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ABSOLUTE CONFIGURATIONS OF METAL COMPLEXES DETERMINED BY X-RAY ANALYSIS

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CONTENTS

A. INTRODUCTION

The absolute configuration of the $(+)_{589}$-tris(ethylenediamine)cobalt^{III} ion[1(i)]* was determined in 1955 by Bijvoet's anomalous dispersion technique[1]. This was the first complex ion of which the absolute configuration was established by means of X-rays. Since that time the number of complexes studied in this way has been growing at an increasing rate. The present article is a bibliography of the absolute configurations of 59 metal complexes determined by means of X-rays. It includes those papers which were published or submitted for publication by the end of 1972.

The X-ray determination of the absolute configuration of transition metal complexes is an elegant means of evaluating many of the assignments of complex ion chirality on the basis of circular dichroism. Another purpose of such an investigation is to provide basic data for constructing a theoretical model for optical activity. Knowledge of the absolute configuration is also of great help in understanding rationally, various aspects of the stereospecific behaviour of optically active complexes.

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* References indicated by [ ] are included in the bibliography (pp. 321–331). Those indicated by superscript refer to the literature listed at the end of this article.

B. PRINCIPLE OF BIJVOET'S METHOD

A crystal is a three-dimensional array of atoms in which the interatomic distances are about 2×10^{-8} cm on average. When the incident beam of X-rays passes over the atoms in a crystal, each atom scatters the incident X-rays. Owing to the periodic arrangement of atoms constructive interference between scattered wavelets takes place to give diffracted beams. The diffraction condition is given in a very simple form by Bragg's law,

$$2d_{hkl}\sin\theta = \lambda \tag{1}$$

Thus diffraction takes place as if the X-ray beam were reflected by the array of crystal planes. The angle of incidence is equal to the angle of reflection, so both are designated as θ. However, the value of θ cannot be arbitrary as in the case of reflection of light by a plane but is strictly restricted by eqn. (1), where d_{hkl} is the spacing between successive atomic planes with Miller index hkl and λ is the wavelength of X-rays. The experimental data obtained from an X-ray diffraction study, after application of the various correction factors appropriate to the particular experiment, are in the form of reduced intensities $I(hkl)$ of the diffracted beam from the array of atomic planes (hkl). $I(hkl)$ is proportional to the quantity $|F(hkl)|^2$, where $F(hkl)$ is given by

$$F(hkl) = \sum_j f_j \exp[2\pi i(hx_j + ky_j + lz_j)] \tag{2}$$

In this equation f_j is called the atomic scattering factor and represents the scattering amplitude of the j-th atom in terms of the scattering amplitude of a free electron under the same experimental conditions. x_j, y_j and z_j are the fractional coordinates of the j-the atom in the unit cell. $F(hkl)$ is usually a complex number and is called the structure factor. It gives the amplitude and the phase of the diffracted beam from one unit cell. The atomic coordinates can be deduced by the various methods of X-ray crystallography on the basis of eqn. (2), since $|F(hkl)|$ can be obtained from observed $I(hkl)$. However, it is not possible by the normal X-ray method to decide whether the optically active complex has a particular configuration or its mirror image. This is because X-ray diffraction patterns are usually obtained under such conditions that 'Friedel's rule' is obeyed: the X-ray wavelength used is nowhere near the absorption edge of any of the atoms in the crystal. In such case f_j in eqn. (2) is real. Consider a dissymetric structure D and its inverted (enantiomorphic) structure L. The structure factors for the hkl and $\overline{hkl}$ reflections can be written

$$\begin{aligned}
F_{\mathrm{D}}(hkl) &= \sum_j f_j \exp[2\pi i(hx_j + ky_j + lz_j)] = A(hkl) + iB(hkl)\\
F_{\mathrm{D}}(\overline{hkl}) &= \sum_j f_j \exp[-2\pi i(hx_j + ky_j + lz_j)] = A(hkl) - iB(hkl)\\
F_{\mathrm{L}}(hkl) &= \sum_j f_j \exp[-2\pi i(hx_j + ky_j + lz_j)] = A(hkl) - iB(hkl)\\
F_{\mathrm{L}}(\overline{hkl}) &= \sum_j f_j \exp[2\pi i(hx_j + ky_j + lz_j)] = A(hkl) + iB(hkl)
\end{aligned} \tag{3}$$

where

$$A(hkl) = \sum_j f_j \cos 2\pi(hx_j + ky_j + lz_j)$$

and

$$B(hkl) = \sum_j f_j \sin 2\pi(hx_j + ky_j + lz_j)\,.$$

Accordingly we have

$$\begin{aligned} F_{\mathrm{D}}(hkl) &= F_{\mathrm{L}}(\overline{hkl}) \\ F_{\mathrm{L}}(hkl) &= F_{\mathrm{D}}(\overline{hkl}) \end{aligned} \tag{4}$$

From eqns. (3) we find

$$I_{\mathrm{D}}(hkl) = I_{\mathrm{D}}(\overline{hkl}) = I_{\mathrm{L}}(hkl) = I_{\mathrm{L}}(\overline{hkl}) \tag{5}$$

This is called Friedel's rule. Equation (5) means that the two enantiomeric structures, D and L, give the same set of intensity data. Accordingly we cannot tell the absolute configuration. However, if the wavelength of the incident X-rays is chosen to lie close to (but necessarily shorter than) an absorption edge of one atom in the crystal, which we denote M, X-rays are scattered anomalously and the anomalous phase shift on scattering has the effect of advancing the wave from M relative to the wave from the rest of atoms. The scattering factor for the atom M is represented by a complex quantity:

$$f_{\mathrm{M}} = f_{0\mathrm{M}} + \Delta f'_{\mathrm{M}} + i\Delta f''_{\mathrm{M}} \tag{6}$$

$\Delta f'_{\mathrm{M}}$ and $\Delta f''_{\mathrm{M}}$ are small correction factors. It can be easily seen that this modification of the scattering factor gives rise to a small difference in intensities between hkl and $\overline{hkl}$, when eqn. (6) is inserted in eqn. (2). However, the relations (4) still hold even after this correction. Consequently we obtain the following important relationship.

$$\text{If } I_{\mathrm{D}}(hkl) \gtrless I_{\mathrm{D}}(\overline{hkl}), \text{ then } I_{\mathrm{L}}(hkl) \lessgtr I_{\mathrm{L}}(\overline{hkl})\,. \tag{7}$$

In other words, the inequality relations observed for one structure are the reverse of those found for its enantiomorph. This is the basis of the determination of absolute configuration by anomalous scattering technique. 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 configuration. Figure 1(a) and (b) show the effect of anomalous scattering. These are Weissenberg photographs of $(-)_{589}$-Λ-[Co(S,S-chxn)$_3$]Cl$_3$.5H$_2$O taken with two different radiations [8]. Figure 1(a) was taken with Fe $K\alpha$ radiation (λ = 1.937 Å). Since this wavelength is away from the K absorption edge wavelength of cobalt (λ_K = 1.608 Å), no effect of anomalous scattering is observed. Intensity distributions of a number of diffraction spots on a characteristic U shaped row-line are

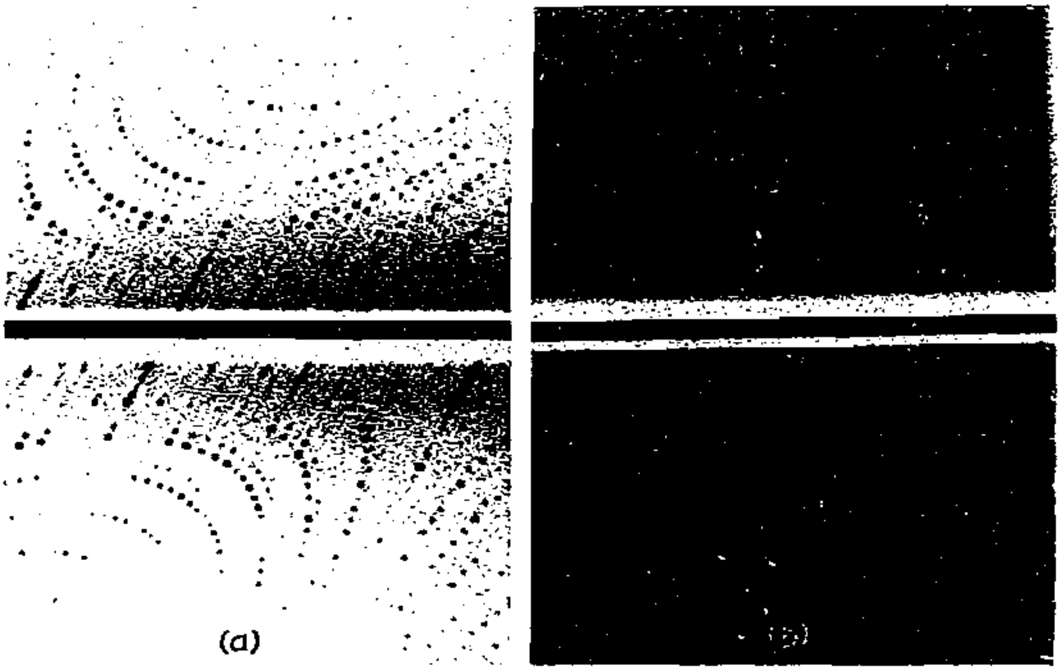

Fig. 1. Weissenberg photographs, showing the effect of anomalous scattering. $(-)_{589}$-Λ-[Co-(S,S-chxn)$_3$]$Cl_3.5H_2O$, *a*-axis rotation, O-th layer. (a) Taken with Fe *Kα* radiation (λ = 1.937 Å) (b) Taken with Cu *Kα* radiation (λ = 1.542 Å).

symmetric with respect to its centre. A pair of reflections located symmetrically on a row-line corresponds to a reflection *hkl* and its counter reflection $\overline{hkl}$ (or its equivalent). Therefore Friedel's rule is obeyed. On the other hand, (b) was taken by Cu *Kα* radiation (λ = 1.542 Å) whose wavelength lies close to and a little shorter than the absorption edge of cobalt. X-rays are then scattered anomalously by the cobalt atom. Copious fluorescent radiation darkens the background of the film. The corresponding reflections on a row-line are no longer equal in intensity and Friedel's rule is violated. If a crystal of Δ-isomer is used under the same experimental conditions, the observed intensity relations will be inverted.

Bijvoet first determined the absolute configuration of d-tartaric acid by this method and showed that Emil Fischer's convention is correct[1]. The reversal of inequality relations for a pair of enantiomorphic structures was first demonstrated by Saito and his collaborators for crystals of $(+)_{589}$- and $(-)_{589}$-$Na[Co(en)_3]_2Cl_7.6H_2O$, and such inequality relations were shown to be certainly due to the effect of anomalous scattering and not to some other effect such as differences in secondary extinction or absorption [1 (i), (ii)].

The inequality relations between a reflection and its counter reflection (or its equivalent) are generally weak but discernible, as shown in Fig. 1, if the wavelength is chosen appropriately. Most of the absolute configurations tabulated in the bibliography were determined in this way. No other physical method is at present capable of determining the absolute configuration unambiguously.

Usually the determination of absolute configuration is carried out by employing completely resolved optical isomers. However, in favourable cases, it is possible to attain the purpose, even if the resolution is incomplete. The absolute configuration of $(-)_{546}$-tris(acetylacetonato)cobalt(III) was determined for quasiracemic crystals [38]. $[Co(acac)_3]$ was partially resolved by column chromatography on D-(+)-lactose. Crystallization of a mixture of partially resolved $[Co(acac)_3]$ and racemic $[Al(acac)_3]$ gave quasiracemic crystals which contain an excess of $(-)_{546}$-$[Co(acac)_3]$. The cell dimensions are nearly identical with those for the isomorphous racemic $[Co(acac)_3]$ and $[Al(acac)_3]$. However, the space group of the quasiracemic crystal is different from centrosymmetric $P2_1/c$ of racemic crystals and is non-centrosymmetric $P2_1$. This is certainly due to unequal substitution of cobalt atom in the two enantiomeric sites. Structure factor calculation revealed that the model with excess Λ-$[Co(acac)_3]$ in the crystal gave the best fit to the observed values. The Λ absolute configuration was further supported by calculation of 19 Friedel pairs (a reflection and its counter reflection).

