whether an inner-sphere path competes with the dominant outer-sphere path for the oxidant $Co(NH_3)_5Cl^{2+}$, the strong indication from stopped-flow experiments that the outer-sphere path contributes less than 20% of the $Co(NH_3)_5N_3^{2+}$ oxidation of V^{2+}, and the knowledge that the electron-transfer-controlled path for $Co(NH_3)_5N_3^{2+}$ may be greater than the observed, substitution-limited rate. It can be seen from Table V that all three outer-sphere systems show the chloride ion system as the more reactive. For the four inner-sphere systems, the two in which a $\sigma(e_g)$ antibonding electron is presumably donated are more reactive with $Co(NH_3)_5Cl^{2+}$ and the two in which a $\pi(t_{2g})$ electron is presumably donated exhibit greater reactivity with $Co(NH_3)_5N_3^{2+}$. One striking difference between Cl^- and N_3^- is the presence of empty π orbitals; it may be that low-lying empty orbitals of π symmetry are necessary for efficient inner-sphere transfer of a t_{2g} electron. Stritar and Taube have discussed some systems in a similar fashion.[50,51]

Finally, some further comments on the activation data obtained in this study are warranted because of the publication of similar data on the Cr^{2+} reduction of various $Co(III)-Cl^-$ complexes.[52] These authors reported data that showed wide variations in $\Delta H^{\ddagger}$ as the nonbridging ligands were changed; they ascribed this behavior to a slightly more expanded version of a mechanism analogous to Scheme II (excluding the last equation), in which, it was reasoned, variations in the thermodynamics of precursor formation and in the relative magnitude of k_2 compared to k_3 would cause widely fluctuating activation parameters as the nonbridging ligands were changed. It is to be noted that the data in Table III, data on a system which presumably follows the same mechanistic scheme as does the Cr^{2+} system,[52] show little variation in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values. Further, studies on a model system[43] and on the Fe^{2+} reduction of $Co(III)-Br^-$ complexes[10] indicate little effect is to be expected from precursor stability variations in which the bridging ligand is kept constant and the nonbridging ligands are varied. In these three systems there appears to be little, if any, anomaly in the equilibrium or rate constants or activation data measured for nonbridging ligand changes in apparent contradistinction to the data on the Cr^{2+} reduction of $Co(III)-Cl^-$ complexes.

Acknowledgment.—This research was supported by the National Science Foundation (Grants GP-8318 and GP-18040) and the U. S. Public Health Service (Grant GM-14830). We are grateful for that support.

[50] J. A. Stritar and H. Taube, *Inorg. Chem.*, **8**, 2281 (1969).

[51] See also C. Norris and F. R. Nordmeyer, *ibid.*, **10**, 1235 (1971), and references therein.

[52] R. C. Patel, R. E. Ball, J. F. Endicott, and R. G. Hughes, *ibid.*, **9**, 23 (1970).

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Stereochemistry and Circular Dichroism of *trans*-Diacidobis(diamine)cobalt(III) Complexes of *N,N'*-Dimethylethylenediamine[1]

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The *trans*-dinitrobis(*N,N'*-dimethylethylenediamine)cobalt(III) and *trans*-dinitroethylenediamine(*N,N'*-dimethylethylenediamine)cobalt(III) ions have been prepared. Active forms arising from the asymmetric secondary amine nitrogens were resolved in each case. Pmr evidence indicates that only one *dl* pair was isolated for each complex in which the configuration about the asymmetric nitrogen centers is identical. The bis(*N,N'*-dimethylethylenediamine) complex gave an AA'BB' methylene multiplet. The nmr parameters are consistent with a gauche chelate ring conformation. The active dinitro complexes were converted to active *trans*-dichloro complexes with the same configurations about the nitrogen centers. The absolute configurations for both dinitro and dichloro complexes were assigned by a comparison of the sign of the CD spectra in the $A_{1g} \rightarrow T_{1g}(O_h)$ region with those for other *trans*-diacidotetramine complexes with *N*-methylamines of known configurations about the nitrogen centers. The contributions of the *N*-methyl substituent and the gauche ring to the CD intensities of the $A_{1g} \rightarrow A_{2g}(D_{4h})$ and the main component of the $A_{1g} \rightarrow E_g(D_{4h})$ bands were shown to be additive for a series of optically active *trans*-dichlorobis(diamine) complexes confirming the validity of the hexadecadal rule by S. F. Mason. A similar additivity was not found for the dinitro complexes.

Introduction

Within the past few years, Sargeson and coworkers have prepared a series of transition metal complexes containing secondary amines.[2-5] In these complexes the inertness of the coordinated nitrogen toward inversion of configuration had been demonstrated. This observation has elicited much interest in the stereochemistry of these complexes. The complexes $[Co(NH_3)_4sar]^{2+}$,[2] $[Co(NH_3)_4Meen]^{3+}$,[3] and $[Pt(en)(Meen)]^{2+}$ [5] (sar = sarcosinate anion, Meen = *N*-methylethylenediamine, en = ethylenediamine) have been resolved into mirror-image forms in which the sole source of dissymmetry is the asymmetric secondary nitrogens. Similarly, meso and racemic forms of *trans,trans*-$[Co(Meen)_2(NO_2)_2]^+$ [4] were isolated. The meso form has the two secondary nitrogens with mir-

[1] A portion of this work was presented before the Inorganic Division, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

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

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

[4] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **89**, 3428 (1967).

[5] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **91**, 5227 (1969).

ror-image configurations, whereas the racemic forms have them with the same configuration.

The origin of the optical activity in these complexes has been a point of controversy. Buckingham, Marzilli, and Sargeson[6] assigned the configuration of (−)D-*trans,trans*-$[\mathrm{Co(Meen)_2Cl_2}]^+$ by comparing the CD bands arising from $A_{1g} \rightarrow T_{1g}(O_h)$ transitions with those for (+)D-*trans*-$[\mathrm{Co(L\text{-}3,8\text{-}Me_2trien)Cl_2}]^+$, (+)D-*trans*-$[\mathrm{Co(trien)Cl_2}]^+$, (+)D-*trans*-$[\mathrm{Co((}S\mathrm{)\text{-}pn)_2Cl_2}]^+$, and (+)D-*trans*-$[\mathrm{Co((+)D\text{-}chxn)_2Cl_2}]^+$ where the absolute configuration of the complex is known (L-3,8-Me$_2$trien = L-3,8-dimethyltriethylenetetramine, trien = triethylenetetramine, (*S*)-pn = (*S*)-1,2-diaminopropane, (+)D-chxn = (+)D-1,2-*trans*-diaminocyclohexane). Because the CD curves for these complexes are essentially mirror images of that for (−)D-*trans,trans*-$[\mathrm{Co(Meen)_2Cl_2}]^+$, they suggested that the chelate ring conformation in this Meen complex must be the mirror image of that of the known compounds. From a study of the stereospecific coordination of N_1-methyl-(*S*)-propylenediamine (N_1-Mepn) in *trans,trans*-$[\mathrm{Co(}N_1\mathrm{\text{-}Mepn)_2Cl_2}]^+$, Saburi, Tsujito, and Yoshikawa[7] concluded that the configuration of (−)-*trans,trans*-$[\mathrm{Co(Meen)_2Cl_2}]^+$ had been assigned incorrectly. When N_1-Mepn is coordinated to a metal ion, the *C*-methyl group is assumed to adopt only an equatorial position. Thus, knowledge of the configuration of the asymmetric carbon enabled them to determine the ring conformation in *trans,trans*-$[\mathrm{Co(}N_1\mathrm{\text{-}Mepn)_2Cl_2}]^+$. The stereospecificity allowed them to conclude that the *N*-methyl group must also prefer an equatorial position, and, thus, its configuration was known. Because of the similarity in CD curves for *trans,trans*-$[\mathrm{Co(}N_1\mathrm{\text{-}Mepn)_2Cl_2}]^+$ and (−)D-*trans,trans*-$[\mathrm{Co(Meen)_2Cl_2}]^+$, they reasoned that the ring conformations in both complexes were the same and enantiomeric to that proposed by Buckingham, *et al.*[6] This assignment was confirmed by an X-ray crystal structure determination for (−)D-*trans,trans*-$[\mathrm{Co(Meen)_2Cl_2}]\mathrm{ClO_4 \cdot O \cdot 5H_2O}$.[8]

Explanations to rationalize these anomalies in the CD spectra have been suggested. Hawkins[9] proposed that the CD curve in the $A_{1g} \rightarrow T_{1g}(O_h)$ region resulted from an additivity of dissymmetric effects from the ring conformation and vicinal contributions from the *C*-methyl and *N*-methyl groups. The vicinal effect from the *N*-methyl group is larger and apparently opposite in sign to the other two effects. Mason[10] proposed a theoretically more pleasing and generally more applicable explanation, the hexadecadal rule, derived from symmetry treatments of Schellman.[11] A hexadecadent rule has also been applied by Martin and coworkers to tetragonal complexes of di- and tripeptides.[12] For *trans*-$\mathrm{CoN_4Cl_2}$ type complexes, it was suggested by Mason that the rotational strength of the $A_{1g} \rightarrow T_{1g}(O_h)$ transition is due to dissymmetric perturbations above and below the $\mathrm{CoN_4}$ plane. In the complexes of interest, the perturbations are due to *N*-methyl groups and the methylene and methylmethylene groups of the diamine chain. The sign and magnitude of the perturbation depend on the location of the perturbing groups. For (−)D-*trans,trans*-$[\mathrm{Co(Meen)_2Cl_2}]^+$, the *N*-methyl groups are in hexadecadents in space of opposite sign to those for the methylenes and lying further from the $\mathrm{CoN_4}$ plane. Therefore, the effects of the *N*-methyl groups should predominate in the optical activity, as has since been suggested by other workers.[7]

