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Three-Dimensional Eight- or Four-Connected Metal−Organic Frameworks Tuned by Hydrothermal Temperatures

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ABSTRACT: Two novel three-dimensional (3D) metal−organic frameworks (MOFs) with cobalt(II) clusters as nodes and mixed bridging ligands as links, $[Co_4(OH)_2(obbz)_3(4,4'-bpy)_2](4,4'-bpy)$ ($obbz^{2-}$ = N,N'-oxamidobis(benzoato), 4,4'-bpy = 4,4'-bipyridine) (**1**) and $[Co_3(H_2O)(obbz)_3(4,4'-bpy)_2](H_2O)_2$ (**2**), were obtained from the same reaction mixture but tuned by different hydrothermal temperatures: the 160 °C product **1** is a 3D MOF based on the novel tetranuclear cluster node $[Co_4(OH)_2]^{6+}$, displaying a new eight-connected $3^64^{14}5^46^4$ topology, whereas the 140 °C product **2** is a 2-fold interpenetrating 3D MOF constructed from not only the binuclear cluster node $[Co_2(\mu^2-H_2O)]^{4+}$ but also the mononuclear node Co^{2+}, showing a distorted diamond network.

Introduction

The construction of metal−organic frameworks (MOFs) has become an exciting and expanding approach to novel materials.[1] The interest is stimulated not only by the MOFs' fine-tuning structure diversity but also by their extensively potential applications in such areas as separation, molecular recognition, ion exchange, gas sorption and storage, nonlinear optics, magnetics, and catalysis.[1,2] Deeply understanding the topology structural aspects of high-dimensional MOFs is one of the most important subjects because it will ultimately accelerate the discovery of new MOF materials for application.[1,2]

To date, the topologies of many three-dimensional (3D) MOFs generally can be analyzed and categorized with some natural prototypes in metallic or binary inorganic solids.[3] For example, recently, the corresponding MOFs' replica of α-Po,[4] NbO,[5] Pt₃O₄,[6] PtS,[7] CdSO₄,[8] CaB₂,[9] SrSi₂,[10] diamond,[11] feldspar,[12] boracite,[13] perovskite,[14] pyrite,[15] quartz,[16] rutile,[17] sodalite,[18] tungsten bronze,[19] fluorite,[3] anatase,[20] and zeolite[21] have been explored gradually. In these mimic and many other 3D MOFs without mineral prototypes, the connectivity of the building blocks exceeding six remains scarce because of the metal centers' limited coordination numbers and the steric hindrance for ligands.[3,22,23] Nevertheless, such drawbacks can be overcome by using large polynuclear clusters instead of simple metal centers as the nodes because the polynuclear cluster-based nodes generally possess larger sizes, more coordination sites, and smaller steric hindrance for ligands with respect to the simple *d*- or *f*-block metal center nodes.[3,22] Herein, we report by using the μ^3-hydroxyl-bridged tetranuclear cobalt-(II) cluster $[Co_4(OH)_2]^{6+}$ as the node and the mixed ligands N,N'-oxamidobis(benzoato) ($obbz^{2-}$, Scheme 1) and 4,4'-bypyridine (4,4'-bpy) as the links. A non-interpenetrating 3D MOF with a new eight-connected $3^64^{14}5^46^4$ topology, $[Co_4(OH)_2(obbz)_3(4,4'-bpy)_2](4,4'-bpy)$ (**1**), was obtained under hydrothermal conditions; interestingly, another 3D MOF, $[Co_3(H_2O)(obbz)_3(4,4'-bpy)_2](H_2O)_2$ (**2**), was formed when a lower hydrothermal temperature was applied to the same reaction

Scheme 1. $obbz^{2-}$
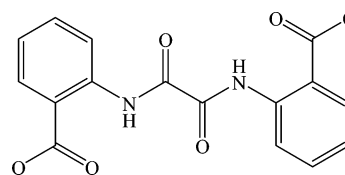
mixture, which shows a 2-fold interpenetrating 3D four-connected (6, 4) distorted diamond network structure based on not only the binuclear cluster node $[Co_2(\mu^2-H_2O)]^{4+}$ but also the mononuclear node Co^{2+}. Interestingly, $obbz^{2-}$ ligand in both complexes adopts the trans-configuration, whereas previously reported obbz complexes generally contain the *cis*-obbz ligand,[24,25] in which not only the carboxylato group but also the oxamido group take part in the coordination roles, and the valence of obbz in the latter is −4.

