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Assembly of Hydrogen Bonded Diamondoid Networks Based on Synthetic Metal-Organic Tetrahedral Nodes

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Reaction of $Mn(ClO_4)_2$ or $Co(PF_6)_2$ with 4,4′-dipyridine-dioxide (dpdo) produced novel molecular species $[M(dpdo)_4(H_2O)_2]^{2+}$, which hold a tetrahedral configuration notwithstanding their octahedral environment around the metal centers. The tetrahedral moieties are further assembled through hydrogen bonds between peripheral NO ends of dpdo ligands and coordinated water molecules, giving rise to 3D diamondoid networks.

Diamondoid networks are of great interest in the field of supramolecular chemistry and crystal engineering because of their predisposition to pack in acentric space groups, which are relevant to NLO properties.[1] Such materials may be obtained from tetrahedral components through covalent linkage, metal coordination, hydrogen bond, donor−acceptor interactions, or van der Waals forces. The organic diamondoid structures are frequently achieved either directly from homo- or heterogeneous tetrahedral building blocks[2] or through the appropriate linear node connectors,[3] while the engineering of most inorganic, metal-organic, or organometallic diamondoid networks is aided by the preferences of certain metal ions for tetrahedral coordination with bridging spacers.[4] The strategy based on tetrahedral nodes and linear spacers for metal-organic diamondoid networks is limited due to the lack of well-defined multiple functionalized T_d symmetric nodes.[1b,5]

In this context, we report two novel supramolecular solids $[M(dpdo)_4(H_2O)_2]X_2{\cdot}2H_2O$ (dpdo = 4,4′-dipyridine-dioxide; $M = Mn^{2+}$, $X = ClO_4^-$ **1**; $M = Co^{2+}$, $X = PF_6^-$ **2**), which constitute tetrahedral nodes consisting of metal ions and linear spacers. These tetrahedral nodes further self-assemble in an unusual fashion into a 3D superdiamond network through hydrogen bonds. We and others have been dedicated to the supramolecular assembly of pyridyl-based dioxide compounds due to their flexible connection modes and strong capability of forming hydrogen bonds.[6] Their use for construction of diamondoid networks with intrinsic tetrahedral ammonium has been recognized very recently.[5]

Both compounds **1** and **2** were prepared by mixing dpdo and the corresponding metal salts in aqueous solution.[7]

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(7) Preparation of **1** follows: To a 5 mL aqueous solution of $Mn(ClO_4)_2{\cdot}6H_2O$ (0.5 mmol, 0.180 g) was added 5 mL of an aqueous solution of 4,4′-dpdo (1 mmol, 0.224 g) under stirring. The clear filtrate was allowed to stand for one week at room temperature, giving rise to orange-red crystals (yield of ca. 52% based on dpdo). Anal. Calcd for $C_{40}H_{40}Cl_2MnN_8O_{20}$: C, 44.54; H, 3.74; N, 10.39%. Found: C, 44.58; H, 3.86; N, 10.35%. Preparation of **2** follows: To an aqueous solution (5 mL) of $Co(NO_3)_2{\cdot}6H_2O$ (0.5 mmol, 0.183 g) was added 5 mL of an aqueous solution of 4,4′-dpdo (1 mmol, 0.224 g) under stirring, which was then followed by the addition of solid $NaPF_6$ (1 mmol, 0.168 g). The clear filtrate was allowed to stand for one week at room temperature, giving rise to red crystals (yield of ca. 40% based on dpdo). Anal. Calcd for $C_{40}H_{40}CoF_{12}N_8O_{12}P_2$: C, 40.94; H, 3.44; N, 9.55%. Found: C, 41.07; H, 3.42; N, 9.51%.

