The Chelate Ring Conformations of the Tris(trimethylenediamine)cobalt(III) Ion

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Summary The temperature-dependence of the solution c.d. spectrum of (+)-[$Co(tn)_3$]$^{3+}$ and the solid-state c.d. of (+)-[$Co(tn)_3$]Br_3,H_2O indicate a conformational equilibrium in solution between a tris-skew-boat and a tris-chair form, the latter being the more stable by 0·5 kcal mol^{-1}.

THE tris-chelated complex ion formed by cobalt(III) with trimethylenediamine (tn) in the crystal (−)-[$Co(tn)_3$]Br_3,H_2O has been shown to have the Λ-configuration and tris-chair conformation by X-ray diffraction analysis.[1] We find that the c.d. spectrum of the enantiomorphous crystal, (+)-[$Co(tn)_3$]Br_3,H_2O, in a microcrystalline form in a potassium bromide matrix, differs from the corresponding spectrum of a solution of the complex ion, and that the latter spectrum is temperature-sensitive (Figure). Thus $[Co(tn)_3]^{3+}$ in solution at ambient temperature exists only partly in the tris-chair conformation (I) adopted in the crystal studied.

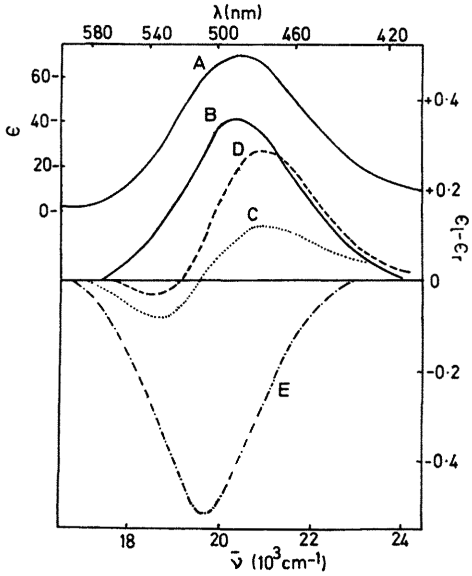
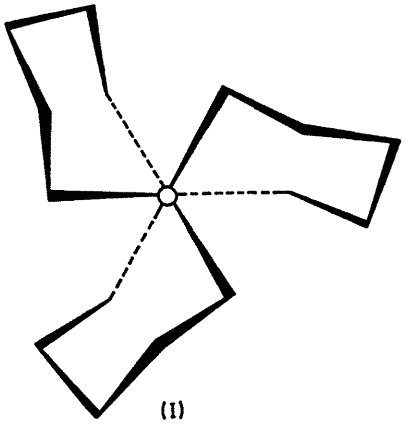


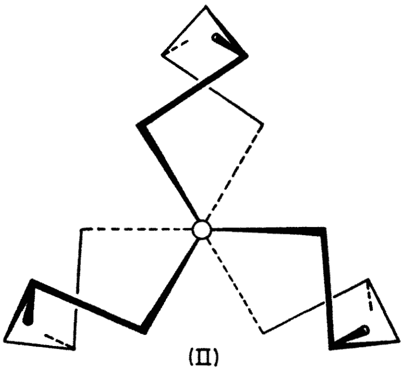
FIGURE. *The absorption spectrum* (A) *and the c.d. spectrum* (B) *of* (+)-$[Co(tn)_3]Br_3,H_2O$ *in a potassium bromide matrix, and the c.d. spectrum of* (+)-$[Co(tn)_3]^{3+}$ *in water at* 330 K (C) *and in ethylene glycol–water* (7 : 3) *at* 198 K (D). *Curve* (E) *represents the c.d. spectrum of* $(-)_{546}$-$[Co(RR\text{-}ptn)_3]^{3+}$ *in water* (*from ref.* 4).