Experimental Section

General Physical Measurements. Materials and Methods. The precursor H₂obbz was prepared according to the published procedures.[24] Other starting materials were commercially available and used as received without further purification. The elemental analyses were performed on a Heraeus Chn-Rapid elemental analyzer. The infrared spectra were recorded on a Pekin-Elmer 2000 spectrophotometer with pressed KBr pallets. The magnetic susceptibility measurements for **1** and **2** were carried out on polycrystalline samples (15.69 mg of **1** and 19.58 mg of **2**) on a Quantum Design MPMS-XL5 SQUID magnetometer in the temperature range of 2−300K. Diamagnetic corrections were estimated from Pascal's constants for all constituent atoms.[26]

Preparation of $[Co_4(OH)_2(obbz)_3(4,4'-bpy)_2](4,4'-bpy)$ (1). A mixture of H₂obbz(1.0 mmol), Co(NO₃)₂·6H₂O (2.0 mmol), 4, 4'-bipy (2.0 mmol), and H₂O (10 mL) was stirred for 20 min. The mixture was then transferred to a Teflon-lined stainless steel autoclave (20 mL) and kept at 160 °C for 6 days. After the autoclave had cooled to room temperature over 6−7 h, purple octahedral crystalline solids of **1** were isolated from the mother liquid, washed with water, and then dried at ambient temperature (35% yield based on cobalt). Anal. Calcd for C₇₈H₅₆Co₄N₁₂O₂₀: C, 54.56; H, 3.29; N, 9.79. Found: C, 54.51; H, 3.33; N 9.75. IR (KBr pallet, cm⁻¹): 3252(m), 1676(s), 1626(s), 1590-(s), 1503(vs), 1438(v), 1378(s), 1292(w), 1220(w), 1163(w), 1067(w), 1046(w), 820(w), 757(w), 667(w), 490(w).

Preparation of $[Co_3(H_2O)(obbz)_3(4,4'-bpy)_2](H_2O)_2$ (2). Hydrothermal reaction using the same mixture as for **1** at 140 °C for 6 days yielded brown block-shaped crystals of **2** in 43% yield based on cobalt.

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Table 1. Crystal Data and Structural Refinement Parameters for 1 and 2

	1	2
chemical formula	$C_{78}H_{56}Co_4N_{12}O_{20}$	$C_{68}H_{52}Co_3N_{10}O_{21}$
fw	1717.07	1521.99
cryst syst	monoclinic	monoclinic
space group	$C2/c$	$P2/c$
a (Å)	28.080(6)	21.293(4)
b (Å)	13.840(3)	7.1590(10)
c (Å)	21.812(4)	22.218(4)
β (deg)	120.14(3)	105.07(3)
V (Å^3)	7331(3)	3270.4(10)
Z	4	2
T (K)	298 (2)	298 (2)
λ(Mo$-$Kα) (Å)	0.71073	0.71073
ρ_{calcd} (g cm^{-3})	1.554	1.546
μ(Mo$-$Kα) (mm^{-1})	0.974	0.839
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0516	0.0739
$wR_2{}^b$ [$I > 2\sigma(I)$]	0.1627	0.1795
S	1.007	1.090

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Complex 1^a

Bond Distances			
Co(1)$-$O(1)	2.070(2)	Co(1)$-$O(9)$^{\#1}$	2.101(3)
Co(1)$-$N(2)$^{\#2}$	2.108(3)	Co(1)$-$O(1)$^{\#1}$	2.112(2)
Co(1)$-$O(2)	2.115(3)	Co(1)$-$O(5)$^{\#3}$	2.178(3)
Co(2)$-$O(1)	1.943(3)	Co(2)$-$O(8)	1.964(3)
Co(2)$-$O(4)$^{\#4}$	1.968(3)	Co(2)$-$N(1)	2.026(3)
N(2)$-$Co(1)$^{\#2}$	2.108(3)	O(1)$-$Co(1)$^{\#1}$	2.112(2)
O(4)$-$Co(2)$^{\#5}$	1.968(3)	O(5)$-$Co(1)$^{\#6}$	2.178(3)
O(9)$-$Co(1)$^{\#1}$	2.101(3)		

Bond Angles			
O(1)$-$Co(1)$-$O(9)$^{\#1}$	174.35(11)	O(1)$-$Co(1)$-$N(2)$^{\#2}$	94.05(10)
O(9)$^{\#1}-$Co(1)$-$N(2)$^{\#2}$	83.83(10)	O(1)$-$Co(1)$-$O(1)$^{\#1}$	83.87(9)
O(9)$^{\#1}-$Co(1)$-$O(1)$^{\#1}$	98.35(9)	N(2)$^{\#2}-$Co(1)$-$O(1)$^{\#1}$	177.58(11)
O(1)$-$Co(1)$-$O(2)	100.74(10)	O(9)$^{\#1}-$Co(1)$-$O(2)	84.51(12)
N(2)$^{\#2}-$Co(1)$-$O(2)	89.80(10)	O(1)$^{\#1}-$Co(1)$-$O(2)	89.37(9)
O(1)$-$Co(1)$-$O(5)$^{\#3}$	87.77(11)	O(9)$^{\#1}-$Co(1)$-$O(5)$^{\#3}$	87.15(13)
N(2)$^{\#2}-$Co(1)$-$O(5)$^{\#3}$	93.78(10)	O(1)$^{\#1}-$Co(1)$-$O(5)$^{\#3}$	87.39(9)
O(2)$-$Co(1)$-$O(5)$^{\#3}$	170.52(11)	O(1)$-$Co(2)$-$O(8)	112.23(10)
O(1)$-$Co(2)$-$O(4)$^{\#4}$	103.95(11)	O(8)$-$Co(2)$-$O(4)$^{\#4}$	121.52(12)
O(1)$-$Co(2)$-$N(1)	109.96(11)	O(8)$-$Co(2)$-$N(1)	101.88(11)
O(4)$^{\#4}-$Co(2)$-$N(1)	106.99(11)		

