

Organically templated three-dimensional open-framework metal selenites with a diamondoid network

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Three-dimensional open-framework metal selenites of the formula, $[\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2]_{0.5}[\text{M}(\text{HSeO}_3)(\text{Se}_2\text{O}_5)]$ ($\text{M} = \text{Zn}, \text{Co}$ or Ni), containing both selenite and diselenite units and intersecting 10-membered channels, have been prepared hydrothermally in the presence of piperazine. The compounds are isomorphous and crystallize in the $P-1$ space group. The structure is built up of MO_6 dimers along with Se_2O_5 and HSeO_3 units, the first two forming sheets, which are connected by the selenite units to yield a three-dimensional non-interpenetrating diamondoid network. The 10-membered channels have an unusual structure, being formed by 4-membered (M_2Se_2) and 6-membered (M_2Se_4) rings.

Introduction

While most of the inorganic open-framework materials involve silicates,¹ phosphates² and carboxylates,^{3–5} there has been some effort recently to prepare open-framework structures, involving the sulfate,⁶ selenite^{7,8} and other such oxyanions. Harrison *et al.*⁷ reported the first organically templated layered zinc selenite. Later, Choudhury *et al.*⁸ prepared organically templated three-dimensional iron selenite of the formula $[\text{C}_2\text{N}_2\text{H}_8]_{0.5}[\text{Fe}_2\text{F}_3(\text{SeO}_3)_2]$. These workers also prepared a three-dimensional zinc selenite of the formula $[\text{C}_2\text{N}_2\text{H}_8]_{0.5}(\text{ZnSeO}_3)$, wherein the amine acts as a pillar.⁸ Larranaga *et al.*⁹ have recently reported two semi-condensed manganese(II) selenite hydrates. Selenium(IV) forms selenite (SeO_3^{2-}), hydrogen selenite (HSeO_3^-) and diselenite ($\text{Se}_2\text{O}_5^{2-}$) anions depending on the conditions in solution.¹⁰ The synthesis of amine templated open-framework structures involving these anions is rendered difficult by the low reduction potential of the $\text{Se}^{\text{IV}}/\text{Se}^0$ couple, which under hydrothermal conditions may cause reduction to metallic selenium. While condensed metal diselenites are known,¹¹ no open-framework structure has been reported to-date for this anion. In the case of open-framework metal phosphates, two low dimensional gallium fluorodiphosphates have been described recently.¹² We have been able to synthesize, for the first time, three-dimensional open-framework compounds of the formula $[\text{NH}_2(\text{CH}_2)_4\text{NH}_2]_{0.5}[\text{M}(\text{HSeO}_3)(\text{Se}_2\text{O}_5)]$, **I**, where $\text{M} = \text{Zn}, \text{Co}$ or Ni , possessing a diamondoid network and containing both the diselenite and the hydrogen selenite anions. The structure possesses intersecting two-dimensional 10-membered channels.

Experimental section

Synthesis and initial characterization

Compound **I** with $\text{M} = \text{Zn}$ was synthesised under hydrothermal conditions in the presence of piperazine (PIP). In a typical synthesis, 0.081 g of ZnO was dispersed in a mixture of 5.4 ml of deionized water and 0.1 ml of 36% HCl. To this solution, 0.45 g of SeO_2 was added followed by the addition of 0.086 g of piperazine under continuous stirring. The resulting mixture of pH 1, with the final molar ratios of 1 ZnO : 4 SeO_2 : 1 PIP : 1.4 HCl : 300 H_2O , was transferred to a polypropylene bottle and heated at 100 °C for 10 days. The reaction mixture

after the above heat treatment did not show any appreciable change in the pH, remaining at pH 1. The solution, after cooling over 48 hours, yielded a good crop of colorless crystals. The crystals were filtered, washed with deionized water and dried in ambient conditions. The final yield of the product was 45%. EDAX analysis indicated the Zn : Se ratio to be 1 : 3, consistent with the formula derived from single crystal data. Elemental analysis was satisfactory: calcd (%) C 5.05, N 2.95, H 1.48; found (%) C 4.85, N 2.77, H 1.37. For the synthesis of the Co and Ni compounds CoCl_2 and NiCl_2 were used in place of ZnO. Initial characterizations were also carried out by powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA). Powder X-ray diffraction with powdered single crystals indicated the formation of new materials and the patterns were in excellent agreement with those simulated from single crystal data, showing phase purity.

