

Syntheses, characterizations and crystal structures of three new organically templated or organically bonded zinc selenates

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Received 7 April 2004; received in revised form 10 June 2004; accepted 13 June 2004

Available online 11 August 2004

Abstract

Three new organically templated or organically bonded zinc selenates, namely, $\{H_2bipy\}Zn(SeO_4)_2(H_2O)_2$ **1** (bipy = 4,4'-bipyridine), $\{H_2pip\}\{Zn(SeO_4)_2(H_2O)_4\} \cdot 2H_2O$ **2** (pip = piperazine), and $Zn(SeO_4)(phen)(H_2O)_2$ **3** (phen = 1,10-phenanthroline) have been synthesized by hydrothermal reactions. The structure of compound **1** features a 1D chain composed of $[Zn(SeO_4)_2(H_2O)_2]^{2-}$ anions. Compound **2** has a 2D layer structure built from $\{Zn(SeO_4)_2(H_2O)_4\}^{2-}$ anions that are cross-linked by doubly protonated piperazine cations via N–H \cdots O hydrogen bonds. The structure of compound **3** contains a 1D chain of $Zn(SeO_4)(phen)(H_2O)_2$, such chains are further interlinked by hydrogen bonds and $\pi\cdots\pi$ interactions to form a $\langle 200 \rangle$ layer. The different roles the templates played have also been discussed.

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Keywords: Hydrothermal synthesis; Crystal structure; Organically templated; Zinc selenates

1. Introduction

A remarkable variety of open-framework organically templated inorganic materials have been reported during the last two decades [1]. Generally, the inorganic skeleton of the materials is built up from two parts: a metal cation and an oxo-anion. The metal elements range from main group elements to transition metal elements and to lanthanide metals. The majority of such work has been focused on the $[PO_4]^{3-}$ phosphate anion [1,2]. In addition to metal phosphates, open frameworks of metal arsenates [3–5], germinates [6,7] and carbonates [8] have also been reported in the literature. Recently, a lot of research efforts have been devoted to the preparations of open-framework structures involving sulfates [9–11], and other such oxy-anions [12–19]. As for the oxy-anions of Se, the first organically templated zinc selenite with a layered structure, $(CN_3H_6)_4[Zn_3(SeO_3)_5]$, was reported by Harrison et al. [12]. The first three-dimensional organically

templated iron(III) selenite, $(C_4N_2H_{12})_{0.5}[Fe_2F_3(SeO_3)_2]$, and an organically pillared zinc selenite, $[C_2N_2H_8]_{0.5}(ZnSeO_3)$, were isolated by Rao et al. [13]. Both organically templated and organically linked vanadium selenites have also been reported [14,15]. More recently, several organically templated selenites, $[H_2en][CdCl_2(HSeO_3)_2]$, $[H_2N(CH_2)_2NH_2]_2Zn_4(SeO_3)_4$ and $[H_3N(CH_2)_3NH_3]_4Zn_4(SeO_3)_8$ have been reported in the literature [16,17]. So far, reports on organically templated metal selenates are still rare [18,19]. The oxy-anions of Se differ from those of S with respect to the stability of the oxidation states and their redox behavior [18]. While the most stable oxidation state of S is +VI as in SO_4^{2-} , that of Se is +IV (SeO_3^{2-} or $Se_2O_5^{2-}$). The reduction potential of the XO_4^{2-}/XO_3^{2-} couple is 0.03 V in alkaline medium in the case of Se and 0.119 V for S, and this has implications on the thermal decomposition and relative stabilities of their compounds. It is, therefore, difficult to stabilize a metal selenate framework under hydrothermal conditions, especially in the presence of the reducing amine templates [19]. The organically templated linear cadmium(II) and organically templated 1D or layered lanthanide(III) selenates

