Inorganica Chimica Acta, 15 (1975) 111–116

Stereochemistry of Complexes of Multidentate Ligands. V. Stereoselective Cobalt(III) Ion Complexes of N,N′-Bis(2-S-Pyrrolidylmethyl)-*trans*-R-1,2-Cyclohexanediamine

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Received December 21, 1974

The synthesis of the ligand, N,N′-bis(2-S-pyrrolidylmethyl)-trans-R-1,2-cyclohexanediamine (SRS-pychxn) and the preparation of the cobalt(III) complexes of SRSpychxn, $[Co(SRS\text{-}pychxn)X_2]^{n+}$ ($X = Cl$, NO_2, and $X_2 = Ox$), are reported. Both cis and trans dichloro cobalt(III) complexes have been isolated. The ligand coordinated stereospecifically in both cis and trans complexes with Λ-β configuration in the case of the cis geometry.

Introduction

It has been shown previously[1,2] that the ligand, 1,6-bis(2-S-pyrrolidyl)-2,5-diazahexane (SS-pyhn), coordinates stereospecifically to cobalt(III) ion to give Λ-*cis*-α configuration and the ligand, 1,7-bis(2-S-pyrrolidyl)-2,6-diazahexane (SS-pyht), gives the optically active *trans* configuration. It was observed that the optically active pyrrolidine ring played a significant role in the stereospecific coordination of these ligands.

The ligand reported here, N,N′-bis(2-S-pyrrolidylmethyl)-*trans*-R-1,2-cyclohexanediamine (SRS-pychxn), was also expected to possess the ability of stereospecific coordination because it contains two optically active pyrrolidine rings. In addition, the ligand is compelled to take the λ conformation in the central chelate ring when coordinated to cobalt(III) ion because of the optically active R-1,2-cyclohexanediamine in its backbone. Therefore, it is of interest to see which "wrapping" or geometrical isomerism (α or β) would be favored in the *cis* cobalt(III) complexes of this ligand.

Experimental

Chemical Reagents

The S-proline and the carbobenzoxy chloride were purchased from Nutritional Biochemical Corp., Cleveland, Ohio, U.S.A. The isobutyl chloroformate was obtained from J. T. Baker Chemical Co., Philipsburg, New Jersey, U.S.A., and the lithium aluminum hydride from Ventron Corp., Beverly, Mass., U.S.A. *Trans*-1,2-diaminocyclohexane was purchased from Aldrich Chemical Co., Milwaukee, Wisconsin, U.S.A. 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 Spectrophotometer using 1-cm cell and using water as the solvent. The pmr spectra were obtained using a Varian A-60 Spectrometer with 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, U.S.A., and by Micro-Tech Laboratories, Skokie, Illinois, U.S.A.

Resolution of Trans-1,2-Cyclohexanediamine

Trans-1,2-cyclohexanediamine was resolved according to the method of Asperger and Liu.[3] The R(–) antipode was obtained as its hydrochloride. The free amine base was obtained by cautious distillation of the hydrochloride neutralized with an excess of sodium hydroxide.

Preparation of N,N′-Bis(Carbobenzoxy-S-Prolyl)-Trans-R-1,2-Cyclohexanediamine

A solution of 15.2 g (0.064 mol) of carbobenzoxy-S-proline[1] and 8.9 ml of triethylamine in 200 ml of toluene was chilled to –5° C and treated with 8.4 ml (0.064 mol) of isobutylchloroformate. After one hour of standing, a cold solution of 5.99 g (0.032 mol) of *trans*-R-1,2-cyclohexanediamine and 8.9 ml of triethylamine in 150 ml of chloroform was added with stirring, and the mixture was allowed to stand overnight at room temperature. The mixture was filtered, washed successively with water, 3% sodium bicarbonate solution,

and water, and finally dried over anhydrous sodium sulfate. Evaporation under reduced pressure gave a pale yellow oil. The oil crystallized overnight to give white crystals, which were recrystallized from hot acetone and ether. Yield: 14.3 g. $[\alpha]_{589} = -136.3$ (c = 0.0033 g/3 ml of acetone). *Anal.* Calcd. for $C_{29}H_{36}N_4O_6$: C, 66.65; H, 6.99; N, 9.72. Found: C, 66.61, H, 7.05; N, 9.63.

