A non-heme dinuclear iron(II) complex containing a single, unsupported hydroxo bridge†‡

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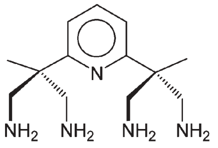
Complexation of the tetrapodal pentadentate NN_4 ligand 2,6-$C_5H_3N[CMe(CH_2NH_2)_2]_2$ (1) with iron(II) perchlorate hydrate in methanol, in the presence of *N*-methylimidazole, produces a diferrous complex with a single, unsupported μ-OH ligand between two {(1)Fe^{II}} coordination modules.

Open-chain aliphatic amine ligands, and primary amines in particular, have been rarely used in the coordination chemistry of iron, in both the +II and +III oxidation states.[1] While imine ligands, heterocyclic or open-chain, can accept metal electron density into their π* orbitals, aliphatic amines are pure σ donors. Some of their complexes have been reported to undergo ready metal- and/or ligand-centred oxidation, the latter resulting in imine formation.[2,3] Observations recently made for the iron(II) complex of a tetrapodal pentadentate polyamine (pyN_4, **1**) are therefore unusual: in this complex of overall octahedral symmetry, the ligand architecture focuses reactivity on a single remaining coordination site. The metal's increased electron density can be utilised for unusual transformations, *e.g.*, the reduction of metal-coordinated nitrite to NO.[4] Similarly, upon reaction with dioxygen, the {(**1**)Fe^{II}} coordination module reacts cleanly to give the corresponding dinuclear iron(III) oxo complex,[5] rather than undergoing oxidative degradation in the ligand.



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Added interest in complexes of this chelator derives from the possibility of spin-state switching, depending on the nature of the sixth ligand. Whereas the bromo complex [(**1**)Fe^{II}Br]Br is high-spin (4 unpaired electrons) at room temperature, the carbonyl complex [(**1**)Fe^{II}(CO)]Br_2 is low-spin and diamagnetic.[4] For mononuclear iron(II) complexes to be bistable, *i.e.*, show temperature-dependent spin crossover (SCO) behaviour,[6] the ligand sphere usually consists of *six* N donors.[7] In order to check for temperature-dependent SCO in complexes of our pyN_4 ligand, we have begun to investigate a series of heterocyclic imines for use as monodentate ligands in the sixth coordination position. Work with 1-methyl-1*H*-imidazole provided both the desired complex, [(**1**)Fe^{II}($C_4H_6N_2$)](OTf)$_2$ (**2**) and, under different reaction conditions, the binuclear iron(II) complex [(**1**)$_2$(Fe^{II})$_2$(μ_2-OH)]Br(ClO_4)$_2$ (**3**), whose unsupported μ-hydroxo bridge is a structural feature hitherto unknown in the coordination chemistry of iron(II).

For the synthesis of **2**, we reacted a well-defined and soluble anhydrous iron(II) precursor, Fe(OTf)$_2$·2MeCN, the free polyamine **1** (prepared by neutralisation of the storage form **1**·4HBr with NaOMe) and 1-methylimidazole in anhydrous methanol; precipitation by ether diffusion produced the desired complex **2** (triflate salt) as a dark red polycrystalline material in about 80% yield. The methanol solution at room temperature contains paramagnetic iron(II) ions, as indicated by strongly broadened signals in the ^1H NMR spectra (methanol-d_4), which span a range of more than 140 ppm. A spin transition in solution at low temperature is immediately apparent from NMR spectra recorded at −80 °C, whose resolution is excellent, indicating complete spin state conversion to diamagnetic complexes (low spin state). The aromatic protons (pyridine AB_2 and imidazole) are clearly distinguishable between 8.0 and 7.1 ppm with correct integrated intensities, as are the aliphatic signals belonging to the imidazole methyl group (3.95 ppm), the diastereotopic methylene protons (2.75 and 2.59 ppm) and the methyl groups on the pyridine-derived ligand (1.45 ppm). The data are compatible with averaged C_{2v} symmetry of the fragment {(**1**)Fe^{II}} in solution, and thus suggest fast rotation (on the NMR timescale) of the 1-methylimidazole ligand about the Fe–N bond.

