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Structural Assignments and Circular Dichroism of Cobalt(III) Complexes Coordinated with N-Methyl-(*S*)-propylenediamine Isomers

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Two geometrical isomers of N-methyl-(*S*)-propylenediamine were synthesized and cobalt(III) complexes of the monodiamine and the *trans*-bisdiamine types were prepared. It was indicated from pmr and circular dichroism (CD) measurements that the N-methyl group adopts preferentially the equatorial position with respect to the five-membered diamine chelate rings for both of the diamines. The *trans,trans* configuration was assigned for the dinitro- and the dichlorobisdiamine complexes of N-methylated (*S*)-propylenediamines. A significant influence of the asymmetric secondary nitrogen atom on the CD spectra was recognized for the several complexes prepared in this study. Tentative assignments of the chelate ring conformation of N-methylethylenediamine in its optically resolved complexes are also discussed.

The absolute configurations of optically active coordination compounds are occasionally presumed by the use of the "ligand stereospecificity" induced by optically active ligands.[1] The study of complexes of active propylenediaminetetraacetate (PDTA), for example, clarified the absolute configuration of the optically active isomer of the Co(EDTA)$^-$ ion (EDTA = ethylenediaminetetraacetate).[2,3] A probable assignment of the absolute configuration of the (+)D-*trans*-Co(trien)Cl_2^+ ion (trien = triethylenetetramine) was made on the basis of the resemblance between the circular dichroism (CD) curve of this complex and that of (+)D-*trans*-Co((*SS*)-3,8-dimetrien)Cl_2^+ ion ((*SS*)-3,8-dimetrien = (*SS*)-3,8-dimethyltriethylenetetramine).[4] A perfect ligand stereospecificity was suggested for the PDTA[2] and (*SS*)-3,8-dimetrien complexes.[5,6] The present study was carried out with a view to elucidating the absolute configuration of the optically active cobalt(III) complexes containing N-methylethylenediamine (N-Meen), utilizing the ligand stereospecificity of N-methylated (*S*)-propylenediamine.

Preparation and assignments of the diastereoisomeric pairs of the *trans,trans*-CoX_2(N-Meen)$_2^+$ ion (X^- = Cl^-, NO_2^-) (*i.e.*, the *meso* and the racemic (*dl*) isomers) were reported in recent publications.[7,8] The *meso* isomer is intrinsically optically inactive, whereas an optically active isomer of the *trans,trans*-Co$(NO_2)_2$(N-Meen)$_2^+$ ion was obtained by an optical resolution of the racemic isomer. Furthermore, an assumption of the absolute configuration of the (−)D-*trans,trans*-$CoCl_2$(N-Meen)$_2^+$ ion, which is derived from the (+)D-Co$(NO_2)_2$(N-Meen)$_2^+$ ion, was made by comparing the CD curve of the present complex with those of *trans*-Co((*S*)-(+)pn)$_2Cl_2^+$ (pn = propylenediamine) and of *trans*-Co((*SS*)-3,8-dimetrien)Cl_2^+.[7,8] However, preparation of the N-methyl-(*S*)-propylenediamine complex, which must have a structure very similar to that of the N-Meen complex, would contribute to the determination of the absolute configuration of the optically active N-Meen complex. Thus, two isomers of N-methyl-substituted (*S*)-propylenediamine were synthesized and are listed in Table I.

It is well recognized that the hydrogen atoms attached to carbon atoms of an ethylenediamine chelate ring can be classified as axial or equatorial in a similar way as for the cyclohexane ring.[9,10] It was established by X-ray diffraction studies that the more stable conformation of a pn chelate ring is that having an equatorial methyl group, rather than that having an axial methyl group.[11,12] Recently, it was shown by a proton magnetic resonance (pmr) study that in aqueous solution the (*R*)-(−)pn chelate rings have a fixed λ[13]-*gauche* form for some diamagnetic complexes at room temperature.[14] This conclusion was drawn from the examination of the exact values of coupling constants. Thus, the possibility of rapid conformational inversion can be ruled out in the case of the propylenediamine chelate ring. This indicates that the methyl group of pn possesses a steric effect by which the conformation of the chelate ring is fixed. We consider that this effect of the C-methyl group also occurs in the N-methylated propylenediamine chelates.

A similar distinction between the axial and equatorial orientations is acknowledged for the hydrogen atoms attached to the amine nitrogen of the ethylenediamine chelate.[9,10] Hence, a new type of stereoisomerism is probable for N-Meen and related N-substituted diamines. Possible structures for the N_1-Mepn and N_2-Mepn chelates are shown in Figure 1, where the C-substituted methyl groups adopt the equatorial positions. The N-substituted methyl groups are in the

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[1] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 334.

[2] F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **83**, 2610 (1961).

[3] D. H. Busch and D. W. Cooke, *J. Inorg. Nucl. Chem.*, **23**, 145 (1961).

[4] D. A. Buckingham, P. A. Marzilli, A. M. Sargeson, S. F. Mason, and P. G. Beddoe, *Chem. Commun.*, 433 (1967).

[5] S. Yoshikawa, T. Sekihara, and M. Goto, *Inorg. Chem.*, **6**, 169 (1967).

[6] M. Goto, M. Saburi, and S. Yoshikawa, *ibid.*, **8**, 358 (1969).

[7] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Am. Chem. Soc.*, **89**, 3428 (1967).

[8] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **7**, 915 (1968).

[9] E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959).

[10] A. M. Sargeson, *Transition Metal Chem.*, **3**, 303 (1966).

[11] Y. Saito and H. Iwasaki, *Bull. Chem. Soc. Japan*, **35**, 1131 (1962).

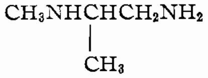
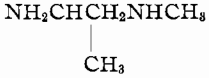
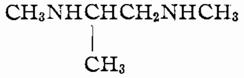
[12] H. Iwasaki and Y. Saito, *ibid.*, **39**, 92 (1966).

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

[14] S. Yano, H. Ito, Y. Koike, J. Fujita, and K. Saito, *Bull. Chem. Soc. Japan*, **42**, 3184 (1969).

TABLE I

LIST OF SYNTHESIZED LIGANDS

Ligand	Name	Abbreviation
 $CH_3NHCH(CH_3)CH_2NH_2$	N_1-methyl-(S)-propylenediamine	N_1-Mepn
 $NH_2CH(CH_3)CH_2NHCH_3$	N_2-methyl-(S)-propylenediamine	N_2-Mepn
 $CH_3NHCH(CH_3)CH_2NHCH_3$	N,N′-dimethyl-(S)-propylenediamine	N,N′-Me_2pn

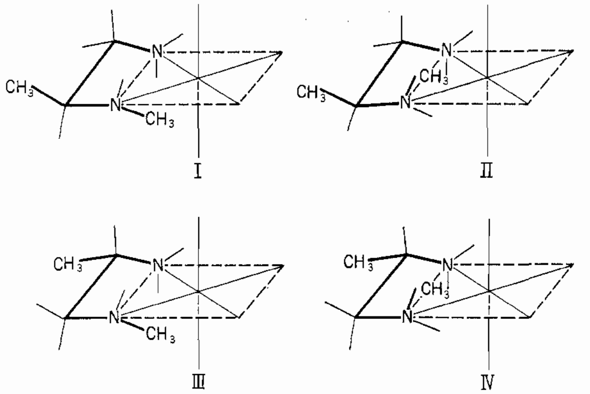


Figure 1.—Possible structures of N_1-Mepn (I and II) and N_2-Mepn (III and IV) chelate rings; I and III have an equatorial N-methyl group; II and IV have an axial N-methyl group.

equatorial orientations for I and III shown in Figure 1 (I, N_1-Mepn; III, N_2-Mepn), whereas the N-methyl groups of II and IV take the axial orientation (II, N_1-Mepn; IV, N_2-Mepn). These structures are in a diastereoisomeric relationship to each other, and therefore an energy difference can be expected between them. Buckingham, Marzilli, and Sargeson have reported the result of a conformational analysis of the N-Meen chelate ring in the tetraammine complex.[15] It was pointed out by these authors that an N-Meen chelate with an equatorial N-methyl group is more stable ($\sim$4 kcal mol^{-1}) than that with an axial N-methyl group. Further, it was indicated that if the chelate ring conformation of N-Meen is λ, the stable form of chelate ring takes the S[16] configuration with respect to the asymmetric secondary nitrogen center (equatorial). This means that the absolute configuration of the secondary nitrogen center (R or S) is closely related to the conformation of N-Meen chelate ring (δ or λ). Since N_1-Mepn and N_2-Mepn, derived from L-alanine, belong to the S series with regard to the asymmetric carbon center, the chelate rings of the diamines both adopt the δ preferred conformation, assuming that the C-methyl group takes the equatorial orientation. The secondary nitrogen center of N-methylated (S)-propylenediamine has an R absolute configuration for the equatorial orientation of N-methyl group and an S configuration for the axial orientation (Figure 1). When the energy difference between the configuration with an equatorial N-methyl group and that with an axial N-methyl group is fairly large, as estimated by Buckingham and coworkers for the N-Meen complex,[15] fixation of the configuration of the secondary nitrogen center will be brought about, probably in the form of I and III in Figure 1.

In a recent conformational analysis study,[17] however, it was pointed out that the energy difference between the most preferred equatorial and axial orientations is much less than that calculated by Buckingham and coworkers for the $Co(NH_3)_4(N\text{-}Meen)^{3+}$ ion, though there is still a preference for the equatorial configuration of the order of 0.8 kcal mol^{-1} or less, depending on the types of van der Waals nonbonded interaction equation used in the calculations. If such an energy difference is negligibly small, stereospecificity of the coordinated secondary nitrogen center would not be observed. It is necessary for discussing the characteristics of the CD spectra of the complex to clarify the exact structure of the N_1-Mepn and N_2-Mepn chelate rings with respect to the secondary nitrogen center.

In a preliminary report,[18] we supposed that the conformation of the N-Meen chelate ring for the (−)D-*trans,trans*-$CoCl_2(N\text{-}Meen)_2^+$ ion would be δ on account of the similarity between the CD curve of this ion and that of the *trans*-$CoCl_2(N_1\text{-}Mepn)_2^+$ ion. This assumption was proved correct in a recent X-ray diffraction study of the (−)D-*trans,trans*-$CoCl_2(N\text{-}Meen)_2^+$ ion.[19] The detailed structure of the N_1-Mepn complex, however, has not been resolved. In the present study, it is proved that the *trans*-$CoX_2(N_1\text{-}Mepn)_2^+$ and *trans*-$CoX_2(N_2\text{-}Mepn)_2^+$ ions ($X^- = NO_2^-, Cl^-$) possess the *trans,trans* configuration. The stereospecificity of coordinated secondary nitrogen atom of N_1-Mepn and N_2-Mepn is also discussed. Finally, the CD spectra of several cobalt(III) complexes with N_1-Mepn and N_2-Mepn are examined, taking into account the influence of the vicinal effect of the assymmetric secondary nitrogen center.

