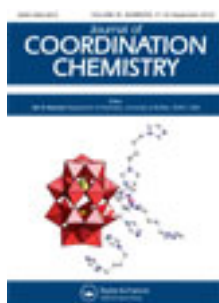


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Solvent effect on condensation of pyramidal $[\text{AsSe}_3]^{3-}$: solvothermal syntheses of new selenidoarsenates containing transition metal(II) complexes with 1,10-phenanthroline

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Solvent effect on condensation of pyramidal $[\text{AsSe}_3]^{3-}$: solvothermal syntheses of new selenidoarsenates containing transition metal(II) complexes with 1,10-phenanthroline

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The reactions As_2O_3 , Se and 1,10-phenanthroline (phen) with NiCl_2 and ZnCl_2 in water at 140°C for 5 days afforded selenidoarsenates $[\text{Ni}(\text{phen})_3]_2[\text{As}_8\text{Se}_{14}]$ (**1**) and $[\text{Zn}(\text{phen})_3]_2[\text{As}_8\text{Se}_{14}]$ (**2**), respectively. The reactions with CoCl_2 and NiCl_2 in CH_3OH aqueous solution produced polyselenidoarsenates $[\text{Co}(\text{phen})_3][\text{As}_2\text{Se}_6]$ (**3**) and $[\text{Ni}(\text{phen})_3][\text{As}_2\text{Se}_6]$ (**4**). All transition metal ions are octahedrally coordinated by six nitrogen atoms and all arsenics are trigonal pyramidally coordinated by three seleniums. In **1** and **2**, eight $[\text{AsSe}_3]^{3-}$ trigonal pyramids joined *via* edge-sharing to form $[\text{As}_8\text{Se}_{14}]^{4-}$ with condensation grade of 0.571. $[\text{As}_8\text{Se}_{14}]^{4-}$ contains two As_3Se_3 and one As_6Se_6 heterocycles. The formations of the selenidoarsenate anion $[\text{As}_8\text{Se}_{14}]^{4-}$ in **1** and **2** and polyselenidoarsenate $[\text{As}_2\text{Se}_6]^{2-}$ in **3** and **4** show solvent effect on condensation of trigonal bipyramidal $[\text{AsSe}_3]^{3-}$ units under solvothermal conditions.

Keywords: Selenidoarsenates; Solvothermal synthesis; X-ray structure determination; Solvent effect; Condensation grade

1. Introduction

Chalcogenidoarsenates have received interest due to their condensation of trigonal bipyramidal $[\text{AsE}_3]^{3-}$ ($\text{E} = \text{S}, \text{Se}$) units and potential applications in optical, electrical and ion exchange materials [1–5]. Hydro- or solvothermal synthesis from 100 – 200°C and extraction technique at room temperature have proven to be useful for access to chalcogenidoarsenate [6–9]. Condensation of trigonal bipyramidal $[\text{AsE}_3]^{3-}$ ($\text{E} = \text{S}, \text{Se}$) units in the presence of organic cations or alkali (and alkaline earth) metal cations leads to a set of binary chalcogenidoarsenate $[\text{As}_x\text{E}_y]^{n-}$ anions, exemplified by $[\text{As}_2\text{E}_4]^{2-}$ [10–12], $[\text{As}_3\text{E}_6]^{3-}$ [13, 14], $[\text{As}_4\text{S}_7]^{2-}$ [15], $[\text{As}_6\text{S}_{10}]^{2-}$ [15, 16], and $[\text{As}_8\text{S}_{13}]^{2-}$ [16–18]. Since the first ternary cobalt chalcogenometalates $[\text{Co}(\text{en})_3]\text{CoSb}_4\text{S}_8$ were prepared in ethylenediamine (en) in 1996 [19], a number of chalcogenidoarsenates combined with transition-metal (TM) complex cations have been synthesized under aminothermal

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conditions in aliphatic ethylene polyamine solvents. The coordinative ethylene polyamines coordinate to TM^{n+} to form complex cations $[\text{TM}(\text{polyamine})_m]^{n+}$, which combined with chalcogenidoarsenates to form TM-containing chalcogenidoarsenates, such as $[\text{Mn}(\text{en})_3]_2[\text{Mn}(\text{en})_2\text{AsS}_4][\text{As}_3\text{S}_6]$ [2], $[\text{TM}(\text{en})_3]_2\text{As}_2\text{Se}_5$ (TM = Mn, Co) [20, 21], $[\text{Fe}(\text{en})_3]\text{As}_2\text{Se}_6$ and $[\text{Mn}(\text{en})_3]\text{As}_2\text{Se}_6$, $[\text{Mn}(\text{dien})_2]_3[\text{As}_3\text{Se}_6]_2$ [22], $[\text{TM}(\text{dien})_2]\text{As}_2\text{Se}_6$ (dien = diethylenetriamine) (TM = Co, Ni), and $[\text{Mn}(\text{dap})_3]\text{As}_2\text{Se}_6$ (dap = 1,2-diaminopropane) [23]. Recently, selenidoarsenates $\mu\text{-As}_2\text{Se}_4$, $\mu\text{-As}_2\text{Se}_5$, $\mu\text{-As}_4\text{Se}_7$, and $\mu\text{-As}_4\text{Se}_8$ were obtained in manganese complexes with the tridentate terpy (terpy = 2,2';6',2''-terpyridine) or tetradentate tren as the coligands [24–26]. Polyselenidoarsenates to Mn(II) are also obtained in $[\{\text{Mn}(\text{terpy})\}_3(\mu\text{-AsSe}_2(\text{Se}_2))_2]$ and $[\{\text{Mn}(\text{cyclam})\}_2(\mu\text{-As}_2\text{Se}_6)]$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) [27].

