OPTICAL ACTIVITY AND MOLECULAR DISSYMMETRY IN COORDINATION CHEMISTRY

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ABSTRACT

Classical and quantum mechanical theories of optical activity are reviewed with particular reference to the coordination compounds of the transition metal ions. The limiting cases of 'the inherently dissymmetric chromophore' and of 'the symmetric chromophore in a chiral molecular environment' are exemplified respectively by a discussion of the non-empirical exciton treatment of the tris-2,2'-bipyridyl and tris-1,10-phenanthroline complexes of the iron-group metals, and of empirical regional rules relating the position of a substituent to the optical activity of amine complexes of cobalt(III) and analogous metal ions.

INTRODUCTION

THE general connection between optical activity and molecular stereochemistry was appreciated more than a century ago, in fact before the advent of any detailed theory of molecular structure, by Pasteur[1] who introduced the term 'dissymmetric' to describe all structures, whether molecular or macroscopic, producing optical rotation. According to Pasteur[1] a dissymmetric structure is not sterically superposable upon its mirror-image by translations and rotations alone, lacking an inversion centre, a reflection plane, or other secondary element of symmetry.

Features of the general relationship, notably, the helical model for molecular dissymmetry and optical activity, were foreshadowed even earlier. The rotation of the plane of linearly polarized light was discovered by Arago[2] for crystalline quartz and by Biot[3] for liquid natural products. Fresnel[4] attributed the optical rotation to the different refractive indices of the active medium for the left- and right-circularly polarized components of the plane-polarized light and, in order to account for the circular birefringence and for the existence of laevorotatory and dextrorotatory forms of an optically active substance, he postulated that the molecules of an active medium were helically arranged, in either a left- or a right-handed structure.

Fresnel's helical model[4] was taken up by Pasteur[1] and, more particularly, by Drude[5], who developed the first of the classical electromagnetic theories of optical activity. Drude postulated[5] that dissymmetric molecules have a stereochemical form which constrains the motions of sub-molecular charged particles (electrons) to a helical path. The electrons are set into forced

335

oscillation in a radiation field with a molecular resonance frequency, and left-circularly polarized light absorbed to the greater degree if the helical path is right-handed, whereas right-circularly polarized light is preferentially absorbed if the path is left-handed, corresponding to a positive and to a negative rotatory power, respectively. As the refraction and the absorption of light are interconnected, the rotatory power of a medium appears as circular birefringence in wavelength regions where the medium is transparent and is manifest as circular dichroism in the wavelength range where light is absorbed. The absorption counterpart of optical rotation, circular dichroism, was first observed in crystals of amethyst quartz by Haidinger[6] and in solutions of copper(II) and chromium(III) tartrate by Cotton[7].

QUANTUM THEORY OF OPTICAL ROTATION

The essentials of the classical helix model carry over into the quantum mechanical theory of optical rotation[8-12]. A charged particle displaced through a helical path undergoes a translatory motion, generating an electric dipole moment, and a rotatory motion, producing a magnetic dipole moment, and the two moments are collinear. In the quantum theory the absorption of light by a dissymmetric molecule promotes a valency electron from one stationary molecular energy state to another, and the reorganization of the electric charge distribution generates a transient electric and magnetic dipole moment. The scalar product of the electric dipole and magnetic dipole transition moment represents the rotational strength R_{n0} of the transition between the electronic states ψ_0 and ψ_n,

$$R_{n0} = Im\langle 0|\boldsymbol{\mu}|n\rangle \langle n|\mathbf{m}|0\rangle \tag{1}$$

where $\boldsymbol{\mu}$ and $\mathbf{m}$ are the electric and magnetic dipole operators, respectively, and Im signifies that the imaginary part of the product is to be taken. Experimentally the rotational strength R_{n0} is obtained from the band area of the circular dichroism absorption due to the transition $\psi_0 \rightarrow \psi_n$.

The detailed quantum theory of optical activity at present assumes one of three distinct forms, depending upon the particular electronic structure of the molecule and the type of electronic transition considered. In the one limiting case, that of molecules containing an inherently dissymmetric chromophore, such as the helicenes[13], each electronic excitation has an intrinsic electric and magnetic dipole transition moment. The calculation of the sign and the magnitude of the rotational strength (equation 1) of particular transitions for a given optical isomer is then straightforward[14], and the absolute stereochemical configuration of the isomer is obtained unambiguously from its circular dichroism spectrum if the electronic transitions are correctly identified.

The second limiting case is that of the symmetric chromophore in a dissymmetric molecular environment where the substituent groups are virtually inert spectroscopically, absorbing radiation only in the vacuum ultra-violet, e.g. alkyl-substituted carbonyl compounds[8, 9]. Here the electronic transitions of the chromophore, which has one or more secondary element

336

of symmetry, are generally either electric- or magnetic-dipole allowed, or the two moments, if concurrent, are orthogonal. No electronic transition of the molecule has a zero-order rotational strength, but the electric and magnetic dipole transitions of the chromophore are mixed by the static perturbing field, V, due to the dissymmetric substituents, and each composite transition acquires a first-order rotatory power.

If the symmetric chromophore has two main transitions from the ground state, ψ_0, one magnetic-dipole allowed to the state, ψ_a, and the other electric-dipole allowed to the state, ψ_b, the first-order rotational strengths are

$$R_{a0} = Im\langle a|\mathbf{m}|0\rangle \langle 0|\boldsymbol{\mu}|b\rangle \langle b|V|a\rangle/(E_b - E_a) \qquad (2)$$

and

$$R_{b0} = Im\langle a|\mathbf{m}|0\rangle \langle 0|\boldsymbol{\mu}|b\rangle \langle b|V|a\rangle/(E_a - E_b) \qquad (3)$$

where E_a and E_b are the respective transition energies.

These two rotational strengths are equal in magnitude and opposite in sign, and an equivalent sum rule applies in the general case where equation 2 is summed over all electric-dipole transitions of the chromophore and equation 3 over all magnetic-dipole transitions[15].

These two limiting approaches are bridged by the coupled-chromophore treatment, due classically to Kuhn[16] and developed quantum-mechanically by Kirkwood[17], in which an optically-active molecule is regarded as a dissymmetric ensemble of symmetric groups, each with its own characteristic electronic properties. The electronic motions of the individual chromophores are coupled by the Coulombic interaction between the instantaneous charge distributions, and the absorption of light results in a delocalized electronic excitation (exciton) embracing the molecule as a whole.

At one extreme of the exciton treatment the individual chromophores have allowed electric-dipole transitions which are close in energy or are degenerate, the groups being chemically similar or equivalent, and the coupling is then strong. When electron interchange between pairs of groups becomes appreciable, this extreme of the coupled-chromophore model merges with that of the inherently dissymmetric chromophore, as in the case of the sterically-hindered biaryls[18].

At the converse extreme the exciton treatment is applicable to the case of a symmetric chromophore in a dissymmetric molecular environment, such as alkyl-substituted ketones[19]. Here the static perturbing field of the substituents, due to the incompletely-screened nuclear charge of the substituents[8], is supplemented by a dynamic perturbing field arising from the high-energy transitions of the alkyl groups in the vacuum ultra-violet and measured by the polarizabilities of the groups[19].

All of the three detailed quantum mechanical models of optical activity are complementary, for they arise as separate terms of a general treatment of rotatory power based upon the interaction of symmetric groups in a dis-symmetric molecule[10]. To date the general and the detailed treatments of optical activity have been applied more extensively to organic molecules than to coordination compounds, although circular dichroism was first

observed in the visible absorption bands of transition metal complexes[7] and the rotary power of ligand-field excitations has long been of theoretical interest[20-28]. More recently the exciton treatment of optical activity has been extended to chelated metal complexes containing conjugated ligands, providing stereochemical and spectroscopic applications[28-31], and a general method has become available[15] for the formulation of regional rules relating stereochemical configuration to optical activity. In subsequent sections the exciton model for the ligand transitions of metal complexes and the regional rules for the optical activity of ligand-field transitions are discussed.

## THE EXCITON OPTICAL ACTIVITY OF COORDINATION COMPOUNDS

In a bis- or tris-chelated coordination compound containing unsaturated ligands a major source of optical activity is the Coulombic coupling of the allowed $\pi \rightarrow \pi^\star$ excitations in the individual ligands, each involving a linear charge displacement, to give an overall resultant helical charge displacement[28-31]. It is assumed in the simplest treatment, employing degenerate exciton theory, that there is no π-electron delocalization between the individual ligands, either through the coordinated atom or between nearest-neighbour atoms of different ligands, and that the main coupling arises from the instantaneous Coulombic interaction between the electric dipoles of the $\pi \rightarrow \pi^\star$ excitations with the same energy in the different ligands of the complex. Electron exchange between the ligands, and between the ligands and the coordinated atom, may be taken into account by perturbation methods[29] or by a variational treatment[31] of the interaction between the exciton configurations and charge-transfer configurations. However, these refinements do not alter the principal stereochemical and spectroscopic conclusions of the simple exciton treatment applied to the open-shell compounds studied to date, mainly, the 2,2'-bipyridyl and 1,10-phenanthroline complexes of the iron-group and other transition-metal ions[28-31], nor the extension of the treatment to heterochelated compounds, notably the mixed phenanthroline-bipyridyl complexes[29, 30], using non-degenerate exciton theory. For the optical activity of complexes containing a coordinated atom with a closed-shell electron configuration and unsaturated ligands the exciton approach provides an even less approximate treatment[29-31].

