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Preparation and Stereochemistry of Cobalt(III) Complexes with Tetramines Derived from 1-(2-Pyridyl)ethylamine

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The optically active ligands, (2*S*,7*S*)-2,7-di(2-pyridyl)-3,6-diazaoctane (*S*,*S*-peaen) and (2*R*,8*R*)-2,8-di(2-pyridyl)-3,7-diazanonane (*R*,*R*-peatn) have been prepared. The dichlorocobalt(III) complexes of these ligands have been prepared and several isomers isolated. The ligand, *S*,*S*-peaen yielded one *cis*-α and two types of *cis*-β isomers, while the *R*,*R*-peatn gave only one *cis*-β isomer. Oxalato and dinitro derivatives of the *R*,*R*-peatn complexes have been isolated and characterized and the stereochemistry of the isolated complexes discussed.

Extensive investigations have been conducted on the stereochemistry of cobalt (III) complexes containing trien (triethylenetetramine) or its methyl substituted derivatives.[1] Tetramines derived from heteroaromatic ligands are quite limited however.[2-5] The quadridentate ligand, 1,6-di(2-pyridyl)-2,5-diazahexane (bispicen) is one of the representative tetramine ligands having pyridyl groups on the terminal arms. There are three topological ways for coordination of the tetramine type ligands to a cobalt(III) ion, *i.e.* *cis*-α, *cis*-β, and *trans*. Gibson and McKenzie isolated and characterized the *cis*-α and *cis*-β isomers of the dichlorocobalt(III) complex of bispicen for the first time.[2] Very recently Utsuno *et al.*, isolated the *cis*-α and two types of *cis*-β isomers of the cobalt(III) complex containing bispicen and ethylenedianime.[5]

Optically active centers may be introduced into the tetramine chain by methyl substitution on the skeletal carbons. The optically active derivatives of bispicen, $(+)_D$-1,6-di(2-pyridyl)-3-methyl-2,5-diazahexane (picpn)[3] and $(+)_D$-1,6-di(2-pyridyl)-3,4-dimethyl-2,5-diazahexane (bnpic)[4] are examples of such ligands having substituent(s) in the central bridge. Stereospecific coordination to a cobalt(III) ion giving a *Δ*-*cis*-β configuration has been found for these ligands.[3,4] The stereospecificity has been explained in relation to the restricted conformation of the central diamine chelate of picpn and bnpic.

The ligands prepared in the present study, (2*S*,7*S*)-2,7-di(2-pyridyl)-3,6-diazaoctane (*S*,*S*-peaen) and (2*R*,8*R*)-2,8-di(2-pyridyl)-3,7-diazanonane (*R*,*R*-peatn) derived from 1-(2-pyridyl)ethylamine (pea) have two methyl groups in the terminal arms as illustrated in Fig. 1. The terminal pea moiety has a structure intermediate between 1,2-propanediamine and 2,2′-bipyridine. It has been demonstrated that the *S*-pea chelate tends to assume a δ-conformation on complexation with the methyl group occupying an equatorial position.[6,7] Therefore on coordination both of the terminal chelate rings of *S*,*S*-peaen and *R*,*R*-peatn may be fixed giving a sterically prefered configuration about the metal ion.

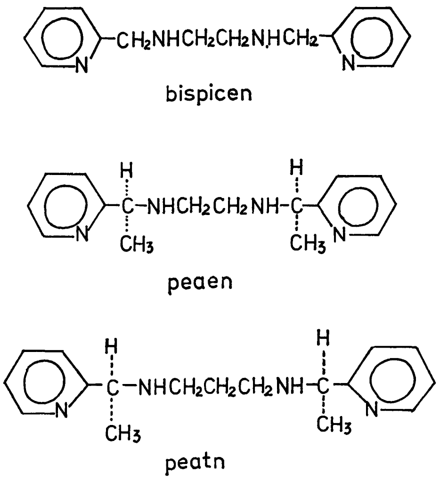

Fig. 1. Abbreviation and structure of ligands.

The preparation and isolation of the isomers of cobalt(III) complexes containing *S*,*S*-peaen and *R*,*R*-peatn are given in this paper and the stereochemistry of the complexes discussed.

