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Three Novel Zinc(II) Sulfonate–Phosphonates with Tetranuclear or Hexanuclear Cluster Units

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Hydrothermal reactions of zinc(II) carbonate with *m*-sulfophenylphosphonic acid (m-HO_3S-Ph-PO_3H_2) and 1,10-phenanthroline (phen) or 4,4′-bipyridine (bipy) lead to three novel zinc(II) sulfonate–phosphonates, namely, $[Zn(phen)_3]_2[Zn_4(m\text{-}O_3S\text{-}Ph\text{-}PO_3)_4(phen)_4]\cdot 20H_2O$ (**1**), $[Zn_6(m\text{-}O_3S\text{-}Ph\text{-}PO_3)_4(phen)_8]\cdot 11H_2O$ (**2**), and $[Zn_6(m\text{-}O_3S\text{-}Ph\text{-}PO_3)_4(bipy)_6(H_2O)_4]\cdot 18H_2O$ (**3**). Compound **1** contains a tetranuclear zinc(II) cluster anion in which four Zn(II) ions are bridged by two tetradentate and two bidentate phosphonate groups, and the four negative charges of the cluster are compensated by two $[Zn(phen)_3]^{2+}$ cations. Compound **2** features a hexanuclear zinc(II) cluster in which the same tetranuclear cluster of **1** is bridged with two additional Zn(II) ions. The structure of **3** features a porous 3D network based on hexanuclear zinc(II) units of $[Zn_6(m\text{-}O_3S\text{-}Ph\text{-}PO_3)_4]$ interconnected by 4,4′-bipy ligands. The hexanuclear cluster in **3** is different from that in **2** in that all four phosphonate groups in **3** are tridentate bridging. Compounds **1**, **2**, and **3** exhibit broad blue fluorescent emission bands at 378, 409, and 381 nm, respectively.

Introduction

The chemistry of metal phosphonates has been a rapidly expanding research field in recent years, mainly because of their potential application in catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry, and materials chemistry.[1] Most of the metal phosphonates have a layered structure in which the metal centers are bridged by the phosphonate groups, although a variety of 1D chains and porous 3D networks have also been reported.[1] Although a large number of open frameworks of V(V) or Mo(VI) phosphonate clusters incorporated by Ni(II) or Cu(II) complex moieties have been reported,[2] metal phosphonates containing a molecular cluster unit are still rare.[3−12] A lanthanide phosphonate cage compound was also reported by Bunzli et al. very recently.[3] Several cage complexes involving vanadium and aluminum have been reported.[4] The redox-active $\{Mn_4\}$ cages described by the Dismukes group are very interesting.[5] A novel dodecanuclear copper(II) cage and a few tri- and hexanuclear zinc cages containing phosphonate and pyrazole were reported,[6] and several polymetallic cobalt and manganese cages with phosphinate and phosphonate ligands have been isolated by the Winpenny group.[7] Two mixed-valence polyoxomolybdenum diphosphonate anions were reported by the Sevov group,[8] and a

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dodecanuclear zincophosphonate aggregate with a $Zn_4(\mu_4\text{-}O)$ core was reported by the Roesky group.[9] Trinuclear, tetranuclear, and hexanuclear zinc(II) cages containing phosphonate and pyrazole ligands were reported by the Chandrasekhar group,[10] and a series zinc phosphonates containing an unusual cluster anion, $\{Zn_6[MeN(CH_2CO_2)(CH_2PO_3)]_6(Zn)\}^{4-}$, which features a unusual $Zn_6(Zn)$-centered octahedron, was reported by our group.[11] The use of phosphonic acid derived from proline instead of $MeN(CH_2CO_2H)(CH_2PO_3H_2)$ produced a compound with a similar heptanuclear cluster unit.[12] The direct reaction of hydroxy(2-pyridyl)methylphosphonic acid with zinc sulfate under hydrothermal conditions resulted in the formation of another type of heptanuclear cluster compound $[Zn_7\{(2\text{-}C_5H_4N)CH(OH)\text{-}PO_3\}_6(H_2O)_6](SO_4)\cdot 4H_2O$ in which the cluster unit can be described as a cylindrical drum made up of six Zn atoms bridged by six $\{CPO_3\}$ units and centered by a seventh Zn atom.[13] The synthesis of multi-zinc clusters is of considerable contemporary interest, as exemplified by the potential application of the trinuclear clusters in biological systems, such as phospholipase C and P1 nuclease.[14]

To prepare metal phosphonates with a polynuclear cluster unit, two methods are commonly applied. The first one is to select a suitable phosphonic acid that serves as a chelating and bridging ligand. The other one is to introduce a second ligand such as 1,10-phenanthroline; the coordination of such a ligand reduces the coordination sites available for the phosphonate ligand, and furthermore, its steric hindrance effect may help to prevent the formation of extended architectures. In our current studies, we use a phosphonate ligand attached by a sulfonate group, $m\text{-}HO_3S\text{-}C_6H_4\text{-}PO_3H_2$, as the main ligand and 1,10-phenanthroline (phen) or 4,4′-bipyridine (bipy) as the auxiliary ligand. The sulfonate group is a weak coordination ligand to most metal ions, and its introduction could improve the solubility and crystallinity of the metal phosphonates because of its acidic nature, in addition to forming hydrogen bonds. So far no metal complexes of sulfonate−phosphonate ligands have been structurally characterized, although a number of metal sulfonate−phosphonate mixed-ligand complexes were reported by our group.[15] Our research efforts yielded three novel zinc(II) sulfonate-phosphonates, namely, $[Zn(phen)_3]_2[Zn_4(m\text{-}O_3S\text{-}Ph\text{-}PO_3)_4(phen)_4]\cdot 20H_2O$ (**1**), $[Zn_6(m\text{-}O_3S\text{-}Ph\text{-}PO_3)_4(phen)_8]\cdot 11H_2O$ (**2**), and $[Zn_6(m\text{-}O_3S\text{-}Ph\text{-}PO_3)_4(bipy)_6(H_2O)_4]\cdot 18H_2O$ (**3**). Compound **1** contains a tetranuclear zinc(II) phosphonate cluster unit, whereas compounds **2** and **3** feature two types of hexanuclear zinc(II) phosphonate cluster units. Herein, we report their syntheses, crystal structures, and characterizations.