Absolute configurations of many biologically important chelating molecules such as α-amino acids were determined by Bijvoet's method. Therefore, a known absolute configuration of one centre in a complex can be utilized to deduce that of other centres. In this case the whole absolute configuration of the complex can be determined by normal X-ray diffraction[2]. Such was the case for α-$(+)_{589}$-tris(L-alaninato)-cobalt(III) (ref. [40]) and $(+)_{496}$-L-glutaminatobis(ethylenediamine)cobalt(III) perchlorate (ref. [18]).

A few words will be given to the theoretical background of eqn. (6). The theory of anomalous dispersion was developed by Hönl classically[3] and quantum mechanically (semi-classical theory)[4]. More advanced quantum field theoretical treatment gives essentially the same result[5]. Calculated values of $\Delta f_M'$ and $\Delta f_M''$ are tabulated in International Tables for X-ray Crystallography[6], which are mainly due to Dauben and Templeton[7]. Experimental verification of these values are rather fragmentary, but the agreement is generally good where experimental values exist except very close to the absorption edge. Relativistic calculations of $\Delta f'$ and $\Delta f''$ improved the agreement with the experimental values considerably[8]. Recent measurements of $\Delta f'$ and $\Delta f''$ by energy dispersive detector also showed very good agreement with the theoretical calculations[9].

C. CIRCULAR DICHROISM AND ABSOLUTE CONFIGURATION

The origin of the optical activity exhibited by dissymmetric transition metal complexes may be classified into two limiting cases. One is that of the symmetric

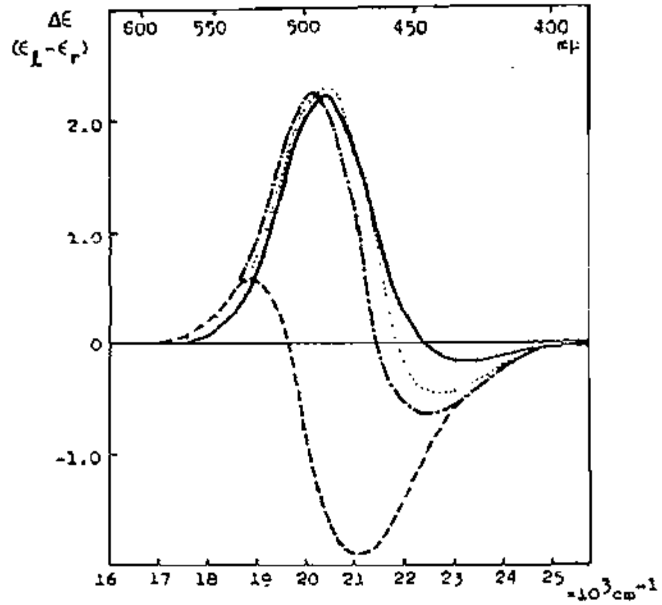

Fig. 2. Circular dichroism spectra of some tris-bidentate cobalt^{III} complex ions in aqueous solutions. ——, $(+)_{589}$-$[Co(en)_3]^{3+}$; . . . ., $(+)_{589}$-$[Co(+pn)_3]^{3+}$; —·—·—, $(-)_{589}$-$[Co(+chxn)_3]^{3+}$; - - - -, $(-)_{589}$-$[Co(+cptn)_3]^{3+}$.

chromophore in a dissymmetric molecular field and the origin of optical activity in this case is ascribed in a number of theories[10-16,18] to a certain kind of distortion of the ligand or their orbitals from regular dispositions such as octahedral or tetragonal arrangement. In another limiting case, an optically active complex is regarded as a dissymmetric ensemble of symmetric chromophores formed by coordination to a central metal atom[19-22]. The complexes listed in the bibliography mostly possess a symmetric chromophore placed in a dissymmetric environment. A dissymmetric ensemble of individual chromophores is exemplified by $(-)_{589}$-$[As(cat)_3]^-$ (ref. [52]), $(+)_{589}$-$[Ni(phen)_3]^{2+}$ (ref. [49]) and $(-)_{589}$-$[Fe(phen)_3]^{2+}$ (ref. [46]). The optically active polyamine complexes of cobalt^{III} provide a particularly comprehensive series of stable coordination compounds in which a symmetric chromophore is located in a dissymmetric environment. About eighty percent of the absolute configurations included in the bibliography are cobalt^{III} complexes. Optical properties of these complexes have been extensively studied both in solution and as single crystals[23-29]. Figure 2 shows the circular dichroism of four tris(bidentate) complex ions in aqueous solution. They all have the absolute configuration Λ(δδδ). The absorption spectra of these complexes consist of two weak ligand field bands, one in the visible and the other in the near ultra-violet, and a strong ligand-to-metal charge transfer band in the far ultra-violet. The ligand field band in the visible region is called the first absorption band and is a magnetic dipole allowed *d–d* transition. In solution the circular dichroism associated with the first absorption band consists of two circular dichroism bands of unequal magnitude and opposite signs. All the longer wavelength bands shown in Fig. 2 have positive rotatory strength, reflecting Λ absolute configuration. McCaffery and Mason[26] measured the circular dichroism of single crystals of Na$(+)_{589}$-$[Co(en)_3]_2Cl_7 . 6H_2O$ and assigned the longer wavelength band to that of E symmetry and the shorter wavelength component to that of A_2 symmetry. The circular dichroism spectra of $(+)_{589}$-$[Co(+pn)_3]^{3+}$ and $(-)_{589}$-$[Co(+chxn)_3]^{3+}$ can be assigned in the same way as those of $(+)_{589}$-$[Co(en)_3]^{3+}$, since the circular dichroism spectra resemble those of $(+)_{589}$-$[Co(en)_3]^{3+}$. The crystal measurements show that the intrinsic rotational strength of the E component of the octahedral T_{1g} transition in $(+)_{589}$-$[Co(en)_3]^{3+}$ is positive and substantially larger than that of the solution circular dichroism. Accordingly the intrinsic rotational strength of the A_2 component must be almost as large and negative, the two rotational strengths overlapping and mutually cancelling to within a few percent when the complex is oriented randomly in solution. The band origins of the E and A_2 components coincide in frequency and the appearance of each circular dichroism band in the solution spectrum arises from the different distribution of rotational strength over the E and A_2 vibronic progressions[28]. Thus the observed circular dichroism is residual, or in other words, it is in the resultant of two large rotational strengths opposite in sign and with nearly equal frequency. Accordingly a small difference in dissymmetric environment may produce a major change in circular dichroism spectra observed in solution. The circular dichroism spectrum of $(-)_{589}$-$[Co(+cptn)_3]^{3+}$ is somewhat different: the longer wavelength band has smaller rotatory strength than the shorter wavelength band, whereas the longer wavelength band predominates in the first three members of the series. Gegen-ion effect and anisotropy in absorption of polarized light of single crystals indicate that the longer wavelength band is assignable to E (ref. [7]). Structure analyses of these complexes revealed that the shape and size of an octahedron formed by six nitrogen atoms around the cobalt atom as well as those of the five-membered chelate ring is practically the same throughout the series of the complex ions. The octahedron is slightly distorted around the threefold axis; the upper triangle formed by three nitrogen atoms is rotated counterclockwise by about 5° with respect to the lower triangle of the three remaining nitrogen atoms. No appreciable strain is introduced in bond angles on forming a chelate ring for the complex ions, $(+)_{589}$-$[Co(en)_3]^{3+}$, $(+)_{589}$-$[Co(+pn)_3]^{3+}$ and $(-)_{589}$-$[Co(+chxn)_3]^{3+}$. In the case of $(-)_{589}$-$[Co(+cptn)_3]^{3+}$, however, the N—N distance of 3.14 Å decreases in length to 2.76 Å when a strain free ligand molecule would form a chelate ring and some bond angles in the chelate ring as well as in the cyclopentane ring are significantly smaller than the normal tetrahedral angle. Such a strain in bond angles due to fused-ring formation might affect the ligand field. This change in the ligand field would cause the shifts of the circular dichroism spectrum as observed. The reversal of the ratio of the rotatory strength of the E and A_2 components of the circular dichroism might also be attributable to this change in the ligand field.

Thus correlation of stereochemistry with optical activity requires some prudence. Various rules, purely empirical or with theoretical background, have been proposed to correlate the circular dichroism and the absolute configuration (see references given in ref. 32). Notably two rules are known: one is Hawkins and Larsen's octant sign rule[30] and the other is the "ring pairing method" of Legg and Douglas[31]. Both methods are essentially empirical and equivalent. They cover the main symmetry types of cobalt^{III} and other metal complexes and the sign of the Cotton effect due to a particular component descended from the octahedral T_{1g} transition in a trigonal, tetragonal or orthorhombic environment is correlated with octant sign or net chirality. Where the configurational and the vicinal effects are opposed the former appears to be generally dominant. Usually substitution on the chelate ring is accompanied by small changes in ring conformation and distortion of the chelating atoms, which may give rise to a change in the circular dichroism spectra. Thus the vicinal effects may be rather indirect. All the cobalt^{III} complexes with multidentate polyamines containing five-membered chelate rings of which the absolute configurations are established by X-ray method [11–13, 15A, 15B, 30–32] predominantly give a positive circular dichroism in the region of the first absorption band for the net chirality Λ (or positive octant sign), or negative for the net chirality Δ (or negative octant sign).

Mason devised regional rules correlating the position of a substituent to tetragonal chromophores, $[CoA_5B]$ and *trans*-$[CoA_4B_2]$ and octahedral chromophore $[CoA_6]$ (ref. 32). These rules are founded on the general symmetry aspects of the theory of the symmetric chromophore in a dissymmetric environment developed by Schellman[33]. The theory shows that the induced rotatory power may be related to the substitution pattern by means of the symmetry properties of the unperturbed chromophore. In the case of centrosymmetric chromophore such as those with octahedral or tetragonal geometry, the zero-order rotational strength vanish, but the first-order rotational strength may be non-zero, if the perturbation potential due to the substituent groups around the chromophore transforms or contains a component which transforms like a pseudo-scalar in the point group to which the symmetric chromophore belongs. There is an infinite number of those potential functions which transform as a pseudo-scalar under the symmetry operations of the point group. Among them, only the simpler potential functions may be useful for the regional rules. Octant sign can be obtained by employing the coordinate function $z(x^2-y^2)$ for each substituent. The coordinate axes are right-handed and they are directed along the metal–ligand bonds. X-ray study of tetragonal complexes, $(-)_{589}$-$[CoCl_2(N\text{-}Meen)_2]^+$ (ref. [25]) and $(-)_{589}$-$[CoCl_2(-pn)_2]^+$ (ref. [23]) showed that the coordinate function $xyz(x^2-y^2)$ must be used to accommodate the observed circular dichroism of these complexes[34,35], which is the simplest pseudo-scalar potential function for a point group D_{4h}. The simplest pseudo-scalar for O_h has a form $xyz(x^2-y^2)(y^2-z^2)(z^2-x^2)$. The functional forms of the simplest pseudo-scalar potential are listed for most of the common point groups[33].

Bosnich and Harrowfield[36] presented a regional rule for the optical activity of the d–d transitions of the conformational isomers of octahedral complexes. It is based upon a more intuitive argument utilising experimental facts. The space demarcation derived is the simplest pseudo-scalar representation of the point group O_h. The effect of donor atom distortion and the contributions of the amino hydrogen atom, which were ignored in the previous regional rules are taken into account. Such donor atom distortion was indeed observed in crystals of $(+)_{546}$-$[Co(NO_2)_2(3,2,3\text{-tet})]Br$ (ref. [34]). The four donor nitrogen atoms of the tetramine ligands in the equatorial plane of the coordination octahedron showed alternate deviation from the plane. These deviations generate two non-orthogonal skew lines, which define a helical system at the cobalt atom.

Shinada calculated the optical rotatory dispersion of D_3 complexes by means of a purely ionic model[15]. Qualitative agreement was obtained for Λ-$(+)_{589}$-$[Cr(ox)_3]^{3-}$ (ref. [41C]). For $[Co(en)_3]^{3+}$, the effect of coordinated nitrogen atoms was replaced by the point dipoles and the rotatory strength was shown to depend upon the direction of these dipoles with respect to the average planes of the chelate rings.

