A New Polycatenated 3D Array of Interlaced 2D Brickwall Layers and 1D Molecular Ladders in \([\text{Mn}_2(\text{bix})_3(\text{NO}_3)_4] \cdot 2\text{CHCl}_3\) [bix = 1,4-bis(imidazol-1-ylmethyl)benzene] That Undergoes Supramolecular Isomerization upon Guest Removal

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Received September 14, 2007; Revised Manuscript Received October 22, 2007

ABSTRACT: The reactions of Mn(II) nitrate with the flexible ligand 1,4-bis(imidazol-1-ylmethyl)benzene (bix) (reagent ratios 1:2–1:3) yield novel interesting coordination networks including, besides the ladder-like species [Mn(bix)1.5(NO3)2] and the 2-fold interpenetrated three-dimensional (3D) cd's network [Mn(bix)2(NO3)2]3, the exceptional [Mn2(bix)3(NO3)4]·2CHCl3, which is comprised of two different supramolecular isomers, namely, brickwall layers and one-dimensional (1D) molecular ladders, polycatenated to give a 3D (2D + 1D) architecture.

Coordination polymeric frameworks have attracted in these years great attention due to their potential applications as functional solid materials in areas such as microelectronics, nonlinear optics, porous materials, and catalysis.1 Crystal engineering concepts have been employed in the attempt to construct networks of desired topologies and properties, but many factors still contribute to make this objective a major challenge. The use of conformationally nonrigid ligands increases the difficulty in controlling the final outcome but, at the same time, offers more chances to obtain motifs with peculiar features that are worth investigation: (i) new topologies and framework entanglements (including polycatenanes and polyrotaxanes);2 (ii) phenomena of conformational polymorphism3 and supramolecular isomerism,4 and (iii) flexibility of the networks (single or entangled) that can result in different kinds of nanoporous behaviors upon external stimuli (third generation materials).5 In this regard, a flexible ligand such as 1,4-bis(imidazol-1-ylmethyl) benzene (bix) and related spacers have shown a certain ability to give with metal salts a variety of two- and three-dimensional (2D and 3D) network topologies and, more interestingly, many new intriguing entanglements of distinct motifs thanks to their different conformations. Examples of these entangled species include polycatenanes,6,7 polyrotaxanes interlaced in inclined8,9 or parallel9 fashion, and interwaved 2D layers exhibiting rotaxane-like links10 or Borromean links.11 Moreover, cases of entangled supramolecular isomers embodied in the same crystal were also observed.6,12

We report here the results of our studies on the reactions of the bix ligand with Mn(II) nitrate that have produced three novel polymeric species, that is, [Mn2(bix)3(NO3)4]·2CHCl3 (1), [Mn(bix)2(NO3)2]2 (2), and [Mn(bix)3(NO3)3] (3), whose structures and transformations are described. Compound 1 is particularly intriguing in that it shows a new case of polycatenation involving one-dimensional (1D) and 2D motifs interlaced in a 3D architecture.

The reactions of Mn(NO3)2·4H2O in EtOH and bix·2H2O in CHCl3 with a reagent ratio of ca. 1:3 were carried out by slow diffusion upon carefully layering the metal salt solution over the bix solution at 30–60 °C. In one or two days, almost colorless tabular crystals of 1 are formed on the walls of the test tube at the solution surface. On the other hand, on leaving the same system (or a similar one with a reagent ratio up to 1:1.5) to stand for longer times, the crystals at the surface disappear, and new colorless saber-shaped crystals form at the CHCl3/EtOH interface, that were shown to be compound 2. The bulk polycrystalline material obtained by mixing the reagents under the same conditions corresponds to almost pure 2, as confirmed by X-ray powder diffraction methods. Compounds 1 and 2 are supramolecular isomers (see below) and represent the kinetic products of these reactions. Compound 3 was first obtained by mixing a MeOH solution of Mn(NO3)2·4H2O with bix·2H2O in MeOH (reagent ratio 1:3), heating the mixture at ca. 60 °C for few minutes to get a clear solution and leaving it to rest for about two months. However, 3 (the thermodynamic product) is also obtained from all the previously described mother solutions when these are allowed to stand for few months. All the crystals are stable in the air for long times, and their structures have been characterized by single crystal X-ray analyses.13

Although compounds 1 and 2 contain polymeric frames of identical composition, their structures are drastically different. The second one consists of simple molecular ladders all extending in the same direction, while in 1 two distinct motifs are present in the same framework, 1D ladder-like polymers and 2D brickwall layers, that are supramolecular isomers and give polycatenation to produce an unique 3D array. Within a crystallographic unit cell, there are two metals for each of the two motifs, shown in Figure

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The 1D ladder motif (Figure 1, top) is significantly undulated and the 4-gons windows are rhombic rather than square shaped, with inside angles well deviating from 90° (Mn⋯Mn⋯Mn angles 111.4° and 68.6°). The side edges and the rungs are 14.44 and 15.64 Å long, respectively. All the ladders run along the same [010] direction and show parallel planes; they form piles stacking in the [100] direction with a stacking distance of 6.0 Å. The second motif (Figure 1, bottom) is a 3-connected layer with 6° topology, as for honeycomb layers, but with a different geometry usually called “brick-wall”, that exhibits rectangular windows (13.05 × 29.52 Å, approximately of double area with respect to the rhombic windows of the 1D motif). The layers stack along the [111] direction with a stacking distance of 7.2 Å. The metal ions in the two motifs exhibit almost the same pentagonal bipyramidal (3N + 4O) environment, with two equatorial chelating nitrate-κ²O anions and three N-donor imidazole groups of different bix ligands in a T-shaped geometry (Mn–N and Mn–O bond lengths 2.198(6)–2.208(6) Å and 2.251(5)–2.467(6) Å, respectively, in the ladders vs 2.188(6)–2.222(6) Å and 2.275(5)–2.388(5) Å, respectively, in the layers).