The coupled-chromophore theory of optical activity is significantly illustrated by the treatment of tris-phenanthroline metal complexes[28-31], as it has been shown recently[32] by the anomalous-scattering x-ray diffraction method that $(-)-[Fe(phen)_3]^{2+}$ has the absolute stereochemical configuration (I). In this isomer the three ligands have a left-handed (M, minus) screw stereochemistry around the metal ion, viewed along the three-fold rotation axis of the complex, C_3, and assume a right-handed aspect (P, plus), viewed along a twofold axis, C_2. The electronic transitions of the complex are polarized along these elements of rotational symmetry, and related excitations directed parallel and perpendicular to the principal axis have optical activities of opposite sign. The configurational helicity $M(C_3)$ of the isomer (I)

(I)
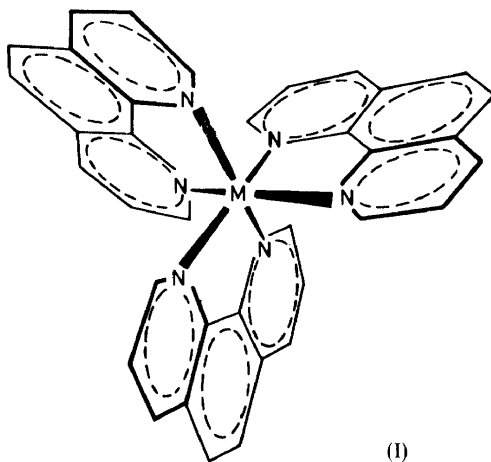
implies the complementary element of chirality $P(C_2)$, and this relationship provides a stereochemical basis for the opposed signs of the Cotton effects of related transitions with different symmetries and, by extension, for the sum rule. According to this rule, both classically[16] and quantum-mechanically[8], the rotational strengths of the various electronic transitions of an optical isomer sum to zero over the spectrum as a whole.

A restricted form of the sum rule emerges in a simple way from the exciton theory of optical activity. The allowed $\pi \to \pi^\star$ transitions of unsaturated molecules involve linear charge displacements in the molecular plane,

(II)
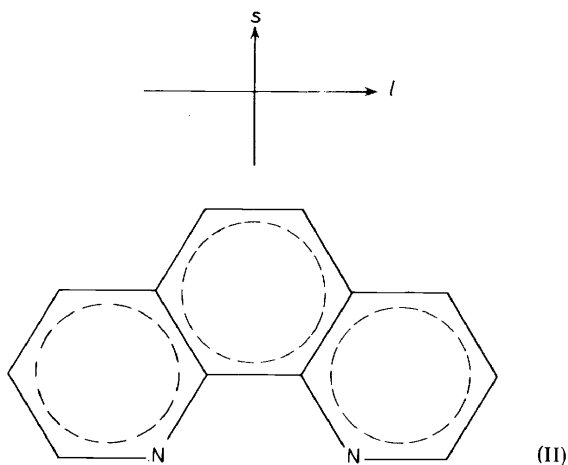
directed, in cases like that of 1,10-phenanthroline (II), either along the short (s) or long (l) in-plane molecular axis. In the corresponding tris-chelated complex (I) a particular ligand excitation gives rise to three coupling modes, two being degenerate. If the ligand excitation is long-axis polarized in the free ligand, the non-degenerate coupling-mode produces a helical charge

339

displacement along and around the threefold rotation axis, C_3, of the complex [*Figure 1*(a)]. For the $M(C_3)$ configuration of the complex ion (I) the helical charge displacement is left-handed [*Figure 1*(a)], producing a negative Cotton effect. The degenerate coupling mode resulting from a long-axis polarized ligand excitation gives rise to helical charge displacements along two mutually orthogonal directions in the plane perpendicular to the C_3 axis [*Figure 1*(b)]. For the $M(C_3)$ configuration of the complex ion (I) the doubly degenerate charge displacement is right-handed [*Figure 1*(b)] and produces a positive Cotton effect, equal in magnitude and opposed in sign to that given by the corresponding non-degenerate coupling mode [*Figure 1*(a)].

The geometrical arrangement of the octahedrally coordinated ligands requires that the instantaneous Coulombic interaction between the transition
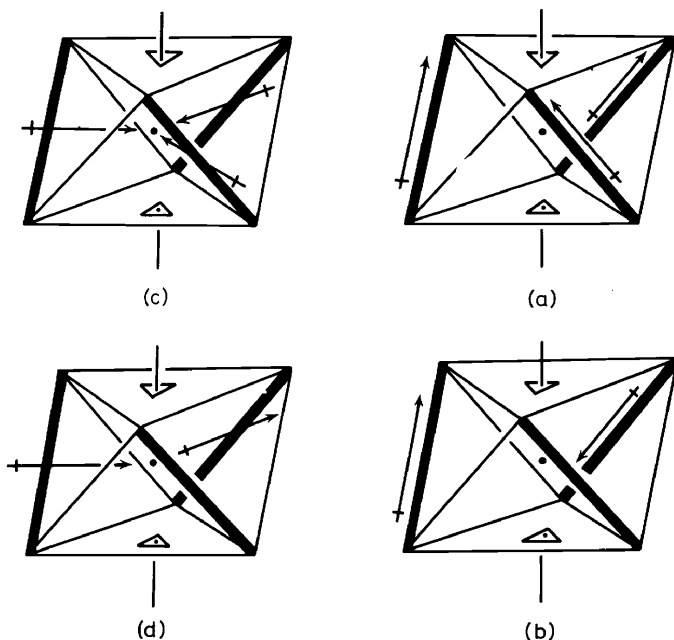

Figure 1. The interaction of long-axis polarized ligand excitations in a tris-chelated complex to give, (a) a non-degenerate coupling mode (A_2 symmetry) and (b) a doubly-degenerate coupling mode (E symmetry); and, for short-axis polarized ligand excitations, (c) the non-degenerate coupling mode (A_1 symmetry) and (d) the doubly-degenerate coupling mode (E symmetry). Only one component of each doubly-degenerate mode is depicted.

charge densities of the long-axis polarized ligand excitations is repulsive in the non-degenerate coupling mode [*Figure 1*(a)] but attractive in the doubly-degenerate mode [*Figure 1*(b)]. Accordingly a tris-chelated complex with the $M(C_3)$ configuration (I) is expected to give, in the wavelength region of the absorption due to an electronic transition which is long-axis polarized in the free ligand (II), a major positive CD band at the lower frequency and a negative CD band with an equal area at the higher frequency.

340

If the $\pi \rightarrow \pi^\star$ excitation of the free ligand (II) is short-axis polarized neither the non-degenerate [*Figure 1*(c)] nor the doubly-degenerate coupling mode [*Figure 1*(d)] of the three excitations in the tris-chelated complex (I) is optically active according to the degenerate exciton treatment, as the excitation dipoles are coplanar in both coupling modes. Even if the de-localization of π-electrons from one ligand to another and to the coordinated metal ion is neglected, however, it is found that the short-axis polarized excitations of one ligand interact Coulombically with the long-axis directed transitions of the other, mixing the two types. In particular, the doubly-degenerate coupling modes [*Figures 1*(b) and *1*(d)] mix on symmetry grounds, both transforming under the E representation of the group D_3 to which the complex (I) belongs, whereas the non-degenerate modes [*Figures 1*(a) and *1*(c)] mix neither with each other nor with the degenerate modes, as they are spanned by the A_2 and the A_1 representation, respectively. Accordingly the complex (I) is expected to show a weak second-order circular dichroism in the wavelength region of the absorption due to an electronic transition which is short-axis polarized in the free ligand (II).

These expectations are in good accord with the observed absorption and circular dichroism spectra of $(-)$-$[Fe(phen)_3]^{2+}$ (*Figure 2*) and other tris-phenanthroline and tris-bipyridyl complexes of transition metal ions[28–31]. The presence of a strong band in the visible region of the absorption spectrum of $[Fe(phen)_3]^{2+}$, responsible for the red colour of the complex, shows that

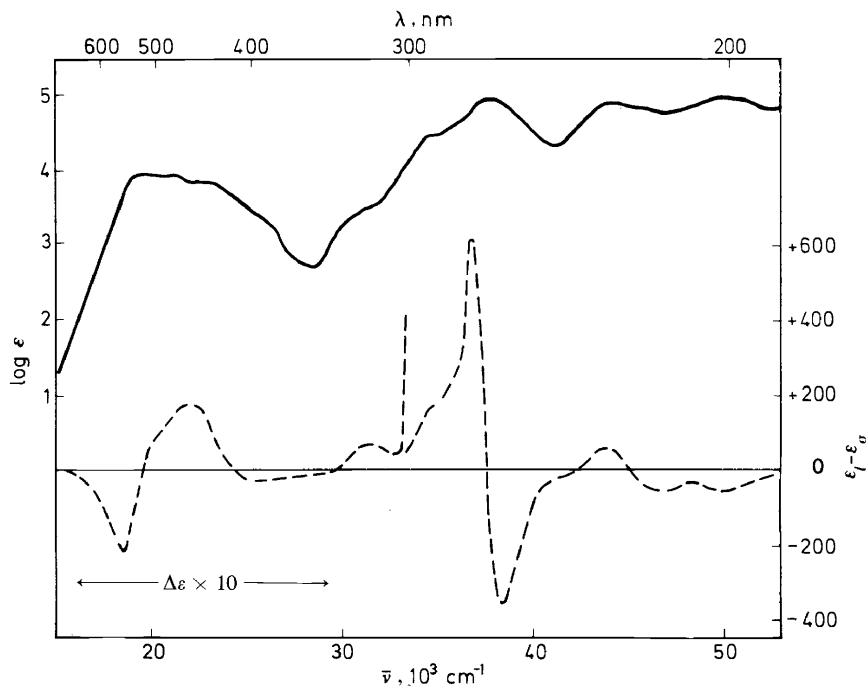*Figure 2.* The absorption spectrum (———) and the circular dichroism (‑‑‑‑‑) of $(-)$-$[Fephen_3]$ $(ClO_4)_2$ in aqueous solution.

the transfer of charge between the metal ion and the ligands is significant. In the ultra-violet region, however, the absorption of the complex corresponds approximately to that of the three ligands, suggesting that charge-transfer and other electronic effects do not greatly affect the ligand transition.