Piper and Karipides calculated the rotatory strength of some trigonal complexes by a static one-electron model[14]. Although this model is not appropriate for accurate quantitative calculations of the rotatory strength, it provides a simple and correct representation of the nodal structure in the electronic states of a symmetric chromophore in a dissymmetric molecular environment. It is particularly attractive in making correlations between circular dichroism spectra and absolute stereochemical configuration of the complexes. In their treatment the sign of rotatory strength does not depend upon the absolute configuration of the chelate ring around the metal ion but is determined by the displacement of the coordinating atoms from the apices of a regular octahedron. Wing and Eiss determined the absolute configuration of bis(tribenzo[b,f,j]-[1,5,9]triazacycloduodecine)cobalt(III) ion (ref. [14]). It is a 'sandwich' type complex like ferrocene with two parallel planar ligand molecules. The octahedron formed by the six nitrogen atoms possess a small twist distortion about the threefold axis. This is in the counterclockwise direction as in the case of Λ-$(+)_{589}$-$[Co(en)_3]^{3+}$, which has a remarkably similar circular dichroism in the region of the first absorption band. This correspondence may indeed constitute experimental support for Piper's model for optical activity in trigonal metal complexes.

Schäffer[16] discussed the optical activity of D_3 complexes of Co^{III} and Cr^{III} in terms of the angular overlap model of bonding in coordination compounds first proposed by Yamatera[17]. The effects of the dissymmetric environment were represented in terms of the small angular parameters representing displacements of ligating atoms away from the regular disposition. Observed molecular geometries of Λ-$[Co(en)_3]^{3+}$ etc. were analysed.

TABLE 1
Geometry of tris-bidentate complex ions

	α	ω	θ	*Reference*
$[Co(ox)_3]^{3-}$	84.3 (30)	54.0	56.4	[39]
$[Co(thiox)_3]^{3-}$	89.7 (2)	57.0	53.8	
$[Cr(ox)_3]^{3-}$	82.4	50.3	56.3	
$[Cr(mal)_3]^{3-}$	91.9 (6)	60.2	53.5	
lel_T-$[Co(en)_3]^{3-}$	85.4 (3)	54.9	55.9	[1 (iv)]
ob_T-$[Co(chxn)_3]^{3+}$	84.3 (1)	50.6	55.2	[9]
lel_T-$[Co(R,R\text{-}ptn)_3]^{3+}$	89.0 (3)	57.0	54.3	[6]
Octahedron	90	60	54.8	

Richardson[18] examined the optical activity of trigonally distorted ML_6 cluster on the basis of ionic model. The perturbation expansion of the wave functions was carried out to the second order. The results obtained to first order in perturbation theory are similar to those obtained by Piper and Karipides and others[10,11,14]. According to this theory, the trigonal splitting parameter $K(= \nu_E - \nu_{A_2})$ of the $^4A_{2g} \rightarrow {}^4T_{2g}(Cr^{III})$ and of the $^1A_{1g} \rightarrow {}^1T_{1g}(Co^{III})$ transition may be controlled by whether an angle θ is greater or less than the octahedral value of 54.75°, where θ is one of the spherical coordinates of the ligating atom and is measured from the trigonal axis of the complex (see Fig. 3). Values of θ can be easily calculated from the atomic coordinates and generally the deviation from the octahedral value is small. Unfortunately the number of structure determinations accurate enough to give reliable θ values is still limited. The angles characterising structures of some trisbidentate complexes of Cr^{III} and Co^{III} are listed in Table 1, of which the crystal structures were determined with sufficient accuracy. It is known that the sign of the ^1E component inverts from the circular dichroism spectrum of Λ-$(+)_{589}$-$[Cr(ox)_3]^{3-}$ to that of Λ-$(+)_{589}$-$[Cr(mal)_3]^{3-}$ (refs. 37,38). This is consistent with the observed change in θ. The reversal in component energies between Λ-$(+)_{589}$-$[Co(thiox)_3]^{3-}$ and Λ-$(-)_{589}$-$[Co(ox)_3]^{3-}$ are also in accord with the theoretical prediction. The observed distortions of the CoN_6 chromophore in the complex ions with five-membered chelate rings are trigonal compression ($\theta > 54.75°$), whereas that of Δ-$[Co(R,R\text{-}ptn)_3]^{3+}$ is a trigonal elongation at a low-significance level. Table 2 lists the angular parameters of each ligating atom in Λ-$[Co(tn)_3]^{3+}$. The angles were calculated from the atomic parameters of $(-)_{589}$-$[Co(tn)_3]Cl_3 \cdot H_2O$, which is isotypic with its bromide analogue and the final R value was 0.033 for 2806 observed reflections collected by the diffractometer methods [4 (iii)]. The values of θ, ω and α indicate that the deviations from a regular octahedron are rather irregular. In contrast to this, the individual angles in the latter three complex ions listed in Table 1 were in accord with the expected D_3 symmetry and by assuming this sym-

TABLE 2
Geometry of the complex ion Λ-$[Co(tn)_3]^{3+}$

Chelate ring		α	ω	θ
A	N(1)[a] N(2)	89.3 (1)	60.8	56.7 125.5 (54.5)[b]
B	N(3) N(4)	89.9 (1)	58.2	55.1 126.9 (53.1)
C	N(5) N(6)	92.0	60.6	52.5 125.4 (54.6)
Average		90.4	59.9	54.3

[a] See Fig. 5. [b] $180° - \theta$.

metry the averaging could be justified. The general trend of the distortion observed for $[Co(tn)_3]^{3+}$ appears to be trigonal elongation, implied by four out of six θ values less than 54.7°. The bromide monohydrate of Δ-$(+)_{589}$-$[Co(tn)_3]^{3+}$ shows a single positive peak in a potassium bromide matrix, and Δ-$(-)_{546}$-$[Co(R,R\text{-}ptn)_3]^{3+}$ shows a single negative peak in solution[43]. The assignments of the symmetry of the circular dichroism band of $(+)_{589}$-$[Co(tn)_3]^{3+}$ are at variance. Those based on a single crystal study assign the high-energy component as that of E symmetry[39], while gegen-ion effect suggests that this is the A_2 component[40–42]. The assignment of symmetry of the circular dichroism band of $[Co(R,R\text{-}ptn)_3]^{3+}$ has not yet been made.

It may be worthwhile to note here that the conformation of the chelate rings observed in the crystal will not always be retained in solution. One should not overlook this point in correlating the solution circular dichroism with the absolute

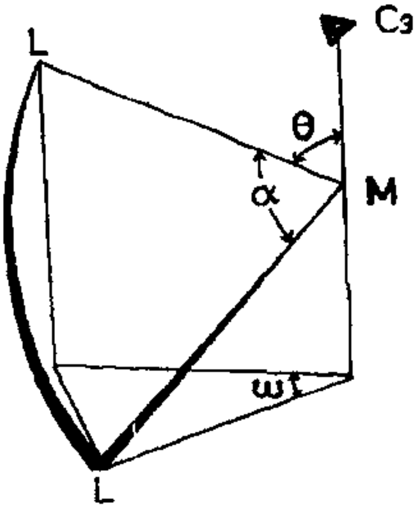

Fig. 3. Angles characterising a tris-bidentate complex.

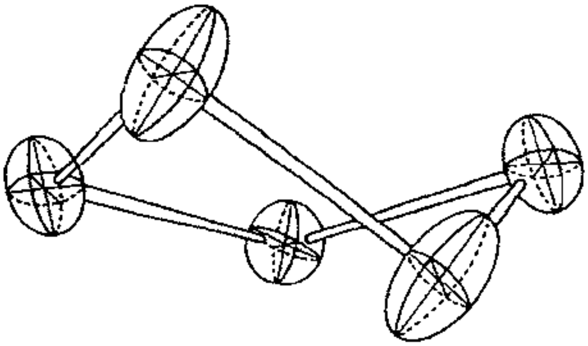

Fig. 4. View of thermal motion ellipsoids of a Co—en ring.

configuration. Such an indication can often be obtained by the study of anisotropic thermal parameters of the atoms in the chelate ring. The thermal ellipsoids of a cobalt ethylenediamine ring which lie on a twofold axis in the crystals of $(+)_{589}$-$[Co(en)_3]Cl_3 . H_2O$ (ref. [1(iv)]) are shown in Fig. 4. Whereas the vibrations of the cobalt atom are nearly isotropic, the two carbon atoms appear to oscillate with large amplitudes nearly perpendicularly to the C—C bond with a mean amplitude of about 0.3 Å. These features of the anisotropic thermal vibrations of the carbon atoms seem to support the existence of a puckering motion of the chelate ring in solution. A six-membered chelate ring such as cobalt-1,3-diaminopropane ring is more flexible. The thermal motion ellipsoids of Λ-$(-)_{589}$-$[Co(tn)_3]^{3+}$ in crystals of its chloride monohydrate is presented in Fig. 5 (ref. [4(iii)]). The three chelate rings have the chair conformation. In one of the chelate rings, the much greater thermal motion of two carbon atoms is particularly striking. The amplitude of thermal motion is primarily perpendicular to the plane formed by the two C—C or C—N bonds for each atom. In fact the chelate ring containing these two carbon atoms is the most loosely packed in the crystal. Such thermal motion suggests a change in conformation of the Co—tn ring from chair to skew-boat form in solution at room temperature, resulting in a conformational equilibrium among different conformers of $[Co(tn)_3]^{3+}$. Δ-$(+)_{589}$-$[Co(tn)_3]Br_3 . H_2O$ shows a single positive peak ($\Delta\epsilon = 0.35$) in a microcrystalline form in a potassium bromide matrix[43]. This is different from the corresponding spectrum of a solution of the complex ion. At room temperature the circular dichroism spectrum of $(+)_{589}$-$[Co(tn)_3]^{3+}$ in solution consists of two bands of opposite sign, the longer wavelength band being negative. On lowering the temperature the circular dichroism changes progressively towards that of the corresponding spectrum in potassium bromide matrix. The circular dichroism spectrum of $(-)_{546}$-$[Co(R,R\text{-}ptn)_3]^{3+}$ in water shows a negative peak ($\Delta\epsilon_{525} = -0.51$) (ref. 44). This complex ion has the absolute configuration $\Delta(\lambda\lambda\lambda)$ and the three chelate rings take skew-boat form [6]. The observed solution circular dichroism spectrum may well be accounted for if there exists a conformational equilibrium in solution

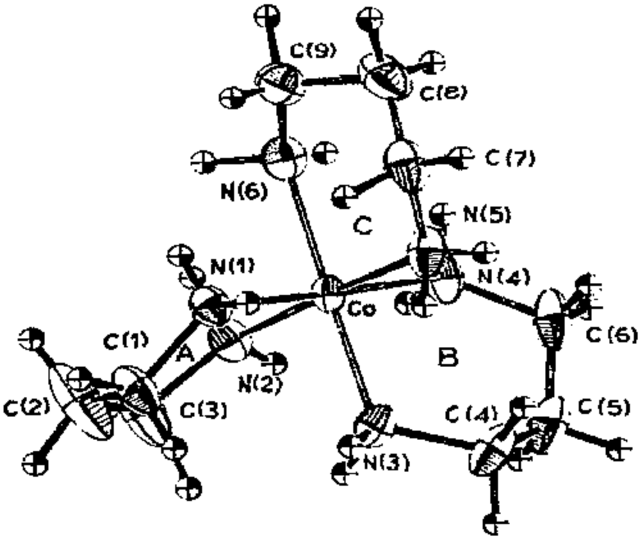

Fig. 5. View of thermal motion ellipsoids of $[Co(tn)_3]^{3+}$.

between a tris-skew-boat and a tris-chair form. If it is assumed that the principal conformers of $(+)_{589}$-$[Co(tn)_3]^{3+}$ in solution are the Δ-tris-chair and Δ-lel-tris-skew-boat form, an analysis of the observed temperature variation of the circular dichroism spectrum indicates that the tris-chair form is the more stable by 0.5 Kcal mol^{-1} in aqueous solution. At 20°C the tris-chair population is 70% in solution.

