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Chiral metal complexes
36*. Stereoselectivity enhanced by *N,N'*-dimethylation of a chiral N_4 tetradentate, including the crystal structure of Δ-α_1,α_2-{[(*N,N'*-dimethyl-3*R*-methyl-1,6-di(2-pyridyl)-2,5-diazahexane)(*S*-alaninato)]-cobalt(III)} perchlorate

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Abstract

N,N'-dimethylation of the N_4 linear tetradentate *R*-picpn (3*R*-methyl-1,6-di(2-pyridyl)-2,5-diazahexane) in DMF in the presence of excess formaldehyde and sodium cyanoborohydride produces, in high yield, *R*-picpnMe$_2$ (*N,N'*-dimethyl-3*R*-methyl-1,6-di(2-pyridyl)-2,5-diazahexane). Reaction of this ligand with cobalt(III) in the presence of excess chloride ion under non-aqueous conditions produces stereospecifically the *Δ-cis-α* dichloro complex in high yield. The chloride donor atoms undergo replacement by water, nitrite, oxalate or *S*-alaninate with retention of this stereochemistry. The alaninato complex crystallises in the orthorhombic space group $P2_12_12_1$, with $a=10.502(3)$, $b=13.623(7)$, $c=18.655(7)$ Å and $Z=4$. The structure was refined by least-squares methods to $R=0.048$ for 2085 diffractometer data collected at −130 °C. The cobalt atom has octahedral coordination with the N_4 tetradentate adopting *Δ-α* topology and with the aminoacidate completing the coordination sphere. The *S*-ala Co–N and Co–O bond distances are 1.965(7) and 1.887(6) Å, and the Co–N(py) and Co–N(tert-amine) distances average 1.95(1) and 1.990(7) Å, respectively. This latter bond distance is significantly longer than Co–N(sec-amine) distances observed for analogous complexes with *cis-β* topology. The two geometric isomers which are possible for this asymmetric complex form, defined herein as *cis*-α_1 and *cis*-α_2, are observed to co-crystallise. In the crystal structure the cation shows positional disorder for the methyl substituent on the central link of the tetradentate, and the indicated 2:1 ratio for these isomers is consistent with NMR data.

Introduction

There have been several reports dealing with coordination of the tetradentate ligand picpn[†] to octahedral cobalt(III) [1–5] and chromium(III) [5, 6]. Invariably the mode of coordination has been non-specific, and four of the six possible configurations, *Λ-α*, *Λ-β*, Δ-*α* and Δ-*β*, have been observed for the *R* enantiomeric form of the ligand. To date, the isolation of *trans* octahedral complexes of this, or analogous mono-substituted ligands, has not been reported. This lack of stereospecificity may be attributed to the absence of the repulsive interactions which would be felt if two vicinal substituents were to be positioned on the tetradentate backbone. This is demonstrated by the ligands *R,R*-picbn, *R,R*-picchxn and *R,R*-picstien, each of which has been shown to adopt *Λ-β* topology stereospecifically on coordination to cobalt(III) [7–9].

Recently we have demonstrated [10] that alkylation of the secondary nitrogen atoms of *R,R*-picchxn causes this *Λ-β* stereospecificity to change to Δ-*α*, attributable to a similar vicinal effect involving the N-substituents. In order to test the stereochemical consequence of such N-alkylation on a non-specific ligand we have synthesised *R*-picpnMe$_2$ (I) which is the subject of this communication.

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*Part 35 is ref. 20.

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[†] picpn is 3-methyl-1,6-di(2-pyridyl)-2,5-diazahexane; picpnMe$_2$ is *N,N'*-dimethyl-3-methyl-1,6-di(2-pyridyl)-2,5-diazahexane; picchxn is *N,N'*-di(2-picolyl)-1,2-diaminocyclohexane; picchxnMe$_2$ is *N,N'*-dimethyl-*N,N'*-di(2-picolyl)-1,2-diaminocyclohexane; picbn is 3,4-dimethyl-1,6-di(2-pyridyl)-2,5-diazahexane; picstien is 3,4-diphenyl-1,6-di(2-pyridyl)-2,5-diazahexane; ala is the *α*-alaninate anion.

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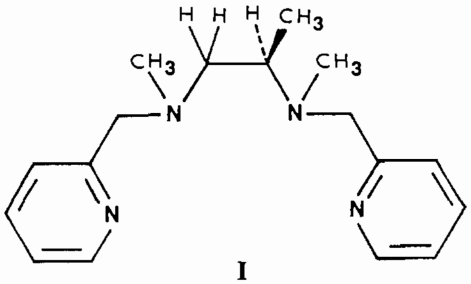
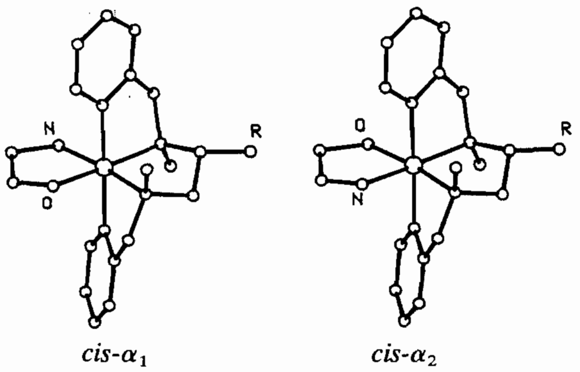


