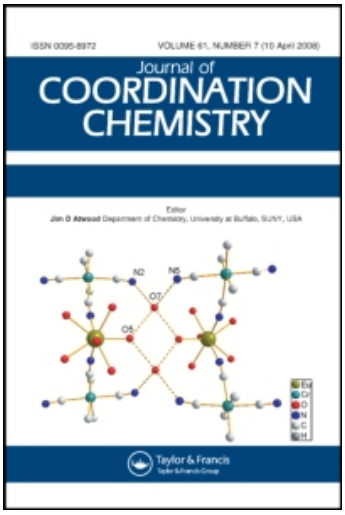

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CHIRAL METAL COMPLEXES. PART 52. THE STRUCTURES OF CO-CRYSTALLISED DIASTEREOISOMERIC DNA PROBES SHOWING INTRAMOLECULAR π-π INTERACTIONS

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CHIRAL METAL COMPLEXES. PART 52.* THE STRUCTURES OF CO-CRYSTALLISED DIASTEREOISOMERIC DNA PROBES SHOWING INTRAMOLECULAR $\pi-\pi$ INTERACTIONS

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The structure of Δ-$\alpha_{1,2}$-[Co(*R*-picpnMe$_2$)(*S*-phe)](ClO$_4$)$_2\cdot$H$_2$O where *R*-picpnMe$_2$ is *N*,*N*′-dimethyl-3*R*-methyl-1,6-di(2-pyridyl)-2,5-diazahexane and *S*-phe is the *S*-phenylalaninate anion has been determined to be orthorhombic, space group $P2_12_12_1$, with $a=9.959(4)$, $b=15.919(7)$, $c=19.59(3)$ Å, $D_c=1.515$ Mg m^{-3} and $Z=4$. The structure was refined by least-squares methods to $R=0.050$ for 2328 independent reflections with $I>2\sigma(I)$ for diffractometer data collected at 293 K. The cobalt atom has the expected octahedral coordination with the N4 tetradentate adopting Δ-α topology and with the phenylalaninate ligand completing the coordination sphere. Two geometric isomers possible for the asymmetric complex, α_1 and α_2 (depending upon the relative mode of coordination of the aminoacidate relative to the *trans* orientation of the methyl group of the tetradentate), are observed to co-crystallise in a 1 : 1 ratio. In these species, the phenyl ring is weakly bonded to one of the pyridyl rings of the tetradentate, as has been found in a number of congeners. The *R*-phe analogue has also been synthesised. The perchlorate salt contains both possible isomers. NMR studies indicate that the $\pi-\pi$ interaction observed in the solid state for Δ-$\alpha_{1,2}$-[Co(*R*-picpnMe$_2$)(*S*-phe)]$^{2+}$ is preserved in solution.

Keywords: Cobalt(III); tetradentate; chiral complexes; van der Waals bonding; DNA; X-ray structure

* Part 51 is Ref. [1].

† Authors for correspondence.

INTRODUCTION

Much of our recent effort has been directed towards the development of chiral metal complexes which can discriminate, enantioselectively and stereoselectively, the helical forms of nucleic acids.[2] In this endeavour we have had occasion to investigate the subtle structural differences evident in complexes of general composition $[M(tetradentate)(bidentate)]^{n+}$. The primary function of the tetradentate is to control the overall handedness of the complex, i.e., with respect to Δ or Λ absolute configuration at the metal centre. Secondary functions include limiting isomerism and providing opportunities for incorporation of secondary substituents which may facilitate base-sequence selectivity. The bidentate component of the complexes reported here is an amino acid, which, by design features an aromatic ring intended for intercalation between the base pairs of nucleic acids.

Related complexes containing a tetradentate based upon the linear N_4 ligand *N,N'*-dimethyl-1,6-di(2-pyridyl)-2,5-diazahexane have been reported,[1] together with analogues containing 1,2-diaminocyclohexane in the central portion of the tetradentate ligand.[3,4] In each of these complexes, the aromatic ring of the amino acid side chain is bonded to one of the pyridyl rings of the tetradentate, both in the solid state and in solution. Such observations indicate the promise of this class of complex as probes of the structure of DNA in that the intramolecular bond is akin to that formed when aromatic species intercalate between the base pairs of the nucleic acid.

