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Chiral Metal Complexes. 26*. Metal Complexes of the New Stereospecific Tetraamine Ligand 3*R*,4*R*- and 3*S*,4*S*-Diphenyl-1,6-di(2-pyridyl)-2,5-diazahexane

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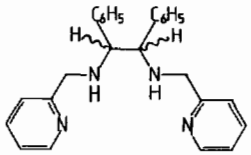
Abstract

The new N_4 tetradentate 2,5-diaza-3,4-diphenyl-1,6-di(2-pyridyl)hexane (picstien), based on stilbenediamine, has been synthesised in its racemic and enantiomeric forms. *R,R*-Picstien coordinates to Co(III) to give the Λ-β-$[Co(R,R\text{-picstien})Cl_2]^+$ cation stereospecifically. This cation may be isolated as its chloride or perchlorate monohydrate salt using several different synthetic procedures, each of which yields products in several crops with identical NMR and chiroptical properties. The chloride donors in this cation undergo substitution by nitrite or oxalate with full retention of its Λ-β topology. A Rh(III) analogue of the dichloro complex also was isolated, and this has the same stereochemistry. The *S,S* antipode of the ligand was used to generate corresponding enantiomeric chelate forms.

Introduction

The several recently reported reactions [1–4] involving substitution of the chloride ligands in α-$[Co(R\text{-picpn})Cl_2]^+$ have demonstrated a variety of isomeric forms for the respective products, thus revealing the optically active tetraamine ligand *R*-picpn# to be quite non-specific in its mode of coordination. By comparison *R,R*-picchxn, a more rigid analogue derived from 1*R*,2*R*-diaminocyclohexane, has demonstrated stereospecific Λ-β coordination to Co(III) in each of the several complexes that have been characterised [5–8]. This stereospecific function has been used to successfully control asymmetric coordination [5, 6] and synthetic reactions of amino acids on this moiety [7, 8].

As part of a systematic study of the coordination behaviour and uses of potentially stereospecific tetradentate ligands of this type, we decided to extend our investigations to the tetraamine analogue derived from 1,2-diphenyl-1,2-diaminoethane (stilbenediamine, stien). This was done in the belief that the two aromatic substituents should provide sufficient steric bulk as to enforce stereospecificity upon coordination in any one enantiomeric form of the optically active ligand. This ligand, picstien (I), has been synthesised in its mesomeric (*R,S*) and two enantiomeric (*R,R* and *S,S*) forms. The coordination behaviour of the *R,S* form has been touched on recently [9]. In this communication we report the synthesis and characterisation of the *R,R* and *S,S* ligands and some of their complexes with cobalt(III).



I

Experimental

Microanalyses were carried out by AMDEL Laboratories, Melbourne. NMR spectra were recorded on a Varian XL-200 spectrometer and are reported in ppm relative to DSS, TMS or known solvent resonances used as internal standards. Circular dichroism (CD) spectra were recorded on a JASCO SP-500C Spectropolarimeter at ambient temperatures. Optical rotations were measured at the sodium-D line (589 nm) on a Perkin-Elmer 141 Polarimeter. Electronic spectra were recorded using a Varian Techtron 635 recording spectrophotometer.

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#picpn = 2,5-diaza-3-methyl-1,6-di(2-pyridyl)hexane; picchxn = *N,N'*-di(2-picolyl)-1,2-diaminocyclohexane; picbn = 2,5-diaza-3,4-dimethyl-1,6-di(2-pyridyl)hexane; picstien = 2,5-diaza-3,4-diphenyl-1,6-di(2-pyridyl)hexane; ox = the oxalate dianion.

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Synthesis of Stilbenediamine

rac-Stilbenediamine was prepared using a combination of published procedures [10, 11]. This involved the synthesis of hydrobenzamide from benzaldehyde in 65.6% yield and its progressive conversion to amarine (56.3% yield), isomarine (88.5% yield), *rac*-*N*-acetyl-*N'*-benzoylstilbenediamine (quantitative) and then the hydrobromide salt of *rac*-stilbenediamine (40.0% yield).

This salt (150.0 g, 0.40 mol) was dissolved in water (600 cm^3), and the solution filtered and made basic using 10 M NaOH while keeping the temperature below 20 °C. The mixture was allowed to stand in an icebath for *ca.* 1 h. The white crystals of *rac*-stien which had formed were collected at the pump, washed with a minimum of cold water and air dried (yield 75.6 g). The product was recrystallised from 60/90 petroleum ether to yield pale straw-yellow needles. Yield: 65.3 g (76.9%). Melting point (m.p.) 80–81 °C (lit. 80–82 °C [10, 11]).

Resolution of Stilbenediamine

rac-Stilbenediamine was resolved using a method adapted from that of Hawn *et al.*, [11].

