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A Three-Dimensional Open-Framework Indium Selenide: $[C_7H_{10}N][In_9Se_{14}]$

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An open-framework indium selenide, $[C_7H_{10}N][In_9Se_{14}]$, has been prepared under solvothermal conditions in the presence of 3,5-dimethylpyridine and characterized by single-crystal X-ray diffraction, thermogravimetry, elemental analysis, Fourier tranform IR spectroscopy, and UV–vis diffuse reflectance. The crystal structure of $[C_7H_{10}N][In_9Se_{14}]$ contains an unusual building unit, in which corner- 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 behavior of metal chalcogenides. Possible areas of application for these novel microporous semiconductors range from molecule-discriminating sensors[3] to selective ion exchange[4] and photocatalysis.[5] Significant progress has already been made in the synthesis of open-framework indium sulfides 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 $[In_{10}Se_{18}]^{6-}$ open framework[8] exhibits a supertetrahedra-based double-diamond lattice, isostructural to the indium sulfide $[(CH_3)_2NH_2][In_{10}S_{18}]$,[9] and that of $[In_4Se_8]^{4-}$ can be described as a non-interpenetrating supertetrahedra-based diamond lattice,[10] the $[In_{33}Se_{56}]^{13-}$ open framework[11] does not contain supertetrahedral clusters. Instead, the structure of $[In_{33}Se_{56}]^{13-}$ can be described as formed by cross-linked chains of corner-sharing $InSe_4^{5-}$ tetrahedra.[11] In $[NH_4]_4[In_{12}Se_{20}]$, nonanuclear indium clusters are the building units of a microporous structure that exhibits ion-exchange properties with heavy-metal ions.[12]

Here we report the synthesis, crystal structure,[13] and optical properties[14] of a three-dimensional open-framework indium selenide, $[C_7H_{10}N][In_9Se_{14}]$. The unique crystal structure of this material contains an unusual building unit, in which corner- and edge-linked $InSe_4^{5-}$ tetrahedra coexist. To prepare $[C_7H_{10}N][In_9Se_{14}]$, 3,5-dimethylpyridine (Aldrich,

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(13) A crystal (dimensions 0.04 × 0.04 × 0.2 mm^3) was mounted on a glass fiber, and X-ray intensity data were collected using a Bruker X8 APEX 2 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 100 K. The structure was solved by direct methods using the program *SIR92*, and models were 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. $BaSO_4$ 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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Table 1. Crystallographic Data for $[C_7H_{10}N][In_9Se_{14}]$

M_r	2138.82
cryst syst	hexagonal
space group	$P6_3/m$
T/K	100
a/Å	12.8786(6)
c/Å	11.7792(12)
V/Å^3	1691.9(2)
Z	2
μ/mm^{-1}	21.066
no. of measd data	43 944
no. of unique data	1470
no. of obsd data [$I > 3\sigma(I)$]	958
R_{merg}	0.039
R	0.0202
R_w	0.0223

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 $[C_7H_{10}N][In_9Se_{14}]$ together with an amorphous brown powder. The red needles of $[C_7H_{10}N][In_9Se_{14}]$ were separated from the brown powder using an ultrasonic bath and further purified by handpicking of crystals under a microscope.

The crystal structure of $[C_7H_{10}N][In_9Se_{14}]$ (Table 1) contains two crystallographically independent In atoms, which are tetrahedrally coordinated by Se 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 indium.[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 $[In_9Se_{14}]^-$ framework is a six-membered In_3Se_3 ring, formed by corner-linked $InSe_4^{5-}$ tetrahedra. Each $In(1)Se_4^{5-}$ tetrahedron in the In_3Se_3 ring shares an edge with a second $In(1)Se_4^{5-}$ tetrahedron of an adjacent ring, forming a chain that 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 found, however, 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.

The individual chains shown in Figure 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 3-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 atoms are taken into account, the effective aperture dimension of the channels is ca. 6 Å. Using *PLATON*,[19] it was established that the $[In_9Se_{14}]^-$ framework contains ca. 25% of solvent-accessible void space. The 3,5-dimethylpyridine molecules

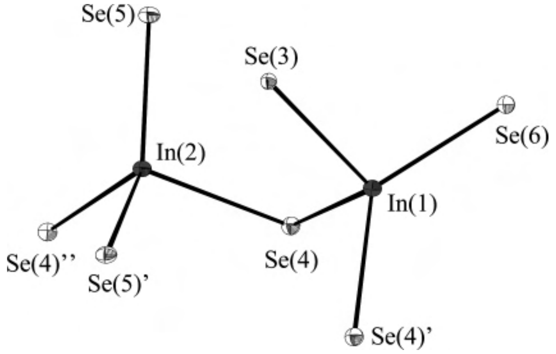

Figure 1. Local coordination diagram showing the atom-labeling scheme and ellipsoids at 50% probability.