Experimental Section

Materials and Instrumentation. All chemicals were obtained from commercial sources and used without further purification. Elemental analyses were performed on a German Elementary Vario EL III instrument. The FT-IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer using KBr pellets in the range of 4000−400 cm^{-1}. Thermogravimetric analyses were carried out on a NETZSCH STA 449C unit at a heating rate of 10 °C/min under an oxygen atmosphere. Photoluminescence analyses were performed on a Perkin Elemer LS55 fluorescence spectrometer. X-ray powder diffraction (XRD) patterns (Cu Kα) were collected on a XPERT-MPD $\theta-2\theta$ diffractometer.

Synthesis of *m*-Sulfophenylphosphonic Acid. *m*-Sulfophenylphosphonic acid ($m\text{-}HO_3S\text{-}C_6H_4-PO_3H_2$) was synthesized according to the procedures previously described by Montoneri et al.[16] Phenylphosphonic acid (20.16 g, 127 mmol) was added to freshly distilled SO_3 (12.5 cm^3, 300 mmol) at 0 °C, and then the mixture was heated at 85−90 °C for 14 h. The conversion of phenylphosphonic acid to *m*-sulfophenylphosphonic acid was nearly quantitative. Residual SO_3 was converted to $BaSO_4$ via the addition of aqueous HCl and $BaCl_2$ to the reaction mixture in water. The excess $BaCl_2$ was removed by concentration, filtration of the saturated solution, and ion-exchange of the residual barium ions on a Dowex 50W-X8 H$^+$ form resin. The eluate was finally concentrated and dried to yield the final product (mp = 164 °C). Its purity was confirmed by ^{31}P NMR, IR, and elemental analyses.

Synthesis of $[Zn(phen)_3]_2[Zn_4(m\text{-}O_3S\text{-}Ph\text{-}PO_3)_4(phen)_4]\cdot 20H_2O$ (1). A mixture of zinc(II) carbonate (0.3 mmol), $m\text{-}HO_3S\text{-}Ph\text{-}PO_3H_2$ (0.3 mmol), and phen (0.5 mmol) in 10 mL of distilled water, with its pH value adjusted to about 7.0 via the addition of a 1 M NaOH solution, was put into a Parr Teflon-lined autoclave (23 mL) and heated at 150 °C for 4 days. Colorless plate-shaped crystals of **1** were collected in a ca. 71% yield based on Zn. Its purity was also confirmed by XRD powder diffraction (see Supporting Information). Anal. Calcd for $C_{144}H_{136}N_{20}O_{44}P_4S_4Zn_6$ (M_r = 3496.06): C, 49.47; H, 3.92; N, 8.01. Found: C, 49.11; H, 3.83; N, 7.89. IR data (KBr, cm^{-1}): 3392(s), 3061(s), 1625(m), 1582(m), 1519(s), 1428(s), 1188(s), 1156(vs), 1103(vs), 1072(s), 1031(s), 999(s), 987(m), 961(m), 867(m), 850(s), 797(m), 725(vs), 700(m), 619(m), 552(m).

Synthesis of $[Zn_6(m\text{-}O_3S\text{-}Ph\text{-}PO_3)_4(phen)_8]\cdot 11H_2O$ (2). A mixture of zinc(II) carbonate (0.3 mmol), $m\text{-}HO_3S\text{-}Ph\text{-}PO_3H_2$ (0.32 mmol), and phen (0.32 mmol) in 10 mL of distilled water, with its pH value adjusted to about 5.0 via the addition of a 1 M NaOH solution, was put into a Parr Teflon-lined autoclave (23 mL) and heated at 150 °C for 4 days. Colorless brick-shaped crystals of **2** were collected in a ca. 54% yield based on Zn. Its purity was also confirmed by XRD powder diffraction (see Supporting Information). Anal. Calcd for $C_{120}H_{102}N_{16}O_{35}P_4S_4Zn_6$ (M_r = 2972.52): C, 48.49; H, 3.46; N, 7.54. Found: C, 48.40; H, 3.38; N, 7.57. IR data (KBr, cm^{-1}): 3392(s), 3061(s), 1625(m), 1582(m), 1519(s), 1428(s), 1188(s), 1156(vs), 1103(vs), 1072(s), 1031(s), 999(s), 987(m), 961(m), 867(m), 850(s), 797(m), 726(vs), 700(m), 619(m), 552(m).