H_2[S,S-Stilbenediamine][R,R,-tartrate]

To a solution of *rac*-stilbenediamine (51.0 g, 0.24 mol) in hot 95% ethanol (410 cm^3) was added $(+)_{589}$-*R,R*-tartaric acid (36.0 g, 0.24 mol) in hot absolute ethanol (250 cm^3). After 15 min the fine white crystals which had formed were filtered off, washed with cold absolute ethanol and air dried. The product was recrystallised from a water/ethanol system to constant rotation. Yield: 27.7 g. $[\alpha]_{589}$ – 11.0° (1% *w/v* in water at 20 °C).

H_2[R,R-Stilbenediamine][S,S-tartrate]

The supernatant and washings from the isolation of the *S,S-R,R* salt were combined and the solvent removed. The resulting white solid was dissolved in water (400 cm^3) and the solution neutralised with 2 M NaOH while keeping the temperature below 20 °C. The yellow oil which formed was extracted into 3 × 300 cm^3 portions of diethyl ether, the extracts dried over anhydrous sodium sulphate and the solvent removed. The resulting white solid (26.7 g) was dissolved in hot ethanol (220 cm^3) then $(-)_{589}$-*S,S*-tartaric acid (18.4 g, 0.12 mol) in hot ethanol (130 cm^3) was added. The fine white crystals that formed were collected and recrystallised from aqueous ethanol until constant optical rotation was achieved. Yield 35.7 g. $[\alpha]_{589}$ + 11.0° (1% *w/v* aqueous solution at 20 °C).

The 1:1 stoichiometry of both salts was confirmed by NMR measurements.

S,S-Stilbenediamine

A sample (26.0 g) of the *S,S-R,R* salt isolated above was dissolved in water (260 cm^3) and the solution neutralised by addition of KOH (10.4 g) in water (100 cm^3) while maintaining a temperature below 20 °C. The yellow oil which formed was extracted into diethyl ether, the extract dried over anhydrous sodium sulphate and the solvent removed. The white solid which resulted was recrystallised from 60/90 petroleum ether (250 cm^3) to yield long pale yellow needles which were collected at the pump (yield 11.1 g). The combined supernatant and washings were reduced to 50 cm^3 on a steambath, and a further crop of crystals was obtained on cooling (yield 1.5 g). Both crops had identical optical rotation. Yield: 49.4% based on available *S,S* enantiomer. $[\alpha]_{589}$ – 106.0° (lit. –108° [11]; 1% *w/v* in methanol at 20 °C).

R,R-Stilbenediamine

This enantiomer was obtained using a method similar to that of the *S,S* form. $[\alpha]_{589}$ + 106.0°.

The total yield of the two optically resolved diamines is approximately 1.5% based on the original benzaldehyde starting material.

Synthesis of R,R- or S,S-Picstien

These ligands were isolated as their hydrochloride salts after initial synthesis and subsequent hydrogenation of their diimine homologues (designated as picstiendii).

R,R- or S,S-Picstiendii

A solution of *R,R*-stilbenediamine (6.0 g, 28.3 mmol) in diethyl ether (200 cm^3) was added dropwise under a positive nitrogen pressure to a solution of freshly distilled pyridine-2-carboxaldehyde (6.13 g, 57.2 mmol) in diethyl ether (50 cm^3) over a period of 1 h. The temperature was maintained below 5 °C during the addition. The solvent then was removed under reduced pressure to leave a yellow oil and some droplets of water. The sides of the reaction vessel were washed down with a small amount of diethyl ether, the nitrogen flow was stopped and the flask sealed and allowed to stand for 12 h. The pale yellow needles of *R,R*-picstiendii which had formed were filtered off, washed with 2 × 5 cm^3 portions of diethyl ether and air dried. Yield: 8.68 g (78.5%); m.p. 100–101 °C. *Anal.* Found: C, 79.65; H, 5.64; N, 14.88. Calc. for $C_{26}H_{22}N_4$: C, 79.97; H, 5.68; N, 14.35%.

A similar yield was obtained using benzene as the reaction solvent, and both methods are equally applicable to the synthesis of either enantiomer.

