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New Examples of Metal Coordination Architectures of 4,4′-Sulfonyldibenzoic Acid: Syntheses, Crystal Structure and Luminescence

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Seven metal–organic coordination polymers, namely $[Cd(sfdb)(phen)_2]_n \cdot 2nH_2O$ (**1**), $[Cd(sfdb)(bpy)_2]_n \cdot nH_2O$ (**2**), $[Cu(sfdb)(phen)(H_2O)]_n \cdot 0.5nH_2O$ (**3**), $[Zn(sfdb)(bpy)(H_2O)]_n \cdot 0.5nCH_3OH$ (**4**), $[Cd(sfdb)(quin)]_n$ (**5**), $[Cd_3(sfdb)_2(Hsfdb)_2(phen)_2]_n$ (**6**), and $[Cd(sfdb)(bpy)]_n$ (**7**) [H_2sfdb = 4,4′-sulfonyldibenzoic acid, phen = 1,10-phenanthroline, quin = 2,2′-biquinoline, bpy = 2,2′-bipyridine] have been synthesized according to the principles of crystal engineering and structurally characterized by elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction analyses. Compounds **1**–**3** form 1D zigzag chains. Two phen ligands chelate to one cadmium atom in **1**, which is rare in similar polymers, while two 2,2′-bpy ligands coordinate one cadmium atom in **2**. The zigzag chains in **3** propagate in two different directions (rotated by 75°) that are assembled by supramolecular forces into an intriguing three-dimensional network. Complexes **4** and **5** form square-wave-like 1D chains, although the results indicate a transformation of 2,2′-bpy into quin during the course of the hydrothermal synthesis of compound **5**. Compound **6** is a 1D grid-chain based on a linear trinuclear unit, and compound **7** shows a 1D double chain containing 28-membered rings with $sfdb^{2-}$ ligands as bridges. Weak hydrogen bonding and intra- and/or intermolecular π···π stacking contacts in compounds **3**–**7** link the discrete 1D chains into high-dimensional supramolecular structures. The $sfdb^{2-}$ ligand displays multiple coordination modes in these seven complexes. Complexes **1**, **2**, and **4**–**7** show blue photoluminescence at room temperature.

Introduction

The design and synthesis of metal–organic compounds has been flourishing in recent years because of their intriguing architectures[1] and potential applications in gas storage, ion exchange, catalysis, and so on.[2] Although a variety of metal coordination frameworks with beautiful topologies and interesting properties have been synthesized to date, the rational control of the construction of polymeric networks remains a great challenge in crystal engineering. One of the most efficient routes to coordination polymers is to employ a multifunctional ligand to link metal ions into an infinite framework. Flexible di- and polycarboxylic acids are good candidates for the construction of novel metal–organic compounds as the carboxyl groups can form C–O–M–O four-membered rings with central metal ions, thereby improving the stability of transition metal–organic frameworks (MOFs). Furthermore, di- and polycarboxylic acids have two or more carboxyl groups that can be completely or partially deprotonated, which results in a rich variety of coordination modes and many interesting structures with higher dimensions. Furthermore, these ligands can act as both hydrogen-bond acceptors and hydrogen-bond donors to generate supramolecular topologies. In light of the above, more and more attention has been paid to the use of flexible di- and polycarboxylate ligands,[3] whereas studies involving semi-rigid V-shaped dicarboxylate ligands are relatively scarce.[4] 4,4′-Sulfonyldibenzoic acid (H_2sfdb) is a typical example of a semi-rigid V-shaped dicarboxylate ligand, and to the best of our knowledge there are only a few reports concerning its coordination compounds.[5]

4,4′-Sulfonyldibenzoic acid is a very versatile ligand for the construction of novel metal–organic compounds as it has six potential donor atoms that allow the formation of variable structures with different topologies and dimensions constructed in different directions. A particular feature of the $sfdb^{2-}$ ligand is the number of coordination modes it can display (Scheme 1). However, the coordination chemistry and structural properties of metal polymers containing $sfdb^{2-}$ ligands have seldom been documented to date.[5] With the aim of understanding the coordination chemistry of $sfdb^{2-}$ and studying its influence on the framework structures of its complexes, we have recently engaged in research

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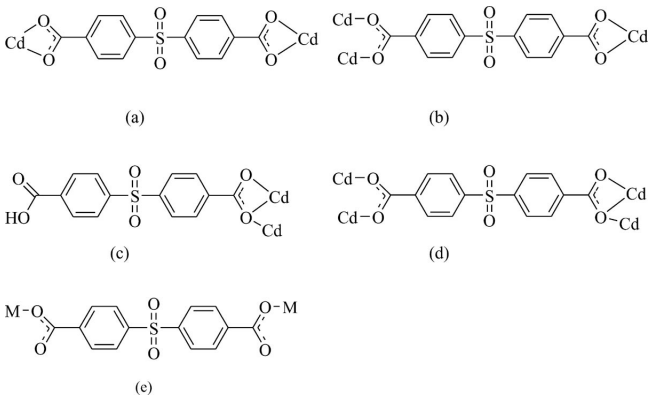
of this kind with coordination polymers. The introduction of N-containing auxiliary ligands, such as phen, 2,2′-bipyridine, etc., into the M/sfdb system may lead to new structural evolution and allow fine-tuning of the structural motif of these metal–organic compounds. We now report the synthesis, structures, and luminescent properties of seven novel complexes of 4,4′-sulfonyldibenzoic acid, namely $[Cd(sfdb)(phen)_2]_n \cdot 2nH_2O$ (**1**), $[Cd(sfdb)(bpy)_2]_n \cdot nH_2O$ (**2**), $[Cu(sfdb)(phen)(H_2O)]_n \cdot 0.5nH_2O$ (**3**), $[Zn(sfdb)(bpy)(H_2O)]_n \cdot 0.5nCH_3OH$ (**4**), $[Cd(sfdb)(quin)]_n$ (**5**), $[Cd_3(sfdb)_2(Hsfdb)_2(phen)_2]_n$ (**6**), and $[Cd(sfdb)(bpy)]_n$ (**7**).



Scheme 1. Coordination modes of the $sfdb^{2-}$ ligand.

Results and Discussion

Description of the Structures

[Cd(sfdb)(phen)$_2$]$_n$·2nH$_2$O (1)

Single-crystal X-ray diffraction analysis revealed that compound **1** is a 1D zigzag coordination polymer. The asymmetric unit of **1** contains one cadmium atom, one $sfdb^{2-}$ ligand, two phen ligands, and two lattice water molecules. As illustrated in Figure 1a, each Cd^{II} atom in **1** is coordinated by four nitrogen atoms [Cd1–N1 2.379(2), Cd1–N2 2.522(3), Cd1–N3 2.419(2), Cd1–N4 2.391(2) Å] from two chelating phen ligands and four oxygen atoms from two chelating carboxylate groups of two $sfdb^{2-}$ ligands [Cd1–O1 2.316(3), Cd1–O2 2.729(3), Cd1–O5A 2.494(3), Cd1–O6A 2.604(3) Å]. However, the Cd1–O2 distance suggests a nonnegligible interaction. Thus, the Cd^{II} atom can be regarded as a monocapped pentagonal bipyramid. Eight-coordinate Cd^{II} is very rare[6] and the structure of **1** is different from previously reported eight-coordinate complexes,[6a] which generally have a distorted tetragonal antiprism geometry.

Each $sfdb^{2-}$ ligand bridges two cadmium atoms in a chelating/chelating bis(bidentate) coordination mode (Scheme 1a) to form a 1D infinite zigzag chain (Figure 1b) with a Cd···Cd distance of 13.977(3) Å. Interestingly, two phen ligands chelate to one cadmium atom in **1**, which is rare in similar coordination polymers.[7] Two adjacent phen

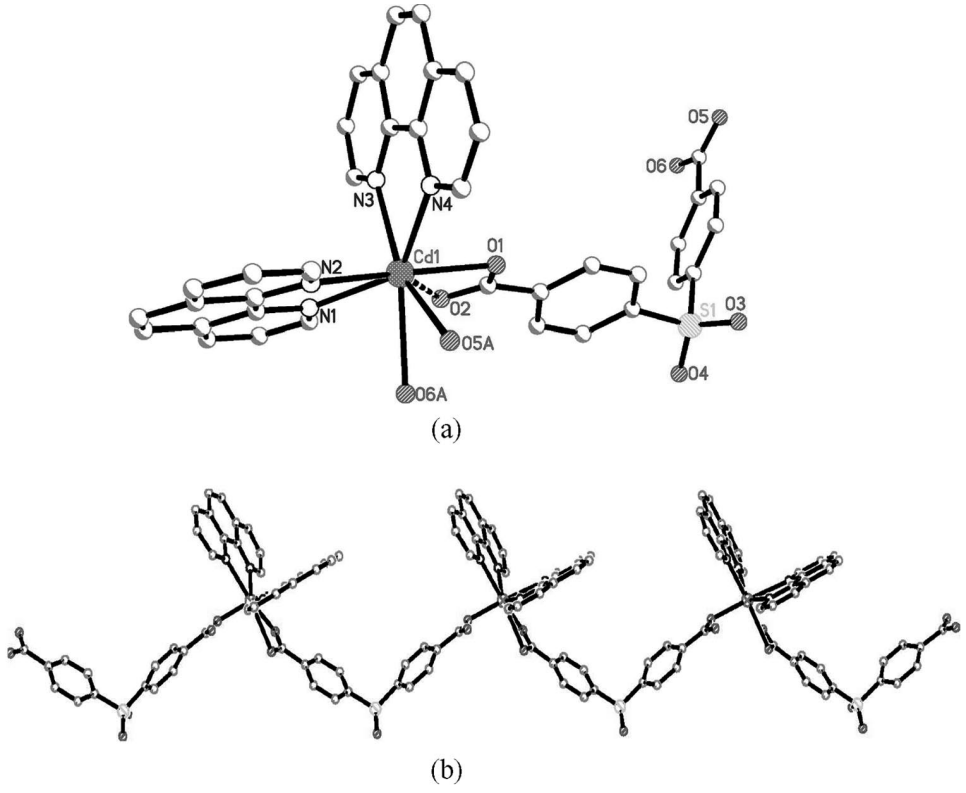


Figure 1. (a) Coordination environment of the Cd^{II} atom in **1**; (b) perspective view of the 1D zigzag chain in **1**. All hydrogen atoms have been omitted for clarity.

