Inorganica Chimica Acta 484 (2019) 214–218

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Research paper

Growing crystalline selenidostannates in deep eutectic solvent

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ARTICLE INFO

Keywords:
Chalcogenides
Deep eutectic solvent
Selenidostannates
Choline chloride

ABSTRACT

By using deep eutectic solvent mixture of ChCl (ChCl = choline chloride) and 1,8-diaminooctane as reaction medium, three new selenidostannates were synthesized, namely $[Cr(en)_3]_{2.5}[SnSe_4]\cdot Cl_{3.5}\cdot(pip)_{0.5}\cdot 1.5H_2O$ (**1**) (en = ethylenediamine, pip = piperazine), $[Ni(en)_3][Sn_3Se_{6.5}(Se_2)_{0.5}]$ (**2**), and $[Ni(en)_3][Sn_3Se_7]$ (**3**). Compound **1** features a primary unit of $SnSe_4$ tetrahedron, in which the $[Cr(en)_3]^{3+}$ complex acts as charge balance agent. In compound **2,** there are two kinds of one dimensional chains, including $[Sn_3Se_7]_n^{2n-}$ and $[Sn_3Se_6(Se)_2]_n^{2n-}$ anionic chains. The $[Sn_3Se_7]_n^{2n-}$ chain is constructed by connecting $[Sn_3Se_9]$ units via edge-sharing Se^{2-} ion, while the $[Sn_3Se_6(Se)_2]_n^{2n-}$ chain is constructed by linking $[Sn_3Se_{10}]$ units via sharing one Se^{2-} ion and one Se_2^{2-} ion. Compound **3** features a lamellar anionic $[Sn_3Se_7]_n^{2n-}$ structure, where the $[Ni(en)_3]^{2+}$ ions are located in inter-lamellar space. The optical absorption spectra indicate band gaps of 2.23 eV for **1**, 1.95 eV for **2**, and 2.01 eV for **3**.

1. Introduction

As an important member of solid-state materials, crystalline chalcogenides have caught extensive attentions due to their fascinating structures as well as unique performances in the areas of photoelectric effect [1], photoluminescence [2], nonlinear optics [3], and thermoelectricity [4]. The traditional synthetic methods involved the utilization of reaction mediums have been widely employed in preparing new crystalline chalcogenides, such as molten flux [5], room temperature solution approach [6], and hydro(solvo)thermal methods [7–10]. Obviously, the properties of solvents are crucial to the reaction processes, which significantly affect the component and structure formation of as-prepared chalcogenides. Based on this strategy, application of new solvents that are quite different from traditional molecular solvents would be attractive to the exploration of novel chalcogenides [11–15]. The unique properties of ionic liquids make them good alternatives to the traditional molecular solvents [16]. Indeed, ionothermal has been proved as a promising synthetic approach in the preparation of crystalline materials, including zeolite analogues [17], chalcogenides [18], and metal-organic frameworks [19]. In recent years, ionothermal synthesis of crystalline chalcogenides has become a new research direction in chalcogenide chemistry.Scheme 1.

Abundant chalcogenides with diverse structures and variable components have been synthesized in various imidazole-based ionic liquids [18,20,21]. However, most of these ionic liquids are very expensive, which limits their large-scale application in the synthetic procedure. There is another type of ionic fluids, namely deep eutectic solvents (DES), which possess the similar properties to the imidazole-based ionic liquids, such as low vapour pressure, high ionic conductivity, and high polarity [22]. Nevertheless, deep eutectic solvents involved the use of ChCl and corresponding hydrogen bond donors are much cheaper than the imidazole-based ionic liquids. Moreover, deep eutectic solvents are produced by mixing various quaternary ammonium halide salts and hydrogen bond donors. This simplified synthetic procedure is performed without purification. In addition, deep eutectic solvents are non-toxic [23] and biodegradable [24]. These characters enable them to be used without environmental concerns. Although deep eutectic solvents have been extensively studied in material synthesis and electrochemistry [25], this type of solvents is rarely used in the synthesis of crystalline chalcogenides [26]. Thus, more efforts are deserved to explore this research area.

