Synthesis and Structures of μ_3-Oxo-centered Mixed-valent Trinuclear Iron Complexes with 1-Methyl-imidazole Ligands

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Treatment of the μ_3-oxo-centered mixed-valent trinuclear iron complex [Fe$_3(\mu_3$-O)(μ-OAc)$_6$(H$_2$O)$_3$] (**1**) in methanol solution with one, two, or three equivalents of 1-methyl-imidazole (C$_4$H$_6$N$_2$) afforded the substitution products [Fe$_3(\mu_3$-O)(μ-OAc)$_6$(H$_2$O)$_2$(C$_4$H$_6$N$_2$)] (**2**), [Fe$_3(\mu_3$-O)(μ-OAc)$_6$(H$_2$O)(C$_4$H$_6$N$_2$)$_2$] (**3**), and [Fe$_3(\mu_3$-O)(μ-OAc)$_6$(C$_4$H$_6$N$_2$)$_3$] (**4**), respectively. Complexes **2** – **4** were characterized by spectroscopic and elemental analyses, and the crystal structures of complexes **3** · 1.5MeOH · 2H$_2$O and **4** have been determined by single-crystal X-ray diffraction. The results indicate that in **2** – **4** the trinuclear core unit [Fe$_3(\mu_3$-O)(μ-OAc)$_6$] of **1** is preserved.

Key words: Synthesis, Crystal Structure, Trinuclear Iron Complex, Mixed-valent Iron Complex

Introduction

Oxo-centered trinuclear iron complexes with the trinuclear core unit [Fe$_3(\mu_3$-O)(μ-O$_2$CR)$_6$L$_3$] (where L is a neutral monodentate ligand, *e. g.* H$_2$O, and R is an alkyl or aryl group), popularly referred to as "basic iron carboxylates", have been known for more than a century [1, 2]. These trinuclear complexes are considered an important class of compounds because the [Fe$_3(\mu_3$-O)] unit has been proposed as the smallest building block for the formation of the iron core in ferritin, an iron storage protein [3]. Moreover, the general goal of the studies of these mixed-valent iron complexes has been to understand what factors determine the rate of electron transfer between well-separated metal ions through variation of the bridge between the metal centers [4 – 6]. The results of experiments carried out in the past two decades have shown that mixed-valent iron acetates of the composition [Fe$_3(\mu_3$-O)(μ-OAc)$_6$L$_3$]S (S is a solvate molecule such as benzene or pyridine) are well-suited as models for determining the importance of the solid-state environment in controlling intramolecular electron transfer [7, 8]. It is interesting to note that the onset of motion of L and/or S leads to an appreciable increase in the rate of electron transfer as the temperature is increased [9, 10]. Thus, bond lengths as determined by regular diffraction methods often show pronounced temperature dependence in this class of mixed-valent iron complexes, which suggested some structural and resonance-diffraction studies at different temperatures [9 – 12]. In the reported mixed-valent iron acetate complexes [Fe$_3(\mu_3$-O)(μ-OAc)$_6$L$_3$], the neutral monodentate ligands are water with an oxygen donor and pyridines with a nitrogen donor [8, 10, 11]. We have become interested in the reactivity of [Fe$_3$-$(\mu_3$-O)(μ-OAc)$_6$(H$_2$O)$_3$] as a good starting material for mixed-valent iron acetate complexes with different Fe-L terminal bonds. In this paper we report the synthesis and structures of complexes with *N*-bonded 1-methyl-imidazole ligands.

Experimental Section

General

Doubly distilled water was used throughout. All other chemical reagents were of analytical-grade purity. The infrared spectra were recorded by using KBr pellets in a Digilab FTS-40 spectrophotometer. Mass spectra were performed on a Finnigan TSQ 7000 spectrometer. Microanalytical (C, H, N) data were obtained with using a Perkin-Elmer 2400 elemental analyzer.

Syntheses

[Fe₃(μ₃-O)(μ-OAc)₆(H₂O)₃] (1)

This compound was prepared by a previously reported method [13]. FeCl$_2$ · 4H$_2$O (1.0 g, 5.0 mmol), NaOAc (1.0 g, 1.2 mmol) and glacial acetic acid (3.0 g, 50 mmol) were

Table 1. Crystal data, data collection parameters and details of the structure refinement.

