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Chiral metal complexes
34*. Stereospecific *cis*-α coordination to cobalt(III) by the new tetradentate ligand *N*,*N*′-dimethyl-*N*,*N*′-di(2-picolyl)-1,2-diaminocyclohexane

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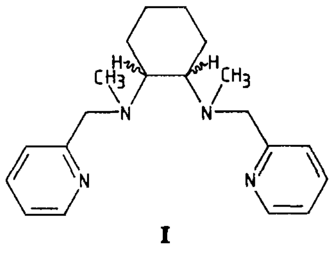
Abstract

The new tetradentate *N*,*N*′-dimethyl-*N*,*N*′-di(2-picolyl)-1,2-diaminocyclohexane (picchxnMe$_2$) has been synthesised, in both optically active enantiomeric forms, by *N*,*N*′-dimethylation of the previously described stereospecific *cis*-β tetradentate *N*,*N*′-di(2-picolyl)-1,2-diaminocyclohexane (picchxn). The ligand has been shown to adopt stereospecific *cis*-α topology when binding to Co(III). *R*,*R*-PicchxnMe$_2$ coordinates to Co(III) to give the Δ-α-[Co(*R*,*R*-picchxnMe$_2$)Cl$_2$]$^+$ cation stereospecifically. The nature of the intramolecular interactions which induce the change of coordination mode are commented on. The chloride donors in this cation may undergo substitution by nitrite, oxalate or aminoacidate ligands with full retention of Δ-α topology as demonstrated by the chiroptical properties of the products. The *S*,*S* antipode of the ligand was used to generate the corresponding enantiomeric chelate forms including the alanine complex Λ-α-[Co(*S*,*S*-picchxnMe$_2$) (*R*-ala)](ClO$_4$)$_2$ for which the crystal structure has been determined. Crystal data: $C_{23}H_{34}N_5O_{10}Cl_2Co$, $M_r = 670.4$, orthorhombic, space group $P2_12_12_1$, with $a = 10.525(5)$, $b = 14.697(12)$, $c = 18.594(8)$ Å and $Z = 4$. The structure was refined by least-squares methods to $R = 0.047$ for 2270 non-zero reflexions and confirms unambiguously the absolute configuration at the metal centre. The tetradentate ligand completes an octahedral coordination sphere on the cobalt ion, with the central chelate ring adopting a δ conformation with a N–C–C–N torsion angle of 50.9(5)°. The average Co–N distance was found to be 1.97(1) Å and the average N–Co–N bite angle is 84.0(3)°.

Introduction

There have been numerous publications on the stereochemistries of Co(III) complexes of N$_4$ tetradentates based on the ligand picen† [1]. Three of these ligands (in their optically active forms) *R*,*R*-picbn [2], *R*,*R*-picchxn [3] and *R*,*R*-picstien [4] adopt the *cis*-Λ-β configuration stereospecifically on coordination to cobalt(III) ions, whereas both *S*,*S*-picchxn and *S*,*S*-picbn adopt *cis*-Δ-α topology on coordination to chromium(III) [5, 6]. The less constrained *R*-picpn ligand has been shown to be non-specific on coordination to cobalt(III) [7–9] and chromium(III) [10]. Methyl substitution on the methylene groups adjacent to the pyridine rings of picen produces the optically active *S*,*S*-pean [11, 12] tetradentate. On coordination to cobalt(III) this ligand has been shown to be non-specific when isolated as the dichloro complex but adopts a Λ-α topology when the chloride donors are replaced by oxalate.



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As yet there have been no reports on the effect of *N*,*N*′-dialkylation on any of these tetradentates.

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*Part 33 is ref. 33.

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†Picen is 2,5-diaza-1,6-di(2′-pyridyl)hexane; picbn is 2,5-diaza-3,4-dimethyl-1,6-di(2′-pyridyl)hexane; picchxn is *N*,*N*′-di(2-picolyl)-1,2-diaminocylohexane; picstien is 3,4-diphenyl-1,6-di(2′-pyridyl)-2,5-diazahexane; picchxnMe$_2$ is *N*,*N*′-dimethyl-*N*,*N*′-di(2-picolyl)-1,2-diaminocyclohexane.

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Molecular models suggest that if the protons on the secondary N atoms were to be replaced by bulky methyl groups then an α topology would be favoured. Furthermore, if this alkylation were on a tetradentate containing a chiral diamine bridge then the ligand also might be expected to be enantioselective. We have therefore carried out the syntheses of the enantiomeric forms of picchxnMe$_2$ (I), and representative cobalt(III) complexes, as an initial investigation into the stereochemistries adopted by such ligands.

Experimental

Microanalyses were carried out by Dr. H.-P. Pham in the microanalytical laboratory of the University of New South Wales, Sydney. Proton 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 calibrants. Circular dichroism (CD) spectra were recorded on a JASCO SP-500C spectropolarimeter at ambient temperatures. Electronic spectra were recorded using a Shimadzu UV-160 recording spectrophotometer. Conductivity measurements were carried out using a Philips PW9506 conductivity meter.

R,R-PicchxnMe$_2$·4HCl

R,R-Picchxn was prepared using published methods [3] and was isolated as a low melting, colourless solid. This solid (8.41 g, 0.028 mol) was dissolved in acetonitrile (100 cm^3), 37% (wt./vol.) aqueous formaldehyde (23 cm^3) was added, and the reaction solution stirred for 0.25 h. Sodium cyanoborohydride (Aldrich, 5.7 g, 0.09 mol) dissolved in acetonitrile (20 cm^3) was carefully added to the mixture with vigorous stirring, which was continued for 1.5 h. The pH was maintained at 7.0 by the dropwise addition of glacial acetic acid.

