can be considered to be virtually identical and consisting of nonionic entities $M(L^+)Cl_3$ where L^+ is the six-coordinate cobalt(III) complex which acts as a positively charged ligand. The divalent metal ion is tetrahedrally surrounded by three chlorine ions and the fourth coordination position is occupied by the nitrogen atom of a bridging cyanide. The pseudotetrahedral coordination of the M(II) ions is supported by the values of the magnetic moments which indicate a high-spin configuration (except for Zn(II)) and are in the range generally found for tetrahedrally coordinated divalent ions (Table I).[10]

The electronic spectra of the $Ni(L^+)Cl_3$ complex also support this formulation showing a broad absorption in the 14,000–17,000-cm^{-1} region which is in agreement with a pseudotetrahedral coordination.[17] Moreover the infrared spectra of all the complexes show two sharp bands in the CN stretching region confirming thus the presence of bridging and terminal cyanide groups. It is pertinent to note that the positive shift observed (19–39 cm^{-1}) is in the range found when organonitriles coordinate through the lone pair of electrons on nitrogen.[18] The small decrease in the ν(CN) for terminal cyanide is in agreement with the observation than when benzodinitriles coordinate to a metal atom through only one cyanide group, the frequency of the remote cyanide is lowered very slightly.[19]

Conclusions

A significant result of this study is the preparation of a novel series of compounds of uncommon stoichiometry and geometry, containing a cobalt(III) complex which acts as a positively charged ligand. The presence of a positive charge which can neutralize by electron delocalization the negative charge of MX_3^- groups probably favors the formation of the compounds $M(L^+)X_3$. The well-known tendency of cyanide to bridge metal atoms[15] affords a viable path to maintain tetracoordination around the divalent ion.

These complexes which may be considered as examples of inorganic zwitterions extend the relatively small number of complexes known to contain a positively charged ligand. In the previously reported $M(L^+)X_3$ complexes L^+ was a cationic phosphorus or nitrogen or arsenic ligand.[20] In the present case L^+ is a transition metal complex containing cyanide groups which behave as an organonitrile coordinated *via* σ bonding to divalent metal ions.

Acknowledgments.—The authors are grateful to Professor A. Turco for stimulating discussion and to Mr. L. Turiaco and G. Gomiero for technical assistance.

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Mixed-Ligand Complexes of Cobalt(III). Complexes with Stereospecific Tetramine Ligands

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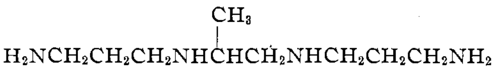
The syntheses, resolution, and properties of some oxalato, malonato, and diacido complexes of cobalt(III) with the stereospecific flexible tetramine ligands 5-methyl-4,7-diaza-1,10-decanediamine (5-Me-3,2,3-tet) and *N,N'*-bis(2-picolyl)-1-methyl-1,2-diaminoethane (picpn) are reported. Stereospecificity is demonstrated by comparison of the optical rotation of the ligand prepared *via* an asymmetric synthesis with that of the ligand isolated from the resolved complex. The stereochemistry of the complexes is deduced from electronic spectra, ORD, and CD measurements.

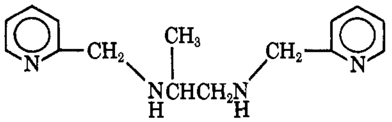
Introduction

To illustrate stereospecific coordination and absolute configuration of some tetramine ligands with cobalt(III), the tetramines 5-methyl-4,7-diaza-1,10-decandiamine, 5-Me-3,2,3-tet (I), and *N,N'*-bis(2-picolyl)-1-methyl-1,2-diaminoethane, picpn (II), were chosen for study. The unique properties of these tetramines lie in the fact that they are not only derivatives of 3,2,3-tet and 2,2,2-tet, respectively, but also contain an optically active center in the ligand affording a means for preparing optically active ligand cobalt(III) complexes. Direct evidence for stereospecific coordination is obtained from a comparison of the cobalt(III) complexes



$$H_2NCH_2CH_2CH_2NH\overset{CH_3}{\overset{|}{C}}HCH_2NHCH_2CH_2CH_2NH_2$$

5-methyl-4,7-diaza-1,10-decanediamine
(5-Me-3,2,3-tet)
I



N,N'-bis(2-picolyl)-1-methyl-1,2-diaminoethane
(picpn)
II

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(1) From the M.S. Thesis of J. C., Jr., Illinois Institute of Technology, 1971.

prepared with the resolved ligand and the resolved cobalt(III) complexes prepared with the ligand racemate.

To date, all investigations of the stereochemistry of cobalt(III) complexes with 3,2,3-tet and its analogs have dealt with either the resolved complexes or active ligand complexes but not both for the same system. No complete study has been made of 5-Me-3,2,3-tet, and only a narrative report of the stereochemistry of a number of (−)picpn–Co(III) complexes, has been recorded in the literature.[2]

Experimental Section

Physical Measurements.—Optical rotatory dispersion curves were recorded using a Cary Model 60 spectropolarimeter. The circular dichroism curves were recorded using a Cary Model 6002 circular dichroism attachment. Both spectra were obtained using 1- or 3-dm cells and a solvent blank was used for the base line determination; the solvent was water or absolute methanol unless otherwise noted. All solutions were approximately 10^{-3} *M*. Rotational measurements were obtained from the Cary Model 60 spectropolarimeter or on a Rudolph Model 340 oscillating photoelectric polarimeter using a 2-dm cell with mercury and sodium lamps. Optical isomers are denoted by (+) or (−), the sign of the rotation at the Na D line, or when another wavelength was used, it appears as a subscript.

The proton magnetic resonance spectra were recorded on a Varian A-60 spectrometer at the ambient probe temperature, 38°. The ligand samples were prepared as 50% solutions with carbon tetrachloride using tetramethylsilane as the internal standard. The electronic absorption spectra were obtained on a Beckman Model DBG spectrophotometer using matched 10-mm silica cells. Elemental analysis for C, N, and H was obtained from M-H-W Laboratories, Garden City, Mich.

Synthetic Procedures.—Preparation of 5-Methyl-4,7-diaza-1,10-decanediamine, 5-Me-3,2,3-tet.—The procedures of Hamilton[3] and Schaefer[4] were used with alteration. To a solution of 1,3-diaminopropane (318 g, 4.3 mol) in 333 ml of absolute ethanol was added 1,2-dibromopropane (202 g, 1 mol) slowly with mechanical stirring. The temperature was maintained at 50° throughout the addition, after which the solution was heated to near reflux and stirred for 3–4 hr. After cooling, 266 g of potassium hydroxide was added and the solution was stirred for 1 hr. The white solid which formed was filtered, 1,3-diaminopropane and ethanol were evaporated under reduced pressure, and the clear oily product was collected by vacuum distillation at 122–124° (0.5 mm); yield, 21.1 g.