^{a} Symmetry transormations: $^{\#1}$ $-x + 1/2$, $-y + 3/2$, $-z + 1$; $^{\#2}$ $-x + 1/2$, $-y + 5/2$, $-z + 1$; $^{\#3}$ x, $-y + 1$, $z - 1/2$; $^{\#4}$ $-x + 1/2$, $y + 1/2$, $-z + 3/2$; $^{\#5}$ $-x + 1/2$, $y - 1/2$, $-z + 3/2$; $^{\#6}$ x, $-y + 1$, $z + 1/2$.

Anal. Calcd for $C_{68}H_{52}Co_3N_{10}O_{21}$: C, 53.66; H, 3.44; N, 9.20. Found: C, 53.61; H, 3.49; N, 9.16. IR (KBr pallet, cm^{-1}): 3461(br. s), 3074-(w), 1690(m), 1664(m), 1630(m), 1590(s), 1510(s), 1442(s), 1389(s), 1300(w), 1221(w), 1172(w), 869(w), 809(w), 755(w), 667(w).

Structure Determination. Crystals with dimensions $0.23 \times 0.33 \times 0.42$ mm^3 for **1** and $0.15 \times 0.24 \times 0.33$ mm^3 for **2** were mounted and data were collected at 298(2) K on a Rigaku RAXIS RAPID IP imaging plate system with Mo$-$Kα radiation ($\lambda = 0.71073$ Å). A total of 29491 reflections were collected in the range $2.39° < \theta < 27.30°$ ($0 \le h \le 36$, $0 \le k \le 17$, $-28 \le l \le 24$), of which 8069 are unique ($R_{int} = 0.0494$) and 5831 with $I > 2\sigma(I)$ were used in the refinement of the structure of **1**. A total of 11062 reflections were collected in the range $1.90° < \theta < 27.52°$ ($-27 \le h \le 27$, $0 \le k \le 9$, $-28 \le l \le 28$), of which 6880 are unique ($R_{int} = 0.0939$) and 4799 with $I > 2\sigma(I)$ were used in the refinement of **2**. Empirical absorption corrections from φ scan were applied. Cell parameters were obtained by the global refinement of the positions of all collected reflections for two complexes. Both structures were solved by direct methods and refined by a full matrix least-squares technique based on F^2 using the SHELXL 97 program. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms but those in hydroxyl groups of **1** were refined as riding atoms. Selected crystallographic data and structure determination parameters for complexes **1** and **2** are given in Table 1. Selected bond lengths and angles for **1** and **2** are listed in Tables 2 and 3, respectively.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of Complex 2^a

Bond Distances			
Co(1)$-$O(4)	2.016(3)	Co(1)$-$O(3)$^{\#1}$	2.069(3)
Co(1)$-$O(1)$^{\#2}$	2.090(3)	Co(1)$-$O(2W)	2.121(4)
Co(1)$-$N(1)	2.143(4)	Co(1)$-$O(1W)	2.147(3)
Co(2)$-$O(8)	2.039(4)	Co(2)$-$O(8)$^{\#3}$	2.039(4)
Co(2)$-$N(2)	2.092(4)	Co(2)$-$N(2)$^{\#3}$	2.092(4)
Co(2)$-$O(7)$^{\#3}$	2.243(4)	Co(2)$-$O(7)	2.243(4)
O(1)$-$Co(1)$^{\#2}$	2.090(3)	O(1W)$-$Co(1)$^{\#1}$	2.147(3)
O(3)$-$Co(1)$^{\#1}$	2.069(3)		

Bond Angles			
O(4)$-$Co(1)$-$O(3)$^{\#1}$	97.58(15)	O(4)$-$Co(1)$-$O(1)$^{\#2}$	89.88(15)
O(3)$^{\#1}-$Co(1)$-$O(1)$^{\#2}$	172.54(14)	O(4)$-$Co(1)$-$O(2W)	176.11(16)
O(3)$^{\#1}-$Co(1)$-$O(2W)	84.42(14)	O(1)$^{\#2}-$Co(1)$-$O(2W)	88.14(15)
O(4)$-$Co(1)-N(1)	87.07(15)	O(3)$^{*1}-$Co(1)$-$N(1)	91.83(15)
O(1)$^{\#2}-$Co(1)$-$N(1)	88.66(15)	O(2W)$-$Co(1)$-$N(1)	89.54(18)
O(4)$-$Co(1)$-$O(1W)	88.21(13)	O(3)$^{*1}-$Co(1)$-$O(1W)	90.85(11)
O(8)$-$Co(2)$-$O(8)$^{\#3}$	159.9(2)	O(8)$-$Co(2)$-$N(2)	99.61(17)
O(8)$^{\#3}-$Co(2)$-$N(2)	93.04(15)	O(8)$-$Co(2)$-$N(2)^{*3}	93.04(15)
N(2)$-$Co(2)$-$N(2)$^{\#3}$	101.9(2)	O(8)$-$Co(2)$-$O(7)$^{\#3}$	103.83(16)
N(2)$-$Co(2)$-$O(7)$^{\#3}$	151.91(15)	O(8)$-$Co(2)$-$O(7)	60.40(14)
O(8)$^{\#3}-$Co(2)$-$O(7)	103.83(16)	N(2)$-$Co(2)$-$O(7)	92.18(16)
N(2)$^{\#3}-$Co(2)$-$O(7)	151.91(15)	O(7)$^{\#3}-$Co(2)$-$O(7)	86.2(2)
Co(1)$-$O(1W)$-$Co(1)$^{\#1}$	114.4(2)	O(7)$^{\#3}-$Co(2)$-$C(27)$^{\#3}$	29.69(15)