A conformational analysis indicates[2] that the tris-chair conformation of $[Co(tn)_3]^{3+}$ is expected to be only 0·5 kcal mol^{-1} per ring more stable than a tris-skew-boat form with an N–Co–N chelate ring angle of 90°. Recent calculations[3] suggest that the particular tris-skew-boat conformation in which the C–C–C plane of each chelate ring is approximately parallel to the C_3 axis of the complex ion, the *lel*-twist form (II), has 0·9 kcal mol^{-1} less strain energy than the tris-chair form in the ideal-gas state. The *ob*-twist form (III), in which the C–C–C of each chelate ring is obliquely inclined with respect to the C_3 axis of the complex, has a substantially higher energy.[3]



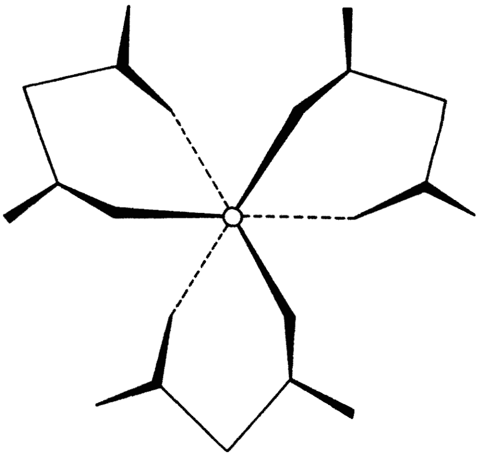
(I)

The ligand (*RR*)-2,4-diaminopentane (*RR*-ptn) forms tris-chelate complexes with cobalt(III) in which the *lel*-twist form (II) is adopted for the Δ-configuration and the *ob*-twist form (III) for the Λ-configuration on account of the equatorial preference of the methyl substituents in the chelate rings.[4] For the same reason *meso*-2,4-diaminopentane (*RS*-ptn) forms a tris-chelate complex with the tris-chair conformation (I). The isomers $(+)_{546}$- and $(-)_{546}$-$[Co(RR\text{-}ptn)_3]^{3+}$ and $(-)_{546}$-$[Co(RS\text{-}ptn)_3]^{3+}$ have been isolated and their c.d. spectra recorded.[4] The solid-state c.d. spectrum of (+)-$[Co(tn)_3]Br_3,H_2O$ closely resembles the solution c.d. spectrum[4] of $(+)_{546}$-$[Co(RS\text{-}ptn)_3]^{3+}$, both representing the tris-chair conformation (I). A recent *X*-ray diffraction analysis of $(+)_{546}$-$[Co(RR\text{-}ptn)_3]Cl_3,H_2O$ shows[5] that the complex ion in this crystal has the *ob*-twist conformation and the Λ-configuration, enantiomeric to (III). Accordingly the isomer $(-)_{546}$-$[Co(RR\text{-}ptn)_3]^{3+}$ has the Δ-configuration and *lel*-twist conformation (II).



(II)

If it is assumed that the principal conformers of (+)-$[Co(tn)_3]^{3+}$ in solution are the Δ-tris-chair (I) and Δ-*lel*-twist form (II) an analysis[6] of the observed temperature-variation of the c.d. spectrum (Figure) indicates that the tris-chair form (I) is the more stable by 0·5 ± 0·1 kcal mol^{-1} in aqueous solution or by 0·7 ± 0·1 kcal mol^{-1} in ethylene glycol–water (7 : 3). At 20° the tris-chair population is 70% in aqueous solution or 77% in the glycol–water mixture, the entropy-difference between the conformations (I) and (II) being 0 ± 1 e.u. in both cases.



(III)

The changes observed[7,8] in the c.d. spectrum of (+)-$[Co(tn)_3]^{3+}$ in aqueous solution at ambient temperature on the addition of polarisable oxy-anions suggest that the tris-chair conformation (I) is stabilised by ion-association. On the addition of selenite or phosphate[9] the c.d. spectrum of a 0·01M aqueous solution of (+)-$[Co(tn)_3]Br_3,H_2O$ changes progressively towards the corresponding spectrum of that salt in a potassium bromide matrix (Figure). At 0·05M-oxy-anion concentration, where the effect saturates, the solution and the solid-state c.d. spectra of (+)-$[Co(tn)_3]Br_3$,-H_2O are virtually superposable. However, the effect of gegenions upon the c.d. spectrum of (+)-$[Co(tn)_3]^{3+}$ is only partly due to conformational changes, at least in non-aqueous solvents, for (+)-$[Co(tn)_3]I_3$ in sulpholane[9] exhibits a c.d. band ($\Delta\epsilon_{485}$ + 0·8) with an area twice as large as that of (+)-$[Co(tn)_3]Br_3,H_2O$ in a potassium bromide matrix (Figure), the additional rotational strength arising from interionic charge transfer.[10]

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