(2.89 Å) and nitrate[5] (2.85 Å) complexes are small enough to require that we consider the possibility of magnetic interactions directly between the cations. Goodenough[10] and Martin[11] have subdivided this type of interaction into three categories: (1) overlap of two half-filled orbitals, (2) overlap of a half-filled and a full orbital, and (3) overlap of a half-filled and an empty orbital. Obviously the third category does not apply to the present d^9–d^9 systems. The first mechanism makes a negative (antiferromagnetic) contribution to J, for the Pauli principle limits a given orbital to one electron of each spin. The second mechanism provides the following pathway for magnetic interaction: an electron may be transferred from the full orbital on atom A to the half-full one on atom B and back again. For this transfer to take place, the spin of the transferred electron must be antiparallel to the spin of the electron in the half-filled orbital. If a second orbital on A is half-filled, Hund's rule favors the transfer of the electron in the filled orbital whose spin is also antiparallel to the unpaired electron in this half-filled orbital. Thus an interaction is favored in which the spin of the transferred electron is antiparallel to the spins of the unpaired electrons on both A and B so that the latter spins must be parallel. This mechanism will make a positive contribution to J. Structural considerations eliminate the possibility of two half-filled orbitals overlapping in the present complexes so that the only contribution from a cation–cation interaction to the final value of J must be positive.

The mechanisms contributing to magnetic coupling through a 90° cation–anion–cation pathway have been discussed in detail elsewhere[10,11] and will be mentioned here only briefly. The two unpaired electrons in the dipyridyl complexes will be located in the $d_{x^2-y^2}$ orbitals of the copper ions. These electrons may be antiferromagnetically coupled through oxygen s orbitals and ferromagnetically coupled through two p orbitals. The latter mechanism is expected to be stronger than the former because of the greater radial extension of the p orbitals.

Since all the major pathways available for magnetic coupling make positive contributions to J, the sign of experimentally measured data is reasonable. The preceding discussion of mechanisms offers no explanation for the different J values determined for the four complexes under study. The assumption used in the above model that the unpaired electrons existed in "pure" $d_{x^2-y^2}$ orbitals is of course naive. The spatial distribution of the unpaired electron spin around the copper ions is very much a function of the environment of the ions. As the spin density changes slightly with changes in anion, changes in the magnitude of the coupling would be expected. We have been able to suggest general mechanisms to explain the sign of J, but much more complete characterization of the complexes is needed before changes in the magnitude of J within this series of compounds can be fully understood. Presumably electronic effects arising from changes in the coordinated counterion(s) and water molecules contribute to the trend, but we do not choose to speculate in the absence of structural data.

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[11] R. L. Martin in "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, London, 1968.

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The Isomers of the Bis(diethylenetriamine)cobalt(III) Ion and a New Source of Optical Activity

By F. R. Keene and G. H. Searle

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The three geometric isomers of the $[Co(dien)_2]^{3+}$ ion s-cis, u-cis, and trans have been separated by various methods, and the u-cis and trans isomers have been resolved into optical isomers through diastereoisomer formation. The configurations have been unequivocally assigned to these geometric forms from the different racemization behavior of the u-cis and trans optical isomers. Factors determining relative isomer stabilities are discussed, and infrared and pmr criteria for assigning isomer configurations are examined.

Introduction

The problem of the existence of the three geometric isomers which are possible for a complex $[M(dien)_2]^{3+}$ (where dien designates the tridentate ligand diethylenetriamine)[1] has remained ever since the cobalt(III) complex ion of this formulation was first isolated as the iodide $[Co(dien)_2]I_3$ by Mann in 1934.[2] The corresponding chromium(III) complex $[Cr(dien)_2]I_3$ has also been prepared[3] and again isomers have not been isolated. This paper describes the isolation and characterization of all the geometric and optical isomers which

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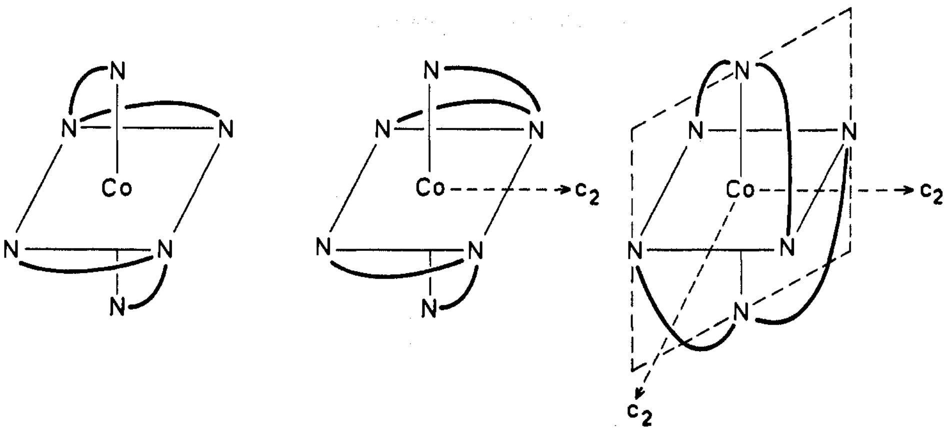
[1] Abbreviations used: en, ethylenediamine; *N*-Meen, *N*-methylethylenediamine; dien, diethylenetriamine; trien, triethylenetetramine; tetraen, tetraethylenepentamine; penten, pentaethylenehexamine (double branched chain isomer); sarc, sarcosinato; tart, tartrate; mal, malonato.

[2] F. G. Mann, *J. Chem. Soc.*, 466 (1934).

[3] V. O. Kling and H. L. Schlafer, *Z. Anorg. Allg. Chem.*, **313**, 187 (1961).



s-cis
s-fac

u-cis
u-fac

trans
mer

(+)D optical isomer
Λ absolute configuration

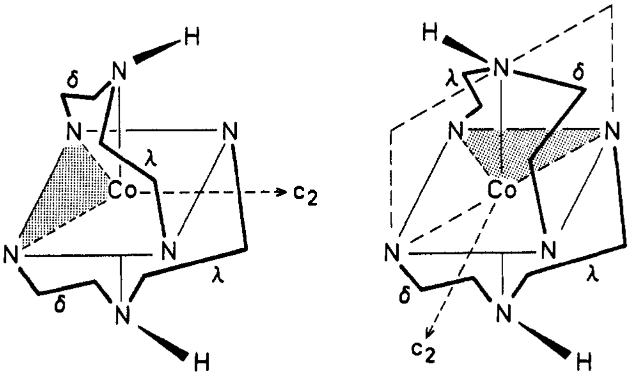
Figure 1.—Topological isomers of $[Co(dien)_2]^{3+}$.

are possible for the $[Co(dien)_2]^{3+}$ ion. The three geometric isomers are shown in Figure 1. These may be designated in terms of the facial or meridional disposition of the ligands or alternatively by the cis or trans positions of the primary amino donor groups of each dien ligand, and an additional specification s or u is necessary to distinguish the two cis forms. The u-cis (unsymmetrical) form has only a twofold rotation axis and should exist in optical isomers, with the dissymmetry arising primarily from a configurational effect. The s-cis (symmetrical) isomer with a center and planes of symmetry is not dissymmetric.

