

## Synthesis, Characterization, and Crystal Structures of Three New Divalent Metal Carboxylate–Sulfonates with a Layered and One-Dimensional Structure

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Hydrothermal reactions of 5-sulfoisophthalic acid ( $\text{HO}_3\text{SC}_6\text{H}_3\text{-1,3-(CO}_2\text{H)}_2$ ,  $\text{H}_3\text{L}$ ) with  $\text{M(II)}$  carbonate (or oxide) and 4,4'-bipyridine (4,4'-bipy) (or 2,2'-bipyridine, 2,2'-bipy) resulted in three new metal carboxylate–sulfonate hybrids, namely,  $[\text{CdL(H-4,4'-bipy)}]$  (**1**) and  $[\text{Cd}_3\text{L}_2(2,2\text{'-bipy)}_4(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$  (**2**) with layered structures and  $[\text{ZnL(H-4,4'-bipy)}(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$  (**3**), whose structure features a one-dimensional double chain. The cadmium(II) ion in complex **1** is seven-coordinated by five carboxylate oxygen atoms and one sulfonate oxygen atom from four ligands and a unidentate 4,4'-bipyridine. The interconnection of the cadmium(II) ions through bridging carboxylate–sulfonate ligands resulted in the formation of a  $\langle 002 \rangle$  double layer with the bipyridyl rings orientated toward the interlayer space. Complex **2** has a different layered structure.  $\text{Cd(1)}$  is seven-coordinated by two bidentate chelating carboxylate groups from two ligands, a bidentate chelating 2,2'-bipy and an aqua ligand, and  $\text{Cd(2)}$  is octahedrally coordinated by two bidentate chelating 2,2'-bipy's, a sulfonate oxygen, and an aqua ligand. The coordination geometry around  $\text{Cd(3)}$  is similar to that of  $\text{Cd(1)}$  with the aqua ligand being replaced by an oxygen atom from the sulfonate group. The carboxylate–sulfonate ligand acts as pentadentate ligand, bridging with three cadmium(II) ions. The bridging of cadmium(II) ions through the carboxylate–sulfonate ligands resulted in the formation of  $\langle 006 \rangle$  and  $\langle 003 \rangle$  layers; the 2,2'-bipy molecules and  $[\text{Cd(2)(2,2'-bipy)}_2(\text{H}_2\text{O})]$  cations are orientated to the interlayer space. Complex **3** features a 1D metal carboxylate–sulfonate double chain along the diagonal of the  $a$ - and  $b$ -axes. The zinc(II) ion is octahedrally coordinated by four carboxylate O atoms from three ligands, a unidentate 4,4'-bipy, and an aqua ligand. Each pair of zinc(II) ions is bridged by two carboxylate groups from two ligands to form a dimer, and such dimeric units are interconnected by bridging ligands to form a double chain. The sulfonate group of the carboxylate sulfonate ligand remains noncoordinated and forms a number of hydrogen bonds with aqua ligands as well as lattice water molecules.

### Introduction

Mixed inorganic–organic hybrids with layered structures have been of interest due to their potential applications in chemical separations and catalysis.<sup>1,2</sup> Much of the work in this area has involved organically functionalized clays and metal phosphonates.<sup>3,4</sup> Similar to phosphonic acids,<sup>4</sup> orga-

nosulfonic acids have been reported to form various types of layered or pillared layered compounds with metal ions, such as silver(I) ion,<sup>5</sup> alkali and alkaline earth metal ions,<sup>6,7</sup> and transitional metal ions as well as lanthanide(III) ions.<sup>8–10</sup> Analogous to that in the metal phosphonate chemistry,<sup>4,11</sup> various functional groups such as amine, hydroxyl, and

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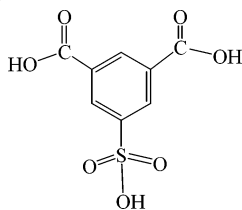
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(1) Clearfield, A. *Comments Inorg. Chem.* **1990**, *10*, 89.

(2) Pinnavaia, F. *Science* **1983**, *220*, 365.

(3) Righor, E.; Tzou, M.; Pinnavaia, T. *J. Catal.* **1991**, *130*, 29.

(4) (a) Stein, E.; Clearfield, A.; Subramanian, M. A. *Solid State Ionics* **1996**, *83*, 113. (b) Alberti, G.; Costantino, U. In *Comprehensive Supramolecular Chemistry*; Lehn, J. M., Ed.; Pergamon-Elsevier Science Ltd.: London, 1996; p 1. (c) Clearfield, A. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 268. (d) Clearfield, A. Metal Phosphonate Chemistry. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; John Wiley & Sons: New York, 1998; Vol. 47, pp 371–510 (and references herein).

Chart 1. 5-Sulfoisophthalic Acid, HO<sub>3</sub>SC<sub>6</sub>H<sub>3</sub>-1,3-(CO<sub>2</sub>H)<sub>2</sub> (H<sub>3</sub>L)

carboxylate groups have been attached to the organosulfonic acids to build new inorganic–organic hybrid materials.<sup>6–10</sup> Reports on metal carboxylate–sulfonates are still rare. 4-Carboxybenzenesulfonic acid has been reported to form a layered compound with potassium(I) ion,<sup>6a</sup> a 1D coordination polymer with Cd(II) ion,<sup>8c</sup> and 3D pillared layered networks with Eu(III) and Gd(III) ions when benzene-1,4-disulfonate is also added in the reactions.<sup>9d</sup> Two copper(II) complexes with a 1D chain structure and three isomorphous layered lanthanide complexes with 5-sulfoisophthalic acid (HO<sub>3</sub>SC<sub>6</sub>H<sub>3</sub>-1,3-(CO<sub>2</sub>H)<sub>2</sub>, H<sub>3</sub>L; Chart 1) have been reported recently.<sup>10</sup> Hydrothermal reactions of 5-sulfoisophthalic acid with M(II) carbonate (or oxide) and a second ligand, 4,4'-bipyridine (4,4'-bipy) (or 2,2'-bipyridine, 2,2'-bipy), afforded three new metal carboxylate–sulfonate hybrids, namely, [CdL(H-4,4'-bipy)] (1) and [Cd<sub>3</sub>L<sub>2</sub>(2,2'-bipy)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O (2) with a layered structure, and [ZnL(H-4,4'-bipy)(H<sub>2</sub>O)]·2H<sub>2</sub>O (3), whose structure features a one-dimensional double chain. Herein we report their syntheses, characterizations, and crystal structures.