The circular dichroism of $(-)$-$[Fe(phen)_3]^{2+}$ in the ultra-violet region consists (*Figure 2*) of two major CD bands with opposed signs and approximately equal area in the region of the $37\,000$ cm^{-1} absorption band and substantially weaker dichroism bands at higher frequencies. These observations indicate that the $37\,000$ cm^{-1} band of phenanthroline (II) is predominantly long-axis polarized whereas the $44\,000$ and $50\,000$ cm^{-1} bands are largely short-axis polarized. The two major CD bands have the signs and relative frequencies expected for the $M(C_3)$ configuration (I) of $(-)$-$[Fe(phen)_3]^{2+}$ (*Figure 2*), a negative band at the higher frequency, due to the long-axis non-degenerate mode [*Figure 1*(a)], and a positive band at the lower frequency, arising from the long-axis doubly-degenerate mode [*Figure 1*(b)].

The sign of the energy interval between the long-axis non-degenerate and doubly-degenerate coupling modes is of crucial importance in assigning the absolute configuration of a tris-chelated complex using the exciton theory, as the two major CD bands associated with a given absorption band are reliably identified by their relative frequencies. The energy interval due to the instantaneous Coulombic interactions between the transitional charge distributions in the different ligands of a complex ion, the exciton splitting, is positive $(+2000$ to $+3000$ cm$^{-1})$, the non-degenerate mode [*Figure 1*(a)] having the higher energy, but this interval is reduced by charge-transfer π-bonding between the metal ion and the ligands, and may be diminished further by inter-ligand π-bonding[29]. However, these effects are of minor importance, even in the case of $[Ru(phen]_3]^{2+}$ where charge-transfer is the most significant[29], and they are counterbalanced by configurational interaction between the long- and short-axis doubly degenerate coupling modes [*Figure 1*(b) and *1*(d)] which shifts the former, giving the major positive CD band of $(-)$-$[Fe(phen)_3]^{2+}$ at $36\,800$ cm^{-1} (*Figure 2*), to lower energies.

The exciton treatment of optical activity and stereochemistry appears to be reliable for the complexes of transition metal ions with neutral conjugated ligands, notably, the α-diimines[29], and for complexes containing anionic ligands and coordinated atoms with a closed shell electron configuration, such as the tris(acetylacetonato)-silicon(IV) ion[33]. However, the absorption and circular dichroism spectra of the complexes of transition metal ions with anionic ligands, such as oxalate or hydroxymethylene camphorate, lack the characteristic exciton form, owing to the probable greater importance of metal–ligand charge-transfer π-bonding. For these cases the metal complex as a whole requires the treatment appropriate to an inherently dissymmetric chromophore.

REGIONAL RULES RELATING CONFIGURATION TO OPTICAL ACTIVITY IN COORDINATION COMPOUNDS

Optically-active complexes composed of a transition metal ion coordinated to σ-bonding ligands, such as the diamine metal complexes, approximate

closely to the case of a symmetric chromophore in a dissymmetric molecular environment. The effect of alkyl substituents upon the isotropic light-absorption properties of the hexammine metal complexes is quite minor, for the electronic transitions of the alkanes lie at particularly high energies and the degree to which they couple with the ligand–field transitions of the metal ion must be small. The optical activity induced by alkyl substitution of the metal ammines is, however, relatively large and it is sensitive to the particular pattern of substitution. A general treatment of the symmetric chromophore in a dissymmetric environment[15] indicates that the induced rotatory power may be related to the substitution pattern by means of the symmetry properties of the unperturbed chromophore, independently of the detailed physical mechanism of the connection. On this basis general regional rules may be derived for correlating stereochemical configuration with the sign of the Cotton effect associated with a given electronic transition in a series of related molecules[15], on the assumption that a common principal dissymmetric perturbation prevails throughout the series[19].

The optically-active ammine complexes of cobalt(III) provide a particularly comprehensive series of coordination compounds in which a symmetric chromophore is located in a dissymmetric alkyl environment. The absolute configurations of a wide range of optically-stable cobalt(III) complexes have been determined by the anomalous-scattering x-ray diffraction method[34–42], and the optical properties of these complexes have been extensively investigated both in solution, and as single crystals[43–49].

(III)
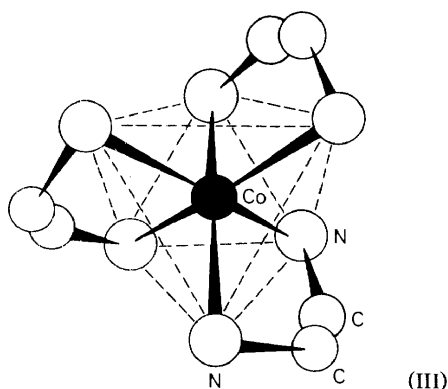
The tris(ethylenediamine)cobalt(III) complex ion, (+)-$[Coen_3]^{3+}$ was early shown[34] to have the M(C_3) configuration (III), or the Λ configuration, following the recent tentative IUPAC convention[50]. According to this convention the octahedral edges of a polydentate complex spanned by two chelate rings without a common vertex define two skew lines which constitute a segment of a helix. The chirality of the segment is given unambiguously as Λ (left-handed) or Δ (right-handed) by the relations between the two octahedral edges considered and their unique common normal, taking either edge as the helix axis. In the case of a polychelated complex all pairs of chelate rings without a common vertex are taken into account, and the overall

configuration of the complex is Δ if the number of right-handed pairs exceeds the number of left-handed pairs, and vice-versa[50]. For $(+)$-$[Coen_3]^{3+}$ (III) all of the three ring-pairs have a mutual Λ relationship.
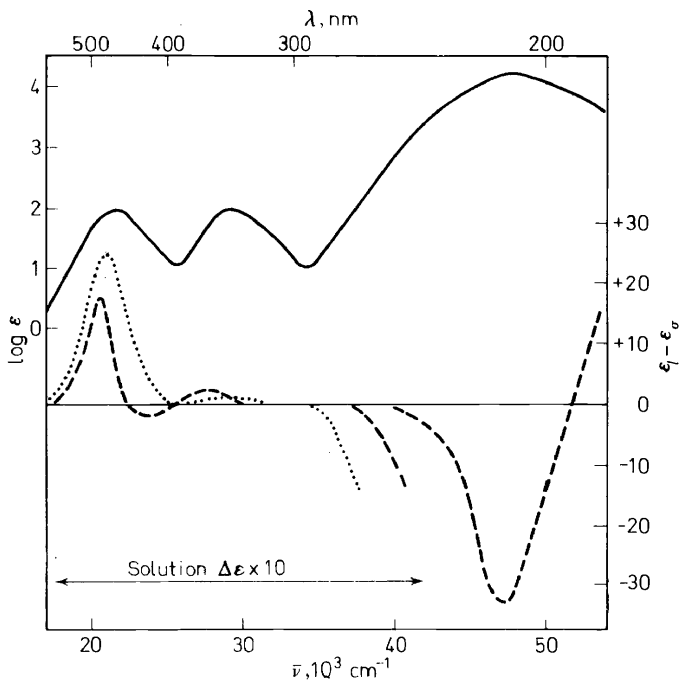

Figure 3. The absorption spectrum (———) and the circular dichroism (— — —) of $(+)$-$[Coen_3]$ $(ClO_4)_3$ in aqueous solution, and the circular dichroism (dotted) of a single crystal with light propagated along the optic axis of $2[(+)$-$Coen_3Cl_3]$. $NaCl.6H_2O$.

The absorption spectra of the hexammine complexes of cobalt(III), containing the octahedral CoN_6 chromophore, 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 (*Figure 3*). From its intensity the charge-transfer band is electric-dipole allowed, whilst the visible, but not the ultra-violet, ligand–field band arises from a magnetic-dipole allowed $d \rightarrow d$ transition[20]. Thus the lower frequency ligand–field band of $(+)$-$[Coen_3]^{3+}$ is substantially more optically active than that at higher frequency, both in solution and in a single crystal (*Figure 3*).

In solution the optical activity associated with the visible absorption band consists of a major positive and a minor negative CD band which are ascribed, respectively, to the E and the A_2 component into which the triply-degenerate T_{1g} octahedral transition is broken down in a trigonal (D_3) environment. The non-degenerate A_2 and doubly-degenerate E component are polarized respectively parallel and perpendicular to the threefold rotation symmetry axis of the complex ion (III), and in a tetragonal[43] or hexagonal[46, 49] halide crystal, where the C_3 axis of each complex ion is oriented parallel to

344

the optic axis of the crystal[34], the optical activity of the E component, and of other transitions with the same symmetry, may be measured separately.

