Brief Communications

New antiferromagnetic tetranuclear pivalate complex containing Fe^{III} and Fe^{II} atoms*

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The interaction of $[K_2Fe^{III}_4(O)_2(OOCCMe_3)_{10}(HOOCCMe_3)_2(H_2O)_2]_n$ with 2-pyridinecarboxaldehyde results in a mixed-valence complex $Fe^{II}Fe^{III}_3(\mu_3\text{-}O)_2(\mu_2\text{-}OOCCMe_3)_7L_2 \cdot 2.5MeCN \cdot 3H_2O$ ($L = 2\text{-}NC_5H_4COOH_{0.75}K_{0.25}$). The structure of the complex was established by X-ray analysis. The magnetic properties of the complex were studied.

Key words: iron complexes, X-ray diffraction study, 2-pyridinecarboxaldehyde.

Heterospin polynuclear coordination compounds are of considerable interest in connection with search for molecular magnetic systems in order to design new-generation electronic devices.[1,2] From this point of view, iron derivatives appear to be convenient materials because they are readily available and cheap. Besides, a distinctive feature of iron pivalate complexes is a high solubility in organic solvents.

Heterospin polynuclear iron carboxylates are mainly known in the form of triangular complexes containing both Fe^{III} ($S = 5/2$) and Fe^{II} ($S = 2$) atoms in various ratios.[3—7] Tetranuclear pivalate complexes with the $Fe_4(\mu_3\text{-}O)_2$ core comprised of two triangles sharing an edge are only known for iron(III).[8,9]

In this work we report on reduction of a tetranuclear dianionic iron(III) oxopivalate complex with 2-pyridinecarboxaldehyde resulting in a complex containing Fe^{III} and Fe^{II} atoms.

Results and Discussion

Recently,[9] we have shown that dissolution of a polymeric complex $[K_2Fe_4(O)_2(OOCCMe_3)_{10}(HOOCCMe_3)_2(H_2O)_2]_n$ (**1**) in MeCN affords the $[K(HOOCCMe_3)(MeCN)]_2[Fe_4(O)_2(OOCCMe_3)_{10}]$ compound (**2**) containing discrete tetranuclear iron(III) dianions (Scheme 1).

* Dedicated to Academician A. L. Buchachenko on the occasion of his 70th birthday.

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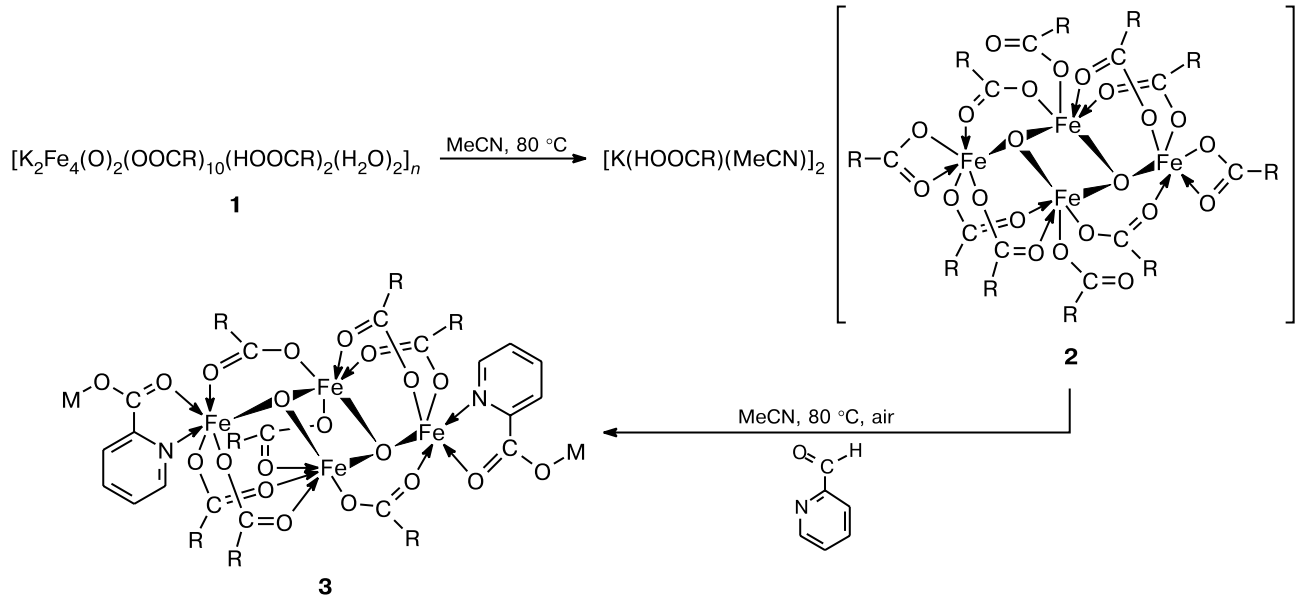
Scheme 1