Experimental

Preparation of Ligands. Optically active 1-(2-pyridyl)-ethylamine (pea) used as the starting materials in the preparation of the tetramines were synthesized according to a method similar to that given by Michelsen.[8] The $(+)_D$-isomer of pea is known to have an *R* configuration.[9]

*(2*S*,7*S*)-2,7-Di(2-pyridyl)-3,6-diazaoctane (*S*,*S*-peaen).* To a vigorously stirred solution of *S*-pea (30.54 g, 0.25 mol) in ethanol (300 cm³) was added dropwise 1,2-dibromoethane (9.40 g, 0.05 mol) over a period of 2 h under nitrogen atmosphere at 50 °C. The mixture was heated to reflux with vigorous stirring under nitrogen for 18 h. The end point of the condensation was correlated with the disappearance of the 1,2-dibromoethane peak found from gas chromatography. The reaction mixture was subsequently cooled to room temperature. To the stirred solution was added granulated metallic sodium (2.3 g) in small portions. The mixture was stirred at 50 °C for a further 2 h and cooled to room temperature. After filtration, the ethanol and excess *S*-pea was removed by distillation under reduced pressure. The residue was purified by alumina column chromatography using hexane as an eluent. After removal of the solvent, a brown syrup (6.8 g) was obtained. Yield 50.3%. The tetramine was isolated as its hydrochloride by the addition of concd HCl (10 cm³) and ethanol (100 cm³). Yield 7.85 g.

Found: C, 46.33; H, 6.31; N, 13.56%. Calcd for $C_{16}H_{22}N_4 \cdot 4HCl$: C, 46.15; H, 6.25; N, 13.46%.

*(2*R*,8*R*)-2,8-Di(2-pyridyl)-3,7-diazanonane (*R*,*R*-peatn).* This ligand was prepared according to a method similar to that for *S*,*S*-peaen using *R*-pea and 1,3-dibromopropane and isolated as the hydrochloride. Yield 48.6%.

Found: C, 47.33; H, 6.82; N, 12.97%. Calcd for $C_{17}H_{24}N_4\cdot 4HCl$: C, 47.45; H, 6.56; N, 13.02%.

cis-β-I-$[CoCl_2(S,S\text{-peaen})]ClO_4\cdot H_2O$. A stream of air was bubbled through a solution of the *S,S*-peaen·4HCl (2.08 g), $LiOH\cdot H_2O$ (0.65 g) and $CoCl_2\cdot 6H_2O$ (1.2 g) in water (50 cm^3) for 3 h. To the solution was added concd HCl (8 cm^3) and 70% $HClO_4$ (2 cm^3). The resulting red solution was evaporated to 30 cm^3 on a water bath (60 °C) and stored in a refrigerator overnight. The violet crystals deposited were filtered, washed with water, ethanol and ether. Yield: 350 mg. The second crop of crystals which were identical with those of the first crop were obtained by evaporating the filtrate to 20 cm^3. Yield: 240 mg.

Found: C, 36.91; H, 4.86; N, 10.69%. Calcd for $C_{16}H_{24}N_4O_5Cl_3Co$: C, 37.17; H, 4.64; N, 10.82%.

cis-β-II-$[CoCl_2(S,S\text{-peaen})]ClO_4\cdot 1/2H_2O$. The filtrate from the separation of *cis-β*-I was stored in a refrigerator for 3 h. The reddish-purple crystals deposited were filtered, washed with a water–ethanol mixture (1:1), ethanol and ether, and air dried. Yield: 200 mg.