This paper further explores these kinds of complexes. We report here a study of the complexes Δ-$\alpha_{1,2}$-$[Co(R\text{-picpnMe}_2)(R^*\text{-phe})]^{2+}$ where *R*-picpnMe$_2$ is *N,N'*-dimethyl-3*R*-methyl-1,6-di(2-pyridyl)-2,5-diazahexane and phe is the phenylalaninate anion. The single-crystal X-ray structure of the co-crystallised *S*-phe isomers has been determined and the above-mentioned intramolecular $\pi-\pi$ interaction again is observed to exist in these cations.

EXPERIMENTAL

Electronic spectra were obtained using a Shimadzu UV-2100 spectrophotometer. Circular dichroism spectra were recorded on a Jasco J-500C spectropolarimeter. Proton NMR spectra were recorded on Varian 200 MHz Unity or Varian 300 MHz Unity Plus spectrometers in dmso-d_6. Chemical shifts are reported in ppm relative to TMS as internal standard. Δ-α-$[Co(R\text{-picpnMe}_2)Cl_2]Cl \cdot 5H_2O$ was synthesised using the method of Fenton *et al.*[5]

Δ-$\alpha_{1,2}$-[Co(*R*-picpnMe$_2$)(*S*-phe)](ClO$_4$)$_2$ · H$_2$O and Δ-$\alpha_{1,2}$-[Co(*R*-picpnMe$_2$)(*R*-phe)](ClO$_4$)$_2$

Δ-α-[Co(*R*-picpnMe$_2$)Cl$_2$]Cl · 5H$_2$O (0.5 g, 0.93 mmol) was dissolved in 50 cm^3 of water and warmed on a steam-bath. A warm solution of *R*-phenylalanine (0.77 g, 4.65 mmol) and 1 mol equivalent of NaOH solution (9.3 cm^3, 0.1 M) was added and the mixture heated for exactly 0.5 h at 70°C, then allowed to cool to room temperature before being applied to a Sephadex® CM-C25 cation exchange resin in the Na$^+$ cycle (longer reaction times or higher temperatures give lower yields). The adsorbed mixture was then eluted with aqueous 0.5 M NaCl. The sole red band which developed was collected in 8 fractions. Electronic and CD spectra of these were recorded before solid NaClO$_4$ was added to each fraction. Fractions were allowed to slowly evaporate at room temperature and after 1 month a very fine, orange, micro-crystalline product was collected in milligram quantities from all fractions except 1 and 2. The *S*-phenylalanine complex was synthesised in the same manner with 7 fractions being collected from the sole red band developed on the Sephadex® CM-C25 column. Fractions 4 and 7 yielded orange micro-crystalline solids of similar form to the *R*-phenylalanine products. However, fractions 3 and 6 produced flattened red prisms, with those of fraction 3 superior in form; these were chosen for the crystallographic analysis. Satisfactory microanalyses were obtained for all solids. Both α_1 and α_2 isomers are present in the solids. Thus we report only qualitative electronic spectroscopic data. For the *R*-phenylalanine complexes, the absorption maximum is at *ca* 494 nm and a negative CD extremum is observed at 495 nm. Corresponding wavelengths for the *S*-phenylalanine species are 492 and 517 nm, respectively; the CD is also negative at these wavelengths.

Crystal Structure of Δ-$\alpha_{1,2}$-[Co(*R*-picpnMe$_2$)(*S*-phe)](ClO$_4$)$_2$ · H$_2$O

The structure determination was performed on crystals of the Δ-α_1,α_2-*R*,*S* diastereoisomer grown from the third fraction of the sole red chromatographic band.

