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Nontrivial Chemical Assembly of a Molecular Complex with Fe^{3+} and Li^{+} Cations

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Abstract—The reaction of Fe(III) and Li(I) pivalates and pyridine (py) in acetonitrile affords a molecular heteronuclear complex $[Fe_4Li_2(O)_2(Piv)_{10}(py)_2]\cdot CH_3CN$ (**I**), where Piv is pivalic acid anion, with the structural assembly nontrivial for Fe(III) and alkaline metals. The X-ray diffraction data show that complex **I** contains the hexanuclear motif $\{Fe_4Li_2O_2\}$ in which, according to the Mössbauer spectroscopy data, the paramagnetic Fe(III) ions exist in the high-spin state ($S = 5/2$) in the symmetric octahedral environment of the O and N atoms.

Keywords: heterometallic pivalate complexes, iron(III) complexes, lithium, crystal structure, Mössbauer spectroscopy

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INTRODUCTION

Heterometallic pivalate (trimethylacetate) complexes based on iron are interesting from different points of view: they can act as components of homo- or heterogeneous catalytic systems and possess unique magnetic (related to the transition to the magnetically ordered state at low temperatures), electroconducting, sorption, and other properties [1–7]. In addition, the variation of the nature of metal heteroatoms and Fe : M ratio (M = Ni, Zn, Co, Mn, etc.) in similar molecules provides their possible use as precursors in technological processes of preparing diverse functional materials (e.g., complex oxides) [8–10]. However, to accomplish specified properties, it is important to understand their origin and be able to “tune” a required structure of the compound. The most productive way to polynuclear iron(III) complexes includes the systematic study of the reaction conditions providing novel molecular structures with new physical properties. The Fe(III) complexes with 3*d* metals (Fe(III)–M, where M = Ni, Zn, Mn, Cd, Ag) were synthesized using the developed methodical approach including “solution procedures” followed by solid-phase thermolysis [11–15]. These complexes are characterized by different nuclearities of the metal fragments (3–9) and diverse physicochemical properties, but the “direct” synthesis of them is almost impossible.

The further studies showed that this synthetic approach also worked in the case of the *s* metal: Li [16, 17]. However, the hexanuclear metal oxide fragment formed in the absence of N-donor ligands of the $[Fe_4Li_2(O)_2(Piv)_{10}(HPiv)_2(H_2O)_2]$ complex [16] is rearranged to form basic trinuclear $\{Fe_2LiO\}$ in the case of 1,10-phenanthroline (Phen) [17].

The synthesis, structure, and properties of the new polynuclear oxopivalate adduct with pyridine containing Fe(III) and Li(I) ions are described in this work.

EXPERIMENTAL

The complexes were synthesized using commercial reagents and solvents without additional purification: pivalic acid (99%, Merck), LiOH (analytical grade), toluene (special purity grade, Khimmed, Russia), and pyridine (analytical grade, Khimmed, Russia). Complex $[Fe_3O(Piv)_6(H_2O)_3]\cdot Piv$ was synthesized using a known procedure [18]. Lithium pivalate (LiPiv) was synthesized by the reaction of equimolar aqueous solutions of LiOH and HPiv followed by evaporation, and the formed solid phase was washed with hexane [19].

Elemental analysis was carried out on a Carlo Erba EA 1108 C,H,N analyzer. The IR spectra of the compound were recorded on a Perkin-Elmer Spectrum 65

FT-IR spectrophotometer in the attenuated internal total reflectance (ATR) mode in the frequency range from 400 to 4000 cm^{-1}.

The ^{57}Fe Mössbauer spectrum of complex **I** was recorded on a Wissel electrodynamic spectrometer (Germany) at 300 K. The accuracy of temperature maintenance was at least ±0.1 K. The sample under study contained "natural" iron in which the ^{57}Fe isotope content did not exceed 3 wt % (owing to this, the Mössbauer effect did not exceed 2%). The source of the Mössbauer radiation was ^{57}Co(Rh) with an activity of 1.1 GBq. Isomeric shifts were counted from the center of the magnetic hyperfine structure (HFS) of metallic iron. The spectrum was processed using the standard calculation and simulation programs for the Mössbauer transition 3/2 → 1/2. The complex processing of the Mössbauer spectrum was performed by least squares using the LRT (Semenov Institute of Chemical Physics, Russian Academy of Sciences) and WINNORMOS programs (Germany).

