



Hydrothermal synthesis of $[C_6H_{16}N_2][In_2Se_3(Se_2)]$: A new one-dimensional indium selenide

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ABSTRACT

A new organically templated indium selenide, $[C_6H_{16}N_2][In_2Se_3(Se_2)]$, has been prepared hydrothermally from the reaction of indium, selenium and trans-1,4-diaminocyclohexane in water at 170 °C. This material was characterised by single-crystal and powder X-ray diffraction, thermogravimetric analysis, UV–vis diffuse reflectance spectroscopy, FT-IR and elemental analysis. The compound crystallises in the monoclinic space group $C2/c$ ($a = 12.0221(16)$ Å, $b = 11.2498(15)$ Å, $c = 12.8470(17)$ Å, $\beta = 110.514(6)^\circ$). The crystal structure of $[C_6H_{16}N_2][In_2Se_3(Se_2)]$ contains anionic chains of stoichiometry $[In_2Se_3(Se_2)]^{2-}$, which are aligned parallel to the $[1\ 0\ 1]$ direction, and separated by diprotonated trans-1,4-diaminocyclohexane cations. The $[In_2Se_3(Se_2)]^{2-}$ chains, which consist of alternating four-membered $[In_2Se_2]$ and five-membered $[In_2Se_3]$ rings, contain perselenide $(Se_2)^{2-}$ units. UV–vis diffuse reflectance spectroscopy indicates that $[C_6H_{16}N_2][In_2Se_3(Se_2)]$ has a band gap of 2.23(1) eV.

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1. Introduction

Reactions performed under solvothermal conditions in the presence of a structure directing agent such as an amine, are a versatile route for the synthesis of a wide range of structurally diverse materials [1]. Solvothermal reactions exploit the mild conditions afforded by solvents under autogeneous pressure [2] to produce metastable phases, which may have markedly different structural and physical properties from materials prepared using high-temperature synthetic techniques. The products of solvothermal reactions are influenced by a large number of parameters, including time, temperature, pressure, choice of solvent and the concentrations of the starting reagents [3].

Since the extension from oxides to sulphides by Bedard et al. [4] of the synthetic methodologies used for the preparation of zeolites, solvothermally prepared metal chalcogenides have been the focus of extensive research due to their wide range of potential applications, which include catalysis, [5] selective ion-exchange [6] and molecule-discriminating sensors [7]. This has resulted in the successful synthesis and characterization of a number of new chalcogenides containing main-group elements from Group 13 (Ga, In) [8,9], Group 14 (Ge, Sn) [10,11,12] and Group 15 (Sb, As) [11,12,13]. A frequently encountered primary building unit in many Group 13 metal chalcogenides is the MQ_4 tetrahedron (where $M = Ga, In$; $Q = S, Se, Te$). Linkage of MQ_4 building blocks by corner- or edge-sharing, results in

a variety of secondary building blocks. For instance, corner-linkage of MQ_4 tetrahedra frequently results in the formation of supertetrahedral clusters, which can be described as tetrahedrally shaped fragments of the ZnS lattice [9]. Discrete T2 supertetrahedral clusters, $[M_4Q_{10}]^{8-}$ ($M = Ga, In$; $Q = S, Se$), have been isolated from aqueous solutions, [14] while linkage of supertetrahedral units by their vertices results in the formation of two- or three-dimensional structures. This includes three-dimensional sulphides and selenides containing T3 units, $[M_{10}Q_{20}]^{10-}$ ($M = Ga, In$; $Q = S, Se$), [15–19] as well as other three-dimensional structures containing larger heterometallic T4 clusters, $[M_4In_16S_{33}]^{10-}$ ($M = Mn, Co, Zn, Cd$) [20] or $[M_4Ga_{16}S_{33}]^{10-}$ ($M = Co, Zn$) [15,16] and T5 clusters, $[Cu_5In_{30}S_{54}]^{13-}$ [21]. By contrast, edge-sharing of MQ_4 tetrahedra ($M = Ga, In$; $Q = S, Se, Te$) often results in the formation of one-dimensional $[MQ_2]^-$ chains [22–25]. Other building blocks of greater complexity have also been reported. For example, the sulphide $[(C_3H_7)_2NH_2]_3[In_6S_{11}H]$ [26] is composed of corner- and edge-sharing InS_4^{5-} tetrahedra, which form layers that stack along the $[1\ 0\ 0]$ direction. Edge- and corner-sharing $InSe_4^{5-}$ tetrahedra coexist in the three-dimensional framework of $[C_7H_{10}N][In_9Se_{14}]$, which contains one-dimensional channels with a diameter of ca. 6 Å [27]. The three-dimensional framework $[In_{33}Q_{56}]^{13-}$ ($Q = S, Se, Te$) is constructed from cross-linking of helical chains of corner-sharing InQ_4^{5-} tetrahedra, [28] whilst in $[NH_4]_4[In_{12}Se_{20}]$, nona-nuclear indium clusters serve as the building units for a microporous structure which exhibits selective ion-exchange properties with heavy-metal ions [29].

