dues give Co(II) complexes whose CD magnitudes are the sums of the two complexes containing one corresponding asymmetric residue per dipeptide. For example, in Figure 1 for both the 400-520- and 520-700nm regions the area under the curve for L-alanyl-Lalanine approximates the sum of the areas under the curves for L-alanylglycine and glycyl-L-alanine. The area under the curve for L-alanyl-D-alanine equals the difference in areas between those for L-alanylglycine and glycyl-L-alanine. Excellent agreement is obtained between magnitudes calculated from sums and observed values for the Co(III) complexes of Table I except for the 535-nm hand of L-alanyl-D-alanine where the sign is reversed. Though the agreement between calculated and observed magnitudes is poor, sign agreement is obtained if the CD over both Co(III) transitions is considered together. Scaling of the CD magnitudes of the Co(III) complexes so that all values refer to a complex with a molar absorptivity of 400 near 520 nm improves the agreement between calculated and observed values for alanyl dipeptides but worsens the agreement for phenylalanyl dipeptides. Excepting the one Co-(III) complex mentioned above, we conclude that the magnitude of the optical activity through four ligand field transitions in both cobalt(II)- and cobalt(III)dipeptide complexes consists of nearly independent and additive contributions from each amino acid residue. Similar conclusions have been reached for tetragonal peptide complexes of nickel(II), palladium(II), and copper(II) where a hexadecant regional rule appears to apply.13,20

Unless their formation is highly stereoselective, solutions of the 2:1 dipeptide complexes of both Co(II)and Co(III) will contain a mixture of diastereomers when at least one amino acid residue is asymmetric.

(20) R. B. Martin, J. M. Tsangaris, and J. W. Chang, J. Amer. Chem.
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While stereoselectivity in the labile Co(II) complexes is only thermodynamic, that in the inert Co(III) complexes may also contain kinetic contributions originating from differential rates of oxygenation. The additivity observed for the CD magnitudes indicates either that equivalent amounts of two diastereomers are present for any one set of dipeptides or that diastereomers exhibit similar CD magnitudes. Preliminary nmr results on solutions show two isomers present in approximately a 2:1 molar ratio for both the L-alanylglycine- and L-phenylalanylglycine-cobalt(III) complexes. Examination of space-filling molecular models reveals that the thermodynamically favored diastereomer possesses side chains directed toward the carboxylate oxygen rather than the amino nitrogen of the other dipeptide in a 2:1 complex. The identical 2:1 ratios for the dipeptides with a small methyl and a large benzyl side chain suggest a kinetic rather than a thermodynamic origin for stereoselectivity. As noted above experimentally it is observed that oxygenation is inhibited in dipeptide complexes containing large or branched side chains in the carboxyl terminal residue. This inhibition might produce lower yields which may account for the low values of the molar absorptivities at 520 nm in the Co(III) complexes of dipeptides with carboxyl terminal side chains. Because of the proximity of the side chains on one dipeptide with the carboxylate oxygen that is released upon oxygenation on the other, the thermodynamically favored diastereomer is not the more active kinetically. The kinetically more active diastereomer, with the side chains directed toward the amino nitrogen of the other dipeptide, leaves the approach to the carboxylate oxygens relatively unhindered. Mixed DL-dipeptides of necessity contain side chains hindering the approach of oxygen molecules, accounting for their observed²¹ slower rate of oxidation compared to that of their LL counterparts.

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Oxalatotetramines of Cobalt(III)

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The syntheses, resolution, electronic structures, and stereochemistry of mixed-ligand complexes of cobalt(III) with the dianion of oxalic acid and ammonia, ethylenediamine (en), 1,3-diaminopropane (tn), triethylenetetramine (trien), 3,7-diaza-1,9-diaminononane (2,3,2-tet), and 4,7-diaza-1,10-diaminodecane (3,2,3-tet) are reported. The instability of cobalt(III) complexes with 4,8-diaza-1,11-diaminoundecane (3,3,3-tet) indicates that the complexes $Co(NH_3)_{40}x^+$, $Co(en)_{20}x^+$, $Co(tn)_{20}x^+$, α -*cis*-Co(trien)ox⁺, β -*cis*-Co(2,3,2-tet)ox⁺, and α -*cis*-Co(3,2,3-tet)ox⁺ comprise the complexe series of oxalatotetramine complexes with unsubstituted amines.

Introduction

The complexes oxalato(tetraammine)cobalt(III), $Co(NH_3)_{40x}$ +, oxalatobis(ethylenediamine)cobalt(III), $Co(en)_{20x}$ +, oxalatobis(1,3-diaminopropane)cobalt(III), $Co(tn)_{20x}$ +, oxalatotriethylenetetraminecobalt(III), Co(2,2,2-tet)ox+, oxalato-4,7-diaza-1,10-decanediaminecobalt(III), $Co(3,2,3,-tet)ox^+$, and oxalato-3,7-diaza-1,9-nonanediaminecobalt(III), $Co(2,3,2-tet)ox^+$, comprise a complete series of mixed-ligand oxalatotetraminecobalt(III) ions. Though numerous other complexes are doubtless formed with N- and C-substituted derivatives of these ligands and with cyclic tetramines, the relative instability of cobalt(III) complexes with 4,8-diaza-1,11-undecanediamine, 3,3,3-tet, in our hands, suggests that there are no other similar complexes with symmetrical unsubstituted linear amines.

Experimental Section

Electronic spectra were obtained with a Beckman Model DBG spectrophotometer equipped with a Beckman Model 1005 10-in. recorder and matched 10-mm silica cells. Optical rotatory dispersion and circular dichroism measurements were obtained with a Cary Model 6002 circular dichroism accessory. Solutions of approximately 10^{-3} *M* concentration and 0.1-, 0.2-, 0.5-, or 1.0-dm cells were employed as appropriate. Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany.

Preparation of α and β -Dichloro(triethylenetetramine)cobalt(III) Chloride, α -Carbonato(triethylenetetramine)cobalt(III) Perchlorate, and β -Carbonato(triethylenetetramine)cobalt(III) Chloride.—The procedures of Sargeson and Searle were employed without modification.¹

Preparation of 3,7-Diaza-1,9-nonanediamine.—1,3-Dibromopropane (240 g) was added slowly to a solution of 500 g of ethylenediamine in 500 ml of ethanol. The temperature of the reaction mixture should not be permitted to rise much above 50° during the course of this exothermic reaction. Potassium hydroxide (400 g) was added and the solution was stirred for 1 hr. After filtration to remove the KBr, excess ethylenediamine and ethanol were removed by distillation and the product was collected by distillation at 140–145° (8 mm).

Preparation of 4,7-diaza-1,10-decanediamine.—The synthetic procedure was identical with that employed for the preparation of 3,7-diaz-1,9-nonanediamine, with the substitution of 1,2-dibromoethane and 1,3-diaminopropane for 1,3-dibromopropane and ethylenediamine, respectively. The product was distilled at $150-160^{\circ}$ (5 mm).

