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Nontrivial structural organization of pivalate complexes with the fragment {$Fe_2Li(\mu_3$-O)}

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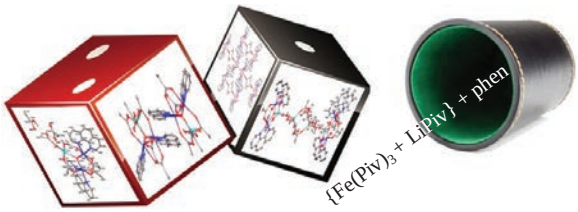
The reaction of Fe^{III} and Li^{I} pivalates with 1,10-phenanthroline (phen) in toluene simultaneously gives the heteronuclear compounds $[Fe_2Li(O)(Piv)_5(phen)_2]\cdot 2HPiv$ and $[\{Li_4(Piv)_4(HPiv)_2\}\{Fe_2LiO(Piv)_5(phen)_2\}_2]\cdot 2PhMe$ with a structural organization uncharacteristic of Fe^{III} and alkali metals. According to X-ray diffraction data, the trinuclear metal oxide moiety {Fe_2Li (μ_3-O)} forms two nonequivalent complex molecules, which form infinite horizontal chains in the crystal due to stacking interactions between aromatic rings.



Keywords: heterometallic pivalate complexes, iron(III), lithium, 1,10-phenanthroline, crystal structure, Mössbauer spectroscopy.

Heterometallic complexes of Fe with *s* metals are of increasing interest primarily due to a search for cathode components as alternatives to cobalt (less toxic, cheaper),[1–3] the synthesis of molecular precursors for oxide materials[4–7] and {Fe–(*s*-M)} catalytic systems for the functionalization of aliphatic C–H bonds and polymerization processes.[8,9] Analysis of the structural database (CSD version 5.40; May 2019) showed that more than 40 complexes of iron with Group IA metals (mainly Na and K) have been obtained.[10–15] Of Fe–Li complexes with monocarboxylic acids, only two molecular compounds that simultaneously contain iron(III) and lithium(I) ions are known: $[Fe_6Li_5(O)_2(Bu^tPO_3)_6(Piv)_8(MeOH)_2(Py)_4]$[16] and $[Fe_4Li_2(O)_2(Piv)_{10}(HPiv)_2(H_2O)_2]$[17] (Piv is the pivalate anion). The structural organization of {Fe^{III}–M^{IA}} compounds is represented by various polynuclear architectures, from four[13,18] to several dozens of metal atoms in a metal moiety.[19–21]

The structural organization of the metal oxide moiety {$Fe_2Li(\mu_3$-O)} obtained in this study is more characteristic of systems with Ni, Co, and Mn ions,[22–24] but it is nontrivial for Fe^{III}–Li^{I} complexes. We isolated two new compounds with the moiety {$Fe_2Li(\mu_3$-O)}, studied their crystal structure, and recorded Mössbauer spectra.

Previously, the $[Fe_4Li_2(O)_2(Piv)_{10}(H_2O)_2]$ hexanuclear complex was obtained from $[Fe_3O(Piv)_6(H_2O)_3]\cdot Piv^-$ and Li(Piv) (1 : 1) in toluene (110 °C).[17] It would be expected that the presence of two water molecules at the terminal iron atoms can result in replacement, for example, with N-donor base molecules without a fundamental rearrangement of the metal core. However, the reaction of Fe^{III}, Li^{I} carboxylates and 1,10-phen in toluene gave green complexes $[Fe_2Li(O)(Piv)_5(phen)_2]\cdot 2\,HPiv$ **1** and $[\{Li_4(Piv)_4(HPiv)_2\}\{Fe_2LiO(Piv)_5(phen)_2\}_2]\cdot 2\,PhMe$ **2**,[†] which were isolated as a hardly separable mixture of crystals (recrystallization did not result in phase separation, while mechanical separation is difficult due to a small size of the crystals) in a **1** : **2** ratio of 3 : 7 according to XRD data (Figure S1, see Online Supplementary Materials).

