A Chemical Correlation of Octahedral Tris-chelate Compounds

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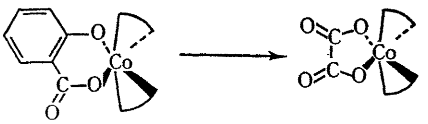
CHEMICAL correlations of optical configuration among octahedral complexes have been achieved previously for (i) a series[1] of bis-chelated compounds of the type $[\mathrm{Co\text{-}en_2XY}]^{n+}$ where X and Y are monodentate ligands such as isothiocyanate or ammonia, (ii) several binuclear series[2] which have been related to the corresponding monomeric compounds, and (iii) tris-cysteinatocobaltate(III) and its sulphinate derivative.[3] Non-trivial chemical correlations between tris-chelated compounds are rare. We report here the first case in which the size of the ring is altered.

(—)-Salicylatobisethylenediaminecobalt(III) (A) reacts slowly ($t_{\frac{1}{2}}$ *ca.* 12 hr.) with hot nitric acid to give finally oxalatobisethylenediaminecobalt(III) (B) which is optically inactive.[4] We find, using ^{14}C, that the carboxyl labelled carbon of A is no longer present in B. Further, the resolved oxalato-complex loses its optical activity readily in the reaction medium ($t_{\frac{1}{2}} \simeq$ 30 min. at 80°).†



However, oxidation with neutral or acid permanganate gives a strongly optically active product, fairly rapidly in very good yield in the cold (*via* several as yet unidentified intermediates). The product B, which has lost the ^{14}C label, has been identified with an authentic sample [i.r. and analysis (solid) and electronic spectra, o.r.d., and c.d. (solution)]. The properties of A and B are shown in the Figure.

Six-membered chelate rings tend in general to give smaller rotational strengths than five-membered rings,[5] since A [six-membered ring; $(\epsilon_L - \epsilon_R)_{max}$ — 0·90] must be at least as optically pure as B (five-membered ring; $(\epsilon_L \pm \epsilon_R)_{max}$ — 2·4). It seems likely that the conversion of A into B occurs without inversion and that the

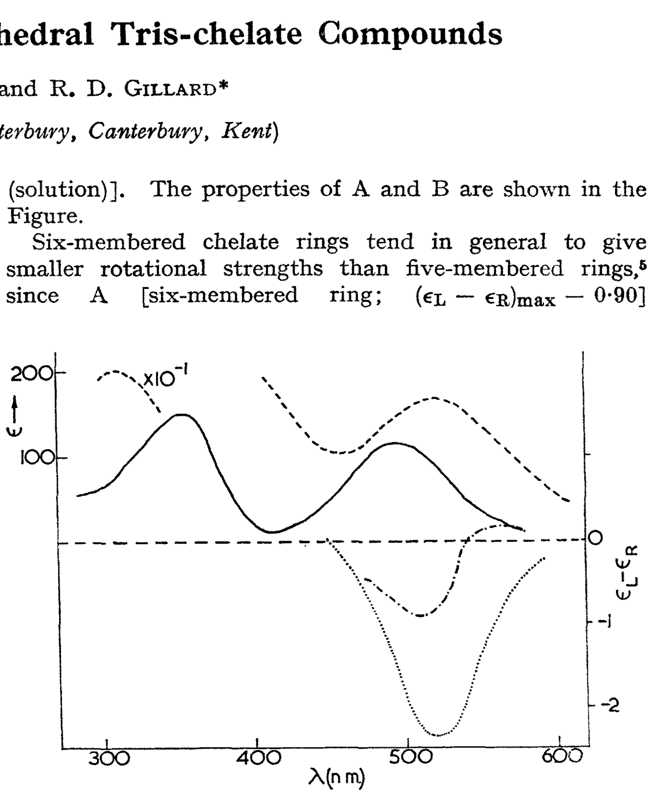


FIGURE. *The absorption* (– – – –) *and circular dichrois m* (– . *of the cation* (—)-[Co en$_2$ sal]$^+$, (A) *and the absorption* (———) *and circular dichroism* (. . . .) *of the cation* (—)-Co en$_2$ ox]$^+$ (B).

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empirical rules[6] relating the dominant sign of the Cotton effect in the visible region to the absolute configuration of a cobalt(III) complex can be applied to molecules of the type [Co(AB)(CD)(EF)] where AB and CD are four- or five membered bidentate chelate rings, and EF is six-membered.

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