I

The unsymmetrical nature of this tetradentate ligand permits two geometrical *cis*-α isomeric forms when the remaining coordination sites are occupied by non-equivalent donor atoms. For convenience, such isomeric pairs may be distinguished according to the substitutional priority of the donor atoms in a manner similar to the Cahn–Ingold–Prelog notation [11]. These forms are designated here as *cis*-α_1 and *cis*-α_2, where the former refers to the isomer in which the higher ranking donor atom completing the coordination sphere is *trans* to the higher-ranked central donor of the tetradentate. By way of example, coordination of a bidentate amino acid would allow the two forms shown in **II**, which are observed in this work.



cis-α_1 *cis*-α_2

II

Experimental

Microanalyses were carried out by Dr H.-P. Pham in the microanalytical laboratory of the University of New South Wales, Sydney. NMR spectra were recorded on a Varian XL-200 spectrometer and are reported in ppm relative to DSS, TMS or known solvent impurity resonances used as internal calibrants. Circular dichroism (CD) spectra were recorded on a JASCO J-500C spectropolarimeter at ambient temperatures. Optical rotations were measured at 589 nm on an Optical Activity AA-10 automatic polarimeter. Electronic spectra were recorded using a Shimadzu UV-160 recording spectrophotometer. Conductivity measurements were carried out using a Philips PW9506 conductivity meter.

R-picpnMe$_2$·2H$_2$O

rac-1,2-Diaminopropane (Aldrich) was resolved as the *S*,*S*-tartrate salt according to the method of Dwyer *et al.* [12] from aqueous acetic acid to constant rotation, $[\alpha]_D = 22.5 \pm 0.5°$ ($c = 1$, H_2O) after ten recrystallisations. To this salt (22.4 g, 0.1 mol) was slowly added 10 M NaOH until it dissolved and the liberated diamine separated as an oil. This was extracted into dichloromethane (3×50 cm^3), the extract dried over anhydrous Na_2SO_4, and the solvent then was removed at 40 °C under reduced pressure to give a pale yellow oil. Yield 5.5 g (74%).

A sample of this *R*-pn product (1.49 g, 0.02 mol) was added to benzene (150 cm^3) and to the mixture was added 2-pyridinecarboxaldehyde (Aldrich, 4.29 g, 0.04 mol). The solution immediately became cloudy due to the release of water on formation of the Schiff's base. The mixture was stirred for 0.25 h, and the azeotrope removed at 50 °C under reduced pressure. The oily residue was dissolved in absolute ethanol (150 cm^3), 10% palladium on charcoal catalyst (0.5 g) was added, and the mixture was hydrogenated at 3 atm. Filtration of the mixture through a small celite pad under suction and subsequent removal of the solvent left a clear yellow oil. Yield 5.1 g (quantitative).

This product (*R*-picpn) was shown by its NMR spectrum [2, 13] to be suitable for use without further purification. It was dissolved in acetonitrile (100 cm^3), aqueous formaldehyde (37% wt./vol., 17 cm^3) was added and the mixture stirred for 0.25 h. In a fume-hood, sodium cyanoborohydride (Aldrich, 4.0 g, 0.06 mol) dissolved in acetonitrile (20 cm^3) was carefully added with vigorous stirring, which was continued for 1.5 h. The pH was maintained at 7.0 throughout by the dropwise addition of glacial acetic acid. Removal of the solvent mixture under reduced pressure yielded a viscous oil, to which was added aqueous NaOH (2 M, 150 cm^3), followed by extraction into diethyl ether (3×60 cm^3). The extract was washed with water, dried and the solvent removed. Further purification was effected using a neutral-alumina/chloroform chromatographic system. The solvent was removed from the eluate to leave a straw-yellow oil. Yield 4.2 g (74%). NMR, solvent DMSO-d$_6$, ppm; 1.00 (d, 3H)*; 2.16 (s, 3H); 2.19 (s, 3H); 2.46 (m, 2H); 2.28 (q, 1H); 3.64 (d, 2H); 4.00 (d, 2H); 7.25 (m, 2H); 7.48 (t, 2H); 7.77 (dd, 2H); 8.48 (dd, 2H). *Anal.* Calc. for $C_{17}H_{28}N_4O_2$: C, 63.7; H, 8.8; N, 17.5%. Found: C, 64.8; H, 7.7; N, 18.5%.

