Supramolecular isomers in the same crystal: a new type of entanglement involving ribbons of rings and 2D (4,4) networks polycatenated in a 3D architecture†

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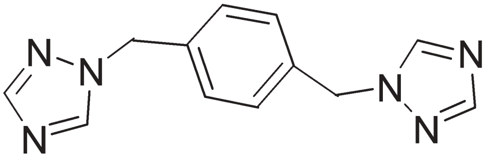
Received (in Cambridge, UK) 9th December 2004, Accepted 7th March 2005
First published as an Advance Article on the web 18th March 2005
DOI: 10.1039/b418392d

The reaction of corresponding cadmium salts with the flexible ligand 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (bbtz) affords the 3D coordination network $[Cd_3(bbtz)_6(H_2O)_6](BF_4)_6\cdot1.75H_2O$ (1), containing ribbons of rings and planar 2D (4,4) networks polycatenated with each other, the undulating 2D (4,4) network $[Cd(bbtz)_2(H_2O)_2](ClO_4)_2\cdot2H_2O$ (2), and ribbons of rings $[Cd(bbtz)_2(H_2O)_2](BF_4)_2\cdot3DMF$ (3) and $[Cd(bbtz)_2(H_2O)_2](ClO_4)_2\cdot3DMF$ (4).

The current interest in the crystal engineering of coordination polymer frameworks stems not only from their potential application as functional materials, but also from their intriguing variety of architectures and topologies.[1–8] A variety of appealing interpenetrating structures have been reported recently and reviewed by Batten and Robson.[2] Among them, particular attention has been recently devoted to entangled polymeric systems such as catenanes, rotaxanes and pseudocatenate/rotaxanes.[3] Robson and coworkers reported two remarkable polyrotaxane-like polymers based on 1,4-bis(imidazol-1-ylmethyl)benzene (bix),[4] while the known examples of polycatenations involving motifs of different dimensionality are rarities.[3,5]

The increasing known examples of coordination polymers based on identical building blocks in the same ratio exhibit different structures.[6,7] Zaworotko and coworkers have introduced the term "supramolecular isomers" to define them.[6] The finding of different polymeric topologies in the same crystal is unusual,[8] especially if these topologies are supramolecular isomers.[7]

Our synthetic approach starts by focusing on the construction of new topological frameworks using flexible ligands such as 1,2-bis(1,2,4-triazol-1-yl)ethane,[9] 1,2-bis(benzotriazol-1-yl)ethane[10] and 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (bbtz, Scheme 1)[11] due to their variety of conformations.[12] In this communication, we report the 3D network $[Cd_3(bbtz)_6(H_2O)_6](BF_4)_6\cdot1.75H_2O$ (**1**) containing ribbons of rings and planar 2D (4,4) networks, the undulating 2D (4,4) network $[Cd(bbtz)_2(H_2O)_2](ClO_4)_2\cdot2H_2O$ (**2**), and ribbons of rings $[Cd(bbtz)_2(H_2O)_2](BF_4)_2\cdot3DMF$ (**3**) and $[Cd(bbtz)_2(H_2O)_2](ClO_4)_2\cdot3DMF$ (**4**).



Scheme 1 Structure of bbtz.

Compounds **1** and **2** are obtained in high yield as colourless block crystals by the reaction of bbtz in methanol with the corresponding cadmium salts in water, irrespective of the stoichiometry of metal-to-ligand. **3** and **4** are obtained by recrystallizing **1** and **2** in DMF, respectively.

The crystal structure of **1**‡ is comprised of two distinct and crystallographically independent polymeric motifs packed together that have the same stoichiometry (Fig. 1). One of these motifs consists of a planar 2D (4,4) network, in which the Cd(1) atom lies on an inversion centre. Four cadmium atoms and four bbtz ligands form a $Cd_4(bbtz)_4$ unit with a side of 14.547 Å × 14.845 Å corresponding to the *a*- and *c*-axis translations, respectively and a diagonal measurement of 19.679 Å × 21.834 Å. The bbtz ligands adopt a *trans-gauche* conformation, with the shortest N···N distance of 10.676 and 10.916 Å between the two donor atoms.