Synthesis of $[Zn_6(m\text{-}O_3S\text{-}Ph\text{-}PO_3)_4(4,4'\text{-}bipy)_6(H_2O)_4]\cdot 18H_2O$ (3). A mixture of zinc(II) carbonate (0.4 mmol), $m\text{-}HO_3S\text{-}Ph\text{-}PO_3H_2$ (0.4 mmol), and bipy (0.4 mmol) in 10 mL of distilled water with an initial pH value of about 4.0 was put into a Parr Teflon-lined autoclave (23 mL) and heated at 140 °C for 4 days. Colorless plate-shaped crystals of **3** were collected in a ca. 75% yield based on Zn. Its purity was also confirmed by XRD powder diffraction (see Supporting Information). Anal. Calcd for $C_{84}H_{108}N_{12}O_{46}P_4S_4Zn_6$ (M_r = 2666.16): C, 37.84; H, 4.08; N, 6.30. Found: C, 37.75; H, 4.01; N, 6.24. IR data (KBr, cm^{-1}): 3854(m), 3747(m), 3672(m), 3650(m), 3464(s), 1613(s), 1537(m), 1419(m), 1217(s), 1191(s),

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Table 1. Summary of Crystal Data and Refinements for Compounds **1**, **2**, and **3**

	1	**2**	**3**
empirical formula	$C_{144}H_{136}N_{20}O_{44}$-$P_4S_4Zn_6$	$C_{120}H_{102}N_{16}O_{35}$-$P_4S_4Zn_6$	$C_{84}H_{108}N_{12}O_{46}$-$P_4S_4Zn_6$
fw	3496.06	2972.52	2666.16
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	14.0927(7)	13.9916(4)	13.5396(1)
b (Å)	14.6020(7)	14.0668(4)	30.4380(5)
c (Å)	19.4740(9)	17.5288(5)	15.7217(3)
α (deg)	95.857(2)	97.816(1)	90
β (deg)	98.831(1)	98.731(1)	110.535(1)
γ (deg)	109.966(1)	114.932(1)	90
V (Å^3)	3670.0(3)	3014.3(2)	6067.5(2)
Z	1	1	2
D_{calcd} (g cm^{-3})	1.581	1.638	1.459
μ (mm^{-1})	1.158	1.387	1.374
GOF on F^2	1.063	1.285	1.059
R1, wR2[a] [$I > 2\sigma(I)$]	0.0457, 0.1198	0.0797, 0.1409	0.0576, 0.1638
R1, wR2[a] (all data)	0.0557, 0.1274	0.1060, 0.1555	0.0636, 0.1689

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

Table 2. Selected Bond Lengths (Å) for Compounds **1**, **2**, and **3**

	1[a]		
Zn(1)−O(23)	1.979(2)	Zn(1)−O(13)	1.999(2)
Zn(1)−N(2)	2.147(2)	Zn(1)−N(1)	2.157(2)
Zn(1)−O(11)#1	2.160(2)	Zn(2)−O(22)	1.935(2)
Zn(2)−O(12)	1.995(2)	Zn(2)−N(4)	2.113(2)
Zn(2)−O(11)#1	2.127(2)	Zn(2)−N(3)	2.179(2)
Zn(3)−N(7)	2.143(2)	Zn(3)−N(9)	2.150(2)
Zn(3)−N(8)	2.171(2)	Zn(3)−N(6)	2.176(2)
Zn(3)−N(10)	2.177(2)	Zn(3)−N(5)	2.180(2)
	hydrogen bonds		
O(32′)···O(1W)	2.72(2)	O(21)···O(5W)	2.726(4)
O(43)···O(2W)	2.566(12)	O(3W)···O(4W)	2.772(6)
O(4W)···O(10W)	2.765(5)	O(4W)···O(5W)	2.787(6)
O(6W)···O(10W)	2.804(5)	O(7W)···O(10W)	2.796(5)
	2[b]		
Zn(1)−O(13)	1.949(4)	Zn(1)−O(33)	2.004(4)
Zn(1)−N(5)	2.126(6)	Zn(1)−N(6)	2.132(5)
Zn(1)−O(31)#1	2.133(4)	Zn(2)−O(32)	1.966(4)
Zn(2)−O(12)	1.970(4)	Zn(2)−N(7)	2.095(5)
Zn(2)−O(31)#1	2.160(4)	Zn(2)−N(8)	2.209(6)
Zn(3)−O(11)	1.932(4)	Zn(3)−N(4)	2.116(6)
Zn(3)−N(3)	2.147(6)	Zn(3)−N(1)	2.164(6)
Zn(3)−N(2)	2.182(6)		
	hydrogen bonds		
O(21)···O(5W)	2.90(1)	O(23)···O(3W)	2.95(1)
O(41)···O(6W)#2	2.76(4)	O(41)···O(2W)#2	2.97(1)
O(42)···O(1W)#3	2.90(2)	O(43)···O(5W)#4	2.94(1)
O(1W)···O(4W)#5	2.92(2)	O(1W)···O(4W)	2.99(2)
O(1W)···O(3W)	3.00(2)	O(4W)···O(5W)	2.75(1)
	3[c]		
Zn(1)−O(13)	2.089(2)	Zn(1)−O(1W)	2.130(3)
Zn(1)−N(3)	2.152(3)	Zn(1)−O(2W)	2.157(3)
Zn(1)−N(2)#1	2.168(3)	Zn(1)−N(5)#2	2.210(3)
Zn(2)−O(12)	1.900(2)	Zn(2)−O(32)#3	1.928(3)
Zn(2)−N(4)#4	2.032(3)	Zn(2)−N(6)	2.038(3)
Zn(3)−O(11)	1.906(3)	Zn(3)−O(31)#3	1.928(3)
Zn(3)−O(33)	1.936(3)	Zn(3)−N(1)	2.037(3)
	hydrogen bonds		
O(21)···O(5W)	2.779(9)	O(22)···O(12W)	2.80(2)
O(23)···O(16W)	2.83(2)	O(41)···O(10W)	2.72(2)
O(42)···O(5W)#1	2.78(1)	O(43)···O(7W)	2.766(2)
O(1W)···O(3W)#6	2.785(4)	O(2W)···O(8W)#2	2.88(1)
O(3W)···O(7W)#7	2.754(9)	O(5W)···O(11W)#8	2.83(2)
O(6W)···O(13W)	2.63(2)	O(7W)···O(11W)	2.70(2)
O(8W)···O(16W)	2.91(3)	O(10W)···O(13W)#6	2.80(2)
O(12W)···O(14W)#3	2.55(3)	O(12W)···O(15W)#9	2.66(3)

