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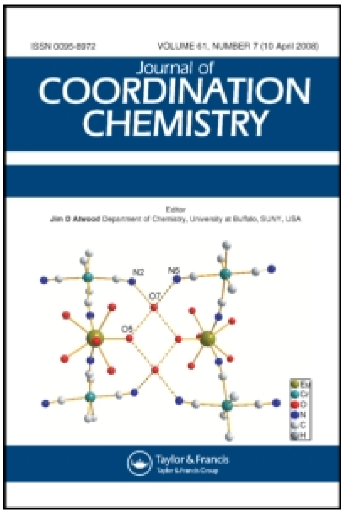

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STEREOCHEMISTRY OF COMPLEXES OF MULTIDENTATE LIGANDS

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STEREOCHEMISTRY OF COMPLEXES OF MULTIDENTATE LIGANDS

IV[1] Stereoselective cobalt(III) ion complexes of 1,7-bis(2-S-pyrrolidyl)-2,6-diazaheptane

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(*Received November 18, 1974, in final form February 18, 1975*)

Dichloro, dinitro, and diacetato cobalt(III) complexes of a new tetramine ligand, 1,7-bis(2-S-pyrrolidyl)-2,6-diazaheptane (SS-pyht) have been prepared and characterized. Only the *trans* isomer has been obtained for each complex. Oxalate ion reacts with *trans*-[Co(SS-pyht)Cl_2]ClO_4 in aqueous media to produce Λ-*cis*-β-[Co(SS-pyht)Ox]ClO_4.

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INTRODUCTION

Synthesis of the dichloro cobalt(III) complexes of 1,4,8,11-tetraazaundecane(2,3,2-tet)[2,3] and 1,5,8,12-tetraazadodecane(3,2,3-tet)[4] have been shown so far to yield *trans* isomers exclusively. A similar marked topological specificity for the *trans* isomer has also been observed in the dichloro cobalt(III) complexes of 2,5,9,12-tetraazatridecane-(1,11-me_2-2,3,2-tet)[5] and 4,8-diaza-2,10-undecane-diamine(dime-2,3,2-tet)[6] ligands.

In a previous paper[1] we reported that the ligand, 1,6-bis(2-S-pyrrolidyl)-2,5-diazahexane(SS-pyhn) which can be considered as a homolog of trien or 2,2,2-tet, formed only the Λ-*cis*-α isomer with cobalt(III) ion. The ligand prepared in the present work, 1,6-bis(2-S-pyrrolidyl)-2,6-diazaheptane-(SS-pyht)[7], is similar to SS-pyhn, but has its alkyl backbone lengthened with the insertion of one more methylene group between the second and third amino groups (See Figure 1). The object then was to see if this new ligand, with its highly constrained, optically active coordinating moieties, would show the topological specificity for the *trans* isomer. Like SS-pyhn, this ligand contains two optically active centers. Each terminal nitrogen and its neighboring asymmetric carbon atom are linked by means of the pyrrolidine rings. It was expected that the pyht ligand would coordinate stereospecifically and that the two pyrrolidine rings, with their unique structural nature, would play a significant role in the details of the stereoselective coordination.

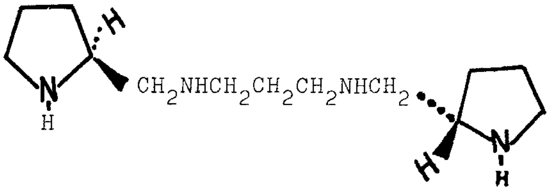

FIGURE 1 Absolute configuration of SS-pyht.

EXPERIMENTAL SECTION

Chemical reagents

The S-proline and the carbobenzoxy chloride were purchased from Nutritional Biochemical Corp., Cleveland, Ohio. The isobutyl chloroformate and the 1,3-propanediamine were obtained from J. T. Baker Chemical Co., Philipsburg, New Jersey, 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

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Spectrophotometer. The ORD and CD curves were measured on a Jasco ORD/CD–5 Spectrophotometer using 1-cm cell and using water as the solvent. The pmr spectra were obtained using a Varian A-60 Spectrometer using 2,2-dimethyl-2-silapentane-5-sulfonate(DSS) as an internal standard. The solvent was D_2O. Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan, and by Micro–Tech Laboratories, Skokie, Illinois.

Preparation of Carbobenzoxy-S-proline

This was prepared according to the method of Berger, et al.[8]: mp 75–77°.

Preparation of N,N'-Bis (carbobenzoxy-S-Prolyl)-1,3-propanediamine

A solution of 24.92 g (0.1 mol) of carbobenzoxy-S-proline and 15.5 ml of triethylamine in 300 ml of toluene was chilled to –5°C and treated with 13.1 ml of isobutylchloroformate. After one hour of standing, a cold solution of 3.7 g (0.05 mol) of 1,3-propanediamine and 15 ml of triethylamine in 200 ml of chloroform was added, and the mixture was allowed to stand overnight at room temperature. The mixture was filtered. The filtrate was washed successively with water, 3% sodium bicarbonate solution, and water, and finally dried over anhydrous sodium sulfate. It was evaporated to dryness to give a pale yellow oil, which crystallized slowly over two days. The white product was recrystallized from ethanol. Yield: 20.2 g (75.4%). $[\alpha]_{589}$–24.1 (c 0.0949 g/3 ml of chloroform). *Anal.* Calc'd. for $C_{29}H_{36}N_4O_6$: C, 64.91; H, 6.76; N, 10.44. Found: C, 64.75, H, 6.78; N, 10.41.

Preparation of N,N'-Bis(S-prolyl)-1,3-propanediamine

21 g of N.N'-bis-(carbobenzoxy-S-prolyl)-1,3-propanediamine and 250 ml of methanol were taken into a 500 ml Paar low-pressure hydrogenation bottle. To this mixture 1.0 g of palladium on charcoal (10%) catalyst was added, the hydrogen gas pressure was adjusted to 15 lb/in^2, and the mixture solution shaken for three hours. The catalyst was filtered and the filtrate was evaporated under reduced pressure to give a pale yellow oil. This was not further characterized.

