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Two (3,10)-Connected 2D Networks Based on Pentanuclear Metal Clusters as Building Blocks

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Self-assembly of a long, V-shaped 4,4′-sulfonyldibenzoato (sdba) ligand and metal salts in the presence of a heterocyclic aromatic ligand affords two (3,10)-connected 2D networks: $[Cd_5(\mu_3\text{-}OH)_2(sdba)_4(2,2'\text{-}bpy)_2(H_2O)_2]\cdot 2H_2O$ (**1**) and $[Mn_5(\mu_3\text{-}OH)_2(sdba)_4(2,2'\text{-}bpy)_2(H_2O)_2]\cdot H_2O$ (**2**) (2,2′-bpy = 2,2′-bipyridine). Their structures were determined by single-crystal X-ray diffraction analysis, and they were further characterized by elemental analysis, IR spectroscopy, and TG analysis. Compounds **1** and **2** are isostructural and represent the highest connected topology presently known for 2D nets. More interestingly, when the strong hydrogen bonds between layers are taken into account, the resulting net becomes a (3,12)-connected 3D network with complex $(3^2.4)_2(3^8.4^{22}.5^{24}.6^{10}.7^2)$ topology, which possesses the highest observed connectivity (twelve connectivity) known to date. The magnetic properties of compound **2** have been studied by measuring its magnetic susceptibility in the temperature range 2–300 K. The results indicate the existence of antiferromagnetic coupling within the pentanuclear manganese cluster. Furthermore, the luminescent properties of **1** are discussed.

Introduction

The crystal engineering of coordination polymer frameworks is of great current interest; not only because of their tremendous potential applications in gas storage, chemical separations, magnetism, microelectronics, nonlinear optics, and heterogeneous catalysis, but also because of their intriguing variety of architectures and topologies.[1–6] Employing the principles of crystal engineering, a variety of appealing metal–organic frameworks (MOFs) with interesting compositions and topologies have been designed[1–14] and well discussed in comprehensive reviews by Yaghi, Kitagawa, Rao, Chen, and their co-workers.[3] However, the major structural types found in MOFs are based on three-, four-, and six-connected topologies.[1–4] Connectivities of seven, eight, or higher are still extremely rare in metal–organic coordination frameworks.[15–18] Therefore, particular attention has recently been turning to the design and synthesis of highly connected MOFs.[15–18] This has been a great challenge in crystal engineering because the construction of highly connected nets is severely hampered by the limited coordination numbers of metal centers and the sterically demanding nature of most commonly used organic ligands. Furthermore, among the few examples of highly connected MOFs – almost all with 3D structures[16–18] – only one 2D coordination polymer with eight-connected topology has been reported by Long et al. very recently.[15b] This may be attributed, at least in part, to the fact that the generation of highly connected planar nodes is more difficult than that of highly connected spatial nodes. Moreover, highly connected MOFs having mixed nodes are surprisingly rare,[18] in contrast to the large majority of highly connected MOFs with uninodal net topology.[15–17] Therefore, the construction of 2D highly connected MOFs having mixed nodes is still a challenging issue in crystal engineering. Fortunately, the concept of using polynuclear metal clusters as nodes has recently provided a feasible route to the rational design of highly connected MOFs.[16–18] Relative to d- or f-block ions, metal-cluster-based nodes generally have larger surface areas (sometimes even nanoscale), and they can therefore accommodate the steric demands of organic linkers more readily.

Inspired by the aforementioned considerations, we attempted to synthesize highly connected 2D MOFs by linking metal cluster building blocks with long, V-shaped 4,4′-sulfonyldibenzoato (sdba) ligands. In our experiments, the sdba and chelate 2,2′-bipyridine (2,2′-bpy) ligands are simultaneously introduced for the following reasons: (i) Multidentate carboxylates are known to be essential in chelating metal ions and locking their position into metal clus-

