

CIRCULAR DICHROISM OF TRANSITION METAL COMPLEXES

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ABBREVIATIONS

big	biguanide
bipy	2,2'-bipyridyl
chxn	<i>trans</i> 1,2-diaminocyclohexane
cptn	<i>trans</i> 1,2-diaminocyclopentane
en	1,2-diaminoethane
Me ₄ pn	<i>N,N,N',N'</i> -tetramethyl 1,2-diaminopropane
ox	oxalate
pd	2,4-pentanedionate
phen	1,10-phenanthroline
ptn	2,4-diaminopentane
tacn	1,4,7-triazacyclononane
tn	1,3-diaminopropane
tmd	1,4-diaminobutane

A. INTRODUCTION

Transitions giving rise to the electronic absorption and circular dichroism spectrum of a typical transition metal ion complex may be divided into three

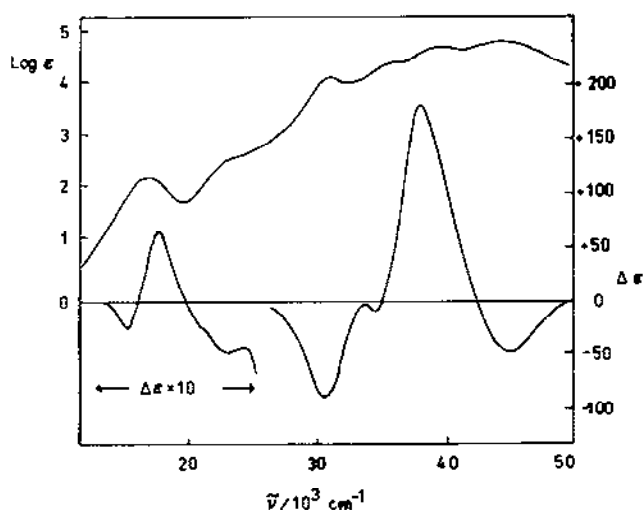


Fig. 1. The absorption (upper curve) and circular dichroism (lower curve) spectra of Λ -[Co(pd)₃] in ethanol.

general types: $d \leftrightarrow d$ (or $f \leftrightarrow f$) transitions of the metal ion; charge-transfer transitions; and internal ligand transitions. The spectrum of Λ -[Co(pd)₃] (Fig. 1) illustrates this division quite well. The lowest energy absorption band at $\sim 17000 \text{ cm}^{-1}$, with its associated circular dichroism couplet, results from the ${}^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ transition of the Co(III) ion which is to a very good

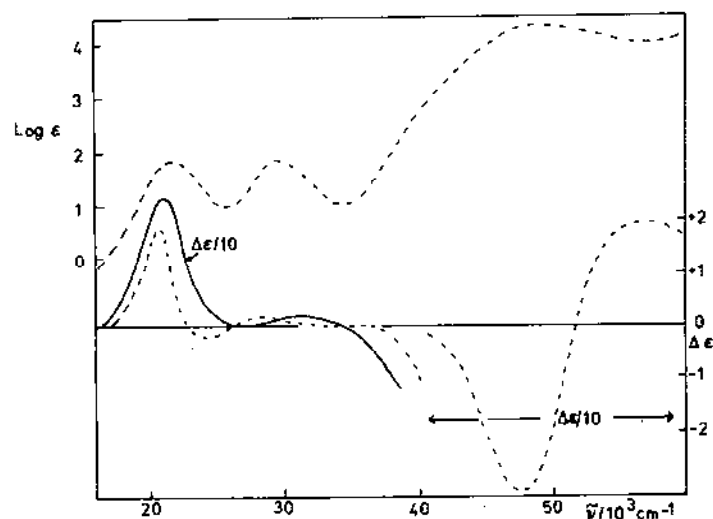


Fig. 2. The axial single-crystal circular dichroism spectrum ($\Delta\epsilon/10$) of $2[\Lambda\text{-Co(en)}_3\text{Cl}_3]_2 \cdot \text{NaCl} \cdot 6 \text{H}_2\text{O}$ (solid curve) and the absorption and circular dichroism spectra of Λ -[Co(en)₃] [ClO₄]₃ in water (upper and lower broken curves respectively).

approximation a metal-localised $d \leftrightarrow d$ transition. The molar extinction coefficient, ϵ , and the differential molar extinction coefficient for left and right circularly polarised light, $\Delta\epsilon$ ($=\epsilon_l - \epsilon_r$), are typical of magnetic-dipole allowed, electric-dipole forbidden transitions within the d -orbital set of a configurationally optically active trigonal transition metal complex. The absorption band at 31000 cm^{-1} and the shoulder at 35000 cm^{-1} with their associated circular dichroism can be assigned to charge-transfer transitions in which an electron is formally transferred from a ligand (in this case π) orbital to the metal e_g orbital set. Finally at highest energy (39000 cm^{-1} and 43000 cm^{-1}) are the exciton-coupled absorption and circular dichroism bands of the internal transitions of the 2,4-pentanedionate ligand. The spectrum of $[\text{Co}(\text{pd})_3]$ is typical of a complex with polarisable ligands which have substantial absorption in the UV region and which has relatively low-energy charge-transfer bands. Complexes with saturated ligands, for example $[\text{Co}(\text{en})_3]^{3+}$, will have no ligand absorption in the near-UV region and the charge-transfer transitions, which originate from σ -bonding ligand orbitals, will be found at higher energy than in complexes with unsaturated ligands (Fig. 2). The assumption that the metal, charge-transfer and ligand transitions can be regarded as being largely independent of one another is a fairly good one for Co(III) complexes but is generally less valid for those of Cr(III).

Measurement of the exciton-coupled circular dichroism spectra of internal ligand transitions is the most reliable method, apart from X-ray crystallography, of establishing the absolute configuration of a transition metal complex provided the ligand excitations occur in an accessible spectral region. The theory of this method has been detailed and its application extensively reviewed [1,2]. There seems no need to paraphrase these excellent accounts. There is no known case where the exciton theory, when correctly applied, has led to the incorrect assignment of the absolute configuration of a metal complex.

The available literature on the circular dichroism of $d \leftrightarrow d$ transitions runs into thousands of references. The general methods of interpreting such spectra are exemplified by concentrating on two classes of complex: the tris-chelates of Co(III) which have been more extensively studied than any other type of complex, and pseudo-tetrahedral complexes of Co(II) which are believed to represent a major area of future study.

Divalent transition metal ions such as Co(II), Ni(II) and Cu(II) have an important role in bioinorganic chemistry. A review of the circular dichroism of metal ions in bioinorganic systems is available [3]. The spectra of these complicated systems have, however, been used only in an empirical way, for example, to distinguish between the sources of the metalloenzyme carbonic anhydrase [4], or to demonstrate the complexing of Co(II) alkaline phos-

phatase by $[\text{HPO}_4]^{2-}$ ions [5]. In the absence of suitable model systems and with no fully adequate theory for the circular dichroism of pseudo-tetrahedral, or lower symmetry, transition metal complexes it is not surprising that the interpretation of the spectra of these complex systems has not proceeded further. The discussion of the circular dichroism of pseudo-tetrahedral Co(II) complexes will indicate how much has been achieved in this field and will, it is hoped, encourage further research.

The circular dichroism of charge-transfer transitions has been neglected compared to that of both $d \leftrightarrow d$ and internal ligand transitions. The reason for this is partly because charge-transfer spectra of complexes of σ -bonding ligands have till recently been only partially accessible and partly because of the difficulty of interpreting such spectra within the framework of a crystal-field theory which assumes no interaction between metal and ligand orbitals. Charge-transfer transitions, however, are a major feature of the spectra of many complexes, especially tris-diimine complexes of the divalent iron group metals whose charge-transfer photochemistry is currently under intensive investigation. An understanding of charge-transfer circular dichroism is of considerable theoretical importance and these spectra have potential applications both in the determination of stereochemistry and in helping to assign charge-transfer spectra.

B. CIRCULAR DICHROISM OF $d \leftrightarrow d$ TRANSITIONS

(i) Trigonal Co(III) complexes with σ -bonding ligands

Trigonal (D_3) symmetry is the highest symmetry commonly found in coordination compounds exhibiting optical activity. It is not surprising, therefore, to find that by far the largest number of circular dichroism measurements and theoretical studies have been performed on the optically stable and easily resolved trigonal complexes of Co(III). Apart from the obvious theoretical convenience of high symmetry, one additional advantage of D_3 complexes is that they may crystallise in a uniaxial space group, thus enabling the single-crystal circular dichroism to be measured without the complications of linear dichroism. Such single-crystal circular dichroism experiments have been, and remain, crucial to our understanding and interpretation of the $d \leftrightarrow d$ optical activity of metal complexes.

With a few exceptions the complexes of most interest are tris-chelates and these may be conveniently divided into two classes. First, there are the tris-(saturated diamines), in which the disposition of the six nitrogens is usually the most important chiral influence on the metal ion wavefunctions and in which the ring backbone is likely to be of minor significance in determining the sign and magnitude of the rotational strengths. The second

class comprises the tris-(unsaturated chelates) such as oxalate, pentane-1,3-dionato and biguanide where the whole chelate ring is involved in a delocalised π -system and in which it is therefore less valid to distinguish the effects of the ligators from those of the ligand backbone. The coordination of the saturated ligands is by σ bonding and, to a good approximation, the ligators may be treated as isotropic perturbers. For the unsaturated ligands both σ and π bonding are present and the perturbation of the metal ion electrons has an anisotropic character.