A suitable single crystal of **I** was carefully selected under a polarizing microscope and mounted at the tip of a thin glass fiber using cyanoacrylate (super glue) adhesive. Single crystal structure determination by X-ray diffraction was performed on a Siemens SMART-CCD diffractometer equipped with a normal focus, 2.4 kW sealed-tube X-ray source (Mo- $\text{K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$) operating at 50 kV and 40 mA. A hemisphere of intensity data was collected at room temperature in 2014 frames with ω scans (width of 0.30° and an exposure time of 20 s per frame) in the 2θ range of $2\text{--}23^\circ$. The structure was solved by direct methods using SHELXS-86,¹³ which readily revealed all the heavy atom positions (Zn, Se) and enabled us to locate the other non-hydrogen (C, N and O) positions from the difference Fourier maps. An empirical absorption correction based on symmetry equivalent reflections was applied using SADABS.¹⁴ All the hydrogen positions were found in the difference Fourier maps. For the final refinement, hydrogen atoms for both the framework as well as the amine were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares structure refinement against $|F^2|$ was carried out using the SHELXTL-PLUS¹⁵ package of programs. Pertinent experimental details and crystallographic data for **I** ($\text{M} = \text{Zn}$) are given below. The structural parameters of **I** ($\text{M} = \text{Zn}$) are listed in Table 1. We discuss the structure of the zinc compound in detail in the next section.

Table 1 Selected bond lengths and angles in **I**

Moiety	Length/Å	Moiety	Length/Å
Se(1)–O(1)	1.650(5)	Zn(1)–O(1) ^{#1}	2.078(6)
Se(1)–O(2)	1.670(5)	Zn(1)–O(8) ^{#2}	2.101(6)
Se(1)–O(3)	1.820(6)	Zn(1)–O(7) ^{#3}	2.116(6)
Se(2)–O(4)	1.679(5)	Zn(1)–O(4)	2.120(5)
Se(2)–O(5)	1.683(5)	Zn(1)–O(5) ^{#4}	2.131(5)
Se(2)–O(6)	1.746(6)	Zn(1)–O(2)	2.137(6)
Se(3)–O(7)	1.655(6)	O(1)–Zn(1) ^{#1}	2.078(6)
Se(3)–O(8)	1.675(6)	O(5)–Zn(1) ^{#4}	2.131(5)
Se(3)–O(3)	1.834(6)	O(7)–Zn(1) ^{#3}	2.116(6)
O(8)–Zn(1) ^{#5}	2.101(6)		
Organic moiety			
Moiety	Length/Å	Moiety	Angle/°
N(1)–C(2)	1.456(13)	C(2)–N(1)–C(1)	110.5(8)
N(1)–C(1)	1.478(13)	N(1)–C(1)–C(2) ^{#6}	109.5(8)
C(1)–C(2) ^{#6}	1.520(13)	N(1)–C(2)–C(1) ^{#6}	110.6(8)
C(2)–C(1) ^{#6}	1.520(13)		

^aSymmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 1, -z + 1$; #2 $x + 1, y, z$; #3 $-x + 1, -y + 2, -z + 1$; #4 $-x + 1, -y + 1, -z$; #5 $x - 1, y, z$; #6 $-x, -y, -z$.