Synthesis of [$Fe_4Li_2(O)_2(Piv)_{10}(py)_2$]·$CH_3CN$ (I). Weighed samples of [$Fe_3O(Piv)_6(H_2O)_3$]·HPiv (100 mg, 0.1 mmol) and LiPiv (10 mg, 0.9 mmol) were dissolved in acetonitrile (25 mL) on heating (70°C), and py (0.14 mL, 1.8 mmol) was added. The reaction mixture was hold for 3 h. The obtained solution was slowly cooled and left for crystallization by the slow evaporation of the solvent at room temperature. The brown crystals precipitated in a day were decanted from the mother liquor and dried in air. The yield of complex **I** was 119 mg (78% based on the initial iron complex).

For $C_{62}H_{103}O_{22}N_3Li_2Fe_4$

Anal. calcd., %	C, 50.42	H, 7.02	N, 2.84
Found, %	C, 50.47	H, 7.05	N, 2.79

IR (ν, cm^{-1}): 2962 m, 2928 w, 2904 vw, 2869 w, 1612 vs, 1577 m, 1548 m, 1480 vs, 1447 w, 1420 vs, 1400 vs, 1377 m, 1354 vs, 1338 vs, 1218 vs, 1156 vw, 1149 vw, 1073 vw, 1040 s, 1031 vw, 1014 vs, 937 vw, 895 s, 786 m, 754 vw, 695 m, 626 m, 598 s, 552 m, 504 s, 430 vs, 423 vs, 415 vs, 403 vs.

X-ray diffraction (XRD) of a single crystal of complex **I** was carried out on a Bruker D8 Venture diffractometer (CCD detector, MoK_α, λ 0.71073 Å, graphite monochromator). A semiempirical absorption correction was applied [20]. The structure was solved by a direct method and refined in the full-matrix least-squares anisotropic approximation (SHELXL-2018/3) [21]. The H atoms in the carboxylate ligands were calculated geometrically and refined by the riding model. The crystallographic parameters and details of structure refinement for complex **I** at T = 100(2) K are as follows: $C_{62}H_{103}Fe_4Li_2N_3O_{22}$, FW = 1479.75 g/mol, brown prismatic crystals, space group $Pca2_1$, a = 24.140(8), b = 16.165(4), c = 19.756(4) Å, V = 7709(4) Å^3, Z = 4, ρ_{calc} = 1.275 g cm^{-3}, μ = 0.805 mm^{-1}, 1.98° ≤ θ ≤ 28.28°, 17762 measured reflections, 14967 reflections with $I > 2\sigma(I)$, R_{int} = 0.0646, GOOF = 1.070, R_1 = 0.0425, wR_2 = 0.0571 ($I > 2\sigma(I)$); R_1 = 0.0931, wR_2 = 0.1002 (all data). $T_{min/max}$ = 0.677/0.746.

The atomic coordinates and other parameters for the structure of complex **I** were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 2189983; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The reflux of a mixture of [$Fe_3O(Piv)_6(H_2O)_3$]·Piv$^-$ and LiPiv (1 : 1) in toluene (110°C) was shown to result in the formation of complex [$Fe_4Li_2(O)_2(Piv)_{10}(H_2O)_2$] [16] characterized by the hexanuclear metal cage. The introduction of chelating Phen into the initial reaction mixture [17] favored the rearrangement of the metal fragment with the formation of trinuclear {Fe_2Li}, which is more characteristic of a combination of Fe(III) ions with other 3*d* metals, for example, Fe(III)–M (M = Mn, Co [8], Ni [11]). It is shown in the present work that the replacement of Phen by py retains the hexanuclear metal cage {$Fe_4Li_2O_2$}, and only the terminal water molecules are substituted by py.