The absorption spectrum (Fig. 2) of $[\text{Co(en)}_3]^{3+}$, typical of the saturated chelate complexes, is very similar to that of the octahedrally coordinated $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion. It shows two spin-allowed $d \leftrightarrow d$ bands well separated from the charge-transfer absorption. These are assigned to the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition (at 22000 cm^{-1}) and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ (at 30000 cm^{-1}) where the octahedral symmetry labels will continue to be used for the moment. Since these transitions are within the d -orbital set they are electric-dipole forbidden (by the $\Delta l = \pm 1$ selection rule) and the explanation of why $d \leftrightarrow d$ transitions have any absorption intensity and circular dichroism at all is a parallel investigation [6,7] to that of explaining the relative signs and magnitudes of the circular dichroism bands.

The ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition arises from the one-electron excitations $xy \rightarrow x^2 - y^2$, $yz \rightarrow y^2 - z^2$ and $zx \rightarrow z^2 - x^2$ which give rise to the three components of a magnetic dipole transition moment along the z , x and y directions respectively. The lowest order electric transition moment produced by the one-electron excitations is an electric hexadecapole. The ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition, in contrast, is magnetic-dipole forbidden; the one-electron transitions $xy \rightarrow z^2$, $yz \rightarrow x^2$ and $zx \rightarrow y^2$ corresponding to three components of an electric quadrupole transition moment.

The allowed magnetic dipole transition moments and higher multipole electric transition moments are responsible for an extremely small light absorption and the observed absorption intensity must arise through some form of forced electric dipole mechanism. In $[\text{Co}(\text{NH}_3)_6]^{3+}$ this mechanism involves vibronic coupling via non-totally symmetric vibrations although in the tris-chelate complexes there will be a contribution from statically induced electric dipole intensity as a result of the reduction in symmetry, $O_h \rightarrow D_3$. In the case of $[\text{Co(en)}_3]^{3+}$, for example, where the distortion of the nitrogen atoms from the O_h positions is not large (small static D_3 perturbation) it seems likely that the static and dynamic contributions to the intensity will be of comparable magnitude. The relative contributions of these mechanisms and the precise details of how they produce the observed electric dipole intensity is a subject of continuing investigation.

While the magnetic dipole transition moment is unimportant in determining the isotropic absorption intensity, it is of crucial importance in the

acquisition of rotational strength, this being equal to the scalar product of the electric and magnetic transition moments. For a transition from a ground state $\langle 0|$ to an excited state $|a\rangle$ the rotational strength R_{0a} is given by the expression [8]

$$R_{0a} = \text{Im} \langle 0 | \hat{\mu} | a \rangle \cdot \langle a | \hat{m} | 0 \rangle$$

$\hat{\mu}$ and \hat{m} being the electric and magnetic dipole moment operators respectively. It is expected, therefore, that the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition of $[\text{Co}(\text{en})_3]^{3+}$ which has an allowed magnetic dipole transition moment should display a very much larger circular dichroism than the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition which is magnetic-dipole forbidden in O_h symmetry. It is clearly seen from Fig. 2 that this is so. If the octahedral parentage were strictly preserved, the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition would have to acquire both its electric and magnetic transition moment by vibronic coupling which would result in an extremely small rotational strength. In the true D_3 symmetry of the complex, however, the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition transforms as ${}^1A_1 \rightarrow {}^1E$ (polarised perpendicular to the C_3 axis) and ${}^1A_1 \rightarrow {}^1A_2$ (polarised parallel to the C_3 axis) while ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transforms as ${}^1A_1 \rightarrow {}^1E$ and ${}^1A_1 \rightarrow {}^1A_1$ (forbidden in D_3). The two 1E states may mix with each other (and with charge-transfer 1E states), giving a small

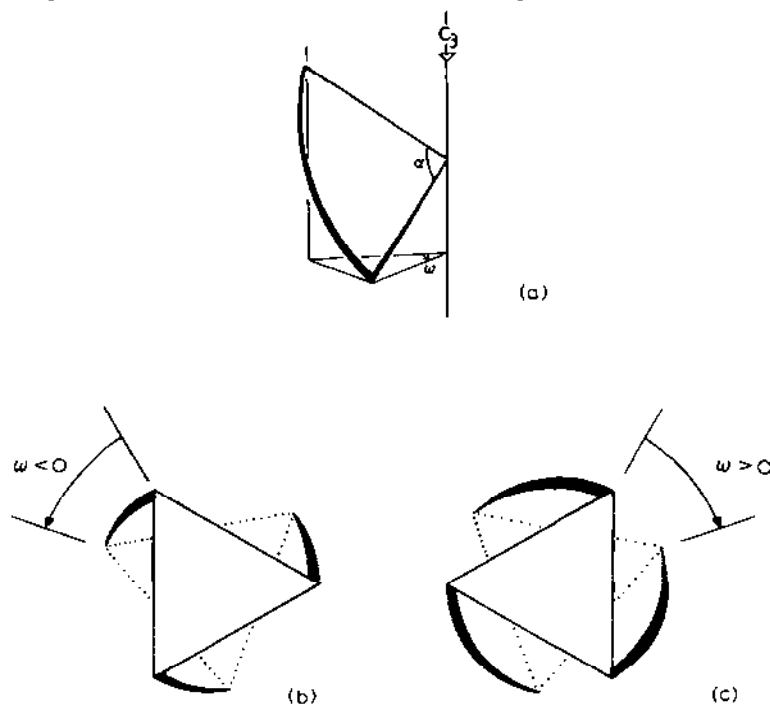


Fig. 3. Angles characterising a tris-bidentate complex of D_3 symmetry. The diagram show how ω can be positive or negative for the same absolute configuration of the chelate rings. Figs. 3b and 3c show the situation in, for example, $\Lambda\text{-}[\text{Co}(\text{en})_3]^{3+}$ and $\Lambda\text{-}[\text{Co}(\text{tn})_3]^{3+}$ respectively.

rotational strength to the ${}^1A_1 \rightarrow {}^1E(T_{2g})$ transition. The observed small circular dichroism of this transition suggests that the trigonal perturbation (at least in the case of saturated diamine complexes) is not large.

Further evidence on the size of the trigonal perturbation comes from the observed splitting of the ${}^1T_{1g}$ state into 1E and 1A_2 components as determined from the polarised absorption spectrum of $[\text{Co(en)}_3]^{3+}$ in single crystals [9,10]. While the Franck-Condon maxima of the ${}^1A_1 \rightarrow {}^1E$ and ${}^1A_1 \rightarrow {}^1A_2$ transitions are separated by about 70 cm^{-1} , the $0 \leftrightarrow 0$ bands (electronic origins) appear to be degenerate to $\pm 2 \text{ cm}^{-1}$ at liquid helium temperature. The sense of the trigonal splitting (that is, which of A_2 or E comes to higher energy) is determined for saturated tris-chelates by the 'bite' angle of the chelate ring (α in Fig. 3). If α is $< 90^\circ$ the octahedron of ligators is trigonally compressed and the 1E state is expected to have lower energy than 1A_2 . If α is $> 90^\circ$ the octahedron is elongated and 1A_1 should occur to lower energy of 1E . In the case of $[\text{Co(en)}_3]^{3+}$ the octahedron is trigonally compressed [11], $\alpha = 85.4^\circ$, which implies that the 1E component would be expected to occur to lower energy of the 1A_2 component. The evidence from the polarised absorption spectrum is, as mentioned above, somewhat ambiguous and it is necessary to turn to single-crystal circular dichroism spectroscopy to obtain the order of the energies of the 1E and 1A_2 components of relevance to the interpretation of the solution optical activity.

Because of the nature of circularly polarised light, single-crystal circular dichroism spectra may only be obtained without the complication of linear dichroism and birefringence if the light is propagated down the unique axis of a uniaxial crystal. Fortunately there are a number of D_3 complexes which crystallise in uniaxial space groups with their C_3 molecular axis parallel to the unique crystal axis. The electric and magnetic vectors of the circularly polarised radiation are always perpendicular to the direction of propagation of the light and so only those transitions which are polarised perpendicular to the C_3 axis of the complex can absorb radiation. The single-crystal circular dichroism experiment [12] uniquely identifies E polarised transitions. The circular dichroism spectrum of an aqueous solution of $[\text{Co(en)}_3]^{3+}$ and of a single crystal of $2[\Lambda\text{-Co(en)}_3\text{Cl}_3] \cdot \text{NaCl} \cdot 6\text{H}_2\text{O}$ is shown in Fig. 2. It can readily be seen that the single-crystal circular dichroism is much larger (approximately ten times) than the solution circular dichroism and, in the case of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition, maximises slightly to long wavelength of the absorption band maximum. Because the circular dichroism must sum to zero independently for each transition in the limit of octahedral symmetry, and because the trigonal perturbation is small, the sum of the rotational strengths of the A_2 and E components must be approximately zero. The couplet seen in the solution circular dichroism spectrum under the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition can be identified with the residual wings of the E and A_2 transitions which

TABLE 1

The rotational strengths R (10^{-40} cgs units) of the ${}^1A_{1g} \rightarrow {}^1T_{1g} (O_h)$ transition for a number of amine complexes of Co(III). Values are listed both for the net rotational strength $R(T_1)$ and for the rotational strengths of the E and A_2 trigonal components obtained from single-crystal measurements. Also included are the angular parameters α and ω defined in Fig. 3 and the relative energy order of the E and A_2 trigonal components. $R(E)$ and $R(A_2)$ have been corrected by the fixed orientation factors of $\frac{2}{3}$ and $\frac{1}{3}$, respectively