Crystal data: $[\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2]_{0.5}[\text{M}(\text{HSeO}_3)(\text{Se}_2\text{O}_5)]$, **I**, with $\text{M} = \text{Zn}$, $M = 475.34$, triclinic, space group = $P-1$, $a = 7.4704(4)$, $b = 8.5931(5)$, $c = 9.300(6)$ Å, $\alpha = 114.805(2)^\circ$, $\beta = 93.823(2)^\circ$, $\gamma = 114.385(2)^\circ$, $V = 472.35(5)$ Å³, $Z = 2$, $\mu = 14.183$ mm⁻¹, total data collected = 2014, $R_{\text{int}} = 0.0254$. Final R : $R_1 = 0.045$, $wR_2 = 0.107$. The lattice parameters of the corresponding Co and Ni compounds were nearly identical.

CCDC reference number 199943.

See <http://www.rsc.org/suppdata/jm/b3/b303323f/> for crystallographic data in CIF or other electronic format.

The infrared spectrum of **I** ($\text{M} = \text{Zn}$) was recorded as a KBr pellet in the frequency range 400–4000 cm⁻¹. The spectrum showed characteristic bands due to the amine and –OH groups in the range 2331–3469 cm⁻¹. A band due to the stretching mode of selenite was observed at 966 cm⁻¹. Bands due to the diselenite unit were found at 550, 581 and 1005 cm⁻¹.

Results and discussion

The asymmetric unit of **I** consists of 15 non-hydrogen atoms out of which 12 belong to the inorganic framework and 3 to the amine as shown in Fig. 1. There are three crystallographically distinct selenium atoms and a unique zinc atom with half of the amine appearing in the asymmetric unit. Each selenium atom, bound to three oxygen atoms, forms a pyramid characteristic of the Se^{IV}O₃ group, with the stereochemically active lone pair of electrons occupying the remaining tetrahedral site. The diselenite group is formed by two SeO₃ units sharing an oxygen atom. In the diselenite group, containing Se(1) and Se(3), the

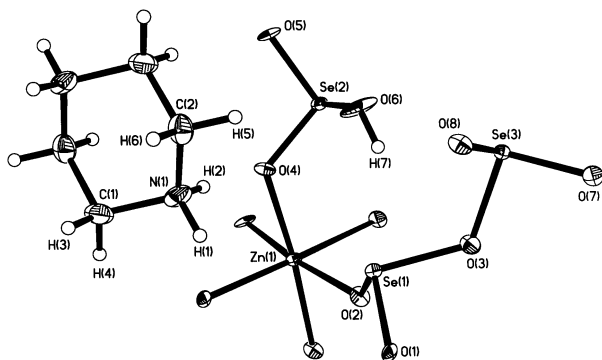


Fig. 1 ORTEP plot of $[\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2]_{0.5}[\text{Zn}(\text{HSeO}_3)(\text{Se}_2\text{O}_5)]$, **I**. The asymmetric unit is labelled. Thermal ellipsoids are given at 50% probability.

bridging Se–O bonds are markedly longer than the other Se–O bonds. In the case of Se(2), one of the oxygens is protonated, forming a hydrogenselenite (HSeO₃) group. The presence of a longer Se(2)–O(6) bond, the nature of the electron density near this oxygen in the difference Fourier map as well as bond valence sum (BVS) calculations¹⁶ support the presence of a terminal –OH group. The anionic framework consists of ZnO₆ octahedra along with SeO₃ and Se₂O₅ units with an extra framework charge of –2. The presence of 0.5[H₂N(CH₂)₄NH₂] accounts for the +1 charge arising from the protonation of the amine. The excess negative charge of –1 is then balanced by the protonation of the SeO₃ unit, as given in the formula. The hexa-coordinated Zn atoms form six Zn–O–Se bonds, four from the diselenite unit and two from the selenite unit. No two oxygens of a diselenite unit are bound to the same zinc atom.

The three-dimensional structure of **I** is derived from two-dimensional sheets made up of ZnO₆ octahedra and the diselenite units, the layers being formed along the *ab*-plane, by the linking of ZnO₆ dimers and the diselenite units (Fig. 2a). The ZnO₆ dimers are bridged by two diselenite units through –Zn–O–Se–O–Zn– linkages, which create a four-membered ring propagating in a zig-zag fashion in the *ab*-plane. The four-membered rings are fused by the diselenite units in a head-to-tail fashion (–Zn–O–Se–O–Se–O–Zn–) by satisfying the coordination of the diselenite unit, creating a six-membered ring. The strictly alternating four- and six-membered rings in the *ab*-plane can be seen in Fig. 2b.

