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Structural Assignments, Reactivity, and Stability of the Isomers of the *trans,trans*-Dinitrobis(N-methylethylenediamine)cobalt(III) Ion

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The *meso* and optically active forms of *trans,trans*-[Co(Meen)$_2$(NO$_2$)$_2$]$^+$ (Meen = N-methylethylenediamine) have been isolated. Proton exchange at the N-methyl center exceeds the rate of isomerization of *meso* form $\rightleftharpoons$ racemate by a large factor, and the equilibrium constant for the latter is 7.1 at 34.3°. The stability difference is discussed in relation to the nonbonded atomic interactions in the two ions, and the circular dichroism of the active *trans,trans*-[Co(Meen)$_2$(NO$_2$)$_2$]$^+$ and *trans,trans*-[Co(Meen)$_2$Cl$_2$]$^+$ ions is analyzed.

Introduction

The resolution of coordinated secondary amines has been described in several recent publications.[1-6] This demonstration of the comparative inertness of these nitrogen centers to racemization is significant for inorganic stereochemistry since it contrasts with the lability of the same centers in organic chemistry and greatly enhances the number of potentially isolable isomers. In this article we are concerned with the properties of these centers in relation to the structure, stability, and reactivity of the possible *trans*-dinitrobis(N-methylethylenediamine)cobalt(III) isomers (N-methylethylenediamine = Meen). The possible structures of *trans*-[Co(Meen)$_2$(NO$_2$)$_2$]$^+$ complexes are given in Figure 1 (A = B = NO$_2^-$). For the *trans,trans* isomer, if the two substituents are different, such as in the chloronitro ions, then the *meso* form of the dinitro complex becomes a racemate, Figure 1c (A = Cl, B = NO$_2$), which has one N–CH$_3$ group directed toward each substituent. The optically active *trans, trans* isomers however, give two internal diastereoisomers where both N–CH$_3$ groups are directed toward one substituent in each isomer, Figure 1d and Figure 2E and F. For the *trans,cis* series, however, the situations are reversed. The *meso*-dinitro isomer becomes two internally compensated geometrical forms for *trans,cis*-[Co(Meen)$_2$ClNO$_2$]$^+$, Figure 1a (A = Cl, B = NO$_2$ or A = NO$_2$, B = Cl), whereas the active isomers each yield only one optical isomer, Figure 1b (A = Cl, B = NO$_2$). These properties allow the structure of the isolated species to be unraveled using primarily rotatory dispersion (RD) and proton magnetic resonance spectroscopy (pmr).

This study is a continuation of earlier work on the kinetics and mechanism of hydrogen isotope exchange and racemization at coordinated asymmetric nitrogen centers. It is specifically related to the reactions of the *trans,trans*-[Co(Meen)$_2$(NO$_2$)$_2$]$^+$ ion[3] where it was proposed that the ion racemized by first isomerizing to a less stable *meso trans,trans*-[Co(Meen)$_2$(NO$_2$)$_2$]$^+$ isomer which then isomerized to the racemic *trans, trans*-[Co(Meen)$_2$(NO$_2$)$_2$]$^+$ isomer which then isomerized to the racemic *trans,trans*-[Co(Meen)$_2$(NO$_2$)$_2$]$^+$. Preliminary rate data[3] supported these proposals and a more detailed investigation into the kinetics and mechanism of these isomerization reactions is now described.

Experimental Section

Optical rotations were measured in a 1-dm tube with a Perkin-Elmer 141 polarimeter fitted with a Zeiss monochromator and a quartz–iodine lamp. Pmr spectra were obtained on a Perkin-Elmer R10 spectrometer using sodium trimethylsilylpropanesulfonate as a standard reference.

Kinetic Studies.—The methods employed for determining the rates of racemization and proton exchange have been discussed.[1,2] The proton-exchange rates were measured in 0.2 *M* acetate buffer containing 0.09 *M* complex. Racemization was studied in 0.05 *M* NaOD–glycine buffers made to μ = 0.14 with KCl (Analar). The same buffer without KCl was employed for studying the *meso* $\rightarrow$ racemate reaction (0.09 *M* in complex). The pH of the solutions was measured at 34.3°, ±0.01 pH unit using a Cambridge bench-type pH meter. The empirical formula pD = pH + 0.4 was used to evaluate [D$^+$].[7]

***meso-trans,trans*-[Co(Meen)$_2$(NO$_2$)$_2$]Cl.**—This compound was obtained contaminated with NaCl in the preparation of (±)-*trans,trans*-[Co(Meen)$_2$(NO$_2$)$_2$]Cl.[3] It was purified by recrystallization of the impure product (1.3 g) from hot aqueous solution (yield 1.0 g). The bromide, iodide, and perchlorate salts were also obtained readily by addition of the respective sodium salts and were less soluble than the chloride. Also since the *meso* complex was unstable toward base, a slight excess of acid in the preparative mixture improved the *meso* to racemate ratio; if in the described preparation[3] the volume of 11.6 *N* HCl was increased from 8.8 to 9.6 ml, the yield of *meso* isomer was increased to 10 g. *Anal.* Calcd for [CoC$_6$H$_{20}$N$_4$(NO$_2$)$_2$]Cl: C, 21.53; H, 6.02; N, 25.12. Found: C, 21.76; H, 6.25; N, 25.23. Calcd for [CoC$_6$H$_{20}$N$_4$(NO$_2$)$_2$]Br·H$_2$O: C, 18.14; H, 5.58; N, 21.17. Found: C, 18.17; H, 5.32; N, 21.12. Calcd for [CoC$_6$H$_{20}$N$_4$(NO$_2$)$_2$]ClO$_4$: C, 18.08; H, 5.06; N, 21.09. Found: C, 18.12; H, 5.00; N, 20.90. Calcd for [CoC$_6$N$_6$H$_{20}$O$_4$]I: C, 16.91; H, 4.73; N, 19.73. Found: C, 16.78; H, 5.13; N, 19.67.

(±)-*trans,trans*-[Co(Meen)$_2$(NO$_2$)$_2$]NO$_2$·0.5H$_2$O.—A solution of N-methylethylenediamine (7.7 g) and LiCl (6 g) in methanol

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

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

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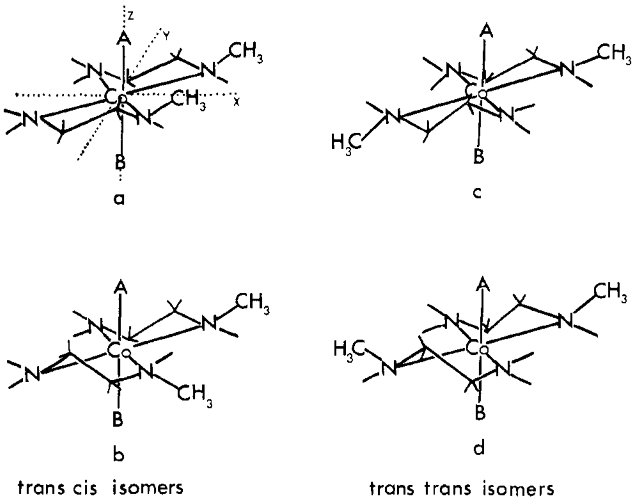

Figure 1.—Some isomeric forms of *trans,trans*- and *trans,cis*-$[Co(Meen)_2AB]^{n+}$ (derived from the *meso* and optically active forms of $[Co(Meen)_2A_2]^{n+}$).

