(H$_2$NC$_4$H$_8$NCH$_2$CH$_2$NH$_2$)$_2$Zn$_2$Sn$_2$Se$_7$: a hybrid ternary semiconductor stabilized by amine molecules acting simultaneously as ligands and counterions†

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A hybrid, organic–inorganic ternary semiconductor with chemical formula (H$_2$NC$_4$H$_8$NCH$_2$CH$_2$NH$_2$)$_2$Zn$_2$Sn$_2$Se$_7$ is reported in which the organic molecules have a dual role, acting simultaneously as ligands and charge balancing cations.

The current intense exploratory work in templated solvothermal syntheses of crystalline metal chalcogenides is primarily driven by the prospect of constructing novel open-framework solids that combine accessible pore space and optoelectronic properties.[1] In a significant 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 the chalcogen elements (mainly sulfur and selenium), for the development of structurally and chemically diverse metal chalcogenides.[2] In the vast majority of such complexes, 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 in the development of organic–inorganic semiconductors in which the organic part is covalently bonded to the inorganic framework.[3] In this way, the organic part could induce dimensional reduction of the inorganic network leading to hybrid materials with unique optoelectronic properties, suitable for advanced applications including photovoltaics and light emitting devices.[2a,d] Despite the significant efforts during the last decade it is still a great challenge to prepare such solids. A representative, and at the same time rare, example is the family of MQ(L)$_x$ (M = Mn, Zn; Q = Se, Te; L = amines) hybrid semiconductors[4] which show very strong quantum confinement effects. Very recently, novel one- and two-dimensional organic–inorganic networks were reported, made from supertetrahedral gallium sulfide clusters bridged by covalently bonded dipyridyl ligands.[5]

We report here the synthesis, characterization and optical properties of a novel polar 2D ternary chalcogenide (H$_2$NC$_4$H$_8$NCH$_2$CH$_2$NH$_2$)$_2$Zn$_2$Sn$_2$Se$_7$ (**1**) synthesized under solvothermal conditions in MeOH. A unique feature of **1** is the dual role of the organic template N-(2-aminoethyl)piperazine;

each molecule is covalently bonded to the inorganic [Zn$_2$Sn$_2$Se$_7$]$^{2-}$ layer through the amino end-group, while the other end is protonated forming a piperazinium cation that compensates for the anionic charge of the adjacent layer (Fig. 1a). To the best of our knowledge this is the first hybrid metal–chalcogenide in which the same organic molecule exhibits simultaneously covalent and ionic bond character.

Initially, **1** was obtained in low yield as yellow, transparent plate-like crystals by reacting K$_4$SnSe$_4$ (0.1 g, 0.169 mmol), ZnSO$_4$·7H$_2$O (0.049 g, 0.169 mmol), 2 ml of N-(2-aminoethyl)-piperazine and 2 ml of CH$_3$OH in a 23 ml Teflon-lined stainless steel autoclave at 200 °C for 2 days. However, we found that almost pure product in high yield (>80% based on Sn) can be obtained by reacting stoichiometric amounts of Zn
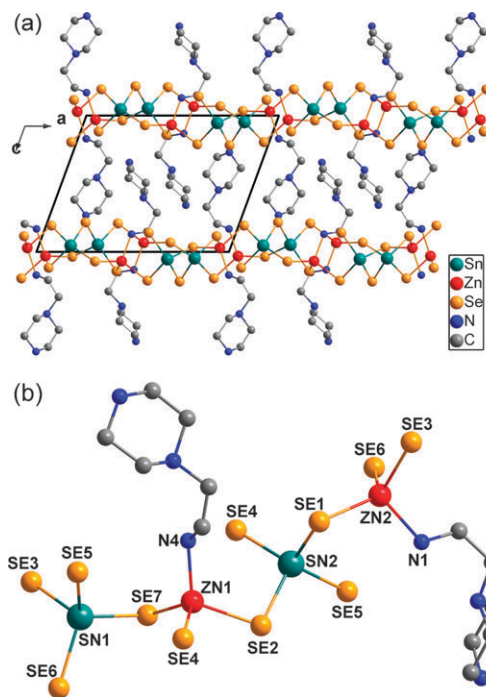

Fig. 1 (a) The layered structure of **1** looking down the b-axis and (b) local coordination of the non-hydrogen atoms with the corresponding labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Sn(1)–Se(3) 2.5274(15), Sn(1)–Se(5) 2.5777(15), Sn(1)–Se(6) 2.5321(16), Sn(1)–Se(7) 2.4903(16), Sn(2)–Se(1) 2.5004(14), Sn(2)–Se(2) 2.5043(14), Sn(2)–Se(4) 2.5143(17), Sn(2)–Se(5) 2.5821(16), Zn(1)–N(4) 2.092(10), Zn(1)–Se(2) 2.461(2), Zn(1)–Se(4) 2.4657(19), Zn(1)–Se(7) 2.4367(19), Zn(2)–N(1) 2.092(10), Zn(2)–Se(1) 2.4349(18), Zn(2)–Se(3) 2.4725(18), Zn(2)–Se(6) 2.4816(19).

