# A soft coordination polymer derived from container molecule ligands†‡

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**Partial collapse of the ladder-shaped tunnels of a crystalline cryptophane derived coordination polymer is monitored by single crystal X-ray diffraction.**

Crystalline coordination polymers and frameworks are receiving considerable attention as they are intrinsically designable.[1] A particularly promising avenue for design involves using ligands that will convey established functionality to the material—chiroselective,[2] catalytic,[3] photoreactive,[4] or recognition properties,[5] for example. To this end, we are pursuing the synthesis of coordination polymers derived from 'container molecule'[6] ligands, as members of this family are known to: (i) select/recognize guests,[6,7] (ii) bind gases (*e.g.* $N_2$, $O_2$, NO, $CH_4$, Xe),[6,8] (iii) store encapsulated species with exceptional kinetic stability,[6,9] and (iv) serve as reaction nanovessels.[10] Though little is known about the binding/storage properties of solids derived from container molecules, what is known is promising.[9,11] We report herein a cryptophane[6a] ligand, (±)-$H_3$**2**, derived from its ester **1**,[9] possessing exterior-positioned carboxylic acid moieties. Reaction of (±)-$H_3$**2** with $Cu(NO_3)_2 \cdot 2.5H_2O$ in the presence of ancillary pyridine ligands yields a crystalline coordination polymer that partially desolvates in a single-crystal-to-single-crystal fashion. Insight into this desolvation process bears general relevance to the properties of other flexible crystalline materials.[12]

Cryptophanes are characterized by two $C_3$-symmetric [1.1.1]-orthocyclophane caps connected by three linkers. Those possessing *m*-xylyl linkers allow the selective positioning of functional groups either interior[13] (2-position) or exterior[9] (5-position) to the molecular cavity. (±)-**1** and (±)-$H_3$**2** (Fig. 1a) possess pseudo-$D_3$ symmetry and are chiral. Preliminary X-ray structures of over twenty (±)-**1**⊂guest complexes, however, reveal that (±)-**1** only rarely adopts a pseudo-$D_3$ symmetric conformation in the solid-state. As exemplified by the (±)-**1**⊂DMF complex (Fig. 1b),‡ a $C_1$ conformation is more common, wherein one of the *m*-xylyl linkers extends in a direction opposite to the two others.

Reaction of racemic (±)-$H_3$**2** with $Cu(NO_3)_2 \cdot 2.5H_2O$ in DMF–MeOH solutions led to an insoluble, likely polymeric, turquoise material. Though the material is crystalline, we have not yet been successful in determining its structure. Addition of pyridine to the reaction mixture, however, afforded deep blue diffraction quality crystals. X-ray analysis of fresh crystals drawn directly from the mother liquor reveals a centrosymmetric coordination polymer of composition $[Cu_{1.5}((\pm)\text{-}\mathbf{2} \subset DMF)(C_6H_5N)_3(MeOH)] \cdot$*solvent*, hereafter **3**·*solvent*.§

The structure of **3** consists of a one-dimensional polymer of (±)-$\mathbf{2}^{3-}$ ligands linked *via* coordination to Cu(II) centers (Fig. 2). The coordination environments of the Cu(II) ions are additionally occupied by ancillary methanol and/or pyridine ligands such that there are two unique Cu(II) sites, **A** and **B**. The **A** sites consist of square planar (or pseudo-octahedral) Cu(II) ions which are *trans*-coordinated by two pyridine ligands and two carboxylate groups from adjacent enantiomers of (±)-**2**. The two carboxylate groups are almost coplanar (C–O1–O3–C = 178°) and arranged such that the carbonyl oxygens are weakly interacting with the metal (Cu1–O2, Cu1–O4 = 2.58(15) Å, avg.). The **B** sites consist of Cu(II) ions situated on a two-fold rotation axis and are similarly coordinated in a transoid fashion by two pyridine ligands and two carboxylate groups from adjacent (±)-**2** ligands, but of the same chirality. At the **B** sites, however, the axial positions of the Jahn–Teller distorted Cu(II) ions are additionally occupied by weakly coordinated MeOH molecules (Cu2–O6 = 2.518(5) Å). The methanolic hydroxyl groups hydrogen bond with the carbonyl oxygen atoms of the carboxylate ligands (O(H)···O = 2.687(6) Å), which lie out of plane (C–O5–O5′–C′ = 131°). The extended 1D structure of **3** consists of centrosymmetric dimers of (*M*)-**2** and (*P*)-**2** ligands doubly connected *via* **A** sites and further linked along the [10-1] crystallographic direction by **B** sites. The stereochemistry of the ligands along the polymer thus follows the order $(\text{-}M\text{-}P\text{-}P\text{-}M\text{-})_\infty$.