In this work, we wish to report some examples which test the validity of a hexadecadal rule. The complexes *trans*-$[\mathrm{Co(}NN'\mathrm{\text{-}Meen)_2X_2}]^+$ and *trans*-$[\mathrm{Co(en)(}NN'\mathrm{\text{-}Meen)X_2}]^+$ (NN'-Meen = N,N'-dimethylethylenediamine, $X^- = NO_2^-$ or Cl^-) have been synthesized. The dinitro complexes have been resolved into optically active forms and converted directly into the corresponding dichloro complexes. These complexes provide interesting possibilities for stereoisomerism because of the asymmetric nitrogen centers as shown in Figures 1 and 2. The stereochemistry of each complex has been characterized. A comparison of $A_{1g} \rightarrow A_{2g}(D_{4h})$ CD peak intensities of (+)-*trans*-$[\mathrm{Co(}NN'\mathrm{\text{-}Meen)_2Cl_2}]^+$ and (+)-*trans*-$[\mathrm{Co(en)(}NN'\mathrm{\text{-}Meen)Cl_2}]^+$ to (+)D-*trans,trans*-$\mathrm{Co(Meen)_2Cl_2}^+$ as the number or position of the *N*-methyl substituents is varied in these complexes has provided a reasonable test of the validity of a hexadecadal rule. In addition, the optically active dinitro complexes provided additional examples

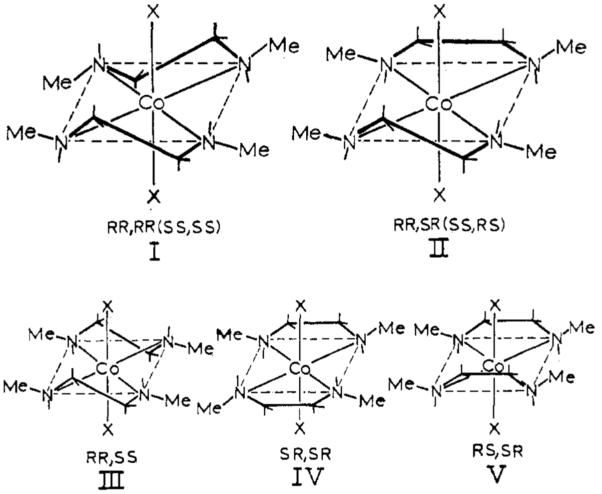

Figure 1.—Possible structures of *trans*-$[\mathrm{Co(}NN'\mathrm{\text{-}Meen)_2X_2}]^+$. I and II are dissymmetric and would exist as *dl* pairs. III–V are meso structures.

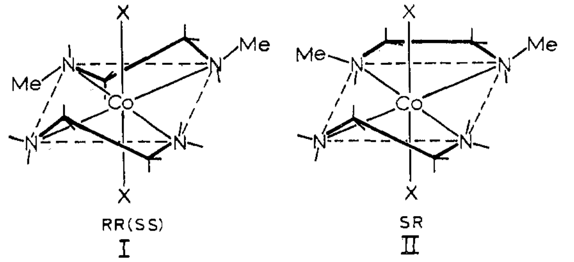

Figure 2.—Possible structures of *trans*-$[\mathrm{Co(en)(}NN'\mathrm{\text{-}Meen)X_2}]^+$. I is dissymmetric and would exist as a *dl* pair. II is a meso structure.

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[7] (a) M. Saburi, Y. Tsujito, and S. Yoshikawa, *Inorg. Nucl. Chem. Lett.*, **6**, 203 (1969); (b) M. Saburi, Y. Tsujito, and S. Yoshikawa, *Inorg. Chem.*, **9**, 1476 (1970).

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[10] S. F. Mason, *ibid.*, 856 (1969).

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with which to utilize CD spectra in predicting absolute configuration.

Experimental Section

Materials.—Silver (+)-α-bromocamphor-π-sulfonate (AgBCS)[4] and trinitroamino(ethylenediamine)cobalt(III), $Co(NH_3)(en)(NO_2)_3$,[13] was prepared using methods described in the literature. *N,N'*-Dimethylethylenediamine was purchased from Ames Laboratories, Inc., Milford, Conn., and tetraphenylarsonium chloride, from Aldrich Chemical Co.

***trans*-Dinitrobis(*N,N'*-dimethylethylenediamine)cobalt(III) Perchlorate, *trans*-[Co(*NN'*-Meen)$_2$(NO$_2$)$_2$]ClO$_4$.**—A cold solution of $CoCl_2\cdot 6H_2O$ (23.8 g, 0.1 mol, in 50 ml of H_2O) was added to a cold solution of *N,N'*-dimethylethylenediamine (17.6 g, 0.2 mol, in 8.1 ml of 12.4 *N* HCl), and $NaNO_2$ (15.9 g, 0.23 mol) was added quickly. The resulting solution was aerated in an ice bath for 30 min, followed by 5 hr at ambient temperature. This solution was evaporated slowly under an air stream at 25° to a paste and dried under vacuum. The residue was ground in methanol (200 ml) and filtered, discarding the light green solid. The filtrate was evaporated to 75 ml, filtered again, and evaporated to dryness at room temperature. The residue was dissolved in 100 ml of H_2O and an $NaClO_4$ solution (12.2 g, 0.1 mol, in 20 ml of H_2O) was added dropwise with stirring. The desired precipitate was collected, washed with ethanol and ether, and dried under vacuum (31.8 g, 0.075 mol). Recrystallization of 1 g of this solid from 50 ml of 50% ethanol at 55° gave well-developed orange crystals. *Anal.* Calcd for $[CoC_8H_{24}N_6O_4]ClO_4$: C, 22.50; H, 5.67; N, 19.67. Found: C, 22.61; H, 5.52; N, 19.85.

Resolution of *trans*-[Co(*NN'*-Meen)$_2$(NO$_2$)$_2$]ClO$_4$.—An aqueous solution of *trans*-[Co(*NN'*-Meen)$_2$(NO$_2$)$_2$]Cl, obtained from *trans*-[Co(*NN'*-Meen)$_2$(NO$_2$)]ClO$_4$ (7.34 g, 0.17 mol), by passing an aqueous solution of that salt through a Dowex 1-X8 (50–100 mesh) anion-exchange resin in the Cl^- form (40–50-fold excess) and evaporating to 100 ml, was vigorously stirred with AgBCS (7.0 g, 0.17 mol). The mixture was filtered to remove AgCl, and the filtrate was evaporated to an oil on a rotary evaporator. Ethanol (100 ml) was added and the solution was reevaporated. The residue was dissolved in 95% ethanol (200 ml) at 50°. The volume was quickly reduced to 90 ml at 35° on a rotary evaporator. The solution was allowed to cool for 5 hr at room temperature and 2 days at 6°. The solid which formed was collected, washed with ethanol and ether, and dried under vacuum (3.0 g, 4.7 mmol, $[\alpha]_{500}$ −244° for 0.1% solution). Additional solid of similar activity was obtained by cooling the filtrate to −20° for several days (1.3 g). The first fraction was dissolved in 95% ethanol (160 ml at 40°), rapidly evaporated to half-volume, and cooled for 5 hr at room temperature and then for several days at −20°. The well-developed orange crystals were collected, washed with ethanol and ether, and dried under vacuum (1.7 g, $[\alpha]_{500}$ −340° for a 0.1% solution). Additional recrystallizations gave only slight improvement in the optical purity of $(-)_{500}$-*trans*-[Co(*NN'*-Meen)$_2$(NO$_2$)$_2$]BCS ($[\alpha]_{500}$ −350° for 0.1% solution).

(−)$_D$-*trans*-[Co(*NN'*-Meen)$_2$(NO$_2$)$_2$]ClO$_4$.—$(-)_{500}$-*trans*-[Co(*NN'*-Meen)$_2$(NO$_2$)$_2$]BCS (3.3 g, 0.47 mol) was dissolved in about 500 ml of 95% ethanol. A solution of $LiClO_4$ (2.2 g in 20 ml of ethanol) was added dropwise with stirring. The resulting solid was collected, washed with ethanol and ether, and dried under vacuum (2.2 g, $[\alpha]_{500}$ −680° for 0.05% solution). *Anal.* Calcd for $[CoC_8H_{24}N_6O_4]ClO_4$: C, 22.50; H, 5.67; N, 19.70. Found: C, 22.42; H, 5.63; N, 19.86.

(+)$_D$-*trans*-Dichlorobis(*N,N'*-dimethylethylenediamine)cobalt(III) Chloride Hydrochloride Dihydrate, (+)$_D$-*trans*-[Co(*NN'*-Meen)$_2$Cl$_2$]Cl·HCl·2H$_2$O.—An aqueous solution of (−)$_D$-*trans*-[Co(*NN'*-Meen)$_2$(NO$_2$)$_2$]ClO$_4$ (0.75 g, 1.15 mmol) was mixed with tetraphenylarsonium chloride (0.6 g, 1.4 mmol) removing most of the ClO_4 as a precipitate. The solution was evaporated on a rotary evaporator to a solid. This was dissolved in HCl (17 ml of 12.4 *N*) and heated on a steam bath for 1 hr at 65–70°. Upon cooling at room temperature, large dark green crystals formed. They were collected, washed with cold 6 *N* HCl, ethanol, and ether, and dried under vacuum ($[\alpha]_D$ +890° for 0.075% solution). *Anal.* Calcd for $[CoC_8H_{24}N_2Cl_2]Cl\cdot HCl\cdot 2H_2O$: C, 23.29; H, 7.05; Cl, 34.26; N, 13.60. Found: C, 22.97; H, 7.28; Cl, 33.95; N, 13.76. Inactive *trans*-[Co(*NN'*-Meen)$_2$Cl$_2$]Cl·HCl·2H$_2$O was prepared in a manner similar to the active form.