- (5) (a) Shimizu, G. K. H.; Enright, G. D.; Ratcliffe, C. I.; Preston, K. F.; Reid, J. L.; Ripmeester, J. A. *Chem. Commun.* **1999**, 1485. (b) Smith, G.; Cloutt, B. A.; Lynch, D. E.; Byriel, K. A.; Kennard, C. H. L. *Inorg. Chem.* **1998**, *37*, 3236. (c) Côté, A. P.; Ferguson, M. J.; Khan, K. A.; Enright, G. D.; Kulynych, A. D.; Dalrymple, S. A.; Shimizu, G. K. H. *Inorg. Chem.* **2002**, *41*, 287. Shimizu, G. K. H.; Enright, G. D.; Ratcliffe, C. I.; Rego, G. S.; Reid, J. L.; Ripmeester, J. A. *Chem. Mater.* **1998**, *10*, 3282.
- (6) (a) Gunderman, B. J.; Squatrito, P. J. *Inorg. Chem.* **1994**, *33*, 2924. (b) Gunderman, B. J.; Kabell, I. D.; Squatrito, P. J.; Dubey, S. N. *Inorg. Chim. Acta* **1997**, *258*, 237. (c) Gunderman, B. J.; Squatrito, P. J. *Inorg. Chem.* **1995**, *34*, 2399.
- (7) (a) Côté, A. P.; Shimizu, G. K. H. *Chem. Commun.* **2001**, 251. (b) Dalrymple, S. A.; Shimizu, G. K. H. *Chem.—Eur. J.* **2002**, *8*, 3010. (c) Yu, J. O.; Côté, A. P.; Enright, G. D.; Shimizu, G. K. H. *Inorg. Chem.* **2001**, *40*, 582.
- (8) (a) Chen, C.-H.; Cai, J.-W.; Liao, C.-Z.; Feng, X.-L.; Chen, X.-M.; Ng, S. W. *Inorg. Chem.* **2002**, *41*, 4967. (b) Cai, J.-W.; Chen, C.-H.; Liao, C.-Z.; Yao, J.-H.; Hu, X.-P.; Chen, X.-M. *J. Chem. Soc., Dalton Trans.* **2001**, 1137. (c) Tisato, F.; Refosco, F.; Bandoli, G.; Pilloni, G.; Corain, B. *Inorg. Chem.* **2001**, *40*, 1394. (d) Henderson, R. K.; Bouwman, E.; Spek, A. L.; Reedijk, J. *Inorg. Chem.* **1997**, *36*, 4616. (e) Yuan R.-X.; Xiong, R.-G.; Xie, Y.-L.; You, X.-Z.; Peng, S.-M.; Lee, G.-H. *Inorg. Chem. Commun.* **2001**, *4*, 384.
- (9) (a) Drljaca, A.; Hardie, M. J.; Johnson, J. A.; Raston, C.-L.; Webb, H. R. *Chem. Commun.* **1999**, 1135. (b) Orr, G. W.; Barbour, L. J.; Atwood, J. L. *Science* **1999**, *285*, 1049. (c) Hardie, M. J.; Johnson, J. A.; Raston, C. L.; Webb, H. R. *Chem. Commun.* **2000**, 849. (d) Xiong, R.-G.; Zhang, J.; Chen, Z.-F.; You, X.-Z.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **2001**, 780. (e) Steed, J. W.; Johnson, C. P.; Barnes, C. L.; Juneja, R. K.; Atwood, J. L.; Reilly, S.; Hollis, R. L.; Smith, P. H.; Clark, D. L. *J. Am. Chem. Soc.* **1995**, *117*, 11426.
- (10) (a) Sun, D.; Cao, R.; Sun, Y.-Q.; Li, X.; Bi, W.; Hong, M.-C.; Zhao, Y.-J. *Eur. J. Inorg. Chem.* **2003**, 94. (b) Wang, Z.; Ströbele, M.; Zhang, K.-L.; Meyer, H.-J.; You, X.-Z.; Yu, Z. *Inorg. Chem. Commun.* **2002**, *5*, 230.
- (11) (a) Mao, J.-G.; Clearfield, A. *Inorg. Chem.* **2002**, *41*, 2319. (b) Mao, J.-G.; Wang, Z.; Clearfield, A. *Inorg. Chem.* **2002**, *41*, 2334. (c) Stock, N.; Stucky, G. D.; Cheetham, A. K. *Chem. Commun.* **2000**, 2277. (d) Sharma, C. V. K.; Clearfield, A.; Cabeza, A.; Aranda, M. A. G.; Bruque, S. *J. Am. Chem. Soc.* **2001**, *123*, 2885.

## Experimental Section

**Materials and Methods.** All chemicals and solvents were of reagent grade and used as received. Elemental analyses were performed on a German Elementary Vario EL III instrument. IR spectra were recorded on a Magna 750 FT-IR spectrometer photometer as KBr pellets in the range of 4000–400 cm<sup>-1</sup>. Thermogravimetric analyses were carried out with a TGA/SBTA851 unit, at a heating rate of 15 °C/min under a nitrogen atmosphere.