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were reported recently by Rao et al. [19]. An organically templated lithium selenate was isolated by the Havlicek group [19d]. We deem that the nature of the template amines used in the reactions has an important effect on the structures of the metal selenates formed. The diamine such as 4,4'-bipyridine can function as templated cation as well as a bidentate ligand to a metal ion. The aim of our current study is to understand the effect of the nature of the templates on the structures of metal selenates thus obtained. By hydrothermal reactions of zinc oxide and selenic acid in the presence of 4,4'-bipyridine (bipy), or piperazine (pip) or 1,10-phenanthroline (phen), three new organically templated or organically bonded zinc selenates, namely, $\{\text{H}_2\text{bipy}\}\text{Zn}(\text{SeO}_4)_2(\text{H}_2\text{O})_2$ **1** featuring a 1D chain of $[\text{Zn}(\text{SeO}_4)_2(\text{H}_2\text{O})_2]^{2-}$, $\{\text{H}_2\text{pip}\}\{\text{Zn}(\text{SeO}_4)_2(\text{H}_2\text{O})_4\} \cdot 2\text{H}_2\text{O}$ **2** with a hydrogen-bonded layered structure, and one-dimensional $\text{Zn}(\text{SeO}_4)(\text{phen})(\text{H}_2\text{O})_2$ **3** in which the template phen ligand is bidentately chelated to a metal center, have been successfully prepared and their crystal structures established by single-crystal X-ray diffraction. Herein we report their syntheses, crystal structures and characterizations.

2. Experimental

All chemicals were obtained from commercial sources and used without further purification. Elemental analyses were performed on a Vario EL III elemental analyser. Se and Zn analyses were carried out with an ICPQ-100 spectrometer. IR spectra were recorded on a Magna 750 FT-IR spectrometer photometer as KBr pellets in the range of 4000–400 cm^{-1} . Thermogravimetric analyses were carried out with a NETZSCH STA 449C unit, at a heating rate of 15°C/min under a nitrogen atmosphere. The XRD powder patterns were collected on a Philips X'Pert-MPD diffractometer using graphite-monochromated $\text{CuK}\alpha$ radiation in the angular range $2\theta = 5\text{--}70^\circ$ with a step size of 0.02° and a counting time of 3 s per step.

2.1. Synthesis of compounds **1**, **2**, and **3**

All three compounds were synthesized by a similar method. Thus only the procedures for the synthesis of compound **1** will be described in detail as an example. 0.0811 g (1 mmol) of ZnO was dissolved completely in 0.77 mL (3 mmol) of selenic acid (Aldrich, 40 wt%), then 0.0792 g (0.5 mmol) of 4,4'-bipyridyl and 5 mL of distilled water and 5 mL of ethanol were added into the solution. The resultant mixture was sealed into an autoclave equipped with a Teflon liner (25 mL) and heated at 110°C for 5 days. The initial and final pH values of the solution are 3.0 and 3.5, respectively. Colorless needle crystals of compound **1** were collected

in a yield of 51.2% base on Zn. Elemental analysis for compound **1**, $\text{C}_{10}\text{H}_{14}\text{ZnN}_2\text{O}_{10}\text{Se}_2$: Zn, 11.8; Se, 28.7; C, 21.19; H, 2.68; N, 5.02. Calcd.: Zn, 11.99; Se, 28.95; C, 22.02; H, 2.59; N, 5.14. IR data (KBr, cm^{-1}): 3220 (vs), 1635 (w), 1601 (w), 1400(s), 1087(w), 867(m), 582(w), 407 (m).

Compounds **2** and **3** were synthesized by hydrothermal reactions in a similar procedure. The reaction temperatures are 100°C and 120°C, respectively, for compounds **2** and **3**. The initial and final pH values of the solution are 4.0 and 4.5 for compound **2**, 3.0 and 3.5 for compound **3**, respectively. Colorless plate-shaped crystals of compounds **2** and **3** were collected in a yield of 60.2% and 68.5% base on Zn, respectively. Elemental analysis for compound **2**, $\text{C}_4\text{H}_{24}\text{ZnN}_2\text{O}_{14}\text{Se}_2$: Zn, 11.7; Se, 28.6; C, 9.22; H, 3.02; N, 5.28. Calcd.: Zn, 11.94; Se, 28.84; C, 8.76; H, 4.41; N, 5.11%. IR data (KBr, cm^{-1}): 3584 (w), 3018 (m), 2735 (m), 2471 (m), 1703 (w), 1651 (w), 1613 (m), 1461 (m), 1210 (w), 1086 (m), 971 (m), 880 (br), 745 (vs), 601 (w), 471 (vs), 439 (vs). Elemental analysis for compound **3**, $\text{C}_{12}\text{H}_{12}\text{ZnN}_2\text{O}_6\text{Se}$: Zn, 15.1; Se, 18.3; C, 33.56; H, 2.57; N, 6.64. Calcd.: Zn, 15.40; Se, 18.60; C, 33.95; H, 2.85; N, 6.60%. IR data (KBr, cm^{-1}): 3093 (br), 2988 (s), 1989 (w), 1951 (w), 1913 (w), 1621 (m), 1581 (s), 1519 (s), 1425 (vs), 1347 (m), 1109 (m), 935 (w), 859 (vs), 728 (vs), 644 (w), 499 (w), 427 (vs), 418 (w).