Complex	$\mathbf{3} \cdot 1.5\text{MeOH} \cdot 2\text{H}_2\text{O}$	$\mathbf{4}$
Empirical formula	$C_{21.5}H_{43}Fe_3N_4O_{17.5}$	$C_{24}H_{36}Fe_3N_6O_{13}$
Formula weight	805.15	784.14
Color, habit	orange, rod	red, block
Crystal size, mm^3	$0.24 \times 0.10 \times 0.05$	$0.20 \times 0.10 \times 0.08$
Crystal system	monoclinic	rhombohedral
Space group	$P2_1/c$	$R3$
a, Å	17.288(3)	17.746(6)
b, Å	8.0688(15)	a
c, Å	28.617(6)	21.129(14)
β, deg	95.499(5)	90
Volume, Å^3	3973.6(13)	5763(5)
Z	4	6
Density (calc.), g cm^{-3}	1.35	1.34
Absorption coefficient, mm^{-1}	1.2	1.2
Temperature, K	293(2)	293(2)
$F(000)$, e	1672	2424
Radiation, wavelength	— MoK_α, $\lambda = 0.71073$ Å —	
Reflections collected	26022	11430
Independence reflections, R_{int}	8231, $R_{\text{int}} = 0.083$	4486, $R_{\text{int}} = 0.077$
Reflections with $I \geq 2\sigma(I)$	1779	3211
Weighting scheme	$W = [\sigma^2(F_o^2) + 0.0780P^2 + 0.0000P]^a$	$W = [\sigma^2(F_o^2) + 0.0791P^2 + 0.0000P]^a$
Parameters refined	414	283
Final R indices (all data)[b]	$R1 = 0.121$, $wR2 = 0.189$	$R1 = 0.103$, $wR2 = 0.159$
Goodness of fit (GoF)[c]	0.93	1.01
x (Flack)	–	0.01(1)
Final difference peaks, e Å^{-3}	$+0.64/-0.32$	$+0.61/-0.44$

[a] $P = (F_o^2 + 2F_c^2)/3$; [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$; [c] GoF $= [\Sigma w(|F_o| - |F_c|)^2/(N_{\text{obs}} - N_{\text{param}})]^{1/2}$.

dissolved in 10 mL of water. The reaction mixture was heated at 70 – 80 °C under reflux for 1 h, while bubbling a constant stream of air. The mixture was cooled to r. t. and the dark-brown precipitate was filtered, washed with ethanol and diethyl ether, and then dried under vacuum. Yield: 0.56 g (56.7 %). – IR (KBr disc, cm^{-1}): ν(O–H) = 3354 (br), ν(CO$_2$) = 1604 (s) 1453 (s), ν_{as}(Fe$_3$O) = 664(s) 621(m). – MS (FAB): m/z = 593 [M+1]$^+$, 574 [M–H$_2$O]$^+$, 556 [M–2H$_2$O]$^+$, 538 [M–3H$_2$O]$^+$. – Anal. calcd. for C$_{12}$H$_{24}$Fe$_3$O$_{16}$: C 24.3, H 4.05; found C 24.1, H 4.02.

### *[Fe$_3$(μ_3-O)(μ-OAc)$_6$(H$_2$O)$_2$(C$_4$H$_6$N$_2$)] (2)*

To a solution of **1** (216 mg, 0.5 mmol) in methanol (10 mL) was added 1-methyl-imidazole C$_4$H$_6$N$_2$ (41 mg, 0.5 mmol). The mixture was stirred overnight at r. t., during which time the color changed from brown to orange-yellow. The solution was cooled to −5 °C, and orange-yellow needle crystals were harvested in a yield of 47.5 % (122 mg). – IR (KBr disc, cm^{-1}): ν(O–H) = 3351 (br), ν(CO$_2$) = 1601 (s) 1455 (s), ν(C=N) = 1493 (s), ν_{as}(Fe$_3$O) = 662(s) 626(m). – MS (FAB): m/z = 656 [M]$^+$, 638 [M–H$_2$O]$^+$, 620 [M–2H$_2$O]$^+$, 538 [M–2H$_2$O–C$_4$H$_6$N$_2$]$^+$. – Anal. calcd. for C$_{16}$H$_{28}$Fe$_3$N$_2$O$_{15}$ · H$_2$O: C 28.5, H 4.45, N 4.15; found C 28.2, H 4.39, N 4.13.

