Geometric and Optical Isomers of the Bis(diethylenetriamine)cobalt(III) Ion

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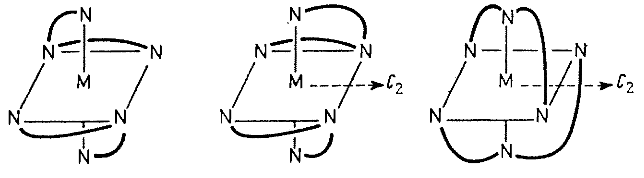
Summary All the geometric and optical isomers possible for the $[Co(dien)_2]^{3+}$ system have been isolated and characterised, and the geometric configurations have been assigned from the difference in racemisation behaviour of the optical forms of the *u-cis-* and *trans-*isomers and from the ^1H n.m.r. spectra.

IN co-ordinating to metals, diethylenetriamine (dien) can adopt either facial (*cis*) or meridional (*trans*) dispositions, so that a bis-complex $[M(dien)_2]^{n+}$ can exist in three topological isomers, *s-cis* (symmetrical-*cis*), *u-cis* (unsymmetrical-*cis*), and *trans* (Figure 1). Also, the *u-cis-* and *trans-*isomers can exist in optical forms. The complex $[Co(dien)_2]Cl_3$ was described many years ago[1] but the isomers have not previously been reported.



s-cis (+)$_D$-u-cis trans

FIGURE 1. *Topological isomers of* $[M(dien)_2]^{3+}$

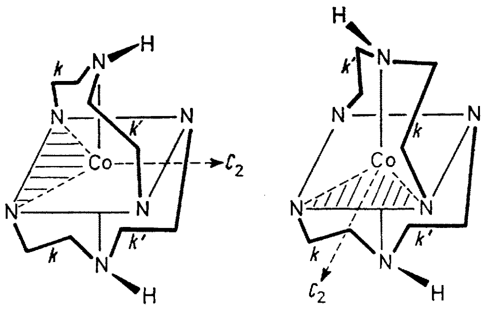


FIGURE 2. *Optical isomers of* trans-$[Co(dien)_2]^{3+}$

The isolation and characterisation of these isomers has been carried out separately and concurrently in our two laboratories. Some sections of the work are accredited to one of our laboratories; these are denoted by Adelaide or Nagoya in parentheses.

The complexes were prepared as mixtures of isomers by the following methods:

(1) $CoX_2 + HX + O_2 + dien + C^* \xrightarrow[\text{or } 80^\circ]{20^\circ} [Co(dien)_2]^{3+}$ (Adelaide);

(2) $[Co(NH_3)_5X]X_2 + dien + H_2O + C^* \rightarrow [Co(dien)_2]^{3+}$;

(3) $K_3[Co(CO_3)_3]^2 + dien + H_2O + C^*$ at 0—3° with precipitation of the complex by addition of bromide ion (Nagoya);

(4) direct mixing of dien with *trans*-$[Co(dien)Cl_3]^{3,4}$ at room temperature (Nagoya). This is not an equilibrium method.

The resulting mixtures contained the *trans-* and *u-cis-*isomers as main components, and a small amount of the *s-cis*-isomer was formed in the reactions (1)—(3) with bromide as anion. No *s-cis*-isomer has been isolated from preparations (2) and (4) involving chlorides. The *s-cis*-isomer was separated cleanly as the least soluble bromide. The *trans-* and *u-cis*-isomers could then be separated from the filtrates by fractional crystallisation as iodides, with *trans* being the less soluble (Adelaide). The first and final fractions thus obtained were isomerically pure.

The mixtures could also be partially separated by paper chromatography, cellulose t.l.c., and ion-exchange. These procedures (Adelaide) were useful in monitoring the *u-cis*/*trans* separation by fractional crystallisation and in determining isomer ratios in equilibrium solution mixtures. The equilibrium isomer proportions (Table) indicate that the *trans*-configuration of the ligand is preferred, which is the configuration assigned to the complexes [Co(dien)Cl_3],[4] [Co(dien)$(NO_2)_3$],[5] and [Cu$(dien)_2$]Br_2,H_2O[6] on the basis of i.r. spectra[4] and *X*-ray structural analysis.[5,6] These results demonstrate that bond-angle strain is not the dominant factor in determining relative stabilities of isomers in amine systems of this type.[7]

TABLE

		s-cis	*u-cis*	*trans*
Isomer proportions in equilibrium solution mixtures of bromides	20°	5%	30%	65%
	80°	8%	40%	52%
Visible absorption spectra maxima (nm) ..		ϵ_{461} 68·5; ϵ_{333} 65·0	ϵ_{468} 96·4; ϵ_{338} 94·1	ϵ_{466} 134; ϵ_{341} 103
^{1}H n.m.r. spectra in deuteriated dimethyl sulphoxide		single NH_2 peak at 4·80 p.p.m. (downfield from Me_4Si)	two NH_2 peaks at 5·08 and 4·68 p.p.m.	two NH_2 peaks at 4·75 and 4·18 p.p.m.
^{1}H n.m.r. spectra in D^+/D_2O		*s-cis* and *trans* similar; *u-cis* spectrum more complex consistent with its lower symmetry		
Rotations of optical isomers from less soluble diastereoisomers with the resolving agents indicated		optical isomers not possible	(+)D-SbO tartrate $[M]_D$ +164°	(+)D-[Co(en)$(mal)_2$]$^-$ $[M]_D$ +28·8°

The mixture of the three geometric isomers was also completely separated by column chromatography (Nagoya). A solution of the mixture in water-saturated n-butanol was poured on to a column of P-cellulose,[8] and the isomers were eluted by a mixture of n-butanol, concentrated HCl, and water (volume ratio 200:15:15). The *trans*-isomer was eluted first, followed by the *s-cis* and *u-cis* successively. The final eluted fractions (*u-cis*) were optically active, indicating partial resolution.