Crystal data: $C_{25}H_{32}N_5O_{11}Cl_2Co$, $M_r = 708.39$, space group, $P2_12_12_1$, $a = 9.959(4)$, $b = 15.919(7)$, $c = 19.59(3)$ Å, orthorhombic, $V = 3107(5)$ Å^3, $Z = 4$, $D_c = 1.515$ Mg m^{-3}, $F(000) = 1464$, μ(MoKα) = 0.79 mm^{-1}. Unit cell parameters were initially determined from single-crystal precession photographs using MoKα radiation and refined via a least-squares fit to diffractometer data. Data for the complex were collected at 293 K on an

Enraf-Nonius FAST area detector diffractometer using documented procedures.[6] Intensity data were determined using a crystal $0.30 \times 0.25 \times 0.05$ mm in size, for reflections in the θ range 2.08–25.09°. Intensities were corrected for Lorentz and polarisation effects but absorption corrections were not applied. A total of 12678 measured reflections were merged to give 4685 unique reflections of which 2328 had $I > 2\sigma(I)$ and these were used for the structure determination. The structure was solved by the heavy atom method using the programs SHELXS86[7] and SHELXS93[8] and refined by full-matrix least-squares techniques in which the function $\sum w(F_o^2 - F_c^2)^2$ was minimised. The weight for each reflection in the final cycles of refinement is given by $w = 1/[\sigma^2(F_o)^2 + (0.100P)^2]$ where $P = (\max(F_o^2, 0) + F_c^2)/3$, as defined by SHELXL93. This weighting scheme gives a uniform analysis of variance in terms of F_c^2. After anisotropic refinement of the structure excluding hydrogen atoms, all hydrogen atoms were positioned using the appropriate geometry and relevant C–H and N–H bond lengths; the accuracy of these positions was confirmed by a subsequent difference Fourier synthesis. Refinement was continued with hydrogen atoms riding on the atoms to which they are bonded, with fixed isotropic thermal parameters, and with ansiotropic temperature factors for all other atoms. The refinement process was terminated when the minimisation factor changed by $< 0.1\%$ and a final difference map showed no residual electron density greater than $|0.5|$ e Å^{-3}. The final R and R_w $[= \{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}^{1/2}]$ values were 0.050 and 0.109, respectively, for 2328 reflections with $I > 2\sigma(I)$. For all 4685 unique data, the corresponding values were 0.095 and 0.128, respectively.

RESULTS AND DISCUSSION

R-Picpn (3*R*-methyl-1,6-di(2-pyridyl)-2,5-diazahexane) is non-stereospecific in its mode of coordination to Co(III), with Λ-α, Λ-β, Δ-α and Δ-β topologies being observed for its complexes.[9–11] *N,N'*-Dimethylation of the picpn ligand, however, changes the mode of coordination to being stereospecifically Δ-α for *R*-picpnMe_2. The change in coordination strereospecificity has been attributed to a substituent vicinal effect whereby the picolyl ligand fragment energetically favours the apical position, where it is disposed anti to the methyl group.[12] Coordination of the unsymmetic tetradentate, however, removes formal C_2 symmetry and thus an unsymmetric bidentate can coordinate in two senses, α_1 or α_2, depending on the disposition of the bidentate in relation to the methyl group of the picpn ligand.[5] In *S*-alanine

congeners of the present complexes both isomers co-crystallised,[5] and so also is the case for the structure reported here. Subtle trends in the electronic absorption and CD spectra of fractions collected indicated only partial separation of the α_1/α_2 isomers on the Sephadex column. This is confirmed by ^{1}H NMR measurements (*vide infra*).

Table I lists final atomic coordinates for non-hydrogen atoms and Table II gives selected bonding and interatomic contacts for the complex. Calculated positions of the hydrogen atoms are given in Table III, because of their relevance to ^{1}H NMR spectroscopic studies of this complex. A stereo view[13] of the Δ-α_1,α_2-[Co(R-picpnMe$_2$)(S-phe)]$^{2+}$ cation illustrating the atom labelling scheme is shown in Figure 1.

