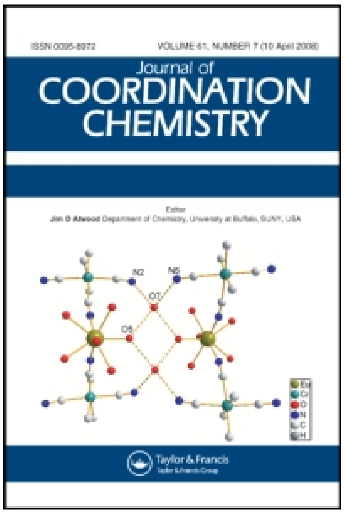

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CHIRAL METAL COMPLEXES 47. THE SOLID STATE AND SOLUTION STRUCTURE OF Λ-α-[(*N,N'*-DIMETHYL-*N,N'*-di(2-picolyl)-1*S*, 2*S*-DIAMINOCYCLOHEXANE)(*S*-PHENYLALANINATO(1-)]COBALT(III) PERCHLORATE

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CHIRAL METAL COMPLEXES 47.[‡] THE SOLID STATE AND SOLUTION STRUCTURE OF Λ-*α*-[(*N,N′*-DIMETHYL-*N,N′*-di(2-picolyl)-1*S*, 2*S*-DIAMINOCYCLOHEXANE) (*S*-PHENYLALANINATO(1-)]COBALT(III) PERCHLORATE

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The structure of the complex Λ-*α*-[Co(*S,S*-picchxnMe$_2$)(*S*-phe)](ClO$_4$)$_2$ where *S,S*-picchxnMe$_2$ is *N,N′*-dimethyl-*N,N′*-di(2-picolyl)-1*S*,2*S*-diaminocyclohexane and *S*-phe is the *S*-phenylalaninate anion, has been determined by X-ray diffraction techniques. The perchlorate salt is monoclinic, space group $P2_1$, with $a = 11.833(1)$, $b = 11.029(2)$, $c = 14.020(2)$ Å, $\beta = 115.63(2)°$ and $Z = 2$. The structure was refined to $R = 0.050$ for 4280 independent reflections with $I > 2\sigma(I)$. In the solid state, the phenyl ring of the phe ligand is hydrophobically bonded to one of the picolyl rings of the tetradentate ligand in intramolecular fashion; the two rings are virtually parallel ($\phi = 13.6°$) and the distance between the rings averages about 3.8 Å. Considerable ring overlap is evident. Remarkably, this structure persists in solution as revealed by nmr experiments. These show that the conformer of the cation, with respect to the three possible staggered rotamers, observed in the crystal structure, predominates in dmso-d_6 solution (population parameter = 0.528).

KEYWORDS: cobalt(III), chirality, tetradentate, amino acid, X-ray structure, conformation

INTRODUCTION

For some time we have been examining the chiral discriminations involved in a series of complexes containing chelating ligands,[1] and especially those containing chiral tetradentate ligands.[2] More particularly, we have begun exploring the interaction of such complexes with DNA.[3] As part of this study, complexes containing a chiral tetradentate, *R*,R**-picchxnMe$_2$, and a bidentate aminoacidate

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[‡] Part 46 is Ref. 1.

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have been synthesised. *N*-Methylation of the tetradentate amino nitrogen atoms enforces α stereochemistry at Co(III) centres.[4,5] Current work focuses on complexes which contain a group which may intercalate between base pairs in DNA or model oligonucleotides. Diasteroisomers of the title complex, whose crystal and molecular structure and behaviour in solution are presented below, have been selected for detailed studies involving DNA, which will be reported elsewhere.

