The Circular Dichroism of the Dodecamminehexa-μ-hydroxotetracobalt(III) Ion

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BY resolving a purely inorganic tris-chelate complex, the dodecamminehexa-μ-hydroxotetracobalt(III) ion (I), Werner[1] disposed of the vitalist contention that organic carbon is an essential concomitant of optical activity. In addition to its historical significance, the complex (I), together with the hexa-ethylenediamine analogue[2] (II), are of interest in connection with metal–metal bonding in polynuclear co-ordination compounds and, more generally, with interactions between the individual chromophores of polymeric systems.

The present work reports the circular dichroism and absorption spectra of optical isomers of the complex ions (I) and (II) (Figure), prepared according to Werner[1,2] and resolved by the method of Goodwin, Gyarfas, and Mellor,[3] using antimonyl-(+)- and -(−)-tartrate. The latter method of resolution, reported[3] for the complex (II), proved to be more expeditious for the resolution of the complex (I) than Werner's method,[1] in which (+)-bromocamphorsulphonic acid is employed. Mellor and his co-workers described[3] the isolation of four of the eight possible isomers of the complex (II). Optically only two isomers are distinguished, however, for the forms of the complex (II) designated[3] D_I and D_{II} are found to have the same circular dichroism spectrum, which is enantiomorphous to that given by both of the forms termed[3] L_I and L_{II}. The successive precipitation of (+)- and then (−)-isomers of (II) by the repeated addition of potassium antimonyl-(+)-tartrate was cited[3] as evidence for the existence of more than two isomers, but the complex ion (I), in which only two forms are possible, is found to behave in a similar way. The addition of sodium perchlorate to solutions of the antimonyl-(+)-tartrate of (I) precipitates the (−)-isomer, whereas the addition of ethanol precipitates the (+)-isomer.

The 6300 and 5000 Å bands in the isotropic absorption spectrum of the complex ions (I) and (II) (Figure) correspond in position and intensity to those due to the $^1A_1 \rightarrow {}^1T_1$ transition of the CoO_6 and three CoN_4O_2 chromophores, respectively, but the corresponding circular dichroism indicates that there is considerable interaction

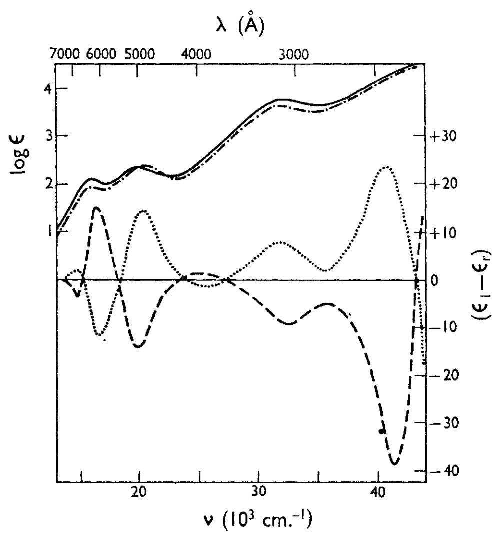
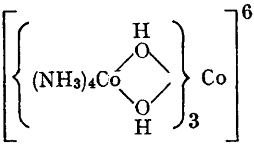
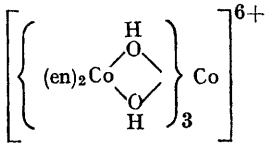


FIGURE. *The circular dichroism* (— — —) *and the absorption spectrum* (———) *of the* (−)*-dodecammine-hexa-μ-hydroxo-cobalt*(III) *ion* (I), *and the circular dichroism* (. . .) *and the absorption spectrum* (— · —) *of the* (+)*-hexakis*(*ethylenediamine*)*hexa-μ-hydroxotetra-cobalt*(III) *ion* (II) *in water.*

between those chromophores. The circular dichroism observed in the visible wavelength region is remarkable in that it is an order of magnitude larger than that generally inhibited by the $d \rightarrow d$ transitions of mononuclear tris-chelate cobalt(III) complexes,[4] and that it is quantitatively similar for corresponding optical isomers of the complex ions (I) and (II), in spite of the six additional chelate rings in the latter (Figure). The circular dichroism bands at 6800 and 6050 Å are ascribed, respectively, to the A_2 and E_a trigonal components of the octahedral T_1 transition of the CoO_6 chromophore from the observation[4] that the E_a circular dichroism band invariably has a larger area than that due to the A_2 component in trigonal cobalt(III) complexes. On this basis the chirality rule[4] connecting the sign of the E_a circular dichroism with the stereochemistry of the complex suggests that the oxy-chelate rings in the (−)-isomers of (I) and (II) have an absolute configuration around the central cobalt(III) ion similar to that of the ethylenediamine rings in the (+)-$[Co(en)_3]^{3+}$ ion.[5]

As yet the chirality of the ethylenediamine rings in the complex ion (II) cannot be specified, for the contribution of these chelate rings to the circular dichroism near 5000 Å, which is due largely to the components of the ${}^1A_1 \rightarrow {}^1T_1$ transition of the CoN_4O_2 chromophores, is relatively small, judged by the measurements reported[6] for the corresponding mononuclear complex, (+)-$[Co(en)_2(H_2O)_2]^{3+}$. The circular dichroism near 5000 Å is quantitatively similar for (I) and (II) (Figure), and in the former complex the CoN_4O_2 chromophores are not inherently dissymmetric. Current studies of the hexapropylenediamine analogues of the complex (I) may elucidate the relative configurations of the diamine and the oxy-chelate rings in the complex (II).


(I)


(II)

The absorption band near 3100 Å and the corresponding circular dichroism of the complexes (I) and (II) have no close counterpart in the spectra of the mononuclear complexes containing the CoO_6 or the CoN_4O_2 chromophore. The nearest analogue[7] is the band at 2550 Å (ϵ_{max} 9500) given by the tris(carbonato)cobaltate(III) ion. On intensity grounds the 3100 Å band of (I) and (II), like the 2550 Å band of $[Co(CO_3)]^{3-}$, is ascribed largely to transitions of the oxygen p_π electrons to metal-ion e_g orbitals, and not primarily to metal–metal interactions. In dimeric cupric acetate and dimeric chromous acetate the bands regarded[8] as diagnostic of metal–metal bonding, at 3700 and 3250 Å, respectively, are relatively weak (ϵ_{max} ~ 100),[9] although these dimers are neither electronically nor stereochemically closely comparable to the tetranuclear complexes (I) and (II).

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