The crystal measurements show that the intrinsic rotational strength of the E component of the octahedral T_{1g} $d \rightarrow d$ transition in $(+)$-$[Coen_3]^{3+}$ is positive and substantially larger than that of the solution CD (*Figure 3*). 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 per cent when the complex ion is randomly oriented in solution. In fact the band origins of the A_2 and E components
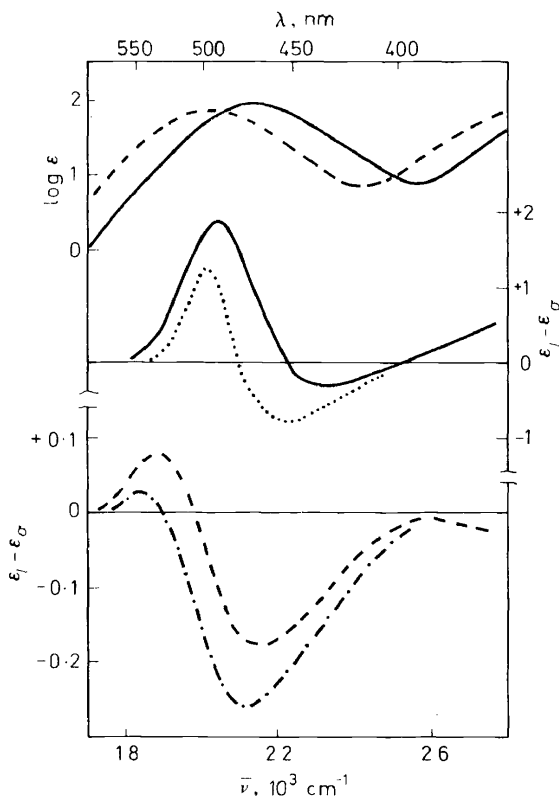

Figure 4. Top curves; the absorption spectra (———) of $[Coen_3](ClO_4)_3$ and (– – – –) of $[Cotn_3](ClO_4)_3$ in water. Middle curves; the circular dichroism (full) of $(+)$-$[Coen_3](ClO_4)_3$ in water, and (· · · · · ·) with the addition of 0·01M selenite. Bottom curves; the circular dichroism of $(-)$-$[Cotn_3](ClO_4)_3$ (– – – –) in water, and (–·–·–·–) with the addition of 0·01M selenite.

coincide in frequency[48], and the appearance of separate CD bands in the solution spectrum arises from the differing distribution of rotational strength over the A_2 and E vibronic progressions.

In these circumstances where the observed solution CD is residual, being the resultant of two large and oppositely-signed rotational strengths close in frequency, the correlation of stereochemistry with optical activity requires

345

some circumspection, for a minor change in the intrinsic rotational strengths may produce a major change in the optical activity observed in solution. It has been suggested[51], for example, that tris-chelated metal complexes giving a predominantly positive circular dichroism in the region of the lower frequency ligand-field band have the same configuration as $(+)$-$[Coen_3]^{3+}$. However, the $(-)$-tris(trimethylenediamine)cobalt(III) complex ion, which has the same $M(C_3)$ or Λ configuration[34] (IV) as $(+)$-$[Coen_3]^{3+}$ (III),

(IV)
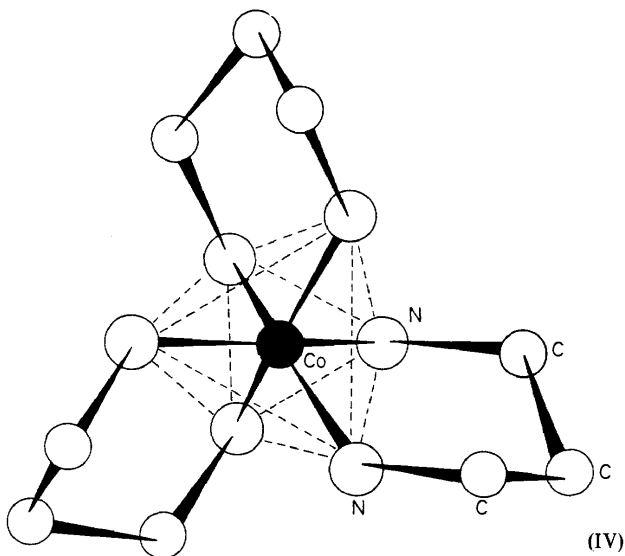
exhibits a predominantly negative circular dichroism in the region of the octahedral T_{1g} transition (*Figure 4*). Like $(+)$-$[Coen_3]^{3+}$, the complex ion $(-)$-$[Cotn_3]^{3+}$ exhibits a positive and a negative CD band at lower and higher frequency, respectively, the areas of these bands being diminished and enhanced, respectively, in the presence of polarizable anions, such as phosphate or selenite[52-54] (*Figure 4*). The gegen-ion effects suggest that the visible CD bands of the two complexes (III) and (IV) are related, the higher-frequency negative band and the lower-frequency positive band arising from the A_2 and the E component of the octahedral T_{1g} transition respectively.

The observed optical activity of the tris-diamine cobalt(III) complexes (III) and (IV) show (*Figure 4*) that stereochemical configuration correlates with the sign of the circular dichroism of a particular trigonal electronic transition[55], the A_2 or the E component, but not with the overall Cotton effect of the two trigonal components with octahedral T_{1g} parentage. The correlation of the absolute configuration of hexacoordinated complexes with their optical activity accordingly requires general methods for characterizing the electronic transitions giving the Cotton effects which are to be compared.

Hitherto, five general procedures have been employed. First, the axial circular dichroism spectrum of a coordination compound in a uniaxial crystal gives unambiguously the sign and the magnitude of the rotational strengths of electronic transitions polarized perpendicularly to the optic

axis. This method is suitable only for complexes forming trigonal, tetragonal or hexagonal crystals, notably the trigonal dihedral tris-chelated complexes[55]. The second and third methods depend upon measurements of the plane-polarized spectra of single crystals, which need not necessarily be uniaxial. Where the energy-splitting between the components descended from the octahedral T_{1g} transition is appreciable, the measurements give directly the frequencies of the components, as in the case of the trisoxalates and trisacetyl-acetonates of cobalt(III) and other metal ions[56]. If the splitting is small or zero, as in the case[47] of $(+)$-$[Coen_3]^{3+}$, the value of the polarization intensity ratio, $I(A_2)/I(E)$, is informative. The ratio is expected to be two if the restricted sum rule[21] holds, namely, $R(A_2) = -R(E)$, and if the ratio is less than two, as is frequently found[56], the major of the two circular dichroism bands may be attributed to the E component of the octahedral T_{1g} transition[55].

The fourth method, based upon the changes in the circular dichroism spectrum produced by outer-sphere coordination (*Figure 4*), is confined largely to chelated hexamine complexes, where the effect is large[52–54]. For
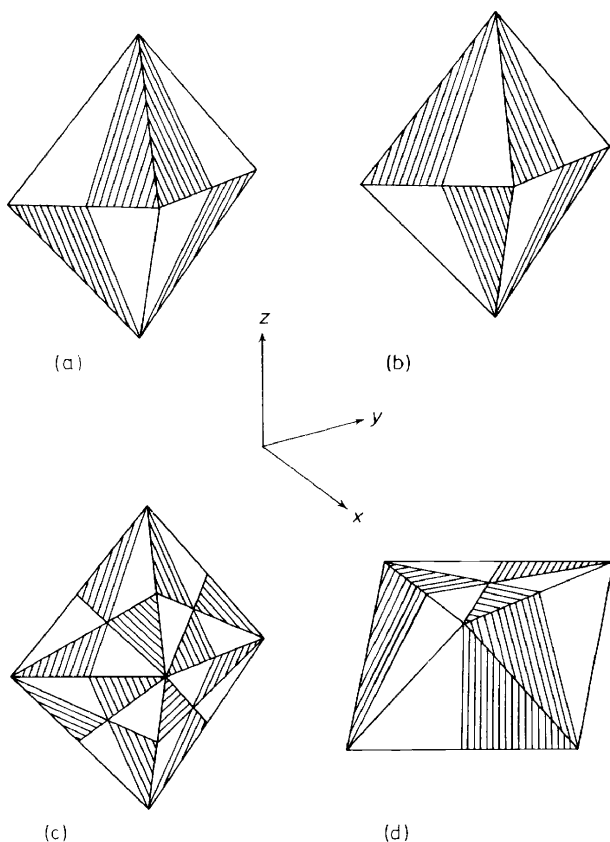

Figure 5. Regional rules relating the position of substitution to optical activity; (a) the octant sign rule, (b) the tetragonal pseudo-scalar potential, (c) the octahedral pseudo-scalar potential, and (d) the trigonal pseudo-scalar potential.

chelated monoacido-pentammine and diacido-tetrammine complexes the gegen-ion effect is minor[57], but in these cases the energy-splitting of the component of the octahedral T_{1g} transition is generally appreciable, and the components may be identified by a fifth method[57], based upon the known position of the ligands in the spectrochemical series[58].

