

Electronic Supplementary Information

Atypical Stoichiometry for a 3D Bimetallic Oxalate-Based Long-range Ordered Magnet Exhibiting High Proton Conductivity

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Experimental

Synthesis

Except where mentioned, all the chemicals were purchased from commercial sources and were used as received. $(\text{NH}_4)_3[\text{Cr}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$ was prepared following the literature procedures.¹ Elemental analyses (C, H, N) were carried by the Microanalytical Service of the University of Grenoble.

$(\text{NH}_4)_5[\text{Mn}_2\text{Cr}_3(\text{ox})_9] \cdot 10\text{H}_2\text{O}$ (**1**).

$(\text{NH}_4)_3[\text{Cr}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$ (85.6 mg, 0.2 mmol) and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (19.8 mg, 0.2 mmol) was dissolved in 8 mL methanol. The resulting mixture was carefully layered to 15 mL solution $\text{CH}_3\text{OH}/\text{CHCl}_3$ 1/1. Tiny violet crystals were obtained after three days in 72% yield. Elemental analysis calculated (%) for $\text{C}_{18}\text{H}_{40}\text{Cr}_3\text{Mn}_2\text{N}_5\text{O}_{46}$ (1328.38): C 16.27, H 3.03, N 5.27; found: C 16.28, H 2.85, N 5.04;

Single-Crystal Studies.

Data was collected at 173(2) K on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo-K α ($\lambda = 0.71073$ Å) radiation. The diffraction data was corrected for absorption and structural determination was achieved using the APEX (1.022) package. The ammonium and water molecules in compound **1** are highly disordered which could not be located successfully from Fourier maps in the refinement cycles. The scattering from the highly disordered lattice guest molecules were removed using the SQUEEZE procedure implemented in the PLATON package². The resulting new file was used to further refine the structures.

CCDC 981441 contains the supplementary crystallographic data for this paper

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- [1] J. C. Bailar and E. M. Jones, *Inorg. Synth.*, 1939, **1**, 37.
[2] A. L. Spek, *J. Appl. Crystallogr.* 2003, **36**, 7.

Table S1 : Crystallographic Parameters for recorded at 173 K. (first column = partially squeeze structure, only one NH₄⁺ cations were refined)

Formula	C ₁₈ H ₄₀ Cr ₃ Mn ₂ N ₅ O ₄₆
Molecular weight	1328.43
Crystal system	monoclinic
Space group	C2/c
a(Å)	8.8345(11)
b(Å)	35.591(4)
c(Å)	16.246(2)
α(deg)	90
β(deg)	93.437(6)
γ(deg)	90
V(Å ³)	5098.8(10)
Z	4
violet	Colourless
Crystal dim (mm ³)	0.12 x 0.03 x 0.02
Dcalc (gcm ⁻³)	1.731
F(000)	2692
μ (mm ⁻¹)	1.224
Wavelength (Å)	0.71073
Number of data meas.	15489
Number of data with I > 2σ(I)	4235
R	0.0732
Rw	0.1734
GOF	1.066
Largest peak in final difference (eÅ ⁻³)	-0.862 and 0.459

