STUDIES OF COBALT(II) COMPLEXES WITH SALICYLIDENEIMINES

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SUMMARY

The reluctance of Schiff's bases of the type N-R-salicylideneimine, where R may be aliphatic or aromatic, to form cobalt(II) complexes when the aniline residue was ortho-substituted, has been attributed to steric hindrance. A primary aim, achieved in this thesis, was the development of suitable methods for preparing these sterically hindered complexes. The ease of preparation of the complexes was observed to depend on both the size and charge of the substituent.

Since the d-d absorption bands of nearly all of the complexes were of similar energy, the sterically strained molecules were considered to have a configuration similar to that found in compounds not bearing an ortho-substituent. The ultraviolet spectra of these compounds suggested that on coordination of cobalt(II), the steric effect is modified by a twisting of the Schiff's base about the carbon-nitrogen single bond.

In Chapter II, the effect that substituents have on the electronic transitions of the Schiff's bases is discussed. The energy of the transitions was nearly

independent of the substituent on the aniline residue, however the intensity of the $^1B \longleftarrow {^1A}$ band was found to vary. This variation was used in evidence for the twisting about the carbon-nitrogen single bond of the Schiff's base when ortho-substitution of the aniline residue occurs.

In Chapter III, the ability of the Schiff's bases to behave as monodentate ligands through the imine-nitrogen was considered. The structures of these bis-Schiff's base-dihalo-cobalt(II) complexes prepared, were assigned on the basis of their spectral and magnetic properties. The possibility that one compound was of a symmetry lower than tetrahedral was considered in the light of its unusual visible spectrum.

In Chapter IV, it was shown that the energies of the d-d spectral bands of the chelates bis(N-R-salicylideneiminato)cobalt(II) were not compatible with a pure tetrahedral configuration, and hence a distorted tetrahedral configuration was suggested. The intensities of the spectral bands were considered in terms of a low metal-ligand orbital intermixing. The energy of the charge transfer bands of the chelates in benzene indicated a transfer from metal to ligand.

These cobalt chelates were found generally to react with pyridine to form mono- and di-pyridinates, the stability of the adducts being largely determined by their solvation. However, in some cases only one type of adduct was detected. The entropy and enthalpy changes accompanying pyridinate formation suggested that steric hindrance to pyridine addition occurred when there was a substituent on the ortho-position of the aniline residue. The spectral and magnetic properties of the mono- and di-pyridinate species were very similar.

The effect of solvation of the Schiff's base complexes was illustrated by the study of the stability of the mono-pyridinate of copper(II) chelates in various solvents.

To the best of my knowledge and belief, this thesis contains no material previously published or written by another person, nor any material previously submitted for a degree or diploma in any University, except where due reference is made in the text.

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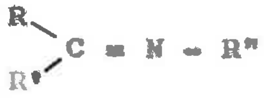
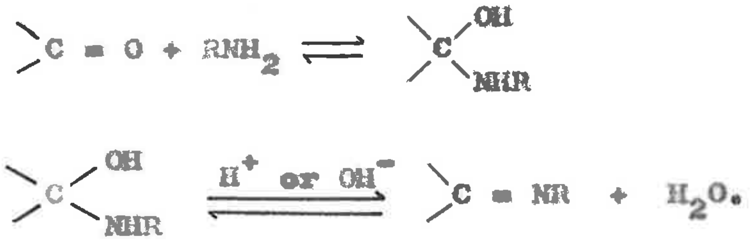
CHAPTER I.

INTRODUCTION.

The condensation products of carbonyl groups with primary amines, known as Schiff's bases, have the general formula



A critical factor in determining the ease of condensation is, of course, the nature of the reactants;[1] an activated carbonyl group as found in salicylaldehyde reacting more readily with aniline than would benzaldehyde. Cordes and Jencks[2] found that the condensation mechanism could be expressed by the equations,



The rate determining process depends on the pH of the reaction solution. Under neutral conditions the rate is determined by the dehydration of the carbinolamine addition product, but in acid, amine attack becomes rate determining.

The imine double bond, a characteristic of Schiff's bases, is less stable chemically than the ethylene linkage.

Thus, Schiff's bases are found to be highly susceptible to both alkaline and acid hydrolysis.[3,4]

The nitrogen of the imine group possesses a lone pair of electrons through which the Schiff's base may coordinate to a transition metal ion. Most Schiff's base-metal reaction studies have involved bidentate Schiff's bases. One of the more common starting materials in the preparation of bidentate Schiff's bases is salicylaldehyde. On coordination with primary amines, Schiff's bases of the type shown in Fig.(I)-1 are formed.

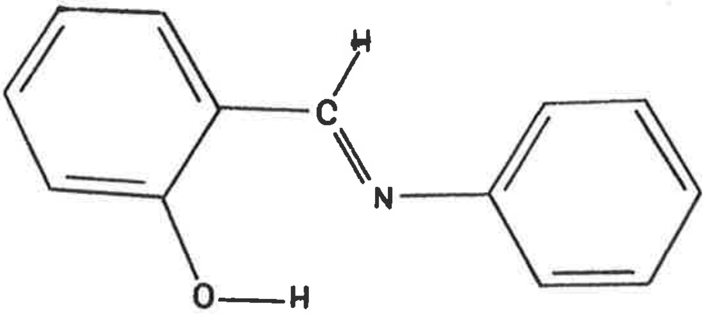


Fig.(I)-1. The structure of N-phenylsalicylideneimine.

Because of the double bond in the imine linkage, there is a possibility of cis-trans isomerism. Hantzsch and Schwab[5], in 1901, claimed to have isolated both the cis and trans isomers of various Schiff's bases. Again, as recently as 1933, a claim was made for the discovery of two forms of N-*o*-tolyl-5-bromosalicylideneimine[6]. However, these early experiments could not be verified[7]. With this in mind, de Gaouck and Le Fevre[7] determined the dipole moment of a series of Schiff's bases in benzene, from which they deduced a trans-configuration for the compounds studied, and that the trans-configuration occurs to the complete exclusion of the cis form. The apparently easy chelation of the ortho-hydroxy Schiff's bases to metal ions was also recognized as additional evidence supporting the trans-structure[8]. Hendricks et.al.[9] investigating the absorption of the hydroxyl group in the 7,100 to 7,400 $cms.^{-1}$ region, suggested that the absence of the hydroxyl stretching band indicated hydrogen bonding. The evidence obtained by Hendricks et.al.[9] and others[7,8,10,11] leaves little doubt that the *o*-hydroxy Schiff's bases, represented by Fig.(I)-1, have a trans-configuration.

Although the bidentate Schiff's bases have been the most thoroughly investigated, quadridentate ligands derived from salicylaldehyde are also well known. These compounds are obtained by condensing salicylaldehyde with diamines.

It is the acidic nature of the phenolic grouping that confers a multidentate character on these ligands. In neutral non-ionising solvents they may behave as unidentate coordinators[12]. Therefore in general, to facilitate the removal of the proton, chelate compounds of Schiff's bases are formed in an acetate buffered reaction mixture[8,13].

The dependence of the properties of the Schiff's base metal chelates on both the properties of the ligands and on the metal has been studied by many techniques. Thus through X-ray analysis, the structure of many compounds have been elucidated[14-20]. Dipole moment measurements have also been employed to assign configurations to a number of chelates[21,22]. Calvin et.al.[23] were able, by polarographic reduction measurements, to correlate the stability of some copper(II) Schiff's base complexes with the electronic properties of substituents on the ligands. Magnetic moments[24] and spectral measurements[25] have also been used to deduce the configuration of Schiff's base chelates.

By these techniques, the configuration of metal(II) Schiff's base complexes were shown to depend on a variety of factors, such as the coordination number of the metal, the number of active groups on the ligands, the stereochemistry of the Schiff's bases and also the preferred configuration of the metal. This latter point is well demonstrated by the chemistry of palladium(II) and platinum(II).

The square planar configuration is well known in the compounds of these metals[26]. Therefore, not surprisingly, Meuthen and Stackelberg[14] in reporting some X-ray studies, suggested that bis(N-methylsalicylideneiminato)palladium(II) had a trans square-planar configuration. Such a configuration was supported by dipole moment measurements[21].

Molecular models of these chelates predict that when a tert-butyl group is on the imine nitrogen, serious steric hindrance occurs[27]. An ultraviolet spectral study of several N-alkylsalicylideneimine Schiff's base complexes of platinum(II) and palladium(II) did in fact suggest a distortion from planarity in the tert-butyl complexes[27]. However, the stability of the planar structure is indicated by the fact that bis(N-isopropylsalicylideneiminato)-platinum(II) and palladium(II) are essentially planar, whereas the copper(II) and nickel(II) compounds show a large distortion from planarity[27]. The configuration of platinum(II) and palladium(II) Schiff's base complexes thus appears to be nearly independent of the ligand. This is, however, not true for copper compounds. Although copper does prefer a planar coordination site, compounds approaching a tetrahedral configuration are known[28,29].

The copper(II) Schiff's base chelates have been investigated more thoroughly than those of other metals. Generally green or brown in colour, these compounds have been known nearly as long as Schiff's bases themselves. The first systematic study of these compounds was instigated by Pfeiffer and collaborators[30-35] in the 1930's.

Although Pfeiffer *et.al.*[34] recognised that these complexes should be planar, this was not proven unambiguously until Stackelberg[16] determined their structures by X-ray analysis. On the basis of displacement reactions, Pfeiffer and Glaser[35] had suggested that the chelate stabilities depended on the amine used in their preparation, in the order aniline < methylamine < *o*-phenylenediamine < ethylenediamine. This order suggested to them that the cis configuration (a property of the diamine) was the more stable one. Stackelberg[16] was surprised to find that all bidentate copper complexes had a trans-configuration, and that the cis-configuration occurred only with the tetradentate ligands by virtue of their geometry. The higher stability of the cis compounds over the trans compounds as found by Pfeiffer and Glaser[35] was attributed to the formation of an additional chelate ring.

From a X-ray analysis of bis(N-methylsalicylideneiminato)copper(II) and the corresponding N-phenyl chelate, Stackelberg[16] and Wei et.al.[20] concluded that in these compounds the copper coordination site was planar. However, in the N-phenyl compound the aniline residues were nearly perpendicular to this plane, thus leading to a chair configuration for this complex.

The copper chelate obtained from the quadridentate ligand N,N'-ethylenedisalicylideneimine should be cis-planar on account of the geometric limitations imposed by the diamine bridge. Such a structure for this chelate has been confirmed independently by Pachler and Stackelberg[15], and also by Hall and Waters[18]. Although these workers concur on the dimeric nature of the complex, there is some disagreement on the nature of the dimeric bonding forces. Pachler and Stackelberg[15] felt that adjacent dimeric molecules were arranged so that the copper atoms were above each other, the nitrogens being placed over the oxygen atoms and vice versa. The combining forces operating between the complex centres produces an approach of these centres to 3.2 Å. Hall and Waters[18] considered the dimeric bonding forces to be two copper-oxygen bonds of length 2.41 Å. As a result of the binding between complex centres, there is a deformation from planarity in the molecule, the aromatic extremities of the dimeric molecules being separated by approximately 4.0 Å. This bending of the molecules illustrates the strength of the intermolecular attraction.

Subnormal magnetic moments have been found in copper(II) Schiff's base chelates, the largest group of these being based on the tridentate ligand derived by condensation of salicylaldehyde with an o-aminophenol[36]. Several of the chelates obtained from the cis-quadridentate ligands described above also possess low magnetic moments[37]. In these complexes the metal-metal distance is quite long, and overlap of the metal $3d_{x^2-y^2}$ orbitals cannot occur. The low magnetic properties of these complexes are attributed to "super exchange". As the intermolecular copper-copper bonds are non-linear (through the phenolic oxygens), the super-exchange is considered to proceed via a pi-path[38].

The relationship between the structure and the stability of copper(II) Schiff's base chelates as suggested by Pfeiffer and Glaser[35] was partially confirmed by Calvin and Bailes[23] in 1946. From a determination of the half wave potentials using a dropping mercury electrode, they found that the copper chelates derived from quadridentate ligands were decidedly more stable than those based on the bidentate ligands. This they concluded, as did Stackelberg, was due to the "chelate effect". However, the findings of Calvin and Bailes[23] suggested that the Pfeiffer-Glaser[35] order of stabilities was in part incorrect, in that the chelates obtained from the aromatic amines were more stable than those from aliphatic ones.

In recent publications, Jabalpurwala <u>et.al.</u>[39], investigating the proton-ligand and metal-ligand stability constants of some Schiff's bases in a dioxane-water system, supported the findings of Calvin and Bailes[23]. They showed that bis(N-phenylsalicylideneiminato)copper(II) was more stable than the corresponding N-methylsalicylideneimine complex, due to the higher basic strength of the nitrogen and the greater acidity of the phenol group of the N-phenylsalicylideneimine ligand.

The tendency to form planar compounds evident in the Schiff's base chelates of platinum(II), palladium(II) and copper(II), is decreased when the chelated metal is nickel. In 1939, Pauling[40] stated that "the factors which determine whether the diamagnetic square or the paramagnetic tetrahedral configuration is assumed by a nickel complex cannot be stated precisely." In recent years many workers have accumulated evidence to furnish an answer to the question implied above.

Recent studies on the magnetic properties of Schiff's base nickel(II) complexes have highlighted the subtle balance that exists between the relative stabilities of the planar and tetrahedral configurations. Many compounds of the type bis(N-alkylsalicylideneiminato)-nickel(II) were found to possess magnetic moments between diamagnetism and the paramagnetism associated with two unpaired electrons[41-43]. The paramagnetism was considered to be indicative of a conformational equilibrium between a spin-paired planar and a spin-free tetrahedral species. However the configuration of the paramagnetic isomer was questionable. Although no spin-free planar nickel complex was known, the possibility of its existence could not be neglected. The electric dipole moments of several N-alkysalicylideneimine nickel(II) chelates in benzene and dioxane were found to be compatible with a spin-free planar formulation of the paramagnetic species[21,44].

Ballhausen and Liehr[45], and also Maki[46], have shown by ligand field theory that nickel(II) in a planar configuration has a number of singlet and triplet states of similar energy, the ground state thus being highly sensitive to both the strength and symmetry (cis, trans) of the ligand field.

In an X-ray structural investigation, Frasson <u>et.al.</u>[47] found that in the diamagnetic N-methylsalicylideneimine chelate the coordinated ligands were in a trans-planar arrangement. The paramagnetic isomer however, could not be obtained in a crystalline state suitable for a structural determination. For this reason, attempts were made to correlate the physical properties of the chelates with a spin-free planar coordination state of nickel.

Sacconi <u>et.al.</u>[48] were able to show that their magnetic susceptibility measurements were in accord with the expression of Ballhausen and Liehr relating the atomic susceptibility of nickel in a planar configuration to the temperature. However, as the paramagnetic N-isopropyl- and N-<u>sec</u>-butylsalicylideneimine Schiff's base chelates of nickel(II) were found to be tetrahedral[19,49], it was concluded that the conformational equilibrium in the nickel(II) Schiff's base compounds was one between tetrahedral and planar isomers, and did not involve a spin-free planar species.

While it was possible to explain the magnetic and spectral properties of some nickel(II) Schiff's base chelates on the basis of a planar $\rightleftharpoons$ tetrahedral equilibrium, Holm and co-workers[50-53] found that molecular association was also of importance in many instances, especially at room temperature. The room temperature paramagnetism of bis(N-methylsalicylideneiminato)nickel(II) in both the solid phase and in solution, was considered to arise from polymerization. The existence of polymerization in chelates of the type bis(N-arylsalicylideneiminato)-nickel(II) was convincingly demonstrated by Holm et.al.[53]

On increasing the bulkiness of the amine residue in the vicinity of the imine nitrogen, the tetrahedral configuration of the nickel chelates is stabilized relative to the planar configuration[54].

In recent years the conformational equilibrium between diamagnetic and paramagnetic nickel(II) compounds has been found in complexes other than those of Schiff's bases. The bulkiness of the ligand, known to be a decisive factor in the Schiff's base chelates, has been found to be an important general structural criterion in the preparation of spin-free pseudotetrahedral nickel(II) compounds[55].

Turning to the cobalt(II) complexes, one finds that the tetrahedral configuration is preferred to the planar one. Although no complete X-ray structural investigation has been completed for cobalt(II) Schiff's base complexes, Frasson and Panattoni[56] suggested that the chelate bis(N-butylsalicylideneiminato)cobalt(II) was tetrahedral as it was isomorphous with the corresponding tetrahedral zinc(II) compound. Dipole moment measurements by Sacconi _et.al._[21] and others[22] and the magnetic moment measurements by West[24] were also in agreement with a tetrahedral configuration for these complexes. A spectral investigation of these cobalt(II) chelates was thus under-taken to determine whether this property is compatible with a tetrahedral structure.

In the preparation of the chelates of the type bis(N-R-salicylideneiminato)cobalt(II), it was found that a substituent in the ortho-position of the aniline residue of the ligand greatly hindered chelate formation[57]. Since the corresponding nickel(II) and copper(II) complexes could be readily obtained, West[57] proposed that the ortho-effect, evident in the cobalt(II) complexes, was due to the non-planarity of cobalt(II) chelates. To elucidate the stereochemical problems involved on chelation of the Schiff's bases with cobalt(II), the work in this thesis was undertaken.

In an initial study, the spectral properties of the Schiff's bases were measured to see whether an ortho-substituent on the aniline residue of the base disturbs the planarity of the ligand. This investigation was subsequently extended to a spectral study of the zinc(II) Schiff's base chelates to gain information on the configuration of Schiff's bases coordinated to a tetrahedral metal.

Extension of the coordination number of cobalt(II) above four is possible. Although the pentacoordination state is not a very stable one for cobalt(II), especially if unidentate ligands are employed, pentacoordinated Schiff's base complexes have been made. A stable complex that has been well characterised is the chelate, N,N'-(3,3'-di-n-propylamine)bis-salicylideneiminatocobalt(II), the ligand being quinquidentate[37]. Sexadentate cobalt(II) compounds are well known. A study of the addition of pyridine to the compounds bis(N-arylsalicylideneiminato)cobalt(II) was made to ascertain the effect the stereochemistry of the amine residue has on the stability of the adducts.

When a quadridentate ligand such as N,N'-ethylenedisalicylideneimine is complexed with cobalt, a planar chelate[58], paramagnetic to the extent of one unpaired electron[37], is obtained. To determine whether the planarity of this chelate is dependent on the length of the diimine bridge, a spectral and magnetic investigation of such compounds in which the diimine bridge had been extended to above seven carbon atoms, was made.

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CHAPTER II.

THE SCHIFF'S BASE LIGANDS.

1. Introduction.

The ease of preparation of Schiff's base chelates, especially those of cobalt(II), was found by West[1] to depend largely on both the nature and position of the substituent on the aniline residue[a]. Although Schiff's bases have been well characterized, the dependence of their chelation properties on the substituent carried by the aniline residue has not been fully appreciated.

Calvin and Bailes[2] noted the importance of the electronic properties of the substituents to the stability of the copper(II) Schiff's base chelates. The enhanced stability of these chelates with increasing electron donating power of the substituent on the amine residue was related to the increased basic strength of the anil[3]. However, as these workers investigated only the para-substituted Schiff's bases, no conclusions could be drawn concerning the magnitude of steric effects involved in chelation.

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[a] Schiff's bases of the type N-R-salicylideneimine will be referred to by the nature of the amine residue, R. Thus, if R is p-tolyl, the ligand is known as the p-tolyl Schiff's base or ligand.

Substituents on an aromatic system can alter conjugated energy levels of the molecule, either by electronic or steric means. The extent by which a substituent will change the separation between the ground and excited energy states of the molecule will depend on both the electronic and steric features imposed on the conjugated system by a particular substituent. An examination of the electronic spectra of a series of Schiff's bases may thus prove a useful tool in correlating the electronic and steric properties of the ligands with their ease of chelation.

With this in mind, the spectra of some Schiff's bases were measured. The position of their band maxima with the corresponding molar extinction coefficients, are tabulated in Appendix A.

2. Electronic Spectra of Schiff's Bases.

(i) Assignment of the Spectral Transitions.

A comparative study of the spectra of Schiff's bases can only be made following an assignment of the spectral transitions. For this purpose it is useful to review in brief, the work of Jaffe et.al.[4] and others[5,6] on the spectral properties of the iso-pi-electronic compounds stilbene, azobenzene, N-phenylbenzylideneimine and several others. Energy level diagrams were calculated by application of the LCAO molecular orbital theory, assuming the molecules to be linear (D_{2h} symmetry). The results of the calculations of Jaffe et.al.[4,7] are presented in Fig.(II)-1.

Following the Platt notation[8], the energy levels shown in Fig.(II)-1 are given in order of increasing stability by e_g, (v_g, v_u), f_u, g_g, (w_g, w_u) and h_u respectively. Transitions other than those between these energy levels are of too high an energy to be found in the readily attainable ultra-violet region. Excitation of the electrons from the ground state species (^1A) having the configuration $e_g^2 v_g^2 v_u^2 f_u^2$ then proceeds in the usual way. (See Table (II)-1).

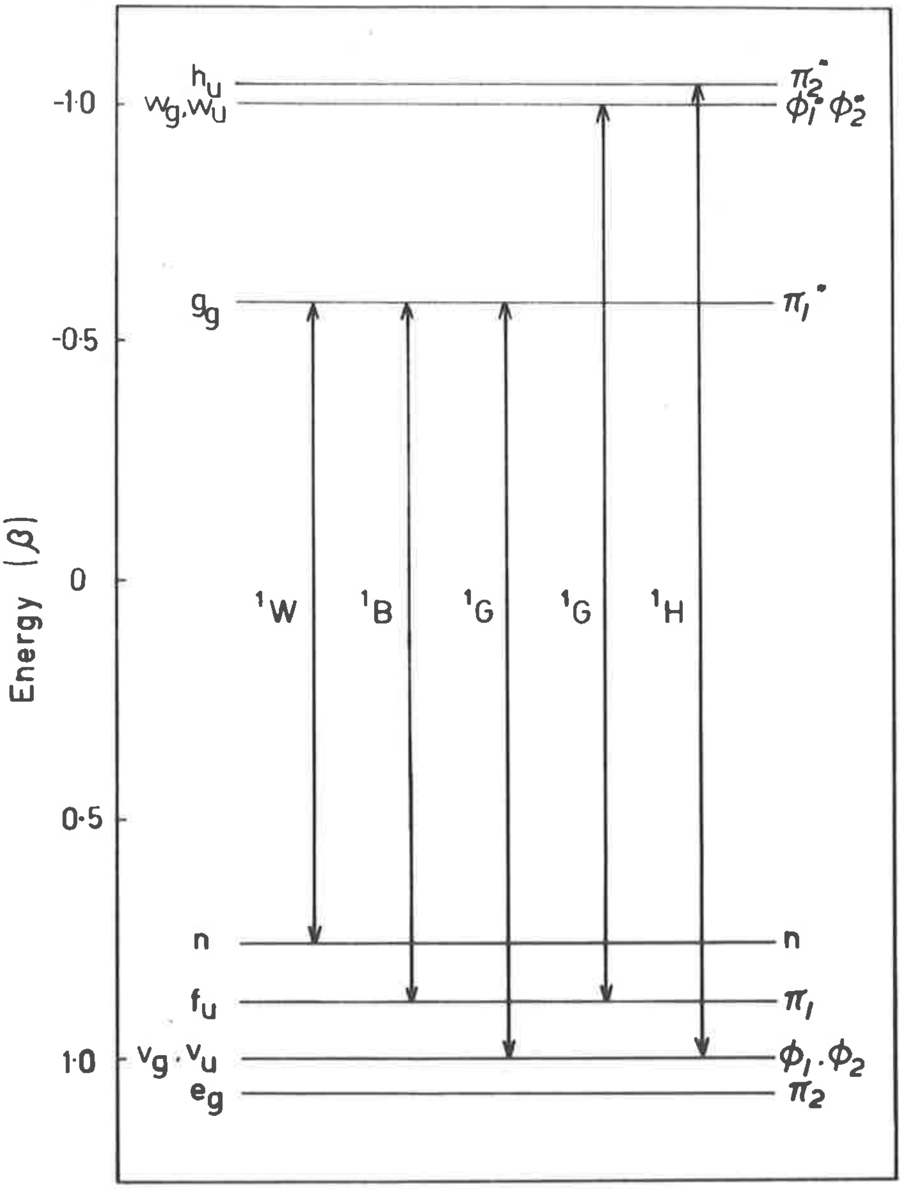

Fig.(II)-1. One-electron orbital energy diagram for N-phenylbenzylideneimine.[4] The symmetry allowed transitions found in the readily attainable ultraviolet spectral region are shown by the vertical arrows bearing Platt's notation. The energy is expressed in terms of β, the resonance integral within the benzene ring.

The LCAO molecular orbital theory predicts that the symmetry allowed transition ${}^1B \longleftarrow {}^1A$, polarised parallel to the longitudinal axis of the molecules, is of the lowest energy and should therefore be found at the longest wavelength[4,5]. At higher energy the transitions involving the doublet ${}^1G \longleftarrow {}^1A$ $(v \longrightarrow g,\ f \longrightarrow w)$ should be found. It should be noted that the v and w states are associated only with the phenyl aromatic ring systems and not with the molecule as a whole. The next highest energy bands may then be assigned to the ${}^1H \longleftarrow {}^1A$ transitions. In the perfectly symmetrical case, this transition is doubly degenerate[4,5,7].

On analysis of the spectrum of N-phenylbenzylideneimine, Jaffe *et.al.*[4,7] identified four transitions, and attributed the lowest energy band to the ${}^1B \longleftarrow {}^1A$ transition. An assignment involving the other bands proved more difficult as both the ${}^1G \longleftarrow {}^1A$ and the ${}^1H \longleftarrow {}^1A$ electron transitions involve two excitations. A guide to the highest energy band in N-phenylbenzylideneimine was obtained from the relative insensitivity of this band to changes in the bridging units between the phenyl systems. (See Table (II)-2.) Since the ${}^1H \longleftarrow {}^1A$ transitions involve only the phenyl rings, and not the "vinyl-bridge", whereas the ${}^1G \longleftarrow {}^1A$ transitions do incorporate this bridging unit, the high energy band was assigned to the ${}^1H \longleftarrow {}^1A$ transition.

TABLE (II)-1.

The excited energy states of Stilbene, in order of increasing energy[7].

Configuration	Platt Notation	Polarization[a]	Forbiddeness[b]
$e_g^2 v_g^2 v_u^2 f_u g_g$	^1B	L	A
$e_g^2 v_g^2 v_u f_u^2 g_g$	^1G	T	A
$e_g^2 v_g v_u^2 f_u^2 g_g$			F
$e_g^2 v_g^2 v_u^2 f_u w_g$			A
$e_g^2 v_g^2 v_u^2 f_u w_u$			F
$e_g^2 v_g^2 v_u f_u^2 w_g$	^1H	T	A
$e_g^2 v_g^2 v_u f_u^2 w_u$			F
$e_g^2 v_g v_u^2 f_u^2 w_g$			F
$e_g^2 v_g v_u^2 f_u^2 w_u$			A

a. Transition polarized longitudinally (L) or transversely (T).

b. Transition forbidden (F) or allowed (A).

TABLE (II)-2.

The energy and molar extinction coefficients of the ${}^1H \longleftarrow {}^1A$ transition of N-phenylbenzylideneimine and some iso-pi-electronic compounds[4]

Compound	cms.$^{-1}$	ϵ
Stilbene	44,250	15,000
N-phenylbenzylideneimine	45,870	14,400
Azobenzene	42,370	7,400
Azobenzene (conj. acid)	42,370	8,000
Azoxybenzene	42,020	8,200

The two intermediate energy bands arise from the ${}^1G \longleftarrow {}^1A$ ($v \longrightarrow g$ and $f \longrightarrow w$) transitions; the $v \longrightarrow g$ one being of lower energy.

N-phenylbenzylideneimine and the other nitrogen containing compounds in Table (II)-2 also give rise to an allowed transition involving the non-bonding electrons on the nitrogen. These $n \longrightarrow g$ transitions, allowed by local symmetry, are designated as ${}^1W \longleftrightarrow {}^1A$ in the Platt notation[8]. It can be seen, by reference to Fig.(II)-1, that this transition occurs at lowest energy. The low intensity of these transitions follows from their "locally" allowed character - overlap with the pi system is small. Because of its low intensity, this band is often hidden under the tail of the $^1B \longleftarrow {}^1A$ transition.

(ii) The Effect of Substituents on Monodentate Schiff's Bases.

a. Effect on spectral features.

The construction of symmetrical bands under the absorption spectrum of N-phenylbenzylideneimine enabled Jaffe et.al.[4,7] to assign energies to the $^1B \longleftarrow {}^1A$, the $^1G \longleftarrow {}^1A$ and the $^1H \longleftarrow {}^1A$ transitions. Although the $^1B \longleftarrow {}^1A$ and $^1G \longleftarrow {}^1A$ transitions could be located, the energy of the $^1H \longleftarrow {}^1A$ bands remained uncertain due to large overlap with shorter wavelength bands present.

In order to produce more conclusive proof of the existence of the postulated electronic transitions in Schiff's bases, the spectra of several substituted ligands were investigated in the present work. If the substituents affect the various energy states by differing extents, a greater separation and hence higher definition of some of the bands may be achieved. Such an effect was indeed observed with all substituents (See Figs.(II)-2 and (II)-3). On construction of symmetrical bands below the spectra, by a series of subtractions of intensities, four bands were found, and in each case identified by reference to the work of Jaffe et.al.[4]

TABLE (II)-3.

The spectral transitions of several N-R-benzylideneimine compounds.

	$^1B \leftarrow {}^1A$		$^1G \leftarrow {}^1A$		$^1H \leftarrow {}^1A$	
Compound	cms.$^{-1}$	ϵ	cms.$^{-1}$	ϵ	cms.$^{-1}$	ϵ
N-phenylbenzylideneimine[4]	32,050	10,000	37,040 39,530	13,500 10,000	45,900	14,400
N-*p*-chlorophenylbenzylideneimine	31,150	9,580	36,600 39,500	16,500 13,800	43,500	13,700
N-*p*-tolylbenzylideneimine-2-benzoate	28,900	19,120	32,600 37,050	14,000 19,300	41,800	21,500
N-phenylsalicylideneimine	29,050	11,230	33,000 37,100	9,130 13,860	42,400	18,500

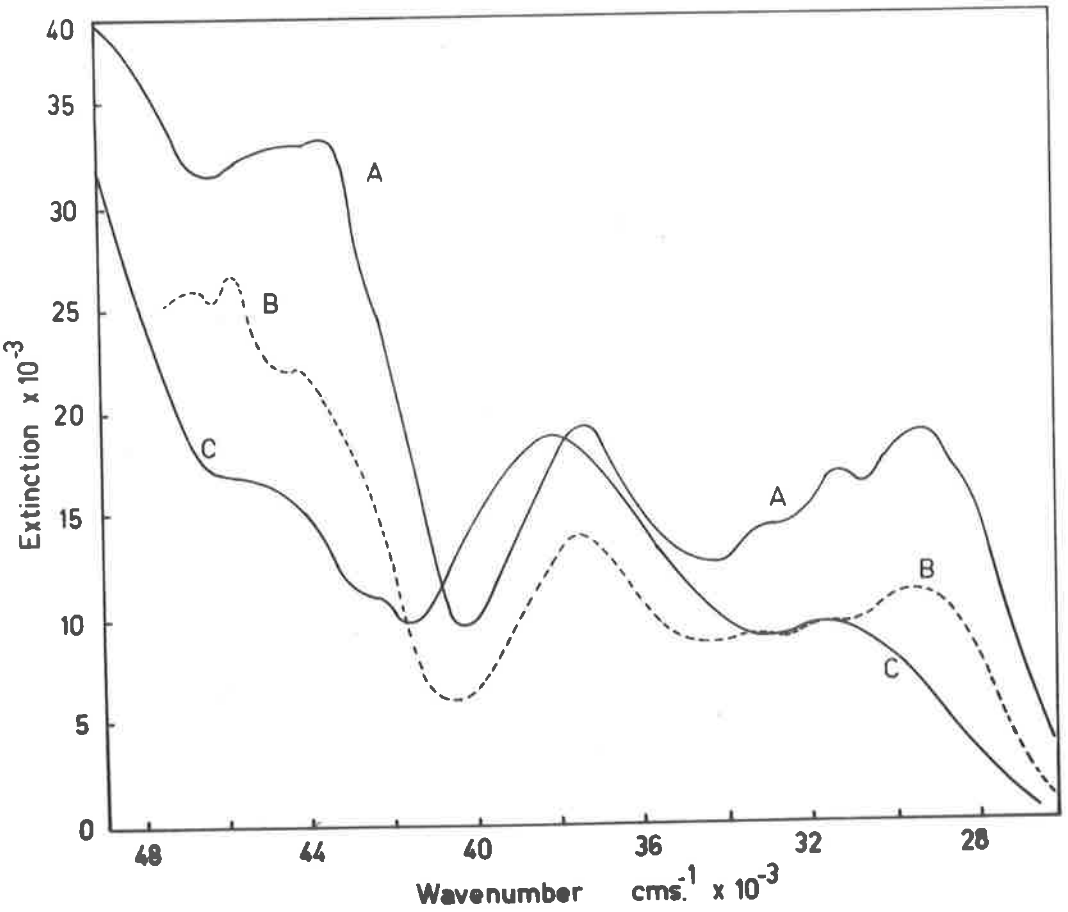

Fig.(II)-2. The electron absorption spectra at 25°C. in cyclohexane of
A. N-p-tolylbenzylideneimine-2-benzoate.
B. N-phenylsalicylideneimine.
C. N-p-chlorophenylbenzylideneimine.

On the basis of the assignments made in Table (II)-3, energy level diagrams can be constructed for the compounds. In Fig.(II)-3, the v_u level has been arbitrarily considered to possess more energy. From such energy level diagrams an estimate of the relative interaction of the substituents with the various energy levels of the parent molecule can be made. It should be noted that there is an uncertainty of approximately 1,500 cms.$^{-1}$ in the placement of the w_g level, this being the difference between the energy calculated from the lowest three energy transitions, and the energy estimated from the absorption spectrum. This correlation between the found and calculated energy of the $^1H \longleftarrow {}^1A$ transitions seems excellent when the uncertainty in the placement of the $^1G \longleftarrow {}^1A$ bands is taken into account.

TABLE (II)-4.

Comparison of the calculated and found energies for the $^1H \longleftarrow {}^1A$ transitions for several Schiff's Base compounds.

Compound	Found	Calculated
N-phenylbenzylideneimine	45,900 cms.$^{-1}$	44,500 cms.$^{-1}$
N-p-chlorophenylbenzylideneimine	43,450	42,060
N-phenylsalicylideneimine	42,400	41,050
N-p-tolylbenzylideneimine-2-benzoate	41,800	40,750

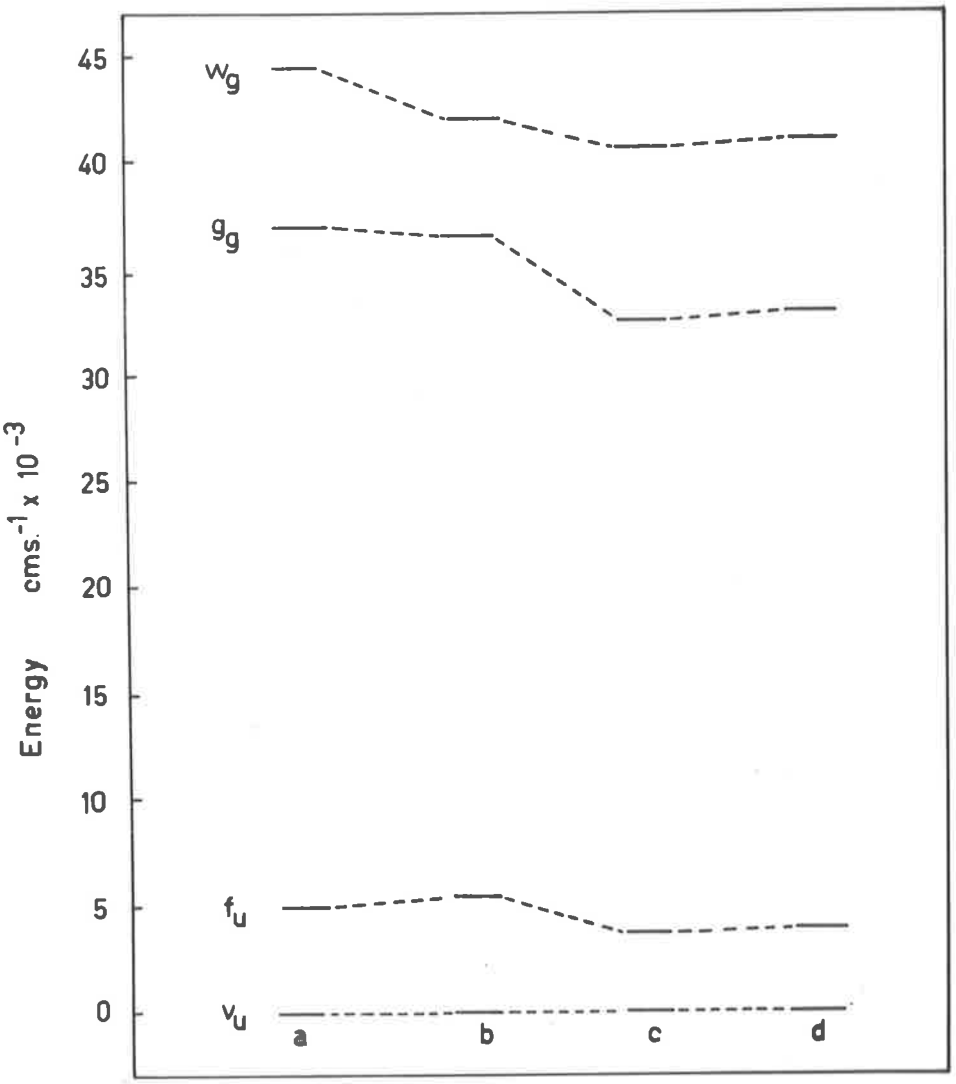

Fig.(II)-3. The energy level diagram for
a. N-phenylbenzylideneimine.
b. N-p-chlorophenylbenzylideneimine.
c. N-p-tolylbenzylideneimine-2-benzoate.
d. N-phenylsalicylideneimine.

b. Participation in conjugation.

Addition of the phenolic-hydroxy grouping to N-phenylbenzylideneimine will alter the spectrum of the parent compound by electronic interactions and by lowering the symmetry of the molecule. The electronic interactions are due to a participation of the hydroxy groups' electron energy states with those of the conjugated parent system and also with that of the non-bonding electrons on the nitrogen.

The presence of hydrogen bonding in salicylaldehyde Schiff's bases has been well established[9]. By a mixing in of the hydroxyl energy levels with the "non-bonding" energy level of the nitrogen, this energy level of the nitrogen will be stabilized, resulting in a hypsochromic shift of the $^1W \longleftarrow {}^1A$ band[10,11,12].

The predominant effect of the hydroxy group on the spectrum of the parent system occurs through a mixing in of the substituent energy levels with those of the aromatic system[10]. This will in general result in a bathochromic shift of the absorption bands[13,14]. The extent of this intermixing of energy levels will, to some extent, be dependent on the strength of the hydrogen bond[15]. The stronger this bond, the more pronounced the bathochromic shift[16]. Since both the n and g levels are therefore stabilised by the hydroxy substituent, it is not possible to predict whether the $n \rightarrow g$ band will experience a blue or a red shift.

The other substituents considered in Table (II)-3 will affect the energy levels of the parent system in a manner similar to the hydroxy group, neglecting the hydrogen bonding. From the energy level diagram (Fig.(II)-3) it can be seen that the extent of interaction of the substituent energy levels with those of the parent depends on both the substituent and the particular electron energy state. On substitution therefore, unequal shifts in the spectral bands are expected, and, in general, found.

(iii) Substitution in Bidentate Schiff's Bases.

The Schiff's bases considered here are those derived from salicylaldehyde and substituted aromatic amines. In this section it is proposed to outline the effect of substitution on the spectral bands of the parent compound, N-phenylsalicylideneimine, attempting to correlate any appreciable spectral change with substituent properties.

a. Substitution in the Para-position.

The energy and intensity of the spectral transitions depend on both the nature and position of the substituent. By reference to Table (II)-4 it can be seen that on para-substitution, all compounds investigated experience a bathochromic shift in the $^1B \leftarrow {}^1A$ band, the magnitude of this shift depending on the extent of intermixing of the substituent energy levels with those of the parent molecule.

TABLE (II)-4.

The spectral transitions for

N-para-X-phenylsalicylideneimine in cyclohexane at 25°C.

X	$^1B \leftarrow {}^1A$		$^1G \leftarrow {}^1A$		$^1H \leftarrow {}^1A$	
	cms.$^{-1}$	ϵ	cms.$^{-1}$	ϵ	cms.$^{-1}$	ϵ
H	29,050	11,230	33,000 37,100	9,130 13,800	42,400	18,500
CH_3	28,900	13,450	32,800 37,100	9,660 13,050	42,400	15,400
OCH_3	28,350	16,610	32,300 37,150	9,060 11,900	42,400	16,300
F	28,900	11,630	32,600 37,100	9,310 14,200	42,800	17,300
Cl	28,650	12,800	32,600 36,800	10,200 14,100	43,050	21,400
Br	28,600	13,050	32,300 36,700	10,820 14,300	43,050	20,500
NO_2	27,800	14,610	32,300 36,400	15,850 9,200	43,100	9,900

Thus as expected, the methoxy group and the nitro group shift the $^1B \longleftarrow {}^1A$ band to the lowest energies, while the methyl group and the fluorine have little effect on the transition energy.

It is not possible to make similar generalizations concerning the trends in the properties of the $^1G \longleftarrow {}^1A$ bands as each substituent reacts to various degrees with all four energy levels involved in these transitions. However, for most $^1G \longleftarrow {}^1A$ transitions, bathochromic shifts are observed.

b. Meta-substitution.

Like para substitution, meta substitution reveals a bathochromic shift in the $^1B \longleftarrow {}^1A$ band, the magnitude of this shift is however decreased. This may presumably arise from either a relatively higher stabilization of the ground g_g state compared to the excited f_u state, or by a lower participation of the substituent with the parent electronic system.

The $^1G \longleftarrow {}^1A$ $(v \longrightarrow g)$ band has, to within ± 100 cms.$^{-1}$, the same energy for all the meta-substituted Schiff's bases, except the nitro compound, while the high energy $^1G \longleftarrow {}^1A$ $(f \longrightarrow w)$ band moves in energy roughly parallelling that of the $^1B \longleftarrow {}^1A$ band. It is therefore tempting to propose that in all cases (nitro compounds excepted) the v_u, the g_g and also the w_g levels are stabilised by equal amounts, the variation in transition energy of the $^1B \longleftarrow {}^1A$ and the $^1G \longleftarrow {}^1A$ ($f \longrightarrow w$) excitations resulting from differences in participation of the substituent with the ground f_u state. While the surprisingly constant values found for the $^1H \longleftarrow {}^1A$ band energy argues in favour of such a scheme, the experimental uncertainty in the placement of this band disqualifies its use in this discussion.

Although meta-substitution has little effect on the intensity of the $^1B \longleftarrow {}^1A$ band and on the $^1G \longleftarrow {}^1A$ ($v \longrightarrow g$) band, the high energy $^1G \longleftarrow {}^1A$ ($f \longrightarrow w$) transition intensity increases appreciably for several compounds, and in particular the *m*-nitrophenyl one. This effect is opposite to that found for para-substitution. The differences found in both spectral intensity and energy between the meta- and para-substituted Schiff's bases may arise from differences in the "mesomeric" interaction of the substituent with the parent molecule. Such changes in electronic effects, viewed in conjunction with the direction of transition polarization, may well explain this inversion in intensity changes between the two groups of Schiff's bases.

TABLE (II)-5.

The spectral transitions for

N-meta-X-phenylsalicylideneimine in cyclohexane at 25°C.

X	$^1B \longleftarrow {}^1A$		$^1G \longleftarrow {}^1A$		$^1H \longleftarrow {}^1A$	
	cms.$^{-1}$	ϵ	cms.$^{-1}$	ϵ	cms.$^{-1}$	ϵ
H	29,050	11,230	33,000 37,100	9,130 13,800	42,400	18,500
CH_3	29,050	11,980	33,000 37,250	9,910 14,140	42,500	18,400
OCH_3	29,000	11,990	32,900 37,200	8,300 13,980	42,300	16,400
F	28,850	11,010	32,900 37,050	9,780 14,980	42,500	14,700
Cl	28,750	11,020	32,800 36,850	9,240 14,550	42,400	15,600
Br	28,750	10,930	33,000 36,800	9,000 14,260	42,400	18,600
NO_2	28,550	10,180	32,400 36,700	9,800 19,900	-	-

The long tail found on the $^1B \longleftarrow {}^1A$ band of the meta-nitro compound suggests the presence of a $^1W \longleftarrow {}^1A$ transition. The high bathochromic shift experienced by this band, making it partially observable, is indicative of the high stabilization of the g_g level on nitration. However, whether this transition arises from the imine-nitrogen or from the nitro-group[13] cannot be said.

c. Ortho-substitution.

On substitution in the ortho-position of the aniline residue of the Schiff's bases the substituent may assume a position trans or cis to the hydrogen bonded phenolic-hydroxy group. Consideration of the symmetry of the molecule suggests a trans substituted compound (See Fig.(II)-4).

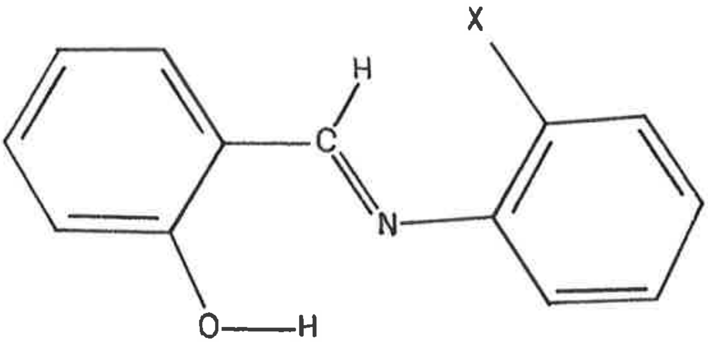

Fig.(II)-4 Trans substituted N-o-X-phenylsalicylideneimine.

Depending on the nature of X, steric interaction between this substituent and the imine hydrogen may occur. Assuming these Schiff's base compounds to be planar, scale drawings show that for N-o-chlorophenylsalicylideneimine, the chlorine - imine hydrogen distance lies between 1.5 and 1.6 Å. Since the sum of Van der Waals radii of these atoms is 2.7 Å, an appreciable steric distortion in the molecule may be postulated. Recently Bregman et.al.[17] found that the phenyl ring of the aniline residue in N-o-chlorophenylsalicylideneimine is rotated through 51.5° about the nitrogen-phenyl bond. This distortion is readily accounted for by steric hindrance.

Even in Schiff's bases bearing no substituents on the aniline residue, steric effects are found. Bregman et.al.[17] postulated that the slight displacement of the nitrogen from the plane of the aldehyde-imine system was due to steric forces between the imine-hydrogen and the hydrogen on the ortho position of the aniline residue. In addition, through the non-planarity of the imine-nitrogen bonding orbitals, all Schiff's bases are bent approximately 7° at the nitrogen atom[17].

The twisting of a "single-bond" in a conjugated system will, of course, affect the electronic spectrum of the molecule[18]. Since the interaction of the pi-orbitals across the bond is a maximum when the system is planar, any deviation from planarity of the molecular configuration will reduce the degree of conjugation and consequently alter the spectral features of the molecule. The relation between the spatial configuration and the intensity and position of the conjugated band has been determined for many systems. In general the position and energy of the conjugated band will vary in the following ways:[18]

1. If the angle of twist is slight, the transition energy remains constant but the intensity is decreased. Such an effect is found only when spatial distortion is small.

2. A further increase in the twist will result in a blue shift of the band, together with a drop in intensity.

3. When the steric distortion is large enough to eliminate almost entirely the pi-pi interaction across the twisted bond, the spectrum will resemble that of the individual components.

TABLE (II)-6.

The spectral properties of

N-ortho-X-phenylsalicylideneimine in cyclohexane at 25°C.

X	$^1B \longleftarrow {}^1A$		$^1G \longleftarrow {}^1A$		$^1H \longleftarrow {}^1A$	
	cms.$^{-1}$	ϵ	cms.$^{-1}$	ϵ	cms.$^{-1}$	ϵ
H	29,050	11,230	33,000 37,100	9,130 13,800	42,400	18,500
CH_3	29,050	11,380	32,900 37,470	7,180 13,930	42,400	14,200
OCH_3	28,450	12,180	32,500 37,300	6,240 13,120	42,800	23,000
F	28,800	11,080	33,000 37,200	9,120 15,800	42,600	18,180
Cl	28,650	9,650	32,700 36,900	7,130 13,300	42,800	18,900
Br	28,600	10,100	32,500 36,900	7,050 14,080	42,400	18,000

On ortho-substitution, in all cases except for the methyl compound, bathochromic shifts are observed in the $^1B \longleftarrow {}^1A$ band. Since these shifts are all very similar to those experienced by the $^1B \longleftarrow {}^1A$ band on para-substitution, the twist about the N-phenyl bond is not sufficiently large to affect the conjugation of the system to any appreciable extent[19]. In all cases however, a decrease in the extinction of the band (compared to the para-substituted compound) does occur.

