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Synthesis and structure of antiferromagnetic dinuclear iron(II) pivalate with a Chinese-lantern-like structure

A. A. Sidorov,[a]★ I. G. Fomina,[a] G. G. Aleksandrov,[a] Yu. V. Rakitin,[b] V. M. Novotortsev,[a] V. N. Ikorskii,[c] M. A. Kiskin,[a] and I. L. Eremenko[a]

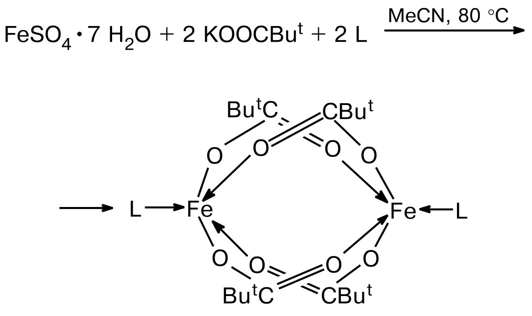
[a]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 954 1279. E-mail: sidorov@igic.ras.ru
[b]*I. V. Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials*
of the Kola Science Center, Russian Academy of Sciences,
26 A ul. Fersmana, 184200 Apatity, Murmansk oblast´, Russian Federation.
Fax: +7 (815 5) 57 5295
[c]*A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,*
3 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 34 4489

Data on dinuclear quadruply-bridged pivalate carboxylate complexes $LM(\mu\text{-}OOCR)_4ML$ (where L is an N,O-donor ligand) with 3d Group VIII elements having a Chinese-lantern-like structure refer primarily to cobalt(II)[1,2] and nickel(II)[3—7] derivatives, whereas analogous Fe^{II} complexes have been poorly studied. Data on the structures and magnetic properties of the latter compounds are very scarce, because such iron(II) complexes are very difficult to isolate in the pure form due to their high sensitivity to oxidizers, including atmospheric oxygen. Apparently, that is the reason why only a few complexes of this type were characterized by X-ray diffraction, among which are the $Fe_2(\mu\text{-}OOCAr)_4L_2$ complex ($L = 4\text{-}Bu^tC_5H_4N$) and its oxidation products $[Fe_2(\mu\text{-}OOCAr)_4L_2]^+$ (L = Py or $4\text{-}Bu^tC_5H_4N$).[8—10] It should be noted that these systems attract attention also in relation to modeling of oxidation processes of natural nonheme iron-containing enzymes.[9,10] In addition, quadruply-bridged carboxylate dimers with high-spin iron(II) atoms (S = 2) extend a series of analogous structures known for other Group VIII elements, *viz.*, cobalt (S = 3/2) and nickel (S = 1). It should be noted that an increase in the spin of the magnetic centers would be expected to give rise to ferromagnetic exchange interactions[11] in dimers with a Chinese-lantern-like structure.

In the present study, we report the synthesis and structure of a dinuclear quadruply-bridged iron(II) pivalate complex and the results of magnetic measurements and calculations of exchange parameters. The detailed theoretical study of the magnetic properties of this unusual compound will be published elsewhere.

The dinuclear iron complex was synthesized as follows. The first step involved the reaction of iron sulfate $FeSO_4 \cdot 7\,H_2O$ with $KOOCCMe_3$ (in a ratio of 1 : 2) in acetonitrile at 80 °C under an atmosphere of pure argon. Then the precipitate of potassium sulfate that formed was filtered off and a one-and-a-half—two-fold excess of 2,3-lutidine was added to the solution. Cooling of the resulting pale-yellow solution afforded pale-yellow needle-like crystals of the $Fe_2(\mu\text{-}OOCCMe_3)_4L_2$ complex (**1**, L = 2,3-lutidine) in high yield (80—85%) (Scheme 1). The crystals are very sensitive to atmospheric oxygen.