EXPERIMENTAL

All materials used were of reagent grade. Δ-α-[Co(*R*,*R*-picchxnMe$_2$)Cl$_2$](ClO$_4$)$_2$ and its enantiomer were synthesised as described previously.[5]

Δ-α-[Co(R,R,-picchxnMe$_2$)(R-phe)](ClO$_4$)$_2$ or its Enantiomer

The complex Δ-α[Co(*R*,*R*-picchxnMe$_2$)Cl$_2$](ClO$_4$)$_2$ (2.000 g, 3.6 mmol) and *R*-phenylalanine (2.984 g, 18 mmol) were added to water (400 cm^3) and the mixture heated on a water bath for 2 h. The resulting burgundy-coloured solution was cooled to room temperature. NaOH (3.6 cm^3, 1.0 M) was added slowly dropwise, and the solution was stirred for 45 min. The solution was loaded onto a CM Sephadex C25 column (30×2 cm) and eluted with 0.3 M NaCl. The first minor pink band was discarded and the second red-orange band collected in fractions. This band contained a single isomer of the desired complex, as revealed by measurements of the absorbtion spectra of the fractions. Solid NaClO$_4$ was added to the eluate and this was allowed to slowly dissolve and diffuse undisturbed through the solution. Reddish orange crystals of the title complex grew slowly during one week. These were collected at the pump, washed with ethanol and air dried. Characteristic spectroscopic data: $\lambda_{max} = 492$ nm, $\varepsilon = 169$ M^{-1} cm^{-1}; $\Delta\varepsilon_{499}$ (extremum) = -9.96; $\Delta\varepsilon_{360}$ (shoulder) = $+2.95$ M^{-1} cm^{-1}, in acetone: water = 40:60 (*v/v*), for the Δ-α-*R*,*R*,*R* diastereoisomer. Δ-α-[Co(*S*,*S*-picchxnMe$_2$)(*S*-phe)](ClO$_4$)$_2$ was synthesised similarly using *S*,*S*-picchxnMe$_2$ and S-pheH. The analytical composition of the complex salt was confirmed by a single-crystal X-ray structure determination (*vide infra*).

X-Ray Structure Analysis

The structure determined was performed on crystals of the Λ-α-*S*,*S*,*S* diastereoisomer. Crystal data: C$_{29}$H$_{38}$N$_5$O$_{10}$Cl$_2$Co, M_r = 746.5, a = 11.833(1), b = 11.029(2), c = 14.020(2)Å, β = 115.63(2)°, V = 1649.61Å^3, $Z = 2$, D_c = 1.503, D_m = 1.51 mg m^{-3}, F(000) = 776.0, μ(Mo Kα) = 0.75 mm^{-1}, monoclinic, space group $P2_1$ (No. 4). Unit cell parameters were initially determined from single-crystal precession photographs using MoKα radiation and refined *via* a least-squares fit to diffractometer data. The crystal used for data collection was 0.11×0.13×0.36 mm in size. Data for the complex were collected at 278 K on an Enraf-Nonius FAST area detector diffractometer using documented procedures.[6] Intensity data were determined for reflections in the range $6° < 2\theta < 72°$. Intensities were corrected for Lorentz and polarization effects but absorption corrections were not applied. A total of 8222 measured reflections was merged to give 5722 unique reflections of which 4284 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 SHELXS-86 and SHELXL-93[7] and refined by full-matrix least-squares techniques in which the function $\Sigma w(F_o^2-F_c^2)^2$ was minimized.[7] The weight for each reflection in the final cycles of refinement is given by $w = 1/[\sigma^2(F_o)^2 + (0.0654P)^2]$ where $P = (\max(F_o^2, 0) + F_c^2)/3$, as defined by SHELXL-93.[7] 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 anisotropic temperature factors for all other atoms. The refinement process was terminated when the minimization 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 value was 0.050 for 4284 reflections with $I>2\sigma(I)$. The final weighted $R = [\{\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}]$ was 0.129 for all 5722 data.

Physical Measurements

Electronic and CD spectra were recorded on a Shimadzu UV-2100 recording spectrophotometer and a Jasco J-500C spectropolarimeter. Nmr spectra of samples dissolved in dmso-d_6 were recorded at 300 MHz for ^{1}H and 75 MHz for ^{13}C using a Varian 300 Unity Plus spectrometer, with TMS as internal standard.

