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# Variation in the Coordination Mode of Arenedisulfonates: Syntheses and Structural Characterization of Mononuclear and Dinuclear Cadmium(II) Arenedisulfonate Complexes with Two- to Zero-Dimensional Architectures

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Seven cadmium(II) arenedisulfonate compounds, namely [Cd(2,2′-bpy)$_2$(H$_2$O)(peds)]·4H$_2$O (**1**), [Cd$_2$(2,2′-bpy)$_4$(H$_2$O)$_2$-(1,5nds)](1,5nds)·4H$_2$O (**2**), [Cd(cyclam)(1,5nds)]$_2$ (**3**), {[Cd(inia)$_2$(H$_2$O)$_2$(2,6nds)]·4H$_2$O}$_n$ (**4**), {[Cd(inia)$_2$(H$_2$O)$_2$(bpds)]·4H$_2$O}$_n$ (**5**), {[Cd$_2$(inia)$_4$(H$_2$O)$_3$(peds)$_2$]·2H$_2$O}$_n$ (**6**), and [Cd(1,5nds)(H$_2$O)$_2$]$_n$ (**7**), where 2,2′-bpy = 2,2′-bipyridyl, cyclam = 1,4,8,11-tetraazacyclotetradecane, inia = isonicotinamide, nds = naphthalenedisulfonate, bpds = 4,4′-biphenyldisulfonate, and peds = 4,4′-phenyletherdisulfonate, have been obtained from aqueous solution by using similar procedures and structurally characterized by X-ray single-crystal diffraction, IR spectroscopy, and thermal gravimetric analysis. In **1**, the peds anion coordinates as a monodentate ligand, leading to a mononuclear unit. In **2** and **3**, the 1,5nds anions coordinate as $\mu_2$-bridging ligands in different modes, producing charged or neutral dinuclear clusters. In **4** and **5**, 2,6nds and bpds behave as $\mu_2$-spacers, resulting in 1-dimensional polymers. While in **6**, the peds acts both as terminal and bridging ligands with the SO$_3^-$ groups being either monodentate or $\mu_2$-bridging, creating a knotted 1-dimensional polymer with dinuclear clusters as the repeating units. In **7**, 1,5nds acts as a bridging ligand with each SO$_3^-$ coordinated as a $\mu_2$-bridging group to adjacent Cd(II) centers, leading to a 2-dimensional polymer. Together with the reported {[Cu(en)$_2$(1,5nds)]·2H$_2$O}$_n$ (**8**), all of the six possible coordination modes adopted by organodisulfonate anions, on the assumption that each SO$_3^-$ group could be monodentate or $\mu_2$-bridging, are realized by introducing nitrogen-containing organic ligands as auxiliaries.

## Introduction

Previously, we have reported that arenedisulfonates can form inorganic−organic lamellar crystalline structures with Group IA and IIA metals,[1] similar to the pillared structures formed by metal phosphonates.[2] Also, a series of 1-dimensional coordination polymers constructed by divalent transition metals Cu(II)[3a] or Cd(II)[3b] and arenedisulfonates demonstrated that the coordination behavior of arenesulfonates with transition metals can be tailored by decorating the metal centers with other amino ligands. Inspired by these results, we initiated a systematic investigation on the coordination chemistry of organosulfonates, which is an attractive research subject for the following reasons: (1) the coordination chemistry of sulfonates is a less-well explored territory,[4] as is also indicated by the limited number of references on

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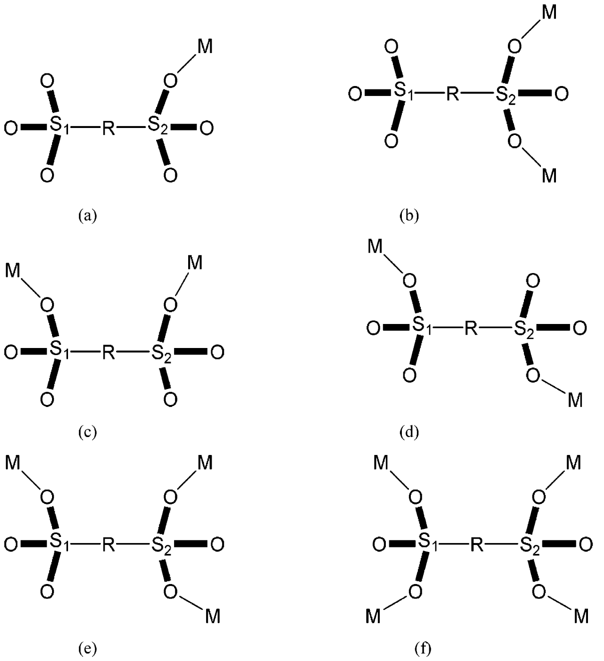
structures of metal sulfonates, and (2) sulfonate anions show weak coordination strength with transition metals. Most of the transition metal sulfonates obtained from aqueous solution are aqua-metal sulfonate salts.[5] However, after introducing other organic ligands as auxiliaries to the metal centers, sulfonate anions can compete with water molecules and coordinate with transition metals.[3] This observation indicates that the coordination strength of sulfonate anions is tunable. With the infinite number of organic ligands available, it opens up a novel research area that could produce numerous materials with interesting coordination and structural features; (2) metal sulfonate materials with potential absorption, inclusion and catalysis functionalities, similar to those reported for their structural analogues—metal phosphonates—could be built and identified, as demonstrated by the inspiring works of Shimizu[6] and others;[7] (3) arenedisulfonate anions are flexible spacers with potential multiple binding sites which can be used to construct coordination polymers with multiple dimensions and variant topologies, as demonstrated previously.[3]

The coordination mode of $SO_3^-$ with Group IA and IIA metal cations ranges from $\mu_3$ to $\mu_5$.[1] A bridging mode of $\mu_6$ was observed in a Ag(I) benzenesulfonate.[4,8] The maximum number of coordination sites provided by sulfonate $SO_3^-$ to divalent transition metal reported so far is two in a zirconocene(II)[9] sulfonate complex. As shown in Scheme 1, there are six possible coordination modes for arenedisulfonate anions represented as $SO_3{-}R{-}SO_3^{2-}$ if each $SO_3^-$ group could be monodentate or $\mu_2$-bridging. Among them, (d), the centro-symmetric trans $\mu_2$-bridging mode, is the most common one observed in our previously reported Cd(II) and Cu(II) compounds.[3]

Herein, we report that by decorating the Cd(II) center with different nitrogen-containing auxiliaries, i.e., 2,2′-bipyridyl (2,2′-bpdy), 1,4,8,11-tetraazacyclotetradecane (cyclam), and isoincotinamide (inia), arenedisulfonates anions, i.e., 1,5- or 2,6-naphthahlenedisulfonate (nds), 4,4′-biphenyldisulfonate (bpds), and 4,4′-phenyletherdisulfonate (peds), can achieve five of the above possible coordination modes and create a series of mononuclear and dinuclear compounds with dimensions ranging from two to zero. The sixth coordination mode, namely the cis $\mu_2$-bridging mode (c), was observed in $\{[Cu(en)_2(1{,}5nds)]{\cdot}2H_2O\}_n$ (**8**).[3a]

**Scheme 1.** Schematic Representation of the Six Possible Coordination Modes of the Disulfonate Anions, if Each $SO_3$− Group Could Be Monodentate or $\mu_2$-Bridging[a]



[a] The S−O bonds could be single or double depending on the nature of the coordination modes and are represented as thicker lines for simplification.

## Experimental Section

**Materials and Methods.** All materials were commercially available and used as received. 4,4′-Phenyletherdisulfonic acid is synthesized according to the method of the synthesis of 4,4′-biphenyldisulfonic acid.[10] Elemental analyses were carried out with an elemental Vario EL elemental analyzer. FTIR spectra were obtained on a Bruker EQUINOX 55 FTIR spectrometer with KBr pellets. TGA was performed with a Netzsch TG-209 analyzer under flowing nitrogen.

**Syntheses and Characterization.** Compounds **2**−**6** were prepared by using the same procedure as that of **1**.

**$[Cd(2{,}2'\text{-}bpy)_2(H_2O)(peds)]{\cdot}4H_2O$ (1):** An aqueous solution (20 mL) of 4,4′-phenthyletherdisulfonic acid (0.5 mmol) was added to $CdCO_3$ (0.08 g, 0.5 mmol) with heating in 60 °C and constant stirring, until all of the solid dissolved. To this solution was added 2,2′-bipyridyl (0.16 g, 1 mmol) with heating and stirring for another 30 min. Colorless crystals of **1** were collected after 2 days (70% yield based on Cd). Required for $C_{32}H_{34}N_4O_{12}S_2Cd$: C, 45.58, H, 4.06, N, 6.64. Found: C, 46.01, H, 4.04, N, 6.93. IR data ($cm^{-1}$, KBr): 3444 s, 3111 s, 3086 s, 2035 w, 1920 w, 1636 m, 1596 s, 1487 s, 1318 m, 1241 s, 1158 s, 1187 s, 1063 m, 1030 s, 1006 s, 910 w, 870 m, 839 m, 816 w, 772 s, 738 m, 707 s, 679 m, 632 m.