As expected, each cryptophane ligand cavity is occupied by one molecule of DMF and the conformation of (±)-**2** ligand in

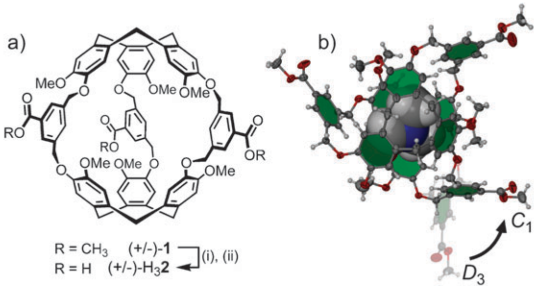

**Fig. 1** (a) Cryptophane ligand (±)-$H_3$**2**, as derived from (±)-**1**. (i) $NMe_4OH$, DMF; (ii) HCl, 87%. (b) The (±)-**1**⊂DMF complex. The major orientation of the disordered DMF is shown. The semi-transparent *m*-xylyl linker depicts a hypothetical pseudo-$D_3$ conformation.

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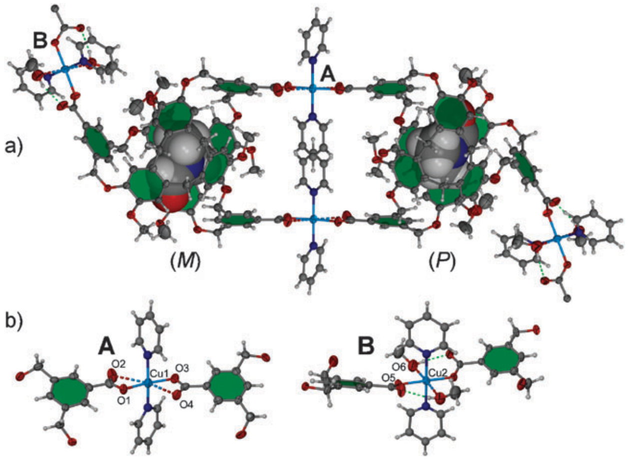

**Fig. 2** (a) The 1D polymeric structure of $[Cu_{1.5}((\pm)\text{-}\mathbf{2}\subset DMF)(C_6H_5N)_3(MeOH)]_\infty$, **3**. The major orientation of the disordered DMF is shown. (b) Two independent Cu(II) coordination sites within **3**.

**3**·*solvent* is similar to that of (±)-**1** in the (±)-**1**⊂DMF complex (Fig. 2). This observation supports the contention that different encapsulated guests may template different coordination polymer topologies by biasing the host conformation. This hypothesis is currently under investigation.

Bulky, ellipsoidal compounds such as (±)-**2** cannot pack efficiently in the solid-state. So, in addition to the molecular cavities defined by (±)-**2**, inefficient packing of the polymers in **3**·*solvent* gives rise to segregated, 1D tunnels along the [001] direction of the crystal. The tunnels are corrugated and contoured, but are best described as ladder-shaped, being intermittently pillared (green, Fig. 3) by the pyridine ligands of the **B** coordination sites. Unfortunately, it is difficult to precisely define a stoichiometric composition for crystals of **3**·*solvent*. X-ray analysis of crystals retrieved directly from the reaction mother liquor and immediately (<5 s) placed into the 173(1) K cold stream of the diffractometer consistently (7 crystals) gave *C*-centered monoclinic unit cells with volumes that average 19 249(26) Å$^3$ (Table 1). Even the highest quality low temperature data set obtained from these crystals reveals highly disordered solvents within the ladder-shaped tunnels. SQUEEZE[14] analysis estimates the electron count to be 72 e$^-$ within 485 Å$^3$ (0.15 e$^-$ A$^{-3}$) of available space per formula unit, suggesting four molecules of MeOH (72 e$^-$). The pre-SQUEEZE refinement model, however, suggests that there are regions of electron density corresponding to one DMF and four methanol molecules (112 e$^-$) per formula unit; the available volume could easily accommodate this number of guests. Other forms of analysis (*e.g.* TGA) are complicated by the fact that the crystals immediately begin to lose solvent once removed from the mother liquor (*vide infra*) or decompose at high temperature. The composition of the fully solvated crystals of **3**·*solvent* is therefore tentatively assigned as **3**·DMF·4MeOH, but it is recognized that the crystals likely have a more complex, perhaps non-stoichiometric, composition.