Preparation of trans-Dichloro(3,7-diaza-1,9-diaminononane)cobalt(III) Chloride.—The procedure described by Hamilton and Alexander was employed.²

Preparation of *trans*-Dichloro(4,7-diaza-1,10-diaminodecane)cobalt(III) Chloride.—The procedure of Alexander and Hamilton was employed.³

Preparation of α -cis-Oxalato(4,7-diaza-1,10-diaminodecane)cobalt(III) Chloride Tetrahydrate.—A solution containing 10.2 g (0.03 mol) of trans-[Co(3,2,3-tet)Cl₂]Cl and 5.6 g (0.03 mol) of potassium oxalate hydrate in 100 ml of water was warmed on a steam bath for 2 hr. The solution was filtered and then evaporated on a steam bath under a stream of air until crystals just started to form after which it was cooled for 3 hr in a refrigerator. The bright red needles were filtered, washed with methanol and ether, and recrystallized once from hot water. Anal. Calcd for CoC₁₀H₂₂N₄O₄Cl·4H₂O: C, 28.01; H, 7.00; N, 13.07. Found: C, 27.77; H, 7.24; N, 13.12.

Resolution of α -cis-Oxalato(4,7-diaza-1,10-diaminodecane)cobalt(III) Chloride Tetrahydrate.—To a constantly stirred solution of α -cis-[Co(3,2,3-tet)ox] Cl·4H₂O (4.28 g, 0.01 mol) in 300 ml of water was added slowly 1.8 g (0.005 mol) of lithium hydrogen *d*-tartrate dibenzoate in 50 ml of warm water. After cooling to room temperature, the diastereoisomer was filtered and washed with water. Purification was effected by stirring the diastereoisomer in 600 ml of hot water and cooling overnight. The diastereoisomer was removed by filtration, washed with cold water and methanol, and air-dried.

The diastereoisomer was then stirred in 50 ml of water containing 20 ml of concentrated HCl. Insoluble *d*-tartaric acid dibenzoate was removed by filtration. To the filtrate was added 5 ml of concentrated HClO₄. On cooling, (+)- α -*cis*-[Co(3,2,3tet)ox]ClO₄ crystallized and was filtered, washed with methanol to remove any remaining *d*-tartaric acid dibenzoate, and airdried; [M]₅₄₆ -2890°, [M]₅₂₁ -5490°. *Anal.* Calcd for CoC₁₀-H₂₂N₄ClO₈: C, 28.50; H, 5.23; N, 13.30. Found: C, 28.57; H, 5.53; N, 12.65.

To the filtrate from the formation of the diastereoisomer was added another 1.8 g of lithium hydrogen *d*-tartrate dibenzoate in 50 ml of warm water. After standing several hours, the solid

was removed and discarded. To this filtrate was added 10 ml of perchloric acid. (-)- α -cis-[Co(3,2,3-tet)ox]ClO₄, crystallized on evaporation under an air stream, was filtered, washed with methanol to remove the *d*-tartaric acid dibenzoate, and air-dried; [M]₅₄₆ 2990°, [M]₅₂₁ 5465°.

Preparation of β -cis-Oxalato(3,7-diaza-1,9-diaminononane)cobalt(III) Iodide.—A solution containing 9.8 g (0.03 mol) of trans-[Co(2,3,2-tet)Cl₂]Cl and 6.0 g of potassium oxalate hydrate in 100 ml of water was warmed on a steam bath for 3 hr. After filtration, 6 g of sodium iodide dissolved in a little water was added to the warm solution. The red crystals which formed on cooling were filtered, washed with cold water and methanol, and air-dried. The product was sometimes contaminated with unreacted trans-[Co(2,3,2-tet)Cl₂]I. This was removed by dissolving the product in the minimum volume of hot water and filtering the sparingly soluble trans-[Co(2,3,2-tet)Cl₂]I. Evaporation of the filtrate produced pure β -cis-[Co(2,3,2-tet)ox]I. Anal. Calcd for CoC₉H₂₀N₄O₄I: C, 24.88; H, 4.61; N, 12.90. Found: C, 24.97; H, 5.21; N, 12.78.

Resolution of β -cis-Oxalato(3,7-diaza-1,9-diaminononane)cobalt(III) Iodide.— β -cis-[Co(2,3,2-tet)ox]I (4.4 g, 0.01 mol) was stirred with 1.7 g of AgNO₃ in 275 ml of water. Silver chloride was removed by filtration and 1.8 g of lithium hydrogen *d*-tartrate dibenzoate in 50 ml of warm water was added to the constantly stirred filtrate. After cooling to room temperature, the diastereoismer was filtered, washed with cold water, and air-dried.

The diastereoisomer was dissolved in 40 ml of water containing 10 ml of concentrated HCl. After filtering the *d*-tartaric acid dibenzoate, 5 ml of concentrated HClO₄ was added. The crystals of (-)- β -cis-[Co(2,3,2-tet)ox]ClO₄ which formed on cooling were filtered, washed with cold water and methanol, and airdried; [M]₅₀₉ -1665°, [M]₅₀₀ 5054°. Anal. Calcd for CoC₉-H₂₀N₄ClO₈: C, 26.60; H, 4.93; N, 13.79. Found: C, 26.95; H, 5.38; N, 13.99.

To the filtrate from the formation of the diastereoisomer was added another 1.7 g of lithium hydrogen *d*-tartate dibenzoate. After standing 1 hr, the solid was filtered and discarded. To this filtrate was added HClO₄. After evaporation under an air stream at room temperature, (+)-[Co(2,3,2-tet)ox]ClO₄ was filtered, washed with methanol to remove *d*-tartartic acid dibenzoate, and air-dried; [M]₅₈₉ 1640°, [M]₅₀₉ - 5034°.

Preparation of β -cis-Oxalato(triethylenetetramine)cobalt(III) Iodide.—A solution containing β -cis-[Co(trien)CO₃]Cl and excess oxalic acid was warmed on a steam bath for 1 hr. On cooling and adding NaI, β -cis-[Co(trien)ox]I crystallized, was removed by filtration, washed with methanol and ether, and air-dried.

Preparation of α -cis-Oxalato(triethylenetetramine)cobalt(III) **Perchlorate.**—A solution containing α -cis-[Co(trien)CO₃]ClO₄ and excess oxalic acid was warmed on a steam bath until crystals began to form. After cooling, α -cis-[Co(trien)OX]ClO₄ was removed by filtration, washed with water and acetone, and airdried. Due to its low solubility, the perchlorate salt could not be used in the resolution procedure. The iodide salt was obtained by stirring the perchlorate salt in a saturated KCl solution, removing KClO₄ by filtration, and adding excess NaI. Other more soluble salts were then easily obtained from the iodide salt by trituration with the appropriate silver salt.

