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X-ray crystal structure of [BPMEN(Cl)$Fe^{III}OFe^{III}$(Cl)BPMEN]$(ClO_4)_2$ [BPMEN = *N,N′*-dimethyl-*N,N′*-bis(2-pyridylmethyl)ethane-1,2-diamine] and the assignment of its ^{1}H NMR peaks in CD_3CN

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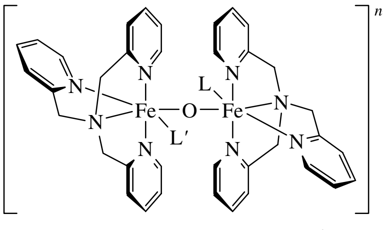
The complex [BPMEN(Cl)$Fe^{III}OFe^{III}$(Cl)BPMEN]$(ClO_4)_2$ [BPMEN = *N,N′*-dimethyl-*N,N′*-bis(2-pyridylmethyl)ethane-1,2-diamine] was prepared and characterised by X-ray crystallography; the ^{1}H NMR peaks of this complex in CD_3CN were assigned based on the integration and proximity of particular protons to a paramagnetic centre.

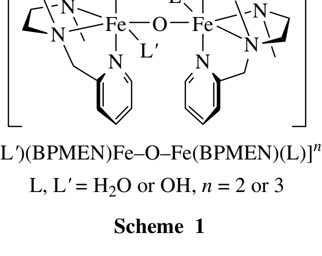
Oxo-bridged diiron complexes with tetradentate aminopyridine ligands, such as tris(2-pyridylmethyl)amine (TPA) and *N,N′*-dimethyl-*N,N′*-bis(2-pyridylmethyl)ethane-1,2-diamine (BPMEN) attracted considerable interest as structural and functional models of nonheme metalloproteins (Scheme 1).[1–14] The use of ^{1}H NMR spectroscopy for studying catalytic systems based on iron complexes with TPA and BPMEN ligands is complicated by paramagnetic line broadening. While for diiron(III) complexes with TPA some of the ^{1}H NMR peaks were assigned based on the integration and proximity of corresponding proton to the perturbing paramagnetic centre,[15–17] the assignment of the ^{1}H NMR peaks of diiron(III) complexes with BPMEN is still absent.

Here, we report the X-ray crystal structure of (μ-oxo)-diiron(III) complex [BPMEN(Cl)$Fe^{III}OFe^{III}$(Cl)BPMEN]$(ClO_4)_2$ **1**[†] and the assignment of its ^{1}H NMR peaks in CD_3CN. Based on this result, the ^{1}H NMR spectra of related (μ-oxo)(μ-hydroxo) diiron(III) complexes were also interpreted.

The cation in **1**, [BPMEN(Cl)$Fe^{III}OFe^{III}$(Cl)BPMEN]$^{2+}$, is depicted in Figure 1. The O atom is in a special position on the inversion centre. Each Fe atom is octahedrally coordinated to the bridging O atom, four N atoms of the BPMEN ligand and a Cl atom. The X-ray structures of similar cations in [BPMEN(Cl)$Fe^{III}OFe^{III}$(Cl)BPMEN]$(ClO_4)_2\cdot 0.751H_2O$ **2**[18] and [BPMEN(Cl)$Fe^{III}OFe^{III}$(Cl)BPMEN]Cl_2 **2′**[19] were described



[(L′)(TPA)Fe–O–Fe(TPA)(L)]$^{n+}$



[(L′)(BPMEN)Fe–O–Fe(BPMEN)(L)]$^{n+}$

L, L′ = H_2O or OH, n = 2 or 3

Scheme 1

[†] *General experimental details*. All commercial reagents were used without further purification. The ligand BPMEN·$3HClO_4$ was synthesised according to a published procedure.[26]

Preparation of [BPMEN(Cl)$Fe^{III}OFe^{III}$(Cl)BPMEN]$(ClO_4)_2$ **1**. The ligand BPMEN (450 mg, 1.66 mmol) and triethylamine (340 μl, 2.49 mmol) dissolved in 5 ml of ethanol were added to $Fe(ClO_4)_3\cdot 6H_2O$ (770 mg, 1.67 mmol) dissolved in 5 ml of ethanol. The solution became reddish brown. Tetrabutylammonium chloride (460 mg, 1.66 mmol) dissolved in 2 ml of water was added to the above mixture. After stirring for 2 h at room temperature, the reaction was allowed to proceed at 4 °C overnight, and a reddish brown precipitate formed. This precipitate was filtered off and dissolved in 50 ml of warm acetonitrile. Diffusion of diethyl ether into the filtered solutions resulted in crystallization of a red product, which was filtered off and washed with diethyl ether. Yield of crystal material, 85 mg (11%).

