

Solutions of complex copper salts in LTTM

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Supplementary materials

Experimental section

Synthesis

Preparation of $\text{Cu}(\text{CF}_3\text{SO}_3)_2 \cdot 6\text{H}_2\text{N}(\text{CH}_2)_2\text{OH}$. Copper(II) triflate (0.400 g, 1.1 mmol) and ethanolamine (0.403 g, 6.6 mmol) were mixed in a vial with cap. The mixture was rapidly heated to 250°C at intensive stirring with magnetic stirrer and then cooled to room temperature. The product appeared to be a very viscous deep blue liquid, which was stored in a desiccator above P_4O_{10} .

Preparation of $\text{Cu}(\text{CF}_3\text{SO}_3)_2 \cdot 6\text{H}_2\text{N}(\text{CH}_2)_6\text{OH}$. Copper(II) triflate (0.400 g, 1.1 mmol) and hexanolamine (0.772 g, 6.6 mmol) were mixed in a vial with cap. The mixture was rapidly heated to 250°C at intensive stirring with magnetic stirrer and then cooled to room temperature. The product appeared to be a very viscous greenish liquid which was stored in a desiccator above P_4O_{10} .

Preparation of $\text{Fe}(\text{CF}_3\text{SO}_3)_3 \cdot 6\text{H}_2\text{N}(\text{CH}_2)_6\text{OH}$. Iron(III) triflate (0.402 g, 0.8 mmol) and hexanolamine (0.562 g, 4.8 mmol) were mixed in a vial with cap. The mixture was rapidly heated to 250°C at intensive stirring with magnetic stirrer and then cooled to room temperature. The product appeared to be a very viscous reddish-brown liquid which was stored in a desiccator above P_4O_{10} .

Preparation of $\text{Fe}(\text{CF}_3\text{SO}_3)_3 \cdot 6\text{HN}(\text{C}_2\text{H}_4\text{OH})_2$. Iron(III) triflate (0.402 g, 0.8 mmol) and diethanolamine (0.504 g, 4.8 mmol) were mixed in a vial with cap. The mixture was rapidly heated to 250°C at intensive stirring with magnetic stirrer and then cooled to room temperature. The product appeared to be a very viscous liquid colored in dark reddish-brown, which was stored in a desiccator above P_4O_{10} .

Preparation of $\text{Cu}(\text{CF}_3\text{SO}_3)_2 \cdot 6\text{HN}(\text{C}_2\text{H}_4\text{OH})_2$. Copper(II) triflate (0.400 g, 1.1 mmol) and diethanolamine (0.693 g, 6.6 mmol) were mixed in a vial with cap. The mixture was rapidly heated to 250°C at intensive stirring with magnetic stirrer and then cooled to room temperature. The product appeared to be a very viscous deep blue liquid which was stored in a desiccator above P_4O_{10} .

Preparation of $\text{CH}_3\text{NC}_3\text{H}_3\text{NC}_4\text{H}_9[\text{FeCl}_4]$. Anhydrous iron(III) chloride was obtained by direct chlorination of iron at 400°C, the product was stored in a sealed ampule. 1-butyl-3-methyl-imidazolium chloride was obtained as follows.

1-methyl-imidazole (1.25 mol) was dissolved in toluene (125 cm³) at 0°C. Solution was mixed with 1-chloro-butane (144 cm³, 1.38 mol). The mixture was refluxed at 110°C for 24 h. Then solution was cooled in a refrigerator at -20°C for 12 h. Toluene was decanted, the remained viscous substance was recrystallized firstly from acetonitrile, then from ethylacetate. The resulting white crystalline product was dried *in vacuo* at 60°C, the yield was 68%.

$\text{CH}_3\text{NC}_3\text{H}_3\text{NC}_4\text{H}_9[\text{FeCl}_4]$ was obtained as follows. Anhydrous iron(III) chloride (0.926 g, 5.8 mmol) and 1-butyl-3-methyl-imidazolium chloride (1.014 g, 5.8 mmol) were mixed in a vial with cap. The mixture was heated due to an exothermic reaction at intensive stirring with magnetic stirrer, then a weighting bottle was cooled to room temperature. The product appeared to be a dark brown liquid, which was stored in a desiccator above P_4O_{10} .