Complex **I**·CH_3CN crystallizes in the orthorhombic crystal system, space group $Pca2_1$. The metal oxide cage of complex {$Li_2Fe_4O_2$} (Fig. 1a) consists of two Fe_3LiO tetrahedra with the common side Fe(1)Fe(2) (Fe(1)...Fe(2) 2.9393(10) Å, Fe(1,2)...Fe(3,4) 3.345(1)–3.439(1) Å, Fe...Li 2.988(8)–3.172(8) Å). In each Fe_3LiO tetrahedron, the metal ions are centered by the μ_4-bridging oxo group (selected bond lengths and angles are given in Table 1). The $Fe_4Li_2O_2$ cage in complex **I** is similar to that described previously in the [$Fe_4Li_2(O)_2(Piv)_{10}(HPiv)_2(H_2O)_2$] complex [16]. The {$Fe_4Li_2$} metal cage is additionally strengthened by eight O,O'-μ_2- and two O,O,O'-μ_3-bridging carboxylate groups. Each peripheral iron atom additionally coordinates one nitrogen atom of the pyridine molecules (Fig. 1b). The coordination environment of the lithium atoms (LiO_4) corresponds to a distorted tetrahedron, and that of the iron atoms (FeO_6 and FeO_5N) corresponds to a distorted octahedron.

The oxidation states and spin state of the iron ions in complex **I** were studied by Mössbauer spectroscopy. The Mössbauer spectrum at room temperature in the zero magnetic field is a single doublet (Fig. 2). The values of isomeric shift and quadrupole splitting in the Mössbauer spectrum (Table 2) suggest the presence of only high-spin iron(III) ions in the octahedral envi-

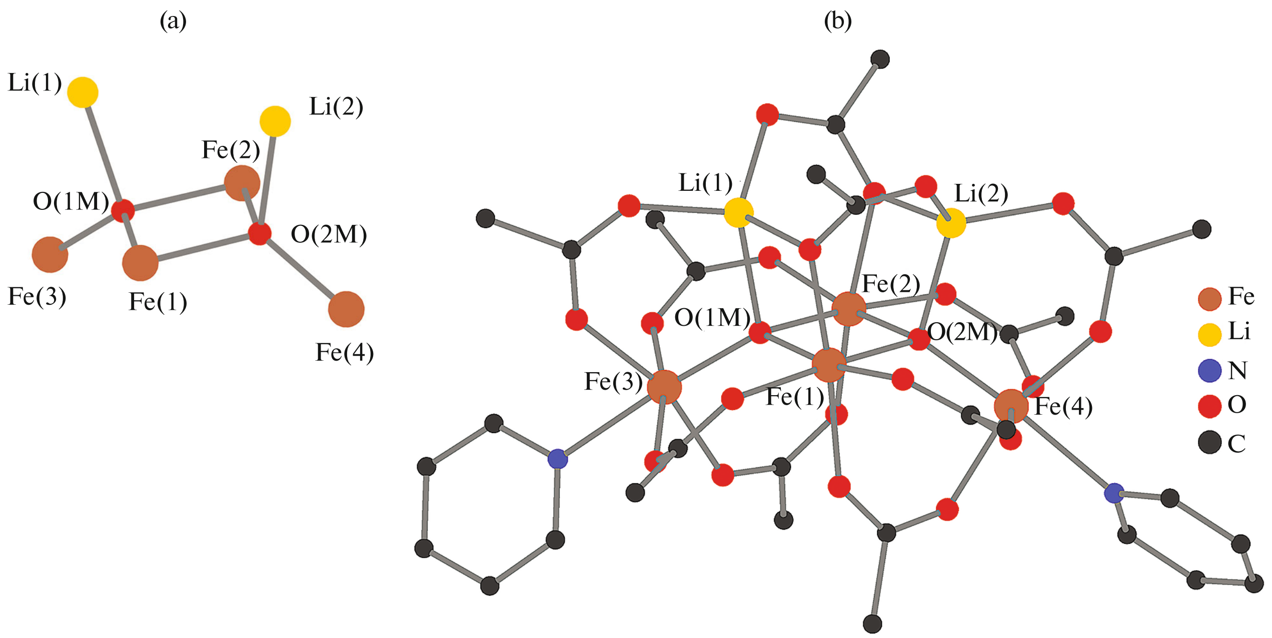

Fig. 1. (a) Structure of the $\{Fe_4Li_2O_2\}$ metal oxide cage and (b) molecular structure of complex **I**.

ronment of the oxygen and nitrogen atoms, which is consistent with the XRD data. Unlike the compounds described previously [16, 17], synthesized complex **I** is characterized by a less distorted polyhedron of the metal, which is indicated by a lower quadrupole splitting parameter.

Based on the obtained and known data, we may assume that the formed hexanuclear heterometallic $Fe_4Li_2O_2$ cage in the carboxylate complex is relatively stable in the presence of monodentate N/O-donor ligands but can dissociate to trinuclear Fe_2LiO due to the action of the chelate N-donors.