According to X-ray data,[‡] complexes **1** and **2** (Figures 1, 2) crystallize as solvates with two pivalic acid molecules in **1** or with two toluene molecules in **2**. In complex **1**, the HPiv solvate

[†] Samples of $[Fe_3O(Piv)_6(H_2O)_3]\cdot HPiv$ (100 mg, 0.09 mmol), Li(Piv) (10 mg, 0.09 mmol) and 1,10-phen (16 mg, 0.09 mmol) were dissolved in toluene on heating and boiled (110 °C) for 1 h. The resulting solution was slowly cooled to room temperature and held for 24 h. The precipitated crystals were separated from the mother liquor by decantation and dried in air. The yield of a mixture of crystals was 115 mg. FT-IR (ATR) (ν/cm^{-1}) (s = strong, m = medium, w = weak): 3365 (br. m), 3061 (w), 1646 (br. w), 1617 (w), 1562 (br. m), 1503 (m), 1421 (s), 1422 (s), 1345 (w), 1217 (w), 1138 (w), 1219 (vw), 1091 (m), 1037 (w), 1036 (w), 987 (w), 883 (w), 852 (s), 778 (w), 692 (br.m), 508 (m), 451 (w), 410 (s).

[‡] X-ray diffraction experiments were carried out at 120 K (**1**) and 296 K (**2**) on a Bruker APEX2 DUO CCD diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å). Using Olex2,[25] the structures were solved with the ShelXT[26] program and refined with the Olex2.refine refinement package using least-squares minimization against F^2 in anisotropic approximation for non-hydrogen atoms.[27] Hydrogen atoms of OH groups were located from difference Fourier synthesis; positions of other hydrogen atoms were calculated. All hydrogen atoms were then refined in an isotropic approximation within the riding model.

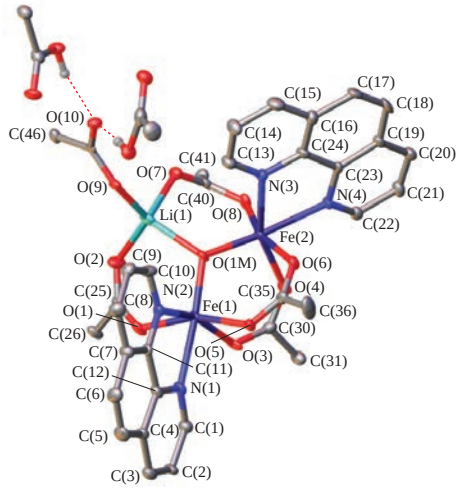


Figure 1 General view of complex **1** in the representation of atoms by ellipsoids of thermal vibrations (ρ = 30%). Hydrogen atoms (with the exception of solvate pivalic acid molecules belonging to the OH groups) and *tert*-butyl groups are not shown for clarity.

molecules are bound by hydrogen bonds [O···O 2.594 (8)–2.601(7) Å, O–H–O 166.9(4)–176.5(4)°], while toluene molecules in **2** are involved in weak intermolecular interactions.

In both metal complexes, the $\{Fe_2LiO\}$ moiety is the metal core in which the lithium(I) and iron(III) ions are linked by a μ_3-bridging oxo group (the main bond lengths are given in Table S1).

The coordination environment of iron(III) ions in complexes **1** and **2** formed by three bridging pivalate anions, a central O_2^- ion and a phenanthroline ligand is a distorted octahedron (FeO_4N_2). The lithium ion has a distorted tetrahedral environment, LiO_4,

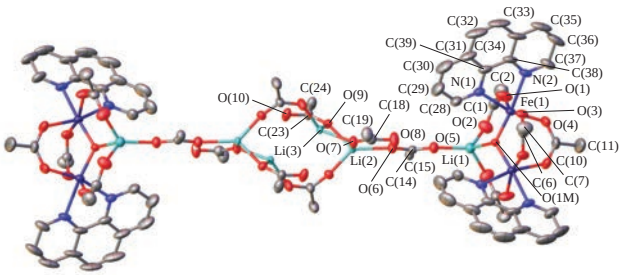


Figure 2 General view of complex **2** in the representation of atoms as ellipsoids of thermal vibrations (ρ = 30%). Hydrogen atoms (with the exception of the solvate molecules of pivalic acid belonging to the OH groups) and *tert*-butyl groups are not shown for clarity. [The names of the atoms are given only for the symmetrically independent part of the unit cell in which the complex molecule occupies a particular position: the plane crossing the bridging pivalate anion, and the second-order axis passing between two Li ions (3)].

