Single-crystal Circular Dichroism Spectra of Tris(pentane-2,4-dionato)-cobalt(III) and Tris(pentane-2,4-dionato)chromium(III) †

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The axial circular dichroism spectrum of the lowest energy electronic transition has been measured for both Λ-[Co(pd)$_3$] (pd = pentane-2,4-dionate) and Λ-[Cr(pd)$_3$] doped in a single crystal of *rac*-[Rh(pd)$_3$]·nCHCl$_3$ (n = *ca.* 20). The rotational strengths so obtained are compared with those of the corresponding oxalato and 1,2-diaminoethane complexes and an explanation is offered for their relative magnitudes.

The various theories developed to explain the circular dichroism (c.d.) spectra of transition-metal ion *d–d* transitions[1,2] have been applied almost exclusively to tris-chelate complexes of Co$^{\text{III}}$ and Cr$^{\text{III}}$ with saturated amine ligands. This is partly due to the greater complexity of the spectra when anisotropic π-bonding ligands are involved, partly due to the difficulty in resolving many of the complexes concerned, and partly because of a lack of single-crystal c.d. spectra and so of unambiguous assignments of the electronic transitions.[3] The only reported single-crystal c.d. spectra of complexes with unsaturated ligands have been for the tris-oxalates of Co$^{\text{III}}$, Cr$^{\text{III}}$, and Rh$^{\text{III}}$[4] and for [Co(Hbig)$_3$]$^{3+}$ (Hbig = biguanide)[3] for which only the signs of the A_2 and E components of the magnetic dipole transition were reported.

The signs of the rotational strengths of the E and A_2 polarised components of the lowest-energy electronic transition of Co$^{\text{III}}$ and Cr$^{\text{III}}$ amine complexes can be correctly predicted by an empirical rule[5] relating these signs to the sense of the angle of twist between the two triangular sets of ligator atoms. The twist angle (ω) is defined as the smaller angle between the upper and lower triangles of ligators (Figure 1) and is positive or negative if the sense of rotation on going from the upper to the lower set of ligators is clockwise or counterclockwise respectively. The rotational strength of the E symmetry component of the $^{1}A_{1g}\rightarrow{}^{1}T_{1g}$ (cobalt) or $^{4}A_{2g}\rightarrow{}^{4}T_{2g}$ (chromium) transition is positive for a negative value of ω and *vice versa*. This empirical rule holds for all those complexes of Co$^{\text{III}}$ and Cr$^{\text{III}}$ for which single-crystal c.d. measurements have been made and can be reproduced for these complexes by calculations based on the ligand polarisation correlation model.[6]

The rule appears to break down, however, when applied to complexes with unsaturated ligands such as the tris(pentane-2,4-dionato) (pd) complexes. If the higher energy c.d. band seen under the $^{1}A_{1g}\rightarrow{}^{1}T_{1g}$ transition in the solution spectrum of [Co(pd)$_3$] is identified as due to the E polarised component, it has a positive rotational strength for the Λ configuration for which ω is also positive. Although the assignment of the E component is based upon a single-crystal linear dichroism spectrum[7] and is therefore very likely to be correct, it is important to have an unambiguous identification of the trigonal components in the c.d. spectrum. It would also be very useful to have an estimate of the absolute magnitudes of the rotational strengths to compare with those of the corresponding transitions in saturated amine complexes: for this a single-crystal c.d. spectrum is required.

The racemic tris(pentane-2,4-dionate) complexes of the trivalent transition metal ions crystallise from chloroform as square or rectangular plates which are uniaxial, in a direction perpendicular to the well developed face, when viewed through a polarising microscope. The crystals contain considerable chloroform of crystallisation (about 20 mol per mol of complex) which is lost slowly at room temperature and pressure. The racemic rhodium complex may be doped with a few per cent of the optically active cobalt or chromium complexes without changing the crystal habit and it is sufficiently transparent to allow the uniaxial single-crystal c.d. spectrum of [Co(pd)$_3$] and [Cr(pd)$_3$] to be measured in the region of the magnetic dipole transition.