The facility of linear polyamine ligands (and related linear multidentate ligands) to coördinate in facial or meridional dispositions over each pair of interlocked five-membered chelate rings is well established. This facility for dien has been demonstrated by extensive studies of mono-dien complexes, and in a number of systems all the possible geometric isomers have been isolated.[4-8] On this basis it seems surprising that the two possible geometric forms of $[Co(dien)X_3]$ ($X^- = Cl^-, NO_2^-, NCS^-$) have not so far been prepared or separated.[5,6,9]

The bis-dien cobalt(III) complex has been used in studies by several workers,[9-13] and from the reported preparative methods it is now apparent that these materials were isomeric mixtures. In the only attempt to assign a configuration, Crayton and Mattern[9] implied that only the most stable isomer in such systems would be isolated. Partly on the basis of failure to resolve their $[Co(dien)_2]^{3+}$ with three resolving agents, they assigned the configuration as trans, and although the rationale for this proposal was invalid (failure to achieve a resolution does not prove that a compound is incapable of being resolved or is not dissymmetric) the present work shows that the trans isomer is indeed the most stable.

An aspect of particular interest in the $[Co(dien)_2]^{3+}$ system is the origin of dissymmetry and the resulting optical activity in the trans isomer. In principle, the configurational and conformational effects are vanishing for this isomer. Figure 1 indicates that if the atoms of each chelate ring are taken to be coplanar, the structure has two planes of symmetry and two C_2 axes (there is also an S_4 axis mutually perpendicular to the two C_2 axes shown in the figure) so that the stereochemical disposition of the chelate rings about the metal ion is nonchiral. Figure 2 shows the chelate ring conformations which must obtain in the optical isomers. When these ring conformations are considered the planes of symmetry in Figure 1 disappear and the S_4 axis is destroyed (although each coordinated ligand retains a mirror plane as in Figure 2), but one of the C_2 axes remains and relates the two ligands in the molecule. The point group is thus reduced from S_2 (ring atoms taken to be coplanar) to C_2 by the ring conformations. A vicinal effect should not arise since the two chelate rings constituting each dien ligand are mirror images. It is also evident that for each dien ligand the conformational effect is internally compensated, one chelate ring having



trans-δ-NH
M(C_2)-NH

trans-λ-NH
P(C_2)-NH

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

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(4) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **5**, 594 (1966).
(5) D. A. House, *Inorg. Nucl. Chem. Lett.*, **3**, 67 (1967).
(6) H. H. Schmidtke and D. Garthoff, *Inorg. Chim. Acta*, **2**, 357 (1968).
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(8) S. H. Caldwell and D. A. House, *J. Inorg. Nucl. Chem.*, **31**, 811 (1969).
(9) P. H. Crayton and J. A. Mattern, *ibid.*, **13**, 248 (1960).
(10) J. Brigando, *Bull. Soc. Chim. Fr.*, 211 (1957).
(11) G. A. Barclay and A. K. Barnard, *J. Chem. Soc.*, 2540 (1958).
(12) F. Basolo, J. W. Palmer, and R. G. Pearson, *J. Amer. Chem. Soc.*, **82**, 1073 (1960).
(13) H. Yoneda and Y. Morimoto, *Bull. Chem. Soc. Jap.*, **39**, 2180 (1966).

a δ conformation and the other the λ conformation (or k and k′, respectively, in the Sargeson–Bailar and Corey designation).[14] Thus the "conventional" sources of chirality, configurational and conformational and vicinal effects, are not present in this molecule.

The dissymmetry of the molecule is due to another chirality type which is exemplified and uniquely described by the stereochemical relationship between the two trans N^2H bonds of the secondary nitrogen atoms in the two ligands (Figure 2). These two NH bonds form a segment of either a right-handed or a left-handed helix taking either NH bond as the helix axis according to the IUPAC convention,[14] and we designate the absolute configurations of the optical forms of the *trans*-$[Co(dien)_2]^{3+}$ complex as trans-δ-NH and trans-λ-NH, respectively (Figure 2). We therefore describe this source of chirality in such amine complexes as the "NH chiral effect".

However the dissymmetry is not due solely to the presence of the N^2H bonds as the structure would retain dissymmetry even if such bonds were absent, for example if a sulfur donor replaced the secondary amine group. The same type of symmetry relationship holds between any of the C_2-related CH, NH, NC, or CC bonds in the two ligands and these individual bond chiralities should all contribute to the overall helicity of the molecule. The absolute configuration can therefore be described by any of these bond relationships (these are not all of the same skew, δ or λ) and we have chosen the N^2H bonds as the simplest description for this complex as this means of nomenclature lends itself more generally to a wider variety of potential ligands. With sulfur donors for example, the lone pair directions might be employed in an analogous stereochemical situation. An alternative designation for the absolute configurations of the *trans*-$[Co(dien)_2]^{3+}$ optical isomers could be in terms of the left-handed (minus) or right-handed (positive) helicity of the two N^2H bonds about the C_2 axis, M(C_2)-NH or P(C_2)-NH, respectively (Figure 2).

Such chiral effects as we have described have not hitherto been realized as contributing effects to optical activity in metal polyamine complexes, but should be present in complex systems such as $[Co(trien)X_2]^+$ in addition to the "conventional" sources of chirality.

It has been known for some time that NH bonds on coordinated nitrogen donor atoms are relatively inert toward hydrogen exchange in acid conditions. However, it has only recently been appreciated from the work of Sargeson, *et al.*,[15] that this inertness of N^2H bonds on coordinated *secondary* amine donor groups is sufficient to allow separation of optical isomers of complexes whose dissymmetry arises from this source. Optical isomers of a number of complexes containing the ligands *N*-methylethylenediamine (*N*-Meen) or sarcosinato (sarc) have been observed to racemize only very slowly in acid conditions, but in solutions of higher pH the NH exchange process becomes facilitated and leads to racemization following the rate law

$$\text{rate} = k_{\text{rac}}[\text{complex}][\text{OH}^-]$$

The situation in *trans*-$[Co(dien)_2]^{3+}$ is analogous to that in the $[Co(NH_3)_4(N\text{-Meen})]^{3+}$ and $[Co(NH_3)_4(sarc)]^{2+}$ complexes. In each of these complexes[16,17] the molecular dissymmetry arises from the alternative possible dispositions of the N^2H bond, and these alternative dispositions are interconvertible in basic solution. These racemization phenomena provide the basis of a method for unequivocally distinguishing the trans isomer from the other two geometric isomers in the $[Co(dien)_2]^{3+}$ system.

Although the contribution of "NH chiral effects" to optical activity of polyamine complexes has not previously been appreciated, the stereochemical basis is not new. An N^2H bond fixed in one of two alternative dispositions will confer isomerism providing these alternative dispositions can be distinguished. In *trans*-$[Co(dien)_2]^{3+}$ the alternative dispositions of one N^2H are distinguished with reference to one fixed disposition of the other N^2H bond in the molecule. Due to the particular symmetry properties of this molecule the "NH chiral effect" is the only contribution to the dissymmetry, since these coordinated nitrogen atoms themselves are not asymmetric. In all complexes of *N*-Meen and sarc, however, the secondary amine nitrogen becomes asymmetric on coordination (a situation described as donor atom asymmetry) and vicinal and conformational effects both contribute to optical activity. In these instances with only one N^2H bond the chiral effect does not arise, yet the kinetic aspects of the racemization should be closely similar.