Δ-α-[Co(R-picpnMe$_2$)Cl$_2$]Cl·5H$_2$O

To a solution of *R*-picpnMe$_2$·2H$_2$O (3.4 g, 0.011 mol) in absolute ethanol (150 cm^3) was added 10 M HCl (5 cm^3) slowly. The solvent then was removed on a rotary evaporator to leave a viscous hygroscopic product

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*d = doublet, m = multiplet; q = quartet; s = singlet; t = triplet; dd = doublet of doublets.

which was redissolved in absolute ethanol (300 cm^3). To this solution was added slowly $CoCl_2 \cdot 6H_2O$ (2.38 g, 0.01 mol) in absolute ethanol (50 cm^3), the rate of addition being such that any solid species formed was allowed to redissolve in the stirred solution before further addition. Hydrogen peroxide (3 cm^3, 30% wt./vol.) was added and stirring continued for a further 0.25 h before the mixture was stored at 0 °C for 12 h. The resulting blue–green solid, which tends to be hygroscopic until completely dry, was collected at the pump, washed with absolute ethanol and dried in a desiccator over silica gel *in vacuo*. Yield 4.01 g (81%). *Anal.* Calc. for $C_{17}H_{34}N_4O_5Cl_3Co$: C, 37.8; H, 6.3; N, 10.4. Found: C, 38.0; H, 4.4, N, 10.1%.

Δ-α$_1$,α$_2$-[Co(R-picpnMe$_2$)(S-ala)](ClO$_4$)$_2$

A solution of Δ-α-[Co(*R*-picpnMe$_2$)Cl$_2$]Cl (0.225 g, 0.5 mmol) in water 40 cm^3 was warmed on a steam-bath, *S*-alanine (0.07 g, 0.75 mmol) was added and the mixture heated for 1 h. The orange solution was cooled, diluted to 300 cm^3 and applied to a column of CM Sephadex®-C25 cation exchange resin in the Na^+ cycle. The adsorbed material was washed with water then eluted with 0.5 M NaCl. The sole mobile orange band was collected in fractions and the CD of each fraction recorded. Since all fractions had qualitatively the same spectral features they were combined, saturated $NaClO_4$ (2 cm^3) was added and the solvent was allowed to slowly evaporate. After two weeks the dark orange needles were collected at the pump, washed with minimum amounts of ice-cold water and absolute ethanol, and air dried. Yield 0.21 g (66.6%). This product was used for the crystallographic analysis reported below. On standing a further crop of crystals was obtained from the mother liquor. Yield 0.04 g (12.7%).

[{Δ-α-Co(R-picpnMe$_2$)}$_2$(ox)](ClO$_4$)$_4$·4H$_2$O

To a warm solution of Δ-α-[Co(*R*-picpnMe$_2$)Cl$_2$]Cl (0.225 g, 0.5 mmol) in water (40 cm^3) was added oxalic acid (0.045 g, 0.5 mmol) and the mixture was heated on a steam-bath for 1 h. Hydrated lithium perchlorate (0.05 g) was then added and the solution filtered and reduced in volume to *c*. 5 cm^3 on the steam-bath. The solution then was cooled and propanol was added to induce precipitation. The solid product obtained was collected at the pump, washed with propanol, followed by a minimum amount of absolute ethanol, then dried *in vacuo* over silica gel. Yield 0.15 g (58%). *Anal.* Calc. for $C_{36}H_{56}N_8O_{24}Cl_4Co_2$: C, 34.7; H, 4.5; N, 9.0. Found: C, 34.7; H, 3.9; N, 9.0%.

TABLE 1. Final atomic coordinates (fractional $\times 10^4$) for non-hydrogen atoms with e.s.d.s in parentheses for Δ-α$_1$, α$_2$-[Co(*R*-picpnMe$_2$)(*S*-ala)](ClO$_4$)$_2$

	Occupancy[a]	*x*	*y*	*z*
Co		229.1(11)	563.6(8)	188.1(6)
N(11)		−725(7)	90(5)	−655(4)
N(21)		1094(8)	1050(5)	1032(4)
N(1)		−1077(8)	−228(5)	695(4)
N(2)		1420(7)	−566(5)	307(4)
N(3)		1372(6)	1412(5)	−370(3)
O(31)		−921(5)	1628(4)	177(3)
O(32)		−1325(5)	3042(4)	−361(3)
C(31)		−605(7)	2383(6)	−208(4)
C(32)		787(8)	2409(6)	−450(4)
Me(3)		942(10)	2801(7)	−1208(5)
C(11)		−380(9)	102(7)	−1351(4)
C(12)		−1227(10)	−98(9)	−1898(5)
C(13)		−2477(9)	−318(9)	−1728(5)
C(14)		−2828(9)	−344(7)	−1013(5)
C(15)		−1948(9)	−152(7)	−502(5)
C(16)		−2261(9)	−130(7)	278(5)
Me(1)		−1362(11)	80(8)	1463(5)
C(1)		−620(9)	−1274(7)	669(6)
C(2)		762(12)	−1261(7)	816(6)
C(3)	0.67	1178(14)	−2319(11)	889(10)
C(3′)	0.33	−1097(43)	−2065(23)	1096(20)
Me(2)		1795(10)	−1071(7)	−376(6)
C(21)		747(10)	1817(6)	1450(5)
C(22)		1475(12)	2109(8)	2030(5)
C(23)		2507(12)	1616(8)	2216(5)
C(24)		2928(9)	825(7)	1786(5)
C(25)		2204(9)	582(7)	1186(4)
C(26)		2585(9)	−167(7)	649(5)
Cl(1)		−1077(2)	4436(3)	1713(1)
O(1a)		−2436(6)	4408(7)	1752(4)
O(1b)		−689(7)	3980(5)	1059(4)
O(1c)	0.55	−746(32)	5471(21)	1606(18)
O(1d)	0.40	−695(59)	3656(45)	2265(29)
O(1e)	0.50	−539(25)	4045(27)	2325(14)
O(1f)	0.55	−547(35)	5313(34)	1926(19)
Cl(2)		4802(3)	3177(2)	3576(1)
O(2a)	0.90	3445(9)	2980(8)	3561(5)
O(2b)	0.75	5468(18)	2850(12)	4162(12)
O(2c)	0.70	4708(13)	4232(9)	3556(8)
O(2d)	0.40	5278(24)	2880(21)	2916(12)
O(2e)	0.40	5049(33)	2180(14)	3312(12)
O(2f)	0.35	5875(35)	3484(29)	3105(13)
O(2g)	0.50	4939(32)	3241(21)	4347(19)