Preparation of 1,7-Bis(2-S-pyrrolidyl)-2,6-diazaheptane tetrahydrochloride monohydrate-(SS-pyht · 4HCl · H_2O)

250 ml of dry tetrahydrofuran and 11.8 g (0.044 mole) of N,N'-bis(S-prolyl)-1,3-propanediamine were placed in a 500-ml three necked round-bottom flask equipped with a mechanical stirrer and a reflux condenser in an ice-bath. Then 15.2 g (0.4 mole) of lithium aluminum hydride was added carefully with vigorous stirring at ice temperature. After being allowed to come slowly to room temperature, the reaction mixture was refluxed and stirred for two days. It was then cooled and transferred into a one-liter three necked round-bottom flask, which was equipped with a mechanical stirrer and placed in an ice bath. A solution of 36 g of water and 200 ml of tetrahydrofuran was added cautiously with vigorous stirring. Solids were 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 oil was dissolved in absolute ethanol. Concentrated hydrochloric acid was added. After being stored in a refrigerator overnight and adding ether, white crystals precipitated. They were washed with absolute ethanol and ether. Yield: 8.6 g(51%). *Anal.* Calc'd. for $C_{13}H_{28}N_4 \cdot 4HCl \cdot H_2O$; C, 38.63; H, 8.48; N, 13.86; Cl, 35.08. Found: C, 38.73; H, 8.46; N, 13.67; Cl, 34.93. The specific rotation for this ligand was $[\alpha]_{589}$ –201.3(c = 0.044 g/3 ml of water).

Preparation of trans-[Co(SS-Pyht)Cl_2]ClO_4 · H_2O

To a mixture of 3.8 g (9.84 x 10^{-3} mol) of 1,7-bis(2S-pyrrolidyl-2,6-diazaheptane tetrahydrochloride (SS-pyht · 4HCl) and 2.34 g (9.84 x 10^{-3} mol) of $CoCl_2 \cdot 6H_2O$ dissolved in 60 ml of water was added 1.65 g of $LiOH \cdot H_2O$. The brown solution was aerated with CO_2-free air for 36 hours. When 10 ml of concentrated hydrochloric acid was added, the solution turned green. Three ml of 70% $HClO_4$ was added to this green solution and it was evaporated under moving air at room temperature until crystals separated. The green product was collected by filtration, washed with a little cold acetone and ethanol, and then air dried. *Anal.* Calc'd. for $CoC_{13}H_{28}N_4Cl_2 \cdot ClO_4 \cdot H_2O$: C, 32.01; H, 6.20; N, 11.45; Cl, 21.81. Found: C, 31.57; H, 5.99; N, 11.82; Cl, 21.71.

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Preparation of trans-[Co(SS-Pyht)(OAc)$_2$] ClO$_4$ · H$_2$O

A solution containing 0.5 g of *trans*-[Co(SS-pyht)-Cl$_2$] ClO$_4$·H$_2$O and 1.0 g of sodium cetate was heated on a steam bath for two hours, after which 0.1 g of LiClO$_4$ was added. The solution was cooled and evaporated until crystals began to form. The red-violet crystals were removed by filtration and recrystallized from hot water. *Anal.* Calc'd. for $CoC_{17}H_{34}N_4ClO_8 \cdot H_2O$: C, 38.17; H, 6.78; N, 10.47. Found: C, 37.95; H, 6.41; N, 10.41.

Preparation of trans-[Co(SS-Pyht)NO$_2$)$_2$] ClO$_4$.

To a solution of 0.582 g (1.5 x 10^{-3} mol) of pyht 4HCl·H$_2$O and 0.252 g (6 x 10^{-3} mol) of LiOH·H$_2$O in 30 ml of water, 0.457 g (1.5 x 10^{-3} mol) of CoCl$_2$·6H$_2$O and 0.21 g (3 x 10^{-3} mol) of NaNO$_2$ were added. The solution was aerated with CO$_2$-free air for 24 hours. The solution was then evaporated under moving air at room temperature to 15 ml and an excess of LiClO$_4$ was added. The yellow-brown product was obtained on standing overnight in a refrigerator, and washed with cold water and ethanol. *Anal.* Calc'd. for $CoC_{13}H_{28}N_4 \cdot 2NO_2 \cdot ClO_4$: C, 31.82; H, 5.75; N, 17.12. Found: C, 31.50; H, 5.71; N, 17.22.

Preparation of Λ-cis-β-[Co(SS-phyt)Ox] ClO$_4$.

A solution containing 0.63 g (1.29 x 10^{-3} mol) of *trans*-[Co(SS-phyt)Cl$_2$] ClO$_4$·H$_2$O and 0.238 g (1.29 x 10^{-4} mole) of potassium oxalate hydrate in 50 ml of water was heated on a steam bath for two hours. The solution was filtered and evaporated on a steam bath under moving air until crystals formed. The solution was cooled and kept in a refrigerator for several hours. The red product was filtered, washed with methanol, and recrystallized once from hot water. *Anal.* Calc'd. for $CoC_{13}H_{28}N_4 \cdot C_2O_4 \cdot ClO_4$: C, 37.01; H, 5.80; N, 11.51. Found: C, 36.89; H, 5.71; N, 11.55.

DISCUSSION

Preparation

The ligand, 1,7-bis(2-S-pyrrolidyl)-2,6-diazaheptane-(SS-pyht), was prepared according to the same general scheme as described previously,[1] using 1,3-propylenediamine in place of ethylenediamine.

The dichloro and dinitro cobalt(III) complexes with SS-pyht were prepared by the usual air oxidation technique. The diacetato and oxalato complexes were obtained by the reaction of the dichloro complex with sodium acetate and potassium oxalate respectively. Only one isomer was isolated for each complex.