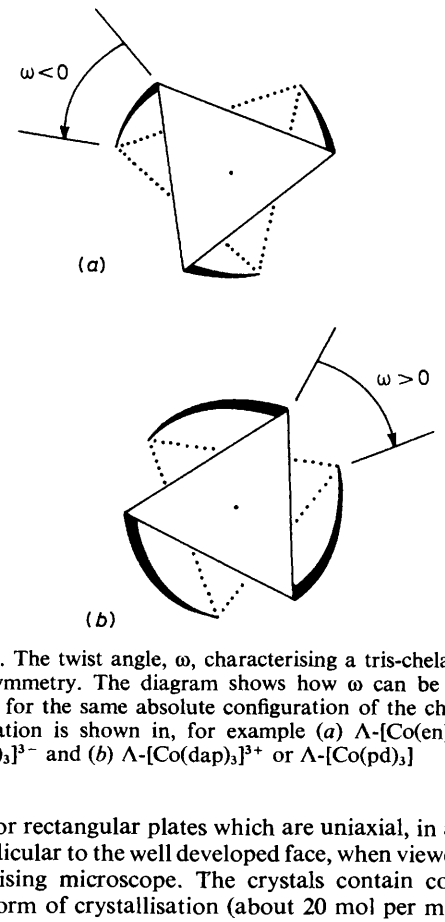

Figure 1. The twist angle, ω, characterising a tris-chelate complex of C_3 symmetry. The diagram shows how ω can be positive or negative for the same absolute configuration of the chelate rings: the situation is shown in, for example (*a*) Λ-[Co(en)$_3$]$^{3+}$ or Λ-[Co(oxa)$_3$]$^{3-}$ and (*b*) Λ-[Co(dap)$_3$]$^{3+}$ or Λ-[Co(pd)$_3$]

Experimental

Λ-[Cr(pd)$_3$] was prepared by asymmetric synthesis.[8] Λ-[Co(pd)$_3$] was resolved *via* the complex with (2*R*,3*R*)-(−)-dibenzoyltartaric acid.[9] Crystals of *ca.* 5% [Co(pd)$_3$] or [Cr(pd)$_3$] in racemic [Rh(pd)$_3$] were grown by slow evaporation from chloroform solution. The crystals, which contain about 20 molecules of CHCl$_3$ of crystallisation per molecule of complex, are square or rectangular plates with typical

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† *Non-S.I. units employed*: D = 3.336 × 10^{-30} C m; B.M. = 9.27 × 10^{-24} A m^2.

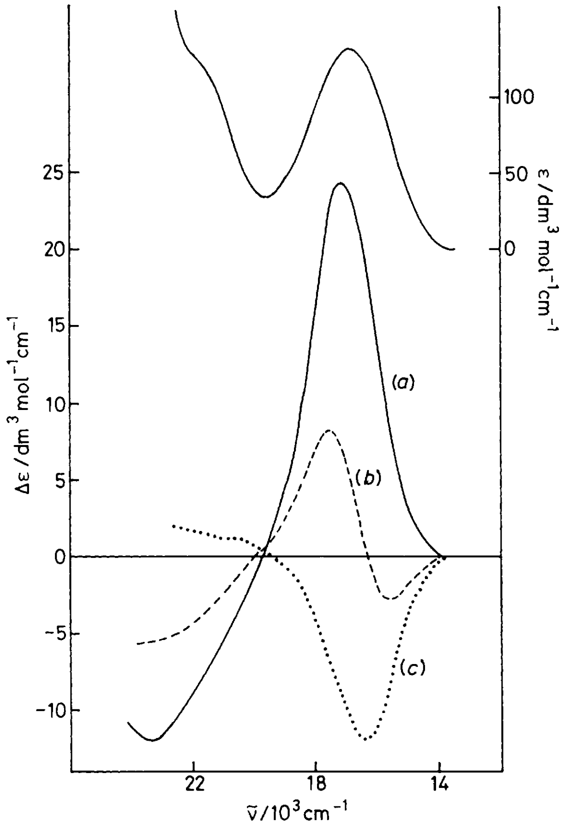

Figure 2. Upper curve: the absorption spectrum of [Co(pd)$_3$] in CHCl$_3$ solution. Lower curves: (*a*) the axial c.d. spectrum of *ca.* 5% Λ-[Co(pd)$_3$] in a single crystal of *rac*-[Rh(pd)$_3$] chloroform solvate [= Δε(*E*)]; (*b*) the c.d. spectrum of a solution of Λ-[Co(pd)$_3$] in CHCl$_3$; (*c*) the difference between the axial and solution c.d. spectra of Λ-[Co(pd)$_3$]. $\Delta\varepsilon(c) = \frac{2}{3}\Delta\varepsilon(a) - \Delta\varepsilon(b) = \frac{1}{3}\Delta\varepsilon(A_2)$