**$[Cd_2(2{,}2'\text{-}bpy)_4(H_2O)_2(1{,}5nds)](1{,}5nds){\cdot}4H_2O$ (2):** 20% yield based on Cd. Required for $C_{60}H_{56}N_8O_{18}S_4Cd_2$: C, 47.10, H, 3.69, N, 7.32. Found: C, 47.21, H, 3.87, N, 7.33.

**$[Cd(cyclam)(1{,}5nds)]_2$ (3):** 85% yield based on Cd. Required for $C_{20}H_{29}N_4O_6S_2Cd$: C, 40.17, H, 4.89, N, 9.37. Found: C, 40.54, H, 5.25, N, 9.59. IR data ($cm^{-1}$, KBr): 3451 w, 3240 s, 2843 s, 1969 w, 1914 w, 1848 w, 1629 w, 1585 w, 1499 m, 1455 m, 1387 w, 1336 m, 1253 s, 1223 s, 1181 s, 1103 s, 1034 s, 962 m, 925 m, 845 m, 801 m, 762 m, 664 w, 608 s.

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**Table 1.** Crystal Data and Structure Refinement for Compounds **1**−**7**

| | **1** | **2** | **3** | **4** | **5** | **6** | **7** |
|---|---|---|---|---|---|---|---|
| formula | $C_{32}H_{34}N_4O_{12}S_2Cd$ | $C_{30}H_{28}N_4O_9S_2Cd$ | $C_{20}H_{29}N_4O_6S_2Cd$ | $C_{22}H_{30}N_4O_{14}S_2Cd$ | $C_{24}H_{32}N_4O_{14}S_2Cd$ | $C_{24}H_{25}N_4O_{11.5}S_2Cd$ | $C_{10}H_{10}O_8S_2Cd$ |
| fw | 843.15 | 765.08 | 597.99 | 751.02 | 777.06 | 730.00 | 434.70 |
| cryst syst | monoclinic | triclinic | monoclinic | triclinic | triclinic | triclinic | triclinic |
| space group | $P2_1/n$ | $P\bar{1}$ | $P2_1/n$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$ (Å) | 14.666(8) | 9.7682(12) | 11.716(6) | 6.823(4) | 6.850(2) | 12.970(7) | 7.7501(15) |
| $b$ (Å) | 18.226(10) | 10.1641(13) | 16.535(8) | 10.356(6) | 10.611(6) | 15.006(8) | 8.0181(16) |
| $c$ (Å) | 15.118(8) | 16.576(2) | 12.435(6) | 11.366(6) | 11.861(8) | 16.528(9) | 21.348(4) |
| $\alpha$ (deg) | 90 | 74.679(2) | 90 | 65.739(9) | 73.90 | 66.000(9) | 94.950(4) |
| $\beta$ (deg) | 118.881(9) | 79.633(3) | 95.128(9) | 80.303(9) | 75.33 | 84.437(10) | 90.845(4) |
| $\gamma$ (deg) | 90 | 76.711(2) | 90 | 81.160(9) | 80.06(10) | 76.130(9) | 97.586(3) |
| $V$ (Å$^3$) | 3539(3) | 1532.3(3) | 2399(2) | 718.6(7) | 796.4(7) | 2853(3) | 1309.6(4) |
| $Z$ | 4 | 2 | 4 | 1 | 1 | 4 | 2 |
| $D_{calcd}$ (g/cm$^3$) | 1.583 | 1.658 | 1.656 | 1.736 | 1.620 | 1.699 | 1.102 |
| $\mu$ (mm$^{-1}$) | 0.803 | 0.911 | 1.128 | 0.981 | 0.888 | 0.980 | 1.012 |
| R1$^a$ $[I > 2\sigma(I)]$ | 0.0379 | 0.0369 | 0.0296 | 0.0558 | 0.0396 | 0.0379 | 0.0456 |
| wR2$^b$ $[I > 2\sigma(I)]$ | 0.0928 | 0.0746 | 0.0700 | 0.1597 | 0.1059 | 0.0966 | 0.1164 |

{**[Cd(inia)$_2$(H$_2$O)$_2$(2,6nds)]·4H$_2$O**}$_n$ **(4):** 75% yield based on Cd. Required for $C_{22}H_{30}N_4O_{14}S_2Cd$: C, 35.18, H, 4.03, N, 7.46. Found: C, 35.74, H, 3.96, N, 7.68. IR data (cm$^{-1}$, KBr): 3418 s, 3308 s, 3179 s, 3067 m, 2770 w, 1705 s, 1609 s, 1553 m, 1492 w, 1417 s, 1386 s, 1329 w, 1256 w, 1234 s, 1128 s, 1144 m, 1090 s, 1034 s, 965 w, 890 w, 847 w, 800 w, 762 m, 645 s, 625 s.

{**[Cd(inia)$_2$(H$_2$O)$_2$(bpds)]·4H$_2$O**}$_n$ **(5):** 85% yield based on Cd. Required for $C_{24}H_{32}N_4CdO_{14}S_2$: C, 37.10, H, 4.15, N, 7.21. Found: C, 37.53, H, 4.17, N, 7.42. IR data (cm$^{-1}$, KBr): 3417 s, 3308 s, 3178 s, 3067 m, 2770 w, 1706 s, 1611 s, 1554 m, 1485 w, 1416 s, 1384 s, 1195 s, 1130 s, 1040 s, 1001 m, 846 w, 819 m, 762 w, 726 s, 619 s.

{**[Cd$_2$(inia)$_4$(H$_2$O)$_3$(peds)$_2$]·2H$_2$O**}$_n$ **(6):** 70% yield based on Cd. Required for $C_{48}H_{50}N_8Cd_2O_{23}S_4$: C, 39.45, H, 3.45, N, 7.67. Found: C, 39.15, H, 3.68, N, 7.73. IR data (cm$^{-1}$, KBr): 3387 s, 3172 s, 2842 w, 2787 w, 2040 w, 1969 w, 1903 w, 1696 s, 1615 s, 1582 s, 1554 s, 1487 s, 1404 s, 1297 w, 1246 s, 1166 s, 1118 s, 1032 s, 1005 s, 859 m, 785 m, 709 s, 644 m.

**[Cd(1,5nds)(H$_2$O)$_2$]$_n$ (7):** An aqueous solution (15 mL) of hexadhydrate naphthalene-1,5-disulfonic acid (0.18 g, 0.5 mmol) was added to $CdCO_3$ (0.08 g, 0.5 mmol) with heating at 60 °C and constant stirring, until all of the solid dissolved. The resulting solution was set out at room temperature in an open beaker. After 6 days, platelike colorless crystals were collected (70% yield based on Cd). Required for $C_{10}H_{10}O_8S_2Cd_2$: C, 27.63; H, 2.32. Found: C, 27.75; H, 2.71. IR data (cm$^{-1}$, KBr): 3379 s, 3237 m, 3100 w, 3067 w, 1969 w, 1903 w, 1843 w, 1604 m, 1502 m, 1246 s, 1222 s, 1172 s, 1151 s, 1049 s, 926 w, 794 s, 769 s, 660 w, 605 s.

TGA results are listed as a table and provided as Supporting Information.

**Crystallography.** Experimental details of the X-ray analyses are provided in Table 1. Diffraction data were collected on a Bruker Smart 1000 CCD or Enraf-Nonius CAD4 diffractometer equipped with graphite monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å) at room temperature. In all cases, the structures were solved by direct methods and refined by using full-matrix least-squares/difference Fourier techniques with SHELXTL.[11] All non-hydrogen atoms were refined with anisotropic displacement parameters. After that, all hydrogen atoms of the ligands were placed at idealized positions and refined as riding atoms with the relative isotropic parameters of the heavy atoms to which they are attached. Hydrogen atoms of some water molecules were located from the difference Fourier map at the final state of refinement and refined as fixed atoms. Selective bond distances and angles are listed in Table 2. Hydrogen bonds are listed in Table 3. The hydrogen atoms of water molecules in **7** could not be located from the different Fourier map; therefore, no hydrogen bonds can be calculated.

In compound **2**, the 1,5nds counteranion is disordered over two sites with 55.7 and 44.3% occupancies. The two naphthalene planes are tilted by 1.4°.