Complex	$R(E)$	$R(A_2)$	$R(T_1)$	ω ($^\circ$)	α ($^\circ$)	Energy order	Ref.
$\Lambda\text{-[Co(en)}_3\text{]}^{3+}$	+62.9	-58.6	+4.3	-54.9	85.4	$E < A_2$	12
$\Lambda\text{-[Co(S-pn)}_3\text{]}^{3+}$	+38.1	-36.6	+1.5	-55	84.2	$E < A_2$	14
$\Lambda\text{-[Co(S, S-chxn)}_3\text{]}^{3+}$	+56.5	-51.1	+5.4	-55	86.7	$E < A_2$	14
$\Lambda\text{-[Co(S, S-cptn)}_3\text{]}^{3+}$	+57.3	-54.5	+2.8	-54.5	86.7	$E < A_2$	14
$\Lambda\text{-[Co(S, S-ptn)}_3\text{]}^{3+}$	+12.5	-14.5	-2.0	-57	89.1	$E < A_2$	14
$\Lambda\text{-[Co(tmd)}_3\text{]}^{3+}$	+31.1	-38.7	-7.6	-55.7	89.2	$E < A_2$	14
$\Lambda\text{-[Co(tn)}_3\text{]}^{3+}$	-10.5	+10.2	-0.3	+53	91	$A_2 < E$	13
$[\text{Co}\{(2R\text{-Me})\text{-tacn}\}_2]^{3+}$	-14.8	+29.7	+14.8	+52.4	elongated	$A_2 \approx E$	17

must of necessity have nearly equal intensity and which, because of the small trigonal splitting, largely cancel each other out. By a comparison of the axial crystal circular dichroism spectrum with the solution circular dichroism spectrum (or better the spectrum of the complex pressed in an alkali halide disc to minimise conformational changes) the rotational strength of the A_2 component may be obtained. The rotational strengths of the ${}^1A_1 \rightarrow {}^1E$ and ${}^1A_1 \rightarrow {}^1A_2$ transitions for all those Co(III) complexes with unsaturated diamine ligands whose single-crystal circular dichroism spectra have been measured [12–14] are collected in Table 1. Also given in Table 1 are the residual rotational strengths, $R(T_1)$, after cancellation in the random orientation and the two structural parameters defined in Fig. 3; the bite of the chelate ring (α) and the angle ω which is defined by viewing the complex as a projection in the plane perpendicular to the trigonal axis. ω is the smallest angle measured from any one of the upper set to one of the lower set of ligator atoms. This angle is positive when its direction, as defined above, is clockwise.

Having identified and determined the sign of the rotational strength of the 1E component of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition of several tris-diamine Co(III) complexes it is relevant to ask if there is a correlation of this sign with the absolute configuration of the tris-chelate. The answer to the question is yes, but the correlation is not with the absolute configuration as conventionally defined in terms of the disposition of the chelate ring backbone atoms about the metal ion. The correlation is between $R(E)$ and the sense of the angular displacement of the two triangles of ligator atoms from the octahedral configuration. If the twist of the top triangle relative to the bottom is counterclockwise (ω negative) then $R(E)$ is positive and $R(A_2)$ negative. This is the case for the Λ configuration of all the five-membered chelate ring complexes studied. If the twist is in the clockwise direction (ω positive) then $R(E)$ is negative and $R(A_2)$ positive. An example of this is seen in the spectrum of Λ -[Co(tn)₃]³⁺.

The correlation between the sign of circular dichroism and the sense of the

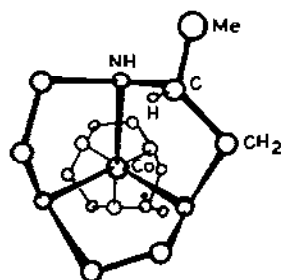


Fig. 4. A projection of the structure of the bis(2*R*)-2-methyl-1,4,7-triazacyclononane] cobalt(III) ion, [Co((2*R*-Me)-tacn)₂]³⁺, viewed down the molecular *z* axis.

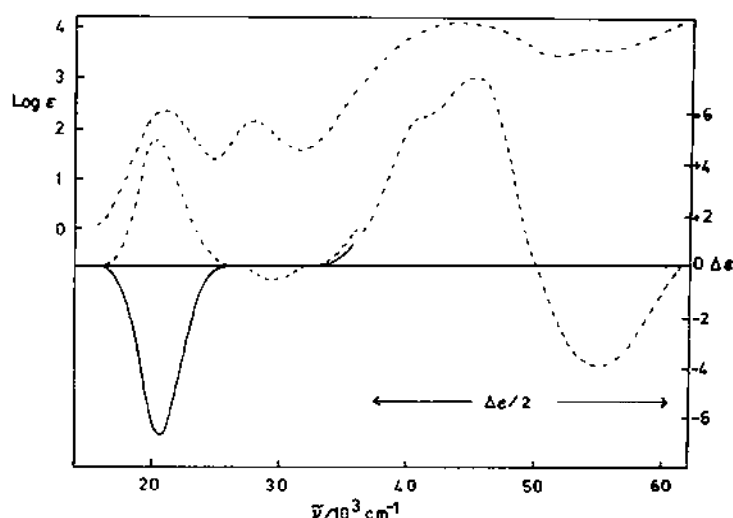


Fig. 5. The absorption spectrum (upper dashed curve) and circular dichroism spectrum (lower dashed curve) of $[\text{Co}\{(2R\text{-Me})\text{-tacn}\}_2][\text{ClO}_4]_3$ in water, or in D_2O for the 160–260 nm region and the circular dichroism spectrum of a single crystal of $[\text{Co}\{(2R\text{-Me})\text{-tacn}\}_2]\text{I}_3 \cdot 5\text{H}_2\text{O}$ with radiation propagated along the crystal c axis (molecular z axis) (full curve).

angle of twist between the planes of ligators can be extended from the tris-chelates to include the unusual 'sandwich' compound [15] $[\text{Co}\{(2R\text{-Me})\text{-tacn}\}_2]^{3+}$ whose structure [16] is shown in Fig. 4. In this complex there are no chelate rings joining the triangles of ligators and so the definition of absolute configuration based on the orientation of chelate rings cannot be made. The crystal structure shows that there is a clockwise rotation of the upper triangle of ligators with respect to the lower triangle and the single-crystal axial circular dichroism [17] (Fig. 5) shows that $R(E)$ is negative. Thus all the available evidence supports the conclusion that the sense of twist of the ligators is the major chiral perturbation in saturated diamine complexes of Co(III) and that the absolute configuration and disposition of the chelate rings, while controlling this sense of twist, does not directly determine the sign of circular dichroism.

While the sign of the rotational strength for saturated diamine complexes is independent of the positions of the non-ligating atoms the same can not be said for the magnitude of the rotational strength. The magnitude is clearly determined by the positions of all the atoms as can be seen by considering the spectra of $\Lambda\text{-}[\text{Co}(\text{en})_3]^{3+}$ and $\Lambda\text{-}[\text{Co}(\text{S-pn})_3]^{3+}$ (Table 1). The ligator positions, and particularly the size of the twist angle, are essentially identical in the two complexes while the rotational strengths $R(E)$ are different by a factor of about 0.6. A comprehensive comparison of configurational and conformational contributions to circular dichroism in saturated Co tris-

chelate complexes has been reported [18].

Both the energies and the sign of the rotational strength of the 1A_2 and 1E components of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition of cobalt tris-diamine complexes can be correlated with structural parameters and can be reproduced reasonably well by calculation [19]. The third important feature of the circular dichroism of this transition, the relative magnitudes of the rotational strengths $R(A_2)$ and $R(E)$, is much less well understood. This is particularly unfortunate since it is only this feature, the overall sign of the ${}^1A_1 \rightarrow {}^1T_1$ transition $R(T_1)$, which can be measured unambiguously from a solution or disc spectrum if no oriented single-crystal data are available. For $[\text{Co(en)}_3]^{3+}$, and for the majority of complexes listed in Table 1, $R(E) > R(A_2)$. Indeed the assumption that $R(E)$ was always greater in magnitude than $R(A_2)$ prevailed for some time but there are now several examples known where this generalisation does not hold, the most recent being $[\text{Co}\{(2R\text{-Me})\text{-tacn}\}_2]^{3+}$.

Without the knowledge of which circular dichroism band corresponds to the ${}^1A_1 \rightarrow {}^1E$ and which to the ${}^1A_1 \rightarrow {}^1A_2$ transition it is impossible to make a prediction about the chirality of the complex in question. If the bite angle of the chelate is known or can be predicted from models or by analogy it is certainly possible to apply the rule that in axially compressed molecules 1E lies to lower energy of 1A_2 . Even this will fail, however, in cases like $[\text{Co}\{(2R\text{-Me})\text{-tacn}\}_2]^{3+}$ where only one sign is seen in the solution circular dichroism. Calculation of the relative magnitudes of $R(E)$ and $R(A_2)$ from crystal structure data has been less successful than the calculation of the signs and absolute magnitudes of these rotational strengths. This is because $R(T_1)$ is small compared to $R(E)$ or $R(A_2)$ and because calculations which involve only transitions within the d -orbital set have proved incapable of correctly predicting this small difference between $R(E)$ and $R(A_2)$. Either a molecular orbital calculation [20] or a treatment in which second-order charge-transfer rotational strength is added to that calculated by the ligand polarisation model [19] can correctly predict $R(T_1)$ in a number of cases. To calculate the charge-transfer contribution, however, a knowledge of the symmetry of the lowest charge-transfer transition is required and this in turn requires a polarised crystal spectrum.

All the foregoing discussion of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ circular dichroism of $[\text{Co(en)}_3]^{3+}$ depends upon the assumption that the two bands seen in the solution spectrum are due to a static trigonal splitting. The fact that the separation of the two resolved circular dichroism components is of the order of 100 cm^{-1} while the vibrations seen [21] in the liquid helium spectrum have wavenumbers of 174, 246, 332, 408, 445 and 491 cm^{-1} casts some doubt on whether a description in terms of a static distortion has meaning. It is also rather worrying that while the crystal structure reveals an undoubted

trigonal distortion in the ground state, the liquid helium absorption spectrum suggests that the electronic origins of the A_2 and E polarised components of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition are essentially degenerate. These arguments have led to the suggestion [21] that the excited state of $[\text{Co(en)}_3]^{3+}$ is Jahn–Teller distorted and that the parallel and perpendicularly polarised circular dichroism and absorption bands are components of the transition to this Jahn–Teller excited state and not trigonal components caused by the static ligand field as is usually supposed. The evidence for or against this suggestion is not conclusive. Very recent work shows, however, that in certain cases the circular dichroism of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition cannot be explained [22] without explicitly considering the vibronic perturbation.