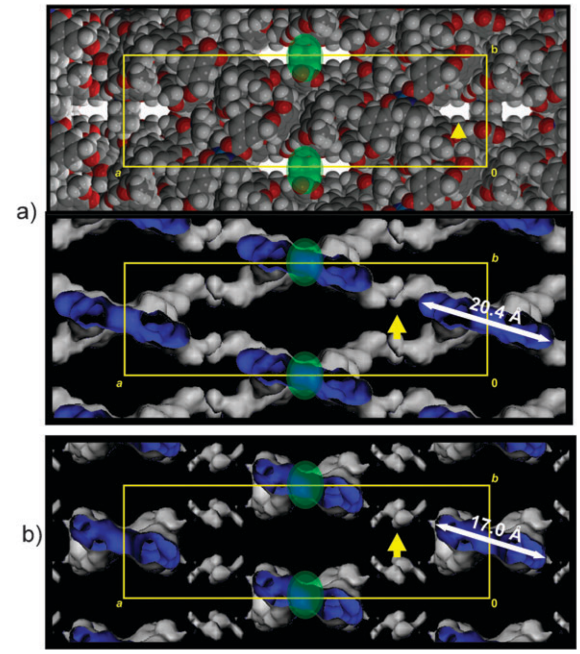

**Fig. 3** Spacefill and solvent accessible surface representations looking down the ladder-shaped 1D tunnels in (a) **3**·DMF·4MeOH and (b) desolvated-**3**. Note the contraction of the tunnels (gray surface, cross-section in blue) in (b) relative to (a).

Crystals of **3**·*solvent* are stable at low temperature (173 K), but immediately begin to lose solvent once exposed to ambient conditions. Remarkably, however, the crystals maintain their integrity for the initial stages of desolvation to the extent that the process can be monitored by single crystal diffraction. For instance, one single crystal of fully solvated **3**·*solvent*, subjected to unit cell determination at 173(1) K and then alternately exposed to ambient conditions for $t$ = 1, 6, 25, 45, and 120 min, gave monoclinic unit cells with volumes measuring $V$ = 19 244(9) ($t$ = 0), 19 028(11), 18 814(10), 18 652(8), 18 644(13), and 18 470(19) Å$^3$, respectively. Other crystals behaved similarly. Notably, the contraction (desolvation) process appears to follow a typical deceleratory rate law consistent with desolvation. The average unit cell volumes (173 K) of several (6) single crystals that had been exposed to ambient conditions for two or more hours measured 18 534(87) Å$^3$ (Table 1). The volume difference between fully solvated crystals of **3**·*solvent* and those exposed to ambient conditions for at least two hours, hereafter desolvated-**3**, is statistically significant, measuring *ca.* 715 Å$^3$ or 3.7% of the crystal volume. Powder diffraction (PXRD) analysis of bulk **3**·*solvent*, initially moist with mother liquor and then allowed to slowly dry, is consistent with the single crystal analysis.‡ These data suggest retention of the overall Cu-(±)-**2** connectivity throughout the desolvation process. Moreover, the desolvation process is entirely reversible according to PXRD.

**Table 1** Average unit cell parameters for single crystals of **3**·*solvent* and partially desolvated-**3** at 173 K

| | **3**·*solvent*[a] | Desolvated-**3**[b] |
|---|---|---|
| $a$/Å | 53.0(1) | 53.3(2) |
| $b$/Å | 16.09(2) | 15.89(4) |
| $c$/Å | 23.13(3) | 22.43(8) |
| $V$/Å$^3$ | 19 249(26) | 18 534(87) |

Lattice constants and errors are derived from averaged unit cell data obtained from[a] seven or [b] six single crystals.

Though the crystals ultimately fragment into powder after prolonged exposure to ambient conditions, a structure determination can nonetheless be performed on partially desolvated-**3** ($V$ = 18 574(3) Å$^3$). Not surprisingly, the structure of desolvated-**3** is nearly identical to that of **3**·*solvent*. Though the quality of the structure is poor due to weakness in the diffraction pattern, a comparison of the structure of desolvated-**3** to **3**·*solvent* gives some insight into the desolvation process. Among the most notable observations is an approximate 23% contraction in the volume of the ladder-shaped tunnels (Fig. 3). Indeed, SQUEEZE analysis estimates the residual solvent accessible volume (that not occupied by the $[Cu_{1.5}((\pm)\text{-}\mathbf{2}\subset DMF)(C_6H_5N)_3(MeOH)]$ polymer) to be 374 Å$^3$ per formula unit in desolvated-**3** *vs.* 485 Å$^3$ in **3**·*solvent*. The tunnels in desolvated-**3** are by no means empty; SQUEEZE in fact estimates the tunnels to be occupied by roughly 57 e$^-$ per formula unit. It is interesting to note that the average electron density within the tunnels of desolvated-**3** and **3**·*solvent* is about the same, approximately 0.15 e$^-$ Å$^{-3}$. The flexibility of the polymer apparently allows for a more or less continuous contraction of the channels as solvent is lost. It is therefore unlikely that this material will exhibit permanent porosity. Interestingly, even at low temperature, the calculated electron density within the tunnels is considerably lower than that of the liquid solvents (DMF = 0.31 e$^-$ Å$^{-3}$, MeOH = 0.27 e$^-$ Å$^{-3}$) at room temperature.

