Brief Communications

New hexanuclear antiferromagnetic heterospin iron complex

M. A. Kiskin,[a]★ G. G. Aleksandrov,[a] Yu. G. Shvedenkov,[b] V. M. Novotortsev,[a] and I. L. Eremenko[a]

[a]N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (495) 955 4835. E-mail: ilerem@igic.ras.ru
[b]A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, 3 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation. Fax: +7 (383) 330 9489

Precise oxidation of $Fe^{II}_4(\mu_3\text{-}OH)_2(OOCBu^t)_6(EtOH)_6$ afforded the mixed-valent hexanuclear complex $[Fe^{II}_4Fe^{III}_2(\mu_4\text{-}O)_2(\mu_3\text{-}OOCBu^t)_4(\mu\text{-}OOCBu^t)_6(HOOCBu^t)_3(EtOH)]\cdot HOOCBu^t$. The structure of the latter was established by X-ray diffraction. The magnetic properties of the new complex were studied.

Key words: polynuclear iron complexes, carboxylate ligands, synthesis, X-ray diffraction study, magnetic properties.

Heterospin polynuclear transition metal complexes hold promise as "spin materials" for the design of molecular magnets.[1—4] Among such structures, homo-[5—12] and heteronuclear[13] compounds containing six metal atoms and having the formula $M^{II}_4M'^{III}_2(O)_2(OOCR)_{10}L_4$ (M = Mn, Co, or Ni; M´ = Mn or Co; R = Me, CMe_3, or Ph; L = THF, DMF, EtOH, $HOOCBu^t$, py, MeCN, or pyrazole) are of great interest. These compounds are convenient synthons in the chemical assembly of new magnetic structures with unusual properties. Recently, it has been demonstrated[4] that molecular magnets can be prepared by combining the $[Mn_6]$ clusters with organic groups serving as ligands L. However, iron derivatives are lacking among available hexanuclear carboxylate clusters, although such derivatives would be high-spin compounds analogously to manganese compounds. In the present study, we synthesized a compound belonging to this group by oxidation of iron(II) hydroxo pivalate $Fe_4(\mu_3\text{-}OH)_2(OOCBu^t)_6(EtOH)_6$ (**1**) (see. Ref. 14) and examined the magnetic properties of the new compound.

One of convenient approaches to the synthesis of hexanuclear heterospin manganese-containing carboxylates is based on oxidation of the starting manganese(II) carboxylates with atmospheric oxygen.[5,11] However, unlike oxidation of the latter compounds, oxidation of iron(II) carboxylates with atmospheric oxygen affords oxo carboxylate complexes containing only iron(III) atoms as the major reaction products.[15,16] Hence, it is necessary to

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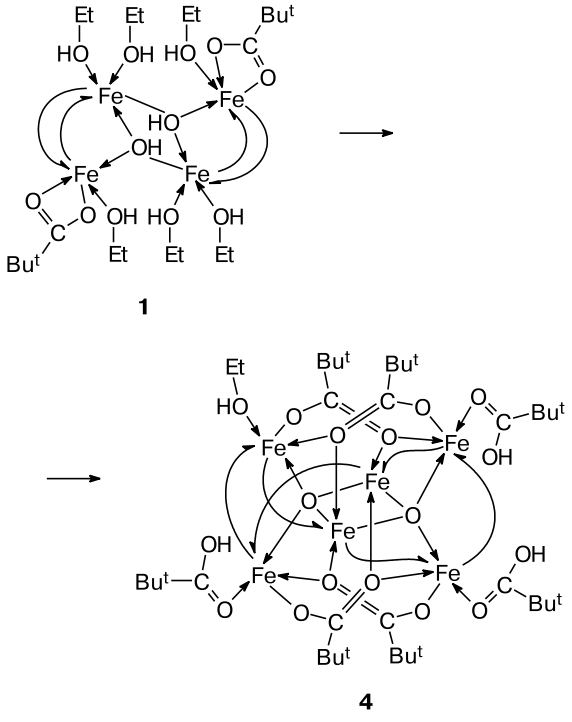
use controlled oxidation of Fe^{II} atoms for the synthesis of mixed-valent compounds. This has been exemplified[17] by the synthesis of the heterospin dodecanuclear complex $Fe^{II}{}_8Fe^{III}{}_4(O)_2(OMe)_{18}(OCCH_2Cl)_{5.3}Cl_{0.7}(MeOH)_4$ (**2**). The latter was prepared by the reaction of a mixture of $FeCl_2$, chloroacetic acid, and LiOMe with a precisely dosed amount of dioxygen.[17] Oxidation of **2** afforded the cyclic iron(III) complex $[Fe(OMe)_2(OCCH_2Cl)]_{10}$ (**3**), which is known under the name of an "iron ring."