10.1021/ic048648q CCC: $30.25

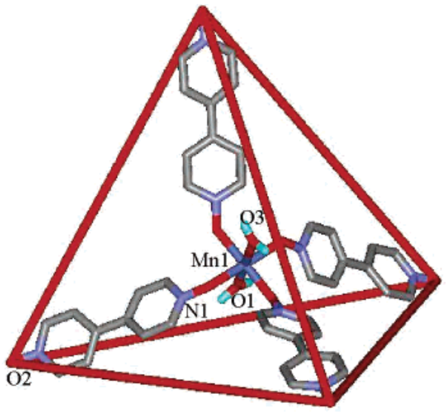

Figure 1. Molecular structure of $Mn(dpdo)_4(H_2O)_2]^{2+}$ unit in **1**. The red solid lines show the tetrahedral geometry of the $[Mn(dpdo)_4(H_2O)_2]^{2+}$ unit. Bond lengths and angles follow for **1**: Mn1−O1= 2.157(4) Å; Mn1−O3 = 2.161(6) Å; Mn2−O4 = 2.195(4) Å; Mn2−O6 = 2.174(6) Å; N1−O1−Mn1 = 131.2(3)°; N3−O4−Mn2 = 129.3(3)°. Bond lengths and angles follow for **2**: Co1−O1 = 2.057(5) Å; Co1−O3 = 2.135(7) Å; Co2−O4 = 2.095(5) Å; Co2−O6 = 2.136(7) Å; N1−O1−Co1 = 130.1(4)°; N3−O4−Co2 = 129.0(4)°.

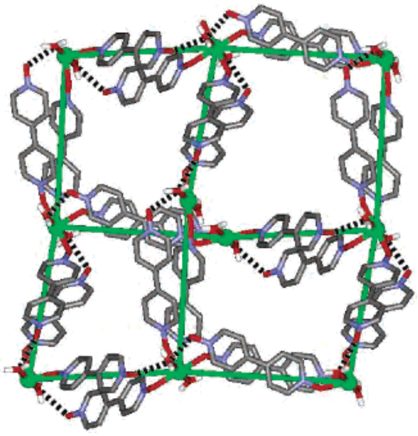

Figure 2. A single diamondoid cage assembled by tetrahedral $[M(dpdo)_4(H_2O)_2]^{2+}$ nodes through hydrogen bonds and $\pi-\pi$ interactions: carbon, gray; oxygen, red; nitrogen, blue; hydrogen, white; metal (Mn or Co), green; hydrogen bonds, black dashed line. The green lines of the connectivity among metal centers give rise to an adamantane.

Single-crystal X-ray diffraction analysis revealed that they are isomorphous and crystallize in a noncentric space group $I\bar{4}$ and form a 3D hydrogen bonded diamondoid network.[8] Two independent metal ions in an asymmetric unit have essentially the same octahedral coordination environments surrounded by four monodentate dpdo ligands and two water molecules, in which metal centers and water molecules are located on a $\bar{4}$ axis. Notwithstanding the four coordinated oxygen atoms of dpdo molecules occupying the planar position of the octahedron, the overall arrangement of $[M(dpdo)_4(H_2O)_2]^{2+}$ unit has a tetrahedral geometry with T_d symmetry as illustrated in Figure 1 due to the angular coordination mode of dpdo. The peripheral O−M−O angles are ca. 104.1° and 120.8° for both compounds. This is one of the remarkable features of dpdo distinct from the corresponding 4,4′-bipyridine, which assumes a linear connectivity. Two pyridyl groups of dpdo spacers twist at 13.9° and 21.8° in **1** and 12.0° and 21.3° in **2**.