Very recently, rigid aromatic chelating ligands 2,2'-bipy and phen were used instead of the traditional aliphatic chelating amines as structure directing agents, and several chalcogenidoarsenates(III) have been prepared under hydrothermal conditions. Examples included thioarsenates(III) $[\text{Mn}_2(2,2'\text{-bipy})\text{As}_2\text{S}_5]$ [28], $[\text{Fe}(\text{phen})_3][\text{As}_3\text{S}_6] \cdot \text{dien} \cdot 7\text{H}_2\text{O}$, $[\text{Mn}_2(\text{phen})_4(\text{As}_2\text{S}_5)] \cdot \text{phen} \cdot 2\text{H}_2\text{O}$ [29], $[\text{Mn}_2(\text{phen})(\text{As}_2\text{S}_5)]_n$ [30] and $[\text{Mn}(\text{phen})_2(\text{As}_2\text{S}_4)]_n$ [31], mixed-valent thioarsenates(III, V) $[\{\text{Mn}(2,2'\text{-bipy})_2]_2(\text{As}^{\text{V}}\text{S}_4)[\text{As}^{\text{III}}\text{S}(\text{S}_5)]$ [31], and $[\{\text{Mn}(\text{phen})\}_3(\text{As}^{\text{V}}\text{S}_4)(\text{As}^{\text{III}}\text{S}_3)]_n \cdot n\text{H}_2\text{O}$ [32], and selenidoarsenate(III) $[\text{Mn}(\text{phen})_2]_n[\text{As}_2\text{Se}_3(\text{Se}_2)]_n$ [33]. In our previous work, polyselenidoarsenates(III) $[\text{TM}(\text{phen})_3][\text{As}_2\text{Se}_2(\mu\text{-Se}_3)(\mu\text{-Se}_5)]$ (TM = Co, Ni), $[\text{Fe}(\text{phen})_3][\text{As}_2\text{Se}_6]$, and mixed-valent thioarsenates(III, V) $[\{\text{Mn}(\text{phen})_2\}_2(\mu\text{-}\eta^2\text{-As}^{\text{V}}\text{Se}_4)_2[\text{As}_2^{\text{III}}\text{Se}_6] \cdot \text{H}_2\text{O}$ [34, 35] were prepared by reactions of TMCl_2 , As_2O_3 , Se, and phen under methanol-thermal conditions. Now, the TM/As/Se/phen system is investigated in water and CH_3OH aqueous solution, and selenidoarsenates(III) $[\text{TM}(\text{phen})_3]_2[\text{As}_8\text{Se}_{14}]$ (TM = Ni (1), Zn (2)) and polyselenidoarsenates(III) $[\text{TM}(\text{phen})_3][\text{As}_2\text{Se}_6]$ (TM = Co (3), Ni (4)) were synthesized and characterized.

2. Experimental

2.1. Materials and physical measurements

All chemicals are analytical grade and used without purification. Elemental analysis was conducted on a MOD 1106 elemental analyzer. Room temperature optical diffuse reflectance spectra of the powdered samples were obtained with a Shimadzu UV-3150 spectrometer. The absorption (α/S) data were calculated from reflectance using the Kubelka-Munk function $\alpha/S = (1-R)^2/2R$ [36], where R is the reflectance at a given angle, α is the absorption, and S is the scattering coefficient.

2.2. Synthesis of the complexes

2.2.1. Synthesis of $[\text{Ni}(\text{phen})_3]_2[\text{As}_8\text{Se}_{14}]$ (1). $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (71 mg, 0.3 mmol), phen (162 mg, 0.9 mmol), As_2O_3 (59 mg, 0.3 mmol), Se (190 mg, 2.4 mmol), and diethylenetriamine (dien) (186 mg, 1.81 mmol) were dispersed in 6 mL of H_2O , and then the dispersion was loaded into a Teflon-lined stainless steel autoclave with an inner volume of 15 mL. The sealed autoclave was heated under autogenous pressure at

140°C for 5 days. Upon cooling to ambient temperature, dark-red block crystals of **1** were obtained with *ca* 59% yield (based on As₂O₃). The compound is stable in dried air and in C₂H₅OH and dimethyl ether. Anal. Calcd for C₇₂H₄₈N₁₂Ni₂As₈Se₁₄ (%): C, 29.79; H, 1.67; N, 5.79. Found (%): C, 29.65; H, 1.53, N, 5.66.