Preparation of N,N′-Bis(S-Propyl)-Trans-R-1,2-Cyclohexanediamine

14.0 g of N,N′-bis(carbobenzoxy-S-prolyl)-*trans*-R-1,2-cyclohexanediamine and 250 ml of methanol were introduced into a 500 ml Paar low-pressure hydrogenation bottle. To this mixture 0.3 g of palladium on charcoal catalyst (10%) was added. After the mixture was shaken for two hours, the catalyst was filtered and the filtrate was concentrated under reduced pressure to give a pale yellow oil.

Preparation of N,N′-Bis(2-S-Pyrrolidylmethyl)-Trans-R-1,2-Cyclohexanediamine Tetrahydrochloride (SRS-Pychxn·4HCl)

250 ml of anhydrous tetrahydrofuran and 8.6 g of N,N′-bis(S-prolyl)-*trans*-R-1,2-cyclohexanediamine were placed in a 1000-ml three-necked round bottom flask equipped with a mechanical stirrer and a reflux condenser. The mixture was cooled in an ice bath. Then, 12.5 g of lithium aluminum hydride was carefully added with vigorous stirring. The reaction mixture was stirred and allowed slowly to warm to room temperature. Then it was refluxed and stirred for two days. The reaction mixture was cooled, and a solution of 29.7 g of water and 250 ml of tetrahydrofuran was carefully added with vigorous stirring. The solid mixture was filtered and the filter-cake was extracted twice with boiling tetrahydrofuran. The combined 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, and the solution was stored in a refrigerator overnight. White crystals were precipitated by adding a small amount of ether. The product was washed with absolute ethanol and ether, and air dried. Yield: 8.2 g. The specific rotation for this ligand was $[\alpha]_{589} = -57.1$ (c = 0.0041 g/ml of water). *Anal.* Calcd. for $C_{16}H_{32}N_4 \cdot 4HCl$: C, 45.08; H, 8.51; N, 13.14; Cl, 33.27. Found: C, 45.21; H, 8.39; N, 13.20, Cl, 32.98.

Preparation of Trans-[Co(SRS-R-Pychxn)Cl_2]$ClO_4 \cdot H_2O$

A solution of 4.7 g (1.1×10^{-2} mol) of N,N′-bis(2-S-pyrrolidyl)-*trans*-R-1,2-cyclohexanediamine tetrahydrochloride (SRS-Pychxn·4HCl), 2.62 g (1.1×10^{-2} mol) of $CoCl_2 \cdot 6H_2O$ and 1.85 g (4.4×10^{-2} mol) of $LiOH \cdot H_2O$ in 50 ml of water and 10 ml of ethanol was aerated for 36 hours with CO_2-free air. The solution was evaporated to one-half its original volume under moving air at room temperature. To this solution 12 ml of concentrated hydrochloric acid were added and evaporation continued until the volume was again halved. When an excess amount of $LiClO_4$ was added, a green compound precipitated. It was removed by filtration. A further crop of green compound was obtained from the filtrate by evaporation and filtration. The combined portions of green compound were washed with cold acetone and ether and recrystallized from methanol. Since a water solution of this compound changes its color from green to brown (and eventually to pinkish red) fairly rapidly, the UV, CD and ORD spectra of this complex were measured in methanol solutions. *Anal.* Calcd. for $CoC_{16}H_{32}N_4Cl_2 \cdot ClO_4 \cdot H_2O$: C, 36.41; H, 6.11; N, 10.62; Cl, 20.15. Found: C, 36.50; H, 5.99; N, 10.47; Cl, 20.33.

Preparation of Λ-Cis-β-[Co(SRS-Pychxn)Cl_2]$ClO_4 \cdot 1/2H_2O$

The solution after removing the *trans* complex as described above was evaporated to dryness under moving air at room temperature. The residue was washed with acetone several times until no additional blue compound appeared in the washings. It was then dissolved in minimal hot methanol. A red product was precipitated by cooling and slowly adding acetone. The red complex was recrystallized from hot methanol. *Anal.* Calcd. for $CoC_{16}H_{32}N_4Cl_2 \cdot ClO_4 \cdot 1/2H_2O$: C, 37.05; H, 6.22; N, 10.80; Cl, 20.50. Found: C, 36.89; H, 5.98; N, 10.64; Cl, 20.72.