2.2. Single-crystal structure determination

Single crystals of compounds **1**, **2** and **3** were mounted on a Siemens Smart CCD diffractometer equipped with a graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Intensity data were collected by the narrow frame method at 293 K. All three data sets were corrected for Lorentz and Polarization factors as well as for absorption by SADABS program [20]. The space groups of compounds **1**, **2** and **3** were determined correctly to be $P\bar{1}$, $P2_1/n$ and $C2/c$, respectively, based on systematic absences as well as E -value statistics, which gave satisfactory refinements for all three compounds. All three structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELXS-97 [20]. All hydrogen atoms, except those for water molecules, were located at geometrically calculated positions. The data collection and refinement parameters are summarized in Table 1, and selected bond lengths and angles are listed in Table 2.

Crystallographic data (excluding structure factors) for the three structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 235492, 235493 and 235494. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; <mailto:deposit@ccdc.cam.ac.uk>).

Table 1
Crystal data and structural refinements for compounds **1**, **2** and **3**

Compound	1	2	3
Formula	C ₁₀ H ₁₄ ZnN ₂ O ₁₀ Se ₂	C ₄ H ₂₄ ZnN ₂ O ₁₄ Se ₂	C ₁₂ H ₁₂ ZnN ₂ O ₆ Se
Fw	545.52	547.54	424.57
space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	5.354(3)	7.0962(9)	15.256(2)
<i>b</i> (Å)	7.529(4)	12.0343(15)	14.3088(19)
<i>c</i> (Å)	10.797(7)	10.5205(14)	6.8608(10)
<i>a</i> (deg)	109.471(14)	90.00	90.00
<i>β</i> (deg)	93.89(2)	113.600(3)	105.757(7)
<i>γ</i> (deg)	105.483(19)	90.00	90.00
<i>V</i> (Å ³)	389.5(4)	865.15(19)	1441.4(4)
<i>Z</i>	1	2	4
<i>D</i> _{calcd} (g cm ⁻³)	2.326	2.102	1.956
<i>μ</i> (mm ⁻¹)	6.307	5.695	4.260
Crystal size	0.35 × 0.07 × 0.05 mm	0.32 × 0.16 × 0.06 mm	0.25 × 0.05 × 0.04 mm
<i>F</i> (000)	266	544	840
Reflections collected	2546	2517	4309
Independent reflections	1366 (<i>R</i> _{int} = 0.0268)	1510 (<i>R</i> _{int} = 0.0433)	1274 (<i>R</i> _{int} = 0.0348)
Observed reflections (<i>I</i> > 2σ(<i>I</i>))	1178	1313	1158
Data/restraints/parameters	1366/0/115	1510/0/106	1274/0/101
GOF on <i>F</i> ²	1.063	1.158	1.123
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0301/0.0702	0.0562/0.1450	0.0370/0.0873
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0384/0.0741	0.0654/0.1535	0.0432/0.0910

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

3. Results and discussion

The synthetic procedures for these three organically templated or organically bonded zinc selenates are worth discussing. As mentioned earlier, the selenate anion can be easily reduced to selenite anion in the presence of the reducing basic template. Therefore, all three compounds were synthesized under acidic media and at relatively lower reaction temperatures.

