Chiral metal complexes
Part 37*. A new stereospecific N_4 tetradentate, *N,N'*-di(2-picolyl)-*N'*-methyl-2*S*-aminomethylpyrrolidine, *S*-picpyrrMe, and the crystal structures of its ternary Λ-α_1-$[Co^{III}(S\text{-picpyrrMe})(L)]^{2+}$ ions (L = *S*- or *R*-alaninate)

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Abstract

A new linear N_4 tetradentate with terminal pyridyl groups, *N,N'*-di(2-picolyl)-*N'*-methyl-2-aminomethylpyrrolidine, *S*-picpyrrMe, has been synthesized via a six-step process in 19% yield from the naturally-occurring α-amino acid *S*-proline. The ligand stereospecifically adopts a Λ-α topology on coordination to cobalt(III) when isolated as the dichloro complex. This configuration is retained on substitution of the chloro ligands by nitrite or *R*- or *S*-alaninate ions. The products were characterised by their electronic absorption and chiroptical properties and by ^1H NMR. The low-temperature crystallographic analyses of the *R*- and *S*-alaninate complexes are reported. Λ-α_1-$[Co(S\text{-picpyrrMe})(R\text{-ala})](ClO_4)_2$ crystallises in the monoclinic space group $P2_1$ with $a = 10.888(4)$, $b = 10.243(4)$, $c = 12.365(6)$ Å, $\beta = 109.37(3)°$ and $Z = 2$; Λ-α_1-$[Co(S\text{-picpyrrMe})(S\text{-ala})](ClO_4)_2 \cdot \frac{1}{2}H_2O$ crystallises in the orthorhombic space group $P2_12_12_1$ with $a = 10.580(8)$, $b = 14.391(8)$, $c = 18.078(7)$ Å and $Z = 4$. The structures were refined by full-matrix least-squares procedures to $R = 0.046$ for 1662 reflections and $R = 0.046$ for 1771 reflections, respectively. In each case the amino acid coordinates as a N,O-bidentate, completing a CoN_5O octahedral coordination sphere with α_1 topology. The average Co–N(pyridine) distance is 1.955(8) Å and the Co–N(tert-amine) distances are 1.996(8) and 1.979(8) Å for the methylated and pyrrolidine amines, respectively. The *R*-alaninate chelate ring is considerably flattened due to a steric interaction between its methyl group and a pyridyl ring of the tetradentate, whereas the *S*-alaninate has an unstrained puckered conformation.

Introduction

For some time, this group has been investigating the effects of C- and/or N-substitution on the stereoselective coordination behaviour of linear N_4 tetradentates containing terminal pyridyl groups, **I**. It has been demonstrated that such C-di-substituted ligands, having the two vicinal asymmetric carbon atoms with the same absolute configuration, stereospecifically adopt a β topology on octahedral coordination to cobalt(III) [1–3]. Moreover, the stereospecific behaviour exhibited by one of these ligands, *R,R*-picchxn† (**I** with R^2, $R^3 = -CH_2-CH_2-CH_2-CH_2-$; $R^1 = R^4 = H$), changes from Λ-β to Δ-α on N,N'-dimethylation of the secondary N atoms [4]. By way of comparison, the C-monosubstituted ligand *R*-picpn (**I** with $R^2 = CH_3$; $R^1 = R^3 = R^4 = H$) has shown non-specific coordination to cobalt(III), with Λ-α, Λ-β, Λ-α and Λ-β forms having been isolated [5, 6]. This non-stereospecificity obviously is due to the rotational flexibility of the central diamine bridge of this tetradentate.

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†Picchxn is *N,N'*-di(2-picolyl)-1,2-diaminocyclohexane; 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; picchxnMe$_2$ is *N,N'*-dimethyl-*N,N'*-di(2-picolyl)-1,2-diaminocyclohexane; picpyrrMe is *N,N'*-di(2-picolyl)-*N'*-methyl-2-aminomethylpyrrolidine; 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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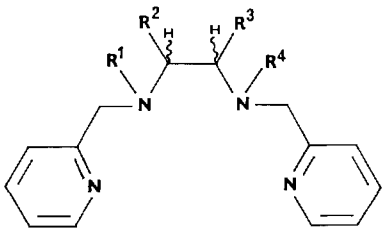
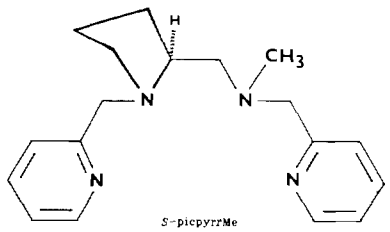


I

It has been demonstrated in this laboratory that by N,N'-dimethylation of *R*-picpn Δ-α_1 or Δ-α_2 topologies are stereospecifically enforced on coordination to cobalt(III), attributable to a vicinal substituent effect involving repulsion of the two vicinal CH_3 groups along the C–N bond [7]. It might be expected that if any portion of these types of tetradentates were to include a ring system which includes a central N atom then the conformation dictated by the resulting loss of flexibility would determine the coordination stereospecificity. An obvious choice as a chiral precursor for the synthesis of such a ligand is the naturally occurring amino acid *S*-proline, which contains both an asymmetric carbon atom and a secondary nitrogen atom as part of a five-membered ring. Such ligands, based on readily available optically pure amino acids, have the advantage that they do not require optical resolution of their synthetic precursors. In order to investigate the stereochemical behaviour of ligands of this type the ligand picpyrrMe **II** (**I** with R^1, $R^2 = -CH_2-CH_2-CH_2-$, $R^3 = H$, $R^4 = CH_3$) has been synthesized and its coordination to trivalent cobalt studied. The results of the investigation are reported below.



II

Experimental

Optical rotations were measured at 589 nm on an Optical Activity AA-10 automatic polarimeter. Circular dichroism (CD) and electronic absorption spectra were recorded on a JASCO J-500C spectropolarimeter or Shimadzu UV-160 recording spectrophotometer at ambient temperature using solution concentrations of *c.* 10^{-3} M. 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. Ionic conductivity measurements were carried out using a Philips PW9506 conductivity meter. Microanalyses were carried out by Dr H.-P. Pham in the microanalytical laboratory of the University of NSW, Sydney.