Preparation of (−)-5(*R*)-Methyl-4,7-diaza-1,10-decanediamine, (−)-5-Me-3,2,3-tet.—The preparation was adapted from a procedure of Goto, *et al.*[5] γ-Bromopropylphthalimide (80 g, 0.3 mol) was melted completely and with mechanical stirring (−)-1,2-diaminopropane[6] (11.1 g, 0.15 mol) was added slowly over a period of 3 hr at a temperature of 130–140°. The resulting viscous mixture was heated for an additional 20 hr and then hydrolyzed for 5 hr with 275 ml of concentrated hydrochloric acid at 110° while stirring. After cooling the mixture to room temperature overnight, the solid was filtered and washed once with water, and the combined washing and filtrate were concentrated under reduced pressure to near dryness. A solution of 150 g of sodium hydroxide in 150 ml of water was then slowly added with heating and the oily layer which formed was extracted with benzene. The benzene extracts were dried over anhydrous sodium sulfate. The benzene was evaporated at reduced pressure and the residue was vacuum distilled to a clear oil at 140–150° (1.2 mm); yield, 4.2 g.

Preparation of *N,N'*-Bis(2-picolyl)-1-methyl-1,2-diaminoethane, picpn.—1,2-Diaminopropane (18 g, 0.24 mol) was treated with pyridine-2-carboxaldehyde (53.5 g, 0.50 mol) by the method described by Goodwin and Lions for ethylenediamine.[7] The product was vacuum distilled as a thick yellow oil, bp 180–190° (1 mm); yield, 28.1 g.

Preparation of (+)-*N,N'*-Bis(2-picolyl)-1(*S*)-methyl-1,2-diaminoethane, (+)-picpn.—The procedure used here was identical with that of the racemic picpn using (+)-1,2-diaminopropane instead of (±)-1,2-diaminopropane. The yellow product was vacuum distilled at 180–190° (1 mm); yield, 10.2 g.

Preparation of *trans*-Dichloro(5-methyl-4,7-diaza-1,10-decanediamine)cobalt(III) Chloride, *trans*-[Co(5-Me-3,2,3-tet)$\mathrm{Cl_2}$]Cl.—A solution of 5-Me-3,2,3-tet (7.52 g, 0.04 mol) and cobalt(II) chloride hexahydrate (9.52 g, 0.04 mol) in 100 ml of water was air oxidized with carbon dioxide free air for 12 hr. Concentrated hydrochloric acid (10 ml) was added to the resulting solution and it was evaporated to near dryness on a steam bath with the aid of a jet of air. The crude green product was filtered, washed with a little cold water, then air-dried, and stored in an oven at 100° overnight. The *trans*-[Co(5-Me-3,2,3-tet)$\mathrm{Cl_2}$]Cl was purified by recrystallization from a minimum of hot water; yield, 2.40 g. *Anal.* Calcd for $\mathrm{CoC_9H_{24}N_4Cl_3}$: C, 30.56; H, 6.79; N, 15.84. Found: C, 29.76; H, 6.23; N, 15.35.

Preparation of *trans*-Dichloro((−)-5(*R*)-methyl-4,7-diaza-1,10-decanediamine)cobalt(III) Chloride, *trans*-[Co((−)-5-Me-3,2,3-tet)$\mathrm{Cl_2}$]Cl.—The procedure used here was identical with that given for *trans*-[Co(5-Me-3,2,3-tet)$\mathrm{Cl_2}$]Cl using (−)-5(*R*)-methyl-4,7-diaza-1,10-decanediamine in place of the racemic tetramine; yield, 2.37 g.

Preparation of *uns-cis*-Oxalato(5-methyl-4,7-diaza-1,10-decanediamine)cobalt(III) Iodide Monohydrate, *uns-cis*-[Co(5-Me-3,2,3-tet)ox]I·$\mathrm{H_2O}$.—A solution containing *trans*-[Co(5-Me-3,2,3-tet)$\mathrm{Cl_2}$]Cl (10.6 g, 0.03 mol) and 5.6 g of potassium oxalate monohydrate in 80 ml of water was heated on a steam bath for 2 hr. The solution was filtered hot and then evaporated on a steam bath to a volume of 25 ml. Solid sodium iodide, 6.0 g, was then added, and on cooling, the pink solid was filtered, washed with cold water and methanol, and recrystallized once from water; yield, 1.5 g. *Anal.* Calcd for $\mathrm{CoC_{11}H_{26}N_4O_5I}$: C, 27.51; H, 5.41; N, 11.67. Found: C, 27.75; H, 6.17; N, 11.48.

Resolution of *uns-cis*-Oxalato(5-methyl-4,7-diaza-1,10-decanediamine)cobalt(III) Iodide, *uns-cis*-[Co(5-Me-3,2,3-tet)ox]I.—The procedure used here is similar to that used by Schaefer[4] for the resolution of *uns-cis*-[Co(2,3,2-tet)ox]Cl·$\mathrm{4H_2O}$. To a constantly stirred solution of *uns-cis*-[Co(5-Me-3,2,3-tet)ox]I (2.30 g, 0.005 mol) in 100 ml of water was added 0.85 g (0.005 mol) of silver nitrate dissolved in 10 ml of water. After digestion for 10 min, the silver halide was removed by filtration and 0.99 g (0.0025 mol) of potassium hydrogen *d*-tartrate dibenzoate was added in 50 ml of warm water. After cooling to room temperature, the solution was evaporated under a jet of air to half the original volume. The *d*-tartrate dibenzoate salt was filtered, washed with cold water, and air dried. Purification was effected by dissolution in 100 ml of hot water, filtering and washing with methanol, and then drying in a vacuum desiccator over calcium chloride.

To the filtrate, from the formation of the tartrate salt, was added another 0.99 g of potassium hydrogen *d*-tartrate dibenzoate. After standing 1 hr the solid was filtered and discarded. To this filtrate was added 2.5 ml of concentrated $\mathrm{HClO_4}$ and with evaporation at room temperature (+)-*uns-cis*-[Co(5-Me-3,2,3-tet)ox]$\mathrm{ClO_4}$ was filtered, washed with methanol, and then air-dried; $[M]_{522} = +2154°$, $[M]_{450} = -1421°$.

The tartrate salt was dissolved in 20 ml of water containing 5 ml of concentrated HCl. D-Tartaric acid dibenzoate was filtered off and 5 ml of concentrated $\mathrm{HClO_4}$ was added. The crystals of (−)-*uns-cis*-[Co(5-Me-3,2,3-tet)ox]$\mathrm{ClO_4}$ which formed on evaporation and cooling were filtered and washed with methanol; $[M]_{522} = -8698°$, $[M]_{450} = +5968°$.

Preparation of *uns-cis*-Oxalato((−)-5(*R*)-methyl-4,7-diaza-1,10-decanediamine)cobalt(III) Iodide Monohydrate, *uns-cis*-[Co((−)-5-Me-3,2,3-tet)ox]I·$\mathrm{H_2O}$. The method used here was the same as for the preparation of *uns-cis*-[Co(5-Me-3,2,3-tet)ox]I using (−)-5(*R*)-methyl-4,7-diaza-1,10-decanediamine in place of the racemic amine; yield, 1.4 g. *Anal.* Calcd for

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(6) (±)-1,2-diaminopropane was resolved using (+)-tartaric acid: F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Amer. Chem. Soc.*, **81**, 290 (1959). The least soluble diastereoisomer was the levo isomer. After ten recrystallizations the diastereoisomer was converted to the hydrochloride by the method of J. C. Bailar, H. B. Jonassen, and A. D. Gott, *J. Amer. Chem. Soc.*, **74**, 3131 (1952). The levo base was obtained by cautious distillation of the hydrochloride mixed with sodium hydroxide. This gave (−)-1,2-diaminopropane $[\alpha]_{546}$ −27.4° (aqueous), in agreement with Bailar, Jonassen, and Gott.