Crystallographic data for **1**: at 295(2) K crystals of $C_{32}H_{44}Cl_4Fe_2N_8O_9$ are monoclinic, space group $P2_1/n$, a = 9.3198(14), b = 9.566(2) and c = 22.785 Å, V = 1995.6(6) Å^3, Z = 2, M = 938.25, d_{calc} = 1.561 g cm^{-3}, λ(MoKα) = 1.056 cm^{-1}, F(000) = 968. Intensities of 7329 reflections were measured and 3506 independent reflections were used in the further refinement. Suitable crystals of **1** were mounted on a glass fiber using glue. Data collection was done with a D094 four-circle diffractometer (Stoe, Darmstadt) using the STADI-4 software,[27] MoKα radiation (λ = = 0.71069 Å), a graphite monochromator and a scintillation counter. 50 reflections in a 2θ range between 20 and 27° were used for cell refinement. Data reduction and absorption corrections (semi-empirical method, ψ-scanning) were performed using the X-RED software.[27] The structure[1] was solved by the direct method using SHELXS-97;[26] a full-matrix least-squares structure refinement in an anisotropic approximation for all non-hydrogen atoms was done using SHELXL-97.[28] Hydrogen atoms were calculated by geometrical methods and refined as riding model.

CCDC 602236 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2007.

^{1}H NMR spectroscopic studies. ^{1}H NMR spectra of paramagnetic iron complexes were measured on a Bruker Avance 400 NMR spectrometer at 400.13 MHz. The following operating conditions were used: spectral width, 125 kHz; spectrum accumulation frequency, 10 Hz; number of scans, 5000–10000; 20–40° pulse at 5 μs. The chemical shifts were referenced to the residual peak of the solvent (CHD_2CN, δ 1.96).

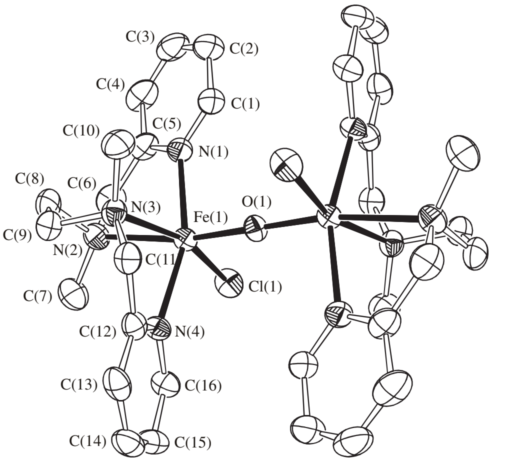


Figure 1 X-ray structure of the cation of **1** showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Fe(1)–O(1) 1.8039(7), Fe(1)–N(1) 2.178(4), Fe(1)–N(2) 2.311(4), Fe(1)–N(3) 2.244(4), Fe(1)–N(4) 2.166(3), Fe(1)–Cl(1) 2.3179(13); bond angles (°): O(1)–Fe(1)–N(1) 99.10(11), O(1)–Fe(1)–N(3) 96.51(10), O(1)–Fe(1)–Cl(1) 98.38(4), N(1)–Fe(1)–N(3) 91.95(14), N(2)–Fe(1)–N(3) 78.47(13), N(3)–Fe(1)–N(4) 75.02(13), N(2)–Fe(1)–Cl(1) 87.97(10), N(4)–Fe(1)–Cl(1) 94.43(10), O(1)–Fe(1)–N(2) 170.50(10), O(1)–Fe(1)–N(4) 95.78(10), N(1)–Fe(1)–N(2) 73.23(14), N(1)–Fe(1)–N(4) 161.25(13), N(2)–Fe(1)–N(4) 90.72(13), N(1)–Fe(1)–Cl(1) 94.62(11), N(3)–Fe(1)–Cl(1) 162.55(10).

previously. The torsional angle Cl–Fe···Fe–Cl is 180° for **1**, 128.2° for **2** and 135° for **2′** indicating flexibility of the considered dinuclear species. Recently, the structure of complex [BPMEN(F)Fe^{III}OFe^{III}(F)BPMEN](ClO$_4$)$_2$·(MeCN)$_2$ was reported.[20] In this complex, the torsional angle F–Fe···Fe–F is 180° as for **1**.