Found: C, 37.89; H, 4.60; N, 10.87%. Calcd for $C_{16}H_{22}N_4O_4Cl_3Co\cdot 1/2H_2O$: C, 37.73; H, 4.52; N, 11.01%.

cis-α-$[CoCl_2(S,S\text{-peaen})]ClO_4\cdot 3/2H_2O$. $CoCl_2\cdot 6H_2O$ (1.2 g) in water (10 cm^3) and 30% H_2O_2 (1 cm^3) were mixed in an ice bath and added dropwise to a solution of $NaHCO_3$ (2.8 g in 50 cm^3 of water) at 0 °C for 30 min.[10] To the solution was added a mixture of *S,S*-peaen·4HCl (2.08 g) and $LiOH\cdot H_2O$ (0.63 g) in water (10 cm^3). The resulting red solution, concd HCl (10 cm^3) and 70% $HClO_4$ (1 cm^3) were added and heated at 80 °C for 20 min, and allowed to stand at room temperature overnight. The violet crystals deposited were filtered, washed with water, ethanol and finally ether. Yield: 300 mg. The crystals were identical with *cis-β*-I obtained by the air oxidation method. The filtrate from the separation of *cis-β*-I was poured onto a column of cation exchanger Dowex 50W-X8 (H^+ form) (ϕ 3.0×20 cm). The column was washed with water, and the adsorbed product was eluted with 5 M HCl. The reddish-purple eluate was evaporated to dryness. The purple residue was dissolved in 5 M HCl (15 cm^3) and the solution filtered. After the addition of 70% $HClO_4$ (1 cm^3), the solution was stored in a refrigerator for three days. The purple crystals deposited were filtered, washed with a water–ethanol mixture (1:1), ethanol and finally ether. Yield: 240 mg.

Found: C, 36.63; H, 4.56; N, 10.64%. Calcd for $C_{16}H_{22}N_4O_4Co\cdot 3/2H_2O$: C, 36.49; H, 4.75; N, 10.63%.

cis-α-$[Co(ox)(S,S\text{-peaen})]ClO_4\cdot H_2O$. A mixture of *cis-α*-$[CoCl_2(S,S\text{-peaen})]ClO_4\cdot 3/2H_2O$ (0.5 g) and sodium oxalate (0.2 g) in water (30 cm^3) was heated at 80 °C for 30 min. The orange solution was evaporated to 10 cm^3 and stored at room temperature. The orange crystals deposited were collected and recrystallized from hot water.

Found: C, 40.58; H, 4.96; N, 10.39%. Calcd for $C_{18}H_{22}N_4O_8ClCo\cdot H_2O$: C, 40.43; H, 4.48; N, 10.48%.

cis-β-$[CoCl_2(R,R\text{-peatn})]ClO_4\cdot H_2O$. The procedure used here was analogous to the preparation of $[CoCl_2(S,S\text{-peaen})]ClO_4\cdot H_2O$. A stream of air was bubbled through a solution of *R,R*-peatn·4HCl (2.15 g), $LiOH\cdot H_2O$ (0.65 g) and $CoCl_2\cdot 6H_2O$ (1.2 g) in water (50 cm^3) for 4 h. To the dark brown solution was added concd HCl (8 cm^3) and 70% $HClO_4$ (2 cm^3). The resulting solution was evaporated to 20 cm^3 on a water bath. On standing at room temperature for 1 h deep violet crystals deposited. The crystals were collected, washed with a small amount of water, acetone and air dried. Yield 1.64 g. The filtrate was poured onto a column of SP-Sephadex (ϕ 3.0×42 cm). The adsorbed band was eluted with 2 M HCl. The eluatant of the purple band was fractionated and the CD spectra recorded. All the fractions gave an identical CD spectra with that of the isolated complex. No indication of the presence of the other isomer was found. The so-called tricarbonato method[10] was also employed in the preparation of dichloro(*R,R*-peatn) complexes. The obtained complex was identical with that prepared by the air oxidation method.

Found: C, 38.28; H, 5.21; N, 10.37%. Calcd for $C_{17}H_{24}N_4Cl_3Co\cdot H_2O$: C, 38.40; H, 4.94; N, 10.53%.

cis-β-$[Co(NO_2)_2(R,R\text{-peatn})]ClO_4$. Sodium nitrate (0.2 g) was added to a hot solution of *cis-β*-$[CoCl_2(R,R\text{-peatn})]ClO_4$ (0.4 g) in water (10 cm^3). The solution was heated at 70 °C for 30 min. On cooling to room temperature for 1 h, the orange-yellow crystals were filtered and washed with water, ethanol and finally ether. Yield: 310 mg.

