# STRUCTURES AND ABSOLUTE CONFIGURATIONS OF COBALT(III) COMPLEXES

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## INTRODUCTION

Although the existence of chelate rings and the general features of the structure of metal chelates have been established by chemical methods of investigation, our knowledge of chelation was greatly strengthened by the confirmation of the correctness of their structures by x-ray crystal analysis. X-ray crystal analysis introduced a metrical element into the understanding of coordination by revealing the lengths and angles of chemical bonds and other structural details that could not be ascertained by other physical and chemical methods.

Normal x-ray methods do not tell us whether the optically active complex has a particular configuration or one related to this as its mirror image. In other words, it is not possible to assign the absolute stereochemical configurations to enantiomorphically related pairs of the complexes. However, if an x-ray wavelength a little shorter than the absorption edge of the heavy atom in the crystal is used, the anomalous phase shift on scattering by the heavy atom has the effect of advancing the wave from it relative to the waves from the rest of the atoms. This will give rise to a slight but discernible change in intensities of pairs of reflections, which are normally equal in intensity because of the requirement of the space group. Bijvoet[1] first pointed out that this effect can be used to determine the absolute configuration of the molecules. The intensities can be calculated by assuming a particular enantiomorphic configuration for the complex and the result can be compared with the observation. If the intensity relations are the reverse of those observed, then the inverted configuration represents the correct absolute stereochemical configuration. No other physical method is, at present, capable of determining the absolute configuration unambiguously.

The knowledge of the absolute configuration of optically active complex ions will not only deepen our understanding of the mechanism of the interaction by which the rotatory power and its close associate, circular dichroism, are exerted, but also enable us to rationalize various chemical phenomena involving stereospecific effects.

## ROTATIONAL ISOMERISM IN COORDINATED LIGANDS (FIVE-MEMBERED CHELATE RINGS)

The first topic is the rotational isomerism possible in coordinated ligands such as ethylenediamine. It is well known that if chelation can take place to

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form five-membered rings, the stability of the compounds is greatly enhanced. Ethylenediamine is the simplest and the most important of chelating bases and these complexes have played an important part in the development of the coordination theory.

The suggestion that the five-membered chelate rings formed by ethylenediamine need not be planar appeared first in a paper on platinum complexes by Rosenblatt and Schleede[2] as early as 1933. In 1939, Kobayashi[3] studied the optical activity of $(+)_D$-[Co(en)$_3$]Br$_3$ and also suggested that the chelate ring was puckered. This was indeed verified by an x-ray study of [Cu(en)$_2$]$^{2+}$ by Scouloudi[4], and then of trans-[CoCl$_2$(en)$_2$]$^+$ by Nakahara, Saito and Kuroya[5]. The existence of puckering in chelate rings has also been established by structural analyses of a number of other metal chelates.

Since there are two possible enantiomorphic 'gauche' conformations for ethylenediamine molecules, two conformations of coordinated ethylenediamine rings are possible as shown in Figure 1. These are mirror images of each other and are called the δ and λ forms according to the nomenclature proposed at the Meeting of the Nomenclature Commission on Inorganic Chemistry of IUPAC (held at Beckenried, Switzerland, 1966).
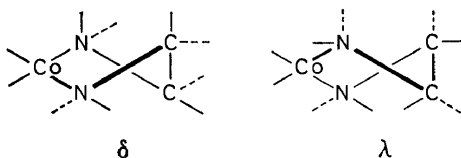


*Figure 1.* Two possible conformations of cobalt–ethylenediamine ring.

In the trans-dihalogenobis(ethylenediamine)cobalt(III) ion, the following three arrangements of two cobalt–ethylenediamine rings can occur: (δδ), (λλ), (δλ). (δδ) and (λλ) are mirror images and have the same relative potential energy. The relative potential energies of (δδ) and (δλ) must, however, be different. This energy difference has been calculated by Corey and Bailar[6] who found that the (δδ) configuration is more stable by about 1 kcal/mole.

The crystal structures of the two isotype crystals of trans-dihalogenobis-(ethylenediamine)cobalt(III) halide hydrogen halide dihydrate, [CoX$_2$(en)$_2$]-X.HX.2H$_2$O(X = Cl[5], Br[7]) have been determined. The complex ion was found, however, to be centrosymmetric and to have the (δλ) conformation as illustrated in Figure 2. In this case the (δλ) form must be favoured by specific intermolecular forces in the crystalline state.

When propylenediamine is introduced in place of ethylenediamine, the stereochemistry is further complicated, since the ligand molecule itself is optically active. From an x-ray examination of trans-dichlorobis(d,l-propylenediamine)* cobalt(III)chloride hydrochloride dihydrate, [CoCl$_2$(d,l-pn)$_2$]

*The symbols d and l attached to organic molecules are used to denote (+) and (−) for the Na D line, respectively. The symbols D and L are used to denote the absolute configurations of optically active organic molecules.

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Cl.HCl.2H$_2$O[8], it was revealed that the general features of the crystal structure resemble those of the ethylenediamine analogue and the complex ion is again centrosymmetric and assumes the ($\delta\lambda$) form, but if optically
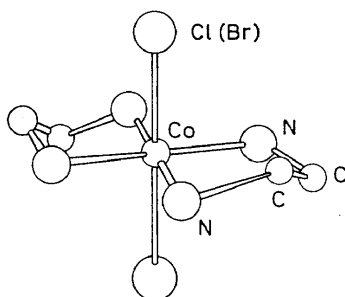


*Figure 2.* A perspective drawing of the complex ion [CoX$_2$(en)$_2$]$^+$, (X = Cl, Br)

active propylenediamine is used, the complex ion is clearly no longer centrosymmetric. It will be readily seen that there are six possible stereo-isomers of the *trans*-[CoX$_2$(*l*-pn)$_2$] ion. First there are two possible directions of each C—CH$_3$ bond with respect to the chelate ring. The C—CH$_3$ bond can lie approximately parallel to the 'plane' of the five membered chelate ring, or it can stand approximately perpendicular to the plane of the chelate ring. These forms are called 'equatorial' and 'axial' respectively. Secondly, there are two possible positions of the methyl groups with respect to the cobalt atom, viz.
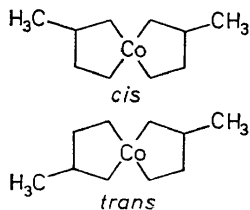


If we denote these two forms as *cis* and *trans* referring to the positions of the methyl groups, the six possible isomers may be represented as follows:

*cis* (ax,ax), *cis* (ax,eq), *cis* (eq,eq),

*trans* (ax,ax), *trans* (ax,eq), *trans* (eq,eq).