^{a} Symmetry transformations: $^{\#1}$ $-x + 1$, y, $-z + 1/2$; $^{\#2}$ $-x + 1$, $-y + 1$, $-z$; $^{\#3}$ $-x$, y, $-z + 1/2$.

Results and Discussion

Syntheses. Both new 3D MOFs were synthesized using the same reaction mixture of H_2obbz(1.0 mmol), Co(NO$_3$)$_2$·6H$_2$O (2.0 mmol), 4,4′-bipy (2.0 mmol), and H$_2$O (10.0 mL), but different hydrothermal temperatures were applied: the non-interpenetrating **1** was obtained at 160 °C, whereas the 2-fold interpenetrating **2** was formed at 140 °C, suggesting that the hydrothermal temperatures have critical impact on the construction of 3D MOFs. It is noted that the change of the hydrothermal temperatures to obtain 3D MOFs' interpenetrating and non-interpenetrating structures was rarely performed before, although several MOFs tuned by the hydrothermal temperatures had been documented.[27] Previous research suggested using large inorganic clusters as the second building units (SBUs)[28] or suitable guest molecules as the templates[1e,1i,1j] could generate non-interpenetrating networks, so the large μ^3-hydroxyl bridged tertranuclear cobalt(II) cluster [Co$_4$(OH)$_2$]$^{6+}$ being utilized as the SBU and the existence of 4,4′-bpy guest molecules maybe are responsible for the non-interpenetrating structure of **1**. On the other hand, it is also noteworthy that obbz^{4-} ligand[24,25] or halogen-substituted obbz^{4-} ligand[29] in previously reported complexes always adopt the *cis*-configuration and not only the carboxylato group but also the oxamido group take part in the coordination roles, however, only the carboxylato group of obbz^{2-} ligand in both **1** and **2** are involved with the connection of metal centers, so obbz^{2-} ligand with the trans-configuration in **1** and **2** actually acts as a long spacer.

Crystal Structures. (a) Complex **1**. The crystal structure of **1** exhibits a 3D network composed of the tetranuclear cluster nodes [Co$_4$(μ^3-OH)$_2$]$^{6+}$, 4,4′-bpy bridging ligands, and obbz^{2-} bridging ligands(Figure 1). Two μ^3-hydroxyl groups bridge four cobalt(II) atoms to form the centrosymmetric tetranuclear cluster [Co$_4$(μ^3-OH)$_2$]$^{6+}$ as the node. There are two crystallographic independent cobalt(II) atoms: Co1 adopts a distorted octahedral [O$_5$N] coordination geometry with three carboxylato oxygen atoms from three obbz^{2-} ligands, two μ^3-hydroxyl groups, and one nitrogen atom of a 4,4′-bpy ligand, whereas Co2 exhibits a distorted tetrahedral [O$_3$N] coordination environment, which is coordinated by two carboxylato oxygen atoms from two obbz^{2-} ligands, one μ^3-hydroxyl group, and one nitrogen atom of a 4,4′-bpy ligand. The Co1$-$N bond distance of 2.108(3)Å is a little
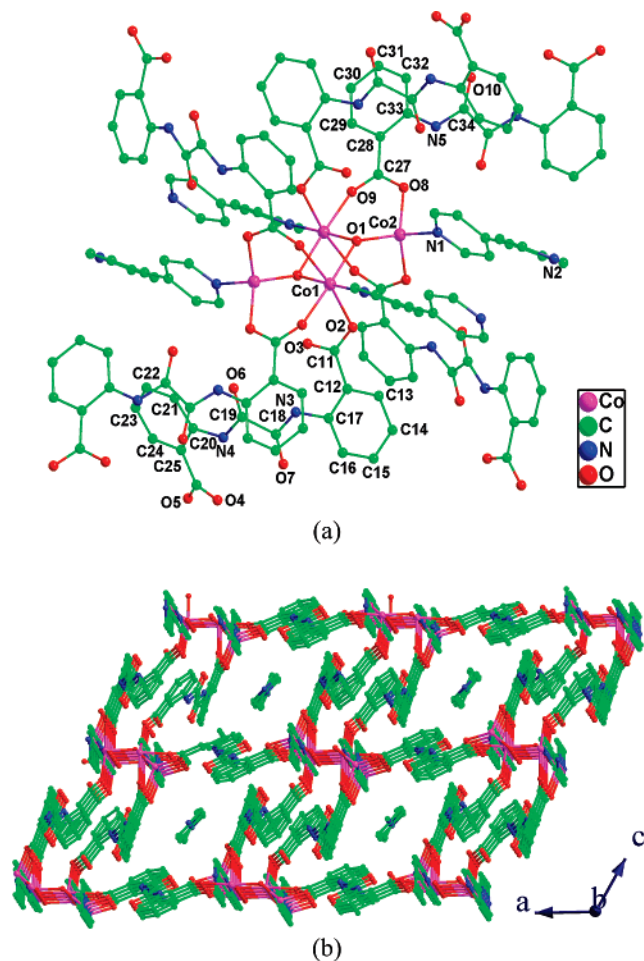
(a)

