

Electronic Supplementary Information

A {Na₂Fe₁₀} isobutyrate cluster, interlinked into 1D chains

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Experimental part

Materials and methods. All reactions were performed under aerobic conditions using chemicals and solvents that were used as received without further purification. The precursor compound [Fe₃O(ib)₆(H₂O)₃]NO₃·2H₂O was prepared using a published procedure (O. Botezat, J. van Leusen, V. Ch. Kravtsov, A. Ellern, P. Kögerler and S. G. Baca, *Dalton Trans.*, 2015, **44**, 20753). **Caution! Care should be taken when using the potentially explosive sodium azide.** A WiseClean ultrasonic bath, operating at 42 kHz with maximum power of 120 W was used for ultrasonic irradiation. FTIR spectrum (4000 – 700 cm⁻¹) was recorded on a FTIR PerkinElmer spectrometer. Thermogravimetric analysis/differential thermal analysis (TGA/DTA) measurements were performed with AUTOSORB 1 in nitrogen atmosphere at a heating rate 10 K·min⁻¹ from 20 – 1000 °C.

Magnetic properties were determined using a Quantum Design MPMS-5XL SQUID magnetometer. A microcrystalline sample of **1** was compacted and immobilized into a cylindrical PTFE sample holder. The data were recorded at 0.1 Tesla in the temperature range 2.0 – 290 K, and at 2.0 K in the field range 0.1 – 5.0 Tesla. They were corrected for the diamagnetic contributions of the sample holder and the intrinsic contribution of the compound ($\chi_{m,dia} = -1.16 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$).

Synthesis of [Na₂Fe₁₀O₆(OH)₄(ib)₁₄(bpy)(MeO)₂(MeCN)₂]□MeOH (1**).** A solution of [Fe₃O(ib)₆(H₂O)₃]NO₃·2H₂O (0.087 g, 0.1 mmol), pyrazole (0.013 g, 0.19 mmol), 4,4'-bipyridine (0.015 g, 0.1 mmol) and NaN₃ (0.02 g; 0.3 mmol) in 10 mL of MeCN was ultrasonicated for 70 min at 60 °C and then filtered. The filtrate was allowed to slowly evaporate at room temperature. After 2 weeks brown crystals of **1** were filtered off, washed with water and isopropanol and dried in air. Yield: 0.051 g (23% based on Fe). Characteristic IR bands (cm⁻¹): ν(OH): 3676 (m); ν(C-H): 2971 (s, br), 2902 (sh); ν(COO): 1585 (vs), 1422 (vs); δ(C-H): 1470 (m), 1376 (m).

Single-crystal X-ray diffraction crystallographic analysis. Single-crystal X-ray diffraction experiment for **1** was performed at 293 K on an Oxford Xcalibur CCD diffractometer with graphite-monochromatized Mo K α radiation. Full crystallographic data and refinement details of **1** are provided in Table S1. The position of metal atoms was located by direct methods. The remaining atoms were found in an alternating series of least-square cycles and difference Fourier maps. All non-hydrogen atoms were refined in full-matrix anisotropic approximation using the SHELX software package. All hydrogen atoms were placed at idealized position and were allowed to ride on the neighboring atoms. Selected bond distances and angles for **1** are listed in Table S2. CCDC 2088628.

Table S1. Crystal data and details of structural determination for compound **1**

[Na ₂ Fe ₁₀ O ₆ (OH) ₄ (ib) ₁₄ (bpy)(MeO) ₂ (MeCN) ₂] \cdot MeOH	
Empirical formula	C ₇₃ H ₁₂₆ Fe ₁₀ N ₄ Na ₂ O ₄₁
M_r / g mol ⁻¹	2320,21
Wavelength / Å	0.71073
Radiation type	MoK α
T / K	293
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	
a / Å	25.2017(13)
b / Å	18.1205(12)
c / Å	24.0709(10)
α	90°
β	105.576(5)°
γ	90°
V / Å ³	10588.7(10)
Z	4
ρ / mg m ⁻³	1.455
μ / mm ⁻¹	1.415
Theta range for data collection	3.062° to 25.049°
Index ranges	$-29 \leq h \leq 30$, $-12 \leq k \leq 21$, $-22 \leq l \leq 28$
Reflections collected	18859
Independent reflections	9353 [R(int) = 0.0806]
Reflections $I \geq 2\sigma(I)$	4589
Data / restraints / parameters	9353 / 85 / 635
Goodness-of-fit on F^2	0.990
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0748$, $wR_2 = 0.1261$
R indices (all data)	$R_1 = 0.1622$, $wR_2 = 0.1537$
Largest diff. peak and hole / e \cdot Å ⁻³	0.555 and -0.476

