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**STRUCTURE AND MAGNETIC PROPERTIES OF THE PENTANUCLEAR COMPLEX
[Fe₂(CN)₁₂Ni₃(L)₆]·27H₂O, WHERE L IS NITRONYL NITROXIDE**© 2009 **H. Higashikawa¹, K. Inoue^{1*}, K.Yu. Maryunina², G.V. Romanenko²,
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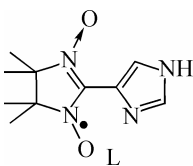
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We succeeded in synthesizing a new high-spin complex [Fe₂(CN)₁₂Ni₃(L)₆]·27H₂O, where L is stable nitroxide 2-(imidazol-4-yl)-4,4,5,5-tetramethyl-2-imidazoline-3-oxide-1-oxyl. According to X-ray diffraction data, the metal core of the pentanuclear [Fe₂(CN)₁₂Ni₃(L)₆] molecule is a trigonal bipyramid with Fe atoms occupying the axial positions and linked via CN bridges to {NiL₂} fragments laying in the equatorial plane. A peculiarity of this coordination compound is a large number of water molecules per the [Fe₂(CN)₁₂Ni₃(L)₆] pentanuclear molecule in the structure. The complex character of the $\mu_{\text{eff}}(T)$ dependence points to many competing channels of exchange interactions between the three types of paramagnetic centers.

Keywords: nickel, iron, cyano bridge, nitroxide, pentanuclear complex, crystal structure, magnetic properties.

Molecular magnets based on metal-nitroxide heterospin complexes were described in many publications [1–10]. Molecular magnets based on metal cyano complexes are also well documented [11–20]. However, examples of molecular magnets containing a metal-nitroxide fragment along with cyanometalate are scarce. In fact, only two solvates ([Fe₂(CN)₁₂Ni₃(Im-2Py)₆]·4H₂O and [Fe₂(CN)₁₂Ni₃(Im-2Py)₆]·2CH₃OH·2H₂O) of a heterospin mixed-metal compound were described and investigated by Vostrikova et al. [21]. It was a Ni(II) imino nitroxide complex with dominant ferromagnetic exchange inside the [Ni(Im-2Py)₂]²⁺ fragment. We succeeded in synthesizing a pentanuclear complex [Fe₂(CN)₁₂Ni₃(L)₆] (**1**) with the nitronyl nitroxide 2-(imidazol-4-yl)-4,4,5,5-tetramethyl-2-imidazoline-3-oxide-1-oxyl (L) possessing a rare ability to crystallize together with a large number of water molecules (**1**·27H₂O). This solvate readily loses water after filtration. In this paper we describe the crystal structure and magnetic properties of **1**·27H₂O.

Experimental. All reagents were of analytical grade and used without further purification. 2-(Imidazol-4-yl)-4,4,5,5-tetramethyl-2-imidazoline-3-oxide-1-oxyl was prepared as described previously [22].



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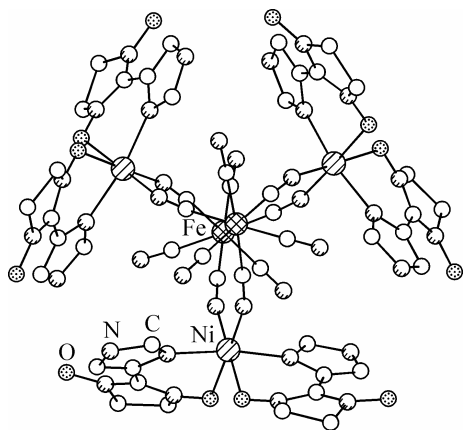


Fig. 1. Structure of pentanuclear molecule of **1**. (H atoms and CH₃ groups are omitted for clarity)

