The *d*-Electron Optical Activity of Tetrahedral Dichloro[(−)-spartein]cobalt(II)

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The absorption and circular dichroism spectra of the title complex, $[CoCl_2L^1]$, have been recorded over the range of the *d–d* transition manifold, 2 000—20 000 cm^{-1}. The spectra are discussed in terms of the dynamic ligand-polarization mechanism for *d–d* transition probabilities.

THE investigation of the optical activity of chiral transition-metal complexes has been confined, hitherto, largely to the optical isomers first isolated by Werner.[1] These enantiomers are mainly six-co-ordinate chelate complexes of the metal(III) ions with a d^3 or spin-paired d^6 configuration, affording an orbitally non-degenerate ground state, and with ligands at a position in the spectrochemical series ensuring *d–d* absorption in the readily accessible visible or quartz u.v. region. The principal features of the *d–d* absorption and circular dichroism (c.d.) spectra of the dihedral (D_3) tris chelate complexes were early established,[2,3] and the first quantum mechanical interpretation of *d*-electron optical activity, employing crystal-field theory, was based upon the c.d. spectra of these complexes.[4]

Crystal-field theory proved to have a limited application to the analysis of *d–d* optical activity.[5] A pseudoscalar crystal field, required for a first-order *d–d* optical activity, was found [6] to give a vanishing contribution in a chiral complex with octahedral co-ordination, while the corresponding second-order approach gave crystal-field *d–d* rotational strengths at variance with the observed c.d. spectra of D_3 complexes.[7] An alternative treatment of *d–d* optical activity, based upon the dynamic polarization of the ligands by the potential of the leading electric moment of the *d–d* transition, an even multipole, provides a less limited analysis of the c.d. spectra of chiral six-co-ordinated complexes of cobalt(III), whether tris chelate,[8] or hexakis unidentate,[9] as in the case of (*R*)-(+)-*all-cis*-$[Co(NH_3)_2(OH_2)_2(CN)_2]^+$.

As yet, few studies have been reported, either experimental or theoretical, of the *d*-electron optical activity of chiral metal complexes with tetrahedral co-ordination, in contrast to the extensive investigation of their octahedrally co-ordinated analogues.[5,10] The main quasi-tetrahedral chiral complexes at present well characterised belong to the $[M^{II}X_2(\text{diamine})]$ series, where M^{II} is a transition-metal ion of the first long period, X is a halide or pseudohalide ion, and the diamine is chiral and ditertiary. The diamines employed [11-14] are (−)-spartein (L^1), and its epimers, (−)-α-isospartein (L^2) and (+)-β-isospartein (L^3), or their antipodes, together with [15] (*R*)-(+)-*NNN′N′*-tetramethyl-1,2-propylenediamine (L^4). The molecular structures of $[CuCl_2L^{3'}]$, $L^{3'}$ = (−)-β-isospartein,[16] $[CoCl_2L^1]$, [17] $[CoCl_2L^2]$,[18] and $[CoCl_2L^4]$,[19] determined by *X*-ray crystallography, show that the co-ordination is tetrahedral, although the molecular and chromophoric (MN_2Cl_2) symmetry at the highest is C_2 (Figure 1).

The present work reports the absorption and c.d. spectrum of $[CoCl_2L^1]$ over the frequency region (2 000—20 000 cm^{-1}) of the *d–d* manifold (Figure 2). The aim of the study is an extension of the analysis of *d–d* optical activity in terms of the dynamic ligand-polarization mechanism to chiral complexes with tetrahedral co-ordination and to analogues with co-ordination polyhedra other than octahedral. Owing to the smaller ligand field of tetrahedral cobalt(II), relative to octahedral cobalt(III), two of the three main *d–d* band systems of $[CoCl_2L^1]$ lie in the i.r. region. The recent development [20-22] of i.r.c.d. spectrophotometers with a sensitivity adequate for the detection of vibrational optical activity permits the characterisation of the electronic *d*-electron optical activity in detail, including a Fano [23] anti-resonance effect in the c.d. spectrum [24] observed [25] between the vibrational C–H stretching modes of the