Conversion of (+)$_D$-*trans*-[Co(*NN'*-Meen)$_2$Cl$_2$]$^+$ to (−)$_D$-*trans*-[Co(*NN'*-Meen)$_2$(NO$_2$)$_2$]$^+$.—A solution (25 ml) of (+)$_D$-*trans*-[Co(*NN'*-Meen)$_2$Cl$_2$]Cl·2H$_2$O (0.1%, 0.06 mmol) and $NaNO_2$ (1.25 g, 20 mmol) in 0.01 *N* $HClO_4$ was prepared, and the change in rotation at 500 nm was followed while the solution was maintained at room temperature. After 2 days, the rotation ceased to change and the absorption spectrum in the 400–600-nm region was indistinguishable from that for a similar solution of (−)$_D$-*trans*-[Co(*NN'*-Meen)$_2$(NO$_2$)$_2$]ClO$_4$. The rotation at 500 nm in a 0.5-cm cell had changed from +0.21 to −0.29° during that time.

***trans*-Dinitroethylenediamine(*N,N'*-dimethylethylenediamine)cobalt(III) Perchlorate, *trans*-[Co(en)(*NN'*-Meen)(NO$_2$)$_2$]ClO$_4$. Method I.**—A suspension of $[Co(NH_3)(en)(NO_2)_3]$[13] (7.5 g, 0.27 mol) in aqueous *N,N'*-dimethylethylenediamine (2.3 g, 0.26 mol, in 235 ml of H_2O) was heated on a steam bath for 40–45 min with occasional agitation. The resulting solution was evaporated to a paste under a stream of air. This was mixed thoroughly with water (300 ml) and filtered. The filtrate was added at a rate of 1.5 ml/min to a column (diameter 5 cm) containing 1 l. of strong-acid cation-exchange resin (Dowex 50W-X8, 100–200 mesh) in the NH_4^+ form. Water was added at the same rate until the liquid above the column was no longer colored. The orange layer at the top of the resin was then eluted with $NaClO_4$ (0.075 *M*) over a period of 2 weeks at a rate of 0.5 ml/min. During this time the orange layer separated into six bands. The slowest three were very minor as compared to the other three. The slowest band remained at the origin, presumably composed of 2+ and 3+ cations. The next slowest band gave electronic[14] and pmr[15] spectra identical with those of *cis*-[Co(en)$_2$(NO$_2$)$_2$]$^+$, and the band in front of it had an electronic spectrum consistent with that of *cis*-[Co(en)(*NN'*-Meen)(NO$_2$)$_2$]$^+$ although it decomposed before further analysis could be performed. The fastest of the three major bands, I, which was 1.8 cm wide, had moved to the bottom of the column (48 cm from the top). The next band, II, which was 6 cm wide and orange-brown, was not completely separated from I (yellow-brown). The slowest of the major bands, III (yellow), which was 3 cm wide, had moved 31 cm from the origin. I–III were removed from the column by means of a suction hose. II was removed in two portions: the 2 cm nearest to I (labeled IIA) and the rest (IIB). The colored material was removed from the resin of each band by elutions on small columns with $NaClO_4$ (0.5 *N*) at a rate of 4 ml/min and the eluted solutions were evaporated to solids in a rotary evaporator. Each solid was evaporated twice to dryness with added ethanol (400 ml) to remove H_2O. The dry solids were then extracted several times with ethanol to ensure complete removal of $NaClO_4$. I, IIA, IIB, and III yielded 0.7, 1.85, 4.4, and 0.9 g of solid, respectively. Thin layer chromatographic analysis of the bromide salts of I, IIA, IIB, and III along with their electronic absorption spectra showed IIB to contain the pure desired *trans*-[Co(en)(*NN'*-Meen)(NO$_2$)$_2$]$^+$ product. IIA contained a mixture of this (86%) and *trans*-[Co(*NN'*-Meen)$_2$(NO$_2$)$_2$]$_2$ClO$_4$ as did I (6%). III was essentially *trans*-[Co(en)$_2$(NO$_2$)$_2$]ClO$_4$. Recrystallization of IIB from 330 ml of 50% ethanol at 55° gave large golden-brown crystals of the desired product. *Anal.* Calcd for $[CoC_6H_{20}N_6O_4]ClO_4$: C, 18.07; H, 5.07; N, 21.07. Found: C, 18.04; H, 4.98; N, 21.20.

Method II.—$CoCl_2\cdot 6H_2O$ (2.38 g), ethylenediamine (0.6 g of 98%), *N,N'*-dimethylethylenediamine (0.88 g), $NaNO_2$ (1.62 g), and HCl (0.82 ml of 12.4 *N*) were allowed to react in a manner similar to the preparation of *trans*-[Co(*NN'*-Meen)$_2$(NO$_2$)$_2$]ClO$_4$. The product was treated on an ion-exchange column as in method I. The solid isolated from bands I, IIA, and IIB weighed 0.15, 0.32, and 1.28 g, respectively, and had compositions similar to the products obtained in method I.

Resolution of *trans*-[Co(en)(*NN'*-Meen)(NO$_2$)$_2$]ClO$_4$.—A solution of *trans*-[Co(en)(*NN'*-Meen)(NO$_2$)$_2$]Cl, obtained from the ClO_4^- salt (9.1 g, 23 mmol) as described above for the other resolutions, was mixed vigorously with AgBCS (9.15 g, 22 mmol) and filtered to remove AgCl. The filtrate was evaporated to an oil and reevaporated after 50 ml of ethanol was added. The residue was dissolved in hot ethanol (140 ml) and cooled to −20°

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[14] F. Basolo, *J. Amer. Chem. Soc.*, **72**, 4393 (1950).

[15] T. E. MacDermott, *Inorg. Nucl. Chem. Lett.*, **5**, 463 (1969), and references therein.

until significant amounts of gelatinous residue formed. The mixture was then warmed with agitation to 55° until all but a small amount of the residue had dissolved. Upon cooling for 3 hr at room temperature with occasional agitation to prevent formation of gelatinous solid, large amounts of a yellow flocculent solid formed throughout the solution. The solid was collected, washed with ethanol and ether, and dried under vacuum (5.0 g, 6.5 mmol, $[\alpha]_{500}$ −170° for a 0.1% solution). An additional fraction of similar activity was obtained upon cooling the filtrate to 6° (0.9 g). The first fraction was recrystallized from ethanol (250 ml) at 45° to give improved optical purity (2.2 g, $[\alpha]_{500}$ −210° for 0.1% solution). Additional recrystallization gave no further improvement in the optical purity of $(-)_{500}$-*trans*-[Co(en)(*NN'*-Meen)$(NO_2)_2$]BCS.

(−)D-*trans*-[Co(en)(*NN'*-Meen)$(NO_2)_2$]ClO_4.—An ethanol solution of $LiClO_4$ (1 g) was added dropwise to a stirred solution of $(-)_{500}$-*trans*-[Co(en)(*NN'*-Meen)$(NO_2)_2$]BCS (2.2 g, 2.9 mmol) in about 170 ml of 95% ethanol. The desired precipitate was collected, washed with ethanol and ether, and dried under vacuum (1.15 g, $[\alpha]_{500}$ −500° for a 0.5% solution). *Anal.* Calcd for $[CoC_6H_{20}N_6O_4]ClO_4$: C, 18.07; H, 5.07; N, 12.07. Found: C, 18.09; H, 5.00; N, 21.15.

Inactive *trans*-Dichloroethylenediamine(*N,N'*-dimethylethylenediamine)cobalt(III) Perchlorate Hemihydrate, *trans*-[Co(en)(*NN'*-Meen)Cl_2]$ClO_4\cdot 0.5H_2O$.—A solution of *trans*-[Co(en)(*NN'*-Meen)$(NO_2)_2$]ClO_4 (2 g, 5 mmol) in HCl (50 ml of 12.4 *N*) was heated on a steam bath for 30 min at 70–75°. The solution was evaporated to a residue on a rotary evaporator. The residue was recrystallized by dissolution in 60° HCl (25 ml of 12.4 *N*) and cooling to 6°. The resulting green needlelike crystals were collected, washed with cold 6 *N* $HClO_4$, ethanol, and ether, and dried under vacuum. *Anal.* Calcd for $[CoC_6H_{20}N_4Cl_2]ClO_4\cdot 0.5H_2O$: C, 18.66; H, 5.49; Cl, 28.17; N, 14.84. Found: C, 18.88; H, 5.58; Cl, 27.78; N, 14.85.

(+)D-*trans*-Dichloroethylenediamine(*N,N'*-dimethylethylenediamine)cobalt(III) Perchlorate, (+)D-*trans*-[Co(en)(*NN'*-Meen)Cl_2]ClO_4.—A solution of (−)D-*trans*-[Co(en)(*NN'*-Meen)$(NO_2)_2$]ClO_4 (0.45 g, 1.1 mmol) in HCl (10 ml of 12.4 *N*) was heated for 1.5 hr at 70°. The resulting green solution was separated on a rotary evaporator to a residue. This was dissolved in 60° HCl (10 ml of 0.6 *N*), $LiClO_4$ (0.15 g, 7 mmol) was added with stirring, and the solution was cooled to 6° overnight. The green crystals were collected, washed with ethanol and ether, and dried under vacuum (0.2 g, $[\alpha]_D$ +350° for 0.075% solution). *Anal.* Calcd for $[CoC_6H_{20}N_4Cl_2]ClO_4$: C, 19.09; H, 5.34; Cl, 28.17; N, 14.84. Found: C, 19.00; H, 5.30; Cl, 28.03; N, 15.05.

Conversion of (+)D-*trans*-[Co(en)(*NN'*-Meen)Cl_2]$^+$ to (−)D-*trans*-[Co(en)(*NN'*-Meen)$(NO_2)_2$]$^+$.—A solution (25 ml) of (+)D-*trans*-[Co(en)(*NN'*-Meen)$(NO_2)_2$]ClO_4 (0.1%, 0.06 mmol) and $NaNO_2$ (1.25 g, 20 mmol) in 0.01 *N* $HClO_4$ was prepared, and the change in rotation at 500 nm was followed. After 2 days the rotation remained constant, and the absorption spectrum in the 400–600-nm region was indistinguishable from that of a similar solution of (−)D-*trans*-[Co(en)(*NN'*-Meen)$(NO_2)_2$]ClO_4. The rotation in a 0.5-dm cell had changed from +0.19 to −0.19° during that time.