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ters,[1a,17b] and it should be feasible to link discrete clusters by the long sdba bridges to give an extended network containing highly connected nodes. (ii) The bulky 2,2′-bpy ligand plays a "passive" role by occupying coordination sites on the metal centers and providing steric constraints,[3d] which prevent the spatial extension of the skeleton and may thus favor the formation of a 2D structure. (iii) Coordination polymers constructed from the sdba ligand remain largely unexplored, and[13b] therefore, much work is still necessary to understand the coordination chemistry of sdba. Fortunately, by trial and error we have isolated two (3,10)-connected 2D MOFs, $[Cd_5(\mu_3\text{-}OH)_2(sdba)_4(2,2'\text{-}bpy)_2(H_2O)_2]\cdot 2H_2O$ (**1**) and $[Mn_5(\mu_3\text{-}OH)_2(sdba)_4(2,2'\text{-}bpy)_2(H_2O)_2]\cdot H_2O$ (**2**), in which pentanuclear metal clusters act as ten-connected nodes and sdba ligands act as three-connected nodes as well as linkers. Compounds **1** and **2** have two unusual features: (i) The (3,10)-connected networks in **1** and **2** represent the highest connected topology presently known for 2D nets. (ii) When the strong hydrogen bonds between layers are taken into account, the resulting net becomes a (3,12)-connected 3D network with complex $(3^2.4)_2(3^8.4^{22}.5^{24}.6^{10}.7^2)$ topology, which possesses the highest observed connectivity (twelve connectivity) known to date.[16]

Results and Discussion

Crystal Structures

Single-crystal X-ray diffraction analysis reveals that compounds **1** and **2** are isostructural, hence only the structure of **1** will be discussed in detail. The secondary building unit (SBU) of **1** is a new pentanuclear cadmium cluster (Figure 2), in which 2.5 crystallographically independent Cd atoms (Figure 1) exhibit different coordination spheres, although all are six-coordinate. Cd1 lies on a center of symmetry and is coordinated to two μ_3-OH groups [Cd–O 2.1868(16) Å, Table 1] and four carboxylate oxygen atoms [Cd–O 2.2632(16)–2.3327(15) Å] from four different sdba ligands (Figure S4). Cd2 is ligated with two carboxylate oxygen atoms [Cd–O 2.2290(17)–2.3686(16) Å] from two sdba ligands, two nitrogen atoms [Cd–N 2.3285(19)–2.332(2) Å] from a 2,2′-bpy ligand, one oxygen atom [Cd–O 2.4337(17) Å] from the sulfonyl group of a sdba ligand, and a μ_3-OH group [Cd–O 2.1977(16) Å], whereas the Cd3 atom is coordinated by four carboxylate oxygen atoms [Cd–O 2.2900(16)–2.3571(17) Å] of four sdba ligands, one aqua ligand [Cd–O 2.3266(16) Å], and a μ_3-OH group [Cd–O 2.2366(15) Å]. The octahedrally coordinated Cd1 is connected to four adjacent Cd centers in a corner- and/or edge-sharing mode to form a $[Cd_5(\mu_3\text{-}OH)_2(\mu_3\text{-}O)_2]$ core via μ_3-OH and μ_3-carboxylate oxygen atoms (O8) with nonbonding Cd···Cd distances of 3.4281(6)–3.871(32) Å (Figure 2).

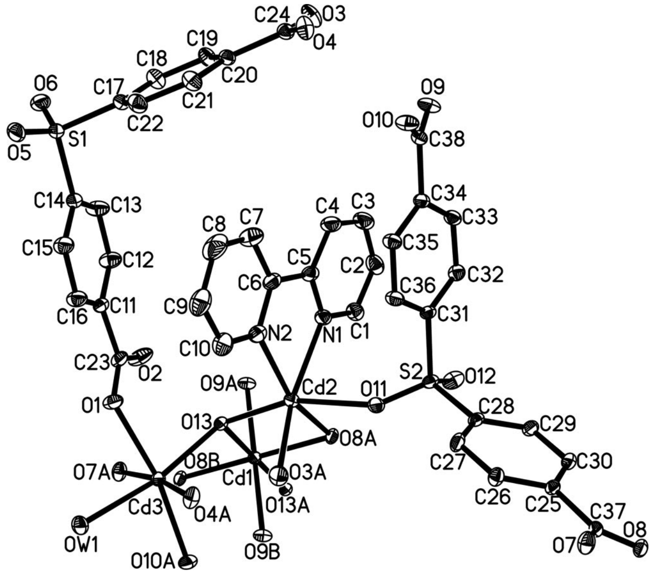

Figure 1. ORTEP drawing of **1** with thermal ellipsoids at 30% probability.