Resolution of α -cis- and β -cis-Oxalato(triethylenetetramine)cobalt(III) Iodide.—These resolutions were carried out analogously to that of β -cis-[Co(2,3,2-tet)ox]I. For (-)- α -cis-[Co-(trien)ox]ClO₄ the ORD curve was identical with that reported; [M]₅₄₆ -5100°. For (-)- β -cis-[Co(2,2,2-tet)ox]ClO₄ an ORD curve somewhat different from that reported⁴ was obtained; [M]₅₄₆ -3825°. Anal. Calcd for (-)- β -cis-CoC₈H₁₈N₄ClO₈. 0.5H₂O: C, 23.88; H, 4.72; N, 13.93. Found: C, 24.05; H, 4.64; N, 13.97.

Preparation of Oxalatobis(1,3-diaminopropane)cobalt(III) Chloride Hemihydrate.—Twenty grams of cobaltous acetate tetrahydrate in 100 ml of water (60°) was added to a solution of 15 g of oxalic acid dihydrate and 18.5 ml of 1,3-diaminopropane. The solution was heated to 80° and 10 g of lead dioxide was added. The solution was boiled for 0.5 hr adding 2 g of lead dioxide after 10 and 20 min. After cooling and filtering, 10 ml of 10 N sulfuric acid was added and the solution was filtered again. Twenty-five milliliters of HCl was added and the solution was evaporated to 100 ml and cooled. The red product was removed by filtration, recrystallized from 60 ml of hot water by adding 20 ml of HCl, and cooling. Anal. Calcd for $CoC_8H_{20}N_4ClO\cdot0.5H_2O$: C,

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28.32; H, 6.19; N, 16.52. Found: C, 28.53; H, 6.27; N, 16.62.

Resolution of Oxalatobis(1,3-diaminopropane)cobalt(III) Chloride Hemihydrate.—The resolution was analogous to the resolution of α -cis-[Co(3,2,3-tet)ox]Cl. The isomer obtained as the least soluble diastereoisomer of the hydrogen *d*-tartrate dibenzoate anion was (-)-[Co(tn)₂ox]ClO₄·0.5H₂O; [M]₅₄₆ 1320°. For (+)-[Co(tn)₂ox]ClO₄·0.5H₂O, [M]₅₄₆ is 1280°. *Anal.* Calcd for (+)-CoC₈H₂O₈N₄ClO₈·0.5H₂O; C, 23.82; H, 5.21; N, 13.89. Found: C, 23.76; H, 5.10; N, 13.86.

Preparation of Oxalatobis(ethylenediamine)cobalt(II) Chloride Hydrate.—This compound was prepared as described by Dwyer, Reid, and Garvan.⁶

Resolution of Oxalatobis(ethylenediamine)cobalt(III) Chloride Hydrate.—The resolution was analogous to that of α -cis-[Co-(3,2,3-tet)ox]Cl except that no perchloric acid was used as the chloride salt of the resolved Co(en)₂ox⁺ isomer could easily be obtained. The rotations observed compared favorably with those reported previously.⁶ The isomer obtained as the least soluble diastereoisomer was (-)-Co(en)₂ox; [M]₅₄₆ -4025°.

Preparation of (-)-trans-(RR)-Dichloro(4,7-diaza-1,10-diaminodecane)cobalt(III) Perchlorate.— $(+)_{546}$ - α -cis-[Co(3,2,3-tet)-ox]ClO₄ (0.3 g) was dissolved in 25 ml of methanol saturated with dry HCl gas. After standing at room temperature for 12 hr, a few drops of concentrated perchloric acid was added. The green crystals of (-)-trans-(RR)- $[Co(3,2,3-tet)Cl_2]ClO_4$ were removed by filtration, washed with a little ether, and air-dried; $[M]_{559} - 390^\circ$, $[M]_{614} - 590^\circ$. Anal. Calcd for CoC₈H₂₂N₄-Cl₅O(3,2,3-tet)Cl_2(2, C, 23.76; H, 5.45; N, 13.86. Found: C, 24.15; H, 5.43; N, 13.67.

Preparation of (-)-trans-(RR)-Dichloro(3,7-diaza-1,9-diaminononane)cobalt(III) Perchlorate.—(-)- β -cis-[Co(2,3,2-tet)-ox]ClO₄ (0.3 g) was refluxed in 2 ml of methanol saturated with dry HCl gas for several hours. Additional HCl gas was added occasionally. On cooling and adding HClO₄ to the solution, (-)-trans-[Co(2,3,2-tet)ox]ClO₄ (crystallized. This was filtered, washed with ether, and air-dried; $[M]_{559} - 880^\circ$, $[M]_{613} - 1650^\circ$. Anal. Calcd for CoC₇H₂₀N₄Cl₃O₄: C, 21.54; H, 5.13; N, 14.36. Found: C, 21.71; H, 5.36; N, 13.80.

14.36. Found: C, 21.71; H, 5.36; N, 13.80. (-)-trans-(RR)·Co(3,2,3-tet)Cl₂⁺ \rightarrow (+)₅₄₆-Co(3,2,3-tet)ox⁺.--(-)-trans-(RR)·[Co(3,2,3-tet)Cl₂]ClO₄ (0.0200 g) was dissolved in 10 ml of water containing 1.0 g of oxalic acid. After heating at 40° for 24 hr, the solution was allowed to stand at room temperature for about 1 week. The visible spectrum of this solution was then identical with that of α -cis-Co(3,2,3-tet)ox⁺. An aliquot (2 ml) of this solution was added to 0.5 g of Ca(NO₃)₂· 4H₂O, diluted to 25 ml, and filtered to remove excess oxalic acid as calcium oxalate. The ORD spectrum of this solution was identical in shape with that of pure (+)₅₄₆ cis-Co(3,2,3-tet)ox⁺. The observed rotation, [M]₅₂₁ 5100°, agreed with that of the resolved isomer, [M]₅₂₁ 5490°.

(-)-trans-(RR)-Co(2,3,2-tet)Cl₂⁺ $\rightarrow (-)$ - β -cis-Co(2,3,2-tet)-ox⁺.--(-)-trans-(RR)-[Co(2,3,2-tet)Cl₂]ClO₄ (0.0200 g) was dissolved in 10 ml of water containing 1.0 g of oxalic acid. After heating at 50° for 24 hr, the visible absorption spectrum of this solution was identical with that of β -cis-Co(2,3,2-tet)ox. An aliquot (2 ml) of this solution was treated similarly to that above. The ORD spectrum of this solution was identical with that of (-)- β -cis-Co(2,3,2-tet)ox⁺, [M]₅₀₃ 5150°. For the resolved complex [M]₅₀₃ is 5054°.

Preparation of (+)-trans-(RR)-Dibromo(4,7-diaza-1,10-diaminodecane)cobalt(III) Perchlorate.—This was prepared in a manner analogous to the preparation of (-)-trans-(RR)-[Co-(3,2,3-tet)Cl₂]ClO₄ using HBr gas in place of HCl gas. It can also be obtained by heating $(+)_{546}$ - α -cis-[Co(3,2,3-tet)Ox]ClO₄ on a steam bath in concentrated HBr containing a little concentrated HClO₄; [M]₅₈₉ 275°, [M]₆₆₈ - 450°. Anal. Calcd for CoC₈H₂₂N₄Br₂ClO₄: C, 19.51; H, 4.47; N, 11.38. Found: C, 20.05; H, 4.46; N, 11.13.

