

VIBRATIONAL SPECTRAL STUDIES AND CRYSTAL ANALYSIS  
OF COORDINATION COMPLEXES

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## General Introduction

There are many physical or physico-chemical methods available for studying the various properties of chemical compounds. These methods can be conveniently classified into classes which are determined by the purpose of the investigation. Those used to elucidate molecular structure fall into two classes.

The first, which includes x-ray, neutron, and electron diffraction yields detailed information about the whole structure of the molecule. These techniques introduce a metrical element into the understanding of the complex, revealing the lengths of the chemical bonds, the angles between them, and other structural details such as the various forms of isomerism in the topological and conformational arrangements of polydentate ligands about the metal centre.

The second gives fragmentary information concerning individual bonds of a particular group of atoms in the molecule. This class includes optical rotatory dispersion, circular dichroism, the measurement of electric and magnetic moments, and various kinds of spectroscopy of the region ranging from microwave to ultraviolet. The last two groups should yield information mostly in the area of the electronic structure of the molecule. The last group covers vibrational

spectroscopy which originates in the vibrations of the nuclei constituting a molecule. Vibrational spectra are observed both as infrared and Raman spectra, and the frequencies of the vibrational transitions are determined by the masses of the constituent atoms, the molecular geometry and the interatomic forces. The intensities of infrared and Raman spectra are related to the changes in dipole moment and polarisability, respectively. Attempts have been made to analyse the vibrational spectra quantitatively. Though there has been some success, work on many aspects (such as intensity in relation to bonding) is sparse. Nevertheless, the understanding of the molecular and the electronic structure of some molecules can be much extended by employing a combination of methods.

This thesis consists of two main sections. The first describes the vibrational spectral studies of diarsine complexes. Most of the spectral work is centred around the low infrared frequency region. Raman spectra of two complexes are reported and characterised by their metal-ligand sensitive absorptions. The frequencies of these assignments are used to calculate the frequencies of the infrared active metal-ligand vibrations. The frequencies assigned to the metal-ligand vibration of diarsine complexes are analysed in terms of the change in electronic configuration of the transition element. It is hoped that the inferences obtained

from the vibrational may elucidate the bonding in these complexes. These results are checked against those derived from the data given in x-ray and electron spin resonance (e.s.r.) spectral studies.

The second main section gives a description of the crystal and the molecular structure of cobalt triethylene-tetramine glycinato dichloride,  $\Delta\text{-}\beta_2'\text{-(RS)-(Co(trien)(gly))Cl}_2\cdot\text{H}_2\text{O}$ . It belongs to a series of cobalt(III) polyamino compounds containing asymmetric nitrogen centres. These polyamino complexes can display various forms of isomerism in their topological and conformational arrangements. The reasons for the study of this particular complex are many, and are given in the Introduction to Crystal Studies. However, the primary reason is that precise molecular geometry is of great importance as a check on the predicted molecular geometry derived from energy minimisation techniques.

PART I

Low Frequency Vibrational Studies of

Diarsine Complexes



ABSTRACT

The different assignments of the frequency of the infrared active antisymmetric cobalt-chlorine vibration for the complexes  $\text{CoD}_2\text{Cl}_2\text{Cl}$  and  $\text{CoD}_2\text{Cl}_2\text{ClO}_4$  were checked by examining whether the values fitted the trends (e.g.,  $\nu(\text{M-Cl})$  vs. Oxidation State (of transition metal),  $\nu(\text{M-Cl})$  vs. Electronic configuration, etc.) formed by the other diarsine complexes. Further investigations arose from the study of the infrared spectra of  $\text{CoD}_2\text{Cl}_2\text{BF}_4$ , and also from the values of the frequencies of the infrared active cobalt-halogen vibrations calculated from the assignments proposed for the Raman active symmetric cobalt halogen vibrations for the complexes  $\text{CoD}_2\text{Cl}_2\text{Cl}$  and  $\text{CoD}_2\text{Br}_2\text{Br}$ .

The low infrared spectra of various diarsine complexes were examined ( $\text{MD}_2\text{Z}_2$ ;  $\text{M} = \text{Co}, \text{Ni}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{ClO}_4$  and  $\text{NO}_3$ ; and  $\text{CoD}_2(\text{BF}_4)_2$ ). Attempts were made to correlate the frequencies of the metal-ligand vibrations of diarsine compounds (whose central metal atom has  $d^6$ ,  $d^7$  or  $d^8$  electronic configuration) with the oxidation state and the electronic configuration of the central metal ion. Inferences drawn from the vibrational data have provided some insight into the bonding in these diarsine systems. An attempt has been made to see how closely these results agree with those derived from x-ray diffraction and electron spin resonance (e.s.r.) spectral studies.

## INTRODUCTION

In the last decade, many studies of transition metal complexes have been reported, and there has been much interest in the assignment of metal-ligand vibrations. Of particular interest has been metal-halogen stretching frequencies of tetrahedral<sup>1</sup> or octahedral<sup>2,3</sup> metal complexes.  $\nu(\text{M-X})$  values are readily obtained from studies of the 200-500  $\text{cm}^{-1}$  region but for some complexes (e.g.,  $\text{CoD}_2\text{Cl}_2^*$ ,  $\text{CoD}_2\text{Br}_2$ ,  $\text{NiD}_2\text{Cl}_2$ )<sup>4</sup>,  $\nu(\text{M-X})$  lie below 200  $\text{cm}^{-1}$ . With the recent development of commercially available interferometers, it is now possible not only to study and locate the metal-halogen stretches in the region below 200  $\text{cm}^{-1}$  but also to check those observed with spectrophotometers covering the range 500-200  $\text{cm}^{-1}$ . As metal-halogen bands occur in many inorganic complexes, the characterisation of M-X frequencies is of considerable interest. By studying series of related complexes, it is possible to relate the frequencies of the vibrations to changes in atomic weight, oxidation state, coordination number and electronic configuration. These factors will be discussed in some detail since this part of the thesis deals primarily with the use of low frequency vibrational spectra in the study of these effects.

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\*For convenience diarsine is referred to throughout this thesis as D.

Generally, the assignment of  $\nu(\text{M-X})$  is reasonably straightforward since they are normally observed as strong absorptions. If the spectra of corresponding halide complexes are available direct comparison shows the 'isotopic' shift of the (M-X) band, thus providing a very reliable method for making assignments. For example, it is commonly found that metal bromine stretching frequencies  $\nu(\text{M-Br})$  parallel  $\nu(\text{M-Cl})$  frequencies, occurring at 0.65 - 0.85 of the value of a directly analogous M-Cl vibration (the most usual value is  $\sim 0.75$  for first-row transition metals)<sup>5</sup>. This method was used in the assignment of the two strong absorption bands of tetrahedral  $\text{CoCl}_2 \cdot \text{py}_2$  at 303 and 334  $\text{cm}^{-1}$  as  $\nu(\text{Co-Cl})$  modes. It was observed that the halogen bands decreased by a factor of  $\sim 0.77$  in going from the chlorides to the corresponding bromides while the ligand bands remained virtually constant.

Assignment of i.r. absorptions of metal-halogen group may be achieved by comparison of the spectra with that of the free ligand by observing the appearance of new absorptions.

The position of an absorption band not only depends on the various characteristics of the metal-ligand bond (e.g., mass, bond strength, oxidation state, etc.) but also on any coupling with other metal-ligand modes, and it is difficult to distinguish these various effects from each other quantitatively. However, an increasing number of vibrational analyses have been attempted in recent years. Quantitative vibrational

analyses are largely confined to simple molecules of high symmetry. These analyses are known as 'normal coordinate analysis'. It involves the classical vibrating molecule whose spectroscopic characteristics (e.g. infrared absorptions, Raman scattering) are assumed to arise from the interaction of its normal vibrations with an electromagnetic field. To reduce mathematical complexities, a particular form of representation of the energy (force field) of the system is assumed. Three commonly used force fields are the 'central' force field, the 'valence' force field, and the Urey-Bradley force field (details of these systems are found in standard texts on vibrational spectroscopy). Such calculations produce the force constants and indicate the form of each vibration in terms of the normal coordinates. These force constants can then be used to interpret bond properties. This method has been performed on simple molecules in the gas phase and even on some complexes; e.g., ammine complexes<sup>6-8</sup>, hexahalo complexes<sup>9</sup>, and oxolato complexes<sup>10</sup>. Nevertheless, it is realised that this semiquantitative method is not very practical for complexes of lower symmetry containing complicated ligands.

A 'simple triatomic model'<sup>11</sup> for calculating metal-ligand vibrations has recently been attempted. This was developed primarily because the simplicity of the calculation would not demand the use of elaborate computations and it was hoped it would prove sophisticated enough to yield useful results.

Various systems were mentioned but as its treatment of complexes with  $D_{4h}$  symmetry is relevant to the study of metal-halogen vibrations in this thesis an outline is included here.

The formulae for the frequencies of the symmetric and asymmetric stretches of a linear triatomic molecule of the type AMB are

$$v_s = K \left\{ \frac{1}{2} \left( \frac{k_1}{\mu_{AM}} + \frac{k_2}{\mu_{MB}} \right) - \sqrt{\left[ \frac{1}{2} \left( \frac{k_1}{\mu_{AM}} - \frac{k_2}{\mu_{MB}} \right) \right]^2 + \frac{k_1 k_2}{m_M^2}} \right\}^2 \quad (1)$$

$$v_a = K \left\{ \frac{1}{2} \left( \frac{k_1}{\mu_{AM}} + \frac{k_2}{\mu_{MB}} \right) + \sqrt{\left[ \frac{1}{2} \left( \frac{k_1}{\mu_{AM}} - \frac{k_2}{\mu_{MB}} \right) \right]^2 + \frac{k_1 k_2}{m_M^2}} \right\}^2 \quad (2)$$

where  $v_s$  = frequency in K ( $\text{cm}^{-1}$ ) of the symmetric stretch

$v_a$  = frequency in K of the asymmetric stretch,

$K$  = conversion factor numerically equal to 1304,

$k_1$  = force constant in md/A for the bond between A and M,

$k_2$  = force constant between atom M and atom B,

$\mu_{AM}$  = reduced mass of A and M,

$\mu_{MB}$  = reduced mass of M and B.

If atoms A and B are identical, the above equations reduce to

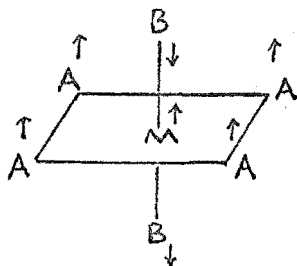
$$v_s = K \sqrt{k/m_A} \quad (3)$$

and

$$v_a = K \sqrt{k \left( \frac{1}{m_A} + \frac{2}{m_M} \right)} \quad (4)$$

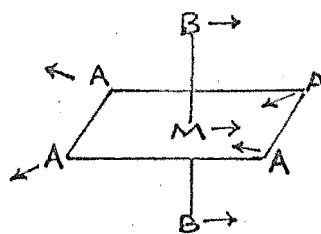
For this model to be generally useful for complexes, three-dimensional fundamental modes are resolved into a one-dimensional model. One of the weaknesses of this model is that it does not include any repulsion terms nor does it allow for any bending modes to mix with the stretching modes. Hence, the most dependable results from this model are the ratios of frequencies of corresponding vibrations of similar molecules.

A trans disubstituted six coordinate complex of the type  $A_4MB_2$  with  $D_{4h}$  symmetry has five stretching modes of vibrations, of which two are infrared active.



$A_{2u}$ ,  $\nu_a(MB)$

$$\nu_a = \sqrt{k_1 \left( \frac{1}{m_B} + \frac{2}{m_T} \right)} \quad (5)$$



$E_u$ ,  $\nu_a(AM)$

$$\nu_a = \sqrt{k_2 \left( \frac{1}{m_A} + \frac{2}{m_S} \right)} \quad (6)$$

It can be seen that  $A_{2u}$  is chiefly an asymmetric M-B stretch for which a formula of type (4) can be applied (using  $m_T = m_M + 4m_A$ ), and  $E_u$  is chiefly an asymmetric A-M stretch with the same formula but  $m_S = m_M + 2m_B$ .

These formulae can be used to predict the frequencies of the vibrations if an independent estimate of the force

constant is available. For example, calculated values for the Co-Cl vibrations for the series of complexes  $\text{CoD}_2\text{Cl}_2\text{Z}$ , where  $\text{Z} = \text{Cl}, \text{ClO}_4$ , can be obtained by using data from the two complexes,  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$  and  $\text{Coen}_2\text{Cl}_2^+$ , and then compared with the observed values. Results of interest are given below.

t-MA <sub>4</sub> B <sub>2</sub>	Source of f	f(md/A)	ν(M-B), in K		Ref.
			calc.	found	
CoD <sub>2</sub> Cl <sub>2</sub> Cl	Co(NH <sub>3</sub> ) <sub>5</sub> Cl <sup>2+</sup>	2.00	326	324	12
CoD <sub>2</sub> Cl <sub>2</sub> ClO <sub>4</sub>	" "	"	326	325	12
CoD <sub>2</sub> Br <sub>2</sub> Br	Co(NH <sub>3</sub> ) <sub>5</sub> Br <sup>2+</sup>	"	232	243	12
CoD <sub>2</sub> Cl <sub>2</sub> Cl	Coen <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>	2.65	376	384±4	13
CoD <sub>2</sub> Cl <sub>2</sub> ClO <sub>4</sub>	" "	"	376	394	12
CoD <sub>2</sub> Br <sub>2</sub> Br	" "	"	267	264	12

Column 4 in the table above compares the calculated and the observed values for the cobalt-halogen vibration. The force constant (column 3) employed in the calculation is obtained from the complex listed in Column 2. It can be seen that the 2.00 value for f gives a better agreement, thus indicating that this value is also appropriate to  $\text{CoD}_2\text{Br}_2\text{Br}$ .

It was reported that some of the bands in both series (i.e., obtained by using both force constants) were fairly

weak; for instance, the spectra of both  $\text{CoD}_2\text{Cl}_2\text{Cl}$  and  $\text{CoD}_2\text{Br}_2\text{Br}$  are almost identical in the region 350 to 400K, where Lewis et al.<sup>4</sup> proposed that the Co-Cl stretches are to be found. Similarly, using both sets of force constants, the Co-Cl stretches for  $[\text{cis-Coen}_2\text{Cl}_2]^+$  and  $[\text{cis-CoD}_2\text{Cl}_2]^+$  have been calculated. It was observed that the agreement with the data of Hughes and McWhinnie<sup>14</sup> was distinctly better for the lower force constants. Hence, it was concluded that this model would indicate that the Co-Cl stretches were to be found in the 280 and 330K region of the spectrum, rather than from 350 to 390K as has been proposed by other authors.

Though the triatomic model is apparently quite promising and some assignments from it are presumably correct, it is still largely dependent on the source of force constant to give reliable calculated frequencies of vibration. Hence, its treatment of metal diarsine halogen complexes is questionable. The studies of Lewis et al.<sup>4</sup> on a large number of these compounds have not only given new assignments but also describe the qualitative approach to the metal-halogen frequency with respect to various properties of the metal. However, frequencies for some of these complexes (e.g.  $\text{CoD}_2\text{Cl}_2$ ,  $\text{NiD}_2\text{Cl}_2$ )<sup>4</sup> were not assigned. For these reasons, bromo analogues of some of the diarsine chloro complexes mentioned above and other diarsine compounds were studied, especially in the low-frequency range.



To check the different assignment of bands to the Co-Cl vibration of the complexes  $\text{CoD}_2\text{Cl}_2\text{Cl}$  and  $\text{CoD}_2\text{Cl}_2\text{ClO}_4$ , the i.r. spectra of the complexes  $\text{CoD}_2\text{Cl}_2\text{Z}$ , where  $\text{Z} = \text{Cl}, \text{ClO}_4$ , and  $\text{BF}_4$ , are examined. If the frequency of the Co-Cl vibration of the  $\text{CoD}_2\text{Cl}_2^+$  ion is not very sensitive to the nature of the counter-ion, then the  $\nu(\text{Co-Cl})$  for the tetrafluoroborate complex should lie about  $385 \text{ cm}^{-1}$ .

Further investigation on the previous assignments on this Co-Cl frequency comes from the Raman spectral studies of the complexes  $\text{CoD}_2\text{Cl}_2\text{Cl}$  and  $\text{CoD}_2\text{Br}_2\text{Br}$ . The force constants calculated from the frequencies assigned to the Raman active symmetric cobalt-halogen vibrations shall be used to predict the frequencies of the i.r. active antisymmetric cobalt-halogen vibrations.

Comparison of the metal-halogen frequencies assignment to the diarsine complexes described in this thesis should permit correlation of these parameters and hence, bond strength in terms of the magnitude of force constant, with the oxidation state and the electronic configuration of the transition metal centre. This should give some insight into the nature of bonding in the metal-halogen bond.

The low i.r. spectra of diarsine complexes with oxy-anions ( $\text{MD}_2\text{Z}_2$ ;  $\text{M} = \text{Co, Ni}$ ;  $\text{Z} = \text{ClO}_4, \text{NO}_3$ )<sup>15</sup> were investigated for the following reasons: firstly, metal-anion sensitive bands were reported to be absent above  $200 \text{ cm}^{-1}$  and

spectra below  $200\text{ cm}^{-1}$  had not been accessible; secondly, results from this study could be correlated with i.r. data on the oxyanions<sup>15</sup>; and thirdly, the overall agreement with other information on the nature of the bonding of the metal-halogen bond would be of interest.

Structural data on some diarsine complexes<sup>16-19</sup> have been reported and it was hoped that the metal-anion and the metal-arsenic bond distances would allow inferences to be drawn on the bonding in the compounds.

Recently, three electron spin resonance studies<sup>19,20,21</sup> of  $d^7$  diarsine complexes have been described. Although their spectral data (namely the g pattern for arsenic) are similar, for the monocation,  $\text{NiD}_2\text{Cl}_2^+$ , the investigators differ somewhat in their interpretation of its electronic structure.

It is envisaged that the results (or data) obtained from these magnetic and x-ray diffraction investigations would be of value in checking or supporting the inferences deduced from the vibrational spectroscopic data.

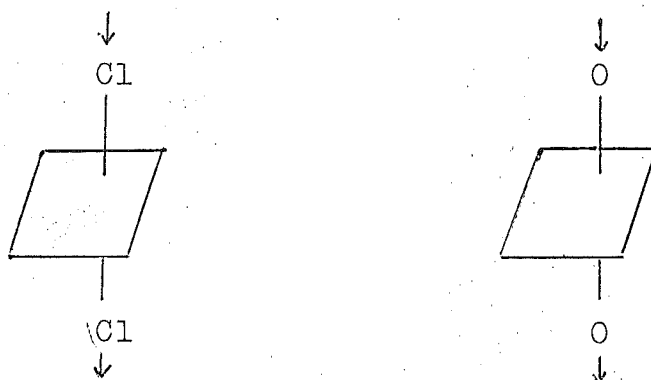
## RESULTS AND DISCUSSION

The following series of complexes has been investigated.

- (a)  $\text{MD}_2\text{Br}_2$ ,  $\text{M(II)} = \text{Co}$ , and  $\text{Ni}$ .  
 $\text{MD}_2\text{Cl}_2$ ,  $\text{M(II)} = \text{Co}$ , and  $\text{Ni}$ .  
 $\text{MD}_2(\text{BF}_4)_2$ ,  $\text{M(II)} = \text{Co}$ .  
 $\text{MD}_2(\text{NO}_3)_2$ ,  $\text{M(II)} = \text{Co}$ , and  $\text{Ni}$ .  
 $\text{MD}_2(\text{ClO}_4)_2$ ,  $\text{M} = \text{Co}$ , and  $\text{Ni}$ .
- (b)  $\text{MD}_2\text{Br}_2 \cdot \text{Br}$ ,  $\text{M(III)} = \text{Co}$ , and  $\text{Ni}$ .
- (c)  $\text{MD}_2\text{Br}_2 \cdot (\text{ClO}_4)$ ,  $\text{M(III)} = \text{Co}$ , and  $\text{Ni}$ , and  
 $\text{MD}_2\text{Cl}_2 \cdot (\text{BF}_4)$ ,  $\text{M(III)} = \text{Co}$ .

Chloro analogues of complexes of the type  $\text{MD}_2\text{Br}_2 \cdot \text{Br}$  and  $\text{MD}_2\text{Br}_2 \cdot (\text{ClO}_4)$  have been studied elsewhere, but data are referred to for comparison.

Table 1 contains the frequencies that have been tentatively assigned to metal-halogen and metal-oxygen infrared-active asymmetric vibrations.



Some of the assignments are difficult to make since the diarsine ligand contains a number of absorptions in the low-

frequency region. Further, it is not to be inferred that these are pure vibrations, because of the possible coupling with ligand and metal-ligand bending vibrations.

Calculated frequencies obtained by the semi-empirical method employing the relationship  $\nu(\text{M-Br})/\nu(\text{M-Cl}) = a$  constant (0.75 here) are presented in Table 2. It may be noted that both Tables 1 and 2 list the force constants corresponding to the assigned frequencies. Table 3 contains the tentative assignments to the  $\nu(\text{M-X})$  Raman active symmetric vibrations and the corresponding force constants.

