

# $(\text{H}_2\text{NC}_4\text{H}_8\text{NCH}_2\text{CH}_2\text{NH}_2)(\text{HNCH}_2\text{CH}_2\text{NH}_2)_3\text{Zn}_2\text{Ge}_2\text{Se}_8$ : A new, templated one-dimensional ternary semiconductor stabilized by mixed organic cations

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Dedicated to Dr. Aris Terzis, in recognition of his great help for the advancement of inorganic chemistry in Greece through single-crystal, X-ray crystallography.

### Keywords:

Chalcogenides  
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Templated synthesis

## ABSTRACT

The novel, 1D semiconductor  $(\text{H}_2\text{NC}_4\text{H}_8\text{NCH}_2\text{CH}_2\text{NH}_2)(\text{HNCH}_2\text{CH}_2\text{NH}_2)_3\text{Zn}_2\text{Ge}_2\text{Se}_8$  has been synthesized under solvothermal conditions using *N*-(2-aminoethyl)piperazine as solvent and templating agent at 200 °C. The material was characterized by single crystal and powder X-ray diffraction, IR and Raman spectroscopy and thermogravimetric analysis. The compound consists of 1D anionic  $[\text{Zn}_2\text{Ge}_2\text{Se}_8]^{4-}$  chains made of alternating edge-shared  $[\text{ZnSe}_4]$  and  $[\text{GeSe}_4]$  tetrahedra that charged balanced by one *N*-(2-aminoethyl)piperazinium and three piperazinium cations. The optical properties were investigated with solid state UV–Vis/near IR spectroscopy and the results show that the solid is a medium gap semiconductor with an absorption edge at 1.8 eV.

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## 1. Introduction

Metal chalcogenides represent an important class of materials associated with advanced technological applications, because of their unique optoelectronic properties [1–5]. The rich and versatile structural chemistry associated with the soft chalcogen atoms (S, Se and Te) offer the possibility to construct novel structures with complex chemical composition using mild synthetic methodologies such as ion-exchange, redox and solvothermal reactions, under thermodynamically or kinetically controlled conditions.

In particular, during the last 15 years, solvothermal and reactive flux reactions have proven unique methodologies for the development of novel chalcogenides with unprecedented structures and important properties [6,7]. In addition, a significant amount of this type of work focuses on templated solvothermal reactions in which organic molecules serve primarily as structure directing agent [8–10]. This particular methodology has been successfully applied for many years for the development of porous oxides including zeolites and related mesoporous solids and also found to be suitable for non-oxidic solids such as metal chalcogenides. In fact, the currently intense exploratory work in templated solvothermal syntheses of crystalline metal chalcogenides is primarily driven by the prospect to construct novel open-framework solids that combine accessible pore space and optoelectronic properties [9,11–14]. In a large part of this research, amine molecules have been used as structure directing agents with a combination of metals from groups 13 (In, Ga), 14 (Ge, Sn), 15 (As, Sb) and chalcogen element (mainly sulfur and sele-

mium), for the development of structurally and chemically diverse metal chalcogenides [15–18]. In their vast majority, the amine molecules enter the host inorganic lattice either as neutral space filling molecules or as extra-framework cations.

In addition to these efforts, there is an increasing interest for the development of hybrid semiconductors in which the organic part is covalently bonded to the inorganic framework [19–22]. In this way, low dimensional inorganic networks could be developed, leading to hybrid materials with unique optoelectronic properties, suitable for advanced applications including photovoltaics and light emitting devices [15,18]. A representative and at the same time rare example, is the family of  $\text{MQ(L)}_x$  ( $M = \text{Mn, Zn}$ ;  $Q = \text{Se, Te}$ ;  $L = \text{amines}$ ) hybrid semiconductors [23,24] which show very strong quantum confinement effects. In another example, novel, one- and two-dimensional organic–inorganic networks have been reported, made from supertetrahedral gallium sulfide clusters bridged by covalently bonded dipyrindyl ligands [25].