Conversion of Perchlorate Salts to Bromide and Chloride Salts.—For proton magnetic resonance measurements, all slightly soluble perchlorate salts were converted to more soluble chloride salts by thoroughly mixing aqueous suspensions of perchlorate salts with equimolar amounts of tetraphenylarsonium chloride. The solutions were filtered and evaporated to dryness. Chloride salts used in resolutions were obtained by passing the perchlorate salts through a column of a strong-base anion-exchange resin (Dowex 1-X8, 50–100 mesh) in the Cl^- form, which had sufficient resin such that the exchange capacity of the column was in 40–50-fold excess. The solutions were then evaporated on a rotary evaporator to the desired solids. Similarly, the bromide salts for thin layer chromatography were prepared using resin in the Br^- form.

Thin Layer Chromatography.—The plates used (10 × 20 or 20 × 20 cm) were coated with Cellex-N1 TLC cellulose (∼0.5 mm thick). Sample applications were made with aqueous solutions (1–2 μl) of the complex bromide salts (100–150 μg). The plates were developed, using a Brinkman development tank with a solvent system suggested for nitroamine complexes by MacDermott[16] (butanol–pyridine–water–acetic acid, 40:30:20:10).

Electronic Absorption Spectra.—Spectra were recorded at room temperature using a Cary Model 14 spectrophotometer and 0.05–0.1% solutions in 1- or 5-cm quartz cells.

Optical Rotations.—Rotations were measured at room temperature using a Beckman Model DU-2 spectrophotometer with a Keston Model D polarimetric attachment (Standard Polarimeter Co., Hackensack, N.J.) and 0.05–0.1% solutions in 5- or 1-cm quartz cells. All measurements of dinitro complexes were performed on 10^{-3} *M* $HClO_4$ solutions. Measurements of dichloro complexes were performed on methanol solutions.

Circular Dichroism Spectra.—Spectra were recorded at room temperature using a Cary Model 60 spectropolarimeter with a CD attachment; 0.067–0.1% solutions in the visible region and 0.001–0.002% solutions in the uv region in 1- and 5-cm quartz cells were used.

Proton Magnetic Resonance Spectra.—Spectra were recorded on either a Varian A-60 or HA-100 spectrometer with sodium trimethylsilylpropanesulfonate as an internal standard, using D_2O solutions or D_2O–DCl solutions, 10–20% in complex. N-Deuterated samples were obtained by allowing D_2O solutions of the complexes to exchange for several hours.

Analysis of the Pmr Spectra of *trans*-[Co(*NN'*-Meen)$_2$$(NO_2)_2$]Cl.—The methylene portion of the 60-MHz pmr spectra of the N-deuterated complex was analyzed using the LAOCN3 iterative program written by Bothner-By[17] which was modified for use by the Upjohn Co., Kalamazoo, Mich., for an IBM 360/30 computer. Calculated spectra were plotted using their EAI-3500 Dataplotter. By trial and error, an AA'BB' spectrum was calculated which approximated the experimental spectrum sufficiently to make line assignments. The experimental line assignments were then used to calculate a best-fit spectrum. Additional modification of the calculated spectrum was achieved by considering long-range coupling of the methylene protons with the N–CH_3 protons.

Analyses.—All elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., or Midwest Microlab, Indianapolis, Ind.

Results

Preparations.—The preparation of the dinitrobis(diamine) complex *trans*-[Co(*NN'*-Meen)$_2$$(NO_2)_2$]$^+$ was similar to that for (±)-*trans,trans*-[Co(Meen)$_2$$(NO_2)_2$]$^+$.[4] When Co^{2+}, *NN'*-Meen, $NaNO_2$, and HCl were allowed to react in the mole ratio of 1:2:2:1, the main impurity was the green *trans*-dichloro complex. If the relative molar quantity of $NaNO_2$ was increased to 2.3, the dichloro complex was essentially eliminated but was replaced by anionic impurities (presumably [Co$(NO_2)_4$(*NN'*-Meen)$_2$]$^-$ and [Co$(NO_2)_6$]$^{3-}$).

Two methods of preparation of the dinitro(mixed-diamine) complex *trans*-[Co(en)(*NN'*-Meen)$(NO_2)_2$]$^+$ produced comparable yields (40–50%). Similarly, each produced significant amounts of cationic side products (*e.g.*, *cis*- and *trans*-[Co(en)$_2$$(NO_2)_2$]$^+$, *trans*-[Co(*NN'*-Meen)$_2$$(NO_2)_2$]$^+$, and another cis complex, presumably *cis*-[Co(*NN'*-Meen)(en)$(NO_2)_2$]$^+$). In this respect the reaction of [Co(NH_3)(en)$(NO_2)_3$] with *NN'*-Meen is similar to that with l-pn which has been shown to lead to significant amounts of disproportionation products.[17]

Treatment of dinitro complexes with concentrated HCl produced the expected dichloro complexes. Starting with the (−)D-dinitrobis(diamine) complex, the green (+)D-dichloro complex was obtained, which, when converted back to the dinitro complex with $NaNO_2$ in dilute acid, gave 100% retention of the optical activity. The (+)D-dichloro–mixed-diamine complex, prepared from the (−)D-dinitro complex, on the other hand, led to product retaining 84% of its activity on conversion back to the nitro complex.

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[16] L. A. Kane-Maguire and T. E. MacDermott, *Inorg. Chem.*, **7**, 768 (1968).

[17] This program is described in P. F. DeTar, Ed., "Computer Programs for Chemistry," Vol. I, W. A. Benjamin, New York, N. Y., 1968, p 10.

This reduction of activity is similar to (−)-*trans,trans*-[Co(Meen)$_2$Cl$_2$]$^+$, which had a retention ratio of 90%.[6]

Spectra.—The visible and ultraviolet absorption spectra and circular dichroism curves for the optically active dinitro and dichloro complexes are given in Figures 3 and 4, respectively. Their band locations and intensities are tabulated in Table I. The low-energy absorption band near 22,000 cm^{-1} for *trans*-[Co(*NN'*-Meen)$_2$(NO$_2$)$_2$]$^+$, *trans*-[Co(en)(*NN'*-Meen)(NO$_2$)$_2$]$^+$, and *trans*-[Co(en)$_2$(NO$_2$)$_2$]$^+$ (23,100 cm^{-1}) shows a band shift to higher energy of 350–400 cm^{-1} for each *N*-methyl substituent removed. The two bands near 29,000 and 40,000 cm^{-1} were not as sensitive to such structural changes. A similar shift was observed for the bands near 22,000 cm^{-1} for the dichloro complexes (about 500 cm^{-1} shift per methyl in each case).

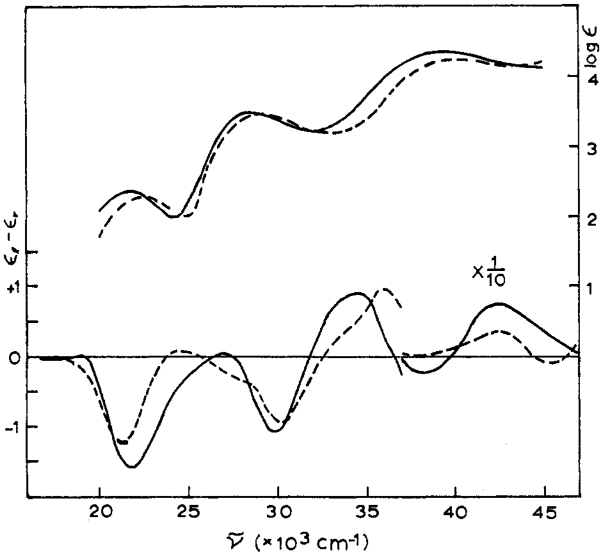

Figure 3.—Absorption and CD spectra of (−)D-*trans*-[Co(*NN'*-Meen)$_2$(NO$_2$)$_2$]$^+$ (——) and (−)D-*trans*-[Co(en)(*NN'*-Meen)(NO$_2$)$_2$]$^+$ (- - -) (in 10^{-3} *M* HClO$_4$).

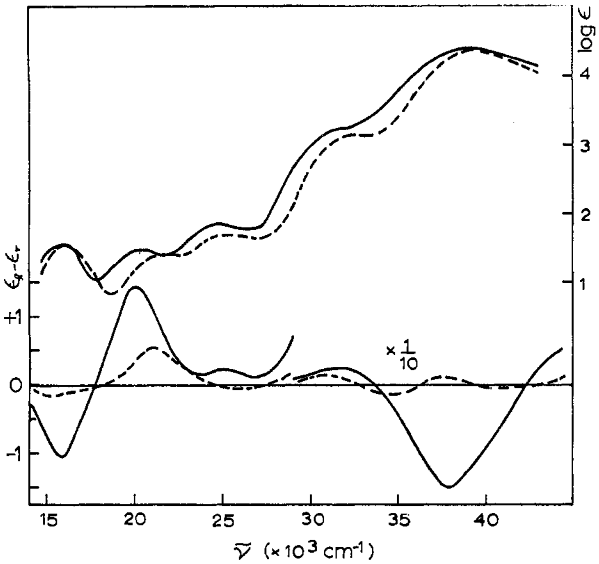

Figure 4.—Absorption and CD spectra of (+)D-*trans*-[Co(*NN'*-Meen)$_2$Cl$_2$]$^+$ (——) and (+)D-*trans*-[Co(en)(*NN'*-Meen)Cl$_2$]$^+$ (- - -) (in methanol).