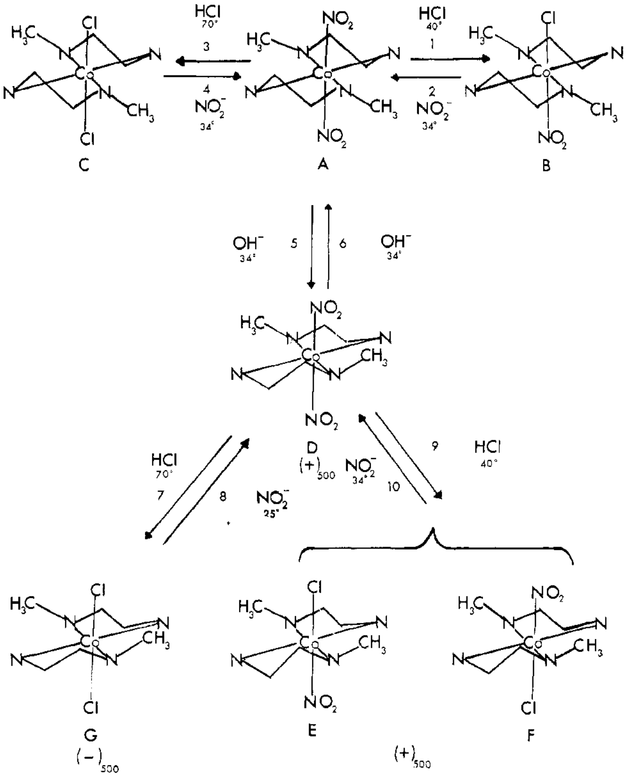

Figure 2.—Summary of principal isomerization and substitution reactions for the *trans,trans*-$[Co(Meen)_2AB]^+$ ions.

(500 ml) containing a suspension of $Na_3[Co(NO_2)_6]$ (20.1 g) was refluxed for 3 hr until only NaCl remained suspended. This was removed, and, on standing overnight, crystals of $[Co(Meen)_2(NO_2)_2]NO_2$ were formed (4.0 g) and collected. The volume was reduced to 75 ml and a second fraction (10.5 g) was collected. The volume was further reduced by half and addition of excess LiBr resulted in the bromide salt (1.5 g). All fractions were identified as the *trans,trans* racemate by their pmr spectra. *Anal.* Calcd for $[CoC_6H_{20}N_6O_4]NO_2 \cdot 0.5H_2O$: C, 20.34; H, 5.98; N, 27.69. Found: C, 20.59; H, 5.82; N, 27.62.

(±)-*trans,trans*-$[Co(Meen)_2(NO_2)Cl]ClO_4 \cdot 0.5H_2O$.—A solution of (±)-*trans,trans*-$[Co(Meen)_2(NO_2)_2]Cl$ (1.9 g) in HCl (7 ml, 10 *N*) was warmed at 40° until it became deep crimson (~5 min) and excess $NaClO_4$ was added. The solution was cooled and the product collected in three fractions (total yield 1.5 g). The pmr spectra were identical for all three fractions. *Anal.* Calcd for $[CoC_6H_{20}N_4(NO_2)Cl]ClO_4 \cdot 0.5H_2O$: C, 18.24; H, 5.36; N, 17.73. Found: C, 18.49; H, 5.34; N, 17.87.

(−)$_D$-*trans,trans*-$[Co(Meen)_2(NO_2)Cl]ClO_4 \cdot 0.5H_2O$.—A solution of (−)$_D$-*trans,trans*-$[Co(Meen)_2(NO_2)_2]Cl$ (0.5 g, α_{495} −0.363° for a 0.1% solution) in HCl (2.5 ml, 10 *N*) was warmed as above. After 5 min, the complex was precipitated by adding ethanol and ether. It was redissolved in a minimum volume of hot water (at pH 3, acetic acid) and recrystallized by adding $NaClO_4$ (yield 0.35 g). *Anal.* Calcd for $[CoC_6H_{20}N_4(NO_2)Cl]ClO_4 \cdot 0.5H_2O$: C, 18.24; H, 5.36; N, 17.73. Found: C, 18.52; H, 5.47; N, 17.70.

***meso-trans,trans*-$[Co(Meen)_2(NO_2)Cl]ClO_4 \cdot 0.5H_2O$.**—This compound was obtained in a similar manner to that for the (±)-*trans,trans* isomer. *Anal.* Calcd for $[CoC_6H_{20}N_4(NO_2)Cl]ClO_4 \cdot 0.5H_2O$: C, 18.24; H, 5.36; N, 17.73. Found: C, 18.08; H, 5.24; N, 17.68.

(−)$_D$-*trans,trans*-$[Co(Meen)_2Cl_2]ClO_4$.—A solution of (+)$_D$-$[Co(Meen)_2(NO_2)_2]ClO_4$ (0.3 g, $[\alpha]_{500}$ +320°) in HCl (10 ml, 11 *N*) was allowed to stand at ambient temperature for 1 hr and was then warmed at 70° for 15 min. It was evaporated to near dryness under reduced pressure and an additional 5 ml of acid was added. The volume was reduced to 3 ml, when crystallization occurred. The crystals were redissolved by warming, the solution was filtered, and 11 *N* $HClO_4$ (1 ml) was added. On cooling, the lustrous, dark emerald green crystals which formed were collected and washed with 5 *M* $HClO_4$ and finally acetone (yield 0.15 g, α_{500} −0.480° for a 0.1% solution in 0.01 *N* $HClO_4$). *Anal.* Calcd for $[CoC_6H_{20}N_4Cl_2]ClO_4$: C, 19.09; H, 5.34; N, 14.84. Found: C, 18.84; H, 5.40; N, 14.91.