A similar situation to that in *trans*-$[Co(dien)_2]^{3+}$ arises in the case where dien is coordinated meridionally in the system $[Co(en)(dien)Cl]^{2+}$, shown in Figure 3. Here the two alternative dispositions of the single N^2H bond can be distinguished by reference to the chloro ligand which is cis to the donor secondary nitrogen. This creates two geometric isomers,[7] but optical isomers are not possible as there is no "NH chiral effect" nor vicinal effect and the conformational contributions in the coordinated dien cancel as in *trans*-$[Co(dien)_2]^{3+}$.

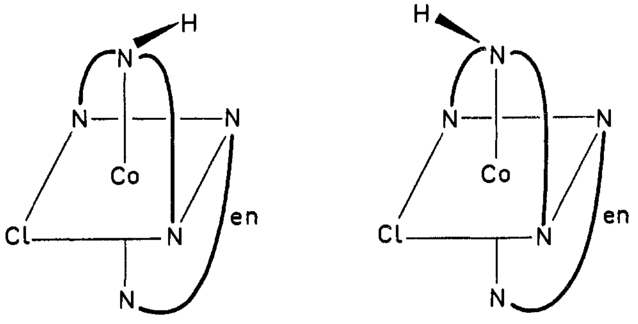

Figure 3.—Isomers of $[Co(en)(dien)Cl]^{2+}$ arising from dien coordinated meridionally.

The optical activity and circular dichroism of *trans*-$[Co(dien)_2]^{3+}$ have been discussed in a previous communication[18] and the kinetics of racemization and exchange will be reported in due course.

The factors which determine relative stabilities of isomers are not well understood, and the number of systems where equilibrium isomer proportions have

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[14] *IUPAC Bull.* **No. 33**, 66 (1968); *Inorg. Chem.*, **9**, 1 (1970).

[15] A. M. Sargeson and G. H. Searle, *ibid.*, **6**, 787 (1967).

[16] B. Halpern, A. M. Sargeson, and K. R. Turnbull, *J. Amer. Chem. Soc.*, **88**, 4630 (1966).

[17] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **89**, 825 (1967).

[18] F. R. Keene, G. H. Searle, and S. F. Mason, *Chem. Commun.*, 893 (1970).

been assessed experimentally is as yet very limited. Much further experimental data are necessary to compare with results from energy minimization computations. Some systems previously studied such as $[Co(trien)X_2]^{n+}$ [15] and $[Co(tetraen)X]^{n+}$ [19] involve factors arising from the acido ligands X, and the present system provides an opportunity to study isomer stabilities as a function of factors in the amine chelate rings only.

Experimental Section

Diethylenetriamine, from either Fluka (puriss) or Union Carbide Australia Ltd., was used without further purification.

Visible spectra were measured on a Unicam SP700 recording spectrophotometer in 1-cm cells against water as a reference. For estimating isomer proportions, spectra of elutes from chromatographic separations were measured at the first band maximum (*ca.* 466 nm) on a manual Shimadzu QR-50 spectrophotometer. The separate isomers in either water or in 0.3 *M* sodium tartrate solution gave identical visible spectra, and extinction coefficients obtained on the two instruments agreed.

Infrared spectra were obtained on a Perkin-Elmer 457 grating infrared spectrophotometer in KBr disks against air reference. Optical rotations were measured on a Perkin-Elmer 141-MC spectropolarimeter in a 1-dm tube at 20°. Signs of rotations refer to the sodium D line unless another wavelength is specified. ORD curves were obtained on a Perkin-Elmer P22 recording spectropolarimeter. Pmr spectra were obtained on a Varian HA-100 spectrometer or a 60-Mc Jeol spectrometer using sodium trimethylsilylpropanesulfonate as a reference.

Preparation of $[Co(dien)_2]^{3+}$ by Aerial Oxidation.—To a solution of $CoCl_2 \cdot 6H_2O$ (47.6 g, 0.20 mol) in water (250 ml) was added dien (34.5 g, 0.33 mol), dien·3HCl (14.5 g, 0.067 mol), and charcoal (25 g). Air was passed through the solution for 36 hr. After filtering, the solution was evaporated to a small volume using a rotary evaporator and the product was then precipitated as completely as possible by the addition of ethanol. The product was filtered off, washed with ethanol and acetone, and then air-dried; yield of $[Co(dien)_2]Cl_3 \cdot xH_2O$, 76.0 g (93% calcd for 2-hydrate).

The complex was prepared as the bromide in an analogous manner using anhydrous $CoBr_2$ (44.0 g, 0.20 mol), dien (34.5 g, 0.33 mol), and dien·3HBr (23.0 g, 0.067 mol) in water (500 ml). After aeration and filtration, the solution was evaporated almost to dryness, and the remaining product was precipitated with ethanol; yield 99.0 g (95% calcd for $[Co(dien)_2]Br_3 \cdot H_2O$).

Preparation of $[Co(dien)_2]^{3+}$ from $[Co(NH_3)_5X]X_2$.—A slurry in water was prepared of charcoal (20 g) and either $[Co(NH_3)_5Cl]Cl_2$ (100 g, 0.40 mol) or $[Co(NH_3)_5Br]Br_2$ (154 g, 0.40 mol). dien (91 g, 0.88 mol) was stirred in, and the mixture was heated on a steam bath for 4 hr. After filtering, the solution was evaporated almost to dryness and the product was precipitated as completely as possible with ethanol. The product was filtered off, washed with ethanol and acetone, and then air-dried; yield of $[Co(dien)_2]Cl_3 \cdot 2H_2O$, 153 g, 94%; yield of $[Co(dien)_2]Br_3 \cdot H_2O$, 200 g, 95%.

Separation of Geometric Isomers from Preparative Mixtures.—The above bromide preparations were recrystallized from warm water by allowing the solution to cool and stand until about 10% of the material had separated. This was filtered off and fractionally recrystallized again from warm water (3 times its weight). As each fraction was filtered off it was washed with 70% ethanol, and the filtrate was evaporated in a rotary evaporator to induce crystallization of the next fraction. The least-soluble fractions comprised pure *s-cis*-$[Co(dien)_2]Br_3$ as relatively large well-formed prisms, and the point at which the more soluble trans isomer commenced to crystallize could be recognized visually from the very much smaller thin needles of *trans*-$[Co(dien)_2]Br_3 \cdot H_2O$. This procedure allows essentially quantitative separation of the s-cis isomer from the mixture.