Synthesis of 1·27H₂O. A water solution (1 ml) of K₃[Fe(CN)₆] (6.6 mg, 0.020 mmol) was added to a preliminarily prepared water solution of NiCl₂·6H₂O (7.2 mg, 0.030 mmol) and L (13.4 mg, 0.0600 mmol). The resulting dark blue solution was kept in an open flask at 5 °C. After 3 days, dark green prismatic crystals were separated by filtration, washed with a small amount of cold water, and dried in air. Yield 0.017 g, 69 %. The complex is soluble in ethanol and methanol and insoluble in water and most organic solvents. When stored in air, the crystals gradually lost H₂O

molecules and became turbid. It was difficult to prevent decomposition of the compound during filtration. In a freshly prepared sample, the C%/N% ratio is 1.69; Ni content 7.4 %. Calculated for C₇₂H₁₄₄Fe₂N₃₆Ni₃O₃₉: C%/N% 1.71; Ni 7.3 %. Dried sample: found: C 42.2, H 4.9, N 25.0; Ni 8.3 %; calculated for C₇₂H₁₀₄Fe₂N₃₆Ni₃O₁₉: C 41.9, H 5.1, N 24.4; Ni 8.5 %.

Magnetic susceptibility measurements. Magnetic susceptibility measurements of [Fe₂(CN)₁₂Ni₃(L)₆]·27H₂O and the dried sample ([Fe₂(CN)₁₂Ni₃(L)₆]·7H₂O) were carried out on an MPMSXL SQUID magnetometer (Quantum Design) at 2–300 K with magnetic field up to 5 kOe. Molar magnetic susceptibility was calculated using diamagnetic corrections for the complexes. The effective magnetic moment was calculated as $\mu_{\text{eff}} = (8\chi T)^{1/2}$.

X-Ray diffraction study. The intensity data for a single crystal of **1**·27H₂O were collected by the standard procedure (Mo radiation) on a SMART APEX CCD (Bruker AXS) automated diffractometer with a Helix (Oxford Cryosystems) accessory. The structure was solved by direct methods and refined by the full-matrix least-squares procedure anisotropically for non-hydrogen atoms and isotropically for hydrogens. Some of H atoms were located in difference electron density syntheses; the others were calculated geometrically. Calculations were carried out with the SHELXTL 6.14 program package.

Crystal data and experimental details. C₇₂H₁₄₄Fe₂N₃₆Ni₃O₃₉; *FW* = 2426.06; *T* = 240 K; monoclinic, *C*2/*c*; *Z* = 8; *a* = 29.210(3), *b* = 14.9932(17), *c* = 51.975(6) Å, β = 91.431(2)°, *V* = 22755(4) Å³; *d_c* = 1.416 g/cm³; μ(MoK_α) = 0.829 cm⁻¹; 1.57 ≤ θ ≤ 25.00°; 101139 *I_{hkl}* measured, 20037 *I_{hkl}* unique, *R_{int}* = 0.1292; the number of refined parameters is 1483; GOOF = 1.109; *R*₁ = 0.0880, *wR*₂ = 0.2006 for *I* > 2σ_{*i*}; *R*₁ = 0.1224, *wR*₂ = 0.2181 for all data.

Results and discussion. The reaction of an aqueous solution of K₃[Fe(CN)₆] with a preliminarily prepared aqueous solution of Ni(L)₂Cl₂ reproducibly led to **1**·27H₂O isolated as a solid. A change in the reagent ratio did not affect the composition of the product. We succeeded in synthesizing **1**·27H₂O as large (up to 5 mm) dark green prismatic crystals. The complex is soluble in ethanol and methanol but insoluble in water and nonpolar organic solvents. According to X-ray diffraction data, the pentanuclear molecule of [Fe₂(CN)₁₂Ni₃(L)₆] (Fig. 1) is a trigonal bipyramid, whose vertices are occupied by Fe atoms bonded via CN bridges with Ni atoms laying in the equatorial plane of the pyramid. In the environment of the Fe atoms, three of the six CN groups, coordinated by the C atoms, are terminal and the other three are bridging. The latter link the {Fe(CN)₆} and {NiL₂} fragments. The Fe—C distances are 1.924(7)—1.957(7) Å. All three Ni atoms have a distorted octahedral environment of two N atoms of the CN groups of two different {Fe(CN)₆} fragments, two N atoms of the imidazoline ring (Ni—N 2.029(6)—2.063(5) Å), and two O atoms of the nitroxyl groups (Ni—O 2.064(4)—2.093(4) Å) of the two nitroxides L laying in the *cis* position. In the paramagnetic ligands, the N—O bond lengths are typical for nitroxides, 1.257(8)—1.306(7) Å; the angles at the coordinated O atom of the NO group do not exceed 117.3(3)—118.9(4)°.