In comparison with sulphides, the number of solvothermally prepared indium selenides that has been reported is relatively small, [17,27–30] although the synthesis of these phases would

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enable tuning of optical and electrical properties. In this work, we report the synthesis, crystal structure and optical properties of a one-dimensional indium selenide prepared hydrothermally using trans-1,4-diaminocyclohexane as the structure-directing agent. Remarkably, the presence of a perselenide (Se_2)²⁻ unit in a solvothermally prepared indium selenide is seen here for the first time.

2. Materials and methods

2.1. Synthesis

For the preparation of $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$, In powder (Alfa Aesar, 99+%, 0.1676 g, 1.46 mmol), Se powder (Aldrich, 99.5%, 0.2369 g, 3 mmol) and ground trans-1,4-diaminocyclohexane (Aldrich, > 98%, 0.3426 g, 3 mmol) were mixed and loaded into a 23 ml Teflon-lined stainless steel autoclave. Deionised water (3 ml) was added to form a mixture with an approximate molar composition $\text{In}:\text{Se}:\text{C}_6\text{H}_{14}\text{N}_2:\text{H}_2\text{O}$ of 1.5:3:3:166. After stirring the mixture, the vessel was closed and heated at 170 °C for 10 days, and then cooled to room temperature at a cooling rate of 0.2 °C min^{-1} . The product was filtered, washed with methylated spirits and acetone, and dried in air at room temperature. Under these conditions, the solid product consisted mainly of small orange/brown crystals, which were later identified by single crystal X-ray diffraction as $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$, together with a small amount of a grey powder. Powder X-ray diffraction data indicate that the grey powder is a mixture of In_4Se_3 and an unidentified phase.

2.2. Characterisation

Powder X-ray diffraction data were collected using a Bruker D8 Advance powder diffractometer, operating with germanium monochromated $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$), or using a Bruker D8 Discover, operating with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Data were collected on ground portions of the bulk products of the reactions.

Elemental analysis on hand-picked crystals of $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$ was carried out using an Exeter CE-440 elemental analyser. Thermogravimetric analysis was performed using a DuPont Instruments 951 thermal analyser. Approximately 10 mg of finely ground crystals was heated under a flow of O_2 over the temperature range of $30 \leq T/\text{°C} \leq 1000$ using a heating rate of 5 °C min^{-1} . Diffuse reflectance measurements were performed using a Perkin Elmer Lambda 35 UV–vis spectrometer. BaSO_4 powder was used as a reference (100% reflectance) and absorption data were calculated from the Kubelka–Munk function [31]. The infrared spectrum of $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$ was obtained using a Perkin Elmer 100 ATR spectrophotometer, on a ground sample of hand-picked crystals.