**Synthesis of [CdL(H-4,4'-bipy)] (1).** CdCO<sub>3</sub> (0.5 mmol) was added to 10 mL of an aqueous solution of 5-sulfoisophthalic acid monosodium salt (0.7 mmol, Aldrich) and heated at 80 °C for 30 min under stirring. The resultant mixture was filtered, and a mixture of the filtrate and 4,4'-bipyridyl (0.5 mmol) was sealed into a bomb equipped with a Teflon liner and then allowed to react at 180 °C for 4 days. Colorless brick-shaped crystals of **1** were recovered in ca. 62.3% yield. Anal. Found for complex **1**: C, 41.85; H, 2.18; N, 5.53. Calcd: C, 42.16; H, 2.36; N, 5.46. IR data (KBr, cm<sup>-1</sup>): 3386 (m), 3055 (w), 1554 (m), 1414 (w), 1362 (s), 1218 (s), 1198 (s), 1043 (m), 806 (s), 755 (w), 727 (w), 631 (s), 492 (w).

**Synthesis of [Cd<sub>3</sub>L<sub>2</sub>(2,2'-bipy)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O (2).** Complex **2** was synthesized by a method similar to that used for complex **1**. 2,2'-Bipyridine was used instead of 4,4'-bipyridine. Colorless brick-shaped crystals of **2** were recovered in ca. 74.5% yield. Anal. Found for complex **2**: C, 43.92; H, 2.88; N, 7.16. Calcd: C, 44.24; H, 3.05; N, 7.3%. IR (KBr, cm<sup>-1</sup>) data: 3375 (m), 3115 (w), 2364 (w), 1668 (w), 1608 (vs), 1439 (vs), 1180 (s), 1018 (s), 876 (w), 766 (s), 729 (m), 652 (m), 627 (m), 579 (w).

**Synthesis of [ZnL(H-4,4'-bipy)(H<sub>2</sub>O)]·2H<sub>2</sub>O (3).** A 0.5 mmol amount of zinc(II) oxide was added to 10 mL of aqueous solution of 5-sulfoisophthalic acid monosodium salt (0.7 mmol, Aldrich) and then heated at 80 °C under stirring until the zinc oxide was dissolved completely. The resultant solution was mixed with 0.5 mmol of 4,4'-bipyridine, sealed into a bomb equipped with a Teflon liner, and allowed to react at 180 °C for 4 days. Colorless plate crystals of **3** were recovered in ca. 54.9% yield. Anal. Found for complex **3**: C, 41.45; H, 3.25; N, 5.28. Calcd: C, 41.60; H, 3.49; N, 5.39. IR (KBr, cm<sup>-1</sup>) data: 3425 (s), 3086 (w), 2598 (w), 1606 (vs), 1371 (s), 1234 (s), 1036 (s), 860 (w), 820 (m), 729 (m), 633 (s), 571 (w), 490 (w).

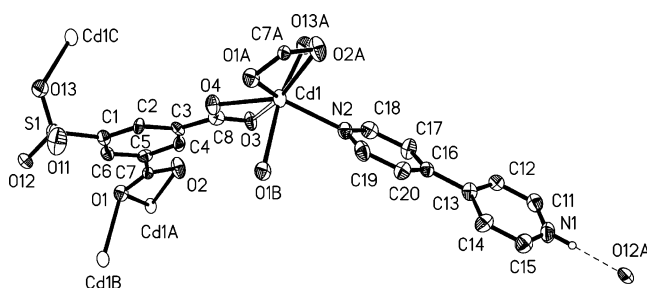
**Crystal Structure Determination.** Single crystals of the title complexes were mounted on a Bruker Smart CCD using Mo Kα radiation (λ = 0.710 69 Å) and a graphite monochromator at room temperature. Intensity data were collected by using the narrow frame method with 0.3°/frame in φ at 293 K. A total of 2960, 9727, and 3473 independent reflections for **1–3**, respectively, were collected among which 2110 (for **1**), 6785 (for **2**), and 2618 (for **3**) reflections with I > 2.0σ(I) were considered observed. Absorption corrections were performed by using the SADABS program.<sup>12</sup> All three structures were solved by direct methods and refined by full-matrix least-squares fitting on F<sup>2</sup> by SHELXL.<sup>12</sup> All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at geometrically calculated positions and refined with isotropic thermal parameters. A summary of the crystallographic data for these three complexes is listed in Table 1. Selected bond distances and angles are given in Table 2. More details on the crystallographic studies as well as atom displacement parameters are given in the Supporting Information.

- (12) (a) Sheldrick, G. M. *Program SADABS*; Universität Göttingen: Göttingen, Germany, 1995. (b) Sheldrick, G. M. *SHELXTL, Crystallographic Software Package, SHELXTL*, version 5.1; Bruker-AXS: Madison, WI, 1998.

**Table 1.** Crystal Data and Structure Refinement Details for Complexes 1–3

param	1	2	3
empirical formula	C <sub>18</sub> H <sub>12</sub> N <sub>2</sub> O <sub>7</sub> -SCd	C <sub>56</sub> H <sub>46</sub> N <sub>8</sub> O <sub>18</sub> -S <sub>2</sub> Cd <sub>3</sub>	C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>10</sub> -SZn
fw	512.76	1520.33	519.77
space group	<i>P</i> 1̄ (No. 2)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	<i>P</i> 1̄ (No. 2)
<i>a</i> (Å)	7.7975(4)	8.53170(10)	8.7273(3)
<i>b</i> (Å)	9.0264(4)	40.5665(2)	9.5184(4)
<i>c</i> (Å)	13.0844(2)	16.63820(10)	13.7818(6)
α (deg)	74.765(2)	90.0	96.608(2)
β (deg)	87.993(3)	104.5090(10)	94.816(2)
γ (deg)	74.033(3)	90.0	117.269(2)
<i>V</i> (Å <sup>3</sup> )	853.59(6)	5574.85(8)	998.67(7)
<i>Z</i>	2	4	2
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.995	1.811	1.729
<i>T</i> (K)	293	293	293
λ (Å)	0.710 73	0.710 73	0.710 73
μ(Mo Kα) (mm <sup>-1</sup> )	1.451	1.293	1.397
R1, wR2 [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.0709, 0.1238	0.0656, 0.1038	0.0701, 0.1695
R1, wR2 (all data) <sup>a</sup>	0.1197, 0.1493	0.1122, 0.1227	0.1019, 0.1997

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR2 = \{ \sum w[(F_o)^2 - (F_c)^2]^2 / \sum w(F_o)^2 \}^{1/2}.$$

**Figure 1.** ORTEP representation of the asymmetric unit of complex 1. Thermal ellipsoids are drawn at 50% probability. The longer Cd–O contacts and hydrogen bonds are represented by the open and dotted lines, respectively.