The coordination environments of the different sites in the inorganic layer of **I** can be represented by the Schläfli symbol, which specifies the connectivity of the various vertex-linked

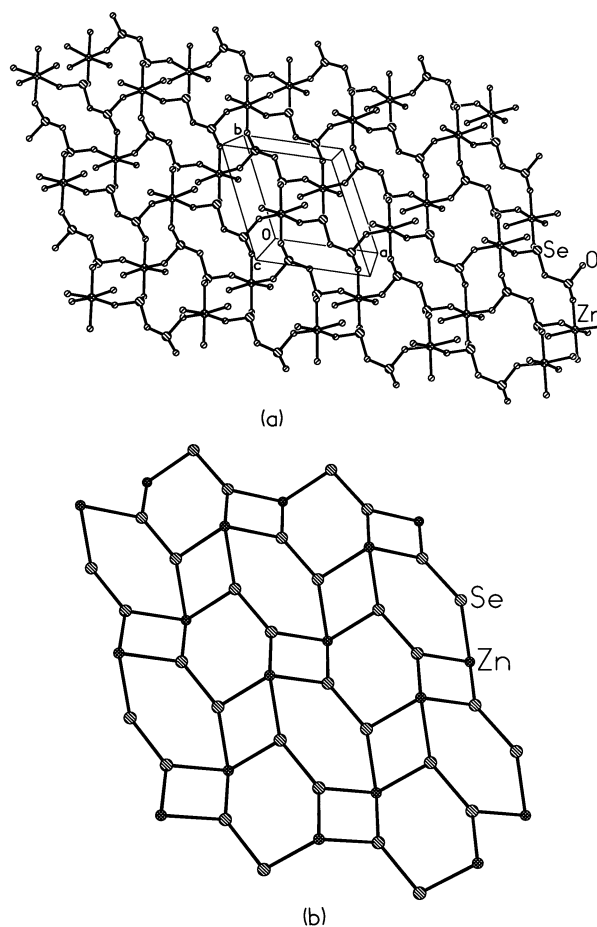


Fig. 2 a) Ball and stick representation of the inorganic layer built up with ZnO₆ octahedra and diselenite units in the *ab*-plane and forming strictly alternating 4- and 6-membered rings. b) T-atom (Zn, Se) connectivity forms a net in the *ab*-plane. Note that T-atom connectivity gives rise to Zn/Se/Se alternation in the *ab*-plane.

polygons.¹⁷ According to the Schläfli notation, the coordination environments of zinc and selenium in **I** are represented as (4,6,4,6) and (6,6,4) respectively. Hence, the circuit symbol that enumerates the smallest T-atom loop pathways, can be written as 4².6² for the octahedral atoms and 4¹.6² for the pseudo-tetrahedral atoms (Fig. 2b).

Along the *c*-axis, selenite units connect the zinc centers from the adjacent layers forming four-membered rings and act as pillars by crosslinking the layers to form the three-dimensional structure. Each ZnO₆ octahedron in a layer is connected to a ZnO₆ octahedron of the adjacent layer through two selenite units, leaving a terminal Se–OH bond. This connectivity results in a distinctive 10-membered two-dimensional channel system, propagating along [100] and [010]. The polyhedral view of the framework of **I** along the [100] direction shown in Fig. 3, clearly reveals the 10-membered channels built up of four ZnO₆ octahedra along with two diselenite and two SeO₃ units. The ZnO₆ octahedra are interconnected by the SeO₃ units along the *c*-axis and the diselenite units in the *ab*-plane. The Zn/Se T-atom alternation is, therefore, maintained along the *c*-axis and the Zn/Se/Se T-atom alternation in the *ab*-plane. These channels are occupied by piperazinium cations, which form hydrogen bonds with the framework oxygens, thereby contributing to the additional structural stability of the compound. The channels are elliptical in shape, with dimensions of 11.12 × 5.45 Å [100] and 14.23 × 2.52 Å [010] (longest atom–atom contact distances).