(±)-*trans,trans*-$[Co(Meen)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$ and (±)-*trans,trans*-$[Co(Meen)_2Cl_2]SCN$.—A solution of (±)-*trans,trans*-$[Co(Meen)_2(NO_2)_2]Cl$ (1.1 g) in HCl (5 ml, 11 *N*) was warmed on a steam bath for 20 min. The solution turned grayish purple and dark green needles formed on cooling. The crystals were collected and washed with 5 *N* HCl and then acetone. The product was recrystallized from dilute HCl (10^{-3} *M*) by the addition of several drops of 11 *N* HCl and cooling. It was also converted to the much less soluble thiocyanate salt by adding LiSCN. *Anal.* Calcd for $[CoC_6H_{20}N_4Cl_2]Cl \cdot HCl \cdot 2H_2O$: C, 18.66; H, 6.52; N, 14.51. Found: C, 18.73; H, 6.57; N, 14.29. Calcd for $[CoC_6H_{20}N_4Cl_2]SCN$: C, 25.01; H, 5.98; N, 20.84. Found: C, 25.29; H, 6.05; N, 20.79.

***meso-trans,trans*-$[Co(Meen)_2Cl_2]ClO_4$.**—This poorly soluble compound was made by treating *meso-trans,trans*-$[Co(Meen)_2(NO_2)_2]ClO_4$ with 11 *N* HCl and warming. After the solution turned green $NaClO_4$ was added and the solution was cooled. The green crystals formed were collected and washed with alcohol and ether and dried. *Anal.* Calcd for $[CoC_6H_{20}N_4Cl_2]ClO_4$: C, 19.09; H, 5.34; N, 14.84. Found: C, 18.89; H, 5.38; N, 14.89.

***meso-trans,trans*-$[Co(Meen)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$.**—A solution of *meso-trans,trans*-$[Co(Meen)_2(NO_2)_2]Cl$ (1.1 g/5 ml of 11 *N* HCl) was heated for 1 hr at 70°. The color changed rapidly from yellow to the red color of the chloronitro complex and then more slowly became red-brown. The solution finally became a deep green after 0.5 hr and dark green crystals deposited. These were collected and washed with 10 *N* HCl and acetone (0.4 g) and dried under vacuum at room temperature. *Anal.* Calcd for $[CoC_6H_{20}N_4Cl_2]Cl_2H_5O_2$: C, 18.66; H, 6.52; N, 14.51. Found: C, 18.54; H, 6.45; N, 14.68. The infrared spectrum (Nujol) and the pmr spectrum (Figure 3) of the corresponding *meso* and racemate salts were indistinguishable, but the visible spectra in methanol were appreciably different.

Conversion of (−)$_D$-*trans,trans*-$[Co(Meen)_2(NO_2)Cl]ClO_4 \cdot 0.5H_2O$ (Isomeric Mixture) to (−)$_D$-*trans,trans*-$[Co(Meen)_2(NO_2)_2]ClO_4$.—To $[Co(Meen)_2(NO_2)Cl]ClO_4 \cdot 0.5H_2O$ (0.01 g/10 ml of 0.01 *N* $HClO_4$) was added $NaNO_2$ (0.175 g). The solution was warmed at 34.3° and maintained at that temperature while the change in optical rotation was followed with time at 500 mμ. A 0.1% solution in 0.1 *M* Hg^{2+} and 0.05 *M* $HClO_4$ was main-

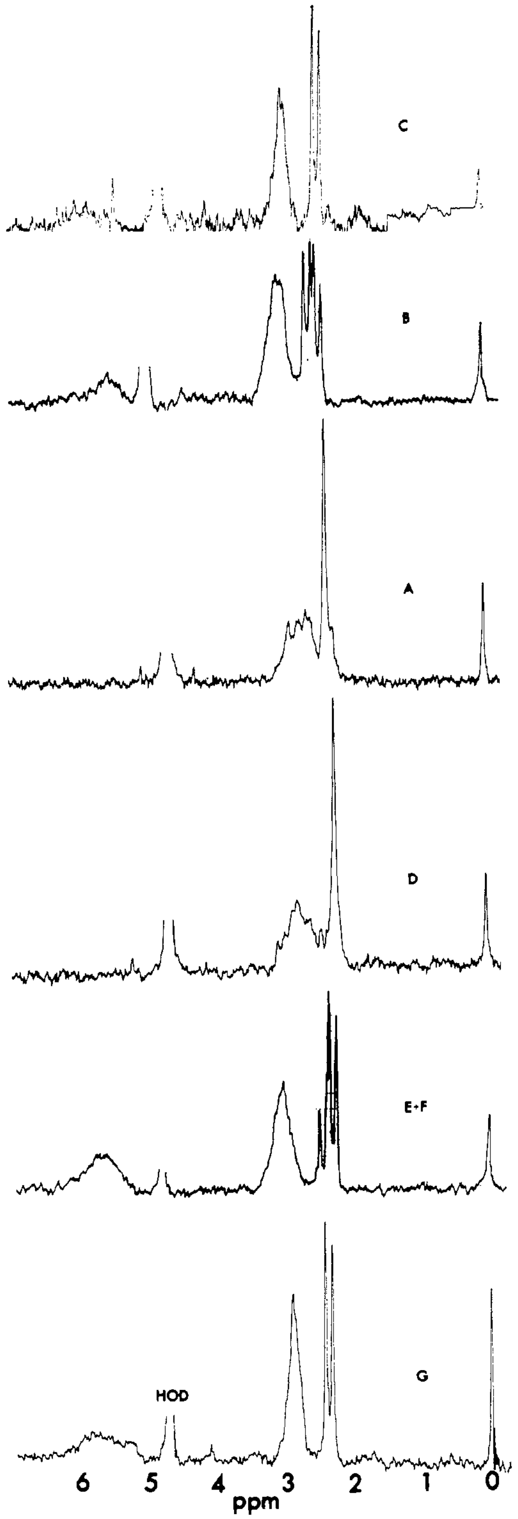

Figure 3.—The pmr spectra of: (A) the *meso*-dinitro-d_6 isomer, in dilute NaOD (pH ~8); (B) the *meso*-chloronitro isomer in 0.1 N DCl; (C) the *meso*-dichloro isomer in 0.01 N DCl; (D) the (±)-dinitro-d_6 isomer, same solution as (A), made by adding more base (pH ~10); (E and F) the two (±)-chloronitro complexes in 0.1 N DCl; (G) the (±)-dichloro complex in 0.01 N DCl.

tained at 34.3° for 1 hr, and then $NaNO_2$ (0.4 g/10 ml of H_2O) was added.

Conversion of (−)$_D$-*trans,trans*-$[Co(Meen)_2Cl_2]ClO_4$ to (+)$_D$-*trans,trans*-$[Co(Meen)_2(NO_2)_2]ClO_4$.—A solution (10 ml) of 0.05% $[Co(Meen)_2Cl_2]ClO_4$ and $NaNO_2$ (0.5 g) in 0.01 N $HClO_4$ was maintained at 25° and the change in optical rotation with time was followed at 500 mμ.