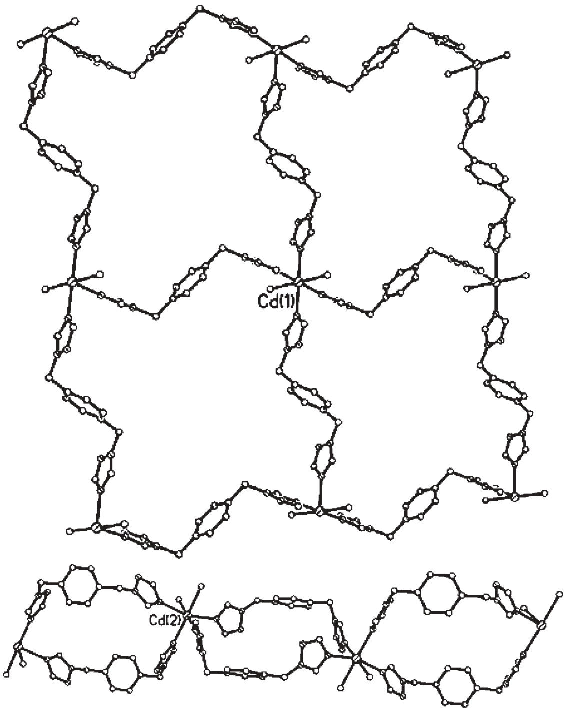


Fig. 1 Two different motifs in **1**: a planar 2D (4,4) network (top) and a ribbon of rings (bottom).

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† Electronic supplementary information (ESI) available: details of synthesis of **1**, **2**, **3** and **4**. See http://www.rsc.org/suppdata/cc/b4/b418392d/
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The metal coordination is octahedral, with four equatorially bonded triazole groups [Cd–N 2.282(3), 2.363(3) Å], and two axial water molecules [Cd–O 2.321(3) Å]. The 2D (4,4) network extends along the *ac*-plane and the neighbouring networks are packed parallel along the *b* direction with the distance 1/2b and show a relative displacement of half of the side lengths (off-set 1/2a in the *a*-direction and 1/2c in the *c*-direction).

The second motif of **1** is composed of ribbons of 26-membered cycles, each ring involving two cadmium atoms and two bbtz molecules, in which the Cd(2) atom is in a general position. The bbtz ligands exhibit a *gauche-gauche* conformation and work as shorter spacers (N···N 9.536 and 9.344 Å). The metal coordination is also octahedral, with four N atoms from four triazole groups [Cd–N 2.289(4), 2.302(4), 2.303(3), 2.319(3) Å] and two water molecules [Cd–O 2.350(3), 2.369(4) Å], similar to that observed in the 2D network. The difference in the coordination geometries is that two water molecules are located at *cis*-positions in the ribbon of the ring but at *trans*-positions in the 2D network. All these rings run parallel to the *b* direction, with a period equal to the *b* axis translation (24.032 Å), corresponding to two successive rings.

The most interesting structural feature of **1** is that the ribbons and the 2D networks are inextricably entangled (Fig. 2) in a unique three-dimensional array. Each ring of the ribbons locks one adjacent 2D network, and each "square" mesh of the 2D network is catenated by four rings belonging to four different ribbons.

The entanglement found here, of the (1D + 2D) type, is unusual. The known examples of polycatenation involving motifs with different dimensionality are true rarities.[3,5] One example with similar (1D + 2D) topology is $[Cu_5(bpp)_8(SO_4)_4(EtOH)(H_2O)_5](SO_4)\cdot EtOH\cdot 25.5H_2O$ [bpp = 1,3-bis(4-pyridyl)-propane] which includes a 3D array formed by ribbons of rings polycatenated with 2D tessellated stacked layers.[5a] The stack mode of the layers and the catenation mode of the ribbons and 2D layers are different from that of **1**. The layers stack with an *ABCD* sequence; each ring of the ribbons locks two adjacent layers and each "square" of the layers is catenated by two rings belonging to two different ribbons in this example. Another example is $[Co(bix)_2(H_2O)_2](SO_4)\cdot 7H_2O$, containing polymeric ribbons of rings which penetrate and catenate a 3D single frame of the $CdSO_4$ topology.[5b]