Experimental Section

Carbobenzoxy-L-alanine Amide.—Carbobenzoxy-L-alanine ethyl ester, obtained from 61 g of L-alanine ethyl ester hydrochlo-

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[15] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Am. Chem. Soc.*, **89**, 825 (1967).

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

[17] J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, **8**, 1168 (1969).

[18] M. Saburi, Y. Tsujito, and S. Yoshikawa, *Inorg. Nucl. Chem. Letters*, **5**, 203 (1969).

[19] W. T. Robinson, D. A. Buckingham, G. Chandler, L. G. Marzilli, and A. M. Sargeson, *Chem. Commun.*, 539 (1969).

ride and 88 g of carbobenzoxy chloride by the usual method,[20] was added to 800 ml of methanol saturated with ammonia. The solution was allowed to stand at room temperature for 7 days and evaporated almost to dryness under reduced pressure. The white crystals that separated were collected, washed with ether, and dried under vacuum. The product was recrystallized from methanol and ether; yield 74 g. *Anal.* Calcd for $C_{11}H_{14}N_2O_3$: C, 59.45; H, 6.35; N, 12.60. Found: C, 59.49; H, 6.57; N, 12.78.

N_1-Methyl-(*S*)-propylenediamine.—To 500 ml of anhydrous tetrahydrofuran in a 1-l. three-necked round-bottomed flask equipped with a mechanical stirrer and a reflux condenser was added 15 g of pulverized lithium aluminum hydride. Powdered carbobenzoxy-L-alanine amide (22 g) was added in small portions with stirring and the suspension was stirred and heated under reflux for 24 hr. Water (29 ml) diluted with 100 ml of tetrahydrofuran was added dropwise with vigorous stirring, and the resultant slurry was filtered off. The residue was extracted by boiling with tetrahydrofuran (150 ml) for 2 hr and filtered again. After this procedure was repeated, the extracts and filtrate were combined, treated with dry hydrogen chloride gas, and concentrated under reduced pressure. To the remaining oily layer was added a large excess of sodium hydroxide pellets, and the liquid layer that separated was extracted with 200 ml of ether. The ether extract was distilled fractionally at atmospheric pressure and the fraction boiling at 110–120° was collected as the product; yield 4.5 g. A small sample was converted to its picrate salt for analysis, and it was recrystallized from warm water. *Anal.* Calcd for $C_4H_{12}N_2\cdot 2C_6H_3N_3O_7\cdot H_2O$: C, 34.05; H, 3.57; N, 19.84. Found: C, 34.14; H, 3.98; N, 20.42.

N_2-Methyl-(*S*)-propylenediamine.—L-Alanine methylamide was obtained by the method described by Bergel and Peutherer[21] with a slight modification. L-Alanine ethyl ester (30 g) was dissolved in 500 ml of methanol saturated with methylamine and the solution was left at room temperature for 7 days. The excess reagent and solvent were removed, and the oily residue was used in the following reaction without further purification. A 25.5-g sample of crude L-alanine methylamide dissolved in 100 ml of anhydrous tetrahydrofuran was added dropwise to a suspension of 14.5 g of lithium aluminum hydride in 300 ml of anhydrous tetrahydrofuran at room temperature and stirred and heated under reflux for 24 hr. Water (27 ml) diluted with 50 ml of tetrahydrofuran was added carefully with vigorous stirring. The subsequent treatments were the same as that mentioned in the case of N_1-methyl-(*S*)-propylenediamine; bp 110–120°; yield 10 g. A small sample was converted to its hydrochloride salt for analysis and recrystallized from water by adding ethanol. *Anal.* Calcd for $C_4H_{12}N_2\cdot 2HCl$: C, 29.82; H, 8.76; N, 17.39. Found: C, 29.68; H, 8.75; N, 17.10.

N,N′-Dimethyl-(*S*)-propylenediamine.—Carbobenzoxy-L-alanine methylamide was obtained by treating carbobenzoxy-L-alanine ethyl ester (60 g) with methylamine in methanol solution for 7 days. After the solution was concentrated to dryness under vacuum, the crystals were collected, washed with ether, and dried under vacuum; yield 45 g. The product was recrystallized from methanol and ether. *Anal.* Calcd for $C_{12}H_{16}N_2O_3$: C, 61.03; H, 6.82; N, 11.85. Found: C, 60.82; H, 6.56; N, 12.03. Carbobenzoxy-L-alanine methylamide (23.6 g) was reduced by lithium aluminum hydride (15.0 g) in a similar manner to that described in the case of N_1-methyl-(*S*)-propylenediamine. The subsequent treatment was also the same. The fraction boiling at 115–120° was collected as the product; yield 5 g. A small sample was converted to its picrate for analysis. *Anal.* Calcd for $C_5H_{14}N_2\cdot 2C_6H_3N_3O_7$: C, 36.43; H, 3.59; N, 19.98. Found: C, 36.16; H, 3.86; N, 20.14.

***trans,trans*-Dinitrobis(N_1-methyl-(*S*)-propylenediamine)cobalt(III) Chloride Monohydrate, *trans,trans*-$[Co(NO_2)_2(N_1\text{-}Mepn)_2]Cl\cdot H_2O$.**—An ice-cold solution of N_1-methyl-(*S*)-propylenediamine (1.0 g in 10 ml of H_2O containing 0.6 g of concentrated HCl) was added to a cold solution of $CoCl_2\cdot 6H_2O$ (1.43 g in 15 ml of H_2O), and $NaNO_2$ (0.83 g) was added quickly. The resultant solution was aerated in an ice bath for 0.5 hr, followed by 5 hr at room temperature. The solution was evaporated to half its volume on a steam bath and left at room temperature for 1–2 days. The crystals that separated were collected, washed with methanol, acetone, and ether, and dried under vacuum; yield 1.8 g. Elemental analysis data of the complexes are summarized in Table II.

***trans,trans*-Dinitrobis(N_2-methyl-(*S*)-propylenediamine)cobalt(III) Iodide, *trans,trans*-$[Co(NO_2)_2(N_2\text{-}Mepn)_2]I\cdot C_2H_5OH$.**—An ice-cold solution of N_2-methyl-(*S*)-propylenediamine (1.0 g in 10 ml of H_2O containing 0.6 g of concentrated HCl) was added to a cold solution of $CoCl_2\cdot 6H_2O$ (1.43 g in 15 ml of H_2O), and $NaNO_2$ (0.83 g) was added quickly. The resultant solution was aerated in an ice bath for 0.5 hr, followed by 5 hr at room temperature. The solution was evaporated to half its volume, excess solid NaI was added, and the solution was further evaporated almost to dryness. The remaining materials were dissolved in methanol (20 ml) and the residue composed of NaCl was removed by filtration. After addition of ethanol (20 ml), the filtrate was allowed to stand at room temperature for several days. The yellow-brown crystals were collected and washed with ethanol and acetone. This product was recrystallized from a minimum volume of water by adding ethanol, filtered, washed with acetone, and dried under vacuum. It contains ethanol, which is proved by elemental analysis and pmr spectral measurement.

***trans,trans*-Dinitrobis(N_2-methyl-(*S*)-propylenediamine)cobalt(III) Perchlorate Monohydrate, *trans,trans*-$[Co(NO_2)_2(N_2\text{-}Mepn)_2]ClO_4\cdot H_2O$.**—An aerated solution obtained by the same procedure as for *trans,trans*-$[Co(NO_2)_2(N_2\text{-}Mepn)]I$ was evaporated to half its volume, and excess $LiClO_4$ was added. The crystals that separated were collected, washed with acetone, and dried under vacuum; yield 1.2 g.

***trans,trans*-Dichlorobis(N_1-methyl-(*S*)-propylenediamine)cobalt(III) Perchlorate, *trans,trans*-$[CoCl_2(N_1\text{-}Mepn)_2]ClO_4$.**—To an aqueous solution of $CoCl_2\cdot 6H_2O$ (1.75 g in 25 ml of H_2O) was added 1.0 g of N_1-methyl-(*S*)-propylenediamine and the solution was aerated for 10 hr with CO_2-free air. After 7 ml of concentrated HCl was added, the solution was concentrated to about 10 ml on a steam bath. An excess amount of $LiClO_4$ was added, and the green crystals formed were filtered off, washed with methanol and acetone, and dried under vacuum. The product was recrystallized from warm dilute HCl by adding $LiClO_4$.

Conversion of *trans,trans*-$[Co(NO_2)_2(N_1\text{-}Mepn)_2]Cl\cdot H_2O$ to *trans,trans*-$[CoCl_2(N_1\text{-}Mepn)_2]ClO_4$.—A solution of *trans,trans*-$[Co(NO_2)_2(N_1\text{-}Mepn)_2]Cl\cdot H_2O$ (0.6 g) in HCl (20 ml, 11 *N*) was warmed at 70° for 1 hr. An excess amount of $LiClO_4$ was added and cooled to 5° overnight. The green crystals that separated were collected, washed with acetone, and dried under vacuum. This product showed an infrared spectrum identical with that of the product obtained by the above-mentioned process.

***trans,trans*-Dichlorobis(N_2-methyl-(*S*)-propylenediamine)cobalt(III) Perchlorate, *trans,trans*-$[CoCl_2(N_2\text{-}Mepn)_2]ClO_4\cdot CH_3OH$.**—This compound was obtained by a method similar to that for *trans,trans*-$[CoCl_2(N_2\text{-}Mepn)_2]ClO_4$, using N_2-methyl-(*S*)-propylenediamine instead of N_1-methyl-(*S*)-propylenediamine. The product was recrystallized from methanol. The elemental analysis data show that this contains methanol of crystallization.

Conversion of *trans,trans*-$[Co(NO_2)_2(N_2\text{-}Mepn)_2]ClO_4$ to *trans,trans*-$[CoCl_2(N_2\text{-}Mepn)_2]ClO_4$.—This reaction was carried out in a similar manner for the corresponding N_2-Mepn complex. The product obtained showed a infrared spectrum slightly different from that of the complex obtained by the above-mentioned process. The visible absorption and CD spectra for *trans,trans*-$CoCl_2(N_2\text{-}Mepn)_2^+$ ion were recorded for the present complex.

