Hydrothermal Syntheses, Crystal Structures and Photoluminescent Properties of Three Metal-Cluster Based Coordination Polymers Containing Mixed Organic Ligands

Jun Tao,*[a] Xin Yin,[a] Zan-Bin Wei,[a] Rong-Bin Huang,[a] and Lan-Sun Zheng[a]

Keywords: Coordination polymers / Zinc / Cadmium / 5-Sulfoisophthalate / 5-Nitroisophthalate

Three novel metal-cluster based coordination polymers (MCCPs) with formulae $[Zn_4(\mu_3\text{-}OH)_2(H_2O)_2(sip)_2(4,4'\text{-}bpy)_2]\cdot 3H_2O$ (MCCP-4), $[Cd_4(\mu_3\text{-}OH)_2(H_2O)_2(sip)_2(4,4'\text{-}bpy)_4]\cdot H_2O$ (MCCP-5) and $[Cd_6(\mu_3\text{-}OH)_4(\mu_2\text{-}OH_2)_2(OH_2)_2(nip)_4(4,4'\text{-}bpy)_3]\cdot 3H_2O$ (MCCP-6) [H_2sip = 5-sulfoisophthalic acid, H_2nip = 5-nitroisophthalic acid and 4,4′-bpy = 4,4′-bipyridyl] were hydrothermally synthesized and characterized by single-crystal X-ray diffraction studies. MCCP-4 crystallizes in the triclinic space group $P\bar{1}$ with a = 10.106(2), b = 10.851(2), c = 11.125(2) Å, α = 105.66(3), β = 112.63(3), γ = 98.18(3)°, V = 1041.8(4) Å^3, and Z = 2. MCCP-5 crystallizes in the monoclinic space group $C2/c$ with a = 25.602(1), b = 16.571(1), c = 13.322(1) Å, β = 92.524(1)°, V = 5646.4(2) Å^3, and Z = 4. MCCP-4 and -5 consist of similar $[M_4(\mu_3\text{-}OH)_2]^{6+}$ tetranuclear building units that are joined through sip and 4,4′-bpy ligands to generate a two-dimensional structure (MCCP-4) and a three-dimensional structure (MCCP-5), respectively. MCCP-6 crystallizes in the triclinic space group $P\bar{1}$ with a = 14.295(2), b = 14.472(2), c = 20.204(3) Å, α = 73.362(3), β = 82.200(3), γ = 62.769(2)°, V = 3560.9(10) Å^3, and Z = 2. MCCP-6 contains unprecedented $[Cd_6(\mu_3\text{-}OH)_4(\mu_2\text{-}OH_2)_2]^{8+}$ hexanuclear building units which are linked through nip and 4,4′-bpy ligands to afford a two-dimensional structure. The infrared spectroscopy, thermal stability and photoluminescence of the three complexes were studied.

Introduction

Coordination polymers have attracted considerable attention in recent years due to their interesting properties and promising applications in the areas of catalysis, gas storage, magnetism and optics.[1] Concurrent with these studies has been the development of highly ordered multi-dimensional frameworks based primarily on combining organic and inorganic units through the assembly of metal centers with di- or multitopic organic ligands.[2] To date, the structures and properties of the vast majority of reported coordination polymers have been finely tuned by closely controlling the molecular properties of the organic ligands such as size, shape, functionality, flexibility and symmetry. One current challenge involves the preparation of coordination polymers in which the inorganic components display different physical properties or have different structural influences. This goal has been recently illustrated by metal-cluster based coordination polymers (MCCPs),[3] whose dimensions, geometries and properties can be controlled by the choice of metal clusters. Metal clusters can be very versatile in terms of coordination properties and rigidity as well as displaying intriguing physical properties in comparison with mono- or dinuclear species. Thus, coordination polymers constructed with metal clusters are usually more stable and promising in terms of potential applications. At present, in addition to utilizing H_2O_2 or excess base to facilitate the formation of metal clusters,[4,5] they can also be obtained from hydrothermal reactions involving in situ hydrolysis of metal ions with or without template ligands. In our group, we have focused our attention on metal-cluster based coordination polymers (particularly of Zn^{II} and Cd^{II}) with respect to their optical properties and we have found that in the presence of mixed organic ligands, metal clusters can form under hydrothermal conditions[6] e.g., $[Zn_4O(ip)_3(4,4'\text{-}bpy)]$ (MCCP-1, where ip = isophthalate), $[Zn_4(OH)_2(fa)_3(4,4'\text{-}bpy)_2]$ (MCCP-2, where fa = fumarate), $[Zn_3(OH)_2(4,4'\text{-}bpy)_{0.5}(4,4'\text{-}oba)_2]\cdot 0.5H_2O$ [MCCP-3, where 4,4′-oba = 4,4′-oxybis(benzoate)]. Based on our experience in this area and with the long-term goal of classifying the factors affecting the formation of metal clusters and metal-cluster based coordination polymers, we have started to synthesize new coordination polymers with metal clusters.

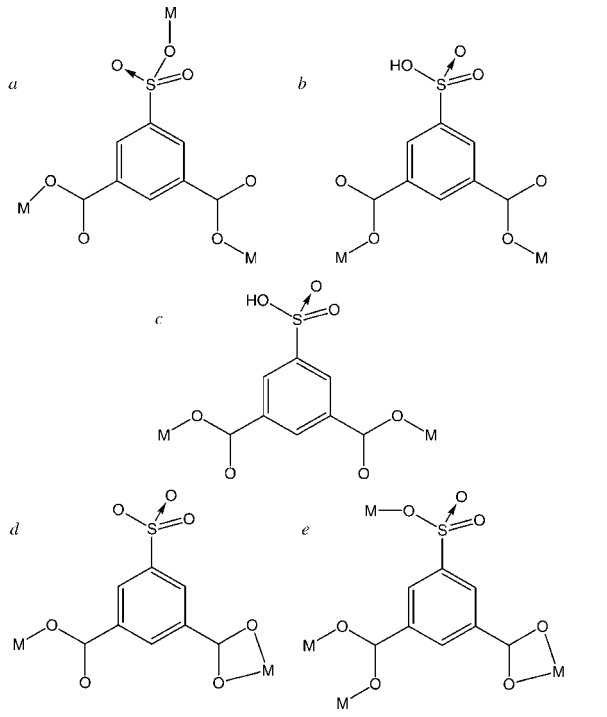
Our previous work on $[Zn_4O(ip)_3(4,4'\text{-}bpy)]$ (MCCP-1)[6a] has led us to consider whether ligands derived from isophthalate can produce similar structures, especially the 5-substituted forms of isophthalate. We selected 5-sul-

[a] Department of Chemistry and State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, China
Fax: (internat.) + 86-592-2183047
E-mail: taojun@jingxian.xmu.edu.cn

