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New Optically Active Metal Ions

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Chiroptical measurements may be useful both stereochemically and spectroscopically. Werner complexes of only a few metal ions {*e.g.* Co(III), Cr(III), Fe(II)} have been resolved, for kinetic reasons. The optical activity of other species, which racemize too readily for classical measurements, may be demonstrated through solid state circular dichroism. We report here an extension of the range of chromophores whose circular dichroism spectra may be measured, with the first such results for d^2 and d^4 high spin configurations.

From solutions of the labile tris-oxalato complexes of vanadium(III), manganese(III) and iron (III) (where the rates of exchange of complexed oxalate with external oxalate are so high that there is little prospect of measuring chiroptical effects in solution) we have now crystallized, with the (+)-$[Co(en)_3]^{3+}$ cation, the isomorphous series (including M = Cr or Co) of diastereoisomeric salts of the composition $\{(+)[Co(en)_3]\}[M(C_2O_4]nH_2O$, in which the anion is dissymmetric as revealed by the circular dichroism in the solid state (alkali halide disc). Even more clear is the situation with the analogous colourless ion of rhodium(III), $(-)[Rh(en)_3]^{3+}$, where any Cotton effect observed for the diastereoisomeric isomorphous salts $\{(-)[Rh(en)_3]\}\{\Lambda[M(C_2O_4)_3]\}pH_2O$ in the visible region must arise from the anion. As expected, no chiroptical absorption was found for the ferric diastereoisomer. The Λ absolute stereochemistries assigned to the anions in the salts $(-)[Rh(en)_3]\cdot\Lambda[M(C_2O_4)_3]$ are an obvious deduction from the rule of isomorphous less soluble diastereoisomers and the known Λ configurations[1] of the enantiomers of $[Crox_3]^{3-}$ and $[Coox_3]^{3-}$ which are present in their salts with $(-)[Rhen_3]^{3+}$.

We may conclude that $\Lambda[V(C_2O_4)_3]^{3-}$ has circular dichroism ($\Delta\epsilon$) at 630 nm ($\Delta\epsilon$ – 0.46) and 430 nm ($\Delta\epsilon$ – 1.94), and that $\Lambda[Mn(C_2O_4)_3]^{3-}$ has circular dichroism at 525 nm ($\Delta\epsilon$ + 0.92) and 455 nm ($\Delta\epsilon$ – 1.14).

References

1 a) K. R. Butler and M. R. Snow, *Chem. Comm.*, 1971, 550; b) *Idem, J. Chem. Soc. (A)*, 1971, 525.