(b)

Figure 1. Bridging ligands coordinating the cluster node $[Co_4(\mu^3\text{-}OH)_2]^{6+}$ in **1** (a) and projection of the 3D network of **1** down the *b*-axis (b).

larger than the Co2−N bond length of 2.026(3) Å, and the Co1−O bond distances (from 2.070(2) to 2.178(3) Å) are larger than the Co2−O bond lengths (from 1.943(3) to 1.968(3) Å). The molecular formula of **1** is confirmed by the bond-valence sums' calculation,[30] which indicates that the valences of Co1 and Co2 are +1.972 and +1.943, respectively. It is noteworthy that the cluster $[Co_4(OH)_2]^{6+}$ in **1** is the only example constructed from four cobalt atoms showing not only the octahedral geometry but also the tetrahedral coordination environment, although many other μ^3-oxygen-bridged tetra-nuclear cobalt clusters that generally possess only one type of coordination configuration had been observed before.[31]

Each tetranuclear cluster node $[Co_4(\mu^3\text{-}OH)_2]^{6+}$ is coordinated by 10 bridging ligands (including four 4,4′-bpy ligands and six $obbz^{2-}$ ligands) but linked to only eight nearest neighbors because of two pairs of 4,4′-bpy ligands acting as two "double bridges"(Figure 1b). This affords a 3D eight-connected frame-work structure, which is not of the familiar CsCl-type. The CsCl-type structure is constructed from perpendicularly intersected 2D (4, 4) nets by sharing the diagonal, showing an eight-connected $4^{24}6^4$ topology, [23a] whereas the topology structure of **1** can be considered as being composed of 2D (3, 6) nets parallel to the *bc*-plane, which intersect with two types of 2D (4, 4) nets parallel to the *ab*-plane but arranged alternatively in a staggered way (Figure 2). The (3, 6) net and two types of (4, 4) nets share the arris along the *c*-axis direction to generate an eight-connected structure, which comprises linked lattices with dimensions of about 13.8 × 12.7 × 12.9 Å³. The formed 1D
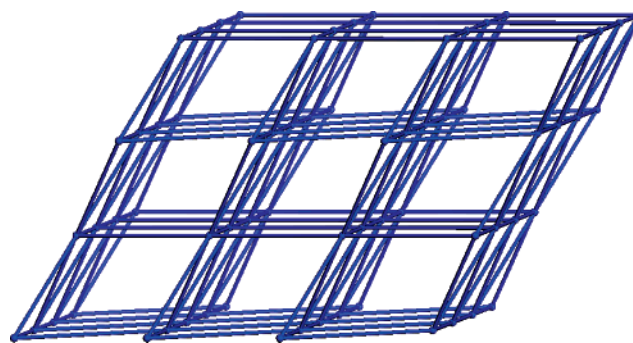

Figure 2. Schematic representation of the $3^64^{14}5^46^4$ topology of **1** viewed down the *b*-axis; the short and long links represent double 4,4′-bpy ligands and $obbz^{2-}$ ligand, respectively.

