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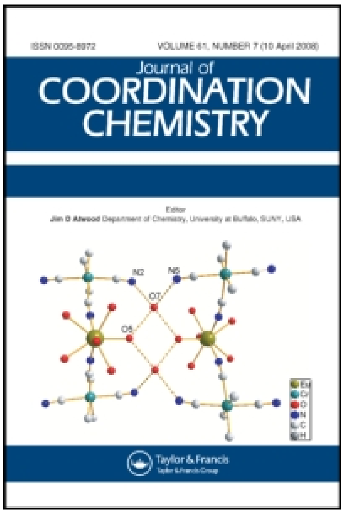

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

CHIRAL METAL COMPLEXES. 51. STRUCTURE OF THE DNA PROBE Δ-α-[*N,N'*-DIMETHYL-l,6-DI(2-PYRIDYL)-2,5-DIAZAHEXANE][S-PHENYLALANINATO(l-)l-COBALT(III) PERCHLORATE

Peter Leverett[a]; Janice Petherick[a]; Peter A. Williams[a]; Robert S. Vagg[b]
[a] School of Science, University of Western Sydney Nepean, Kings wood, New South Wales, Australia [b] School of Chemistry, Macquarie University, New South Wales, Australia

To cite this Article Leverett, Peter , Petherick, Janice , Williams, Peter A. and Vagg, Robert S.(1999) 'CHIRAL METAL COMPLEXES. 51. STRUCTURE OF THE DNA PROBE Δ-α-[*N,N'*-DIMETHYL-l,6-DI(2-PYRIDYL)-2,5-DIAZAHEXANE][S-PHENYLALANINATO(l-)l-COBALT(III) PERCHLORATE', Journal of Coordination Chemistry, 49: 2, 91 — 100

To link to this Article: DOI: 10.1080/00958979908030748

URL: http://dx.doi.org/10.1080/00958979908030748

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J. Coord. Chem., 1999, Vol. 49, pp. 91–100
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CHIRAL METAL COMPLEXES. 51.* STRUCTURE OF THE DNA PROBE Λ-α-[*N*,*N*′-DIMETHYL-1,6-DI(2-PYRIDYL)-2,5-DIAZAHEXANE][*S*-PHENYLALANINATO(1-)]-COBALT(III) PERCHLORATE

PETER LEVERETT[a], JANICE PETHERICK[a],
PETER A. WILLIAMS[a,†] and ROBERT S. VAGG[b,†]

[a]*School of Science, University of Western Sydney Nepean, P.O. Box 10, Kingswood, New South Wales 2747, Australia;* [b]*School of Chemistry, Macquarie University, New South Wales 2103, Australia*

(Received 20 January 1999)

The ternary complex Λ-α-[*N*,*N*′-dimethyl-1,6-di(2-pyridyl)-2,5-diazahexane][*S*-phenylalaninato(1-)]cobalt(III) perchlorate has been isolated from aqueous solution as the least soluble diastereoisomer. Crystals are orthorhombic, space group $P2_12_12_1$ with $a = 10.462(2)$, $b = 12.895(3)$, $c = 22.560(3)$ Å, $V = 3043.4$ Å^3, $Z = 4$, $D_c = 1.480$ and $D_m = 1.48$. The structure was refined by full-matrix least-squares to a final R value of 0.054 for 1797 reflections with $I > 2\sigma(I)$. In the structure, the phenyl ring of the phenylalanine ligand is bonded face-to-face, albeit slightly offset, to one of the pyridine rings of the tetradentate. ^{1}H NMR measurements show that this indicated weak interaction between the rings persists in solution.

Keywords: Cobalt(III); tetradentate; phenylalanine; van der Waals bond; X-ray structure; DNA

INTRODUCTION

We have been developing structural probes of DNA[1–3] based on an aromatic amino acid capable of intercalating between base pairs,[4–6] and a chiral tetradentate, which can be chosen to fix the absolute configuration of an

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* Part 50 is Ref. [1].
[†] Authors for correspondence.

octahedral metal centre so as to be complementary to the helical sense of the polynucleotide. Complexes of the type Δ-α-[Co(*R*,*R*-picchxnMe$_2$)(*R**-phe)](ClO$_4$)$_2$ (*R*,*R*-picchxn is *N*,*N*′-dimethyl-*N*,*N*′-di(2-picolyl)-1*R*,2*R*-diaminocyclohexane; phe is phenylalaninato) have been synthesised and it has been shown[1,7] that the phenyl group of the amino acid is bonded face-to-face by π–π interactions to one of the pyridyl rings of the tetradentate. Furthermore, this weak bond is maintained in solution, as evidenced by NMR measurements.

