

crystallize at 25° for 24 hr. The violet needles of the *cis-α* complex were collected, washed with cold water, and dried. It was finally recrystallized from methanol (25 ml), acetone (25 ml), and acetonitrile (20 ml) by the slow addition of ether (275 ml). The pure product (3.1 g) deposited as deep violet needles or flakes.  $\Lambda_M = 64 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  ( $5.93 \times 10^{-4} M$  in methanol at 25°). Anal. Calcd for  $[\text{Co}(\text{C}_{24}\text{H}_{30}\text{As}_4)\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$ : C, 35.9; H, 4.0; Cl, 13.3; As, 37.4; Co, 7.4. Found: C, 36.4; H, 4.1; Cl, 13.1; As, 37.0; Co, 7.3.

*trans*- $[\text{Co}(\text{R},\text{S}\text{-qars})\text{Cl}_2]\text{Cl}$ . The acetonitrile filtrate derived from the initial isolation of the *cis-α* complex was evaporated to dryness. It was recrystallized three times from hot HCl (0.1 M) solution to give the green *trans* complex as green needles. It was finally purified by crystallization from methanol by the careful addition of ether (1.5 g).  $\Lambda_M = 63 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  ( $1.07 \times 10^{-3} M$  in methanol at 25°). Anal. Calcd for  $[\text{Co}(\text{C}_{24}\text{H}_{30}\text{As}_4)\text{Cl}_2]\text{Cl}$ : C, 36.8; H, 3.9; Cl, 13.6; Co, 7.5. Found: C, 36.9; H, 4.1; Cl, 13.3; Co, 7.3.

*cis-β*- $[\text{Co}(\text{R},\text{S}\text{-qars})\text{CO}_3]\text{ClO}_4$ . *trans*- $[\text{Co}(\text{R},\text{S}\text{-qars})\text{Cl}_2]\text{Cl}$  (1 g) was dissolved in methanol (10 ml) and water (10 ml). Lithium carbonate (0.2 g) was then added and the solution was refluxed on a steam bath for 20 min to give a red solution. After filtration,  $\text{NaClO}_4$  (2 g) in water (100 ml) was added and the solution was extracted with methylene chloride (five 20-ml portions). The organic solvent was dried and removed under vacuum to give a red solid. This was taken up in acetonitrile (10 ml) and methanol (5 ml) and the product was crystallized by the slow addition of ether (30 ml). The carbonate compound deposited as red needles (0.45 g). Anal. Calcd for  $[\text{Co}(\text{C}_{24}\text{H}_{30}\text{As}_4)\text{CO}_3]\text{ClO}_4$ : C, 35.9; H, 3.6; Cl, 4.2. Found: C, 35.9; H, 3.6; Cl, 4.2.

*cis-β*- $[\text{Co}(\text{R},\text{S}\text{-qars})\text{Cl}_2]\text{ClO}_4$ . This compound was prepared by the method described for *cis-β*- $[\text{Co}(\text{R},\text{S}\text{-fars})\text{Cl}_2]\text{ClO}_4$  using *cis-β*- $[\text{Co}(\text{R},\text{S}\text{-qars})\text{CO}_3]\text{ClO}_4$  (0.3 g) as starting material. It was recrystallized from acetonitrile (15 ml) by slowly adding ether (45 ml). It deposited as dark brown blocks (0.2 g).  $\Lambda_M = 84 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  ( $4.73 \times 10^{-4} M$  in methanol at 25°). Anal. Calcd for  $[\text{Co}(\text{C}_{24}\text{H}_{30}\text{As}_4)\text{Cl}_2]\text{ClO}_4$ : C, 34.0; H, 3.6; Cl, 12.6. Found: C, 34.0; H, 3.6; Cl, 12.6.

**Topological Equilibria.** The complexes ( $1.5 \times 10^{-3} M$ ) were refluxed for 24 hr in 1 M HCl. All the complexes after a certain time suddenly isomerized by a Co(II) electron-transfer reaction.<sup>3</sup> This may occur within 1 hr but all of the reactions consistently occurred within 24 hr. The solutions were cooled and extracted with  $\text{CH}_2\text{Cl}_2$ . After removal of the solvent under vacuum the homogeneous residue was analyzed by NMR using the integrated methyl peak heights. In all cases the NMR spectrum only represented the appropriate isomeric mixture of complexes. For the methanol solution equilibrations  $1.5 \times 10^{-3} M$  complex solutions were used and the solutions were refluxed for 50 hr. The methanol was taken off under vacuum, the residue

was taken up in water, and the isomers were extracted and analyzed as before. All of the equilibrations generate a small amount of Co(II) which is effectively retained in the aqueous layer.