## Results and Discussion

**Syntheses.** All the above crystalline materials were obtained from aqueous solution by using the same procedure, and metal-to-sulfonate stoichiometric ratio, as that reported for the 1-dimensional Cd(II) arenedisulfonate polymers.[3b] Only **4** and **5** were the expected 1-dimensional coordination polymers with repeating mononuclear units. This suggests that the various coordination modes of both the Cd(II) cation and disulfonate anions are controlled by the nature of the organic R groups of the sulfonate anions and the N-containing auxiliaries, instead of reaction conditions. In **1** and **2**, with the same auxiliary 2,2′-bpy, when the flexible and nonlinear peds was altered to rigid and linear 1,5nds (with the two S−C bonds antiparallel to each other), a dinuclear cluster cation was generated, instead of a neutral mononuclear unit. Another type of neutral dinuclear cluster was observed in **3** when the two 2,2′-bpy were replaced by one, less bulkier, cyclam. The most dramatic change was observed in **4**, **5**, and **6**. When the spacer was altered from linear 2,6nds/bpds to nonlinear peds (where the two phenyl rings display more conformational freedom, compared with that of bpds), the coordination and linking features were diversified, unpredictably, from the centrosymmetric trans $\mu_2$-bridging mode (d) to noncentrosymmetric modes (b) and (e).

**Spectral Characterization and Thermal Analyses.** The IR spectra show the N−H and H−O−H stretching vibrations at 3100−3500 cm$^{-1}$ for **1** and **3**−**7**. The well-resolved frequencies of aromatic rings span over the regions of 1250−1750 and 600−900 cm$^{-1}$. Bands characteristic of the fundamental and split $\nu_3$ S−O stretching modes are observed in the range of 1000−1240 cm$^{-1}$.[3]

TGA analysis showed that the first weight losses for compounds **1**, **2**, **4**, **5**, and **6** were recorded at 50−96, 70−100, 60−120, 60−89, and 58−82 °C, respectively,

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**Table 2.** Selected Bond Distances(Å) and Angles (deg) for Compounds **1**−**7**[a]

[Cd(2,2′-bpy)$_2$(H$_2$O)(peds)]·4H$_2$O (**1**)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cd(1)−O(1) | 2.279(3) | Cd(1)−N(2) | 2.320(3) | S(1)−O(1) | 1.467(3) | S(1)−C(30) | 1.772(4) |
| Cd(1)−O(5W) | 2.277(3) | Cd(1)−N(3) | 2.334(3) | S(1)−O(2) | 1.440(3) | | |
| Cd(1)−N(1) | 2.384(3) | Cd(1)−N(4) | 2.338(3) | S(1)−O(3) | 1.445(3) | | |
| O(1)−Cd(1)−O(5W) | 84.63(13) | O(1)−Cd(1)−N(2) | 97.90(10) | O(1)−Cd(1)−N(4) | 98.29(10) | O(1)−S(1)−O(3) | 112.27(18) |
| O(1)−Cd(1)−N(1) | 167.66(9) | O(5W)−Cd(1)−N(2) | 93.86(15) | O(5W)−Cd(1)−N(4) | 168.34(13) | O(2)−S(1)−O(3) | 113.29(18) |
| O(5W)−Cd(1)−N(1) | 90.77(14) | O(1)−Cd(1)−N(3) | 103.00(9) | N(2)−Cd(1)−N(4) | 96.90(10) | O(1)−S(1)−C(30) | 105.76(15) |
| N(2)−Cd(1)−N(1) | 70.94(9) | O(5W)−Cd(1)−N(3) | 96.83(14) | N(3)−Cd(1)−N(4) | 71.52(10) | O(2)−S(1)−C(30) | 107.04(16) |
| N(3)−Cd(1)−N(1) | 88.89(9) | N(2)−Cd(1)−N(3) | 157.29(10) | O(1)−S(1)−O(2) | 110.93(17) | O(3)−S(1)−C(30) | 107.04(17) |
| N(4)−Cd(1)−N(1) | 88.51(10) | | | | | | |

[Cd$_2$(2,2′-bpy)$_4$(H$_2$O)$_2$(1,5nds)](1,5nds)·4H$_2$O (**2**)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cd(1)−O(1W) | 2.261(3) | Cd(1)−N(2) | 2.337(3) | S(1)−O(1) | 1.467(2) | S(1)−C(22) | 1.784(3) |
| Cd(1)−O(1) | 2.320(2) | Cd(1)−N(3) | 2.344(3) | S(1)−O(2) | 1.451(2) | | |
| Cd(1)−N(1) | 2.348(3) | Cd(1)−N(4) | 2.328(3) | S(1)−O(3) | 1.445(2) | | |
| O(1)−Cd(1)−N(1) | 89.03(8) | O(1W)−Cd(1)−N(3) | 99.00(11) | N(1)−Cd(1)−N(4) | 101.12(9) | O(1)−S(1)−O(3) | 112.24(14) |
| O(1)−Cd(1)−N(2) | 101.34(9) | O(1W)−Cd(1)−N(4) | 96.50(11) | N(2)−Cd(1)−N(3) | 95.21(9) | O(2)−S(1)−O(3) | 113.77(16) |
| O(1)−Cd(1)−N(3) | 163.45(8) | O(1W)−Cd(1)−O(1) | 79.90(10) | N(2)−Cd(1)−N(4) | 163.77(9) | O(1)−S(1)−C(22) | 107.22(14) |
| O(1)−Cd(1)−N(4) | 92.36(9) | N(1)−Cd(1)−N(2) | 70.77(9) | N(3)−Cd(1)−N(4) | 71.29(9) | O(2)−S(1)−C(22) | 105.13(14) |
| O(1W)−Cd(1)−N(1) | 159.55(11) | N(1)−Cd(1)−N(3) | 96.43(9) | O(1)−S(1)−O(2) | 111.13(15) | O(3)−S(1)−C(22) | 106.79(15) |
| O(1W)−Cd(1)−N(2) | 94.45(11) | | | | | | |

[Cd(cyclam)(1,5nds)]$_2$ (**3**)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cd(1)−O(5)$^{i}$ | 2.281(2) | Cd(1)−N(2) | 2.329(3) | S(2)−O(4) | 1.449(2) | S(2)−C(18) | 1.780(3) |
| Cd(1)−O(4) | 2.313(2) | Cd(1)−N(3) | 2.283(3) | S(2)−O(5) | 1.456(2) | | |
| Cd(1)−N(1) | 2.302(3) | Cd(1)−N(4) | 2.340(3) | S(2)−O(6) | 1.424(3) | | |
| O(4)−Cd(1)−N(1) | 100.44(10) | O(5)$^{i}$−Cd(1)−N(2) | 175.77(10) | N(1)−Cd(1)−N(4) | 77.40(11) | O(4)−S(2)−O(6) | 114.09(16) |
| O(4)−Cd(1)−N(2) | 82.31(8) | O(5)$^{i}$−Cd(1)−N(3) | 106.24(11) | N(2)−Cd(1)−N(3) | 77.97(11) | O(5)−S(2)−O(6) | 113.72(16) |
| O(4)−Cd(1)−N(3) | 93.39(10) | O(5)$^{i}$−Cd(1)−N(4) | 86.66(9) | N(2)−Cd(1)−N(4) | 93.94(9) | O(4)−S(2)−C(18) | 105.48(14) |
| O(4)−Cd(1)−N(4) | 175.75(9) | N(1)−Cd(1)−N(2) | 88.57(12) | N(3)−Cd(1)−N(4) | 87.75(10) | O(5)−S(2)−C(18) | 104.85(14) |
| O(5)$^{i}$−Cd(1)−O(4) | 96.94(8) | N(1)−Cd(1)−N(3) | 159.26(10) | O(4)−S(2)−O(5) | 110.51(15) | O(6)−S(2)−C(18) | 107.35(15) |
| O(5)$^{i}$−Cd(1)−N(1) | 87.47(11) | | | | | | |

{[Cd(inia)$_2$(H$_2$O)$_2$(2,6nds)]·4H$_2$O}$_n$ (**4**)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cd(1)−N(1) | 2.284(4) | Cd(1)−O(1) | 2.329(3) | S(1)−O(1) | 1.461(4) | S(1)−O(3) | 1.440(4) |
| Cd(1)−O(1W) | 2.294(4) | S(1)−C(3) | 1.768(4) | S(1)−O(2) | 1.435(4) | | |
| N(1)−Cd(1)−N(1)$^{i}$ | 180.000(1) | N(1)−Cd(1)−O(1W)$^{i}$ | 92.86(14) | O(1W)−Cd(1)−O(1W)$^{i}$ | 180.000(1) | O(1)−S(1)−C(3) | 104.6(2) |
| N(1)−Cd(1)−O(1) | 89.15(13) | O(1)−Cd(1)−O(1)$^{i}$ | 180.000(1) | O(1)−S(1)−O(2) | 112.6(3) | O(2)−S(1)−C(3) | 108.4(2) |
| N(1)−Cd(1)−O(1)$^{i}$ | 90.85(13) | O(1)−Cd(1)−O(1W) | 82.11(15) | O(1)−S(1)−O(3) | 110.6(2) | O(3)−S(1)−C(3) | 106.0(2) |
| N(1)−Cd(1)−O(1W) | 87.14(14) | O(1)−Cd(1)−O(1W)$^{i}$ | 97.89(15) | O(2)−S(1)−O(3) | 114.0(3) | | |