Preparation of $[\text{DH}_3^+]\text{OTf}^-$, $[(\text{DH}_2)_3\text{H}^+]\text{OTf}^-$ and $[(\text{DH}_2)_4\text{H}^+]\text{OTf}^-$. (designations given in the main text). The reagents – diethanolamine and trifluoromethylsulfuric acid – were mixed at stirring in ice bath. Stoichiometric ratios were 1:1, 3:1 and 4:1 for obtaining $[\text{DH}_3^+]\text{OTf}^-$, $[(\text{DH}_2)_3\text{H}^+]\text{OTf}^-$ and $[(\text{DH}_2)_4\text{H}^+]\text{OTf}^-$, respectively. The products were stored in a desiccator above P_4O_{10} .

Results of analyses

EXAFS of $\text{Fe}(\text{CF}_3\text{SO}_3)_3 \cdot 6\text{HN}(\text{CH}_2)_6\text{OH}$. As shown in Fig. S1, EXAFS spectrum of $\text{Fe}(\text{OTf})_3 \cdot 6\text{HH}$ sample looks more complicated than the spectra of $\text{Cu}(\text{OTf})_2 \cdot 6\text{EH}$ and $\text{Cu}(\text{OTf})_2 \cdot 6\text{HH}$ spectra. The FT plot of EXAFS function for this IL appeared to be surprisingly similar to the known function for crystalline magnetite Fe_3O_4 . However, fitting using a model based only on the local structure of magnetite appeared to be unsatisfactory.

To attain the better correspondence, **Fe-O₆** model consisting of Fe atoms in the octahedral environment of oxygen atoms O_{oct} forming one coordination sphere was added to the model of magnetite structure.

For description of the local environment of Fe atoms in magnetite, we used seven independent coordination spheres, because there are two different atomic positions of Fe in magnetite. Thus, for experimental data interpretation, we used a model of double-phase material composed of a liquid with one-sphere coordination of the resonantly absorbing Fe centers surrounded with six O atoms and the formed magnetite crystals distributed in this liquid. A satisfactory description of EXAFS data for this sample is attained with the model parameters presented in table S1. The phase composition of material was refined together with the structural parameters.

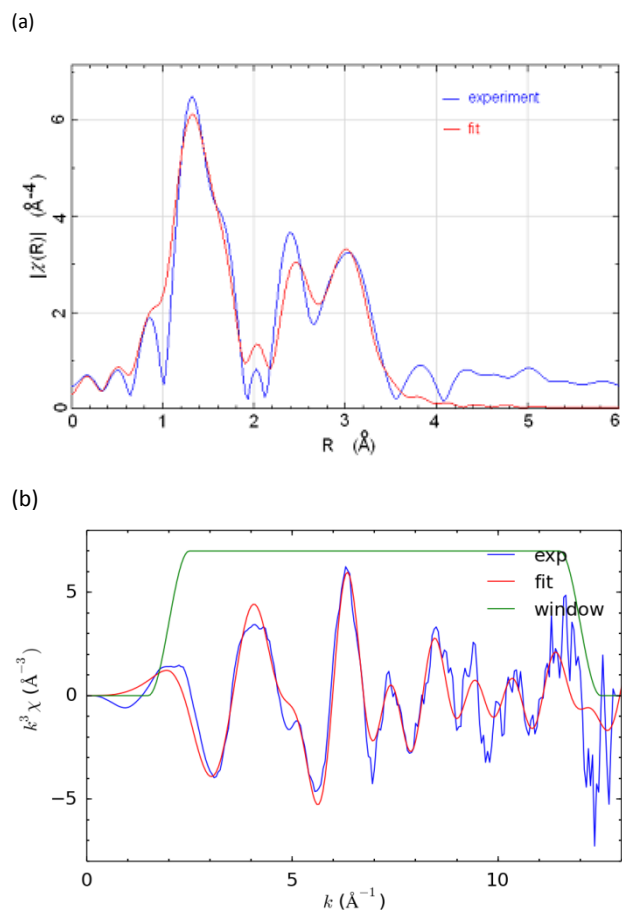


Fig. S1. Fourier transformation of EXAFS function for $\text{Fe}(\text{OTf})_3 \cdot 6\text{DH}_2$ sample in (a) metrical space R ; (b) wave space k .

