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A ‘three-in-one’ crystal of coordination networks†

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Three types of coordination polymers are formed together in one crystal when a linear bifunctional ligand of length 15.7 Å is reacted with $Cd(NO_3)_2$ in the presence of mesitylene or *m*-xylene or *o*-xylene, which is also included in the crystal as a guest.

The linear and bifunctional ligand 4,4′-bipyridine and its longer analogs upon reaction with transition metals are known to form several types of coordination networks that include 3D-networks (octahedral and diamondoid),[1,2] 2D-networks (square and rectangular grids, brick-wall and bilayers),[3–5] and 1D-networks (ladders, linear chains, helices and railroads).[6–11] The formation of the networks was shown to depend upon several factors such as the presence of guest, the mode of coordination by metal atom, the type of anions present and metal : ligand ratios. Here we present a very unusual example in which 4,4′-bis(4-pyridyl)biphenyl (**1**) upon reaction with $Cd(NO_3)_2$ results in the crystallization of three types of coordination polymers and guest molecules in one crystal.[12] This unusualness is found to be consistent for three guest molecules such as mesitylene, *m*-xylene and *o*-xylene.

Recently we have shown that ligand **1** upon reaction with $Ni(NO_3)_2$ in the presence of *o*-xylene forms an open 2D-network containing square grids of dimension 20 × 20 Å.[13] Accordingly we anticipated similar type of network upon reaction of ligand **1** with $Cd(NO_3)_2$. The diffusion of an MeOH (1 ml) solution of $Cd(NO_3)_2$ (3.1 mg, 0.001 mmol) into the mesitylene solution (5 ml) of **1** (6.2 mg, 0.002 mmol) resulted in the crystals of complex **2** suitable for X-ray diffraction.‡

To our surprise the crystal structure analysis revealed that **2** consisted of three types of polymers (Fig. 1): desired 2D-layer containing grids of 20 × 20 Å $[Cd(\mathbf{1})_2(NO_3)_2]$ (**A**), double linear chain $[Cd_4(\mathbf{1})_4(NO_3)_6(MeOH)_6]^{2+}$ (**B**), and linear chain $[Cd(\mathbf{1})(NO_3)_3]^-$ (**C**). In total, complex **2** can be formulated as $\{(\mathbf{A})(\mathbf{B})(\mathbf{C})NO_3\cdot 2(\text{mesitylene})\cdot 3MeOH\}_n$.

The polymer **A** consists of the anticipated square grid polymer with grid dimensions of 20 × 20 Å (Fig. 1(a)). The Cd atom has distorted octahedral geometry and exhibited no symmetry in coordination. As a result there are two Cd–ONO_2 distances (2.525 and 2.382 Å) and four Cd–N distances (2.327, 2.379, 2.286 and 2.360 Å) around the Cd atom. Further, the grid layers pack on each other such that there exist channels of dimension *ca.* 10 × 20 Å with large interlayer separation of 10.9 Å.

In polymer **B**, four Cd atoms form two linear chains with four ligands of **1** which are joined together by nitrate anions with Cd···Cd separations of 4.2 and 5.1 Å. These double linear chains are nicely fitted in the channels that are formed across the packing of grid **A** to form a 3D-polyrotaxane type arrangement (Fig. 2).[14] The four Cd atoms in **B** are symmetrically independent: each of them has different coordination environments (Fig. 1(b)). All Cd atoms complete six-coordination with a different number of NO_3 anions and MeOH molecules. The Cd–N, Cd–OMe and Cd–ONO_2 distances are in the range 2.260–2.300, 2.326–2.387 and 2.314–2.515 Å respectively.