Table 1. Selected bond lengths [Å] for **1** and **2**.[a]

1			
Cd(1)–O(13)#1	2.1868(16)	Cd(1)–O(9)#3	2.2632(16)
Cd(1)–O(13)	2.1868(16)	Cd(1)–O(8)#4	2.3327(15)
Cd(1)–O(9)#2	2.2632(16)	Cd(1)–O(8)#5	2.3327(15)
Cd(2)–O(13)	2.1977(16)	Cd(2)–N(2)	2.332(2)
Cd(2)–O(3)#2	2.2290(17)	Cd(2)–O(8)#4	2.3686(16)
Cd(2)–N(1)	2.3285(19)	Cd(2)–O(11)	2.4337(17)
Cd(3)–O(13)	2.2366(15)	Cd(3)–O(4)#2	2.3294(17)
Cd(3)–O(10)#2	2.2900(16)	Cd(3)–O(7)#5	2.3559(16)
Cd(3)–OW1	2.3266(16)	Cd(3)–O(1)	2.3571(17)
2			
Mn(1)–O(13)	2.1208(12)	Mn(1)–O(9)#3	2.1263(13)
Mn(1)–O(13)#1	2.1208(12)	Mn(1)–O(8)#4	2.2326(12)
Mn(1)–O(9)#2	2.1263(13)	Mn(1)–O(8)#5	2.2326(12)
Mn(2)–O(13)	2.0987(12)	Mn(2)–N(1)	2.2692(17)
Mn(2)–O(3)#3	2.1029(15)	Mn(2)–N(2)	2.2858(17)
Mn(2)–O(8)#5	2.2234(13)	Mn(2)–O(11)	2.3580(13)
Mn(3)–O(13)	2.1495(13)	Mn(3)–O(4)#3	2.2484(13)
Mn(3)–O(10)#3	2.2017(13)	Mn(3)–O(1)	2.2565(13)
Mn(3)–OW1	2.2381(15)	Mn(3)–O(7)#4	2.2571(13)

[a] Symmetry transformations used to generate equivalent atoms: for **1**: #1 $-x + 1, -y + 1, -z$; #2 $x, -y + 3/2, z - 1/2$; #3 $-x + 1, y - 1/2, -z + 1/2$; #4 $-x + 1, -y+2, -z$; #5 $x, y - 1, z$; for **2**: #1 $-x, -y + 1, -z$; #2 $-x, y + 1/2, -z + 1/2$; #3 $x, -y + 1/2, z - 1/2$; #4 $x, y + 1, z$; #5 $-x, -y, -z$.

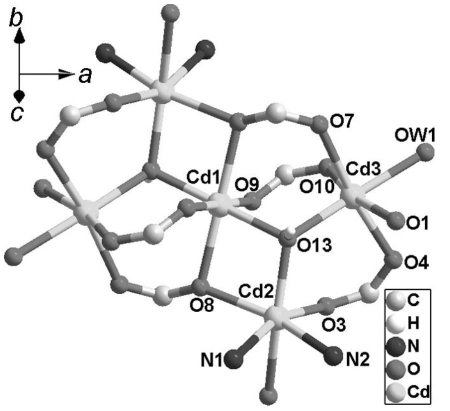

Figure 2. View of the pentanuclear cadmium cluster.