[Fe$_3$(μ_3-O)(μ-OAc)$_6$(H$_2$O)(C$_4$H$_6$N$_2$)$_2$] (3)

To a solution of **1** (216 mg, 0.5 mmol) in methanol (10 mL) was added C$_4$H$_6$N$_2$ (82 mg, 1.0 mmol). The mixture was stirred overnight at r. t., during which time the color changed from brown to orange. The solution was cooled to −5 °C, and orange crystals were obtained in a yield of 59.2 % (176 mg). – IR (KBr disc, cm^{-1}): ν(H$_2$O) = 3538 (br), ν(O–H) = 3346 (br), ν(CO$_2$) = 1603 (s) 1451 (s), ν(C=N) = 1498 (s), ν_{as}(Fe$_3$O) = 668(s) 632(m). – MS (FAB): m/z = 721 [M+1]$^+$, 702 [M–H$_2$O]$^+$, 620 [M–H$_2$O–C$_4$H$_6$N$_2$]$^+$, 538 [M–H$_2$O–2C$_4$H$_6$N$_2$]$^+$. – Anal. calcd. for C$_{20}$H$_{32}$Fe$_3$N$_4$O$_{14}$ · 2 H$_2$O · 1.5 CH$_4$O: C 32.7, H 5.32, N 7.09; found C 32.4, H 5.27, N 7.01.

[Fe$_3$(μ_3-O)(μ-OAc)$_6$(C$_2$H$_6$N$_2$)$_3$] (4)

To a solution of **1** (216 mg, 0.5 mmol) in methanol (10 mL) was added C$_4$H$_6$N$_2$ (123 mg, 1.5 mmol). The mixture was stirred overnight at r. t., during which time the color changed from brown to red. The solution was cooled to −5 °C, and red crystals were obtained in a yield of 63.4 % (215 mg). – IR (KBr disc, cm^{-1}): ν(O–H) = 3353 (br), ν(CO$_2$) = 1600 (s) 1448 (s), ν(C=N) = 1492 (s), ν_{as}(Fe$_3$O) = 661(s) 627(m). – MS (FAB): m/z = 784 [M]$^+$, 702 [M–C$_4$H$_6$N$_2$]$^+$, 620 [M–2C$_4$H$_6$N$_2$]$^+$, 538 [M–3C$_4$H$_6$N$_2$]$^+$. –
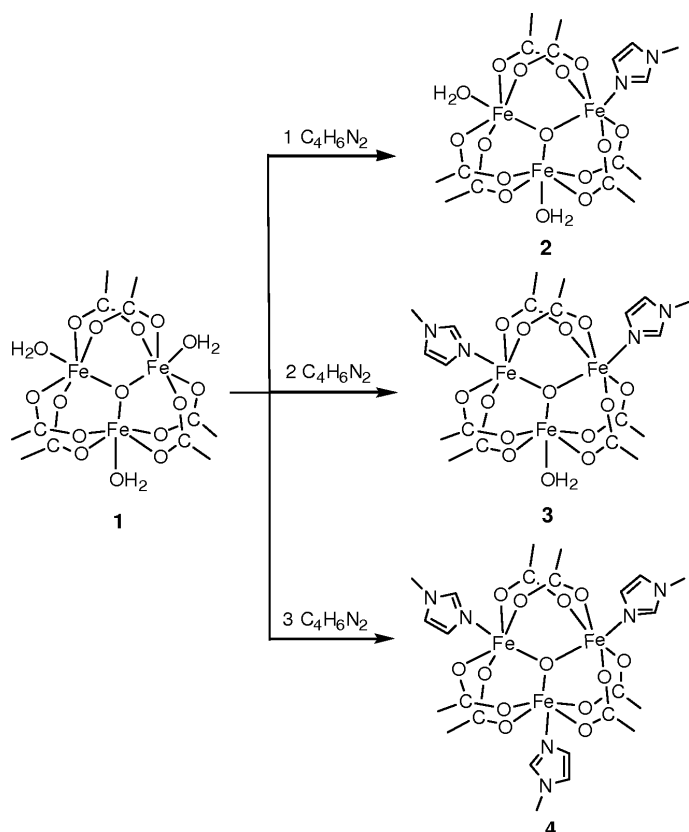
Scheme 1.

