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Metal-Coordination-Directed Assembly of Binuclear Trigonal Prisms and Three-Dimensional Hydrogen-Bonded Networks

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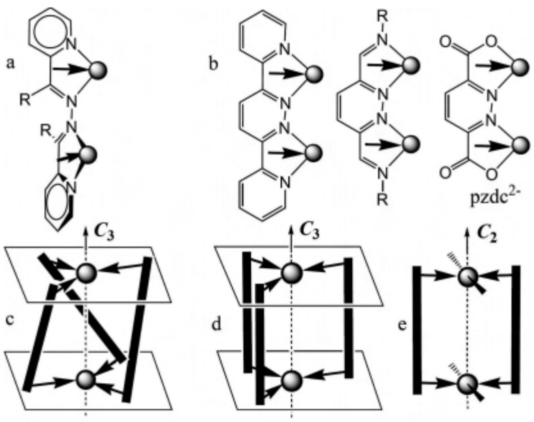
The coordination of pyridazine-3,6-dicarboxylate by manganese(II) leads to unusual anionic binuclear trigonal prisms, which coassemble with the hexaaquamanganese(II) antiprisms to generate a hydrogen-bonded CsCl-type three-dimensional network.

The self-assembly of discrete metallosupramolecular entities with specific shapes directed by metal−ligand coordination has attracted considerable interest.[1] By the judicious selection/design of metal ions and organic ligands with definite coordination preferences, a large variety of supramolecular motifs, such as helicates, polygons, polyhedrons, and prisms, have been constructed.[1,2] The semiflexible bis(bidentate) diazine ligands exemplified in Chart 1a are the simplest ligands that have been used to construct binuclear triple helicates (M_2L_3) with octahedral metal ions.[3] The crucial helicating element is that the ligands can twist around N−N to produce a spiral conformation with the two chelate vectors pointing in different directions (Chart 1c). By contrast, for the pyridazine-based ligands (Chart 1b), the rigidity dictates that the chelate vectors point in the same direction. With six-coordinative metal ions, binuclear trigonal-prismatic entities (M_2L_3; Chart 1d) can be expected. However, such species are extremely rare.[4] A possible reason is the geometrical mismatch: the prismatic arrangement of three ligands defines two trigonal-prismatic binding cavities, while the preferred environment for most six-coordinative metal ions is octahedral; thus, the outcomes of the self-assembly are usually binuclear species (Chart 1e) with two side-by-side ligands, with the octahedral coordination being completed by axial ligands.[5,6] Only recently has a trigonal-prismatic species with the geometrically flexible silver(I) ion, $[Ag_2(bptz)_3]^{2+}$ [bptz = 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine], been reported, where the assembly is assisted by the anion−π interaction between AsF_6^- or SbF_6^- and the π−acidic tetrazine ring.[4] Here, we report the structure and magnetic properties of a novel ionic species, $[Mn(H_2O)_6][Mn_2(pzdc)_3]$ (**1**; $pzdc^{2-}$ = pyridazine-3,6-dicarboxylate), which contains the unusual binuclear trigonal-prismatic motif. The supramolecular structure of the side-by-side $[M_2(pzdc)_2(H_2O)_4]$ (M

Chart 1



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(6) (a) The molecular structure of **3** has been reported elsewhere (ref 6b), together with the magnetic properties of **2** and **3**, but without any discussion about intermolecular interactions and the supramolecular networks, which are presented in this paper for comparison with **1**. (b) Escuer, A.; Vicente, R.; Mernari, B.; El Gueddi, A.; Pierrot, M. *Inorg. Chem.* **1997**, *36*, 2511.

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= Co for **2** and Ni for **3**[6]) species is also described for comparison.