The spectra (both i.r. and Raman) are presented in line form to allow better comparison of spectra. Weak absorptions have not been included because the interferometer spectra sometimes give a comparatively high background noise.

For convenience the discussion is divided into five parts: (1) Cobalt(III) complexes, (2) Nickel(III) complexes, (3)  $\text{MD}_2\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}$  and  $\text{BF}_4$ ) complexes, (4)  $\text{MD}_2\text{X}_2$  ( $\text{X} = \text{NO}_3$  and  $\text{ClO}_4$ ) complexes, and (5) Bonding in Diarsine complexes. The final section describes the correlation of conclusions derived from the spectra reported on the above complexes with those obtained by other physicochemical methods on some of these diarsine compounds.

### 1. Cobalt(III) Complexes

Figure 1 presents the spectra for the cobalt (III) complexes,  $\text{CoD}_2\text{X}_2 \cdot \text{ClO}_4$ , and  $\text{CoD}_2\text{X}_2 \cdot \text{X}$ , where X = Cl and Br. The characteristic bands for these complexes are:

$\text{CoD}_2\text{Cl}_2 \cdot \text{ClO}_4$	388(w)		217(s)
$\text{CoD}_2\text{Br}_2 \cdot \text{ClO}_4$		239(w)	
$\text{CoD}_2\text{Cl}_2 \cdot \text{Cl}$	384±4(w)		209(m)
$\text{CoD}_2\text{Br}_2 \cdot \text{Br}$		247(w)	227(w) 192(m)
$\text{CoD}_2\text{Cl}_2 \cdot \text{BF}_3$	389(w)		220(vs)

Assignments for some of these complexes have been reported. Lewis et al.<sup>4</sup> have assigned the  $\nu(\text{Co-Cl})$  i.r. active bands for the complexes  $\text{CoD}_2\text{Cl}_2 \cdot \text{Cl}$  and  $\text{CoD}_2\text{Cl}_2 \cdot \text{ClO}_4$  at 384±4 and 388  $\text{cm}^{-1}$  respectively by comparing the spectra of these complexes with those of their bromo analogs. However, Baylis recently reported the  $\nu(\text{Co-Cl})$  frequencies to be located at 324 and 325  $\text{cm}^{-1}$  respectively.<sup>11</sup> The support and weakness of both sets of assignments will now be discussed. The 384  $\text{cm}^{-1}$  band is discussed first.

A weak but definite band at about 387  $\text{cm}^{-1}$  is observed in the spectra of  $[\text{CoD}_2\text{Cl}_2]^+$  complexes including  $\text{CoD}_2\text{Cl}_2 \cdot \text{BF}_4$ . This absorption band is apparently both ligand (halogen) and metal sensitive since it is not observed in the bromo analogs nor in the nickel (III) diarsine chloro complexes.

The absorption band at about  $385 \text{ cm}^{-1}$  is dependent on the nature of the counter-anion as normally observed for  $\nu(\text{M-Cl})$  frequencies of compounds of this type. For example, the bands for the complexes  $\text{CoD}_2\text{Cl}_2 \cdot \text{Z}$ , where  $\text{Z} = \text{ClO}_4$ , and  $\text{BF}_4$  are  $388$  and  $389 \text{ cm}^{-1}$  respectively while for  $\text{Z} = \text{Cl}$  the band is at a lower energy as found for other diarsine compounds (Table 4).

Table 4

<u>M(III)</u>	<u><math>\nu(\text{M-Cl})(\text{cm}^{-1})</math></u>	<u>M(III)</u>	<u><math>\nu(\text{M-Cl})(\text{cm}^{-1})</math></u>	<u><math>\Delta\nu(\text{cm})</math></u>
Rh	349	Rh	358(?)	9
Tc	335	Tc	343	8
Ir	320	Ir	335	15
Re	317	Re	325	8

However, the difference between the bands at about  $384 \text{ cm}^{-1}$  for the complexes  $\text{CoD}_2\text{Cl}_2\text{X}$  where  $\text{X} = \text{Cl}$  and  $\text{ClO}_4$  ( $\Delta\nu = 4 \text{ cm}^{-1}$ ) is not as great as those exemplified above.

The 'mass effect' on the  $\nu(\text{M-Cl})$  vibrational frequencies on some diarsine complexes has been reported by Lewis et al.<sup>4</sup> For example, Table 5 shows that for complexes involving metals (Fe, Ru and Os) of the same charge and electron configuration, the frequency of the band falls as the mass of the metal increases.

Table 5

<u>MD<sub>2</sub>Cl<sub>2</sub>·ClO<sub>4</sub></u>		
<u>M(III)</u>	<u><math>\nu(M-Cl)</math> (cm<sup>-1</sup>)</u>	<u>AtW of M</u>
Fe	373	59
Ru	340	101
Os	322	190

Table 6 illustrates how the 'mass effect' on the  $\nu(M-Cl)$  vibrational frequencies of cobalt, rhodium and iridium complexes of the type  $MD_2Cl_2Z$ ,  $Z = Cl$  or  $ClO_4$ , strongly suggests that the  $\nu(Co-Cl)$  band lies in the region about  $384\text{ cm}^{-1}$ .

Table 6

<u>MD<sub>2</sub>Cl<sub>2</sub>·Cl</u>			<u>MD<sub>2</sub>Cl<sub>2</sub>·ClO<sub>4</sub></u>	
<u>M(III)</u>	<u><math>\nu(M-Cl)</math></u>	<u>At.Wt. of M</u>	<u>M(III)</u>	<u><math>\nu(M-Cl)</math></u>
Co	384	59	Co	388
Rh	349	103	Rh	358(?)
Ir	320	192	Ir	335

This absorption band is not very intense but quite distinct, especially in the spectrum recorded by the DM4. The low intensity of this band was not unexpected since the  $\nu(M-Cl)$  vibration for the  $FeD_2Cl_2$  complex (where the metal ion also has the  $d^6$  configuration) gives a weak band at  $349\text{ cm}^{-1}$ . The exact relationship between the low intensity

of these bands and the  $d^6$  electronic configuration of the metal ion is not very clear. However, it has been observed that in octahedral  $MX_6$  system (e.g.  $[PtCl_6]^{2-}$ ,  $[PtBr_6]^{2-}$ ) the intensity of the i.r. active bending metal-halogen mode is relatively greater than that of the antisymmetric stretching mode.<sup>21</sup> Woodward postulated that the unusual pattern was caused by  $d\pi-d\pi$  bonding from the  $(t_{2g})^6$  orbitals to vacant orbitals on the chlorine or bromine ligand.<sup>21</sup> The spectrum for the complex  $CoD_2Cl_2 \cdot ClO_4$  shows a very strong band at  $217 \text{ cm}^{-1}$ , and that for  $CoD_2Cl_2 \cdot Cl$  shows a strong band at  $209 \text{ cm}^{-1}$ . These are tentatively assigned to  $\nu(\text{Co-Cl})$  bending modes.

Further support of the band at about  $384 \text{ cm}^{-1}$  comes from consideration of the 'charge effect'. It is commonly observed that all other things being equal, increase in charge on the central metal ion gives an increase in the  $\nu(\text{M-X})$  frequency. For example, for a given electronic configuration (e.g.  $d^5$ ), the  $\nu(\text{M-X})$  frequency is higher for the complex (when comparing the complexes  $MD_2Cl_2 \cdot Cl$ ,  $M = Tc, Mo$ ) whose metal ion has a higher charge ( $Tc(\text{III})$ ,  $335 \text{ cm}^{-1}$ ;  $Mo(\text{II}) = 299 \text{ cm}^{-1}$ ;  $\Delta\nu = 36 \text{ cm}^{-1}$ ). Hence for  $d^6$  configuration and with  $\nu(\text{Fe-Cl})$  stretching frequency for the  $Fe(\text{II})D_2Cl_2$  equal to  $349 \text{ cm}^{-1}$  the  $\nu(\text{Co-Cl})$  stretching frequency for the complex  $CoD_2Cl_2Z$ ,  $Z = Cl$  or  $ClO_4$  is expected to be about  $385 \text{ cm}^{-1}$  (since  $349 + 36 = 385 \text{ cm}^{-1}$ ). This is further supported by the case of the complexes  $Ru(\text{II})D_2Cl_2$  and



$\text{RhD}_2\text{Cl}_2\cdot\text{Cl}$  (with  $d^6$  electronic configuration;  $\nu(\text{Ru-Cl}) = 316$ ;  $\nu(\text{Rh-Cl}) = 349$ ;  $\Delta\nu = 33 \text{ cm}^{-1}$ ). Increase in frequency gives an increase in force constant for the metal-halogen bond, assuming all other things being equal. The 'charge effect' may be accounted for by relating covalent character of the bond with the charge on the metal ion.

Baylis in her paper on the 'triatomic model' gave two assignments for the Co-Cl stretches. She reported that if the force constants determined from the  $[\text{Co}(\text{NH}_3)_5\text{X}]^{+2}$  calculations were used, the assignments for the complexes  $\text{Coen}_2\text{X}_2\cdot\text{X}$ ,  $\text{CoD}_2\text{X}_2\cdot\text{X}$  and  $\text{CoD}_2\text{X}_2\cdot\text{Y}$ , where X = Cl or Br, Y =  $\text{ClO}_4$ , would seem quite reasonable. If, however, the higher energy bands were chosen, a Co-Cl force constant of 2.00 md/A could be calculated for  $\text{Coen}_2\text{Cl}_2^+$ , from which a series of cobalt-halogen stretches could be calculated which would also correspond to bands in the spectra. Table 7 lists part of the data of Table 6 in Baylis' paper.

It was also reported that some bands in both series were fairly weak; for instance, the spectra of  $\text{CoD}_2\text{Cl}_2\cdot\text{Cl}$  and  $\text{CoD}_2\text{Br}_2\cdot\text{Br}$  were almost identical in the region 350 to 400K, where Rodley proposed that the Co-Cl stretch should be found. Baylis concluded that the model would indicate that the Co-Cl stretches were to be found in the 280 to 330K region of the spectrum, rather than from 350 to 390K.

Table 7

M-B Stretching Frequencies for trans-Dihalo Complexes

t-MA <sub>4</sub> B <sub>2</sub>	Source of f	f, md/A	$\nu(M-B)$ , cm <sup>-1</sup>	
			calc.	found
Co(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> .Cl		1.12		290
Co(NH <sub>3</sub> ) <sub>4</sub> Br <sub>2</sub> .Br		1.08		228
Coen <sub>2</sub> Cl <sub>2</sub> .Cl	Co(NH <sub>3</sub> ) <sub>5</sub> Cl <sup>+2</sup>	1.35	301	295
Coen <sub>2</sub> Br <sub>2</sub> .Br	Co(NH <sub>3</sub> ) <sub>5</sub> Br <sup>+2</sup>	1.35	234	230
CoD <sub>2</sub> Cl <sub>2</sub> .Cl	Co(NH <sub>3</sub> ) <sub>5</sub> Cl <sup>+2</sup>	2.00	326	324
CoD <sub>2</sub> Cl <sub>2</sub> .ClO <sub>4</sub>	Co(NH <sub>3</sub> ) <sub>5</sub> Cl <sup>+2</sup>	2.00	326	325
CoD <sub>2</sub> Br <sub>2</sub> .Br	Co(NH <sub>3</sub> ) <sub>5</sub> Br <sup>+2</sup>	2.00	232	243
Co(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> .Cl		1.67		353
Co(NH <sub>3</sub> ) <sub>4</sub> Br <sub>2</sub> .Br		2.11		318
Coen <sub>2</sub> Cl <sub>2</sub> .Cl		2.00		366
Coen <sub>2</sub> Br <sub>2</sub> .Br	Coen <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>	2.00	284	290
CoD <sub>2</sub> Cl <sub>2</sub> .Cl	Coen <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>	2.65	376	384 <sub>±4</sub>
CoD <sub>2</sub> Br <sub>2</sub> .Br	Coen <sub>2</sub> Br <sub>2</sub> <sup>+</sup>	2.65	276	391

Figures 1 and 5(2) clearly reveal that the ion CoD<sub>2</sub>Cl<sub>2</sub><sup>+</sup> has a distinct persistent band at about 387 cm<sup>-1</sup>. The ion CoD<sub>2</sub>Br<sub>2</sub><sup>+</sup> can also be seen to have its own characteristic band. Otherwise, the spectra for these two ions are very similar in the region from 230 to 400 cm<sup>-1</sup>. It was previously noted that these absorptions are not very intense.

To check the Co-Cl and the Co-Br assignments, the Raman spectra of the two complexes  $\text{CoD}_2\text{Cl}_2 \cdot \text{Cl}$  and  $\text{CoD}_2\text{Br}_2 \cdot \text{Br}$  in the region  $400 - 70 \text{ cm}^{-1}$  are recorded and examined. Figure 2 presents the Raman line spectra for these complexes and the frequencies of the tentatively assigned cobalt-halogen bands with their corresponding force constants are given in Table 3. The spectrum of either complex shows weak absorptions at 222, 254 and  $354 \text{ cm}^{-1}$ . These are probably intra-ligand bands. However, each of these compounds has its characteristic bands.

$\text{CoD}_2\text{Cl}_2 \cdot \text{Cl}$  shows two distinct strong absorptions at 275 and  $288 \text{ cm}^{-1}$  respectively. The band at  $254 \text{ cm}^{-1}$  is more intense than that for the bromo analogue; the higher intensity probably arises through the superimposition of vibrational bands. The  $275 \text{ cm}^{-1}$  band is the most prominent Raman absorption observed and is markedly absent in the bromo complex. The force constant calculated for this band on the assumption that it arises from the cobalt-chlorine symmetric vibration is equal to 1.44 md/A (that for the cobalt-chlorine anti-symmetric vibration is 2.56 md/A). The ratio of the force constants  $k_{v_s}(\text{Co-Cl})/k_{v_a}(\text{Co-Cl})$  is equal to 0.56.

The characteristic absorptions for the complex  $\text{CoD}_2\text{Br}_2 \cdot \text{Br}$  occur at 182 and  $140 \text{ cm}^{-1}$  respectively. Though both bands are comparatively strong, the higher energy absorption is more intense and is assigned to the Raman active cobalt(III)-bromine vibration. The corresponding force constant calculated for the  $182 \text{ cm}^{-1}$  band is 0.88 md/A.

The ratio of these frequencies,  $\nu_s(\text{Co(III)-Br})$ ,  $\nu_s(\text{Co(III)-Cl})$ , is equal to about 0.66 which is not significantly different from that (0.60) calculated from the frequencies of the i.r. active  $\text{Co(III)-X}$  vibrations. However, it must be emphasized at this stage that the ratio employed is an empirical relationship. Examination of results derived from the vibrational spectra of the complexes  $\text{CoX}_4^{2-}$ , where  $X = \text{Cl}$  and  $\text{Br}$ , shows that the difference between the corresponding ratios is of about the same magnitude as that found for the diarsine compounds.

Table 8

Compound	I.R.	R	$\nu_s(\text{Co-Br})/\nu_s(\text{Co-Cl})$	$\nu_a(\text{Co-Br})/\nu_a(\text{Co-Cl})$
$\text{CoCl}_4^{2-}$	245	269	0.63	0.60
$\text{CoBr}_4^{2-}$	146	166		
$\text{CoD}_2\text{Cl}_2 \cdot \text{Cl}$	384	275	0.66	0.60
$\text{CoD}_2\text{Br}_2 \cdot \text{Br}$	227	182		

The results above suggest the assignments of the frequencies to the i.r. active and the Raman active cobalt-halogen bands for  $\text{CoD}_2\text{Cl}_2 \cdot \text{Cl}$  and  $\text{CoD}_2\text{Br}_2 \cdot \text{Br}$  are reasonably accurate.

To check whether the expressions (relating the frequency of a given type of vibration to the corresponding force constant and the masses of the atoms of interest) given by

the 'simple triatomic model' for the  $D_{4h}$  system is applicable to the complexes  $\text{CoD}_2\text{Cl}_2 \cdot \text{Cl}$  and  $\text{CoD}_2\text{Br}_2 \cdot \text{Br}$ , the frequencies obtained from the Raman spectral studies are used in the relevant expression to give the corresponding force constants which are then introduced in the proper expression to give the frequencies of the corresponding i.r. active vibrations. The formulae employed in these calculations are presented below, and the results are tabulated in Table 9:

FORMULAE RELATING VIBRATIONAL FREQUENCY AND CORRESPONDING FORCE CONSTANT

$$\nu_s = K \sqrt{\frac{k\nu_s}{m_{\text{CoX}}}}, \quad \nu_a = K \sqrt{k\nu_a \frac{1}{m_{\text{CoX}}} + \frac{1}{m_{\text{Co}} + 4m_X}}$$

Since there is no clear-cut relationship between the force constants of the symmetric and the anti-symmetric vibrations for a given bond, it is assumed here that both are of the same magnitude.

Table 9

X	$\nu_s(\text{Co-X})(\text{cm}^{-1})$	$k(k_{\nu_s} = k_{\nu_a})(\text{md}/\text{A}^\circ)$	$\nu_a(\text{Co-Br})(\text{cm}^{-1})$	
			Calc.	Obs.
Cl	275	1.66	311	384
Br	182	1.55	218	227

The results above show that the calculated cobalt(III)-bromine frequency is only  $9 \text{ cm}^{-1}$  below that observed, whereas there is a rather large difference ( $70 \text{ cm}^{-1}$ ) between the calculated and the observed frequency of the cobalt(III)-chlorine vibration. The expression used for the symmetric vibration assumes that the metal has no influence on this motion. Results given in Table 10 show that inclusion of the mass of the metal (cobalt) in the expression improves the overall agreement between the calculated and the observed frequencies of the i.r. active cobalt-halogen vibrations.

Table 10

<u>X</u>	<u><math>\nu(\text{Co-X})(\text{cm}^{-1})</math></u>	<u><math>k(\text{md/\AA})</math></u>	<u><math>\nu(\text{Co-X})(\text{cm}^{-1})</math></u>	
			<u>calc.</u>	<u>obs.</u>
Cl	275	2.20	360	384
Br	182	1.35	204	227

Modified expression: 
$$\nu_s = K \sqrt{k \frac{2}{m_{\text{Co}} + m_X}}$$

Hence it may be concluded that the assignment of the i.r. active Co-Cl vibrations of the complex  $\text{CoD}_2\text{Cl}_2 \cdot \text{Cl}$  to the absorption at about  $384 \text{ cm}^{-1}$  is further supported by Raman spectral studies and application of a modified version of the 'triatomic model'.

## 2. Nickel(III) Complexes

Figure 3 presents the far infrared spectra of the diarsine nickel(III) complexes  $\text{NiD}_2\text{X}_2 \cdot \text{X}$  and  $\text{NiD}_2\text{X}_2 \cdot \text{ClO}_4$ , where X = Cl or Br. The characteristic absorption bands for these complexes are given below:

$\text{NiD}_2\text{Cl}_2 \cdot \text{ClO}_4$	261(vs)	209(m)		142(w)	128(w)	97(m)
$\text{NiD}_2\text{Cl}_2 \cdot \text{Cl}$	239(vs)	198(m)	180(w)	167(w)	104(s)	96(s)
$\text{NiD}_2\text{Br}_2 \cdot \text{ClO}_4$	221(w)	192(2)	185(s)	171(w)		127(m)
$\text{NiD}_2\text{Br}_2 \cdot \text{Br}$		190(vs)	178(sh)	156(w)		129(w)

The frequencies of the i.r. active nickel-halogen vibrations and their corresponding force constants calculated using the triatomic model are listed in Tables 1 and 2.

Lewis et al.<sup>4</sup> have reported values for the Ni-Cl frequencies of the complexes  $\text{NiD}_2\text{Cl}_2 \cdot \text{Cl}$  and  $\text{NiD}_2\text{Cl}_2 \cdot \text{ClO}_4$  to be 238 and 260  $\text{cm}^{-1}$  respectively. It was noted that although the value of 238  $\text{cm}^{-1}$  for  $\text{NiD}_2\text{Cl}_2 \cdot \text{Cl}$  is about 135  $\text{cm}^{-1}$  lower than the  $\nu(\text{Co-Cl})$  value for  $\text{CoD}_2\text{Cl}_2 \cdot \text{Cl}$ , both these complexes have the same powder patterns. The corresponding perchlorate compounds  $\text{CoD}_2\text{Cl}_2 \cdot \text{ClO}_4$  and  $\text{NiD}_2\text{Cl}_2 \cdot \text{ClO}_4$ , which have  $\nu(\text{M-Cl})$  absorptions differing by 128  $\text{cm}^{-1}$  were reported to give similar powder patterns and single-crystal X-ray photographs, which show that they have the same structure with a slight difference in one of the unit cell dimensions.

The bands assigned to the i.r. active anti-symmetric Ni(III)-Cl vibrations in the compounds  $\text{NiD}_2\text{Cl}_2\cdot\text{Cl}$  and  $\text{NiD}_2\text{Cl}_2\cdot\text{ClO}_4$  are observed to be very strong in intensity and to be comparatively sharp in band-width, which is in sharp contrast to the band properties of the corresponding absorptions in the analogous cobalt complexes. Since the characteristics (other than frequency) of these cobalt-halogen (Co-Cl, Co-Br) bands are largely unaffected by the type of halogen (Cl or Br), the same is expected of the nickel-halogen absorptions. Hence the nickel(III)-bromine bands should neither be weak nor broad.