Recently, our group reported the synthesis, characterization and optical properties of a novel polar 2D ternary chalcogenide  $(\text{H}_2\text{NC}_4\text{H}_8\text{NCH}_2\text{CH}_2\text{NH}_2)_2\text{Zn}_2\text{Sn}_2\text{Se}_7$  (**1**) in which the organic template *N*-(2-aminoethyl)piperazine (**2**) is covalently bonded to the inorganic  $[\text{Zn}_2\text{Sn}_2\text{Se}_7]^{2-}$  layer through the amino end-group, while from the other end is protonated forming a piperazinium cation that compensates the anionic charge of the adjacent layer [26]. In our efforts to synthesize the isostructural analogue of germanium and in this way to systematically tune the optical properties in this type of materials, we isolated a new one-dimensional (1D) polar semiconductor with a chemical formula  $(\text{H}_2\text{NC}_4\text{H}_8\text{NCH}_2\text{CH}_2\text{NH}_2)(\text{HNCH}_2\text{CH}_2\text{NH}_2)_3\text{Zn}_2\text{Ge}_2\text{Se}_8$  (**3**). To the best of our knowledge, the 1D chains  $[\text{Zn}_2\text{Ge}_2\text{Se}_8]^{4-}$  in **3** are observed for the first

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time and also **3** is a rare templated semiconductor that contains two different charge balancing organic cations. We report here the synthesis and structural characterization of **3** as well as its optical and thermal properties.

## 2. Experimental

### 2.1. Reagents

*N*-(2-aminoethyl)piperazine (98%) and zinc powder (99.9%) were purchased from Alfa Aesar. Germanium (99.99%) and selenium (99.5%) were purchased from Aldrich. All chemicals were used as received.

### 2.2. Synthesis of $(H_2NC_4H_8NCH_2CH_2NH_2)(HNCH_2CH_2NH_2)_3Zn_2Ge_2Se_8$ (**3**)

In a typical synthesis, an amount of Zn (0.052 g, 0.795 mmol), Ge (0.029 g, 0.399 mmol), Se (0.219 g, 2.774 mmol) and 6 ml of *N*-(2-aminoethyl)piperazine were placed in a 45 ml Teflon-lined stainless steel autoclave (Parr Instruments) and heated at 200 °C for 62 h. The product, in the form of transparent, yellow–orange rod like crystals, was isolated by suction filtration and washed with copious amount of CH<sub>3</sub>OH. Yield 0.210 g based on Ge.

### 2.3. Single crystal X-ray crystallography

A STOE IPDS II diffractometer was used to collect intensity data at room temperature, operated at 2000 W power (50 kV, 40 mA) with graphite monochromatized Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation. An analytical absorption correction was applied using the program X-RED (routine within the X-AREA software package). The structure was solved with SHELXL software (Sheldrick, SHELXL, University of Göttingen, 2002). All non-hydrogen atoms were refined anisotropically except the carbon atom C9 (–CH<sub>2</sub>– group in a piperazinium cation) which was refined using the isor command (six restraints) because the ADPs were found physically not very sensible. The hydrogen atoms were generated with idealized geometries.

### 2.4. Physical measurements

Powder X-ray diffraction patterns were collected on a Rigaku D/MAX-2000H rotating anode diffractometer (Cu K $\alpha$  radiation) equipped with a secondary pyrolytic graphite monochromator operated at 40 kV and 178 mA. The scan rate was 0.15°/min with a step size of 0.01°. Simulated PXRD patterns were calculated from the corresponding single crystal data using the program POWDER CELL 2.3. Thermogravimetric analyses (TGA) were performed using a TA SDT Q 600 analysis system. An amount of 20 mg of sample was placed inside an alumina cup and heated up to 600 °C under Argon flow with a heating rate of 5 °C/min. ATR-IR spectra were recorded on a Thermo-Electron Nicolet 6700 FT-IR optical spectrometer with a DTGS KBr. Raman spectrum was recorded at room temperature on a single crystal using a Nicolet Almega XR Raman spectrometer with a 473 nm blue laser (25% of the 15 mW laser power). The beam was focused on the sample through a confocal microscope using a 10 $\times$  objective lens. Solid state UV–Vis/near IR electronic absorption spectrum was obtained at room temperature on a Perkin Elmer LAMBDA 950 UV/Vis/NIR spectrophotometer in the wavelength range of 200–2500 nm. BaSO<sub>4</sub> powder was used as a reference (100% reflectance) and base material on which the powder sample was coated. Reflectance data were converted to absorbance data as described elsewhere [27].