Preparation of $(+)_{b46}$ -trans-(RR)-Dibromo(3,7-diaza-1,9-diaminononane)cobalt(III) Perchlorate.—This was prepared in a manner analogous to the separation of (-)-trans-(RR)-[Co-(2,3,2-tet)Cl₂]ClO₄ using HBr gas in place of HCl gas or by heating (-)- β -cis-[Co(2,3,2-tet)Ox]ClO₄ on a steam bath in concentrated HBr containing a little HClO₄. The product is spectrophotometrically identical with that previously reported; [M]₅₅₉ 80°, [M]₆₆₉ - 1280°.

 $(-)-trans-(RR)-\operatorname{Co}(2,3,2-\operatorname{tet})\operatorname{Cl}_{2^{+}} \rightarrow \Delta(+)_{548}-\beta-\operatorname{Co}(2,3,2-\operatorname{tet})-$

Cl(H₂O)²⁺.—Aquation of (-)-trans-(RR)-[Co(2,3,2-tet)Cl₂]ClO₄ (0.03000 g) is allowed to proceed in 25 ml of 0.02 M HClO₄ at room temperature until formation of (+)₅₄₆- β -cis-Co(2,3,2-tet)-Cl(H₂O)⁺ is complete (approximately 4 hr). The circular dichroism curve of this solution was then measured; $\Delta \epsilon_{550} - 0.56$.

Results and Discussion

Syntheses.—Oxalatotetraminecobalt(III) chloride was prepared by the action of oxalic acid on a carbonatotetraminecobalt(III) salt.⁶ The oxalatobis(ethylenediamine)cobalt(III) ion, $Co(en)_2ox^+$, was prepared by the reaction of dichlorobis(ethylenediamine)cobalt-(III) chloride and ammonium oxalate⁷ or by direct oxidation of cobalt(II) acetate in the presence of oxalic acid and ethylenediamine.⁵ Oxalatobis(1,3-diaminopropane) cobalt(III) ion, $Co(tn)_2ox^+$, was prepared by the oxidation of a solution of cobalt(II) acetate, 1,3-diaminopropane, and oxalic acid with lead dioxide.

oxalatotriethylenetetraminecobalt(III) The ion. $C_0(trien)ox^+$, was first reported by Basolo⁸ as a product of the reaction of the carbonatotriethylenetetraminecobalt(III) ion with oxalic acid. No attempt was made to assign the geometrical configuration of this complex. Bailar subsequently reported the preparation of α -Co-(trien)ox⁺ from α - $[Co(trien)Cl_2]Cl$ and potassium oxalate.9 We find that the latter reaction produces primarily β -Co(trien)ox⁺, but high yields of the α isomer are obtained from the reaction of α -Co(trien)CO₃⁺ with oxalic acid. The acidic medium prevents the isomerization of α -diaquo- and α -hydroxoaquotriethylenetetraminecobalt(III) complexes to the β -cis forms.⁹⁻¹¹ Similarly, pure β -Co(trien)ox⁺ may be prepared from β -Co(trien)CO₃+.

The complexes α -oxalato-4,7-diaza-1,10-diaminodecanecobalt(III), α -Co(3,2,3-tet)ox⁺, and β -oxalato-3,7-diaza-1,9-diaminononanecobalt(III), β-Co(2,3,2tet)ox+, were prepared by heating the respective transdichloro complexes with an excess of potassium oxalate. The two ions so prepared were fractionally crystallized as both the iodide and the chloride salts; all fractions were spectrophotometrically identical. Both Co(2,3,2)tet) ox^+ and $Co(3,2,3-tet)ox^+$ yield only one band when adsorbed on a Dowex 50W-X8 ion-exchange column in the sodium form and eluted with 0.25 M sodium chloride, a method which has been used to separate similar sets of geometrical isomers.¹² Following resolution, the electronic spectra of the (+) and (-) isomers of $Co(2,3,2-tet)ox^+$ are identical, and the ORD curves are true mirror images, as are the corresponding curves for the (+) and (-) isomers of Co(3,2,3-tet)ox⁺. We are confident that there is only one geometrical isomer produced for each of the complexes; details of the assignments of configurations will be discussed with the ORD-CD results.

Resolution of the Complexes.—All of the oxalatotetramine complexes described in this work were resolved with the hydrogen *d*-tartrate dibenzoate anion, dbdt. The isomers obtained as the least soluble dbdt diastereoisomers are (-)-Co $(en)_2ox^+$, (-)-Co $(tn)_2ox^+$, (-)- β -Co $(trien)ox^+$, (-)- β -Co $(trien)ox^+$, (-)- β -Co-(2,3,2-tet)ox⁺, and (-)- α -Co(3,2,3-tet)ox⁺.

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Figure 1.—Electronic spectra: $Co(NH_3)_{40x^+}$, ---; α -Co-(3,2,3-tet)ox⁺, ----; β -Co(2,3,2-tet)ox⁺, ···.

Electronic Spectra.—The two broad symmetrical bands which appear in the visible region (Figure 1) may be assigned to the spin-allowed ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}(\nu_{1})$ and ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}(\nu_{2})$ electronic transitions of the cobalt(III) ion in pseudooctahedral symmetry. On comparing the spectral data for Co(NH₃)₄ox⁺ with those for the other oxalatotetramine complexes, it is evident that the chelate rings have little effect on the energies of the electronic transitions. There is no apparent correlation between the number and/or size of chelate rings and ν_{max} ; indeed, ν_{max} varies by less than 6% throughout the series (Table I).

	TABLE I			
ELECTRONIC SP	ECTRAL PAR	AMETERS	of Some	
Oxalatotetram	INE COMPLE	EXES OF C	OBALT(III	.)
Compd	νmax, kK	\$emax	Δr, kK	10³fa
Co(NH ₃) ₄ ox +	19.65	8 0	3.39	1.2
	27.93	122	4.31	2.4
$Co(en)_{2}ox^{+}$	20.08	114	3.39	1.8
	28.09	142	4.50	2.9
$Co(tn)_2 ox^+$	19.60	79	3.68	1.3
	27.93	147	3.99	2.7
α -cis-Co(trien)ox+	20.28	110	3.21	1.6
	28.01	123	4.38	2.5
β -cis-Co(trien)ox ⁺	20.12	179	3.38	3.3
	28.01	179	4.01	3.3
8-cis-Co(2,3,2-tet)ox+	20.00	140	3.32	2.1
	27.77	175	4.35	3.5
α -cis-Co(3,2,3-tet)ox+	19.53	118	3.65	2.0
	27.54	177	4.08	3.3
		· ·		

^a Estimated from the relationship $f \approx 4.6 \times 10^{-9} \epsilon \Delta \nu$ (see text).