The circular dichroism of the ${}^1A_{1g} \rightarrow {}^1T_{2g}(O_h)$ transition of saturated tris-chelate complexes of Co(III) has been largely ignored by most workers. For example no low-temperature measurements have been published. The transition (in O_h parentage) is magnetic-dipole forbidden and the most obvious explanation of why it shows circular dichroism is that its 1E component can borrow rotational strength from the ${}^1A_1 \rightarrow {}^1E(T_{1g})$ transition in D_3 symmetry. This explains both the weak rotational strength of the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition and also the observation that the rotational strength is invariably of one sign, since the ${}^1A_1 \rightarrow {}^1A_1$ component cannot mix with any other transition to acquire a magnetic dipole moment. The only worrying feature of this explanation is that the wavenumber of the circular dichroism maximum shifts to higher energy on going from solution to single crystal and the intensity increases by a factor of ~ 10 . It has been suggested [23] that the single-crystal rotational strength has a different origin from that observed in random orientation. In the oriented case the allowed electric quadrupole transition moment of the ${}^1A_1 \rightarrow {}^1T_{2g}(O_h)$ transition may give rise to a rotational strength which will average to zero in random orientation.

(ii) Trigonal Co(III) complexes with π -bonding ligands

The relatively simple picture presented above for saturated diamine ligands becomes more complicated when complexes with unsaturated ligands are considered. Table 2 shows the signs of $R(E)$, $R(A_2)$ and $R(T_1)$ for the ${}^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ transition of $[\text{Co}(\text{pd})_3]$, $[\text{Co}(\text{big})_3]$ and $[\text{Co}(\text{ox})_3]^{3-}$ along with the appropriate structural parameters. The first thing to be noticed is that the correlation between the sense of the trigonal splitting and the bite angle of the chelate ring, which held for the saturated diamine complexes, does not hold in these cases. $[\text{Co}(\text{pd})_3]$ is trigonally elongated ($\alpha = 96.6^\circ$) and, in agreement with the relationship found to hold in the saturated chelate case, has 1A_2 to lower energy of 1E . The same energy order also holds, however, for $[\text{Co}(\text{big})_3]$ ($\alpha = 89.2^\circ$) and in $[\text{Co}(\text{ox})_3]^{3-}$ which is markedly

TABLE 2

The rotational strengths R (10^{-40} cgs units) of the ${}^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ transition for some complexes of Co(III) with unsaturated chelate ligands. Values are listed for both the net rotational strength $R(T_1)$ and, where known, for the rotational strengths of the E and A_2 trigonal components obtained from single-crystal measurements. Also included are the angular parameters α and ω defined in Fig. 3 and the relative energy order of the E and A_2 components. $R(E)$ and $R(A_2)$ have been corrected by the fixed orientation factors of 2/3 and 1/3, respectively

Complex	$R(E)$	$R(A_2)$	$R(T_1)$	ω ($^\circ$)	α ($^\circ$)	Energy order	Ref.
$\Lambda\text{-[Co(ox)}_3\text{]}^{3-}$	+114	-101	+13	-54	84.3	$A_2 \approx E$	18
$\Lambda\text{-[Co(big)}_3\text{]}$	+	-	+7.4	-58.4	89.2	$A_2 < E$	24
$\Lambda\text{-[Co(pd)}_3\text{]}$	+	-	+16.2	+52.7	96.6	$A_2 < E$	24

compressed ($\alpha = 84.3^\circ$) the energies of the two components are essentially equal. The sense of the trigonal splitting can in fact be rationalised [24] in terms of the effect of metal-ligand π -bonding but although the order of the 1E and 1A_2 components may be explained a posteriori, the assignment of the circular dichroism spectrum of the ${}^1A_1 \rightarrow {}^1T_{1g}(O_h)$ transition for a complex with unsaturated ligands is even less certain, unless a single-crystal circular dichroism spectrum is available, than for complexes of saturated ligands.

The correlation between the sign of $R(E)$ and the sense of the trigonal twist, which was seen to hold for all saturated diamine complexes whose spectra have been unambiguously assigned, clearly does not hold for the three unsaturated tris-chelate complexes considered. Both $\Lambda\text{-[Co(ox)}_3\text{]}^{3-}$ and $\Lambda\text{-[Co(pd)}_3\text{]}$ show strong positive $R(E)$ despite having trigonal twists of (nearly) equal magnitude and opposite sense. This must be taken as direct evidence that the ligands are not isotropic and a treatment of the circular dichroism of unsaturated ligand complexes in which the chiral perturbation is considered to be anisotropic would seem to be necessary. A good account of the present status of the circular dichroism of tris-chelate complexes with unsaturated ligands has recently been published [24].

(iii) Pseudo-tetrahedral complexes of Co(II)

By comparison with the trigonal pseudo-octahedral complexes, those with a distorted tetrahedral coordination geometry have been almost totally neglected. This is understandable since tetrahedrally coordinated transition metal ion complexes are substitutionally labile and so cannot be resolved into configurational isomers, any chirality having to be induced by chiral ligands. Furthermore, in the case of Co(II), Ni(II) and Cu(II) tetrahedral

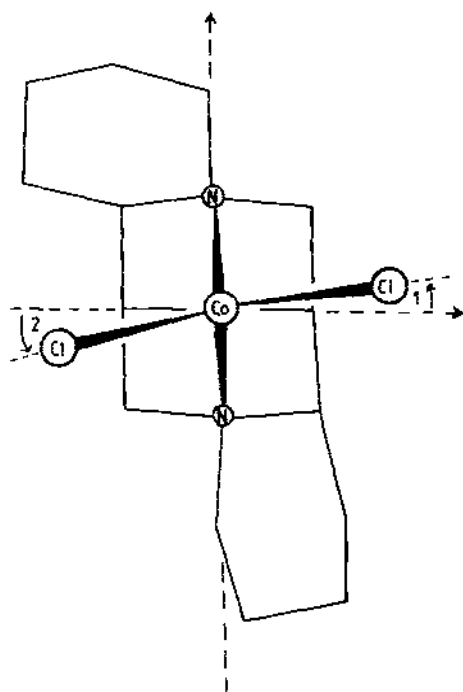


Fig. 6. A projection of the structure of $[\text{Co}\{(-)\text{-spartein}\}\text{Cl}_2]$ on the XY plane perpendicular to the pseudo- $C_2(Z)$ axis. In the projection the distortion angles are 6.2° for $\text{Cl}(1)$ and 10° for $\text{Cl}(2)$.

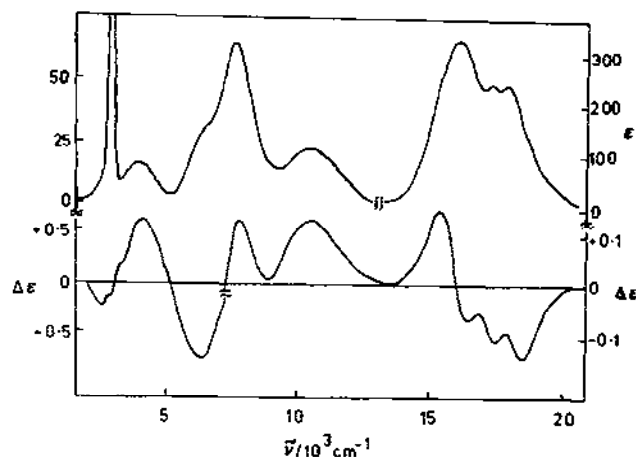


Fig. 7. The absorption spectrum (upper curve) and circular dichroism spectrum (lower curve) of $[\text{Co}\{(-)\text{-spartein}\}\text{Cl}_2]$ in CHCl_3 or CDCl_3 solution. Note the change in scale for the absorption (at 13000 cm^{-1}) and for the circular dichroism (at 7000 cm^{-1}).

complexes many of the $d \leftrightarrow d$ transitions are in the near-IR region and a study of their circular dichroism has had to wait for suitable instrumentation [25] to be developed. This neglect is unfortunate, however, since many biologically important chiral metal ion sites, such as the Cu^{2+} site in the copper blue proteins and the Zn^{2+} site in carbonic anhydrase are pseudo-tetrahedral. The situation is unusual in that there are a large number of uninterpreted circular dichroism spectra of these complicated systems and little spectral information about optically active model complexes.

The only extensive series of pseudo-tetrahedral complexes of known structure whose circular dichroism has been measured throughout the whole $d \leftrightarrow d$ spectral range are the complexes of cobalt, nickel and copper halides with the alkaloid (-)-spartein [26,27] and in certain cases with its isomers (-)- α -isospartein [28] and (+)- β -isospartein [29]. The structure of $[\text{Co}((-)\text{-spartein})\text{Cl}_2]$ [30] is shown in Fig. 6. The complex has only C_1 symmetry in the solid state but it may be conveniently assumed that the metal-ligand core has C_2 symmetry in solution where all spectral measurements have been made. The major chirality is configurational in that the chiral ligand forces the two pairs of ligands to deviate from the C_{2v} configuration to an extent of about 98° between the CoN_2 and CoCl_2 planes. The absorption and circular dichroism spectra of the complex are illustrated in Fig. 7.