N-Carbobenzoxy-S-proline-N'-methylamide

The amino acid precursor, the *p*-nitrophenylester of *N*-carbobenzoxy-*S*-proline, was synthesized using a combination of published procedures [8]. This involved the protection of the secondary amine nitrogen atom of *S*-proline via benzyloxycarbonyl chloride under basic conditions, and the consequent formation of the *p*-nitrophenyl ester with dicyclohexylcarbodiimide as the coupling agent. The product was isolated as colourless needles and its authenticity confirmed by NMR: solvent DMSO-d_6, ppm; 1.98 (dt, 2H)*; 2.36 (m, 2H); 3.52 (m, 2H); 4.62 (dq, 1H); 5.14 (q, 2H); 7.28 (q, 2H); 7.40 (m, 5H); 8.30 (m, 2H). m.p. 96–97 °C uncorr. (lit. 94–96 °C corr.). Yield 79%.

A sample of the *N*-carbobenzoxy-*S*-proline-*p*-nitrophenylester product (20 g, 0.054 mol) was dissolved in warm absolute ethanol (400 cm^3) and aqueous methylamine (25–30%, 40 cm^3) was added and the solution stirred for 12 h. The solvent then was removed on a rotary evaporator, the yellow residue was redissolved in chloroform (500 cm^3) and to this solution was added neutral activated alumina (50 g) and the mixture stirred. The alumina was filtered off by suction through a pad of activated alumina and the solvent was removed at reduced pressure to leave a colourless oil. Yield 14.0 g (99%). NMR: solvent DMSO-d_6, ppm; 1.82 (m, 3H); 2.12 (m, 1H); 2.59 (t, 3H); 3.46 (m, 2H); 4.15 (dt, 1H); 5.06 (q, 2H); 7.36 (m, 5H); 7.83 (t, 1H).

N'-Methyl-2(S)-aminomethylpyrrolidine

The cleavage of the N-carbobenzoxy group was carried out by a modification of the method of Ben-Ishai and Berger [9]. To *N*-carbobenzoxy-*S*-proline-*N'*-methylamide (14 g, 0.053 mol) in a round-bottom flask was added dry HBr (36% in acetic acid, 50 g, 36 cm^3) and the mixture warmed on a steam-bath until fumes started to evolve. After the reaction had ceased, the solvent was removed under reduced pressure at 70 °C on a rotary evaporator, leaving a crystalline residue. Acetone (20 cm^3) was added and the crystalline HBr salt was collected at the pump, washed with a minimum amount of acetone and air dried. Yield 9.56 g (86%). NMR: solvent D_2O, ppm; 2.08 (m, 3H); 2.44 (m, 1H); 2.82 (s, 3H); 3.46 (m, 2H); 4.40 (m, 1H).

This colourless salt was neutralized with excess 10 M NaOH and extracted with chloroform (3×50 cm^3).

*br = broad, d = doublet, s = singlet, t = triplet, m = multiplet, q = quartet.

The extracts were then dried with anhydrous Na_2SO_4 and the solvent removed at reduced pressure to leave the amide compound as a colourless oil. NMR: solvent DMSO-d_6, ppm; 1.62 (m, 3H); 1.94 (m, 1H); 2.62 (d, 3H); 2.82 (m, 2H); 3.00 (br, 1H); 3.50 (dd, 1H); 7.90 (br, 1H). The method used for the reduction of the secondary amide was adapted from a published procedure [10]. The oil obtained above was dissolved in sodium-dried THF (150 cm^3), cooled to ice temperature and excess lithium aluminium hydride (7.0 g, 0.18 mol) was added slowly. The resulting mixture was stirred for 1 h and then left to slowly warm to room temperature, after which is was refluxed for 48 h. The mixture was then cooled and a solution of water (12 cm^3) in THF (100 cm^3) was added slowly with vigorous stirring. The resulting paste was filtered off under suction through a pad of celite and the solid residue was then washed with two 150 cm^3 portions of hot THF. The filtrate and washings were combined, and removal of the solvent on a rotary evaporator left the diamine as a pale-yellow oil. Yield 3.62 g (69%). NMR: solvent DMSO-d_6 + 1 drop D_2O, ppm; 1.28 (m, 1H); 1.64 (m, 2H); 2.28 (s, 3H); 2.38 (d, 1H); 2.72 (m, 2H); 3.04 (m, 1H).

N,N'-Di(2-picolyl)-N'-methyl-2(S)-aminomethylpyrrolidine disesquihydrate, S-PicpyrrMe·2½H_2O

N'-Methyl-2(*S*)-aminomethylpyrrolidine (3.62 g, 0.032 mol) was suspended in water (150 cm^3) and 2-picolyl chloride hydrochloride (Aldrich, 10.50 g, 0.064 mol) was added. The pH of the mixture was adjusted to, and maintained at, 9.0 by dropwise addition of 2 M NaOH until the reaction was complete (*c.* 48 h). The pH then was increased to 13 and the crude ligand extracted into dichloromethane (4 × 50 cm^3). The extract was dried over anhydrous Na_2SO_4 and the solvent removed on a rotary evaporator. Purification of the

TABLE 1. Summary of crystal data, data collection and structure refinement for the complexes Λ-α_1-[Co(*S*-picpyrrMe)L]$(ClO_4)_2 \cdot xH_2O$

Compound			
L	*R*-alaninato		*S*-alaninato
x	0		0.5
Crystal data			
Formula	$C_{21}H_{30}N_5O_{10}Cl_2Co$		$C_{21}H_{31}N_5O_{10.5}Cl_2Co$
M_r	642.3		651.3
System	monoclinic		orthorhombic
Space group	$P2_1$ (No. 4)		$P2_12_12_1$ (No. 19)
a (Å)	10.888(4)		10.580(8)
b	10.243(4)		14.391(8)
c	12.365(6)		18.078(7)
β (°)	109.37(3)		
U (Å^3)	1301.0		2752.5
D_m (flotation)			1.56
Z	2		4
D_c (g cm^{-3})	1.640		1.572
μ (Mo Kα) (cm^{-1})	9.59		9.09
F(000)	664		1348
Data collection			
Crystal size (mm)	0.12 × 0.36 × 0.52		0.32 × 0.21 × 0.26
Temperature (°C)	−130		−120
Instrument	Nicolet XRD P3 [12] four-circle diffractometer		
Radiation	graphite monochromatised Mo Kα		
2θ (min., max.)	5.0, 50.0		5.0, 50.0
Absorption correction		empirical [12]	
Transmission (min., max.)	0.829, 0.897		0.670, 0.970
Total no. reflections	2544		2774
No. with $I > 3\sigma(I)$	1662		1771
Refinement			
Least-squares		full-matrix	
Min. Fn.		$\sigma w\Delta^2$	
Weighting scheme	counter statistics		unity
Anisotropic		all non-hydrogen atoms	
H atoms		included, not refined	
R	0.046		0.046
$R'[(\Sigma w\Delta^2/\Sigma w\|F_o\|^2)^{1/2}$	0.024		0.050
Final Δ map (ρ, e Å^{-3})	<|0.55|		<|0.5|