[a] Symmetry codes: #1 $-x + 1, -y, -z$. [b] Symmetry codes: #1 $-x + 2, -y + 1, -z + 2$; #2 $x, y - 1, z$; #3 $-x + 1, -y, -z + 1$; #4 $x + 1, y, z$; #5 $-x, -y, -z + 1$. [c] Symmetry code: #1 $-x, -y, -z + 1$; #2 $-x + 1, y + 1/2, -z + 3/2$; #3 $-x + 1, -y, -z + 1$; #4 $-x + 2, -y, -z + 2$; #5 $x - 1, y, z - 1$; #6 $x - 1, y, z$; #7 $x + 1, -y + 1/2, z + 1/2$; #8 $-x, y - 1/2, -z + 3/2$; #9 $x, -y - 1/2, z - 1/2$.

1102(vs), 1072(vs), 1033(s), 1012(s), 809(m), 697(m), 641(m), 619(m), 571(m).

Single-Crystal Structure Determination. Data collections for compounds **1** and **3** were performed on a Mercury CCD diffractometer, whereas the data collection for compound **2** was performed on a Siemens Smart CCD diffractometer. Both diffractometers were equipped with a graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The intensity data were collected by the narrow-frame method at 293 K. The data sets were corrected for Lorentz and polarization factors, as well as for absorption, by the SADABS program or multiscan method.[17a,17b] All structures were solved by the direct method and refined by full-matrix least-squares fitting on F^2 by SHELX-97.[17c] All non-hydrogen atoms, except O(14w), O(15w), and O(16w) of compound **3**, were refined with anisotropic thermal parameters. All hydrogen atoms were generated geometrically and refined isotropically. The hydrogen atoms for the water molecules are not included in the refinements. The sulfonate groups in compound **1** are severely disordered, and each of five sulfonate oxygens (O(31), O(32), O(41), O(42), and O(43)) displays two orientations with 50% occupancy for each site. O(43) of the sulfonate group in compound **3** is also disordered and exhibits two orientations (O(43) and O(43′)) with 50% occupancy. O(6w) of compound **2** which is 1.60(6) Å from its symmetrically generated atoms (symmetry code $2 - x, 2 - y, 2 - z$) is also considered to be disordered, and its occupancy factor is reduced to 50%. The occupancy factors of O(7w) to O(16w) in compound **3** were reduced to 50% because of their larger thermal parameters. Crystallographic data and structural refinements for compounds **1**, **2**, and **3** are summarized in Table 1, and important bond lengths are listed in Table 2. More details on the crystallographic studies, as well as atom displacement parameters, are given in the Supporting Information.

Results and Discussion

Hydrothermal reactions of zinc(II) carbonate with *m*-sulfophenylphosphonic acid (*m*-HO_3S−Ph-PO_3H_2) and 1,-10-phenanthroline (phen) or 4,4′-bipyridine (bipy) lead to three novel zinc(II) sulfonate−phosphonates, namely, $[Zn(phen)_3]_2[Zn_4(m\text{-}O_3S\text{-}Ph\text{-}PO_3)_4(phen)_4]\cdot 20H_2O$ (**1**), $[Zn_6(m\text{-}O_3S\text{-}Ph\text{-}PO_3)_4(phen)_8]\cdot 11H_2O$ (**2**), and $[Zn_6(m\text{-}O_3S\text{-}Ph\text{-}PO_3)_4(bipy)_6(H_2O)_4]\cdot 18H_2O$ (**3**). All three compounds contain tetranuclear or hexanuclear sulfonate−phosphonate clusters. They represent also the first structurally characterized metal complexes of phosphonic acid attached with a sulfonate group.

The formula of compound **1** contains a tetranuclear cluster of $[Zn_4(m\text{-}O_3S\text{-}Ph\text{-}PO_3)_4(phen)_4]^{4-}$ anion and two $[Zn(phen)_3]^{2+}$ cations, as well as twenty lattice water molecules. There are three crystallographically independent zinc(II) ions in the structure. Both the Zn(1) and Zn(2) ions are five-coordinated by three phosphonate oxygen atoms from three $(m\text{-}O_3S\text{-}Ph\text{-}PO_3)^{3-}$ anions, as well as a bidentate chelating

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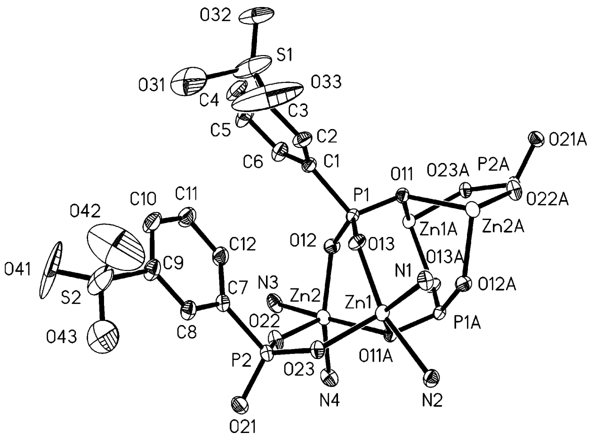
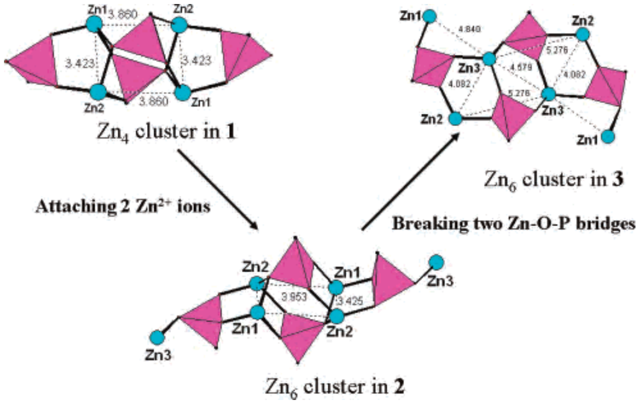