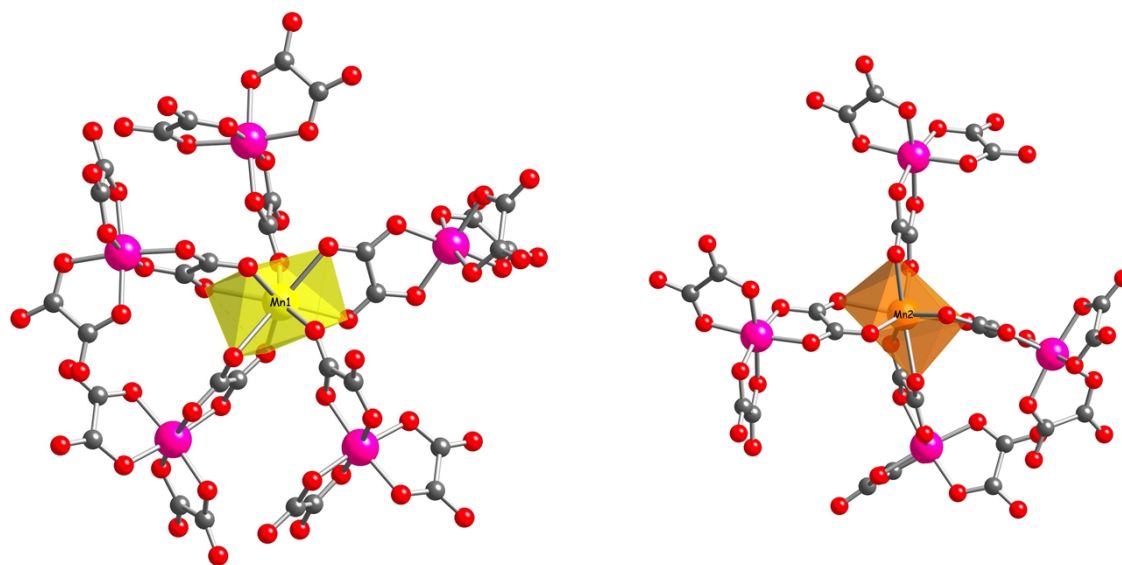


Figure S1: Representation of the Mn coordination environments in **1** for Mn1 (left) and Mn2 (right).

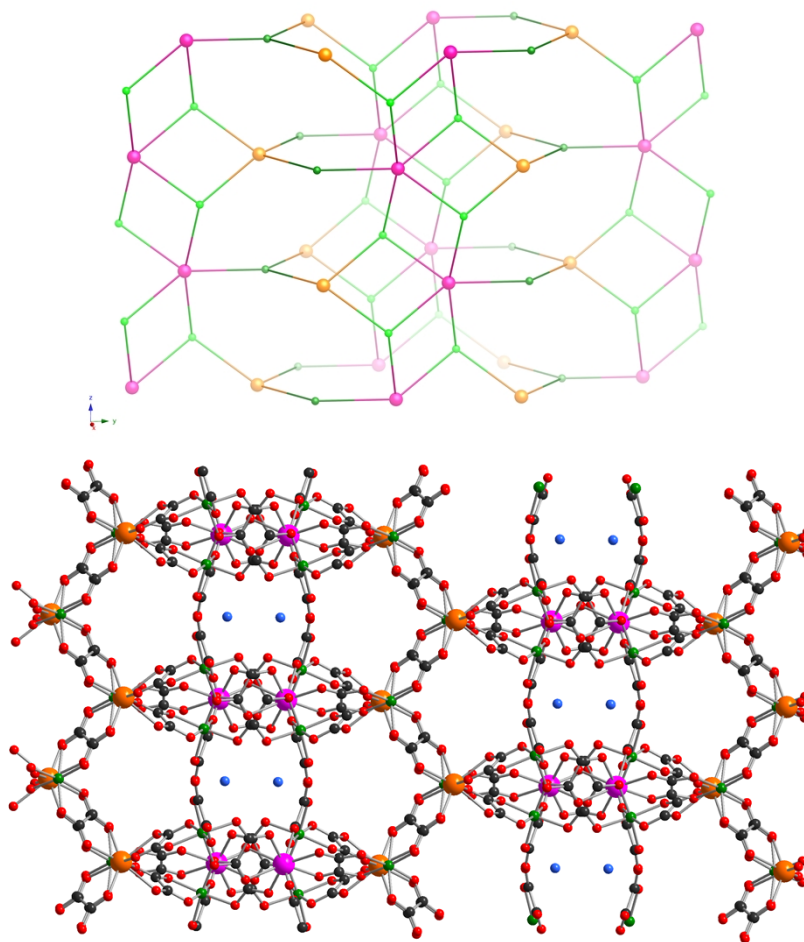


Figure S2: Topological representation of the metallic network encountered in 1 (fuschia= Mn1, gold = Mn2, light green= Cr1, dark green= Cr2; top); Representation of the structure of 1 with the resolved ammonium ions in the cavities of the network (bottom).

Powder X-ray Diffraction (PXRD)