We found that the interaction of complex **1** (or **2**) with 2-pyridinecarboxaldehyde in a MeCN solution results in a tetranuclear oxopivalate complex containing coordinated molecules of 2-pyridinecarboxylic acid (see Scheme 1). The formal composition of the isolated green-brown crystals of complex **3** corresponds to the formula $[Fe_4(\mu_3\text{-}O)_2(\mu_2\text{-}OOCCMe_3)_7L_2]\cdot 2.5MeCN\cdot 3H_2O$, where L = $2\text{-}NC_5H_4COOH_{0.75}K_{0.25}$ (**3**$\cdot 2.5MeCN\cdot 3H_2O$). According to X-ray analysis data, the metal carboxylate core is built of four iron atoms and comprises two triangular fragments sharing the Fe(2)...Fe(4) edge to which the pivalate bridge is coordinated (Fe...Fe, 2.862(8) Å). The tridentate-bridging oxygen atoms (Fe—O, 1.80(1)—1.96(2) Å) are similarly displaced from the planes of corresponding Fe_3 triangles by 0.36 and 0.27 Å. Other Fe...Fe distances in the triangular fragments lie in the range 3.290(7)—3.423(7) Å. The triangular fragments are arranged in a "butterfly" fashion (Fe(1)...Fe(3), 5.682(7) Å), the dihedral angle between the Fe(1)Fe(2)Fe(4) and Fe(2)Fe(3)Fe(4) planes is 138.7(9)°). The iron atoms acquire the octahedral coordination involving the O atoms of the chelate pivalate groups (Fig. 1) and the one-quarter potassium salt of pyridinecarboxylic acid $2\text{-}NC_5H_4COOH_{0.75}K_{0.25}$ (Fe—N, average 2.18(4) Å; Fe—O, average 2.03(4) Å). The crystal contains two potassium cations, which occupy particular positions on the crystallographic axis *4* and have populations of 0.25. Hence, the H atoms at the O(16) and O(17) terminal atoms should have populations of 0.75. We failed to locate the positions of H atoms in this structure; therefore, the ionic structure with $NC_5H_4COO^-$ anions and mixed μ_3-OH and μ_3-O bridges can not be ruled out. This interpretation of the composition, namely, $K^+\{Fe_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OOCCMe_3)_7(NC_5H_4COO)_2][Fe_4(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}OOCCMe_3)_7(NC_5H_4COO)_2]^-\}$, requires that a 1 : 1 mixture of the neutral and anionic tetranuclear complexes be present in the crystal.

Earlier,[10] oxidation of the γ-isomer of pyridinecarboxaldehyde to the corresponding acid was observed in the presence of lanthanide nitrates or perchlorates with the nitrate or perchlorate anions acting as oxidizing agents. In the reaction studied in this work both the oxygen molecules (because the reaction was carried out in air) and the iron(III) atoms of the starting dianionic complexes **1** or **2** can serve this function. In the latter case one can expect that reaction products can contain reduced heterospin structures with Fe^{II} atoms. Magnetic measurement data for complex **3** show that the compound exhibits antiferromagnetic properties and that its magnetic moment, μ_{eff}, per molecule decreases from 9.256 to 1.648 μ_B in the temperature range 280—2 K (Fig. 2). The magnetic moment of the molecule **3** at 2 K is similar to the pure spin value corresponding to one unpaired electron (1.73 μ_B). Under assumption of antiferromagnetic intramolecular exchange interactions typical of iron oxocarboxylate clusters[11,12] the magnetic behavior of **3** can formally be described using two models, namely, (1) a complex containing three Fe^{III} (S = 5/2) atoms and one Fe^{II} (S = 2) atom and (2) a complex containing three Fe^{II} atoms and one Fe^{III} atom. The latter seems to be unlikely because pyridinecarboxyaldehyde can hardly be considered as a strong reducing agent. However, in any case it is probable