Figure 1. ORTEP representation of the tetranuclear zinc(II) cluster unit in compound **1**. The thermal ellipsoids are drawn at 30% probability. Only one orientation was shown for the sulfonate groups for clarity. The carbon atoms of the phen ligands are omitted for clarity. Symmetry codes for the generated atoms: a $1 - x$, $-y$, $-z$.

Scheme 1. Comparison and Relationship between Cluster Cores in Compounds **1**, **2**, and **3**[a]



[a] The CPO_3 groups are shaded in pink.

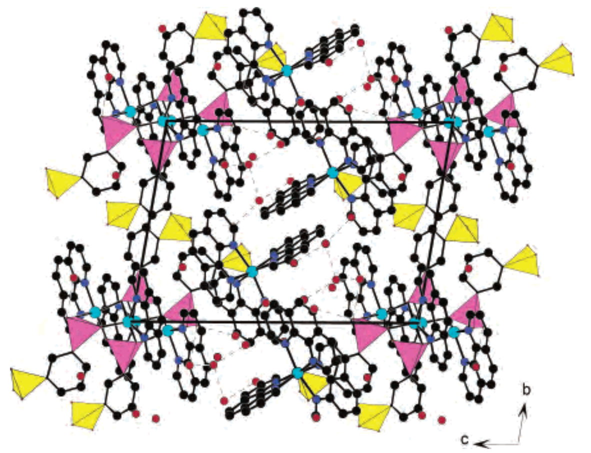


Figure 2. View of the structure of **1** down the *a* axis. The CPO_3 and CSO_3 tetrahedra are represented in pink and yellow, respectively. The Zn, N, O, and C atoms are drawn as cyan, blue, red, and black circles, respectively. The hydrogen bonds are represented by dashes.

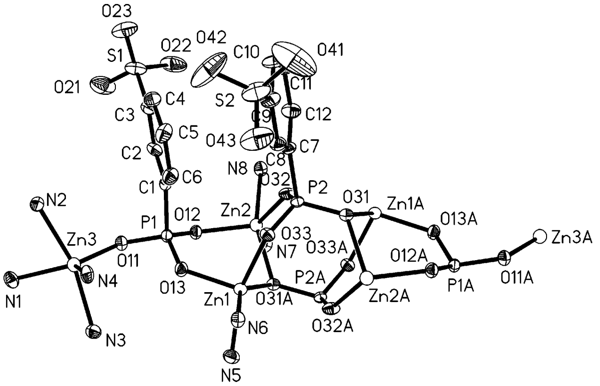


Figure 3. ORTEP representation of the hexanuclear zinc(II) cluster unit in compound **2**. The thermal ellipsoids are drawn at 30% probability. The carbon atoms of the phen ligands are omitted for clarity. Symmetry codes for the generated atoms: a $2 - x$, $1 - y$, $2 - z$.

phen ligand. Their coordination geometry can be described as a distorted trigonal bipyramid. The Zn(3) ion is octahedrally coordinated by three bidentate chelating phen ligands. The Zn−O (1.935(2)−2.160(2) Å) and Zn−N (2.113(2)−2.180(2) Å) distances are comparable to those reported for other zinc phosphonates.[9−13]

There are two unique $(m\text{-}O_3S\text{-}Ph\text{-}PO_3)^{3-}$ ligands in compound **1**. The one containing P(1) and S(1) atoms is tetradentate. All three phosphonate oxygens are involved in metal coordination. O(11) functions as a μ^2-bridging ligand. The sulfonate group is disordered and remains noncoordinated. The second sulfonate−phosphonate containing P(2) and S(2) is bidentate. It bridges with two zinc(II) ions via its two phosphonate oxygen atoms. The third phosphonate oxygen (O(21)) is noncoordinated. Its sulfonate group is also disordered and noncoordinated. Two Zn(1) and two Zn(2) ions are bridged by four sulfonate−phosphonate ligands into a tetranuclear cluster unit (Figure 1). The four zinc(II) ions form a slightly distorted rectangle (Scheme 1). The two Zn−Zn edges are 3.423(1) and 3.860 (1) Å. The Zn−Zn−Zn angles of 92.7 and 87.3° are deviated slightly from the ideal 90°. Two tetradentate phosphonate groups cap above and below the rectangle, respectively, whereas the two bidentate phosphonate groups cap on the two short edges from the left and right sides, respectively. This tetranuclear zinc cluster unit is different from the one previously reported in which the zinc(II) ions are interconnected solely by Zn−O−P−O−Zn bridges.[10a] The four negative charges of the $[Zn_4(m\text{-}O_3S\text{-}Ph\text{-}PO_3)_4(phen)_4]^{4-}$ anion are compensated by two $[Zn(phen)_3]^{2-}$ cations. The lattice water molecules are located at the voids of the structure. A number of hydrogen bonds are formed among the lattice water molecules and the noncoordinated phosphonate and sulfonate oxygens (Figure 2, Table 2).

