

Supplementary Information

Synthesis, structure and magnetic properties of a novel high-nuclearity oxo-carboxylate $[\text{Zn}_x\text{Co}_{13-x}(\mu_4\text{-O})_4(\text{O}_2\text{CPh})_{18}]$ cluster

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General Remarks: All manipulations were conducted under nitrogen by using standard Schlenk techniques. Cobalt benzoate was prepared according to the literature method.^[1] Solvents were dried and distilled prior to use. Deionized water was deoxygenated by vacuum treatment upon sonication followed by bubbling of N₂.

IR spectra were recorded with an FTIR Bruker-Tensor II System.

PXRD measurement was performed using PANalytical Empyrean diffractometer equipped with Ni-filtered Cu K α radiation (40 kV, 40 mA). Sample for the PXRD analysis was sealed between two layers of kapton foil and measured in transmission geometry.

Optical absorption spectrum was collected on a Shimadzu UV-2600 spectrophotometer.

Magnetochemical Measurements. The magnetic data of **1** were collected using a Quantum Design MPMS-5XL SQUID magnetometer. The polycrystalline sample was compacted and immobilized into a cylindrical PTFE capsule. The data were recorded as a function of the magnetic field (0.1–5.0 T at 2.0 K) and the temperature (2–290 K at 0.1 T), and were corrected for the diamagnetic contributions of the sample holder and the compound ($\chi_{m,dia} = -1.56 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$).

Synthesis of 1: Et₂Zn (2.18 M in hexane, 0.5 mL, 1.09 mmol) was added dropwise to a solution of benzoic acid (133 mg, 1.09 mmol) in THF (10 mL) at –78 °C. The mixture was warmed to room temperature, and after 4 h cobalt benzoate (328 mg, 1.09 mmol) was added. The suspension was then stirred for few minutes until cobalt benzoate had dissolved. Afterwards, to a vigorously stirred reaction degassed water (10 μ L, 0.55 mmol) was introduced. After 4 hours the mixture was dried under vacuum for 1 hour and subsequent recrystallized from 1:1 CH₂Cl₂/hexane mixture at room temperature for 1 d. Cobalt-blue crystals of **1** were obtained in a moderate isolated yield (228 mg, ~42% based on zinc).

Elemental analysis, calc.(found), %: Zn, 11.74 (11.63 \pm 0.17); Co, 13.99 (13.73 \pm 0.17); C 48.53(48.7 \pm 0.26); H 3.17 (3.3 \pm 0.05).

We note that the conducted FT-ICR mass spectrometry analysis on single crystals of **1** appeared as a featureless method and provided only fragmentated species with the molecular ion peaks less than the molecular weight (~3055 g/mol). The positive and negative ionization analyses are shown in Figure S5 and S6, respectively.

[1] K. S. Gavrilenko, S. V. Punin, O. Cador, S. Golhen, L. Ouahab, V. V. Pavlishchuk, *J. Am. Chem. Soc.*, **2005**, 127, 12246–12253.

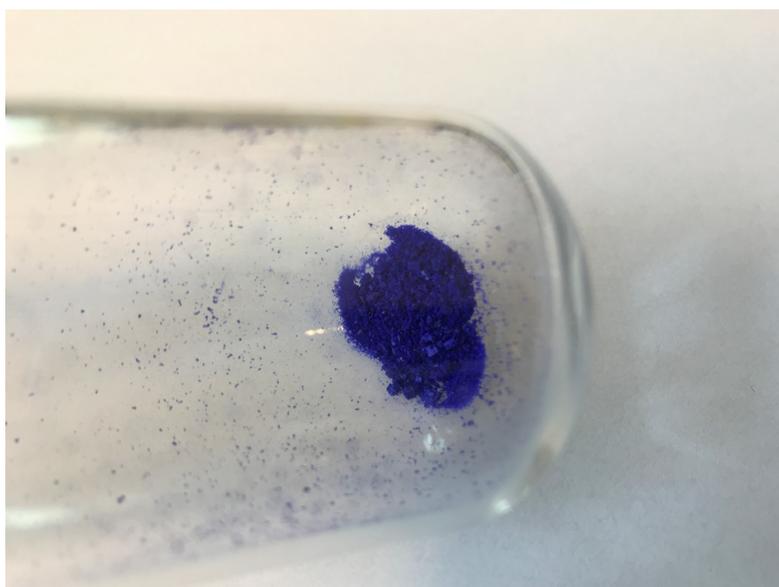


Figure S1. Image of single crystals of **1**.

