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The dipyrrolide ligand as a template for the spontaneous formation of a tetranuclear iron(II) complex†

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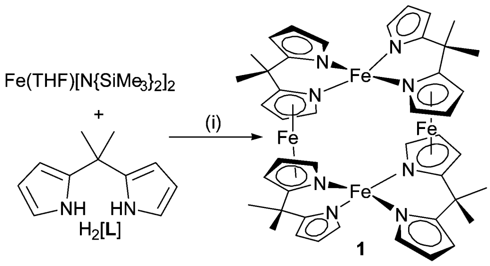
The *meso*-disubstituted dipyrrolide ligand (L) has promoted the formation of a unique tetranuclear iron(II) compound that contains both diazaferrocenyl and distorted-tetrahedral iron centres.

The combined σ- and π-bonding ability of the pyrrolide group makes it an attractive ligand to encourage the spontaneous formation of multimetallic complexes. This is especially true for *meso*-disubstituted dipyrrolides, which have been shown to promote the formation of reactive macrocyclic clusters in f-element chemistry;[1] low valent octa- and hexanuclear Sm^{II} dipyrrolide compounds retain sufficient reactivity to activate dinitrogen.[2] With this in mind, we have initiated a study towards the spontaneous formation[3] of potentially reactive, polynuclear iron compounds and saw the dipyrrolide ligand as an appropriate support for low valent iron. The prevalence of polynuclear iron sites in metalloenzymes (*e.g.* nitrogenases)[4] and the potential use of multi-iron compounds as spin crossover[5] and single molecule magnetic systems[6] has made the syntheses of new polynuclear iron compounds a target of considerable interest.

The reactions between the dilithio salt of the *meso*-disubstituted dipyrrolide, **L** and iron(II) and iron(III) halides proved inconclusive. However, our recent success in forming Group 4 dipyrrolide compounds *via* transamination routes led us to consider this approach to form iron dipyrrolide compounds.[7] The transamination reaction between $Fe(THF)[N(SiMe_3)_2]_2$ and $H_2[\mathbf{L}]$ was successful at elevated temperature, and led to the formation of the highly air and moisture sensitive tetranuclear iron complex, $\{Fe[\mathbf{L}]\}_4$ **1** that was isolated in moderate yield (see Scheme 1). Monitoring this reaction in d_8-THF by ^1H NMR spectroscopy confirmed that quantitative conversion to **1** occurs, with no easily assignable intermediates (see later for NMR details). Crystals suitable for X-ray diffraction studies were grown from a THF–toluene–Et_2O mixture and the solid state structure is shown in Fig. 1.‡ Two distinct types of iron co-ordination are observed, one distorted-tetrahedral in which the iron is σ-bound to four pyrrolide nitrogens, the other octahedral with η^5-bonding to two pyrrolide rings so forming a diazaferrocene unit; the rings are eclipsed but have staggered pyrrolic nitrogens, and the two diazaferrocenyl units are in an approximate orthogonal orientation to each other (81.9°). Similar distorted tetrahedral geometries have been observed in Fe(II) tropocoronand,[8] amidinate,[9] guanidinate,[10] and iminopyrrolide complexes;[11] such a distortion is presumably a consequence of the constrained (~90°) bite angle of the N–N chelating ligands. Diazaferrocenes have been isolated and characterised using strategies that sterically or co-ordinatively protect the pyrrolic nitrogen.[12] In the case of **1**, the unsubstituted 5,5′-positions on the pyrrolic ring offer no steric protection, so pyrrolic nitrogen coordination to the Lewis acidic Fe^{II} is uninhibited and may therefore promote the formation of **1**. The different iron centres are well separated and form a rhombohedral motif with intranuclear Fe···Fe distances and angles of 3.636 and 3.605 Å and 101.2 and 78.8° respectively. Confirmation of the tetrametallic nature of **1** in the solid state is provided by the mass spectrum, which shows a molecular ion at *m*/*z* 912 with the correct isotopic pattern for four iron atoms.



Scheme 1 Synthesis of **1**. (i) THF–toluene, 80 °C, 48 h.