## 3. Results and discussion

### 3.1. Synthesis

In templated solvothermal syntheses of metal chalcogenides usually a common solvent such as water, methanol, ethylenediamine, pyridine or acetonitrile is required in addition to the templating molecules. That was the case in the successful synthesis of **1** in which a mixture of CH<sub>3</sub>OH and **2** was used under solvothermal reaction conditions. Interestingly, when germanium was used instead of tin, under otherwise the same reaction conditions, we did not observe the isostructural phase of **1** or any other ternary Zn/Ge/Se crystalline phase. In contrast, when only **2** was used as solvent and template we obtained the ternary phase **3** in pure form (see below the powder X-ray data) and high yield (>80%). As we report below, the crystal structure of **3** consists of 1D [Zn<sub>2</sub>Ge<sub>2</sub>Se<sub>8</sub>]<sup>4–</sup> chains made of edge sharing [ZnSe<sub>4</sub>] and [GeSe<sub>4</sub>] tetrahedra. Alternatively, the chains can be viewed as made of [GeSe<sub>4</sub>]<sup>4–</sup> anions bridged by Zn<sup>2+</sup> cations. These results could be explained based on solvent effects as follows: the highly basic nature of the [GeSe<sub>4</sub>]<sup>4–</sup> anions requires a relatively strong basic environment in order to be stabilized and therefore, the fact that the synthesis of **3** requires only the amine **2** as a solvent (basic environment) and not a mixture of **2**/CH<sub>3</sub>OH could be explained in terms of the relative basicity of the reaction medium. In fact, the effect of basicity in the stabilization of different germanium chalcogenide species, for example in aqueous solutions, has been documented [28]. Accordingly, in highly basic solutions the anions [GeQ<sub>4</sub>]<sup>4–</sup> (Q = S, Se) are stable, while at lower pH, condensation reactions occur leading to the formation of dimeric [Ge<sub>2</sub>Q<sub>6</sub>]<sup>4–</sup> and tetrameric, adamantane type [Ge<sub>4</sub>Q<sub>10</sub>]<sup>4–</sup> species. We note that the pH dependence of metal chalcogenide clusters has also been used as a tool for the controlled formation of ordered mesostructured metal chalcogenides [29].

### 3.2. X-ray diffraction characterization

The powder X-ray diffraction pattern of **3** is in full agreement with that calculated from the corresponding crystal structure (see Fig. 1) and confirms that the as-made, bulk material is a pure phase.

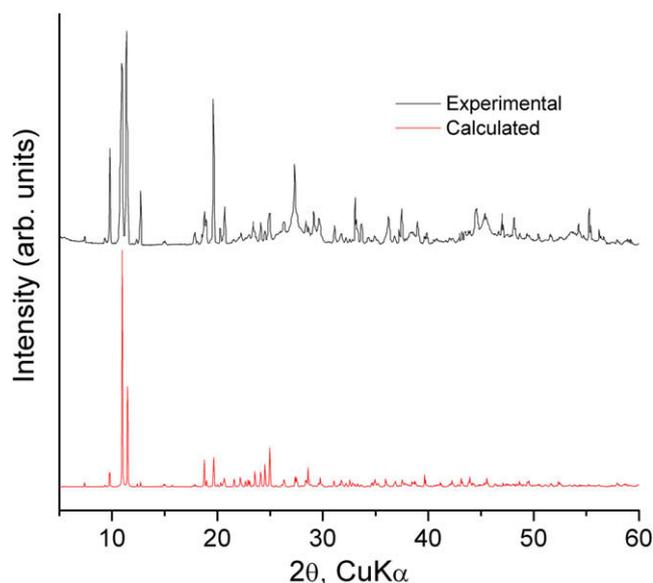


Fig. 1. Experimental (black line) and calculated (red line) powder X-ray diffraction pattern of **3**. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Compound **3** crystallize in the orthorhombic non-centrosymmetric space group  $P2_12_12$  (see Table 1). The unit cell is shown in Fig. 2. The inorganic network consists of 1D  $[\text{Zn}_2\text{Ge}_2\text{Se}_8]^{4-}$  chains made of edge sharing  $[\text{ZnSe}_4]$  and  $[\text{GeSe}_4]$  tetrahedral, running down the  $c$ -axis (see Fig. 3). Selected bond distances and bond angles are shown in Tables 2 and 3, respectively. The Zn–Se and

Ge–Se bond distances lie between 2.4700(15)–2.5171(16) and 2.3416(15)–2.3580(16) Å, respectively, in the same range to those reported in some crystalline metal chalcogenides, as for example in ZnSe and GeSe<sub>2</sub>.

