Topological isomerism in the formation of a novel three-dimensional metal-organic polycatenane

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The self-assembly of cadmium nitrate with sodium dicyanamide and 1,3-bis(4′-pyridyl)propane generates a kinetic 1D isomer and a thermodynamic 2D isomer, which presents an unusual pattern of 3D supramolecular entanglement.

The design and construction of metal-organic coordination polymers has attracted intense interest not only for their potential applications as new functional materials, but also for their fascinating structural and superstructural diversity.[1–3] One of the most intriguing phenomena related to this diversity is interpenetration and a wide range of interpenetrating polymeric networks have been recognized recently.[2] Particularly attractive are polymeric systems sustained by supramolecular entanglement of constituent motifs that are of lower dimensionality than the resulting overall architecture.[4–7] Many supramolecular 3D assemblies have been generated by inclined interpenetration of 2D networks (2D inclined interpenetration).[2–4] Dimensional increase can also be achieved by 2D networks interpenetrating in a parallel fashion (2D → 3D parallel interpenetration), but examples are still rather rare.[6,7]

Besides interpenetration, another remarkable phenomenon contributing to structural diversity is supramolecular isomerism.[3] Various different isomers from simple building blocks such as T-shaped nodes have been reported.[3,8] Recently, Schröder and his coworkers described two isomers from CuI and bis(4-pyridyl)disulfide and preferred the term "topological isomerism" to emphasize the differences in the topology and connectivity of the networks.[9] Here we report an unusual example of topological isomerism related to the *cis* or *trans* geometry around the metal ion. Interestingly, the thermodynamic phase presents a novel 3D architecture sustained by the catenation of the "arcs" on the surfaces of adjacent layers.

The evaporation of a methanol–water solution of sodium dicyanamide [Na(dca)], cadmium(II) nitrate and 1,3-bis(4′-pyridyl)propane (bpp) yields two kinds of crystals of different shape but identical stoichiometry, $[Cd(dca)_2(bpp)]_\infty$. If the crystals were allowed to remain in the solution, the column-shaped crystals (**1**) disappeared and transformed into the block crystals (**2**). This indicated that **1** is a kinetic product with **2** being thermodynamically more stable. The transformation occurred possibly by re-dissolution of the former, followed by recrystallization of the latter. Indeed, when we recrystallized the mixture of **1** and **2** from methanol, only **2** was obtained. This phenomenon of isomerization is similar to that observed for the two isomers of $[CuBr(L)]_\infty$ (L = 3,3′-dipyridylethyne).[10]

The structures of both isomers were determined by X-ray crystallography. The Cd(II) atom in **1** is octahedrally coordinated by two pyridyl and four nitrile nitrogens with the two pyridyl groups in *trans* positions. The polymeric structure of **1** can be described as three sinusoidal ribbons, one $[Cd(\mu\text{-}bpp)]_n$ and two $[Cd(\mu\text{-}NCNCN)]_n$, intersecting at the Cd atoms, thus producing an infinite 1D chain (Fig. 1). The chain contains the 12-membered $M(dca)_2M$ rings that have been found in some 1D complexes of the $[M(dca)_2(L)_2]$ type (L = pyridine and analogous monodentate ligands, also in *trans* positions).[11] Interestingly, the rings in **1** adopt an unusual boat conformation to facilitate coordination of the arc-shaped bpp bridges in the *GG* conformation, while the rings in the previously reported complexes are rather flat with a slight chair conformation, producing a linear chain of $M(dca)_2$. The chains in **1** are aligned in parallel and interdigitated with the $(CH_2)_3$ groups overlapping, resulting an overall 2D sheet (Fig. 1). Another interesting feature of the structure is the unusual conformation of the bpp ligand. It has been noted that this flexible ligand usually assume *TT*, *TG* or *GG*′ conformations with quite different N-to-N distances (within the 6.7–10.1 Å range).[12] It is only very recently that the first example of the *GG* conformation was recognized by Carlucci and his