The Mössbauer spectrum of **1** (Fig. 2)† is consistent with the presence of two different iron sites in the solid state. At 77 K, two signals are observed at δ 0.60 (ΔE_q 2.56) and 0.77 mm s^{-1} (1.59 mm s^{-1}), plus a small impurity, and are consistent with both high-spin Fe^{II} atoms in a distorted tetrahedral geometry and with Fe^{II} of diazaferrocene.[13] The higher quadrupole splitting of the signal at 0.60 mm s^{-1} is similar to those observed for azaferrocene and its substituted analogues, and so can be assigned to the diazaferrocene moiety in **1**.

^1H NMR studies in CD_2Cl_2 show that the asymmetric dipyrrolide structure observed in the solid state is retained in solution.† Although the resonances are broad features and cover

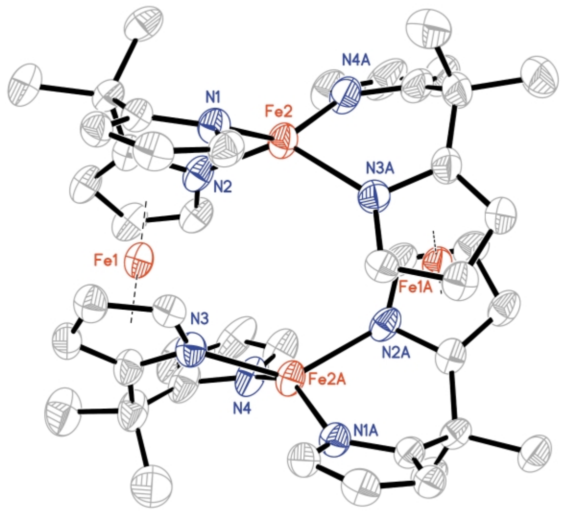


Fig. 1 The solid state structure of $\{Fe[\mathbf{L}]\}_4$ **1** (50% ellipsoids). Selected bond lengths (Å) and angles (°): Fe(2)–N(1) 1.987(3), Fe(2)–N(2) 2.120(4), Fe(2)–N(3A) 2.109(3), Fe(2)–N(4A) 1.975(4), Fe(1)–cent 1.374/1.377, cent–Fe(1)–cent′ 179.4, N(1)–Fe(2)–N(2) 92.23(14), N(3A)–Fe(2)–N(4A) 91.52(14), N(2)–Fe(2)–N(3A) 133.88(14), N(1)–Fe(2)–N(4A) 146.57(16).

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† Electronic supplementary information (ESI) available: full experimental and characterisation data. See http://www.rsc.org/suppdata/cc/b3/b303485b/

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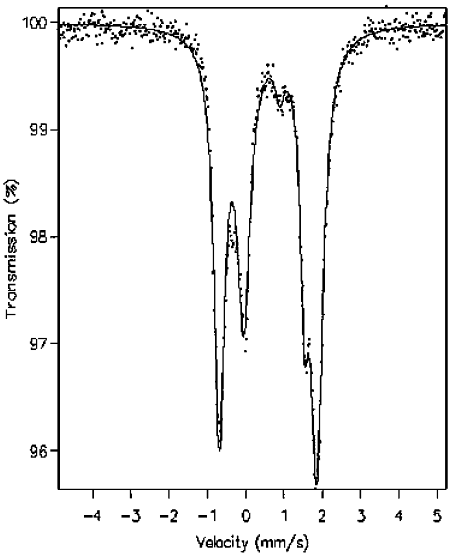

Fig. 2 Mössbauer spectrum of **1** at 77 K.

a wide chemical shift range, the six unique pyrrolic protons are clearly visible at 101.5, 65.1, 58.8, 43.2, 37.7, and 11.9 ppm, along with two different *meso*-methyl group protons at 7.76 and −41.6 ppm. The assignment of these latter resonances by integration was confirmed by using the deuterium-labelled ligand $H_2[\mathbf{L^{d6}}]$, which substitutes CH_3 for CD_3 groups in the *meso*-position; as expected, these signals were absent from the ^1H NMR spectrum of $\{Fe[\mathbf{L^{d6}}]\}_4$.

