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FULL PAPER

Novel iron(II) complexes with hexadentate nitrogen ligands obtained *via* intramolecular redox reactions

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Two novel complexes: $[Fe(L^{2'})][BPh_4]_2$, **1**, and $[Fe(L^{3'})][BPh_4]_2$, **2**, with the hexadentate nitrogen ligands, $L^{n'}$ = 1,9-bis(2′-pyridyl)-5-[(R-2″-pyridyl)methyl]-2,5,8-triazanon-1-ene, where R = ethoxy for $L^{2'}$ and methoxy for $L^{3'}$, were obtained from the iron(III) complex of the pentadentate ligand, L^1 = 1,9-bis(2′-pyridyl)-2,5,8-triazanonane. Complexes **1** and **2** were also obtained by making the hexadentate ligands: 1,9-bis(2′-pyridyl)-5-[(ethoxy-2′-pyridyl)methyl]-2,5,8-triazanonane (L^2) and 1,9-bis(2′-pyridyl)-5-[(methoxy-2″-pyridyl)methyl]-2,5,8-triazanonane (L^3) react with Fe(III), respectively. The structures of complexes **1** and **2** were characterized by COSY, HMBC, HMQC and NOESY NMR studies, and both structures were also confirmed by X-ray analysis. In both cases, the geometry around iron is a distorted octahedron. Since **1** and **2** are diamagnetic at 298 K they are low-spin iron(II) species. Both preparative methods are examples of oxidative dehydrogenation of a Fe(III) polyamine complex, in which the thermodynamically and kinetically stable final product is a low spin Fe(II) imine complex. In the case of the first method an increase in the size and denticity of the starting ligand is observed.

Introduction

Transition metal ions play an important role in different types of oxidation of coordinated organic ligands. An example is the conversion of coordinated alcohols to aldehydes and ketones.[1] Another example is the intramolecular oxidation of coordinated amines *via* oxidative dehydrogenation, where bound amines are transformed to imines coordinated to the reduced central ion. These oxidations have been reported to occur with iron,[2] copper,[3] nickel,[4] ruthenium,[5] osmium,[6] platinum[7] and cobalt.[8] In the case of iron, these reactions have been explained by different reaction mechanisms.[2,9] Iron(III) complexes containing primary or secondary amines can undergo oxidative dehydrogenation to yield thermodynamically and kinetically stable imine iron(II) complexes. However, little is known about oxidation reactions where there is an increase in the size and denticity of the starting ligand in the isolated final products.[10] In this paper, we describe proposed key steps between iron(III) and the pentadentate ligand: 1,9-bis(2′-pyridyl)-2,5,8-triazanonane (L^1), to produce the new hexadentate ligands: 1,9-bis(2′-pyridyl)-5-[(R-2″-pyridyl)methyl]-2,5,8-triazanon-1-ene, where R = ethoxy, ($L^{2'}$), or methoxy, ($L^{3'}$), coordinated to Fe(II): **1** and **2**, respectively. In addition, the hexadentate ligands 1,9-bis(2″-pyridyl)-5-[(ethoxy-2″-pyridyl)methyl]-2,5,8-triazanonane (L^2) and 1,9-bis(2″-pyridyl)-5-[(methoxy-2″-pyridyl)methyl]-2,5,8-triazanonane (L^3) were synthesised separately and reacted with Fe(III). Again, the final products prove to be the monoimine derivatives: $[Fe(L^{n'})][BPh_4]_2$ (**1**, **2**). For details of the ligand structures see Fig. 1. The characterisation of these complexes is also reported.

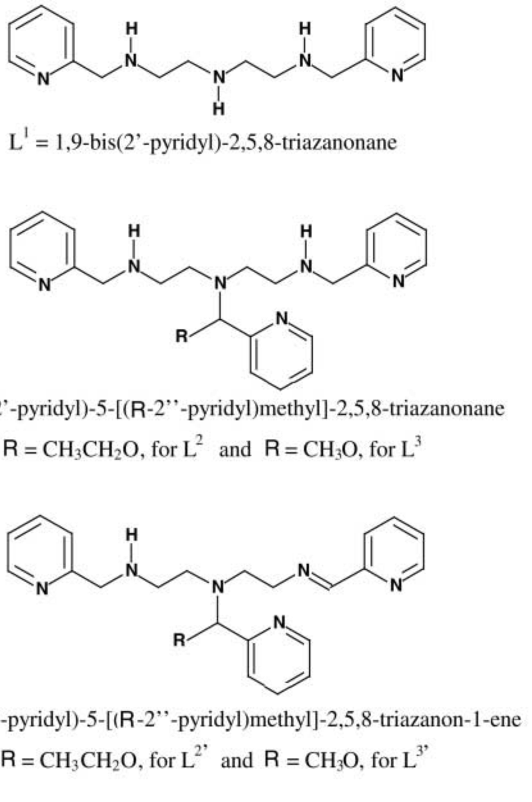

Fig. 1 Structures of the ligands.

Experimental

Physical measurements

Fourier transform infrared spectra on KBr pellets of the complexes were recorded on a Perkin-Elmer 599-B instrument in the range 4000–200 cm^{-1}. Electronic absorption spectra were recorded on a Hewlett-Packard 8452 diode array spectrophotometer at room temperature. The ^1H and ^{13}C NMR spectra

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of the compounds were obtained in acetone-d_6, in acetonitrile d_3 and dimethylsulfoxide-d_6 solutions on Varian NMR Unity Plus 500 and Varian 300 NMR Unity-Inova spectrometers respectively using TMS as a standard. Electrochemical measurements were performed on an EG&G PAR Potentiostat-Galvanostat model 273-A, using a three-electrode potentiostatic system in ethanol containing 0.10 M LiCl as supporting electrolyte in each case. Cyclic voltammetric measurements were carried out using a double platinum electrode and Ag°–AgCl as reference electrode. Potentials are given in V referenced to ferrocene–ferrocenium ($\Delta E = 0.73$ V). Elemental analyses C, H and N were carried out in the Chemistry Department at the University College London. The magnetic susceptibility data were obtained on a Faraday balance at room temperature; the set up was calibrated with $Hg[Co(SCN)_4]$ as standard.

Syntheses

1,9-Bis(2′-pyridyl)-2,5,8-triazanonane trihydrochloride (picdien·3HCl = L^1·3HCl). Was prepared as described in the literature.[8] $[Fe(DMSO)_6](NO_3)_3$ was synthesised according to the method already reported.[11] L^1·3HCl was dissolved in D_2O and its ^1H NMR spectrum corresponded to the reported one.[8b]

1,9-Bis(2′-pyridyl)-5-[(ethoxy-2″-pyridyl)methyl]-2,5,8-triazanonane (L^2). Absolute ethanol (100 mL) was added to L^1·3HCl (0.488 g, 1.24 mmol) and LiOH (0.089 g, 3.71 mmol). This mixture was heated (60 °C) until the solid dissolved; then, 2-pyridylcarboxyaldehyde (0.131 g, 1.24 mmol) was added to this solution and allowed to react for 2 h. A chromatography test was performed in order to ensure complete reaction of the aldehyde. The solvent was evaporated under vacuum at 50–60 °C until a yellow solid was obtained. The ^1H NMR spectrum of this compound confirmed the presence of the hexadentate ligand.