The solvent was removed on a rotary evaporator at 50 °C, aqueous 2 M potassium hydroxide (230 cm^3) was added and the residue extracted with diethyl ether (3×50 cm^3). The ether extracts were washed with water (2×25 cm^3) then extracted with 1 M hydrochloric acid (3×50 cm^3). The combined acidic extracts were washed with dichloromethane (50 cm^3) and most of the water removed under reduced pressure at 65 °C. Any remaining water was removed as an azeotrope with ethanol. The white hygroscopic solid which remained was triturated with acetone (100 cm^3), collected at the pump, washed well with acetone and dried *in vacuo* over silica gel. Yield: 11.64 g (87%). After absorption of atmospheric moisture the hygroscopic product analysed as a tetrahydrate. However, the compound was stored and used in its anhydrous form.

Anal. Calc. for $C_{20}H_{40}N_4O_4Cl_4$: C, 44.29; H, 7.43; N, 10.33. Found: C, 43.56; H, 6.78; N, 10.61%.

Δ-α-[Co(R,R-picchxnMe$_2$)Cl$_2$]ClO$_4$

A sample of the anhydrous tetrahydrochloride salt (4.70 g, 0.01 mol) was dissolved in absolute ethanol (400 cm^3), concentrated hydrochloric acid was added (2 cm^3), and to the stirred solution was added slowly a solution of $CoCl_2 \cdot 6H_2O$ (2.38 g, 0.01 mol) in absolute ethanol (50 cm^3). The rate of addition was maintained so as to allow any solid produced to dissolve to give a clear blue solution before further addition. When this process was complete the mixture was stirred for 0.25 h, 30% (wt./vol.) hydrogen peroxide (2 cm^3) was added, and stirring then was continued for a further 0.5 h. A solution containing hydrated $LiClO_4$ (1 g) in absolute ethanol (50 cm^3) was added, and the mixture stirred for 0.25 h before cooling to 0 °C. The resulting grey–blue fine crystalline product was collected at the pump, washed with absolute ethanol (2×10 cm^3), then diethyl ether (2×20 cm^3) and air dried.

Yield: 5.15 g. *Anal.* Calc. for $C_{20}H_{28}N_4O_4Cl_3Co$: C, 43.38; H, 5.10; N, 10.12. Found: C, 43.12; H, 5.22; N, 9.82%.

Δ-α-[Co(R,R-picchxnMe$_2$)(R-ala)](ClO$_4$)$_2$·H$_2$O

A suspension of Δ-α-[Co(*R,R*-picchxnMe$_2$)Cl$_2$]-ClO$_4$ (1.106 g, 2 mmol) in water (100 cm^3) was heated on a steam bath until a clear mauve solution was produced. *R*-Alanine (0.22 g, 2.5 mmol) dissolved in water (20 cm^3) was added and the solution heated further until the colour had changed to orange. Solid hydrated $LiClO_4$ (0.2 g) was added and the solution filtered. The filtrate then was reduced slowly on a steam bath to *c.* 10 cm^3, and on cooling to room temperature the liquid became viscous. Ethanol (3 cm^3) was added, whereby orange crystals started to form, and the mixture was stored at 0 °C for 12 h. The resulting fine, orange crystalline product was collected at the pump, washed with a few drops of ice-cold water, then absolute ethanol and air dried.

Yield: 1.0 g (73%) *Anal.* Calc. for $C_{23}H_{36}N_5O_{11}Cl_2Co$: C, 40.13; H, 5.27; N, 10.17. Found: C, 39.91; H, 5.16; N, 9.87%.

Δ-α-[Co(R,R-picchxnMe$_2$)(S-ala)](ClO$_4$)$_2$ and Λ-α-[Co(S,S-picchxnMe$_2$)(R-ala)](ClO$_4$)$_2$

These complexes were prepared by a method similar to that used for the *R*-alanine analogue described above. Upon reduction in volume to *c.* 20 cm^3 on a steam bath, fine orange needles of the *R,R*-picchxnMe$_2$ complex formed in the hot solution.

The mixture was left to cool to room temperature, then at 0 °C for 2 days. The orange product was collected at the pump, washed with a few drops of ice-cold water, then absolute ethanol, and was air dried. Yield: 1.04 g (77.6%). The antipode derived from *S*,*S*-picchxnMe$_2$ and *R*-alanine was prepared by a similar means, the orange needle crystals being used for the crystal structure determination reported below.

Δ-α-$[Co(R,R\text{-}picchxnMe_2)(NO_2)_2]ClO_4 \cdot H_2O$

A suspension of Δ-α-[Co(*R*,*R*-picchxnMe$_2$)Cl$_2$]ClO$_4$ (0.30 g, 0.54 mmol) in water (40 cm^3) was heated on a steam bath until all the complex dissolved to leave a clear mauve solution. To this solution was added sodium nitrite (0.1 g, 1.45 mmol) dissolved in water (5 cm^3) and the mixture heated until a clear orange solution resulted. Solid hydrated LiClO$_4$ (0.2 g) was added and the solution filtered. The filtrate was evaporated slowly on a steam bath to a volume of *c.* 15 cm^3, then left to stand for 10 days. The resulting deep orange plates, up to 3 mm in dimension, were collected at the pump, washed with a few drops of ice-cold water and air dried.

