

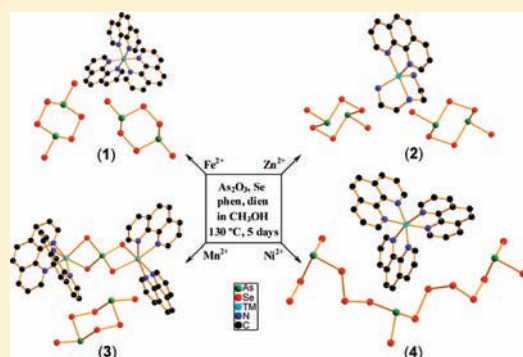
# Solvothermal Synthesis and Characterization of Polyselenidoarsenate Salts of Transition Metal Complex Cations

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Supporting Information

**ABSTRACT:** The polyselenidoarsenates  $[\text{Fe}(\text{phen})_3][\text{As}_2\text{Se}_6]$  (1),  $[\text{Zn}(\text{phen})(\text{dien})][\text{As}_2\text{Se}_6] \cdot 2\text{phen}$  (2),  $[\{\text{Mn}(\text{phen})_2\}_2(\mu-\eta^2, \eta^2-\text{AsSe}_4)]_2[\text{As}_2\text{Se}_6] \cdot \text{H}_2\text{O}$  (3), and  $[\text{Ni}(\text{phen})_3][\text{As}_2\text{Se}_2(\mu-\text{Se}_3)(\mu-\text{Se}_5)]$  (4) (dien = diethylenetriamine and phen = 1,10-phenanthroline) were prepared by the reaction of  $\text{As}_2\text{O}_3$ , Se, dien, and phen in the presence of transition metals in a methanol solvent under solvothermal conditions. Compounds 1–3 consist of  $[\text{As}_2\text{Se}_6]^{2-}$  anions with  $[\text{Fe}(\text{phen})_3]^{2+}$ ,  $[\text{Zn}(\text{phen})(\text{dien})]^{2+}$ , and  $[\{\text{Mn}(\text{phen})_2\}_2(\mu-\eta^2, \eta^2-\text{AsSe}_4)]^+$  complex counter cations, respectively. The  $[\text{As}_2\text{Se}_6]^{2-}$  anion is formed from two  $\text{As}^{\text{III}}\text{Se}_3$  trigonal pyramids linked through two Se–Se bonds. Compound 3 is the first example of a mixed-valent selenidoarsenate(III,V) and exhibits the coexistence of  $\text{As}^{\text{III}}\text{Se}_3$  trigonal pyramidal and  $\text{As}^{\text{V}}\text{Se}_4$  tetrahedral units. Compound 4 is composed of a helical chain of  $[\text{As}_2\text{Se}_2(\mu-\text{Se}_3)(\mu-\text{Se}_5)]^{2-}$  and octahedral  $[\text{Ni}(\text{phen})_3]^{2+}$  cations. The  $[\text{As}_2\text{Se}_2(\mu-\text{Se}_3)(\mu-\text{Se}_5)]^{2-}$  chain is constructed from  $\text{AsSe}^+$  units alternatively linked by  $\mu-\text{Se}_3^{2-}$  and  $\mu-\text{Se}_5^{2-}$  bridging ligands. When the structures of compounds 1–4 are compared, the transition metal ions show different structural directing effects during the synthesis of arsenic polyselenides in methanol. Compounds 1, 2, 3, and 4 exhibit semiconducting properties with band gaps of 1.88, 2.29, 1.82, and 2.01 eV, respectively.



## INTRODUCTION

Multinary chalcogenidoarsenates have received significant interest due to their potential applications in optical, electrical, and ion exchange materials,<sup>1–7</sup> and numerous transition metal (TM)-containing chalcogenidoarsenates have been prepared and characterized.<sup>1–4,6–14</sup> These arsenic chalcogenide structures are based upon the condensation of  $[\text{AsQ}_3]^{3-}$  trigonal pyramids ( $\text{Q} = \text{S}, \text{Se}$ ) via  $\text{Q}–\text{Q}$  and  $\text{As}–\text{Q}$  bond formation, which leads to polychalcogenides and chalcogenides, respectively. Polymeric anions of  $[\text{As}_x\text{Q}_y]^{z-}$  exhibit binding to thiophilic metal ions including  $\text{Cu}^+$ ,  $\text{Ag}^+$ , and  $\text{Hg}^{2+}$ , yielding extended ternary selenidoarsenates(III).<sup>6–11</sup> Since the cobalt thioantimonate complex  $[\text{Co}(\text{en})_3]\text{CoSb}_4\text{S}_8$  was prepared in ethylenediamine (en) under mild solvothermal conditions in 1996,<sup>15</sup> solvothermal reactions in polyamine solutions have become a versatile route for synthesizing ternary main group chalcogenidometalates containing TM complexes. Kromm and Sheldrick recently prepared coordinative selenidoarsenates using the tridentate N-donor ligand 2,2',6',2''-terpyridine (terpy) and the tetradentate N-donor ligand tris(2-aminoethyl)amine (tren) as templates in the presence of Mn(II) under solvothermal conditions. The  $\mu-\text{As}_2\text{Se}_4$ ,  $\mu-\text{As}_2\text{Se}_5$ ,  $\mu-\text{As}_4\text{Se}_7$ , and  $\mu-\text{As}_4\text{Se}_8$  bridging ligands were found to coordinate to  $\text{Mn}^{2+}$  in  $[\text{Mn}(\text{tren})]^{2+}$  and  $[\text{Mn}(\text{terpy})]^{2+}$  complexes.<sup>16–18</sup> Polyselenidoarsenate ligands coordinated to Mn(II) centers are also observed in  $[\{\text{Mn}(\text{terpy})\}_3(\mu-\text{AsSe}_2(\text{Se}_2))_2]$  and  $[\{\text{Mn}(\text{cyclam})\}_2(\mu-\text{As}_2\text{Se}_6)]$  where cyclam = 1,4,8,11-

tetraazacyclotetradecane.<sup>19</sup> In these compounds,  $\text{Mn}^{2+}$  ions form unsaturated coordinated complexes with amino ligands, and selenidoarsenate units further coordinate to  $\text{Mn}^{2+}$ , completing the 6-fold coordinate environment.