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**Registry No.** *cis-α*- $[\text{Co}(\text{R},\text{R}:\text{S},\text{S}\text{-fars})\text{Cl}_2]\text{ClO}_4$ , 56143-06-7; *cis-β*- $[\text{Co}(\text{R},\text{R}:\text{S},\text{S}\text{-fars})\text{Cl}_2]\text{ClO}_4$ , 55648-81-2; *trans*- $[\text{Co}(\text{R},\text{R}:\text{S},\text{S}\text{-fars})\text{Cl}_2]\text{ClO}_4$ , 55700-27-1; *cis-β*- $[\text{Co}(\text{R},\text{S}\text{-fars})\text{CO}_3]\text{ClO}_4$ , 55648-79-8; *cis-β*- $[\text{Co}(\text{R},\text{S}\text{-fars})\text{Cl}_2]\text{ClO}_4$ , 55700-29-3; *trans*- $[\text{Co}(\text{R},\text{S}\text{-fars})\text{Cl}_2]\text{ClO}_4$ , 55700-31-7; *cis-α*- $[\text{Co}(\text{R},\text{R}:\text{S},\text{S}\text{-fars})\text{Br}_2]\text{Br}$ , 55648-82-3; *trans*- $[\text{Co}(\text{R},\text{S}\text{-fars})\text{Br}_2]\text{Br}$ , 55721-18-1; *cis-α*- $[\text{Co}(\text{R},\text{R}:\text{S},\text{S}\text{-qars})\text{Cl}_2]\text{Cl}$ , 55648-83-4; *trans*- $[\text{Co}(\text{R},\text{S}\text{-qars})\text{Cl}_2]\text{Cl}$ , 55700-32-8; *cis-β*- $[\text{Co}(\text{R},\text{S}\text{-qars})\text{CO}_3]\text{ClO}_4$ , 55648-85-6; *cis-β*- $[\text{Co}(\text{R},\text{S}\text{-qars})\text{Cl}_2]\text{ClO}_4$ , 55722-69-5; *trans*- $[\text{Co}(\text{R},\text{S}\text{-fars})\text{Cl}_2]\text{Cl}\cdot\text{HCl}$ , 55700-33-9; *o*-phenylenebis(dimethylarsine), 13246-32-7; *o*-phenylenebis(methylbromoarsine), 52120-03-3;  $\gamma$ -chloropropylidimethylarsine, 26900-75-4; *o*-phenylenebis(dimethylarsino- $\gamma$ -propylmethylarsine), 55637-97-3; *o*-bromophenylidimethylarsine, 4457-88-9; *o*-phenylenebis(*o*-dimethylarsinophenylmethylarsine), 55637-98-4.

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## Stereochemistry of Complexes of Multidentate Ligands. III.<sup>1</sup>

### Stereoselective Cobalt(III) Ion Complexes of 1,6-Bis(2(*S*)-pyrrolidyl)-2,5-diazahexane

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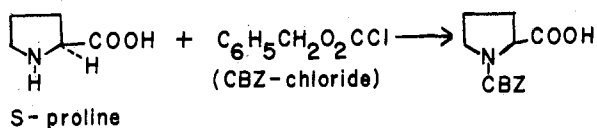
The synthesis of a new flexible tetraamine ligand, 1,6-bis(2(*S*)-pyrrolidyl)-2,5-diazahexane (*SS*-pyhn), is reported. Cobalt(III) complexes of *SS*-pyhn have been prepared and characterized. Only one isomer,  $\Lambda$ -*cis-α*- $[\text{Co}(\text{SS}\text{-pyhn})\text{X}_2]^{n+}$  ( $\text{X} = \text{Cl}, \text{H}_2\text{O}, \text{NO}_2$ ;  $\text{X}_2 = \text{CO}_3, \text{Ox}$ ), was observed in the synthesis. The absolute configuration of this isomer is assigned on the basis of electronic absorption and CD spectra along with other chemical data.

## Introduction

It has been observed that, when the cobalt(III) complexes of substituted derivatives of triethylenetetramine (trien) are synthesized, those flexible tetraamines which have asymmetric centers usually coordinate stereospecifically to the cobalt(III)

ion. The absolute configurations of the complexes can be rationalized in terms of the positions of the substituents in the trien skeleton.<sup>2-6</sup>

The ligand prepared in this work, 1,6-bis(2(*S*)-pyrrolidyl)-2,5-diazahexane (*SS*-pyhn),<sup>7</sup> is expected to possess



S-proline

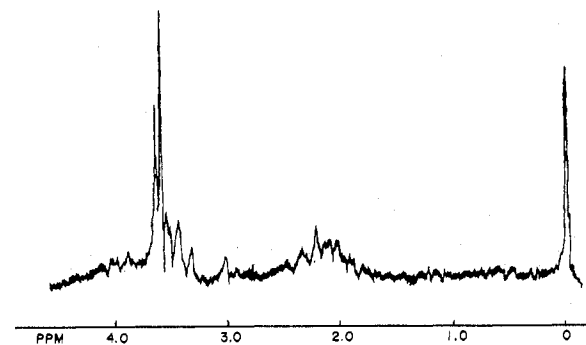
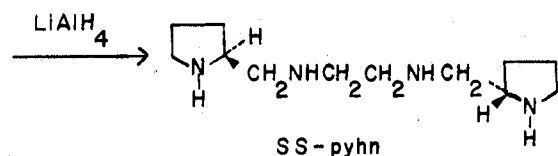
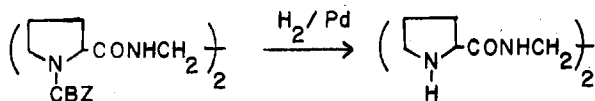
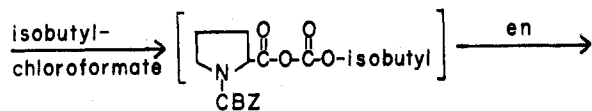


Figure 1. Synthetic route to SS-pyhn and the pmr spectrum of SS-pyhn-4HCl in D<sub>2</sub>O.

a pronounced tendency toward stereospecific coordination; it not only contains two asymmetric centers, but also each terminal nitrogen and its nearby asymmetric carbon atom are locked together by means of the pyrrolidine ring. The two pyrrolidine rings, because of their unique structural nature, were expected to play a significant role in stereospecific coordination. The resultant complexes were expected to offer background material for the study of other stereoselective reactions.

(S)-Proline was used as the starting material for the synthesis of the ligand. Since the absolute configuration of (S)-proline is known, the absolute configuration of the pyhn ligand derived from it is known. The synthesis of the ligand was accomplished through a series of reactions depicted in Figure 1.

