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Novel Formation of a Linear Trinuclear Ferric Complex Containing a μ-Oxo Bis(μ-acetato) and a μ-Hydroxo Bis(μ-acetato) Bridge

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The reaction of monomeric five-coordinate iron(II) complexes such as Fe(OBz)(HB(3,5-iPr$_2$pz)$_3$) (**1**) with dioxygen was recently shown to give μ-peroxo iron(III) dimers that are reasonably stable and characterizable.[1] However, irreversible thermal decomposition proceeds above -20 °C, and it is of interest to learn about the nature of the ultimate product(s).

Efforts to identify the irreversible oxidation product from the reaction of dioxygen with **1** have not been successful owing to poor crystallinity. This prompted us to explore a related complex, Fe(acac)(HB(3,5-iPr$_2$pz)$_3$) (**2**), where the carboxylate in **1** has been replaced by the structurally similar bidentate monoanionic oxygen-donor ligand acetylacetonate.[2] This new complex is easily prepared by ligand displacement with Fe(Cl)(HB(3,5-iPr$_2$pz)$_3$) and Na(acac).[3] It binds acetonitrile readily, as does **1**, to form the six-coordinate Fe(acac)(MeCN)(HB(3,5-iPr$_2$pz)$_3$) (**3**), whose structure has been determined by X-ray crystallography.[3] The reaction chemistry of **2** parallels that of **1**. In toluene at -78 °C, it reacts with dioxygen to give a bluish green product, presumably a μ-peroxo adduct. However, this adduct is much less stable than in the case of **1** and it decomposes to a reddish brown complex within 1 h even at -78 °C.

In order to isolate the irreversibly oxidized product, an acetonitrile solution of **2** was allowed to stand for 1 week under aerobic conditions. This afforded greenish brown crystals of **4** (55% yield) suitable for X-ray diffraction.[4] Figure 1 indicates its molecular structure. It is found to contain a linear trinuclear iron structural motif with a crystallographically imposed center of symmetry. Surprisingly, the acetylacetonate ligand of **2** is no longer present in **4**. Instead, it contains acetate bridges as evidenced by elemental analysis and ν(CO) at 1596 cm^{-1} in the IR spectrum. From labeling experiments, we have determined that the acetate groups originate from the acetylacetonate ligands, not from the solvent. While the mechanism of this transformation is unknown, it is clear that the assembly of the trimeric structure has considerably thermodynamic driving force. An IR band at 3636 cm^{-1} for **4** indicates the presence of a hydroxo group. The analytical data together with the X-ray structure clearly establish that **4** is neutral overall. Given the uninegative charge of the tridentate pyrazolylborate capping ligand, these data are consistent with two possible formulations: (a) a mixed-valence Fe(III)-Fe(II)-Fe(III) complex with two μ-hydroxo bis(μ-acetato) bridges or (b) an all-ferric Fe(III)-Fe(III)-Fe(III) compound with crystallographic disorder of μ-oxo bis(μ-acetato) and μ-hydroxo bis(μ-acetato) bridges. On the basis of magnetic susceptibility and Mössbauer data (*vide infra*), we conclude that the latter assignment is correct. Consistent with this formulation, the relevant Fe-O bond lengths of **4** (Fe1-O3 and Fe2-O3 in Figure 1) average to 1.91 Å. This value lies between the short values found in familiar μ-oxo bis(μ-carboxylato) diferric species (1.77-1.83 Å)[5] and the longer value reported for a μ-hydroxo bis(μ-carboxylato) dimer (1.96 Å).[6] It is also shorter than the Fe-O distances of 1.96 and 1.93 Å reported very recently for a closely related μ-hydroxo bis(μ-carboxylato) linear trimer.[7]

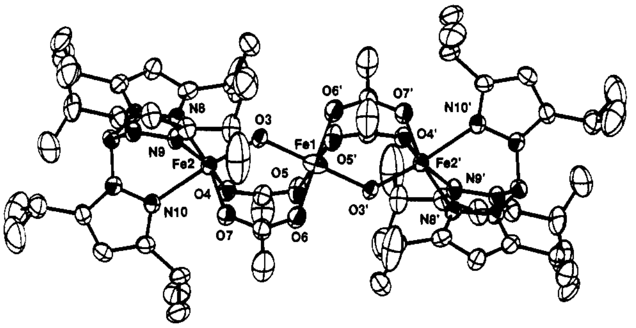

Figure 1. Molecular Structure of the trimer **4** (50% probability). The MeCN molecule of crystallization is omitted for clarity. Selected bond distances (Å) and angles (deg): Fe1-O3, 1.961(5); Fe1-O5, 2.047(7); Fe1-O6, 2.070(4); Fe2-O3, 1.858(5); Fe2-O4, 2.028(6); Fe2-O7, 2.040(5); Fe2-N8, 2.129(6); Fe2-N9, 2.141(6); Fe2-N10, 2.208(6); Fe1⋯Fe2, 3.392(1); Fe1-O3-Fe2, 125.3(2).