Anal. calcd. for $C_{24}H_{36}Fe_3N_6O_{13}$: C 36.7, H 4.59, N 10.7; found C 36.1, H 4.46, N 10.4.

Crystal structure determination

Single crystals of **3**·1.5MeOH·2H$_2$O (0.24 × 0.10 × 0.05 mm³) and **4** (0.20 × 0.10 × 0.08 mm³) were mounted in random orientation on a glass fiber. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer with MoK_α radiation (λ = 0.71073 Å) at 293 K using an ω scan mode. The collected frames were processed with the software SAINT [14]. The data was corrected for absorption using the program SADABS [15]. Structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [16]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C_{sp^3}–H = 0.96 and C_{sp^2}–H = 0.93 Å) and included in the structure factor calculations with fixed isotropic displacement parameters but were not refined. The methanol solvent molecules in **3**·1.5MeOH·2H$_2$O were isotropically refined without hydrogen atoms due to heavy disorder. The hydrogen atoms of the water molecules of **3**·1.5MeOH·2H$_2$O were also excluded. The Flack value of zero for **4** indicated the correct absolute structure. Crystal data, data collection parameters and details of the structure refinement are given in Table 1.

Crystal data (excluding structure factors) have been deposited with The Cambridge Crystallographic Data Centre as supplementary publications CCDC 637503 and CCDC 637504. Copies of the data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

The known μ_3-oxo-centered mixed-valent trinuclear iron complex [Fe$_3$(μ_3-O)(μ-OAc)$_6$(H$_2$O)$_3$] (**1**) has three terminally coordinated hydrate molecules which are labile to substitution by strong donor ligands. Thus, treatment of **1** in methanol solution with one, two, or three equivalents of 1-methyl-imidazole (C$_4$H$_6$N$_2$) results in the isolation of accordingly substituted complexes in moderate yields with elemental analyses data consistent with formulae [Fe$_3$(μ_3-O)(μ-OAc)$_6$(H$_2$O)$_2$(C$_4$H$_6$N$_2$)] (**2**), [Fe$_3$-(μ_3-O)(μ-OAc)$_6$(H$_2$O)(C$_4$H$_6$N$_2$)$_2$] (**3**), and [Fe$_3$(μ_3-O)(μ-OAc)$_6$(C$_4$H$_6$N$_2$)$_3$] (**4**), respectively (Scheme 1). The IR spectra in general show features attributable
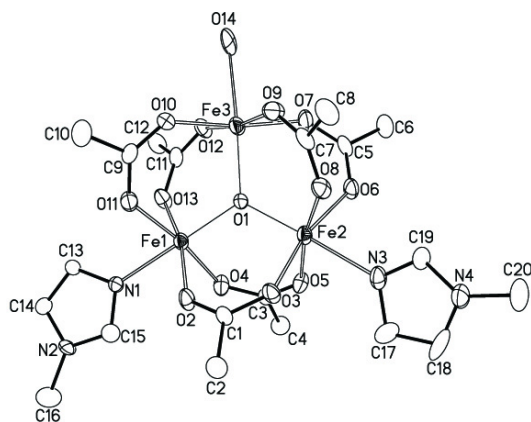
Fig. 1. ORTEP plot of the structure of $[Fe_3(\mu_3\text{-O})(\mu\text{-OAc})_6$-$(H_2O)(C_4H_6N_2)_2]$ (**3**) in the methanol water solvate at 293 K with displacement ellipsoids at the 40 % probability level. Solvent molecules and hydrogen atoms are omitted for clarity.
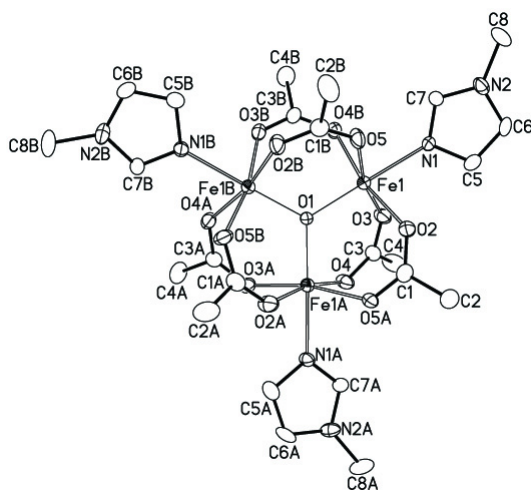