TABLE I

ELECTRONIC ABSORPTION AND CIRCULAR DICHROISM DATA OF COMPLEXES[a]

Complex ion	Absorption		CD	
	ν_{max}	ϵ_{max}	ν_{max}	$\Delta\epsilon_{max}$
(−)D-*trans*-[Co(*NN'*-Meen)$_2$(NO$_2$)$_2$]$^{+\,b}$	21.6	234	18.9	+0.01
	28.6	3,080	21.9	−1.62
	39.1	21,800	27.0	+0.05
	48.5	13,400	29.8	−1.07
			34.4	+0.93
			38.2	−2.2
			42.4	+7.5
(−)D-*trans*-[Co(en)(*NN'*-Meen)(NO$_2$)$_2$]$^{+\,b}$	22.4	189	21.4	−1.23
	29.0	2,980	24.5	+0.07
	39.5	17,600	30.3	−0.92
	48.1	18,600	36.2	+0.96
			42.6	+3.9
			45.4	−0.7
(+)D-*trans*-[Co(*NN'*-Meen)$_2$Cl$_2$]$^{+\,c}$	15.6	34.1	15.8	−1.07
	20.4	29.0	20.0	+1.42
	24.6	69.8	25.2	+0.22
	31.6[d]	1,680	31.8	+2.3
	38.8	24,760	37.9	−15
(+)D-*trans*-[Co(en)(*NN'*-Meen)Cl$_2$]$^{+\,c}$	16.1	33.1	15.3	−0.17
	21.5	24.0	21.1	+0.52
	25.4	48.8	25.6	−0.05
	31.4	1,250	31.2	+1.3
	39.2	23,500	37.7	+0.8
			40.8	−0.5

[a] All energies in 10^3 cm^{-1}. [b] In 10^{-3} *M* HClO$_4$. [c] In methanol. [d] Shoulder.

The pmr spectra of N-protonated and N-deuterated *trans*-[Co(*NN'*-Meen)$_2$(NO$_2$)$_2$]$^+$ are given in Figure 5. The spectral assignments for the dinitro and dichloro complexes are tabulated in Table II. The spectra for the inactive forms were indistinguishable from

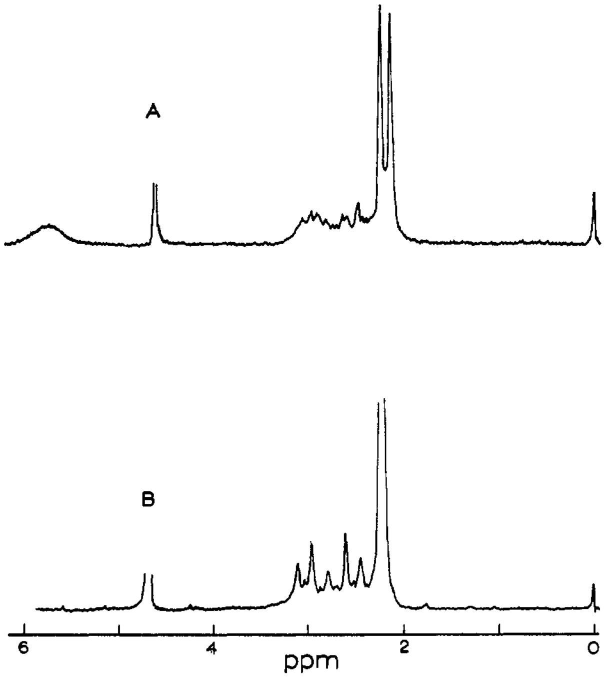

Figure 5.—Pmr spectra of *trans*-[Co(*NN'*-Meen)$_2$(NO$_2$)$_2$]: (A) in 0.01 *N* DCl; (B) in D$_2$O after several hours of solution.

TABLE II

ASSIGNMENT OF CHEMICAL SHIFTS (PPM)[a] FOR PMR SPECTRA OF COMPLEXES

Complex ion	N–CH$_3$	–CH$_2$–	=NH	–NH$_2$
trans-[Co(*NN'*-Meen)$_2$(NO$_2$)$_2$]$^{+\,b}$	2.20	2.3–3.3		5.8
trans-[Co(en)(*NN'*-Meen)(NO$_2$)$_2$]$^{+\,b}$	2.27	2.4–3.2	5.3	5.9
trans-[Co(*NN'*-Meen)$_2$Cl$_2$]$^{+\,c}$	2.43	2.5–3.4		5.9
trans-[Co(en)(*NN'*-Meen)Cl$_2$]$^{+\,c}$	2.46	2.6–3.3	5.6	5.9

[a] Sodium trimethylsilylpropanesulfonate as internal standard reference. [b] In 0.01 *N* DCl. [c] In 0.1 *N* DCl.

those of the resolved complexes. In general, the *N*-methyl protons exhibited sharp doublets in the N-protonated forms and singlets in the N-deuterated forms (N-deuterated spectra were obtained only for the dinitro complexes). The methylene resonances were always complex multiplets in which differences between protonated and deuterated spectra can be assigned to proton coupling. N-Deuterated *trans*-$[Co(NN'\text{-Meen})_2(NO_2)_2]^+$ gave a reasonably symmetrical methylene multiplet which was analyzed successfully by computer methods.

Pmr Spectral Analysis.—If the diamine chelate rings of *trans*-$[Co(NN'\text{-Meen})_2(NO_2)_2]^+$ are in a symmetrical gauche or an eclipsed conformation, there exist two pairs of equivalent protons: two axially and two equatorially located protons. These should then exhibit an AA′BB′ splitting with a coupling scheme

$$\begin{tikzcd}
A \arrow[r, leftrightarrow, "J_{AB}"] \arrow[d, leftrightarrow, "J_{AA'}"'] \arrow[dr, leftrightarrow, "J_{AB'}"] & B \arrow[d, leftrightarrow, "J_{BB'}"] \\
A' & B'
\end{tikzcd}$$

A spectrum was readily calculated resembling the methylene part of the N-deuterated spectrum of *trans*-$[Co(NN'\text{-Meen})_2(NO_2)_2]^+$ (Figure 6A) if (1) chemical shifts of the A and B protons used were estimated as the midpoints of the two pairs of major peaks, *e.g.*, 152.5 and 183.5 Hz, and (2) coupling constants used were those reasonable for a gauche chelate ring,[18] *e.g.*, 4 and 10 Hz for trans and gauche vicinal coupling constants, respectively, and −12 Hz for geminal coupling constants. An iteration on 17 lines assigned from the experimental spectrum gave a best-fit spectrum (Figure 6B) in good agreement with Figure 6A. The parameters obtained were $J_{AA'} = 10.7$ Hz, $J_{AB} = -13.1$ Hz, $J_{AB'} = 4.6$ Hz, $J_{BB'} = 4.3$ Hz, and δ_{AB} 0.500 ppm. The root-mean-square deviation from the 17 assigned lines was 0.083 Hz. The axial and equatorial protons are assigned as the A and B protons, respectively (Figure 7). This is the only assignment that is consistent with $J_{AA'}$ being large and $J_{BB'}$ being small as expected for trans and gauche vicinal coupling constants, respectively.

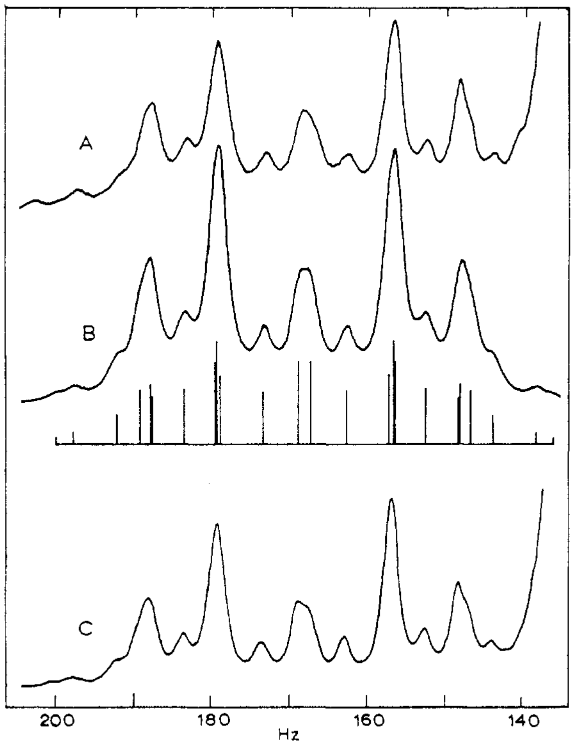

Figure 6.—Pmr spectra of N-deuterated *trans*-$[Co(NN'\text{-Meen})_2(NO_2)_2]^+$ in D_2O: (A) experimental spectrum; (B) spectrum and line assignments calculated from best-fit AA′BB′ splitting parameters; (C) spectrum calculated as in (B) with the long-range methyl–methylene coupling and the overlapping *N*-methyl resonance added.

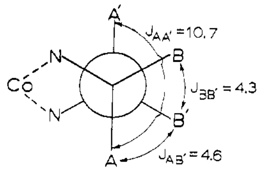

Figure 7.—Assignments of vicinal coupling constants (hertz) for *N,N′*-dimethylethylenediamine in N-deuterated *trans*-$[Co(NN'\text{-Meen})_2(NO_2)_2]^+$.

The 60-MHz results were confirmed by a 100-MHz analysis which gave δ_{AB} 0.502 ppm and coupling constants within 0.1 Hz of the 60-MHz result. The experimental spectrum in Figure 6 is somewhat dissymmetric (the two major peaks at 157 and 179 Hz have unequal heights and the smaller peak at 168 Hz is noticeably dissymmetric) which is not expected for an AA′BB′ pattern. This dissymmetry can be rationalized when long-range coupling of the methylene protons with the *N*-methyl group is considered. These parameters are estimated from the semiempirical coupling constant–dihedral angle relationship developed by Barfield[19] from data on methylcyclohexanes. Using approximate values of 35 and 75° (obtained from molecular models) for the dihedral angle between the presumed equatorial methyl group and the axial A and equatorial B protons gave values for the coupling constants of 0.5 and 0.1 Hz, respectively. The spectrum was recalculated (Figure 6C) using these coupling constants adjusting the half-bandwidth from 2.7 to 2.0 Hz to counteract line broadening caused by this additional coupling and incorporating the *N*-methyl absorption band. The dissymmetry in Figure 6C closely resembles the experimental spectrum (Figure 6A) indicating that the pmr spectrum in the methylene region can indeed be interpreted as an AA′BB′ spectrum with stereochemistry shown in Figure 7 influenced by long-range *N*-methyl coupling as expected for two equivalent gauche chelate rings with their *N*-methyl groups oriented in an equatorial position.