1,9-Bis(2′-pyridyl)-5-[(methoxy-2″-pyridyl)methyl]-2,5,8-triazanonane (L^3). This ligand was prepared in the same way as L^2, except that in this case absolute methanol was used.

$[Fe(L^{2'})][BPh_4]_2$, 1. *Method (i).* The trihydrochloride salt of ligand L^1, (L^1·3HCl) (0.509 g, 1.29 mmol) was placed in the filter thimble of a Soxhlet extractor together with metallic lithium (0.026 g, 3.80 mmol). $[Fe(DMSO)_6](NO_3)_3$ (0.917 g, 1.29 mmol) in anhydrous ethanol (50 mL) was added to the reservoir flask and flushed with nitrogen (orange solution). The neutralised ligand was extracted into the flask and allowed to react slowly with the iron compound to produce a green solution. The reaction was kept at reflux for 16 h, whereby the colour of the solution changed to deep purple. The addition of a 1 M sodium tetraphenylborate ethanolic solution (4 mL) to the cold reaction mixture produced a dark red precipitate which was filtered off and washed with cold methanol. The recovered solid was air-dried. The yield was 0.245 g (20%). (Found: C, 77.25; H, 6.41; N, 7.45%. $C_{72}H_{70}B_2FeN_6O$ requires C, 77.71; H, 6.34; N, 7.55%). IR (KBr) of **1** : 3241m [ν(NH)], 2981m [$\nu(CH_2)$], 1602m [ν(C=N)], 1578m [ν(C=C)], 1323m [$\delta_{sym}(CH_3)$], 1091s [ν(C–O)] cm^{-1}.

Method (ii). To a solution of L^2 (2.46 mmol) in ethanol at 60 °C, $[Fe(DMSO)_6](NO_3)_3$ (1.748 g, 2.46 mmol) was added in small portions, over a period of 1.5 h. The purple solution was stirred at the same temperature for an extra hour. To the cold solution, 20 mL of 0.24 M sodium tetraphenylborate ethanolic solution were added. The reaction mixture was then placed in a fridge for 30 min. The solid formed was recovered by filtration, washed with cold ethanol, dichloromethane and finally air-dried under vacuum (1.566 g, 59%). The yield of the compound by this second method increased substantially from 20 to 59%. (Found: C, 77.38; H, 6.19; N, 7.66%. $C_{72}H_{70}B_2FeN_6O$ requires C, 77.71; H, 6.34; N, 7.55%). The IR (KBr) spectrum showed exactly the same peaks as for **1** obtained *via* the first method.

NMR of $[Fe(L^{2'})][BPh_4]_2$, 1. Since the assignment of every signal was not possible using only 1D ^1H and ^{13}C NMR, it was necessary to use 2D methods: COSY, NOESY, HMBC, HMQC. The unequivocal assignments are shown in Tables 1 and 2.

$[Fe(L^{3'})][BPh_4]_2$, 2. This compound was prepared by both the first and second method mentioned in the above for complex **1**, except that methanol was used as solvent. A substantial increase in reaction yield was again observed using the second method (14 to 44%). (Found: C, 77.31; H, 6.35; N, 7.74%. $C_{71}H_{68}B_2FeN_6O$ requires C, 77.61, H 6.24, N, 7.65%). IR (KBr) of **2**: 3254m [ν(NH)], 2982m [$\nu(CH_2)$], 1602m [ν(C=N)], 1542m, [ν(C=C)], 1325m [$\delta_{sym}(CH_3)$], 1093s [ν(C–O)] cm^{-1}.

X-Ray analysis

A summary of the crystallographic data for compounds **1** and **2** is listed in Table 3. The diffraction data for complex **1** were analysed by using a CCD area detector, the Laue symmetry was found to be $2/m$: $R_{int} = 17\%$ for this monoclinic cell. However, because of the poor diffraction of the crystal, it was not possible to collect data at a better resolution than 1.15 Å ($\theta = 18°$ for Mo-K_α radiation). The measured intensities were reduced to $F_o{}^2$ by using a classical procedure and corrected for absorption with SHELXTL-plus[12] (min. and max. transmission factors: 0.84 and 0.96 respectively). The structure was solved by direct methods (SIR 92)[13] and refined by full matrix least-squares by using SHELX-97.[14] The crystal was considered as twinned by pseudo-merohedry, which could explain the β angle for the unit cell close to 90°. Using the twin matrix law [1 0 0 0 − 1 0 0 0 − 1] and contributions of 88 and 12% for each individual twin domain, the R_1 index[14] for reflections having $I > 2\sigma(I)$ was reduced from 16.71 to 9.03% for an isotropic model including all non-hydrogen atoms. In the last refinement cycles hydrogen atoms were placed in idealised positions and the remaining atoms were refined anisotropically with neither restraints nor constraints for the geometry.

The diffraction data of compound **2** were collected to a maximum θ of 28.00° with 2424 frames (complete sphere) *via* ω-rotation ($\Delta/\omega = 0.3°$) at 10 s per frame on a BRUKER-AXS APEX diffractometer with a CCD area detector. The measured intensities were reduced to F^2 and corrected for absorption with SADABS by the BRUKER-AXS software package.[15] The structure was solved by direct methods and refined by full-matrix least-squares calculations using all measured F^2 data and SHELXTL-NT 98.[16] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions using a riding model. The molecular structure was created by the CRYSTALS software package.[17]

CCDC reference numbers 168495 and 168496.

See http://www.rsc.org/suppdata/dt/b1/b100915j/ for crystallographic data in CIF or other electronic format.

Results and discussion

The reaction in anhydrous ethanol between the $[Fe(DMSO)_6]$-$(NO_3)_3$ complex and the trihydrochloride of the ligand L^1 which was prepared in high purity, produced compound **1**: $[Fe(L^{2'})][BPh_4]_2$. This reaction was repeated several times and the same product was always obtained. The ^1H NMR spectrum for **1** in acetone-d_6 at 298 K is shown in Fig. 2. The unequivocal ^1H and ^{13}C NMR assignments for compound **1** were achieved by 2D correlated COSY (Fig. 3), NOESY, HMBC and HMQC (Fig. 4) experiments, the assignments for each hydrogen and carbon atom of the molecules **1** and **2** are listed in Tables 1 and 2. The ^1H NMR and ^{13}C NMR spectra confirmed the formation of the imine function with chemical shifts of $\delta = 9.55$ and 170.6 for H-11 and C-11, respectively. The hemiaminal function at carbon C-17 can be identified by the corresponding chemical

Table 1 ^{1}H NMR data, in acetone-d$_6$, for **1** (500 MHz) and **2** (300 MHz) with TMS as internal reference[a]

