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"D_3 CHROMOPHORES - geometric distortion in trigonal-dihedral transition metal chromophores and its relevance to optical circular dichroism."

a thesis submitted for the
Degree of Doctor of Philosophy
at the University of Adelaide
in May, 1973.

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SUMMARY

The crystal structures of the inorganic salts, sodium $(+)_{546}$-bis(malonato)1,2-diaminoethane cobaltate(III) dihydrate, Na $(+)_{546}[Co(C_3H_2O_4)_2(C_2H_8N_2)].2H_2O$, $(-)_{589}$-tris($(-)_{589}$1,2-diaminopropane)cobalt(III) $(+)_{589}$-tris(malonato)chromate(III) trihydrate, $(-)_{589}[Co(-)_{589}(C_3H_{10}N_2)_3](+)_{589}[Cr(C_3H_2O_4)_3].3H_2O$, and potassium calcium $(+)_{589}$-tris(dithiooxalato)cobaltate(III) tetrahydrate, K.Ca $(+)_{589}[Co(C_2O_2S_2)_3].4H_2O$, have been determined and refined by a full-matrix least-squares procedure with conventional *R* factors at convergence of 0.050, 0.073 and 0.062 respectively. The absolute configurations of the complex anions in the respective structures were assigned as Δ,Λ and Λ.

The absolute configurations of the complex ions in the previously determined structure, potassium $(+)_{589}$-tris(1,10-phenanthroline)nickel(II) $(-)_{589}$-tris(oxalato)cobaltate(III) dihydrate, $K(+)_{589}[Ni(C_{12}H_8N_2)_3](-)_{589}[Co(C_2O_4)_3].2H_2O$, have both been determined as Λ using the technique of X-ray anomalous dispersion. The complex ions $(+)_{589}$-tris(oxalato)chromate(III), $(+)_{589}[Cr(C_2O_4)_3]^{3-}$, $(-)_{600}$-tris(malonato)cobaltate(III), $(-)_{600}[Co(C_3H_2O_4)_3]^{3-}$, $(-)_{400}$-tris(1,3-diaminopropane)chromium(III), $(-)_{400}[Cr(C_3H_{10}N_2)_3]^{3+}$ and $(+)_{589}$-tris(1,10-phenanthroline)ruthenium(II), $(+)_{589}[Ru(C_{12}H_8N_2)_3]^{2+}$, have all been assigned a Λ absolute configuration on the basis of X-ray powder diffraction patterns of the relevant least-soluble diastereoisomers.

Angular distortion parameters of the ML_6 coordination polyhedra in several inorganic structures of pseudo-D_3 symmetry have been computed from the crystal coordinates; the distortion of this core from O_h symmetry in tris-bidentate complexes has been correlated with the size of the ligand bite angle, α, on the basis of a repulsive electrostatic potential operative between the six ligand donor atoms. This theoretical model predicts a distortion towards trigonal-prismatic geometry for tris-complexes containing bidentate ligands which subtend angles, α, less than 90^o at the coordinated metal atom; for $\alpha > 90^o$ the model predicts a geometry more flattened relative to the three-fold axis than that in which the three bidentate ligands are orthogonal.

The computed ML_6-core distortions of relevant tris-bidentate transition metal complexes have been considered in assessing the validity of a limited crystal-field trigonal distortion model proposed by Piper and Karipides for correlating the absolute configuration of a chiral trigonal-dihedral (D_3) chromophore with the sign of the observed rotatory strength. It is concluded that this model does not adequately explain the observed Cotton effects for all pseudo-D_3 transition metal complexes.