Preparation of Λ-Cis-β-[Co(SRS-Pychxn)$(NO_2)_2$]ClO_4

To a mixture of 0.71 g (1.65×10^{-3} mol) of SRS-pychxn·4HCl and 0.28 g of $LiOH \cdot H_2O$ dissolved in 50 ml of water, 0.39 g (1.65×10^{-3} mol) of $CoCl_2 \cdot 6H_2O$ and 0.23 g (3.3×10^{-3} mol) of $NaNO_2$ were added successively. The solution was aerated with CO_2-free air for 24 hours and evaporated at room temperature to 25 ml. An excess of $LiClO_4$ was added and evaporation continued until the volume was less than 10 ml. The solution was stored in a refrigerator for one day. The precipitated crystals were filtered and recrystallized from hot water. *Anal.* Calcd. for $CoC_{18}H_{32}N_4 \cdot 2NO_2 \cdot ClO_4$: C, 36.20; H, 6.08; N, 16.05. Found: C, 36.01; H, 5.89; N, 16.05.

An alternative way to prepare this complex is described in the fellowing. To 0.12 g of *Λ-cis-β*-[Co(SRS-pychxn)Cl_2]$ClO_4 \cdot 1/2H_2O$ was added 10 ml of $HClO_4$ (0.001 *M*) and the solution was aquated for 24 hours at room temperature. An excess amount of $NaHCO_3$ was added and after three hours excess $HClO_4$ (0.6 ml of 1*M*) was added to the solution, followed by excess $NaNO_2$ after two hours. After standing overnight, the solution was evaporated to less than half its original volume under moving air at room temperature. The product

crystallized slowly, was removed by filtration, and was washed with acetone.

Preparation of Λ-Cis-β-[Co(SRS-Pychxn)Ox]ClO_4

To a solution of 0.1 g of *trans*-[Co(SRS-pychxn)Ox]$ClO_4 \cdot H_2O$ dissolved in 30 ml of water was added 0.04 g of potassium oxalate hydrate. The solution was heated on a steam bath for three hours. Then the solution was evaporated under moving air on a steam bath to near dryness. The red product was recrystallized from hot water. *Anal.* Calcd. for $CoC_{18}H_{32}N_4 \cdot C_2O_4 \cdot ClO_4$: C, 41.04; H, 6.12; N, 10.63. Found: C, 40.98; H, 6.05; N, 10.42.

When the *Λ-cis-β* dichloro SRS-pychxn complex was used to prepare the oxalato complex in place of the *trans* dichloro complex, the same *Λ-cis-β* oxalato complex was obtained: visible–UV absorption, CD and ORD spectra were identical in both cases.

Results and Discussion

Preparation of Ligands and Complexes

The synthetic route employed to prepare the ligand, N,N'-bis(2-S-pyrrolidylmethyl)-*trans*-R-1,2-cyclohexanediamine (SRS-pychxn) is shown in Figure 1 along with the absolute configuration of the ligand. S-proline was used as the starting material and R-cyclohexanediamine in the third step.

The dichloro cobalt(III) complexes with this ligand were prepared by the usual air oxidation. Two isomeric dichloro complexes were obtained: optically active *trans* and optically active *cis-β*. The green *trans* isomer was isolated before the pinkish red *cis* isomer and the yields were 12 to 1 predominant in the *trans*. Also, the dinitro cobalt(III) complex was prepared by air oxidation, but only the optically active *cis-β* isomer was obtained. The oxalato cobalt(III) complex was prepared by heating the *trans* dichloro complex with potassium oxalate to give a *cis-β* isomer. When the *cis-β* dichloro complex was treated in the same way with potassium oxalate, the same optically active *cis-β* isomer was obtained.