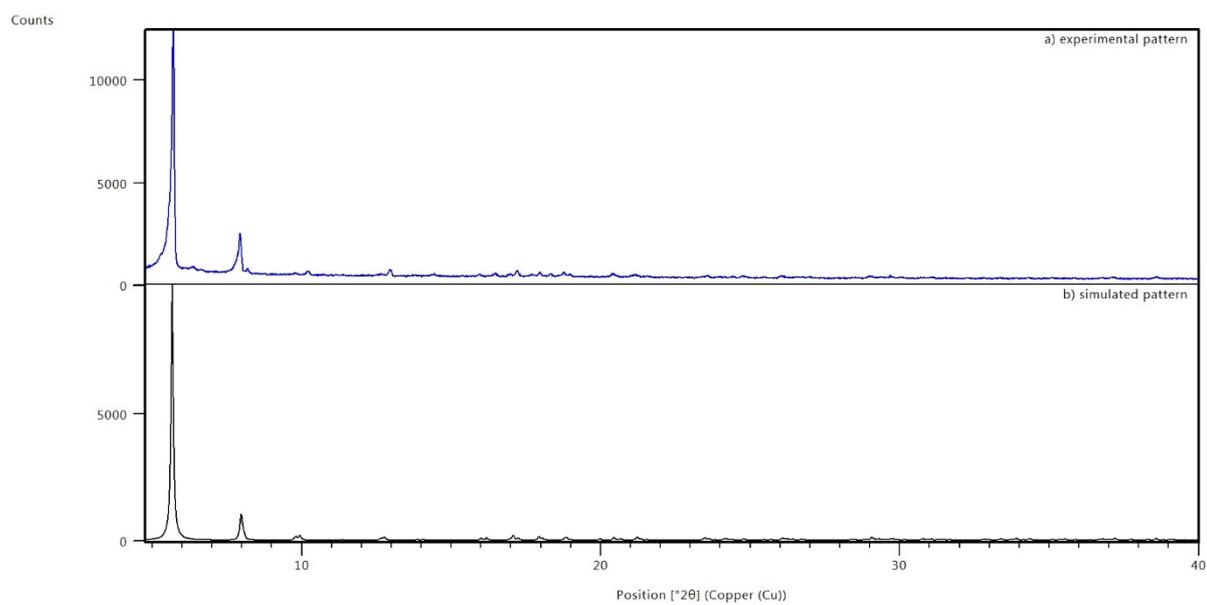


Figure S2. a) Experimental and b) simulated PXRD pattern of **1**.

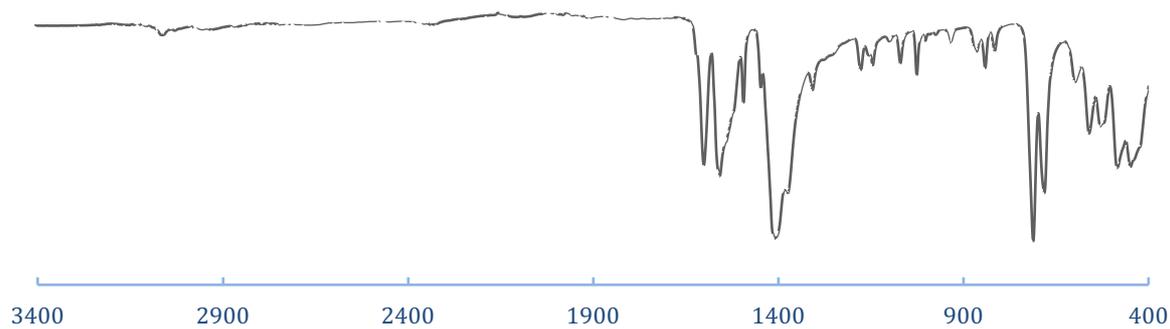


Figure S3. Fourier-transform infrared spectroscopy (FTIR) of **1**.