When the reactions were carried out at a lower pH value with a higher Zn/phen ratio, $[Zn_6(m\text{-}O_3S\text{-}Ph\text{-}PO_3)_4(phen)_8]\cdot 11H_2O$ (**2**) was isolated. Compound **2** features an isolated hexanuclear zinc(II) cluster unit (Figure 3). Among the three independent zinc atoms in compound **2**, Zn(1) and Zn(2) are five-coordinated by three phosphonate oxygen atoms from three $(m\text{-}O_3S\text{-}Ph\text{-}PO_3)^{3-}$ anions, as well as a bidentate chelating phen ligand, as in compound **1**. The Zn(3) ion is five-coordinated by one phosphonate oxygen atom and two bidentate chelating phen ligands. The Zn−O (1.932(4)−2.160(4) Å) and Zn−N (2.095(5)−2.209(6) Å) distances are comparable to those in compound **1**, as well as other zinc phosphonates reported.[9−13]

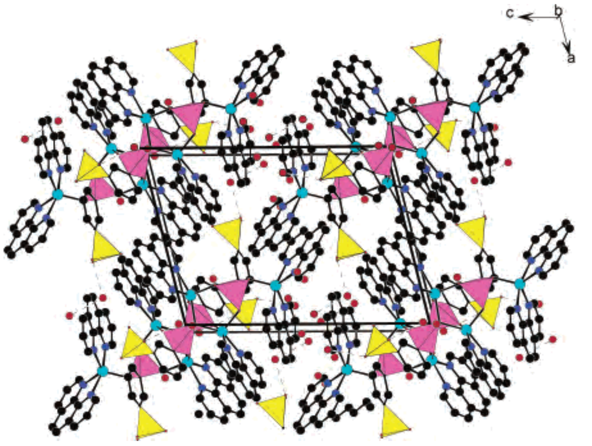


Figure 4. View of the structure of **2** along the *b* axis. The CPO_3 and CSO_3 tetrahedra are represented in pink and yellow, respectively. Zn, N, O, and C atoms are drawn as cyan, blue, red, and black circles, respectively. Hydrogen bonds are represented by dashed lines.

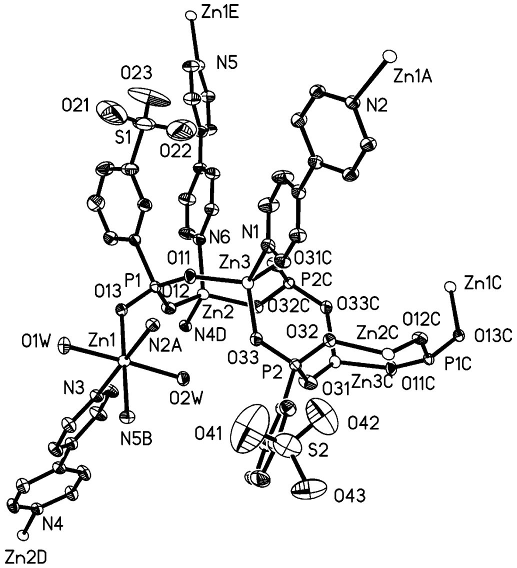


Figure 5. ORTEP representation of the selected unit in compound **3**. The thermal ellipsoids are drawn at 30% probability. Only one orientation was shown for the sulfonate groups for clarity. The lattice water molecules have been omitted for clarity. Symmetry codes for the generated atoms: a $-x$, $-y$, $-z + 1$; b $-x + 1$, $y + 1/2$, $-z + 3/2$; c $-x + 1$, $-y$, $-z + 1$; d $-x + 2$, $-y$, $-z + 2$; e $-x + 1$, $y - 1/2$, $-z + 3/2$.

The four $(m\text{-}O_3S\text{-}Ph\text{-}PO_3)^{3-}$ anions in $[Zn_6(m\text{-}O_3S\text{-}Ph\text{-}PO_3)_4(phen)_8]\cdot 11H_2O$ (**2**) adopt two types of coordination modes. Similar to those in compound **1**, all sulfonate groups are noncoordinated. The $(m\text{-}O_3S\text{-}Ph\text{-}PO_3)^{3-}$ anion containing P(2) and S(2) is tetradentate and bridges with four zinc(II) ions by using its three phosphonate oxygens; this type of coordination mode is found in compound **1**. The second type of $(m\text{-}O_3S\text{-}Ph\text{-}PO_3)^{3-}$ anion containing P(1) and S(1) atoms is tridentate; each phosphonate oxygen connects with a zinc(II) ion. The interconnection of zinc(II) ions by the above two types of $(m\text{-}O_3S\text{-}Ph\text{-}PO_3)^{3-}$ anions resulted in a novel hexanuclear cluster unit. Such cluster unit can be viewed as being derived from the tetranuclear zinc(II) cluster in compound **1** through the coordination of the third phosphonate oxygens of its two bidentate $(m\text{-}O_3S\text{-}Ph\text{-}PO_3)^{3-}$ anions (Scheme 1). The six zinc(II) ions form a Zn_6 ring in the "chair" conformation. The Zn(1)···Zn(2) distances (3.425(1) and 3.953(1) Å) are similar to those in compound **1**. The Zn(3)···Zn(1) and Zn(3)···Zn(2) separations are much longer (5.210(3) and 6.170(1) Å, respectively).

The lattice water molecules are located at the cavities of the structure (Figure 4). A large number of hydrogen bonds are formed among the noncoordinated sulfonate oxygen atoms and the lattice water molecules. The O···O contacts range from 2.75(1) to 3.00(2) Å (Table 2).