The next topic is the non-empirical determination of the absolute configuration from the observed circular dichroism spectrum. The absolute configuration of an optically active metal complex can be determined non-empirically by the study of its circular dichroism, when it can be regarded as a dissymmetric ensemble of symmetric chromophores. In a tris-chelated coordination compound containing unsaturated ligands a major source of optical activity is the Coulombic coupling of the allowed $\pi \rightarrow \pi^*$ transitions in the individual ligands, yielding component transitions which are intrinsically optically active and which have Cotton effects whose signs are determined by the phase relationships of the individual transition dipoles. The X-ray method and this non-empirical method should give the same result for one particular complex. The X-ray determinations of the absolute configurations of $(-)_{589}$-Λ-$[Fe(phen)_3]^{3+}$ (ref. [46]), $(+)_{589}$-Λ-$[Ni(phen)_3]^{2+}$ (ref. [49]) and $(-)_{589}$-$[As(cat)_3]^-$ (ref. [52]) indeed verified that both methods can give an identical conclusion. Studies on $[As(cat)_3]^-$ will be briefly explained[45] (ref. [52]). 1,2-Benzenediol exhibits three electronic absorption bands in the ultraviolet region. In Fig. 6 its absorption spectrum is drawn by broken line with the intensity scale multiplied by a factor of three (curve 2). The spectrum of $(-)_{589}$-K$[As(cat)_3]$ also consists of three bands with slightly different frequencies, which is shown by thick

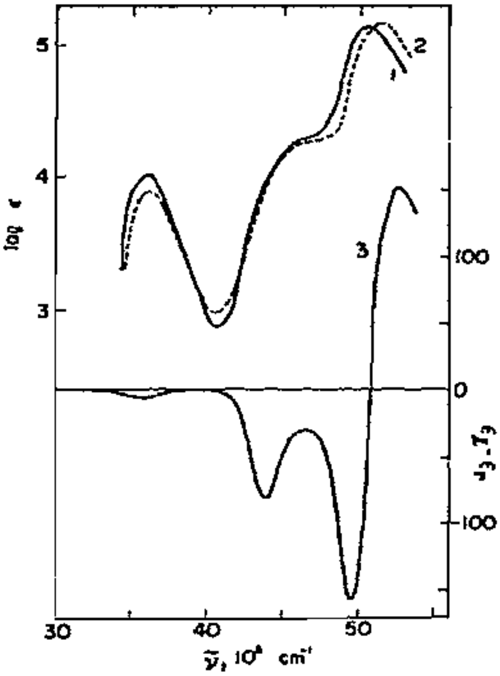

Fig. 6. The absorption spectrum of 1,2-benzenediol in an aqueous solution (2) (with the intensity scale multiplied by a factor of three) and the absorption spectrum (1) and the circular dichroism spectrum (3) of $(-)_{589}$-K[As(cat)$_3$] . 1.5H$_2$O in an aqueous solution.

line in Fig. 6 (curve 1). These three bands are denoted hereafter as I, II (shoulder) and III from longer to shorter wavelengths. The similarity of the two curves indicates that the metal ligand interaction by charge transfer is small. Accordingly, the $\pi \rightarrow \pi^*$ transitions of the ligand, 1,2-benzenediol, which has the transition dipole moment either parallel (x; long axis) or perpendicular (y; short axis) to the oxygen–oxygen direction. The y-polarised transition cannot produce zero-order rotatory power in tris-chelated complexes, since it has no magnetic moment. On the other hand, the x-polarised transitions of the three ligands in the complex couple each other to give two electronic transitions, $A_1 \rightarrow A_2$ and $A_1 \rightarrow E$. It was found that the $A_1 \rightarrow E$ band appears at longer wavelength than the $A_1 \rightarrow A_2$ band[46,47]. A negative circular dichroism band appears in the region of band II, and a strong negative and a strong positive peak was observed from longer to shorter wavelengths in the region of band III, whereas band I exhibited very weak optical activity. Consequently band I may be designated y-polarised, and bands II and III x-polarised. The fact that in the region of band III the $A_1 \rightarrow E$ transitions at longer wavelength have a negative rotatory strength and the $A_1 \rightarrow A_2$ transition at shorter wavelength has a positive rotatory strength indicates that the absolute configuration of $(-)_{589}$-[As(cat)$_3$]$^-$ is Δ, in agreement with the result by X-ray analysis.

Recent improvements in experimental and computational techniques in X-ray crystallography have made it possible to determine the atomic charges as well as distribution of bonding electrons based on accurate X-ray diffraction data. Perhaps the most challenging result is the determination of number of electrons around the central metal atom of complexes. Let us consider a CoN_6 cluster. If the Co—N bond is purely ionic the cobalt atom bears a charge 3+ and if the Co—N bond is completely covalent, then the charge on the central cobalt atom should be 3− due to donation of an electron from each of the six coordinating atoms. An accurate determination of electron density distribution in crystals of $[Co(NH_3)_6]$ $[Co(CN)_6]$ was carried out[48]. The direct integration of the electron density around the cobalt atom within a sphere of radius 1.22 Å (covalent radius of cobalt atom) showed that each metal atom has largely neutralized resultant charges: $[Co(NH_3)_6]^{3+}$, 26.3 ± 0.3 e and $[Co(CN)_6]^{3-}$, 26.8 ± 0.3 e. The positive charge in $[Co(NH_3)_6]^{3+}$ is mainly distributed on the eighteen hydrogen atoms of the six ammonia molecules. Likewise, the negative charge on $[Co(CN)_6]^{3-}$ is distributed on the six cyano groups and the metal atom has a small positive charge. In $(+)_{589}$-$[Co(R,R\text{-}chxn)_3]^{3+}$ (ref. [9]), the number of electrons around the cobalt atom was estimated to be 25.8 ± 0.7. This latter value is less accurate because the intensity data were not good enough to warrant such detailed analysis. A recent electron population analysis by Coppens et al.[49] for [*N,N'*-di-(2-aminoethyl)malondiamidato] nickel(II) trihydrate has shown that the nickel atom has a small positive charge of about 0.5 e, which is in good agreement with the values obtained for the cobalt^{III} complexes. All these results imply that the ionic character of a metal—ligand bond is about 50%. In the difference Fourier synthesis of $[Co(NH_3)_6]$ $[Co(CN)_6]$ distribution of bonding electrons was clearly discernible. It is clear that a large amount of information can be obtained from these accurate determinations of electron density to construct a theoretical model for optical activity.

To summarize, optical activity may be classified as a second-order optical property and its extreme sensitivity to the details of the electronic structure of the overall system requires very accurate structural parameters as well as very accurate wavefunctions for theoretical calculations. At present, in the absence of accurate wavefunctions, a theoretical analysis of the optical rotatory properties may be best accomplished by determining the symmetry-controlled aspects of the problem. The need for accurate structural data deserves special emphasis in this respect. As discerned from the Metal Index (p. 331) the paucity of absolute configurations of complexes of elements other than cobalt is still a distinct handicap and it is hoped that more extensive work will be done in this area. Secondly, accurate determinations of positional coordinates and electron density distributions are highly desirable. Such accurate determinations are difficult and are still small in number.

D. TABLE OF ABSOLUTE CONFIGURATIONS OF METAL COMPLEXES DETERMINED BY X-RAY ANALYSIS

This table contains the absolute configurations of coordination compounds determined by means of X-rays. It includes those papers which were published or submitted for publication up to 31st December, 1972, but cannot claim completeness. The author should very much appreciate receiving suggestions for new entries to this table, so that possible later editions would be more comprehensive.

(i) Designation of absolute configuration

The symbols used to denote the absolute configurations of metal complexes in the text are according to the IUPAC proposal (1968)*, while those used in the titles of papers are the same as those adopted by the authors in the original papers.

(ii) Abbreviation of the ligands

		No. of complex
acac	acetylacetonate	16, 38
ala	alaninate	40
arg	arginate	29
atc	acetylcamphorate	42
bigua	biguanide	45
cat	1,2-benzenediolate	52
chxn	*trans*-1,2-diaminocyclohexane (*trans*-1,2-cyclohexanediamine)	8, 9
cptn	*trans*-1,2-diaminocyclopentane (*trans*-1,2-cyclopentanediamine)	7
dien	diethylenetriamine	11
3,8-dimetrien	3,8-dimethyltriethylenetetramine	31, 32, 33
en	ethylenediamine	1, 10, 18, 21, 22A, 22B, 27, 41, 48, 54
glut	glutamate	18
mal	malonate	22B, 41A, 41B
N-meen	*N*-methylethylenediamine	25
mepenten	*N,N,N',N'*-tetrakis(2'-aminoethyl)-1,2-diaminopropane	13
5-metrien	5-methyltriethylenetetramine	30

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* (1) IUPAC Information Bulletin, No. 33 (1968) 68–77. (2) *Inorg. Chem.*, 9 (1970) 1–5. (3) *Nomenclature of Inorganic Chemistry*, 2nd edn., Butterworths, London, 1972, pp. 75–83.

ox	oxalate	36, 41C, 49B
phen	1,10-phenanthroline	46, 49
penten	*N,N,N',N'*-tetrakis(2'-aminoethyl)-1,2-diaminoethane	12
pn	propylenediamine	2, 3, 23, 24, 51
pro	prolinate	19, 20, 53
ptn	2,4-diaminopentane	5, 6
$(sal)_2$-bmp	2,2'-bis(salicylideneiminato)-6,6'-dimethylbiphenyl	44
sar	sarcosinate	17
3,2,3-tet	1,10-diamino-4,7-diazadecane	34
tetraen	tetramethylenepentamine	15A, 15B
thiox	1,2-dithiooxalate	39
tn	1,3-diaminopropane(trimethylenediamine)	4, 10, 16, 28
trdta	trimethylenediaminetetraacetate	37
TRI	tribenzo[b,f,j]-[1,5,9]triaza-cycloduodecine	14
trien	*N,N'*-bis(2'-aminoethyl)-1,2-diaminoethane(trimethylenetetraamine)	19, 20

1. $(+)_{589}$-$[Co(en)_3]^{3+}$

   (i) Determination of the absolute configuration of optically active complex ion, $[Co(en)_3]^{3+}$ by means of X-rays.
   Y. Saito, K. Nakatsu, M. Shiro and H. Kuroya, *Acta Crystallogr.*, 8 (1955) 729.

   (ii) Studies on crystals of metallic tris-ethylenediamine complexes. III. The determination of the absolute configuration of optically active complex ion, $[Co(en)_3]^{3+}$, by means of X-rays.
   Y. Saito, K. Nakatsu, M. Shiro and H. Kuroya, *Bull. Chem. Soc. Jap.*, 30 (1957) 795.
   * $(+)_{589}$-$2[Co(en)_3]Cl_3 . NaCl . 6H_2O$, trigonal, $P3$, $a = 11.47$ Å, $c = 8.06$ Å, $Z = 1$, $\Lambda(\delta\delta\delta)$.

   (iii) The crystal structure of D-tris-ethylenediamine-cobalt(III) bromide monohydrate, D-$[Co(en)_3]Br_3.H_2O$, and the absolute configuration of the D-tris-ethylenediamine-cobalt(III) ion, D-$[Co(en)_3]^{3+}$.
   K. Nakatsu, *Bull. Chem. Soc. Jap.*, 35 (1962) 832.
   * $(+)_{589}$-$[Co(en)_3]Br_3.H_2O$, tetragonal, $P4_32_12$, $a = 9.95$ Å, $c = 16.73$ Å, $Z = 4$, $\Lambda(\delta\delta\delta)$.

   (iv) The crystal structure of $(+)_D$-tris(ethylenediamine)cobalt(III) chloride monohydrate, $(+)_D$-$[Co(en)_3]Cl_3.H_2O$.
   M. Iwata, K. Nakatsu and Y. Saito, *Acta Crystallogr. Sect. B*, 25 (1969) 2562.
   * $(+)_{589}$-$[Co(en)_3]Cl_3.H_2O$, tetragonal, $P4_32_12$, $a = 9.682$ Å, $c = 16.287$ Å, $Z = 4$, $\Lambda(\delta\delta\delta)$.

(v) The crystal structure of $(+)_{D}$- tris(ethylenediamine)cobalt(III) nitrate.
D. Witiak, J.C. Clardy and D.S. Martin Jr., *Acta Crystallogr. Sect. B*, 28 (1972) 2694; *Coord. Chem. Rev.*, 11 (1973) 80.
* $(+)_{589}$-$[Co(en)_3](NO_3)_3$, orthorhombic, $P2_12_12_1$, $a = 14.570$ Å, $b = 12.607$ Å, $c = 8.756$ Å, $Z = 4$, $\Lambda(\delta\delta\delta)$.