{[Cd(inia)$_2$(H$_2$O)$_2$(bpds)]·4H$_2$O}$_n$ (**5**)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cd(1)−N(1) | 2.298(3) | Cd(1)−O(3W) | 2.309(3) | S(1)−O(1) | 1.471(3) | S(1)−O(3) | 1.447(3) |
| Cd(1)−O(1) | 2.343(2) | S(1)−C(1) | 1.775(3) | S(1)−O(2) | 1.458(3) | | |
| N(1)−Cd(1)−N(1)$^{i}$ | 180.0 | N(1)−Cd(1)−O(3W)$^{i}$ | 91.86(10) | O(3W)−Cd(1)−O(3W)$^{i}$ | 180.000(1) | O(1)−S(1)−C(1) | 105.37(15) |
| N(1)−Cd(1)−O(1) | 89.09(9) | O(1)−Cd(1)−O(1)$^{i}$ | 180.0 | O(1)−S(1)−O(2) | 110.23(16) | O(2)−S(1)−C(1) | 106.71(15) |
| N(1)$^{i}$−Cd(1)−O(1) | 90.91(9) | O(1)−Cd(1)−O(3W) | 81.79(11) | O(1)−S(1)−O(3) | 112.74(19) | O(3)−S(1)−C(1) | 106.80(16) |
| N(1)−Cd(1)−O(3W) | 88.14(10) | O(1)−Cd(1)−O(3W)$^{i}$ | 98.21(11) | O(2)−S(1)−O(3) | 114.34(18) | | |

{[Cd$_2$(inia)$_4$(H$_2$O)$_3$(peds)$_2$]·2H$_2$O}$_n$ (**6**)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cd(1)−N(1) | 2.283(3) | Cd(2)−N(5) | 2.286(3) | S(1)−O(1)$^{ii}$ | 1.459(3) | S(2)−O(12) | 1.441(3) |
| Cd(1)−N(3) | 2.308(3) | Cd(2)−N(7) | 2.267(3) | S(1)−O(2) | 1.455(3) | S(2)−C(37) | 1.776(4) |
| Cd(1)−O(1) | 2.383(3) | Cd(2)−O(14)$^{i}$ | 2.339(3) | S(1)−O(6) | 1.434(3) | S(4)−O(15) | 1.432(3) |
| Cd(1)−O(2) | 2.336(3) | Cd(2)−O(16) | 2.361(3) | S(1)−C(30) | 1.761(4) | S(4)−O(14) | 1.448(3) |
| Cd(1)−O(3) | 2.288(3) | Cd(2)−O(4W) | 2.299(3) | S(2)−O(3) | 1.465(3) | S(4)−O(16) | 1.450(3) |
| Cd(1)−O(3W) | 2.265(3) | Cd(2)−O(5W) | 2.318(3) | S(2)−O(11) | 1.437(3) | S(4)−C(46) | 1.765(4) |
| N(1)−Cd(1)−N(3) | 171.31(11) | O(1)−Cd(1)−O(2) | 89.03(11) | O(4W)−Cd(2)−O(14)$^{i}$ | 166.64(11) | O(3)−S(2)−O(11) | 111.17(18) |
| N(1)−Cd(1)−O(1) | 88.35(11) | O(1)−Cd(1)−O(3) | 84.03(10) | O(4W)−Cd(2)−O(16) | 79.23(11) | O(3)−S(2)−O(12) | 110.71(18) |
| N(1)−Cd(1)−O(2) | 91.59(10) | O(2)−Cd(1)−O(3) | 172.52(10) | O(4W)−Cd(2)−O(5W) | 89.92(12) | O(11)−S(2)−O(12) | 114.89(19) |
| N(1)−Cd(1)−O(3) | 91.00(10) | N(5)−Cd(2)−N(7) | 173.91(11) | O(5W)−Cd(2)−O(14)$^{i}$ | 84.61(13) | O(3)−S(2)−C(37) | 105.22(16) |
| N(1)−Cd(1)−O(3W) | 94.39(12) | N(5)−Cd(2)−O(14)$^{i}$ | 93.17(11) | O(5W)−Cd(2)−O(16) | 166.41(11) | O(11)−S(2)−C(37) | 106.91(18) |
| N(3)−Cd(1)−O(1) | 83.78(10) | N(5)−Cd(2)−O(16) | 86.02(11) | O(14)$^{i}$−Cd(2)−O(16) | 107.70(12) | O(12)−S(2)−C(37) | 107.34(17) |
| N(3)−Cd(1)−O(2) | 84.61(10) | N(5)−Cd(2)−O(4W) | 98.78(11) | O(2)−S(1)−O(6) | 112.25(17) | O(14)−S(4)−O(16) | 110.02(19) |
| N(3)−Cd(1)−O(3) | 91.84(10) | N(5)−Cd(2)−O(5W) | 87.59(12) | O(2)−S(1)−O(1)$^{ii}$ | 112.26(17) | O(14)−S(4)−O(15) | 113.7(2) |
| N(3)−Cd(1)−O(3W) | 93.71(12) | N(7)−Cd(2)−O(14)$^{i}$ | 83.39(11) | O(6)−S(1)−O(1)$^{ii}$ | 112.33(19) | O(15)−S(4)−O(16) | 112.03(19) |
| O(3W)−Cd(1)−O(1) | 175.47(11) | N(7)−Cd(2)−O(16) | 90.23(11) | O(1)$^{ii}$−S(1)−C(30) | 105.71(16) | O(14)−S(4)−C(46) | 107.42(17) |
| O(3W)−Cd(1)−O(2) | 94.50(12) | N(7)−Cd(2)−O(4W) | 85.20(11) | O(2)−S(1)−C(30) | 106.46(17) | O(15)−S(4)−C(46) | 107.21(17) |
| O(3W)−Cd(1)−O(3) | 92.29(12) | N(7)−Cd(2)−O(5W) | 97.06(12) | O(6)−S(1)−C(30) | 107.29(18) | O(16)−S(4)−C(46) | 106.02(16) |

[Cd(1,5nds)(H$_2$O)$_2$]$_n$ (**7**)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cd(1)−O(1)$^{i}$ | 2.273(3) | Cd(2)−O(7)$^{i}$ | 2.284(2) | S(1)−O(3) | 1.456(3) | S(3)−O(8) | 1.445(3) |
| Cd(1)−O(2) | 2.264(2) | Cd(2)−O(15) | 2.246(3) | S(1)−C(1) | 1.766(3) | S(3)−O(9) | 1.470(2) |
| Cd(1)−O(10) | 2.338(2) | Cd(3)−O(6) | 2.250(3) | S(2)−O(4) | 1.455(3) | S(3)−C(11) | 1.772(3) |
| Cd(1)−O(12)$^{ii}$ | 2.279(2) | Cd(3)−O(9)$^{ii}$ | 2.342(2) | S(2)−O(5) | 1.459(2) | S(4)−O(10) | 1.472(2) |
| Cd(1)−O(13) | 2.240(3) | Cd(3)−O(16) | 2.224(3) | S(2)−O(6) | 1.447(3) | S(4)−O(11) | 1.442(3) |
| Cd(1)−O(14) | 2.220(3) | S(1)−O(1) | 1.445(3) | S(2)−C(6) | 1.766(3) | S(4)−O(12) | 1.457(3) |
| Cd(2)−O(5) | 2.277(2) | S(1)−O(2) | 1.457(2) | S(3)−O(7) | 1.453(3) | S(4)−C(14) | 1.778(3) |