Fig. 2. ORTEP plot of one of the two crystallographically independent molecules $[Fe_3(\mu_3\text{-O})(\mu\text{-OAc})_6(C_4H_6N_2)_3]$ in the crystals of **4** at 293 K with displacement ellipsoids at the 40 % probability level. Hydrogen atoms are omitted for clarity.

to all components of the structure, *i. e.* the $[Fe_3(\mu_3\text{-}$O$)]$ core [18], the bridging acetate ligand and the neutral 1-methyl-imidazole ligand (see Experimental Section) [19]. A clear assignment for $\nu(H_2O)$ can be made for a very broad band at *ca.* 3540 cm^{-1} in the IR spectrum of the solvate of **3**, while the stretching vibration $\nu(O–H)$ due to the coordinating water molecule is observed at *ca.* 3352 cm^{-1} for **2** and **3**. Positive-ion FAB mass spectra show the retention of the $[Fe_3(\mu_3\text{-}$O$)(\mu\text{-OAc})]$ core ($m/z = 538$) and the incorporation of ligands, as in $[Fe_3(\mu_3\text{-O})(\mu\text{-OAc})(C_4H_6N_2)]^+$ and

Table 2. Selected bond lengths (Å) and bond angles (°) for complex **3** · 1.5MeOH · 2H$_2$O.

Fe(1)–O(1)	1.924(5)	Fe(2)–O(5)	2.037(7)
Fe(1)–O(2)	2.014(6)	Fe(3)–O(1)	1.923(5)
Fe(1)–O(13)	2.012(6)	Fe(3)–O(9)	2.000(7)
Fe(1)–O(11)	2.016(7)	Fe(3)–O(10)	2.008(7)
Fe(1)–O(4)	2.030(6)	Fe(3)–O(7)	2.014(7)
Fe(2)–O(1)	1.901(5)	Fe(3)–O(12)	2.030(7)
Fe(2)–O(8)	1.995(7)	Fe(1)–N(1)	2.147(7)
Fe(2)–O(3)	2.025(6)	Fe(2)–N(3)	2.142(8)
Fe(2)–O(6)	2.033(6)	Fe(2)–O(14)	2.169(9)
O(1)–Fe(1)–O(2)	97.6(2)	O(6)–Fe(2)–O(5)	88.5(3)
O(1)–Fe(1)–O(13)	96.0(2)	O(1)–Fe(2)–N(3)	178.1(3)
O(2)–Fe(1)–O(13)	166.3(2)	O(8)–Fe(2)–N(3)	84.9(4)
O(1)–Fe(1)–O(11)	94.1(2)	O(3)–Fe(2)–N(3)	81.7(3)
O(2)–Fe(1)–O(11)	90.3(3)	O(6)–Fe(2)–N(3)	85.4(3)
O(13)–Fe(1)–O(11)	90.9(3)	O(5)–Fe(2)–N(3)	86.1(3)
O(1)–Fe(1)–O(4)	93.8(2)	O(1)–Fe(3)–O(9)	94.9(3)
O(2)–Fe(1)–O(4)	88.3(3)	O(2)–Fe(3)–O(10)	93.8(2)
O(13)–Fe(1)–O(4)	88.6(3)	O(9)–Fe(3)–O(10)	86.2(3)
O(11)–Fe(1)–O(4)	172.1(3)	O(1)–Fe(3)–O(7)	93.2(3)
O(1)–Fe(1)–N(1)	179.3(3)	O(9)–Fe(3)–O(7)	90.1(3)
O(2)–Fe(1)–N(1)	83.1(3)	O(10)–Fe(3)–O(7)	172.3(3)
O(13)–Fe(1)–N(1)	83.4(3)	O(1)–Fe(3)–O(12)	93.4(3)
O(11)–Fe(1)–N(1)	85.6(3)	O(9)–Fe(3)–O(12)	171.7(3)
O(4)–Fe(1)–N(1)	86.5(3)	O(10)–Fe(3)–O(12)	92.5(3)
O(1)–Fe(2)–O(8)	95.5(3)	O(7)–Fe(3)–O(12)	90.1(3)
O(1)–Fe(2)–O(3)	96.4(2)	O(1)–Fe(3)–O(14)	177.3(2)
O(8)–Fe(2)–O(3)	89.8(3)	O(9)–Fe(3)–O(14)	86.1(3)
O(1)–Fe(2)–O(6)	96.4(2)	O(10)–Fe(3)–O(14)	83.7(3)
O(8)–Fe(2)–O(6)	89.2(3)	O(7)–Fe(3)–O(14)	89.3(3)
O(3)–Fe(2)–O(6)	167.2(2)	O(12)–Fe(3)–O(14)	85.6(3)
O(1)–Fe(2)–O(5)	93.6(2)	Fe(2)–O(1)–Fe(3)	120.1(3)
O(8)–Fe(2)–O(5)	170.8(3)	Fe(2)–O(1)–Fe(1)	119.9(3)
O(3)–Fe(2)–O(5)	90.4(3)	Fe(3)–O(1)–Fe(1)	120.0(2)