We prepared a heterospin iron complex with the use of a milder oxidant, *viz.*, trimethylamine *N*-oxide. It appeared that precise oxidation of tetranuclear complex **1** with trimethylamine *N*-oxide in ethanol under argon afforded the hexanuclear complex $[Fe^{II}{}_4Fe^{III}{}_2(\mu_4\text{-}O)_2(\mu_3\text{-}OOCBu^t)_4(\mu\text{-}OOCBu^t)_6(HOOCCMe_3)_3(EtOH)]\cdot\cdot HOOCBu^t$ (**4**$\cdot$HOOCBu^t) (Scheme 1).

Scheme 1



Reagents and conditions: Me_3NO ({Fe} : [O] = 1 : 6) Ar, EtOH.
$\frown$ = μ-OOCBu^t

Oxidation of **1** with atmospheric oxygen gave the known ionic complex $[Fe^{III}{}_3(\mu_3\text{-}O)(\mu\text{-}OOCBu^t)_6(H_2O)_3]^+[OOCBu^t]^-\cdot 3EtOH$ (**5**) as the major reaction product.[16]

X-ray diffraction study showed that the $Fe_6O_2(OOCR)_{10}$ core of complex **4** is analogous to the core of the manganese derivatives[5—11] (Fig. 1). Six iron atoms form two distorted edge-sharing tetrahedra (Fe(cnt)...Fe(cnt), 2.9178(19) Å; Fe(cnt)...Fe(prf), 3.033(2)—3.502(2) Å; Fe(prf)...Fe(prf), 3.454(2) and 3.457(2) Å, where cnt and prf are the central and peripheral positions, respectively), inside which there are two μ_4-bridging oxygen atoms (Fe(cnt)—O(μ_4-O), 1.950(5)—1.981(5) Å; Fe(prf)—O(μ_4-O), 1.998(5)—2.041(5) Å). The iron atoms are linked to each other by four μ_3- and six μ-bridging carboxylate groups (Fe(cnt)—O(OOCR), 1.995(6)—2.070(5) Å; Fe(prf)—O(OOCR), 2.051(6)—2.431(6) Å; C—O, 1.233(9)—1.313(9) Å; O—C—O, 122.0(9)—126.6(9)°). The coordination environment of the central atoms can be described as a distorted octahedron. The coordination number of four peripheral iron atoms is 6 due to coordination by the oxygen atoms of three pivalic acid molecules and one ethanol molecule (Fe—O(HOOCR), 2.138(6)—2.192(6) Å; C—O, 1.221(10)—1.312(11) Å; O—C—O, 121.4(9)—123.9(9)°; Fe—O(HOEt), 2.169(6) Å). Analysis of the metal—oxygen bond lengths demonstrated that two iron(III) atoms occupy the central positions, whereas four iron(II) atoms are peripheral. The average Fe—O(OOCR) bond lengths are 2.04 and 2.16 Å for the central and peripheral metal atoms, respectively. The difference in these bond lengths is approximately equal to the difference in the ionic radii of Fe^{II} (0.92 Å) and Fe^{III} (0.785 Å).[18] The difference in the average Fe—O(μ_4-O) distances is substantially smaller (2.02 and 1.97 Å for the peripheral and central metal atoms, respectively).

The magnetic properties of complex **4** provide evidence for the occurrence of exchange antiferromagnetic interactions (in the temperature range of 300—2 K, μ_{eff} = 9.327—2.745 μ_B per overall molecule, see Fig. 2).

Therefore, the hexanuclear heterospin iron oxo pivalate complex can be synthesized with the use of a mild oxidant, *viz.*, trimethylamine *N*-oxide, by the reaction with polynuclear Fe^{II} pivalate. Due to solubility in organic solvents (acetonitrile, ethanol, or benzene) and the presence of labile terminal ligands, this compound can be used as a synthon for the design of new magnetoactive polynuclear systems analogous to manganese(II,III) derivatives.[4,19] New iron cluster **4** proved to be antiferromagnetic like its analogs containing manganese[5—11] or cobalt[12] atoms and dodecanuclear complex **2**.