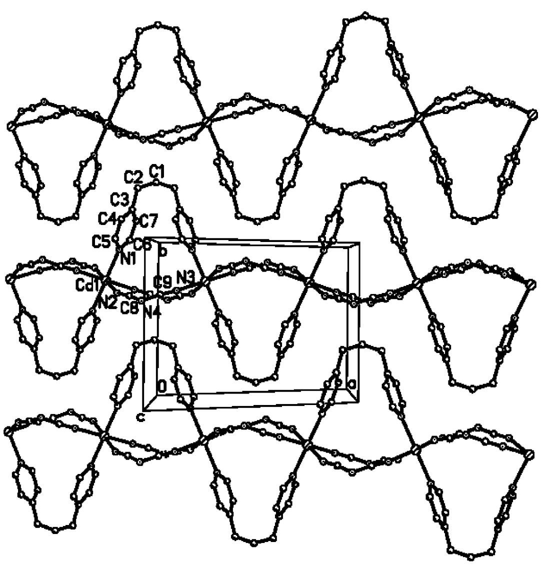

Fig. 1 View down the *c* axis showing the 1D chains and the quasi-2D sheet resulting from interdigitation in **1**; hydrogen atoms are omitted for clarity.

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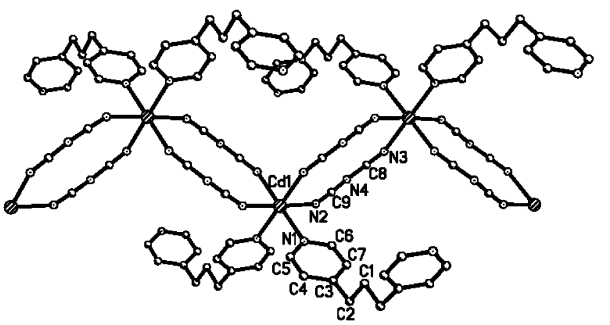

Fig. 2 View with the atom labeling scheme, showing the metal environment and one of the zigzag [Cd(dca)$_2$] chains in **2**. Hydrogen atoms have been omitted for clarity.

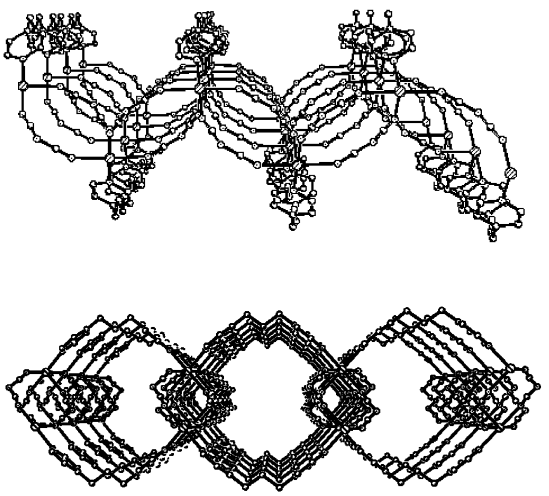

Fig. 3 Two side views of one of the layers in **2**, showing the undulation (top) and the "channels" (bottom, down the [Cd(dca)$_2$] chains). Hydrogen atoms have been omitted for clarity.

co-workers in a binuclear species, [Cu$_2$(μ-bpp)$_2$(μ-NO$_3$)$_2$-(NO$_3$)$_2$]·2CH$_2$Cl$_2$ (**3**).[12a] The two pyridyl rings of the bpp ligand in **1** are in facing positions, as observed in **3**, but exhibit a significantly larger dihedral angle (38.7° *vs.* 13°) and hence a significantly longer N-to-N distance (5.23 *vs.* 3.87 Å). The differences reflect the flexibility of the *GG* conformation and its adaptability to co-bridges of different lengths.