$[Fe_3(\mu_3\text{-O})(\mu\text{-OAc})(C_4H_6N_2)_2]^+$ observed at $m/z = 620$ and 702, respectively, and in $[Fe_3(\mu_3\text{-O})(\mu\text{-OAc})$-$(C_4H_6N_2)(H_2O)]^+$ and $[Fe_3(\mu_3\text{-O})(\mu\text{-OAc})(H_2O)_2]^+$ at $m/z = 638$ and 528, respectively.

The structures of complexes **3** · 1.5MeOH · 2H$_2$O and **4** were determined by r. t. single-crystal X-ray diffraction, and the results are shown in Figs. 1 and 2, respectively. Selected bond lengths and angles are given in Tables 2 and 3. Complex **3** crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$. The solvate molecules are disordered at two resolvable positions. There is no crystallographically imposed symmetry for the $[Fe_3(\mu_3\text{-O})]$ core. Complex **4** crystallizes in the rhombohedral crystal system with two molecules in slightly different conformations. No significant differences in bonding parameters between these two molecules (A and B) were found. The structure is of high symmetry with the three-fold axis passing through the oxygen atom of the $[Fe_3(\mu_3\text{-O})]$ core.

Table 3. Selected bond lengths (Å) and bond angles (deg) for complex **4**.

Molecule I		Molecule II	
Fe(1)–O(1)	1.9143(13)	Fe(2)–O(6)	1.9129(13)
Fe(1)–O(2)	2.062(7)	Fe(2)–O(7)	2.072(6)
Fe(1)–O(3)	2.067(7)	Fe(2)–O(8)	2.052(6)
Fe(1)–O(4)#1	2.065(7)	Fe(2)–O(9)	2.073(6)
Fe(1)–O(5)	2.070(6)	Fe(2)–O(10)	2.064(6)
Fe(1)–N(1)	2.168(7)	Fe(2)–N(3)	2.171(7)
O(1)–Fe(1)–O(2)	95.2(3)	O(6)–Fe(2)–O(8)	95.3(3)
O(1)–Fe(1)–O(4)#1	96.0(3)	O(6)–Fe(2)–O(10)	97.3(3)
O(2)–Fe(1)–O(4)#1	168.6(2)	O(8)–Fe(2)–O(10)	88.3(3)
O(1)–Fe(1)–O(3)	95.2(3)	O(6)–Fe(2)–O(7)	95.0(3)
O(2)–Fe(1)–O(3)	90.1(3)	O(8)–Fe(2)–O(7)	89.6(3)
O(4)#1–Fe(1)–O(3)	90.5(3)	O(10)–Fe(2)–O(7)	167.6(2)
O(1)–Fe(1)–O(5)	97.1(3)	O(6)–Fe(2)–O(9)	96.5(3)
O(2)–Fe(1)–O(5)	88.2(3)	O(8)–Fe(2)–O(9)	168.2(2)
O(4)#1–Fe(1)–O(5)	88.8(3)	O(10)–Fe(2)–O(9)	89.0(3)
O(3)–Fe(1)–O(5)	167.7(2)	O(7)–Fe(2)–O(9)	90.7(3)
O(1)–Fe(1)–N(1)	179.0(3)	O(6)–Fe(2)–N(3)	178.7(3)
O(2)–Fe(1)–N(1)	84.5(2)	O(8)–Fe(2)–N(3)	84.4(2)
O(4)#1–Fe(1)–N(1)	84.3(2)	O(10)–Fe(2)–N(3)	84.0(3)
O(3)–Fe(1)–N(1)	83.9(3)	O(7)–Fe(2)–N(3)	83.7(3)
O(5)–Fe(1)–N(1)	83.8(3)	O(9)–Fe(2)–N(3)	83.9(2)
Fe(1)#1–O(1)–Fe(1)	119.97(2)	Fe(2)#3–O(6)–Fe(2)	119.96(2)
Fe(1)–O(1)–Fe(1)#2	119.97(2)	Fe(2)–O(6)–Fe(2)#4	119.97(2)