channels along the *b*-axis are occupied by the guest 4,4′-bpy molecules. Interestingly, from another view-angle, the structures of both **1** and CsCl can be considered to comprise (4, 4) nets, which are cross-linked by zigzag chains displaced by transla-tion: in CsCl, the zigzag chains bridge across the diagonal of the parallel (4, 4) nets, [23b] whereas in **1**, the zigzag chains bridge the border parallel to the *b*-axis of two types of (4, 4) nets that are alternatively arranged parallel to the *ab*-plane(Figure 2). The Schälfli symbol[32] for the net of **1** is $3^64^{14}5^46^4$; this 8-coordinated net was analyzed using Systre (gavrog.org), indicating that it is completely new within the reported 3D MOFs (this means it is not found in RCSR, see rcsr.anu.edu.au), and it possesses the symmetry *Cccm*, which is clearly a subnet of the 10-coordinated RCSR net *bct*. The topology of another recently reported 3D non-natural eight-connected MOF, $La(L)_4(ClO_4)_3$ (L = 4, 4′-bipyridine-*N,N*′-dioxide),[23b] is constructed from parallel (4, 4) nets and cross-linked zigzag chains too; however, the neighbor-ing zigzag chains are displaced by translation with a rotation angle of 61.5°. One zigzag chain bridges across the diagonal, whereas its translation analog bridges the border of the (4, 4) net, displaying an eight-connected topology of $3^34^{15}5^86^2$. To the best of our knowledge, **1** also represents the first 3D eight-connected MOF constructed from tetranuclear transition metal cluster nodes and mixed bridging ligands. Another quite recently reported 3D MOF $[Cd_3(bdc)_3(L)_2(H_2O)_2]$ (bdc = 1,4-benzene-dicarboxylate; L = 1,4-bis(1,2,4-triazol-1-yl)butane) is a self-penetrating coordination framework composed of trinuclear cadmium clusters as the nodes and mixed ligands 1,4-benzene-dicarboxylate and 1,4-bis(1,2,4-triazol-1-yl)butane as the bridges, exhibiting an interesting eight-connected $4^{20}6^8$ topology.[33]

(b) Complex **2**. The architecture of 3D homometallic coor-dination polymers based on both dinuclear cluster node and mononuclear node is extremely rare. However, not only the dinuclear cluster node $[Co_2(\mu^2\text{-}H_2O)]^{4+}$ but also the mononuclear node Co^{2+} are observed in **2**, which are connected by 4,4′-bpy and $obbz^{2-}$ bridging ligands, generating a 3D extended structure-(Figure 3). There are two crystallographic independent cobalt-(II) atoms: Co1 possesses a slightly distorted octahedral $[O_5N]$ coordination environment, which comprised three carboxylato oxygen atoms from three $obbz^{2-}$ ligands, one nitrogen atom of a 4,4′-bpy ligand, one terminal hydrate molecule, and one bridging hydrate molecule, whereas Co2 is coordinated in a distorted octahedral $[O_4N_2]$ geometry, with four carboxylato oxygen atoms from two $obbz^{2-}$ ligands and two nitrogen atoms from two 4,4′-bpy ligands. Co1 and its symmetry equivalent Co1[#1]([#1] −x + 1, y, −z + 1/2) are one hydrate molecule bridged, with a Co1··Co1[#1] distance of 3.61 Å and a Co1−O$_{hydrate}$−Co1[*1] bond angle of 113.9°, forming the dinuclear cluster node $[Co_2(\mu^2\text{-}H_2O)]^{4+}$, whereas Co2 acts as the mononuclear node.

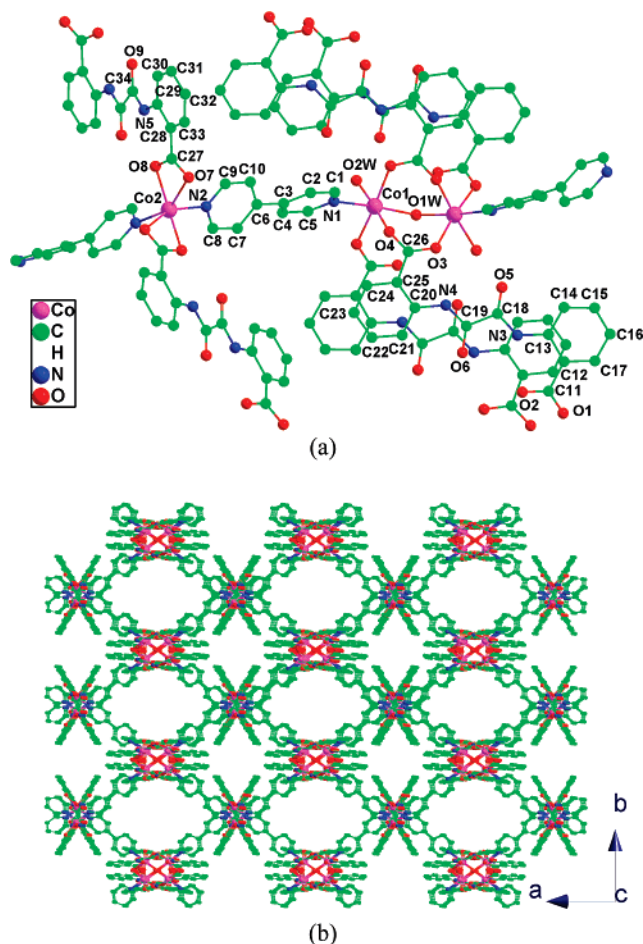**Figure 3.** Fragment of the structure of **2** (a) and one of 2-fold interpenetrating networks in **2** viewed down the *c*-axis (b).

Figure 4. Schematic representations of the 6^6 topology based on mononuclear node (in red)−dinuclear node (in blue) connections in **2** (viewed down the *Y*-axis), the blue−red, blue, and red links represent 4,4′-bpy ligand, single $obbz^{2-}$ ligand, and double $obbz^{2-}$ ligands, respectively, (a) and two interpenetrating 3D networks in **2** (viewed down the *Z*-axis), one of which is shown as green for clarity (b).