Following the formulation of the successful octant rule for dissymmetric ketones[59], a number of regional rules relating the molecular structure of coordination compounds to their optical activity have been proposed[60-64]. In the most general of these rules, the octant sign rule[61], covering the main symmetry types of cobalt(III) and other metal complexes, 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 the sign of 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. Conventionally, the chelate ring of a monochelate complex, or the reference chelate ring of a bis- or poly-chelated complex, span the region between the $+ x$ and $+ y$ axes[61]. In the version of the octant sign rule depicted [*Figure 5*(a)], a substituent placed in a shaded region induces a positive Cotton effect, or in an unshaded region a negative effect, for the E component of the octahedral T_{1g} transition in trigonal complexes belonging to the C_3 or D_3 point groups, and for the A_2 or A_{2g} component in tetragonal complexes containing the C_{4v} chromophore, CoN_5L, or the D_{4h} chromophore, *trans*-CoN_4L_2, respectively. For complexes of lower symmetry, such as those containing the orthorhombic C_{2v} chromophore, *cis*-CoN_4L_2, parentage arguments are adopted, linking the T_{1g} components to those of a related trigonal complex[57], or it is assumed that the sign of the major circular dichroism band associated with the octahedral T_{1g} absorption correlates with the octant sign of the coordinate function, $z(x^2 - y^2)$, summed for each substituent[61].

Hitherto the octant sign rule has been generally successful in correlating the stereochemistry with the optical activity of cobalt(III) coordination compounds, but recent x-ray structure determinations[39, 40], together with studies of the circular dichroism of complexes containing stereospecific chelate ligands[65, 66], show that a more complex regional rule, at the minimum a double octant[63, 64] [*Figure 5*(b)], is required for dissymmetric tetragonal complexes. X-ray diffraction studies show that the $(-)_D$-*trans,trans*-dichloro-bis(N-methylethylenediamine)cobalt(III) ion[40], $[Co(Meen)_2Cl_2]^+$, and the $(+)_{546}$-*trans*-dichloro-bis-(d-propylenediamine)cobalt(III) ion[67], $[Co(+ pn_2)Cl_2]^+$, have the same absolute configuration, (V) and (VI), respectively, yet their circular dichroism spectra are virtually enantiomorphous in the region of the octahedral cobalt(III) T_{1g} absorption[64, 68] (*Figure 6*). Further the circular dichroism[66] of the *trans*-dichloro-bis(N_1-methyl-d-propylenediamine)cobalt(III) ion, which on conformational grounds[69] has the absolute stereochemistry (VII), is also enantiomorphous with that of the parent complex (VI) (*Figure 6*).

These observations indicate that the dissymmetric perturbation arising from the N-methyl groups of the chelate ligands in a *trans*-bisdiamine cobalt(III) complex has an opposite sign to that due to the CH_2 or $CHCH_3$ groups of the diamine chain, and that the dissymmetric potential deriving
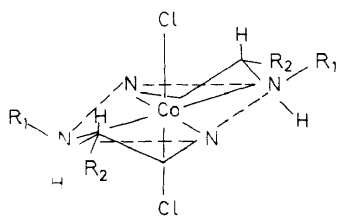
FB (V) R_1 = Me , R_2 = H
FB (VI) R_1 = H , R_2 = Me
FB (VII) R_1 = R_2 = Me

from the alkyl substituents which lower the tetragonal (D_{4h}) symmetry of the *trans*-CoN_4Cl_2 chromophore in the complexes, (V), (VI) and (VII), is nodal in each of the three planes containing four metal–ligand bonds

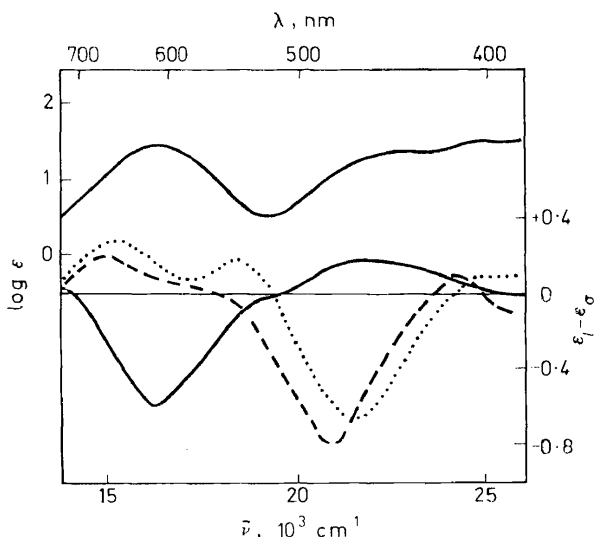*Figure 6.* The absorption spectrum (upper curve) and circular dichroism (lower curve) of *trans*-[Co(+pn)$_2$Cl$_2$]Cl (VI) (———), and the circular dichroism (-----) of *trans*-[Co(N$_1$-Me(+)pn)$_2$Cl$_2$]Cl (VII) and (········) of (−)-*trans,trans*-[Co(Meen)$_2$Cl$_2$]Cl (V) in water.

[*Figure 5*(b)]. In order to accommodate these results the coordinate function, $z(x^2 - y^2)$, of the octant sign rule [*Figure 5*(a)], must be augmented to the function, $xyz(x^2 - y^2)$. The form of the latter function depicted [*Figure 5*(b)] gives the sign of the Cotton effect associated with the $A_{2g}(D_{4h})$ component of the octahedral T_{1g} absorption as positive for alkyl substitution in a shaded region or negative for substitution in an unshaded region. In the case of the *trans*-CoN_4L_2 chromophore the A_{2g} tetragonal component, due to the $d(xy) \rightarrow d(x^2 - y^2)$ transition when the ligands, L, are oriented along the z axis, lies close to the frequency of the triply-degenerate T_{1g} transition of the octahedral CoM_6 chromophore (21 500 cm^{-1}).

349

Whilst the octant sign rule[61] [*Figure 5*(a)] is essentially empirical, the double octant of hexadecadal rule[63, 64] [*Figure 5*(b)] is founded upon the general symmetry aspects of the theory of the symmetric chromophore in a dissymmetric molecular environment[15]. The crystal and solution circular dichroism spectrum of (+)-[Coen$_3$]$^{3+}$ shows, for example, that the intrinsic rotational strength of the E component of the octahedral T_{1g} transition is approximately equal in magnitude but opposite in sign to that of the accessible charge-transfer circular dichroism band, which is also of E symmetry[46] [*Figure 3*]. Thus the magnetic-dipole allowed $d \rightarrow d$ transition and the electric-dipole allowed charge-transfer transition with E symmetry mix to give equal and opposite rotational strengths (equations 2 and 3), and although other electric-dipole transitions may mix also their contribution is likely to be smaller owing to the larger energy-denominators involved (equations 2 and 3).

The mixing is mediated by the potential, V (equations 2 and 3), due possibly to the static field of the incompletely-screened nuclear charges[8] of the atoms in the chelate rings, or to the dynamic field depending upon the polarizabilities[19] of the methylene groups in the chelate rings, or to other mechanisms[12]. Whatever the particular physical basis, however, the potential, V, must have the appropriate symmetry properties in the point group of the unperturbed symmetric chromophore if the optical activity of the chromophore perturbed by substitution is to be non-zero[15].

The rotational strength of an electronic transition, representing the scalar product of a polar vector, the electric moment, with an axial vector, the magnetic moment (equation 1), is a pseudo-scalar property, changing sign under inversion, reflection, or any other secondary symmetry operation. If the rotational strength of a transition is non-zero, it is totally-symmetric with respect to all symmetry operations of the point group to which the molecule belongs, by Neumann's principle[70], so that an optically-active molecule must be devoid of all secondary elements of symmetry. If the principal chromophore of a dissymmetric molecule contains secondary symmetry elements the zero-order rotational strengths (equation 1) vanish, but the first-order rotational strengths (equations 2 and 3) may be non-zero if the perturbation potential, V, due to the substituent groups around the chromophore, transforms, or contains a component which transforms, like a pseudo-scalar property in the point group to which the symmetric chromophore belongs[15].

For a given point group there is an infinite number of potential functions which transform under the pseudo-scalar representation of that group, but only the simpler functions are significant for the regional substitution rules governing optical activity. The simplest pseudo-scalar potential function of a group may be derived by transforming all the symmetry planes into nodal planes where the potential changes sign, e.g. the simplest pseudo-scalar potential for the tetragonal group D_{4h} is as depicted [*Figure 5*(b)] for the double octant rule, and is represented by the potential function, $xyz(x^2 - y^2)$. The functional forms of the simplest pseudo-scalar potential have been listed[15] for the majority of the common point groups.

Whilst the double octant rule [*Figure 5*(b)] for relating the stereochemistry of tetragonal complexes to their optical activity satisfies Schellman's pseudo-

scalar potential criterion[15], it does not necessarily represent the significant dissymmetric field obtaining in optically-active tetragonal and other complexes. The alkyl substituents of the *trans*-bisdiamine complexes, (V), (VI) and (VII), are located near to the equatorial xy plane, and they give little information regarding the form of the dissymmetric potential due to substituents near to the xz or yz plane.

Two levels of chromophoric symmetry prevail in the complexes, (V), (VI) and (VII), the approximate octahedral symmetry of the parent CoN_6 group and the actual tetragonal symmetry of the *trans*-CoN_4Cl_2 group. The simplest pseudo-scalar potential for the octahedron [*Figure* 5(c)] with the functional form[15], $xyz(x^2 - y^2)(y^2 - z^2)(z^2 - x^2)$, is pseudo-scalar also in the tetragonal group, D_{4h}, and has a similar dependence upon the coordinates of the substituents in regions close to the xy plane.