***trans,trans*-Chloronitrobis(N_1-methyl-(*S*)-propylenediamine)cobalt(III) Perchlorate, *trans,trans*-$[CoCl(NO_2)(N_1\text{-}Mepn)_2]ClO_4$.**—A solution of *trans,trans*-$[Co(NO_2)_2(N_1\text{-}Mepn)_2]Cl\cdot H_2O$ (0.8 g) in HCl (2.8 ml, 10 *N*) was warmed at 40° until it became deep red (~5 min), and excess $LiClO_4$ was added, followed by ethanol.

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[20] J. P. Greenstein and M. Winitz, "Chemistry of Amino Acid," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1961, p 951.

[21] F. Bergel and M. A. Peutherer, *J. Chem. Soc.*, 3965 (1964).

TABLE II

ELEMENTAL ANALYSIS DATA

Complex	% calcd			% found		
	C	H	N	C	H	N
trans(Br)-$[CoBr_2(NH_3)_2(N_1\text{-}Mepn)]Br\cdot 2H_2O$	10.51	4.85	12.26	10.56	4.75	12.19
trans(Br)-$[CoBr_2(NH_3)_2(N_2\text{-}Mepn)]Br\cdot 2H_2O$	10.95	4.55	12.76	10.11	4.31	13.01
$[Co(NH_3)_4(N_1\text{-}Mepn)]Br_3\cdot H_2O$	10.15	5.54	17.76	10.25	5.52	17.30
$[Co(NH_3)_4(N_2\text{-}Mepn)]Br_3\cdot 0.5H_2O$	10.36	5.43	18.12	10.74	5.38	17.73
trans,trans-$[Co(NO_2)_2(N_1\text{-}Mepn)_2]Cl\cdot H_2O$	25.22	6.88	22.05	25.64	7.12	22.46
trans,trans-$[CoCl_2(N_1\text{-}Mepn)_2]ClO_4$	23.68	5.96	13.81	23.62	5.70	13.46
trans,trans-$[CoCl(NO_2)(N_1\text{-}Mepn)_2]ClO_4$	23.10	5.77	16.83	22.85	5.45	16.50
trans,trans-$[Co(NO_2)_2(N_2\text{-}Mepn)_2]I\cdot C_2H_5OH$	24.01	6.04	16.80	23.76	6.07	16.92
trans,trans-$[Co(NO_2)_2(N_2\text{-}Mepn)_2]ClO_4\cdot H_2O$	21.61	5.89	18.90	21.25	5.66	18.69
trans,trans-$[CoCl_2(N_2\text{-}Mepn)_2]ClO_4\cdot CH_3OH$	24.70	6.45	12.80	24.44	6.37	12.84
trans,trans-$[CoCl_2(N_2\text{-}Mepn)_2]ClO_4$	23.68	5.96	13.81	23.97	6.26	13.67
trans,trans-$[CoCl(NO_2)(N_2\text{-}Mepn)_2]ClO_4$	23.10	5.77	16.83	22.83	5.83	16.99
trans-$[CoBr_2(N_1\text{-}Mepn)_2]_2[CoBr_4]$[a]	16.44	4.10	9.58	16.47	4.20	9.36
trans-$[CoBr_2(N_2\text{-}Mepn)_2]Br$	20.23	5.05	11.79	20.39	5.28	11.50
trans-$[Co(NH_3)_2(N_1\text{-}Mepn)_2]Br_3\cdot 2H_2O$	17.63	6.24	15.41	17.73	6.80	15.35
trans-$[Co(NH_3)_2(N_2\text{-}Mepn)_2]Br_3$	18.83	5.89	16.51	18.50	5.90	16.58
trans-$[Co(NO_2)_2(N,N'\text{-}Me_2pn)_2]I\cdot H_2O$	24.01	6.04	16.80	23.38	6.08	17.06

[a] Br analysis: calcd, 54.72%; found, 55.71%.

The crystals that separated were filtered off, washed with ethanol and acetone, and dried under vacuum.

***trans,trans*-Chloronitrobis(N$_2$-methyl-(*S*)-propylenediamine)cobalt(III) Perchlorate, *trans,trans*-$[CoCl(NO_2)(N_2\text{-}Mepn)_2]ClO_4$.**—This compound was obtained by a method similar to that for preparing *trans,trans*-$[CoCl(NO_2)(N_2\text{-}Mepn)_2]ClO_4$ using *trans,trans*-$[Co(NO_2)_2(N_2\text{-}Mepn)_2]ClO_4$ as the starting material.

***trans*-Dibromobis(N$_1$-methyl-(*S*)-propylenediamine)cobalt(III) Tetrabromocobaltate(II), *trans*-$[CoBr_2(N_1\text{-}Mepn)_2]_2[CoBr_4]$.**—N$_1$-Methyl-(*S*)-propylenediamine (1.19 g) was added to an aqueous solution of $CoBr_2\cdot 6H_2O$ (2.5 g in 25 ml of H_2O) and the solution was aerated with CO_2-free air for 10 hr. Concentrated hydrobromic acid (7 ml) was added and the resultant solution was evaporated to half its volume. The yellow-green crystals that separated were collected and washed with acetone; yield 1.1 g. This product could not be recrystallized from 2 *N* HBr or methanol. The composition of this compound, $[CoBr_2(N_1\text{-}Mepn)_2]_2[CoBr_4]$, was determined based on the result of elemental analysis.

***trans*-Dibromobis(N$_2$-methyl-(*S*)-propylenediamine)cobalt(III) Bromide, *trans*-$[CoBr_2(N_2\text{-}Mepn)_2]Br$.**—This compound was prepared in a procedure similar to that for corresponding N$_1$-Mepn complex. The product was recrystallized from 2 *N* HBr and washed with acetone; yield 0.65 g.

***trans*-Diamminebis(N$_1$-methyl-(*S*)-propylenediamine)cobalt(III) Bromide Dihydrate, *trans*-$[Co(NH_3)_2(N_1\text{-}Mepn)_2]Br_3\cdot 2H_2O$.**—*trans*-$[CoBr_2(N_1\text{-}Mepn)_2]_2[CoBr_4]$ (1.4 g) was added to liquid ammonia (50 ml). A white precipitate formed was filtered off, and the filtrate was evaporated almost to dryness at room temperature. The orange crystals that remained were recrystallized from 1 *N* HBr by adding ethanol.

***trans*-Diamminebis(N$_2$-methyl-(*S*)-propylenediamine)cobalt(III) Bromide, *trans*-$[Co(NH_3)_2(N_2\text{-}Mepn)_2]Br_3$.**—This was prepared by a method similar to that for preparing *trans*-$[Co(NH_3)_2(N_1\text{-}Mepn)_2]Br_3$ using *trans*-$[CoBr_2(N_2\text{-}Mepn)_2]Br$ was the starting complex.

Ammonium Disulfitodiammine-N$_1$-methyl-(*S*)-propylenediaminecobaltate(III), $NH_4[Co(SO_3)_2(NH_3)_2(N_1\text{-}Mepn)]$.—Ammonium disulfitotetraamminecobaltate(III)[22] (8.1 g) was suspended in water (110 ml) and N$_1$-methyl-(*S*)-propylenediamine (2.0 g) was added dropwise with stirring. The resultant solution was stirred for 3 hr and reduced to half its volume under vacuum. The yellow product was obtained by adding ethanol and cooling to 5°, collected, washed with ethanol and acetone, and dried under vacuum; yield 7.5 g. The product was analytically impure but was used in the following reaction without further purification.

Diammine-*trans*-dibromo-N$_1$-methyl-(*S*)-propylenediaminecobalt(III) Bromide Dihydrate, *trans*(Br)-$[CoBr_2(NH_3)_2(N_1\text{-}Mepn)]Br\cdot 2H_2O$.—A 7.2-g sample of crude $NH_4[Co(SO_3)_2(NH_3)_2(N_1\text{-}Mepn)]$ was added rapidly to a hot solution of HBr (30 ml of 47% at 60°). Heating was continued until the color of the solution changed from yellow to green. After cooling quickly, the resultant green solution was stirred at room temperature for 3 hr and concentrated at 30–35° under reduced pressure. The yellow-green precipitates separated were collected, washed with acetone and ethanol, and dried under vacuum; yield 7.0 g. A sample was recrystallized from warm HBr (2 *N*), washed with acetone, and dried under vacuum.

Tetraammine-N$_1$-methyl-(*S*)-propylenediaminecobalt(III) Bromide Monohydrate, $[Co(NH_3)_4(N_1\text{-}Mepn)]Br_3\cdot H_2O$.—$[CoBr_2(NH_3)_2(N_1\text{-}Mepn)]Br$ (4.0 g) was added to liquid ammonia (50 ml). After the ammonia was evaporated at room temperature, the residue was extracted twice with boiling ethanol (50 ml). It was recrystallized from warm HBr (1 *N*) and the orange crystals that separated were collected, washed with ethanol and acetone, and dried under vacuum.

Ammonium Disulfitodiammine-N$_2$-methyl-(*S*)-propylenediaminecobaltate(III), $NH_4[Co(SO_3)_2(NH_3)_2(N_2\text{-}Mepn)]$.—This complex was prepared by a method similar to that for the N$_1$-Mepn complex, using N$_2$-Mepn, and was used without further purification.

Diammine-*trans*-dibromo-N$_2$-methyl-(*S*)-propylenediaminecobalt(III) Bromide, *trans*(Br)-$[CoBr_2(NH_3)_2(N_2\text{-}Mepn)]Br$.—This was prepared according to a similar procedure mentioned in the corresponding N$_1$-Mepn complex. The product obtained was slightly impure probably due to contamination by a tetrabromocobaltate(II) salt, *i.e.*, $[CoBr_2(NH_3)_2(N_2\text{-}Mepn)]_2[CoBr_4]$.

Tetraammine-N$_2$-methyl-(*S*)-propylenediaminecobalt(III) Bromide Hemihydrate, $[Co(NH_3)_4(N_2\text{-}Mepn)]Br_3\cdot 0.5H_2O$.—This was also obtained according to a method similar to that for the corresponding N$_1$-Mepn complex.

***trans*-Dinitrobis(N,N'-dimethyl-(*S*)-propylenediamine)cobalt(III) Iodide Monohydrate, *trans*-$[Co(NO_2)_2(N,N'\text{-}Me_2pn)_2]I\cdot H_2O$.**—A mixture of $K_3[Co(NO_2)_6]$ (4.5 g) and N,N'-dimethyl-(*S*)-propylenediamine (2.0 g) in H_2O (50 ml) was stirred and heated at 80° for 3 hr. The remaining $K_3[Co(NO_2)_6]$ was removed by filtration, excess solid NaI was added, and the solution was evaporated at room temperature. The precipitated product was collected, washed with acetone, and dried under vacuum.