Discussion

Structural Assignments.—It is generally acknowledged that the visible and uv spectra of cobalt(III)–diacidobis(diamine) complexes are characteristic of their geometry.[14] Dinitro complexes with either trans or cis arrangements of the nitro groups are brown. However the trans complexes have the middle absorption

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[18] (a) S. Yano, H. Ito, Y. Koike, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, **42**, 3184 (1969); (b) J. K. Beattie and H. Elsbernd, *J. Amer. Chem. Soc.*, **92**, 1946 (1970).

[19] M. Barfield, *J. Chem. Phys.*, **41**, 2825 (1964).

band maximum occurring near 28,600 cm^{-1}, while for the cis forms, it occurs at about 30,300 cm^{-1}. Similarly, dichloro complexes with trans geometry are green, while the cis complexes are violet. The dinitrobis(diamine) and -(mixed-diamine) complexes described here have absorption bands at 28,600 and 29,000 cm^{-1}, respectively, and can be assigned trans geometries. Likewise, both green dichloro complexes have visible and uv spectra similar to known trans bis-diamine complexes with *N*-methyldiamines.[6,7]

The order of elution of the complexes on ion-exchange columns and pmr results provide additional support for these assignments. It has been shown that the elution order on ion-exchange resins can be used as criteria for the identification of geometric isomers of octahedral complexes.[20] In general, trans isomers of diacidotetramine complexes elute faster than cis isomers. For example, *trans*-$[\mathrm{Co(en)_2(NO_2)_2}]^+$ elutes considerably faster on a strong-acid cation-exchange resin than does the cis isomer. Both the bis- and mixed-diamine dinitro complexes eluted at slightly faster rates than did *trans*-$[\mathrm{Co(en)_2(NO_2)_2}]^+$, suggesting that they also have trans geometry. In addition several bands identified as cis isomers eluted at a slower rate. Finally, the pmr spectrum for each of the dinitro and dichloro complexes prepared shows only one methyl signal. In each case only the trans geometry can give rise to structures with all *N*-methyl groups in chemically equivalent environments.

The inert asymmetric secondary nitrogen centers of the trans bis-diamine complex allows for the existence of seven possible stereoisomers as shown in Figure 1. (The conformations of the diamine chelate rings presented in Figures 1 and 2 are those resulting from equatorial placement of *N*-methyl substituents and are not necessarily the most stable thermodynamically.) The frequency of the methyl pmr resonance and the splitting pattern of the methylene resonance should both be reasonably sensitive to the structural differences of these possibilities. The optically active form of the dinitrobis(diamine) complex gave a pmr spectrum indistinguishable from that of the isolated inactive form. This would suggest that the inactive material is composed of only one enantiomeric pair and that the active form is one of the enantiomers. If the meso forms and the other possible enantiomeric pair were present, they were there in such small amounts as to be undetected by pmr. Structure I has all four nitrogens with the same configuration. Assuming that the methyl groups take equatorial positions,[21,22] all four methyls would be equivalent and a single methyl resonance would be observed. On this basis the bis-diamine complex can be assigned structure I. The enantiomeric pair with structure II has three asymmetric secondary nitrogens with the same configuration and one with the mirror-image configuration, resulting in four nonequivalent methyl groups which would give a complicated methyl resonance. Buckingham and coworkers found that the *N*-methyl resonance on similar complexes was sensitive to slight changes in chemical environment.[4] In *trans*,-*trans*-$[\mathrm{Co(Meen)_2(NO_2)_2}]^+$, resonances of 2.34 and 2.23 ppm were found for the meso and racemic forms of the compound due to differences in interaction between the equatorial *N*-methyl group and the neighboring amine proton as discussed by Dabrowiak and Cooke[23] in terms of steric compression arguments. In structure II similar differences would be expected when comparing interactions between two *R* amines on different ligands (which are staggered and would have interactions comparable to those of the *N*-methyl groups in I) and those between an *S* and *R* amine (which are eclipsed). Some of this interaction between an *S* and *R* amine can be relieved by displacing the *N*-methyl group from an equatorial orientation. However, this also should influence the chemical shift. In these compounds we found differences between axial and equatorial protons on the chelate ring of 0.500 ppm comparable to differences found by others in similar compounds.[18] Woldbye[24] found that the pmr spectrum of tris(*meso*-2,3-diaminobutane)cobalt(III) showed two doublets at 1.73 and 1.85 ppm assigned to the axial and equatorial methyl groups.

Structure I should also have two types of methylene protons: four equivalent axial and four equivalent equatorial protons. Structure II should have eight nonequivalent methylene protons. If structure I has been assigned correctly to the bis-diamine complex, the methylene resonance of the *N*-deuterated complex (Figure 6A) should be an AA′BB′ multiplet of up to 24 lines, with coupling constants expected for a gauche chelate ring conformation. Structure II, on the other hand, should give rise to a much more complex multiplet. The simplest spectrum expected for structure II would be two overlapping nonequivalent AA′BB′ patterns, one from a gauche chelate ring and the other from either an eclipsed chelate ring shown in Figure 1 or another gauche conformation. The results of the computer analysis performed on the methylene resonances are consistent with only one AA′BB′ splitting pattern. The methylene coupling constants obtained are those expected for a gauche conformation (Figure 7). Furthermore, $J_{\mathrm{AB'}}$ and $J_{\mathrm{BB'}}$, the two gauche vicinal coupling constants, are nearly equal, consistent with an undistorted gauche conformation. The values of the long-range methyl coupling constants for the axial (0.5 Hz) and equatorial protons (0.1 Hz) are consistent with the methyl being equatorial to the chelate ring.[19] The pmr evidence, then, strongly supports the assignment of structure I to the dinitrobis(diamine) complex isolated.

There are three possible stereoisomers for the *trans*-diacido(mixed-diamine) complexes (Figure 2): one meso form and one racemic pair. As was true for the bis-diamine case, the pmr spectrum of the active dinitro(mixed-diamine) complex was indistinguishable from that for the inactive material. For the same reasons discussed above, it appears that only one racemic pair was isolated in any detectable amount, which can be assigned structure I.

Although the methylene resonance of this complex is

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(20) L. F. Druding, *Coord. Chem. Rev.*, **3**, 409 (1968).

(21) Buckingham, *et al.*,[3,4] determined the equatorial methyl group in complexes of Meen to be more stable than the axial methyl group by ~5 kcal mol^{-1}, using conformational analysis considerations. On similar grounds, Gollogly and Hawkins[22] found the difference to be much smaller (1 kcal mol^{-1}). However, Yoshikawa, *et al.*,[7] concluded on the basis of the stereospecific coordination of N_1-Mepn and N_2-Mepn that the difference should be considerably more than this.

(22) J. R. Gollogly and C. J. Hawkins, *ibid.*, **8**, 1168 (1969).

(23) J. C. Dabrowiak and D. W. Cooke, *J. Amer. Chem. Soc.*, **92**, 1097 (1970).

(24) F. Woldbye, "Studier over Optisk Aktivitet," Polyteknisk Forlag, Copenhagen, 1969.

too complex to be analyzed (two nonequivalent overlapping AA′BB′ splitting patterns are expected with 48 possible lines for the N-deuterated complex), the similarity of the methyl resonances for the two dinitro complexes suggests that in both complexes, the methyl groups are in similar positions relative to the nitro groups. The *NN*′-Meen ring conformation in both cases should also be similar. The en ring, on the other hand, should be less restricted and interconvertible from one gauche ring conformation to the other.[25] However, the λλ or δδ[26] ring conformation for the *NN*′-Meen–en pair is presumably thermodynamically more stable than λδ or δλ. The relative stability in this case would be expected to be comparable to that between the *meso*- and *dl-trans,trans*-$[Co(Meen)_2(NO_2)_2]^+$ (1.2 kcal mol^{-1} [4]). The meso form has δλ and the *dl* form has δδ or λλ ring conformations. The principal interactions to compare are those between the *N*-methyl group on one ligand molecule and the adjacent amine proton on the other ligand. In the trans,trans Meen complexes two such interactions exist, one for each *N*-methyl group. In the meso form the interactions are more severe than in the *dl* form as evidenced by the fact that only 4% of meso product was obtained[4] and by the shift in the pmr signal explained by steric compression.[23] For the mixed *NN*′-Meen, although both *N*-methyl groups are on the same ligand two *N*-methyl–amine interactions exist and an analogous situation to the bis-Meen complexes would be expected to exist between conformers with both interactions more severe in the δλ conformation than in the λλ case. Consequently the predominant conformation is the one determined by the *NN*′-Meen conformation as shown for structure I.

The structures of the *trans*-dichloro derivatives can be reasonably assigned as well. Both dichloro complexes must have the same configurations about the asymmetric nitrogen centers as the dinitro complexes because they are converted back to the dinitro complexes from which they were prepared with almost complete retention of activity. The single sharp methyl doublet observed for each dichloro complex supports this assignment.

From the above, it can be concluded that all of the complexes were obtained in only one racemic form, described by structure I in Figures 1 and 2, in which all of the coordinated secondary amine nitrogens have the same configuration, *e.g.*, either all *R* or all *S*.[27] The diamine conformations are determined by the configuration of the asymmetric nitrogen atom. The en conformation is an equilibrium mixture of δ and λ *gauche* rings, the predominant one having the same chirality as the coordinated *NN*′-Meen ring.

