Outer-sphere Co-ordination and Optical Activity in Transition-metal Complexes

S. F. MASON and (Miss) B. J. NORMAN
(*School of Chemical Sciences, University of East Anglia, Norwich*)

IT has been suggested[1] that inner- and outer-sphere co-ordination to transition-metal ions may be distinguished in the case of optically-active ligands by means of the criterion that inner-sphere co-ordination induces a Cotton effect in the wavelength region of the $d \rightarrow d$ transitions of the metal ion whereas outer-sphere co-ordination does not. Thus $[Co(NH_3)_4(D\text{-tart})]$ (ClO_4) and $[Co(NH_3)_5(D\text{-tart})]$ (ClO_4), where D-tart is the (+)-tartrate dianion, exhibit in aqueous solution a Cotton effect near 5000 Å in the region of the $^2A_{1g} \rightarrow {}^1T_{1g}$ absorption of cobalt(III) but $[Co(NH_3)_6]_2(D\text{-tart})_3$ gives throughout the visible wavelength range a plain optical rotatory dispersion curve.[1]

However, we find that hexamminecobalt(III) perchlorate in an aqueous solution containing an excess of the (+)-tartrate anion or dianion or, more particularly, (+)-tartaric acid or diethyl-(+)-tartrate, exhibits a marked Cotton effect near 5000 Å (Figure). The optimum rotational strength induced in the $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption of $Co(NH_3)_6{}^{3+}$ diethyl-(+)-tartrate is in fact somewhat larger in magnitude than that produced[1] by the inner-sphere co-ordination of the optically-active ligand in $[Co(NH_3)_4(D\text{-tart})]^+$ or $[Co(NH_3)_5(D\text{-tart})]^+$ and it is of opposite sign (Figure). The magnitude of the induced rotational strength shows an approximate proportionality to the concentration of diethyl-(+)-tartrate over the range (0·4—3M, and an inverse proportionality to the hexamminecobalt(III) perchlorate concentration over the range 5—20 mM. Analysis of the concentration-dependence[2] fails to reveal, however, a well-defined outer-sphere co-ordination complex, or a series of such complexes, characterised by a precise ligand co-ordination number.

The circular dichroism of $[Co(NH_3)_6]^{3+}$ induced by outer-sphere co-ordination is accompanied by an increase in the absorption of unpolarized radiation (Figure). The new absorption band with an onset near 3000 Å is probably due to the transfer of an electron from the outer-sphere ligand to the complex ion, and the enhanced intensity of the ligand-field bands arises from the mixing of the $d \rightarrow d$ transitions of the metal ion with this charge-transfer transition. The electric moment of the component of the charge-transfer transition mixed with the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition of cobalt(III) couples with the intrinsic magnetic moment of the latter to give the rotational strength responsible for the circular dichroism band observed at 4800 Å (Figure). The observed circular dichroism implies that the outer-sphere co-ordination of diethyl-(+)-tartrate to $[Co(NH_3)_6]^{3+}$ is non-random, and that

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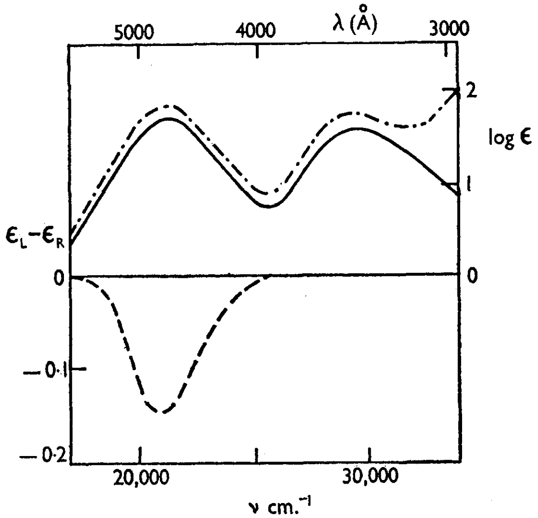
[1] D. C. Bhatnagar and S. Kirschner, *Inorg. Chem.*, 1964, **3**, 1256.
[2] R. Larsson and B. Folkeson, *Acta Chem. Scand.*, 1965, **19**, 53.

the outer-sphere complex or complexes have a structure, determined by a preferred mutual orientation of the two species, devoid of secondary elements of symmetry, notably a centre or a plane.



The electronic absorption spectrum of $[Co(NH_3)_6](ClO_4)_3$ ——————————*in water, and* ——·——·——·——· —— *in aqueous diethyl-*(+)*-tartrate* (4M), *and the circular dichroism* —— —— —— —— —— —— *of* $[Co(NH_3)_6](ClO_4)_3$ *in aqueous diethyl-*(+)*-tartrate* (4M).

Chelate hydrogen-bonding may govern the preferred mutual orientation of the two species in the optically-active outer-sphere complexes of $[Co(NH_3)_6]^{3+}$ since solutions of this ion containing (+)-camphorsulphonic acid, but not those containing the same concentration of (+)-camphor, give a circular dichroism band at 4800 Å. It has been tentatively suggested[3] that a Cotton effect is induced in the $d \rightarrow d$ transitions of a transition-metal complex by an optically-active ligand only if that ligand is a chelate. This criterion does not apply generally to the inner-sphere co-ordination of dissymmetric ligands,[1,4] but it appears applicable to the corresponding case of outer-sphere co-ordination. The steric requirements for the induction of a Cotton effect in the $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption region of $[Co(NH_3)^6]^{3+}$ by outer-sphere chelate hydrogen-bonding are exacting, for this ion gives no measurable circular dichroism in the visible wavelength range in solutions containing an excess of L-malic acid, the L-amino-acids, or sucrose.

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[3] E. Larsen and I. Olsen, *Acta. Chem. Scand.*, 1964, **18**, 1025.

[4] G. Paiaro and A. Panunzi, *J. Amer. Chem. Soc.*, 1964, **86**, 5148; *Tetrahedron Letters*, 1965, **441**; and private communication. J. Fujita, T. Yasui, and Y. Shimura, *Bull. Chem. Soc. Japan*, 1965, **38**, 654.