Homochiral H-bonded proline based metal organic frameworks†

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Two L-proline based homochiral frameworks synthesised *via* diffusion and solvothermal methods display distinct L-proline bonding modes, one N,O chelating and one O,O bridging with amine nitrogen not bound to the metal, with binding mode dependent upon the degree of protonation of the amino acid.

Porous materials such as zeolites have widespread applications in catalysis, sorption and separation.[1] Coordination chemistry offers an alternative route to regular porous arrays,[2,3] with the advantages of larger pores[4] and more diverse building units[5] and network topologies[6] to set against reduced thermal and chemical stability. This chemistry is particularly advantageous in the synthesis of chiral porous materials, which is difficult with zeolites, but can be achieved either through control of helix handedness[7] or the use of chiral building units.[8–12] Recently amino acid–based extended networks[13,14] with accessible porosity[15,16] have been prepared. We were interested in incorporating proline (*c*-NHCH(COOH)$CH_2CH_2CH_2$, H-Pro) into metal organic frameworks (MOFs) as this amino-acid would not only prove useful for enantioselective separation but also as a heterogenized organocatalyst. Deprotonated amino acid coordination chemistry is dominated by the formation of the N,O chelate motif producing the geometrically (and energetically) favoured five-membered metallocycle;[17] indeed the only metal proline containing coordination polymers that we are aware of contain proline bonded through the amine functionality in the N,O chelate mode.[18,19] Herein we report the synthesis and characterisation of two new homochiral two dimensional frameworks containing the amino acid proline in distinct coordination modes, including one where the amine functionality is not involved in metal bonding.

The slow diffusion of a bipy (bipy = 4-4′-bipyridyl) EtOH solution into a MeOH solution containing $Cd(NO_3)_2$ and 2 equivalents of [Et_3NH][L-Pro] yielded the homochiral material; $[Cd(NO_3)$(L-Pro)(bipy)]$_n$, **1**.‡ Containing only one enantiomer of the amino-acid, **1** crystallises in the chiral orthorhombic $P2_12_12_1$ space group with Flack parameters close to zero.§ With the proline deprotonated the amine lone pair is available, thus L-proline unsurprisingly chelates to one cadmium centre in the N,O mode. The structure is then extended in one dimension through the non-chelate carboxylate oxygen connecting to an adjacent cadmium (Fig. 1) *trans* to the chelating O; this is an analogous bonding mode to the only other proline containing extended framework material, KH_2[(L-Pro)$_4$(H_2O)Cu_3][$BW_{12}O_{40}$]·$5H_2O$.[18] In **1** bipy acts orthogonally to pillar the corrugated, one-dimensional cadmium–proline chains generating a 2D sheet. The octahedral coordination environment at cadmium is completed by a monodentate NO_3 anion bound *trans* to the proline amine. This ligand set at the Cd centre offers an additional stabilising hydrogen-bonding interaction between a nitrate N–O and an adjacent proline N–H. Layers of **1** stack efficiently in an ABAB repeating motif, resulting in a non-porous material with no void space or guests (see ESI†). The solid-state structural assignment is supported by elemental microanalysis, the non-porous nature confirmed by TGA analysis and bulk phase purity verified by comparison of experimental and simulated powder X-ray diffraction patterns (see ESI†). **1** is insoluble in H_2O and common organic solvents (*e.g.*, MeOH, EtOH, acetone, acetonitrile). The bipy pillars separate the Cd centres to prevent oligomer formation typically seen in proline chemistry[14–16] and makes **1** only the second example of a proline-containing extended net. It is interesting that **1** could equally be synthesised *via* solvothermal methods (120 °C, 24 h), with the weakly coordinating nitrate anion not displaced even in the presence of excess bipy and/or [Et_3NH][Pro] – thus **1** is not a 'kinetically trapped' phase (*i.e.* an initially formed insoluble lower dimensionality phase). The repeated inability to displace the second NO_3^- from the cadmium coordination sphere implies that this anion, and in particular the hydrogen bonding interaction to the proximal proline N–H, is critical in the stability of **1**.

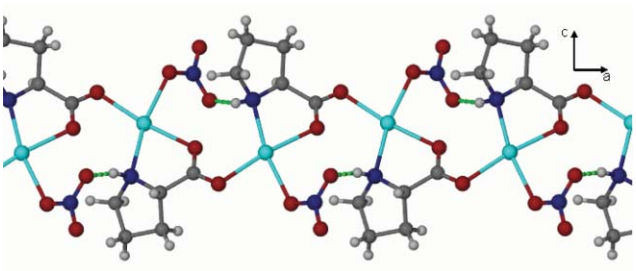

Fig. 1 View down the *b* axis of **1** showing the proline bridged chains (bipy pillars orthogonal to plane removed for clarity, dashed green bonds indicates hydrogen bonds). Cd cyan, C grey, O red, N blue, H light grey.

