Crystal Circular Dichroism and Spin-forbidden Optical Activity of Tris(diamine)cobalt(III) Complexes

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The axial crystal circular dichroism spectrum of $2\{\Lambda(+)[Co(en)_3]Cl_3\}\cdot NaCl\cdot 6H_2O$ (en = ethylenediamine) at liquid-nitrogen and ambient temperature has been measured, together with the corresponding aqueous-solution spectrum and those of $\Lambda(+)[Co\{(S)(pn)\}_3]^{3+}$ and $\Lambda(-)[Co(pd)_3]^{3+}$, over the range 500—1 000 nm (pn = propylenediamine and pd = propane-1,3-diamine). The optical activity associated with the spin-forbidden transitions to the $^3T_1$ and $^3T_2$ octahedral states has distinctive features which are accounted for satisfactorily by spin–orbit coupling between these states and, principally, the corresponding $^1T_1$ state.

THE optical activity associated with the spin-allowed *d*-electron transitions of chiral tris(diamine)cobalt(III) complexes has been accounted for recently by means of a dynamic-coupling ligand-polarisation model.[1] In this model a non-vanishing rotational strength is provided by the coupling of induced electric-dipole moments in the groups of the chelate rings with the intrinsic magnetic-dipole moment of the *d*-electron transition in the metal ion through the leading electric-multipole moment of the transition. The analysis is based on

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[1] S. F. Mason and R. H. Seal, *J.C.S. Chem. Comm.*, 1975, 331; *Mol. Phys.*, 1976, **31**, 755.

single-crystal linear dichroism[2] and circular dichroism (c.d.)[3] studies of $2\{\Lambda(+)[Co(en)_3]Cl_3\}\cdot NaCl\cdot 6H_2O$ (en = ethylenediamine) and of other tris(diamine)cobalt(III) salts with a known crystal structure and absolute configuration.[4]

In order to analyse the optical activity connected with the corresponding spin-forbidden *d*-electron transitions, the axial c.d. study of the crystal $2\{\Lambda(+)[Co(en)_3]Cl_3\}\cdot NaCl\cdot 6H_2O$ has been extended in the present work to the 525—1 000 nm wavelength region of the singlet–triplet transitions with ${}^1A_1 \rightarrow {}^3T_1, {}^3T_2$ octahedral parentage in the $[Co^{III}N_6]$ chromophore. The single-crystal linear dichroism of the corresponding racemic salt over the same wavelength range has been reported recently.[5]

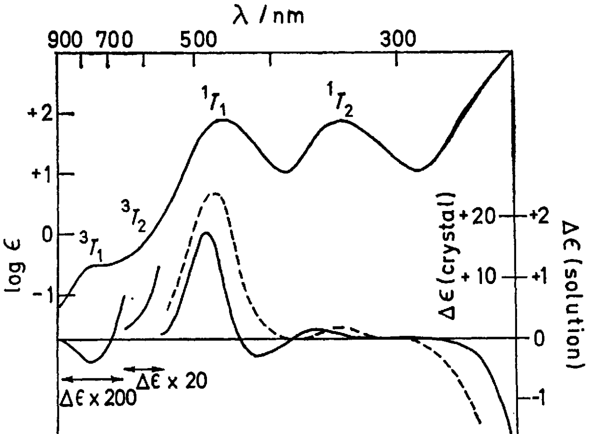

FIGURE 1 Absorption (upper curve) and circular dichroism spectra (lower curves) of $\Lambda(+)[Co(en)_3]^{3+}$ in aqueous solution (full curves) and in a single crystal of $2\{\Lambda(+)[Co(en)_3]Cl_3\}\cdot NaCl\cdot 6H_2O$ for radiation propagated along the optic axis (broken curve)

RESULTS AND DISCUSSION

The c.d. spectra were recorded with the crystal at liquid-nitrogen and at room temperature (Table, Figures 1 and 2), and the corresponding c.d. spectra of aqueous solutions at ambient temperature were measured for the tris complexes obtained from (*S*)(+)-propylenediamine, $\Lambda(+)[Co\{(S)(pn)\}_3]^{3+}$ and propane-1,3-diamine, $\Lambda(-)[Co(pd)_3]^{3+}$, as well as ethylenediamine, $\Lambda(+)$-$[Co(en)_3]^{3+}$ (Figure 3).