The complexes  $\text{NiD}_2\text{Br}_2\cdot\text{Br}$  and  $\text{NiD}_2\text{Br}_2\cdot\text{ClO}_4$  give strong absorptions at 190 and 192  $\text{cm}^{-1}$  respectively. These stretches are assigned to the antisymmetric i.r. active Ni(III)-Br vibrations. It is possible that these strong bands result from the superimposition of these Ni-Br stretching modes with Ni-As bending or antisymmetric vibrations since weak absorptions occur at about 190  $\text{cm}^{-1}$  for the analogous chloro compounds.

The ratio  $\nu_a(\text{Ni-Br})/\nu_a(\text{Ni-Cl})$  for the complexes  $\text{NiD}_2\text{X}_2\cdot\text{X}$  and  $\text{NiD}_2\text{X}_2\cdot\text{ClO}_4$  are 0.80 and 0.74 respectively, whose magnitude is quite close to that (0.77) given for octahedral structures.<sup>5</sup>

The force constant calculated for the i.r. active anti-symmetric nickel-halogen vibration of the complexes



$\text{NiD}_2\text{Cl}_2\cdot\text{Cl}$ ,  $\text{NiD}_2\text{Cl}_2\cdot\text{ClO}_4$ ,  $\text{NiD}_2\text{Br}_2\cdot\text{Br}$  and  $\text{NiD}_2\text{Br}_2\cdot\text{ClO}_4$  are 0.95, 1.18, 1.16 and 1.16 md/A respectively. The magnitude of these values suggests that the strength of the nickel-halogen bond in these compounds is about the same. Here, as in other calculations involving the 'triatomic model' no consideration is taken of the type of counter-ion.

Little attention has been given to the use of intensity to derive information about the nature of the metal-ligand bond. So far, only relative intensities of certain i.r. active spectral bands have been studied. For example, Shimanouchi found in a study of amino transition metal complexes that as the metal-nitrogen force constant decreases the corresponding band increases in intensity.<sup>23</sup> The observation was rationalised by the postulate that the ionic character of the M-N bond increases as the force constant decreases and the increased ionic character leads to a larger value for the transition moment. If increase in ionic character of a bond implies weakening and hence lengthening of the bond, then diffraction studies would confirm this. Although crystallographic studies of the series of diarsine complexes  $\text{M(III)D}_2\text{Cl}_2\cdot\text{Cl}$  are not extensive enough to prove that there is a definite relation between intensity of ionic character and length of metal-chlorine bond, investigation of data available is of much interest.

The bands assigned to the i.r. active antisymmetric metal(III)-chlorine vibration for the nickel complexes is relatively more intense than those assigned for the cobalt analogues. This coupled with the observation that the nickel complex gives a frequency and the corresponding force constant both of which are significantly lower than those for the cobalt compound strongly suggests that the metal-halogen bond is weaker for the nickel compound, which is expected to be reflected in the lengthening of the nickel-chlorine bond. Structural studies of the complexes  $\text{NiD}_2\text{Cl}_2 \cdot \text{Cl}$  and  $\text{CoD}_2\text{Cl}_2 \cdot \text{Cl}$ <sup>34</sup> have allowed comparison of their metal-chlorine bond (Ni(III)-Cl, 2.43; Co(III)-Cl, 2.22A), which supports the inference made from analysis of their vibrational spectra.<sup>4</sup> However, these data are not sufficient to allow a detailed description of the nature of the metal-halogen bond. The effect of the change in electronic configuration ( $d^6 \rightarrow d^7$ ) on the metal-chlorine bond can be studied in greater detail by employing magnetic methods. Nevertheless, it is hoped that results of similar studies on the  $d^7$  and  $d^8$  complexes,  $\text{Co(II)D}_2\text{Cl}_2$  and  $\text{Ni(II)D}_2\text{Cl}_2$ , will elucidate the nature of the metal-halogen bond in diarsine complexes.

### 3. M(II)D<sub>2</sub>X<sub>2</sub> (M = Co, Ni; X = Cl, Br) Complexes

Crystallographic and infrared spectroscopic (450 - 200 cm<sup>-1</sup>) studies of the diarsine complexes CoD<sub>2</sub>Cl<sub>2</sub>, CoD<sub>2</sub>Br<sub>2</sub>, NiD<sub>2</sub>Cl<sub>2</sub> and NiD<sub>2</sub>Br<sub>2</sub> have been reported.<sup>13</sup>

The X-ray powder photographs indicate that the complexes CoD<sub>2</sub>Cl<sub>2</sub> and NiD<sub>2</sub>Cl<sub>2</sub> are isostructural. Single-crystal X-ray studies have provided evidence for the trans-configuration in these two complexes. The space group and cell dimensions of NiD<sub>2</sub>Br<sub>2</sub>, isomorphous with NiD<sub>2</sub>Cl<sub>2</sub>, have been determined. The space group P2<sub>1</sub>/c, with two molecules per unit cell, can accommodate either six coordinate trans-molecules or planar NiD<sub>2</sub><sup>2+</sup> and Br<sup>-</sup> ions.

Recently, Kakazai and Melson described their studies of nickel(II) and cobalt(II) complexes with two and three molecules of the aromatic diamines, o-phenylenediamine, 1,8-diaminonaphthalene, and 2-2'-diaminobiphenyl.<sup>6</sup> The complexes have been characterised by magnetic and infrared and visible spectral measurements. Those complexes containing two molecules of diamine have been shown to have D<sub>4h</sub> symmetry. These diamino compounds are presumed to be structurally very similar to the corresponding diarsine complexes, and it is hoped that comparison of the frequencies of the i.r. active antisymmetric metal(II)-anion of the structural analogues lends support to the present assignments and elucidates the nature of the bonding in the diarsine complexes.

Figure 4 represents the far-infrared spectra of the diarsine compounds, and the frequencies of the tentatively assigned i.r. active asymmetric metal-halogen bands are given in Table 1 together with the corresponding force constants.

The complexes  $\text{CoD}_2\text{Cl}_2$ ,  $\text{CoD}_2\text{Br}_2$ ,  $\text{NiD}_2\text{Cl}_2$  and  $\text{NiD}_2\text{Br}_2$  give almost identical spectra above  $200\text{ cm}^{-1}$ . They show a band of medium intensity at  $99\text{ cm}^{-1}$ . It probably arises from some intra-diarsine ligand vibration. However, they exhibit characteristic metal and anion sensitive absorptions in the far-infrared region where some authors have reported skeletal vibrations to exist. The assignment of the i.r. active antisymmetric metal-halogen vibrations in these diarsine complexes is described below.

The spectrum of the complex  $\text{CoD}_2\text{Cl}_2$  shows two distinct absorptions of high intensity at  $158$  and  $152\text{ cm}^{-1}$  respectively. Both are absent in the bromo analogue, but a weak band is present in the spectrum of the compound  $\text{NiD}_2\text{Cl}_2$  at about  $150\text{ cm}^{-1}$ . Hence, the band with frequency  $158\text{ cm}^{-1}$  is assigned to the i.r. active antisymmetric vibration. So far, no vibrational spectral data is available for the complex  $\text{trans-Co}(\text{opda})_2\text{Cl}_2$  that would be of use as a check on the above assignment since this compound is structurally similar to  $\text{CoD}_2\text{Cl}_2$ . However, an analogous diamino complex  $\text{Co}(\text{dan})_2\text{Cl}_2$  has been spectrally characterised. The frequency

( $132\text{ cm}^{-1}$ ) of its cobalt-chlorine band is  $26\text{ cm}^{-1}$  lower than that assigned to the diarsine analogue. Comparison of frequencies should show how the different chelating ligands (e.g., diarsine, 1,8-diaminonaphthalene) affect the cobalt-chlorine bond strength and hence the distribution of the unpaired electron of the cobalt (II) ion. Such information could also be obtained by comparing force constants for these frequencies. If the force constants calculated by employing the 'simple triatomic model' were to give a measure of the strength of the bond, then comparison of force constants should give more reliable conclusions.

The force constants calculated from the Co(II)-Cl frequency of the complexes  $\text{Co}(\text{dan})_2\text{Cl}_2$  and  $\text{CoD}_2\text{Cl}_2$  are 0.40 and 0.43 md/A respectively. Either method of comparison shows that the Co(II)-Cl bond is weaker in the 1,8-diaminonaphthalene compound. This indicates diamino ligand increases repulsion in the bond, probably by enhancing localisation of the unpaired electron of cobalt(II) ion into some antibonding orbital.

For the complex  $\text{CoD}_2\text{Br}_2$ , the Co(II)-Br band is assigned to the sharp intense, anion and metal dependent absorption at  $107\text{ cm}^{-1}$ . The frequencies of the corresponding Co(II)-Br vibration in  $\text{Co}(\text{opda})_2\text{Br}_2$  and  $\text{Co}(\text{dan})_2\text{Br}_2$  are 120 and  $198\text{ cm}^{-1}$  respectively. The force constant calculated for the characteristic band in the spectrum of  $\text{CoD}_2\text{Br}_2$  (0.29 md/A) is

markedly close to that for  $\text{Co}(\text{opda})_2\text{Br}_2$  (0.28 md/Å), and is higher than that for  $\text{Co}(\text{dan})_2\text{Br}_2$  (0.23 md/Å). The small differences in the band parameters suggest close similarity in the cobalt-bromine bonding in these three compounds. The ratio,  $\nu(\text{M-Br})/\nu(\text{M-Cl})$ , for the cobalt complexes with diarsine and 1,8-diaminonaphthalene chelating ligand are 0.68 and 0.82 respectively. Though the magnitudes of these values have about the same deviation (0.06) from the value (0.77) quoted in the literature, they differ in sign. Spatial or electronic interaction may cause significant distortion and hence, the deviation.

Comparison of the spectra for the four diarsine complexes reveals that each of the nickel compounds has its own characteristic absorption which is both anion and metal dependent. The spectrum of  $\text{NiD}_2\text{Cl}_2$  gives a comparatively strong band at  $106 \text{ cm}^{-1}$  which is assigned to the i.r. active antisymmetric vibration. The corresponding band for the amino complexes  $\text{Ni}(\text{opda})_2\text{Cl}_2$  and  $\text{Ni}(\text{dan})_2\text{Cl}_2$  occur at 220 and  $144 \text{ cm}^{-1}$  respectively.<sup>6</sup> The force constants calculated for these three chloro compounds are 0.20, 0.63 and  $0.27 \text{ md}/\text{Å}^0$  respectively. This certainly shows that the Ni-Cl bond for the diarsine complex is about three times weaker than that of the structural analog  $\text{Ni}(\text{opda})_2\text{Cl}_2$  (assuming that these force constants give a reasonable measure of the strength of the bond).

The Ni-Br absorption for  $\text{NiD}_2\text{Br}_2$  occurs at  $64 \text{ cm}^{-1}$ . The very low energy of this band suggests marked weakening and hence, lengthening of the Ni-Br bond. The amino complexes  $\text{Ni}(\text{opda})_2\text{Br}_2$  and  $\text{Ni}(\text{dan})_2\text{Br}_2$  give much higher energy Ni-Br bands ( $135$  and  $144 \text{ cm}^{-1}$  respectively). The marked weakness of the Ni-Br bond in the diarsine compound is well illustrated by comparing the force constants ( $0.14$ ,  $0.36$  and  $0.26 \text{ md/\AA}$ ) of these complexes. Structural analysis of  $\text{NiD}_2\text{Br}_2$  is expected to reveal significant tetragonal distortion or departure from octahedral structure.

Kakazai and Melson<sup>6</sup> noted in their studies of the diamino complexes that the positions of  $\nu(\text{M-X})$  for all the nickel complexes are of the order of  $10 \text{ cm}^{-1}$  higher than the corresponding cobalt(II) complexes as expected from the Irving-Williams order of stabilities. In contrast, the frequencies of the M-X vibrations in the nickel-diarsine compounds are about  $40 \text{ cm}^{-1}$  lower than those of the corresponding cobalt(II) diarsine compounds. Discussion of this observation is given in Section 5 (Bonding in Diarsine Complexes).

For the four  $\text{M}(\text{II})\text{D}_2\text{X}_2$  ( $\text{M}=\text{Co}, \text{Ni}$ ;  $\text{X}=\text{Cl}, \text{Br}$ ) complexes discussed in this section, only one  $\nu(\text{M-X})$  vibration is detected, suggesting that these compounds have the  $\text{trans}(\text{D}_{4h})$  configuration. This is in good agreement with the x-ray powder and crystal studies.

4. MD<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> and MD<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>, M = Co, Ni

Rodley and Smith<sup>15</sup> have reported and interpreted the infrared data for the oxyanions in trans-MD<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> and MD<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>, M = Ni, Co, in terms of the association of the anions with the metal ions. Kakazai and Melson and other workers have described their studies on amino analogues (M(opda)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>, M(opda)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>, M(dan)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>, and M(dan)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>) of these complexes. The results from the above sources are considered in the discussion of the assignments made to the diarsine compounds.

The low i.r. spectra of these complexes are presented in Figure 6 and the frequencies of the bands assigned to the i.r. active antisymmetric metal-oxygen vibrations with the corresponding force constants are tabulated in Table 1.

Comparison of the spectra for the diarsine perchlorates shows that the spectrum of the cobalt compound shows a strong absorption at 103 cm<sup>-1</sup> which is assigned to the cobalt-oxygen asymmetric stretch. It was noted that the nickel analogue has no characteristic absorption except for a very weak band at 114 cm<sup>-1</sup> which probably arises from combination of bands for vibrations. The absence of the nickel-oxygen absorption indicates very weak bonding between the perchlorate anion and the metal ion.

The above observations are in line with the results obtained from the studies of the oxyanions. It was



postulated that if the degree of the splitting of the  $T_2$  band of perchlorate anion were taken as a measure of the strength of perchlorate bonding (with the assumption that the crystal lattice effect is negligible for isomorphous complexes where the site symmetry remains the same), then the values for the isomorphous complexes  $NiD_2(ClO_4)_2$  and the monoclinic form of  $CoD_2(ClO_4)_2$ , 30 and 82  $cm^{-1}$  respectively, suggests that the perchlorate ion is quite strongly coordinated in the cobalt complex.

Moore et al.<sup>28</sup> observed in their spectral studies of the perchlorate anions in the amino analogues,  $Co(opda)_2(ClO_4)_2$  and  $Co(dan)_2(ClO_4)_2$ , that the oxyanions all showed strong broad absorptions indicative of uncoordinated perchlorate ions. This was confirmed by further studies which showed that the amino compounds  $(M(opda)_2(ClO_4)_2, M(dan)_2(ClO_4)_2; M = Co, Ni)$  gave no bands characteristic of metal-anion absorptions.

The low i.r. spectra of the nitrates  $CoD_2(NO_3)_2$  and  $NiD_2(NO_3)_2$  show that these complexes are characterised by the strong absorptions at 121 and 100  $cm^{-1}$  respectively, which are assigned to the i.r. active metal-oxygen vibration. The corresponding force constant calculated from these frequencies are 0.40 and 0.27 md/A respectively. Either set of parameters strongly suggests weaker nitrate coordination in the nickel complex, which agrees well with the results obtained from spectral studies of the nitrate anions.

It was concluded in the spectral analysis of the oxy-anions that bonding is stronger in the cobalt( $d^7$ ) complexes than in the corresponding nickel ( $d^8$ ) compounds, which is substantiated by the lower magnitude of the frequency and force constant for the nickel-oxygen vibrations.

Nitrogen and arsenic are well-established to be electron donors especially to class b elements (which includes Co), and it would be of interest to check how the difference between their electron donating power is reflected in the bonding between the metal ion and the anion.

The fluoborate diarsine complex,  $\text{CoD}_2(\text{BF}_4)_2$  is included in this section because it is assumed that close similarity exists between the mode of coordination of the fluoborate anion and that of the oxyanions to the cobalt metal centre. These three anions, all of  $\text{AB}_4$  structure, are coordinated to the metal atom via B atom(s). The infrared spectrum of yellow  $\text{CoD}_2(\text{BF}_4)_2$  was recorded over the range  $2000-40 \text{ cm}^{-1}$  at room temperature. Spectra were obtained from 2000 to 400 with i.r. spectrometer 337, from 500 to 200 with DM4 i.r. spectrophotometer. It was initially hoped that comparison of these results with those found for  $\text{CoD}_2\text{Cl}_2 \cdot \text{BF}_4$ , the diarsine ligand, and  $\text{O}_2^+\text{BF}_4^-$  (dioxygenyl fluoborate) would prove the presence of the fluoborate ion ( $\text{BF}_4^-$ ), and show whether coordination of this anion to the cobalt(II) centre exists.

Although the spectrum of  $\text{CoD}_2(\text{BF}_4)_2$  above  $500 \text{ cm}^{-1}$  shows coordinated diarsine bands together with some of the

fluoborate absorptions which suggests the presence of  $\text{BF}_4^-$ . Ambiguity arises in some regions where important  $\text{BF}_4^-$  bands (e.g.  $\nu_1$ ) are not easily detected, probably because of the superposition of strong diarsine ligand bands. However, the low frequency spectrum gives not only absorptions which characterize the  $\text{BF}_4^-$  anion, but also additional bands, one of which is attributed to the i.r. active antisymmetric vibration. For these reasons, only the bands in the low i.r. region are considered. The spectrum of  $\text{CoD}_2(\text{BF}_4)_2$  in this range is presented in Figure 5.

Loos et al.<sup>29</sup> have described the infrared spectrum of dioxygenyl fluoborate in the region  $2000-300 \text{ cm}^{-1}$ . In their description of the fundamental vibrations of  $\text{BF}_4^-$ , the isolated  $\text{BF}_4^-$  ion was reported to have  $T_d$  symmetry and nine fundamental modes of vibration. These include a doubly degenerate deformation,  $\nu_2$ , which is Raman active only. Goubeau and Bues<sup>30</sup> have previously observed the doubly degenerate deformation only in the Raman spectrum of  $\text{KBF}_4$  at  $353 \text{ cm}^{-1}$ . However, infrared spectra of  $\text{O}_2^+\text{BF}_4^-$  have shown the presence of two weak bands at  $374$  and  $362 \text{ cm}^{-1}$ . It was noted that if the crystal symmetry is lower than that of the isolated ion, transitions normally forbidden may now appear as a consequence of the reduced symmetry present at the site of the ion. Hence the two absorptions were assigned to the  $\nu_2$  vibration.

$\text{CoD}_2(\text{BF}_4)_2$  gives two very strong absorptions at 374 and 366  $\text{cm}^{-1}$  which are both almost the same in intensity. The nature of these bands indicates the presence of two absorptions contributed by  $\text{BF}_4^-$  which are superimposed onto the coordinated diarsine bands at about 374 and 366  $\text{cm}^{-1}$ , and the former pair of bands are assigned to the doubly degenerate deformation,  $\nu_2$ , of the  $\text{BF}_4^-$  anion. This suggests lower crystal symmetry which probably arises from hydrogen-bonding or from coordination of the anion to cobalt atom.

Comparison of the spectra of  $\text{CoD}_2(\text{BF}_4)_2$  and  $\text{CoD}_2\text{Cl}_2 \cdot \text{BF}_4$  shows that the former gives two additional bands in the 280-350  $\text{cm}^{-1}$  region (Figure 5). These may be associated with vibrational modes of the  $\text{M}=\text{BF}_4$  grouping. The 314  $\text{cm}^{-1}$  band is tentatively assigned to the i.r. active antisymmetric  $\text{Co(II)}-\text{F}$  vibration. This assignment is supported by comparison of the spectrum of  $\text{CoD}_2(\text{BF}_4)_2$  with those of the diarsine complexes described in the previous section which shows that the 314  $\text{cm}^{-1}$  absorption characterises the fluoborate complex. The presence of only one anion and metal dependent absorption for  $\text{CoD}_2(\text{BF}_4)_2$  would indicate that the complex has trans ( $\text{D}_{4h}$ ) configuration. The force constant calculated from the frequency of the cobalt-fluorine vibration is 2.64 md/A. Both parameters, frequency and force constant, suggest the cobalt-fluorine(fluoborate) bond is much stronger than the cobalt-halide bonds in other cobalt(II)

diarsine complexes. This may be accounted for by the small mass of the fluorine atom and its high electronegativity.

## 5. Bonding in Diarsine Complexes

Diarsine complexes of the first row transition elements with  $d^6$ ,  $d^7$  and  $d^8$  configurations have been studied by methods to investigate mainly the bonding in these compounds.<sup>4,16-20,31,32</sup> The results of these studies are briefly discussed below, and any correlation between them and those obtained from the i.r. data reported in this thesis are considered.

Feltham and Silverthorn<sup>32</sup> described visible and near-infrared spectral studies of several diarsine complexes of Cr(III), Co(III) and Fe(III) both in solution and in the solid state. The electronic transitions which were observed were found to be d-d transitions and were assigned on the basis of a ligand field model. It was also reported that an evaluation of the ligand field parameters,  $Dq$ ,  $B$  and  $C$  for these compounds indicated that there was considerable amount of  $\sigma$  bonding between the metal ions and diarsine but there was no evidence for  $d_{\pi}-d_{\pi}$  bonding between the metal and the ligand in these complexes. This work was concentrated largely on the  $d^6$  system of diarsine complexes, and no detailed description is given on metal-anion bonding.