The existence of only one racemic form for each complex is reasonable in light of approximate conformational stability considerations. The meso isomer of *trans,trans*-$[Co(Meen)_2(NO_2)_2]^+$ was formed in only 4% yield (compared to the racemic compound) under preparative conditions similar to those used in the present study.[4] Conformational analysis studies of models of these two forms are consistent with these results and show that the difference in stability is 0–1 kcal, depending on the number of interactions considered.[4] Conformational energy differences between the possible forms of the dinitro complexes under study here appear to be much larger to a first approximation. These differences arise because of significant energy differences among (1) axial and equatorial placement of the methyl substituent (equatorial placement is more stable by much more than 1 kcal mol^{-1}),[21] (2) eclipsed and gauche chelate ring conformations (gauche conformation of an en ring is more stable by about 5 kcal mol^{-1}),[28] and (3) eclipsed and staggered placement of cis methyl groups on different diamines (staggered placement is more stable by more than 10 kcal mol^{-1} [29]). The importance of cis methyl–methyl interactions is illustrated by the fact that no trans,cis forms of $[Co(Meen)_2(NO_2)_2]^+$ were reported.[6]

In the structures assigned to the dinitro complexes (structure I, Figures 1 and 2), all of these interactions are minimized. The other possible racemic bis-diamine structure, structure II (Figure 1), requires that one chelate ring take an eclipsed conformation and two cis methyl groups be eclipsed. A conformation for II more closely approximating a minimum energy conformation would be to make the eclipsed ring conformation gauche. However, this conformation would require an axial methyl group and the structure should be less stable than I by more than 1 kcal mol^{-1}. The meso forms (III–V) should all be much less stable than I because of at least one of considerations (1)–(3) above. For the dinitro(mixed-diamine) complex, II is less stable than I by about 5 kcal mol^{-1} because of an eclipsed chelate ring conformation. Making the eclipsed *NN*′-Meen ring gauche would still make II much less stable than I because of an axial methyl group. From these considerations, it is evident that the other forms of the dinitro complexes should not be obtained in isolable amounts under reaction conditions in which thermodynamic stability is important.

Circular Dichroism and Structure.—It has been shown recently for *trans*-dichlorotetraminecobalt(III) complexes of *N*-methyl and *C*-methyl ethylenediamines[7,9] and triethylenetetramines[30] that the sign of the CD band near 22,000 cm^{-1} ($A_{1g} \rightarrow A_{2g}(D_{4h})$ CD band) can be related to the configuration of the asymmetric nitrogen centers. This apparently applies whether the methyl substituents are on adjacent or opposite nitrogens. For example, *trans*-[Co(L,L-1,3,8,10-Me_4trien)$Cl_2]^+$ [30] (Me_4trien = tetramethyltriethylenetetramine) with cis *N*-methyl groups and *trans,trans*-[Co(N_1-Mepn)$_2Cl_2]^+$ [7] with trans *N*-methyl groups are known to have *R* configurations around the nitrogens. Both have negative $A_{1g} \rightarrow A_{2g}(D_{4h})$ CD bands as well. On this basis, (−)D-*trans*-[Co(*NN*′-Meen)$_2Cl_2]^+$ and (−)D-*trans*-[Co(en)(*NN*′-Meen)$Cl_2]^+$ (enantiomers of the complexes isolated here) can be assigned *R* configurations around the nitrogen because they have negative CD bands in this region. From steric considera-

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[25] J. R. Gollogly, C. J. Hawkins, and J. K. Beattie, *Inorg. Chem.*, **10**, 318 (1971).

[26] The nomenclature of a diamine chelate ring is based on the proposal in *Inorg. Chem.*, **9**, 1 (1970).

[27] R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966).

[28] Gollogly, Hawkins, and Beattie[25] have shown recently by conformational analysis that for an isolated ethylenediamine ring, gauche conformations ($\omega \approx 60°$) are more stable than eclipsed conformations ($\omega \approx 0°$) by 4–5 kcal mol^{-1}.

[29] Crude calculations from molecular models considering only H–H and C–H interaction between methyls estimated from Hill's or Bartell's van der Waals energy curves[21] indicate that eclipsed methyl groups are less stable than staggered by considerably more than 10 kcal mol^{-1}.

[30] M. Goto, A. Okubo, T. Sawai, and S. Yoshikawa, *Inorg. Chem.*, **9**, 1488 (1970).

tions discussed earlier, the *N*-methyl group has the least amount of interaction when it is in an equatorial orientation with respect to the ring. Placing the *N*-methyl groups in equatorial positions restricts the *NN′*-Meen ring to the δ^{26} conformation. The ethylenediamine ring in the more stable conformation would also be δ.

The dinitro complexes can be assigned the same configurations as the corresponding chloro complexes. Thus, (+)D-*trans*[Co(*NN′*-Meen)$_2$(NO$_2$)$_2$]$^+$ and (+)D-*trans*-[Co(en)(*NN′*-Meen)(NO$_2$)$_2$]$^+$, which convert to the (−)D-dichloro complexes, are assigned *R* nitrogen configurations and δ ring conformations. Assignments for the dinitro complexes can also be determined from a comparison of their major CD bands near 22,000 cm^{-1}. The dinitro compounds *trans,trans*-[Co(N_1-Mepn)$_2$(NO$_2$)$_2$]$^+$,[7] *trans,trans*-[Co(N_2-Mepn)$_2$(NO$_2$)$_2$]$^+$,[7] (+)D-*trans,trans*-[Co(Meen)$_2$(NO$_2$)$_2$]$^+$,[8] and *trans*-[Co(*NN′*-Me$_2$pn)$_2$(NO$_2$)$_2$]$^+$ [7] (*NN′*-Me$_2$pn = *N,N′*-dimethyl-(*S*)-1,2-diaminopropane) with known *R* configurations around the nitrogen centers have positive CD bands near 22,000 cm^{-1} in contrast to the negative bands for the dichloro compounds. (+)D-*trans*-[Co(*NN′*-Meen)(NO$_2$)$_2$]$^+$ and (+)D-*trans*-[Co(en)(*NN′*-Meen)(NO$_2$)$_2$]$^+$, which were assigned *R* nitrogen configurations on the basis of the dichloro assignments, have positive CD bands near 22,000 cm^{-1}. Thus, the two methods of assignment are consistent.

The circular dichroism spectra of the dichloro complexes can be interpreted in a more detailed fashion with the use of the hexadecadal rule of Mason.[10] The activity for these complexes in the $A_{1g} \rightarrow T_{1g}(O_h)$ region is proposed to arise from additive dissymmetric perturbing effects from amine substituents situated out of the tetragonal plane which lower the tetragonal symmetry. Accordingly, the regions of space above and below this plane defined by the nitrogens can be divided into octants in a nodal manner. The sign of an octant depicts the contribution to an $A_{1g} \rightarrow T_{2g}(O_h)$ CD band of a perturbing substituent located in that octant. This is shown in Figure 8 for (−)D-*trans*-[Co(*NN′*-Meen)$_2$Cl$_2$]$^+$, (−)D-*trans*-[Co(en)(*NN′*-Meen)Cl$_2$]$^+$, and (−)D-*trans,trans*-[Co(Meen)$_2$Cl$_2$]$^+$. The signs indicate the contributions to the $A_{1g} \rightarrow A_{2g}(D_{4h})$ CD band of substituents in the +*Z* direction. Those in the −*Z* direction are of opposite sign. Solid circles represent carbons in +*Z* space, and open circles represent carbons in −*Z* space. It can be seen that the CD intensity for (−)D-*trans*-[Co(*NN′*-Meen)$_2$Cl$_2$]$^+$ should arise from four negative N–CH$_3$ contributions and four positive CH$_2$ contributions (*i.e.*, two rings in the δ configuration). For the other two complexes, it should arise from two negative N–CH$_3$ contributions and four positive CH$_2$ contributions.

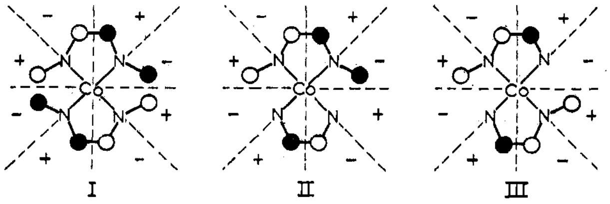

Figure 8.—The regional sign arrangement above the CoN$_4$ plane of contributions by diamine moieties to the $A_{1g} \rightarrow A_{2g}(D_{4h})$ CD bands in (I) (−)-*trans*-[Co(*NN′*-Meen)$_2$Cl$_2$]$^+$, (II) (−)D-*trans*-[Co(en)(*NN′*-Meen)Cl$_2$]$^+$, and (III) (−)D-*trans,trans*-[Co-(Meen)$_2$Cl$_2$]$^+$. Carbons above the CoN$_4$ plane (+*Z*) are represented as solid circles and below by open circles.

A reasonable approach to determine the magnitude of CH$_2$ and N–CH$_3$ contributions to the $A_{1g} \rightarrow A_{2g}(D_{4h})$ CD band is as follows. The band intensity of the $A_{1g} \rightarrow A_{2g}(D_{4h})$ CD band of *trans*-[Co((*S*)-pn)$_2$Cl$_2$]$^+$ is +0.11.[31] Contributions to this intensity come from the two CH$_2$ groups and two CHCH$_3$ groups in the two rings. Comparison of this band intensity with that of *trans*-[Co((*R*)-chxn)Cl$_2$]$^+$ (+0.07)[32] where the ring is retained but additional ring substitution is added suggests that the principal contribution is from the δ rings and that the methyl group has only a minor contribution as suggested by Hawkins.[9] The small vicinal effect for (*S*)-pn in complexes of cobalt(III) with ethylenediaminediacetic acid type ligands (−0.01 to −0.03)[33,34] and the small change in the $A_{1g} \rightarrow A_{2g}(D_{4h})$ CD band intensity for *trans*-[Rh((*R*)-diamine)$_2$Cl$_2$]$^+$ complexes of pn (+0.12) and 2,3-butanediamine (+0.11)[35] support this. Because the band intensities change little, in an apparently random manner as the number and types of alkyl substituents are varied, it is assumed for our calculations that to a first approximation, the value +0.11 is the contribution due to four CH$_2$ groups in two δ rings. The contribution of four N–CH$_3$ groups can be determined by subtracting this δ ring contribution (+0.11) from the CD band intensity for (−)D-*trans*-[Co(*NN′*-Meen)$_2$Cl$_2$]$^+$ (−1.42), to give −1.53 or −0.38 for each *N*-methyl group. The CD band for this complex is probably a reasonable choice to be used for determining a representative N–CH$_3$ contribution. From pmr results of the dinitro derivative, it would be expected that the dichloro complex has gauche diamine rings and equatorial methyl groups which are reasonably distortion free. Also, the band intensity for this complex results more from the N–CH$_3$ complex than for the other complexes, and using it should introduce less relative error from the assumed CH$_2$ contribution.