Double-phase model allows to change the ratio of Fe atoms with octahedral and tetrahedral first coordination spheres fixed as 2:1 in magnetic structure; on addition of liquid with one-sphere coordination of the resonantly absorbing Fe centers surrounded by six O atoms this ratio is exceeded. Formation of a phase with the magnetite-like structure comes from specific composition and sample preparation conditions. Hexanolamine does not form metallocycles due to its length and coordinates Fe atom mainly by its hydroxyl group, because iron affinity to O atoms is higher than to N atoms. The amino groups of

hexanolamine bind to hydrogen cations arising from hydrolysis of iron triflate by air moisture (aerobic reaction conditions and fast heating of samples).

The OH groups, the products of hydrolysis, can form cubane structures with triflate ions, and coordination polyhedra of Fe ions are supplemented to octahedra⁵⁴. So, in the absence of chelation hydrolysis of Fe(III) triflate appears to be possible.

EXAFS of $\text{Fe}(\text{CF}_3\text{SO}_3)_3 \cdot 6\text{HN}((\text{CH}_2)_2\text{OH})_2$. The data presented in Table S2 unambiguously indicate that coordination number of Fe atom in the first coordination sphere of $\text{Fe}(\text{OTf})_3 \cdot 6\text{DH}_2$ sample is 6. Since monodentate ligands with oxygen atoms of the hydroxyl groups in the inner coordination sphere of complexes do not protect iron(III) triflate from hydrolysis by air moisture, three DEA molecules are supposed to form five-membered metallocycles with each Fe atom. Consequently, there are three O atoms and three N atoms in the inner coordination sphere.

As for $\text{Fe}(\text{OTf})_3 \cdot 6\text{DH}_2$ preparation, it differs from its copper analog, not only in coordination number of Fe atom (see above), but also in the character of TGA curves (Fig. S2). Mass spectra indicate that at 240 and 300°C water vapor is evolved, and this is possibly a result of DH_2 condensation reaction, but at 300–400°C DH_2 evaporates. At 410°C DH_2 and/or the products of its condensation decompose.

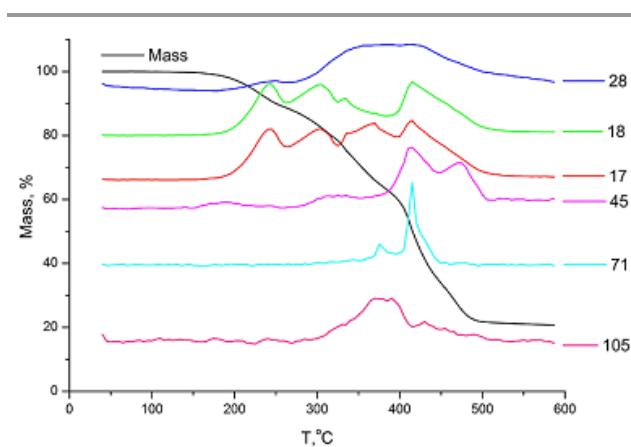


Fig. S2. TGA curve of $\text{Fe}(\text{OTf})_3 \cdot 6\text{DH}_2$ preparation and the simultaneously recorded mass spectra of exit vapors and gases.

The MALDI spectrum (Supplementary Materials, Fig. S6) of $\text{Fe}(\text{OTf})_3 \cdot 6\text{DH}_2$ preparation indicates the presence of DH_2 before heating of preparation. Structure and properties of $\text{Fe}(\text{OTf})_3 \cdot 6\text{DH}_2$ preparation differ significantly from those of $\text{Cu}(\text{OTf})_2 \cdot 6\text{DH}_2$ and require additional studies.

