TRANSITION METAL CHELATES WITH SCHIFF BASES
DERIVED FROM
SALICYLALDEHYDE AND DIAMINO ETHANE

ALVIN PAUL SUMMERTON, B.SC.

UNIVERSITY OF ADELAIDE,
DEPARTMENT OF PHYSICAL AND INORGANIC CHEMISTRY

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SUMMARY

The following study of transition metal complexes with Schiff base ligands comprises two related studies.

PART I
Complexes of the quadridentate ligand, salen.

A number of complexes of general formula Fe(III)salenX, where X = Cl, Br, I, NO₃, N₃, NCS and C₆H₅COO, have been prepared. Of these species, two (X = NO₃ and N₃) have not been previously reported and only one (X = Cl) has been intensively studied. In addition, two novel octahedral complex salts K[Fe(salen)(CN)₂] and Fe(saen)₂Cl.H₂O, which involve a low spin central metal ion, have been obtained. The salt Fe(saen)₂Cl.H₂O has several unusual properties which have been examined in Part II of this thesis.

This investigation of the salen complexes has involved:

1. confirmation of structure by microanalysis, i.r. spectra and magnetism;
2. a study of the u.v.-visible solution spectra;
3. determination of the Moessbauer spectral parameters.

The solution spectra indicated that the species were involved in dissociative equilibria which were utilized to estimate the relative stability of the covalent bond between the metal and the anionic ligand occupying the fifth coordination position. In contrast to previous studies, where a correlation between magnetic properties and the Moessbauer data was indicated, the results of this work suggested that the magnitude of the quadrupole splitting may be related to the nature of the Fe-X bond.
PART II
Complexes of the tridentate ligand, saen.

Cationic salts of general formula M(III)(saen)$_2$X$_n$H$_{2O}$, where X = Cl, Br, I, NO$_3$, NCS, ClO$_4$, BF$_4$ and PF$_6$, n = 0 or 1, have been prepared and confirmed by microanalysis for M = Cr, Fe and Co. The properties of these salts have been studied in the solid state utilizing a variety of techniques including i.r. spectra, X-ray powder diffraction, magnetic susceptibility and dehydration in vacuo. The characteristic i.r. spectra obtained allowed classification of the salts into one of three general spectral types. This classification was found to be dependent on the nature of both the metal and anion in addition to the presence or absence of water of hydration.

The chloride salts of all three complex metal cations were found to be isostructural monohydrates of particular interest. The water molecule appeared to be unusual in that it:

1. produced two sharp absorptions in the O-H stretching region of the i.r. spectrum;
2. stabilized the low spin state of Fe(III) in Fe(saen)$_2$Cl. H$_{2O}$.

The solution properties of the salts were studied via n.m.r. and u.v.-visible spectra, conductance and magnetic susceptibility measurements. In contrast to the results obtained in water and alcohol, association of the chloride salts was observed in the aprotic solvent DMSO, with the evidence supporting the conclusion that the water molecule also remained bound.

In order to rationalize the behaviour of the water mole-
cule, the molecular structure of Fe(saen)_2Cl.H_2O was determined by the single crystal X-ray diffraction technique. The water molecule was found to be strongly bound into the crystal lattice via unusual, specific hydrogen bonding interactions. These specific interactions involve one cation ammine hydrogen atom with the water oxygen and one water hydrogen atom with the anion. The mode of bonding of the water molecule has enabled the above-mentioned unusual features to be explained.