The trans and u-cis isomers in the remaining solution were separated by fractional precipitation by adding LiI in small amounts. The trans isomer is the less soluble, but the precipitated products appeared (halide analyses) to be mixed bromide–iodides. This separation was monitored by running thin-layer chromatograms on cellulose of the various fractions (developing solvent *sec*-butyl alcohol:water:concentrated HCl = 70:20:10). The first and last fractions were isomerically pure trans and u-cis, respectively, but middle fractions contained both isomers. The mixed halide precipitates of the separated isomers were converted to pure bromides or iodides using an anion exchanger. The trans and u-cis iodides are anhydrous. *Anal.* Calcd for *s-cis*-$[Co(C_4H_{13}N_3)_2]Br_3$: C, 19.0; H, 5.19; N, 16.6; Br, 47.5. Found: C, 19.4; H, 5.40; N, 16.7; Br, 47.7. Calcd for *trans*-$[Co(C_4H_{13}N_3)_2]Br_3 \cdot H_2O$: C, 18.4; H, 5.40; N, 16.1; Br, 45.8. Found: C, 18.0; H, 5.12; N, 16.1; Br, 45.7. Calcd for *u-cis*-$[Co(C_4H_{13}N_3)_2]Br_3 \cdot 0.5H_2O$: C, 18.7; H, 5.29; N, 16.3; Br, 46.6. Found: C, 18.6; H, 5.29; N, 16.2; Br, 46.5.

Isomeric purity was checked by chromatography on a column of SE-Sephadex C-25 cation exchanger (Na^+ form), column dimensions 40 × 0.9 cm. A dilute aqueous solution of a small portion (*ca.* 0.1 g) of a particular fraction was absorbed on the column and eluted with 0.3 *M* sodium tartrate solution. Two hours was required to ensure a clean separation on the column of the bands of the three isomers (if present), the band order being s-cis (fastest moving), u-cis, and trans (slowest).

Estimation of Equilibrium Isomer Proportions.—Solutions containing the three isomers were prepared by synthesis involving aerial oxidation as above, with equilibrium between the isomeric products being established by the presence of charcoal. The reaction mixtures in all cases involved the stoichiometry

$$\text{aqueous } CoX_2 + 1.67\text{dien} + 0.33(\text{dien}\cdot 3HX) \xrightarrow{\text{air, charcoal}} [Co(dien)_2]^{3+} + 3X^-$$

and air was passed through the solutions at 20° for 36 hr.

After filtering off the charcoal from such reaction mixtures a small sample of each solution (from which crystallization of products was prevented) was extracted, and in suitable dilution was applied to a column of SE-Sephadex C-25 as described earlier. The eluate bands (0.3 *M* sodium tartrate solution) were collected separately and made up to convenient exact volumes, and the relative amounts were estimated spectrophotometrically at the first absorption band maxima (4-cm cells).

For preparations involving quantities as described earlier, but with a solution volume of 500 ml in each instance, the isomer proportions (chloride or bromide preparation) obtained for equilibration at 20°, with [Co] = 0.4 *M*, were as follows: 65% trans, 28% u-cis, 7% s-cis. These figures were obtained from duplicate preparations of bromides and duplicate preparations of chlorides. Each preparation was analyzed by two chromatographic separations and spectral determinations. The above figures were reproducible to ±1 in the eight determinations. The charcoal used was freshly finely ground B.D.H. granulated activated charcoal for gas absorption, and before use in the equilibrations its catalytic ability was tested to ensure that it satisfied the criterion of causing racemization of $(+)[Co(en)_3]^{3+}$ within 2 min at 90°.[20]

Resolution of *u-cis*-$[Co(dien)_2]^{3+}$.—To a solution of *u-cis*-$[Co(dien)_2]Cl_3 \cdot 2H_2O$ (8.2 g, 0.02 mol) in warm water (200 ml) was added Ag(+)[SbOtart] (23.6 g, 0.06 mol). After shaking, the precipitated silver chloride was filtered off and the filtrate volume was made up to 250 ml. Scratching the beaker induced crystallization of the diastereoisomer (+)*u-cis*-$[Co(dien)_2](+)$-$[SbO\,tart]_3 \cdot 2H_2O$, and after cooling at 0° for several hours it was filtered off, washed with 75% ethanol, absolute ethanol, and then acetone, and then air-dried; yield 9.2 g, 80% of one optical form. It was recrystallized from water (discarding the most soluble portions) until constant rotation was attained. $\alpha_D = +0.533°$ for a 0.44% solution in water, whence $[\alpha]_D = 121°$. *Anal.* Calcd for (+)*u-cis*-$[Co(C_4H_{13}N_3)_2](+)[SbO(C_4H_4O_6)]_3 \cdot 2H_2O$: C, 20.9; H, 3.65; N, 7.2. Found: C, 20.9; H, 3.65; N, 7.0.

This recrystallized diastereoisomer (2.6 g) was ground with NaI in an aqueous slurry, and the (+)*u-cis*-$[Co(dien)_2]I_3$ which separated was filtered off, washed with ice-cold NaI solution, ethanol, and acetone, and then air-dried. Recrystallization from hot water did not increase the rotation; yield 1.0 g (8%). $\alpha_D = +0.033°$ for a 0.13% aqueous solution, $[\alpha]_D = +25.6°$. *Anal.* Calcd for (+)*u-cis*-$[Co(C_4H_{13}N_3)_2]I_3$: C, 14.9; H, 4.06; N, 13.0. Found: C, 14.9; H, 3.95; N, 13.0.

The diastereoisomer remaining in the aqueous solution above was fractionally precipitated by gradually adding ethanol and

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(19) M. R. Snow, D. A. Buckingham, I. E. Maxwell, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **92**, 3610, 3617 (1970).

(20) F. P. Dwyer and A. M. Sargeson, *Nature (London)*, **187**, 1022 (1960).

cooling. The most soluble of these fractions (4.0 g) was ground with sodium iodide as before, and the (−)*u-cis*-$[Co(dien)_2]I_3$ obtained was recrystallized three times from water to give constant rotation. The optical isomer was less soluble than the racemate; yield 1.3 g (10%); $[\alpha]_D = -24.9°$.

Resolution of *trans*-$[\mathbf{Co(dien)_2}]^{3+}$.—*trans*-$[Co(dien)_2]Cl_3 \cdot 2.5H_2O$ (8.3 g, 0.02 mol) was dissolved in water acidified with acetic acid (100 ml of water containing 0.5 ml of glacial acetic acid, giving a solution of pH 3–4). Ag(+)$[Co(en)(mal)_2] \cdot 2H_2O$[15] (28 g, 0.06 mol) was added, and after shaking the solution in a stoppered flask, the precipitated silver chloride was filtered off. Water (100 ml) and methanol (200 ml) were added to the filtrate, then ethanol (about 500 ml) was added carefully to incipient crystallization. Crystallization of the diastereoisomer is somewhat difficult, but with the above conditions (+)*trans*-$[Co(dien)_2]$(+)-$[Co(en)(mal)_2]_3 \cdot 10H_2O$ crystallized on cooling the solution for several days in a refrigerator; yield 7.3 g, 52% of one optical form. The diastereoisomer was filtered off, washed with methanol, ethanol, and acetone, and then air-dried. Because of the difficulty with crystallization and the relatively poor discrimination between the two diastereoisomers with this resolving agent, optical purification of the diastereoisomer was difficult. *Anal.* Calcd for (+)*trans*-$[Co(C_4H_{13}N_3)_2]$(+)$[Co(C_2H_8N_2)(C_3H_2O_4)_2]_3 \cdot 10H_2O$: C, 27.1; H, 5.8; N, 11.9. Found: C, 26.7; H, 5.2; N, 12.1.