### Experimental Section

**Chemical Reagents.** The (S)-proline and the carbobenzyloxy chloride were purchased from Nutritional Biochemical Corp., Cleveland, Ohio. The isobutyl chloroformate was obtained from J. T. Baker Chemical Co., Philipsburg, N. J., and the lithium aluminum hydride from Ventron Corp., Beverly, Mass. All other chemicals used were commercial reagent grade.

**Physical Measurements.** The infrared spectra of the solid samples were recorded using potassium bromide disks on a Perkin-Elmer Model 337 grating spectrophotometer. The spectra of liquid samples were taken of neat smears on KBr plates. The electronic absorption spectra were obtained using a Unicam SP 800A UV spectrophotometer. The ORD and CD curves were measured on a Jasco ORD/CD-5 spec-

trophotometer using 1-cm cell and using water as the solvent. The PMR spectra were obtained using a Varian A-60 spectrometer and using 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal standard. The solvent was D<sub>2</sub>O. Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich., and by Micro-Tech Laboratories, Skokie, Ill.

**Preparation of Carbobenzyloxy-(S)-proline.** This was prepared according to the method of Berger et al.,<sup>8</sup> mp 75–77°.

**Preparation of N,N'-Bis(carbobenzyloxy-(S)-prolyl)ethylenediamine.** A solution of 17.9 g (0.072 mol) of carbobenzyloxy-(S)-proline and 12 ml of triethylamine in 200 ml of toluene was chilled to –5° and treated with 9.7 ml of isobutyl chloroformate. After 1 hr of standing, a cold solution of 2.16 g (0.036 mol) of ethylenediamine and 12 ml of triethylamine in 150 ml of chloroform was added, and the mixture was allowed to stand overnight at room temperature. An additional 25 ml of chloroform was added. The mixture was washed successively with water, 3% sodium bicarbonate solution, and water, and finally dried over anhydrous sodium sulfate. After evaporation to dryness under reduced pressure the white crystalline product was collected; yield 16.8 g (89%);  $[\alpha]_{589} -20.8^\circ$  ( $c = 0.2845$  g/4 ml of chloroform). Anal. Calcd for C<sub>28</sub>H<sub>34</sub>N<sub>4</sub>O<sub>6</sub>: C, 64.35; H, 6.56; N, 10.72. Found: C, 64.48; H, 6.58; N, 10.53.

**Preparation of N,N'-Bis(S)-prolyl)ethylenediamine.** N,N'-Bis(carbobenzyloxy-(S)-prolyl)ethylenediamine (17 g) and 180 ml of methanol were taken into a 500-ml Paar low-pressure hydrogenation bottle. To the mixture 1.0 g of palladium on charcoal (10%) catalyst was added, the hydrogen gas pressure was adjusted to 15 lb/in.<sup>2</sup>, and the mixture was shaken for 3 hr. The catalyst was filtered and the filtrate was concentrated under reduced pressure to give a pale yellow oil. This oil was not further characterized. It can be transformed into a solid salt by dissolving in absolute ethanol, adding concentrated hydrochloric acid, and storing in a refrigerator for 2 days. The resultant white crystals are hygroscopic.

**Preparation of 1,6-Bis(2(S)-pyrrolidyl)-2,5-diazahexane-4-Hydrochloride (SS-pyhn-4HCl).** Anhydrous tetrahydrofuran (400 ml) and 25 g of N,N'-bis(2(S)-prolyl)ethylenediamine were placed in a 1000-ml three-necked round-bottom flask equipped with a mechanical stirrer and a reflux condenser. Lithium aluminum hydride (20.0 g) was carefully added with vigorous stirring in an ice bath. After the reaction mixture reached room temperature, it was refluxed and stirred for 36 hr. It was then cooled, and a solution of 39 g of water in 250 ml of tetrahydrofuran was cautiously added with vigorous stirring in an ice-salt bath. The solid was filtered off and the filter cake was extracted three times with boiling tetrahydrofuran. The combined tetrahydrofuran filtrate and washings were concentrated under reduced pressure to give a pale yellow oil. The oily residue was dissolved in absolute ethanol. Concentrated hydrochloric acid was added. Again concentration under reduced pressure gave a yellow oil. This oil was taken up in absolute ethanol and stored in a refrigerator for 2 days. The precipitated white crystals were collected, washed with absolute ethanol several times, and recrystallized from 10% water-ethanol solution; yield 22.4 g (62%). Anal. Calcd for C<sub>12</sub>H<sub>26</sub>N<sub>4</sub>·4HCl: C, 38.72; H, 8.12; N, 15.05. Found: C, 38.80; H, 8.05; N, 15.18. The specific rotation for this ligand was –158.1° ( $c = 0.2278$  g/2 ml of water) at 589 nm.

