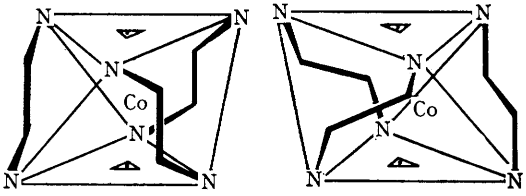
The Effect of Ring Conformation on The Optical Activity of Transition-Metal Complexes

By A. J. McCAFFERY*, S. F. MASON, and MISS B. J. NORMAN
(*School of Chemical Sciences, University of East Anglia, Norwich*)

COREY and BAILAR[1] have shown that the ethylenediamine ring in a chelated complex can adopt one of two enantiomorphous conformations, *k* and *k'*, in which the N–C–C–N chain forms a segment of a left-handed and a right-handed helix, respectively. The *kkk* arrangement of the three rings gives the more stable *lel* conformation (Figure 1a) and the less stable *ob* conformation (Figure 1b) in tris-diamine complexes with the same absolute configuration as (+)- and (−)-Co(en)$_3^{3+}$, respectively.[1] Equilibration studies[2] demonstrate that the *lel* conformation is more stable than the *ob* by a free-energy increment of 0·6 kcal. per ring.

Recently it has been suggested[3] that the large positive and small negative circular dichroism bands of (+)-Co(en)$_3^{3+}$ in the visible wavelength region are due to complex ions respectively in the *lel* and in the *ob* or mixed *kkk'* or *kk'k'* conformation. (+)-Propylenediamine forms chelate rings predominantly with the *k*-configuration, in which the methyl group is equatorial with respect to the ring, since the axial methyl group of the *k'*-conformation increases the energy of the ring by 2 kcal.[1] Thus (+)- and (−)-Co(+pn)$_3^{3+}$ have the *lel* (Figure 1a) and *ob* conformation (Figure 1b), respectively, and the circular dichroism spectra of these complex ions are now reported (Figure 2).



(a) (b)

FIGURE 1. (a) *The* lel *conformation* (kkk) *of the diamine chelate rings in* (+)–Co(en)$_3^{3+}$ *or* (+)–Co(+pn)$_3^{3+}$, *and* (b) *the* ob *conformation* (kkk) *of the rings in* (−)–Co(en)$_3^{3+}$ *or* (−)–Co(+pn)$_3^{3+}$.

* Present address: Chemistry Department IV, University of Copenhagen.

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It is found that (+)-Co(+pn_3)$^{3+}$ gives two circular dichroism bands with opposed signs in the visible region (Figure 2). These bands cannot be due to different conformations of the complex ion, and they are ascribed to different electronic transitions of the ion, following the previous interpretation based on single-crystal studies[4] of the corresponding bands of (+)-Co$(en)_3^{3+}$.

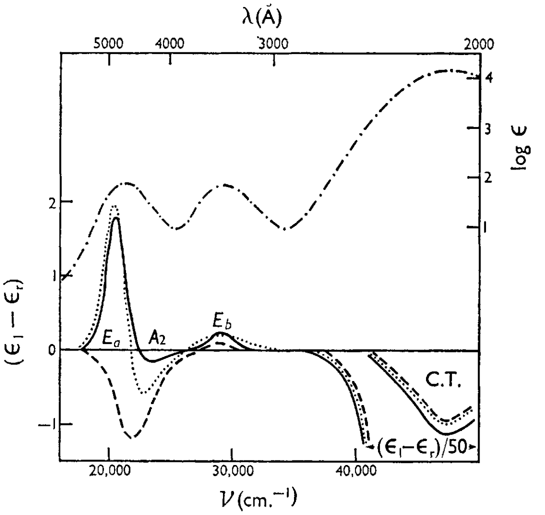

FIGURE 2. *The electronic absorption spectra* —·—· *of* (+)- *and* (−)-Co(+pn)$_3^{3+}$, *and the circular dichroism spectrum of* —— (+)-Co(en)$_3^{3+}$, ----- (−)-Co(+pn)$_3^{3+}$, *and* ········ (+)-Co(+pn)$_3^{3+}$.

The A_2 circular dichroism band at shorter wavelengths is substantially weaker in (+)-Co(en_3^{3})$^+$ than in (+)-Co(+pn)$_3^{3+}$, whilst in (−)-Co(+pn)$_3^{3+}$ it is absent, presumably because it is overlaid by the stronger E_a band which is of opposite sign (Figure 2). This observation suggests that different conformations of Co(en)$_3^{3+}$ co-exist in solution, and it is consistent with the thermodynamic data[2] which show that (+)-Co(en)$_3^{3+}$ in aqueous solution at 25° exists in the *kkk* (*lel*), *kkk'*, *kk'k'*, and *k'k'k'* (*ob*), conformations in the proportions, 59%, 29%, 8%, and 4%, respectively.

The absolute configuration of the chelate rings around the metal ion is the same[5] in (+)-Co(+pn)$_3^{3+}$ as in[6] (+)-Co(en)$_3^{3+}$ (Figure 1a), but (−)-Co(+pn)$_3^{3+}$ has the enantiomeric configuration[1] (Figure 1b). The sign of the E_a circular dichroism band in the visible region reflects these configurational relationships,[7] but the charge-transfer circular dichroism band near 2200 Å is negative in all three cases (Figure 2). Since the diamine chelate rings in each of the three complexes have predominantly the *k*-conformation, this observation suggests that the positive or negative sign of the charge-transfer circular dichroism band depends upon, respectively, the right- or left-handed configuration of the N–C–C–N chain of the diamine.

A similar correlation is found in studies of diamine complexes with lower symmetries. The only elements of dissymmetry in *trans*-(−)-Co(−pn)$_2$Cl$_2^+$ are the asymmetric carbon atom and the *k'*-conformation[8] of the (−)-propylenediamine rings, and this complex gives a positive charge-transfer circular-dichroism band at 2400 Å in accord with the right-handed stereochemistry of both of the N–C–C–N chains. Similarly the charge-transfer circular-dichroism band at 2300 Å of each of the bis-(−)-propylenediamine oxalato-complexes, (+)- and (−)-Co(−pn)$_2$(ox)$^+$, has a differential extinction coefficient $(\epsilon_l - \epsilon_r)_{max}$ which is displaced to a more positive value from that of the corresponding band of the respective ethylenediamine complex, (+)- and (−)-Co(en)$_2$(ox)$^+$.

The correlation observed between the sign of the circular dichroism in the charge-transfer region and the chirality of the diamine chain, irrespective of the absolute configuration of the chelate rings about the metal ion, suggests that current theories[9–12] which ascribe the optical activity of metal complexes solely to distortions of the ligand atoms, or their orbitals, from the octahedral disposition are of limited application.

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