The dextro isomer was obtained by dissolving the diastereoisomer in 0.1 *M* HBr and absorbing the cation on a column of cation-exchange resin (Bio-Rad AG 50W-X2, 200–400 mesh, in H^+ form). The resolving anion was washed from the column with 0.1 *M* HBr, then the (+)$[Co(dien)_2]^{3+}$ cation was eluted with 3 *M* HBr. (+)*trans*-$[Co(dien)_2]Br_3 \cdot H_2O$ crystallized on evaporating the elute, and the product was recrystallized from 0.1 *M* HBr four times to constant rotation, the active bromide being less soluble than the racemate; yield 0.6 g. $\alpha_{546} = +0.089°$ for a 0.308% solution in 0.1 *M* HBr, whence $[\alpha]_{546} = +28.9°$.

Further diastereoisomer was crystallized from the cold solution by careful addition of further portions of ethanol over several days. The product was removed in fractions until the total diastereoisomer obtained was about 80% of the total (both optical forms). The solution which then contained essentially only (−)*trans*-$[Co(dien)_2]$(+)$[Co(en)(mal)_2]_3$ was passed through the cation exchanger as above, and (−)*trans*-$[Co(dien)_2]Br_3 \cdot H_2O$ crystallized from the 3 *M* HBr elute. Recrystallization to constant rotation gave $[\alpha]_{546} = -29.2°$; yield 0.8 g. *Anal.* Calcd for (−)*trans*-$[Co(C_4H_{13}N_3)_2]Br_3 \cdot H_2O$: C, 18.4; H, 5.40; N, 16.1; Br, 45.8. Found: C, 18.4; H, 5.30; N, 15.9; Br, 44.7.

trans-$[\mathbf{Cu(dien)_2]Br_2 \cdot 0.5H_2O}$.—A solution of $CuBr_2$ in ethanol was added to dien (2.1 molar ratio) in ethanol. After cooling the solution, the deep blue crystals were filtered off, washed with ethanol, and then air-dried. The product was recrystallized slowly from hot methanol; yield 70%. *Anal.* Calcd for *trans*-$[Cu(C_4H_{13}N_3)_2]Br_2 \cdot 0.5H_2O$: C, 21.9; H, 6.20; N, 19.2; Br, 36.4. Found: C, 21.7; H, 6.20; N, 19.0; Br, 36.4. The configuration of this product has been established as trans by X-ray structure analysis.[21]

$[\mathbf{Ni(dien)_2]Br_2 \cdot H_2O}$.—A solution of $NiBr_2 \cdot 3H_2O$ in water was added to dien (2.1 molar ratio) in water. The product was precipitated by addition of ethanol, filtered off and washed with ethanol and acetone, and then air-dried. Slow recrystallization from hot water gave a yield of 70%. *Anal.* Calcd for $[Ni(C_4H_{13}N_3)_2]Br_2 \cdot H_2O$: C, 21.7; H, 6.37; N, 19.0; Br, 36.1. Found: C, 21.7; H, 6.33; N, 19.0; Br, 36.0.

Reaction *cis*-$[\mathbf{Co(dien)(H_2O)_3}]^{3+}$ + **dien.**—*cis*-$[Co(dien)(H_2O)_3]^{3+}$ was prepared and purified chromatographically by methods given previously,[8,22] except that the complex was eluted from Bio-Rad AG 50W-X4 cation-exchange resin with a 2.9 *M* $NaClO_4$–0.1 *M* $HClO_4$ solution (replacing 3 *M* $HClO_4$,[22] to reduce the acidity).

dien was added dropwise to portions of the red-violet elute to adjust the pH to either 6 or 9; one set of these solutions was warmed on a steam bath (1 hr) and another set was allowed to stand at room temperature. The $[Co(dien)_2]^{3+}$ constituents of these yellow reaction mixtures were assessed by chromatography on Sephadex. A faster moving violet band of unreacted monodien species was also obtained from all reactions but was more prominent in the less complete reactions at pH 6.

Results and Discussion

$[Co(dien)_2]^{3+}$ was prepared as a mixture of the three geometric isomers by two general methods, the standard method of aerial oxidation of cobalt(II) chloride or bromide in the presence of dien, and by a substitution method involving reaction of dien with $[Co(NH_3)_5X]X_2$ (X = Cl, Br). All preparations were carried out in aqueous solution at room temperature in the presence of charcoal catalyst to establish equilibrium.

The resulting mixtures contained all three isomers; the trans isomer was the major component and the s-cis isomer was present in smallest proportion. The presence of the s-cis isomer in both chloride and bromide preparations was demonstrated by separations of the product mixtures by a chromatographic procedure using Sephadex (see later).

The three isomers could be separated by fractional crystallization, but the s-cis could be isolated only from the preparations involving bromides, as the least-soluble bromide. No s-cis isomer could be separated by fractional crystallization of the product mixtures from preparations involving chlorides. Even when the complex in a chloride solution was fractionally precipitated as complex bromide by adding lithium bromide, the least soluble fractions obtained were always predominantly the trans isomer. The inability to isolate s-cis by these methods from any preparation in the presence of chloride ion has also been noted by Yamasaki,[23] so that the presence of chloride evidently modifies the solubility relationships between the bromides of the three isomers. This may be due to crystallization as mixed chlorides–bromides, since this effect was noticed with iodide precipitation of the u-cis and trans isomers.

On a preparative scale the remaining trans and u-cis isomers (after removal of *s-cis*-$[Co(dien)_2]Br_3$) were separated from the mixtures by fractional crystallization as iodides, iodide giving a better discrimination than bromide. This separation required a chromatographic monitoring technique, and either thin-layer chromatography on cellulose or chromatography using a Sephadex column was suitable, although Sephadex was preferable for checking isomeric purity. The early and later fractions thus obtained were *trans*-$[Co(dien)_2]I_3$ and *u-cis*-$[Co(dien)_2]I_3$, respectively (these are actually mixed halides; see Experimental Section), and the intermediate mixed fractions were discarded.