**Preparation of  $\Lambda$ -cis- $\alpha$ -[Co(SS-pyhn)Cl<sub>2</sub>]Cl·1/2H<sub>2</sub>O.** To a mixture of 11.2 g (0.03 mol) of 1,6-bis(2(S)-pyrrolidyl)-2,5-diazahexane-4-hydrochloride (SS-pyhn-4HCl) and 7.13 g (0.03 mol) of Co-Cl<sub>2</sub>·6H<sub>2</sub>O in 250 ml of water was added 5.0 g (0.12 mol) of LiOH·H<sub>2</sub>O. The brown solution was aerated with CO<sub>2</sub>-free air for 36 hr. The solution was evaporated to one-fourth its original volume under moving air at room temperature. To this solution 50 ml of concentrated hydrochloric acid was added and the evaporation was continued until half the volume remained. The precipitated purple crystals were filtered and washed with acetone and ether several times. A second crop of the purple crystals was obtained by adding 20 ml of concentrated hydrochloric acid to the filtrate and by evaporating the solution to less than its half-volume under moving air at room temperature. After the second crop of the product was filtered off, the filtrate was evaporated to near dryness. The residue was repeatedly extracted with hot acetone until no additional blue compound dissolved. It was then dissolved in a minimum amount of water and concentrated hydrochloric acid was added at room temperature until the third crop of the purple crystals separated. The total yield of the three fractions was 68% of the theoretical. The product was recrystallized from methanol-acetone. The three fractions described above have the same

ORD and CD, and the final filtrate also has the same ORD and CD as the product. Anal. Calcd for  $[\text{Co}(\text{C}_{12}\text{H}_{26}\text{N}_4)\text{Cl}_2]\text{Cl}\cdot\frac{1}{2}\text{H}_2\text{O}$ : C, 35.97; H, 6.54; N, 13.98; Cl, 26.55. Found: C, 36.46; H, 6.31; N, 14.22; Cl, 27.15.

**Preparation of  $\Delta$ -*cis*- $\alpha$ - $[\text{Co}(\text{SS-pyhn})\text{CO}_3]\text{ClO}_4$ .**  $\Delta$ -*cis*- $\alpha$ - $[\text{Co}(\text{SS-pyhn})\text{Cl}_2]\text{Cl}\cdot\frac{1}{2}\text{H}_2\text{O}$  (0.2 g) was dissolved in  $\text{HClO}_4$  (0.01 M) and after 24 hr of standing at room temperature 0.1 g of  $\text{NaHCO}_3$  and 0.09 g of  $\text{NaClO}_4$  were added. The red solution was evaporated under moving air at room temperature until crystals were formed. The product was removed by filtration and recrystallized from hot water. Anal. Calcd for  $[\text{Co}(\text{C}_{12}\text{H}_{26}\text{N}_4)\text{CO}_3]\text{ClO}_4$ : C, 35.11; H, 5.89; N, 12.60. Found: C, 34.88; H, 5.61; N, 12.51.

**Preparation of  $\Delta$ -*cis*- $\alpha$ - $[\text{Co}(\text{SS-pyhn})(\text{H}_2\text{O})_2]^{3+}$  in Situ.**  $\Delta$ -*cis*- $\alpha$ - $[\text{Co}(\text{SS-pyhn})\text{CO}_3]\text{ClO}_4$  ( $7.25 \times 10^{-2}$  g) was dissolved in water. To this solution 70%  $\text{HClO}_4$  was added dropwise until the pH of the solution was 2 and  $\text{CO}_2$  evolution stopped. The ORD and CD curves of the diaquo complex so formed were measured after several hours.

**Preparation of  $\Delta$ -*cis*- $\alpha$ - $[\text{Co}(\text{SS-pyhn})(\text{NO}_2)_2]\text{ClO}_4$ .** To 0.294 g of  $\Delta$ -*cis*- $\alpha$ - $[\text{Co}(\text{SS-pyhn})\text{Cl}_2]\text{Cl}\cdot\frac{1}{2}\text{H}_2\text{O}$  was added 15 ml of  $\text{HClO}_4$  (0.001 M) and the solution was aquated for 24 hr at room temperature. An excess amount of  $\text{NaHCO}_3$  (0.11 g) was then added, followed by excess  $\text{HClO}_4$  (1.0 ml of 1 M) after 3 hr. After 2 hr excess  $\text{NaNO}_2$  was added. After standing overnight, the solution was evaporated to less than half of its original volume under moving air at room temperature. The orange product crystallized slowly, was removed by filtration, and was washed with a small amount of cold water and acetone. Anal. Calcd for  $[\text{Co}(\text{C}_{12}\text{H}_{26}\text{N}_4)(\text{NO}_2)_2]\text{ClO}_4$ : C, 30.23; H, 5.50; N, 17.63. Found: C, 29.98; H, 5.42; N, 17.83.

**Preparation of  $\Delta$ -*cis*- $\alpha$ - $[\text{Co}(\text{SS-pyhn})\text{Ox}]\text{Cl}\cdot\text{H}_2\text{O}$ .** A solution containing 0.4 g of  $\Delta$ -*cis*- $\alpha$ - $[\text{Co}(\text{SS-pyhn})\text{Cl}_2]\text{Cl}\cdot\frac{1}{2}\text{H}_2\text{O}$  and 0.12 g of oxalic acid in 50 ml of water was heated on a steam bath for 3 hr. After about one-fourth of the original volume of the solution was evaporated under moving air, the solution was filtered, and the evaporation was continued under moving air at room temperature until crystals formed. The red product was filtered, washed with methanol, and recrystallized once from water. Anal. Calcd for  $\text{CoC}_{12}\text{H}_{26}\text{N}_4(\text{C}_2\text{O}_4)\text{Cl}\cdot\text{H}_2\text{O}$ : C, 39.40; H, 6.61; N, 13.13. Found: C, 39.28; H, 6.49; N, 13.01.

## Results and Discussion

**Preparation.** The ligand, 1,6-bis(2(*S*)-pyrrolidyl)-2,5-diazahexane (SS-pyhn), was prepared according to the scheme depicted in Figure 1 along with its PMR spectrum. It has two optically active centers; both have the *S* absolute configuration. All the spectroscopic and analytical data are consistent with the structural assignment of this compound.

