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Chiral Metal Complexes.
25*. Cobalt(III) Complexes of some Linear *Mesomeric* Tetramine Ligands

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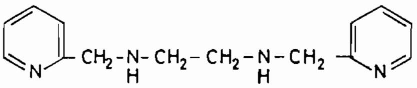
Abstract

The complexes of Λ-α-[Co(R,S-picbn)Cl_2]ClO_4 (where R,S-picbn is 3R,4S-dimethyl-1,6-di(2-pyridyl)-2,5-diazahexane) together with its Δ-Λ-α and Δ,Λ-β *exo* congeners, Δ-Λ-β-*exo*-[Co(picchmn)Cl_2]ClO_4 (where picchmn is N,N'-di(2-picolyl)-1R, 2S-diaminocyclohexane) as well as Δ,Λ-β-*endo*-[Co(R,S-picstien)Cl_2]$ClO_4 \cdot 2H_2O$, [Co(R,S-picstien)(ox)]$ClO_4 \cdot 0.5H_2O$ and [Co(R,S-picstien)(mal)]$ClO_4 \cdot 3H_2O$ (where picstien is 3R,4S-diphenyl-1,6-di(2-pyridyl)-2,5-diazahexane, ox is the oxalate dianion and mal is the malonate dianion) have been synthesised. The nature of the compounds was determined using a combination of ^{1}H NMR and, for certain chiral species, chiroptical techniques. In the various β complexes, the tetradentate is observed to adopt either the *exo* or *endo* geometry, specifically. Factors which influence coordination geometry include steric interactions and hydrophobic bonding effects.

A number of chemical transformations between dinitro and dichloro complexes of Co(III) with R,S-picbn have been examined, as has the reaction of Δ,Λ-β-*exo*-[Co(R,S-picbn)Cl_2]$^+$ with S-alanine in aqueous solution. The resulting product mixture contains eight of the sixteen possible β diastereoisomers, of which three have been isolated and characterised. The eight are composed of four β_1 and four β_2 isomers, however, and it is noted that isomerisation at the in-plane amine nitrogen atom is restricted by the overall geometry of the complexes formed. Discriminatory forces in these complexes are small in magnitude, and *exo*/*endo* isomerisation is somewhat dependent upon the choice of ligand(s) used to complete the coordination sphere.

Introduction

For some time we have been studying the properties of ternary complexes of Ru(II) and Co(III). In particular we have examined the sources of chiral discriminations in these complexes and their influence on coordination geometries [1, 2]. Considerable attention has been focused on complexes containing linear tetradentates based on 1,6-di(2-pyridyl)-2,5-diazahexane, picen (**1**). When the central chelate ring formed by ligands akin to **1** is derived from an optically active diamine such as 1R,2R- or 1S,2S-diaminocyclohexane or 1R,2R- or 1S,2S-diaminobutane, considerable stereospecificity is observed in complexes of Co(III) [3, 4].



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Somewhat different patterns of coordination would be expected to be enforced in complexes of similar ligands in which the central ring is derived from a *mesomeric* di-substituted 1,2-diamine. In order to explore the stereochemistry of complexes containing such ligands, we have undertaken a study of Co(III) species of these linear tetradentates based on 1R,2S-diaminocyclohexane, 2R,3S-diaminobutane and 1,2-diamino-1R,2S-diphenylethane. The results of this study are reported below.

Experimental

Analyses were carried out either by Mrs A. Dams at University College, Cardiff, or by the AMDEL Analytical Service, Melbourne. High-resolution ^{1}H NMR spectra were recorded at either 360 or 200 MHz using a Bruker WM360 or Varian XL-200 spectrometer, respectively, at 298 K. Saturated solutions

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were used throughout. Electronic spectra were recorded using a Beckman DK2A ratio-recording spectrophotometer or a Varian Techtron 635 spectrophotometer. Circular dichroism (CD) spectra were obtained using a Jobin Yvon CNRS Dichrographe III.

2R,3S- and 2R,3R- or 2S,3S-Diaminobutane

Isomeric mixtures of the amine 2,3-diaminobutane were prepared by Raney nickel reduction of dimethylglyoxime following the method of Dickey *et al.*, [5]. The complete separation of the *meso* and *rac* forms of the diamine is notoriously difficult [6, 7], and incomplete separations have given rise to errors in past work concerning complexes of these ligands [8]. Exhaustive recrystallisation is necessary to ensure complete purity, and yields are correspondingly low. This fact is of particular significance with respect to the isolation of Λ-α-[Co(*R*,*S*-picbn)Cl_2]-ClO_4 from a mixture containing a large excess of Δ-β-[Co(*S*,*S*-picbn)Cl_2]$^+$ (*vide infra*). Impure *R*,*S*-bn was obtained by fractionally crystallising its dihydrochloride salt from methanol [1]. Five recrystallisations from dry methanol were necessary before the salt was judged to be pure by reference to its infrared spectrum [6]. Yields of pure *R*,*S*-bn were typically 20% based on the amount of dimethylglyoxime used.

Purification of *rac*-bn was considerably more difficult. Even after twelve recrystallisations of its dihydrochloride salt from dry methanol, a small amount of the *meso* isomer was still present in the product (yield 37% based on dimethylglyoxime). Nevertheless, this product is suitable for resolution, and the subsequent preparation of *S*,*S*- or *R*,*R*-picbn as described elsewhere [4]. However, we repeat the details of the resolution process here, since the apparently pure diastereoisomeric salt of *S*,*S*-bnH_2^{2+} with *R*,*R*-(+)$_D$-tartrate still does in fact contain a trace of *R*,*S*-bn, even after several recrystallisations.

2S,3S-Diaminobutane

A sample of *rac*-bn·2HCl (124 g) was mixed with flakes of solid NaOH (100 g) and the mixture dry-distilled to yield *rac*-bn (64 g, boiling point (b.p.) 120–125 °C). Resolution was effected according to the literature method [9] to yield the salt [*S*,*S*-bnH_2] [*R*,*R*-(+)$_D$-tartrateH]$_2$ which was recrystallised from H_2O/MeOH (1:2, *v*/*v*) to constant rotation. Four recrystallisations were necessary. One further recrystallisation yielded 126 g of the apparently pure diastereoisomeric salt. The salt was dissolved in the minimum of hot water (70 °C) and treated with two equivalents of KCl dissolved in the minimum of cold water. Upon cooling to room temperature, sparingly soluble potassium hydrogen tartrate separated. After being left to stand for 24 h at room temperature, the mixture was filtered and the supernatant evaporated under reduced pressure to give a dry solid. This mixture was dry-distilled with excess solid NaOH to yield 23 g of *S*,*S*-bn contaminated with a trace of the *meso*-diamine. The first crop of diastereoisomeric salt containing *S*,*S*-bn that was isolated had $[\alpha]_D^{25} = +14.8°$ ($c = 1$, H_2O), At the end of the series of recrystallisations this value had risen to +15.6° (literature [9], +15.8°). Pure *R*,*R*-bn may be isolated from the supernatant by treatment with *S*,*S*-(−)$_D$-tartaric acid.