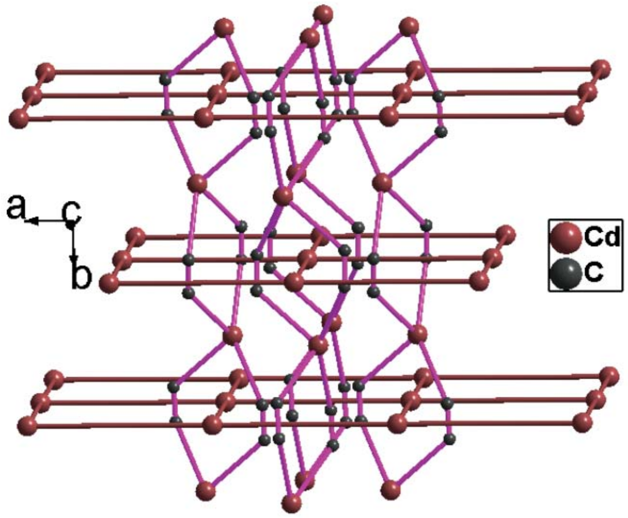

Fig. 2 Schematic view of the overall entanglement of **1**. The bbtz ligands of the planar 2D (4,4) networks are omitted for clarity. The representation of the bbtz ligands of the ribbons of rings is simplified by showing only the methylene atoms.

2 has the same stoichiometry of metal-to-ligand (1 : 2) as **1**, with the difference of ClO_4^- counter anions in **2** and BF_4^- counter anions in **1**. The crystal structure of **2** is composed of only undulating 2D (4,4) networks (Fig. 3),[13] while **1** has two motifs, the planar 2D (4,4) networks and ribbons of rings. The undulating 2D network of **2** is reasonable because the bbtz ligands have a *gauche-gauche* conformation. The coordination geometry of the cadmium atom [Cd–N 2.324(2), 2.332(2) Å and Cd–O 2.286(3) Å] is very similar to that in the planar 2D (4,4) networks of **1**. The bbtz ligands work as the shorter spacers (N···N 9.193 Å). Four cadmium atoms and four bbtz ligands form a $Cd_4(bbtz)_4$ unit with a side of 11.568 Å × 11.568 Å, and a diagonal measurement of 15.744 Å × 16.954 Å corresponding to the *a*- and *b*-axis translations, respectively.

The crystal structures of **3** and **4** are similar, with the difference of BF_4^- counter anions in **3** and ClO_4^- counter anions in **4**, also composed of ribbons of 26-membered cycles $Cd_2(bbtz)_2$ (Fig. 4) similar to the ribbons of rings in **1**. The metal coordination is also octahedral, with four N atoms from four triazole groups [Cd–N 2.305(2), 2.309(2), 2.328(2), 2.346(2) Å in **3**, and Cd–N 2.287(2), 2.290(2), 2.309(2), 2.327(2) Å in **4**] and two water molecules [Cd–O 2.318(2), 2.368(2) Å in **3**, and Cd–O 2.312(2), 2.384(2) Å in **4**], similar to that observed in the ribbons of rings in **1**. The difference in coordination geometries is two water molecules at *trans*-positions in **3** and **4** but at *cis*-positions in **1**. The ligands exhibit a *trans-gauche* conformation and work as the middle spacers (N···N 10.340 and 10.349 Å, Cd···Cd 13.507 Å in **3**; N···N 10.235 and 10.251 Å, Cd···Cd 13.346 and 13.379 Å in **4**).

The solvent system and the counter anions play a fundamental role in the synthesis of the coordination polymers. Compounds **1**

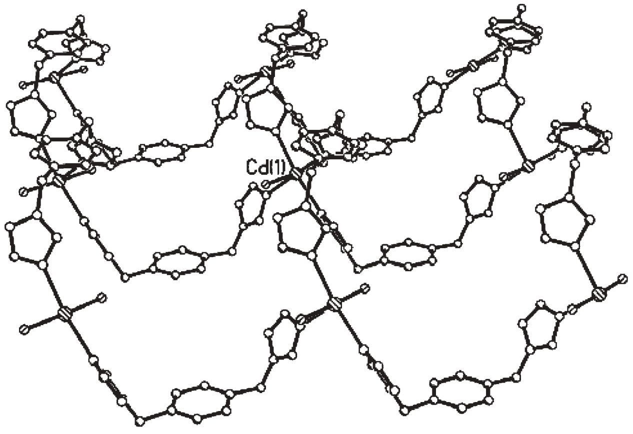

Fig. 3 An undulating 2D (4,4) network in **2**.