Found: C, 38.15; H, 4.54; N, 15.84%. Calcd for $C_{17}H_{24}N_6O_8ClCo$: C, 38.18; H, 4.52; N, 15.71%.

cis-β-$[Co(ox)(R,R\text{-peatn})]ClO_4\cdot 1/2H_2O$. A solution of *cis-β*-$[CoCl_2(R,R\text{-peatn})]ClO_4$ (0.52 g) and sodium oxalate (0.2 g) in water (10 cm^3) was heated at 50 °C for 2 h. The cherry-red crystals deposited were collected and recrystallized from hot water. Yield: 220 mg.

Found: C, 42.06; H, 4.61; N, 10.38%. Calcd for $C_{19}H_{24}N_4O_8ClCo\cdot 1/2H_2O$: C, 42.27; H, 4.67; N, 10.38%.

Measurements. The visible and ultraviolet absorption were recorded with a Shimadzu Double 40-R spectrophotometer. The CD spectra were recorded on a JASCO J-20 spectropolarimeter. The spectra of the dichloro complexes were recorded in concd HCl, while those of the other complexes were recorded in water. The PMR spectra in DMSO-d_6 were obtained with a JNM-PMX60 spectrometer using tetramethylsilane (TMS) as an internal standard. All the measurements were conducted at room temperature.

Results and Discussion

Ligands. The quadridentate ligands, *S,S*-peaen and *R,R*-peatn were prepared from optically active 1-(2-pyridyl)ethylamine (pea) with 1,2-dibromoethane and 1,3-dibromopropane, respectively. The absolute configuration of the tetramine ligands is expected to be the same as that of the mother pea whose absolute configuration has been determined.[9]

S,S-Peaen Complexes. Dichlorocobalt(III) complexes of *S,S*-peaen were prepared according to the reaction scheme:

1) $Na_3[Co(CO_3)_3] + S,S\text{-peaen}$

$$\xrightarrow[HClO_4]{HCl}\left\{\begin{array}{c} cis\text{-}\alpha\text{-}[CoCl_2(S,S\text{-peaen})]^+ \\ \text{(purple)} \\ cis\text{-}\beta\text{-I-}[CoCl_2(S,S\text{-peaen})]^+ \\ \text{(violet)} \end{array}\right.$$

2) $Co(II)Cl_2\cdot 6H_2O + S,S\text{-peaen}$

$$\xrightarrow[HCl,\ HClO_4]{O_2}\left\{\begin{array}{c} cis\text{-}\beta\text{-I-}[CoCl_2(S,S\text{-peaen})]^+ \\ \text{(violet)} \\ cis\text{-}\beta\text{-II-}[CoCl_2(S,S\text{-peaen})]^+ \\ \text{(reddish-purple)} \end{array}\right.$$

Two types of stereoisomers were isolated by fractional crystallization from both reactions. The violet isomer (*cis-β*-I) was a major product in both reactions. Elemental analyses of the isomers are in good accord with the formulation and the geometrical configurations were confirmed by visible absorption and PMR spectral data. No *trans*(Cl–Cl) isomer was obtained. The trans geometry of the peaen complex would be unstable presumably due to steric hindrance between the hydrogen atoms of the two terminal pyridine residues. The PMR spectra of the isolated isomers measured in deuterated DMSO are given in Fig. 2. The purple isomer which was obtained *via* tricarbonatocobaltate(III) showed a single methyl doublet at approximately 1.9 ppm, indicating that the two methyl groups of peaen are equivalent; the geometrical configuration is therefore *cis*-α. The violet (*cis*-β-I) and reddish-purple (*cis*-β-II) complexes gave signals for the two types of methyl groups. Thus, the geometries may be assigned as *cis*-β. For the *cis*-α isomer of the cobalt(III) complex of the trien type ligand, only one enantiomer is possible, whereas two types of diastereomers are expected for the *cis*-β geometry. The two *cis*-β geometries arise from a combination of the configuration of the coordinated secondary nitrogen atoms.[11] Similar isomers are expected for the complexes of bispicen type ligands as shown in Fig. 3.[12]