R,R- or S,S-Picstien·4HCl·1.5H_2O

To a sample of *S,S*-picstiendii (2.48 g, 6.35 mmol) dissolved in glacial acetic acid (25 cm^3) was added dropwise a solution of dimethylaminoborane (Fluka, 1.4 g) in glacial acetic acid (25 cm^3), the temperature

being maintained below 20 °C. The reaction mixture was stirred at room temperature for 3 h, then water (150 cm^3) was added, thus generating an emulsion. This mixture was neutralised using 10 M NaOH while again maintaining the temperature below 20 °C. A yellow oil separated, which was extracted into 3×50 cm^3 portions of chloroform. The extracts were combined and to them was added slowly 0.6 M HCl (150 cm^3), causing methylamine to be liberated. The mixture was shaken vigorously and the aqueous phase isolated. This was washed with 3×50 cm^3 portions of chloroform before being evaporated under reduced pressure at 25 °C. When the total volume had reduced to *ca.* 20 cm^3 absolute ethanol (100 cm^3) was added and the remainder of the water removed as an azeotrope. When a white solid had begun to form a further 100 cm^3 of ethanol was added and the mixture left to stand for 12 h. This white solid was collected at the pump, washed with ethanol and acetone and air dried. This first less-soluble product proved to be the triamine by-product, 1,4-diaza-2*S*,3*S*-diphenyl-5-(2-pyridyl)-pentane trihydrochloride monohydrate, a potential tridentate ligand. Yield: 0.31 g; m.p. 222–223 °C (decomp.). *Anal.* Found: C, 55.42; H, 5.77; N, 9.49. Calc. for $C_{20}H_{26}N_3Cl_3O$: C, 55.76; H, 6.08; N, 9.76%.

The filtrate and washings were taken to dryness under reduced pressure at 25 °C. The resulting off-white tetraamine solid was broken up in acetone, filtered off, washed with acetone (at this stage it is quite hygroscopic), and was then dried *in vacuo*. Yield: 2.19 g (61%); m.p. 217–218 °C (decomp.). *Anal.* Found: C, 55.16; H, 6.02; N, 9.86; Cl, 23.6. Calc. for $C_{26}H_{33}N_4Cl_4O_{1.5}$: C, 55.04; H, 5.86; N, 9.87; Cl, 25.00%.

Synthesis of Picstien Metal Complexes

Although each of the following syntheses would be equally applicable to both the *R,R* or *S,S* ligand forms, details are given according to which enantiomer was used.

β-[Co(R,R- or S,S-picstien)Cl_2]X·nH_2O (X = Cl, n = 0; X = ClO_4, n = 1)

This complex cation was prepared by three different methods. In each case the complex initially was precipitated as its chloride salt from the reaction mixture. The mother liquor was then treated with perchloric acid which precipitated the perchlorate salt. Using the three methods all crops of the corresponding salts gave identical NMR spectra and had the same chiroptical properties. The anhydrous nature of the chloride salt was confirmed by thermogravimetric analysis.

Method 1. To a stirred solution of *R,R*-picstien·4HCl·1.5H_2O (1.235 g, 2.18 mmol) dissolved in 95% ethanol (20 cm^3) was added $CoCl_2 \cdot 6H_2O$ (0.519 g, 2.18 mmol) in 95% ethanol (20 cm^3). This dark blue–purple solution was acidified by the dropwise addition of 10 M HCl (3.0 cm^3). Hydrogen peroxide (30% *w/v*, *ca.* 2 cm^3) was then added dropwise until the solution turned to a deep red–purple. The mixture was stirred for a further 10 min after which time a lavender solid had begun to form, and then was allowed to stand for 1 h. The fine lavender crystals were collected at the pump, washed with a minimum amount of cold water and air dried (Yield: 0.470 g). The mother liquor was allowed to stand for 2 days, when a second crop was collected (0.026 g). Total yield of Λ-β-[Co(*R,R*-picstien)Cl_2]Cl: 0.496 g (43.4%). *Anal.* Found: C, 55.61; H, 4.68; N, 9.66. Calc. for $C_{26}H_{26}N_4Cl_3Co$: C, 55.78; H, 4.68; N, 10.01%.

Perchloric acid (2 cm^3) was added dropwise to the mother liquor and the purple solid, which began to form immediately, was collected after 2 h. Yield: 0.261 g. The mother liquor was left for 2 weeks then a further crop of fine purple crystals was collected (0.102 g). The total yield of Λ-β-[*R,R*-picstien)Cl_2]-$ClO_4 \cdot H_2O$ was 0.363 g (26.0%). *Anal.* Found: C, 48.38; H, 4.09; N, 8.46. Calc. for $C_{26}H_{28}N_4O_5Cl_3Co$: C, 48.65; H, 4.40; N, 8.73%.

Method 2. S,S-Picstien was synthesised *in situ* from stilbenediamine (2.0 g, 9.42 mmol) and pyridine-2-carboxaldehyde (2.04 g, 19.0 mmol), the resulting Schiff base being hydrogenated with dimethylaminoborane/acetic acid as described above. The crude ligand was extracted into diethyl ether, which then was taken to dryness under reduced pressure. The yellow oil which resulted was dissolved in 95% ethanol (25 cm^3), and to this solution was added $CoCl_2 \cdot 6H_2O$ (2.24 g, 9.42 mmol) dissolved in 95% ethanol (20 cm^3). To the resulting blue–green solution was added 10 M HCl (3.0 cm^3) followed by dropwise addition of hydrogen peroxide (30% *w/v*), and the chloride (1.10 g, 22.3%) and perchlorate (0.69 g, 11.4%) salts (Δ forms) were isolated as described above.