**Table 2** (Continued)

| [Cd(1,5nds)($H_2O$)$_2$]$_n$ (**7**) | | | | | | | |
|---|---|---|---|---|---|---|---|
| O(1)$^{i}$−Cd(1)−O(2) | 90.00(9) | O(12)$^{ii}$−Cd(1)−O(14) | 95.11(10) | O(6)−Cd(3)−O(9)$^{iv}$ | 94.81(9) | O(3)−S(1)−C(1) | 106.59(16) |
| O(1)$^{i}$−Cd(1)−O(10) | 85.05(9) | O(13)−Cd(1)−O(14) | 176.37(10) | O(6)−Cd(3)−O(9)$^{ii}$ | 85.19(9) | O(4)−S(2)−O(5) | 111.62(17) |
| O(1)$^{i}$−Cd(1)−O(12)$^{ii}$ | 177.91(8) | O(5)−Cd(2)−O(5)$^{iii}$ | 180.000(1) | O(6)−Cd(3)−O(16) | 86.21(11) | O(6)−S(2)−O(4) | 113.36(18) |
| O(1)$^{i}$−Cd(1)−O(13) | 96.99(11) | O(5)−Cd(2)−O(7)$^{i}$ | 87.74(9) | O(6)$^{v}$−Cd(3)−O(16) | 93.79(11) | O(6)−S(2)−O(5) | 112.16(16) |
| O(1)$^{i}$−Cd(1)−O(14) | 86.23(11) | O(5)−Cd(2)−O(7)$^{iv}$ | 92.26(9) | O(9)$^{iv}$−Cd(3)−O(9)$^{ii}$ | 180.000(1) | O(4)−S(2)−C(6) | 106.78(16) |
| O(2)−Cd(1)−O(12)$^{ii}$ | 88.28(9) | O(5)−Cd(2)−O(15) | 87.64(11) | O(9)$^{iv}$−Cd(3)−O(16) | 90.96(9) | O(5)−S(2)−C(6) | 106.43(15) |
| O(2)−Cd(1)−O(13) | 85.96(11) | O(5)$^{iii}$−Cd(2)−O(15) | 92.36(11) | O(9)$^{ii}$−Cd(3)−O(16) | 89.04(9) | O(6)−S(2)−C(6) | 105.91(16) |
| O(2)−Cd(1)−O(14) | 95.75(11) | O(5)$^{iii}$−Cd(2)−O(15)$^{iii}$ | 87.64(11) | O(16)−Cd(3)−O(16)$^{v}$ | 180.00(12) | O(11)−S(4)−O(12) | 114.45(16) |
| O(2)−Cd(1)−O(10) | 171.55(9) | O(7)$^{iv}$−Cd(2)−O(7)$^{i}$ | 180.000(1) | O(1)−S(1)−O(2) | 112.56(16) | O(10)−S(4)−O(11) | 111.91(16) |
| O(10)−Cd(1)−O(12)$^{ii}$ | 96.52(9) | O(7)$^{i}$−Cd(2)−O(15) | 81.92(10) | O(1)−S(1)−O(3) | 113.47(18) | O(10)−S(4)−O(12) | 110.31(14) |
| O(10)−Cd(1)−O(13) | 87.83(10) | O(7)$^{iv}$−Cd(2)−O(15) | 98.08(10) | O(2)−S(1)−O(3) | 111.36(17) | O(10)−S(4)−C(14) | 106.92(15) |
| O(10)−Cd(1)−O(14) | 90.77(10) | O(15)−Cd(2)−O(15)$^{iii}$ | 180.00(14) | O(1)−S(1)−C(1) | 106.05(16) | O(11)−S(4)−C(14) | 106.92(15) |
| O(12)$^{ii}$−Cd(1)−O(13) | 81.72(10) | O(6)−Cd(3)−O(6)$^{v}$ | 180.0 | O(2)−S(1)−C(1) | 106.20(15) | O(12)−S(4)−C(14) | 105.80(15) |

[a] Symmetry code for **3**: (*i*) $-x, -y + 2, -z + 1$. Symmetry code for **4**: (*i*) $-x - 1, -y + 1, -z + 3$. Symmetry code for **5**: (*i*) $-x, -y, -z + 2$. Symmetry code for **6**: (*i*) $-x + 1, -y - 1, -z + 1$; (*ii*) $-x, -y + 1, -z$. Symmetry code for **7**: (*i*) $-x + 1, -y + 1, -z$; (*ii*) $-x, -y, -z$; (*iii*) $-x + 2, -y + 1, -z + 1$; (*iv*) $x + 1, y, z + 1$; (*v*) $-x + 1, -y, -z + 1$.

corresponding to the loss of lattice water molecules. **3** is stable up to 370 °C. While for compound **7**, the release of coordinated water molecules was recorded at 163−262 °C, followed by another weight loss at 528 °C.

**Coordination Geometry of the Cd(II) Centers.** The Cd(II) cations in all compounds are 6-coordinated with octahedral geometry distorted to different degrees. The distances between Cd(II) and the coordinate sulfonate oxygen (∼2.3 Å) are very consistent. Both the syn and anti[12] coordination modes of the metal sulfonate fragments are observed in these compounds. The most diverse geometrical parameter around the Cd(II) coordination core is the planarity of the C−S−O−Cd fragment, represented as the absolute value of $90 - |\theta|$ ($\theta$ = torsion angle of C−S−O−Cd), the smaller the more planar. It ranges from 1.4 (in **6**) to 70.2° (in **3**).

**Description of the Structures. The mononuclear unit [Cd(2,2′-bpy)$_2$($H_2O$)(peds)]·4$H_2O$ (1)−coordination mode (a):** Cd(II) is coordinated by four nitrogen atoms from two 2,2′-bpy ligands in cis fashion, one water molecule and one $SO_3^-$ oxygen atom of the peds anion; however, the $SO_3^-$ group on the other end of the peds ligand is not anchored by any covalent bond. The overall structure of the unit is very “polar”, carrying positive and negative charges at the metal center and the ligand, respectively. The noncoordinated $SO_3^-$ group is stabilized by two water molecules by strong hydrogen bonds, as shown in Figure 1a. Four $SO_3^-$ groups from four coordination units form a hydrophilic cavity that hosts a water cluster, as shown in Figure 1b. The peds ligand is highly twisted, with a dihedral angle of 71.1° formed between the planes of the two phenyl rings.

**The dinuclear cluster [Cd$_2$(2,2′-bpy)$_4$($H_2O$)$_2$(1,5nds)](1,5nds)·4$H_2O$ (2)−coordinaion mode (d):** Each of the Cd(II) centers has a similar coordination environment as that in **1**. However, both the $SO_3^-$ groups coordinate with Cd(II), monodentately, in trans fashion, resulting in a dinuclear cation, as shown in Figure 2a. The two 2,2′-bpy and naphthalene planes are almost coplanar. The dihedral angle of the planes is 3.5° and the distance is 3.4 Å, indicative of significant intramolecular $\pi-\pi$ stacking. The free 1,5nds anions connect two dinuclear clusters via hydrogen bonds formed by the coordinated water molecules and $SO_3^-$ oxygens, extending the dinuclear clusters into 1-dimensional chains, as shown in Figure 2b.

**The neutral dinuclear cluster [Cd(cyclam)(1,5nds)]$_2$ (3)−coordination mode (b):** Cd(II) is six-coordinated by four nitrogen atoms from one cyclam ligand in cis fashion and two $SO_3^-$ oxygen atoms from two different 1,5nds anions. The Cd(II) centers are double-bridged by two $\mu_2$-$SO_3^-$ groups, resulting a dinuclear cluster, as illustrated in Figure 3a. The cis coordination mode of the cyclam ligand is only reported in a limited number of compounds.[13] Also, it is the first example observed in Cd(II) complexes. 1,5nds adopts a terminal $\mu_2$-bridging mode connecting two Cd(II) centers, with Cd···Cd = 5.39 Å. It is interesting to note that when the metal center in [Cu(cyclam)(1,5nds)]$_n$ [3a] was substituted by Cd(II), the resulting structure changes from a 1-dimensional polymer, in which 1,5nds is a $\mu_2$-bifunctional spacer, to a dinuclear cluster. The coordination environment of Cd(II) can be described as a highly distorted octahedron, with the cis bond angles ranging from 77.40(11) to 106.24(11)° and the trans bond angles from 159.26(10) to 175.77(10)°. The two noncoordinated $SO_3^-$ groups of the cluster are anchored by strong intermolecular hydrogen bonds with the amino hydrogen atoms of adjacent clusters, as shown in Figure 3b, leading to 1-dimensional chains which are further extended into the 3-dimensional network through extensive interchain hydrogen bonds.

