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A three-dimensional open-framework indium selenide: $[\text{C}_7\text{H}_{10}\text{N}][\text{In}_9\text{Se}_{14}]$

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ABSTRACT An open-framework indium selenide, $[\text{C}_7\text{H}_{10}\text{N}][\text{In}_9\text{Se}_{14}]$, has been prepared under solvothermal conditions in the presence of 3,5-dimethylpyridine, and characterized by single crystal diffraction, thermogravimetry, elemental analysis, FTIR spectroscopy and UV-Vis diffuse reflectance. The crystal structure of $[\text{C}_7\text{H}_{10}\text{N}][\text{In}_9\text{Se}_{14}]$ contains an unusual building unit, in which corner-linked and edge-linked InSe_4^{5-} tetrahedra coexist. The presence of one-dimensional circular channels, of ca. 6 Å diameter, results in approximately 25% of solvent accessible void space.

There have been extensive research efforts to develop new microporous materials during the last few decades, because of their technological importance for applications such as catalysis or molecular sieves.¹ Although research has focused primarily on oxygen-based frameworks, in recent years there has been an increasing interest in the preparation of microporous chalcogenide materials,² given their technological potential as multifunctional materials, capable of combining the ion-exchanging and catalytic features of zeolites with the semiconducting behaviour of metal chalcogenides. Possible areas of application for these novel microporous semiconductors range from molecule discriminating sensors³ to selective ion-exchange⁴ and photocatalysis.⁵ A significant progress has already been made in the synthesis of open-framework indium sulphides built from supertetrahedral clusters, which can be described as tetrahedrally shaped fragments of the ZnS structure.⁶ In comparison with sulfides, very few indium selenides are known, but their development is desirable to allow tuning of the electronic and optical properties of the resulting chalcogenides. Given that selenides and tellurides tend to have higher electrical conductivities (and smaller band gaps) than sulfides and that the disorder of the template generally found in microporous chalcogenides may lead to low thermal conductivities,⁷ these materials could also find applications in the area of thermoelectricity.

The very few examples of microporous indium selenides reported so far have revealed a greater degree of structural complexity than that found in the corresponding indium sulfides. While the three-dimensional structure of the

$[\text{In}_{10}\text{Se}_{18}]^{6-}$ open-framework⁸ exhibits a supertetrahedra-based double-diamond lattice, isostructural to the indium sulphide $[(\text{CH}_3)_2\text{NH}_2][\text{In}_{10}\text{S}_{18}]$,⁹ and that of $[\text{In}_4\text{Se}_8]^{4-}$ can be described as a non-interpenetrating supertetrahedra-based diamond lattice,¹⁰ the $[\text{In}_{33}\text{Se}_{56}]^{13-}$ open-framework¹¹ does not contain supertetrahedral clusters. Instead the structure of $[\text{In}_{33}\text{Se}_{56}]^{13-}$ can be described as formed by cross-linked chains of corner-sharing InSe_4^{5-} tetrahedra.¹¹ In $[\text{NH}_4]_4[\text{In}_{12}\text{Se}_{20}]$, nona-nuclear indium clusters are the building units of a microporous structure which exhibits ion-exchange properties with heavy-metal ions.¹²

Here we report the synthesis, crystal structure¹³ and optical properties¹⁴ of a three-dimensional open-framework indium selenide, $[\text{C}_7\text{H}_{10}\text{N}][\text{In}_9\text{Se}_{14}]$. The unique crystal structure of this material contains an unusual building unit, in which corner-linked and edge-linked InSe_4^{5-} tetrahedra coexist. To prepare $[\text{C}_7\text{H}_{10}\text{N}][\text{In}_9\text{Se}_{14}]$, 3,5-dimethylpyridine (Aldrich, 98+%, 2.5 mL, 21.9 mmol) was added to a Teflon-lined 23 ml stainless steel autoclave containing indium metal (Aldrich, 99.99%, 168 mg, 1.46 mmol) and selenium (Aldrich, 99.5%, 196 mg, 2.48 mmol). The vessel was sealed and heated at 200°C for 16 days. After cooling to room temperature overnight, the reaction mixture was filtered, washed with ethanol and acetone and dried in air at room temperature. The reaction product consists of red needles of $[\text{C}_7\text{H}_{10}\text{N}][\text{In}_9\text{Se}_{14}]$ together with an amorphous brown powder. The red needles of $[\text{C}_7\text{H}_{10}\text{N}][\text{In}_9\text{Se}_{14}]$ were separated from the brown powder using an ultrasonic bath, and further purified by handpicking of crystals under a microscope.