Wavenumbers ($\tilde{\nu}/10^3$ cm^{-1}), absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}), dissymmetry factors (*g*), and rotational strengths ($R/10^{-40}$ c.g.s. units) of the bands observed in the axial single-crystal absorption and circular dichroism spectrum of $2\{\Lambda(+)[Co(en)_3]Cl_3\}\cdot NaCl\cdot 6H_2O$ and in the corresponding spectra in aqueous solution. The crystal measurements over the triplet region refer to 80 K and the other data to ambient temperature

					R		
$\tilde{\nu}_{abs.}$	ε	$\tilde{\nu}$(c.d.)	$\varepsilon_L - \varepsilon_R$	10^2g	obs.	calc.	Upper state
(*a*) Crystal							
13.5	0.6	14.0	+0.025	4	+0.068	+0.046	${}^3E_a$
18.0	2.0	18.0	+0.15	7	+0.32	+0.55	${}^3E_b$
21.3	95	21.1	+23	24	+53		${}^1E_a$
29.4	110	29.0	+0.9	0.8	+1.3		${}^1E_b$
(*b*) Solution							
13.5	0.3	13.5	−0.002 2	0.7	−0.005 5	−0.009 3	${}^3T_1$
17.0	1.0	16.5	+0.025	3	+0.07	+0.04	${}^3T_2$
21.3	84	20.3	+1.89	2	+4.8		} ${}^1T_1$
		23.7	−0.17		−0.4		
29.4	74	28.5	+0.25	0.3	+0.7		${}^1T_2$

The tris(diamine) complexes of Co^{III} have D_3 or effective D_3 symmetry and the triply degenerate octahedral excited states, whether of singlet or triplet spin multiplicity, are each broken down into two dihedral components, T_1 to A_2 and E, and T_2 to A_1 and E. The two dihedral component states with E symmetry are conveniently distinguished as E_a (from T_1) and E_b (from T_2). Electronic transitions from the A_1 ground state are formally electric-dipole allowed to A_2 dihedral states, with a polarisation parallel to the three-fold rotational symmetry axis C_3 of the tris(chelate) complex, and to the doubly degenerate E dihedral states polarised in the plane perpendicular to the C_3 axis of the complex ion. Insofar as the electronic transition of the complex ion

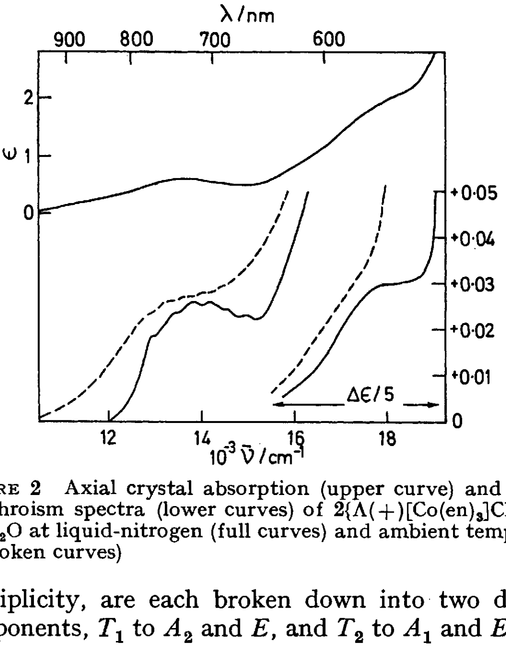

FIGURE 2 Axial crystal absorption (upper curve) and circular dichroism spectra (lower curves) of $2\{\Lambda(+)[Co(en)_3]Cl_3\}\cdot NaCl\cdot 6H_2O$ at liquid-nitrogen (full curves) and ambient temperature (broken curves)

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[2] R. Dingle and C. J. Ballhausen, *Mat. Fys. Medd.*, 1967, **35**, no. 12.

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

[4] R. Kuroda and Y. Saito, *Bull. Chem. Soc. Japan*, 1976, **49**, 433.