Notably, although in the system Zn/Sn/Se a number of crystalline ternary and quaternary compounds have been discovered and structurally characterized [30–33], in the system Zn/Ge/Se only the synthesis of  $\text{Zn}_2\text{GeSe}_4$  and  $\text{Zn}_2\text{GeSe}_3$  has been reported. The  $[\text{ZnSe}_4]$  tetrahedra in **3** are highly distorted and the Se–Zn–Se bond angles lie in the range 93.09(7)–119.92(4)° (see Table 3). This large distortion from the ideal  $T_d$  symmetry of the zinc cations have been observed in other tetrahedral, transition metal containing metal chalcogenides including the isostructural series  $(\text{Me}_4\text{N})_2\text{M}[\text{Ge}_4\text{S}_{10}]$  ( $\text{M} = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}$ ) [34–37],  $(\text{Me}_4\text{N})_2\text{M}[\text{Ge}_4\text{Se}_{10}]$  ( $\text{M} = \text{Fe}^{2+}, \text{Cd}^{2+}$ ) [38],  $(\text{Me}_4\text{N})_2\text{M}[\text{Sn}_4\text{Se}_{10}]$  ( $\text{M} = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}$ ) [39,40] and  $(\text{Me}_4\text{N})_2\text{Mn}[\text{Ge}_4\text{Te}_{10}]$  [39]. The Se–Ge–Se bond angles lie in the range 100.34(7)–116.21(5)° which is typical for main-group metal chalcogenides [10].

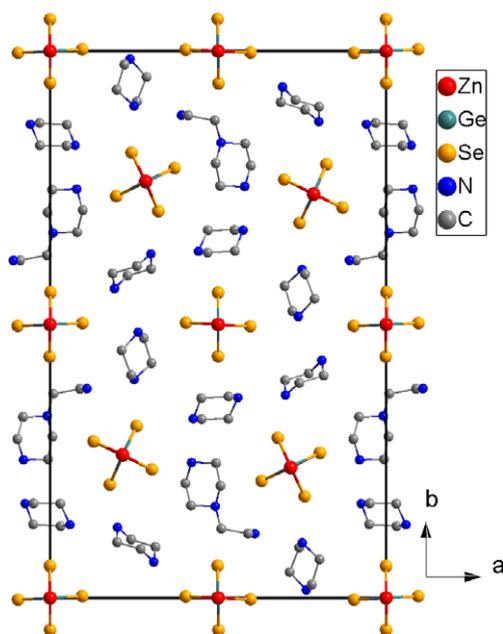
A unique feature in **3** is that the anionic chains  $[\text{Zn}_2\text{Ge}_2\text{Se}_8]^{4-}$  are charged balanced by two different organic cations. The asymmetric unit of **3** contains one templating molecule **2** and three piperazine molecules (**4**). Because compound **4** was not included in the starting reaction mixture, their formation indicates that **2** are partially decomposed during the reaction forming **4** and presumably ethylamine. In compound **3**, looking down the  $c$ -axis, the chain  $[\text{Zn}_2\text{Ge}_2\text{Se}_8]^{4-}$  located at the center of the unit cell ( $\text{Zn}^{2+}$  and  $\text{Ge}^{4+}$  atoms at  $+1/2, +1/2, z$ ), is surrounded by six molecules **4**, while all the other are surrounded by four molecules **4** and two molecules **2** (see Fig. 2). Taking into account charge balancing considerations, the observed packing indicates that the molecule **2** and the three molecules **4** of the asymmetric unit are monoprotonated forming  $N$ -(2-aminoethyl)piperazinium and piperazinium cations, respectively that compensate the anionic charge of the chains. Accordingly, the overall charged balanced formula of **3** is  $(\text{H}_2\text{NC}_4\text{H}_8\text{NCH}_2\text{CH}_2\text{NH}_2)(\text{HNCH}_2\text{CH}_2\text{NH}_2)_3\text{Zn}_2\text{Ge}_2\text{Se}_8$ .

**Table 1**

Crystal data and structure refinement for **3** at 298(2) K.