Method 3. A mixture of *R,R*-picstien·4HCl·1.5H_2O (0.20 g, 0.35 mmol) and *trans*-[Co(py)$_4Cl_2$]-Cl·6H_2O (0.215 g, 0.352 mmol) in 95% ethanol (20 cm^3) was stirred until dissolved. The clear olive green solution was left to stand, with the colour changing to a deep red–purple with pale lavender crystals forming during a period of 1 h. The mixture was cooled in an ice-bath, and the lavender crystals of Λ-β-[Co(*R,R*-picstien)Cl_2]Cl were collected at the pump, washed with a minimum amount of cold water and air dried. Yield: 0.075 g (40.5%). Perchloric acid (2 cm^3) was added dropwise to the mother liquor and the mixture left to stand for 12 h. The fine purple crystals of Λ-β-[Co(*R,R*-picstien)Cl_2]$ClO_4 \cdot H_2O$ which formed were collected at the pump, washed with water and air dried. Yield: 0.064 g (28.2%).

rac-β-[Co(picstien)Cl$_2$]X·nH$_2$O (X = Cl, n = 0; X = ClO$_4$, n = 1)

These pale purple compounds were prepared according to Method 2 above, only substituting *rac*-stilbenediamine as reactant.

X = Cl; yield: 21.4%. *Anal.* Found: C, 55.00; H, 4.96; N, 10.05; H$_2$O, 0.0. Calc. for $C_{26}H_{26}N_4Cl_3Co$: C, 55.78; H, 4.68; N, 10.01; H$_2$O, 0.0%.

X = ClO$_4$; yield: 20.3%. *Anal.* Found: C, 48.46; H, 4.40; N, 8.76; H$_2$O, 3.0. Calc. for $C_{26}H_{28}N_4Cl_3O_5Co$: C, 48.65; H, 4.40; N, 8.73; H$_2$O, 2.7%.

Δ-β-[Co(S,S-picstien)(ox)]ClO$_4$·H$_2$O

To a stirred solution of Δ-β-[Co(*S,S*-picstien)Cl$_2$]-Cl (0.20 g, 0.38 mmol) dissolved in DMSO (2.0 cm^3) was added water (5.0 cm^3) and sodium oxalate (0.051 g, 0.38 mmol), the latter having been dissolved in a minimum amount of DMSO. Over 15 min the deep purple solution turned to a bright orange–pink. Saturated sodium perchlorate solution (2.0 cm^3) then was added and after 10 min the solution turned opalescent. The mixture was covered and allowed to stand for 12 h. The resulting salmon pink crystals were filtered off, washed with 2 × 1 cm^3 portions of water, 1 cm^3 of absolute ethanol and air dried. Yield: 0.19 g (75.9%). *Anal.* Found: C, 51.00; H, 4.02; N, 8.67. Calc. for $C_{28}H_{28}N_4O_9Cl_1Co$: C, 51.03; H, 4.28; N, 8.50%.

Δ-β-[Co(S,S-picstien)(NO$_2$)$_2$]ClO$_4$·H$_2$O

To a solution of Δ-β-[Co(*S,S*-picstien)Cl$_2$]ClO$_4$·H$_2$O (0.10 g, 0.156 mmol) dissolved in DMSO (1.0 cm^3) was added water (5.0 cm^3) and sodium nitrite (0.022 g, 0.31 mmol). Ethanol (10 cm^3) then was added and the mixture slowly warmed until the colour of the suspension turned to a definite yellow–orange. The mixture then was left to digest for 12 h, after which time the yellow–orange solid was filtered off, washed with minimum amounts of cold water and ethanol and air dried. Yield: 0.043 g (41.6%). *Anal.* Found: C, 47.53; H, 3.99; N, 12.24. Calc. for $C_{26}H_{28}N_6O_9Cl_1Co$: C, 47.10; H, 4.26; N, 12.68%.

Λ-β-[Co(R,R-picstien)(NO$_2$)$_2$]Cl·2H$_2$O

To a stirred solution of Λ-β-[Co(*R,R*-picstien)Cl$_2$]-Cl (0.10 g, 0.19 mmol) dissolved in DMSO (1 cm^3) was added water (10 cm^3) and sodium nitrite (0.026 g, 0.38 mmol). The purple solution soon turned orange accompanied by precipitation of a fine yellow solid. The mixture was left to stand for 12 h, then the solid product was filtered off, washed with a minimum amount of cold water and air dried. Yield: 0.072 g (61.1%). *Anal.* Found: C, 50.20; H, 4.47; N, 13.94. Calc. for $C_{26}H_{30}N_6O_6Cl_1Co$: C, 50.61; H, 4.90; N, 13.63%.