ligands are almost perpendicular to each other in **1** (the dihedral angle is 86.35°). To the best of our knowledge, only a few examples have been reported to date in which two phen ligands chelate to one cadmium atom in coordination polymers.[7]

[Cd(sfdb)(bpy)$_2$]$_n$·nH$_2$O (2)

To further examine the influence of the auxiliary ligands on the structure of **1**, we used the smaller aromatic chelating ligand 2,2′-bpy instead of phen. This ligand forms a similar 1D zigzag polymeric coordination chain. As shown in Figure 2a, the asymmetric unit of **2** contains one Cd^{II} atom, one $sfdb^{2-}$ ligand, two 2,2′-bpy ligands, and one lattice water molecule. Each Cd^{II} atom is six-coordinated by four nitrogen atoms [Cd1–N1 2.411(2), Cd1–N2 2.419(2), Cd1–N3 2.403(2), Cd1–N4 2.440(2) Å] from two chelating 2,2′-bpy ligands and two oxygen atoms [Cd1–O1 2.299(2), Cd1–O6A 2.272(2) Å] from two monodentate carboxylate groups of two $sfdb^{2-}$ ligands. The coordination geometry of the Cd^{II} center can therefore be described as a distorted octahedron. The Cd^{II} atoms are linked into a zigzag chain with a Cd···Cd distance of 13.089 Å, which is shorter than that in **1**. There are some distinct differences between the crystal structures of **1** and **2**, although both of them exhibit similar 1D chain structures. Thus, the $sfdb^{2-}$ ligand in **2** shows a different coordination mode (Scheme 1e) from that of **1** and the environment of the Cd^{II} atom in **2** is modified by incorporation of a bridging bis(monodentate) $sfdb^{2-}$ ligand instead of a chelating/chelating bis(bidentate) ligand in **1**. Similar to **1**, the bpy ligands in **2** are coordinated to the Cd^{II} atom in a chelating fashion and the pyridine rings are on the same side of the one-dimensional chain (Figure 2b); two adjacent bpy ligands are almost perpendicular to each other in **2** (the dihedral angle is 80.58°). The H_2sfdb ligands in **2** are completely deprotonated and are strongly bent at the sulfone sulfur site [C–S–C 101.74(14), O–S–O 120.2(2)°].

[Cu(sfdb)(phen)(H$_2$O)]$_n$·0.5nH$_2$O (3)

The asymmetric unit of **3** contains one Cu atom, one $sfdb^{2-}$ ligand, one phen, and one coordinated and half a lattice water molecule. Each Cu^{II} atom is five-coordinated by two nitrogen atoms [Cu1–N1 2.042(2), Cu1–N2 2.029(2) Å] from one chelating phen ligand, two oxygen atoms (O1, O5A) from two carboxylate groups of two $sfdb^{2-}$ ligands, and one oxygen atom (O7) from one coordinated water molecule (Figure 3a). The Cu^{II} atom exhibits an approximately square-pyramidal environment with the atoms N1, N2, O1, and O5A in the equatorial plane and a water molecule in the axial position. The Cu–O7(water) distance of 2.340(2) Å is significantly longer than the average Cu–O(carboxyl) distances of 1.932(2) Å. As shown in Figure 3b, each Cu^{II} atom is joined to another one by an $sfdb^{2-}$ ligand in a bis(monodentate) fashion (Scheme 1e) to generate a 1D zigzag chain. The angle between the phen nitrogen atoms and the metal atom is far from the ideal value of 90° [N1–Cu–N2 80.98(9)°] because of the geometrical constraints imposed by the phen ligand.

The structure of **3** consists of 1D polymeric zigzag chains that form a 2D undulating network (Figure 3c) due to hydrogen-bonding interactions between the lattice water mole-

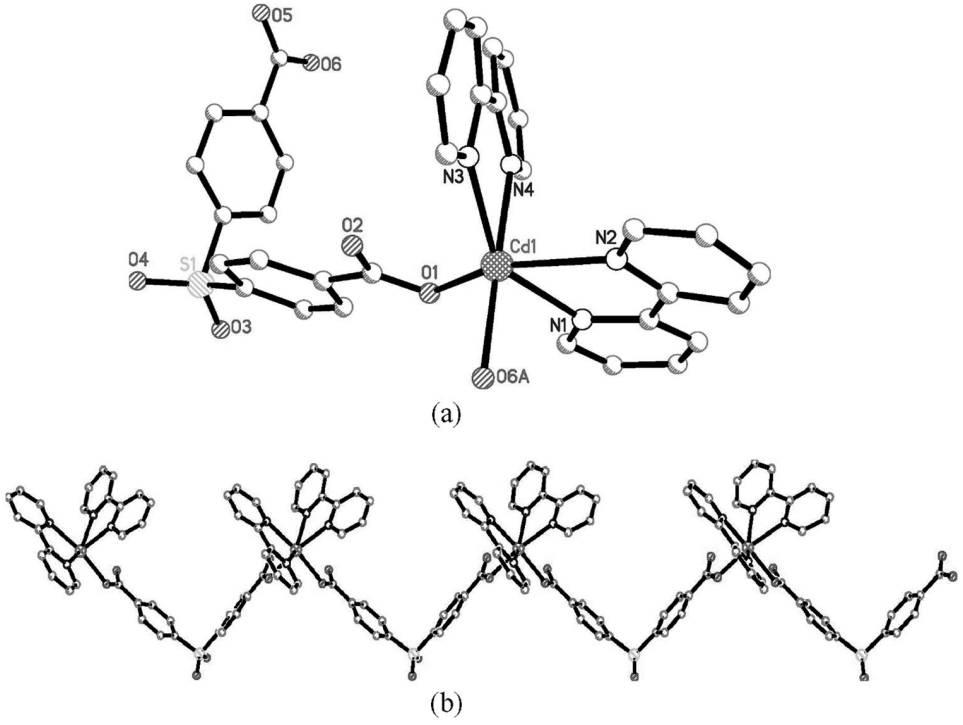


Figure 2. (a) Coordination environment of the Cd^{II} atom in **2**; (b) perspective view of the 1D zigzag chain in **1**. All H atoms have been omitted for clarity.

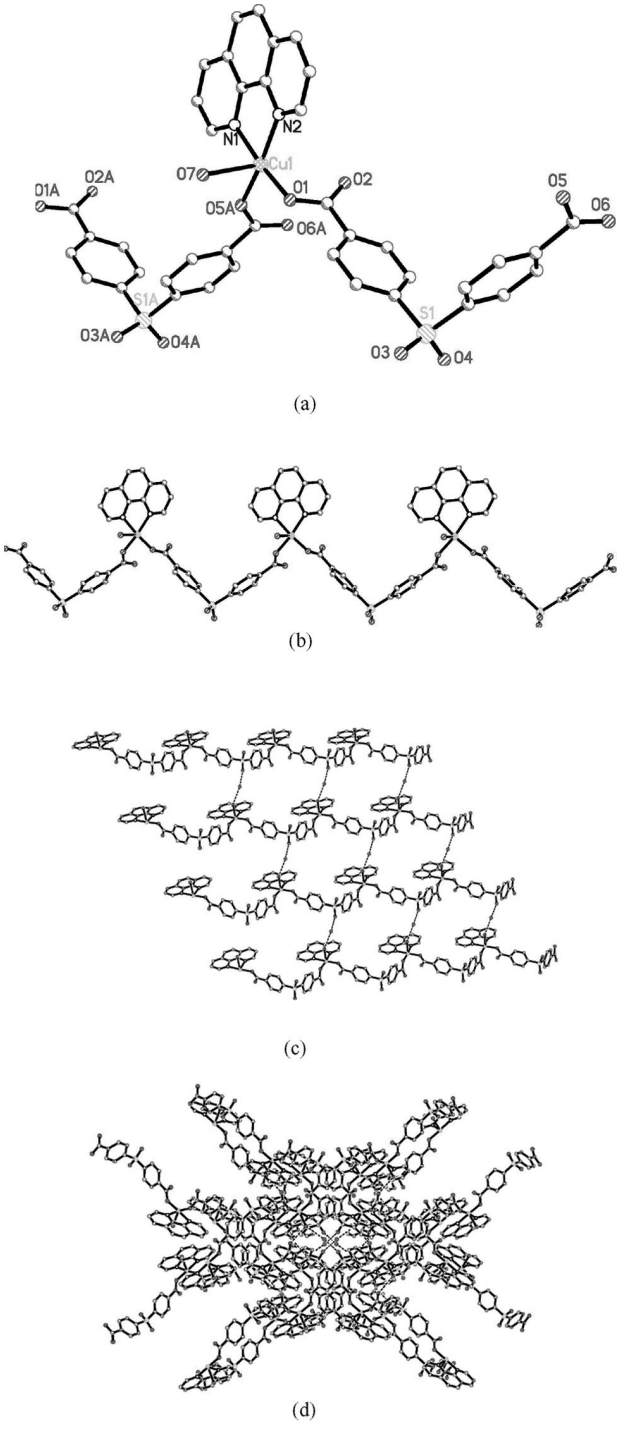


Figure 3. (a) Coordination environment of the Cu^{II} ion in **3**; (b) perspective view of the 1D zigzag chain in **3**; (c) perspective view of the 2D undulating network in **3**; d) polymeric chains arranged in different propagation directions. All H atoms have been omitted for clarity.

cule and the oxygen atoms of the coordinated water molecule and sulfone (O8–H8A···O7 2.724, O8–H8B···O4 2.780 Å). Adjacent 2D networks are ultimately extended into a 3D supramolecular structure through interlayer hydrogen-bonding interactions [O7–H7A···O3 2.938(3) Å and 168(4)°; O7–H7B···O6 2.789(3) Å and 176(4)°].

