



GEOMETRIC ISOMERS AND CONFORMATIONAL ANALYSIS
OF SOME COBALT(III) COMPOUNDS CONTAINING
ETHYLENEDIAMINE AND PROPYLENEDIAMINE

Thesis presented for Degree of
Master of Science
by

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1972.

This thesis contains no material accepted for the award of any other degree or diploma in the University of Adelaide and to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

Signed:

ACKNOWLEDGEMENTS

Sincere thanks to my supervisor, Dr. M.R. Snow for his interest and for assistance in the way of helpful discussions and practical guidance throughout the course of my study for this degree. His continued interest has been invaluable in the completion of this thesis.

I wish to thank the following,

:Professors D.O. Jordan and D.R. Stranks for the opportunity to use the facilities of this Department.

:Dr. T.E. MacDermott for providing crystal samples.

:K.R. Butler, F.R. Keene and R.J. Geue for helpful discussions.

:The University of Adelaide for provision of a University Research Grant and for the use of computing facilities.

:Miss Beverley Willason for the competent typing of this thesis.

Thanks are also due to fellow students and staff of the Physical and Inorganic Chemistry Department who have been of assistance in any way.

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1.

SUMMARY



A survey of nine salts of the complex ions cis and trans Δ -tris[(-)-propylenediamine]cobalt(III) has been undertaken using single-crystal and X-ray powder data. It is found to be impossible to directly prove the existence of the trans isomer by X-ray structure analysis because of disorder. The compounds studied were prepared from the bromide derivatives of cis and trans Δ -[Co{(-)-pn}₃]³⁺ and fall into two classes with regard to disorder of the complex ions.

In the first class, typified by the dithionate and tris(malonato)-chromate(III) salts, the two geometric isomers are indistinguishable since the cations are disordered giving rise to an average D₃ symmetry.

In the second class, typified by the bromide salt, the cis isomer has an ordered structure with C₃ symmetry. In this case the lattice does not have the space to accommodate the disordered cation or the trans isomer. The trans isomer thus does not crystallise but forms an amorphous glass.

A conformational analysis of isomers of the complex systems [Co{en/(-)pn}₃]³⁺ and [Co{(+)pn}₃]³⁺ has been carried out using an energy-minimization

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technique. The most stable conformations adopted by the metal-chelate rings present in isomers of these complexes are those which have the lowest strain energy. An evaluation of the strain energy of an isomer is made considering energies arising from nonbonded interactions between atoms, torsional interactions about bonds within the metal-ligand ring, bond length and bond angle distortion interactions.

Energies obtained for different isomers are compared with those of an experimental conformational analysis^{4,5,6} of these complexes, some original calculations^{2,3} as applied to these particular complexes, in which the energies of isomers were calculated using only nonbonded interactions, and those of a related energy minimization procedure.^{3,9,40,41}

3.

ABBREVIATIONS

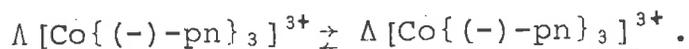
<u>Abbreviation</u>	<u>Full Name</u>
en	ethylenediamine
pn	propylenediamine
Me	methyl
ox	oxalate
mal	malonate
edda	ethylenediamine- NN'diacetate

PART I.STRUCTURAL DISORDER IN THE GEOMETRIC ISOMERS OF
 Δ -TRIS{(-)PROPYLENEDIAMINE}COBALT(III) SALTS.1:1 INTRODUCTION

The synthesis of a cobalt(III) complex containing three molecules of the bidentate chelate propylenediamine was first carried out by Pfeiffer and Grassman¹ using the racemic form of the ligand. Later, the same ion was isolated as the bromide derivatives $D[\text{Co}(d\text{-pn})_3]\text{Br}_3 \cdot 2\text{H}_2\text{O}^2$ and $L[\text{Co}(l\text{-pn})_3]\text{Br}_3 \cdot 2\text{H}_2\text{O}^3$ using resolved propylenediamine. The method of synthesis involved aerial oxidation of a mixture of a cobalt(II) salt and the optically pure diamine in the presence of charcoal and hydrochloric acid.

Dwyer and co-workers^{4,5,6} repeated this synthesis and isolated the $[\text{Co}\{(-)\text{-pn}\}_3]^{3+}$ ion as chloride or iodide derivatives. Using the techniques of fractional crystallisation⁴ and paper chromatography⁵, Λ and Δ isomers⁷ of the cation have been separated quantitatively. By equilibrating a solution of the complex using charcoal and separating the two diastereoisomers, Dwyer and co-workers obtained a value of 14.6 as the equilibrium constant for the system. represented by:

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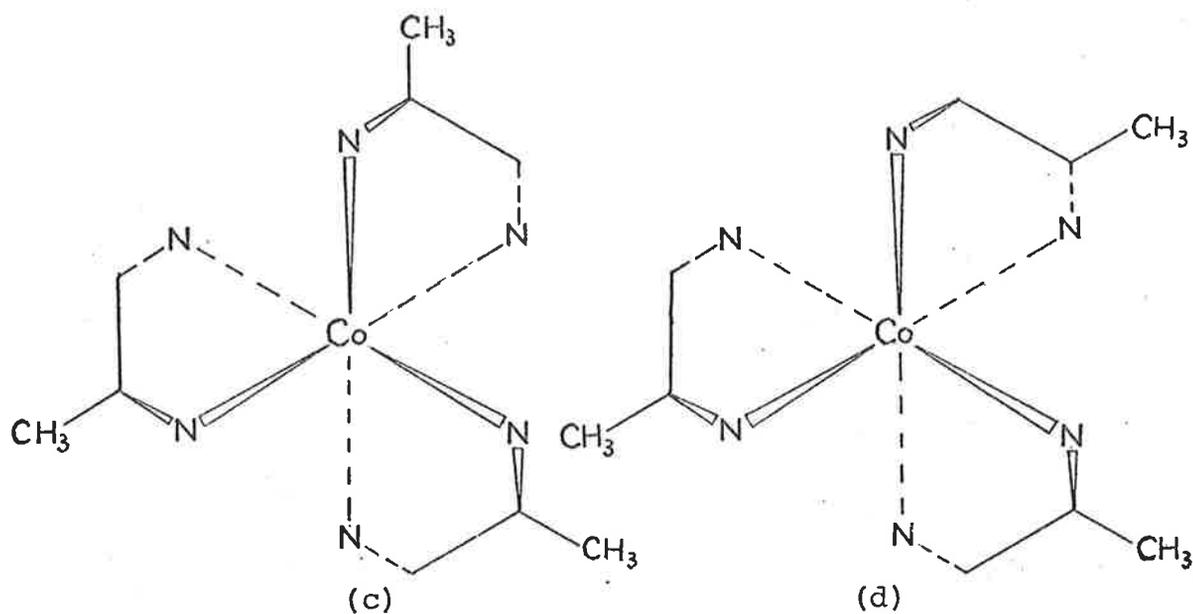
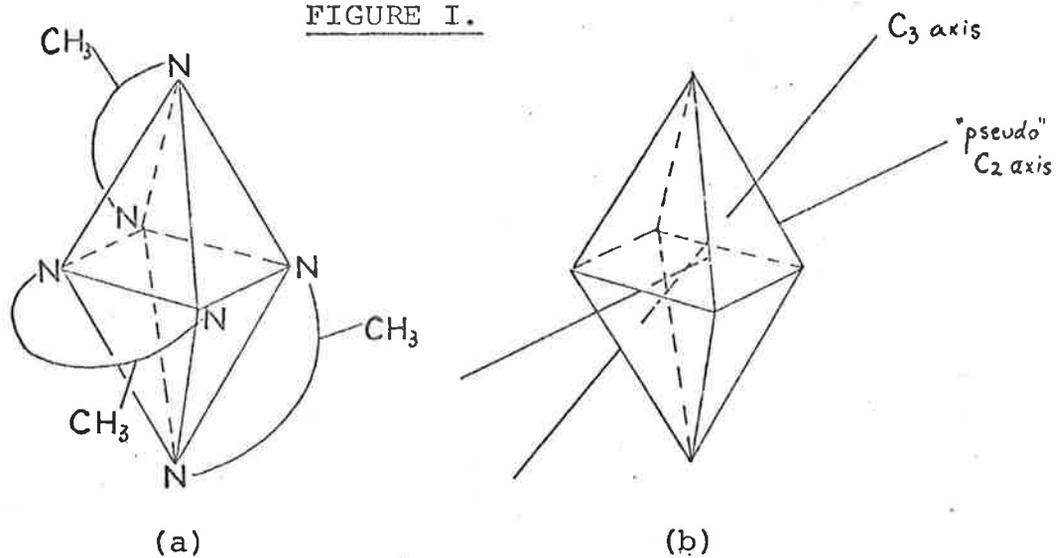


The Δ form of the ion is the most abundant of the two isomers and for it, as well as for the Λ isomer, two geometric isomers are possible.

The geometric isomerism arises because of the different orientations possible for the three dissymmetric $(-)\text{-pn}$ ligands. The three methyl groups of the ligands may have either a cis or a trans orientation relative to one another - as is shown diagrammatically in Figure I. For the cis isomer, the three methyl groups are positioned on the same side of the complex ion, giving it C_3 symmetry. The trans isomer is obtained by rotation of one pn ligand of the cis isomer about its "pseudo" C_2 axis. This results in the methyl group of the ligand being on the opposite side of the complex ion to the other two methyl groups. The trans cation now has no overall symmetry and only approximate three fold symmetry. There are three possible ways of forming the trans isomer (by rotation of any one of the three pn ligands) and thus the expected ratio of cis: trans isomer is 1:3 (if prepared under equilibrium conditions).

6.

FIGURE I.



- (a) $\text{cis-}\Lambda\text{-[Co}\{-\text{pn}\}_3\text{]}^{3+}$ showing positions of three ligands.
- (b) octahedron showing direction of C_3 axis and "pseudo" C_2 axis relative to ligand positions in (a) - Ligands have not been included to preserve clarity.
- (c) $\text{cis-}\Lambda\text{-[Co}\{-\text{pn}\}_3\text{]}^{3+}$ looking along C_3 axis.
- (d) $\text{trans-}\Lambda\text{-[Co}\{-\text{pn}\}_3\text{]}^{3+}$ looking along same direction as (c)

7.

The two geometric isomers still have the same configuration about the central metal ion and the asymmetric C atom and the same conformation of the ligand. They differ from one another only in the positioning of the methyl groups relative to one another.

In their preparation and separation of these complexes, Dwyer et. al.⁴ found no indication of the existence of both cis and trans isomers even though they carried out repeated fractionation of the stable Λ isomer. Also, a crystal structure analysis by Iwasaki and Saito⁸ of the compound $L[Co\{(-)-pn\}_3]Br_3$ prepared by a different method indicated the existence of the cis isomer only. Despite this, the peculiar behaviour of the pn ligand in giving rise to geometrical isomerism in metal complexes has been observed on several occasions. In Werners study⁹ of cis $[Co(en)(pn)(NO_2)_2]^+$, he found that for a given absolute configuration about the metal ion (Λ or Δ) and using optically pure pn $\{(+)$ or $(-)\}$, two distinct crystal forms could be obtained. These two isomeric compounds have identical rotations of plane polarised light but differ in that one form crystallises as

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needles while the other is prismatic. Structures corresponding to the two isomers, which differ only in the relative position of the methyl groups attached to the pn ligand, are shown in Figure II.

Legg¹⁰ has separated geometric isomers of the complex anion $[\text{Co}(\text{edda}) (-)\text{-pn}]^+$ (edda ethylenediamine-NN'-diacetate) which differ only in the way in which the (-)pn ligand is attached to the metal ion. Using ion exchange chromatographic methods he separated and identified four bands corresponding to four geometric isomers (with respect to the orientation of the methyl groups of the pn ligands) of cis $[\text{Co}(\text{edda}) (-)\text{-pn}]^+$. Structures corresponding to two of the four possible isomers are shown in Figure III. Two isomers of this type were separated in the same manner for trans $[\text{Co}(\text{edda}) (-)\text{-pn}]^+$.

Gollogly and Hawkins¹¹ have presented chromatographic evidence which indicates the existence of the two isomers of trans $[\text{Co}\{(-)\text{-pn}\}_2\text{Cl}_2]^+$ differing only in the positions of the pn methyl groups with respect to one another. Also, the crystal structure analysis and absolute configuration determination of (+) cis $[\text{Co}\{(-)\text{-pn}\}_2(\text{NO}_2)_2]^{+12}$ shows this ion to have the methyl groups of the

9.

FIGURE II.

