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Hexanuclear methanediolate-bridged iron(III) complex

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The hexanuclear complex $[Fe_6(O)_2(CH_2O_2)(OOCCMe_3)_{12}(THF)_2] \cdot THF$ was synthesized. The characteristic feature of this complex is the presence of the methanedithiolate bridge.

Key words: iron(III), polynuclear compounds, methanediolate, X-ray diffraction analysis.

Recently,[1] we have described a modified procedure for the synthesis of the $[Mn_6(O)_2(OOCCMe_3)_{10}(THF)_4] \cdot THF$ complex (**1**), whose hexanuclear fragment $[Mn_6(O)_2(OOCCMe_3)_{10}]$ appeared to be an efficient structural block, which initiates self-assembly of heterospin molecular magnetics in reactions with nitronyl nitroxide radicals. Taking into account that nitroxide radicals are weak donors,[2] we expected monodentate-coordinated THF molecules to play a special role in molecule **1**. In this complex, THF molecules act as good leaving groups, which are replaced by the O atoms of the nitronyl nitroxide group of the radical. This allowed us to prepare the first heterospin compounds starting from polynuclear trimethylacetate complexes of metals and nitroxides. As an extension of this approach, we prepared an analogous hexanuclear iron trimethylacetate complex using a procedure for the synthesis of complex **1**. No data on the structures of iron trimethylacetate complexes containing coordinated THF molecules are available in the Cambridge Structural Database (CSD).[3]

Results and Discussion

Under the conditions used, the trinuclear $[Fe_3(O)(OOCCMe_3)_6(THF)_3][FeCl_4] \cdot THF$ complex (**2**) was prepared as the major reaction product in 70—80% yield. However, in certain experiments, the hexanuclear $[Fe_6(O)_2(CH_2O_2)(OOCCMe_3)_{12}(THF)_2] \cdot THF$ complex (**3**) was initially obtained as the solid phase. Attempts to recrystallize this complex led to its transformation into complex **2**. In some cases, compound **3** was isolated in higher yield (~30%). Nevertheless, we failed to find controlled conditions, under which complex **3** was reproducibly formed.

The structural feature of compound **3** is the presence of the methanediolate μ_4-bridge (Fig. 1, *a*). Since no structural data on polynuclear 3d metal compounds containing these fragment are available in the CSD, we give a brief description of the structure of compound **3**.

X-ray diffraction study demonstrated that molecule **3** includes two trinuclear $\{Fe_3O\}$ fragments. In these fragments, two Fe—O distances involving the "inner" Fe atoms (1.929(4)—1.953(4) Å) are somewhat longer than the Fe—O distances with the "terminal" Fe atoms (1.860(4)—1.862(4) Å). The $\{Fe_3O\}$ fragments are linked to each other *via* two μ_2-bridging $OOCCMe_3$ anions (d_{Fe-O} = 1.988(5)—2.000(5) Å) and the μ_4-bridging $H_2CO_2^{2-}$ anion (d_{Fe-O} = 1.983(4)—2.007(4) Å). The coordination environment about all Fe atoms can be described as a distorted octahedron. For the terminal Fe atoms, the coordination polyhedra are formed by four O_{OOCCMe_3} atoms, one O_{THF} atom, and one μ_3-O atom. The Fe—O_{OOCCMe_3} distances vary in a rather narrow range (1.981(4)—2.052(5) Å), whereas the Fe—O distances to the O_{THF} atom are substantially longer (2.194(5) and 2.195(5) Å). The coordination environment about the inner Fe atoms is formed by four O_{OOCCMe_3} atoms of the μ_2-trimethylacetate anions, one μ_3-O atom, and one O atom of the methanediolate μ_4-bridge. The octahedral environment is less distorted compared to that of the terminal Fe atoms, because all Fe—O distances with the inner Fe atoms are in the range of 1.929(4)—2.046(5) Å. The angles between the planes of the $\{Fe_3O\}$ fragments and the plane formed by the inner Fe atoms are 151.87(5) and 152.48(5)°. Since the terminal iron atoms deviate in the same direction from the plane of the inner iron atoms, the metal core can be described as a "twisted boat" (Fig. 1, *b*). The μ_4-bridging $H_2CO_2^{2-}$ ligand is located inside the boat above the plane of its bottom. In the $H_2CO_2^{2-}$ fragment, the C—O distances are 1.409(8) Å and the angle between the C—O bonds is 108.8(5)°. These values are close to the analogous characteristics in the structure of dimethoxymethane (1.403 Å and 113.7°).[4]

Of all d-metal compounds retrieved from the CSD, only one tetranuclear molybdenum complex contains the