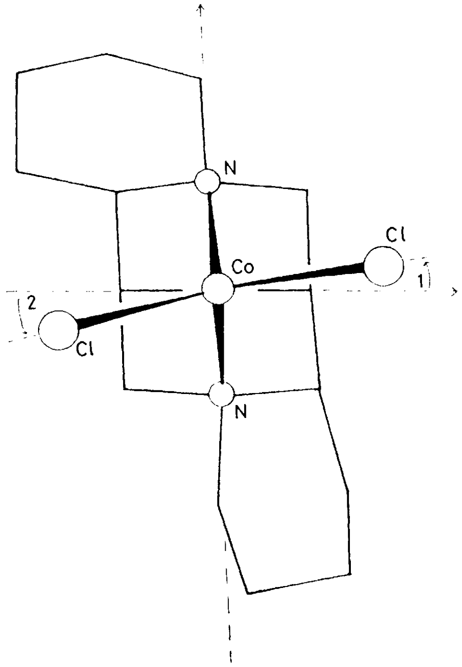
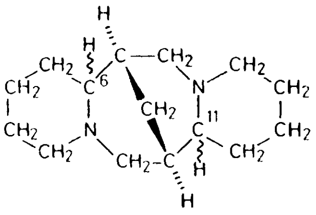
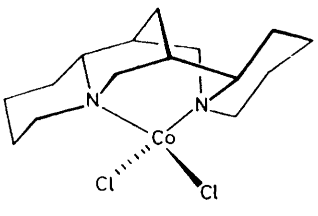


FIGURE 1 A projection of the molecular structure of $[CoCl_2L^1]$ on the *XY* plane perpendicular to the pseudo-$C_2(Z)$ axis. In the projection the distortion angles are 6.2° for Cl(1) and 10.0° for Cl(2)

ligand (L^1) and the electronic *d–d* transition in $[CoCl_2L^1]$. As the complex is insufficiently soluble in CCl_4, a solution of $[CoCl_2L^1]$ in $CDCl_3$ was required over the C–H stretching vibration region of the ligand (2 750—2 900 cm^{-1}), solutions in $CHCl_3$ being otherwise employed, since hydroxylic solvents are precluded below *ca.* 1.0 μm.



(L^1) (6*R*, 11*S*)
(L^2) (6*R*, 11*R*)
(L^3) (6*S*, 11*S*)



$[CoCl_2L^1]$

RESULTS AND DISCUSSION

The absorption and c.d. spectra of the complex $[CoCl_2L^1]$ over the range of the *d–d* manifold divide into three regions, characterised by the dissymmetry ratio of Kuhn,[3] $g = (\Delta\varepsilon/\varepsilon)$. The *g* ratio differs by an order of magnitude between the three regions, having the values $|g|$ *ca.* 4×10^{-2} (2 000—7 000 cm^{-1}), *ca.* 3×10^{-3} (7 000—12 000 cm^{-1}), and *ca.* 4×10^{-4} (15 000—20 000 cm^{-1}) (Figure 2). The absorption and c.d. in each of the three regions corresponds to the low-symmetry components of the tetrahedral cobalt(II) *d–d* transitions, $^4A_2 \rightarrow {}^4T_2(F)$, $^4T_1(F)$, and $^4T_1(P)$ respectively. Over the band areas of an absorption feature as a whole, the *g* factor represents the ratio of the rotational strengths to the dipole strength of the transition, $g = 4R/D$. The rotational strength, *R*, is given by the scalar product of the magnetic-dipole, *m*, and the electric-dipole, μ, transition moments, while the dipole strength, *D*, is the square modulus of the latter moment, $|\mu|^2$. A substantial *g* ratio ($g \geqslant 10^{-2}$) indicates that the corresponding transition has a large magnetic dipole moment, with generally, but not necessarily, a small electric dipole moment.[26]