Aquation of (−)$_D$-*trans,trans*-$[Co(Meen)_2Cl_2]ClO_4$.—A 0.05% solution of (−)$_D$-$[Co(Meen)_2Cl_2]ClO_4$ in 0.01 N $HClO_4$ was maintained at 25°, and the change in optical rotation with time at 500 and 630 mμ was followed.

Conversion of Perchlorate Salts to Chloride Salts.—Since all perchlorate salts were too insoluble in D_2O for pmr measurements, analytically pure samples of the perchlorate salts were converted to chloride salts by shaking an aqueous suspension with an equimolar amount of tetraphenylarsonium chloride. The solutions were then filtered and evaporated to dryness.

Results

The preparation of *meso-trans,trans*-$[CO(Meen)_2(NO_2)_2]Cl$ (A) (minor product) and (±)-*trans,trans*-$[Co(Meen)_2(NO_2)_2]Cl$ (D) (major product) has been reported previously,[3] and the resolution of the latter has also been described. The pmr spectra and the optical properties of these isomers were also presented, but the evidence for the structural assignment was postponed until this publication. The evidence used to assign structure to these species is derived mainly from the near-uv spectra, circular dichroism (CD) curves, pmr spectra, and the reactions of the complexes and their derivatives as shown in Figure 2. The dichloro and dinitro isomers denoted as $(+)_{500}$ or $(-)_{500}$ are identical with the designation $(+)_D$ or $(-)_D$, respectively.

Reactions 1 and 2.—Treatment of A with HCl at 40° for 5 min resulted in *trans,trans*-$[Co(Meen)_2(NO_2)Cl]^+$ (B) isolated as the perchlorate and then converted to the chloride. The pmr spectrum of this ion in 0.01 M DCl is given in Figure 3B. Two methyl doublet signals of equal intensity appear at 2.4 and 2.57 ppm. Excess $NaNO_2$ was then added to this solution and the spectrum retaken after 1 day. Apart from the appearance of a small peak at the center of the methyl doublet resulting from some proton exchange (~10%), the final spectrum was identical with that for *meso-trans,trans*-$[Co(Meen)_2(NO_2)_2]^+$, Figure 3A.

Reactions 9 and 10.—Similar treatment of (−)$_D$-*trans,trans*-$[Co(Meen)_2(NO_2)_2]ClO_4$ with HCl, followed by the addition of $NaClO_4$, resulted in the isolation of an isomeric mixture (E and F) of (−)$_D$-*trans,trans*-$[Co(Meen)_2(NO_2)Cl]ClO_4$. The pmr spectrum of this mixture is given in Figure 3E and F. Again two methyl signals appear, one at 2.46 ppm and the other at 2.29 ppm, but they are of unequal intensity. Treatment of the solution with $NaNO_2$ gave (−)$_D$-$[Co(Meen)_2(NO_2)_2]ClO_4$ ($[\alpha]_{500}$ −323°, optically pure). The racemic dinitro complex D treated the same way gave the same pmr spectrum for the product, and addition of $NaNO_2$ reconverted the isomeric mixture of chloronitro ions to the racemic dinitro species as shown by the pmr spectrum.

The mixture of chloronitro ions (E and F) was converted to a mixture of nitroaquo isomers using Hg^{2+} ions in dilute acid, and this mixture was reconverted to the dinitro ion with full retention of optical activity and configuration using $NaNO_2$. The result suggests that the Hg^{2+}-induced hydrolysis occurs with complete retention of the *trans* configuration.

Reactions 7 and 8.—(+)$_D$-*trans,trans*-[Co(Meen)$_2$(NO$_2$)$_2$]ClO$_4$ treated with HCl at 70° for 15 min and addition of HClO$_4$ gave the sparingly soluble salt (−)$_D$-*trans,trans*-[Co(Meen)$_2$Cl$_2$]ClO$_4$ (G). The circular dichroism (CD) and spectral curves for this complex and the parent dinitro ion are given in Figures 4 and 5. The optical rotation slowly changed with time as the complex aquated to the optically active chloroaquo ion. Addition of NaNO$_2$ to a dilute acid solution of the dichloro salt resulted in the formation of the parent dinitro complex with 90% retention of activity. The pmr spectrum of the more soluble racemic salt *trans,trans*-[Co(Meen)$_2$Cl$_2$]Cl·HCl·2H$_2$O is given in Figure 3G. Treatment of this solution with LiNO$_2$ results in the (±)-dinitro ion as the major product.

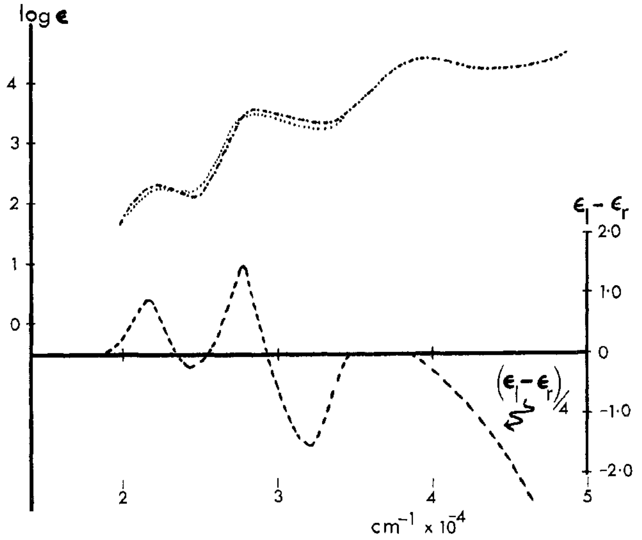

Figure 4.—Absorption spectrum (–·–·–·) and CD curve (– – –) for (+)$_D$-[Co(Meen)$_2$(NO$_2$)$_2$]ClO$_4$ and absorption spectrum of *meso-trans,trans*-[Co(Meen)$_2$(NO$_2$)$_2$]Cl (····) in H$_2$O.

Reactions 3 and 4.—*meso-trans,trans*-[Co(Meen)$_2$(NO$_2$)$_2$]Cl (A), when treated with HCl at 70° for 0.5 hr, gave *meso*-[Co(Meen)$_2$Cl$_2$]Cl·2H$_2$O (C). The pmr spectrum of this compound in dilute DCl solution is given in Figure 3. Treatment of this solution with excess LiNO$_2$ resulted in the *meso*-dinitro complex (A).