(7) H. A. Goodwin and F. Lions, *J. Amer. Chem. Soc.*, **82**, 5021 (1960).

$CoC_{11}H_{26}N_4O_5I$: C, 27.51; H, 5.41; N, 11.67. Found: C, 28.02; H, 6.12; N, 11.57. $[M]_{522}$ +8689°, $[M]_{450}$ −5958°.

Preparation of *uns-cis*-Malonato(5-methyl-4,7-diaza-1,10-decanediamine)cobalt(III) Chloride, *uns-cis*-[Co(5-Me-3,2,3-tet)-mal]Cl.—A solution containing *trans*-[Co(5-Me-3,2,3-tet)Cl_2]Cl (3.5 g, 0.01 mol) and disodium malonate monohydrate (1.66 g, 0.01 mol) in 33 ml of water was warmed on a steam bath for 2 hr. The solution was then reduced on a steam bath with the aid of a jet of air until a crust formed on the surface. After cooling in ice, the pink precipitate was filtered, washed with methanol, air-dried, and recrystallized from a minimum of hot water; yield, 2.4 g. *Anal.* Calcd for $CoC_{12}H_{28}N_4O_5Cl$: C, 35.78; H, 6.95; N, 13.91. Found: C, 35.62; H, 6.93; N, 13.74.

Preparation of *uns-cis*-Dichloro(*N,N* -bis(2-picolyl)-1-methyl-1,2-diaminoethane)cobalt(III) Perchlorate, *uns-cis*-[Co(picpn)-Cl_2]ClO_4.—The procedure used here is analogous to the preparation of *uns-cis*-[Co(bnpic)Cl_2]ClO_4 reported by Bosnich.[8] A stream of carbon dioxide free air was bubbled through a solution of picpn ligand (10.24 g, 0.04 mol) and cobalt(II) chloride hexahydrate (9.52 g, 0.04 mol) in water (370 ml) for 6 hr. To the dark brown solution was then added 5 ml of concentrated HCl and 10 ml of concentrated $HClO_4$ and the resulting solution was evaporated on a steam bath to a volume of 50 ml. On standing at room temperature for 2 days the deep violet product precipitated, was collected, washed with a little water and acetone, and then air dried. A second crop of crystals could be obtained from the mother liquor by doubling the volume with methanol and allowing the resulting solution to stand at room temperature; yield, 7.7 g. *Anal.* Calcd for $CoC_{15}H_{20}N_4O_4Cl_3$: C, 37.07; H, 4.11; N, 11.53. Found: C, 36.87; H, 4.26; N, 11.20.

Preparation of *uns-cis*-Dichloro((+)-*N,N'*-bis(2-picolyl)-1(*S*)-methyl-1,2-diaminoethane)cobalt(III) Perchlorate, *uns-cis*-[Co((+)picpn)Cl_2]ClO_4.—The procedure used here was identical with that given for *uns-cis*-[Co(picpn)Cl_2]ClO_4 using (+)-*N,N'*-bis(2-picolyl)-1(*S*)-methyl-1,2-diaminoethane in place of the racemic amine; yield, 7.15 g, $[M]_{558}$ −5572°.

Preparation of *uns-cis*-Dibromo(*N,N'*-bis(2-picolyl)-1-methyl-1,2-diaminoethane)cobalt(III) Perchlorate, *uns-cis*-[Co(picpn)-Br_2]ClO_4.—The method was the same as for the preparation of *uns-cis*-[Co(picpn)Cl_2]ClO_4 using 47% HBr in place of concentrated HCl; yield, 7.9 g. *Anal.* Calcd for $CoC_{15}H_{20}N_4O_4Br_2Cl$: C, 31.33; H, 3.48; N, 9.74. Found: C, 31.13; H 3.30; N, 9.65.

Preparation of *uns-cis*-Oxalato(*N,N'*-bis(2-picolyl)-1-methyl-1,2-diaminoethane)cobalt(III) Iodide, *uns-cis*-[Co(picpn)ox]I.—A solution of *uns-cis*-[Co(picpn)Cl_2]ClO_4 (1.45 g, 0.0003 mol) and 0.55 g of potassium oxalate monohydrate in 60 ml of water was warmed on a steam bath for 2 hr. To the hot solution, sodium iodide (0.74 g, 0.005 mol) was added and the solution was evaporated on a steam bath until a crust formed on the surface. After cooling to room temperature the bright orange crystals were filtered, washed with methanol, and recrystallized from water; yield, 1.2 g. *Anal.* Calcd for $CoC_{17}H_{20}N_4O_4I$: C, 38.49; H, 3.77; N, 10.57. Found: C, 38.51; H, 3.78; N, 10.58.

Preparation of *uns-cis*-Oxalato((+)*N,N'*-bis(2-picolyl)-1(*S*)-methyl-1,2-diaminoethane)cobalt(III) Iodide, *uns-cis*-[Co((+)-picpn)ox].—The procedure used here was identical with that given for *uns-cis*-[Co(picpn)ox]I using *uns-cis*-[Co((+)picpn)Cl_2]ClO_4 in place of *uns-cis*-[Co(picpn)Cl_2]ClO_4; yield, 1.15 g, $[M]_{516}$ −3010°.

Preparation of *uns-cis*-Dinitro(*N,N'*-bis(2-picolyl)-1-methyl-1,2-diaminoethane)cobalt(III) Perchlorate, *uns-cis*-[Co(picpn)-(NO_2)$_2$]ClO_4.—A solution of sodium nitrite (0.912 g, 0.013 mol) and *uns-cis*-[Co(picpn)Cl_2]ClO_4 (3.1 g, 0.0064 mol) in water (100 ml) was heated on a steam bath for 10 min and then filtered directly into a solution of sodium perchlorate (8 g) in 25 ml of water. After cooling in ice, the yellow solid was filtered, washed with a little cold water, air-dried, and recrystallized from water; yield, 2.5 g. *Anal.* Calcd. for $CoC_{15}H_{20}N_6O_8Cl$: C, 34.54; H, 3.94; N, 16.58. Found: C, 34.56; H, 3.90; N, 16.16.

Preparation of *uns-cis*-Dinitro((+)-*N,N'*-bis(2-picolyl)-1(*S*)-methyl-1,2-diaminoethane)cobalt(III) Perchlorate, *uns-cis*-[Co((+)picpn)(NO_2)$_2$]ClO_4.—The procedure used here is similar to the preparation of *uns-cis*-[Co(bnpic)(NO_2)$_2$]ClO_4 reported by Bosnich.[8] Sodium nitrite (0.228 g, 0.0033 mol) in water (10 ml) was added to a hot solution of *uns-cis*-[Co((+)picpn)Cl_2]ClO_4 (0.776 g, 0.0016 mol) in 20 ml of water. The solution was boiled for 0.5 min and filtered hot into a solution of sodium perchlorate (2 g) in 10 ml of water. On cooling in ice, bright yellow crystals precipitated, were filtered, washed once with cold water, and recrystallized from a minimum of water; yield 0.15 g; $[M]_{490}$ −3343°, $[M]_{430}$ +4603°.