The lowest-energy tetrahedral cobalt(II) transition, $^4A_2 \rightarrow {}^4T_2(F)$, is made up, together with two equivalent orthogonal excitations, of the single *d*-orbital promotion, $d_{x^2-y^2} \rightarrow d_{xy}$, which has a magnetic dipole ($m_z = 2$ B.M.*) and an electric hexadecapole, $H_{xy(x^2-y^2)}$, as the leading transition moments.[8] The field of the electric 2^4-pole transition moment, $H_{xy(x^2-y^2)}$, in a complex with regular tetrahedral co-ordination produces no overall constructive correlation of the electric dipoles induced in each of the co-ordinated ligand atoms, but a D_2 or lower-symmetry distortion of the complex affords a constructive correlation, giving a non-vanishing resultant induced electric dipole (Figure 3). The resultant constitutes the first-order ligand-polarization electric-

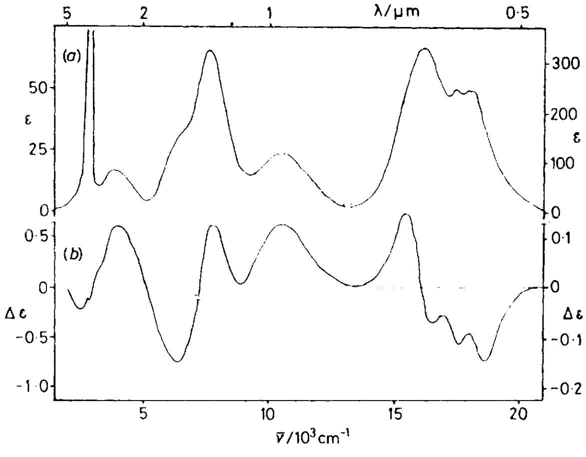


FIGURE 2 The absorption spectrum (*a*) and circular dichroism (*b*) of $[CoCl_2L^1]$ in $CHCl_3$ or $CDCl_3$ solution over the *d–d* transition range. The absorption due to the ligand C–H stretching vibrations ($\varepsilon_{max.}$ 300 dm^3 mol^{-1} cm^{-1}) is truncated. Note the change in scale for the c.d. ($\Delta\varepsilon$) at 7000 cm^{-1} and the absorption spectrum (ε) at 13 000 cm^{-1}

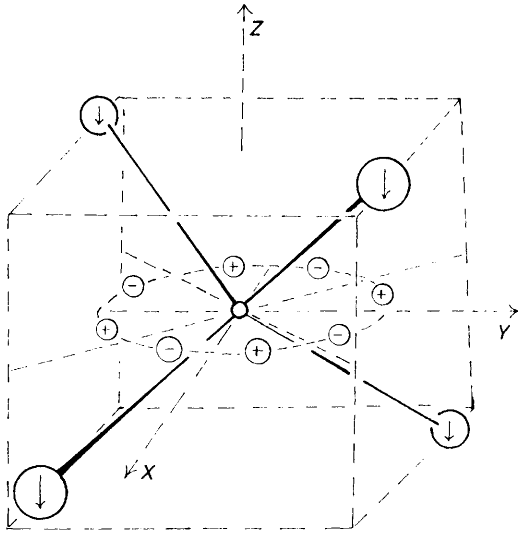


FIGURE 3 The Coulombic correlation of the z component of the electric dipole induced in each of the co-ordinated ligand atoms by the $xy(x^2 - y^2)$ component of the electric-hexadecapole transition moment for the $d_{x^2-y^2} \rightarrow d_{xy}$ excitation in a chirally distorted tetrahedral metal complex of D_2 or lower symmetry

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* Throughout this paper: 1 B.M. $= 9.274 \times 10^{-24}$ A m^2.

dipole moment of the *d–d* transition, and it has *z* polarization in the isotropic ligand-polarizability approximation,[10] equation (1).

$$\mu_z^{dd'} = -H'_{xy(x^2-y^2)}{}^{dd} \sum_{\mathrm{L}} \bar{\alpha}(\mathrm{L})\ G_{xyz,x^2-y^2)}{}^{\mathrm{L}} \qquad (1)$$