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(0.043 g, 0.657 mmol), Sn (0.078 g, 0.657 mmol) and Se (0.181 g, 2.299 mmol) in the presence of the organic template and methanol under the same solvothermal reaction conditions. Compound **1** crystallizes in the monoclinic non-centrosymmetric space group $P2_1$.‡ The local coordination of the non-hydrogen atoms is shown in Fig. 1b. The $[Zn_2Sn_2Se_7]^{2-}$ layers in **1** are built from $[SnSe_4]$ and $[ZnSe_3N]$ tetrahedra. The nitrogen atom in $[ZnSe_3N]$ originates from the covalently bonded amino end-group of the organic template. As shown in Fig. 2, $[SnSe_4]$ and $[ZnSe_3N]$ tetrahedra share corners alternately *via* Zn–Se–Sn bonds to form infinite zig-zag chains running along the *a*-axis and fused together along the *b*-axis through additional Zn–Se–Sn and Sn–Se–Sn bonds. This type of connectivity results in the formation of 8-membered rings (four $SnSe_4$ and four $ZnSe_3N$ tetrahedra) with an aperture of approximately 2×7 Å, excluding the van der Waals radii (see Fig. 2). All layers are stacked along the *c*-axis in the eclipsed configuration resulting in straight 8-ring channels. Similar types of layers with the same anionic charge have been observed in the crystal structure of $[enH_2][(Ga_4S_7(en)_2]^6$ and $[enH_2]_2[(Ga_4Se_7(en)_2]^7$ (en: ethylenediamine); however, in both cases the structure is centrosymmetric and in marked contrast to **1**, different en molecules serve as counterions and coordinating ligands to gallium atoms. It is noteworthy that four Ga^{3+} cations in the above chalcogenogallates or the combination of two Zn^{2+} and two Sn^{4+} in **1** results in the formation of structurally equivalent hybrid inorganic layers. This implies that it may be possible to accommodate more complex chemical compositions (*e.g.* $2Ga^{3+} : Zn^{2+} : Sn^{4+}$) in this type of inorganic layer, leading to a family of materials with tunable properties.

Powder X-ray diffraction (PXRD) data indicate that **1** is the major crystalline phase (see Fig. S1 in ESI†). Small crystalline impurities are observed which do not match with metallic Zn or Sn, binary metal selenides (ZnSe, SnSe and SnSe$_2$) or Se.

Infrared spectroscopy confirmed the presence of piperazinium cations and –NH$_2$ groups[8] in **1** (see Fig. S2 in ESI†). Thermogravimetric analysis (TGA) shows that **1** does not contain any solvent molecules and is stable up to 230 °C (see Fig. S3 and the related text in ESI†).

[119]Sn Mössbauer spectroscopy was used to characterize the tin local environment and formal oxidation state in **1**. The corresponding spectrum recorded at 80 K is shown in Fig. 3. The major component (81% area) of the spectrum consists of
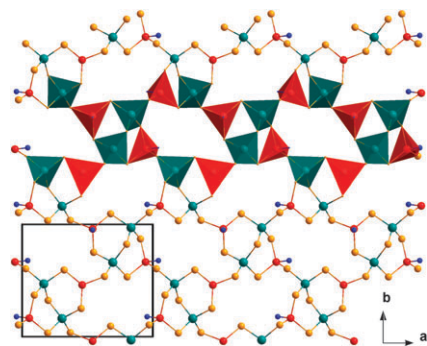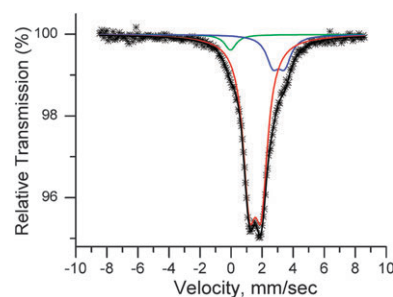

Fig. 3 [119]Sn Mössbauer spectrum for compound **1** recorded at 80 K. The spectrum was obtained with a constant acceleration spectrometer using a 5 mCi CaSnO$_3$ source (source kept at room temperature). The corresponding isomer shift values are reported relative to CaSnO$_3$.

a doublet with an isomer shift $\delta = 1.56$ mm s^{-1} and a quadrupole splitting ΔE_q of 0.76 mm s^{-1}. These are consistent with Sn^{4+} in a distorted tetrahedral environment of selenide ligands,[9] in full agreement with the crystallographic data of **1**. The spectrum also contains in small amounts two more components with parameters 3.06/0.76 (15.1%) mm s^{-1} (blue line) and 0.04/0.0 (3.9%) mm s^{-1} (green line). The latter (singlet) could be assigned to SnO$_2$ which is not detectable in the PXRD pattern due to its very low quantity (area 3.9%). The doublet, with high isomer shift (3.06 mms^{-1}), is consistent with Sn^{2+} in selenides.[9] Given the fact that SnSe was not observed in the PXRD pattern, the origin of this component remains at present unclear.