Empirical formula	$\text{C}_{18}\text{H}_{49}\text{N}_9\text{Zn}_2\text{Ge}_2\text{Se}_8$
Formula weight	1299.19
$T$ (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	$P2_12_12$
<i>Unit cell dimensions</i>	
$a$ (Å)	18.928(4)
$b$ (Å)	30.849(6)
$c$ (Å)	6.3954(13)
$\alpha$ (°)	90.00
$\beta$ (°)	90.00
$\gamma$ (°)	90.00
Volume (Å <sup>3</sup> )	3734.3(13)
$Z$	4
Density (calculated) g/cm <sup>3</sup>	2.295
Absorption coefficient (mm <sup>-1</sup> )	10.
$F(000)$	2428
Crystal size (mm <sup>3</sup> )	$0.3 \times 0.1 \times 0.1$
$\theta$ Range for data collection	1.26–29.23°
Index ranges	$-25 \leq h \leq 25, -42 \leq k \leq 42, -8 \leq l \leq 8$
Reflections collected	56 328
Independent reflections	10 084 [ $R_{\text{int}} = 0.1783$ ]
Completeness to $\theta = 29.23^\circ$	100%
Refinement method	full-matrix least-squares on $F^2$
Data/restraints/parameters	10 084/6/354
Goodness-of-fit (GOF) on $F^2$	0.899
Final $R$ indices [ $>2\sigma(I)$ ]	$R_{\text{obs}} = 0.0589, wR_{\text{obs}} = 0.1075$
$R$ indices (all data)	$R_{\text{all}} = 0.1052, wR_{\text{all}} = 0.1224$
Largest differences in peak and hole (e Å <sup>-3</sup> )	1.017 and $-1.762$

$R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR = \{ \sum [w(|F_o|^2 - |F_c|^2)^2] / \sum [w(|F_o|^4)] \}^{1/2}$  and calc.  $w = 1 / [\sigma^2(F_o^2) + (0.0448P)^2 + 0.0000P]$  where  $P = (F_o^2 + 2F_c^2) / 3$ .



**Fig. 2.** The unit cell of **3** looking down the  $c$ -axis. Hydrogen atoms are omitted for clarity.

### 3.3. Infrared and Raman spectroscopy

Infrared spectroscopy confirmed the presence of  $-\text{NH}_2^+$ ,  $-\text{NH}-$  and  $-\text{NH}_2$ , groups [41] in **3** (see Fig. 4).

Raman spectroscopy was used to further characterize the inorganic part in **3**. The Raman spectrum of **3** in the range 0–500  $\text{cm}^{-1}$ , recorded at room temperature on a single crystal, is shown in Fig. 5. At least five vibrational modes were observed and provide information about the local environment of the germanium atoms in the structure. Normally, an ideal  $[\text{GeSe}_4]^{4-}$  tetrahedron should show only a single Raman peak due to the symmetric (Ag) mode of vibration. The observation of multiple peaks suggests a local symmetry lowering of the tetrahedron, in full agreement with the crystallographic data of **3**. A comparison with the Raman spectra of  $\text{ASmGeSe}_4$  ( $\text{A} = \text{K}^+, \text{Rb}^+, \text{Cs}^+$ ) [42],  $\text{KCeGeSe}_4$  [43],  $\text{M}_{0.5}\text{Pb}_{1.75}\text{GeSe}_4$  ( $\text{M} = \text{Ag}^+, \text{Na}^+$ ) [44] and  $\text{GeSe}_2$  [45] all of which contain linked  $[\text{GeSe}_4]^{4-}$  distorted tetrahedra, allows for a qualitative assignment of the observed bands. Accordingly, the sharp, intense peak centered at 213  $\text{cm}^{-1}$  can be assigned to the primary symmetric Ge–Se stretching modes (A1 mode,  $\nu_1$ ) of  $[\text{GeSe}_4]$  tetrahedra. The peaks at 300 and 284  $\text{cm}^{-1}$  can be assigned to the asymmetric Ge–Se stretching modes (F) while those at 166 and 101  $\text{cm}^{-1}$  to the partially overlapping antisymmetric Se–Ge–Se bends (E).