The three lowest energy transitions of tetrahedral Co(II) are ${}^4A_2 \rightarrow {}^4T_2$ (at $\sim 4500 \text{ cm}^{-1}$), ${}^4A_2 \rightarrow {}^4T_1(F)$ ($\sim 9000 \text{ cm}^{-1}$) and ${}^4A_2 \rightarrow {}^4T_1(P)$ ($\sim 17000 \text{ cm}^{-1}$). The lowest energy transition (transforming as T_1 in tetrahedral symmetry) is magnetic-dipole and electric-octupole allowed while the other two are electric-quadrupole allowed but magnetic-dipole forbidden. In the C_2 point group each of these triply degenerate transitions splits into two transitions of B symmetry and one of A symmetry. Finally, all the B transitions are mixed together and all the A transitions are mixed together by the C_2 ligand field. There is a further complication in that the low-symmetry ligand field perturbation is of the same order of magnitude as both the energy of the metal-ligand vibrations and the perturbation due to spin-orbit coupling. A detailed analysis of even the absorption spectrum of a low-symmetry pseudo-tetrahedral Co(II) complex is therefore rather difficult.

The overall magnitude of the circular dichroism spectrum (Fig. 7) is quite large especially in the region of the ${}^4A_2 \rightarrow {}^4T_2(T_d)$ transition where it reaches values comparable with those found for configurationally active D_3 tris-chelate Co(III) complexes. The circular dichroism between 14000 and 20000 cm^{-1} can clearly be identified as arising from the ${}^4A_2 \rightarrow {}^4T_1(P)$ (T_d) transition which is split into two components of B and one of A symmetry by the low-symmetry ligand field and further split by spin-orbit and vibronic effects. The ${}^4A \rightarrow {}^4A$ component of the ${}^4A_2 \rightarrow {}^4T_1(P)$ transition is expected to

have a very small rotational strength (the rotational strength would be zero in C_{2v} symmetry, see below) and the two ${}^4A \rightarrow {}^4B$ components are expected to mix with each other to give a circular dichroism couplet. As can be seen in Fig. 7, this is exactly the behaviour which is observed. The sign of the circular dichroism couplet is determined solely by the sense of twist about the C_2 axis. It seems, therefore, that it may be possible in favourable cases to predict the sense of twist of a pseudo-tetrahedral complex from the circular dichroism of the ${}^4A_2 \rightarrow {}^4T_1(P)$ transition although this possibility will certainly depend upon the low-symmetry ligand field splitting being large enough to dominate the spin-orbit and vibronic perturbations.

The two lower energy transitions are much more difficult to analyse. This is largely because, being closer in energy to each other, the low-symmetry components may overlap and in any case are extensively mixed. All the magnetic dipole transition moment arises (in the parent tetrahedral symmetry) from the ${}^4A_2 \rightarrow {}^4T_2$ transition and substantial circular dichroism is only observed in the ${}^4A_2 \rightarrow {}^4T_1$ transitions due to mixing by the low-symmetry ligand field. The problem of calculating the circular dichroism, especially for the two lowest energy transitions where the mixing is considerable, is almost entirely one of obtaining accurate eigenfunctions for a low-symmetry complex, a task which has been largely ignored by ligand field theory to date. The two positive circular dichroism bands seen between 8000 and 14000 cm^{-1} are certainly components of the ${}^4A_2 \rightarrow {}^4T_1(F)$ transition but it has not been possible as yet to identify any of the lower energy transitions without ambiguity.

A different kind of chiral pseudo-tetrahedral complex is typified by dichloro[$R(+)-N,N,N',N'$ -tetramethyl-1,2-propanediamine]cobalt(II) ($[\text{Co}(R\text{-Me}_4\text{pn})\text{Cl}_2]$). The structure of this complex is shown in Fig. 8 and its

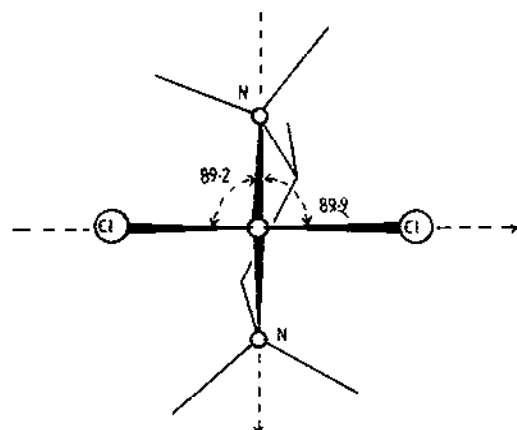


Fig. 8. A projection of the structure of $[\text{Co}(R\text{-Me}_4\text{pn})\text{Cl}_2]$ on a plane perpendicular to the pseudo- C_2 axis, and the angular distortions of the $[\text{CoN}_2\text{Cl}_2]$ cluster from C_{2v} symmetry.

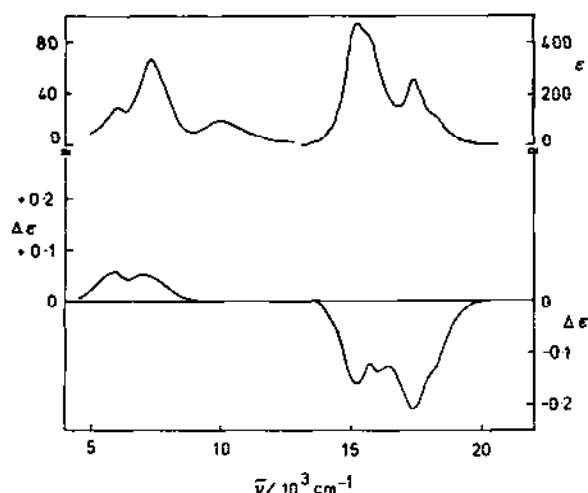


Fig. 9. The absorption spectrum (upper curve) and circular dichroism spectrum (lower curve) of $[\text{Co}(\text{R-Me}_4\text{pn})\text{Cl}_2]$ in CHCl_3 . Note the change in scale for the absorption spectrum (at 13000 cm^{-1}).

absorption and circular dichroism spectra in Fig. 9. To a very good approximation the CoN_2Cl_2 core has C_{2v} symmetry [31] (although the symmetry of the complex as a whole is C_1). This higher C_{2v} symmetry results in major differences in the electronic structure and spectra of $[\text{Co}(\text{R-Me}_4\text{pn})\text{Cl}_2]$ when compared with $[\text{Co}\{(-)\text{-spartein}\}\text{Cl}_2]$. In C_{2v} symmetry the ${}^4A_2 \rightarrow {}^4T_1(T_d)$ transitions split into ${}^4A_2 \rightarrow {}^4A_2 + {}^4B_1 + {}^4B_2$ (C_{2v}) and the ${}^4A_2 \rightarrow {}^4T_2$ transition into ${}^4A_2 \rightarrow {}^4A_1 + {}^4B_1 + {}^4B_2$ (C_{2v}). The ${}^4A_2 \rightarrow {}^4A_2$ transitions (transforming as A_1 in C_{2v} symmetry) are both electric- and magnetic-dipole forbidden and so should have no rotational strength. The energy region between 9000 and 13000 cm^{-1} (where there is absorption) was carefully searched [29] for circular dichroism. None could be detected and an upper limit of $|\Delta\epsilon| < 2 \times 10^{-3}\text{ l mol}^{-1}\text{ cm}^{-1}$ can be calculated from the sensitivity of the instrument. The absence of circular dichroism confirms that the ligator symmetry is effectively C_{2v} and unambiguously identifies the absorption band at 10000 cm^{-1} as the ${}^4A_2 \rightarrow {}^4A_2(T_1)$ transition. A second difference is that the two B components of the 4T_1 states transform differently (as B_1 and B_2) and so cannot mix with each other. This results in the circular dichroism of the ${}^4A_2 \rightarrow {}^4T_1(P)$ (T_d) transition being of one sign in contrast to the couplet pattern seen under the same transition in $[\text{Co}\{(-)\text{-spartein}\}\text{Cl}_2]$ which is caused by the mixing of the two $B(C_2)$ components of the ${}^4A_2 \rightarrow {}^4T_1(P)$ transition. The magnitude of the rotational strengths shown by $[\text{Co}(\text{R-Me}_4\text{pn})\text{Cl}_2]$ is perhaps surprisingly large since it must be induced by the vicinal effect of the diamine ligand rather than from a direct configurational effect as in $[\text{Co}\{(-)\text{-spartein}\}\text{Cl}_2]$. This may be mainly due to the

cancelling of rotational strength in the latter complex because of the extensive couplet structure and suggests that the optical activity of such compounds is even more comparable with the more familiar tris-chelate cases.

Despite the small number of spectra available at the moment, and our inability to fully interpret even these, the discussion above may give some hope that pseudo-tetrahedral complexes will play an important role in assigning configuration to sites in biological molecules in the future. More work is needed on model complexes, especially of strict D_2 and C_2 symmetry, and on the calculation of good eigenvalues for low-symmetry complexes.

C. CHARGE-TRANSFER CIRCULAR DICHROISM

(i) σ -Bonding tris-chelate complexes

While $d \leftrightarrow d$ (or $f \leftrightarrow f$) transitions are necessarily electric-dipole forbidden and have to acquire both dipole and rotational strength through some form of perturbation of the d orbitals, the intense charge-transfer transitions frequently seen in the UV (and sometimes visible) regions of the spectra of d transition metal complexes are electric-dipole allowed, arising from the transfer of an electron from a predominantly ligand orbital to a metal orbital or vice versa. Again, unlike the $d \leftrightarrow d$ transitions where it is possible to consider the chirality of the ligands or ligators as a perturbation on the achiral metal orbitals, the whole molecule must be considered as the chiral chromophore when dealing with charge-transfer transitions. This has the effect of making a theoretical treatment of charge-transfer circular dichroism more difficult or more prone to approximation than that for $d \leftrightarrow d$ circular dichroism but also means that in a sense charge-transfer circular dichroism should be a more direct function and probe of the chirality of the metal-ligand system as a whole.