The Co2−O8 bond distance of 2.039(4) Å is obviously smaller than that of Co2−O7 (2.243(4) Å), but compared with the Co1−$O_{carboxylato}$ bond lengths (average 2.058(3)Å), whereas the Co1−N1 bond distance of 2.143(4)Å is a little larger than the Co2−N bond lengths (2.092(4) Å). The bond-valence sums' calculation[30] gives the valence of Co1 as +2.055, whereas the valence of Co2 is +1.887, affirming that H_2O rather than OH is the μ^2-O bridging unit between Co1 and Co1#1 (#1 −x + 1, y, −z + 1/2).

Each dinuclear cluster node $[Co_2(\mu^2-H_2O)]^{4+}$ is only four-connected, although it is coordinated by six bridging ligands, which include two 4,4′-bpy ligands and two pairs of $obbz^{2-}$ ligands acting as two double bridges. The mononuclear node Co^{2+} is also four-connected, but links to each other by single $obbz^{2-}$ ligand. Although the dinuclear node $[Co_2(\mu^2-H_2O)]^{4+}$ links to the mononuclear node Co^{2+} through a 4,4′-bpy bridging ligand. Consequently, a self-penetrating 3D framework is formed (Figures 3 and 4). To fully appreciate this network structure, we present the topology of node−node connections as Figure 4, which exhibits a 2-fold interpenetrating 3D (6, 4) distorted diamond network with the Schälfli symbol of 6^6. All four-connected nodes in the diamond structure possess an ideal tetrahedral connection configuration, whereas the (6, 4) network in **2** is constructed from two types of four-connected nodes: the mononuclear node Co^{2+} (red, Figure 4) with a distorted tetrahedral connection geometry, and the dinuclear cluster node $[Co_2(\mu^2-H_2O)]^{4+}$ (blue, Figure 4) possessing a special "quaternity truss" connection configuration, where its four linked neighbors are located at the same side. As a result, a new 3D (6, 4) network structure is formed.
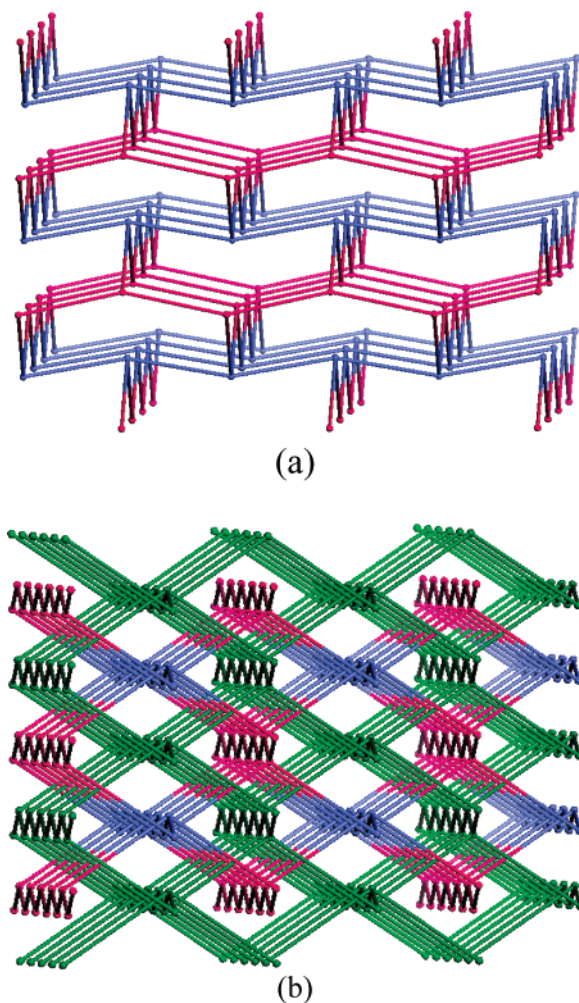
There are extensive intramolecular hydrogen bonds among the oxamido group and the carboxylato groups within $obbz^{2-}$ ligand (N(3)···O(2), 2.575(5) Å; N(3)···O(6), 2.613(5) Å; N(4)···O(3), 2.622(5) Å; N(4)···O(5), 2.707(5) Å; N(5)···O(8), 2.609-(5) Å; N(5)···O(9)#2, 2.652(6) Å; #2 −x, −y − 1, −z + 1), between the bridging hydrate molecule and the carboxylato group in $obbz^{2-}$ ligand (O(1W)···O(2)#3, 2.511(4) Å, #3 −x + 1, −y + 1, −z), as well as among the terminal hydrate molecule and the oxamido groups in $obbz^{2-}$ ligands (O(2W)···O(6)#4, 2.835(6) Å; O(2W)···O(5)#5, 2.740(6) Å; #4 x, −y + 1, z + 1/2; #5 −x + 1, y, −z + 1/2). These weak interactions play important roles in the stabilization of the crystal structure of **2**.