The asymmetric unit of compound **1**, {H₂bipy} Zn(SeO₄)₂(H₂O)₂, consists of 13 independent non-hydrogen atoms, 7 of which belong to the inorganic framework (one Zn, one Se and five oxygens) and 6 to the 4,4'-bipyridine (one N and five C atoms). The zinc atom lies on a position with a -1 symmetry and is octahedrally coordinated by four SeO₄²⁻ groups and two aqua ligands. The Zn–O distances range from 2.070(3) to 2.117(3) Å, which are comparable to those reported in the ethylenediamine-templated zinc selenites [16,17]. The Zn–O(aqua) distances are slightly longer than those of Zn–O(selenate) bonds (Table 2). The selenate group forms a tetrahedron, it acts as a bidentate bridging metal linker. The template ligand bipy is doubly protonated.

Two neighboring zinc octahedra are bridged by a pair of selenate tetrahedra via corner-sharing to form a 1D chain along *a*-axis (Fig. 1). This type of 1D chain is similar to that reported in the ethylenediamine-templated cadmium selenate [19]. Such neighboring chains are further interlinked by {H₂bipy}²⁺ cations via strong hydrogen bonds into a <022> 2D layer (Fig. 1). The N–H...O hydrogen bond distance and angle are

2.608(5) Å and 169.2°, respectively (Table 2). The aqua ligand also forms a hydrogen bond with the non-coordination oxygen (O4) from the selenate group. Adjacent 2D layers are held together via weak Van der Waals force (Fig. 2).

When piperazine was used as the template molecule instead of 4,4'-bipyridine, compound **2** was isolated. The asymmetric unit of compound **2** consists of 12 independent non-hydrogen atoms, 8 of which belong to the anionic framework (one Zn, one Se and six oxygens), and 3 atoms to the piperazine (one N and two C atom) and one to the lattice water (Fig. 3). As shown in Fig. 3, the zinc atom is located at a position with a -1 symmetry; it is octahedrally coordinated by two unidentate SeO₄²⁻ groups and four aqua ligands. The Zn–O distances range from 2.069(6) to 2.120(5) Å, which are comparable to those in compound **1** and those reported in organically templated zinc selenites [16,17]. Unlike that in compound **1**, each selenate group in compound **2** is monodentate. This may be result from the stronger Zn–H₂O bonds than the Zn–O (selenate) bonds (Table 2). The piperazine ligand is doubly protonated and carries two positive charges.

The isolated {Zn(SeO₄)₂(H₂O)₄}²⁻ anions, template cations and lattice water molecules are interlinked via hydrogen bonds into a 3D network (Fig. 4, Table 2). The N–H...O hydrogen bond distance and angle are 2.748(9) Å and 163.3°, respectively (Table 2).

The use of 1,10-phenanthroline as the template molecule lead to an organically bonded zinc selenate with a 1D chain structure. As shown in Fig. 5, the

Table 2
Selected bond lengths (Å) and angles (deg) for compounds **1**, **2** and **3**