The structural parameters of **2** in the solid state at 100 K, when compared with those of [(**1**)Fe^{II}Br]Br (high spin) and [(**1**)Fe^{II}CO]Br_2 (low spin),[4] confirm a low-spin electronic configuration. Specifically, all iron–nitrogen bonds have lengths around 2.0 Å (Fe–N_{eq}: 2.026(3)–2.033(3) Å) as in the carbonyl complex; this value increases by 10% in the high-spin bromo complex.[4] The FeN_6 core is an only slightly distorted octahedron. The angle between the planes of the pyridine and imidazole rings is 86.23(9)°, suggesting appreciable π interaction between the d_{xz} and d_{yz} orbitals on iron and each of the heteroaromatic axial donors. The axial bond lengths Fe–N11 (1.952(3) Å, pyridyl) and Fe–N30 (2.009(3) Å, 1-methylimidazole) are significantly different (Fig. 1), unlike the situation in a low-spin iron(II) porphyrinato complex with two axial imidazole ligands (2-methylimidazole), where the

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‡ Dedicated to Professor Jörn Müller on the occasion of his 70th birthday.

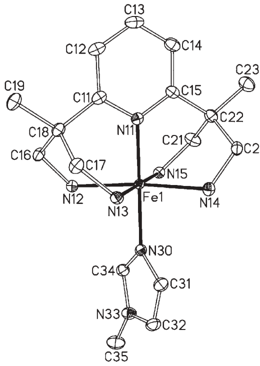

Fig. 1 Molecular structure of the dication in $[(\mathbf{1})Fe^{II}(C_4H_6N_2)](OTf)_2$, **2** (50% thermal probability ellipsoids; hydrogen atoms omitted). Distances in Å and angles in °: Fe1–N11: 1.952(2); Fe1–N12: 2.026(2); Fe1–N13: 2.033(2); Fe1–N14: 2.030(2); Fe1–N15: 2.028(2); Fe1–N30: 2.009(2); N11–Fe1–N30: 178.97(9); N12–Fe1–N14: 173.97(9); N13–Fe1–N15: 179.55(9).

corresponding bonds have almost identical lengths around 2.03 Å.[8] The close approach of the pyridine nitrogen atom in **2** is *not* enforced by the chelating nature of the ligand; the corresponding bond in the low-spin carbonyl complex, $[(\mathbf{1})Fe^{II}CO]Br_2$, is 2.02(1) Å long.[4]

The magnetic susceptibility of **2** (Fig. 2), measured at 200 K, points to a diamagnetic sample, corresponding to the low spin state of the complex. Above 300 K, the $\chi_M T$ values start to rise. At 400 K, the value of $\chi_M T$ indicates a spin conversion of about 35% of the iron(II) low spin species to the high spin state. Experiments to follow the spin transition above 400 K require different equipment and are in preparation. A ^{57}Fe Mössbauer spectrum (Fig. 2, inset), measured at 300 K, supports the diamagnetic character of the sample. The isomer shift of 0.521(3) mm s^{-1} (relative to α-iron) is in the range expected for iron(II) low spin species. Despite the relatively low symmetry of the structure (C_{2v}), the quadrupole splitting at 0.156(9) mm s^{-1} is remarkably small; in the case of an iron(II) low spin compound, the electric field gradient arises *only* from a lattice contribution, whereas the valence electrons do not contribute. In order to follow the spin transition by Mössbauer spectroscopy well above room temperature, the compound will be prepared with enriched ^{57}Fe to compensate for the decreasing Debye–Waller factor at higher temperatures.

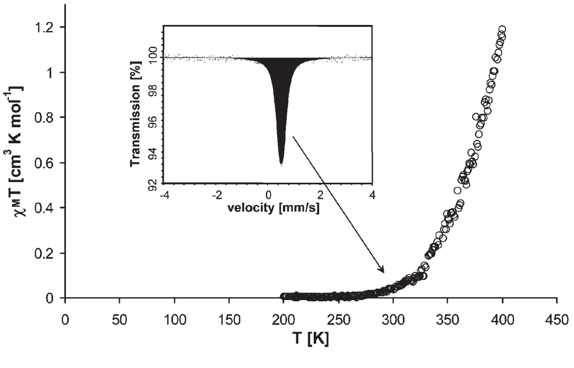

Fig. 2 The magnetic behaviour of **2** indicates a low spin state below room temperature and the beginning of a spin transition above 300 K. The ^{57}Fe Mössbauer spectrum at 300 K confirms the presence of an iron(II) low spin species.