Braude and Sondheimer[20] suggested that in cases where the angle of twist is small, and the bands are not shifted, the ratio of the intensity of the daughter (ϵ) and parent (ϵ_o) compounds was proportional to $\cos^2\theta$, where θ is the angle of twist. Thus,

$$\frac{\epsilon}{\epsilon_o} = \mathrm{Cos}^2\theta$$

Application of this empirical expression to the spectra of ortho substituted Schiff's bases would necessitate an assumption concerning the nature of the parent compound. Since both ortho- and para-substituents "activate" similar positions on the phenyl ring systems, the para-substituted Schiff's bases were chosen as best representing the hypothetical ortho-substituted bases exhibiting no steric strain. When the substituent is uncharged, such as in the methyl-substituted compound, this assumption should represent a nearly true picture. The possible difference in the $^1B \longleftarrow {}^1A$ transition moment between the ortho- and para-substituted compounds when the substituent is charged, or reacts strongly with the molecular electronic configurations, may to some extent invalidate calculations based on a "para" parent compound. However, it is rather interesting that the smallest substituent, the fluorine atom, does in fact show the smallest angle of twist on application of the Braude-Sondheimer expression.

TABLE (II)-7.

The angle of twist about the N-phenyl bond in N-ortho-X-phenylsalicylideneimine, calculated from the empirical expression of Braude and Sondheimer[20].

X	Angle of twist, θ°.
methyl	23
methoxy	31
fluoro	12
chloro	30
bromo	29

A comparison of the calculated angle of twist for N-o-chlorophenylsalicylideneimine with that found by Bregman et.al.[17] (51.5°) suggests that the Braude-Sondheimer expression predicts angles that are too small. Alternatively, this decrease in the twist may be a solution property. For chloro, bromo, methoxy and even methyl substitution rather similar angles of twist are calculated. Suzuki[21] found a similar situation in the case of substituted biphenyl compounds. Thus 2-methyl-, 2-ethyl-, 2,2'-dimethyl- and even 2,2'-diethyl- biphenyl show similar angles of twist about the central "single" bond.

The hydrogen on the imine-carbon would, by reason of the electron absorbing properties of the imine double bond and the phenyl rings, be to some extent acidic. Thus, besides steric strain, electronic interactions may also be possible between the sterically interfering atoms. A proton magnetic resonance study of these ortho substituted compounds would be of some interest.

Comparison of Table (II)-4 with Table (II)-6 reveals that in all cases the $^1G \longleftarrow {}^1A$ bands are at higher energies on ortho-substitution. The low energy $^1G \longleftarrow {}^1A$ $(v_u \longrightarrow g_g)$ transitions of the ortho-substituted compounds have an intensity some 3,000 extinction units below that for the corresponding para-substituted compounds. It is noteworthy that only the ortho-fluoro-substituted base does not show this large hypochromic shift. Since the $^1G \longleftarrow {}^1A$ transitions occur between configurations involving the whole electron system and the energy states localised on the phenyl rings, the behaviour observed for this band is readily accounted for on the grounds of steric hindrance.

However, in the methyl, methoxy and especially the fluoro compounds, the high energy $^1G \longleftarrow {}^1A$ $(f_u \longrightarrow w_g)$ bands increase in intensity on movement of the substituent from the para- to the ortho- position of the aniline residue. It is not possible to propose an explanation of this effect without a more detailed knowledge of the charge dispersion in both the ground and excited states of this transition.

Again, due to the uncertainty in placement of the $^1H \longleftarrow {}^1A$ bands, little information can be gleaned from these measurements. However since these bands arise from transitions localised on the phenyl groups, twisting of the molecule should have little effect on the band properties.

(iv) Substitution on the aldehyde residue.

It is of interest to consider in brief the changes in the spectral properties of the parent Schiff's bases on substitution in the salicylaldehyde residue. If interaction of the substituent with the phenolic-hydroxy group is important, placement of the substituent on the aldehyde ring system would magnify any such effect[22]. The compounds studied were the 5-bromosalicylaldehyde, the 4-hydroxysalicylaldehyde and the 2-hydroxy-1-naphthaldehyde Schiff's bases with aromatic amines.

a. 5-bromosalicylaldehyde Schiff's bases.

In the previous section it was shown that bromination in the aniline residue resulted in a bathochromic shift of between 300 and 450 cms.$^{-1}$ in the $^{1}B \longleftarrow {}^{1}A$ band. In the 5-bromosalicylaldehyde Schiff's bases, the longest wavelength band experiences a bathochromic shift of between 800 and 1,000 cms.$^{-1}$. This large shift suggests that a considerable amount of reinforcement in the participation of both the hydroxy group and the bromine with the parent pi electronic configuration occurs[22].

The most spectacular shifts are seen in the $^{1}G \longleftarrow {}^{1}A$ and $^{1}H \longleftarrow {}^{1}A$ transitions, the $^{1}G \longleftarrow {}^{1}A$ $(v_u \longrightarrow g_g)$ bands being moved 1,700 to 1,800 cms.$^{-1}$ to lower energies; the $^{1}G \longleftarrow {}^{1}A$ $(f \longrightarrow w)$ bands by 3,000 to 3,700 cms.$^{-1}$ while the $^{1}H \longleftarrow {}^{1}A$ bands experience a red shift of about 5,500 cms.$^{-1}$. These extremely large energy changes, on bromination of the aldehyde residue, would tend to cast some doubt on both the location (determined by construction of symmetric curves under the spectra) and assignment of the bands. If all the observed transitions do occur between the four energy states as postulated in Table (II)-8, it is possible using three of the found transition energies to calculate the energy of the fourth. For the above

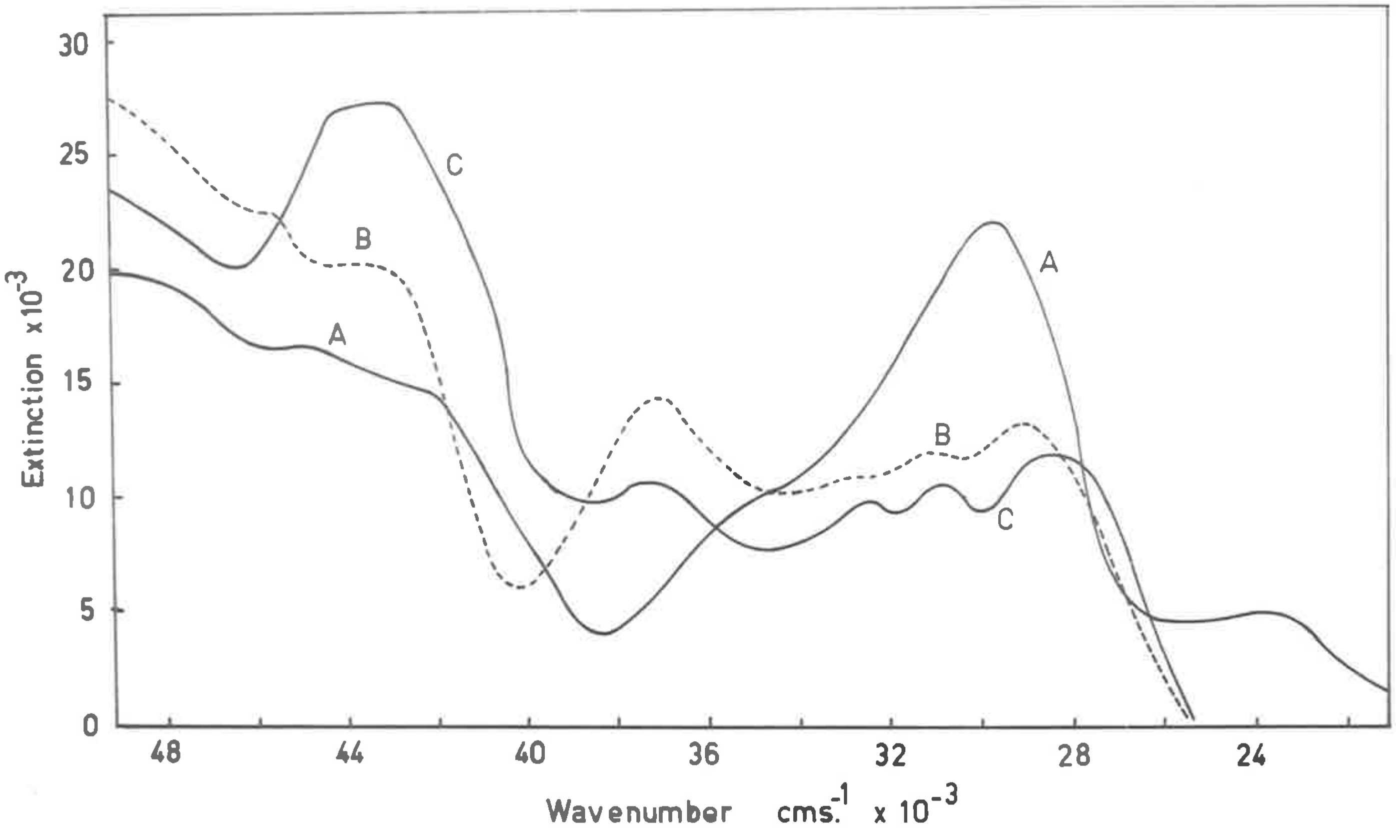

Fig.(II)-5. The electron absorption spectra at 25°C. of
A. N-p-tolyl-4-hydroxysalicylideneimine in methanol.
B. N-p-bromophenylsalicylideneimine in cyclohexane.
C. N-p-tolyl-5-bromosalicylideneimine in cyclohexane.

compounds a difference of less than 500 cms.$^{-1}$ is found between the calculated and observed transition energy of the $^1H \longleftarrow {}^1A$ band. This excellent agreement argues strongly in favour of both the transition assignments and energies given in Table (II)-8.

TABLE (II)-8.

The spectral properties of

N-X-phenyl-5-bromosalicylideneimine in cyclohexane at 25°C.

X	$^1B \longleftarrow {}^1A$		$^1G \longleftarrow {}^1A$		$^1H \longleftarrow {}^1A$	
	cms.$^{-1}$	ϵ	cms.$^{-1}$	ϵ	cms.$^{-1}$	ϵ
H	28,250	9,810	31,300 34,050	7,900 7,200	36,900	11,460
p-CH$_3$	27,950	11,890	31,000 33,400	8,650 7,430	36,900	10,600
m-CH$_3$	28,050	10,330	31,300 34,000	7,580 7,430	37,000	10,900
m-F	27,900	9,210	31,100 33,700	7,900 7,900	36,800	11,720

The low intensity found for the $^1H \longleftarrow {}^1A$ band may result from a lifting of the degeneracy of this transition ($v_u \rightarrow w_g$, $v_g \rightarrow w_u$), resulting from the greater assymmetry of the Schiff's bases bearing a second substituent on the aldehydo residue. A possible decrease in the transition moment may also be suggested.

b. N-p-tolyl-4-hydroxysalicylideneimine.

Addition of a second hydroxy group to the aldehyde residue of the Schiff's base is, by comparison with the 5-bromosalicylaldehyde compounds, expected to give rise to a bathochromic shift in all bands. That such a shift has in fact occurred in the longest wavelength band is obvious from the orange-red colour of the compound.

Assignment of the spectral transitions of this compound is rather difficult as only three bands are found with an energy below 42,000 cms.$^{-1}$. Since the bathochromic shift on addition of the second hydroxy group to the aldehyde residue is presumably greater than that occurring on 5-bromination, the ${}^1H \longleftarrow {}^1A$ band in the 4-hydroxysalicylaldehyde Schiff's base will appear at energies less than 37,000 cms.$^{-1}$. One may thus assign the band at 34,800 cms.$^{-1}$ to the ${}^1H \longleftarrow {}^1A$ excitation. This then leaves two bands at longer wavelengths to assign to the two ${}^1G \longleftarrow {}^1A$ transitions and to the ${}^1B \longleftarrow {}^1A$ transition.

The low intensity, longest wavelength band presumably arises from the ${}^1B \longleftarrow {}^1A$ transition. Such a low intensity for this band seems reasonable since the ground (f_u) state would already be highly polarized, decreasing the transition moment of the ${}^1B \longleftarrow {}^1A$ excitation. Although a similar argument can be presented for the low intensity

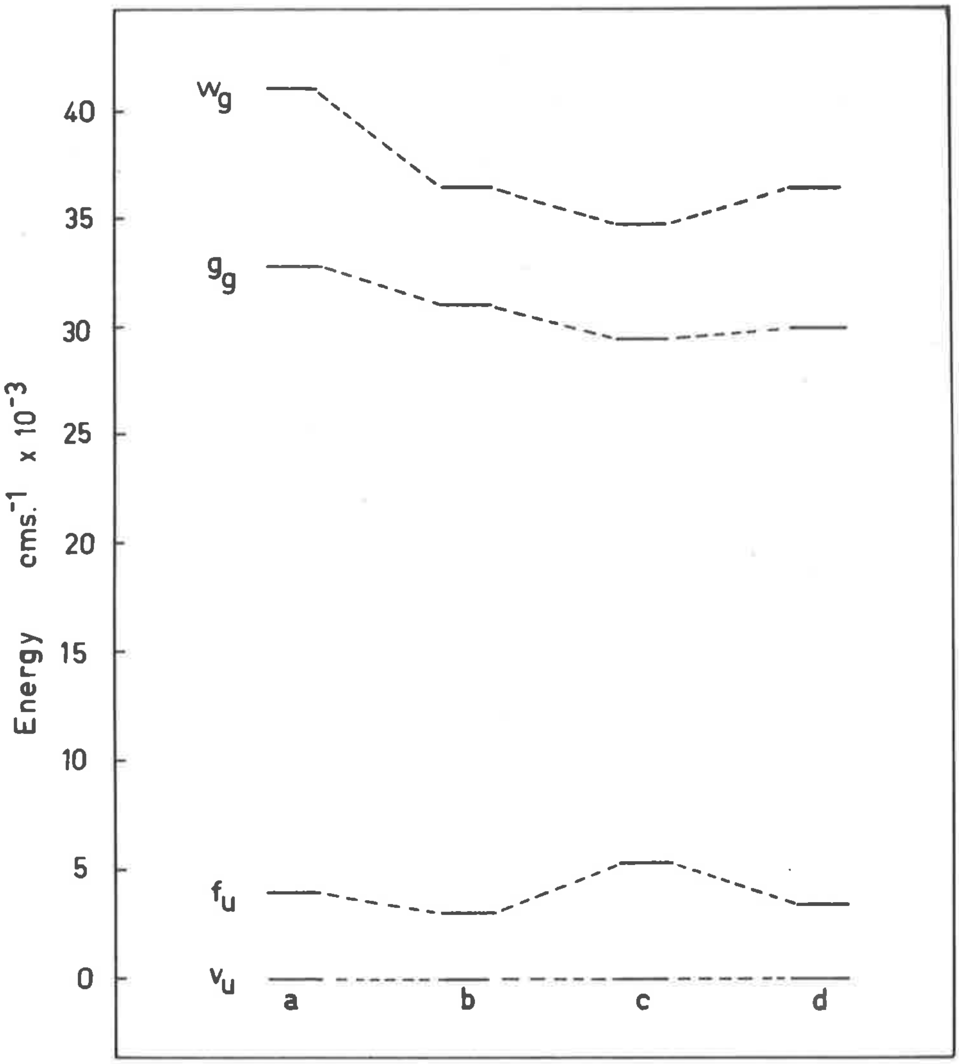

Fig.(II)-6. The energy level diagram for
a. N-p-tolylsalicylideneimine.
b. N-p-tolyl-5-bromosalidylideneimine.
c. N-p-tolyl-4-hydroxysalicylideneimine.
d. N-p-tolyl-2-hydroxy-1-naphthylideneimine.

of the ${}^1H \longleftarrow {}^1A$ band, an alternative explanation, based on the degeneracy of this band may also be considered.

TABLE (II)-10.

The spectral properties of

N-p-tolyl-4-hydroxysalicylideneimine

in dry methanol at 25°C.

Transition	cms.$^{-1}$	ϵ
${}^1B \longleftarrow {}^1A$	24,050	4,770
${}^1G \longleftarrow {}^1A$ ${}^1G \longleftarrow {}^1A$	29,400	22,000
${}^1H \longleftarrow {}^1A$	34,800	9,430

The band at 29,400 cms.$^{-1}$ can now be assigned to both the ${}^1G \longleftarrow {}^1A$ transitions, the high symmetry of the band suggesting that both transitions are of nearly equal energy. The plausibility of such a postulate is supported by the fact that in the 5-bromosalicylaldehyde Schiff's bases the high energy ${}^1G \longleftarrow {}^1A$ $(f_u \rightarrow w_g)$ transition experiences a bathochromic shift approximately 30% larger than the low energy ${}^1G \longleftarrow {}^1A$ transitions. Again, the high intensity of the band is indicative of two overlapping bands.

Besides inducing changes on the spectral properties of the parent compound, the 4-hydroxy group has a marked effect on the solubility of the Schiff's base. Its insolubility in cyclohexane and ready solution in methanol was ascribed to intermolecular hydrogen bonding of the 4-hydroxy group. Since no hydroxy stretching band was found in the infrared spectrum, the hydrogen bonding is strong[23].

e. 2-hydroxy-1-naphthaldehyde Schiff's bases.

In an investigation of the spectral properties of these compounds, Voss et.al.[24] and Cohen et.al.[25] found that the long wavelength bands experience large bathochromic shifts on replacement of non-polar solvents by polar ones. Voss and co-workers associated this shift with changes in the character of the hydrogen bond. Whereas in non-polar solvents, the hydrogen bond is of the form OH....N, in polar solvents this bond may be best represented by the structure O····HN. The increased negative charge on the oxygen, together with the higher positive charge on the nitrogen found in the O····HN form was considered to stabilize the lowest energy anti-bonding pi state. Cohen et.al.[25] arrived at the same conclusion and demonstrated that the spectral change was also temperature dependent.

The occurrence of this tautomerism in the naphthaldehyde compounds but not in the corresponding salicylaldehyde Schiff's bases, was considered by these workers[25] to be a result of the electron withdrawing effect of the naphthaldehyde residue.

The spectra of several of these Schiff's bases were determined at 25°C in cyclohexane. Assuming a similar set of electronic energy levels as found in the salicylaldehyde Schiff's bases, the spectral assignments given in Table (II)-11 can be made.

TABLE (II)-11.

The spectral properties of

N-X-phenyl-2-hydroxy-1-naphthylideneimine

in cyclohexane at 25°C.

X	$^1B \longleftarrow {}^1A$		$^1G \longleftarrow {}^1A$		$^1H \longleftarrow {}^1A$	
	cms.$^{-1}$	ϵ	cms.$^{-1}$	ϵ	cms.$^{-1}$	ϵ
$\underline{o}$-CH_3	26,450	13,150	30,800 32,400	7,360 5,690	38,000	9,800
$\underline{p}$-CH_3	26,400	13,020	30,100 32,100	9,580 7,400	37,800	7,800
$\underline{m}$-CH_3	26,500	15,130	29,900 32,000	8,300 8,850	37,200	7,500

These naphthaldehyde Schiff's bases show a similar convergence in the energies of the $^1G \longleftarrow {}^1A$ bands as is the case in the 5-bromosalicylaldehyde Schiff's bases, and in particular in the 4-hydroxysalicylaldehyde compound. The explanation based on the high stabilization of the w_g state again appears feasible.

Application of the Braude-Sondheimer expression to the o-tolyl compound gives a value of 21° for the angle of twist about the carbon-nitrogen "single" bond. This angle of twist is strikingly similar to that calculated for N-o-tolylsalicylideneimine (23°).

(v) Solvent Effects

The energy of the transitions will presumably depend in part on the solvent sphere[26] about the Schiff's base molecules. The main effects may be summarized thus:[27]

1. When both solute and solvent are polar, the interaction is of the dipole-dipole type, an increase in the dipole moment on excitation leading to a red shift and a decrease in moment resulting in a blue shift.

2. In the case of a non-polar solute, a polar solvent will stabilize the more polar excited states to a greater extent than the ground states, leading to a red shift.

TABLE (II)-12.

The absorption characteristics of the $^1B \longleftarrow {}^1A$ transition of several N-X-phenylsalicylideneimine Schiff's bases in cyclohexane, dimethylformamide (DMF) and pyridine at 25°C.

R	Cyclohexane		DMF		Pyridine	
	cms.$^{-1}$	ϵ	cms.$^{-1}$	ϵ	cms.$^{-1}$	ϵ
o-CH_3	29,050	11,380	29,200	11,630		
p-CH_3	28,900	13,450	28,950	13,450	28,700	12,560
o-OCH_3	28,450	12,180	28,250	11,680		
p-OCH_3	28,350	16,610	28,250	17,140		
o-F	28,800	11,080	29,050	11,780		
p-F	28,900	11,630	29,200	11,750	29,000	11,600

Replacement of cyclohexane by dimethylformamide (See Table (II)-12) is followed by a slight increase in the band intensities. This trend however, has an exception in N-*o*-anisylsalicylideneimine. The intensity of the *p*-fluorophenyl Schiff's base $^1B \longleftarrow {}^1A$ band is apparently independent of the solvent. Although the same is true for the *p*-tolyl compound in cyclohexane, and dimethylformamide, a large decrease in intensity is found in pyridine.

Both bathochromic and hypsochromic shifts are observed on changing the solvent from cyclohexane. These shifts are little larger than the error in their measurement, thus suggesting that the OH····N hydrogen bond is unaltered by the various solvents.

The angles of twist about the nitrogen-carbon "single" bond of the substituted Schiff's bases, calculated using the Braude-Sondheimer formula, were found to be unaltered by dimethylformamide, except in the case of N-o-fluorophenylsalicylideneimine for which a planar structure was predicted.

(vi) Schiff's base chelates of zinc.

Bregman et.al.[17] showed, by X-ray analysis, that salicylaldehyde Schiff's bases substituted in the ortho position of the aniline residue were twisted about the carbon-nitrogen "single" bond, while the Schiff's bases not carrying this ortho-substituent were essentially planar. Wei et.al.[28] and von Stackelberg[29] demonstrated - also by X-ray analysis - the non-planarity of the unsubstituted Schiff's base on coordination to copper. It is thus tempting to postulate a non-planar structure for Schiff's bases tetrahedrally coordinated about a metal. Again, while copper chelates of most ortho-substituted Schiff's bases are obtained with ease, the corresponding cobalt(II) compounds could not be readily prepared[1]. This presumably is due to a higher distortion of the ligand on tetrahedral coordination[1]. To demonstrate the accuracy of these postulates, a spectral investigation of tetrahedrally coordinated Schiff's bases was undertaken.

The zinc(II) Schiff's base chelates lend themselves readily to such a spectral study since, through the absence of charge transfer bands, all ligand transitions are observable. Since on zinc chelation, the $O\cdots H\cdots N$ bond is in effect replaced by an $O\cdots Zn\cdots N$ linkage, little change should be affected on the ligand properties.

TABLE (II)-13.

The spectral properties of the $^1B \longleftarrow {}^1A$ band for bis(N-R-salicylideneiminato)zinc(II) in benzene at 25°C.

R	cms.$^{-1}$	ϵ
m-tolyl	28,850	21,150
p-tolyl	28,900	21,370
o-anisyl	24,250	14,470
p-anisyl	28,150	29,410
m-chlorophenyl	28,900	22,180
p-chlorophenyl	28,800	26,360

The small change in the energy of the $^1B \longleftarrow {}^1A$ transition found for the meta- and para-substituted Schiff's bases on zinc chelation supports the notion that the configuration of these bases is not altered drastically on chelation with "tetrahedral" metals. Although little change in the energy of the band is found, all the compounds experience a drop in extinction (per Schiff's base) except the p-chlorophenyl compound. It is interesting to observe that this compound is also the only zinc chelate to be phototropic at room temperature. The observed decreases in intensity may, in part, arise from a twisting of the bases away from planarity on chelation.

The zinc chelates of the ortho-substituted ligands could not be prepared using the methods developed for preparation of cobalt(II) Schiff's base compounds[30]. Hence a comparison of the angles of twist, calculated from the spectral intensities of the para- and ortho-substituted Schiff's base zinc chelates, cannot be made.

The ortho-anisyl Schiff's base was atypical, as the zinc chelate is easily obtained. This parallels the findings of West[1] in the Schiff's base chemistry of cobalt(II). He proposed an octahedral configuration for bis(N-o-anisylsalicylideneiminato) cobalt(II). The low intensity and the high bathochromic shift of 4,600 cms.$^{-1}$ found for the zinc complex are in accord with such a

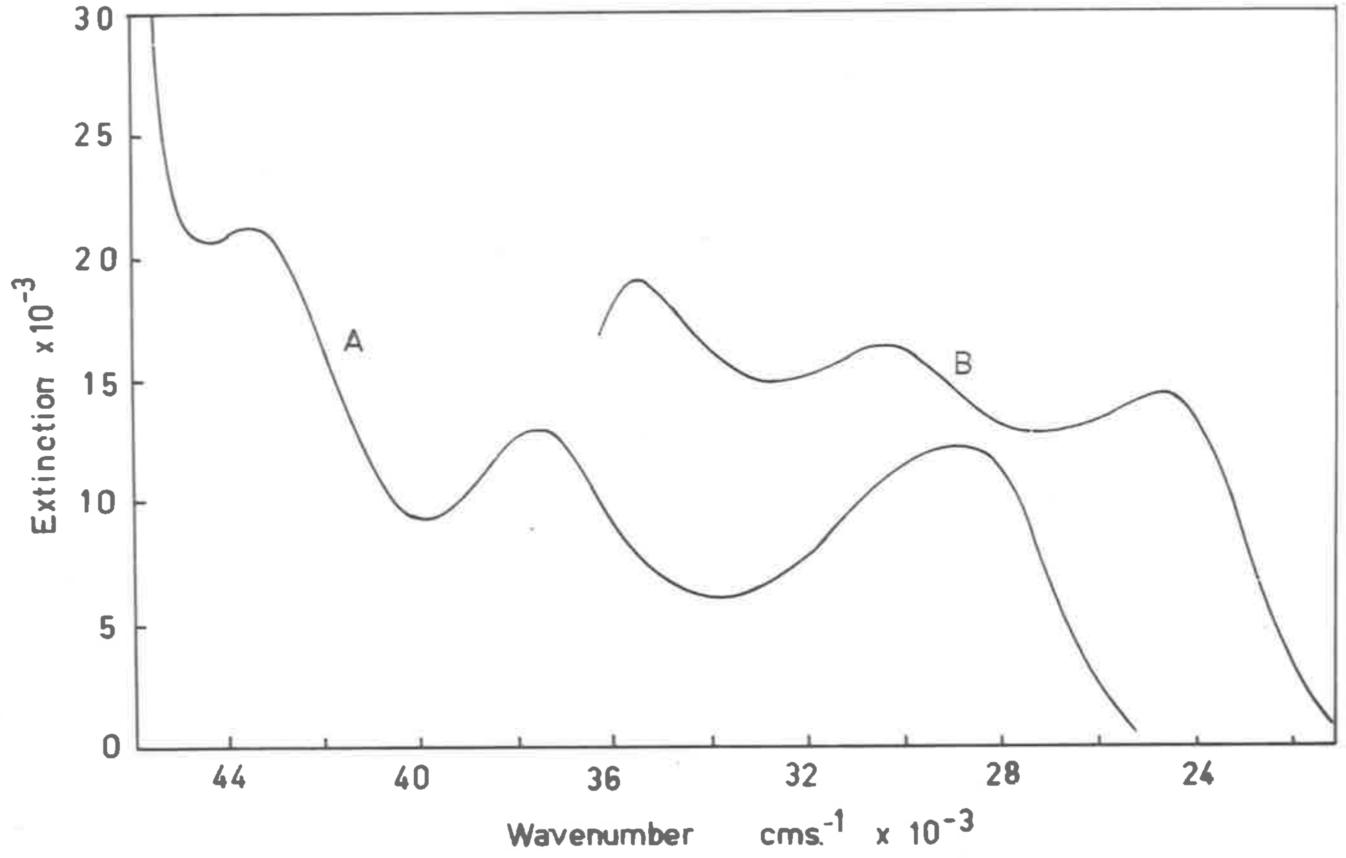

Fig.(II)-7. The electron absorption spectra at 25°C. of
A. N-*o*-anisylsalicylideneimine in cyclohexane.
B. Bis(N-*o*-anisylsalicylideneiminato)zinc(II) in benzene.

proposal. The absence of a bathochromic shift on complexing the p-anisyl Schiff's base with zinc argues against intermolecular bonding through the methoxy group.

3. Summary

The similarity in the spectra of N-phenylsalicylideneimine Schiff's bases with those of N-R-benzylideneimine suggests that similar spectral assignments can be made for both type of compounds. A comparison with the work of Jaffe et.al.[4,7] and others[5,22] led to the assignments for all the low energy ultraviolet transitions found in the salicylaldehyde Schiff's bases.

Variation in the nature and position of the substituent on the aniline residue has little effect on the spectral properties, except in the case of nitro- and methoxy-substitution in which appreciable participation of the substituent with the parent electron system does occur. On these grounds, substitution on the amine residue should not effect the coordination ability of the ligand to any extent.

The work of Bregman et.al.,[17] extended to other ortho substituted Schiff's bases by the use of the Braude-Sondheimer formula, shows that these ligands are distorted from planarity. Because of the inability to prepare the ortho-substituted Schiff's base zinc chelates, no comparison of the angle of twist about the carbon-nitrogen "single" bond in the free base and the complexed one could be made. However, since steric strain is the only apparent difference between the various Schiff's bases the preparational difficulties presumably arise from steric strain.

The surprising ease of preparation of the ortho-methoxy Schiff's base zinc(II) chelate, together with the large spectral changes incurred on chelation, strongly supports an "octahedral" configuration for this compound.

The greater dependence of the spectral properties of the Schiff's bases on substitution in the aldehyde ring system as compared to substitution on the aniline residue indicates by comparison with the work of Smith[22], that the $^1B \longleftarrow {}^1A$ transition involves a migration of electrons into the aniline residue. This effect, reverse to that found in the N-phenylbenzylideneimine, is presumably due to hydrogen bonding.

It may be noted that an infra-red spectral investigation of all Schiff's bases proved to be fruitless, as no definite substitution trends were observed.

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CHAPTER III.

NON-AQUEOUS COORDINATION OF SCHIFF'S BASES.

1. Introduction.

Schiff's bases derived from salicyladehyde possess functional groups in the imine nitrogen and in the phenolic hydroxy group. The bidentate nature of these Schiff's bases on reaction with metal salts in acetate buffered or alkaline solutions has been well established.[1,2] However, under neutral, non-aqueous conditions the Schiff's bases may presumably act as monodentates, the hydrogens remaining attached to the phenolic groups. To test the validity of this postulate, a study of the reaction of Schiff's bases with cobalt halides under non-aqueous conditions was undertaken.

From the formation of a series of monodentate-Schiff's base cobalt halide complexes a comparison of the amount of strain involved in the metal-imine nitrogen bond with the position of the substituent on the amine residue can be made. The use of such a study is that it can give a knowledge of the importance of steric effects operating in the bidentate complexes of the form bis(N-R-salicylideneiminato) cobalt(II).

The studies on cobalt complexes have been extended, in part, to cover the behaviour of other metal halides with Schiff's bases. Several interesting variations in the coordination tendencies of the metals were observed.

2. Cobalt(II) Complexes.

The interaction of cobalt(II) halides with N-arylsalicylideneimines in ethanol produces a 1:2 complex (cobalt:ligand) as determined by a continuous variation study involving cobalt chloride and either the *p*-tolyl or *o*-tolyl-salicylideneimines. Green compounds could be isolated from such reaction mixtures and analysis showed the complexes to have the empirical formula $Co(BH)_2X_2$, where BH represents a molecule of Schiff's base and X is a halide or thiocyanate ion.

The compounds were slightly soluble in solvents which were capable of strong hydrogen bonding such as alcohols or dimethylformamide, but were virtually insoluble in other common solvents.

The magnetic moments of the compounds all lie in the range 4.3 - 4.8 B.M. which is characteristic of cobalt(II) complexes having a tetrahedral arrangement of the ligands about the metal.[3,4] Similarly the reflectance spectra of the compounds all showed the intense multicomponent band in the region 18,000-13,000 $cms.^{-1}$ which is diagnostic for tetrahedral cobalt(II) complexes.[5] The type of spectra obtained are shown in Figs. (III)-2 and (III)-3. The complexes were easily dissociated in

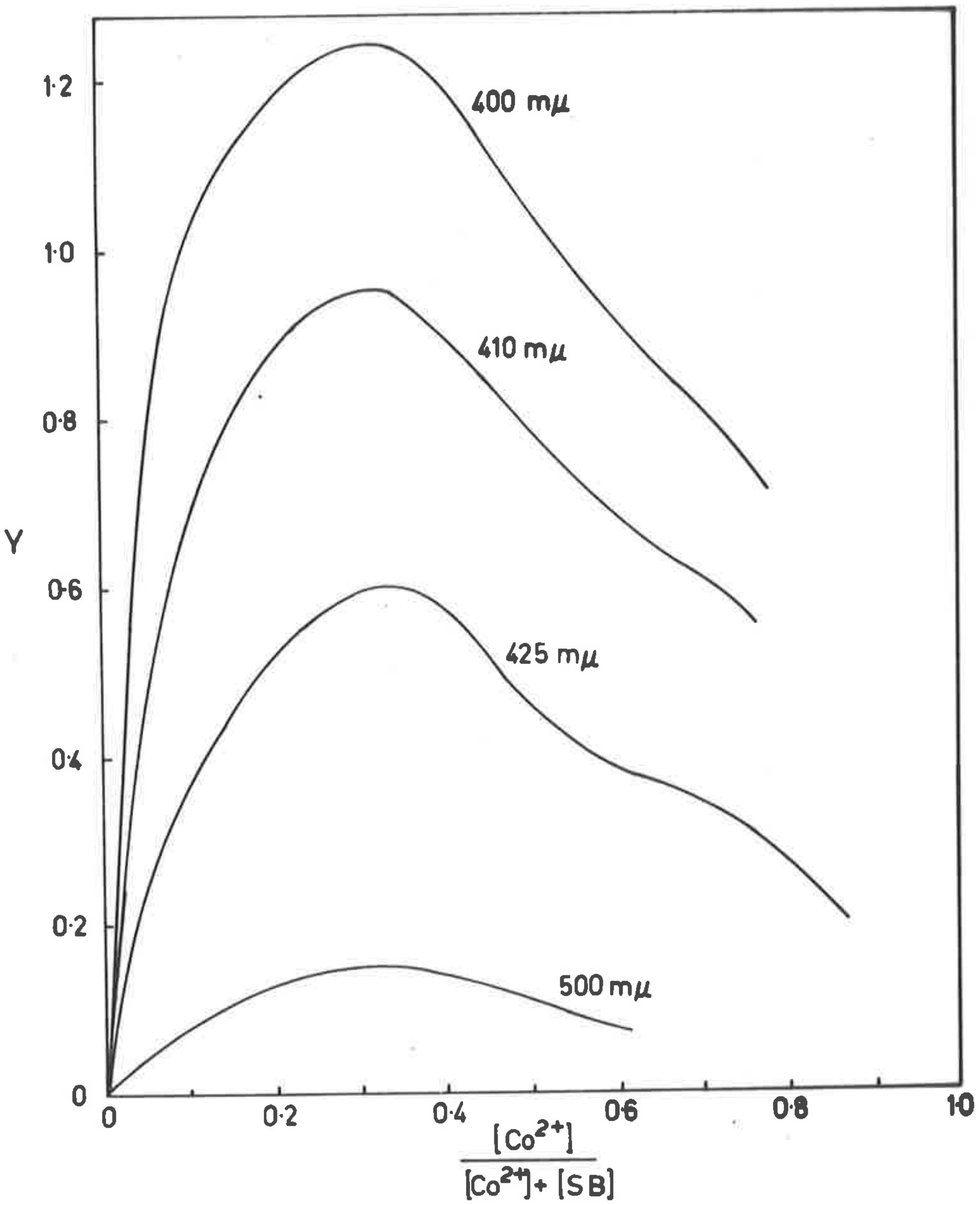


Fig.(III)-1. Continuous variation results for the reaction of cobalt chloride with N-p-tolylsalicylideneimine in ethanol. Y is a function of the solution optical density.

donor solvents. Thus the spectra of dilute solutions (10^{-4}M.) of the compounds in ethanol or n-propanol were identical with the spectra of the free Schiff's bases and no longer showed the "tetrahedral" cobalt(II) bands.

The p-tolyl-cobalt chloride complex was sufficiently soluble in ethanol for an ebullioscopic molecular weight determination to be attempted, but the low value obtained (373) compared to the theoretical value based on an assumed composition of $Co(BH)_2X_2$, (552), indicated that extensive dissociation had occured.

(i) The structure of the complexes.

There are three possible formulae for these pseudo-tetrahedral complexes having the empirical formula $Co(BH)_2X_2$, namely:

$$\underset{\text{I}}{\left[Co(BH)_2\right]^{2+} X_2^{\;2-}}, \quad \underset{\text{II}}{Co(BH)_2X_2} \quad \text{and} \quad \underset{\text{III}}{\left[Co(BH)_4\right]^{2+}\left[CoX_4\right]^{2-}}.$$

In these formulae above BH refers to a Schiff's base still possessing the phenolic hydrogen and X is a halogen or thiocyanate ion. Structures II and III assume the Schiff's bases to be unidentate and to coordinate through the imine nitrogen, whereas the structure I proposes that the coordination is through both the nitrogen and the hydroxy oxygen atoms.

TABLE (III)-1.

The Spectral Properties[a] of

bis(N-R-salicylideneimine)dihalocobalt(II) complexes.

R	Halogen	$^4A_2 \longrightarrow ^4T_1(F)$ cms.$^{-1}$	$^4A_2 \longrightarrow ^4T_1(P)$ cms.$^{-1}$
o-tolyl	Cl	7,250(s)	17,200
		5,900	15,650
		5,300(s)	14,850
m-tolyl	Cl	7,700	17,000
		6,100	16,100
		5,500(s)	15,050
p-tolyl	Cl	7,500(s)	17,200
		6,150	15,700
		5,150(s)	14,850
o-anisyl	Cl	7,600	17,100
		5,800	16,250
		5,600(s)	14,850
p-anisyl	Cl	6,700	16,750
		6,000	16,200
		5,400	14,400
cyclohexyl	Cl	7,300	16,750
		6,000	15,800
		5,400(s)	14,950
p-tolyl/pyridine[b]	Cl	8,450	16,950
		6,900	15,150
		5,450	15,250
o-tolyl	Br	7,000	17,350
		6,000	15,300
		5,200(s)	14,450

contd...

TABLE (III)-1. (contd.)

R	Halogen	$^4A_2 \longrightarrow {}^4T_1(F)$ cms.$^{-1}$	$^4A_2 \longrightarrow {}^4T_1(P)$ cms.$^{-1}$
m-tolyl	Br	7,300 5,900 5,000(s)	17,000 15,300 14,300
p-tolyl	Br	7,450 5,800 5,200	16,750 16,000 14,700
p-chlorophenyl	I	7,250 5,900 5,100	16,500 15,270 13,700
p-tolyl	SCN	8,250 7,300(s)	17,500(s) 16,400

a. From the mull transmission spectra.

b. Refers to the complex monopyridine(N-*p*-tolyl-salicylideneimine)dichlorocobalt(II).

If the complexes can be represented by structure III above, the effect of both the anion and cation configuration must be considered. While the tetra-halo cobalt(II) anions have been shown to be tetrahedral[6], the cation $Co(BH)_4^{2+}$ may be planar or tetrahedral. Assuming equal spectral intensities for both ions, a complex visible spectrum is expected due to the differences in ligand field strengths between the Schiff's bases and the halide ions. However, the identification of only two three-component bands in the mull transmission spectrum (visible and near infra-red) suggests that only one absorbing species is important. (See Fig.(III)-3 and Table (III)-1).

If the absorption is then due to the CoX_4^{2-} ions, absorption bands in the regions given in Table (III)-2 are expected.

TABLE (III)-2.

The position of the absorption bands of the cobalt(II) tetrahalide ions. (From reference 5).

	$^4A_2 \rightarrow {}^4T_1(F)$	$^4A_2 \rightarrow {}^4T_1(P)$
Cl^-	5,220 - 5,700 $cms.^{-1}$	14,600 - 14,800 $cms.^{-1}$
Br^-	4,880 - 5,080	13,800 - 14,200
I^-	4,500 - 4,700	13,000 - 13,500

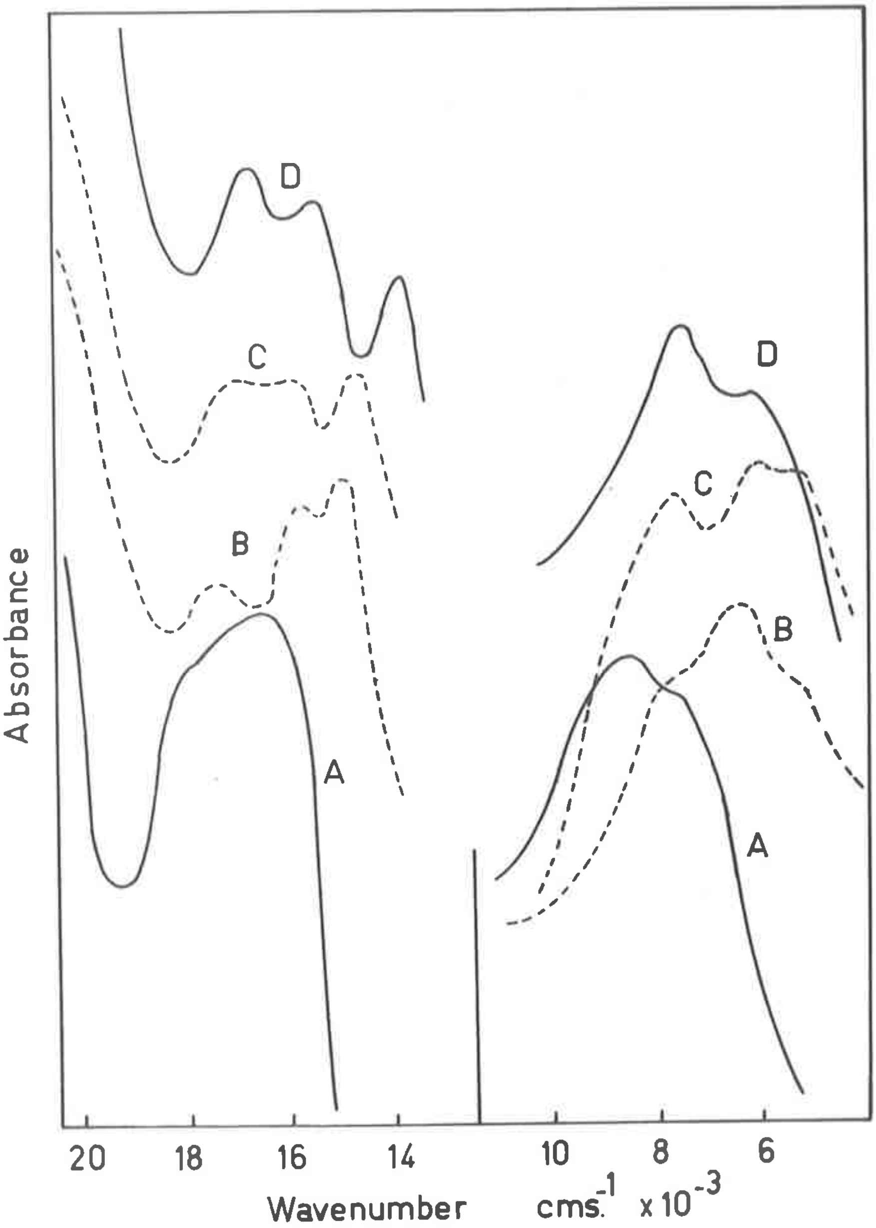


Fig.(III)-3. The mull transmission spectra of
A. Bis(N-p-tolylsalicylideneimine)-dithiocyanatocobalt(II).
B. Bis(N-p-tolylsalicylideneimine)dichlorocobalt(II).
C. Bis(N-p-tolylsalicylideneimine)dibromocobalt(II).
D. Bis(N-p-chorophenylsalicylideneimine)-diiodocobalt(II).

Since the bands found (see Table (III)-1) do not coincide with the regions given in Table (III)-2, the absorbing species cannot be the CoX_4^{2-} ion. The high values found for the spectroscopic parameters B' and $10D_q$ confirms this conclusion[5]. (See Table (III)-4.)

The absorption characteristics are also inexplicable on the basis of the $Co(BH)_4^{2+}$ species as the spectral properties of the complexes vary appreciably with the nature of the halogen, suggesting that the absorptions arise from a species in which the halogens are attached to the metal. (See Table (III)-3.)

TABLE (III)-3.

The effect of the halogen on the absorption band energies[a] of bis(N-p-tolylsalicylideneimine)dihalocobalt(II) complexes.

Halogen	$^4A_2 \longrightarrow {}^4T_1(F)$	$^4A_2 \longrightarrow {}^4T_1(P)$
SCN^-	7,780 $cms.^{-1}$	16,950 $cms.^{-1}$
Cl^-	6,270	15,920
Br^-	6,150	15,820

a. The energies correspond to the band baricentre.

On the basis of the above evidence it can be concluded that the complexes do not have the structures

$$\left[Co(BH)_4\right]^{2+}\left[CoX_4\right]^{2-} \quad or \quad \left[Co(BH)_2\right]^{2+} \; X_2{}^{2-}.$$

Hence the structure $Co(BH)_2X_2$, with which the magnetic and spectral results are found to be in good accord, can be taken as representing the formula of these cobalt halide Schiff's base complexes.

On reaction, of cobalt chloride with N-p-tolylsalicylideneimine in absolute ethanol containing pyridine, a heterogeneous precipitate containing orange, pink and green crystals formed. By heating this product in air the green complex mono-pyridine(N-p-tolylsalicylideneimine)cobalt(II)dichloride was obtained. Recrystallization of the initial reaction product from a dilute solution of pyridine in ethanol gave the same compound. In the absence of pyridine, recrystallization gave a mixture of di- and tetra- pyridinates of cobalt dichloride. While the initial reaction product could not be obtained in a pure state, it lost sufficient pyridine on heating to suggest that it was initially a six coordinated complex.

The formation of this monopyridinate Schiff's base cobalt dichloride complex suggests that the coordination of the Schiff's base to the metal proceeds through the imine nitrogen.

The presence of an acidic hydrogen in these complexes was confirmed by alkali titration, when red compounds of the type bis(N-R-salicylideneiminato)cobalt(II) where obtained in good yields.

The insolubility of these cobalt dihalide Schiff's base complexes may possibly be related to intermolecular hydrogen bonding involving the hydroxy groups. Negative evidence for this was found in that no hydroxy stretching bands were observed in their infrared spectra. The low stability of these complexes in solution suggests that their isolation is dependent on their insolubility.

An attempt was made to prepare complexes of cobalt dichloride with N-p-tolylbenzylideneimine-2-benzoate. However, only the compound bis(N-p-tolylsalicylideneimine)-dichlorocobalt(II) was obtained. Apparently, under the reaction conditions, hydrolysis of the ester grouping occurs.

(iii) Spectral properties.

The quartet ground state term of cobalt(II) will be split into three levels on application of a tetrahedral ligand field, the lowest being non-generate ($^4A_2$) while the upper two ($^4T_2$ and $^4T_1$ in order of increasing energy) are triply degenerate. A $^4T_1(P)$ term arising from the ^4P term of the free gaseous ion, lies above the $^4T_1(F)$ level. These terms are the only spin free terms possible for ions of a d^7 electron configuration in a tetrahedral ligand field.

The spin allowed transitions which may then ensue on excitation are the $^4A_2 \longrightarrow {}^4T_2$, the $^4A_2 \longrightarrow {}^4T_1(F)$ and the $^4A_2 \longrightarrow {}^4T_1(P)$ transitions. In general, for tetrahedral cobalt(II), the transition to the $^4T_2$ state occurs in the vicinity of 3,000 cms.$^{-1}$, the $^4T_1(F)$ transition at roughly 6,000 cms.$^{-1}$, with the highest energy transition ($^4A_2 \longrightarrow {}^4T_1(P)$) being in general found in the visible spectral region (15,000 - 17,000 cms.$^{-1}$).[5]

Thus, following these assignments, the multicomponent band in the vicinity of 16,000 cms.$^{-1}$ in the Schiff's base cobalt halide complexes can be considered to arise from the $^4A_2 \longrightarrow {}^4T_1(P)$ transition, with the band in the near infra-red region being attributed to the $^4A_2 \longrightarrow {}^4T_1(F)$ excitation. (See Table (III)-1.)

TABLE (III)-4.

The Electronic Spectral Parameters of
bis(N-R-salicylideneimine)dihalocobalt(II) complexes.

R	Halogen	100Dq[b] cms.$^{-1}$	B'[c] cms.$^{-1}$	β'[d]
o-tolyl	Cl	3,530	763	0.789
m-tolyl	Cl	3,700	758	0.784
p-tolyl	Cl	3,610	758	0.784
o-anisyl	Cl	3,650	765	0.791
p-anisyl	Cl	3,460	762	0.788
cyclohexyl	Cl	3,580	754	0.780
p-tolyl/pyridine[a]	Cl	4,010	734	0.759
o-tolyl	Br	3,490	754	0.780
m-tolyl	Br	3,490	742	0.767
p-tolyl	Br	3,530	758	0.784
p-chlorophenyl	I	3,500	716	0.740
p-tolyl	SCN	4,530	743	0.768

a. Complex is monopyridine(N-*p*-tolylsalicylideneimine)-dichlorocobalt(II).

b. Ligand field splitting parameter.

c. The interelectronic repulsion parameter.

d. The nephelauxetic ratio. (B for the free ion is 971 cms.$^{-1}$)

On the basis of these assignments it is possible to compute the ligand field parameters 10Dq and B'. (See Table (III)-4.) The values calculated for these parameters are very similar to those found by Cotton et.al.[8,9] for the cobalt halide diphosphines.