TABLE 2. Final atomic coordinates (fractional $\times 10^4$) for the non-hydrogen atoms with e.s.d.s in parentheses for the crystal structures of Λ-α_1-[Co(*S*-picpyrrMe)(L)]$(ClO_4)_2$

	L=*R*-alaninato			L=*S*-alaninato[a]		
	x	*y*	*z*	*x*	*y*	*z*
Co	3549(1)	2500	2784(1)	−140.2(10)	574.5(9)	206.1(7)
N(11)	2106(7)	3591(7)	2880(6)	835(8)	67(6)	−620(4)
N(21)	4999(7)	1436(8)	2698(6)	−1067(8)	1080(5)	1047(5)
N(1)	3727(7)	3927(7)	1752(6)	1033(8)	−217(5)	803(4)
N(2)	2589(6)	1517(8)	1403(6)	−1382(6)	−467(5)	293(4)
N(3)	3403(6)	1268(7)	3946(5)	−1094(7)	1416(5)	−433(4)
O(31)	4633(5)	3482(6)	4031(5)	1067(6)	1540(4)	255(4)
O(32)	5365(5)	3630(6)	5942(5)	1790(6)	2766(5)	−371(3)
C(31)	4756(8)	3036(9)	5036(9)	979(8)	2178(6)	−261(5)
C(32)	4190(8)	1699(8)	5106(8)	−216(10)	2145(6)	−745(5)
Me(3)	3429(8)	1658(9)	5956(7)	−826(9)	3097(7)	−785(7)
C(11)	1116(9)	3230(8)	3221(7)	539(9)	35(7)	−1345(5)
C(12)	302(9)	4142(11)	3477(8)	1387(11)	−260(7)	−1880(6)
C(13)	537(10)	5438(10)	3346(9)	2588(10)	−531(9)	−1665(6)
C(14)	1515(10)	5822(10)	2930(10)	2897(9)	−500(8)	−927(5)
C(15)	2281(9)	4839(8)	2703(8)	2018(9)	−223(6)	−424(6)
C(16)	3334(10)	5139(9)	2244(8)	2289(9)	−193(7)	403(6)
Me(1)	5006(8)	4104(10)	1610(8)	1247(10)	63(7)	1579(6)
C(1)	2720(8)	3684(9)	599(8)	530(9)	−1184(7)	771(6)
C(2)	2755(8)	2216(10)	388(7)	−900(11)	−1159(7)	865(6)
C(3)	1587(9)	1771(10)	−693(8)	−1531(10)	−2096(7)	691(7)
C(4)	685(9)	962(9)	−194(8)	−2278(10)	−1944(8)	−23(7)
C(5)	1132(7)	1325(9)	1069(7)	−1712(10)	−1051(7)	−368(6)
C(21)	6282(8)	1636(9)	3311(7)	−702(9)	1799(6)	1484(6)
C(22)	7211(9)	739(10)	3221(8)	−1429(10)	2085(8)	2084(6)
C(23)	6854(9)	−332(10)	2525(8)	−2519(12)	1607(7)	2251(5)
C(24)	5532(9)	−514(9)	1888(8)	−2898(10)	878(7)	1795(5)
C(25)	4656(9)	387(9)	2032(8)	−2188(8)	654(7)	1183(5)
C(26)	3203(8)	193(9)	1493(8)	−2555(9)	−25(7)	599(5)
O(w)				2425(14)	2283(9)	2366(8)
Cl(1)	7567(2)	2333(3)	567(2)	1109(2)	4409(2)	1646(2)
O(1a)	7989(5)	2583(8)	−409(5)	2478(6)	4418(7)	1697(4)
O(1b)	7625(6)	3527(6)	1179(5)	659(8)	5330(6)	1727(6)
O(1c)	8383(6)	1384(8)	1291(6)	760(9)	4031(7)	947(5)
O(1d)	6240(5)	1871(6)	135(5)	627(9)	3834(8)	2233(5)
Cl(2)	−787(2)	4062(3)	6046(2)	5276(3)	3258(2)	3427(2)
O(2a)	−1193(8)	3972(8)	7037(6)	6627(8)	3271(7)	3302(5)
O(2b)	−638(6)	5431(6)	5774(6)	4855(13)	2313(8)	3361(10)
O(2c)	−1739(6)	3470(6)	5094(5)	5113(13)	3484(11)	4231(8)
O(2d)	411(5)	3391(6)	6267(6)	4500(14)	3867(11)	3035(9)
O(2e)				5104(25)	3243(18)	3485(20)
O(2f)				4853(29)	2983(29)	2648(15)
O(2g)				4735(33)	2786(25)	3937(16)

[a]For the *S*-alaninato structure the occupancies for the atoms O(2b), O(2c), O(2d) are 0.67 and for O(2e), O(2f), O(2g) are 0.33.

ligand was effected by applying it to a column of neutral activated alumina (3×40 cm) and eluting with chloroform. The fast moving yellow band was collected and the solvent removed at reduced pressure to give the product as a pale-yellow oil. Yield 3.86 g (35%). NMR: solvent DMSO-d_6 ppm; 1.62 (m, 3H); 1.94 (m, 1H); 2.21 (q, 1H); 2.23 (s, 3H); 2.36 (q, 1H); 2.54 (m, 1H); 2.82 (m, 2H); 3.48 (d, 1H); 3.64 (s, 2H); 4.28 (d, 1H); 7.26 (dt, 2H); 7.44 (dt, 2H); 7.77 (dt, 2H); 8.50 (d, 2H). Anal. Calc. for $C_{18}H_{29}N_4O_{2.5}$: C, 63.3; H, 8.6; N, 16.4. Found: C, 63.5; H, 7.3; N, 16.1%.