[5] W. R. Mason, *Inorg. Chem.*, 1976, **15**, 1741.

connects two d orbitals, the excitation is electric-dipole forbidden by the Laporte selection rule and the leading electric-transition moment is an even multipole, a quadrupole, or hexadecapole. However, hexadecapolar d-electron transitions of the type ${}^1A_1 \rightarrow {}^1T_1$ of octahedral Co^{III} are magnetic-dipole allowed, as exemplified by the component $d_{xy} \rightarrow d_{x^2-y^2}$ which has a z-polarised magnetic moment of 2 B.M.*

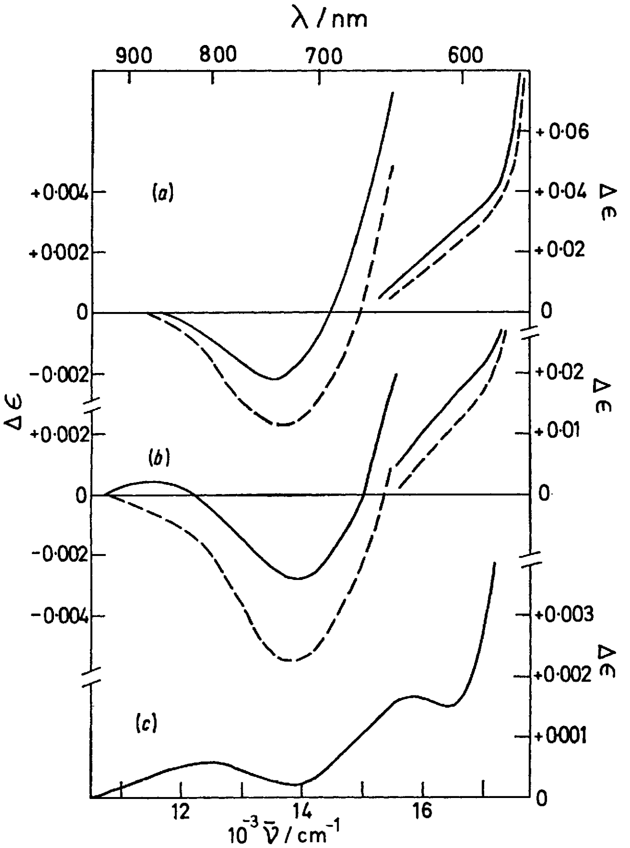

FIGURE 3 Circular dichroism spectra in aqueous solution (full curves) and in 1.0 mol dm^{-3} selenite (broken curves) of (*a*) $\Lambda(+)[Co(en)_3]^{3+}$, (*b*) $\Lambda(+)[Co\{(S)(pn)\}_3]^{3+}$, and (*c*) $\Lambda(-)[Co(pd)_3]^{3+}$

In a tris(diamine) complex of Co^{III} the electric-hexadecapole moment of each of the corresponding component excitations, ${}^1A_1 \rightarrow {}^1A_2, {}^1E_a$, coulombically correlates transient electric moments induced in the amino- and methylene groups of the chelate rings, and the resulting electric-dipole moment forms a non-zero scalar product with the intrinsic magnetic-dipole moment of that component excitation.[1] Thus the hexadecapolar transitional-charge distribution of the excitation, $d_{xy} \rightarrow d_{x^2-y^2}$, with the angular form $[xy(x^2-y^2)/r^4]$, couples the induced moments of the chelate ring groups to give a resultant electric-dipole transition moment with a non-vanishing z component. If this component is parallel to the intrinsic z-polarised magnetic moment of the excitation, the rotational strength, measured by the corresponding c.d. band area, has a positive value or, if antiparallel, the rotational strength is negative.

