

Molecular and electronic structure of a mixed-valent class II, dinuclear complex containing a linear $[\text{Fe}^{\text{II}}\text{--O--Fe}^{\text{III}}]^{3+}$ core

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One-electron reduction of $[\{\text{LFe}^{\text{III}}(\text{Ph}_2\text{acac})\}_2(\mu\text{-O})]$ $[\text{BPh}_4]_2$ $1[\text{BPh}_4]_2$ ($\text{L} = 1,4,7$ -trimethyl-1,4,7-triazacyclononane, $\text{Ph}_2\text{acac}^- = 1,3$ -diphenylpropane-1,3-dionate) in CH_2Cl_2 -toluene by 1 equiv. of cobaltocene produces the mixed-valent complex $[\{\text{LFe}(\text{Ph}_2\text{acac})\}_2(\mu\text{-O})][\text{BPh}_4] \cdot \text{C}_6\text{H}_5\text{Me}$ $2[\text{BPh}_4] \cdot \text{C}_6\text{H}_5\text{Me}$ which is characterized by X-ray crystallography; **2 has an $S = \frac{1}{2}$ ground state (antiferromagnetically coupled high-spin Fe^{III} and high-spin Fe^{II} with $J = -65 \text{ cm}^{-1}$) and exhibits class II behaviour according to the Robin and Day classification.**

Mixed-valent $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ forms have been spectroscopically identified for the non-haem metalloproteins hemerythrin, the R2 subunit of ribonucleotide reductase and methane monooxygenase.¹ In their active sites an antiferromagnetically exchange coupled pair of a high-spin iron(II) and a high-spin iron(III) bridged by a μ -hydroxo or a μ -oxo group give rise to a characteristic, EPR-active $S = \frac{1}{2}$ ground state with g values < 2.0 . We have recently reported the first μ -hydroxo bridged, mixed-valent complex $[\text{L}_2\text{Fe}_2(\mu\text{-OH})(\mu\text{-O}_2\text{CBu}^t)_2][\text{ClO}_4]_2$ ($\text{L} = 1,4,7$ -trimethyl-1,4,7-triazacyclononane) which displays a rhombic EPR signal at 10 K with g values of 1.95, 1.52 and 1.43.² A structurally characterised dinuclear complex containing a linear $[\text{Fe}^{\text{II}}\text{--O--Fe}^{\text{III}}]^{3+}$ core has not been described to date. Here we report the molecular and electronic structure of such a species.

The reaction† of $[\text{LFe}^{\text{III}}\text{Cl}_3]^{3-}$ and potassium 1,3-diphenylpropane-1,3-dionate (1 : 1) in MeCN–H₂O (8 : 1) yields upon addition of NEt₃ and NaClO₄ orange crystals of $[\{\text{LFe}^{\text{III}}(\text{Ph}_2\text{acac})\}_2(\mu\text{-O})][\text{ClO}_4]_2$ **1** $[\text{ClO}_4]_2$ which was converted to **1** $[\text{BPh}_4]_2$ by metathesis. One-electron reduction of **1** $[\text{BPh}_4]_2$ in dry CH_2Cl_2 -toluene by 1 equiv. of cobaltocene‡ afforded deep-green microcrystals of $[\{\text{LFe}(\text{Ph}_2\text{acac})\}_2(\mu\text{-O})]\text{BPh}_4 \cdot \text{C}_6\text{H}_5\text{Me}$ **2** $[\text{BPh}_4] \cdot \text{C}_6\text{H}_5\text{Me}$ which crystallises in the triclinic space group *P*1 with two formula units per unit cell.§ Two independent μ -oxo atoms [O(1) and O(4)] lie on a crystallographic centre of symmetry and, consequently, both $\text{Fe}^{\text{II}}\text{--O--Fe}^{\text{III}}$ cores are linear. The methylene carbon atoms C(1)–C(6) of the macrocyclic amine coordinated to Fe(1) and Fe(1') display small, 'normal' anisotropic thermal parameters ($U_{\text{eq}} \approx 0.029 \text{ \AA}^2$) whereas those of the corresponding atoms of the macrocycle coordinated to Fe(2) and Fe(2') are significantly larger ($U_{\text{eq}} \approx 0.062 \text{ \AA}^2$). The five-membered Fe--N--C--C--N chelate rings adopt either ($\lambda\lambda\lambda$) or ($\delta\delta\delta$) conformation. In the monocation composed of Fe(1) and Fe(1') these two conformations are related by a crystallographic inversion centre and the resulting achiral *meso* isomer is ordered (Fig. 1). In contrast, the other cation comprising Fe(2) and Fe(2') shows a static disorder because the two enantiomeric forms, ($\lambda\lambda\lambda$) $\text{FeFe}(\lambda\lambda\lambda)$ and ($\delta\delta\delta$) $\text{FeFe}(\delta\delta\delta)$, occupy this position. Note that a statistical ratio of the two diastereomeric forms of 1 : 1 is expected from the synthesis. The $\text{Fe--O}_{\text{oxo}}$ distances at 1.877(1) and 1.901(1) Å are slightly longer than in oxo-bridged diiron(III) complexes (*ca.* 1.80 Å).⁴