Table S2. Selected bond distances for **1**

Atom 1	Atom 2	Length / Å	Atom 1	Atom 2	Length / Å
Fe1	O1	1.891(4)	Fe4	O10	2.001(5)
Fe1	O2	1.899(5)	Fe4	O5 ¹	2.054(4)
Fe1	O3	1.931(4)	Fe4	O19 ¹	2.071(5)
Fe1	O6	2.210(5)	Fe4	O4	2.112(5)
Fe1	O8	2.214(5)	Fe5	O2	1.906(4)
Fe1	N1	2.249(5)	Fe5	O9	1.974(5)
Fe1	Na1 ¹	3.211(3)	Fe5	O12	2.010(5)
Fe2	O3 ¹	1.947(4)	Fe5	O18	2.045(5)
Fe2	O20	1.971(4)	Fe5	O4 ¹	2.053(4)
Fe2	O1	1.989(4)	Fe5	O5	2.119(4)
Fe2	O4	2.050(4)	Na1	O16	2.383(6)
Fe2	O14	2.062(5)	Na1	O14	2.399(6)
Fe2	O11	2.108(5)	Na1	O8 ¹	2.409(5)
Fe2	Fe3	2.9300(14)	Na1	N2	2.417(9)
Fe2	Na1	3.337(3)	Na1	O6 ¹	2.444(6)
Fe3	O3 ¹	1.939(4)	Na1	O3 ¹	2.460(5)
Fe3	O20	1.970(4)	Na1	Fe1 ¹	3.211(3)
Fe3	O2	1.975(4)	O3	Fe3 ¹	1.939(4)
Fe3	O16	2.041(5)	O3	Fe2 ¹	1.947(4)
Fe3	O5	2.042(4)	O3	Na1 ¹	2.460(5)
Fe3	O13	2.103(5)	O4	Fe5 ¹	2.053(4)
Fe3	Na1	3,340(3)	O5	Fe4 ¹	2.054(4)
Fe4	O1	1.905(4)	O19	Fe4 ¹	2.071(5)
Fe4	O7	1.980(5)			

¹ 1/2-x, 3/2-y, 1-z

Table S3. Bond valence sums for selected atoms in **1** (K. Knížek, *Kalvados – Software for crystal structure and powder diffraction*; see <http://www.fzu.cz/~knizek/kalvados/index.html>)

Atom	BVS	Atom	BVS
Fe1	2.91	O9	-1.95
Fe2	2.99	O10	-1.94
Fe3	3.06	O11	-1.95
Fe4	3.01	O12	-1.99
Fe5	3.03	O13	-1.92
O1	-1.87	O14	-1.96
O2	-1.87	O15	-1.58
O3	-1.93	O16	-1.96
O4	-1.37	O17	-1.56
O5	-1.37	O18	-1.97
O6	-1.95	O19	-1.88
O7	-1.94	O20	-2.09
O8	-1.93		

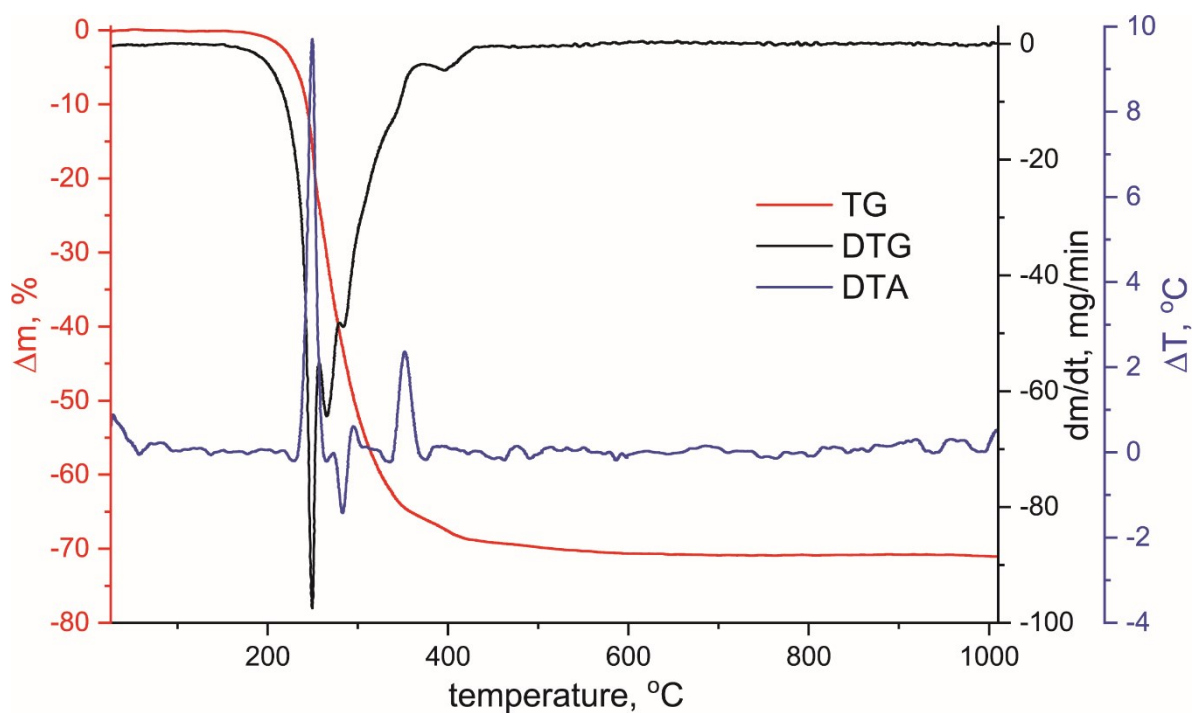


Figure S1. TGA/DTG/DTA curves of **1**.