With −0.38 and +0.11 as the contributions of an *R* N–CH$_3$ group and four CH$_2$ groups from two δ diamine rings, respectively, the CD intensities can be calculated for the other two complexes in Figure 8. Also, considering the CH$_2$ group to be equivalent to an equatorial CHCH$_3$, the intensities for the bis-N_1-Mepn and -N_2-Mepn complexes can be calculated. The results are shown in Table III for complexes with *R* nitrogen configurations and δ ring conformations.

The agreement with calculated values for the mixed-diamine and bis-Meen complexes is reasonably close. These complexes had been converted back to the dinitro complexes with 84 and 90% optical purity, respectively. These racemizations may have occurred during the preparation of the dichloro from the dinitro complexes, which is carried out in strong acid, but more likely occurred in the conversion back to the dinitro compounds, carried out in more dilute acid where a greater possibility for racemization would exist. In any case, the results confirm that the hexadecadal rule has predicted correctly that the cis methyl contributions in the mixed-

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[31] R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 202 (1965).

[32] C. J. Hawkins, E. Larsen, and I. Olsen, *Acta Chem. Scand.*, **19**, 1915 (1965).

[33] J. I. Legg, D. W. Cooke, and B. E. Douglas, *Inorg. Chem.*, **6**, 7004 (1967).

[34] L. N. Schoenberg, D. W. Cooke, and C. F. Liu, *ibid.*, **7**, 2386 (1968).

[35] S. K. Hall and B. E. Douglas, *ibid.*, **7**, 333 (1968).

TABLE III

CALCULATED CD INTENSITIES IN THE $A_{1g} \rightarrow T_{1g}(O_h)$ REGION FOR THE DICHLORO COMPLEXES

		CD max			
		$A_{1g} \rightarrow A_{2g}$		$A_{1g} \rightarrow Eg$	
Complex ion	Expected contributions	Calcd	Obsd	Calcd	Obsd
(−)D-*trans,trans*-[Co(Meen)$_2$Cl$_2$]$^+$	2 N–CH$_3$, 4 CH$_2$	−0.65	−0.62	+0.18	+0.22
(−)D-*trans*-[Co(en)(*NN'*-Meen)Cl$_2$]$^+$	2 N–CH$_3$, 4 CH$_2$	−0.65	−0.52	+0.18	+0.17
trans,trans-[Co(N_1-Mepn)$_2$Cl$_2$]$^+$	2 N–CH$_3$, 4 CH$_2$^{b}	−0.65	−0.77	+0.18	+0.20
trans,trans-[Co(N_2-Mepn)$_2$Cl$_2$]$^+$	2 N–CH$_3$, 4 CH$_2$^{b}	−0.65	−0.51	+0.18	+0.05
(−)D-*trans*-[Co(*NN'*-Meen)$_2$Cl$_2$]$^+$	4 N–CH$_3$, 4 CH$_2$	−1.42^a	−1.42	+1.07^a	+1.07
trans-[Co((*S*)-pn)$_2$Cl$_2$]$^+$	4 CH$_2$^{b}	+0.11^a	+0.11	−0.71^a	−0.71

[a] These values were used to calculate the other values. [b] Assuming that the contribution for $CHCH_3$ is the same as for CH_2.

diamine complex are comparable to the trans methyl contributions of the bis-Meen complex. Furthermore, the four N–CH$_3$ groups in the bis-*NN'*-Meen complex contribute twice as much as two *N*-methyl groups in the other two complexes as predicted.

The predicted intensity for the N_1-Mepn complex is −0.12 smaller than experimentally observed. Examination of molecular models suggests that interactions between the N–CH$_3$ and C–CH$_3$ are important here. Such interactions could result in a small distortion of the ligand conformation in which both methyl groups are less equatorial. The change in the CD intensity from the C–CH$_3$ would probably be small. The change in the much larger N–CH$_3$ contribution could be more significant. This possible additional contribution from adjacent C–CH$_3$ and N–CH$_3$ interactions is consistent with the observation that the intensity of *trans*-[Co(*NN'*-Mepn)Cl$_2$]$^+$ (−1.59)[36] is 0.17 smaller than that of the bis-*NN'*-Meen complex. In the N_2-Mepn complex the absence of interaction between the N–CH$_3$ and C–CH$_3$ complexes apparently allows both methyl groups to assume an even more equatorial orientation (placing the groups in less negative CD regions) and a lower methyl contribution as is observed. A similar case exists for the mixed *NN'*-Meen complex where both methyls are on the same ligand. Finally, the N–CH$_3$ contribution found here is in approximate agreement with that obtained from CD data for complexes of *N*-methyltriethylenetetramines.[30]

The $A_{1g} \rightarrow Eg(D_{4h})$ CD bands for the dichloro complexes should, also, lend themselves to interpretation by the hexadecadal rule.[10] However, this region of the spectrum is more complicated. It has been proposed for the complexes of Meen,[6] N_1-Mepn,[7] and N_2-Mepn[7] that the double degenerate $A_{1g} \rightarrow Eg(D_{4h})$ transition splits into two components in the C_2 symmetry of N-substituted amines: A → A and A → B. The CD spectrum which results from the overlap of these two CD bands of opposite sign would be expected to be unreliable for analysis by the hexadecadal rule. A treatment of the $A_{1g} \rightarrow Eg(D_{4h})$ region similar to the $A_{1g} \rightarrow A_{2g}(D_{4h})$ region follows. The CD band intensity for *trans*-[Co((*S*)-pn)$_2$Cl$_2$]$^+$ (−0.71)[31] in this region is assumed to be the contribution of two rings on the same grounds as discussed above for the $A_{1g} \rightarrow A_{2g}(D_{4h})$ CD band. Experimental evidence confirms this assumption.[32,35] Then, by subtracting this intensity from that for (−)D-*trans*-[Co(*NN'*-Meen)$_2$Cl$_2$]$^+$ (+1.07), the contribution of one N–CH$_3$ would be +0.44. Using these values, the expected activity for the $A_{1g} \rightarrow Eg(D_{4h})$ bands of other complexes can be calculated. These are tabulated in Table III with the $A_{1g} \rightarrow A_{2g}(D_{4h})$ results. In cases where there are two maxima in the $A_{1g} \rightarrow Eg(D_{4h})$ region, the dominant low-energy component is the one treated. As can be seen, the agreement between experimental and calculated values is surprisingly good for all but the N_2-Mepn complex. It appears that the main difference between the $A_{1g} \rightarrow A_{2g}(D_{4h})$ and $A_{1g} \rightarrow Eg(D_{4h})$ regions, apart from the overlapping component bands, is the ring contributions (estimated at −0.11 and 0.71, respectively). The N–CH$_3$ contributions are almost the same.

For the dinitro complexes, an overlap is expected for all three C_2 component $A_{1g} \rightarrow T_{2g}(O_h)$ CD bands[6,7] which should make a rigorous treatment of their activity, using the hexadecadal rule, impossible. In addition, Mason[10] has pointed out that the rule probably will not hold if cylindrical symmetry about the metal–acid group bond direction does not exist, as in the case of the nitro complexes. The sign of the octants cannot be assigned without knowing the positions of the nitro oxygens, and these positions may vary with different complexes.

With this in mind, the major $A_{1g} \rightarrow T_{1g}(O_h)$ CD band for the dinitro derivatives can be examined. Since there is no reliable CD spectrum of *trans*-[Co(pn)$_2$(NO$_2$)$_2$]$^+$ available,[6,7] it will not be considered. (+)D-*trans*-[Co(en)(*NN'*-Meen)(NO$_2$)$_2$]$^+$ and (+)D-*trans,trans*-[Co(Meen)$_2$(NO$_2$)$_2$]$^+$ should have CD band maxima of equal intensities for the same reasons as mentioned for the dichloro complexes. Yet, they are grossly different (1.23 *vs.* 0.7[4]). Because the intensities of the major CD bands of *trans,trans*-[Co(N_1-Mepn)$_2$(NO$_2$)$_2$]$^+$ and *trans,trans*-[Co(N_2-Mepn)$_2$(NO$_2$)$_2$]$^+$ (0.80 and 0.92[7]) are similar to that for (+)D-*trans,trans*-[Co(Meen)$_2$(NO$_2$)$_2$]$^+$, one would conclude that the C–CH$_3$ substituent contributes little to the induced activity. (+)D-*trans*-[Co(*NN'*-Meen)$_2$(NO$_2$)$_2$]$^+$ and *trans*-[Co(*NN'*-Me$_2$pn)(NO$_2$)$_2$]$^+$, which differ by only two C–CH$_3$ substituents, should have similar CD intensities from application of the hexadecadal rule. Again, the CD intensities are grossly different (1.6 *vs.* 2.5[7]).

CD results can be summarized as follows. The hexadecadal rule cannot be used to predict the activity, with any great precision, of the dinitro complexes. However, considering all examples available to date, the $A_{1g} \rightarrow A_{2g}(D_{4h})$ CD bands of dichlorobis(diamine) complexes (and to a lesser extent the $A_{1g} \rightarrow Eg(D_{4h})$ CD bands) are interpreted consistently using the principles of the hexadecadal rule.

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(36) Yoshikawa, *et al.*,[7] attempted unsuccessfully to prepare this complex. It has been prepared and characterized recently in our laboratory and will be reported, shortly.