Yield: 0.22 g (69%). *Anal.* Calc. for $C_{20}H_{30}N_6O_9ClCo$: C, 40.52; H, 5.10; N, 14.17. Found: C, 40.77; H, 5.05; N, 13.74%.

$[\Delta$-α-$\{Co(R,R\text{-}picchxnMe_2)\}_2ox](ClO_4)_4 \cdot 3.5H_2O$

To a warm solution of Δ-α-[Co(*R*,*R*-picchxnMe$_2$)Cl$_2$]ClO$_4$ (0.30 g, 0.54 mmol) in water (40 cm^3) was added sodium oxalate (0.1 g, 0.75 mmol) dissolved in water (5 cm^3) and the reaction solution warmed until a clear orange–red colour resulted. Solid hydrated LiClO$_4$ (0.2 g) was added and the solution filtered and evaporated slowly on a steam-bath to a volume of *c.* 25 cm^3. The mixture was then left to stand undisturbed for 10 days. The resulting large, deep orange crystals were collected at the pump, washed with a few drops of ice-cold water and air dried.

Yield: 0.23 g (64%). *Anal.* Calc. for $C_{42}H_{63}N_8O_{23.5}Cl_4Co_2$: C, 38.34; H, 4.83; N, 8.52. Found: C, 38.29; H, 4.49; N, 8.51%.

Crystal and molecular structure of Λ-α-$[Co(S,S\text{-}picchxnMe_2)(R\text{-}ala)](ClO_4)_2$

Crystal data

$C_{23}H_{34}N_5O_{10}Cl_2Co$, $M_r = 670.4$, orthorhombic, $a = 10.525(5)$, $b = 14.697(12)$, $c = 18.594(8)$ Å, $U = 2876.8$ Å^3, $Z = 4$ $D_c = 1.548$ g cm^{-3}, $F(000) = 1392$, μ(Mo Kα) = 8.71 cm^{-1}, space group $P2_12_12_1$ (No. 19).

Unit cell parameters initially were determined from precession photographs using Mo Kα radiation. Accurate cell parameters were obtained from a least-squares fit to diffractometer data. The crystal used for data collection had dimensions 0.64 × 0.72 × 0.76 mm. Intensities were collected at -130 °C on a Nicolet XRD-P3 four-circle diffractometer [13] in the range $5 < 2\theta < 50°$ using Mo Kα radiation. Reflexions were corrected for Lorentz, polarisation and absorption effects [13]. With respect to the latter, the maximum and minimum transmission factors were 0.775 and 0.687, respectively. Of the 2891 reflexions measured 2270 gave counts for which $I > 3\sigma(I)$, and these were used for the structure determination.

Structure determination

The structure was solved by the heavy atom method and was refined by full-matrix least-squares calculations in which the function minimised was $\Sigma w\Delta^2$, the weights used being based on counting statistics. Difference maps were used to locate the approximate positions of the hydrogen atoms, which were optimised assuming C–H and N–H to be 1.0 Å and O–H 0.9 Å, and the appropriate geometries of the atoms to which they were bonded. The refinement was terminated when the maximum change in any parameter was <0.1 σ. Final values for R and R' $[=(\Sigma w\Delta^2/\Sigma w|F_o|^2)^{1/2}]$ were 0.047 and 0.032, respectively. A final difference map showed no density $>|0.5|$ e Å^{-3}. All calculations were carried out on a FACOM 340S computer using programs written by F.S.S. Neutral atom scattering factors, corrected for anomalous dispersion, were taken from ref. 14.

The final non-hydrogen atomic parameters are given in Table 1.

Results and discussion

Several methods for the methylation of the secondary amine atoms of the picchxn tetradentate were investigated. The addition of methyl iodide under a variety of conditions produced a mixture of products, which proved impossible to separate. Reaction of picchxn with formaldehyde/methanol and sodium borohydride, adapted from a literature procedure [15], formed an octahydrobenzimidazole derivative in essentially quantitative yield, which resulted from a single methylene group joining the two central tertiary nitrogen atoms. Adaption of the general method of Borch and Hassid [16] for the methylation of secondary amines using a large excess of formaldehyde and sodium cyanoborohydride in acetonitrile provided a facile method for the controlled *N*,*N*′-dimethylation of the linear tetradentate, with the relatively pure product being produced in high yield.

TABLE 1. Final atomic coordinates (fractional $\times 10^4$) for the non-hydrogen atoms of Λ-α-[Co(*S*,*S*-picchxnMe$_2$)(*R*-ala)](ClO$_4$)$_2$ with e.s.d.s in parentheses