The  $\text{Cl}_2(\text{SS-pyhn})\text{Co}^{\text{III}}$  complex ion was prepared by a typical air oxidation. The carbonato and dinitro complexes were obtained from the reaction of the dichloro complex with sodium bicarbonate and sodium nitrite, respectively. The  $\text{Ox}(\text{pyhn})\text{Co}^{\text{III}}$  complex was prepared by the reaction of oxalic acid with the  $\text{Cl}_2(\text{pyhn})\text{Co}^{\text{III}}$  complex ion.

**Electronic Absorption Spectra.** The electronic absorption spectra of the dichlorocobalt(III) complex of SS-pyhn and the oxalatocobalt(III) complex with this ligand are shown in Figures 2 and 3. The  $[\text{Co}(\text{SS-pyhn})\text{Cl}_2]^+$  ion shows a broad first absorption band in the visible region at about 555 nm. This is the region where the *cis* geometrical isomer's first absorption band is reported in *cis*- $\alpha$ - $[\text{Co}(\text{trien})\text{Cl}_2]^+$ <sup>9</sup> and *cis*- $\alpha$ - $[\text{Co}(2\text{S},9\text{S-dimetrien})\text{Cl}_2]^+$ .<sup>10</sup> Further, the absorption spectrum shows a shoulder at a low-energy side of the first absorption band. This suggests that the bluish purple dichlorocobalt(III) complex of SS-pyhn, the only isomer obtained, has the *cis*- $\alpha$  configuration.<sup>9,10</sup> In the electronic spectrum for the  $\text{Ox}(\text{SS-pyhn})\text{Co}^{\text{III}}$  complex (Figure 3) the two broad symmetrical bands which appear in the visible region may be assigned the spin-allowed  $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$  and  $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$  electronic transitions of the cobalt(III) ion in pseudo-octahedral symmetry. It is interesting to note that, on comparing the spectroscopic data for  $[\text{Co}(\text{NH}_3)_4\text{Ox}]^+$  with those for other oxalatotetraamine complexes,<sup>11</sup> the presence of the chelate rings exerts little effect on the energies of the electronic transitions.

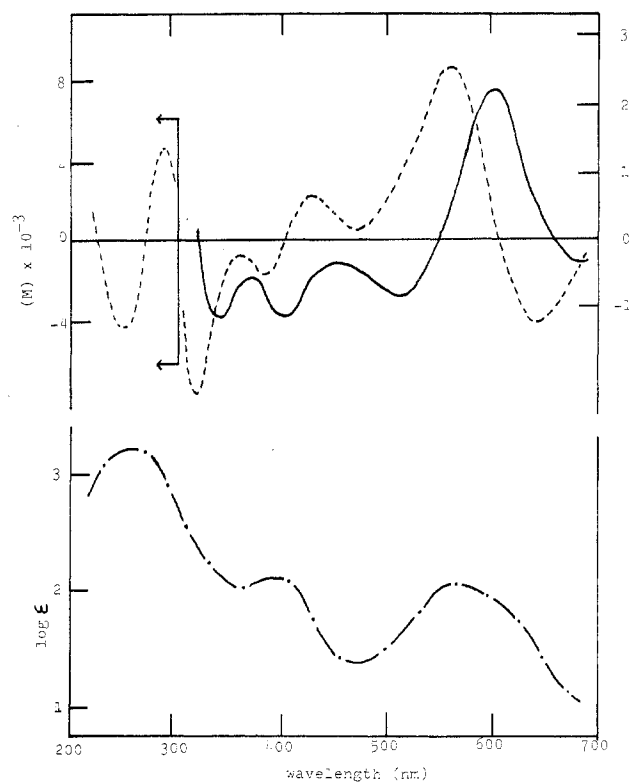


Figure 2. ORD (—), CD (---), and electronic absorption (- · - ·) spectra of  $\Delta$ -*cis*- $\alpha$ - $[\text{Co}(\text{SS-pyhn})\text{Cl}_2]^+$ .

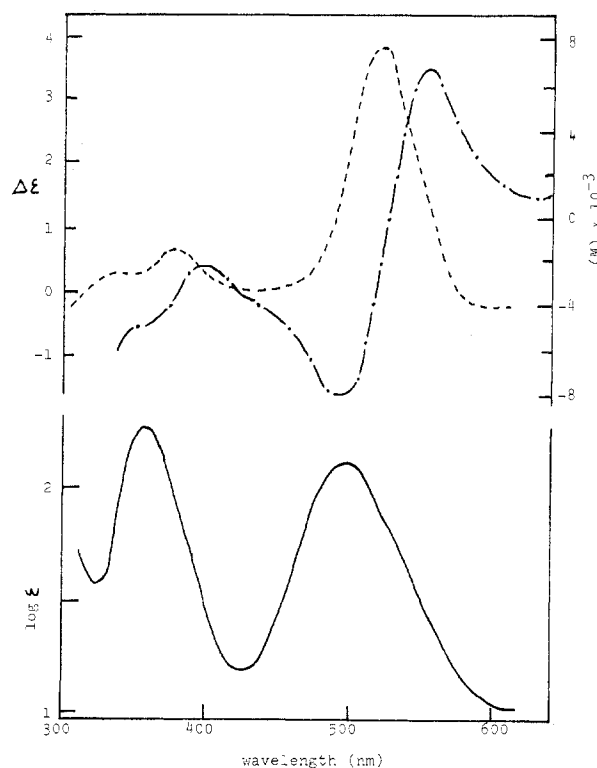


Figure 3. Electronic absorption (—), ORD (---), and CD (- · - ·) spectra of  $\Delta$ -*cis*- $\alpha$ - $[\text{Co}(\text{SS-pyhn})\text{Ox}]^+$ .