The potential of **1** to show interesting magnetic phenomena *via* superexchange coupling between the four Fe^{II} nuclei led us to investigate the magnetic properties of **1**; dc-magnetic susceptibility measurements were carried out between 5 and 300 K and are shown as χ and μ_{eff} *vs. T* plots in Fig. 3.† The observed moment of 7.44 μ_B at 295 K in the solid state (and also in solution by Evans' method, $\mu_{eff} = 7.15\ \mu_B$) is consistent with two magnetically independent tetra-coordinate Fe^{II} centres and two diamagnetic Fe^{II} diazaferrocenes, *i.e.* a $2 \times S = 2$, $g = 2$ spin state ($\mu_{calc} = 6.93\ \mu_B$). Upon cooling, antiferromagnetic coupling is observed following Curie–Weiss behaviour ($\theta = -5.0$ K).

It is difficult to postulate a plausible mechanism for the formation of **1**; NMR spectroscopic monitoring of the reaction yielded little information (see above). However, it was found important to conduct the synthesis of **1** in the presence of THF, as without it an orange powder $\{Fe[\mathbf{L}]\}_n$ **2**, incorporating a small quantity of **1** (by NMR spectroscopy), precipitates from hot toluene.† Combustion analysis of **2** revealed the same empirical formula as **1**, and judging by the insolubility of **2** in CH_2Cl_2 and THF, is presumably polymeric in nature; in comparison, **1** shows good solubility in these solvents. Also, preliminary NMR experiments show that the dissolution of either **1** or **2** (slowly) in d_5-pyridine yields a new paramagnetic compound in which the dipyrrolide ligand is symmetrically coordinated. This implies that **1** and **2** are structurally similar.

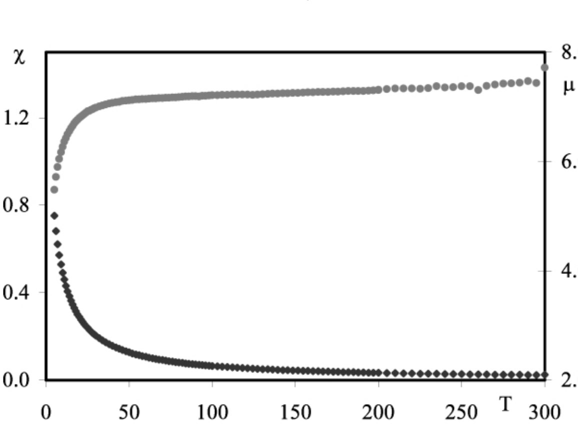

Fig. 3 Variable temperature magnetic measurements for **1**.

We are at present studying this transformation further and are investigating the redox and small molecule reactivity of **1**. Initial cyclic voltammetry studies in CH_2Cl_2 show three oxidations with no reverse waves at E_{pa} + 0.38, + 0.60 and + 1.22 V ($^nBu_4NBF_4$, $FeCp_2/FeCp_2^+$); no reduction was observed to −2.0 V. Azaferrocene has been shown to undergo a reversible oxidation at $E°$ + 0.33 V ($FeCp_2/FeCp_2^+$) using fast scan rates, although the resultant cation is highly reactive at the α-carbon of the pyrrolide ligand.[14] Similarly, the lack of reverse waves for **1** indicates that the cationic species formed during oxidation may undergo rapid reaction.

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Notes and references

‡ *Crystal data*: $\{Fe[\mathbf{L}]\}_4$ **1**, orange prism, 0.14 × 0.13 × 0.08 mm³, $C_{52}H_{68}Fe_4N_8O_2$, tetragonal, a = 15.049(3), b = 15.049(3), c = 42.623(11) Å, $\alpha = \beta = \gamma = 90°$, U = 9653(4) Å³, space group $I4(1)/a$, Z = 8, μ = 1.228 mm⁻¹, $F(000)$ = 4448, 18802 collected reflections, 5426 unique (R_{int} = 0.09). Data were collected at 150(2) K on a Bruker SMART1000 CCD, λ = 0.71073 Å, θ = 1.97 to 27.35°, semi-empirical absorption correction applied from equivalents, solved by direct methods and refined using SHELXL-97. Final full-matrix least-squares refinement on F^2 converged at R_1 = 0.0574 for 5341 reflections with $I > 2\sigma(I)$, wR_2 = 0.1387, S = 0.916 for all data and 277 parameters. CCDC reference number 207435. See http://www.rsc.org/suppdata/cc/b3/b303485b/ for crystallographic files in .cif format.

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