These six forms are distinguishable from each other by ordinary x-ray methods without recourse to anomalous scattering effects. In fact, the *trans*-[CoCl$_2$(*l*-pn)$_2$]$^+$ ion has been shown[9] to have the *trans* (eq,eq) form, which is illustrated in *Figure 3.*

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*Figure 3* also represents the absolute configuration of *trans*-dichlorobis-(*l*-propylenediamine)cobalt(III) ion. The complex ion has an approximate twofold axis of symmetry through the central cobalt atom. Accordingly, the most stable form present in the solid state corresponds to the ($\lambda\lambda$) form with respect to the conformation of the chelate ring.
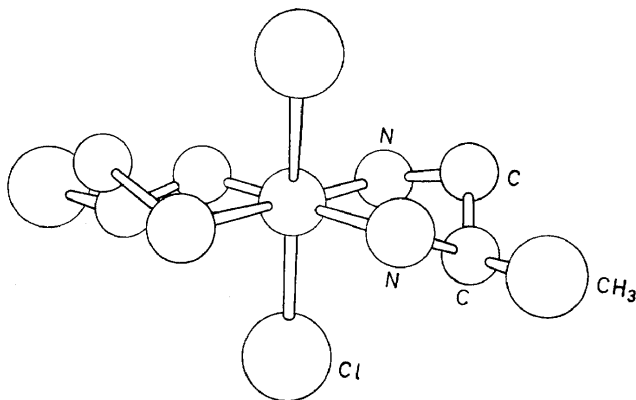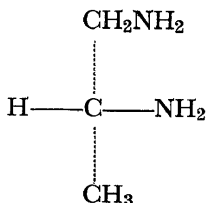


*Figure 3.* A perspective drawing of the complex ion $(-)_D-[CoCl_2(l-pn)_2]^+$

The absolute configuration of *l*-propylenediamine molecule is represented by the formula:

$$\begin{array}{c} CH_2NH_2 \\ | \\ H—C—NH_2 \\ | \\ CH_3 \end{array}$$

This is in agreement with the result determined chemically with reference to D($-$)-alanine[10, 11]. It is to be noted here that when a molecule of *l*-propylenediamine is coordinated to a metal atom to form a chelate ring with its C—CH$_3$ bond in the equatorial position, the conformation of the chelate ring necessarily becomes $\lambda$.

When three bidentate ligands are coordinated octahedrally to a central metal atom, two optically active isomers can occur. In *Figure 4*, the isomers are viewed along a threefold axis of the octahedron. We call these isomers $\varDelta$ and $\varLambda$.† This isomerism has been proved for a number of compounds. The first investigation by x-ray diffraction was that of the tris-(oxalato)chromate(III) ion performed by Niekerk and Schoening[12]. In this case oxalate groups are planar, but if the metal–chelate rings are not planar, the situation becomes more complicated. One of the best examples is provided again by ethylenediamine. If we denote the two enantiomorphic

†According to the new proposals of the IUPAC Commission on the Nomenclature of Inorganic Chemisty (August 1968), the use of $\varDelta$ and $\varLambda$ are opposite to those reported here.

$$\Delta\,(C_2) \qquad\qquad \Lambda\,(C_2)$$

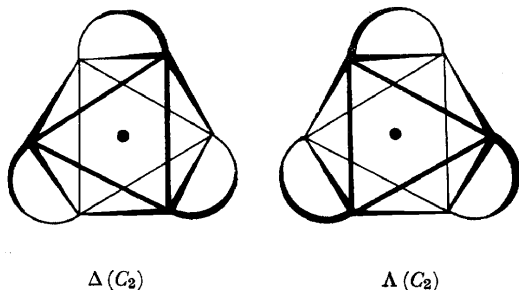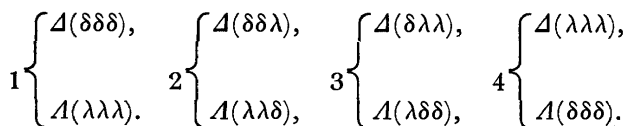**Figure 4.** Two possible isomers of an octahedral tris(bidentate) complex.

conformations of the metal–ethylenediamine rings as $\delta$ and $\lambda$, and represent the two possible configurations of the chelate ring around the metal atom as $\Delta$ and $\Lambda$, then there are eight possible configurations for an octahedral tris ethylenediamine complex, viz.

$$1\begin{cases}\Delta(\delta\delta\delta),\\[4pt]\Lambda(\lambda\lambda\lambda).\end{cases}\quad 2\begin{cases}\Delta(\delta\delta\lambda),\\[4pt]\Lambda(\lambda\lambda\delta),\end{cases}\quad 3\begin{cases}\Delta(\delta\lambda\lambda),\\[4pt]\Lambda(\lambda\delta\delta),\end{cases}\quad 4\begin{cases}\Delta(\lambda\lambda\lambda),\\[4pt]\Lambda(\delta\delta\delta).\end{cases}$$