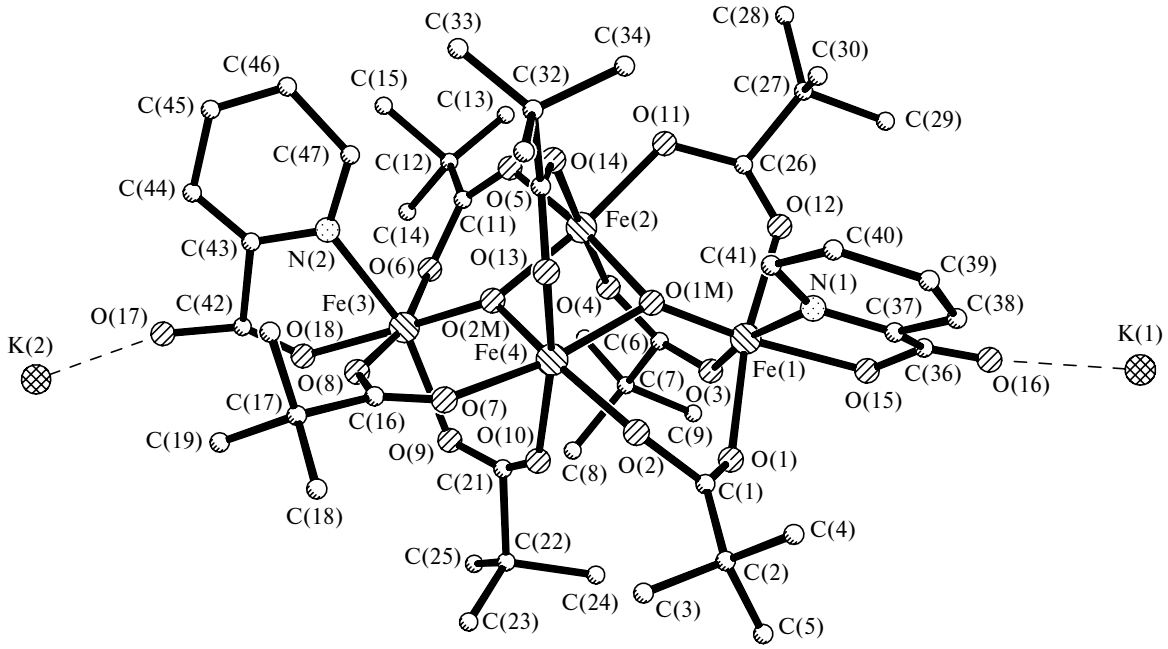


Fig. 1. Structure of complex **3** established by X-ray analysis (solvated MeCN and water molecules are not shown).

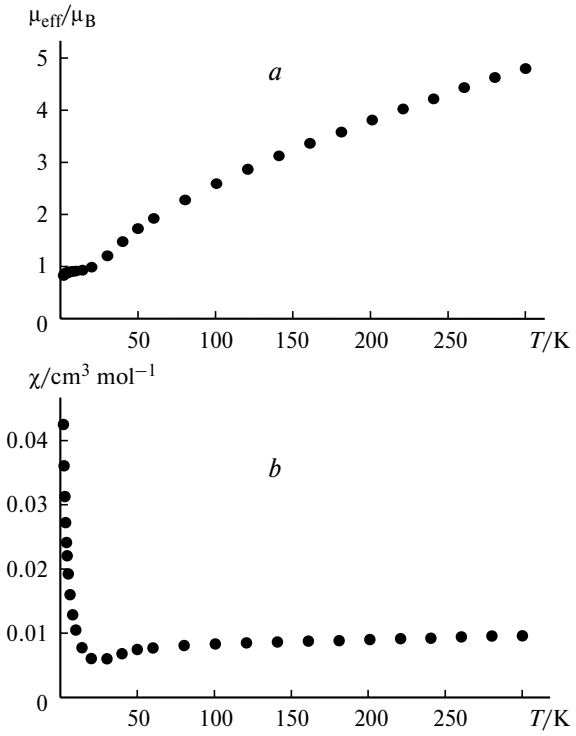


Fig. 2. Effective magnetic moment (μ_{eff}) (*a*) and static magnetic susceptibility (χ) (*b*) of compound **3**·2.5MeCN·$3H_2O$ plotted *vs.* temperature; the μ_{eff} and χ are given per Fe atom.

that complex **3** contains Fe^{II} atoms, which can indicate the oxidative ability of the starting iron(III) dianions in compounds **1** and **2**.