The charge-transfer bands seen in the UV spectra of the saturated diamine tris-chelates of Co(III) and Cr(III) arise from the promotion of an electron from the t_{1u} symmetry σ -bonding orbitals of the nitrogen ligator set to the e_g^* σ -antibonding metal orbitals. In O_h symmetry this $t_{1u} \rightarrow e_g^*$ excitation leads to three transitions from the $^1A_{1g}$ ground state to excited states of $^1T_{1u}$, 1E_u and $^1A_{1u}$ symmetry, of which only the first is electric-dipole and none of which is magnetic-dipole allowed. In the D_3 symmetry of the complex ion the $^1T_{1u}$ state is split into components of 1E and 1A_2 symmetry and we would therefore expect the circular dichroism in the charge-transfer region to show a couplet of opposite and approximately equal rotational strengths. In fact in the quartz UV region of the spectrum of $[\text{Co}(\text{en})_3]^{3+}$ only one charge-transfer circular dichroism band is seen (at 48000 cm^{-1}) but on proceeding to the vacuum UV the second transition can be detected at 57000 cm^{-1} (Fig. 2).

The charge-transfer circular dichroism bands have opposite and nearly equal rotational strength in isotropic solution and the edge of the lower energy one has been shown to be *E* polarised in the single crystal. The dissymmetry factor ($\Delta\epsilon/\epsilon$) for the ${}^1A_{1g} \rightarrow {}^1T_{1u}$ charge-transfer transition is much lower than that for the magnetic-dipole allowed ${}^1A_{1g} \rightarrow {}^1T_{1g}$ ($d \leftrightarrow d$) transition ($\sim 3 \times 10^{-3}$ for the charge-transfer compared to $\sim 2 \times 10^{-2}$ for the $d \leftrightarrow d$ transition in isotropic solution) consistent with the former being magnetic-dipole forbidden in zero order. The combination of low dissymmetry factor and the difficulty of measuring circular dichroism in the far-UV region has resulted in the study of charge-transfer circular dichroism of saturated tris-chelate complexes being relatively neglected.

If the ${}^1A_1 \rightarrow {}^1E$ and 1A_2 transitions are considered to be directed along the bonds connecting the metal and the ligating atoms, the bond dipole-bond dipole interaction gives the energy order of the 1E and 1A_2 components as 1E lower than 1A_2 if the octahedron of ligators is trigonally compressed ($\alpha < 90^\circ$) and 1A_2 lower than 1E if the octahedron of ligators is trigonally expanded ($\alpha > 90^\circ$). The cobalt tris(ethylenediamine) ion is trigonally compressed ($\alpha = 85.4^\circ$) and so the lower energy charge-transfer band is expected to have *E* polarisation as is experimentally observed. It is interesting to note that the sense of the trigonal splitting is expected to be the same for the ${}^1T_{1u}$ charge-transfer and ${}^1T_{1g}$ *d*-electron states in the case of saturated tris-diamine complexes. If it is assumed that the position of the ligating atoms is the major source of chirality for the charge-transfer transitions, as it is for the magnetic-dipole allowed $d \leftrightarrow d$ transitions, then the sign of the charge-transfer circular dichroism should change as the angle of twist between the two triangles of ligating atoms changes sign. Since the sense of the trigonal distortion and the sign of the twist angle changes on going from Λ -

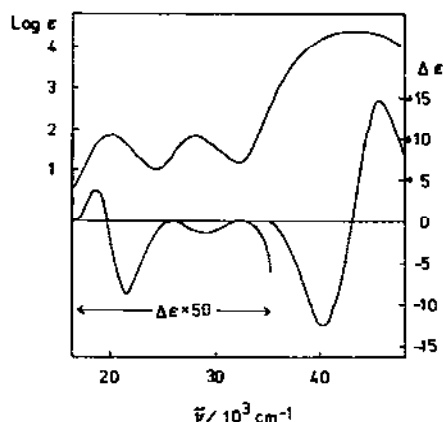


Fig. 10. The absorption spectrum (upper curve) and circular dichroism spectrum (lower curve) of Λ -[Co(en)₃][ClO₄]₃ in water.

TABLE 3

Calculated and experimental values of $\Delta\epsilon$ for the lowest charge-transfer circular dichroism band of $[\text{Co}(\text{en})_n(\text{S-pn})_{3-n}]^{3+}$ measured in aqueous solution

Complex	Conformation	$\Delta\epsilon$ (calc.)	$\Delta\epsilon$ (expt.)
$\Lambda\text{-}[\text{Co}(\text{en})_3]^{3+}$	$\delta\delta\delta$	-34	{ -32 ^a
	$\delta\delta\lambda$	-28	
$\Lambda\text{-}[\text{Co}(\text{S-pn})_3]^{3+}$	$\delta\delta\delta$	-34	-37
$\Lambda\text{-}[\text{Co}(\text{en})(\text{S-pn})_2]^{3+}$	$\delta\delta\lambda$	-28	-31
$\Lambda\text{-}[\text{Co}(\text{en})_2(\text{S-pn})]^{3+}$	$\delta\lambda\lambda$	-25	-25
$\Delta\text{-}[\text{Co}(\text{S-pn})_3]^{3+}$	$\delta\delta\delta$	+16	+16
$\Delta\text{-}[\text{Co}(\text{en})(\text{S-pn})_2]^{3+}$	$\delta\delta\lambda$	+21	+19
$\Delta\text{-}[\text{Co}(\text{en})_2(\text{S-pn})]^{3+}$	$\delta\lambda\lambda$	+28	+25

^a The $\delta\delta\lambda$ conformation is probably the major conformation in aqueous solution [35].

$[\text{Co}(\text{en})_3]^{3+}$ to $\Lambda\text{-}[\text{Co}(\text{tn})_3]^{3+}$ an identical sign pattern is expected in the charge-transfer circular dichroism of the Λ configuration of both ions with the lower energy transition being A_2 polarised in the case of $[\text{Co}(\text{tn})_3]^{3+}$. Unfortunately there is no single-crystal polarised circular dichroism spectrum available for the charge-transfer edge of $[\text{Co}(\text{tn})_3]^{3+}$ but the predicted sign pattern is found [32] experimentally in solution (Fig. 10). A comparison of the charge-transfer spectra of the five-membered ring tris(ethylenediamine) complex and the six-membered ring tris(trimethylenediamine) complex, however, shows that the energy and magnitude of the circular dichroism bands are very sensitive to ring conformation. (The Co-N bond lengths are identical within experimental error and the difference in the NCoN angles between the two complexes is unlikely to shift the baricentre of the charge-transfer transition by 10000 cm^{-1} .) Only one other saturated amine complex, $[\text{Co}\{(2R\text{-Me})\text{tacn}\}_2]^{3+}$, has had its circular dichroism measured [17] in the vacuum UV region; the charge-transfer circular dichroism is seen (Fig. 5) not to be a simple couplet but to consist of three bands which have a distinctly non-conservative rotational strength. It is not clear whence the extra transition arises, but charge transfer to the solvent is a possibility and a splitting of the E state in the lower (C_2) symmetry of the complex cannot be discounted.

The effect of ring conformation on the charge-transfer circular dichroism of the five-membered ring chelates can be illustrated by considering the series $[\text{Co}(\text{S-pn})_n(\text{en})_{3-n}]^{3+}$ (Table 3). The configurational and conformational contributions to the circular dichroism of the lowest energy charge-transfer transition can be shown to be approximately additive [18,33] with the Λ and Δ configurations contributing -25 and +25 $\Delta\epsilon$ units respectively while each chelate with a δ conformation contributes -3 and each chelate

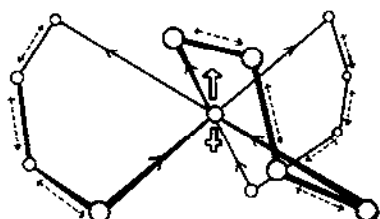


Fig. 11. The phase relationships between the charge displacements along the Co-N bonds (small arrows) of $\Lambda\text{-}[\text{Co}(\text{en})_3]^{3+}$ giving rise to the ${}^1A_1 \rightarrow {}^1A_2$ component (large arrow) of the ${}^1A_{1g} \rightarrow {}^1T_{1u}$ ligand-to-metal charge-transfer transition, and the coulombically correlated phases of the transient electric dipoles (broken arrows) induced in the C-C and C-N bonds by the radiation field.

with a λ conformation contributes $+3 \Delta\epsilon$ units. This shows clearly that any theoretical model for calculating the circular dichroism of the charge-transfer transitions of saturated diamine complexes must take the ring conformation into account and cannot rely on the ligand atoms as the only chiral perturbation. One possible source for the rotational strength of the charge-transfer transitions which takes into account the conformation of the ligand backbone is the ligand or bond polarisability model [18,34]. The required magnetic dipole moment is considered to arise from the correlation of the transient electric moments along the C-C and C-N bonds by the electric dipole transition moment of the charge-transfer transition (Fig. 11). The rotational strength of the charge-transfer transition is given [18] by

$$R_{\text{CT}} = \pi \tilde{\nu}_{\text{CT}} \sum_{\text{bonds}} \sum_{\text{transitions } o \rightarrow j} \frac{2 E_{oj}^l}{E_{\text{CT}}^2 - E_{oj}^2} V_{ml} \vec{\mu}_{\text{CT}} \cdot \vec{R}_{ml} \times \vec{\mu}_{oj}^t$$

where the summation is over all electric-dipole allowed transitions $o \rightarrow j$ of all the bonds l of the ligands (not the Co-N bonds), $\tilde{\nu}_{\text{CT}}$, E_{CT} and $\vec{\mu}_{\text{CT}}$ are respectively the wavenumber, energy and electric dipole transition moment vector of the charge-transfer transition, \vec{R}_{ml} is the vector connecting the metal centre to the mid-point of each bond l and V_{ml} is the coulombic correlation potential between the charge-transfer transition moment and the induced electric dipole moments along the bonds.