	x	*y*	*z*
Co	540.1(10)	4305.3(7)	5147.6(5)
N(11)	−472(6)	4662(4)	4297(3)
N(21)	1487(6)	3933(4)	5994(3)
N(1)	−699(6)	5097(4)	5645(3)
N(2)	1716(5)	5357(4)	5173(3)
N(3)	1633(6)	3475(4)	4603(3)
O(31)	−585(5)	3312(3)	5212(3)
O(32)	−1079(5)	2019(3)	4652(2)
C(31)	−325(7)	2629(5)	4812(4)
C(32)	1038(7)	2558(5)	4551(4)
Me(3)	1181(7)	2135(5)	3812(4)
C(11)	−178(7)	4574(5)	3589(4)
C(12)	−1079(8)	4651(6)	3054(4)
C(13)	−2328(8)	4831(6)	3244(4)
C(14)	−2649(8)	4957(6)	3961(4)
C(15)	−1683(8)	4868(5)	4466(4)
C(16)	−1937(8)	4963(5)	5270(4)
Me(1)	−953(7)	4839(5)	6421(4)
C(1)	−269(8)	6069(5)	5560(4)
C(2)	1151(8)	6077(5)	5660(4)
C(3)	1728(8)	7023(5)	5590(4)
C(4)	1110(9)	7662(6)	6130(5)
C(5)	−322(9)	7693(6)	5998(4)
C(6)	−922(8)	6769(5)	6048(4)
Me(2)	2013(7)	5743(6)	4442(4)
C(21)	1155(7)	3255(5)	6455(4)
C(22)	1899(8)	3064(5)	7063(4)
C(23)	2964(8)	3589(5)	7193(4)
C(24)	3302(7)	4272(5)	6719(4)
C(25)	2564(7)	4401(5)	6104(4)
C(26)	2926(7)	5021(5)	5508(4)
Cl(1)	−877(2)	822(2)	6764(1)
O(1a)	−554(6)	1039(4)	6032(3)
O(1b)	−210(6)	1426(4)	7235(3)
O(1c)	−505(6)	−102(3)	6913(3)
O(1d)	−2231(5)	912(4)	6854(3)
Cl(2)	4763(2)	1883(1)	8600(1)
O(2a)	5756(5)	1457(3)	8221(3)
O(2b)	4491(6)	1372(4)	9246(3)
O(2c)	3647(5)	1936(4)	8167(3)
O(2d)	5148(6)	2785(4)	8779(4)

The *cis*-α dichloro intermediate was isolated in high yield from the reaction of the tetrahydrochloride salt of the ligand and cobaltous chloride in ethanol using hydrogen peroxide as the oxidant, under essentially non-aqueous conditions. The presence of excess water produces the highly soluble, characteristically purple, chloro-aquo species [17]. So also does dissolution of the isolated *cis*-α dichloro species in water under neutral conditions. This solution initially has a molar conductivity of 121 S cm^{-1}, which rises to 225 S cm^{-1} after 1 h ($t_{1/2}$=*c.* 5 min). These values are consistent with those of 1:1 and 1:2 electrolytes, respectively [18]. Potentiometric titration of the complex with AgNO$_3$ [19] indicates that only one chloride ion is released in solution; the other remains bound even in the presence of five equivalents of AgNO$_3$. On filtration, this solution had the same electronic spectral properties as an equilibrated aqueous solution derived from the dichloro complex.

The electronic spectral data for the complexes are given in Table 2, and CD spectra are shown in Fig. 1. Representative ^{1}H NMR spectra are shown in Fig. 2. The absolute configurations of the complexes are assigned on the basis of their CD spectral features, and in comparison with those of the Λ-α-[Co(*S*,*S*-picchxnMe$_2$)(*R*-ala)](ClO$_4$)$_2$ complex used for the structural determination (*vide infra*).

An α complex of such a tetradentate, containing also two like unidentates or a symmetrical bidentate, would have C_2 symmetry, and this is reflected in the relatively simple ^{1}H NMR spectrum observed for the dichloro species (Fig. 2). Indeed the spectral

TABLE 2. Electronic spectral data for picchxnMe$_2$ metal complexes

Complex[a]	λ (nm)	$\epsilon \times 10^{-3}$ (dm^2 mol^{-1})	$\Delta\epsilon$ (dm^2 mol^{-1})
Δ-α-[Co(R,R-L)Cl$_2$]$^+$	647		+3.79
(solvent: conc HCl)	569	0.79	
	565		−5.69
	425		−21.67
	345		+37.37
Δ-α-[Co(*R*,*R*-L)Cl$_2$]$^+$	655		+4.80
(solvent: DMSO)	575		−7.60
	570	0.80	
	493		−0.40
	430		−9.59
	365		+28.78
Δ-α-[Co(*R*,*R*-L)(NO$_2$)$_2$]$^+$	528		−2.79
(solvent: H$_2$O)	472		−3.10
	350	16.52	
	340		+34.09
[Δ-α-{Co(*R*,*R*-L)}$_2$ox]$^{4+}$	530		−19.04[b]
(solvent: H$_2$O)	509	0.55	
	446		+2.18
Δ-α-[Co(*R*,*R*-L)(*R*-*ala*)]$^{2+}$	500		−18.34
(solvent: H$_2$O)	498	1.14	
	420		+0.25
	397		−0.19
	362	1.72	
	360		+3.48
Δ-α-[Co(*R*,*R*-L)(*S*-ala)]$^{2+}$	507		−19.34
(solvent H$_2$O)	498	1.12	
	410		−0.52
	390		−0.79
	360	1.88	+1.31

[a] L = picchxnMe$_2$. [b] Calculated per mole of Co.