**Optical Activity, Absolute Configuration, and Stereospecific Coordination.** All the cobalt(III) complexes with SS-pyhn prepared in this work, *cis*- $\alpha$ - $[\text{Co}(\text{SS-pyhn})\text{X}_2]^{n+}$  ( $\text{X}_2 = \text{Cl}_2, \text{ClH}_2\text{O}, \text{CO}_3, (\text{H}_2\text{O})_2, \text{Ox}$ ), have  $\text{C}_2$  symmetry (except for the chloroaquo complex which is treated as though it possesses

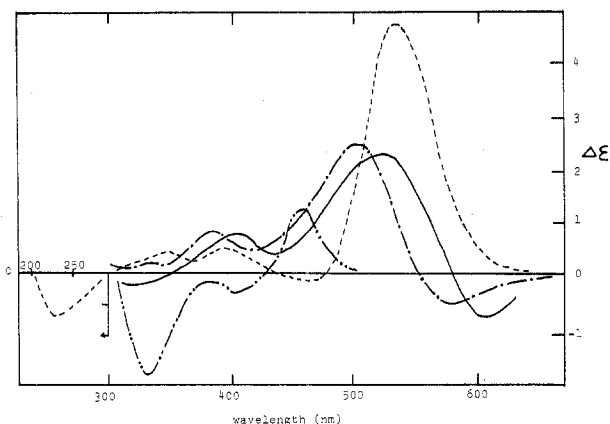


Figure 4. CD spectra of  $\Lambda$ -*cis*- $\alpha$ -[Co(SS-pyhn)ClH<sub>2</sub>O]<sup>2+</sup> (—),  $\Lambda$ -*cis*- $\alpha$ -[Co(SS-pyhn)CO<sub>3</sub>]<sup>+</sup> (---),  $\Lambda$ -*cis*- $\alpha$ -[Co(SS-pyhn)(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup> (- · - ·), and  $\Lambda$ -*cis*- $\alpha$ -[Co(SS-pyhn)(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> (- · · - ·).

a C<sub>2</sub> symmetry). The *cis*- $\alpha$ -[Co(SS-pyhn)Cl<sub>2</sub>]<sup>+</sup> ion shows a long-wavelength negative Cotton effect followed by a larger positive Cotton effect (Figure 2). Since the chloro group has a lower ligand field strength than the amine group, the CD band should be shifted toward longer wavelengths.<sup>12,13</sup> Therefore, the negative band is assigned to the <sup>1</sup>A<sub>1</sub> → <sup>1</sup>B<sub>1</sub> transition and the larger, positive band is assigned to the <sup>1</sup>A<sub>1</sub> → <sup>1</sup>A<sub>2</sub>(E<sub>g</sub>) transition. Applying Mason's formalism,<sup>14,15</sup> the dominant CD band is related to the <sup>1</sup>A<sub>1</sub> → <sup>1</sup>A<sub>2</sub>(E<sub>g</sub>) transition and, as it is positive for the ion (+)<sub>546</sub>- $\alpha$ -[Co(SS-pyhn)Cl<sub>2</sub>]<sup>+</sup>, is assigned the  $\Delta$ <sup>16</sup> absolute configuration. Saito et al.<sup>17</sup> showed that *cis*- $\alpha$ -[Co(3S,8S-dimetrien)(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> takes the absolute configuration. Comparison of the CD spectra of *cis*- $\alpha$ -[Co(SS-pyhn)Cl<sub>2</sub>]<sup>+</sup> with those of other complexes reported in the literature<sup>9,10,18</sup> also confirms the assignment of the  $\Delta$  absolute configuration.

The CD spectra of the other cobalt(III) complexes with SS-pyhn are shown in Figures 3 and 4. The chloroquo, diaquo, and oxalato complexes follow the same pattern as the dichloro complex. Using reasoning similar to that given for the dichloro complex, their dominant positive CD bands are related to the <sup>1</sup>A<sub>1</sub> → <sup>1</sup>A<sub>2</sub>(E<sub>g</sub>) transition and they are all assigned the  $\Delta$  absolute configuration. The main CD band of the carbonato complex is also positive and assigned the  $\Delta$  absolute configuration. For the dinitro compound the higher energy negative CD band is assigned to the <sup>1</sup>B<sub>1</sub> transition and the lower energy positive band to the <sup>1</sup>A<sub>1</sub> + <sup>1</sup>B<sub>2</sub> transition,<sup>18</sup> consistent with the assignment of the  $\Delta$  configuration to the complex.

A recent X-ray diffraction study<sup>19</sup> showed that the two outside chelate rings of the  $\Lambda$ -*cis*- $\alpha$ -[Co(trien)ClNH<sub>3</sub>]<sup>2+</sup> complex adopt the  $\delta$ <sup>16</sup> conformation. Crystallographic studies of the (+)<sub>589</sub>-*cis*- $\alpha$ -[Co(2S,9S-dimetrien)(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> and the (+)<sub>589</sub>-*cis*- $\alpha$ -[Co(3S,8S-dimetrien)(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> ions showed that the two outside chelate rings also adopt the  $\delta$  conformation.<sup>17,20</sup> In both complexes the middle chelate ring takes the  $\lambda$  conformation. The two asymmetric carbon atoms of the SS-pyhn ligand have the *S* absolute configuration, since all the asymmetric centers are derived from the (*S*)-proline used as a starting material. The SS-pyhn ligand resembles closely the 2S,9S-dimetrien; both are substituted at the second and ninth carbon atoms. By comparison then to the tetraamine ligands mentioned above, the SS-pyhn ligand also would take a conformation in which the two outside chelate rings were  $\delta$ . Therefore, all the  $\Lambda$ -*cis*- $\alpha$  cobalt(III) complexes of SS-pyhn isolated in this work should have the  $\delta\lambda\delta$  conformation in their chelate rings.