Λ-β-[Rh(R,R-picstien)Cl$_2$]ClO$_4$·H$_2$O

To a stirred solution of *R,R*-picstien·4HCl·1.5H$_2$O (0.10 g, 0.176 mmol) dissolved in water (10 cm^3) was added RhCl$_3$·3H$_2$O (0.046 g, 0.176 mmol) dissolved in water (2 cm^3). A pale pink solid formed almost immediately which redissolved with gentle heating to give a clear yellow solution. Saturated sodium perchlorate solution was added dropwise until a solid just began to form. The resulting mixture was allowed to cool slowly to room temperature. The canary yellow solid which had formed was filtered off, washed with a minimum amount of cold water and air dried. Yield: 0.046 g (38.1%). *Anal.* Found: C, 45.20; H, 4.04; N, 7.71. Calc. for $C_{26}H_{28}N_4O_5Cl_3Rh$: C, 45.53; H, 4.12; N, 8.17%.

Results and Discussion

Several points were noted during the synthesis of the ligands that are worthy of comment. The Schiff base *meso*-picstiendii could be prepared from *meso*-stilbenediamine using conventional procedures [9]. However, the corresponding products from the optically active diamines were much more difficult to prepare. It appears that the optically active Schiff bases, once formed, are very sensitive to heat, light, choice of solvent and the presence of oxygen. Even when prepared under nitrogen atmosphere and the water by-product removed it was found that if the pale yellow needles were not collected immediately and reduced to the tetraamine they decomposed relatively quickly to a green oil.

Again, hydrogenation of the *meso* diimine using palladium on charcoal catalyst gave the corresponding tetraamine in relatively high yield [9]. By comparison, hydrogenation of the chiral forms by this method proved to be impossible. The successful method of using dimethylaminoborane was selected since this is known to give higher yields at low temperatures [12]. The ligands also proved to be sensitive to heat, oxygen and high pH, which was restrictive to their use in the formation of their Co(III) complexes. Conventional methods involving aerial oxidation or high temperature often resulted in a characteristic odour of benzaldehyde from the hydrolysed ligand. Details of the ^{1}H NMR spectrum derived from either isomeric form of picstien are given in Table I.

A list of electronic absorption and chiroptical data for the complexes is given in Table II, and Fig. 1 shows a comparison of the CD spectrum of the Λ-β-[Co(*R,R*-picstien)Cl$_2$]$^+$ cation with those of previously reported analogues. Here it may be seen that the CD spectrum of Λ-β-[Co(*R,R*-picstien)Cl$_2$]$^+$ is dominated by three large positive peaks in the visible region. These spectral features are almost identical to those of Λ-β-[Co(*R,R*-picchxn)Cl$_2$]$^+$ [5, 6] and almost enantiomeric to those of Δ-β-[Co(*S,S*-picbn)Cl$_2$]$^+$ [13]. These data provide strong evidence that, as expected, the *R,R* form of picstien

TABLE I. ^{1}H and ^{13}C NMR Data for Picstien and its Metal Complexes[a]

δ or *J*	A	B	C	D	E
H(11)	8.60(d)	9.33(d)	9.02(d)	8.40(d)	9.48(d)
H(12)	7.88(t)	7.88(t)	7.90(t)	7.16(t)	7.80(t)
H(13)	8.41(t)	8.25(t)	8.29(t)	8.28(t)	8.24(t)
H(14)	7.86(d)	7.82(d)[b]	7.79(d)[b]	7.90(d)[b]	7.90(d)
H(21)		7.13(d)	7.24(d)	[c]	7.58(d)
H(22)		[c]	7.58(t)	7.61(t)	7.70(t)
H(23)		8.10(t)	8.20(t)	8.24(t)	8.20(t)
H(24)		7.84(d)[b]	7.82(d)[b]	7.86(d)[b]	7.90(d)
H(phenyl)[d]	7.1–7.3	7.2–7.4	7.2–7.3	7.3–7.4	7.2–7.4
		7.5–7.6	7.4–7.5	7.5–7.6	
			7.7–7.8		
H(1)	4.56(s)	5.27(t)	5.00(t)	4.92(t)	5.38(t)
H(2)		4.29(dd)	4.35(dd)	4.39(t)	4.28(t)
H(16a)	4.25(d)[b]	3.68(dd)	4.00(dd)	3.97(dd)	3.92(dd)
H(16b)	4.41(d)[b]	4.59(dd)	4.27(dd)	4.62(dd)	4.66(dd)
H(26a)		4.09(d)	4.02(d)	4.04(d)	4.02(d)
H(26b)		4.91(dd)	4.43(dd)	4.46(dd)	5.00(dd)
H(N1)	[e]	8.20(bm)	8.18(bm)	8.00(dd)	8.44(b)
H(N2)		7.70(bm)	6.80(bm)	7.74(bm)	[c]
$\lvert J_{16a,\,16b}\rvert$	16.0	15.9	15.2	16.0	16.4
$\lvert J_{26a,\,26b}\rvert$		17.0	16.5	16.8	15.8
$J_{1,\,2}$		11.9	12[f]	12.0	12.0
$J_{16a,\,N1}$		4.9	5[f]	4.8	4.5
$J_{16b,\,N1}$		9.3	9.2	9.8	9.0
$J_{1,\,N1}$		11.5	12[f]	10.5	10.0
$J_{2,\,N2}$		9.1	6[f]	9.5	10.0
$J_{26a,\,N2}$		*ca.* 0	*ca.* 0	*ca.* 0	*ca.* 0
$J_{26b,\,N2}$		5.5	5.6	4.8	4.3

