Chemical Communications

(The Journal of The Chemical Society, Section D)

NUMBER 15/1970 5 AUGUST

The Circular Dichroism and the Chirality of the Unsymmetric-*cis*- and the *trans*-$(+)_D$-Bis(diethylenetriamine)cobalt(III) Ion

By F. R. KEENE and G. H. SEARLE*

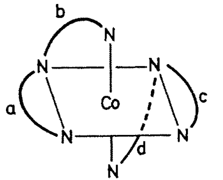
(*Department of Physical and Inorganic Chemistry, The University of Adelaide, Adelaide, South Australia* 5001)

and S. F. MASON

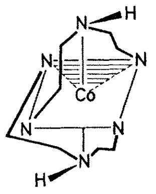
(*School of Chemical Sciences, University of East Anglia, Norwich*)

Summary The circular dichroism of the systems u-*cis*-$(+)_D$-$[Co(dien)_2]^{3+}$ and *trans*-$(+)_D$-$[Co(dien)_2]^{3+}$ indicates the stereochemical configuration of the former, and indicates in the latter a new type of chirality which has hitherto not been realized, but which will be present in metal–polyamine complexes.

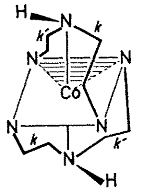
THE three geometric isomers of $[Co(dien)_2]^{3+}$ have been isolated recently, and the unsymmetrical *cis* (u-*cis*) (I) and the *trans* isomer (II), each having only C_2 symmetry, have been resolved into optical antipodes.[1] The third isomer,[1] symmetrical *cis* (s-*cis*), is not dissymmetric (C_{2h} symmetry).



(I) u-*cis*-$(+)_D$-$[Co(dien)_2]^{3+}$



(IIa) *trans* – δ–NH



(IIb) *trans* – λ–NH

The c.d. spectra of the u-*cis*-$(+)_D$- and the *trans*-$(+)_D$-$[Co(dien)_2]^{3+}$ optical isomers have now been measured (Figure) in order to determine the stereochemical configuration of the former and to evaluate the optical effect of a new type of chirality in the latter. The results show (Figure) that u-*cis*-$(+)_D$-$[Co(dien)_2]^{3+}$ in aqueous solution gives a major positive and a minor negative c.d. band, at a lower and a higher frequency, respectively, in the spectral region of the octahedral $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption of the

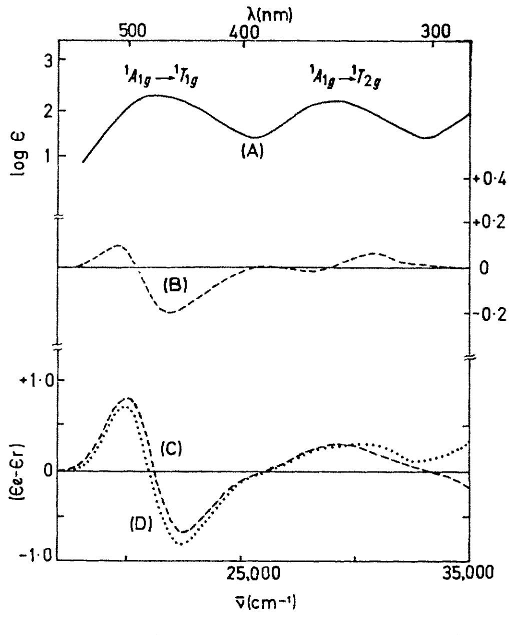


FIGURE. *The absorption spectrum* (A) *and the c.d.* (B) *of trans*-$(+)_D$-$[Co(dien)_2]^{3+}$ *in* 0·1 M-$HClO_4$ *and the c.d. of* u-*cis*-$(+)_D$-$[Co(dien)_2]^{3+}$ (C) *in water and* (D) *in* 0·2 M-*sodium selenite.*

$Co^{III}N_6$ chromophore, the areas of these c.d. bands being diminished and enhanced, respectively, by the addition of a polarisable oxyanion. The signs and relative frequencies and magnitudes of the lower-energy c.d. bands of u-*cis*-$(+)_D$-$[Co(dien)_2]^{3+}$, and the changes in band area on the addition of selenite are similar[2] to the corresponding properties of the analogous c.d. bands of $(+)_D$-$[Co(en)_3]^{3+}$, $(+)_D$-*cis*-$[Co(en)_2(NH_3)_2]^{3+}$, and $(+)_D$-$[Co(penten)]^{3+}$, and it is concluded that the former complex has the same configuration (I) as that of the latter group of complex ions, which also contain the $Co^{III}N_6$ chromophore.

Crystal structure analysis by the anomalous *X*-ray scattering method shows[3,4] that both $(+)_D$-$[Co(en)_3]^{3+}$ and $(+)_D$-$[Co(penten)]^{3+}$ have the Λ configuration, in terms of the ring-pairing nomenclature of the IUPAC commission.[5]

The application of the ring-pairing procedure to u-*cis*-$(+)_D$-$[Co(dien)_2]^{3+}$ indicates that whilst the chelate rings *b* and *d* of (I) have a mutual Δ chirality, both of the pairs *a* and *d*, and *b* and *c*, have a mutual Λ chirality. Thus the overall configuration of (I) is Λ, like that[4] of $(+)_D$-[Co-(penten)]$^{3+}$ where the ring-pairing relations are closely analogous,[6] the two complex ions differing only in that a fifth chelate ring, joining the nitrogen atoms which are secondary in the former (I), is present in the latter complex.