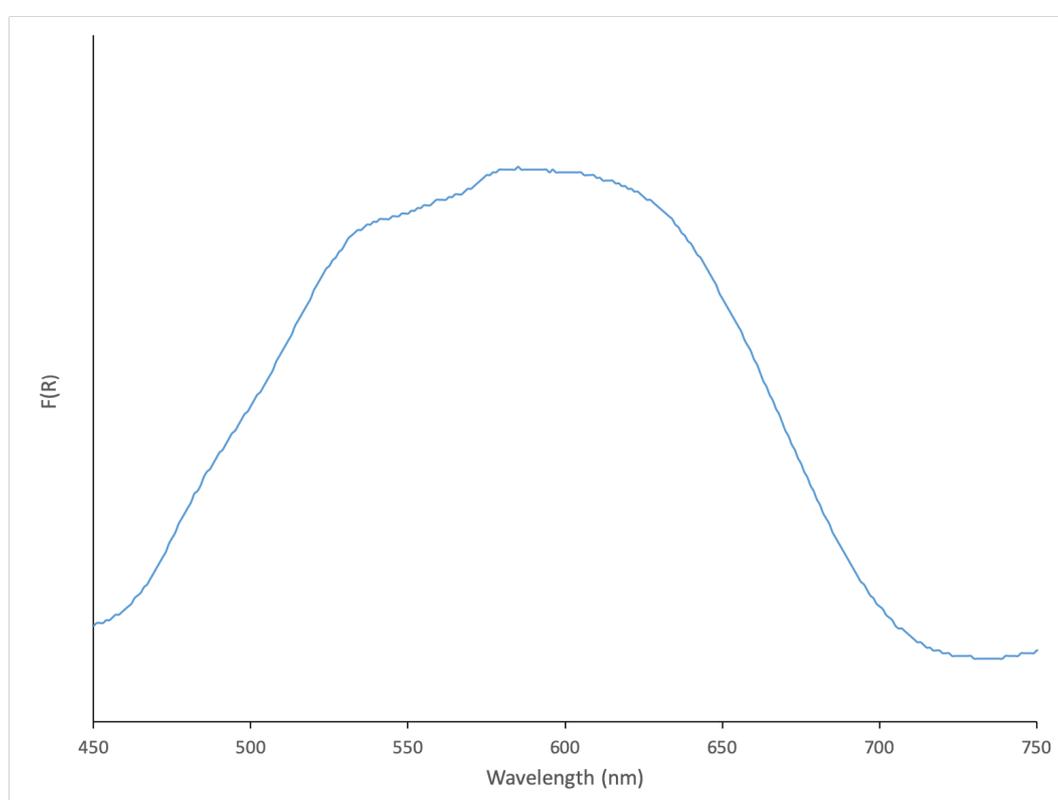


Figure S4. UV-vis diffuse reflectance spectroscopy of **1**.