Electronic Absorption Spectra

Electronic absorption spectra for *trans*-[Co-(SS-pyht)Cl$_2$]$^+$, *trans*-[Co(SS-pyht)(NO$_2$)$_2$]$^+$, and *trans*-[Co(SS-pyht)(OAc)$_2$]$^+$ are shown in Figures 2–4, along with CD and ORD spectra. All of the electronic absorption spectra show split bands in the long-wavelength region where the *cis* configuration would show a broad band. Therefore, these complexes have been assigned the *trans* configuration on the basis of their visible spectra.

Comparison of the spectra of *trans*-[Co(SS-pyht)-(OAc)$_2$] ClO$_4$ with those of the *trans* isomers of [Co(en)$_2$(OAc)$_2$]$^+$, [Co(NH$_3$)$_4$(OAc)$_2$]$^+$, and *trans*-[Co(2,3,2-tet)(OAc)$_2$] ClO$_4$[9] confirms the *trans* configuration. The first band of [Co(NH$_3$)$_4$(OAc)$_2$]$^+$ shows distinct splitting in the *trans* isomer but no splitting in the *cis* isomer[10] as do the corresponding [Co(en)$_2$(OAc)$_2$]$^+$ isomers.[11] The *trans*-[Co-(SS-pyht)(OAc)$_2$] ClO$_4$ complex shows a splitting in the first band. The electronic spectra of these species are in accord with those expected for complex ions of the CoA$_4$B$_2$ type from crystal field theory.[12] Although the *trans*-[Co(SS-Pyht)(OAc)$_2$]$^+$ is not of D$_{4h}$ symmetry, its visible spectrum is closely approximated by this model. Thus, for this complex the long wavelength band is assigned to the transition approximating the ^1E_g and the next shorter wavelength band assigned to that approximating the $^1A_2$ transition.

Optical Activity and Absolute Configuration

The CD and ORD spectra of *trans*-[Co-(SS-pyht)Cl$_2$]$^+$, *trans*-[Co(SS-pyht)(NO$_2$)$_2$]$^+$, and *trans*-[Co(SS-pyht)(OAc)$_2$]$^+$ are shown in Figures 2–4.

The CD curves of *trans*-CoN$_4$Cl$_2$ ions have been measured with ligands trien[13], SS-3,8-Me$_2$trien[14], R-1,5,10-Me$_3$trien[5], SS-1,2,9,10-Me$_4$trien[5], SS-1,3,8,10-Me$_4$trien[5], 2,3,2,-tet[15], and SS-Me$_2$-2,3,-2-tet[6].

The CD curves of (+)-*trans*-SS-[Co(trien)Cl$_2$]$^+$ and (+)-*trans*-[Co(3,8-Me$_2$-trien)Cl$_2$]$^+$ (3,8-Me$_2$trien-3,8-dimethyltrietylenetetramine) both show a dominant negative band at about 650 nm, a smaller positive band at about 570 nm, and another positive band at about 455 nm. The two components of the E(D$_4$)

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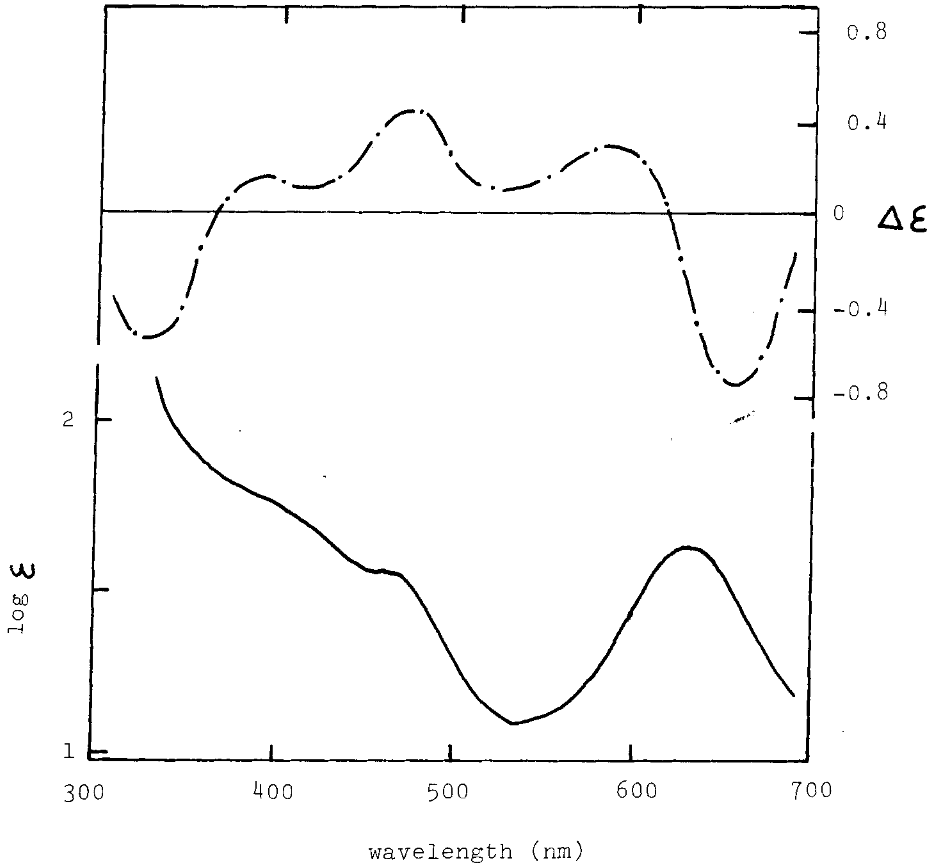

FIGURE 2 Electronic absorption(————) and CD(— · — ·) spectra of *trans*-[Co(SS-pyht)Cl$_2$]$^+$ ion.