Measurements.—Visible and ultraviolet absorption spectra were measured using a Shimadzu QV-50 spectrophotometer and a 1-cm cell. Circular dichroism was measured using a JASCO Model ORD/UV-50 spectrophotometer or a Shimadzu QV-50

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[22] J. C. Bailar, Jr., and D. F. Peppard, *J. Am. Chem. Soc.*, **62**, 105 (1940).

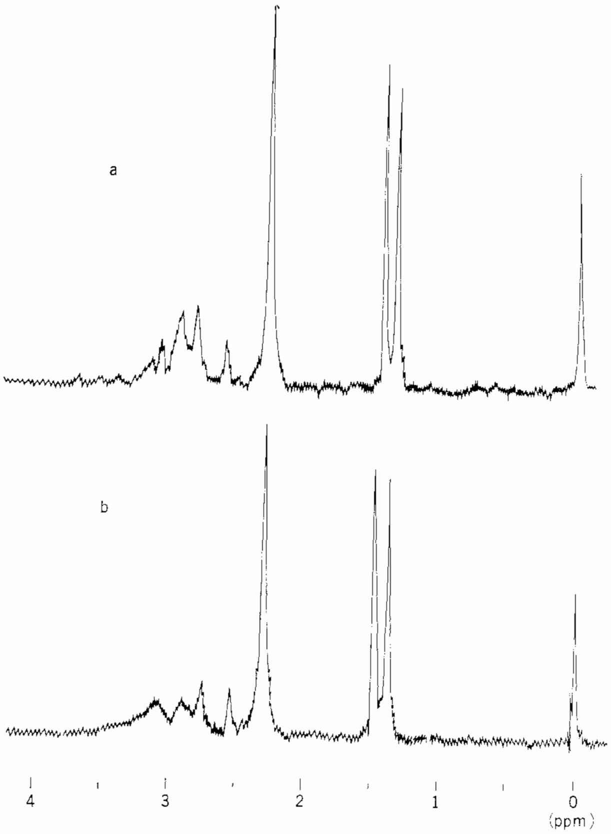

Figure 2.—Pmr spectra of $[Co(NH_3)_4(N_1\text{-Mepn})]Br_3$ (a) and $[Co(NH_3)_4(N_2\text{-Mepn})]Br_3$ (b) in D_2O.

spectrophotometer fitted with a CD attachment. Proton magnetic resonance spectra were measured using a Japan Electronic Optics Laboratory Model C-60 spectrometer and sodium trimethylsilylpropanesulfonate as an internal standard reference. Since several perchlorate salts were very insoluble in D_2O for pmr measurements, analytically pure samples of perchlorate salts were converted to chloride salts by shaking an aqueous supension with an equimolar amount of tetraphenylarsonium chloride. The solutions were then filtered and evaporated to dryness.

Results and Discussion

Structure of Monodiamine Complexes.—There are two significant subjects to be clarified in examining the structures of the N_1-Mepn and N_2-Mepn complexes. The first is the possibility of rapid conformational inversion of the diamine chelate rings, and the second is the orientations of the N-methyl group with regard to the diamine chelate ring. It was suggested in recent publications that the pmr measurement is very useful for proving the conformational fixation of (*R*)-(−)pn chelate rings[14] and the stereoisomerism of the N-Meen complexes with respect to the N-methyl group.[8]

The pmr spectra for monodiamine complexes of the tetraammine type containing either N_1-Mepn or N_2-Mepn are shown in Figure 2. Assignments of the chemical shifts for the complexes are summarized in Table III. The signal of the C-methyl protons was observed at about 1.4 ppm as a single doublet for both complexes. The signals of the methylene and methyne protons were observed in the region 2.5–3.4 ppm. The signals assigned to the methylene and methyne were also observed as a set of sharp bands in a similar region for the (*R*)-(−)pn chelate in the $Co(CN)_4((R)\text{-pn}^-)$ ion.[14] According to the result of the exact calculations of coupling constants between these protons, the conformation of (*R*)-(−)pn chelate ring was proved to be fixed in the λ-*gauche* form. The fact that the signals for the methylene and methyne protons are composed of several sharp bands was also pointed out in the pmr spectra of the tetraammine complexes of N_1-Mepn and N_2-Mepn, though there is some ambiguity, partly due to the use of a 60-MHz spectrometer (the spectrum for (*R*)-(−)pn complex was recorded with a 100-MHz spectrometer) and partly due to the low solubility of the complexes. This observation, along with the fact that the signal for the C-methyl protons is a single doublet, suggests that the conformations of the N_1-Mepn and the N_2-Mepn chelate rings are fixed in the stable structure, in which the C-methyl group adopts an equatorial position. If the conformational interchange between two *gauche* forms is rapid, the C-methyl protons can be observed as a single doublet. In such a case, however, the pmr signals for the methylene and methyne protons should be observed as a single broad peak. Therefore, the possibility of rapid conformational inversion can be ruled out for the N-methylated (*S*)-propylenediamine chelates. On this basis, the preferred conformation of the N_1-Mepn and the N_2-Mepn chelates should be the δ form, as expected previously.

Table III

Assignments of Chemical Shifts (ppm)[a] for Pmr Spectra of N_1-Mepn and N_2-Mepn Complexes

Complex	C–CH_3	N–CH_3	–CH_2CH
$[Co(NH_3)_4(N_1\text{-Mepn})]Br_3$[b]	1.39	2.28	2.6–3.3
$[Co(NH_3)_4(N_2\text{-Mepn})]Br_3$[b]	1.42	2.30	2.5–3.4
trans(Br)-$[CoBr_2(NH_3)_2(N_1\text{-Mepn})]ClO_4$[c]	1.43	2.54	
trans,trans-$[Co(NO_2)_2(N_1\text{-Mepn})_2]Cl$[b]	1.36	2.28	2.4–3.2
trans,trans-$[Co(NO_2)_2(N_2\text{-Mepn})_2]I$[b]	1.39	2.20	2.4–3.2
trans,trans-$[CoCl(NO_2)(N_1\text{-Mepn})_2]Cl$[d]	1.32	2.13 (2.27)	2.8–3.3
trans,trans-$[CoCl(NO_2)(N_2\text{-Mepn})_2]Cl$[d]	1.53	2.22 (2.53)	2.6–3.1
trans,trans-$[CoCl_2(N_1\text{-Mepn})_2]Cl$[e]	1.44	2.42	2.6–3.1
trans,trans-$[CoCl_2(N_2\text{-Mepn})_2]Cl$[e]	1.38	2.40	2.6–3.1
trans-$[Co(NO_2)_2(N,N'\text{-Me}_2pn)_2]I$[b]	1.37	2.17	2.4–3.2

[a] Sodium trimethylsilylpropanesulfonate as standard reference. [b] In D_2O. [c] In 48% DBr. [d] In 0.1 *N* DCl. [e] In 1 *N* DCl.

It was a fundamental assumption for discussing the stereospecificity of the N-methyl-L-alanine complex with respect to the N-methyl group[23] that an N-methyl group located in a fixed orientation should have a chemical shift different from that of the N-methyl group in the other fixed orientation. This anticipation would be applicable to the N-methylated (*S*)-propylenediamine chelates. For a few N-Meen complexes, for example, the N-methyl groups situated in different circumstances could be distinguished by means of the pmr spectral measurement.[8] Therefore, it was presumed that the equatorial N-methyl group should have a chemical shift different from that of the axial N-methyl group for the N_1-Mepn and N_2-Mepn chelates.

Since protons attached to ammine and amine nitrogen atoms are commonly deuterated in neutral D_2O

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(23) M. Saburi and S. Yoshikawa, *Inorg. Chem.*, **7**, 1890 (1968).

solution, the signal of an N-methyl group in the particular orientation should be observed as a singlet. If both the diastereomeric configurations depicted as I and II or III and IV in Figure 1 are stable enough and arise in appropriate concentrations for detecting in the pmr measurement, the pmr signal of the N-methyl protons should be observed generally as two singlets of different intensities. It is observed, however, that the pmr signal of the N-methyl group is only one singlet (~2.3 ppm) for both tetraammine complexes, as shown in Figure 2.

In the case where the chelate ring conformations are fixed as for the N_1-Mepn and the N_2-Mepn complexes, the diastereomeric pair of configurations, such as I and II or III and IV, may exist at equilibrium provided the inversion at the asymmetric secondary nitrogen center occurs readily. It was indicated that the rate constant of the racemization (k_{obsd}) is on the order of 10^{-4} sec^{-1} at pH ~7 for the optically active $Co(NH_3)_4$-(N-Meen)$^{3+}$ ion.[8] Thus, the equilibrium between I and II or III and IV would be achieved sufficiently in the course of standing in D_2O solution for at least 1 day. The pmr spectra given in Figure 2 are those taken after the solution has stood for 2 or 3 days, which would be long enough to establish the equilibrium mentioned above. On this basis, the observation that the pmr signal of the N-methyl protons is only one singlet can indicate that the $Co(NH_3)_4(N_1\text{-Mepn})^{3+}$ and the $Co(NH_3)_4(N_2\text{-Mepn})^{3+}$ ions are composed of the single species in aqueous solution. This means that the N-methyl group is restricted in a specific orientation with regard to the diamine chelate rings and so the stereospecificity of the asymmetric secondary nitrogen atom is almost perfect for these complexes within the limit of pmr spectral measurement.

Based on the conclusion of conformational studies of the N-Meen complex,[15,17] it is obvious that the preferred configurations of the N_1-Mepn and the N_2-Mepn chelate rings are those shown as I and III in Figure 1, respectively, which possess the N-methyl groups oriented in an equatorial position. The absolute configuration of the asymmetric secondary nitrogen center is *R* for these structures.

In order to explore the stereospecificity with respect to the N-methyl group in another system, we examined the *trans*(Br)-dibromodiammine complexes with N_1-Mepn and N_2-Mepn. However, it was very difficult to purify the N_2-Mepn complex, *trans*(Br)-$[CoBr_2(NH_3)_2(N_2\text{-Mepn})]Br$, due to its high solubility in aqueous or methanol solution and contamination by cobalt(II) species such as $[CoBr_2(NH_3)_2(N_2\text{-Mepn})]_2[CoBr_4]$. Satisfactory elemental analyses have not been obtained yet for this complex, so its pmr spectrum is not reported in the present paper. Only the pmr spectrum of the *trans*(Br)-$[CoBr_2(NH_3)_2(N_1\text{-Mepn})]Br$, which could be purified by recrystallization, is shown in Figure 3. This spectrum was taken in 48% DBr solution. In acidic solution, the deuterium exchange of N–H protons is retarded sufficiently for cobalt(III) complex, so that the pmr signal of the N-methyl protons in a particular orientation should be observed as a doublet.