Symmetry transformations used to generate equivalent atoms: #1 $y - x - 1$, $1 - x$, z; #2 $1 - y$, $x - y + 2$, z; #3 $1 - y$, $x - y + 1$, z; #4 $y - x$, $1 - x$, z.

The structures of **3** and **4** contain the same neutral tri-nuclear [Fe$_3$(μ_3-O)(μ_3-OAc)$_6$] core in which the three iron atoms form an equilateral triangle with a central μ_3-oxygen atom. The central oxygen atom deviates from the Fe$_3$ plane by 0.014 Å in **3** and 0.026 Å in **4**. Although there are mixed-valent Fe^{II} and Fe^{III} in the two complexes, no obvious difference of the Fe–μ_3-O bond lengths [av. 1.916(5) Å for **3** and av. 1.914(1) Å for **4**] was observed in the r. t. structures. Thus, the "ferric" and "ferrous" sites cannot be defined by crystallographic parameters only; it requires the low-temperature Mössbauer spectra to reflect the "ferric" and "ferrous" signals in the ratio of 2 : 1 [4, 5].

Each iron atom adopts an octahedral coordination geometry. The average Fe–O$_{ac}$ bond lengths in the two complexes are essentially identical and similar to related μ_3-oxo-centered mixed-valent trinuclear iron complexes. The average terminal Fe–N bond lengths are 2.145(7) Å for **3** and 2.170(7) Å for **4**, which are shorter than those in similar complexes with *N*-bound pyridine ligands, such as [Fe$_3$(μ_3-O)(μ-OAc)$_6$(py)$_3$] (2.224(12) Å) [6], [Fe$_3$(μ_3-O)(μ-OAc)$_6$(4-Me-py)$_3$] (2.195(3) Å) [20] and [Fe$_3$(μ_3-O)(μ-OAc)$_6$(3-Me-py)$_3$] (2.227(2) Å) [6]. The terminal Fe–O(H$_2$O) bond length of 2.169(9) Å in **3** can be compared with that of 2.162(5) Å in [Fe$_3$(μ_3-O)(μ-OAc)$_6$(H$_2$O)$_3$] [8, 13]. The angles at the iron atoms involving the central oxygen atom and the terminal nitrogen/oxygen atoms are in the ranges of 177.3(2)–179.3(3)° in **3** and 178.7(3)–179.0(3)° in **4**. In **3**, the plane of one imidazole ligand is nearly parallel to that of the three iron atoms; the dihedral angle is 3.1°. The dihedral angle with the other imidazole ligand is 14.8°. The dihedral angle of the planes of the two imidazole ligands is 14.7°. In **4**, the dihedral angle of the plane of the imidazole ligand with the [Fe$_3$(μ_3-O)] plane is 8.7°, and the dihedral angle of the planes of the two imidazole ligands is 15.0°. The difference of this orientation is also observed in the related complexes [Fe$_3$(μ_3-O)-(μ-OAc)$_6$(R-py)$_3$] with pyridine ligands (R = H, 3-Me, 4-Et) [6, 20, 21]. The average Fe $\cdots$ Fe separations are 3.319(3) and 3.314(2) Å for **3** and **4**, respectively, indicative of no significant electronic interaction at r. t.

In summary, we have explored substitution reactions of [Fe$_3$(μ_3-O)(μ-OAc)$_6$(H$_2$O)$_3$] with 1-methyl-imidazole ligands in different stoichiometry and isolated mono-, di- and tri-substituted complexes with *N*-bonded ligands. The results of spectroscopic and structural studies reflect the structural stability of the core [Fe$_3$(μ_3-O)(μ-OAc)$_6$] for different numbers and orientations of imidazole ligands in these complexes. Further investigations on [Fe$_3$(μ_3-O)(μ-OAc)$_6$(L)$_3$] complexes with bulky imidazole ligands including their magnetic properties and temperature-dependent crystal structures will be carried out in this laboratory.

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