Experimental

All operations associated with the synthesis and isolation of complex **3** were carried out in freshly distilled MeCN in air. 2-Pyridinecarboxaldehyde was purchased from Aldrich. IR spectra were recorded on a Specord M-80 instrument (KBr pellets).

Bis(μ_3-oxo)heptakis(μ_2-*O*,*O*′-trimethylacetato)bis(η^2-*N*,*O*-2-pyridinecarboxylic acid)iron(II), triiron(III) one-quarter potassium salt, $Fe^{II}Fe^{III}_3(\mu_3\text{-}O)_2(\mu_2\text{-}OOCCMe_3)_7(NC_5H_4COOH_{0.75}K_{0.25})_2$ (3). A weighed sample of complex **1** (0.20 g, 0.123 mmol) was dissolved in MeCN (20 mL) and an excess of 2-pyridinecarboxaldehyde (0.55 g, 0.51 mmol) was added. The brown solution that formed was heated at 80 °C for 30 min. The greenish-brown solution thus obtained was concentrated to 10 mL and kept at 20 °C for 48 h to form dark green-brown crystals. The crystals were separated from the solution by decantation and washed with cold MeCN. Crystals of the composition **3**·2.5MeCN·$3H_2O$ were studied by X-ray analysis. The yield was 0.08 g (47%). Found (%): C, 44.9; H, 6.5; N, 4.5. $C_{52}H_{86}Fe_4K_{0.5}N_{4.5}O_{23}$. Calculated (%): C, 45.09; H, 6.26; N, 4.55. IR, ν/cm^{-1}: 3552 m, 3476 m, 3416 m, 2960 m, 2928 m, 2868 m, 1664 m, 1652 m, 1572 s, 1564 s, 1552 s, 1536 m, 1512 m, 1484 s, 1460 m, 1420 s, 1376 s, 1360 s, 1292 w, 1260 w, 1224 m, 1172 w, 1152 w, 1092 w, 1044 w, 1024 w, 940 w, 896 w, 856 w, 792 w, 760 w, 700 m, 644 m, 604 s, 520 m, and 436 s.

The static magnetic susceptibility measurements were carried out with a Quantum Desing SQUID MPMS-5S magnetometer in the temperature range 2—300 K; H = 5000 Oe; the effective magnetic moments were calculated by the equation $\mu_{eff} = (8\chi_M T)^{1/2}$.[11]

X-ray study of complex 3. X-Ray diffraction experiments were carried out at the X-ray Structural Centre (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of

Sciences) with a Bruker AXS SMART 1000 diffractometer[13,14] equipped with a CCD detector (Mo-Kα radiation, graphite monochromator, 110 K, ω scan technique, 0.3° scan increment, 30 s frame exposure time, $2\theta_{max} = 48°$).

The structure of the complex was solved by the direct method. Crystals of the compound are twins with 4/*mmm* pseudosymmetry. The compound crystallizes in tetragonal system (*P*4/*n*, class 4/*m*). Calculations were carried out with allowance for twinning ("twin" instruction 0 1 0 1 0 0 0 0 – 1) using the SHELX-97 program package.[15] The hydrogen atoms of the Me groups were placed in calculated positions and refined using a riding model. The structure was refined by the full-matrix least-squares method in the anisotropic approximation for the Fe and K atoms and isotropically for other non-hydrogem atoms.

The space group is *P*4/*n*, $a = 25.160(4)$, $c = 24.130(5)$ Å; $V = 15275(4)$ Å^3, $Z = 8$, $\mu = 0.837$ mm^{-1}, number of measured reflectins was 9629, number of reflections with $I > 2\sigma$ was 4585, $R_1 = 0.1092$, and $wR_2 = 0.3079$.

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