Spectra

Assignment of *cis* and *trans* isomers can be made on the basis of the electronic absorption spectra of the compounds (Figure 2 through 5). The first absorption band of the *cis*-[Co(SRS-pychxn)Cl_2]$^+$ (Figure 2) is observed at about 550 nm with no indication of any shoulder at the longer wavelength side. Such a shoulder has been taken to be characteristic of *cis-α*-[Co(trien)Cl_2]$^+$ as compared with the *cis-β* isomer and was also observed in *Λ-cis-α*-[Co(SS-pyhn)Cl_2]$^+$.[1] The only *cis* isomer obtained formed crystals of a color more similar to that of other known *cis-β* compounds[4,5,6] and quite unlike *cis-α* complexes. It is possible on the basis of

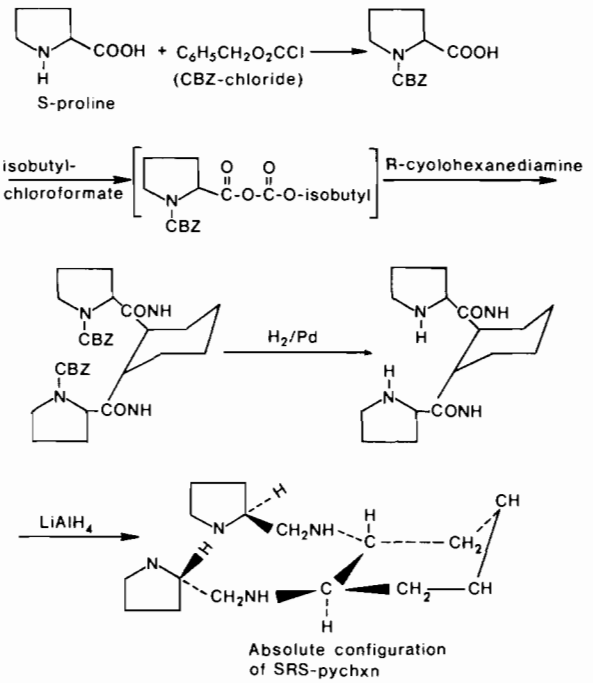

Figure 1. Synthetic route to SRS-pychxn.

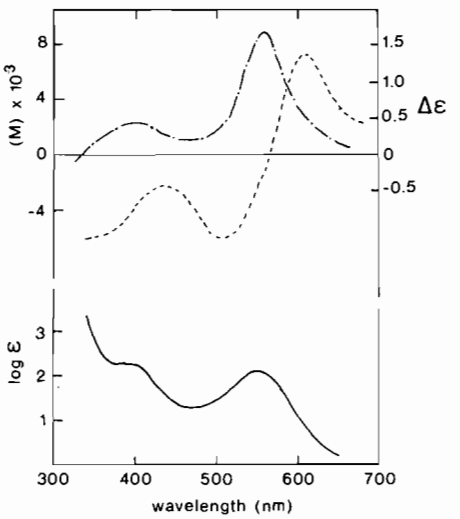

Figure 2. Electronic absorption (——), CD(——·——·), and ORD(-----) spectra of *Λ-cis-β*-[Co(SRS-pychxn)Cl_2]$^+$ ion.

these results to assign the *cis* dichloro complex of SS-pychxn to the *cis-β* isomer. For this *cis-β* isomer the band near 500 nm is assigned $^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ and the band near 400 nm to the $^1A_{1g} \rightarrow T_{2g}(O_h)$ electronic transition of cobalt(III) ion.

A splitting of the lower energy band is expected for the *trans* complex (Figure 3). The *trans* dichloro com-

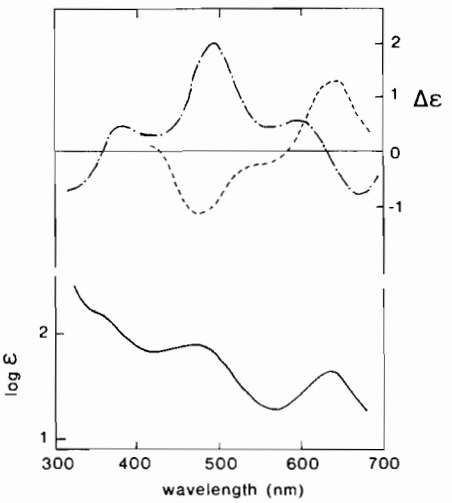

Figure 3. Electronic absorption (——) and CD(——·——·) spectra of *trans*-[Co(SRS-pychxn)Cl_2]$^+$ ion, and the contribution from the R-asymmetric nitrogens suggested by Yoshilawa, *et al.* composite curbe for *trans*-[Co(SS-1,3,8,10-Me_4trien)Cl_2]$^+$–*trans*-[Co(SS-3,8-Me_2trien)Cl_2]$^+$ (-----).