The cyclic voltammogram of **1** $[\text{ClO}_4]_2$ in MeCN (0.1 M NBu₄PF₆) in the potential range +1.3 to –1.8 V vs. Fc^+/Fc displays one reversible one-electron transfer wave at

$E_{1/2} = -0.966 \text{ V vs. Fc}^+/\text{Fc}$ which is assigned to the couple **1**–**2**.

From temperature-dependent magnetic susceptibility measurements using a SQUID magnetometer (4–300 K) an $S = 0$ ground state was established for **1** $[\text{ClO}_4]_2$ with $J = -95 \text{ cm}^{-1}$, $g = 2.0$ (fixed) and a paramagnetic impurity ($S = 5/2$) of 2.6% ($H = -2J \cdot S_1 \cdot S_2$, $S_1 = S_2 = 5/2$). This antiferromagnetic coupling is typical for complexes with a linear $[\text{Fe}^{\text{III}}\text{--O--Fe}^{\text{III}}]^{4+}$ core.⁴ For **2** $[\text{BPh}_4] \cdot \text{C}_6\text{H}_5\text{Me}$ a similar antiferromagnetic coupling was detected yielding an $S = \frac{1}{2}$ ground state with $J = -65 \text{ cm}^{-1}$, $g = 2.0$ (fixed) ($S_1 = 5/2$, $S_2 = 2$) and a weakly coupled ($J = -10 \text{ cm}^{-1}$) dinuclear Fe^{II} impurity of 5% which most probably corresponds to the fully reduced, μ -OH bridged form of **2**.

The $S = \frac{1}{2}$ ground state for **2** $[\text{BPh}_4] \cdot \text{C}_6\text{H}_5\text{Me}$ was confirmed by its X-band EPR-spectrum measured at 4 K in CH_2Cl_2 . A rhombic signal is observed (Fig. 2) at g -values of 1.99, 1.93 and 1.84. In contrast, **1** $[\text{ClO}_4]_2$ is EPR silent.§ The rhombic signal of **2** displays a significantly narrower spread of g -values as compared to the μ -hydroxo bridged $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ species in ref. 1. This observation agrees nicely with spectra reported for the mixed-valent μ -oxo- and μ -hydroxo-bridged mixed-valent forms of the R2 subunit of ribonucleotide reductase, methane monooxygenase and hemerythrin.¹

The electronic spectrum of **2** $[\text{BPh}_4] \cdot \text{C}_6\text{H}_5\text{Me}$ in CH_2Cl_2 solution displays an intervalence absorption maximum at 635 nm ($\epsilon = 1.2 \times 10^3 \text{ m}^{-1} \text{ cm}^{-1}$) which is absent in the spectrum of **1**. A similar but much weaker maximum has been observed at 1350 nm ($\epsilon = 138 \text{ m}^{-1} \text{ cm}^{-1}$) for the μ -hydroxo bridged analogue.²

Temperature-dependent zero-field Mössbauer spectra of crystalline samples of **1** $[\text{ClO}_4]_2$ and **2** $[\text{BPh}_4] \cdot \text{C}_6\text{H}_5\text{Me}$ characterise **2** as a class II mixed-valent species.