Assignment	**1**					**2**				
Nucleus	δ	m(i)	$J$1/Hz	$J$2/Hz	$J$3/Hz	δ	m(i)	$J$1/Hz	$J$2/Hz	$J$3/Hz
H24	1.30	t(1)		J_{24-23}(7)		—	—	—	—	—
H7a	3.00	dd(1)	J_{7a-7b}(14)	J_{7a-8a}(5)		3.16	dd(1)	J_{7a-7b}(14)	J_{7a-8a}(5)	
H8a	3.13	dd(1)	J_{8a-8b}(15)	J_{8a-7a}(5)		3.13	dd(1)	J_{8a-8b}(10)	J_{8a-7a}(4)	
H9a,b	3.17	m(2)				3.28	m(2)			
H8b	3.19	dd(1)	J_{8b-8a}(14)	J_{8b-7b}(5)		3.33	dd(1)	J_{8b-8a}(10)	J_{8b-7b}(4)	
H7b	3.37	m(1)				3.49	m(1)			
NH	3.83	t(1)		J_{NH-6a}(6)		4.00	t(1)		J_{NH-6a}(7)	
H23a	3.94	qd(1)		J_{23a-24}(7)		3.85	s(3)			
H23b	4.08	qd(1)		J_{23b-24}(7)						
H6a	4.11	dd(1)	J_{6a-6b}(18)	J_{6a-NH}(6)		4.21	dd(1)	J_{6a-6b}(18)	J_{6a-NH}(7)	
H6b	4.18	d(1)	J_{6b-6a}(18)			4.34	d(1)	J_{6b-6a}(18)		
H10a	4.30	ddd(1)	$J_{10a-10b}$(9)	J_{10a-9a}(5)	J_{10a-9b}(1)	4.46	ddd(1)	$J_{10a-10b}$(16)	J_{10a-9a}(6)	J_{10a-9b}(1)
H10b	4.56	m(1)				4.71	m(1)			
H17	5.38	s(1)				5.04	s(1)			
H4	6.59	dd(1)		J_{4-3}(5)	J_{4-2}(1)	6.66	ddd(1)	J_{4-3}(5)	J_{4-2}(1)	J_{4-1}(1)
H$_p$(Bφ_4)	6.74	t(8)		J_{m-p-o}(7)		6.75	t(8)			J_{m-p-o}(7)
H$_m$(Bφ_4)	6.89	t(16)		J_{o-m-p}(7)		6.90	dd(16)		J_{m-o}(8)	J_{m-p}(7)
H3	7.21	ddd(1)	J_{3-2}(7)	J_{3-4}(6)	J_{3-1}(1)	7.29	m(1)			
H13	7.23	d(1)		J_{13-14}(6)		7.28	m(1)			
H$_o$(Bφ_4)	7.31	m(16)				7.32	m(16)			
H14	7.36	ddd(1)	J_{14-15}(7)	J_{14-13}(6)	J_{14-16}(1)	7.44	ddd(1)	J_{14-15}(7.5)	J_{14-13}(6)	J_{14-16}(1)
H20	7.52	dd(1)	J_{20-21}(7)	J_{20-19}(6)	J_{20-22}(1)	7.60	dd(1)	J_{20-21}(7)	J_{20-19}(5)	J_{20-22}(1)
H1	7.64	d(1)	J_{1-2}(8)			7.64	ddd(1)	J_{1-2}(7.5)	J_{1-3}(1)	J_{1-4}(1)
H19	7.73	d(1)		J_{19-20}(6)	J_{19-21}(1)	7.78	dd(1)		J_{19-20}(5)	J_{19-21}(1)
H22	7.77	d(1)	J_{22-21}(8)			7.85	d(1)	J_{22-21}(7)		
H2	7.98	ddd(1)	J_{2-1}(8)	J_{2-3}(7)	J_{2-4}(1)	8.04	ddd(1)	J_{2-1}(7.5)	J_{2-3}(6)	J_{2-4}(1)
H15	8.02	ddd(1)	J_{15-16}(8)	J_{15-14}(7)	J_{15-13}(1)	8.09	ddd(1)	J_{15-16}(8)	J_{15-14}(7)	J_{15-13}(1)
H21	8.08	ddd(1)	J_{21-22}(8)	J_{21-20}(7)	J_{21-19}(1)	8.16	ddd(1)	J_{21-22}(7)	J_{21-20}(7)	J_{21-19}(1)
H16	8.25	d(1)	J_{16-15}(8)			8.53	d(1)	J_{16-15}(8)		
H11	9.55	s(1)				9.74	s(1)			

[a] δ = Chemical shift; m = multiplicity; (i) = integration; J = coupling constant; (Bϕ_4) = *ortho* (*o*), *meta* (*m*) and *para* (*p*) proton of tetraphenylborate.

Table 2 ^{13}C NMR data, in acetone-d$_6$, for **1** (125 MHz) and **2** (75 MHz), TMS as internal reference[a]

Assignment Nucleus	**1** δ	**2** δ	Identification
C24	15.87	—	
C9	56.04	55.93	HMQC C17
C7, C10	58.94	59.00	HMQC C11
C8	60.43	60.53	HMQC C17
C6	60.69	60.66	
C23	70.19	61.65	HMQC C17
C17	99.55	100.77	
C$_p$(Bφ_4)	122.33	122.24	COSY
C22	123.43	123.31	HMQC C6
C1	125.90	125.90	HMQC C17
C$_m$(Bφ_4)	126.09	126.00	COSY
C20	127.07	127.01	
C14	127.26	127.26	
C3	127.74	127.18	
C16	129.15	127.66	
C$_o$(Bφ_4)	137.08	136.96	COSY
C15	138.00	137.71	
C2	139.53	139.48	
C21	139.57	153.15	
C19	153.19	153.20	
C4	154.58	154.54	
C13	155.44	155.44	
C12	163.50	163.48	HMQC H11
C$_Q$(Bφ_4)	165.03	164.88	q; (J_{B-C}) 49.1 Hz
C18	164.45	164.31	HMBC H17
C$_Q$ (Bφ_4)	165.03	164.88	q; (J_{B-C}) 49.1 Hz
C$_Q$ (Bφ_4)	165.03	164.88	q; (J_{B-C}) 49.1 Hz
C$_Q$ (Bφ_4)	165.03	164.88	q; (J_{B-C}) 49.1 Hz
C5	166.89	166.89	HMQC H6
C11	170.59	170.55	

[a] δ = Chemical shift; J_{B-C} = boron–carbon coupling constant; (Bϕ_4) = *ortho* (*o*), *meta* (*m*), *para* (*p*) and quaternary (Q) carbon atom of tetraphenylborate.