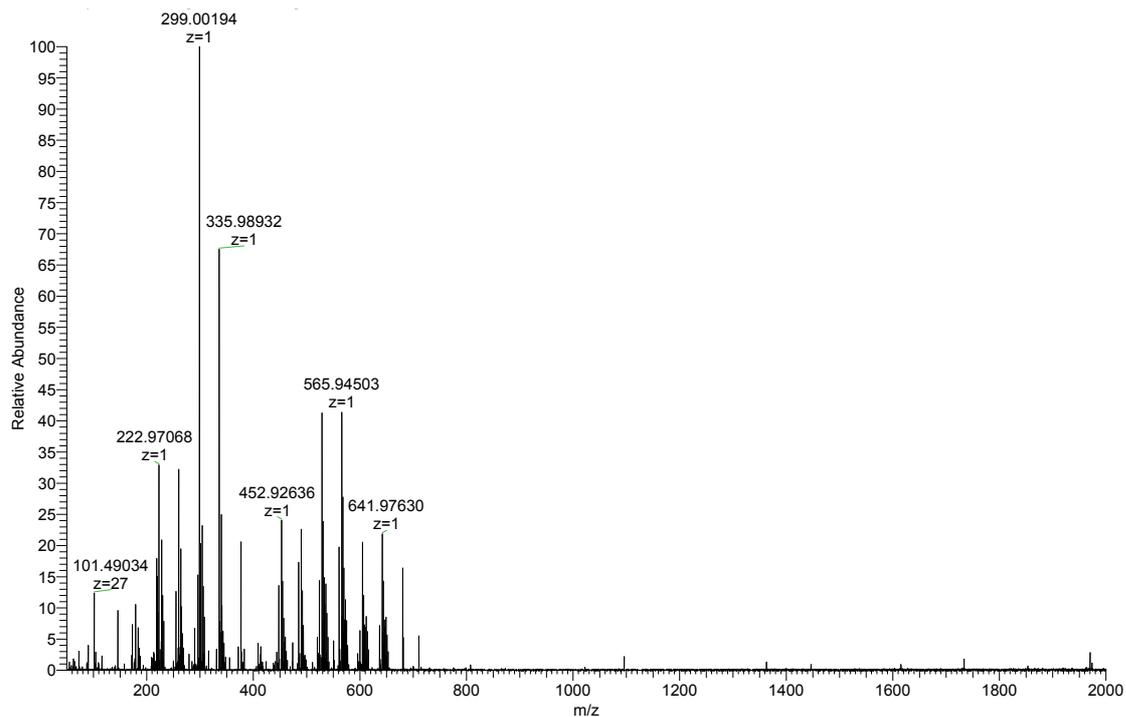


Figure S5. The positive FT-ICR mass spectrum of **1**.

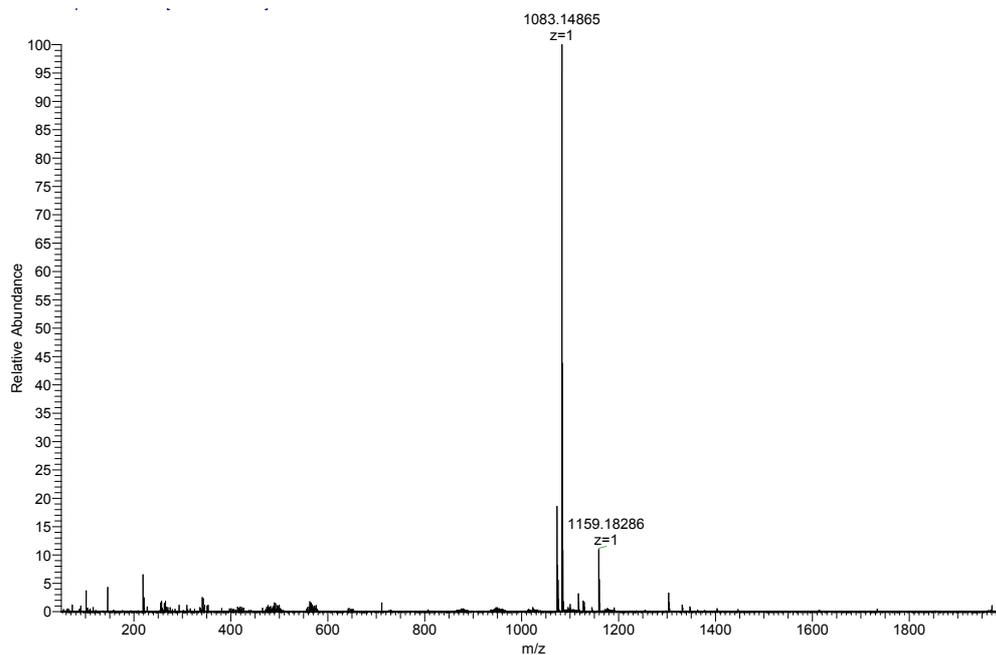


Figure S6. The negative FT-ICR mass spectrum of **1**.