appear as A(C_2) and B(C_2) components of opposite sign in the long wavelength region and the $A_2(D_4)$ as the band at 455 nm. These results agree with the conclusion that two outside chelate rings have the same δ conformation, which has been confirmed by a recent X-ray crystallographic study.[16] The substituted trien ligands with methyl substitution at the terminal nitrogens, R-1,5,10-Me$_3$trien, SS-1,2,9,10-Me$_4$trien, and SS-1,3,8,10-Me$_4$trien show the similar dominant negative CD bands with A(C_2) and B(C_2) components of opposite sign in the long wave-length region and the $A_2(D_4)$ as the band at 455 nm. These results agree with the conclusion that two outside chelate rings have the same δ conformation, which has been confirmed by a recent X-ray crystallographic study.[16] The substituted trien ligands with methyl substitution at the terminal nitrogens, R-1,5,10-Me$_3$trien, SS-1,2,9,10-Me$_4$trien, and SS-1,3,8,10-Me$_4$ trien show the similar dominant negative CD bands with A(C_2) and B(C_2) components of opposite sign in the long wave-length region. Thus, the outside chelate ring in these complexes have been assigned the δ conformation. However, these dichloro complexes have a CD band near 460 nm whose sign is opposite that of *trans*-[Co(SS-3,8-Me$_2$trien)Cl$_2$]$^+$ ion. This CD band near 460 nm has been ascribed to the $^1A_1 \rightarrow {}^1A_2(D_{4h})$ transition because the ligand field difference between these ions should be small. This difference has been interpreted by means of the vicinal effect from the R-asymmetric nitrogen at the end of the chelate ring.[5,16] The vicinal effect has a positive Cotton effect for the $A_{1g} \rightarrow E_g$ (D_{4h}) component and a negative Cotton effect for the $A_1 \rightarrow A_2$ component.

The CD curves of *trans*-[Co(SS-Me$_2$-2,3,2-tet)-Cl$_2$]$^+$ and *trans*-(RR)-[Co(2,3,2-tet)Cl$_2$]$^+$ both show a dominant negative band at about 650 nm, a smaller positive band at about 570 nm, and a negative band at about 450 nm. The two components of the E(D_4) appear as A(C_2) and B(C_2) components of opposite

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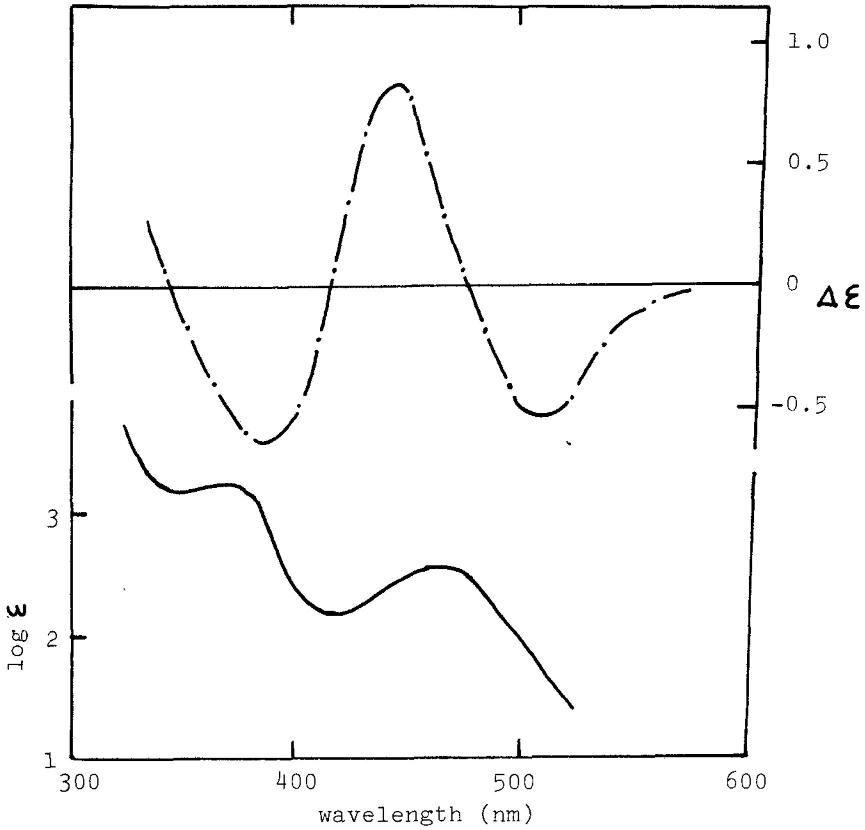

FIGURE 3 Electronic absorption(———)and CD(– — — •) spectra of *trans*-[Co(SS-pyht)$(NO_2)_2$]$^+$ ion.

sign in the long wavelength region and the $A_2(D_4)$ as the band at 450 nm. Both 2,3,2-tet and SS-Me_2-2,3,2-tet complexes have a six-membered middle chelate ring. There are two possible conformations for the six-membered middle chelate ring in the CO(III) complexes: the skew-boat conformation and the chair conformation. From the pmr spectrum of the SS-Me_2-2,3,2-tet complex, the CD spectra of both complexes and the stereochemical points of view, the skew-boat conformation has been assigned in both cases,[6,18] and the absolute configuration of the middle nitrogens has ben shown to be R.†

The CD curve for *trans*-[Co(SS-pyht)Cl_2]$^+$ show in Figure 7 shows a dominant negative band at about 660 nm and a smaller positive band at about 590 nm, although it appears as a shoulder. This pattern of CD spectrum has been observed for all the *trans* dichloro tetramine complexes described above in which the outside chelate ring conformation has been determined to be δ. Thus, these two CD Cotton effects of opposite sign in the first absorption band region are assigned the two components of the $E(D_4)$ transition, and the two outside chelate rings are assigned the δ conformation for the *trans*-[Co(SS-pyht)Cl_2]$^+$ion.

