SUPPORTING INFORMATION

Ambient pressure synthesis of MIL-100(Fe) MOF from homogeneous solution using a redox pathway

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Experimental Procedure

Note: DMSO and iron(III) nitrate are listed as incompatible chemicals. Precipitation of $Fe(NO_3)_3 \cdot 6$ DMSO (yellow crystals) was observed if the fresh reaction mixture was allowed to sit at RT over a longer period, especially if the prescribed water content was not maintained. $Fe(NO_3)_3 \cdot 6$ DMSO was patented as an explosive.

Reagents and Reactants

Benzene-1,3,5-tricarboxylic acid (trimesic acid, ≥ 98 %, TCI) was used as received.

Ethanol (96 %, Carl Roth, 1% methyl ethyl ketone) was distilled prior to use.

N,N-dimethyl formamide (≥ 99.9 %, anhydrous, BDH Prolabo) was distilled prior to use. The first and the last 10 % of the distillate were discarded.

Dimethylsulfoxide (≥ 99.5 %, Carl Roth) was used as received. After opening, bottles were used within 2 weeks.

Iron(III)-nitrate nonahydrate (≥ 96 %, Carl Roth), *iron(III)-sulfate nonahydrate* (reagent quality, VWR chemicals) and *iron(III)-chloride hexahydrate* (≥ 98 %, Carl Roth) were used as received.

Preparation of the metal salt solutions

Iron(III) nitrate: 3.24 g of iron(III) nitrate nonahydrate (8 mmol) were dissolved in 8 mL of deionized water. pH = 0.

Iron(III) chloride: 2.16 g of iron(III) chloride hexahydrate (8 mmol) were dissolved in 8 mL of deionized water. pH = 0 was adjusted with conc. hydrochloric acid.

Iron(III) mesylate: To a solution of 3.24 g (8 mmol) of iron(III) nitrate nonahydrate (≥ 96 %, Carl Roth) in 30 ml of deionized water, ammonium hydroxide solution (25%) was added in drops until no further precipitation of Fe(O)(OH) could be noticed and pH ≥ 10 was achieved. The resulting solid was removed by centrifugation, thoroughly washed with deionized water until pH = 7 and finally redispersed in 8 ml of deionized water. 1.56 mL (24 mmol) of methanesulfonic acid were added. The mixture turned clear. pH = 0 was adjusted with methanesulfonic acid.

Iron(III) sulfate / hydrogen sulfate buffer system: To a solution of 2.25 g (4 mmol) of iron(III) sulfate hydrate in 8 mL of deionized water, 12 mmol (1.18 g), 8 mmol (0.78 g), or 4 mmol (0.39 g) of conc. sulfuric acid were added. pH = 0 was adjusted with conc. sulfuric acid.