That the intensities of the absorption bands increase with decreasing symmetry is not surprising, though the effect should be small in descent from C_{2v} (Co(NH₃)ox⁺) to C_1 (β -Co(trien)ox⁺, for example). The variation in intensity is perhaps best correlated with the increase in the number of normal modes of vibration which accompanies the increasing number of atoms within this series. For Co(NH₃)₄ox⁺ there are 27 normal vibrational modes (excluding hydrogen atoms): 10 A₁, 4 A₂, 8 B₁, 5 B₂. All of these molecular vibrations interact with one or another of the electronic transitions in the complex, thereby contributing to both the bandwidth and to the intensity of the spectrum. For β -Co(trien)ox⁺ there are 45 totally symmetric normal vibrational modes contributing to spectral intensity.

The half-bandwidths, $\Delta \nu$, vary by as much as 20%. However, again, there is no apparent correlation between half-bandwidth and molecular symmetry. Oscillator strengths, f, were estimated from half-bandwidths and molar extinction coefficients under the pseudooctahedral approximation—the assumption that each broad band may be attributed to a single electronic transition. The values so obtained are reasonable for this class of compound (for Co(en)₃³⁺, ν_1 21.40 kK, ϵ 85, $f = 1.2 \times 10^{-3}$; ν_2 29.40 kK, ϵ 72, $f = 1.2 \times 10^{-3}$) but provide no meaningful correlation with the symmetry of the complexes under study.

It is obvious from even the most casual inspection that the electronic spectra do not contribute materially to an understanding of the symmetry of these complexes. The ${}^{1}T_{1g}$ and ${}^{1}T_{2g}$ states of the spin-paired octahedral cobalt(III) ion are split into three nondegenerate levels by the lower symmetry of the oxalatotetramine ligand field (the C_{2v} symmetry of Co(NH₃)₄ox⁺ is the highest in this series). Symmetry-allowed transitions from the ground state to each of these levels should result in broad and relatively intense absorption bands in the electronic spectra. Splitting of the octahedral states of cobalt(III) is rarely observed at room temperature; the observed bandwidths and the magnitude of the oscillator strengths suggest, however, that there is a noncubic component in the ligand field which is too small to cause a significant deviation from an average octahedral environment of four nitrogen and two oxygen donors.

Stereochemistry.—There is, of course, only one geometrical isomer possible for the complexes $Co(NH_3)_{4^-}$ ox^+ , $Co(en)_2ox^+$, and $Co(tn)_2ox^+$. The geometric configurations of α - and β -Co(trien) ox^+ are assigned on the basis of the known configurations of the α - and β -Co(trien) CO_3^+ starting materials. The electronic spectra agree with those reported previously.⁴

Only one geometric isomer was isolated for each complex, $Co(2,3,2-tet)ox^+$ and $Co(3,2,3-tet)ox^+$. Each complex was fractionally crystallized as both the iodide and the chloride salts, and all fractions were spectrophotometrically identical. Both [Co(3,2,3-tet)ox]Cland [Co(2,3,2-tet)ox]Cl yield only one band when adsorbed on a Dowex 50W-X8 ion-exchange column in the sodium form and eluted with 0.25 M sodium chloride. This method has been used previously to separate similar types of geometric isomers. The electronic absorption spectra for both (+)- and (-)- α - [Co(3,2,3-tet)ox]- ClO_4 are identical with that obtained for the racemic compound and the optical rotatory disperion curves of the (+) and (-) isomers are mirror images. Similar results are obtained for the optical isomers of β -Co(2,3,-2-tet)ox⁺. These observations indicate that there is only one geometrical isomer present for each of the two complexes.

Optical Activity. Absolute Configuration.—Circular dichroism is more sensitive than electronic spectra to the individual components of the absorption bands. The circular dichroism spectra of (+)-Co $(en)_{20x}^+$, (+)- α -Co $(trien)_{0x}^+$, and (+)- β -Co $(trien)_{0x}^+$ are shown in Figure 2; those of (+)-Co $(tn)_{20x}^+$, (+)- β -Co(2,3,2-tet)_{0x}^+, and $(+)_{546}$ - α -Co(3,2,3-tet)_{0x}^+ are shown in Figure 3. Mason¹³ found in a study of complexes Co $(en)_{2}LL^{n+}$, where LL is a bidentate conjugated ligand, that only one band is seen in the circular dichro-

(13) A. J. McCaffery, S. F. Mason, and B. J. Norman, J. Chem. Soc., 5094 (1965).



Figure 2.—Circular dichroism spectra: (+)-Co(en)₂ox⁺, \cdots ; (+)- α -Co(trien)ox⁺, ——; (+)- β -Co(trien)ox⁺, ---.



Figure 3.—Circular dichroism spectra: (+)-Co $(tn)_{20}x^{+}$, \cdots ; $(+)_{546}$ - α -Co(3,2,3-tet)ox⁺, ---; (+)- β -Co(2,3,2-tet)ox⁺, ---.

ism spectrum in the region of the ${}^{1}A_{1s} \rightarrow {}^{1}T_{1h}(O_{h})$ transition. The most noticeable feature of the CD spectra of the oxalatotetramine complexes is that, whereas there is only one low-energy band observable for (+)- $Co(en)_{2}ox^{+}$, (+)- $Co(tn)_{2}ox^{+}$, (+)- α - $Co(trien)ox^{+}$, and (+)- β - $Co(trien)ox^{+}$, there are two distinct bands of opposite sign for both (+)₅₄₆- α -Co(3,2,3-tet)ox⁺ and (+)- β -Co(2,3,2-tet)ox⁺.

All of the optically active complexes have C_2 symmetry except for the cis- β isomers and we have assumed that these approximate C_2 symmetry. The assignment of absolute configuration for the C_2 complexes $Co(en)_2$ - L_2^{n+} has been described by Mason.^{13,14} The results are analyzed in terms of a model in which the complexes are regarded as intermediate between $Co(en)_3^{3+}$ with D_3 symmetry and cis-Co(NH₃)₄L₂ⁿ⁺ with C_{2v} symmetry. The ${}^{1}T_{1g}(O_{\hbar})$ state is split in trigonal complexes into ${}^{1}A_{2}$ and ${}^{1}E_{s}$ components. For (+)-Co(en) ${}^{3+}$ of known absolute configuration A, the ${}^{1}A_{1} \rightarrow {}^{1}E_{a}$ transition is positive and the ${}^{1}A_{1} \rightarrow {}^{1}A_{2}$ is negative.¹⁵ In complexes of C_2 symmetry, the ${}^{1}T_{1g}(O_h)$ state is split into one component with A symmetry and two components with B symmetry as shown in Figure 4. The transition with A symmetry derives from the component of the ${}^{1}E_{a}(D_{3})$ state and has a wave function which is invariant in form throughout the series $Co(en)_3^{3+}$, $cis-Co(en)_2L_2^{n+}$, and cis-Co(NH₃)₄L₂ⁿ⁺. The wave function describing the ${}^{1}A_{1} \rightarrow {}^{1}B_{2}(E_{a})$ and ${}^{1}A_{1} \rightarrow {}^{1}B_{1}(A_{2})$ transitions are not symmetry determined in these complexes. The sign of the ${}^{1}A_{1} \rightarrow {}^{1}A_{2}(E_{a})$ transition may be used for the corre-(14) P. G. Beddoe and S. F. Mason, Inorg. Nucl. Chem. Lett., 4, 433 (1968).