From the similarity in the shape of CD bands (I_a band) of *trans*-[Co(SS-pyht)Cl_2]$^+$, *trans*-[Co(SS-Me_2-2,3,2-tet)Cl_2]$^+$, and *trans*-(RR)-[Co(2,3,2-tet)Cl_2]$^+$, the conformation of the six-membered middle chelate ring in the SS-pyht complex is believed to be skew-boat[6,18] as shown in Figure 5(a). The absolute configuration of the nitrogens in the central chelate ring is R. An alternative structure for the *trans*-[Co(SS-pyht)Cl_2]$^+$ complex has the six-membered ring in the chair conformation and the five-membered chelate rings in conformations of opposite chirality with the absolute configuration of one of two nitrogens in the central ring being S.

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†In the case of (+)-trans-SS-[Co(trien)Cl_2]$^+$, the absolute configuration of the central nitrogens becomes S due to the changes in priorities of substituents surrounding those nitrogens, even though hydrogens on the asymmetric nitrogen atoms are on the same side with respect to the central chelate ring.

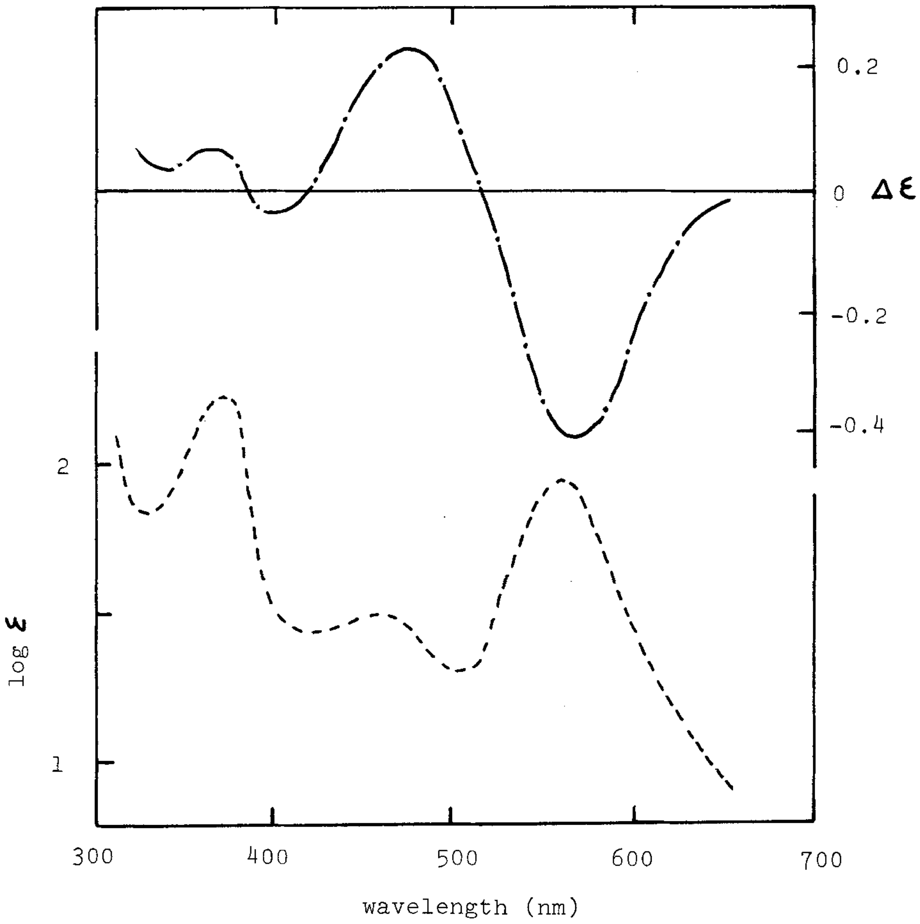

FIGURE 4 Electronic absorption(– – – – –) and CD(—— · —— ·) spectra of *trans*-[Co(SS-pyht)(OAc)$_2$]$^+$ ion.

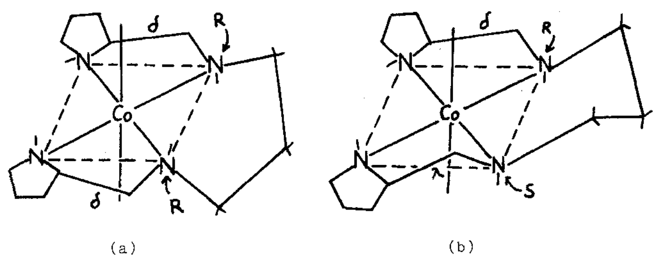

FIGURE 5 Possible structures of *trans*-[Co(SS-pyht)Cl$_2$]$^+$: (a) six-membered ring in skew-boat conformation, and (b) six-membered ring in chair conformation.

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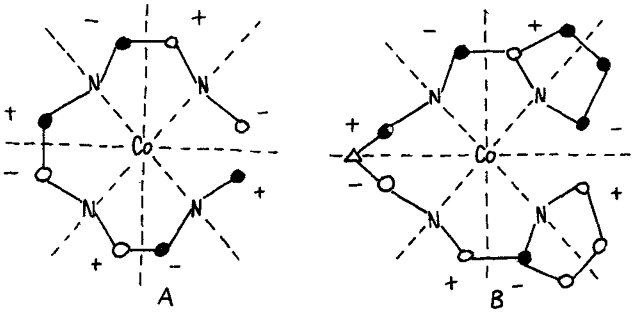

FIGURE 6 The structure of (A) *trans*-[Co(SS-1,3,8,10-Me_4trien)Cl_2]$^+$ and (B) *trans*-[Co(SS-pyht)Cl_2]$^+$ in the hexadecadal region; the location of the carbon atoms in the chelate ring below the CoN_4 plane (●) and above the CoN_4 plane (○).