The amino-acid N,O chelation bonding motif is pervasive in all reported metal–amino-acid extended frameworks.[13–16,18–20] In order to form structures where the proline amino functionality is not coordinated to the metal, this group needs to be engaged in alternate bonding, or "protected".[21] This can be achieved simply by protonation if the zwitterionic form of proline (H-Pro) is used to coordinate to the metal. Diffusion of an alcoholic (MeOH or EtOH) solution of bipy into a H_2O solution containing $Zn(BF_4)_2$·$5H_2O$ and 2 equivalents of L-proline resulted in the formation of colourless platelets over the course of three weeks.

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† Electronic supplementary information (ESI) available: Full experimental information, data and crystallographic details for **1** and **2**. See DOI: 10.1039/b706557d

Single-crystal X-ray diffraction§ revealed the formation of the cationic coordination polymer $[Zn(\mu\text{-}F)(H\text{-}Pro)(bipy)]_n^{n+}[BF_4]_n \cdot n(H_2O)$, **2** (Fig. 2); with proline present as only one enantiomer, indicated by the chiral monoclinic space group $P2_1$ and an effectively zero Flack parameter. The structure of **2** consists of zwitterionic proline molecules connecting octahedral Zn centres *via* an O,O bridging motif, supported by a μ-F linkage forming a 1D chain. Both ligands are essentially symmetrically bridged (Zn–F 2.036(4) and 2.040(4) Å, Zn–O 2.101(3) and 2.129(3) Å). The structure is extended orthogonally into 2D sheets by bipy ligands. The μ-F and proline ligands alternate positions along the 1D corrugated chain, resulting in a linear assembly; in contrast to related systems with regular, *syn*, proline/μ-F arrangements that form molecular wheels of varying sizes due to chain curvature caused by the smaller bite angle of the carboxylate chelate relative to the μ-F. Framework **2** is constructed from bipy connection of chains with μ-F and bridging proline connecting the metal centres and occupying alternate sides of the chain and (Fig. 2(a), (d)), the formation of a polymeric structure for **2** may well be enforced by the rigorously *trans* ligating bipy pillar.

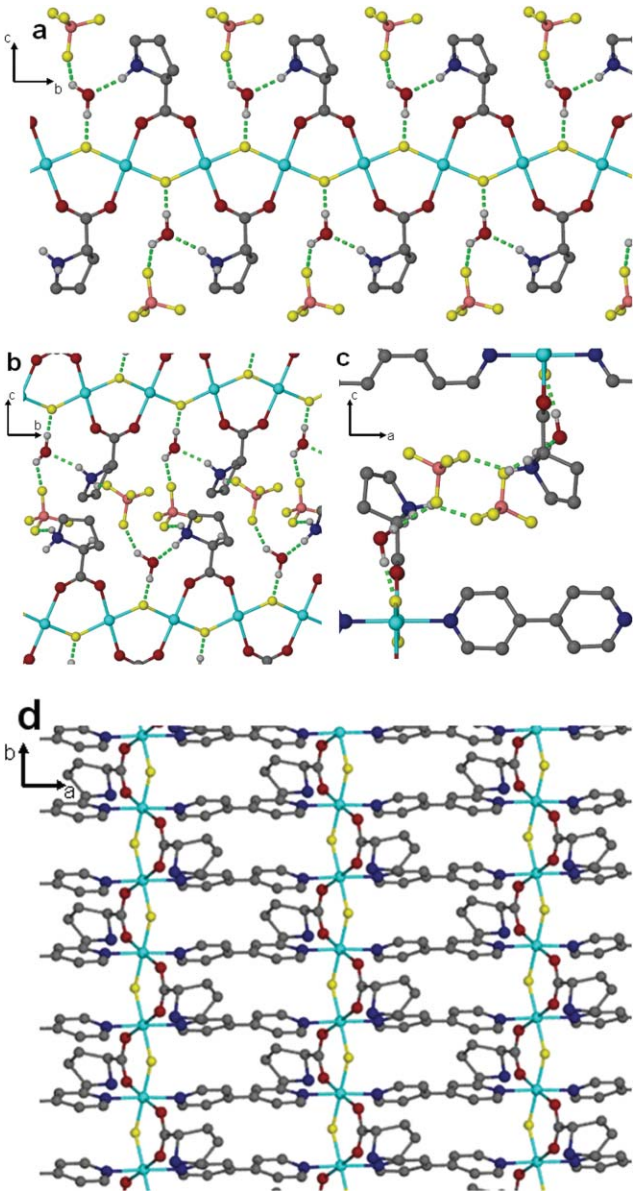

Fig. 2 (a) The one-dimensional proline/(μ-F) bridged chain in framework **2** displaying the proline O,O bridging motif, the protonated amine and the hydrogen bonded water molecule. (b) The interlayer hydrogen bonding in **2** viewed down the *a* axis. (c) The interlayer hydrogen bonding viewed down the *b* axis. (d) The 2D layers of **2** (BF_4 and H_2O removed for clarity). In (a) and (b) the bipy molecules, all hydrogens not involved in hydrogen bonding and one of each of the disordered proline and BF_4 molecules are removed for clarity. Zn cyan, O red, N dark blue, C grey, F yellow, H light grey, hydrogen bonds green.