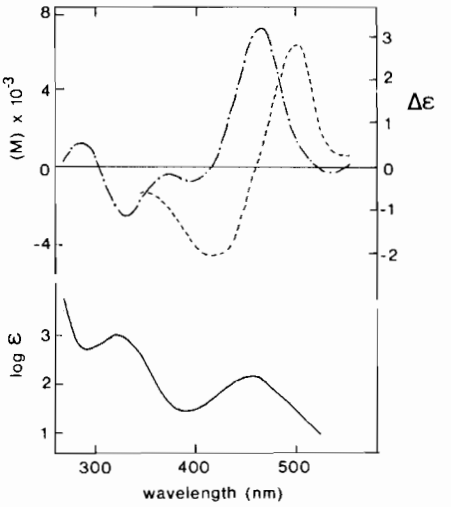

Figure 4. Electronic absorption (——), CD(——·——·), and ORD(-----) spectra of *Λ*-*cis*-*β*-[Co(SRS-pychxn)$(NO_2)_2$]$^+$ ion.

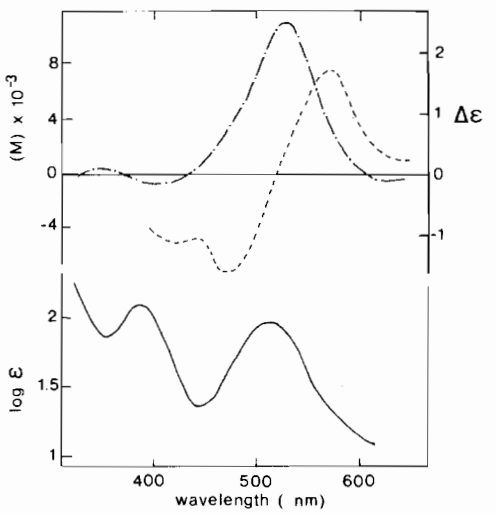

Figure 5. Electronic absorption (——), CD(——·——·), and ORD(-----) spectra of *Λ*-*cis*-*β*-[Co(SRS-pychxn)Ox]$^+$ ion.

plex has a band at about 620 nm and another band near 480 nm, which are assigned $^1A_1 \rightarrow {}^1E_a(D_4)$ and $^1A_1 \rightarrow A_2(D_4)$ electronic transitions respectively.

Electronic spectra of the dinitro and the oxalato complexes are shown in Figure 4 and Figure 5, respectively. The first absorption bands (near 460 nm for the dinitro complex and near 510 nm for the oxalato complex) are assigned $^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ electronic transition. The second absorption bands (near 325 nm for the dinitro complex and near 380 nm for the oxalato complex) are assigned $^1A_{1g} \rightarrow T_{2g}(O_h)$ electronic transition. When the dinitro and the oxalato complexes were prepared from the *cis*-*β* dichloro complex, their electronic absorption, CD and ORD spectra were identical with those of dinitro and oxalato complexes prepared by the methods described in the experimental section.

The CD and ORD spectra of the *cis*-*β*-isomer (Figure 2) show only one dominant positive peak in the first absorption band region. In applying Mason's[7] and MacDermott's[8] formalisms to this *cis*-*β*-[Co(SRS-pychxn)Cl_2]$^+$ the dominant $^1A_1 \rightarrow {}^1A_2$ low-energy Cotton effect, assuming the complex approximates to C_2 symmetry, is assigned to the major CD and ORD components centered between 520 and 620 nm. Since these bands are positive, the *Λ* absolute configuration is assigned. The same assignment can be made from the similarity of the CD and ORD spectra of this isomer with those of *cis*-*β*-[Co(trien)Cl_2]$^+$, *cis*-*β*-[Co(R-ECE)Cl_2]$^+$,[9] and *cis*-*β*-[Co(5R-metrien)Cl_2]$^+$,[9] which have been assigned the *Λ* absolute configuration.