Geometric isomers of $\text{cis}[\text{Co}(\text{en})(\text{pn})(\text{NO}_2)_2]^+$

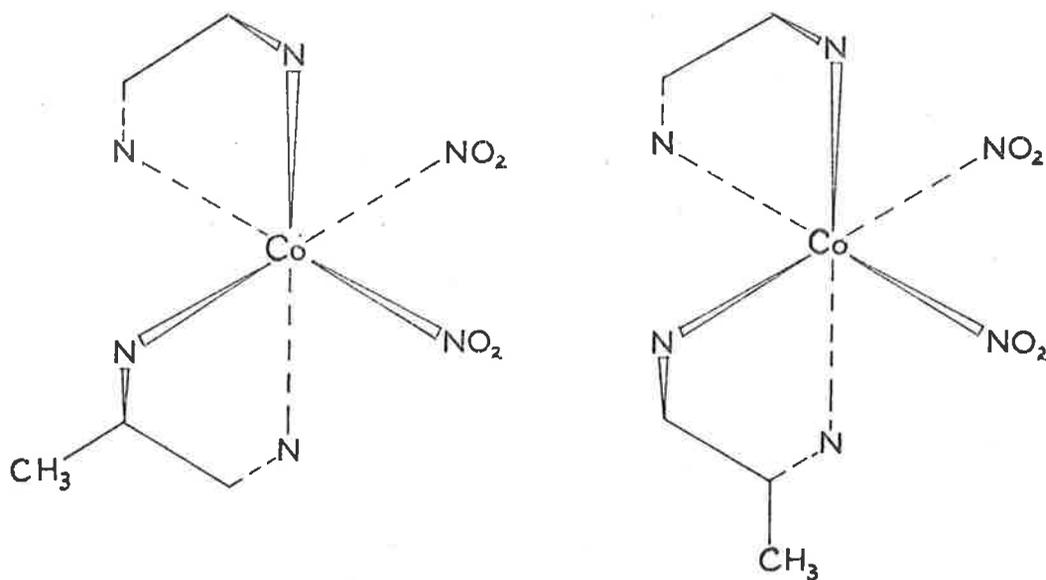
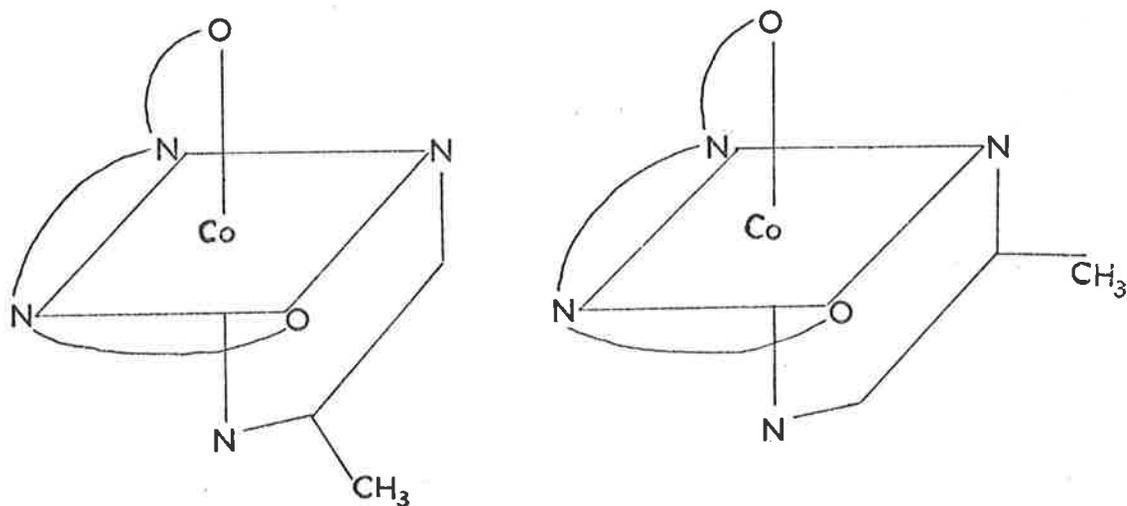


FIGURE III.

Geometric isomers of $\text{cis}[\text{Co}(\text{edda})(-)\text{pn}]^+$

(two of the four possible isomers).



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pn ligands in positions trans to one another.

The above examples refer to the possibility of geometrical isomerism due to the unsymmetrical nature of the ligand, pn. However, geometrical isomers have been observed for other octahedral tris-chelate metal complexes containing unsymmetrical bidentate ligands. Fay and Piper^{1,3,14} have separated cis-trans geometric isomers for several tris-chelate complexes of the type:-

$[M(\underline{t}fac)_3]^{3+}$ {M=Co, Cr, Rh ; tfac=1,1,1-trifluoro-2,4,-pentandione}. Geometrical isomerism in this case has been established by proton and fluorine - N.M.R. spectroscopy and X-ray powder photographs.

All these observations show that it is possible for geometric isomers of the $\Delta[Co\{(-)-pn\}_3]^{3+}$ ion to exist even though both the experimental preparations^{4,6} and crystal structure analysis⁸ failed to give any indication for the existence of the trans isomer.

11.

1:2 MacDermott's Preparations.

T.E. MacDermott¹⁵ has prepared bromide and dithionate derivatives of the $\Delta[\text{Co}\{(-)\text{-pn}\}_3]^{3+}$ ion and claims to have separated both cis and trans isomers of these compounds. The bromides were prepared from the chlorides, $\Delta[\text{Co}\{(-)\text{-pn}\}_3]\text{Cl}_3$ which had first been synthesized and separated into Λ and Δ isomers using the methods of Dwyer et. al.^{4,5}. MacDermott then treated a concentrated aqueous solution of the chromatographically pure Δ isomer with excess concentrated hydrochloric acid to precipitate the orange coloured $\Delta[\text{Co}\{(-)\text{-pn}\}_3]\text{Br}_3$ in a quantitative manner.

Two solid phases appeared on slow, careful crystallisation of the bromide from aqueous solution; large needles (28%) of anhydrous $\Delta[\text{Co}\{(-)\text{-pn}\}_3]\text{Br}_3$ were first formed followed by an amorphous glass (72%) of composition $\Delta[\text{Co}\{(-)\text{-pn}\}_3]\text{Br}_3 \cdot 2\text{H}_2\text{O}$. The crystalline phase corresponds to the sample used in the X-ray structure analysis⁸ while the amorphous phase, MacDermott concluded, contained only the trans isomer. The respective yields of the two isomers corresponded well with the ratio of 1:3 which is

predicted from the statistical distribution of the cis : trans isomers. The two compounds were distinguished by their crystal forms and differences in their infra-red spectra and X-ray powder patterns. The infra-red spectra showed only slight variations while the X-ray powder patterns were markedly different. The powder pattern for the cis isomer was sharp and clear showing distinct lines and is in good agreement with the pattern calculated¹⁶ from the single crystal data of Saito.⁸ A blurred image with some indication of two broad lines appeared in the pattern for the trans isomer. MacDermott converted both the cis and trans bromide derivatives to the corresponding dithionate compounds by mixing hot, concentrated solutions of the bromide and sodium dithionate. On cooling the mixture, identical crystals with composition, $\Delta[\text{Co}\{(-)\text{-pn}\}_3]_2[\text{S}_2\text{O}_6]_3 \cdot 3\text{H}_2\text{O}$ were obtained. These two compounds were distinguished only by their infra-red spectra, which showed an even greater similarity than do the bromide compounds, and their X-ray powder patterns. The X-ray powder patterns of both cis and trans dithionates showed many distinct lines.

13.

A single crystal X-ray structure analysis of the compound trans- Δ -[Co{(-)-pn}₃]₂[S₂O₆]₃·3H₂O was planned in an attempt to confirm unambiguously the formation and separation of the cis and trans isomers.

1:3 X-RAY STRUCTURAL INVESTIGATIONS

Crystals of the bromide and dithionate derivatives of $\Delta[\text{Co}\{(-)\text{-pn}\}_3]^{3+}$ were kindly provided by Dr. MacDermott. Single crystal X-ray photographs of both cis and trans dithionate compounds were taken using both Weissenburg and Precession cameras. The crystals, needle-like in appearance were first mounted on glass fibres in a direction along the needle axis. Photographs were taken of the hko,okl and ikl reciprocal levels. The photographs obtained were identical, both in the relative positions of spots and their intensities. The unit cell data obtained is recorded on Table I. The size of the unit-cell was found to be rather large (length of C axis = 48.18Å), in fact too large to permit a ready structure analysis. The photographs also showed heavy streaking between reflections in the [001] direction: The results obtained were rather disturbing since the object of this single-crystal structure analysis had been to obtain evidence for the existence of the trans isomer. It was apparent that the dithionate salt was quite unsuitable for this as it did not distinguish between the cis and trans isomers.

15.

Accordingly, a survey was undertaken to find a more suitable derivative for use in a structure analysis determination of the trans isomer.

A number of derivatives of both the cis and trans- Δ [Co{(-)-pn}₃]³⁺ cation with several different anions were prepared using samples of the respective bromides. The compounds prepared fell into two different categories. They were either similar to the bromide derivatives (i.e. the cis isomer forming a crystalline phase while the trans isomer formed an amorphous glassy phase) or the dithionate derivatives (i.e. both cis and trans isomers forming crystalline products).

Sulphate and phosphate salts of both cis and trans isomers behaved in a similar manner to the bromide salts. The X-ray powder pattern of the cis salt showed many distinct lines while that of the trans salt gave no lines at all. X-ray "d" spacings for the cis bromide and sulphate derivatives are shown on Table II.

Derivatives of both cis and trans- Δ -[Co{(-)-pn}₃]³⁺ with the following ions were similar to the dithionates:- tris(oxalato)metallates (metal=Al, Cr, Co), tris(malonato)chromate, cobaltinitrite, tetraphenylborate and thiosulphate.

TABLE 1.

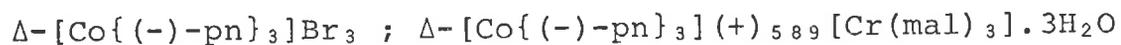
SINGLE-CRYSTAL DATA FOR Δ -[Co{(-)-pn}₃]³⁺ SALTS.

Anion	Br§	(+) ₅₈₉ Cr(mal) ₃ *	S ₂ O ₆ ²⁻	S ₂ O ₃ ²⁻
Space Group	R6 ₃	R32	P4,22	P4,22
Crystal Glass	Hexagonal		Tetragonal	
<u>a</u> (Å)	11.08	16.12	9.69	9.39
<u>c</u> (Å)	8.59	10.07	48.18	43.65
<u>U</u> (Å ³)	913	2265	4523	3849
<u>Dm</u>	1.91	1.52	1.63	1.59
<u>Z</u>	2	3	4	4
<u>Dc</u>	1.90	1.53	1.64	1.60
<u>M</u>	520.6	693.6	1115.1	917.7

§ From reference 8.

* From reference 17.

Formulae of the salts are:-



The number of water molecules in the last two salts have been deduced by best fit of Dm and Dc.

The tris(oxalato)metallates, cobaltinitrite and tetraphenylborate derivatives were isolated as either water-insoluble microcrystals or small needles and were unsuitable for single-crystal work. X-ray powder photographs have been obtained for these derivatives and the results, in the form of "d" spacings, are shown on Table II. The powder photographs were identical for both cis and trans isomers of each of these derivatives. The tris(malonato)chromate and thiosulphate derivatives formed small crystals suitable for use in a single-crystal structure analysis.

Preliminary photographs for both isomers of each of the derivatives were identical. As for the dithionate derivatives, the unit-cell sizes for the thiosulphate salts were too large to permit a ready structure analysis and the photographs once again showed heavy streaking between reflections.

An X-ray structure analysis of the tris(malonato)chromate derivative of trans[Co{(-)-pn}₃]³⁺ with the formula; (-) [Co{(-)-pn}₃] (+) 589 [Cr(malonate)₃].3H₂O has been determined by Butler and Snow.¹⁷ Unit-cell data for each of these derivatives is recorded on Table I. The X-ray patterns (single-crystal) obtained for both these

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derivatives gave identical results for both geometric isomers. Thus, none of these prepared derivatives are able to distinguish between the two isomers in terms of a full crystal structure analysis.

1:4 DISCUSSION OF RESULTS(a) Disorder in Salts Containing the Δ -[Co{(-)-pn}₃]³⁺ Ion.

The reason for this failure to distinguish between the cis and trans isomers and hence to obtain crystal structural evidence for the existence of the trans isomer became apparent when the results of the structure analysis of the tris(malonato)chromate derivative mentioned above were examined.¹⁷

The X-ray structure analysis showed the cobalt cation to reside on a crystal site of 32 (D₃) symmetry. The cis cation (symmetry 3(C₃) - see Figure I.) and the trans cation (approximate 3-fold symmetry and no overall symmetry - see Figure I.) become equivalent when statistically disordered in the crystal on these 32 symmetry sites. The very similar nature of the X-ray patterns for both isomers arises because of this disorder.

In the case of the dithionate and thiosulphate compounds, the space group (P4,22) does not require disorder by space group considerations as in the above case. Disorder is still possible however, if the larger volume of the disordered cation is permitted by crystal packing effects.

21.