Λ-α-[Co(S-picpyrrMe)Cl₂]Cl·5½H₂O

$CoCl_2 \cdot 6H_2O$ (2.01 g, 8.43 mmol) was dissolved in absolute ethanol (100 cm^3) and was added slowly to a stirred solution of *S*-picpyrrMe·$2\frac{1}{2}H_2O$ (2.9 g, 8.43 mmol) in absolute ethanol (100 cm^3) and concentrated HCl (4 cm^3). The rate of addition was controlled so

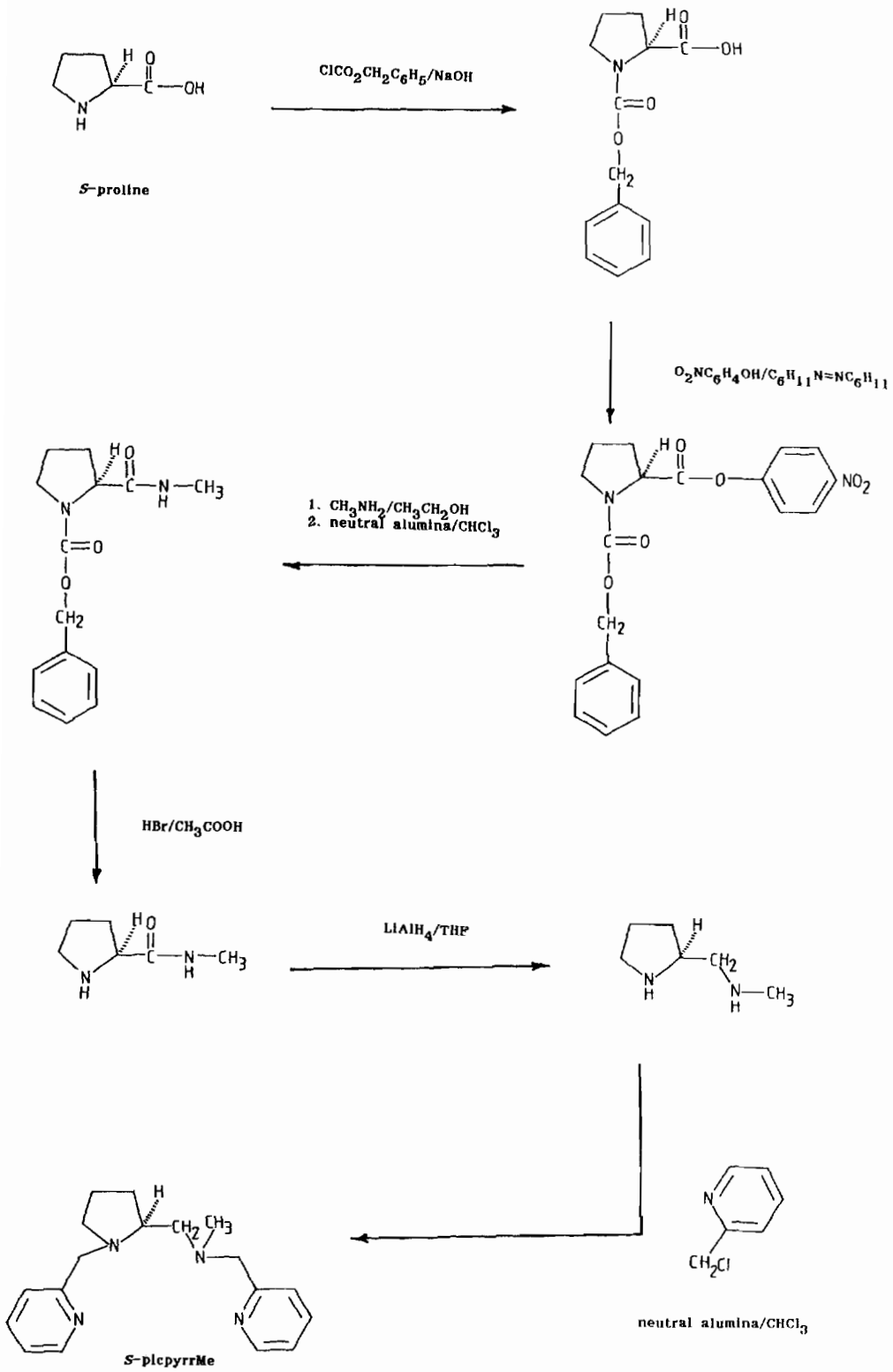


Fig. 1. The synthetic scheme for the preparation of *N*,*N*′-di(2-picolyl)-*N*′-methyl-2(*S*)-aminomethylpyrrolidine.

that any solid produced was allowed to dissolve before any further addition took place. When the addition was complete the mixture was stirred for 0.25 h after which 30% wt./vol. hydrogen peroxide (2 cm^3) was added and stirring was continued for a further 0.5 h. The resulting fine blue–green crystalline product was collected at the pump, washed with absolute ethanol (2×10 cm^3), acetone (10 cm^3) and air dried. The mother

