The Resolution and the Stereochemistry of Di-μ-hydroxo-tetrakis-(α-di-imine)dichromium(III) Ions

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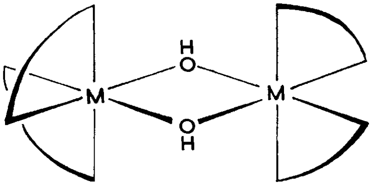
THE binuclear complex ions,[1-3] $[L_2M(OH)_2ML_2]^{4+}$ (I), where L is 1,10-phenanthroline or 2,2'-bipyridyl and M is iron(III) or chromium(III), give rise in principal to *meso*- and (+)- and (−)-isomers in the statistical ratio of 2 : 1 : 1. We find, however, that the incremental precipitation of the binuclear chromium(III) ions from solutions of the nitrate at pH 4 by the successive addition of portions of potassium antimonyl (+)-tartrate up to equivalence yields fractions which contain only optically active complex cations. In the case of both the phenanthroline and the bipyridyl binuclear chromium(III) ion the (−)-isomer forms the less-soluble diastereoisomer with antimonyl (+)-tartrate, and, together with the corresponding (+)-isomer, it accounts for at least 95% of the starting material. Models indicate that the *meso*-isomer if formed would be grossly hindered sterically whereas the (+)- and (−)-isomers are relatively free from steric constraints.



(I)

Antimonyl (+)-tartrate was removed from the less-soluble diastereoisomers as the silver salt, and the phenanthroline binuclear chromium ion (I) was isolated as the anhydrous chloride, $[\alpha]^{20}_{D}$ − 1095°, whilst the corresponding bipyridyl complex was obtained as the perchlorate monohydrate, $[\alpha]^{20}_{D}$ − 850°. The circular dichroism and absorption spectra of the phenanthroline and bipyridyl binuclear chromium(III) ions are qualitatively similar to those of the mononuclear analogues,[4] $(-)$-$[Cr(phen)_2ox]^+$ and $(-)$-$[Cr(bipy)_2ox]^+$, respectively (Figure), and to those of the hydrolysis products, $(-)$-$[Cr(phen)_2(H_2O)_2]^{3+}$ and $(-)$-$[Cr(bipy)_2(H_2O)_2]^{3+}$, formed by heating the corresponding binuclear complexes at 70° in 1M-nitric acid for 14 hours.[3] The circular dichroism observed in the 30,000—40,000 cm.$^{-1}$ region (Figure) is of the typical exciton form, consisting of two major bands with opposed signs and nearly equal areas. These circular dichroism bands arise from the coupling of excitations which are polarised in the direction of the longer in-plane axis of the free ligands,[5] and calculations of the exciton splitting, based upon the Coulombic interaction energy between the transition monopoles of different ligands in the complex,[6] show that the $(-)$-isomers, giving a major negative and positive dichroism band at lower and higher frequencies, respectively, in the 30,000—40,000 cm.$^{-1}$ region (Figure), have the $M(C_2)$ stereochemical configuration (I). The $(-)$-isomers of the analogous mononuclear complexes similarly are found to have the $M(C_2)$ configuration, and accordingly the acid-catalysed cleavage reaction[3] of the binuclear chromium(III) ions proceeds largely with retention of configuration.

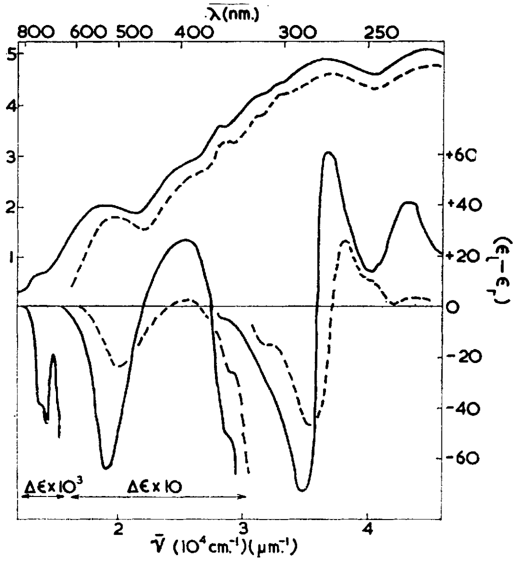


FIGURE. *The absorption spectra (upper curves) and circular dichroism (lower curves) in water of* $(-)$-*di-μ-hydroxy-tetrakis-*(1,10-*phenanthroline*)*dichromium* (III) *tetrachloride* (———) *and of* $(-)$-*oxalatobis-*(1,10-*phenanthroline*)*chromium*(III) *perchlorate* (— — —).

(*Received, September 12th*, 1968; *Com.* 1241.)

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