$R_1 = Me$, $R_2 = H$ (VIII)
$R_1 = H$, $R_2 = Me$ (IX)
$R_1 = R_2 = Me$ (X)
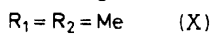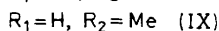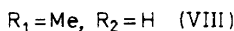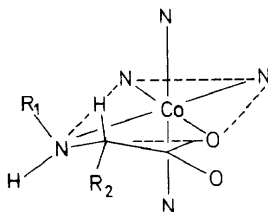
In principle, the significant dissymmetric field in optically-active tetragonal complexes may have the form of either the tetragonal [*Figure* 5(b)] or the octahedral [*Figure* 5(c)] pseudo-scalar potential, but the properties of a further series of tetragonal complexes, the tetrammine (aminoacid)cobalt(III) ions. (VIII), (IX) and (X), support the latter alternative. The absolute configuration of $(-)_D$-$[Co(NH_3)_4sarc]^{2+}$ is established as (VIII) from an x-ray diffraction study of the enantiomer[39], whilst the configurations of $[Co(NH_3)_4(L-ala)]^{2+}$ and the corresponding complex obtained from N-methyl-L-alanine[65] are (IX) and (X), respectively, on conformational grounds[69] and from extensive investigations of the structures of the amino acid complexes with metal ions by x-ray diffraction methods[71].

The circular dichroism spectra of the complex ions, (VIII)[39], (IX)[65] and (X)[65] show again (*Figure* 7) than an N-methyl group induces a Cotton effect in the tetragonal A_2 component of the octahedral T_{1g} transition, near 21 500 cm^{-1}, with a sign opposite to that generated by the atoms of the chelate ring, including the C-methyl group of the L-alanine complexes. In the C_{4v} chromophore, CoN_5O, of the complex ions, (VIII), (IX) and (X), the amino acid chelate ring lies in the xz (or yz) plane, the orientation of the z axis being determined by the Co—O bond direction. A consideration of the double-octant regional rule, based on the tetragonal pseudo-scalar potential [*Figure* 5(b)], shows that both the N-methyl and the C-methyl groups of the complex
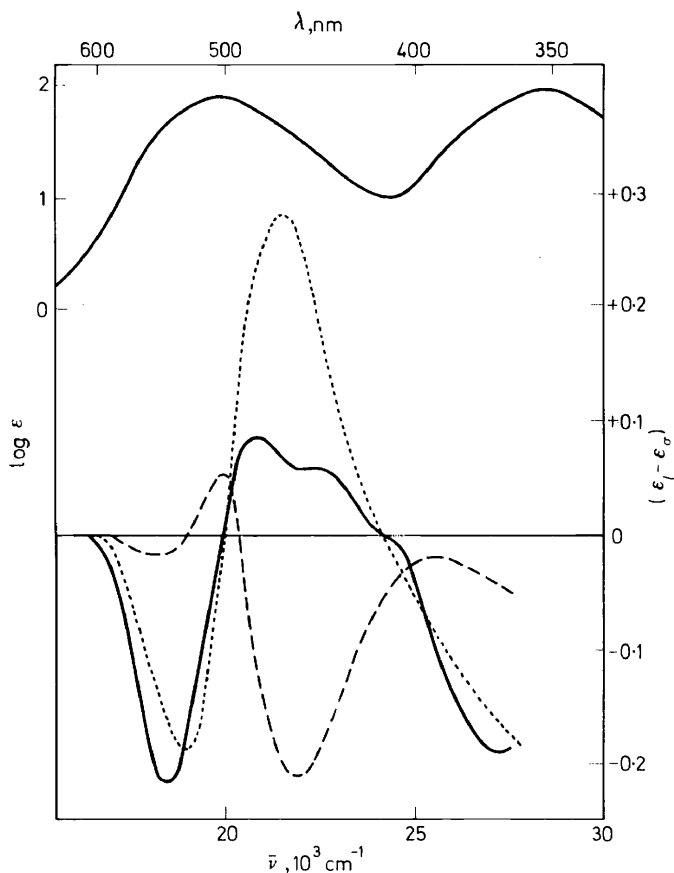
351

Figure 7. The absorption spectrum (upper curve) and circular dichroism (lower curve) (———) of $[Co(NH_3)_4(N\text{-Me-L-ala})]^{2+}$ (X) and the circular dichroism (–––––) of $[Co(NH_3)_4(L\text{-ala})]^{2+}$ (IX) and (········) of $(-)\text{-}[Co(NH_3)_4(sarc)]^{2+}$ (VIII) in water.
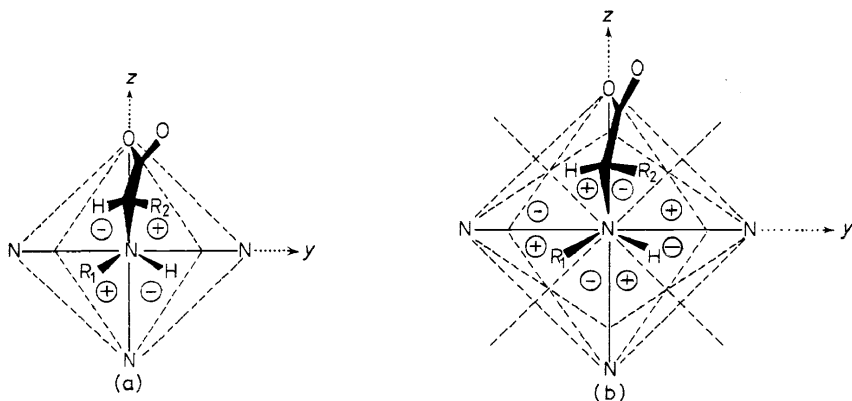

Figure 8. The projection of the molecular model of the complex ions, (VIII), (IX) and (X), (a) upon the *yz*-planar section of the tetragonal pseudo-scalar potential and (b) upon the corresponding section of the octahedral pseudo-scalar potential.

352

ions, (VIII), (IX) and (X), are expected to induce a positive circular dichroism in the region of the A_2 tetragonal component of the octahedral T_{1g} transition [*Figure 8*(a)], contrary to the observed result (*Figure 7*).

However, the octahedral pseudo-scalar potential [*Figure 5*(c)] provides a more general regional rule, which accommodates the observation (*Figure 7*) that, in the series of complex ions, (VIII), (IX) and (X), the N-methyl group induces a positive Cotton effect and the C-methyl group a negative effect [*Figure 8*(b)] associated with the A_2 (C_{4v}) component of the T_{1g} (O_h) transition near 21 500 cm^{-1}. The series of *trans*-bisdiamine complex ions, (V), (VI) and (VII) is also covered by the octahedral pseudo-scalar rule [*Figure 5*(c)], since the latter has the same sign alteration as the double octant rule [*Figure 5*(b)] in regions close to the xy plane. Accordingly it is concluded that the effective dissymmetric field inducing optical activity in the lowest energy ligand-field band of mono-chelate, *trans*-bis-chelate, and poly-chelate metal complexes in which the rings have a common average plane, has the form of the octahedral pseudo-scalar potential [*Figure 5*(c)].

Such a potential is not adequate, however, to account for the optical activity of metal complexes in which the chelate rings do not possess a common mean plane. Complexes containing planar chelate rings, such as the tris-oxalates, are strongly optically-active, but all of the atoms in such complexes lie in the nodal planes of the octahedral potential [*Figure 5*(c)]. Thus a dissymmetric field of a different type must obtain in metal complexes containing chelate rings without a common vertex or a common mean plane.

The tetragonal pseudo-scalar potential [*Figure 5*(b)] is obtained from the corresponding octahedral potential [*Figure 5*(c)] by removing the threefold rotational elements of symmetry of the octahedron. An alternative simplification of the octahedral potential is achieved by suppressing the fourfold rotational elements of symmetry of the octahedron to produce a trigonal potential [*Figure 5*(d)]. The trigonal potential has the functional form, $y(3x^2-y^2)$ where the z direction lies along the trigonal axis, and it represents[15] the simplest pseudo-scalar function for the group C_{3v}.

In the groups C_3 and D_3, to which tris-chelated metal complexes belong, pseudo-scalar properties are themselves totally-symmetric and the simplest pseudo-scalar potential is spherically symmetrical. However, the effective dissymmetric field in the tetragonal complexes, (V) to (X), does not correspond to the simplest tetragonal pseudo-scalar potential [*Figure 5*(b)], but to the more complex octahedral form [*Figure 5*(c)]. In the same way it appears that the effective dissymmetric field in metal complexes containing chelate rings without a common vertex or a common mean plane is more complex than totally-symmetric, being represented by the trigonal potential [*Figure 5*(d)]. For the trigonal potential depicted [*Figure 5*(d)], a substituent located in a shaded region induces a positive Cotton effect, or in an unshaded region a negative effect, in the $E(D_3)$ component of the T_{1g} (O_h) transition, or in components related by parentage considerations to the trigonal E transition for complexes of lower than trigonal symmetry.

The form of the trigonal potential indicates [*Figure 5*(d)] that the ligand atoms directly bonded to the metal ion lie in a nodal plane and do not contribute to the dissymmetric field if the coordination is perfectly octahedral with ligand–metal–ligand bond angles of 90°. If the L–M–L bond angle

within a chelate ring is less than 90° the ligand atoms are disposed in the same spatial sextant, and contribute an additional potential of the same sign as the chelate chain atoms of that ring [*Figure 5*(d)]. On the other hand, if the L–M–L bond angle within a chelate ring is greater than 90° the ligand atoms cross the nodal planes and are constrained to lie in the sextants immediately adjacent to that containing the chain atoms of the chelate ring, and they contribute a potential of opposite sign to that produced by the chelate ring atoms. Accordingly the overall dissymmetric field is expected to be smaller in the latter than in the former case.