2. $(-)_{589}$-$[Co(-pn)_3]^{3+}$:
(i) The absolute configuration of the tris-propylenediamine-cobalt(III) ion, L-$[Co\ l\text{-}pn]^{3+}$.
Y. Saito, H. Iwasaki and H. Ota, *Bull. Chem. Soc. Jap.*, 36 (1963) 1543.
(ii) The crystal structure of tris(*l*-propylenediamine)cobalt(III) bromide and the absolute configuration of the complex ion, $[Co\ l\text{-}pn_3]^{3+}$.
H. Iwasaki and Y. Saito, *Bull. Chem. Soc. Jap.*, 39 (1966) 92.
* $(-)_{589}$-$[Co(-pn)_3]Br_3$, hexagonal, $P6_3$, $a = 11.08$ Å, $c = 8.59$ Å, $Z = 2$, $\Delta(\lambda\lambda\lambda)$, $-$pn, R.

3. $(-)_{589}$-$[Co(+pn)_3]^{3+}$.
Cited in 'Structure and Absolute Configuration of Cobalt(III) Complexes'.
Y. Saito, *Pure and Appl. Chem.*, 17 (1968) 21.
* $(-)_{589}$-$[Co(+pn)_3][Co(CN)_6].3H_2O$, cubic, $P2_13$, $a = 13.643$ Å, $Z = 4$, $\Delta(\delta\delta\delta)$.

4. $(-)_{589}$-$[Co(tn)_3]^{3+}$.
(i) The absolute configuration of the tris(trimethylenediamine)cobalt(III) ion, $(-)_{D}$-$[Co(tn)_3]^{3+}$.
Y. Saito, T. Nomura and F. Marumo, *Bull. Chem. Soc. Jap.*, 41 (1968) 530.
(ii) The crystal structure of $(-)_{D}$-tris(trimethylenediamine)cobalt(III) bromide monohydrate.
T. Nomura, F. Marumo and Y. Saito, *Bull. Chem. Soc. Jap.*, 42 (1969) 1016.
* $(-)_{589}$-$[Co(tn)_3]Br_3.H_2O$, monoclinic, $P2_1$, $a = 16.274$ Å, $b = 7.863$ Å, $c = 9.48$ Å, $\beta = 126.42°$, $Z = 2$, Λ.
(iii) The crystal structure of $(-)_{589}$-tris(trimethylenediamine)cobalt(III) chloride monohydrate, $(-)_{589}$-$[Co(tn)_3]Cl_3.H_2O$.
R. Nagao, F. Marumo and Y. Saito, *Acta Crystallogr. Sect. B*, 29 (1973) 2438.
* $(-)_{589}$-$[Co(tn)_3]Cl_3.H_2O$, monoclinic, $P2_1$, $a = 12.871$ Å, $b = 7.545$ Å, $c = 9.436$ Å, $\beta = 91.76°$, $Z = 2$, Λ.

5. $(+)_{546}$-$[Co(R,R\text{-}ptn)_3]^{3+}$.
(i) The structure and the absolute configuration of $(+)_{546}$-tris(R,R-2,4-diaminopentane)cobalt(III) ion, $(+)_{546}$-$[Co(R,R\text{-}2,4\text{-}ptn)_3]^{3+}$.
A. Kobayashi, F. Marumo, Y. Saito, J. Fujita and F. Mizukami, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 777.
(ii) The crystal structure of $(+)_{546}$-tris(R,R,-2,4-diaminopentane)cobalt(III) chloride monohydrate, $(+)_{546}$-$[Co(R,R\text{-}ptn)_3]Cl_3.H_2O$.
A. Kobayashi, F. Marumo and Y. Saito, *Acta Crystallogr. Sect. B*, 28 (1972) 3591.
* $(+)_{546}$-$[Co(R,R\text{-}ptn)_3]Cl_3.H_2O$, orthorhombic, $P2_12_12_1$, $a = 17.516$ Å, $b = 13.537$ Å, $c = 11.048$ Å, $Z = 4$, $\Lambda(\lambda\lambda\lambda)$, $(ob)_3$.

6. $(-)_{546}$-$[\mathrm{Co(R,R\text{-}ptn)_3}]^{3+}$.
The crystal structure of $(-)_{546}$-tris(R,R-2,4-diaminopentane)cobalt(III) chloride dihydrate, $(-)_{546}$-$[\mathrm{Co(R,R\text{-}ptn)_3}]\mathrm{Cl_3.2H_2O}$.
A. Kobayashi, F. Marumo and Y. Saito, *Acta Crystallogr. Sect. B*, 29 (1973) 2443.
* $(-)_{546}$-$[\mathrm{Co(R,R\text{-}ptn)_3}]\mathrm{Cl_3.2H_2O}$, tetragonal, $P4_32_12$, $a = 11.369$ Å, $c = 20.193$ Å, $Z = 4$, $\Delta(\lambda\lambda\lambda)$.

7. $(-)_{589}$-$[\mathrm{Co(+cptn)_3}]^{3+}$
(i) The structure and the absolute configuration of tris(*trans*-1,2-diaminocyclopentane)cobalt(III) ion, $(-)_{589}$-$[\mathrm{Co(+cptn)_3}]^{3+}$.
M. Ito, F. Marumo and Y. Saito, *Inorg. Nucl. Chem. Lett.*, 6 (1970) 519.
(ii) Crystal structure of $(-)_{589}$-tris[(+)-*trans*-1,2-diaminocyclopentane] cobalt(III) chloride tetrahydrate, $(-)_{589}$-$[\mathrm{Co(+cptn)_3}]\mathrm{Cl_3.4H_2O}$.
M. Ito, F. Marumo and Y. Saito, *Acta Crystallogr. Sect. B*, 27 (1971) 2187; *Coord. Chem. Rev.*, 8 (1972) 285.
* $(-)_{589}$-$[\mathrm{Co(+cptn)_3}]\mathrm{Cl_3.4H_2O}$. hexagonal, $P6_122$, $a = 11.871$ Å, $c = 30.803$ Å, $Z = 6$, $\Lambda(\delta\delta\delta)$, +cptn, S,S.

8. $(-)_{589}$-$[\mathrm{Co(+chxn)_3}]^{3+}$.
The crystal structure of $(-)_{589}$-tris[(+)-*trans*-1,2-diaminocyclohexane]cobalt(III) chloride pentahydrate, $(-)_{589}$-$[\mathrm{Co(+chxn)_3}]\mathrm{Cl_3.5H_2O}$.
F. Marumo, Y. Utsumi and Y. Saito, *Acta Crystallogr. Sect. B*, 26 (1970) 1492; *Coord. Chem. Rev.*, 6 (1971) Bibl. 12.
* $(-)_{589}$-$[\mathrm{Co(+chxn)_3}]\mathrm{Cl_3.5H_2O}$, hexagonal, $P6_1$, $a = 12.34$ Å, $c = 33.52$ Å, $Z = 6$, $\Lambda(\delta\delta\delta)$, +chxn, S,S.

9. $(+)_{589}$-$[\mathrm{Co(-chxn)_3}]^{3+}$.
The crystal structure of $(+)_{589}$-tris[(−)-*trans*-1,2-diaminocyclohexane] cobalt(III) chloride monohydrate, ('ob' isomer).
A. Kobayashi, F. Marumo and Y. Saito, *Acta Crystallogr. Sect. B*, 28 (1972) 2709; *Coord. Chem. Rev.*, 11 (1973) 80.
* $(+)_{589}$-$[\mathrm{Co(-chxn)_3}]\mathrm{Cl_3.H_2O}$, monoclinic, $C2$, $a = 13.922$ Å, $b = 10.720$ Å, $c = 8.777$ Å, $\beta = 108.93°$, $Z = 2$, $\Lambda(\lambda\lambda\lambda)$, −chxn, R,R.

10. $(+)_{589}$-$[\mathrm{Co(en)_2(tn)}]^{3+}$.
The structure and absolute configuration of bis(ethylenediamine)trimethylenediaminecobalt(III) bromide.
H.V.F. Schousboe-Jensen, *Acta Chem. Scand.*, 26 (1972) 3413.
* $(+)_{589}$-$[\mathrm{Co(en)_2(tn)}]\mathrm{Br_3}$, orthorhombic, $P2_12_12_1$, $a = 18.629$ Å, $b = 10.774$ Å, $c = 8.719$ Å, $Z = 4$, $\Lambda(\delta\delta$ chair).

11. $(-)_{589}$-*u*-*fac*-$[\mathrm{Co(dien)_2}]^{3+}$.
The crystal structure of $(-)_{589}$-*u*-*facial*-bis(diethylenetriamine)cobalt(III) hexacyanocobaltate(III) dihydrate, $(-)_{589}$-*u*-*facial*-$[\mathrm{Co(dien)_2}]\,[\mathrm{Co(CN)_6}]\,.\mathrm{2H_2O}$.
M. Konno, F. Marumo and Y. Saito, *Acta Crystallogr. Sect. B*, 29 (1973) 739.
* $(-)_{589}$-*u*-*fac*-$[\mathrm{Co(dien)_2}]\,[\mathrm{Co(CN)_6}]\,.\mathrm{2H_2O}$, orthorhombic, $B22_12$, $a = 13.942$ Å, $b = 32.370$ Å, $c = 9.418$ Å, $Z = 8$, $\Delta(\delta\lambda)$, $\Delta(\lambda\lambda)$.

12. (+)$_{589}$-[Co(penten)]$^{3+}$.

(i) The structure and the absolute configuration of (+)$_{D}$-*N,N,N′,N′*-tetrakis-(2′-aminoethyl)-1,2-diaminoethanecobalt(III) ion, [Co(penten)]$^{3+}$.

A. Muto, F. Marumo and Y. Saito, *Inorg. Nucl. Chem. Lett.*, 5 (1969) 85.

(ii) The crystal structure of (+)$_{D}$-[*N,N,N′,N′*-tetrakis-(2′-aminoethyl)-1,2-diaminoethane] cobalt(III) hexacyanocobaltate(III) dihydrate.

A. Muto, F. Marumo and Y. Saito, *Acta Crystallogr. Sect. B*, 26 (1970) 226.

* (+)$_{589}$-[Co(penten)] [Co(CN)$_6$]. 2H$_2$O, orthorhombic, $P2_12_12_1$, $a = 15.471$ Å, $b = 16.036$ Å, $c = 9.253$ Å, $Z = 4$, ΛΔΛ, (Λ).

13. (–)$_{540}$-[Co(–mepenten)]$^{3+}$.

(i) The absolute configuration of cobalt(III) complexes of penten and its methyl derivative.

Y. Saito, A. Muto and F. Marumo, *Proceedings of the XII International Conference on Coordination Chemistry*, H.C. Freeman (ed.), 1969, p. 90.

(ii) The crystal structure of (–)$_{589}$-*N,N,N′,N′*-tetrakis-(2′-aminoethyl)-1,2-diaminopropane cobalt(III) hexacyanocobaltate(III) dihydrate.

A. Kobayashi, F. Marumo and Y. Saito, *Acta Crystallogr. Sect. B*, in press.

* (–)$_{540}$-[Co(–menpenten)] [Co(CN)$_6$]. 2H$_2$O, orthorhombic, $P2_12_12_1$, $a = 10.84$ Å, $b = 26.76$ Å, $c = 8.59$ Å, $Z = 4$, ΔΛΔ, (Δ), –mepenten, R.

14. [Co(TRI)$_2$]$^{3+}$.

Bis(tribenzo[b,f,j]-[1,5,9]triazacycloduodecine)cobalt(III) ion, (+)$_{546}$-[Co(TRI)$_2$]$^{3+}$, evidence for Piper's model of optical activity. The structure and absolute configuration of (+)$_{5461}$-bis(tribenzo[b,f,j]-[1,5,9]triazaduodecine)cobalt(III) iodide.

R.M. Wing and R. Eiss, *J. Amer. Chem. Soc.*, 92 (1970) 1929.

* (+)$_{546}$-[Co(TRI)$_2$]I$_3$.3H$_2$O, orthorhombic, $P2_12_12_1$, $a = 19.592$ Å, $b = 14.609$ Å, $c = 14.508$ Å, $Z = 4$, Λ.

15A. (+)$_{540}$-αβS-[CoCl(tetraen)]$^{2+}$.

15B. (+)$_{540}$-αβR-[CoCl(tetraen)]$^{2+}$.

(i) The absolute configurations and conformations of chlorocobalt(III) tetraethylenepentamine complexes.