Table 3 Crystallographic data for compounds **1** and **2**

	1	**2**
Formula	$C_{72}H_{70}B_2FeN_6O$	$C_{71}H_{68}B_2FeN_6O$
M	1112.81	1098.78
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
T/K	293(2)	293(2)
a/Å	18.1077(2)	17.850(5)
b/Å	17.2455(1)	12.015(3)
c/Å	39.8316(4)	26.864(7)
β/°	90.0977(7)	91.227(5)
U/Å^3	12438.4(2)	5760(3)
Z	8	4
D_c/Mg m^{-3}	1.188	1.267
μ(Mo-K$_\alpha$)/mm^{-1}	0.29	0.31
Crystal dimensions/mm	0.28 × 0.10 × 0.06	0.39 × 0.24 × 0.06
Total reflections measured	83289	54868[c]
No. unique reflections	8537	10155
No. observed reflections	6217 [$F_o > 4\sigma(F_o)$]	5011 [$F_o > 4\sigma(F_o)$]
No. variables	1479	732
GOOF	1.160	0.829
R[a]	0.0729	0.0560
wR[b]	0.1505	0.0817

[a] R is for data with $I > 2\sigma(I)$, $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] wR is for all data, $wR = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w^{-1} = \sigma^2F_o^2 + (0.0174P)^2 + 0.00P$; $P = [\max(F_o^2, 0) + 2\,F_c^2]/3$. [c] θ-range from 1.14 to 25.00°.

shifts of H-17, δ = 5.38, and C-17, δ = 99.6. The coordinated ligand has three asymmetric centres, namely C-17, the central nitrogen atom and N–H so that in the ^{1}H NMR spectrum the signals of the neighbouring methylene groups to C-17 are diasterotopic.

The signals of the three pyridine rings were identified by the aid of a COSY spectrum and assigned by HMBC, this permitted the identification of H-19 (correlated with H-17) and

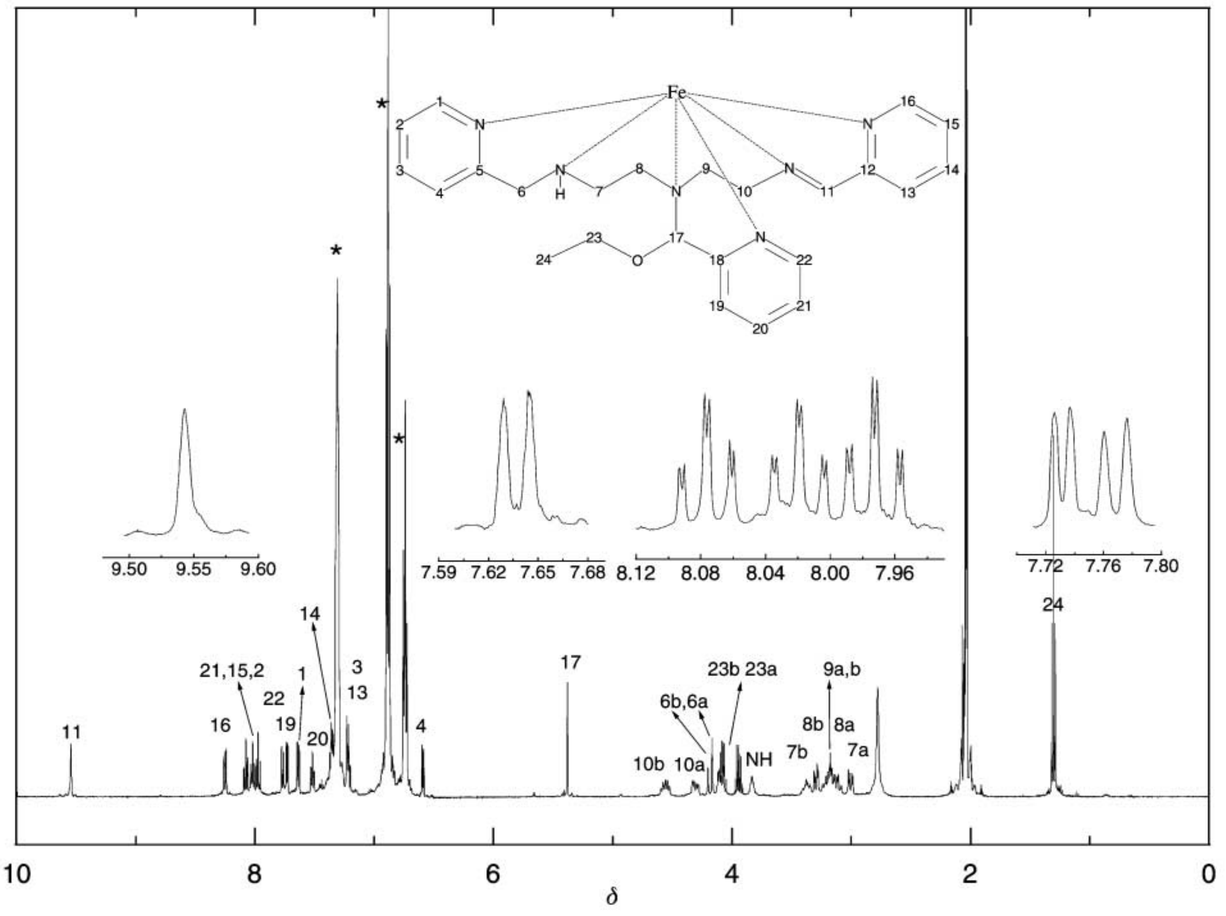


Fig. 2 ^1H NMR spectrum in acetone-d_6 for **1** (500 MHz) at 298 K, TMS as internal reference, * represents counterion signals.

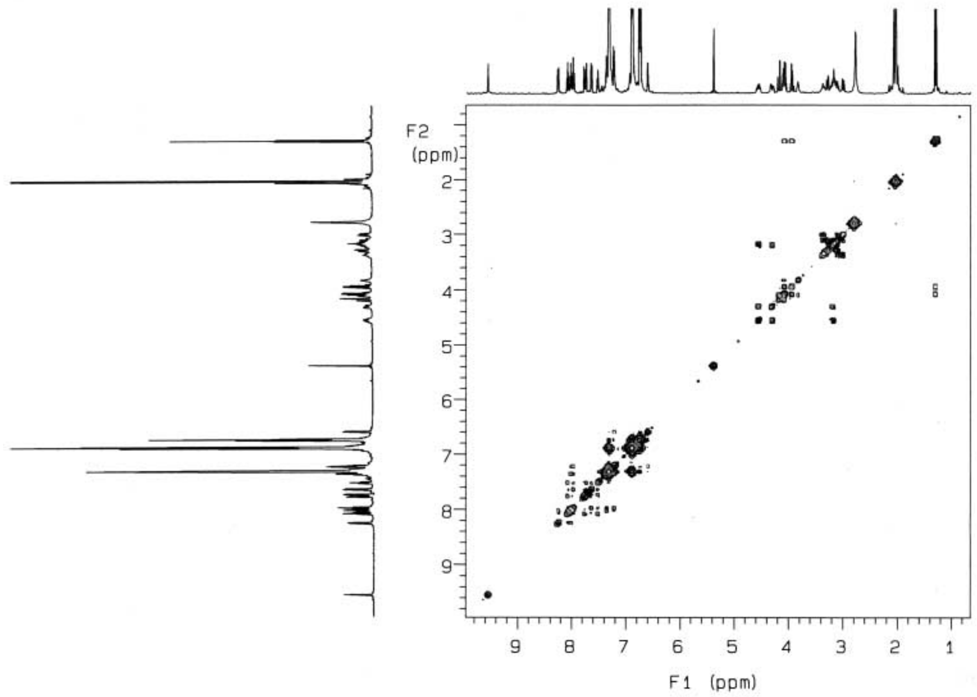


Fig. 3 COSY spectrum of **1**.