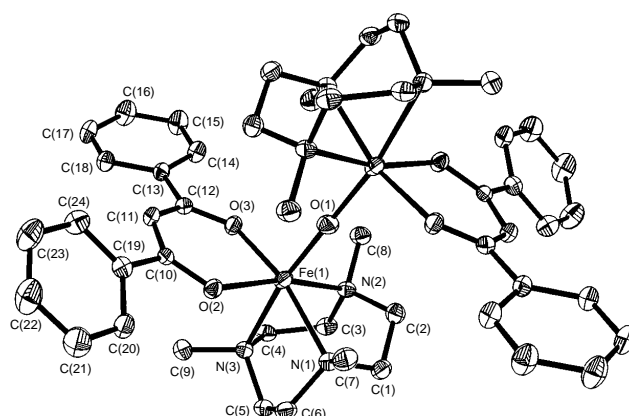


Fig. 1 Structure of one of the monocations in crystals of **2** $[\text{BPh}_4] \cdot \text{C}_6\text{H}_5\text{Me}$ at 100(2) K (the ordered *meso* form is shown). Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses: Fe(1)–O(1) 1.877(1), Fe(1)–O(2) 2.063(2), Fe(1)–O(3) 2.056(2), Fe(1)–N(1) 2.232(3), Fe(1)–N(2) 2.234(3), Fe(1)–N(3) 2.341(3); Fe(1)–O(1)–Fe(1') 180.

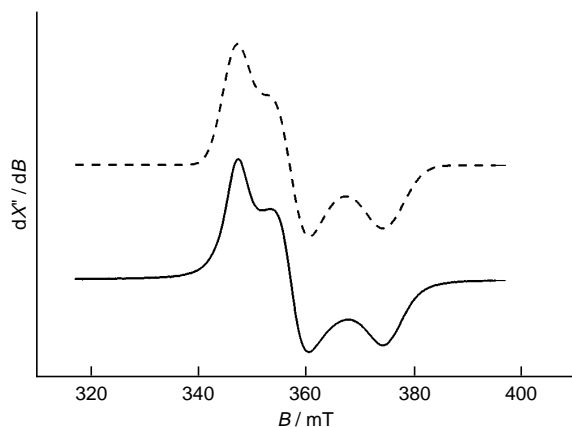


Fig. 2 X-Band EPR spectrum of $2[\text{BPh}_4]\cdot\text{C}_6\text{H}_5\text{Me}$ in CH_2Cl_2 at 4 K: the solid line represents the experimental spectrum and the dashed line is a simulation with $g_x = 1.99$, $g_y = 1.93$, $g_z = 1.84$ (with linewidths: $w_x = 2.93$, $w_y = 3.30$, $w_z = 4.12$ mT).

At temperatures > 200 K the spectra of **2** consist of a symmetric quadrupole doublet with isomer shift $\delta = 0.78$ mm s^{-1} and quadrupole splitting $\Delta E_Q = 0.37$ mm s^{-1} . This value of δ is intermediate between that of **1** ($\delta = 0.48$ mm s^{-1} , $\Delta E_Q = 1.30$ mm s^{-1} at 80 K) and that of the diiron(ii) reference compound $[\text{L}_2\text{Fe}^{\text{II}}_2(\mu\text{-OH})(\mu\text{-O}_2\text{CMe})_2][\text{ClO}_4]_5$ ($\delta = 1.15$ mm s^{-1} at 77 K). Due to the observed temperature-dependent line broadening in the spectrum of **2** we propose that this species exhibits class-II type⁶ dynamic valence detrapping of the $[\text{Fe}^{\text{II}}\text{-O-Fe}^{\text{III}}]^{3+}$ core with electron hopping at 200 K being fast on the Mössbauer timescale (10^{-7} s) rather than quantum-mechanical valence delocalisation (class III).⁷ The Mössbauer linewidths of **2** increase drastically with decreasing temperature ($\Gamma = 0.47$ mm s^{-1} at 200 K, 0.76 mm s^{-1} at 160 K and 1.16 mm s^{-1} at 120 K). Further lineshape distortions at temperatures < 40 K can be assigned to the onset of spin-relaxation processes. Therefore, it is not possible to record unperturbed quadrupole spectra in the slow limit of electron hopping at cryogenic temperatures (< 10 K).