Crystal data for **1** (120 K). $C_{59}H_{81}Fe_2LiN_4O_{15}$, M = 1204.91, monoclinic, brown, $P2_1/n$, a = 25.11(2), b = 19.714(12) and c = 27.49(3) Å, V = 13115(18) Å^3, Z = 2. Total of 41835 reflections were collected, from which 25409 were independent. The final refinement parameters were R_1 = = 0.0936, wR_2 = 0.2161 for the reflections with $I > 2\sigma(I)$. GOOF = 1.018. Residual electronic density max/min was 1.024/–0.971 eÅ^{-3}.

Crystal data for **2** (296 K). $C_{128}H_{176}Fe_4Li_6N_8O_{34}$, M = 2635.80, monoclinic, green, $C2/m$, a = 33.4503(11), b = 18.2998(6) and c = 12.4081(5) Å, V = 7561.0(5) Å^3, Z = 2. Total of 37436 reflections were collected, from which 7623 were independent. The final refinement parameters were R_1 = 0.0799, wR_2 = 0.1269 for the reflections with $I > 2\sigma(I)$. GOOF = 1.037. Residual electronic density max/min was 1.752/0.857 eÅ^{-3}.

CCDC 1963095 and 1963096 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Figure 3 Fragment of an infinite chain formed by complex molecules in a crystal of **1** due to stacking interactions between phenanthroline ligands.

which consists of two bridging pivalate anions, a central O_2^- ion and a pivalate anion, which occupies a terminal position in **1** and binds the $\{Fe_2LiO\}$ metal core with the central $\{Li_4(Piv)_4(HPiv)_2\}$ moiety. The O^{2-} central anion deviates from the Fe–Li–Fe plane by 0.257(6) and 0.287(6) Å in two symmetrically independent molecules of complex **1**. The corresponding value in **2** is 0.359(5) Å. Note that, in complex **2** (see Table S1), the Li–μ_3-O and Li–O(Piv-bridging) bonds are stretched by 0.03 and 0.04 Å, respectively, due to a central homometallic tetranuclear Li moiety through which two hetero-moieties are bound.

In a crystal of **1**, the complex molecules form infinite chains due to stacking interactions between the phenanthroline ligands; the corresponding distances and angles between their root-mean-square planes lie in the ranges of 3.489(7)–3.562(7) Å and 1.40(10)–4.47(9)°, respectively (Figure 3).

In a crystal of **2**, similar stacking interactions with distances of 3.301(9) Å and angles of 0.000(3)° between the planes of phenanthrolines bind the complex molecules into infinite layers (Figure 4).

The formation of a trinuclear oxo-centered metal core is most characteristic of carboxylate complexes of 3*d* transition metals with the general formula $[M_3O(O_2CR)_6L_3]^z$, where M = Fe, Ni, Mn, Cr, Zn, *etc.*; L = H_2O, HOAc, Py, MeOH, THF; R = Me, Ph, C_5H_4NH,[28–31] and also of M_2M'-heterometallic complexes (M = Cr, Fe, Mn; M′ = Co, Ni, Zn, Fe, Mn, Cr) with similar structures.[22–24]

Using Mössbauer spectroscopy,§ we studied the oxidation states and spin state of iron ions in a crystalline sample of a mixture of

