1D→1D Two-Fold Parallel Interpenetrated Coordination Polymers with a Bis(pyridylurea) Ligand

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Experimental details

Experimental

S1. General

^{1}H NMR spectra were recorded on a Mercury plus-400 spectrometer with calibration against the solvent signal (DMSO-d_6 2.50 ppm for ^{1}H). IR spectra were obtained using a Nicolet AVATAR 360 FT-IR spectrometer as KBr pallets. Elemental analyses were done on a VarioEL instrument from Elementaranalysensysteme GmbH. ESI-MS measurements were carried out using a Waters ZQ4000 spectrometer in methanol. Melting points were detected on an X-4 Digital Vision MP Instrument.

S2. Synthesis

L. Isonicotinoyl azide (1.50 g, 10.1 mmol) was dissolved in dry toluene (50 mL) and refluxed for 2 h until no more N_2 was evolved. The solution was cooled to room temperature and 1,3-diaminopropane (0.37g, 5.0 mmol) was added. A mass of precipitate appeared immediately. After filtration, the crude solid was recrystallized from CH_3OH/H_2O (1:2) as colorless crystals. Yield: 1.25 g (80%); Mp: 127−128 °C.

Anal. Calcd for $C_{15}H_{18}N_6O_2 \cdot H_2O$: C, 54.21; H, 6.07; N, 25.29%. Found: C, 54.24; H, 5.68; N, 25.42%. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 1.59 (t, J = 6.8 Hz, 2H, CH$_2$CH_2CH$_2$), 3.13 (dd, J = 12.8, 6.8 Hz, 4H, NHCH_2), 6.46 (t, J = 5.6 Hz, 2H, NH), 7.37 (dd, J = 4.8, 1.6 Hz, 4H, m-Py), 8.28 (dd, J = 5.2, 1.2 Hz, 4H, o-Py), 9.03 (s, 2H, Py-NH). ^{13}C NMR (DMSO-d_6, 400 MHz, ppm): δ 154.72 (C=O), 149.93, 147.10, 111.77, 36.48, 30.30. IR (KBr disk, ν/cm^{-1}): 3377 (m, NH), 1704 (s, CO), 1597 (s, NH). ESI-MS: m/z = 315 [M+H]$^+$, 337 [M+Na]$^+$, 651 [2M+Na]$^+$.

{[CdL$_2$(H$_2$O)$_2$]Cl$_2$·2H$_2$O}$_n$ (1).   The ligand L (62.8 mg, 0.2 mmol) and CdCl$_2$·2.5H$_2$O (45.6 mg, 0.2 mmol) were dissolved in a mixed solvent of DMF (10 mL) and H$_2$O (5 mL). Slow evaporation at r.t. for a week yielded colorless crystals of **1** (62 mg, 55%); Mp: 192−194 °C. Anal. Calcd for $C_{30}H_{36}N_{12}O_4CdCl_2 \cdot 5H_2O$: C, 39.94; H, 5.14; N, 18.63%. Found: C, 39.83; H, 5.58; N, 18.15%. IR (KBr disk, ν/cm^{-1}): 3379 (m, NH), 1701 (s, CO), 1595 (s, NH).

{[CdL$_2$(H$_2$O)$_2$](NO$_3$)$_2$}$_n$ (2).   Cd(NO$_3$)$_2$·4H$_2$O (61.6 mg, 0.2 mmol) was dissolved in H$_2$O (2 mL). A buffer layer of methanol/H$_2$O (1:1) (5 mL) was carefully added, followed by a methanol solution (1 mL) of ligand L (62.8 mg, 0.2 mmol). Slow diffusion of the mixture at r.t. for a week yielded colorless crystals of **2** (51 mg, 50%); Mp: 183−185 °C. Anal. Calcd for $C_{30}H_{36}N_{14}O_{10}Cd \cdot 6H_2O$: C, 37.02; H, 4.97; N, 20.15%. Found: C 36.83; H 4.88; N 20.61%. IR (KBr disk, ν/cm^{-1}): 3328 (m, NH), 1692 (s, CO), 1593 (s, NH), 1383 (s, N-O).

{[CoL$_2$(H$_2$O)$_2$]Cl$_2$·2H$_2$O}$_n$ (3).   L (62.8 mg, 0.2 mmol) and CoCl$_2$·6H$_2$O (47.6 mg, 0.2 mmol) were dissolved in a mixed solvent of DMF (10 mL) and H$_2$O (5 mL). Slow evaporation of the mixture at r.t. for a week yielded pink crystals of **3** (60 mg, 55%); Mp: 188−190 °C. Anal. Calcd for $C_{30}H_{36}N_{12}O_4CoCl_2 \cdot 5H_2O$: C, 42.46; H, 5.46; N, 19.81%. Found: C, 42.22; H, 5.64; N, 19.58%. IR (KBr disk, ν/cm^{-1}): 3322 (m, NH), 1701 (s, CO), 1592 (s, NH).

{[CoL$_2$(H$_2$O)$_2$]SO$_4$·6H$_2$O}$_n$ (4).   CoSO$_4$·7H$_2$O (56.2 mg, 0.2 mmol) was dissolved in H$_2$O (2 mL). A buffer layer of methanol/H$_2$O (1:1) (5 mL) was carefully added, followed by a methanol solution (1 mL) of ligand L (62.8 mg, 0.2 mmol). Slow diffusion of the components at r.t. for a month yielded pink crystals of **4** (45 mg, 40%); Mp: 220−222 °C. Anal. Calcd for $C_{30}H_{36}N_{12}O_8CoS \cdot 7H_2O$: C, 39.60; H, 5.54; N, 18.47%. Found: C, 39.54; H, 5.02; N, 18.03%. IR (KBr disk, ν/cm^{-1}): 3252 (m, NH), 1685 (s, CO), 1599 (s, NH), 1095 (s, S-O).