Racemization and Deuteration Reactions 5 and 6.—The pmr spectra of the *meso* and active isomers, both N deuterated, are given in Figure 3A and D, and the assignments of the absorptions are given in Table I. The principal difference between the spectra for the two isomers occurs for the methyl doublets which arise from the coupling of the methyl group with the N proton.[3] Similarly in the deuterated isomers (Figure 3) the singlet absorptions for the methyl groups are well separated. Thus the proton exchange for both isomers was followed by the collapse of the methyl doublet to a singlet in D$_2$O or *vice versa* in H$_2$O.[3]

The racemization of the (+)$_D$ isomer was followed as previously[3] and no activity remained after 10 half-lives. The isomerization of the *meso* form to racemate was measured by the collapse of the methyl signal at 2.34 ppm (*meso*) and also by the growth of the signal at 2.23 ppm (racemate) (Figure 6). This change was accompanied by a small shift in the visible spectrum from a maximum at 354 to 347 mμ. The combined rate constants ($k_m + k_r$) for the isomerization

$$\textit{meso}\ \text{form} \underset{k_r}{\overset{k_m}{\rightleftarrows}} \text{racemate}$$

are given in Table II. Included also in this table are rate constants (k_r) for racemization measured in the same buffers and at the same ionic strength as the *meso* → racemate reaction in both D$_2$O and H$_2$O. In Table III the rate constants for proton exchange at the secondary N for the *meso* and racemic isomers at $\mu = 0.3$ are recorded. Plots of log [(peak height)$_t$ − (peak height)$_\infty$] or log α_t against time were linear for at least 2 half-lives and some *meso* → racemate reactions were followed for longer than 3 half-lives and no curvature was observed in the plots. This suggests that only one isomeric species is present.

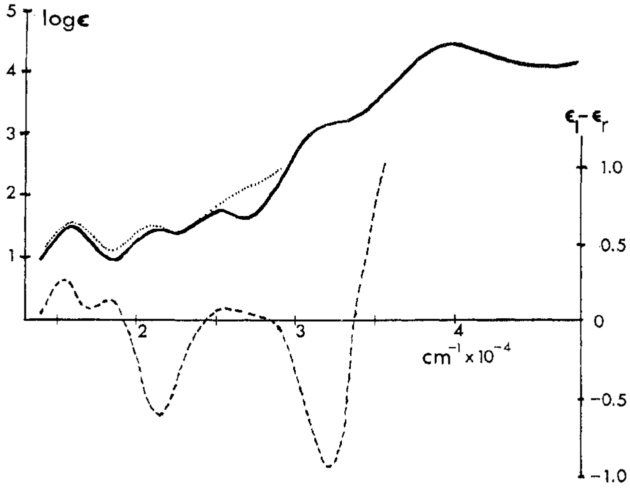

Figure 5.—The absorption spectrum (——) and CD curve (– – –) for (−)$_D$-*trans,trans*-[Co(Meen)$_2$Cl$_2$]ClO$_4$ and absorption spectrum (····) for *meso-trans,trans*-[Co(Meen)$_2$Cl$_2$]Cl·HCl·2H$_2$O (in methanol).

Table I

Assignments of Chemical Shifts (ppm) for Pmr Spectra of Complexes A-G,[a] Figure 3

	—CH$_3$	—CH$_2$CH$_2$—	—NH$_2$, =NH
C	2.4	~2.9	~5.7
B	2.4, 2.57	~3.0	~5.5
A	2.34	~2.7	...
D	2.23	~2.8	...
E	2.46	~3.0	~5.7
F	2.29	~3.0	~5.7
G	2.37	~2.9	~5.7

[a] Sodium trimethylsilylpropanesulfonate as standard reference. Letters correspond to pmr spectra in Figure 3 and structures in Figure 2.

Both the racemization and proton-exchange reactions obey the same rate law

$$R = k[\text{complex}][\text{OD}^-]$$

although the rates differ widely.

Discussion

Structure Assignment.—The visible and uv spectra of bis-diamine complexes of Co(III) do not vary greatly

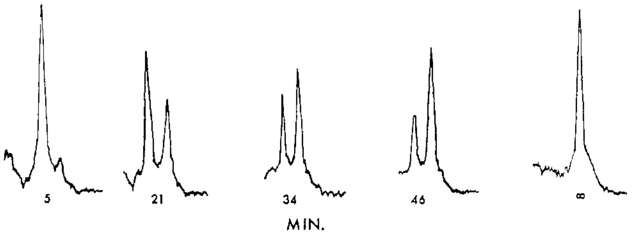

Figure 6.—The isomerization of deuterated *meso-trans,trans*-$[Co(Meen)_2(NO_2)_2]^+$ to the *racemic* form followed by the change in the methyl singlets of the two ions with time at pD 10.45.

TABLE II

RATE CONSTANTS FOR THE ISOMERIZATION OF THE *meso* AND ACTIVE ISOMERS OF *trans,trans*-$[Co(Meen)_2(NO_2)_2]^+$ IN GLYCINE BUFFER[a] AT 34.3°

pD	$k_{obsd} \times 10^4$, sec^{-1}	k_{calcd},[b] $M^{-1}\,sec^{-1}$
	Loss of *meso*	
9.45	0.98	10.2
10.14	5.02	10.7
10.45	10.04	10.4
	Formation of Racemate	
9.45	0.91	9.5
10.14	5.25	11.1
10.45	9.63	9.9
	Formation of *meso*	
10.45	1.24	1.29
10.14	0.58	1.23
9.34[c]	0.44	1.15

[a] 0.05 *M* glycine, [Co] = 0.09 *M*, μ = 0.14 *M*, D_2O. [b] $k_{calcd} = k_{obsd}[D^+]/0.195 \times 1.75 \times 10^{-14}$. [c] H_2O, $k_{calcd} = k_{obsd}[H^+]/1.75 \times 10^{-14}$.

TABLE III

RATE CONSTANTS FOR SECONDARY N-PROTON EXCHANGE IN THE *meso* AND RACEMIC ISOMERS OF *trans,trans*-$[Co(Meen)_2(NO_2)_2]^+$ ION AT 34.3°

pD[a]	$k_{obsd} \times 10^5$, sec^{-1}	$k_{calcd} \times 10^{-5}$,[d] $M^{-1}\,sec^{-1}$
4.09[b]	2.46	5.84
5.62[b]	50.2	5.60
6.15[b]	269	5.60
6.15[c]	67.9	1.41

[a] pD = pH + 0.4.[7] [b] *meso* isomer, [Co] = 0.09 *M*, μ = 0.3 *M*. [c] (±) isomer, [Co] = 0.09 *M*, μ = 0.3 *M*. [d] $K_{D_2O} = 3.4 \times 10^{-15}$.

with change in diamine.[8] For example, the dichloro complexes are green for the *trans* series and violet for the *cis*. The *trans*-dinitro complexes show λ_{max} at 330 mμ for the *cis* isomers and at 350 mμ for the *trans* series. Thus, *cis*-$[Co(en)_2(NO_2)_2]^+$ absorbs maximally at 325 mμ, whereas the *trans* isomer absorbs at 347 mμ.[8] A similar result obtains for the *cis*-$[Co((-)\text{-}pn)_2(NO_2)_2]^+$ ion[9] (pn = 1,2-diaminopropane). The *meso* and racemic dinitro complexes recorded here absorb maximally at 354 and 347 mμ, respectively, and on this basis are assigned the *trans*-dinitro configuration.