Solvents are thought to play an important role in the solvothermal synthesis of chalcogenidometalates,<sup>20–22</sup> and there have been precedents for the aminothermal and hydrothermal syntheses of TM-containing chalcogenidometalates.<sup>23–25</sup> However, the methanolothermal synthesis of chalcogenidometalates has been less explored, although this method was used to prepare alkali chalcogenidometalates many years ago.<sup>7,26–29</sup> We recently reported a helical polyselenidoarsenate  $[\text{Co}(\text{phen})_3][\text{As}_2\text{Se}_2(\mu-\text{Se}_3)(\mu-\text{Se}_5)]$  from the methanolothermal reaction of  $\text{CoCl}_2$ ,  $\text{As}_2\text{O}_3$ , Se, and phen in  $\text{CH}_3\text{OH}$  at 130 °C.<sup>30</sup> In the current study, the TM/As/Se/ $\text{CH}_3\text{OH}$  (TM = Fe, Mn, Ni, Zn) system was investigated using the coordinative phen ligand as a template, and polyselenidoarsenates with TM complex counter cations  $[\text{Fe}(\text{phen})_3][\text{As}_2\text{Se}_6]$  (1),  $[\text{Zn}(\text{phen})(\text{dien})][\text{As}_2\text{Se}_6] \cdot 2\text{phen}$  (2),  $[\{\text{Mn}(\text{phen})_2\}_2(\mu-\eta^2, \eta^2-\text{AsSe}_4)]_2[\text{As}_2\text{Se}_6] \cdot \text{H}_2\text{O}$  (3), and  $[\text{Ni}(\text{phen})_3][\text{As}_2\text{Se}_2(\mu-\text{Se}_3)(\mu-\text{Se}_5)]$  (4) have been prepared and characterized. The influence of the TM on methanolothermal synthesis is discussed.

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Table 1. Crystal Data and Summary of X-Ray Data Collection

	1	2	3	4
empirical formula	C <sub>36</sub> H <sub>24</sub> N <sub>6</sub> FeAs <sub>2</sub> Se <sub>6</sub>	C <sub>40</sub> H <sub>37</sub> N <sub>9</sub> ZnAs <sub>2</sub> Se <sub>6</sub>	C <sub>96</sub> H <sub>66</sub> N <sub>16</sub> OMn <sub>4</sub> As <sub>4</sub> Se <sub>14</sub>	C <sub>36</sub> H <sub>24</sub> N <sub>6</sub> NiAs <sub>2</sub> Se <sub>10</sub>
fw	1220.06	1332.76	3084.52	1538.76
color, shape of crystal	dark-red, block	orange, prism	black, block	dark-red, block
cryst syst	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	C2 (no. 5)
<i>a</i> , Å	13.1258(7)	11.857(2)	11.394(4)	24.412(7)
<i>b</i> , Å	13.1882(7)	13.738(3)	12.975(4)	11.263(2)
<i>c</i> , Å	13.6521(6)	15.815(3)	17.797(6)	19.406(5)
$\alpha$ , deg	117.090(13)	78.836(9)	80.302(12)	90.00
$\beta$ , deg	99.308(15)	69.160(8)	89.540(11)	127.749(5)
$\gamma$ , deg	105.732(18)	65.066(8)	74.714(9)	90.00
<i>V</i> , Å <sup>3</sup>	1909.7(4)	2180.3(7)	2499.7(13)	4218.9(19)
<i>Z</i>	2	2	1	4
<i>T</i> , K	223(2)	223(2)	223(2)	223(2)
calcd density, Mg m <sup>-3</sup>	2.122	2.030	2.049	2.423
<i>F</i> (000)	1156	1280	1470	2864
2 $\theta$ (max), deg	50.70	50.70	50.70	50.70
Flack value				0.15(4)
total reflns collected	18754	14870	17674	20790
unique reflns	6958	7941	9093	7400
<i>R</i> <sub>int</sub>	0.0599	0.0464	0.0592	0.0860
no. params	461	524	578	469
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0430	0.0318	0.0425	0.0406
<i>wR</i> <sub>2</sub> (all data)	0.1025	0.0671	0.1171	0.1269
GOF on <i>F</i> <sup>2</sup>	1.110	0.985	1.013	1.118

## EXPERIMENTAL SECTION

**Materials and Methods.** All starting chemicals were of analytical grade and were used as received. Elemental analyses were conducted using an EA1110-CHNS-O elemental analyzer. Fourier transform infrared (FT-IR) spectra were recorded using a Nicolet Magna-IR 550 spectrometer on dry KBr discs over the 4000–400 cm<sup>-1</sup> range. Room-temperature optical diffuse reflectance spectra of powder samples were obtained using a Shimadzu UV-3150 spectrometer. Absorption ( $\alpha/S$ ) data were calculated from the reflectance using the Kubelka–Munk function  $\alpha/S = (1-R)^2/2R$ .<sup>31</sup>

**Syntheses.** All compounds were synthesized under methanolothermal conditions. In a typical synthetic procedure, reactants in the desired molar ratio were dispersed in CH<sub>3</sub>OH by stirring, and the dispersion was loaded into a polytetrafluoroethylene (PTFE) lined stainless steel autoclave with a volume of 15 mL. The sealed autoclave was heated to 130 °C for 5 days. After cooling to ambient temperature, the crystals were filtered off, washed with ethanol, and stored under vacuum conditions.