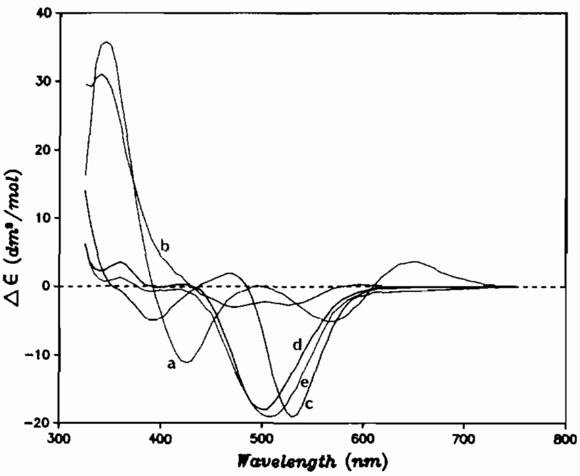


Fig. 1. Visible circular dichroism spectra of the R,R-picchxnMe$_2$ Co(III) complex cations: a, Δ-α-[Co(R,R-picchxnMe$_2$)Cl$_2$]$^+$ in 10 M HCl; b, Δ-α-[Co(R,R-picchxn-Me$_2$)(NO$_2$)$_2$]$^+$ in H_2O; c, [{Δ-α-[Co(R,R-picchxnMe$_2$)]}$_2$-ox]$^{4+}$ in H_2O; d, Δ-α-[Co(R,R-picchxnMe$_2$)(R-ala)]$^{2+}$ in H_2O; e, Δ-α-[Co(R,R-picchxnMe$_2$)(S-ala)]$^{2+}$ in H_2O.

patterns observed are in complete contrast with those found for related unsymmetrical β diastereoisomers [3]. The spectra of the alaninato complexes are somewhat more complex due to the unsymmetrical bidentate nature of the aminoacid, resulting in an α complex with C_1 symmetry. This is reflected in the resonances attributable to the pyridyl H atoms, which are clearly grouped in pairs, and the N-methyl group signals also appear as individual singlets. The chemical shifts of the alaninato Λ-α complexes are diagnostic of the hand of the amino acid. The R-alanine methyl doublet, and its downfield pyridyl doublet, appear at *c.* 0.05 and 0.2 ppm to lower field, respectively, and the methine quartet at 1.4 ppm higher field, when compared with the spectrum of the S-alanine form.

The unusual binuclear oxalate complex presumably contains the oxalate group bridging as a bis-bidentate to the two Co atoms and retaining C_2 symmetry. This bonding mode is akin to other complexes reported previously [20, 21]. The stoichiometry is established by the analytical results, and the CD spectrum of the complex demonstrates the Δ absolute configuration at the metal. Such a structure is consistent with the symmetrical ^{1}H NMR spectrum of the complex, which is closely related to those of the mononuclear species described above. Indeed, if a Δ-α/Λ-β pair were to be present in the dimer, then four sets of pyridyl signals would be observed, corresponding to the two diastereoisomeric modes of coordination possible for the homochiral tetradentate.

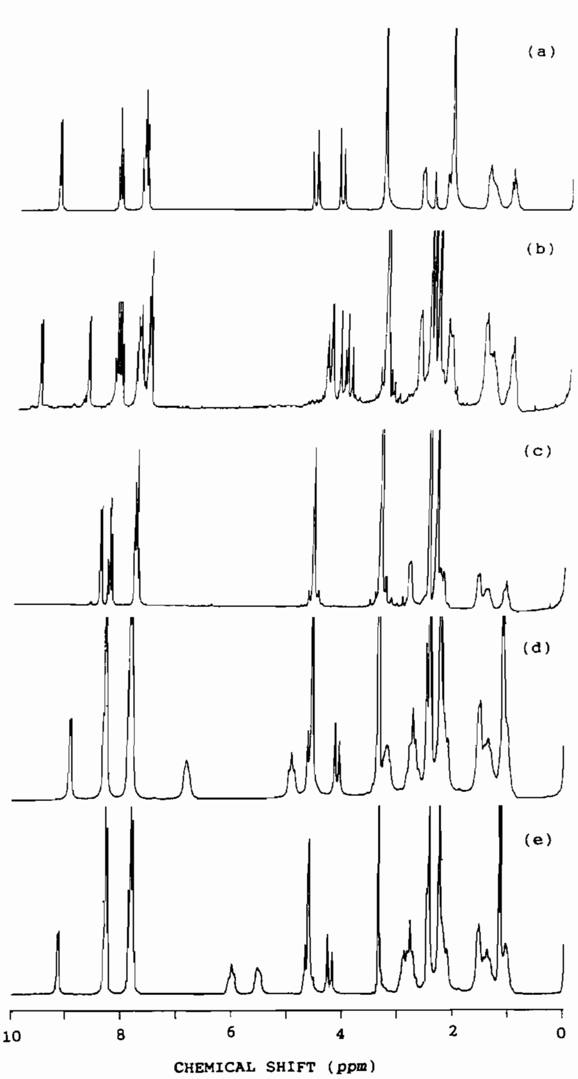


Fig. 2. Proton NMR spectra of the R,R-picchxnMe$_2$ Co(III) complexes recorded in DMSO-d$_6$: (a) Δ-α-[Co(R,R-picchxnMe$_2$)Cl$_2$]$^+$; (b) Δ-α-[Co(R,R-picchxnMe$_2$)(NO$_2$)$_2$]$^+$; (c) [{Δ-α-[Co(R,R-picchxnMe$_2$)]}$_2$ox]$^{4+}$; (d) Δ-α-[Co(R,R-picchxnMe$_2$)(R-ala)]$^{2+}$; (e) Δ-α-[Co(R,R-picchxnMe$_2$)(S-ala)]$^{2+}$.