TABLE I Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$). *U(eq)* is defined as one third of the trace of the orthogonalised *Uij* tensor

	x/a	*y/b*	*z/c*	*U(eq)*
Co	9997(1)	248(1)	9348(1)	29(1)
O(31)	9442(4)	−147(3)	8493(2)	38(1)
N(11)	8554(5)	−333(4)	9819(3)	31(1)
N(2)	11330(5)	−680(4)	9366(3)	39(2)
N(21)	11477(5)	835(4)	8903(3)	37(2)
N(1)	10542(5)	513(3)	10300(3)	36(2)
N(31)	8718(5)	1174(4)	9183(3)	32(2)
Cl(2)	10205(2)	3653(1)	9823(1)	43(1)
O(21)	9824(6)	4210(4)	9284(3)	75(2)
O(22)	9988(6)	4097(4)	10438(3)	72(2)
O(23)	9400(4)	2913(3)	9790(3)	56(2)
O(24)	11578(4)	3437(4)	9764(3)	66(2)
Cl(1)	9798(2)	−2289(1)	11448(1)	50(1)
O(11)	9633(6)	−1445(4)	11661(3)	68(2)
O(12)	9241(6)	−2397(5)	10798(3)	100(3)
O(13)	9116(8)	−2803(4)	11928(4)	100(2)
O(14)	11141(6)	−2490(5)	11416(4)	101(3)
C(1)	11357(6)	−221(5)	10545(4)	35(2)
C(15)	8349(6)	−94(5)	10464(4)	34(2)
C(2)	12215(7)	−522(5)	9963(4)	42(2)
C(31)	8391(7)	205(5)	8219(4)	39(2)
C(16)	9301(6)	565(4)	10705(4)	36(2)
C(11)	7699(7)	−915(5)	9552(4)	42(2)
O(32)	7832(5)	−78(4)	7697(3)	47(2)
C(12)	6701(8)	−1270(6)	9928(5)	51(3)
C(14)	7356(7)	−445(5)	10881(4)	48(2)
C(25)	12374(7)	327(6)	8581(4)	44(2)
C(13)	6542(8)	−1048(5)	10595(5)	52(2)
C(3A)	13084(15)	−1189(12)	10217(10)	59(5)
C(24)	13384(8)	620(7)	8176(4)	59(3)
C(2M)	10768(7)	−1547(5)	9391(5)	58(2)
C(1M)	11309(7)	1309(5)	10416(4)	38(2)
C(26)	12107(8)	−573(7)	8719(4)	65(3)
C(3B)	12129(11)	−143(11)	11193(8)	45(5)
C(23)	13576(9)	1459(9)	8133(5)	76(4)

TABLE I (*Continued*)

	x/a	*y/b*	*z/c*	*U(eq)*
C(32)	7789(6)	925(5)	8605(4)	35(2)
C(22)	12721(7)	1993(7)	8456(4)	58(3)
C(21)	11685(7)	1663(6)	8839(4)	41(2)
C(33)	7451(7)	1668(5)	8130(4)	41(2)
C(34)	8659(7)	2098(5)	7821(4)	33(2)
C(35)	9009(8)	2908(5)	8008(4)	47(2)
C(39)	9487(7)	1691(5)	7346(4)	41(2)
C(36)	10112(9)	3317(5)	7740(4)	53(2)
C(38)	10588(8)	2097(5)	7087(4)	45(2)
C(37)	10891(8)	2907(5)	7281(4)	45(2)
OW	5388(6)	−844(5)	7350(3)	87(2)

TABLE II Selected bond lengths (Å) and angles (°) for the complex

(a) *Bond lengths*			
Co–N(1)	1.988(7)	N(31)–C(32)	1.514(9)
Co–N(2)	1.988(6)	C(32)–C(31)	1.498(10)
Co–N(11)	1.942(6)	C(31)–O(31)	1.304(8)
Co–N(21)	1.951(6)	C(31)–O(32)	1.248(8)
Co–N(31)	1.974(5)	C(32)–C(33)	1.543(10)
Co–O(31)	1.873(5)	C(34)–C(35)	1.385(10)
		C(35)–C(36)	1.380(11)
		C(36)–C(37)	1.356(11)
		C(37)–C(38)	1.376(11)
		C(38)–C(39)	1.370(9)
		C(39)–C(34)	1.402(10)
(b) *Bond angles*			
N(11)–Co–N(21)	178.2(3)	N(31)–Co–O(31)	85.0(2)
O(31)–Co–N(1)	172.3(2)	Co–O(31)–C(31)	117.5(5)
N(31)–Co–N(2)	171.5(3)	O(31)–C(31)–C(32)	116.2(7)
		C(31)–C(32)–N(31)	109.5(6)
		C(32)–N(31)–Co	108.8(4)
(c) *Non-bonded contacts between the two hydrophobically bonded rings*			
	N(21)···C(34)	4.05	
	C(25)···C(39)	4.34	
	C(21)···C(35)	3.70	
	C(24)···C(38)	4.22	
	C(22)···C(36)	3.63	
	C(23)···C(37)	3.91	