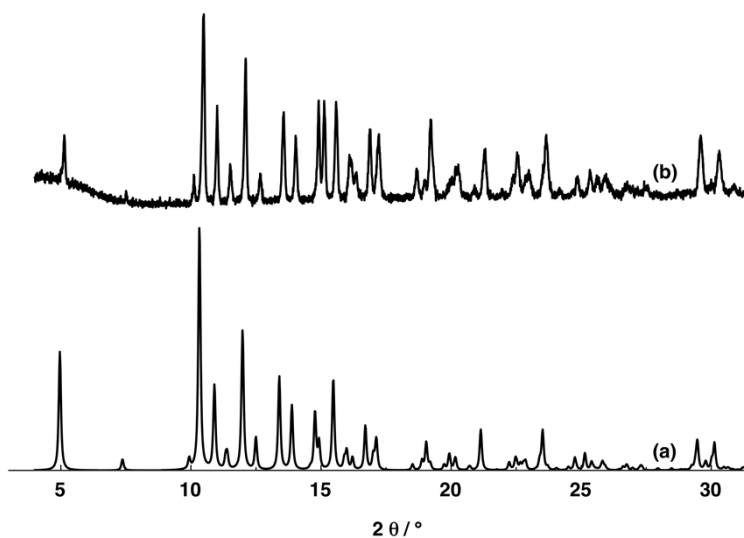


Figure S3: Comparison of the calculated (a) and observed (b) PXRD patterns for **1**.



Figure S4: Comparison of the simulated (a), observed dehydrated (b), observed rehydrated after 2h (c), and observed rehydrated after 24h (d), PXRD patterns for **1**.

Thermogravimetric (TGA) Studies

TGA measurements have been performed on Pyris 6 TGA Lab System (Perkin-Elmer), using a N_2 flow of 20 ml/mn and a heat rate of $4^\circ C/ mn$ (figure ESI-2).

The measurements reveal that **1** is stable up to $220^\circ C$. The first weight loss of 13.67% between $30-115^\circ C$ corresponds to the removal of 10 water molecules (calc.: 13.55%), that were refined by single-crystal XRD measurements. When dehydrated, the crystallinity of the compound dramatically decreases.