R,S-picbn

Freshly distilled pyridine-2-carboxaldehyde (9.02 g, 85 mmol) was refluxed in dry ethanol (50 cm^3) under dinitrogen and a solution of *R*,*S*-bn (3.73 g, 42 mmol) in dry ethanol (50 cm^3) was added dropwise during one hour. The mixture was refluxed and the solvent removed at reduced pressure to yield a pale yellow syrup, which crystallised overnight at 0 °C. The crystals were washed with cold diethylether and collected at the pump (yield 9.33 g, 83%). An 8.8 g sample of this product was dissolved in boiling ethanol (200 cm^3) and was treated with a large excess of $NaBH_4$. The mixture was refluxed for 4 h, was cooled, and water (100 cm^3) was added slowly. The solution was saturated with K_2CO_3 and was extracted with diethylether (5 × 100 cm^3). The combined extracts were dried over anhydrous K_2CO_3, filtered, and the solvent removed *in vacuo* to yield the ligand as a pale yellow oil (8.40 g, 94%). The ligand was ued for the preparation of complexes without further purification.

S,S-picbn

This ligand was prepared as described earlier [4], but contains a trace of the *meso*-tetradentate (*vide infra*).

Δ,Λ-β-[Co(R,S-picbn)Cl₂]ClO₄ and Δ,Λ-α-[Co(R,S-picbn)Cl₂]ClO₄

$CoCl_2 \cdot 6H_2O$ (7.9 g, 33 mmol) and *R*,*S*-picbn (13.3 g, 49 mmol) were dissolved in H_2O (300 cm^3) and oxygen was bubbled through the solution overnight. To the resulting dark yellow–brown solution was added conc. HCl (8.5 cm^3) and conc. $HClO_4$ (8.5 cm^3), and it was transferred to an evaporating dish on a steam bath. The mixture quickly turned to a deep red colour, and after some time a pale orange precipitate formed. This was removed by filtration, and the filtrate was further evaporated until purple crystals began to form. The mixture was cooled to room temperature and the crystals of Δ,Λ-β-[Co(*R*,*S*-picbn)Cl_2]ClO_4 were filtered off, washed with a little ice-cold water, then acetone, and dried at the pump. Yield: 5.5 g (35%). *Anal.* Calc. for $C_{16}H_{22}N_4O_4Cl_3Co$: C, 38.5; H, 4.4; N, 11.3. Found: C, 38.3; H, 4.3; N, 11.2%.

In several experiments, the same racemate was obtained, but in one case, using as starting materials *R,S*-picbn and $CoCl_2 \cdot 6H_2O$ in equimolar amounts, Δ,Λ-α-[Co(*R,S*-picbn)Cl_2]ClO_4 crystallised under the same conditions as detailed above. Yield: 55%. *Anal.* Found: C, 38.5; H, 4.2; N, 11.2%.

Λ-α-[Co(R,S-picbn)Cl_2]ClO_4

A reaction was carried out in the same manner as described above, except that $CoCl_2 \cdot 6H_2O$ (4.23 g, 18 mmol) and *S,S*-picbn (4.67 g, 17 mmol) containing a trace of *R,S*-picbn were used. Prior to evaporation of the solvent on the steam-bath, 2.5 cm^3 of conc. HCl and 4.2 cm^3 of conc. $HClO_4$ were added to the reaction mixture. As evaporation proceeded the mixture was stirred occasionally, and after a short time crystals were observed to have grown around the edge of the red solution. The mixture was cooled to room temperature and the crystals were filtered off, washed with ice-cold H_2O, then acetone, and were dried at the pump (yield 0.45 g, 5%). ^1H NMR measurements showed that this salt was a mixture of α-(*R,S*-picpn) and Δ-β-(*S,S*-picpn) diastereoisomers in the respective ratio of 1.0:0.3. Fractional recrystallisation of the mixture from hot aqueous HCl (4.0 mol dm^{-3}) afforded the pure Λ-α-[Co(*R,S*-picpn)Cl_2]ClO_4 salt as the least soluble diastereoisomer (0.21 g). Further recrystallisation from this medium, or from hot conc. HCl, did not change the optical activity of the product. All fractions isolated had the same chiroptical properties and thus the compound was adjudged to be optically pure. Subsequent evaporation of the supernatant from the reaction mixture afforded pure Δ-β-[Co(*S,S*-picbn)Cl_2]ClO_4 [3, 4]. *Anal.* for the Λ-α isomer. Found: C, 38.5; H, 4.4; N, 11.3%.

Δ,Λ-β-[Co(R,S-picpn)(NO_2)$_2$]ClO_4

Δ,Λ-β-[Co(*R,S*-picbn)Cl_2]ClO_4 (0.08 g, 0.17 mmol) and sodium nitrite (0.024 g, 0.34 mmol) were dissolved in H_2O (5 cm^3) on a steam bath. After a few minutes the solution had turned to a golden-orange colour. Aqueous $NaClO_4$ solution (1 cm^3, 20% *w/v*) then was added. The solution was cooled to room temperature and after 12 h the orange crystals which had formed were filtered off, washed with a few drops of ice-cold water and dried at the pump. Yield: 0.073 g, 83%. *Anal.* Calc. for $C_{16}H_{22}N_6O_8Cl_1Co$: C, 36.9; H, 4.3; N, 16.1. Found: C, 36.7; H, 4.1; N, 16.2%.

The same racemic complex was isolated in 64% yield when Λ-α-[Co(*R,S*-picpn)Cl_2]ClO_4 was used as starting material. In both cases the electronic spectrum of the reaction supernatant was identical, within experimental error, to that obtained for aqueous solutions of the isolated products. Furthermore, Δ,Λ-β-[Co(*R,S*-picbn)(NO_2)$_2$]ClO_4 may be converted quantitatively to the same β-dichloro species mentioned above by treatment with conc. HCl and evaporation of the purple solution so obtained to dryness on the steam bath.

Reaction of Δ,Λ-β-[Co(R,S-picbn)Cl_2]ClO_4 with S-Alanine

To a suspension of Δ,Λ-β-[Co(*R,S*-picbn)Cl_2]ClO_4 (1.0 g, 2 mmol) and *S*-alanine (*S*-alaH, 0.73 g, 10 mmol) in water (25 cm^3) was added 1.0 M aqueous NaOH (2.0 cm^3). The mixture was heated on a steam bath for 30 min and the resulting orange solution was diluted to 500 cm^3 with water and applied to a CM-Sephadex® C-25 column (100 × 2.5 cm) in the Na^+ cycle. The column was flushed with water and the complexes then eluted with 0.1 M aqueous $NaClO_4$. Two broad orange bands developed and these were collected in fractions using an LKB Ultrorac® II fraction collector. Measurements of electronic absorbance and circular dichroism (CD) spectra for each fraction allowed an estimation of the degree of separation of the complexes in the reaction mixture. Plots of both absorbance and differential absorbance against fraction number are shown in Fig. 1. It is obvious by inspection of these plots that both of the cleanly separated orange bands that had developed contain several diastereoisomers. With respect to the faster moving band, fractions from the leading and trailing edges were too dilute to permit the isolation of any solid product. However, all the fractions in this band had CD spectra characteristic of β_2 species [1, 4].