The stereochemistry of the complex is established unambiguously along similiar lines used for related complexes in that the coordinated tetradentate and aminoacidate act as internal labels of known chirality. Thus the tetradentate ligand dictates Δ-α stereochemistry at the metal centre. Examination of bond lengths and angles (Table II) does not reveal any anomaly. The structure determined here demonstrates that co-crystallisation of α_1 and α_2 isomers occurs in the single crystal. This is evidenced by the disordered nature of the methyl group in the central ring of the tetradentate ligand,

TABLE III Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$)

	x/a	*y/b*	*z/c*	*U(eq)*
H(31A)	8237(5)	1275(4)	9563(3)	38
H(31B)	9167(5)	1645(4)	9072(3)	38
H(1)	10706(6)	−672(5)	10626(4)	42
H(2)	12803(7)	−53(5)	9838(4)	50
H(16A)	8899(6)	1116(4)	10652(4)	43
H(16B)	9503(6)	481(4)	11185(4)	43
H(11)	7801(7)	−1074(5)	9098(4)	50
H(12)	6129(8)	−1662(6)	9731(5)	61
H(14)	7250(7)	−277(5)	11332(4)	57
H(13)	5881(8)	−1306(5)	10857(5)	63
H(3A1)	13669(74)	−968(19)	10563(39)	89
H(3A2)	13611(77)	−1409(46)	9848(14)	89
H(3A3)	12544(15)	−1630(32)	10408(49)	89
H(24)	13928(8)	251(7)	7933(4)	70
H(2M1)	10147(40)	−1622(12)	9021(17)	87
H(2M2)	10310(44)	−1630(11)	9816(12)	87
H(2M3)	11484(10)	−1948(5)	9350(27)	87
H(1M1)	10843(24)	1769(6)	10205(19)	57
H(1M2)	12189(17)	1258(11)	10220(19)	57
H(1M3)	11386(37)	1412(15)	10897(4)	57
H(26A)	12951(8)	−873(7)	8753(4)	78
H(26B)	11602(8)	−811(7)	8342(4)	78
H(3B1)	12403(76)	−691(12)	11344(25)	67
H(3B2)	11574(34)	112(53)	11536(16)	67
H(3B3)	12909(52)	199(48)	11118(15)	67
H(23)	14294(9)	1671(9)	7883(5)	91
H(32)	6947(6)	728(5)	8808(4)	42
H(22)	12833(7)	2572(7)	8420(4)	69
H(21)	11107(7)	2031(6)	9062(4)	49
H(33A)	6882(7)	1465(5)	7764(4)	49
H(33B)	6941(7)	2079(5)	8387(4)	49
H(35)	8481(8)	3187(5)	8327(4)	56
H(39)	9290(7)	1146(5)	7207(4)	49
H(36)	10316(9)	3863(5)	7872(4)	64
H(38)	11139(8)	1822(5)	6776(4)	54
H(37)	11637(8)	3174(5)	7095(4)	54

with an observed occupancy ratio for the co-crystallisation of 1 : 1. The central five-membered chelate ring has a λ conformation with the N(1)–C(1)–C(2)–N(2) torsion angle equal to −53.4(8)°. Fenton *et al.*[5] found the complex Δ-$\alpha_{1,2}$-[Co(*R*-picpnMe$_2$)(*S*-ala)](ClO$_4$)$_2$ to have a similiar torsion angle of 53.9°, and noted that for both α_1 and α_2 forms the methyl group attached to the central chelate ring occupied a *quasi* equatorial position. This also is apparent for the structure determined here.