X-ray diffraction study of a freshly prepared sample showed that per each of the [Fe₂(CN)₁₂Ni₃(L)₆] pentanuclear fragments there are 27 water molecules linked by a complex system of hydrogen bonds

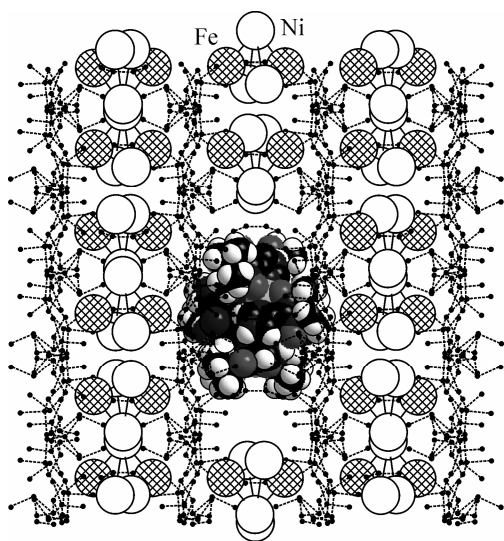


Fig. 2. Water framework (small red balls) in solid $1 \cdot 27\text{H}_2\text{O}$ (space-filling representation of the pentanuclear molecule in the center; for other pentanuclear molecules only metal atoms are shown)

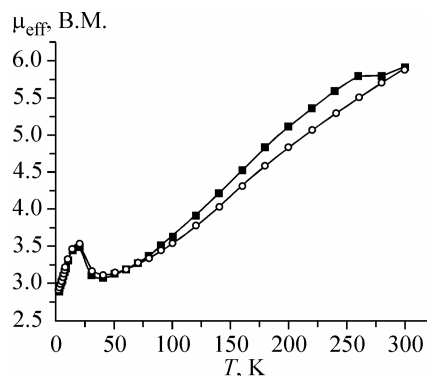


Fig. 3. Temperature dependence of the effective magnetic moment of the freshly prepared sample $1 \cdot 27\text{H}_2\text{O}$ (■) and the dried sample $1 \cdot 7\text{H}_2\text{O}$ (○)

with each other and the complex molecule into a framework (Fig. 2). The reasons for the formation of this complex hydrogen-bonded framework are not clear as yet. After drying $1 \cdot 27\text{H}_2\text{O}$ in vacuum, the number of included water molecules decreased to seven and did not change any longer.

The temperature dependence of magnetic susceptibility for $1 \cdot 27\text{H}_2\text{O}$ and $1 \cdot 7\text{H}_2\text{O}$ at 5 kOe is shown in Fig. 3. The solvates show almost the same behavior. For both solvates, μ_{eff} is 5.9 B.M. at 300 K. Due to strong antiferromagnetic interactions between different paramagnetic centers, this value of μ_{eff} is some less than theoretical one of 6.93 B.M. corresponding to the additive spin-only contribution from two low-spin Fe^{3+} ions ($S = 1/2$), three Ni^{2+} ions ($S = 1$), and six L ($S = 1/2$) for $g = 2$. The effective magnetic moment μ_{eff} has a minimum (40 K, 3.1 B.M.) and a maximum (20 K, 3.6 B.M.) at low temperatures. The molecule has a complex structure of exchange channels involving 11 paramagnetic centers. The ratio between the exchange interaction energies is not evident and requires special quantum-chemical calculations [23].

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