Single crystal X-ray diffraction was carried out at 293 K using a Bruker X8 Apex diffractometer ($\text{MoK}\alpha$ $\lambda = 0.71073 \text{ \AA}$) [32]. The crystal, a block with dimensions $0.3 \times 0.1 \times 0.08 \text{ mm}^3$, was mounted with cyanoacrylate adhesive onto a glass fibre. Intensity data were collected at 10 s intervals per rotation. The structure was solved by direct methods using the program SIR92 [33], which located the indium and selenium atoms. Subsequent Fourier calculations and least squares refinements on F were carried out using the CRYSTALS program [34]. The carbon and nitrogen atoms of the amine were located in the difference Fourier maps. Hydrogen atoms were placed geometrically, and their coordinates refined using riding constraints. Crystallographic data for the structure reported in this paper have been deposited at the

Cambridge Crystallographic Data Centre, with the CCDC number 818282.

3. Results and discussion

The local coordination diagram and atom labelling scheme for $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$ is shown in Fig. 1, with selected crystallographic data presented in Table 1. The atomic coordinates and isotropic thermal parameters are given in Table 2. The structure of $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$ contains one crystallographically independent indium atom, which is tetrahedrally coordinated to four selenium atoms, at distances in the range of 2.5742(3)–2.6019(3) Å (Table 3). These distances are comparable with those

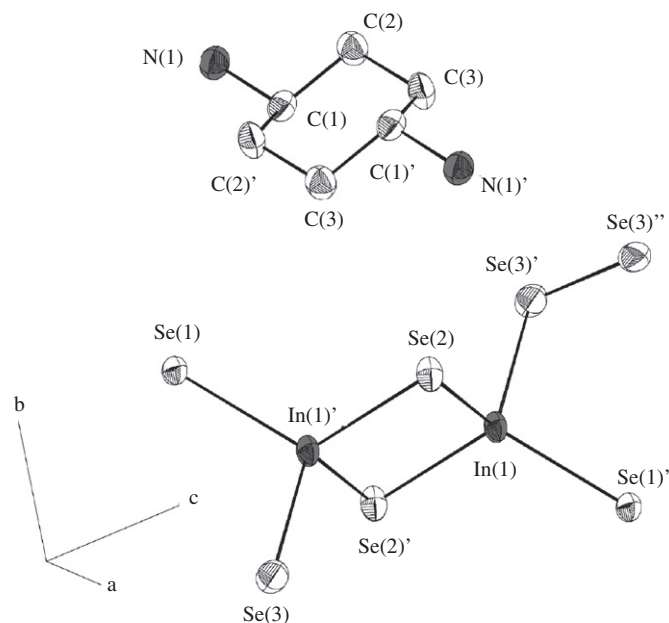


Fig. 1. Local coordination diagram of non-hydrogen atoms showing the atom labelling scheme and ellipsoids at 50% probability.

Table 1
Selected crystallographic data for $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$.

Formula	$[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$
Mr	740.65
Crystal size/mm	$0.3 \times 0.1 \times 0.08$
Crystal habit	Brown block
Crystal system	Monoclinic
Space group	$C2/c$
$a/\text{\AA}$	12.0221(16)
$b/\text{\AA}$	11.2498 (15)
$c/\text{\AA}$	12.8470(17)
$\beta/\text{°}$	110.514(6)
Unit cell volume/ \AA^3	1627.3(4)
Z	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	3.023
$\theta_{\text{max}}/\text{°}$	26.402
Temperature/K	293
R_{merge}	0.029
Number of parameters refined	49
Measured data	14833
Unique data	1656
Observed data ($I > 3\sigma(I)$)	1450
Residual electron density $\text{max}/\text{e \AA}^{-3}$	0.62
Residual electron density $\text{min}/\text{e \AA}^{-3}$	−0.43
R	0.014
R_w	0.016

Table 2
Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for non-hydrogen atoms of $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$.

Atom	Site	x	y	z	U_{iso}
In(1)	8(f)	0.11909(1)	0.24682 (1)	0.39453(1)	0.0238
Se(1)	4(e)	0	0.40235(3)	1/4	0.0250
Se(2)	8(f)	0.16762(2)	0.29863(2)	0.60092 (2)	0.0276
Se(3)	8(f)	-0.00056(2)	0.04947(2)	0.34277(2)	0.0337
N(1)	8(f)	0.2540(2)	0.3971(2)	0.18224(18)	0.0309(4)
C(1)	8(f)	0.2299(2)	0.3028(2)	0.0947(2)	0.0267(5)
C(2)	8(f)	0.3441(3)	0.2350(2)	0.1097(2)	0.0317(6)
C(3)	8(f)	0.3222(2)	0.1405(2)	0.0193(2)	0.0319(5)

Table 3
Selected bond lengths (\AA) and angles (deg.) for $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$.