If V_{ml} is expanded and the sum over bond-located transition moment replaced by the parallel and perpendicular components of the electric-dipole polarisability, α_{\parallel} and α_{\perp} , the following expression [18] for the rotational strength of the ${}^1A_1 \rightarrow {}^1A_2$ transition is obtained

$$R_{\text{CT}}^{(A_2)} = -\pi \tilde{\nu}_{\text{CT}} |\vec{\mu}_{\text{CT}}|^2 \sum_{\text{bonds}} (\alpha_{\parallel} - \alpha_{\perp})_l [\vec{R}_{ml} \cdot (\vec{l}_m \times \vec{l}_l)] G_{ml}$$

where \mathbf{l}_m and \mathbf{l}_l are unit vectors along the molecular C_3 axis and the bond l respectively, and G_{ml} is the geometric factor for the coulombic correlation between two point dipoles. Clearly since the rotational strength is dependent upon both the polarisability and the orientation of the ligand bonds, configuration and conformational effects are taken into account by this mechanism.

If the C-H and N-H bonds of ethylenediamine are assumed to have isotropic polarisability and so not to contribute to the rotational strength, the major contributions to the rotational strength of the ${}^1A_1 \rightarrow {}^1A_2$ transition of $[\text{Co}(\text{en})_3]^{3+}$ will come from the C-C and C-N bonds. For $\Lambda\text{-}[\text{Co}(\text{en})_3]^{3+}$, which adopts the *lel* conformation ($\delta\delta\delta$) in the crystal, the major contribution will be from the C-N bonds; the C-C bonds, being nearly parallel to the C_3 axis of the ion, giving only a minor contribution (Fig. 11). Using literature values of polarisability and structural parameters the rotational strength of the ${}^1A_1 \rightarrow {}^1A_2$ charge-transfer transition of $\Lambda\text{-}[\text{Co}(\text{en})_3]^{3+}$ is calculated [18] to be $+1.8 \times 10^{-38}$ c.g.s. units which can be compared with the experimental value of $\sim +1.0 \times 10^{-38}$ c.g.s. units for the ion in solution. The complex ion exists as an equilibrium mixture [35] of conformational isomers in aqueous solution, the predominant conformation being $\delta\delta\lambda$. Since this isomer is expected to have a smaller charge-transfer rotational strength than the $\delta\delta\delta$ conformer used for the calculation, agreement between calculation and experiment is quite good. With the increasing availability of far-UV circular dichroism spectra it should be possible to test the theories of charge-transfer circular dichroism of tris-diamine complexes more thoroughly. Such spectra have a potential use not only in establishing absolute configuration but also in probing ligand conformation.

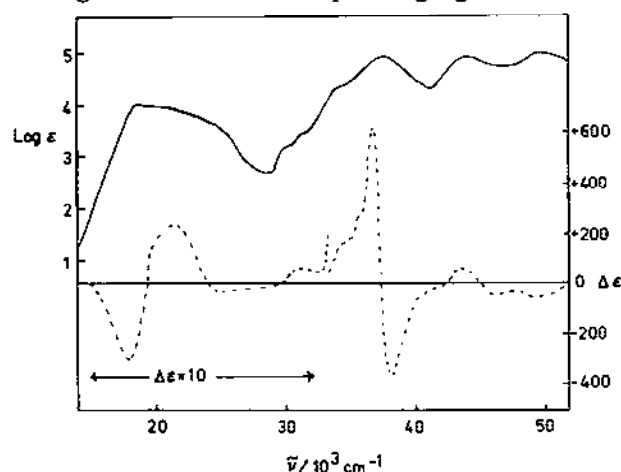


Fig. 12. The absorption spectrum (upper curve) and circular dichroism spectrum (lower curve) of $\Lambda\text{-}[\text{Fe}(\text{phen})_3]^{2+}$ in water.

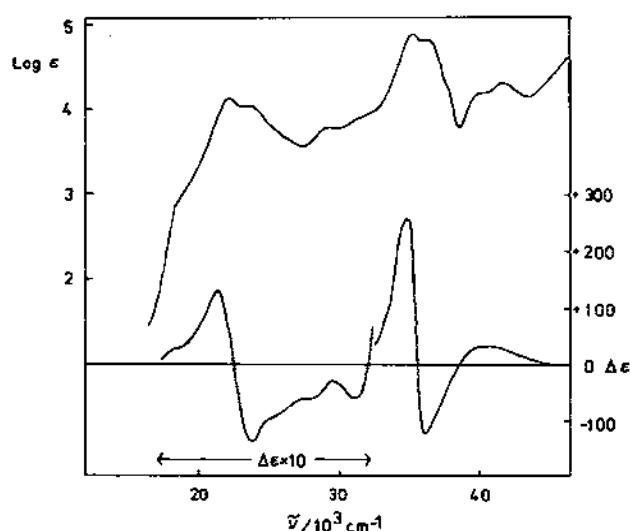


Fig. 13. The absorption spectrum (upper curve) and circular dichroism spectrum (lower curve) of Λ -[Ru(bipy) $_3$] $^{2+}$ in water.

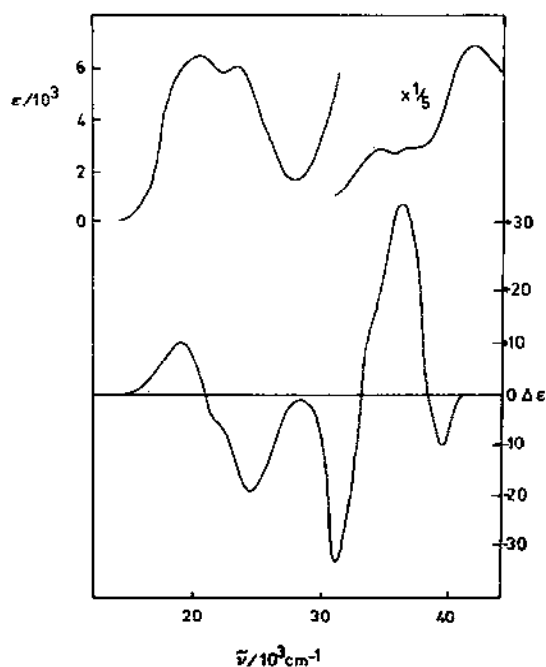


Fig. 14. The absorption spectrum (upper curve) and circular dichroism spectrum (lower curve) of (3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dionedioximato)nickel(IV) as the perchlorate salt in water. (The circular dichroism is of the enantiomer eluted first from an SP-Sephadex cation exchange column by a solution of potassium (+) antimonyl tartrate.)

(ii) π -Bonding tris-chelate complexes

In contrast to the tris-diamine complexes discussed above where the charge-transfer transitions occur in the UV region and are not always readily accessible, the charge-transfer transitions of tris-diimine complexes of the divalent and trivalent iron group metals [1] and tetravalent nickel [36] are found in the visible region. They are, in general, strong, well separated from the internal ligand transitions and overlay and obscure the $d \leftrightarrow d$ transitions of the metal ion (Figs. 12–14).

The charge-transfer transitions of the Fe(II), Ru(II) and Os(II) tris(bipyridyl) and tris(phenanthroline) complexes arise from the transfer of an electron from the filled t_{2g} orbital set on the metal ion to the vacant π -antibonding set of ligand orbitals of t_{1u} symmetry. This $t_{2g} \rightarrow t_{1u}$ one-electron excitation gives rise to four spin-allowed transitions in octahedral symmetry: ${}^1A_{1g} \rightarrow {}^1A_{2u}$, 1E_u , ${}^1T_{1u}$ and ${}^1T_{2u}$. Only ${}^1A_{1g} \rightarrow {}^1T_{1u}$ is electric-dipole allowed and this splits into two transitions, ${}^1A_1 \rightarrow {}^1A_2$ and ${}^1A_1 \rightarrow {}^1E$, in the D_3 symmetry of the complex ion. Although both of these transitions are symmetry allowed, only the E polarised transition has substantial electric dipole intensity; the A_2 transition can be shown to have no zero-order dipole strength by both calculation [37] and by orbital overlap considerations. The two other E polarised transitions, arising from ${}^1A_{1g} \rightarrow {}^1E_u$ and ${}^1A_{1g} \rightarrow {}^1T_{2u}$, can acquire dipole strength in D_3 symmetry by mixing with the ${}^1E({}^1T_{1u})$ state. The charge-transfer spectrum of, for example, $[\text{Ru}(\text{bipy})_3]^{3+}$ is expected, therefore, to be predominantly E polarised and this is observed experimentally [38,39] (Fig. 15).

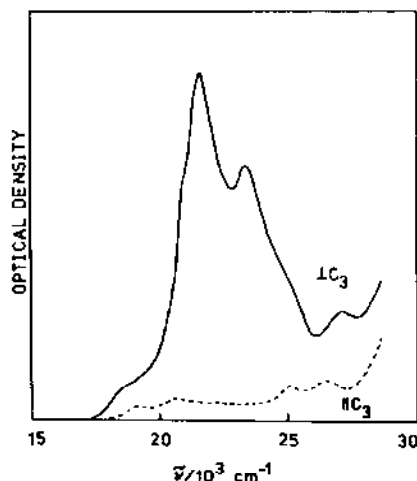


Fig. 15. The absorption spectrum of a single crystal of $[\text{Ru}(\text{bipy})_3]^{2+}$ doped in $[\text{Zn}(\text{bipy})_3][\text{SO}_4] \cdot 7\text{H}_2\text{O}$ with the light polarised perpendicular (full line) and parallel (dashed line) to the molecular C_3 axis.