(15) R. E. Ballard, A. J. McCaffery, and S. F. Mason, Proc. Chem. Soc., London, 331 (1962).



Figure 4.—Energy levels for tetragonal and dihedral complexes of low-spin Co(III).

lation of absolute configurations for a series of complexes of C_2 symmetry. If the transition with ${}^{1}A_{1} \rightarrow$ ${}^{1}E_{s}(D_{2})$ parentage, ${}^{1}A_{1} \rightarrow {}^{1}A_{2}(E_{a})$, is positive, the complex is assigned the Λ absolute configuration; if negative, the complex is assigned the Δ absolute configuration. The ${}^{1}A_{1} \rightarrow {}^{1}A_{2}(E_{a})$ transition is distinguished as the more intense band. In the complexes of C_{2} symmetry, this band is usually assigned as the composite transition ${}^{1}A_{1} \rightarrow {}^{1}A_{2}(E_{a}) + {}^{1}B_{2}(E_{a})$; that is, accidental degeneracy is assumed for the components of the trigonal ${}^{1}E_{a}$ state. Indeed, the CD spectra often appear to fit the trigonal or tetragonal model.

Using Mason's formula, the (+)-Co $(en)_2 ox^+$ ion is assigned the absolute configuration Λ in agreement with previous assignment.¹³ It shows a positive dominant low-energy Cotton effect which has been related to the composite transition ${}^{1}A_1 \rightarrow {}^{1}A_2(E_a) + {}^{1}B_2(E_a) +$ ${}^{1}B_1(A_2)$. Similarly, the ions (+)- α -Co $(trien)ox^+$ all have positive dominant low-energy Cotton effects (which can be related to the composite ${}^{1}A_1 \rightarrow {}^{1}A_2(E_a) +$ ${}^{1}B_2(E_a) + {}^{1}B_1(A_2)$ transition and can thus be assigned the same absolute configuration as (+)-Co $(en)_2 ox^+$).

In contrast to these oxalatotetramine complexes, the ion $(+)_{546}$ - α -Co(3,2,3-tet)ox⁺ shows a low-energy negative Cotton effect followed by a larger positive Cotton effect. The (+)- β -Co(2,3,2-tet)ox⁺ ion shows a longwavelength dominant positive Cotton effect at 535 nm followed by a smaller, negative component in the region of the ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}(O_{\hbar})$ transition. Adhering to Mason's formalism, the dominant band is related to the ${}^{1}A_{1} \rightarrow$ ${}^{1}A_{2}(E_{g})$ transition and as it is positive for these ions, $(+)_{546}$ - α -Co(3,2,3-tet)ox⁺ and (+)- β -Co(2,3,2-tet)ox⁺ are assigned Λ absolute configuration.

From these data alone it is impossible to assign the other electronic transitions which appear. It has been proposed^{16,17} for the $Co(en)_2L_2^{n+}$ complexes that, when L lies below amine in the spectrochemical series, the state of E_a parentage lies at higher energy than does the ¹A₂ while the reverse is true when L lies above amine. This has proved applicable for $L = Cl^-$, H_2O , NO_2^- , Br^- , etc. Since there are three transitions possible for the complexes $Co(3,2,3-\text{tet})ox^+$ and $Co(2,3,2-\text{tet})ox^+$ of C_2 or approximately C_2 symmetry and only the ¹A₁ \rightarrow

- (16) R. Wentworth and T. S. Piper, Inorg. Chem., 4, 202 (1965).
- (17) H. Yamatera, Bull. Chem. Soc. Jap., 31, 95 (1958).

 ${}^{1}A_{2}(E_{a})$ has been identified, several assignments are possible. However, keeping the same ordering of energy levels for both complexes as indicated by the similarity of their electronic absorption spectra, it appears that the ${}^{1}A_{1} \rightarrow {}^{1}A_{2}(E_{a})$ occurs as the middle transition with the ${}^{1}A_{1} \rightarrow {}^{1}B_{2}(E_{a})$ and ${}^{1}A_{1} \rightarrow {}^{1}B_{1}(A_{2})$ on either side.

The reasons for observing splitting of the ${}^{1}A_{1z} \rightarrow {}^{1}T_{1g}(O_{h})$ band in the circular dichroism spectra of α -Co(3,2,3-tet)ox⁺ and β -Co(2,3,2-tet)ox⁺ but not in the spectra of the other oxalatotetramine complexes are not readily apparent. Observable splitting of any band depends on several factors including the energy separation of the states and the relative signs and intensities of the transitions involved. It is expected that splitting might be observed in α -Co(3,2,3-tet)ox⁺ if the energy separation between any two of the ${}^{1}A_{2}$, ${}^{1}B_{2}$, and ${}^{1}B_{1}$ components is significantly greater in α -Co(3,2,3-tet)ox⁺ than it is in the other oxalatotetramine complexes. Perhaps it is merely that two overlapping transitions of opposite signs rather than the same sign are more easily observed.

There is some evidence that larger rings tend to increase the intensity of the ${}^{1}A_{2}(D_{3})$ transition relative to the E_a which would have the effect of making this component more readily observable. For Co(EDTA)-, in which all the chelate rings are five membered, the transition related to the E_s state is dominant, but in Co- $(EDTP)^{-}(EDTP = ethylenediaminetetrapropionate)$ and $Co(1,3-PDTA)^-$ (1,3-PDTA = 1,3-propanediaminetetraacetate), in which some six-membered chelate rings appear, the transition related to the ${}^{1}A_{2}$ state is the dominant transition.¹⁸ Similarly, the ${}^{1}A_{1} \rightarrow$ ${}^{1}E_{a}$ transition is dominant in Co(en)₃³⁺ (five-membered rings) but is the minor band in $Co(tn)_3^{3+}$ (six-membered rings).¹⁴ Thus we can explain the occurrence of splitting in the CD spectra of α -Co(3,2,3-tet)ox⁺ and β -Co-(2,3,2-tet)ox⁺ but not the lack of observable splitting for $Co(tn)_{2}ox^{+}$.

Using McDermott and Sargeson's method for the assignment of absolute configurations from ORD data,¹⁹ we note that the ORD curves for the ions (+)-Co(en)₂ox⁺; (+)- α -Co(trien)ox⁺, (+)- β -Co(trien)ox⁺, (+)- $Co(tn)_{2}ox^{+}$, and $(+)-\beta$ - $Co(2,3,2-tet)ox^{+}$ have essentially the same shape and show dominant positive lowenergy Cotton effects (Figures 5, 6). We have assigned the same absolute configuration to these ions as (+)- $Co(en)_{3^{3+}}$, that is, Λ . The ORD curve of $(+)_{546-\alpha}$ - $Co(3,2,3-tet)ox^+$ is slightly different from the others, showing first a small negative Cotton effect at about 569 nm and a larger positive Cotton effect at about 489 nm. The higher energy Cotton effect is related to the ${}^{1}A_{1} \rightarrow {}^{1}A_{2}(E_{s})$ transition as explained in the discussion of the CD curves. On the basis of this dominant, positive Cotton effect, $(+)_{546}-\alpha$ -Co(3,2,3-tet)ox⁺ is assigned absolute configuration Λ . In addition, the negative sign of the Cotton effect as the ORD curves trail off into the ultraviolet indicates that all the ions whose ORD curves are shown in Figures 5 and 6 have the same absolute configuration.