PXRD of $[Fe(DMSO)_6](NO_3)_3$

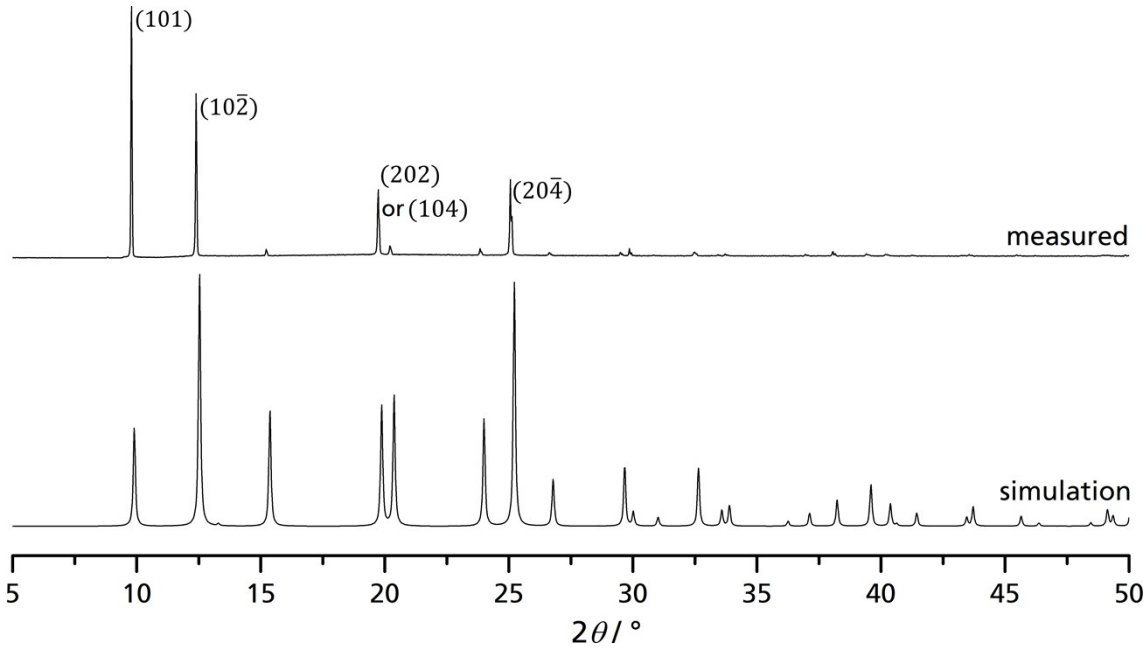

Figure S1 Comparison of the PXRDs acquired for the precipitated crystals with cif-file simulation for $Fe(NO_3)_3$ ❿ 6 DMSO (CCDC-No. 125872).[1] Indices are given for intense reflections. Cu-Kα radiation. Note: Preparation and handling (grinding etc.) of this compound is strongly discouraged.

[1] J. R. Tzou, M. Mullaney, R. E. Norman and S. C. Chang, *Acta Crystallogr. C*, 1995, **51**, 2249-2252. DOI: 10.1107/s0108270195005695