The structural scaffold of **2** is cationic due to the zwitterionic nature of L-proline, and to achieve charge balance each unit has an associated $[BF_4]^-$ anion. The $[BF_4]^-$ is involved in hydrogen bonding interactions with a guest water molecule and to two proline ammonium functionalities (Fig. 2(b), (c)). The water molecule is additionally hydrogen bonded to the μ-F and an ammonium cation (Fig. 2(a)). The 2D layers are efficiently interdigitated with the disordered BF_4 anions residing in a channel enclosed by two prolines from adjacent layers that are both orientated to participate in the multiple F···HN hydrogen bonds (Fig. 2(c)). The extensive hydrogen bonding between the ammonium cation, H_2O, (μ-F) and BF_4 anion provides robust interlayer linkage. These multiple hydrogen bonds may be the origin of the atypical alternating carboxylate/μ-F chain arrangement instead of the ubiquitous *syn* arrangement observed in 'molecular wheels' species.

The bridging fluoride in **2** originates from the hydrolysis of one equivalent of the BF_4 anion, a well documented phenomenon that has also been recently utilised to yield a fluoride bridged zinc MOF, $[ZnF(AmTAZ)]_n$ (AmTaz = 3-amino-1,2,4-triazole).[22] The assignment of the bridging fluoride and BF_4 anion in **2** is unambiguously confirmed by ^{19}F NMR (1F integral singlet at −123.3 ppm and a combined integral 4F resonance for the ^{10}B and ^{11}B isotopes of BF_4 at −150.4 and −150.5 ppm) spectroscopy, that displays the expected 1 : 4 ratio for (μ-F) : BF_4. The $[BF_4]^-$ is also observed by mass spectroscopy with no products from anion hydrolysis observed (*e.g.*, $[BF_3OH]^-$). The structural assignment is further supported by elemental analysis. Bulk phase purity is established by powder X-ray diffraction and by scanning electron microscopy that confirmed a single-crystal morphology (see Supporting Information). The infrared spectrum for **2** is complex but reveals a number of bands in the region expected for an ammonium cation $N\text{–}H^+$ (2200–3000 cm^{-1}) and close to those observed in the parent zwitterionic HPro amino acid.

Framework **2** is insoluble in common organic solvents (MeOH, EtOH, acetone, MeCN) but dissolves rapidly in H_2O; dynamic light scattering (no species above 1 nm observed) and mass spectroscopy (monomeric Zn species) reveal this process proceeds *via* framework breakdown to molecular species. However, removal of the H_2O solvent *in-vacuo* regenerates framework **2** (by powder XRD) resulting in an overall dissolution/reassembly process. The process involves the aqueous displacement of fluoride ligand from the metal coordination sphere *via* a four- or five-coordinate zinc centre (coordination numbers well documented for Zn) as all observed metal containing species in the mass spectra (ESI mode) were fluoride free.

Thermogravimetric analysis of **2** under a nitrogen flow reveals a mass loss of 4.2% between 30 and 120 °C, this is attributed to the loss of the guest water molecules (calc. mass loss 3.9%) from the

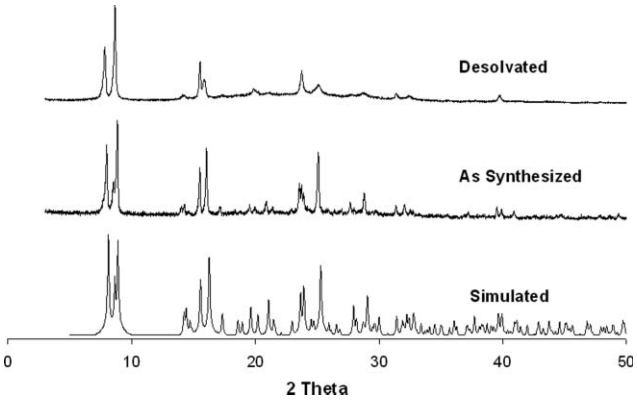

Fig. 3 Powder X-ray diffraction patterns for **2** showing the pattern simulated from single crystal data, the as synthesised experimental pattern and **2** after desolvation overnight *in vacuo* at 120 °C.