[a] Fractional occupancies are included for the relevant atoms.

Crystal structure determination of Δ-α$_1$,α$_2$-[Co(R-picpnMe$_2$)(S-ala)](ClO$_4$)$_2$

Crystal data. $C_{20}H_{30}N_5O_{10}Cl_2Co$, $M_r = 630.3$, orthorhombic, $a = 10.502(3)$, $b = 13.623(7)$, $c = 18.655(7)$ Å, $U = 2668.9$ Å^3, $Z = 4$, $F(000) = 1304$, μ(Mo Kα) = 9.33 cm^{-1}, space group $P2_12_12_1$ (No. 19).

Unit cell parameters were initially 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 [14] in the range $5.0 < 2\theta < 50.0°$ using Mo Kα radiation. Reflexions were corrected for Lorentz, polarisation and absorption effects [14]. With respect to the latter, the maximum and minimum transmission factors were 0.715 and 0.681, respectively. Of the 2690 reflexions measured 2085 gave counts for which $I > 3\sigma(I)$, and these were used for the structure determination.

The structure, solved by the heavy atom method, was refined by full-matrix least-squares calculations in which $\Sigma w\Delta^2$ was minimised. The weight applied to each reflexion was based on counting statistics. Difference maps showed disorder in the position of the methyl group on the central ethylene link, the peak heights being consistent with occupancies of 1/3 and 2/3 for the methyl groups on atoms C(1) and C(2), respectively, and with both asymmetric carbon atoms having *R* absolute configuration. The two perchlorate anions also showed disorder with only two oxygen atoms, on Cl(1), having full occupancy. For the six other oxygen atoms twelve positions were indicated, and the peak heights of these were used to assign initial occupancies. The occupancies for these oxygen atoms were subsequently adjusted during refinement so that their isotropic thermal parameters remained approximately the same as the other oxygen atoms in these ions having full occupancy. The difference maps were used further to locate the approximate positions of the hydrogen atoms, and these were optimised assuming C–H and N–H to be 1.0 Å and the appropriate geometry for each C or N atom. The final anisotropic refinement for all non-hydrogen atoms was terminated when the change in any parameter was $<0.1\sigma$. Final values for *R* and *R'* $[=(\Sigma w\Delta^2/\Sigma w|F_o|^2)^{1/2}]$ were 0.048 and 0.052, respectively. A final difference map showed no density $>|0.8|$e Å^{-3}. All structure refinement and analysis calculations were carried out on a FACOM M340S computer using programs written by F.S.S. Neutral atom scattering factors, with corrections being applied for anomalous dispersion, were taken from ref. 15.

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

Results and discussion

An earlier report of the chiroptical properties of metal complexes of *R*-1,2-diaminopropane (*R*-pn) [16] has been the subject of dispute due to difficulties involved in effecting a complete resolution of the diamine. However it is considered that ten recrystallisations from an acetic acid/water solvent system produces a tartrate salt of the diamine of very high optical purity [12]. Following this method we obtained [*R*-pnH$_2$][*S*,*S* (−)tart], $[\alpha]_D = 22.5 \pm 0.5°$ ($c = 1$, H$_2$O), the 1:1 stoichiometry being confirmed by NMR measurements. Isolation of the resolved free diamine was effected by dichloromethane extraction under strongly basic conditions, a method more facile and higher yielding than the previously reported dry distillation of the dihydrochloride salt from solid NaOH [17].

The ^{1}H NMR spectra of the complexes synthesised are shown in Fig. 1 and their absorption and circular dichroism spectral data are given in Fig. 2 and Table 2. These data are closely comparable with those reported recently for picchxnMe$_2$ analogues [10]. The observed simplicity of the NMR spectra again confirms the α topology of each complex in solution.