Sn^{4+} ion tends to coordinate with chalcogen elements (S, Se, Te) in four-, five- and six-coordinated geometries, leading to the formation of three primary building units, including SnQ_4 tetrahedron, SnQ_5 hexahedron, and SnQ_6 octahedron [27,28].The condensation of these primary building units (PBUs) could generate a variety of secondary building units (SBUs) through corner-sharing and edge-sharing, such as $[Sn_2Q_6]$ dimers and $[Sn_4Q_{10}]$ (Q = S, Se) clusters [29,30]. Thus, a series

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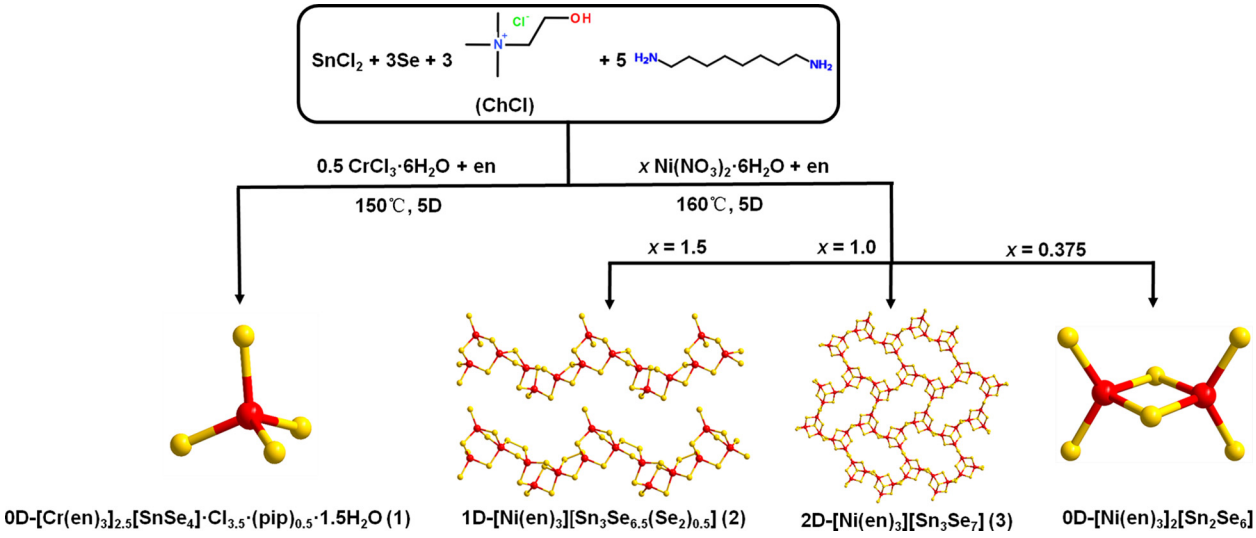
https://doi.org/10.1016/j.ica.2018.09.046
Received 25 August 2018; Received in revised form 18 September 2018; Accepted 18 September 2018
Available online 20 September 2018



Scheme 1. Schematic illustration of the synthetic procedures for **1**–**3**.

of chalcogenidostannates with different structural dimensionalities have been constructed by the assembly of these SBUs, such as one dimensional chains (e.g. $[Sn_2Q_5]_n^{2n-}$ [31], $[Sn_2Q_6]_n^{2n-}$ [32]), two dimensional layers (e.g. $[Sn_3Q_7]_n^{2n-}$ [33], $[Sn_4Q_9]_n^{2n-}$ [31]), and three dimensional frameworks (e.g. $[Sn_9Se_{20}]_n^{4n-}$ [33], $[Sn_{18}Se_{40}]_n^{8n-}$ [34]). In this work, by using deep eutectic solvent mixture of ChCl and 1,8-diaminooctane as reaction medium, we synthesized three new selenidostannates with structures ranging from zero-dimensional discrete cluster to two-dimensional layer, namely $[Cr(en)_3]_{2.5}[SnSe_4]\cdot Cl_{3.5}\cdot(pip)_{0.5}\cdot 1.5H_2O$ (**1**), $[Ni(en)_3][Sn_3Se_{6.5}(Se_2)_{0.5}]$ (**2**), and $[Ni(en)_3][Sn_3Se_7]$ (**3**). The deep eutectic solvent was crucial to the synthesis of **1**–**3**, since no crystals can be obtained due to the removal of these two chemicals from the reactions.

2. Experimental section

2.1. Materials and general methods

All reagents and chemicals were purchased from commercial sources and used without further purification. Elemental analyses for C, H and N were characterized by a German Elementary Vario EL III instrument. Energy-dispersive X-ray analysis (EDXA) was performed on a JEOL JSM-6700F scanning electron microscope. Optical diffuse reflectance spectra were measured at room temperature with an UV-vis-NIR Varian 86 Cary 500 Scan spectrophotometer using a $BaSO_4$ plate as a standard (100% reflectance). The absorption (α/S) data were calculated from reflectance spectra by using the Kubelka–Munk function: $\alpha/S = (1 - R^2)/2R$, where α is the absorption coefficient, S is the scattering coefficient, and R is the reflectance. Powder X-ray diffraction (PXRD) patterns were recorded in the angular range of 2θ = 5–60° on a Miniflex II diffractometer using CuKα radiation (λ = 1.5406). A NETZSCH DSC214Polyma thermogravimetric analyzer was used to obtain the thermogravimetry (TG) curves in a N_2 atmosphere with a heating rate of 10 °C min^{-1} in the temperature range of 30–750 °C.