In the case of the trans cation in the compounds which form an amorphous glass, (the bromide, sulphate and phosphate derivatives), it appears that the trans cation can interfere with the crystal packing giving rise to a structure which only grossly resembles that of the cis crystalline compounds. Evidence of this resemblance is provided by the powder photographs of the two geometric isomers of the bromide salts (see Table II). The pattern for the trans isomer reveals only diffuse indications of two broad lines which correspond in position to the two most intense lines in the pattern of the cis isomer. MacDermott suggests¹⁵ that the appearance of these lines may be due to a slight contamination of the trans isomer with some of the cis isomer.

(b) Re-Investigation of X-ray Crystal Structure of
cis- Δ -[Co{(-)-pn}₃]Br₃.⁸

In order to deduce whether or not the above mentioned interference takes place, the structure of cis Δ -[Co{(-)-pn}₃]Br₃ has been re-examined using the published X-ray single-crystal intensity data.⁸

22.

Computer programmes used in this structure refinement are those of the CRYST. system which has been described previously.¹⁸

A Fourier map based on the published coordinates does not show any evidence of disorder at all, no electron density being found at the position corresponding to that predicted for the methyl group of one pn ligand in the trans position. A cycle of full matrix least-squares refinement was undertaken with half methyl carbon atoms (occupancy factor 0.5) at each of the six possible sites (attached to each of the six carbon atoms of the three pn ligands). During this full matrix refinement the overall R-factor dropped from the originally reported value of 0.100⁸ to 0.077. The occupancy factor at the original (cis) methyl site increased from 0.5 to converge at 1.07 while that at the potentially disordered (trans) site converged at 0.06. This means that methyl groups are present only at cis sites of the pn ligand in the complex ion.

The refinement once again gives no indication of any disorder in the cis crystal. Furthermore, a methyl group substituted in the disordered (trans)

position makes three close contacts to N and C atoms of other nearby complex ions in the range 2.5 to 3.0 Å. Since Van der Waals' radii data¹⁹ suggest that the lower limit for these values is 3.2 to 3.4 Å it is physically impossible for the trans complex cation to exist in the lattice of the cis cation.

Neither the trans complex ion nor the disordered cis or trans complex ions are able to crystallize in the lattice of the cis complex ion.

(c) Conclusions

Unfortunately, neither the original compounds of MacDermott nor any of the derivatives which have been prepared from them are able to provide direct evidence (via a full X-ray crystal-structure analysis) for the existence of the trans isomer of Δ -[Co{(-)-pn}₃]³⁺. Some of the trans isomers of these derivatives have been isolated as non-crystalline, amorphous, glassy products unsuitable for single-crystal work. Those which do form as crystalline products are indistinguishable from their corresponding cis isomer due to disorder of the complex cations in the crystal lattice. A separation of the two isomers has been reported recently (see reference 73 of the

24.

review by Buckingham and Sargeson³⁰). The separation was achieved by the use of elaborate chromatographic methods.

It is concluded²⁰ that it is unlikely that an ordered trans - isomer structure will be found, the combination of a high pseudo-symmetry C_3 with no overall symmetry gives rise to the possibility of entropy gain by disorder of the cation alone or by irregular packing of the whole structure (resulting in the formation of the amorphous glass). This conclusion is reinforced by the calculations of the least strain energy of both cis and trans geometric isomers using the energy minimization technique set out in Part II. of this thesis. The results (see Section 2:5) show that there is very little difference in total strain energy between cis and trans Δ -[Co{(-)-pn}₃]³⁺ and thus little difference in their stabilities.

25.

1:5 EXPERIMENTAL PROCEDURES

The following salts were prepared using analytically pure cis $\Delta[\text{Co}\{(-)\text{-pn}\}_3]\text{Br}_3$ and trans $\Delta[\text{Co}\{(-)\text{-pn}\}_3]\text{Br}_3 \cdot 2\text{H}_2\text{O}$. The scale of the preparations was too small for analysis. The cis - salts were prepared in a similar manner to the trans salts.

Sulphate Salts.

The bromides were passed down an anion exchange resin (Deacidite FF) in the sulphate form and eluted with distilled water. The eluant was tested for bromide ion and the complex sulphate crystallised by evaporation over calcium chloride.

Cis salt; large hexagonal plates and some needle crystals.

Trans salt; glassy material, the powder pattern shows no distinct lines.

Phosphate Salts.

The bromides were converted into the phosphates with silver phosphate following the method of Chang et.al.²¹

Cis salt; large needles.

Trans salt; glassy material; the powder pattern shows no distinct lines.

Silver phosphate was prepared by the method of Baxter and Jones.^{21a}

Salts of the Complex Anions

$[M(\text{oxalate})_3]^{3+}$, M=Al, Cr, Co.

A solution of the bromide salt (0.5mg./0.5ml.) was layered on a solution of $K_3[M(\text{oxalate})_3]$ of equal concentration. Crystals grew at the solution interface (interfacial growth). Both cis and trans - isomers of all anions formed insoluble microcrystalline derivatives.

Tris(malonato) Chromate (III) Salts.

The same method as employed for the oxalato - anions was used. Both cis and trans - isomers gave long needle crystals. $K_3[\text{Cr}(\text{malonate})_3] \cdot 3\text{H}_2\text{O}$ was prepared by the method of Chang.²²

Cobaltinitrite, Tetraphenylborate and Thiosulphate Salts.

These salts were prepared by interfacial growth using the reagents $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$, NaBPh_4 and $\text{Na}_2\text{S}_2\text{O}_3$ respectively. The cis and trans - isomers of the first two salts gave microcrystals.

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Cis-thiosulphate salt; small needles.

Trans-thiosulphate salt; large tabular crystals.

The X-ray powder patterns were identical for each set of salts.

X-ray Powder Pattern and Single Crystal Data.

X-ray Powder Patterns were recorded using a Nonius general-purpose camera (radius = 28.65mm) with Co-K α radiation filtered through an iron foil. The films were uncalibrated.

Weissenburg and Precession cameras were used to obtain single-crystal data.

Mo-K α , Zr filter $\lambda_{\text{Mo-K}\alpha} = 0.7107\text{\AA}$ or

Cu-K α , Ni filter $\lambda_{\text{Cu-K}\alpha} = 1.542\text{\AA}$.

Computer programs of the CRYST. system described previously¹⁸ were run on the CDC 6400 computer at the University of Adelaide.

PART II.CONFORMATIONAL ANALYSIS OF COBALT(III) COMPLEXES OF
ETHYLENEDIAMINE AND PROPLYENEDIAMINE USING AN ENERGY
MINIMIZATION TECHNIQUE2.1 Introduction

The stereochemistry of inorganic coordination compounds has interested chemists greatly over recent years. In particular, the stereochemistry of chelate ring systems formed when a multidentate ligand coordinates with a metal atom has been the subject of a considerable amount of research. Metal complexes containing these ligands (such as ethylenediamine which forms a 5-membered metal-chelate ring) are able to adopt different conformations. These are different (non superimposable) spatial arrangements of the atoms constituting the ring. The conformers are energetically equivalent in the isolated state (when a single metal-ligand ring is considered) but in a complex containing more than one of these rings eg. $[\text{Co}(\text{en})_3]^{3+}$, energy differences arise since there are several arrangements possible for the complex ion corresponding to the different conformations which each ring may have.

A conformational analysis of this type of system considers the factors giving rise to the energy differences between possible conformers and aims to find out which of the conformers exist and the extent to which they do. It also takes into account the absolute configuration about the central metal ion. Much of the research done has been concerned with Co(III) complexes containing en and pn ligands and it is these complexes which are of particular interest in this thesis. Dwyer, Sargeson and co-workers^{4,5,6} have carried out quantitative preparations of these complexes and separated the various isomers. Corey and Bailar^{2,3} on the other hand, have made theoretical calculations on the Co-en and Co-pn rings present in these complexes. Both these methods have aided in the determination of the affect the different conformations have on the stabilities of the various isomers.

Originally it was Mathieu^{2,4} who pioneered work of this type when he used London dispersion forces in an approximate calculations of the relative energies for various possible isomers of $[\text{Co}(\text{pn})_2(\text{NO}_2)_2]^+$. Recent developments in the conformational analysis

of organic molecules has led to a more rigorous approach to the calculation of the energy differences between conformers. Techniques of minimization of the potential energy of conformations have been used with great efficiency in both organic and polymer molecules.^{2 5,2 6,2 7} One of these procedures has recently been applied successfully to several inorganic multidentate metal complexes. The procedure considers the energies due to a large number of interactions within the complex ion and results in an equilibrium energy and geometry being obtained by minimization of the strain energy of the complex.

This thesis presents the results of the application of Boyds' minimization procedure^{2 5} (with some modification by M.R. Snow) to the fundamental chelate ring systems considered by Corey and Bailar^{2 3} and to the $[\text{Co}(\text{en}/\text{pn})]^{3+}$ and $[\text{Co}\{\text{(+)}\text{pn}\}_3]^{3+}$ systems prepared by Dwyer et. al.^{4,5,6} Such a study allows a comparison of the usefulness of each of the techniques in calculating energy differences between conformers and thus the determination of the most stable conformer. A comparison between the experimental and calculated measures of stereospecificity on isomers of the same compound is thus enabled and such results are rare.

2:2 Conformations of Metal Chelate Rings

(a) Co-ethylenediamine chelate ring

X-ray structural evidence showing the staggered or puckered nature of the Co-en ring in the $[\text{Co}(\text{en})_3]^{3+}$ cation has been provided by Saito et.al. in their determination of the crystal structures of $(+)[2[\text{Co}(\text{en})_3]\text{Cl}_3 \cdot \text{NaCl} \cdot 6\text{H}_2\text{O}]^{31}$, $(+)[\text{Co}(\text{en})_3]\text{Br}_3 \cdot \frac{1}{2}\text{H}_2\text{O}^{32}$ and more recently $(+)[\text{Co}(\text{en})_3]\text{Cl}_3 \cdot \text{H}_2\text{O}^{33}$. The latter structure provides the most accurate detailed geometry of the complex ion. These results, together with I.R. and N.M.R. spectral results which have also been carried out help confirm the concept first put forward by Thielacker in 1937.³⁶ He used molecular models of the square planar $[\text{Pt}(\text{en})_2]^{+2}$ cation to show that for metal-chelate ring complexes, the rings themselves were likely to be twisted or puckered. The hydrogen atoms attached to the ring forming atoms are almost completely staggered (see Figure IV) and have a non-eclipsed axial or equatorial character (similar to the hydrogen atoms of the 5-membered organic ring compound cyclopentane). Hydrogen atoms attached to C atoms of the ring have the most pronounced axial or equatorial character.

The fact that the N-Co-N bond angle in the ring is near 90° is a further reason for the skewed nature of the ring since the remainder of the ring must skew to prevent distortion at the C and N ring atoms which have a tetrahedral environment.

The strain-free gauche arrangement of the ring corresponds to a minimum energy form and as such has two different conformations. These are non-superimposable, enantiomeric (mirror-image) forms which are energetically and geometrically equivalent. They have been designated δ or λ conformers⁷ and are shown in Figure IV (b) and (c) with the axial and equatorial hydrogen atoms being indicated.

In a metal complex containing more than one of these rings eg. $[\text{Co}(\text{en})_3]^{3+}$, there are several arrangements of the chelate rings possible for each absolute configuration (Λ or Δ) about the central metal ion.

The different arrangements arise because each of the Co-en rings may exist in either the δ or λ form.

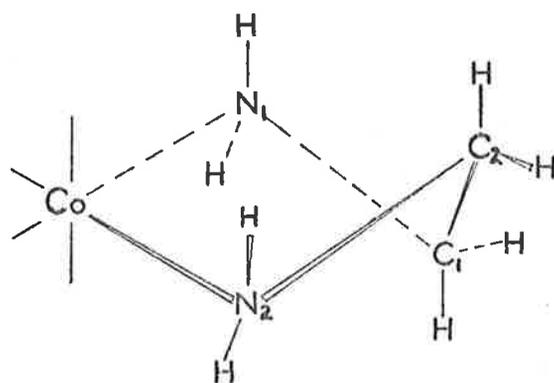
For $[\text{Co}(\text{en})_3]^{3+}$ there are four possible conformational isomers for each absolute configuration (see Table III).

Corey and Bailar^{2,3} have carried out theoretical calculations of the energy differences between the

33.

FIGURE IV.

(a) Co-ethylenediamine ring.