The detailed assignment of the charge-transfer spectrum of $[\text{Ru}(\text{bipy})_3]^{3+}$ is still controversial but the identification of the two strong E polarised bands with the ${}^1A_1 \rightarrow {}^1E({}^1T_{1u})$ and ${}^1A_1 \rightarrow {}^1E({}^1E_u)$ transitions appears to be a strong possibility [40]. The solution circular dichroism spectrum of Λ - $[\text{Ru}(\text{bipy})_3]^{3+}$ in the charge-transfer region can be resolved convincingly [41] into five Gaussian bands, four of which coincide with E polarised features in the absorption spectrum. The band at 19100 cm^{-1} is a spin-forbidden transition, the one at 25300 cm^{-1} is a ligand localised transition and the two at 21900 cm^{-1} and 23600 cm^{-1} are the ${}^1A_1 \rightarrow {}^1E$ transitions referred to earlier. The fifth circular dichroism band at 21000 cm^{-1} , which does not correspond to a detectable feature in the solution absorption spectrum correlates with a weak A_2 polarised band in the crystal spectrum and is consequently assigned to A_2 symmetry.

The charge-transfer circular dichroism in tris-diimine complexes can be treated by the ligand polarisability theory in an analogous manner to that developed for tris-diamine complexes. The rotational strength resulting from the correlation of transient dipole moments induced in the ligands by the large electric moment of the charge-transfer transition is given by [34]

$$R_{\text{CT}} = \pi \tilde{\nu}_{\text{CT}} \sum_L \sum_{o \rightarrow j} \frac{2E_{oj}^2}{E_{\text{CT}}^2 - E_{oj}^2(L)} V_{\text{ML}} \vec{\mu}_{\text{CT}} \cdot \vec{R}_{\text{ML}} \times \vec{\mu}_{oj}^L$$

where the sum is taken over all transitions $o \rightarrow j$ of the ligands L .

Unlike the tris-diamine complexes, where the induced moments must be along the bonds of the ligand backbone, the major source of rotational strength in the tris-diimine complexes is expected to be from coupling with the long-axis polarised $\pi \rightarrow \pi^*$ transitions of the bipyridyl or phenanthroline ligand. Writing μ_L for the long-axis polarised transition moment of a single ligand and evaluating the vector cross product for the Λ configuration, the expression for the A_2 polarised rotational strength becomes

$$R_{\text{CT}}^{(A_2)} = -\frac{3}{2} \pi \tilde{\nu}_{\text{CT}} \left(\frac{2E_L}{E_{\text{CT}}^2 - E_L^2} \right) \frac{|\mu_{\text{CT}}^{A_2}|^2 |\mu_L^{A_2}|^2}{R_{\text{ML}}^2}$$

The expression can also be written in terms of the rotational strength of the exciton-coupled ligand transition of appropriate symmetry, $R_{\text{ex}}^{(A_2)}$

$$R_{\text{CT}}^{(A_2)} = -\left(\frac{2E_L}{E_L^2 - E_{\text{CT}}^2} \right) \frac{|\mu_{\text{CT}}^{A_2}|^2 R_{\text{ex}}^{(A_2)}}{R_{\text{ML}}^3}$$

and in this form reveals the expectation that the rotational strength of the charge-transfer transition should be of opposite sign to that of the ligand exciton transition with the same symmetry. The analogous expression for an

E polarised transition is

$$R_{CT}^{(E)} = - \left(\frac{E_{CT}}{E_L^2 - E_{CT}^2} \right) \frac{|\mu_{CT}^E|^2 R_{ex}^{(E)}}{R_{ML}^3}$$

The reason why the charge-transfer rotational strength should be of opposite sign to the ligand exciton rotational strength for transitions of the same symmetry is illustrated in Fig. 16. The charge-transfer electric dipole moment induces a resultant parallel electric moment in the ligands. This moment must be correlated in the opposite direction from μ_{CT} to minimise the dipole-induced dipole energy. Since the magnetic moment is the very same for the charge-transfer and the ligand transitions, the resulting rotational strengths are, of necessity, of opposite sign.

The alternative source of rotational strength for charge-transfer transitions, direct borrowing from ligand transitions, would result in the charge-transfer transition having the same sign of rotational strength as the ligand transition of appropriate symmetry. The two mechanisms should, if the assignments of ligand and charge-transfer transitions are known, be distinguishable.

Using experimentally determined values of the *E* polarised charge-transfer dipole strengths, the *E* polarised ligand exciton rotational strength and the appropriate energies, and taking the distance between the metal and the

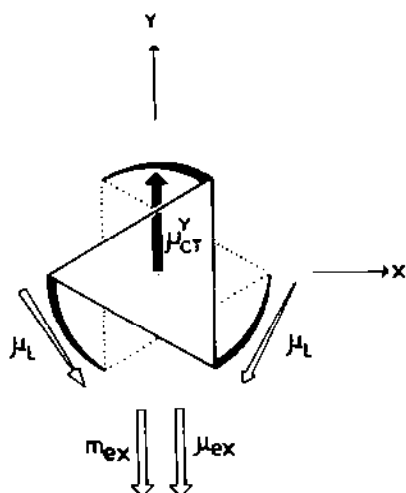


Fig. 16. The phase relationships between the *Y* component (μ_{CT}^Y) of a metal-to-ligand charge-transfer transition of *E* symmetry and the long-axis polarised ligand electric dipole transitions (μ_L) induced by the radiation field showing how the resultant magnetic dipole transition moment $\vec{m}_{ex} [= \sum_L (\vec{R}_{HL} \times \vec{\mu}_L)^Y]$ in the *Y* direction gives rise to rotational strengths with opposing signs for the charge-transfer ($R_{CT} = i\vec{\mu}_{CT} \cdot \vec{m}_{ex}$) and exciton-coupled ligand ($R_{ex} = -i\vec{\mu}_{ex} \cdot \vec{m}_{ex}$) transitions of the same symmetry.

induced dipole on the bipyridyl ligand as 300 pm, the two *E* polarised charge-transfer circular dichroism bands of Λ -[Ru(bipy)₃]³⁺ are calculated to have $\Delta\epsilon_{\text{max}}$ values of approximately -10 and -11 (dm³ mol cm⁻¹) which can be compared with the experimental values of -12 and -4. The ligand polarisation model can, then, clearly predict the sign and order of magnitude of the *E* polarised charge-transfer circular dichroism of tris-diimine complexes although the closeness of the agreement in magnitude may be somewhat fortuitous. The model cannot, however, account for the magnitude of the *A*₂ polarised circular dichroism since the *A*₂ polarised charge-transfer absorption is very small (about one twentieth of the magnitude of the *E* polarised absorption) and the calculated value (+0.1) of $\Delta\epsilon_{\text{max}}$ for the transition is too small by a factor of ~100. Direct borrowing of rotational strength from the *A*₂ polarised ligand exciton transition would give the wrong sign of circular dichroism and the only obvious explanations are either that the rotational strength is being borrowed from very high-energy transitions or that the circular dichroism is not that of a charge-transfer band at all. Unfortunately neither [Ru(bipy)₃]³⁺, nor any other tris-diimine complex, has had its single-crystal circular dichroism measured and in the absence of this information the final assignment of the circular dichroism spectrum of the complex must remain open.

D. CONCLUDING REMARKS

Our understanding of the circular dichroism spectra of transition metal ion complexes has come a long way since the pioneering single crystal study of 2Co(en)₃Cl₃ · NaCl · 6 H₂O by McCaffery and Mason [12]. There are, however, a number of significant areas in which this understanding is still rather limited or where experimental measurements have not kept pace with the development of theoretical models.

Probably the most important aspect of circular dichroism which is still imperfectly understood is the contribution made by vibronic interactions to the rotational strength of *d* ↔ *d* transitions. Only two experimental studies have been published of vibronic structure in the spectra of Co(III) complexes with saturated diamine ligands [21,22] and both of these have posed more questions than they have answered. The major reason why so little work has been done in this area is that the spin-allowed transitions of Co(III) and Cr(III) complexes are notorious for showing little resolved vibronic structure even at low temperatures in single crystals. The intraconfigurational spin-forbidden ⁴A₂ ↔ ²E transitions of Cr(III) complexes do show considerable vibronic structure both in absorption and emission and have been studied recently for the [Cr(en)₃]³⁺ ion by both circular dichroism [42] and circularly polarised luminescence [43] spectroscopy. Detailed studies of the circular

dichroism and circularly polarised luminescence of the intraconfigurational transitions of a variety of Cr(III) complexes will, we believe, place our appreciation of the relative importance of the vibronic and static contributions to the optical activity of tris-chelate complexes on a firmer footing.

The polarised single crystal circular dichroism spectra of remarkably few complexes have been measured despite the unique ability of this technique to assign transitions without ambiguity. There are, for example, no uniaxial single crystal circular dichroism spectra of the $d \leftrightarrow d$ transitions of tris-chelated complexes with unsaturated ligands; nor has the single crystal circular dichroism of a charge-transfer spectrum of any tris-diimine complex been published. The problem is experimental: the absence of a suitable transparent uniaxial host into which the complex can be doped. The absence of such spectra severely restricts our understanding of the optical activity in the types of complex concerned. The problem is particularly acute in the case of the tris-diimine complexes such as $[\text{Ru}(\text{bipy})_3]^{2+}$ where an assignment of the circular dichroism spectra could be of considerable help in understanding the electronic spectrum as a whole.

Finally, we feel that the circular dichroism spectra of the pseudo-tetrahedral complexes of the divalent transition metal ions are an area ripe for future investigation. So far spectra have been obtained for complexes of relatively low symmetry (C_2 molecular symmetry with, at highest, C_{2v} chromophoric symmetry) where the calculation of accurate eigenfunctions is an extremely difficult task. The problem could be solved more easily if complexes of higher symmetry, for example D_2 , could be prepared. A fuller appreciation of such model systems should make the interpretation of the circular dichroism spectra of many bio-inorganic complexes a real possibility for the future.

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