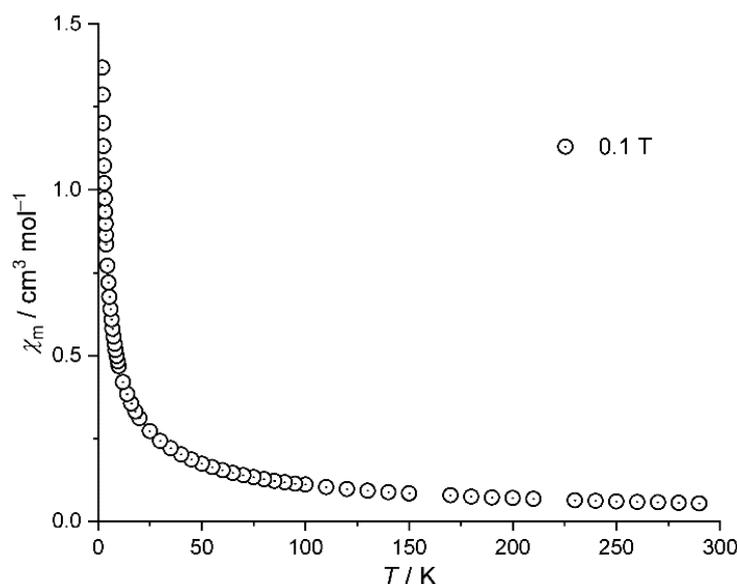


Figure S7. The plot of χ_m vs T .

Single-Crystal X-ray Diffraction:

The crystal was selected under Paratone-N oil, mounted on the nylon loops and positioned in the cold stream on the diffractometer. The X-ray data for complex **1** were collected at 100(2) K on a SuperNova Agilent diffractometer using MoK α radiation ($\lambda = 0.71073$ Å). The data were processed with *CrysAlisPro*.^[2] Structure was solved by direct method and refined using *SHELXL-2016/4*.^[3] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added to the structure model at geometrically idealized coordinates and refined as riding atoms. For compound **1** we have observed significant residual electron densities within the pores. Therefore, the initial dataset was subjected to the SQUEEZE function within the PLATON software.^[4]

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). CCDC – 1917490.

[2] Agilent Technologies, *CrysAlisPro*, Version 1.171.35.21b

[3] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122

[4] A. L. Spek, *Acta Cryst.* **2015**, *C71*, 9

Crystal data for **1**, $C_{126}H_{90}O_{40}Co_6Zn_7$: $M = 3055.14$, crystal dimensions $0.12 \times 0.08 \times 0.04 \text{ mm}^3$, trigonal, space group $R\bar{3}$ (no. 146), $a = 22.1339(5) \text{ \AA}$, $b = 22.1339(5) \text{ \AA}$, $c = 26.6450(6) \text{ \AA}$, $U = 11304.8(6) \text{ \AA}^3$, $Z = 3$, $F(000) = 4614$, $D_c = 1.346 \text{ g cm}^{-3}$, $T = 100(2) \text{ K}$, $\mu(\text{Mo-K}\alpha) = 1.801 \text{ mm}^{-1}$, $\theta_{\text{max}} = 28.863^\circ$, 10951 unique reflections. Refinement converged at $R1 = 0.0682$, $wR2 = 0.1471$ for all data and 539 parameters ($R1 = 0.0512$, $wR2 = 0.1351$ for 8939 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal 1.082. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P)]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = $+1.20 / -0.80 \text{ e\AA}^{-3}$.