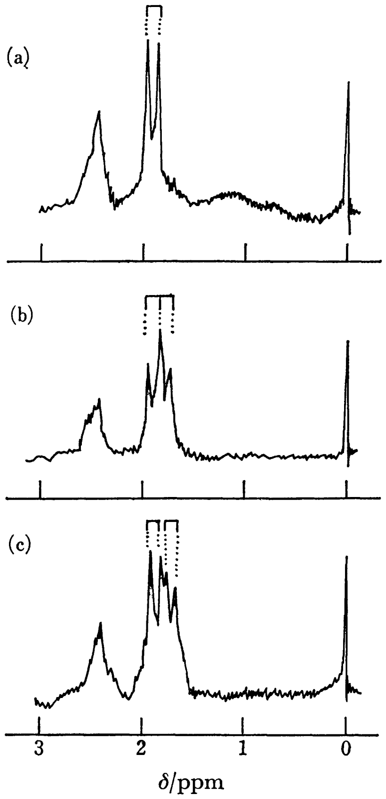

Fig. 2. PMR spectra of (a) *cis*-α-$[CoCl_2(S,S\text{-peaen})]^+$, (b) *cis*-β-I-$[CoCl_2(S,S\text{-peaen})]^+$ and (c) *cis*-β-II-$[CoCl_2(S,S\text{-peaen})]^+$ in DMSO(d_6).

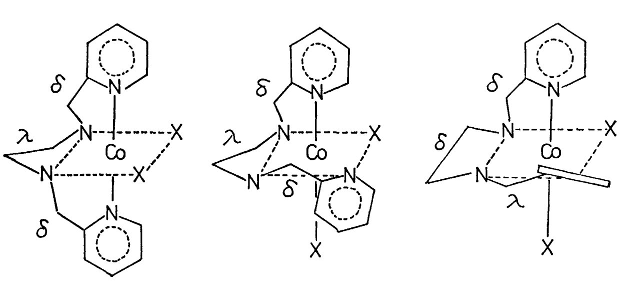

Fig. 3. Three diastereomers of *cis*-$[CoX_2(\text{bispicen})]^+$. (a) Λ-*cis*-α-($R_N$,$R_N$), (b) Δ-*cis*-β-($R_N$,$S_N$), (c) Δ-*cis*-β-($R_N$,$R_N$).

According to a recent X-ray analysis of Λ-*fac*-$[Co(S\text{-pea})_3](ClO_4)_3 \cdot H_2O$, the *S*-pea chelate has been shown to take a puckered δ-conformation with the C-methyl group occupying an equatorial position.[6] The terminal chelate rings of *S*,*S*-peaen in the present complex would also favour the δ-conformation in a similar manner to the chelate ring of the mother *S*-pea. A molecular model predicts that whenever the terminal chelates of *S*,*S*-peaen are fixed in a δ-conformation, the *cis*-α and *cis*-β geometries uniquely yield Λ-*cis*-α-(R_N,R_N) and Δ-*cis*-β-(R_N,S_N) configuration, respectively. Thus the present *cis*-α and one of the *cis*-β isomers are most likely to have the above configurations, respectively. Since two types of *cis*-β isomers were obtained in the present study, one must be either the Δ-*cis*-β-(R_N,R_N) or the Λ-*cis*-β-(S_N,S_N) (see Fig. 3-c). In these enantiomeric configurations, the two outer chelate rings should have opposed conformations, *i.e.*, one of the terminal chelate rings should take a λ-conformation in which the methyl group takes an axial position.