Without considering anomalous dispersion, x-ray methods can identify the forms 1–4, but the two enantiomorphic forms in each pair cannot be identified., unless the absorption edge technique is used. In crystals of $[Co(en)_3]Cl_3.3H_2O$, the complex ion was found to possess a threefold axis of symmetry, requiring the complex ion to be either 1 or 4. The difference between structures 1 and 4 can be stated as follows: In form 1 the direction of the central C—C bond in an ethylenediamine molecule is approximately parallel to the threefold axis of the complex ion, while it is largely slanted obliquely in form 4. Corey and Bailar[6] labelled these two isomers as the 'lel' and 'ob' forms, respectively. They are shown in *Figure 5*[13].
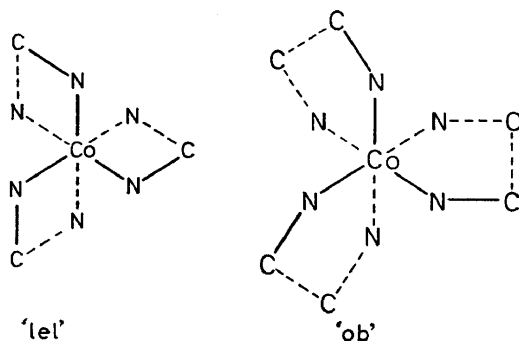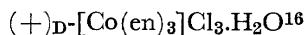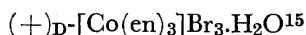


'lel' 'ob'

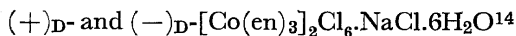**Figure 5.** The 'lel' and 'ob' forms of the complex ion $[Co(en)_3]^{3+}$.

The result of x-ray analysis showed that the tris(ethylenediamine)-cobalt(III) ion has the 'lel' form. This agrees with the result of calculation that the 'lel' form is more stable by about 2 kcal/mole than the 'ob' form. This was confirmed also for other complexes shown below:

$$(+)_D\text{- and }(-)_D\text{-}[Co(en)_3]_2Cl_6.NaCl.6H_2O^{14}$$

$$(+)_D\text{-}[Co(en)_3]Br_3.H_2O^{15}$$

$$(+)_D\text{-}[Co(en)_3]Cl_3.H_2O^{16}$$

Saito *et al.*[17] have determined the absolute configuration of the complex ion by using the double salt listed above, and then Nakatsu[15] confirmed the result by using $(+)_D$-tris(ethylenediamine)cobalt(III) bromide monohydrate. Complete three dimensional analysis of $(+)_D$-tris(ethylenediamine)cobalt (III) chloride monohydrate has been finished recently[16]. In these studies the shape and size of the tris(ethylenediamine)cobalt(III) ion was completely established, and it was concluded that the ion has $D_3$ symmetry within the limits of the experiments. The shape and size of the cobalt–ethylenediamine ring are summarized as follows:

$$Co\text{—}N = 1{\cdot}991 \pm 0{\cdot}009\,Å \quad \angle CoNC = 108{\cdot}71° \pm 0{\cdot}70°$$

$$N\text{—}C = 1{\cdot}494 \pm 0{\cdot}015\,Å \quad \angle NCC = 105{\cdot}36° \pm 0{\cdot}86°$$

$$C\text{—}C = 1{\cdot}567 \pm 0{\cdot}015\,Å \quad \angle NCoN = 85{\cdot}45° \pm 0{\cdot}39°$$

These studies of $[Co(en)_3]^{3+}$ ions show that the displacement of the nitrogen atoms from the octahedral position is insignificant or very small. The upper face of the octahedron, formed by the three nitrogen atoms, is rotated approximately 5° from the position required as a perfect octahedron. The $\angle NCoN$ is 85·5° on the average.

Here, a few words will be added about the thermal vibration of the chelate ring in crystals of $(+)_D$-$[Co(en)_3]Cl_3.H_2O$. The anisotropic thermal parameters of the atoms of the chelate rings were transformed to obtain the axes of the ellipsoids of vibration. *Figure 6* shows the results obtained for the chelate
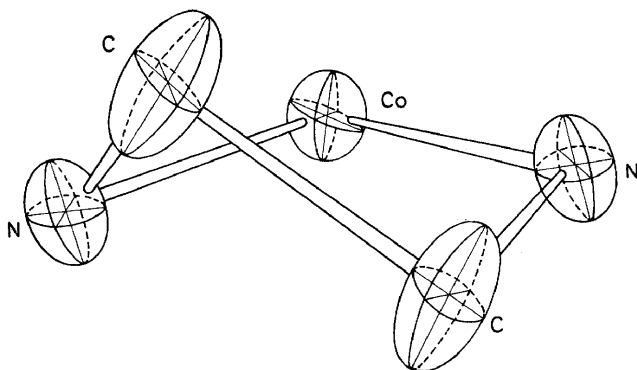


*Figure 6.* View of the ellipsoids of thermal vibration.

ring which lies on a twofold axis. The vibrations are represented dia-grammatically. The axes of the ellipsoids are proportional to the mean square amplitude. The anisotropy of vibration of the atoms is consider-able. The vibrations of the central cobalt atom and the two nitrogen atoms have the smaller amplitude, those of the cobalt atoms being nearly iso-tropic. The two carbon atoms appear to oscillate perpendicularly to the C—C bond with greater amplitude. These features of the anisotropic vibrations of the atoms seem to suggest the existence of a puckering motion of the chelate ring in solution. The mean amplitude of vibration is about 0·3 Å. However, in the other ring which is not on the twofold axis, the vibrations of the carbon atoms are smaller. This is due to the presence of a chloride ion at 3·62 Å from each carbon atom. On the other hand, the corresponding C—Cl distances found for the chelate ring on the twofold axis are 3·86 Å, long enough to allow such vibrations of the carbon atoms. In fact, Mason *et al.* measured the circular dichroism spectra of $[Co(en)_3]^{3+}$ ions in solution and suggested that different conformations of $[Co(en)_3]^{3+}$ coexist in solution[18]. This was supported by the thermodynamic data obtained by Dwyer *et al*[19].