The crystal structure of $[\text{C}_7\text{H}_{10}\text{N}][\text{In}_9\text{Se}_{14}]$ (Table 1) contains two crystallographically independent indium atoms, which are tetrahedrally coordinated by selenium atoms (Figure 1). The In-Se distances lie in the range 2.5243(9)–2.6669(6) Å, similar to those reported for other indium selenides containing tetrahedrally coordinated In.¹⁵ The InSe_4^{5-} tetrahedra are significantly distorted as evidenced by Se-In-Se angles varying between 128.83(2) and 94.34(2)° for In(1) and between 136.38(5) and 98.52(3) for In(2). The building unit of the $[\text{In}_9\text{Se}_{14}]^-$ framework is a six-membered In_3Se_3 ring, formed by corner-linked InSe_4^{5-} tetrahedra. Each $\text{In}(1)\text{Se}_4^{5-}$ tetrahedron in the In_3Se_3 ring shares an edge with a second $\text{In}(1)\text{Se}_4^{5-}$ tetrahedron of an adjacent ring, forming a chain which runs

parallel to the *c*-axis (Figure 2). While all solvothermally-prepared indium selenides reported to date are built from corner-linked InSe_4^{5-} tetrahedra, edge-linked tetrahedra have been previously found in condensed structures, such as TlInSe_2 .¹⁶ Edge-sharing of InSe_4^{5-} tetrahedra results in relatively short In-In distances, of *ca.* 3.58 and 3.42 Å in the title compound and TlInSe_2 respectively. Much shorter In-In distances (*ca.* 2.77 Å) have been however found in indium-rich selenides such as InSe ¹⁷ or In_4Se_3 .¹⁸ This suggests that In-In interactions in the title compound are very weak.

Table 1. Crystallographic data for $[\text{C}_7\text{H}_{10}\text{N}][\text{In}_9\text{Se}_{14}]$.

M_r	2138.82
Crystal system	Hexagonal
Space group	$P6_3/m$
T/K	100
$a/\text{\AA}$	12.8786(6)
$c/\text{\AA}$	11.7792(12)
$V/\text{\AA}^3$	1691.9(2)
Z	2
μ/mm^{-1}	21.066
Measured data	43944
Unique data	1470
Observed data ($I > 3\sigma(I)$)	958
R_{merge}	0.039
R	0.0202
R_w	0.0223

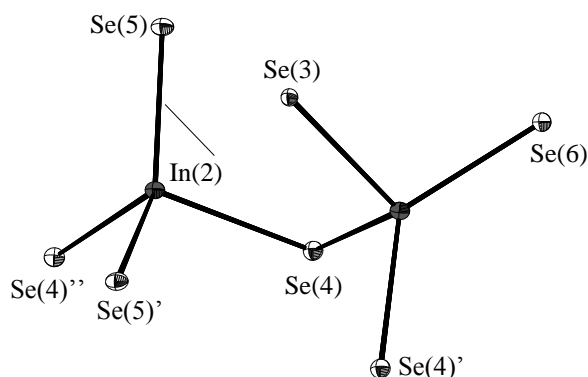


Figure 1. Local coordination diagram showing the atoms labeling scheme and ellipsoids at 50% probability.