Spectral studies on cobalt complexes containing halogen ions have shown that the ligand field splitting of the halogen ions varies in the order $NCS^- > Cl^- > Br^- > I^-$. A similar variation in 10Dq with halide ion in the cobalt halide Schiff's base complexes is both expected and found.

TABLE (III)-5.

Variation of the parameters 10Dq and B' with the halogen ion in the complexes bis(N-R-salicylideneimine)dihalocobalt(II).

R	Halogen	10Dq $cms.^{-1}$	B' $cms.^{-1}$
p-tolyl	NCS^-	4,530	743
p-tolyl	Cl^-	3,610	758
p-tolyl	Br^-	3,530	758
p-chlorophenyl	I^-	3,500	716

The high value of 10Dq for the thiocyanate complex leaves no doubt that the thiocyanate ion is bound to the cobalt through the nitrogen[10]. This postulate is strengthened by the low magnetic moment of the complex. (See Table (III)-6.) Supporting infra-red spectral evidence was also obtained. A strong thiocyanate C-N stretching band was found at 2,035 cms.$^{-1}$ which was weakly split into a doublet; a shoulder appeared at 2,038 cms.$^{-1}$. Although this band is not as diagnostic as the C-S stretching band[10] found in the 700-900 cms.$^{-1}$ region, its slightly depressed value is indicative of nitrogen coordination in the thiocyanate group[11,12]. The low energy band could not be observed among the strong Schiff's base absorptions.

The assumption that the ligand field strength in the complexes under investigation can be divided into contributions from the halide ions and the Schiff's base ligands, allows the approximate calculation of the Schiff's base ligand field strength to be made. On this basis, using the values given by Cotton et.al.[10] for the ligand field strengths of the halide ions, the value of 10Dq for the Schiff's bases was computed to lie between 4,000 and 4,500 cms.$^{-1}$. This is roughly equal in magnitude to that associated with the thiocyanate ion.

The separation of the components of the ligand field spectral bands depends on both the extent of spin-orbit coupling[13] and on the ligand field symmetry[8]. As the ligand field strengths of the thiocyanate ion and the Schiff's bases are nearly of equal magnitude, the multi-component bands of this compound are expected to show a minimum in energy spread. This was in fact found, the width of the band being only half that for the other complexes.

Since the monopyridinate complex has a higher 10Dq value than the corresponding bis-Schiff's base complex, the pyridine presumably lies above the Schiff's bases in the spectrochemical series.

The interelectronic repulsion parameter B is defined in terms of the Racah parameters F_2 and F_4 ($B = F_2 - 5F_4$) such that the separation of the two spectroscopic states of maximum multiplicity is given by a multiple of B. Thus, the separation of the baricentres of the quartet states ^4P and ^4F in cobalt(II) is given by 15B. A lowering in B then indicates a decreased electronic repulsion between the ^4P and ^4F states, which can be associated with an increase in covalent bonding in complexes.[14] The relative tendency for a particular ligand to form covalent bonds with a metal can be readily gauged from its position in the nephelauxetic series.

The order of the halide ions in the complexes under investigation in the nephelauxetic series is

$I^- > NCS^- > Cl^-$, Br^-.

Taking the values of B' obtained from the bis-Schiff's base cobalt chloride complexes, the neutral ligands give rise to the nephelauxetic series

Pyridine > cyclohexyl- > m-tolyl-; p-tolyl- > p-anisyl- > o-tolyl- > o-anisyl- salicylideneimine Schiff's base.

Because of the similarity in the B' values, the order of the ligands in the above series is highly dependent on small errors. However, the position of pyridine at the head of the series is unlikely to be challenged. Possibly the main error introduced into the B' value of the cobalt complexes arises from the coupling of the spin-paired doublets $^2E(G)$ and $^2T_1(G)$ with the quartet $^4T_1(P)$ level[14].

In the spectrum of the cyclohexyl Schiff's base cobalt chloride complex a third transition is found above the $^4A_2 \longrightarrow {}^4T_1(P)$ excitation. This weak band appearing at 19,400 $cms.^{-1}$ is ascribed to the spin forbidden $^4A_2 \longrightarrow {}^2E(G)$ excitation. The intensity of this band arises from an admixture of the $^2E(G)$ state with the $^4T_1(P)$ one[15].

(iii) Magnetic properties.

Since tetrahedral cobalt(II) is spin-free, a magnetic moment equal to or greater than the spin only moment ($\mu_{s.o.}$) is predicted. The non-degenerate character of the lowest energy level (the $^4A_2$ state) suggests that the magnetic moment may be expressed by the formula

$$\mu_{eff.} = \sqrt{4S(S+1)}\ \text{B.M.} \qquad \text{(III)-1.}$$

However, by spin-orbit coupling the $^4A_2$ level can "mix in" with the higher energy quartet states possessing angular momentum[16]. This admixture of energy states is dependent on both the energy separation between the $^4A_2$ and $^4T_2$ states (10Dq) and upon the spin-orbit coupling constant (λ), such that

$$\mu_{eff.} = \mu_{s.o.}(1 - \frac{4\lambda'}{10Dq}) \qquad \text{(III)-2.}$$

In contrast to the tetrahedral case, octahedral cobalt(II) has a triply degenerate quartet ground state ($^4T_{1g}$). On this point rests the diagnostic value of magnetic moments in deciding on the configuration of cobalt(II) complexes[3,4]. Whereas the octahedral compounds have moments in excess of 4.8 B.M., "tetrahedral" moments are generally found between the spin-only value and 4.8 B.M.

The paramagnetism shown by the mixed Schiff's base - halogen cobalt complexes is then explicable only on the basis of a tetrahedral configuration. (See Table (III)-6.)

The moments determined for the complexes may, on correction for the temperature independent paramagnetism[8,17] be used to compute values for λ'. This spin-orbit coupling parameter, like the electron repulsion parameter B', is decreased from the free ion value on complex formation. The increase in the spin-orbit coupling parameter over that of the free ion value (-178 cms.$^{-1}$) for several of the complexes given in Table (III)-6 results, presumably, from a magnification of the errors in the determination of the magnetic moments by the subtraction implied in Equation (III)-2. Furthermore, no account was taken of the Curie-Weiss temperature in the susceptibility calculations. In conjunction with this increase in spin-orbit coupling it is of interest to note that Lew[18], attempting to find a set of parameters to fit the spectral data of d^5 ions, had to assume a value for the spin-orbit coupling constant some 20 to 25% above that of the free ion.

TABLE (III)-6.

The solid magnetic properties of bis(N-R-salicylideneimine)dihalocobalt(II) complexes.

R	Halogen	Temp.(°A)	μ_{eff} (B.M.)[b]	λ' cms.$^{-1}$ [c]
o-tolyl	Cl	291.8	4.49	141
m-tolyl	Cl	291.8	4.70	198
p-tolyl	Cl	290.0	4.51	149
o-anisyl	Cl	290.8	4.69	193
p-anisyl	Cl	290.7	4.73	192
cyclohexyl	Cl	291.8	4.61	171
p-tolyl/pyridine[a]	Cl	287.7	4.38	132
o-tolyl	Br	292.0	4.52	146
m-tolyl	Br	291.2	4.68	182
p-tolyl	Br	292.1	4.60	166
p-chlorophenyl	I	291.4	4.59	163
p-tolyl	SCN	291.2	4.28	120

a. Refers to the Complex monopyridine(N-p-tolylsalicylideneimine)dichlorocobalt(II).

b. Corrected for temperature independent paramagnetism.

c. Spin-orbit coupling constant (free ion value is -178 cms.$^{-1}$).

(iv) A spin-free planar complex.

On refluxing bis(N-p-tolylsalicylideneimine)-dichlorocobalt(II) in absolute ethanol (under nitrogen) an insoluble brown crystalline precipitate of identical composition to the starting material was obtained. The X-ray powder patterns of the brown and green compounds differ appreciably, the green one having more lines. A magnetic moment of 4.20 B.M. at 19°C. was found for the brown compound, compared with a moment of 4.51 B.M. for the green one. The reflectance spectra of the two compounds are highly dissimilar, the brown complex showing a band maximum at 12,400 $cms.^{-1}$. (See Fig.(III)-4.) No bands of lower energy were found in the mull transmission spectrum.

Whereas the magnetic data is in accord with a tetrahedral configuration for the brown complex, the spectral results argue strongly against such an assignment. The spectrum is possibly explicable on the assumption of an octahedral configuration (high 10Dq), but this is in turn contradictory to the magnetic data. It is therefore reasonable to propose some lower symmetry for this complex, such as the planar configuration (D_{4h}). A structure of this symmetry may, in part, be stabilized by weak tetragonal bonds between the phenolic oxygens and the cobalt.

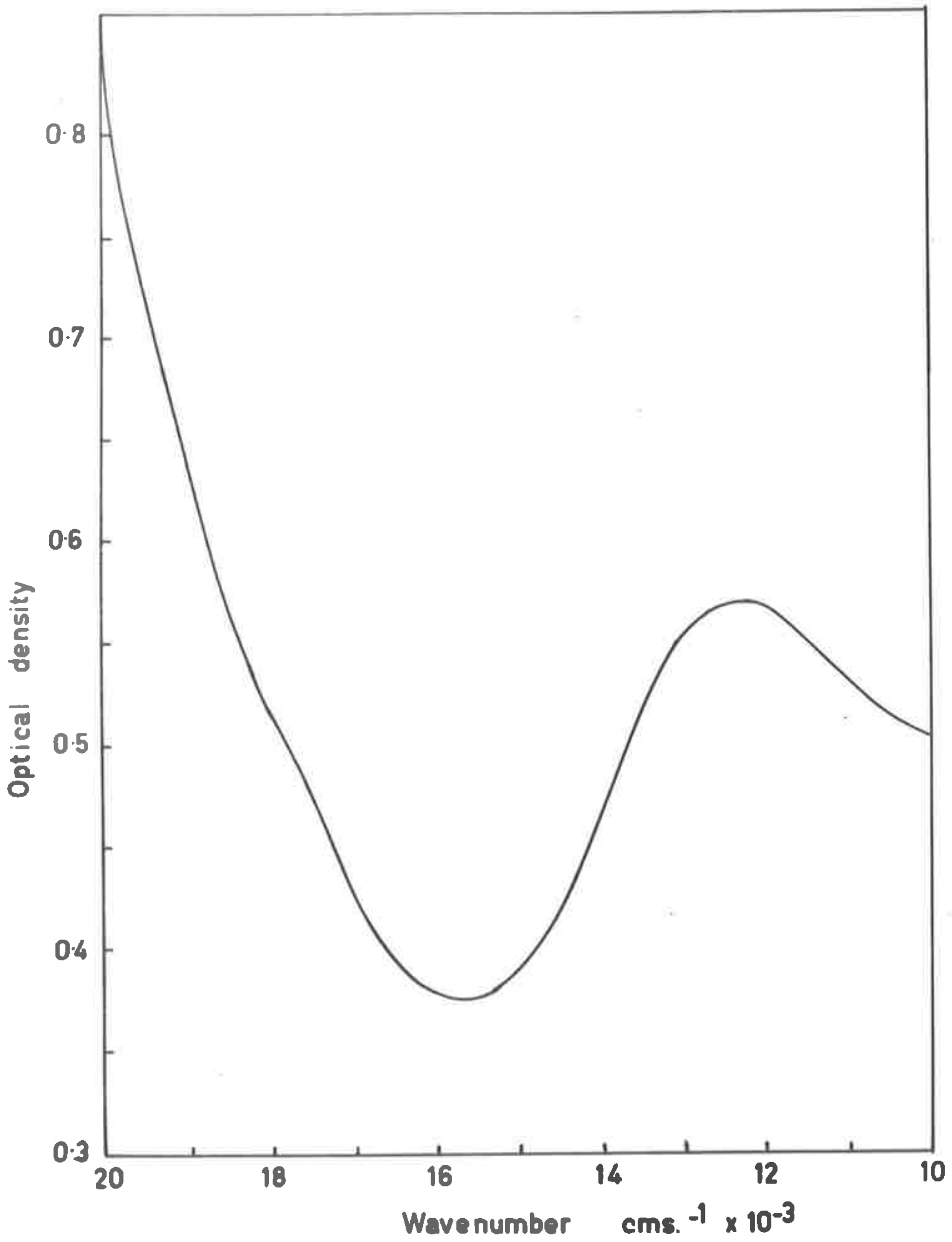


Fig.(III)-4. The powder reflectance spectrum of the brown sample of bis(N-p-tolylsalicylideneimine)dichlorocobalt(II).

In the energy level diagram for spin-free, planar cobalt(II) suggested by Cotton and Holm[19], the ground state has ${}^{4}E_{g}$ symmetry. On this basis a low magnetic moment may be predicted for spin-free planar cobalt(II) complexes. However, no estimate of the magnitude of the orbital moment can be made, as this is dependent on the extent of spin-orbit coupling[19]. The low moment found for the brown sample of bis(N-p-tolylsalicylideneimine)dichlorocobalt(II) is not in contradiction with the predicted ${}^{4}E_{g}$ ground state.

The spectral band at 12,400 cms.$^{-1}$ may, on the basis of the Cotton-Holm energy level diagram[21], be assigned to the ${}^{4}E_{g}(F) \longrightarrow {}^{2}G$ or to the ${}^{4}E_{g}(F) \longrightarrow {}^{4}P$ transitions. The apparent strength of the band in the powder reflectance spectrum suggests that it arises from the spin allowed excitation.

Thus the 'planar' structure for this complex, as suggested on spectral and magnetic grounds, awaits confirmation by X-ray analysis or possibly e.s.r. studies[20].

(v) Summary.

The reaction of cobalt halides with salicylideneimine Schiff's bases in anhydrous solvents led to the formation of compounds of the type bis(N-R-salicylideneimine)-dihalocobalt(II), in which the Schiff's base was monodentate, the cobalt being tetrahedrally coordinated. These complexes were highly insoluble in organic solvents incapable of strong hydrogen bonding. The instability of the complexes in alcohol was indicated by the change in spectral properties between the solid complex and its solution.

The spectral and magnetic properties were explicable on the basis of a tetrahedral ligand field about the metal. Values for the spectral parameters 10Dq and B' were computed and found to compare closely with literature values[5] for "mixed" halogen complexes.

Since the o-tolyl and the p-tolyl Schiff's base cobalt halide complexes had comparable values of 10Dq and B', the steric effects of the ortho-methyl group on imine-nitrogen coordination are small. Thus, in the preparation of the bis(N-R-salicylideneiminato)cobalt(II) complexes, steric factors arising from the substitution on the ortho-position of the amine residue become of importance only on the attachment of the oxygen to the metal.

A brown complex of identical composition to the Schiff's base cobalt chloride complexes was made. The spectral and magnetic properties of this complex militated against an octahedral or tetrahedral structural assignment.

Although no conclusive evidence was presented concerning its configuration, a structure of symmetry D_{4h} has been suggested.

3. Complexes of metals other than cobalt.

(i) Copper(II) complexes.

The reaction of copper chloride with p-tolyl and o-tolyl salicylideneimine Schiff's bases in absolute ethanol yielded brown precipitates of bis(N-tolylsalicylideneimine)dichlorocopper(II).

On solution of these complexes in ethanol, considerable dissociation occurs. This was illustrated by a comparison of the solution and powder reflectance spectra. (See Fig.(III)-5.) Supporting evidence was obtained from the low molecular weight of 324 found for the p-tolyl Schiff's base copper chloride complex, and from the large deviations from Beer's law. In dilute solution the spectrum was that of the Schiff's base.

The complexes had an ill-defined absorption maximum in the vicinity of 11,900 $cms.^{-1}$ in their reflectance spectra. On this basis a planar structure can be proposed[21]. This view is strengthened by the planarity found in the dichlorocopper(II)dipyridinate complex[22].

Magnetic moments of 2.00 B.M. and 2.06 B.M. at 17°C. were found for the para- and ortho- substituted Schiff's base complexes respectively.

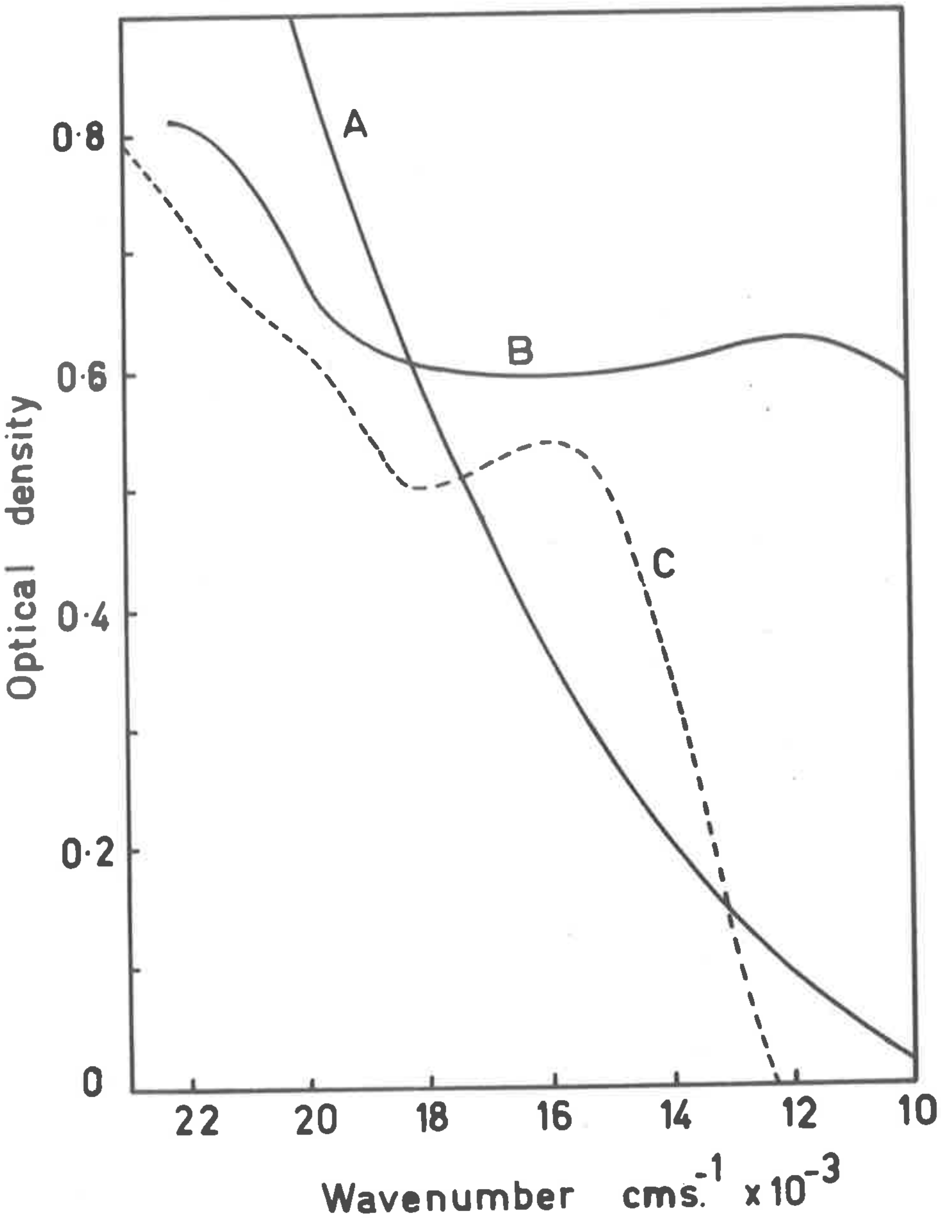


Fig.(III)-5.

The absorption spectra of
- A. Bis(N-p-tolylsalicylideneimine)dichlorocopper(II) in ethanol; concentration is $2.37_2 \times 10^{-2}$M, the cell length being one mm.
- B. The powder reflectance spectrum of bis(N-p-tolylsalicylideneimine)dichlorocopper(II).
- C. The mull transmission spectrum of N-p-tolylsalicylideneiminatomonochloroiron(II).

The absorbance scale refers to the solution spectrum only.

(ii) A Manganese(II) complex.

On reaction of manganese chloride with N-cyclohexylsalicylideneimine in anhydrous ethanol, a yellow complex bis(N-cyclohexylsalicylideneimine)dichloromanganese(II) was formed.

In ethanol this complex oxidises readily to manganese dioxide, suggesting an oxidation state below four for the manganese in this complex. The value of 6.09 B.M. found for the magnetic moment confirms that the manganese is divalent, the phenolic hydrogens still being attached to the Schiff's bases. The absence of hydroxy stretching bands in the infra-red spectrum, together with the insolubility of the complex in non-hydrogen bonding solvents, suggests that the phenolic hydrogens on the Schiff's bases take part in intermolecular hydrogen bonding. The Schiff's base thus behaves as a unidentate ligand.

As all d ⟶ d transitions are spin-forbidden and occur under the $^1B \longleftarrow {}^1A$ Schiff's base band, no structural assignment based on spectral data is possible. Again, since the ground term is a non-degenerate sextet ^6S term, magnetic measurements have no configurational diagnostic value. However, on comparison of the X-ray powder reflectance patterns of this compound with that of the corresponding cobalt(II) compound, it was evident that the complexes were isomorphous.

(iii) A Nickel(II) complex.

In recent years the dependence of the tetrahedral ⇌ planar conformational equilibrium on the stereochemistry of the ligands, noted by Holm and Sacconi in nickel(II) Schiff's base chelates[23], has been found in systems of the type NiL_2X_2 where X is a halogen and L a phosphine or arsine[24]. The importance of ligand size on the configuration of nickel complexes is thus well established.

All attempts to prepare complexes of the type bis(N-R-salicylideneimine)dihalonickel(II) were fruitless. However, from the reaction of N-o-anisylsalicylideneimine with nickel chloride, the complex N-o-anisylsalicylideneiminatomonochloronickel(II) was isolated. On the assumption that the nickel is tetra-coordinated, either a binuclear structure bridged through the halogens or a monomeric one can be proposed, the Schiff's base being tridentate by reason of the methoxy group.

The relatively small bulk of the ligand suggests that this complex may be spin-paired and planar. Since the magnetic moment of this insoluble yellow complex was found to be 3.56 B.M., the nickel is presumably in a pseudotetrahedral ligand environment.

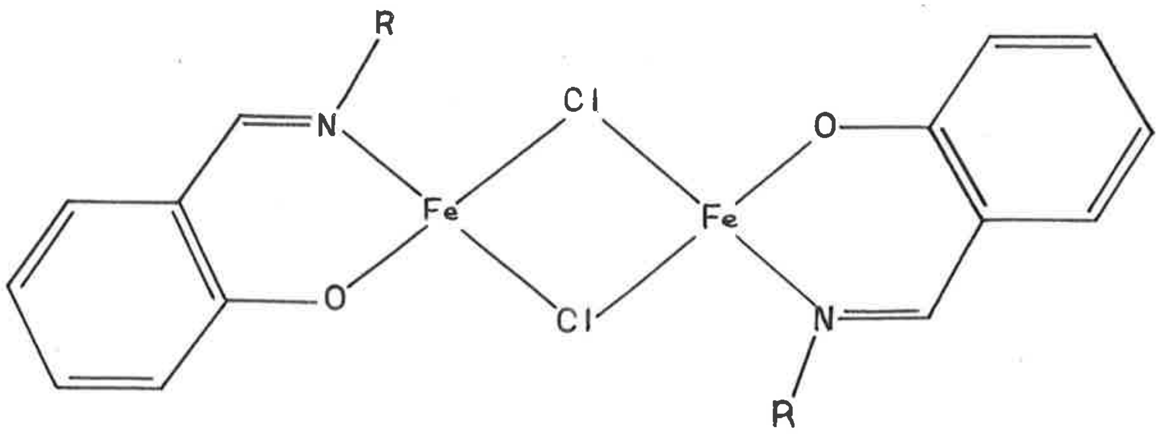
In a tetrahedral ligand field the ^3F ground state term of spin-free nickel is split into the levels $^3T_1$, $^3T_2$ and $^3A_2$ (in order of increasing energy). Above the $^3A_2$ levels lies the $^3T_1(P)$ energy state. The two spectral bands observed for the o-anisyl Schiff's base nickel chloride complex at 8,350 cms.$^{-1}$ and 13,600 cms.$^{-1}$ are explicable only on the basis of a tetrahedral ligand field, and are assigned respectively to the $^3T_1 \longrightarrow {}^3A_2$ and $^3T_1 \longrightarrow {}^3T_1(P)$ transitions. No spin forbidden transitions were observed in the mull transmission spectrum.

By application of the Liehr-Ballhausen expressions[25] assuming the spin-orbit coupling constant to be -275cms.$^{-1}$ and $F_2 = 14F_4$, a value of 4,050 cms.$^{-1}$ was computed for the ligand field strength 10Dq, and a value of 648 cms.$^{-1}$ for the parameter B'. This low value of B' (the nephelauxetic ratio is 0.614) indicates considerable covalency in this complex. It is interesting to note that the ligand field splitting parameter is only a little larger than those found in the "mixed" halogen - Schiff's base cobalt(II) complexes.

(iv) Complexes of Iron.

a. A Ferrous Complex.

Since only the reactions of ferrous halides with Schiff's bases in aqueous solution are well known[26,27], a study of the reaction between ferrous chloride and N-p-tolylsalicylideneimine in absolute ethanol was undertaken. From this reaction mixture the complex N-p-tolylsalicylideneiminatomonochloroiron(II) was isolated. The postulate that the iron(II) is tetra-coordinated necessitates the assumption that the complex is dimeric, dimerization being achieved through two chlorine bridges.



The molecular weight of 540 (theoretical value is 603) found by depression of freezing point in benzene is in accord with the dimeric configuration suggested. The solution dissociation inferred by the low molecular weight was confirmed by solution and solid spectral studies.

The unusual behaviour of the Schiff's bases with ferrous chloride (and also nickel chloride) may perhaps be explicable by solubility and pH considerations.

In the mull transmission spectrum, one absorption band (near 15,900 cms.$^{-1}$) was found, together with a weak shoulder at 20,200 cms.$^{-1}$ (See Fig.(III)-5). Since the band associated with the tetrahedral ferrous ion should occur in the vicinity of 5,000 cms.$^{-1}$, the complex under study cannot possess tetrahedral symmetry[28]. On this basis it is tempting to postulate some lower symmetry, such as D_{4h}, in the crystalline complex.

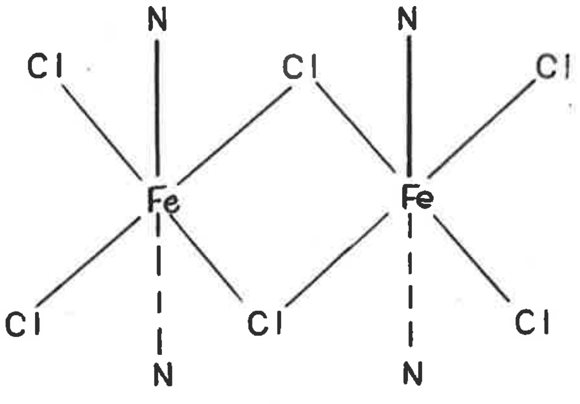
A magnetic moment of 4.28 B.M. at 21°C. was found for this ferrous complex, this value being appreciably lower than the spin only moment of 4.90 B.M. associated with a quintuplet ground state. Moments below the spin-only value suggest some form of spin pairing between metal ions. Whether this process eventuates by a direct overlap of the metal orbitals, or via a super-exchange mechanism cannot be stated[29].

b. A Ferric Complex.

The products from the reaction of ferric chloride with both bidentate and tetradentate salicylideneimine Schiff's bases have been well characterised through preparative[30], magnetic[31] and structural[32] studies.

In this work, on reaction of ferric chloride with N-p-tolylsalicylideneimine in absolute ethanol, a brown crystalline product of bis(N-p-tolylsalicylideneimine)-trichloroiron(III) was obtained. Rather surprisingly the Schiff's bases appear to be monodentate, suggesting that the product isolated was the least soluble one in the reaction mixture. The insolubility of the complex in benzene, in conjunction with the absence of an hydroxy stretching band, is indicative of strong intermolecular hydrogen bonding.

A structure for this complex based on the Fe_2Cl_6 backbone - the Schiff's bases occupying the octahedral positions - can be proposed.



The magnetic moment of 5.98 B.M. found, conforms with the non-degenerate sextet ground state of d^5 ions.

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CHAPTER IV.

COBALT(II) SCHIFF'S BASE CHELATES.

1. Introduction.

Interest in the cobalt(II) complexes of N-R-salicylideneimines was aroused by the reluctance of the Schiff's bases substituted in the ortho-position of the phenyl ring in N-aryl derivatives to form complexes of the form bis(N-R-salicylideneiminato)cobalt(II). This "ortho" effect, evident in the cobalt(II) complexes, was attributed to their tetrahedral configuration as the corresponding planar copper(II) complexes were easily obtained[1]. The preparation and the ultraviolet spectral properties of the cobalt(II) chelates were studied in order to gain a closer understanding of the steric forces involved.

The ease of oxidation of the chelates in solution is dependent on the nature of the amine residue. Thus, while the benzyl[a] Schiff's base chelate oxidizes rapidly, the cyclohexyl complex is very stable in solution. This property, together with the ortho-effect, were investigated by a quantitative study of the reaction of the cobalt(II) Schiff's base complexes with pyridine. To determine

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[a] The chelates bis(N-R-salicylideneiminato)metal(II) are referred to by the nature of the amine residue, R.

whether the same steric effects found in the cobalt complexes were applicable to the planar copper(II) Schiff's base chelates, an examination of the reaction of these copper complexes with pyridine was made.

The complex N,N'-ethylenedi(salicylideneiminate)-cobalt(II) is believed to be planar[2]. A brief study of the effect lengthening the diimine bridge has on the configuration of the chelate was made.

2. Configuration of Cobalt(II) Schiff's Base Chelates.

In recent years evidence has been mounting - from magnetic studies[3,4], dipole moment measurements[5,6] and X-ray measurements[7] - for the assignment of a tetrahedral configuration for the complexes bis(N-R-salicylideneiminato)-cobalt(II). An investigation of the visible absorption spectra of these complexes in non-coordinating solvents and in the solid state was undertaken to determine if their spectral properties were explicable on the basis of a tetrahedral configuration. While this work was being completed the spectra of several analogous cobalt(II) complexes were published by Yamada[8,9] and Sacconi[4]. The results obtained in the present work (See Appendix B) were in accord with the published data.

(i) Ligand Field Spectra.

In the spectral region between 20,000 cms.$^{-1}$ and 4,100 cms.$^{-1}$ three bands of approximate energy 7,400 cms.$^{-1}$, 11,000 cms.$^{-1}$ and 17,500 cms.$^{-1}$ were found. The presence or absence of the high energy band was governed largely by the position of the charge transfer band. The maximum of this band at 17,500 cms.$^{-1}$ could best be estimated from those chelates in which the amine residue was aliphatic. (See Figs.(IV)-1, (IV)-2 and (IV)-4.) The weak shoulder observed on the high energy side of the infra-red band arises, presumably, from the overlap with

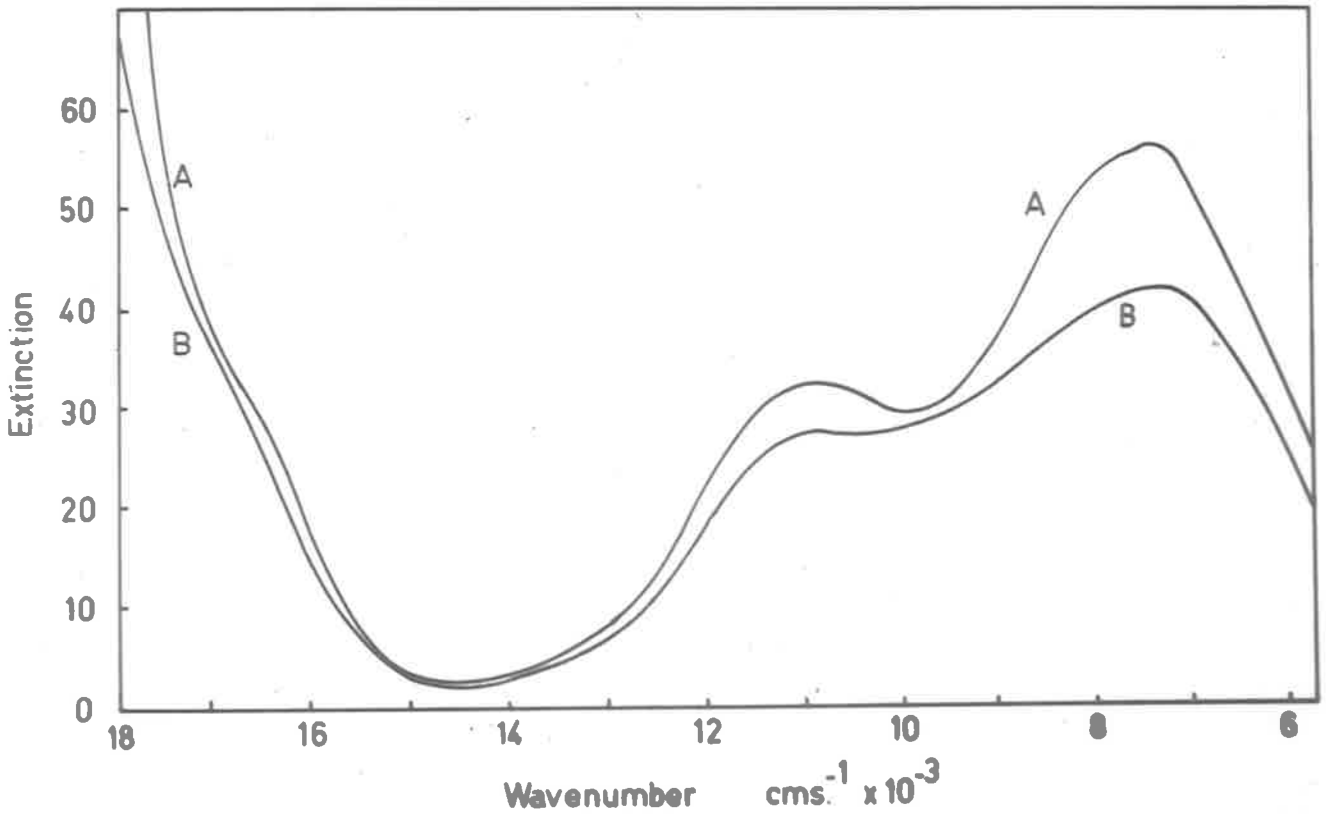


Fig.(IV)-1. The electronic spectral properties (at 25°C) of
A. Bis(N-phenylsalicylideneiminato)cobalt(II) in benzene.
B. Bis(N-*o*-bromophenylsalicylideneiminato)-cobalt(II) in chlorobenzene.

the 11,000 cms.$^{-1}$ band. For most complexes the intensity of the 7,400 cms.$^{-1}$ band lies between 47 and 58 extinction units, the intensity of the 11,000 cms.$^{-1}$ transition being roughly half that. When observed, the high energy band has an intensity of about 60.

On varying both the nature and position of the substituent on the aniline residue of the Schiff's base, little change is found in both the energy and intensity of the spectral bands. Exceptions are found in several compounds, namely in the *o*-anisyl, the *m*-nitrophenyl-, the *o*-chlorophenyl- and the *o*-bromophenyl-salicylideneimine bis Schiff's base complexes. (See Figs.(IV)-1 and (IV)-7.) The spectral properties of these four complexes are discussed in later sections of this chapter.

It is apparent that the spectral properties of the chelates bis(N-R-salicylideneiminato)cobalt(II) are not in accord with those generally found for tetrahedral cobalt(II) complexes [10]. The intensity of the absorption bands are appreciably lower than those found for the cobalt(II) tetrahalide ions. Ballhausen and Liehr[11] observed that the intensity of the $^4A_2 \longrightarrow {}^4T_1(P)$ excitation in tetrahedral cobalt(II) complexes arises in part from the covalency in the metal-ligand bonds. Thus a low covalency in these bonds leads to a low spectral intensity. A decrease in the metal-ligand orbital-intermixing is reflected in a greater repulsion between the ^4P and ^4F energy states. The spectral parameter B', being a measure of this energy separation, can be used as a guide to the degree of metal-ligand covalency. Cotton[12] has applied such an argument to explain the low extinction (40) of the visible absorption band of the tetrahedral dipivaloylmethane cobalt(II) complex. On this basis the low extinctions found for the transitions in the cobalt(II) Schiff's base complexes require these chelates to be largely ionic.

On raising the temperature the covalency of the metal-ligand bond will decrease. It follows, therefore, that on heating tetrahedral complexes, their spectral intensity will fall[13]. This is opposite to that found in octahedral complexes in which the intensity arises from vibronic coupling. The spectra of all cobalt(II) Schiff's base chelates, in inert solvents, showed a steady decrease in intensity (1 to 1.5 extinction units) on increasing the temperature from 25°C to 45°C. Thus the transition intensities of these chelates arise from the partial covalency of the metal-ligand bonds.

The intensities of the spectral bands of these complexes are nearly independent of the nature and position of the substituent on the aniline residue of the Schiff's base. This is not unexpected as the electronic energy bands of the Schiff's bases are not affected significantly by substituents on the aniline residue (See Chapter II of this Thesis). However, substitution on the salicylaldehyde residue produces large bathochromic shifts in all the electronic transitions of the Schiff's base, indicating a high stabilization of the anti-bonding molecular energy states. The importance of this decrease in energy of the Schiff's base orbitals on the extent of covalency in the metal-ligand bonds is seen in the higher intensity of the d-d spectral transitions in these aldehyde-substituted Schiff's base chelates. (See Table (IV)-1 and Fig.(IV)-2.)

TABLE (IV)-1.

The variation in intensity of the spectral band at 7,400 cms.$^{-1}$ of some cobalt(II) bis- Schiff's base chelates with the energy of the $^{1}B \leftarrow {}^{1}A$ excitation of the Schiff's base, (at 25°C).

Schiff's base	$^{1}B \leftarrow {}^{1}A$ cms.$^{-1}$	$\epsilon_{7,400}$
N-phenylsalicylideneimine	29,050	58.6
N-p-tolylsalicylideneimine	28,900	57.9
N-p-tolyl-4-hydroxysalicylideneimine[a]	24,050	74.7
N-p-tolyl-2-hydroxy-1-naphthylideneimine	26,400	73.4

[a] The cobalt(II) chelate is a monohydrate.

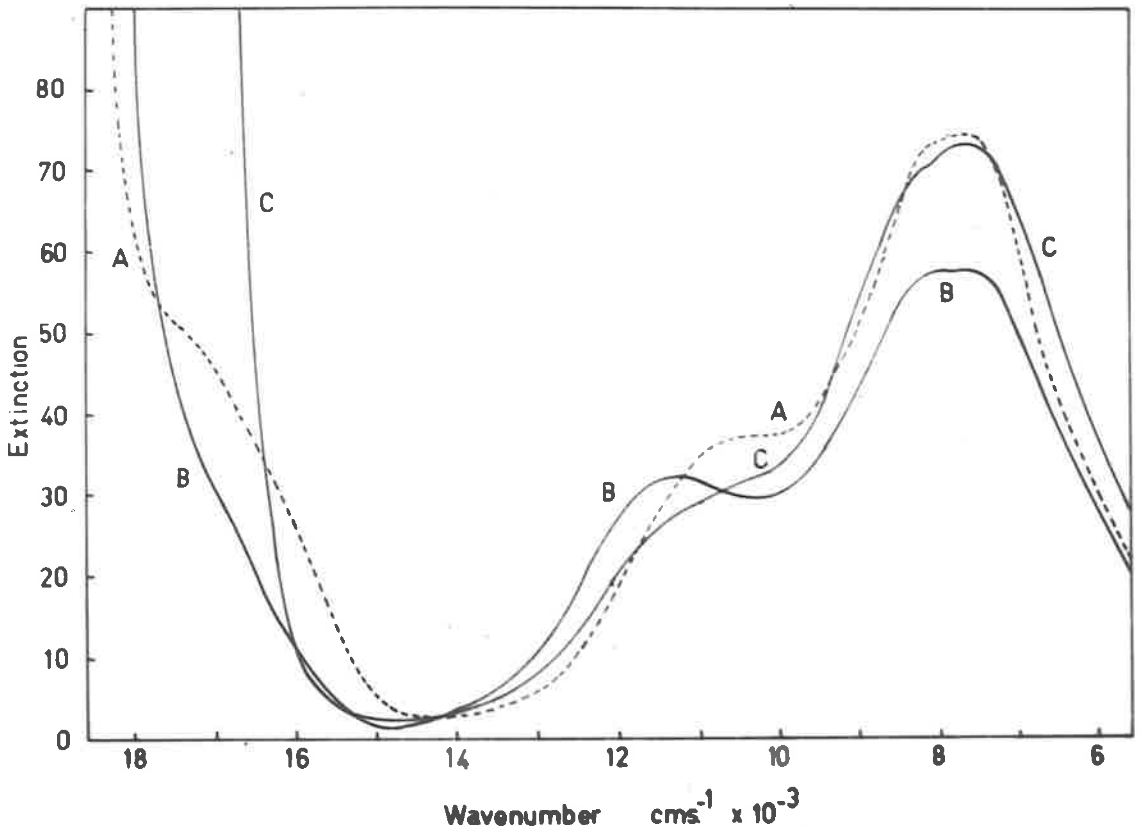


Fig.(IV)-2. The electronic spectra (at 25°C) of
A. Bis(N-p-tolyl-4-hydroxysalicylideneiminato)-cobalt(II)monohydrate in dimethylformamide.
B. Bis(N-p-tolylsalicylideneiminato)cobalt(II) in benzene.
C. Bis(N-p-tolyl-2-oxy-naphthylideneiminato)-cobalt(II) in chlorobenzene.

The energies of the d-d spectral transitions indicate that all the complexes are distorted from the tetrahedral symmetry. This assymmetry arises, presumably, from a distortion of the tetrahedral angles on account of the stereochemical requirements of the coordinated Schiff's base[14]. Differences in the strength of the metal-nitrogen and metal-oxygen bonds will also affect the symmetry of the chelate. Because of the distortions from Td symmetry no estimate of the parameters B' and 10Dq is possible.

Since the energies of the spectral transitions in solution and in the solid state are similar, no change in the configuration of the complexes occurs on solution. The weak band in the solid transmission spectra at 8,000 - 9,000 cms.^{-1} is attributed to the overlap between the 11,000 cms.^{-1} and the 7,400 cms.^{-1} bands.

(ii) Magnetic Properties.

The use of magnetic moments as a confirmatory test for the structure of complexes was first applied to cobalt(II) Schiff's base complexes by West[3]. He found that the complexes investigated had, in both the solid state and in benzene, magnetic moments below 4.6 B.M., suggesting that they are tetrahedral. Bis(N- β -naphthyl-salicylideneiminato)cobalt(II) was shown[3] to deviate only slightly from the Curie law, indicating that inter-molecular interactions were small. Sacconi et.al.[4]

arrived at a similar conclusion from a temperature study on the magnetic properties of the corresponding N-cyclohexyl chelate.

In the present investigation the room-temperature magnetic work of West[3] and Sacconi[4] was confirmed (in part) and extended to cover additional cobalt(II) Schiff's base complexes. The results obtained are tabulated in Appendix C. A tetrahedral structure can be assigned to all the complexes studied, as their magnetic moments were below 4.61 B.M.

3. Steric Hindrance.

(i) Preparative Evidence.

The reaction of cobalt(II) acetate with preformed Schiff's base in an acetate buffered reaction mixture leads to the formation of complexes of the type bis(N-R-salicylideneiminato)cobalt(II) only when the substituent on the aniline residue is not in the ortho-position. This apparent instability of the ortho-substituted Schiff's base chelates has been attributed to steric hindrance, there being no correlation between the basicity of the parent amine and the ease of complex formation[1].

That the complex bis(N-*o*-tolylsalicylideneimine)-dichlorocobalt(II) could be readily obtained, suggests that the major strain in the formation of the bis(N-R-salicylideneiminato)cobalt(II) complexes arises on chelate formation. In order to facilitate the reaction of the phenolic group with the metal, competitive anions must be removed. Thus, the titration of bis(N-*o*-tolylsalicylideneimine)dichlorocobalt(II) in absolute alcohol with caustic soda leads to high yields of bis(N-*o*-tolylsalicylideneiminato)cobalt(II), the halogen ions being precipitated as sodium chloride. Several alternative preparative techniques for the preparation of ortho-substituted Schiff's base cobalt(II) chelates have been summarised in Table (IV)-2.

TABLE (IV)-2.

The methods of preparation available for bis(N-R-salicylideneiminato)cobalt(II), where R is an ortho-substituted phenyl group. + is indicative of a successful preparative method.

R	NaAc[a]	Na_2CO_3[b]	$CoSal_2/EtOH$[c]	$CoSal_2/PhCl$[d]
o-anisyl	+	+	+	+
o-fluorophenyl		+	+	+
o-tolyl		+	+	+
o-chlorophenyl			+	+
α-naphthyl			+	+
o-bromophenyl				+

a. Reaction of Schiff's base with cobalt acetate in a sodium acetate buffered reaction mixture.

b. The sodium acetate is replaced by sodium carbonate.

c. Bis-salicylaldehydocobalt(II)dihydrate is refluxed with amine in alcohol.

d. The ethanol in method 'c' is replaced by a high boiling point solvent, usually chlorobenzene.

On increasing the size of the ortho- group, an increased "strain" on chelation is expected. This is borne out in part by the preparative evidence, the ease of formation of the complexes decreasing with the amine residue in the order *o*-anisyl > *o*-fluorophenyl > *o*-tolyl > *o*-chlorophenyl > α - naphthyl > *o*-bromophenyl. The position of the *o*-anisyl chelate at the head of the series results from the weak coordination of the methoxy-group to the metal[1]. Such a notion has received support from the study of the spectra of the Schiff's bases and their zinc(II) chelates. (See Chapter II.) The visible spectrum of bis(N-*o*-anisylsalicylideneiminato)cobalt(II) in dimethylformamide (Fig.(IV)-7) is also in agreement with this view. Although the transition energies are unaltered compared to the other Schiff's base chelates - thereby suggesting that the ligand field has a distorted tetrahedral symmetry - the intensities of the spectral transitions are markedly decreased. The magnetic moment data of West[3] and that presented in this Thesis are in accord with the postulated $^4A_2$ ground state for this *o*-anisyl complex. On increasing the temperature of a solution of this complex in dimethylformamide (DMF) from 25° to 45°C, the spectral intensity at 7,300 cms.$^{-1}$ increases from 17.8 to 19.2 extinction units. The direction of this intensity change is opposite to that expected for tetrahedral compounds, suggesting that it arises from a change in the symmetry of the complex. Solvation effects by the DMF however, may also be important. By omitting the o-anisyl complex, from the series above, and separating the electronegative substituents from the hydrocarbon ones, the relations o-fluorophenyl > o-chlorophenyl > o-bromophenyl, and o-tolyl > α-naphthyl are obtained. The importance of substituent size on the ease of preparation of the cobalt(II) chelates is indicative that steric hindrance to chelation does in fact occur.

In order to determine whether strain exists in the chelates of these ortho-substituted Schiff's bases, an investigation of their ultraviolet spectra was undertaken.

(ii) The Ultraviolet Spectra.

In an investigation of the ultraviolet spectrum of bis(N-o-tolylsalicylideneiminato)cobalt(II) in ethanol, large deviations from Beer's law were observed. Below concentrations of 2.3×10^{-5}M in complex, the spectrum in ethanol was identical to that of the Schiff's base. On increasing the concentration an absorption band appears near 25,000 cms.$^{-1}$. A plot of the molar extinctions of these solutions - of varying concentrations - revealed isosbestic points at 38,600 cms.$^{-1}$, 36,000 cms.$^{-1}$ and at

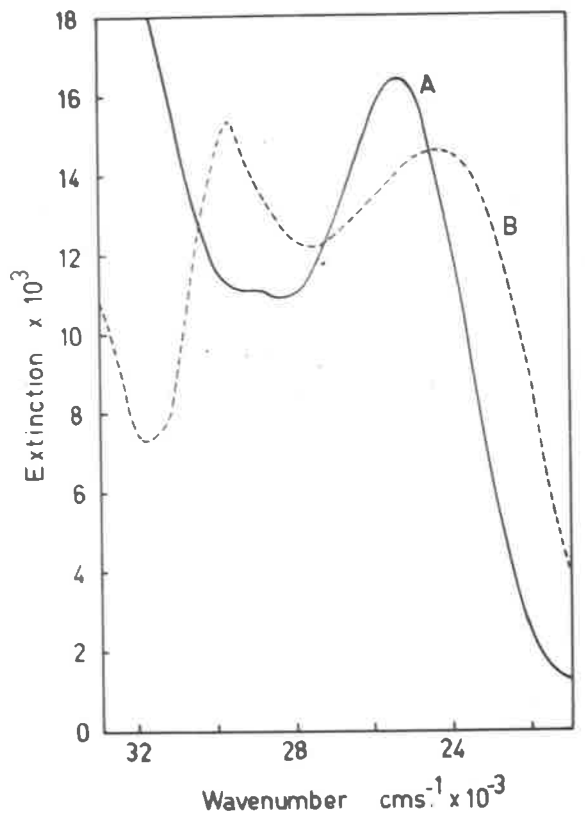
32,300 cms.$^{-1}$. On this basis, the deviations from Beer's law were attributed to an equilibrium between two absorbing species.

The spectrum of this p-tolyl complex in anhydrous benzene obeyed Beer's law over a wide concentration range (concentrations $> 2x10^{-5}M$). Furthermore, this spectrum in anhydrous benzene passed through the isosbestic point at 32,300cms.$^{-1}$, indicating that the two absorbing species in the ethanol solution were the Schiff's base and its cobalt(II) chelate.