According to the first-order ligand-polarisation model[1] or to first-order crystal-field theory,[6] the rotational strengths of transitions to the two dihedral components of the octahedral ${}^1T_1$ state are equal in magnitude and opposite in sign, obeying a restricted sum rule (1) if

$$R({}^1A_2) + R({}^1E_a) = 0 \qquad (1)$$

each chelate ring of a tris(diamine)cobalt(III) complex is achiral, *e.g.* $\Lambda(-)[Co(pd)_3]^{3+}$ where each chelate ring has a chair conformation with a mirror plane in either the bromide[7] or the chloride[8] crystal. In the $2\{\Lambda(+)\text{-}[Co(en)_3]Cl_3\}\cdot NaCl\cdot 6H_2O$ crystal the C_3 axis of each complex ion is oriented parallel to the trigonal optic axis of the crystal,[9] and radiation propagated along the optic axis gives rise only to transitions with E dihedral symmetry in the complex. The axial c.d. spectrum of this crystal indicates that the d-electron transitions of $\Lambda(+)[Co(en)_3]^{3+}$ from the ${}^1A_1$ ground state to the excited states ${}^3E_a$, ${}^3E_b$, ${}^1E_a$, and ${}^1E_b$, at 14 000, 18 000, 21 000, and 29 000 cm^{-1}, respectively, have positive rotational strengths and that the crystal c.d. absorption is an order of magnitude larger than that of the corresponding solution spectrum over the frequency regions of the transitions to the ${}^3T_1$ and ${}^1T_1$ octahedral states (Figures 1—3).

In solution, where the complex ions have a statistically random orientation, both the dihedral components of a given transition to an octahedral T_1 state couple to the radiation field and the solution c.d. spectrum records the overall rotational strength (2). If the rotational

$$R(T_1) = R(A_2) + R(E_a) \qquad (2)$$

strengths are wholly first order in origin, and the two dihedral components with a common octahedral parentage are degenerate, both $R({}^1T_1)$ and $R({}^3T_1)$ go to zero by the restricted sum rule [equation (1)]. The solution c.d. spectrum of $\Lambda(+)[Co(en)_3]^{3+}$ shows that equation (1) is obeyed only approximately, to within *ca.* 10% (Table, Figures 1—3), and that overall $R({}^1T_1)$ is positive, *i.e.* $|R({}^1E_a)| > |R({}^1A_2)|$, whereas $R({}^3T_1)$ is negative owing to the converse inequality, $|R({}^3E_a)| < |R({}^3A_2)|$. The two residual wing c.d. absorptions resulting from the overlap of the positive $R(E_a)$ and the negative $R(A_2)$ were observed in the solution c.d. spectrum of $\Lambda(+)\text{-}[Co(en)_3]^{3+}$ over the ${}^1T_1$ frequency region and of $\Lambda(+)\text{-}[Co\{(S)(pn)\}_3]^{3+}$ over the ${}^3T_1$ frequency range (Figures 1 and 3).

The inequality of magnitude, $|R({}^1E_a)| > |R({}^1A_2)|$, arises from a second-order mixing of the dihedral components of the ${}^1A_1 \rightarrow {}^1T_1$ d-electron transition with the corresponding components of the allowed ligand–metal charge-transfer transition at higher frequency.[1] The

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* Throughout this paper 1 B.M. ≈ 9.27×10^{-24} A m^2.

[6] S. Sugano, *J. Chem. Phys.*, 1960, **33**, 1883.

[7] T. Nomura, F. Marumo, and Y. Saito, *Bull. Chem. Soc. Japan*, 1969, **42**, 1016.

[8] R. Nagao, F. Marumo, and Y. Saito, *Acta Cryst.*, 1973, **B29**, 2438.

[9] K. Nakutsu, M. Shiro, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, 1957, **30**, 158.

frequency interval between the two ^1E components is smaller than that separating the two components of $^1A_2$ symmetry so that the second-order augmentation of $R(^1E_a)$ is greater than that of $R(^1A_2)$. The converse inequality for the corresponding triplet rotational strengths, $|R(^3E_a)| < |R(^3A_2)|$, is ascribed to the larger spin–orbit mixing of the $^3A_2$ and $^1A_2$ dihedral *d*-electron states, due to the circumstance that the wavenumber interval $\bar{\nu}(^1A_2) - \bar{\nu}(^3A_2)$ is smaller than $\bar{\nu}(^1E_a) - \bar{\nu}(^3E_a)$. While the *d*-electron transitions to the $^1A_2$ and ^1E_a states of $[\mathrm{Co(en)_3}]^{3+}$ are virtually degenerate, with a common band origin [2] at 18 960 cm^{-1}, the band maxima of the corresponding transitions to $^3A_2$ and ^3E_a lie at [5] 14 530 and 13 790 cm^{-1}, respectively. The $^1A_1 \rightarrow {}^3E_a$ band of the axial crystal c.d. spectrum at 80 K shows a vibronic progression of six members with an interval of 350—400 cm^{-1}, corresponding to the totally symmetric Co–N stretching mode in the electronically excited state (Figure 2), and the wavenumber of the first member, 12 950 cm^{-1}, is taken as the band origin. The origin of the $^1A_1 \rightarrow {}^3A_2$ transition is placed 740 cm^{-1} to higher frequency, corresponding to the observed blue shift between the two band maxima,[5] so that the relevant singlet–triplet wavenumber separations, $\Delta_1 = \bar{\nu}(^1A_2) - \bar{\nu}(^3A_2)$ and $\Delta_2 = \bar{\nu}(^1E_a) - \bar{\nu}(^3E_a)$, are 5 270 and 6 010 cm^{-1} respectively.