In equation (1), the sum is taken over the ligand atoms or groups, L, each with the mean polarizability, $\bar{\alpha}$(L), at the *d–d* transition frequency, and $G_{xyz(x^2-y^2)}{}^{\mathrm{L}}$ is the geometric tensor of angular and radial factors governing the potential between the electric hexadecapole, $H_{xy(x^2-y^2)}$, centred on the metal ion and the *z* component of an electric dipole, μ_z, located in the ligand group or atom, L, where *X*, *Y*, *Z* refer to the Cartesian co-ordinates of

$$G_{xyz(x^2-z^2)}{}^{\mathrm{L}} = 315XYZ(Y^2 - X^2)/R_{\mathrm{ML}}{}^{11} \qquad (2)$$

the ligand group, L, in the tetrahedral frame with the metal ion as origin (Figure 3). As the geometric tensor [equation (2)] vanishes for regular tetrahedral co-ordination, the minor angular distortions of the co-ordinated ligand atoms in [CoCl$_2$L^1] from the tetrahedral location (Figure 1) give the $d_{x^2-y^2} \rightarrow d_{xy}$ transition, and the two equivalent excitations producing the $^4T_2(F)$ tetrahedral cobalt(II) state, only a small first-order electric-dipole transition moment [equation (1)]. The first-order electric dipole moment is, however, collinear with the zero-order magnetic dipole moment, giving each of the three components of the tetrahedral $^4A_2 \rightarrow {}^4T_2(F)$ cobalt(II) transition in [CoCl$_2$L^1] a large rotational strength, while the corresponding dipole strength is small. Thus the *g* ratio is large for each of the three c.d. and absorption bands of [CoCl$_2$L^1] observed over the 2 000—7 000 cm^{-1} region (Figure 2).

In the cubic description, the higher-energy *d–d* transitions of a tetrahedral cobalt(II) complex, $^4A_2 \rightarrow {}^4T_1(F)$, $^4T_1(P)$, derive a non-zero transition probability from the one-electron promotion, $d_{z^2} \rightarrow d_{xy}$, and two equivalent orthogonal excitations. Both the $^4T_1(F)$ and the $^4T_1(P)$ excited state are represented by linear combinations of one-electron ($e^3t_2{}^4$) and two-electron ($e^2t_2{}^5$) excited configurations, and promotions from the ground configuration ($e^4t_2{}^3$) to the two-electron excited configuration have a vanishing transition probability in a radiation field. The leading moment of the one-electron excitation, $d_{z^2} \rightarrow d_{xy}$, is the *xy* component of an electric quadrupole, θ_{xy}, but there is no accompanying magnetic-dipole moment in this case, nor that of the equivalent orthogonal excitations.

The constructive correlation of the electric dipoles induced in each co-ordinated ligand atom or group by the field of the *d–d* quadrupole transition moment, θ_{xy}, is an optimum [27] in four-co-ordinate complexes at regular tetrahedral co-ordination for a given metal–ligand bond distance (Figure 4). The resultant first-order electric-dipole transition moment, located wholly in the ligands, is relatively large in this case, being given by the expression (3). The geometric tensor in equation (3) governing

$$\mu_z^{dd'} = -\theta_{xy}{}^{dd'} \sum_{\mathrm{L}} \bar{\alpha}(\mathrm{L})\ G_{xyz}{}^{\mathrm{L}} \qquad (3)$$

the potential between the *z* component of an electric dipole and the *xy* component of an electric quadrupole has the form (4) where *X*, *Y*, *Z* represent the Cartesian

$$G_{xyz}{}^{\mathrm{L}} = -15(XYZ/R_{\mathrm{ML}}{}^7) \qquad (4)$$

co-ordinates of the ligand, L, in the tetrahedral frame centred on the metal ion, with a metal–ligand bond length, R_{ML} (Figure 4).