RESULTS AND DISCUSSION

Solid-state Structure

Table 1 lists final atomic coordinates of non-hydrogen atoms and Table 2 gives selected bonding parameters and interatomic distances for the complex. A perspective view of the complex cation Λ-α-[Co(*S,S*-picchxnMe$_2$)(*S*-phe)]$^{2+}$ showing the atom labelling scheme, is shown in Fig. 1.

The stereochemistry of the complex is established unambiguously; use of *S*-pheH and *S,S*-picchxnMe$_2$ as internal chiral labels leads to the conclusion that the tetradentate ligand of this hand enforces the Λ-α stereochemistry at the metal centre. Thus isomerism at the tertiary amine centres also is established. These observations are in line with others made with respect to analogous complexes[4,5] and reinforces the notion that tetradentate ligands of this kind can be used in a rational way to enforce a predetermined, chiral coordination mode.

Examination of bond lengths and angles (Table 2) in the complex does not reveal any anomaly. However, Fig. 1 clearly shows a notable interaction in the solid state between one of the pyridyl rings of the tetradentate ligand and the phenyl ring of the coordinated aminoacidate. Hydrophobic bonding between the rings is suggested in that the rings lie almost parallel to each other. The pyridyl ring in question (Fig. 1) is flat with a rms deviation of 0.006 Å for all six atoms; the mean plane of the phenyl ring is also flat with a rms deviation of 0.013 Å. The dihedral angle between the two planes is 13.6°.

Extent of overlap of the two planes is illustrated in Fig. 2. The inclination of one

Table 1 Final atomic coordinates for the non-hydrogen atoms with their estimated standard deviations in parentheses.

	x/a	*y/b*	*z/c*
Co	0.7542(1)	0.3000	0.1284(1)
N1	0.8780(4)	0.4341(4)	0.1875(4)
N11	0.8179(3)	0.2950(5)	0.0221(3)
N2	0.8802(4)	0.1897(4)	0.2321(3)
N21	0.6876(3)	0.3046(5)	0.2345(3)
N31	0.6171(4)	0.3977(3)	0.0237(3)
O31	0.6451(4)	0.1659(3)	0.0628(3)
O32	0.4656(4)	0.1140(3)	-0.0692(3)
C1	1.0064(5)	0.3756(5)	0.2531(4)
C11	0.7994(5)	0.2047(5)	-0.0492(4)
C12	0.8343(6)	0.2195(8)	-0.1297(5)
C13	0.8888(7)	0.3235(11)	-0.1385(5)
C14	0.9102(7)	0.4137(7)	-0.0661(5)
C15	0.8737(5)	0.3987(5)	0.0144(4)
C16	0.8811(6)	0.4953(5)	0.0929(4)
C1M	0.8431(6)	0.5291(5)	0.2474(5)
C2	0.9847(5)	0.2696(5)	0.3111(4)
C21	0.6050(6)	0.3852(6)	0.2416(4)
C22	0.5593(7)	0.3716(8)	0.3148(6)
C23	0.5975(7)	0.2766(10)	0.3832(6)
C24	0.6827(7)	0.1946(8)	0.3788(5)
C25	0.7262(5)	0.2109(5)	0.3027(4)
C26	0.8157(5)	0.1265(5)	0.2883(4)
C2M	0.9282(6)	0.0959(5)	0.1823(5)
C3	1.1086(6)	0.2011(6)	0.3760(5)
C31	0.5392(5)	0.1909(5)	-0.0107(4)
C32	0.5015(5)	0.3241(5)	-0.0225(4)
C33	0.4139(6)	0.3642(6)	-0.1368(4)
C34	0.4735(6)	0.3654(6)	-0.2107(5)
C35	0.4757(7)	0.2655(7)	-0.2689(5)
C36	0.5352(8)	0.2750(11)	-0.3360(6)
C37	0.5939(9)	0.3758(14)	-0.3403(7)
C38	0.5910(9)	0.4751(9)	-0.2841(7)
C39	0.5320(7)	0.4703(7)	-0.2217(6)
C4	1.2063(6)	0.2867(9)	0.4499(5)
C5	1.2269(6)	0.3956(7)	0.3883(6)
C6	1.1065(6)	0.4593(6)	0.3280(5)
Cl1	0.2293(1)	0.2943(2)	0.0809(1)
O11	0.1955(7)	0.3134(10)	-0.0298(5)
O12	0.1331(5)	0.2238(5)	0.0844(5)
O13	0.3409(6)	0.2306(7)	0.1142(7)
O14	0.2371(9)	0.4045(7)	0.1260(7)
Cl2	0.9638(2)	0.3176(2)	0.5921(1)
O21	0.9720(6)	0.2073(4)	0.5422(4)
O22	0.8671(7)	0.3134(10)	0.6234(5)
O23	0.9419(8)	0.4119(5)	0.5200(5)
O24	1.0739(7)	0.3378(5)	0.6851(5)