[*Fe*(phen)<sub>3</sub>][As<sub>2</sub>Se<sub>6</sub>] (**1**). Dark-red block crystals of **1** were prepared by the reaction of FeCl<sub>2</sub>·4H<sub>2</sub>O (60 mg, 0.3 mmol), phen (162 mg, 0.9 mmol), As<sub>2</sub>O<sub>3</sub> (59 mg, 0.3 mmol), Se (190 mg, 2.4 mmol), and dien (206 mg, 2 mmol) in 6 mL of CH<sub>3</sub>OH, in 65% yield based on As<sub>2</sub>O<sub>3</sub>. Elemental analysis calcd for C<sub>36</sub>H<sub>24</sub>N<sub>6</sub>FeAs<sub>2</sub>Se<sub>6</sub>: C, 35.44; H, 1.98; N, 6.89. Found: C, 35.28; H, 1.85; N, 6.72. IR (KBr, cm<sup>-1</sup>): 3736 (w), 3564 (w), 3049 (w), 2914 (w), 1666 (s), 1619 (m), 1580 (w), 1522 (s), 1490 (w), 1419 (s), 1381 (m), 1341 (w), 1219 (w), 1139 (w), 1096 (m), 1057 (w), 867 (w), 845 (s), 772 (m), 724 (s), 639 (m), 534 (w), 427 (w).

[*Zn*(phen)(dien)][As<sub>2</sub>Se<sub>6</sub>]·2phen (**2**). Orange prism crystals of **2** were prepared by the reaction of ZnCl<sub>2</sub> (41 mg, 0.3 mmol), phen (162 mg, 0.9 mmol), As<sub>2</sub>O<sub>3</sub> (59 mg, 0.3 mmol), Se (190 mg, 2.4 mmol),

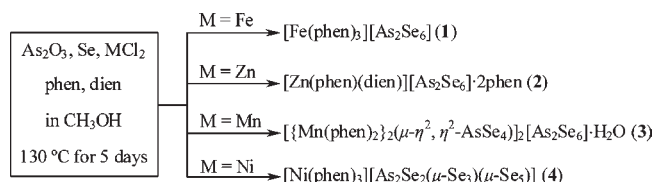
and dien (206 mg, 2 mmol) in 6 mL of CH<sub>3</sub>OH, in 67% yield based on As<sub>2</sub>O<sub>3</sub>. Elemental analysis calcd for C<sub>40</sub>H<sub>37</sub>N<sub>9</sub>ZnAs<sub>2</sub>Se<sub>6</sub>: C, 36.05; H, 2.80; N, 9.46. Found: C, 35.87; H, 2.66; N, 9.31. IR (KBr, cm<sup>-1</sup>): 3736 (w), 3448 (br), 3276 (br), 3184 (br), 2914 (w), 2870 (w), 2362 (s), 2074 (w), 1638 (s), 1568 (s), 1479 (m), 1452 (s), 1387 (w), 1136 (m), 1089 (s), 1011 (s), 974 (s), 886 (w), 672 (s), 639 (s), 528 (s), 454 (s).

[{*Mn*(phen)<sub>2</sub>}<sub>2</sub>( $\mu$ - $\eta^2$ , $\eta^2$ -AsSe<sub>4</sub>)<sub>2</sub>][As<sub>2</sub>Se<sub>6</sub>]·H<sub>2</sub>O (**3**). Black block crystals of **3** were prepared by the reaction of MnCl<sub>2</sub>·4H<sub>2</sub>O (59 mg, 0.3 mmol), phen (162 mg, 0.9 mmol), As<sub>2</sub>O<sub>3</sub> (59 mg, 0.3 mmol), Se (190 mg, 2.4 mmol), and dien (206 mg, 2 mmol) in 6 mL of CH<sub>3</sub>OH, in 49% yield based on As<sub>2</sub>O<sub>3</sub>. Elemental analysis calcd for C<sub>96</sub>H<sub>66</sub>N<sub>16</sub>OMn<sub>4</sub>As<sub>4</sub>Se<sub>14</sub>: C, 37.38; H, 2.16; N, 7.27. Found: C, 37.25; H, 2.02; N, 7.12. IR data (KBr, cm<sup>-1</sup>): 3699 (w), 3695 (w), 3472 (br), 3058 (w), 1595 (s), 1469 (m), 1433 (s), 1309 (s), 1243 (w), 1155 (w), 1102 (w), 1011 (s), 953 (m), 890 (w), 763 (s), 731 (w), 674 (w), 649 (w), 527 (w), 470 (w), 439 (m), 406 (s).

[*Ni*(phen)<sub>3</sub>][As<sub>2</sub>Se<sub>2</sub>( $\mu$ -Se<sub>3</sub>)( $\mu$ -Se<sub>3</sub>)] (**4**). Dark-red block crystals of **4** were prepared by the reaction of NiCl<sub>2</sub>·6H<sub>2</sub>O (71 mg, 0.3 mmol), phen (162 mg, 0.9 mmol), As<sub>2</sub>O<sub>3</sub> (59 mg, 0.3 mmol), Se (190 mg, 2.4 mmol), and dien (206 mg, 2 mmol) in 6 mL of CH<sub>3</sub>OH, in 67% yield based on As<sub>2</sub>O<sub>3</sub>. Elemental analysis calcd for C<sub>36</sub>H<sub>24</sub>N<sub>6</sub>NiAs<sub>2</sub>Se<sub>10</sub>: C, 28.10; H, 1.57; N, 5.46. Found: C, 27.95; H, 1.50; N, 5.32. IR data (KBr, cm<sup>-1</sup>): 3741 (w), 3035 (w), 1621 (w), 1597 (w), 1510 (s), 1419 (s), 1336 (w), 1305 (w), 1217 (w), 1144 (w), 1095 (w), 989 (w), 848 (s), 779 (w), 720 (w), 639 (m), 501 (w), 423 (w).