Scheme 1



$$FeSO_4 \cdot 7\,H_2O + 2\,KOOCBu^t + 2\,L \xrightarrow{\text{MeCN, 80 °C}}$$

L = 2,3-lutidine

According to the results of X-ray diffraction analysis, two Fe^{II} atoms in centrosymmetrical molecule **1** are linked by four bridging carboxylate ligands (Fe—O, 2.094(2)—2.049(2) Å; O—C, 1.264(4)—1.258(4) Å; O—C—O, 124.9(3)—125.1(3)°) and are separated by a distance of 2.866(9) Å. Each metal atom is coordinated by the nitrogen atom of the apical lutidine ligand (Fe—N, 2.135(3) Å). The N—Fe...Fe—N fragment in molecule **1** is nonlinear (N—Fe...Fe, 164.9(1)°). On the whole, the geometry of complex **1** (Fig. 1) is similar to that observed for analogous nickel and cobalt derivatives.[1—7]

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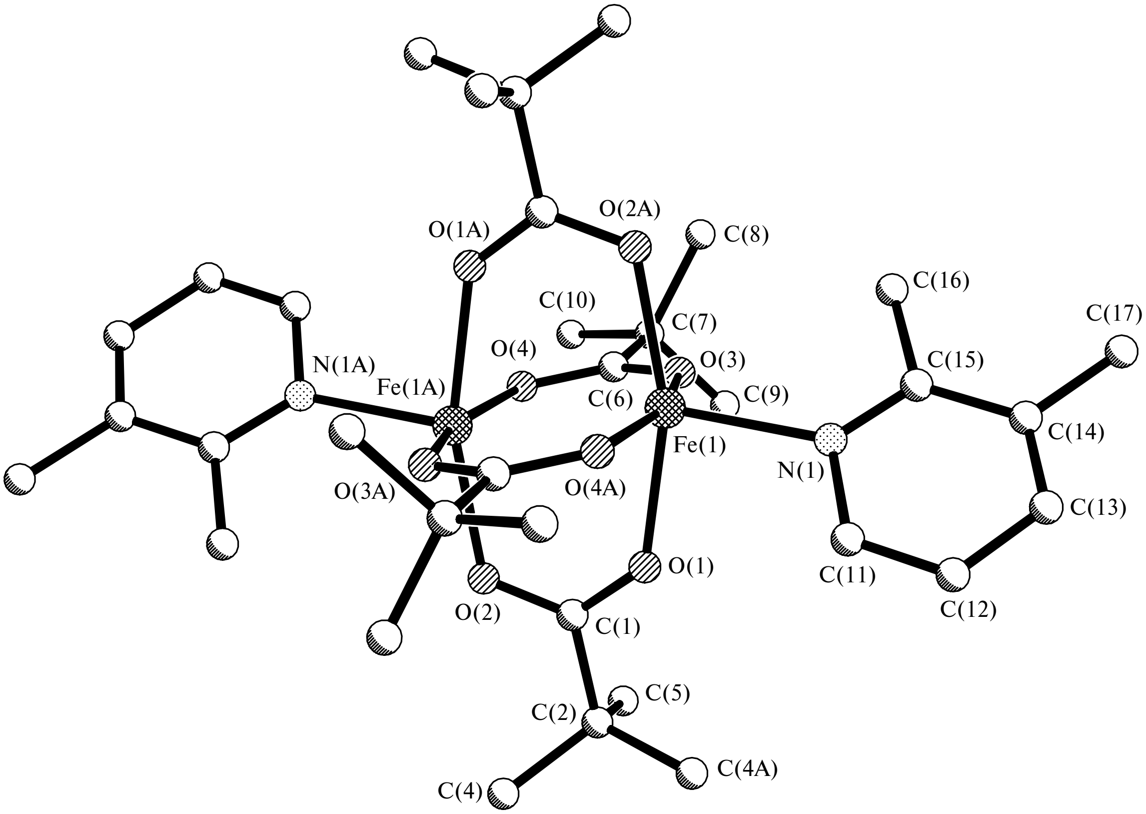

Fig. 1. Molecular structure of the dinuclear complex $(2,3\text{-Me}_2C_5H_3N)_2Fe_2(\mu\text{-OOCCMe}_3)_4$ (**1**).