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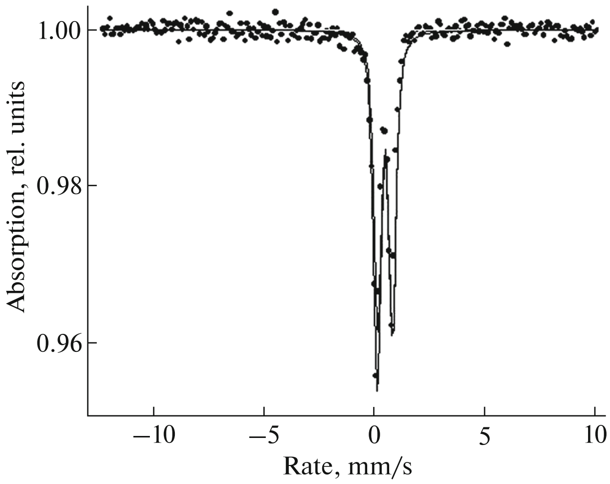

Fig. 2. Mössbauer spectrum of a solid sample of complex **I**.

Table 1. Selected bond lengths (*d*, Å) and bond angles (ω, deg) in complex **I**

Bond	*d*, Å	Bond	*d*, Å
M–O(μ_4-O)			
Fe(1)–O(1M)	1.968(3)	Fe(3)–O(1M)	1.879(3)
Fe(1)–O(2M)	1.970(3)	Fe(4)–O(2M)	1.881(3)
Fe(2)–O(1M)	1.967(3)	Li(1)–O(1M)	2.125(9)
Fe(2)–O(2M)	1.988(3)	Li(2)–O(2M)	2.043(8)
M–O(Piv)/M–N(py)			
Fe(1)–O	2.015(3)–2.036(3)	Fe(4)–O	1.984(3)–2.056(3)
Fe(2)–O	2.006(3)–2.038(3)	Fe(4)–N	2.222(4)
Fe(3)–O	1.992(3)–2.038(3)	Li(1)–O	1.839(9)–1.970(9)
Fe(3)–N(1)	2.233(4)	Li(2)–O	1.887(8)–1.964(9)
Angle	**ω, deg**	**Angle**	**ω, deg**
Fe(1)O(1M)Fe(2)	96.65(12)	Fe(1)O(1M)Li(1)	95.3(3)
Fe(1)O(1M)Fe(3)	123.74(14)	Fe(2)O(1M)Li(1)	98.8(3)
Fe(2)O(1M)Fe(3)	123.38(15)	Fe(3)O(1M)Li(1)	113.1(3)
Fe(1)O(2M)Fe(2)	95.92(11)	Fe(1)O(2M)Li(2)	104.4(3)
Fe(1)O(2M)Fe(4)	120.59(14)	Fe(2)O(2M)Li(2)	95.7(3)
Fe(2)O(2M)Fe(4)	125.44(14)	Fe(4)O(2M)Li(2)	110.6(3)
OFe(1)O	83.92(11)–100.43(12), 170.29(12)–174.02(12)	OFe(2)O	83.22(12)–103.02(13), 166.84(13)–174.85(13)
OFe(3)O	88.56(14)–103.53(12), 161.60(13), 168.49(12)	OFe(4)O	85.11(15)–102.68(13), 161.72(13), 168.70(13)
NFe(3)O	81.72(14)–85.62(13), 174.62(13)	NFe(4)O	81.17(13)–87.07(13), 175.54(14)
OLi(1)O	81.9(3)–123.0(5)	OLi(2)O	83.9(3)–119.1(5)

Table 2. Parameters of the Fe(III) forms (*T* = 300 K)*

Complex	Form of Fe	δ	Δ	Γ	A	Literature
		±0.03 mm/s			±0.05 mm/s	
I	Fe^{3+} paramagnetic	0.43	0.66	0.35	1.00	This work
$[Fe_4Li_2(O)_2(Piv)_{10}(HPiv)_2(H_2O)_2]$	Fe^{3+} paramagnetic	0.40	0.75	0.48	1.00	[16]
$[Fe_2Li(O)(Piv)_5(Phen)_2]$	Fe^{3+} paramagnetic	0.43	1.20	0.37	0.62	[17]

* δ is the isomeric shift relative to α-Fe, Δ is the quadrupole splitting (quadrupole shift); Γ is the linewidth, and A is the relative content.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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