A number of chromatographic procedures were examined for their ability to separate the three isomers, and a column of SE-Sephadex C-25 cation exchanger proved the most effective. The separation appears to be greatly dependent on the developing electrolyte, sodium (+)tartrate solution producing a clean separation in 2 hr. NaCl gave no separation, so that the mechanism is not purely ion exchange with Na^+ ion but some form of differential association between the complex cations and solvent anion $[Co(dien)_2]^{3+}$–(+)$tart^{2-}$ must be involved. The three bands we obtain are the three geometric isomers, since separate samples of (±)u-cis and (±)trans each give only one band when passed down the column. Yamasaki[23] reports that this chromatographic medium and eluent will separate the u-cis isomer into optical forms al-

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TABLE I

	s-cis	u-cis	trans
Sephadex C-25, elution order of isomers	1	2	3
TLC on cellulose, eluent sec-BuOH:H_2O:HCl = 70:20:10 Paper chromatography, eluent as above (30 hr) or 80:10:10 for sharper bands	1	2	1
Solubility order in water (chloride, bromide, or iodide)	3 (least soluble)	1 (most soluble)	2
Visible absorption maxima, nm	ϵ_{461}, 68.5; ϵ_{333}, 65.0	ϵ_{468}, 96.4; ϵ_{338}, 94.1	ϵ_{466}, 137; ϵ_{341}, 105
Rotations of optical isomers from less soluble diastereoisomers with the resolving agents indicated	Optical isomers not possible	(+)DSbO tartrate $[M]_D$ = +165° $[M]_{533}$ = +852° (peak) $[M]_{476}$ = −3540° (trough) $[M]_{415}$ = +506° (peak) Zero at 512, 435, 367 nm	(+)D$[Co(en)(mal)_2]^-$ $[M]_D$ = +84° $[M]_{546}$ = +153° (peak) $[M]_{482}$ = −675° (trough) $[M]_{423}$ = +382° (peak) Zero at 518, 456 nm

though the effective column length to achieve the resolution is many times the length we use for the above separation. Sephadex has a relatively low capacity and thus we do not find it particularly suitable for isomer separations on a large preparative scale.

Paper and thin-layer chromatography gave only partial separations of mixtures, yet tlc proved to be useful for monitoring fractional crystallization separations. Although a wide range of solvent mixtures and compositions and tl support media were examined, under no conditions was a suggestion of a third band obtained. On paper, sec-BuOH:H_2O:HCl (80:10:10) eluent and for tlc on cellulose sec-BuOH:H_2O:HCl (70:20:10) gave the best separations, but in both instances the s-cis and trans isomers ran together in the faster band.

The separated isomers were characterized by a number of methods (Table I) but of these only racemization behavior and pmr spectra allowed unequivocal assignment of the geometric configurations.

The u-cis isomer was resolved into optical isomers through diastereoisomer formation with antimonyl (+)tartrate, and the ORD curve of the (+) optical isomer is given in Figure 4. Comparison of the circular dichroism spectrum with that of (+)$[Co(penten)]^{3+}$, supported by a study of ion-pairing effects,[18] allows the absolute configuration of (+)*u-cis*-$[Co(dien)_2]^{3+}$ to be assigned as Λ^{14} as shown in Figure 1.

A solution of active u-cis isomer in pH 8 buffer showed no change in rotation after standing for 2 months. This isomer, like $[Co(en)_3]^{3+}$, is thus optically stable in base since the optical activity is ascribed predominantly to a configurational effect, and racemization would have to involve a gross rearrangement of the chelate rings.

The trans isomer was resolved with (+)$[Co(en)(mal)_2]^-$ ion. The active *trans*-$[Co(dien)_2]^{3+}$ complex should be handled in acid conditions to avoid racemization, and although in principle acid conditions are not essential to obtain the solid less soluble diastereoisomer, such conditions were used throughout the resolution procedure to avoid racemization of the more soluble diastereoisomer left in solution. Since both optical forms were obtained from the resolution and could be recrystallized to constant rotation, this was taken to indicate that optical purity had been achieved.

In contrast to the u-cis isomer, active trans racemizes in basic media according to the same rate law as observed previously for other systems involving racemization due to N^2H hydrogen exchange. For instance the half-lives for racemization of aqueous buffer solutions (collidine–HNO_3) at 35° are 93 min at pH 7.42 and 17 min at pH 8.10. These observations allow the u-cis and trans assignments to these isomers.

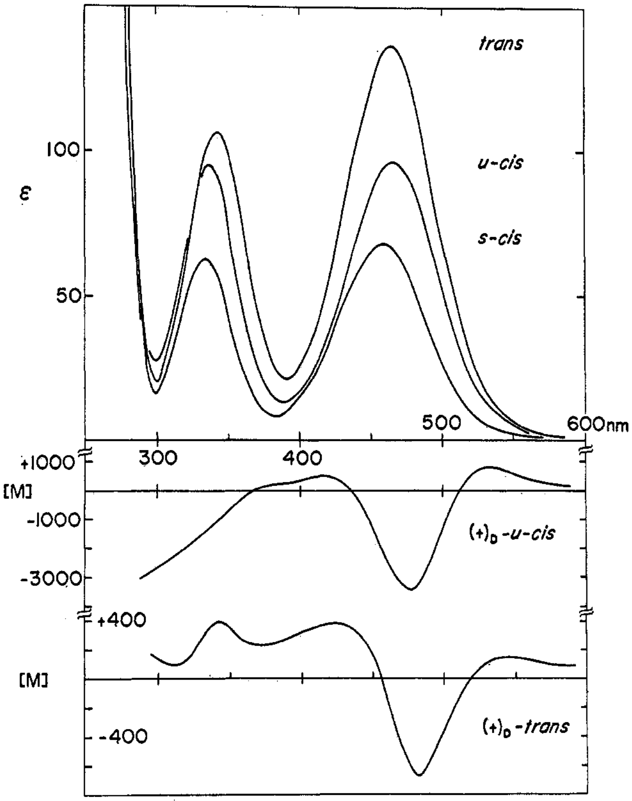

Figure 4.—Absorption and ORD spectra of the $[Co(dien)_2]^{3+}$ isomers.

The ORD (Figure 4) and CD spectra[18] of the active trans isomer in the spectral region of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ absorption of the $Co^{III}N_6$ chromophore are of similar forms to those of the u-cis isomer, and the ORD curves of the optically pure isomers indicate that the rotatory power of the "N^2H chiral effect" only (in trans) is an order of magnitude lower than the rotatory power due to the configurational effect (u-cis). The absolute configuration of the active trans isomer cannot be deduced from the ORD or CD at this stage since no suitable reference structures are available, and the assignment awaits our absolute X-ray crystal structure analysis.

Although the visible spectra are closely similar in form for the three isomers (although differing significantly in intensities) (Figure 4), the infrared spectra are much more distinctive and are useful for characterizing the isomers. The region most useful for characterization is 800–300 cm^{-1} and peaks in this region are listed in Table II.

Table II

Infrared Frequencies[a] of $[Co(dien)_2]Br_3$ Isomers in the 800–300-cm^{-1} Range (KBr disks)

s-cis	u-cis	trans
803 s	810 sh, 802 m	
779 m	777 w	761 s, 742 sh
758 s	755 mw, 743 sh	
	702 vw	
683 s, 671 sh	671 sh, 667 mw	675 vw
592 s	609 m	589 m
	581 m, 568 sh	575 568 } d, mw
	540 vw	
521 sh, 516 m	525 mw	528 m
	501 mw	487 w
	482 vw	472 w
460 sh, 451 w	457 mw	
	445 w 432 w	446 438 } d, mw
		414 vw
389 w	388 w	395 vw
374 s		375 sh, 370 m
	339 m	324 mw
307 sh, 301 m	310 m, 305 sh	

[a] Estimated intensities: s, strong; m, medium; w, weak; sh, shoulder; d, doublet.