2.2. Synthesis

Synthesis of **$[Cr(en)_3]_{2.5}[SnSe_4]\cdot Cl_{3.5}\cdot(pip)_{0.5}\cdot 1.5H_2O$ (1).** $CrCl_3\cdot 6H_2O$ (0.50 mmol, 0.133 g), $SnCl_2$ (1.03 mmol, 0.196 g), Se (3.14 mmol, 0.248 g), ChCl (3.00 mmol, 0.419 g), 1,8-diaminooctane (4.98 mmol, 0.719 g) and ethylenediamine (0.30 mL) were mixed and sealed in an autoclave equipped with a Teflon liner (20 mL), then heated at 150 °C for 5 days and cooled to room temperature. The products were filtrated and washed several times with ethanol to obtain yellow cubic crystals of **1** with a yield of 42% (0.523 g, based on Sn). Elemental analysis calcd (%) for $C_{17}H_{68}N_{16}O_{1.50}Cl_{3.50}Cr_{2.50}SnSe_4$: C 16.88, H 5.68, N 18.53; found(%): C 16.74, H 5.54, N 18.64.

Synthesis of **$[Ni(en)_3]$ $[Sn_3Se_{6.5}(Se_2)_{0.5}]$ (2).** $Ni(NO_3)_2\cdot 6H_2O$ (1.00 mmol, 0.291 g), $SnCl_2$ (1.06 mmol, 0.200 g), Se (3.00 mmol, 0.237 g), ChCl (3.10 mmol, 0.435 g), 1,8-diaminooctane (5.20 mmol, 0.749 g) and ethylenediamine (0.30 mL) were mixed and sealed in an autoclave equipped with a Teflon liner (20 mL), then heated at 160 °C for 5 days and cooled to room temperature. The products were filtrated and washed several times with ethanol to obtain dark-red rod like crystals of **2** with a yield of 25.6% (0.236 g, based on Sn). Elemental analysis calcd (%) for $C_6H_{24}N_6NiSn_3Se_{7.5}$: C 6.07, H 2.04, N 7.08; found (%): C 5.97, H 1.97, N 6.92.

Synthesis of **$[Ni(en)_3]$ $[Sn_3Se_7]$ (3).** $Ni(NO_3)_2\cdot 6H_2O$ (1.51 mmol, 0.439 g), $SnCl_2$ (1.03 mmol, 0.195 g), Se (3.00 mmol, 0.237 g), ChCl (3.01 mmol, 0.421 g), 1,8-diaminooctane (5.00 mmol, 0.721 g) and ethylenediamine (0.30 mL) were mixed and sealed in an autoclave equipped with a Teflon liner (20 mL), then heated at 160 °C for 5 days and cooled to room temperature. The products were filtrated and washed several times with ethanol to obtain dark-red prismatic crystals of **3** with a yield of 26.6% (0.316 g, based on Sn). Elemental analysis calcd (%) for $C_6H_{24}N_6NiSn_3Se_7$: C 6.28, H 2.11, N 7.32; found(%): C 6.67, H 2.04, N 7.30.

The crystals of **1**–**3** are stable in air and insoluble in common solvents. The phase purity of these crystals is confirmed by a PXRD study (Figs. S1–S3).

2.3. Single-crystal structure determination

Single-crystal X-ray diffraction data of **1**–**3** were collected on a Bruker APEX-II CCD with graphite-monochromated MoKα radiation (λ = 0.71073 Å) at room temperature. The absorption corrections were determined using a multi-scan technique. The structures of **1**–**3** were analyzed by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-2016 program package [35]. Non-hydrogen atoms were refined with anisotropic displacement parameters. The empirical formulae were confirmed by thermogravimetric analyses (TGA) and element analyses (EA) results. The relevant crystallographic data and structure refinement details are listed in Table 1. The corresponding selected bond lengths, bond angles and hydrogen bonds data are listed in Tables S1–S6 in the Supporting Information (SI).

3. Results and discussion

The mixture of ChCl and 1,8-diaminooctane with a mole ratio of 3 :