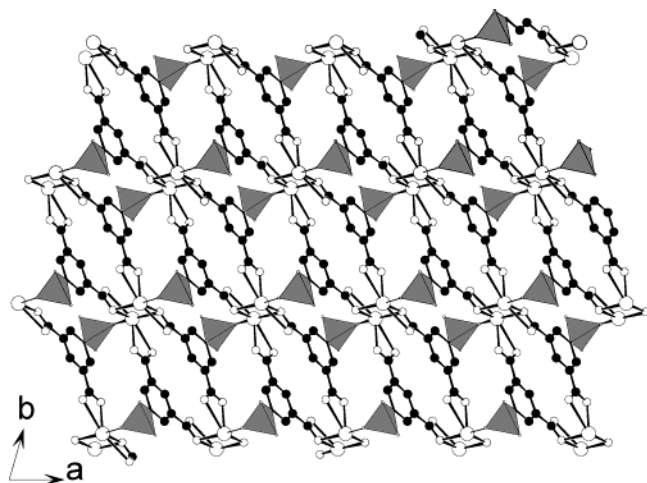
## Results and Discussion

As shown in Figure 1, the Cd(II) ion in complex 1 is seven-coordinated by five carboxylate and one sulfonate oxygen atoms from four ligands as well as a unidentate 4,4'-bipy nitrogen. The Cd(1)–O(3) distance of 2.732(7) Å is much larger than the remaining Cd–O distances which range from 2.195(6) to 2.502(7) Å. The Cd–N bond length is 2.268(8) Å. These distances are comparable to those reported in other Cd(II) sulfonates.<sup>8</sup> Different from that in the copper(II) and lanthanide complexes, the carboxylate–sulfonate ligand in complex 1 adopts a hexadentate bridging and chelating coordination mode; one carboxylate group chelates with a cadmium(II) ion bidentately (O(3), O(4)), and the other carboxylate group (O(1), O(2)) adopts a  $\mu_3$  chelating and bridging coordination mode and connects with two metal ions. The sulfonate group is unidentate (O(13)). The carboxylate–sulfonate ligand in its copper(II) complexes bridges with two copper(II) ions using two unidentate carboxylate groups, and the sulfonate group remains noncoordinated. In its lanthanide complexes, the carboxylate groups are bidentate chelating and the sulfonate group is unidentate.<sup>10</sup> On the basis of the close C–O or S–O distances (Table 2), the carboxylate–sulfonate ligand is assumed to be completely deprotonated. For the sake of charge balance, the noncoordinated nitrogen atom of the 4,4'-bipy should be protonated; it forms

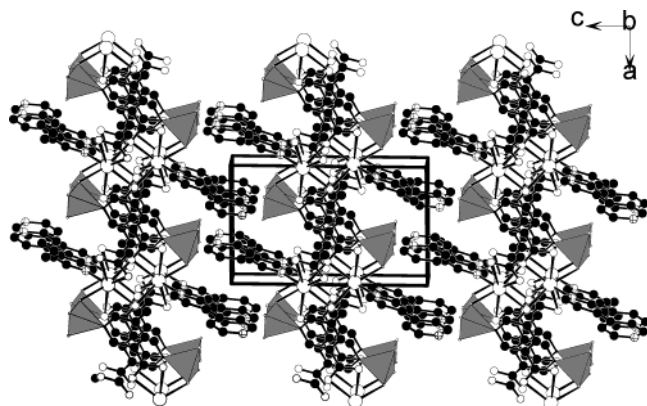
**Table 2.** Bond Lengths (Å) and Angles (deg) for Complexes 1–3<sup>a</sup>