The signal for the N-methyl protons as well as that for the C-methyl protons was a single doublet for the *trans*(Br)-$[CoBr_2(NH_3)_2(N_1\text{-Mepn})]Br$ as shown in Figure 3. The splitting of the signals for the methylene and methyne protons was also recognized in the present complex, though a slight ambiguity, compared with the tetraammine complex, was observed. Therefore, the N_1-Mepn chelate ring would have a preferred structure like I of Figure 1 even in the *trans*(Br)-dibromodiammine framework, by the same reasoning for the tetraammine complex.

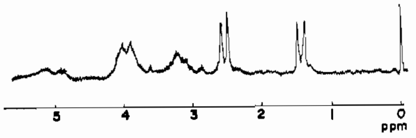

Figure 3.—Pmr spectrum of *trans*(Br)-$[CoBr_2(NH_3)_2(N_1\text{-Mepn})]$-Br in 48% DBr.

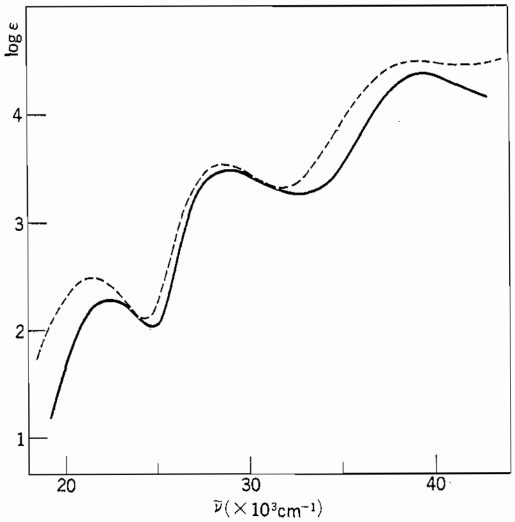

Figure 4.—Visible and ultraviolet absorption spectra of *trans*,-*trans*-$Co(NO_2)_2(N_1\text{-Mepn})_2^+$ (——) and *trans*-$Co(NO_2)_2(N,N\text{-}Me_2pn)_2^+$ (----).

Structures of Bisdiamine Complexes.—The visible and ultraviolet spectra of bisdiamine complexes of cobalt(III) do not vary significantly with change in diamine. It is recognized that dinitro complexes show λ_{max} at ~330 mμ for the *cis* isomers and at ~350 mμ for the *trans* isomers. The dinitro complexes of N_1-Mepn and of N_2-Mepn show λ_{max} at 346 mμ (28,900 cm^{-1}) and at 347 mμ (28,800 cm^{-1}), respectively (see Figure 4). This indicates that these complexes have the *trans* configuration with respect to the two nitro groups. The dichloro complexes of N_1-Mepn and of N_2-Mepn are green, which is characteristic of the *trans*-$CoCl_2N_4^+$ type of complex. The absorption spectrum of the N_1-Mepn complex given in Figure 5 is almost identical with that of the N_2-Mepn complex and is very similar to that of the *trans,trans*-$CoCl_2$-(N-Meen)$_2^+$ complex. Thus, it is clear that the

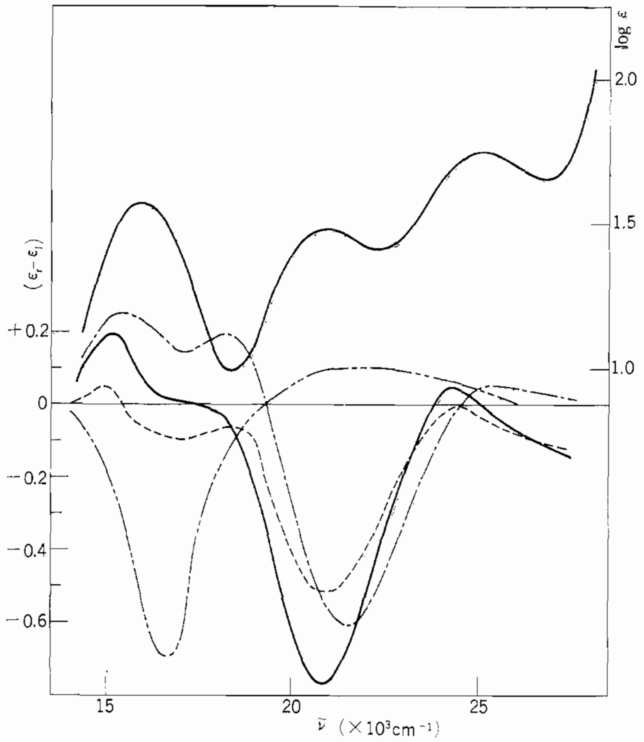

Figure 5.—Visible absorption and CD spectra of *trans,trans*-$CoCl_2(N_1\text{-}Mepn)_2^+$ (——) and CD spectra of *trans,trans*-$CoCl_2$-$(N_2\text{-}Mepn)_2^+$ (----), (−)D-*trans,trans*-$CoCl_2(N\text{-}Meen)_2^+$ (-·-·-), and trans-$CoCl_2$(*d*-pn)$_2^+$ (-·····-) (in methanol solutions).

dinitro and dichloro complexes are *trans* with respect to the anionic substituents.

The pmr spectra of the dinitro and the dichloro complexes are shown in Figure 6. For both ligands and for both anionic ligands, the signals for the C-methyl and the N-methyl groups were observed as the single bands. The splitting features for the signals of the methylene and methyne protons were observed clearly in the case of dinitro complexes, indicating that the possibility of rapid conformational inversion of the chelate rings can be excluded for these complexes. This situation is also noticed for the dichloro complexes with slight ambiguity due to overlapping of the N–H proton signals. These results require that the dinitro and the dichloro complexes are composed of the single species. The probable structures of *trans*-diacido complex of N_1-Mepn and N_2-Mepn are those shown in Figure 7. When X and Y are equivalent as in the case of dinitro and dichloro complexes, it is difficult to distinguish between *trans,trans* and *trans,cis* by means of pmr spectra. For both configurations, two C-methyl groups and also two N-methyl groups are in the same environment, respectively.

However, in the case in which X and Y are not the same, the *trans,trans* isomer is easily distinguishable from the *trans,cis* isomer. The two C-methyl and two N-methyl groups are not equivalent for the *trans,cis* isomers, whereas they are equivalent for the *trans,trans* isomers. Buckingham, Marzilli, and Sargeson utilized the differences of the pmr spectra of the chloronitro complexes for the assignments of the *meso* and (±) isomers of the *trans,trans*-CoX_2(N-Meen)$_2^+$ ion. Two diastereoisomers can arise for the *trans,trans* isomer of the chloronitro complexes ($X^- = Cl^-$, $Y^- = NO_2^-$; $X^- = NO_2^-$, $Y^- = Cl^-$). These isomers will not necessarily occur in equal amounts. Therefore, the pmr signals of the C- and N-methyl groups will be observed as two bands of unequal intensities for the chloronitro isomers of *trans,trans* configuration. In contrast, such a new isomerism does not occur for the *trans,cis* configuration even in the chloronitro form: the pmr signals of C- and N-methyl groups should be observed as two bands of equal intensity for this configuration.

The pmr spectra of chloronitro isomers of the N_1-Mepn and of the N_2-Mepn complexes are also shown in Figure 6. The intensities of pairs of signals, which can be assigned to the C- and N-methyl groups, are not equivalent for both ligands. In the case of N_2-Mepn complex, the pmr spectrum taken after 24 hr of the first measurement show slight differences from the initial spectrum. The signal at 2.53 ppm becomes higher in intensity after 24 hr, while the signal at 2.22 ppm is lowered. These signals are both assigned to the N-methyl protons, and, therefore, we consider that the former signal corresponds to the N-methyl group of the aquated species, rather than the one isomer of the chloronitro complexes. Although a similar phenomenon has not been confirmed for the N_1-Mepn complex, it is apparent that two bands of equal intensities are not observed in the signals of the C- and N-methyl groups for the N_1-Mepn and N_2-Mepn complexes. This indicates that the dinitro and the dichloro complexes with N-methyl-(*S*)-propylenediamines adopt the *trans,trans* configuration.

The dibromobisdiamine complexes were also prepared for the purpose of comparing the CD curve of monodiamine complex with that of bisdiamine types of complexes. The elemental analysis data suggest the composition $[Co(C_4H_{12}N_2)_2]_2[CoBr_4]$ for the N_1-Mepn complex. A similar composition had been indicated for the *trans*-dichlorocobalt(III) complexes with N-alkylethylenediamines.[24] One of the present authors has also noted the presence of $CoCl_4^{2-}$ as the counterion of dichlorocobalt(III) complexes of triethylenetetramine derivatives.[25] Therefore, it seems reasonable to consider such an anomalous constitution for this complex, though other evidence has not yet been collected.

The dibromo complexes obtained are yellow-green and showed visible absorption spectra given in Figure 8, suggesting that these complexes are *trans* with respect to the bromide coordinated. The pmr spectra were not measured for the dibromo complexes. However, the *trans,trans* configuration would be more probable than the *trans,cis* configuration, since the dichloro complexes obtained directly from the aerated solution in a procedure similar to that for preparing the dibromo complexes have been shown to be *trans,trans*.

The structure of the diamminebisdiamine type of

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(24) E. W. Gillow and G. M. Harris, *Inorg. Chem.*, 7, 394 (1968).

(25) M. Saburi and S. Yoshikawa, unpublished result.