Experimental

The new complex was synthesized under argon in freshly distilled ethanol. The starting compound $Fe_4(\mu_3\text{-}OH)_2(OOCBu^t)_4(OOCBu^t)_2(EtOH)_6$ (**1**) was prepared according to a known procedure.[14] Triethylamine *N*-oxide was purchased from Fluka. The IR spectra of the complexes were recorded on a Specord M-80 instrument in KBr pellets.

Bis(μ_4-oxo)tetrakis(μ_3-trimethylacetato-*O*,*O*,*O*′)hexakis(μ_2-trimethylacetato-*O*,*O*′)tris(η^1-trimethylacetic acid)(η^1-ethanol)tetrairon(II),diiron(III), solvate with trimethylacetic acid,

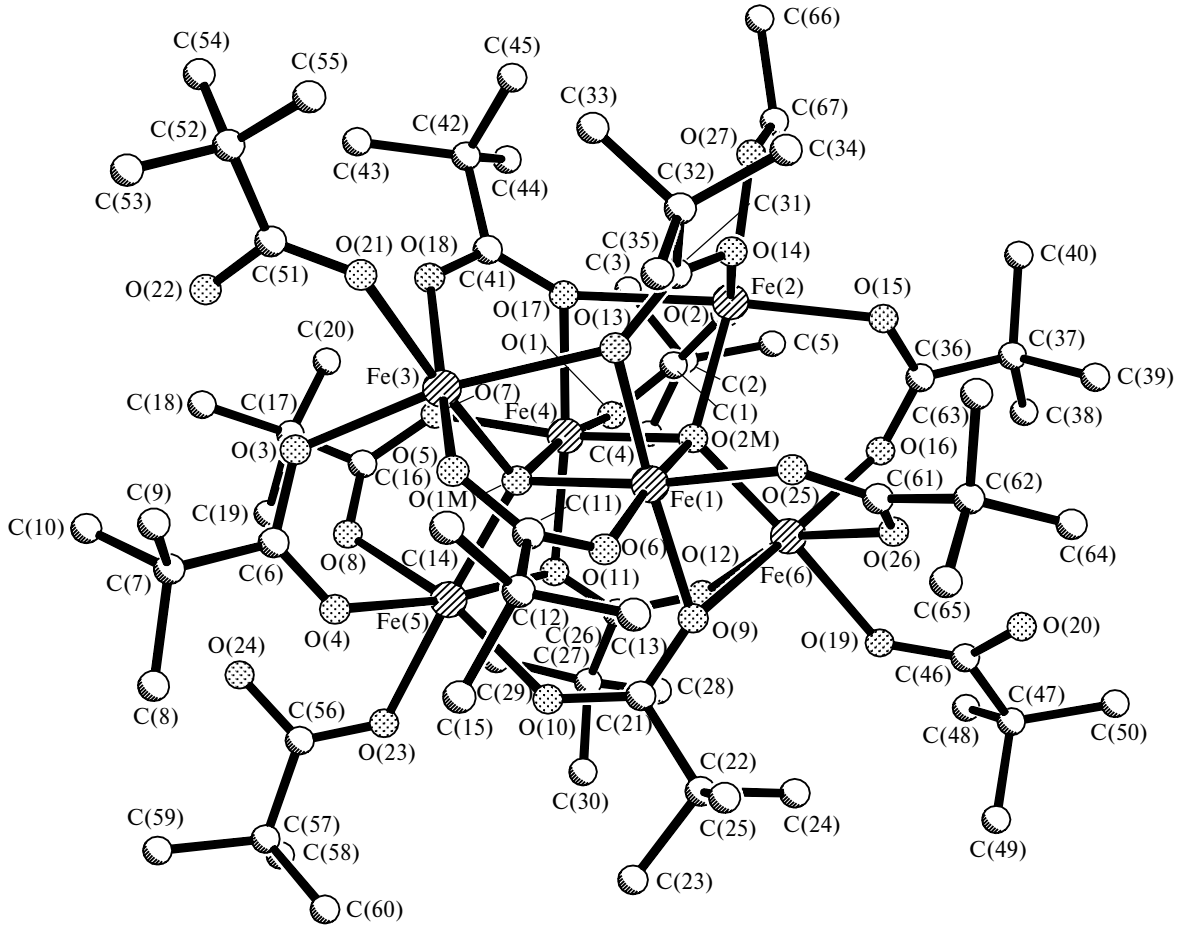


Fig. 1. Structure of complex **4**.