	B	C[g]	D
C(11)	152.23	151.95, 151.72	152.61
C(21)	151.56	151.47, 150.60	149.63
C(13)	140.44	141.02, 140.67[h]	141.26
C(23)	139.84	140.08, 140.67[h]	140.56
C(14)	125.87	126.24, 125.86	126.52
C(24)	124.94	125.41, 124.79	124.99
C(12)	123.81	124.17[h]	124.00
C(22)	122.84	123.30, 122.95	123.15
C(P11)	133.91	134.17. 134.01	133.60
C(P21)	132.22	132.44, 131.84	132.63
C(P12)			
C(P22)	129.31	129.35, 129.12	129.32
C(P13)	129.15	129.04, 128.96	128.97
C(P23)	128.95	128.89, 128.80	128.82
C(P14)	128.61	128.68, 128.54	128.68
C(P24)			
C(1)	75.06	74.89, 74.66	73.35
C(2)	70.56	69.89, 68.92	69.23
C(16)	59.60	56.72, 56.17	55.61
C(26)	54.30	54.37, 54.03	53.40
C(ox)[i]			166.74, 165.67

[a]Recorded in DMSO-d_6 except for the free ligand (D_2O); chemical shifts are reported ± 0.1 ppm (*H*) or ± 0.02 ppm (*C*) relative to TMS or DSS as internal standards at room temperature; A: L·4HCl, B: β-$[Co(L)Cl_2]^+$, C: β-$[Co(L)(NO_2)_2]^+$, D: β-$[Co(L)(ox)]^+$, E: β-$[Rh(L)Cl_2]^+$; L = *R,R*- or *S,S*-picstien; b = broad, s = singlet, d = doublet, t = triplet, m = multiplet. [b]We do not distinguish between these pairs of resonances. [c]Obscured by *H*-phenyl resonances. [d]Complex multiplets. [e]Exchanged. [f]Coupling constants are ± 1 Hz; all other coupling constants are ± 0.5 Hz. [g]DMSO-nitro adducts – see text. [h]Double integral peaks. [i]Oxalate carbon atoms.

coordinates to trivalent cobalt in an identical fashion to that of *R,R*-picchxn, which has demonstrated a stereospecific Λ-β bonding mode [5–8]. The absolute configuration of the Λ-β-[Rh(*R,R*-picstien)Cl_2]$^+$ cation is confirmed by virtue of the close correspondence of the ^{1}H NMR coupling constant data as compared with those of the analogous Co(III) complex (*vide infra*).

The *cis*-β topology of these picstien dichloro complexes is confirmed by their ^{1}H and ^{13}C NMR spectra, Table I. The atomic numbering schemes are shown in II and III. Figure 2 shows the proton NMR spectrum of the Co(III) complex cation. All resonances may be

TABLE II. Electronic and CD Spectral Data for Picstien Metal Complexes

Complex[a]	λ (nm)	$\epsilon \times 10^{-3}$ (dm^2 mol^{-1})	Δε (dm^2 mol^{-1})
Λ-β-[Co(*R,R*-L)Cl_2]$^+$	390		+4.62
	425		+4.85
	510		+3.82
	540	1.67	
	597		+7.31
Λ-β-[Co(*R,R*-L)$(NO_2)_2$]$^+$	410	4.72	
	457		−18.70
	560		−0.75
Λ-β-[Co(*S,S*-L)(ox)]$^+$	362		+9.19
	410	4.68	
	494		−19.78
	500	2.70	
	565		+0.20
	620		−0.40
Λ-β-[Rh(*R,R*-L)Cl_2]$^+$	302		+6.97
	350	4.11	−7.80
	405		+7.60

[a]L = picstien.