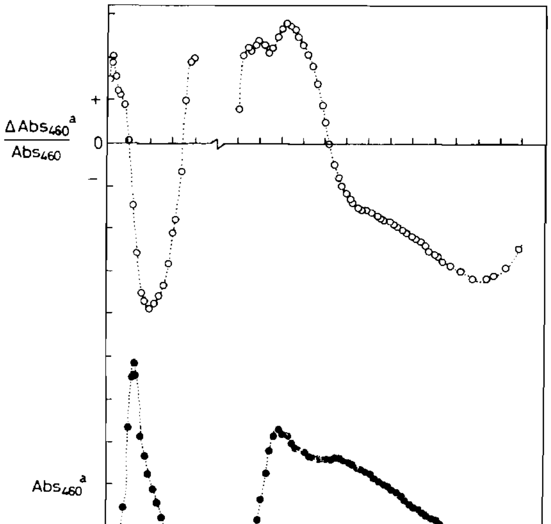


Fig. 1. Electronic absorption and CD spectral properties measured at 460 nm (in arbitrary units) of product fractions eluted on a Sephadex® C-25 column from the reaction mixture of Δ,Λ-β[Co(*R,S*-picbn)Cl_2]$^+$ with *S*-alanine. ^{a}Arbitrary units.

Fractions from the centre of the centre of the band, which had approximately constant $\Delta A/A$ values (fractions 15–25), were combined and evaporated to dryness *in vacuo* at 30 °C. The residue was dissolved in warm water (*ca.* 40 °C, 20 cm^3) and the resulting solution slowly evaporated over silica gel at room temperature. During several days a crop of small orange prisms crystallised, and these were filtered off, washed with a minimum of ice-cold water and dried at the pump. A detailed discussion of the nature of the two isomers present in this substance, which is Δ-β_2-*exo,endo*-[Co(*R,S*-picbn)(*S*-ala)](ClO$_4$)$_2$, is given in the following section. Yield: 0.12 g. *Anal.* Calc. for $C_{19}H_{28}N_5O_{10}Cl_2Co$: C, 37.0; H, 4.6; N, 11.4. Found: C, 37.3; H, 4.6; N, 11.4%.

Fractions from the slower-moving band, which had CD spectra characteristic of β_1 diastereoisomers of this type [9, 10], showed that this band also contained a number of species. Nevertheless, it was evident that the leading fractions contained only one diastereoisomer, so these were combined and worked up as described above, yielding fine orange needles of Δ-β_1-*exo*-[Co(*R,S*-picbn)(*S*-ala)](ClO$_4$)$_2$ (*vide infra*). Yield: 0.07 g. *Anal.* Found: C, 36.8; H, 5.0; N, 11.7%.

Solid complex salts could be isolated from the remaining fractions of the slower moving band in the usual way, but these proved to be mixtures of, in total, four β_1 diastereoisomers. No other pure β_1 species could be separated chromatographically using the Sephadex® employed, but it is evident that of the four complexes, two have Λ and two have Δ absolute configurations. Thus, by virtue of the fact that no equilibration of the absolute configuration of the in-plane amine nitrogen atom is observed upon N–*H* proton exchange in the three complexes isolated above, or in related species [9, 10 and refs. therein], the four complexes in the slower moving band are the Δ,Λ-β_1-*exo,endo* diastereoisomers.

N,N'-di(2-picolyl)-1R,2S-diaminocyclohexane (picchmn)

1*R*,2*S*-diaminocyclohexane (chmn) was purified from a mixture of isomers of the diamine (Aldrich) by forming the complex Ni(chmn)$_2$Cl$_2$ stereoselectively [10]. Treatment of this yellow salt with 3M H_2SO_4, then strong base, freed the amine which was extracted into diethylether. Chmn was isolated by vacuum distillation and the product stored under dinitrogen.

A sample of chmn (16.6 g, 145 mmol) and freshly distilled pyridine-2-carboxaldehyde (33.6 g, 313 mmol) were dissolved in dry dmf (140 cm^3) and the mixture was left to stand overnight. The solution was reduced in volume by one half on a rotary evaporator, and then was cooled in a refrigerator over 24 h. The white crystals of the Schiff base which had formed were collected by filtration, washed with ice-cold water and dried under suction (yield: 35.4 g, 83%). All of this product was dissolved in ethanol (100 cm^3) and 0.25 g of 10% Pd on carbon catalyst was added. The mixture was hydrogenated at room temperature until no more hydrogen was taken up, the catalyst was filtered off, and the filtrate was evaporated down to yield a deep yellow oil. This oil was vacuum distilled (220–226 °C, 0.3 mm Hg) to give a yellow oil which solidified on cooling. This solid was recrystallised from boiling ethanol to give pale yellow flakes of the tetradentate picchmn (yield: 6.5 g, 19%). *Anal.* Calc. for $C_{18}H_{24}N_4$: C, 72.9; H, 8.2; N, 18.9. Found: C, 72.8; H, 7.6 N, 19.0%.

Δ,Λ-β-[Co(picchmn)Cl$_2$]ClO$_4$

A solution of $CoCl_2 \cdot 6H_2O$ (1.16 g, 4.9 mmol) in H_2O (10 cm^3) was cooled to 0 °C and to it was added 30% H_2O_2 (1 cm^3). To the resulting pink solution was added dropwise, over 30 min, a solution of $NaHCO_3$ (2.8 g) in water (50 cm^3). To the green reaction solution was added picchmn (2.16 g, 7.3 mmol) and on warming to room temperature the solution changed to red. To this was added conc. HCl (10 cm^3) and conc. $HClO_4$ (1 cm^3) and the solution was heated for 30 min on a steam bath. As the volume slowly reduced crystals separated from the deep purple solution. The mixture was cooled to room temperature and the crystals were filtered off, washed with water and dried at the pump. Yield: 1.03 g, 40%. *Anal.* Calc. for $C_{18}H_{24}N_4Cl_3O_4Co$: C, 41.1; H, 4.6; N, 10.7. Found: C, 40.8; H, 4.7; N, 10.4%.

3R,4S-diphenyl-1,6-di(2-pyridyl)-2,5-diazahexane, R,S-picstien

The preparation of 1*R*,2*S*-diaminodiphenylethane (*meso*-stilbenediamine) was carried out according to literature methods [11, 12]. *meso*-Stilbenediamine (22.5 g, 110 mmol) and freshly distilled pyridine-2-carboxaldehyde (23.6 g, 220 mmol) were dissolved in dry benzene (350 cm^3) in a round-bottomed flask fitted with a Dean-Stark trap and a condenser. The mixture was refluxed for 4 h, during which time the stoichiometric amount of water had collected in the trap, and then the solution was left to stand at room temperature. After several hours pale yellow needles of the di-Schiff base had crystallised. These were collected at the pump, washed with benzene and air-dried. Yield: 33.6 g, 81%. Melting point (m.p.) 182–183 °C. *Anal.* Calc. for $C_{26}H_{22}N_4$: C, 80.0; H, 5.7; N, 14.4. Found: C, 80.8; H, 5.7; N, 14.2%.

The Schiff base (3.0 g, 7.7 mmol) was dissolved in absolute ethanol (150 cm^3) by vigorous stirring, and to the solution was added 10% palladium on charcoal catalyst (0.5 g). The mixture was hydrogenated at 40 p.s.i. using a Parr hydrogenator for 4 days, at which time hydrogen uptake had ceased. Upon filtration and solvent evaporation crude *R*,*S*-picstien was obtained as an off-white solid. This solid was dissolved in absolute ethanol (250 cm^3) and conc. HCl (3.0 cm^3) was added dropwise with stirring. The solution volume was reduced to *ca.* 30 cm^3 and a further 100 cm^3 of absolute ethanol was added. Upon cooling the mixture, white crystals of *R*,*S*-picstien·4HCl·$2H_2O$ slowly formed. After cooling the mixture in ice for two hours the product was collected at the pump, was washed with absolute ethanol (5 cm^3) then acetone (2 X 10 cm^3) and was air-dried. Yield: 3.5 g, 90%. *Anal.* Calc. for $C_{26}H_{34}N_4Cl_4O_2$: C, 54.2; H, 6.0; N, 9.8; Cl, 24.6. Found: C, 54.8; H, 5.9; N, 10.0; Cl, 24.0%.