**The 1-dimensional chain {[Cd(inia)$_2$($H_2O$)$_2$(2,6nds)]·4$H_2O$}$_n$ (4) and the {[Cd(inia)$_2$($H_2O$)$_2$(bpds)]·4$H_2O$}$_n$ (5)−coordination mode (d): 4** and **5** have very similiar metal coordination structures and packing arrangement. The Cd(II) centers are located on inversion centers and adopt a slightly distorted octahedral geometry. Two water molecules, two isonicotinamide, and two $SO_3^-$ groups coordinate in trans fashion. The 2,6nds/bpds anions behave as bifunctional spacers coordinated trans to two Cd(II) centers, resulting in steplike one-dimensional coordination polymers. Adjacent chains are connected by N−H···O hydrogen bonds formed

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**Table 3.** Selected Hydrogen Bond Interactions for Compounds **1**−**6** (Å, deg)

| D−H···A | *d*(D−H) | *d*(H···A) | *d*(D···A) | ∠(DHA) |
|---|---|---|---|---|
| $[Cd(2,2'\text{-}bpy)_2(H_2O)(peds)]\cdot 4H_2O$ (**1**) | | | | |
| O(1W)−H(1WA)···O(4W)$^{i}$ | 1.04 | 1.97 | 3.017(16) | 176.2 |
| O(1W)−H(1WB)···O(5) | 1.06 | 1.96 | 2.803(6) | 134.0 |
| O(2W)−H(2WA)···O(6) | 1.00 | 1.84 | 2.825(6) | 171.5 |
| O(2W)−H(2WB)···O(3W)$^{ii}$ | 1.05 | 2.16 | 2.716(8) | 110.3 |
| O(5W)−H(5WA)···O(3W)$^{iii}$ | 0.82 | 2.47 | 3.291(8) | 177.7 |
| O(5W)−H(5WB)···O(4)$^{iv}$ | 0.87 | 1.93 | 2.715(5) | 149.4 |
| $[Cd_2(2,2'\text{-}bpy)_4(H_2O)_2(1,5nds)](1,5nds)\cdot 4H_2O$ (**2**) | | | | |
| O(1W)−H(1W1)···O(4) | 0.846(10) | 1.85(2) | 2.665(5) | 163(5) |
| O(1W)−H(1W1)···O(4′) | 0.846(10) | 2.10(4) | 2.821(9) | 143(5) |
| O(1W)−H(1W2)···O(2W) | 0.850(10) | 1.886(13) | 2.734(5) | 176(7) |
| O(2W)−H(2W1)···O(5)$^{i}$ | 0.848(10) | 2.03(3) | 2.834(9) | 159(6) |
| O(2W)−H(2W1)···O(5′)$^{i}$ | 0.848(10) | 1.90(3) | 2.684(12) | 152(5) |
| O(2W)−H(2W2)···O(3W) | 0.848(10) | 2.029(17) | 2.867(7) | 170(7) |
| O(3W)−H(3W1)···O(6)$^{ii}$ | 0.844(10) | 2.21(2) | 3.010(8) | 158(5) |
| O(3W)−H(3W1)···O(6′)$^{ii}$ | 0.844(10) | 1.86(3) | 2.637(8) | 153(5) |
| $[Cd(cyclam)(1,5nds)]_2$ (**3**) | | | | |
| N(1)−H(1C)···O(1)$^{i}$ | 0.91 | 2.14 | 2.980(4) | 153.5 |
| N(2)−H(2B)···O(2)$^{ii}$ | 0.91 | 2.10 | 2.969(4) | 160.5 |
| N(3)−H(3C)···O(3)$^{iii}$ | 0.91 | 2.03 | 2.890(4) | 157.3 |
| N(4)−H(4C)···O(2)$^{ii}$ | 0.91 | 2.08 | 2.959(4) | 160.7 |
| $\{[Cd(inia)_2(H_2O)_2(2,6nds)]\cdot 4H_2O\}_n$ (**4**) | | | | |
| O(1W)−H(1WA)···O(3)$^{i}$ | 0.84(7) | 1.98(7) | 2.810(5) | 174(7) |
| O(1W)−H(1WB)···O(2W)$^{ii}$ | 0.88(8) | 1.85(8) | 2.720(6) | 171(7) |
| O(2W)−H(2WA)···O(4)$^{iii}$ | 0.75(7) | 1.94(7) | 2.695(6) | 177(7) |
| O(2W)−H(2WB)···O(3W)$^{iv}$ | 0.70(12) | 2.22(13) | 2.916(9) | 171(13) |
| O(2W)−H(2WB)···O(3W)$^{v}$ | 0.70(12) | 2.53(12) | 2.891(9) | 114(12) |
| N(2)−H(2B)···O(2)$^{vi}$ | 0.86 | 2.20 | 3.047(6) | 169.1 |
| N(2)−H(2C)···O(2W)$^{vii}$ | 0.86 | 2.13 | 2.953(7) | 159.3 |
| $\{[Cd(inia)_2(H_2O)_2(bpds)]\cdot 4H_2O\}_n$ (**5**) | | | | |
| O(1W)−H(1WA)···O(4)$^{i}$ | 0.86(6) | 1.87(6) | 2.708(4) | 166(6) |
| O(1W)−H(1WB)···O(2W) | 0.87(5) | 1.86(5) | 2.729(6) | 178(4) |
| O(2W)−H(2WA)···O(2) | 0.67(9) | 2.28(8) | 2.931(6) | 164(11) |
| O(2W)−H(2WB)···O(3)$^{ii}$ | 1.18(10) | 1.76(10) | 2.823(6) | 146(7) |
| O(3W)−H(3WA)···O(1W)$^{iii}$ | 0.90(5) | 1.84(5) | 2.732(4) | 172(5) |
| O(3W)−H(3WB)···O(2)$^{iv}$ | 0.72(5) | 2.11(5) | 2.825(4) | 168(5) |
| N(2)−H(2B)···O(3)$^{v}$ | 0.86 | 2.19 | 3.036(4) | 167.0 |
| N(2)−H(2C)···O(1W)$^{vi}$ | 0.86 | 2.14 | 2.961(5) | 159.2 |
| $\{[Cd_2(inia)_4(H_2O)_3(peds)_2]\cdot 2H_2O\}_n$ (**6**) | | | | |
| O(1W)−H(1WA)···O(6)$^{ii}$ | 0.75 | 2.00 | 2.742(5) | 169.7 |
| O(1W)−H(1WB)···O(9)$^{iii}$ | 0.84 | 2.08 | 2.876(5) | 157.9 |
| O(2W)−H(2WA)···O(15)$^{iv}$ | 1.11 | 1.70 | 2.809(6) | 176.7 |
| O(2W)−H(2WB)···O(5W)$^{v}$ | 0.87 | 2.34 | 3.101(5) | 145.3 |
| O(3W)−H(3WA)···O(2W)$^{vi}$ | 0.79(6) | 1.98(6) | 2.763(5) | 168(5) |
| O(3W)−H(3WB)···O(11)$^{vii}$ | 0.84(5) | 1.98(5) | 2.807(5) | 167(5) |
| O(4W)−H(4WB)···O(1W)$^{viii}$ | 0.79(5) | 1.89(5) | 2.680(5) | 176(5) |
| O(5W)−H(5WA)···O(9)$^{i}$ | 0.82(6) | 1.92(6) | 2.735(5) | 176(6) |
| O(5W)−H(5WB)···O(10)$^{ix}$ | 0.83(6) | 1.94(6) | 2.767(5) | 169(6) |
| N(2)−H(2B)···O(5)$^{x}$ | 0.86 | 2.08 | 2.934(4) | 173.6 |
| N(2)−H(2C)···O(16)$^{x}$ | 0.86 | 2.19 | 3.014(5) | 161.1 |
| N(4)−H(4B)···O(4)$^{iii}$ | 0.86 | 2.11 | 2.959(4) | 169.6 |
| N(4)−H(4C)···O(8)$^{iii}$ | 0.86 | 2.18 | 2.975(4) | 154.6 |
| N(6)−H(6A)···O(18)$^{x}$ | 0.86 | 2.04 | 2.899(4) | 175.5 |
| N(6)−H(6B)···O(12)$^{xi}$ | 0.86 | 2.07 | 2.909(4) | 164.0 |
| N(8)−H(8B)···O(17)$^{iii}$ | 0.86 | 2.07 | 2.934(4) | 177.6 |
| N(8)−H(8C)···O(1)$^{iii}$ | 0.86 | 2.47 | 3.260(5) | 152.2 |
| N(8)−H(8C)···O(3)$^{iii}$ | 0.86 | 2.65 | 3.180(5) | 121.0 |