There are other significant differences between the structures of **3**·*solvent* and partially desolvated-**3**. For instance, there is a strong indication that some loss of the weakly coordinated pyridine and methanol ligands occurs concomitantly with solvent loss. The X-ray data of desolvated-**3** are best modeled such that, on average relative to **3**·*solvent*, nearly one equivalent of pyridine and half an equivalent of methanol are lost from the Cu(II) centers. Notably, the **B** coordination sites lining the tunnels are more susceptible to ligand loss than the **A** sites. There are also some subtle changes in the conformation of the (±)-**2** ligands upon desolvation. For example, the methoxy substituents and portions of the xylyl linkers that line the tunnels of the structure are more disordered in desolvated-**3** than in **3**·*solvent*. It is clear that the portions of the structure that line the tunnels are the most significantly affected by desolvation.

Finally, it is important to note that, despite the ready loss of lattice-included and coordinated guests, the cryptophane cavity remains fully occupied by DMF during the initial stages of desolvation. Such behavior is a design feature of materials derived from container molecules; the closed surface nature of the cryptophane ligand provides a greater kinetic barrier to loss of the encapsulated guests. So, the container-like properties of the ligand are manifested in the desolvation properties of this material. Further experiments will reveal whether this feature can be exploited for separations based upon differences in guest sorption kinetics.

## Notes and references

§ Crystal data for **3**·*solvent* (**3**·DMF·4MeOH): $C_{101}H_{112}N_5O_{25}Cu_{1.5}$, $M$ = 1891.27, blue prism, 0.44 × 0.24 × 0.18 mm$^3$, monoclinic, $C2/c$ (No. 15), $a$ = 52.867(10), $b$ = 16.102(3), $c$ = 23.170(4) Å, $\beta$ = 102.582(3)°, $V$ = 19 250(6) Å$^3$, $Z$ = 8, $D_c$ = 1.305 g cm$^{-3}$, $F_{000}$ = 7972, Siemens SMART 1K CCD, MoK$\alpha$ radiation ($\lambda$ = 0.71073 Å), $T$ = 173(2) K, $2\theta_{max}$ = 50.0°, 49 632 reflections collected, 16 928 unique ($R_{int}$ = 0.0674). Final *GooF* = 0.929, $R1$ = 0.0701, $wR2$ = 0.1779, based on 8710 reflections with $I > 2\sigma(I)$ (refinement on $F^2$), 1068 parameters, 18 restraints.
Crystal data for desolvated-**3**, formulated as $[Cu_{1.5}((\pm)\text{-}\mathbf{2}\supset DMF)(C_6H_5N)_{2.15}(MeOH)_{0.5}]\cdot DMF\cdot MeOH$: $C_{93.25}H_{93.75}Cu_{1.50}N_{4.15}O_{21.50}$, $M$ = 1711.88, 0.36 × 0.18 × 0.14 mm$^3$, monoclinic, space group $C2/c$ (No. 15), $a$ = 53.319(6), $b$ = 15.9118(16), $c$ = 22.444(2) Å, $\beta$ = 102.719(2)°, $V$ = 18 574(3) Å$^3$, $Z$ = 8, $D_c$ = 1.224 g cm$^{-3}$, $F_{000}$ = 7182, MoK$\alpha$ ($\lambda$ = 0.71073 Å), $T$ = 173(2) K, $2\theta_{max}$ = 44.2°, 51 505 reflections collected, 11 478 unique ($R_{int}$ = 0.0965). Final *GooF* = 0.866, $R1$ = 0.0946, $wR2$ = 0.2458, based on 4431 reflections with $I > 2\sigma(I)$ (refinement on $F^2$), 958 parameters, 0 restraints. Structures were treated with SQUEEZE‡.

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