Δ,Λ-β-[Co(R,S-picstien)Cl_2]ClO_4·$2H_2O$

To a stirred solution of *R*,*S*-picstien·4HCl·$2H_2O$ (2.0 g, 3.5 mmol) dissolved in a mixture of 95% ethanol (25 cm^3) and water (5 cm^3) was added $CoCl_2$·$6H_2O$ (0.83 g, 3.5 mmol) dissolved in 95 ethanol (25 cm^3). The resulting deep blue solution was stirred for 15 min and 30% H_2O_2 was added dropwise until the solution turned a deep red–purple colour (*ca.* 3.5 cm^3). After a further 30 min, conc. $HClO_4$ (2 cm^3) was added dropwise and the mixture left to stand at room temperature. During 4 days, the title complex crystallised as fine deep purple needles. Yield: 0.84 g, 37%. *Anal.* Calc. for $C_{26}H_{30}N_4Cl_3Co$: C, 47.3; H, 4.6; N, 8.5. Found: C, 47.1; H, 4.2; N, 8.9%.

Δ,Λ-β-[Co(R,S-picstien)(mal)]ClO_4·$3H_2O$

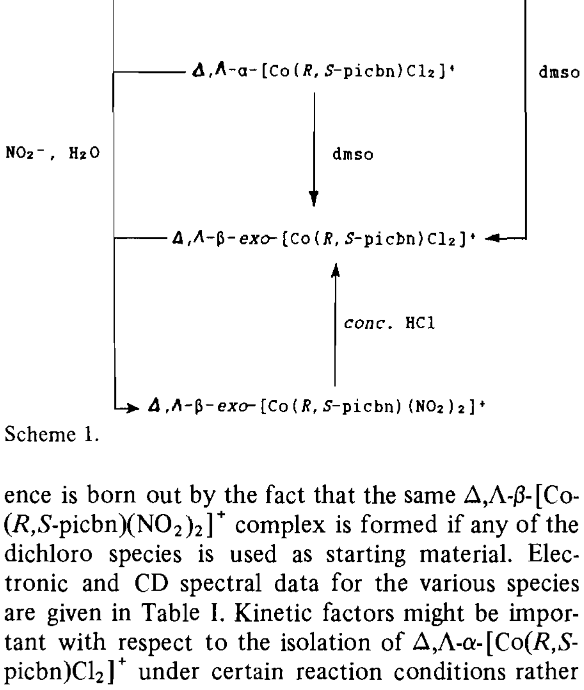
To a stirred suspension of Δ,Λ-β-[Co(R,S-picstien)Cl_2]ClO_4·$2H_2O$ (0.10 g, 0.15 mmol) in water (5 cm^3) was added disodium propanedicarboxylate (Na_2mal, 0.022 g, 0.15 mmol). All solids slowly dissolved (a few drops of ethanol aids dissolution) and the solution turned from a purple colour to a rose-pink. Red crystals of the title complex separated slowly over several hours. These were filtered off, washed with water (2 X 1 cm^3) and air-dried. Yield: 0.08 g, 74%. *Anal.* Calc. for $C_{29}H_{34}N_4O_{11}Cl_1Co$: C, 49.1; N, 7.9. Found: C, 49.1; N, 8.0%.

Δ,Λ-β-[Co(R,S-picstien)(ox)]ClO_4·$0.5H_2O$

To a solution of Δ,Λ-β-[Co(*R*,*S*-picstien)Cl_2]ClO_4·$2H_2O$ (0.1 g, 0.15 mmol) in H_2O (5 cm^3) and dimethylsulfoxide (DMSO, 2 cm^3) was added a solution of disodium oxalate (0.025 g, 0.23 mmol) in water (2 cm^3 and DMSO (1 cm^3). The reaction mixture was stirred until it had turned to a pink–orange colour and then saturated aqueous sodium perchlorate (2 cm^3) was added. Orange–red crystals of the title complex grew from solution over several hours at room temperature. These were filtered off, washed with a little cold water and air-dried. Yield: 0.08 g, 81%. *Anal.* Calc. for $C_{28}H_{29}N_4O_{8.5}Cl_1Co$: C, 51.8; H, 4.3; N, 8.7. Found: C, 51.7; H, 4.3, N, 8.8%.

Results and Discussion

Some chemical interconversions observed between complexes containing *R*,*S*-picbn are shown in Scheme 1. Since both Λ-α- and Δ,Λ-α-[Co(*R*,*S*-picbn)Cl_2]$^+$ are isomerised in DMSO solution to Δ,Λ-β-[Co(*R*,*S*-picbn)Cl_2]$^+$, these reactions being observed during NMR spin-decoupling experiments on solutions of the α complexes. It appears that the β complex is the more thermodynamically stable one for this *meso* tetradentate. The half-life for the isomerisation is about 45 min at 80 °C. This energetic preference is born out by the fact that the same Δ,Λ-β-[Co(*R*,*S*-picbn)(NO_2)$_2$]$^+$ complex is formed if any of the dichloro species is used as starting material. Electronic and CD spectral data for the various species are given in Table I. Kinetic factors might be important with respect to the isolation of Δ,Λ-α-[Co(*R*,*S*-picbn)Cl_2]$^+$ under certain reaction conditions rather than the β racemate, but the reasons for this are not obvious. In the case of Λ-α-[Co(*R*,*S*-picbn)Cl_2]$^+$, isolated as its perchlorate salt from a mixture containing mostly Δ-β-[Co(*S*,*S*-picbn)Cl_2]$^+$, solubility phenomena no doubt are responsible (*vide supra*). The optical activity is induced by the chiral medium from which it crystallizes. The CD spectrum of the complex is virtually enantiomorphic with that of Δ-α-[Cr(*S*-picpn)Cl_2]$^+$ (where *S*-picpn is 3*S*-methyl-1,6-di(2-pyridyl)-2,5-diazahexane), whose absolute configuration is known from a crystallographic study [13]. It also bears a close relationship to the CD spectrum of Λ-α-[Co(*R*-picpn)Cl_2]$^+$ whose configuration is known as well [14, 15]. All optical activity is lost when Λ-α-[Co(*R*,*S*-picbn)Cl_2]$^+$ isomerises to the β complex in DMSO solution.



Scheme 1.