The thermodynamic isomer **2** consists of 2D coordination layers polycatenated into an overall 3D architecture. Again, the metal atom is octahedrally coordinated to four dca and two bpp bridging ligands with similar bond distances. Now, however, the two pyridyl groups are in *cis* positions. This *cis* coordination geometry generates a zigzag chain of M(dca)$_2$ (Fig. 2), which has only been recognized in two 1D coordination polymers, M[N(CN)$_2$]$_2$(2,2′-bipy) (M = Mn[11f,g] and Cd[11h]), where the *cis* geometry is dictated by the chelating 2,2′-bipyridine ligand. In **2**, the arc-shaped bpp ligands, which now adopt the *TT* conformation with a much longer N-to-N distance (9.41 Å), act as "arch bridges" between parallel adjacent zigzag chains, yielding an undulating 2D layer with a (4,4) network (Fig. 3). A remarkable feature of the layer is that the arc-shaped bpp ligands protrude from both sides of the layer, increasing the "empty" space within the layer. This is evidenced by the existence of the 1D infinite channels that run parallel to the M(dca)$_2$ chains (Fig. 3, bottom). In the crystal, each arc (*i.e.*, the bpp ligand) protruding from a layer is catenated with the adjacent arc from another layer generated by a 2-fold axis that threads through the arcs and parallels the layers but not the M(dca)$_2$ chains. Therefore, each layer is entangled with two adjacent (one above, one below) identical motifs, filling the "empty" space and generating an interesting 3D polycatenane. Fig. 4 illustrates the 3-fold interpenetrating topology.

The structure of **2** represents a novel type of 2D → 3D parallel interpenetration. Parallel 2D networks usually interpenetrate without dimensional increase,[2,13] and they must be highly undulating or "thick" in order to increase the dimensionality.[2b] To our knowledge, there have been only two examples of undulating layers interpenetrating in parallel into 3D arrays, and in both cases, the catenation is actually sustained by short interlayer metal-metal contacts.[6,14] The other known examples of 2D → 3D parallel interpenetration involve "thick" double, triple or even quintuple layers composed of (4,4) or other sheets.[7] In the present case, the unusual dimension-increasing parallel interpenetration is made possible not only by the undulation of the single (4,4) layers built of zigzag chains, but more remarkably, by the arc-like feature of the bpp ligands protruding from the "surface" of the layers.

It is worthwhile to compare the two structures to find some clues to the thermodynamic preference of **2** to **1**. Although the bond lengths and angles around the metal atoms are similar, the geometries of the bpp ligand and the M(dca)$_2$M ring in **1** are very different from those in **2**. The unusual *GG* conformation of bpp in **1** suffers an extra strain and is obviously unfavoured in energy by comparison with the usual *TT* conformation in **2** (the *GG* conformation in **3** may be stabilized by the double nitrate bridges between metal atoms). On the other hand, the M(dca)$_2$M ring in **2** and the previously reported *cis* and *trans* complexes[11,12] with double dca bridges is rather flat with the two dca bridges on opposite sides of the M···M line, and thus the repulsive interaction between the two anions is minimized. In **1**, the peculiar bent conformation of the M(dca)$_2$M ring imposes a decreased distance between the two dca bridges and hence an increased repulsive interaction.

In summary, we have described two kinetic/thermodynamic isomers that exhibit remarkably different topologies based on

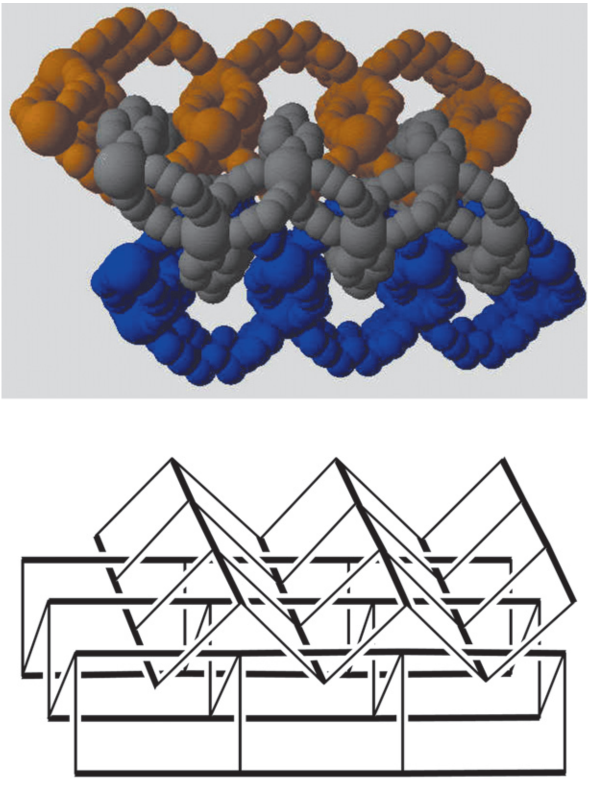

Fig. 4 Space-filling (top) and schematic (bottom, only two layers are shown for clarity) representations of the polycatenation between adjacent (4,4) layers in **2**. In the schematic drawing, bold lines stand for the bpp linkages and thin lines for the double dca linkages.