Though the electronic method has useful applications, especially in determining energies of d-d transitions and

in allowing semiquantitative inference of the extent of electron delocalisation in metal complexes, it is not suitable for detailed studies. Hence, some other experimental technique must be used to measure the electron density distribution and to find the orbitals corresponding to this electron density.

Methods which make use of magnetic properties of unpaired electrons are now commonly employed in the study of d electrons of the transition metals in certain paramagnetic complexes. Neutron diffraction is the most direct technique which is in principle capable of giving sufficiently accurate measurements of unpaired electron densities. However, only paramagnetic (electron) resonance studies on diarsine complexes with  $d^7$  electron configuration have been reported<sup>19,20,31</sup>.

Corjava and Nordio<sup>20</sup> described in their paper on e.s.r. spectra of  $\text{Ni(III)D}_2\text{Cl}_2 \cdot \text{ClO}_4$  how they arrived at their tentative assumption that the unpaired electron of the nickel centre is placed in an antibonding  $\pi$  orbital. It was assumed to be predominantly on the ligand, and to result from mixing of the vacant 4d orbitals of the arsenic atoms with the nickel orbitals. It was noted that the presence of a  $d\pi$  molecular orbital had been suggested by the shortening of the Pd-As or Pt-As bond lengths in similar diarsine complexes, and that the absence of chlorine hyperfine interaction may

arise from the electron delocalisation on 4d arsenic orbitals. Two other e.s.r. spectral studies on the cation  $\text{Ni(III)D}_2\text{Cl}_2^+$  have been reported<sup>19,31</sup>. It is of interest that although the three studies give very similar descriptions of the three g pattern of the powder spectrum of  $\text{NiD}_2\text{Cl}_2^+$ , they give different interpretations of the electronic structure. Further, each paper differs in its report on the localisation of the unpaired electron on the metal-anion bond.

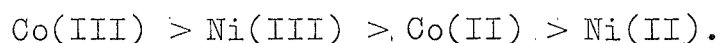
Kriesman et al.<sup>19</sup> included in their studies the spectrum of the uncomplexed diarsine radical cation which was reported to give a g pattern very similar to that of  $\text{NiD}_2\text{Cl}_2^+$ . It was inferred that the unpaired electron in the complex is derived from that in the radical cation itself. The authors proposed a 'metal-stabilised radical' model for the ground state of  $\text{NiD}_2\text{Cl}_2^+$ .

It was suggested that the lone pairs on the As atoms give rise to two delocalised orbitals ( $\sigma^+, \sigma^-$ ), the higher of which bears the unpaired electron in diars<sup>+</sup>. As the lone-pair orbitals of the two diarsine ligands give four symmetry orbitals, the highest filled level, ( $b_{1g}(1)$ ), is of proper symmetry to combine with the metal  $b_{1g}(xy)$  orbitals. Hence, the molecular orbital bearing the unpaired cation electron

in the complex is thus directly derived from the ligand radical.

The third and most recent paper<sup>31</sup> describes two series of  $d^7$  complexes,  $NiD_2X_2^+$  and  $CoD_2X_2$ , where  $X = Cl, Br,$  and  $NCS$ . Only the nickel halogen complexes exhibit a three g pattern, while the thiocyanate gives an almost isotropic pattern. The cobalt compounds, apparently isoelectronic with the corresponding analogues, give e.s.r. spectra characteristic of axial symmetry. Large isotropic splittings are observed for  $^{35,37}Cl,$   $^{79,81}Br,$  which indicate that the two halogens are bonded to the central atom. This proves six-coordination, and shows that unpaired electron density is present on the axial ligands.

Examination of the frequencies assigned to the metal-anion vibrations shows that for either oxidation state (III or II) the cobalt-anion bond is stronger or more stable than that of the corresponding nickel complex. Hence, for a given anion the order of stabilities is



The effect of filling of the  $e_g$  electron levels on the metal-halogen bond is very noticeable when the frequency of the i.r. active metal-chlorine vibration of the following diarsine complexes;  $Co(d^6)D_2Cl_2Cl,$   $Ni(d^7)D_2Cl_2Cl,$   $Co(d^7)D_2Cl_2$  and  $Ni(d^8)D_2Cl_2,$  are compared (Table 11).



Table 11

<u>Complex</u>	<u>CoD<sub>2</sub>Cl<sub>2</sub>Cl</u>	<u>NiD<sub>2</sub>Cl<sub>2</sub>Cl</u>	<u>CoD<sub>2</sub>Cl<sub>2</sub></u>	<u>NiD<sub>2</sub>Cl<sub>2</sub></u>
$\nu(\text{M-Cl})(\text{cm}^{-1})$	384	239	158	107
Oxidation State	III	III	II	II
Electron configuration	d <sup>6</sup>	d <sup>7</sup>	d <sup>7</sup>	d <sup>8</sup>

If the effect of the differing oxidation states is removed, then more reliable comparison of the frequencies may be obtained. Data on the complexes with partially filled  $t_{2g}$  electron levels show that for a given electronic configuration change in oxidation state (III  $\rightarrow$  II) lowers the metal-anion frequency by about  $35 \text{ cm}^{-1}$  (section 1, p. 15-16), whereas, here the lowering is more pronounced ( $\Delta\nu = 85 \text{ cm}^{-1}$ ; Ni(O.S., III; d<sup>7</sup>), 239; Co(O.S., II; d<sup>7</sup>),  $158 \text{ cm}^{-1}$ ). The corresponding change for the bromo analogues is about  $70 \text{ cm}^{-1}$ .

Table 12

<u>Complex</u>	<u>CoD<sub>2</sub>Cl<sub>2</sub>Cl</u>	<u>NiD<sub>2</sub>Cl<sub>2</sub>Cl</u>	<u>CoD<sub>2</sub>Cl<sub>2</sub></u>	<u>NiD<sub>2</sub>Cl<sub>2</sub></u>
Electron configuration	d <sup>6</sup>	d <sup>7</sup>	d <sup>7</sup>	d <sup>8</sup>
$\nu(\text{M-Cl})(\text{cm}^{-1})$	300	155	155	105

The 'modified' frequencies given in the above Table 12 show that introduction of the first electron (d<sup>6</sup>  $\rightarrow$  d<sup>7</sup>) into the  $e_g$  electron orbitals gives a drop of about  $145 \text{ cm}^{-1}$  ( $300-155 \text{ cm}^{-1}$ ), whereas that of the second (d<sup>7</sup>  $\rightarrow$  d<sup>8</sup>) lowers

the frequency by about  $50 \text{ cm}^{-1}$  ( $155 - 105 \text{ cm}^{-1}$ ). Since the  $d^8$  complex is diamagnetic, the difference between these changes in frequencies suggests that pairing of the two  $e_g$  electrons stabilises the M-Cl bond by about  $95 \text{ cm}^{-1}$  ( $145 - 50 \text{ cm}^{-1}$ ). The magnitude of the parameters I.E. and Pr.E. (Introduction of Electron, and Pairing of Electrons in  $t_{2g}$  energy levels respectively) indicates that the orbitals into which the  $e_g$  electrons are accommodated are strongly anti-bonding in character. This is strongly supported by comparison of the M-Cl bond lengths for  $\text{CoD}_2\text{Cl}_2\text{Cl}$  <sup>16</sup> and  $\text{NiD}_2\text{Cl}_2\text{Cl}$  <sup>19</sup> ( $2.22$  and  $2.43\text{\AA}$  respectively). It is hoped that structural studies on  $\text{CoD}_2\text{Cl}_2$  and  $\text{NiD}_2\text{Cl}_2$  would be attempted in the near future, and it is predicted that the Co(II)-Cl bond will be shorter than the Ni(II)-Cl bond. However, metal-arsenic bond distances of diarsine complexes have been reported. Consideration of these bond lengths (namely, Co(III)-As, Ni(III)-As, Co(II)-As, and Ni(II)-As) in terms of the electronic configuration and oxidation state of the central metal atom should give some insight into the bonding in the metal-arsenic bonds which would then be useful in checking whatever had been proposed on the bonding in the metal-anion bond.

If it were assumed that delocalisation of the  $e_g$  electron(s) into the metal-anion bond is marginal or nil, then comparison of the metal-arsenic bond distances (Table 13) of transition metal diarsine complexes (even with different anions) should show <sup>whether</sup> the postulate is valid.

Table 13

Metal(O.S.)	Co(III)	Ni(III)	Co(II)	Ni(II)
M-As(A)	2.34	2.34-2.37	2.30	2.28-2.30
Electronic configuration	d <sup>6</sup>	d <sup>7</sup>	d <sup>7</sup>	d <sup>8</sup>
Complex	CoD <sub>2</sub> Cl <sub>2</sub> Cl <sup>16</sup>	NiD <sub>2</sub> Cl <sub>2</sub> Cl <sup>19</sup>	CoD <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> <sup>17</sup>	NiD <sub>2</sub> I <sub>2</sub> <sup>18</sup>

The table above reveals that the electronic configuration apparently has no effect on the metal-arsenic bond length, and that change in oxidation state is probably the main contributing factor to variation in bond length. Comparison of metal-arsenic bond distance for Ni(III)D<sub>2</sub>Cl<sub>2</sub>Cl and Co(II)D<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub><sup>17</sup> shows that for the d<sup>7</sup> electron configuration the Ni(III)-As bond length is greater than that for Co(II)-As by about 0.05Å. Further, comparison of this metal-metal distance for Co(d<sup>6</sup>)D<sub>2</sub>Cl<sub>2</sub>Cl and Ni(d<sup>7</sup>)D<sub>2</sub>Cl<sub>2</sub>Cl reveals that for the higher bond length oxidation state (III) of the transition metal the Ni(d<sup>7</sup>)-As is only marginally greater (0.01Å) than that of the Co(d<sup>6</sup>)-As bond. Although bond distance is not a very accurate measure of electron distribution or density, the above observations indicate that the metal-arsenic bond length is marginally susceptible to e<sub>g</sub> electron configuration and that there must be weak e<sub>g</sub> electron delocalisation into the metal-arsenic bond. This is also supported by comparison of the metal-arsenic bond lengths for Co(d<sup>7</sup>)D<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> and Ni(d<sup>8</sup>)D<sub>2</sub>I<sub>2</sub> which shows that introduction of the second

$e_g$  electron lowers the bond distance by an almost negligible amount (0.01). The reverse direction of change in length is probably accounted for by a marked reduction in antibonding effect (i.e., increase in stability of molecular system) arising from pairing of the two  $e_g$  electrons. Hence, the alternative postulate that the electron (s) is largely accommodated in the molecular orbitals arising from the metal and the anion atomic orbitals would be more promising. This proposition is supported by the results of the low i.r. studies mentioned previously. Further confirmation is given by e.s.r. studies<sup>31</sup> of the diarsine complexes with  $d^7$  configuration ( $NiD_2X_2X$ ,  $CoD_2X_2$  where  $X = Cl$ , and  $Br$ ) which showed that unpaired electron density was located in the metal-anion bond.

It now appears that the  $e_g$  electron(s) is located in a molecular orbital which closely approximates the  $d_{z^2}$  orbital. This is in line with the structural data on  $NiD_2Cl_2Cl$  and  $CoD_2(ClO_4)_2$  which reveal that these molecules have an axially elongated, six-coordinate structure which belongs to a system approximating that of  $D_{2h}$ . Further support on the assumption that the  $e_g$  electron is present in the M-anion bond comes from e.s.r. studies of  $d^7$  diarsine complexes mentioned earlier. It was observed that spin density was located on the arsenic and halogen atoms, and that there were sizable differences in the arsenic splittings when the

axial ligands are changed indicating that the unpaired electron was present in a molecular orbital containing all the ligands.

## EXPERIMENTAL

### 1. Preparation of Samples

The methods of preparation of most complexes studied are described in papers by Nyholm et al. However, schematic diagrams of the preparations of these compounds and the metal (Co, Ni) diarsine nitrates are given in Figs 1 and 2.

Preparation and study of  $\text{NiD}_2\text{Br}_2 \cdot \text{ClO}_4$  have not been mentioned elsewhere. It was isolated by the same method used for the chloro analogue. Its purity was checked by fingerprinting with i.r. spectra and powder photographs.

### 2. Physical Measurements

#### (a) Infrared Spectra (400-2000 $\text{cm}^{-1}$ )

Infrared spectra in the range 400-2000  $\text{cm}^{-1}$  were recorded on a Perkin-Elmer 337 spectrometer for the complexes in nujol mulls between KBr plates. A spectrum of the diarsine ligand was recorded as a film between KBr plates.

#### (b) Infrared Spectra (40-400 $\text{cm}^{-1}$ ; 200-500 $\text{cm}^{-1}$ )

Polystyrene discs were used in the region below 400  $\text{cm}^{-1}$  where they are transparent except for a band at 72  $\text{cm}^{-1}$ .

A Grubb-Parsons DM4 spectrometer was employed to measure spectra in the range 200-500  $\text{cm}^{-1}$ . An atmosphere of dry air was needed to prevent any absorption by water vapour.

Fourier Spectrophotometer FS-720, with range 40-400  $\text{cm}^{-1}$  operates under vacuum. An interferogram is produced which yields the absorption spectrum after Fourier transformation (accuracy,  $\pm 2 \text{ cm}^{-1}$ ).

(c) X-ray Powder Photographs

X-ray powder photographs were obtained with a Philips-Scherer camera.

(d) Raman Spectra

A 1 watt Argon laser (with the laser line at  $4880\overset{\circ}{\text{Å}}$ ) was used as the incident light source. Light scattered through  $90^\circ$  from a powder sample was analysed using a Jarrell-Ash monochromator and photon counting detection. Optimal slit widths were found to be  $100\mu$ .

The sample was prepared by sprinkling the compound over a thin film of glue on a glass plate. It was found that the glue had no effect on the Raman Spectra.

Although the  $\text{CoD}_2\text{Cl}_2 \cdot \text{Cl}$  and  $\text{CoD}_2\text{Br}_2 \cdot \text{Br}$  samples were green in colour, the green ( $\lambda = 4880\overset{\circ}{\text{Å}}$ ) light gave reasonable spectra. Later, blue radiation (laser line at  $4545\overset{\circ}{\text{Å}}$ ) was employed to give spectral bands of better form.

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Complexes of the type MD<sub>2</sub>Br<sub>2</sub>

Electron configuration	M(II)	$\nu(\text{M-Br})$	Force constant(md/A)
d <sup>8</sup>	Ni	72	0.14
d <sup>7</sup>	Co	107	0.29

Complexes of the type MD<sub>2</sub>Cl<sub>2</sub>

	M(II)	$\nu(\text{M-Cl})$	
d <sup>8</sup>	Ni	106	0.20
d <sup>7</sup>	Co	158	0.43

Complexes of the type MD<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>

	M(II)	$\nu(\text{M-O})$	
d <sup>8</sup>	Ni	100	0.27
d <sup>7</sup>	Co	121	0.40

Complexes of the type MD<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>

	M(II)	$\nu(\text{M-O})$	
d <sup>8</sup>	Ni	-	
d <sup>7</sup>	Co	103	

Complexes of the type MD<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub>

	M(II)	$\nu(\text{M-F})$	
d <sup>7</sup>	Co	314	2.64

Complexes of the type MD<sub>2</sub>Br<sub>2</sub>.ClO<sub>4</sub>

	M(III)	$\nu(\text{M-Br})$	
d <sup>7</sup>	Ni	192	1.16
d <sup>6</sup>	Co	239	1.55

Complexes of the type MD<sub>2</sub>Cl<sub>2</sub>.ClO<sub>2</sub>

	M(III)	$\nu(\text{M-Br})$	
d <sup>7</sup>	Ni	260	1.16
d <sup>6</sup>	Co	388	2.56

Table 1. M-L stretching frequencies (cm<sup>-1</sup>) and corresponding force constants for diarsine complexes.

Complex	(a) from $\frac{\nu(\text{M-Br})}{\nu(\text{M-Cl})} \cdot 0.75$	(b) from S.T.A.M <sup>1</sup> ;	force constant <sup>2</sup> , k	(c) Obs.
NiD <sub>2</sub> Br <sub>2</sub>	79	79	0.20	64
CoD <sub>2</sub> Br <sub>2</sub>	118	115	0.43	107
NiD <sub>2</sub> Br <sub>2</sub> .Br	179	190	1.18	190
CoD <sub>2</sub> Br <sub>2</sub> .Br	288	280	2.56	227
		258	2.20	
		224	1.66	
NiD <sub>2</sub> Br <sub>2</sub> .ClO <sub>4</sub>	195	188	1.16	192
CoD <sub>2</sub> Br <sub>2</sub> .ClO <sub>4</sub>	298	280	2.56	239
		258	2.20	
		224	1.66	

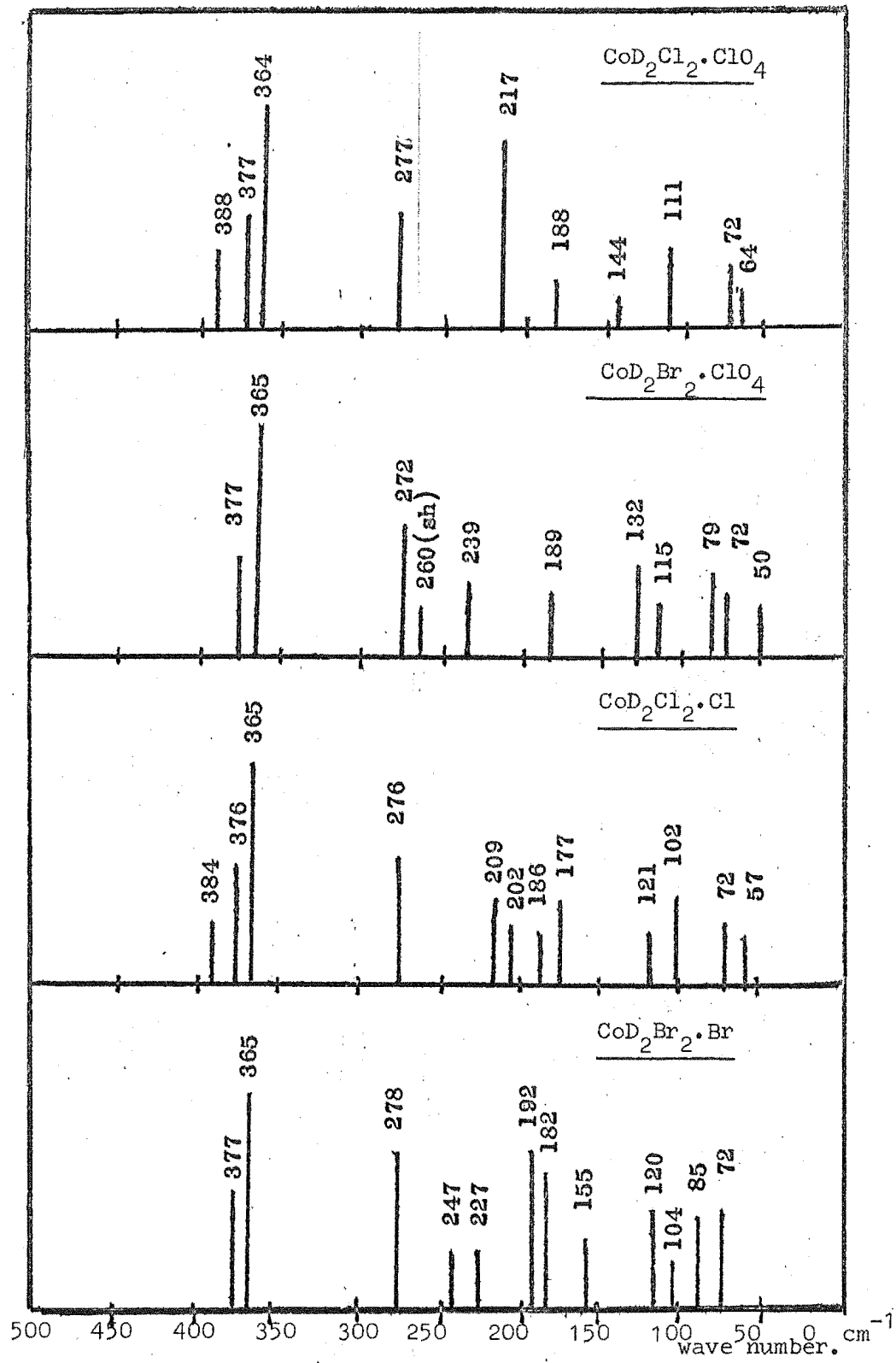
Table 2. Calculated frequencies. (cm<sup>-1</sup>) of M-Br vibrations

1. Simple triatomic model
2. Assume  $k_{\text{M-Cl}} = k_{\text{M-Br}}$  as an approximation

<u>Complex</u>	<u><math>\nu(\text{Co-X})(\text{cm}^{-1})</math></u>	<u>Force Constant(<math>\text{md}/\text{A}</math>)<sup>1</sup></u>
$\text{CoD}_2\text{Cl}_2 \cdot \text{Cl}$	275	1.66
$\text{CoD}_2\text{Br}_2 \cdot \text{Br}$	182	1.55

Table 3. Tentative Assignments to the  $\nu(\text{M-X})$  Raman active Symmetric Vibrations and the Corresponding Force Constants.