ring with respect to the other, as shown in the Figure, is such that the "hinge" of the two planes containing the rings is constituted by two pairs of *ortho* atoms. At the hinge, the C12-C36 and C13-C37 distances are 3.52 and 3.46 Å, respectively. As the rings diverge, the most distant contacts are those involving N11-C34 and C15-C39, these both being 4.04 Å (see Table 2). The average distance between the rings thus

Table 2 Selected bond lengths (Å) and angles (°) for the complex.

(a) Bond Lengths			
Co-N(11)	1.940(4)	N(31)-C(32)	1.477(6)
Co-N(1)	1.992(4)	C(32)-C(31)	1.523(8)
Co-N(2)	1.985(4)	C(31)-O(31)	1.261(6)
Co-N(21)	1.962(4)	C(31)-O(32)	1.238(6)
Co-N(31)	1.972(4)	C(32)-C(33)	1.550(7)
Co-O(31)	1.917(3)	C(34)-C(35)	1.378(9)
		C(35)-C(36)	1.402(11)
		C(36)-C(37)	1.326(14)
		C(37)-C(38)	1.359(14)
		C(38)-C(39)	1.336(11)
		C(39)-C(34)	1.391(10)
		C(34)-C(33)	1.483(9)
(b) Bond angles			
N(11)-Co-N(21)	179.2(2)	N(31)-Co-O(31)	84.1(2)
O(31)-Co-N(1)	173.7(1)	Co-O(31)-C(31)	116.6(3)
N(31)-Co-N(2)	174.6(2)	O(31)-C(31)-C(32)	116.1(5)
		C(31)-C(32)-N(31)	108.0(4)
		C(32)-N(31)-Co	109.5(3)
(c) Non-bonded contacts between the two hydrophobically bonded rings (see text)			
N(11)...C(34)	4.04		
C(15)...C(39)	4.04		
C(11)...C(35)	3.80		
C(14)...C(38)	3.75		
C(12)...C(36)	3.52		
C(13)...C(37)	3.46		

amounts to 3.8 Å. The situation observed here in the solid state parallels that found for a related complex[9] Λ-β-[Co(*R*,*R*-picchxn)(*S*-AMBA)]$^+$ (where picchxn = *N*,*N'*-di(2-picolyl)-1*R*;2*R*-diaminocyclohexane and AMBA is the anion of aminobenzylmalonic acid). In this complex, as well, the phenyl ring of the phenylalanine precursor is aligned parallel to one of the coordinated picolyl residues. Such