The cobalt(III) *cis*-α dichloro complex was synthesised under essentially non-aqueous conditions in high yield, similar to analogous compounds [9, 10]. Again like those complexes, this dichloro species is highly susceptible to aquation, with the rapid replacement of one chloride donor atom by a water molecule [7, 10]. Immediately on dissolution a solution of the dichloro complex displayed a molar conductivity of 258 S cm^{-1} which rose rapidly to 283 S cm^{-1} ($t_{1/2}$ *c.* 1 min), a value which remained unchanged after 1 h. These values are consistent with those for 1:2 electrolytes [18]. Potentiometric titration with silver ion demonstrates the

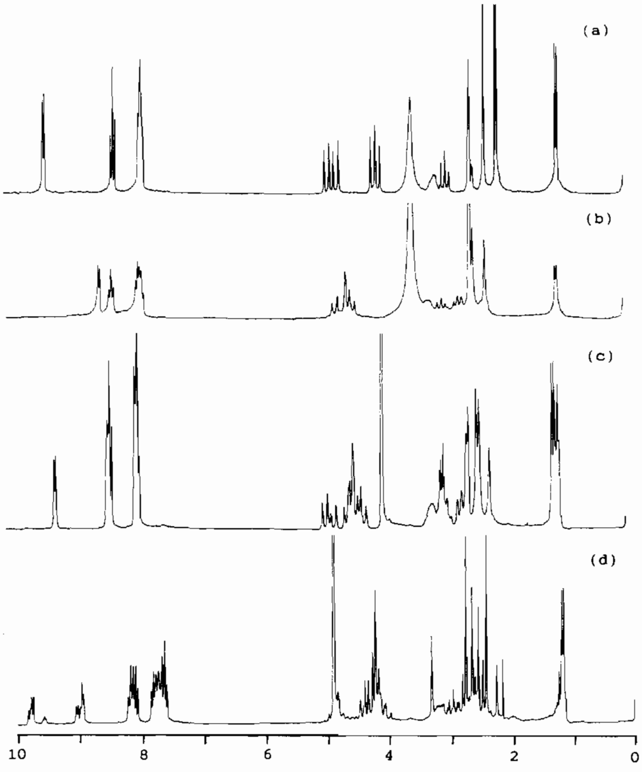

Fig. 1. 200 MHz ^{1}H NMR spectra of the Co(III)–picpnMe$_2$ complex cations: (a) Δ-α-[Co(*R*-picpnMe$_2$)Cl$_2$]$^+$ in dmso-d$_6$; (b) [Δ-α-{Co(*R*-picpnMe$_2$)}$_2$(ox)]$^{4+}$ in dmso-d$_6$; (c) Δ-α_1,α_2-[Co(*R*-picpnMe$_2$)(*S*-ala)]$^{2+}$ in dmso-d$_6$; (d) Δ-α-[Co(*R*-picpnMe$_2$)(NO$_2$)$_2$]$^+$ in CD$_3$OD.

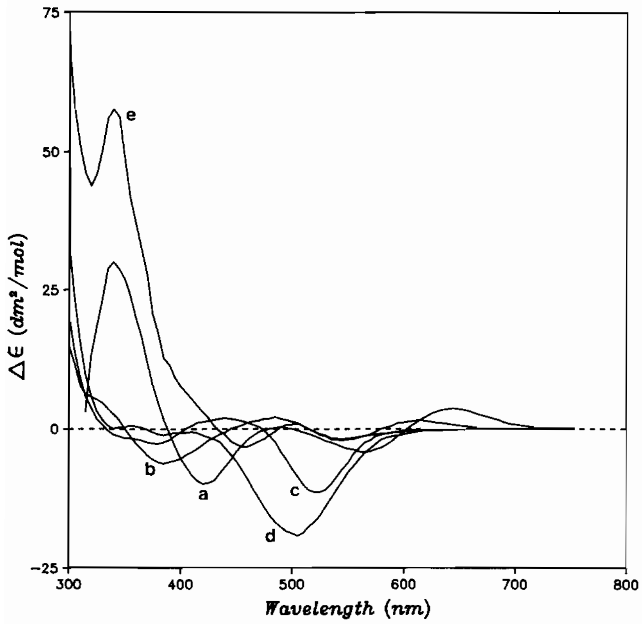

Fig. 2. CD spectra of the Co(III)–picpnMe$_2$ complex cations: (a) Δ-α-[Co(R-picpnMe$_2$)Cl$_2$]$^+$ in 10 M HCl; (b) Δ-α-[Co(R-picpnMe$_2$)Cl(H$_2$O)]$^{2+}$ in H$_2$O; (c) [Δ-α-{Co(R-picpnMe$_2$)}$_2$(ox)]$^{4+}$ in H$_2$O; (d) Δ-α_1,α_2-[Co(R-picpnMe$_2$)(S-ala)]$^{2+}$ in H$_2$O; (e) Δ-α-[Co(R-picpnMe$_2$)(NO$_2$)$_2$]$^+$ in CH$_3$OH. Spectra were recorded at concentrations of c. 10^{-3} M.

presence of the two free chloride ions in solution, with the coordinated chloride remaining bound even after addition of silver ion in significant excess. It is of interest that this aqua-chloro hydrolysis product could exist in cis-α_1 or cis-α_2 isomeric forms.