**X-Ray Crystal Structure Determination.** Data were collected on a Rigaku Mercury CCD diffractometer at 223(2) K using graphite monochromated Mo K $\alpha$  radiation with a  $\omega$ -scan method to a maximum 2 $\theta$  value of 50.70°. An absorption correction was applied for all compounds using multiscan. Structures were solved with direct methods using the program SHELXS-97,<sup>32</sup> and refinement was performed against

## Scheme 1. Solvothermal Syntheses of Compounds 1–4



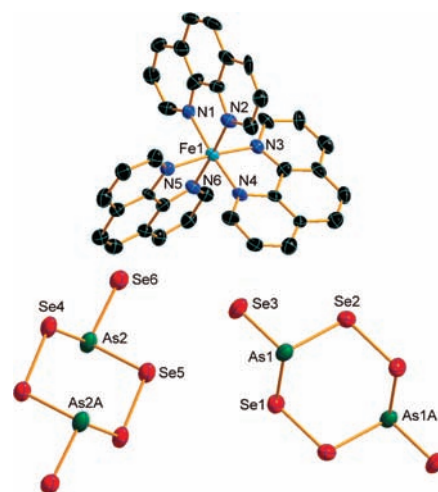
$F^2$  using SHELXL-97.<sup>33</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added geometrically and refined using the riding model. Technical details of data acquisition and selected refinement results are summarized in Table 1.

## RESULTS AND DISCUSSION

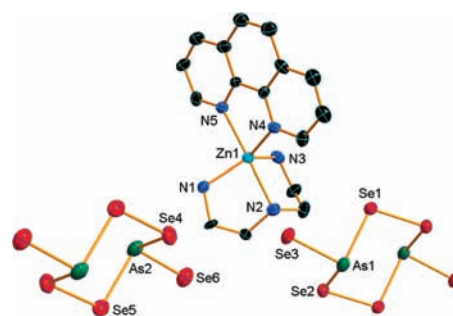
**Synthesis and Infrared Spectra.** TM-containing polyselenidoarsenate compounds 1–4 were prepared by reactions of  $\text{As}_2\text{O}_3$ , Se, dien, and phen in the presence of the TM with methanol as the solvent under solvothermal conditions (Scheme 1).  $\text{Fe}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Mn}^{2+}$  ions led to the formation of the polyselenide  $[\text{As}_2\text{Se}_6]^{2-}$  compounds (1–3), and these compounds contain different complex cation structures. Reaction with  $\text{Ni}^{2+}$  yielded the  $[\text{As}_2\text{Se}_2(\mu\text{-Se}_3)(\mu\text{-Se}_5)]^{2-}$  infinite polyselenide chain in 4, which is isostructural to the previously reported Co analogue  $[\text{Co}(\text{phen})_3][\text{As}_2\text{Se}_2(\mu\text{-Se}_3)(\mu\text{-Se}_5)]$ .<sup>30</sup> The TM ions are coordinated by three phen ligands, forming  $[\text{TM}(\text{phen})_3]^{2+}$  complex counter cations to the polyselenide anions, with the exception of complexes containing  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ . In 2 and 3, the  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$  ions bind with dien and  $\text{AsSe}_4$  ligands, respectively, in addition to phen, giving the mixed  $[\text{Zn}(\text{phen})(\text{dien})]^{2+}$  and  $[\{\text{Mn}(\text{phen})_2\}_2(\mu\text{-AsSe}_4)]^+$  complexes, respectively. To verify the influence of dien on the synthesis, excess dien was used in synthesis for the other TM compounds, but no TM–phen–dien mixed complexes could be obtained for  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Ni}^{2+}$ . For  $\text{Ni}^{2+}$ , an increase of dien concentration to 5 mmol resulted in a small amount of purple compound being formed, in addition to the title compound, which was found to be  $[\text{Ni}(\text{dien})_2]\text{Cl}_2$  by elemental analysis. Similarly, excess  $\text{As}_2\text{O}_3$  and Se starting materials did not yield any TM–phen– $\text{AsSe}_4$  mixed complexes, except for that using  $\text{Mn}^{2+}$ .

In the IR spectra of 1–4 (Figures S1–S4, Supporting Information), the relatively weak absorption bands at 3736–3035  $\text{cm}^{-1}$  are due to C–H vibrations of the aromatic ring hydrogen atoms. Strong and broad absorptions at 3448–3181  $\text{cm}^{-1}$  in 2 are assigned to N–H stretching modes of dien ligands. Broad absorption arises from the presence of hydrogen bonding, which is confirmed in the crystal structure determination below. Other characteristic absorption bands of phen are observed at 1666–1381  $\text{cm}^{-1}$ .

**Crystal Structures.** Compounds 1 and 2 crystallize in the triclinic crystal system and contain two formula units in the unit cell (Table 1). Compound 1 consists of  $[\text{As}_2\text{Se}_6]^{2-}$  and  $[\text{Fe}(\text{phen})_3]^{2+}$ , while 2 is composed of  $[\text{As}_2\text{Se}_6]^{2-}$ ,  $[\text{Zn}(\text{phen})(\text{dien})]^{2+}$ , and free phen molecules. There are two crystallographically distinct As(III) atoms in 1 and 2, and both As(1) and As(2) are coordinated by three Se atoms, yielding  $\text{AsSe}_3$  trigonal pyramids. Two As(1)Se<sub>3</sub> trigonal pyramids are linked through two Se–Se bonds, forming the bimeric anion  $[\text{As}(1)_2\text{Se}_6]^{2-}$ . The  $[\text{As}(2)_2\text{Se}_6]^{2-}$  anion is similarly formed from two As(2)Se<sub>3</sub> trigonal pyramids (Figures 1 and 2). Each  $[\text{As}_2\text{Se}_6]^{2-}$  anion



**Figure 1.** Crystal structure of 1, showing atom labels (thermal ellipsoids are shown at 50% probability). Hydrogen atoms are omitted for clarity.