On standing the benzene solution in a damp, inert atmosphere, the spectrum of bis(N-p-tolylsalicylideneiminato)-cobalt(II) reverts to that of the Schiff's base. The rate and extent of the dissociation of the complex in solution was shown to be highly dependent on the amount of water present. For this reason, all spectra of the cobalt Schiff's base chelates, both in the visible and in the ultraviolet regions, were studied in anhydrous solvents.

Because of the insolubility of the complexes in cyclohexane and other such non-aromatic solvents, the ultraviolet spectral study was carried out in benzene. The use of this solvent limited the investigation to the spectral bands of energy below 35,000 cms.$^{-1}$.

The main spectral feature observed was a band in the vicinity of 25,000 cms.$^{-1}$ to 27,000 cms.$^{-1}$, with an intensity between 11,000 and 17,000 extinction units. (Table (IV)-3, Fig.(IV)-3.) As this Laporte allowed transition arises only on complex formation, it has been



Fig(IV)-3a.
The ultraviolet spectra in benzene at 25°C of
A. Bis(N-phenylsalicylideneiminato)-cobalt(II)
B. Bis(N-o-anisylsalicylideneiminato)-cobalt(II)

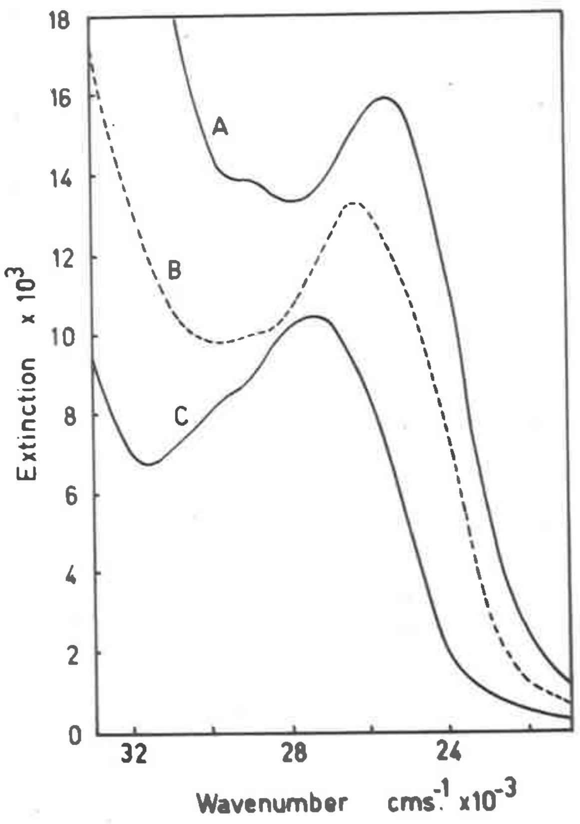


Fig.(IV)-3b.
The ultraviolet spectra in benzene of
A. Bis(N-p-tolylsalicylideneiminato)cobalt(II)
B. Bis(N-o-tolylsalicylideneiminato)cobalt(II
C. Bis(N-cyclohexylsalicylideneiminato)-cobalt(II).

assigned to a metal-ligand charge transfer band. The two types of pi-bonding to consider are those involving either a metal-to-ligand or ligand-to-metal electron transfer. In the former case, the more stable pi-orbital is on the metal, whereas in the second case the more stable pi-orbital is on the ligand[15]. A destabilization of the ligand molecular orbitals would therefore increase the transition energy for a metal-to-ligand electron transfer and decrease the energy of the ligand-to-metal electron transfer. The high energy of the electron transfer band in the complexes bis(N-cyclohexylsalicylideneiminato)cobalt(II) and bis(N-benzylsalicylideneiminato)cobalt(II), supports strongly that the electron transfer is one from the metal to the ligands. This is in agreement with both the strong electron acceptor properties of the imine-group of the Schiff's base and with the high ease of oxidation of these cobalt(II) chelates.

The stability of the ligand molecular orbitals will be dependent on the amount of twisting about the carbon-nitrogen single bond of the Schiff's base. That the charge transfer band is found at higher energies in the *p*-tolyl, the *p*-chlorophenyl and the *p*-bromophenyl chelates (Table (IV)-3) suggests that the planarity of the coordinated Schiff's bases in these complexes is more highly disturbed. In line with this postulate, the *p*-fluorophenyl chelate exhibits a charge transfer band of lower energy. On this basis it may be proposed that strain does exist in these chelates, the strain being removed, not by a distortion in the metal-ligand bonds (See Chapter IV, Section 2 - (i)), but by a twisting of the Schiff's bases away from planarity.

The twisting about the carbon-nitrogen single bond of the Schiff's base, bringing about an increase in the energy of the ligand orbitals, may result in a decrease in the covalency of the metal-ligand bonds. A lowering of the intensity (oscillator strength) of the ligand field spectral transitions may thus ensue. This was in fact found for the *p*-chlorophenyl and the *p*-bromophenyl compounds, their extinctions at 7,400 cms.$^{-1}$ being 39.4 and 42.3 respectively. (See Fig.(IV)-1.) However no relationship between the energy of the ligand orbitals and the intensity of the ligand field spectral bands can be suggested for the *p*-tolyl chelate, in which the extinction at 7,300 cms.$^{-1}$ is 57.1.

The ultraviolet spectrum of bis(N-*p*-anisylsalicylideneiminato)cobalt(II) is exceptional, in that two bands are found in benzene solution. (Fig.(IV)-3a.) This again suggests that an interaction between the methoxy-group and the metal does occur.

TABLE (IV)-3.

The energy and intensity of the charge transfer bands of some bis(N-R-salicylideneiminato)cobalt(II) chelates in benzene.

R	Band Energy cms.$^{-1}$	ϵ_M
phenyl	25,250	16,400
o-tolyl	26,200	13,300
m-tolyl	25,700	14,150
p-tolyl	25,450	15,900
o-anisyl	24,150	14,600
m-anisyl	25,650	14,900
p-anisyl	25,200	16,200
o-fluorophenyl	25,400	14,500
m-fluorophenyl	25,100	15,300
p-fluorophenyl	25,100	15,900
o-chlorophenyl	26,000	11,500
m-chlorophenyl	25,300	16,650
p-chlorophenyl	25,300	16,650
o-bromophenyl	26,300	11,150
m-bromophenyl	25,050	15,950
p-bromophenyl	25,200	16,300
α-naphthyl	24,700s	12,200
benzyl	27,100	10,900
cyclohexyl	27,300	10,450.

In conclusion it may be stated that a "steric effect", evident in the preparation of the ortho-substituted chelates, also exists in the chelates once formed.

To understand further, the dependence of the properties of the cobalt(II) bis-Schiff's base chelates on the position and nature of the substituent on the aniline residue of the Schiff's base, an investigation of the reaction of these chelates with pyridine was undertaken.

4. The Reaction of Cobalt(II) Schiff's Base Chelates with Pyridine.

The addition of pyridine to complexes in which the coordination number of the metal is not completely satisfied, has been investigated by several workers. Thus Graddon and Watton[16] determined the equilibrium constants of pyridine addition to β-diketocopper(II) complexes. In all cases only the penta-coordinated species was formed. However, on reaction of pyridine type bases with planar diacetyl-disbenzoylhydrazonenickel(II) in benzene, Sacconi *et.al.*[17] could only identify the dipyridinate complex. Similarly, King *et.al.*[18] found only the octahedral dipyridinate on reacting bis-pyridine dihalocobalt(II) with pyridine. Recently, Fackler, in an interesting study of the reaction of pyridine with the acetylacetonates of nickel(II)[19] and cobalt(II)[20] found, in addition to the dipyridinate, a dimeric species of the type $[Co(acac)_2]_2Pyr.$, where acac. refers to acetylacetone and Pyr. to pyridine. In the case of the cobalt complex, a monomeric monopyridinate was also detected.

The reaction of pyridine on cobalt(II) Schiff's base complexes can be represented by the equations,

$$CoB_2 + Pyr. \rightleftharpoons \underset{\text{Penta-coordinated}}{CoB_2Pyr.} \qquad (IV)\text{-}1$$

$$CoB_2Pyr. + Pyr. \rightleftharpoons CoB_2Pyr._2 \qquad (IV)-2$$

octahedral

where CoB_2 is the bis-Schiff's base complex. The overall reaction then is

$$CoB_2 + 2Pyr. \rightleftharpoons CoB_2Pyr._2 \qquad (IV)-3$$

The differences found in the spectra of the complexes in pyridine and in non-coordinating solvents suggested that the reactions above could be investigated spectroscopically. The charge transfer band proved unsuitable here as at the low concentrations required (5×10^{-5}M), complex dissociation and oxidation became important. Good reproducibility of spectra was possible however, using the less intense absorption region 8,600 to 7,200 $cms.^{-1}$. (See Fig.(IV)-4.)

The spectral properties of these Schiff's base complexes of cobalt(II) in solutions containing pyridine were explicable only on the assumption that both the monopyridinate and the dipyridinate formed. The relationship found between the equilibrium constants and the measurable quantities (See Appendix D, Section 1) had the form

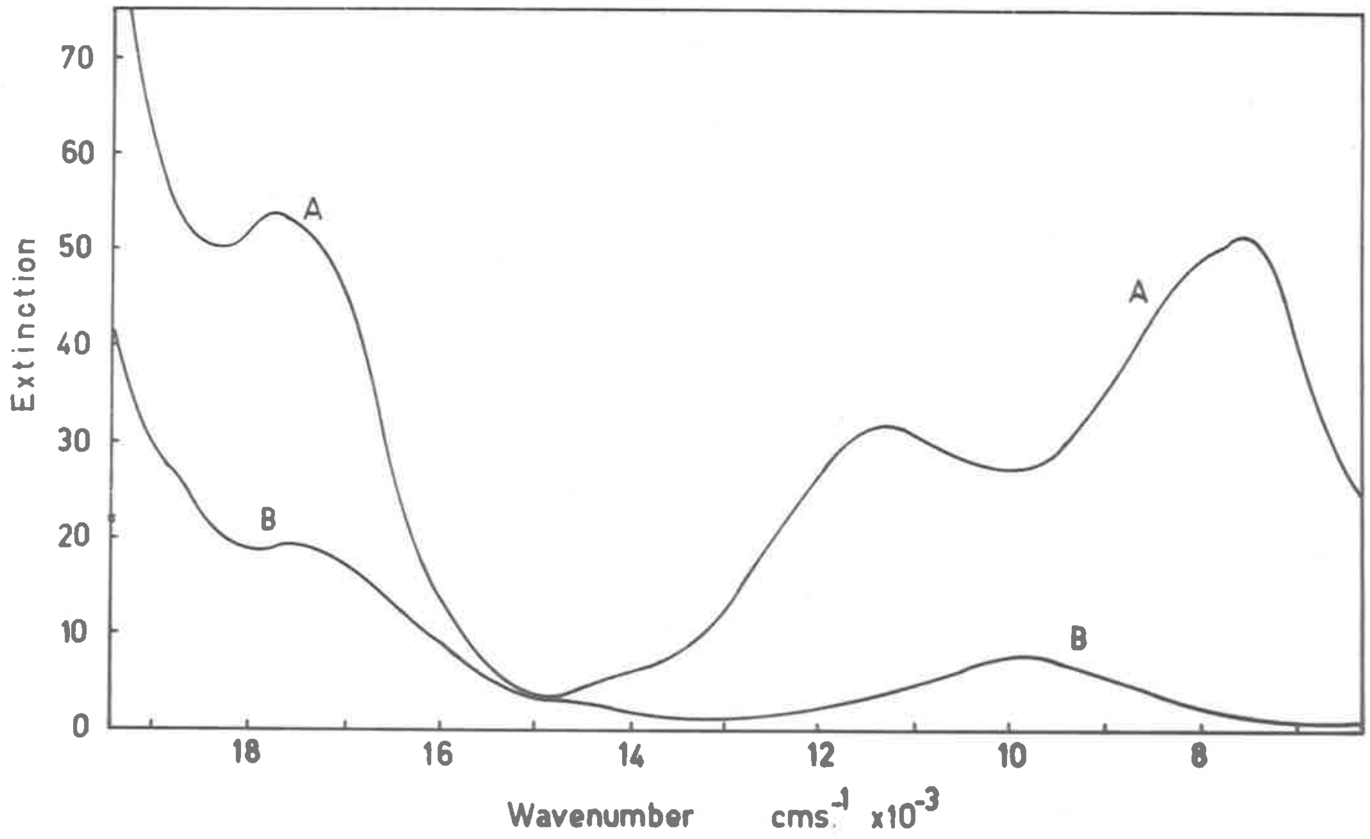


Fig.(IV)-4. The spectrum of bis(N-benzylsalicylideneiminato)cobalt(II) at 25°C in,
A. Benzene,
B. Pyridine. The concentration of complex in pyridine was 1.373×10^{-2}M.

$$\epsilon_T - \epsilon_1 = \frac{1}{K_1}\left[a + K_T b \right] \qquad \text{(IV)-4}$$

in which ϵ_T is the extinction of the reaction solution; ϵ_1 the extinction of the monopyridinate species, and K_1 the equilibrium constant (in litres/mole) associated with equation (IV)-1.

$$a = \frac{\epsilon_0 - \epsilon_T}{C_{Pyr.}} \qquad \text{(IV)-5}$$

where ϵ_0 is the extinction of the reaction solution in the absence of pyridine and $C_{Pyr.}$ is the equilibrium pyridine concentration. K_T is the stability constant for reaction (IV)-3 (in litres^2/mole^2), and

$$b = C_{Pyr}(\epsilon_2 - \epsilon_T) \qquad \text{(IV)-6}$$

where ϵ_2 is the extinction of the dipyridinate species, which may be estimated from the spectrum of the complex in pyridine. It is not possible to say a priori that the spectrum in pyridine is in fact that of the dipyridinate species. However, for most complexes no change in the spectrum is experienced on increasing the pyridine concentration above 5M., which strongly suggests that the only absorbing species present in pure pyridine is in fact the dipyridinate. This has been subsequently confirmed by the stability constant calculations.

Evaluation of Equation (IV)-4 is difficult as it contains three unknowns, namely ϵ_1, K_1 and K_T. However ϵ_1 can be estimated (it varies from 0.7 to 1.5 extinction units over the range 8,600 to 7,200 cms.$^{-1}$) and Equation (IV)-4 can then be solved graphically.

From the plot of log K against $\frac{1}{T}$, the standard enthalpy changes (ΔH^o) for the reactions (IV)-1, (IV)-2, and (IV)-3 were evaluated. Fig.(IV)-5 shows a typical plot. On introduction of these values into the equation

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} \qquad \text{(IV)-7}$$

the standard entropy changes (ΔS^o) can be found, since ΔG^o, the standard free energy change, is given by the expression

$$\Delta G^o = -RT\ln K \qquad \text{(IV)-8}$$

The magnitude of the entropy changes found on the addition of pyridine to the bis(N-R-salicylideneiminate)-cobalt(II) type complexes arises from several factors, the main one being bond formation. This negative entropy effect is however decreased numerically by the weakening of the cobalt-Schiff's base bonds resulting from the

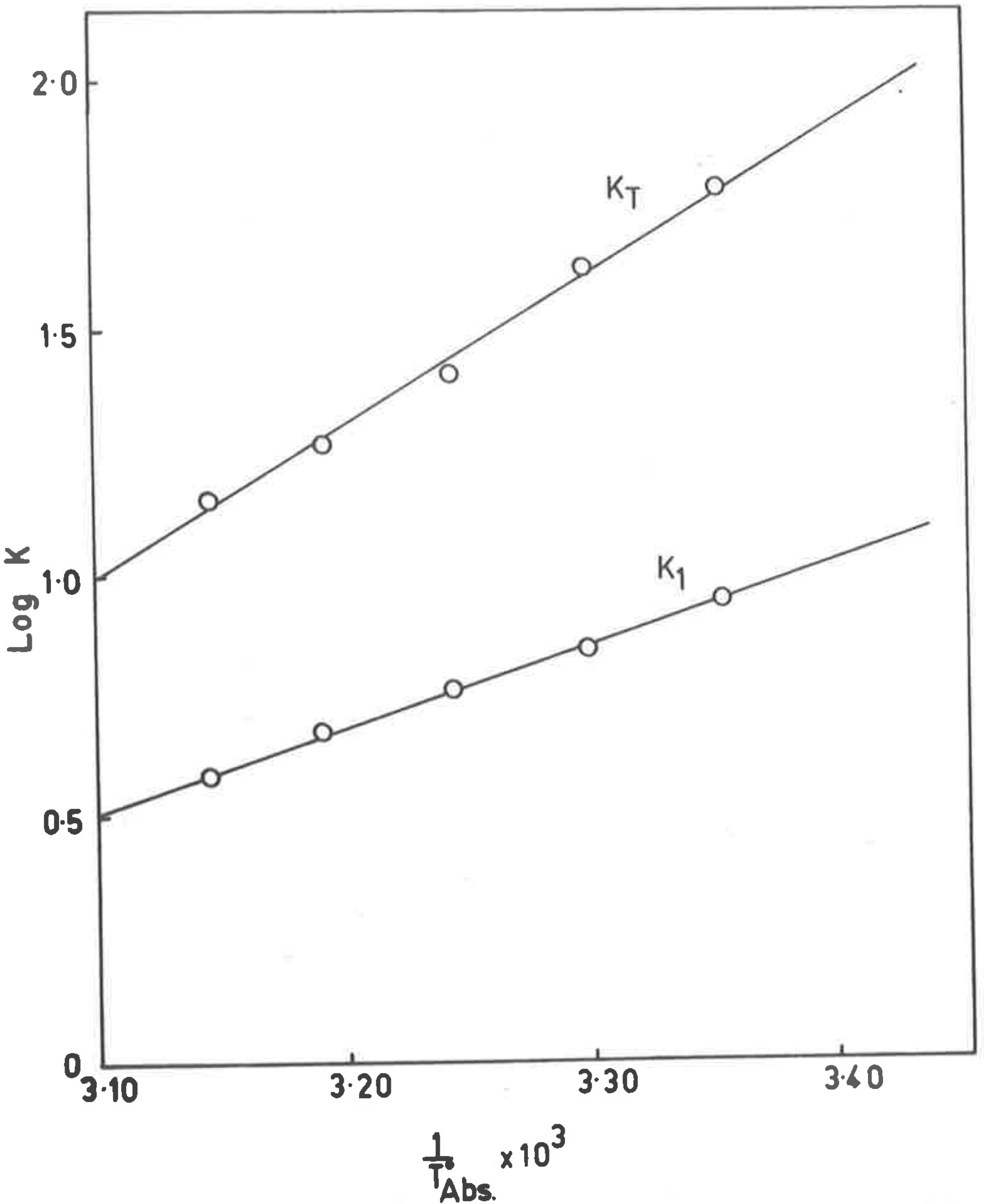


Fig.(IV)-5. The plots of the logarithm of the equilibrium constants K_1 and K_T as a function of the reciprocal of the absolute temperature for the complex bis(N-m-fluorophenylsalicylideneiminato)-cobalt(II) in benzene.

expansion of the coordination number of the metal[21]. Differences in the ligand field stabilization energies between the tetrahedral and the octahedral complexes will also contribute to the entropy changes. Also, on coordination, the number of degrees of freedom available to the pyridine are reduced, resulting in a loss of entropy by the system.

Since the spectral transitions of most complexes change in energy by a common amount on dipyridinate formation (See Appendix B) a similar overall entropy change (ΔS°_{T}) presumably occurs. Some variation in these entropy values is expected due to the differences in solvation and steric properties of the chelates. A comparison of the total entropy changes may thus lead to some information on both the solvation and stereochemical properties of the complexes.

No comparison of the individual entropy changes (ΔS°_{1} and ΔS°_{2}) for the various complexes can be made due to the lack of knowledge on the structure and solution properties of the penta-coordinated mono-pyridinate species.

The first group of chelates considered below are those bearing a substituent on the para-position of the aniline residue. With a substituent in this position, steric hindrance to the approach and coordination of a pyridine molecule will be a minimum. Information on the importance of solvation may thus be gained.

The ease of oxidation of the complexes necessitated the use of solvents in which solution could be rapidly attained at room temperature. Suitable solvents for the complexes studied were benzene, chlorobenzene and dimethylformamide.

(i) Para-substituted Schiff's base Complexes.

The thermodynamic properties for the reaction of pyridine with the first three complexes in Table (IV)-4 were determined in benzene. Since the substituents are removed from the metal coordination sites, they cannot hinder the approach and subsequent coordination of the pyridines. However, the overall stability constants (K_T), for these three complexes with pyridine vary appreciably suggesting differing extents of solvation of these complexes.

A solvent such as benzene may interact electronically with solute molecules either through the aromatic pi-system[22] or via its positively charged hydrogens[23,24]. When the solute does not possess a highly charged (or easily polarizable) negative group, the interaction is likely to proceed through the pi-electrons. Such a polarization interaction is proposed for these Schiff's base complexes, the strength of solvation being dependent on the Schiff's base properties. Thus, a negative group on the Schiff's base will repel the solvent while a positive group would facilitate the interaction.

The higher solvation of the p-tolyl and the p-anisyl complexes compared to the phenyl compound is suggested by the higher stability of the pyridine adducts of the phenyl compound. This is rather unexpected as the methyl and the methoxy groups should hinder solvation of the Schiff's base by both their electronic and steric properties. On this basis, an interaction between benzene solvent molecules and the hydrogens of the methyl groups on the p-tolyl or p-anisyl complexes may be proposed, this attraction with the solvent being stronger in the p-anisyl complex by virtue of the inductive effect of the methoxy-oxygen. Such an interaction would be similar to that found between benzene and chloroform, which proceeds through the chloroform hydrogen[25]. The strength of this chloroform-benzene adduct (-1.97 Kcals./mole[25]) is indicative of the high solvation power of the benzene. The variations in K_T for the phenyl, p-tolyl and p-anisyl compounds can hence be explained on the basis of the postulate on the solvation of the coordinated Schiff's bases.

TABLE (IV)-4.

The thermodynamic properties for the reaction of pyridine with bis(N-para-X-phenylsalicylideneiminato)cobalt(II) at 25°C.

X	Solvent	K_1[a]	K_2[a]	K_T[b]	ΔG°_1[c]	ΔG°_2	ΔG°_T
hydrogen	benzene	1.8	2.8	5.1	-340	-610	-950
	DMF	0.48	0.53	0.25	440	270	710
methyl	benzene	0.87	2.1	1.8	80	-420	-340
methoxy	benzene	0.42	2.3	0.98	510	-500	12
fluoro	chlorobenzene	3.2	4.4	14.4	-700	-880	-1580
	DMF	1.2	0.77	0.89	-90	160	70
chloro	DMF	2.1	0.58	1.2	-430	320	-110
bromo	DMF	1.9	0.76	1.3	-360	190	-170

a. The equilibrium constants K_1 and K_2 are expressed in litres/mole.

b. The overall equilibrium constant, $K_T=K_1K_2$, is in litres^{2}mole^{-2}.

c. All free energy terms are expressed in calories/mole.

TABLE(IV)-4. (contd.)

X	Solvent	$-\Delta H^{\circ}_{1}$[a]	$-\Delta H^{\circ}_{2}$	$-\Delta H^{\circ}_{T}$	$-\Delta S^{\circ}_{1}$[b]	$-\Delta S^{\circ}_{2}$	$-\Delta S^{\circ}_{T}$
hydrogen	benzene	5.8	7.3	13.1	19	21	40
methyl	benzene	7.1	4.4	11.5	24	13	37
methoxy	benzene	4.9	6.1	11.0	18	19	37
fluoro	chlorobenzene	9.1	2.7	11.8	28	6	34
	DMF	5.8	4.3	10.1	19	15	34
chloro	DMF	6.7	2.0	8.7	24	6	30
bromo	DMF	5.7	3.7	9.4	18	13	31

a. Enthalpy changes for pyridine addition are in K.cals./mole.

b. Entropy changes are in entropy units (cals./degree/mole).

The lack of knowledge of the structure and hence extent of solvation of the monopyridinate adduct prevents a quantitative comparison of the equilibrium properties of the step-wise reactions of pyridine addition from being made.

The entropy changes of the reactions studied should reflect differences in the solvation between the reactants and the products. Since the total entropy change for pyridination, (ΔS^{o}_{T}) of the phenyl, the p-tolyl and the p-anisyl complexes are comparable, the relative extents of solvation of their tetrahedral and octahedral species may be similar.

Pyridine can also solvate these complexes. However, as the equilibrium plots for the reactions of pyridine addition are linear, this effect is considered to be small. This is not surprising since in all cases the ratio of solvent to pyridine was above 11:1.

As the p-bromophenyl and the p-chlorophenyl complexes are nearly insoluble in benzene or chlorobenzene at room temperature, their reactions with pyridine were studied in DMF. The use of this solvent introduces several complications through its high solvation and its coordination properties[26]. The ultraviolet and visible spectral properties of the phenyl, the p-tolyl and p-anisyl and the m-chlorophenyl complexes were identical in DMF and in benzene. On this basis it was considered that no cobalt-DMF coordination occurs in the bis(N-R-salicylideneiminato)cobalt(II) complexes.

The strong solvation properties of the DMF can be seen from the low equilibrium constants in DMF. (See Table (IV)-4.) A direct comparison of the relative extents of solvation by various solvents cannot be made from the stability constant measurements as solvation, not only of the complexes but also of the pyridine, varies with the solvent. It is evident however, from the high value found for the equilibrium constant K_T for the p-fluorophenyl compound in chlorobenzene, that the solvation of these complexes is highly important in deciding the magnitudes of the equilibrium constants.

Hatton and Richards[27], studying the nuclear magnetic resonance of DMF in aromatic solvents, suggested that an interaction occurred between the aromatic pi-orbitals and the positively charged nitrogen of the DMF. The unequal shifts to higher fields of the two methyl resonances on increasing the concentration of the aromatic compound (in cyclohexane) led them to propose that one methyl group was located in the centre of the aromatic ring, the other lying outside the pi-system. A similar interaction may be considered to exist between the Schiff's base ligands and DMF. The strength of the solvation will depend on the nature of the substituent on the base. Neutral groups will prevent solvation, by steric hindrance. Support for such an effect was found by Hatton and Richards[27], who noticed that a direct relationship appeared to exist between the extent of the interaction of DMF with methylated benzenes and the molecular volume of the substituted benzenes. A drastic reduction in the shift of the methyl resonances was also noticed on halogen substitution of the benzene. Whether this was due to the formation of a looser solvate or an alternative interaction mechanism was not deduced[27].

A similar dependence of the extent of solvation on the size and charge of the substituent on the Schiff's base was evident from the data obtained (Table (IV)-4). The very low K_T for the N-phenyl chelate in DMF, compared to that in benzene, indicated the higher solvation of this complex by the DMF. On halogen substitution, the stability constants change in parallel with the halogen size. The lower values of the total entropy change found for the para-halogen substituted compounds may reflect the importance of substituent charge on the extent of solvation; the smaller the entropy changes the more solvent being released (or less gained) during the reaction of the cobalt Schiff's base complex with pyridine to form the pyridine adduct.

Further evidence for a solvent effect when the p-halophenyl complexes are dissolved in DMF is gained from their visible spectra. While other Schiff's base chelates have like extinctions for their ligand field absorption bands in DMF, benzene and chlorobenzene, the p-halophenyl complexes have a lower absorption in DMF. (See Table (IV)-5 and Fig.(IV)-6.)

TABLE(IV)-5.

The extinction coefficients of bis(N-X-phenylsalicylideneiminato)cobalt(II) at 7,600 cms.$^{-1}$ X is a para-halogen substituent.

X	Solvent	$\epsilon_{25^\circ C}$	$\epsilon_{45^\circ C}$
F	DMF	43.4	46.3
	Chlorobenzene	52.9	50.6
Cl	DMF	38.3	42.3
	benzene	51.5	
Br	DMF	36.4	41.3
	benzene	46.8	

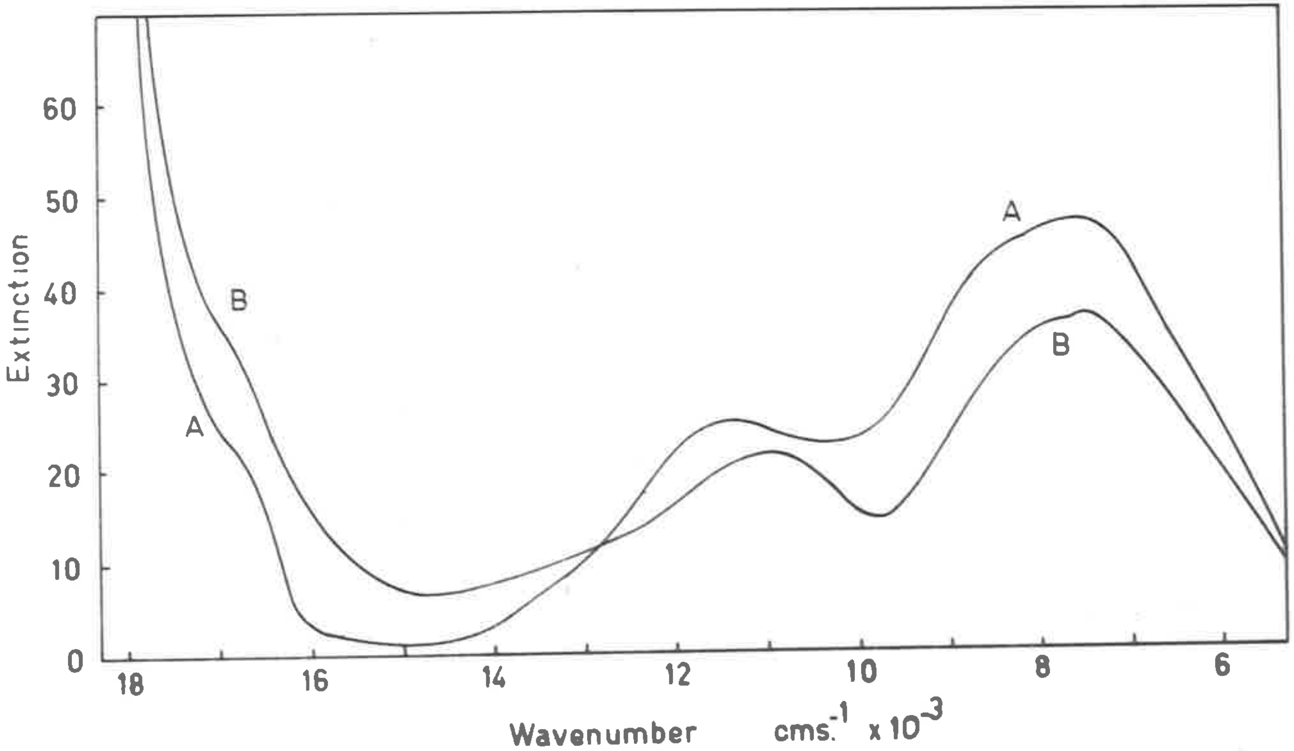


Fig.(IV)-6. The electronic spectral properties of bis(N-p-bromophenylsalicylideneiminato)cobalt(II) in

A. Benzene
B. Dimethylformamide.

The decrease in intensity of the p-fluorophenyl complex in chlorobenzene on raising the temperature is as expected on the basis of a tetrahedral structure. No comparison can be drawn between the K_T values for the p-halogen compounds and their extinction coefficients in DMF, as the K_T values contain information on the extent of solvation of both the mono- and di-pyridinate adducts. A parallel relationship between the extinction coefficients in DMF and the halogen electronegativities is observed.

The intensity changes in the d-d bands on solvation with DMF can arise from either a change in the symmetry of the ligand field or through a reduction of the metal-ligand orbital intermixing. A study of the ultraviolet spectra of these complexes in several solvents was undertaken to elucidate the nature of the intensity reducing mechanism. In benzene and chlorobenzene, the cobalt(II) Schiff's base complexes have charge transfer bands in the vicinity of 25,000 cms.$^{-1}$. Changing the solvent to DMF had little effect on this band, except in the case of the p-halophenyl complexes in which this band disappears. The loss of the charge transfer band in DMF was taken to indicate that the reduction in the intensity of the ligand field bands on solution of the para-halophenyl complexes in DMF resulted from a decrease in the metal-ligand pi-bonding.

The increase in intensity of the 7,400 cms.$^{-1}$ band on raising the temperature from 25°C to 45°C (Table (IV)-5) is explicable on the basis of the formation of a weak solvate. However, the linearity of the Beer's law plots of these p-halophenyl complexes in DMF (for complex concentrations greater than 1.5×10^{-3}M.) indicates that the solvation is complete. Furthermore, on the basis of the spectral intensity results presented above, the solvation occurs in the vicinity of the cobalt - Schiff's base bonds.

(ii) Meta-substituted Schiff's base Complexes.

The importance of solvation, demonstrated above for the para-substituted Schiff's base complexes, necessitates the consideration of both the effect of substituent charge and size on the pyridine coordination tendencies of the meta-substituted Schiff's base complexes. Placement of the substituent closer to the metal coordination sites may increase steric effects.

The results of the equilibrium studies of the reaction of pyridine with the meta-substituted Schiff's base complexes are shown in Table(IV)-6. It is evident from the higher values of the equilibrium constants, that solvation near the metal coordination sites in these complexes is appreciably lower than that found in the corresponding para-substituted compounds.

The increase in the stability constants for the m-tolyl and the m-anisyl complexes over those of the corresponding para-compounds may arise from an increase in the steric hindrance to solvation near the metal. Then, on the formation of the pyridine adducts, solvation increases resulting in a higher stabilization of the reaction products. This is in agreement with the higher $-\Delta S^{o}_{T}$ and $-\Delta H^{o}_{T}$ values found for the m-tolyl and m-anisyl complexes compared to the corresponding para-substituted compounds.

On movement of the methoxy group from the para- to the meta- position, a larger increase in the equilibrium constants of pyridine addition is expected than for a similar shift of the methyl group. This was found to be the case. The greater increase in the equilibrium energy parameters for the m-anisyl complex on monopyridinate formation is indicative of the relatively higher solvation of the adduct compared to the original reactant. Thus on the basis of solvent stabilization of the species in the reaction solution, the enthalpies and entropies of pyridine additions to the m-tolyl and m-anisyl complexes can be understood.

TABLE (IV)-6.

The thermodynamic properties for the reaction of pyridine with bis(N-meta-X-phenylsalicylideneiminato)cobalt(II) at 25°C.

X	Solvent	$K_1{}^a$	$K_2{}^a$	$K_T{}^b$	$\Delta G^{\circ}{}_1{}^c$	$\Delta G^{\circ}{}_2$	$\Delta G^{\circ}{}_T$
hydrogen	benzene	1.8	2.8	5.1	-340	-610	-950
methyl	benzene	1.3	3.9	4.9	-140	-800	-940
methoxy	benzene	1.4	3.9	5.4	-200	-800	-1,000
fluoro	benzene	8.8	7.0	61	-1,290	-1,150	-2,440
chloro	benzene	8.7	11.9	103	-1,350	-1,400	-2,750
	chlorobenzene	9.2	4.8	44	-1,310	-930	-2,240
bromo	benzene	10.2	10.0	102	-1,380	-1,370	-2,750

a. The equilibrium constants K_1 and K_2 are expressed in litres/mole.

b. The overall equilibrium constants $K_T = K_1.K_2$ is in litres^{2}mole^{-2}.

c. All free energy terms are expressed in calories/mole.

TABLE (IV)-6. (contd.)

X	Solvent	$-\Delta H^{\circ}_{1}$[a]	$-\Delta H^{\circ}_{2}$	$-\Delta H^{\circ}_{T}$	$-\Delta S^{\circ}_{1}$[b]	$-\Delta S^{\circ}_{2}$	$-\Delta S^{\circ}_{T}$
hydrogen	benzene	5.8	7.3	13.1	19	21	40
methyl	benzene	7.6	5.1	12.7	25	14	40
methoxy	benzene	6.8	6.5	13.3	22	19	42
fluoro	benzene	6.2	5.1	11.3	22	18	41
chloro	benzene	8.4	4.01	12.4	24	9	33
	chlorobenzene	9.0	1.7	10.8	28	4	32
bromo	benzene	8.0	4.2	12.2	22	10	32

a. Enthalpy changes for pyridine addition are in K.cals./mole.

b. Entropy changes are in entropy units (cals./degree/mole.)

The stability of the pyridine adducts of the *m*-halophenyl chelates are quite large (See Table(IV)-6). This is attributed to a low solvation of the Schiff's bases in the vicinity of the metal due to the meta-halogens which tend to repel the solvent.

In benzene, the overall equilibrium constant K_T for the reaction of pyridine with the *m*-chlorophenyl complex is greater than in chlorobenzene. A lower solvation by the benzene is hence suggested. It is not possible, at first sight, to attribute the decrease in K_T in chlorobenzene to the greater solvation of the complex by this solvent as stronger pyridine-chlorobenzene interaction would have a similar effect on K_T. However, if the differences in the solvent effects lie only in the strengths of the pyridine solvates, both K_1 and K_2 should be reduced in chlorobenzene. This is not the case, as K_1 is found to be larger in this solvent.

An explanation based on the greater solvent stabilization of the monopyridinate adduct by the chlorobenzene is in accord with both the high K_1 value and the high (numerically) enthalpy and entropy of formation of this intermediate species. The low value of K_2, $- \Delta H^\circ_2$ and $- \Delta S^\circ_2$ for the *m*-chlorophenyl complex in chlorobenzene supports this postulate of a high solvent stabilization of the monopyridinate.

The m-halophenyl complexes are more readily soluble than the corresponding para-substituted compounds. This apparent decrease in intermolecular bonding is also noted in their lower melting points.

When a saturated solution of the m-bromophenyl complex in chlorobenzene, was heated to boiling, a fine precipitate of the complex formed. On cooling this precipitate redissolved. Presumably at elevated temperatures the solvation of the complex is reduced sufficiently to allow precipitation to occur. This effect was not observed in the lower boiling-point solvent benzene.

The preparation of the m-halophenyl complexes was difficult on account of their unwillingness to crystallize readily. This was especially true for the m-fluorophenyl complex which tended to precipitate as a gel from benzene or a benzene/ethanol mixture.

(iii) Ortho-substituted Schiff's base complexes.

On coordination of a pyridine molecule to the cobalt atom in a complex, a loss in both the rotational and translational entropy is incurred by the pyridine. The amount of rotational entropy lost will depend on the restriction to rotation imposed on the pyridine following coordination. While the rotation about the two pyridine axes is completely removed, rotation about the two-fold axis through the nitrogen remains possible. If, however, the pyridine is also pi-bonded to the cobalt, this entropy will also be lost.

The importance of steric effects on the entropy for the addition of picolines to diacetylbisbenzoylhydrazonenickel(II) was taken by Sacconi <u>et.al</u>.[17] to infer that pyridine attached to the metal in this complex can rotate. The entropy change found by these workers for the addition of two pyridines to the nickel complex was -33 entropy units, while the coordination of two $\underline{\alpha}$ -picolines to the same compound resulted in an entropy change of -41 e.u. With the saturated base piperidine, which cannot form pi-bonds, an entropy change of approximately -20e.u. was found. On this basis it appeared probable that only weak pi-bonds exist when pyridine is coordinated to nickel. This has recently been confirmed by Happe and Ward[28] who found that spin-density was transferred only through the sigma-orbital system when pyridine is coordinated to bis-acetylacetonate-nickel(II). In an extension of this study, they were able to show that the same is true for the corresponding cobalt complexes. Thus, presumably in the cobalt(II) Schiff's base complexes, the pyridine can rotate about the nitrogen-cobalt bond.

Calculation of the rotational partition function, $q_{rot.}$, of the pyridine about the two-fold axis through the nitrogen (See Appendix E), and the introduction of this function into the expression

$$S = R + R \ln q_{rot} \qquad (IV)-9$$

allows an estimation of the entropy, S, associated with this rotation. A value of 14.1 entropy units was found. This differs appreciably from the value of 7.8 e.u. calculated by King _et.al._[18]

Inspection of Table(IV)-7 shows that in the reaction of the _o_-tolyl complex with pyridine, the overall entropy change is -63e.u. This value is 23 e.u. more negative than that estimated for the phenyl complex. An increase in entropy of this magnitude is explicable only on the assumption of a steric interaction between the pyridine and the _o_-methyl groups, so restricting the rotation of the coordinated pyridines. On the basis of the calculation above (Equation (IV)-9), the entropy difference between free rotation of the two pyridines about the cobalt-nitrogen bonds and completely restricted rotation is 28.2 e.u. Since the observed entropy change is only a little less than this, it suggests that rotation of the pyridine in the dipyridinate is highly restricted. As $-\Delta S^{o}_{1}$ is low, and $-\Delta S^{o}_{2}$ is high for this compound, the strain is introduced only on the formation of the dipyridinate.

TABLE (IV)-7.

The thermodynamic properties for the reaction of pyridine with bis(N-ortho-X-phenylsalicylideneiminato)cobalt(II) at 25°C.

X	Solvent	K_1[a]	K_2[a]	K_T[b]	ΔG°_1[c]	ΔG°_2	ΔG°_T
hydrogen	benzene	1.8	2.8	5.1	-340	-610	-950
methyl	benzene	2.4	0.68	1.6	-510	290	-280
fluoro	chlorobenzene	12.1	4.9	59	-1,480	-940	-2,420
chloro	chlorobenzene	15.8	1.2	18.4	-1,640	-90	-1,730
bromo	chlorobenzene	18.9			-1,740		

a. The equilibrium constants K_1 and K_2 are expressed in litres/mole.

b. The overall equilibrium constant, $K_T = K_1.K_2$, is in litres^{2}mole^{-2}.

c. All free energy terms are expressed in calories/mole.

TABLE (IV)-7. (contd.)

X	Solvent	$-\Delta H^{\circ}_{1}$[a]	$-\Delta H^{\circ}_{2}$	$-\Delta H^{\circ}_{T}$	$-\Delta S^{\circ}_{1}$[b]	$-\Delta S^{\circ}_{2}$	$-\Delta S^{\circ}_{T}$
hydrogen	benzene	5.8	7.3	13.1	19	21	40
methyl	benzene	5.2	13.8	19.0	16	47	63
fluoro	chlorobenzene	6.4	4.7	11.1	22	18	40
chloro	chlorobenzene	7.3	9.4	16.7	19	31	50
bromo	chlorobenzene	7.4			19		

[a] Enthalpy changes for pyridine addition are in K.cals./mole.

[b] Entropy changes are in entropy units (cals./degree/mole.).

The ease of preparation of the o-fluorophenyl complex has been ascribed to the low distortion from planarity of the Schiff's base due to the small size of the substituent. On reaction of the complex with pyridine, the entropy changes for the reaction are, as expected, similar to those found in the phenyl complex. The large value of K_T for the pyridine addition to this o-fluorophenyl complex is considered to be due to low solvation near the metal.

On increasing the size of the halogen from fluorine to chlorine, steric strain again becomes important in the Schiff's base. This was made evident by the X-ray analysis by Bregman et.al.[29] on N-o-chlorophenylsalicylideneimine. An angle of twist of 54° from planarity about the carbon - nitrogen bond was observed. The large value of the entropy change on formation of the dipyridinate of the o-chlorophenyl cobalt(II) complex was attributed to the steric interaction between the pyridine and the o-chloro atoms. Again, as found in the o-tolyl complex, $-\Delta S^{o}_{2}$ makes the major contribution to the overall entropy change, indicating that the strain is introduced on formation of the octahedral species. Since the chlorine atoms are smaller than the methyl groups, it is not surprising that the steric hindrance to the rotation of the pyridine is greater in the o-tolyl complex than in the o-chlorophenyl one.

The increase in strain on formation of the dipyridinate is also reflected in the equilibrium constants. Thus, as the strain is increased, K_2 decreases. This is emphasised by the o-bromophenyl complex for which no dipyridinate species could be detected.

For an accurate estimation of both K_1 and K_2 using Equation (IV)-4, these two equilibrium constants must be of comparable order of magnitude. Since K_2 is very small for the o-bromophenyl complex, K_1 can be determined using the expression

$$\epsilon_T = \frac{\epsilon_o - \epsilon_T}{K_1 C_{pyr}} + \epsilon_1 \qquad \text{(IV)-10}$$

(See Appendix D). Here no allowance is made for dipyridinate formation.

(iv) Some additional Schiff's base complexes.

In Table (IV)-8 the thermodynamic properties of the reaction of pyridine with some additional cobalt(II) Schiff's base chelates are given. These complexes have been grouped separately as their structural features differ from those described above.

a. Bis(N-*o*-anisylsalicylideneiminato)cobalt(II).

The unusual properties of this chelate - mentioned earlier in this thesis - arise from the possible coordination of the *o*-methoxy groups to the metal. While the spectral properties of this compound support such an interaction between the metal and these groups, it was of interest to determine whether this type of bonding could be confirmed by the reaction of this compound with pyridine.

Unlike the *p*-anisyl and the *m*-anisyl complexes, the *o*-anisyl compound is highly insoluble in the more common organic solvents such as benzene. It is however soluble in DMF, and this solvent was used for the equilibrium determinations.

It was noted above that as the size of the ortho-substituent on the Schiff's base was increased, so the value of K_2 decreased. On this basis a low value of K_2 for this *o*-anisyl compound is expected. In fact K_2 was found to be too small to be measured by the spectrophotometric technique employed. Bonding through the methoxy groups would stabilise the chelate against reaction with pyridine. This stabilization would be reflected in a low K_1 value. While K_1 was shown experimentally to be small (0.36 litres/mole), it was not possible to form any structural conclusions from this data since solvation by the DMF could not be accounted for.

However, the small ΔH^{o}_{1} value of -2.4 K.cals./mole, tends to support the assumption of metal - methoxy bonding.

The spectrum of bis(N-*o*-anisylsalicylideneiminato)-cobalt(II) in pyridine should, as was found to be the case with the *o*-bromophenyl complex, be described by Equation (IV)-10. However, on application of the spectral intensities to this expression, smooth curves were obtained. This effect can be attributed to differences in the solvation of this compound by the DMF and pyridine. The importance of the pyridine effect in this system arises from the low value of the equilibrium constant, necessitating the use of high pyridine concentrations to affect an appreciable change in the solution extinctions. The accuracy of the stability plot (Equation (IV)-10) rests mainly on the difference $\epsilon_0 - \epsilon_T$. Since the extinction (ϵ_0) of bis(N-*o*-anisylsalicylideneiminato)-cobalt(II) in DMF at 25°C. is only 17.3, (See Fig.(IV)-7) the term $\epsilon_0 - \epsilon_T$ is small, thus introducing large errors into the determination of the equilibrium constant.

By rearrangement of Equation (IV)-10, it is possible to obtain the relationship

$$\epsilon_T = -K.C_{pyr.}(\epsilon_1 - \epsilon_T) + \epsilon_0 \quad \text{(IV)-11}$$

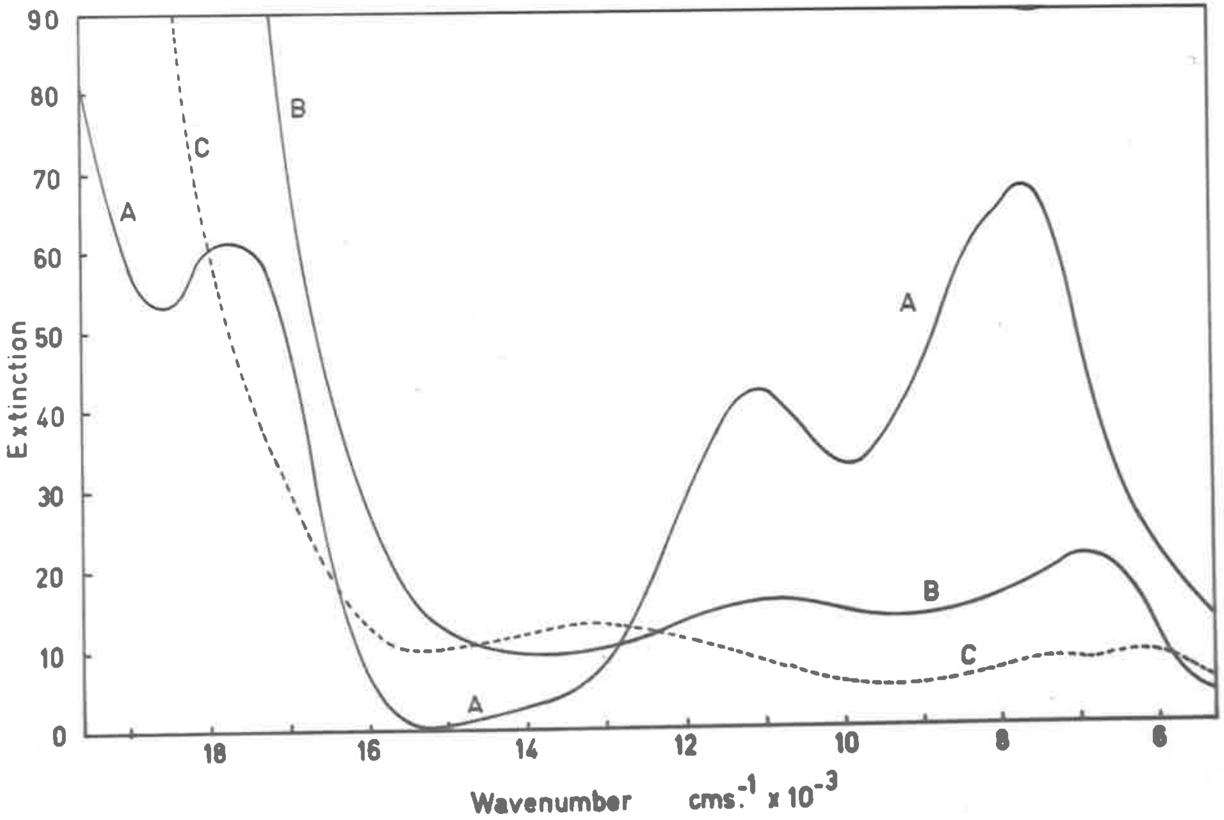


Fig.(IV)-7. The visible and near infrared spectra (at 25°C) of
A. Bis(N-cyclohexylsalicylideneiminato)cobalt(II) in benzene.
B. Bis(N-o-anisylsalicylideneiminato)cobalt(II) in dimethylformamide.
C. Bis(N-m-nitrophenylsalicylideneiminato)cobalt(II) in dimethylformamide.