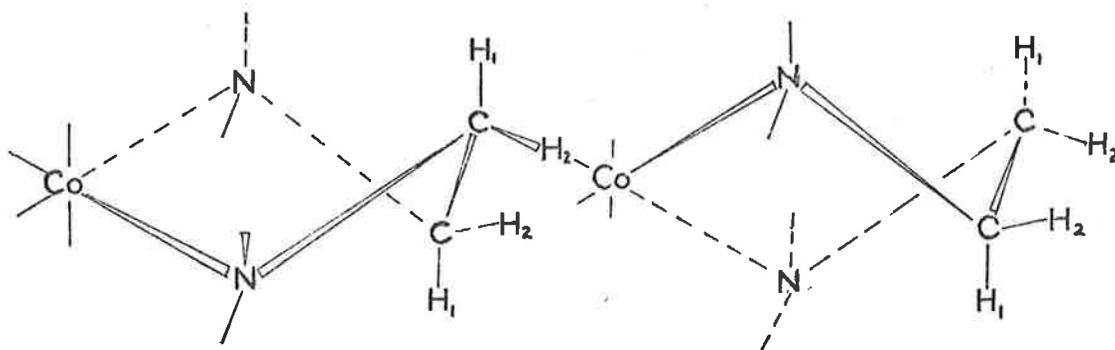


(b) δ conformation

(c) λ conformation

$H_1 = H$ axial

$H_2 = H$ equatorial



two extreme arrangements - the "lel" and "ob" isomers^{2 3} - of the Co-en ring in $\Lambda[\text{Co}(\text{en})_3]^{3+}$. They likened the coordinated en ring to cyclopentane and used a method similar to those employed to investigate conformations in organic compounds. The geometry of the Co-en ring was first calculated by vector analysis (using the normal values of bond distances and angles). This also showed the ring to be puckered in its strain free form with all hydrogen atoms staggered. The most significant nonbonded distances between rings were then calculated for the $\Lambda(\delta\delta\delta)$ and $\Lambda(\lambda\lambda\lambda)$ isomers and substituted into a potential function^{3 8} in order to obtain the energy difference between the two forms. An energy difference of 1.8K-cal./mole (0.6K-cal./mole for each ring) was obtained (see Table III). The "lel" isomer, in which the C-C bonds of the three rings are all parallel to the C_3 axis was found to be the most stable, for both Λ and Δ isomers of $[\text{Co}(\text{en})_3]^{3+}$.

TABLE III.Conformations of Co-en Rings in [Co(en)₃]³⁺

<u>ISOMER</u>	$\Delta[\text{Co}(\text{en})_3]^{3+}$	$\Delta[\text{Co}(\text{en})_3]^{3+}$	
		<u>Ring Conformations</u>	<u>$\Delta G_{\text{calc.}}$</u> *
stability decreases	$\delta\delta\delta$	$\lambda\lambda\lambda$ ("lel")	0
	$\delta\delta\lambda$	$\lambda\lambda\delta$	0.6
- minimum energy	$\delta\lambda\lambda$	$\lambda\delta\delta$	1.2
increases ↓	$\lambda\lambda\lambda$	$\delta\delta\delta$ ("ob")	1.8

* $\Delta G_{\text{calc.}}$ (Kcal/mole) - Free energy differences calculated.^{2 3}

(b) Co-propylenediamine chelate ring.

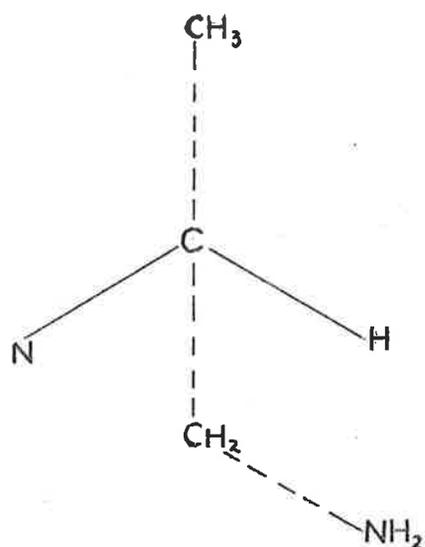
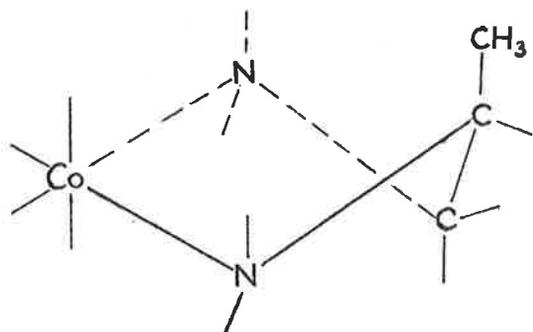
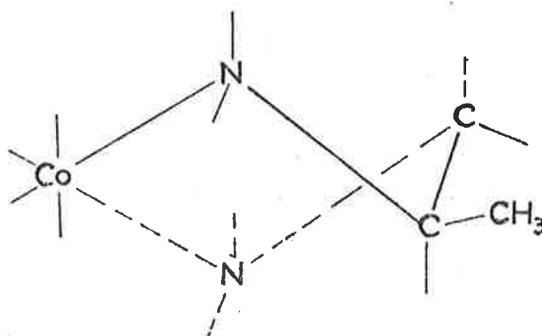
Propylenediamine also coordinates forming a 5-membered metal-ligand ring. The ring has a puckered nature similar to that of the Co-en ring with the methyl group of the pn ligand occupying either an axial or equatorial position (see Figure V). The pn molecule is optically active and the absolute configuration of the (-)pn isomer is also shown in Figure V. The absolute configuration of (-)pn, the skewed nature of the Co-(-)pn ring and the fact that the attached methyl group always occupies an equatorial position has been shown from the X-ray structure determinations of compounds containing $\Delta[\text{Co}\{(-)\text{-pn}\}_3]^{3+ 8}$ and cis(+) $[\text{Co}\{(-)\text{-pn}\}_2(\text{No}_2)_2]^+ 12$.

Corey and Bailar^{2 3} have also carried out theoretical calculations of the energy differences between the two conformations (λ or δ) of the Co-(-)pn ring. They found the λ conformation (with the methyl group in an equatorial position - see Figure V) to be more stable than the δ conformer (methyl group in axial position) by an energy value in excess of 2Kcal/mole.

For $\Lambda[\text{Co}\{(-)\text{-pn}\}_3]^{3+}$ the λ conformation of the $\text{Co-}(-)\text{pn}$ ring will be favoured since the methyl group is equatorial (by 2Kcal/mole per ring) while the δ conformation will be favoured (by 0.6Kcal/mole per ring) since the isomer has the Λ absolute configuration.

For $\Delta[\text{Co}\{(-)\text{-pn}\}_3]^{3+}$ the λ conformation is favoured by both effects. Thus for this complex ion, the $(-)\text{pn}$ will be coordinated exclusively in the λ conformation, for both Λ and Δ absolute configurations. The two possible isomers (Λ or Δ) of this dissymmetric complex are not obtained in equal amounts since they are not of equal stability. This preference for one particular isomer over another in a metal complex is known as stereospecificity and is observed on many occasions when both the metal complex and the coordinated ligand are of dissymmetric nature.

FIGURE V.

(a) Absolute configuration of $\Lambda(-)$ pn(b) Co-(-)pn
 δ conformation
CH₃ axial(c) Co-(-)pn
 λ conformation
CH₃ equatorial.

2.3 Isomers of the $[\text{Co}(\text{en}/\text{pn})_3]^{3+}$ and $[\text{Co}\{(\pm)\text{-pn}\}_3]^{3+}$ Ions.

Dwyer, Sargeson and co-workers^{4,5,6} have prepared Co(III) complexes containing en and pn ligands in order to study the stereospecificity influences involved in such syntheses. Optical isomers of octahedral tris-Co(III) complexes containing both en and pn as well as isomers of the $[\text{Co}(\text{pn})_3]^{3+}$ ion containing either (+)pn, (-)pn or a mixture of both have been isolated. The experimental methods used consisted of identifying the relative proportion of each of the isomers present under equilibrium conditions. The equilibrium between isomers was established rapidly in solution using a charcoal catalyst. Chromatographic methods were used extensively to separate the isomers present in the equilibrium mixtures and the products analysed to determine the proportion of each isomer present.

The calculations of Corey and Bailar^{2,3} gave a theoretical basis to explain the difference in relative stabilities of the isomers observed in the above preparations. Their calculations rationalise these stabilities in terms of the possible conformations which may be adopted by the en or pn ring.

The two sets of results for isomers of the $[\text{Co}\{\text{en}/(-)\text{-pn}\}_3]^{3+}$ system of complexes are set out on Table IV. The observed isomer proportions for various racemic pairs of ions of the $[\text{Co}\{(\underline{+})\text{-pn}\}_3]^{3+}$ system together with the observed free energy differences between these pairs are also shown (see Table V).

Comparison between the results of the experimental preparations (energy differences between isomers given by ΔG_{obs} on Table IV) and the theoretical calculations (energy differences given by ΔG_{calc} on Table IV) gives a comparison between the observed and calculated stereospecificity for the same set of isomers.

Such a comparison will be made in conjunction with a third set of results, giving computed energy differences between the same systems of isomers which have been considered above. The latter calculations form a major part of the work presented herein and were accumulated using an alternative, more flexible method of calculating the energies of isomers by an energy minimization procedure. Details of the techniques used in this energy minimization process are now presented.

41.

TABLE IV.

ISOMERS OF THE [Co{en/(-)pn}₃]³⁺ SYSTEM.

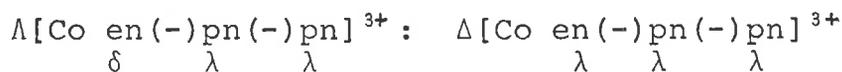
<u>Complex</u>	<u>Ring Conformations</u>	<u>Ratio Λ:Δ</u>	<u>ΔGobs.</u>	<u>ΔGcalc.</u>	<u>ΔU</u>
Co en en en	Λδδδ:Δλλλ	1:1	0	0	0
Co en en(-)pn	Λδδλ:Δλλλ	1:2.1	0.45	0.6	0.40
Co en(-)pn(-)pn	Λδλλ:Δλλλ	1:7.5	1.2	1.2	0.76
Co(-)pn(-)pn(-)pn	Λλλλ:Δλλλ	1:14.6	1.6	1.8	0.66

ΔGobs. (Kcal/mole) Observed free energy difference from ratio of isomers formed in preparations.⁵

ΔGcalc. (Kcal/mole) Calculated free energy difference for isomer pairs from original conformational analysis.

ΔU (Kcal/mole) Computed difference in TOTAL STRAIN ENERGY for isomer pair from minimization procedure.

N.B. The preparations⁵ refer to isomer pairs of the type:-



whereas the minimization computations were carried out with all isomers in the Λ form. The corresponding isomer pair is thus:-



The relative energies measured in both cases remains the same since Δ[Co en(-)pn(-)pn]³⁺ and Λ[Co en(+)pn(+)pn]³⁺ are energetically equivalent enantiomers.

TABLE V.

(a) STRAIN ENERGY VALUES FOR ISOMERS OF THE
 $\Lambda[\text{Co}\{(\pm)\text{pn}\}_3]^{3+}$ SYSTEM.

<u>ISOMER</u>	<u>TOTAL STRAIN ENERGY (Kcal/mole)</u>	<u>$\Delta U \S$ (Kcal/mole)</u>
Co(+) ₃ pn(+) ₃	11.94	0.42
Co(+) ₂ pn(+) ₂ pn(-) ₁	12.36	0.36
Co(+) ₁ pn(+) ₁ pn(-) ₂	12.72	-0.12
Co(-) ₃ pn(-) ₃	12.60	

(b) ISOMER PROPORTIONS OF RACEMIC PAIRS OF
 $[\text{Co}\{(\pm)\text{pn}\}_3]^{3+}$

<u>RACEMIC PAIR</u>	<u>% found *</u>	<u>K *</u>	<u>$\Delta G_{\text{obs.}}^*$ (Kcal/mole)</u>	<u>$\Delta U \S$ (Kcal/mole)</u>
$\Lambda_{+++} : \Delta_{---}$	40.5	$\frac{\Lambda_{+++}}{\Lambda_{++-}} = 1$	0	0.42
$\Lambda_{++-} : \Delta_{--+}$	40.3	$\frac{\Lambda_{++-}}{\Lambda_{+--}} = 2.4$	-0.52	0.36
$\Lambda_{+--} : \Delta_{-++}$	16.5	$\frac{\Lambda_{+--}}{\Lambda_{---}} = 6.1$	-1.1	-0.12

* From reference 6. : $\Delta G_{\text{obs.}}$ = Observed free energy difference from proportions of each isomer pair.

\S ΔU = Computed differences in Total Strain Energy for isomer pairs from Minimization procedure.

N.B.

See footnote at bottom of Table IV.

2:4 ENERGY MINIMIZATION PROCEDURE

(a) Force Field and Potential Functions.

A modified version of Boyds' energy minimization procedure was used. Initially, he used the procedure in order to determine the minimum potential energy conformations of some organic molecules but recently the method has been adapted and used with some considerable success in the calculation of energies of conformational isomers of some inorganic metal-chelate complexes.^{28,29} An adequate detailed description of this procedure and its application to the quantitative conformational analysis of metal complexes has already been given.^{28,29,30}

Briefly, the procedure uses a general force field to calculate the minimum strain energy of a given compound in terms of a number of different types of atomic interactions. Interactions between atoms give rise to the following energy terms:-

- (1) torsional energy (E_{ϕ}) - twisting about bonds in the ligand skeleton.
- (2) bond length distortion energy (E_r)
- (3) bond angle distortion energy (E_{θ})
- (4) non bonded interaction energy (E_{nb}) - between atoms

in one metal-ligand ring or between different rings.

