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Electronic Supplementary Information

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

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Experimental

All reactions were carried out at room temperature in dried solvents under an atmosphere of dry dinitrogen, using standard Schlenk techniques. $pyN_4 \cdot 4\ HBr \cdot MeOH$ and $Fe(OTf)_2 \cdot 2\ MeCN$ were prepared according to literature procedures.[1, 2] Other reagents were purchased from Fluka or Aldrich and used without further purification. IR spectra of solids were measured using KBr disks. Spectroscopic data were obtained using the following instruments: ir spectroscopy: Nicolet Magna System 750; nmr spectroscopy: Bruker ARX 200, Bruker ARX 400, Jeol FT-NMR ALPHA 500. Signs of coupling constants in the ^1H and ^{13}C NMR spectra were not determined. Elemental analyses were carried out using Thermo Finnigan, Flash EA, 1112 series analysers.

$[(1)Fe^{II}(C_4H_6N_2)](OTf)_2$, 2: To a suspension of $pyN_4 \cdot 4\ HBr \cdot MeOH$ (0.14 g, 0.23 mmol) in methanol (5 ml) was added NaOMe (0.95 ml of a 1M 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 $Fe(OTf)_2 \cdot 2\ MeCN$ (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 color 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 (%) calcd for $C_{19}H_{31}F_6FeN_7O_6S_2$: 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 cm^{-1}. ^1H NMR (20 °C, 500 MHz, [d_4]-MeOH, all signals broadened due to paramagnetism): δ = 142.80 (s), 100.47 (s), 89.72 (s), 52.17 (s), 30.27 (s), 25-0 (m) ppm. ^1H NMR (–80 °C, 500 MHz, [d_4]-MeOH): 8.0 – 7.1 (m; 1 + 2 H, pyridine AB_2; 3 H, imidazole), 3.95 (s, 3 H, imidazole, methyl), 2.75/2.59 (AB, 4H/4H, methylene), 1.45 (s, 6 H, amine ligand, methyl).

$[(1)_2(Fe^{II})_2(\mu_2\text{-}OH)]Br(ClO_4)_2$, 3: To a suspension of $pyN_4 \cdot 4\ HBr \cdot MeOH$ (0.14 g, 0.23 mmol) in methanol (8 ml) was added LiOMe (0.92 ml of a 1M stock solution in MeOH, 0.92 mmol). The resulting solution was stirred at room temperature for 5 min. $Fe(ClO_4)_2$ (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 (r. t.) into the solution led to the formation of orange crystals, which were filtered and dried *in vacuo* (37 mg, 35 %). Elemental analysis (%) calcd for $C_{26}H_{51}BrCl_2Fe_2N_{10}O_9$: C 34.31, H 5.65, N 15.39; found C 34.33, H 5.49, N 15.09. IR(KBr disc): 3459m (OH), 3363m, 3342m, 3306m, 3271m, 3106sh, 2973m, 2922m, 2880m, 2013w, 1598s, 1582s, 1470s, 1419m, 1396m, 1366m, 1353m, 1110 vs, 1073vs, 1010s, 993s, 829m, 815m, 772w, 757m, 624s, 578m, 538m, 502m cm^{-1}.

X-ray crystallography:

A more comprehensive selection of bond lengths and angles is listed in Table 1. Cation structures are presented in Figures 1, 2. All structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 using SHELXTL NT 6.12 (Bruker AXS, 2002). All nonhydrogen atoms were refined anisotropically. Compound **3**: The crystal used for measurements was an inversion twin (ratio of individuals approx. 1 : 1, Flack parameter: 0.50(2)). The dinuclear trication lies on the fourfold position 2*c* of space group $P\bar{4}2_1m$ and has D_{2d} symmetry. The perchlorate anion is disordered around the vector O11–Cl1. Treatment of hydrogen atoms: Compound **2**: The hydrogen atoms were geometrically positioned; their isotropic displacement parameters were tied to those of the adjacent C and N atoms by a factor 1.2 and 1.5, respectively. Compound **3**: The positions of all hydrogen atoms, including that of the hydroxo bridge, were determined from difference Fourier syntheses. The positional parameters were refined, while a common isotropic displacement parameter was kept constant during refinement.