When we take into account the asymmetric feature of the secondary amino groups in the trien complex of cobalt(III),

there is only one enantiomeric pair for the *cis*- $\alpha$  isomer,  $\Lambda$ -*cis*- $\alpha$ -RR and  $\Delta$ -*cis*- $\alpha$ -SS, where *R* and *S* indicate the absolute configuration of the central nitrogen atoms in the trien complex. SS-pyhn has a methylene group on each asymmetric carbon atom by means of a pyrrolidine ring. Because of the presence of these substituted methylene groups, priorities of the substituents surrounding an asymmetric nitrogen atom are reversed when we consider the absolute configuration of the asymmetric nitrogen atoms in the central chelate ring in the trien complex and the SS-pyhn complex. Therefore, the  $\Lambda$ -*cis*- $\alpha$ -RR configuration in the trien complex becomes the  $\Delta$ -*cis*- $\alpha$ -SS configuration in the SS-pyhn complex, even though the protons of those nitrogen atoms lie on the same side with respect to the central chelate ring.

Since both terminal nitrogen atoms in SS-pyhn are secondary, they become asymmetric upon coordination to the cobalt(III) ion. In the  $\Lambda$ -*cis*- $\alpha$ -SS configuration of SS-pyhn complexes, the favorable absolute configuration of both terminal nitrogen atoms is believed to be *S*, because in this case the asymmetric C-methylene groups are in the equatorial position and the nonbonded interactions between chelate rings are minimized. The alternative absolute configuration is *R*. However, a conformational analysis using Drieding molecular models indicates that there would be an enormous amount of nonbonded interaction between chelate rings, too much ring strain on the part of both outside chelate rings and pyrrolidine rings, and further the asymmetric C-methylene groups would be in the axial position. Therefore, the *S* absolute configuration on the part of the terminal nitrogen atoms should be much more stable.

Although the SS-pyhn ligand was expected to possess the ability of stereospecific coordination, the fact that only one optically active isomer,  $\Lambda$ -*cis*- $\alpha$ , was obtained in this work is quite remarkable. The  $\Delta$ - $\alpha$  isomer, in which the pyrrolidine rings should adopt the axial orientations, is energetically quite unstable compared with the  $\Lambda$  isomer. Since the preferred conformation of the outside chelate ring of SS-pyhn is the  $\delta$ -gauche form, it is reasonable that the *cis*- $\alpha$  isomer gives rise to the  $\Lambda$  configuration. In the *cis*- $\alpha$  geometry both ring strain and nonbonded interaction either between chelate rings or between the central chelate ring and the pyrrolidine ring are much less than in either the *cis*- $\beta$  or the *trans* geometry. The nonbonded interaction between the central chelate ring and the pyrrolidine ring should be the most prominent factor. Therefore, it is believed that both the presence of the pyrrolidine rings in the ligand and the preferred conformation of the outside chelate rings play decisive roles in the stereospecific coordination of SS-pyhn.

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**Registry No.** *N,N'*-Bis(carbobenzoxy-(*S*)-prolyl)ethylenediamine, 54985-57-8; *N,N'*-bis((*S*)-prolyl)ethylenediamine, 54985-58-9; 1,6-bis(2(*S*)-pyrrolidyl)-2,5-diazahexane-4-hydrochloride, 54985-59-0;  $\Lambda$ -*cis*- $\alpha$ -[Co(SS-pyhn)Cl<sub>2</sub>]Cl, 54986-00-4;  $\Lambda$ -*cis*- $\alpha$ -[Co(SS-pyhn)CO<sub>3</sub>]ClO<sub>4</sub>, 54986-02-6;  $\Lambda$ -*cis*- $\alpha$ -[Co(SS-pyhn)(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup>, 54986-03-7;  $\Lambda$ -*cis*- $\alpha$ -[Co(SS-pyhn)(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub>, 54986-05-9;  $\Lambda$ -*cis*- $\alpha$ -[Co(SS-pyhn)(Ox)]Cl, 54986-06-0; carbobenzoxy-(*S*)-proline, 1148-11-4; ethylenediamine, 107-15-3.

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## Complex Ion Kinetics. Reaction Rates on Ion-Exchange Resins Compared to Those in Water

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A comparison has been made between the rates in water and on an ion-exchange resin for the aquation of  $[(\text{NH}_3)_5\text{CoOReO}_3]^{2+}$  and  $[(\text{H}_2\text{O})_5\text{CrCl}]^{2+}$  and for the  $^{18}\text{O}$  isotopic exchange of water with  $[(\text{NH}_3)_5\text{Co}(\text{OH}_2)]^{3+}$  and  $\text{ReO}_4^-$ . The rate of water exchange on  $[(\text{NH}_3)_5\text{Co}(\text{OH}_2)]^{3+}$  was not changed by association with Dowex 50W resins. Aquation of  $[(\text{NH}_3)_5\text{CoOReO}_3]^{2+}$  and water exchange on  $\text{ReO}_4^-$  had modified pH dependencies when associated with a resin. With the cobalt complex the rates were faster on the resin in the acidic region and slower on the resin in the basic region. A new term in the rate equation was observed when  $\text{ReO}_4^-$  was on the resin, first order in  $\text{H}^+$ , while the other terms appear to be unchanged. Aquation of  $[(\text{H}_2\text{O})_5\text{CrCl}]^{2+}$  was much slower when it was absorbed on the resin. This was related to the known ionic strength effect of the reaction.