An energy value for each of these four terms is obtained from a consideration of the contribution that each atomic interaction makes to the energy of the relevant term. The total strain energy is then obtained from the summation of the overall energy values obtained for each of the four interaction types.

$$\text{i.e. } U = \Sigma (E\phi + E_r + E\theta + E_{nb})$$

The contribution of all relevant atomic interactions to the energy terms is calculated by a series of potential functions representative of each type of interaction. Potential functions and their force constants used to describe the calculations described herein are detailed in the reports of the previous calculations of this type.^{28,29,30}

Table VI. shows the force constants for the nonbonded interactions.

(b) Coordinates of Ring Atoms - Symmetry Matrices

To calculate the energy of a particular conformer, a set of trial coordinates for all atoms were obtained and orthogonalised. The Co atom of the octahedral complex was placed at the origin (0,0,0) with the

TABLE VI.POTENTIAL FUNCTION CONSTANTS - NONBONDED INTERACTIONPARAMETERS #

<u>Atoms (i,j)</u>	<u>d(ij) (A)</u>	<u>a(ij)</u>	<u>b(ij)</u>	<u>c(ij)</u>	
H-H	d(min)	2.97	45.8	4.08	0.34
	d(incr)	3.27	78.3	4.08	0.34
	d(decr)	2.67	27.9	4.08	0.34
C-H	d(min)	3.15	218.0	4.20	0.84
	d(incr)	3.45	405.4	4.08	0.84
	d(decr)	2.85	124.2	4.08	0.84
N-H	d(min)	3.03	195.0	4.32	0.69
	d(incr)	3.33	373.3	4.32	0.69
	d(decr)	2.73	112.2	4.32	0.69
C-C	d(min)	3.50	1640	4.32	2.07
C-N	d(min)	3.37	1472	4.44	1.695
N-N	d(min)	3.27	1295	4.55	1.39

From reference 28,29. A Buckingham Function $E(nb) = A(ij) \exp(-b(ij)d(ij)) - c(ij)/d(ij)^6$ was used. $a(ij)$, $b(ij)$, $c(ij)$ = parameters of potential function.

$d(ij)$ = distance between atoms i and j
 $d(\text{min})$ = minimum value of this function.
 $d(\text{incr})$, $d(\text{decr})$ - minimum value increased or decreased by 0.3Å for H-H, C-H, N-H interactions.

Co-N bond directions being along the directions of the x, y and z coordinate axes. The trial coordinates were those reported in the crystal structure analysis^{8,33} (giving coordinates for one Co-en or Co-pn ring) or from molecular models constructed using the normal values for bond distances and angles. Since coordinates were provided for only one Co-ligand ring, the coordinates of the second and third rings of the tris-complex were generated from the original coordinates using a symmetry matrix. The coordinates of any point P(x,y,z) in the original ring were rotated about the C₃ axis (see Figure I) using a matrix of transformation. The use of two of these matrices (transformation operators) transformed the coordinates of P(x,y,z) in the first ring to P'(-y,-z,x) and P''(+z,-x,-y), P' and P'' being the coordinates of the corresponding atom in the second and third rings respectively. (see Figure VI. (a)).

To change the ring conformation from δ to λ (or vice-versa) the coordinates for the C atoms of the original Co-ligand ring and their attached H atoms were transformed from:-

47.



For the other two rings, this coordinate transformation to change the ring from a δ to λ conformation were carried out in a similar manner.

(c) Minimization Method

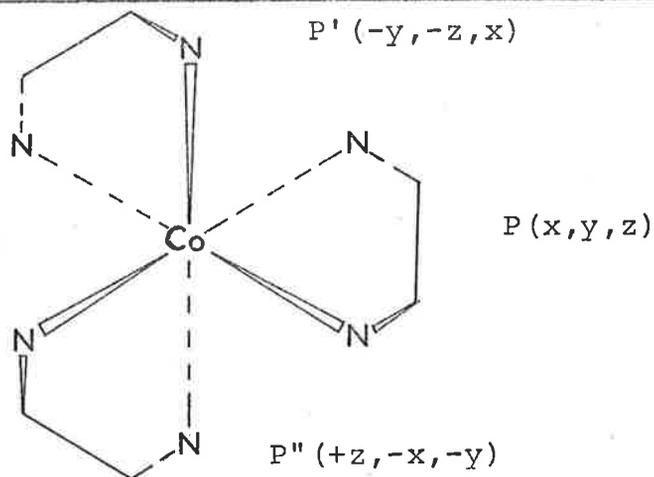
Using a computer, the atomic coordinates for all atoms in the complex ion were allowed to vary simultaneously (except for the central Co atom, the coordinates of which remained fixed and for two of the N atoms of one ring. The coordinates of these two atoms were allowed to vary in one direction and two directions respectively). The calculated strain energy of the complex was minimized by this continual refinement of atomic coordinates. For each molecule considered, a minimum value of strain energy and a set of atomic coordinates corresponding to this energy minimum were obtained.

A quantitative conformational analysis of all the isomers of both the $[\text{Co}\{\text{en}/(-)\text{pn}\}_3]^{3+}$ and $[\text{Co}\{(+)\text{pn}\}_3]^{3+}$ systems has been carried out. Total strain energy (T.S.E.) values have been obtained for all isomers of the above systems which have been prepared by Dwyer et.al.^{4,5,6} and also those discussed in the original conformational analysis.^{2,3}

48.

FIGURE VI.

(a) [Co(en)₃]³⁺ showing Matrices of Transformation



The transformations may be represented by:-

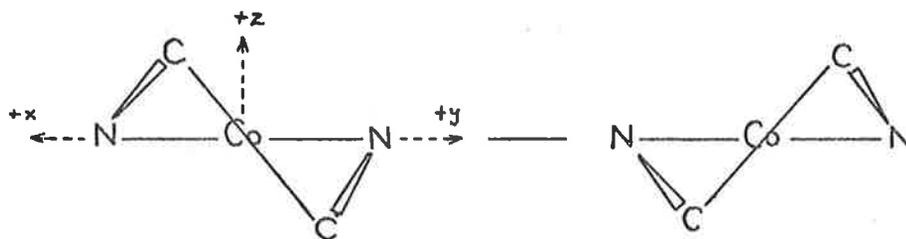
$$\begin{bmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -y \\ -z \\ x \end{bmatrix}$$

Matrix 1 P P'

$$\begin{bmatrix} 0 & 0 & 1 \\ -1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} z \\ -x \\ -y \end{bmatrix}$$

Matrix 2 P P''

(b) Transformation to change ring conformation from δ to λ



$C(x, y, z) \longrightarrow C'(x, y, -z)$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ -z \end{bmatrix}$$

Matrix C C'

49.

All isomers considered in these computations were those with a Λ absolute configuration of ligands about the central metal ion.

2:5 RESULTS AND DISCUSSIONS(a) Conformations of the $\Lambda[\text{Co}(\text{en})_3]^{3+}$ ion.

Using this minimization procedure the energy difference between the two isomers of $\Lambda[\text{Co}(\text{en})_3]^{3+}$ in the extreme "lel" and "ob" conformations (i.e. $\Lambda(\delta\delta\delta)$ and $\Lambda(\lambda\lambda\lambda)$) is calculated to be 0.58Kcal/mole (see Table VII). As can be seen from the table, a large portion of this energy difference arises from differences in torsional interaction energies between the two isomers. This value is substantially less than the value of 1.8 Kcal/mole (0.6 Kcal/mole for each Co-en ring) estimated from the original calculations^{2,3} and considered to be due mainly to differences in the nonbonded interactions between Co-en rings. Their method of calculation consisted of calculating energies due to the most significant nonbonded interactions between the ligand rings in the complex for the two conformations (δ or λ). This method is a rather rigid means of calculation since a rather rigid structure of the complex ion was assumed. The structure was not varied and did not allow for the effect of the nonbonded interactions (both within a single Co-en ring and between two such rings) upon the actual ring conformation and



such effects are rather important.

Gollogly and Hawkins^{3,9,40,41} have also carried out a series of conformational analysis calculations on these two isomers under various conditions and obtained a value of the order of 1 Kcal/mole⁴¹ for the energy difference. They used nonbonded interaction, torsional interaction and bond angle deformation energies to map the strain energy of one Co-en ring as a function of a number of selected and independent geometric variables (among them being the torsion or dihedral angle between the plane containing the atoms N1,C1,C2 and that containing the atoms N2,C2,C1 in the Co-en ring - see Figure IVa.)

N.M.R. spectral results³⁷ for the two isomers of $[\text{Ni}(\text{en})_3]^{3+}$ in the two extreme conformations report the free energy barrier is as small as 0.9Kcal/mole.

The smaller energy differences between the two isomers reported here and by Gollogly and Hawkins means that the energy barrier between successive conformers will be much smaller than the value of 0.6Kcal/mole predicted by Corey and Bailar's work. Indeed the energy differences are so small that they have been found to be critically dependant upon the

TABLE VII.

TOTAL STRAIN ENERGIES (Kcal/mole) FOR ISOMERS OF
 $\Lambda[\text{Co}(\text{en})_3]^{3+}$

<u>Ring Conformations</u>			
<u>Interaction Type</u>	<u>$\delta\delta\delta$</u>	<u>$\lambda\lambda\lambda$</u>	<u>ΔU</u>
<u>Total Interactions</u>	269	264	5
<u>Bond Length</u>	1.77	1.76	0.01
<u>Nonbonded</u>	4.46	4.25	0.21
<u>Bond Angle</u>	1.23	1.52	-0.29
<u>Torsion</u>	3.52	2.87	0.65
<u>Total Strain Energy</u>	<u>10.98</u>	<u>10.40</u>	<u>0.58</u>

TABLE VIII.

STRAIN ENERGIES FOR $\Lambda[\text{Co}(\text{en})_3]^{3+}$ ISOMERS (Kcal/mole)
- DIFFERENT FORCE CONSTANTS FOR N-H, C-H, H-H

<u>NONBONDED INTERACTIONS</u>			
<u>Potential Function Type #</u>	<u>$\Lambda(\lambda\lambda\lambda)$</u>	<u>$\Lambda(\delta\delta\delta)$</u>	<u>ΔU</u>
d(min). decreased by 0.3A	-0.01	0.29	-0.30
d(min). original	10.98	10.40	0.58
d(min). increased by 0.3A	31.74	30.63	1.11

#. Values of d(min), d(incr), d(decr), given on Table VI. Energy values refer to isomers with original, increased and decreased values of d(min): Contact distances for nonbonded interactions between N-H, C-H, H-H atoms.

potential functions used to calculate the nonbonded interactions within and between rings. Gollogly and Hawkins⁴⁰ have calculated energies of the two conformers of the bis-(en)Co(III) system ($\Lambda(\delta\delta)$ and $\Lambda(\lambda\lambda)$) using three different potential functions. Potential functions due to Mason and Kreevoy,³⁸ Bartell⁴² and Hill⁴³ were considered and it was found that by varying the type of function used, the nonbonded interactions would alter the strain energies of the conformers such that their relative stabilities would change.

A similar result was observed using the minimization procedure described herein. Instead of altering the potential function for nonbonded interactions however, the minimum distances for nonbonded interactions between N-H, C-H and H-H atoms were decreased or increased by 0.3Å in turn (see Table VI). This had the effect of altering the force constants for the one potential function considered. A change in the total strain energy for each particular conformer was observed. This also led to an alteration in the relative stabilities of the two isomers, with the $\Lambda(\lambda\lambda)$ isomer becoming the more stable

when the minimum distance for the three interactions indicated was decreased by 0.3\AA (see Table VIII).

Because of this small difference in energies between the two extreme forms, there is a definite likelihood that conformers other than $\Lambda(\delta\delta\delta)$ (or its enantiomer $\Delta(\lambda\lambda\lambda)$) could be isolated but until recently, all reports of X-ray crystal structures of complexes containing the $[\text{Co}(\text{en})_3]^{3+}$ ion agreed with the preference for the $\Lambda(\delta\delta\delta)$ conformation.

Ibers et.al.^{4,4,5,6} have reported results of crystal structures of the $[\text{Cr}(\text{en})_3]^{3+}$ ion with several different anions in which all possible conformations of the M-en ring were observed. These results, together with ring conformations obtained from other crystal structure analysis which also show variations in the conformations are shown on Table IX.

It is likely that the different environments of the complex ion in the crystal lattice (resulting from the presence of different anions) has led to the stabilisation of new, different conformations of the complex ion. Ibers et.al.^{4,6} suggest that hydrogen bonding (between the hydrogen atoms attached

to N ring atoms and the anions or the water molecules of crystallisation present in the lattice) plays a major part in the stabilisation of these new conformers. The energy released on formation of these hydrogen bonds enables a conformer other than $\Lambda(\delta\delta\delta)$ to become the most stable one.