The construction of infinite supramolecular architectures with specific net topology from discrete molecular components (tectons) through hydrogen bonds is another attractive subject in the field of supramolecular chemistry.[7] To get a well-defined net, it is crucial that the hydrogen-bonding groups (recognition sites) in the tectons are properly predisposed in space in a divergent and complementary fashion. In this Communication, we show how metal coordination predisposes the hydrogen-bonding sites in **1**−**3** in a complementary (**1**) or self-complementay (**2** and **3**) way to generate a binodal or uninodal eight-connected three-dimensional (3D) net. Compared to lower-connected hydrogen-bonding 3D nets,[8] eight-connected hydrogen-bonding nets are still rare,[9,10] reflecting the challenge of incorporating a high number of divergent and complementary hydrogen-bonding sites into the tectons. Evidently, metal coordination represents an efficient way of gathering and predisposing hydrogen-bonding sites.

The compounds were prepared by the solvothermal reactions of dimethyl pyridazine-3,6-dicarboxylate and the appropriate metal(II) chlorides in aqueous ethanol (Supporting Information). X-ray crystallographic analyses[11] revealed that the manganese(II) compound consists of $[Mn_2(pzdc)_3]^{2-}$ anions and $[Mn(H_2O)_6]^{2+}$ cations (Figure 1a). As expected, each $pzdc^{2-}$ chelates two Mn1 ions, and the two chelate rings linked by the pyridazine ring are coplanar and lock the two metal ions in a line nearly parallel to the N−N bond. Thus, two equivalent Mn1 atoms that reside on a C_3 axis with Mn···Mn = 4.085(1) Å are bridged by three N−N bonds from equivalent $pzdc^{2-}$ ligands, each of which is bisected by a C_2 axis perpendicular to the C_3 axis, generating a binuclear moiety with D_3 symmetry. Constrained by the rigidity of the ligand, the $[MnN_3O_3]$ moiety adopts the uncommon trigonal-prismatic geometry with a twist angle of 4.8° (this angle is 0° for an ideal trigonal prism and 60° for an octahedron). The ligand constraints also dictate a trigonal-prismatic geometry for the binuclear moiety, with the overall shape closely resembling a revolving door.

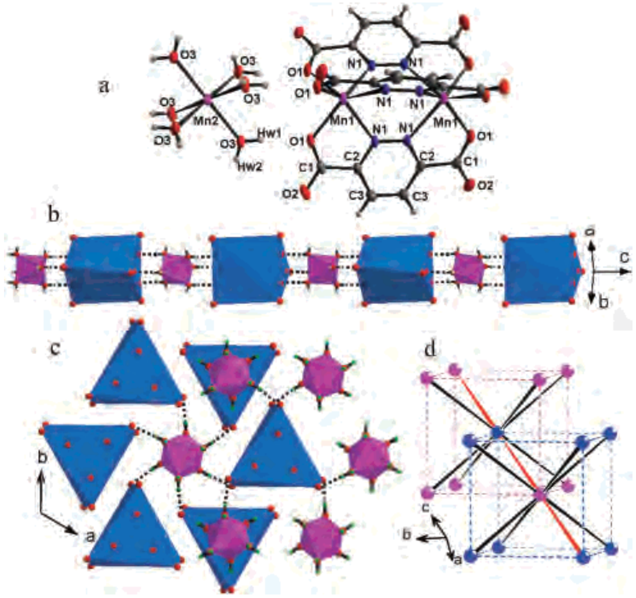

Figure 1. Structure of **1**: (a) the molecular structure; (b) the chain via the triple hydrogen bonding; (c) the single hydrogen bonds around the cation and anion; (d) the binodal bcc net (red and black lines for the triple and single hydrogen-bonding connections, respectively).