So far, pentanuclear clusters of any metal are rare, as evidenced in a recent work by Henderson and co-workers.[17g] While a few polynuclear cadmium clusters[12b,17b,19] have been reported, such a pentanuclear $[Cd_5(\mu_3\text{-OH})_2(\mu_3\text{-O})_2]$ core containing mixed μ_3-OH and μ_3-O bridges has never been presented before. Moreover, there are two types of sdba ligands in **1**. The first type acts as a hexadentate ligand (^{a}sdba, Figure S2a); one carboxylate group adopts a bidentate bridging mode, while the other exhibits an unusual tridentate bridging mode. The sulfonyl group adopts a monodentate coordination mode, which is still very rare in the system of metal–organic complexes.[3] The second type of sdba ligand adopts a monodentate–bidentate coordination mode (^{b}sdba, Figure S2b); one carboxylate group bridges two Cd^{II} ions in a bidentate mode, and the other exhibits a monodentate coordination mode. On the basis of these connection modes, each pentanuclear cadmium cluster is further linked to six others through six triply bridging ^{a}sdba (Figure S5a) and four doubly bridging ^{b}sdba ligands (Figure S5b) to generate a 2D network (Figure 3) with a thickness of 18.2 Å, which falls well in the nano region (Figure S3).

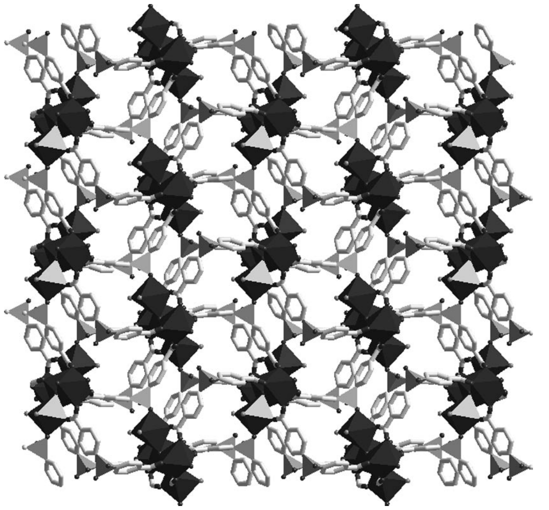

Figure 3. The 2D layer in **1** viewed along the [601] direction (2,2′-bpy are omitted for clarity).

The most fascinating and peculiar structural feature of **1** is that the 2D nanoscale layer can be rationalized as a (3,10)-connected binodal net with $(3^2.4)_2(3^8.4^{14}.5^{12}.6^9.7^2)$ topology (Figure 4). As illustrated in Figure S4, there are twelve organic ligands (six ^{a}sdba, four ^{b}sdba, and two 2,2′-bpy ligands) surrounding each pentanuclear $[Cd_5(\mu_3\text{-OH})_2(\mu_3\text{-O})_2]$ core. Being end-capping units, two 2,2′-bpy ligands are disregarded from a topological perspective; therefore, the pentanuclear cadmium cluster is defined as a ten-connected node (Figure S5c). Likewise, each ^{a}sdba ligand is linked to three pentanuclear cadmium clusters and thus acts as a three-connecting node (Figure S5b). On the basis of the above simplification principle, the resulting structure of compound **1** is a unique 2D binodal network containing alternating three-connected (^{a}sdba ligand) and ten-connected nodes (pentanuclear cadmium cluster) with a topology of $(3^2.4)_2(3^8.4^{14}.5^{12}.6^9.7^2)$, which is the highest connected topology ever found in 2D compounds. It is worth mentioning here that a whole lot of 2D and 3D high-symmetry nets have been listed within the RCSR (Reticular Chemistry Structure Resource), EPINET, and Topos databases.[20] To further analyze the topology of **1**, all (3,10)-connected nets contained in the RCSR, EPINET, and Topos databases have been carefully examined. None of those have the same topology as that of **1**. Therefore, the 2D network of **1** represents a (3,10)-connected topology that is not only unobserved but also unlisted. The discovery of this new topology is useful at the basic level in the crystal engineering of coordination networks.

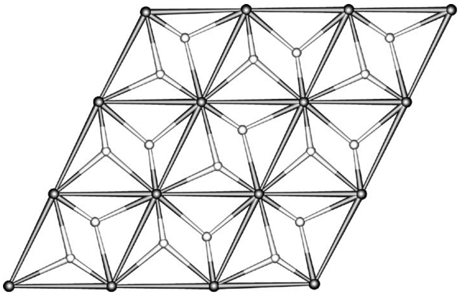

Figure 4. Schematic representation of the 2D (3,10)-connected net of **1**.