Table S1. Analysis of EXAFS data for Fe(OTf)₃·6HH sample using structural model consisting of magnetite mixed with IL, fitting performed in the range $k = 2.000\text{--}14.000 \text{ \AA}^{-1}$ and $R = 1.2\text{--}4.0 \text{ \AA}$

Substance	Fe concentration, %	Scattering pathway	N_j	$R, \text{ \AA}$	$\sigma^2, \text{ \AA}^2 \times 10^{-3}$	$R_f, \%$
Fe-O₆	31 ± 16	Fe-O _{oct}	6	1.843 ± 0.03	2.9 ± 5	6.3
Fe ₃ O ₄	69 ± 16	Fe-O1	1.33	1.81 ± 0.06	1.2 ± 2.6	
		Fe-O2	4.0	2.01 ± 0.03	1.2 ± 2.6	
		Fe-Fe1	4.0	2.96 ± 0.05	14 ± 5	
		Fe-Fe2	8.0	3.45 ± 0.06	14 ± 5	
		Fe-O3	1.33	3.64 ± 0.05	14 ± 5	
		Fe-Fe3	4.0	3.4 ± 0.1	4.0 ± 3.5	
		Fe-O4	5.66	3.72 ± 0.05	4.0 ± 3.5	

Table S2. The local structure parameters of samples containing DH₂ ligand defined from EXAFS data. Calculations performed for $S_0^2 = 0.8$, fitting in the range $k = 2\text{--}12 \text{ \AA}^{-1}$, $R = 1.2\text{--}3.2 \text{ \AA}$

Sample	S_0^2	Scattering pathway	N_j	$R, \text{ \AA}$	$\sigma^2, \text{ \AA}^2 \times 10^{-3}$	$R_f, \%$
Fe(OTf) ₃ ·6DH ₂	0.8	Fe-(O/N)	5.5 ± 1.7	1.98 ± 0.02	9 ± 3	2.67
		Fe-C1	1 ± 2	2.8 ± 0.1	0 ± 9	
		Fe-C2	2.9 ± 3.9	2.96 ± 0.06		
		Fe-C3	3.4 ± 4.2	3.18 ± 0.04		

**Fig. S3.** MALDI (Matrix Assisted Laser Desorption/Ionization) mass spectrum of $[\text{Cu}^{2+}\text{DH}_2(\text{DH}^-)][(\text{DH}_2)_4\text{H}^+](\text{OTf}^-)_2$ preparation