**Figure 2.** Crystal structure of 2, showing atom labels (thermal ellipsoids are shown at 50% probability). Hydrogen atoms are omitted for clarity.

contains a six-membered  $\text{As}_2\text{Se}_4$  ring in the chair conformation with a centrosymmetric structure and has two sets of As–Se bond lengths. Terminal As–Se<sub>t</sub> bonds are shorter than bridging As–Se<sub>b</sub> bonds (Table 2). As–Se and Se–Se bond lengths of  $[\text{As}_2\text{Se}_6]^{2-}$  anions are similar to corresponding values observed in other compounds containing bimeric  $[\text{As}_2\text{Se}_6]^{2-}$  anions.<sup>34–37</sup> The  $\text{Fe}^{2+}$  ion in 1 is coordinated by six N atoms of three phen ligands in a slightly distorted octahedral geometry with facial N–Fe–N angles in the range of 82.6(4)–95.3(4)° and axial N–Fe–N angles in the range of 173.5(4)–176.7(4)° (Table 2). Interestingly, the  $\text{Zn}^{2+}$  ion in 2 is coordinated by two N atoms of one phen ligand and three N atoms of one dien ligand, yielding the novel mixed coordinated complex cation  $[\text{Zn}(\text{phen})(\text{dien})]^{2+}$ . The 5-fold coordinated  $\text{Zn}^{2+}$  ion is in a distorted trigonal bipyramidal environment. The axial and facial N–Zn–N angles are 177.04(12)° and 107.17(13)–128.01(13)°, respectively. The Fe–N [1.970(9)–1.984(9) Å] and Zn–N [2.038(3)–2.195(3) Å] bond lengths (Table 2) are similar to those in reported phen-containing iron(II) and zinc(II) complexes, respectively.<sup>38,39</sup>

In 1, the aromatic plane of the phen molecule containing N3 and N4 is parallel to that of the neighboring complex molecule containing N3 and N4. The interplane distance between the centroids of the two phen molecules is 3.288 Å, indicating a weak intermolecular  $\pi$ – $\pi$  stacking interaction (Figure S5, Supporting Information). The interplane distances are in the range of those



Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1, 2, and 4

	1 (M = Fe)	2 (M = Zn)	4 (M = Ni)
As–Se <sup>a</sup>	2.271(2), 2.285(3)	2.2712(7), 2.2844(7)	2.251(4), 2.251(4)
As–Se <sup>b</sup>	2.371(4)–2.542(4)	2.3508(7)–2.4306(8)	2.375(4)–2.487(4)
Se–Se	2.335(3), 2.350(2)	2.3508(7), 2.3509(7)	2.303(4)–2.342(5)
M–N	1.970(9)–1.984(9)	2.038(3)–2.195(3)	2.058(19)–2.14(2)
Se–As–Se	94.07(7)–99.93(7)	92.94(3)–101.26(3)	89.28(12)–109.53(14)
<i>cis</i> -N–M–N	82.6(4)–95.3(4)	77.96(13)–128.01(13)	79.0(7)–98.5(7)
<i>trans</i> -N–M–N	173.5(4)–176.7(4)	177.04(12)	167.0(6)–177.6(8)

<sup>a</sup> Terminal bond lengths. <sup>b</sup> Bridging bond lengths.

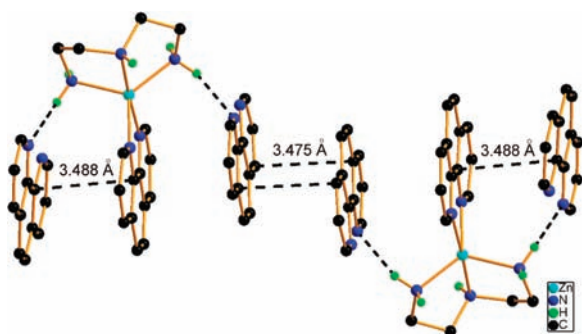


Figure 3. Sectional crystal packing in 2, showing  $\pi$ – $\pi$  stacking and N–H $\cdots$ N intermolecular interactions. Hydrogen atoms of C–H bonds are omitted for clarity.

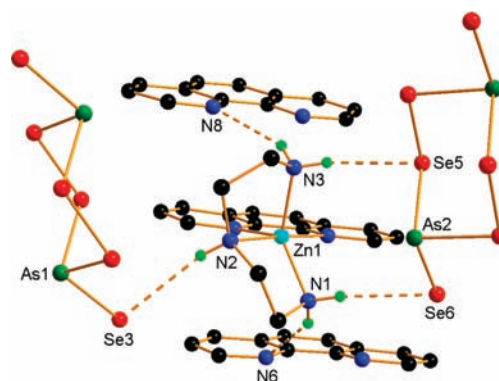


Figure 4. Sectional crystal packing in 2, showing N–H $\cdots$ Se and N–H $\cdots$ N intermolecular interactions. Hydrogen atoms of C–H bonds are omitted for clarity.

for phen complexes reported in the literature.<sup>40,41</sup> The three phen molecules in 2 (one ligand and two free) are parallel to each other (Figure 3). The coordinated phen ligand in  $[\text{Zn}(\text{phen})(\text{dien})]^{2+}$  is located between the two free phen molecules with interplane distances of 3.488 and 3.475 Å, indicating weak intermolecular  $\pi$ – $\pi$  stacking interactions (Figure 3). The  $\text{NH}_2$  and  $\text{NH}$  groups of dien in the  $[\text{Zn}(\text{phen})(\text{dien})]^{2+}$  ion interact with  $[\text{As}_2\text{Se}_6]^{2-}$  anions, with N $\cdots$ Se distances between 3.525(4) and 3.767(4) Å, indicating N–H $\cdots$ Se hydrogen bonding interactions (Table S5, Supporting Information). The  $\text{NH}_2$  groups interact with the two free phen molecules via N–H $\cdots$ N hydrogen bonds, with N $\cdots$ N distances of 3.007(5) and 3.218(5) Å (Figure 4). From the N–H $\cdots$ N and  $\pi$ – $\pi$  stacking interactions, the  $[\text{Zn}(\text{phen})(\text{dien})]^{2+}$  and phen moieties are arranged into a column structure (Figure 3), while the  $[\text{As}_2\text{Se}_6]^{2-}$  anions are distributed in an array via N–H $\cdots$ Se hydrogen bonds (Figure 4; Figure S7, Supporting Information).