In addition, the $(+)_D$-dinitro isomer racemizes at one rate without change in the absorption spectrum which is consistent with the *trans* configuration. A *cis* isomer would mutarotate to a constant rotation unless the resolution procedure accidentally gave equal amounts of the D and L configurations about the cobalt center while resolving the asymmetric N centers. Moreover, racemization at one N center would give a new *cis* isomer with nonequivalent methyl groups, and equivalence would be observed only if the second N center then racemized much more rapidly. Also both *cis* diastereoisomers are required to racemize and exchange protons with the solvent at the same rate. This collection of coincidences is so improbable that it can be discounted as an explanation for the complete racemization at one rate.

Finally, the pmr spectra of the two dinitro ions indicate only one type of methyl group is present in each instance. This is also observed for the green *trans*-dichloro salts derived from the dinitro ions. In summary then the evidence requires the complexes to be *trans* with respect to the anionic substituents.

The asymmetric secondary nitrogen centers in these compounds are inert to inversion at pH <8, which increases the number of potentially isolable *trans*-dinitro isomers from two, *cis*-methyl and *trans*-methyl, to six. Both the *cis*-CH_3 and *trans*-CH_3 have one *meso* form and a racemic pair. The principal difference between the possible *meso* forms is that *cis*-CH_3 has a mirror plane (Figure 1a, *xz* plane) and *trans*-CH_3 has a center of inversion. The difference between the active forms is the direction of the C_2 axis. Both methyl groups are equivalent in all of the structures shown, but resolution will distinguish (±) from *meso*, and interconversion from *meso* to (±) or *vice versa* will relate a given pair as either *cis*-CH_3 or *trans*-CH_3.

When the *meso-trans*-methyl- and (±)-*cis*-methyl-dinitro ions are converted to the chloronitro derivatives, only one *trans* isomer will form from each species, respectively, but the *meso-cis*-CH_3 and (±)-*trans*-CH_3 species will form two isomers each having equivalent CH_3 groups. However, the new species will not necessarily occur in equal amounts.

These requirements lead to only one solution for our observations. The $(-)_D$-dinitro ion gave a mixture of two optically active chloronitro ions in unequal amounts from which only one optically active *trans*-dichloro ion was obtained. The pmr spectra of the chloronitro species indicate that methyl groups are adjacent to the chloro substituent for one species and to the nitro group for the other. Also the optically active dichloro ion when treated with NO_2^- ion gave almost optically pure parent dinitro complex. These results coupled with the previous analysis require all of the complexes (D, E, F) to be *trans* with respect to the anionic substituents and *trans* with respect to the methyl group. Also, since the methyl signal of the dichloro ion is downfield from that of the dinitro complex, structure F is assigned to the major chloronitro product.

The pmr spectrum of the chloronitro product B obtained from the *meso*-dinitro compound indicates

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(8) F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950).

(9) G. A. Barclay, E. Goldschmeid, N. C. Stephenson, and A. M. Sargeson, *Chem. Commun.*, 540 (1966).

the presence of only one compound with two types of methyl groups. That these groups are *trans* to each other in compounds A and B is evident since A and D must have the *trans,trans* structure since they interconvert during proton exchange.

Circular Dichroism and Absolute Configuration.—The first transition in the absorption spectrum of cobalt(III) in an octahedral ligand field is ${}^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ which splits in a tetragonal field (*e.g.*, *trans*-$[CoN_4X_2]^+$) into ${}^1A_{1g} \rightarrow E_g(D_{4h})$ and ${}^1A_{1g} \rightarrow {}^1A_{2g}(D_{4h})$ components, respectively.[10] In Yamatera's theory,[10a] where the results for an orthoaxial chromophore are equivalent with those of the angular overlap model,[10b–d] the position of the split components depends, in the approximation of pure cubic subconfigurations, on the spectrochemical parameter Δ for the ligands. For example, in this approximation, *trans*-$[Co(en)_2X_2]^+$ has its orbitally nondegenerate transition ${}^1A_1 \rightarrow {}^1A_2(D_{4h})$ situated at Δ_{en} and its twice degenerate transition ${}^1A_1(D_{4h}) \rightarrow {}^1E(D_{4h})$ at ${}^1/_2(\Delta_{en} + \Delta_X)$ so that *trans*-$[Co(en)_2Cl_2]^+$ has the ${}^1E(D_{4h})$ level lying at a lower wave number than the ${}^1A_2(D_{4h})$ level whereas the opposite is true of *trans*-$[Co(en)_2(NO_2)_2]^+$ because $\Delta_{NO_2} > \Delta_{en}$. This description is particularly suited for discussing low-symmetry splittings, since the interelectronic repulsion terms remain the same[10d] for the three components of ${}^1T_1(O_h)$. These theoretical results are supported by the analysis of the dichroism exhibited by crystals of $[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$ along the Cl–Co–Cl axis and perpendicular to it.[11] The band at $\sim$16,000 cm^{-1} was ascribed to the ${}^1A_1 \rightarrow {}^1E(D_{4h})$ transition and that at $\sim$22,000 to the ${}^1A_1 \rightarrow {}^1A_2(D_{4h})$ transition.