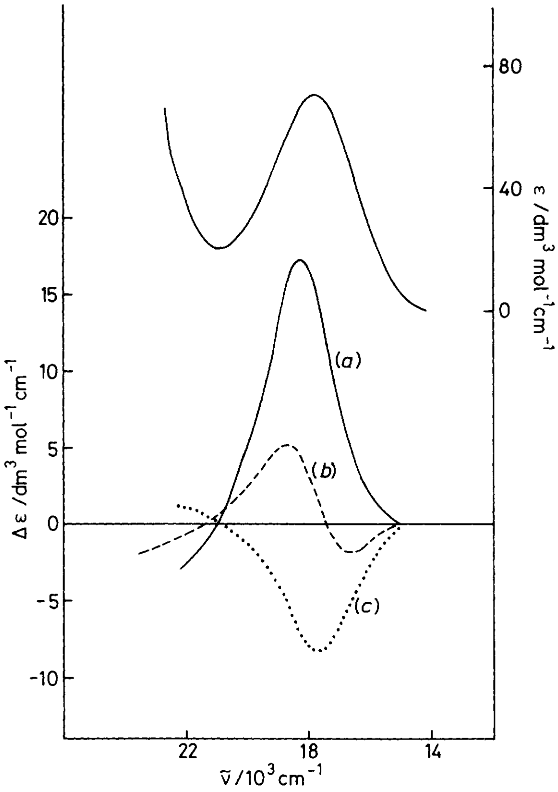

Figure 3. Upper curve: the absorption spectrum of [Cr(pd)$_3$] in CHCl$_3$ solution. Lower curves: (*a*) the axial c.d. spectrum of *ca.* 5% Λ-[Cr(pd)$_3$] in a single crystal of *rac*-[Rh(pd)$_3$] chloroform solvate [= Δε([illegible] (*b*) the c.d. spectrum of a solution of Λ-[Cr(pd)$_3$] in CHCl$_3$; (*c*) the difference between the axial and solution c.d. spectra of Λ-[Cr(pd)$_3$]. $\Delta\varepsilon(c) = \frac{2}{3}\Delta\varepsilon(a) - \Delta\varepsilon(b) = \frac{1}{3}\Delta\varepsilon(A_2)$

dimensions 4 × 4 × 0.5 mm. The chloroform of crystallisation is lost slowly (3—4 h at room temperature and pressure) but the crystals can be preserved by coating with Nujol or in an atmosphere of chloroform.

The crystals appear uniaxial under the polarising microscope. Three further experiments confirm that the crystals are isotropic in the plane perpendicular to the unique axis. (1) They show no linear dichroism (detected by modulation techniques) for any orientation about the unique axis. (2) They do not depolarise circularly polarised light when it is propagated down the unique axis. This was established by measuring the c.d. spectrum of a solution of Λ-[Co(en)$_3$]$^{3+}$ (en = 1,2-diaminoethane) before and after the light was passed through a crystal of [Rh(Λ-Cr)(pd)$_3$]. The two spectra were identical. (3) The axial c.d. spectra of the crystals is independent of their orientation about the unique axis.

Circular and linear dichroism spectra were measured on an instrument consisting of a 0.6 m Jobin-Yvon monochromator, a Morvue photoelastic modulator, and a Bentham lock-in amplifier. The instrument was calibrated with an aqueous solution of Λ-[Co(en)$_3$]$^{3+}$. The values of Δε for the crystal spectra were obtained by measuring the area of the crystal and then dissolving it in ethanol and measuring the c.d. of the resulting solution to obtain the total number of moles of the optically active complex. $\Delta\varepsilon_{\text{cryst.}}$ can then be calculated from equation (i), where $\Delta A_{\text{cryst.}}$ is the difference between the absorbance of left and right circularly polarized light by the crystal. Values of $\Delta\varepsilon_{\text{cryst.}}$ are estimated to be accurate to about ±15%.

$$\Delta\varepsilon_{\text{cryst.}} = \frac{\Delta A_{\text{cryst.}} \times \text{area (cm}^2) \times 10^{-3}}{\text{number of moles}} \qquad \text{(i)}$$

Results and Discussion

The axial c.d. spectra of Λ-[Co(pd)$_3$] and Λ-[Cr(pd)$_3$] doped in the racemic rhodium host are shown in Figures 2 and 3 respectively. Also included are the appropriate solution absorption and c.d. spectra.