Compound 3 consists of an  $[\text{As}_2\text{Se}_6]^{2-}$  anion, two  $[\{\text{Mn}(\text{phen})_2\}_2(\mu\text{-}\eta^2, \eta^2\text{-AsSe}_4)]^+$  counter cations, and a water molecule. The  $[\text{As}_2\text{Se}_6]^{2-}$  anion is isostructural to anions in 1 and 2 (Tables 2 and 3). The crystal structure of the  $[\{\text{Mn}(\text{phen})_2\}_2(\mu\text{-}\eta^2, \eta^2\text{-AsSe}_4)]^+$  ion is shown in Figure 5. Each  $\text{Mn}^{2+}$  ion is coordinated by two phen ligands, forming an unsaturated  $[\text{Mn}(\text{phen})_2]^{2+}$  unit. The  $\text{AsSe}_4^{3-}$  anion links two  $[\text{Mn}(\text{phen})_2]^{2+}$  cations into the binuclear complex as a tetradentate  $\mu\text{-}\eta^2, \eta^2\text{-AsSe}_4$  bridging ligand, completing the six-coordinate environment around the  $\text{Mn}^{2+}$  ion. The highly distorted octahedral geometry of  $\text{Mn}^{2+}$  is formed by four N and two Se atoms. The axial and facial N–Mn–N angles are 158.4(3)–167.86(18) $^\circ$  and 72.4(2)–103.47(18) $^\circ$ , respectively (Table 3). The chelating coordination to the  $\text{Mn}^{2+}$  ion also causes distortion in the

$\text{AsSe}_4^{3-}$  tetrahedron. The Se–As–Se angles of  $\text{AsSe}_4^{3-}$  vary in the range 104.76(5)–112.66(5) $^\circ$  (Table 3).

The selenidoarsenate(III) units  $\text{As}_2\text{Se}_4$ ,  $\text{As}_2\text{Se}_5$ ,  $\text{As}_2\text{Se}_6$ , and  $\text{As}_4\text{Se}_7$  have been observed to coordinate to  $\text{Mn}^{2+}$  in the reported complexes  $[\{\text{Mn}(\text{tren})\}(\text{As}_2\text{Se}_4)]$ ,<sup>16</sup>  $[\{\text{Mn}(\text{tren})\}_2(\mu\text{-As}_2\text{Se}_5)]$ ,<sup>17</sup>  $[\{\text{Mn}(\text{tren})\}_2(\mu\text{-As}_2\text{Se}_6)]$ ,<sup>17</sup>  $[\{\text{Mn}(\text{tren})\}(\text{As}_4\text{Se}_7)]$  (tren = tris(2-aminoethyl)amine),<sup>16</sup> and  $[\{\text{Mn}(\text{cyclam})\}_2(\mu\text{-As}_2\text{Se}_6)]$  (cyclam = 1,4,8,11-tetraazacyclotetradecane).<sup>19</sup> The first chelating ligand for a selenidoarsenate(V)  $\text{AsSe}_4$  unit was observed in  $\text{Cs}[\{\text{Mn}(\text{tren})\}\text{AsSe}_4]$ .<sup>42</sup> The  $[\{\text{Mn}(\text{phen})_2\}_2(\mu\text{-}\eta^2, \eta^2\text{-AsSe}_4)]^+$  cation in 3 is the first example to contain a bridging  $\mu\text{-}\eta^2, \eta^2\text{-AsSe}_4$  ligand between two TM atoms. The presence of the  $\text{AsSe}_4$  unit results in 3 being the only reported example of a mixed-valent selenidoarsenate(III,V) containing coexisting  $\text{As}^{\text{III}}\text{Se}_3$  trigonal pyramidal and  $\text{As}^{\text{V}}\text{Se}_4$  tetrahedral units. Interestingly, the first mixed-valent selenidoarsenate(II,IV) was observed in  $[\text{AsSe}_2(\text{AsSe}_3)]^{4-}$  of  $\text{K}_5\text{Ag}_2\text{As}_3\text{Se}_9$ , which also contains trigonal pyramidal and tetrahedral units, albeit with a central As–As bond.<sup>6</sup>

Compound 4 is isostructural to the reported cobalt analogue  $[\text{Co}(\text{phen})_3][\text{As}_2\text{Se}_2(\mu\text{-Se}_3)(\mu\text{-Se}_5)]$ .<sup>30</sup> It consists of the  $[\text{Ni}(\text{phen})_3]^{2+}$  complex cation and  $[\text{As}_2\text{Se}_2(\mu\text{-Se}_3)(\mu\text{-Se}_5)]^{2-}$  polymeric anion. There are two crystallographically distinct  $\text{Ni}^{2+}$  ions. Both  $\text{Ni}^{2+}$  ions are coordinated by three bidentate phen ligands at distances in the range 2.058(19)–2.14(2) Å in a distorted octahedral geometry with facial N–Ni–N angles in the range 79.0(7)–98.5(7) $^\circ$  and axial N–Ni–N angles in the range 167.0(6)–177.6(8)1 $^\circ$  (Table 2). The bond lengths and angles are consistent with those of reported nickel complexes containing phen ligands.<sup>43</sup> The  $[\text{As}_2\text{Se}_2(\mu\text{-Se}_3)(\mu\text{-Se}_5)]^{2-}$  ion

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 3

As–Se <sup>a</sup>	2.3040(14)–2.3349(14)	As–Se <sub>t</sub> <sup>b</sup>	2.2801(15)
As–Se <sub>b</sub> <sup>b</sup>	2.4131(15), 2.4388(16)	Se–Se	2.3474(14)
Mn–Se	2.6620(18)–2.7323(17)	Mn–N	2.257(7)–2.311(7)
Se–As–Se <sup>a</sup>	104.76(5)–112.66(5)	Se–As–Se <sup>b</sup>	93.64(5)–102.64(5)
cis-N–Mn–N (Se)	72.4(2)–103.47(18)	trans-N–Mn–N (Se)	158.4(3)–167.86(18)

<sup>a</sup> Bond lengths and angles for the AsSe<sub>4</sub> unit. <sup>b</sup> Bond lengths and angles for the As<sub>2</sub>Se<sub>6</sub> unit.

