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Symmetric, triply interlaced 3-D anionic MOF that exhibits both magnetic order and SMM behaviour

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I. Preparation, elemental analysis, IR spectra and TGA for compound 1.

Preparation of compound 1: Reagents were commercial and used as received. No additional purifications were necessary.

The polymer $K_{4n}[[Co_4(C_6H_4O_7)_4]\mu-[Co(H_2O)_4]_2]_n \cdot 8n(H_2O)$ **1** was obtained by addition of $CoCO_3 \cdot xH_2O$ (o.5 g, 3.7 mmol, for x = 1) to a stirred aqueous solution of citric acid monohydrate (10 mL, 0.47 M). After the reaction was complete, the resulting mixture was gravity-filtered and then an aqueous solution of KOH (0.5 M) was added dropwise until a pH of 7-8 was reached. The solvent was evaporated at 90 °C to reach the initial volume. The addition of a commercial solution of 1,2propanediol (99% pure) (H₂O/1,2-propanediol 2/1) gives well-formed red-pink cubic-shaped crystals of **1** after several days at room temperature (0.47 g, 0.30 mmol). Yield: 48.7%.

Elemental analysis of 1 was carried out on a Perkin Elmer 2400 CHNS/O analyser. Calculated analysis for $(C_{24}H_{48}C_{06}K_4O_{44})$ is: C, 18.59%; H, 3.12%. Results obtained were C, 18.59%; H, 3.12%.

FT-IR spectra of 1 were measured on a Perkin-Elmer Spectrum 100 FT-IR Spectrophotometer with ATR accessory in the range of 4000 - 300 cm⁻¹ (Figure S1).



Figure S1. IR spectrum of 1.

IR (neat compound, cm⁻¹): ν (OH) 3414.80 (w) and 3102.34 (w); ν (C=O) 1541.71 (w); ν (C-H) 1427.52 (w), 1410.84 (w) and 1382.12 (w); ν (CO) 1082.11 (t).

Thermogravimetric analysis (TGA) was carried out using a Universal V4.5A TA Instrument, model 2960 SDT V3.0F in the range of 25 - 500 °C (Figure S2).



Figure S2. TGA for 1.

II. Crystallography and basic structural features of 1.

Single crystal X-Ray diffraction was performed in an Xcalibur S₃ CCD-based four-circle diffractometer (Oxford Diffraction and Agilent Technologies). The program CrysAlis Pro¹ was used for data collection and processing. The structure was solved ab initio by direct methods² and refined by full-matrix least-squares analysis.³ Non-hydrogen atoms were refined with anisotropic displacement parameters. The methylene H atoms of the citrate ligands were placed at idealized positions and refined as riders on their respective parent C atoms with isotropic displacement parameters set to 1.2 times the equivalent isotropic U of the C atom. Hydrogen atoms of the water molecules were found in a difference map. Their isotropic displacement parameters were set to 1.2 times the equivalent isotropic U of the corresponding O atom. Material for publication was prepared using Diamond⁴ and Mercury.⁵ Data collection and structure solution information and refinement details are shown in Table S1.

Powder diffraction measurements were made by the X-ray Diffraction and Fluorescence Service of the Servicio General de Apoyo a la Investigación of the University of Zaragoza, using a Rigaku D/MAX-2500 diffractometer equipped with Cu Kα radiation.

Table S1. Crystallographic data for 1.					
Formula	^a C ₂₄ H ₄₈ Co ₆ K ₄ O ₄₄	Crystal size (mm ³)	0.41 X 0.32 X 0.22		
fw (g mol ⁻¹)	1550.60	θ(min,max) (°)	4.385, 30.740		
Radiation	X-Rays (Mo k α)	Reflns collected	13258		
Wavelength (Å)	0.71073	Indep reflns	3514		
Crystal system	tetragonal	$R(int), R(\sigma)$	0.0137, 0.0131		
Space group	I 41/a	Completeness (<i>θ</i>)	0.996 (27.500)		
temp (K)	105(1)	Abs corr	multi-scan		
a (Å)	20.7872(3)	T(min,max)	0.7458, 1.0000		

c (Å)	11.3290(2)	restraints/parms	0, 223		
V (Å ³), Z	4895.35(13), 4	Goodness-of-fit	1.139		
ρ calc (Mg/m³)	2.104	R1, wR2 (obs) ^b	0.0294, 0.0730		
μ (mm ⁻¹)	2.451	R1, wR2 (all)	0.0301, 0.0734		
F (000)	3128	∆⁄ơ(max,mean)	0.002, <0.001		
		<i>Δρ</i> range (e Å ⁻³)	0.661, -0.555		
${}^{a}K_{4n}\{[Co_{4}(C_{6}H_{4}O_{7})_{4}]\mu-[Co(H_{2}O)_{4}]_{2}\}_{n}\cdot 8n(H_{2}O)$ ${}^{b}threshold I > 2\sigma(I).$					

Compound 1 crystallises in the tetragonal system, space group I_{4_1}/a . The asymmetric unit was chosen so as to permit the simplest possible description of the extended structure, with the Co_4O_4 cubane unit centred at (1/2, 1/2, 1/2). For this purpose it was necessary to use Origin Choice 1 for this space group as given in the International Tables.⁶



Figure S3: Schematic representation of three 3-D polymeric nets showing their interpenetration, viewed along a direction near the *a*-axis. Only the cubes, each represented by a point at its centre of gravity (Cg1), the Co(II) units (bold circles) and the bridging O-C-O atoms are represented. The coordinates of the three labeled Cg1 are (red) *xyz*, (blue) *x*, *y*, *1*+*z*, and (green) *x*, *y*, *2*+*z*, in which *xyz* is (1/2, 1/2, 1/2).



III. Complementary magnetic measurements of 1

Figure S4: Magnetization versus field at low fields for 1.

Table S2. Energy barrier for previously reported Co_4O_4 cubane core SMM				
Formula	ΔΕ	τ₀		
[NMe4]3Na{Co4(cit)4[Co(H2O)5]2} ·7H2O 7	26 K	8.2 × 10-9 s		
[(NMe4)4{Co4-(cit)4[Co(H2O)5]2}]·6H2O 7	32K	2.1× 10-9 s		
[C(NH2)3]8{Co4(cit)4} ·4H2O ⁸	24 K,	3.4 × 10-8 s		



Figure S5. Simulated (red) and experimental (room temperature, green) powder diffraction patterns for **1**.



Figure S6. Environment of the two partially occupied K⁺ sites in the structure of **1**. K1, K2 occupancies are 0.87 and 0.13, respectively. O5 and O7 are peripheral citrate carboxylate oxygen atoms from cubanes. O1W and O2W are from aqua ligands bound to bridging Co2. The remaining oxygen atoms are from uncoordinated water.

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