The electronic absorption and CD spectra of the Λ-*cis*-α dichloro(*S*,*S*-peaen) complex and its oxalato derivative are shown in Fig. 4. The Λ-*cis*-α dichloro(*S*,*S*-peaen) complex shows a well defined shoulder at the longer wavelength side of the first absorption band. A similar feature in the first absorption band has been observed for the *cis*-α dichloro complex of trien[13] and methyl substituted trien.[14] The CD spectrum in the first absorption band region gives positive and negative components with nearly equal

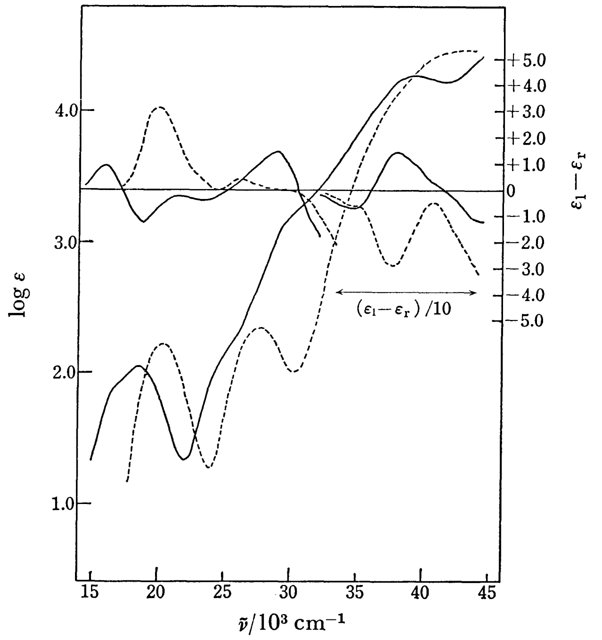

Fig. 4. Absorption and CD spectra of *cis*-α-$[CoCl_2(S,S\text{-peaen})]^+$ (——) in concd hydrochloric acid and *cis*-α-$[Co(ox)(S,S\text{-peaen})]^+$ (----) in water.

intensity from the longer to shorter wavelength. This CD pattern is vertually enantiomeric with that of Λ-*cis*-α-[$CoCl_2$(trien)]$^+$,[13] and Λ-*cis*-α-[$CoCl_2$(3*S*,8*S*-dimetrien)]$^+$ (3*S*,8*S*-dimetrien=(2*S*,7*S*)-2,7-dimethyl-3,6-diazaoctane-1,8-diamine).[14] The *cis*-α oxalato (*S*,*S*-peaen) complex which was obtained from the dichloro complex by a treatment with sodium oxalate in aqueous solution gave CD spectrum very similar to that of Λ-*cis*-α-[Co(ox)(trien)]$^+$.[15] The PMR spectrun of the oxalato complex showed a singel methyl doublet, indicating that the *cis*-α configuration is maintained in the course of reaction.

The absorption and CD spectra of the two types of *cis*-β isomers are shown in Fig. 5. Obviously these *cis*-β isomers give different absorption and CD spectra in the first absorption band region. The absorption maximum of *cis*-β-I appears at a longer wavelength than that of *cis*-β-II and the band has a well defined shoulder on the longer wavelength side. The CD associated with the first absorption band of *cis*-β-I gives two components, positive and negative Cotton effects from longer to shorter wavelength, while that of *cis*-β-II gives only one negative CD component. In contrast to the *S*,*S*-peaen complex only one *cis*-β isomer of structure Δ-*cis*-β-(R_N,S_N) has been obtained for the dichlorocobalt(III) complexes of 3*S*,8*S*-dimetrien and 2*S*,9*S*-dimetrien (2*S*,9*S*-dimetrien=(1*S*,8*S*)-1,8-dimethyl-3,6-diazaoctane-1,8-diamine).[14] The absorption and CD spectra in the first absorption band region for these *cis*-β complexes resembles those of the *cis*-β-II isomer rather than the *cis*-β-I isomer in the following points: (1) no shoulder of the first absorption band was detected; (2) only one negative CD peak was observed in the first absorption band region. Thus, the present *cis*-β-II isomer is most likely to have a Δ-*cis*-β-(R_N,S_N) configuration in which both of the two outer chelates have a δ-conformation.