The $^3T_1$ and the $^1T_1$ *d*-electron states of $[\mathrm{Co(en)_3}]^{3+}$ have components of T_1 spin–orbit symmetry in common, and these components of the triplet state, corrected to first order, become [10] as in (3) where ξ is the spin–orbit

$$|^3T_1,T_1\rangle = |^3T_1,T_1\rangle - (\xi/(2^{\frac{3}{2}}\Delta)|^1T_1,T_1\rangle \qquad (3)$$

coupling constant for Co$^{\mathrm{III}}$ and $\Delta = \bar{\nu}(^1T_1) - \bar{\nu}(^3T_1)$ is the energy difference between the singlet and triplet T_1 states. If the triplet transition with dihedral symmetry Γ acquires both an electric moment and a magnetic moment by spin–orbit coupling with the corresponding singlet transition the rotational strengths are related by (4), where $\Delta = \Delta_1$ for $\Gamma = A_2$ and $\Delta = \Delta_2$ for $\Gamma = E_a$.

$$R(^3T_1,\Gamma) = (\xi/2^{\frac{3}{2}}\Delta)^2R(^1T_1,\Gamma) \qquad (4)$$

Thus corresponding singlet and triplet *d*-electron transitions necessarily have rotational strengths of the same sign, and, since $\Delta_2 > \Delta_1$ for the dihedral states of $\Lambda(+)[\mathrm{Co(en)_3}]^{3+}$ descended from singlet and triplet octahedral *d*-electron states of T_1 orbital symmetry, it follows that $R(^3A_2)$ is the major of the two triplet rotational strengths so that $R(^3T_1)$ is negative [equation (2)]. Values of $R(^3E_a)$ and $R(^3T_1)$, calculated from equation (4) with [10] ξ 500 cm^{-1}, and experimental values for the other quantities required, are listed in the Table. A comparison with the corresponding experimental values obtained from the axial crystal and solution c.d. spectrum of $\Lambda(+)[\mathrm{Co(en)_3}]^{3+}$, respectively, shows that the calculated $R(^3E_a)$ and $R(^3T_1)$ values have the correct sign and magnitude (Table).

The *d*-electron transition $^1A_1 \rightarrow {}^1T_2$ of the $[\mathrm{Co^{III}N_6}]$ chromophore is devoid of a zero-order magnetic-dipole moment and the optical activity associated with that transition is relatively small. A measure of the relative optical activity connected with different electronic transitions is provided by Kuhn's dissymmetry factor [11] (5), where D is the dipole strength of the transition.

$$g = 4R/D \simeq \Delta\varepsilon_{\mathrm{max.}}/\varepsilon_{\mathrm{max.}} \qquad (5)$$

The $^1A_1 \rightarrow {}^1T_2$ transition of $\Lambda(+)[\mathrm{Co(en)_3}]^{3+}$ or its allowed dihedral component $^1A_1 \rightarrow {}^1E_b$ has the smallest g factor of the *d*-electron transitions of the complex ion in either the axial crystal or the solution spectrum (Table). The rotational strength $R(^1E_b)$ from the crystal spectrum is larger than its solution counterpart, $R(^1T_2)$ (Table), although they or, more restrictively, the corresponding g factors are expected to be equal given the same mechanism for optical activity in the crystal as in solution. The enhancement of $R(^1E_b)$ in the crystal probably owes its origin to the coupling between the electric dipole and the electric-quadrupole moment of the $^1A_1 \rightarrow {}^1E_b$ transition, a mechanism for optical activity which is singular to statistically orientated chiral species.[12]