(b) $[\text{Co}(\text{en})_2(-)\text{pn}]^{3+}$ with Methyl group axial or equatorial

The minimization procedure predicts the conformer of $\Lambda[\text{Co}(\text{en})_2(-)\text{pn}]^{3+}$ which has the pn ligand with the methyl group in an equatorial position to be more stable by 1.8Kcal/mole than the same conformer with the methyl group in the axial position (see Table X).

Corey and Bailar^{2 3} have predicted an energy difference of approx 2Kcal/mole and suggest that severe nonbonded interactions (between the axial methyl group and other axial substituents) to be responsible for this. The computed results are in agreeance with this fact but indicate that torsional interactions and bond-angle deformation interactions are also important in stabilising the conformer with the equatorial methyl group.

TABLE IX.VARIOUS CONFORMATIONS OF $[M(en)_3]^{3+}$ ION

<u>Compound</u>	<u>Absolute Configuration about Metal and Ring conformations.</u>	<u>Reference</u>
$[Ni(en)_3](NO_3)_2$	$\Lambda(\delta\delta\delta)$	47
$[Co(en)_3]Cl_3 \cdot 3H_2O$	$\Lambda(\delta\delta\delta)$	48
(+) $[Co(en)_3]Cl_3 \cdot H_2O$	$\Lambda(\delta\delta\delta)$	33
$\Lambda[Co(en)_3]Br_3 \cdot H_2O$	$\Lambda(\delta\delta\delta)$	32
$\Lambda[Co(en)_3]Cl_3 \cdot NaCl \cdot 6H_2O$	$\Lambda(\delta\delta\delta)$	31
$[Cr(en)_3][Ni(CN)_5]1\frac{1}{2}H_2O$	$\Lambda(\delta\delta\lambda)$ $(\delta\lambda\lambda)$	44
$[Cr(en)_3][Co(CN)_6] \cdot 6H_2O$	$\Lambda(\lambda\lambda\lambda)$	45
$[Cu(en)_3]SO_4$	$\Lambda(\delta\delta\delta)$	49
$[Cr(en)_2ox][Cr(OX)_2en]$	$\Lambda(\lambda\lambda)$ cation $\Lambda(\delta), \Lambda(\lambda)$ anion	50
$Na(+)_546[Co(mal)_2en]$	$\Delta(\delta)$	17.

With this relatively large difference in energy it is not surprising that the conformer containing the equatorial methyl group is the one which has been observed in reported crystal structure analyses (e.g. $[\text{Co}\{(-)\text{-pn}\}_3]\text{Br}_3$ ⁸) and will be the one which predominates in solution.

(c) The $\Lambda[\text{Co}\{\text{en/pn}\}_3]^{3+}$ system.

Table X. shows the minimum strain energy values for the isomer pairs of the $[\text{Co}\{\text{en/pn}\}_3]^{3+}$ system which have been prepared and characterised by Dwyer et.al.⁵ The main contribution to the energy differences between these pairs is once again seen to be the torsional interactions with the nonbonded and bond-angle deformation interactions also being significant. The most important (highest energy) nonbonded interactions are H-H type interactions between hydrogen atoms attached to C ring atoms and those attached to the N ring atoms of the same or adjacent rings. H-H and C-H nonbonded interactions of H atoms attached to C ring atoms are also important. Table IV. compares the energy differences between the isomer-pairs calculated by

this minimization procedure (ΔU) with the ΔG_{obs} . and ΔG_{calc} . values introduced earlier.

The computed energy differences (ΔU) give the same relative stability for the isomer pairs as that observed in the experimental preparations (ΔG_{obs}).

However for isomers of the type $[\text{Co}(\text{en})\{(-)\text{pn}\}_2]^{3+}$ and $[\text{Co}\{(-)\text{-pn}\}_3]^{3+}$ the computed energy differences are much smaller than those observed. A factor responsible for this disagreement is that the ΔU values refer to a difference in minimum strain energy of the isomers in an isolated state (an enthalpy effect). The ΔG_{obs} . values however, take into account both enthalpy and entropy contributions to the energy differences between the isomers in solution. The comparison thus has a limited value. The minimization procedure predicts that there is not a large energy barrier separating the isomers of each particular pair from each other. This is in agreement with the ΔG_{obs} . values obtained on isolating the isomers from solution.

Values of ΔG_{calc} . and ΔG_{obs} . correlate remarkably well but in the light of the conclusions previously made, that the ΔG_{calc} . values do not

give a complete estimation of the energies of isomers of the $[\text{Co}\{\text{en}\}_3]^{3+}$ system, this agreement now seems rather fortuitous. The $\Delta G_{\text{calc.}}$ values, because of the use of the rather rigid potential function;³⁸ tend to overestimate the energy differences between isomers and also take no account of entropy effects or differences in solvation energies which can occur in solution.

(d) Isomers of the $[\text{Co}\{\text{(+)-pn}\}_3]^{3+}$ system.

Table $\bar{\text{V}}$. shows total strain energy values of isomers of this system and compares the free energy differences computed (ΔU) with those observed ($\Delta G_{\text{obs.}}$) in their preparations.⁶ Once again, torsional interactions are responsible for a major part of this energy difference. The decrease in energy for the $\Lambda[\text{Co}\{\text{(-)-pn}\}_3]^{3+}$ ion relative to the energies of the other three isomers is due to a significant decrease in intra and inter-ring non-bonded interactions of the type mentioned above (see p57).

The $\Delta G_{\text{obs.}}$ and ΔU . values both show a decrease in magnitude as the value of K , the equilibrium constant for each particular isomer pair, increases.

TABLE X.

TOTAL STRAIN ENERGY VALUES (Kcal/mole) FOR ISOMERS

OF Λ -[Co{en/pn}₃]³⁺ SYSTEM

<u>Isomer</u>	<u>Bond Stretch</u>	<u>Non- bonded</u>	<u>Bond Angle</u>	<u>Tors- ional</u>	<u>T.S.E.</u>
Λ [Co en en(-)pn] ³⁺ ($\delta\delta\lambda$) Me equatorial	1.86	4.88	1.50	3.12	11.36
Λ [Co en en(-)pn] ³⁺ ($\delta\delta\lambda$) Me axial	1.91	5.54	1.98	3.78	13.21
<u>ΔU</u>	<u>0.05</u>	<u>0.66</u>	<u>0.48</u>	<u>0.66</u>	<u>1.85</u>
Λ [Co en en(-)pn] ³⁺ ($\delta\delta\lambda$)	1.86	4.88	1.50	3.12	11.36
Λ [Co en en(+)pn] ³⁺ ($\delta\delta\delta$)	1.83	4.65	1.64	2.84	10.96
<u>ΔU</u>	<u>0.03</u>	<u>0.23</u>	<u>-0.14</u>	<u>0.28</u>	<u>0.40</u>
Λ [Co en(-)pn(-)pn] ($\delta\lambda\lambda$)	1.97	5.29	1.56	3.33	12.15
Λ [Co en(+)pn(+)pn] ($\delta\delta\delta$)	1.84	4.97	1.77	2.81	11.39
<u>ΔU</u>	<u>0.13</u>	<u>0.32</u>	<u>-0.21</u>	<u>0.52</u>	<u>0.76</u>
Λ [Co(-)pn(-)pn(-)pn] ³⁺ ($\lambda\lambda\lambda$)	2.02	5.59	1.61	3.38	12.60
Λ [Co(+)pn(+)pn(+)pn] ³⁺ ($\delta\delta\delta$)	1.98	5.31	1.88	2.77	11.94
<u>ΔU</u>	<u>0.04</u>	<u>0.28</u>	<u>-0.27</u>	<u>0.61</u>	<u>0.66</u>
<u>cis</u> - Λ [Co{(+)-pn} ₃] ³⁺ ($\delta\delta\delta$)	1.98	5.31	1.88	2.77	11.94
<u>trans</u> - Λ [Co{(+)-pn} ₃] ³⁺ ($\delta\delta\delta$)	1.99	5.36	1.89	2.76	12.00
<u>ΔU</u>	<u>0.01</u>	<u>0.05</u>	<u>-0.01</u>	<u>0.01</u>	<u>0.06</u>

It is worth noting that the ΔG_{obs} . values refer to preparative conditions in which (+)pn and (-)pn were present in a 1:1 ratio. With a different ratio of ligand molecules present (e.g. (+)pn: (-)pn = 2:1) different % yields of each particular diastereo isomer will be obtained. This results in a corresponding change in the equilibrium constant, K and ΔG_{obs} . values for each isomer pair. The computed energy values (ΔU) do not take into account any statistical preferences for one isomer over another.

(e) cis and trans Λ -[Co{(+)pn}₃]³⁺

It was considered relevant to calculate strain energy values for both cis and trans isomers of this ion. Values of the four energy types, leading to the total strain energy value for each geometrical isomer are shown on Table X. The calculations confirm the very small energy difference between the two geometrical isomers. With this extremely small barrier it is not surprising that the experimental preparations of Dwyer and co-workers,^{4,5,6} while distinguishing between other isomer pairs with larger energy differences separating them due to different ring conformations, failed to give any

62.

indication of the trans isomer.

2:6 CONCLUSIONS

A meaningful comparison between the computed (using minimization procedure) and observed (using experimental preparations) conformational analyses for the isomers considered is rather hard to make. With the basic differences in the two techniques used, a quantitative agreement can hardly be expected. Even so, the two methods are in good qualitative agreement as far as the relative order of stabilities of isomers is concerned.

The minimization technique calculates the minimum energy of the isomer cations in an isolated state. In this respect however, the procedure which has been used is more comprehensive than any other available since it encompasses almost all inter-atomic interactions (bonded or otherwise) which occur in a complex ion or molecule. The effects of all these interactions on the positions of the atoms is taken into account since the atomic positions are allowed to vary until the geometry corresponding to the least strain energy is found.

The preparative experimental methods however, involve separating the complex cations from solution.

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In solution, the ion is far from being in an isolated state and other factors must be taken into account when determining which conformations of the ligand rings in a particular isomer will be most stable.

Solvation energies, hydrogen bonding between the cations and the anions or solvent molecules present and electrostatic interaction between ions in solution will all have an effect on the conformations which a ligand ring may adopt and none of these have been considered by the minimization technique. In addition to this, the strain energy values computed take no account of any entropy contributions whereas the ΔG_{obs} . values obtained from the preparations include both enthalpy and entropy contributions.

The disagreement between the calculated and observed energy values will thus give some measure of the overall contribution which these other solution effects will make to the energies of different isomers. An estimate of the contribution which these other effects (e.g. solvation energies, hydrogen bonding, entropy etc.) make individually

may possibly be obtained from a consideration of the relative yields of the various isomers formed under different preparative conditions. Some preliminary investigations have been made into this but no significant results have as yet been obtained.

Application of the energy minimization technique to inorganic complex systems has been carried out in conjunction with several crystal structure analyses.^{2,8,29,51} Results reported so far indicate excellent reproduction of molecular geometry and conformations observed in crystal lattices by the energy minimization calculations. The procedure reproduces well any ring distortions which occur in the crystal lattice. A good comparison can thus be made between the molecular geometry and conformations predicted as the most stable by this method with the actual geometry and conformations which are observed in the solid state.

An estimation of crystal packing forces which may effectively stabilise a higher energy conformation can be made as well as an evaluation of specific crystal forces (for example, hydrogen bonding between

complex cations and either the anions or water molecules of crystallisation present, as considered by Ibers and co-workers^{4,4,4,5,4,6}).

The future value of the energy minimization calculations may, perhaps, lie in this area since the technique also provides an accurate theoretical molecular geometry to aid in the determination of crystal structures.

REFERENCES

1. P. Pfeiffer and I. Grassman, Liebigs. Ann. Chem., 1905, 346, 45.
2. L. Tschugaeff and W. Sokoloff, Berichte, 1909, 42, 55.
3. A.P. Smirnoff, Helv. Chim. Acta, 1920, 3, 177, 194.
4. F.P. Dwyer, F.L. Garvin and A. Shulman, J. Amer. Chem. Soc., 1959, 81, 290.
5. F.P. Dwyer, T.E. MacDermott and A.M. Sargeson, J. Amer. Chem. Soc., 1963, 85, 2913.
6. F.P. Dwyer, A.M. Sargeson and L.B. James, J. Amer. Chem. Soc., 1964, 86, 590.
7. Nomenclature according to:- I.U.P.A.C. Information Bulletin, 1968, 33, 68. and Inorg. Chem., 1970, 9, 1.
8. H. Iwasaki and Y. Saito, Bull. Chem. Soc. Japan, 1966, 39, 92.
9. A. Werner, Helv. Chim. Acta, 1918, 1, 5.
10. J.I. Legg, Chem. Comm., 1967, 675.
11. J.R. Gollogly and C.J. Hawkins, Acta. Chim. Scand., 1965, 19, 1915.
12. G.A. Barclay, E. Goldschmied, N.C. Stephenson and A.M. Sargeson, Chem. Comm., 1966, 540.
13. R. Fay and Piper, J. Amer. Chem. Soc., 1963, 85, 500.
14. R. Fay and Piper, Inorg. Chem., 1964, 3, 348.

REFERENCES (contd.)