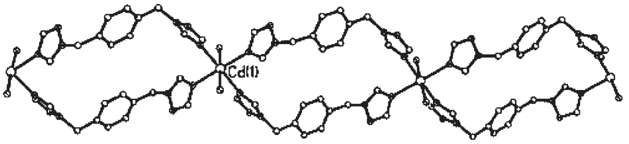

Fig. 4 A ribbon of rings in **3** and **4**.

and **2** are obtained in methanol/H_2O, while **3** and **4** are obtained by recrystallizing **1** and **2** in DMF, respectively.

In conclusion, two groups of supramolecular isomers (**1** and **3**, **2** and **4**) were synthesized. **2** consists of an undulating 2D (4,4) network, **3** and **4** are composed of chain structures containing ribbons of macrocyclic rings, and **1** corresponds to the interpenetration of the two motifs (the planar 2D (4,4) network and the chain). The structure of **1** is very interesting; it has topological isomers in the same crystal and has the new (1D + 2D) type of entanglement. The thermal behaviours, anion-exchange properties of the compounds and the synthesis of the new interesting coordination polymers are under investigation.

The Natural Science Foundation of the University of Jiangsu Province (grant No. 03KJB150118) and the Funds of the Key Laboratory of Organic Synthesis of Jiangsu Province, P. R. China, are thanked for financial support.

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Notes and references

‡ X-ray single-crystal diffraction data collections: **1**, **2**, **3** and **4** were collected on a Rigaku Mercury CCD at 193.15 K. The structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs. **1**: $C_{72}H_{87.5}B_6Cd_3F_{24}N_{36}O_{7.75}$, M_r = 2439.34, monoclinic, space group $P2_1/n$, a = 14.5472(14), b = 24.032(2), c = 14.8451(14) Å, β = 95.943(2)°, V = 5161.9(8) Å^3, Z = 2, D_c = 1.569 g·cm^{-3}, μ = 0.723 mm^{-1}, 11781 [R(int) = 0.0293] unique reflections, 10230 data with $I > 2\sigma(I)$, 710 parameters, R_1 = 0.0625, wR_2 = 0.1740, S = 1.173. **2**: $C_{24}H_{32}CdCl_2N_{12}O_{12}$, M_r = 863.92, monoclinic, space group $C2/c$, a = 15.744(3), b = 16.954(3), c = 14.824(3) Å, β = 118.91(3)°, V = 3463.7(12) Å^3, Z = 4, D_c = 1.657 g·cm^{-3}, μ = 0.861 mm^{-1}, 3772 [R(int) = 0.0246] unique reflections, 3555 data with $I > 2\sigma(I)$, 247 parameters, R_1 = 0.0379, wR_2 = 0.1075, S = 1.077. **3**: $C_{33}H_{49}B_2CdF_8N_{15}O_5$, M_r = 1021.89, triclinic, space group $P\bar{1}$, a = 9.9995(4), b = 11.6029(5), c = 20.2826(10) Å, α = 82.925(3), β = 88.436(3), γ = 77.008(2)°, V = 2275.55(17) Å^3, Z = 2, D_c = 1.491 g·cm^{-3}, μ = 0.569 mm^{-1}, 8259 [R(int) = 0.0201] unique reflections, 7779 data with $I > 2\sigma(I)$, 600 parameters, R_1 = 0.0432, wR_2 = 0.1191, S = 1.123. **4**: $C_{33}H_{49}CdCl_2N_{15}O_{13}$, M_r = 1047.17, triclinic, space group $P\bar{1}$, a = 11.6707(7), b = 14.1256(11), c = 14.9212(9) Å, α = 89.544(5), β = 71.742(4), γ = 82.640(4)°, V = 2315.4(3) Å^3, Z = 2, D_c = 1.502 g·cm^{-3}, μ = 0.662 mm^{-1}, 8403 [R(int) = 0.0284] unique reflections, 7408 data with $I > 2\sigma(I)$, 618 parameters, R_1 = 0.0406, wR_2 = 0.0990, S = 1.010. CCDC 256591–256594. See http://www.rsc.org/suppdata/cc/b4/b418392d/ for crystallographic data in CIF or other electronic format.

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