Supramolecular Chemistry

DOI: 10.1002/ange.200501373

Entangled Coordination Networks with Inherent Features of Polycatenation, Polythreading, and Polyknotting**

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The current interest in coordination polymer frameworks not only stems from their potential applications in microelectronics, nonlinear optics, porous materials, and catalysis, but also from their intriguing variety of topologies and entanglement motifs.[1] Interpenetration has been the most investigated type of entanglement, as shown by the two comprehensive reviews by Batten and Robson.[2] More recently, a complete analysis of all the 3D interpenetrated structures contained in the CSD database was also carried out with a rationalization and classification of the topology of the interpenetration.[3] The increasing number of coordination polymers reported in the literature has led to new and more complex types of entanglement being recognized[2b,4,5] in polycatenated, polythreaded, and polyknotted species that are reminiscent of molecular catenanes, rotaxanes, and knots, respectively.

According to Ciani and co-workers,[5] polycatenation differs from interpenetration in that the whole catenated array has a higher dimensionality than that of the component motifs, and that each individual motif is catenated only with the surrounding ones and not with all the others. Polythreaded structures are characterized by the presence of closed loops, as well as of elements that can thread through the loops, and can be considered as extended periodic analogues of molecular rotaxanes and pseudorotaxanes, depending on the "ideal" possibility of being extricated. Polyknotting is typical of self-penetrating nets, that is, single nets having the peculiarity that the smallest topological rings are catenated by other smallest rings belonging to the same net.

Apart from their intrinsic aesthetic appeal, interest in these new families of entangled structures has been heightened by the fact that their resulting overall architectures are more flexible than the usual networks based entirely on coordination bonds[6]—a functional property that has potential applications ranging from drug-delivery vehicles to sensor devices.[7] Therefore, the exploitation of such species not only increases the structural diversity of coordination polymers, but also provides new insights into the relationships between the structure and function of these materials.

We report here three new entangled frames that were obtained from the use of the rigid 4,4′-bipyridine (bpy) and the long V-shaped 4,4′-oxybis(benzoate) (oba) ligands: $[Ni_2(oba)_2(bpy)_2(H_2O)_2]\cdot bpy$ (**1**) is the first example of a polycatenated array of 1D nanotubes, $[Ni_3(oba)_2(bpy)_2(Hoba)_2(H_2O)_2]\cdot bpy\cdot 2H_2O$ (**2**) is a new type of 2D polythreaded architecture involving five polymeric units at a time, and $[Ni(oba)(bpy)]\cdot 2H_2O$ (**3**) is an intriguing self-penetrating 3D net with an unprecedented topology. The magnetic susceptibilities of compounds **1**–**3** were also investigated (see the Supporting Information).

The crystal structure of compound **1**[8] consists of cationic $[\{Ni(bpy)\}_4]^{8+}$ squares (crystallographically equivalent in pairs), with Ni···Ni separations of 11.180(7) and 11.269(5) Å; these square units are joined by anionic oba^{2-} bridges to give one-dimensional nanotubes containing large cubelike boxes of approximate dimensions 11.2 × 11.3 × 14.9 Å (Figure 1, top). The two differnt types of nickel(II) centers are coordi-

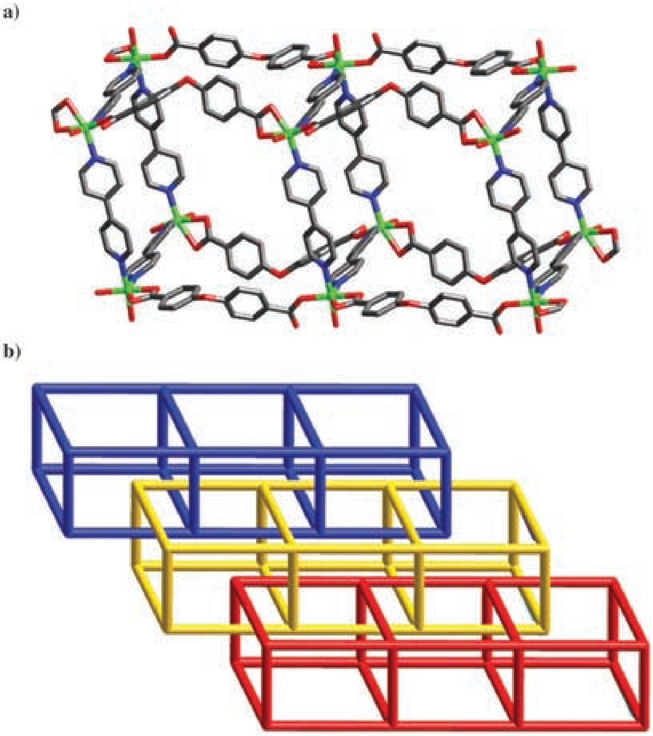

Figure 1. Compound **1**: a) a portion of two cubelike boxes of a single nanotube; b) a schematic view of the parallel polycatenation of three different nanotube motifs.