<sup>1</sup>Simple Triatomic Model.



I.R. Line Spectra of Complexes  $\text{CoD}_2\text{X}_2 \cdot \text{X}$  and  $\text{CoD}_2\text{X}_2 \cdot \text{ClO}_4$

Figure 1

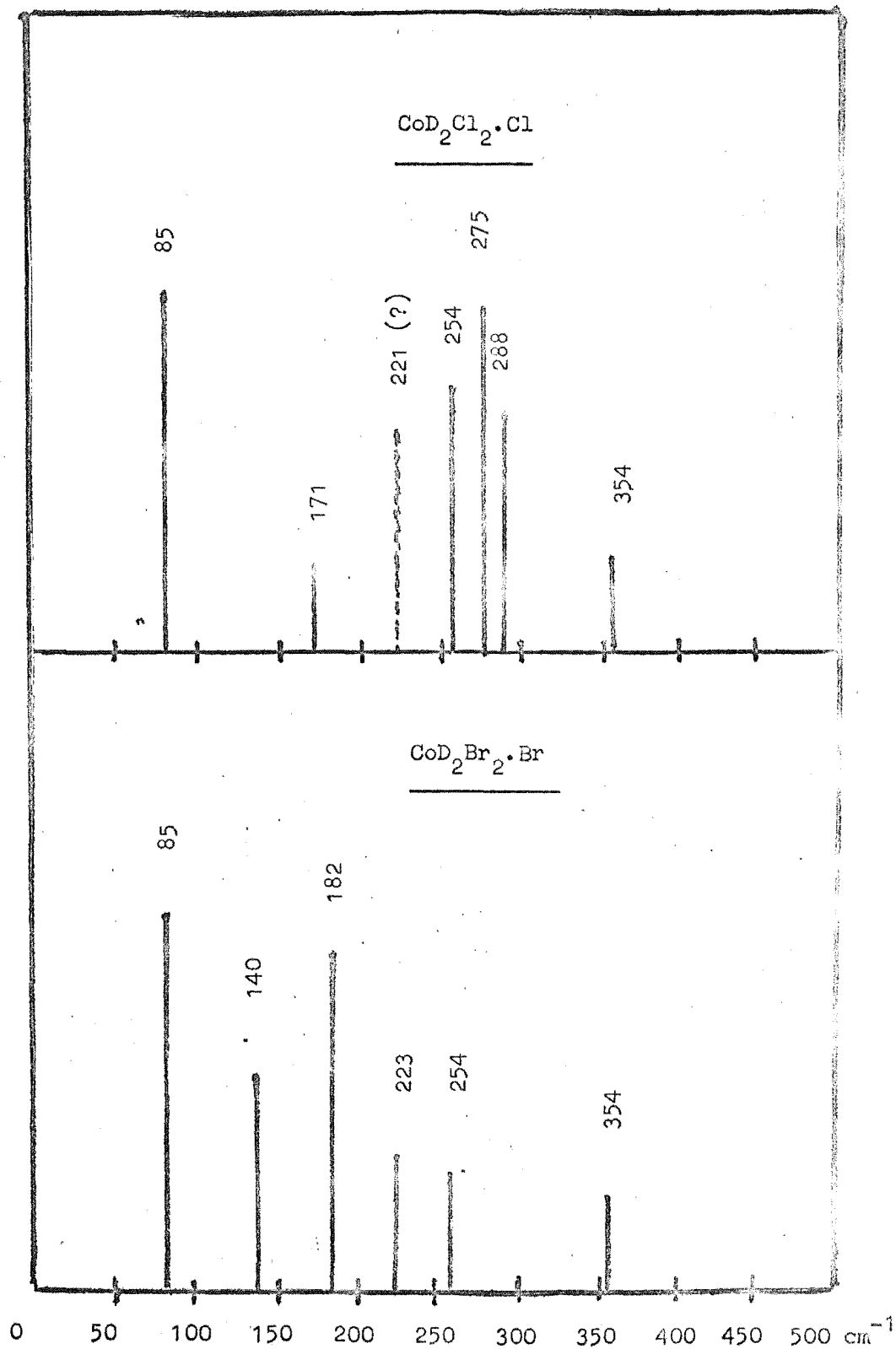
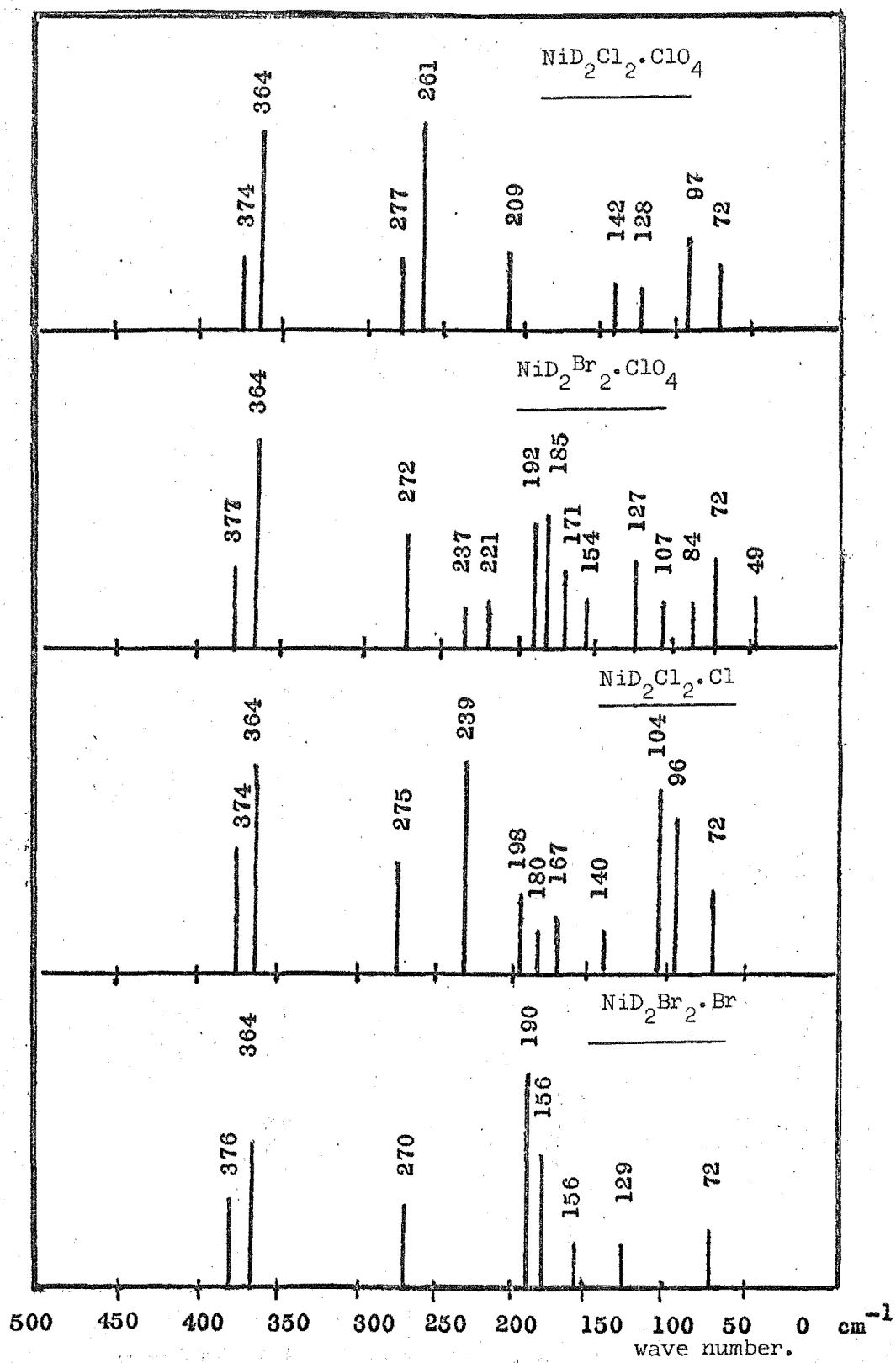


Figure 2 Raman Line Spectra of Complexes  $\text{CoD}_2\text{X}_2 \cdot \text{X}$ , X = Cl, Br



I.R. Line Spectra of Complexes  $\text{NiD}_2\text{X}_2 \cdot \text{X}$  and  $\text{NiD}_2\text{X}_2 \cdot \text{ClO}_4$

Figure 3



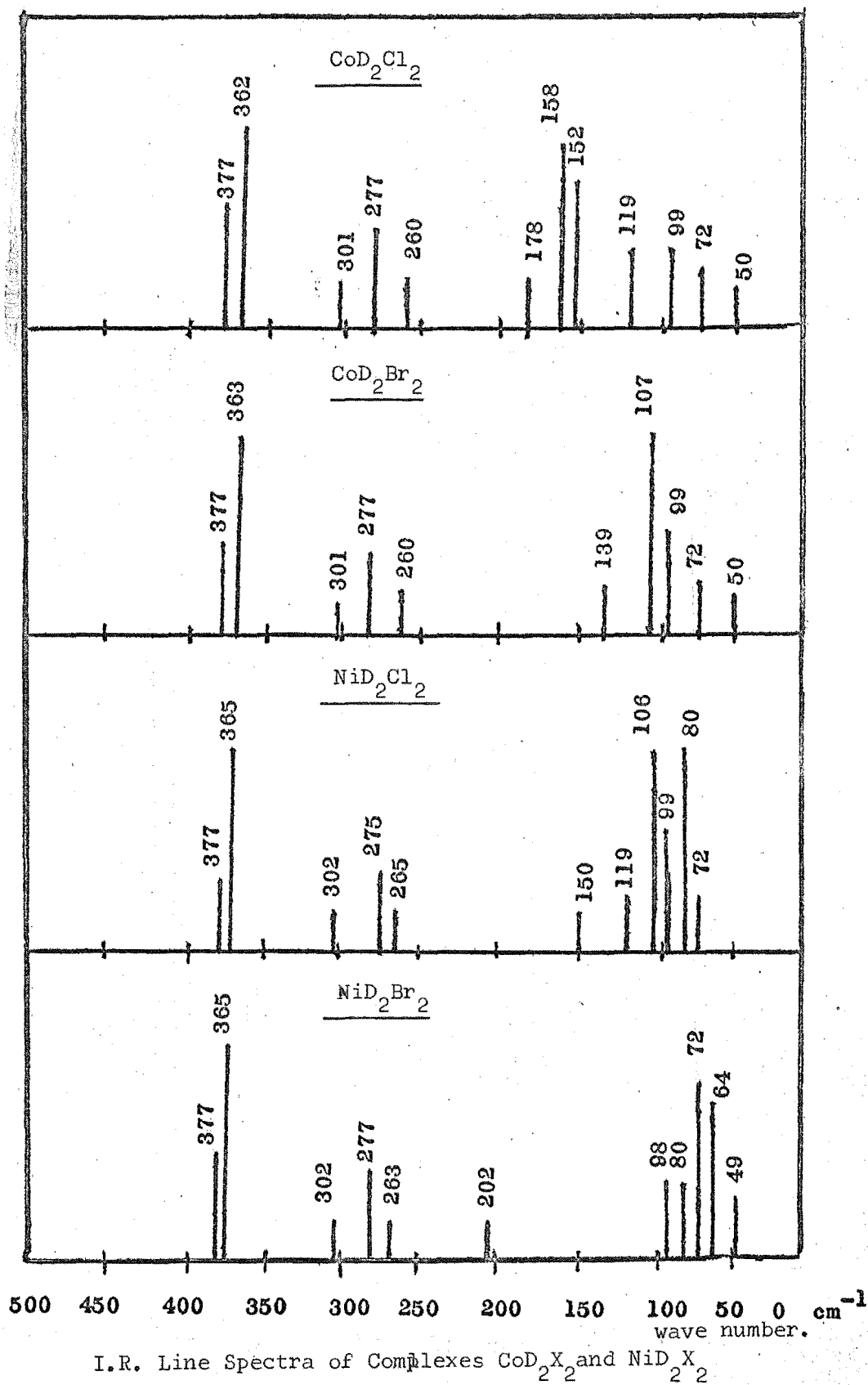


Figure 4

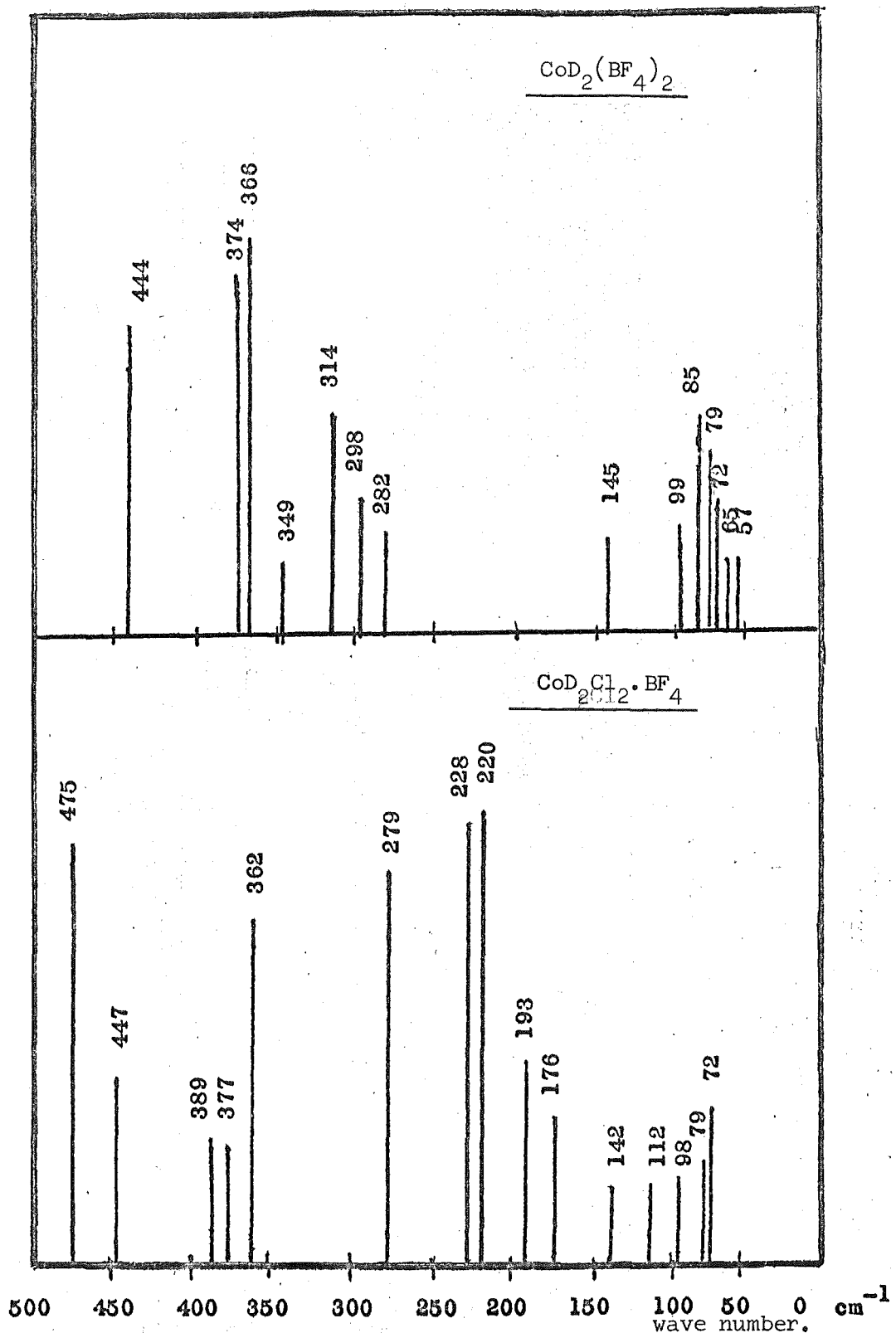


Figure 5 I.R. Line Spectra of the Complexes  $\text{CoD}_2(\text{BF}_4)_2$  and  $\text{CoD}_2\text{Cl}_2 \cdot \text{BF}_4$

2 4 2 2 2 4

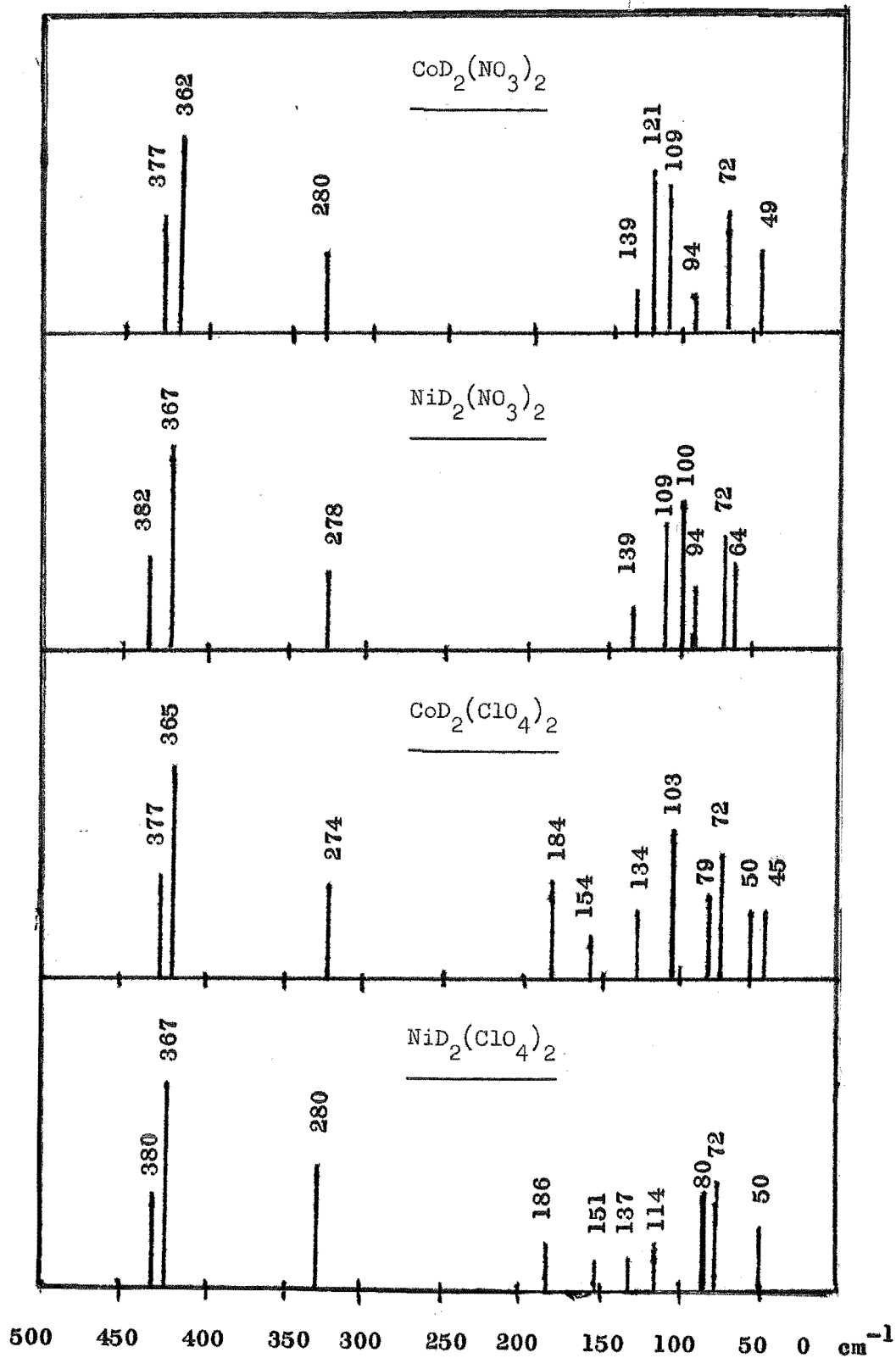


Figure 6 I.R. Line Spectra of Complexes  $\text{M(II)D}_2(\text{NO}_3)_2$  and  $\text{M(II)D}_2(\text{ClO}_4)_2$

PART II

The Crystal and Molecular Structure of  
Racemic- $\beta_2$ -(cobalt triethylenetetramine glycinato)  
Dichloride Monohydrate

THE CRYSTAL AND MOLECULAR STRUCTURE OF  
RACEMIC-B<sub>2</sub>-(COBALT TRIETHYLENETETRAMINE GLYCINATO)  
DICHLORIDE MONOHYDRATE

THE CRYSTAL AND MOLECULAR STRUCTURE OF  
RACEMIC- $\beta_2$ -(COBALT TRIETHYLENETETRAMINE GLYCINATO)  
DICHLORIDE MONOHYDRATE

ABSTRACT

The crystal and molecular structure of racemic- $\beta_2'$ -(RS)- (cobalt triethylenetetramine glycinato) dichloride monohydrate,  $\beta_2'$ -(RS)-(Co(trien)(gly))Cl<sub>2</sub>·H<sub>2</sub>O, have been determined from three-dimensional X-ray data collected by counter methods. The compound crystallises in space group P2<sub>1</sub>/c (C<sub>2h</sub><sup>5</sup>, no. 14) with a = 8.349(3), b = 14.927(8), c = 24.31(9) Å,  $\beta = 103.58(2)^\circ$ , and Z = 8. Measured and calculated densities are, respectively, 1.65 and 1.68 gm<sup>-3</sup>. The structure has been refined by full-matrix least-squares techniques to give a conventional R-factor of 0.117 for 1726 independent reflections whose intensities were greater than their estimated standard deviations. The crystal is composed of discrete isomeric  $\beta_2'$ -(Co(trien)(gly))<sup>2+</sup> cations, Cl<sup>-</sup> anions and connecting hydrogen bonds. The coordination about the metal ion is octahedral, the

trien ligand being quadridentately coordinated in the  $\beta_2$  configuration. A nitrogen and an oxygen atom, both from the glycine ligand, occupy the two remaining sites. For the first time,  $\lambda$  conformation of the apical  $\beta_2$  trien ring has been observed.