framework. Heating beyond 120 °C results in a breakdown of the framework (with powder XRD revealing only amorphous material) and a second mass loss of 9.8% to 300 °C; further heating resulted in a more dramatic mass loss of 59.2% (see ESI†), the remaining material (experimental 26.8%) is identified by powder X-ray diffraction as ZnO and HBO_2 (calculated mass 27.2%). The similarity of the powder X-ray diffraction patterns for the as-synthesised and desolvated (*in vacuo* 120 °C, 18 h) framework **2** (Fig. 3) demonstrates that **2** is relatively robust, and is stable to loss of the guest water molecule involved in multiple hydrogen bonding. Though the interlayer hydrogen bonding must be significantly perturbed by H_2O loss, the N–H···F interactions are still strong enough to maintain framework integrity. The de-solvated powder X-ray diffraction pattern for **2** is significantly less crystalline suggesting a loss of order in the material which can be envisaged to arise due to the increase in freedom of motion now afforded the proline molecules on removal of the locking H-bonded water molecule. Framework **2** can alternatively be produced solvothermally at 100 °C in 24 h from $Zn(BF_4)_2{\cdot}5H_2O$–Bipy–HPro (1 : 2 : 2) in 4 ml of a 1 : 3 H_2O–EtOH solution, again confirming that the observed structure is not a kinetically trapped species but a thermodynamic metastable phase.

Extended networks are accessible by combining bipyridyl and proline as framework-forming ligands. The synthesis of **2**, in which the amino group is "protected" by protonation, avoids the common N–O chelate proline coordination mode and the structure is retained after guest loss, suggesting that open-framework systems may be accessible from N-protected derivatives of proline, offering the possibility that a subsequent deprotection could afford free proline N–H centres.

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Notes and references

‡ Compound **1**: *Method A*: An 'H-Cell' is charged in one arm with a 1 ml MeOH solution containing L-proline (0.44 mmol), Et_3N (0.44 mmol) and $Cd(NO_3)_2.4\ H_2O$ (0.22 mmol) and the other arm with a 1 ml EtOH solution of bipy (0.44 mmol). Both sides are carefully layered with MeOH and diffusion over a period of two weeks yielded colourless platelet crystals (0.062 g, 14 mmol. Isolated yield based on $Cd(NO_3)_2{\cdot}4H_2O$ is 64%). *Method B*; An 18 ml Teflon-lined autoclave was charged with 0.05 g $Cd(NO_3)_2{\cdot}4H_2O$ (0.16 mmol), 0.038 g of L-proline (0.33 mol), 46 μl Et_3N (0.33 mmol), 0.05 g bipy (0.32 mmol) and 4 ml of MeOH, sealed and heated at 120 °C for 24 h to yield a microcrystalline colourless solid (0.045 g, 0.1 mmol. Isolated yield based on $Cd(NO_3)_2{\cdot}4H_2O$ is 63%). Microanalysis (%): found (calc. for $CdN_4O_5C_{15}H_{16}$): C 40.28 (40.36); H 3.56 (3.62); N 12.65 (12.56). Compound **2**: *Method A*: One arm of an 'H-cell' is charged with $Zn(BF_4)_2{\cdot}5H_2O$ (0.18 mmol) and L-proline (0.45 mmol) and 1 ml H_2O, the other arm with bipy (0.20 mmol) in 1 ml EtOH. Both are carefully layered with EtOH and slow diffusion over a period of three weeks yielded colourless platelets (0.032 g, 0.07 mmol. Isolated yield based on $Zn(BF_4)_2{\cdot}5H_2O$ = 39%). *Method B*: An 18 ml Teflon lined autoclave is charged with $Zn(BF_4)_2{\cdot}5H_2O$ (0.15 mmol), L-Proline (0.30 mmol), 3 ml EtOH, 0.5 ml H_2O and bipy (0.30 mmol), sealed and heated to 100 °C for 24 h, yielding colourless platelets (0.047 g, 0.1 mmol yield based on $Zn(BF_4)_2{\cdot}5H_2O$ = 67%). Microanalysis (%): found (calc. for $ZnBF_5N_3O_3C_{15}H_{19}$): C 39.24 (39.21), H 4.05 (4.17), N 9.05 (9.15). IR (4000 to 1000 range) ν cm^{-1} (KBr); 3607 (s), 3402 (br), 3214 (br), 2985 (br), 2759 (br), 2593 (br), 1613 (br), 1536 (s), 1490 (s), 1416 (br), 1322 (s), 1296 (s), 1257 (s), 1220 (s), 1072 (br).

§ CCDC 645631 and 645632. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b706557d

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