The spectral results for the dinitro complex are somewhat ambiguous in that the CD spectrum of the reaction solution consists of two main bands, one of positive sign at ≈550 nm and a negative band at ≈485 nm, which implies a simple Δ-α species. However, this is not consistent with the spectrum obtained when the crystalline product is redissolved in water (Fig. 1). The ^{1}H NMR spectrum of the crystalline material in DMSO-d$_6$ does not have the simple symmetrical pattern expected, and this spectrum changes with time. A sample heated in DMSO rapidly changes its chiroptical properties, whereas in water no change is observed. This contrasts with the behaviour of the dichloro species in DMSO, which shows minor spectral shifts in both CD absorption bands compared with aqueous solutions (Fig. 1 and Table 2), but the complex is kinetically stable. Unfortunately the limited solubility of the crystalline product in water precludes the use of D_2O as an NMR solvent. Dissolution in warm concentrated HCl quantitatively reverts the complex to the *cis*-α dichloro species, as evidenced by electronic spectral measurements.

Changes in stereochemistries on reaction of *cis*-dichloro complexes with nitrite ions [7, 9], anomalous CD spectra of related bis-dinitro species [22], the existence of conformational isomerism due to restricted rotation of coordinated nitrite groups observed for $[Co(en)(NH_3)(NO_2)_3]$ [23] and *cis*-β-$[Co(bispictn)(NO_2)_2]^+$ [24], and the substitution of bound nitrite by DMSO [4], have all been reported. Each would provide a possibile explanation for the properties observed in this case, and hence the geometry of the complex remains indefinite.

Crystal and molecular structure of Λ-α-[Co(S,S-picchxnMe₂)(R-ala)](ClO₄)₂

A perspective drawing [25] of the cationic species, together with the atom labelling scheme, is shown in Fig. 3. The structure confirms the Λ-α topology around the octahedral cobalt(III) ion, with the *S*,*S*-1,2-diaminocyclohexane fragment in the central five-membered chelate ring adopting a δ conformation. As a result, the picolyl and methyl group substituents are disposed in quasi equatorial and axial positions, respectively. The *R* absolute configuration of the α-amino acid is confirmed. The cobalt–(*S*,*S*-picchxnMe$_2$) fragment has approximate C_2 symmetry, in accord with the NMR data represented in Fig. 2. The bond lengths and angles for the structure are given in Table 3. Although the bite angles for the tetradentate chelate rings are similar to those found for complexes of the unsubstituted ligand picchxn, in which a β topology is always adopted [26–29], there appears to be a lengthening by about

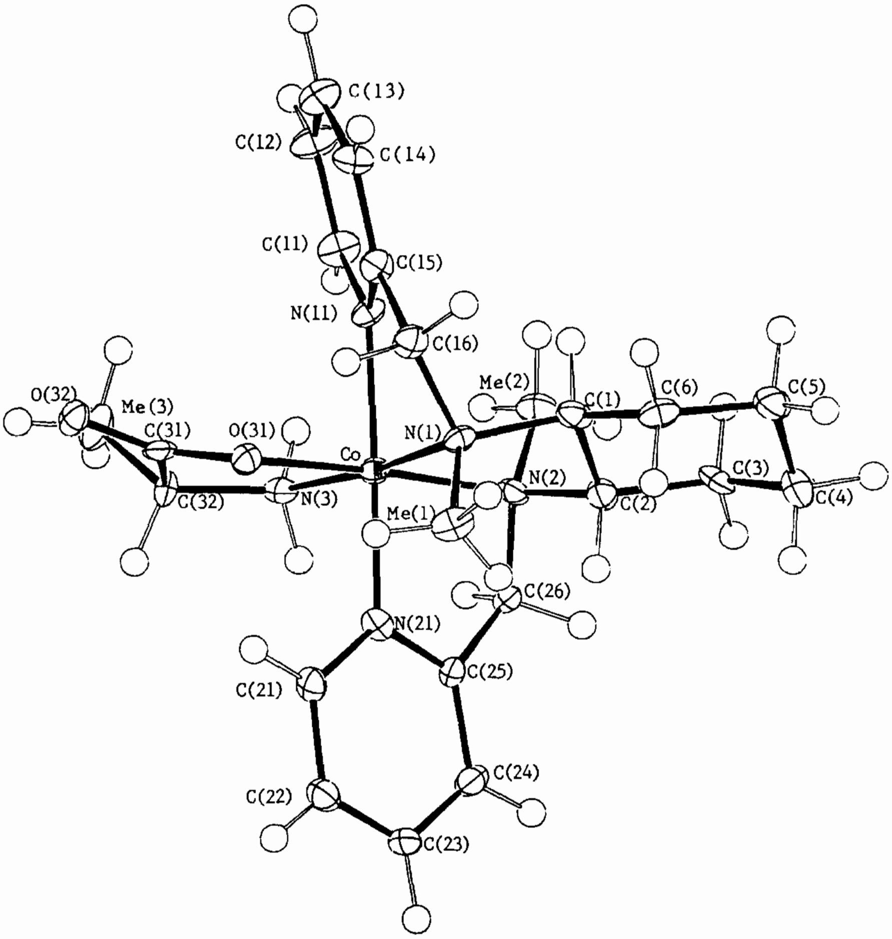


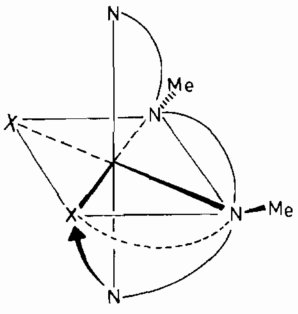
Fig. 3. Perspective drawing of the Λ-α-[Co(*S*,*S*-picchxnMe$_2$)(*R*-ala)]$^{2+}$ cation showing the atom labelling scheme; thermal ellipsoids are drawn to include 35% probability.