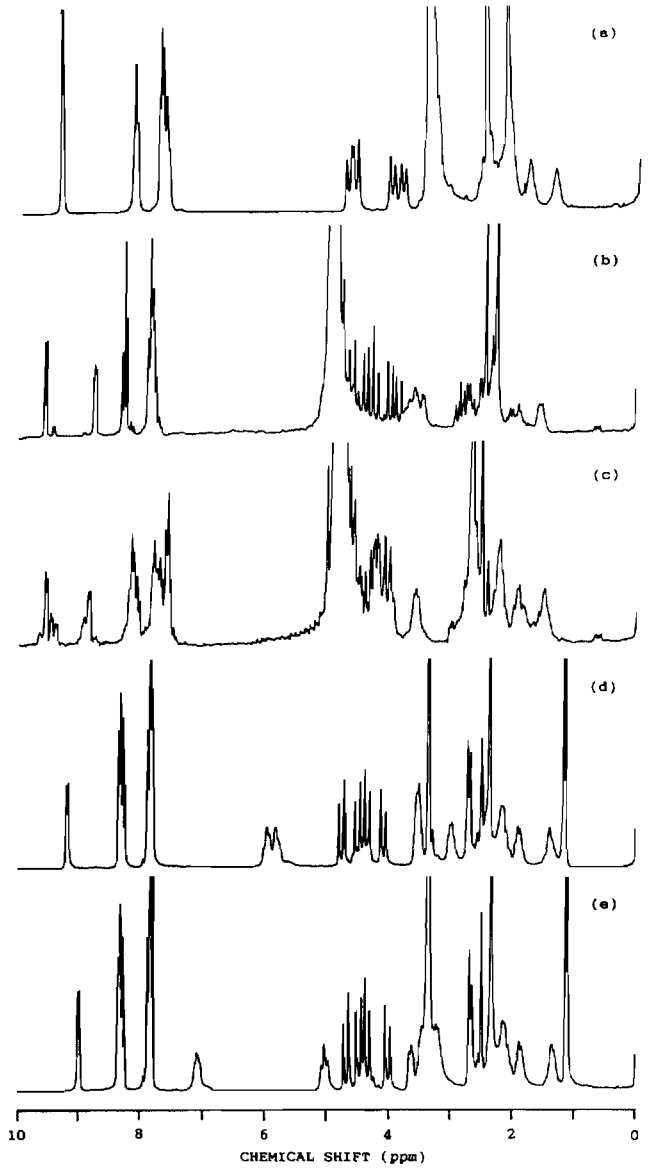


Fig. 2. The ^{1}H NMR spectra of the picpyrrMe cobalt(III) complexes. (a) *Λ*-*α*-[Co(*S*-L)Cl_2]$^+$, solvent: DMSO-d_6; (b) *Λ*-*α*-[Co(*S*-L)(Cl)(D_2O)]$^{2+}$, solvent: D_2O; (c) *Λ*-*α*-[Co(*S*-L)(NO_2)$_2$]$^+$, reaction solution; (d) *Λ*-α_1-[Co(*S*-L)(*R*-ala)]$^{2+}$, solvent: DMSO-d_6; (e) *Λ*-α_1-[Co(*S*-L)(*S*-ala)]$^{2+}$, solvent: DMSO-d_6.

liquor and washings were combined and reduced in volume to c. 40 cm^3 on a rotary evaporator at 50 °C and then left at 0 °C for 12 h. An additional product was collected as above. Both product crops have identical ^{1}H NMR spectra and chiroptical properties. Yield: 2.93 g (62%). *Anal.* Calc. for $C_{18}H_{35}N_4O_{5.5}Cl_3Co$: C, 38.5; H, 6.3; N, 10.0. Found: C, 38.5; H, 4.4; N, 9.9%.

The low hydrogen analyses obtained for this complex may be attributed to the loss of water after weighing but prior to combustion, as has been found for related complexes [11].

TABLE 3. Electronic spectral data for picpyrrMe metal complexes

Complex[a]	λ (nm)	$\epsilon \times 10^{-3}$ (dm^2 mol^{-1})	Δε (dm^2 mol^{-1})
Λ-*α*-[Co(*S*-L)Cl_2]$^+$	692	3.21	
(Solvent: conc. HCl)	661	3.21	
	637		−6.49
	561	1.21	
	555		+10.74
	480		+1.12
	420		+11.64
	345		−31.33
	295		+38.03
Λ-*α*-[Co(*S*-L)Cl(H_2O)]$^{2+}$	610		−4.07
(Solvent: H_2O)	539	0.78	
	525		+8.32
	460		+1.30
	390		+8.87
	330		−3.69
	290	26.72	
Λ-*α*-[Co(*S*-L)(NO_2)$_2$]$^+$	555		+2.20
(Solvent: methanol)	517	4.00	
	505		−9.16
	460		+6.38
	405		−19.62
	349	60.39	
	345		−85.01
	320		−49.05
	282	75.82	
Λ-α_1-[Co(*S*-L)(*R*-ala)]$^{2+}$	500		+20.45
(Solvent: H_2O)	491	1.03	
	405		+0.24
	385		+0.97
	360	1.48	−0.49
	282	24.20	
Λ-α_1-[Co(*S*-L)(*S*-ala)]$^{2+}$	497		+18.66
(Solvent: H_2O)	486	0.99	
	415		−0.91
	390		−0.15
	355		−2.43
	335		−1.52
	279	21.96	

[a]L = picpyrrMe.

Λ-α$_1$-[Co(S-picpyrrMe)(R-ala)](ClO$_4$)$_2$

A solution of *Λ*-*α*-[Co(*S*-picpyrrMe)Cl_2]Cl·5½H_2O (0.25 g, 0.45 mmol) and *R*-alanine (Sigma, 0.16 g, 1.80 mmol) in water (40 cm^3) was heated on a steam bath until the volume had been reduced to *c.* 20 cm^2, saturated sodium perchlorate solution (1 cm^3) was added and the mixture left to stand for 12 h. The resulting dark-orange crystals were collected at the pump, washed with a few drops of ice-cold water then with a minimum amount of absolute ethanol and air dried. Yield 0.13 g (45%). These crystals were used in the X-ray analysis reported below. The mother liquor was left to slowly evaporate to produce a further crop of crystals which were collected as above. Yield 0.15 g (52%). Both crops of crystals had identical ^{1}H NMR spectra and chiroptical

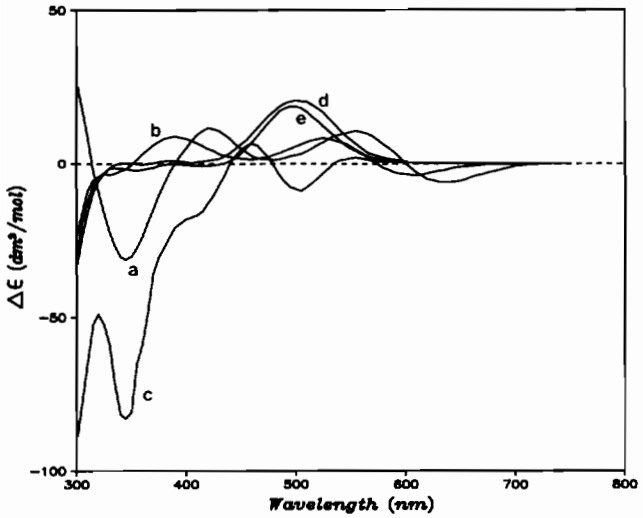


Fig. 3. The CD spectra of the picpyrrMe cobalt(III) complexes. (a) Λ-α-[Co(*S*-L)Cl_2]$^+$, solvent: 10 M HCl; (b) Λ-α-[Co(*S*-L)(Cl)(H_2O)]$^{2+}$, solvent: H_2O; (c) Λ-α-[Co(*S*-L)(NO_2)$_2$]$^+$, solvent: MeOH; (d) Λ-α_1-[Co(*S*-L)(*R*-ala)]$^{2+}$, solvent: H_2O; (e) Λ-α_1-[Co(*S*-L)(*S*-ala)]$^{2+}$, solvent: H_2O.