Neither the CD spectra nor the pmr spectra of the other complexes[6] is consistent with this structure, however.

The *trans* dichloro cobalt(III) complex of SS-pyht ion has a CD band near 460 nm whose sign is opposite to that of the analogous complex of SS-Me_2-2,3,2-tet[6] as well as opposite to the sign of the same CD band of the analogous complex of SS–1,3,8,10-Me_4trien.[5] The CD band near 460 nm has been ascribed to the $^1A_1 \rightarrow {}^1A_2(D_4)$ transition. The SS-pyht complex bears methylene groups at each terminal nitrogen by means of pyrrolidine rings, while the SS-1,3,8,10-Me_4trien complex has a free methyl group at each terminal nitrogen. The opposite signs in the $^1A_1 \rightarrow {}^1A_2$ band for *trans*-[Co(SS-pyht)Cl_2]$^+$ and *trans*-[Co(SS-1,3,8,10-Me_4trien)Cl_2]$^+$ suggest that these two complexes have different absolute configurations at the terminal nitrogens: S absolute configuration for *trans*-[Co(SS-pyht)Cl_2]$^+$ and R absolute configuration for *trans*-[Co(SS-1,3,8,10-Me_4trien)Cl_2]$^+$.

The positive Cotton effect for the $^1A_1 \rightarrow {}^1A_2$ component for *trans*-[Co(SS-pyht)Cl_2]$^+$ ion may be explained by means of Mason's semi-empirical hexadecadal rule[19,20] assuming that the terminal nitrogens take the S-asymmetric configuration.

The regional sign depicted in Figure 6 indicates the sign of the Cotton effect induced by substituents in the +z hemisphere for the $A_{1g} \rightarrow A_{2g}(D_{4h})$ components; the signs given (Figure 6) are reversed for substituents in the –z hemisphere for the $A_{1g} \rightarrow A_{2g}(D_{4h})$ components. The [Co(tetramine)Cl_2]$^+$ ion studied here has chelate rings and N-methylene substituents as shown in Figure 6 B. Carbon atoms in the +z hemisphere are indicated with open circles and carbon atoms in the –z hemisphere with black circles. Note that the central carbon atom in the middle ring lies in the boundary surface. It is observed that CH_2 and CH groups of the outside chelate rigns lie in positive sectors whereas $CHCH_2$ groups in the pyrrolidine rings and CH_2 groups in the central chelate ring lie in negative sectors. However, N–CH_2 groups in the pyrrolidine groups lie in the positive sectors.

The dissymmetric potential, $xyz(x^2 - y^2)$, has a larger absolute value for the N-methylene group than for the CH_2 and $CHCH_2$ groups of the tetramine rings. As a result, the Cotton effect for the $A_{1g} \rightarrow A_{2g}$ component is positive for *trans*-[Co(SS-pyht)Cl_2]$^+$ and negative for both *trans*-[Co(SS-1,3,8,10-Me_4trien)Cl_2]$^+$ and for *trans*-[Co(SS-Me_2-2,3,2-tet)Cl_2]$^+$.

The conclusion that *trans*-[Co(SS-pyht)Cl_2]$^+$ synthesized in the present work has an S-asymmetric configuration at each terminal nitrogen has been further supported by the vicinal effect[21,22] from these S-asymmetric nitrogens. The vicinal effect from these S-asymmetric nitrogens shown in Figure 7 has been obtained from the CD spectra of *trans*-[Co(SS-pyht)Cl_2]$^+$ and *trans*-[Co(SS-Me_2-2,3,2-tet)Cl_2]$^+$, both of which have a six-membered chelate ring in the middle. Also indicated is the vicinal effect from an R-asymmetric nitrogen.[5] This was obtained from the CD spectra of *trans*-[Co(SS-1,3,8,10-Me_4trien)Cl_2]$^+$ and *trans*-[Co(SS-3,8-Me_2trien)-Cl_2]$^+$, both of which have a five-membered chelate ring in the middle. It has been established that the chirality of six-membered ring contributes less to the

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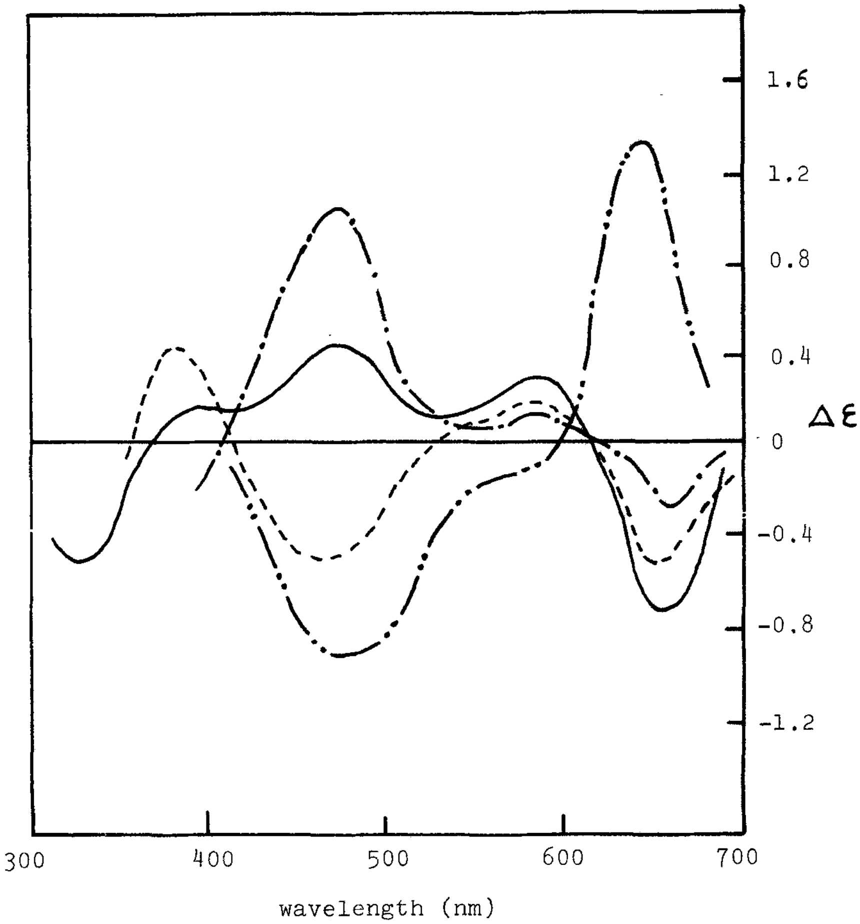