However, Figure 1 shows a notable interaction between one of the pyridyl rings of the tetradentate ligand and the phenyl ring of the coordinated phenylalanine ligand. This ring interaction is similiar to that observed[1,3,4] for the related complexes α-[Co(*R**,*R**-picchxnMe$_2$)(*R**-phe)](ClO$_4$)$_2$ and

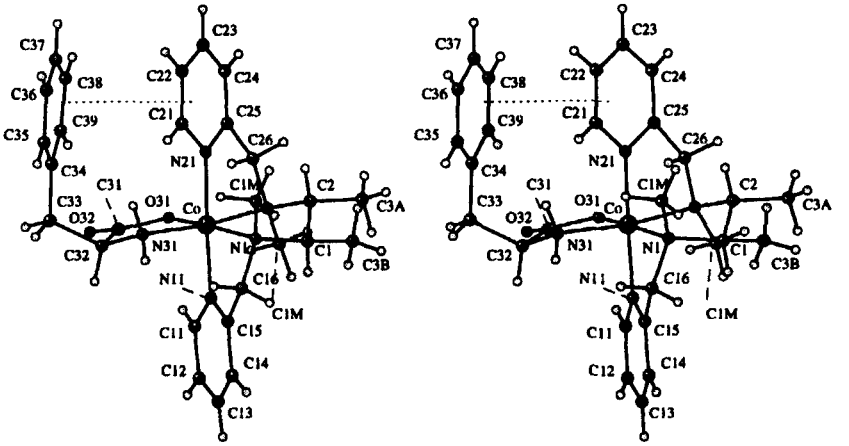

FIGURE 1 Stereoscopic view of the Δ-α_1,α_2-[Co(*R*-picpnMe$_2$)(*S*-phe)]$^{2+}$ cation showing the atom labelling scheme. Labels for hydrogen atoms are taken from the labels of heavy atoms to which they are bonded. When more than one hydrogen is bonded to a centre they are distinguished by the suffix a, b or c. The disordered methyl groups in the central ring of the tetradentate ligand are C3A and C3B.

Λ-α-[Co(picenMe$_2$)(*S*-phe)](ClO$_4$)$_2$. The pyridyl ring involved is flat with an rms deviation of 0.004 Å for all six atoms; the phenyl ring also is flat with an rms deviation of 0.015 Å. The dihedral angle between these rings is 20.3°. Perspective views[13] of the two rings are shown in Figure 2. Leverett *et al.*[4] found for the Δ-α-[Co(*R*,*R*-picchxnMe$_2$)(*R*-phe)](ClO$_4$)$_2$ complex that the inclination of one ring with respect to the other is such that the 'hinge' of the two planes containing the rings is constituted by two pairs of *ortho* atoms; this also is evident in the complex structure determined here. These 'hinge' pairs are C(36)···C(22) and C(35)···C(21), 3.63 and 3.70 Å apart, respectively. The most divergent pairs of atoms are C(24)···C(38) and C(25)···C(39), 4.22 and 4.34 Å apart, respectively. The average distance between the rings is thus 4.0 Å

Hydrophobic $\pi-\pi$ or van der Waals ring interactions of this nature are of considerable interest, and have been identified as providing opportunities to incorporate ligands which may intercalate with the base pairs of DNA.[1-4] NMR studies indicate that this interaction for the isomeric forms reported here also persists in solution although 'deceptively simple' ABX patterns for the aliphatic protons of the coordinated phenylalaninato ligands prohibit any detailed analysis of rotamer populations in dmso solution.[4]

Characteristic ^{1}H NMR data for the complexes in dmso-d_6 are given in Table IV. Assignments are made on the basis of those for analogous