S3. X-ray crystallography

Diffraction data were collected on a Bruker SMART APEX II diffractometer at 173 K with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction using SADABS was applied for all data.[1] The structures were solved by direct methods using the SHELXS

program.[2] All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 by the use of the SHELXL program.[2] Hydrogen atoms bonded to carbon and nitrogen were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Hydrogen atoms on the water oxygens for compounds **1** and **3** were located from the difference Fourier map and then refined by considering their chemical environments with restraints [O–H = 0.85(2) Å] and U(H) fixed at 0.08 Å^2.

For the compound {[CoL$_2$(H$_2$O)$_2$]SO$_4$·6H$_2$O}$_n$ **(4)**, the sulfate anion is severely disordered and there are unsolved residual peaks for solvent molecules. Increasing the exposure time at 173 K did not ameliorate the quality of data in this case. Repeated measurements of the unit cell dimensions from different single crystals at 173 K confirmed the composition and structure of **4**. However, it was difficult to determine the accurate positions of the solvent molecules. Thus, eight unidentified peaks within void spaces were modeled as isolated oxygen atoms O11 to O18. The occupancy factors for these oxygen atoms have been carefully refined to avoid new high residual peaks. Isotropic refinement was applied to these atoms with similar environment. Finally, the Ueq values of O11−O17 are below 0.3. The disordered sulfate group was divided into two parts; the same anisotropic displacements were used to O7−O10 and O7A−O10A. Hydrogen atoms were not included for the crystal water molecules (O11−O18).
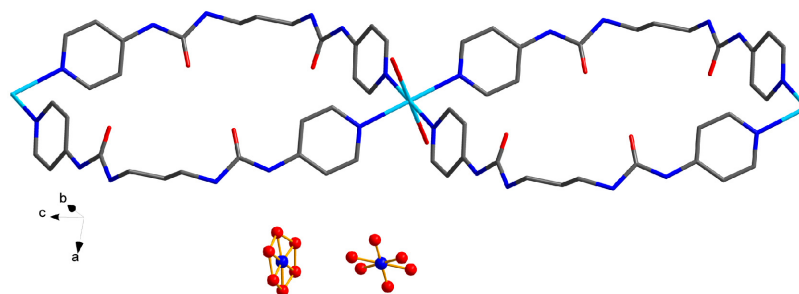

Figure S1. 1D chain motif of **2** with Cd-fused metallacycles and two disordered NO$_3^-$ anions.
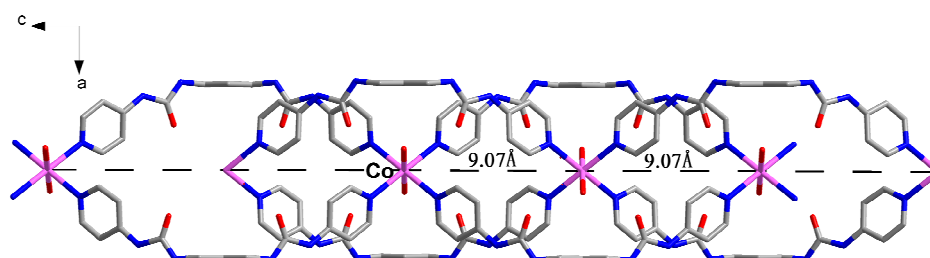

Figure S2. 1D→1D parallel interpenetration in **3** with equidistant Co···Co interchain distances.

S4. DFT computations

DFT computations for the L molecule were carried out at the B3LYP/6-31G level. For symmetric L, the starting point for the calculations was that one of the N-pyridylurea substituents (the right half in the numbering Scheme 1) was constrained according to the global minimum. Then another pyridylurea was allowed to rotate around the C(2)–N(a) bond such that the C(3)–N(a)–C(2)–C(1) torsion angle changed from −180 to 180°. Each point on the potential energy surface was determined by constraining the C(3')–N(a')–C(2')–C(1) torsion angle (Scheme 1) and optimizing the molecular geometry.
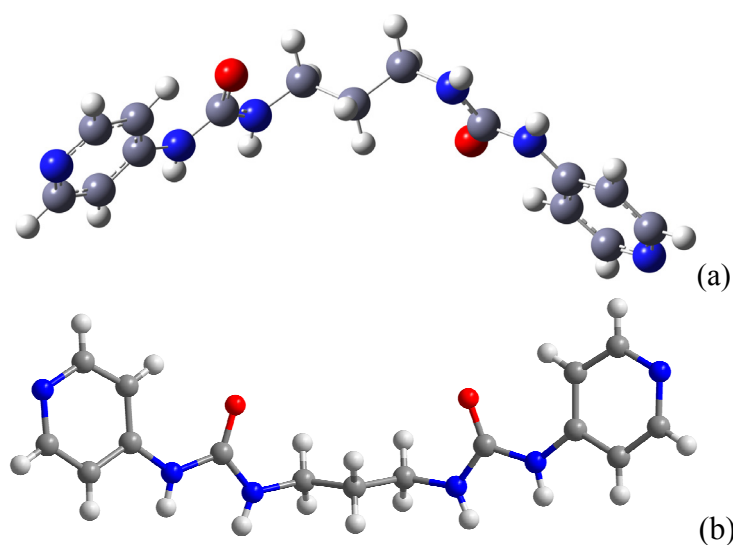
(a)

(b)

Figure S3. (a) The B3LYP/6-31G optimized[3] global minimum for L. (b) The structure of L in $\{[CdL_2(H_2O)_2]Cl_2 \cdot 3H_2O\}_n$(**1**) where two urea carbonyls assume the *syn* conformation.

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