The ^{1}H NMR spectrum of **1** at 60 °C in CD$_3$CN (Figure 2) displays peaks in the range of δ 6 to 40 ppm: 39.7 (4H, $\Delta\nu_{1/2}$ 1800 Hz, C*H*H–N or CH*H*–C*H*H), 30.0 (6H, $\Delta\nu_{1/2}$ 900 Hz, Me), 26.5 (6H, $\Delta\nu_{1/2}$ 900 Hz, Me), 22.7 (2H, $\Delta\nu_{1/2}$ 500 Hz, picolinic α-H), 20.5 (2H, $\Delta\nu_{1/2}$ 500 Hz, picolinic α-H), 18.8 (2H, $\Delta\nu_{1/2}$ 200 Hz, picolinic β-H), 17.4 (2H, $\Delta\nu_{1/2}$ 200 Hz, picolinic β-H), 16.6 (2H, $\Delta\nu_{1/2}$ 200 Hz, picolynic β-H), 15.2 (2H, $\Delta\nu_{1/2}$ 200 Hz, picolinic β-H), 7.6 (2H, $\Delta\nu_{1/2}$ 45 Hz, picolinic γ-H), 6.6 (2H, $\Delta\nu_{1/2}$ 45 Hz, picolinic γ-H). The remaining C*H*H–N and C*H*H–C*H*H protons are too broad to be detected or are masked by the peaks of picolinic β-H and α-H protons. It is seen that the ^{1}H NMR peaks of picolinic and Me protons of **1** can be reliably assigned. The assignment of the resonances of C*H*H–N or CH*H*-C*H*H protons is less clear. The ^{1}H NMR data obtained for **1** were used for the interpretation of the ^{1}H NMR spectra of related (μ-oxo)(μ-hydroxo)diiron(III) complexes [Fe$_2^{III}$(μ-O)(μ-OH)(BPMEN)$_2$](ClO$_4$)$_3$ **3** and [Fe$_2$^{III}(μ-O)(μ-OH)(BPMCN)$_2$](ClO$_4$)$_3$ **4** [BPMCN = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridylmethyl)-*trans*-1,2-diaminocyclohexane].

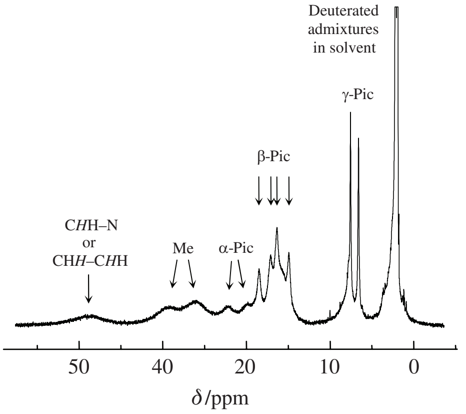


Figure 2 ^{1}H NMR spectrum of [BPMEN(Cl)Fe^{III}OFe^{III}(Cl)BPMEN](ClO$_4$)$_2$ **1** in CD$_3$CN at 60 °C.

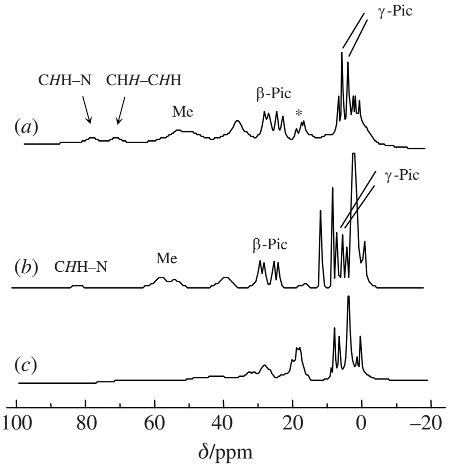


Figure 3 ^{1}H NMR spectra of (*a*) [Fe$_2^{III}$(μ-O)(μ-OH)(BPMEN)$_2$](ClO$_4$)$_3$ **3**, (*b*) [Fe$_2^{III}$(μ-O)(μ-OH)(BPMCN)$_2$](ClO$_4$)$_3$ **4** and (*c*) [Fe$_2^{III}$(μ-O)(OH)(OH$_2$)(BPMEN)$_2$](ClO$_4$)$_3$ **5** in CD$_3$CN at room temperature reproduced from references 14 and 25. The peak marked by an asterisk belongs to complex **5**.