The isomers differ in their i.r. and electronic spectral properties (Table) and while these served to characterise and distinguish the isomers they were not particularly useful in assigning these configurations. The ^{1}H n.m.r. spectra, however, (Table) clearly differentiated the *u-cis*-isomer from the two more symmetrical forms. Whereas the four primary amine groups are equivalent in the *s-cis*-isomer (one NH_2 resonance observed) they are not equivalent in the *u-cis*- and *trans*-isomers (two peaks observed), the two NH_2 groups on each dien ligand being in different environments. The *k*/*k'* designations of the chelate ring conformations in the *trans*-isomer (Figure 2) follow Sargeson's nomenclature.

The isomeric products (8% *u-cis*, 92% *trans*) from method (4) involving *trans*-[Co(dien)Cl_3] are consistent with the topological assignment to the *trans*-[Co$(dien)_2$]$^{3+}$ isomer, provided extensive isomerisation does not occur in this reaction.

The *u-cis*-isomer was completely resolved into optical isomers by two methods.

(1) An aqueous solution was adsorbed on a column of SE-Sephadex C-25 and eluted by 0·15 M-sodium (+)-tartrate solution (Nagoya). The (+)D-isomer was eluted first. Details of this resolution will be published elsewhere.

(2) Diastereoisomer formation with (+)D-antimonyl tartrate and recrystallisation of the active iodides to maximum rotation gave the results shown in the Table (Adelaide). A solution of the complex at pH 8 showed no measureable change in rotation after 2 weeks at 20°.

A comparison of the c.d. spectrum of (+)D-*u-cis*-[Co$(dien)_2$]$^{3+}$ (Figure 3) with that of (+)D-[Co(penten)]$^{3+}$ as previously determined,[9] supported by a study of ion-pairing effects, allows the absolute configuration to be assigned as that shown in Figure 1. A more detailed analysis of the dichroism will be reported elsewhere.

Optical activity in the *trans*-[Co$(dien)_2$]$^{3+}$ isomer arises predominantly from chirality of the N^2–H bonds about the C_2 axis (Figure 2). It does not arise from a configurational effect, and Figure 1 implies two planes of symmetry for this isomer. Sargeson *et al.*[10] have demonstrated that such N^2–H bonds in cobalt(III) complexes are rendered sufficiently inert towards hydrogen exchange in acid conditions to allow separation of optical isomers whose dissymmetry arises from this source. In solutions of higher pH the N–H exchange process becomes facilitated and leads to racemisation at rates which are proportional to hydroxide ion concentration.

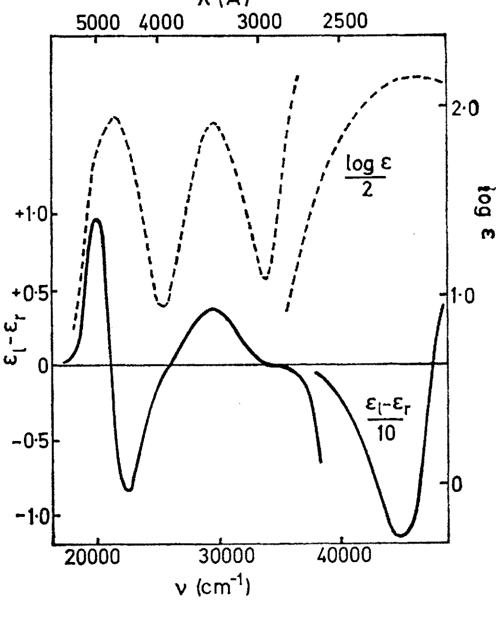


FIGURE 3. *Absorption (– – – –) and c.d. (———) spectra of* (+)D-*u-cis*-[Co$(dien)_2$]Cl_3,$2H_2O$ *in water.*

The *trans*-isomer was resolved with the (+)D-[Co(en)$(mal)_2$]$^-$ ion in acid conditions (Adelaide). The optical isomer obtained from the less soluble diastereoisomer as the perchlorate had rotation $[\alpha]_D$ +3·4°, and on fractional recrystallisation the highest rotation obtained (least soluble fraction) was $[\alpha]_D$ +5·1°, $[M]_D$ +28·8°. The optical purity is probably high, but the diastereoisomer crystallises with difficulty and only a small amount of the active perchlorate has so far been obtained. The active *trans*-isomer was optically stable in solution pH 2 at 20°, but on raising the pH of this solution to pH 10 by addition of lithium hydroxide, complete racemisation had occurred within 5 min. This behaviour contrasts with the optical stability of the *u-cis*-isomer where the activity is ascribed predominantly to a configurational effect, and these results unequivocally assign the geometric configurations to these complexes. The kinetics of this racemisation of *trans*-$[Co(dien)_2]^{3+}$ are at present being studied (Adelaide).

The *X*-ray determination of the crystal structures of the *s-cis*-, optically active *u-cis*-, and racemic *trans*-$[Co(dien)_2]^{3+}$ isomers is in progress (Professor Y. Saito, University of Tokyo). The absolute *X*-ray structural analysis of optically active *trans*-$[Co(dien)_2]^{3+}$ will be undertaken at the University of Adelaide, and the c.d. of this isomer will also be reported later.

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