The Sign of the Cotton Effect for $d \rightarrow d$ Transitions of Trigonal Metal Complexes

By J. R. GOLLOGLY and C. J. HAWKINS

(*Department of Chemistry, University of Queensland, St. Lucia, Queensland, Australia*)

ACCORDING to various theories concerning the rotational strengths of the $d \rightarrow d$ transitions of "octahedral" metal complexes that are dissymmetric due to the distribution of their chelate rings, the displacement of the donor atoms from the regular octahedral positions due to the chelation is important in determining the size and the sign of the Cotton effects.[1] The common bidentate chelates, such as 1,2-diaminoethane,[2] 1,2-diaminopropane,[3] and oxalate,[4] form complexes with cobalt(III) in which the ring angle, α, between the two co-ordinate bonds is less than 90°. For the tris-complexes of these ligands it has been well established that for the D-configuration (positive octant sign)[5] the E and A_2 components of the low-energy ligand-field band (T_{1g}, O_h) show positive and negative Cotton effects, respectively.[6] It has been suggested that if α was greater than 90° this would lead to a reversal in signs for the same distribution of chelates.[7] We report experimental data to show that this is not the case for the tris-(1,3-diaminopropane)cobalt(III) complex, $[\mathrm{Co\ pn_3}]^{3+}$, in which α is 94·5°.

By the anomalous X-ray diffraction study of its bromide salt, the absolute configuration of (—)-[Co pn_3]$^{3+}$ has been found to be D, the chelate rings possessing a flattened chair conformation.[8] This flattening, which is necessary to alleviate considerable steric interactions, gives rise to the α value greater than 90°.†

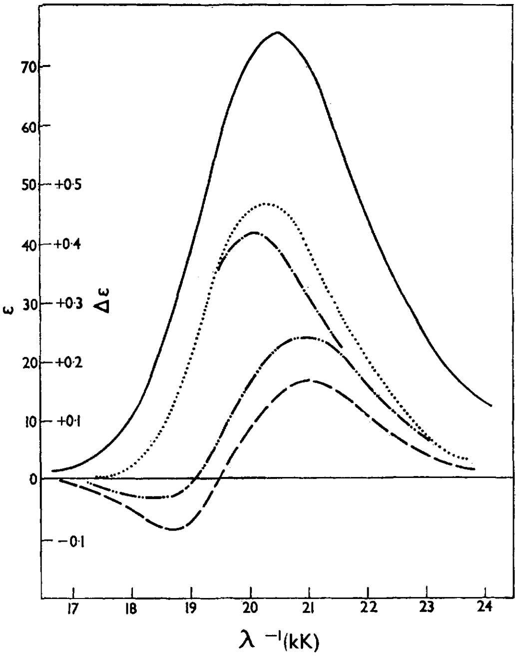

FIGURE. *The absorption spectrum of* (+)-[Co pn_3]I_3 (0·01M) *in water* (———) *c.d. in water* (- - - -) *in approx.* 0·05M-*selenite* (· · · · · ·) *in* 0·05M-*phosphate* (-··-) *and in* 0·05M-*sulphate* (-···-) *for the low-energy ligand field band.*

The c.d. spectrum for (+)-[Co pn_3]$^{3+}$ is given in the Figure. The two c.d. bands under the first ligand-field band are both small. The problem reduces to the assignment of transitions to these bands. Mason has proposed that for diamines it is possible to distinguish the E and A_2 transitions by the additon of selenite, phosphate, or sulphate to the solution of the complex: the A_2 is increased in size and the E decreased.[9] For tris-complexes of the type, [Co en_3]$^{3+}$, these anions are thought to hydrogen-bond to the three hydrogen atoms (bound to nitrogen donor atoms) which are directed parallel to the C_3-axis of the complex ion in the L-configuration.[9] It is found that these atoms are approximately 2·5 Å apart, which corresponds to the O–O distances in the oxy-anions.[10] The structure for [Co pn_3]$^{3+}$ determined by X-ray analysis[8] possesses three hydrogen atoms in this orientation which are separated by approximately this distance.‡ Therefore it is expected that the addition of the above oxy-anions will affect the E and A_2 transitions in the same way. The c.d. spectra for (+)-[Co pn_3]$^{3+}$ (L-configuration) with the added oxy-anions are given in the Figure. It is seen that the high-energy component increases dramatically at the expense of the low-energy component, and thus the former is assigned to the A_2 transition (positive Cotton effect) and the latter to the E transition (negative Cotton effect). It would seem therefore, that the E transition has a positive Cotton effect for complexes with the D-configuration, irrespective of the angle α. This lends further support to the empirical rules which have been proposed for complexes that gain their dissymmetry in this way, relating the sign of the Cotton effect with the distribution of their chelates.[11]

We thank the Australian Research Grants Committee for financial support.

(*Received, April 26th*, 1968; *Com.* 509.)

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† The steric interactions would also enforce this geometry in solution.

‡ The positions of the hydrogen atoms were determined by constructing a model of the complex from the given geometrical data.

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