The most peculiar structural feature of this compound is the unique supramolecular organization of these polymeric chains, which extend in two different directions (Figure 3d). These polymeric chains are arranged on parallel levels in different propagating directions, rotated by 75° on passing from one level to the successive one, which results in an ABAB sequence. As far as we know, the packing of 1D polymers usually occurs with a parallel orientation of all chains, although, less commonly, they can span two different directions in other alternate layers.[8]

[Zn(sfdb)(bpy)(H$_2$O)]$_n$· 0.5nCH$_3$OH (4)

The Zn^{II} atom in the structure of **4** is five-coordinate with a distorted square-pyramidal coordination environment (Figure 4a) made up of one Zn^{II} atom, one $sfdb^{2-}$ ligand, one 2,2′-bpy ligand, one coordinated water molecule, and half a methanol molecule. Each Zn^{II} atom is coordinated by two nitrogen atoms [Zn1–N1 2.1119(9), Zn1–N2 2.1456(9) Å] from one chelating 2,2′-bpy ligand and two oxygen atoms from two monodentate carboxylate groups of two $sfdb^{2-}$ ligands in the equatorial plane, with another oxygen atom (O7) from one coordinated water molecule in the axial position. The Zn–O distances fall in the range 1.9764(7)–2.0368(8) Å and are similar to those found in other zinc carboxylate coordination polymers.[9] The axial Zn–O distance is slightly longer than those of the equatorial Zn–O bonds. As shown in Figure 4b, the Zn^{II} atoms are joined by an $sfdb^{2-}$ ligand in a bis(monodentate) fashion (Scheme 1e), similar to that in **3**, to generate a 1D square-wave-like chain. The dihedral angle between the two phenyl rings of the $sfdb^{2-}$ ligand is 87.9°.

The 1D chains are linked into a 2D layer through a hydrogen-bonding interaction [O7–H7B···O2 2.706(1) Å and 161.9(9)°] between the carboxylate oxygen atoms and coordinated water molecules along the *a* axis (Figure 4c). Interestingly, these layers are further packed into a 3D structure (Figure 4d) by π···π stacking interactions, with centroid–centroid distances of 3.564 and 3.714 Å and plane–plane distances of 3.361 and 3.375 Å between the pyridine rings.

[Cd(sfdb)(quin)]$_n$ (5)

Compound **5** crystallizes in the monoclinic space group $P2_1/n$, and the asymmetric unit consists of one Cd^{II} atom, one $sfdb^{2-}$ anion, and one quin ligand, as shown in Figure 5a. The quin ligand is formed in situ from 2,2′-bpy during the hydrothermal synthesis. Cd1 has a distorted octahedral coordination environment containing two nitrogen atoms from one chelating quin ligand and four oxygen atoms from two chelating carboxylate groups of two $sfdb^{2-}$ ligands [Cd1–O1 2.446(4), Cd1–O2 2.246(4), Cd1–O5A 2.379(4), Cd1–O6A 2.291(3) Å]. These distances are similar to those reported for [Cd(bdc)(phen)·dmf] (H_2bdc = benzene-1,4-dicarboxylic acid).[7a] As shown in Figure 5b, the Cd^{II} centers are joined by two $sfdb^{2-}$ ligands to generate a square-wave-like 1D chain. One $sfdb^{2-}$ ligand assumes a chelating/chelating bis(bidentate) bonding mode

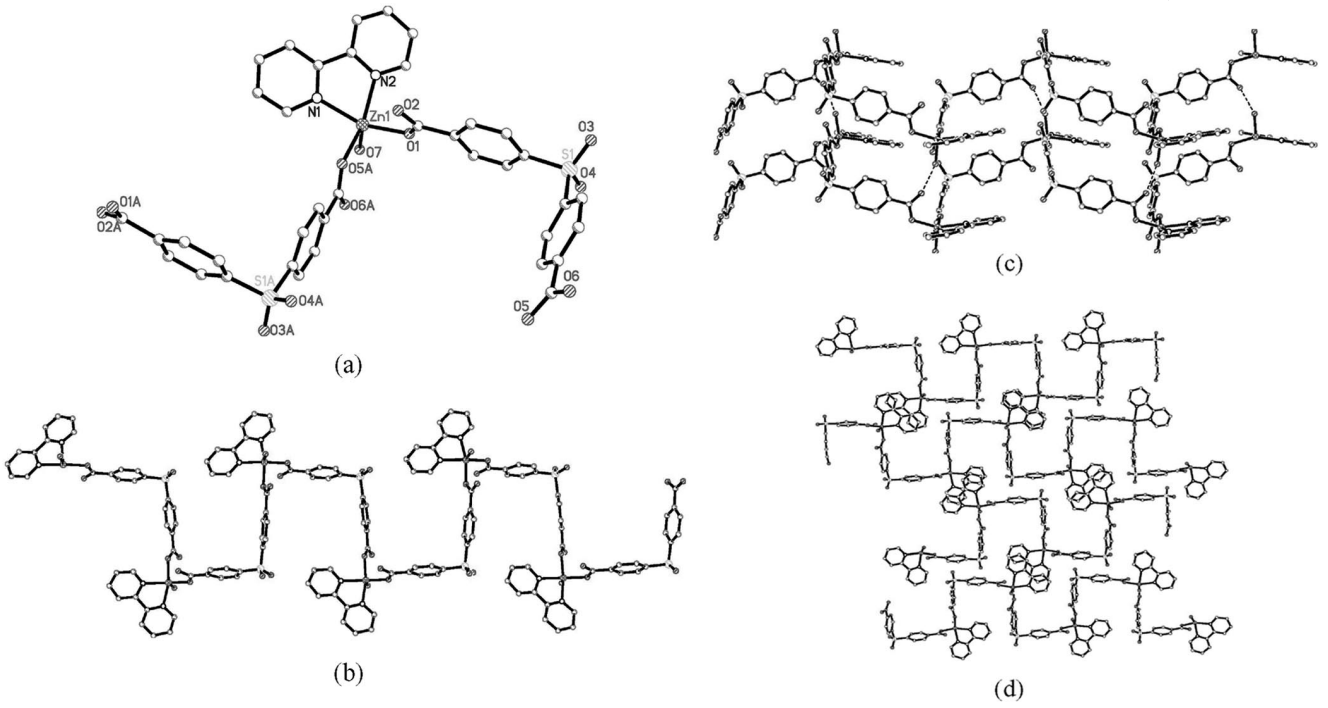


Figure 4. (a) Coordination environment of the Zn^{II} atom in **4**; (b) a perspective view of the 1D chain in **4**; (c) perspective view of the 2D layer formed by hydrogen-bonding interactions; (d) 3D structure formed by π···π stacking interactions. H atoms have been omitted for clarity.

(Scheme 1a), similar to that in **1**, to connect two Cd^{II} atoms with a Cd···Cd distance of 14.669 Å. The dihedral angle between two phenyl rings of the $sfdb^{2-}$ ligand is 82.47°.

Although 2,2′-bpy was used as the original organic reagent in the preparation of this compound, it was rather unexpectedly not found in the final product, which indicates a transformation of 2,2′-bpy into quin during the course of the hydrothermal treatment. This transformation of 2,2′-bpy into quin only happens during the synthesis of compound **5**, where the hydrothermal synthesis conditions and metal/ligand ratio are different from those used to synthesize compounds **2** and **7**, although they have the same reagents. Additionally, C–H···O hydrogen bonds are observed between C22–H22 and C25–H25 of the quin molecule and the other coordinated carboxylate oxygen atoms (O1) of the adjacent chains. The quin molecules also participate in C–H···π interactions with a contact distance of 2.860 Å. All these interactions lead to the formation of a 3D supramolecular structure (Figure 5c).