Compound 1			
Cd(1)–O(4)	2.195(6)	Cd(1)–N(2)	2.268(8)
Cd(1)–O(13) <sup>#1</sup>	2.338(7)	Cd(1)–O(1) <sup>#2</sup>	2.356(7)
Cd(1)–O(2) <sup>#2</sup>	2.498(7)	Cd(1)–O(1) <sup>#3</sup>	2.502(7)
Cd(1)–O(3)	2.732(7)	O(1)–Cd(1) <sup>#4</sup>	2.356(7)
O(1)–Cd(1) <sup>#3</sup>	2.502(7)	O(2)–Cd(1) <sup>#4</sup>	2.498(7)
N(1)···O(12) <sup>#5 b</sup>	2.707(11)	N(1)–H(0a)···O(12) <sup>#5 b</sup>	167.9
O(4)–Cd(1)–N(2)	143.3(3)	O(4)–Cd(1)–O(13) <sup>#1</sup>	102.8(2)
N(2)–Cd(1)–O(13) <sup>#1</sup>	89.2(3)	O(4)–Cd(1)–O(1) <sup>#2</sup>	86.6(2)
O(2)–Cd(1)–O(1) <sup>#2</sup>	118.1(3)	O(13) <sup>#1</sup> –Cd(1)–O(1) <sup>#2</sup>	118.6(3)
N(4)–Cd(1)–O(2) <sup>#2</sup>	132.7(3)	N(2)–Cd(1)–O(2) <sup>#2</sup>	83.2(3)
O(13) <sup>#1</sup> –Cd(1)–O(2) <sup>#2</sup>	79.9(3)	O(1) <sup>#2</sup> –Cd(1)–O(2) <sup>#2</sup>	53.7(2)
O(4)–Cd(1)–O(1) <sup>#3</sup>	81.3(2)	N(2)–Cd(1)–O(1) <sup>#3</sup>	79.3(3)
O(13) <sup>#1</sup> –Cd(1)–O(1) <sup>#3</sup>	164.7(2)	O(1) <sup>#2</sup> –Cd(1)–O(1) <sup>#3</sup>	76.1(3)
O(2) <sup>#2</sup> –Cd(1)–O(1) <sup>#3</sup>	108.4(2)	Cd(1) <sup>#4</sup> –O(1)–Cd(1) <sup>#3</sup>	103.9(3)
Compound 2			
Cd(1)–O(1)	2.213(6)	Cd(1)–O(3W)	2.322(6)
Cd(1)–N(4)	2.330(7)	Cd(1)–N(3)	2.343(7)
Cd(1)–O(8) <sup>#1</sup>	2.377(6)	Cd(1)–O(7) <sup>#1</sup>	2.494(6)
Cd(2)–N(2)	2.295(7)	Cd(2)–N(7)	2.297(7)
Cd(2)–N(8)	2.313(7)	Cd(2)–N(1)	2.320(7)
Cd(2)–O(4W)	2.384(6)	Cd(2)–O(11)	2.482(5)
Cd(3)–O(5)	2.246(5)	Cd(3)–O(4)	2.261(5)
Cd(3)–O(22) <sup>#2</sup>	2.273(6)	Cd(3)–N(5)	2.330(7)
Cd(3)–N(6)	2.361(7)	Cd(3)–O(3)	2.517(6)
O(7)–Cd(1) <sup>#3</sup>	2.494(6)	O(8)–Cd(1) <sup>#3</sup>	2.377(6)
O(22)–Cd(3) <sup>#4</sup>	2.273(6)		
O(1w)···O(3w) <sup>b</sup>	2.883(10)	O(1w)···O(13) <sup>#2 b</sup>	2.756(8)
O(2w)···O(12) <sup>#2 b</sup>	2.814(8)	O(2w)···O(23) <sup>#5 b</sup>	2.795(9)
O(3w)···O(4w) <sup>#6 b</sup>	2.940(10)		
O(1)–Cd(1)–O(3W)	100.5(2)	O(1)–Cd(1)–N(4)	114.8(2)
O(3W)–Cd(1)–N(4)	143.8(2)	O(1)–Cd(1)–N(3)	123.5(2)
O(3W)–Cd(1)–N(3)	84.1(2)	N(4)–Cd(1)–N(3)	70.4(2)
O(1)–Cd(1)–O(8) <sup>#1</sup>	85.8(2)	O(3W)–Cd(1)–O(8) <sup>#1</sup>	98.3(2)
N(4)–Cd(1)–O(8) <sup>#1</sup>	92.0(2)	N(3)–Cd(1)–O(8) <sup>#1</sup>	149.9(2)
O(1)–Cd(1)–O(7) <sup>#1</sup>	136.7(2)	O(3W)–Cd(1)–O(7) <sup>#1</sup>	74.8(2)
N(4)–Cd(1)–O(7) <sup>#1</sup>	84.1(2)	N(3)–Cd(1)–O(7) <sup>#1</sup>	99.2(2)
O(8) <sup>#1</sup> –Cd(1)–O(7) <sup>#1</sup>	53.49(19)	N(2)–Cd(2)–N(7)	163.7(3)
N(2)–Cd(2)–N(8)	106.1(3)	N(7)–Cd(2)–N(8)	73.1(3)
N(2)–Cd(2)–N(1)	72.1(2)	N(7)–Cd(2)–N(1)	110.9(2)
N(8)–Cd(2)–N(1)	172.1(2)	N(2)–Cd(2)–O(4W)	107.1(2)
N(7)–Cd(2)–O(4W)	89.2(2)	N(8)–Cd(2)–O(4W)	92.1(2)
N(1)–Cd(2)–O(4W)	81.3(2)	N(2)–Cd(2)–O(11)	84.5(2)
N(7)–Cd(2)–O(11)	79.2(2)	N(8)–Cd(2)–O(11)	85.9(2)
N(1)–Cd(2)–O(11)	101.4(2)	O(4W)–Cd(2)–O(11)	168.3(2)
O(5)–Cd(3)–O(4)	100.8(2)	O(5)–Cd(3)–O(22) <sup>#2</sup>	84.6(2)
O(4)–Cd(3)–O(22) <sup>#2</sup>	90.7(2)	O(5)–Cd(3)–N(5)	115.0(2)
O(4)–Cd(3)–N(5)	138.1(2)	O(22) <sup>#2</sup> –Cd(3)–N(5)	112.8(2)
O(5)–Cd(3)–N(6)	88.9(2)	O(4)–Cd(3)–N(6)	90.6(2)
O(22) <sup>#2</sup> –Cd(3)–N(6)	173.5(2)	N(5)–Cd(3)–N(6)	70.0(2)
O(5)–Cd(3)–O(3)	154.8(2)	O(4)–Cd(3)–O(3)	54.43(19)
O(22) <sup>#2</sup> –Cd(3)–O(3)	99.0(2)	N(5)–Cd(3)–O(3)	86.9(2)
N(6)–Cd(3)–O(3)	87.0(2)		
Compound 3			
Zn(1)–O(3) <sup>#1</sup>	1.986(4)	Zn(1)–O(1)	2.000(5)
Zn(1)–N(1)	2.051(6)	Zn(1)–O(1W)	2.162(5)
Zn(1)–O(4) <sup>#2</sup>	2.222(5)	O(3)–Zn(1) <sup>#3</sup>	1.986(4)
O(1w)···O(13) <sup>#4 b</sup>	2.790(8)	O(2w)···O(12) <sup>#5 b</sup>	2.898(9)
O(2w)···O(13) <sup>b</sup>	2.801(8)	O(2w)···O(3w) <sup>b</sup>	2.806(10)
N(2)···O(3w) <sup>#6 b</sup>	2.644(9)	N(2)–H(0a)···O(3w) <sup>#6 b</sup>	162.8
O(3) <sup>#1</sup> –Zn(1)–O(1)	110.9(2)	O(3) <sup>#1</sup> –Zn(1)–N(1)	98.5(2)
O(1)–Zn(1)–N(1)	150.6(2)	O(3) <sup>#1</sup> –Zn(1)–O(1W)	92.8(2)
O(1)–Zn(1)–O(1W)	94.4(2)	N(1)–Zn(1)–O(1W)	85.2(2)
O(3) <sup>#1</sup> –Zn(1)–O(4) <sup>#2</sup>	102.48(19)	O(1)–Zn(1)–O(4) <sup>#2</sup>	90.7(2)
N(1)–Zn(1)–O(4) <sup>#2</sup>	81.5(2)	O(1W)–Zn(1)–O(4) <sup>#2</sup>	161.01(18)

