



# Syntheses, crystal and band structures, and optical properties of a selenidoantimonate and an iron polyselenide

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## ABSTRACT

A new selenidoantimonate  $(\text{CH}_3\text{NH}_4)[\text{Mn}(\text{phen})_2](\text{SbSe}_4) \cdot \text{phen}$  (**1**, phen = 1,10-phenanthroline) and an iron polyselenide  $[\text{Fe}(\text{phen})_2](\text{Se}_4)$  (**2**) were obtained under hydro(solvo)thermal conditions. Compound **1** represents the first example of a selenidoantimonate anion as a ligand to a transition-metal  $\pi$ -conjugated ligand complex cation. Compound **2** containing a  $\kappa^2\text{Se}^1, \text{Se}^4$  chelating tetraselenide ligand, represents the only example of a tetraselenide ligand to a Fe complex cation. Compounds **1** and **2** exhibit optical gaps of 1.71 and 1.20 eV, respectively and their thermal stabilities have been investigated by thermogravimetric analyses. The electronic band structure along with the density of states calculated by the DFT method indicate that the optical absorptions mainly originate from the charge transitions from the Se 4p and Mn 3d states to the phen  $p-\pi^*$  orbital for **1** and the Se 4p and Fe 3d states to the phen  $p-\pi^*$  orbital for **2**.

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## 1. Introduction

Current increasing interest in TM-containing (TM = transitional-metal) chalcogenides arises not only from their fascinating structural features [1], but also as a result of their potential applications in semiconductors, nonlinear optics, ion exchange, photocatalysis, and fast-ion conductivity, etc. [2]. The mild hydro(solvo)thermal syntheses with aliphatic chelating amines, such as ethylenediamine, diethylenetriamine, triethylenetetramine, tris(2-aminoethyl)amine and tetraethylenepentamine as solvents have been proved to be a promising synthetic strategy for the preparation of TM-containing chalcogenides [1f,3]. In the reactions, the aliphatic chelating amines not only can act as reaction mediums, but also can act as organic ligands connecting with TM ions to form TM aliphatic chelating amine complexes that have diverse spatial configurations, flexibilities and H-bonding sites and can direct the syntheses of different TM-containing chalcogenides [3b,4]. It should be noted that such studies have been well performed [3b,5], and a large number of chalcogenides with TM aliphatic chelating amine complex cations have been reported.

In these compounds, the organic aliphatic chelating amines either chelate with TM ions to form saturated TM complex cations, which act as a space filler or a structure director in chalcogenides, or saturate part of the coordinate sites at the TM ions, allowing the TM ions to make TM–Q (Q = S, Se, Te) bonds with chalcogenide anions to form covalent chalcogenide architectures.

Compared with aliphatic chelating amines, chelating  $\pi$ -conjugated ligands featuring delocalized electrons over their aromatic rings can confer peculiar photochemical and electrochemical properties on their TM complex cations [6], which also have unusual structure directing abilities [2b,7]. So, it is very attractive to incorporate TM  $\pi$ -conjugated ligand complex cations into main-group metal chalcogenide frameworks to form TM-containing chalcogenidometalates, which may have fascinating structures and combined features of magnetic, electrical, and optical properties from both components. For example, it was recently reported that TM  $\pi$ -conjugated ligand complex cations can stabilize well the chalcogenide anions with characteristic self-condensation inclination to form novel TM-containing chalcogenides that exhibit interesting optical and magnetic properties [2f,8]. However, research in this area is still in its early stage. In the domain of chalcogenidoantimonates, despite a large number of chalcogenidoantimonates with TM aliphatic chelating amines complexes have been reported [9], the TM  $\pi$ -conjugated ligand complex-containing

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chalcogenidoantimonate is only known in two thioantimonates [7c,10]. To our knowledge, the TM  $\pi$ -conjugated ligand complex-containing selenidoantimonate has never been reported up to now.

In this work, we report the synthesis, crystal and band structures, and optical properties of the first TM  $\pi$ -conjugated ligand complex-containing selenidoantimonate,  $(\text{CH}_3\text{NH}_4)[\text{Mn}(\text{phen})_2](\text{SbSe}_4) \cdot \text{phen}$  (**1**, phen = 1,10-phenanthroline). Meanwhile, a novel iron polysele-nide  $[\text{Fe}(\text{phen})_2](\text{Se}_4)$  (**2**) was obtained during the synthesis research of **1**, and its synthesis, crystal and band structures, and optical properties were also reported here. Compound **2** represents the only example of a tetraselenide anion  $(\text{Se}_4)^{2-}$  as a ligand to a Fe complex cation.

## 2. Experimental section

### 2.1. Materials and physical measurements

All reagents were purchased commercially and used without further purification. Elemental analyses of C, H, and N were performed on an Elementar Vario EL III microanalyzer. Powder X-ray diffraction (PXRD) patterns were recorded on Bruker D8 Focus diffractometer using Cu  $K\alpha$  radiation. A Perkin-Elmer Diamond thermogravimetric analyzer was used to obtain thermogravimetric analyses (TGA) curves in  $\text{N}_2$  with a flow rate of 20 mL/min and a ramp rate of  $10^\circ\text{C min}^{-1}$  in the temperature range 30–1000  $^\circ\text{C}$ . An empty  $\text{Al}_2\text{O}_3$  crucible was used as the reference. The FT-IR spectra were obtained on a Perkin-Elmer spectrophotometer using KBr disk in the range 4000–400  $\text{cm}^{-1}$ . Optical diffuse reflectance spectra were measured at room temperature with a Shimadzu UV-310 PC UV-vis spectrophotometer. The instrument was equipped with an integrating sphere and controlled with a personal computer. The samples were ground into fine powder and pressed onto a thin glass slide holder. A  $\text{BaSO}_4$  plate was used as a standard (100% reflectance). The absorption spectra were calculated from reflectance spectrum using the Kubelka–Munk function [11]:  $\alpha/S = (1 - R)^2/2R$  where  $\alpha$  is the absorption coefficient,  $S$  is the scattering coefficient (which is practically wavelength independent when the particle size is larger than 5  $\mu\text{m}$ ), and  $R$  is the reflectance.