[$Cd_3(sfdb)_2(Hsfdb)_2(phen)_2$]$_n$ (6)

The X-ray crystallographic analysis revealed that **6** contains linear trinuclear cadmium units that are linked by two $sfdb^{2-}$ bridges into a 1D grid chain. The structure contains two crystallographically nonequivalent Cd^{II} atoms. As shown in Figure 6a, Cd1 is surrounded by two nitrogen atoms [Cd1–N1 2.364(3), Cd1–N2 2.299(3) Å] from a chelating phen ligand, two oxygen atoms (O1, O2) from one chelating carboxylate group of the $Hsfdb^-$ ligand, two oxygen atoms (O7, O8) from a chelating carboxylate group of the $sfdb^{2-}$ ligand, and one oxygen atom (O11A) from a bridging carboxylate group of another $sfdb^{2-}$ ligand. The Cd1–O distances fall in the range 2.270(2)–2.605(3) Å and are similar to those found in other cadmium carboxylate coordination polymers.[10] The coordination geometry of the Cd1 center can be described as a distorted pentagonal bipyramid with atoms O2, O7, O8, N1, and N2 in the equatorial plane and another two atoms (O1 and O11A) in the axial positions. Cd2 lies at a crystallographic inversion center and coordinates to six oxygen atoms from six carboxylate groups of four $sfdb^{2-}$ and two $Hsfdb^-$ ligands. Two oxygen atoms (O2, O2A) come from two chelating-bridging tridentate carboxylate groups of two $Hsfdb^-$ ligands, two oxygen atoms (O8, O8B) come from two chelating-bridging tridentate carboxylate groups of two $sfdb^{2-}$ ligands, and two oxygen atoms (O12A, O12B) come from bridging bidentate carboxylate groups of two $sfdb^{2-}$ ligands. The Cd2–O distances fall in the range 2.214(2)–2.284(2) Å and are very similar to each other. Likewise, the distances to the two oxygen atoms situated at the diagonals are equivalent.

An interesting feature of **6** is that it contains completely deprotonated $sfdb^{2-}$ and partially deprotonated $Hsfdb^-$ ligands, which show two different coordination modes. Thus, the completely deprotonated $sfdb^{2-}$ ligand acts as a bridging bidentate/chelating-bridging tridentate coordination ligand (Scheme 1d), while the partially deprotonated $Hsfdb^-$ ligand binds in a chelating-bridging tridentate coordination mode (Scheme 1c) and shows a significantly different coordination fashion to those ligands in compounds **1**–**5** and **7**. Each $sfdb^{2-}$ ligand links four cadmium atoms and each Cd1 atom is connected to two $sfdb^{2-}$ ligands and one $Hsfdb^-$ ligand, whereas each Cd2 atom is connected to four $sfdb^{2-}$

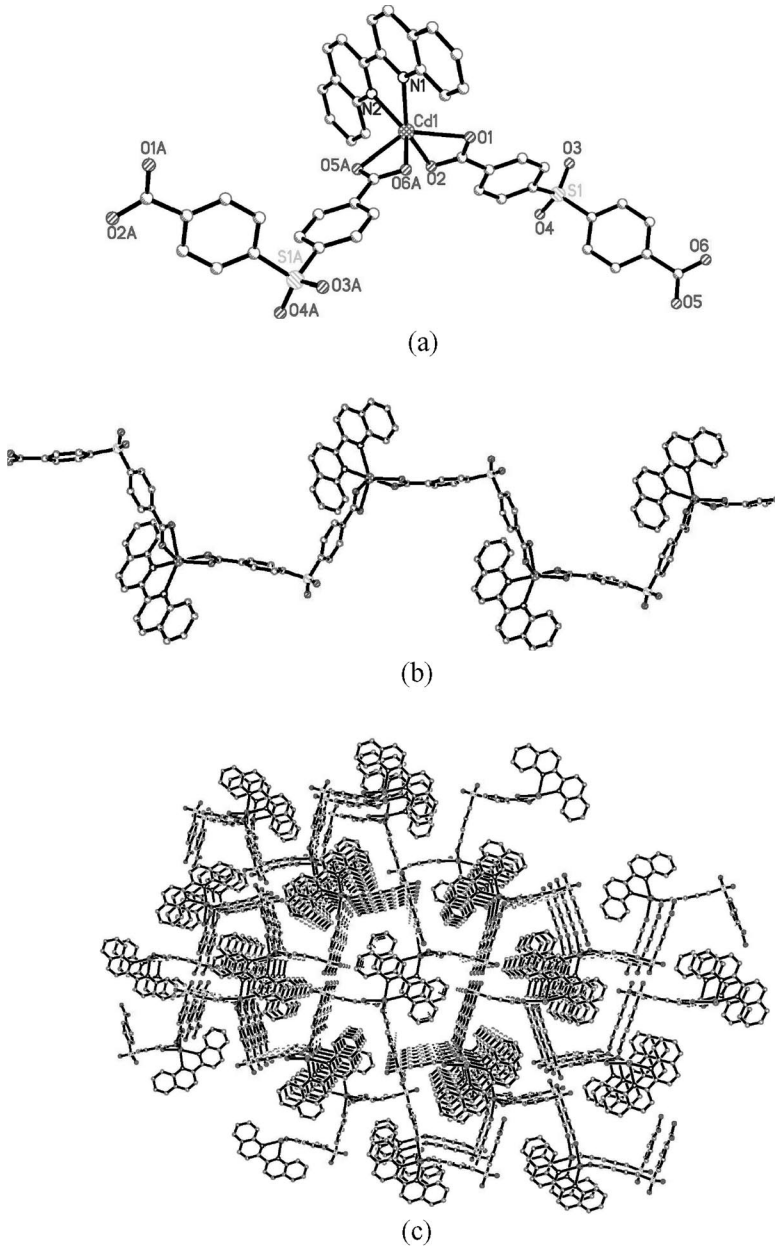


Figure 5. (a) Coordination environment of the Cd^{II} ion in **5**; (b) perspective view of the 1D chain in **5**; (c) view of the 3D supramolecular structure. All H atoms have been omitted for clarity.

ligands in a bridging bidentate/chelating-bridging tridentate coordination mode (Scheme 1d) and two $Hsfdb^-$ ligands with a chelating-bridging tridentate coordination mode (Scheme 1c).

Another interesting feature is that a novel trinuclear cadmium unit is found in **6**. Three cadmium atoms (Cd1, Cd2, and Cd1A) are located in a line with Cd1···Cd1A and Cd1···Cd2 distances of 7.000 and 3.499 Å, respectively. To the best of our knowledge, this situation is very rare and differs from the situation in other Cd carboxylate coordination polymers containing trinuclear cadmium units,[11] where the three Cd^{II} atoms are not in line (Cd1···Cd2···Cd1A 133.5°). Two trinuclear cadmium units are connected by four carboxylate groups of two $sfdb^{2-}$ ligands to form a novel $\{Cd_6O_8C_{20}S_2\}$ 36-membered ring containing a micropore with a size of around 13.7×9.53 Å^2 (based on the Cd2···Cd2 and S2···S2 distances). All the rings are further linked to form a one-dimensional grid chain (Figure 6b).

The most significant feature of **6** is that adjacent chains form a 2D rectangular grid framework along the *a* axis through hydrogen-bonding interactions between the uncoordinated carboxyl oxygen of the $Hsfdb^-$ ligands and the oxygen atom of another $Hsfdb^-$ ligand [O5–H5A···O6B 2.623(5) Å and 176.0°; Figure 6c]. More remarkably, the hydrogen bonds pass through the $\{Cd_6O_8C_{20}S_2\}$ 36-membered ring of the adjacent chain to form a 2D interpenetrated framework (Figure 6d). These 2D interpenetrated