TABLE (IV)-8.

The thermodynamic properties for the reaction of pyridine with cobalt(II) Schiff's base chelates, at 25°C.

Schiff's base	Solvent	K_1[a]	K_2[a]	K_T[b]	ΔG°_1[c]	ΔG°_2	ΔG°_T
N-phenylsalicylideneimine	benzene	1.8	2.8	5.1	-340	-610	-950
N-*o*-anisylsalicylideneimine	DMF	0.36			600		
N-*m*-nitrophenylsalicylideneimine	DMF	2.1	1.4	2.9	-450	-180	-630
N-α-naphthylsalicylideneimine	benzene	5.8	1.6	9.1	-1,040	-270	-1,310
N-benzylsalicylideneimine	chlorobenzene	4.1	2.3	9.6	-830	-500	-1,330
N-cyclohexylsalicylideneimine	benzene	0.10			1,200		
N-*p*-tolyl-2-hydroxy-1-naphthylideneimine	chlorobenzene	0.56	3.3	1.8	300	-810	-510
N-*p*-tolyl-4-hydroxysalicylideneimine	DMF			0.012			2,600

a. The equilibrium constants K_1 and K_2 are expressed in litres/mole.

b. The overall equilibrium constant, $K_T = K_1.K_2$, is in litres^{2}mole^{-2}.

c. All free energies are expressed in calories/mole.

TABLE (IV)-8. (contd.)

Schiff's base	Solvent	$-\Delta H^\circ_1$ [a]	$-\Delta H^\circ_2$	$-\Delta H^\circ_T$	$-\Delta S^\circ_1$ [b]	$-\Delta S^\circ_2$	$-\Delta S^\circ_T$
N-phenylsalicylideneimine	benzene	5.8	7.3	13.1	19	21	40
N-*o*-anisylsalicylideneimine	DMF	2.4			10		
N-*m*-nitrophenylsalicylideneimine	DMF	5.5	5.1	10.6	17	17	34
N-*α*-naphthylsalicylideneimine	benzene	6.4	7.3	13.7	18	23	41
N-benzylsalicylideneimine	chlorobenzene	4.2	15.0	19.2	11	49	60
N-cyclohexylsalicylideneimine	benzene	7.5			30		
N-*p*-tolyl-2-hydroxy-1-naphthylideneimine	chlorobenzene	6.5	6.7	13.2	23	20	43
N-*p*-tolyl-4-hydroxysalicylideneimine	DMF			5.7			28

a. Enthalpy changes for pyridine addition are in K.cals./mole.

b. Entropy changes are in entropy units (cals./degree/mole.)

In this expression, since ϵ_1 is always small (between 0.8 and 2.0 in the spectral region 8,400 - 7,200 cms.$^{-1}$), the difference $\epsilon_1 - \epsilon_T$ will be numerically larger than $\epsilon_0 - \epsilon_T$, thus decreasing the percentage error incurred when using Equation (IV)-10. This was found, the plot of ϵ_T against $C_{pyr}(\epsilon_1 - \epsilon_T)$ being a straight line.

From the intercept of this slope, ϵ_0 was estimated. On the introduction of this value into Equation (IV)-10 straight line plots were also obtained. From these an improved value of ϵ_1 could be found, and then used in Equation (IV)-11 so increasing the precision of the equilibrium constant determination. In Table (IV)-9, a comparison of the extinctions found for the unreacted chelate in DMF, and those determined using Equation (IV)-11, is made. As the temperature is increased the two values for ϵ_0 converge, suggesting that the solvation by the pyridine approaches that of the complex in DMF. The solvation of this complex by DMF differs from that found in the p-halophenyl complexes as the charge transfer band of the p-anisyl complex had similar properties in both benzene and DMF.

TABLE (IV)-9.

The extinction of

bis(N-*o*-anisylsalicylideneiminato)cobalt(II)

at 7,600 cms.$^{-1}$, in DMF ($\epsilon_{0,\ DMF}$) and that determined

from Equation (IV)-11 ($\epsilon_{0,\ Pyr.}$).

Temp. ^{o}C.	$\epsilon_{0,\ DMF}$	$\epsilon_{0,\ Pyr.}$
25	17.3	16.2
30	17.8	16.8
35	18.4	17.0
40	18.8	17.8
45	18.9	18.3

b. Bis(N-*m*-nitrophenylsalicylideneiminato)cobalt(II).

The solution spectrum of this chelate is unique among the group of cobalt(II) Schiff's base complexes studied in that a band, of intensity 13.2 extinction units, was found at 13,400 cms.$^{-1}$. (See Fig.(IV)-7.) Two more weak ligand field bands were found, one at 7,200 cms.$^{-1}$ having an extinction of 8.2, and the other at 6,200 cms.$^{-1}$ with extinction 8.8. While the low intensity of the spectral bands suggests an octahedral configuration, the magnetic moments, both in DMF solution (4.52 B.M.) and in the solid (4.28 B.M.) are indicative of a "non-magnetic" quartet ground state. Such a ground state is provided for by the tetrahedral configuration (${}^4A_2$), or by a planar one (${}^4E_g$). Since the spectral properties are unaccountable for on the basis of a tetrahedral structure, a configuration of lower symmetry is suggested. On account of the spectral band at 13,400 cms.$^{-1}$, the distortion from the tetrahedral configuration is presumably greater in the case of the *m*-nitrophenyl compound than for the *p*-anisyl chelate.

If a D_{4h} symmetry is assumed for the *m*-nitrophenyl compound with two weak tetragonal bonds to the metal along the "z" direction, it is possible to assign the 13,400 cms.$^{-1}$ band to the ${}^4E_g(F) \longrightarrow {}^4P$ transition. The two bands at 6,200 cms.$^{-1}$ and 7,200 cms.$^{-1}$ may then be attributed to transitions within the ${}^4F$ energy state. It is of interest for comparison, to recall that the brown complex bis(N-*p*-tolylsalicylideneimine)dichlorocobalt(II) had an absorption band at 12,800 cms.$^{-1}$

The distortion from tetrahedral symmetry may arise from either a metal-nitro or metal-DMF interaction. Since the mull transmission spectrum of this *m*-nitrophenyl complex is similar to that found for the other cobalt(II) Schiff's base complexes (See Appendix B), it is suggested that metal-DMF interactions are important. The study of the reaction of this complex with pyridine in DMF did not yield any further information on the nature of the distorting force.

An interesting feature of the solution spectrum of this m-nitrophenyl complex is that on increasing the temperature, the extinction of the 13,400 cms.$^{-1}$ band falls, while that of the 7,200 cms.$^{-1}$ band and the 6,200 cms.$^{-1}$ band increases. This is shown (in part) in Table (IV)-10.

TABLE (IV)-10.

The spectral properties of

bis(N-m-nitrophenylsalicylideneiminato)cobalt(II) in DMF.

Temp. °C.	$\epsilon_{13,400}$	$\epsilon_{6,200}$
25	13.2	8.8
30	12.8	9.2
35	12.6	9.4
40	12.6	10.4
45	12.4	10.8

Furthermore, on increasing the temperature, the width of the 13,400 cms.$^{-1}$ band increases, the band maximum being 300 cms.$^{-1}$ lower in energy at 45°C. than at 25°C. These changes presumably reflect a weakening in the tetragonal bonds, the configuration of the compound changing to a more tetrahedral one.

In common with the o-anisyl complex, this m-nitrophenyl chelate is highly insoluble in the more common organic solvents. Solutions of concentrations up to about $2 \times 10^{-2}M$ can however be obtained in DMF. These solutions are quite stable to oxidation by air at room temperature.

e. Bis(N-α-naphthylsalicylideneiminato)cobalt(II)

This complex, next to the o-bromophenyl chelate, is the most difficult to prepare, suggesting that the Schiff's base is strongly distorted from planarity. Like all the other chelates not bearing an electronegative substituent, it is quite soluble in benzene.

On the addition of pyridine to a solution of the complex in benzene, both the mono- and di-pyridinate species are formed. From a consideration of the entropy values of these reactions, only a little strain can be considered to occur between the pyridine and the α-naphthyl ring systems. This tends to indicate that in the octahedral species, the Schiff's base molecules are not twisted far from planarity.

d. Bis(N-benzylsalicylideneiminato)cobalt(II).

This chelate is the most easily oxidised of the cobalt Schiff's base complexes investigated. Although it is soluble in benzene, its reaction with pyridine was studied in chlorobenzene to hasten solution and so minimise oxidation.

Since the aromatic ring system of the amine residue is further removed from the metal, solvent effects should be less than those found in the N-phenyl complex. The larger values of K_T and especially K_1 for the benzyl chelate suggest that this is so. A restriction to the rotation of the pyridine and the benzyl residue is suggested by the large overall entropy change associated with the pyridine adduct formation. The high value of 49 e.u. for $-\Delta S^{\circ}_{2}$, together with the low value of $-\Delta S^{\circ}_{1}$ (11 e.u.) indicates that the strain on pyridine coordination is introduced only on dipyridinate formation.

e. Bis(N-cyclohexylsalicylideneiminato)cobalt(II).

Because the conjugation of the Schiff's base is destroyed by the saturated cyclohexylamine residue, free rotation of the cyclohexyl system about the carbon-nitrogen single bond is possible. Such a large rotating substituent would interact very strongly with a coordinated pyridine.

In a study of the reaction of pyridine with this chelate, only the equilibrium constant for the addition of one pyridine could be evaluated. That no dipyridinate forms, even in pure pyridine can be ascribed to the large volume occupied by the cyclohexyl groups, preventing the approach of a second pyridine molecule. The low value for K_1 (0.10 litres/mole) and the high entropy value (ΔS^o_1 is -29.6 e.u.) indicate that the onset of strain occurs on monopyridinate formation.

In a pyridine solution, the concentration of the unreacted species (C_0) and the monopyridinate species (C_1) is given by the relationship

$$\frac{C_1}{C_0} = K_1.C_{pyr.} \qquad \text{(IV)-12}$$

or

$$\frac{C_1}{C_T} = \frac{K_1.C_{pyr}}{K_1.C_{pyr} + 1} \qquad \text{(IV)-13}$$

where $C_T = C_0 + C_1$, the total complex concentration. Taking a pure pyridine solution, $C_{pyr.}$ is approximately

12M., and $C_1/C_T = 0.55$. Thus in pure pyridine, 55% of bis(N-cyclohexylsalicylideneiminato)cobalt(II) is converted to the monopyridinate. This is contrary to the results of Sacconi _et.al._[4] who considered such a solution to contain 50% of the dipyridinate, and no monopyridinate.

On account of the low equilibrium constant, an appreciable change in the extinction of a solution of the cyclohexyl complex can only be affected by large additions of pyridine. The solvation of the unreacted complex by the pyridine must therefore be considered. The importance of this effect is demonstrated in Table (IV)-11.

TABLE (IV)-11.

The extinction at 7,400 cms.$^{-1}$ of bis(N-cyclohexylsalicylideneiminato)cobalt(II) in benzene ($\epsilon_{0,\ \text{benzene}}$) and that determined from Equation (IV)-11, ($\epsilon_{0,\ \text{Pyr.}}$).

Temp. °C.	$\epsilon_{0,\ \text{benzene}}$	$\epsilon_{0,\ \text{Pyr.}}$
19.6	68.8	70.6
30	67.5	68.8
45	66.9	67.6

The lower solvation by the pyridine on raising the temperature is reflected in the convergence of the extinction coefficients ($\epsilon_{0,\ \text{benzene}}$) and ($\epsilon_{0,\ \text{pyr.}}$).

Unlike the o-anisyl complex, the extinction of the cyclohexyl compound calculated from Equation (IV)-11 is higher than that found in benzene.

At high pyridine concentrations, a deviation from linearity in the plot of Equation (IV)-11 is found. This deviation, tending to decrease the equilibrium constant, cannot be explained on the basis of dipyridinate formation. However, by comparison with the reactions of copper(II) Schiff's base chelates with pyridine in cyclohexane (See Chapter IV, Section 7), the deviation from linearity may be ascribed to differences in the strength of solvation of the complex by the pyridine and by benzene. Thus, at high pyridine concentrations a stronger solute - pyridine interaction will depress the equilibrium constant. This effect appears to be important only at pyridine concentrations above 8M in benzene.

Previously, only the role of the substituent on the amine residue of the Schiff's base in determining the extent of the reaction of pyridine with the cobalt(II) Schiff's base chelates has been discussed. The effect of a substituent on the aldehyde residue, causing large changes in the degree of pyridine addition, is shown in Table(IV)-12.

TABLE (IV)-12.

The extinctions in benzene and pyridine at 7,400 cms.$^{-1}$ for bis(N-cyclohexylsalicylideneiminato)cobalt(II), ($\epsilon_{0,H}$) and bis(N-cyclohexyl-5-bromosalicylideneiminato)cobalt(II) ($\epsilon_{0,\ Br}$), at 25°C.

The concentrations of the two complexes in pyridine are 6.850×10^{-3}M and 1.148×10^{-2}M respectively.

Solvent	$\epsilon_{0,\ H}$	$\epsilon_{0,\ Br}$
Benzene	68.0	71.2
Pyridine	32.0	6.6

No steric interaction between the pyridine and the bromine is possible. In fact, if such an interaction did occur, a lower equilibrium constant for the addition of pyridine to the complex is predicted. The low extinction of the bis(N-cyclohexyl-5-bromosalicylideneiminato)cobalt(II) complex in pyridine is therefore only explicable on the basis of a decrease in solvent - solute interaction.

To examine more closely the importance of the nature of the aldehyde residue on the reaction of pyridine with the cobalt Schiff's base complex, a study of the coordination of pyridine to bis(N-p-tolyl-2-oxy-1-naphthylideneiminato)cobalt(II) and bis(N-p-tolyl-4-hydroxysalicylideneiminato)cobalt(II) was undertaken.

e. Bis(N-p-tolyl-2-oxy-1-naphthylideneiminato)cobalt(II).

The reaction of this bright red complex with pyridine was carried out in chlorobenzene. As found for bis(N-p-tolylsalicylideneiminato)cobalt(II), K_2 is larger than K_1, indicating the absence of any appreciable steric strain in the dipyridinate. On the basis of the planarity of the aldimine residue this result is as expected. The major difference in the equilibrium properties between these two complexes lies in the slightly higher $-\Delta S^{\circ}_2$ for the naphthylideneimine complex. This might well arise from variations in the strength of the solute - solvent interactions. A strict comparison between the equilibrium parameters of these two p-tolyl complexes, however, cannot be made on account of the different solvents used.

g. Bis(N-p-tolyl-4-hydroxysalicylideneiminato)cobalt(II).

This chelate is readily obtained on reaction of cobalt acetate with the Schiff's base in an acetate buffered, reaction mixture. On recrystallisation from an ethanol-benzene mixture, the monohydrate is obtained as an orange-brown powder.

The spectral bands of this monohydrated complex are of a similar energy in both DMF and in the solid state (See Appendix B), indicating that the water is not coordinated to the metal. On this basis it is considered that the water molecules may reside near the 4-hydroxy groups. The presence of a strong, narrow absorption band at 3,605 cms.$^{-1}$ indicates that the water is only loosely held to the complex. However, the water cannot be removed by drying in vacuo over phosphorus pentoxide for several days at room temperature. On elevating the temperature to 135°C., all the water was released within a period of ten hours. No change in colour of the complex accompanied this dehydration.

Since the solubility of the complex is very low in aromatic solvents, the reaction of pyridine with the monohydrate was studied in DMF.

The reaction of this monohydrate complex with pyridine was very limited. This was borne out by the spectral results. For a solution of concentration 8.183 x 10^{-3}M the extinction in DMF at 7,800 cms.$^{-1}$ was 74.6, while in pyridine, at 25°C, it decreased only to 24.4 extinction units.

Unlike the cyclohexyl compound, this decrease in extinction is due to the formation, not of the monopyridinate species, but of the dipyridinate adduct. The existence of a monopyridinate adduct could not be ascertained, the spectral properties of the reaction solutions being described exactly by the relationship

$$\epsilon_T = -K_T(C^2_{pyr.})\ (\epsilon_T - \epsilon_2) + \epsilon_0 \qquad \text{(IV)-14}$$

(See Appendix D). The overall stability constant K_T, so calculated was 0.012 litre^2.mole^{-2}, at 25°C.

The absence of the monopyridinate in the reaction solution suggests that K_2 is very much larger than K_1. Thus, when the monopyridinate forms, the concentration of pyridine (0.5 to 12 M) present is sufficient to convert it completely to the dipyridinate.

The reluctance of the pyridine to react with this complex can be attributed to a high steric hindrance to the approach of the pyridine to the metal. This may either be due to intermolecular water bridges, or strong solvation of the complex by the DMF. The existence of intermolecular water bridges in DMF however, seems unlikely. Furthermore, the spectral intensity of the 7,800 cms.$^{-1}$ band of the dehydrated species decreases by the same extent in pyridine as does the monohydrate, (of equal concentration), suggesting that the low equilibrium constant for pyridine addition arises from DMF solvation. The low overall enthalpy change (ΔH^{o}_{T} = -5.7 K.cal./mole) is in agreement with the small K_T value, and tends to confirm the postulate that solvent-solute bonds are cleaved on pyridine addition.

Since the low K_T value necessitates the use of high pyridine concentrations in the equilibrium study, the value of ϵ_0 given in Equation (IV)-14, will differ from that found for the complex in DMF. From the equilibrium plot (Equation (IV)-14), ϵ_0 at 25°C. is estimated to be 67.8 at 7,800 cms.$^{-1}$, while in DMF the extinction at this wavenumber and temperature is 74.6.

5. Nature of the Pyridine Adducts.

The instability of solid pyridine adducts of cobalt(II) Schiff's base chelates has been demonstrated by West[3], who, in an attempt to isolate the pyridinate of the *m*-tolyl and the *p*-tolyl complexes, found that they released pyridine spontaneously at room temperature.

The equilibrium studies above have illustrated that both the mono- and the di-pyridinate adducts form on solution of most cobalt(II) Schiff's base chelates in pyridine. Unless the K_1 and K_2 values have been measured it is not possible to predict *a priori* what kinds of complexes will be formed by pyridine with a particular chelate. Thus, on solution of bis(N-cyclohexylsalicylideneiminato)cobalt(II) in pyridine, only the monopyridinate forms. The same is true for the *o*-bromophenyl and the *o*-anisyl complexes. However, bis(N-*p*-tolyl-4-hydroxysalicylideneiminato)cobalt(II) monohydrate forms only the dipyridinate adduct in pyridine.

A direct interpretation of the magnetic and spectral properties of the cobalt(II) Schiff's base complexes in pyridine solution cannot be made owing to a lack of knowledge of the properties of the monopyridinate adduct. However, in conjunction with the equilibrium studies it is possible, from such measurements, to gain information on both the spectral and magnetic properties of the two pyridinates.

(i) The dipyridinate.

From the equilibrium results presented in the previous section of this chapter, it can be seen that most complexes in pure pyridine exist nearly completely as the dipyridinate.

a. Ligand Field Spectra.

The ligand field spectra of the dipyridinates consists of two bands, one at 9,800 cms.$^{-1}$ ($\epsilon \approx 10$) and the other at about 18,000 cms.$^{-1}$ ($\epsilon \approx 20$). (See Appendix B and Fig. (IV)-4.) The appearance of this high energy band is dependent on the energy of the charge transfer band.

The low extinction of the band at 9,800 cms.$^{-1}$ indicates that the intensity of the transition arises from a vibronic coupling mechanism. The dipyridinates are hence considered to have a distorted octahedral configuration. The transition at 9,800 cms.$^{-1}$ can therefore be attributed to the $^4T_{1g}(F) \longrightarrow {}^4T_{2g}$ excitation.

Some ambiguity does arise in the assignment of the band at 18,000 cms.$^{-1}$, as this transition can be assigned to either the $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ or the $^4T_{1g}(F) \longrightarrow {}^4A_{2g}$ excitation. The intensity of the $^4T_{1g}(F) \longrightarrow {}^4A_{2g}$ excitation is expected to be very small (oscillator strength of about 4.8×10^{-6}) as this transition represents a two-electron jump.[30] However, it is not possible to assign this band at 18,000 cms.$^{-1}$ on the basis of intensity as in all cases it overlaps with the charge transfer band. Calculations using either assignment for the high energy transition lead to unreasonable values[a] for the parameters B' and 10Dq, suggesting that the complexes are distorted from octahedral symmetry.

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a. In these calculations the bands found for the bis(N-benzylsalicylideneiminato)cobalt(II) complex in pyridine were employed as the charge transfer band does not hide the maximum at 17,700 cms.$^{-1}$ (See Fig.(IV)-4). Assignment of this transition to the $^4T_{1g}(F) \longrightarrow {}^4A_{2g}$ excitation leads to a negative value of B'. The alternative assignment ($^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$) necessitates B' being 596 cms.$^{-1}$ with 10Dq = 10,800 cms.$^{-1}$. This value of B' is much lower than that expected for octahedral cobalt(II).

b. Magnetic Properties.

West[3] found that the magnetic moments of several of these Schiff's base complexes in pyridine were in the range 4.7 - 4.97 B.M. This work has been extended to other Schiff's base complexes (See Appendix C). The moments found were all within the range 4.70 - 5.06 B.M. These chelates which do not add on pyridine readily (i.e. $K_T < 1$) had, in general, moments between 4.70 and 4.80 B.M. The m-halophenyl complexes, which have the highest stability constants for their pyridine adducts, also have high magnetic moments in pyridine.

The increase in magnetic moment on solution in pyridine of those Schiff's base complexes which have a high K_T for pyridine addition reflects the spectral results in that they indicate an inversion of the tetrahedral d^7 Stark energy pattern.

(ii) The Monopyridinate.

The initial reaction product of all Schiff's base complexes in pyridine solution is the mono-pyridinate adduct. No prediction on the true structure of this species is possible on the information available.

a. Ligand Field Spectra.

Since the dipyridinate of the o-bromophenyl complex could not be detected, and as the equilibrium constant for the formation of the monopyridinate is large (18.9 litres.mole^{-1}), the spectrum of this complex in pyridine will closely resemble that of the monopyridine adduct. (See Fig. (IV)-8). Two absorption maxima were found, one at 9,800 cms.$^{-1}$ (ϵ = 8.6) and the other at 17,100 cms.$^{-1}$ (ϵ = 28.8). The high extinction of the latter band arises in part from overlap with the tail of the charge transfer band. The spectral properties of this monopyridinate are very similar to those of the dipyridinate (See Fig.(IV)-8.)

Recently Cotton et.al.[31] have isolated and examined the visible spectrum of the penta-coordinated complex cyclohexylaminebis(pentane-2,4-dieno)cobalt(II). An absorption maximum was observed at approximately 18,000 cms.$^{-1}$ with an extinction of 37. The energy of this band is thus similar to that found for the monopyridinate of the o-bromophenyl Schiff's base complex.

Using Equation (IV)-4, the spectral properties of the monopyridinate may be calculated. This was done (graphically) for the o-tolyl complex. A band of

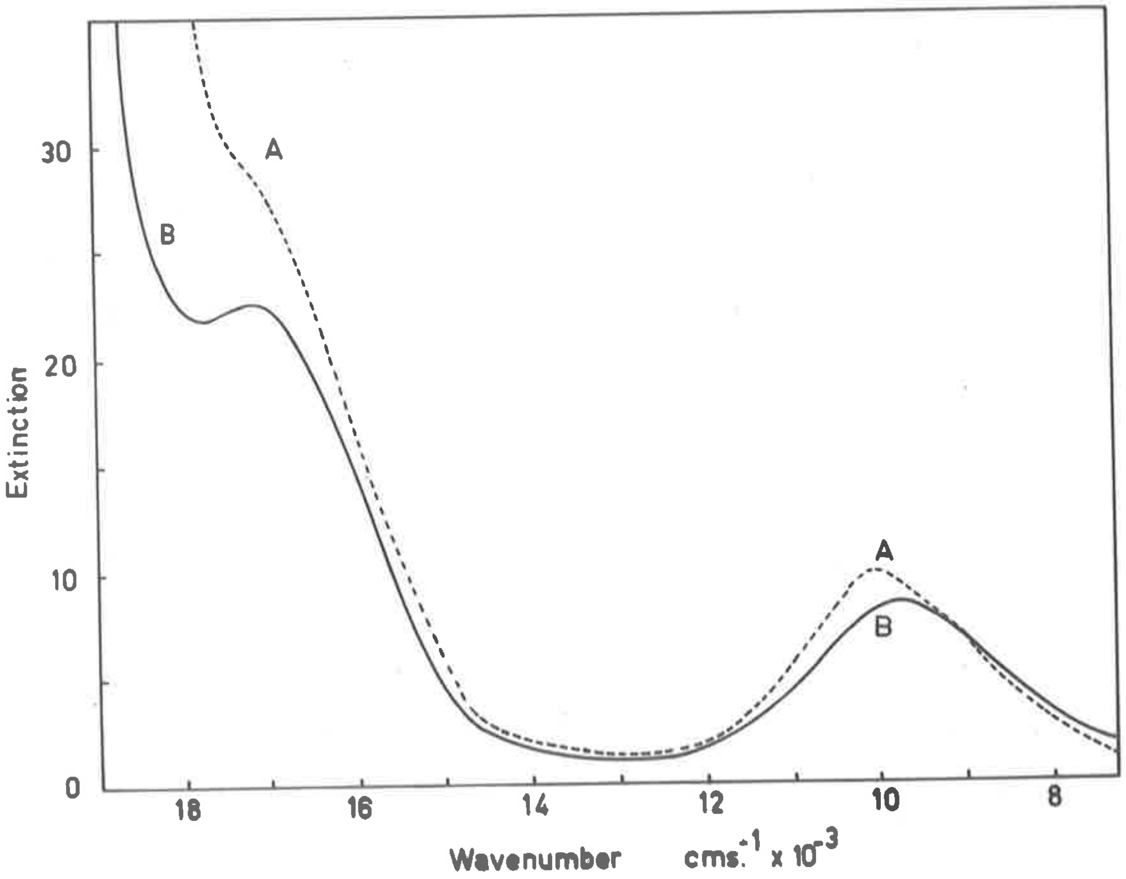

Fig.(IV)-8. The visible and near infrared spectra at 25°C of
A. Bis(N-m-bromophenylsalicylideneiminato)-cobalt(II) (1.149×10^{-2}M) in pyridine.
B. Bis(N-o-bromophenylsalicylideneiminato)-cobalt(II) (1.103×10^{-2}M) in pyridine.

extinction 4.8 was observed at 9,600 cms.$^{-1}$. (See Fig.(IV)-9.)

Even though the complexes have no centre of symmetry, the oscillator strength of the d-d bands are small. On this basis, the intensity of the transitions are considered to arise from a vibronic coupling mechanism.

b. Magnetic Moments.

The increased magnetic moment found on dissolving the o-bromophenyl complex (4.79 B.M.) and the cyclohexyl complex (4.75 B.M.) in pyridine, suggests that the ground state of the monopyridinate possesses a higher orbital angular momentum than the non-pyridinated species. Whether this arises from a removal of the $^4A_2$ state from the lowest energy, or is due to a greater intermixing of the ^4F energy levels, cannot be said.

Hence as the magnetic moment of the monopyridinate, like the dipyridinate adduct, is greater than that of the tetrahedral species, care must be taken in the interpretation of the magnetic moments of cobalt(II) Schiff's base complexes dissolved in pyridine.

(iii) The Ultraviolet Spectra in Pyridine.

Both on mono- and di-pyridinate formation, the charge transfer bands of the Schiff's base complexes experience a hypsochromic shift. (See Appendix B.) This increase in energy is, for most complexes, between 1,500 and 2,500 cms.$^{-1}$. An exception was noted in the o-anisyl complex.

The energy of the charge transfer bands is in part dictated by the energy of the ligand orbitals. For the o-anisyl complex in benzene, the low energy of the charge transfer band can be attributed to a stabilisation of the ligand molecular orbitals through the formation of metal-methoxy bonds. Cleavage of these bonds, which occurs on pyridination, will raise the energy of the ligand orbitals, resulting in the larger (3,150 cms.$^{-1}$) hypsochromic shift.

6. The Ease of Aerial Oxidation.

The ease of aerial oxidation of the complexes of the type bis(N-R-salicylideneiminato)cobalt(II) in solution is greatly dependent on the nature of the amine residue, R. When R is a straight chain aliphatic residue, oxidation of the chelate is rapid. However, when R is a branched aliphatic chain, oxidation is slow. An aromatic amine gives rise to cobalt(II) Schiff's base complexes whose ease of oxidation is intermediate between these two extreme cases.

Air oxidation of these chelates in solution can only proceed when the oxygen approaches the metal so permitting the charge transfer to occur. Thus the ease of oxidation will be governed by some of the factors involved in pyridine adduct formation.

When the approach of the oxygen to the metal is sterically hindered, a reduced rate of oxidation is expected. On this basis, it is possible to predict that the ease of oxidation will decrease with R in the order aliphatic straight chain > aromatic > aliphatic branched chain. Hence, the cyclohexyl complex is expected, and is found, to oxidise very slowly, whereas the benzyl chelate, in which the phenyl rings are further removed from the metal, oxidises very rapidly.

The p-anisyl compound is oxidised only slowly in solution because of the strong shielding of the metal by the methoxy groups.

Solvent stabilisation of the reactants was found to be of high importance in the pyridine addition reactions. A parallel dependence is expected with oxidation. This is borne out by the resistance to oxidation of the para-halogen substituted Schiff's base chelates in DMF, and by the ease of their oxidation in chlorobenzene.

The stability constants of the pyridine adducts were greatest when the aniline residue bore a meta-substituent. In agreement with this, these compounds were found to oxidise extremely readily.

An ortho-substituent lowers the rate of oxidation, by steric hindrance, to below that found in the case of the meta-substituted compounds.

7. The Reaction of Copper(II) Schiff's base Complexes with Pyridine.

The importance of solvation of cobalt(II) Schiff's base complexes in their reaction with pyridine was further emphasised by a quantitative study of the addition of pyridine to the corresponding copper(II) complexes. The copper Schiff's base complexes were used in this investigation as copper shows little tendency to increase its coordination number above five. This greatly simplifies the determination of accurate stability constants. Furthermore the steric effects are expected to be less important than with the cobalt Schiff's base complexes on account of the planarity of the copper-ligand bonds.

Pentacoordinated copper(II) is found in many chelates. Waters et.al.[32] have shown that in many instances the green colour of the copper chelates can be associated with the penta-coordination state of the metal. On solution in pyridine, most copper chelates give a green solution, indicative of the monopyridinate adduct. Such behaviour was found to occur with all the copper Schiff's base chelates investigated.

The first quantitative work on the addition of pyridine to copper chelates was carried out by Gradden and Watton[16]. On addition of pyridine to some β-diketone copper chelates only the monopyridinate was found in the solution. Significant differences in the stability constant of the monopyridinate adduct were found both on varying the nature of the ligand and the solvent. The dependence of the stability of the monopyridinate on the nature of the ligand was considered to be related to the residual positive charges on the copper atoms. The changes in the stability of the pyridine adduct with solvent (chloroform < acetone < benzene) were attributed to changes in the solvation energies of the pyridine.

The reaction of copper(II) Schiff's base chelates with pyridine is described by the equation

$$CuB_2 + Pyr. \rightleftharpoons CuB_2Pyr. \qquad (IV)-15$$

where CuB_2 is the copper chelate. Isosbestic points found in the visible spectral region (See Fig.(IV)-10) also support such a reaction scheme.

The high stability of copper(II) Schiff's base chelates in anhydrous solvents[33] enables the study of the reaction (IV)-15 to be made in solutions of lower complex concentration than those required in the corresponding reaction of the cobalt(II) Schiff's base complexes with pyridine. Cyclohexane was found to be a suitable solvent for some complexes.

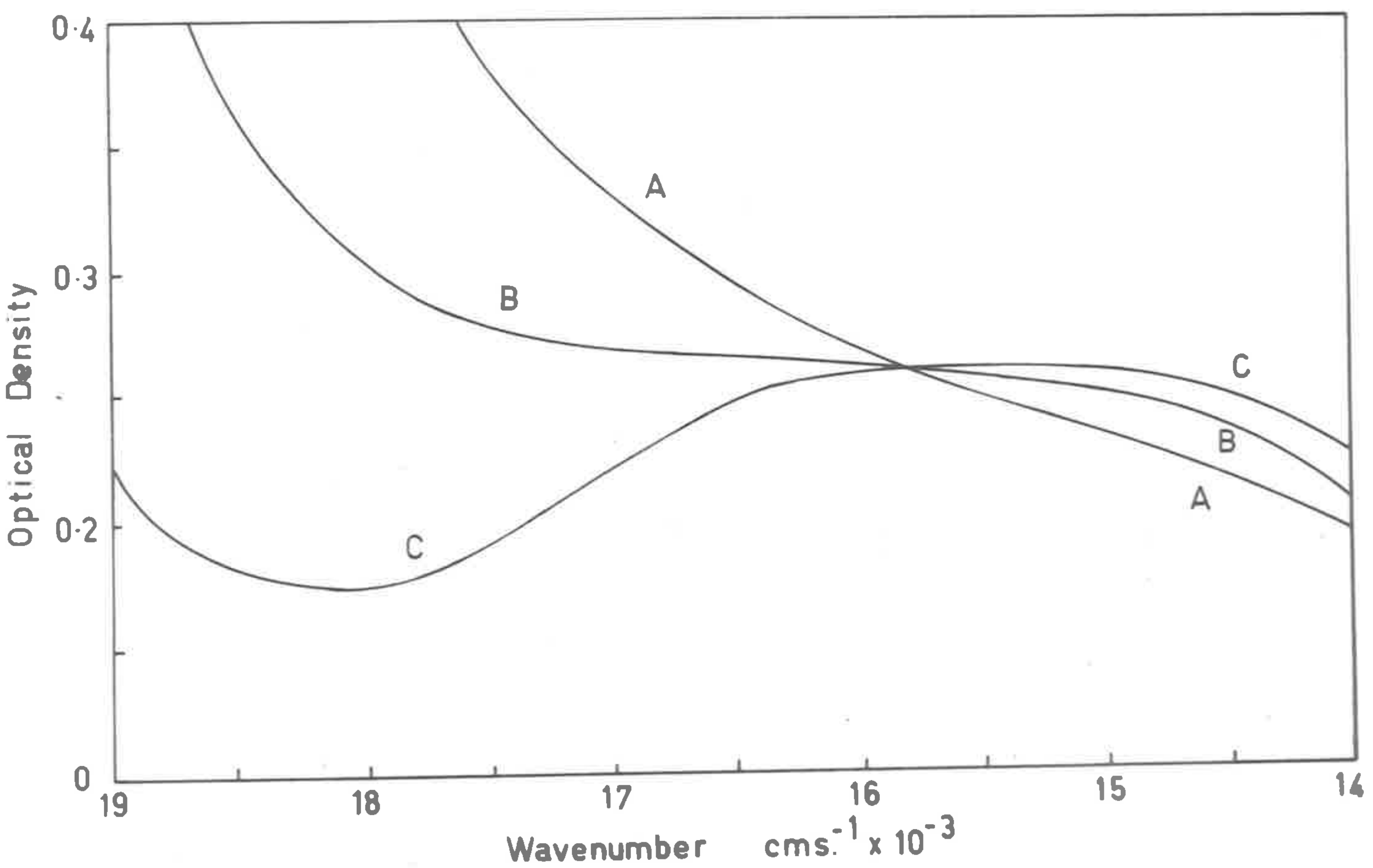

Fig.(IV)-10. The spectra of bis(N-m-fluorophenylsalicylideneiminato)-copper(II) in chlorobenzene/pyridine mixtures at 25°C.
A. The spectrum in chlorobenzene
B. The spectrum in 0.4970M pyridine.
C. The spectrum in 9.881M pyridine.

(i) Hydrocarbon Substituents on the Schiff's base.

Neglecting solvation, the stability constants for the monopyridinate adducts of the complexes bis(N-R-salicylideneiminato)copper(II) are expected to decrease with R in the direction

phenyl > p-tolyl > m-tolyl > o-tolyl,

as this is the predicted order of increasing steric crowding about the metal. A reversal of this order may occur if solvation of the complexes is important. Inspection of Table (IV)-13 shows that the stability constants do not increase in the way described above in either cyclohexane or chlorobenzene, suggesting that the complexes are solvated. Furthermore, since the entropy change for the o-tolyl complex is little larger than that found for the other complexes, the steric interaction between the substituents and the attached pyridine is small.

A dipolar interaction between the solvent and complex or pyridine would decrease in the order chlorobenzene > benzene > cyclohexane. The stability constants and enthalpy terms were found to vary in the opposite direction to the strengths of the solvates.

TABLE (IV)-13.

The thermodynamic properties for the reaction of pyridine with bis(N-R-salicylideneiminato)copper(II).

R	Solvent	$K_1{}^a$	$\Delta G^\circ_1{}^b$	$-\Delta H^\circ_1{}^c$	$-\Delta S^\circ_1{}^d$
phenyl	chlorobenzene	0.957	26	5.01	16.9
	benzene	1.82	-354	5.82	18.3
	DMF	0.186	998	4.70	19.2
	cyclohexane	5.99	-1,060	6.41	17.9
o-tolyl	chlorobenzene	0.965	21	5.59	18.9
	cyclohexane	5.74	-1,030	7.16	20.6
m-tolyl	chlorobenzene	0.774	152	4.04	14.1
	cyclohexane	4.35	-871	4.53	12.3
p-tolyl	chlorobenzene	0.724	191	4.27	15.0
	cyclohexane	5.08	-963	6.58	18.9
o-anisyl	chlorobenzene	0.159	1,090	-1.08	0.42
m-anisyl	cyclohexane	7.40	-1,190	7.16	20.0
p-anisyl	chlorobenzene	0.527	380	1.95	7.71
o-fluorophenyl	chlorobenzene	1.22	-119	5.86	19.3
m-fluorophenyl	chlorobenzene	2.55	-554	4.84	14.4
	benzene	4.03	-826	5.50	15.7
	cyclohexane	13.9	-1,560	8.52	23.5
p-fluorophenyl	chlorobenzene	1.62	-287	4.84	15.3
	benzene	2.32	-499	4.16	12.3

contd......

TABLE (IV)-13. (contd.)

R	Solvent	K_1	ΔG°_1	$-\Delta H^\circ_1$	$-\Delta S^\circ_1$
	cyclohexane	10.7	-1,400	6.41	16.8
o-chlorophenyl	chlorobenzene	0.506	403	3.50	13.1
m-chlorophenyl	cyclohexane	16.8	-1,670	9.00	24.6
p-chlorophenyl	cyclohexane	16.8	-1,670	7.42	19.3
o-bromophenyl	chlorobenzene	3.30	-708	4.95	14.2
m-bromophenyl	cyclohexane	8.47	-1,270	6.12	16.1
p-bromophenyl	cyclohexane	17.2	-1,680	8.92	24.4
m-nitrophenyl	chlorobenzene	7.48	-1,190	4.66	11.6
cyclohexyl	chlorobenzene	0.145	1,150	3.41	15.3
benzyl	chlorobenzene	0.321	674	2.27	9.87

a. K_1 is the equilibrium constant (litres.mole^{-1}) of monopyridinate formation at 25°C.

b. ΔG°_1 is the standard free energy change (cals.mole^{-1}) at 25°C.

c. ΔH°_1 is the standard enthalpy change in K.cals.mole^{-1}.

d. ΔS°_1 is the standard entropy change in entropy units (cals./degree/mole).

It is not possible to predict whether this arises mainly from the solvent-pyridine or the solvent-complex interactions. However, the differences found in the thermodynamic quantities for the addition of pyridine to these copper(II) Schiff's base chelates in a particular solvent, indicate the importance of solvation of the complexes.

The addition of pyridine to these copper complexes was followed by the measurement of the drop in the optical density of the complexes which accompanies coordination with pyridine. In chlorobenzene and benzene straight line equilibrium plots were obtained, even on increasing the pyridine concentration to as high as 8M. But in cyclohexane deviations from linearity were observed at pyridine concentrations above 2.5M. On increasing the concentration of pyridine above this value, the optical density of the solutions began to increase instead of decreasing. (See Fig.(IV)-11.) This increase in optical density was inexplicable on the basis of the formation of a dipyridinate adduct. It was therefore attributed to the fact that the pyridine-pyridine and the pyridine-complex interactions were stronger than the corresponding cyclohexane-pyridine and cyclohexane-complex interactions. This leads to the unusual, and

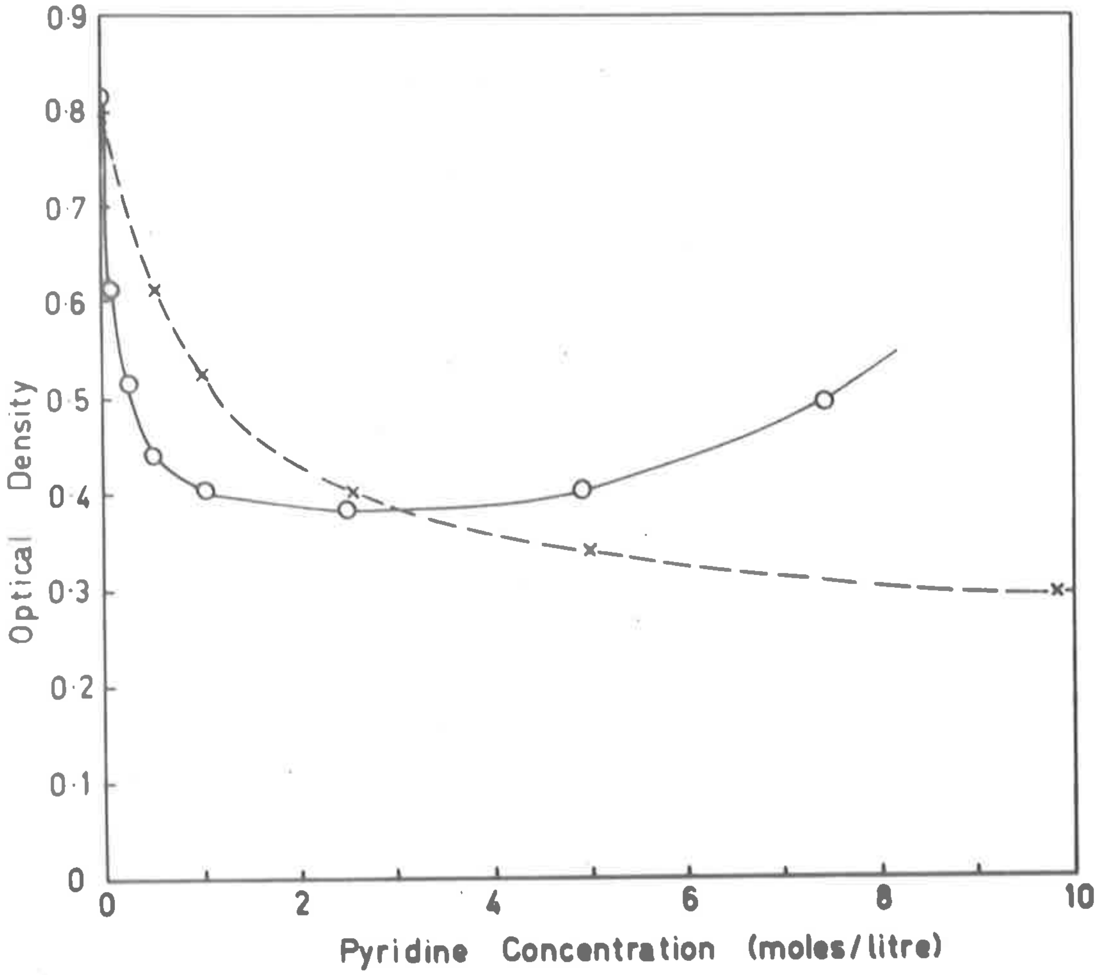

Fig.(IV)-11. The optical density of a solution of bis(N-phenylsalicylideneiminato)copper(II) at 25°C.
as a function of the pyridine concentration
-------; the solvent is chlorobenzene
_______; the solvent is cyclohexane.

surprising, conclusion that the extent of an equilibrium reaction may be retarded by increasing the concentration of a reactant. Thus, for maximum reaction of the pyridine with the Schiff's base chelates - and also presumably with other complexes - a careful choice of solvents must be made.

(iii) Electronegative Substituents on the Schiff's base.

Since the equilibrium constants for the formation of the pyridine adducts are increased when the hydrocarbon substituents on the aniline residue of the Schiff's bases are replaced by more electronegative groups (See Table (IV)-13), the solvation of these complexes must be reduced. A similar dependence of the stability of the pyridine adduct in solution on the nature of the substituent on the aniline residue was found in the cobalt(II) chelates. The more electronegative substituents apparently repel solvent molecules.

The equilibrium constants for the formation of the monopyridinate adducts of the m-fluorophenyl and the p-fluorophenyl complexes varied with solvent, decreasing in the order cyclohexane > benzene > chlorobenzene. This is the order predicted if solvation of the complex or the pyridine is an important factor in determining the value of the equilibrium constant.

The enthalpy changes ($-\Delta H^{\circ}_{1}$) for the addition of pyridine to these copper complexes are expected to vary with the solvent in the same direction as the equilibrium constants. While this is in fact found for most complexes, the p-fluorophenyl compound is exceptional in that the enthalpy of pyridine addition to this complex in benzene is less exothermic than for the same reaction in chlorobenzene. No explanation for this behaviour suggests itself.

Since the equilibrium constants in any one solvent vary from complex to complex, solvation of the complexes must occur with all three solvents used. Thus not even cyclohexane can be considered as a completely inert solvent.

The small entropy changes involved on forming the monopyridinate of the p-chlorophenyl and the p-bromophenyl complexes indicates that steric hindrance between the pyridine and the ortho-substituents is small. The similarity of the ultraviolet spectral properties (charge transfer region) of the copper complexes in benzene (See Appendix F) suggests that all Schiff's bases have virtually the same structure on coordination. This agrees with the configuration deduced for the phenyl complex, in which the copper coordination site is planar, but the amine residue projects nearly at right angles to this plane.

On this account, little steric crowding is expected in the vicinity of the metal. Thus the conjugation of all the Schiff's bases is reduced by a similar extent on chelation to copper.

(iii) Methoxy-substituted Schiff's bases.

The exceptional properties of the *p*-anisyl complex of cobalt(II) were attributed to a methoxy-metal interaction. Since the addition of pyridine to the corresponding copper(II) complex was an endothermic reaction, ($\Delta H^{\circ} = 1.08$ K.cals./mole.), a similar methoxy-metal bond may exist in this complex. The very low equilibrium constant of pyridine addition (0.159 litres.mole^{-1}) is in agreement with this postulate. Further support is found in the low energy of the charge transfer band of this complex (See Appendix F).

The low enthalpy change found for the reaction of pyridine with the *p*-anisyl complex may arise from strong solvation of the methoxy group by chlorobenzene. A similar mechanism may, in part, be responsible for the endothermicity of the reaction of pyridine with the *p*-anisyl complex in chlorobenzene.

(iv) Schiff's bases derived from aliphatic amines.

The monopyridinates of the cyclohexyl and benzyl complexes of copper have a low stability in chlorobenzene solution. (See Table (IV)-13.) However, as the entropy changes for the formation of these adducts are also small, little steric hindrance towards the coordinated pyridine occurs.

The results obtained show that solvation of the reactants is of major importance in determining the stability of the equilibrium product. The absence of strain between the pyridine and the substituents on the amine residue of the Schiff's base in the copper complexes can be ascribed to the planarity of the copper coordination site.

Since the copper(II) has only one unpaired d-electron, little structural information can be gleaned from magnetic measurements. The magnetic moments have been measured for some of the copper Schiff's base complexes listed in Table (IV)-13 in both the solid state and in solution. The values obtained were in the range 1.79 to 2.26 B.M. (See Appendix F.) Magnetic moments of a similar magnitude were found for several of these chelates by Calvin *et.al.*[34]

8. Cobalt(II) chelates of tetradentate Schiff's bases.

The preparation and properties of the complex N,N'-ethylenedi(salicylideneiminate)cobalt(II) have been investigated by many workers. Calvin and Barkelew[34] showed that the solid magnetic moment of this chelate was equivalent to one unpaired electron. On this basis, together with the stereochemical requirements of the ligand, a planar structure was considered likely, and this was subsequently confirmed by X-ray analysis[2].

Whereas the spectral properties of cobalt(II) in a tetrahedral or octahedral ligand environment are well known, no information is available on the spectral characteristics of square planar, spin-paired cobalt(II). With this in mind, the spectrum of the above complex was measured.

In the solid, reflectance spectrum, a band was found at 11,400 $cms.^{-1}$ which was, on solution in dichloromethane, displaced to 8,300 $cms.^{-1}$, its extinction being 20.6 in this solvent. (See Fig.(IV)-12a). This shift in energy can be attributed to solvent interaction. The ability of haloforms to form solid mono-adducts with this compound has been well established[35].

Although solvation of the complex would tend to destabilise the ground state - derived from the ^2G state of the free metal ion - the complex remains spin-paired. Thus West found a magnetic moment of 2.3 B.M. for the complex in dichloromethane[36]. The monochloroform adducts also possess one unpaired electron[35].

On increasing the length of the diimine bridge chelation with cobalt is made more difficult. Diehl et.al.[37] attempted to prepare a series of such cobalt compounds in which the di-imine bridge varied in length from 4 carbon atoms to 10. Only impure samples of the 1,4- and the 1,6-diimine chelates were obtained.