Compound 1			
Zn(1)–O(2)	2.070(3)	Zn(1)–O(2)#1	2.070(3)
Zn(1)–O(1)#2	2.114(3)	Zn(1)–O(1)#3	2.114(3)
Zn(1)–O(1W)	2.117(3)	Zn(1)–O(1W)#1	2.117(3)
Hydrogen bonds			
N(1)⋯O(3)#4	2.608(5)	O(1W)⋯O(4)	2.711(5)
N(1)–H(01A)⋯O(3)#4	169.2		
O(2)–Zn(1)–O(2)#1	180.00(19)	O(2)–Zn(1)–O(1)#2	92.09(12)
O(2)#1–Zn(1)–O(1)#2	87.91(12)	O(2)–Zn(1)–O(1)#3	87.91(12)
O(2)#1–Zn(1)–O(1)#3	92.09(12)	O(1)#2–Zn(1)–O(1)#3	180.0(2)
O(2)–Zn(1)–O(1W)	94.43(12)	O(2)#1–Zn(1)–O(1W)	85.57(12)
O(1)#2–Zn(1)–O(1W)	90.27(13)	O(1)#3–Zn(1)–O(1W)	89.73(13)
O(2)–Zn(1)–O(1W)#1	85.57(12)	O(2)#1–Zn(1)–O(1W)#1	94.43(12)
O(1)#2–Zn(1)–O(1W)#1	89.73(13)	O(1)#3–Zn(1)–O(1W)#1	90.27(13)
O(1W)–Zn(1)–O(1W)#1	180.0		
Compound 2			
Zn(1)–O(1W)	2.069(6)	Zn(1)–O(1W)#1	2.069(6)
Zn(1)–O(2W)	2.101(5)	Zn(1)–O(2W)#1	2.101(5)
Zn(1)–O(3)#1	2.120(5)	Zn(1)–O(3)	2.120(5)
Hydrogen bonds			
O(1)⋯O(2W)#2	2.732(9)	O(1)⋯O(3W)#3	2.865(11)
O(4)⋯O(2W)	2.716(8)	O(4)⋯O(1W)#4	2.721(8)
O(1W)⋯O(3W)#5	2.680(9)	O(2)⋯O(3W)	2.787(10)
N(1)⋯O(2)	2.748(9)	N(1)–H(01B)⋯O(2)	163.3
O(1W)–Zn(1)–O(1W)#1	180.0(4)	O(1W)–Zn(1)–O(2W)	90.9(2)
O(1W)#1–Zn(1)–O(2W)	89.1(2)	O(1W)–Zn(1)–O(2W)#1	89.1(2)
O(1W)#1–Zn(1)–O(2W)#1	90.9(2)	O(2W)–Zn(1)–O(2W)#1	180.0(2)
O(1W)–Zn(1)–O(3)#1	88.8(2)	O(1W)#1–Zn(1)–O(3)#1	91.2(2)
O(2W)–Zn(1)–O(3)#1	86.1(2)	O(2W)#1–Zn(1)–O(3)#1	93.9(2)
O(1W)–Zn(1)–O(3)	91.2(2)	O(1W)#1–Zn(1)–O(3)	88.8(2)
O(2W)–Zn(1)–O(3)	93.9(2)	O(2W)#1–Zn(1)–O(3)	86.1(2)
O(3)#1–Zn(1)–O(3)	180.000(1)		
Compound 3			
Zn(1)–O(1W)#1	2.075(3)	Zn(1)–O(1W)	2.075(3)
Zn(1)–N(1)#1	2.115(4)	Zn(1)–N(1)	2.115(4)
Zn(1)–O(1)#1	2.222(3)	Zn(1)–O(1)	2.222(3)
Hydrogen bonds			
O(1W)⋯O(2)#1	2.647(4)	O(1W)⋯O(2)#2	2.700(5)
O(1W)#1–Zn(1)–O(1W)	95.72(18)	O(1W)#1–Zn(1)–N(1)#1	171.33(13)
O(1W)–Zn(1)–N(1)#1	92.86(13)	O(1W)#1–Zn(1)–N(1)	92.86(13)
O(1W)–Zn(1)–N(1)	171.33(13)	N(1)#1–Zn(1)–N(1)	78.58(19)
O(1W)#1–Zn(1)–O(1)#1	91.23(12)	O(1W)–Zn(1)–O(1)#1	90.38(11)
N(1)#1–Zn(1)–O(1)#1	89.90(13)	N(1)–Zn(1)–O(1)#1	88.24(12)
O(1W)#1–Zn(1)–O(1)	90.38(11)	O(1W)–Zn(1)–O(1)	91.23(12)
N(1)#1–Zn(1)–O(1)	88.24(12)	N(1)–Zn(1)–O(1)	89.90(13)
O(1)#1–Zn(1)–O(1)	177.60(17)		

Symmetry transformations used to generate equivalent atoms:

For **1**: #1, $-x, -y + 1, -z$; #2, $-x - 1, -y + 1, -z$; #3, $x + 1, y, z$; #4, $-x + 1, -y + 2, -z$.

For **2**: #1, $-x + 2, -y + 1, -z + 1$; #2, $-x + 1/2, -y + 1/2, -z + 1/2$; #3, $-x + 3/2, y - 1/2, -z + 1/2$; #4, $1 - x, 1 - y, 1 - z$; #5, $x + 1/2, -y + 3/2, z + 1/2$.