Polymer **C** consists of linear chains which are packed between the 2D layers of polymer **A** such that they make an angle of 90° with the polymer **B** (Fig. 3). The Cd-atom has seven coordination as it coordinates to two moieties of **1** and five O atoms of three NO_3 anions, two coordinated in a bidentate fashion and one in a monodentate fashion (Fig. 1(c)). As a result of seven-coordination, Cd–ONO_2 distances are somewhat longer than usual (2.442–2.556 Å). Further the uncoordinated MeOH molecule links the polymers **C** and **B** *via* O–H···O hydrogen bonds (**B**-MeO(H)···(Me)OH···ONO_2-**C**, O···O 2.61 and 2.73 Å). The mesityline and MeOH molecules and remaining nitrate anion fills the cavities that are formed between the packing of these polymers.

A similar type of complex formation was observed when the reaction was repeated by using *m*-xylene (**3**) or *o*-xylene (**4**) instead of mesitylene. The crystal structures of complexes **3** and **4** are essentially identical to the crystal structure of **2** but contain one additional H_2O molecule.‡ The inclusion of H_2O molecule in **3** and **4** could be due to the fact that *m*-xylene and *o*-xylene

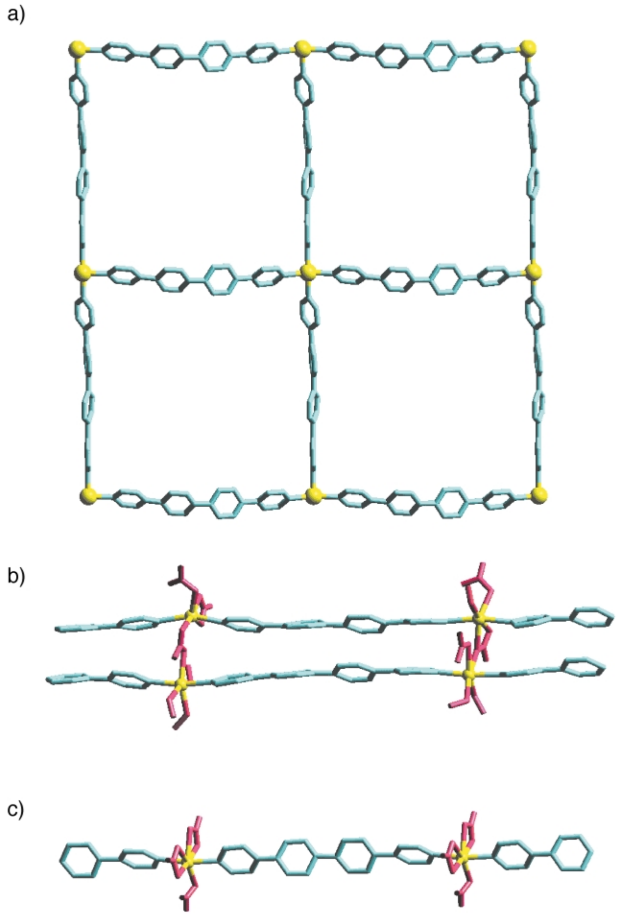

Fig. 1 Illustrations for the three coordination polymers exhibited in the crystal structure of **2**: (a) square grid (**A**); (b) double linear chain (**B**) and (c) linear chain (**C**). **1** = light blue; Cd = yellow; NO_3 and MeOH = pink.

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† Electronic supplementary information (ESI) available: ORTEP drawings for **2**, **3** and **4**. See http://www.rsc.org/suppdata/cc/b2/b203025j/

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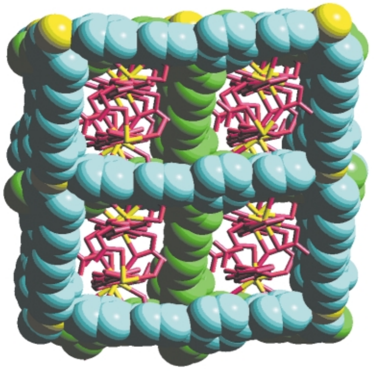

Fig. 2 Top view showing the insertion of polymer **B** through the channels formed across the layers of **A** to form 3D-polyrotaxane type arrangement. **B** = pink, Cd = yellow, alternate layers of **A** = light blue or green.