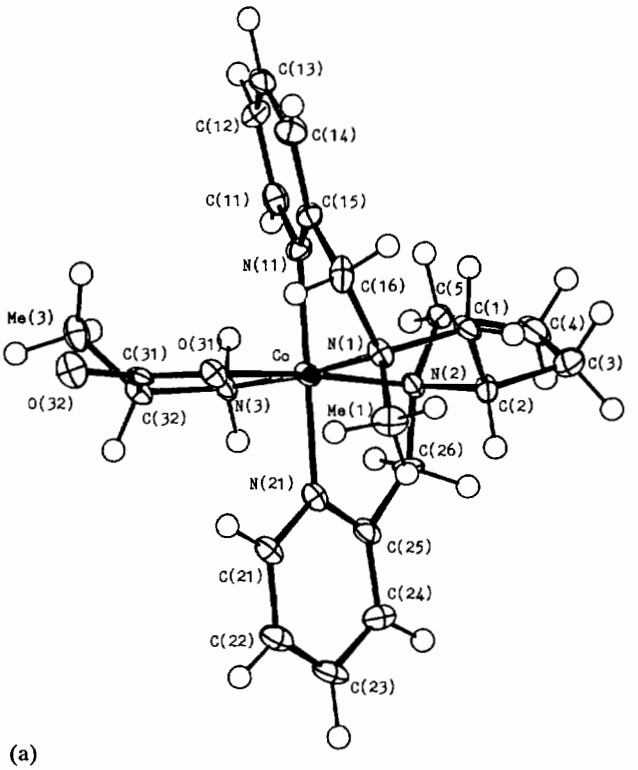
properties and the remaining mother liquor had qualitatively the same CD spectrum as solutions prepared from the solid products.

Λ-α_1-[Co(S-picpyrrMe)(S-ala)]$(ClO_4)_2 \cdot \frac{1}{2}H_2O$

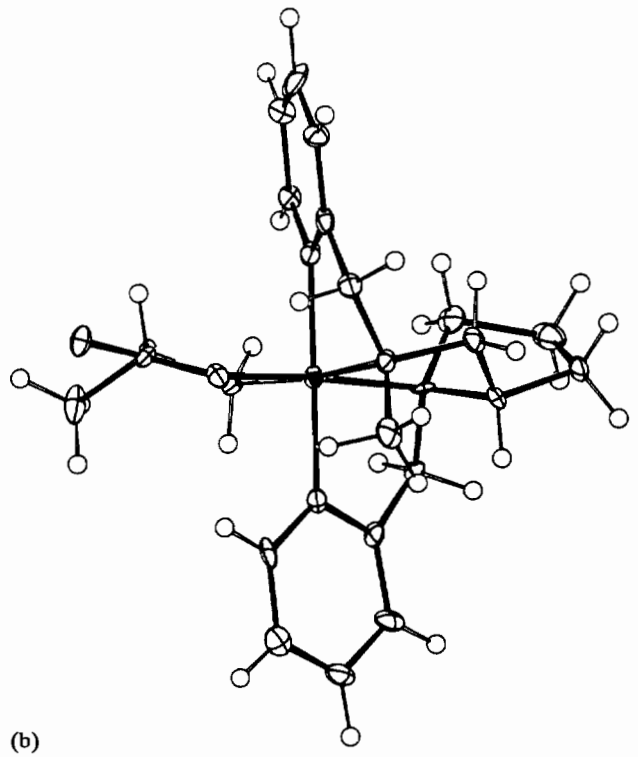
The synthesis above was repeated substituting *S*-alanine for *R*-alanine. Reduction of the reaction solution to near dryness resulted in the production of an oil, which was dispersed with a small amount of ethanol. Over a period of a few weeks deep-orange crystals appeared, which were collected at the pump, washed with a few drops of cold water and air dried. These crystals were used for the structure analysis reported below. Yield 0.04 g (14%).

Crystal structure determinations of Λ-α_1-[Co(S-picpyrrMe)(R-ala)]$(ClO_4)_2$ *and* Λ-α_1-[Co(S-picpyrrMe)(S-ala)]$(ClO_4)_2 \cdot \frac{1}{2}H_2O$

Crystal data, data collection and refinement details [12] are summarized in Table 1. The structures were solved by the heavy-atom method. Difference maps indicated the approximate positions of hydrogen atoms of the cations, their coordinates were optimised assuming C–H, N–H 1.0 Å and the appropriate geometries of the atoms to which they are bonded. For the *S*-ala complex these maps indicated disorder in the positions for the oxygen atoms of one of the perchlorate ions. The positions and peak heights were consistent with two ions being present in the approximate ratio of 2:1, and this formed the basis for the assignment of the occupancies for the oxygen atoms. The maps further showed a peak for the lattice water molecule, the height being consistent with the hemihydrate formulation.



(a)



(b)

Fig. 4. Perspective drawings of the Λ-α_1-[Co(*S*-picpyrrMe)L]$^{2+}$ cations: (a) L = *R*-ala, (b) L = *S*-ala. Thermal ellipsoids are drawn to include 35% probability. The same atom labelling scheme is used in both structures.

TABLE 4. Selected bond lengths and angles with e.s.d.s in parentheses for the complex cations Λ-α_1-[Co(*S*-picpyrrMe)(L)]$^{2+}$