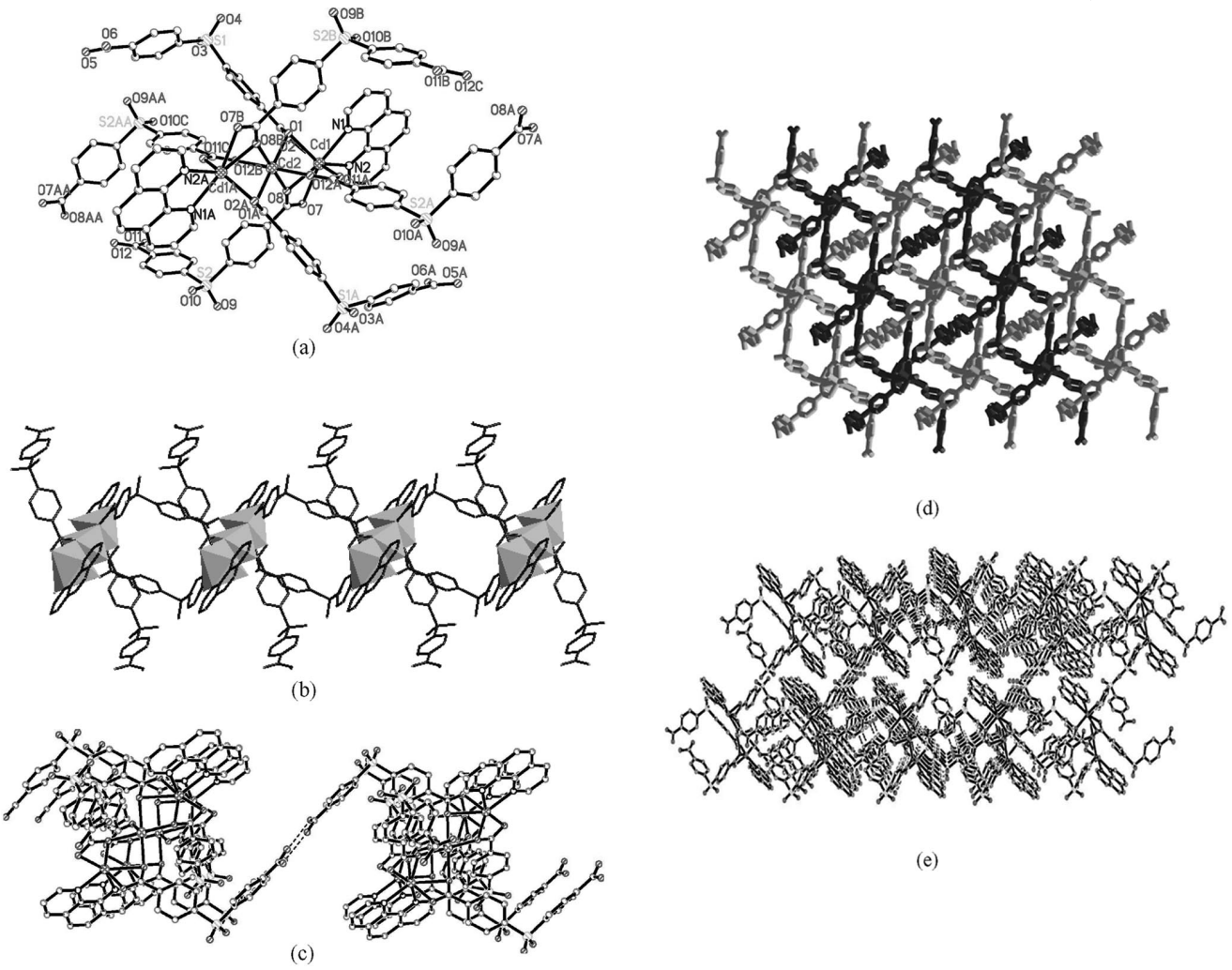


Figure 6. (a) Coordination environment of the Cd^{II} atom in **6**; (b) perspective view of the 1D chain in **6**; (c) perspective view of the 2D layer formed by hydrogen bonds; (d) perspective view of the interpenetrating 2D network formed by hydrogen bonds (phen ligands omitted for clarity); (e) 3D structure formed by C–H···O hydrogen bonds and weak C–H···π interactions viewed along the *b* axis. All H atoms have been omitted for clarity.

frameworks are found to pack on top of each other in a slipped geometry that is stabilized by C–H···O hydrogen bonds and weak C–H···π interactions with a distance of 3.333 Å to form a 3D architecture (Figure 6e).

[Cd(sfdb)(bpy)]$_n$ (7)

The crystal structure of **7** reveals that it is a one-dimensional double chain containing 28-membered rings with $sfdb^{2-}$ ligands as the bridges. The asymmetric unit of **7** contains one Cd^{II} atom, one $sfdb^{2-}$ ligand, and one bpy ligand. As shown in Figure 7a, the Cd^{II} atom is in a distorted octahedral geometry and is coordinated by two nitrogen atoms from one chelating 2,2′-bpy ligand and four carboxylate oxygen atoms from three $sfdb^{2-}$ ligands. The Cd–O and Cd–N bond lengths are similar to those in other Cd carboxylate coordination polymers.[12] Each pair of Cd^{II} atoms is bridged by six carboxylate oxygen atoms from two $sfdb^{2-}$ ligands to form a 28-membered ring. These dimeric Cd_2 units feature a 1D double chain interconnected by the carboxylate groups of $sfdb^{2-}$ ligands along the 101 direction (Figure 7b). The H_2sfdb ligands in **7** are completely deprotonated ($sfdb^{2-}$) and are bent at the sulfone sulfur site [C–S–C 105.25(14)°, O–S–O 119.2(2)°]; the dihedral angle between the two phenyl rings is 87.57°.

It is worth to note that the Cd^{II} center is connected to three $sfdb^{2-}$ ligands, while one $sfdb^{2-}$ ligand is connected to three Cd^{II} atoms in a bridging/chelating bis-bidentate coordination fashion (Scheme 1b), which is different from the situation in complexes **1**–**6**. To the best of our knowledge, only five examples of complexes containing an $sfdb^{2-}$ ligand, where each ligand binds to two metal atoms in bridging/bridging bis-bidentate and bis-monodentate modes, have been reported to date.[5] A similar bridging/chelating bis-bidentate coordination mode has never been described before for metal complexes containing an $sfdb^{2-}$ ligand.

The most significant feature of **7** is that adjacent chains are intercalated in a zipper fashion to generate a 2D undulating sheet through hydrogen bonds (C1–H1···O3 2.416 Å and 134.4°; C13–H13···O3 2.533 Å and 148.4°; C17–

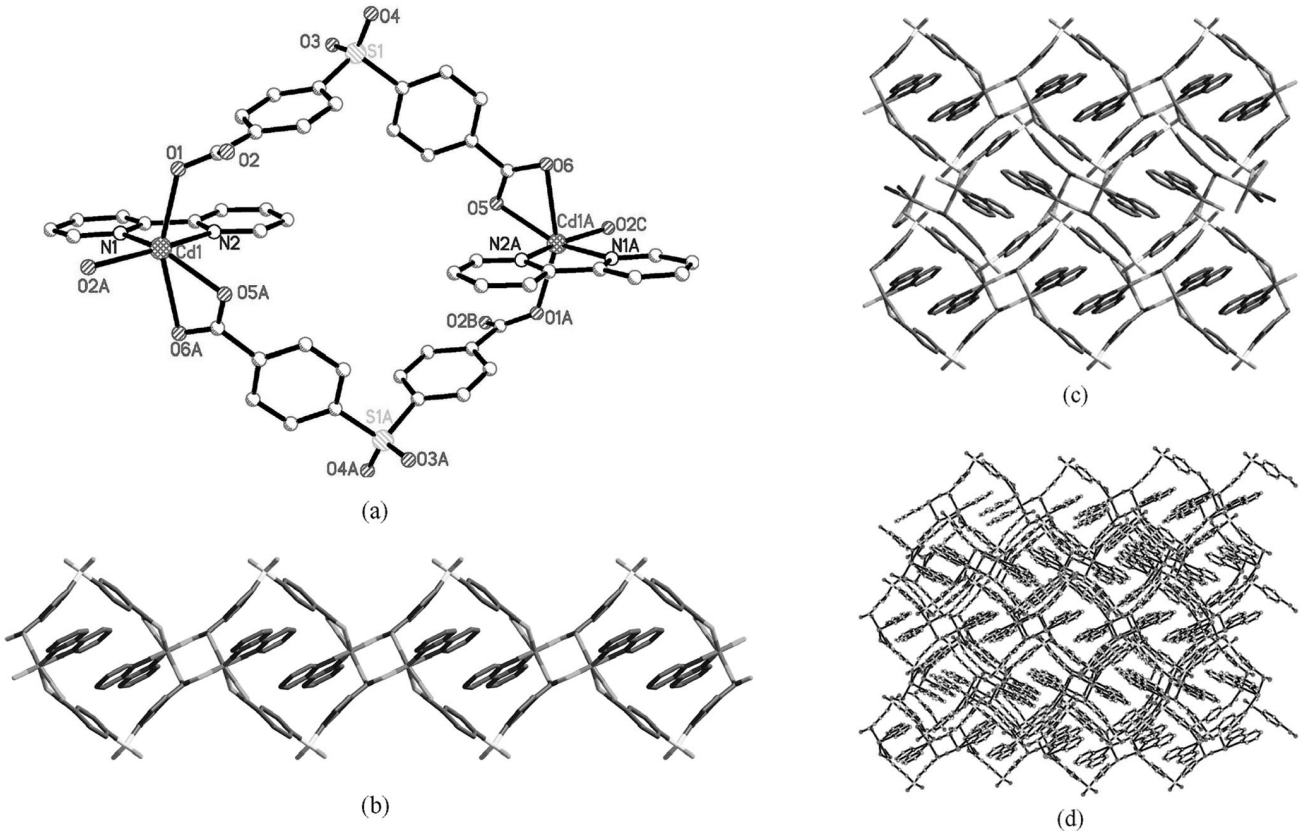


Figure 7. Coordination environment of the Cd^{II} atom in **7**; (b) perspective view of the 1D double chain in **7**; (c) 2D layer produced by hydrogen bonds viewed along the *a* axis; (d) perspective view of the 3D network viewed along the *a* axis. All H atoms have been omitted for clarity.

H17···O6 2.503 Å and 134.3°; C20–H20···O4 2.621 Å and 151.3°; C23–H23···O5 2.626 Å and 139.5°; C24–H24···O1 2.716 Å and 149.8°; C8–H8···π 2.770, 2.682 Å and 174.0, 144.6°; S1=O3···C1 3.318 Å and 114.9°) and π···π stacking interactions, with a centroid–centroid distance of 3.377 Å between the pyridine rings and the phenyl rings of the adjacent chain. This 2D undulating sheet has two types of pores with sizes of about 12.5×11.3 Å^2 (28-membered rings, based on the Cd1···Cd1A and S1···S1A distances) and 5.0×4.0 Å^2 (eight-membered rings, based on the O2···O2A and Cd1A···Cd1B distances; Figure 7c). The real volume of the cavity in each pore structure is further reduced due to significant offset stacking of adjacent metallamacrocycles. This 2D network is further packed into a 3D structure through C–H···π interactions (C4–H4···π 2.854 Å; Figure 7d).