Footnotes

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† Preparation of complexes: To a mixture of MeCN (80 ml) and water (10 ml) was added $[\text{LFe}^{\text{III}}\text{Cl}_3]$ (1.0 g, 3.0 mmol) and $\text{K}[\text{Ph}_2\text{acac}]$ (1.0 g, 3.8 mmol) with stirring at ambient temperature. To the deep-red solution were

added a few drops of NEt_3 . After 2 h of stirring the orange–yellow solution was filtered and NaClO_4 (1.0 g) was added. Within a few days orange crystals of $1[\text{ClO}_4]_2$ were obtained in 67% yield (1.10 g). $1[\text{BPh}_4]_2$ was prepared from an acetone solution of $1[\text{ClO}_4]_2$ by adding NaBPh_4 .

The following reduction was performed under strictly anaerobic conditions (argon) using Schlenk glassware. A solution of $1[\text{BPh}_4]_2$ (0.3 g, 0.20 mmol) and $[\text{Co}(\eta\text{-C}_5\text{Me}_5)_2]$ (0.05 g, 0.25 mmol) in dry, deoxygenated CH_2Cl_2 (40 ml) was stirred at room temp. for 30 min. From the deep-green solution yellow microcrystals of $[\text{Co}(\eta\text{-C}_5\text{H}_5)_2][\text{BPh}_4]$ precipitated which were filtered off under argon. After addition of dry, O_2 -free toluene (40 ml) and reduction of the reaction volume by slow evaporation deep-green crystals of $2[\text{BPh}_4]\cdot\text{C}_6\text{H}_5\text{Me}$ precipitated (0.05 g, 20%) which were suitable for X-ray crystallography. Satisfactory elemental analyses for all complexes were obtained.

UV–Vis spectra: $1[\text{ClO}_4]_2$ in MeCN: $\lambda_{\text{max}} = 283$ nm ($\epsilon = 3.9 \times 10^4$ $\text{m}^{-1} \text{cm}^{-1}$), 367 (2.9×10^4), 432 (1.65×10^4), 510 (2.2×10^3).

$2[\text{BPh}_4]\cdot\text{C}_6\text{H}_5\text{Me}$ in CH_2Cl_2 : $\lambda_{\text{max}} = 228$ nm (2.5×10^4 $\text{m}^{-1} \text{cm}^{-1}$), 362 (1.7×10^4), 635 (1.2×10^3).

‡ Crystal data: $\text{C}_{79}\text{H}_{92}\text{BFe}_2\text{N}_6\text{O}_5$ $2[\text{BPh}_4]\cdot\text{C}_6\text{H}_5\text{Me}$, $M = 1328.1$, triclinic, space group $P\bar{1}$, $a = 11.193(2)$, $b = 15.181(3)$, $c = 22.123(3)$ Å, $\alpha = 83.30(2)$, $\beta = 88.76(2)$, $\gamma = 69.77(2)^\circ$, $U = 3502.5(10)$ Å³, $Z = 2$, $D_c = 1.259$ g cm^{-3} , $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, $F(000) = 1410$, $\mu = 0.47$ mm^{-1} , $T = 100(2)$ K, 11311 independent reflections were used in the refinement of which 7254 were observed [$F_o > 4\sigma(F_o)$]; $R = 0.053$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/391.

§ The sample investigated displayed a weak signal at $g = 4.3$ at 10 K due to the mononuclear impurity ($S = 5/2$).

References

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