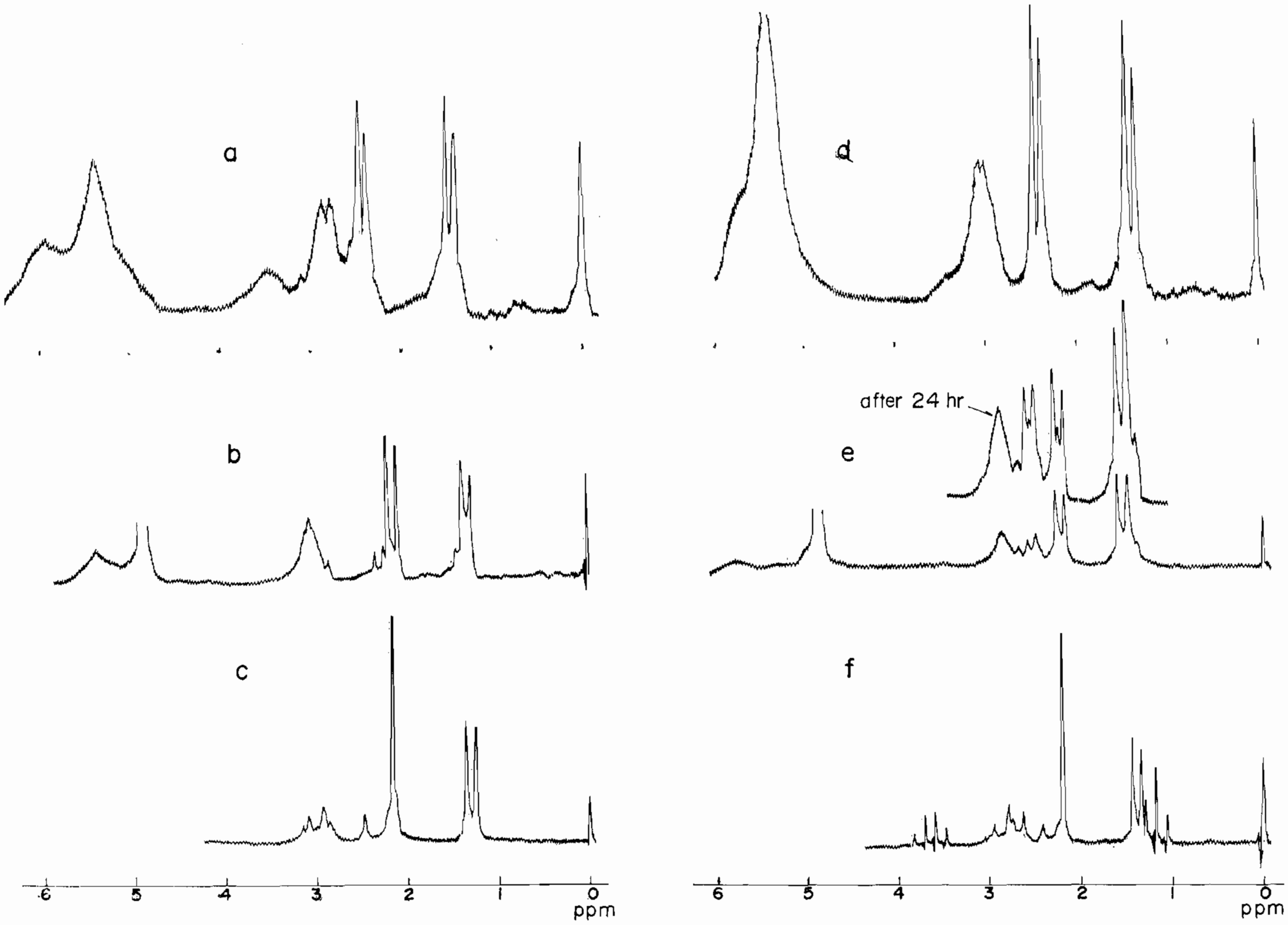

Figure 6.—Pmr spectra of (a) *trans,trans*-[$CoCl_2(N_1\text{-Mepn})_2$]Cl in 1 *N* DCl, (b) *trans,trans*-[$CoCl(NO_2)(N_1\text{-Mepn})_2$]Cl in 0.1 *N* DCl, (c) *trans,trans*-[$Co(NO_2)_2(N_1\text{-Mepn})_2$]Cl in D_2O, (d) *trans,trans*-[$CoCl_2(N_2\text{-Mepn})_2$]Cl in 1 *N* DCl, (e) *trans,trans*-[$CoCl(NO_2)(N_2\text{-Mepn})_2$]Cl in 0.1 *N* DCl, and (f) *trans,trans*-[$Co(NO_2)_2(N_2\text{-Mepn})_2$]I·$C_2H_5OH$ in D_2O.

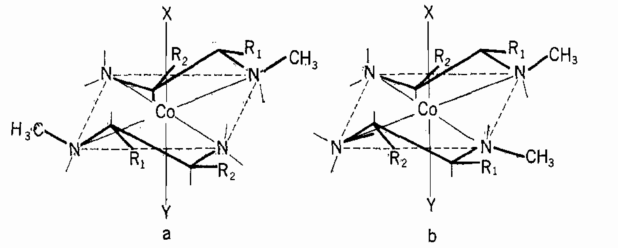

Figure 7.—Possible structures of bisdiamine complexes with N_1-Mepn (R_1 = CH_3, R_2 = H) or N_2-Mepn (R_1 = H, R_2 = CH_3): (a) *trans,trans;* (b) *trans,cis*.

complexes could not be determined from the absorption spectral data. The procedure employed for preparing the diammine complexes in this study is found to give solely the *trans*-diammine isomer for the active propylenediamine complex,[26] though the *trans*-dibromo complex was used instead of the *trans*-dichloro complex. Hence, we consider that the diammine complexes take *trans* configurations with regard to the two ammonia molecules.

Circular Dichroism and Structural Factors of Complexes.—The asymmetric features of the complexes discussed in this work are attributed to the conformation, the asymmetric carbon atom, and the asymmetric secondary nitrogen center of coordinated N-methylated propylenediamines. Any contribution from the chirality about the central cobalt(III) ion cannot be postulated here. The contribution from the conformation and the asymmetric carbon atom are present for the active propylenediamine complex, while the contribution from the conformation and the asymmetric secondary nitrogen center are expected for the resolved N-methylethylenediamine complexes. Hence, it becomes possible to investigate individually the significance of these factors in affecting the circular dichroism of complexes.

The first absorption band of cobalt(III) complex in an octahedral ligand field is ${}^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ which splits into ${}^1A_{1g} \rightarrow {}^1E_g(D_{4h})$ and ${}^1A_{1g} \rightarrow {}^1A_{2g}(D_{4h})$ transitions in a tetragonal field such as *trans*-$CoN_4X_2^+$. It was recognized that the cobalt(III) complexes of the type *trans*-$CoN_4Cl_2^+$ show their absorption maxima in the vicinity of 16,000 and 21,000 cm^{-1} which are assigned to the ${}^1A_{1g} \rightarrow {}^1E_g(D_{4h})$ and ${}^1A_{1g} \rightarrow {}^1A_{2g}(D_{4h})$ transitions, respectively.[27] Hawkins, Larsen, and Olsen have proposed an empirical rule which correlates the signs of Cotton effect in a particular d–d transition

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(26) T. D. O'Brien, J. P. McReynolds, and J. C. Bailar, *J. Am. Chem. Soc.*, **70**, 749 (1948).

(27) R. Dingle, *J. Chem. Phys.*, **46**, 1 (1967), and references therein.

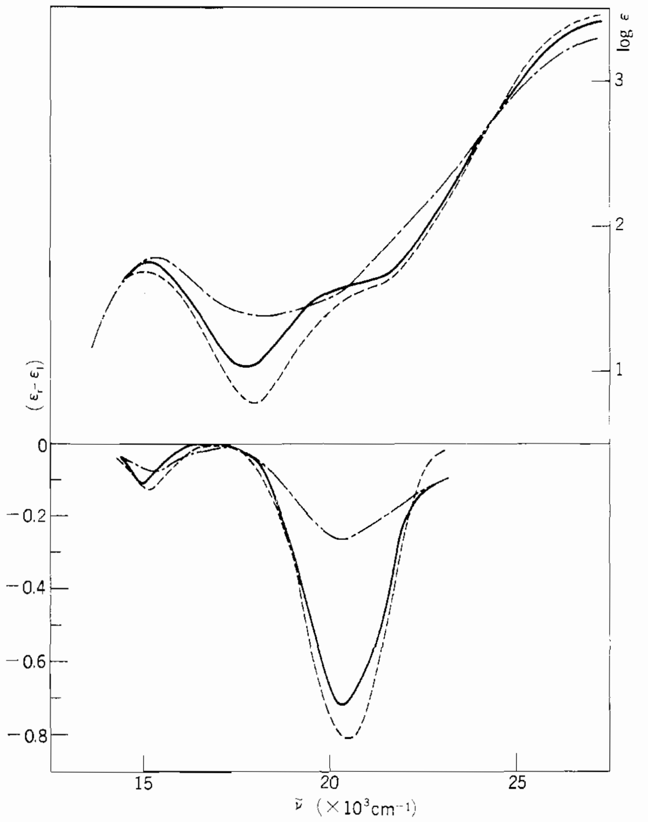

Figure 8.—Visible absorption and CD spectra of *trans*-$CoBr_2(N_1\text{-}Mepn)_2^+$ (——), *trans*-$CoBr_2(N_2\text{-}Mepn)_2^+$ (----), and *trans*-(Br)-$CoBr_2(NH_3)_2(N_1\text{-}Mepn)^+$ (-·-·-) (in methanol solutions).

of cobalt(III) complexes of the monodiamine and *trans*-bisdiamine types, in which the diamines are optically active, with the preferred conformation of diamines through a study of *l*-propylenediamine and *l*-cyclohexanediamine complexes.[28,29] They supposed that complex ions in which the coordinated diamines adopt the δ conformation show a positive CD maximum at the $^1A_1 \rightarrow {}^1B_1(D_2)$ (or its C_2 equivalent) transition derived from the $^1A_{1g} \rightarrow {}^1A_{2g}(D_{4h})$ transition. This rule was revealed to be applicable to the *trans*-dichlorocobalt(III) complexes with triethylenetetramine or its optically active derivatives.[4,6] Based on this rule, Buckingham, Marzilli, and Sargeson[8] considered that the chelate ring conformation of (−)D-*trans,trans*-$CoCl_2(N\text{-}Meeen)_2^+$ ion would be λ, since this ion shows a negative CD maximum at 21,300 cm⁻¹, which can be assigned to the $^1A \rightarrow {}^1B(C_2)$ transition derived from the $^1A_{1g} \rightarrow {}^1A_{2g}(D_{4h})$ transition.