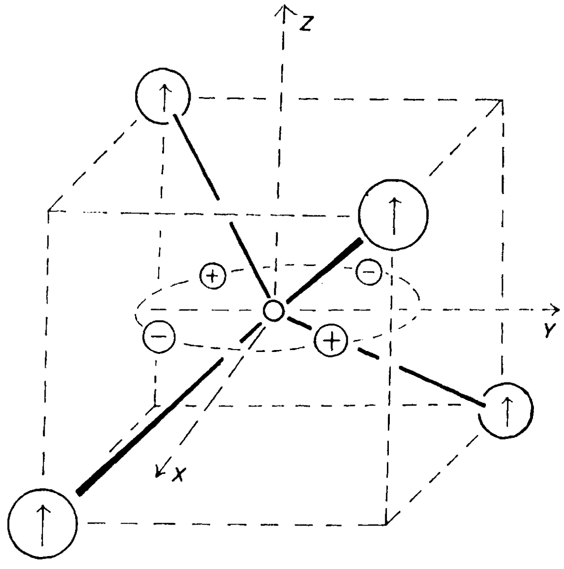

FIGURE 4 The Coulombic correlation of the *z* component of the electric dipole induced in each of the co-ordinated ligand atoms by the *xy* component of the electric-quadrupole transition moment for the $d_{z^2} \rightarrow d_{xy}$ excitation in a tetrahedral metal complex

Steric distortions from regular tetrahedral co-ordination reduce the resultant first-order electric-dipole transition moment induced in the ligands by the *d–d* electric quadrupole moment [equations (3) and (4)], but the moment remains substantial in complexes, such as [CoCl$_2$L^1], where the angular distortions are not large. More significantly, the distortions limit the validity of the cubic description, and the allowed and the forbidden magnetic-dipole *d–d* transitions become mixed to a degree dependent, among other factors, upon the inverse of the energy separation between the allowed and the forbidden magnetic-dipole transition types. The magnetic-dipole allowed *d–d* transitions of [CoCl$_2$L^1], with $^4A_2 \rightarrow {}^4T_2(F)$ tetrahedral cobalt(II) parentage, lie in the 2 000—7 000 cm^{-1} region, and the *g* ratios of the higher-energy band systems, those with $^4A_2 \rightarrow {}^4T_1(F)$, $^4T_1(P)$, tetrahedral parentage in the 7 000—12 000 cm^{-1} and 15 000—20 000 cm^{-1} region respectively, reflect the reduced mixing of allowed and forbidden magnetic-dipole *d–d* transitions with increasing energy separation (Figure 2).

A detailed treatment of the absorption and c.d. spectrum of [CoCl$_2$L^1] requires a quantitative knowledge of the mixing of the *d–d* transition types or, what is equivalent, of the particular composition of the *d*-electron states. General observations, not requiring such detailed information, are that equation (1) and its analogues for the two other components of the tetrahedral $^4A_2 \rightarrow {}^4T_2$ transition give the correct order of magnitude and the signs of the three major c.d. bands observed over the 2 000—7 000 cm^{-1} region, and that equation (3) and its analogues for the two other components of the $^4A_2 \rightarrow {}^4T_1(e^3t_2^4)$ excitation account for a substantial fraction of the total dipole strength measured over the 7 000—20 000 cm^{-1} region (Table). For both regions, the *X*-ray crystallographic data[17] for the complex [CoCl$_2$L^1] were employed to evaluate the appropriate geometric tensors [equations (2) and (4)] for the co-ordinated atoms of the CoN$_2$Cl$_2$ chromophore (Figures 3 and 4). The Cartesian *X*, *Y*, *Z* co-ordinate frame of equations (2) and (4) is not symmetry-determined in quasi-tetrahedral complexes of lower than D_2 point symmetry. Accordingly the *Z* axis was taken as the quasi-C_2 axis of [CoCl$_2$L^1], and the bisectors of the larger and the smaller dihedral angle between the NCoN and the ClCoCl planes were chosen as the *X* and the *Y* axis, respectively, so that the CoN$_2$Cl$_2$ chromophore is considered essentially as a perturbed D_2 system (Figure 3).