In contrast to the values for the corresponding singlets, the g factors for the transition $^1A_1 \rightarrow {}^3T_2$ of $\Lambda(+)[\mathrm{Co(en)_3}]^{3+}$ in the crystal or in solution are larger than those of the $^1A_1 \rightarrow {}^3T_1$ transition and its dihedral components (Table). The triplet state $^3T_2$ of the $[\mathrm{Co^{III}N_6}]$ chromophore has components of T_1 spin–orbit symmetry, like the $^1T_1$ state,[10] and in a tris(diamine)cobalt(III) complex the transition $^1A_1 \rightarrow {}^3T_2$ acquires rotational strength by spin–orbit coupling from $R(^1A_2)$ and $R(^1E_a)$, and also through its T_2 spin–orbit components from $R(^1E_b)$, although this last source is relatively unimportant. Corrected to first order, the T_1 spin–orbit components of the triplet state $^3T_2$ have the form [10] (6), where

$$|^3T_2,T_1\rangle = |^3T_2,T_1\rangle - [6^{\frac{1}{2}}\xi/4\Delta_3]|^1T_1,T_1\rangle \qquad (6)$$

$\Delta_3 = \bar{\nu}(^1T_1) - \bar{\nu}(^3T_2)$ expresses the energy separation between the singlet $^1T_1$ and triplet $^3T_2$ states. The wavenumber interval Δ_3 is the same for the A_2 and E dihedral components of $^3T_2$ with a common T_1 spin–orbit parentage, since the linear dichroism of the crystal $2\{[\mathrm{Co(en)_3}]\mathrm{Cl_3}\}\cdot\mathrm{NaCl}\cdot 6\mathrm{H_2O}$ in the $^3T_2$ frequency region shows the same maximum at 18 180 cm^{-1} for radiation polarised parallel or perpendicular to the C_3 rotation axis of the complex ion.[5] Vibronic structure is absent from the crystal absorption [5] and c.d. band in the $^3T_2$ region at low temperature and the band origin is taken to lie near to the onset frequency of strong $^3T_2$ c.d. absorption at 16 000 cm^{-1} (Figure 2), *i.e.* $\Delta_3 \simeq 3\,000$ cm^{-1}.

From equation (6) the rotational strengths of the dihedral components Γ with a common T_1 spin–orbit ancestry of the transition $^1A_1 \rightarrow {}^3T_2$ are given by expression (7). As the frequency interval Δ_3 is the same

$$R(^3T_2,\Gamma) = [6^{\frac{1}{2}}\xi/4\Delta_3]^2R(^1T_1,\Gamma) \qquad (7)$$

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[10] J. S. Griffith, 'The Theory of Transition Metal Ions,' Cambridge University Press, 1961, pp. 422 and 437.

[11] W. Kuhn, *Trans. Faraday Soc.*, 1930, **46**, 293.

[12] L. D. Barron, *Mol. Phys.*, 1971, **20**, 241.

for the two optically active dihedral components of $^3T_2$, $\Gamma = A_2$ or E in equation (7), each of the triplet rotational strengths, $R(A_2,{}^3T_2)$ and $R(E,{}^3T_2)$, directly reflects the sign and the magnitude of the corresponding singlet rotational strength, $R(^1A_2)$ and $R(^1E_a)$, respectively, and the common proportionality factor also relates the sum of the rotational strengths over the dihedral components for the triplet, $R(^3T_2)$, to the corresponding sum for the singlet, $R(^1T_1)$. For $\Lambda(+)$-$[\mathrm{Co(en)_3}]^{3+}$ the triplet strengths, $R(^3E_b)$, *i.e.* $R(E,{}^3T_2)$, and $R(^3T_2)$ are found to be positive like the singlet counterparts, $R(^1E_a)$ and $R(^1T_1)$, respectively, from which they are derived by spin–orbit coupling (Figures 1—3). Values of $R(^3E_b)$ and $R(^3T_2)$ calculated from equation (7) with [10] ξ 500 cm^{-1} agree in sign and magnitude with the corresponding observed quantities (Table).