Infrared criteria for assigning the configuration of a coordinated dien ligand as facial or meridional have been proposed[6–8] on the basis of experimental data for a number of monodiethylenetriamine complexes. We find that Schmidtke's criteria[6] at 1500–1400, 1250, and 850–700 cm^{-1} are not sustained in our bis-dien complexes, and it is likely that each dien ligand in $[M(dien)_2]^{n+}$ systems will be in a less symmetric environment due to interligand interactions than will dien in complexes of types $[M(dien)X_3]$, or $[M(dien)X]^+$ (planar). If this is so, greater splitting of absorbances would be expected in $[M(dien)_2]^{n+}$, and our spectra do appear more complicated than those on which the above criteria were established.

The 950–800-cm^{-1} region appears to be more distinctive, however. *trans*-$[Co(dien)_2]Br_3 \cdot H_2O$ and *trans*-$[Cu(dien)_2]Br_2 \cdot 0.5H_2O$ both show a band quartet in this region (attributed to CH_2–, NH_2–, and NH– rocking modes and CN skeletal vibrations) whereas both *cis*-$[Co(dien)_2]Br_3$ (facial) isomers exhibit either fewer peaks or broad unsymmetric absorptions (Figure 5). $[Ni(dien)_2]Br_2 \cdot H_2O$ (configuration undetermined) also shows the band quartet. This quartet–triplet distinction has also been noted in mono-dien systems.[6–8]

Our results support the observation[6] that the CH_2 stretching vibrations (3000–2800 cm^{-1}) are very weak for facial dien, but strong for meridional dien, in $[M(dien)X_3]$ (M = Rh, Co, Cr; X = Cl, Br). Figure 5 shows that the CH_2 bands are very weak for *s-cis-* and *u-cis-*$[Co(dien)_2]^{3+}$, but are quite pronounced for the trans isomers of $[Co(dien)_2]^{3+}$ and $[Cu(dien)_2]^{2+}$. On this criterion the corresponding nickel(II) complex may be assigned as trans, which is consistent with the quartet criterion above and also with trans appearing to be the most stable isomer in all these bis-dien systems.

It is of interest to consider the use of pmr spectra as a criterion to assign geometric configurations to these complexes. The solvent we investigated particularly was D_2O (neutral, or acidified with D_2SO_4), and the spectra have also been recorded in dimethyl-d_6 sulfoxide by Yamasaki.[23] We find that the three spectra run in one solvent do not in general distinguish all three isomers, but may allow one assignment to be made. Only from spectra taken under various conditions is it possible to assign all three configurations by this method alone.

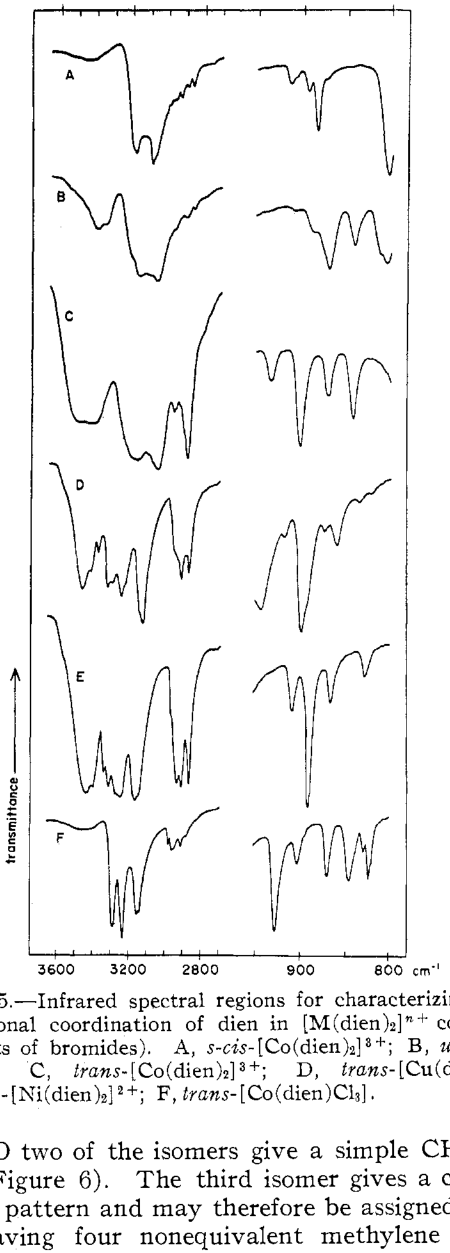

Figure 5.—Infrared spectral regions for characterizing facial or meridional coordination of dien in $[M(dien)_2]^{n+}$ complexes (KBr disks of bromides). A, *s-cis*-$[Co(dien)_2]^{3+}$; B, *u-cis*-$[Co(dien)_2]^{3+}$; C, *trans*-$[Co(dien)_2]^{3+}$; D, *trans*-$[Cu(dien)_2]^{2+}$; E, *trans*(?)-$[Ni(dien)_2]^{2+}$; F, *trans*-$[Co(dien)Cl_3]$.

In D_2O two of the isomers give a simple CH_2 resonance (Figure 6). The third isomer gives a complex splitting pattern and may therefore be assigned as the u-cis, having four nonequivalent methylene groups (Figure 1). The s-cis and trans isomers should have only two nonequivalent CH_2 groups, since in neutral solution the rapid conformational interchange in the trans isomer should make each chelate ring equivalent on a time average.

Spectra in acidic D_2O were all distinctive (Figure 6) with only one isomer showing a single NH_2 peak (4.73 ppm from TMP) whereas multiple NH_2 resonances were apparent for the other two isomers. These observations can be interpreted on the basis of chelate ring conformations.

Figure 6.—Pmr spectra of $[Co(dien)_2]Cl_3 \cdot xH_2O$ isomers: (a) in $D_2O-D_2SO_4$, and (b) in D_2O (containing trace of sodium carbonate), in ppm with respect to sodium trimethylsilypropanesulfonate. Spectra (a) are 100-Mc, obtained on a Varian HA-100 spectrometer. Spectra (b) were run on a 60-Mc Jeol spectrometer.

For the s-cis isomer there are (in principle) five possible types of combinations for the four ring conformations: $\lambda\delta-\lambda\delta$, $\lambda\delta-\delta\lambda$, $\lambda\lambda-\lambda\delta$, $\lambda\lambda-\delta\delta$, and $\lambda\lambda-\lambda\lambda$. Conformational interchange in this isomer is not dependent on N^2H dissociation, so that such interchange should be facile even in acid solution. On a time average therefore all four primary amine groups should be equivalent and on this basis this isomer may be regarded as having a center and planes of symmetry. The s-cis configuration may therefore be assigned to the isomer showing the single NH_2 resonance in D_2O/D^+, and a single resonance is also obtained from this isomer in dimethyl-d_6 sulfoxide.[23]

The NH_2 groups on each dien ligand are in nonequivalent environments in the u-cis and trans isomers, and this is apparent from Figures 1 and 2, respectively. Conformational interchange in trans must involve N^2H dissociation as discussed previously and will not take place in the acidic solvent, and multiple resonance could be expected. Although conformational interchange could take place in the u-cis isomer (as with s-cis discussed above) the two NH_2 groups of each ligand would still remain in nonequivalent environments due to the configurational symmetry being C_2, and this is consistent with the two resonances observed both in D_2O/D^+ (Figure 6) and in dimethyl-d_6 sulfoxide.[23]

The three spectra in trifluoroacetic acid were qualitatively similar, and were less useful as criteria for configurations.