### 3.4. Thermal analysis

The thermal stability of **3** was studied by thermogravimetric analysis (TGA). As shown in Fig. 6, the material is stable up to  $\sim 105^\circ\text{C}$ . Between 105 and  $450^\circ\text{C}$  weight loss occur in two steps,

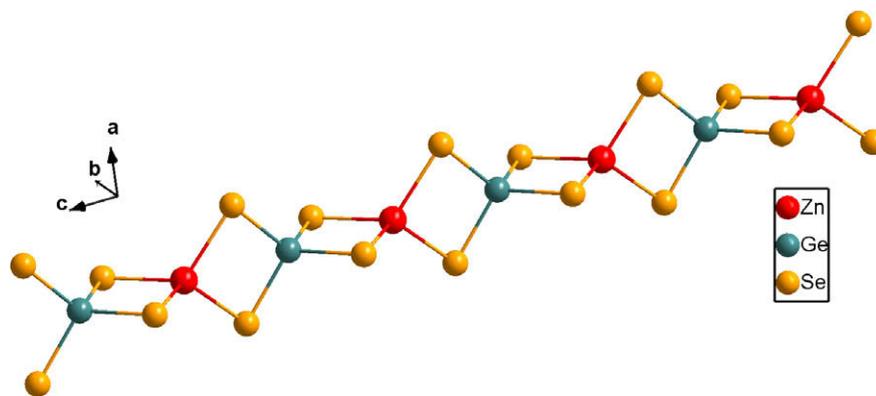


Fig. 3. The 1D  $[\text{Zn}_2\text{Ge}_2\text{Se}_8]^{4-}$  chains in **3**.

Table 2

Selected bond lengths [Å] for **3** at 298(2) K with estimated standard deviations in parentheses.

Label	Distances	Label	Distances
Zn(1)–Se(2) <sup>#1</sup>	2.4924(15)	Ge(1)–Se(3) <sup>#4</sup>	2.3416(15)
Zn(1)–Se(2)	2.4924(15)	Ge(1)–Se(6)	2.3563(15)
Zn(1)–Se(8) <sup>#1</sup>	2.5041(15)	Ge(1)–Se(4)	2.3580(16)
Zn(1)–Se(8)	2.5041(15)	Ge(2)–Se(1) <sup>#2</sup>	2.3436(14)
Zn(2)–Se(6)	2.4759(17)	Ge(2)–Se(1)	2.3436(14)
Zn(2)–Se(5)	2.4845(17)	Ge(2)–Se(7)	2.3556(14)
Zn(2)–Se(3)	2.4871(17)	Ge(2)–Se(7) <sup>#2</sup>	2.3556(14)
Zn(2)–Se(4)	2.5171(16)	Ge(3)–Se(2) <sup>#4</sup>	2.3485(13)
Zn(3)–Se(1)	2.4700(15)	Ge(3)–Se(2) <sup>#5</sup>	2.3485(13)
Zn(3)–Se(1) <sup>#2</sup>	2.4700(15)	Ge(3)–Se(8)	2.3559(13)
Zn(3)–Se(7) <sup>#3</sup>	2.4804(15)	Ge(3)–Se(8) <sup>#1</sup>	2.3559(13)
Zn(3)–Se(7) <sup>#4</sup>	2.4804(15)	Ge(2)–Se(1) <sup>#2</sup>	2.3436(14)

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

Table 3

Bond angles [°] for **3** at 298(2) K with estimated standard deviations in parentheses.