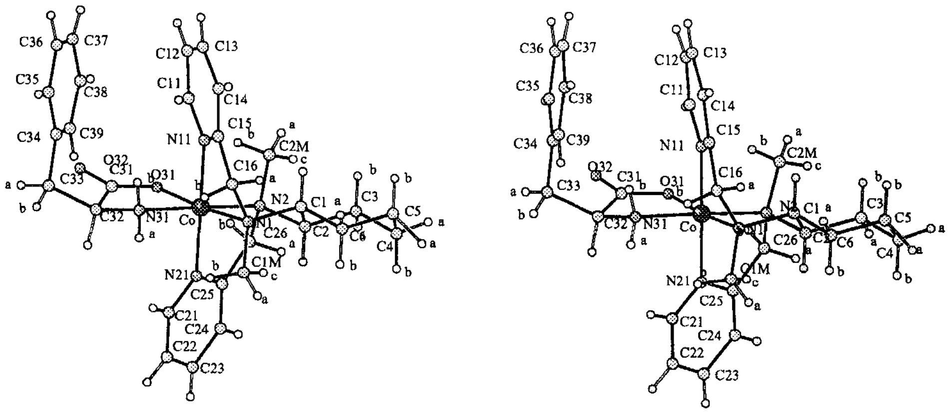


Figure 1 A stereo view[8] drawing of the Λ-α-[Co(*S*,*S*-pichhxnMe$_2$)(*S*-phe)]$^{2+}$ cation showing the atom labelling scheme. Labels for hydrogen atoms are taken from the labels of heavy atoms to which they are bonded. Thus, H11 is bonded to C11, H39 is bonded to C39, *etc.* When more than one hydrogen is bonded to a centre it is distinguished by the suffix a, b or c.

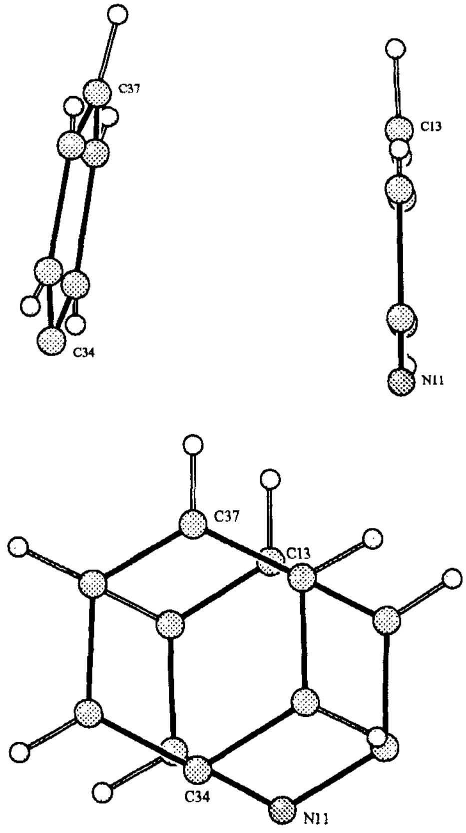


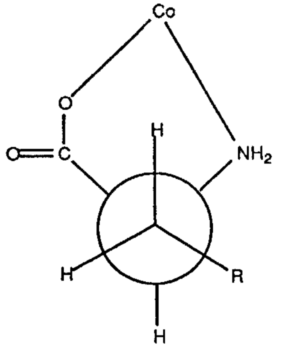
Figure 2 Perspective views[8] of the orientations of the two hydrophobically bonded rings illustrating (a) the inclination of the planes (ϕ = 13.6°), and (b) the extent of overlap. The two views are orthogonal to each other, and the rotation axis used to generate the two projections passes through N11 and C13.

hydrophobic interactions are difficult to evaluate in energy terms and solvation effects might be expected to dominate in solution. Nevertheless, they have been identified as being important in reactions involving these kinds of ligands[9] and their very existence is of considerable interest with respect to the rationale for their synthesis, *viz*, that it may be possible to incorporate ligands which can intercalate with the base pairs of DNA.

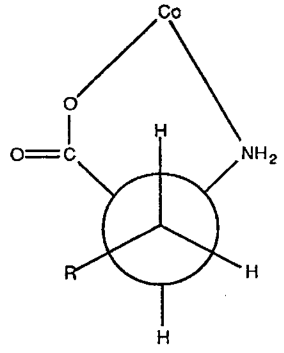
In the crystal lattice, the perchlorate groups are generally constrained. The central chlorine atom of each perchlorate ion was readily located in the initial Patterson map and the oxygen atoms in different maps. Final refinement revealed that one oxygen atom in each perchlorate group had significant anisotropic thermal vibration, which might indicate slight disorder of the anions within the structure. The perchlorate ions are otherwise normal and are not involved in hydrogen bonding. Complex cations are however linked in chains along *a* by a weak hydrogen bond between H31a and O32 at $1-x$, $1/2+y$, $-z$ (1.898 Å).