M.R. Snow, D.A. Buckingham, P.A. Marzilli and A.M. Sargeson, *Chem. Commun.*, (1969) 891.

(ii) Structure and conformational analysis of coordination complexes. Part III. A diastereoisomeric pair of αβ-chloro(tetraethylenepentamine)cobalt(III) cations.

Michael R. Snow, *J. Chem. Soc. Dalton*, (1972) 1627; *Coord. Chem. Rev.*, 10 (1973) 430.

* (+)$_{540}$-αβS-[CoCl(tetraen)](ClO$_4$)$_2$, orthorhombic, $P2_12_12_1$, $a = 17.37$ Å, $b = 12.44$ Å, $c = 8.43$ Å, $Z = 4$, Λ.

(+)$_{540}$-αβR-[CoCl(tetraen)](ClO$_4$)$_2$, orthorhombic, $P2_12_12_1$, $a = 17.26$ Å, $b = 12.03$ Å, $c = 8.72$ Å, $Z = 4$, Λ.

16. $(-)_{589}$-$[Co(acac)(tn)_2]^{2+}$.
The absolute configuration of the $(-)_{589}$-acetylacetonato-bis(trimethylenediamine)cobalt(III) ion.
H. Kawaguchi, K. Matsumoto, H. Kuroya and S. Kawaguchi, *Chem. Lett.*, (1972) 125.
* $(-)_{589}$-$[Co(acac)(tn)_2]$ $[As\text{-}(+)\text{-}tart]_2.H_2O$, monoclinic, $P2_1$, $a = 12.02$ Å, $b = 13.73$ Å, $c = 9.02$ Å, $\beta = 107.4°$, $Z = 2$, Δ.

17. $(+)_{436}$-$[Co(sar)(NH_3)_4]^{2+}$.
The absolute configuration of the $(+)_{436}$-sarcosinatotetraammine-cobalt(III) ion.
S. Larsen, K.J. Watson, A.M. Sargeson and K.R. Turnbull, *Chem. Commun.*, (1968) 847.
* $(+)_{436}$-$[Co(sar)(NH_3)_4](NO_3)_2$, orthorhombic, $P2_12_12_1$, $a = 11.865$ Å, $b = 14.88$ Å, $c = 7.279$ Å, $Z = 4$, S, λ.

18. $(+)_{495}$-$[Co(en)_2(L\text{-}glut)]^+$.
Crystal and molecular structure of $(+)_{495}$-L-glutamatobis(ethylenediamine)-cobalt(III) perchlorate: the product of a kinetically stereoselective reaction.
R.D. Gillard, N.C. Payne and G.B. Robertson, *J. Chem. Soc. A*, (1970) 2579; *Coord. Chem. Rev.*, 6 (1971) Bibl. 16.
* $(+)_{495}$-$[Co(L\text{-}glu)(en)_2]ClO_4$, orthorhombic, $P2_12_12_1$, $a = 13.54$ Å, $b = 12.08$ Å, $c = 10.06$ Å, $Z = 4$, $\Lambda(\delta\delta)$.

19. $(-)_{589}$-β_2-RRS-$[Co(S\text{-}pro)(trien)]^{2+}$.
The crystal structure and absolute configuration of L$(-)_{589}$-β_2-RRS-(triethylenetetramine-S-prolinato)cobalt(III) diiodide dihydrate.
H.C. Freeman and I.E. Maxwell, *Inorg. Chem.*, 9 (1970) 649.
* $(-)_{589}$-β_2-RRS-$[Co(S\text{-}pro)(trien)]I_2.2H_2O$, orthorhombic, $P2_12_12_1$, $a = 9.12$ Å, $b = 14.43$ Å, $c = 14.90$ Å, $Z = 4$, $\Delta(\delta\delta\lambda)$, asymmetric N atoms: R,R.

20. $(+)_{589}$-β_2-SSS-$[Co(S\text{-}pro)(trien)]^{2+}$.
The crystal structure and absolute configuration of D-β_2-SSS-(triethylenetetramine-S-prolinato)cobalt(III) tetrachlorozincate.
H.C. Freeman, L.G. Marzilli and I.E. Maxwell, *Inorg. Chem.*, 9 (1970) 2408; *Coord. Chem. Rev.*, 6 (1971) Bibl. 9.
* $(+)_{589}$-β_2-SSS-$[Co(S\text{-}pro)(trien)]$ $[ZnCl_4]$, monoclinic, $P2_1$, $a = 7.01$ Å, $b = 15.58$ Å, $c = 9.66$ Å, $\beta = 109.9°$, $Z = 2$, $\Lambda(\lambda\lambda\delta)$, asymmetric N atoms: S,S.

21. $(+)_{589}$-$[CoCl_2(en)_2]^+$.
The crystal structure of $(+)_{589}$-dichlorobis(ethylenediamine)cobalt(III) chloride monohydrate.
K. Matsumoto, S. Ooi and H. Kuroya, *Bull. Chem. Soc. Jap.*, 43 (1970) 3801.
* $(+)_{589}$-$[CoCl_2(en)_2]Cl.H_2O$, monoclinic, $P2_1$, $a = 12.07$ Å, $b = 11.52$ Å, $c = 8.33$ Å, $\beta = 96.9°$, $Z = 2$, $\Lambda(\delta\delta)$.

22A. $(-)_{589}$-$[Co(NO_2)_2(en)_2]^+$.
22B. $(+)_{589}$-$[Co(mal)_2(en)]^-$.
The crystal structure of $(-)_{589}$-dinitrobis(ethylenediamine)cobalt(III) $(+)_{589}$-bis-

(malonato)ethylenediaminecobaltate(III).
K. Matsumoto and H. Kuroya, *Bull. Chem. Soc. Jap.*, 45 (1972) 1755.
* $(-)_{589}$-$[Co(NO_2)_2(en)_2]$.$(+)_{589}$-$[Co(mal)_2(en)]$, triclinic, $P1$, $a = 10.58$ Å, $b = 7.98$ Å, $c = 7.99$ Å, $\alpha = 122.8^\circ$, $\beta = 105.3^\circ$, $\gamma = 74.6^\circ$, $Z = 1$, cation: $\Delta(\delta\delta)$; anion: Δ. (See No. 41B).

23\. $(-)_{589}$-*trans*-$[CoCl_2(-pn)_2]^+$.
The crystal structure of *trans*-dichloro-bis-*l*-propylenediaminecobalt(III) chloride hydrochloride dihydrate and the absolute configuration of the complex ion, $[Co(l\text{-}pn)_2Cl_2]^+$.
Y. Saito and H. Iwasaki, *Bull. Chem. Soc. Jap.*, 35 (1962) 1131.
* $(-)_{589}$-$[CoCl_2(-pn)_2]Cl.HCl.2H_2O$, monoclinic, $C2$, $a = 22.092$ Å, $b = 8.406$ Å, $c = 9.373$ Å, $\beta = 99^\circ39'$, $Z = 2$, R, $\lambda\lambda$.

24\. $(+)_{589}$-*cis*-$[Co(NO_2)_2(-pn)_2]^+$.
The crystal structure and absolute configuration of $(+)_{589}$-*cis*-dinitrobis[$(-)_{589}$-1,2-propylenediamine]cobalt(III) chloride.
G.A. Barclay, E. Goldschmied and N.C. Stephenson, *Acta Crystallogr. Sect. B*, 26 (1970) 1559; *Coord. Chem. Rev.*, 6 (1971) Bibl. 12.
* $(+)_{589}$-*cis*-$[Co(NO_2)_2(-pn)_2]Cl$, orthorhombic, $P2_12_12_1$, $a = 646$ Å, $b = 9.62$ Å, $c = 22.36$ Å, $Z = 4$, $\Delta(\lambda\lambda)$.

25\. $(-)_{589}$-$[CoCl_2(N\text{-}meen)_2]^+$.
The absolute configuration of $(-)_{589}$-*trans*-dichlorobis(*N*-methylethylenediamine)cobalt(III) perchlorate hemihydrate.
W.T. Robinson, D.A. Buckingham, G. Chandler, L.G. Marzilli and A.M. Sargeson, *Chem. Commun.*, (1969) 539.
* $(-)_{589}$-$[CoCl_2(N\text{-}meen)_2]ClO_4.0.5H_2O$, orthorhombic, $P2_12_12_1$, $a = 10.72$ Å, $b = 15.02$ Å, $c = 9.29$ Å, $Z = 4$, RR; $\delta\delta$.

26\. $(+)_{589}$-*trans*-[dichloro-{$(-)_{589}$-*N*,*N'*-bis-(S-2-amino-3-phenylpropyl)-*trans*-R-cyclohexane-1,2-diamine $\delta\lambda\delta$}cobalt(III)] ion.
The crystal structure and absolute configuration of a novel tetradentate ligand in a cobalt(III) ion complex.
J.W. Turley, F.P. Boer and F. van Remoortere, *Chem. Commun.*, (1970) 720.
* $CoC_{24}H_{36}Cl_3N_4O_4$(perchlorate), monoclinic, $P2_1$, $a = 13.237$ Å, $b = 16.671$ Å, $c = 12.988$ Å, $\beta = 94.806^\circ$, $Z = 4$.

27\. $(+)_{589}$-$[Co(CN)_2(en)_2]^+$.
The crystal structure of $(+)_{589}$-dicyanobis(ethylenediamine)cobalt(III) chloride monohydrate.
K. Matsumoto, S. Ooi and H. Kuroya, *Bull. Chem. Soc. Jap.*, 44 (1971) 2721; *Coord. Chem. Rev.*, 8 (1972) 278.
* $(+)_{589}$-$[Co(CN)_2(en)_2]Cl.H_2O$, monoclinic, $P2_1$, $a = 8.23$ Å, $b = 11.74$ Å, $c = 6.65$ Å, $\beta = 107.8^\circ$, $Z = 2$, $\Lambda(\lambda\lambda)$.

28\. $(-)_{589}$-$[Co(NCS)_2(tn)_2]^+$.
The absolute configuration of the $(-)_{589}$-$[Co(NCS)_2(tn)_2]$(Sb-(+)-tart).$2H_2O$ diastereomer.

K. Matsumoto, M. Yonezawa, H. Kuroya, H. Kawaguchi and S. Kawaguchi, *Bull. Chem. Soc. Jap.*, 43 (1970) 1269.

* $(-)_{589}$-[Co(NCS)$_2$(tn)$_2$](Sb-(+)-tart).2H$_2$O, orthorhombic, $P2_12_12_1$, $a = 12.14$ Å, $b = 19.51$ Å, $c = 9.13$ Å, $Z = 4$, Λ.

29. $(+)_{589}$-*cis*-[Co(NO$_2$)$_2$(L-arg)$_2$]$^{+}$.

The structure of (+)-dinitrobis(L-arginato)cobalt(III) nitrate dihydrate.

W.H. Watson, D.R. Johnson, M.B. Celap and B. Kamberi, *Inorg. Chim. Acta*, 6 (1972) 591.

* $(+)_{589}$-*cis*-[Co(NO$_2$)$_2$(L-arg)$_2$]NO$_3$.2H$_2$O, triclinic, $P1$, $a = 11.250$ Å, $b = 9.867$ Å, $c = 5.701$ Å, $\alpha = 89°29'$, $\beta = 99°26'$, $\gamma = 93°13'$, $Z = 1$, Λ.

30. $(+)_{589}$-*cis*-β-[Co(NO$_2$)$_2$(R-5-metrien)]$^{+}$.

The crystal structure of $(+)_{589}$-*cis*-β-dinitro(R-5-methyl-triethylenetetramine)-cobalt(III) chloride, $(+)_{589}$-*cis*-β-[Co(NO$_2$)$_2$(R-metrien)]Cl.

K. Tanaka, F. Marumo and Y. Saito, *Acta Crystallogr. Sect. B*, 29 (1973) 733.

* $(+)_{589}$-*cis*-β-[Co(NO$_2$)$_2$(R-5-metrien)]Cl, orthorhombic, $P2_12_12_1$, $a = 12.696$ Å, $b = 14.364$ Å, $c = 7.542$ Å, $Z = 4$, $\Lambda(\lambda\lambda\delta)$, asymmetric nitrogen atoms: S.

31. $(-)_{589}$-*cis*-α-[Co(NO$_2$)$_2$(L-3,8-dimetrien)]$^{+}$.