$[Zn_6(m\text{-}O_3S\text{-}Ph\text{-}PO_3)_4(4,4'\text{-bipy})_6(H_2O)_4]\cdot 18H_2O$ (**3**) was obtained when 4,4′-bipy was used as the second metal linker. The structure of compound **3** features a novel porous 3D network composed of hexanuclear zinc(II) sulfonate−phosphonate cluster units cross-linked by bridging 4,4′-bipy ligands. The open-framework skeleton of compound **3** is composed of three unique zinc(II) ions, two $(m\text{-}O_3S\text{-}Ph\text{-}PO_3)^{3-}$ anions, three 4,4′-bipy ligands, and two aqua ligands. The coordination geometries for the zinc(II) ions differ significantly from those in compounds **1** and **2**. As shown in Figure 5, Zn(1) is octahedrally coordinated by one phosphonate oxygen atom from a $(m\text{-}O_3S\text{-}Ph\text{-}PO_3)^{3-}$ anion, three nitrogen atoms from three 4,4′-bipy ligands, and two aqua ligands. Zn(2) is tetrahedrally coordinated by two phosphonate oxygens from two $(m\text{-}O_3S\text{-}Ph\text{-}PO_3)^{3-}$ anions and two nitrogen atoms from two 4,4′-bipy ligands. Zn(3) is tetrahedrally coordinated by three phosphonate oxygens from three $(m\text{-}O_3S\text{-}Ph\text{-}PO_3)^{3-}$ anions and one nitrogen atom from a 4,4′-bipy ligand. The Zn−O (1.900(2)−2.157(3) Å) and Zn−N (2.032(3)−2.210(3) Å) distances are comparable to those reported in compounds **1** and **2**.

All four $(m\text{-}O_3S\text{-}Ph\text{-}PO_3)^{3-}$ anions in the formula unit are tridentate with each phosphonate oxygen atom linking to a Zn(II) ion. The sulfonate groups are noncoordinated as in compounds **1** and **2**. The interconnection of six Zn(II) ions via four bridging $(m\text{-}O_3S\text{-}Ph\text{-}PO_3)^{3-}$ anions led to a hexanuclear cluster unit in also the "chair" conformation, which is similar to the one in the zinc(II) complex containing *tert*-butylphosphonic acid and 3,5-dimethylpyrazole.[10b] This cluster unit is different from that in compound **2** in that all four $(m\text{-}O_3S\text{-}Ph\text{-}PO_3)^{3-}$ anions are tridentate bridging; hence, the rectangle formed by the four middle Zn(II) ions is much more expended (Scheme 1). The edges of the rectangle are 4.082 and 5.276 Å, respectively, which are much larger than those in compounds **1** and **2**. The distances from the "head" and "tail" zinc(II) ions (Zn(3) and Zn(3a)) in compound **2** to the plane defined by the central rectangle are 1.5894 Å, whereas the corresponding ones in compound **3** are 4.4046 Å; therefore, the Zn_6 cluster in compound **2** is much more flattened than that in compound **3**.

The hexanuclear zinc(II) cluster units are cross-linked by bridging 4,4′-bipy ligands into a 3D open framework with tunnels along *c* axis (Figure 6). The tunnel is formed by rings composed of 4 cluster units and four 4,4′-bipy ligands. The sulfonate groups of the $(m\text{-}O_3S\text{-}Ph\text{-}PO_3)^{3-}$ anions are orientated toward the center of the tunnels; hence, the tunnels are hydrophilic and can accommodate a number of lattice water molecules (Figure 6). These lattice water molecules form a complicated hydrogen bonding network (Table 2).

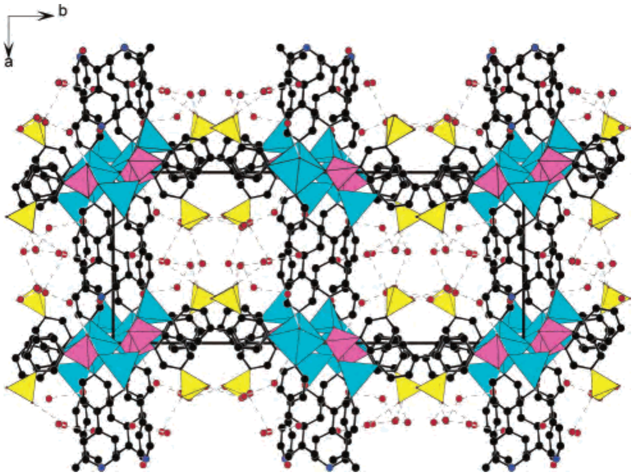


Figure 6. View of the structure of **3** along the *c* axis. The CPO_3 and CSO_3 tetrahedra are represented in pink and yellow, respectively. The zinc(II) polyhedra are shaded in cyan. The N, O, and C atoms are drawn as blue, red, and black circles, respectively. Hydrogen bonds are represented by dashed lines.