	L=*R*-alaninato	L=*S*-alaninato
Distances (Å)		
Co–N(11)	1.963(7)	1.957(8)
Co–N(21)	1.951(7)	1.950(8)
Co–N(1)	1.991(7)	2.001(8)
Co–N(2)	1.959(7)	1.999(8)
Co–N(3)	1.958(7)	1.954(7)
Co–O(31)	1.891(6)	1.890(6)
C(31)–O(31)	1.289(10)	1.312(10)
C(31)–O(32)	1.254(10)	1.221(10)
C(31)–C(32)	1.516(10)	1.538(13)
C(32)–N(3)	1.474(11)	1.510(12)
C(32)–Me(3)	1.539(11)	1.516(13)
N(21)–C(25)	1.329(11)	1.357(12)
C(25)–C(26)	1.512(12)	1.491(14)
N(2)–C(26)	1.499(10)	1.500(11)
N(2)–C(5)	1.513(9)	1.502(12)
N(2)–C(2)	1.506(10)	1.523(13)
C(1)–C(2)	1.529(13)	1.523(14)
C(2)–C(3)	1.577(11)	1.537(14)
C(3)–C(4)	1.560(12)	1.529(16)
C(5)–C(4)	1.520(11)	1.549(14)
N(1)–Me(1)	1.472(10)	1.478(13)
N(1)–C(1)	1.504(10)	1.491(13)
N(1)–C(16)	1.505(11)	1.512(12)
N(11)–C(15)	1.321(11)	1.366(12)
C(15)–C(16)	1.470(12)	1.522(15)
Angles (°)		
N(11)–Co–N(21)	179.2(3)	178.3(4)
N(1)–Co–N(3)	172.8(3)	172.7(3)
N(2)–Co–O(31)	172.9(3)	172.7(3)
N(11)–Co–N(1)	82.6(3)	82.6(3)
N(21)–Co–N(2)	82.7(3)	83.6(3)
N(1)–Co–N(2)	87.5(3)	84.5(3)
O(31)–Co–N(3)	85.7(3)	85.5(3)
N(11)–Co–N(2)	98.0(3)	97.3(3)
N(11)–Co–N(3)	93.5(3)	93.0(3)
N(11)–Co–O(31)	86.8(3)	87.3(3)
N(21)–Co–N(1)	97.0(3)	96.0(3)
N(21)–Co–N(3)	86.8(3)	88.3(3)
N(21)–Co–O(31)	92.5(3)	91.6(3)
N(1)–Co–O(31)	88.0(3)	88.5(3)
N(2)–Co–N(3)	99.1(3)	99.9(3)
Co–N(3)–C(32)	111.0(5)	109.5(6)
Co–O(31)–C(31)	115.8(6)	115.6(6)
O(31)–C(31)–O(32)	123.0(9)	123.4(8)
O(31)–C(31)–C(32)	117.5(9)	116.2(8)
O(32)–C(31)–C(32)	119.4(9)	120.4(8)
N(3)–C(32)–Me(3)	112.7(7)	112.5(7)
N(3)–C(32)–C(31)	109.3(8)	108.3(5)
C(31)–C(32)–Me(3)	112.6(8)	110.4(8)
Co–N(1)–C(1)	106.9(5)	106.8(6)
Co–N(1)–C(16)	104.2(5)	105.9(6)
Co–N(1)–Me(1)	117.6(6)	116.8(6)
C(1)–N(1)–C(16)	107.7(7)	110.2(8)
C(1)–N(1)–Me(1)	109.1(7)	108.5(7)
C(16)–N(1)–Me(1)	110.7(7)	108.2(8)
Co–N(2)–C(2)	107.7(5)	108.9(6)
Co–N(2)–C(26)	107.7(5)	104.7(6)
Co–N(2)–C(5)	120.8(5)	120.6(6)
Angles (°)		
C(2)–N(2)–C(26)	108.5(7)	107.7(7)
C(2)–N(2)–C(5)	103.8(6)	104.6(7)
C(26)–N(2)–C(5)	107.7(7)	109.7(7)
N(1)–C(1)–C(2)	105.8(7)	109.1(8)
C(1)–C(2)–N(2)	108.0(7)	105.8(9)
C(1)–C(2)–C(3)	111.7(8)	112.8(9)
N(2)–C(2)–C(3)	106.4(7)	106.8(9)
C(2)–C(3)–C(4)	104.7(7)	105.7(9)
C(3)–C(4)–C(5)	104.3(8)	105.0(9)
C(4)–C(5)–N(2)	105.2(7)	103.5(8)
Co–N(11)–C(15)	112.2(7)	113.5(7)
N(11)–C(15)–C(16)	116.1(9)	114.8(9)
C(15)–C(16)–N(1)	110.2(7)	107.6(8)
Co–N(21)–C(25)	114.8(6)	114.3(7)
N(21)–C(25)–C(26)	114.7(8)	113.3(8)
C(25)–C(26)–N(2)	106.8(7)	108.8(7)

Neutral atom scattering factors, corrected for anomalous dispersion, were taken from ref. 13, and all calculations were carried out on FACOM M340S or M380S computers with programmes written by F.S.S. The final atomic coordinates of the non-hydrogen atoms for the two compounds are given in Table 2.

Results and discussion

The six-part synthetic scheme used for the preparation of the ligand is shown in Fig. 1. At each step in the synthesis the authenticity of the product was confirmed by ^{1}H NMR analysis. The tetradentate was produced in 19% overall yield based on the *S*-proline precursor. Although this yield is relatively low, it is nevertheless much higher than that which was achieved for the synthesis of the optically active ligands picbn and picstien [1, 3], where the respective diamine precursors first require synthesis and subsequent resolution. The use of coupling, substitution and reduction reactions that do not involve the asymmetric carbon atom of *S*-proline avoids ambiguity as to the optical purity of the ligand, and in any case this has been confirmed by the X-ray analysis of the amino acid complexes, as detailed below.

The *cis*-dichloro cobalt(III) complex was produced and isolated under essentially non-aqueous conditions. This complex, like its picchxnMe$_2$ [4] and picpnMe$_2$ [7] analogues, rapidly aquates to produce the characteristic purple Λ-α-[Co(*S*-picpyrrMe)(H$_2$O)Cl]$^{2+}$ species; this shows a molar conductivity of 240 S cm^{-1} immediately on dissolution rising to a constant 326 S cm^{-1} with $t_{1/2} \sim 1$ min.