Solution Studies

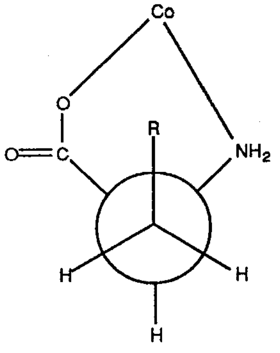
Selected ^{1}H NMR data for the complex in dmso-d_6 are given in Table 3, and H atom positions are listed in Table 4, in view of their relevance to the nmr study. Assignments are made on the basis of those for analogous complexes.[4,5,9] Here, however, it was possible to unambiguously assign the relevant portions of the spectrum arising from the phe ligand using a series of 2D COSY correlations. An assessment of the rotamer populations for I to III has been carried out using published methods.[10]



I



II



III

The conformers are drawn for *S*-phe, and the nmr experiments were performed using solutions of the Δ-α-*R*,*R*,*R* diastereoisomer. For phenylalanine itself, the coupling constants J_{gauche} = 2.60 Hz and J_{trans} = 13.56 Hz have been determined previously,[10] and these values were used in the calculations, assuming that no changes to them would occur upon coordination of the aminoacidate.

Rotomer populations of 0.188 and 0.284 were found for conformers **I** and **II.** Conformer **III** dominates in dmso solution (population parameter = 0.528) at room temperature. This major conformer is the one which is revealed in the X-ray structure of the perchlorate salt. Thus it must be concluded that the hydrophobic interaction persists in solution, at least in dmso.

The unexpected preservation of the hydrophobic bond in solution explains other effects in the nmr. Notably, there is a marked difference between the chemical shifts of the amine hydrogen atoms of the phenylalanine ligand (δ H31a = 7.06, δ H31b = 4.03 ppm). This assignment is in accord with the observation that while the H31a signal is partially obscured by phenyl proton resonances, that of H31b is a well-resolved triplet (doublet of doublets) with J_{av} = 11.7 Hz. Contributions to J_{av} will come from the separate vicinal coupling constant to the methine proton *trans* to it (X of the ABX portion of the phenylalanine fragment) and the geminal N*H*-N*H* coupling constant. The significant chemical shift differences are thus simply explained by the fact that H31a will be contact deshielded through non-bonded interactions with H11, H16b and the adjacent (C1) methyl group. Contrary to this arrangement, H31b points towards the region between the two hydrophobically bonded rings and thus would be expected to experience considerable shielding effects.

Table 3 Characteristic ^1H nmr data for Δ-α-[Co(*R*,*R*-pichhxnMe$_2$)(*R*-phe)](ClO$_4$)$_2$ in dmso-d_6 at 298K.

Proton	Chemical shift (ppm)** or coupling constant (Hz)
H11	8.05(d)
H12	7.60(t)
H13	8.23(t)
H14	7.82(d)
CH_3	2.21(s), 2.45** (s)
H21	9.06(d)
H22	7.86(t)
H23	8.30(t)
H24	7.84(d)
H32	3.40(m)
H33a	2.91(dd)
H33b	2.80(m)
H35–H39	7.1(m), overlapped
H31a	7.06‡
H31b	4.03(*t*); J_{av} = 11.7
$J_{32,33b}$	5.7_1
$J_{32,33a}$	4.6_6
$J_{33a,33b}$	13.8
$J_{11,12}$	5.7
$J_{12,13}$	9.0
$J_{13,14}$	6.6
$J_{11,13}$	0.9
$J_{21,22}$	5.7
$J_{22,23}$	7.8
$J_{23,24}$	7.8
$J_{21,23}$	<0.5

*S = singlet, d = doublet, t = triplet, m = multiplet. **We do not distinguish between the two methyl resonances. ‡Partially obscured by phenyl resonances.