Bond	(\AA)	Angle	(Deg.)
In(1)–In(1) ^b	3.3583(3)	Se(1)–In(1)–Se(2)	117.05(1)
In(1)–In(1) ^a	3.8127(3)	Se(1)–In(1)–Se(2) ^b	116.31(1)
In(1)–Se(1)	2.5876(4)	Se(2)–In(1)–Se(2) ^b	98.97(1)
In(1)–Se(2)	2.5742(4)	Se(1)–In(1)–Se(3)	106.04(1)
In(1)–Se(2) ^b	2.5952(5)		
In(1)–Se(3)	2.6019(5)	Se(2)–In(1)–Se(3)	111.22(1)
		Se(2) ^b –In(1)–Se(3)	106.92(1)
Se(3)–Se(3) ^a	2.3884(5)		

^a Symmetry transformations used to generate equivalent atoms: $-x, y, (1/2)-z$.

^b Symmetry transformations used to generate equivalent atoms: $(1/2)-x, (1/2)-y, 1-z$.

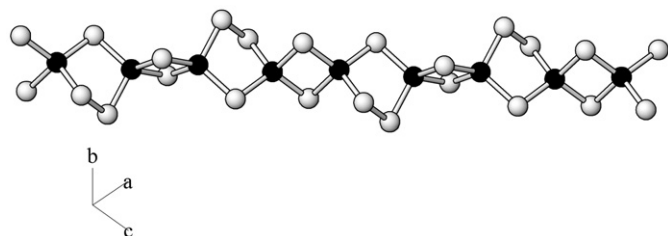


Fig. 2. View along $[\bar{1}11]$ of a $[\text{In}_2\text{Se}_3(\text{Se}_2)]^{2-}$ chain. Key: indium, solid circles; selenium, open circles.

reported for other selenides containing tetrahedrally coordinated indium [27]. The InSe_4 tetrahedra are slightly distorted, as evidenced by the Se–In–Se bond angles, which lie in the range of $98.972(8)$ – $117.043(10)^\circ$. In the crystal structure of $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$, pairs of InSe_4 tetrahedra are linked through common vertices to yield dimers of composition In_2Se_7 . Within this unit, two terminal selenium atoms, one from each of the tetrahedra, are separated by a distance of $2.3882(7) \text{\AA}$, which is less than the sum of the van der Waals' radii of two Se atoms (3.80\AA) [35]. This is consistent with the formation of a perselenide bond. Although this is the first reported example of a one-dimensional indium selenide with this linkage of InSe_4 tetrahedra, perselenide units have been observed at similar Se–Se distances in discrete complexes, [36,37] in rare-earth clusters, [38] and when selenium was used as a ligand [39]. When the perselenide moiety is taken into account, the dimeric In_2Se_7 unit is more correctly formulated as $[\text{In}_2\text{Se}_5(\text{Se}_2)]^{6-}$. The $[\text{In}_2\text{Se}_5(\text{Se}_2)]^{6-}$ dimeric units are linked through shared edges formed from the remaining terminal selenium atoms (Se(2)) to create a chain of stoichiometry $[\text{In}_2\text{Se}_3(\text{Se}_2)]^{2-}$. These one-dimensional chains are composed of alternating four-membered $[\text{In}_2\text{Se}_2]$ and five-membered $[\text{In}_2\text{Se}_3]$ rings (Fig. 2), with the indium atom being common to both ring systems, and where the perselenide linkage completes the five-membered $[\text{In}_2\text{Se}_3]$