Raman spectroscopy was used to further characterize the inorganic framework. The Raman spectrum of **1** in the range 0–600 cm^{-1}, recorded at room temperature on a single crystal, is shown in Fig. 4. A comparison with the Raman spectrum of the isolated $[SnSe_4]^{4-}$ anion in Na$_4$SnSe$_4$·2en[10] allows for a qualitative assignment of the observed bands. At least five vibrational modes were observed in the region of 50–600 cm^{-1}. The sharp, intense peak centred at 191 cm^{-1} can be assigned to the totally symmetric Sn–Se stretching mode of the $[SnSe_4]^{4-}$ anion, corresponding to the 199 cm^{-1} peak in the spectrum of Na$_4$SnSe$_4$·2en but slightly shifted due to coordination to the Zn^{2+} centers in **1**. The observed slight downshift is in accordance with the average longer Sn–Se bond distance in **1** (2.529 Å) as compared to that found in the crystal structure of Na$_4$SnSe$_4$[11] (2.519 Å). The peaks at 235 cm^{-1} and 255 cm^{-1} can be assigned to the asymmetric Sn–Se stretching modes,

Fig. 2 A single layer of **1** looking down the *c*-axis. Note the 8-membered rings formed by alternating corner shared $[SnSe_4]$ and $[ZnSe_3N]$ tetrahedra.
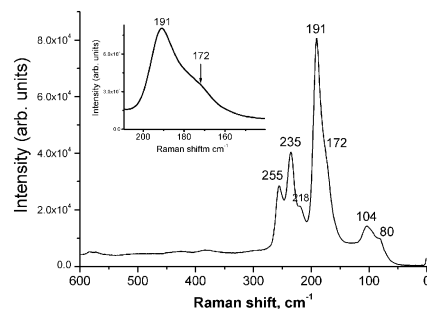

Fig. 4 Raman spectrum for compound **1** recorded at room temperature on a single crystal. The measurement was performed using a Nicolet Almega XR Raman spectrometer with a 473 nm blue laser (25% of the 15 mW laser power). The beam was focused on the sample through a confocal microscope using a 10× objective lens.

corresponding to 239 cm^{-1} and 247 cm^{-1} in the spectrum of the free $[SnSe_4]^{4-}$ anions. The broad peaks at 104 cm^{-1} and 80 cm^{-1} can be assigned to the partially overlapping anti-symmetric Se–Sn–Se bends.[10] The shoulder at 172 cm^{-1} (see inset in Fig. 4) is absent in the spectrum of free $[SnSe_4]^{4-}$ and could be assigned to the Zn–Se vibrational mode.

Diffuse reflectance UV-vis/near IR spectroscopy was used to investigate the optical properties of **1**. As shown in Fig. 5, a well defined optical absorption associated with a band-gap transition at 2.3 eV is observed, indicating that this is a wide gap semiconductor. Interestingly, the observed band-gap is close to that found in the open-framework solids $(Me_4N)_2Zn[Sn_4Se_{10}]$[12] and $[Zn(H_2O)_4][Zn_2Sn_3Se_9(MeNH_2)]$[13] (2.23 eV and 2.03 eV, respectively) made from the same elements as **1**, indicating that the elemental composition in these structurally different, but not dense, materials controls their optical properties. This is also confirmed from the fact that the structurally related solid $[enH_2]_2[(Ga_4Se_7(en)_2]$, having different metal cations (four Ga^{3+} instead of the combination of two Zn^{2+} and two Sn^{4+} in **1**), shows a band-gap transition at 1.69 eV.[7]

The polar structure of **1** and its optically transparent nature make it attractive for NLO (non-linear optic) studies. Preliminary powder SHG (second-harmonic generation) measurements on a polycrystalline sample were performed on a modified Kurtz-NLO system[14] using 1064 nm radiation. A detailed description of the equipment and the methodology used has been published.[15] No index matching fluid was used in any of the experiments, and the powders were not sieved. Green light was observed with an efficiency slightly less than α-SiO$_2$, confirming the acentricity of the material.

In conclusion, we have shown that it is possible to construct novel, ternary hybrid semiconductors in which the organic molecules serve not only as templates but also as ligands and counterions. This combination is highly attractive because it could expand the structural and chemical diversity in multinary chalcogenides, leading to materials with unique optical and electronic properties.
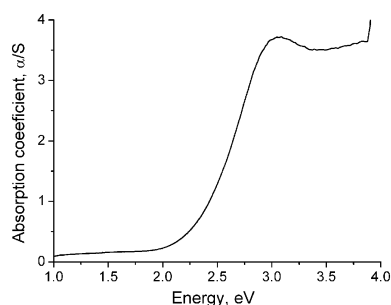
Fig. 5 Solid state UV-vis/near IR electronic absorption spectrum for compound **1**. The spectrum was obtained at room temperature on a PerkinElmer LAMBDA 950 UV/Vis/NIR spectrophotometer in the wavelength range of 200–2500 nm. BaSO$_4$ powder was used as a reference (100% reflectance) and base material on which the powder sample was coated. Reflectance data were converted to absorbance data as described elsewhere.[16]

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