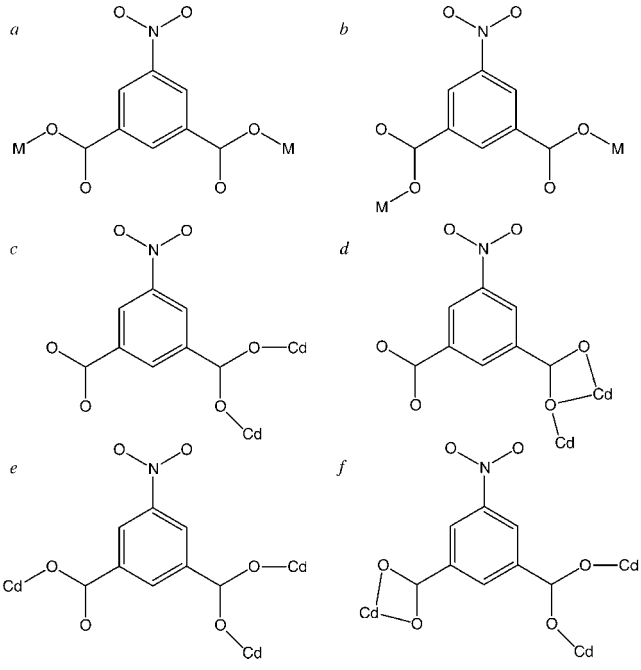
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

foisophthalate (sip) and 5-nitroisophthalate (nip) as ligands in which the sulfonate group shows weak coordination strength towards transition metals[7] and both sulfonate and nitro groups are suitable H-bonding acceptors.[8] As such they may be helpful for stabilizing these complexes. Herein we report three novel coordination polymers constructed from zinc and cadmium clusters and mixed organic ligands: $[Zn_4(\mu_3\text{-}OH)_2(H_2O)_2(sip)_2(4,4'\text{-}bpy)_2]\cdot 3H_2O$ (MCCP-4), $[Cd_4(\mu_3\text{-}OH)_2(H_2O)_2(sip)_2(4,4'\text{-}bpy)_4]\cdot H_2O$ (MCCP-5) and $[Cd_6(\mu_3\text{-}OH)_4(\mu_2\text{-}OH_2)_2(OH_2)_2(nip)_4(4,4'\text{-}bpy)_3]\cdot 3H_2O$ (MCCP-6).

The sip ligand was studied recently as a building block for extended frameworks. Shimizu[9] has reported a pseudo-honeycomb coordination polymer $\{[Cu_{1.5}(sip)(py)_5]\cdot(py)\cdot(H_2O)_{6.76}\}_n$, and Cao[10] reported two zeolite-like supramolecular complexes $\{[Cu(H_2O)_2(Hsip)]\cdot(H_2O)_2\cdot(pip)_{0.5}\}_n$ and $\{[Cu(H_2O)_3(Hsip)]\cdot(H_2O)_6\cdot(hmt)_{0.5}\}_n$ (pip = piperazine, hmt = hexamethylenetetramine). To date the above three Cu(sip) coordination complexes are the only transition metal sip complexes reported. In these three complexes, the sip ligands exhibit three different coordination modes, henceforth denoted as *a*-sip, *b*-sip and *c*-sip and depicted in Scheme 1. The sip ligands reported here (MCCP-4 and -5) coordinate to metal atoms in different coordination modes, namely as *d*-sip in MCCP-4 and *e*-sip in MCCP-5, respectively. With regards to the nip ligand, the only other metal-(nip) complexes which have been prepared are two Cu(nip) supramolecular isomers[11] and two Zn(nip) supramolecular structures, namely $\{[Zn(nip)(py)(H_2O)]\cdot(H_2O)\}_n$ and $\{[Zn(nip)(4,4'\text{-}bpy)_{0.5}(H_2O)_2]\cdot(H_2O)\}_n$. In the two zinc complexes that have been reported by our group,[8c,8d] the nip ligand displays two slightly different coordination modes, namely *a*-nip and *b*-nip as illustrated in Scheme 2. Interestingly, the nip ligand in MCCP-6 exhibits four different coordination modes, viz. *c*-nip, *d*-nip, *e*-nip, and *f*-nip as shown in Scheme 2.



Scheme 1. The five different coordination modes of the sip ligand in refs.[9,10] (*a*, *b*, *c*), MCCP-4 (*d*) and MCCP-5 (*e*)



Scheme 2. The six different coordination modes of the nip ligand in refs.[8c,8d,11a] (*a*, *b*) and MCCP-6 (*c*−*f*)

Results and Discussion

Syntheses and Characterization

The hydrothermal method has been proven to be very effective for the synthesis of zeolites, nanomaterials and more recently coordination polymers. It is well known that small changes in one or more of the hydrothermal parameters, such as temperature, reaction time, pH value, and molar ratios of reactants may exert a profound influence on the final reaction products. During the past few years, we have explored the synthesis of MCCPs containing mixed organic ligands under typical hydrothermal conditions (i.e., 120−180 °C for 2−7 d), and found that a pH of 7−8 and the existence of 4,4′-bpy are most suitable in forming metal clusters as well as MCCPs. These conditions have been used directly to prepare MCCP-4, -5 and -6, where it is believed that the formation of metal clusters can be attributed to the hydrolysis of metal ions in neutral systems under hydrothermal conditions.

The FT-IR spectra of MCCP-4, -5 and -6 show no bands in the region 1690−1730 cm^{-1}, indicating complete deprotonation of the carboxyl groups. The spectra exhibit broad absorption bands in the range of 3260−3570 cm^{-1} due to the ν(OH) vibrations of coordinated water molecules. The absorptions in the region 1000−1230 cm^{-1} for MCCP-4 and -5 are typical for a sulfonate group,[12] and those at

1360−1460 cm^{-1} for MCCP-6 characterize the asymmetric and symmetric vibrations of the nitro group.[13] The strong bands at 1360−1610 cm^{-1} for all MCCPs are characteristic of a carboxylate group. In MCCP-6 these bands probably overlap partially with those of the nitro group.

The thermogravimetric analyses (TGA) of MCCP-4 and -6 showed the occurrence of three consecutive processes, namely dehydration, ligand pyrolysis (or volatilization) and inorganic residue formation. The TGA for MCCP-4 showed the complete loss of five water molecules at ca. 135 °C (found 7.61%; calcd. 8.68%). The dehydrated compound remained stable up to ca. 360 °C without any weight loss, however, MCCP-4 decomposed when heated to 140 °C at 0.05 Torr for 12 h as evidenced by the diffraction lines observed in its X-ray powder diffraction pattern (see Supporting Information) and at a temperature range of 360−580 °C the pyrolysis (or volatilization) of both sip and 4,4′-bpy ligands occurred leaving residual ZnO (remaining weight: found 26.60%; calcd. 4ZnO: $[Zn_4(\mu_3\text{-}OH)_2(H_2O)_2(sip)_2(4,4'\text{-}bpy)_2]\cdot 3H_2O$ 27.48%). The TGA for MCCP-6 showed an initial weight loss of 3.06% from 180 to 215 °C corresponding to the removal of three lattice water molecules per formula unit (calcd. 2.49%), followed by another weight loss of 60.98% from 307 °C for elimination of the nip ligands and 4,4′-bpy pillars from the framework, the remaining residue was probably $Cd(OH)_2$. (as calcd. 6$Cd(OH)_2$: $[Cd_6(\mu_3\text{-}OH)_4(\mu_2\text{-}OH_2)_2(OH_2)_2(nip)_4(4,4'\text{-}bpy)_3]\cdot 3H_2O$ 40.42%). The TGA curve of MCCP-5 was somewhat different from those of MCCP-4 and -6. MCCP-5 remained stable under nitrogen up to 186 °C before it suffered a weight loss of 22.24% of the total weight between 186 and 335 °C. This can be assigned to the evaporation of one lattice water molecule, two-coordinated water molecules and two one-end-bound 4,4′-bpy ligands per formula (calcd. 22.22%). The second distinct weight loss appeared in the temperature range 335−550 °C and was caused by the pyrolysis (or volatilization) of the sip and μ_2-4,4′-bpy ligands resulting in a residue of $Cd(OH)_2$ (found 35.81%; calcd. 35.52%).