In the present study an attempt was made to show that non-planar complexes could be formed if the diimine bridge was made long enough.

The preparative technique employed involved the refluxing of bis(salicylaldehyde)cobalt(II)dihydrate with a diamine in ethanol. The complexes so prepared are listed in Table (IV)-14.

These compounds are all highly insoluble in organic solvents other than pyridine, in which partial solubility could be attained.

TABLE (IV)-14.

The magnetic properties of
N,N'-alkyldi(salicylideneiminato)cobalt(II)
in the solid state

Alkyl	T°A.	$10^6 \chi_g$	μ eff. B.M.
1,7-heptamethylene	291.6	22.99	4.68
1,8-octamethylene	294.3	21.49	4.65
1,9-nonamethylene	293.9	20.94	4.63
1,10-decamethylene	297.4	20.02	4.65

The magnetic and spectral properties of the solid chelates indicate that a change in structure has occurred on increasing the diimine bridge above two carbon atoms in length. The room temperature magnetic moments of the complexes are in the range expected for tetrahedral cobalt(II) complexes[38], while the solid transmission spectra (See Table (IV)-15, and Fig. (IV)-12b) are similar to those obtained for the cobalt(II) complexes with bidentate N-R-salicylideneimines, and also agree with a tetrahedral configuration for the compounds.

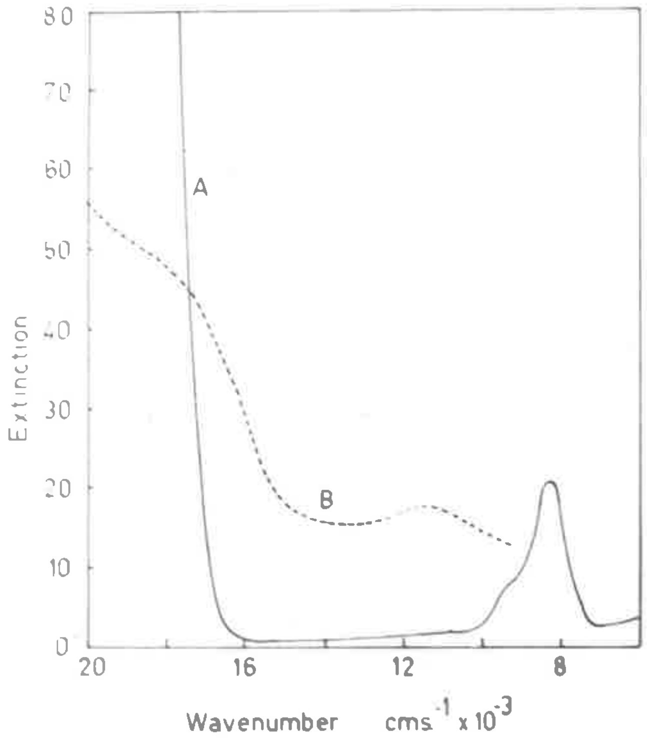

Fig.(IV)-12.a The spectrum of N,N'-ethylenedi(salicylideneiminato)cobalt(II).
A. In dichloromethane.
B. Solid reflectance spectrum.
The intensity scale refers only to the solution spectrum.

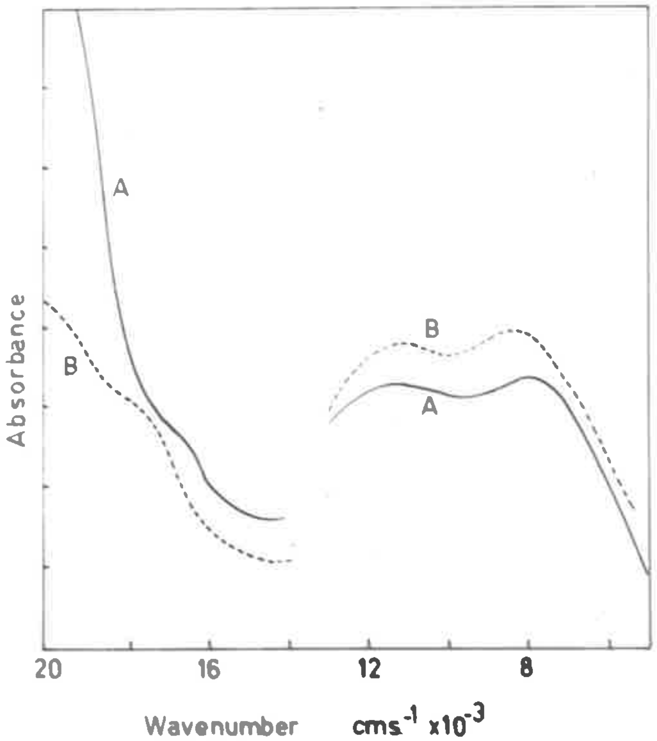

Fig.(IV)-11.b. The solid transmission spectrum of
A. Bis(N-phenylsalicylideneiminato)cobalt(II).
B. N,N'-1,7-heptamethylenedi(salicylideneiminato)-cobalt(II).

TABLE (IV)-15.

The solid mull transmission spectral properties of N,N'-alkylbis(salicylideneiminato)cobalt(II)

Alkyl	Visible Band cms.$^{-1}$	Near Infrared Bands cms.$^{-1}$	
1,7-heptamethylene	19,700(s)	11,000	8,200
	17,850(s)		7,500(s)
1,8-octamethylene	19,700(s)	11,000	8,250
	17,800(s)		7,400(s)
1,9-nonamethylene	19,800(s)	11,300	8,050
	17,800(s)		7,550
1,10-decamethylene	19,650(s)	10,700	8,640(s)
	18,570(s)		7,540(s)
	17,610(s)		

The complexes may not possess a perfectly tetrahedral configuration, but the flexible nature of the chelating agents will enable the coordinating sites to be grouped around the cobalt ion as close to a tetrahedral arrangement as possible.

Thus the spin-pairing observed in the N,N'-ethylene cobalt(II) complex arises because a square planar cis configuration is forced on the metal complex due to the steric requirements of the ligand which cannot assume a tetrahedral arrangement about the metal ion. The ligands having a long chain of methylene groups between the imine nitrogen donor groups can apparently twist themselves readily to occupy close to tetrahedral positions about the cobalt. This stereochemical arrangement may be assumed to possess the lowest energy for cobalt(II) complexes in the absence of competing steric or electronic (conjugative) factors associated with the ligand.

9. Reactions of Cobalt(II) with Schiff's Bases derived from 2-hydroxyacetophenone.

The strain, preventing planarity in N-arylsalicylideneimine Schiff's bases, arises from the steric interaction between the imine hydrogen and the amine residue. Replacement of the imine hydrogen by a larger group would tend to greatly increase this strain. This was found to be true, as no complex of cobalt(II) could be prepared with the Schiff's base N-(p-tolyl)-α-methylsalicylideneimine.

From the reaction mixture of this ligand with cobalt acetate in ethanol, a blue compound was isolated which was identified by analysis, as 2-oxy-acetophenonatocobalt(II) acetate.

In the mull transmission spectrum, two multi-component bands were found, one at 16,200 cms.$^{-1}$, and the other at 7,100 cms.$^{-1}$. On this basis a distorted tetrahedral configuration can be assigned to the complex. The high energy band is attributed to the $^4A_2 \longrightarrow {}^4T_1(P)$ excitation, while the band at 7,100 cms.$^{-1}$ results from the $^4A_2 \longrightarrow {}^4T_1(F)$ transition. The ligand field parameters 10Dq and B' were thus estimated at 4,130 cms.$^{-1}$ and 729 cms.$^{-1}$ respectively. ($\beta' = 0.754$). These results are in accord with a tetrahedral configuration.

The acetate groups may be chelated to a single metal, or bridged between two adjacent molecules. As the magnetic moment of the solid (at 19.8°C) is 3.92 B.M., a dimeric structure may be proposed. No confirmatory evidence for the existence of dimers could be obtained by molecular weight measurements because of the insolubility of the complex in benzene and other solvents suitable for molecular weight determinations.

10. Summary.

The energies of the d-d spectral transitions of the bis(N-R-salicylideneiminato)cobalt(II) complexes do not agree with those expected for regular tetrahedral complexes. The intensity of these bands was found to arise, in part, from the covalency in the metal-Schiff's base bonds. Such an intensity gaining mechanism has been shown to be of importance in tetrahedral cobalt(II) complexes[11]. Hence it was suggested that the d → d spectral properties of the Schiff's base complexes of cobalt were compatible with a distorted tetrahedral configuration in these complexes. The magnetic moments of these compounds were all less than 4.7 B.M., in accord with a $^4A_2$ ground state.

Strong support for a tetrahedral structure for these complexes comes from the X-ray work of Frasson and Panattoni[6]. Since they did not carry out a complete X-ray analysis on the n-butyl complex, no estimate of the deviation from tetrahedral symmetry can be made.

Ciampolini et.al.[5] and Sacconi et.al.[4] found that the dipole moment of these cobalt(II) Schiff's base complexes were explicable on the basis of a tetrahedral configuration. It may be mentioned, however, that measurements of this type would be difficult to interpret unambiguously when evidence on the structure of the coordinated ligand is lacking. Thus, while the spectral properties of the coordinated Schiff's base (to zinc) and the free Schiff's base appear to be similar, no conclusion can be reached concerning the stereochemistry of the coordinated Schiff's base molecules. This is due to the fact that the Schiff's bases can twist an appreciable amount about the carbon-nitrogen single bond with little effect on either the energy or intensity of the spectral bands.

The difficulty in the preparation of the cobalt(II) Schiff's base complexes bearing an ortho-substituent on the aniline residue, has been attributed to the non-planarity of the free Schiff's bases. On coordination, all Schiff's bases impose a ligand field of approximately equal strength and symmetry on the cobalt. From the charge-transfer spectra it was seen that the configuration of the coordinated Schiff's base is dependent on the nature of the ortho-substituent. The increase in energy of the o-tolyl, the o-chlorophenyl and the o-bromophenyl complexes over the corresponding para-substituted ones, was found to be between 600 and 1,100 cms.$^{-1}$

On reaction of cobalt(II) Schiff's base complexes with pyridine, both mono-pyridine and di-pyridine adducts formed in solution. The stability of these adducts is dependent both on their extent of solvation by the solvent used and on the stereochemistry of the Schiff's base ligands. The low stability of the dipyridinate adduct (compared to the monopyridinate adduct) of those complexes bearing large substituents in the ortho-position of the aniline residue of the Schiff's base ligand, was attributed to the steric shielding of the sixth metal coordination site by the ortho-substituents.

The d-d spectra and the magnetic characteristics of both the mono- and di-pyridinates were found to be similar. Both species have absorption bands of similar intensity near 10,000 cms.$^{-1}$ and 17,500 cms.$^{-1}$, and magnetic moments greater than 4.7 B.M.

The ease of oxidation of the complexes is solution was observed to depend on both the solvent and the nature of the amine residue. A parallel relationship between the stability of the pyridine adducts and the ease of oxidation of the complexes was noted.

The importance of solvation on the stability of the pyridine adduct was illustrated by a study of the reaction of pyridine with copper(II) Schiff's base complexes. These complexes lent themselves well to such an investigation as steric interaction between the attached pyridine and the amine-substituents was small.

A brief study of the dependence of the configuration of cobalt(II) complexes of the type N,N'-ethylenedi(salicylideneiminato)cobalt(II) on the length of the diimine bridge was made. On lengthening the bridge to seven carbon atoms, the spectral and magnetic properties of the complexes were indicative of a distorted tetrahedral structure.

In an attempt to prepare the cobalt complex with N-(p-tolyl)-α-methylsalicylideneimine, only the product 2-oxy-acetophenonatocobalt(II) acetate was isolated. The instability of the iminato complex was attributed to the steric hindrance between the amine residue and the keto-methyl group.

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CHAPTER V

EXPERIMENTAL

1. Analyses
   - (i) Cobalt and Copper.
   - (ii) Halide ions.
   - (iii) Schiff's bases.
   - (iv) Water.

2. Preparations.
   - (i) Schiff's bases.
   - (ii) Metal halide Schiff's base complexes.
     - a. Cobalt(II).
     - b. Copper(II).
     - c. Manganese(II).
     - d. Nickel(II).
     - e. Iron(II) and Iron(III).
   - (iii) Cobalt(II) Schiff's base chelates.
   - (iv) Copper(II) Schiff's base chelates.
   - (v) Zinc(II) Schiff's base chelates.
   - (vi) Cobalt(II) chelates with quadridentate Schiff's bases.
   - (vii) 2-oxy-acetophenonatocobalt(II) acetate.

8. Magnetic Moment Determinations.

(i) Solid measurements.

(ii) Solution measurements.

References to Chapter V.

1. Analyses.

The carbon, hydrogen and nitrogen analyses reported in this thesis were determined by the Micro-analytical Laboratories of the C.S.I.R.O., Melbourne.

(i) Determination of Cobalt and Copper.

The complexes bis(N-R-salicylideneiminato)metal(II) were destroyed by boiling for 3-4 hours with a mixture of 'Analar' grade sulphuric and nitric acids. During the process of oxidation, the nitric acid was replenished in small amounts until the solution became clear. The remaining sulphuric acid was then evaporated to near dryness by strong heating. The resulting metal-sulphate precipitate was dissolved in water and analysed for the metal by treatment with pyridine and ammonium thiocyanate as described by Vogel[1].

The analysis of the metal in the complexes bis(N-R-salicylideneimine)dihalometal(II) was easier as these complexes dissociate readily. Their complete dissociation was affected by boiling weighed samples for 10 minutes in 100 mls. of a 50/50 mixture of redistilled alcohol and water. This concentration of alcohol was found to be sufficient to keep the free Schiff's bases in solution. Analysis of the metal was carried out on this solution in an identical manner to that described above.

(ii) Halide Determinations.

The Schiff's base-metal halide complexes were decomposed as in (i) above. After dilute nitric acid had been added, the solution was analysed for the halogen with silver nitrate in the usual way[2].

(iii) Schiff's base Analysis.

The number of Schiff's base molecules per metal atom have been determined for several Schiff's base metal halide complexes. These compounds were all readily decomposed in aqueous ethanolic solutions. A Beer's law plot of the complex bis(N-p-tolylsalicylideneimine)dichlorocobalt(II) in 1MHCl served to show that dissociation and hydrolysis of the imino bond was complete is this solvent.

The analytical procedure involved wetting a weighed amount of the complex with 10 mls. of ethanol and then making the solution up to 100 mls. with approximately 1M.HCl. The optical density of this solution was then measured at 30,800 cms.$^{-1}$ in a 1 cm. silica cell using a Unicam SP-500 Spectrophotometer. By reference to a previously constructed Beer's law plot of the Schiff's base in the same solvent, the concentration of the Schiff's base in the complex solution was estimated.

The hydrolysed Schiff's bases have two absorption bands, one at 30,800 cms.$^{-1}$ (extinction ca. 3,000) and the other at 39,000 cms.$^{-1}$ (extinction ca. 12,000). Since the high energy band is sharp, the broad band at 30,800 cms.$^{-1}$ was used in the analyses.

The results so obtained were in all cases correct to within 1% of their theoretically predicted values.

(iv) Determination of Water.

The water in the complex bis(N-p-tolyl-4-hydroxysalicylideneiminato)cobalt(II)monohydrate was analysed for by heating the complex to 135°C under vacuum and over phosphorus pentoxide to constant weight. This took 10 hours of heating.

2. Preparations.

(i) Preparation of Schiff's bases.

The Schiff's bases used in this study have all been prepared previously[3,45].

They were readily obtained in yields of 30-70% by the direct reaction of equimolar quantities of the aldehyde with a primary amine in ethanol. On boiling for 10 to 20 minutes and then cooling, the Schiff's base, in general, precipitated. Purification of the compounds was affected by recrystallisation twice from ethanol or from an ethanol-benzene solution. When a Schiff's base failed to crystallise on cooling, water was added to the solution until precipitation of the base began.

The recrystallised compounds were partially dried by suction on a sintered glass Buchner funnel, and then were kept _in vacuo_, at room temperature, over phosphorus pentoxide for two days.

The compounds listed below were prepared by this method.

N-phenylsalicylideneimine. Yellow needles, m.pt. 49°C.

Calc. for $C_{13}H_{11}NO$: C, 79.16; H, 5.62.

Found : C, 78.91; H, 5.74.

N-o-tolylsalicylideneimine.	Yellow crystals, m.pt. 47°C.
Calc. for $C_{14}H_{13}NO$:	C, 79.60; H, 6.20.
Found :	C, 79.33; H, 6.20.
N-m-tolylsalicylideneimine.	Yellow phototropic crystals, m.pt. 50°C.
Calc. for $C_{14}H_{13}NO$:	C, 79.60; H, 6.20.
Found :	C, 79.15; H, 6.20.
N-p-tolylsalicylideneimine.	Yellow needles, m.pt. 95°C.
Calc. for $C_{14}H_{13}NO$:	C, 79.60; H, 6.20.
Found :	C, 79.61, H, 6.23.
N-o-anisylsalicylideneimine.	Yellow crystals, m.pt. 57°C.
Calc. for $C_{14}H_{13}NO_2$:	C, 73.99; H, 5.77.
Found :	C, 74.21; H, 5.45.
N-m-anisylsalicylideneimine.	Yellow crystals, m.pt. 60°C.
Calc. for $C_{14}H_{13}NO_2$:	C, 73.99; H, 5.77.
Found :	C, 74.36; H, 5.74.
N-p-anisylsalicylideneimine.	Pale yellow plates, m.pt. 82°C.
Calc. for $C_{14}H_{13}NO_2$:	C, 73.99; H, 5.77.
Found :	C, 74.04; H, 5.71.

N-*o*-fluorophenylsalicylideneimine. Yellow crystals, m.pt.69°C

Calc. for $C_{13}H_{10}NOF$: C, 72.54; H, 4.68.
Found : C, 71.97; H, 4.52.

N-*m*-fluorophenylsalicylideneimine. Yellow plates, m.pt. 44°C.

Calc. for $C_{13}H_{10}NOF$: C, 72.54; H, 4.68.
Found : C, 72.83; H, 4.74.

N-*p*-fluorophenylsalicylideneimine. Yellow crystals, m.pt. 84°C.

Calc. for $C_{13}H_{10}NOF$: C, 72.54; H, 4.68.
Found : C, 72.46; H, 4.29.

N-*o*-chlorophenylsalicylideneimine. Yellow crystals, m.pt. 81°C.

Calc. for $C_{13}H_{10}NOCl$: C, 67.39, H, 4.35.
Found : C, 67.51; H, 4.48.

N-*m*-chlorophenylsalicylideneimine. Yellow crystals, m.pt. 93°C.

Calc. for $C_{13}H_{10}NOCl$: C, 67.39; H, 4.35.
Found : C, 67.91; H, 4.44.

N-*p*-chlorophenylsalicylideneimine. Yellow crystals, m.pt. 103°C.

Calc. for $C_{13}H_{10}NOCl$: C, 67.39; H, 4.35; N, 6.05.
Found : C, 67.25; H, 4.29; N, 6.03.

N-*o*-bromophenylsalicylideneimine. Yellow crystals, m.pt. 86°C.

Calc. for $C_{13}H_{10}NOBr$: C, 56.54; H, 3.65.

Found : C, 56.72; H, 3.68.

N-*m*-bromophenylsalicylideneimine. Yellow crystals, m.pt. 96°C.

Calc. for $C_{13}H_{10}NOBr$: C, 56.54; H, 3.65.

Found : C, 56.66; H, 3.71.

N-*p*-bromophenylsalicylideneimine. Yellow needles, m.pt. 109°C.

Calc. for $C_{13}H_{10}NOBr$: C, 56.54; H, 3.65.

Found : C, 56.49; H, 3.60.

N-*m*-nitrophenylsalicylideneimine. Yellow crystals, m.pt. 127°C.

Calc. for $C_{13}H_{10}N_2O_3$: C, 64.45; H, 4.16.

Found : C, 64.08; H, 4.11.

N-*p*-nitrophenylsalicylideneimine. Orange crystals, m.pt. 162°C.

Calc. for $C_{13}H_{10}N_2O_3$: C, 64.45; H, 4.16.

Found : C, 64.33; H, 4.32.

N-*o*-tolyl-2-hydroxy-1-naphthylideneimine. Yellow crystals, m.pt. 129°C.

Calc. for $C_{18}H_{15}NO$: C, 82.73; H, 5.79.
Found : C, 82.35; H, 5.86.

N-*m*-tolyl-2-hydroxy-1-naphthylideneimine. Yellow crystals, m.pt. 87°C.

Calc. for $C_{18}H_{15}NO$: C, 82.73; H, 5.79.
Found : C, 82.97; H, 5.92.

N-*p*-tolyl-2-hydroxy-1-naphthylideneimine. Yellow crystals, m.pt. 139°C.

Calc. for $C_{18}H_{15}NO$: C, 82.73; H, 5.79.
Found : C, 82.68; H, 5.73.

N-*p*-tolyl-4-hydroxysalicylideneimine. Orange-red crystals, m.pt. 167°C.

Calc. for $C_{14}H_{13}NO_2$: C, 73.67; H, 5.74; N, 6.14.
Found : C, 73.91; H, 5.92; N, 6.05.

5-bromosalicylaldehyde. This compound was prepared by bromination of salicylaldehyde by the method of Auwers and Buerger[6]. The following 5-bromosalicylideneimine Schiff's bases were obtained in good yields by the procedure described above.

N-phenyl-5-bromosalicylideneimine. Yellow crystals, m.pt. 122°C.

Calc. for $C_{13}H_{10}NOBr$: C, 56.56; H, 3.65.
Found : C, 56.74; H, 3.81.

N-*m*-tolyl-5-bromosalicylideneimine. Yellow needles, m.pt. 103°C.

Calc. for $C_{14}H_{12}NOBr$: C, 57.96; H, 4.17.
Found : C, 57.84; H, 4.15.

N-*p*-tolyl-5-bromosalicylideneimine. Long yellow prisms, m.pt. 163°C.

Calc. for $C_{14}H_{12}NOBr$: C, 57.96; H, 4.17; N, 4.83.
Found : C, 58.01; H, 4.13; N, 4.69.

N-*m*-fluorophenyl-5-bromosalicylideneimine. Orange crystals, m.pt. 101°C.

Calc. for $C_{13}H_9NOFBr$: C, 53.08; H, 3.08.
Found : C, 53.16; H, 3.02.

N-p-tolylbenzylideneimine-2-benzoate. This compound was prepared by condensation of benzoylated salicylaldehyde[7] with *p*-toluidine in ethanol. The product was recrystallised twice from ethanol as long, yellow needles, m.pt. 90°C.

Calc. for $C_{21}H_{17}NO_2$: C, 79.62; H, 5.73.
Found : C, 79.28; H, 6.12.

N-p-chlorophenylbenzylideneimine was prepared by boiling equimolar quantities of *p*-chloroaniline with benzaldehyde in ethanol for 20 minutes. The precipitate was recrystallised twice from ethanol as white flakes, m.pt. 61°C.

Calc. for $C_{13}H_{10}NCl$: C, 72.38; H, 4.67.
Found : C, 72.76; H, 4.67.

(ii) Preparation of metal halide Schiff's base Complexes.

a. Complexes of cobalt(II).

These complexes were prepared by boiling preformed Schiff's base (0.1M) with a cobalt(II) halide (hydrated) (0.05M) in 100 mls. of absolute ethanol for 10-15 minutes. On cooling the reaction mixture to room temperature, a green-black, crystalline precipitate formed. Yields of all complexes were greater than 60%. The products were recrystallized from a filtered ethanol solution, and then washed with redistilled absolute ethanol and dried by suction.

The following compounds were prepared by this method.

Bis(N-*o*-tolylsalicylideneimine)dichlorocobalt(II).

Dark green crystals, m.pt. 271°C.

Calc. for $CoCl_2(C_{14}H_{13}NO)_2$: C, 60.85; H, 4.75; N, 5.08.
Found: C, 61.26; H, 4.65; N, 5.32.

Two Schiff's base molecules per cobalt atom were found by analysis.

Bis(N-*m*-tolylsalicylideneimine)dichlorocobalt(II).

Dark green crystals, m.pt. 185°C.

Calc. for $CoCl_2(C_{14}H_{13}NO)_2$: C, 60.85; H, 4.75; N, 5.08.
Found: C, 60.99; H, 4.78; N, 4.84.

Bis(N-*p*-tolylsalicylideneimine)dichlorocobalt(II).

Dark green crystals, m.pt. 270°C.

Calc. for $CoCl_2(C_{14}H_{13}NO)_2$: C, 60.85; H, 4.75; N, 5.08;
Co, 10.72; Cl, 12.89.
Found: C, 61.16; H, 4.96; N, 5.05;
Co, 10.41; Cl, 12.66.

Two Schiff's base molecules per cobalt atom were found by analysis.

Bis(N-*o*-anisylsalicylideneimine)dichlorocobalt(II).

Dark green crystals, m.pt. 230°C.

Calc. for $CoCl_2(C_{14}H_{13}NO_2)_2$: C, 57.55; H, 4.47; N, 4.80
Found: C, 57.96; H, 4.71; N, 4.82.

Bis(N-*p*-anisylsalicylideneimine)dichlorocobalt(II).

Dark green crystals, m.pt. 196°C.

Calc. for $CoCl_2(C_{14}H_{13}NO_2)_2$: C, 57.55; H, 4.47; N, 4.80.
Found : C, 57.34; H, 4.67; N, 5.01.

Bis(N-cyclohexylsalicylideneimine)dichlorocobalt(II).

Calc. for $CoCl_2(C_{13}H_{17}NO)_2$: C, 58.22; H, 6.39; N, 5.22.
Found: C, 58.61; H, 6.23; N, 5.34.

Bis(N-*o*-tolylsalicylideneimine)dibromocobalt(II).

Dark green crystals, m.pt. 241°C.

Calc. for $CoBr_2(C_{14}H_{13}NO)_2$: C, 52.44; H, 4.09; N, 4.37;
Co, 9.22; Br, 25.00.
Found: C, 51.87; H, 4.20; N, 4.11;
Co, 8.97; Br, 24.77.

Bis(N-*m*-tolylsalicylideneimine)dibromocobalt(II).

Dark green crystals, m.pt. 211°C.

Calc. for $CoBr_2(C_{14}H_{13}NO)_2$: C, 52.44; H, 4.09; N, 4.37.
Found: C, 52.71; H, 4.18; N, 4.54.

Bis(N-p-tolylsalicylideneimine)dibromocobalt(II).

Dark green crystals, m.pt. 234°C.

Calc. for $CoBr_2(C_{14}H_{13}NO)_2$: C, 52.44; H, 4.09; N, 4.37 ; Co, 9.22.

Found: C, 52.36; H, 4.29; N, 4.55; Co, 9.16.

Bis(N-p-chlorophenylsalicylideneimine)diiodocobalt(II).

Dark green crystals, m.pt. 226°C.

Calc. for $CoI_2(C_{13}H_{10}NOCl)_2$: C, 40.23; H, 2.60; N, 3.61.

Found : C, 40.17; H, 2.78; N, 3.46.

Bis(N-p-tolylsalicylideneimine)dichlorocobalt(II).

(Brown Sample.)

When bis(N-p-tolylsalicylideneimine)dichlorocobalt(II) was refluxed for 3-4 hours in ethanol under nitrogen, the colour of the complex changed from green to brown. After cooling, the mother liquor was replaced by absolute alcohol and the brown complex was recrystallized from this solvent under a continuous stream of nitrogen. The brown crystals obtained were filtered and dried under nitrogen in a sintered glass Buchner funnel fitted to the recrystallization flask. The dried compound was then kept *in vacuo* over phosphorus pentoxide for one day. M.Pt. 149°C. The preparation of this brown complex thus differed to that of the corresponding green compound only in the length of time the complex was refluxed in ethanol during recrystallization. For the green complexes recrystallization was generally completed in 20 minutes.

Calc. for $CoCl_2(C_{14}H_{13}NO)_2$: C, 60.85; H, 4.75; N, 5.08;
Cl, 12.89.
Found : C, 60.05, H, 4.85; N, 5.02;
Cl, 12.56.

Bis(N-p-tolylsalicylideneimine)dithiocyanatocobalt(II).

This complex was prepared by the reaction of cobalt(II) nitrate hexahydrate (5.70 gms., 0.025M) in 25mls. of absolute alcohol and N-p-tolylsalicylideneimine (10.6 gms. 0.05M) in 100mls. absolute alcohol. On addition of the sodium thiocyanate to the reddish mixture of Schiff's base and cobalt nitrate, the reaction solution turned dark green. After refluxing for 15 minutes, the precipitated sodium nitrate was removed by filtration of the hot solution. 1.8 gms. (52%) of the sodium nitrate was removed. Dark green crystals (7.7 gms., 64% yield) were obtained on cooling the reaction mixture. The complex was then dissolved in ethanol, filtered hot, and allowed to recrystallize. The product was dried in the manner described for the other green cobalt(II)dihalo Schiff's base complexes. M.Pt. 206°C.

An alternative procedure, based on the reaction of sodium thiocyanate on bis(N-p-tolylsalicylideneimine)-dichlorocobalt(II) in absolute ethanol was also used. However, the yields were low (10-15%), the major product being the Schiff's base.

Calc. for $CO(NCS)_2(C_{14}H_{13}NO)_2$: C, 60.30; H, 4.38; N, 9.38.
Found : C, 60.91; H, 4.48; N, 9.45.

N-p-tolylsalicylideneiminedichlorocobalt(II)monopyridinate.

This complex was prepared by reacting cobalt chloride hexahydrate (5.7 gms. 0.025M) with N-p-tolylsalicylideneimine (10.6 gms., 0.05M) in 100 mls. in absolute alcohol and then treating the reaction mixture with 25 mls. of pyridine. After boiling for 10 minutes, and then cooling, an orange product (19 gms.) was isolated from the reaction solution. On drying this complex in an oven at 120°C for two hours, it turned green. This complex was then recrystallized from ethanol and air dried on a sintered glass funnel in the usual way. M.Pt. 182°C.

Calc. for $C_{19}H_{18}N_2OCl_2Co$: C, 54.31; H, 4.32; N, 6.67; Cl, 16.88.
Found: C, 54.41; H, 4.44; N, 6.50; Cl, 17.02.

By analysis, only one mole of Schiff's base was found per molecule of complex.

The higher solubility of this complex compared to the other Schiff's base dihalo cobalt complexes has been attributed to a lower extent of intermolecular hydrogen bonding.

On drying the orange compound in air at 120°C in an oven for five hours, no further decrease in weight was observed. The total loss in weight found was 39.36%. A loss of four pyridines per molecule of complex would represent a loss in weight of 42.9%. On this basis it was considered that the initial reaction product was N-p-tolylsalicylideneiminedichlorocobalt(II)monopyridinate, solvated by four pyridines. Recrystallization of this complex to confirm its composition was not possible. In ethanol, dissociation to the blue dipyridinatedichlorocobalt(II) occurred, while in a pyridine/ethanol mixture, a considerable amount of the pink tetrapyridinatedichlorocobalt(II) was found.

(ii) Complexes of Copper.

These compounds were prepared by the reaction of anhydrous copper chloride (4.0 gms., 0.03M) with the Schiff's base (12.7 gms. 0.06M) in absolute alcohol (100 mls.).

The brown reaction solution was refluxed for 15 minutes and then let cool to room temperature. Crystallization of the product was allowed to proceed for two days, after which the precipitate was collected. The product was recrystallized from ethanol and dried by suction as before. The khaki-green, crystalline complexes so obtained were stored for one day under vacuum, over phosphorus pentoxide.

Bis(N-*o*-tolylsalicylideneimine)dichlorocopper(II).

Small Khaki green crystals, m.pt. 124°C.

Calc. for $CuCl_2(C_{14}H_{13}NO)_2$: Cu, 11.46; Cl, 12.78.
Found : Cu, 11.28; Cl, 12.52.

Two Schiff's bases per copper atom were found by analysis.

Bis(N-*p*-tolylsalicylideneimine)dichlorocopper(II).

Small khaki-green crystals, m.pt. 151°C.

Calc. for $CuCl_2(C_{14}H_{13}NO)_2$: Cu, 11.46; Cl, 12.78.
Found : Cu, 11.28; Cl, 12.56.

Two Schiff's bases per copper atom were found by analysis.

c. A Complex of Manganese(II).

Bis(N-cyclohexylsalicylideneimine)dichloromanganese(II).

This complex was prepared by reacting manganese chloride tetrahydrate with N-cyclohexylsalicylideneimine in

100 mls. of absolute alcohol. A yellow precipitate was readily obtained which was recrystallized from ethanol, collected on a sintered glass Buchner funnel, and dried in a stream of nitrogen. Unless nitrogen was present when drying the complex, it oxidised on the exposed surfaces to a fine black powder, which was presumably a manganese(IV) compound. M.pt. 195°C (darkens).

Calc. for $MnCl_2(C_{13}H_{17}NO)_2$: C, 58.62; H, 6.44; N, 5.26.
Found : C, 58.25; H, 6.38; N, 5.28.

d. A Complex of Nickel(II).

N-o-anisylsalicylideneiminatomonochloronickel(II).

This complex was prepared in excellent yields (85%) by the reaction of nickel chloride hexahydrate (8 gms., 0.035M) with N-o-anisylsalicylideneimine (16 gms., 0.07M) in 100 mls. of absolute ethanol. After boiling for 15 minutes a yellow precipitate formed which was found to be insoluble in ethanol and other common organic solvents. The complex was hence purified by washing well with alcohol on a sintered glass Buchner funnel and dried by suction of air through the filter. M.pt. 198°C.

Calc. for $C_{14}H_{13}NO_2ClNi$: C, 52.29; H, 4.08; N, 4.36.
Found : C, 52.32; H, 4.07; N, 4.05.

e. Complexes of Iron.

N-p-tolylsalicylideneiminatomonochloroiron(II).

This complex was obtained from the reaction, under nitrogen, of ferrous chloride tetrahydrate (4 gms., 0.02M) with the Schiff's base (8.2 gms., 0.04M) in 75 mls. of absolute alcohol. The brown reaction solution was refluxed for 10 minutes and then let stand under nitrogen in a stoppered flask at room temperature for two days to crystallise. The precipitate was collected, recrystallized from ethanol (under nitrogen), dried in a stream of nitrogen and then kept in a vacuum dessicator over phosphorus pentoxide for one day. The shiny brown flakes obtained had a melting point of 206°C.

Calc. for $C_{14}H_{13}NOClFe$: C, 55.73; H, 4.01; N, 4.64.

Found : C, 54.98; H, 4.48; N, 4.80.

Bis(N-p-tolylsalicylideneimine)trichloroiron(III).

From the reaction mixture of ferric chloride hexahydrate (5.4 gms., 0.02M) with N-p-tolylsalicylideneimine (8.4 gms., 0.04M) in 75 mls. of absolute alcohol, a brown crystalline precipitate was obtained. This was collected after the reaction solution had been let stand in a stoppered flask for three days at room temperature. The yield was 3.4 gms., 29%. The product was recrystallized from ethanol and then air dried on a sintered glass Buchner funnel and kept under vacuum over phosphorus pentoxide for two days. M.pt. 211°C.

Calc. for $FeCl_3(C_{14}H_{13}NO)_2$: C, 57.41; H, 4.48; N, 4.97; Cl, 18.18.

Found : C, 57.27; H, 4.60; N, 4.97; Cl, 17.84.

(iii) Preparation of cobalt(II) Schiff's base chelates.

The complexes not bearing a substituent in the ortho-position on the aniline residue of the Schiff's base have, in the main, been prepared previously[8,9]. However, at the time the preparative work on the ortho-substituted Schiff's base complexes was begun, no successful synthesis for these complexes was available. Most of the preparative work was hence directed towards the preparation of these strained complexes.

The four general methods of preparation employed were:-

Method A. This method was used by Hunter *et.al.*[10], and others[8,9]. The method involved the reaction of cobalt acetate hexahydrate (0.05M) in 30 mls. of water with the Schiff's base (0.1M) in 150 mls. of ethanol. The reaction solution was buffered with sodium acetate. After boiling for 20 minutes, good yields of product were isolated from the cooled reaction mixture. The reddish precipitates so obtained were recrystallised from a filtered solution, washed with redistilled ethanol and then dried in air by suction. The complexes were then stored under vacuum, over phosphorus pentoxide for two days. This drying procedure was used for all compounds, independent of their method of preparation.

The sodium acetate of the buffer above may be replaced by caustic soda (a little less than 0.1M). The reaction, however, must then be carried out under nitrogen as the cobalt is readily oxidised under basic conditions. Furthermore, to prevent the formation of the cobalt hydroxide, the alkali must be added dropwise to the refluxing reaction mixture.

The following complexes were prepared by this method.

Bis(N-phenylsalicylideneiminato)cobalt(II).

Red crystals from benzene-ethanol, m.pt. 185°C.

Calc. for $Co(C_{13}H_{10}NO)_2$: C, 69.18; H, 4.47; N, 6.21.

Found : C, 69.34; H, 4.49; N, 6.06.

Bis(N-*m*-tolylsalicylideneiminato)cobalt(II).

Dark red crystals from benzene-ethanol, m.pt. 192°C.

Calc. for $Co(C_{14}H_{12}NO)_2$: C, 70.14; H, 5.04; N, 5.84.

Found: C, 70.40; H, 5.33; N, 5.68.

Bis(N-*p*-tolylsalicylideneiminato)cobalt(II).

Dark red-brown crystals from benzene-ethanol, m.pt. 195°C.

Calc. for $Co(C_{14}H_{12}NO)_2$: C, 70.14; H, 5.04; N, 5.84.

Found: C, 70.23; H, 5.07; N, 6.01.

Bis(N-*o*-anisylsalicylideneiminato)cobalt(II).

Dark red crystals from DMF, m.pt. 275°C.

Calc. for $Co(C_{14}H_{12}NO_2)_2$: C, 65.81; H, 4.73; N, 5.48.

Found: C, 65.31; H, 4.72; N, 5.44.

Bis(N-*p*-anisylsalicylideneiminato)cobalt(II).

Red crystals from benzene, m.pt. 181°C.

Calc. for $Co(C_{14}H_{12}NO_2)_2$: C, 65.81; H, 4.73; N, 5.48.

Found: C, 65.32; H, 5.02; N, 5.54.

Bis(N-*p*-fluorophenylsalicylideneiminato)cobalt(II).

Red crystals from chlorobenzene, m.pt. 224°C.

Calc. for $Co(C_{13}H_9NOF)_2$: C, 64.08; H, 3.72; N, 5.75.

Found: C, 64.38; H, 3.85; N, 5.64.

Bis(N-p-chlorophenylsalicylideneiminato)cobalt(II).

Red crystals from chlorobenzene, m.pt. 284°C.

Calc. for $Co(C_{13}H_9NOCl)_2$: C, 60.02; H, 3.49; N, 5.39.

Found : C, 60.62; H, 3.62; N, 5.38.

Bis(N-p-bromophenylsalicylideneiminato)cobalt(II).

Orange-red crystals from chlorobenzene, m.pt. 294°C.

Calc. for $Co(C_{13}H_9NOBr)_2$: C, 51.28; H, 2.98; N, 4.60.

Found : C, 51.49; H, 3.18; N, 4.19.

Bis(N-cyclohexylsalicylideneiminato)cobalt(II).

Dark red crystals from benzene, m.pt. 185°C.

Calc. for $Co(C_{13}H_{16}NO)_2$: C, 67.37; H, 6.95; N, 6.05.

Found: C, 67.20; H, 6.92; N, 6.58.

Bis(N-benzylsalicylideneiminato)cobalt(II).

Orange-red crystals from benzene-ethanol, m.pt. 182°C.

Calc. for $Co(C_{14}H_{12}NO)_2$: C, 70.14; H, 5.04; N, 5.84.

Found: C, 70.51; H, 5.02; N, 5.77.

Bis(N-p-tolyl-5-bromosalicylideneiminato)cobalt(II).

Red crystals from bromobenzene, m.pt. 321°C.

Calc. for $Co(C_{14}H_{11}NOBr)_2$: C, 52.78; H, 3.48; N, 4.40.

Found : C, 51.96; H, 3.53; N, 4.68.

Bis(N-cyclohexyl-5-bromosalicylideneiminato)cobalt(II).

Red crystals from chlorobenzene, m.pt. 238°C.

Calc. for $Co(C_{13}H_{16}NOBr)_2$: C, 50.31; H, 5.20; N, 4.51.

Found : C, 50.71; H, 4.83; N, 4.39.

Bis(N-p-tolyl-2-oxy-1-naphthylideneiminato)cobalt(II).

Bright red crystals from chlorobenzene, m.pt. 248°C.

Calc. for $Co(C_{18}H_{14}NO)_2$: C, 74.61; H, 4.87; N, 4.84.

Found : C, 74.98; H, 5.02; N, 4.69.

Bis(N-p-tolyl-4-hydroxysalicyl deneiminato)cobalt(II)-monohydrate.

Orange-brown powder from ethanol, m.pt. 282°C.

Calc. for $Co(C_{14}H_{12}NO_2)_2H_2O$: C, 63.53; H, 4.95; N, 5.29; H_2O, 3.40.

Found : C, 63.83; H, 5.00; N, 5.44; H_2O, 3.38.

<u>Method B</u>. As a first step in this preparative scheme, the complex bis(N-R-salicylideneimine)dichlorocobalt(II) was prepared. Thus, cobalt chloride hexahydrate (0.025M) was refluxed with the Schiff's base (0.05M) in 150 mls. of absolute ethanol in a three-necked reaction flask for 15 minutes. Through one arm, a continuous flow of nitrogen was passed to remove the oxygen from above the reaction mixture

and also to stir the reaction solution. In the third arm of the flask was a separating funnel which contained sodium hydroxide (a little less than the required 0.05M) in 10 mls. of water, diluted with 30 mls. of ethanol. The caustic soda solution was added slowly, drop-wise into the refluxing and stirred reaction mixture. The green colour of the solution gradually changed to red as the caustic soda was introduced; the colour change being accompanied by the precipitation of sodium chloride. When all the caustic soda had been added, the reaction solution was refluxed for a further 15 minutes. On cooling, a red precipitate of the required cobalt(II) Schiff's base chelate was obtained in 60-80% yields. The product was purified by recrystallization from a filtered benzene solution and then dried as in Method A.

This preparative method was found to lend itself well to the formation of the complexes listed under Method A. In addition the *m*-chlorophenyl and the *m*-bromophenyl chelates were also readily obtained. The sterically hindered *o*-tolyl complex was also prepared by this method in 72% yield.

Method C. In this method the sodium acetate or sodium hydroxide of Method A was replaced by sodium bicarbonate.

Cobalt acetate (0.025M) in as little water as possible was added to a solution of Schiff's base (0.05M) in 100 mls. of absolute alcohol. Sodium bicarbonate, in the solid or as a saturated aqueous solution, was slowly introduced to the boiling reaction mixture until effervescence ceased. A little excess bicarbonate was then added and the reaction solution boiled gently with stirring for a further 10 minutes. The yields of the complex thus obtained were between 50 and 85%, depending on the solubility of the complex formed. The products were recrystallised from filtered solutions.

This preparative method was thus very simple, and gives good yields of product. It is recommended for the preparation of all complexes that were made by Methods A or B, and those listed below.

Bis(N-*p*-tolylsalicylideneiminato)cobalt(II).

Red crystals from benzene, m.pt. 190°C.

Calc. for $Co(C_{14}H_{12}NO)_2$: C, 70.14; H, 5.04; N, 5.84;
Co, 12.31.

Found: C, 70.14; H, 5.13; N, 6.21;
Co, 12.64.

Bis(N-*m*-anisylsalicylideneiminato)cobalt(II).

Red crystals from benzene, m.pt. 172°C.

Calc. for $Co(C_{14}H_{12}NO_2)_2$: C, 65.81; H, 4.73; N, 5.48.

Found : C, 65.25; H, 4.99; N, 5.42.

Bis(N-*o*-fluorophenylsalicylideneiminato)cobalt(II).

Small red crystals from benzene, m.pt. 222°C.

Calc. for $Co(C_{13}H_9NOF)_2$: C, 64.08; H, 3.72; N, 5.75.

Found: C, 64.47; H, 4.22; N, 5.93.

Bis(N-*o*-chlorophenylsalicylideneiminato)cobalt(II).

Red crystals from benzene-ethanol, m.pt. 190°C.

Calc. for $Co(C_{13}H_9NOCl)_2$: C, 60.02; H, 3.49; N, 5.39.

Found: C, 59.90; H, 3.57; N, 5.09.

Bis(N-*o*-bromophenylsalicylideneiminato)cobalt(II).

Red crystals from benzene-ethanol, m.pt. 193°C.

Calc. for $Co(C_{13}H_9NOBr)_2$: C, 51.28; H, 2.98; N, 4.60.

Found: C, 51.79; H, 3.19; N, 4.34.

Bis(N-*o*-nitrophenylsalicylideneiminato)cobalt(II).

Small red crystals from DMF, m.pt. 267°C.

Calc. for $Co(C_{13}H_9N_2O_3)_2$: C, 57.67; H, 3.36; N, 10.35.

Found: C, 58.18; H, 3.56; N, 10.09.

Method D. This reaction method, first used by Pfeiffer et.al.[11] for the preparation of copper(II) Schiff's base complexes, involves the treatment of bis-salicylaldehydocobalt(II)dihydrate (0.025M) with a primary amine (0.013M) in a suitable solvent (150mls.). The two reactants were refluxed together, under nitrogen, for 1½-2 hours. The product, collected after cooling the reaction vessel, was purified by recrystallization from a filtered benzene or chlorobenzene solution and then dried as described for Method A.

The reaction solution used in all cases except for the o-bromophenyl complex was alcohol. Both alcohol and benzene were found to be unsuitable as a reaction solvent in the preparation of this o-bromophenyl complex. When the reaction was carried out in chlorobenzene, a good yield (58%) of the complex was obtained. The reluctance of the o-bromophenyl complex to form in alcohol or benzene has been ascribed to their low boiling points, and hence the low reaction temperature.

The complexes listed below could only be prepared by Method D.

Bis(N-*o*-chlorophenylsalicylideneiminato)cobalt(II).

Small yellow-brown crystals from chlorobenzene, m.pt. 174°C.

Calc. for $Co(C_{13}H_9NOCl)_2$: C, 60.02; H, 3.49; N, 5.39.
Found : C, 59.42; H, 3.47; N, 5.15.

Bis(N-*o*-bromophenylsalicylideneiminato)cobalt(II).

Small yellow-brown crystals from chlorobenzene, m.pt. 177°C.

Calc. for $Co(C_{13}H_9NOBr)_2$: C, 51.28; H, 2.98; N, 4.60.
Found : C, 52.55; H, 3.28; N, 4.43.

Bis(N-*α*-naphthylsalicylideneiminato)cobalt(II).

Red crystals from benzene, m.pt. 201°C.

Calc. for $Co(C_{17}H_{12}NO)_2$: C, 74.31; H, 4.40; N, 5.10.
Found : C, 73.27; H, 4.41; N, 4.92.

Bis(N-*m*-fluorophenylsalicylideneiminato)cobalt(II)

This complex could be prepared by both Methods C and D. However if Method C is used, recrystallization from benzene or ethanol was difficult as gels tended to form. The product obtained by Method D could easily be purified by recrystallization from ethanol. Red crystals, m.pt. 159°C

Calc. for $Co(C_{13}H_9NOF)_2$: C, 64.08; H, 3.72; N, 5.75.
Found: C, 64.42; H, 3.69; N, 5.75.

(iv) Preparation of the copper(II) Schiff's base chelates.

All the copper(II) Schiff's base complexes studied except the m-anisyl one, had been prepared previously[9,10,12]. The preparations involved the reaction of copper(II) acetate tetrahydrate (0.025M) in 20 mls. of water with the Schiff's base (0.05M) in 150 mls. of ethanol. This reaction mixture was buffered with sodium acetate. After boiling for 10 minutes, the solution was cooled and the precipitate collected. Yields of the crude product varied between 65% and 95%. Purification was affected by recrystallization from a filtered ethanol, benzene or chlorobenzene solution. The crystals of pure product were air dried and kept under vacuum over phosphorus pentoxide for one day.

Difficulty in the preparation of the m-anisyl complex arose from its high solubility and its reluctance to crystallise from ethanol. Copper acetate tetrahydrate (0.025M, 5 gms.) in 40 mls. of water was added to the N-m-anisylsalicylideneimine (0.05M, 11.3 gms.) in 150 mls. ethanol. Sodium bicarbonate powder was added to the boiling reaction mixture until effervescence ceased.

On cooling to room temperature, a black oil was obtained. This was separated from the reaction mixture by solidifying it by cooling to -15°C. This mass was dissolved in ethanol, filtered and precipitated as small brown crystals by the addition of cyclohexane.

The copper(II) complexes listed below were prepared.

Bis(N-phenylsalicylideneiminato)copper(II).

Brown crystals, m.pt. 233°C.

Calc. for $Cu(C_{13}H_{10}NO)_2$: C, 68.40; H, 4.39; N, 6.14.
Found : C, 68.64; H, 4.47; N, 6.02.

Bis(N-*o*-tolylsalicylideneiminato)copper(II).

Brown crystals, m.pt. 239°C.

Calc. for $Cu(C_{14}H_{12}NO)_2$: C, 69.40; H, 4.98; N, 5.78.
Found : C, 69.22; H, 5.23; N, 5.45.

Bis(N-*m*-tolylsalicylideneiminato)copper(II).

Red-brown crystals, m.pt. 183°C.

Calc. for $Cu(C_{14}H_{12}NO)_2$: C, 69.40; H, 4.98; N, 5.78.
Found : C, 70.03; H, 5.12; N, 5.74.