Like substitution reactions on the dichloro species to those performed with Δ-α-[Co(S, S-picchxnMe$_2$)Cl$_2$]$^+$ [10] were investigated. Unfortunately the high solubility of the dinitro species in water precluded its isolation in a pure form, which is in contrast with the relatively insoluble Δ-α-[Co(R,R-picchxnMe$_2$)(NO$_2$)$_2$]ClO$_4$ analogue [16]. Aqueous and methanolic solutions of the dinitro species were prepared by dissolving the dichloro precursor with five equivalents of anhydrous sodium nitrite in the appropriate solvent, and the NMR, CD and visible spectra recorded. The reaction is extremely rapid at room temperature, producing the characteristic orange–yellow of the N$_6$ chromophore. The NMR results confirm that one isomeric species predominates and it is assumed that at such high nitrite concentrations this is the dinitro species. Again the simplicity of the NMR spectrum of the oxalato complex confirms the retention of its bridged structure in solution with an α-topology for each cobalt atom. A structure analogous to that proposed for the S, S-picchxnMe$_2$ complex [10] is envisaged, consistent with the similar electronic spectral features observed for that complex.

TABLE 2. Electronic spectral data for picpnMe$_2$ metal complexes in the form of absorption maxima and circular dichroism extrema

Complex[a]	λ (nm)	$\epsilon\times10^{-3}$ (dm^2 mol^{-1})	$\Delta\epsilon$ (dm^2 mol^{-1})
Δ-α-[Co(R-L)Cl$_2$]$^+$	690	0.56	
(solvent: conc. HCl)	664	0.63	
	645		+3.71
	565		−4.97
	562	0.87	
	490		+0.31
	420		−9.88
	340		+29.96
Δ-α-[Co(R-L)(H$_2$O)Cl]$^{2+}$	615		+1.56
(solvent: H$_2$O)	545		−2.08
	512	0.63	
	485		+2.08
	385		−6.23
Δ-α-[Co(R-L)(NO$_2$)$_2$]$^+$	545		−1.84
(reaction soln. MeOH)	505		+0.92
	457		−3.34
	360	72.03	
	340		+57.62
	337	94.69	
	320		+43.80
[Δ-α-{Co(R-L)}$_2$(ox)]$^{4+}$	523		−11.65
(solvent: H$_2$O)	497	1.07	
	440		+1.89
	380		−2.74
Δ-α-[Co(R-L)(S-ala)]$^{2+}$	505		−19.11
(solvent: H$_2$O)	497	0.99	
	410		−0.59
	385		−1.17
	355		+0.59
	340		0.00

[a] L = picpnMe$_2$.

The NMR spectra of the S-aminoacidate complex products show the presence of both geometric isomers. For the first crop, comparative integration of the singlet resonances in the range 2.3 to 2.8 ppm attributable to the N-methyl group protons provides an approximate 2:1 ratio for the α_1 and α_2 isomers, respectively. This is in agreement with the isomeric occupancies observed in the crystal structure, and demonstrates that this product is not a mixture of separate crystals of each form. It is of interest that the NMR spectrum of the second crop obtained from the mother liquor shows a lower α_1:α_2 ratio. Unlike the unsymmetrical β_1 and β_2 isomeric analogues formed with picpn [3], which may be separated under like conditions, the use of CM Sephadex®-C25 cation exchange chromatography did not provide a resolution of these alaninato α-isomers. Presumably the small structural difference between the α_1 and α_2 forms of this complex is insufficient to permit discriminative separation by this method.

In the crystal lattice both α_1 and α_2 stereoisomers of the molecular cation co-crystallise in a 2:1 ratio, respectively, which is in accord with the NMR measurements of solutions of the same crystalline form.

Figure 3 shows a perspective drawing [19] of the α_1 isomer, which is the major constituent for the molecular cation, together with the atom labelling scheme. In this species the cobalt atom has octahedral coordination with the tetraaza ligand adopting a Δ-α topology, and with the alaninato bidentate completing the coordination sphere. The central five-membered ring has a λ conformation with the N(1)–C(1)–C(2)–N(2) torsion angle of −53.9°. In both α_1 and α_2 forms the methyl group attached to the central link occupies a quasi equatorial position. The molecular dimensions of the coordinated *S*-alaninate ion agree well with those found in similar structures [4, 10], and its absolute configuration acts as a chiral marker to confirm the *R* configuration of the tetradentate. Molecular dimensions in the cations are given in Table 3 and are similar to those reported for the closely related Λ-α-[Co(*S*, *S*-picchxnMe$_2$)(*R*-ala)](ClO$_4$)$_2$ complex [10].

A hydrogen bond network which includes both alaninato amine protons is apparent (Fig. 4(a)), and details of this together with other close intermolecular contacts are given in Table 4. The molecular packing in this structure is remarkably similar to that of the picchxnMe$_2$ complex, which crystallises in the same space group and has similar cell parameters [10]. However, it is apparent from the packing diagrams (Fig. 4) that the observed disorder of the perchlorate ions in the present structure is allowed by the less bulky central link of the tetradentate affording a larger volume for these ions to occupy.