It is noteworthy that in **I** that the Zn centers are connected to form a 3D diamondoid framework based on adamantoid cages, as shown in Fig. 4. Many metal–organic diamondoid networks have been synthesized and characterized over the past decade.^{18–26} The Zn⋯Zn connectivity in **I** is somewhat similar to that in the coordination polymer reported by Xiong *et al.*,²⁴ where the Zn centers are connected through the PEBA [bis{4-[2-(4-pyridyl)ethenyl]benzoate}] bridges. In **I**, however, we do not have an interpenetrating diamondoid network as in the other systems discussed in the literature.

The Zn–O bond length in **I** ranges from 2.078(6) to 2.137(6) Å [$d(\text{Zn}(1)\text{--O})_{\text{av}} = 2.114(6)$ Å]. The *cis*-O–Zn–O bond angles are between 83.5(2) and 96.9(2)°, (ave = 90.09(2)°) and the *trans*-O–Zn–O bond angles are between 172.9(2) and 177.7(2)°,

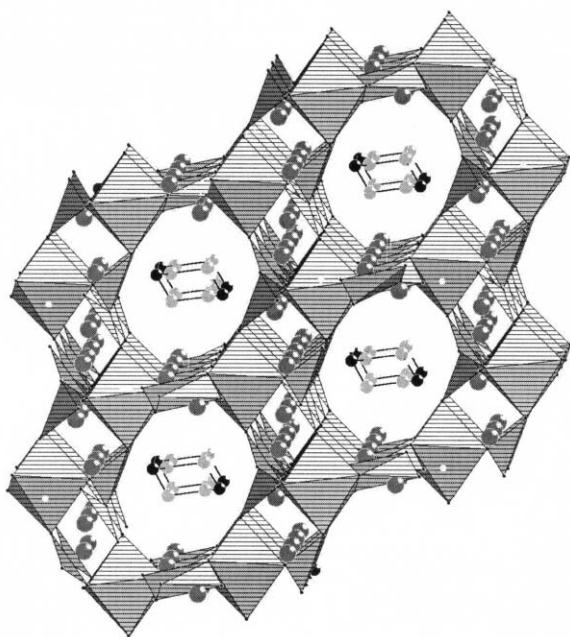


Fig. 3 Polyhedral view of the inorganic framework structure of **I** along the [100] direction, showing 10-membered channels and the amine molecules that form hydrogen bonds with the framework oxygens.

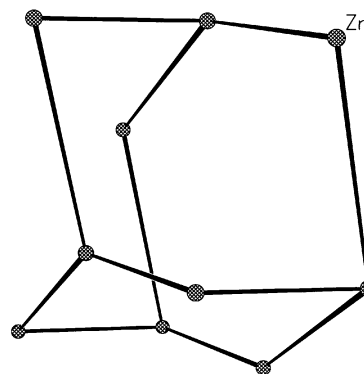


Fig. 4 A schematic representation of the Zn⋯Zn connectivity that results in an adamantoid network.