The Mössbauer spectrum of **4** is shown in Figure 2. It reveals high-spin iron(III) states for all three iron atoms. The predominant doublet at $\delta_{\mathrm{Fe}} = 0.47$ with $\Delta E_{\mathrm{q}} = 1.71$ mm·s^{-1} is assigned to the two iron atoms involved in the μ-oxo bridge. There is a close analogy with many characterized oxo-bridged ferric dimers whose ΔE_{q} values lie in the range 1.27-1.80 mm·s^{-1}.[5] It is notable

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(1) Kitajima, N.; Fukui, H.; Moro-oka, Y.; Mizutani, Y.; Kitagawa, T. *J. Am. Chem. Soc.* **1990**, *112*, 6402.

(2) Abbreviations used in this paper: HB(3,5-iPr$_2$pz)$_3$ = hydrotris(3,5-diisopropyl-1-pyrazolyl)borate(1-); acac = acetylacetonate(1-).

(3) Satisfactory analytical data were obtained for **2** and **3**. **3**·2MeCN crystallized in the monoclinic space group $P2_1/n$ with $a = 18.628(7)$ Å, $b = 16.197(12)$ Å, $c = 14.789(6)$ Å, $\beta = 91.67(3)°$, $V = 4460(4)$ Å^3, and $Z = 4$. The current R (R_w) values are 8.6% (8.2%) for 4108 reflections recorded at -50 °C. The details are provided as supplementary material.

(4) Anal. Calcd for **4** ($C_{62}H_{105}N_{12}B_2O_{10}Fe_3$): C, 54.45; H, 7.74; N, 12.29. Found: C, 53.99; H, 7.72; N, 12.29. IR (KBr; cm^{-1}): ν(OH) 3636, ν(BH) 2533, ν_a(COO) 1596, ν_s(COO) 1390. UV-vis (in CH$_2$Cl$_2$; λ/nm (ϵ/cm^{-1}·M^{-1})): 330 (sh, 14 600), 330 (19 200), 480 (sh, 2600). **4**·4MeCN ($C_{70}H_{117}N_{16}B_2O_{10}Fe_3$, fw = 1531.96) crystallized in the triclinic space group $P\bar{1}$ with $a = 11.958(4)$ Å, $b = 17.317(9)$ Å, $c = 11.952(6)$ Å, $\alpha = 119.88(3)°$, $\beta = 92.89(4)°$, $\gamma = 91.74(4)°$, $V = 2136(2)$ Å^3, and $Z = 1$. The data were collected at -50 °C ($2° \leq 2\theta \leq 48°$). The structure was solved by the Patterson method. All non-hydrogen atoms were refined anisotropicaly by the full-matrix least-squares methods. Hydrogen atom positions except those of the methyl groups and solvent molecule were calculated and fixed in the final refinement cycles isotropically. The refinement converged with R (R_w) = 7.0% (7.3%) for 4439 reflections ($F_o \geq 6\sigma(F_o)$).

(5) (a) Kurtz, D. M., Jr *Chem. Rev.* **1990**, *90*, 585. (b) Que, L., Jr.; True, A. E. *Prog. Inorg. Chem.* **1990**, *38*, 97.

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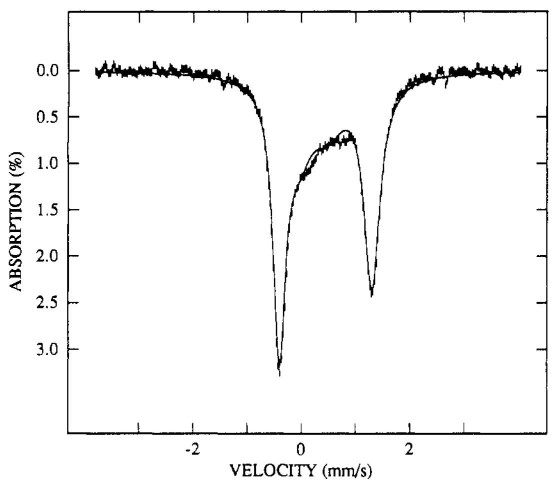

Figure 2. Room-temperature Mössbauer spectrum of the trimer 4. Fitting parameters: $\delta_1 = 0.47$, $\Delta E_q = 1.71$, $\Gamma_L = 0.28$, $\Gamma_R = 0.35$ mm·s^{-1}; $\delta_2 = 0.24$, $\Delta E_q = 0.52$, $\Gamma_L = 0.59$, $\Gamma_R = 0.77$ mm·s^{-1}. Isomer shifts are relative to Fe foil at room temperature. Area ratio = 71:33.

that the line widths of the fitted peaks (0.28 and 0.35 mm·s^{-1}) are narrow. Thus, despite their formal inequivalence in the unsymmetrical trimeric structure, the two μ-oxo-linked iron atoms bear remarkable identity with those in symmetric μ-oxo bis(μ-carboxylato) dimers. The third iron atom of the trimer appears as a proportionately less intense, poorly resolved signal that can be roughly approximated to a doublet with $\delta \sim 0.24$ and $\Delta E \sim 0.52$ mm·s^{-1}. These parameters, and the poor resolution, are similar to those seen in both reported examples of μ-hydroxo bis(μ-carboxylato) ferric dimers[6,8] and in the corresponding trimer.[7] At 4.2 K, a broad multiline spectrum is observed, indicating magnetic hyperfine interactions from a paramagnetic ground state.