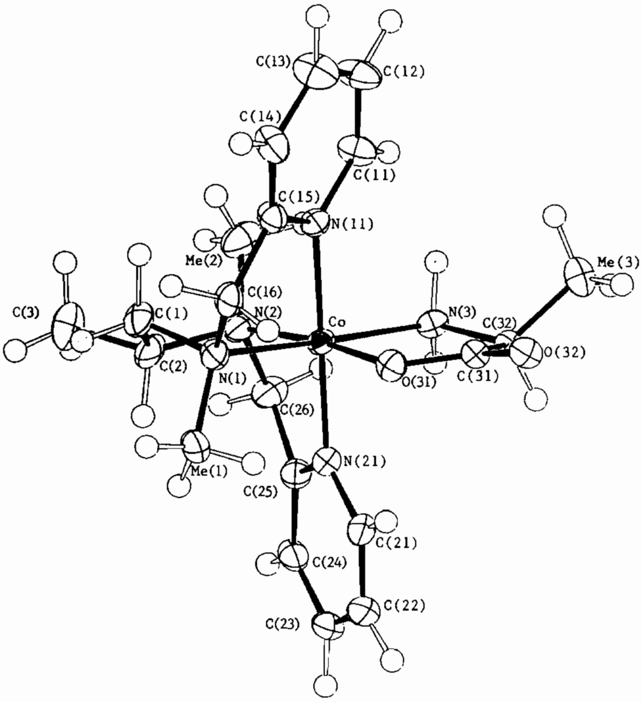

Fig. 3. Perspective drawing of the Δ-α_1-[Co(*R*-picpnMe$_2$)(*S*-ala)]$^{2+}$ cation showing the atom labelling scheme with thermal ellipsoids drawn to include 35% probability.

TABLE 3. Bond lengths and angles with e.s.d.s in parentheses for the Δ-α_1, α_2-[Co(*R*-picpnMe$_2$)(*S*-ala)]$^{2+}$ cations

Distances (Å)			
Co–N(11)	1.973(7)	Co–N(21)	1.934(7)
Co–N(1)	1.985(7)	Co–N(2)	1.995(7)
Co–N(3)	1.965(7)	Co–O(31)	1.887(6)
N(3)–C(32)	1.498(10)	O(31)–C(31)	1.298(9)
C(1)–C(2)	1.477(15)	O(32)–C(31)	1.207(9)
C(2)–C(3)	1.513(17)	C(31)–C(32)	1.531(11)
C(1)–C(3′)	1.431(34)	C(32)–Me(3)	1.520(13)
	$n=1$	$n=2$	
N(*n*)–C(*n*)	1.503(13)	1.509(13)	
N(*n*)–Me(*n*)	1.523(12)	1.500(12)	
N(*n*)–C(*n*6)	1.473(12)	1.483(11)	
C(*n*6)–C(*n*5)	1.493(12)	1.486(13)	
N(*n*1)–C(*n*1)	1.348(10)	1.353(11)	
N(*n*1)–C(*n*5)	1.357(10)	1.359(12)	
C(*n*1)–C(*n*2)	1.380(12)	1.384(13)	
C(*n*2)–C(*n*3)	1.384(14)	1.321(16)	
C(*n*3)–C(*n*4)	1.384(13)	1.414(14)	
C(*n*4)–C(*n*5)	1.353(12)	1.393(11)	
Angles (°)			
N(11)–Co–N(1)	81.5(3)	N(11)–Co–N(21)	177.5(3)
N(21)–Co–N(2)	83.1(3)	N(1)–Co–N(3)	173.9(3)
N(1)–Co–N(2)	87.8(3)	N(2)–Co–O(31)	174.2(3)
O(31)–Co–N(3)	86.1(3)	N(21)–Co–N(1)	97.0(3)
N(11)–Co–N(2)	98.9(3)	N(21)–Co–N(3)	86.7(3)
N(11)–Co–N(3)	94.6(3)	N(21)–Co–O(31)	92.7(3)
N(11)–Co–O(31)	85.2(3)	N(1)–Co–O(31)	88.9(3)
Co–O(31)–C(31)	116.9(5)	N(2)–Co–N(3)	97.4(3)
O(31)–C(31)–O(32)	124.1(7)	N(1)–C(1)–C(2)	107.2(8)
O(31)–C(31)–C(32)	115.1(7)	N(1)–C(1)–C(3′)	125.8(20)
O(32)–C(31)–C(32)	120.7(7)	C(2)–C(1)–C(3′)	104.4(19)
C(31)–C(32)–N(3)	110.0(7)	N(2)–C(2)–C(1)	109.9(8)
C(31)–C(32)–Me(3)	112.6(7)	N(2)–C(2)–C(3)	121.5(11)
N(3)–C(32)–Me(3)	111.6(7)	C(1)–C(2)–C(3)	106.8(10)
Co–N(3)–C(32)	109.6(5)		
	$n=1$	$n=2$	
Co–N(*n*)–Me(*n*)	115.8(6)	115.1(5)	
Co–N(*n*)–C(*n*)	106.2(6)	105.5(6)	
Co–N(*n*)–C(*n*6)	106.4(5)	106.4(5)	
Me(*n*)–N(*n*)–C(*n*)	110.7(7)	111.5(7)	
Me(*n*)–N(*n*)–C(*n*6)	107.8(8)	108.5(7)	
C(*n*)–N(*n*)–C(*n*6)	109.8(7)	109.7(7)	
N(*n*)–C(*n*6)–C(*n*5)	109.1(8)	108.6(7)	
Co–N(*n*1)–C(*n*1)	128.9(6)	127.3(7)	
Co–N(*n*1)–C(*n*5)	113.1(6)	114.5(6)	
C(*n*1)–N(*n*1)–C(*n*5)	117.4(7)	118.0(8)	
N(*n*1)–C(*n*1)–C(*n*2)	122.4(8)	121.6(10)	
C(*n*1)–C(*n*2)–C(*n*3)	119.0(9)	120.8(10)	
C(*n*2)–C(*n*3)–C(*n*4)	118.6(9)	119.6(9)	
C(*n*3)–C(*n*4)–C(*n*5)	119.5(8)	117.8(9)	
C(*n*4)–C(*n*5)–N(*n*1)	123.0(8)	121.8(9)	
C(*n*4)–C(*n*5)–C(*n*6)	122.8(8)	123.9(9)	
N(*n*1)–C(*n*5)–C(*n*6)	114.1(8)	114.2(7)	