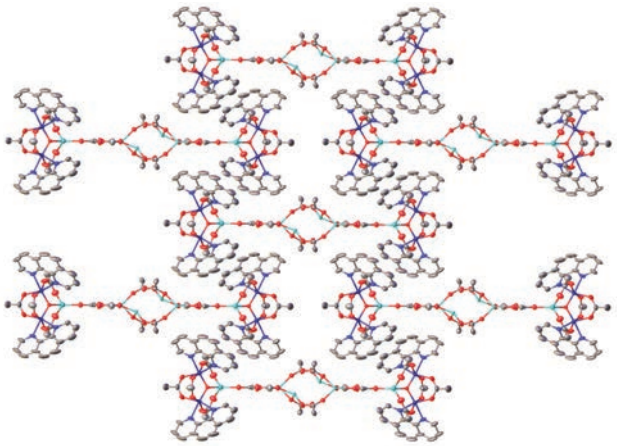


Figure 4 Fragment of an infinite layer formed by complex molecules in a crystal of **2** due to stacking interactions between phenanthroline ligands.

§ The Mössbauer spectra ^{57}Fe were obtained on a Wissel electrodynamic type spectrometer (Germany) at 300 K. The test sample contained natural iron, the ^{57}Fe isotope content of which did not exceed 3 wt%. As a consequence, the magnitude of the Mössbauer effect did not exceed 2%. The activity of ^{57}Co(Rh) as a Mössbauer radiation source was 1.1 GBk. The isomer shifts were measured from the center of the magnetic hyperfine structure (STS) of metallic iron. The spectra were processed by standard counting and simulation programs for the Mössbauer transition 3/2 → 1/2. Complex processing of Mössbauer spectra was carried out by the least squares method using the LRT programs at the N. N. Semenov Institute of Chemical Physics of the Russian Academy of Sciences and WINNORMOS (Germany).

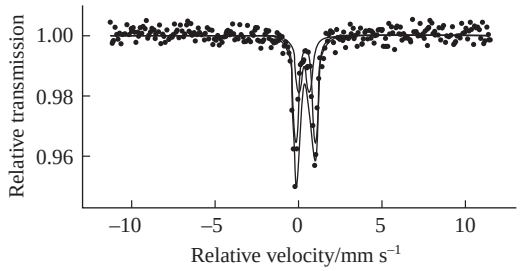


Figure 5 Mössbauer spectra of **1** and **2** (solid sample, T = 300 K).

complexes **1** and **2** in a ratio of 3 : 7 according to XRD data. The Mössbauer spectrum of the sample at room temperature in a zero magnetic field has two doublets (Figure 5). The isomeric shifts (δ) and quadrupole splittings (Δ) in the Mössbauer spectra of the complex make it possible to conclude that it contains only high-spin iron(III) ions in an octahedral environment of oxygen atoms, which agrees with X-ray single crystal diffraction data.

The observed isomeric shifts and quadrupole splittings of the complexes in ranges of 0.36–0.43 mm s^{-1} (for δ) and 0.75–0.85 mm s^{-1} (for Δ) are comparable with published data for heterometallic {Fe^{III}–M^{II}} complexes (M^{II} = Mn, Zn, Ni) (Table S2).[22,32] The spectrum contains two types of structurally nonequivalent iron(III) atoms with a ratio of 62 : 38 (as confirmed by the X-ray single crystal diffraction and X-ray powder diffraction data) (see Figure 5).

Thus, a new type of trinuclear moiety {$Fe_2Li(\mu_3\text{-}O)$}, an analogue of the {M_3O} trinuclear moiety originally described by Weinland in 1908,[33] was obtained. It is of interest for the preparation of new coordination compounds, including polymers, due to binding with polycarboxylic acids. In this case, the driving force that generates the {$Fe_2Li(\mu_3\text{-}O)$} moiety is a chelating phen ligand since a tetrahedral moiety {$Fe_3Li(\mu_4\text{-}O)$} was formed previously under similar conditions.[17] Complex **1** is a precursor of complex **2** in which the neutral {$Fe_2LiO(Piv)_5(phen)_2$} moieties are linked by tetranuclear {$Li_4(Piv)_4(HPiv)_2$}.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.05.003.

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