The binuclear dianion is counterpoised by $[Mn(H_2O)_6]^{2+}$, which, with $\bar{3}$ symmetry, assumes an octahedral or, more exactly, trigonal-antiprismatic geometry furnished by six equivalent water ligands. Remarkably, the anion and cation are perfectly complementary in hydrogen-bonding sites. In the prismatic anion, the six uncoordinated oxygens (O2) occupy the vertices of the prism, and the six coordinated oxygens (O1) are disposed as two small triangles on the bases. In the antiprismatic cation, six equivalent hydrogens (Hw2) point away from the C_3 axis of the $[MnO_6]$ antiprism, and the other six hydrogens (Hw1) are displaced from the bases of the antiprism along the C_3 axis to constitute two small triangles above and below the antiprism, respectively. The arrangement of the O1 atoms and that of the Hw1 atoms are well matched, and hence a triple hydrogen-bonding motif with prismatic geometry is formed and consists of three quasi-linear O3···O1 hydrogen bonds [O−H···O, 172(3)°, O···O, 2.834(2) Å]. This unusual hydrogen-bonding motif sets up a triple bridge between Mn1 and Mn2 $[Mn2\text{-}(O{-}H\cdots O)_3Mn1]$ with a separation of 5.466(1) Å and directs the prisms and antiprisms to be alternately stacked in a base-to-base fashion along a common C_3 axis, producing a columnlike infinite chain (Figure 1b). The chain as a whole is self-complementary for interchain hydrogen bonding. Each prism or antiprism from a chain is linked to six antiprisms or prisms from six different chains (Figure 1c) via the vertex-to-vertex O3−Hw2···O2 single hydrogen bonds [O−H···O, 175(3)°; O···O, 2.732(3) Å]. On the whole, each anion/cation is connected to eight cations/anions via two triple hydrogen-bonding bridges and six single hydrogen bonds, and the 3D stacking of the eight-connected ions is

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(11) Crystal data for **1**: $C_{18}H_{18}Mn_3N_6O_{18}$, M_r = 771.20, trigonal, space group $R\bar{3}c$, a = 12.190(3) Å, c = 30.035(3) Å, V = 3865.1(15) Å^3, Z = 6, μ(Mo Kα) = 1.549 mm^{-1}, ρ_{calcd} = 1.988 g cm^{-3}, T = 293(2) K, R1 = 0.0302, wR2 = 0.0612. Crystal data for **2**: $C_{12}H_{12}Co_2N_4O_{12}$, M_r = 522.12, orthorhombic, space group *Pbca*, a = 13.267(3) Å, b = 8.7549(18) Å, c = 14.685(3) Å, V = 1705.6(6) Å^3, Z = 4, μ(Mo Kα) = 2.025 mm^{-1}, ρ_{calcd} = 2.033 g cm^{-3}, T = 293(2) K, R1 = 0.0327, wR2 = 0.0476.

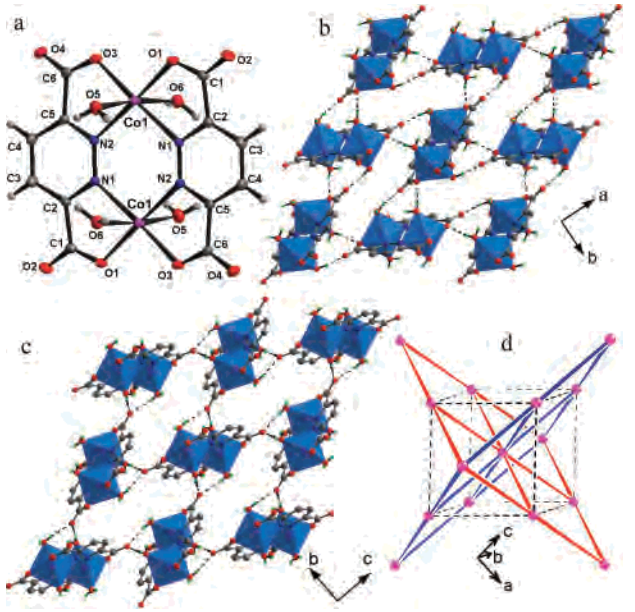

Figure 2. Views of the structure of **2**, showing the molecular structure (a), the 2D hydrogen-bonded sheets (b and c), and the uninodal bcc net (d).

similar to that in CsCl, generating a binodal body-centered-cubic (bcc) net (Figure 1d). Obviously, metal−ligand coordination plays a decisive role in facilitating the prismatic triple hydrogen bonding, which, with enhanced strength and directionality, should be the most important directing force for intermolecular recognition and the 3D assembly.