The *R*- and *S*-alaninato complexes were readily obtained, but attempts to isolate solid dinitro and oxalato complexes were unsuccessful. However, NMR and CD

TABLE 5. Intermolecular contacts[a] with e.s.d.s in parentheses

Λ-α_1-[Co(*S*-picpyrrMe)(*R*-ala)]$(ClO_4)_2$			
Proposed hydrogen bonding			
N(3)H(N3a)···O(32^{i})	2.999(9)	N(3)H(N3b)···O(2b^{ii})	3.257(9)
Contact distances <3.3 Å			
C(26)···O(1a^{i})	3.079(11)	C(23)···O(1c)	3.245(10)
O(32)···C(25^{iii})	3.091(12)	C(11)···O(2b^{ii})	3.245(10)
C(5)···O(1c^{iv})	3.095(10)	C(14)···O(2a^{vi})	3.247(11)
Me(1)···O(1b)	3.126(10)	O(32)···C(24^{iii})	3.265(11)
C(22)···O(1c)	3.128(11)	C(3)···O(2c^{vi})	3.281(11)
C(23)···O(2d^{i})	3.140(10)	N(3)···O(2a^{ii})	3.245(10)
C(21)···O(2e^{v})	3.143(10)		
Λ-α_1-[Co(*S*-picpyrrMe)(*S*-ala)]$(ClO_4)_2\cdot\frac{1}{2}H_2O$			
Proposed hydrogen bonding			
N(3)H(N3a)···O(32^{vii})	2.92(1)	O(w)···O(1d)	2.94(2)
N(3)H(N3b)···O(1a^{vii})	2.99(1)	O(w)···O(2b)	3.14(2)
		O(w)···O(2f)	2.81(3)
Contact distances <3.3 Å			
C(13)···O(w^{viii})	3.07(2)	C(13)···O(1b^{x})	3.26(1)
C(23)···O(2a^{ix})	3.19(1)	C(23)···O(1b^{xi})	3.26(1)
O(32)···C(24^{x})	3.25(1)	C(14)···O(1b^{x})	3.27(1)
C(12)···O(2b^{viii})	3.26(1)	C(4)···O(2g^{xi})	3.28(3)

[a]Roman numeral superscripts refer to the following equivalent positions relative to x, y, z: $^{i}1-x, y-\frac{1}{2}, 1-z$; $^{ii}-x, y-\frac{1}{2}, 1-z$; $^{iii}1-x, y-\frac{1}{2}, 1-z$; $^{iv}x-1, y, z$; $^{v}1+x, y, z$; $^{vi}-x, \frac{1}{2}+y, 1-z$; $^{vii}x-\frac{1}{2}, \frac{1}{2}-y, -z$; $^{viii}\frac{1}{2}-x, -y, z-\frac{1}{2}$; $^{ix}x-1, y, -z$; $^{x}\frac{1}{2}+x, \frac{1}{2}-y, -z$; $^{xi}-x, \frac{1}{2}-y, \frac{1}{2}-z$.

spectra for the dinitro complex were obtained by reaction of the *cis*-dichloro complex with a large excess of sodium nitrite in D_2O or methanol, respectively. The ^1H NMR spectra of the complexes (Fig. 2) show, by virtue of their simplicity in the aromatic region [6], that each has an α topology. The spectra of the alaninate complexes show that in each case there is only one isomer present, which contrasts with the analogous picpnMe$_2$ product, in which both the α_1 and α_2 isomers co-crystallise [7].

The electronic spectral data for the complexes are given in Table 3 and Fig. 3. The metal ion absolute configurations are assigned on the basis of these CD spectral features and in comparison with those for which the structure determinations are reported herein (*vide infra*) and the results of previous work [4, 7].

Drawings [14] of the two aminoacidate cations derived from the crystal structure analyses are shown in Fig. 4, and their selected bond lengths and angles are given in Table 4. The molecular structures are closely similar, particularly that of each Co(*S*-picpyrrMe) fragment. The absolute configurations of the metal ions and amino acid and tetradentate asymmetric carbons, and the ligands' α geometries, are all confirmed by these analyses. The N(1) amine nitrogen atoms have *S* absolute configuration, as designated by the Cahn–Ingold–Prelog convention [15]. Each cation has pseudo two-fold symmetry if the pyrrole ring and the alaninate ligand are disregarded. A like arrangement is found in the structures of the analogous picchxnMe$_2$ [4] and picpnMe$_2$ [7] complexes and the intermolecular discriminations that determine the absolute configurations of the cobalt atoms in those latter structures are again applicable to the present ones. In fact, the relative inflexibility of the pyrrolidine ring in picpyrrMe should serve to enhance these discriminations. Again the Co–N(tert-amine) distances, with the exception of Co–N(2) for the *R*-ala complex, are lengthened by c. 0.04 Å compared with similar complexes of N-unsubstituted ligands [16], in which the β topology is always adopted.

A difference in the conformation of the alaninate chelate rings is apparent in the two cations. The *S*-alaninate ring is relatively unstrained with a puckered conformation, whereas that of the *R*-alaninate is severely flattened; the average and maximum deviations from the respective mean planes are 0.103 and 0.148, and 0.028 and 0.048 Å. This situation is analogous to that found in the Λ- and Δ-[Ru(bipy)$_2$(*S*-ala)]$^+$ species [17], where the enantiomeric form of Δ-*S*-ala would correspond to the present Λ-*R*-ala complex. Again, to alleviate a steric interaction between the methyl group and the N(11) pyridyl ring, rotation about the N(3)–C(32) bond occurs so as to orientate the methyl group into an essentially equatorial position, and as a consequence flattening of the chelate ring results. A similar ring flattening is observed in the complexes Λ-α-[Co(*S*,*S*-picchxnMe$_2$)(*R*-ala)]$(ClO_4)_2$ [4] and Δ-α-[Co(*R*-picpnMe$_2$)(*S*-ala)]$(ClO_4)_2$ [7], presumably for the same reason.

In both of the present structures, the alaninate nitrogen atom acts as a donor centre for hydrogen bonding, the details of which are given in Table 5 together with other close intermolecular contacts. It is possible for these α-alaninate species to adopt two different geometric forms, designated α_1 or α_2, as defined for the complexes of the analogous picpnMc$_2$ [7], where both isomers co-crystallised in varying ratio. For the present ligand, however, both the *R*-ala or *S*-ala complexes are shown by their respective ^{1}H NMR spectra to be isomerically pure. In both cases, the crystal structures show this to be the α_1 forms, which corresponds to the major isomer of the analogous picpnMe$_2$ complex [7]. The α_1-*R*-ala complex isolated here, although demonstrating some internal steric strain in its molecular structure, was obtained in almost quantitative yield. Hence, it is possible that even though both tetradentates are stereospecific in their coordination behaviour, the inherent lower degree of flexibility in picpyrrMe compared with that in picpnMe$_2$ may cause enhanced discrimination in controlling coordination of other unsymmetric ligands. Indeed this very well may be the reason why only α_1 isomers were obtained.

Supplementary material

Lists of anisotropic thermal parameters, hydrogen atom parameters, complete Tables of bond lengths and angles and observed and calculated structure factors are available from F.S.S. on request.

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