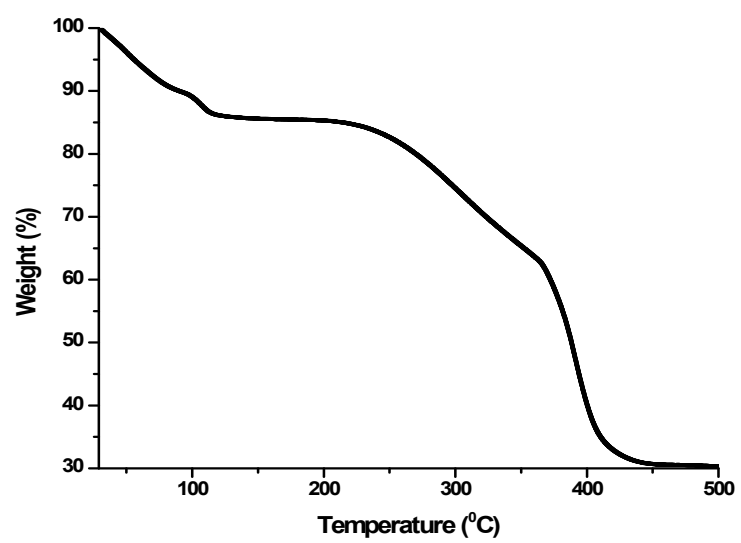


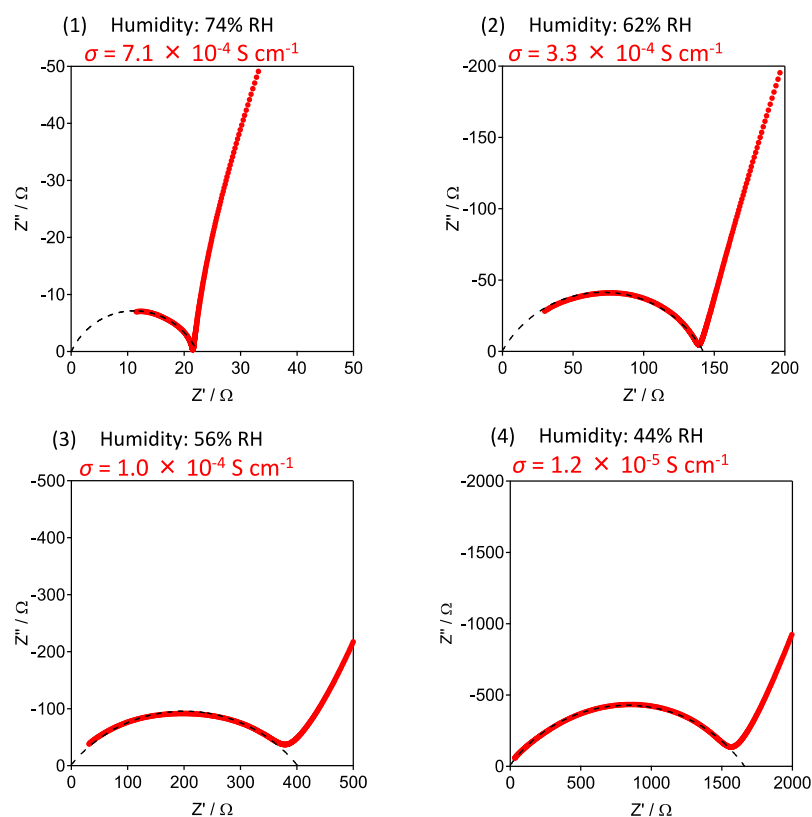
Figure S5: TGA trace for compound 1

Magnetic properties

Magnetic measurements were carried out on powdered samples of **1** whose quality has been checked by PXRD (see Figure ESI-1) using a Quantum Design SQUID magnetometer. Variable-temperature (1.8-300 K) direct current magnetic susceptibility (dc) was measured under applied magnetic fields of 0.1 T. The susceptibility data were corrected for the diamagnetism of the constituent atoms and the sample holder. The field cooled (FC) behaviour was established by measurements between 14 and 2 K in a 0.1 T field.

Proton Conductivity Measurements

The conductivity measurements were carried out using a an Agilent 4294A precision impedance analyzer by a quasi-four-probe method in the frequency range from 40 Hz to 110 MHz. For the measurement, the powdered sample was compressed into diameter of 7 mm and thickness of 0.10 cm using a sample holder between two steel electrodes. The humidity of the sample holder for each measurement was tuned using dry N₂ that had been passed through water or a saturated aqueous solution of NaBr. The measurement of the conductivity was performed between 74 and 9.5 %RH and fitted accordingly (Fig. S5).



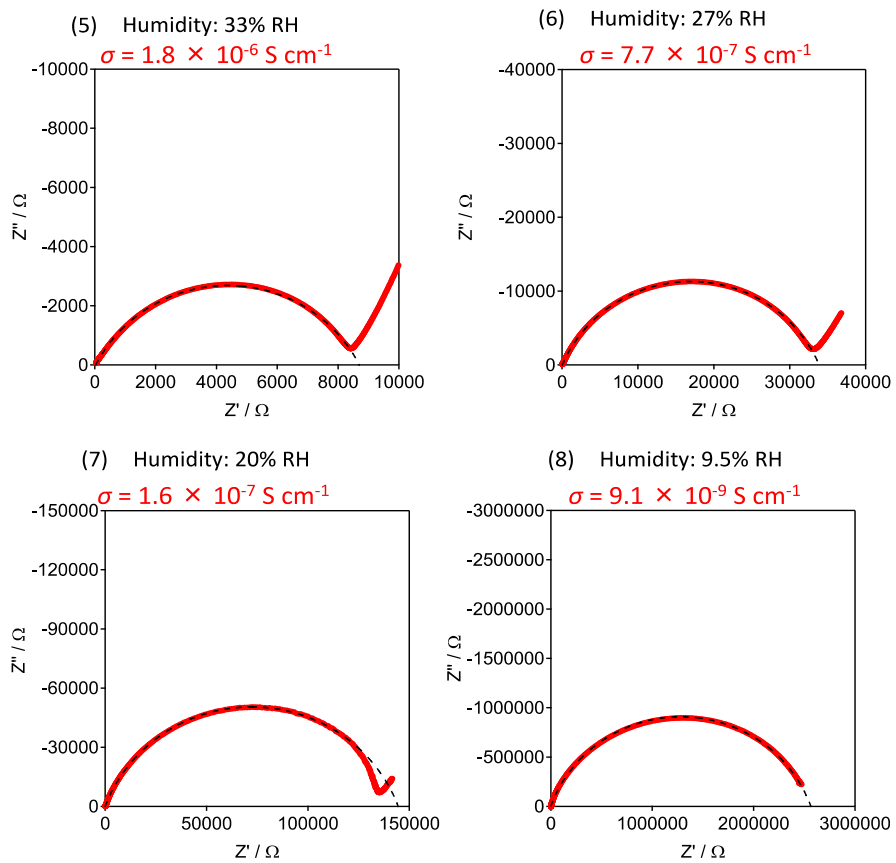


Figure S6: Conductivity of **1** for high values of %RH.