Here we report the crystal and molecular structure of the related diastereoisomeric salt Λ-α-[Co(picenMe$_2$)(*S*-phe)](ClO$_4$)$_2$ (picenMe$_2$ is *N*,*N*′-dimethyl-1,6-di(2-pyridyl)-2,5-diazahexane), which shows the same kind of π–π interaction in the solid state. Solution NMR studies show that again this weak bond is maintained in solution, and this in turn suggests that complexes of this type may be suitable archetypes for probing the structure of DNA.

EXPERIMENTAL

Electronic and CD spectra were recorded on a Shimadzu UV-2100 recording spectrophotometer and a Jasco J-500C spectropolarimeter, respectively. NMR spectra were recorded using a Varian 300 Unity Plus spectrometer, with TMS as internal standard.

Picen

1,2-Diaminoethane (10 g, 0.17 mol) was dissolved in benzene (100 cm^3) and pyridine-2-carboxaldehyde (38 g, 0.36 mol) was added. A Dean-Stark distillation unit was used to collect water from the formation of the Schiff base. Solvent was removed *in vacuo* to give a thick red oil which crystallised overnight. The Schiff base and sodium borohydride (27.4 g, 0.72 mol) were dissolved in dry isopropanol (120 cm^3). The mixture was left to stir overnight, then refluxed for 1 h, allowed to cool, and 2 M hydrochloric acid added very slowly to pH 1. **CAUTION**: the acidification reaction is EXTREMELY violent. Aqueous NaOH was then added to pH 10 and the mixture extracted with chloroform. Solvent was removed *in vacuo* to give a thick red-brown oil (yield, 38.5 g).

PicenMe$_2$

A mixture of picen (5.68 g, 16 mmol) in acetonitrile (100 cm^3) and 37% (w/v) aqueous formaldehyde (20 cm^3) was stirred for 15 min before addition of a solution of sodium cyanoborohydride (3.85 g, 60 mmol) in acetonitrile (20 cm^3). The pH was maintained at 7.0 by minimal addition of glacial acetic acid, and after a further 1.5 h was reduced in volume and 1 M sodium hydroxide (230 cm^3) added. This mixture was extracted with diethylether (3 × 50 cm^3) and the combined extracts were washed with water (2 × 25 cm^3) and hydrochloric acid (1 M, 3 × 50 cm^3). The acid extracts were combined, the pH was adjusted to 10 with 5 M sodium hydroxide (*ca* 60 cm^3), and extracted with dichloromethane (2 × 50 cm^3). The extracts were dried over anhydrous sodium sulphate and then evaporated to dryness to give a yellow solid (yield, 4.4 g).

Δ,Λ-α-[Co(picenMe$_2$)Cl$_2$]ClO$_4$

This reaction was carried out in an evaporating dish on a steam bath. PicenMe$_2$ · 4HCl (3.09 g, 7.4 mmol) and $Na_3[Co(CO_3)_3] \cdot 3H_2O$ (2.27 g, 6.3 mmol) were mixed together and deionised water (40 cm^3) was added. The reaction mixture turned dark burgundy in colour. Hydrochloric acid (12 M, 4 cm^3) was added to the reaction mixture, which turned dark purple. Concentrated perchloric acid (2.5 cm^3) was added and the solution allowed to evaporate to approximately one third its original volume, then cooled. The resulting blueish/green crystalline product was collected at the pump, washed with a small amount of cold deionised water and allowed to dry in air. The mother liquor was reduced to yield a second crop (yield, 1.33 g). Satisfactory microanalyses were obtained.