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[**] This work was supported financially by the National Natural Science Foundation of China (No. 20371011).

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

nated in a distorted octahedral geometry to two oba ligands (one monodentate: Ni-O 1.998(3) and 2.033(3) Å, and one chelate: Ni-O in the range 2.064(3)–2.200(4) Å), two bpy ligands (Ni-N 2.066(4)–2.159(4) Å), and one water molecule (Ni-O 2.045(4) and 2.103(4) Å). A large number of molecular squares have been thoroughly investigated to date,[9] all of which were held together by van der Waals interactions except in one case, in which cationic squares were interconnected by axial chloride bridges into a 3D network.[10] Therefore, to our knowledge, this is the first nanosized tubular structure constructed by the covalent linkage of molecular squares.

The most fascinating and peculiar structural feature of **1** is that each nanotube, which is aligned parallel to the *b* axis, is interlocked in a parallel fashion (along the *a* axis) with the two nearest neighboring ones to give rise to a 2D polycatenated layer (Figure 1, bottom). This kind of entanglement is still quite uncommon and the known examples are based exclusively on infinite 1D molecular ladders.[4,11] Therefore, compound **1**, besides providing a remarkable new structural motif, represents the first example of a 2D array of such motifs polycatenated in a parallel manner. It is also a rare example having both polyrotaxane and polycatenane characteristics[12] and could equally well be considered as formed by interconnected 1D polyrotaxane columns. Free void space is also present within the structure (25.5 % of the crystal volume as calculated by PLATON) which is occupied by guest molecules, with each "box" encapsulating two uncoordinated bpy molecules.

Compound **2** is an extended threaded framework involving 2D coordination layers of square (4^4) topology with dangling ligands. The nodes within the layers are alternately represented by single metal centers (Ni2) of distorted octahedral geometry (Ni-O in the range 2.051(3)–2.119(3) and Ni-N 2 × 2.100(4) Å), and dinuclear units of Ni1 atoms that are bridged by two pairs of oba carboxylate ligands into a paddle wheel moiety (Ni-O in the range 1.971(3)–1.993(4), Ni-N 2.075(4), and Ni···Ni 2.6174(13) Å). All the nodes are connected through oba and bpy ligands to give a 2D motif with very large rhombic windows (dimensions 12.50 × 15.00 Å); dangling oba ligands are coordinated in the axial sites of dinuclear nodes only, and disposed in a mutual *anti* orientation with respect to the layer plane (Figure 2a). The layers are stacked in a parallel manner along the [−1 −1 2] direction in an ABCABC sequence at a distance of approximately 5.4 Å. Each dangling arm has an effective length of about 13.5 Å. As result, the dangling oba ligands of each layer are threaded into the rhombic voids of the two adjacent layers above and below, thus every rhombic window of each layer is threaded by only two dangling ligands that come from opposite directions (this is expected considering that the dangling arms reside on the dinuclear nodes only, Figure 2a). Finally, this unique simultaneous threading fashion of five adjacent polymeric motifs gives the novel (2D→3D) polythreaded array observed for compound **2** (Figure 2b).

Polythreaded structures containing finite components are, at present, rare.[5] The few species known include polythreaded 0D rings with side arms that give 1D[13a] or 2D arrays,[13b] as well as molecular ladders with dangling arms that result in (1D→2D)[13c] or (1D→3D)[13d] polythreaded arrays. Until now, the only known example of a (2D→3D) polythreaded network assembled from 2D motifs is the complex $[Zn(Hbtc)(4,4'\text{-bpy})]_n$ (btc = 1,2,4-benzenetricarboxylate) reported by us very recently,[14] in which the threading involves the two nearest layers only because of the shorter length of the dangling arms.