Resolution of *uns-cis*-Dinitro(*N,N'*-bis(2-picolyl)-1-methyl-1,2-diaminoethane)cobalt(III) Perchlorate, *uns-cis*-[Co(picpn)(NO_2)$_2$]-ClO_4.—The procedure used here was analogous to that reported by Douglas for the partial resolution of cobalt(III) chelated complexes using ion-exchange cellulose.[9] In the resolution, 20 g of Cellex-CM cation-exchange cellulose in the sodium form (Bio-Rad Laboratories) was stirred with 400 ml of 0.01 *M* $NaClO_4$. After allowing the cellulose to settle for 45 min, the clear solution was decanted and the process was repeated. After adding 100 ml of 0.01 *M* $NaClO_4$ the cellulose mixture was rapidly stirred and immediately poured into a column. The cellulose was allowed to settle for 1 hr and the surface was protected by pouring in a layer of sand. First 100 ml of 0.10 *M* $NaClO_4$ and then 100 ml of water were passed through the column. A solution of 0.2 g of *uns-cis*-[Co(picpn)(NO_2)$_2$]ClO_4 in 100 ml of water was then loaded on the column and eluted over a period of 4 hr with 0.01 *M* $NaClO_4$. Fifteen fractions were collected and the process was repeated using the first three fractions.

The first four fractions on the second pass through the column all contained optically pure (−)-*uns-cis*-[Co(picpn)(NO_2)$_2$]$^+$. The fractions were combined and concentrated to dryness. After further drying in a vacuum oven the solid was dissolved in methanol to obtain the ORD and CD spectra; $[M]_{490}$ −3348°, $[M]_{430}$ +4608°.

Removal of Optically Pure Ligand from (−)-*uns-cis*-[Co(picpn)-(NO_2)$_2$]ClO_4 and (−)-*uns-cis*-[Co(5-Me-3,2,3-tet)ox]I·H_2O.—The method used to determine if 5-methyl-4,7-diaza-1,10-decanediamine and *N,N'*-bis(2-picolyl)-1-methyl-1,2-diaminoethane coordinated stereospecifically was identical with that reported by Worrell.[10] A sample of optically pure oxalato or nitro complex, 30 mg, was weighed into a 25-ml volumetric flask. To this 0.15 g of KCN and 4 drops of 1.0 *N* NaOH were added and the sample was diluted to the mark with water and allowed to stand at room temperature for 3 hr. The rotation was then measured in a 2-dm polarimeter tube at 546 and 589 nm (Table I).

TABLE I

OPTICAL ROTATIONS OF SOME TETRAMINE LIGANDS PREPARED FROM RESOLVED DIAMINES AND ISOLATED FROM RESOLVED COMPLEXES

Amine	λ, nm	[α], deg	[M], deg
(−)-5-Me-3,2,3-tet	589	−29.1	−54.7
	546	−27.3	−51.3
(+)-5-Me-3,2,3-tet	589	30.4	57.1
removed from the complex	546	28.9	54.3
(+)-picpn	589	20.8	53.2
	546	20.2	51.7
(+)-picpn	589	21.6	55.2
removed from the complex	546	20.9	53.5

Results and Discussion

Ligand Synthesis.—5-Me-3,2,3-tet was prepared by the reaction of 1,2-dibromopropane with 1,3-diaminopropane in absolute ethanol. A different synthesis was employed for (−)-5-Me-3,2,3-tet in which the product was obtained through the hydrolysis of (−)-*N,N'*-bis(3-propylphthalimide)-1,2-diaminopropane. The picpn and (+)-picpn ligands were obtained by the reaction of 1,2-diaminopropane and (+)-1,2-diaminopropane with excess pyridine-2-carboxaldehyde by reduction with zinc and acetic acid.

The pmr spectrum of 5-Me-3,2,3-tet is shown in Figure 1a. For 5-Me-3,2,3-tet the integrated intensities are correct if it is assumed that the high-field doublet centered at τ 9.10 arises from the side-chain methyl protons. The large singlet at τ 8.87 then repre-

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[9] J. I. Legg and B. E. Douglas, *ibid.*, **7**, 1452 (1968).

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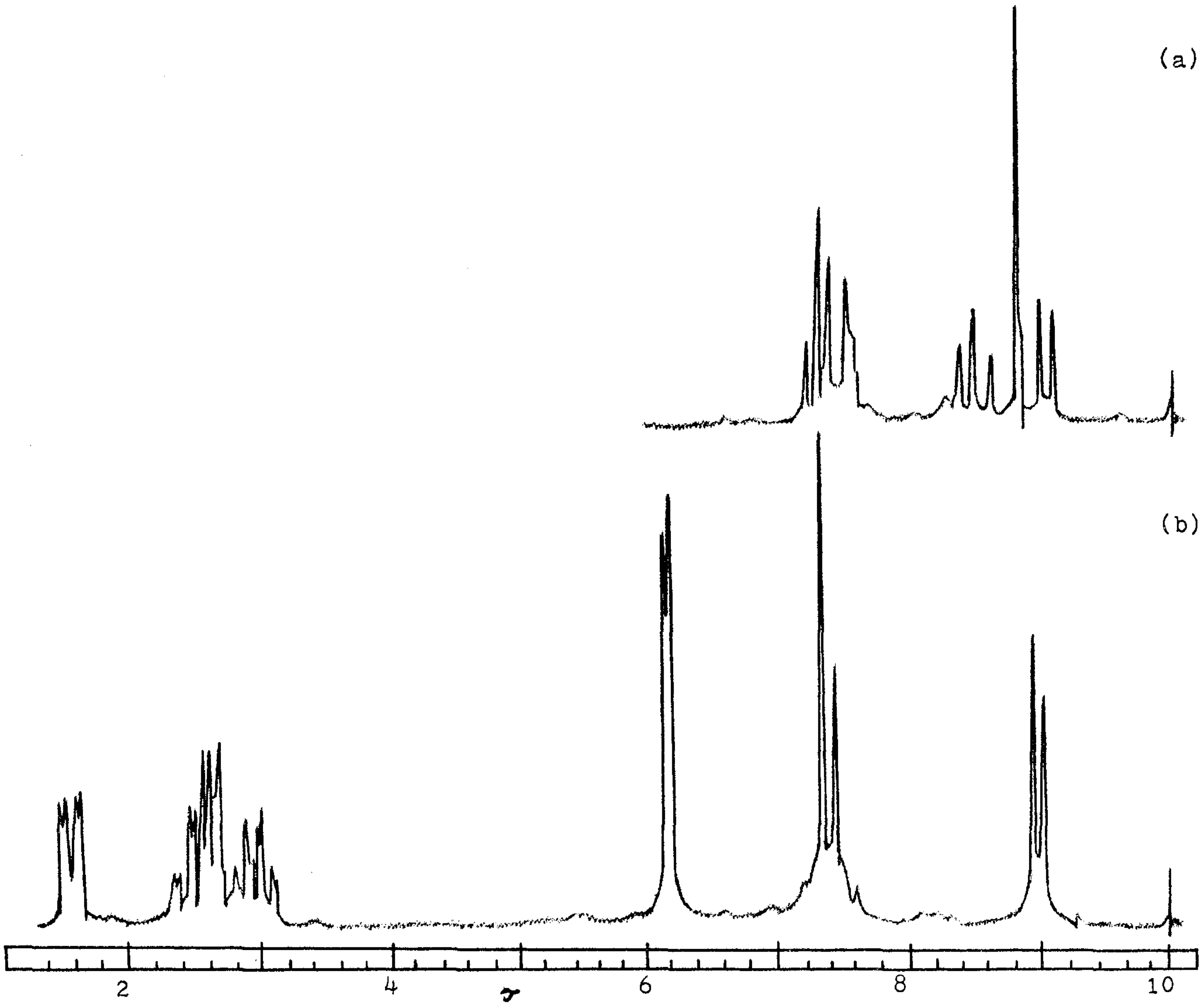

Figure 1.—Pmr spectra for 5-Me-3,2,3-tet (a) and picpn (b) in carbon tetrachloride.

sents all the NH protons and the quintet centered at τ 8.49 integrates to the CH protons on the second and ninth carbons, respectively. The other CH protons apparently overlap each other at about τ 7.4.