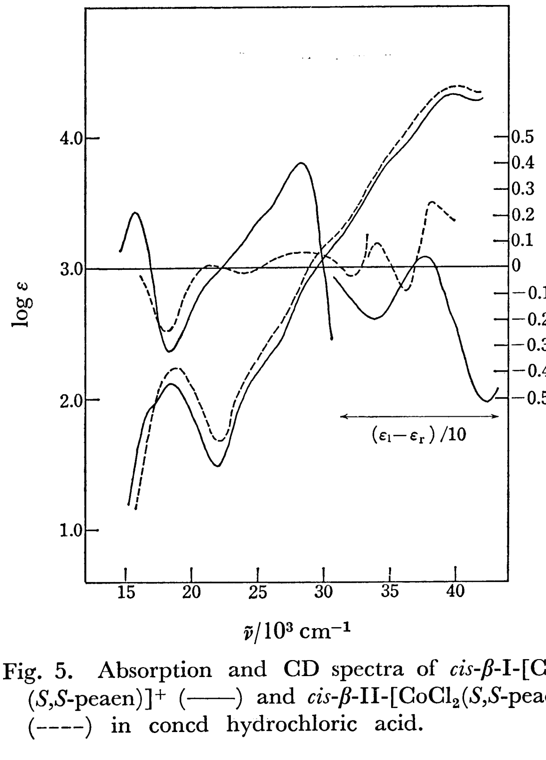

Fig. 5. Absorption and CD spectra of *cis*-β-I-[$CoCl_2$-(*S*,*S*-peaen)]$^+$ (——) and *cis*-β-II-[$CoCl_2$(*S*,*S*-peaen)]$^+$ (----) in concd hydrochloric acid.

The absorption spectra and CD pattern of the *cis*-β-I isomer resemble the *cis*-α more than the *cis*-β II, although the CD magnitude of the *cis*-β-I is smaller than that of *cis*-α. At present it is impossible to be unambiguous about the absolute configuration of the *cis*-β-I based on the CD pattern. Saburi *et al.*, have isolated a novel *cis*-β isomer of dinitro and carbonato (3*S*,8*S*-dimetrien)cobalt(III) complexes whose absolute configuration has been deduced to be Λ-*cis*-β-(S_N,S_N) on the basis of the PMR and CD spectra.[16] The molecular structure of Λ-*cis*-β-[Co(CO_3)(3*S*,8*S*-dimetrien)]-ClO_4 has been determined by the X-ray diffraction method[17] where it has been shown that the methyl group on the apically ligated chelate ring has an axial orientation. It is said that the apically ligated chelate ring inthe *cis*-β-(trien) complexes is less restricted than the side chelate ring coplanar with the central chelate.[1] Thus the structure of the present *cis*-β-I would also be in a Λ-*cis*-β-(S_N,S_N) configuration.

R,R-*peatn Complexes*. Dichlorocobalt(III) complexes with *R*,*R*-peatn were prepared according to the same method as those of the peaen complexes. In both methods, only one purple isomer was stereospecifically obtained. The PMR spectra of the dichloro complex shown in Fig. 6 gives two types of methyl doublets due to the terminal pea in the 1.8—2.0 ppm region, indicating that the complex has *cis*-β geometry.

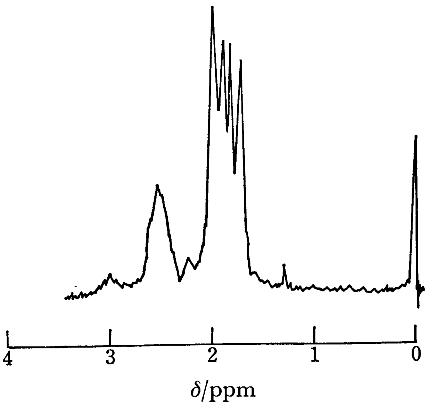

Fig. 6. PMR spectra of *cis*-β-[$CoCl_2$(*R*,*R*-peatn)]$^+$ in DMSO(d_6).