Initial attempts to prepare **2** failed; in the presence of water of crystallisation (as introduced by employing commercially available iron(II) perchlorate, approx. heptahydrate [Aldrich]), highly basic **1** and/or 1-methylimidazole abstract a proton from H_2O, and the only isolable product is a dinuclear complex (**3**) with a single μ-hydroxo bridge between two $\{(\mathbf{1})Fe^{II}\}$ coordination modules. This product forms as a yellow–orange crystalline material in moderate yield (from methanol, 35%). Elemental analysis confirms the composition $[(\mathbf{1})_2(Fe^{II})_2(\mu_2\text{-}OH)]Br(ClO_4)_2$, and the IR spectrum has, in addition to the chelator's fingerprint, prominent bands attributable to the OH bridge (3459 cm^{-1}) and perchlorate (1073 cm^{-1}). Preliminary NMR data obtained at room temperature suggest **3** to be paramagnetic. Cyclic voltammetry (MeOH; rt, scan rate 100 mV s^{-1}) shows one quasi-reversible redox wave at −0.34 V as the only feature (*vs.* NHE; internal standard ferrocene; working/reference/counter electrode: glassy carbon/Pt/Pt; ΔE = 171 mV; i_{pa}/i_{pc} = 0.9, one electron). We assign this redox process to the formation of a mixed-valent species, Fe^{II}–(μ-OH)–Fe^{II} → Fe^{III}–(μ-OH)–Fe^{II}; the formation of the doubly oxidised, *i.e.* bis(ferric), μ-hydroxo complex is not observed. The redox potential recorded in a separate experiment for the one-electron reduction of the bis(ferric) μ-oxo complex, Fe^{III}–(μ-O)–Fe^{III} → Fe^{II}–(μ-O)–Fe^{III}, is −0.24 V.[5] The solid-state structure, as determined from single crystal X-ray data, suggests high-spin iron(II) centres; all bonds emanating from the iron centres have lengths between 2.18 and 2.23 Å, the axial bond to the pyridine ring being the longest at 2.230(3) Å (see Fig. 3). The pentadentate amine ligand again acts as a square-pyramidal coordination cap, albeit with stronger distortions compared to **2**. The iron–oxygen bond length is 2.008(2) Å and thus virtually the same as the iron-imidazole nitrogen distance in **2** (2.009(3) Å). The Fe–O–Fe angle is 146.7(2)°, in keeping with the presence of a hydroxyl group (which, in addition to the IR spectroscopic evidence, is further supported by the anion balance); the significant increase over the value of 120° for a regular trigonal arrangement is most likely due to the steric requirements of the two polyamine–iron fragments. The proton of the hydroxo bridge was located in the crystal structure analysis with a distance d(O–H) of 0.85(1) Å, and an Fe–O–H angle of 106.7(1)°. The hydroxyl group is involved in a weak O–H···Br contact with the Br^- counterion (d(O1···Br1) = 3.370(4) Å, angle (OHBr) = 180° [the complex has crystallographically imposed *mm* symmetry; the O1–H1 and Br1 atoms

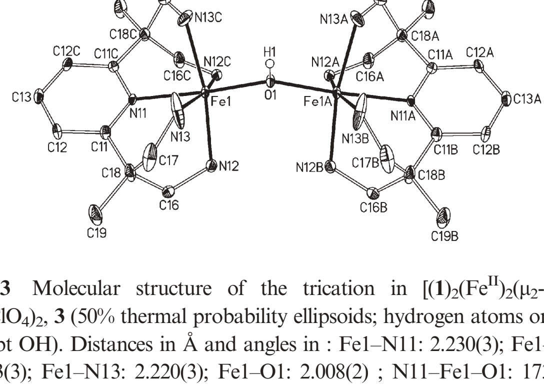

Fig. 3 Molecular structure of the trication in $[(\mathbf{1})_2(Fe^{II})_2(\mu_2\text{-}OH)]$-$Br(ClO_4)_2$, **3** (50% thermal probability ellipsoids; hydrogen atoms omitted except OH). Distances in Å and angles in : Fe1–N11: 2.230(3); Fe1–N12: 2.183(3); Fe1–N13: 2.220(3); Fe1–O1: 2.008(2) ; N11–Fe1–O1: 173.8(2); Fe1–O1–Fe1A: 146.7(2). Letters A, B, C in the atom labels refer to equivalent positions ($1 - x, -y, z$), ($\tfrac{1}{2} - y, \tfrac{1}{2} - x, z$) and ($\tfrac{1}{2} + y, -\tfrac{1}{2} + x, z$), respectively.