The x-ray diffraction studies of Saito and his co-workers[34] show that the N—Co—N bond angle within a chelate ring has an average value of 85·5° for (+)-$[Coen_3]^{3+}$ (III) and of 94·5° for (−)-$[Cotn_3]^{3+}$ (IV). Thus the circular dichroism of (+)-$[Coen_3]^{3+}$ (III) in the region of the octahedral T_{1g} absorption is found to be virtually an order of magnitude larger than that of (−)-$[Cotn_3]^{3+}$ (IV) (*Figure 4*).

In metal complexes containing puckered chelate rings without a common vertex or a common mean plane the octahedral [*Figure 5*(c)] and the trigonal potential [*Figure 5*(d)] appear to make additive contributions to the total dissymmetric field, as expected for first order perturbations. From studies of the circular dichroism of chelated metal complexes containing optically-active ligands a distinction has been drawn between the configurational effect of the ligands on the one hand, and their vicinal or conformational effect on the other[72–74]. The configurational optical activity of a chelated metal complex is that which would be produced by analogous planar chelate rings, or rings in which conformational lability averages the positions of the chelate ring atoms to the plane of the terminal metal–ligand bonds. The conformational or vicinal optical activity is that due to the preferred conformation of the chelate ring atoms above or below the plane of the terminal metal–ligand bonds, or to an asymmetric centre in the chelate ring chain, and it is the sole source of optical activity in mono-chelate complexes, such as (VIII) to (X), or *trans*-bis-chelated complexes, such as (V) to (VII).

(XI)
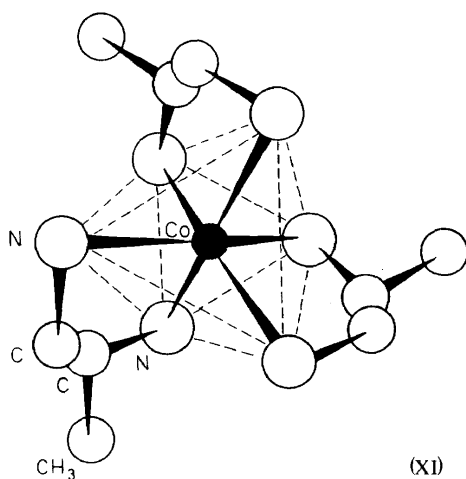
In a conformational analysis of five-membered diamine chelate rings Corey and Bailar showed[69] that d-propylenediamine forms the more stable tris-complex, $(+)$-$[Co(+pn)_3]^{3+}$, with the lel conformation (XI), in which the carbon–carbon bond of each chelate ring is parallel to the threefold

(XII)
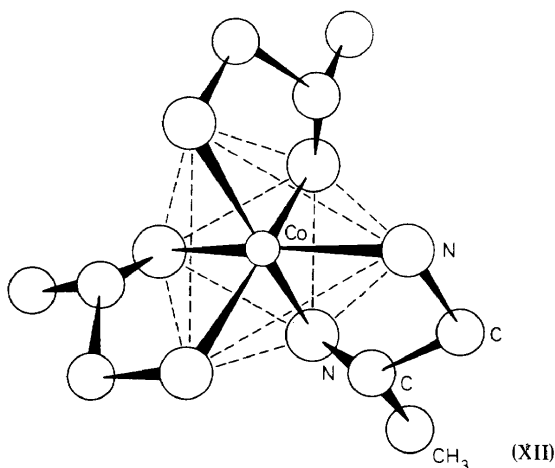
rotation axis of the complex, and the less stable tris-complex, $(-)$-$[Co(+pn)_3]^{3+}$, with the ob conformation (XII), in which the ring carbon–carbon bonds are obliquely inclined with respect to the C_3 axis. These conclusions are confirmed by the thermodynamic studies of Dwyer and his co-workers[75] of the equilibrium between the tris-chelated isomers, and by the x-ray determination of the structures (XI) and (XII) by Saito and his collaborators[34].

The circular dichroism spectra of the isomers (XI) and (XII) in the region of the T_{1g} (O_h) absorption have different forms (Figure 9) owing to the combination of the same conformational or vicinal effect with configurational effects of opposite sign. The two effects are separable by the addition or subtraction of the circular dichroism curves observed for the isomers (XI) and (XII), followed by the appropriate weighting[72–74]. The configurational circular dichroism curve (Figure 9) represents the contribution of the trigonal potential [Figure 5(d)] to the total dissymmetric field, for all of the alkyl groups in either the lel (XI) or the ob (XII) conformation lie in sextants with a common sign, positive for $(+)$-$Co(+pn)_3]^{3+}$ (XI) and negative for $(-)$-$[CO(+pn)_3]^{3+}$ (XII). The configurational circular dichroism resembles more closely[72] that of $(+)$-$[Coen_3]^{3+}$ (III) than that of either of the complex ions (XI) or (XII) [Figures 4 and 9], although the conformational effect cannot be entirely absent in the former complex, as the lel conformation is preferred[69] amongst the mixture of conformers of (III).

The conformational or vicinal circular dichroism curve [Figure 9] represents the contribution of the octahedral pseudo-scalar potential [Figure 5(c)] to the total dissymetric field of the complex ions (XI) and (XII). In both of these ions all of the alkyl groupings lie in regions of the octahedral pseudo-scalar potential [Figure 5(c)] where substituents induce a positive

Cotton effect in the A_{2g} (D_{4h}) component of the T_{1g} (O_h) transition. Suitably weighted to allow for the appropriate number of chelate rings, the conformational or vicinal circular dichroism resembles that of trans-[Co(+pn)$_2$-(NH$_3$)$_2$]$^{3+}$ (*Figure 9*), and that[74] of [Co(NH$_3$)$_4$(+pn)]$^{3+}$.
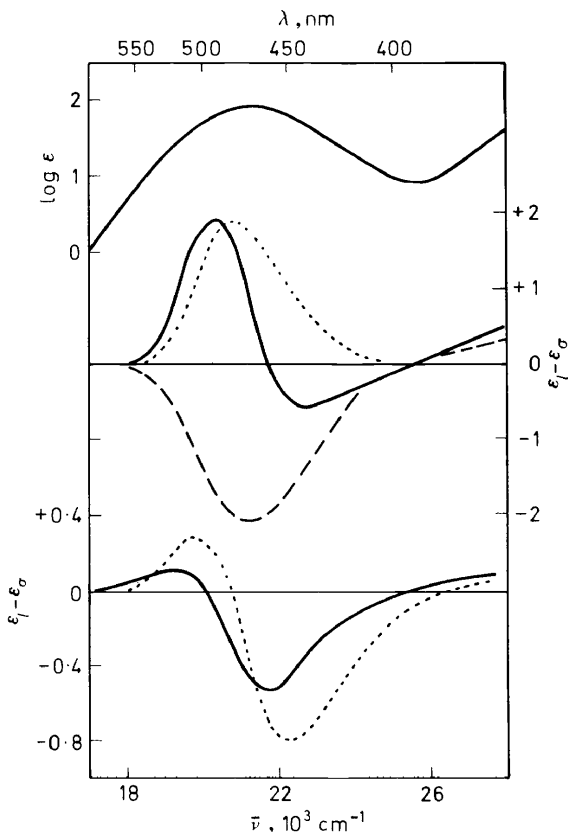

Figure 9. Top curve; the absorption spectrum of (+)-[Co(+pn)$_3$]$^{3+}$ in water. Middle curves: the circular dichroism (_____) of (+)-[Co(+pn)$_3$]$^{3+}$ (XI), and (_ _ _ _) of (−)-[Co(+pn)$_3$]$^{3+}$ (XII) and (............) of the configurational effect of a tris-diamine complex with the $M(C_3)$ or Λ configuration (one-half of the difference between the former two curves). Bottom curves; the circular dichroism (_____) of trans-[Co(+pn)$_2$(NH$_3$)$_2$]$^{3+}$ and of the conformational effect (............) of two (+)-pn chelate rings (one-third of the sum of the CD curves of (+)- and (−)-[Co(+pn)$_3$]$^{3+}$.

The configurational effect is generally stronger than the conformational or vicinal effect, inducing a substantially larger circular dichroism (*Figure 9*). Where they are superposed, the trigonal potential [*Figure 5*(d)] is expected[15] to make a larger contribution to the total dissymmetric field than the octahedral pseudo-scalar potential [*Figure 5*(c)], on account of the smaller

number of nodal planes in the former potential, namely, three, as opposed to nine in the latter. The nodal planes divide the environment of the metal-ion chromophore into six regions of alternating potential phase in the trigonal case [*Figure 5*(d)], but into 48 regions in the octahedral case [*Figure 5*(c)]. A given point source of potential is correspondingly the more effective in the trigonal case, owing to the more rapid attenuation of the field with its extension in the octahedral case[15].

Where the configurational and the vicinal or conformational effects are superposed the former appears to be generally dominant in polychelated complexes of cobalt(III) containing five-membered rings. For such complexes the ring-pairing convention for the nomenclature of absolute configuration, from the mutual chirality of pairs of octahedral edges without a common vertex or common plane spanned by chelate rings[50], may be connected with the optical activity induced by the groups of the chelate rings through the trigonal potential [*Figure 5*(d)]. All of the polychelated cobalt(III) complexes containing five-membered rings, with an absolute configuration established by an x-ray structure determination[34–38,41,42], give predominantly a positive circular dichroism in the region of the T_{1g} (O_h) absorption for the Λ configuration, or negative for the Δ configuration. Where the ring-pairing procedure gives as many Λ and Δ chelate ring pairs, or is not applicable, as in the case of the complex ions (V)[40] and (VIII)[39], there remains only the conformational or vicinal effect, giving an induced optical activity governed by the octahedral potential [*Figure 5*(c)].