The total solvent accessible space is about 30% of the cell volume according to our calculations.[18]

The TGA curves of compound **1** exhibit three weight losses (see Supporting Information). The first step started at 40 °C and ended at 217 °C, which corresponds to the release of 20 lattice water molecules. The observed weight loss of 10.0% is very close to the calculated value (10.3%). The second phase started at 240 °C and ended at 320 °C, which corresponds to the loss of SO_3 from the sulfonate−phosphonate ligand. The observed weight loss of 9.5% is very close to the calculated value (9.2%). The third step began at 380 °C and ended at 850 °C, which corresponds to the combustion of the phen and phosphonate ligands. The total weight loss at 1000 °C is 78.0%. The final residuals are not characterized; however, they are probably a mixture of ZnO and $Zn_2P_2O_7$ in a 1:1 ratio (calculated weight loss of 77.9%). The TGA curves of compound **2** also exhibit four main weight losses. The first started at 40 °C and was complete at 160 °C, which corresponds to the release of the 11 lattice water molecules. The observed weight loss of 6.8% matches well with the calculated value (6.7%). The second started at 280 °C and ended at 440 °C, which corresponds to the loss of SO_3 from the sulfonate−phosphonate ligand. The weight loss of 13.0% is slightly larger than the calculated one (10.8%). The third started at 450 °C and continued to 580 °C, which may be from the release of phen ligands. The forth step began at 460 °C and continued to 1000 °C, which corresponds to the further combustion of the compound. The total weight loss is 73.6% at 1000 °C. The final residuals are not characterized. The TGA curves of compound **3** also reveal three main weight losses. The first began at 40 °C and endeded at 130 °C, corresponding to the release of 18 lattice water molecules. The observed weight loss of 13.0% is slightly larger than the calculated value (12.1%). The second started at 130 °C and was complete at 480 °C, and the observed weight loss was 23.1%, which may correspond to the partial decomposition of the 4,4′-bipy and sulfonate−phosphonate ligands. The third phase started at 485 °C and ended at 630 °C, during which the 4,4′-bipy and sulfonate−phsophonate ligands were further combusted. The total observed weight loss is 73.1% at 1000 °C, and the final residues were not characterized further.

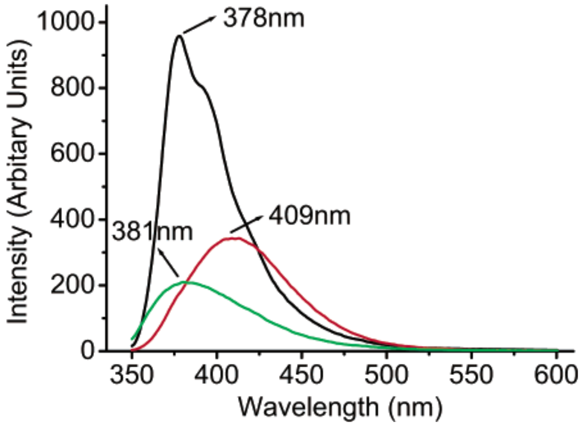


Figure 7. Solid-state emission spectra of compounds **1** (black), **2** (red), and **3** (green).

The solid-state luminescent spectra of compounds **1**, **2**, and **3** were investigated at room temperature (Figure 7). The free *m*-sulfophenylphosphonate ligand shows only a fluorescent emission band at $\lambda_{max} = 370$ nm under 308 nm excitation. The phen ligand displays a fluorescent emission band at $\lambda_{max} = 381$ nm with a shoulder at 364 nm upon excitation at 339 nm. Upon complexation of both ligands with the zinc(II) ions, compound **1** displays a strong fluorescent emission band at $\lambda_{max} = 378$ nm ($\lambda_{excitation}= 308$ nm), and compound **2** exhibits a strong fluorescent emission band at $\lambda_{max} = 409$ nm ($\lambda_{excitation}= 308$ nm). The bipy ligand displays a broad fluorescent emission band at $\lambda_{max} = 423$ nm ($\lambda_{excitation}= 345$ nm). Upon complexation of the *m*-sulfophenylphosphonate ligand and bipy ligand with the zinc(II) ions, compound **3** displays a fluorescent emission band at $\lambda_{max} = 381$ nm ($\lambda_{excitation}= 295$ nm). The emission bands are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature, but rather, the emission is attributed to an intraligand emission state, as reported for other zinc(II) phosphonates containing an N-donor second ligand such as 4,4′-bipy.[19]

Conclusion

In summary, the syntheses, crystal structures, and characterizations of three novel zinc(II) sulfonate−phosphonates with tetranuclear or hexanuclear cluster units, namely, $[Zn(phen)_3]_2[Zn_4(m\text{-}O_3S\text{-}Ph\text{-}PO_3)_4(phen)_4]\cdot 20H_2O$ (**1**), $[Zn_6(m\text{-}O_3S\text{-}Ph\text{-}PO_3)_4(phen)_8]\cdot 11H_2O$ (**2**), and $[Zn_6(m\text{-}O_3S\text{-}Ph\text{-}PO_3)_4(bipy)_6(H_2O)_4]\cdot 18H_2O$ (**3**), have been reported. The nature of the clusters formed is strongly affected by the amount and coordination nature of the second metal linker. The $[Zn(phen)_3]^{2+}$ cation in compound **1** is formed because a larger phen/Zn molar ratio applied. The hexanuclear cluster in

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[18] Spek, A. L. *Platon: A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2001.

[19] (a) Wang, S. *Coord. Chem. Rev.* **2001**, *215*, 79. (b) Song, J.-L.; Zhao, H.-H.; Mao, J.-G.; Dunbar, K. R. *Chem. Mater.* **2004**, *16*, 1884.

compound **2** is isolated, whereas those in compound **3** are interconnected to form a porous network, which can be attributed to the bidentate chelating nature of phen and the bidnetate bridging nature of 4,4′-bipy. The different hexanuclear cluster units in compounds **2** and **3** also result from the different coordination modes of the sulfonate−phosphonate ligands. The results of our studies indicate that the attachment of a weak coordination sulfonate group to the phosphonic acid and the selection of a suitable second metal linker may be a new synthetic route for cluster compounds of metal phosphonates. We are currently extending such a synthetic technique to lanthanide compounds and results will be published in another paper soon.

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Supporting Information Available: X-ray crystallographic files in CIF format, TGA diagrams, and simulated and experimental XRD patterns for the three compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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