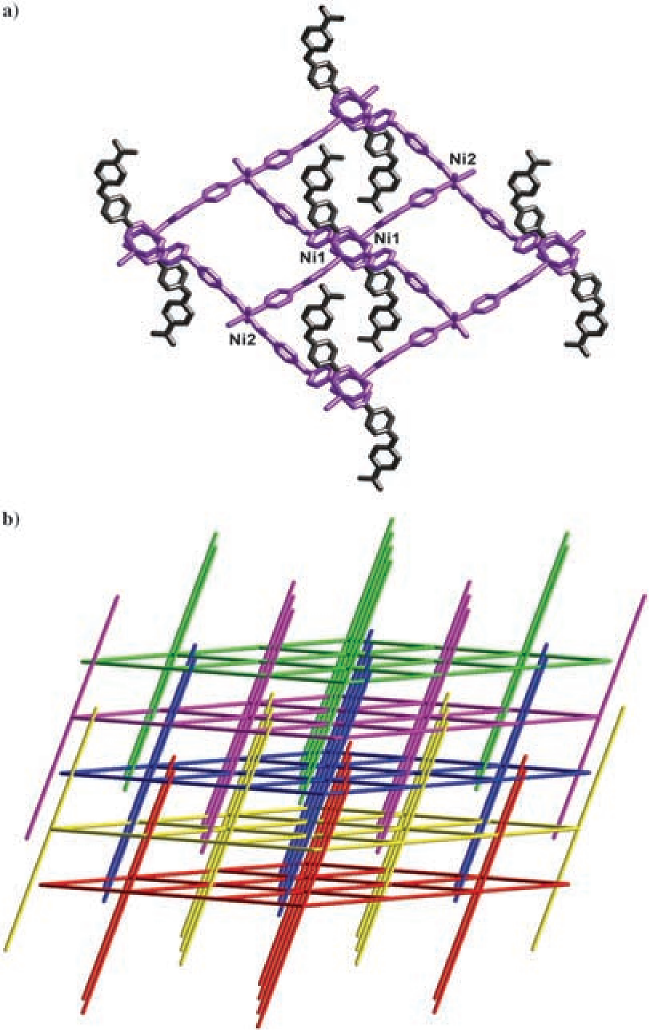

Figure 2. Compound **2**: a) a single 2D square (4^4) layer showing the alternating nodes: single Ni2 atoms and $(Ni1)_2$ paddle wheel units which carry the dangling arms; b) a schematic illustration of the mutual polythreading of five layers.

The threading observed in **2** is stabilized by two weak interactions: a π–π stacking arising from the aromatic rings of the oba ligands penetrating into the same void (interplanar distance: 3.65 Å, offset: 1.39 Å), and strong hydrogen bonding involving the uncoordinated carbonyl oxygen atoms from a dangling ligand and a coordinated water molecule of a mononuclear metal center on the third nearest neighboring layer (O···O 2.82 Å). When these hydrogen bonds are taken into account, the resulting structure displays a threefold interpenetrated 3D 6-connected net with α-Po (primitive cubic, pcu) ($4^{12}.6^3$) topology. A distorted cubelike unit of the resulting α-Po nets (Figure 3a) shows dimensions of 12.5 ×

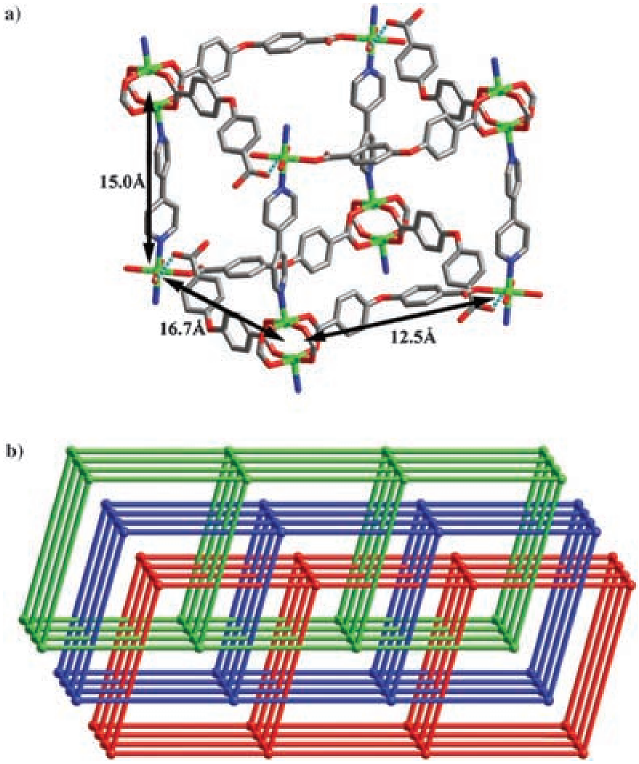

Figure 3. Compound **2**: a) a single distorted cubelike unit of the α-Po net with the relative dimensions 12.5 × 15.0 × 16.7 Å; b) a schematic view of the threefold interpenetrating α-Po network that is formed when H bonds are taken into account.