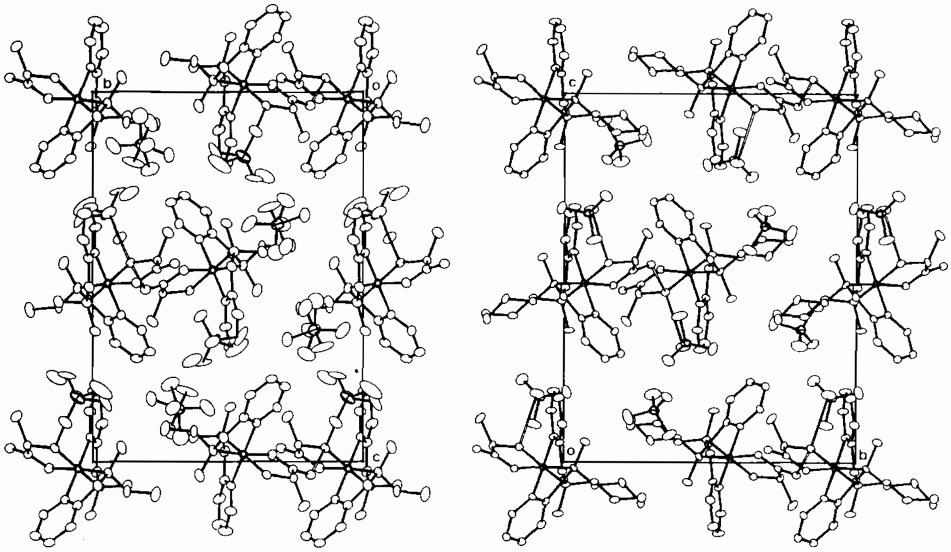
(a) (b)

Fig. 4. A comparison of the packing of the molecular ions in the crystal lattices of (a) Δ-α_1,α_2-[Co(*R*-picpnMe$_2$)(*S*-ala)](ClO$_4$)$_2$ and (b) Λ-α-[Co(*S*, *S*-picchxnMe$_2$)(*R*-ala)](ClO$_4$)$_2$. Hydrogen bonding is indicated by open bonds. For the picpnMe$_2$ complex only the α_1 isomer is depicted.

TABLE 4. Intermolecular distances (Å) with e.s.d.s in parentheses for Δ-α_1,α_2-[Co(*R*-picpnMe$_2$)(*S*-ala)](ClO$_4$)$_2$

Proposed hydrogen bonding[a]			
N(3)H(N3a)...O(32^{I})	2.875(9)	N(3)H(N3b)...O(1a^{I})	3.077(9)
Contacts <3.3 Å (disordered O atoms excluded)[a]			
O(32)...C(25^{II})	2.88(1)	C(31)...O(1b)	3.21(1)
O(32)...O(1b)	3.02(1)	N(21)...O(32^{I})	3.23(1)
O(32)...C(26^{II})	3.16(1)	C(11)...O(1a^{I})	3.25(1)
O(32)...C(24^{II})	3.17(1)		

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

In our earlier report on the complexes of picchxnMe$_2$ we commented on the intra-molecular discriminations that determine the choice of Δ-α or Λ-α topologies adopted by the *R*,*R* and *S*,*S* enantiomeric ligand forms, respectively. Similar arguments would hold for that half of the *R*-picpnMe$_2$ ligand which contains the asymmetric carbon atom, where substituent vicinal pairs would energetically favour an *anti* conformation. For the other half of the ligand the methyl group on the tertiary chiral nitrogen atom would lie *anti* to both the picolyl residue and the central C–C bond, and thus these vicinal substituent effects would determine the stereochemical choices observed. Hence the study shows that, as a result of these intramolecular interactions, the stereoselectivity of a non-stereospecific ligand such as picpn can be optimised by N,N′-dialkylation.

Supplementary material

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

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