In the solution spectra of the tris(diamine)cobalt(III) complexes containing five-membered chelate rings, $\Lambda(+)[\mathrm{Co(en)_3}]^{3+}$ and $\Lambda(+)[\mathrm{Co}\{(S)(\mathrm{pn})\}_3]^{3+}$, the $^1A_1 \rightarrow {}^3T_2$ c.d. band appears only as a shoulder on a rising background due to the $^1A_1 \rightarrow {}^1T_1$ c.d. absorption, the frequency separation between the two transitions being small (Figure 3). The corresponding frequency interval in the case of the six-membered chelate-ring complex, $\Lambda(-)[\mathrm{Co(pd)_3}]^{3+}$, is larger so that the $^1A_1 \rightarrow {}^3T_2$ c.d. band is now distinct in the solution spectrum, but the larger interval Δ_3 has the result [equation (7)] that the rotational strength $R(^3T_2)$ of this complex is smaller than that of $\Lambda(+)[\mathrm{Co(en)_3}]^{3+}$ (Figure 3). The $^1A_1 \rightarrow {}^3T_1$ c.d. band of $\Lambda(-)[\mathrm{Co(pd)_3}]^{3+}$ is similarly shifted to the red and is smaller in area relative to that of $\Lambda(+)[\mathrm{Co(en)_3}]^{3+}$ (Figure 3).

Polarisable anions have a marked effect on the c.d. spectrum of tris(diamine)cobalt(III) complexes in aqueous solution over the frequency region of the $^1A_1 \rightarrow {}^1T_1$ transition.[13] For complexes containing five-membered chelate rings the effect consists of an enhancement of $R(^1A_2)$ and a diminution of $R(^1E_a)$ with an increasing anion concentration.[13] The effect extends to the frequency region of the corresponding triplet transition, $^1A_1 \rightarrow {}^3T_1$. Thus the addition of selenite ions increases the area of the negative c.d. band near 720 nm, due to the $^1A_1 \rightarrow {}^3A_2$ dihedral component, in the solution spectrum of $\Lambda(+)[\mathrm{Co(en)_3}]^{3+}$ and $\Lambda(+)$-$[\mathrm{Co}\{(S)(\mathrm{pn})\}_3]^{3+}$ and reduces the area of the positive c.d. band of the latter complex near 850 nm, due to the $^1A_1 \rightarrow {}^3E_a$ component (Figure 3).

EXPERIMENTAL

Materials.—The complexes were prepared by standard methods: $(+)[\mathrm{Co(en)_3}]\mathrm{Cl_3}$ by an asymmetric synthesis,[14] $(+)[\mathrm{Co}\{(S)(\mathrm{pn})\}_3]\mathrm{Br_3}$ by the procedure of Dwyer *et al.*,[15] and $[\mathrm{Co(pd)_3}]\mathrm{Cl_3}$ by the method of Bailar and Work.[16] Conversion into the iodide (+)-tartrate gave the less-soluble diastereoisomer [17] $(-)[\mathrm{Co(pd)_3}]\mathrm{I}[(+)$-tartrate].

Spectra.—Crystals of $2\{\Lambda(+)[\mathrm{Co(en)_3}]\mathrm{Cl_3}\}\cdot\mathrm{NaCl}\cdot6\mathrm{H_2O}$, grown by the method of Nakutsu *et al.*,[9] with well developed (0001) faces, *ca.* 40 mm^2 in cross section and 1—3 mm thick, were studied over the 500—1 000 nm region using a Cary 14 spectrophotometer and a laboratory-constructed c.d. spectrometer equipped with a red-sensitive photomultiplier.[18]

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[15] F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Amer. Chem. Soc.*, 1959, **81**, 290.

[16] J. C. Bailar and J. B. Work, *J. Amer. Chem. Soc.*, 1946, **68**, 232.

[17] A. M. Sargeson, personal communication.

[18] R. Grinter, M. J. Harding, and S. F. Mason, *J. Chem. Soc. (A)*, 1970, 667.