heteroring. The plane of the four- and five-membered rings rotates by approximately 90° on moving from one ring to another along the $[\text{In}_2\text{Se}_3(\text{Se}_2)]^{2-}$ chain. The five-membered ring in the $[\text{In}_2\text{Se}_3(\text{Se}_2)]^{2-}$ chain however is distorted from a planar conformation, where the selenium atoms of the perselenide bond are above and below the plane of the ring. This results in a torsion angle of $-19.73(1)^\circ$ for $\text{Se}(3)\text{--In}(1)\text{--Se}(1)\text{--In}(1)$. As a result of the nature of the chains, two different In–In distances are observed. In the five-membered ring the In–In distance is $3.8127(3) \text{\AA}$, whilst the edge-sharing of the InSe_4 units within the four-membered rings results in a fairly short In–In distance of $3.3583(3) \text{\AA}$. This is comparable to the average metal–metal distance of indium metal of 3.34\AA [40]. Similarly short In–In distances are found within the four-membered rings in $[\text{InQ}_2]^-$ ($Q=\text{S}, \text{Te}$) chains [23,25]. Despite the relatively short In–In distances found in the $[\text{In}_2\text{Se}_3(\text{Se}_2)]^{2-}$ chains, the bond valence sum, [41] of around $+2.90$ v.u. for In(1), is consistent with a formal oxidation state of In(III), indicating localization of electrons. The $[\text{In}_2\text{Se}_3(\text{Se}_2)]^{2-}$ chains found here can be considered to be related to the frequently encountered $[\text{MQ}_2]^-$ chains, which are formed by edge-sharing of MQ_4 tetrahedra [22–25]. By replacing a Se^{2-} ion by a perselenide (Se_2^{2-}) ion per $[\text{M}_2\text{Se}_4]^{2-}$ formula unit, a $[\text{M}_2\text{Se}_3(\text{Se}_2)]^{2-}$ chain can be generated from a $[\text{MSe}_2]^-$ chain.

The $[\text{In}_2\text{Se}_3(\text{Se}_2)]^{2-}$ chains are packed parallel to the $[101]$ crystallographic direction and separated from each other by diprotonated 1,4-diaminocyclohexane cations (Fig. 3). These cations adopt two orientations with respect to the $[\text{In}_2\text{Se}_3(\text{Se}_2)]^{2-}$ chains, with successive protonated amines along the $[101]$ direction rotated by approximately 90° . As shown in Fig. 3, each nitrogen atom is pointing towards selenium atoms in two adjacent $[\text{In}_2\text{Se}_3(\text{Se}_2)]^{2-}$ chains. All hydrogen atoms in the N–H bonds are involved in N–H \cdots Se bonding interactions (Supplementary information), with each ammonium group exhibiting a total of four hydrogen-bonding interactions, with nitrogen to selenium distances within the range of $3.411(2)$ – $3.535(2) \text{\AA}$. As a result of these interactions, a three-dimensional hydrogen-bonding network, which is illustrated in Fig. 3, is formed.

The one-dimensional chains of $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$, formed by alternating four- and five-membered rings, constitute a new structural motif for Group 13 chalcogenides. As far as we are aware, compounds containing $[\text{In}_2\text{Se}_3]$ heterorings have not been described previously, although isolated anions containing

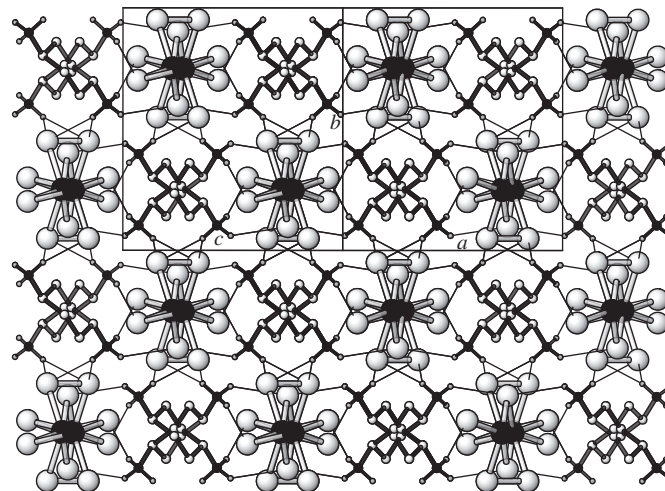


Fig. 3. View of $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$ along the $[101]$ direction showing the anionic $[\text{In}_2\text{Se}_3(\text{Se}_2)]^{2-}$ chains separated by diprotonated organic amines. Hydrogen bonds are indicated by lines. Hydrogen atoms on the carbon backbone have been omitted for clarity. Key: indium, large solid circles; selenium, large open circles; carbon, medium open circles; nitrogen, medium solid circles and hydrogen, small grey circles.