Λ-α-[Co(picenMe$_2$)(*S*-phe)](ClO$_4$)$_2$

Δ,Λ-α-[Co(picenMe$_2$)Cl$_2$]ClO$_4$ (0.504 g, 1.0 mmol) and *S*-pheH (0.830 g, 5.0 mmol) were mixed together and deionised water (100 cm^3) was added. The resulting solution was heated on a hot water bath for *ca* 2 h, when it turned a burgundy colour. It was then cooled and sodium hydroxide (1 M, 1 cm^3) was added slowly to give a deep orange solution. This solution was loaded onto a CM Sephadex C25 column and eluted with 0.3 M sodium chloride. Minor pink to light orange bands were discarded. The primary red-orange band was collected in fractions. CD and electronic absorption spectra of these fractions indicated that they contained two diastereoisomers in varying proportions. The most concentrated fractions were combined and solid sodium perchlorate was added to the eluate and allowed to slowly dissolve and diffuse undisturbed through the solution. Crystals of the title complex grew over a period of a week. These were collected at the pump, washed with ice-cold water and air-dried. The complex was, as far as the chirality of the cobalt centre is concerned, resolved by the method of least soluble diastereoisomers. In this case, the resolving agent is the coordinated *S*-phenylalaninato anion. The perchlorate salts of the two possible diastereoisomers have markedly different solubilities in water. An ^{1}H NMR spectrum showed that there was only one diastereoisomer present in the isolated solid product and the analytical composition of the complex salt was confirmed by a single-crystal X-ray structure determination. In the visible region of the CD spectrum, an extremum is observed at 497 nm with $\Delta\varepsilon = +1.43\,M^{-1}\,cm^{-1}$. In the electronic spectrum, the absorption maximum is at 482 nm with $\varepsilon = 130\,M^{-1}\,cm^{-1}$.

X-ray Structure Analysis of Λ-α-[Co(picenMe$_2$)(*S*-phe)](ClO$_4$)$_2$

Crystal data: $C_{24}H_{30}N_5O_{10}Cl_2Co$, $M_r = 678.3$, $a = 10.462(2)$, $b = 12.895(3)$, $c = 22.560(3)$ Å, $V = 3043.4$ Å^3, $Z = 4$, $D_c = 1.480$, $D_m = 1.48\,Mg\,m^{-3}$, $F(000) = 1400.0$, $\mu(MoK\alpha) = 0.80\,mm^{-1}$, orthorhombic, space group $P2_12_12_1$ (No. 19). 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.[8] Intensity data were determined for reflections in the range $3.6° < 2\theta < 50°$. Intensities were corrected for Lorentz and polarisation effects but absorption corrections were not applied. A total of 8222 measured reflections was merged to give 4572 unique reflections of which 1797 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[9] and SHELXL-93[10] 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 was given by $w = 1/[\sigma^2(F_o)^2 + (0.0638P)^2]$ where $P = (\max(F_o^2, 0) + F_c^2)/3$, as defined by SHELXL-93.[10] This weighting scheme gave 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 minimisation factor changed by $<0.1\%$ and a final difference map showed no residual electron density greater than $|0.5|\,e\,\text{Å}^{-3}$. The final R value was 0.054 for 1797 reflections with $I > 2\sigma(I)$. The final weighted R [$= \{w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}^{1/2}$] was 0.133 for all 4572 data.

RESULTS AND DISCUSSION

Crystal and Molecular Structure

A perspective view of the complex cation Λ-α-[Co(picenMe$_2$)(*S*-phe)]$^{2+}$ showing the atom labelling scheme is shown in Figure 1. The chirality of the metal centre is unambiguously established as Λ because of the presence of *S*-phenylalanine as a chiral label. Tables I and II list the final atomic coordinates of non-hydrogen atoms and hydrogen atoms, respectively (in view of the importance of the latter to the NMR discussion) and Table III gives selected bonding parameters and interatomic distances for the complex.

Examination of the bond lengths and angles (Table III) in the complex does not reveal any anomaly. This complex (Figure 1) also contains an intramolecular hydrophobic bond between the phenyl ring of the amino acidate and one of the pyridyl rings of the tetradentate ligand, similar to that found[1,7] in the α-[Co(*R**,*R**-picchxnMe$_2$)(*R**-phe)]$^{2+}$ complexes, and in

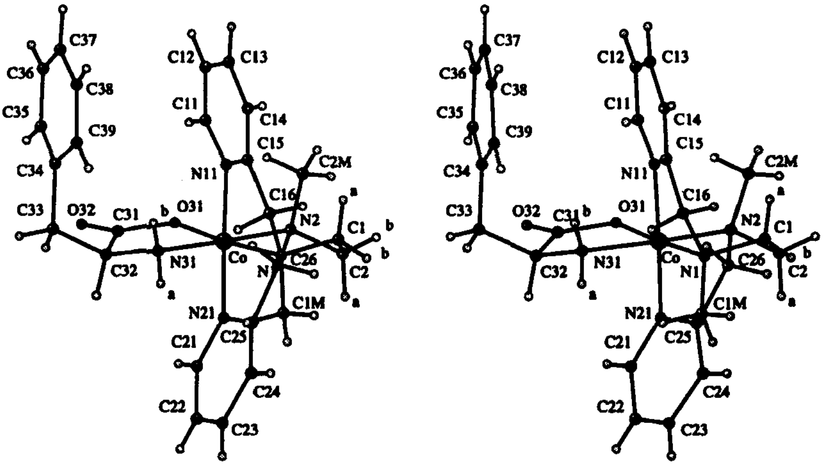

FIGURE 1 A perspective view[43] of the Δ-α-[Co(picenMe$_2$)(*S*-phe)]$^{2+}$ cation showing the atom labelling scheme. Numeric labels for hydrogen atoms correspond to those of the heavy atoms to which they are bonded. When more than one hydrogen atom is bonded to a centre it is distinguished by the suffix a, b or c.