Label	Angles	Label	Angles
Se(2) <sup>#1</sup> –Zn(1)–Se(2)	94.18(7)	Se(3) <sup>#4</sup> –Ge(1)–Se(6)	115.72(6)
Se(2) <sup>#1</sup> –Zn(1)–Se(8) <sup>#1</sup>	115.96(4)	Se(3) <sup>#4</sup> –Ge(1)–Se(4)	113.12(6)
Se(2)–Zn(1)–Se(8) <sup>#1</sup>	119.92(4)	Se(6)–Ge(1)–Se(4)	101.35(5)
Se(2) <sup>#1</sup> –Zn(1)–Se(8)	119.92(4)	Se(3) <sup>#4</sup> –Ge(1)–Se(5) <sup>#4</sup>	100.89(5)
Se(2)–Zn(1)–Se(8)	115.96(4)	Se(6)–Ge(1)–Se(5) <sup>#4</sup>	112.92(6)
Se(8) <sup>#1</sup> –Zn(1)–Se(8)	93.09(7)	Se(4)–Ge(1)–Se(5) <sup>#4</sup>	113.43(6)
Se(6)–Zn(2)–Se(5)	119.13(6)	Se(1) <sup>#2</sup> –Ge(2)–Se(1)	100.34(7)
Se(6)–Zn(2)–Se(3)	118.71(7)	Se(1) <sup>#2</sup> –Ge(2)–Se(7)	116.21(5)
Se(5)–Zn(2)–Se(3)	93.70(5)	Se(1)–Ge(2)–Se(7)	112.21(5)
Se(6)–Zn(2)–Se(4)	93.83(5)	Se(1) <sup>#2</sup> –Ge(2)–Se(7) <sup>#2</sup>	112.21(5)
Se(5)–Zn(2)–Se(4)	118.35(6)	Se(1)–Ge(2)–Se(7) <sup>#2</sup>	116.21(5)
Se(3)–Zn(2)–Se(4)	115.14(6)	Se(7)–Ge(2)–Se(7) <sup>#2</sup>	100.45(8)
Se(1)–Zn(3)–Se(1) <sup>#2</sup>	93.55(7)	Se(2) <sup>#4</sup> –Ge(3)–Se(2) <sup>#5</sup>	102.02(7)
Se(1)–Zn(3)–Se(7) <sup>#3</sup>	119.79(5)	Se(2) <sup>#4</sup> –Ge(3)–Se(8)	111.45(4)
Se(1) <sup>#2</sup> –Zn(3)–Se(7) <sup>#3</sup>	116.07(5)	Se(2) <sup>#5</sup> –Ge(3)–Se(8)	115.76(4)
Se(1)–Zn(3)–Se(7) <sup>#4</sup>	116.07(5)	Se(2) <sup>#4</sup> –Ge(3)–Se(8) <sup>#1</sup>	115.76(4)
Se(1) <sup>#2</sup> –Zn(3)–Se(7) <sup>#4</sup>	119.79(5)	Se(2) <sup>#5</sup> –Ge(3)–Se(8) <sup>#1</sup>	111.45(4)
Se(7) <sup>#3</sup> –Zn(3)–Se(7) <sup>#4</sup>	93.75(7)	Se(8)–Ge(3)–Se(8) <sup>#1</sup>	101.00(7)

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

corresponding to the removal of the organic molecules, with a total weight loss of 22.5%. This value is close to that calculated from the chemical formula of **3** (30 wt%), assuming complete removal of the organic part. The difference between the observed and the calculated weight loss could be explained by remaining carbon in the form of coke, due to the calcination of **3** under inert (flow of argon) conditions.

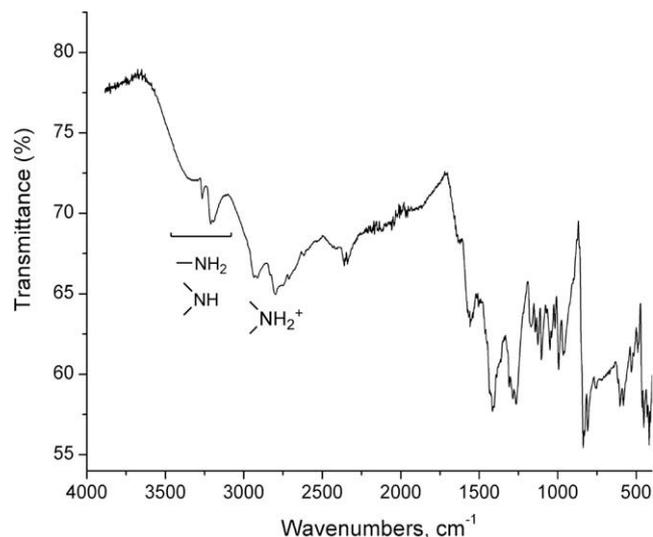


Fig. 4. ATR-IR spectrum of **3**.

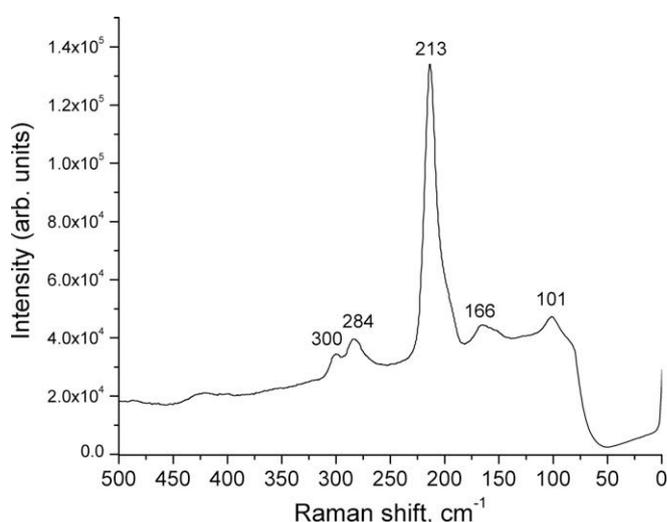


Fig. 5. Raman spectrum for compound **3** recorded at room temperature on a single crystal.