TABLE I. Spectral Data for the Complexes[a]

Complex	λ (nm)	10^{-3} a (dm^2 mol^{-1})	$\Delta\epsilon$ (dm^2 mol^{-1})
Λ-α-[Co(*R*,*S*-picbn)Cl_2]$^+$ [b]	535	1.44	
	598		−18.8
	518		+20.3
	414		+9.7
	332		−28.1
Δ,Λ-β-[Co(*R*,*S*-picbn)Cl_2]$^+$ [b]	525	1.85	
Δ,Λ-β-[Co(*R*,*S*-picbn)(NO_2)$_2$]$^+$ [c]	445	3.80	
Δ,Λ-β-[Co(picchmn)Cl_2]$^+$ [a]	538	1.74	
Δ,Λ-β-[Co(*R*,*S*-picstien)Cl_2]$^+$ [d]	550	1.75	
Δ,Λ-β-[Co(*R*,*S*-picstien)(mal)]$^+$	503	2.29	
Δ,Λ-β-[Co(*R*,*S*-picstien)(ox)]$^+$	508	2.11	
Δ-β_2-*exo,endo*-[Co(*R*,*S*-picbn)(*S*-ala)]$^{2+}$ [e]	480	2.07	
	354	1.78	
	558		−0.5
	504		+4.0
	454		−7.9
	352		+2.9
Δ-β_1-*exo*-[Co(*R*,*S*-picbn)(*S*-ala)]$^{2+}$ [e]	490	2.15	+13.2
	354	1.80	−7.4

[a] Wavelength values correspond to maxima and extrema in the electronic and CD spectra, respectively. [b] Recorded in conc. HCl. [c] Recorded in methanol solution. [d] Recorded in DMSO solution. [e] Recorded in aqueous solution.

A number of isomeric and conformational possibilities exist for these complexes. NMR spectral studies have been of help in distinguishing between these for the particular species isolated. With α-[Co(*R*,*S*-picbn)Cl_2]$^+$, only one geometric isomer is possible, and this has C_1 symmetry. Thus the pyridyl hydrogen atoms lie in non-equivalent positions and all eight are observed separately in the 360 MHz ^{1}H NMR spectrum, although they do occur as expected in four pairs. Neither *H*(6) nor *H*(6′) is shielded by a pyridyl ring as is the case with β diastereoisomers [14, 15], and both are found at low field (9.43 and 9.35 ppm). Spin-decoupling experiments define the resonances for each pyridyl ring uniquely, but we are unable to distinguish between particular rings. ^{1}H NMR data are given in Table II. While this aspect of the ^{1}H NMR spectrum of the complex (and also that of the Δ,Λ-α-racemate) is straightforward, two conformations of the central chelate ring are permitted. A close inspection of the relevant sections of the NMR spectrum, however, shows that one is favoured over the other and the pattern of measured coupling constants allows its unequivocal assignment.

Here we concentrate on the Λ-α enantiomer for the purposes of discussion. It is not posssible for both methyl groups of Λ-α-[Co(*R*,*S*-picbn)Cl_2]$^+$ to lie in an equatorial position in the central chelate ring. As a consequence of this, should either the λ or δ conformer be adopted, one methyl group in an equatorial position forces the other to lie in such

TABLE II. 360 MHz ^{1}H NMR Data[a] for Co(III) Complexes of picbn and picchmn as Dichloro or Dinitro Salts

	δ or *J* for complex			
	A[b]	B	C	D
H(3)	7.69[c]	7.89	7.87	7.94
H(4)	8.15[d]	8.27	8.30	8.36
H(5)	7.73[e]	7.84	7.82	7.95
H(6)	9.43[f]	9.25	8.89	9.36
H(3′)	7.69[c]	7.71	7.72	7.83
H(4′)	8.15[d]	8.03	8.12	8.15
H(5′)	7.73[e]	7.37	7.45	7.49
H(6′)	9.35[f]	6.95	7.03	7.07
H(11)	5.00	4.10	4.33	4.31
H(12)	4.00	3.91	3.95	3.97
H(41)	4.66	4.30	4.22	4.40
H(42)	4.36	5.05	4.93	5.16
H(21)	2.93	3.45	3.26	
C(M2)H_3	0.27	1.46	1.17	
H(31)	2.56	2.55	2.86	
C(M3)H_3	1.12	1.10	1.12	
H(N2)	7.01	6.90	[g]	7.28
H(N3)	7.64	7.59	[g]	7.80
$J_{3,4}$	7.8	7.8	7.5	7.7
$J_{4,5}$	8.0	7.7	8.0	7.3
$J_{5,6}$	5.6	5.6	5.5	5.2
$J_{3',4'}$	7.8	7.5	7.8	7.5
$J_{4',5'}$	8.0	7.6	7.7	7.8
$J_{5',6'}$	5.7	5.8	5.6	5.7
$\lvert J_{11,12}\rvert$	17.0	16.3	16.5	16.7
$J_{11,N2}$	6.7	5.3		5.2

(continued)

TABLE II. *(continued)*

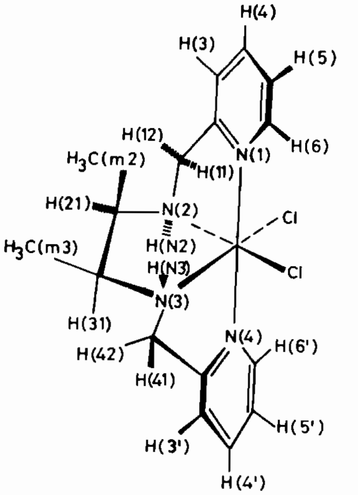
	δ or J for complex			
	A^b	B	C	D
$J_{12,N2}$	*ca.* 0	10.0		10.1
$J_{21,N2}$	6.6	6.6		
$J_{21,M2}$	7.5	7.2	7.2	
$J_{21,31}$	6.8	6.1	6.5	
$J_{31,M3}$	6.9	6.4	6.4	
$J_{31,N3}$	6.4	*ca.* 0		
$\lvert J_{41,42}\rvert$	18.1	17.3	18.2	16.2
$J_{41,N3}$	8.1	*ca.* 0		*ca.* 0
$J_{42,N3}$	*ca.* 0	6.6		6.5

[a] Recorded in DMSO-d_6. Chemical shifts in ppm relative to TMS as internal standard, coupling constants in Hz. [b] Complexes are A: Λ-α or Δ,Λ-α-[Co(*R*,*S*-picbn)Cl_2]$^+$; B: Δ,Λ-β-[Co(*R*,*S*-picbn)Cl_2]$^+$; C: Δ,Λ-β-[Co(*R*,*S*-picbn)$(NO_2)_2$]$^+$; D: Δ,Λ-[Co(picchmn)Cl_2]$^+$. [c–f] We do not distinguish between these pairs of resonances.

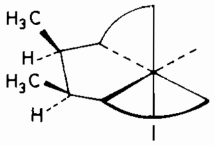
an environment that it would experience a pronounced shielding effect from an adjacent pyridyl ring. Thus one CH_3 resonance is observed at an unusually high field [15] in the spectrum at 0.27 ppm. With such an arrangement, on the other hand, the λ conformer in the Λ-α complex would give rise to non-bonded steric interactions between the two methyl groups and a neighbouring methylene bridge in the tetradentate, as revealed by molecular models. While this suggests that the δ conformer would be the more stable, a study of the appropriate dihedral angles between protons in the central chelate ring, together with measured coupling constants, confirms that the δ conformer is that which is assumed.

Molecular models show that the two hydrogen atoms located on carbons in the central ring in the δ conformer make dihedral angles of 30 and 150° with their adjacent N–*H* protons. The dihedral angle between these two C–*H* protons is about 40°. Alternatitively, in the λ conformer, the appropriate angles are 40, 90 and 50°, respectively. All of the coupling constants associated with these protons are significantly large (Table II), being 6.6, 6.4 and 6.8 Hz respectively, and these values would serve to eliminate the λ conformer, which would have one coupling constant *ca.* 0 Hz. Therefore, the conformation of the Λ-α-[Co(*R*,*S*-picbn)Cl_2]$^+$ ion is that shown in 2, with the central chelate ring in the δ conformation; the methyl group adjacent to the tetradentate fold is that which experiences ring shielding. Other coupling constants involving the bridging methylene groups are fully in accord with this structure.