Comparison of the Structures of Complexes 1–7

Seven new complexes have been obtained by self-assembly with the V-shaped ligand $sfdb^{2-}$, which shows five different coordination modes (Scheme 1). To the best of our knowledge, only five complexes containing an $sfdb^{2-}$ ligand, in which each ligand binds to two metal ions in bridging/bridging bis-bidentate and bis-monodentate coordination modes, have been reported to date,[5] and coordination modes such as those shown in Scheme 1a–d have never been described before in metal complexes containing an $sfdb^{2-}$ ligand.

Complexes **1**–**7** are readily synthesized under the same hydrothermal reaction conditions in the presence of different auxiliary ligands (phen and 2,2′-bpy). Interestingly, two complexes with different structures, different coordination modes, and different luminescence properties are obtained. A comparison of the structures of **1** and **7** shows that the size of the auxiliary ligands has a significant effect on the formation and structures of the resulting complexes.

It should be noted that other factors, such as the pH of the reaction mixture, the hydrothermal reaction conditions, and the metal/ligand ratios, also affect the overall structure obtained. A comparison of complexes **2**, **5**, and **7** shows that the transformation of the 2,2′-bpy ligand into quin only happens during the hydrothermal treatment of complex **5**, where the synthesis conditions and metal/ligand ratio are different from those of **2** and **7**, although they use the same reactants. Moreover, **2** and **7** are obtained according to the same procedure but at different pH. Complex **2** contains 1D zigzag chains, whereas **7** contains a one-dimen-

sional double chain containing 28-membered rings. These results suggest that an increase in pH results in a higher connectivity level of the $sfdb^{2-}$ ligands, which in turn affects the formation of the final structure.

In addition, although **1** and **6** both contain a Cd^{II} atom, an $sfdb^{2-}$ ligand, and phen, and are formed under the same hydrothermal reaction conditions, except for different metal/ligand ratios, they have a remarkable structural and compositional diversity that is achieved due to the different coordination modes of the ligands and the coordination geometry of the metal center. A comparison of the structures of **1** and **6** shows that the metal/ligand ratios are a critical factor for the formation and structure of the resulting complexes.

In order to examine the effect of metal salt and solvent on the syntheses, hydrothermal reactions were carried out under the same conditions with $Cu(NO_3)_2$ and $Zn(NO_3)_2$ instead of $Cd(NO_3)_2$ and ethanol instead of H_2O. The resulting complexes **2**–**4** show a similar 1D polymer chain with the same coordination mode, which shows that the metal salt and solvent have little influence on the reaction.

A comparison of the structures of **1**–**7** shows that the formation of MOFs is influenced by many factors, such as the organic ligands, metal/ligand ratios, solvent molecules, hydrothermal reaction conditions, and pH of the reaction mixture, etc. Among these factors, the size of the auxiliary ligands, the hydrothermal reaction conditions, and the metal/ligand ratios are the most important aspects and have very significant effects on the formation and structures of the resulting complexes and their distinct supramolecular structures.

Luminescent Properties

The emission spectra of **1**, **2**, and **4**–**7** in the solid state at room temperature are shown in Figure 8. The ligand exhibits one weak emission band at λ = 329 nm upon excitation at 253 nm. Complexes **1** and **2** exhibit two similar emission peaks at $\lambda \approx$ 380 and 396 nm upon excitation at 310 nm for **1** and at $\lambda \approx$ 365 and 388 nm upon excitation at 335 nm for **2**, which is due to their similar structures. Complex **6** also exhibits an emission peak at λ = 394 nm upon excitation at 253 nm. The emission peaks in **1**, **2** and **6** are redshifted relative to that of the free ligand (λ_{max} = 329 nm), which might also be attributed to intraligand (π–π*) fluorescence.[13] Excitation at λ = 335 nm gives intense emissions at λ = 359 nm for **4**, λ = 385 nm for **5**, and λ = 365 nm for **7**, which are assigned to ligand-to-metal charge-transfer (LMCT) transitions.[14] According to the ligand-field theory of coordination compounds and previously reported molecular orbital calculation for related Cd^{II} coordination polymers,[6c] we can conclude that the HOMO is associated with π-bonding orbitals from the ring and that the LUMOs are mostly Cd–O antibonding orbitals, which are localized more on the metal centers for complexes **4**, **5**, and **7**. A comparison of the emission spectra of complexes **4**, **5**, **7**, and the ligand shows that the enhancement of luminescence in the complexes may be due to their rigidity. This rigidity favors the energy transfer and reduces the loss of energy through nonradiative pathways.[6c,14] On the other hand, the different redshifts of **1**–**2**, **5**–**7** compared with the free $sfdb^{2-}$ ligand may be attributed to the different coordination modes (Scheme 1) of the ligands.[6c,15] The luminescence properties of these metal–organic compounds indicate that they may be excellent candidates for use as photoluminescent materials.

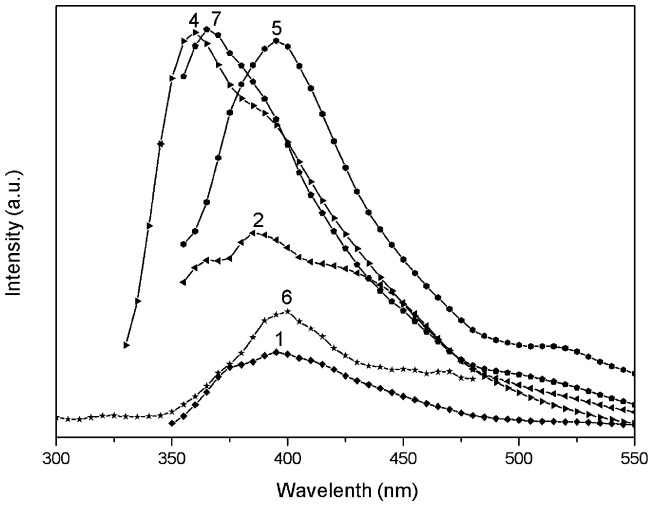


Figure 8. Emission spectra of **1**, **2**, and **4**–**7** in the solid state at room temperature.

Conclusions

We have investigated the coordination chemistry of 4,4′-sulfonyldibenzoic acid with transition metal salts (Cd, Zn, and Cu). Different auxiliary ligands lead to a series of 1D chain structures with different coordination modes of the bridging ligands and different coordination geometries at the metal centers. The different structures of complexes **1**–**7** indicate that the V-shaped $sfdb^{2-}$ dicarboxylate ligand has the ability to adjust its coordination configuration in different reaction systems. Our studies also show that the size of the auxiliary ligands, the hydrothermal reaction conditions, and the metal/ligand ratios have significant effects on the formation and structures of the resulting complexes and result in distinct supramolecular structures. In addition, weak hydrogen-bonding, intra- and/or intermolecular π···π stacking contacts, and C–H···π interactions play a crucial role in linking the discrete 1D chains into high-dimensional supramolecular structures. Obviously, the appropriate combination of bridging dicarboxylate, aromatic chelate, and metal ion could lead to the design of metal–organic compounds with novel structures and properties. Compounds **1**, **2**, and **4**–**7** show photoluminescence at room temperature.

Experimental Section

Materials and Methods: All chemicals and reagents were used as received from commercial sources without further purification. All

reactions were carried out under hydrothermal conditions. Elemental analyses (C, H, and N) were determined with a Elementar Vario EL III elemental analyzer. IR spectra were recorded as KBr pellets with a Bruker EQUINOX55 spectrophotometer in the 4000–400 cm^{-1} region. Fluorescence spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

Synthesis of $[Cd(sfdb)(phen)_2]_n \cdot 2nH_2O$ (1): A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (30.8 mg, 0.1 mmol), 4,4′-sulfonyldibenzoic acid (30.6 mg, 0.1 mmol), and phen (39.6 mg, 0.2 mmol) in a 1:1:2 molar ratio was stirred in water (10 mL) and the pH of the mixture adjusted to 6.5 with a 0.5 M NaOH solution. It was then sealed in a 25-mL Telfon-lined stainless-steel container, which was heated to 160 °C for 72 h and then cooled to room temperature at a rate of 5 °C h^{-1}. Pale-yellow block crystals were obtained. Yield: 45.5 mg (56% based on Cd). $C_{38}H_{26}CdN_4O_8S$ (813.10): calcd. C 53.52, H 3.43, N 7.34; found C 53.54, H 3.40, N 7.29. IR (KBr): $\tilde{\nu}$ = 3442 m, 2360 m, 1597 s, 1555 s, 1398 s, 1327 w, 1162 m, 1101 m, 848 m, 815 m, 745 s, 696 w, 619 m cm^{-1}.

Synthesis of $[Cd(sfdb)(bpy)_2]_n \cdot nH_2O$ (2): This complex was synthesized as for **1** but with 2,2′-bpy instead of phen (solution pH 5.5). Colorless crystals. Yield: 43.3 mg (58% based on Cd). $C_{34}H_{26}CdN_4O_7S$ (747.05): calcd. C 54.66, H 3.51, N 7.50; found C 54.69, H 3.47, N 7.53. IR (KBr): $\tilde{\nu}$ = 3425 w, 3066 w, 2360 s, 1598 s, 1552 s, 1439 m, 1393 s, 1296 m, 1145 w, 1069 w, 1014 w, 849 w, 746 s, 615 m cm^{-1}.