If these considerations are applied to the spectra of the *trans* ions $[Co((+)pn)_2Cl_2]^+$,[12–14] $[Co((+)\text{-}chxn)_2Cl_2]^+$,[13,15] $(+)_D$-$[Co(trien)Cl_2]$,[14] $(+)_D$-$[Co\text{-}((+)_D\text{-}L\text{-}3,8\text{-}Me_2trien)Cl_2]^+$[14,16] (chxb = 1,2-*trans*-diaminocyclohexane; trien = triethylenetetramine), and $(+)_D$-$[Co(Meen)_2Cl_2]^+$, the same conclusions are reached. All species show absorption bands in the vicinity of 16,000 and 22,000 cm^{-1}. However, the CD curves of these ions indicate that more than two transitions exist and this extra structure can be considered as caused by the chiral perturbation[10d] which in these complexes acts on top of orthoaxial perturbation of symmetry D_{4h}. The CD curves of $(+)_D$-$[Co(trien)Cl_2]^+$ and $(+)_D$-$[Co(3,8\text{-}Me_2trien)Cl_2]^+$ both show a dominant negative CD maximum at 15,400 cm^{-1}, a smaller positive CD maximum at $\sim$17,500 cm^{-1}, and another positive CD maximum at $\sim$22,000 cm^{-1}. Both ions have C_2 symmetry and the $E(D_{4h})$ components are distinguishable therefore as $A(C_2)$ and $B(C_2)$ components and the $A_2(D_{4h})$ component may be distinguished as one of $B(C_2)$ symmetry. The $A(C_2)$ and $B(C_2)$ excited levels derived from the $E(D_{4h})$ level have been assigned[14] to the CD bands of opposite sign at longer wavelengths and the $B(C_2)$ component derived from the $A_2(D_{4h})$ level has been assigned to that remaining at $\sim$22,000 cm^{-1}. The circular dichroism of the ions *trans*-$[Co((+)pn)_2Cl_2]^+$ and *trans*-$[Co((+)chxn)_2Cl_2]^+$ shows less resolution:[13,15] a negative band at $\sim$16,400 cm^{-1} and a positive band at $\sim$22,000 cm^{-1} in methanol. However, the *trans*-$[Co((+)pn)_2Cl_2]^+$ ion does show a slight positive CD wing at 14,000 cm^{-1} ($(\epsilon_l - \epsilon_r) = +0.012$) in 4 *M* HCl[13] which implies the dominant negative band has obscured a less significant positive transition at approximately the same wavelength. In short, it has been experimentally shown for most of these systems that the ${}^1A_1 \rightarrow {}^1T_1(O_h)$ transition exhibits three CD bands whose frequencies vary slightly: a dominant negative transition and a less dominant positive transition in the vicinity of 15,000 cm^{-1} and a less dominant positive transition in the vicinity of 22,000 cm^{-1}. The relative contributions of these transitions to the CD appear to vary considerably from those complexes containing coordinated asymmetric N centers to the complexes containing ligands with asymmetric C centers solely. The CD spectra of the former are much more pronounced than those of the latter but in all instances the ${}^1A_1 \rightarrow {}^1E(D_{4h})$ transition appears to dominate the dichroism.

If we assign to the *trans* species, which show this pattern, the same absolute configuration, then the analysis agrees with the absolute configurations of $(+)_D$-*trans*-$[Co((+)L\text{-}3,8\text{-}Me_2trien)Cl_2]^+$,[14] $(+)_D$-*trans*-$[Co(trien)Cl_2]^+$,[14] $(+)_D$-*trans*-$[Co((+)pn)_2Cl_2]^+$,[17] and $(+)_D$-*trans*-$[Co((+)chxn)_2Cl_2]^+$,[15] known from other sources. The asymmetric carbon centers have the same configuration and the chelate conformations (terminal for trien) also have the same configuration. These arguments suggest that the CD curve of the complex ion $(-)_D$-*trans*-$[Co(Meen)_2Cl_2]^+$, Figure 5, is derived from three transitions: overlapping dominant positive (16,500 cm^{-1}) and less significant negative (17,300 cm^{-1}) bands and a negative band at 21,300 cm^{-1}. This analysis is depicted qualitatively in Figure 7a. It might be inferred therefore that the complex has the antimeric configuration to those described above, namely, the configuration shown in Figure 2.

It can be stated with certainty, however, that the configurations about the asymmetric N centers in $(-)_D$-*trans*-$[Co(Meen)_2Cl_2]^+$ and $(+)_D$-*trans*-$[Co(Meen)_2(NO_2)_2]^+$ are identical. As stated below, Yamatera's theory requires the $E(D_{4h})$ and $A_2(D_{4h})$ excited levels for the transition ${}^1A_1 \rightarrow {}^1T_1(O_h)$ to invert on going from the dichloro to the dinitro ion since NO_2^- is higher in the spectrochemical series than amine NH_2. However, since the dinitro species is not too different

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[10] (a) H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958); (b) C. E. Schäffer and C. K. Jørgensen, *Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd.*, **34**, No. 13 (1965); (c) C. E. Schäffer, *Theroret. Chim. Acta*, **4**, 166 (1966); (d) C. E. Schäffer, *Proc. Roy. Soc.* (London), **A297**, 96 (1967).

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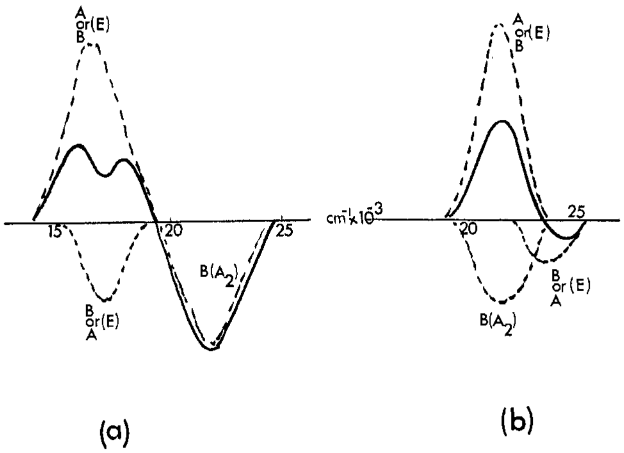

Figure 7.—Qualitative illustration of the proposed contributions of the transitions to the CD in (a) $(-)_D$-*trans,trans*-$[Co(Meen)_2Cl_2]ClO_4$ and (b) $(+)_D$-*trans,trans*-$[Co(Meen)_2(NO_2)_2]ClO_4$.

from the CoN_6 chromophore, the transitions are close together.

We interpret the CD spectrum in such a way that the positive CD band at 21,500 cm^{-1} is assigned as one of the components of $^1A_1 \rightarrow {}^1E(D_{4h})$, dominating and quenching the appearance of the $^1A_1 \rightarrow {}^1A_2(D_{4h})$ transition, and the negative CD wing at 24,500 cm^{-1} is assigned as the residue of the other component of $^1A_1 \rightarrow {}^1E(D_{4h})$. Qualitatively the analysis is shown in Figure 7. Here the $E(D_{4h})$ components have been classified as $A(C_2(Y))$ and $B(C_2(Y))$ where Y refers to the approximate twofold axis, which passes through the middle of the two chelate rings (Figure 1d) and which does not coincide with the proper molecular twofold axis (see Figure 1a for the orientation of the axes). An alternative to this explanation is that the CD bands change sign indiscriminately. Correlation of the CD of the dinitro ion with that of similar dinitro complexes is not yet possible because of a lack of reliable standards. It seems likely that the "*trans*-$[Co((-)pn)_2(NO_2)_2]^+$" ion described previously[12] is in fact *cis* ($\lambda_{max} \ll 350$ mμ) and similarly the supposed "*trans*-$[Co((-)chxn)_2(NO_2)_2]^+$" ion[15] is almost certainly *cis* (λ_{max} 322 mμ). Both complexes have visible and uv spectra and CD closely analogous to those of the authentic *cis*-$[Co((-)pn)_2(NO_2)_2]^+$ ion.[9]

Proton Exchange and Isomerization.—The rate laws for the proton exchange of *meso*-$[Co(Meen)_2(NO_2)_2]^+$ and the isomerization *meso* $\rightleftarrows$ racemate are consistent with earlier observations for similar compounds. The large rate ratio of proton exchange to isomerization, 60,000, is also consistent and indicates the configurations about the N centers are retained for a large number of exchanges.