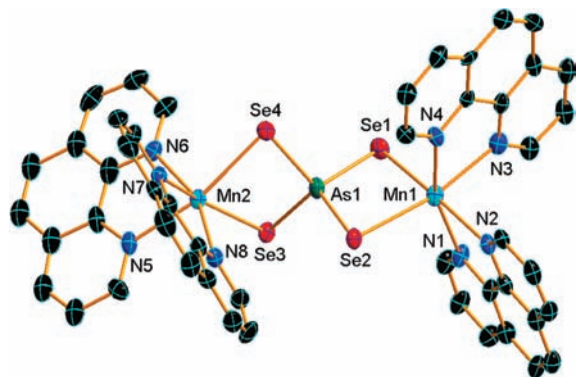


Figure 5. Crystal structure of the  $[\{\text{Mn}(\text{phen})_2\}_2(\mu\text{-}\eta^2,\eta^2\text{-AsSe}_4)]^+$  ion in 3 showing atom labels (thermal ellipsoids are shown at 50% probability). Hydrogen atoms are omitted for clarity.

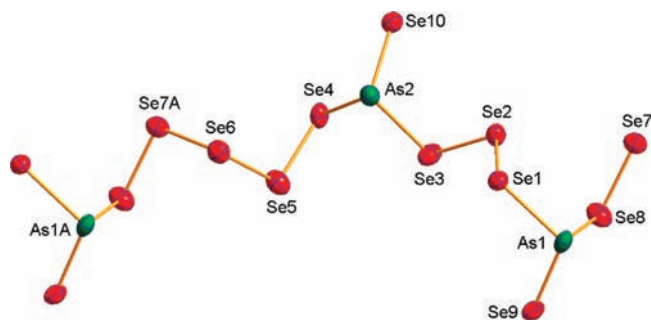


Figure 6. Crystal structure of the  $[\text{As}_2\text{Se}_2(\mu\text{-Se}_3)(\mu\text{-Se}_5)^{2-}]_\infty$  chain in 4 showing atom labels (thermal ellipsoids are shown at 50% probability).

chain contains two crystallographically distinct As(III) centers, and each is coordinated by a terminal Se<sup>2-</sup> to give AsSe<sup>+</sup> units. The AsSe<sup>+</sup> units are joined together by  $\mu\text{-Se}_3^{2-}$  and  $\mu\text{-Se}_5^{2-}$  bridging ligands, yielding the one-dimensional (1-D)  $[\text{As}_2\text{Se}_2(\mu\text{-Se}_3)(\mu\text{-Se}_5)^{2-}]_\infty$  chain, in which  $\mu\text{-Se}_3^{2-}$  and  $\mu\text{-Se}_5^{2-}$  units occur alternatively. Thus, the chain is based on repeating  $[\text{AsSe}-\text{Se}_5-\text{AsSe}-\text{Se}_3-\text{AsSe}]_\infty$  units (Figure 6). The only other reported  $[\text{As}_2\text{Se}_2(\mu\text{-Se}_3)(\mu\text{-Se}_5)^{2-}]_\infty$  chain is observed in  $[\text{Co}(\text{phen})_3][\text{As}_2\text{Se}_2(\mu\text{-Se}_3)(\mu\text{-Se}_5)]$ .<sup>30</sup> Each As atom is surrounded by three Se atoms to form the AsSe<sub>3</sub> trigonal pyramid with As–Se bond lengths and Se–As–Se angles in the ranges 2.251(4)–2.487(4) Å and 89.28(12)–109.53(14)°, respectively (Table 2). The Se–Se bond lengths (2.303(4)–2.342(5) Å) compare favorably with those found in other polyselenides, e.g.,  $\text{RbAsSe}_3 \cdot 0.5\text{H}_2\text{O}$  and  $\text{CsAsSe}_3 \cdot 0.5\text{H}_2\text{O}$  [Se–Se: 2.347(1), 2.349(1) Å],<sup>44</sup>  $\text{KPdCu}(\text{Se}_2)(\text{Se}_3)$  [Se–Se: 2.338(2), 2.390(1) Å],<sup>45</sup> and  $[\text{V}_2(\text{Se}_2)_2(\mu\text{-Se}_2)_2(\mu\text{-Se}_5)]^{2-}$  [Se–Se: 2.339(3)–2.453(3) Å].<sup>46</sup>

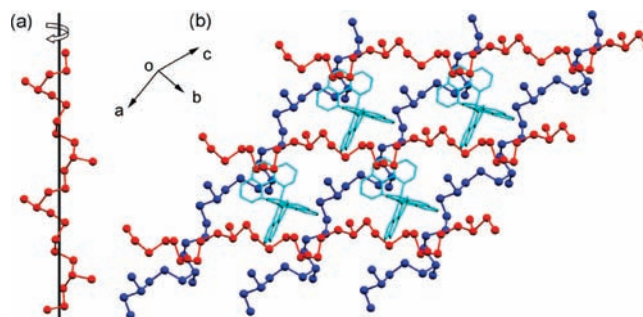


Figure 7. (a) The right-handed  $[\text{As}_2\text{Se}_2(\mu\text{-Se}_3)(\mu\text{-Se}_5)^{2-}]_\infty$  helix in 4. (b) Perspective view of the cross-stacking of helices A (red) and B (blue) in 4.