### Introduction

Ion-exchange processes have played a highly significant role in studies involving reactions of inorganic and complex ions. Use of ion-exchange resins has been made in determining the charge of ions,<sup>2</sup> the degree of polymerization,<sup>3</sup> the number and type of products of a reaction,<sup>4</sup> and the rate of reaction<sup>5</sup> and in preparative experiments.<sup>6</sup> It has been especially valuable in the reaction product separation of complex ions for analytical<sup>7</sup> and preparative<sup>8</sup> purposes. Considerable time is required for many of these separations during which reactions may occur on the complex ions being separated. These reactions may or may not differ from those occurring in the aqueous phase and can occur during the process of absorption and/or desorption from the resin or during association with the resin. Considerable effort has been made in the study of ion-exchange resins as catalysts for many reactions<sup>9</sup> and the case of an absorbed ion reacting to form a new ion during chromatographic separation has been mathematically developed.<sup>10</sup> Hydrolysis of polypeptides by reaction with complexes immobilized on ion-exchange resins has been of extreme value in recent years.<sup>11</sup> The question of changes in rates of reaction due to interaction with the resin does not appear to have been directly measured. In a qualitative sense it is generally accepted that for the usual inert Werner type complexes neither the products nor the reaction rates change drastically when absorbed on a resin.

This study compares reaction rates on a resin with those in water for four fairly representative systems: aquation of  $[\text{Co}(\text{NH}_3)_5\text{OReO}_3]^{2+}$  and  $[\text{Cr}(\text{OH}_2)_5\text{Cl}]^{2+}$  and the  $^{18}\text{O}$  water exchange with  $[\text{Co}(\text{NH}_3)_5\text{OH}_2]^{3+}$  and with  $\text{ReO}_4^-$ . The products of these reactions were found to be identical on the resin and in water and the kinetics in aqueous media is well known. It was hoped that the results of this study would allow a prediction of the magnitude and direction of changes in reaction rate of complex ions when associated with ion-exchange resins.

### Experimental Section

**A. Aquation of Resin- $[\text{Co}(\text{NH}_3)_5\text{OReO}_3]$  in Water.**  $[\text{Co}(\text{NH}_3)_5\text{OReO}_3](\text{ReO}_4)_2$  was prepared as previously described.<sup>6</sup> Dowex 50W-X4 or 50W-X2 (50–100 mesh) was freshly purified each day

by exhaustive washing with 6 M HCl, 2 M NaOH, 1 M NaCl, and water leaving it neutral in the sodium ion form.

About 2 ml of resin was suspended in 25 ml of pure water at 0° and about 50 mg of complex was added. With stirring it took about 5 min for the complex ion to dissolve and be absorbed by the resin. The resin complex was collected on a filter and washed exhaustively with water (0°). At this point it was about 50% in the complex form. It was then added to 100 ml of buffer solution or water at the appropriate reaction temperature and approximately 0.3-ml aqueous samples were collected at timed intervals. Stirring was intermittent. The  $[\text{ReO}_4^-]$  in each of these samples was determined by exact dilution of 100  $\mu\text{l}$  to 50.00 ml with a color-developing solution consisting of HCl, acetone,  $\text{SnCl}_2$ , and either DMG<sup>12</sup> or furil dioxime (FDO).<sup>13</sup> After 3 hr of color development the light absorption was measured at 445 nm (DMG) and 532 nm (FDO), and  $[\text{ReO}_4^-]$  was determined from standard curves. Graphs of  $-\ln(1-F)$  vs. time were linear over at least 3–4 half-times giving values for  $k_{\text{obsd}}$  (Table I, Figure 1).

Buffer solutions utilized 2,6-lutidine-HCl mixtures, a poorly coordinating amine, since the reaction is general acid-base catalyzed. However, they were not entirely satisfactory and the solution pH changed upon addition of the resin. This was due apparently to replacement of  $\text{Na}^+$  from the resin by 2,6-lutH<sup>+</sup> with a consequent increase in solution basicity. This occurred instantaneously however, and the final pH represents the reaction conditions. The concentration of either cobalt complex in solution at any time in the reaction was extremely small being estimated at less than 0.001 of the total cobalt. This was maintained by having the resin less than two-thirds saturated with the cobalt complex.

**B. Oxygen Exchange between Resin- $\text{ReO}_4$  and Water.**  $\text{NaReO}_4$  ( $^{18}\text{O}$  enriched) was prepared from  $\text{HReO}_4$  by equilibration with  $\text{H}_2^{18}\text{O}$  (1 hr at 25°) followed by neutralization with solid NaOH. Recrystallization was from MeOH-acetone solution. Dowex 1-X4 (50–100 mesh) was washed with 8 M HCl, 4 M NaOH, and saturated NaCl solutions in that order and then exhaustively with twice distilled water. CsCl and NaCl were recrystallized from water until their solutions were neutral. 2,6-Lutidine was distilled and the middle third used with HCl to formulate buffer media.

To a 5.0-cm column containing approximately 20 ml of freshly cleaned and washed resin-Cl<sup>14</sup> at 0° 150 ml of a cooled solution containing 5.0 g of  $\text{NaReO}_4$  ( $^{18}\text{O}$  enriched) was added. This constituted about two-thirds of the capacity of the resin. The resin- $\text{ReO}_4$  was washed with cold water, dried by aspiration, and added to 100 ml of water or appropriate buffer solution at the proper temperature in a water bath. (On occasion, the resin-Cl was prewashed with the buffer solution or converted to the  $\text{OH}^-$  form before  $\text{NaReO}_4$  addition.)