A Chemical Correlation of Octahedral Configurations

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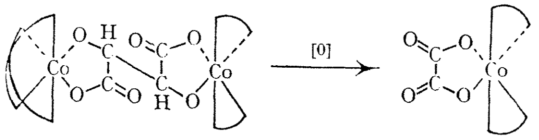
THE current uncertainty[1] regarding the electronic origin of optical activity in transition-metal complexes has led us to search for meaningful chemical correlations of octahedral configurations. We report here the novel conversion of a binuclear complex (A) to monomeric oxalatobisethylenediamine-cobalt(III) (B) as shown below.



(A) (B)

When (+)-tartaric acid reacts in water with DL-carbonatobisethylenediaminecobalt(III), the product is primarily a mixture of two dimeric diastereoisomers. Stereoselective reactions of this mixture with such nucleophiles as chloride, nitrite, and ethylenediamine have been discovered,[2] leading to such complexes as D(+)-[Co en_2 $(NO_2)_2]^+$.

We have obtained, by chromatography on Sephadex G10 and fractional crystallisation, crystalline samples of the perchlorate of one of the dimeric diastereoisomers, which we have characterized as (A). Analysis shows that for each tartrate ligand there are four ethylenediamine ligands, and the electronic spectrum is typical of a $Co^{III}N_4O_2$ chromophore. The ^1H n.m.r. confirms the analytical conclusion (τ 5·68 and 7·25 intensity ratio 1 : 8), and shows that the two protons of the tartrate bridging group are equivalent. Complex (A) undergoes rapid and reversible protonation. The molar conductivity of (A) as its perchlorate is consistent with its being a 1 : 2 electrolyte.

The c.d. spectrum of (A) shows a large negative band in the region of the lowest energy *d–d* absorption (Figure), and we confirm our assignment of the absolute configuration (L at each cobalt) by oxidation with cold, neutral potassium permanganate solution. This gives L(—)-oxalatobisethylenediamine cobalt(III) perchlorate, which we have identified by comparison with an authentic sample (electronic, c.d., and i.r. spectra). The more water-soluble product of the preparative reaction has similarly been shown to be the bridged tartrate dimer with the D-configuration at each cobalt.

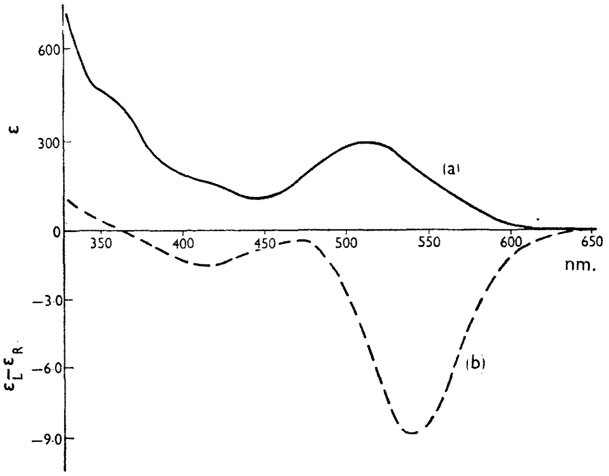


FIGURE. *The absorption spectrum* (a) *and circular dichroism* (b) *of* (—)$[en_2Co_L\{(+)tartrate\}Co_Len_2](ClO_4)_2$ *in water.*

The present example encourages us in our belief that empirical comparisons (from Cotton effects)[3] of the optical configurations of metal complexes are useful.

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[1] R. D. Gillard, "O.R.D, and C.D", in "Physical Methods in Advanced Inorganic Chemistry" ed. H. A. O. Hill and P. Day, Interscience, 1968, page 167.

[2] H. B. Jonassen, J. C. Bailar, and E. H. Huffman, *J. Amer. Chem. Soc.*, **1948**, **70**, 756.

[3] R. D. Gillard, *Chem. in Britain*, **1967**, 205.