A plot of the effective magnetic moment[9] per cluster is shown in Figure 3. A distinctive feature is the 5.9-μ_B plateau as the temperature decreases to 50 K. This is indicative of strong antiferromagnetic coupling between the three high-spin iron(III) centers, with spin frustration, to give an overall $S = {}^5/_2$ ground state. The spin Hamiltonian appropriate to such a linear trimer formally involves three coupling constants: J_{oxo}, $J_{hydroxo}$, and J_{term}, if spin coupling between the terminal iron atoms is included. On the basis of precedents from structurally similar dimers having μ-oxo and μ-hydroxo bridges,[5,6,8] chemically reasonable values for the first two could be $J_{oxo} = -108$ to -132 cm^{-1} and $J_{hydroxo} = -17$ cm^{-1}. Fitting the temperature dependence of μ_{eff} from 300 to 50 K shows there is a significant correlation of the spin Hamiltonian parameters. In particular, for J_{oxo} in the range -110 to -140 cm^{-1}, equally good fits can be found with $J_{hydroxo}$ and J_{term} ranging from -22 to -10 cm^{-1} and 24 to 11 cm^{-1}, respectively (see Figure 3). Fits excluding J_{term} are significantly poorer. The value of J_{term} is not unreasonable,[10] and since J_{oxo} is of intermediate magnitude, it can be specified more narrowly than in structurally related, sulfur-bridged systems.[11] Although there is no unique fit, the magnetic susceptibility data are clearly consistent with an $S = {}^5/_2$ ground state arising from strong antiferromagnetic coupling of the μ-oxo iron(III) atoms, weaker antiferromagnetic coupling to the hydroxo-bridged iron atom, and possible ferromagnetic coupling between the terminal iron atoms. The low-temperature data can be fit to a simple $S = {}^5/_2$ spin Hamiltonian with axial zero-field splitting ($g = 2.00$, $D = 0.79$ cm^{-1}, Figure 3b). The X-band EPR spectrum at 6 K in frozen toluene/acetonitrile solution shows an anisotropic derivative signal at $g = 4.3$ ($\Delta H = 60$ G) and a minor feature at $g = 9.7$. This is diagnostic of an overall $S = {}^5/_2$ state with $D > g\beta H$ and is typical of rhombic high-spin iron(III).[12] Thus, the magnetic data corroborate the chemical reasonableness of the μ-oxo-dominated description of the electronic structure that is suggested by the Mössbauer spectra.

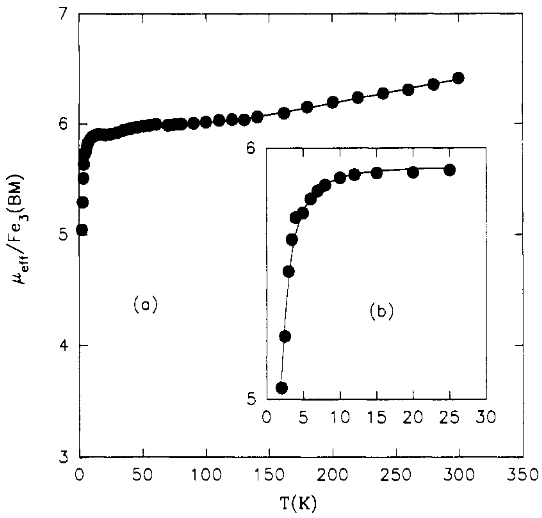

Figure 3. Plot of effective magnetic moment per trinuclear cluster of 4 versus temperature (data taken at 10 kG): (a) The 50–300 K fit with $g = 2.025$, $J_{oxo} = -110$ (fixed), $J_{hydroxo} = -9.6$, and $J_{term} = +10.6$ cm^{-1} using a spin Hamiltonian of the form §ch = $-2J_{oxo}S_1 \cdot S_2 - 2J_{hydroxo}S_2 \cdot S_3 - 2J_{term}S_1 \cdot S_3$; (b) insert showing the 2–25 K fit with $g = 2.00$ and $D = 0.79$ cm^{-1}. The jump in the data near 30 K is an instrumental artifact. It leads to slightly different g factors in the upper and lower temperature data but has an insignificant effect on J values.

While this work was in progress, a closely related linear trimer with symmetrical μ-hydroxo bis(μ-carboxylato) bridges was reported.[7] Both structures involve rather sterically encumbered tripodal capping ligands which destabilize their respective dimeric structures. The assembly of the present example and the asymmetry of its electronic structure, as dictated by the oxo bridge, are particularly notable. It adds to the increasingly rich area of polynuclear iron carboxylate chemistry[13] and is one of very few known linear trimeric structures.[11,14] Possibly, it will be found in biology.

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Supplementary Material Available: A textural presentation of the experimental crystallographic details, tables of crystal data, atomic coordinates, temperature factors, and intramolecular bond distances and angles, and an ORTEP view with atomic numbering for 3·2MeCN and 4·4MeCN (23 pages). Ordering information is given on any current masthead page.

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