For **3**: #1, $-x, y, -z - 1/2$; #2, $-x, -y + 1, -z$.

asymmetric unit of compound **3** consists of 12 independent non-hydrogen atoms, 5 of which belong to the inorganic framework (one Zn, one Se and three

oxygens), and 7 to the 1,10-phenanthroline (one N and six C atoms). The zinc atom sits on a two-fold axis, it is octahedrally coordinated by a bidentate chelating phen

ligand, two SeO_4^{2-} groups in a unidentate fashion and two aqua ligands. The Zn–N distances are 2.115(4) Å, and the Zn–O(aqua) distances of 2.075(3) Å are significantly shorter than those of Zn–O (selenate) (2.222(3) Å). Hence, the zinc octahedron in compound **3** is much more distorted than those in compounds **1** and **2**. The selenate group adopts a bidentate bridging coordination mode.

The interconnection of the ZnO_4N_2 octahedra via bridging selenate groups results in the formation of a 1D chain along *c*-axis. Two such neighboring chains are interlinked via hydrogen bonds formed between the non-coordinated oxygen atoms of the selenate groups and aqua ligands into a double chain (Fig. 6, Table 2). The $[\text{Zn}(\text{H}_2\text{O})_2\text{SeO}_4]$ double chains are further held together via $\pi \cdots \pi$ interactions between phen ligands to form a $\langle 200 \rangle$ layer (Fig. 6). The distance between two

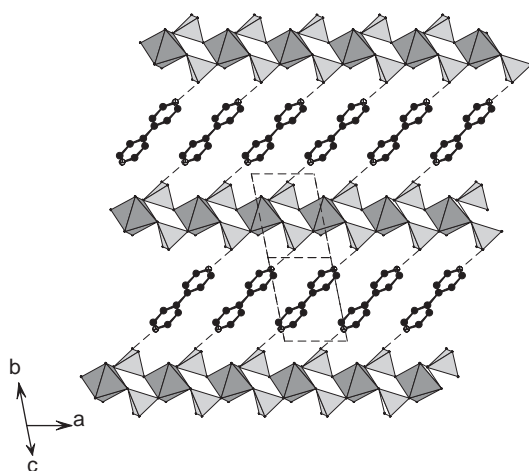


Fig. 1. A hydrogen bonded layer in compound **1**. Hydrogen bonds are drawn as dotted lines. Zinc octahedra and selenate tetrahedra are shaded in medium and light gray, respectively. N and C atoms are drawn as octanted and black circles, respectively.

parallel C_6 rings (the middle ring of the phen ligand) from two neighboring chains is 3.453 Å. These $\langle 200 \rangle$ layers are further interact through weak Van der Waals force.

From above discussions, we know that the template can play different roles in its metal selenates. In compound **1** or **2**, the 4,4'-bipyridine or piperazine molecules are doubly protonated and involved in hydrogen bonding with the zinc selenate moiety. 1,10-phenanthroline is a good chelating ligand, hence it is directly chelated to the metal center to form an organically bonded zinc selenate.

The experimental XRD powder patterns for compounds **1**, **2** and **3** match well with those simulated from single-crystal structure data, indicating that all three compounds were isolated as single phases.

IR spectra of compounds **1**, **2** and **3** all exhibit characteristic absorption bands at around $830\text{--}880\text{ cm}^{-1}$ and $407\text{--}439\text{ cm}^{-1}$ associated with the stretching and bending vibrations of SeO_4 groups, respectively. The bands at around $1519\text{--}1651$ and $2471\text{--}3584\text{ cm}^{-1}$ originate from the bending vibrations of water molecules and template ligands.

TGA curves of compounds **1** and **2** are similar to those reported for the ethylenediamine-templated cadmium selenate, $\{\text{H}_2\text{en}\}\text{Cd}(\text{SeO}_4)_2(\text{H}_2\text{O})_2$ [19]. The first weight loss occurs in a broad temperature range of $70\text{--}499^\circ\text{C}$ for compound **1** and $80\text{--}485^\circ\text{C}$ for compound **2**, during which the templates, water molecules and SeO_2 are released. The second step corresponds to the further decomposition of the compounds. The final residuals were a mixture of ZnO and ZnSe in a molar ratio close to 4:1 (JCPDS file, card nos: 21-1486 and 05-0566) based on the XRD powder pattern. The total weight losses are 80.3% for compound **1** and 82.1% for compound **2**. The thermal decomposition mechanism has been explained in the literature [19]. TGA curves of the compound **3** also indicate two main weight losses. The first one