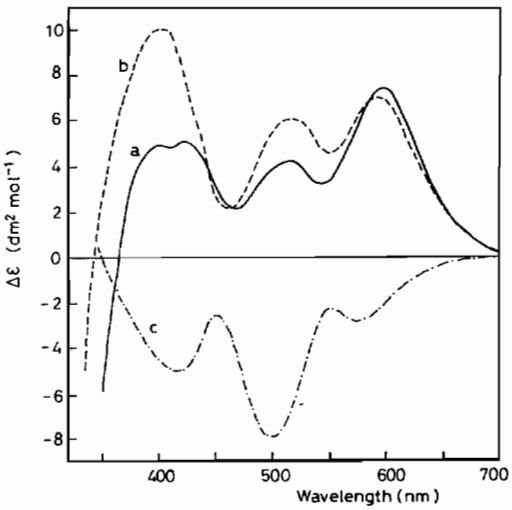


Fig. 1. A comparison of the CD spectrum of (a) Λ-β-[Co(*R,R*-picstien)Cl_2]$^+$ in DMSO, with those of (b) Λ-β-[Co(*R,R*-picchxn)Cl_2]$^+$ in conc. HCl [6], and with (c) Δ-β-[Co(*S,S*-picbn)Cl_2]$^+$ in methanol [13].

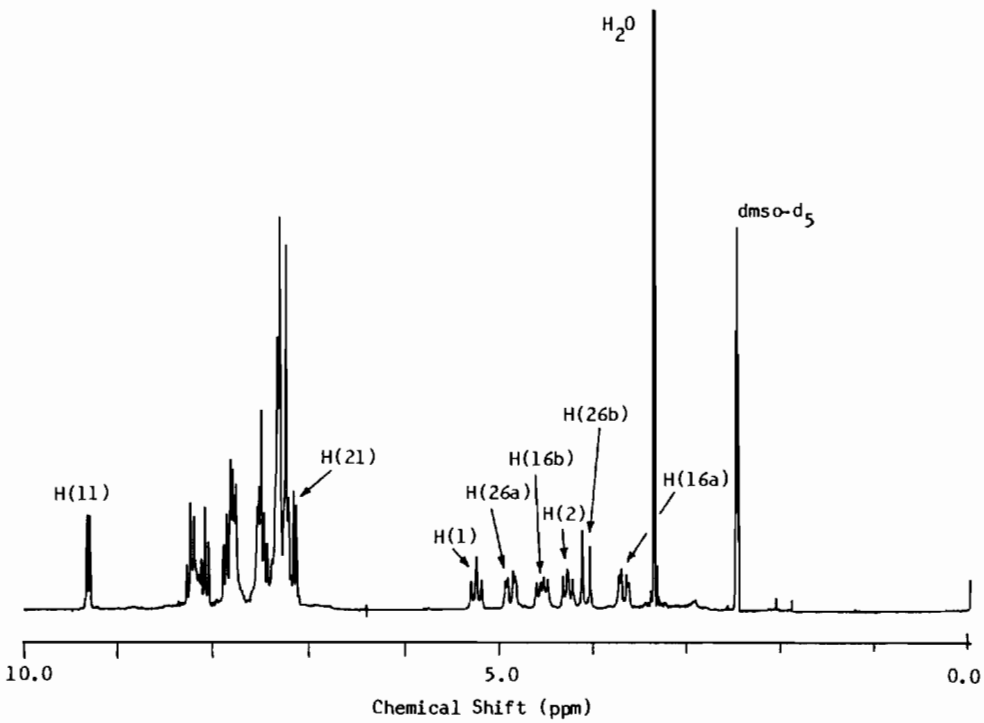
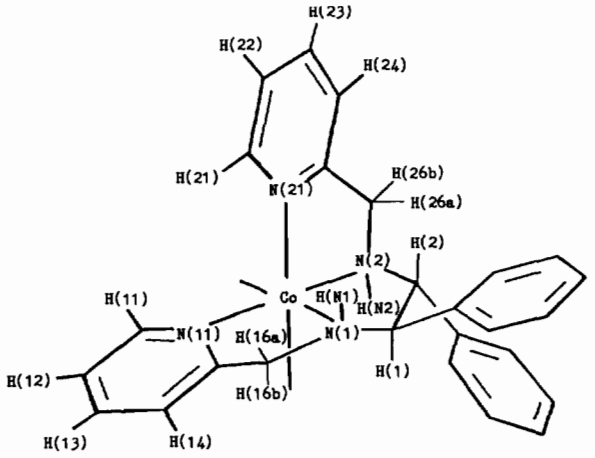
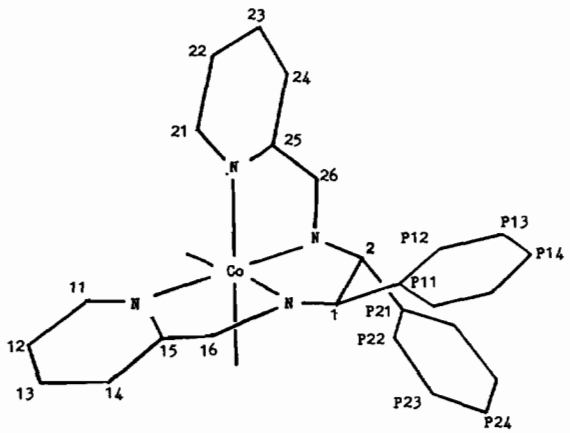