The assignments of absolute configurations from ORD and CD data are consistent with familiar observation that similar compounds with the same absolute

(19) T. E. MacDermott and A. M. Sargeson, Aust. J. Chem., 16, 334 (1963).



Figure 5.—ORD curves: (+)-Co $(en)_{2}$ ox⁺, \cdots ; (+)- α -Co-(trien)ox⁺, ---.



Figure 6.—ORD curves: $(+)-C_0(tn)_{20}x^+, \cdots; (+)_{546}-\alpha-C_0(3,2,3-tet)ox^+, ----; (+)-\beta-C_0(2,3,2-tet)ox^+, ----.$

configuration form the less soluble diastereoisomer with a given resolving agent.²⁰ The ions (-)-Co(en)₂ox⁺, (-)-Co(tn)₂ox⁺, (-)- α -Co(trien)ox⁺, (-)- β -Co(trien)ox⁺, (-)- β -Co(2,3,2-tet)ox⁺, and (-)₅₄₆- α -Co(3,2,3tet)ox⁺ form less soluble diastereoisomers in the form [CoN₄ox][dbdt].

Optical Activity. Topology of Flexible Tetramine Ligands.-To determine the geometrical configuration of the tetradentate tetramine ligands, each optically active cis-oxalatotetramine complex was converted into its corresponding dichlorotetramine complex by treating the complex with methanol saturated with HCl or by warming the complex in concentrated aqueous hydrochloric acid. Under these conditions, $(+)-\alpha$ - and (+)- β -Co(trien)ox⁺ ions produce (+)- α - and (+)- β -Co- $(trien)Cl_2^+$. The ORD curves of the Co $(trien)Cl_2^+$ ions correspond to the reported curves.²¹ No trans-Co- $(trien)Cl_2^+$ is produced in this reaction in agreement with the known instability of the trans-dichlorotriethylenetetramine species. In contrast, $Co(en)_2ox^+$, Co- $(tn)_2 ox^+$, β -Co(2,3,2-tet)ox⁺, and α -Co(3,2,3-tet)ox⁺ react with concentrated hydrochloric acid to produce the corresponding trans-dichloro species. Since trans- $Co(en)_2Cl_2^+$ and trans- $Co(tn)_2Cl_2^+$ are optically inactive, all optical activity is lost when this reaction is carried out using the active $Co(en)_2 ox^+$ or $Co(tn)_2 ox^+$ ions.

The ligands 2,3,2-tet and 3,2,3-tet contain secondary nitrogen atoms which, when coordinated, become asymmetric. The $trans-(2,3,2-tet)Cl_2$ and $trans-(3,2,3-tet)Cl_2$

⁽¹⁸⁾ C. Van Saun and B. E. Douglas, Inorg. Chem., 8, 1145 (1969).

⁽²⁰⁾ A. Werner, Chem. Ber., 45, 1229 (1912).

⁽²¹⁾ A. M. Sargeson and G. H. Searle, Inorg. Chem., 4, 45 (1965).

tet)Cl₂ complexes can exist as the optically active trans-RR and trans-SS species or as the inactive meso-trans-SR. Molecular models indicate that the secondary nitrogen atoms coordinate stereospecifically in the cis isomers. The RS (meso) form can be found only in the β isomer and not in the α . Moreover, when comparing the β isomer having the active RR or SS configuration of the secondary amines to the α isomer, it is seen that the configuration of the secondary amines is opposite for α and β complexes of the same absolute configuration. Conversion of cis-(3,2,3-tet)ox or cis-(2,3,2-tet)ox complexes of absolute configuration Λ to a trans-dichloro complex without changing the asymmetry of the secondary nitrogen atoms can produce any one of three isomers of the trans-dichloro complex depending on the geometrical configuration of the original Λ -cis isomer as shown in Figure 7. Notice that the Λ - α -cis isomer pro-



Figure 7.—The interrelation of absolute configurations of the secondary nitrogen atoms for various cis and trans tetramine complexes.

duces a trans isomer having opposite configuration from that produced by the Λ - β -cis isomer.

For a β -diacidotriethylenetetramine complex, β -Co-(trien)L₂ⁿ⁺, the β -SR isomer has been shown to be less stable than the β -RR and -SS isomers.²² Molecular models indicate that the same analysis should apply to mixed-ligand 2,3,2-tet and 3,2,3-tet complexes. In the basic media used for preparing the ox-2,3,2-tet and -3,2,3-tet complexes, rapid amine proton exchange takes place leading to the expectation that the β isomer will adopt the more stable RR,SS configurations.

Recent studies show that in acidic media, exchange rates of the coordinated secondary amine protons are sufficiently slow to render them inert²³ and, as a result, isolation of *RR* and *SS* isomers has been effected in the case of *trans*-Co(trien)Cl₂⁺.²² The (3,2,3-tet)ox and

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- (23) B. Halpern, A. M. Sargeson, and K. R. Turnbull, J. Amer. Chem. Soc., 88, 4630 (1966).

(2,3,2-tet)ox complexes of absolute configuration Λ react in methanol saturated with anhydrous HCl—acidic conditions under which configurations of the secondary amines should be retained—to produce optically active *trans*-dichloro species which are of opposite configurations as indicated by the shapes of their ORD curves. This series of reactions is summarized in the scheme

$$(+)-\Lambda-\beta-\operatorname{Co}(2,3,2-\operatorname{tet})\operatorname{ox}^{+} \xrightarrow{\operatorname{HCl}} (+)-\operatorname{trans-Co}(2,3,2-\operatorname{tet})\operatorname{Cl}_{2}^{+}$$
$$(+)_{546}-\Lambda-\alpha-\operatorname{Co}(3,2,3-\operatorname{tet})\operatorname{ox}^{+} \xrightarrow{\operatorname{HCl}} (-)-\operatorname{trans-Co}(3,2,3-\operatorname{tet})\operatorname{Cl}_{2}^{+}$$

The optical rotatory dispersion curves of (+)-trans-Co-(2,3,2-tet)Cl₂+, (-)-trans-Co(3,2,3-tet)Cl₂+, and (+)trans-(SS)-Co(trien)Cl₂+ are shown in Figure 8. The



Figure 8.—ORD curves: (+)-trans-Co(2,3,2-tet)Cl₂+, ...; (+)-trans-(SS)-Co(trien)Cl₂+, ...; (-)-trans-Co(3,2,3-tet)-Cl₂+, ---.

latter complex has been assigned SS configuration on the basis of the configuration of the optically active β -Co(trien)Cl₂⁺ ion from which it is obtained²² and also by comparison of its circular dichroism curve to that of trans-Co((-)pn)Cl₂⁺ (pn = propylenediamine), of known configuration.²⁴ From the similarity in shapes of the ORD curves of (+)-trans-(SS)-Co(trien)Cl₂⁺ and (+)-trans-Co(2,3,2-tet)Cl₂⁺, the latter ion is assigned the same configuration. This is expected if the precursor oxalato complex is of the β configuration. Similarly, the (-)-trans-Co(3,2,3-tet)Cl₂⁺ ion is assigned the opposite RR^{25} configuration consistent with the assignment of the α configuration to the precursor Co(3,2,3-tet)ox⁺ ion.^{26, 27}

(24) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, Chem. Commun., 433 (1967).