## INTRODUCTION

In recent years there have been numerous studies on cobalt(III) polyamine compounds containing asymmetric nitrogen centres. These compounds can exhibit various forms of isomerism in their topological and conformational arrangements. However, not all these isomers have been prepared or isolated. The difficulty in assigning structures to these types of complexes has been well documented.

A recent paper<sup>1</sup> has stated that a knowledge of the structures of these isomers is essential to any comprehensive/understanding of the mechanisms of hydrolysis in these complexes. It is also realised now that an accurate knowledge of the geometry of triethylenetetramine coordinated in various modes is important in understanding the interconversion reactions between the various forms.

Precise molecular geometry is of great importance to more recent studies on the prediction of molecular geometries of multi-dentate amine complexes using energy minimisation techniques.

For these reasons, the crystal structure of racemic- $\beta'_2$ -(Co(trion)(gly))Cl<sub>2</sub>.H<sub>2</sub>O was undertaken. The general stereochemistry of this complex has been discussed in literature. It was found that



the glycine ligand could coordinate in either of two ways, one with the terminal oxygen in the planar site (thus giving the  $\beta_1$  isomer) and the other with the terminal nitrogen atom of the glycine residue in this coordination site. The main product would largely depend on the type of glycine residue used, and the pH of the solution. The crystals used in this structure analysis are obtained from reaction product by fractionation.

The molecular geometry of this complex has been predicted.<sup>2,3</sup> The thermodynamic stabilities of two isomeric configurations,  $\beta_2$ -(RR)- and  $\beta_2$ -(RS)-, have been calculated. It was hoped that comparison of the results of the latter with those obtained from this structure analysis would elucidate the interaction of atomic forces controlling stability in the isomers.

EXPERIMENTAL SECTION

Crystal Data

Orange crystals of what proved to be  $\beta'_2$ -(RS)-  
 (Co(trien)(gly))Cl<sub>2</sub>·H<sub>2</sub>O were kindly supplied by Dr D.A. Buckingham  
 from Australian National University and were used without further  
 recrystallisation. Preliminary precession photographs taken with  
 Ni filtered CuK $\alpha$  radiation indicated that the crystals were mono-  
 clinic. The conditions limiting possible reflections amongst all  
 recorded spectra ( $h0l$ ,  $h + l = 2n$ ,  $k = 2n$ ) are uniquely consistent  
 with space group  $C_{2h}^5 - P2_1/c$ . At  $24 \pm 2^\circ$ , the cell constants are  
 $a = 8.349(3)$ ,  $b = 14.927(8)$ ,  $c = 24.31(9)\text{\AA}$ ,  $\beta = 103.58(2)^\circ$ . These  
 parameters were determined from least-squares refinement of 11  
 reflections which had been accurately centred on a Hilger and Watts  
 four-circle automatic diffractometer. In this refinement the wave-  
 length of MoK $\alpha_1$  radiation was taken as  $0.7093\text{\AA}$ . The crystal density,  
 determined as  $1.65(3)\text{gcm}^{-3}$  by gradient-tube density measurement  
 method, is in good agreement with that of  $1.68\text{gcm}^{-3}$  calculated for  
 eight formula units in the unit cell.

X-ray Data Collection and Reduction

For data collection a crystal with approximate dimensions  $0.19 \times 0.38 \times 0.09 \text{ mm}^3$  was mounted on a thin glass fibre in a random orientation on a Hilger and Watts computer controlled four-circle diffractometer. After alignment of the diffractometer, 11 reflections from the data set were centred at a take-off angle of  $3.0^\circ$ . These reflections formed the basis for the least-squares refinement of cell constants and the orientation defining matrix. Three strong axial reflections (200, 020, and 004) were chosen as standards which also served for determining the scan ranges and mosaicity. The mosaicity of the crystal was checked from open counter omega scans at a take-off angle  $3.0^\circ$  on the three independent reflections given above. All scans of these low-angle reflections had peak widths at half-height of  $0.17^\circ$  which is normal for crystals suitable for intensity experiments.<sup>4</sup>

Intensity data were collected at a take-off angle of  $3.0^\circ$ . The primary and secondary collimators were 1.0 and 5.0mm respectively. The data were collected by the  $\theta - 2\theta$  scan technique at a scan rate of  $0.6^\circ/\text{min}$ . Stationary counter background counts of 16 seconds were

taken at each end of the scan range. No attenuators were used as no reflections exceeded 7000 counts/sec during a scan.

During the data collections, the intensities of three standard reflections in diverse regions of reciprocal space were monitored periodically to check on electronic and crystal stability. The three standards showed different degrees of variation in intensity during the four days required to collect the data. However, the background counts were reasonably stable. Initially it was thought that the drop in intensity was caused by crystal decomposition. But it was later proved more likely that the goniometer head and crystal had moved during the data collection.

The linear absorption coefficient of the compound for  $\text{MoK}\alpha$  radiation is  $17.35 \text{ cm}^{-1}$ . Because  $\text{CuK}\alpha$  radiation is known to create fluorescence and has higher absorption,  $\text{MoK}\alpha$  radiation was used to collect intensity data. The crystal was carefully measured by using a microscope equipped with a micrometer eye-piece. The major faces of the crystal were indexed and the possible absorption corrections were calculated using program DABS. A total of 3448 intensities were recorded for the two equivalent forms  $(hkl, h\bar{k}l)$  of this monoclinic crystal. Lorentz and Polarisation corrections were carried out using

program HILGOUT. Equivalent forms were averaged yielding 3475 independent reflections of which 1726 had  $I^2 \geq \sigma_p^2$ . No corrections were made for absorption because a test calculation indicated that the correction was small and because it is intended to recollect a better data set.

### Solution of Structure

The structure was successfully solved by means of the symbolic addition procedure (Hauptman and Karle, 1953; Karle and Karle, 1966) using a locally modified version of the symbolic addition program NRC-4, written by S.R. Hall and revised by F.R. Ahmed.

Initially the program SHNORM is used to calculate the overall isotropic temperature and scale factors and the normalised structure factors  $|E|$  for all the reflections. Calculated E statistics were in good agreement with the theoretical values for centrosymmetric structures.

## STATISTICS FOR NORMALISED STRUCTURE FACTORS

	E	E <sup>2</sup>	E <sup>2</sup> -1	E <sup>3</sup>	E <sup>2</sup>	E <sup>1</sup>
Obs.	0.8567	1.0067	0.8419	0.16	3.23	33.17
cent.	0.7980	1.0000	0.9690	0.30	5.00	32.00
Theo. noncent.	0.8860	1.0000	0.7360	0.01	1.80	37.00

The 289 largest normalised structure factors were used in the symbolic addition procedure. A search for triplets of reflections satisfying the  $\sum_2$  relationship yielded 1384 triplets for subsequent calculations. The calculations were made at successively lowered probability limits at which the  $\sum_2$  relationships held. The variables A, B, and C were assigned to the reflections 6, 4, and 23 respectively. Values for the symbols were then obtained by a cross-correlation of all the  $\sum_2$  relationships having regard to the probabilities involved. The results of these are summarised as follows, where the accumulation of tentative signs for each symbol is presented.

## ACCUMULATED SIGNS FOR THE SYMBOLS

	A	B	C	AB	AC	BC	ABC
Number+	23	16	0	17	0	0	0
Number-	72	66	0	53	0	0	0

---

From these results, the symbols A and B were therefore given the signs -, - respectively and the sign of C was considered undetermined. Initially a -ve sign is assigned to C, and the set of values (A, -; B, -; C, -) were applied to the 289 reflections used in the basic sign determination procedure, with the result that 280 of them had phases assigned. A Fourier synthesis was then calculated using the signed E values as coefficients. However, no chemically reasonable structure could be deduced from the E-map. Consequently, C was reassigned as +ve, and the phases of the reflections recalculated.

The origin defining reflections were then selected according to the parity criteria (even/odd Miller index combinations) demanded by the space group, and also in descending order for the number of triplets found for each defining reflection. The first, sixth and third reflections were chosen in that order by the automatically programmed procedure, and given arbitrary '+' phases. A series of passes

through the entire set of reflections resulted in 289 reflections having phases assigned. Another E-map was calculated, and this revealed likely positions for cobalt and chlorine atoms.

Two cycles of full-matrix least-squares refinement of positional coordinates and isotropic temperature factors for the two cobalt and four atoms, and the overall scale factor gave the agreement factors,  $R_1$  and  $R_2$ , values of 44.4 and 45.5% respectively, where

$$R_1 = \frac{\sum (|F_o| - |F_c|)}{\sum F_o}$$

$$R_2 = \left( \frac{\sum w(|F_o| - |F_c|)^2}{\sum w/F_o^2} \right)^{\frac{1}{2}}$$

and the function minimised was  $w(F_o - F_c)^2$

with  $w$  = weight of each reflection,

and  $|F_o|$  and  $|F_c|$  are the observed and calculated structure

amplitudes. The strategy then was to run successive difference

Fourier calculations each followed by distance and angle calculations and

line printer diagrams to facilitate the search for

remaining atoms. Program CUCLS was used at every stage to refine

the developing model. All non-hydrogen atoms belonging to the two

complex molecules in the asymmetric unit were ultimately located



and refined to give  $R_1 = 18.5\%$  and  $R_2 = 18.2\%$ . The last difference Fourier showed two distinct peaks which were thought to be due to oxygen atoms in solvent molecules and their inclusion led to values for  $R_1$  and  $R_2$  of 14.4% and 12.6% respectively. The location of residual peaks suggested anisotropic temperature factors would be appropriate for Co and Cl atoms. Such refinement would involve 183 variables, and the computing facilities available then limited the number to a maximum of 155. Hence the refinement was executed in two blocks, one containing the C, N, and O atoms for one molecule, the other with the corresponding atoms for the second molecule in the asymmetric unit. Each block also contained the Co, Cl, and O (solvent) atoms. The agreement factors  $R_1$  and  $R_2$  were 11.7% and 10.0% respectively. No significant features could be found in the three-dimensional difference Fourier where the highest peak had a density of  $1.6e/\text{\AA}^3$  or about 0.4 the height of the last atom located. No more atoms were refined anisotropically because the calculations would consume much computing time, and no structure factor listing is presented in this thesis since it is anticipated that a better data set will be collected in the near future.

The program RANGER was used to check the weighting scheme. It

showed that the R-factor was almost independent of  $|F|_o$  or  $\sin \theta/\lambda$ , which implied that the relative weighting scheme was reasonable. Scattering factor table used for  $\text{Co}^{3+}$ ,  $\text{Cl}^-$ , O, N, and C were those of Cromer and Waber,<sup>5</sup> and the anomalous scattering terms were those listed by Cromer.<sup>6</sup> Preliminary diagrams drawn at this stage revealed that the cations in the asymmetric unit had opposite configurations ( $\Delta, \Lambda$ ) about cobalt. The positional coordinates and vibrational parameters and their estimated standard deviations obtained from the final cycle of least-squares refinement using program CORFFE are listed in Table 1, together with the root-mean-square amplitudes of vibration of the cobalt and chlorine atoms.

DESCRIPTION OF THE STRUCTURE

Description of the isomeric  $\beta_2'$  - (Co(trien)(gly))<sup>2+</sup> cations

The structure analysis revealed that the crystal contains two types of conformationally isomeric cations in equal abundance, together with chloride anions and water molecules. This is the first structure containing two cations with opposite conformations at the out-of-plane  $\beta$ -trien ring which shall be described as the 'apical ring'. Using the nomenclature described in a recent paper<sup>7</sup> these cations are labelled as  $\Delta\text{-}\beta_2\text{-(RS)-(Co(trien)(gly))}^{2+}$  and  $\Delta\text{-}\beta_2\text{-(SR)-(Co(trien)(gly))}^{2+}$ . Further, the crystal structure is said to have a  $\beta_2'$  configuration. For convenience, both isomers are depicted in the  $\Delta$ -configuration (except in the unit-cell diagrams). To distinguish between the isomers, the one with a  $\delta$  conformation at the apical ring is termed isomer A and the other, with a  $\lambda$  conformation at the corresponding ring, isomer B. Perspective views of both isomers are given in Figure 1. The atom numbering scheme is largely based on that proposed by Dr I.E. Maxwell<sup>2</sup>. However, the numbers of the atoms of isomer B have a prefix (1) to distinguish them from the corresponding atoms of isomer A. Likewise, the oxygen atoms of the solvent

molecules have their own prefix (2).

The crystal structure is characterised by four pairs of isomeric cations connected by hydrogen bonds. Figure 2, which is a stereoscopic pair of the contents of the unit-cell projected onto the plane (100), depicts such pairs of cations.

Intramolecular bond distances/with their standard deviations and angles are presented in Tables 2 and 3 respectively. The mean Co(III)-N(trien) bond distances for the two isomers are equal (1.99(2), 1.99(2)Å). These values are slightly greater than those for related compounds, 1.933Å and 1.915Å in the  $\Delta$ - $\beta_1$ -(RR)- and  $\Delta$ - $\beta_1$ -(RS) - (Co(trien)(gly))I<sub>2</sub>.½H<sub>2</sub>O<sup>8</sup> isomers respectively, 1.955Å in  $\Delta$ - $\beta_2$ -(SSS)-Co(trien)(S-Pro))(ZnCl<sub>4</sub>)<sup>9</sup>, 1.96Å in  $\Delta$ - $\beta_2$ -(RRS)-(Co(trien)(S-Pro))I<sub>2</sub>.2H<sub>2</sub>O<sup>10</sup> and 1.93Å in  $\beta$ -(Co(trien)(Cl H<sub>2</sub>O)(ClO<sub>4</sub>)<sub>2</sub>)<sup>11</sup>. For the present complexes, the difference between the Co(III)-N(gly) bond lengths is within experimental error.

The Co(III)-O(gly) bond lengths (1.91(2)Å and 1.93(3)Å for isomers A and B respectively) are comparable with 1.880(14)Å in  $\Delta$ - $\beta_2$ -(RS)-(Co(trien)(S-Pro))I<sub>2</sub>.H<sub>2</sub>O<sup>10</sup> and those (1.906(5) and 1.914(6)Å for  $\beta_1$ -(RR)- and  $\beta_1$ -(RS)- isomers) in  $\beta_1$ -(Co(trien)(gly))I<sub>2</sub>.½H<sub>2</sub>O<sup>8</sup>. Mean values of the C-N bond distances in isomer A and isomer B are 1.51(1)Å and 1.51(1)Å respectively. They

are comparable to that (1.499(3)Å) of  $\Delta$ - $\beta_2$ -(RRS)-(Co(trien)(S-Pro))I<sub>2</sub>.H<sub>2</sub>O<sup>10</sup> and to those (1.483(3)Å and 1.488(3)Å) for  $\Delta$ - $\beta_1$ -(RR)- and  $\Delta$ - $\beta_1$ -(RS)-(Co(trien)(gly))I<sub>2</sub>. $\frac{1}{2}$ H<sub>2</sub>O isomers<sup>8</sup>. The mean C-C bond distances for the present structure are 1.54(2)Å and 1.53(2)Å respectively. These lengths are slightly greater than those found in other trien complexes. It was reported<sup>2</sup> that the minimisation calculations showed that the C-C and C-N bond lengths are sensitive to inclusion of H atoms at calculated positions and their exclusion would give significantly longer bond distances. It may be noted that hydrogen atoms were not included in the appropriate positions for the structure.

The C(8)-O(1) and C(8)-O(2) bond lengths (1.29(3)Å, 1.27(3)Å) are almost equal, taking the error into consideration. This also occurs for the corresponding atoms in isomer B (C(18)-O(1), 1.27(3)Å; C(18)-O(12), 1.26(3)Å). This suggests that the carbonyl bond in each isomer is polarised probably through interaction with neighbouring proton-donating species. If polarisation is absent or almost insignificant, the C=O bond distance would be relatively shorter.

The angles subtended at the cobalt by the puckered trien chelate rings of isomer A (N(1)-Co(1)-N(2), 86.8(8)°);

$N(2)-Co(1)-N(3)$ ,  $85.0(8)^\circ$ ;  $N(3)-Co(1)-N(4)$ ,  $85.7(7)^\circ$   
 are comparable to those  $(86.6(8)^\circ, 85.7(8)^\circ, \text{ and } 87.3(8)^\circ)$   
 found for isomer B. Either set of values is comparable  
 to that  $(85.4(4)^\circ, 84.5(3)^\circ, \text{ and } 85.8(4)^\circ)$  in  
 $\Lambda-\beta_2'-(SSS)-(Co(\text{trien})(S\text{-Pro}))(\text{ZnCl}_4)^9$  and to that  
 $(85.5(9)^\circ, 85.8(3)^\circ \text{ and } 86.3(4)^\circ)$  in  $\Lambda-\beta_2-(RRS)-$   
 $(Co(\text{trien})(S\text{-Pro}))I_2 \cdot H_2O^{10}$ . These angles, coupled with  
 those of the glycine chelate ( $N(5)-Co(1)-O(2)$ ,  $86.9(7)^\circ$ ;  
 $N(15)-Co(11)-O(12)$ ,  $85.0(7)^\circ$ ) combine to produce  
 significant distortions from regular octahedral  
 coordination about the cobalt ion in each isomer.

The bonds from  $Co(1)$  to  $O(2)$ ,  $N(2)$ ,  $N(4)$  and  $N(5)$   
 are coplanar (Table 4, plane 3), but significant  
 distortions occur from the other two coordination planes  
 (planes 1 and 2). A similar situation occurs in isomer  
 B as shown in Table 5. These distortions are comparable  
 to those observed in  $\Lambda-\beta_2-(RRS)-\frac{1}{2}(Co(\text{trien})(S\text{-Pro}))I_2 \cdot H_2O^{10}$

The most significant angular distortions occur in  
 the following bond angles. The values for  $C(2)-N(2)-C(3)$   
 and  $C(12)-N(12)-C(13)$  are  $118(2)^\circ$  and  $121(2)^\circ$   
 respectively. In strain-free conditions, pure  
 tetrahedral angles ( $109.5^\circ$ ) would be expected. The  $N(2)-$   
 $Co(1)-N(4)$  and  $N(12)-Co(11)-N(14)$  bond angles are  
 $97(1)^\circ$  and  $97(1)^\circ$  respectively, where the strain-free

values are  $90^\circ$ . The significance of these distortions is discussed in following sections.

### CONFORMATIONS OF THE CHELATE RINGS

The most significant difference in the conformation of the two cations lies in the outer trien chelate ring. This ring adopts an unsymmetrical-skew conformation for isomer A, in contrast to the almost symmetrical envelope found in isomer B. The distances of the ring carbon atoms from the relevant N-Co-N planes are given in Table 6. Hence, for the A configuration about the metal ion the chiralities of the trien chelate rings are as follows; N(1)-C(1)-C(2)-N(2),  $\delta$ ; N(2)-C(3)-C(4)-N(3),  $\lambda$ ; N(3)-C(5)-C(6)-N(4),  $\delta$ ; N(11)-C(11)-C(12)-N(12),  $\delta$ ; N(12)-C(13)-C(14)-N(13),  $\lambda$ ; N(13)-C(15)-C(16)-N(14),  $\lambda$ . It is noted that the hydrogen atom at the asymmetric nitrogen atoms (N(2) and N(12)) points away from the apical ring of the coordinated trien ligand.

Conformations are determined primarily by the configuration of the two asymmetric secondary nitrogen atoms which link the chelate rings. Hence it appears that the chiralities of the rings must be enantiomeric and these chelate rings cannot invert without synchronous

inversion at the secondary centre. However, models indicate that inversion at the apical trien ring could occur with retention of configuration at the secondary nitrogen atom, N(3). This was not observed in the structures of trien complexes previously reported, and it was thought that this was so because of the increase in conformational strain energy for the  $\lambda$  form. But this phenomenon occurs in isomer B.

The conformations of the chelate rings of the two isomers are compared quantitatively in two different ways.

First, the deviations of the chelate ring carbon atoms from their N-Co-N planes are compared in Table 6 and Figure 3. The C(5) and C(6) deviations in isomer A have opposite signs, whereas the corresponding deviations in isomer B have the same sign. The deviation of C(5) has almost the same magnitude as that for C(16), but the directions of the deviations are opposite. The deviations of the amino acid carbon atoms, C(7) and C(8) for isomer A, from the N-Co-N plane is also given in Table 6 and Figure 3.