In the packing arrangement of **1**, adjacent 2D nanometer-scale layers are interconnected by strong hydrogen bonding interactions [OW1···O4 2.779(2) Å and OW1···O1 2.852(2) Å] to generate a 3D supramolecular network (Figure S6). Very intriguingly, when these hydrogen bonds are taken into account,[2a,13b] the resulting structure can be simplified to a unique (3,12)-connected 3D network symbolized as $(3^2.4)_2(3^8.4^{22}.5^{24}.6^{10}.7^2)$ (Figure 5), which possesses the highest observed connectivity known to date[16] and has never been described before in the field of coordination polymers. A notable topological feature is that the twelve-connected pentanuclear cadmium cluster in **1** has a distorted decagonal bipyramid coordination (Figure S7) that makes it exceptional in that the only three comparable examples adopt the cuboctahedral or trigonal icosahedral coordination configuration.[16] Furthermore, a search in the RCSR, EPINET, and Topos databases[20] reveals that the 3D net of **1** has never been listed hitherto.

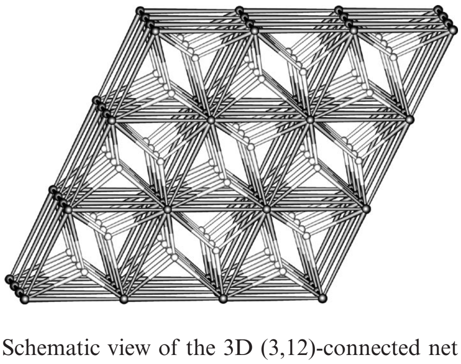

Figure 5. Schematic view of the 3D (3,12)-connected net of **1**.

Thermal Stability Analysis

In order to examine the thermal stability of the two compounds, thermal gravimetric (TG) analysis of **1** was performed representatively. The TG curve of **1** exhibits three steps of weight loss (Figure S9). The first weight loss is 3.62% in the temperature range 70–300 °C, which corresponds to the loss of lattice water, coordinated water, and water from hydroxy groups (calcd. 4.10%). The second weight loss is 49.05% from 300 to 525 °C, and the third step is 2.64% from 525 to 625 °C, both assigned to the decomposition of 2,2′-bpy and sdba ligands (calcd. 52.11%). The remaining weight (44.69%) indicated that the final product was a mixture of $CdSO_4$ and CdO in a molar ratio of 4:1 (calcd. 43.79%).

Luminescent Properties

The luminescence of **1** was investigated, because the introduction of d^{10} metal–hydroxy (or –oxy) clusters can improve the luminescence performance of coordination polymers.[21] Compound **1** exhibits an intense blue radiation emission maximum at 469 nm upon excitation at 400 nm (Figure 6). In order to understand the nature of the emission band, the photoluminescence properties of the H_2sdba ligand were analyzed. It was found that a weak emission (λ_{max} = 329 nm) could be observed for the free H_2sdba ligand (Figure S8). Thus, according to the literature, the luminescence of **1** might be assigned to ligand-to-metal charge transfer.[21] The enhancement of luminescence may be attributed to ligand chelation to the metal center, which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay.[22] Similar to other d^{10} metal–hydroxy-cluster-based complexes,[12b,19d,21] the lifetime of **1** is about 13 ns, which is significantly longer than those for complexes without metal–hydroxy clusters. The longer lifetime may be ascribed to the presence of the metal clusters, since the μ_3-OH ligand may tighten the whole skeleton, resulting in much weaker vibrations.

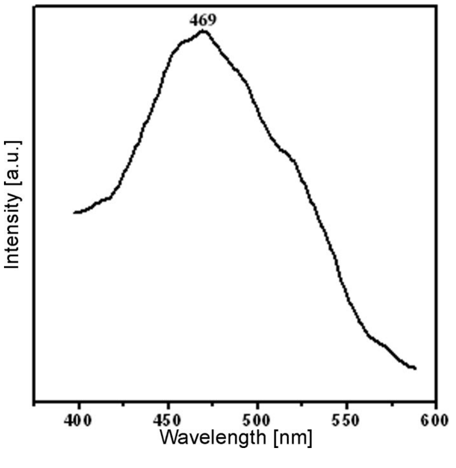

Figure 6. Solid-state emission spectrum of compound **1** at room temperature.