The carbon atoms in the ring are arranged symmetrically 0·34 Å above and below the plane determined by the cobalt and nitrogen atoms. Unlike the symmetrical gauche form observed in the cobalt–ethylenediamine complexes, Brown and Lingafelter[20] found that the ethylenediamine ring in the copper complex, $[Cu(en)_2]$ $(SCN)_2$ has an unsymmetrical gauche form. One carbon atom is 0·16 Å and the other carbon atom is −0·53 Å from the plane of copper and two nitrogen atoms. The same kind of asym-metry has been observed on other copper(II) complexes[4, 21, 22].
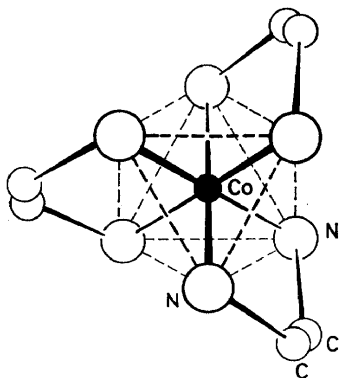


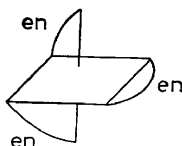*Figure 7.* A drawing of the complex ion $(+)_D$-$[Co(en)_3]^{3+}$.

The absolute configuration of $(+)_D[Co(en)_3]^{3+}$ is shown in *Figure 7*[17]. It can be represented as $\varDelta(\delta\delta\delta)$. In the usual manner this can be written as:

C—CH$_3$ bonds lie in an equatorial position relative to the plane of the five-membered ring, in agreement with the prediction of Corey and Bailar based on the conformational analysis of the chelate ring[6]. The absolute configuration of the complex ion $(-)_D$-[Co($l$-pn)$_3$]$^{3+}$ can be denoted as $\Lambda(\lambda\lambda\lambda)$. If three methyl groups of $(-)_D$[Co($l$-pn)$_3$]$^{3+}$ are replaced by hydrogen atoms, the absolute configuration of the complex ion $(-)_D$-[Co(en)$_3$]$^{3+}$ is obtained. Smirnoff[25] found that the o.r.d. curves of these complex ions correspond well to each other. From this fact it has been deduced that these two ions possess the same absolute configuration. The present investigation has revealed that this is actually the case. Thus the conventional method of correlating the absolute configurations with the o.r.d. curves has been proved for the first time to be useful and reliable in the field of metal complexes.

We have also prepared single crystals of $(-)_D$-[Co($d$-pn)$_3$] [Co(CN)$_6$]. 3H$_2$O which contain the less stable form of the complex ion and determined its crystal structure completely[26]. The cubic crystals are ionic and consist of octahedral hexacyanocobaltate(III) ions and the complex cations. They are packed in much the same way as the ions in sodium chloride. *Figure 9* is a drawing of $(-)_D$-tris($d$-propylenediamine)cobalt(III) ion viewed along its threefold axis. The complex ion has a threefold axis because of the requirement of the space group. Thus the three methyl groups are again attached
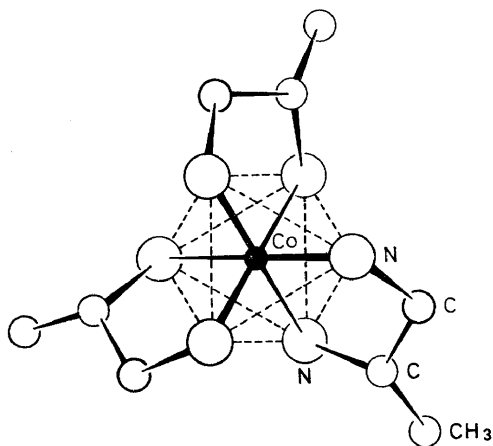


*Figure 9.* A drawing of the complex ion $(-)_D$-[Co($d$-pn)$_3$]$^{3+}$.

in the facial positions. The five-membered chelate rings resemble those found in other related complexes. The C—CH$_3$ bonds are in equatorial positions, but the central C—C bond in the chelate ring is slanted obliquely by about 60° from the threefold axis. Thus the complex ion takes the 'ob' form. All the C—C and C—N bond lengths and angles are normal. Comparing this fact with that obtained for the more stable 'lel' form, we can easily realize that the 'lel' form is favoured mainly because of the less severe non-bonded hydrogen interactions.

The absolute configuration of $(-)_D$-[Co($d$-pn)$_3$]$^{3+}$ can be represented as $A(\delta\delta\delta)$. In *Table 1* the relationships of these stereoisomers to $D(-)$-alanine is shown.

*Table 1*

$$D(-)\text{–alanine}$$
$$\downarrow$$
$$l\text{–pn}$$

| | |
|---|---|
| $(-)_D$-[Co($l$-pn)$_3$]$^{3+}$ | $(+)_D$-[Co($l$-pn)$_3$]$^{3+}$ |
| $A(\lambda\lambda\lambda)$ | $\Delta(\lambda\lambda\lambda)$ |
| more stable isomer 'lel' | less stable isomer 'ob' |

| | | |
|---|---|---|
| Symmetry | $C_3$ | $C_3$ |
| Position of CH$_3$ groups | fac | fac |

The 'ob' conformation of metal–ethylenediamine ring is frequently found in various *cis*-isomers of dihalogeno-bis(ethylenediamine)cobalt(III) and nickel(II) complexes[27, 28].