The fact that a crystal is uniaxial does not necessarily imply that the C_3 axes of the individual molecules are parallel to the unique crystal axis; the molecules may be arranged round the optic axis with their C_3 axes inclined at a constant angle α. Under those conditions the single-crystal circular dichroism, $\Delta\varepsilon_{\text{cryst.}}$, is given in terms of the circular dichroism of the E and A_2 trigonal components ($\Delta\varepsilon_E$ and $\Delta\varepsilon_{A_2}$) by equation (ii).[10]

$$\Delta\varepsilon_{\text{cryst.}} = \Delta\varepsilon_E(\cos^2\alpha + 1)/2 + \Delta\varepsilon_{A_2}(\sin^2\alpha)/2 \qquad \text{(ii)}$$

Since the value of α is unknown for the [Rh(pd)$_3$] chloroform solvate crystal, the value of $\Delta\varepsilon_E$ may be larger than that of $\Delta\varepsilon_{\text{cryst.}}$. There is no sign of asymmetry on the long wavelength side of the single-crystal c.d. spectrum, however, and so it is felt that any contribution from $\Delta\varepsilon_{A_2}$ must be rather small.

A second reason for suspecting that the value of α must be close to zero is that when the spectra are decomposed into E and A_2 polarised components using α = 0, the energies of

Table. Rotational strengths (D B.M.) of the trigonal components, $R(E)$ and $R(A_2)$, of the octahedral magnetic dipole *d*-electron transition $^1A_{1g} \longrightarrow {}^1T_{1g}$ (cobalt) or $^4A_{2g} \longrightarrow {}^4T_{2g}$ (chromium) and the corresponding sum $R(T)$[a]

Complex	ω (°)	$R(E)$	$R(A_2)$	$R(T)$	Ref.
Λ-$[Co(en)_3]^{3+}$	−54.9	+0.678	−0.632	+0.046	10
Λ-$[Co(oxa)_3]^{3-}$	−54	+1.23	−1.09	+0.14	4
Λ-$[Co(pd)_3]$	+52.7	+0.59	−0.42	+0.17	*b*
Λ-$[Cr(en)_3]^{3+}$	−52.2	+0.313	−0.265	+0.048	4, *c*
Λ-$[Cr(oxa)_3]^{3-}$	−47.4	+0.56	−0.46	+0.10	4
Λ-$[Cr(pd)_3]$	+59	+0.42	−0.31	+0.11	*b*

[a] $R(E)$ and $R(A_2)$ have been corrected by the fixed-orientation factors of $\frac{2}{3}$ and $\frac{1}{3}$ respectively. The angle ω is defined in the text and in Figure 1. [b] This work. [c] U. Geiser and H. U. Gudel, *Inorg. Chem.*, 1981, **20**, 3013.

these (Figures 1 and 2) correspond rather well to those determined from the linear dichroism (l.d.) spectra [7,11] of the complexes doped in $[Al(pd)_3]$: $[Co(pd)_3]$, $\tilde{\nu}(E)_{c.d.} = 17\,150$ cm^{-1}, $\tilde{\nu}(E)_{l.d.} = 17\,150$ cm^{-1}, $\tilde{\nu}(A_2)_{c.d.} = 16\,250$ cm^{-1}, $\tilde{\nu}(A_2)_{l.d.} = 16\,225$ cm^{-1}; $[Cr(pd)_3]$, $\tilde{\nu}(E)_{c.d.} = 18\,400$ cm^{-1}, $\tilde{\nu}(E)_{l.d.} = 18\,400$ cm^{-1}, $\tilde{\nu}(A_2)_{c.d.} = 17\,700$ cm^{-1}, $\tilde{\nu}(A_2)_{l.d.} = 17\,600$ cm^{-1}.

The rotational strengths $R(E)$, $R(A_2)$, and $R(T)$ (for random orientation in chloroform solution) along with the values of ω are collected in the Table for the cobalt and chromium tris(pentane-2,4-dionate) complexes. The values for the tris(1,2-diaminoethane) and tris(oxalato) complexes are included in the Table for comparison.

It is clear that the higher energy component of the magnetic dipole transition of both $[Co(pd)_3]$ and $[Cr(pd)_3]$ seen in the solution c.d. spectrum does correspond to the E polarised trigonal component, and that its rotational strength is positive for the Λ configuration of both complexes despite ω being positive. In contrast, the tris(oxalato) complexes, in common with those tris-chelated complexes with saturated amine ligands, do obey the rule relating the sign of rotational strength to the sign of ω. It is also noticeable that while the tris(oxalato) complexes have larger rotational strengths than the corresponding tris(1,2-diaminoethane) complex, as might be expected from the larger polarisability of the oxalate ligand, the tris(pentane-2,4-dionato) complexes have either smaller (cobalt), or at best a little larger (chromium), rotational strengths than the amine complexes. It has been suggested [3] that the anomalous behaviour of the tris(unsaturated chelate) complexes compared to that of the saturated amine complexes can be explained by the anisotropic bonding and polarisability of the unsaturated ligands while the saturated amine ligators can be considered isotropic to a first approximation. This explanation should certainly be considered but must wait for detailed calculations to test it. An alternative, simpler rationalisation can, however, be suggested.