Figure 1b shows the pmr spectrum of the picpn ligand. The pyridine protons occur between τ 1 and 3.3, the methylene protons occur at τ 6.2, and the methyl side chain occurs at τ 9.1. The remaining CH and NH protons overlap around τ 7.5. Both pmr spectra for the (+)picpn and (−)-5-Me-3,2,3-tet were identical with those of their racemic analogs.

Complex Synthesis and Resolution.—The dichloro and dibromo 5-Me-3,2,3-tet– and picpn–Co(III) complexes were prepared by the generally accepted technique of air oxidation of aqueous cobalt(II) chloride and ligand followed by acidification with the appropriate acid. *trans*-[Co(5-Me-3,2,3-tet)Cl_2]Cl was obtained as a light green solid and both *cis*-[Co(picpn)Cl_2]ClO_4 and *cis*-[Co(picpn)Br_2]ClO_4 were obtained as deep violet crystals. The cis oxalato amd malonato complexes of 5-Me-3,2,3-tet were prepared from *trans*-[Co(5-Me-3,2,3-tet)Cl_2]Cl by heating an aqueous solution of the complex with a stoichiometric amount of potassium oxalate or sodium malonate. *cis*-[Co(picpn)ox]I was prepared in a similar manner using potassium oxalate with *cis*-[Co(picpn)Cl_2]ClO_4 and the *cis*-[Co(picpn)-$(NO_2)_2$]ClO_4 complex was prepared from the chloro species by reaction with NO_2^- ions. The active ligand complexes were prepared using the same methods as for the racemic ligand complexes. In all cases fractional crystallization failed to reveal any species having properties different from those of the first isolated complexes.

Complete resolution of *cis*-[Co(5-Me-3,2,3-tet)ox]$^+$ was obtained using the hydrogen *d*-tartrate dibenzoate anion as the resolving agent. The extreme insolubility of the diastereoisomeric salt precluded recrystallization from common solvents. Once separated from the resolving agent, this complex, like the complexes prepared from the resolved ligands, was recrystallized from water to constant rotation.

Attempted resolutions of *cis*-[Co(picpn)ox]$^+$, *cis*-[Co(picpn)Br_2]$^+$, and *cis*-[Co(picpn)$(NO_2)_2$]$^+$ through diastereoisomer formation were unsuccessful. The complex *cis*-[Co(picpn)$(NO_2)_2$]$^+$ was resolved chromatographically on ion-exchange cellulose. The repeated slow elution of *cis*-[Co(picpn)$(NO_2)_2$]$^+$ with aqueous sodium perchlorate through the sodium form of Cellex CM cation-exchange cellulose (Bio-Rad Laboratories) produced optically pure (−)-*cis*-[Co(picpn)-

$(NO_2)_2]^+$. Optical purity was established by repeating the chromatographic procedure until constant rotation was achieved (two passes suffice).

Stereochemistry.—Only one geometrical isomer was isolated for each complex, $[Co(5\text{-}Me\text{-}3,2,3,\text{-}tet)ox]^+$ and $[Co(5\text{-}Me\text{-}3,2,3\text{-}tet)mal]^+$. Each complex was fractionally crystallized as the iodide and chloride salts, respectively, and all fractions were spectrophotometrically identical. For $[Co(picpn)ox]^+$ and $[Co(picpn)X_2]^{n+}$ (X = Cl, Br, NO_3) the iodide and perchlorate salts were obtained. Both the dichloro and dibromo complexes dissociated rapidly in water yielding chloride or bromide and an aquo species. The dinitro and oxalato complexes appear to be relatively stable in water and all species are stable in methanol. For each complex fractional crystallization from methanol produced fractions that were spectrophotometrically identical. The electronic absorption spectra for all the active ligand complexes are identical with those obtained for the racemic compounds. These observations indicate that there is only one geometrical isomer present for each of the complexes.

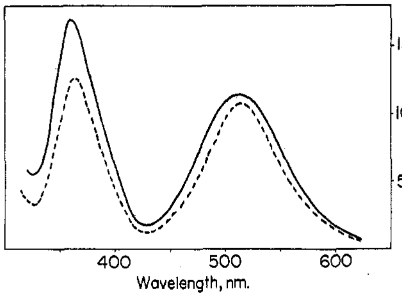

Figure 2.—Electronic absorption spectra for *uns-cis*-$[Co(5\text{-}Me\text{-}3,2,3\text{-}tet)ox]^+$ (—) and *uns-cis*-$[Co(5\text{-}Me\text{-}3,2,3\text{-}tet)mal]^+$ (- - - -).

Electronic Spectra.—The electronic absorption spectra for the oxalato and malonato complexes of 5-Me-3-2,3-tet are shown in Figure 2 and the data are presented in Table II.

TABLE II

ELECTRONIC SPECTRAL PARAMETERS FOR SOME picpn, 5-Me-3,2,3-tet, AND trien COMPLEXES OF COBALT(III)

Compound	λ_{max}, nm	ϵ_{max}
uns-cis-$[Co(trien)ox]^+$	497	179
	357	179
s-cis-$[Co(trien)ox]^+$	493	110
	357	123
uns-cis-$[Co(5\text{-}Me\text{-}3,2,3\text{-}tet)ox]^+$	512	115
	364	170
uns-cis-$[Co(5\text{-}Me\text{-}3,2,3\text{-}tet)mal]^+$	514	105
	367	125
uns-cis-$[Co(picpn)ox]^+$	495	211
	362	231
s-cis-$[Co(picpn)ox]^+$	393	164
	362	187
uns-cis-$[Co(picpn)Cl_2]^+$	544	141
uns-cis-$[Co(picpn)(NO_2)_2]^+$	445	361
uns-cis-$[Co(picpn)Br_2]^+$	543	124

Figure 3 shows the electronic absorption spectra of $[Co(picpn)ox]^+$ and $[Co(picpn)X_2]^{n+}$ (X = Cl, Br, NO_2) in methanol solution. These complexes are assigned the cis configuration on comparison with the related *uns-cis*-$[Co(bnpic)(NO_2)_2]^+$ and *cis*-[Co(*l*-picpn)XY] (X = Y = Cl, OH, N_3; X = NO_2, Y = OH_2) complexes.[2,8]

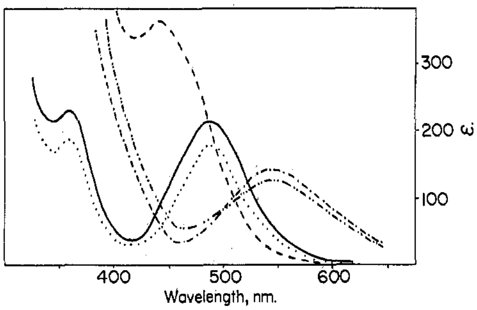

Figure 3.—Electronic absorption spectra for *uns-cis*-$[Co(picpn)ox]^+$ (—), *uns-cis*-$[Co(picpn)(NO_2)_2]^+$ (- - -), *uns-cis*-$[Co(picpn)Cl_2]^+$ (- - - -), *uns-cis*-$[Co(picpn)Br_2]^+$ (–· · –), and *s-cis*-$[Co(picpn)ox]^+$ (· · · ·) in methanol.