The ^{1}H NMR spectrum of **3** in CD$_3$CN at room temperature[14] [Figure 3(*a*)] resembles that of **1** (Figure 2). However, **3** displays paramagnetically shifted ^{1}H peaks in a broader range than **1**. This is consistent with a weaker antiferromagnetic interaction for diiron complexes with two bridges (μ-O, μ-OH) than for those with one μ-O bridge.[21] The reported values of J are 84 cm^{-1} for [Fe$_2$^{III}(μ-O)(μ-OH)(BPMEN)$_2$](ClO$_4$)$_3$ **3**[22] and 184 cm^{-1} for [Fe$_2^{III}$(μ-O)(OH)(OH$_2$)(BPMEN)$_2$](ClO$_4$)$_3$ **5**[23] ($\hat{H} = JS_1S_2$). The J value for **1** estimated from the variation of chemical shifts of its ^{1}H NMR peaks[24] with temperature is about 196±20 cm^{-1}. On the basis of the results for **1**, the following assignment of the ^{1}H NMR peaks of **3** [Figure 3(*a*)] could be made: δ 78 (4H, C*H*H–N), 71 (4H, CH*H*-C*H*H), 54 (6H, Me), 49 (6H, Me), 36.5 (12H, picolinic α-H, C*H*H–C*H*H and C*H*H-N), 28.8 (2H, picolinic β-H), 27.8 (2H, picolinic β-H), 25.3 (2H, $\Delta\nu_{1/2}$ 200 Hz, picolinic β-H), 23.5 (2H, $\Delta\nu_{1/2}$ 200 Hz, picolinic β-H), 7.0 (2H, $\Delta\nu_{1/2}$ 45 Hz, picolinic γ-H), 5.5 (2H, $\Delta\nu_{1/2}$ 45 Hz, picolinic γ-H). Complex **4** differs from **3** only in the diamine bridge (1,2-diaminoethylene for **3** and 1,2-diaminocyclohexane for **4**). The ^{1}H NMR spectrum of **4**: (δ, CD$_3$CN, room temperature) 81.0 (4H), 57.5 (6H), 54.2 (6H), 38.9 (8H), 28.8 (2H), 27.6 (2H), 25.1 (2H), 23.5 (2H), 7.3 (2H), 6.4 (2H)[25] closely resembles that for **3**. However, only one peak is observed in the range 70–80 ppm [Figure 3(*b*)]. This corroborates our assignment of the peak at δ 71 in the ^{1}H NMR spectrum of **3** to CH*H*–C*H*H protons.

The ^{1}H NMR spectrum of [Fe$_2^{III}$(μ-O)(OH)(OH$_2$)(BPMEN)$_2$](ClO$_4$)$_3$ **5** [Figure 3(*c*)] is more poorly resolved (if compared to those of **1**, **3** and **4**). The range of chemical shifts for **5** is smaller than that for **3** due to stronger antiferromagnetic interaction. In this case, even tentative assignment of the ^{1}H NMR peaks of **5** is hardly possible.

Thus, for (μ-oxo)(μ-hydroxo)diiron(III) complexes of BPMEN and related ligands, most of their ^{1}H NMR peaks could be reliably assigned based on the integration and proximity of particular protons to the perturbing metal centre (complexes **3** and **4**). For (μ-oxo)diiron(III) complexes of BPMEN, the antiferromagnetic interaction is stronger than that for (μ-oxo)(μ-hydroxo)diiron(III) counterpart. In this case, the ^{1}H NMR spectra could be poorly resolved as in the case of complex **5**. The ^{1}H NMR spectrum of **1** is better resolved than that of **5**, probably, due to higher symmetry.

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