lie at sites with *mm* symmetry, hence the O–H···Br hydrogen bond is necessarily linear]). In a structurally characterised hydroxo-bridged dinuclear porphyrinato iron(III) complex with no other supporting bridging ligands, the Fe–O bonds are shorter (1.924(3) and 1.952(3) Å), as expected for a more highly oxidised species, but the Fe–O–Fe angle at 146.2(2)° is virtually identical to the value observed for **3**. All cation structural parameters in **3** differ strongly from those of the related dinuclear ferric oxo complex, $[(\mathbf{1})_2(\mathrm{Fe^{III}})_2(\mu_2\text{-O})]\mathrm{Br_4}$, where, specifically, the $\mathrm{Fe{-}N_{aliphatic}}$ bonds fall in the range 2.12–2.15 Å, while $d(\mathrm{Fe{-}N_{py}})$ = 2.276(3) Å; d(Fe–O) is 1.7935(5) Å.[5]

Magnetic measurements of this exceedingly oxidation sensitive material show a gradual increase of the $\chi_M T$ values over the whole temperature range between 4 K and 300 K (see ESI† for a graphical representation). The $\chi_M T$ value of 3.2 $\mathrm{cm^3\ K\ mol^{-1}}$ at room temperature is about half the spin-only value for the two iron(II) high spin centres, and is the result of strong antiferromagnetic coupling between the two iron(II) centres *via* the bridging oxygen atom. The J value is calculated to be *ca.* $-30\ \mathrm{cm^{-1}}$, from a preliminary theoretical adjustment to a dinuclear species with two $S = 2$ centres, and allowing for a ferric contribution of *ca.* 10% which most likely arises from partial oxidation of Fe(II)–(OH)–Fe(II) to Fe(II)–(OH)–Fe(III). The ^{57}Fe Mössbauer spectrum recorded at room temperature shows two quadrupole doublets. One of these, with an isomer shift of 1.001(14) mm $\mathrm{s^{-1}}$ and a quadrupole splitting of 2.74(3) mm $\mathrm{s^{-1}}$, is characteristic of high spin iron(II). The other, with an isomer shift of 0.41(5) mm $\mathrm{s^{-1}}$ and a quadrupole splitting of 0.91(8) mm $\mathrm{s^{-1}}$, is typical of high spin iron(III) and confirms partial oxidation of the sample under the prevailing conditions of measurement. Mössbauer measurements will be repeated on a fresh sample prepared with enriched ^{57}Fe in order to improve the signal to noise ratio; it is poor in the sample under study owing to the presence of bromide, which is a strong absorber for the 14.4 keV γ-quanta. Particular care will be taken to avoid oxidation to mixed-valent dimers, and magnetic measurements will also be repeated.

To the best of our knowledge, compound **3** represents the only case in the coordination chemistry of iron so far, where a μ-hydroxo bridge is the single connector between two *ferrous* centres. In view of the importance of oxo- and hydroxo-bridged diiron species in biological systems, such as certain oxidases and non-heme iron enzymes[9] (*e.g.*, methane monooxygenase and hemerythrin), and of an understanding of their interconversion, work is currently under way to obtain the effective magnetic moments of **2** and **3** in solution, and study the deprotonation of **3** and its reactivity towards stoichiometric amounts of dioxygen.[10]§