## SIX-MEMBERED CHELATE RINGS

Next six-membered chelate rings will be discussed. As pointed out by Bailar and Work[29] it is an interesting fact that the presence of trimethylenediamine in place of ethylenediamine produces changes which seem to depend upon strains in the complex molecule rather than upon the strength of the cobalt–nitrogen bond. While the *cis*-isomer of dichlorobis(ethylenediamine)cobalt(III) chloride is obtained readily and is comparable in stability to the *trans* form, the *cis* form of the trimethylenediamine analogue is extremely difficult to prepare. The salts of tris(trimethylenediamine)cobalt(III) are purple red, which is in contrast to the orange red colour of tris(ethylenediamine cobalt(III) bromide. This change in colour is evidently inherent in the structure of the complex ions in the crystal, for it is not evident in solution but it reappears upon recrystallization. This complex ion contains a six-membered chelate ring. Even simple molecular models show at once that three boat forms cannot be accommodated to form an octahedral complex and that three chair forms can be accommodated subject to severe non-bonded hydrogen interactions between rings. Thus Woldbye[30] proposed that the chelate rings would assume a twist conformation analogous to the twist form of the flexible cyclohexane conformation.

The crystal structure of $(-)_D$-tris(trimethylenediamine)cobalt(III) bromide has been determined[31]. The crystals are ionic and consist of the complex ions, bromide ions and molecules of water of crystallization. The crystals were kindly supplied by Dr. Woldbye of the Technical University of Denmark. A drawing of the $(-)_D$-tris(trimethylenediamine)cobalt(III) ion is shown in *Figure 10*. The complex ion has approximately a threefold

axis through the central cobalt atom. The three six-membered chelate rings are nearly but not exactly identical and take chair forms. The six-membered ring seems to be more flexible than the five-membered ring. Its conformation may be easily affected by the specific intermolecular forces in the crystal. The chelate ring is rather flattened out due to non-bonded hydrogen interaction. Bond angles $\angle$ CoNC are much larger than the normal tetrahedral angle, the average value being 117·4°. The average
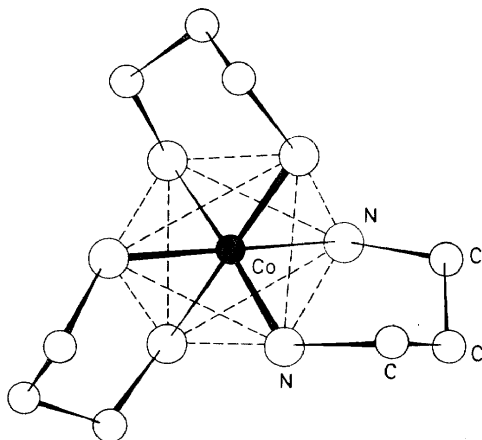


*Figure 10.* A drawing of the complex ion $(-)_D$-$[Co(tn)_3]^{3+}$.

value of $\angle$ NCC and $\angle$ CCC is 112·8°, which is closer to the normal tetrahedral angle. The NCoN angle is larger than 90°, the average value being 94·5°. The Co—N distances are normal and are in the range of 1·999Å~2·022Å. The displacement of the nitrogen atoms from the octahedral position is rather significant and quite irregular. Such a distortion of the chelate rings and the displacement of ligand nitrogen atoms from octahedral positions appear to make the complex less stable than that having five-membered rings and give the crystals an unusual pinkish tint. Such a chair conformation of the cobalt–trimethylenediamine ring has been found in crystals of *trans*-dichlorobis(trimethylenediamine)cobalt(III) chloride hydrochloride dihydrate[32]. It is to be noted here that the puckered conformation of the cobalt–ethylenediamine ring as well as the chair conformation of the cobalt–trimethylenediamine ring are maintained in various complexes with multidentate chelate ligands that contain these amines as their fragments. For example, in *trans*-dichloro(1,4,8,11-tetraazacyclotetradecane)nickel(II)[33], the conformations of the five- and six-membered chelate rings have the same conformations as those found in $[Co(en)_3]^{3+}$ and $[Co(tn)_3]^{3+}$, respectively.

The absolute configuration of this complex ion can be represented as $\Delta$. This configuration is enantiomeric to that assigned on the basis of the sign of the prominent Cotton effect[34].

In *Table 2*, the structures of tris(bidentate)cobalt(III) complexes are summarized together with optical and other data. From the results listed

$$
\begin{array}{c}
\underset{N}{\diagup}\overset{(CH_2)_3}{\diagdown}\underset{N}{} \\
(CH_2)_2 \quad Ni \quad (CH_2)_2 \\
N \diagdown_{(CH_2)_3}\diagup N
\end{array}
$$
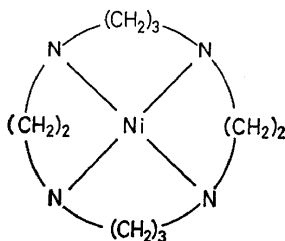
(Cl atoms are not drawn)

in *Table 2*, we can summarize the principles determining the configurations of the complex ions:

1. The most stable form of the complex ion occurring in the crystals is the one having the highest attainable symmetry, as pointed out by Jaeger[35]. Thus all the tris (bidentate) complexes listed in *Table 2* have at least approximately threefold symmetry and the three bidentate rings become identical with one another.

2. When a bidentate ligand like ethylenediamine or a related compound coordinates to a metal atom to form a five-membered ring, the chelate ring is puckered. Two carbon atoms of the ring are symmetrically or asymmetrically arranged above and below the plane defined by the metal atom and the two ligand nitrogen atoms. When the bidentate ligands forms a six-membered ring, the chelate ring assumes a chair conformation.

3. When three bidentate ligands coordinate to a metal atom to form puckered five-membered rings, the central C—C bond prefers the 'lel' conformation to the 'ob' conformation.

4. The substituent attached to the carbon atom of the chelate ring has a tendency to take the equatorial conformation rather than the axial one.