The individual chains shown in Fig. 2 are linked into a three-dimensional honeycomb structure by sharing the terminal Se(3) and Se(5) atoms with four adjacent chains (Figure 3). These individual chains are related to each other by 120° rotations around the three-fold axes located at $1/3, 2/3, z$ and $2/3, 1/3, z$. Large circular channels of *ca.* 9 Å (measured from coordinate to coordinate) are formed parallel to the *c*-axis. When the van der Waals radii of In and Se are taken into account, the effective aperture dimension of the channels is *ca.* 6 Å. Using PLATON,¹⁹ it was established that the $[\text{In}_9\text{Se}_{14}]$ framework contains *ca.* 25% of solvent accessible void space. The 3,5-dimethylpyridine molecules are therefore assumed to be located within the channels and, given the anionic nature of the framework, protonated for charge balance. The FTIR spectrum (Supplementary Information) of the title

compound is consistent with the presence of aromatic and amine functional groups. A peak at *ca.* 3450 cm^{-1} can be tentatively assigned to N-H stretching vibrations, those at *ca.* 3000 cm^{-1} can be attributed to C-H stretching vibrations, while those over the region 1600-1400 cm^{-1} are characteristic of aromatic compounds. Elemental analysis is also consistent with the presence of one protonated 3,5-dimethylpyridinium cation per formula unit.²⁰

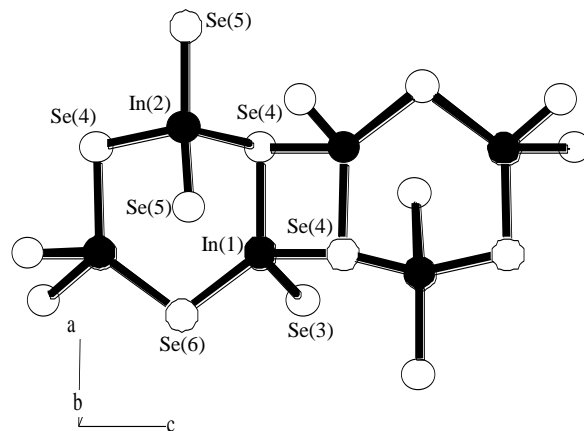


Figure 2. $\text{In}_3\text{Se}_7^{5-}$ chains running parallel to the *c* axis. The labeling scheme is shown.

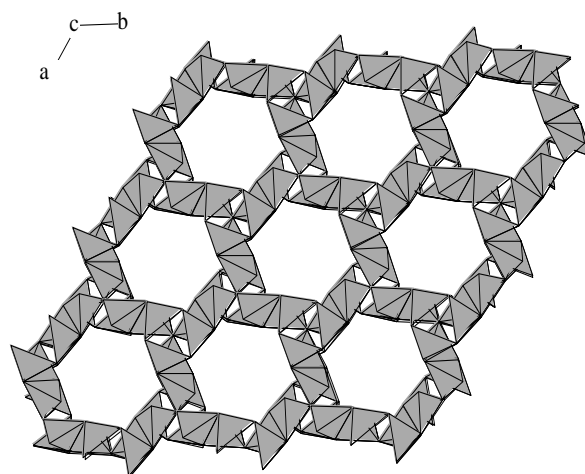


Figure 3. Polyhedral representation of the $[\text{C}_7\text{H}_{10}\text{N}][\text{In}_9\text{Se}_{14}]$ structure viewed along [001]. The 3,5-dimethylpyridinium cations are disordered and located within the one-dimensional channels of the $[\text{In}_9\text{Se}_{14}]$ framework.

Thermogravimetric analysis²¹ indicates that, under a nitrogen atmosphere, $[\text{C}_7\text{H}_{10}\text{N}][\text{In}_9\text{Se}_{14}]$ is stable up to *ca.* 250°C (Supplementary Information). The weight loss (6.0%) is larger than that expected for the total removal of the amine (calculated 4.8%). This may indicate the concomitant loss of a fraction (*ca.* 2.4 at.%) of the selenium, which would result in a decomposition product with a composition close to In_2Se_3 . Although heating of open-framework chalcogenides often results in the collapse of the crystal structure, a number of studies^{4,12,22} have

demonstrated that ion exchange can be used for the removal of the organic species. This suggests that it may be possible to access the microporosity of $[\text{C}_7\text{H}_{10}\text{N}][\text{In}_9\text{Se}_{14}]$ by ion exchange.