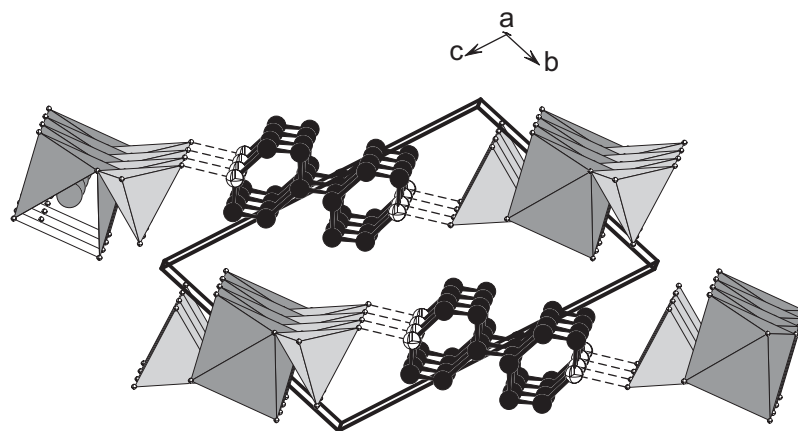


Fig. 2. View of the structure of compound **1** down the *a*-axis. Hydrogen bonds are drawn as dotted lines. Zinc octahedra and selenate tetrahedra are shaded in medium and light gray, respectively. N and C atoms are drawn as octanted and black circles, respectively.

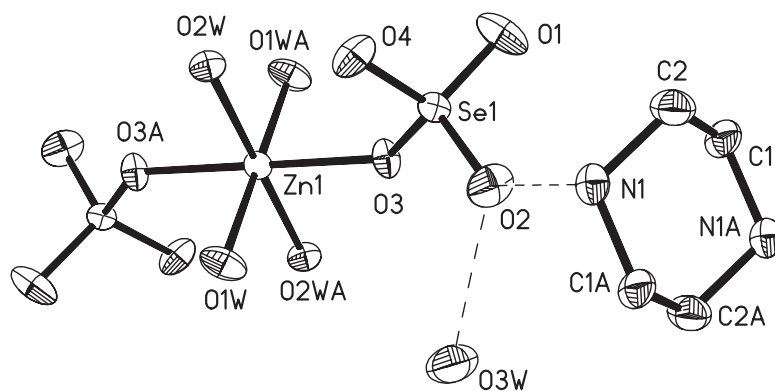


Fig. 3. ORTEP representation of the selected unit in compound **2**. The thermal ellipsoids are drawn at 50% probability. Hydrogen bonds are represented by dotted lines. Symmetry operators for the generated atoms: (a) $2-x, 1-y, 1-z$; (b) $-x, -y+1, z$.

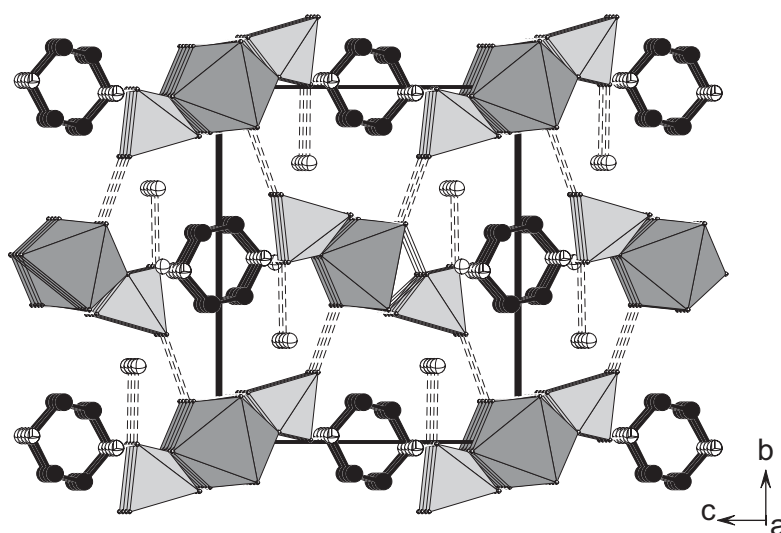


Fig. 4. View of the structure of compound **2** down the a -axis. Hydrogen bonds are drawn as dotted lines. Zinc octahedra and selenate tetrahedra are shaded in medium and light gray, respectively. N, O and C atoms are drawn as octahed, crossed and black circles, respectively.