Taking the strong capability of forming hydrogen bonds of dpdo and possible coordination to metal ions into account, the $[M(dpdo)_4(H_2O)_2]^{2+}$ moiety has potential in constructing diamondoid network. In general, self-complementarity of T_d molecules through hydrogen bonding requires dual functional groups (donor and acceptor) such as carboxylic acid, pyridone, and diaminotriazine. Interestingly, though the dpdo molecule can function only as a hydrogen bond acceptor, the $[M(dpdo)_4(H_2O)_2]^{2+}$ moieties indeed self-assemble through hydrogen bonds into a 3D cationic diamondoid network with equal intraframe M···M distance of ca. 11.77 Å (Figure 2). The connection between the tetrahedral nodes is furnished in a way that the uncoordinated oxygen atoms of terminal dpdo molecules in one set form hydrogen bonds with coordinated water molecules from adjacent units belonging to another set [O3···O5a = 2.779(6) Å, O6···O2b = 2.718(5) Å in **1**; O3···O5a = 2.757(3) Å, O6···O2b = 2.724(4) Å in **2**; $a = x + 1/2, y - 1/2, z + 1/2$; $b = -x + 1, -y + 1, z$]. As a matter of fact, the $[M(dpdo)_4(H_2O)_2]^{2+}$ unit can be virtually viewed as two tetrahedral moieties $[M(dpdo)_4]^{2+}$ and $[M(H_2O)_2]^{2+}$ (the array of four hydrogen atoms on two coordinated water molecules has a tetrahedral geometry), which serve as hydrogen bond acceptor and donor, respectively. The assembly is different from the hydrogen bonded self-complementarity observed in carboxylic acid, pyridone, and diaminotriazine systems, in which the hydrogen bond donor and acceptor come from the same molecule. The two coordinated water molecules on each metal ion play a decisive role in facilitating self-complement of the resulting diamondoid network of **1** and **2**. The double dpdo spacers, which bridge two adjacent metal centers, form significant $\pi-\pi$ interactions with interplanar distance of ca. 3.38 Å to further stabilize the 3D network. It is a well-known fact that diamondoid frameworks have a high propensity to interpenetration,[9] which, nevertheless, is avoided in compounds **1** and **2**. This should be attributed to the bulky double dpdo linkers, which efficiently fill part of the void spaces of the diamondoid network. The remaining channels along the [001] direction are accommodated by water molecules and counteranions (Figure 3).

Among the reported transition metal complexes with dpdo, compounds $[Cu_3(H_2O)_6(dpdo)_8](ClO_4)_6\cdot2dpdo\cdot 6H_2O$[6b] and $[Zn(MeOH)_2(dpdo)_3](SiF_6)\cdot3MeOH$[6f] contain octahedral metal centers coordinated with four dpdo ligands and two solvent molecules, similar to that found in **1** and **2**. However, the four dpdo ligands form a square planar geometry, rather than

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(8) Crystal data follow for compound **1**: $C_{40}H_{40}Cl_2MnN_8O_{20}$, M = 1078.64, tetragonal, $I\bar{4}$, $a = b = 23.150(3)$ Å, $c = 8.150(2)$ Å, U = 4367.8(12) Å^3, $Z = 4$, $D_c = 1.640$ Mg m^{-3}, $\mu = 0.519$ mm^{-1}, $F(000)$ = 2220, GOF = 1.075, crystal size 0.24 mm × 0.16 mm × 0.10 mm. R1 and wR2 are 0.0662 and 0.1966, respectively, for 310 parameters and 2419 reflections [$I > 2\sigma(I)$]. Crystal data follow for compound **2**: $C_{40}H_{40}CoF_{12}N_8O_{12}P_2$, M = 1173.67, tetragonal, $I\bar{4}$, $a = b = 23.169(3)$ Å, $c = 8.2203(16)$ Å, U = 4412.8(12) Å^3, $Z = 4$, $D_c = 1.767$ Mg m^{-3}, $\mu = 0.587$ mm^{-1}, $F(000)$ = 2388, GOF = 1.073, crystal size 0.28 mm × 0.24 mm × 0.20 mm. R1 and wR2 are 0.0726 and 0.1739, respectively, for 340 parameters and 2009 reflections [$I > 2\sigma(I)$]. The data were collected on a Nonius Kappa CCD with Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. The structures were solved by direction methods and refined by a full-matrix least-squares technique based on F^2 using SHELXL 97 program.

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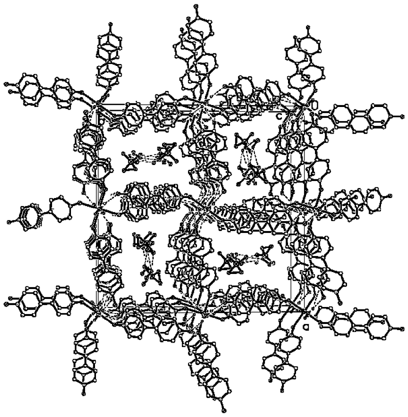

Figure 3. The packing diagram of diamondoid network in **1** and **2**, showing the mircrochannels along the *c* direction, in which water molecules and counterions are included.