The CD spectra for the *trans,trans*-$CoCl_2(N_1\text{-}Mepn)_2^+$ and the *trans,trans*-$CoCl_2(N_2\text{-}Mepn)_2^+$ ions are shown in Figure 5, along with those for the (−)D-*trans,trans*-$CoCl_2(N\text{-}Meen)_2^+$ and *trans*-$CoCl_2(d\text{-}pn)_2^+$ ions. The spectral data are summarized in Table IV. The CD spectra for all of the dichloro complexes with N-methyl-substituted diamines are very similar to each other and are markedly different from that of the *d*-pn complex. The similarity in CD spectra of N-methylated diamine complexes indicates the coincidence of the absolute configuration of the significant structural features, *i.e.*, the conformation of chelate ring and the configuration about the asymmetric secondary nitrogen atom. The preferred conformations of the N_1-Mepn and N_2-Mepn are considered to be δ, as mentioned earlier, and so the conformation of the N-Meen chelates in the (−)D-*trans,trans*-$CoCl_2(N\text{-}Mepn)_2^+$ ion is regarded as δ. This assumption has been proved to be correct by a recent X-ray diffraction study.[19]

The CD spectra for N-methylated diamines show a dominant negative maximum at about 21,000 cm⁻¹ exclusively, though the chelate ring conformations for these complexes are δ. This is in contrast to the *d*-pn complex, the preferred conformation of which is also δ. This complex shows a less significant positive CD maximum in this region and obeys the empirical rule proposed by Hawkins and his coworkers.[28,29] Thus, the empirical rule mentioned above appears not to be applicable to the N-methyl-substituted diamine complexes. A similar result was obtained for the *trans*-dichloro complexes with 2,5,8,11-tetraazadodecane derivatives.[30] It has been indicated that the absolute configuration of the secondary nitrogen is restricted stereospecifically to the *R* configuration for all of the N-methylated diamines which adopt the δ conformation. It is suggested, therefore, that not only the conformation of the chelate ring but also the asymmetric secondary nitrogen center influences significantly the CD spectra of N-substituted diamine complexes. In contrast, the resemblance of the CD curves between the active N-Meen complex and the N_1-Mepn or N_2-Mepn complex would suggest that the asymmetric C-methyl group exhibits very little effect for determining the shapes of CD curves.

Slight differences are observed among the signs of CD bands of the dichloro complexes with N_1-Mepn, N_2-Mepn, and N-Meen in the region 15,000–19,500 cm⁻¹. The doubly degenerate transition, $^1A_{1g} \rightarrow {}^1E_g$ in D_{4h} symmetry, splits into two components, $^1A \rightarrow {}^1A$ and $^1A \rightarrow {}^1B$ in the C_2 symmetry of the N-substituted diamine complexes. It was indicated for the N-Meen complex[8] that the signs of CD bands for these transitions are opposite to each other; a dominant positive band at the lower frequency and a less dominant negative band at the higher frequency are postulated. These two CD bands are expected to compensate each other, and, in some cases, a relatively smaller CD band will be observed in this region. The resultant CD curves arising from the superposition of CD bands of opposite sign at slightly different frequencies should vary considerably from one to the other ligand, reflecting the existence or nonexistence of substituents and its position. This may be a reason for the variations with CD curves mentioned above.

The CD spectra for the *trans*-$CoBr_2(N_1\text{-}Mepn)_2^+$ and *trans*-$CoBr_2(N_2\text{-}Mepn)_2^+$ ions are shown in Figure 8. Although the small positive CD bands in the lowest

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

[29] C. J. Hawkins and E. Larsen, *ibid.*, **19**, 1969 (1965).

[30] M. Goto, A. Okubo, T. Sawai, and S. Yoshikawa, *Inorg. Chem.*, **9**, 0000 (1970).

TABLE IV

ELECTRONIC ABSORPTION AND CIRCULAR DICHROISM OF N-METHYLATED PROPYLENEDIAMINECOBALT(III) COMPLEXES

Complex ion	Absorption		CD	
	$\tilde{\nu}$, cm^{-1}	ϵ_{max}	$\tilde{\nu}$, cm^{-1}	$\Delta\epsilon_{max}$
trans,trans-$Co(NO_2)_2(N_1\text{-Mepn})_2^+$ [a]	22,470	196	21,740	+0.80
			24,510	−0.08
	28,900	3150	27,780	+1.97
trans,trans-$Co(NO_2)_2(N_2\text{-Mepn})_2^+$ [a]	22,470	199	21,650	+0.92
			24,390	−0.10
	28,800	3500	27,780	+2.02
trans,trans-$CoCl_2(N_1\text{-Mepn})_2^+$ [b]	15,870	36.9	15,150	+0.20
			17,500	...
	20,940	30.3	20,830	−0.77
trans,trans-$CoCl_2(N_2\text{-Mepn})_2^+$ [b]	15,870	37.5	14,930	+0.05
			16,950	−0.09
	21,050	29.6	21,050	−0.51
trans-$CoBr_2(N_1\text{-Mepn})_2^+$ [b]	15,150	53.3	14,930	−0.11
	20,000	34.8	20,400	−0.72
trans-$CoBr_2(N_2\text{-Mepn})_2^+$ [b]	15,150	48.0	15,150	−0.13
	20,400	31.2	20,490	−0.81
trans(Br)-$CoBr_2(NH_3)_2(N_1\text{-Mepn})^+$ [a]	14,930	68.6	15,380	−0.07
			20,410	−0.26
$Co(NH_3)_4(N_1\text{-Mepn})^{3+}$ [a]	21,280	73.5	19,010	+0.08
			21,500	−0.37
	29,150	59.3	28,730	+0.06
$Co(NH_3)_4(N_2\text{-Mepn})^{3+}$ [a]	20,830	79.8	19,230	+0.13
			21,730	−0.33
	29,230	63.6	29,200	+0.06
trans-$Co(NH_3)_2(N_1\text{-Mepn})_2^{3+}$ [b]	20,700	66.5	18,870	+0.33
			21,740	−0.55
trans-$Co(NH_3)_2(N_2\text{-Mepn})_2^{3+}$ [b]	20,960	69.0	19,230	+0.36
			21,930	−0.55

[a] CD spectra were measured with a JASCO ORD/UV-50 spectrophotometer. [b] CD spectra were measured with a Shimadzu QV-50 spectrophotometer fitted with a CD attachment.

wave number side could not be measured, these curves are closely similar to those for the corresponding dichloro complexes. This suggests that the structure and arrangement of the ligands are the same for both of the dichloro and dibromo complexes (*trans,trans* configuration). Both of the dibromo complexes exhibit a dominant negative CD band in the vicinity of 21,000 cm^{-1}, which can be assigned to the transition to ${}^1B(C_2)$ excited level with ${}^1A_{2g}(D_{4h})$ parentage. The effect of the asymmetric secondary nitrogen on the CD spectra is also observed, since the *trans*-$CoBr_2(d\text{-pn})_2^+$ ion has a small positive CD maximum for this transition.[28]

It was found[28] that the CD curve of the *trans*(X)-$CoX_2(NH_3)_2(l\text{-pn})^+$ ion resembles that of the *trans*-$CoX_2(l\text{-pn})^{2+}$ ion ($X^- = Cl^-$ or Br^-), though the intensity of each CD band for the former complex is about half that of the corresponding band for the latter complex. Preparation of the dichlorodiammine complexes of N_1-Mepn was not attempted in this work. Only the *trans*(Br)-$CoBr_2(NH_3)_2(N_1\text{-Mepn})^+$ ion is available for the measurement of CD spectrum, since the stereospecificity with respect to the secondary nitrogen center is not ascertained for the *trans*(Br)-$CoBr_2(NH_3)_2(N_2\text{-Mepn})^+$ ion.

As shown in Figure 8, the CD spectrum for the *trans*-$CoBr_2(NH_3)_2(N_1\text{-Mepn})^+$ ion is similar to that for the *trans*-$CoBr_2(N_1\text{-Mepn})^+$ ion, though the band intensity for the former is considerably weaker than for the latter. If the effective symmetry of C_2 would be applied to the monodiamine complex, the dominant negative CD band at 20,410 cm^{-1} observed for the *trans*-$CoBr_2(NH_3)_2(N_1\text{-Mepn})_2^+$ ion is assigned to the ${}^1A \rightarrow {}^1B(C_2)$ transition derived from ${}^1A_{1g} \rightarrow {}^1A_{2g}(D_{4h})$. The CD curve of the *trans*-$CoBr_2(NH_3)_2(d\text{-pn})^+$ ion (enantiomorphous to *trans*-$CoBr_2(NH_3)_2(l\text{-pn})^+$ ion[28]) should exhibit a dominant negative band at 15,320 cm^{-1}. The CD band near 21,000 cm^{-1} was too weak to be observable for this complex, but its sign should be plus, considering the CD of the *trans*-$CoCl_2(NH_3)_2(l\text{-pn})^+$ ion. Thus, the significant effect of the asymmetric secondary nitrogen center on the CD curve is noticed even in the case of the monodiamine complex.

It was observed that the CD spectra for the $Co(NH_3)_4(N_1\text{-Mepn})^{3+}$ and the $Co(NH_3)_4(N_2\text{-Mepn})^{3+}$ ions resemble closely the CD spectrum of the $Co(NH_3)_4(d\text{-pn})^{3+}$ ion, as shown in Figures 9 and 10, respectively. This is in contrast to the case of *trans*-dichloro and *trans*-dibromo complexes discussed earlier. The excited levels for CoN_6^{3+} system are very close together and therefore assignment of the CD bands for the present complexes is somewhat difficult. Hawkins and coworkers proposed assignments of CD bands for the $Co(NH_3)_4(l\text{-pn})^+$ ion, assuming the effective symmetry of D_2 for this ion. Based on their assignments and the fact that the CD spectra of dibromodiammine complexes with N_1-Mepn and with *d*-pn are markedly different, we consider that the main transitions which contribute to the dominant negative CD bands in the

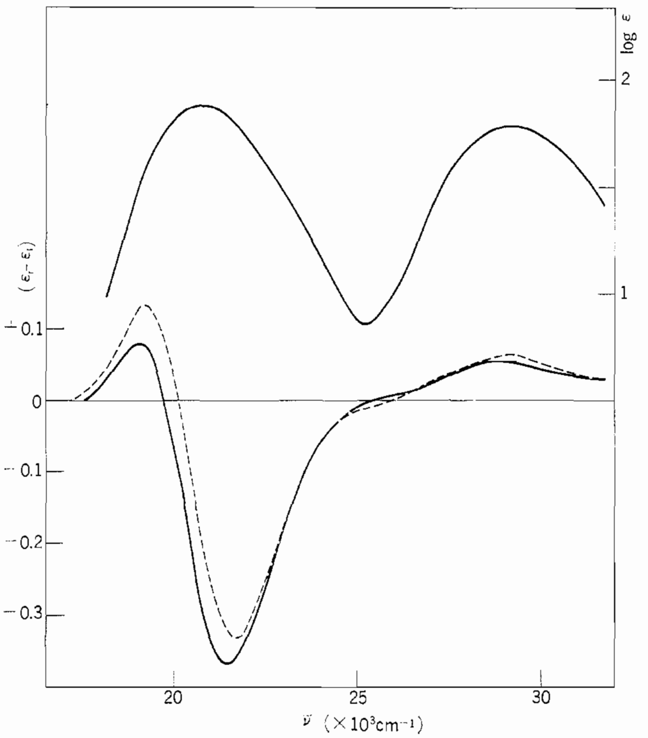

Figure 9.—Visible absorption and CD spectra of $Co(NH_3)_4(N_1\text{-Mepn})^{3+}$ (——) and CD spectrum of $Co(NH_3)_4(N_2\text{-Mepn})^{3+}$ (----).