Secondly, the torsion angles about the C-N and C-C bonds are compared in Table 7 and Figure 4. The torsion angles were defined as follows: for atoms A, B, C and D



bonded in a chain, the torsion angle about the bond BC is taken as positive if the bond ZB is required to be rotated clockwise to lie in the BCD plane. This system was adopted by Dr I.E. Maxwell<sup>2</sup> and it follows the suggestions of Klyne and Prelog<sup>12</sup> and more recently Allen and Rodgers<sup>13</sup>. Moreover, for the N-C-C-N chains of the trien chelate rings the method leads to a positive sign for the torsion angle about the C-C bond when the conformation is blank and a negative sign for the blank conformation. Comparison of the torsion angles, numbered from 1 to 6, for the isomers reveals that the isomer B is less strained in the planar chelate rings. However, a marked difference is obvious at torsion angles numbered 7 and 8, where the values for isomers A and B are  $44^\circ$ ,  $46^\circ$  and  $2^\circ$ ,  $22^\circ$  respectively. Here isomer A exhibits greater stability. Clearly, there must be some explanation to account for greater strain and hence the  $\lambda$  conformation in the apical chelate ring.

Each method of comparison shows that the conformations of the apical trien ring of the isomers are distinctively different, and that the conformations of the planar rings are similar. This is surprising in view of the fact that both isomers are produced in the same reaction. It would be easy to assume that the same

The results above show that the calculated cobalt(III)-bromine frequency is only  $9 \text{ cm}^{-1}$  below that observed, whereas there is a rather large difference ( $70 \text{ cm}^{-1}$ ) between the calculated and the observed frequency of the cobalt(III)-chlorine vibration. The expression used for the symmetric vibration assumes that the metal has no influence on this motion. Results given in Table 10 show that inclusion of the mass of the metal (cobalt) in the expression improves the overall agreement between the calculated and the observed frequencies of the i.r. active cobalt-halogen vibrations.

Table 10

<u>X</u>	<u><math>\nu(\text{Co-X})(\text{cm}^{-1})</math></u>	<u><math>k(\text{md/\AA})</math></u>	<u><math>\nu(\text{Co-X})(\text{cm}^{-1})</math></u>	
			<u>calc.</u>	<u>obs.</u>
Cl	275	2.20	360	384
Br	182	1.35	204	227

Modified expression: 
$$\nu_s = K \sqrt{k \frac{2}{m_{\text{Co}} + m_{\text{X}}}}$$

Hence it may be concluded that the assignment of the i.r. active Co-Cl vibrations of the complex  $\text{CoD}_2\text{Cl}_2 \cdot \text{Cl}$  to the absorption at about  $384 \text{ cm}^{-1}$  is further supported by Raman spectral studies and application of a modified version of the 'triatomic model'.

The two remaining bonds have a geometrical configuration which can be described best by a bifurcated interaction to the two glycine oxygen atoms (O(1) and O(2)) and the nitrogen atom N(14). The distances from N(14) to O(1) and O(2) are 2.85 $\text{\AA}$  and 2.95 $\text{\AA}$  respectively. The angle O(1)...N(14)...O(2) is 45°. If a proton is placed 1.0 $\text{\AA}$  from N(14) and along the bisector of angle O(1)...N(14)...O(2), then the distances H---O(1) and H---O(2) are 1.98 $\text{\AA}$  and 2.00 $\text{\AA}$  respectively. This hydrogen bonding geometry is similar to that reported for the crystal structure  $\Delta$ - $\beta_2$ -(RRS)-(Co(trien)(S-Pro))I<sub>2</sub>.H<sub>2</sub>O,<sup>10</sup> and to that found in crystals of perdeuterated violuric acid monohydrate<sup>14</sup>, with the exception that a nitrogen atom is involved here instead of the oxygen from the water molecule.

Eight hydrogen bonds of the type N--H.....Cl, where the N atom is the donor, are given in Table 8. The first three have bond distances  $3.3 \leq X \dots Y \leq 3.4 \text{\AA}$  which magnitudes suggest weak hydrogen bonding. The remaining N--H.....Cl hydrogen bonds have magnitudes less than the 3.3 $\text{\AA}$  quoted in the literature<sup>15</sup>. There are two hydrogen bonds of the type O--H.....Cl whose bonding distances and corresponding angles (3.15 $\text{\AA}$ , 106°; 3.024 $\text{\AA}$ , 104°) are within accepted values (3.2 $\text{\AA}$ , 109°). It is of interest that hydrogen bonding to three atoms occurs quite

frequently with the O(water molecule) atoms and the Cl anions in the structure studied.

The list of nonbonded contacts reveals that there are eleven contacts involving carbon atoms which would most probably participate as donors to some extent. The effect of these contacts on the intramolecular nonbonded repulsions is not easy to envisage. It may be nevertheless advantageous at this stage to note which particular atoms, especially carbon and nitrogen, are involved in these contacts and the frequency of their participation (C(12), 1; C(13), 2; C(16), 2; C(1), 1; C(3), 1; C(4), 2; C(6), 1; C(7), 1; N(11), 2; N(12), 1; N(13), 1; N(4), 1; N(5), 1.).

Tables 7 and 8 certainly show that the ions forming this structure are held together by a well-developed system of hydrogen bonds and nonbonded contacts.

#### COMPARISON OF OBSERVED AND CALCULATED MOLECULAR GEOMETRY

##### FOR THE $\Delta$ - $\beta_2$ (RS)-(Co(trien)(gly))<sup>2+</sup> CATION

Strain energy minimisation calculations for the  $\Delta$ - $\beta_2$ -(RS)-(Co(trien)(gly))<sup>2+</sup> cation have been carried out by Dr I.E. Maxwell<sup>2,3</sup>. The possibility of an alternative conformation, ( $\lambda$ ) for the apical trien chelate ring was

considered. However, no structural data were available then for the  $\Delta$ -(RS) isomer. Hence the results on the  $\Delta$ -(RS)-(Co(trien)(gly))<sup>2+</sup> cation with  $\delta$  conformation on the outer ring are compared with those of the corresponding isomer from the structure analysis.

The most important nonbonded interactions for this isomer occur between the H atoms on the apical trien nitrogen atom N(4) and the apical hydrogens on the glycine nitrogen atom N(5) and the  $\beta$ -trien carbon atom C(2), and between an H atom on C(6) with the apical H atom C(3). Major angular distortions occur at the metal ion (N(2)-Co(1)-N(4), calculated  $97.0^\circ$ , observed  $97.0^\circ$ ), and at the planar secondary nitrogen atom N(2) (C(2)-N(2)-C(3), calculated  $115.0^\circ$ , observed  $117.8^\circ$ ). It was predicted that no bond lengthening of the Co-N(5) bond length would occur, which is supported by the crystal structure analysis (mean,  $1.99\text{\AA}$ ; Co--N(5),  $1.99\text{\AA}$ ). Agreement is very good, which indicates that the calculations have accurately reproduced the observed results for the isomer A.

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TABLE 1

ATOMIC COORDINATES AND ANISOTROPIC TEMPERATURE FACTORS<sup>a</sup>

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>
Co(1)	0.7239(4)	0.1642(2)	0.2344(1)
Co(11)	0.1679(4)	0.2716(2)	-0.0033(1)
Cl(1)	0.2156(8)	0.5646(4)	0.0715(3)
Cl(2)	0.7119(7)	0.1631(5)	0.0506(2)
Cl(3)	0.8304(9)	0.5318(5)	0.1612(3)
Cl(4)	0.1647(8)	0.0863(5)	0.1382(3)

<sup>a</sup>The expression used for the atomic temperature factor was  

$$[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$$

<u>Atom</u>	<u>B<sub>11</sub></u> <sup>a</sup>	<u>B<sub>22</sub></u>	<u>B<sub>33</sub></u>	<u>B<sub>12</sub></u>	<u>B<sub>13</sub></u>	<u>B<sub>23</sub></u>
Co(1)	0.0039(2)	0.0038(1)	0.0009(1)	-0.0006(13)	-0.0010(2)	-0.0000(1)
Co(11)	0.0045(6)	0.0042(2)	0.0009(1)	0.0003(3)	-0.0008(2)	0.0002(1)
Cl(1)	0.0081(12)	0.0049(5)	0.0012(1)	0.0003(7)	-0.0005(4)	0.0000(2)
Cl(2)	0.0044(11)	0.0084(6)	0.0013(1)	-0.0016(8)	-0.0008(4)	0.0005(2)
Cl(3)	0.0085(14)	0.0065(6)	0.0030(2)	0.0004(8)	-0.0011(5)	-0.0008(3)
Cl(4)	0.0067(13)	0.0071(5)	0.0016(2)	-0.0014(7)	-0.0001(4)	0.0001(2)



ATOMIC COORDINATES AND TEMPERATURE FACTORS

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>B</u>
O(1)	0.874(2)	0.779(1)	0.1781(6)	2.97(4)
O(2)	0.109(2)	0.705(1)	0.2014(6)	2.86(4)
O(11)	0.306(2)	0.316(1)	0.2014(6)	3.75(4)
O(12)	0.300(2)	0.280(1)	0.0721(6)	2.61(3)
O(21)	0.193(2)	0.934(1)	0.2263(7)	5.24(5)
O(22)	0.652(2)	0.359(1)	0.1232(7)	6.31(5)
N(1)	0.598(2)	0.278(1)	0.2377(7)	2.30(4)
N(2)	0.391(2)	0.615(1)	0.2109(7)	2.36(4)
N(3)	0.821(2)	0.042(1)	0.2351(7)	2.04(4)
N(4)	0.563(2)	0.124(1)	0.1646(7)	1.96(4)
N(5)	0.861(2)	0.219(1)	0.1859(7)	2.36(4)
N(11)	0.775(2)	0.603(1)	0.0215(7)	2.62(5)
N(12)	0.629(2)	0.767(1)	0.0269(7)	3.00(5)
N(13)	0.127(2)	0.141(1)	0.0045(7)	2.38(4)
N(14)	0.982(2)	0.735(1)	0.0787(7)	2.84(4)
N(15)	0.983(2)	0.312(1)	0.0308(7)	2.49(4)

ATOMIC COORDINATES AND TEMPERATURE FACTORS

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	
C(1)	0.494(3)	0.767(2)	0.215(1)	4.0(6)
C(2)	0.547(3)	0.669(2)	0.215(1)	1.9(5)
C(3)	0.407(3)	0.515(2)	0.217(1)	2.4(5)
C(4)	0.240(3)	0.487(2)	0.223(1)	2.9(6)
C(5)	0.781(3)	0.006(2)	0.175(1)	2.6(5)
C(6)	0.592(3)	0.028(2)	0.151(1)	4.0(6)
C(7)	0.008(3)	0.260(2)	0.222(1)	3.2(6)
C(8)	0.988(3)	0.744(2)	0.216(1)	3.3(6)
C(11)	0.599(3)	0.604(2)	0.029(1)	3.6(6)
C(12)	0.595(3)	0.690(1)	0.063(1)	2.4(5)
C(13)	0.646(3)	0.856(2)	0.048(1)	2.6(5)
C(14)	0.282(3)	0.092(2)	-0.005(1)	4.1(6)
C(15)	1.017(3)	0.890(2)	0.040(1)	4.3(7)
C(16)	0.096(3)	0.814(2)	0.078(1)	5.0(7)
C(17)	0.049(3)	0.342(2)	0.091(1)	3.5(6)
C(18)	0.233(3)	0.316(2)	0.108(1)	2.9(6)

TABLE 2

INTRAMOLECULAR DISTANCES FOR  $\beta_2^1\text{-(Co(trien)(gly)Cl}_2$ Distances within isomeric  $\beta_2^1\text{-RS-(Co(trien)(gly))}^{2+}$  cations.

<u>Atoms</u>	<u>Distance(A)</u> <sup>o</sup>	<u>Atoms</u>	<u>Distance(A)</u> <sup>o</sup>
Co(1)—N(1)	2.01(2)	Co(11)—N(11)	2.00(2)
Co(1)—N(2)	1.96(2)	Co(11)—N(12)	1.99(2)
Co(1)—N(3)	1.99(2)	Co(11)—N(13)	1.99(2)
Co(1)—N(4)	2.00(2)	Co(11)—N(14)	1.96(2)
Co(1)—N(5)	1.99(2)	Co(11)—N(15)	2.01(2)
Co(1)—O(2)	1.52(3)	N(11)—C(11)	1.52(3)
C(1)—C(2)	1.52(3)	C(11)—C(12)	1.55(3)
N(2)—C(3)	1.50(3)	N(12)—C(13)	1.51(3)
C(3)—C(4)	1.52(3)	C(13)—C(14)	1.53(3)
N(3)—C(4)	1.49(3)	N(13)—C(14)	1.55(3)
N(3)—C(5)	1.52(3)	N(13)—C(15)	1.49(3)
C(5)—C(6)	1.58(3)	C(15)—C(16)	1.50(3)
N(4)—C(6)	1.49(3)	N(14)—C(16)	1.52(3)
N(5)—C(7)	1.47(3)	N(15)—C(17)	1.50(3)
C(7)—C(8)	1.53(3)	C(17)—C(18)	1.53(3)
O(1)—C(8)	1.29(3)	O(11)—C(18)	1.27(3)
O(2)—C(8)	1.27(3)	O(12)—C(18)	1.26(3)

TABLE 3

INTRAMOLECULAR BOND ANGLES FOR  $\beta_2$ -RS-(Co(trien)(gly))Cl<sub>2</sub>  
 ANGLES WITHIN ISOMERIC  $\beta_2$ -RS-(Co(trien)(gly))<sup>2+</sup> CATIONS

<u>Atoms</u>	<u>Angle, deg.</u>	<u>Atoms</u>	<u>Angle, deg.</u>
N(1)-Co(1)-N(2)	87(1)	N(11)-Co(11)-N(12)	87(1)
N(2)-Co(1)-N(3)	85(1)	N(12)-Co(11)-N(13)	86(1)
N(3)-Co(1)-N(4)	86(1)	N(13)-Co(11)-N(14)	87(1)
O(2)-Co(1)-N(5)	87(1)	O(12)-Co(11)-N(15)	85(1)
N(1)-Co(1)-N(4)	92(1)	N(11)-Co(11)-N(14)	89(1)
N(2)-Co(1)-N(4)	97(1)	N(12)-Co(11)-N(14)	97(1)
N(1)-Co(1)-N(5)	94(1)	N(11)-Co(11)-N(15)	93(1)
N(5)-Co(1)-N(4)	89(1)	N(15)-Co(11)-N(14)	91(1)
N(1)-Co(1)-O(2)	89(1)	N(11)-Co(11)-O(12)	92(1)
N(2)-Co(1)-O(2)	87(1)	N(12)-Co(11)-O(12)	87(1)
N(3)-Co(1)-O(2)	94(1)	N(13)-Co(11)-O(12)	93(1)
N(3)-Co(1)-N(5)	95(1)	N(13)-Co(11)-N(15)	95(1)
Co(1)-N(1)-C(1)	108(1)	Co(11)-N(11)-C(11)	108(2)
C(1)-N(1)-C(2)	105(2)	C(11)-N(11)-C(12)	106(12)
Co(1)-N(2)-C(3)	110(1)	Co(11)-N(12)-C(13)	111(2)
N(2)-C(3)-C(4)	103(2)	N(12)-C(13)-C(14)	104(2)

TABLE 3. (contd)

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<u>Atoms</u>	<u>Angle, deg.</u>	<u>Atoms</u>	<u>Angle, deg.</u>
C(2)-N(2)-C(3)	118(2)	C(12)-N(12)-C(13)	121(2)
C(3)-C(4)-N(4)	113(2)	C(13)-C(14)-N(14)	110(2)
C(4)-N(3)-Co(1)	108(1)	C(14)-N(13)-Co(11)	106(1)
Co(1)-N(3)-C(5)	108(1)	Co(11)-N(13)-C(15)	110(1)
Co(1)-N(2)-C(2)	108(1)	Co(11)-N(12)-C(12)	104(1)
C(6)-N(4)-Co(1)	111(1)	C(16)-N(14)-Co(11)	107(1)
Co(1)-N(5)-C(7)	110(1)	Co(11)-N(15)-C(17)	110(1)
N(5)-C(7)-C(8)	110(2)	N(15)-C(17)-C(18)	108(2)
C(8)-O(2)-Co(1)	112(2)	C(18)-O(12)-Co(11)	116(2)
O(2)-C(8)-O(1)	119(2)	O(12)-C(18)-O(11)	120(2)
C(4)-N(3)-C(5)	114(2)	C(13)-N(13)-C(15)	107(2)
C(2)-C(1)-N(1)	108(2)	C(12)-C(11)-N(11)	103(2)
C(1)-C(2)-N(2)	105(2)	C(11)-C(12)-N(12)	106(2)
N(2)-C(3)-C(4)	103(2)	N(12)-C(13)-C(14)	105(2)
N(3)-C(4)-C(3)	112(2)	N(13)-C(14)-C(13)	109(2)
N(3)-C(5)-C(6)	106(2)	N(13)-C(15)-C(16)	112(2)
N(5)-C(7)-C(8)	110(2)	N(15)-C(17)-C(18)	109(2)
O(1)-C(8)-C(7)	120(2)	O(11)-C(18)-C(17)	120(2)
O(2)-C(8)-C(7)	121(2)	O(12)-C(18)-C(17)	119(2)
C(5)-C(6)-N(4)	109(2)	C(15)-C(16)-N(14)	114(2)

TABLE 3 (contd)

<u>Atoms</u>	<u>Angle, deg.</u>	<u>Atoms</u>	<u>Angle, deg.</u>
O(1)-C(8)-O(2)	119(2)	O(11)-C(18)-O(12)	119(2)
C(5)-N(3)-C(4)	114(2)	C(15)-N(13)-C(14)	109(2)

(a) Normal equation for plane is referred to the orthogonal set of axes, is  $lX + mY + nZ - p = 0$  where  $l, m, n$  are the direction cosines of the normal to the plane and  $p$  is the distance of the plane from the origin.

Atoms included in the plane	Plane no.	A	B	C	D
Co(1),N(1),N(2),N(3),N(5)	1	-0.5474	-0.2823	-0.7878	7.6553
Co(1),O(2),N(1),N(3),N(4)	2	0.7065	0.3897	-0.5907	-0.9756
Co(1),O(2),N(2),N(4),N(5)	3	-0.5089	0.8607	-0.0154	0.3789

(b) Deviations of Atoms from Planes ( $\text{\AA}$ )

Atoms	Plane 1	Plane 2	Plane 3
Co(1)	0.02	0.03	0.01
O(2)		0.10	-0.01
N(5)	-0.08		0.00
N(1)	0.07	-0.11	
N(2)	-0.09		0.00
N(3)	0.07	0.12	
N(4)		0.10	-0.00

(a) Normal equation for plane is referred to the orthogonal set of axes, is  $lX + mY + nZ - p = 0$  where  $l, m, n$  are the direction cosines of the normal to the plane and  $p$  is the distance of the plane from the origin.

Atoms included in the plane	no.	A	B	C	D
Co(11),N(11),N(12),N(13),N(15)	1	-0.3756	0.0533	-0.9253	10.16
Co(11),O(12),N(11),N(13),N(14)	2	0.8907	0.2835	-0.3554	4.4538
Co(11),O(12),N(12),N(14),N(15)	3	0.2503	-0.9541	-0.1643	5.5414

(b) Deviations of Atoms from Planes ( $\text{\AA}$ )

Atoms	Plane 1	Plane 2	Plane 3
Co(11)	0.02	-0.03	0.00
O(12)		-0.09	-0.01
N(15)	-0.10		0.01
N(11)	0.10	0.11	0.01
N(12)	-0.12		0.01
N(13)	0.10	0.11	
N(14)		-0.10	-0.01



TABLE 6

COMPARISON OF DEVIATIONS OF CHELATE RING CARBON ATOMS

FROM N-Co-N PLANES FOR ISOMERIC

 $\beta_2$ -(RS)-(Co(trien)(gly))<sup>2+</sup> CATIONS<sup>a</sup>

<u>Atom</u>	<u>Isomer A</u>	<u>Isomer B</u>
C(1)	-0.19	-0.33
C(2)	0.53	0.52
C(3)	0.58	0.53
C(4)	-0.05	-0.16
C(5)	0.61	-0.32
C(6)	-0.04	-0.60
C(7)	0.02	0.26
C(8)	-0.05	0.18

<sup>a</sup> For convenience, the corresponding atoms of the two isomers are given the same numbers.

For the glycine carbons (C(7), C(8)), the deviations are from the N-Co-O plane.

TABLE 7

COMPARISON OF TORSION ANGLES FOR  
 ISOMERIC  $\beta_2$ -(RS)-(Co(trien)(gly))<sup>2+</sup> CATIONS<sup>a</sup>

<u>Plane 1</u>	<u>Plane 2</u>	<u>Isomer A</u>	<u>Isomer B</u>
Co(1), N(1), C(1)	N(1), C(1), C(2)	35.2	42.3
N(1), C(1), C(2)	C(1), C(2), N(2)	52.7	61.5
C(1), C(2), N(2)	C(2), N(2), Co(1)	45.5	50.4
Co(1), N(2), C(3)	N(2), C(3), C(4)	43.6	45.7
N(2), C(3), C(4)	C(3), C(4), N(4)	46.5	51.6
C(3), C(4), N(3)	C(4), N(3), Co(1)	28.5	33.1
Co(1), N(3), C(5)	N(3), C(5), C(6)	44.4	1.6
N(3), C(5), C(6)	C(5), C(6), N(4)	46.2	22.0
C(5), C(6), N(4)	C(6), N(4), Co(1)	26.8	31.6

<sup>a</sup> For convenience, the corresponding atoms of the two isomers are given the same numbers.