The crystal structure of $(-)_{589}$-*cis*-α-dinitro(L-3,8-dimethyltriethylenetetramine)-cobalt(III) perchlorate, *cis*-α-[Co(NO$_2$)$_2$(L-3,8-dimetrien)]ClO$_4$.

M. Ito, F. Marumo and Y. Saito, *Acta Crystallogr. Sect. B*, 28 (1972) 457; *Coord. Chem. Rev.*, 9 (1972/3) 205.

* $(-)_{589}$-*cis*-α-[Co(NO$_2$)$_2$(L-3,8-dimetrien)]ClO$_4$, orthorhombic, $P2_12_12_1$, $a = 12.395$ Å, $b = 16.829$ Å, $c = 7.864$ Å, $Z = 4$, $\Lambda(\delta\lambda\delta)$, asymmetric nitrogen atoms: SS.

32. $(-)_{546}$-*cis*-β-[Co(NO$_2$)$_2$(L-3,8-dimetrien)]$^{+}$.

(i) Structure and absolute configuration of $(-)_{\mathrm{D}}$-*cis*-β-dinitro(L-3,8-dimethyl-triethylenetetramine)cobalt(III) ion, $(-)_{\mathrm{D}}$-[Co(NO$_2$)$_2$(L-3,8-dimetrien)]$^{+}$.

M. Ito, F. Marumo and Y. Saito, *Inorg. Nucl. Chem. Lett.*, 5 (1969) 377.

(ii) The crystal structure of $(-)_{546}$-*cis*-β-dinitro(L-3,8-diemthyltriethylene-tetramine)cobalt(III) perchlorate, $(-)_{546}$-*cis*-β-[Co(NO$_2$)$_2$(L-3,8-dimetrien)]ClO$_4$.

M. Ito, F. Marumo and Y. Saito, *Acta Crystallogr. Sect. B*, 26 (1970) 1408; *Coord. Chem. Rev.*, 7 (1971) Bibl. 11.

* $(-)_{546}$-*cis*-β-[Co(NO$_2$)$_2$(L-3,8-dimetrien)]ClO$_4$, orthorhombic, $P2_12_12_1$, $a = 11.89$ Å, $b = 13.07$ Å, $c = 10.28$ Å, $Z = 4$, $\Delta(\delta\lambda\delta)$, asymmetric nitrogen atoms: RS.

33. $(-)_{589}$-*trans*-[Co(NO$_2$)$_2$(L-3,8-dimetrien)]$^{+}$.

The crystal structure of $(-)_{589}$-*trans*-dinitro(L-3,8-dimethyltriethylenetetramine)-cobalt(III) perchlorate, *trans*-[Co(NO$_2$)$_2$(L-3,8-dimetrien)]ClO$_4$.

M. Ito, F. Marumo and Y. Saito, *Acta Crystallogr. Sect. B*, 28 (1972) 463; *Coord. Chem. Rev.*, 9 (1972/3) 205.

* $(-)_{589}$-*trans*-[Co(NO$_2$)$_2$(L-3,8-dimetrien)]ClO$_4$, orthorhombic, $P2_12_12_1$, $a = 12.82$ Å, $b = 19.91$ Å, $c = 6.52$ Å, $Z = 4$, $\delta\lambda\delta$, asymmetric nitrogen atoms: SS.

34. $(+)_{546}$-$[Co(NO_2)_2(3,2,3\text{-tet})]^+$.
The crystal structure and absolute configuration of $(+)_{546}$-*trans*-dinitro(1,10-diamino-4,7-diazadecane)cobalt(III) bromide.
N.C. Payne, *Inorg. Chem.*, 11 (1972) 1376; *Coord. Chem. Rev.*, 9 (1972/3) 394.
* $(+)_{546}$-$[Co(NO_2)_2(3,2,3\text{-tet})]Br$, monoclinic, $P2_1$, $a = 7.848$ Å, $b = 14.756$ Å, $c = 6.397$ Å, $\beta = 99.5°$, $Z = 2$, asymmetric nitrogen atoms: RR. c.f. 3,2,3-tet = $H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$.

35. $(-)_{546}$-$[Co(C_3H_7N_2O_2)_2]^+$.
The structure and absolute configuration of $(-)_{546}$-*cis, trans, cis*-bis(diaminopropionato)cobalt(III) bromide, $[Co(C_3H_7N_2O_2)_2]Br$.
C.F. Liu and J.A. Ibers, *Inorg. Chem.*, 8 (1969) 1911.
$(-)_{546}$-$[Co(C_3H_7N_2O_2)_2]Br$, orthorhombic, $P2_12_12_1$, $a = 11.76$ Å, $b = 7.49$ Å, $c = 5.91$ Å, $Z = 2$.

36. $(-)_{546}$-$[Co(C_4H_8NO_2)_2(ox)]^-$.
Absolute configuration of sodium $(-)_{546}$-bis(*trans*-N-methyl(S)-alaninato)-oxalatocobaltate(III) dihydrate by an X-ray crystal structure determination.
G.W. Svetich, A.A. Voge, J.B. Brushmiller and E.A. Berends, *Chem. Commun.*, (1972) 701.
* $Na(-)_{546}$-$[Co(C_4H_8NO_2)_2(ox)].2H_2O$, hexagonal, $P6_5$, $a = 13.752$ Å, $c = 15.546$ Å, $Z = 6$, Λ, asymmetric nitrogen atom: R.

37. $(-)_{546}$-$[Co(trdta)]^-$.
The crystal structure of potassium $(-)_{546}$-trimethylenediaminetetraacetatocobaltate(III) dihydrate.
R. Nagao, F. Marumo and Y. Saito, *Acta Crystallogr. Sect. B*, 28 (1972) 1852.
* $K(-)_{546}$-$[Co(trdta)].2H_2O$, orthorhombic, $B22_12$, $a = 10.984$ Å, $b = 16.638$ Å, $c = 8.851$ Å, $Z = 4$, ΛΔΛ, conformation of the six-membered chelate ring is δ (skew-boat).

38. $(-)_{546}$-$[Co(acac)_3]$.
X-ray determination of the absolute configuration of metal complexes in quasi-racemic crystals. Λ-$(-)_{546}$-cobalt(III) acetylacetonate.
R.B. von Dreele and R.C. Hay, *J. Amer. Chem. Soc.*, 93 (1971) 4936.
* $(-)_{546}$-$[Co(acac)_3].[Al(acac)_3]$, monoclinic, $P2_1$, $a = 13.96$ Å, $b = 7.53$ Å, $c = 16.32$ Å, $\beta = 98.66°$, $Z = 2$, Λ.

39. $(+)_{589}$-$[Co(thiox)_3]^{3-}$.
The structure and absolute configuration of the $(+)_{589}$-tris(1,2-dithiooxalato)-cobaltate(III) ion.
K.R. Butler and M.R. Snow, *Inorg. Nucl. Chem. Lett.*, 8 (1972) 541; *Coord. Chem. Rev.*, 9 (1972/3) 414.
* $KCa(+)_{589}$-$[Co(thiox)_3].4H_2O$, orthorhombic, $P2_12_12_1$, $a = 12.381$ Å, $b = 12.791$ Å, $c = 11.801$ Å, $Z = 4$, Λ.

40. $(+)_{589}$-α-[Co(L-ala)$_3$].

The absolute configuration of α-(+)-tris-L-alaninatocobalt(III).

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

* $(+)_{589}$-α-[Co(L-ala)$_3$], orthorhombic, $P2_12_12_1$, $a = 18.550$ Å, $b = 14.459$ Å, $c = 5.09$ Å, $Z = 4$, Λ.

41A. $(+)_{589}$-[Cr(mal)$_3$]$^{3-}$.

41B. $(+)_{546}$-[Co(mal)$_2$(en)]$^-$.

41C. $(+)_{589}$-[Cr(ox)$_3$]$^{3-}$.

Piper's model for optical activity: absolute configuration of the complex ions, $(+)_{589}$-[Cr(malonate)$_3$]$^{3-}$, $(+)_{546}$-[Co(malonate)$_2$(ethylenediamine)]$^-$, and $(+)_{589}$-[Cr(oxalate)$_3$]$^{3-}$.

K.R. Butler and M.R. Snow, *Chem. Commun.*, (1971) 550.

* Na[Co(mal)$_2$(en)].2H$_2$O, orthorhombic, $P2_12_12_1$, $a = 13.46$ Å, $b = 14.24$ Å, $c = 7.34$ Å, $Z = 4$, Δ. (See No. 22B.)

[Co(−pn)$_3$] [Cr(mal)$_3$]. 3H$_2$O, rhombohedral, $R32$, $a = 16.12$ Å, $c = 10.07$ Å (hexagonal setting), $Z = 3$, [Cr(mal)$_3$]$^{3-}$: Λ.

K$(+)_{589}$-[Ni(phen)$_3$].$(+)_{589}$-[Cr(ox)$_3$].2H$_2$O is isomorphous with K$(+)_{589}$-[Ni(phen)$_3$].$(-)_{589}$-[Co(ox)$_3$].2H$_2$O (see No. 47). Therefore $(+)_{589}$-[Cr(ox)$_3$]$^{3-}$ is Λ.

42. $(+)_{589}$-[Cr(+atc)$_3$].

Establishment of absolute configuration in tris-β-diketonatochelate complexes by X-ray methods. The structure of Λ$(+)_{589}$-*trans*-tris-[(+)-3-acetylcamphorato]-chromium(III).

W. DeW. Horrocks Jr., D.L. Johnston and D. MacInnes, *J. Amer. Chem. Soc.*, 92 (1970) 7620.

* $(+)_{589}$-[Cr(+atc)$_3$], $C_{36}H_{51}CrO_6$, monoclinic, $P2_1$, $a = 12.915$ Å, $b = 7.790$ Å, $c = 17.590$ Å, $\beta = 93.06°$, $Z = 2$, Λ.

43. Vitamin B$_{12}$.

The structure of Vitamin B$_{12}$.

D.C. Hodgkin, J. Kamper, J. Lindsey, M. Mackay, J. Pickworth, J.H. Robertson, C.B. Shoemaker, J.G. White, R.J. Prosen and K.N. Trueblood, *Proc. Roy. Soc. Ser. A*, 242 (1957) 228.

* Vitamin B$_{12}$ hexacarboxylic acid, $C_{46}H_{58}O_{13}N_6CoCl$, orthorhombic, $P2_12_12_1$, $a = 24.58$ Å, $b = 15.52$ Å, $c = 13.32$ Å, $Z = 4$.

44. [Co(sal)$_2$-(R)-bmp].

The absolute configuration of a dissymmetric pseudotetrahedral coordination compound containing a restricted biphenyl. Molecular structure of Δ-2,2′-bis-(salicylidenaminato)-$(+)_D$-(R)-6,6′-dimethylbiphenyl-cobalt(II).

L.H. Pignolet, R.P. Taylor and W. DeW. Horrocks Jr., *J. Amer. Chem. Soc.*, 91 (1969) 5457.

* $[Co(sal)_2$-(R)-bmp], orthorhombic, $P2_12_12_1$, $a = 17.978$ Å, $b = 11.206$ Å, $c = 11.628$ Å, $Z = 4$, right hand screw chirality $\Delta(C_2)$.

45. $(-)_{589}$-$[Cr(bigua)_3]^{3+}$.
The absolute configuration of tris(biguanide)chromium(III).
G.R. Brubaker and W.E. Webb, *J. Amer. Chem. Soc.*, 91 (1969) 7199.
* $C_6H_{21}CrN_{15}{}^{3+}.3C_{10}H_{15}O_4S^-$, $(-)_{589}$-tris(biguanide)chromium(III) d-10-camphorsulphonic acid trihydrate, monoclinic, $P2_1$, $a = 16.393$ Å, $b = 10.753$ Å, $c = 16.666$ Å, $\beta = 117.68°$, $Z = 2$, Λ.

46. $(-)_{589}$-$[Fe(phen)_3]^{2+}$.
Structure and absolute configuration of ferrous phenanthroline antimony *d*-tartrate hydrate.
D.H. Templeton, A. Zalkin and T. Ueki, *Acta Crystallogr.*, 21 (1966) A155.
* $(-)_{589}$-$[Fe(phen)_3](SbC_4H_2O_6)_2.8H_2O$, hexagonal, $P3_221$, $a = 18.58$ Å, $c = 12.04$ Å, $Z = 3$, Λ.