Description of Crystal Structures

Single-crystal X-ray diffraction analysis has revealed that MCCP-4 is a 2D-framework constructed from $[Zn_4(\mu_3\text{-}OH)_2]^{6+}$ clusters and two organic ligands. The structure contains a crystallographic inversion center located at the center of the $[Zn_4(\mu_3\text{-}OH)_2]^{6+}$ cluster with the two crystallographically nonequivalent zinc atoms assuming two different coordination geometries. Zn1 is in a distorted trigonal-bipyramidal environment and is coordinated in the equatorial plane to one μ_3-OH group, one 4,4′-bpy nitrogen atom and one oxygen atom from the monodentate carboxylate group of a *d*-sip ligand (Scheme 1). In the axial positions it is also coordinated to one μ_3-OH group and one oxygen atom from the bidentate carboxylate group of another *d*-sip ligand, as shown in Figure 1. However, the Zn1···O4B distance of 2.826(2) Å suggests a nonnegligible interaction with the uncoordinated oxygen atom of the monodentate carboxylate group of a *d*-sip ligand, which may be described as a semichelating coordination mode.[14] Hence, Zn1 may also be regarded as being in a pseudooctahedral environment. Selected bond lengths and angles are given in Table 1. Zn2 is tetrahedrally surrounded by one μ_3-OH group, one bpy nitrogen atom, one water molecule and one oxygen atom from the bidentate carboxylate group of a *d*-sip ligand. The average bond lengths around Zn2 (1.976 Å) are somewhat shorter than those of Zn1 (2.077 Å) and this is consistent with the fact that bond lengths in a tetrahedral geometry are generally shorter than those in other geometries. Two pairs of symmetry-related zinc atoms are then joined by two triply bridging μ_3-OH groups to generate the basic structural building unit $[Zn_4(\mu_3\text{-}OH)_2]^{6+}$ and the Zn−O(hydroxo) distances [1.962(2)−2.172(2) Å] are in the range of those previously reported in the literature.[4,6,15]

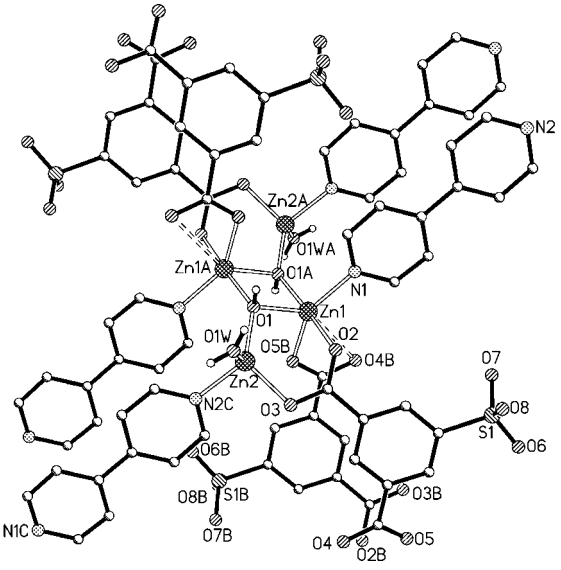


Figure 1. Perspective view of the coordination environments of zinc atoms in MCCP-4; lattice water molecules have been omitted for clarity

Table 1. Selected bond lengths [Å] and angles [°] for MCCP-4; symmetry codes A: $-x+1, -y+1, -z+1$; B: $-x+2, -y+1, -z+2$, C: $x, y+1, z+1$

Zn1−O1	2.029(2)	Zn1−O2	2.220(2)
Zn1−O1A	2.172(2)	Zn1−O5B	1.959(2)
Zn1−N1	2.005(2)	Zn1···O4B	2.826(2)
Zn2−O1	1.962(2)	Zn2−O3	1.963(2)
Zn2−O1W	1.955(2)	Zn2−N2	2.025(2)
O1−Zn1−N1	119.5(1)	O1−Zn1−O2	88.9(1)
O1−Zn1−O5B	95.6(1)	O1−Zn1−O1A	85.2(1)
N1−Zn1−O5B	144.6(1)	O1A−Zn1−O2	173.8(1)
O1−Zn2−O3	119.2(1)	O1−Zn2−O1W	109.1(1)
O3−Zn2−O1W	106.6(1)	O3−Zn2−N2C	97.8(1)

It is interesting that the $[Zn_4(\mu_3\text{-}OH)_2]^{6+}$ clusters are interlinked by the carboxylate groups of *d*-sip in mono- and bidentate fashions, resulting in one-dimensional $[Zn_4(\mu_3\text{-}OH)_2(H_2O)_2(sip)_2]_n$ chains, which are further bridged

through μ-4,4′-bpy ligands to generate an infinite two-dimensional sheet, with uncoordinated sulfonate groups deviating from the plane and orientated on both sides (Figure 2). The distances S1−O6, S1−O7 and S1−O8 are 1.429(2), 1.462(2) and 1.442(2) Å, respectively, and all fall within the typical range of S−O bond lengths in a sulfonate anion (1.40−1.49 Å).[16] Two oxygen atoms of the sulfonate group are involved in hydrogen bonding with the μ_3-OH group and zinc-bound water molecule [O8···O1 2.703(3) Å and O7···O1 W 2.713(3) Å] on the adjacent sheets, and these hydrogen bonds serve to increase the order of the structure of MCCP-4 from two to three-dimensional.

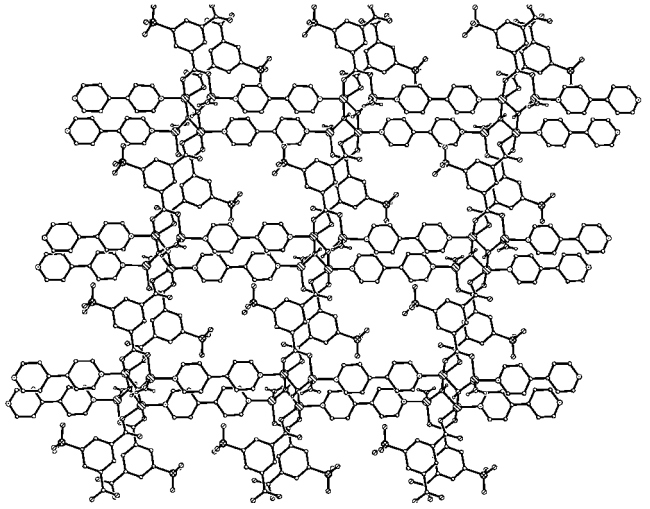


Figure 2. Perspective view of the two-dimensional sheet of MCCP-4; lattice water molecules and hydrogen bonds have been omitted for clarity

The structure of MCCP-5 is constructed from $[Cd_4(\mu_3\text{-}OH)_2]^{6+}$ clusters similar to that of MCCP-4, and also contains a crystallographic inversion center located at the center of the $[Cd_4(\mu_3\text{-}OH)_2]^{6+}$ cluster but its coordination environment around the Cd atoms is somewhat different from that of the Zn centers in MCCP-4. Selected bond lengths and angles are given in Table 2. The octahedral Cd1 atom is bound to one 4,4′-bpy nitrogen atom, three oxygen atoms from the bidentate and chelating carboxylate groups of two different *e*-sip ligands, respectively (Scheme 1). The remaining two coordination sites of the octahedron are filled by one μ_3-OH group and a sulfonate oxygen of an *e*-sip ligand (Figure 3). Cd2 adopts a slightly distorted octahedral geometry and is coordinated to two μ_3-OH groups, one 4,4′-bpy nitrogen atom and one carboxylate oxygen atom of an *e*-sip ligand in the equatorial plane, and to one water molecule and one 4,4′-bpy nitrogen atom in the axial positions. It is noteworthy that the latter 4,4′-bpy ligand uses only one nitrogen atom (N3) to coordinate to Cd2 leaving the other nitrogen (N4) free, as found in $[Zn(C_4H_4O_4)(4,4'\text{-bpy})]$ and the Co-4,4′-bpy molecular railroad.[17]