TABLE 3. Bond lengths and angles for Λ-α-[Co(*S*,*S*-picchxnMe$_2$)(*R*-ala)](ClO$_4$)$_2$ with e.s.d.s in parentheses

Distances (Å)			
Co–N(11)	1.978(6)	Co–N(21)	1.942(6)
Co–N(1)	1.977(6)	Co–N(2)	1.981(5)
Co–N(3)	1.959(6)	Co–O(31)	1.884(5)
N(3)–C(32)	1.489(9)	C(31)–O(31)	1.279(8)
C(32)–Me(3)	1.517(10)	C(31)–O(32)	1.234(8)
C(32)–C(31)	1.518(10)		
C(1)–C(2)	1.507(10)	C(4)–C(5)	1.528(12)
C(2)–C(3)	1.523(10)	C(5)–C(6)	1.500(10)
C(3)–C(4)	1.521(11)	C(6)–C(1)	1.533(10)
	n = 1	*n* = 2	
N(n)–C(n)	1.508(9)	1.513(9)	
N(n)–C(n6)	1.491(9)	1.507(8)	
N(*n*)–Me(*n*)	1.516(8)	1.502(9)	
N(n1)–C(*n*1)	1.358(8)	1.359(8)	
N(n1)–C(n5)	1.348(9)	1.341(8)	
C(n1)–C(n2)	1.379(10)	1.404(10)	
C(n2)–C(n3)	1.388(11)	1.383(10)	
C(n3)–C(n4)	1.388(10)	1.382(10)	
C(n4)–C(n5)	1.390(10)	1.395(9)	
C(n5)–C(n6)	1.525(9)	1.486(10)	
Cl(n)–O(na)	1.439(5)	1.407(5)	
Cl(n)–O(nb)	1.431(5)	1.445(6)	
Cl(n)–O(nc)	1.439(50	1.426(6)	
Cl(n)–O(nd)	1.441(5)	1.426(6)	
Angles (°)			
N(11)–Co–N(1)	82.1(2)	N(21)–Co–N(2)	83.1(2)
N(1)–Co–N(2)	86.7(2)	O(31)–Co–N(3)	85.4(2)
N(11)–Co–N(21)	178.2(3)	N(1)–Co–N(21)	97.2(2)
N(1)–Co–N(3)	174.6(3)	N(1)–Co–O(31)	90.6(2)
N(2)–Co–O(31)	174.9(2)	N(2)–Co–N(3)	97.6(2)
N(11)–Co–N(2)	98.6(2)	N(21)–Co–O(31)	93.0(2)
N(11)–Co–N(3)	93.9(2)	N(21)–Co–N(3)	86.7(2)
N(11)–Co–O(31)	85.3(2)		
Co–N(3)–C(32)	110.5(5)	Co–O(31)–C(31)	115.9(5)
N(3)–C(32)–Me(3)	112.8(5)	O(31)–C(31)–O(32)	124.9(7)
N(3)–C(32)–C(31)	108.4(4)	O(31)–C(31)–C(32)	116.2(7)
C(31)–C(32)–Me(3)	114.3(6)	O(32)–C(31)–C(32)	118.8(7)
N(1)–C(1)–C(2)	107.0(6)	N(2)–C(2)–C(1)	108.1(7)
N(1)–C(1)–C(6)	116.1(7)	N(2)–C(2)–C(3)	115.5(6)
C(2)–C(1)–C(6)	111.6(7)	C(1)–C(2)–C(3)	113.1(7)
C(1)–C(6)–C(5)	112.5(7)	C(2)–C(3)–C(4)	109.7(7)
C(6)–C(5)–C(4)	112.3(7)	C(3)–C(4)–C(5)	109.6(8)
	n = 1	*n* = 2	
Co–N(n)–C(n)	108.1(5)	108.3(4)	
Co–N(n)–C(n6)	106.3(4)	106.4(4)	
Co–N(n)–Me(n)	114.5(5)	113.7(4)	
C(n)–N(n)–C(n6)	109.8(6)	108.4(6)	
C(n)–N(n)–Me(n)	112.9(6)	111.0(5)	
C(n6)–N(n)–Me(n)	104.9(6)	108.7(6)	
Co–N(n1)–C(n1)	128.9(5)	125.8(5)	
Co–N(n1)–C(n5)	112.4(5)	114.4(5)	
C(n5)–N(n1)–C(n1)	117.6(6)	119.8(7)	
N(n1)–C(n1)–C(n2)	122.4(7)	120.7(7)	
C(n1)–C(n2)–C(n3)	118.9(7)	118.8(7)	
C(n2)–C(n3)–C(n4)	120.0(8)	120.2(7)	
C(n3)–C(n4)–C(n5)	117.3(7)	118.5(7)	
C(n4)–C(n5)–N(n1)	123.7(7)	121.8(7)	
C(n4)–C(n5)–C(n6)	121.7(7)	123.5(7)	
N(n1)–C(n5)–C(n6)	114.6(7)	114.7(6)	
C(n5)–C(n6)–N(n)	108.4(6)	107.0(6)	
O(na)–Cl(n)–O(nb)	109.0(3)	109.4(4)	
O(na)–Cl(n)–O(nc)	109.1(4)	110.7(3)	
O(na)–Cl(n)–O(nd)	108.8(4)	108.6(4)	
O(nb)–Cl(n)–O(nc)	109.5(4)	109.5(4)	
O(nb)–Cl(n)–O(nd)	110.9(4)	110.2(4)	
O(nc)–Cl(n)–O(nd)	109.5(4)	108.4(4)	