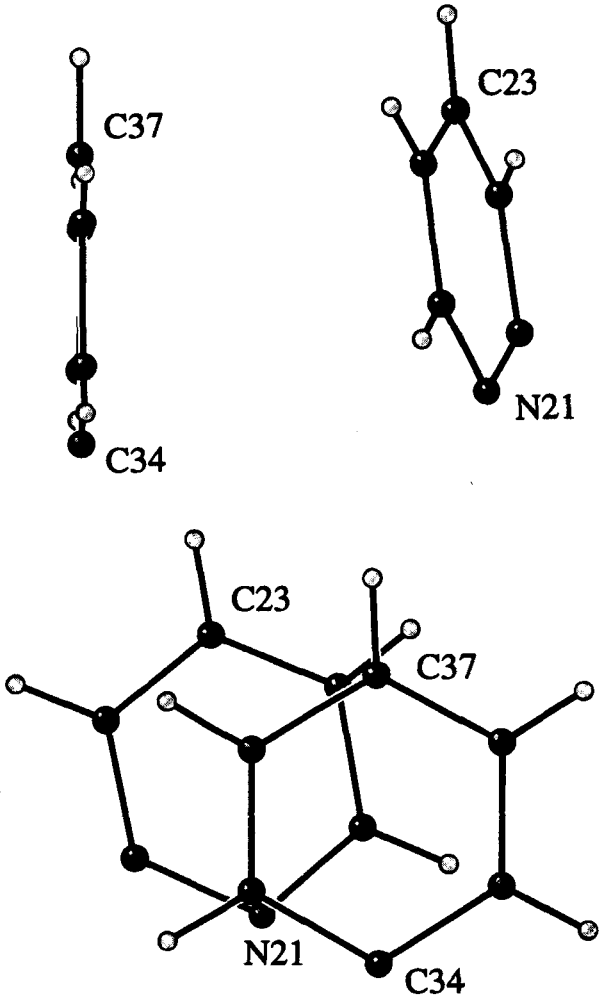

FIGURE 2 Orthogonal views of the orientations of the two hydrophobically bonded rings illustrating the extent of overlap and their relative inclination. The dihedral angle between the rings is 20.3°. The rotation axis used to generate the two orthogonal projections passes through N21 and C23.

complexes.[4,5,12] Data for *S*-alaninato analogues[5] also are listed for comparison. All complexes possess *pseudo* C_2 symmetry and give ^{1}H NMR spectra, particularly in the aromatic region, that are considerably overlapped, not only with respect to signals from the same molecule, but also with respect to signals fom the separate α_1 and α_2 isomers present in solution. Considerable differences ($\sim$ 1 ppm) are evident in the chemical shifts of protons *ortho* to

TABLE IV Characteristic ^{1}H NMR data for the complexes[a]

	Chemical shift (ppm) *or coupling constant* (Hz) *for the complexes*		
	Δ-α_1,α_2-[Co(*R*-L)(*S*-phe)]$^{2+}$	Δ-α_1,α_2-[Co(*R*-L)(*R*-phe)]$^{2+}$	Δ-α_1,α_2-[Co(*R*-L)(*S*-ala)]$^{2+}$ [b]
H11	7.89 (d) 7.96 (d)[c]	8.12 (d), 8.16 (d)[c]	8.30 (dd)
H12	7.45 (t)	7.64 (t), 7.66 (t)[d]	7.85 (m)
H13	8.17 (t)	8.27 (t)[e]	8.30 (t)
H14	7.80 (m)[f]	7.90 (m)[f]	7.85 (m)
H3A,B	1.02 (dd)	1.05 (dd)	1.02 (d)
H21	8.48 (d)	9.03 (d), 9.06 (d)[c]	9.25 (d)
H22	7.80 (m)	7.90 (m)	7.85 (m)
H23	8.30 (t)	8.33 (t)	8.30 (t)[f]
H24	7.80 (m)	7.90 (m)	7.85 (m)
H32	[g]	3.45 (m)	
H33	[g]	2.85 (d)	1.06 (d)
H35–39	7.20 (m)	7.16 (m)	
H31a	7.12 (broad)[h]	7.00 (broad)	5.9
H31b	8.31 (broad)	4.08 (broad)	5.9
H16,26	4.5 (m)	4.45 (m)	4.4 (m)
H1M	2.59 (s), 2.38 (s)	2.57 (s), 2.38 (s)	2.58 (s)
H2M[i]	2.33 (s), 2.17 (s)	2.35 (s), 2.14 (s)	2.38 (s)