five-membered $[\text{InSe}_4]$ heterorings, such as $[\text{In}_2(\text{Se}_4)_4(\text{Se}_5)]^{4-}$, $[\text{In}_2\text{Se}_2(\text{Se}_4)_2]^{2-}$ and $[\text{In}_3\text{Se}_3(\text{Se}_4)_3]^{3-}$, have been reported [42]. There are a limited number of examples of $[\text{M}_2\text{Q}_3]$ ($\text{M}=\text{Ga}, \text{In}$; $\text{Q}=\text{Se}, \text{Te}$) heterorings in the literature, which include those found in $[\text{In}_2(\text{Te}_2)_2\text{Te}_2]^{2-}$ chains [43] and in the $[\text{Ga}_3\text{Se}_6\text{Se}_{2/2}(\text{en})]^{3-}$ bicyclo units of $[\text{Ga}(\text{en})_3][\text{Ga}_3\text{Se}_7(\text{en})] \cdot \text{H}_2\text{O}$ [44]. Polymeric chains containing $[\text{Hg}_2\text{Te}_3]$ rings, including $[\text{Hg}_2\text{Te}_9]^{4-}$ and $[\text{Hg}_2\text{Te}_4]^{2-}$, are also known, [45] and alternating chains of four- and five-membered rings, of stoichiometry $[\text{In}_2\text{As}_5]^{7-}$, have been found in $\text{KBa}_2\text{InAs}_3$ [46]. In sharp contrast to the highly distorted conformation of the $[\text{In}_2\text{Se}_3]$ rings found in the chains reported here, the $[\text{In}_2\text{As}_3]$ heterorings in $\text{KBa}_2\text{InAs}_3$ are planar. It has been suggested that the planarity of the $[\text{In}_2\text{As}_3]$ ring is a consequence of π conjugation, involving $p_\pi-d_\pi$ interactions between empty d -orbitals from the indium atoms and filled p -orbitals of the arsenic atoms [46]. This is reflected in shorter than usual As–As distances, but a similar shortening of the Se–Se distances when compared to other compounds containing $(\text{Se}_2)^{2-}$ units, [36–39] was not found here.

The powder X-ray diffraction pattern (Supplementary information) of the bulk product of the reaction shows that $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$ is the main solid product. The lattice parameters determined for $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$ using powder X-ray diffraction data, $a=12.0377(8)$ Å, $b=11.2231(6)$ Å, $c=12.8450(7)$ Å and $\beta=110.766(4)^\circ$, are in reasonable agreement with those determined by single-crystal X-ray diffraction. As the initially prepared product contained a small amount of In_4Se_3 and an unidentified phase, a range of temperatures and molar ratios were investigated, in an attempt to produce a single-phase material. It was observed that by increasing the reaction temperature to 200 °C, the amount of $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$ was reduced, whilst by increasing the amount of selenium in the reaction mixture, a $[\text{In}_{12}\text{Se}_{20}]^{4-}$ framework, isostructural to the $[\text{NH}_4]_4[\text{In}_{12}\text{Se}_{20}]$ phase previously prepared by Manos et al. [29] in concentrated NH_4OH , was obtained. Given that previously reported Group 13 polyselenides [42,44] were prepared under very mild conditions, these results suggest that the solvothermal synthesis of phases containing $(\text{Se}_2)^{2-}$ or larger $(\text{Se}_n)^{2-}$ units may be favored by low reaction temperatures.