Table 2. Selected bond lengths [Å] and angles [°] for MCCP-5; symmetry codes A: $-x + 1/2, -y + 1/2, -z + 1$; B: $x, -y, -z + 1$, C $-x + 1/2, -y + 1/2, -z + 3/2$; D: $-x + 2, y + 1/2, -z + 1/2$; E: $-x, -y, -z + 1$

Cd1−O1	2.221(3)	Cd1−O2	2.451(3)
Cd1−O3	2.365(3)	Cd1−N1	2.323(3)
Cd1−O4B	2.252(3)	Cd1−O7C	2.436(4)
Cd2−O1	2.330(3)	Cd2−O1A	2.312(3)
Cd2−O1W	2.362(3)	Cd2−O5D	2.305(3)
Cd2−N3	2.417(3)	Cd2−N2E	2.385(3)
O1−Cd1−N1	113.0(1)	O1−Cd1−O4B	85.2(1)
O2−Cd1−O3	54.1(1)	O1−Cd1−O2	136.1(1)
O4B−Cd1−N1	158.2(1)	O1−Cd2−O1A	78.9(1)
O1−Cd2−O1W	81.8(1)	O1−Cd2−N3	100.3(1)
O1−Cd2−O5D	174.4(1)		

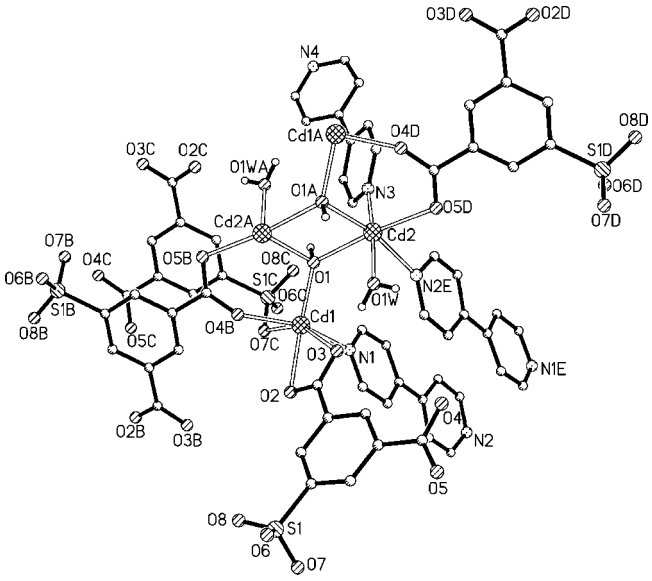


Figure 3. Perspective view of the coordination environments of cadmium atoms in MCCP-5; the coordination spheres around Cd1A and Cd2A have been drawn incompletely for clarity

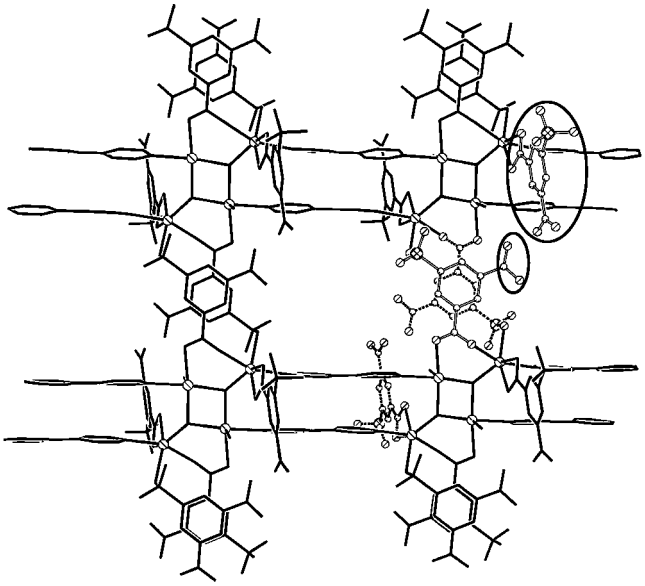


Figure 4. A section of MCCP-5 showing how the two-dimensional sheets are intersected with each other through the *e*-sip ligands

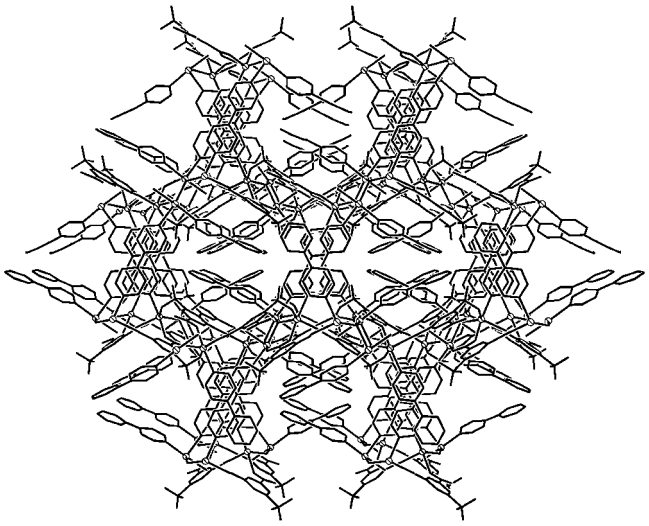


Figure 5. Perspective view of the three-dimensional structure of MCCP-5; lattice water molecules have been omitted for clarity

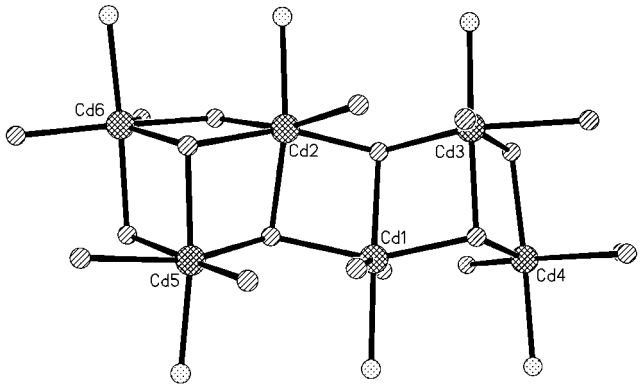


Figure 6. Perspective view of the hexanuclear cadmium cluster in MCCP-6

The most striking feature in MCCP-5 is the connection of all $[Cd_4(\mu_3\text{-}OH)_2]^{6+}$ clusters through *e*-sip ligands using their bridging bidentate carboxylate and sulfonate groups and 4,4′-bpy ligands to form an infinite two-dimensional sheet. The remaining chelating carboxylate groups orientate themselves up and down, as shown in the small circle in Figure 4. The two *e*-sip ligands drawn in open line are indeed symmetrically related (x, $-y$ +2, z − 1/2), and the chelating carboxylate group (small circle) and the *e*-sip ligand (large circle) are further coordinated to the nearest $[Cd_4(\mu_3\text{-}OH)_2]^{6+}$ cluster in the adjacent sheet which is intersected with the first one. Similarly, the two *e*-sip ligands drawn with a dashed line also are coordinated likewise. Thus, the intersected two-dimensional sheet is inter-linked through the chelating carboxylate groups of *e*-sip ligands to form an actual three-dimensional structure containing nearly hexagonal channels that are occupied by pendant 4,4′-bpy ligands and lattice water molecules, as illustrated in Figure 5. To the best of our knowledge, whereas three basic cadmium clusters have been found,[18] this is the first example of a coordination polymer constructed from $Cd_4(\mu_3\text{-}OH)_2$ clusters.