The optical absorption spectrum of the title compound is shown in Figure 4. The band gap, which was estimated from the absorption edge, has a value of 1.91(6) eV. This is consistent with the red color of $[\text{C}_7\text{H}_{10}\text{N}][\text{In}_9\text{Se}_{14}]$, and confirms the semiconducting nature of this material. The band gap of $[\text{C}_7\text{H}_{10}\text{N}][\text{In}_9\text{Se}_{14}]$ lies within the energy range suitable for photocatalytic applications using light in the visible region,⁵ and is comparable to those found for other microporous indium selenides.¹² However, when compared with condensed phases such as $\alpha\text{-In}_2\text{Se}_3$ ($E_g \approx 1.4$ eV),²³ the title compound as well as the small number of known microporous indium selenides, exhibit larger band gaps. It has been proposed that there is a correlation between the magnitude of the optical band gap and the framework density, through analysis of data for a wide range of antimony sulfides of differing dimensionality.²⁴

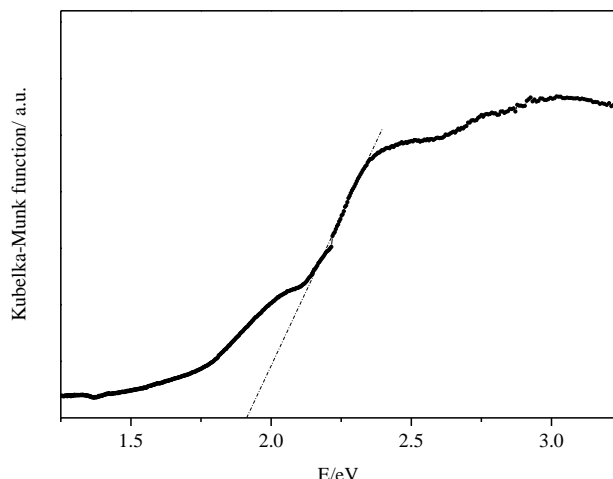


Figure 4. Optical absorption spectrum of $[\text{C}_7\text{H}_{10}\text{N}][\text{In}_9\text{Se}_{14}]$. The dashed line shows the extrapolation from the high-energy end of the absorption edge used to determine the band gap.

In conclusion, $[\text{C}_7\text{H}_{10}\text{N}][\text{In}_9\text{Se}_{14}]$ has a unique open-framework structure, containing one-dimensional circular channels of ca. 6 Å diameter. Our current efforts are directed towards the use of ion exchange to access the microporosity within this structure.

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Supporting Information Available: Crystallographic data in CIF format, FTIR and TGA data. This material is available free of charge via the Internet at <http://pubs.ac.org>.

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- (13) A crystal (dimensions $0.04 \times 0.04 \times 0.2$ mm³) was mounted on a glass fibre and X-ray intensity data collected using a Bruker X8 APEX 2 diffractometer with graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å) at 100 K. The structure was solved by direct methods using the program SIR92 and models refined using CRYSTALS. The data were treated with SQUEEZE, to correct the effect of the disordered organic component.
- (14) Diffuse reflectance measurements were collected using a Perkin Elmer Lambda 35 UV-Vis Spectrometer. BaSO₄ powder was used as a reference and the absorption data were calculated from the reflectance data using the Kubelka-Munk function.
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- (20) Elemental analysis: found: C = 3.58%, H = 0.32%, N = 0.33% ; calc.: C = 3.74%, H = 0.45%, N = 0.62%.
- (21) Thermogravimetric analysis was performed using a DuPont Instruments 951 thermal analyser. Approximately 7 mg of finely ground crystals were heated under a flow of dry nitrogen over the temperature range 25–400°C at a heating rate of 5°C min⁻¹.
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