TABLE I Final atomic coordinates for non-hydrogen atoms with estimated standard deviations in parentheses for the complex Λ-α-[Co(picenMe$_2$)(*S*-phe)](ClO$_4$)$_2$

	x/a	*y/b*	*z/c*
Co	0.7782(2)	0.8868(1)	0.1024(1)
N1	0.6369(13)	0.9268(10)	0.1565(7)
N11	0.7726(16)	1.0284(9)	0.0789(6)
N2	0.8953(14)	0.9113(10)	0.1682(7)
N21	0.7908(17)	0.7449(10)	0.1274(6)
N31	0.6713(11)	0.8579(8)	0.0341(5)
O31	0.9148(10)	0.8591(8)	0.0514(5)
O32	0.9704(11)	0.7893(7)	−0.0352(5)
C1	0.7030(20)	0.9715(13)	0.2081(9)
C11	0.8580(19)	1.0794(13)	0.0466(8)
C12	0.8374(25)	1.1850(16)	0.0294(10)
C13	0.7322(26)	1.2293(16)	0.0451(9)
C14	0.6311(21)	1.1777(16)	0.0750(9)
C15	0.6583(19)	1.0774(14)	0.0925(9)
C16	0.5669(17)	1.0112(13)	0.1264(8)
C1M	0.5466(17)	0.8438(14)	0.1733(9)
C21	0.7198(20)	0.6626(16)	0.1133(8)
C22	0.7395(23)	0.5629(15)	0.1307(9)
C23	0.8534(23)	0.5410(17)	0.1646(11)
C24	0.9322(20)	0.6282(20)	0.1798(9)
C25	0.8939(20)	0.7259(17)	0.1610(9)
C26	0.9777(17)	0.8190(13)	0.1726(8)
C2M	0.9855(18)	1.0006(12)	0.1663(9)
C31	0.8902(17)	0.8162(12)	−0.0007(8)
C32	0.7504(14)	0.8022(10)	−0.0121(6)
C33	0.7120(17)	0.8339(10)	−0.0748(7)
C34	0.7336(19)	0.9482(11)	−0.0912(7)
C35	0.8478(20)	0.9784(13)	−0.1145(9)
C36	0.8676(25)	1.0837(18)	−0.1301(10)
C37	0.7767(27)	1.1548(15)	−0.1217(9)
C38	0.6570(24)	1.1246(16)	−0.1014(10)
C39	0.6325(19)	1.0214(14)	−0.0829(8)
Cl1	1.2739(7)	0.7750(4)	0.2693(3)
O11	1.2720(21)	0.7069(13)	0.2238(9)
O12	1.1698(20)	0.7514(14)	0.3052(9)
O13	1.2655(17)	0.8726(12)	0.2445(7)
O14	1.3879(23)	0.7570(15)	0.2980(10)
Cl2	1.2725(7)	0.0091(4)	0.0392(3)
O21	1.1642(16)	0.0164(11)	0.0026(7)
O22	1.2962(20)	0.1002(15)	0.0689(9)
O23	1.2544(17)	−0.0654(11)	0.0814(7)
O24	1.3731(23)	−0.0270(15)	0.0046(10)

other related β diastereoisomers of *R,R*-picchxn.[11,12] The pyridyl ring in question is flat with an rms deviation of 0.019 Å for all six atoms; the mean plane of the phenyl ring is also flat with and rms deviation of 0.011 Å. The dihedral angle between the two planes is 9.1°.