Boiling curve DMSO-water

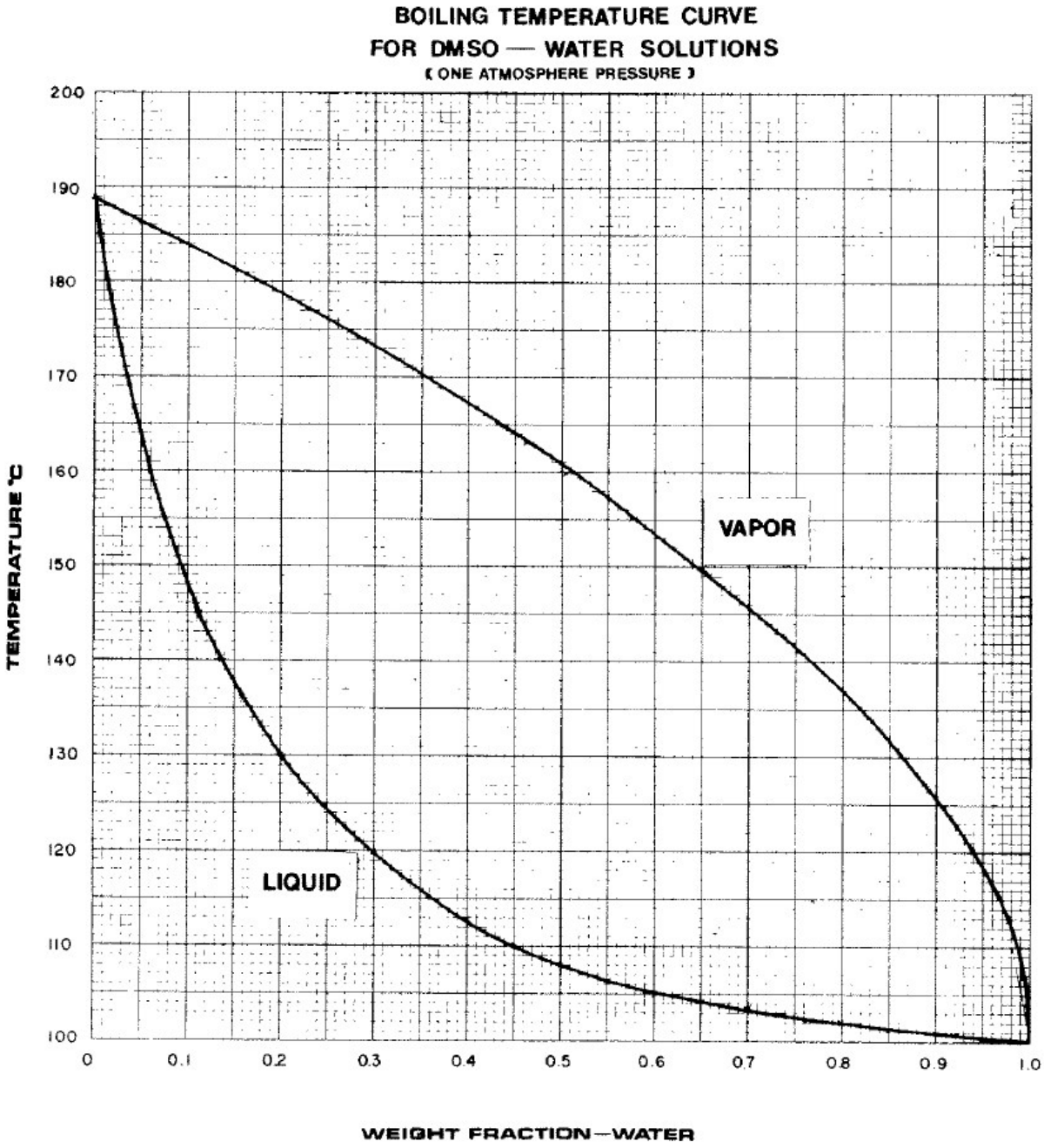

Figure S2 Boiling curve of DMSO/water mixtures. Retrieved from: Gaylord Chemical, Dimethyl Sulfoxide (DMSO) Physical Properties - Bulletin # 101, http://www.gaylordchemical.com/65-2/literature/101b-dmso-physical-properties/, 2005.

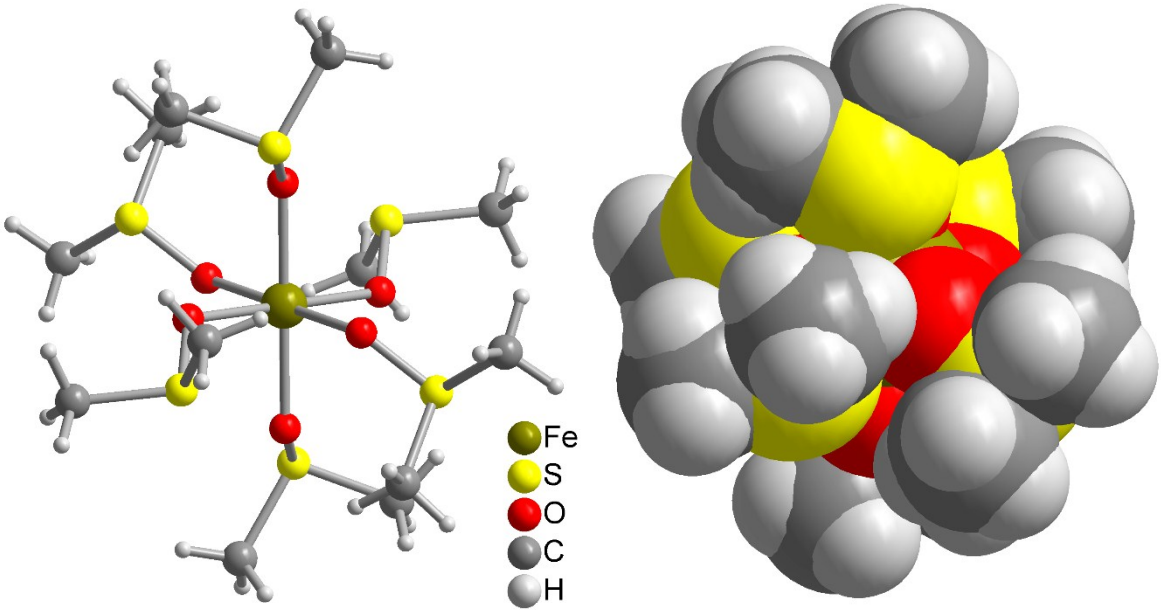

Figure S3 Molecular structure of the $[Fe(DMSO)_6]^{3+}$ cation in $[Fe(DMSO)_6](NO_3)_3$ (= $Fe(NO_3)_3$ ❿ 6 DMSO). Drawing prepared from deposited cif-file (CCDC-No. 125872).[1]