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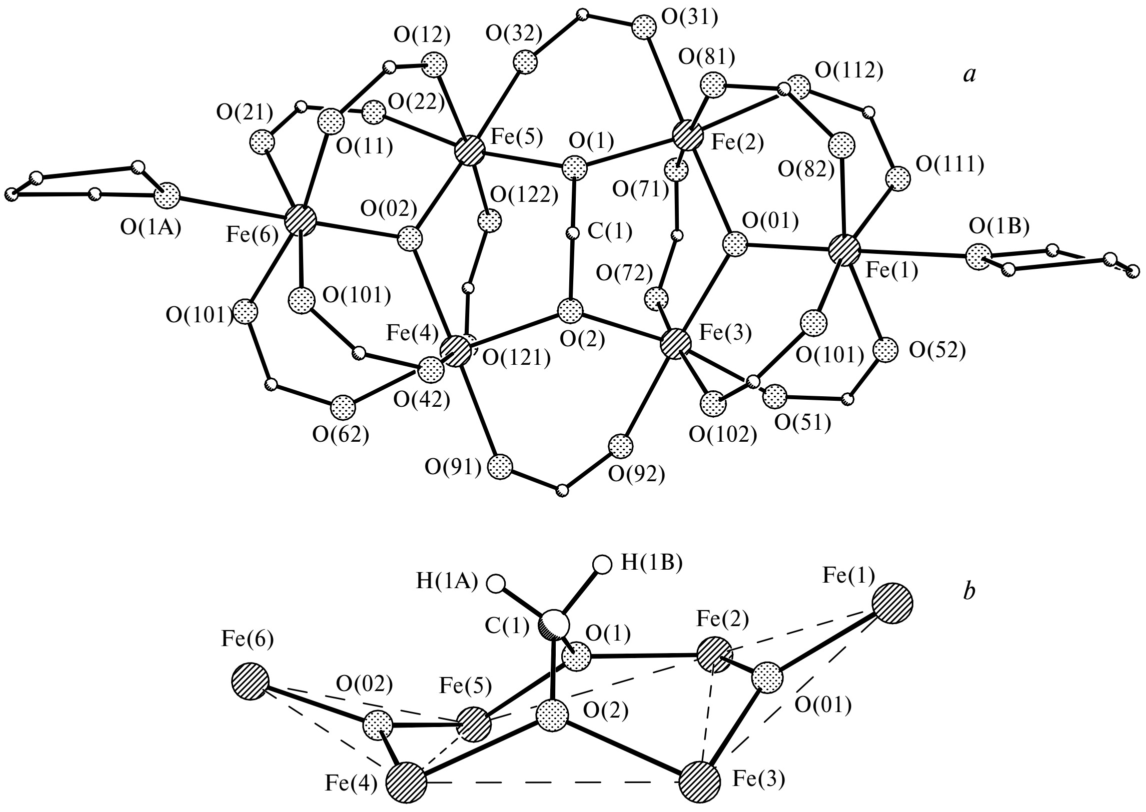

Fig. 1. (*a*) Molecular structure of the $[Fe_6(O)_2(CH_2O_2)(OOCCMe_3)_{12}(THF)_2]$ complex (Bu^t groups, H atoms, and the THF solvate molecule are omitted); (*b*) the schematic structure of the metal core in **3** with the μ_4-bridging methanediol anion.

bridging $H_2CO_2^{2-}$ group. This complex was prepared by the reaction of tetrabutylammonium dimolybdate with formaldehyde.[5] In the synthesis of complex **3**, formaldehyde was not added to the reaction mixture. Apparently, formaldehyde was produced from methanol, which was gradually oxidized during the reaction. The fact that deprotonated methanediol is stabilized in the complex with the polymetallic core is not surprising, because the heminal diols are unstable.[6] It should also be noted that the synthesis of the $[Fe_6(O)_2(CH_2O_2)(OOCCMe_3)_{12}Py_2]$ complex (**4**) and its structure have been described recently.[7] The molecule of the latter compound differs from molecule **3** in that the former contains the monodentate-coordinated Py molecules instead of the monodentate-coordinated THF molecules present in **3**.

The molecular structure of complex **2** (Fig. 2) is typical of trinuclear Fe^{III} complexes. The main characteristic feature of complex **2** is that it is the first compound, in which the THF molecules serve as monodentate coordinated ligands.

Experimental

Synthesis of μ_3-oxohexakis(μ_2-trimethylacetato-*O,O′*)tris(tetrahydrofuran)triiron(III) tetrachloroferrate(III) monotetrahydrofuran solvate (2) and bis(μ_3-oxo)dodecakis(μ_2-trimethylacetato-*O,O′*)(μ_4-dioxamethane-*O,O,O′,O′*)bis(tetrahydrofuran)hexairon(III) monotetrahydrofuran solvate (3). A solution of potassium trimethylacetate (2.82 g, 0.02 mmol) in MeOH (20 mL) was added to a solution of $FeCl_2 \cdot 4H_2O$ (2.0 g, 0.01 mmol) in MeOH (20 mL) at room temperature. The reagents were mixed, after which KCl precipitated and the solution turned brown. The reaction mixture was stirred for 24—26 h, during which it was warmed to ~50 °C from time to time. This led to almost complete removal of MeOH from the reaction mixture. Tetrahydrofuran (50—60 mL) was added to the paste-like residue, KCl was filtered off, and the dark-brown filtrate was kept at ~20 °C for 5—6 days, during which the major portion of the solvent was evaporated and dark-brown crystals of complex **3** precipitated from the saturated solution (several milliliters). Recrystallization of these crystals from THF afforded complex **2**. Stirring of the reaction mixture in MeOH over a shorter period of time afforded complex **2**. Found (%): C, 41.2; H, 6.5. $C_{42}H_{78}Cl_4Fe_4O_{16}$. Calculated with respect to desolvated **2** (%): C, 41.8; H, 6.5. Found (%): C, 44.4; H, 6.8. $C_{61}H_{110}Fe_6O_{28}$. Calculated with respect to desolvated **3** (%): C, 45.0; H, 6.8.