The empirical rule obeyed by trigonally distorted amine complexes can be understood if the assumption is made that the chelate backbone is a minor chiral perturbation compared with the set of ligator atoms, and it is therefore the latter which determine the sign of the c.d. spectrum. If the twist angle ω is negative for the Λ configuration then the chirality of the ligators and of the chelate ring backbones are in the same sense [Figure 1(*a*)] and so the effects reinforce each other, *e.g.* in Λ-$[Co(en)_3]^{3+}$. If, however, ω is positive for the Λ configuration then the chirality of the ligator set and of the chelate backbones are in the opposite sense [Figure 1(*b*)] and the two effects will act against each other, *e.g.* in Λ-$[Co(dap)_3]^{3+}$ (dap = 1,3-diaminopropane). In this case, because the ligators are the larger perturbation, the overall effect and so the sign of the circular dichroism is given by the angle of twist of the ligators and not by the absolute configuration of the chelate ring backbones. Although the signs of the rotational strengths appear to be always controlled by the ligator positions for saturated chelate systems, the magnitude of the rotational strengths will clearly depend upon whether the two chiral perturbations are reinforcing or opposing. For example, in the case of Λ-$[Co(en)_3]^{3+}$, where the twist of the ligators away from the octahedral positions is some 5° counterclockwise, $R(E)$ is +0.68 Debye Bohr magneton (D B.M.); however, for Λ-$[Co(dap)_3]^{3+}$ $R(E)$ is −0.11 D B.M. despite the complex having a larger twist of 7° in the clockwise direction away from octahedral geometry.

In the case of complexes with unsaturated ligands, however, it is expected that the chiral perturbation due to the chelate ring backbone may be comparable to, or even larger than, that due to the ligators. Under those circumstances the sign of the circular dichroism will be given not by the disposition of ligator atoms but by the absolute configuration of the chelate rings as conventionally defined. For the tris(oxalato) (oxa) complexes the twist angle is negative for the Λ configuration, the two chiral perturbations reinforce, and the resulting rotational strengths are large. In the case of the pentane-2,4-dionates, however, the effects oppose and the correct signs for the rotational strengths are predicted only if it is assumed, in contrast to the saturated tris-chelates, that the dominant chiral perturbation is the chiral disposition of the chelate ring backbones. The fact that the overall chirality of the pentane-2,4-dionates is due to competing rather than reinforcing effects explains why the rotational strengths of the cobalt complex are smaller than those of both $[Co(en)_3]^{3+}$ and $[Co(oxa)_3]^{3-}$ despite the pentane-2,4-dionate complex having the largest twist away from octahedral geometry. In $[Cr(pd)_3]$ the ligators are extremely close to the octahedral positions and the rotational strengths must be almost entirely due to the chiral disposition of the ring backbones. This is reflected in the relatively large rotational strength found for $[Cr(pd)_3]$.

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References

1 S. F. Mason, *Struct. Bonding* (*Berlin*), 1980, **39**, 43.
2 F. S. Richardson, in ' Optical Activity and Chiral Discrimination,' ed. S. F. Mason, Reidel, Dordrecht, 1979, ch. 6, p. 107.
3 N. C. Moucharafieh, P. G. Eller, J. A. Bertrand, and D. J. Royer, *Inorg. Chem.*, 1978, **17**, 1220.
4 S. F. Mason, in ' Fundamental Aspects and Recent Developments in Optical Rotatory Dispersion and Circular Dichroism,'

eds. F. Ciardelli and P. Salvadori, Heyden, London, 1973, ch. 3.6, p. 196.
5 R. D. Peacock and B. Stewart, *Coord. Chem. Rev.*, 1982, **46**, 129.
6 S. F. Mason and R. H. Seal, *Mol. Phys.*, 1976, **31**, 755.
7 T. S. Piper, *J. Chem. Phys.*, 1961, **35**, 1240.
8 S. F. Mason, R. D. Peacock, and T. Prosperi, *J. Chem. Soc., Dalton Trans.*, 1977, 702.
9 A. F. Drake, J. M. Gould, S. F. Mason, C. Rosini, and F. J. Woodley, *Polyhedron*, in the press.
10 R. Kuroda and Y. Saito, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 433.
11 T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, 1962, **36**, 3330.

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