### 3.5. Solid-state diffuse reflectance spectroscopy

Diffuse reflectance UV-Vis/near IR spectroscopy was used to investigate the optical properties of **3**. As shown in Fig. 7, a well

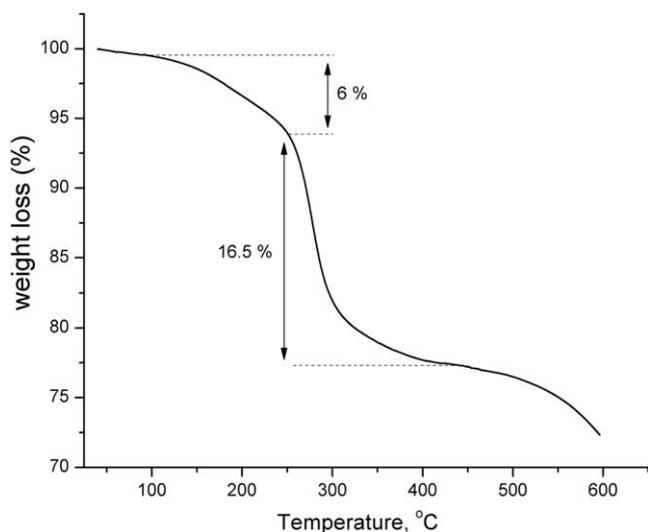


Fig. 6. Thermogravimetric analysis (TGA) curve of **3** recorded under Argon flow.

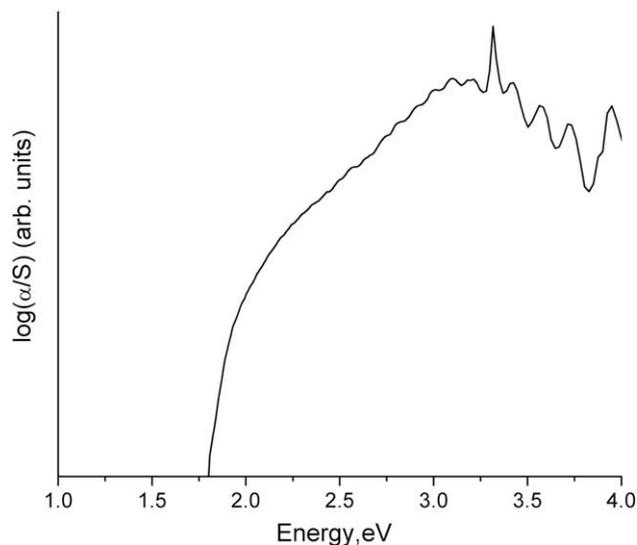


Fig. 7. Solid state UV-Vis/near IR electronic absorption spectrum for compound **3**.

defined optical absorption associated with a band-gap transition at 1.8 eV is observed, indicating that this is a medium gap semiconductor, in the same range of some important chalcogenides such as GaAs (1.43 eV) and CdSe (1.70 eV). Interestingly, the observed band-gap is lower to that found in **1** (2.3 eV). One would expect a higher band-gap in **3** in comparison to **1**, because **1** is a two-dimensional (2D) solid and also contains a heavier main-group metal (Sn instead of Ge). These results indicated that the chemical composition of the inorganic part in **3** is not the decisive factor that controls the optical properties of the material and structural parameters should also be considered. Band structure calculations may shed light into the optical properties of **3** and currently are performed. It is important to note here that similar surprising observations have been reported in other low-dimensional semiconductor structures such as in the case of the 2D compound  $\text{Ga}_4\text{Se}_7(\text{en})_2(\text{enH})_2$  [46].

#### 4. Conclusions

In conclusion, we have synthesized and characterized the first organically templated semiconductor in the system Zn/Ge/Se. The compound features 1D anionic chains made of alternating

edge-shared  $[\text{ZnSe}_4]$  and  $[\text{GeSe}_4]$  tetrahedra that charged balanced by two different organic cations. The material is a medium gap semiconductor with an absorption edge at 1.8 eV. Currently, we are exploring other amine-based organic molecules as templating agents for the development of novel transition metal containing group 14 (Ge and Sn) chalcogenides.

#### 5. Supplementary data

CCDC 721564 contains the supplementary crystallographic data for **3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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