In spite of a rather short Fe...Fe distance in complex **1**, the direct metal—metal bond is, apparently, absent and the complex exhibits paramagnetic properties (Fig. 2). The high effective magnetic moment (μ_{eff} (300 K) ≈ 4.78 μ_B per Fe atom) indicates that complex **1** contains high-spin Fe^{2+} ions (S = 2). The magnetic moment μ_{eff} rapidly decreases with decreasing temperature due to the presence of strong antiferromagnetic interactions, which are also typical of analogous dinuclear nickel and cobalt carboxylates.[1,3,6,7] It should be noted that the experimental dependence $\mu_{\text{eff}}(T)$ for compound **1** is not described by the model of isotropic exchange interactions, which is true for orbital-singlet systems (Fig. 2).

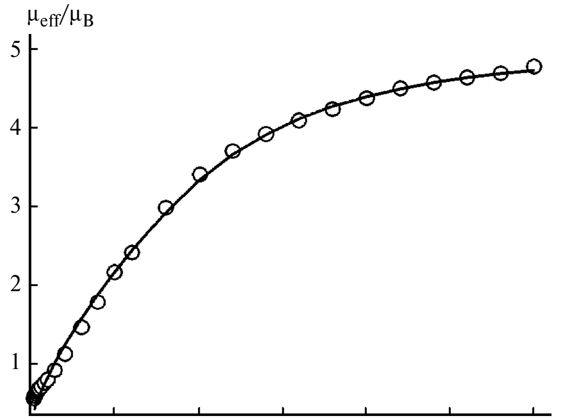

Fig. 2. Magnetic properties of complex **1** (experimental data are represented by empty circles, the calculated data are indicated by a solid curve).

Hence, the experimental data were interpreted in terms of the theory of orbital-dependent exchange[11,12] adapted to the structural features and electronic structure of complexes of type **1**.

The splitting parameter of the magnetic orbitals $\Delta = -134(10)$ cm^{-1} shows that the weakly split triplet $^5T_2$ is the ground state of Fe^{2+} ions. This fact is somewhat surprising, because stronger splitting should be expected in the formally pentacoordinate mononuclear fragment.[11] In addition, the small exchange parameter $-2J(x,z) = 6(1)$ cm^{-1} is, presumably, indicative of the presence of a channel of strong ferromagnetic exchange in dinuclear iron pivalate **1**. Apparently, dimeric complexes of this class would be expected to exhibit strong ferromagnetic properties if the electronic configurations of the metal ions are such that this channel becomes dominant.

Bis(2,3-dimethylpyridino)tetrakis(μ-trimethylacetato)diiron(II). Found (%): C, 56.20; H, 7.70; N, 3.90. $C_{34}H_{54}O_8N_2Fe_2$. Calculated (%): C, 55.90; H, 7.45; N, 3.83. IR (in KBr pellets, under argon), ν/cm^{-1}: 2964 m, 2932 m, 2876 w, 1664 m, 1600 s, 1484 m, 1456 w, 1424 s, 1384 s, 1360 m, 1260 s, 1228 s, 1096 s, 1024 s, 936 w, 896 m, 872 m, 792 s, 748 w, 724 w, 696 m, 604 s, 530 w, 436 s.

The static 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 moments were calculated by the equation $\mu_{eff} = (8\chi_M T)^{1/2}$.

X-ray diffraction study. Experimental data for complex **1** were collected on an automated Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (Mo-Kα radiation (λ = 0.71073 Å), graphite monochromator, 110 K, ω scanning technique, scan step was 0.3°, frames were exposed for 30 s) using a standard procedure.[13] The semiempirical absorption correction was applied.[14] The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. The hydrogen atoms of the benzene ring and methyl groups were generated geometrically and refined using the riding model. All calculations were carried out using the SHELX97 program package.[15] The space group $P\bar{1}$, a = 9.598(3), b = 10.916(3), c = 11.082(3) Å; V = 961.0(4) Å^3, Z = 1, μ = 0.802 mm^{-1}, 7400 reflections were measured, of which 4890 reflections were with $I > 2\sigma$, R_1 = 0.0662, wR_2 = 0.1815.

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