Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Eight coordination with bis(bidentate) bridging ligands: zeolitic topology versus square grid networks

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Syntheses.

$[Cd(pymc)_2]\cdot 7H_2O$ 1. Hydrothermal treatment of the mixture of $Cd(OAc)_2\cdot 2H_2O$(0.25 mmol, 0.067 g), pymCN (0.50 mmol, 0.053 g), H_2O (4 mL) and ethanol (4 mL) over 4 days at 115ºC yielded prism crystals of **1**. The yield was about 84% on pymCN. The phase purity of the bulk product was confirmed by powder X-ray diffraction (PXRD) experiments. Anal. Calcd. for $C_{10}H_{20}N_4O_{11}Cd$: C, 24.78; H, 4.16; N, 11.56. Found: C, 24.14; H, 4.39; N, 10.97. Main IR band (KBr, cm-1): 3467 (br), 3400 (br), 1628 (vs), 1574 (vs), 1440 (m), 1381 (s).

$[Cd(pymtz)_2]_n$ 2-α. Hydrothermal treatment of $CdCl_2$ (0.25 mmol, 0.057 g), pymCN (0.50 mmol, 0.053 g), NaN_3 (0.75 mmol, 0.049 g) and DMF (6 mL) over 4 days at 115 ºC yielded colorless crystals of **2-α**. The yield was about 46% on $CdCl_2$. The phase purity of the bulk product was confirmed by PXRD experiments. Anal. Calcd. for $C_{10}H_6N_{12}Cd$: C, 29.54; H, 1.49; N, 41.33. Found: C, 29.64; H, 1.79; N, 41.79. Main IR band (KBr, cm^{-1}): 1634 (w), 1570 (vs), 1526 (w), 1452(s), 1400 (vs), 1262 (m), 1187 (m), 1125 (m).

$[Cd(pymtz)_2]_n$ 2-β. Crystals of **2-β** are synthesized by a procedure similar to that for **2-α**, using H_2O (6 mL) instead of DMF (6 mL) as the solvent. Yield, 56%. The phase purity of the bulk product was confirmed by PXRD experiments. Found: C, 29.71; H, 1.60; N, 42.06: Main IR band (KBr, cm-1): 1630 (w), 1573 (vs), 1536 (m), 1444 (m), 1391 (s), 1309 (w), 1251 (w), 1197 (m), 1137(m).

Crystallographic Studies.

Diffraction intensity data were collected on a Bruker APEX II diffractometer equipped with a CCD area detector and graphite-monochromated Mo Kα radiation (λ = 0.71073). Empirical absorption corrections were applied using the SADABS program. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2.All non-hydrogen atoms in the structures, except for the disordered water oxygen atoms in **1**, were refined with anisotropic thermal parameters, and all the hydrogen atoms in the frameworks were placed in calculated positions and refined using the riding model. Although well shaped, the crystals of **1** scattered weakly and gave a data set of limited quality, which may be due to the presence of large cavities in the structure and heavily disordered water molecules in the cavities. The refinements were carried out using the reflections in the $3.44 \leq\theta\leq 24.03$ range. According to analytic data and TGA analysis, the compound contains about seven water molecules per Cd atom. We managed to locate the oxygen atoms of the disordered water molecules from the difference map. The final refinement was satisfactory, although the checkCIF/PLATON report gave some alerts of levels A and B arising from the limited resolution of the data set and the severe disorder of the water molecules in the large cavities.

Crystal data. 1: $C_{10}H_{20}N_4O_{11}Cd$, Mr = 484.70, cubic, space group $Im\bar{3}m$, a = 30.1740(10) Å, V = 27472.5(16) Å^3, Z = 48, μ(Mo Kα) = 1.003 mm^{-1}, ρ_{calcd} = 1.406 g cm^{-3}, T = 298 K, S = 0.959, $R1$ = 0.0540 for 952 observed reflections with $I > 2\sigma(I)$, and $wR2$ = 0.1582 for 2095 independent reflections. **2-α**: $C_{10}H_6N_{12}Cd$ Mr = 406.67, tetragonal, space group $I4_1/amd$, a = 6.4690(3) Å, c = 32.806(3) Å, V = 1372.86(16) Å^3, Z = 4, μ(Mo Kα) = 1.612 mm^{-1}, ρ_{calcd} = 1.968 g cm^{-3}, T = 273 K, S = 1.161, $R1$ = 0.0345 for 463 observed reflections with $I > 2\sigma(I)$, and $wR2$ = 0.0347 for 470 independent reflections. CCDC 666270 and 666271. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b717233h.

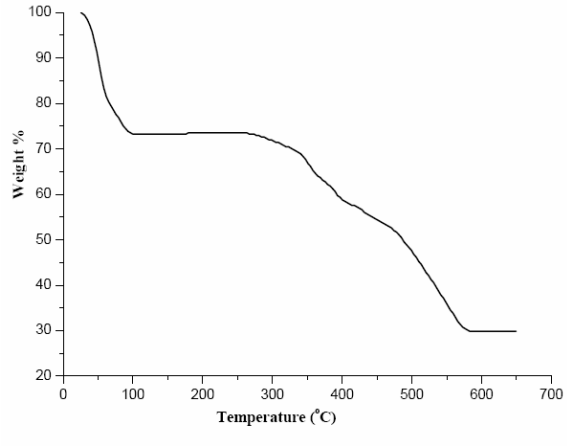

Figure S1. TGA of compound **1**.

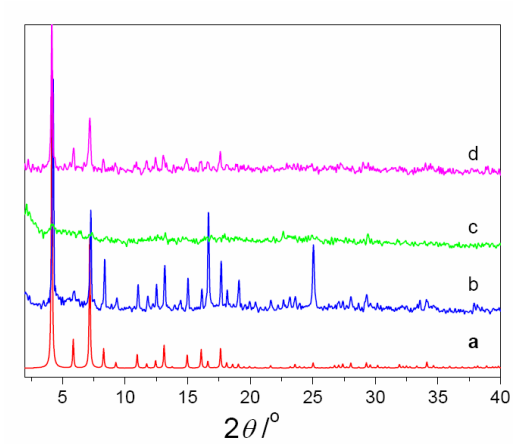

Figure S2. PXRD patterns for different samples of **1**. a, calculated; b, as-synthesized; c, evacuated by heating at 100°C for 1 h; d, immersed in water at 70°C for 24 h after evacuation.

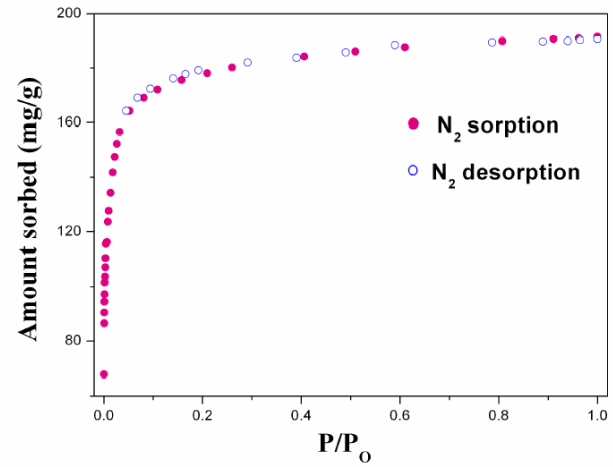

Figure S3. N_2 sorption curves (77 K) of **1** evacuated under vacuum at 60 ºC for 2 h.