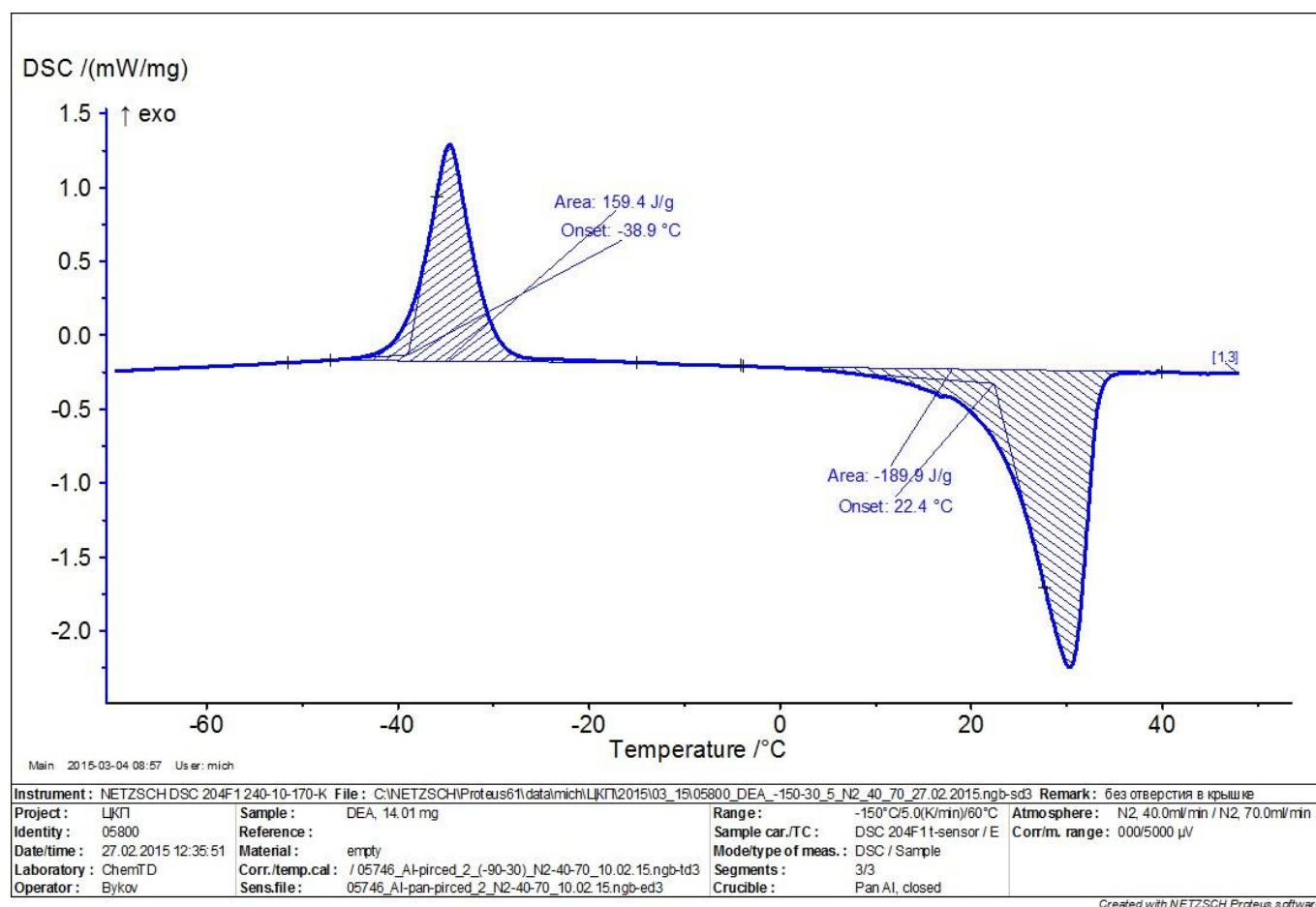


Fig. S4. DSC (Differential Scanning Calorimetry) plot of DH_2 preparation at heating.