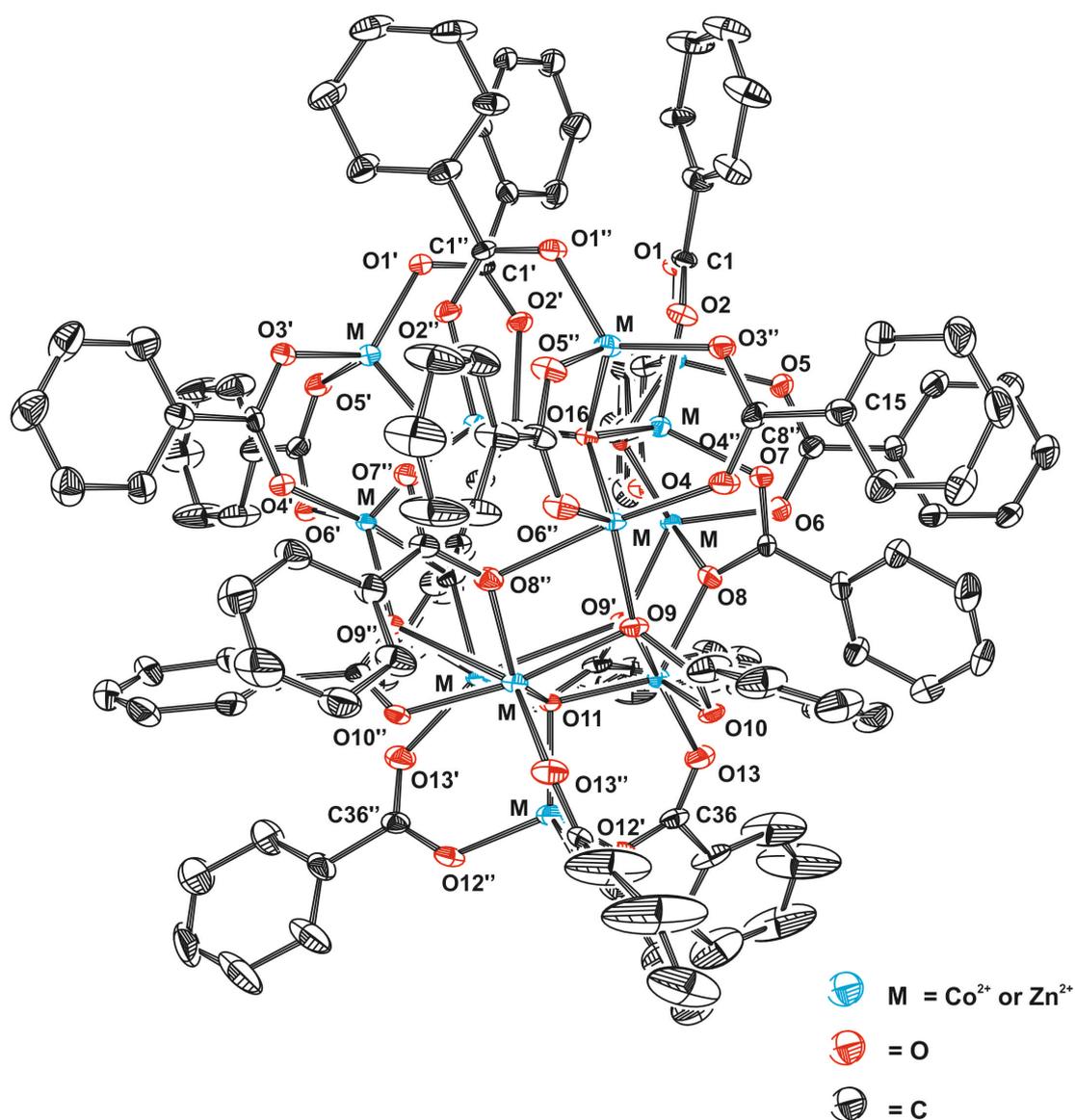


Figure S8. ORTEP diagram of molecular structure of **1** with thermal ellipsoids set at 35% probability; hydrogen atoms have been omitted for clarity. Operators for generating equivalent atoms: $(-x+y+I, -x+I, z)$, $(-y+I, x-y, z)$.