Optical Activity, Absolute Configuration, and Stereospecific Coordination. *N,N′*-Bis(2-picolyl)-1(*S*)-methyl-1,2-diaminoethane.—The circular dichroism and optical rotatory disperion spectra for *cis*-$[Co((+)picpn)Cl_2]^+$, *cis*-$[Co((+)picpn)ox]^+$, and *cis*-$[Co((+)picpn)(NO_2)_2]^+$ are shown in Figures 4 and 5, respectively. The similarity in the major bands of both the CD and ORD indicate that only one geometrical isomer is present. The assignment of a cis configuration was made on the basis of the electronic spectra, and molecular models indicate that the picpn tetramine may easily accommodate either the s-cis or uns-cis configurations.

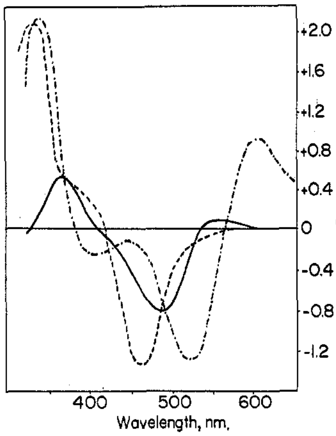

Figure 4.—Circular dichroism spectra for *uns-cis*-$[Co((+)picpn)ox]^+$ (—), *uns-cis*-$[Co((+)picpn)(NO_2)_2]^+$ (- - -), and *uns-cis*-$[Co((+)picpn)Cl_2]^+$ (–·–·).

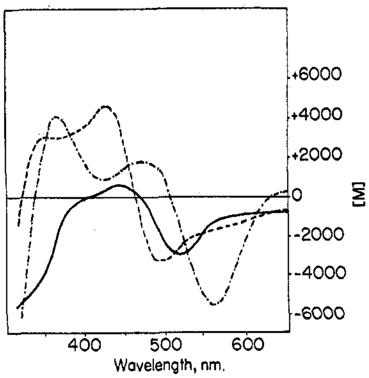

Figure 5.—Optical rotatory dispersion curves for *uns-cis*-$[Co((+)picpn)ox]^+$ (—), *uns-cis*-$[Co((+)picpn)(NO_2)_2]^+$ (- - -], and *uns-cis*-$[Co((+)picpn)Cl_2]^+$ (–·–·).

The assignment of absolute configuration is then based on the most stable conformation of the pyridine rings about the predetermined conformation of the five-membered chelate ring (+)-1(*S*)-methyl-1,2-diaminoethane (Figure 6a) in which the substituent occupies an equatorial position.

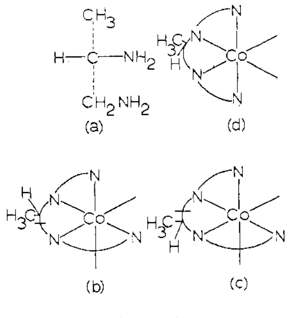

Figure 6.

For the uns-cis isomer, two possibilities arise depending on the position of the substituent (Figure 6b, 6c), but the Δ absolute configuration may be assigned to each. If the configuration of the central chelate ring is preserved by the requirement that the substituent occupy an equatorial position, the single s-cis isomer (Figure 6d) may be assigned the Λ absolute configuration.[11]

In applying Mason's[12] and MacDermott's[13] formalisms to *cis*-[Co((+)picpn)ox]$^+$ and *cis*-[Co((+)-picpn)X$_2$]$^{n+}$ (X = NO$_2$, Cl) the dominant $^1A_1 \rightarrow {}^1A_2$ low-energy Cotton effect, assuming the complexes approximate to C_2 symmetry, is assigned to the major CD and ORD components centered between 450 and 575 nm. For all three complexes this band is negative and a Δ absolute configuration is assigned. By relation to the previous models this defines an uns-cis configuration for the picpn ligand. The optically pure isomer (−)-*cis*-[Co(picpn)(NO$_2$)$_2$]$^+$ obtained by cellulose chromatography has ORD and CD spectra, Figure 7, identical with those of the corresponding active ligand dinitro complex.

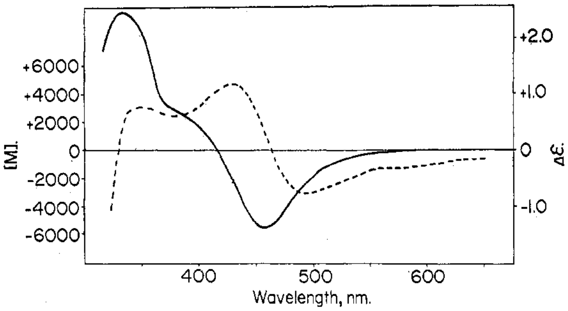

Figure 7.—Circular dichroism spectrum (—) and optical rotatory curve (- - -) for (−)-*uns-cis*-[Co(picpn)(NO$_2$)$_2$]$^+$.

Stereospecific coordination of the ligand picpn is unequivocally demonstrated by comparison of the optical rotation of the ligand prepared from resolved 1,2-propanediamine with that of the ligand prepared from racemic 1,2-propanediamine and subsequently removed from the resolved complex (Table I). These data clearly show that resolving the complex is tantamount to resolving the ligand.

In examining the ligand exciton CD bands for the pyridine π → π* transitions of *cis*-[Co((+)picpn)-(NO$_2$)$_2$]$^+$, *cis*-[Co((+)picpn)Cl$_2$]$^+$, and *cis*-[Co((+)-picpn)ox]$^+$ (Figure 8) a negative band centered at 290 mμ followed by a major positive band at 263 nm is observed for the dichloro and dinitro complexes. For *cis*-[Co((+)picpn)ox] overlapping negative bands are evident. As defined by Bosnich,[14] a *large* negative band at high energies will represent an absolute configuration related to (—)-[Fe(phen)$_3$]$^{2+}$ which is Λ. In general Mason[15] has determined that only the long- and perpendicular-axis polarization of the ligand excitation contribute to CD intensity as defined for a ligand coordinated on an octahedral edge (*e.g.*, 1,10-phenanthroline (Figure 9)). In this way the short-axis-polarized transitions which point toward the metal are not optically active and the component exciton moments have a vanishing resultant.

