## A coordinatively saturated sulfate encapsulated in a metal-organic framework functionalized with urea hydrogen-bonding groups

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## **Supplementary Data**

Synthesis. Tris(2-aminoethyl)-amine, 3-cyanophenyl isocyanate, and silver sulfate were purchased from Aldrich and used as received.

1b. Tris(2-aminoethyl)-amine (0.44 g, 3 mmol) in 5 mL CHCl<sub>3</sub> was added over 3cyanophenyl isocyanate (1.30 g, 9 mmol) in 30 mL CHCl<sub>3</sub>. A white precipitate formed immediately. The mixture was stirred at room temperature under Ar for 18 h, then filtered and washed with CHCl<sub>3</sub> to give **1b**·H<sub>2</sub>O (1.53 g, 85%). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$ 2.62 (t, J = 6.4 Hz, 6H, CH<sub>2</sub>), 3.21 (q, J = 5.9 Hz, 6H, CH<sub>2</sub>), 6.32 (t, J = 5.2, 3H, NH), 7.31 (d, J = 6.9 Hz, 3H, Ph), 7.40 (t, J = 7.9 Hz, 3H, Ph), 7.54 (d, J = 8.2, 3H, Ph), 7.91 (s, 3H, Ph), 8.91 (s, 3H, NH); <sup>13</sup>C NMR (100.61 MHz, DMSO-*d*<sub>6</sub>) δ 37.6 (CH<sub>2</sub>), 53.7 (CH<sub>2</sub>), 111.4 (CN), 119.0 (Ph), 120.1 (Ph) 122.2 (Ph), 124.4 (Ph), 130.0 (Ph), 141.4 (Ph), 155.0 (C=O). M.p. = 208-209 °C. Anal. Calcd. for  $C_{30}H_{32}N_{10}O_4$ : C, 60.39; H, 5.41; N, 23.48. Found: C, 60.20; H, 5.11; N, 23.10.

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**2.** A solution of **1b**·H<sub>2</sub>O (0.060 g, 0.1 mmol) in 20 mL acetone and 5 mL water was added over a suspension of  $Ag_2SO_4$  (0.015 g, 0.05 mmol) in 1 mL water. Slow evaporation of acetone in the dark over a period of four days yielded **2** (0.056 g, 69%) as a white crystalline solid that was collected by filtration and washed with acetone. The powder X-ray diffraction pattern of the bulk material corresponded with the calculated pattern from the single-crystal X-ray diffraction data. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  2.11 (s, 4.6H, acetone), 2.50 (t, *J* = 5.2 Hz, 6H, CH<sub>2</sub>), 3.19 (q, *J* = 5.2 Hz, 6H, CH<sub>2</sub>), 7.14 (m, 6H, Ph), 7.16 (s, 3H, NH), 7.57 (d, *J* = 6.7 Hz, 3H, Ph), 7.76 (s, 3H, Ph), 9.39 (s, 3H, NH); <sup>13</sup>C NMR (100.61 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  37.3 (CH<sub>2</sub>), 54.0 (CH<sub>2</sub>), 111.1 (CN), 118.9 (Ph), 120.0 (Ph) 122.0 (Ph), 124.1 (Ph), 129.5 (Ph), 141.4 (Ph), 154.9 (C=O). M.p. = 192-195 °C (dec). Anal. Calcd. for [Ag<sub>2</sub>SO<sub>4</sub>(**1b**)<sub>2</sub>]·(acetone)<sub>1.5</sub>·(H<sub>2</sub>O)<sub>3.7</sub>: C, 47.74; H, 4.75; N, 17.26. Found: C, 48.25; H, 4.71; N, 17.50.

**X-Ray Crystallography.** Single-crystal X-ray data were collected on a Bruker SMART APEX CCD diffractometer with fine-focus  $Mo_{k\alpha}$  radiation ( $\lambda = 0.71073$  Å), operated at 50 kV and 30 mA. Structure **1b** was solved by direct methods and structure **2** was solved by the Patterson method. Both structures were refined on  $F^2$  using the SHELXTL<sup>S1</sup> software package. Absorption corrections were applied using SADABS, part of the SHELXTL package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and refined with a riding model, except for the hydrogen atoms on one of the water molecules in **2**, which could not be located. The severe disorder of the included acetone in **2** prevented proper refinement of its atomic positions. The corresponding residual electronic density was therefore treated with SQUEEZE, part of the PLATON software package,<sup>S2</sup> which found 45 e/unit cell,

corresponding to 1.4 molecules of acetone (1.5 found by NMR). One of the CN ligands in **1b** is disordered over two sites, with occupancies of 44% and 56%. Pertinent crystallographic data for **1b** and **2** are listed in Table S1.

	1b	2
formula	$C_{30}H_{30}N_{10}O_{3}\\$	$C_{30}H_{34}N_{10}O_7S_{0.5}Ag$
М	578.64	770.57
crystal size [mm]	0.21×0.07×0.07	0.15×0.12×0.05
crystal habit	colorless needle	colorless plate
crystal system	triclinic	triclinic
space group	P-1	P-1
a [Å]	13.0827(18)	10.3995(12)
b [Å]	13.993(2)	13.5437(15)
c [Å]	18.274(3)	14.6455(17)
α [°]	73.362(3)	66.289(2)
β [°]	85.694(3)	76.241(2)
γ [°]	63.147(2)	87.576(2)
V [Å <sup>3</sup> ]	2853.9(7)	1831.2(4)
Z	4	2
T (K)	173(2)	173(2)
$\rho_{calcd} \left[g \ cm^{\text{-}3}\right]$	1.347	1.398
2θ <sub>max</sub> [°]	50.0	56.7
μ [mm <sup>-1</sup> ]	0.092	0.635
reflns collected	20199	22524
independent reflns	10021	9083
no parameters	794	465
R <sub>int</sub>	0.0651	0.0326
$R_1, wR_2 (I > 2\sigma(I))$	0.0752, 0.1920	0.0659, 0.1448
GOF	0.997	1.252

 Table S1. Crystallographic data for 1b and 2.



**FigS1** Hydrogen-bonded chain formed by **1b** in the solid state. Each ligand molecule forms a total of five urea---urea interactions: one intramolecular hydrogen bond between urea groups in the same ligand, and four intermolecular hydrogen bonds with urea groups from adjacent ligands.

**Job's Plot Analysis.** The1b:Ag<sub>2</sub>SO<sub>4</sub> binding stoichiometry in DMSO was determined by monitoring the changes in chemical shifts for the two NH protons from urea as a function of the molar fraction  $x = [1b]/\{[1b] + [Ag_2SO_4]\}$  (x = 1, 0.83, 0.66, 0.5, 0.33), with [1b] + [Ag<sub>2</sub>SO<sub>4</sub>] kept constant at 60 mM.



## References

- (S1) SHELXTL 6.12, Bruker AXS, Inc., Madison, WI, 1997.
- (S2) A. L. Spek,, Acta Crystallogr. A, 1990, 46, C34.