cis/*trans* coordination geometries and different ligand conformations. In particularly, the unusual interpenetrating topology presented by the *cis* species has been highlighted. This study further illustrates the remarkable structural diversity afforded by supramolecular isomerism and interpenetration and the great challenges faced by crystal engineering.

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Experimental

Synthesis

A methanol solution (25 mL) of 1,3-bis(4′-pyridyl)propane (0.2 mmol) was added to an aqueous solution (10 mL) containing sodium dicyanamide (0.4 mmol) and cadmium(II) nitrate (0.2 mmol). The mixture was stirred for a few minutes and then filtered. The filtrate was allowed to evaporate at room temperature. Both **1** (column-shaped) and **2** (block-shaped) appeared overnight. If the crystals were allowed to remain in the solution for two months, **1** disappeared and the amount of **2** increased. In another experiment, the crystal mixture of **1** and **2** was filtered off and re-dissolved in methanol, and the solution was left to stand. Only crystals of **2** were obtained. Anal. calcd. for $C_{17}H_{14}CdN_8$: C, 46.12; H, 3.19; N, 25.31; found for **1**: C, 45.93; H, 3.39; N, 25.46; found for **2**: C, 46.43; H, 3.28; N, 25.30%.

Crystallography

Data were collected on a NONIUS KappaCCD diffractometer using Mo-Kα radiation. Absorption corrections were made empirically. The structures were solved by direct methods (SHELXS-97) and refined on F^2 using the full-matrix least-squares method (SHELXL-97). Crystal data for **1**: $C_{17}H_{14}CdN_8$, $M = 442.76$, monoclinic, $C2/c$, $a = 16.3548(5)$, $b = 10.4935(4)$, $c = 13.0115(4)$ Å, $\beta = 122.0231(19)°$, $u = 1893.23(11)$ Å^3, $Z = 4$, $D_c = 1.553$ g cm^{-3}, μ(Mo-Kα) = 1.171 mm^{-1}, $T = 293$ K, 16206 reflections measured, 2132 unique ($R_{int} = 0.076$). $R_1 = 0.0341$ [$I > 2\sigma(I)$, 1255 reflections], $wR_2 = 0.0801$ (all data). Crystal data for **2**: $C_{17}H_{14}CdN_8$, $M = 442.76$, Orthorhombic, $Fddd$, $a = 13.2140(2)$, $b = 21.7332(4)$, $c = 28.7125(5)$ Å, $u = 8245.7(2)$ Å^3, $Z = 16$, $D_c = 1.427$ g cm^{-3}, μ(Mo-Kα) = 1.075 mm^{-1}, $T = 293$ K, 36198 reflections measured, 2346 unique ($R_{int} = 0.056$). $R_1 = 0.0438$ [$I > 2\sigma(I)$, 1692 reflections], $wR_2 = 0.1493$ (all data).

CCDC reference numbers 185726 and 185727. See http://www.rsc.org/suppdata/nj/b2/b204324f/ for crystallographic files in CIF or other electronic format.

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14 In ref. 6(b), the authors claimed inclined interpenetration for the compounds $Cu_6(CN)_5(trz)$ (Htrz = triazolate), but the structure actually consists of highly undulating layers interpenetrating into 3D arrays, as has been pointed out by Batten.[2b] We have further inspected the structure, and the layers seem, taking the $Cu_3(\mu_3\text{-trz})$ moiety as the 4-connected node, to have a (4,4) net topology similar to that of compound **2**. But the interpenetrating topology is quite different from that of **2**. In $Cu_6(CN)_5(trz)$, each of the shortest 4-node circuits is interlocked with twelve others, six from the upper layer and six from the lower layer. Furthermore, the catenation is sustained by short Cu···Cu contacts [2.7053 (6) Å].