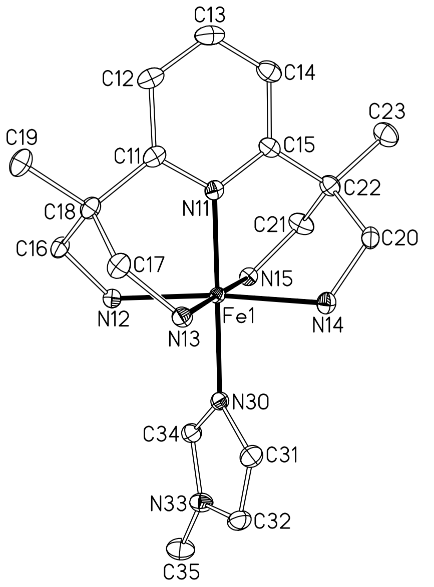

Fig. 1. Molecular structure of the dication in $[(\mathbf{1})Fe^{II}(C_4H_6N_2)](OTf)_2$, **2** (50 % thermal probability ellipsoids; hydrogen atoms omitted).

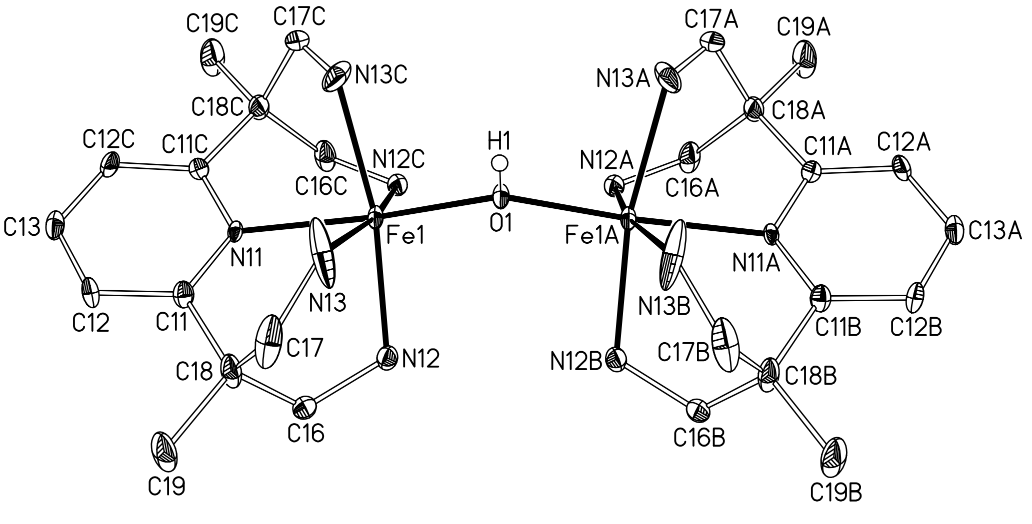

Fig. 2. Molecular structure of the trication in $[(\mathbf{1})_2(\mathrm{Fe^{II}})_2(\mu_2\text{-OH})]\mathrm{Br}(\mathrm{ClO_4})_{2,}$ **3** (50 % thermal probability ellipsoids; hydrogen atoms omitted except OH).

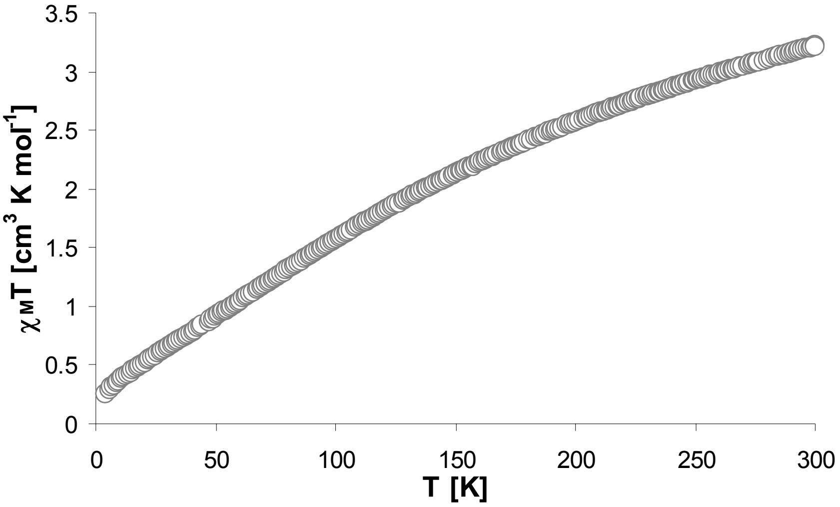

Fig. 3: Compound **3**: The magnetic response of the sample indicates an antiferromagnetic coupling of the iron(II) centres via the oxygen atom with a coupling constant, *J*, of about $-30\ \mathrm{cm^{-1}}$.

References:

[1] A. Grohmann and F. Knoch, *Inorganic Chemistry*, 1996, **35**, 7932.
[2] K. S. Hagen, *Inorganic Chemistry*, 2000, **39**, 5867.