Notes and references

§ Financial support of this work by Deutsche Forschungsgemeinschaft (SFB 658) is gratefully acknowledged. Preparation of **2**: To a suspension of $\mathrm{pyN_4{\cdot}4HBr{\cdot}MeOH}$ (0.14 g, 0.23 mmol) in methanol (5 ml) was added NaOMe (0.95 ml of a 1 M stock solution in MeOH, 0.95 mmol). The resulting solution was taken to dryness, and the remaining solid triturated by stirring in THF (15 ml). Sodium bromide was removed by cannula filtration and the filtrate taken to dryness. The resulting oil was dissolved in MeOH (2 ml). A colourless solution of $\mathrm{Fe(OTf)_2{\cdot}2MeCN}$ (0.10 g, 0.23 mmol) in MeOH (3 ml) was added to give a light red solution. Upon addition of 1-methylimidazole (18 μl, 19 mg, 0.23 mmol) the colour changed to deep red. Isothermal diffusion of diethyl ether (rt) into the solution led to the formation of deep red crystals which were suitable for X-ray diffraction analysis (130 mg, 79%). Elemental analysis (%) calc. for $\mathrm{C_{19}H_{31}F_6FeN_7O_6S_2}$: C 33.20, H 4.55, N 14.26, S 9.33; found C 33.14, H 4.73, N 13.74, S 8.95. IR (KBr disc): 3319vs, 3195s, 3124m, 3082w, 2979s, 2936s, 2876w, 2317w, 1631s, 1610s, 1579m, 1569m, 1541s, 1528w, 1473vs, 1423s, 1397vs, 1224vs, 1164vs, 1094vs, 1028vs, 936w, 834m, 816s, 789w, 769s, 757s, 743s, 692m, 680s, 635vs, 619vs, 573vs, 519vs, 469w, 415w $\mathrm{cm^{-1}}$. Crystallographic data: $\mathrm{C_{19}H_{31}F_6FeN_7O_6S_2}$, M_r 687.48 g $\mathrm{mol^{-1}}$; space group $P2_1/n$ (monoclinic, no. 14); a = 10.1099(6), b = 11.2823(9), c = 24.199(3) Å; β = 90.774(7)°; V = 2760.0(4) $\mathrm{Å^3}$; Z = 4; ρ_{calc} 1.654 g $\mathrm{cm^{-3}}$; μ = 0.787 $\mathrm{mm^{-1}}$; T = 100(2) K; 2Θ range: 6.2 to 54.2°; meas. refl. 80280, unique 6085, obs. $[I > 2\sigma(I)]$ 5220; wR2 (all data) 0.0856; R1 $[I > 2\sigma(I)]$ 0.0391. Preparation of **3**: To a suspension of $\mathrm{pyN_4{\cdot}4HBr{\cdot}MeOH}$ (0.14 g, 0.23 mmol) in methanol (8 ml) was added LiOMe (0.92 ml of a 1 M stock solution in MeOH, 0.92 mmol). The resulting solution was stirred at room temperature for 5 min. $\mathrm{Fe(ClO_4)_2}$ (58 mg, 0.23 mmol) was then added as the solid heptahydrate (Aldrich) in one portion, to give a yellow–orange solution. To this solution was added 1-methylimidazole (18 μl, 19 mg, 0.23 mmol), and the colour of the solution changed to red. Isothermal diffusion of diethyl ether (rt) into the solution led to the formation of orange crystals, which were filtered and dried *in vacuo* (37 mg, 35%). Elemental analysis (%) calcd for $\mathrm{C_{26}H_{51}BrCl_2Fe_2N_{10}O_9}$: C 34.31, H 5.65, N 15.39; found C 34.33, H 5.49, N 15.09. Crystallographic data: $\mathrm{C_{26}H_{51}BrCl_2Fe_2N_{10}O_9}$, M_r 910.28 g $\mathrm{mol^{-1}}$; space group $P\bar{4}2_1m$ (tetragonal, no. 113); a = 15.094(1), b = 15.094(1), c = 8.1109(4) Å; V = 1847.9(2) $\mathrm{Å^3}$; Z = 2; ρ_{calc} 1.636 g $\mathrm{cm^{-3}}$; μ = 2.073 $\mathrm{mm^{-1}}$; T = 100(2) K; 2Θ range: 6.0 to 58.1°; meas. refl. 32119, unique 2575, obs. $[I > 2\sigma(I)]$ 2101; wR2 (all data) 0.0727; R1 $[I > 2\sigma(I)]$ 0.0363. There is no resolvable disorder in the ligand (C17/N13 and symmetry equivalents). CCDC 293017 (**2**) and 293018 (**3**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517635b

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