(25) The configurations of the coordinated secondary amine atoms of linear tetramine ligands are designated by application of the rules devised by R. S. Cahn, C. K. Ingold, and V. Prelog, Angew. Chem., Int. Ed. Engl., 5, 385 (1966); in general, it is insufficient to assign high priority to the longest chain. Consider the linear tetramines trien (2,2,2-tet), 2,3,2-tet, and 3,2,3-tet

H H H NCCNCCNCCN NCCNCCCNCCN NCCCNCCNCCN 32101234 32101234 43210123

To determine the configuration of the secondary nitrogen atom (0), the priority of the groups bound to the nitrogen atom must be established. The proton is assigned the lowest priority, and the coordinated metal is assigned the highest priority; priorities are assigned to the remaining substituents by counting outward along each chain until a substituent with higher priority than carbon is reached. For 2,2,2-tet, the first substituent of higher priority, N, lies equidistant to the right and left as shown above. However, the substituents on the nitrogen to the right have greater priority than those to the left producing an R configuration. For the tetramine 2,3,2-tet, the first nitrogen is found on the left, so the configuration is designated S even though the prolons of the secondary nitrogen aloms lie on the same side of the chelate ring. The configuration assigned to the tetramine 3,2,3-tet is the same as that of 2,2,2-tet. The configurations of substituted derivatives must be individually assigned by application of these rules.

(26) G. R. Brubaker and D. P. Schaefer, Inorg. Nucl. Chem. Lett., 6, 237 (1970).

(27) G. R. Brubaker and D. P. Schaefer, Inorg. Chem., 9, 2373 (1970).

Scaled molecular models can be used to show some of the steric interactions involved in these complexes.²⁸ In trans complexes of triethylenetetramine there is marked strain involved in the ring system in agreement with the observed instability of the trans configuration. However, the α -cis and β -cis models can be constructed with little difficulty and with seemingly little preference for either α or β configuration. In complexes containing 2,3,2-tet, the trans-RS (meso) configuration appears the most stable and is the isomer produced experimentally under what appear to be equilibrium conditions. The trans-*RR*, SS configuration can also be constructed with little difficulty and has also been observed experimentally. In cis complexes containing the 2,3,2-tet ligand, molecular models show that the α configuration leads to highly unfavorable steric interactions between protons on adjacent chelate rings for all conformations of the chelate rings. These interactions are very much relieved in the β configuration so that a relatively strainfree and nonsterically hindered model of the β isomer can be constructed. Proceeding to the 3,2,3-tet ligand, we find that for the β isomer the ligand either blocks the remaining coordination sites or folds into itself resulting in unfavorable proton-proton interactions. The α configuration is to be preferred although the distinctions seem less obvious in the 2,3,2-tet complex. The exper-

 $(28)\,$ J. R. Gollogly and C. J. Hawkins, Inorg. Chem., 9, 57 (1970), and references cited therein.

imental results are in complete accord with simple, qualitative concepts of strain differences and steric hindrance among the various chelate rings in a complex.

Finally, we wish to comment on the use of infrared and nuclear magnetic resonance spectroscopy. Though Buckingham and Jones²⁹ correctly deduced the topology of some triethylenetetramine complexes from infrared evidence, recent reports on other systems cast doubt on the utility of these spectra.³⁰ We have made no effort to obtain infrared spectra. We believe that pmr spectra could be extremely useful in elucidating the configurations of these complexes; the only observable signals must come from the flexible tetramine ligand. We have not succeeded in overcoming several experimental difficulties including the low solubility of the complexes in suitable solvents and insufficient resolution at 60 MHz. Our limited observations are, however, consistent with the conclusions drawn from other spectroscopic studies.

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Competition of Chromium(II) Species Present in Aqueous Ethylenediamine Solutions in Electron-Transfer Reactions with Chloropentaamminecobalt(III) Cation¹

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The electron-transfer reactions between $Co(NH_8)_5Cl^{2+}$ and Cr(II) in aqueous ethylenediamine solutions have been studied as a function of changing pH for constant total ethylenediamine concentration. A procedure was developed to determine the distribution of Cr(III) among the product species, $Cr(OH_2)_5Cl^{2+}$, $Cr(en)(OH_2)_3Cl^{2+}$, and $Cr(en)_2(OH_2)_Cl^{2+}$, and this distribution was compared to the calculated amounts of Cr_{aq}^{2+} , $Cr(en)^{2+}$, and $Cr(en)_2^{2+}$ initially available for reaction. Rate constant ratios were calculated assuming that the mole fractions of the Cr(II) reactants remain constant throughout the reactions, and from these ratios and a previously reported rate constant for the $Cr_{aq}^{2+}-Co(NH_3)_5Cl^{2+}$ reaction, $k_0 = (2.2 \pm 0.5) \times 10^6 M^{-1} \sec^{-1}$, the rate constants for reaction of $Co(NH_3)_6Cl^{2+}$ with $Cr(en)^{2+}$, $k_1 = (4.0 \pm 2.3) \times 10^7 M^{-1} \sec^{-1}$, and with $Cr(en)_2^{2+}$, $k_2 = (1.6 \pm 0.8) \times 10^8 M^{-1} \sec^{-1}$, were found at 25° and an ionic strength of 1.4 M. The regular increases in rate as amine coordination is increased are discussed in terms of increased ligand field strength.

Introduction

Previous studies of the electron-transfer reaction between $Cr(OH_2)_6^{2+}$ and $Co(NH_3)_5Cl^{2+2,3}$ have shown the reaction occurs by a bridged mechanism with little motion of the nonbridging Co(III) ligands in the formation of the activated complex. Other work using $Co(NH_3)_5OH^{2+}$ as oxidant has indicated the rearrangement of the bridging ligand may be important

(1) Work partly supported under Contract AT(04-3)-34, Project No. 170, between the U. S. Atomic Energy Commission and the University of California. This paper constitutes Report No. UCLA-34P170-12 to the AEC.

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in reaching the transition state.^{4,5} Finally ¹⁸O isotopic fractionation studies of the Cr(III) product of this reaction in strong ethylenediamine solutions (*i.e.*, Cr-(en)₂(OH₂)Cl²⁺) suggest that motion of nonbridging Cr(II) ligands also occurs.⁶ The involvement of the nonbridging Cr(II) ligands may also be investigated by varying the ligands coordinated to Cr(II) in the activated complex. If motion of these ligands is required to form the transition state, then variation

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