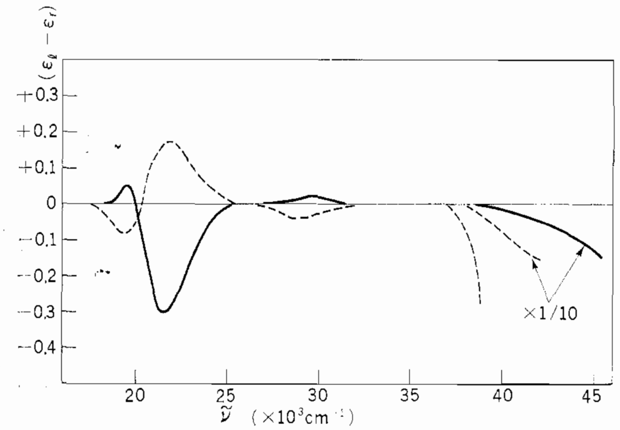

Figure 10.—CD spectra of $Co(NH_3)_4(d\text{-pn})^{3+}$ (——) and $(+)_{490}$-$Co(NH_3)_4(N\text{-Meen})^{3+}$ (----).

vicinity of 21,500 cm^{-1} are due to different excited levels for the N_1-Mepn (and N_2-Mepn) complex and the *d*-pn complex, that is, ^1B with the $^1A_{2g}(D_{4h})$ parentage for the former and the ^1A (or ^1B) with $^1E_g(D_{4h})$ parentage for the latter, assuming for convenience the effective symmetry of C_2 for both types of complexes.

The *trans*-$Co(NH_3)_2(N_1\text{-Mepn})_2^{3+}$ ion and the *trans*-$Co(NH_3)_2(N_2\text{-Mepn})_2^{3+}$ ion have positive and negative CD bands in the vicinity of 19,000 and 21,800 cm^{-1}, respectively. This situation is similar to corresponding *d*-pn complex.[28] Further, the behavior of these CD spectra are fairly similar to that of the tetraammine type, though each CD band for the tetraammine complexes has an intensity about half that for the present complexes. A similar observation has been made in the case of *trans*-dibromo complexes with N_1-Mepn (and with *d*-pn), as mentioned previously. As far as the diamminebisdiamine complexes are concerned, however, the intensity of the CD bands at lower wave number (~19,000 cm^{-1}) for the N_1-Mepn and N_2-Mepn complexes is considerably higher than that for the *d*-pn complex. Although a clear-cut structure of *trans,trans* has not been acertained for the former complexes, the slight difference in CD observed here could be due to the influence of the asymmetric nature of the coordinated secondary nitrogen atom of the ligands, which is not obviously noted for the tetraammine complexes mentioned above. The CD bands for the *trans*-diammine complexes would be assigned to the same transitions as in the case of the tetraammine complexes.

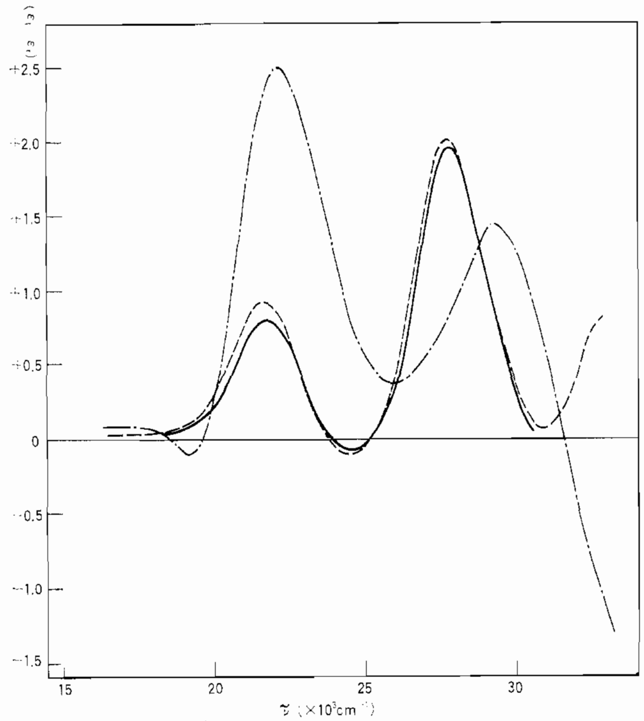

Figure 11.—CD spectra of *trans,trans*-$Co(NO_2)_2(N_1\text{-Mepn})_2^+$ (———), *trans,trans*-$Co(NO_2)_2(N_2\text{-Mepn})_2^+$ (----), and *trans*-$Co(NO_2)_2(N,N'\text{-Me}_2pn)_2^+$ (-·-·-).

The CD spectra for the *trans,trans*-$Co(NO_2)_2(N_1\text{-Mepn})_2^+$ and *trans,trans*-$Co(NO_2)_2(N_2\text{-Mepn})_2^+$ ions are shown in Figure 11. The structures of these complexes are the same as those of the corresponding dichloro complexes (Figure 7). The N_1-Mepn and N_2-Mepn chelate rings take a δ preferred conformation. The absolute configuration with respect to the secondary nitrogen center is *R* for these ligands. The CD spectrum for the (+)D-*trans,trans*-$Co(NO_2)_2(N\text{-Meen})_2^+$ ion reported by Buckingham and coworkers[8] is very similar to those for the N_1-Mepn and N_2-Mepn complexes. Therefore, the conformation of the N-Meen chelate ring in this complex should be δ, as found for the corresponding dichloro complex. Since no reliable CD spectrum for the *trans*-$Co(NO_2)_2(d\text{-pn})_2^+$ ion has been reported as yet, it is not possible to elucidate the effect of the asymmetric secondary nitrogen center on the CD of the *trans*-dinitrobisdiamine complexes.

The CD curve of *trans*-[Co(NO_2)$_2$(N,N′-Me$_2$pn)]I is also shown in Figure 11. This and the corresponding dichloro complex could not be obtained by usual air-oxidation procedures. The conversion of the dinitro to the dichloro isomer by a reaction with HCl in aqueous or in methanol solutions was also unsuccessful, which probably suggests the instability of the dichloro isomer. The *trans* configuration with respect to the nitro groups is indicated by the absorption spectrum. This complex shows an absorption maximum at 350 mμ (28,600 cm^{-1}) (Figure 4). The pmr spectrum of *trans*-[Co(NO_2)$_2$(N,N′-Mepn)$_2$]I in D_2O shows a doublet at 1.37 ppm and a singlet at 2.17 ppm, which can be assigned to the C- and N-methyl groups, respectively. The fact that the two N-methyl groups are not distinguishable in the pmr spectrum indicates not only that the complex has the *trans* configuration with respect to the nitro groups but also that the absolute configurations about the two kinds of N-methyl group (adjacent and not adjacent to the C-methyl group) are the same (probably *R*). If the present complex takes a *cis* configuration with respect to the nitro groups or if one of the two N-methyl groups is situated in an axial position even in *trans* form, the two N-methyl groups should have different chemical shifts to each other. Further, the chemical shifts for the two N-methyl groups should be slightly different in principle even in the case where their absolute configurations are the same, owing to their spatial inequivalence with respect to the C-methyl group. In such a case, however, it seems likely that the signals for both the N-methyl groups are superimposed because of the negligible difference of the chemical shifts. There is a marked difference between the CD curve of the N,N′-Me$_2$pn complex and those of the N_1-Mepn and N_2-Mepn complexes. This demonstrates again the significance of the influence of the asymmetric secondary nitrogen atom on the CD spectrum.

No fundamental difference has been observed between the CD curves of N_1-Mepn complexes and those of corresponding N_2-Mepn complexes. This suggests that the position of the C-methyl group (adjacent to the N-methyl group or not) has a negligible effect on the CD spectra. Furthermore, the CD curves of the N_1-Mepn and N_2-Mepn complexes resemble the CD curves of the N-Meen complexes with similar structures, as illustrated in the *trans,-trans*-dichloro complexes. It may be concluded that the contribution from the asymmetric C-methyl group(s) to the CD is practically negligible in the case of N-methylated diamine complexes. On this basis, the absolute structure of active Co(NH_3)$_4$(N-Meen)$^{3+}$ ion can be determined by comparing the CD curve of this ion with that of Co(NH_3)$_4$(N_1-Mepn)$^{3+}$ ion or the analogous N_2-Mepn complex.

The CD spectrum of (+)$_{490}$-[Co(NH_3)$_4$(N-Meen)]I_3 obtained by Buckingham, Marzilli, and Sargeson[15] is shown in Figure 10. In this spectrum, two CD bands are observed in the first absorption band region, a minor band at 19,500 cm^{-1} ($\Delta\epsilon$ −0.085) and a dominant band at 21,800 cm^{-1} ($\Delta\epsilon$ +0.17). In this region, the behavior of the CD curve of this ion is similar to that of the tetraammine complex containing N_1-Mepn or N_2-Mepn (see Figure 9). Further, the shapes of these curves are similar to one another on the whole, though the intensity of each CD band for the N-Meen complex is about half that for the N-methylated propylenediamine complexes. On this basis, it is possible to assume the chelate ring conformation of the optically active N-Meen complex. Each CD band of the (+)$_{490}$-Co(NH_3)$_4$(N-Meen)$^{3+}$ ion shows a sign opposite to that of the corresponding CD band of the Co(NH_3)$_4$(N_1-Mepn)$^{3+}$ and Co(NH_3)$_4$(N_2-Mepn)$^{3+}$ ions. It is considered therefore that the N-Meen chelate in the (+)$_{490}$-Co(NH_3)$_4$(N-Meen)$^{3+}$ ion adopts a conformation antimeric to those of the N_1-Mepn and N_2-Mepn chelates. Since the preferred conformation of the chelate ring of N_1-Mepn and N_2-Mepn is δ, that of the N-Meen in the present complex would be considered as λ.

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