Other isomeric elaborations attend the corresponding β diastereoisomers. The methyl groups may occupy *exo* or *endo* positions with respect to the fold of the tetradentate, as shown diagramatically in 3 and 4, and the in-plane amine nitrogen atom may adopt either an *R* or *S* absolute configuration. This is unlike the case of α isomers where these configurations are fixed by the overall geometry of the complex. However, ^{1}H NMR measurements (Table II) show that only one enantiomeric pair is in fact formed. The question then arises as to which pair this is. It is appropriate to deal with each of the four possibilities for a Δ diastereoisomer in turn, using the NMR data for the complex in conjunction with molecular models.

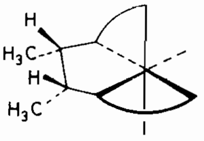


2



Δ-β-endo

3

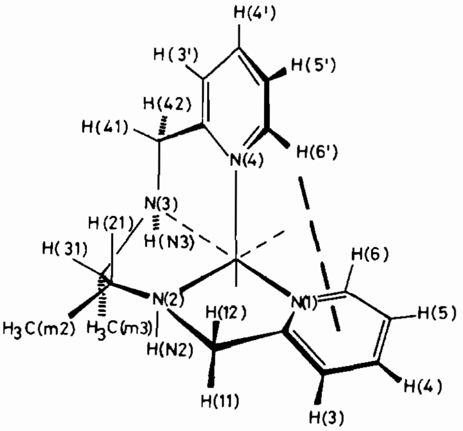


Δ-β-exo

4

First it should be noted that, in the β isomer, neither methyl group is shielded by an adjacent pyridyl ring. The two CH_3 resonances are observed at 1.46 and 1.10 ppm in DMSO solution. Secondly, it is found that one of the amine protons has a coupling constant equal to *ca.* 0 Hz with its adjacent C*H* proton in the central chelate ring. These two facts serve to eliminate several of the isomeric possibilities. In a Δ-β-*endo*-(*R R*) isomer (the *R,S* convention refers here to the absolute configurations of the secondary amine nitrogen atoms) the dihedral angle between the N–*H* and C–*H* protons of the 2,3-diaminobutane fragment is such as to give rise to significant coupling in all cases irrespective of the conformation of the central chelate ring. This is true also for the Δ-β-*endo*-(*S,R*) diastereoisomer in which the central chelate ring is locked in a rigid conformation, one methyl group being in close proximity to the adjacent pyridyl ring.

It is clear therefore that the complex has the *exo* geometry. Both *exo* isomers can satisfy the requirements with respect to N–*H*–C–*H* coupling constants by the appropriate pair of protons next to the tetradentate fold describing a dihedral angle of *ca.* 85°. However, in the (*R*,*R*) diastereoisomer, this angle only can be achieved by the central chelate ring adopting a fully-eclipsed conformation. Such an arrangement would be energetically unfavourable, and we are led to the conclusion that the complex is the Δ-β-*exo*-(*R*,*S*)-$[\mathrm{Co}(R,S\text{-picbn})\mathrm{Cl}_2]^+$ isomer (and its enantiomer, as shown in **5**). A λ conformation is adopted by the central chelate ring, and the methyl group remote from the tetradentate fold is forced to lie in an equatorial position.



5

Finally, it should be noted that the upfield position of the *H*(6′) resonance relative to that of *H*(6) (*i.e.* 6.95 and 9.25 ppm respectively) confirms the overall β geometry of the complex [1].

All $[\mathrm{Co}(R,S\text{-picbn})\mathrm{Cl}_2]^+$ complexes react with aqueous nitrite ion to yield Δ,Λ-β-$[\mathrm{Co}(R,S\text{-picbn})(\mathrm{NO}_2)_2]^+$, again enantiomeric species with the same geometry as that of the Δ-β-*exo* dichloro complex. This conclusion is born out by the fact that the dinitro complex reacts with concentrated HCl to give Δ,Λ-β-*exo*-(*R*,*S*)-$[\mathrm{Co}(R,S\text{-picbn})\mathrm{Cl}_2]^+$. Selected ^{1}H NMR data for the yellow dinitro salt are given also in Table II, as are those for Δ,Λ-β-$[\mathrm{Co(picchmn)Cl}_2]^+$.

For this complex, which contains the tetradentate derived from 1*R*,2*S*-diaminocyclohexane, the same proton numbering scheme as shown in **5** is used, except for the aliphatic hydrogen atoms of the cyclohexane ring. The pattern of pyridyl proton resonances clearly indicates that the complex possesses β geometry, and the very close correspondance between the chemical shift and proton coupling of the N–*H* and bridging C*H*$_2$ groups for this complex and that containing *R*,*S*-picbn leads us to conclude that the former also consists of the Δ-β-*exo*-(*R*,*S*)-$[\mathrm{Co(picchmn)Cl}_2]^+$ cation and its enantiomer. With this geometry, the cyclohexane ring may adopt a chair conformation with ease. Molecular models suggest that no non-bonded steric interactions would exist between the cyclohexane ring and the rest of the ligand chain. This is not the case for either diastereoisomeric arrangement of *endo* isomers.

Notwithstanding the isolation of certain α complexes of Co(III) with *R*,*S*-picbn, the results outlined above indicate a preference for an *exo* geometry in β diastereoisomers. However, the reaction of Δ,Λ-β-*exo*-$[\mathrm{Co}(R,S\text{-picbn})\mathrm{Cl}_2]^+$ with *S*-alanine shows that the chiral discrimination energy between Δ-β-*exo* and Δ-β-*endo* isomers is not very large, a conclusion in accord with observations made concerning related complexes containing picpn [16, 17]. Reference to Fig. 1 makes it obvious that many species in fact are produced in this reaction.

As is reported in 'Experimental', a clean chromatographic separation of β_1 and β_2 isomers was achieved. In the faster moving band containing the latter species, four diastereoisomers were present. Two of these, with absolute configuration Δ as deduced from CD spectral measurements, were isolated as a mixture of their individual perchlorate salts. This solid contained the two Δ-β_2 diastereoisomers in the ratio 1.0:0.85, which was measured by integration of their methyl resonances in the ^{1}H NMR spectrum. Electronic and CD spectral data for this mixture, and characteristic ^{1}H NMR data, are given in Tables I and III, respectively.

We have shown elsewhere [16, 17] in studies on related complexes that isomeric ratio differences do not arise as a result of the variation in absolute configuration of the in-plane amine nitrogen atom in β diastereoisomers. Measurements of ^{1}H NMR spectra of mixtures of these kinds of complexes show that no equilibration of isomer populations takes place upon exchange of the N–*H* protons, a fact we have confirmed in this case by separate measurements in both DMSO-d$_6$ and D$_2$O solution. Proton exchange is fast in the latter solvent; no N–*H* resonances are observed. Thus we are inevitably led to conclude that the two isomers present in this particular case are the *exo* and *endo* forms of Δ-β_2-$[\mathrm{Co}(R,S\text{-picbn})(S\text{-ala})]^{2+}$. The other two isomers in the band eluting faster from the chromatographic column are thus the Λ-β-*exo* and -*endo* species, but these were present in amounts too small to permit their isolation as pure salts.