*Table 2.* Structural and other data of tris(bidentate)cobalt(III) complexes

| No. | Active species | Sign of $[\alpha]_D$ | Absolute configuration (X-ray method) | Symmetry | Signs of | | Halo-genotart. |
|---|---|---|---|---|---|---|---|
| | | | | | longer wavelength c.d. band in the visible region | charge transfer c.d. band | |
| 1 | $[Co(en)_3]^{3+}$ | $+$ | $\varDelta$ ($\delta\delta\delta$) 'lel' | $D_3$ | $+$ | $-$ | L. sol. |
| 2 | $[Co(d-pn)_3]^{3+}$ | $+$ | $\varDelta$ ($\delta\delta\delta$) 'lel' | $C_3$ | $+$ | $-$ | L. sol. |
| 3 | $[Co(d-pn)_3]^{3+}$ | $-$ | $\varLambda$ ($\delta\delta\delta$) 'ob' | $C_3$ | $-$ | $-$ | ———— |
| 4 | $[Co(d-cptn)_3]^{3+}$ | — | $\varDelta$ ($\delta\delta\delta$) 'lel' | $D_3$ | $+$ | $-$ | L. sol. |
| 5 | $[Co(d-chxn)_3]^{3+}$ | $-$ | $\varDelta$ ($\delta\delta\delta$) 'lel' | $D_3$ | $+$ | $-$ | L. sol. |
| 6 | $[Co(tn)_3]^{3+}$ | $-$ | $\varDelta$ | $C_3$ | $+$ | ———— | ———— |

## ABSOLUTE CONFIGURATION AND OPTICAL PROPERTIES

The last topic concerns the optical rotatory dispersion, circular dichroism spectra and the absolute configurations of these complex ions. The ultimate goal of the study of optical rotatory dispersion and circular dichroism may be stated as follows: (i) To establish the relationship between optical rotatory power or its close associate, circular dichroism and the absolute stereochemical configuration of the complex. (ii) To elucidate the mechanism of the interaction between light and the complex by which the rotatory power and the circular dichroism are exerted.

X-ray crystal analysis is the ultimate means of determining the absolute configuration of the complex. It provides an absolute standard for the configuration of the complex. The first example is $[Co(en)_3]^{3+}$. The absolute configurations of a number of cobalt(III) complexes have been related through o.r.d. curves and c.d. spectra to that of $[Co(en)_3]^{3+}$ [34, 36-38]. X-ray crystal analysis also gives information concerning the shape and size of the chelate rings and their arrangement about the metal atom. This information will certainly give a clue to the construction of theoretical models for optical activity. The determination of the absolute configuration of these and other complexes may permit a judgement of the appropriateness of the types of models proposed for optical activity.

The optical rotatory dispersion of the trigonal complex ions listed in *Table 2* were measured and analysed. Predictions about their absolute configurations were made by Corey and Bailar[6], Woldbye[39] and others[34, 36-38]. The circular dichroism of these complex ions have also been measured. It is found that they usually give two circular dichroism bands with opposed signs in the visible region and a strong charge transfer band in the near ultraviolet region. The former bands in the visible region are ascribed to different *d–d* transitions of the ion.

On the other hand, various quantum mechanical treatments of different models of the chromophore with trigonal symmetry were made, notably by Liehr[40], Karipides and Piper[41], Poulet[42], Shinada and Sugano[43,44], and Hamer[45]. Their results indicated that two transitions responsible for the first band in the visible region should acquire optical activities of opposite sign and equal intensity. That the two rotatory strengths within the first band are of different sign agrees with the experimental results, but it turned out by experiment that they are in fact not equal in magnitude.

(i) $(+)_D-[Co(en)_3]^{3+}$ [46, 47]: The long wavelength band is split into two components of opposite rotatory strength. The longer wavelength component has positive sign. Mason[48, 49] measured the circular dichroism of the single crystals of the double salt, of which the crystal structure was already known[14]. He assigned the longer wavelength component to the transition of $E$ symmetry and the shorter wavelength component to that of $A_2$ symmetry.

(ii) $(+)_D-[Co(d\text{-pn})_3]^{3+}$ [50]: The optical rotatory dispersion curve closely resembles that of $(+)_D-[Co(en)_3]^{3+}$. The complex ion gives two circular dichroism bands with opposed signs in the visible

region. They can be assigned in the same way as those of $(+)_D$-$[Co(en)_3]^{3+}$.

(iii) $(-)_D$-$[Co(d\text{-pn})_3]^{3+}$ [18]: The optical rotatory dispersion curve resembles that of $(-)_D$-$[Co(en)_3]^{3+}$. The $E$ circular dichroism band is of negative sign.

From *Table 2*, it may be seen that there exists a simple relationship between the sign of the longer wavelength circular dichroism band in the visible region and the absolute configuration of the chelate rings about the cobalt atom. The upper three species in *Table 2* show that if the sign is plus the absolute configuration is $\Delta$ and if it is minus the absolute configuration is $\Lambda$. The sign of the charge transfer circular dichroism band near $240m\mu$ is negative for all three of these complexes, reflecting the $\delta$ conformation of the chelate ring. Later Mason *et al.*[60] reported that both the configurational and conformational effects contribute to the c.d. of charge transfer bands.

(iv) $(-)_D$-$[Co(d\text{-cptn})_3]^{3+}$ [51]: The salts of tris($d$-cyclopentanediamine)-cobalt(III) are pink, which is in contrast to the orange colour of the hexaammine cobalt(III) salts. This pink colour persists even in solution, unlike that of tris(trimethylenediamine)cobalt(III) salts. The o.r.d. curve of this complex ion has a somewhat different shape from that of $[Co(en)_3]^{3+}$; thus the evidence for the absolute configuration in this case is ambiguous. The long wavelength band in the c.d. spectra is split into two components of opposite sign. The sign of the longer wavelength band is positive. This fact suggests that the absolute configuration is $\Delta$. The crystal structure analysis of $(-)_D$-tris($d$-cyclopentanediamine)cobalt(III) chloride tetrahydrate is now in progress. The crystals are hexagonal and consist of octahedral complex ions, $[Co(d\text{-cptn})_3]^{3+}$, chloride ions and water molecules. This is not in agreement with the claim that the complex ion is the binuclear complex, $[Co_2(cptn)_7(H_2O)_2]^{6+}$ [52].