H-13 (correlated with H-11). The quaternary carbon atoms of the pyridine rings were assigned by HMQC. The broad ^1H NMR signal of the N–H group is located at $\delta = 3.83$. The *ipso* carbon atoms of the phenyl rings of the tetraphenylborate anions were identified from the ^{13}C NMR spectrum, because they show a quartet signal of 1 : 1 : 1 : 1 intensity at $\delta = 165.03$ as a consequence of the coupling between the ^{13}C and ^{11}B nuclei ($J = 49.1$ Hz). The same analysis was carried out for compound **2**, and the assignment is very similar to compound **1** except that the ethoxy group of **1** ($\delta = 3.94, 4.08, 1.30$) does not appear in this case, instead there is a singlet at $\delta = 3.85$ due to the methoxy group (Tables 1 and 2).

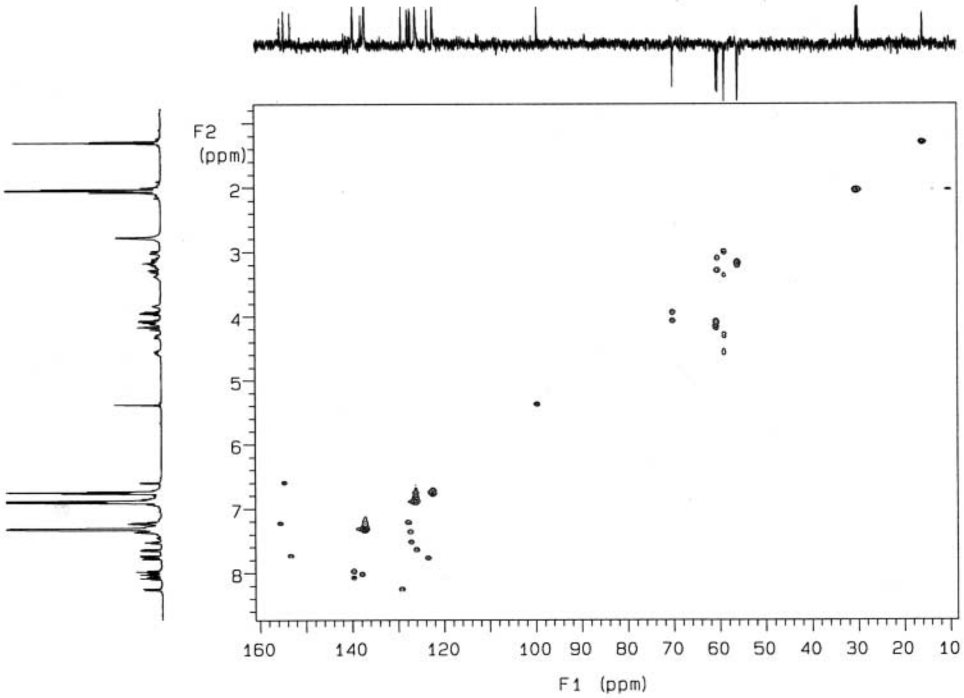


Fig. 4 HMQC spectrum of **1**.

The UV-Vis spectrum of **1** in acetone shows bands that correspond to the transitions in the region expected for a d^6 low spin species: $^1A_{1g} \longrightarrow {}^1T_{1g}$ and $^1A_{1g} \longrightarrow {}^1T_{2g}$,[18] one at 394 nm ($\varepsilon$ = 8036 M^{-1} cm^{-1}) and the other one at 575 (ε = 6984 M^{-1} cm^{-1}). However, the high extinction coefficients might suggest that the d–d transitions are masked by the charge transfer bands that are usually found in complexes with unsaturated ligands.[19] In acetonitrile **1** shows two peaks, one at 394 (ε = 8237 M^{-1} cm^{-1}) and one at 576 nm (ε = 7178 M^{-1} cm^{-1}). The spectra of **1** and **2** in acetone and in acetonitrile are very similar, however in dimethylsulfoxide both complexes show absorptions at 402 and 581 nm. The changes in the UV-Vis spectra in DMSO must be due to a change in the compounds structures due perhaps to a nucleophilic attack on the molecule by the solvent. This is consistent with the changes observed in the ^{1}H NMR spectra in DMSO.

The iron product **1** was obtained with the starting ligand L^1, which therefore might have suffered an oxidation reaction and later have been transformed into a hexadentate ligand. There are several examples known in the literature in which a polydentate amine coordination compound, for instance with cobalt(II), suffers an oxidative dehydrogenation and converts to the imine complex.[8] Therefore, we propose that in our case the coordinated ligand L^1 was oxidized to the monoimine with the double bond being conjugated to the pyridine ring, whereby the original oxidation state of the central iron(III) atom changed to iron(II). A support for this proposal is the diamagnetism found in **1**, consistent with a low spin iron(II) species.

In a second reaction the imine carbon suffers a nucleophilic attack by two ethanol molecules, leading to decomposition and the formation of a ketal moiety. The final product, compound **1**, can be explained by a nucleophilic attack of the central nitrogen in the secondary coordinated amine, of a still intact polydentate imine, to the electron deficient carbon of the ketal moiety (Scheme 1).

Proposed key steps for reaction

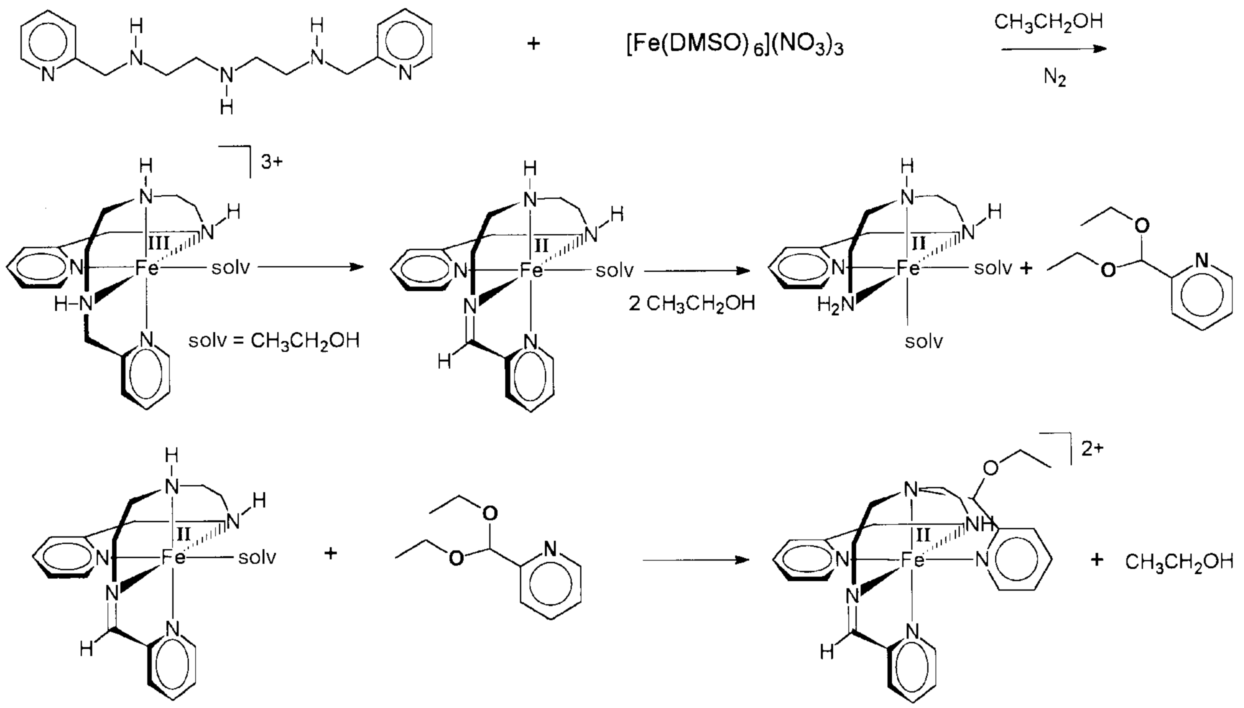
In order to provide some chemical evidence for the proposed reaction mechanism above (Scheme 1), L^1 was reacted with an equivalent amount of 2-pyridylcarboxyaldehyde, thus obtaining the product L^2. It is worthwhile to mention that while the ^{1}H NMR spectrum of L^2 in acetone-d_6 does not show the imine hydrogen, it does show the hydrogen at δ 4.33, on the chiral carbon. When this reaction was carried out in methanol, the obtained product was the methoxy derivative, L^3. Thus, this is further evidence in support of the attack on the ketal moiety.