<sup>a</sup> Symmetry transformations used to generate equivalent atoms are as follows. Complex 1: #1,  $-x, -y + 1, -z + 1$ ; #2,  $x - 1, y + 1, z$ ; #3,  $-x + 1, -y + 1, -z + 1$ ; #4,  $x + 1, y - 1, z$ ; #5,  $x, y + 2, z - 1$ . Complex 2: #1,  $x + 1, y, z - 1$ ; #2,  $x + 1, y, z$ ; #3,  $x - 1, y, z + 1$ ; #4,  $x - 1, y, z$ ; #5,  $-x - 1, -y, 1 - z$ ; #6,  $x + 2, y, z$ . Complex 3: #1,  $x - 1, y - 1, z$ ; #2,  $-x + 3, -y + 2, -z$ ; #3,  $x + 1, y + 1, z$ ; #4,  $x - 1, y, z$ ; #5,  $-x + 4, -y + 2, -z + 1$ ; #6,  $x - 2, y, z - 1$ . <sup>b</sup> Hydrogen bonding parameters.



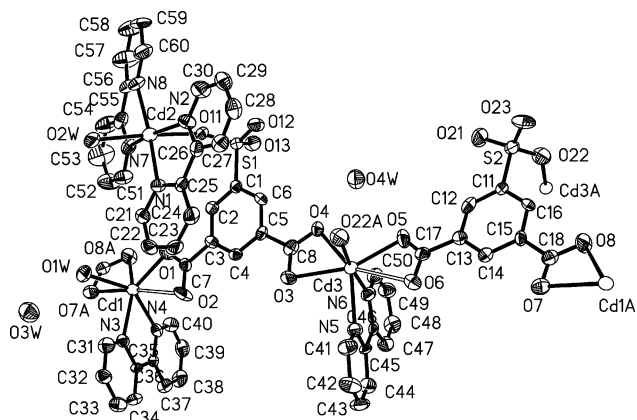
**Figure 2.** A  $\langle 002 \rangle$  layer of complex **1**. The  $\text{CSO}_3$  tetrahedra are shaded in gray, and Cd, C, and O atoms are drawn as open (large), black, and open (small) circles, respectively. The 4,4'-bipy ligands have been omitted for clarity.



**Figure 3.** View of structure of complex **1** down the  $b$ -axis. The  $\text{CSO}_3$  tetrahedra are shaded in gray. Cd, N, C, and O atoms are drawn as open (large), crossed, black, and open (small) circles, respectively.

a hydrogen bond with the noncoordinated sulfonate oxygen atom (O(12)) from a neighboring formula unit (symmetry operator:  $x, y + 2, z - 1$ ). The  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bond length and angle are 2.707(11) Å and 167.9°, respectively.

The interconnection of the Cd(II) ions through bridging carboxylate–sulfonate ligands results in a  $\langle 002 \rangle$  double-sided layer (Figure 2). Three types of rings formed within the double layer; one is a  $\text{Cd}_2\text{O}_2$  four-membered ring, the second type is the 18-membered ring formed by two Cd(II) ion and the carboxylate moieties of two ligands, and the third one is the 16-membered ring created by two Cd(II) ions and the sulfonate moieties of two ligands. The double layers of complex **1** are held together by weak van de Waals' force (Figure 3). The pyridyl rings are orientated toward the interlayer space and stacked one above the other, and the distance from the center of the pyridyl ring (N(1), C(11), C(12), C(13), C(14), C(15)) to that of a parallel neighboring one is 3.548 Å. Thus, there are also weak  $\pi-\pi$  interactions between these rings, which further stabilizes the structure. Similar  $\pi-\pi$  interaction between pyridine rings has also been reported in a number of transition metal 1,10-phenanthroline succinates.<sup>13</sup>

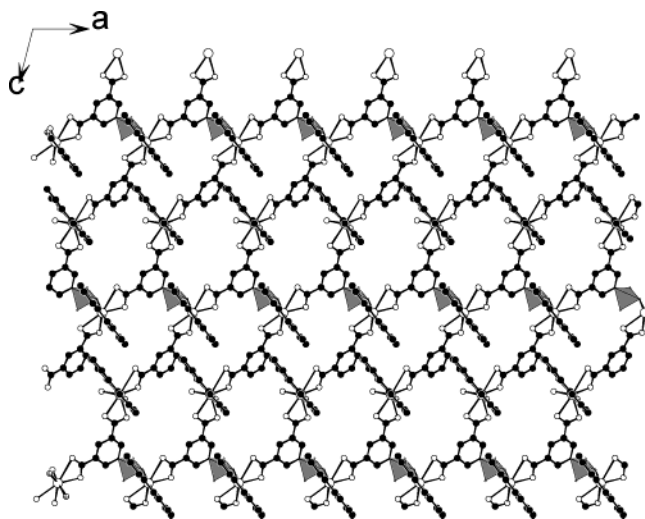


**Figure 4.** ORTEP representation of the asymmetric unit of complex **2**. Thermal ellipsoids are drawn at 50% probability. The longer Cd–O contacts are represented by the open lines.