While the pattern of resonances arising from the aromatic fragments of the cations proves that both Δ cations possess β geometry, it is not possible in the absence of X-ray crystallographic information to

TABLE III. Characteristic 360 MHz ^{1}H NMR Data[a] for the [Co(*R*,*S*-picbn)(*S*-ala)]$^{2+}$ Complexes

	δ or *J* for complex		
	Δ,Λ-β_2-*exo,endo*-[Co(*R*,*S*-picbn)(*S*-ala)]$^{2+}$		Λ-β_1-*exo*-[Co(*R*,*S*-picbn)(*S*-ala)]$^{2+}$
	major isomer[b]	minor isomer[b]	
$H(3)$	7.86(d)[c]	7.86(d)	7.89(d)
$H(4)$	8.30(t)	8.30(t)	8.36(t)
$H(5)$	7.85(t)	7.85(t)	7.89(t)
$H(6)$	8.52(d)	8.52(d)	8.29(d)
$H(3')$	7.72(d)	7.70(d)	7.84(d)
$H(4')$	8.11(t)	8.09(t)	8.15(t)
$H(5')$	7.36(t)	7.37(t)	7.46(t)
$H(6')$	6.97(d)	6.82(d)	6.97(d)
$H(21)$	3.24(m)	3.52(m)	3.67(m)[f]
$H(31)$	3.56(m)	3.17(m)	2.81(m)[f]
$C(M2)H_3$	1.40(d)	1.42(d)	1.20(d)
$C(M3)H_3$	1.39(d)	1.39(d)	1.50(d)
H_α[e]	4.19(q)	4.33(q)	4.04(q)
CH_3[e]	1.73(d)	1.68(d)	1.43(d)
$H(11)$			4.44(d)[g]
$H(12)$			4.14(d)[g]
$H(41)$			4.48(d)[h]
$H(42)$			4.84(d)[h]
$\lvert J_{11,12} \rvert$			16.9
$\lvert J_{41,42} \rvert$			17.3
$J_{21,31}$			5.9
$J_{21,M2}$			6.3
$J_{31,M3}$			7.2
$J_{\alpha,CH3}$[e]			7.2

[a] Recorded in D_2O solution. Chemical shifts in ppm relative to TSS as internal standard. Coupling constants in Hz. [b] Isomers present in the ratio 1.0:0.85. [c] d = doublet, t = triplet, q = quintet, m = multiplet. [d] Aminoacid protons. [f–h] It is not possible on the basis of spectral measurements in D_2O to distinguish between these pairs of signals.

TABLE IV. Characteristic 200 MHz ^{1}H NMR Data[a] for the Complexes Containing *R*,*S*-picstien

	δ or *J* for complex		
	Δ,Λ-β-[Co*L*Cl$_2$]$^+$	Δ,Λ-β [Co*L*(ox)]$^+$	Δ,Λ-β-[Co*L*(mal)]$^+$
$H(6)$	9.26(d)[c]	8.38(d)	8.55(d)
$H(6')$	7.02(d)	7.06(d)	7.02(d)
$H(11)$	4.33	b	f
$H(12)$	4.44	b	f
$H(21)$	5.26	5.15	5.16
$H(31)$	5.89	5.29	5.41
$H(41)$	3.46	3.47	3.47[h]
$H(42)$	4.87	b	4.62
$H(N2)$	8.56	8.12	7.89[g]
$H(N3)$	9.30	8.92	9.01
$H(mal)$[e]			2.70
$H'(mal)$[e]			3.10
$\lvert J_{11,12} \rvert$	16.0		
$\lvert J_{41,42} \rvert$	16.8	17.6	17.2
$J_{21,31}$	7.4	7.0	7.2
$J_{21,N2}$	8.4	7.6	7.8
$J_{31,N3}$	11.5	11.6	11.9
$J_{11,N2}$	5.4		
$J_{12,N2}$	8.6		
$J_{41,N3}$	*ca.* 0	*ca.* 0	*ca.* 0
$J_{42,N3}$	6.2	6.8	6.0

[a] L = *R*,*S*-picstien. Chemical shifts in ppm relative to TSS as internal standard. Coupling constants in Hz. All spectra were recorded in DMSO-d_6. d = doublet. [b] These three signals overlap at 4.48 ppm. [c] A trace of DCl was added to move the interfering H_2O signal downfield. [e] Malonate hydrogen atoms are not distinguished. [f] 'Deceptively simple' doublet centred at 4.36 ppm. [g] Partially obscured by aromatic signals. [h] Partially obscured by the H_2O signal.

distinguish which isomer is present in the greater amount. It is possible that both cations crystallise in the same unit cell, as has been found with related complexes containing *R*- or *S*-picpn [16], but the isolated prisms of the complex were too small to allow NMR measurements to be performed on solutions of individual crystals. X-ray crystallographic work is being undertaken to clarify this point.

Finally, concerning these β_2 species, it should be mentioned briefly that another possible interpretation of the NMR and CD data is possible. The two isomers may yet have opposite absolute configurations. This suggestion is prompted by the somewhat unusual CD spectrum of the mixture in the region of the visible transitions. This possibility only could be fully discounted by crystallographic structure determinations of the isolated salt. However, it is noted that the presence of *S*-alanine in the complexes does not give rise to any significant discriminatory effects.

A similar pattern of results is found upon examination of the CD spectra of fractions containing β_1-[Co(*R*,*S*-picbn)(*S*-ala)]$^+$ isomers in the slower-moving chromatographic band. Mixtures of isomers with overlapping NMR spectra too complex to analyse were obtained from the majority of fractions from the slower-moving band by concentrating eluates containing perchlorate ion. However, from the leading fractions of the band one pure diastereoisomeric salt was obtained as fine orange needles. Spectral data for this complex also are given in Tables I and III.

The ^{1}H NMR spectrum of the complex, recorded in D_2O, shows that the β isomer does not equilibrate in solution to mixtures which would indicate isomerisation of amine N(2). Furthermore, its CD and NMR spectrum clearly established it to be a Λ-β_1 diastereoisomer [16, 17]. It is evident that, by comparison with data for the corresponding dichloro complex (Table III) that the pure isomer isolated from the band is Λ-β_1-*exo*-[Co(*R*,*S*-picbn)(*S*-ala)]$^{2+}$, although, the other three possible β_1 diastereoisomers, disregarding isomerism at N(2), are also present in the reaction mixture. We conclude that discriminatory forces between these isomers are thus rather small, a suggestion that seems justified in terms of the isomeric distribution found in the complexes of *R*,*S*-picstien that we have synthesised. Spectral data for the racemic β complexes of *R*,*S*-picstien and oxalate, malonate or chloride are given in Tables I and IV.