REFERENCES

[1] L. Pasteur, *Ann. Chim. Phys.*, (3), **24**, 442 (1848); 'Researches on molecular asymmetry of natural organic products', (1860), *Alembic Club Reprint, No. 14*, E. and S. Livingstone: Edinburgh (1948).

[2] T. Arago, *Mém. Classe Sci. Math. Phys. Inst. Impér. France*, **12**, 93 and 115 (1811).

[3] J. B. Biot, *Mém. Acad. Sci., Paris*, **2**, 41 (1817).

[4] A. Fresnel, *Ann. Chim. Phys.* **28**, 147 (1825).

[5] P. Drude, *Nachr. Akad. Wiss. Göttingen*, 366 (1892).

[6] W. Haidinger, *Ann. Phys., Lpz.* **70**, 531 (1847).

[7] A. Cotton, *C.R. Acad. Sci., Paris*, **120**, 989 and 1044 (1895).

[8] W. Kauzmann, J. Walter and H. Eyring, *Chem. Rev.* **26**, 339 (1940).

[9] A. Moscowitz, *Advanc. Chem. Phys.* **4**, 67 (1962).

[10] I. Tinoco, *Advanc. Chem. Phys.* **4**, 113 (1962).

[11] S. F. Mason, *Quart. Rev. Chem. Soc.* (*London*), **17**, 20 (1963).

[12] H. Eyring, H. C. Lin and D. Caldwell, *Chem. Rev.* **68**, 525 (1968).

[13] M. S. Newman, R. S. Darlak and L. Tsai, *J. Am. Chem. Soc.* **89**, 6191 (1967).

[14] A. Moscowitz, *Thesis*, Harvard (1957).

[15] J. A. Schellman, *J. Chem. Phys.* **44**, 55 (1966).
J. A. Schellman, *Accounts Chem. Res.* **1**, 144 (1968).

[16] W. Kuhn, *Trans. Faraday Soc.* **26**, 293 (1930).
W. Kuhn, *Annu. Rev. Phys. Chem.* **9**, 417 (1958).

[17] J. G. Kirkwood, *J. Chem. Phys.* **5**, 479 (1937).

[18] R. Grinter and S. F. Mason, *Trans. Faraday Soc.* **60**, 274 (1964).

[19] E. G. Höhn and O. E. Wiegang, *J. Chem. Phys.* **48**, 1127 (1968).

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

[21] S. Sugano, *J. Chem. Phys.* **33**, 1883 (1960).

[22] T. S. Piper and A. Karipides, *Molec. Phys.* **5**, 475 (1962).
T. S. Piper and A. Karipides, *J. Chem. Phys.* **40**, 674 (1964).

S. F. MASON

23 N. K. Hamer, *Molec. Phys.* **5**, 339 (1962).
24 H. Poulet, *J. Chim. Phys.* **59**, 584 (1962).
25 M. Shinada, *J. Phys. Soc. Japan*, **19**, 1607 (1964).
26 A. D. Liehr, *J. Phys. Chem.* **68**, 665 and 3629 (1964).
27 C. E. Schaffer, *Proc. Roy. Soc. A*, **297**, 96 (1967).
28 D. Boone, R. Klingbiel, D. Caldwell and H. Eyring, *Rev. Chim. Min.* **6**, 305 (1969).
29 S. F. Mason, *Inorg. Chim. Acta. Rev.* **2**, 89 (1968).
30 B. Bosnich, *Accounts Chem. Res.* **2**, 266 (1969).
31 I. Hanazaki and S. Nagakura, *Inorg. Chem.* **8**, 654 (1969).
32 D. H. Templeton, A. Zalkin and T. Ueki, *Acta Cryst.*, Suppl. **A21**, 154 (1966).
33 E. Larsen, S. F. Mason and G. H. Searle, *Acta Chem. Scand.* **20**, 191 (1966).
34 Y. Saito, *Pure Appl. Chem.* **17**, 21 (1968) and references therein.
35 A. Muto, F. Marumo and Y. Saito, *Inorg. Nucl. Chem. Lett.* **5**, 85 (1969).
36 M. Ito, F. Marumo and Y. Saito, *Inorg. Nucl. Chem. Lett.* **5**, 377 (1969).
37 G. A. Barclay, E. Goldschmied, N. C. Stephenson and A. M. Sargeson, *Chem. Commun.* 540 (1966).
38 J. F. Blount, H. C. Freeman, A. M. Sargeson and K. R. Turnbull, *Chem. Commun.* 324 (1967).
39 S. Larsen, K. J. Watson, A. M. Sargeson and K. R. Turnbull, *Chem. Commun.* 847 (1968).
40 W. T. Robinson, D. A. Buckingham, L. G. Marzilli and A. M. Sargeson, *Chem. Commun.* 539 (1969).
41 D. A. Buckingham, L. G. Marzilli, I. E. Maxwell, A. M. Sargeson and H. C. Freeman, *Chem. Commun.* 583 (1969).
42 M. R. Snow, D. A. Buckingham, P. A. Marzilli and A. M. Sargeson, *Chem. Commun.* 891 (1969).
43 J. P. Mathieu, *C.R. Acad. Sci., Paris*, **236**, 2395 (1953).
44 S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, **33**, 98 (1960).
45 S. Yamada, *Coord. Chem. Rev.* **2**, 83 (1967).
46 A. J. McCaffery and S. F. Mason, *Molec. Phys.* **6**, 359 (1963).
47 R. Dingle and C. J. Ballhausen, *Mat.-Fys. Medd. Dan. Vid. Selsk.* **35**, No. 12 (1967).
48 R. Dingle, *J. Chem. Phys.* **46**, 1 (1967).
49 R. G. Denning, *Chem. Commun.* 120 (1967).
50 *IUPAC Inform. Bull. No. 33*, 68 (1968).
51 J. P. Mathieu, *J. Chim. Phys.* **33**, 78 (1936).
52a S. F. Mason and B. J. Norman, *Proc. Chem. Soc. (London)*, 339 (1964).
   S. F. Mason and B. J. Norman, *Chem. Commun.* 73 (1965).
52b H. L. Smith and B. E. Douglas, *J. Am. Chem. Soc.* **86**, 3885 (1964).
53 J. R. Gollogly and C. J. Hawkins, *Chem. Commun.* 689 (1968).
54 P. G. Beddoe and S. F. Mason, *Inorg. Nucl. Chem. Lett.* **4**, 433 (1968).
55 R. E. Ballard, A. J. McCaffery and S. F. Mason, *Proc. Chem. Soc. (London)*, 331 (1962).
   R. E. Ballard, A. J. McCaffery and S. F. Mason, *J. Chem. Soc.* 2883 (1965).
56 A. G. Karipides and T. S. Piper, *J. Chem. Phys.* **40**, 674 (1964).
57 A. J. McCaffery, S. F. Mason and B. J. Norman, *J. Chem. Soc.* 5094 (1965).
58 H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958).
59 W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne and C. Djerassi, *J. Am. Chem. Soc.* **83**, 4013 (1961).
60 L. L. Jones and H. Eyring, *J. Chem. Educ.* **38**, 601 (1961).
61 C. J. Hawkins and E. Larsen, *Acta Chem. Scand.* **19**, 185 and 1969 (1965).
62 K. M. Wellman, W. Mungall, T. G. Mecca and C. R. Hare, *J. Am. Chem. Soc.* **89**, 3547 (1967).
63 R. B. Martin, J. M. Tsangaris and J. W. Chang, *J. Am. Chem. Soc.* **90**, 821 (1968).
64 S. F. Mason, *Chem. Commun.* 856 (1969).
65 M. Saburi and S. Yoshikawa, *Inorg. Chem.* **7**, 1890 (1968).
66 M. Saburi, Y. Tsujito and S. Yoshikawa, *Inorg. Nucl. Chem. Lett.*, **5**, 203 (1969).
67 Y. Saito and H. Iwasaki, *Bull. Chem. Soc. Japan*, **35**, 1131 (1962).
68 D. A. Buckingham, L. G. Marzilli and A. M. Sargeson, *Inorg. Chem.* **7**, 915 (1968).
69 E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.* **81**, 2620 (1959).
70 J. von Neumann, *Nachr. Akad. Wiss. Göttingen*, 1 (1927).
71 H. C. Freeman, *Advanc. Protein Chem.* **22**, 257 (1967).
72 B. E. Douglas, *Inorg. Chem.* **4**, 1813 (1965).
73 S. F. Mason, A. M. Sargeson, R. Larsson, B. J. Norman, A. J. McCaffery and G. M. Searle, *Inorg. Nucl. Chem. Lett.* **2**, 333 (1966).

358

S. F. Mason, A. M. Sargeson, R. Larsson, B. J. Norman, A. J. McCaffery and G. M. Searle, *J. Chem. Soc.* 1304 and 1310 (1968).

[74] K. Ogino, K. Murano and J. Fujita, *Inorg. Nucl. Chem. Lett.* **4**, 351 (1968).

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

F. P. Dwyer, T. E. MacDermott and A. M. Sargeson, *J. Am. Chem. Soc.* **85**, 2913 (1963).

F. P. Dwyer, A. M. Sargeson and L. B. James, *J. Am. Chem. Soc.* **86**, 590 (1964).