The basic building unit in MCCP-6 is the $[Cd_6(OH)_4(OH_2)_4]^{8+}$ cluster (Figure 6), which is constructed from hexameric units composed of six octahedral Cd^{II} centers in which four nip ligands doubly bridge the six cadmium clusters in *e* and *f* modes, and two nip ligands are doubly bound to four cadmium atoms in terminal *c* and *d* modes (Figure 7 and Scheme 2). Selected bond lengths and angles are listed in Table 3. Cd1 is coordinated to three μ_3-OH groups (O1, O2 and O3) and one 4,4′-bpy nitrogen

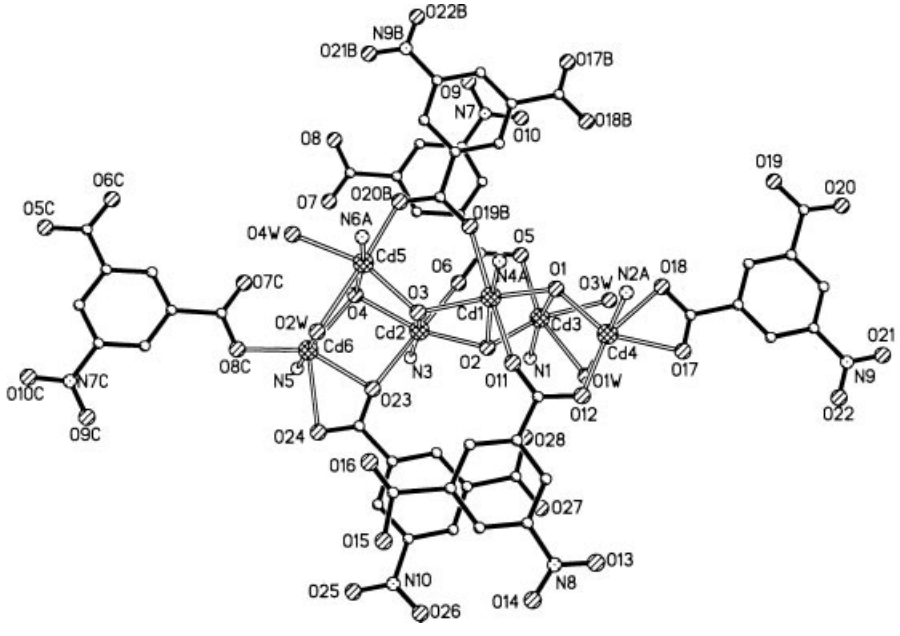


Figure 7. Perspective view of the coordination environments of cadmium atoms in MCCP-6; the carbon atoms of 4,4′-bpy ligands and lattice water molecules have been omitted for clarity

Table 3. Selected bond lengths [Å] and angles [°] for MCCP-6; symmetry codes A: x, $y + 1$, z; B: $-x$, $-y + 1$, $-z$, C: $-x$, $-y$, $-z + 1$

Cd1−O1	2.206(6)	Cd1−O2	2.360(6)	Cd1−O3	2.219(6)	Cd1−N4A	2.284(4)
Cd1−O11	2.333(9)	Cd1−O19B	2.378(8)	Cd2−O2	2.222(6)	Cd2−O3	2.304(6)
Cd2−O4	2.282(7)	Cd2−N3	2.301(4)	Cd2−O6	2.306(8)	Cd2−O23	2.373(7)
Cd3−O1	2.259(6)	Cd3−O2	2.222(6)	Cd3−N1	2.295(5)	Cd3−O3W	2.408(8)
Cd3−O5	2.279(8)	Cd3−O1W	2.517(7)	Cd4−O1	2.247(7)	Cd4−O12	2.268(7)
Cd4−O17	2.338(7)	Cd4−O18	2.495(7)	Cd4−O1W	2.389(6)	Cd4−N2A	2.329(5)
Cd5−O3	2.217(7)	Cd5−O4	2.293(6)	Cd5−O4W	2.325(8)	Cd5−N6A	2.339(4)
Cd5−O2W	2.523(7)	Cd5−O20B	2.244(7)	Cd6−O4	2.260(6)	Cd6−O8C	2.200(8)
Cd6−O23	2.325(7)	Cd6−O24	2.610(8)	Cd6−O2W	2.369(6)	Cd6−N5	2.316(4)
O1−Cd1−O2	77.8(2)	O2−Cd1−O3	80.3(2)	O1−Cd1−N4A	103.5(2)	O3−Cd1−N4A	100.8(2)
O11−Cd1−O19B	169.5(3)	O1−Cd1−O11	93.3(4)	O2−Cd2−O3	81.5(2)	O3−Cd2−O4	78.0(2)
O2−Cd2−N3	103.5(2)	O4−Cd2−N3	98.7(2)	O3−Cd2−N3	167.9(2)	O6−Cd2−O23	162.8(3)
O1−Cd3−O2	79.7(2)	O1−Cd3−O3W	90.3(3)	O2−Cd3−N1	96.7(2)	N1−Cd3−O3W	89.5(3)
O1−Cd3−N1	167.8(3)	O5−Cd3−O1W	160.2(3)	O1−Cd4−O12	117.9(3)	O12−Cd4−O17	103.2(3)
O17−Cd4−O18	53.8(3)	O1−Cd4−O18	84.9(3)	N2A−Cd4−O1W	176.9(2)	O1−Cd4−N2A	99.3(2)
O3−Cd5−O4	79.6(2)	O4−Cd5−O4W	86.3(3)	O4 W−Cd5−N6A	90.1(3)	O3−Cd5−N6A	101.0(2)
O20B−Cd5−O2W	175.3(3)	N6A−Cd5−O2W	91.5(2)	O4−Cd6−O23	81.1(2)	O23−Cd6−O24	52.3(2)
O8C−Cd6−O24	94.9(3)	O4−Cd6−O8C	130.1(3)	N5−Cd6−O2W	177.0(2)	O4−Cd6−N5	100.4(2)

atom in the equatorial plane, and to two oxygen atoms from the bridging bidentate carboxylate group of a *c*-nip ligand (O11) and the bridging bidentate carboxylate group of an *f*-nip ligand (O19B) in the axial positions. Cd2 has a similar coordination environment and is bound to three μ_3-OH groups (O2, O3 and O4) and one nitrogen atom from the 4,4′-bpy ligand. The remaining two coordination sites of the octahedron are filled by two oxygen atoms from the bidentate carboxylate group (O6) of an *e*-nip ligand and the chelating/bridging carboxylate group (O23) of a *d*-nip ligand. Cd3 lies in the center of a distorted octahedron and is coordinated to one μ_3-OH group (O2), one μ_2-bridging water molecule (O1W), one terminal water molecule (O3W) and one oxygen atom from the bidentate carboxylate group (O5) of an *e*-nip ligand in the equatorial plane. The coordination sphere is completed by one μ_3-OH group (O1) and one nitrogen atom from the 4,4′-bpy ligand in the axial positions. Cd4 is octahedrally coordinated by one μ_3-OH group (O1), one oxygen atom from the bridging bidentate carboxylate group (O12) of a *c*-nip ligand, two oxygen atoms from the chelating carboxylate group (O17, O18) of an *f*-nip ligand, one μ_2-bridging water molecule (O1W) and one 4,4′-bpy nitrogen atom. The coordination environments around Cd5 and Cd6 are somewhat similar to those of Cd3 and Cd4, respectively, except for the different coordination modes of the nip ligands. It is noteworthy that the six cadmium atoms are interlinked through four triply bridging μ_3-OH groups to form four basic $Cd_3(OH)$ subunits, in which the Cd−O distances of between 2.211 and 2.368 Å are consistent with those of other μ_3-OH-bridged cadmium motifs.[18,19] The assignment of μ_3-OH groups was based on the near tetrahedral angles around the central O atoms with average angles between 101.1 and 106.9°, which are a little larger than those found in the $(F_5C_5CdOH)_4$ cubane.[19]

The most striking feature of MCCP-6, however, is the connection of all $[Cd_6(\mu_3\text{-}OH)_4(\mu_2\text{-}OH_2)_2(OH_2)_2]^{8+}$ building blocks through linking *e*- and *f*-nip ligands to form a slightly corrugated, infinite 1D-chain with the formula $[Cd_6(\mu_3\text{-}OH)_4(\mu_2\text{-}OH_2)_2(OH_2)_2(nip)_4]_n$ (Figure 8), in which pairs of *c*- and *d*-nip ligands are located on both sides. Obviously, the large bulk combined with short nip links does not allow for high coordination of the hexanuclear cluster because of the steric hindrance. Their links by *e*- and *f*-nip ligands are made to bind in a pairwise manner to two hexanuclear cluster as observed for ip in MOF-49.[20] As shown in Figure 7, each hexanuclear cluster is coordinated to six nitrogen atoms from six μ_2-4,4′-bpy ligands up and down, thus the adjacent 1D-chains are further interlinked through these μ_2-4,4′-bpy ligands to generate an infinite undulating 2D-sheet (Figure 9).