The dipole strengths, *D*, and rotational strengths, *R*, observed for the [CoCl$_2$L^1] complex and calculated for the component *d–d* transitions of the CoN$_2$Cl$_2$ chromophore. The calculated quantities refer to the expectation values, $\langle r^2 \rangle = 0.366$ Å^2 and $\langle r^4 \rangle = 0.443$ Å^4, appropriate for a dipositively charged cobalt ion, and to the mean polarizability values, $\bar{\alpha}(\text{N}) = 1.50$ Å^3 and $\bar{\alpha}(\text{Cl}^-) = 3.50$ Å^3

Transition from $^4A_2(e^4t_2^3)$		Theor.		Expt.		
		10^2R/dβ[a]	10^2D/d^2	10^2R/dβ	10^2D/d^2	$10^{-3}\nu$/cm^{-1}
$^4T_2(e^3t_2^4)$	*x*	−6.92	0.12	−0.8	*b*	2.5
	y	15.88	0.63	4.4	4.3	4.0
	z	−8.96	0.20	−3.9	*c*	6.5
$^4T_1(e^3t_2^4)$		0	36.70	0.28	11.6	7.7
				0.50	4.2	10.6
				0.21	37.5	16.0
				−0.45	24.5	18.2

[a] 1 d ≈ 3.336 × 10^{-30} C m (10^{-18} c.g.s. units); 1 dβ (Debye Bohr magneton) = 3.094 × 10^{-53} A C m^3 (9.27 × 10^{-39} c.g.s. units). [b] Overlaid by the absorption due to the C–H stretching fundamentals of the (−)-spartein ligand. [c] Shoulder absorption (Figure 2).

The electric-multipole transition moments of equations (1) and (3) were obtained by the method of Griffith.[28] In units of the electron charge, the values are those given in (5) and (6). The radial expectation values for

$$\langle d_{z^2}|\theta_{xy}|d_{xy}\rangle = -\langle r^2\rangle\ (2/7\sqrt{3}) \tag{5}$$

$$\langle d_{x^2-y^2}|H_{xy(x^2-y^2)}|d_{xy}\rangle = \langle r^4\rangle\ (2/21) \tag{6}$$

a 3*d* electron of cobalt were calculated from double-exponent wavefunctions[29] for the range from the dipositively charged ion to the neutral atom, representing the limiting effective charge states of the cobalt atom in the complex [CoCl$_2$L^1]. The values of $\langle r^2\rangle$ obtained are 0.569 and 0.366 Å^2 for neutral and dipositively charged cobalt respectively, and the corresponding $\langle r^4\rangle$ values are 0.835 and 0.443 Å^4 respectively. The calculated dipole and rotational strengths recorded (Table) are based upon the radial expectation values for dipositively charged cobalt. The corresponding values for neutral cobalt increase the theoretical rotational and dipole strengths of the $^4A_2 \rightarrow {}^4T_2$ components by a factor of 1.9 and 3.5 respectively, and the total dipole strength of the $^4A_2 \rightarrow {}^4T_1(e^3t_2^4)$ components by a factor of 2.4. The mean polarizability values[30] employed in the calculations are 1.50 and 3.50 Å^3 for the nitrogen and the chloride ligand, respectively.

It is concluded from the observed spectrum and the ligand-polarization analysis that the degree of mixing between the $^4A_2 \rightarrow {}^4T_2$ and the $^4A_2 \rightarrow {}^4T_1(e^3t_2^4)$ transition components in the complex [CoCl$_2$L^1] is surprisingly small, in view of the large perturbations from tetrahedral symmetry in the CoN$_2$Cl$_2$ chromophore. Most of the rotational strength remains localised in the magnetic-dipole allowed components of the $^4A_2 \rightarrow {}^4T_2$ manifold, and the major part of the dipole strength is restricted to the electric-quadrupole allowed components of the $^4A^2 \rightarrow {}^4T_1(e^3t_2^4)$ manifold, for which the ligand-polarization mechanism is particularly effective (Table). The calculated rotational strengths of the $^4A_2 \rightarrow {}^4T_2$ compounds are too large, due in part to the overlap on the frequency ordinate of the major rotational strengths with opposed signs and in part to the minor sequestration of rotational strength by the $^4A_2 \rightarrow {}^4T_1(e^3t_2^4)$ components (Table, Figure 2).

EXPERIMENTAL

Materials.—The complex [CoCl$_2$L^1] was prepared as previously described.[11]

Spectra.—These were measured with a Cary 17 (absorption) and a Jasco J 40 CS (circular dichroism) over the 10 000—20 000 cm^{-1} range. A laboratory-constructed instrument, recording both absorption and circular dichroism,[22] was employed over the 2 000—10 000 cm^{-1} range.

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