Bis(N-*p*-tolylsalicylideneiminato)copper(II).

Brown crystals, m.pt. 207°C.

Calc. for $Cu(C_{14}H_{12}NO)_2$: C, 69.40; H, 4.98; N, 5.78.
Found : C, 69.35; H, 4.66; N, 5.66.

Bis(N-*o*-anisylsalicylideneiminato)copper(II).

Blue-black crystals, m.pt. 217°C.

Calc. for $Cu(C_{14}H_{12}NO_2)_2$: C, 65.17; H, 4.69; N, 5.43.

Found : C, 65.24; H, 4.83; N, 5.01.

Bis(N-*m*-anisylsalicylideneiminato)copper(II).

Brown crystals, m.pt. 141°C.

Calc. for $Cu(C_{14}H_{12}NO_2)_2$: C, 65.17; H, 4.69; N, 5.43.

Found : C, 65.12; H, 4.86; N, 5.16.

Bis(N-*p*-anisylsalicylideneiminato)copper(II).

Black-brown crystals, m.pt. 173°C.

Calc. for $Cu(C_{14}H_{12}NO_2)_2$: C, 65.17; H, 4.69; N, 5.43.

Found : C, 65.49; H, 4.81; N, 5.35.

Bis(N-*o*-fluorophenylsalicylideneiminato)copper(II).

Dark brown crystals, m.pt. 288°C.

Calc. for $Cu(C_{13}H_9NOF)_2$: C, 63.48; H, 3.69; N, 5.69.

Found: C, 63.48; H, 3.97; N, 5.21.

Bis(N-*m*-fluorophenylsalicylideneiminato)copper(II).

Brown plates, m.pt. 206°C.

Calc. for $Cu(C_{13}H_9NOF)_2$: C, 63.48; H, 3.69; N, 5.69.

Found: C, 63.73; H, 3.60; N, 5.92.

Bis(N-*p*-fluorophenylsalicylideneiminato)copper(II).

Black shiny crystals, m.pt. 237°C.

Calc. for $Cu(C_{13}H_9NOF)_2$: C, 63.48; H, 3.69; N, 5.69.

Found : C, 63.59; H, 3.41; N, 5.80.

Bis(N-*o*-chlorophenylsalicylideneiminato)copper(II).

Brown crystals, m.pt. 281°C.

Calc. for $Cu(C_{13}H_9NOCl)_2$: C, 59.50; H, 3.46; N, 5.34.

Found : C, 59.16; H, 3.22; N, 5.41.

Bis(N-*m*-chlorophenylsalicylideneiminato)copper(II).

Brown crystals, m.pt. 207°C.

Calc. for $Cu(C_{13}H_9NOCl)_2$: C, 59.50; H, 3.46; N, 5.34.

Found : C, 60.05; H, 3.29; N, 5.60.

Bis(N-*p*-chlorophenylsalicylideneiminato)copper(II).

Red-brown plates, m.pt. 233°C.

Calc. for $Cu(C_{13}H_9NOCl)_2$: C, 59.50; H, 3.46; N, 5.34.

Found : C, 59.23; H, 3.38; N, 5.17.

Bis(N-*o*-bromophenylsalicylideneiminato)copper(II).

Brown-black crystals, m.pt. 227°C.

Calc. for $Cu(C_{13}H_9NOBr)_2$: C, 50.87; H, 2.96; N, 4.56.

Found : C, 51.20; H, 3.01; N, 4.82.

Bis(N-*m*-bromophenylsalicylideneiminato)copper(II).

Brown crystals, m.pt. 213°C.

Calc. for $Cu(C_{13}H_9NOBr)_2$: C, 50.87; H, 2.96; N, 4.56.

Found : C, 50.95; H, 3.16; N, 4.75.

Bis(N-*p*-bromophenylsalicylideneiminato)copper(II).

Red-brown crystals, m.pt. 245°C.

Calc. for $Cu(C_{13}H_9NOBr)_2$: C, 50.87; H, 2.96; N, 4.56.

Found : C, 50.28; H, 3.14; N, 4.27.

Bis(N-benzylsalicylideneiminato)copper(II).

Olive-green crystals, m.pt. 207°C.

Calc. for $Cu(C_{14}H_{12}NO)_2$: C, 69.48; H, 5.00; N, 5.79.
Found: C, 69.93; H, 5.45; N, 5.74.

Bis(N-cyclohexylsalicylideneiminato)copper(II).

Brown crystals, m.pt. 172°C.

Calc. for $Cu(C_{13}H_{17}NO)_2$: C, 66.71; H, 6.89; N, 5.99.
Found : C, 67.31; H, 6.70; N, 5.49.

Bis(N-*m*-nitrophenylsalicylideneiminato)copper(II).

Red-brown plates, m.pt. 263°C.

Calc. for $Cu(C_{13}H_9N_2O_3)_2$: C, 57.19; H, 3.23; N, 10.26.
Found : C, 57.78; H, 3.46; N, 10.07.

Bis(N-*α*-naphthylsalicylideneiminato)copper(II).

Brown crystals, m.pt. 253°C.

Calc. for $Cu(C_{17}H_{12}NO)_2$: C, 73.43; H, 4.35; N, 5.04.
Found : C, 73.79; H, 4.56; N, 5.11.

(v) Preparation of zinc(II) Schiff's base chelates.

These complexes were prepared by the reaction of zinc acetate (0.025M.) in 50 mls. of water with the Schiff's base (0.05M.) in 150 mls. ethanol. Powdered sodium bicarbonate was slowly added to the boiling reaction mixture until effervescence ceased. After cooling to room temperature the yellow crystalline precipitate was collected. This was recrystallized from a filtered benzene solution. The air dried product was then kept in vacuo over phosphorus pentoxide for three days.

This preparative technique was successful only in the preparation of the zinc chelates with Schiff's bases not substituted in the ortho-position of the aniline residue. (The o-anisyl complex was exceptional in that it was readily obtained). Not even the chelate derived from the o-fluorophenyl Schiff's base could be isolated.

Replacement of the sodium bicarbonate by sodium acetate was found to be unsatisfactory.

The following chelates were obtained in good yields.

Bis(N-p-tolylsalicylideneiminato)zinc(II).

Yellow crystals, m.pt. 201°C.

Calc. for $Zn(C_{14}H_{12}NO)_2$: C, 69.21; H, 4.98; N, 5.76.
Found : C, 69.39; H, 5.08; N, 5.56.

Bis(N-*o*-anisylsalicylideneiminato)zinc(II).

Yellow crystals, m.pt. 239°C.

Calc. for $Zn(C_{14}H_{12}NO_2)_2$: C, 64.94; H, 4.67; N, 5.41.
Found : C, 65.35; H, 4.84; N, 5.49.

Bis(N-*p*-anisylsalicylideneiminato)zinc(II).

Yellow crystals, m.pt. 184°C.

Calc. for $Zn(C_{14}H_{12}NO_2)_2$: C, 64.94; H, 4.67; N, 5.41.
Found : C, 65.21; H, 4.78; N, 5.64.

Bis(N-*m*-chlorophenylsalicylideneiminato)zinc(II).

Yellow crystals, m.pt. 280°C.

Calc. for $Zn(C_{13}H_9NOCl)_2$: C, 59.27; H, 3.44; N, 5.32.
Found : C, 59.62; H, 3.47; N, 5.20.

Bis(N-*p*-chlorophenylsalicylideneiminato)zinc(II).

Yellow crystals, phototropic at room temperature, m.pt. 220°C.

Calc. for $Zn(C_{13}H_9NOCl)_2$: C, 59.27; H, 3.44; N, 5.32.
Found : C, 60.19; H, 3.62; N, 5.24.

(vi) Preparation of cobalt(II) chelates with quadridentate ligands.

The complex N,N'-ethylenedi(salicylideneiminato)-cobalt(II) used in the spectral study was prepared by the method of West[13].

The other complexes were prepared by refluxing for 3-4 hours, bis-salicylaldehydocobalt(II)dihydrate (0.025M.) with a diamine (slightly in excess of 0.025M.) in 200 mls. of ethanol. A slow flow of nitrogen was passed continuously through the reaction mixture to prevent oxidation. On refluxing the mixture for 1-2 hours, all the bis-salicylaldehydocobalt(II)dihydrate dissolved, the reaction solution being orange-red in colour. After refluxing for approximately 3½ hours, a precipitate suddenly formed in the reaction vessel. This precipitate was removed from the boiling ethanolic solution by filtration under nitrogen. The products were then washed with boiling redistilled ethanol. Because of their extreme insolubility, they could not be recrystallized. The complexes so prepared were found to be highly resistant to oxidation and so were dried in air. The last traces of moisture and ethanol were removed by storing the complexes in vacuum over phosphorus pentoxide for several days.

The complexes listed below were obtained in yields of 50-70%.

N,N'-ethylenedi(salicylideneiminato)cobalt(II).

Dark red-brown crystals.

Calc. for $C_{16}H_{14}O_2N_2Co$: C, 59.01; H, 4.34; N, 8.62.

Found : C, 59.38; H, 4.67; N, 8.44.

N,N'-heptamethylenedi(salicylideneiminato)cobalt(II).

Orange-red crystals, m.pt. 246°C.

Calc. for $C_{21}H_{24}O_2N_2Co$: C, 63.78; H, 6.12; N, 7.08.

Found : C, 62.36; H, 6.09; N, 6.53.

N,N'-octamethylenedi(salicylideneiminato)cobalt(II).

Orange-red Crystals, m.pt. 222°C.

Calc. for $C_{22}H_{26}O_2N_2Co$: C, 64.54; H, 6.40; N, 6.84.

Found: C, 63.56; H, 6.57; N, 6.97.

N,N'-nonamethylenedi(salicylideneiminato)cobalt(II).

Orange-red crystals, m.pt. 242°C.

Calc. for $C_{23}H_{28}O_2N_2Co$: C, 65.24; H, 6.67; N, 6.61.

Found: C, 64.79; H, 6.34; N, 6.44.

N,N'-decamethylenedi(salicylideneiminato)cobalt(II).

Yellow-brown crystals, m.pt. 220°C.

Calc. for $C_{24}H_{30}O_2N_2Co$: C, 65.89; H, 6.91; N, 6.40.

Found: C, 65.30; H, 6.83; N, 6.32.

(vii) Preparation of 2-oxy-acetophenonatocobalt(II)acetate.

This complex was obtained from the reaction of N-(*p*-tolyl)-α-methylsalicylideneimine with cobalt acetate. The Schiff's base was prepared by refluxing *o*-hydroxyacetophenone (2.7 gm., 0.02M.) with *p*-toluidine. (2.15 gms., 0.02M.) in 150 mls. of ethanol for 15 minutes. The resulting solution became faintly yellow in colour. Cobalt acetate hexahydrate was then added, (2.5 gms., 0.01N) in 50 mls. of water, to the solution of the Schiff's base. This reaction mixture was boiled for 15 minutes. After cooling, the small red-brown product was removed by filtration. This gummy substance was not identified.

The supernatant liquor was let stand in a stoppered flask for about 3 weeks, during which time a blue crystalline product formed. This was collected and recrystallized from a filtered ethanol solution. The compound was then air dried and kept under vacuum over phosphorus pentoxide for two days. On heating to 246°C, the compound darkened, melting over a temperature range in the vicinity of 260°C. A sodium fusion test for nitrogen on this complex was negative.

Calc. for $C_{10}H_{10}O_4Co$: C, 47.44; H, 3.98.
Found : C, 47.44; H, 4.13.

3. Purification of Solvents.[14,15]

The solvents purified by the methods described below were found suitable for the magnetic and spectral work undertaken in this thesis.

(i) Ethanol.

S.V.R. alcohol was purified for use as a solvent in the ultraviolet spectral region by refluxing and fractional distillation from over caustic soda. The caustic soda both dehydrates the alcohol (partially) and removes the optically absorbing carbonyl compounds. The fraction of b.pt. 78-79°C was collected.

(ii) Methanol.

The commercial solvent (B.D.H., grade) was dried by treatment with magnesium. It was then fractionally distilled, the central fraction of b.pt. 64-65°C. being kept.

(iii) n-Propanol.

This solvent (B.D.H. grade) was purified by the method used for methanol. B.pt. 97-98°C.

(iv) Pyridine.

The pyridine (B.D.H. grade) was purified by refluxing over caustic soda, followed by fractional distillation. The solvent, b.pt. 115-116°C. was collected.

(v) Benzene.

Thiophene was removed by treatment of the benzene (B.D.H. and Unilab grades) with concentrated sulphuric acid as recommended by Vogel[14]. Sodium was used to dry the benzene, which was then fractionally distilled, b.pt. 80-81°C.

(vi) Cyclohexane.

This solvent (Unilab grade) was purified as for benzene. B.pt. 80.5 - 81.5°C.

(vii) Chlorobenzene.

This solvent (B.D.H. grade) was also purified as for benzene, except that dehydration was affected with calcium chloride. B.pt. 132°C.

(viii) Dimethylformamide.

The B.D.H. grade reagent was dried by fractional distillation at reduced pressure under dry nitrogen. Only the central fraction, b.pt. 73.5 - 74.0°C. at a pressure of 4.2 cms. of mercury, was collected.

(ix) Dichloromethane.

This solvent (B.D.H. grade) was washed with sodium bicarbonate solution, water and then dried with calcium chloride as described by Weissberger et.al.[15] On fractional distillation, the portion b.pt. 40°C was collected. While not in use this solvent was stored under nitrogen in the dark to prevent decomposition.

4. Continuous Variation Studies.

This work was instigated to determine the nature of the complex formed when cobalt chloride and a Schiff's base were reacted in ethanol at room temperature.

Solutions of cobalt chloride hexahydrate ('Analar' grade), N-p-tolylsalicylideneimine and N-o-tolylsalicylideneimine were shown to obey Beer's law in ethanol at concentrations greater than 2 x 10^{-4}M. Stock solutions of 3.911 x 10^{-3}M of the cobalt salt and the Schiff's bases were made in ethanol. Solutions of equal overall concentration containing cobalt chloride to Schiff's base in ratios varying from 8:1 to 1:8 were made in 10.0 ml. volumetric flasks. The optical density of nine such solutions were measured in 1 cm. silica cells with an Unicam SP-500 Spectrophotometer. The wavelengths used were 400, 410, 425 and 500 mμ.

On correction of the optical density readings obtained to account for the optical densities of the Schiff's base and the cobalt chloride present in each solution, a maximum optical density was found for the solutions in which the cobalt Schiff's base ratio was 1:2. To place the position of the maximum more accurately, two additional solutions with concentrations of cobalt to Schiff's base of 2.5 : 6.5 and 3.5 : 5.5 were used.

5. Molecular Weights.

The molecular weights of the complexes listed below were determined by the depression of freezing point of benzene[16]. The constant for the system, determined using 'Analar' grade naphthalene, was found to be 5.32. Complex was added to the benzene (20 mls.) in approximately 0.05 - 0.07 gm. amounts, until saturation point was reached. The benzene used had been purified as described in Section 3 of this Chapter.

Bis(N-cyclohexylsalicylideneiminato)cobalt(II).

Found 461; formula weight is 459.

Bis(N-p-anisylsalicylideneiminato)cobalt(II).

Found 488; formula weight is 511.

Bis(N-phenylsalicylideneiminato)copper(II).

Found 447; formula weight is 456.

Bis(N-p-tolylsalicylideneiminato)dichlorodiiron(II).

Found 540; formula weight is 603.

N-o-anisylsalicylideneimine.

Found 234; formula weight is 237.

Since the complexes of the type bis(N-R-salicylideneimine)dihalometal(II) were insoluble in benzene, their molecular weights were measured in redistilled absolute alcohol (30 mls.) by the elevation of the boiling point[16]. The apparatus consisted of a Cottrell pump well insulated from its surroundings by asbestos rope. The reproducibility of the boiling points was not good, repetitive readings varying at times by as much as 0.03°C. Experimental errors in the molecular weights determined by this method were estimated to be about 10%.

The molecular weights of the Schiff's base halogen complexes found are listed below.

Bis(N-*p*-tolylsalicylideneimine)dichlorocobalt(II).

Found 368, formula weight is 552.

Bis(N-*o*-tolylsalicylideneimine)dichlorocobalt(II).

Found 334, formula weight is 552.

Bis(N-*p*-anisylsalicylideneimine)dichlorocobalt(II).

Found 401, formula weight is 584.

Bis(N-*p*-tolylsalicylideneimine)dichlorocopper(II).

Found 324, formula weight is 557.

6. Spectrophotometry.

The spectrophotometers employed in this work were the Unicam SP-500 and the Unicam SP-700. The photoelectric response of both instruments was tested by measurements of the extinction coefficients of a standard potassium chromate solution in the wavelength range 45,000 - 20,000 cms.$^{-1}$. All values found were within 1.5% of the values quoted by Lothian[17].

The wavelength scale was checked with the hydrogen line at 15,237 cms.$^{-1}$. The wavelength scale of the SP-700 was found to increase in wavenumber by 200 ± 30 cms.$^{-1}$ during the first hour after switching the instrument on. After this initial period the wavenumber remained steady (± 30 cms.$^{-1}$). Hence, at all times the instrument was switched on one hour before measurement of a spectrum. All spectra recorded in this thesis were adjusted for the discrepancy in the wavelength.

The range of the SP-700 recording spectrophotometer was from 50,000 - 4,100 cms.$^{-1}$, while that of the manual SP-500 was 50,000 - 10,000 cms.$^{-1}$.

A solid reflectance attachment was available for the SP-500. Since the optics were of glass, this attachment was suitable only to measure the solid visible spectrum. Samples (powdered) of too high an optical density were diluted with 'Analar' grade magnesium carbonate. A block of magnesium carbonate was used as a reference.

Solid mull transmission spectra were measured with the SP-700 spectrophotometer. The complex was crushed, wetted with nujol and placed on a Whatman No. 1 filter paper (2.5 cms.). The filter paper was then mounted between two glass plates held in place in the spectrophotometer by two parallel brass plates screwed together. This arrangement rested loosely on a base plate to facilitate its easy removal and replacement. The reference cell was identical in all respects except that no complex was placed on the nujol-wetted filter paper. The resolution of the spectra obtained was highly dependent on the amount of complex on the filter paper. Best results were obtained when the optical density was in the range 0.9 - 2.0.

An electrically heated cell block was also used in the SP-700 instrument. Only solution spectra could be measured at elevated temperatures (as high as 70^{o}C.).

This apparatus is described in greater detail under the 'Equilibrium Constant' section of this chapter.

Both 1 mm. unstoppered cells and 1 cm. silica cells fitted with silica stoppers were used. In each case the reference and solution cells were found to match, within the limits of the instrument.

The spectral parameters B' and 10Dq were calculated from the spectral bands of the tetrahedral cobalt(II) complexes from the expressions given by Griffith[18]. For tetrahedral cobalt(II) when both the V_2, $({}^4A_2 \longrightarrow {}^4T_1(F))$ and V_3, $({}^4A_2 \longrightarrow {}^4T_1(P))$ transitions were observed, these expressions can be simplified to

$$B'^2 - 2.74\,B'(V_3 - V_2)\,10^{-2} + 3.268\,(V_3 + V_2)^2 10^{-4} - 2.941\,(V_3 - V_2)^2 10^{-3} = 0.$$

and

$$10Dq = \frac{V_2 + V_3}{3} - 5B'$$

From these equations B' and 10Dq were readily calculated.

The ligand field parameters for the complex N-p-anisylsalicylideneiminatomonochloronickel(II) were calculated from the Ballhausen-Liehr expressions[19] using an IBM 1620 computer. The approach used was to estimate the terms F_4 and Dq and then calculate the energy of the two observed spectral transitions. An excellent agreement (to better than 40 cms.$^{-1}$) was found between the energies calculated and observed for the spectral bands.

All infrared spectra were measured using a Perkin-Elmer Model 21 double beam infrared spectrophotometer.

7. Equilibrium Constant Determination.

(i) Cobalt complexes with pyridine.

This study involved the determination of the concentration of the cobalt(II) species in solution as a function of the pyridine concentration. The results were obtained by the method described below.

a. The solutions used.

The major difficulty in the study of the cobalt(II) complexes in solution arose from their ease of oxidation. On this account a minimum of time was allowed to elapse between the addition of solvent to the complexes and the measurement of their spectra. Hence, as no stock solutions could be made, all solutions were obtained by individually weighing the powdered complex into a 25.0 ml. volumetric flask. In general 0.1 to 0.25 gms. of compound were used for each solution. When the complexes were not powdered beforehand, their solution was difficult at room temperature and oxidation problems arose.

Solvent was added to the complex immediately prior to its spectral investigation. No special precautions against oxidation were taken during the addition of solvent or pyridine. The pyridine was introduced into the reaction vessel only after the compound had been wetted with the solvent. If pyridine was added directly to the powdered complex, a hard crust was formed around the powder making it difficult to dissolve. The required amount of solvent was added to the complex with a glass siphon under nitrogen pressure. The flow of solvent could be closely controlled by a tap.

The concentration of complex used was in the range 7×10^{-3}M to 2.5×10^{-2}M. The pyridine concentration varied between zero and 12M. The temperature at which these solutions were prepared was recorded with a thermometer ($\pm 0.1^{\circ}$C) which was protected from its surroundings by immersion in a stoppered 250 ml. flask filled with water. It was found that the temperature thus determined agreed well ($\pm 0.5^{\circ}$C) with that of the solvent. The reference solution was always made up immediately prior to the reaction solution.

All the volumetric glass-ware was standardised. The volume of the flasks was checked with boiled, distilled water, while the pipettes were calibrated with the solvent they were used to deliver, usually pyridine. In the equilibrium study of several complexes in which K_T was greater than 8, the pipettes used were calibrated with pure solvent (benzene or chlorobenzene) since diluted solutions of pyridine (10 mls. per 100 mls. solution) were pipetted into the reaction flasks.

For stability runs at 25°C., eight solutions were used. At other temperatures only seven solutions were taken, the 100% pyridine solution being omitted. This however was the case only when K_T was greater than 1.

After use, the volumetric flasks were washed well with acetone, rinsed with redistilled acetone and dried at room temperature under reduced pressure.

b. Spectroscopy.

All solution absorptions were measured with a Unicam SP-700 recording Spectrophotometer in 1.00 cms. stoppered silica cells.

A strict control was kept over the temperature of the reaction solution in the spectrophotometer. This was affected by using a heated cell carriage, (only for the solution) the temperature of which was controlled to ±0.02°C by an Eilco Type 2A temperature regulator. One quarter inch asbestos sheeting was used to insulate the heated cell block. Cells up to 4 cms. in length could be accommodated. The temperature regulator was calibrated by measurement of the temperature of a solution in the block with a calibrated thermistor, using an Eilco conductivity bridge.

Warming up time for a cell filled with water from room temperature to 45°C. - the block temperature - was 7 minutes. The temperature did not overshoot the mark by more than 0.05°C. To warm the block itself by 5°C. took 15 minutes. During an equilibrium run the cell containing complexes was left between 13 and 15 minutes (in the heated cell holder) for temperature equilibrium to be attained.

At all times, before the cells were placed into the spectrophotometer, the base lines of the recorder were checked and adjusted. A slow scan speed was chosen (4) with a damping and resolution setting of 3. The chart speed was 80 inches per hour. Under these conditions the reproducibility of a spectrum was found to be within 0.002 optical density units.

Over the time taken to measure a spectrum, oxidation was found to be negligible. This was ascertained by the measurement of the room temperature spectrum of bis(N-benzylsalicylideneiminato)cobalt(II). This complex was noted to be the most reactive with oxygen. On oxidation, a charge transfer band associated with the Co(III) species was found in the visible region. As the intensity of this band was strong, this method afforded a sensitive test for oxidation. For the complex above, no change in the spectrum was observed over a period of twenty minutes.

Although the reference cell was not heated, it was shown that this did not introduce any significant errors into the extinctions of the reaction solutions over the spectral range employed, (8,200 - 7,400 cms.$^{-1}$).

c. Equilibrium constants.

In a preliminary investigation, all complexes were shown to obey Beer's law in the solvent used for the stability study.

As a first step in the evaluation of the equilibrium constants, the pyridine concentration used was corrected for the temperature of the day. A further temperature correction to consider arose from the heating of the solution in the spectrophotometer. The expansion of the solvent was expressed by the formula[15]

$$V_t = V_o(1 + \alpha \Delta t)$$

where V_t was the volume at temperature t; V_o was the volume of the solution made up (25.0 mls.) and Δt was the temperature change. The function $\alpha = x/d_t$ where d_t was the density at t°C. and x the change in density per degree.

α and hence V_t were calculated for all solvents used and at all temperatures at which the equilibrium constants were determined. The densities of the solvents were obtained from the literature[15,20].

The monomeric nature of several of the complexes was demonstrated by the molecular weight measurements carried out in this study and also by Sacconi et.al.[21] It was therefore assumed that on reaction with pyridine only the mono- and di-pyridinate adducts were formed by these cobalt complexes. On this basis, the equations given in Appendix D, Section (i)a were developed. The general expression had the form

$$\epsilon_T - \epsilon_1 = \frac{1}{K_1} (a + K_T b) \qquad \text{(V)-1}$$

The definition of the characters in this equation were discussed in Chapter IV and also in Appendix D.

Since Equation (V)-1 contains three unknowns, (ϵ_1, K_1, and K_T), it cannot readily be solved. Taking two reaction solutions of differing pyridine concentration, with extinction ϵ_T and ϵ'_T at a given wavenumber, one can by subtraction remove ϵ_1. The expression then becomes

$$\Delta\epsilon_T = \frac{1}{K_1}(A + K_T B) \qquad (V)\text{-}2.$$

where $\Delta\epsilon_T = \epsilon_T - \epsilon'_T$; $A = a-a'$ and $B = b-b'$. Equation (V)-2 was evaluated by solving simultaneous equations. This was done for the p-tolyl complex. The spectral region chosen for this evaluation was the band at 8,200 - 7,400 cms.$^{-1}$, as in this region strong spectral changes were found on pyridine addition to the complex. (See Fig.(V)-1.)

As Equation (V)-2 was obtained by subtraction of Equation (V)-1, the errors found in Equation (V)-2 were correspondingly much larger. Hence 45 simultaneous equations were solved to obtain reasonably accurate equilibrium constant for the reaction of pyridine with the p-tolyl complex. ϵ_1 was also calculated for this compound (See Appendix D). Over the spectral range used,

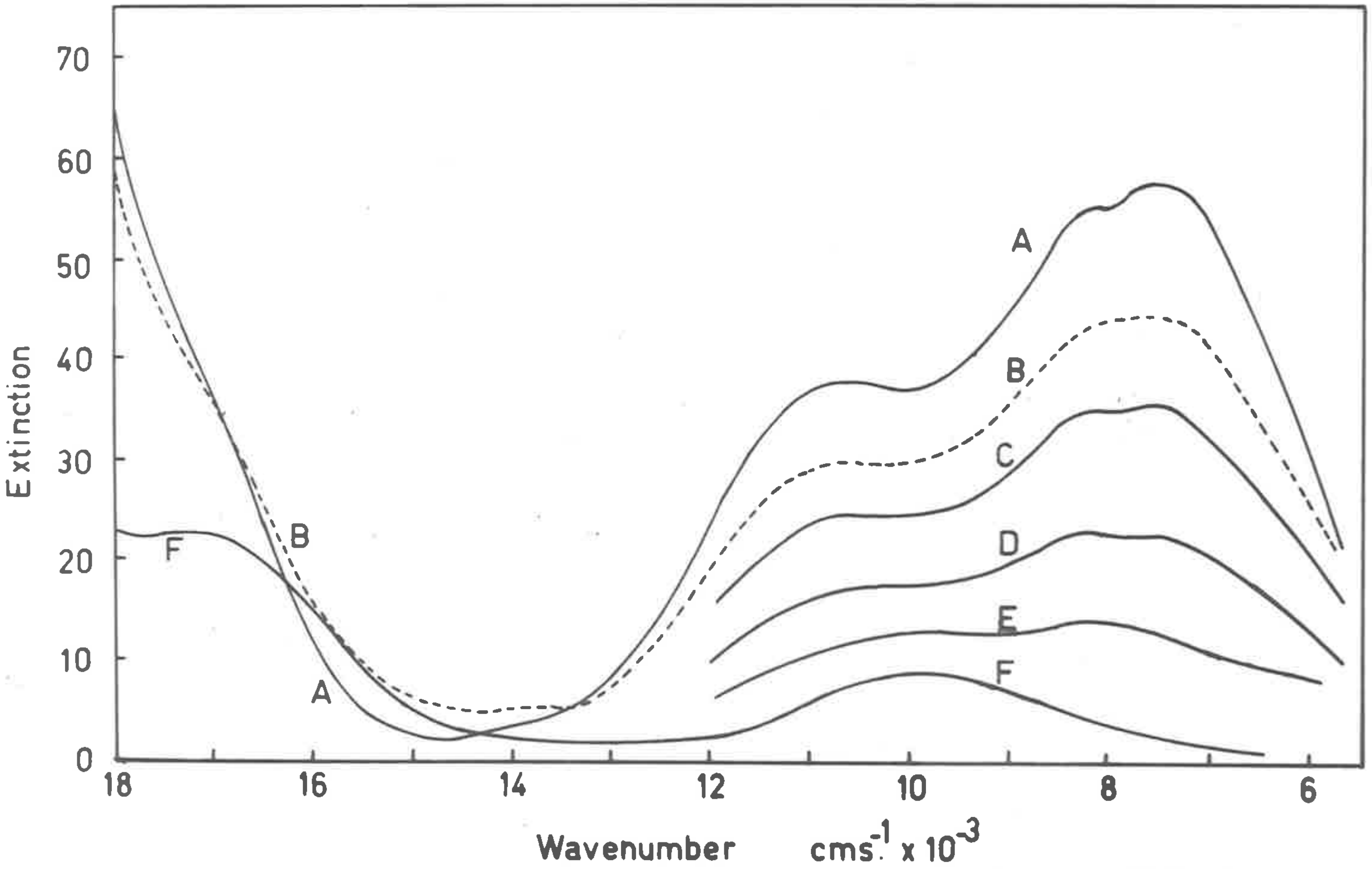

Fig.(V)-1. The spectra of bis(N-o-tolylsalicylideneiminato)cobalt(II) in benzene/pyridine mixtures at 25°C.

this extinction coefficient was found to vary between 0.7 and 1.5. Thus ϵ_1 was a small correction factor applied to ϵ_T, which in general varied between 10 and 50. The stability constants for nearly all complexes were calculated from Equation (V)-1, on the assumption that ϵ_1 was unity.

Equation (V)-1 was solved graphically after rearrangement to the form, (See Appendix D)

$$\frac{\epsilon_T - \epsilon_1}{a} = K_2 \cdot \frac{b}{a} + \frac{1}{K_1} \qquad (V)-3$$

Hence a plot of $\frac{\epsilon_T - \epsilon_1}{a}$ against $\frac{b}{a}$ is linear with slope K_2 and intercept $1/K_1$.

Equation (V)-3 was evaluated using six reaction mixtures. Some typical experimental results are given in Tables (V)-1, 2, 3 and 4, and in Figs. (V)-2 and 3.

TABLE (V)-1.

The spectral properties of
bis(N-phenylsalicylideneiminato)cobalt(II) in DMF,
as a function of the pyridine concentration
(at 25°C).

$C_T^a \times 10^2$	$C_{pyr.}^b$	ϵ_T	a	-b	$\frac{\epsilon_T - \epsilon_1}{a}$	$-\frac{b}{a}$
1.972	0.2569	50.99	27.25	12.48	1.838	0.4579
1.735	0.3551	48.42	26.95	16.34	1.763	0.6062
1.697	0.5028	44.81	26.22	21.32	1.675	0.8134
1.615	0.7448	39.07	25.40	27.30	1.503	1.075
1.764	1.495	26.75	20.89	36.39	1.237	1.742
2.164	2.729	16.41	16.81	34.62	0.922	2.059

Data refer to 7,800 cms.$^{-1}$. $\epsilon_e = 57.99$; $\epsilon_2 = 2.41$ and $\epsilon_1 = 0.9$.

a. C_T refers to the total concentration of complex (Molar) in the reaction solution.

b. $C_{pyr.}$ refers to the equilibrium pyridine concentration (Molar) in the reaction solution.

TABLE (V)-2.

The spectral properties of
bis(N-*o*-bromophenylsalicylideneiminato)cobalt(II) as a
function of the pyridine concentration
in chlorobenzene at 25°C.

$C_T \times 10^2$	$C_{pyr.} \times 10^2$	ϵ_T	a
1.298	9.947	15.10	265.9
1.113	19.80	9.61	161.3
1.136	29.61	7.26	115.8
0.7789	39.73	5.38	90.03
0.9746	49.37	4.92	74.20

Data refer to 7,800 cms.$^{-1}$, ϵ_o = 41.53.

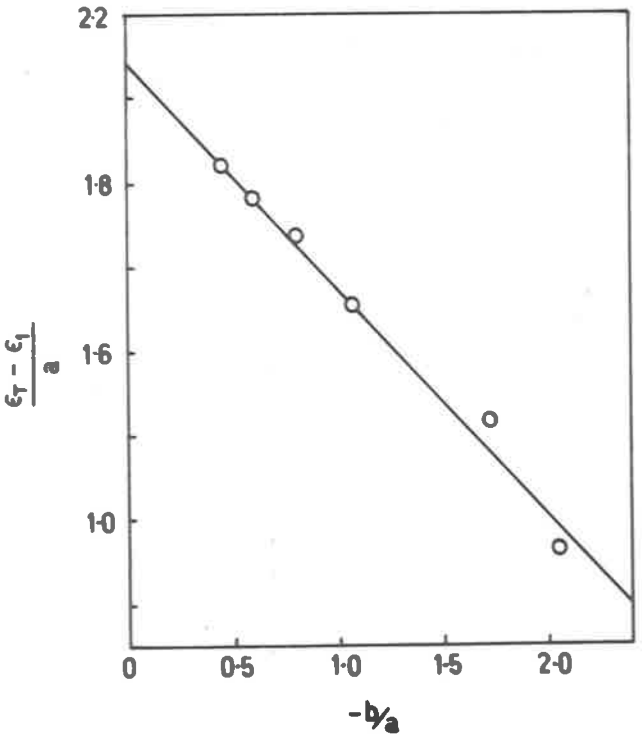

Fig.(V)-2a The plot of (ϵ_T - ϵ_1)/a as a function of -b/a for bis(N-phenylsalicylideneiminato)cobalt(II) in dimethylformamide at 25°C.

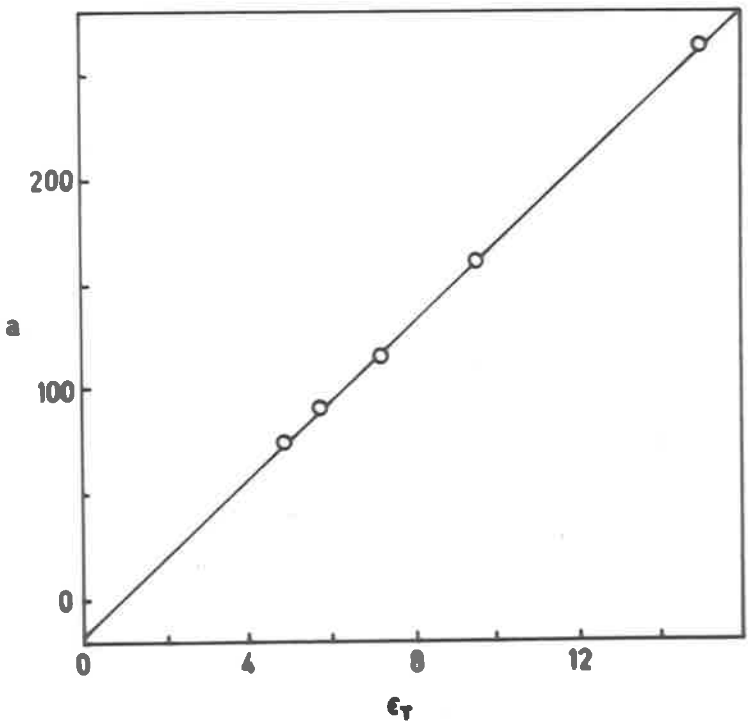

Fig.(V)-2b. The plot of a as a function of ϵ_T for bis(N-o-bromophenylsalicylideneiminato)-cobalt(II) in chlorobenzene at 25°C.

TABLE (V)-3.

The spectral properties of bis(N-*p*-chlorophenylsalicylideneiminato)cobalt(II) as a function of the pyridine concentration in chlorobenzene at 25°C.

$C_T \times 10^2$	$C_{pyr.} \times 10^2$	ϵ_T	a	-b	$\frac{\epsilon_T - \epsilon_1}{a}$	$-\frac{b}{a} \times 10^2$
1.021	2.358	42.38	391.0	1.031	0.1057	0.2657
1.455	3.090	39.11	374.7	1.311	0.1018	0.3498
1.592	4.336	35.33	341.9	1.667	0.1035	0.4888
0.930	6.982	28.71	313.5	2.019	0.0916	0.5116
0.932	15.01	16.04	227.0	2.257	0.0705	0.9940
0.8177	24.41	9.68	165.3	1.986	0.0584	1.200

Data refers to 7,800 cms. , ϵ_o = 52.35, ϵ_2 = 1.93 and ϵ_1 = 1.0.

TABLE (V)-4.

The Spectral properties of bis(N-*o*-anisylsalicylideneiminato)cobalt(II) in DMF as a function of the pyridine concentration, at 25°C.

$C_T \times 10^2$	$C_{pyr.} \times 10^2$	ϵ_T	a
0.8814	0.2568	14.86	3.802
0.9743	0.5027	13.96	6.610
0.9418	1.495	11.15	15.45
1.080	2.472	8.80	19.74
1.203	4.937	6.53	28.23

The data refer to 7,800 $cms.^{-1}$, $\epsilon_o = 17.33$; $\epsilon_1 = 0.81$.

To obtain reasonably accurate values of the equilibrium constants, the calculations for the constants were carried out at five wavenumbers between 8,200 and 7,400 $cms.^{-1}$. Relative percentage errors in the equilibrium constants were calculated. Since the accuracy of the determination rests on the magnitude of the spectral changes on pyridine addition (ϵ_o - ϵ_T), the smaller the equilibrium constant the greater the error. Thus it was found, on the basis of their reproducibility, that for K_1 and K_2 greater than 1, the

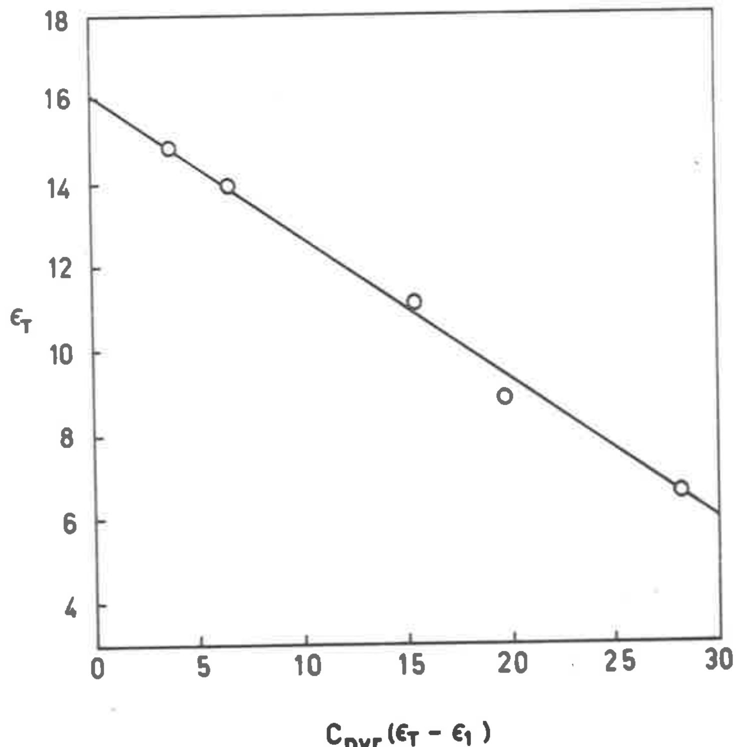

Fig.(V)-3a. The plot ϵ_T as a function of $C_{Pyr.}$ (ϵ_T - ϵ_1) for bis(N-*o*-anisyl-salicylideneiminato)cobalt(II) in dimethylformamide at 25°C.

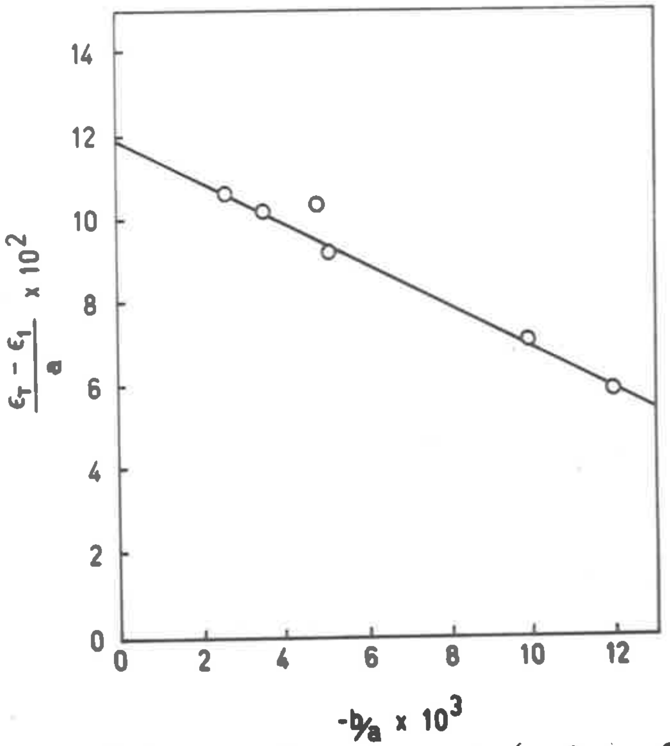

Fig.(V)-3b. The plot of (ϵ_T- ϵ_1)/a as a function of -b/a for bis(N-*m*-chlorophenyl-salicylideneiminato)cobalt(II) in chlorobenze at 25°C.

uncertainty of their values was ± 3%. When the equilibrium constants were less than one, the errors were estimated at ±5%. As K_T was found from the product of K_1 and K_2, the percentage error in this constant lies between 6 and 10% depending on the values of K_1 and K_2.

Before detailed calculations on the stability constants were attempted, preliminary K values were determined (using only one wavenumber, generally 7,800 cms.$^{-1}$). This was done to enable a correction to be applied to the pyridine concentration to evaluate the equilibrium pyridine concentration. The formulae derived for this correction are given in Appendix D. Some typical experimental values showing the magnitude of this correction, are given in Table (V)-5.

It can be seen from Table (V)-5 that the equilibrium pyridine concentration was between 1% and 12% lower than the amount of pyridine added.

The complex bis(N-o-bromophenylsalicylideneiminato)-cobalt(II) did not form the dipyridinate in detectable amounts. This followed from the observation that the plot of ϵ_T against a was a straight line (See Appendix D, and Fig. (V)-2b).

TABLE (V)-5.

The concentration of pyridine added ($C'_{pyr.}$) to a solution of bis(N-R-salicylideneiminato)cobalt(II) and the calculated equilibrium concentration ($C_{pyr.}$)

R	K_T	$C'_{pyr.}$	$C_{pyr.}$	$C_T \times 10^2$
p-bromophenyl	1.3	0.2078	0.2052	0.7881
p-tolyl	1.6	0.1108	0.1080	1.095
phenyl	5.1	0.2080	0.2015	1.281
α-naphthyl	9.1	0.1078	0.1029	1.049
benzyl	9.6	0.04938	0.04757	1.053
m-bromophenyl	102	0.02062	0.01819	1.138

Several complexes, namely the p-anisyl one, the cyclohexyl one and bis(N-p-tolyl-4-hydroxysalicylideneiminato)cobalt(II)monohydrate were found to be exceptional in that the plots of $\frac{\epsilon_T - \epsilon_1}{a}$ against -b/a were smooth curves. The evaluation of the equilibrium constants of these compounds is discussed with reference to the chelate bis(N-p-anisylsalicylideneiminato)cobalt(II).

In the preliminary investigation, the plot of Equation (V)-3 was found to be a curve, assuming ϵ_1 to be unity. Since the o-bromophenyl complex did not form the dipyridinate species, it was postulated that the o-anisyl complex also, on account of the large ortho-group, would only form the monopyridinate in pyridine. The relationship (See Appendix D),

$$\epsilon_T = \frac{1}{K_1}\left[\frac{\epsilon_0 - \epsilon_T}{C_{pyr.}}\right] + \epsilon_1 \qquad (V)\text{-}4.$$

should thus describe the extinction of the complex in solution as a function of the pyridine concentration. However, as expected, since this expression was identical to Equation (V)-3, (b=0), a non-linear equilibrium plot was obtained.

As the concentration of pyridine was high, it was considered that the pyridine may possibly affect the value of ϵ_0. An error in ϵ_0 would seriously affect the stability plot as $\epsilon_0 - \epsilon_T$ was small (less than 15). Equation (V)-4 can be rearranged to the form

$$\epsilon_T = -K_1.C_{pyr.}(\epsilon_T - \epsilon_1) + \epsilon_0 \qquad (V)\text{-}5$$

Since ϵ_1 is small (although unknown) the error in $\epsilon_T - \epsilon_1$ may be less than in $\epsilon_0 - \epsilon_1$ for most pyridine concentrations. Such was found to be the case, the plot of ϵ_T against $C_{pyr.}(\epsilon_T - \epsilon_1)$ being linear, assuming $\epsilon_1 = 1$. Both K_1 and ϵ_0 were thus found. ϵ_0 was seen to differ appreciably from that determined in pure DMF (See Chapter IV-4-(iv).).

To determine the value of ϵ_1, the ϵ_0 value found from Equation (V)-5 was reintroduced into Equation (V)-4. The plot of ϵ_T against $(\epsilon_0 - \epsilon_T)/C_{pyr.}$ was now found to be linear, the intercept, ϵ_1, being 0.81. The final value for the equilibrium constant was then determined by using this value of ϵ_1 in Equation (V)-5.

By a similar approach the equilibrium constant for pyridine addition to the cyclohexyl complex was found.

The procedure for determining the equilibrium constants for pyridine addition to the complex bis(N-p-tolyl-4-hydroxy-salicylideneiminato)cobalt(II)monohydrate differed in that only the dipyridinate was detected.

ϵ_2 could not be determined experimentally. (See Chapter IV-4-(iv).). However, since ϵ_2 was found for all the complexes investigated to lie between 1.5 and 2.5 in the 8,200 - 7,400 cms.$^{-1}$ range, it was estimated to be 2 in the preliminary equilibrium calculation. Hence, as ϵ_T was large (between 70 and 24) a small error in ϵ_2 would be insignificant. Thus no improvement to the value of 2 for ϵ_2 could be made.

From the stability constants, the standard free energy changes (ΔG°) were evaluated using the relationship

$$\Delta G^\circ = -RT\ln K \qquad (V)-6$$

As the equilibrium constants were near unity, ΔG° was small. The percentage error in the free energy changes was the same as that found in K.

The enthalpy changes (ΔH°) of the reactions were found by application of the van't Hoff Isochore. This function was solved using the stability constants determined at five temperatures, namely, 25, 30, 35, 40, and 45°C. The temperatures were accurate to within ±0.1°C. The plot of logK against 1/T was linear in all cases. It was found graphically, that the enthalpy terms ΔH_1° and ΔH_2° were subject to an error of

$\pm$400 cals. ΔH^{o}_{T} was calculated by addition of ΔH^{o}_{1} and ΔH^{o}_{2} and therefore was assigned an uncertainty of $\pm$800 cals.

The entropies of the reactions were determined from the relation

$$\Delta S^{o} = \frac{\Delta H^{o} - \Delta G^{o}}{T} \qquad (V)-7.$$

The error in ΔS^{o} is mainly due to that of the ΔH^{o} as ΔG^{o} was small.

All calculations were carried out using a Friden Model STW calculator.

(ii) Copper Complexes with Pyridine.

The determination of the stability constants of the pyridine adducts was simpler in the case of the complexes of copper(II) than for the complexes of cobalt(II). This arose from the fact that the copper complexes were stable to oxidation, and furthermore only the mono-pyridinate adduct formed in solution. The absence of dipyridinate species in a solution of the complex containing pyridine was established from both the linearity of the equilibrium plots and by the occurrence of an isosbestic point in the spectra of such solutions.

The isosbestic points, found in the region 14,000 to 15,000 cms.$^{-1}$ were determined at 25°C. in benzene and in chlorobenzene, but not in cyclohexane as these solutions were too dilute. All complexes were shown to obey Beer's law at 25°C. in the solvent used for the equilibrium runs.

Many of the practical details in this study were similar to those used for the cobalt complexes. Only the differences in technique are discussed below.

As the problem of oxidation did not exist, stock solutions (250 mls.) of the complexes were made. From these solutions 5 ml. samples were pipetted into clean 25.0 ml. volumetric flasks. For a particular stability determination, the same 5 ml. pipette was always used to ensure that the concentration of complex in each flask was equal. Then the required amounts of pyridine were added and the volume made up to 25 mls. with purified solvent. For any one stability constant determination, five reaction solutions were used.

Since the total complex concentration was constant for all the solutions in the equilibrium run, Equation (V)-4 reduced to

$$OD_T = \frac{OD_0 - OD_T}{K_1 C_{pyr.}} + OD_1 \qquad (V)-8$$

Here OD represents optical density. The plot of this equation was linear, with slope $1/K_1$.

For stability constants less than one, no correction was applied to the pyridine concentration to account for the loss due to adduct formation. However all temperature effects on the pyridine concentration were corrected for.