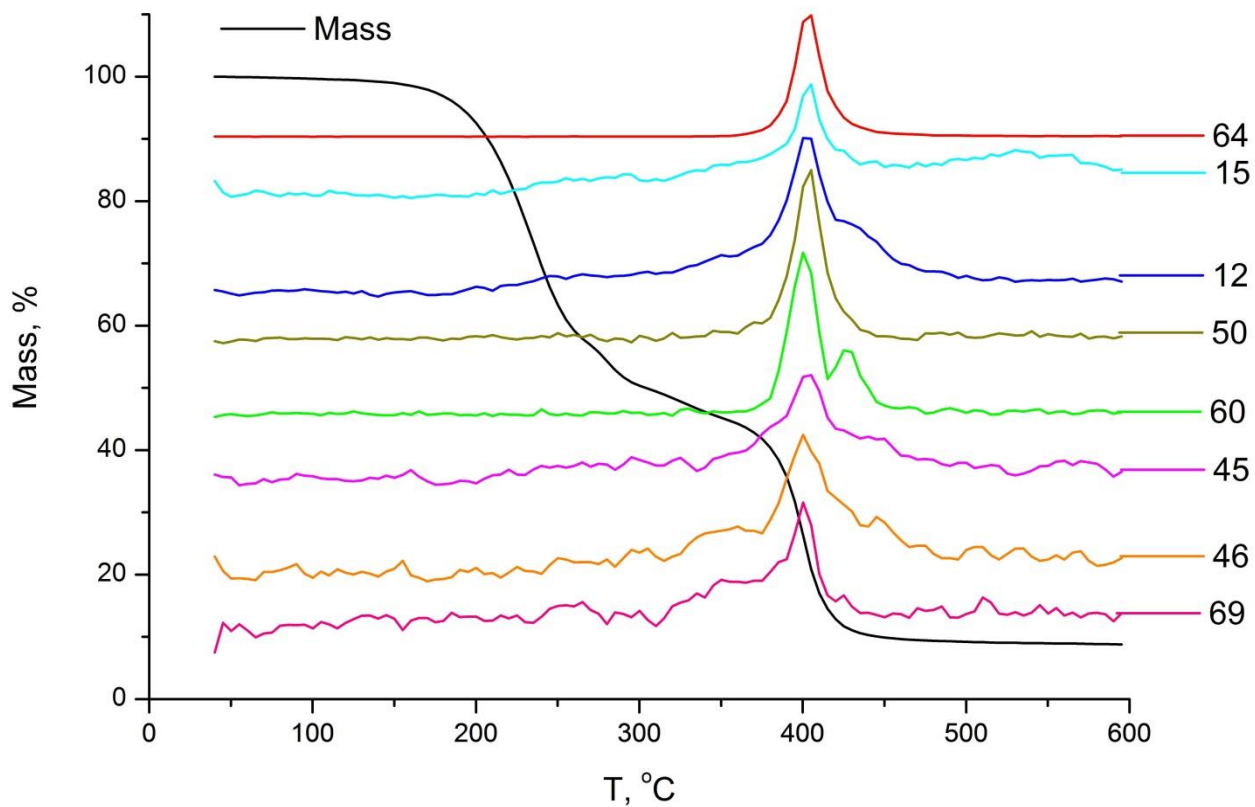


Fig. S5. TGA (Thermal Gravimetry Analysis) curve of $(\text{DH}_2)_4\text{H}^+\text{OTf}^-$ preparation and simultaneously recorded mass spectra of exit vapors and gases (in addition to Fig. 5 of the paper).

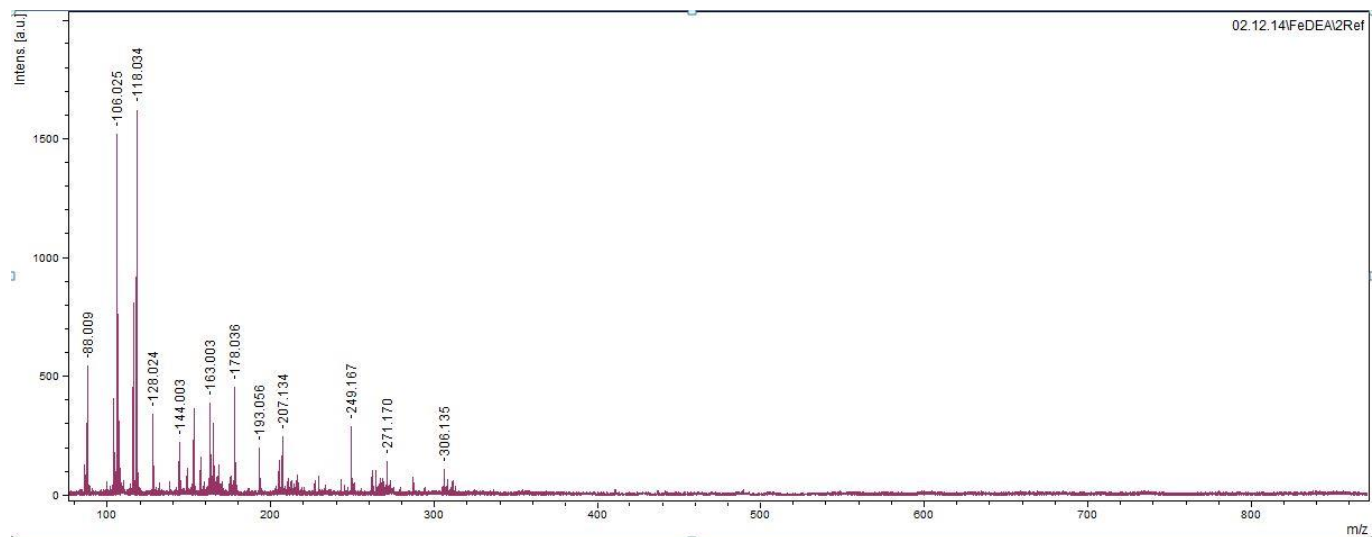


Fig. S6. MALDI mass spectrum of $\text{Fe}(\text{OTf})_3 \cdot 6\text{DH}_2$ preparation.