The extent of the overlap of the two planes is illustrated in Figure 2. When this is compared to Δ-α-[Co(*R,R*-picchxnMe$_2$)(*R*-phe)]$^{2+}$ and its *S*-phe

TABLE II Final atomic coordinates for hydrogen atoms with estimated standard deviations in parentheses for Λ-α-[Co(picenMe$_2$)(*S*-phe)]-(ClO$_4$)$_2$

	x/*a*	*y*/*b*	*z*/*c*
H31a	0.6046(11)	0.8181(9)	0.0450(5)
H31b	0.6406(11)	0.9176(8)	0.0191(5)
H21	0.6495(20)	0.6746(16)	0.0890(8)
H1Ma	0.4979(78)	0.8233(63)	0.1393(15)
H1Mb	0.4899(75)	0.8689(32)	0.2036(38)
H1Mc	0.5934(18)	0.7853(37)	0.1881(49)
H26a	1.0459(17)	0.8225(13)	0.1436(8)
H26b	1.0154(17)	0.8145(13)	0.2118(8)
H16a	0.5039(17)	0.9821(13)	0.0997(8)
H16b	0.5224(17)	1.0532(13)	0.1556(8)
H22	0.6817(23)	0.5108(15)	0.1213(9)
H23	0.8746(23)	0.4739(17)	0.1761(11)
H2a	0.7958(18)	0.8454(13)	0.2375(9)
H2b	0.8631(18)	0.9503(13)	0.2555(9)
H24	1.0069(20)	0.6195(20)	0.2017(9)
H2Ma	1.0224(90)	1.0057(58)	0.1275(17)
H2Mb	1.0522(67)	0.9902(47)	0.1950(37)
H2Mc	0.9403(27)	1.0634(16)	0.1754(54)
H1a	0.7260(20)	1.0427(13)	0.1993(9)
H1b	0.6449(20)	0.9722(13)	0.2416(9)
H11	0.9327(19)	1.0460(13)	0.0350(8)
H12	0.8983(25)	1.2207(16)	0.0074(10)
H13	0.7219(26)	1.2992(16)	0.0364(9)
H32	0.7321(14)	0.7279(10)	−0.0082(6)
H33a	0.6221(17)	0.8182(10)	−0.0800(7)
H33b	0.7594(17)	0.7912(10)	−0.1026(7)
H14	0.5526(21)	1.2090(16)	0.0823(9)
H37	0.7934(27)	1.2212(15)	−0.1297(9)
H35	0.9127(20)	0.9301(13)	−0.1201(9)
H38	0.5923(24)	1.1739(16)	−0.0998(10)
H39	0.5547(19)	1.0023(14)	−0.0663(8)
H36	0.9452(25)	1.1044(18)	−0.1463(10)

analogue,[1,7] the extent of overlap is seen to be intermediate between the two. The closest interatomic contact between the two rings is 3.84 Å and the longest distance is 4.05 Å, between C11 ⋯ C35 and C14 ⋯ C38, respectively; the distance between the centroids of the two rings is 3.95 Å (Table III).

In the crystal lattice, the perchlorate groups are generally constrained. Final refinement revealed that one oxygen atom from Cl2 and two oxygen atoms from Cl1 had significant anisotropic thermal vibration, which might indicate slight disorder of the anions within the structure. The perchlorate ions are otherwise normal and not involved in hydrogen bonding. Complex cations are however linked in chains by a weak hydrogen bond between H31a (N31) and O32 at $-\frac{1}{2}x$, $\frac{1}{2}-y$, $-z$ (1.973 Å). The related complex

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

(a) *Bond lengths* (Å)			
Co–N11	1.901(7)	N31–C32	1.500(9)
Co–N1	1.985(8)	C32–C31	1.513(12)
Co–N2	1.960(8)	C31–O31	1.334(10)
Co–N21	1.938(8)	C31–O32	1.192(10)
Co–N31	1.938(6)	C32–C33	1.526(10)
Co–O31	1.870(6)	C34–C35	1.367(12)
		C35–C36	1.384(13)
		C36–C37	1.293(16)
		C37–C38	1.376(17)
		C38–C39	1.416(15)
		C39–C34	1.415(12)
		C34–C33	1.541(10)
(b) *Bond angles*			
N11–Co–N21	178.0(4)	N31–Co–O31	85.2(3)
O31–Co–N1	176.3(3)	Co–O31–C31	118.6(6)
N31–Co–N2	175.9(3)	O31–C31–C32	112.3(8)
		C31–C32–N31	111.3(7)
		C32–N31–Co	109.4(5)
(c) *Non-bonded contacts between the two hydrophobically bonded rings* (Å; *see text*)			
N11···C34	3.99		
C11···C35	3.86		
C12···C36	3.84		
C13···C37	3.92		
C14···C38	4.05		
C15···C39	4.03		

Δ-α-[Co(R,R-picchxnMe$_2$)(R-phe)](ClO$_4$)$_2$ is also linked through the cations in a similar manner.[7]