Fig. 2. 200 MHz ^{1}H NMR spectrum of Λ-β-[Co(*R,R*-picstien)Cl_2]Cl in DMSO-d_6.

uniquely assigned via spin-decoupling experiments, and coupling constant data give values which establish the coordination of the complexes unambiguously. Both internal nitrogen atoms have an *S* absolute configuration in the Λ diastereoisomer. In the ^{13}C NMR spectra all resonances are doubled, as expected for β topology. However, some of the phenyl carbon resonances do overlap.



II



III

The most striking feature of the ^{1}H NMR spectrum is the low-field doublet resonance attributable to only one of the α-pyridyl protons of the ligand (H(11) of Fig. 3). The suggested asymmetry of the cation's stereochemistry is confirmed by the observation of independent multiplet resonances in the 3.5–5.5 ppm range for each of the ligand's six methine or methylene protons. This asymmetry is evident also in the cation's ^{13}C spectrum (Table I), where resonances attributable to each individual carbon atom in the tetraamine backbone may be identified. This method of structural analysis has been used previously in identifying the complex isomers derived from picpn [4] and picen [14].

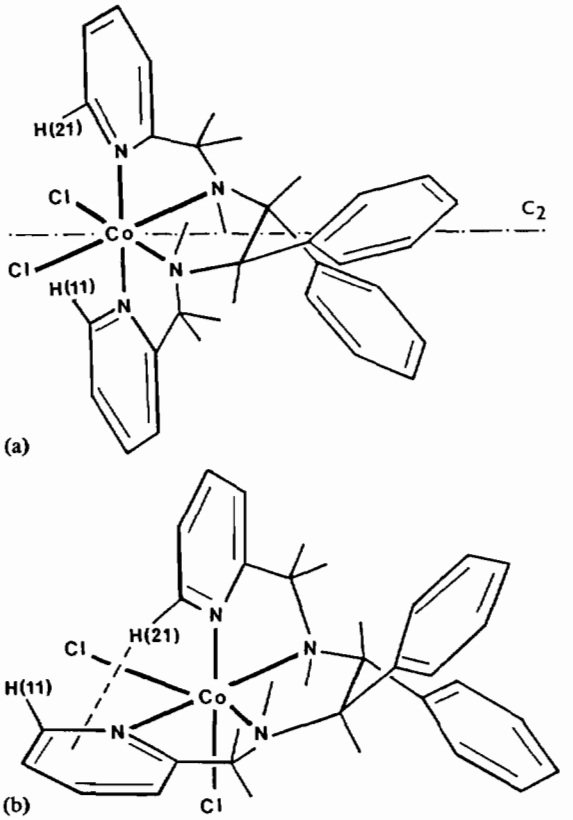


Fig. 3. Representation of the different symmetries and pyridyl proton environments in (a) the Δ-α isomer and (b) the Λ-β isomer of the $[Co(R,R\text{-picstien})Cl_2]^+$ molecular cation.

On substitution of the chloride donors in the dichloro cations by other ligands (ox or nitrite) this asymmetry in the ^{1}H and ^{13}C NMR spectra is retained. Once again the proton NMR spectra of each product shows an isolated low-field doublet resonance attributable to a single H(11) pyridyl proton of a β isomer. It should be noted that substitution of coordinated nitrite by solvent DMSO is observed after a short time. Accordingly, the ^{13}C NMR spectrum (Table I) shows a doubling of the number of resonances observed. The ratio of the two isomers present on prolonged standing is unity, and thus it may be concluded that these are simply the two possible DMSO-nitro β diastereoisomers.

The important fact to be noted here is that *R,R*-picstien or its enantiomer does coordinate stereospecifically to cobalt(III). The preferred topology remains unchanged during substitution at the remaining coordination sites, at least during the preparation of the complexes reported here. This no doubt is due to the steric requirements of the phenyl substituents in the tetradentate, and is completely consistent with our previously reported observations concerning complexes of this type [9, and refs. therein].

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