For each complex in DMSO-d$_6$, only one isomer is present, together with its enantiomer. Reference to the chemical shifts of the pyridyl hydrogen resonances indicates that the β geometry is adopted in Δ,Λ-[Co(*R*,*S*-picstien)Cl$_2$]$^+$. However, the spectral pattern found for the methine and methylene C–*H* resonances is somewhat different from the corresponding picbn and picchmn complexes. Figure 2 shows the relevant regions of the ^{1}H NMR spectra of Δ,Λ-β-[Co(*R*,*S*-picstien)Cl$_2$]$^+$, Δ,Λ-β-[Co(*R*,*S*-picstien)(ox)]$^+$ and Δ,Λ-β-[Co(*R*,*S*-picstien)(mal)]$^+$. As far as the dichloro complex is concerned, the magnitudes of the observed coupling constants indicate which of the signals derive from the CH$_2$ bridging groups. These in turn may be grouped into pairs on the basis of changes observed in spin-decoupling experiments. Signals arising from *H*(21) and *H*(31) appear as a doublet of doublets and a triplet at 5.26 and 5.89 ppm. The vicinal coupling constant between these protons is 7.4 Hz, and they both are coupled to adjacent N–*H* protons as well (J = 8.4 and 11.5 Hz). One of the protons in the methylene bridges does not couple to the adjacent amine proton. Each of the other three does, with coupling constants of 5.4, 6.2 and 8.6 Hz.

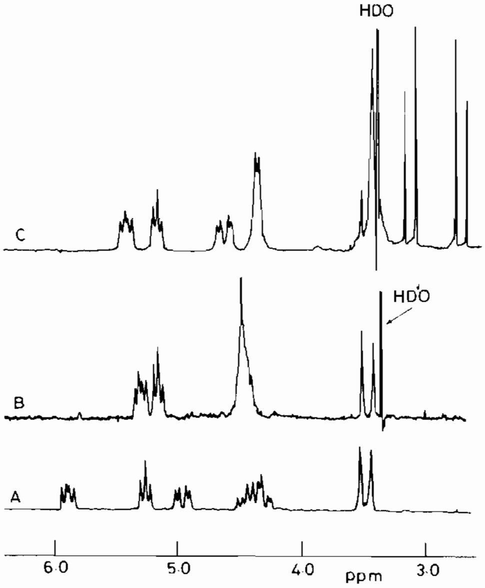
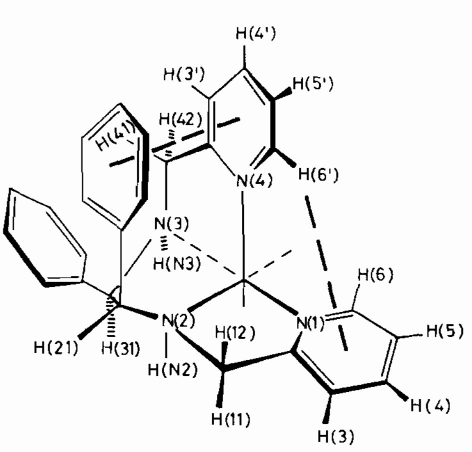


Fig. 2. 200 MHz ^{1}H NMR spectrum in DMSO-d$_6$ of the aliphatic C–*H* region for (a) Δ,Λ-β[Co(*R*,*S*-picstien)Cl$_2$]$^+$, (b) Δ,Λ-β-[Co(*R*,*S*-picstien)(ox)]$^+$, and (c) Δ,Λ-β-[Co(*R*,*S*-picstien)(mal)]$^+$. The H$_2$O signal was suppressed during the recording of the spectrum of the oxalate complex. For the dichloro complex a trace of DCl was added to its solution to move the H$_2$O/HDO signal downfield.

Molecular models reveal that only one of the several possible diastereoisomers for this complex can give rise to this observed spectral pattern. It is Δ-β-*endo*-(*R*,*S*)-[Co(*R*,*S*-picstien)Cl$_2$]$^+$, as shown in **6** (together with its enantiomer). Inspection of the model, together with the coupling constant data, allows the unequivocal assignment of all of the ^{1}H NMR data for the aliphatic C–*H* protons. In the Δ-β-*endo* (*R*,*S*) isomer *H*(41) and *H*(N3) subtend a dihedral angle of *ca.* 95°, and this allows the assignment of the doublet at 3.46 ppm to *H*(41). As a consequence of the spin-decoupling experiments the resonance arising from *H*(42) at 4.87 ppm is defined uniquely. An inspection of the torsion angles between *H*(21) and *H*(N2), and *H*(31) and *H*(N3) indicates that the larger N*H*–C*H* coupling will be associated with *H*(31). This is found with the signal at lower field (5.89 ppm). Contact deshielding effects involving this proton and a coordinated chloride ion are possibly responsible for the low-field position for this proton with respect to that found in the malonate and oxalate derivatives (*vide infra*).



6

The C*H*–N*H* coupling constant data also serve to distinguish the resonances arising from *H*(11) and *H*(12). They are coupled to *H*(N2) with $J_{11,\mathrm{N2}}$ and $J_{12,\mathrm{N2}}$ equal to 5.4 and 8.6 Hz, respectively. A molecular model indicates that the torsion angles associated with these pairs of protons are, in turn, *ca.* 40 and 160°. A noteworthy result of the adoption of this stereochemistry by the complex cation (and its enantiomer) is that the phenyl group remote from the tetradentate fold may lie aligned parallel and adjacent to the apical pyridyl ring (**6**). Any other orientation would be highly unfavourable on steric grounds, and the structure suggests the presence of a significant attractive hydrophobic interaction between the two rings. Such an interaction would serve to explain the preference for *endo* rather than *exo* geometry in these *R,S*-picstien complexes.

A few chemical shift differences with respect to the aliphatic C–*H* resonances are noticed for Δ,Λ-β-[Co(*R,S*-picstien)(ox)]$^+$ and its malonate analogue (Fig. 2). The most significant of these concerns *H*(31), which is shifted to higher field. The loss of deshielding influences on passing from the dichloro to the carboxylic acid derivatives explains these shifts simply, as does the similar chemical shift effect observed for *H*(42). In the oxalate complex, the *H*(42) resonance is submerged by those arising from *H*(11) and *H*(12), which, as is the case with the malonate complex also, gives rise to 'deceptively simple' spectral patterns. However, all the coupling constant data which otherwise can be measured are exactly analogous to those seen for the dichloro complex. Therefore, it seems clear that both of the other complexes also have the β-*endo*-(*R,S*) geometry and that the same hydrophobic effects evident in the dichloro complex serve to stabilise the oxalate and malonate diastereoisomers as well. In the complex Δ,Λ-β-*endo*-(*R,S*)-[Co(*R,S*-picstien)(mal)]$^+$, the CH_2 group in the malonate ligand is observed as a simple AB pair (Fig. 2, Table IV); these protons lie in dissimilar chemical environments.

Subtle steric and hydrophobic effects, together with the possible involvement of solvation influences, have been shown to be important in the determination of the exact molecular geometry adopted of any particular complex containing the *meso* tetradentate reported here. Furthermore the relative energetic differences between several of them, particularly those containing *R,S*-picbn, appear to be slight. Thus, unlike analogous complexes containing certain chiral tetradentates [1, 4], mixtures of isomers can be obtained under certain circumstances. We also wish to note that this also is evidently the case with certain complexes of *R,S*-picstien. Depending on the nature of the ligand(s) completing the coordination sphere, various coordination geometries may be adopted. Preliminary experiments, which will form the basis of a future communication, indicate that both *exo* and *endo* complexes of β-*[Co(R,S*-picstien)-$(NO_2)_2]^+$ and β-[Co(*R,S*-picstien)(1,10-phenanthroline)]$^{3+}$ can be synthesised.

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