The central diamine moiety of *R*,*R*-peatn forms a six-membered chelate ring on complex formation. The conformational behavior of the six-membered chelate ring parallels that of cyclohexane. Among the three possible conformers of the six-membered chelate, *i.e.*, chair, skew and boat, the chair conformation is known to be most stable.[18–20] For the *cis*-β configuration of *R*,*R*-peatn complex, the following isomers are possible, Δ-*cis*-β-(S_N,S_N), Λ-*cis*-β-(R_N,R_N), Δ-*cis*-β-(R_N,S_N) and Λ-*cis*-β-(S_N,R_N). An examination of the molecular models indicates that for the Δ-*cis*-β-(S_N,S_N) configuration, the central six-membered ring can assume the chair conformation and at the same time both *R*-pea chelates take an λ-conformation with the methyl groups occupying equatorial positions. Accordingly, the most probable configuration of the *cis*-β-(*R*,*R*-peatn) complex is Δ-*cis*-β-(S_N,S_N).

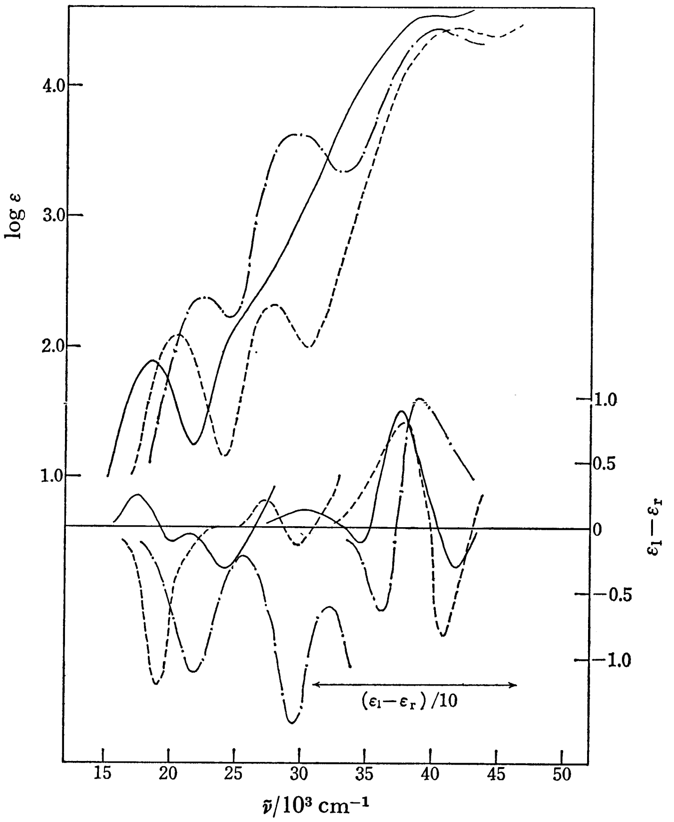

Fig. 7. Absorption and CD spectra of *cis*-β-$[CoCl_2(R,R\text{-peatn})]^+$ (——) in concd hydrochloric acid, *cis*-β-$[Co(ox)(R,R\text{-peatn})]^+$ (----) and *cis*-β-$[Co(NO_2)_2(R,R\text{-peatn})]^+$ (—·—·) in water.

The cis dinitro and oxalato complexes of *R*,*R*-peatn were prepared from *cis*-β-$[CoCl_2(R,R\text{-peatn})]ClO_4$ by heating an aqueous solution of the complex with sodium nitrate or sodium oxalate, respectively. In all cases, absorption and CD spectra of the reacted solution were identical with those obtained for the isolated complexes and no other isomers were formed. Thus, it appears that the relative configurations of the dinitro and oxalato complexes are the same as that of the dichloro species.

The absorption and CD curves of dichloro, dinitro and oxalato complexes are shown in Fig. 7. The CD corresponding to the first absorption band of the dichloro complex gives two components, positive and negative signs from longer to shorter wavelengths. In contrast, the dinitro and oxalato complexes of *R*,*R*-peatn give one negative component in the first absorption band region. The Δ-configuration can be assigned for these complexes on the basis of the signs of the dominants CD peaks in the first absorption band region.[21] This assignment is in accord with that based on the stereomodels.

It has been revealed that the stereochemical behavior of the peaen and peatn complexes is very similar to the corresponding complexes of methyl substituted trien[14,16,22] and 2′,3,2′-tet ligands.[23] This indicates that the conformational effects of the terminal pea chelate moieties of peaen and peatn complexes are essentially the same as those of the chiral diamine chelates.

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