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

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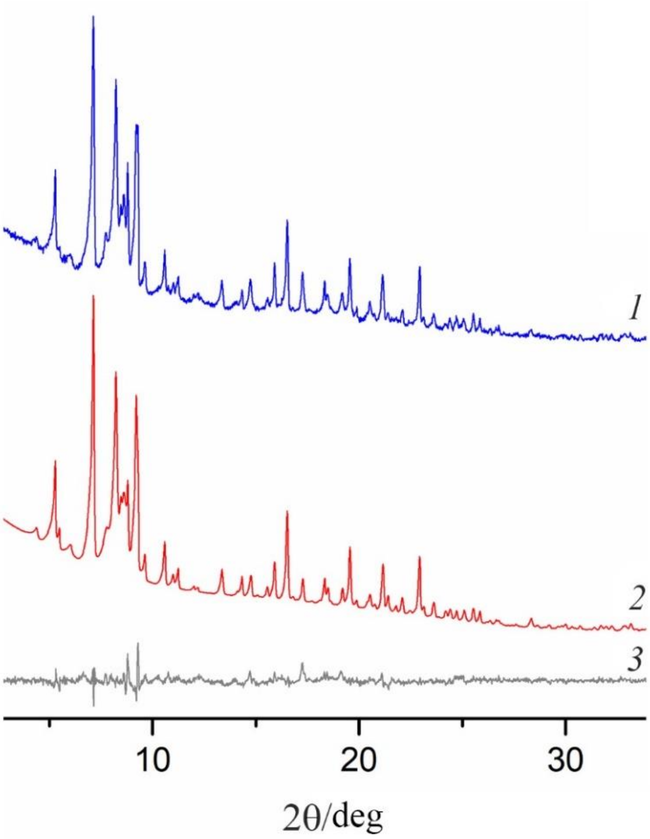

Figure S1 Experimental (*1*) and theoretical (*2*) powder patterns of the complexes **1, 2** and their difference (*3*).

The synthesis of the complexes was carried out using commercial reagents and solvents without further purification: pivalic acid (99%, «Merck»), LiOH (≥99%), toluene (≥99%), 1,10-phenanthroline (99%, «Alfa Aesar»). The complex $[Fe_3O(Piv)_6(H_2O)_3]\cdot Piv$ was obtained by a known method.[S1] Lithium pivalate, Li(Piv), is synthesized by the interaction of equimolar aqueous solutions of LiOH and HPiv, followed by evaporation; the resulting solid phase is washed with hexane. IR spectra were recorded in the 400–4000 cm^{-1} region using a Spectrum-65 Perkin Elmer

FT- IR spectrometer. Microprobe analyses were carried out using an Carlo Erba EA 1108 Series CHN Elemental Analyser (Center of Collective Use of IGIC RAS). The powder pattern was measured on Bruker D8 Advance diffractometer with LynxEye detector and Ge (111) monochromator, λ(CuKα1) = 1.5406 Å, θ/2θ scan from 4° to 40°, step size 0.02°. The measurement was performed in transmission mode, the compounds were deposited between two Mular films. The powder pattern refinement was performed in TOPAS 5 software using low-temperature single-crystal structures. The preferred orientation was described with 4th order spherical harmonics.

Table S1 Selected distances (Å) for **1** and **2**.

	1	**2**
Fe–O(μ_3-O)	1.804(4)–1.821(4)	1.821(2)
Fe–O(Piv)	1.973(6)–2.076(6)	1.961(4)–2.057(4)
Fe–N	2.154(7)–2.233(6)	2.181(4)–2.224(4)
Li–O(μ_3-O)	2.02(2)–2.03(2)	2.054(12)
Li–O(Piv-bridg)	1.86(2)–1.944(14)	1.89(4)–1.981(11)
Li–O(Piv-terminal)	1.867(13)–1.884(12)	-
Li–O(Piv-centr)	-	1.867(10)–2.090(11)

Table S2 Mössbauer parameters for **1** and **2** (T = 300 K).

Complex	Metal core	δ	Δ	*Γ*	*A*, ±0.05	Ref.
		±0.03 mm/s				
1, 2	$\{FeO_4N_2\}$	0.43	1.20	0.37	0.62	This work
	$\{FeO_4N_2\}$	0.34	0.68	0.34	0.38	
$[Fe_4Li_2(O)_2(Piv)_{10}(HPiv)_2(H_2O)_2]$	$\{FeO_6\}$	0.40	0.75	0.48	1.00	[S2]
$[Fe_2Zn_4(O)_2(Piv)_{10}]$	$\{FeO_6\}$	0.36	0.77	0.44	1.00	[S3]
$[Fe_4Zn_3(O)_3(Piv)_{12}(H_2O)]\cdot$	$\{FeO_6\}$	0.40	0.90	0.64	1.00	[S3]
$[Fe_2Mn_4(O)_2(Piv)_{10}(HPiv)_4]$	$\{FeO_6\}$	0.42	0.67	0.44	1.00	[S4]
$[Fe_3Zn_2(O)_2(Piv)_9(phen)]$	$\{FeO_6\}$	0.39	0.85	0.54	0.79	[S3]
	$\{FeO_4N_2\}$	0.47	1.27	0.57	0.21	
$[Fe_2Ni_2(OH)_2(Piv)_8(phen)_2]$	$\{FeO_6\}$	0.39	0.75	0.52	0.63	[S5]
	$\{FeO_6\}$	0.44	1.21	0.53	0.37	

δ – isomer shift relative α-Fe;
Δ – quadrupole splitting;
Γ – line width;
A – abundance.

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