(ave = 174.5(2)°). The bond lengths and angles indicate that the Zn(1) octahedron is slightly distorted. Bond valence sum (BVS) calculations for the Se atoms (Se(1) = 3.985, Se(2) = 4.034 and Se(3) = 3.908) as well as the values of the average bond lengths indicate the oxidation state of all the Se atoms to be +4. The pseudo-tetrahedral Se–O bond lengths are in the range 1.65(5) to 1.834(6) Å, with average Se(1)–O, Se(2)–O and Se(3)–O lengths of 1.713(5), 1.703(5) and 1.721(5) Å respectively and O–Se–O bond angles in the range 96.3(3)–103.5(3)° [(O–Se(1)–O)_{av} = 98.93(3)°, (O–Se(2)–O)_{av} = 99.53(3)°, (O–Se(3)–O)_{av} = 99.53(3)°] are in agreement with the literature values.¹¹ The bridging Se(1)–O(3) and Se(3)–O(3) distances are 1.820(6) Å and 1.834(6) Å respectively while the bridging Se(1)–O(3)–Se(3) angle is 118.9(3)°, which are typical for diselenite containing materials.¹¹ The terminal Se–OH bond length in the HSeO₃ unit is Se(2)–O(6) = 1.746(6) Å. The oxygens O(2), O(8) and O(4) of the inorganic framework interact with the N–H group of the piperazinium cation through N–H⋯O hydrogen bonding with $d(\text{H1}\cdots\text{O2}) = 2.23(1)$, $d(\text{H1}\cdots\text{O8}) = 2.35(1)$ and $d(\text{H2}\cdots\text{O4}) = 2.02(1)$ Å. The oxygens O(5) and O(7) are involved in the C–H⋯O hydrogen bonding linkage, $d(\text{H3}\cdots\text{O5}) = 2.51(1)$ and $d(\text{H6}\cdots\text{O7}) = 2.51(1)$ Å. The OH-group of the selenite unit is also involved in intramolecular hydrogen bonding with the diselenite oxygens as O(6)–H(7)⋯O(3) ($d(\text{H7}\cdots\text{O3}) = 2.495(8)$ Å). The hydrogen bond parameters are listed in Table 2.

Thermogravimetric analysis of **I**, carried out in a flowing N₂ atmosphere (flow rate = 50 ml min^{−1}) in the temperature range 25–900 °C (heating rate = 5° min^{−1}), showed two sharp weight losses. A weight loss of 49.83% occurs at 275.57 °C, corresponding to the loss of the diselenite and a water molecule (calcd 50.4%). The second weight loss of 33.38% occurs at around 438 °C and corresponds to the decomposition of SeO₃ units and the amine molecule (calcd 32.4%). The amine residing in the channel decomposes at a relatively high temperature. The diselenite group decomposes at a lower temperature than that of SeO₃ group. The calcined product diffracted poorly and showed reflections of ZnO.

Table 2 Hydrogen bonding interactions in **I**

Moiety	Bond length/Å			D–H⋯A angle/°
	D–H	H⋯A	D⋯A	
N(1)–H(1)⋯O(2)	0.90(1)	2.23(1)	2.95(1)	136.0(1)
N(1)–H(1)⋯O(8)	0.90(1)	2.35(1)	3.15(1)	147.9(1)
N(1)–H(2)⋯O(4)	0.90(1)	2.02(1)	2.92(1)	173.7(1)
O(6)–H(7)⋯O(3) ^a	0.82(8)	2.49(8)	3.28(8)	161.4(1)
C(1)–H(3)⋯O(5)	0.97(1)	2.51(1)	3.44(1)	161.6(1)
C(2)–H(6)⋯O(7)	0.97(1)	2.51(1)	3.30(1)	138.3(1)

^aIntramolecular hydrogen bonding.

Conclusions

Three-dimensional open-framework metal selenites of formula $[\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2]_{0.5}[\text{M}(\text{HSeO}_3)(\text{Se}_2\text{O}_5)]$, with $\text{M} = \text{Zn}, \text{Co}$ or Ni , containing diselenite units have been synthesised successfully by the hydrothermal method. The materials possess two-dimensional intersecting 10-membered channels, with the protonated piperazine molecules residing in the channels. The unique feature of these compounds is that the $\text{M}\cdots\text{M}$ connectivity creates a diamondoid framework based on adamantanoid cages. These are the first examples of organically templated metal selenites containing a diselenite unit. In addition, the Co and Ni analogues of **I** are the first examples of organically templated open-framework selenites formed by these metals. The present study suggests there is the possibility of building up other novel open-framework structures using of both selenite and diselenite as the building units.

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