Magnetic Properties

The magnetic susceptibility of **2** was investigated over the temperature range 2–300 K (Figure 7). At 300 K, the $\chi_M T$ value is 21.027 $cm^3 K mol^{-1}$, which is slightly smaller than the expected value (21.875 $cm^3 K mol^{-1}$) of five isolated spin-only Mn^{II} ions ($S = 5/2$, $g = 2.0$). As T is lowered, $\chi_M T$ decreases continuously to a value of 1.496 $cm^3 K mol^{-1}$ at 2 K. This behavior indicates a dominant antiferromagnetic interaction between the Mn^{II} ions in the structures. Because the pentanuclear manganese clusters are interconnected by large sdba ligands, the overall antiferromagnetic interaction should be attributed to the magnetic exchange coupling within the pentanuclear manganese cluster. The fit of the curve for the $1/\chi_M$ vs. T plot to the Curie–Weiss law gives a good result in the temperature range 8–300 K with C = 22.604 $cm^3 K mol^{-1}$ and θ = –19.119 K.

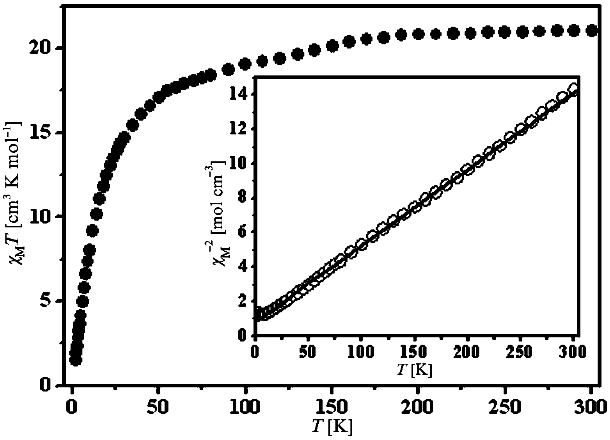

Figure 7. Thermal variation of $\chi_M T$ for **2**. Inset: Plot of thermal variation of χ_M^{-1} for **2**.

Conclusions

We have synthesized two interesting (3,10)-connected 2D MOFs by linking pentanuclear metal clusters with long, V-shaped ligands, which represent the highest connected topology ever found in 2D compounds. Furthermore, the 3D supramolecular networks of **1** and **2** possess the highest observed connectivity (twelve connectivity) known to date. The successful isolation of both compounds not only provides intriguing examples of chemical topology, but also further demonstrates the significant potential of constructing highly connected MOFs by using metal clusters as nodes.

Experimental Section

Materials and General Methods: All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H, and N) were performed with a Perkin–Elmer 2400 CHN Elemental Analyzer. Cd and Mn were determined with a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were recorded in the range 400–4000 cm^{-1} with an Alpha Centaurt FT/

IR spectrophotometer by using KBr pellets. TG analysis was performed with a Perkin–Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C min^{-1}. The steady-state fluorescence and fluorescence lifetimes were determined with a EI FLS920 fluorescence spectrophotometer by using a laser light resource. Variable-temperature magnetic susceptibility data were obtained with a SQUID magnetometer (Quantum Design, MPMS-7) in the temperature range 2–300 K by using an applied field of 1 kG.