15.0 × 16.7 Å. The three interpenetrating nets of the 3D array originate from layers of A, B, and C type (Figure 3b). An analysis of the topology of interpenetration according to a recent classification[3] reveals that compound **2** belongs to Class Ia (all the interpenetrated nets are generated only by translation and the translating vector is [100] (9.90 Å). The overall entanglement still leaves voids that are occupied by two water molecules and one bpy guest molecule that form an intricate net of H bonds across different layers.

Compound **3** is a new (3,5)-connected 3D self-penetrating network with an unprecedented topology whose structure can be described as follows. First of all, it comprises neutral layers of composition [Ni(oba)]. Within these layers the nickel atoms are coordinated by four oxygen atoms from one chelating and two μ_2-bridging carboxylate ions of oba ligands (Ni-O in the range 2.004(3)–2.162(4) Å) to give dinuclear units that are further extended by bridging oba ligands into 2D layers (Figure 4a). From consideration of the Ni and C atoms of the μ_2-carboxylate groups as nodes, we can see that the layers are comprised of octagonal and rhombic meshes with a 3-connected (4.8^2) topology. The diagonals of the distorted rhombic windows are about 4.3 and 4.4 Å, while the dimensions of the distorted octagonal windows, estimated from the maximum distances between opposite vertices, are about 16.9 × 22.9 Å. The resulting layers are highly undulated as a consequence of the bent geometry of the dicarboxylate ligands and the twisting of its phenyl rings (dihedral angle of ca. 83°). The corrugation of the sheets makes the parallel interpenetration of two such layers possible (the average planes of the layers are coincident) to give a twofold interpenetrated array. Entanglement of layers with (4.8^2) topology are rare compared to layers that show the more common square (4^4) or hexagonal (6^3) topologies, and only few examples are known that include sheets that are interpenetrated in a parallel twofold[15] and threefold[16] manner. These sets of twofold interpenetrated layers generate elliptic-shaped channels running along the *c* axis (Figure 4b) that are populated by the guest water molecules. The twofold layers stack in an ABAB sequence parallel to the plane defined by the (**a**,**b**) and **c** vectors, and are interconnected to the two closest layers (above and below the average plane) through bpy bridges disposed along the crystallographic *a* and *b* axes. Two bpy ligands are *trans*-coordinated to each metal center in an axial position (Ni···N 2.096(3) Å) to give a unique (3,5)-connected 3D framework with an unprecedented $(4.8^2)(4.6^4.8^4.10)$ topology. In this simplification the 5-con-