The α diastereoisomer possess formal C_1 symmetry, the C_2 symmetry of the starting dichloro complex being removed by coordination of the unsymmetrical bidentate ligand. Protons *ortho* to nitrogen in the pyridyl rings (H11 and H21) are constrained to orientations adjacent to the aminoacid carboxylate or amino groups. The difference in magnetic environment is manifested by a chemical shift difference of about 1 ppm for the two protons. H11, aligned over the carboxylate group, is somewhat more shielded (δ 8.05 ppm) than H21 lying over the $-NH_2$ group (δ 9.06 ppm). This difference is exactly analogous to that used to distinguish β_1 and β_2 diastereoisomers of Co(III) complexes of aminoacidates and *R**,*R**-picchxn.[2,4,8,11] Minor differences are seen for the chemical shifts of the remaining pyridyl hydrogen resonances. They are grouped in pairs with small chemical shift changes which reflect the *pseudo* C_2 symmetry of the complex cation.

Acknowledgements

The authors wish to thank the ARC and the Macquarie University Research Grant Scheme for financial support and UWS Nepean for the award of a scholarship to JP.

Table 4 Final atomic coordinates for hydrogen atoms with estimated standard deviations in parentheses.

	x/a	*y/b*	*z/c*
H1	1.0368(5)	0.3430(5)	0.2034(4)
H11	0.7628(5)	0.1323(5)	-0.0432(4)
H12	0.8204(6)	0.1575(8)	-0.1785(5)
H13	0.9117(7)	0.3330(11)	-0.1937(5)
H14	0.9493(7)	0.4851(7)	-0.0709(5)
H16a	0.9580(6)	0.5413(5)	0.1141(4)
H16b	0.8108(6)	0.5506(5)	0.0612(4)
H1Ma	0.8476(37)	0.4948(11)	0.3118(16)
H1Mb	0.7593(15)	0.5569(26)	0.2048(13)
H1Mc	0.9002(23)	0.5961(17)	0.2637(28)
H2	0.9549(5)	0.3021(5)	0.3612(4)
H21	0.5792(6)	0.4509(6)	0.1956(4)
H22	0.5020(7)	0.4272(8)	0.3181(6)
H23	0.5659(7)	0.2671(10)	0.4331(6)
H24	0.7104(7)	0.1299(8)	0.4258(5)
H26a	0.8770(6)	0.0984(5)	0.3567(4)
H26b	0.7708(5)	0.0565(5)	0.2476(4)
H2Ma	0.9810(33)	0.1337(8)	0.1547(30)
H2Mb	0.8589(6)	0.0571(27)	0.1258(22)
H2Mc	0.9757(34)	0.0366(21)	0.2343(9)
H31a	0.6041(4)	0.4639(4)	0.0551(3)
H31b	0.6381(4)	0.4222(4)	-0.0278(3)
H32	0.4561(5)	0.3379(5)	0.0207(4)
H33a	0.3423(6)	0.3101(6)	-0.1648(4)
H33b	0.3829(6)	0.4450(6)	-0.1344(4)
H35	0.4384(7)	0.1931(7)	-0.2638(5)
H36	0.5334(8)	0.2094(11)	-0.3783(6)
H37	0.6373(9)	0.3786(14)	-0.3820(7)
H38	0.6301(9)	0.5464(9)	-0.2890(7)
H39	0.5299(7)	0.5394(7)	-0.1844(6)
H3a	1.0938(6)	0.1368(6)	0.4164(5)
H3b	1.1387(6)	0.1645(6)	0.3283(5)
H4a	1.2847(6)	0.2436(9)	0.4870(5)
H4b	1.1799(6)	0.3169(9)	0.5021(5)
H5a	1.2874(6)	0.4513(7)	0.4377(6)
H5b	1.2599(6)	0.3664(7)	0.3402(6)
H6a	1.1198(6)	0.5249(6)	0.2880(5)
H6b	1.0779(6)	0.4944(6)	0.3772(5)

SUPPLEMENTARY DATA

Full lists of isotropic thermal parameters for the H atoms, anisotropic temperature factors for the heavy atoms, and observed and calculated structure factors have been deposited with the editor and can be obtained upon request. ^{13}C NMR data for the complex in dmso-d_6 and ^{1}H and ^{13}C NMR spectra have also been deposited.

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