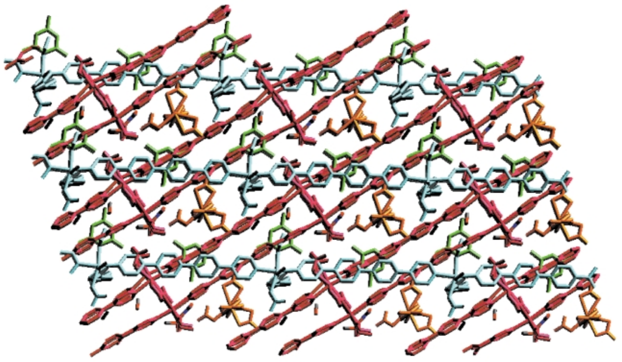

Fig. 3 Crystal packing of complex **2** showing all components. **A** (side view) = light blue; **B** = pink; **C** = orange; mesitylene = green. Note the free methanol and nitrate anions (O = red, C = gray, N = blue).

are smaller in size than mesitylene. The repetitive formation of this unusual complex in three solvents suggests that the packing of three polymers together is more highly robust than packing of any of these polymers with themselves. Further, it is noteworthy that the crystal structure of Ni-analogue of polymer **A** ontains 60% of guest occupied volume whereas in the present structures it is only 33%. The interpenetration of the nets mostly of the same kind is well known to reduce the space available for the guest molecules in the crystal. These structures demonstrate that the formation of more types of polymers in one crystal is an alternative method to reduce the available space for guest molecules since the voids or channels formed by one polymer (**A**) are occupied by the remaining polymers **B** and **C**.

Notes and references

‡ *Crystal data* for **2**: $C_{181}H_{172}N_{26}O_{45}Cd_6$, triclinic, space group $P1$, a = 14.586(1), b = 15.938(1), c = 20.461(2) Å, α = 79.171(1), β = 74.183(1), γ = 82.219(1)°, U = 4477.3(6) Å^3, T = 193 K, Z = 1, D_c = 1.523 g cm^{-3}, λ = 0.7107 Å, 29163 reflections measured, 23974 unique (R_{int} = 0.0180) which are used in all calculations; $R1$ = 0.0340 and $wR2$ = 0.0776.

Crystal data for **3**: $C_{179}H_{170}N_{26}O_{46}Cd_6$, triclinic, space group $P1$, a = 14.583(1), b = 15.648(1), c = 20.393(2) Å, α = 78.869(1), β = 75.705(1), γ = 83.175(1)°, U = 4412.4(6) Å^3, T = 193 K, Z = 1, D_c = 1.541 g cm^{-3}, λ = 0.7107 Å, 28676 reflections measured, 23631 unique (R_{int} = 0.0160) which are used in all calculations; $R1$ = 0.045 and $wR2$ = 0.1163.

Crystal data for **4**: $C_{179}H_{170}N_6O_{46}Cd_6$, triclinic, $P1$, a = 14.692(2), b = 15.522(2), c = 20.387(3) Å, α = 79.360(3), β = 74.950(3), γ = 83.088(4)°, U = 4399.7(11) Å^3, T = 193 K, Z = 1, D_c = 1.546 g cm^{-3}, λ = 0.7107 Å, 29098 reflections measured, 24102 unique (R_{int} = 0.0664) which are used in all calculations; $R1$ = 0.0682 and $wR2$ = 0.1218.

In all structures H-atoms of water and of OH of MeOH were not located. Some of the C and N-atoms in **4** were refined isotropically as they are going non positive definates in anisotropic refinement.

CCDC reference numbers 184121–184123. See http://www.rsc.org/suppdata/cc/b2/b203025j/ for crystallographic data in CIF or other electronic format.

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14 The double chains of polymer **B** also interact with each other to form 2D-layers *via* O–H···O hydrogen bonds (MeO(H)···ONO_2 2.77 Å).