15. T.E. MacDermott, Inorganica Chim.Acta, 1968,2,81.
16. M.R. Snow, private communication.
17. K.R. Butler and M.R. Snow, Chem.Comm., 1971,550.
18. In K.R. Butler and M.R. Snow, J.Chem.Soc.(A), 1971,565, reference 22.
19. A. Bondi, J.Phys.Chem., 1964,68,441.
20. P.F. Crossing and M.R. Snow, J.Chem.Soc.(Dalton), 1972,295.
21. J.C. Chang, J.P. Redfern and J.E. Salmon, J.Chem.Soc., 1964,2811.
- 21a. G.P. Baxter and G. Jones, J. Amer.Chem.Soc., 1910,32,298.
22. J.C. Chang, J.Inorg.Nuclear Chem., 1968,30,945.
23. E.J. Corey and J.C. Bailar jun., J.Am.Chem.Soc., 1959,81,2620.
24. J.P. Mathieu, Ann.Phys.(Paris), 1944,19,335.
25. R.H. Boyd, J.Chem.Phys., 1968,49,2574.
26. H.A. Scheraga, Advan.Phys.Org.Chem., 1968,6,103.
27. S. Lifson and A. Warshel, J.Chem.Phys., 1968,49,5116.
28. M.R. Snow, J.Am.Chem.Soc., 1970,92,3610.
29. D.A. Buckingham, I.E. Maxwell, A.M. Sargeson and M.R. Snow, J.Am.Chem.Soc., 1970,92,3617.
30. D.A. Buckingham and A.M. Sargeson, Topics in Stereochem., 1971,6,219-277.

REFERENCES (contd.)

31. K. Nakatsu, M. Shiro, Y. Saito and H. Kuroya, Bull. Chem. Soc. Japan, 1957, 30, 158.
32. K. Nakatsu, Bull. Chim. Soc. Japan, 1962, 35, 832.
33. M. Iwata, K. Nakatsu and Y. Saito, Acta Cryst., 1969, B25, 2562.
34. J. Quagliamo and S. Mizushima, J. Am. Chem. Soc., 1953, 75, 6084.
35. D.B. Powell and N. Shepherd, J. Chem. Soc., 1959, 791.
36. W. Thielacker, Z. Anorg. Chem., 1937, 234, 161.
37. F.F-L. Ho and C.N. Reilly, Anal. Chem., 1970, 42, 600.
38. E.A. Mason and M.M. Kreevoy, J. Am. Chem. Soc., 1955, 77, 5808.
39. J.R. Gollogly and C.J. Hawkins, Inorg. Chem., 1969, 8, 1168.
40. J.R. Gollogly and C.J. Hawkins, Inorg. Chem., 1970, 9, 576.
41. J.R. Gollogly and C.J. Hawkins, Inorg. Chem., 1971, 10, 317.
42. L.S. Bartell, J. Chem. Phys., 1960, 32, 827.
43. T.L. Hill, J. Chem. Phys., 1948, 16, 399.
44. K.N. Raymond, P.W.R. Corfield and J.A. Ibers, Inorg. Chem., 1968, 7, 842.

REFERENCES (contd.)

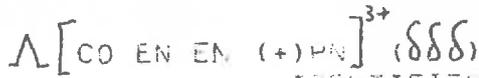
45. K.N. Raymond, P.W.R. Corfield and J.A. Ibers, Inorg.Chem., 1968,7,1362.
46. K.N. Raymond and J.A. Ibers, Inorg.Chem., 1968,7,2333.
47. L.N. Swink and M. Atoji, Acta.Cryst., 1960,13,639.
48. K. Nakatsu, Y. Saito and H. Kuroya, Bull.Chem. Soc.Japan, 1956,29,428.
49. D.L. Cullen and E.C. Lingafelter, Inorg.Chem., 1970,9,1858.
50. J.W. Lethbridge, L.S. DentGlassen and H.F.W. Taylor, J.Chem.Soc., 1970,1862.
51. R.J. Geue and M.R. Snow, J.Chem.Soc.(A), 1971,2981.

Λ [CO EN EN (-)PN]³⁺ (SSS) ME EQUATORIAL

ATOM	IDENTIFIER	X	Y	Z
CO	27.000000	0.000000	0.000000	0.000000
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N1	7.000000	-.242048	1.957661	0.000000
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C2	6.000000	2.163612	1.786013	.275788
C1H1	1.000000	1.190947	2.529487	-1.474992
C1H2	1.000000	1.105044	3.606927	-.069369
C2H1	1.000000	3.130992	2.098891	-.122729
C2H2	1.000000	2.152534	1.976348	1.349895
N1H1	1.000000	-.962478	2.241816	-.079867
N1H2	1.000000	-.515926	2.310325	.927613
N2H1	1.000000	2.377948	.085557	-.900651
N2H2	1.000000	2.395534	-.225918	.739175
N1 A	7.000000	-.873207	-.008018	-1.971282
N2 A	7.000000	.334614	-1.941593	-.097067
C1 A	6.000000	-.129534	-1.431492	-2.424743
C2 A	6.000000	.727267	-2.253275	-1.504886
C1H1 A	1.000000	-1.156346	-1.799091	-2.402633
C1H2 A	1.000000	.246445	-1.511868	-3.446859
C2H1 A	1.000000	.573853	-3.315143	-1.708480
C2H2 A	1.000000	1.779521	-2.015254	-1.666219
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N1H2 A	1.000000	.747980	.451929	-2.388992
N2H1 A	1.000000	-.502686	-2.486082	.152695
N2H2 A	1.000000	1.100461	-2.218044	.534625
N2 B	7.000000	-.003723	-.061018	1.972721
N1 B	7.000000	-1.951361	-.281022	.086368
C1 B	6.000000	-2.288063	-.712410	1.477706
C2 B	6.000000	-1.423734	.008534	2.428952
C1H1 B	1.000000	-3.341636	-.511021	1.682793
C1H2 B	1.000000	-2.107198	-1.781536	1.596161
C2H1 B	1.000000	-1.725720	1.117205	2.403599
C3 B	60.000000	-1.582311	-.443504	3.840580
N1H1 B	1.000000	-2.454091	.591206	-.133073
N1H2 B	1.000000	-2.260267	-1.004632	-.577831
N2H1 B	1.000000	.555492	.704936	2.373849
N2H2 B	1.000000	.393511	-.954497	2.296897
C3H1 B	1.000000	-1.310392	-1.498347	3.896860
C3H2 B	1.000000	-2.616929	-.325011	4.165588
C3H3 B	1.000000	-.935558	.123605	4.511233

Λ [CO EN EN (-)PN] (SSS)

ATOM	IDENTIFIER	X	Y	Z
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N1	7.000000	-.225096	1.964433	0.000000
C1	6.000000	1.079008	2.557211	-.426351
C2	6.000000	2.177079	1.790121	.251427
C1H1	1.000000	1.190191	2.488411	-1.510763
C1H2	1.000000	1.127285	3.609182	-.133526
C2H1	1.000000	3.145117	2.093527	-.156766
C2H2	1.000000	2.168513	1.997458	1.324329
N1H1	1.000000	-.958844	2.241865	-.009347
N1H2	1.000000	-.479327	2.338873	.926588
N2H1	1.000000	2.375204	.007508	-.899817
N2H2	1.000000	2.403846	-.216667	.743203
N1 A	7.000000	-.087378	-.034635	-1.967276
N2 A	7.000000	.288017	-1.905117	-.050685
C1 A	6.000000	-.236225	-1.409263	-2.504820
C2 A	6.000000	.039890	-2.294744	-1.465867
C1H1 A	1.000000	-1.275999	-1.703231	-2.255275
C1H2 A	1.000000	.008201	-1.604670	-3.406532
C2H1 A	1.000000	.470203	-3.306490	-1.057873
C2H2 A	1.000000	1.089559	-2.000980	-1.058907
N1H1 A	1.000000	-.898584	.502312	-2.309177
N1H2 A	1.000000	.762345	.306275	-2.400313
N2H1 A	1.000000	-.508425	-2.506993	.231947
N2H2 A	1.000000	1.090260	-2.204110	.053704
N1 B	7.000000	-1.958757	-.202967	.148678
N2 B	7.000000	.054875	-.011083	1.980152
C1 B	6.000000	-2.338967	.248061	1.542546
C2 B	6.000000	-1.327081	-.297424	2.521434
C1H1 B	1.000000	-2.347840	1.347898	1.595650
C1H2 B	1.000000	-3.339282	-.123011	1.600592
C2H1 B	1.000000	-1.458622	.212555	3.492471
C3 B	6.000000	-1.535022	-1.786163	2.738819
N1H1 B	1.000000	-2.430148	.402885	-.544203
N1H2 B	1.000000	-2.270405	-1.101001	-.012352
N2H1 B	1.000000	.385580	.903305	2.349352
N2H2 B	1.000000	.720509	-.755431	2.293522
C3H1 B	1.000000	-.671541	-2.172506	3.302261
C3H2 B	1.000000	-1.592751	-2.298550	1.789507
C3H3 B	1.000000	-2.465894	-1.930651	3.309631



ATOM	IDENTIFIER	X	Y	Z
CO	27.000000	0.000000	0.000000	0.000000
N2	7.000000	1.944202	.333042	0.000000
N1	7.000000	-.253119	1.956431	0.000000
C1	6.000000	1.066142	2.568563	-.342680
C2	6.000000	2.142045	1.774294	.340918
C1H1	1.000000	1.221036	2.549729	-1.422588
C1H2	1.000000	1.097661	3.005234	-.000926
C2H1	1.000000	3.123330	2.108765	-.602153
C2H2	1.000000	2.079622	1.918105	1.420714
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N1H2	1.000000	-.570461	2.308568	.914252
N2H1	1.000000	2.372868	.132296	-.914614
N2H2	1.000000	2.414830	-.250187	.707191
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N2 A	7.000000	.327540	-1.943763	-.079967
C1 A	6.000000	-.188150	-1.440553	-2.396042
C2 A	6.000000	.680911	-2.209862	-1.494626
C1H1 A	1.000000	-1.224927	-1.771731	-2.318538
C1H2 A	1.000000	.140270	-1.551050	-3.431552
C2H1 A	1.000000	.509104	-3.330713	-1.688470
C2H2 A	1.000000	1.731779	-2.044024	-1.682252
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N1H2 A	1.000000	.772125	.404374	-2.392776
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N2H2 A	1.000000	1.111462	-2.207520	.534621
N1 B	7.000000	-1.953986	-.258140	.076809
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C1H1 B	1.000000	-2.462539	1.054699	1.074626
C1H2 B	1.000000	-3.337913	-.490091	1.678922
C3 B	6.000000	-1.607768	-.276472	3.837830
C2H2 B	1.000000	-1.329044	-1.697566	2.278335
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C3H1 B	1.000000	-1.632037	.804630	3.980726
C3H2 B	1.000000	-.827260	-.698589	4.472061
C3H3 B	1.000000	-2.569349	-.696631	4.136058

$$\Lambda [CO EN(-)PN (-)PN]^{3+} (\delta\lambda)$$

ATOM	IDENTIFIER	X	Y	Z
CO	27.000000	0.000000	0.000000	0.000000
N2	7.000000	1.944597	.333042	0.000000
N1	7.000000	-.232983	1.959027	0.000000
C1	6.000000	1.085293	2.584372	-.326971
C2	6.000000	2.109886	1.775189	.324492
C1H1	1.000000	1.239008	2.612018	-1.406294
C1H2	1.000000	1.114209	3.608079	.052212
C2H1	1.000000	3.142864	2.093207	-.055995
C2H2	1.000000	2.153372	1.932493	1.403646
N1H1	1.000000	-.922546	2.234401	-.714976
N1H2	1.000000	-.557438	2.304018	.914115
N2H1	1.000000	2.366490	.117848	-.914179
N2H2	1.000000	2.405378	-.248305	.715695
N2 A	7.000000	.309118	-1.948642	-.097333
N1 A	7.000000	-.064644	-.014619	-1.971235
C1 A	6.000000	.458012	-1.334431	-2.441642
C2 A	6.000000	-.015572	-2.397353	-1.488126
C1H1 A	1.000000	.082092	-1.543672	-3.445389
C1H2 A	1.000000	1.598190	-1.317047	-2.474661
C2H1 A	1.000000	-1.094776	-2.519238	-1.094734
C3 A	60.000000	.645910	-3.720514	-1.791610
N1H1 A	1.000000	-1.034241	.112103	-2.298913
N1H2 A	1.000000	.509389	.708055	-2.575689
N2H1 A	1.000000	-.280367	-2.402430	.572049
N2H2 A	1.000000	1.294589	-2.155691	.119945
C3H1 A	1.000000	1.730410	-3.631945	-1.715312
C3H2 A	1.000000	.385069	-4.044022	-2.800430
C3H3 A	1.000000	.302911	-4.473614	-1.081065
N2 B	7.000000	.003935	-.008670	1.971779
N1 B	7.000000	-1.955401	-.206652	.095755
C1 B	6.000000	-2.293486	-.697968	1.483480
C2 B	6.000000	-1.412431	.056307	2.441628
C1H1 B	1.000000	-3.342097	-.477926	1.094893
C1H2 B	1.000000	-2.137112	-1.772107	1.588075
C2H1 B	1.000000	-1.708531	1.107090	2.442346
C3 B	60.000000	-1.565818	-.484463	3.843597
N1H1 B	1.000000	-2.443973	.627231	-.108823
N1H2 B	1.000000	-2.265633	-.904450	-.574568
N2H1 B	1.000000	.502239	.696741	2.374408
N2H2 B	1.000000	.410727	-.902129	2.284924
C3H1 B	1.000000	-1.295594	-1.542040	3.874755
C3H2 B	1.000000	-2.591411	-.366090	4.181163
C3H3 B	1.000000	-.903728	.003920	4.519739