Synthesis of $[Cu(sfdb)(phen)(H_2O)]_n \cdot 0.5nH_2O$ (3): This complex was synthesized as for **1** but with $Cu(CH_3COO)_2 \cdot H_2O$ (20.0 mg, 0.1 mmol) instead of $Cd(NO_3)_2 \cdot 4H_2O$. Blue crystals. Yield: 35.1 mg (61% based on Cu). $C_{26}H_{19}CuN_2O_{7.50}S$ (575.03): calcd. C 54.30, H 3.33, N 4.87; found C 54.37, H 3.31, N 4.83. IR (KBr): $\tilde{\nu}$ = 3544 m, 3070 s, 2360 w, 1641 s, 1567 m, 1427 m, 1352 s, 1295 m, 1160 m, 1101 m, 1013 w, 854 m, 777 s, 695 m, 620 s cm^{-1}.

Synthesis of $[Zn(sfdb)(bpy)(H_2O)]_n \cdot 0.5n(CH_3OH)$ (4): $Zn(NO_3)_2 \cdot 4H_2O$ (101.2 mg, 0.4 mmol), 4,4′-sulfonyldibenzoic acid (30.6 mg, 0.1 mmol), and 2,2′-bpy (15.6 mg, 0.1 mmol) in a 4:1:1 molar ratio were stirred in water (5 mL) and methanol (5 mL) and the pH adjusted to 6.5 with 0.5 M NaOH solution. The hydrothermal synthesis of **4** followed the same procedure as for **1**. Colorless crystals. Yield: 34.7 mg (62% based on H_2sfdb). $C_{24.5}H_{20}N_2O_{7.50}SZn$ (559.85): calcd. C 52.56, H 3.60, N 5.00; found C 52.58, H 3.57, N 4.96. IR (KBr): $\tilde{\nu}$ = 3506 w, 2361 w, 1600 s, 1561 s, 1403 s, 1320 m, 1295 m, 1163 s, 1135 w, 1101 m, 1012 w, 869 w, 742 s, 693 w, 620 m cm^{-1}.

Synthesis of $[Cd(sfdb)(quin)]_n$ (5): A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (30.8 mg, 0.1 mmol), 4,4′-sulfonyldibenzoic acid (30.6 mg,

Table 1. Crystal data and structural refinement parameters for compounds **1**–**4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{38}H_{28}CdN_4O_8S$	$C_{34}H_{26}CdN_4O_7S$	$C_{26}H_{19}CuN_2O_{7.5}S$	$C_{24.50}H_{20}N_2O_{7.50}SZn$
Formula mass	813.10	747.05	575.03	559.85
Space group	$P2_1/c$	$C2/c$	$C2/c$	$P2_1/n$
a [Å]	13.9769(18)	23.5920(15)	22.995(5)	6.8234(4)
b [Å]	19.184(2)	13.0888(8)	12.265(2)	16.4101(10)
c [Å]	12.5471(16)	22.7312(14)	17.901(3)	24.0987(15)
α [°]	90	90	90	90
β [°]	94.410(2)	115.0520(10)	110.871(4)	90.6350(10)
γ [°]	90	90	90	90
V [Å^3]	3354.4(7)	6358.8(7)	4717.5(16)	2698.2(3)
Z	4	8	8	4
$D_{calcd.}$ [Mg m^{-3}]	1.610	1.561	1.619	1.378
$F(000)$	1648	3024	2352	1148
Reflections collected	16617	15617	11594	13387
S on F^2	1.042	1.011	1.032	1.040
R_1, wR_2 [$I > 2\sigma(I)$]	0.0327, 0.0770	0.0301, 0.0691	0.0361, 0.0916	0.0450, 0.1238
R_1, wR_2 (all data)	0.0432, 0.0825	0.0382, 0.0734	0.0465, 0.0982	0.0697, 0.1403

Table 2. Crystal data and structural refinement parameters for compounds **5**–**7**.

	5	**6**	**7**
Empirical formula	$C_{32}H_{20}CdN_2O_6S$	$C_{80}H_{50}Cd_3N_4O_{24}S_4$	$C_{24}H_{16}CdN_2O_6S$
Formula mass	672.96	1916.68	572.85
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a [Å]	8.1894(9)	10.413(2)	12.3570(9)
b [Å]	21.468(2)	13.732(3)	15.3292(12)
c [Å]	16.5536(18)	14.915(3)	12.3221(9)
α [°]	90	107.390(2)	90
β [°]	101.536(2)	108.286(2)	110.3440(10)
γ [°]	90	100.380(2)	90
V [Å^3]	2851.5(5)	1842.0(7)	2188.5(3)
Z	4	1	4
$D_{calcd.}$ [Mg m^{-3}]	1.568	1.728	1.739
$F(000)$	1352	958	1144
Reflections collected	14253	9328	10857
S on F^2	0.954	1.039	1.061
R_1, wR_2 [$I > 2\sigma(I)$]	0.0515, 0.0796	0.0325, 0.0806	0.0255, 0.0610
R_1, wR_2 (all data)	0.1263, 0.1016	0.0407, 0.0869	0.0310, 0.0653

0.1 mmol), and 2,2′-bpy (15.6 mg, 0.1 mmol) in a 1:1:1 molar ratio was stirred in water (10 mL) and the pH adjusted to 7 with 0.5 M NaOH solution. This mixture was sealed in a 25-mL Telfon-lined stainless-steel container, which was heated to 170 °C for 72 h. Cooling to room temperature at a rate of 3 °C h^{-1} gave pale-yellow crystals. Yield: 23.5 mg (35% based on H_2sfdb). $C_{32}H_{20}CdN_2O_6S$ (672.96): calcd. C 57.11, H 3.00, N 4.16; found C 57.14, H 3.02, N 4.12. IR (KBr): ṽ = 1573 s, 1508 m, 1420 m, 1374 vs, 1146 w, 1098 w, 851 s, 815 m, 779 vs, 727 s, 664 w cm^{-1}.

Synthesis of $[Cd_3(sfdb)_2(Hsfdb)_2(phen)_2]_n$ (6): A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (30.8 mg, 0.1 mmol), 4,4′-sulfonyldibenzoic acid (61.2 mg, 0.2 mmol), phen (19.8 mg, 0.1 mmol) and NaOH (40.0 mg, 0.1 mmol), in a 1:2:1:1 molar ratio, was stirred in water (10 mL) in air for 30 min, then sealed in a 25-mL Telfon-lined stainless-steel container. The synthesis of compound **6** followed the same procedure as for **1** and gave colorless crystals. Yield: 42.1 mg (66% based on Cd). $C_{80}H_{50}Cd_3N_4O_{24}S_4$ (638.89): calcd. C 50.17, H 2.63, N 2.91; found C 50.14, H 2.65, N 2.93. IR (KBr): ṽ = 2535 w, 1696 s, 1594 s, 1556 s, 1476 w, 1397 s, 1323 s, 1291 s, 1160 m, 1146 m, 1098 m, 1013 w, 864 w, 761 s, 692 m, 616 s cm^{-1}.

Synthesis of $[Cd(sfdb)(bpy)]_n$ (7): The synthesis of compound **7** followed the same procedure as for **2** but with a different pH (solution pH 7). Colorless crystals. Yield: 30.4 mg (53% based on Cd).

Table 3. Selected bond lengths [Å] and bond angles [°] for **1**–**4**.[a]