Further support for the proposed scheme is provided by cyclic voltammetry. Fig. 5(a) shows the cyclic voltammogram of $L^1 \cdot 3HCl$ where three non-reversible reduction signals with a cathodic potential peak at $E_{pc} = -1.187$, -1.371 and -1.527 V are observed with their corresponding oxidation signals. Fig. 5(b) shows the cyclic voltammogram of $[Fe(DMSO)_6](NO_3)_3$; a half wave potential ($E_{1/2}$) of a quasi reversible signal at -0.559 V for the redox couple Fe(III)/Fe(II) is observed. Finally, Fig. 5(c) shows the cyclic voltammogram of a stoichiometric mixture (1 : 1) of $[Fe(DMSO)_6](NO_3)_3$ and $L^1 \cdot 3HCl$. The quasi reversible signal at ($E_{1/2}$) = -0.475 V corresponds to the redox couple Fe(III)/Fe(II) and since the potential of this mixture is shifted compared to the one previously described in Fig. 5(b), we propose that at this stage the ligand is already coordinated to the iron(III) species. Besides, a non reversible signal at $E_{pc} = -1.126$ V is observed and that can be assigned to the free protons formed by the following reaction:

$$Fe^{3+} + (H_3L^1)^{3+} \longrightarrow (FeL^1)^{3+} + 3H^+$$

It is worthwhile to mention that this signal is three times more intense than each one assigned to the free ligand [Fig. 5(a)], that is consistent with our proposal. Thus the first formed compound should correspond to an iron(III) species. In order to confirm the oxidation state of the iron compound, the cyclic voltammetry has also been recorded by starting the linear sweep in the positive direction (anodic sweep). At the beginning, (0 μmol) no oxidation signals were observed [see Fig. 6(a)] therefore, it was concluded that the first compound is an iron(III) species. The observed signals in the whole voltammogram are identical to those observed in Fig. 5(c).

When a cyclic voltammogram is recorded under the same conditions as before with gradual addition of a 0.2 M lithium ethoxide solution to an ethanolic solution of a stoichiometric mixture (1 : 1) of $[Fe(DMSO)_6](NO_3)_3$ and $L^1 \cdot 3HCl$, [Fig. 6(a)], it is observed that an anodic current is generated at the beginning, which gradually increases according to the amount of LiOEt added. Therefore, the oxidation signal which appears at



Scheme 1 Proposed key steps for the formation of **1** *via* an oxidative dehydrogenation.

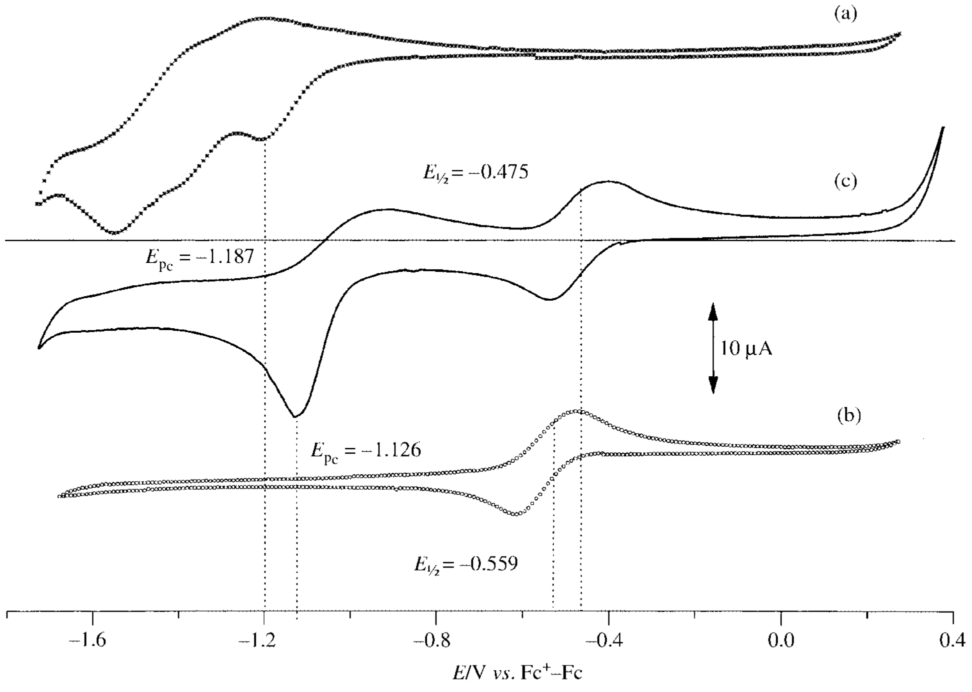


Fig. 5 Cyclic voltammetry of (a) --*-- 10^{-3} M L^1·3HCl, (b) --O-- 10^{-3} M of $[Fe(DMSO)_6](NO_3)_3$ and (c) —— 10^{-3} M of a stoichiometric mixture of both (a) and (b).

anodic potential (E_{pa} = −0.403 V), can be unambiguously assigned to an iron(II) species. When the inversion potential is reached and the linear sweep is in the negative direction (cathodic sweep), a signal at −0.435 V is observed that corresponds to the electrochemically generated reduced iron(III) species. The signal at E_{pc} = −1.125 V corresponds to the reduction of free protons and decreases as LiOEt is added. At the end of the neutralisation (18 μmol of LiOEt) the anodic current becomes constant and only one redox system is observed at $E_{1/2}$ = −0.364 V [see Fig. 6(b)].

Thus from these cyclic voltammetry results we have shown the formation of an iron(III) complex with L^1 which under basic conditions suffers a transformation to an iron(II) complex.