0.04 Å of the Co–N (amine) distances by comparison. The bonding parameters observed for the alanine fragment are consistent with expected values [30]. The cations are involved in intermolecular hydrogen bonding, which also involves the perchlorate anions. Details of these and other close intermolecular contacts are given in Table 4.

The conformations adopted by the three five-membered chelate rings determine the overall topology of the complex and accurate molecular models show that a change from a Λ-β to a Δ-α form is governed by the bonding requirements of atom N(1). Such a change is analogous to an edge-displacement inversion [31], as shown in II. During this process there would be no significant change required of any torsion angles in the complex other than those between N(1) and the terminal pyridyl ring. Therefore it is appropriate to centre attention on the factors that influence the orientation of the bonds geminal and vicinal to this atom, in order to explain the stereospecific topology adopted by this type of ligand on coordination.



II

By examination of molecular models of the free *R*,*R* form of the ligand* (considering one half of the molecule) it may be seen that for the *R* absolute configuration at the asymmetric carbon atom C(1)

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*For discussion purposes we will refer to the *R*,*R* form of the ligand and the consequent Λ-β and Δ-α isomers; the analogous arguments would apply for their enantiomers.

TABLE 4. Intermolecular contacts for Λ-α-[Co(S,S-picchxnMe$_2$)(R-ala)](ClO$_4$)$_2$ with e.s.d.s in parentheses

Proposed hydrogen bonding[a]			
N(3)H(N3a)···O(32$^{\text{I}}$)	2.871(7)	N(3)H(N3b)···O(1$^{\text{I}}$)	3.095(8)
Contacts < 3.5 Å[a]			
O(32)···C(25$^{\text{II}}$)	2.893(9)	O(32)···C(24$^{\text{II}}$)	3.244(7)
O(32)···O(1a)	2.994(7)	N(3)···O(1a$^{\text{I}}$)	3.267(8)
C(23)···O(2c)	3.115(10)	C(31)···O(1a)	3.267(9)
O(32)···C(26$^{\text{II}}$)	3.189(9)	C(12)···O(2c$^{\text{II}}$)	3.268(10)
C(22)···O(2c)	3.218(9)	C(11)···O(1d$^{\text{I}}$)	3.288(9)
C(6)···O(2c$^{\text{III}}$)	3.228(10)	C(22)···O(1b)	3.290(9)

[a]Roman numeral superscripts refer to the following equivalent positions relative to x, y, z: I: $\frac{1}{2}+x$, $\frac{1}{2}-y$, $1-z$; II: $x-\frac{1}{2}$, $\frac{1}{2}-y$, $1-z$; III: $-x$, $\frac{1}{2}+y$, $1\frac{1}{2}-z$.

the tetrahedral spatial arrangement of the geminal bonds on this atom dictates the configuration of the adjacent achiral N(1) atom, which in turn determines the orientation of the vicinal N(1)–C(16) bond. As a result atom N(1) on coordination must adopt, by the Chan–Ingold–Prelog [32] definition, an S absolute configuration, with the two vicinal bonds arranged in the energetically favoured *anti* conformation. The terminal picolyl group then could adopt either of the two alternative positions on the coordination sphere, i.e. in the central plane or in the apical position (**II**). If the hydrogen atom on the secondary nitrogen were to be replaced by a bulkier group such as methyl, however, then the picolyl group would adopt the energetically favoured apical position where it is disposed *anti* (at $\approx 180°$) to this methyl substituent.

The combination of these two orientations (in plane or apical) for each half of the molecule would give rise to the three possible isomers, *trans*, *cis*-Λ-β and *cis*-Δ-α. For the *trans* isomer there would be an unfavourable non-bonded H···H interaction between the two pyridyl protons adjacent to the hetero atoms in those rings (described previously as B-strain [23]). This would seem to be the main reason why *trans* complexes of these ligands on octahedral metal ions have not been reported.

Hence octahedral complexes of R,R-picchxnMe$_2$ should adopt a stereospecific *cis*-Δ-α coordination due to these energetic considerations, and, provided that substituents in the remaining two octahedral sites do not sterically interact with the pyridyl groups, this stereospecificity should be retained during substitution at these sites. This, of course, is fully consistent with the results reported herein.

It is possible that increased torsional constraints arising from N-alkylation of C-substituted tetradentates of this picen type, as discussed above, could be used to enforce a high degree of both enantio- and stereospecificity in the coordination behaviour of such ligands. These factors are being investigated further, and the results will be reported in future articles.

Supplementary material

Lists of anisotropic thermal parameters and of observed and calculated structure factors are available from F.S.S. on request.

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