a tetrahedral configuration as observed in **1** and **2**. Apparently, the geometric configuration of the four peripheral dpdo ligands is associated with their relative orientations. The rotation of dpdo around the M−O bond would produce cone-shaped connection points due to its angular coordination, allowing that the distal oxygen has multidirectional access to metal ions or hydrogen bond donors, unlike the 4,4′-bipyridine whose rotation around M−N bond does not affect the mutual orientation of the two nitrogen sites, retaining the linearity of such a spacer. The adoption of an up−down−up−down fashion of four dpdo with respect to the MO_4 plane results in a T_d symmetry in **1** and **2**, while the random orientation in compounds $[Cu_3(H_2O)_6(dpdo)_8](ClO_4)_6 \cdot 2dpdo \cdot 6H_2O$ and $[Zn(MeOH)_2(dpdo)_3](SiF_6) \cdot 3MeOH$ leads to the almost planar geometry of four ligated dpdo molecules.

It was noted that most of the assembly of metal ions with symmetric or asymmetric bifunctional spacers directly gave the diamondoid network sustained through coordination bond without separation of a tetrahedral immediate.[4,10] The assembly process of the diamondoid networks **1** and **2** is obviously involved in two distinct steps. Metal ion is first coordinated with four linear spacers to yield a tetrahedral node via metal coordination, which then is further extended into a diamondoid network through secondary interactions including hydrogen bonds and $\pi-\pi$ interactions. A similar tiered assembly of diamondoid network has been observed in compounds $Cu(Hcmp)_4X$ (Hcmp = 3-cyano-6-methyl-2(1*H*)-pyridinone; X = PF_6^-, $CF_3SO_3^-$).[11] However, significantly different assembly process between what is mentioned above and our cases exists in two aspects: (1) The tetrahedral configuration in $Cu(Hcmp)_4X$ is created by virtue of the preferred tetrahedral metal center, whereas in compounds **1** and **2** it is facilitated by the coordination orientation of the ligand (metal center has an octahedral environment); (2) the hydrogen bonding interactions in $Cu(Hcmp)_4X$ are accomplished by the same component, which contains hydrogen bonding donor and acceptor groups, whereas the hydrogen bonding assembly is furnished through two different species in **1** and **2**. Thus, compounds **1** and **2** represent the first example of a metal-organic diamondoid network assembled from an octahedral metal center and a linear spacer at two distinct levels.

In contrast to considerably rich functionalized organic tetrahedral molecules, the tetrafunctionalized metal coordination compounds with tetrahedral geometry are less common. The present tetrafunctionalized $[M(dpdo)_4(H_2O)_2]^{2+}$ moieties could be used as a starting point to construct novel supramolecular diamondoid frameworks with other components such as T_d symmetric hydrogen bond donors, linear hydrogen bond donor spacers, or metal ions. Replacement of $Co(PF_6)_2$ with $Cd(PF_6)_2$ gives essentially the same framework,[12] indicating the robustness of the tetrahedral $[M(dpdo)_4(H_2O)_2]^{2+}$ node.

Bulk phase purity was identified for **1** and **2** by X-ray powder diffraction (see Supporting Information). Thermogravimeric analysis showed 6.00% and 6.11% weight loss between room temperature and 180 °C for **1** and **2**, respectively, in agreement with the corresponding calculated values of 6.68% and 6.13% for **1** and **2**. The dehydrated compounds are thermally stable up to 340 and 310 °C for **1** and **2**, respectively. X-ray powder diffraction pattern showed that the evacuated samples of **1** and **2** under 190 °C for 4 h do not match the original ones, though they are still crystalline. One possibility is that the structural symmetry altered after evacuation. The details need to be further explored. A preliminary second harmonic generation measurement on compounds **1** and **2** with a homemade optical setup gave a negligible signal response (see Supporting Information for details).

In conclusion, a novel robust tetrahedral metal-organic complex building block has been revealed, which has potential use to assemble supramolecular diamondoid networks by judicious choice of modular components. The further investigation on this issue is under way.

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Supporting Information Available: SHG measurement setups, CIF files, TGA analysis, and XRPD patterns for freshly prepared and evacuated samples **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Unit cell parameters: $a = b = 23.523(3)$ Å, $c = 8.145(2)$ Å, $\alpha = \beta = \gamma = 90°$, $U = 4506.89(12)$ Å^3.