Compound **1**			
Cd(1)–O(1)	2.316(3)	Cd(1)–N(2)	2.522(3)
Cd(1)–O(5)#1	2.494(3)	Cd(1)–N(3)	2.419(2)
Cd(1)–O(6)#1	2.604(3)	Cd(1)–N(4)	2.391(2)
Cd(1)–N(1)	2.379(2)		
O(1)–Cd(1)–N(1)	131.85(9)	N(1)–Cd(1)–N(2)	67.44(8)
O(1)–Cd(1)–N(2)	159.55(9)	N(1)–Cd(1)–O(6)#1	75.52(9)
O(1)–Cd(1)–N(3)	88.64(9)	N(2)–Cd(1)–O(6)#1	84.30(9)
O(1)–Cd(1)–N(4)	84.14(9)	N(3)–Cd(1)–O(5)#1	153.75(9)
O(1)–Cd(1)–O(5)#1	85.51(9)	N(3)–Cd(1)–N(2)	101.45(8)
O(1)–Cd(1)–O(6)#1	93.90(10)	N(3)–Cd(1)–O(6)#1	155.45(9)
O(5)#1–Cd(1)–N(2)	77.57(8)	N(4)–Cd(1)–O(5)#1	84.80(9)
O(5)#1–Cd(1)–O(6)#1	50.71(10)	N(4)–Cd(1)–O(6)#1	135.41(9)
N(1)–Cd(1)–N(4)	135.59(8)	N(4)–Cd(1)–N(2)	82.97(8)
N(1)–Cd(1)–N(3)	84.63(8)	N(4)–Cd(1)–N(3)	69.13(8)
N(1)–Cd(1)–O(5)#1	117.92(9)		
Compound **2**			
Cd(1)–O(1)	2.299(2)	Cd(1)–N(2)	2.419(2)
Cd(1)–O(6)#1	2.272(2)	Cd(1)–N(3)	2.403(2)
Cd(1)–N(1)	2.411(2)	Cd(1)–N(4)	2.440(2)
O(1)–Cd(1)–N(1)	81.82(8)	O(6)#1–Cd(1)–N(4)	169.24(9)
O(1)–Cd(1)–N(2)	150.44(9)	N(1)–Cd(1)–N(2)	68.77(7)
O(1)–Cd(1)–N(3)	117.66(8)	N(1)–Cd(1)–N(4)	87.46(7)
O(1)–Cd(1)–N(4)	80.20(8)	N(2)–Cd(1)–N(4)	95.13(7)
O(6)#1–Cd(1)–O(1)	91.29(9)	N(3)–Cd(1)–N(1)	143.86(7)
O(6)#1–Cd(1)–N(1)	84.81(9)	N(3)–Cd(1)–N(2)	86.59(8)
O(6)#1–Cd(1)–N(2)	89.04(8)	N(3)–Cd(1)–N(4)	68.21(8)
O(6)#1–Cd(1)–N(3)	122.06(9)		
Compound **3**			
Cu(1)–O(1)	1.9420(19)	Cu(1)–N(1)	2.042(2)
Cu(1)–O(5)#1	1.922(2)	Cu(1)–N(2)	2.029(2)
Cu(1)–O(7)	2.340(2)		
O(1)–Cu(1)–N(1)	174.45(8)	O(5)#1–Cu(1)–N(2)	171.57(9)
O(1)–Cu(1)–N(2)	93.80(9)	O(5)#1–Cu(1)–O(7)	84.70(9)
O(1)–Cu(1)–O(7)	89.75(8)	N(1)–Cu(1)–O(7)	92.70(8)
O(5)#1–Cu(1)–O(1)	94.54(9)	N(2)–Cu(1)–N(1)	80.98(9)
O(5)#1–Cu(1)–N(1)	90.64(9)	N(2)–Cu(1)–O(7)	96.56(9)
Compound **4**			
Zn(1)–O(1)	1.9764(7)	Zn(1)–N(1)	2.1119(9)
Zn(1)–O(5)#1	2.0309(8)	Zn(1)–N(2)	2.1456(9)
Zn(1)–O(7)	2.0368(8)		
O(1)–Zn(1)–O(5)#1	94.10(3)	O(5)#1–Zn(1)–N(1)	90.02(3)
O(1)–Zn(1)–O(7)	103.71(3)	O(5)#1–Zn(1)–N(2)	160.02(3)
O(1)–Zn(1)–N(1)	150.68(3)	O(7)–Zn(1)–N(1)	105.03(3)
O(1)–Zn(1)–N(2)	91.06(3)	O(7)–Zn(1)–N(2)	104.28(3)
O(5)#1–Zn(1)–O(7)	93.23(3)	N(1)–Zn(1)–N(2)	76.35(3)

[a] Symmetry codes for **1**: #1: $x + 1, y, z$; #2: $x - 1, y, z$; **2**: #1: $x, y - 1, z$; #2: $x, y + 1, z$; **3**: #1: $x - 1/2, y + 1/2, z$; #2: $x + 1/2, y - 1/2, z$; **4**: #1: $-x + 1/2, y - 1/2, -z + 1/2$; #2: $-x + 1/2, y + 1/2, -z + 1/2$.

Table 4. Selected bond lengths [Å] and bond angles [°] for **5**–**7**.[a]

Compound **5**			
Cd(1)–O(1)	2.446(4)	Cd(1)–O(6)#1	2.291(4)
Cd(1)–O(2)	2.246(4)	Cd(1)–N(1)	2.304(5)
Cd(1)–O(5)#1	2.379(4)	Cd(1)–N(2)	2.321(5)
O(2)–Cd(1)–O(1)	55.85(15)	O(6)#1–Cd(1)–O(5)#1	55.31(16)
O(2)–Cd(1)–O(5)#1	100.27(16)	O(6)#1–Cd(1)–O(1)	93.74(16)
O(2)–Cd(1)–O(6)#1	102.08(17)	N(1)–Cd(1)–O(5)#1	108.98(15)
O(2)–Cd(1)–N(1)	150.65(17)	N(1)–Cd(1)–N(2)	71.98(19)
O(2)–Cd(1)–N(2)	104.55(18)	N(1)–Cd(1)–O(1)	100.83(17)
O(5)#1–Cd(1)–O(1)	138.43(14)	N(2)–Cd(1)–O(1)	123.63(15)
O(6)#1–Cd(1)–N(1)	96.59(17)	N(2)–Cd(1)–O(5)#1	93.36(16)
O(6)#1–Cd(1)–N(2)	142.03(17)		
Compound **6**			
Cd(1)–O(1)	2.322(3)	Cd(1)–N(1)	2.364(3)
Cd(1)–O(2)	2.605(3)	Cd(1)–N(2)	2.299(3)
Cd(1)–O(7)	2.588(3)	Cd(2)–O(2)	2.284(2)
Cd(1)–O(8)	2.326(2)	Cd(2)–O(8)	2.282(2)
Cd(1)–O(11)#1	2.270(2)	Cd(2)–O(12)#1	2.214(2)
O(1)–Cd(1)–O(8)	87.46(10)	N(1)–Cd(1)–O(7)	154.91(9)
O(1)–Cd(1)–O(7)	94.62(10)	N(2)–Cd(1)–O(1)	105.16(10)
O(1)–Cd(1)–O(2)	52.91(8)	N(2)–Cd(1)–O(2)	145.47(9)
O(1)–Cd(1)–N(1)	92.97(10)	N(2)–Cd(1)–O(7)	83.31(10)
O(2)–Cd(2)–O(2)#3	180.000(1)	N(2)–Cd(1)–O(8)	134.87(10)
O(7)–Cd(1)–O(2)	120.89(8)	N(2)–Cd(1)–N(1)	71.62(10)
O(8)–Cd(1)–O(2)	75.79(8)	O(8)–Cd(2)–O(2)	83.37(9)
O(8)–Cd(1)–N(1)	152.25(9)	O(8)#3–Cd(2)–O(2)	96.63(9)
O(8)–Cd(1)–O(7)	52.16(8)	O(8)#3–Cd(2)–O(8)	180.000(2)
O(11)#1–Cd(1)–O(1)	144.04(9)	O(12)#1–Cd(2)–O(2)	93.96(9)
O(11)#1–Cd(1)–O(8)	83.20(10)	O(12)#1–Cd(2)–O(8)	90.81(9)
O(11)#1–Cd(1)–O(7)	106.42(10)	O(12)#1–Cd(2)–O(12)#2	180.000(1)
O(11)#1–Cd(1)–O(2)	91.13(8)	O(12)#1–Cd(2)–O(2)#3	86.04(9)
O(11)#1–Cd(1)–N(1)	80.26(10)	O(12)#2–Cd(2)–O(2)#3	93.96(9)
O(11)#1–Cd(1)–N(2)	105.98(10)	O(12)#2–Cd(2)–O(8)	89.19(9)
N(1)–Cd(1)–O(2)	82.40(9)	O(12)#2–Cd(2)–O(8)#3	90.81(9)
Compound **7**			
Cd(1)–O(1)	2.2915(19)	Cd(1)–O(6)#2	2.543(2)
Cd(1)–O(2)#1	2.2358(18)	Cd(1)–N(1)	2.316(2)
Cd(1)–O(5)#2	2.2638(18)	Cd(1)–N(2)	2.404(2)
O(1)–Cd(1)–O(6)#2	156.16(6)	O(5)#2–Cd(1)–O(1)	105.47(7)
O(1)–Cd(1)–N(1)	99.28(7)	O(5)#2–Cd(1)–N(1)	139.98(7)
O(1)–Cd(1)–N(2)	83.44(7)	O(5)#2–Cd(1)–N(2)	82.41(7)
O(2)#1–Cd(1)–O(1)	105.37(8)	O(5)#2–Cd(1)–O(6)#2	54.55(7)
O(2)#1–Cd(1)–O(5)#2	112.77(8)	N(1)–Cd(1)–O(6)#2	92.22(7)
O(2)#1–Cd(1)–O(6)#2	95.45(8)	N(1)–Cd(1)–N(2)	69.60(8)
O(2)#1–Cd(1)–N(1)	89.69(8)	N(2)–Cd(1)–O(6)#2	81.10(7)
O(2)#1–Cd(1)–N(2)	158.74(8)		

[a] Symmetry codes for **5**: #1: $x - 3/2, -y + 1/2, z - 1/2$; #2: $x + 3/2, -y + 1/2, z + 1/2$; **6**: #1: $x, y + 1, z$; #2: $-x + 2, -y + 1, -z + 2$; #3: $-x + 2, -y + 2, -z + 2$; #4: $x, y - 1, z$; **7**: #1: $-x + 2, -y + 2, -z + 1$; #2: $-x + 1, -y + 2, -z$.

$C_{24}H_{16}CdN_2O_6S$ (572.85): calcd. C 50.32, H 2.82, N 4.89; found C 50.34, H 2.80, N 4.90. IR (KBr): $\tilde{\nu}$ = 3443 w, 3085 m, 1985 w, 1553 s, 1474 s, 1406 s, 1296 s, 1158 s, 1099 m, 1013 m, 849 m, 846 m, 787 s, 724 w, 613 s cm^{-1}.

X-ray Crystallography: Intensity data were collected with a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at room temperature. Empirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on F^2 using SHELXTL-97.[16] All non-hydrogen atoms were refined anisotropically and the hydrogen atoms of organic ligands were generated geometrically. Crystal data and structural refinement parameters for **1**–**7** are summarized in Tables 1 and 2. Selected bond lengths and bond angles are listed in Tables 3 and 4. CCDC-647395 to -647401 (**1**–**7**, respectively) 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.

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