Syntheses

$[Cd_5(\mu_3\text{-}OH)_2(sdba)_4(2,2'\text{-}bpy)_2(H_2O)_2]\cdot 2H_2O$ (1): A mixture of $Cd(NO_3)_2\cdot 4H_2O$ (231 mg, 0.75 mmol), H_2sdba (184 mg, 0.6 mmol), 2,2′-bpy (47 mg, 0.3 mmol), triethylamine (0.3 mL), and water (8 mL) was stirred for 30 min in air, then transferred into and sealed in a Teflon-lined autoclave (18 mL), which was heated at 160 °C for 60 h. After the mixture was slowly cooled to the room temperature, yellow block crystals of **1** were filtered off, washed with distilled water, and dried at ambient temperature (yield: 185 mg, 56% based on Cd). Elemental analysis results of the yellow crystals are consistent with the stoichiometry of **1**. $C_{76}H_{58}Cd_5N_4O_{30}S_4$ (2197.50): calcd. C 41.54, H 2.66, Cd 25.58, N 2.55; found C 41.18, H 2.89, Cd 25.27, N 2.81. FT-IR (KBr): $\tilde{\nu}$ = 3406 (s), 3085 (w), 2344 (w), 1831 (w), 1611 (s), 1562 (s), 1489 (m), 1476 (m), 1439 (m), 1403 (s), 1358 (m), 1322 (w), 1295 (s), 1164 (s), 1132 (s), 1101 (s), 1068 (m), 1014 (s), 871 (m), 855 (w), 841 (w), 772 (m), 742 (s), 693 (s), 649 (w), 616 (s), 579 (s), 484 (m), 464 (w), 426 (w) cm^{-1}.

$[Mn_5(\mu_3\text{-}OH)_2(sdba)_4(2,2'\text{-}bpy)_2(H_2O)_2]\cdot H_2O$ (2): The preparation of **2** was similar to that of **1** except that $Mn(OAc)_2\cdot 4H_2O$ was used instead of $Cd(NO_3)_2\cdot 4H_2O$. Brown block crystals of **2** were obtained in 64% (182 mg) yield based on Mn. Elemental analysis results of the brown crystals are consistent with the stoichiometry of **2**. $C_{76}H_{56}Mn_5N_4O_{29}S_4$ (1892.19): calcd. C 48.24, H 2.98, Mn 14.52, N 2.96; found C 47.91, H 2.77, Mn 14.75, N 3.14. FT-IR (KBr): $\tilde{\nu}$ = 3423 (s), 3090 (w), 2344 (w), 1832 (w), 1617 (s), 1563 (s), 1489 (m), 1476 (w), 1405 (s), 1362 (s), 1326 (m), 1294 (s), 1163 (s), 1133 (s), 1101 (s), 1067 (m), 1014 (s), 929 (w), 874 (m), 842 (m), 785 (m), 766 (m), 739 (s), 719 (w), 694 (s), 646 (w), 616 (s), 579 (s), 487 (m), 427 (m) cm^{-1}.

X-ray Crystallography: Suitable single crystals with dimensions of 0.51 × 0.48 × 0.43 mm for **1** and 0.55 × 0.53 × 0.49 mm for **2** were glued on a glass fiber. Diffraction intensity data were collected with a Rigaku R-AXIS RAPID IP diffractometer with Mo-K_α monochromated radiation (λ = 0.71073 Å) at 293 K. Empirical absorption correction was applied. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 by using the SHELXL-97 software.[23] All of the non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically. In **1**, exact positions of the hydrogen atoms attached to OW1 and O13 were located from difference Fourier maps, and the hydrogen atoms attached to OW2 were not located. In **2**, the position of the hydrogen atom attached to O13 was located from difference Fourier maps, and the aqua hydrogen atoms were not located. Selected bond lengths for **1** and **2** are listed in Table 1. The crystal data and structure refinement of compounds **1** and **2** are summarized in Table 2.

Table 2. Crystal data and structure refinement for compounds **1** and **2**.

Complex	1	2
Formula	$C_{76}H_{58}Cd_5N_4O_{30}S_4$	$C_{76}H_{56}Mn_5N_4O_{29}S_4$
Formula mass	2197.50	1892.19
T [K]	293(2)	293(2)
λ [Å]	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	12.526(3)	12.380(3)
b [Å]	13.766(3)	13.579(3)
c [Å]	22.042(4)	21.912(4)
β [°]	90.40(3)	91.06(3)
V [Å^3]	3800.9(13)	3682.8(13)
Z	2	2
D_c [g cm^{-3}]	1.920	1.706
μ [mm^{-1}]	1.578	1.040
R_1[a] [$I > 2\sigma(I)$]	0.0239	0.0301
wR_2[b] (all data)	0.0677	0.0880

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

CCDC-665217 and CCDC-665218 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.

Supporting Information (see footnote on the first page of this article): IR spectra, TG curve of **1**, ORTEP drawing of **2**, and additional plots of the structures.

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