[a]L = *R*-picpnMe2. [b]Ref. [5]. [c]Partially overlapped doublets. [d]Two partially overlapped triplets. [e]Partially overlapped with H23. [f]Multiplet resulting from overlapped H14, H24 and H22 resonances. [g]Obscured by solvent peak. [h]Partially obscured by phenyl resonance. [i]*N*-Methyl resonances not distinguished.

the nitrogen atoms in the pyridyl rings for the pair of *R*-phe diastereoisomers. These are consistent with those reported[4] for analogous protons in Δ-α-[Co(*R*,*R*-picchxnMe$_2$)(*R*-phe)](ClO$_4$)$_2$ and result from the different magnetic environments experienced by the respective pyridyl rings. Atom H21 is in the vicinity of the amino group of the phenylalanine bidentate, and is more deshielded (δ 9.03, 9.06) than the other *ortho* proton, H11 (δ 8.12, 8.16), positioned over the carboxylate group. For the other diastereoisomers, this difference is comparable (H21 δ 8.48 (both isomers), H11 δ 7.89, 7.96) and any differences must reflect the relative orientations of the pyridyl rings in the two sets of diastereoisomeric pairs. That is expected, in that the five membered aminoacidate chelate rings are buckled in different senses for *R*-aa and *S*-aa with a Δ configuration at the Co atom centre, as expected.

Curiously, the ^{1}H NMR spectrum of Δ-$\alpha_{1,2}$-[Co(*R*-picpnMe$_2$)(*S*-phe)]$^{2+}$, shows near perfect, albeit fortuitous, resonance overlap for the α_1 and α_2 isomers in the aromatic region. However, ^{1}H NMR spectra of Δ-$\alpha_{1,2}$-[Co(*R*-picpnMe$_2$)(*R*-phe)]$^{2+}$ show distinct separation of some resonances pairs, particularly in the aromatic region. This is only in part attributable to the co-crystallisation of α_1 and α_2 isomers. Thus the resonance due to H11, for example, normally expected to appear as a doublet, manifests itself as a *pseudo* triplet (overlap of two doublets), while H13, normally expected to

appear as a triplet, is a *pseudo* quartet (due to the overlap of the two α_1 and α_2 triplets). The symmetrical nature of the partial overlap is due to the fact that the isomeric α_1/α_2 ratio is close to 1 : 1.

The signal separation arises as a result of the *pseudo* C_2 symmetry being further perturbed by the persistence of the $\pi-\pi$ interaction in solution. Attention is drawn to the very different chemical shifts of the resonances observed for the amine protons of the phenylalanine bidentate, H31a and H31b, (H31a $\delta \sim 7.0$, H31b $\delta \sim 4.0$ for the *R*-phe, and H31a $\delta \sim 8.3$, H31b $\delta \sim 7.1$ for the *S*-phe diastereoisomers). The larger difference observed for Δ-$\alpha_{1,2}$-[Co(*R*-picpnMe$_2$)(*R*-phe)]$^{2+}$ is consistent with shifts established[4] for the closely related Δ-α-[Co(*R*,*R*-picchxnMe$_2$)(*R*-phe)](ClO$_4$)$_2$ complex, and is highly indicative of ring–ring interaction in solution. The chemical shift difference results from the H31b proton experiencing significant shielding due to its orientation between the weakly bonded rings. Corresponding protons in the ^{1}H NMR spectrum of the other pair of diastereoisomers, Δ-$\alpha_{1,2}$-[Co(*R*-picpnMe$_2$)(*S*-phe)]$^{2+}$, are not so separated, indicative of less ring–ring overlap and differing aminoacidate chelate ring conformation, as confirmed by this and related[1,3,4] X-ray structure studies.

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Supplementary Data Available

Full lists of crystallographic data are available from the authors upon request.

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