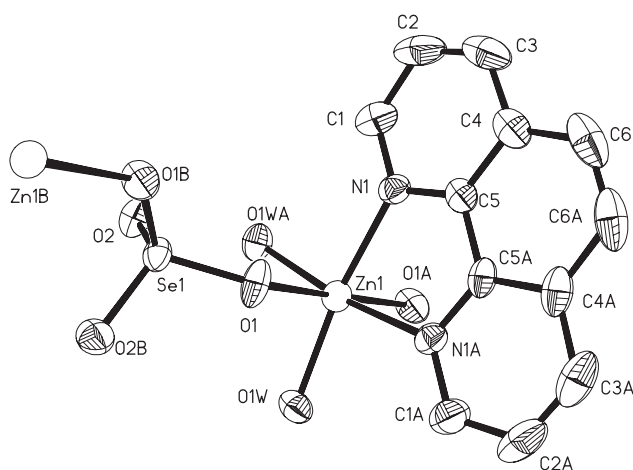


Fig. 5. ORTEP representation of the selected unit in compound **3**. The thermal ellipsoids are drawn at 50% probability. Symmetry operators for the generated atoms: (a) $-x, y, -1/2-z$; (b) $-x, y, 1/2-z$.

started at 113°C and was completed at 174°C , corresponding to the release of its three lattice water molecules. The observed weight loss of 7.94% is in good agreement with the calculated value (8.44%). The second weight loss covers a temperature range from 315°C to 998°C , corresponding to the burning of the 1,10-phenanthroline, and the release of aqua ligand and SeO_2 . The final residuals were a mixture of ZnO and ZnSe based on the XRD powder pattern. The total weight loss is 76.8%. The mechanism of the decomposition for compound **3** is slightly different from that for compounds **1** and **2**. For compounds **1** and **2**, the formation of ZnSeO_3 is accompanied by the loss of SeO_2 , O_2 as well as the template and water molecules, whereas for compound **3** no SeO_2 is released in this process. The remaining steps concerning the decomposition of ZnSeO_3 are the same for all three compounds.

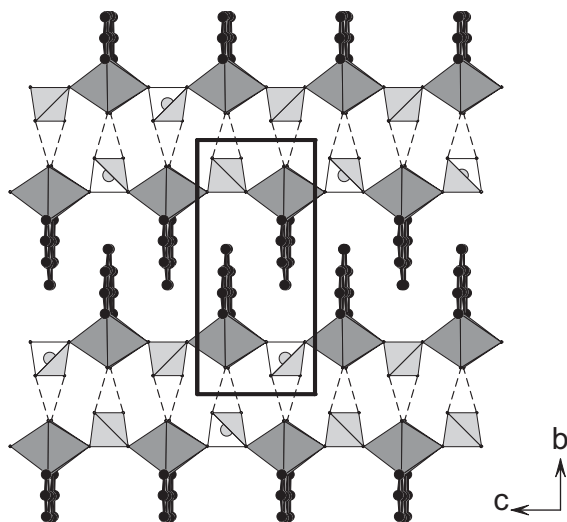


Fig. 6. A $\langle 200 \rangle$ layer formed by the cross-linkage of the hydrogen bonded double chains of $\text{Zn}(\text{SeO}_4)(\text{phen})(\text{H}_2\text{O})_2$ via π - π interaction. Zinc octahedra and selenate tetrahedra are shaded in medium and light gray, respectively. N and C atoms are drawn as octahed and black circles, respectively.

4. Conclusions

In conclusion, three new organically templated or organically bonded zinc selenates have been synthesized successfully by the hydrothermal reactions. The present study again confirms that the acidic media and low reaction temperature are very important to prevent reduction of the selenate group. We deem that a variety of other organically templated open frameworks of metal selenates can be synthesized by using a similar technique. Our future research efforts will be devoted to the organically templated lanthanide selenates.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 20371047).

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