Electronic Supporting Information

Tetrahedral μ_4 -chloride and *in situ* generated octahedral μ_6 -sulfide templating Co₈ complexes with different distortions of the cube

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Measurement details

All starting reagents were of A.R. grade and used as purchased without further purification. The X-ray powder diffraction patterns (XRPD) were conducted at 40 kV and 100 mA on a Rigaku D/Max-2500 diffractometer, using a graphite monochromator and a Cu-target tube under ambient conditions. Elemental analyses of C, H and N were determined on a Perkin-Elmer 240 Elemental analyzer. IR spectrum was recorded with KBr pellets on a Tensor 27 OPUS (Bruker) FT-IR spectrometer in the 4000-400 cm⁻¹ range. The energy dispersive spectroscopy (EDS) analyses of single crystals were determined on a JEOLJSM6700F field-emission scanning electron microscope equipped with an Oxford INCA system. Thermogravimetric analysis (TGA) experiments were recorded at a heating rate of 10 °C /min from 40 to 800 °C on a NETZSCH STA 449F3 thermal analyzer under N₂. The crystal data were collected on a Bruker Apex II CCD diffractometer. Magnetic susceptibility measurements were performed on a powder sample fixed with Eicosane on a Quantum Design MPMS-XL7 SQUID magnetometer.

Synthesis of Complex [Cl@Co₈ (TEOA)₄(CH₃CN)Cl₃] (1)

A mixture of CoCl₂·6H₂O (1 mmol, 238 mg), triethanolamine (H₃TEOA) (1 mmol, 149 mg), CH₃ONa (1mmol, 54 mg), acetonitrile (6 mL) and methanol (6 mL) was sealed in a Teflon-lined stainless vessel (15 mL) and heated at 120 °C for 48 h under autogenous pressure. The vessel was then cooled by air cooling to room temperature spontaneously. Dark-red and cubic single crystals were obtained by filtration, washed with methanol, and dried in air. Yield: 0.101 g (65%, based on Co). Elemental analysis: calcd (found) for $C_{26}H_{51}Cl_4N_5O_{12}Co_8$ (%): C, 25.20(25.32); H, 4.15(4.02); N, 5.65(5.76). IR (KBr, cm⁻¹): 3367(w), 3140(w), 2858(m), 1593(s), 1458(w), 1350(s) and 1022(s).

Synthesis of Complex [S@Co₈(DEOA)₆(NCS)₂] (2)

A mixture of $CoCl_2 \cdot 6H_2O$ (1 mmol, 238 mg), diethanolamine (H₂DEOA) (2 mmol, 210 mg), CH₃ONa (2 mmol, 108 mg), KSCN (0.5 mmol, 49 mg), methanol (10 mL) was sealed in a Teflon-lined stainless vessel (15 mL) and heated at 140 °C for 48 h under autogenous pressure. The vessel was then cooled by air cooling to room temperature spontaneously. Dark-red and cubic single crystals were obtained by filtration, washed with methanol, and dried in air. Yield: 0.110 g (71%, based on Co).

Elemental analysis: calcd (found) for $C_{26}H_{48}N_8O_{12}S_3Co_8$ (%): C, 25.34(25.42); H, 3.93(3.79); N, 9.09(9.16). IR (KBr, cm⁻¹): 3360(m), 2945(w), 2881(m), 2829(m), 1472(w), 1440(m) and 1056(s).

X-ray Crystallography Data

All data were collected on a Bruker Apex II CCD diffractometer equipped with a graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at room temprature. All the structures were solved by direct methods and refined on F^2 by full matrix least-squares using new SHELXL program.^{1, 2} Nonhydrogen atoms were refined anisotropically, and the hydrogen atoms were added theoretically, riding on the concerned atoms and refined with fixed thermal factors. CCDC 1974403 (1) and 1973952 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

	1	2
Empirical formula	$C_{26}H_{51}Cl_4Co_8N_5O_{12}\\$	$C_{26}H_{54}N_8O_{12}S_3Co_8\\$
Formula weight (g mol ⁻¹)	1238.95	1238.39
Crystal system	Trigonal	Trigonal
Space group	R3m	$R\bar{3}$
<i>T</i> (K)	296 K	296 K
<i>a</i> [Å]	14.8782(8)	13.4577(3)
<i>b</i> [Å]	14.8782(8)	13.4577(3)
<i>c</i> [Å]	16.9496(9)	20.3224(4)
α [°]	90	90
β[°]	90	90
γ [°]	120	120
V[Å ³]	3249.3(4)	3187.48(16)
Ζ	3	3
$ ho_{ m calcd} [{ m g} { m cm}^{-3}]$	1.899	1.937
F (000)	1866.0	1869.0

 Table S1. Crystallographic data for complexes 1 and 2.

Reflns collected	13610	13093
Unique reflns	1996	1766
$R_{ m int}$	0.0465	0.0156
Parameters / restraints	125/4	87/0
GOF	1.329	1.242
R_1 [all data]	0.0284	0.0480
R_1 [I>2sigma(I)]	0.0379	0.0371
wR_2 (all data)	0.1198	0.1492
wR_2 (I>2sigma(I))	0.0819	0.1199
Largest diff. peak/hole [e Å ⁻ ³]	0.899 /-1.272	1.380/-1.289



Fig. S1 IR spectra of 1.



Fig. S2 IR spectra of 2.



Fig. S3 TG curves for complexes 1 and 2.



Fig. S4 X-ray powder diffraction (XRPD) patterns of 1 measured in air.



Fig. S5 X-ray powder diffraction (XRPD) patterns of 2 measured in air.



Fig. S6 EDS analyses for 2.

Magnetic Properties

Magnetic susceptibility measurements have been carried out with a Quantum Design MPMS-XL7 SQUID magnetometer upon cooling from 300 to 2 K in variable applied fields. Ac susceptibility measurements have been performed at frequencies of between 1 and 1500 Hz with an ac field of 3.5Oe and with variable dc applied field. Powder samples were embedded in icosane to avoid any field induced crystal reorientation. A diamagnetic correction has been calculated from Pascal constants and embedding eicosane has been applied to the observed magnetic susceptibility.



Fig. S7 The χ_m^{-1} versus *T* plots and Curie-Weiss fitting of **1** and **2**.



Fig. S8 Isothermal magnetization curves for 1 collected from 2 K to 5 K.



Fig. S9 Isothermal magnetization curves for 2 collected from 2 K to 5 K.



Fig. S10 Magnetic hysteresis loop for 1 at 2 K.

References

- G. M. Sheldrick, Acta Crystallographica Section A: Foundations of Crystallography, 2008, 64, 112-122.
- 2. G. M. Sheldrick, Acta Crystallographica Section C: Structural Chemistry, 2015, 71, 3-8.