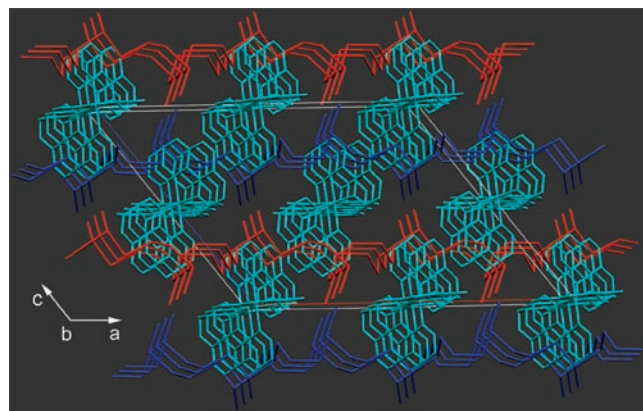
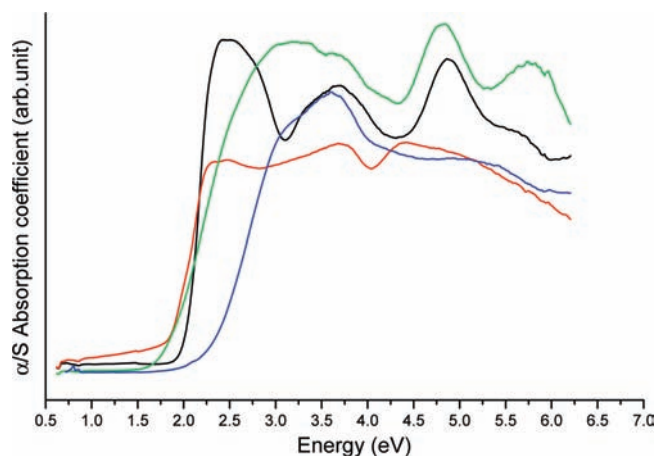


Figure 8. Crystal packing of 4 viewed down the crystallographic *b* axis, showing layers A (red) and B (blue) formed by helices A and B, respectively.

The striking feature of 4 is the existence of the 1-D helical  $[\text{As}_2\text{Se}_2(\mu\text{-Se}_3)(\mu\text{-Se}_5)^{2-}]_\infty$  chain and its unique stacking. The  $[\text{As}_2\text{Se}_2(\mu\text{-Se}_3)(\mu\text{-Se}_5)^{2-}]_\infty$  chain exhibits a right-handed screw axis (Figure 7a). There are two different directional helical chains in the crystal lattice, hereafter referred to as helices A and B, which cross at an angle of 52.7°. Helices A run parallel to each other to form a layer (referred to as layer A). Layer B is similarly formed by helices B (Figure 7b). Both layers A and B propagate parallel to the (001) lattice plane. They alternately stack in a crossed manner creating pseudoparallelogram channels with a size of ca. 7.7 Å × 12.6 Å to accommodate the  $[\text{Ni}(\text{phen})_3]^{2+}$  cations (Figures 7b and 8). The two independent  $[\text{Ni}(\text{phen})_3]^{2+}$  cations exhibit crystallographic C<sub>2</sub> symmetry and display  $\delta$  and  $\lambda$  configurations, respectively. They are similar with those of octahedral complex cations in  $[\text{Co}(\text{phen})_3]_2[\text{SiMo}_8\text{Mo}_4\text{V}_2\text{O}_{42}]$  and  $[\text{Co}(\text{en})_3]\text{CoSb}_4\text{S}_8$ .<sup>15,47</sup> Thus, there is a racemic mixture of



**Figure 9.** Solid state optical absorption spectra of **1** (red), **2** (blue), **3** (green), and **4** (black).

$[\text{Ni}(\text{phen})_3]^{2+}$  cations in the crystal. The helical  $[\text{As}_2\text{Se}_2(\mu\text{-Se}_3)(\mu\text{-Se}_5)^{2-}]_\infty$  chain leads to compound **4** having a chiral space group.

**Optical Properties.** The UV–vis reflectance spectroscopic measurements of the four compounds were recorded from powder samples at room temperature. Absorption data from the reflectance spectroscopy via the Kubelka–Munk function<sup>31</sup> demonstrates that compounds **1**, **2**, **3**, and **4** exhibit steep absorption edges with corresponding band gaps of 1.88, 2.29, 1.82, and 2.01 eV, respectively (Figure 9). This indicates that these compounds exhibit semiconducting properties, and band gaps are in accordance with the compounds color. This intense absorption likely results from charge-transfer transitions from the selenium-dominated filled valence band to the transition metal dominated empty conduction band.<sup>48,49</sup>

## CONCLUSIONS

In summary, the  $\text{As}_2\text{O}_3/\text{Se}/\text{dien}$  system has been investigated in a methanol solvent in the presence of  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$  with phen as a template, and four polyselenidoarsenates were prepared. The  $\text{Fe}^{2+}$  and  $\text{Ni}^{2+}$  ions form octahedral complexes of  $[\text{TM}(\text{phen})_3]^{2+}$  and lead to the bimeric polyselenidoarsenate anion  $[\text{As}_2\text{Se}_6]^{2-}$  and polymeric polyselenidoarsenate anion  $[\text{As}_2\text{Se}_2(\mu\text{-Se}_3)(\mu\text{-Se}_5)^{2-}]_\infty$ , respectively. The  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$  ions form  $[\text{Zn}(\text{phen})(\text{dien})]^{2+}$  and  $[\{\text{Mn}(\text{phen})_2\}_2(\mu\text{-AsSe}_4)]^+$  mixed complexes under the same conditions, respectively. The novel binuclear  $[\{\text{Mn}(\text{phen})_2\}_2(\mu\text{-AsSe}_4)]^+$  complex is the first reported mixed-valent polyselenidoarsenate(III,V) compound.

## ASSOCIATED CONTENT

**Supporting Information.** Crystallographic data of compounds **1–4** in CIF format, selected bond lengths and angles for **1–4** (Tables S1–S5), IR spectra (Figures S1–S4), and structural figures (Figures S5–S8). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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