### 2.2. Computational details

The X-ray crystallographic data of **1** and **2** was used to calculate its electronic structure. The calculations of band structure along with density of states (DOS) were carried out using density functional theory (DFT) with one of the three nonlocal gradient-corrected exchange-correlation functionals (GGA-PBE) and performed with the CASTEP code [12], which uses a plane wave basis set for the valence electrons and norm-conserving pseudopotential for the core electrons [13]. The number of plane waves included in the basis was determined by a cutoff energy,  $E_c$ , of 280 eV for **1** and 300 eV for **2**. Pseudo-atomic calculations were performed for Mn  $3d^54s^2$ , Fe  $3d^64s^2$ , Sb  $5s^24p^3$ , Se  $4s^24p^4$ , C,  $2s^22p^2$ , N  $2s^22p^3$  and H  $1s^1$ . The parameters used in the calculations and convergence criteria were set by the default values of the CASTEP code [12].

### 2.3. Preparations for **1** and **2**

#### 2.3.1. Preparation for **1**

A mixture of Sb (0.061 g, 0.50 mmol),  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (0.099 g, 0.50 mmol), Se (0.158 g, 2.00 mmol), and phen  $\cdot \text{H}_2\text{O}$  (0.198 g, 1.00 mmol) in 4 mL methylamine aqueous solution (28% in  $\text{H}_2\text{O}$ ) was sealed in a 25-mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure and then heated at

120  $^\circ\text{C}$  for 5 days and finally cooled to room temperature. The product consists of deep red block crystals of **1** and a few bits of unidentified powder. The crystals of **1** were selected by hand and washed with ethanol and diethyl ether (yield: 5% based on Sb). Elemental analysis calcd. (%) for  $\text{C}_{37}\text{H}_{30}\text{MnN}_7\text{SbSe}_4$ : C 41.72, H 2.84, N 9.20; found: C 41.23, H 2.27, N 8.92.

#### 2.3.2. Preparation for **2**

The attempts to prepare Fe analog of **1** under conditions similar to those of **1** using  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  or  $\text{FeCl}_3$  instead of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  were unsuccessful. Instead, an iron polyselenide, compound **2**, was isolated. An optimized synthesis method of **2** is as follows:

A mixture of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (0.100 g, 0.50 mmol), Se (0.158 g, 2.00 mmol), and phen  $\cdot \text{H}_2\text{O}$  (0.198 g, 1.00 mmol) in 1 mL methylamine alcoholic solution (33% in absolute ethanol) and 3 mL distilled water was sealed in a 25-mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure and then heated at 150  $^\circ\text{C}$  for 5 days and finally cooled to room temperature. The product consists of black red chunk crystals of **2** and a few bits of unidentified powder. The crystals of **2** were selected by hand and washed with ethanol and diethyl ether (yield: 20% based on Fe). Elemental analysis calcd. (%) for  $\text{C}_{24}\text{H}_{16}\text{FeN}_4\text{Se}_4$ : C 39.37, H 2.20, N 7.65; found: C 39.12, H 2.46, N 7.28.

Both compounds are stable in air and insoluble in common solvents. Pure crystals of **1** and **2** for physical property measurements were handpicked under a microscope and their phase purities were confirmed by PXRD studies (Fig. S5a and b).

### 2.4. Single-crystal structure determination

The intensity data sets were collected on a Agilent Xcalibur, Eos, Gemini CCD diffractometer for **1** and a Rigaku SCXmini CCD diffractometer for **2**, each diffractometer being equipped with a graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293 K. The data sets were reduced by the CrysAlisPro [14] and CrystalStructure [15] programs, respectively. The structures were solved by direct methods using the Siemens SHELXL package of crystallographic software [16]. The difference Fourier maps created on the basis of these atomic positions to yield the other non-hydrogen atoms. The structures were refined using a full-matrix least-squares refinement on  $F^2$ . All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of phen ligand were added geometrically and refined as riding on their parent atoms with fixed isotropic displacement parameters [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ]. Crystallographic data and structural refinements for **1** and **2** are summarized in Table 1. Important bond lengths and angles are listed in Table S1.

## 3. Results and discussion

### 3.1. Synthesis considerations

The hydro(solvo)thermal reactions have been used to prepare compounds **1** and **2**, where the Mn/Fe phen complex cations are formed *in-situ* and further form covalent TM–Se bonds with the selenidoantimonate anion for **1** and tetraselenide anion for **2**. Compounds **1** and **2** are gained in relatively low yields (5% for **1** and 20% for **2**) despite a broad variation of the synthesis conditions. The described synthesis conditions are the best ones to yield the corresponding product up to now and the reproducibility of the two compounds are good. Note that methylamine aqueous or alcoholic solution, acting as an organic base, offers the alkaline condition in the syntheses of **1** and **2**. Compound **1** cannot be obtained when the concentration of the methylamine aqueous solution is lower than 19%. Compound **2** can be obtained with the

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