Piper's Model for Optical Activity: Absolute Configurations of the Complex Ions, $(+)_{589}[Cr(malonate)_3]^{3-}$, $(+)_{546}[Co(malonate)_2(ethylenediamine)]^-$, and $(+)_{589}[Cr(oxalate)_3]^{3-}$

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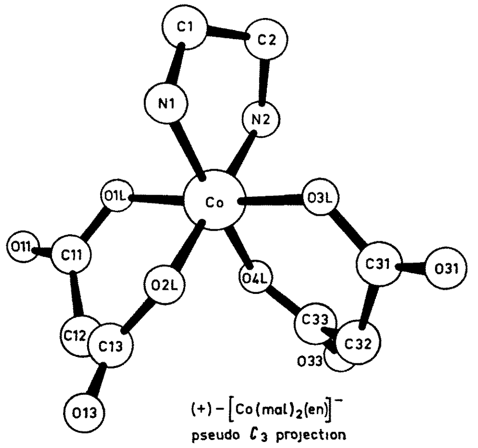
Summary The absolute configurations of the title ions have been assigned as Λ, Δ, and Λ by X-ray studies; the first and third structures support Piper's model for optical activity.

ASSIGNMENT of the absolute configurations of tris-bidentate transition metal complexes by X-ray structure analysis provides data for evaluating spectroscopic methods and their basis models. Pairs of trigonally symmetric complexes having identical ligand atoms in five- and six-membered chelate rings with the same metal are especially useful for this purpose. We present the first such data for oxygen ligands with oxalate and malonate complexes of chromium(III). X-Ray studies of co-ordinated malonate ion have not been previously reported and the conformational possibilities of the six-membered chelate ring confer additional interest on the malonate complexes.



FIGURE

The structure A of $Na(+)_{546}[Co(mal)_2(en)]$ (mal = $CH_2(CO_2)_2^{2-}$ en = ethylenediamine) has been refined to $R = 0{\cdot}058$ by full-matrix least-squares using 838 integrated Weissenberg and precession Mo-K_α reflections. The complex ion is assigned the Δ absolute configuration (Figure) on the basis of 37 Friedel pairs of Cu-K_α Weissenberg data. The absolute configuration of $(-)_{589}[Co(-)\text{-}(pn)_3](+)_{589}[Cr(mal)_3]$ (pn = 1,2-diaminopropane), B, was assigned from the known configuration of the cation;[1] the anion has the Λ absolute configuration. Refinement is continuing with R presently 0·072 for 376 non-zero integrated Mo-K_α data. In both A and B the refinements have included anisotropic temperature factors for the metal atoms and isotropic temperature factors for the remaining atoms.

In A the complex ion exhibits an approximate non-crystallographic two-fold axis; the malonate rings adopt boat conformations and fold towards each other. In the notation of the Figure the Co and C(32) atoms lie 0·42 and 0·45 Å on the same side of the O(3L), O(4L), C(31), C(33) plane; the corresponding distances for the other malonate boat are 0·61 and 0·36 Å. In structure B the cations and anions occupy sites of symmetry 32 although both ions have only a 3-fold symmetry axis. This disorder results in two sites for the methyl group of $[Co(pn)_3]^{3+}$ and two sites for the methylene and non-ligating oxygens of $[Cr(mal)_3]^{3-}$. In the latter case the chromium, the ligand oxygens, and the carboxylcarbon atoms are planar, corresponding to 32 symmetry. The methylene carbon lies 0·69 Å from this plane; the conformation may be described as a boat flattened at one end. Dreiding models give no clear indication of the most favourable conformation for a chelated malonate ring and n.m.r. studies of the $[Co(mal)_2(en)]^-$ complex were also indefinite.[2] In both structures hydrogen bonding with lattice water plays an important part in determining the precise conformation of the ring though intramolecular effects are the most probable cause of ring flattening in the $[Cr(mal)_3]^{3-}$ case.

A previous determination of the structure of $K(+)_{589}[Ni(o\text{-phenanthroline})_3](-)_{589}[Co(oxalate)_3],2H_2O$[3] has shown the absolute configuration of both complex ions to be Λ. X-Ray powder photographs indicate that this structure is isomorphous with the $K(+)_{589}[Ni(o\text{-phenanthroline})_3](+)_{589}[Cr(oxalate)_3],2H_2O$ salt; the chromium anion must also be Λ.

The absolute configurations of the $(+)[Co(mal)_2en]^-$ and $(+)[Cr(oxalate)_3]^{3-}$ ions are as predicted from o.r.d. and c.d. studies;[4,5] the configuration of the $(+)[Cr(mal)_3]^{3-}$ ion is opposite that derived from some c.d. studies.[5] However, if the components of the c.d. spectrum have been correctly assigned, this result for $(+)[Cr(mal)_3]^{3-}$ supports the qualitative aspects of Piper's model of optical activity for trigonally symmetric transition metal complex ions.[6] This model requires the sign of the Cotton effect of the low energy absorption band to be determined by distortions of the octahedron of ligand atoms rather than by the absolute configuration of the complex ion. In terms of Piper's model, the values of the trigonal distortion angle, δ (60° minus the angle between the ligand oxygens in a chelate ring projected on a plane perpendicular to the three fold axis of the complex), are $+6{\cdot}0(1{\cdot}5)$ and $-0{\cdot}6(1{\cdot}1)°$ for the $(-)[Co(oxalate)_3]^{3-}$ and $(+)[Cr(mal)_3]^{3-}$ ions respectively; the intraligand angles at the metal are 84·3(1·5) and 92·4(1·1)°. Racemic $(NH_4)_3[Cr(oxalate)_3],2H_2O$[7] is computed to have an average δ value of 9° and the $(+)[Cr(oxalate)_3]^{3-}$ ion should be closely similar to $(-)[Co(oxalate)_3]^{3-}$. While the significance level of δ for the oxalate complexes is high, that for the malonate is low.

It is known[5] that the sign of the E_a component inverts from the c.d. spectrum of $\Lambda(+)Cr(oxalate)_3$ to that of $\Lambda(+)\text{-}Cr(mal)_3$. If the assignments of the E_a component are correct, the above results are explained in terms of Piper's model at a low significance level. The alternative model relating the absolute configuration of tris complex ions to the sign of the E_a component is not supported.

Crystal data. A: $Na[Co(C_3H_2O_4)_2(C_2H_8N_2)],2H_2O$; M = 382·1; Orthorhombic, $P2_12_12_1$; a = 13·46(2), b = 14·24(2), c = 7·34$_4$(1) Å, U = 1408(5) Å,^{3} D_m = 1·78(2) g cm^{-3}, Z = 4, D_c = 1·80. B: $[Co(C_3H_{10}N_2)_3][Cr(C_3H_2O_4)_3],3H_2O$; M = 693·6; Rhombohedral, R_{32}; hexagonal parameters, a = 16·12(2), c = 10·07(2) Å, U = 2265(7) Å^3, D_m = 1·52(2) g cm^{-3}, Z = 3, D_c = 1·53.

Estimated standard deviations are given in parentheses.

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