Isomerization *meso* → racemate, as measured by the collapse of the *meso*-methyl signal at 2.23 ppm and the growth of that for the racemate at 2.34 ppm, gave a composite rate constant $(k_m + k_r) = 10.4 \pm 0.3\ M^{-1}\ sec^{-1}$ at 34.3°. However, k_r was measured independently by the racemization rate for the active isomer at $1.26 \pm 0.03\ M^{-1}\ sec^{-1}$ at 34.3° and it follows that $k_m = 9.1\ M^{-1}\ sec^{-1}$ and that the equilibrium constant $K = k_m/k_r = 7.1$ and $\Delta G_{34.3°} = 1.2$ kcal/mole.

Since the *meso* → racemate reaction was studied in D_2O and at a low ionic strength, the D → *meso* reaction was examined again under the same conditions. The racemization step was also repeated in H_2O at the same ionic strength (Table II) and as for the previous studies the rate was faster in D_2O than in H_2O. Some uncertainty arises from the empirical method of evaluating pD, but it can be said that the application of the method in a consistent manner leads to a similar isotope effect for all of the systems studied so far. The influence of ionic strength $\mu = 0.14–1.05$[3] for the rate of racemization was small (~10% decrease as μ increases when allowance is made for the change in K_{H_2O}) although the rate of proton exchange was considerably greater than ~50% at the lower ionic strength.[3]

Stability and Conformational Analysis.—The relative thermodynamic stability of the *meso* and active isomers is of some interest in relation to the prediction of a conformational analysis of the two species. Analogies have been drawn between saturated carbocyclic ring systems and some chelate rings, but apart from the pioneering work of Corey and Bailar[18] on the conformational analysis of the latter, few calculations have been reported which can be correlated with an equilibrium measurement. Corey and Bailar discussed the stabilities of the two forms of *trans*-$[Co(en)_2Cl_2]^+$ where both Co–en chelates have the same conformation kk or k′k′ and where the conformations are mirror images kk′. They calculated an energy difference of 1 kcal/mole between the two forms in favor of the kk or k′k′ form, but no experimental value has yet been obtained for this conformational equilibrium constant. The energy difference arises primarily from the H–H nonbonded interactions of the opposing NH_2 groups in the two species of *trans* complex (calculated using the potential function of Mason and Kreevoy[19]). In the *meso* k′k form these interactions are eclipsed and are therefore less stable than in the kk or k′k′ forms, where the staggered arrangement of opposing N–H groups leads to a minimum of interaction.

In the system under consideration here, the *trans,trans*-$[Co(Meen)_2(NO_2)_2]^+$ ion, the two varieties of conformations can be stabilized by the asymmetric nitrogen centers. The preference for the most equatorial arrangement of the $N–CH_3$ group (~5 kcal/mole more stable than the most axial form) in the cobalt–N-methylethylenediamine chelate has been discussed previously.[2,3] Therefore if both possible configurations of the asymmetric N center occur in the complex ion (*meso*) the conformations of the rings must also be mirror images with the opposing NH_2 groups eclipsed. Inversely the NH_2 interactions are staggered in the active ions where the chelate rings have the same conformation.

In previous publications on this type of problem[2,3,6] we have used the potential function formu-

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lated by Hill[20] which places less emphasis on the H···H interactions than that of Mason and Kreevoy.[19] Using this expression in the present circumstances for the complex configurations where all interactions are minimized we obtained practically zero energy difference between the *meso* and active forms for the nonbonded H···H interactions but calculated 1 kcal/mole in favor of the active form from all nonbonded interactions. This calculation agrees substantially with the observed free energy difference whereas that derived from Mason and Kreevoy's expression would be substantially greater. It remains to be seen which potential function gives the most reliable result for those instances where the equilibrium position can be measured.

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Proton Nuclear Magnetic Resonance Studies of Nitrilotriacetic Acid, N-Methyliminodiacetic Acid, and Iminodiacetic Acid Complexes of Cobalt(III) and Rhodium(III) in Aqueous Solutions

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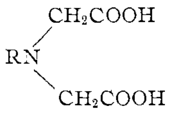
Several 1:1 and 1:2 (metal ion:ligand) complexes of Co(III) and Rh(III) with nitrilotriacetic acid (NTA), N-methyliminodiacetic acid (MIDA), and iminodiacetic acid (IDA) have been prepared and their proton nmr spectra studied in aqueous solutions (D_2O) as a function of pH. The spectra exhibit characteristic multiplet splitting patterns for the ligand acetate protons, indicating that both the metal–nitrogen and the metal–carboxylate bondings are relatively nonlabile (long-lived). The metal ions form both 1:1 and 1:2 complexes with NTA, in which the latter functions as a tetradentate and tridentate ligand, respectively. In addition, Rh(III) forms 1:2 complexes with MIDA and IDA; both ligands form *trans*-facial isomers while IDA also has a *cis* isomer. With the exception of the 1:1 Co(III)–NTA complex, this represents the first reported synthesis and isolation of the complexes. The infrared and visible absorption spectra of the complexes have been measured further to characterize their structures.

Numerous studies (mainly employing pH titrimetric, electrochemical, and spectrophotometric methods) of the metal complexes formed by nitrilotriacetic acid (NTA), N-methyliminodiacetic acid (MIDA), and iminodiacetic acid (IDA)



NTA, R = CH_2COOH
MIDA, R = CH_3
IDA, R = H

have been reported and the stability constants for many of the complexes have been determined.[1] Schwarzenbach and co-workers have established that NTA functions as a tetradentate ligand while both MIDA and IDA act as tridentate ligands.[2,3]

Recently, several proton nmr studies of both diamagnetic[4-9] and paramagnetic[10,11] metal–NTA, –MIDA, and –IDA complexes have been discussed. These studies and those reported for the closely related diamagnetic metal–ethylenediaminetetraacetic acid (EDTA) complexes[4,12-14] have indicated that with certain metal ions an AB splitting pattern is observed for the ligand acetate protons. Cooke has prepared and characterized the 1:2 Co(III)–MIDA and –IDA complexes and has studied their aqueous nmr spectra;[7] AB patterns are observed for the acetate protons in all of the complexes.

The present paper reports the preparation of several Co(III)– and Rh(III)–NTA, –MIDA, and –IDA complexes and summarizes the results of a detailed study of their proton nmr spectra in aqueous solutions (D_2O). The octahedral geometry of both metal ions is well established and both are expected to form complexes

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