The torsion angles are expressed in degrees.

TABLE 8

HYDROGEN BONDING IN  $\beta_2$ -RS-(Co(trien)(gly))Cl<sub>2</sub>·H<sub>2</sub>O CRYSTAL.

<u>Atoms X...H...Y</u>	<u>d(X...Y), Å</u>	<u>Atoms</u>	<u>Angle, deg.</u>
N(1)---H...O(11)	2.77	Co(1)N(1)O(11) C(1)N(1)O(11)	122 91
N(1)---H...O(21)	2.92	Co(1)N(1)O(21) C(1)N(1)O(21)	114 103
N(5)---H...O(22)	2.91	Co(1)N(5)O(22) C(7)N(5)O(22)	104 108
N(14)---H...O(1)	2.85	Co(11)N(14)O(1) C(16)N(14)O(1)	123 99
N(14)---H...O(2)	2.95	Co(11)N(14)O(2) C(16)N(14)O(2)	59 93
N(3)---H...Cl(3)	3.37	Co(1)N(3)Cl(3) C(4)N(3)Cl(3)	109 81
N(4)---H...Cl(2)	3.35	Co(1)N(4)Cl(2) C(6)N(3)Cl(3)	110 82
N(5)---H...Cl(2)	3.34	Co(1)N(5)Cl(2) C(7)N(5)Cl(2)	110 119
N(12)---H...Cl(2)	3.20	Co(11)N(12)Cl(2) C(13)N(12)Cl(2)	128 85
N(13)---H...Cl(4)	3.29	Co(11)N(13)Cl(4) C(15)N(13)Cl(4)	111 121
N(14)---H...Cl(1)	3.24	Co(11)N(14)Cl(1) C(16)N(14)Cl(1)	100 108
N(15)---H...Cl(1)	3.22	Co(11)N(15)Cl(1) C(17)N(15)Cl(1)	99 127
N(15)---H...Cl(2)	3.29	Co(11)N(15)Cl(2) C(17)N(15)Cl(2)	119 100

TABLE 8 (contd)

<u>Atoms X—H...Y</u>	<u>d(X...Y), Å</u>	<u>Atoms</u>	<u>Angle, deg.</u>
O(21)—H...Cl(4)	3.10	N(1)O(21)Cl(3)	106
O(21)—H...Cl(3)	3.15	Cl(3)O(21)Cl(4)	104
O(22)—H...Cl(3)	3.02	N(5)O(22)Cl(3)	105
O(22)—H...O(12)	3.14	Co(11)O(12)O(22)	133
		C(18)O(12)O(22)	95
O(22)—H...O(11)	3.28	C(17)O(11)O(22)	118
		C(18)O(11)O(22)	89

TABLE 9

NONBONDED CONTACTS 3.5<sup>o</sup>Å IN $\beta_2$ -(Co(trien)(gly))Cl<sub>2</sub>·H<sub>2</sub>O CRYSTAL.

<u>Atoms(X.....Y)</u>	<u>d(X.....Y)<sup>o</sup>Å</u>	<u>Atoms(X.....Y)</u>	<u>d(X.....Y)<sup>o</sup>Å</u>
O(1).....C(16)	3.42	Cl(1).....N(11)	3.39
O(1).....C(12)	3.45	Cl(1).....N(12)	3.44
O(1).....C(13)	3.47	Cl(2).....N(5)	3.34
O(2).....C(16)	3.38	Cl(4).....N(13)	3.29
O(2).....Cl(3)	3.47	Cl(2).....C(13)	3.38
O(2).....O(21)	3.49	Cl(2).....C(6)	3.48
O(11).....C(4)	3.10	Cl(3).....C(4)	3.46
O(11).....C(1)	3.19	Cl(3).....N(11)	3.49
O(11).....C(7)	3.30	Cl(4).....N(4)	3.28
O(11).....C(3)	3.31		

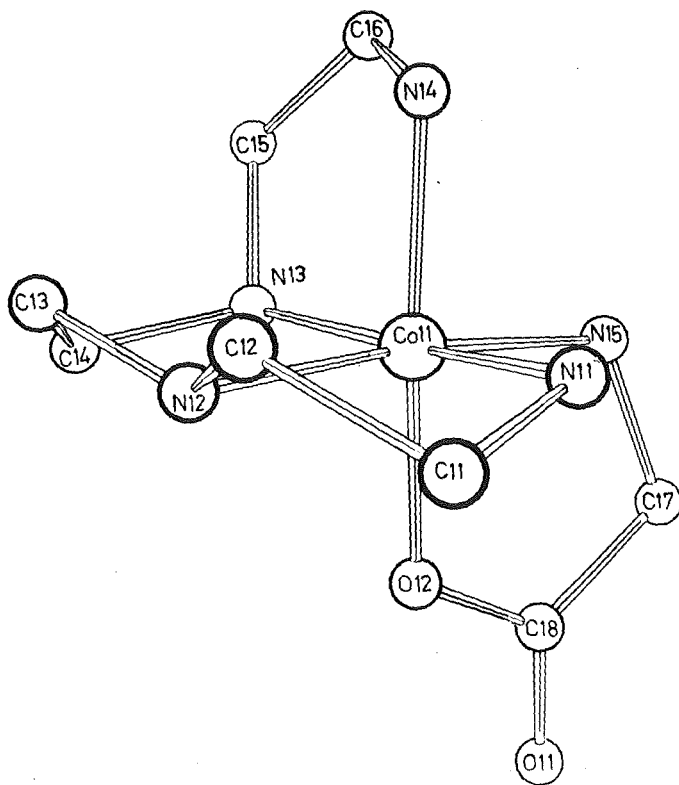
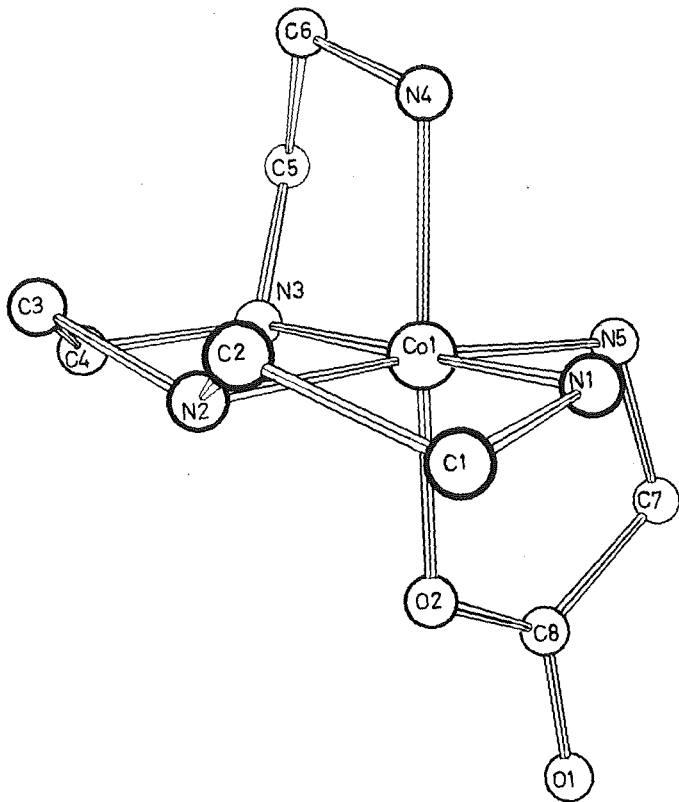


Figure 1

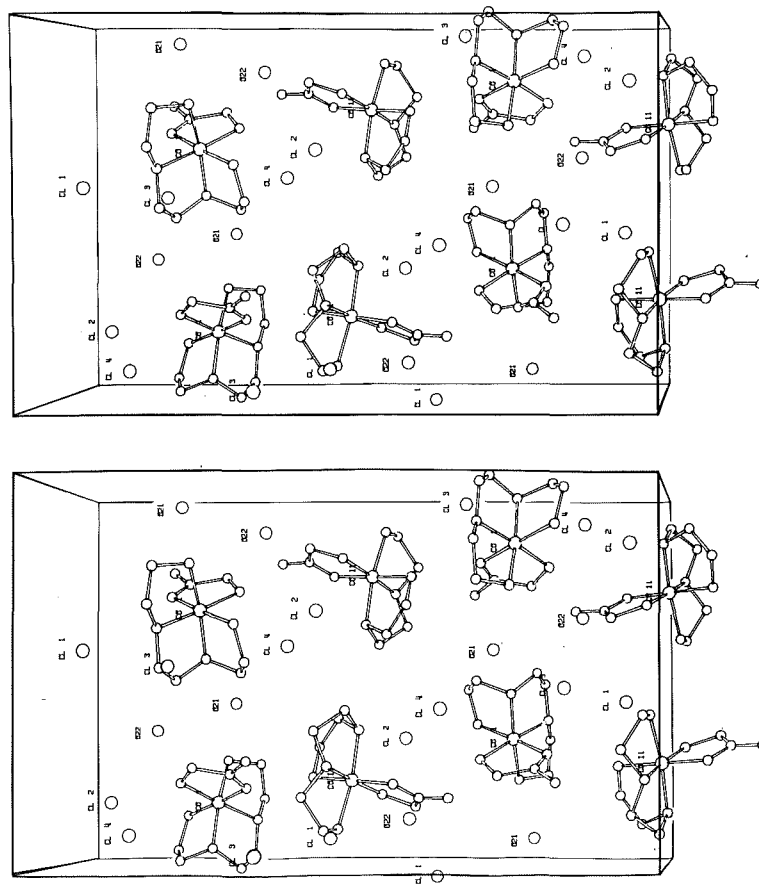
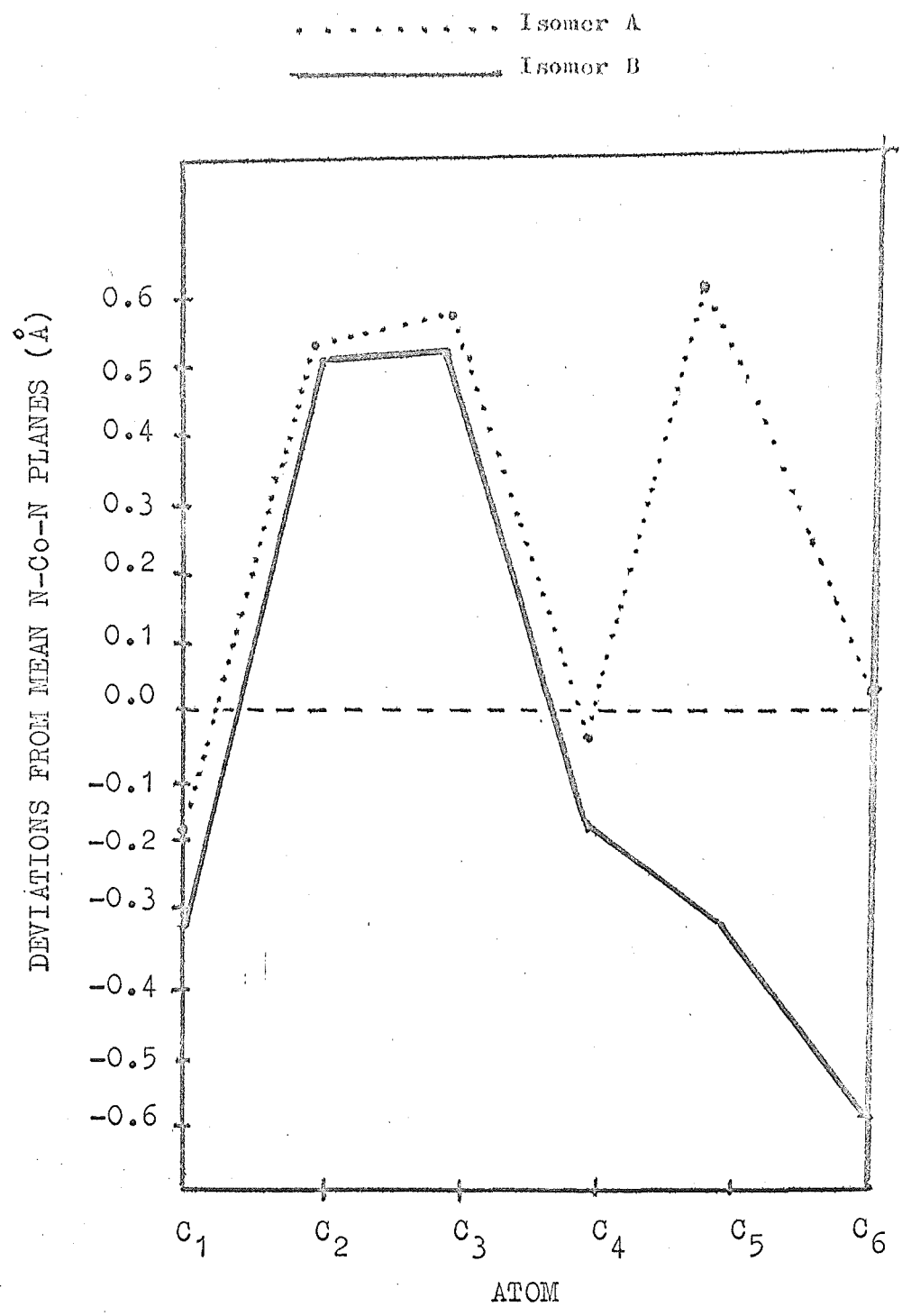


Figure 2

Figure 3.--Comparison of deviations of carbon atoms from their respective N-Co-N planes for the  $\beta_2^1$  - trien chelate rings.





TORSION ANGLE NUMBERS

1 = Co(1)-N(1)-C(1)-C(2)

2 = N(1)-C(1)-C(2)-N(2)

3 = C(1)-C(2)-N(2)-Co(1)

4 = Co(1)-N(2)-C(3)-C(4)

5 = N(2)-C(3)-C(4)-N(3)

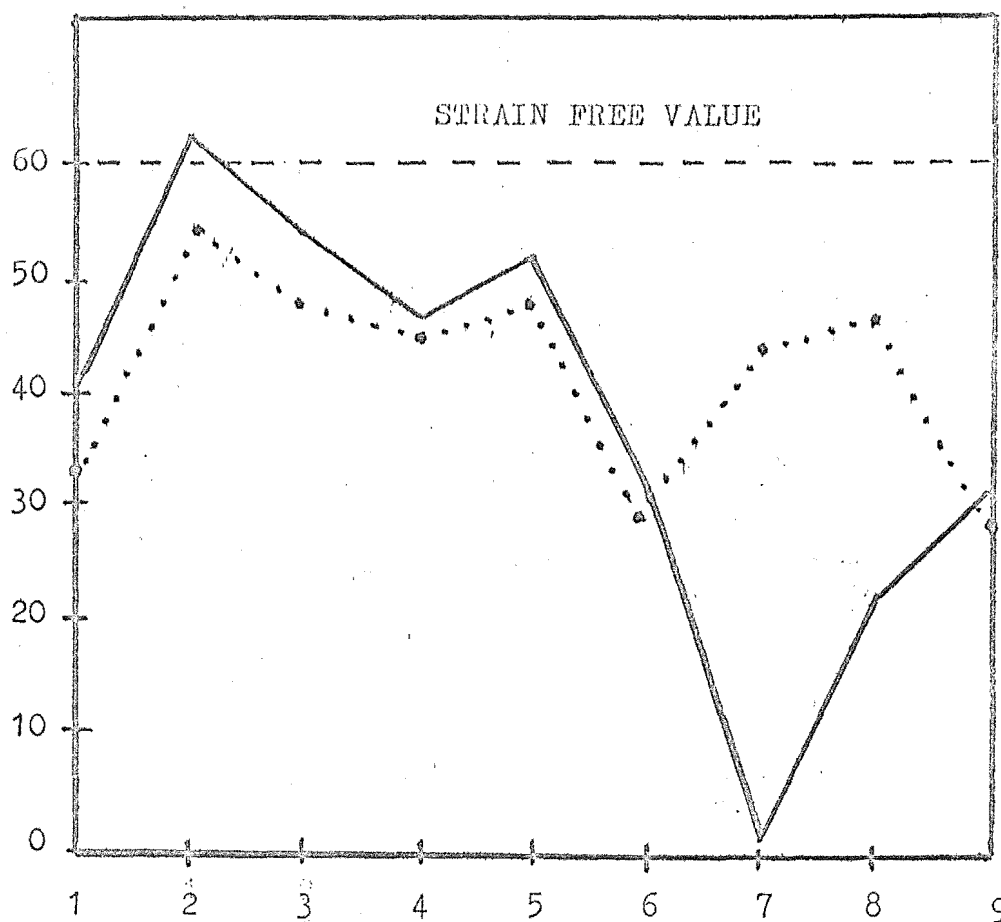
6 = C(3)-C(4)-N(3)-Co(1)

7 = Co(1)-N(3)-C(5)-C(6)

8 = N(3)-C(5)-C(6)-N(4)

9 = C(5)-C(6)-N(4)-Co(1)

..... Isomer A  
 \_\_\_\_\_ Isomer B



are 4.--Comparison of torsion angles for

$\beta_2^+$ -trien chelate rings.

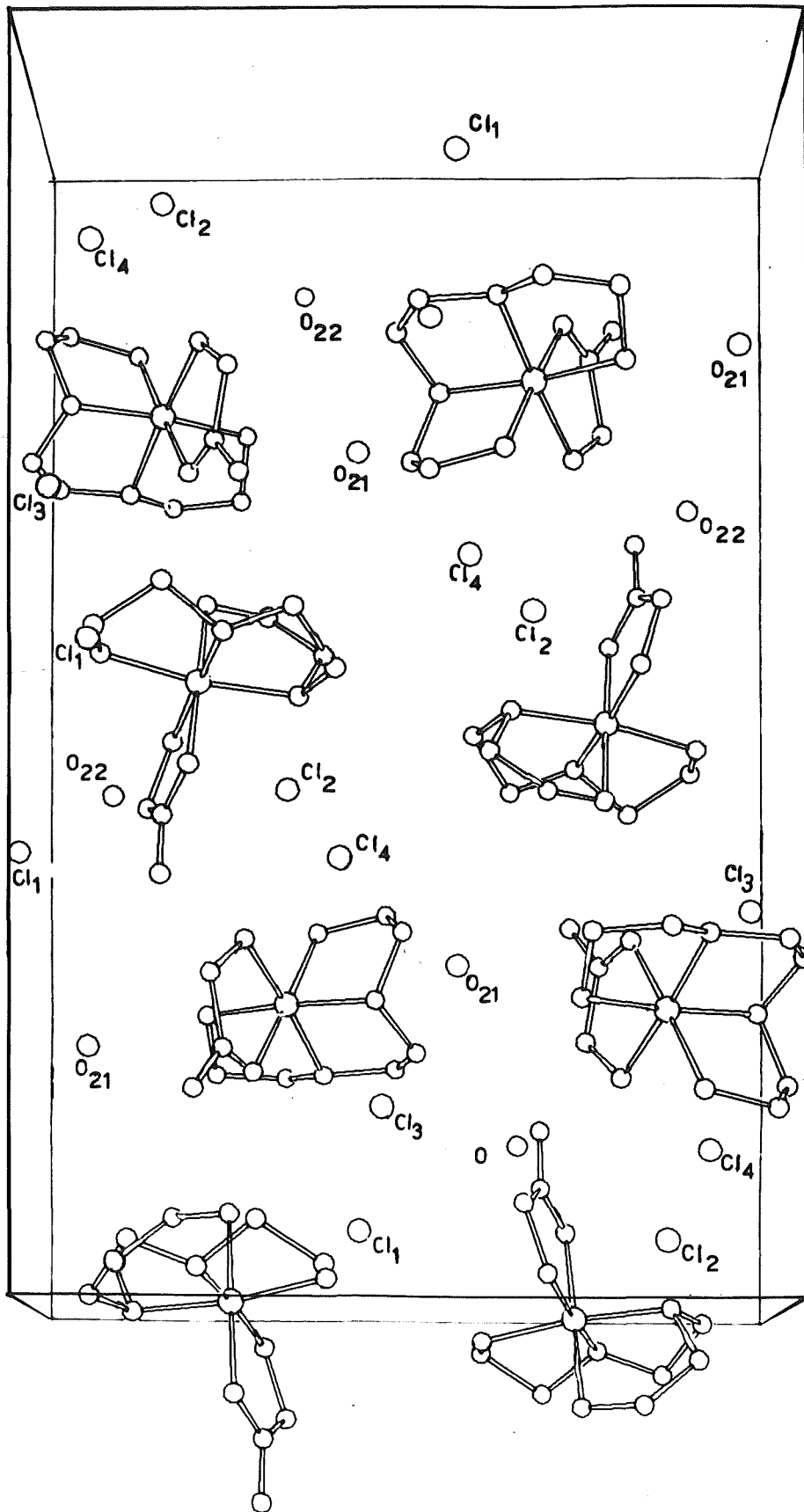


Figure 5