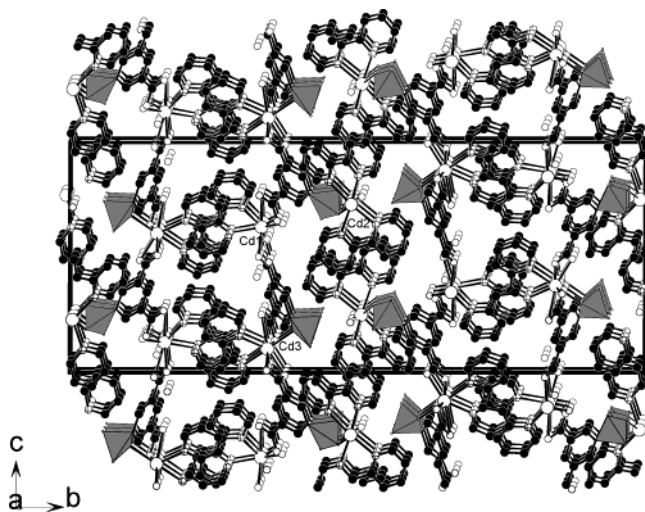
When 2,2'-bipy was used instead of 4,4'-bipy, complex **2** with a different layered structure was obtained. The asymmetric unit of complex **2** contains three Cd(II) ions, two carboxylate–sulfonate ligands, four 2,2'-bipy, two aqua ligands, and two lattice water molecules (Figure 4). Cd(1) is seven-coordinated by two bidentate chelating carboxylate groups from two ligands, a bidentate chelate 2,2'-bipy, and an aqua ligand. Cd(2) is octahedrally coordinated by two bidentate chelating 2,2'-bipy, a sulfonate oxygen, and an aqua ligand. The coordination geometry around Cd(3) is similar to that of Cd(1) with the aqua ligand being replaced by a sulfonate oxygen. Cd(1)–O(2) (2.873(6) Å) and Cd(3)–O(6) (2.775(5) Å) distances are much larger than all remaining Cd–O bonds which range from 2.213(6) to 2.517(6) Å. The Cd–N bonds are in the range 2.295(7)–2.361(7) Å. These distances are comparable with those in complex **1**. Similar to that in the layered lanthanide complexes,<sup>10b</sup> the carboxylate–sulfonate ligand in complex **2** acts as a pentadentate ligand, bridging with three cadmium(II) ions. This coordination mode is slightly different from that in complex **1**. Both carboxylate groups of ligand in complex **2** are bidentate chelating whereas one of the carboxylate groups in complex **1** is tridentate chelating and bridging. The bridging of cadmium(II) ions through bridging carboxylate–sulfonate ligands resulted in the formation of  $\langle 006 \rangle$  (Figure 5) and  $\langle 003 \rangle$  layers which are related by a mirror plane. The 2,2'-bipy molecules and  $[\text{Cd}(2)(2,2'\text{-bipy})_2(\text{H}_2\text{O})]$  cations are orientated to the interlayer space (Figure 5). The  $\text{Cd}(2)(2,2'\text{-bipy})_2(\text{H}_2\text{O})$  units are packed in such a way as to form a  $\langle 020 \rangle$  layer through weak  $\pi-\pi$  interactions between the pyridyl rings (Figure 6). The inter-ring distances are in the range 3.882–4.356 Å, and the corresponding dihedral angles between two pyridyl rings are 6.4 and 11.3°, respectively. The lattice water molecules are located at the cavities of the structure, forming a number of hydrogen bonds with noncoordinated sulfonate oxygen atoms as well as the aqua ligands (Table 2).

The structure of complex **3** features a 1D zinc(II) carboxylate double chain (Figure 7). The zinc(II) ion is octa-

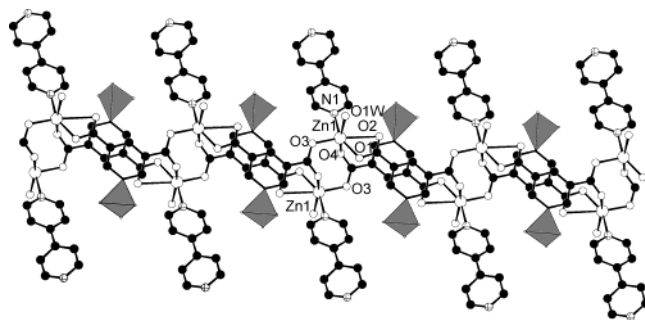
(13) (a) Zheng, Y.-Q.; Lin, J.-L. *Z. Kristallogr.—New Cryst. Struct.* **2000**, 215, 157. (b) Fleck, M.; Tillmannse, E.; Bohaty, L. *Z. Kristallogr.—New Cryst. Struct.* **2000**, 215, 619. (c) Zheng, Y.-Q.; Liu, W.-H.; Lin, J.-L. *Z. Anorg. Allg. Chem.* **2002**, 628, 620.



**Figure 5.** A  $\langle 003 \rangle$  layer of cadmium(II) sulfono-carboxylate in complex **2**. The  $\text{SO}_3\text{C}$  tetrahedra are shaded in gray, and Cd, C, and O atoms are drawn as open (large), black, and open (small) circles, respectively. The  $\text{Cd}(2)(2,2'\text{-bipy})_2(\text{H}_2\text{O})$  cations have been omitted for clarity.