[a] Symmetry code for **1**: (*i*) $-x, -y + 2, -z + 2$; (*ii*) $-x - {}^1/_2, y + {}^1/_2, -z + {}^3/_2$; (*iii*) $x - {}^1/_2, -y + {}^3/_2, z - {}^1/_2$; (*iv*) $-x - {}^1/_2, y - {}^1/_2, -z + {}^3/_2$. Symmetry code for **2**: (*i*) $-x, -y + 1, -z$; (*ii*) $x, y + 1, z$. Symmetry code for **3**: (*i*) $-x + {}^1/_2, y + {}^1/_2, -z + {}^3/_2$; (*ii*) $x, y, z - 1$; (*iii*) $x - {}^1/_2, -y + {}^3/_2, z - {}^1/_2$. Symmetry code for **4**: (*i*) $-x, -y + 1, -z + 3$; (*ii*) $-x, -y + 1, -z + 2$; (*iii*) $-x + 1, -y, -z + 2$; (*iv*) $x, y, z - 1$; (*v*) $-x + 1, -y + 1, -z + 1$; (*vi*) $-x, -y, -z + 3$; (*vii*) $-x, -y, -z + 2$. Symmetry code for **5**: (*i*) $x, y + 1, z - 1$; (*ii*) $-x + 1, -y, -z + 1$; (*iii*) $x - 1, y, z + 1$; (*iv*) $-x + 1, -y, -z + 2$; (*v*) $-x + 1, -y - 1, -z + 2$; (*vi*) $x - 1, y - 1, z + 1$. Symmetry code for **6**: (*i*) $-x, -y + 1, -z$; (*ii*) $-x, -y + 1, -z + 1$; (*iii*) $x, y - 1, z + 1$; (*iv*) $x, y + 1, z$; (*v*) $-x + 1, -y, -z + 1$; (*vi*) $-x + 1, -y + 1, -z + 1$; (*vii*) $-x + 1, -y + 1, -z$; (*viii*) $x, y - 1, z$; (*ix*) $x, -2, z + 1$; (*x*) $x, y + 1, z - 1$; (*xi*) $-x + 1, -y, -z$.

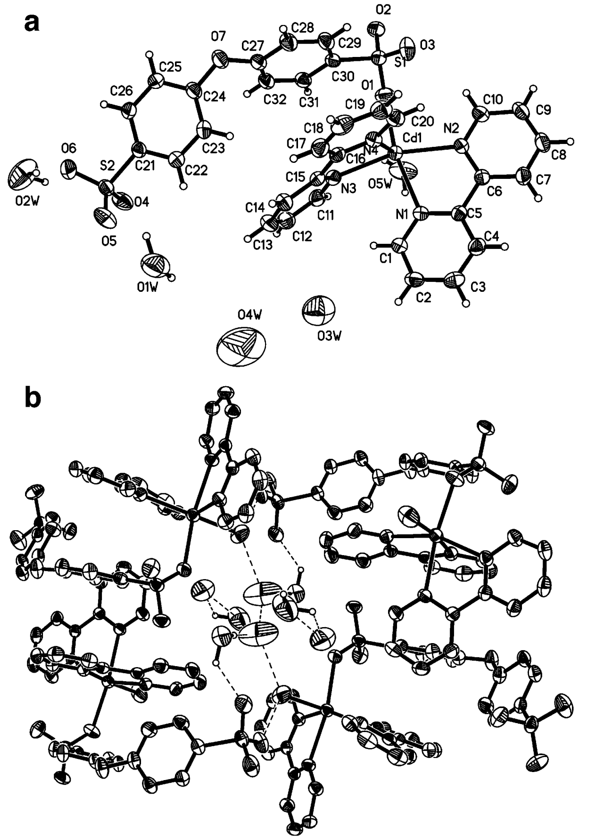

**Figure 1.** (a) The component of the asymmetric unit in **1**, with 30% probability displacement ellipsoids. (b) Four complex units forming a hydrophilic cavity that hosts a water cluster.

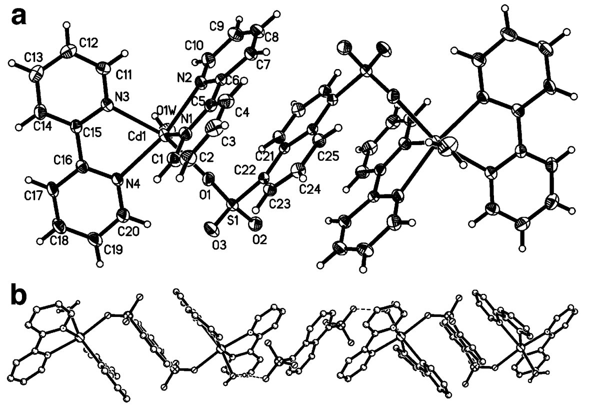

**Figure 2.** (a) The dinuclear cluster cation in **2**, with 30% probability displacement ellipsoids. (b) The extended 1-dimensional chain along the diagonal of the *a* and *c* axes, formed by the dinuclear cluster cations and free 1,5nds anion via hydrogen bonds. Note that the 1,5nds counteranion is disordered over two sites and only one is being shown for clarity.

between amide moieties and sulfonate groups, leading to extended two-dimensional sheets, as illustrated in Figure 4a and Figure 5a. All the phenyl rings of the inia and 2,6nds/bpds ligands align along the *c* axis. When looking down along the *a* axis, the packing arrangement can be described as an inorganic−organic layered network, with the metal centers, $SO_3^-$ groups, and coordinated and crystalline water molecules constructing the inorganic layers, as shown in Figure 4b and Figure 5b.

It is noteworthy that the extended 2-dimensional layer structures in **4** and **5** are very similar, despite the fact that

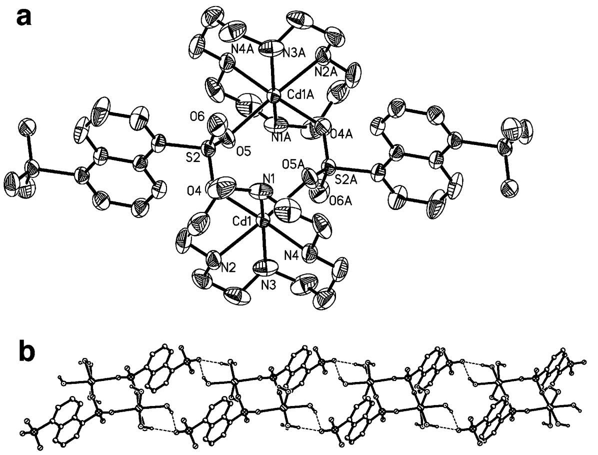

**Figure 3.** (a) The neutral dinuclear cluster in **3**, with 30% probability displacement ellipsoids**.** (b) The 1-dimensional chain along the *c* axis, constructed by hydrogen.

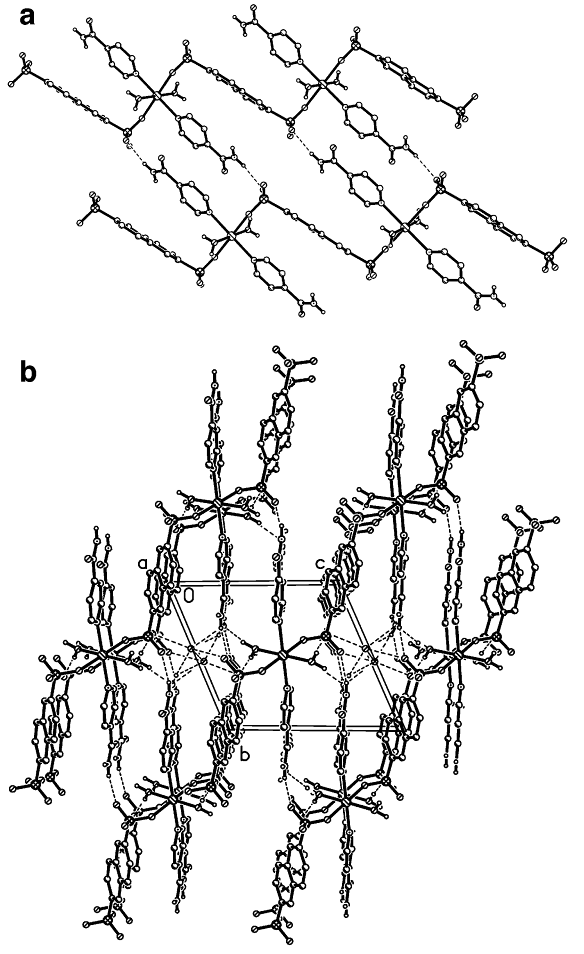

**Figure 4.** (a) The 2-dimensional network along the *bc* plane, constructed by hydrogen bonds in **4**. (b) Packing arrangement when looking down along the *a* axis.

the length of the spacer is 8.49 and 10.66 Å in 2,6nds and bpds (distance between the two S atoms), respectively. In other words, the directing forces for the assembly of the polymers, **4** and **5**, into 2-dimensional structures are the same, similar to the supramolecular synthon reported previously for the Cd(N4)(nds/bpds) system.[3b] In both **4** and **5**, interchain hydrogen bonds construct two rectangular grids. The smaller one is assembled by two inia ligands and two $SO_3$−Cd fragments, while the larger one is assembled by two pairs of the nds/bpds and inia ligands and two $SO_3$−Cd fragments. This construction suggests that if the length of the inia and disulfonate anions is not compatible, the interchain hydrogen bonds leading to a 2-dimensional network cannot be formed. An effort using the 1,5nds anion to obtain a structural analogue failed. This could be caused by the fact that, because of the shortness of the 1,5nds spacer (6.90 Å), the $SO_3^-$ groups are not able to reach out for stable intermolecular hydrogen bonding interactions with the amide hydrogen atoms of adjacent chains.