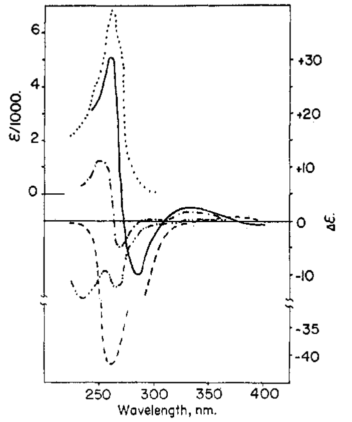

Figure 8.—Circular dichroism exciton bands for *uns-cis*-[Co((+)picpn)Cl$_2$]$^+$(—), *uns-cis*-[Co((+)picpn)(NO$_2$)$_2$]$^+$(–·–·), *uns-cis*-[Co((+)picpn)ox]$^+$ (–··–··), and *s-cis*-[Co((+)picpn)ox]$^+$ (- - -) and the electronic absorption spectrum for (+)picpn (····).

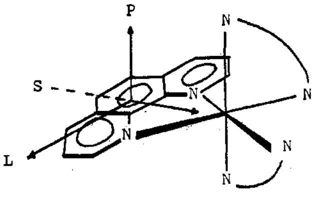

Figure 9.

In the active ligand picpn complexes the selection rules may not apply since neither the long-axis nor the perpendicular-axis polarization of the π → π* transitions for the pyridine rings occupies an octahedral edge. Most probably the overall symmetry is considerably lowered to result in more observed bands.

If it is assumed that the first major positive component at high energy represents a ligand exciton band, then *cis*-[Co((+)picpn)Cl$_2$]$^+$ and *cis*-[Co((+)picpn)-(NO$_2$)$_2$]$^+$ have Δ absolute configurations in agreement

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[11] *Inorg. Chem.*, **9**, 1 (1970).

[12] A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965); S. F. Mason, *Quart. Rev. Chem. Soc.*, **17**, 20 (1963).

[13] T. E. MacDermott and A. M. Sargeson, *Aust. J. Chem.*, **16**, 334 (1963).

[14] B. Bosnich, *Accounts Chem. Res.*, **2**, 266 (1969).

[15] S. F. Mason, *Inorg. Chim. Acta*, **89** (1968).

with the assignments made using the dominant Cotton effects in the d–d regions of the CD spectra. Once again this defines a uns-cis geometry for both complexes. The absence of a positive exciton band for *cis*-[Co((+)picpn)ox]$^+$ is unexplained but can be rationalized when it is considered that the oxalate dianion should also produce an exciton band which would add to the number of observed exciton transitions.

In aqueous solution, the sign of the major Cotton effect for *cis*-[Co((+)picpn)ox]$^+$ is reversed relative to that observed in fresh methanolic solutions (Figure 10). This apparent inversion is also observed on standing either in the solid state or in methanolic solution and implies conversion to the Λ absolute configuration and s-cis topology (*vide supra*). Indeed, comparison of the ORD and CD curves of *cis*-[Co((+)picpn)ox]$^+$ with (+)-*s-cis*-[Co(trien)ox]$^{+4}$ shows considerable likeness. The comparison of the electronic absorption spectra for two samples of *cis*-[Co((+)picpn)ox]$^+$ is shown in Figure 3. For a freshly prepared sample a substantially larger molar extinction coefficient is observed which decreases after standing in the solid state. This decrease is instantaneous in aqueous solution. An increase in the molar extinction coefficient has previously been shown to accompany s-cis → uns-cis isomerization in the triethylenetetramine system.[16] Therefore, a decrease could indicate a uns-cis → s-cis geometrical isomerization which is in agreement with the observed inversion of the ORD and CD spectra. The observed exciton band for *cis*-[Co((+)picpn)ox]$^+$ is also negative in aqueous solution, in agreement with s-cis geometry. Identical results are also obtained from the complex prepared with the ligand racemate.

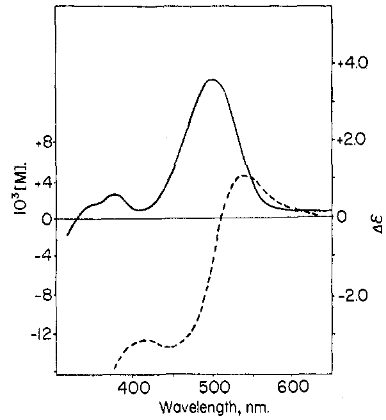

Figure 10.—Circular dichroism spectrum (—) and optical rotatory dispersion curve (- - -) for *s-cis*-[Co((+)picpn)ox]$^+$.

5-Methyl-4,7-diaza-1,10-decanediamine.—The circular dichroism spectra and the optical rotatory dispersion curves of (−)-*cis*-[Co((−)-5-Me-3,2,3-tet)ox]$^+$ and (+)-*cis*-[Co((−)-5-Me-3,2,3-tet)ox]$^+$ are shown in Figure 11. Here, as in the picpn–Co(III) complexes, s-cis and uns-cis geometries are possible. By approximating C_{2v} symmetry, the major band centered at 492 nm in the CD and 525 nm in the ORD may be assigned to the $^1A_1 \rightarrow {}^1A_2$ transition. Using Mason's and McDermott's formalisms the dominant low-energy Cotton effect is positive for (+)-*cis*-[Co((−)-5-Me-3,2,3-tet)ox]$^+$ and negative for (−)-*cis*-[Co(5-Me-3,2,3-tet)ox]$^+$. Thus (+)-*cis*-[Co((−)-5-Me-3,2,3-tet)ox]$^+$ is assigned the Λ absolute configuration and (−)-*cis*-[Co(5-Me-3,2,3-tet)ox]$^+$ is assigned the Δ absolute configuration. Furthermore, by comparison with the previous assignments for the picpn complexes, both complexes may also be assigned the uns-cis geometry, in contrast with the conclusions drawn from an earlier study in this laboratory.[17] There is no evidence for a topological shift such as that observed for complexes with the ligand picpn, either in solution or in the solid state.

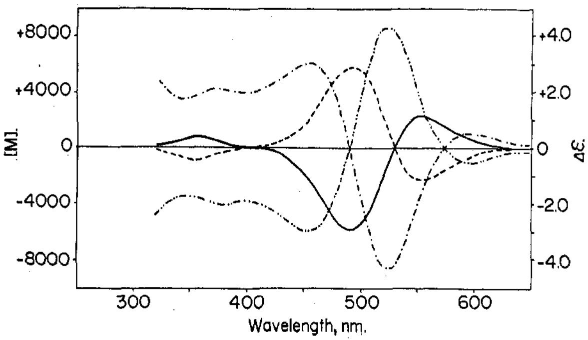

Figure 11.—Circular dichroism spectra for (−)-*uns-cis*-[Co(5-Me-3,2,3-tet)ox]$^+$ (—) and *uns-cis*-[Co((−)-5-Me-3,2,3-tet)ox]$^+$ (- - -) and the optical rotatory dispersion curves for (−)-*uns-cis*-[Co(5-Me-3,2,3-tet)ox]$^+$ (–·–·) and *uns-cis*-[Co((−)-5-Me-3,2,3-tet)ox]$^+$ (–··–··).

Stereospecific coordination is demonstrated by comparison of the optical rotations of the ligand prepared from the resolved diamine with that of the ligand prepared from the racemic diamine and subsequently isolated from the resolved complex (Table I). As shown for the ligand picpn, these data indicate that resolving the complex is tantamount to resolving the ligand.