47. Ferrichrome-A.
Determination of the crystal and molecular structure of ferrichrome-A tetrahydrate.
A. Zalkin, J.D. Forrester and D.H. Templeton, *J. Amer. Chem. Soc.*, 88 (1966) 1810; see also *Science*, 146 (1964) 261.
* $C_{41}H_{58}N_9O_{20}Fe.4H_2O$, monoclinic, $P2_1$, $a = 11.02$ Å, $b = 13.26$ Å, $c = 18.22$ Å, $\beta = 99.48°$, $Z = 2$, Λ.

48. $[Ni(en)_3]^{2+}$.
New silicon–oxygen radical. Ternary two-level Si_6O_{15} ring in the structure of $[Ni(en)_3]Si_2O_5.8.7H_2O$.
Yu.I. Smolin, *Sov. Phys.–Crystallogr.*, 15 (1970) 23.
* $[Ni(en)_3]Si_2O_5.8.7H_2O$, hexagonal, $P6_3$, $a = 17.375$ Å, $c = 15.185$ Å, $Z = 6$, $\Lambda(\delta\delta\delta)$?

49A. $(+)_{589}$-$[Ni(phen)_3]^{2+}$.
49B. $(-)_{589}$-$[Co(ox)_3]^{3-}$.
Absolute configuration of the tris-(1,10-phenanthroline)nickel(II) and tris-(oxalato)cobaltate(III) complex ions by X-ray structure analysis.
K.R. Butler and M.R. Snow, *J. Chem. Soc. A*, (1971) 565.
* $K(+)_{589}$-$[Ni(phen)_3].(-)_{589}$-$[Co(ox)_3].2H_2O$, cubic, $P2_13$, $a = 16.225$ Å, $Z = 4$, $(+)_{589}$-$[Ni(phen)_3]^{2+}$: Λ, $(-)_{589}$-$[Co(ox)_3]^{3-}$: Λ.

50. $[NiC_{42}H_{42}INP_3]^+$.
Crystal and molecular structure of the low-spin five-coordinate complex iodo-(tris-(2-diphenylphosphinoethyl)amino)nickel(II) iodide.
P. Dapporto and L. Sacconi, *J. Chem. Soc. A*, (1970) 1804.
* $C_{42}H_{42}INNiP_3{}^+.I^-$, trigonal, $R3$, $a = 16.363$ Å, $c = 12.398$ Å, $Z = 3$.

51. $(-)_{589}$-$[Cu(-pn)_3]^{2+}$.
The absolute configuration of the tris-*l*-propylenediamine copper(II) ion, $(-)_{589}$-$[Cu(l\text{-}pn)_3]^{2+}$.

T. Okamoto, K. Matsumoto and H. Kuroya, *Bull. Chem. Soc. Jap.*, 43 (1970) 1915.

* $(-)_{589}$-[Cu($-$pn)$_3$]Br$_2$. 2H$_2$O, monoclinic, $P2_1$, a = 10.71 Å, b = 8.93 Å, c = 10.88 Å, β = 107.2°, Z = 2, $\Delta(\lambda\lambda\lambda)$.

52. $(-)_{589}$-[As(cat)$_3$]$^-$.

(i) The absolute configuration of $(-)_{589}$-tris(1,2-benzenediolate)arsenate(V) ion, $(-)_{589}$-[As(cat)$_3$]$^-$.

T. Ito, A. Kobayashi, F. Marumo and Y. Saito, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 1097.

(ii) The crystal structure of potassium $(-)_{589}$-tris(1,2-benzenediolato)arsenate(V) sesquihydrate, $(-)_{589}$-K[As(cat)$_3$] . 1.5H$_2$O.

A. Kobayashi, T. Ito, F. Marumo and Y. Saito, *Acta Crystallogr. Sect. B*, 28 (1972) 3441.

* K$(-)_{589}$-[As(cat)$_3$] . 1.5H$_2$O, orthorhombic, $P2_12_12_1$, a = 12.901 Å, b = 24.852 Å, c = 11.888 Å, Z = 8, Δ.

53. $(+)_{589}$-[Pd(L-pro)$_2$].

The crystal structure of bis(L-prolinato)palladium(II).

T. Ito, F. Marumo and Y. Saito, *Acta Crystallogr. Sect. B*, 27 (1971) 1062; *Coord. Chem. Rev.*, 7 (1972) 418.

* $(+)_{589}$-[Pd(L-pro)$_2$], orthorhombic, $B22_12$, a = 10.31 Å, b = 12.17 Å, c = 9.71 Å, Z = 4, proline: S.

54. $(+)_{450}$-*cis*-[PtCl$_2$(en)$_2$]$^{2+}$.

The structure and absolute configuration of $(+)_{450}$-*cis*-dichlorobis(ethylenediamine)platinum(IV) chloride, [Pt(C$_2$H$_8$N$_2$)$_2$Cl$_2$]Cl$_2$.

C.F. Liu and J.A. Ibers, *Inorg. Chem.*, 9 (1970) 773.

* $(+)_{450}$-*cis*-[PtCl$_2$(en)$_2$]Cl$_2$, monoclinic, $C2$, a = 10.668 Å, b = 10.687 Å, c = 11.339 Å, β = 101.21°, Z = 4, $\Lambda(\lambda\lambda)$.

E. METAL INDEX

F. AUTHOR INDEX

G. REMARKS ON IUPAC PROPOSAL FOR DESIGNATION OF ABSOLUTE CONFIGURATION

Almost all the absolute configurations listed in the bibliography can be designated according to IUPAC proposal (1968)*. However, there are some exceptions. For example the IUPAC scheme cannot be straightforwardly applied for assigning a label to the absolute configuration of $(-)_{546}$-*cis, trans, cis*-bis(diaminopropionato)-cobalt(III) ion (ref. [35]), *cis*(N)-*trans*(O_5)-bis(L-aspartato)cobaltate(III) and *cis*-(N)-*trans*(O_6)-bis(L-aspartato)cobaltate(III) ions. The latter two complex ions are shown in Fig. 7 (ref. 50, 51). In all these complex ions three chelate rings join on a

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* See references on p. 320.

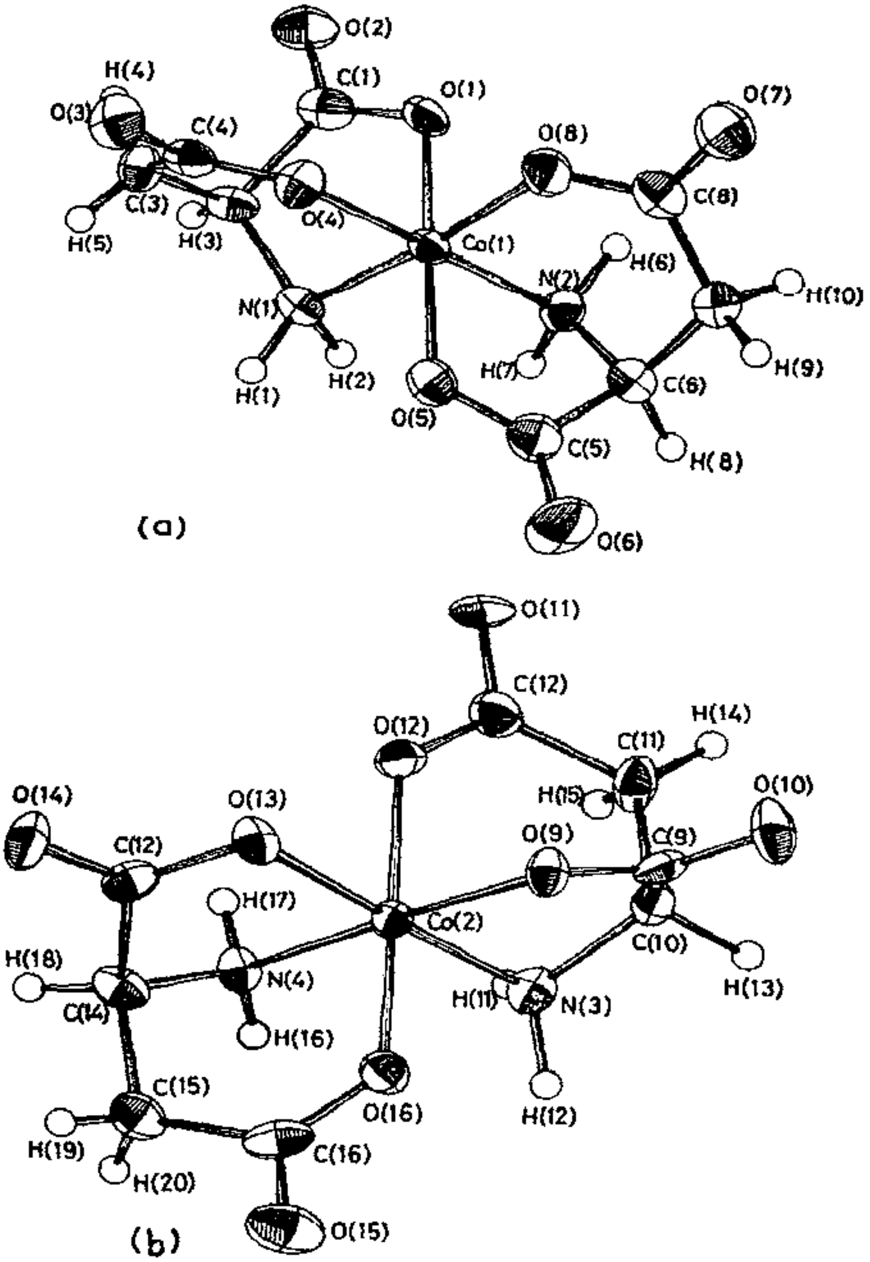

Fig. 7. The two isomers of bis(L-aspartato)cobaltate^{III} ion. (a) *cis*(N)-*trans*(O$_5$) isomer, (b) *cis*-(N)-*trans*(O$_6$) isomer.

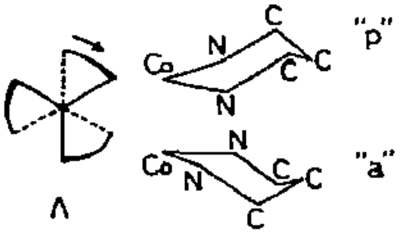

Fig. 8. Two chair conformers of Co–tn rings. The upper ring is the "p" conformer and the lower ring is the "a" form.

face of an octahedron at non-coordinating carbon atoms so that the rings do not define edges of an octahedron. Even if number of skew chelate pairs could be counted, it is impossible to obtain net chirality. Such a difficulty generally arises when a multidentate has a branch with a coordinating atom at its end and this branch is bonded to a non-coordinating atom. On the other hand a multidentate ligand like edta, trdta or penten, does not give rise to such difficulties.

A sandwich type complex ion, $(+)_{546}$-$[Co(TRI)_2]^{3+}$ provides another example [14]. In this case the absolute configuration can be designated as Λ, providing that the helicity is defined by the distortion of an octahedron formed by six ligating nitrogen atoms, as discussed in Section C. A trigonal bipyramidal complex such as $[NiC_{42}H_{42}INP_3]^+$ (ref. [50]) cannot be properly designated. This complex ion has an approximate threefold axis of rotation and the handedness of propeller shaped ring system should be defined. In fact, a pseudotetrahedral coordination compound, $(+)_{589}$-$[Co(sal)_2$-(R)-bmp] has been designated as $\Delta(C_2)$ (ref. [44]).

Finally a few words will be added concerning the six-membered chelate ring. The chair form of a six-membered chelate ring is not chiral and there is no basis for its name in the IUPAC scheme. However, when three, say, 1,3-diaminopropane molecules are coordinated to a metal atom and three chelate rings with chair conformation are formed, chirality is generated. It can be seen from Fig. 5 that the complex ion, $(-)_{589}$-Λ-$[Co(tn)_3]^{3+}$ (ref. [4]), has left handed chirality when viewed along the threefold axis. The chair ring may then fold in such a way that the central carbon atoms define a direction parallel or antiparallel to the direction defined by the three chelate rings. Raymond[52] designated the two conformations as p and a, respectively (see Fig. 8). The fold direction is determined by the orientation of the C–C–C plane. Thus the complex can be designated as Λ ppp according to his scheme. The skew-boat conformer is chiral and its conformation can be defined based on the IUPAC proposal (for example see [5] and [6]).

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