The CD and ORD spectra of *cis*-*β*-[Co(SRS-pychxn)$(NO_2)_2$]$^+$ and *cis*-*β*-[Co(SRS-pychxn)Ox]$^+$ complexes shown in Figure 4 and 5, respectively, also have dominant positive peaks in the first absorption band region and are therefore assigned a *Λ* absolute configuration. It is noted that the CD and ORD spectra of *cis*-*β*-[Co(SRS-pychxn)$(NO_2)_2$]$^+$ closely resemble those of *cis*-*β*-[Co(trien)$(NO_2)_2$]$^+$ and *cis*-*β*-[Co(R-ECE)$(NO_2)_2$]$^+$ ions[9], which have also been assigned *Λ* absolute configurations.

The CD spectra for *trans*-[Co(SRS-pychxn)Cl_2]$^+$ (Figure 3) shows a dominant negative band at about 650 nm and a smaller positive band at about 600 nm in its first absorption band region. This pattern of CD

spectrum closely follows the CD spectrum of *trans*-$[Co(SS\text{-}pyht)Cl_2]^+$.[1] Thus, these two bands 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 the δ conformation. The central chelate ring should adopt the λ conformation for reasons which will be discussed in more detail later.

Like the *trans* dichloro cobalt(III) complex of SS-pyht[2] (SS-pyht = 1,7-bis(2-S-pyrrolidyl)-2,6-diazaheptane) the *trans* dichloro cobalt(III) complex of SRS-pychxn has a dominant positive CD band near 500 nm whose sign is opposite that of *trans*-$[Co(SS\text{-}1,3,8,10\text{-}Me_2trien)Cl_2]^+$ [10] (see Figure 3). This is the indication that the absolute configuration at the terminal nitrogen is S, which can be interpreted by means of Mason's hexadecadal rule and the vicinal effect from S-asymmetric nitrogens in the same way as the *trans* SS-pyht complexes.[2] Although the exact vicinal effect from S-asymmetric nitrogens could not be obtained because there is no reference compound whose CD spectrum has been measured and which has primary terminal nitrogens, the vicinal effect from S-asymmetric nitrogens may be simulated from the vicinal effect from R-asymmetric nitrogens obtained from the CD spectra of *trans*-$[Co(SS\text{-}1,3,8,10\text{-}Me_4trien)Cl_2]^+$ and *trans*-$[Co(SS\text{-}3,8\text{-}Me_2trien)Cl_2]^+$ (Figure 3). Then the sign of the Cotton effect of the vicinal effect from S-asymmetric nitrogens may be positive in the region near 500 nm like that of the *trans*-$[Co(SS\text{-}pyht)Cl_2]^+$ and thus the S absolute configuration may be assigned to the terminal nitrogens in the chelating rings in the *trans*-$[Co(SRS\text{-}pychxn)Cl_2]^+$ complex. The highly intense CD curve even after subtracting the vicinal effect of S-asymmetric nitrogens should be the contribution of the vicinal effect of the two asymmetric carbon atoms in the central chelate ring of the SRS-pychxn complex.

Chelate Ring Conformation and Stereospecificity

Substituted alkyl groups should prefer the equatorial position in the five membered chelate ring, since the conformation with an equatorial methyl group is considered to be more stable than that with an axial methyl group in the propylenediamine chelate ring. The SRS-pychxn ligand has been viewed as having two substituted methyl groups in the central "ethylenediamine bridge" linked by means of a six-membered cyclohexane ring.