FIGURE 7 CD spectra of *trans*-[Co(SS-pyht)Cl$_2$]$^+$(————), *trans*-[Co(SS-Me$_2$-2,3,2-tet)Cl$_2$]$^+$(– – – – –), the composite curve for *trans*-[Co(SS-pyht)Cl$_2$]$^+$ – *trans*-[Co(SS-Me$_2$-2,3,2-tet)Cl$_2$]$^+$(— • — •), and the contribution from the R asymmetric nitrogens suggested by Yoshikawa *et al.*[5] composite curve for *trans*-[Co(SS-1,3,8,10-Me$_4$-trien)Cl$_2$]$^+$ – *trans*-[Co(SS-3,8-Me$_2$ trien)Cl$_2$]$^+$(———••—— • ••).

CD than that of five-membered ring in the complexes. Thus, as expected, the intensity of the vicinal effect from S-asymmetric nitrogen in the *trans*-[Co(SS-pyht)Cl$_2$]$^+$ is lower than that of the vicinal effect from R-asymmetric nitrogen in the *trans*-[Co(SS-1,3,8,10-Me$_4$trien)Cl$_2$]$^+$. Note that, although the signs of the Cotton effect are opposite, these two vicinal effects are similar in shape. The vicinal effect from S-asymmetric nitrogen has a negative Cotton effect for the $A_{1g} \rightarrow E_g(D_4)$ component and a positive Cotton effect for the $A_{1g} \rightarrow A_{2g}$ component. As a result, the Cotton effect for the $A_{1g} \rightarrow A_{2g}$ component is positive for *trans*-[Co(SS-pyht)Cl$_2$]$^+$.

The dinitro complex, *trans*-[Co(SS pyht)(NO$_2$)$_2$]$^+$ synthesized in this work, and *trans*-[Co(SS-1,3,8,10-Me$_4$trien)(NO$_2$)$_2$]$^+$, reported in the literature,[5] have apparently opposite CD bands in the visible and ultraviolet region. The difference in the CD bands for these complexes probably results from the vicinal effects of the S- and R-asymmetric nitrogens. *Trans*-[Co(SS-1,3,8,10-Me$_4$trien)(NO$_2$)$_2$]$^+$ has the R absolute configuration at the terminal nitrogens. The vicinal effect from the R asymmetric nitrogens has been obtained from the subtraction of the CD spectrum of the *trans*-[Co(SS-3,8-Me$_2$trien)(NO$_2$)$_2$]$^+$ from that of the *trans*-[Co(SS-1,3,8,10-Me$_4$trien)(NO$_2$)$_2$]$^+$. The vicinal effect has a positive Cotton effect at near 500 nm, a negative Cotton effect at near 430 nm, and a positive Cotton effect at near 340 nm. Like the *trans*-[Co(SS-pyht)-

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$Cl_2]^+$, the *trans*-$[Co(SS\text{-}pyht)(NO_2)_2]^+$ is expected to have the S-asymmetric terminal nitrogens. Although the exact vicinal effect from the S-asymmetric nitrogens of the *trans*-$[Co(SS\text{-}pyht)(NO_2)_2]^+$ could not be obtained (due to the lack of a reference compound such as the *trans*-$[Co(SS\text{-}Me_2\text{-}2,3,2\text{-}tet)(NO_2)_2]^+$), the vicinal effect from the S-asymmetric nitrogens may have a negative Cotton effect at near 500 nm, a positive Cotton effect at near 430 nm, and a negative Cotton effect at near 340 nm, which are opposite to the signs of Cotton effects of the vicinal effect from the R-asymmetric nitrogens. Then the signs of the Cotton effects of the *trans*-$[Co(SS\text{-}pyht)(NO_2)_2]^+$ may be explained via the vicinal effect from the S-asymmetric nitrogens. Thus, the *trans*-$[Co(SS\text{-}phyt)(NO_2)_2]^+$ has a negative Cotton effect at about 520 nm, and a positive Cotton effect at near 450 nm. From the Yamatera theory,[12] the lower energy band may be the $^1A_1 \to {}^1A_2(D_4)$ component and the higher energy band may be the $^1A_1 \to {}^1D_g \to (D_4)$ component of the $^1A_1 \to {}^1T_1)O_h)$d–d electronic transition.

The CD spectrum of the diacetato complex, *trans*-$[Co(SS\text{-}pyht)(OAc)_2]^+$, somewhat resembles that of the *trans* dichloro complex: a dominant negative CD band on the low energy side and other CD bands on the higher energy side. However, there are only two CD maxima in the first absorption band region and this makes the assignment unreliable with respect to the sign of the CD bands according to Yamatera's theory.

Stereospecificity

There are three possible geometrical isomers from the coordination of SS-pyht to cobalt(III) ion to make diacido complexes: *cis-α*, *cis-β*, and *trans*. However, only one geometrical isomer, *trans*, was isolated in this work. Previously[1] we observed that SS-pyhn yielded only a *cis* isomer. The only difference between SS–pyht and SS–pyhn is the chain length; i,e., the number of methylene groups in the central chelate ring, where SS pyht has three and SS-pyhn two. Thus, it is observed that chain length shows a significant effect on the synthesis of complexes, as have been observed in other cases, where the effects of chelate ring size have been explained in terms of two effects: ring strain and steric hindrance.[23]

The effect of ligand asymmetry on the stereochemistry is also dramatic. Without asymmetric centers in the ligand, *trans* tetramine complexes display optical activity due to ring conformation only.