(v) $(-)_D$-$[Co(d\text{-chxn})_3]^{3+}$ [53, 54]: Although this complex ion is laevorotatory at Na D line, its o.r.d. curve and c.d. spectra resemble those of $(+)_D$-$[Co(en)_3]^{3+}$ so closely that one can safely assign to it the $\Delta$ configuration. The crystal structure analysis of $(-)_D$-tris(d-cyclohexanediamine)cobalt(III) chloride tetrahydrate is now in progress.

(vi) $(-)_D$-$[Co(tn)_3]^{3+}$: The o.r.d. curve and c.d. spectra of $(-)_D$-$[Co(tn)_3]^{3+}$ have been measured by Woldbye[55, 39]. The same relationship as that found for tris-bidentate complexes with five-membered chelate ring, holds for $[Co(tn)_3]^{3+}$ between the sign of the longer wavelength c.d. band in the visible region and the absolute configuration. The rotatory strength of $[Co(tn)_3]^{3+}$ was found to be smaller than that of $[Co(en)_3]^{3+}$ by a factor of ten. This ring size effect seems natural in view of Moffitt's[56] model for the tris-(bidentate) complexes, in which he ascribed the optical activity to the crowding of sixtants in space by the carbon chains of the ligands, this crowding becoming greater the shorter the chain. This

difference in rotatory strength may also be attributable to the difference in the conformation of the chelate ring. In the cobalt–ethylenediamine ring the two carbon atoms are arranged symmetrically above and below the plane formed by the central metal atom and the two nitrogen atoms, while in the cobalt–trimethylenediamine ring the three methylene groups are located on one side of the plane of the cobalt and the two nitrogen atoms and each chelate ring has approximately a mirror symmetry.

The results obtained for these trigonal complexes may permit a judgement of the appropriateness of the two types of models proposed for optical activity. Liehr[40] uses a molecular orbital model in which the coordinated nitrogen atoms are located on the regular octahedral axes. In this treatment the numerical values of the rotatory strength are determined by the absolute configuration of the complex and depend upon the numerical value of the 'angle of cant' between the axes of the overlapping orbitals from the central and ligand atoms but are independent of the sign of this angle. In Piper and Karipides[41] treatment the sign of rotatory strength is independent of the absolute configuration of the chelate ring around the metal ion and is determined instead by the displacement of the coordinated atoms from the apices of the regular actahedron.

Besides these tris(diamine)cobalt(III) complexes, the absolute configurations of ($\alpha$-aminoacidato)cobalt(III) complexes, $1,2,6(+)$-[Co(L-ala)$_3$] [57] and $(+)$D-[Co(L-glut)(en)$_2$] [58], were determined. The empirical rule relating the sign of the longer wavelength c.d. band in the visible region and the absolute configuration was found to hold in both cases. Kuroya *et al.*[27] determined the absolute configuration of $(+)$D*cis*-dicyanobis(ethylenediamine)cobalt(III) ion and showed that it can be represented as $\varDelta$ ($\lambda\lambda$). Perhaps this is the first example of the determination of the absolute configuration of a digonal complex. Templeton[59] determined the absolute configuration of Ferrichrome A and found that the three hydroxamate rings around the iron atom are arranged like a left-handed propeller: absolute configuration $\varDelta$.

The complexes for which the absolute configurations were determined by means of x-rays are still small in number. However, they were perhaps enough to show that the knowledge of absolute stereochemical configuration is of a great help not only in improving our understanding of the mechanism of interactions between light and the optically active complex, but also in understanding rationally various aspects of the stereospecific behaviour of optically active complexes. The study of the absolute configuration of inorganic complexes is still in its infancy. Obviously, more data are necessary and I am sure that the structural study of optically active complexes offers a wide variety of interesting problems.

## References

[1] J. M. Bijvoet, A. F. Peerdeman and A. J. van Bommel. *Nature, Lond.* **168**, 271 (1951).
[2] F. Rosenblatt and A. Schleede. *Liebigs Ann.* **505**, 54 (1933).
[3] M. Kobayashi. *J. Chem. Soc. Japan* **64**, 648 (1939).
[4] H. Scouloudi and C. H. Carlisle. *Acta Cryst.* **6**, 651 (1953); *Nature, Lond.* **166**, 357 (1950).
[5] A. Nakahara, Y. Saito and H. Kuroya. *Bull. Chem. Soc. Japan* **25**, 331 (1952).

[6] E. J. Corey and J. C. Bailar, Jr. *J. Am. Chem. Soc.* **81**, 2620 (1959).

[7] S. Ooi, Y. Komiyama, Y. Saito and H. Kuroya. *Bull. Chem. Soc. Japan* **32**, 263 (1959).

[8] Y. Saito and H. Iwasaki. *Advances in the Chemistry of Coordination Compounds*, S. Kirschner, Ed., p. 562 (1961).

[9] Y. Saito and H. Iwasaki. *Bull. Chem. Soc. Japan* **35**, 1131 (1962).

[10] H. Reihlen, E. Weinbrenner and G. v. Hessling. *Liebigs Ann.* **494**, 143 (1932).

[11] S. Schnell and P. Karrer. *Helv. Chim. Acta* **38**, 2036 (1955).

[12] J. N. van Niekerk and F. R. L. Schoening. *Acta Cryst.* **5**, 196, 475, 499 (1952).

[13] K. Nakatsu, Y. Saito and H. Kuroya. *Bull. Chem. Soc. Japan* **29**, 428 (1956).

[14] K. Nakatsu, M. Shiro, Y. Saito and H. Kuroya. *Bull. Chem. Soc. Japan* **30**, 158 (1957).