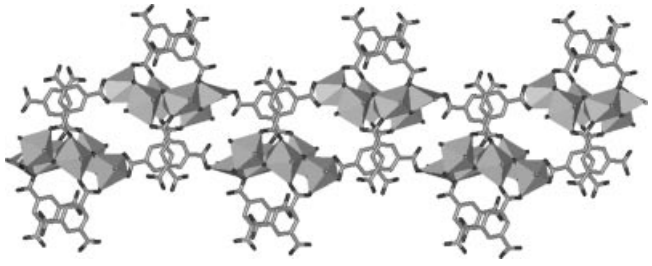


Figure 8. Perspective view of the one-dimensional chain constructed with hexanuclear cadmium clusters and nip ligands; coordinated 4,4′-bpy ligands have been omitted for clarity

Photoluminescent Properties

As we and others previously reported, coordination polymers containing zinc or cadmium oxide or hydroxide motifs exhibit photoluminescent properties[6,18b] and in this study we also investigated the photoluminescent properties of MCCP-4, -5 and -6 (Figure 10). In the solid state, the maximum of the emission bands of MCCP-4 is located at

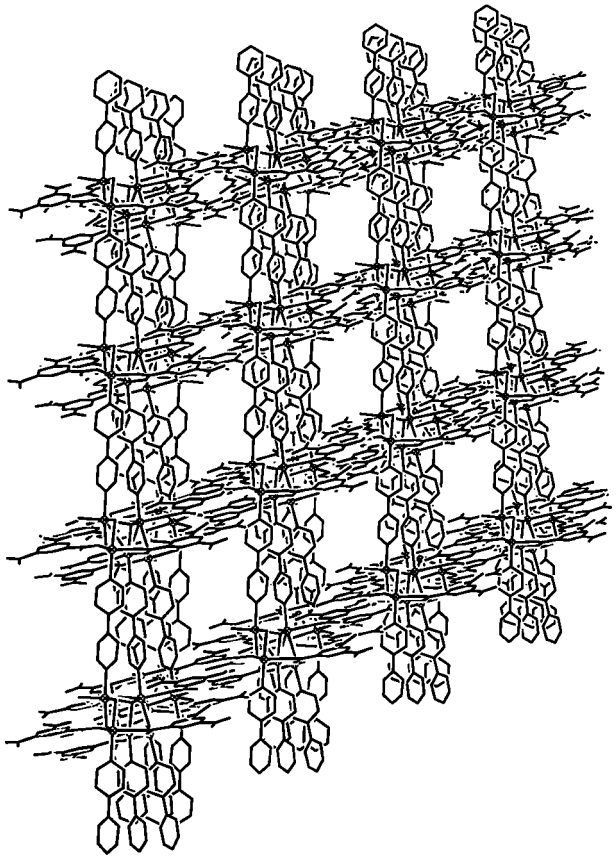


Figure 9. Perspective view of the two-dimensional structure of MCCP-6

562 nm (λ_{ex} = 505 nm), while MCCP-5 shows two emission bands at 370 nm and 468 nm (λ_{ex} = 340 nm), respectively. Since free H_2sip exhibits photoluminescence emission at 355 nm, the emission band at 370 nm of MCCP-5 may be due to the ligand donation, while the emission bands at 562 nm and 468 nm of MCCP-4 and -5 might be attributable to the formation of $[M_4(\mu_3\text{-}OH)_2]^{6+}$ (M = Zn^{II}, Cd^{II}) clusters and/or to ligand-to-metal charge transfer (LMCT).[6,21] MCCP-6 also exhibits intense photoluminescence with the maximum at 470 nm. Because the free H_2nip ligand does not emit any luminescence in the range 400−800 nm, the emission of MCCP-6 might also be assigned to the formation of $[Cd_6(\mu_3\text{-}OH)_4]^{8+}$ clusters and/or to ligand-to-metal charge transfer (LMCT).[6,21]

In conclusion, we have synthesized three novel metal-cluster-based coordination polymers, in which the sip and nip ligands show versatile coordination modes. The sulfonate groups in MCCP-4 and -5 are uncoordinated and monodentate, respectively. Furthermore, the sulfonate and nitro groups are involved in extensive inter-framework hydrogen bonding, which thus leads to extended structures with a higher order of dimensions.

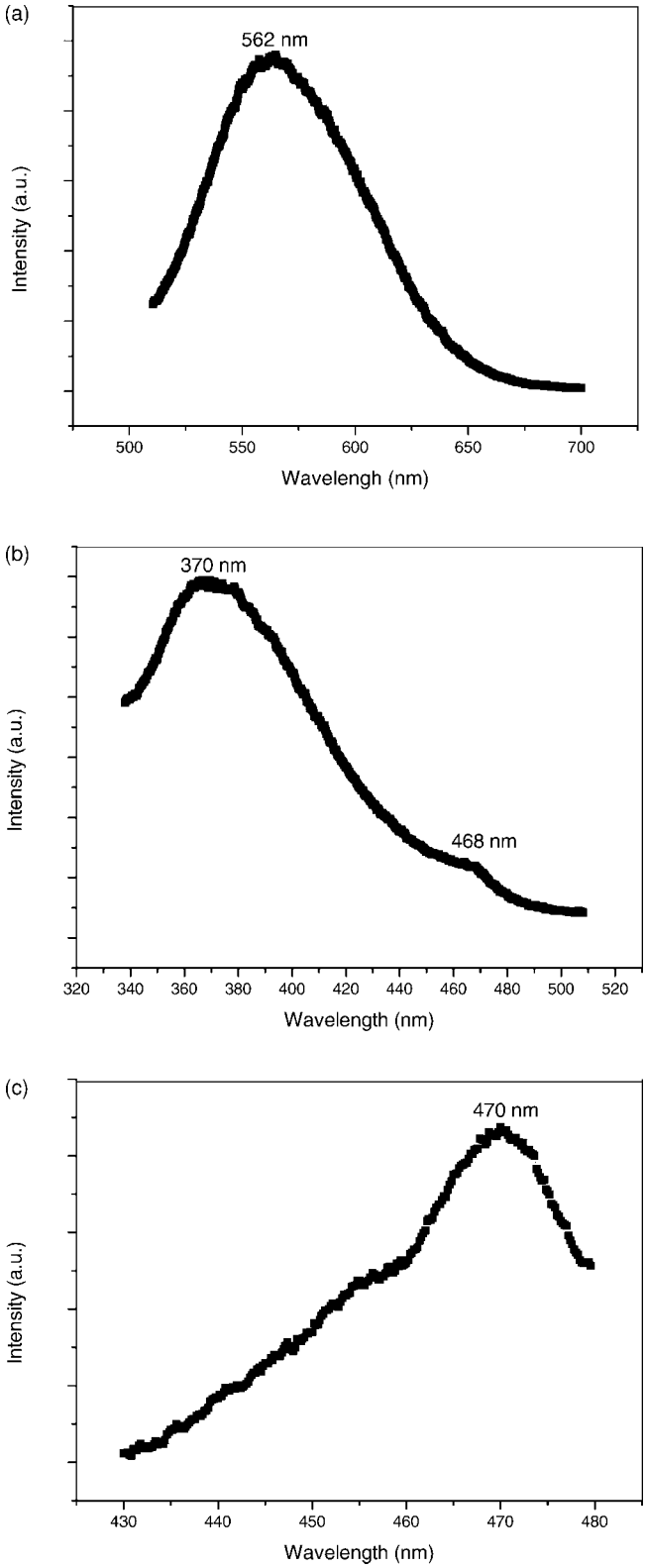


Figure 10. The solid-state photoluminescent spectra of MCCP-4 (a), -5 (b) and -6 (c) at room temperature