Although both types of motifs are rather common when considered separately, the fascinating polycatenated architecture observed in 1 is exceptional (Figure 2). Polycatenation has been defined as the phenomenon in which the whole catenated array has a higher dimensionality than that of each of the component motifs, that are interlocked via topological Hopf links. Each motif can be catenated with a finite or with an infinite number of other independent motifs but not with all. Compound 1 represents a case of inclined polycatenation with motifs of different dimensionality (1D + 2D) forming a 3D array. The ladders cross the brickwall layers at a small angle of 30.0°; in this way, each window of the layers is catenated by three ladders via four Hopf links and each window of the ladders is catenated by two layers again via four Hopf links, as shown in Figure 2 (bottom). Note that this misfit between the number of entangled motifs and the number of topological links is a novelty in inclined polycatenation, that can arise from the small value of the inclination angle.

Previously reported cases of polycatenation involving 1D motifs of the same type are rare: these include parallel catenation of ladders (1D → 2D) and inclined and parallel catenation of ribbons (1D → 2D) and of ladders (1D → 3D). Even more rare are the cases of true polycatenation of motifs of different dimensionality (1D + 2D → 3D). Only two examples were reported, which differ from 1 in the type of the entangled motifs, being both comprised of 2D 4° layers and 1D ribbons of rings: in [Cu5(bpp)3(SO4)4(EtOH)(H2O)5][SO4]·EtOH.25.5H2O [bpp = 1,3-bis(4-pyridyl)propane] each ring of the ribbons locks two adjacent layers, and each “square” of the layers is catenated by two rings belonging to different ribbons, while in [Cd10(bbtz4)(H2O)8] (BF4)3·1.75H2O [bbtz = 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene] a ring of the ribbons interlocks two adjacent layers, but each window of the layers is catenated by four rings of four different ribbons. One recent additional polycatenated example (1D + 2D → 3D) sustained by hydrogen bonds has been reported by Zaworotko et al.21

The entangled array of 1 contains free voids that are ca. 20% of the cell volume and that are filled by solvated CHCl3 molecules that are not lost even after leaving the crystals in the air for long time periods. This can be explained considering that the guest molecules are encapsulated in pairs within internal chambers (see Figure S1, Supporting Information), that have no open windows. Indeed, the crystals left in the mother solution convert (via a dissolution and recrystallization process) into the supramolecular isomeric species 2, that simply consists of parallel 1D ladders (see Figure S2, Supporting Information) with no guest solvents. On the other hand, when the crystalline material is recovered from these solutions and submitted, after grinding, to X-ray powder diffraction (XRPD, see Figure S4, Supporting Information) a ca. 50% mixture of 1 and 2 is observed, which transforms into pure 2 in one day.22 Very probably in polycrystalline form the increased surface area allows a faster loss of the CHCl3 molecules, leading to supramolecular isomerization of 1 to 2 in a crystal-to-crystal process. Thus the solvent system plays a fundamental role in the formation and stability of 1, and the templating role of chloroform is evident. Thermogravimetric analysis (TGA) of 1 monitored by XRPD has confirmed this transformation: the CHCl3 molecules are completely removed in the range 160–190 °C and the X-ray powder pattern collected after this event corresponds to that simulated from the single crystal structure of 2 (Figure 3).

When the same reaction mixtures are left to stand for few months the initially formed crystals of 1 and 2 dissolve to slowly form crystals of compound 3, [Mn(bix)2(NO3)2]. The structure of 3 consists of two identical interpenetrating 3D networks of four-connected nodes with the CdSO4 (6°-8-cds) topology (Figure 4). There are two independent Mn atoms, both lying on inversion centers, that alternate as nodes in each net. The framework structure is highly distorted with respect to the “ideal” reference tetragonal cnds net. The coordination geometry of the metal atoms is octahedral,
species are expected on further investigating these systems by changing the metallic nodes and the counter-anions.

The results reported here are of interest for different reasons: compound 1 is a new example of polycatenated 3D architecture (2D + 1D), comprised of two supramolecular isomers (layers and ladders) embedded in the same crystal. Moreover, the two polycatenated motifs are supramolecular isomers of compound 2 (simply ladders). Finally, the templating role of chloroform molecules in the assembly of 1 and in its transformation into 2 during the desolvation process has also been clarified.

Acknowledgment. This work was supported by MIUR within the project PRIN 2006-2007 “POLYM2006: Innovative experimental and theoretical methods for the study of crystal polymorphism- a multidisciplinary approach.”

Supporting Information Available: Experimental details, TG analyses, CIF files, and supplementary figures and a table are available free of charge via the Internet at http://pubs.acs.org.

References


wR2 = 0.1815. CCDC-655792 (1), CCDC-655793 (2), CCDC-655794 (3) contain the supplementary crystallographic data and can be obtained free of charge via http://www.ccdc.cam.uk/conts/retrieving.html (or from The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB21EZ, UK; fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

(14) The previously defined parameter “density of catenation” (Doc, ref 2a) is here equal to (4/4), but as has already been observed for other examples,15 it seems to be not adequate in the present case.


(16) Recently also infinite polycatenation of 0D motifs (0D → 1D) has been reported, see Jin, C.-M.; Lu, H.; Wu, L.-Y.; Huang, J. Chem. Commun. 2006, 5039, 5041.


(22) Although the detailed mechanism of the 1 → 2 transformation is difficult to be fully envisaged, a simple process leading from a brickwall layer to a set of parallel ladders is shown in Figure S3, Supporting Information.


CG700884Q