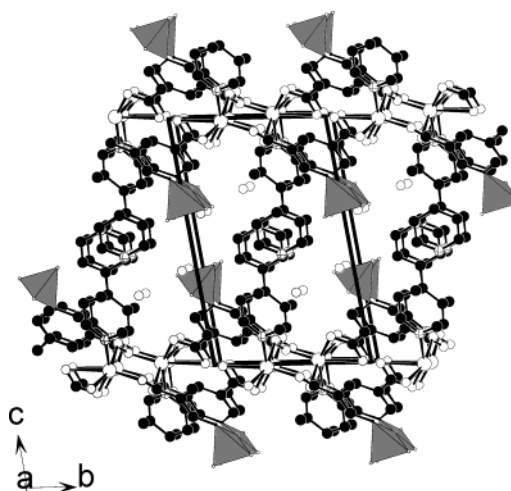


**Figure 6.** View of the structure of complex **2** down the  $a$ -axis. The  $\text{CSO}_3$  tetrahedra are shaded in gray. Cd, N, C, and O atoms are drawn as open (large), crossed, black, and open (small) circles, respectively.



**Figure 7.** A 1D metal carboxylate-sulfonate double chain of complex **3** along the diagonal of  $a$ - and  $b$ -axes. The  $\text{SO}_3\text{C}$  tetrahedra are shaded in gray, and Zn, N, C, and O atoms are drawn as open (large), crossed, black, and open (small) circles, respectively.

hedrally coordinated by four carboxylate oxygen atoms from three ligands, a unidentate 4,4'-bipy, and an aqua ligand. The  $\text{Zn}(1)\text{-O}(2)$  separation of  $2.622(5)$  Å is much longer than those of the remaining ones, which range from  $1.986(4)$  to  $2.222(5)$  Å. The  $\text{Zn}\text{-N}$  bond length is  $2.051(5)$  Å (Table 2).



**Figure 8.** View of structure of complex **3** down the  $a$ -axis. The  $\text{SO}_3\text{C}$  tetrahedra are shaded in gray, and Zn, N, C, and O atoms are drawn as open (large), crossed, black, and open (small) circles, respectively.

Those distances are comparable with those reported in other zinc(II) sulfonates.<sup>14</sup> Unlike that in complexes **1** and **2**, the carboxylate-sulfonate ligand adopts a different coordination mode: its sulfonate group remains noncoordinated; one carboxylate group chelates with a zinc(II) ion whereas the other one bridges with two Zn(II) ions. Similar to that in complex **1**, the 4,4'-bipy is assumed to be 1H-protonated for the sake of charge balance; this is similar to an acid-base reaction. A sulfonate group or a carboxylate group transfers its proton to the noncoordinated amine group, and the other two protons have been replaced by a zinc(II) cation.

Each pair of zinc(II) ions is bridged by a pair of carboxylate groups, forming an eight-membered ring, and each pair of such rings is interconnected by two carboxylate-sulfonate ligands to form a 1D double chain along the diagonal between the  $a$ - and  $b$ -axes. Within the double chain, there are also 16-membered rings which are formed by two zinc(II) ions and the carboxylate moieties of two ligands, which is similar to that found in complex **2**. These double chains are held together via hydrogen bonds as well as weak  $\pi\text{-}\pi$  interactions between the pyridyl rings, forming large pores. The distance between two neighboring parallel pyridyl rings is  $4.060$  Å. The sulfonate groups are orientated toward the pores; thus, such pores are hydrophilic (Figure 8). The lattice water molecules are located in the pore, forming hydrogen bonds with the aqua ligand and the protonated amine group of the 4,4'-bipy as well as the noncoordinated sulfonate oxygen atoms (Table 2). The strongest hydrogen bond is between the protonated pyridylamine and lattice water molecule (O(3w); symmetry operator:  $x - 2, y, z - 1$ ), with a bond distance of  $2.644(9)$  Å and a donor atom-acceptor angle of  $162.8^\circ$ .

The TGA diagram of complex **1** shows two steps of weight losses. The compound is stable up to  $310$  °C. The weight loss from  $310$  to  $625$  °C corresponds to the burning of the

(14) (a) Kimura, K.; Kimura, T.; Kinoshita, I.; Nakashima, N.; Kitano, K.; Nishioka, T.; Isobe, K. *Chem. Commun.* **1999**, 497. (b) Brandsch, T.; Schell, F.-A.; Weis, K.; Ruf, M.; Müller, B.; Vahrenkamp, H. *Chem. Ber.* **1997**, *130*, 283.

4,4-bipy and carboxylate–sulfonate. The second weight loss starts from 725 °C and continues up to 1000 °C, which corresponds to the further decomposing of the compound. The final product is CdSO<sub>4</sub>. The total weight loss of 59.6% matches with the calculated one (59.4%). The TGA curves of complex **2** also show two main weight losses. The first one from 111 to 180 °C corresponds to the loss of two lattice water molecules and two aqua ligands. The observed weight loss of 4.60% is in good agreement with the calculated value (4.74%). The dehydrated compound is stable up to 320 °C and then starts to decompose at 320 °C and continues on up to 1000 °C. The total weight loss of 62.0% is slightly less than the calculated one (64.2%) if the final product is assumed to be a mixture of CdSO<sub>4</sub> and CdO in a molar ratio of 2:1. The TGA curve of complex **3** indicates three main weight losses. The first one from 120 to 200 °C corresponds to the loss of two lattice water molecules and an aqua ligand. The observed weight loss of 9.3% is in agreement with the calculated one (10.4%). The dehydrated compound is stable up to 325 °C. The second weight loss from 325 to 630 °C

corresponds to the burning the organic groups. The third weight loss starts from 750 °C and continues up to 1000 °C, which corresponds to the decomposing of the compound. The total weight loss of 56.0% is much less than the calculated value of 69.0% if the final product is assumed to be ZnSO<sub>4</sub>; hence, the decomposing process is not complete due to the use of N<sub>2</sub> atmosphere.

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**Supporting Information Available:** X-ray crystallographic files for complexes **1–3** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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