The spectral range used (Unicam SP-700 spectrophotometer) depended on the concentration of the solution. Thus, for dilute solutions - as obtained with cyclohexane - the tail of the charge transfer band was used (20,000 - 23,000 cms.$^{-1}$). When the complex could be obtained in sufficient concentration, the visible region (17,000 - 19,000 cms.$^{-1}$) was used. The stability runs were then calculated graphically at five wavenumbers. Some typical experimental results obtained are given below in Tables (V)-6, and 7.

TABLE (V)-6.

The spectral properties of bis(N-phenylsalicylideneiminato)copper(II) in chlorobenzene as a function of the pyridine concentration at 25°C.

$C_{pyr.}$	OD_T	$\frac{OD_0 - OD_T}{C_{pyr.}}$
0.4970	0.682	0.41
0.9920	0.574	0.317
2.472	0.435	0.183
4.938	0.359	0.107
9.881	0.308	0.0587

Data refer to 18,400 cms.$^{-1}$, OD_0 = 0.888.

TABLE (V)-7.

The spectral properties of bis(N-*m*-fluorophenylsalicylideneiminato)copper(II) in cyclohexane as a function of the pyridine concentration at 25°C.

$C_{pyr.}$	OD_T	$\frac{OD_0 - OD_T}{C_{pyr.}}$
0.05820	0.578	2.664
0.1078	0.525	1.930

Cont...

TABLE (V) - 7 contd.

$C_{pyr.}$	OD_T	$\frac{OD_0 - OD_T}{C_{pyr.}}$
0.2568	0.459	1.067
0.7415	0.446	0.5775
1.575	0.434	0.3014

Data refer to 22,200 cms.$^{-1}$, OD_0= 0.733.

The relative errors found for the equilibrium constants were less than 1.5%. The *p*-anisyl complex is exceptional in that the percentage error was 7%. This large error in K_1 for the *p*-anisyl compound was due to the small spectral changes observed when pyridine was added to a solution of this compound.

ΔH_1^0 was found by determining the equilibrium constants at five temperatures (25, 30, 35, 40, 45°C) and then solving the van't Hoff Isochore graphically. The percentage errors found (graphically) in the enthalpy terms was ± 300 cals. The *p*-anisyl complex possessed an uncertainty of ± 700 cals. in its enthalpy term.

Errors of a similar magnitude to those for ΔH_1^o were found in the entropy terms.

8. Magnetic moment Determination.

(i) Solid Measurements.

The magnetic moments of the powdered complexes were measured by the Gouy method. The apparatus consisted of a permanent U shaped magnet placed beneath a Mettler balance weighing to within 0.01 mgms. The Gouy tube was of Pyrex glass and was approximately 10 cms. long, with an external diameter of 4mms. Mercury tetrathiocyanatocobalt(II) was used to standardise the Gouy tubes. This complex was prepared by the method of Figgis and Nyholm[22]. The field strength of the magnet was capable of affecting an increase in weight of 4.70 mgms. (corrected for the diamagnetism of the tube) on 0.3491 gms. of the tetrathiocyanatocobalt(II) complex.

For cobalt complexes, reproducibility of the magnetic moments was better than ± 1% in all cases. However, as the change in weight on application of a magnetic field is very small in the case of the copper(II) complexes, the errors in the magnetic moments were estimated at ± 5%.

All magnetic moments were corrected for diamagnetism in the complex. Only for the complexes of the type bis(N-R-salicylideneimine)dihalocobalt(II) was the temperature independent paramagnetism determined[23].

(ii) Solution measurements.

The solution magnetic moments were also found by the Gouy method. The apparatus used consisted of a water cooled electromagnet placed beneath a Mettler balance weighing to 0.01 mgms. The magnet was a water-cooled Newport 4 inch Type 2A electromagnet. The voltage was stabilised to within 2% at currents below 16 amps. In the measurement of magnetic moments the field strength was controlled manually.

Each solution was weighed at field strengths equivalent to 14 and 15 amps.

The stoppered, Pyrex-glass Gouy tube was 14 cms. long and had a diameter of 1.2 cms. 8.778_1 mls. of solution were employed in all measurements. Standardization of the apparatus was achieved using boiled, redistilled water which had been cooled under nitrogen[24]. The decrease in weight experienced by 8.778_1 mls. of this water (at 22°C.) was 23.05 mgms. at 14 amps., and 23.99mgms. at 15 amps. The temperature of the solutions was measured by immersion of a thermometer into the solution at the completion of the weighings.

The susceptibilities of the solvents used were measured for each lot of solvent purified. Values of the gram susceptibilities found were

Benzene; -0.7071×10^{-6} and $- 0.7015 \times 10^{-6}$
Literature value[25]; -0.712×10^{-6}

Chlorobenzene; -0.6217×10^{-6}
Literature value, -0.639×10^{-6}

Dimethylformamide; -0.6122×10^{-6}

Pyridine; -0.6073×10^{-6}
Literature value, -0.623×10^{-6}

Due to the small amount of complex used in the magnetic determinations, the experimental errors in the moments were found to be double those associated with the solid measurements.

During the magnetic measurements no precautions were taken against oxidation, as all measurements were completed within 20 minutes.

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APPENDICES:

Appendix A.

The spectral properties of the Schiff's bases and their zinc(II) chelates.

Appendix B.

The spectral properties of cobalt(II) Schiff's base complexes.

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Appendix D.

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APPENDIX A.

The Spectral Properties of the Schiff's bases and their zinc(II) chelates.

TABLE (A)-1.

The spectral properties of N-R-salicylideneimine Schiff's bases at 25°C.

R	Solvent	Band Wavenumber	Band Intensity
phenyl	cyclohexane	42,250	26,550
		43,800(s)	22,000
		42,200(s)	16,900
		37,100	13,800
		33,000	9,150
		31,250	9,800
		29,050	11,250
o-tolyl	cyclohexane	44,100	21,300
		43,200(s)	20,850
		41,400(s)	12,750
		37,450	13,950
		30,500(s)	10,250
		29,050	11,400
	DMF	30,550(s)	10,900
		29,200	11,650
m-tolyl	cyclohexane	45,400	37,200
		43,200	21,750
		41,500	14,600
		37,250	14,150
		32,800(s)	9,200
		31,100	10,450
		29,050	12,000
p-tolyl	cyclohexane	44,950	21,550
		43,150	21,900
		41,800	14,850
		37,300	13,050
		32,600	9,900
		31,050	11,700
		28,900	13,450

Contd...

TABLE (A)-1. (contd.)

R	Solvent	Band Wavenumber	Band Intensity
	DMF	32,700(s)	10,800
		31,000	12,300
		28,950	13,450
	pyridine	30,900	11,500
		28,700	12,550
o-anisyl	cyclohexane	45,450(s)	34,550
		43,050	21,400
		37,300	13,100
		29,500(s)	11,550
		28,450	12,200
	DMF	30,000(s)	10,300
		28,250	11,700
m-anisyl	cyclohexane	45,500(s)	34,400
		41,500(s)	20,550
		37,200	14,000
		32,900(s)	8,300
		29,000	12,000
p-anisyl	cyclohexane	45,300	36,800
		43,300(s)	21,100
		37,150	11,900
		34,100	8,350
		30,450(s)	13,450
		28,350	16,600
	DMF	33,900	8,550
		32,600(s)	9,500
		30,450(s)	13,850
		28,250	17,150
o-fluorophenyl	cyclohexane	43,750(s)	21,850
		42,400(s)	18,000
		37,200	15,800
		33,000(s)	9,300
		30,900	9,900
		28,800	11,100

Contd...

TABLE (A)-1. (contd.)

R	Solvent	Band Wavenumber	Band Intensity
	DMF	32,600	10,700
		31,050	11,400
		29,050	11,800
o-fluorophenyl	cyclohexane	43,500(s)	20,950
		42,500(s)	18,150
		37,050	15,000
		32,900	9,800
		31,150	9,900
		28,850	11,000
p-fluorophenyl	cyclohexane	43,200(s)	19,350
		37,100	14,200
		32,800	9,300
		31,300	10,200
		28,900	11,650
	DMF	33,200	10,250
		31,450	10,950
		29,200	11,750
	pyridine	31,250	10,650
		29,000	11,600
o-chlorophenyl	cyclohexane	43,400	20,000
		40,900(s)	10,900
		36,900	13,300
		32,000(s)	7,700
		30,100(s)	9,000
		28,650	9,650
m-chlorophenyl	cyclohexane	45,400(s)	26,700
		43,000	21,400
		41,400(s)	13,500
		36,850	14,550
		32,800(s)	9,250
		31,000	9,650
		28,750	11,000

Contd...

TABLE (A)-1. (contd.)

R	Solvent	Band Wavenumber	Band Intensity
p-chlorophenyl	cyclohexane	45,200	21,050
		43,050	21,400
		36,800	14,100
		32,500	10,400
		30,900	11,600
		28,650	12,800
o-bromophenyl	cyclohexane	45,400(s)	26,650
		43,250	20,600
		40,300	11,500
		36,900	14,100
		30,850	7,800
		30,100	9,450
		28,600	10,100
m-bromophenyl	cyclohexane	45,400(s)	27,600
		43,100(s)	21,200
		40,800(s)	11,200
		36,800	14,300
		32,700(s)	9,050
		30,950	9,400
		28,750	10,950
p-bromophenyl	cyclohexane	45,250	22,550
		43,050	20,500
		36,700	14,300
		32,300	10,800
		30,800	11,900
		28,600	13,050
m-nitrophenyl	cyclohexane	45,200	25,050
		44,200(s)	24,000
		36,700	19,900
		33,400(s)	11,450
		28,550	10,200
p-nitrophenyl	cyclohexane	46,900	32,950
		43,800	16,750
		32,100	15,950
		27,800	14,600

TABLE (A)-2.

The spectral properties of N-R-salicylideneimine Schiff's bases substituted in the aldehyde residue, (at 25°C.).

R	X[a]	Solvent	Band Wavenumber	Band Intensity
p-tolyl	4-hydroxy	methanol	44,350	16,550
			42,200(s)	14,700
			35,000(s)	9,450
			29,400	22,000
			24,050	4,750
phenyl	5-bromo	cyclohexane	43,250	27,150
			41,950(s)	24,700
			36,900	11,450
			34,200(s)	7,900
			32,400	8,600
			30,800	8,350
			28,250	9,800
m-tolyl	5-bromo	cyclohexane	43,400(s)	26,400
			42,400	26,800
			41,000(s)	21,550
			37,000	10,900
			32,200	8,450
			30,500	8,800
			28,050	10,350
p-tolyl	5-bromo	cyclohexane	42,600	27,300
			41,250	22,250
			36,900	10,650
			32,000	9,800
			30,450	10,450
			27,950	11,900
m-fluorophenyl	5-bromo	cyclohexane	43,000	24,750
			36,800	11,700
			32,350	8,850
			30,700	8,200
			27,900	9,200

a. The substituent on the aldehyde residue.

TABLE (A)-3.

The spectral properties of Schiff's bases of the type N-R-2-hydroxy-1-naphthylideneimine at 25°C.

R	Solvent	Band Wavenumber	Band Intensity
o-tolyl	cyclohexane	40,250(s)	22,600
		38,800(s)	15,850
		32,300(s)	8,600
		31,100	11,800
		29,600(s)	8,950
		26,450	13,150
m-tolyl	cyclohexane	40,300(s)	22,400
		38,700(s)	13,950
		32,400(s)	8,000
		31,150	11,800
		30,000(s)	10,050
		26,400	13,000
p-tolyl	cyclohexane	42,500	45,050
		38,800(s)	15,100
		32,100	8,800
		31,050	12,600
		29,800	10,950
		26,500	15,100

TABLE(A)-4.

The spectral properties of N-R-benzylideneimines substituted in the benzylidene residue (in cyclohexane at 25°C.)

R	Substituent	Band Wavenumber	Band Intensity
p-chlorophenyl	hydrogen	45,200	17,200
		43,900	15,800
		41,900	11,200
		37,700	18,900
		31,150	9,600
p-tolyl	*p*-benzoate	44,300	32,950
		44,050	33,100
		41,600(s)	22,800
		37,050	19,300
		32,550(s)	14,400
		31,000	16,850
		28,900	19,100

TABLE (A)-5.

The spectral properties of

bis(N-R-salicylideneiminato)zinc(II) in benzene at 25°C.

R	Band Wavenumber	Band Intensity
m-tolyl	32,600(s)	19,500
	31,150	19,050
	28,850	21,150
p-tolyl	32,600(s)	19,900
	31,050	21,300
	28,900	21,350
o-anisyl	33,000	13,800
	30,050	16,200
	24,250	14,450
p-anisyl	30,500(s)	22,500
	28,150	29,400
m-chlorophenyl	32,450	19,100
	30,800	20,300
	28,900	22,200
p-chlorophenyl	32,500(s)	22,100
	30,900	24,850
	28,800	26,350

APPENDIX B.

The spectral properties of cobalt(II) Schiff's base complexes.

TABLE (B)-1.

The visible and near infrared spectral properties of some bis(N-R-salicylideneiminato)cobalt(II) complexes in solution at 25°C.

R	Solvent	Band Wavenumber	Band Intensity
phenyl	benzene	16,750(s)	32.9
		10,900	32.3
		7,800(s)	58.0
		7,400	58.6
	DMF	17,100(s)	39.3
		10,950	32.4
		7,700	58.1
o-tolyl	benzene	16,700(s)	34.4
		10,400	37.3
		7,900(s)	55.0
		7,350	57.1
m-tolyl	benzene	16,700(s)	31.7
		10,800	33.4
		7,900(s)	57.3
		7,500	58.2
p-tolyl	benzene	16,800(s)	27.0
		11,200	32.1
		7,950(s)	56.3
		7,550	57.9
	DMF	16,950(s)	34.0
		10,900	32.1
		8,100(s)	56.2
		7,650	57.5

Contd...

TABLE (B)-1.

R	Solvent	Band Wavenumber	Band Intensity
o-anisyl	DMF	11,000	16.0
		7,300	17.8
	dichloromethane	10,500	19.6
		7,100	21.3
m-anisyl	benzene	16,750(s)	39.4
		11,100	31.9
		7,950(s)	56.7
		7,600	57.0
p-anisyl	chlorobenzene	10,900	26.9
		7,800(s)	46.8
		7,400	47.8
o-fluorophenyl	chlorobenzene	16,750(s)	38.4
		10,700	32.3
		8,000(s)	46.3
		7,400	47.5
m-fluorophenyl	benzene	16,700(s)	31.1
		11,200	30.3
		8,000(s)	52.0
		7,400	54.4
p-fluorophenyl	chlorobenzene	16,800(s)	32.8
		11,150	31.4
		7,900(s)	47.8
		7,400	52.9
	DMF	17,000(s)	35.6
		11,100	26.2
		7,900(s)	42.4
		7,550	43.3
o-chlorophenyl	chlorobenzene	16,850(s)	34.4
		10,500	27.8
		7,950(s)	38.2
		7,300	39.4

TABLE (B)-1. - (contd.)

R	Solvent	Band Wavenumber	Band Intensity
m-chlorophenyl	benzene	16,800(s)	36.0
		11,300	31.1
		7,950(s)	50.9
		7,500	52.1
	chlorobenzene	16,500(s)	32.0
		10,950	30.6
		7,800(s)	52.3
		7,350	52.9
p-chlorophenyl	benzene	16,800(s)	24.6
		11,400	29.3
		7,950(s)	50.7
		7,600	51.5
	DMF	16,850(s)	46.2
		10,500	22.9
		7,950(s)	37.4
		7,300	38.5
o-bromophenyl	chlorobenzene	16,900(s)	34.4
		10,700	27.8
		7,900(s)	40.3
		7,300	42.3
m-bromophenyl	benzene	16,600(s)	36.9
		11,050	29.0
		7,900(s)	46.7
		7,400	48.1
p-bromophenyl	benzene	16,800(s)	22.0
		11,400	25.2
		8,050(s)	45.3
		7,500	46.8
	DMF	16,800(s)	32.5
		11,000	21.6
		7,800(s)	33.6
		7,400	36.7

Contd...

TABLE (B)-1. (contd.)

R	Solvent	Band Wavenumbers	Band Intensity
α-naphthyl	benzene	10,500	35.0
		7,900(s)	55.2
		7,300	57.6
benzyl	chlorobenzene	17,700	60.5
		17,100(s)	53.8
		11,050	32.1
		7,900(s)	30.3
		7,550	31.5
cyclohexyl	benzene	17,500	63.3
		17,150(s)	61.6
		10,650	42.8
		7,800(s)	66.9
		7,500	68.0
p-nitrophenyl	DMF	13,200	13.2
		7,200	8.2
		6,200	8.9
[a] p-tolyl-4-OH.	DMF	16,900(s)	44.1
		10,400(s)	37.4
		7,700	74.6
	methanol	10,000(s)	38.9
		7,900	69.4
[b] p-tolyl-naphth.	chlorobenzene	10,750(s)	30.4
		7,950(s)	71.7
		7,500	73.4

a. The complex is bis(N-p-tolyl-4-hydroxysalicylideneiminato)-cobalt(II)monohydrate.

b. The complex is bis(N-p-tolyl-2-oxy-1-naphthylideneiminato)-cobalt(II).

TABLE(B)-2.

The solid spectral properties of bis(N-R-salicylideneiminato)cobalt(II) in the visible and the near infrared regions.

R	Band Wavenumbers.		
phenyl	17,050(s)	11,050	8,150(s) 7,600
o-tolyl	17,250(s)	11,200	8,550(s) 7,200
m-tolyl		11,200	9,150 7,050
p-tolyl	16,850(s)	11,100	8,000
o-anisyl	17,490(s)	11,700	8,250
m-anisyl	17,400(s)	11,650	8,450(s) 7,750
p-anisyl	17,800(s)	11,250	8,150
o-fluorophenyl	18,500(s)	11,050	8,450 7,500
m-fluorophenyl	17,500(s) 17,000(s)	10,900(s)	8,050(s) 7,650
p-fluorophenyl	17,000(s)	10,750(s)	7,950(s) 7,550
o-chlorophenyl	16,950	10,450	7,050(s)
m-chlorophenyl	16,450(s)	11,200	9,100(s) 6,850(s)
p-chlorophenyl	16,850(s)	11,700	8,400
o-bromophenyl	16,850	10,600	8,450 6,850

Contd...

TABLE (B)-2. (contd.)

R	Band Wavenumbers		
m-bromophenyl	17,700(s)	11,150	9,000 6,800
p-bromophenyl	16,750(s)	11,300	8,330
benzyl	18,800	10,600	7,000(s)
cyclohexyl	17,950	11,200	7,950
α-naphthyl	16,850(s)	10,700	8,300 7,400(s)
p-nitrophenyl	16,600(s)	11,300	8,600(s) 7,600
[a]*p*-tolyl-5-Br.	18,000(s)	11,100	8,000 7,100(s)
[b]cyclohexyl-5-Br.	17,950(s)	10,700	7,550
[c]*p*-tolyl-4-OH.	17,350	10,950	8,550 7,330(s)
[d]*p*-tolyl-naph.	17,350(s)		8,360(s) 8,000 7,550(s)

a. Bis(N-*p*-tolyl-5-bromosalicylideneiminato)cobalt(II).

b. Bis(N-cyclohexyl-5-bromosalicylideneiminato)cobalt(II).

c. Bis(N-*p*-tolyl-4-hydroxysalicylideneiminato)cobalt(II)monohydrate.

d. Bis(N-*p*-tolyl-2-oxy-1-naphthylideneiminato)cobalt(II).

TABLE (B)-3.

The visible and near infrared spectral properties of bis(N-R-salicylideneiminato)cobalt(II) in pyridine at 25°C.

R	Conc.x10^2(M)	Band Wavenumber	Band Intensity
phenyl	2,032	17,050(s) 16,200(s) 9,800	25.5 17.9 8.6
o-tolyl	2,065	17,000 9,800	22.5 8.9
m-tolyl	1.657	17,000(s) 9,700	25.4 8.8
p-tolyl	1.320	17,300(s) 10,100	26.4 8.6
o-anisyl	0.9083	9,800	9.4
m-anisyl	1.385	17,000(s) 9,800	27.8 7.9
p-anisyl	1.319	16,800(s) 9,800	22.7 7.6
o-fluorophenyl	1.986	17,500(s) 10,100	26.5 9.9
m-fluorophenyl	1.373	17,500(s) 10,000	27.0 10.1
p-fluorophenyl	1.555	17,800(s) 10,000	26.0 9.6
o-chlorophenyl	1.003	17,250 9,800	22.0 8.7
m-chlorophenyl	1.034	17,100(s) 9,800	27.6 10.0
p-chlorophenyl	1.353	17,100(s) 9,900	26.8 9.7

Contd...

TABLE (B)-3. (contd.)

R	Conc.x10^2(M)	Band Wavenumber	Band Intensity
o-bromophenyl	1.103	17,100 9,800	28.8 8.6
m-bromophenyl	1.149	17,150(s) 9,900	29.0 9.6
p-bromophenyl	1.043	17,000(s) 10,000	25.9 9.9
α-naphthyl	1.095	17,000(s) 9,800	24.0 8.6
benzyl	1.454	17,700 10,000	19.7 8.0
cyclohexyl	0.874	17,700 17,050(s) 10,300 7,700	42.3 38.3 22.9 32.0
m-nitrophenyl	1.341	10,100	11.0
[a] p-tolyl-4-OH.	1.179	16,300(s) 10,700(s) 8,100	44.4 16.1 24.1
[b] p-tolyl-naphth.	0.7354	9,900	12.0

For compounds a and b see footnotes c and d of Table (B)-2, respectively.

TABLE (B)-4.

The ultra-violet spectral properties of bis(N-R-salicylideneiminato)cobalt(II) in pyridine at 25°C.

R	Band Wavenumber	Band Intensity
phenyl	27,700 25,900(s)	13,400 11,500
o-tolyl	30,000(s) 28,900	11,600 12,050
m-tolyl	27,700	10,400
p-tolyl	27,800	15,350
o-anisyl	29,900 27,300 25,300(s)	15,150 15,050 6,700
m-anisyl	27,400	13,750
p-anisyl	27,300	14,400
o-fluorophenyl	27,900	13,250
m-fluorophenyl	26,800	12,100
p-fluorophenyl	27,400 25,900(s)	12,800 11,250
o-chlorophenyl	28,300	14,050
m-chlorophenyl	26,700	12,750
p-chlorophenyl	27,600	14,050
o-bromophenyl	28,150	13,950
m-bromophenyl	26,600	13,050
p-bromophenyl	27,250	13,950
α-naphthyl	27,700	19,100

Contd....

TABLE (B)-4. (contd.)

R	Band Wavenumber	Band Intensity
benzyl	27,800	10,350
cyclohexyl	30,600 27,850	8,150 7,740
m-nitrophenyl	26,500	12,850
[a]*p*-tolyl-5-Br.	26,250	13,300
[b]cyclohexyl-5-Br.	27,700	9,500
[c]*p*-tolyl-4-OH.	28,200	7,600
[d]*p*-tolyl-naphth.	31,050 25,050	21,700 17,600

For compounds a, b, c and d see footnotes in Table (B)-2.

APPENDIX C.

The magnetic properties of cobalt(II) Schiff's base complexes.

TABLE (C)-1.

The magnetic properties of bis(N-R-salicylideneiminato)cobalt(II) in the solid.

R	T°A.	$10^6 \chi_g$.	B.M.
phenyl	291.6	18.01	4.44
o-tolyl	283.3	17.81	4.48
m-tolyl	291.0	16.34	4.36
p-tolyl	287.9	16.76	4.39
o-anisyl	291.2	16.02	4.46
m-anisyl	291.0	15.19	4.35
p-anisyl	291.9	14.99	4.33
o-fluorophenyl	291.6	15.81	4.33
p-fluorophenyl	291.7	16.12	4.37
m-fluorophenyl	298.6	16.36	4.45
o-chlorophenyl	291.5	15.89	4.48
m-chlorophenyl	290.7	14.91	4.34
p-chlorophenyl	291.5	15.42	4.42
o-bromophenyl	291.6	12.73	4.35
m-bromophenyl	291.8	13.32	4.45
p-bromophenyl	291.5	12.42	4.30

Contd...

TABLE (C)-1. (contd.)

R	T°A	$10^6 \chi_g$.	B.M.
benzyl	294.0	17.46	4.50
cyclohexyl	297.1	17.27	4.46
α-naphthyl	291.6	14.34	4.39
m-nitrophenyl	291.8	13.88	4.28
[a]p-tolyl-4-OH.	291.7	15.78	4.51
[b]p-tolyl-naphth.	294.2	13.60	4.39

a. Bis(N-p-tolyl-4-hydroxysalicylideneiminato)cobalt(II)-monohydrate.

b. Bis(N-p-tolyl-2-oxy-1-naphthylideneiminato)cobalt(II).

TABLE (C)-2.

The magnetic properties of bis(N-R-salicylideneiminato)cobalt(II) in non-coordinating solvents.

R	Solvent	Conc.*	T°A.	B.M.
phenyl	chlorobenzene	7.199	296.0	4.53
	DMF	8.951	291.6	4.44
o-tolyl	benzene	8.398	290.5	4.57
m-tolyl	chlorobenzene	6.981	296.2	4.57
p-tolyl	chlorobenzene	6.832	295.9	4.33
o-anisyl	DMF	5.564	293.1	4.59
m-anisyl	benzene	8.070	299.2	4.55
p-anisyl	chlorobenzene	6.175	295.5	4.43
o-fluorophenyl	chlorobenzene	6.769	291.5	4.44
m-fluorophenyl	benzene	5.417	299.6	4.57
p-fluorophenyl	chlorobenzene	6.894	292.3	4.44
	DMF	6.975	290.8	4.52
o-chlorophenyl	chlorobenzene	6.713	297.0	4.37
m-chlorophenyl	benzene	7.045	291.2	4.58
	chlorobenzene	6.091	295.5	4.58
p-chlorophenyl	DMF	6.276	294.6	4.59
o-bromophenyl	chlorobenzene	4.047	300.0	4.49
m-bromophenyl	chlorobenzene	6.034	296.7	4.61
p-bromophenyl	DMF	6.689	295.1	4.52
α-naphthyl	benzene	11.15	298.2	4.61

Contd..

TABLE (C)-2. (contd.)

R	Solvent	Conc.[c]	T°A.	B.M.
benzyl	chlorobenzene	4.412	295.5	4.30
cyclohexyl	chlorobenzene	8.576	297.1	4.52
m-nitrophenyl	DMF	6.742	295.8	4.52
[a]p-tolyl-4-OH.	DMF	7.998	295.0	4.37
[b]p-tolyl-naphth.	chlorobenzene	4.827	296.8	4.54

For a and b see the corresponding footnotes of Table (C)-1 of Appendix C.

[c] Concentration is in gms./1000 gms. of solvent.

TABLE (C)-3.

The magnetic moments of bis(N-R-salicylideneiminato)cobalt(II) in pyridine.

R	Conc.^{a}	T°A.	B.M.
phenyl	8.597	294.9	4.91
o-tolyl	8.798	290.6	4.84
m-tolyl	7.038	295.7	4.87
p-tolyl	9.648	295.5	4.76
o-anisyl	7.666	294.3	4.71
m-anisyl	8.649	294.4	4.90
p-anisyl	7.848	295.3	4.70
o-fluorophenyl	9.784	295.5	4.84
m-fluorophenyl	6.837	300.0	4.99
p-fluorophenyl	7.705	296.9	4.88
o-chlorophenyl	5.292	295.2	4.80
m-chlorophenyl	7.895	295.6	4.93
p-chlorophenyl	5.328	295.5	4.89
o-bromophenyl	6.814	296.7	4.79
m-bromophenyl	6.622	293.7	5.06
p-bromophenyl	7.942	295.2	4.83
α-naphthyl	11.07	295.4	4.97
benzyl	7.116	294.7	4.91
cyclohexyl	11.14	295.2	4.75

Contd...

TABLE (C)-3. (contd.)

R	Conc.[e]	T°A.	B.M.
p-nitrophenyl	8.525	294.8	4.73
[a]*p*-tolyl-4-CH.	6.326	295.4	4.77
[b]*p*-tolyl-naphth .	6.883	295.9	4.90

For superscripts a and b see corresponding footnotes in Table (C)-1 of Appendix C.

e. Concentration is in gms./1000 gms. solvent.

APPENDIX D.

Stability Constants.

(i) Derivation of the equilibrium expressions.

a. General equations.

If CoB_2 represents the complex bis(N-R-salicylideneiminato)cobalt(II) and Pyr. represents pyridine, the reaction of the cobalt(II) Schiff's base complex with pyridine (in solution) is described by the relations:

$$CoB_2 + Pyr. \rightleftharpoons CoB_2Pyr. \qquad (D)\text{-}1$$

$$CoB_2Pyr. + Pyr. \rightleftharpoons CoB_2Pyr._2 \qquad (D)\text{-}2$$

The equilibrium constants for these reactions are given by:

K_1^{a} = stability constant of the monopyridinate

$$= \frac{C_1}{C_0 \times C_{Pyr.}} \qquad (D)\text{-}3$$

---

[a] The stability constants are expressed in terms of molar concentration (C). The subscripts 0, 1 and 2 of C refer to species CoB_2, $CoB_2Pyr.$ and CoB_2Pyr_2 respectively. $C_{Pyr.}$ is the equilibrium pyridine concentration.

K_2 = stability constant of the dipyridinate,

$$= \frac{C_2}{C_1 \times C_{Pyr.}} \qquad (D)\text{-}4.$$

$K_T = K_1K_2$, the overall stability constant

$$= \frac{C_2}{C_0 \times C^2_{Pyr.}} \qquad (D)\text{-}5.$$

Here the assumption has been made that the activity of all species in solution is unity. This approximation seems reasonable as all species are uncharged and furthermore organic solvents were used.

It has been shown that the reactions (D)-1 and (D)-2 can be investigated spectrophotometrically. Thus the optical density of the reaction solution, OD_T, is given by the sum of the optical densities of all the absorbing species in solution.

$$OD_T = OD_0 + OD_1 + OD_2 \qquad (D)\text{-}6.$$

The subscripts $_0$, $_1$, and $_2$ refer to the species CoB_2, $CoB_2Pyr.$ and $CoB_2Pyr._2$ respectively. Now on substituting for the optical densities of the solutions the molar extinctions, one obtains the relation

$$\epsilon_T C_T = \epsilon_0 C_0 + \epsilon_1 C_1 + \epsilon_2 C_2 \qquad (D)\text{-}7.$$

where C_T, the total complex concentration,

$$= C_0 + C_1 + C_2 \qquad (D)\text{-}8.$$

On substituting Equation (D)-8 into (D)-7 and rearrangement, the expression

$$c_1(\epsilon_T - \epsilon_1) = c_0(\epsilon_0 - \epsilon_T) + c_2(\epsilon_2 - \epsilon_T) \qquad \text{(D)-9.}$$

is obtained. This can be further rearranged by use of Equations (D)-5 and then (D)-3 to the form

$$\epsilon_T - \epsilon_1 = \frac{1}{K_1}\left[\frac{\epsilon_0 - \epsilon_T}{C_{Pyr.}} + K_T C_{Pyr.}(\epsilon_2 - \epsilon_T)\right] \qquad \text{(D)-10.}$$

$$= \frac{1}{K_1}(a + K_T b) \qquad \text{(D)-11.}$$

where and

$$a = \frac{\epsilon_0 - \epsilon_T}{C_{Pyr.}} \qquad b = (\epsilon_2 - \epsilon_T)C_{pyr.}$$

Equation (D)-11 contains three unknowns, namely ϵ_1, K_1 and K_T.

If the spectral data from two solutions of the same complex (different pyridine concentration) are substituted into Equation (D)-11, subtraction of these resulting equations gives

$$\Delta\epsilon_T = \frac{1}{K_1}(A + K_T B) \qquad \text{(D)-12.}$$

Here $\Delta\epsilon_T = \epsilon_T - \epsilon_T'$; $A = a - a'$; and $D = b - b'$.

Equation (D)-12 can then be solved graphically or solved simultaneously.

b. Equilibrium expression if ϵ_1 is known.

In this case Equation (D)-11 can be used. Thus

$$\epsilon_T - \epsilon_1 = \frac{1}{K_1}(a + K_T b)$$

$$= \frac{a}{K_1} + \frac{K_T b}{K_1}$$

$$= \frac{a}{K_1} + K_2 b$$

$$\frac{\epsilon_T - \epsilon_1}{a} = \frac{K_2 b}{a} + \frac{1}{K_1} \qquad \text{(D)-13.}$$

Hence the plot of Equation (D)-13 will have a slope of K_2, the intercept being $\frac{1}{K_1}$.

c. The equilibrium expression when K_2 is very small compared to K_1.

Reference to Equation (D)-13 shows that if K_2 is very small, this Equation reduces to:

$$\epsilon_T - \epsilon_1 = \frac{a}{K_1} \qquad \text{(D)-14.}$$

Hence the plot of ϵ_T against a will possess a slope of $\frac{1}{K_1}$, the intercept being ϵ_1.

If the uncertainty in ϵ_1 is less than in ϵ_0, Equation (D)-14 may, with advantage, be rearranged to the form:

$$\epsilon_T - \epsilon_0 = -K_1(\epsilon_T - \epsilon_1)C_{Pyr.} \qquad (D)\text{-}15.$$

This plot of ϵ_T against $(\epsilon_T - \epsilon_1)C_{Pyr.}$ is linear with slope $-K_1$ and intercept ϵ_0.

d. The equilibrium expression when K_1 is very small compared to K_2.

From Equation (D)-11 it is seen that if K_1 is very small compared to K_2, the extinction of a solution of complex can be expressed as a function of the pyridine concentration by:

$$a = -K_T b \qquad (D)\text{-}16.$$

which on expansion gives

$$\epsilon_T = -K_T(\epsilon_T - \epsilon_2)C^2_{Pyr.} + \epsilon_0 \qquad (D)\text{-}17.$$

From this expression K_T can be readily found graphically.

If K_T is small so that ϵ_2 cannot be determined experimentally, Equation (D)-17 can be used in the alternate form, namely,

$$\epsilon_T = \frac{a}{K_T C_{Pyr.}} + \epsilon_2 \qquad (D)\text{-}18.$$

e. Evaluation of ϵ_1.

The value of ϵ_1 can be readily found at any wavenumber from Equation (D)-13 after both K_1 and K_2 have been determined. Thus,

$$\epsilon_T - \epsilon_1 = K_2 b + \frac{a}{K_1} \qquad (D)\text{-}19.$$

is the equation of a straight line, intercept ϵ_1.

f. Determination of the equilibrium pyridine concentration.

Due to adduct formation the equilibrium pyridine concentration will always be less than the amount of pyridine introduced into the reaction flask. This decrease in pyridine concentration will be of particular importance for those compounds in which K_T is greater than about 5.

Using Equations (D)-3 and (D)-4 one can define two parameters x and y, where

$$x = \frac{1}{K_1 C_{Pyr.}} = \frac{C_o}{C_1} \quad \text{and } y = \frac{1}{K_2 C_{Pyr.}} = \frac{C_1}{C_2}.$$

Since C_T, the total complex concentration,

$$= C_0 + C_1 + C_2$$

$$= xC_1 + C_1 + C_2$$

$$= C_1(x + 1) + C_2$$

$$= C_2(1 + y + xy).$$

$$C_2 = \frac{C_T}{(1 + y + xy)}. \qquad \text{(D)-20.}$$

Similarly $C_1 = \dfrac{C_T}{(1 + x + 1/y)}$. (D)-21.

The equilibrium pyridine concentration, $C_{Pyr.}$ can then be evaluated by introduction of Equations (D)-20 and (D)-21 into Equation (D)-22 below.

$$C_{Pyr.} = C^T_{Pyr.} - 2C_2 - C_1 \qquad \text{(D)-22.}$$

Here $C^T_{Pyr.}$ is the overall pyridine concentration.

(ii) The stability of the pyridine adducts.

TABLE (D)-1.

The stability constants of the pyridine adducts of bis(N-R-salicylideneiminato)cobalt(II)

R	Solvent	T°C.	K_1	K_2	K_T
phenyl	benzene	30.0	1.21	3.49	4.21
		35.0	0.99_2	2.99	2.96
		40.0	0.90_0	2.38	2.14
		45.0	0.78_0	1.98	1.54
o-tolyl	benzene	30.0	2.06	0.45_6	0.93_9
		35.0	1.76	0.25_8	0.45_4
		40.0	1.47	0.23_4	0.34_3
		45.0	1.35	0.13_4	0.18_1
m-tolyl	benzene	30.0	0.93	3.81	3.56
		35.0	0.79	2.83	2.24
		40.0	0.62	2.93	1.82
		45.0	0.55	2.18	1.20
p-tolyl	benzene	30.0	0.71	1.99	1.40
		35.0	0.64	1.60	1.03
		40.0	0.49	1.51	0.73
		45.0	0.41	1.33	0.55

TABLE (D)-1. (contd.).

R	Solvent	T°C	K_1	K_2	K_T
o-anisyl	DMF	30.0	0.32		
		35.0	0.31		
		40.0	0.29		
		45.0	0.28		
m-anisyl	benzene	30.0	1.24	2.48	3.07
		35.0	1.01	2.12	2.14
		40.0	0.85	1.79	1.52
		45.0	0.73	1.49	1.09
p-anisyl	chlorobenzene	30.0	0.45	1.49	0.67
		35.0	0.35	1.03	0.47
		40.0	0.28	1.33	0.38
		45.0	0.27	1.10	0.29
o-fluorophenyl	chlorobenzene	30.0	9.49	4.32	41.0
		35.0	8.17	3.39	27.7
		40.0	6.13	3.63	22.3
		45.0	5.47	2.27	12.4
m-fluorophenyl	benzene	30.0	7.01	5.97	41.8
		35.0	5.77	4.36	25.2
		40.0	4.75	3.90	18.5
		45.0	3.86	3.67	14.1

Contd...

TABLE (D)-1. (Contd.)

R	Solvent	T°C	K_1	K_2	K_T
p-fluorophenyl	chlorobenzene	30.0	2.53	3.87	9.80
		35.0	1.99	3.53	7.01
		40.0	1.65	3.22	5.32
		45.0	1.18	3.76	4.44
	DMF	30.0	0.99	0.66	0.66
		35.0	0.85	0.60	0.51
		40.0	0.74	0.54	0.40
		45.0	0.66	0.47	0.31
o-chlorophenyl	chlorobenzene	30.0	13.22	0.72	9.54
		35.0	11.53	0.52	5.96
		40.0	9.11	0.55	5.05
		45.0	7.93	0.40	3.17
m-chlorophenyl	benzene	30.0	7.70	8.02	61.8
		35.0	5.37	7.74	41.6
		40.0	4.81	6.90	33.2
		45.0	4.17	6.23	25.4
	chlorobenzene	30.0	7.35	4.02	29.6
		35.0	5.89	3.85	22.6
		40.0	4.20	4.22	17.7
		45.0	3.39	4.02	13.6
p-chlorophenyl	DMF	30.0	1.40	0.65	0.91
		35.0	1.41	0.50	0.71
		40.0	0.99	0.61	0.61
		45.0	0.97	0.49	0.48

Contd...

TABLE (D)-1. (contd.)

R	Solvent	T°C	K_1	K_2	K_T
o-bromophenyl	chlorobenzene	30.0	16.60		
		35.0	12.97		
		40.0	11.13		
		45.0	8.75		
m-bromophenyl	benzene	30.0	8.36	9.33	78.0
		35.0	5.80	9.89	57.4
		40.0	5.26	7.48	39.3
		45.0	4.56	6.47	29.5
p-bromophenyl	DMF	30.0	1.34	0.79	1.07
		35.0	1.26	0.71	0.89
		40.0	1.02	0.58	0.59
		45.0	1.00	0.48	0.48
α-naphthyl	benzene	30.0	4.41	1.57	6.93
		35.0	3.80	1.28	4.88
		40.0	3.33	0.91	3.03
		45.0	2.83	0.81	2.30
benzyl	chlorobenzene	30.0	3.77	1.51	5.70
		35.0	3.30	0.98	3.24
		40.0	3.00	0.55	1.64
		45.0	2.33	0.61	1.42
cyclohexyl	benzene	19.6	0.122		
		30.0	0.083		
		45.0	0.044		

Contd...

TABLE (D)-1. (contd.)

R	Solvent	T°C	K_1	K_2	K_T
p-nitrophenyl	DMF	30.0	1.88	1.21	2.27
		35.0	1.56	0.99	1.54
		40.0	1.37	0.86	1.17
		45.0	1.20	0.80	0.97
[a]*p*-tolyl-4-OH.	DMF	30.0			0.0098
		35.0			0.0085
		40.0			0.0075
		45.0			0.0061
[b]*p*-tolyl-naphth.	chlorobenzene	30.0	0.49	2.57	1.26
		35.0	0.38	2.40	0.92
		40.0	0.36	1.82	0.65
		45.0	0.28	1.73	0.48

a. Bis(N-*p*-tolyl-4-hydroxysalicylideneiminato)cobalt(II)monohydrate.

b. Bis(N-*p*-tolyl-2-oxy-1-naphthylideneiminato)cobalt(II).

TABLE (D)-2.

The equilibrium constants for the addition of pyridine to bis(N-R-salicylideneiminato)copper(II).

R	Solvent	T°C	K_1
phenyl	chlorobenzene	30.0	0.831
		35.0	0.727
		40.0	0.648
		45.0	0.558
	benzene	30.0	1.51
		35.0	1.34
		40.0	1.15
		45.0	0.970
	cyclohexane	30.0	5.08
		35.0	4.15
		40.0	3.50
		45.0	3.15
	DMF	30.0	0.157
		35.0	0.141
		40.0	0.128
		45.0	0.109
p-tolyl	chlorobenzene	30.0	0.772
		35.0	0.661
		40.0	0.584
		45.0	0.523
	cyclohexane	30.0	4.36
		35.0	3.73
		40.0	3.22
		45.0	2.60
m-tolyl	chlorobenzene	30.0	0.698
		35.0	0.636
		40.0	0.565
		45.0	0.487
	cyclohexane	30.0	3.62
		35.0	3.22
		40.0	2.99
		45.0	2.70

Contd...

TABLE (D)-2. (contd.)

R	Solvent	T°C	K_1
p-tolyl	chlorobenzene	30.0	0.618
		35.0	0.555
		40.0	0.495
		45.0	0.455
p-tolyl	cyclohexane	30.0	3.88
		35.0	3.26
		40.0	2,81
		45,0	2.58
o-anisyl	chlorobenzene	30.0	0.161
		35.0	0.170
		40.0	0.167
		45.0	0.192
m-anisyl	cyclohexane	30.0	6.47
		35.0	5.19
		40.0	4.08
		45.0	3.64
p-anisyl	chlorobenzene	30.0	0.522
		35.0	0.520
		40.0	0.467
		45.0	0.446
o-fluorophenyl	chlorobenzene	30.0	1.00
		35.0	0.845
		40.0	0.727
		45.0	0.658
m-fluorophenyl	chlorobenzene	30.0	2.19
		35.0	1.88
		40.0	1.67
		45.0	1.53
	benzene	30.0	3.26
		35.0	2.84
		40.0	2.60
		45.0	2.17
	cyclohexane	30.0	9.53
		35.0	8.10
		40.0	6.69
		45.0	5.50

Contd...

TABLE (D)-2. (contd.).

R	Solvent	T°C	K_1
p-fluorophenyl	chlorobenzene	30.0	1.40
		35.0	1.21
		40.0	1.07
		45.0	0.965
	benzene	30.0	2.04
		35.0	1.92
		40.0	1.73
		45.0	1.45
p-fluorophenyl	cyclohexane	30.0	8.83
		35.0	7.38
		40.0	6.16
		45.0	5.65
o-chlorophenyl	chlorobenzene	30.0	0.471
		35.0	0.419
		40.0	0.371
		45.0	0.366
m-chlorophenyl	cyclohexane	30.0	12.5
		35.0	10.2
		40.0	8.29
		45.0	6.16
p-chlorophenyl	cyclohexane	30.0	12.6
		35.0	10.9
		40.0	9.10
		45.0	7.45
o-bromophenyl	chlorobenzene	30.0	2.83
		35.0	2.40
		40.0	2.13
		45.0	2.40
m-bromophenyl	cyclohexane	30.0	7.69
		35.0	7.25
		40.0	5.62
		45.0	4.52
p-bromophenyl	cyclohexane	30.0	12.5
		35.0	9.34
		40.0	7.76
		45.0	6.64

Contd...

TABLE (D)-2. (contd.)

R	Solvent	T°C	K_1
m-nitrophenyl	chlorobenzene	35.0	5.92
		40.0	5.01
		45.0	4.61
cyclohexyl	chlorobenzene	30.0	1.129
		35.0	0.117
		40.0	0.110
		45.0	0.099
benzyl	chlorobenzene	30.0	0.302
		35.0	0.274
		40.0	0.268
		45.0	0.252

APPENDIX E.

The rotational entropy associated with a coordinated pyridine.

In Chapter IV of this thesis it had been assumed that the pyridine coordinated to cobalt(II) Schiff's base complexes could rotate about the metal-nitrogen bond. The entropy associated with this rotation can be estimated[1].

The basic relationship for the entropy of rotation about a single axis is

$$S_{rot.} = R + R\ln q_{rot.} \qquad (E)\text{-}1.$$

In this expression $S_{rot.}$ is the rotational entropy, R is the gas constant and $q_{rot.}$ is the rotational partition function. This latter function is, for the case in point, defined by the equation

$$q_{rot.} = \frac{1}{\sigma} \cdot \frac{8\pi^2 IkT}{h^2} \qquad (E)\text{-}2.$$

where σ the symmetry element, is two; I is the moment of inertia, of the pyridine about the two fold symmetry axis (in gms. x cms.^{2}), and T is the absolute temperature. k and h are the Boltzmann and Planck constants.

Equation (E)-2 reduces to the form

$$q_{rot.} = \frac{T \times I^1}{2.8776 \times 16.858} \qquad (E)\text{-}3$$

where I' is the moment of inertia expressed in atomic units (amu. x A^2). For pyridine, I' about the symmetric axis through the nitrogen is 83.701 amu. x A^2.[2] Thus assuming free rotation about the metal-pyridine bond, the entropy associated with this rotation is

$$S_{rot.} = 1.99 + 12.42$$

$$= 14.41 \text{ e.u.}$$

REFERENCES TO APPENDIX E.

1. Davidson, N., in "Statistical Mechanics", McGraw-Hill, New York, (1962), pp.123-125.

2. Bak, B., Hansen-Nygaard, L., and Rastrup-Andersen, J., J. Mol. Spectroscopy, 2, 361, (1958).

APPENDIX F.

The spectral and magnetic properties of some copper(II) Schiff's base complexes.

TABLE (F)-1.

The solid magnetic properties of some bis(N-R-salicylideneiminato)copper(II) compounds.

R	T°A.	$10^6 \chi_g$.	B.M.
phenyl	288.0	3.037	1.94
o-tolyl	289.2	2.391	1.79
m-tolyl	290.7	2.855	1.97
p-tolyl	290.7	2.920	1.99
o-anisyl	288.9	2.356	1.87
m-anisyl	289.0	2.308	1.85
p-anisyl	288.8	2.470	1.90
o-fluorophenyl	288.8	2.500	1.86
m-fluorophenyl	288.0	2.766	1.93
p-fluorophenyl	289.5	2.331	1.81
o-chlorophenyl	289.5	2.409	1.90
m-chlorophenyl	288.0	2.735	1.99
p-chlorophenyl	289.6	2.125	1.81
o-bromophenyl	289.2	2.607	2.11
m-bromophenyl	288.0	2.069	1.90
p-bromophenyl	289.5	2.107	1.93

TABLE (F)-2.

The magnetic properties of some bis(N-R-salicylideneiminato)copper(II) compounds in non-coordinating solvents

R	Solvent	T°A.	Conc.^{a}	B.M.
phenyl	chlorobenzene	292.6	4.680	2.02
	benzene	290.8	6.374	2.25
	DMF	290.6	6.633	2.10
o-tolyl	chlorobenzene	292.0	4.720	2.18
m-tolyl	chlorobenzene	291.2	4.339	1.96
p-tolyl	chlorobenzene	291.2	5.763	2.04
o-anisyl	chlorobenzene	291.5	4.851	2.13
m-anisyl	chlorobenzene	292.7	19.36	2.11
p-anisyl	chlorobenzene	291.8	4.973	2.23
m-fluorophenyl	chlorobenzene	291.6	4.275	2.00
	benzene	290.9	6.158	2.26
p-fluorophenyl	chlorobenzene	289.0	4.550	2.10
	benzene	290.2	5.901	2.32
benzyl	chlorobenzene	291.7	4.794	1.94
cyclohexyl	chlorobenzene	291.2	4.525	1.99

a. Concentration in gms./1000gms.solvent.

TABLE (F)-3.

The ultraviolet spectral properties of bis(N-R-salicylideneiminato)copper(II) in chlorobenzene at 25°C.

R	Band Wavenumber	Band Intensity
phenyl	25,400	12,400
o-tolyl	27,500 25,800(s)	12,600 10,500
m-tolyl	27,300 25,350	11,900 11,450
p-tolyl	28,650 25,350(s)	13,100 11,750
o-anisyl	25,150(s) 24,400	12,850 13,200
m-anisyl	27,150 25,450	11,700 11,300
p-anisyl	25,800	16,650
o-fluorophenyl	25,300	12,900
m-fluorophenyl	25,300	12,300
p-fluorophenyl	25,300	12,700
o-chlorophenyl	25,400	12,850
m-chlorophenyl	25,300	12,150
p-chlorophenyl	25,300	13,650
o-bromophenyl	25,300	12,100
m-bromophenyl	25,300	13,500
p-bromophenyl	25,250	14,350
α-naphthyl	25,100	15,050
benzyl	26,650	11,200
cyclohexyl	26,900	10,450
m-nitrophenyl	25,200	12,750