Chemical
Communications

NUMBER 14/1969 23 JULY

Vicinal and Conformational Contributions to the Circular Dichroism of Tetragonal Diaminecobalt(III) Complexes

By C. J. Hawkins

(Department of Chemistry, University of Queensland, St. Lucia, Australia 4067)

Summary The circular dichroism spectra of complexes of the type, *trans*-[Co diamine$_2$Cl$_2$]$^+$, have been interpreted as arising principally from the conformational effect for *C*-substituted diamines, and from both vicinal and conformational effects for *N*-substituted diamines.

Rotational strengths of metal complexes *d–d* transitions are principally governed by the distribution of chelate rings about the central metal ion (configurational effect), the conformations of the chelate rings (conformational effect), and the vicinal effects of asymmetric ligands. The contributions from these three are thought to be additive, and the available experimental evidence strongly supports this.[1] In complexes of the type, (−)-*trans,trans*-[Co meen$_2$Cl$_2$]$^+$ and *trans*-{Co(*R*)-pn$_2$Cl$_2$}$^+$, where meen is *N*-methylethylenediamine, the rotational strengths are derived from the conformational and vicinal effects. However, the relative contributions are presently unknown, and it is suggested here that the lack of this information has led to an incorrect assignment[2] of configuration to the former compound.

The circular dichroism (c.d.) of (−)-*trans,trans*-[Co meen$_2$Cl$_2$]$^+$ has been compared to that of (+)-*trans*-[Co trienCl$_2$]$^+$, (+)-*trans*-[Co(+)-3,8-Me$_2$trienCl$_2$]$^+$, *trans*-[Co (*S*)-pn$_2$Cl$_2$]$^+$, and *trans*-[Co (+)-chxn$_2$Cl$_2$]$^+$, which are of known configuration, and it was tentatively concluded that, for this isomer, the *N*-methylethylenediamine had the (*S*) configuration.[2] Subsequently, the absolute configuration has been determined by *X*-ray diffraction, and the ligand has been found to have the (*R*)-configuration and to exist in the complex with the δ-conformation.[3]

Comparison of the c.d. spectra of cobalt(III),[4,5] and rhodium(III)[6] complexes of the type *trans*-[M (*R*)-diam$_2$-X$_2$]$^{n+}$ where diam is propylenediamine, which contains one asymmetric centre, with those where diam is diasymmetric, *e.g.* *trans*-1,2-diaminocyclohexane and 2,3-diaminobutane, suggests that the vicinal contribution for diamines is slight, and that the c.d. derives from a conformational effect. This conclusion is supported by the observation that the vicinal effect from asymmetric *C*-substituted unidentate amines is small, in contrast to similar asymmetric carboxylate complexes.[7]

The c.d. spectrum for (−)-*trans,trans*-[Co meen$_2$Cl$_2$]$^+$ has a different form to that of the previous compounds (Figure).

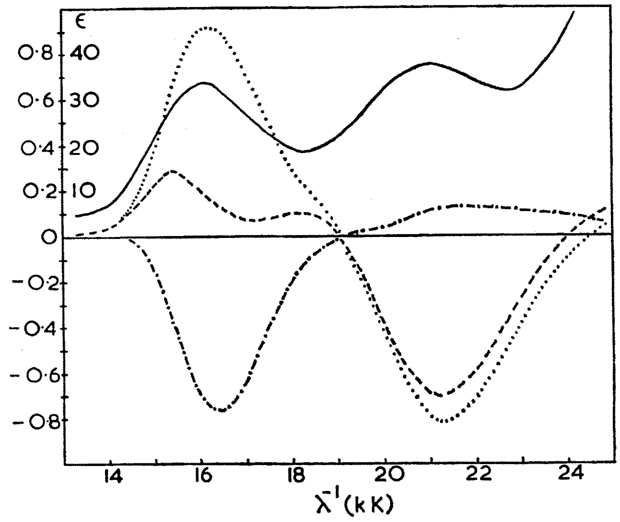

Figure. *Absorption (———) and circular dichroism (– – – –) spectra of* (−)-*trans,trans*-[Co meen$_2$Cl$_2$]$^+$ *in methanol showing the suggested contributions from the δ-conformation (— · —) and the* (R)-*asymmetric nitrogen (· · · · · ·).*

As the c.d. spectra of the meen compound in methanol, and in the crystalline form as a perchlorate in a KBr disc, in which the δ-conformation is known to be exclusively present,[3] show the same sign pattern and the same relative intensities for the Cotton effects, the δ-conformation must be dominant in solution, and would be expected to enforce the same signs of Cotton effects for the three components of the T_{1g} band as were found for (*S*)-propylenediamine. The fact that the observed A_{2g} band has the opposite sign indicates that the vicinal effect from the (*R*)-asymmetric nitrogen must be dominating the c.d. spectrum. In the Figure, the c.d. spectrum of *trans*-[Co (*S*)-$pn_2Cl_2]^+$ has been taken to represent the conformational effect from the δ-conformation of *N*-methylethylenediamine. The whole spectrum has been moved 300 cm.$^{-1}$ to lower energy as the E_g absorption bands of the two complexes are separated by this energy. The approximate vicinal effect so determined for the (*R*)-asymmetric nitrogen has a positive Cotton effect dominating the E_g transition and a negative band for the A_{2g} component.

The conclusion that the vicinal and conformationa effects are opposing one another for the *N*-methyl compound is supported by a comparison of the c.d. spectra[5,8] of [Co(*R*)-pn$(NH_3)_4]^{3+}$, and $(+)_{400}$-[Co meen$(NH_3)_4]^{3+}$. The ratio of the rotational strengths of the two observed Cotton effects are different for the *C*-methyl and *N*-methyl complexes, and the rotational strength of the dominant positive band for the latter is approximately half that of the former.

(*Received, April 28th,* 1969; *Com.* 593.)

---

[1] See, for example, C. T. Liu and B. E. Douglas, *Inorg. Chem.*, 1964, **3**, 1356.
[2] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 1968, **7**, 915.
[3] W. T. Robinson, D. A. Buckingham, G. Chandler, L. G. Marzilli, and A. M. Sargeson, *Chem. Comm.*, 1969, 539.
[4] R. A. D. Wentworth and T. S. Piper, *Inorg, Chem.*, 1965, **4**, 202.
[5] C. J. Hawkins, E. Larsen, and I. Olsen, *Acta Chem. Scand.*, 1965, **19**, 1915.
[6] S. K. Hall and B. E. Douglas, *Inorg. Chem.*, 1968, **7**, 533.
[7] C. J. Hawkins and P. J. Lawson, to be published.
[8] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1967, **89**, 825.