[15] K. Nakatsu. *Bull. Chem. Soc. Japan* **35**, 832 (1962).

[16] M. Iwata, K. Nakatsu and Y. Saito. *Acta Cryst.*, To be published.

[17] Y. Saito, K. Nakatsu, M. Shiro and H. Kuroya. *Acta Cryst.* **8**, 729 (1955); *Bull. Chem. Soc. Japan* **30**, 795 (1957).

[18] A. J. McCaffery, S. F. Mason and B. J. Norman. *Chem. Commun.* 49 (1965).

[19] F. P. Dwyer, F. L. Galvan and L. Shulman. *J. Am. Chem. Soc.* **81**, 290 (1959).

[20] B. W. Brown and E. C. Lingafelter. *Acta Cryst.* **17**, 254 (1964).

[21] Y. Komiyama and E. C. Lingafelter. *Acta Cryst.* **17**, 1145 (1964).

[22] F. Mazzi. *Rend. Sci. mineralog Ital.* **9**, 148 (1953).

[23] F. P. Dwyer and F. L. Garvan. *J. Am. Chem. Soc.* **81**, 1043 (1959).

[24] H. Iwasaki and Y. Saito. *Bull. Chem. Soc. Japan* **39**, 92 (1966).

[25] A. P. Smirnoff. *Helv. Chim. Acta* **3**, 177 (1920).

[26] H. Iwasaki, K. Tano and Y. Saito, To be published.

[27] H. Kuroya, K. Matsumoto and Y. Kushi. *Proceedings of the Xth International Conference on Coordination Chemistry*, Ed. K. Yamasaki, p. 90 (1967).

[28] M. A. Porai-Koshits, A. S. Antsishkina, A. E. Shvelashvilli and L. H. Minacheva, *Proceedings of the IXth International Conference on Coordination Chemistry*, Ed. W. Schneider, p. 413 (1966).

[29] J. C. Bailar, Jr. and J. B. Work. *J. Am. Chem. Soc.* **68**, 232 (1946).

[30] F. Woldbye. *Proc. Roy. Soc.* **A.297**, 79 (1967).

[31] T. Nomura, F. Marumo and Y. Saito. *Bull. Chem. Soc. Japan*, To be published.

[32] K. Matsumoto, S. Ooi and H. Kuroya, Presented at the 17th Annual Meeting of the Chemical Society of Japan, 1964.

[33] B. Bosnich, C. K. Poon and M. L. Tobe. *Inorg. Chem.* **4**, 1102, 1109 (1965).

[34] R. D. Gillard and G. Wilkinson. *J. Chem. Soc.* 1368 (1964).

[35] F. M. Jaeger and L. Bijkerk. *Z. anorg. u. allgem. Chem.* **233**, 97 (1937), earlier articles by Jaeger.

[36] J. H. Dunlop, R. D. Gillard and G. Wilkinson. *J. Chem. Soc.* 3160 (1964).

[37] J. H. Dunlop and R. D. Gillard. *J. Inorg. Nucl. Chem.* **27**, 361 (1965).

[38] T. E. MacDermott and A. M. Sargeson. *Australian J. Chem.* **16**, 334 (1963).

[39] F. Woldbye. *Rec. Chem. Progr.* **24**, 197 (1963).

[40] A. D. Liehr. *J. Phys. Chem.* **68**, 665 (1964).

[41] A. G. Karipides and T. S. Piper. *J. Chem. Phys.* **40**, 674; see also T. S. Piper and A. G. Karipides. *Inorg. Chem.* **4**, 923 (1965).

[42] H. Poulet. *J. Chem. Phys.* **59**, 584 (1962).

[43] M. Shinada and S. Sugano, Lecture presented at the International Symposium on Molecular Spectroscopy. Tokyo, Sept. 1962.

[44] M. Shinada. *J. Phys. Soc. Japan* **19**, 1607 (1964).

[45] N. K. Hamer. *Mol. Phys.* **5**, 339 (1962).

[46] J.-P. Mathieu. *J. Chim. Physique* **33**, 78 (1936).

[47] M. Kobayashi. *J. Chem. Soc. Japan* **64**, 648 (1943).

[48] R. E. Ballard, A. J. McCaffery and S. F. Mason. *Proc. Chem. Soc.* 331 (1962).

[49] A. J. McCaffery and S. F. Mason. *Mol. Phys.* **6**, 359 (1963).

[50] J.-P. Mathieu. *Ann. Physique* **19**, 335 (1944).

[51] F. M. Jaeger. *Proc. Acad. Sci. Amsterdam* **40**, 108 (1937).

[52] J. F. Phillips and D. J. Royer. *Inorg. Chem.* **4**, 616 (1965).

[53] F. M. Jaeger and L. Bijkerk. *Proc. Acad. Sci. Amsterdam* **40**, 246 (1937).

[54] F. M. Jaeger. *Proc. Acad. Sci. Amsterdam* **40**, 2 (1937).

[55] F. Woldbye. *Optical Rotatory Dispersion of Transition Metal Complexes*, European Research Office, U. S. Army, Frankfurt a. M., (1959).

[56] W. Moffitt. *J. Chem. Phys.* **25**, 1189 (1956).

[57] M. G. B. Drew, J. H. Dunlop, R. D. Gillard and D. Rogers. *Chem. Commun.* 42 (1966).

[58] J. H. Dunlop, R. D. Gillard, N. C. Payne and G. B. Robertson. *Chem. Commun.* 874 (1966).

[59] A. Zalkin, J. D. Forrester and D. H. Templeton. *Science* **146**, 261 (1964); *J. Am. Chem. Soc.* **88**, 1810 (1966).

[60] S. F. Mason, A. M. Sargeson, R. Larsson, B. J. Norman, A. J. McCaffery and G. H. Searle. *Inorg. Nucl. Chem. Letters* **2**, 333 (1966).