In order to confirm the formation of the Fe(II) species and the imine in the new ligand, ($L^{2'}$), $[Fe(DMSO)_6](NO_3)_3$ and L^2 were reacted in ethanol under a argon atmosphere in a stoichiometric ratio of 1 : 1, (second method). The ^{1}H NMR spectrum of the solid obtained (yield 43%) corresponds to that of **1**. From this experiment and the results of the cyclic voltammetry, we can conclude that an intramolecular redox reaction took place in an initially formed iron(III) complex giving rise to an iron(II) complex with an imine in the coordinated ligand. Besides, the product yield of 43% indicates that two equivalents of Fe(III) are required oxidise the ligand L^2 completely. Thus, under these conditions the expected optimum yield would be 50%. According to the

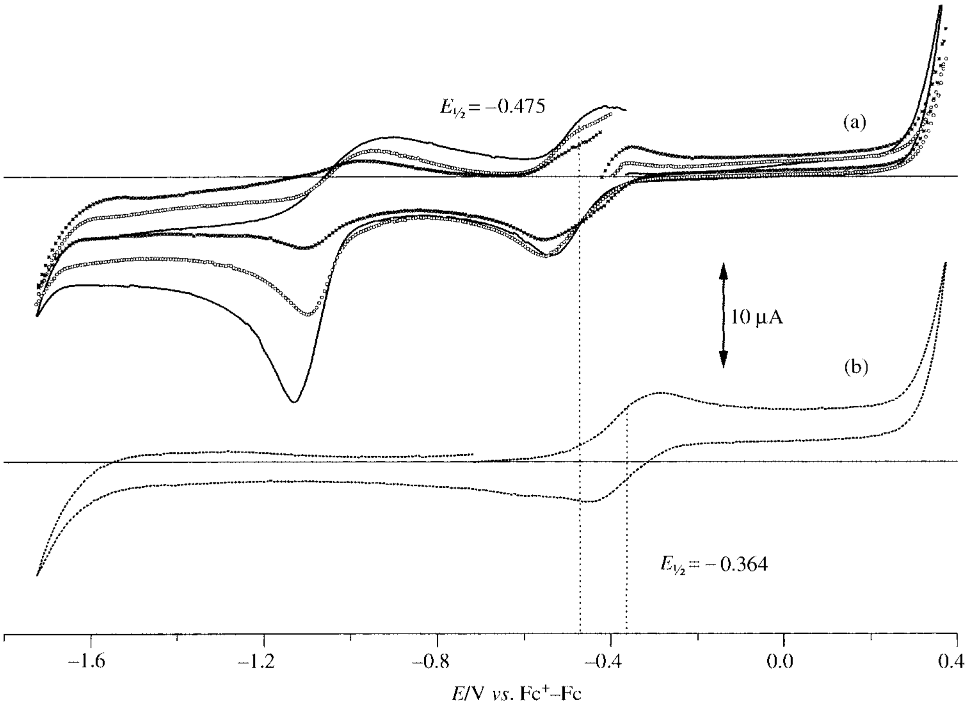


Fig. 6 Cyclic voltammetry of (a) the neutralisation of a mixture of 5 μmol of $[Fe(DMSO)_6](NO_3)_3$ and 5 μmol $L^1 \cdot 3HCl$ with LiOEt (—— 0 μmol; --○-- 6 μmol; --*-- 12 μmol) and (b) --●-- 18 μmol.

previous findings, we propose that the reaction proceeds as follows:

$$R^1\text{–}NH^+{}_2\text{–}CH_2\text{–}R^2\ Cl^- + LiOEt \rightleftarrows R^1\text{–}NH\text{–}CH\text{–}R^2 + LiCl + EtOH$$

$$2\ Fe^{III} + R^1\text{–}NH\text{–}CH_2\text{–}R^2 \longrightarrow 2\ Fe^{II} + R^1\text{–}N{=}CH\text{–}R^2 + 2H^+$$

It is important to mention that this redox reaction takes place with the ligand coordinated to the iron atom. When the reaction is carried out with iron(III) and the equivalent ligand L^3 in methanol, the diamagnetic compound **2** was produced.

The preparation of **1** by the second method resulted in a substantial increase in the product yield (from 20 to 59%) compared to the first method, where several products are formed and purification requires several steps. The second method is more direct and clean. Complexes of iron(II) with very similar ligands have been reported previously,[20] however they are extremely air sensitive, due to the absence of the primary or secondary amines in the ligands.

From previous study we conclude that compounds **1** and **2** form octahedral complexes with the hexadentate ligands $L^{2'}$ and $L^{3'}$, respectively. In order to establish the nature of the complexes in the solid state, suitable single crystals of **1** and **2** were studied by X-ray diffraction.

Solid state structures

In order to confirm the molecular structures of the dark red complexes **1** and **2**, an X-ray diffraction study was carried out for both molecules. Although the resolution of the data is low for compound **1**, they agree very well with the data obtained for complex **2** and it is not surprising that the geometries of the molecular framework of the two complexes are almost identical (see Table 4 for selected interatomic distances and angles).

For compound **1**, the asymmetric unit of the monoclinic cell contains two crystallographically independent cations and four tetraphenylborate counterions, with all atoms lying in general positions. The space group for **1**, with $Z = 8$, was confirmed using the ADDSYM module of PLATON,[21] which did not

Table 4 Selected bond lengths (Å) and angles (°) for compounds **1** and **2**

	1[a]	**2**
Fe(1)–N(1)	1.977(9)	1.981(3)
Fe(1)–N(2)	2.007(8)	2.013(2)
Fe(1)–N(3)	2.007(9)	1.998(2)
Fe(1)–N(4)	1.853(9)	1.848(3)
Fe(1)–N(5)	1.946(9)	1.959(3)
Fe(1)–N(6)	1.942(9)	1.953(3)
N(1)–C(1)	1.347(13)	1.348(3)
N(1)–C(5)	1.353(12)	1.344(4)
N(2)–C(6)	1.474(12)	1.463(4)
N(2)–C(7)	1.488(11)	1.490(3)
N(3)–C(8)	1.483(12)	1.484(3)
N(3)–C(9)	1.510(13)	1.507(3)
N(3)–C(17)	1.491(13)	1.483(3)
N(4)–C(10)	1.460(13)	1.452(4)
N(4)–C(11)	1.271(14)	1.286(4)
N(5)–C(12)	1.376(13)	1.361(4)
N(5)–C(16)	1.342(13)	1.335(3)
N(6)–C(18)	1.368(13)	1.347(4)
N(6)–C(22)	1.356(13)	1.337(3)
C(17)–O(1)	1.384(12)	1.389(3)
N(1)–Fe(1)–N(2)	82.8(5)	82.94(12)
N(1)–Fe(1)–N(3)	97.9(4)	98.56(11)
N(2)–Fe(1)–N(3)	86.1(4)	86.04(11)
N(1)–Fe(1)–N(4)	172.9(5)	173.77(12)
N(2)–Fe(1)–N(4)	90.8(4)	92.90(12)
N(3)–Fe(1)–N(4)	84.7(5)	85.72(12)
N(1)–Fe(1)–N(5)	96.0(5)	94.37(11)
N(2)–Fe(1)–N(5)	95.3(3)	97.11(10)
N(3)–Fe(1)–N(5)	166.2(5)	166.97(12)
N(4)–Fe(1)–N(5)	81.6(6)	81.51(12)
N(1)–Fe(1)–N(6)	93.1(5)	93.21(11)
N(2)–Fe(1)–N(6)	166.6(6)	166.61(11)
N(3)–Fe(1)–N(6)	81.8(6)	81.85(11)
N(4)–Fe(1)–N(6)	94.0(4)	91.87(11)
N(5)–Fe(1)–N(6)	97.9(6)	95.97(11)
N(4)–C(11)–C(12)	115.8(13)	114.3(3)

[a] Average bond lengths and angles have been calculated for the two independent molecules in the asymmetric unit.