Magnetic Properties. The magnetic susceptibilities of complexes **1** and **2** have been investigated. For **1**, the product χT continuously decreases upon cooling (Figure 5), indicating an overall antiferromagntic (AF) coupling between the adjacent Co^{2+} ions. At room temperature, the χT value is 8.45 emu K mol^{-1}, which is larger than the value of 7.5 emu K mol^{-1} expected for four isolated spin-only $S = 3/2$ Co^{2+} cations (assuming $g = 2$). The $1/\chi$ data above 100 K follow the Curie−Weiss law well, with $C = 11.41$ emu K mol^{-1} and $\theta = -102.8$ K. The large negative Weiss constant suggests a net strong AF coupling among Co^{2+} ions. Because of the extreme difficulty of modeling the tetranuclear cobalt(II) cluster system with four
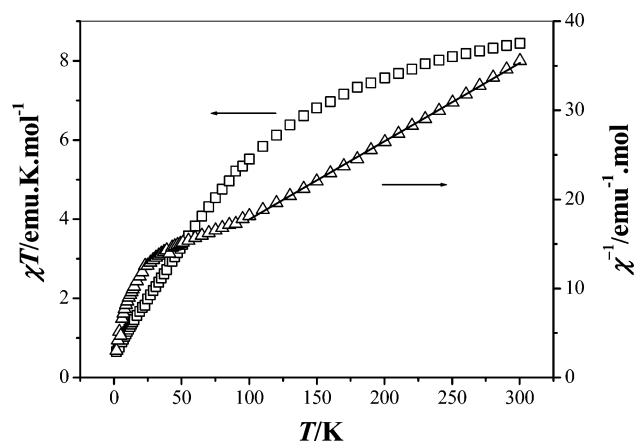
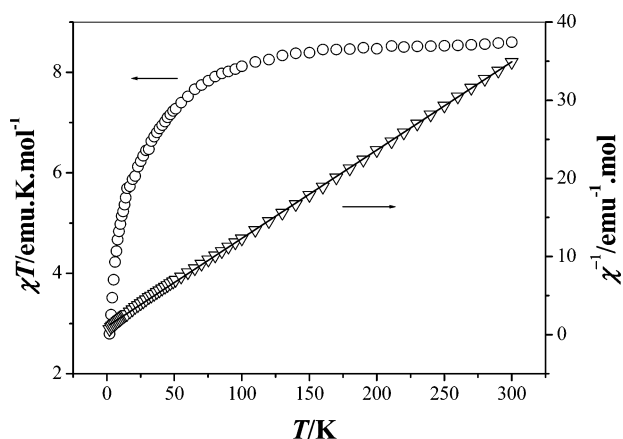**Figure 5.** Plots of χT and $1/\chi$ vs T of complex **1**.

Figure 6. Plots of χT and $1/\chi$ vs T of complex **2**.

different J,[31a] it is also impossible to fit the magnetic data of the more complicated **1** given current theory, even if the Co^{2+} centers are orbitally degenerate. For **2**, the observed χT value of 8.60 emu K mol^{-1} at 300 K is slightly smaller than the expected value of 8.79 emu K mol^{-1} for three non-interacting $S = 3/2$ Co^{2+} cations (assuming $g = 2.5$). The χT value decreases slightly to 8.12 emu K mol^{-1} at 100 K, and then dramatically decreases to 2.79 emu K mol^{-1} at 2 K (Figure 6). Best-fitting the data with the Curie–Weiss law gives $C = 8.87$ emu K mol^{-1} and a negative θ value of -9.9 K. The C value corresponds to $g = 2.51$, which is significantly larger than the spin-only value, being attributed to the orbital contribution of high spin Co(II) ions in the octahedral environment, but is consistent with the values observed in many other high spin octahedral Co(II) complexes.[26] The slight decrease of χT value in high-temperature range does not imply an antiferromagnetic coupling between Co(II) ions, as it is mainly due to the single-ion behavior of Co(II) ion.

Conclusions

Two novel 3D MOFs containing polynuclear cluster nodes and mixed bridging ligands, $[Co_4(OH)_2(obbz)_3(4,4'-bpy)_2](4,4'-bpy)$ (**1**) and $[Co_3(H_2O)(obbz)_3(4,4'-bpy)_2](H_2O)_2$(**2**), have been hydrothermally synthesized and characterized. **1** exhibits a unique 3D eight-connected $3^64^{14}5^46^4$ topology structure based on the tetranuclear cobalt(II) cluster node $[Co_4(\mu^3-OH)_2]^{6+}$ and mixed bridging ligands, whereas **2** possesses a 2-fold interpenetrating 3D distorted diamond network structure constructed from not only the binuclear cluster node $[Co_2(\mu^2-H_2O)]^{4+}$ but

also the mononuclear node Co^{2+}. This study demonstrates that using polynuclear transition metal cluster node and mixed bridging ligands can provide 3D MOFs with novel topology structures, and the hydrothermal technique can be utilized to obtain quite different 3D MOFs by controlling the temperatures only.

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