Experimental Section

General Remarks: All reagents were purchased from commercial sources and used without further purification. Elemental analyses

Table 4. Crystallographic data for MCCP-4, -5 and -6

	MCCP-4	MCCP-5	MCCP-6
Empirical formula	$C_{18}H_{17}N_2O_{10.5}SZn_2$	$C_{56}H_{46}Cd_4N_8O_{19}S_2$	$C_{62}H_{54}Cd_6N_{10}O_{35}$
Formula mass	592.14	1648.73	2173.55
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
a [Å]	10.106(2)	25.602(1)	14.295(1)
b [Å]	10.851(2)	16.571(1)	14.472(1)
c [Å]	11.125(2)	13.322(1)	20.204(1)
α [°]	105.66(3)	90	73.362(1)
β [°]	112.63(3)	92.524(1)	82.200(1)
γ [°]	98.18(3)	90	62.769(1)
V [Å^3]	1041.8(4)	5646.4(2)	3560.9(3)
Z	2	4	2
D_c [g·cm^{-3}]	1.888	1.940	2.027
μ [mm^{-1}]	2.467	1.646	1.862
R_1, wR_2 (obsd.)[a]	0.0273, 0.0657	0.0367, 0.0805	0.0674, 0.1234

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

were performed with a CE EA 1110 elemental analyzer. IR spectra were recorded from 4000 to 400 cm^{-1} with a Nicolet AVATAR FT-IR360 instrument. The thermal gravimetric analyses (TGA) were carried out under nitrogen with a NETZSCH STA 449C differential thermal analyzer with a rate of 10 °C/min.

Synthesis of MCCP-4: An aqueous solution (5 mL) of H_2sip (0.134 g, 0.50 mmol) was adjusted to pH = 7 with 1 M NaOH, and transferred into a Parr Teflon-lined stainless steel vessel (23 mL) containing $Zn(NO_3)_2{\cdot}6H_2O$ (0.158 g, 0.50 mmol) and 4,4′-bpy (0.078 g, 0.50 mmol). To the resultant mixture was added an additional 3 mL of water. The vessel was then sealed and heated to 180 °C for 3 d, followed by cooling at 2.5 °C/h to room temperature. Colorless block-like crystals were collected by hand, washed with distilled water and dried in air at ambient temperature [yield: ca. 75% based on $Zn(NO_3)_2$]. $C_{18}H_{17}N_2O_{10.5}SZn_2$ (592.14): calcd. C 36.51, H 2.89, N 4.73; found C 36.30, H 2.75, N 4.80. IR (KBr): $\tilde{\nu}$ = 3416 m, 3269 m, 3019 m, 3022 m, 1610 vs, 1560 vs, 1498 m, 1441 s, 1372 s, 1255 s, 1228 m, 1205 m, 1171 m, 1104 m, 1077 m, 1038 s, 1016 w, 912 w, 876 w, 822 m, 772 m, 731 m, 678 w, 643 m, 625 m, 593 w, 548 w, 453 w cm^{-1}.

Synthesis of MCCP-5: The synthesis of MCCP-5 was similar to the above description for MCCP-4 except that zinc nitrate hexahydrate was replaced by cadmium nitrate tetrahydrate. Yield: ca. 60% based on $Cd(NO_3)_2$. $C_{56}H_{46}Cd_4N_8O_{19}S_2$ (1648.73): calcd. C 40.79, H 2.81, N 6.80; found C 40.40, H 2.90, N 6.66. IR (KBr): $\tilde{\nu}$ = 3569 w, 3367 w, 3104 w, 3073 w, 3042 w, 3017 w, 1600 s, 1560 s, 1534 s, 1492 m, 1430 m, 1415 m, 1367 s, 1223 m, 1202 m, 1166 m, 1101 m, 1067 m, 1035 s, 996 m, 934 w, 877 w, 859 w, 821 m, 775 s, 728 s, 676 m, 619 vs, 576 m, 516 w, 464 m, 441 m cm^{-1}.

Synthesis of MCCP-6: An aqueous solution (5 mL) of H_2nip (0.106 g, 0.50 mmol) was adjusted to pH = 7 with 1 M NaOH, and transferred into a Parr Teflon-lined stainless steel vessel (23 mL) containing $Cd(NO_3)_2{\cdot}4H_2O$ (0.154 g, 0.50 mmol) and 4,4′-bpy (0.078 g, 0.50 mmol). To the resultant mixture was added an additional 3 mL of water and the vessel was then sealed and heated to 140 °C for 3 d, followed by cooling at 5 °C/h to room temperature. Colorless block-like crystals were collected by hand, washed with distilled water, and dried in air at ambient temperature [yield: ca. 40% based on $Cd(NO_3)_2$]. $C_{62}H_{54}Cd_6N_{10}O_{35}$ (2173.55): calcd. C 34.26, H 2.50, N 6.44; found C 34.10, H 2.55, N 6.15. IR (KBr): $\tilde{\nu}$ = 3410 m, 3094 m, 2914 m, 1610 vs, 1566 s, 1529 m, 1455 m, 1418 m, 1365 vs, 1219 w, 1076 w, 1009 w, 927 w, 809 m, 731 s, 630 m cm^{-1}.

Crystallographic Analyses: Diffraction data were collected with an Enraf Nonius CAD-4 diffractometer for MCCP-4 and with a Bruker APEX CCD diffractometer for MCCP-5 and MCCP-6 with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The three structures were solved by direct methods and refined anisotropically by full-matrix least squares based on F^2 using the SHELXTL crystallographic software package.[22] Non-hydrogen atoms in all structures were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were calculated and included as riding atoms. In the final difference Fourier map of MCCP-6 was a peak larger than 1 e·Å^{-3}. The unit cell, however, contains no residual Solvent Accessible Area as calculated by PLATON.[23] Crystal parameters and details of the data collection and refinement for the structures of MCCP-4, -5 and -6 are listed in Table 4. CCDC-201032 (MCCP-4), -201033 (MCCP-5) and -202206 (MCCP-6) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was granted financial support from the Innovation Foundation for Young Scientific Talents of Fujian Province (No. 2002J004), the NNSF of China (No. 20023001), the Department of Science and Technology of China (No. 2002CCA01600) and the Research Program of Xiamen University (No. Y07015).

[1] [1a] J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982. [1b] R. Kitaura, S. Kitagawa, Y. Kubota, T. C. Kobayashi, K. Kindo, Y. Mita, A. Matsuo, M. Kobayashi, H.-C. Chang, T. C. Ozawa, M. Suzuki, M. Sakata, M. Takata, *Science* **2002**, *298*, 2358. [1c] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469. [1d] G. J. Halder, C. J. Kepert, B. Mouba-

raki, K. S. Murray, J. D. Cashion, *Science* **2002**, *298*, 1762. [1e] P. Ayyappan, O. R. Evans, Y. Cui, K. A. Wheeler, W. B. Lin, *Inorg. Chem.* **2002**, *41*, 4978.