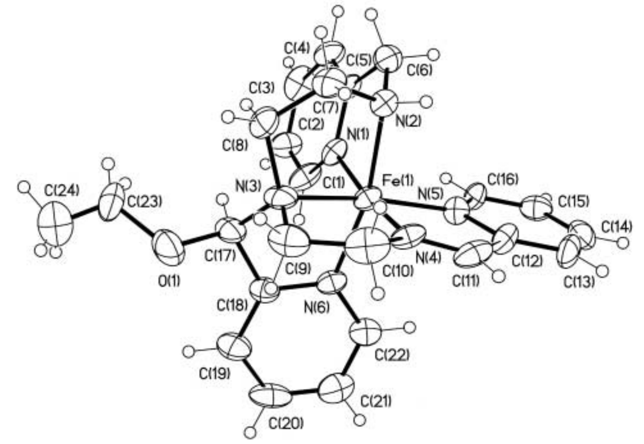


Fig. 7 Perspective view of the [Fe(L$^{2'}$)]$^{2+}$ cation, thermal ellipsoids with 30% probability.

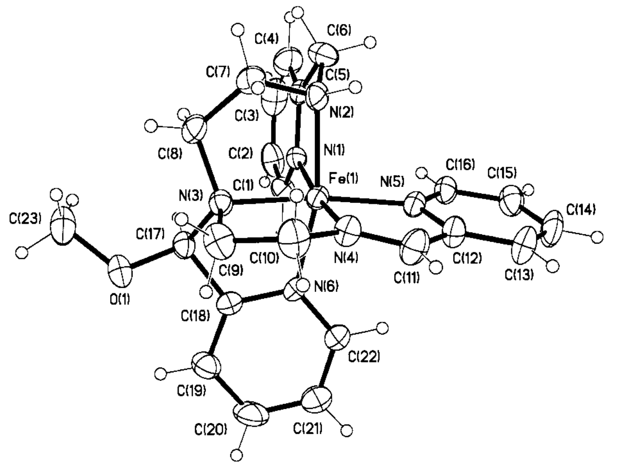


Fig. 8 Perspective view of the [Fe(L$^{3'}$)]$^{2+}$ cation, thermal ellipsoids with 30% probability.

detect any missed symmetry. For compound **2** only one cation and two counterions are found in this unit. The geometry of anions is unexceptional and will not be discussed in detail. From the cation moieties depicted in Figs. 7 and 8 it can be observed that the hexadentate ligands L$^{2'}$ and L$^{3'}$ are coordinated to the metal centre, which implies that the starting material L^1·3HCl suffered a chemical modification during the course of the reaction, as was discussed earlier.

A striking feature of complex **1** is that the two independent cations of the asymmetric unit are enantiomers, *i.e.* compound **1** is a racemic mixture of two configurations for the coordination of the hexadentate ligand to the iron centre. Aside from this inversion of configuration both independent cations present a virtually similar geometry. A fitting of one cation with the inverted independent cation as a model shows that the largest deviation is 0.279 Å for the C74/C24 atoms, with a r.m.s. deviation for the overall cation of only 0.106 Å. This means that the differences in bond lengths and angles for the two cations are not crystallographically significant at the 3σ level, and therefore only averaged data have been listed. The space group for complex **2** is achiral ($P2_1/c$), which means that also in this crystal structure both enantiomers are present, although not in the same asymmetric unit. Due to the similarity between the two structures and the fact that the crystallographic data of compound **2** are more accurate, in the following only the data of **2** will be discussed because both structures are virtually the same.

The metal centre displays a slightly distorted octahedral geometry with three angles close to 180°: N(6)–Fe(1)–N(2) = 166.61(11), N(5)–Fe(1)–N(3) = 166.97(12) and N(4)–Fe(1)–N(1) = 173.77(12)° The remaining angles vary in the range of 81.51(12)–98.56(11) °. The bond lengths between the metal ion and the three N atoms of the pyridine rings are in the range of 1.953(3)–1.981(3) Å and are in agreement with a low spin Fe(II) as metal centre.[22] This is confirmed by the distance of the secondary amine, Fe(1)–N(2) = 2.013(2) Å. Finally, the shortest coordination bond length, Fe(1)–N(4) = 1.848(3) Å, is in the lowest limit of those reported in the CSD.[23] The C(11)–C(12) and N(4)–C(11) bond lengths with values of 1.425(4) and 1.286(4) Å, respectively, confirm the presence of the imine group and indicate a π delocalised system including the N(5) pyridine ring, N(4) and C(11). This is confirmed by the angles around these atoms: C(10)–N(4)–Fe(1) = 118.8(2), C(11)–N(4)–C(10) = 122.5(3), C(11)–N(4)–Fe(1) = 118.7(3) and N(4)–C(11)–C(12) = 114.3(3)°, in agreement with sp^2 hybridisation for N(4) and C(11). As a consequence, the π system is planar with a maximum deviation from the calculated mean plane of 0.016 Å for N(4). On the other hand, this short bond pertains to a five-membered ring containing two double bonds, and consequently, a bite angle of only 81.6(6)° is observed at the metal centre.

Numerous complexes with transition metals containing the 2-pyridylmethyleneamino fragment were reported, for instance: with Co(II),[24] Ni(II)[25] and Cu(II).[26] Thereby, the C–N bond length for the Schiff base is in the range of 1.180 to 1.291 Å. The C–C bond α to the nitrogen atom has an expected bond length of 1.516(4) Å and is typical for a formal σ bond. No significant intermolecular interactions are observed in the packing of **1** and **2**, and cations and anions are well separated in the unit cell.

Conclusions

The pathway to the final products obtained by the first method is a complicated series of steps wherein the initial Fe(II) complex, that is obtained with ligand oxidation of the Fe(III) analogue, is unstable and releases a pyridyl arm to form a ketal in the presence of the solvent. The ketal back-reacts with more of the starting dehydrogenated Fe(II)-complex to increase the size and denticity of the coordinated ligand, whereby the dehydrogenated imine centre is then protected from further decomposition steps. This type of reaction is an interesting alternative for the synthesis of coordination compounds, particularly if the nucleophilic reaction is stereoselective. Additionally, we describe an alternative synthesis, second method, of complexes **1** and **2** *via* intramolecular oxidation of an amino group to an imine function from previously prepared hexadentate ligands and Fe(III) which is a straighter, easier and cleaner procedure compared to those generally reported in the literature.

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