The proportions of the three isomers at equilibrium were found to be independent of the anion being chloride or bromide. Replicate determinations of the isomer proportions (under standardized conditions) gave the ratios trans:u-cis:s-cis = 65:28:7. These figures demonstrate the stability of the trans or meridional arrangement over facial coordination of the dien ligand, but the proportions also indicate that there is an even greater difference in stabilities of the two cis isomers. It is now generally agreed that a number of structural factors affect relative isomer stabilities in metal complex systems.[19] In the present system these will include bond angle strain at the secondary nitrogens bridging chelate rings, and nonbonded atomic interactions. The above results clearly show that bond angle strain is not the major factor involved, since scale molecular models indicate that considerable strain exists between two adjacent en chelate rings when in the meridional disposition, as in *trans*-$[Co(dien)_2]^{3+}$ and *trans*-$[Co(trien)X_2]^+$. Nonbonded interactions are likely to be important, although it must be appreciated that the relative contributions from factors such as solvation energy are difficult to assess.

Preliminary experiments suggest that the isomer proportions in the $[Co(dien)_2]^{3+}$ system also depend to some extent on environmental factors such as temperature (the proportions of s-cis and u-cis increase at the expense of trans, with rise in temperature), cobalt concentration, and nature of the anion (other than chloride–bromide). We also find that charcoal samples differ in their capacity to establish equilibrium. The figures quoted above were obtained with a charcoal sample whose high catalytic efficiency was established by quantitative measurement of its effect on racemization of $[Co(en)_3]^{3+}$. These further results will be discussed along with energy minimization calculations in a subsequent article.

In seeking a method to obtain the *s-cis*-$[Co(dien)_2]^{3+}$ isomer in higher yield, the reaction of a solution claimed[8] to contain *cis*-$[Co(dien)(H_2O)_3]^{3+}$ with excess dien was examined under various conditions of pH. The reaction was most complete in alkaline conditions pH 8–9 (as judged by the color change), and product analysis by chromatography on Sephadex showed that the $[Co(dien)_2]^{3+}$ reaction products were almost all trans with only a trace of the u-cis isomer, with no evidence of any s-cis. This product proportion, while quantitatively similar to that obtained by synthesis, involves an even higher proportion of trans/cis. If the starting complex was in fact *cis*-$[Co(dien)(H_2O)_3]^{3+}$, these results would suggest that substitution of the second dien ligand on a cis-mono-dien arrangement evidently leads to substantial isomerization. This would accord with the greater stability of the trans configuration in the bis complex as indicated by all other preparative methods.[23]

The starting triaquo complex was obtained by the reaction sequence[8]

$$\textit{trans}\text{-}[Co(dien)Cl_3] \xrightarrow{NaOH} \textit{trans}\text{-}[Co(dien)(OH)_3] \xrightarrow{HClO_4} \textit{trans}\text{-}[Co(dien)(H_2O)_3]^{3+}$$

and it is reported that on standing the trans triaquo isomerizes completely to the cis.[22] The cis disposition of coordinated dien would thus appear to be considerably stabilized only by coordinated water. This might be attributed to more favorable hydrogen bonding between the aquo ligands all cis, as this factor may be used to rationalize the greater stability of β-$[Co(trien)(H_2O)(OH)]^{2+}$ compared with the α configuration.[24] The identity of the complex species purported to be *cis*-$[Co(dien)(H_2O)_3]^{3+}$ remains in some doubt however since it has been obtained only in solution.

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Conformational Analysis of Coordination Compounds. V. Six-Membered Diamine Chelate Rings

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The conformational preferences for the chelate ring formed by 1,3-diaminopropane in its octahedral mono, bis, and tris complexes have been studied by *a priori* calculations of conformational energies. The chair conformation was found to be the most stable for each of the compounds studied. The minimum energy geometries were found to agree well with the solid state structures determined by X-ray crystallography. The lowest energy pathway for converting one chair conformation into the other possible chair conformation was similarly studied, and the barrier of activation was calculated to be of the order of 7 kcal mol^{-1}.

The six-membered carbocyclic ring system has been extensively studied by conformational analysis. In contrast, the analogous diamine chelate ring formed by 1,3-diaminopropane (tn) has attracted little attention since the early comments of Corey and Bailar.[1]

As found for the cyclohexane ring, there are two basic types of conformations available to the six-membered diamine chelate ring: (i) a chair form in which the metal atom and the central carbon atom lie on different sides of a plane containing the other four atoms of the ring, and (ii) a flexible boat which corresponds to a wide range of conformations that contains two special symmetrical forms, (a) the symmetrical boat in which the metal and central carbon atoms lie on the same side of a plane containing the remaining four atoms, and (b) the symmetrical skew boat in which the central carbon, the metal, and the two nitrogen atoms are coplanar, with the remaining carbon atoms lying, respectively, above and below this plane (see Figure 1).

In this paper, the methods of analysis developed by the present authors for the five-membered diamine systems[2-4] have been applied to the systems $M(tn)b_2$, $M(tn)a_2b_2$, *trans*-$M(tn)_2a_2$, and $M(tn)_3$ with a M–N bond length of 2.0 Å. Both the ground-state conformations and the activated complexes for conformational interconversion have been studied in order to determine the preferred geometries of the conformations, the energy differences between the stable conformations, and the energy barrier that exists in the chair-to-chair interconversion.

Geometrical Model

The chelate ring is initially placed in a right-hand Cartesian coordinate system as shown in Figure 2 with the coordinate bonds in the xy plane equidistant from the x and y axes. The conformations have been specified by a constant set of bond lengths and by a set of internal coordinates, z_1, z_2, z_3, α, γ, and γ' where z_1, z_2, and z_3 are the z coordinates of the ring carbon atoms C(1), C(2), and C(3) and the angles are as specified in Figure 2.

The positions of the unidentate ligands have been determined and varied in the manner outlined previously.[2] The apical ligands, a, have been permitted to bend back away from the z axis in order to relieve unfavorable interactions where necessary, and also have been allowed to rotate freely to minimize the interactions.

For the bis and tris complexes, the rings have been first constructed in the position shown in Figure 2, and then transformed to their correct position in the octahedron. Reorientation of the rings and groups has been carried out in the way described previously for $M(en)_3$.[4]

Energy Calculations

The set of empirical van der Waals energy equations derived from free energy data for the cobalt(III)–(R)-propylenediamine–(S)propylenediamine system has been applied to the present system.[4,5] The methods for calculating the torsional and angle-bending energies have also been described previously.[2]

Conformational energy calculations for six-membered rings are potentially much more laborious than those for

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