[2] [2a] S. R. Batten, R. Robson, *Angew. Chem. Int. Ed.* **1998**, *37*, 1460. [2b] O. M. Yaghi, H. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **1998**, *31*, 474. [2c] O. R. Evans, W. B. Lin, *Acc. Chem. Res.* **2002**, *35*, 511. [2d] G. K. M. Shimizu, G. D. Enright, C. I. Ratcliffe, J. A. Ripmeester, *Chem. Commun.* **1999**, 461. [2e] M. Kondo, T. Toshitomi, K. Seki, H. Matsuzaka, S. Kitagawa, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1725.

[3] [3a] L. A. Gerrard, P. T. Wood, *Chem. Commun.* **2000**, 2107. [3b] M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319. [3c] M. Kondo, M. Miyazawa, Y. Irie, R. Shinagawa, T. Horiba, A. Nakamura, T. Naito, K. Maeda, S. Utsuno, F. Uchida, *Chem. Commun.* **2002**, 2156.

[4] [4a] D. T. Vodak, M. E. Braun, J. Kim, M. Eddaoudi, O. M. Yaghi, *Chem. Commun.* **2001**, 2534. [4b] N. L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe, O. M. Yaghi, *Angew. Chem. Int. Ed.* **2002**, *41*, 284.

[5] [5a] S. O. H. Gutschke, D. J. Price, A. K. Powell, P. T. Wood, *Eur. J. Inorg. Chem.* **2001**, 2739. [5b] S. O. H. Gutschke, M. Molinier, A. K. Powell, P. T. Wood, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 991.

[6] [6a] J. Tao, M.-L. Tong, J.-X. Shi, X.-M. Chen, S. W. Ng, *Chem. Commun.* **2000**, 2043. [6b] J. Tao, J.-X. Shi, M.-L. Tong, X.-X. Zhang, X.-M. Chen, *Inorg. Chem.* **2001**, *40*, 6328.

[7] [7a] S. A. Dalrymple, M. Parvez, G. K. H. Shimizu, *Inorg. Chem.* **2002**, *41*, 6986. [7b] S. A. Dalrymple, G. K. H. Shimizu, *Chem. Commun.* **2002**, 2224. [7c] C.-H. Chen, J.-W. Cai, C.-Z. Liao, X.-L. Feng, X.-M. Chen, S. W. Ng, *Inorg. Chem.* **2002**, *41*, 4967, and references cited therein.

[8] [8a] B. Szczęsna, Z. Urbańczyk-Lipkowska, *New J. Chem.* **2002**, *26*, 243. [8b] J. M. A. Robinson, D. Philp, K. D. M. Harris, B. M. Kariuki, *New J. Chem.* **2000**, *24*, 799. [8c] J. Tao, X. Yin, S.-Y. Yang, R.-B. Huang, L.-S. Zheng, *Main Group Metal Chem.* **2002**, *25*, 707. [8d] X. Yin, J. Tao, R.-B. Huang, L.-S. Zheng, *Main Group Metal Chem.* **2002**, *25*, 691. [8e] J. Tao, X. Yin, R.-B. Huang, L.-S. Zheng, S. W. Ng, *Acta Crystallogr., Sect. E* **2003**, *59*, 473.

[9] A. D. Kulynych, G. K. H. Shimizu, *Cryst. Eng. Comm.* **2002**, *4*, 102.

[10] D.-F. Sun, R. Cao, Y.-Q. Sun, X. Li, W.-H. Bi, M.-C. Hong, Y.-J. Zhao, *Eur. J. Inorg. Chem.* **2002**, 94.

[11] [11a] H. Abourahma, B. Moulton, V. Kravtsov, M. J. Zaworotko, *J. Am. Chem. Soc.* **2002**, *124*, 9990. As this manuscript was being revised, two Zn-nip and two Cd-nip coordination polymers were reported: [11b] J. Tao, X. Yin, Y.-B. Jiang, L.-F. Yang, R.-B. Huang, L.-S. Zheng, *Eur. J. Inorg. Chem.* **2003**, 2678. [11c] J. Luo, M. Hong, R. Wang, R. Cao, L. Han, Z. Lin, *Eur. J. Inorg. Chem.* **2003**, 2705.

[12] [12a] G. Socrates, *Infrared Characteristic Group Frequencies*, John Wiley & Sons, Stonebridge Press, Bristol, **1980**. [12b] Z. Wang, M. Ströbele, K.-L. Zhang, H. J. Meyer, X.-Z. You, Z. Yu, *Inorg. Chem. Commun.* **2002**, *5*, 230. [12c] J.-W. Cai, C.-H. Chen, C.-Z. Liao, J.-H. Yao, Y.-P. Hu, X. M. Chen, *J. Chem. Soc., Dalton Trans.* **2001**, 1137.

[13] [13a] D. H. Williams, I. Fleming, *Spectroscopic Methods in Organic Chemistry*, 4th ed., John Wiley & Sons, New York, **1989**. [13b] V. T. Yilmez, T. K. Yazicilar, O. Andac, H. Kutuk, Y. Bekdemir, W. T. A. Harrison, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1908.

[14] [14a] J. Tao, M.-L. Tong, X. M. Chen, *J. Chem. Soc., Dalton Trans.* **2000**, 3669. [14b] G. Guilera, J. W. Steed, *Chem. Commun.* **1999**, 1563.

[15] M. Alexiou, C. Dendrinou-Samara, C. P. Raptopoulou, A. Terzis, D. P. Kessissoglou, *Inorg. Chem.* **2002**, *41*, 4732.

[16] A. Onoda, Y. Yamada, M. Doi, T. Okamura, N. Ueyama, *Inorg. Chem.* **2001**, *40*, 516.

[17] [17a] J. Tao, Y.-L. Fu, S.-L. Zheng, X.-M. Chen, S. W. Ng, *Main Group Metal Chem.* **2001**, *24*, 289. [17b] K. V. Domasevitch, G. D. Enright, B. Moulton, M. J. Zaworotko, *J. Solid State Chem.* **2000**, *152*, 280.

[18] [18a] W. Lin, Z. Wang, L. Ma, *J. Am. Chem. Soc.* **1999**, *121*, 11249. [18b] X. Xue, X.-S. Wang, L.-Z. Wang, R.-G. Xiong, B. F. Abrahams, X.-Z. You, Z.-L. Xue, C.-C. Che, *Inorg. Chem.* **2002**, *41*, 6544. [18c] T. Konno, Y. Kageyama, K. I. Okamoto, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1957.

[19] M. Weidenbruch, M. Herrndorf, A. Schafer, S. Pohl, W. Saak, *J. Organomet. Chem.* **1989**, *361*, 139.

[20] D. T. Vodak, M. E. Braun, J. Kim, M. Eddaoudi, O. M. Yaghi, *Chem. Commun.* **2001**, 2534.

[21] [21a] A. Meijerink, G. Blasse, M. Glasbeek, *J. Phys., Condens. Matter* **1990**, *2*, 6303. [21b] R. Bertoncello, M. Bettinelli, M. Cassrin, A. Gulino, E. Tondello, A. Vittadini, *Inorg. Chem.* **1992**, *31*, 1558.

[22] G. M. Sheldrick, *SHELX97*, University of Göttingen, Göttingen, Germany, **1997**.

[23] A. L. Spek, *PLATON*, University of Glasgow, Glasgow, UK, **1998**.

Received June 9, 2003
Early View Article
Published Online October 23, 2003