The optical rotatory dispersion and circular dichroism curves for *trans*-[Co((−)-5-Me-3,2,3-tet)Cl$_2$]$^+$ are shown in Figure 12. The complex has been assigned an *SS* configuration about the secondary nitrogens using the hexadecadal or double-octant rule of Mason.[18] This assignment is in agreement with a recent study.[19]

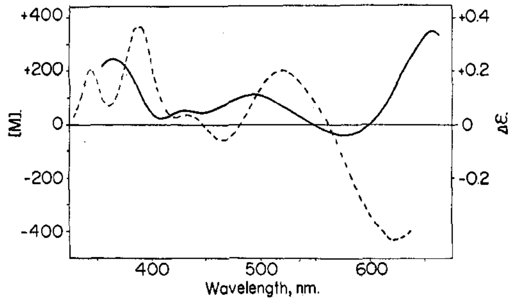

Figure 12.—Circular dichroism spectrum (——) and optical rotatory dispersion curve (- - -) for (−)$_{589}$-*trans*-(*SS*)-[Co((−)-5-Me-3,2,3-tet)Cl$_2$]$^+$ in acetonitrile.

In constructing molecular models using 5(*R*)-methyl-4,7-diaza-1,10-decanediamine, the *R* configuration of the asymmetric carbon fixes the five-membered

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[16] G. R. Brubaker and D. P. Schaefer, *Inorg. Chem.*, **8**, 1794 (1969).

[17] G. R. Brubaker and D. P. Schaefer, *ibid.*, **10**, 968 (1971).

[18] S. F. Mason, *Chem. Commun.*, 865 (1969).

[19] L. T. DeHays, D. H. Busch, and M. D. Alexander, private communication.

chelate ring in the λ conformation which, in turn, fixes the adjacent sedondary amines in the *S* configuration. Since the λ conformation is fixed in both the trans and cis geometries, the trans ion has a λ chirality for the central ring and the six-membered rings have chair conformations. Thus, the assignments made using the molecular models are in complete agreement with those obtained for the spectra. Using the major rotation of the ORD curve, the complex may be labeled $(-)_{589}$-*trans*-$[\mathrm{Co}(5(R)\text{-Me-}3,2,3\text{-tet})\mathrm{Cl_2}]^+$.

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Inner-Sphere Electron-Transfer Reactions of Vanadium(II) with Azidoamine Complexes of Cobalt(III)

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The rates of reduction by V^{2+} of *cis*-$\mathrm{Co(en)_2NH_3N_3}^{2+}$, *trans*-$\mathrm{Co(en)_2(N_3)_2}^{+}$, *trans*-$\mathrm{Co(en)_2H_2ON_3}^{2+}$, and *cis*- and *trans*-$\mathrm{Co(NH_3)_4H_2ON_3}^{2+}$ have been measured. At 25° and unit ionic strength the observed rate constants are (in M^{-1} sec^{-1}) 10.3, 26.6, 18.1, 16.6, and about 100, respectively. The respective activation parameters for the first four complexes mentioned above and for $\mathrm{Co(NH_3)_5Cl}^{2+}$ are as follows ($\Delta H^{\ddagger}$, kcal mol^{-1}, $\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}): 12.6, −11.6; 12.2, −11.2; 11.0, −16.0; 12.1, −12.5; 7.4, −29.5. Observation of $\mathrm{VN_3}^{2+}$ as an unstable intermediate in the reduction of $\mathrm{Co(NH_3)_5N_3}^{2+}$ has been made. The implications of these data on the mechanism of reduction of Co(III) complexes by V^{2+} are discussed. It is concluded that chloride is not a bridging ligand in the V^{2+} reduction of $\mathrm{Co(NH_3)_5Cl}^{2+}$.

Introduction

The investigation of means to determine whether oxidation–reduction reactions take place by an inner-sphere or outer-sphere mechanism has been the subject of a great many studies.[1,2] There are many systems for which no direct information concerning the mechanism exists; and for those systems in which indirect arguments have been made, there are still valid doubts about the assignment of mechanism. One example of this sort will serve to illustrate the point. The rate at which a given reductant reacts with $\mathrm{Co(NH_3)_5N_3}^{2+}$ relative to its rate with $\mathrm{Co(NH_3)_5NCS}^{2+}$ is an often quoted means of determining mechanism.[3] For inner-sphere reactions, the former complex is reduced much more rapidly by those agents that do not have an extraordinary preference for bonding to the sulfur end of $\mathrm{NCS^-}$. Upon inspection of this argument, however, it is clear that the conclusion should be that a large rate ratio implies the inner-sphere mechanism for the azide ion containing system, but no conclusion can be reached about the thiocyanate ion system: it can be either inner-sphere or outer-sphere and the large rate ratio might be found. The difficulty with this approach and most others is that the perturbing influence in the relative rate comparison is the potential bridging ligand. This study is part of a program designed to probe the question of indirect mechanism determinations by means of other types of perturbations—in this case, that of the nonbridging ligands.

The determination of the mechanism of reduction of Co(III) complexes by V(II) has been greatly aided by the observation that the rate of substitution of water on the V(II) center is slow compared to most other dipositive reductants.[4–6] Those reactions between V^{2+} and another cationic reagent that take place at rates greater than about 40 M^{-1} sec^{-1} must therefore occur by the outer-sphere mechanism.[5,7] Even though $\mathrm{Co(NH_3)_5Cl}^{2+}$ reacts at a rate less than this limit, it has been previously suggested[8] that the mechanism of oxidation of V^{2+} by this reagent was outer sphere. This conclusion was based on the reduction of several Co(III) complexes containing chloride ion as the most likely bridging ligand that reacted faster than the limit of substitution-controlled reactivity. Nevertheless both these more rapidly reacting complexes as well as those that were less reactive followed a reactivity order as the "nonbridging" ligands[9] were changed that is very similar to the order observed for several other reductants[2,10,11] and related to them by linear free energy relationships. If $\mathrm{Co(NH_3)_5Cl}^{2+}$ reacted by an inner-sphere path whereas, for instance, *trans*-$\mathrm{Co(en)_2H_2OCl}^{2+}$ reacted by an outer-sphere path, it would seem likely that the *same* linear free energy relationship would not hold for both classes of reactions. The observation of Espenson[12] that the reduction of *cis*-

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(1) For a recent review, see A. G. Sykes, *Advan. Inorg. Chem. Radiochem.*, **10**, 153 (1967).

(2) R. G. Linck in "Homogeneous Catalysis," G. N. Schrauzer, Ed., Marcel Dekker, New York, N. Y., 1971.

(3) J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965).

(4) H. J. Price and H. Taube, *ibid.*, **7**, 1 (1968).

(5) N. Sutin, *Accounts Chem. Res.*, **1**, 225 (1968).

(6) M. V. Olson, Y. Kanazawa, and H. Taube, *J. Chem. Phys.*, **51**, 289 (1969).

(7) For a recent tabulation see R. G. Linck in "MTP International Review of Science, Inorganic Chemistry," Series 1, Vol. 9, M. L. Tobe, Ed., University Park Press, Baltimore, Md., 1971.

(8) P. R. Guenther and R. G. Linck, *J. Amer. Chem. Soc.*, **91**, 3769 (1969).

(9) See footnote 3 of ref 8.

(10) R. G. Linck, *Inorg. Chem.*, **9**, 2529 (1970), and references therein.

(11) J. E. Earley, *Progr. Inorg. Chem.*, **13**, 243 (1970).

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