NMR Studies

Table IV gives selected ^{1}H NMR data for the complex dissolved in dmso-d_6. Assignments are based on those of related compounds.[1,7]

Rotamer populations for Λ-α-[Co(picenMe$_2$)(S-phe)]$^{2+}$ in dmso-d_6 could not be calculated, as the AB portion of the ABX spectrum of the aliphatic protons of phenylalanine gave a 'deceptively simple' spectrum. There are close similarities between the ^{1}H NMR of this complex and that of the *quasi* enantiomorphic species Δ-α-[Co(R,R-picchxnMe$_2$)(R-phe)]$^{2+}$ in dmso-d_6, such as the differences in chemical shifts for H11 and H21 protons. H11 lies over the carboxylate group (δ 8.12), and H21 interacts with the amine group (δ 9.03). However, more important is the marked difference between the chemical shifts of the amine protons of the phenylalanine ligand (H31a δ 7.1, H31b δ 4.15). This assignment is in accord with the fact that while the H31a signal was obscured by the phenyl resonances, its position was established through a COSY correlation to the well resolved triplet of H31b.

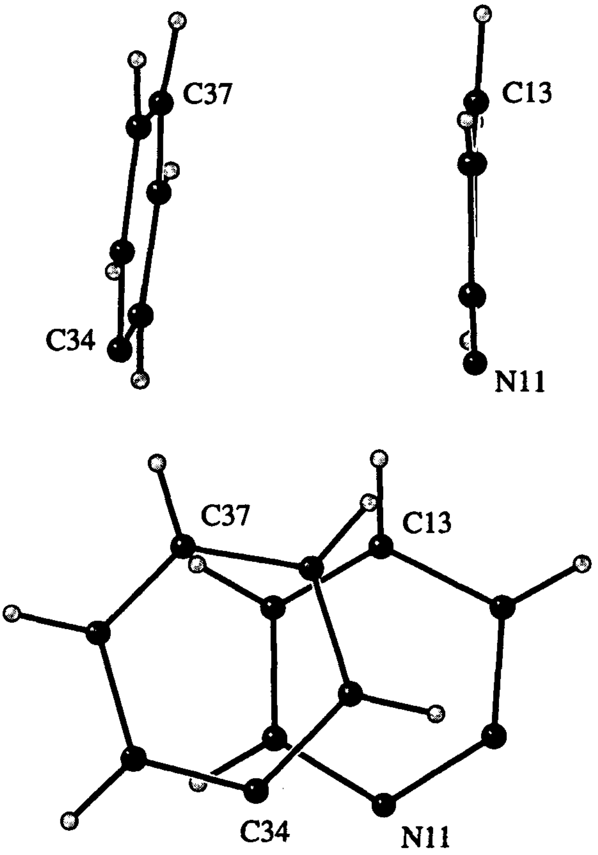

FIGURE 2 Perspective views[2] of the orientations of the two hydrophobically bonded rings illustrating the inclination of the planes ($\phi = 9.1°$) and the extent of overlap. The two views are orthogonal to each other, and the rotation axis used to generate the two projections passes through N11 and C13.

The chemical shift difference results from the H31b proton experiencing significant shielding effects due to its orientation towards the space between the weakly bonded rings, if the interaction were to persist in solution.[1,7] This phenomenon thus appears to be general for this class of coordination complex.

Acknowledgements

We gratefully acknowledge the Australian Research Council for financial support.

TABLE IV Characteristic ^1H NMR data for Λ-α-[Co(picenMe$_2$)(*S*-phe)]$^{2+}$ in dmso-d_6 at 298 K

Proton	*Chemical shift* (ppm)* *or coupling constant* (Hz)
H11	8.12 (d)
H12	8.25 (t)
H13	7.64 (t)
H14	~7.88 (d) overlapped
HM1	2.54 (s)
HM2	2.31 (s)
H21	9.03 (d)
H22	~7.88 (t) overlapped
H23	8.31 (t)
H24	~7.88 (d) overlapped
H32	3.43 (m)
H31a	7.1†
H31b	4.15 (t); $J_{av} = 10.2$ Hz
H35, H39	7.10–7.13, overlapped
H36–H38	7.16–7.18, overlapped
H33	2.8 (m)
$J_{11,12}$	5.4
$J_{21,22}$	5.7

*S = singlet, d = doublet, t = triplet, m = multiplet.
†Obscured by phenyl resonances.

Supplementary Material Available

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

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