Compounds **2** and **3** are isomorphous,[6,12] and **2** is described below. The structure consists of centrosymmetric neutral $[Co_2(pzdc)_2(H_2O)_4]$ dimers, in which two cobalt(II) ions are locked between two $dcpz^{2-}$ ligands in a side-by-side fashion [Co⋯Co, 3.842(1) Å], with the octahedral coordination geometry being completed by two axial water molecules (Figure 2a). Unlike the $[Mn_2(pzdc)_3]^{2-}$ entity, which contains only hydrogen acceptors, $[M_2(pzdc)_2(H_2O)_4]$ contains both hydrogen acceptors and donors. Interestingly, the acceptors and donors are arranged in a self-complementary way, and each dimer is connected to 8 neighbors via a total of 16 hydrogen bonds. Taking the dimers as eight-connected nodes, the resulting 3D network also exhibits the bcc topology, but now it is uninodal (all of the nodes are identical). The structure can be considered as being composed of two intersecting sets of two-dimensional (2D) (4, 4) nets with different hydrogen-bonding connections. In the (002) planes (Figure 2b), the connection is completed by the double hydrogen-bonding motif involving two water molecules from a dimer and two carboxylate oxygens (O1 and O2) from another dimer [O−H⋯O, 164(3)°; O⋯O, 2.702(3) and 2.743(3) Å]. In the (200) planes (Figure 2c), the connection is the bifurcated double hydrogen-bonding motif involving two water molecules from a dimer and an uncoordinated oxygen (O4, as the bifurcated acceptor) from another dimer [O−H⋯O, 152(3)° and 176(3)°; O⋯O, 2.799(3) and 2.741(3) Å]. The two sets of 2D nets are perpendicular and intersect at the nodes to generate the 3D bcc net (Figure 2d).

It is worthwhile to justify why the cobalt(II) and nickel(II) species do not adopt the trigonal-prismatic structure observed for manganese(II). First, the size of the metal ion may be important. For given M−L distances, the interligand repulsion in the trigonal-prismatic environment is higher than that in the octahedral environment. Cobalt(II) and nickel(II) are smaller than manganese(II) and require shorter M−L distances for coordination. While manganese(II) can compromise to occupy the prismatic cavity dictated by three ligands, with the interligand repulsion compensated for by M−L interactions, cobalt(II) and nickel(II) cannot because the ligands would be pulled closer and the increased interligand repulsion could not be compensated for. Second, while high-spin manganese(II) has no ligand-field stabilization in either the octahedral or trigonal-prismatic environment, cobalt(II) and nickel(II) gain more ligand-field stabilization energy in the octahedral field than in the trigonal-prismatic field.

The magnetic susceptibility of **1** was measured in the 2−300 K range. Upon cooling, χT decreases and χ increases continuously. The χ^{-1} vs T plot above 10 K follows the Curie−Weiss law with $C = 13.13$ emu K mol^{-1} and $\theta = -7.07$ K. These features indicate weak antiferromagnetic interactions. The best fit of the data to the susceptibility expression including both contributions from the binuclear and mononuclear motifs led to $J = -2.46$ cm^{-1} with $g = 2.01$, where J refers to the exchange through the triple N−N bridges. Alternatively, the system can be considered as consisting of chains with two alternating bridges, $[(O\cdots H{-}O)_3M_B(O{-}H\cdots O)_3M_A(N{-}N)_3M_A]_n$. The fit of the data to the expression proposed by Escuer et al.[12] for such alternating chains led to $J_2 = -2.44$ cm^{-1} for the triple N−N bridges and $J_1 = -0.028$ cm^{-1} for the triple hydrogen-bonding bridges (Supporting Information). The very small J_1 value confirms that the exchange via the hydrogen-bonding bridges is negligible.

In conclusion, we have shown how the coordination of the $pzdc^{2-}$ ligand by manganese(II) leads to an unusual binuclear trigonal-prismatic species and how the perfect complementarity between the binuclear prisms and the hexaaquamanganese(II) antiprisms generates a 3D network with the binodal bcc net. We have also described the uninodal bcc networks constructed from the self-complementary binuclear cobalt(II) and nickel(II) molecules. The arrangement of the peripheral oxygen atoms makes the anionic binuclear prism a unique and versatile building block for the engineering of hydrogen-bonded and coordination networks. Further investigations along this line are being attempted in our laboratory.

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Supporting Information Available: Synthetic procedures, χT and χ vs T plots and X-ray crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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