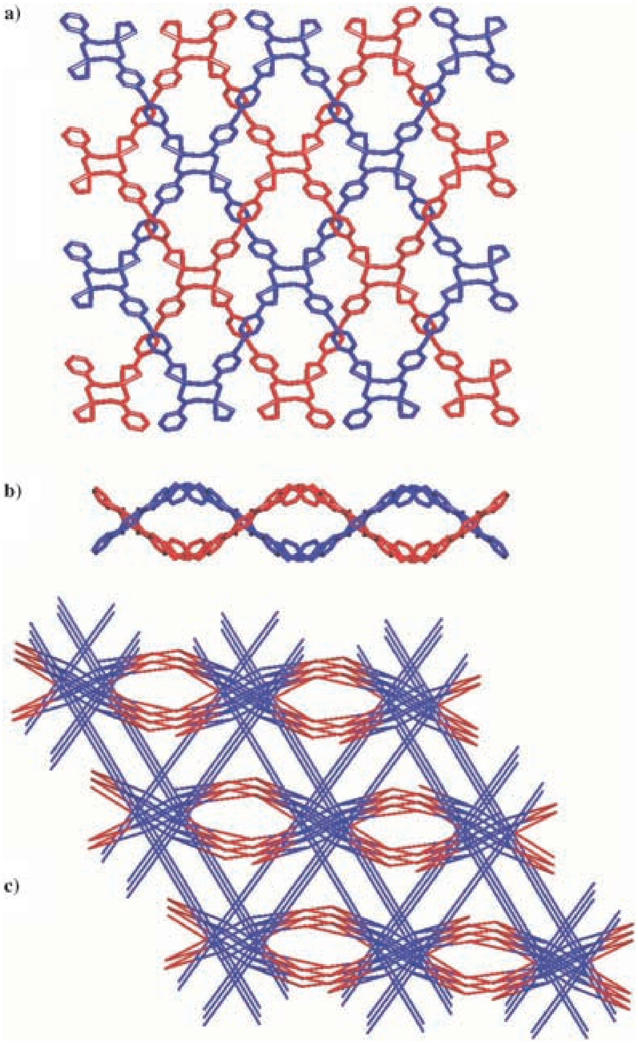

Figure 4. Compound **3**: a) twofold parallel interpenetrating layers of (4.8^2) topology; b) a view down the *c* axis of the twofold interpenetrating layers showing the elliptic-shaped channels; c) a schematic representation of the (3,5)-connected self-penetrating 3D net of $(4.8^2)(4.6^4.8^4.10)$ topology.

nected nodes are the metal atoms and the 3-connected ones are the carbon atoms of the oba ligands bridging the dimetallic unit (Figure 4c).

The network of compound **3** clearly results in self-penetrating since it is generated from linking twofold-interpenetrated sheets. The self-penetration feature is not very common within coordination polymers and only a limited number of self-penetrated nets have been reported to date.[4] A drastic simplification of compound **3** is that it is a 6-connected uninodal net with an unprecedented topology.[17]

In conclusion, although the three compounds described herein were obtained from the same starting building blocks they display quite different structures (ranging from 1D to 3D) and show unusual features of polycatenation, polythreading, and polyknotting. Thus, this study highlights an intriguing feature of coordinative network chemistry in producing rich architectures and topologies.

Experimental Section

1–3: A mixture of $Ni(NO_3)_2 \cdot 6H_2O$ (145 mg, 0.5 mmol for **1–3**), 4,4′-oxybisbenzoate (129 mg, 0.5 mmol for **1–3**), 4,4′-bipyridyl (156 mg, 1 mmol for **1** and **2**; 78 mg, 0.5 mmol for **3**), and water (10 mL) was placed in a 23-mL teflon reactor. After the pH values had been adjusted to 6.5, 5.5, and 7.8 for **1**, **2**, and **3**, respectively, by addition of triethylamine, the mixture was heated at 140°C for 3 days. Green crystals of **1–3** were obtained on cooling the mixture to room temperature at $10\,^{\circ}C\,h^{-1}$.

Received: May 20, 2005

Keywords: coordination modes · networks · nickel · self-assembly · supramolecular chemistry

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[8] Crystal data for **1** ($C_{58}H_{44}Ni_2N_6O_{12}$): $M_r = 1134.41$, triclinic, space group $P\bar{1}$, $a = 12.430(3)$, $b = 14.913(16)$ Å, $c = 15.905(5)$ Å, $\alpha = 88.04(3)$, $\beta = 73.07(3)$, $\gamma = 70.08(3)^{\circ}$, $V = 2644.6(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.425\ mg\,m^{-3}$, final $R1 = 0.0785$ for 11611 independent reflections [$I > 2\sigma(I)$]. Crystal data for **2** ($C_{86}H_{66}Ni_3N_6O_{24}$): $M_r = 1743.58$, triclinic, space group $P\bar{1}$, $a = 9.903(2)$ Å, $b = 12.966(3)$ Å, $c = 16.223(3)$ Å, $\alpha = 92.44(3)$, $\beta = 92.66(3)$, $\gamma = 106.50(3)^{\circ}$, $V = 1991.7(7)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.454\ mg\,m^{-3}$, final $R1 = 0.0733$ for 8648 independent reflections [$I > 2\sigma(I)$]. Crystal data for **3** ($C_{24}H_{20}NiN_2O_7$): $M_r = 507.13$, monoclinic, space group $C2/c$, $a = 18.911(4)$ Å, $b = 12.318(5)$ Å, $c = 19.885(4)$ Å, $\beta = 95.58(3)^{\circ}$, $V = 4610(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.461\ mg\,m^{-3}$, final $R1 = 0.0663$ for 5272 independent reflections [$I > 2\sigma(I)$]. The data were collected at 173(2) K on a Rigaku R-AXIS RAPID IP diffractometer with $Mo_{K\alpha}$ monochromated radiation ($\lambda = 0.71073$ Å). The structures were solved by direct method using SHELXS-97 and extended using Fourier techniques. CCDC-266679–266681 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[17] If the dinuclear units are simplified to their baricentres (new nodes) joined by pairs of bpy ligands (new links) the net becomes 6-connected self-penetrating with a ($4^4.6^{11}$) topology, unprecedented within coordination polymers.[1f]