X-ray diffraction study. X-ray diffraction data sets were collected on a Bruker AXS Smart Apex diffractometer. The structures were solved by direct methods and refined by the full-matrix least-squares method (SHELX97 program package). The positions of certain H atoms were revealed from difference electron density maps. The positions of the other H atoms were calculated geometrically and refined in the rigid-group approximation. The crystallographic characteristics of complex **2**:

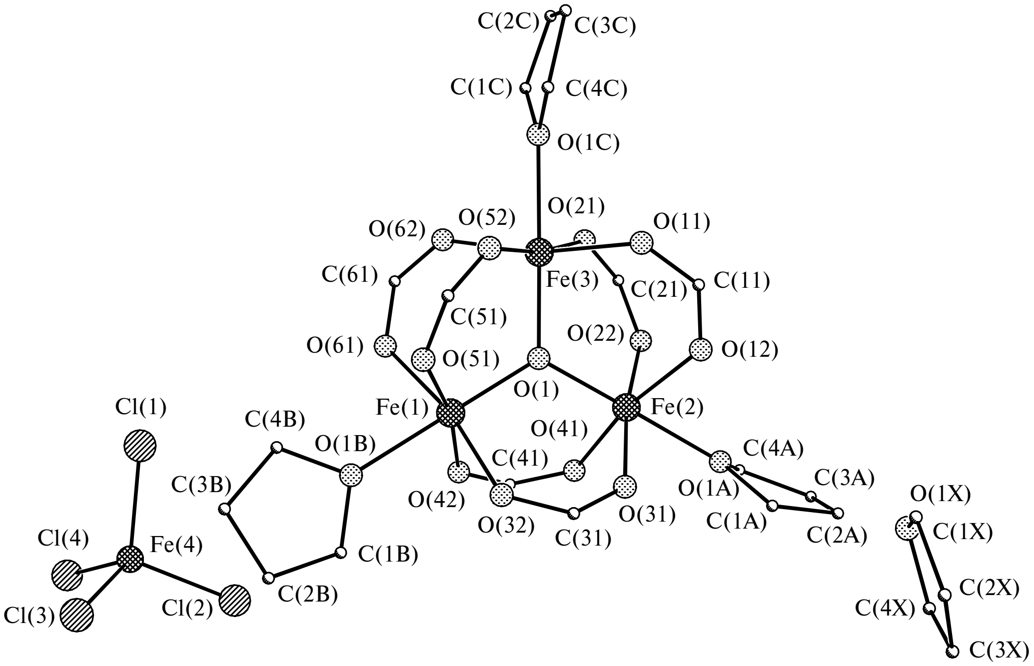

Fig. 2. Fragment of the structure of complex **2** (Bu^t groups and the H atoms are omitted).

a = 13.506(9) Å, b = 13.517(8) Å, c = 18.997(12) Å, α = 80.37(2)°, β = 80.893(9)°, γ = 84.60(1)°, V = 3368(4) $Å^3$, $P\bar{1}$, Z = 2, d_{calc} = 1.259 g cm^{-3}, μ(Mo-Kα) = 1.057 mm^{-1}, 1.74 < θ < 23.15°, a total of 13722 reflections (I_{hkl}) were measured, of which 9105 reflections were independent (R_{int} = 0.0303), 5883 $I_{hkl} > 2\sigma(I)$, 707 parameters were refined, GOOF = 0.955, R_1 = 0.0774, wR_2 = 0.2323 for $I > 2\sigma(I)$, R_1 = 0.1085, wR_2 = 0.2575 for all reflections I_{hkl}. The crystallographic characteristics of complex **3**: a = 24.096(7) Å, b = 19.278(6) Å, c = 24.645(7) Å, β = 116.149(6)°, V = 10277(5) $Å^3$ (T = 240 K), $P2_1/c$, Z = 4, d_{calc} = 1.186 g cm^{-3}, μ(Mo-Kα) = 0.890 mm^{-1}, 1.84 < θ < 23.37°, a total of 44139 reflections (I_{hkl}) were measured, of which 14813 reflections were independent (R_{int} = 0.1098), 7739 $I_{hkl} > 2\sigma(I)$, 1139 parameters were refined, GOOF = 0.893, R_1 = 0.0619, wR_2 = 0.1530 for $I > 2\sigma(I)$, R_1 = 0.1186, wR_2 = 0.1706 for all reflections I_{hkl}.

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