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The Circular Dichroism of Dissymmetric Cobalt(III) Complexes in the Solid State

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The crystal circular dichroism spectra of a number of dissymmetric transition-metal complexes have been measured in order to identify the symmetry and evaluate the magnetic moments of the electronic transitions responsible for the optical activity, and to provide a basis for relating stereochemical configurations through the comparison of Cotton effects with an analogous origin in a series of different compounds.[1–3] These applications involve the comparison of the crystal and the solution circular dichroism of a complex ion, and they rest on the assumption that the crystal circular dichroism is a molecular property which is not greatly affected by the site symmetry of the complex ion or the nature of the anion. The assumption has been questioned on two grounds.[4,5] Firstly, the observation[4,6,7] that in solution some anions change the relative areas, but not the relative frequencies, of the circular dichroism bands given by trisdiamine cationic complexes suggests that the corresponding anion perturbations in the crystal may be large anough to invalidate comparisons between the crystal and the solution circular dichroism spectra.[4] Secondly, the spectrum of the crystal $2[Co(en)_3Cl_3],NaCl,6H_2O$, measured with plane-polarised light over the temperature range 5—300°K, shows that the band maximum due to the ^1E component of the $^1T_{1g}$ octahedral transition lies at a higher frequency than that arising from the $^1A_2$ component, and that the electric dipole band origins of the two components coincide.[5] From these observations it is suggested[5] that the circular dichroism results,[1,2] which place the ^1E component at a lower frequency than the $^1A_2$ (Figure), cannot be transferred from the crystal to solution owing to perturbations in the crystal arising from the site symmetry of the complex ion.

The validity of comparing crystal and solution circular dichroism measurements has been studied in the present work by determining the circular dichroism spectra of a number of complex salts in KCl and KBr discs, where the complex ions have a random average orientation, as in solution, but are subject to perturbations arising from the particular site symmetry and anion, as in a single crystal. The crystalline salts* investigated are, $(+)$-$Co(en)_3Cl_3,3H_2O$, $2[(+)$-$Co(en)_3Cl_3],NaCl,6H_2O$, where the complex ion has trigonal site symmetry,[8,9] $(+)$-$Co(en)_3Br_3,H_2O$, where the site symmetry of the complex ion is digonal,[10] and $(+)$-$Co(en)_3(ClO_4)_3$, $(+)$-$Co(en)_3Cl_3$ diluted in $Rh(en)_3Cl_3,3H_2O$, and $(-)$-$K_3Co(ox)_3,H_2O$, where the site symmetries of the complex ions are as yet unknown. In all cases the circular dichroism spectra given by the complex salt in a KCl or KBr disc and in dilute

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* The abbreviations used are:—(en) = ethylenediamine, (ox) = oxalate.

aqueous solution are closely similar (Figure), indicating that the crystal circular dichroism is largely a molecular property. As the particle-size of the crystallites of the complex salt is increased, the ${}^1E$ and the ${}^1A_2$ circular dichroism bands diminish in area, owing to the increasing depolarisation of the circularly polarised light during transmission through the disc, but under all of the conditions studied the ${}^1E$ circular dichroism band has the larger area and lies at the lower frequency than the ${}^1A_2$ band.

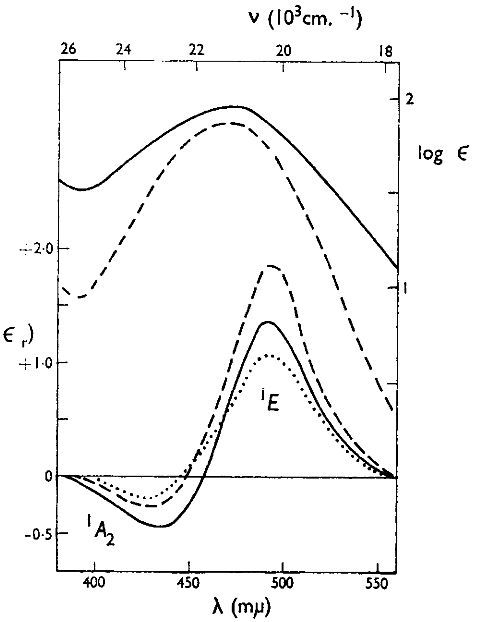

FIGURE. *The circular dichroism (lower curves) and absorption spectra (upper curves) of* (+)-Co(en)$_3$(ClO$_4$)$_3$, ———————*in a* KBr *disc, and* (+)-Co(en)$_3$Cl$_3$,3H$_2$O — — — — — *in aqueous solution and*. . . . . *in a* KBr *disc.*

The gegen-ion effect in solution, where in general the area of the ${}^1A_2$ circular dichroism band is enhanced at the expense of that due to the ${}^1E$ component by polarisable anions,[4,6,7] is small for the halides and is not measurable for perchlorate,[6] and the minor differences observed (Figure) between the solution and the salt-disc circular dichroism show that the corresponding effect of the latter anions in the crystal is not large.

It has long been known[11] that the frequencies of an absorption band and the corresponding circular dichroism band in the electronic spectrum of a dissymmetric molecule do not, in general, coincide, particularly in the case of bands due to transitions formally allowed in magnetic dipole radiation fields. Although the two are related, the rotational strength of an electronic transition, measured by the circular dichroism band area, is a quantity different from the electric dipole strength, measured by the plane-polarised or isotropic absorption band area, and the frequencies of neither the apparent band origins nor the band maxima obtained by the two methods are necessarily identical. In particular, the true band origins of both the ${}^1E$ and ${}^1A_2$ transitions of the Co(en)$_3{}^{3+}$ ion are magnet-dipole allowed, but no magnetic dipole components were detected[5] in the plane-polarised crystal study of 2[Co(en)$_2$Cl$_3$],NaCl,6H$_2$O, since the magnetic dipole strength of the band system is no more than 1% of the electric dipole strength, as the circular dichroism of the crystal shows.[2]

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