Because of the R-absolute configuration of its asymmetric carbons and the cyclohexane ring, SRS-pychxn is compelled to take the λ conformation in the central chelate ring upon coordination to cobalt(III) ion. Taking all the possible combinations of the configurations of the two coordinated secondary nitrogen centers, there is a possible total of four optically active *cis*-β isomers: Λ-β(SS), Δ-β(RR), Λ-β(SR) and Δ-β(RS). However, only Λ-β(SS) and Δ-β(RS) can accommodate a λ conformation in the central chelate ring. It has been shown that the absolute configurations of the cobalt(III) complexes with substituted trien analogs are governed by the conformations of the central diamine chelate.[11] When the central "ethylenediamine bridge" is set to adopt the λ conformation, the substituted trien ligand coordinates stereospecifically to the cobalt(III) ion to give the Λ-*cis*-β(SS) or Δ-*cis*-β(RS). Since the absolute configuration of the complex turns out to be Λ, it follows that not only did the SRS-pychxn ligand stereospecifically coordinate to cobalt(III) ion to give the Λ-*cis*-β configuration but also the complex obtained belongs to the SS type as far as the absolute configuration of its asymmetric secondary nitrogens in the central chelate ring is concerned. The experimental data are in agreement with this assignment and with other studies reported in the literature.[9,11] It has been shown by X-ray diffraction studies[12,13] that in complexes of the type $[Co(trien)X_2]^{n+}$ the conformations of the outside chelate rings are different (δ and λ) for the Λ-cis-β(SS) geometry, when there are no substituted alkyl groups in the outside chelate rings. However, when a ligand has one or more substituted alkyl groups with S absolute configuration on carbon atoms in its outside chelate ring in a complex, the prefered conformation of the outside rings is δ in which the substituted alkyl groups take equatorial positions. Thus, the conformation of the outside chelate ring coplanar with the central chelate ring in the Λ-*cis*-β(SS) complex of SRS-pychxn becomes δ (Figure 6). The conformation of the other outside chelate ring above the plane containing the two coplanar chelate rings should also be δ. Not only does the asymmetric C-methylene group in the pyrrolidine ring take an equatorial position in this conformation but also the nonbonded interaction between this chelate ring and the central chelate ring is minimized in the δ conformation. The alternative structure, in which the conformation of this chelate ring is λ, would suffer an enormous amount of nonbonded interaction between the pyrrolidine ring and the central chelate ring. Further the asymmetric C-methyl group in the pyrrolidine ring would take an axial position. This δ assignment of the chelate ring conformation is supported by a literature

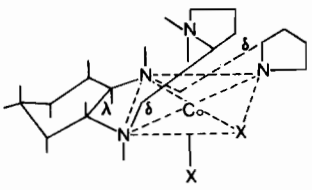

Figure 6. Probable structure of Λ-*cis*-β(SS)-$[Co(SRS\text{-}pychxn)X_2]^{n+}$ ions.

report that an X-ray crystallographic study of $(-)_{589}$-*cis*-[3S,8S-Me_2trien)$(NO_2)_2$]ClO_4 was found to have the configuration $\Lambda(\delta\lambda\delta)$,[14] in which the substituted methyl groups are in the equatorial position in each outside chelate ring. Therefore, the structure shown in Figure 6 is the most probable one for Λ-*cis*-β-[Co(SRS-pychxn)Cl_2]$^+$ ion. The cyclohexane ring should have a chair conformation as it is the most stable conformation.

In conclusion, the SRS-pychxn ligand showed remarkable stereospecificity in its coordination to cobalt (III) ion. The cobalt(III) complexes with this ligand stereospecifically gave Λ-*cis*-β(SS)-($\delta\lambda\delta$) configuration in the *cis*-β geometry and *trans*-(SS)-($\delta\lambda\delta$) with S absolute configuration at the terminal nitrogens in the *trans* geometry. No *cis*-α geometry was observed. The SRS-pychxn is forced to adopt the λ conformation in the central chelate ring because of the asymmetrically substituted cyclohexane ring. It prefers to take the δ conformation in the outside chelate rings due to the asymmetrically substituted pyrrolidine rings. Therefore, it is concluded that conformational preference of the chelate rings of this ligand is chiefly responsible for its stereospecificity more than other factors such as the orientation of the coordinated secondary amine protons. From the comparison of the cobalt(III) complexes of this ligand with those of SS-pyhn (which gave only the *cis*-α geometry) it is observed that the substitution on the central "ethylenediamine bridge" must play a deciding role in determining the geometrical preference as well as the overall absolute configuration. The asymmetrically substituted pyrrolidine ring is responsible, because of its unique structure, for the great conformational preference of this ligand in the outside chelate rings. The preference may exceed that of the usual substituents such as, for example, the methyl group.

Acknowledgement

Financial assistance from the National Institute of Health in the form of a research grant is gratefully acknowledged.

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