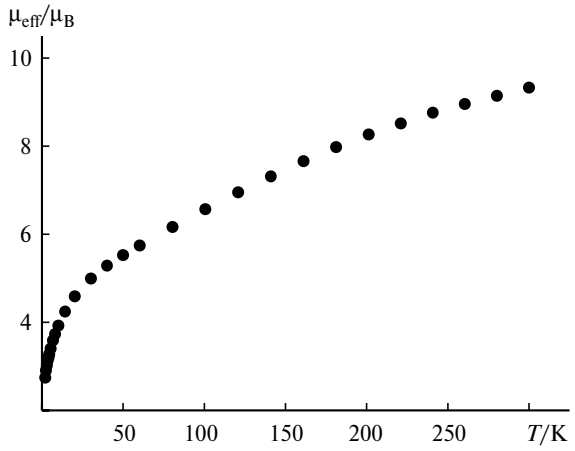


Fig. 2. Plot $\mu_{eff}(T)$ for complex **4**.

$[Fe_6(\mu_4\text{-}O)_2(\mu_3\text{-}OOCBu^t)_4(\mu\text{-}OOCBu^t)_6(HOOCBu^t)_3(EtOH)] \cdot \cdot HOOCBu^t$ (4 · $HOOCBu^t$). A mixture of complex **1** · 2EtOH (0.09 g, 0.07 mmol) and $Me_3NO \cdot 2H_2O$ (0.006 g, 0.05 mmol) in EtOH (10 mL) was stirred under argon at 80 °C for 1 h. The color of the solution gradually changed from brown to dark-green. The solution was concentrated to 5 mL and kept at room temperature for 20 h. Dark-green crystals of complex **4** · $HOOCBu^t{}_3$ suitable for X-ray diffraction were separated from the solution by filtration, washed with cold EtOH (0 °C), and dried under a stream of argon. The yield was 0.04 g (40%). Found (%): C, 47.3; H, 7.6. $C_{72}H_{136}Fe_6O_{31}$. Calculated (%): C, 47.18; H, 7.48. IR, ν/cm^{-1}: 2960 s, 2932 m, 2868 m, 1969 m, 1588 s, 1548 m, 1484 s, 1460 w, 1424 s, 1376 m, 1360 m, 1260 m, 1228 m, 1208 w, 1100 m, 1028 m, 896 w, 872 w, 800 m, 604 m, 536 w, 508 w, 440 m.

The magnetic susceptibility was measured on a SQUID MPMS-5S Quantum Design magnetometer in the temperature range of 2—300 K; H = 5000 Oe. The effective magnetic moment was calculated according to the equation $\mu_{eff} = (8\chi_M T)^{1/2}$, where k is the Boltzmann constant, N_A is Avogadro's number, and β is the Bohr magneton.[20]

X-ray diffraction study of the complex 4 · $HOOCBu^t$. X-ray diffraction study was carried out in the X-Ray Structural Center (A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences) on a Bruker AXS SMART 1000 diffractometer[21,22] equipped with a CCD detector (Mo-Kα, graphite monochromator, 120 K, ω scanning technique with a step of 0.3°, exposure time per frame was 30 s, $2\theta_{max}$ = 50°). The structure of complex **4** was solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for all nonhydrogen

atoms. The hydrogen atoms of the *tert*-butyl groups of the pivalate ligands were placed in calculated positions and refined using a riding model. The calculations were performed with the use of the SHELX97 program package.[23] The space group $P\bar{1}$, a = 13.3719(14) Å, b = 15.7318(15) Å, c = 25.019(2) Å, $\alpha = 73.259(3)°$, $\beta = 79.599(4)°$, $\gamma = 65.903(3)°$, $V = 4588.9(8)$ Å^3, Z = 2, μ = 9.96 cm^{-1}, 20667 reflections were measured, 10925 reflections were with $I > 2\sigma$, $R_1 = 0.0679$, $wR_2 = 0.1192$.

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