$\Lambda [CO EN (+)PN (+)PN]^{3+} (888)$

ATOM	IDENTIFIER	X	Y	Z	
CO	27.000000	0.000000	0.000000	0.000000	
N2	7.000000	1.941867	.333042	0.000000	
N1	7.000000	-.255593	1.955823	0.000000	
C1	6.000000	1.065448	2.568757	-.335177	
C2	6.000000	2.138553	1.771967	.350623	
C1H1	1.000000	1.224661	2.552511	-1.414538	
C1H2	1.000000	1.096050	3.604476	.009533	
C2H1	1.000000	3.121463	2.108297	.014130	
C2H2	1.000000	2.070735	1.909849	1.430796	
N1H1	1.000000	-.948653	2.232531	-.710503	
N1H2	1.000000	-.578019	2.307746	.912530	
N2H1	1.000000	2.374443	.138450	-.914078	
N2H2	1.000000	2.401798	-.262407	.704320	
N2	A	7.000000	.344017	-1.939090	-.077511
N1	A	7.000000	-.070881	-.014932	-1.971031
C1	A	6.000000	-.196229	-1.443421	-2.391325
C2	A	6.000000	.686401	-2.270196	-1.496186
C1H1	A	1.000000	-1.234013	-1.758077	-2.302088
C1H2	A	1.000000	.119326	-1.553713	-3.430957
C3	A	60.000000	.494416	-3.743301	-1.765819
C2H2	A	1.000000	1.730111	-2.012634	-1.687799
N1H1	A	1.000000	-.867950	.512318	-2.311803
N1H2	A	1.000000	.772813	.397747	-2.393556
N2H1	A	1.000000	-.469600	-2.466884	.235659
N2H2	A	1.000000	1.144959	-2.170950	.528461
C3H1	A	1.000000	-.546481	-4.027685	-1.606307
C3H2	A	1.000000	1.125835	-4.324474	-1.092624
C3H3	A	1.000000	.772467	-3.972845	-2.795408
N2	B	7.000000	.003098	-.070797	1.973278
N1	B	7.000000	-1.952288	-.267658	.075941
C1	B	6.000000	-2.373509	-.021059	1.488159
C2	B	6.000000	-1.327410	-.610427	2.394802
C1H1	B	1.000000	-2.466629	1.051260	1.666730
C1H2	B	1.000000	-3.339377	-.494806	1.675879
C3	B	60.000000	-1.613796	-.268794	3.837374
C2H2	B	1.000000	-1.330551	-1.696809	2.285284
N1H1	B	1.000000	-2.436746	.397685	-.543878
N1H2	B	1.000000	-2.223944	-1.220960	-.204200
N2H1	R	1.000000	.157839	.800721	2.383596
N2H1	B	1.000000	.747068	-.697048	2.313998
C3H1	R	1.000000	-1.540187	.812919	3.975137
C3H2	R	1.000000	-.333055	-.666513	4.474972
C3H3	R	1.000000	-2.575135	-.689235	4.135897

$$\Lambda[\text{CO}(-)\text{PN}(-)\text{PN}(-)\text{PN}]^{3+}(\lambda\lambda\lambda)$$

ATOM	IDENTIFIER	X	Y	Z
CO	27.000000	0.000000	0.000000	0.000000
N2	7.000000	1.972721	.004000	.061000
N1	7.000000	.086287	1.950860	.281000
C1	6.000000	1.477214	2.295939	.707717
C2	6.000000	2.437151	1.422803	-.054584
C1H1	1.000000	1.679888	3.346214	.487318
C1H2	1.000000	1.592234	2.139261	1.780857
C2H1	1.000000	2.438939	1.725085	-1.103306
C3	60.000000	3.839941	1.571671	.486495
N1H1	1.000000	-.140695	2.445921	-.594011
N1H2	1.000000	-.576201	2.263741	1.004032
N2H1	1.000000	2.376605	-.548650	-.707913
N2H2	1.000000	2.290128	-.408909	.951075
C3H1	1.000000	3.872048	1.298271	1.541936
C3H2	1.000000	4.172969	2.604329	.376036
C3H3	1.000000	4.517094	.921292	-.067512
N2 A	7.000000	-.005738	-1.940872	-.358259
N1 A	7.000000	-.000377	.200424	-1.955618
C1 A	6.000000	.326898	-1.050000	-2.597112
C2 A	6.000000	-.335905	-2.144281	-1.804521
C1H1 A	1.000000	-.046222	-1.060476	-3.623422
C1H2 A	1.000000	1.406992	-1.199249	-2.620158
C2H1 A	1.000000	-1.416282	-2.084195	-1.947253
C3 A	60.000000	.131804	-3.501316	-2.273427
N1H1 A	1.000000	-.928514	.578596	-2.271182
N1H2 A	1.000000	.692811	.962532	-2.249037
N2H1 A	1.000000	-.701879	-2.430867	.220588
N2H2 A	1.000000	.922410	-2.333156	-.142659
C3H1 A	1.000000	1.213654	-3.590519	-2.165878
C3H2 A	1.000000	-.134357	-3.645127	-3.321540
C3H3 A	1.000000	-.346952	-4.280132	-1.678571
N2 B	7.000000	-.080152	-.337312	1.942977
N1 B	7.000000	-1.971693	.061632	.029812
C1 B	6.000000	-2.432186	-.488921	1.341561
C2 B	6.000000	-1.471415	-.037664	2.408441
C1H1 B	1.000000	-3.433765	-.115838	1.565811
C1H2 B	1.000000	-2.469782	-1.578120	1.301058
C2H1 B	1.000000	-1.585242	1.037194	2.559836
C3 B	60.000000	-1.759231	-.736075	3.715961
N1H1 B	1.000000	-2.298528	1.033972	-.071744
N1H2 B	1.000000	-2.384195	-.493167	-.732814
N2H1 B	1.000000	.584896	.256006	2.458292
N2H2 B	1.000000	.157748	-1.322100	2.131190
C3H1 B	1.000000	-1.676135	-1.817241	3.597774
C3H2 B	1.000000	-2.767106	-.491773	4.054488
C3H3 B	1.000000	-1.044779	-.468153	4.472070

CIS- Λ [CO(+)₃PN(+)₃]³⁺ (888)

ATOM	IDENTIFIER	X	Y	Z
CO	27.000000	0.000000	0.000000	0.000000
N2	7.000000	1.972277	-0.000000	.072000
N1	7.000000	.378458	1.954477	.258000
C1	6.000000	1.493440	2.371702	.019728
C2	6.000000	2.394099	1.323292	.014198
C1H1	1.000000	1.678504	2.404194	-1.051564
C1H2	1.000000	1.681005	3.337116	.494438
C3	60.000000	3.839299	1.605994	.280679
C2H2	1.000000	2.270563	1.326542	1.099939
N1H1	1.000000	-.534703	2.430370	-.415497
N1H2	1.000000	-.209600	2.234020	1.206405
N2H1	1.000000	2.383920	-.159101	-.059156
N2H2	1.000000	2.310	-.752	.690
C3H1	1.000000	3.983258	1.051799	-.800247
C3H2	1.000000	4.472895	.824365	.702177
C3H3	1.000000	4.137028	2.506687	.702604
N2 A	7.000000	-.001711	-1.944854	-.335618
N1 A	7.000000	-.001905	.254540	-1.956505
C1 A	6.000000	-.344204	-1.004111	-2.570002
C2 A	6.000000	.347182	-2.140080	-1.777523
C1H1 A	1.000000	-1.424012	-1.214809	-2.547609
C1H2 A	1.000000	-.306182	-1.090137	-3.008097
C3 A	60.000000	-.074580	-3.510196	-2.251944
C2H2 A	1.000000	1.426872	-2.041699	-1.907060
N1H1 A	1.000000	-.707900	.951194	-2.233506
N1H2 A	1.000000	.913228	.572325	-2.508390
N2H1 A	1.000000	-.919861	-2.302931	-.130258
N2H2 A	1.000000	.702	-2.415	.252
C3H1 A	1.000000	-1.153837	-3.631655	-2.156208
C3H2 A	1.000000	.421305	-4.274443	-1.051783
C3H3 A	1.000000	.208102	-3.645497	-3.297000
N2 B	7.000000	-.080038	-.327341	1.944618
N1 B	7.000000	-1.971572	.073481	.014319
C1 B	6.000000	-2.395439	.194153	1.442185
C2 B	6.000000	-1.496446	-.603318	2.270196
C1H1 B	1.000000	-2.313248	1.232180	1.768107
C1H2 B	1.000000	-3.433294	-.120001	1.550133
C3 B	60.000000	-1.772911	-.496655	3.742774
C2H2 B	1.000000	-1.677979	-1.728053	2.009872
N1H1 B	1.000000	-2.309995	.093528	-.509877
N1H2 B	1.000000	-2.395703	-.707301	-.402570
N2H1 B	1.000000	.212072	.502250	2.479782
N2H2 B	1.000000	.530624	-1.110203	2.206642
C3H1 B	1.000000	-1.021077	.544681	4.030183
C3H2 B	1.000000	-1.097592	-1.124688	4.525175
C3H3 B	1.000000	-2.801303	-.702477	3.967765

TRANS- Λ [CO(+)PN(+)PN(+)PN]³⁺ (888)

ATOM	IDENTIFIER	X	Y	Z	
CO	27.000000	0.000000	0.000000	0.000000	
N2	7.000000	1.972422	-0.006000	.072000	
N1	7.000000	.079283	1.954487	.258000	
C1	6.000000	1.493450	2.371265	.014487	
C2	6.000000	2.394786	1.324526	.010693	
C1H1	1.000000	1.676019	2.459996	-1.057551	
C1H2	1.000000	1.682277	3.338256	.485520	
C3	60.000000	3.839710	1.000627	.275481	
C2H2	1.000000	2.279676	1.330166	1.696516	
N1H1	1.000000	-.536789	2.436989	-.412410	
N1H2	1.000000	-.203500	2.233597	1.208090	
N2H1	1.000000	2.383924	-.162035	-.058759	
N2H2	1.000000	2.310323	-.750059	.699708	
C3H1	1.000000	3.982913	1.629617	-.805612	
C3H2	1.000000	4.473477	.826301	.698674	
C3H3	1.000000	4.138507	2.508512	.694639	
N2	A	7.000000	-.000724	-1.945220	-.333706
N1	A	7.000000	-.000978	.252963	-1.956609
C1	A	6.000000	-.346776	-1.065700	-2.568719
C2	A	6.000000	.344141	-2.142185	-1.776425
C1H1	A	1.000000	-1.427339	-1.214982	-2.545468
C1H2	A	1.000000	-.009815	-1.092853	-3.007137
C3	A	60.000000	-.080677	-3.511975	-2.248631
C2H2	A	1.000000	1.423728	-2.045927	-1.908557
N1H1	A	1.000000	-.706506	.900841	-2.234085
N1H2	A	1.000000	.913799	.508464	-2.309088
N2H1	A	1.000000	-.917366	-2.304307	-.123470
N2H2	A	1.000000	.706104	-2.413641	.251764
C3H1	A	1.000000	-1.160398	-3.051464	-2.150042
C3H2	A	1.000000	.414963	-4.276612	-1.049187
C3H3	A	1.000000	.198553	-3.648598	-3.294307
N2	B	7.000000	-.079991	-.328070	1.943916
N1	B	7.000000	-1.972350	.072310	.014156
C1	B	6.000000	-2.394355	.200792	1.443954
C2	B	6.000000	-1.495581	-.677134	2.271735
C1H1	B	1.000000	-2.276377	1.237527	1.765892
C3	B	60.000000	-3.840613	-.197712	1.015683
C2H1	B	1.000000	-1.683739	-.507024	3.333936
C2H2	B	1.000000	-1.681990	-1.728048	2.045170
N1H1	B	1.000000	-2.389279	.890064	-.014603
N1H2	B	1.000000	-2.384929	-.771643	-.406930
N2H1	B	1.000000	.207157	.496126	2.490555
N2H2	B	1.000000	.532701	-1.113734	2.206957
C3H1	B	1.000000	-4.472490	.436454	.992501
C3H2	B	1.000000	-3.986799	-1.259140	1.325811
C3H3	B	1.000000	-4.138787	-.074250	2.057815