Hitherto the optical activity of dissymmetric metal complexes has been ascribed to two principal sources,[7-9] firstly, the configurational effect due to the chiral disposition of two or more chelate rings (which may be planar) around the metal ion, and secondly, the conformational and vicinal effect due to a preferred dissymmetric conformation of non-coplanar chelate rings augmented by a vicinal perturbation from the asymmetric carbon or nitrogen centre or centres which determine the ring conformation. For *trans*-$(+)_D$-$[Co(dien)_2]^{3+}$ (II) the configurational and the conformational or vicinal effects are vanishing. The stereochemical disposition of the chelate rings about the metal ion in (II) is non-chiral, the symmetry of the complex being D_{2d} if the atoms of each ring are taken to be coplanar. For each dien ligand the conformational effect is internally compensated in (II), one chelate ring having the *k* and the other the *k′* conformation in the Corey and Bailar nomenclature,[10] or the δ and the λ conformation in the IUPAC system.[5]

However *trans*-$(+)_D$-$[Co(dien)_2]^{3+}$ gives a minor positive and a major negative c.d. band at a lower and a higher frequency, respectively, in the spectral region of the $^1A_{1g} \rightarrow {^1T_{1g}}$ absorption of the octahedral $Co^{III}N_6$ chromophore (Figure), these bands having the same sign and similar magnitudes to those given by[9] [Co-(+)-(pn)$(NH_3)_4]^{3+}$ or by[11] $(-)_D$-[Co(NMe-en)$(NH_3)_4]^{3+}$, where the optical activity derives in each case, from a single asymmetric centre in the ligand and a single puckered chelate ring. The sole element of chirality in the complex ion, *trans*-$[Co(dien)_2]^{3+}$ is the stereochemical relationship between the two *trans* N–H bonds of the secondary nitrogen atoms in the ligands. These two N–H bonds form a segment of either a right-handed (IIa) or a left-handed helix (IIb), taking either N–H bond as the helix axis according to the IUPAC convention,[5] and they are designated the *trans*-δ-NH and the *trans*-λ-NH isomers, respectively. The c.d. spectrum of *trans*-$(+)_D$-$[Co(dien)_2]^{3+}$ (Figure) indicates that the *trans*-NH chiral element gives rise to optical effects comparable in magnitude to those of the conformational and vicinal effect of a single optically-active chelate ring, but the c.d. recorded does not distinguish between the structures (IIa) and (IIb) for this isomer. An absolute *X*-ray crystal analysis of an optical isomer of the *trans*-complex is in progress.

Although measurements were taken throughout the u.v. region down to 185 nm on a Jouan CD 185 Dichrographe (c.d. optical density detection limit 1 in 10^5), no c.d. response was recorded over this region for the *trans*-isomer. Thus the c.d. in this charge transfer region, where $\epsilon_{max} = 39{,}000$ at 222 nm cannot be larger than about 0·3, compared with -30 for $(+)_D$-$[Co(en)_3]^{3+}$ or $+12$ for *trans*-[Co-(−)-$(pn)_2$-$(NH_3)_2]^{3+}$.[8] We take this to indicate that the conformational contribution to the optical activity is negligible (hence our assignment of the observed c.d. bands in the ligand field region to the N–H chiral effect).

A molecular model indicates some crowding in one quadrant of the *trans*-molecule (shown shaded in the diagram). Such crowding could be relieved by distortion of the conformation of one chelate ring of each dien ligand. Optical activity could then also arise from asymmetry of charge around the nitrogen (a small vicinal effect) together with a conformational effect since the *k′* helical contributions would not then completely cancel those of *k*. Such distortion will be checked in the *X*-ray structure analysis, although any distortion is evidently too small to be detectable from the dichroism.

Since this is the first complex observed to give no c.d. in the charge transfer region, this result lends support to the hypothesis[8] that configurational and conformational effects are the principal contributors to the c.d. of the charge transfer region in metal complexes.

A contribution to optical activity from this N–H chiral effect should also be present in complexes of all linear polyamines forming gauche five-membered chelate rings, such as triethylenetetramine, tetraethylenepentamine, and (linear) pentaethylenehexamine, but in these instances it would not be separately distinguishable from the conformational and vicinal effects.

(*Received, February 2nd*, 1970; *Com.* 149.)

---

[1] F. R. Keene, G. H. Searle, Y. Yoshikawa, A. Imai, and K. Yamasaki, *Chem. Comm.*, 1970, 784.

[2] S. F. Mason and B. J. Norman, *Chem. Comm.*, 1965, 73.

[3] K. Nakatsu, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, 1956, **29**, 428.

[4] A. Muto, F. Marumo, and Y. Saito, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 85.

[5] IUPAC Bulletin, 1968, No. 33, 68; *Inorg. Chem.*, 1970, **9**, 1.

[6] S. F. Mason and B. J. Peart, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 491.

[7] B. E. Douglas, *Inorg. Chem.*, 1965, **4**, 1813.

[8] S. F. Mason, A. M. Sargeson, R. Larsson, B. J. Norman, A. J. McCaffery, and G. H. Searle, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 333; *J. Chem. Soc.* (*A*), 1968, 1304 and 1310.

[9] K. Ogino, K. Murano, and J. Fujita, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 351.

[10] E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 2620.

[11] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1967, **89**, 825.