The role of the pyrrolidine rings is also significant, because they force the two terminal nitrogens to take the S absolute configuration. When the outside chelate rings assume their favored δ conformation, the hydrogen atom on the asymmetric terminal nitrogen and the hydrogen atom on the asymmetric carbon are favored to be on the same side of the pyrrolidine ring, thus, imparting the S configuration to the chelate terminal nitrogen. A study using Dreiding model indicates that those hydrogen atoms can be forced to be on the opposite side of each other with respect to the pyrrolidine ring while maintaining δ conformation, thus, giving R absolute configuration to the terminal nitrogen. However, all the chelate rings will suffer much greater ring strains in this case, and therefore this alternative structure tends to be ruled out. An N-substituted methyl group on the terminal nitrogen of a coordinated tetramine ligand should have the N-methyl group in the favored equatorial position, giving R configuration to the terminal nitrogen. Therefore, our observation shows that the pyrrolidine rings are chiefly responsible for the S absolute configuration of the terminal nitrogens.

Oxalato Complex

Since dichloro, dinitro, and diacetato complexes of SS-pyht ligand yielded only *trans* compounds, it is interesting to observe that the complex ion $[Co(SS\text{-}pyht)Ox]^+$ occurs only as the *cis* modification.

Cis-$[Co(SS\text{-}pyht)Ox]^+$ was prepared by heating the *trans* dichloro complex with an excess of potassium oxalate. The electronic absorption, CD and ORD spectra are shown in Figure 8. The two broad symmetrical bands which appear in the visible region of the electronic spectrum may be assigned to the spin-allowed $^1A_1 \to {}^1T_2$ and $^1A_1 \to {}^1T_2$ electronic transitions of the cobalt(III) ion in pseudooctahedral symmetry. Although the electronic spectrum alone is not helpful in determining the geometric configurations, comparison of CD and ORD spectra and other data reported in the literature indicate that this complex has *cis-β* geometry.[18]

The CD spectrum of (+)-*cis-β*-$[Co(2,3,2\text{-}tet)Ox]^+$ ion[18] show a dominant positive band at near 540 nm and a smaller negative band at about 480 nm, and this isomer has been assigned Λ absolute configuration. The CD spectrum of *cis-β*-$[Co(SS\text{-}pyht)Ox]^+$ ion has essentially the same shape as the analogous Λ-*cis-β*-$[Co(2,3,2\text{-}tet)Ox]^+$ ion: a dominant positive band at about 540 nm and a tiny but negative band at near 480 nm. Assuming that the *cis*-oxalato complex of

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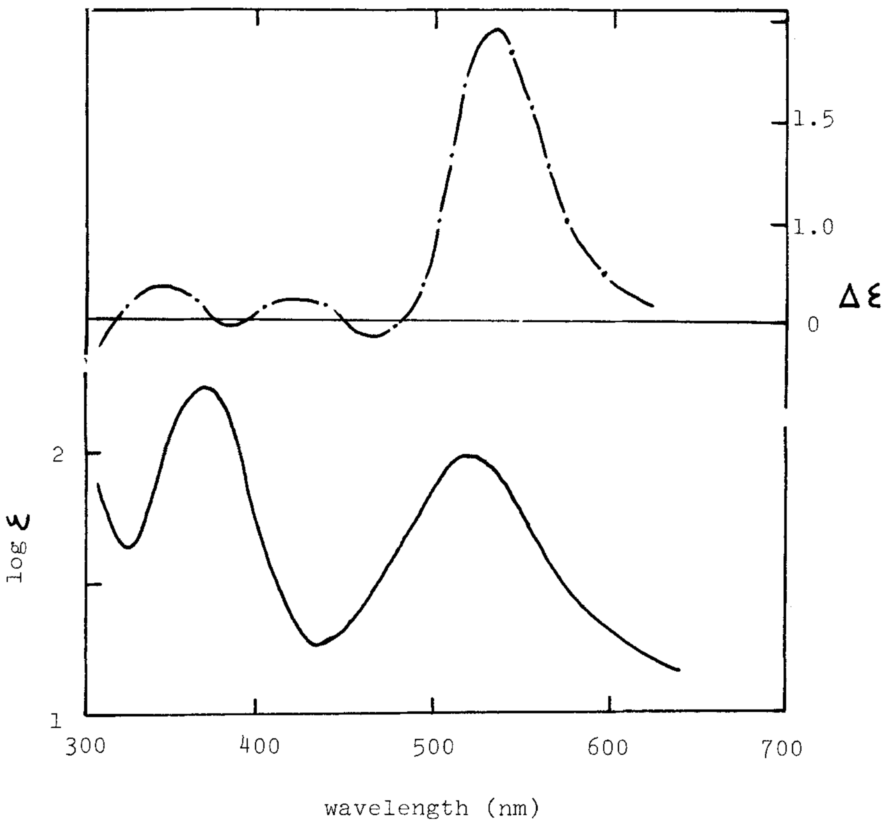

FIGURE 8 Electronic absorption(————) and CD(— · — ·) spectra of -*cis*-α-[Co(SS-pyht)Ox]$^+$ ion.

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SS pyht approximates to C_2 symmetry, this complex is assigned the Λ absolute configuration. This assignment is also made on the basis of the ORD curve. Both Λ-cis-β[Co(SS-pyht)Ox]$^+$ and Λ-cis-β-[Co(2,3,2-tet)Ox]$^+$ have essentially the same shape in their ORD spectra and show dominant low energy positive Cotton effects at about 500 nm.

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