FTIR data (Supplementary information) for $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$ are consistent with the presence of aliphatic amines. A peak at ca. 3400 cm^{-1} can be assigned to N–H stretching vibrations from the primary amine groups within the trans-1,4-diaminocyclohexane molecules. A broad peak at ca. 2890 cm^{-1} can be attributed to C–H stretching vibrations. Other peaks at lower wavenumbers are typical of C–H deformations in aliphatic compounds [47]. Elemental analysis on hand-picked single crystals gave C 8.67, H 1.78, N 3.16% which agrees reasonably well with the values calculated from the crystallographically determined formula of $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$ (C 9.73, H 2.18 and N 3.78%). Thermogravimetric analysis indicated that, under an oxygen atmosphere, $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$ is stable up to ca. 200 °C (Supplementary information). An overall weight loss of 62.8% was observed, which is in very good agreement with the calculated weight loss of 62.5% for decomposition of the title compound into In_2O_3 . The identity of the decomposition product, which was a white powder, was confirmed as In_2O_3 by powder X-ray diffraction (Supplementary information).

The optical absorption spectrum of the title compound is shown in Fig. 4. The optical band gap of $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$, which was estimated from the absorption edge, has a value of 2.23(1) eV at room temperature. This is consistent with the orange/brown colour of the $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$ crystals and confirms the semiconducting nature of this material. When compared with condensed phases such as $\alpha\text{-In}_2\text{Se}_3$ ($E_g \approx 1.4$ eV), $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$ exhibits a significantly larger band gap.

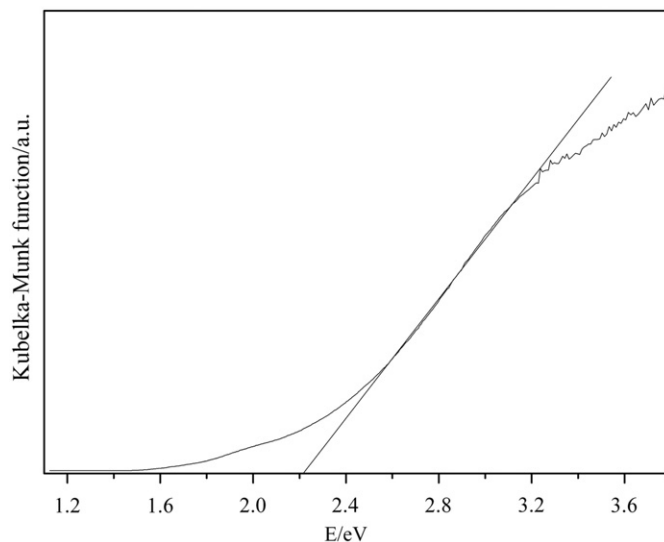


Fig. 4. The optical absorption spectrum of $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$. The black line shows the extrapolation from the high energy end of the absorption edge used to determine the band gap.

Other solvothermally prepared indium selenides, which adopt three-dimensional structures, have band gaps in the range of 1.8–2.1 eV [27,29]. Analysis of a wide range of antimony sulphides [48] led to the identification of a correlation between the magnitude of the optical band gap and the framework density of main-group metal centres. Similar behaviour appears to hold here, as $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$ is less dense than previously reported phases, [27,29] and consequently exhibits a larger band gap.

4. Conclusions

In the material reported here, the incorporation of a per-selenide unit into a solvothermally prepared indium selenide is seen for the first time. This suggests that the solvothermal synthesis of indium polyselenides in which $(\text{Se}_n)^{2-}$ chains act as bridging units between indium polyhedra, may be feasible. Whilst super-tetrahedral clusters are a frequently encountered building unit in solvothermally prepared indium sulphides, the limited number of reports available to date on indium selenides suggests that a greater structural diversity may be possible, [27,29] and the results described here indicate that this structural diversity may be further increased through the incorporation of polyselenide moieties.

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Supplementary information

Crystallographic data in CIF format, powder X-ray diffraction, FTIR and TGA data, and table of hydrogen bonds for $[\text{C}_6\text{H}_{16}\text{N}_2][\text{In}_2\text{Se}_3(\text{Se}_2)]$, are available.

Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2011.05.021.

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