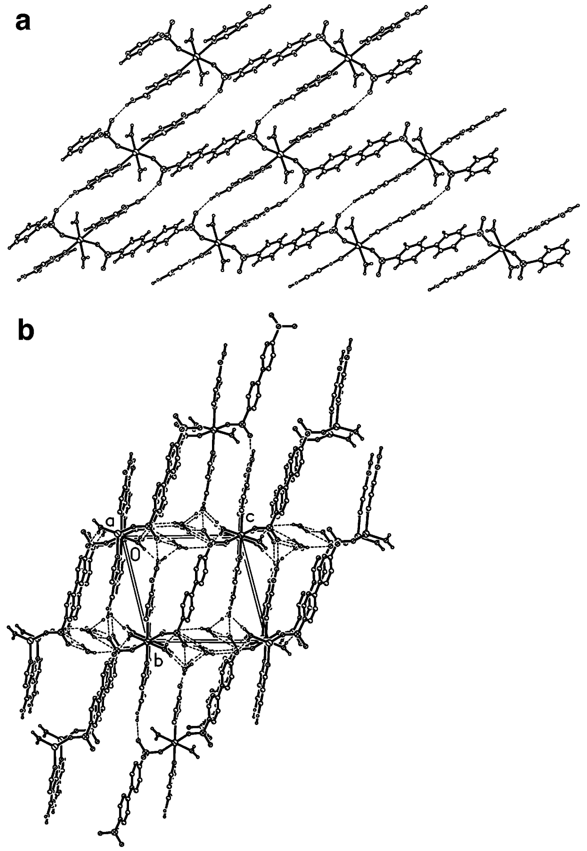

**Figure 5.** (a) The 2-dimensional network along the *bc* plane, constructed by hydrogen bonds in **5**. (b) Packing arrangement when looking down along the *a* axis.

**The 1-dimensional knotted chain {[$Cd_2$(inia)$_4$($H_2O$)$_3$(peds)$_2$]·2$H_2O$}$_n$ (6)−coordinaion modes (b) and (e):** Figure 6a shows the coordination environment of the Cd(II) centers. There are two independent Cd(II) centers with different coordination geometry in the asymmetric unit. Cd(1) is coordinated by one water molecule, two nicotinamide nitrogen atoms, and three sulfonate anions, and Cd(2) is coordinated by two water molecules, two nicotinamide nitrogen atoms, and two sulfonate anions. Each of the Cd(II) centers is double-bridged by two $\mu_2$-$SO_3^-$ groups, resulting in two dinuclear clusters with a Cd···Cd separation of 4.942 and 5.505 Å, respectively. The clusters are linked by peds spacers into 1-dimensional knotted chains, as shown in Figure 6b. The 1-dimensional knotted chains are further extended into a 2-dimensional sheet via hydrogen bonds between the free $SO_3^-$ groups and coordinated water

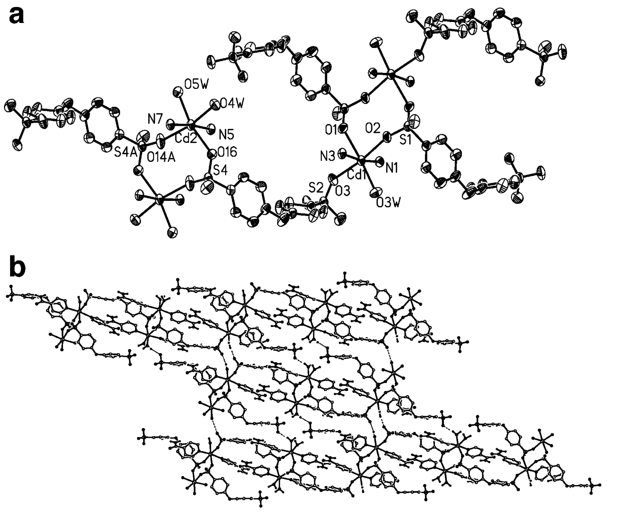

**Figure 6.** (a) The coordination environment of Cd(II) in **6**. Only the coordinated N atom of inia was shown for clarity. (b) The 2-dimensional sheet along the *ab* plane formed by the 1-dimensional knotted chains via hydrogen bonds.

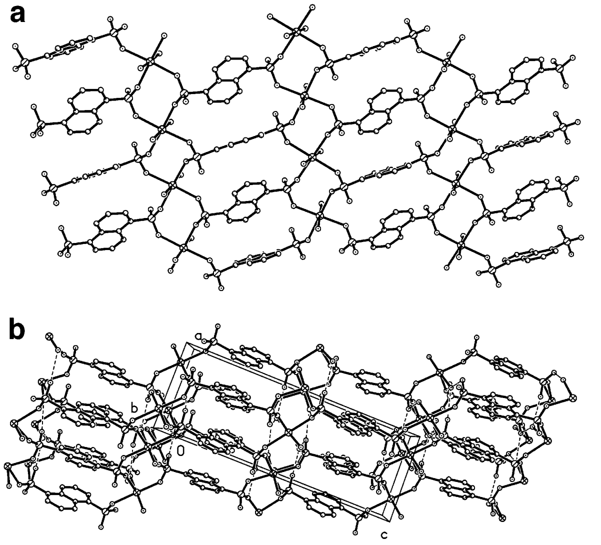

**Figure 7.** (a) The 2-dimensional polymer of **7**. (b) Packing arrangement when looking down along the *b* axis.

molecules of adjacent chains, as shown in Figure 6b. The interlayered head-to-head hydrogen bonds formed between the amide groups produce a hydrogen-bonded 3-dimensional network.

It is interesting to observe that both the spacer and terminal peds anions in the asymmetric unit coordinate with Cd(II) in an asymmetric fashion. The one serving as spacer displays a $\mu_2\mu_1$ mode, one end $\mu_2$-bridging and the other end monodentate, while the second peds coordinates only with one end as a $\mu_2$-bridge and the other end free. Accordingly, the conformations of the peds ligands are different, with the dihedral angle formed by the two phenyl rings changing from 119.2° to 101.4°.

**The 2-dimensional sheet [Cd(1,5nds)($H_2O$)$_2$]$_n$ (7)−coordination mode (f):** The Cd(II) cation is coordinated by four $SO_3^-$ groups and two water molecules. Each $SO_3^-$ group behaves as a $\mu_2$-ligand bridging two Cd(II) centers, constructing a two-dimensional network with alternating organic−inorganic components, as shown in Figure 7a. It is the first two-dimensional structure constructed from a transition metal and arenedisulfonate, an isostructure with [Ca(1,5nds)-($H_2O$)$_2$]$_n$.[1] The inorganic portion consists of three differently conformed eight-membered rings, represented as (Cd−O−S−O)$_2$, with Cd···Cd separations of 5.472, 5.195, and 5.53 Å, respectively. Strong interlayered hydrogen bonding interactions formed between the coordinated water molecules and the free $SO_3^-$ oxygen atoms extend the layers into a 3-dimensional network, as shown in Figure 7b. It is noteworthy that the packing of the sheets along the *b* axis adopts an organic−inorganic layered arrangement reminiscent of that observed in **4** and **5**.

## Conclusions

The reported seven Cd(II) sulfonates, together with the previously reported Cu(II) analogue {[Cu(en)$_2$(1,5nds)]·$2H_2O$}$_n$ (**8**) (coordination mode (c)), show that all of the 6 possible coordination modes of organodisulfonate anions, on the assumption that each $SO_3^-$ group is a potential monodentate or $\mu_2$-bridging ligand, can be achieved with the help of N-containing auxiliaries. Furthermore, the $SO_3^-$ oxygens are involved in extensive intermolecular hydrogen bonds which could be directive and leading to extended structures with higher order of dimension, as that observed in compounds **2**−**7**. These results illustrate vividly the richness of the structural chemistry of transition metal sulfonates. The materials reported herein could display selective absorption properties toward small organic molecules after excluding the crystalline or coordination water molecules, as that reported for the Ag(I) and Ba(II) sulfonates.[6] Further investigations on this aspect are being conducted.

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**Supporting Information Available:** Spectral and TGA data for **1**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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