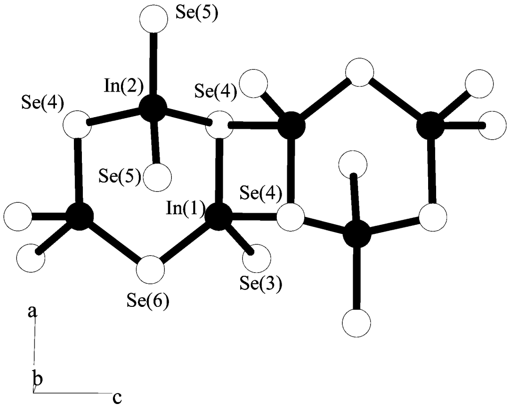

Figure 2. $In_3Se_7^{5-}$ chains running parallel to the c axis. The labeling scheme is shown.

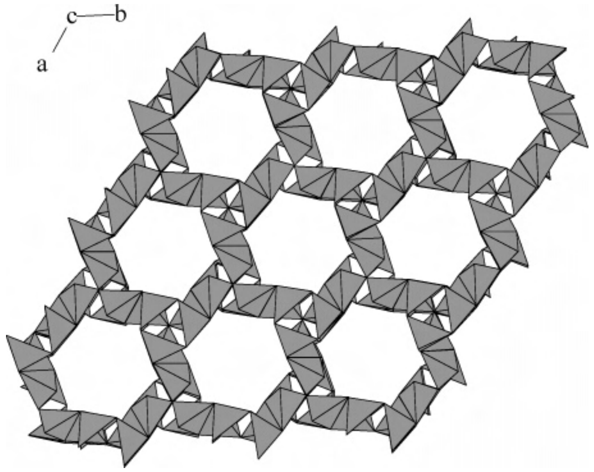

Figure 3. Polyhedral representation of the $[C_7H_{10}N][In_9Se_{14}]$ structure viewed along [001]. The 3,5-dimethylpyridinium cations are disordered and located within the one-dimensional channels of the $[In_9Se_{14}]^-$ framework.

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are therefore assumed to be located within the channels and, given the anionic nature of the framework, protonated for charge balance. The Fourier transform (FTIR) spectrum (Supporting 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]

Thermogravimetric analysis (TGA)[21] indicates that, under a nitrogen atmosphere, $[C_7H_{10}N][In_9Se_{14}]$ is stable up to ca. 250 °C (Supporting 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 atom %) 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 $[C_7H_{10}N][In_9Se_{14}]$ 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 $[C_7H_{10}N][In_9Se_{14}]$ and confirms the semiconducting nature of this material. The band gap of $[C_7H_{10}N][In_9Se_{14}]$ 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 α-In_2Se_3 ($E_g \approx 1.4$ eV),[23] the title compound, as well as the small number of known microporous indium selenides, exhibits 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]

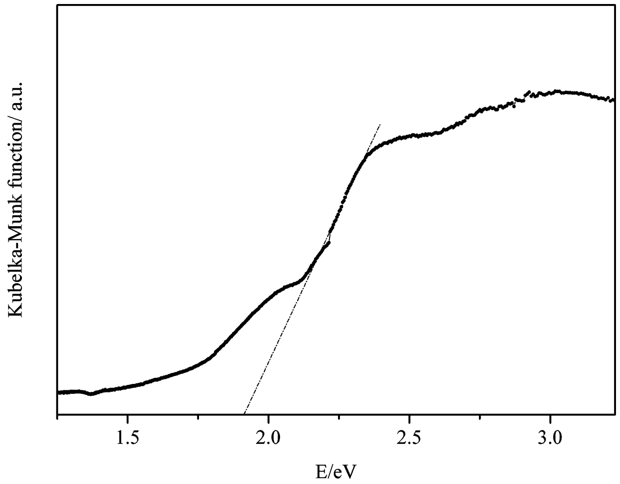

Figure 4. Optical absorption spectrum of $[C_7H_{10}N][In_9Se_{14}]$. The dashed line shows the extrapolation from the high-energy end of the absorption edge used to determine the band gap.

In conclusion, $[C_7H_{10}N][In_9Se_{14}]$ has a unique open-framework structure, containing one-dimensional circular channels of ca. 6 Å diameter. Our current efforts are directed toward the use of ion exchange to access the microporosity within this structure.

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

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(20) Elem anal. Calcd: C, 3.74; H, 0.45; N, 0.62. Found: C, 3.58; H, 0.32; N, 0.33.

(21) TGA was performed using a DuPont Instruments 951 thermal analyzer. Approximately 7 mg of finely ground crystals was 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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