2.2.2. Synthesis of [Zn(phen)₃]₂[As₈Se₁₄] (2). Yellow block crystals of **2** were prepared with a procedure similar to that for synthesis of **1**, except that ZnCl₂ was used instead of NiCl₂ · 6H₂O (54% yield based on As₂O₃). **2** is stable in dried air and in C₂H₅OH and dimethyl ether. Anal. Calcd for C₇₂H₄₈N₁₂Zn₂As₈Se₁₄ (%): C, 29.65; H, 1.66; N, 5.76. Found (%): C, 29.49; H, 1.54; N, 5.61.

2.2.3. Synthesis of [Co(phen)₃][As₂Se₆] (3). CoCl₂ · 6H₂O (71 mg, 0.3 mmol), phen (162 mg, 0.9 mmol), As₂O₃ (59 mg, 0.3 mmol), Se (190 mg, 2.4 mmol), and dien (198 mg, 1.9 mmol) were dispersed in 6 mL of 45% CH₃OH aqueous solution, and then the dispersion was loaded into a Teflon-lined stainless steel autoclave with an inner volume of 15 mL. The sealed autoclave was heated under autogenous pressure at 140°C for 5 days. Upon cooling to ambient temperature, black block crystals of **3** were obtained with *ca* 51% yield (based on As₂O₃). **3** is stable in dried air and in C₂H₅OH and dimethyl ether. Anal. Calcd for C₃₆H₂₄N₆CoAs₂Se₆ (%): C, 35.36; H, 1.98; N, 6.87. Found (%): C, 35.22; H, 1.82, N, 6.73.

2.2.4. Synthesis of Ni(phen)₃[As₂Se₆] (4). Black block crystals of **4** were prepared with a procedure similar to that for synthesis of **3**, except that NiCl₂ · 6H₂O was used instead of CoCl₂ · 6H₂O (48% yield based on As₂O₃). Compound **4** is stable in dried air and in C₂H₅OH and dimethyl ether. Anal. Calcd for C₃₆H₂₄N₆NiAs₂Se₆ (%): C, 35.36; H, 1.98; N, 6.87. Found (%): C, 35.25; H, 1.88, N, 6.68.

2.3. X-ray structure determination

Intensity data were collected on a Rigaku Saturn CCD diffractometer for **1** and **4** and a Rigaku Mercury CCD diffractometer for **2** and **3** using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) with a ω -scan method to a maximum 2θ value of 50.00° for **1** and 50.70° for **2**, **3**, and **4**. An absorption correction was applied for all the compounds using multi-scan methods. The structures were solved with direct methods using SHELXS-97 [37] and refinement was performed against F^2 using SHELXL-97 [38]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters using a riding model. Technical details of data collections and refinement are summarized in table 1.

3. Results and discussion

3.1. Synthesis of the compounds

Products of solvothermal reactions of As₂O₃, Se, dien, and phen in the presence of TMCl₂ are influenced by the reaction solvents. Solvothermal reactions with NiCl₂ and

Table 1. Crystallographic data and structure refinement details for 1–4.

	1	2	3	4
Empirical formula	$C_{72}H_{48}Ni_{12}Ni_{12}As_{14}Se_{14}$	$C_{72}H_{48}Ni_{12}Zn_2As_8Se_{14}$	$C_{36}H_{24}Ni_6CoAs_2Se_6$	$C_{36}H_{24}Ni_6NiAs_2Se_6$
Formula weight	2903.44	2916.76	1223.14	1222.92
Wavelength (\AA)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P-1 (2)$	$P-1 (2)$	$P-1 (2)$	$P-1 (2)$
Unit cell dimensions (\AA , $^\circ$)				
a	10.3554(8)	10.3682(14)	13.1405(3)	13.0546(3)
b	12.7339(8)	12.7834(11)	13.3007(3)	13.1712(5)
c	17.4755(17)	17.524(3)	14.0142(2)	13.6412(4)
α	76.601(6)	76.444(12)	60.24(2)	117.048(9)
β	88.083(7)	87.986(15)	65.42(2)	99.380(10)
γ	66.684(5)	66.711(10)	74.20(2)	105.67(3)
Volume (\AA^3), Z	2054.2(3), 1	2069.6(5), 1	1926.9(5), 2	1896.6(7), 2
Calculated density (g cm^{-3})	2.347	2.340	2.108	2.142
Absorption coefficient (mm^{-1})	9.908	9.959	7.911	8.038
$F(000)$	1360	1364	1160	1160
Reflections collected	17,033	20,219	18,223	15,404
Independent reflections	7178 [$R(\text{int}) = 0.0642$]	7526 [$R(\text{int}) = 0.0847$]	7001 [$R(\text{int}) = 0.0696$]	6889 [$R(\text{int}) = 0.0474$]
Goodness-of-fit on F^2	0.913	1.094	0.987	1.095
Final R indices [$I > 2\sigma(I)$]	4798	5561	4974	5440
Parameters	164	245	249	242
R_1 [$I > 2\sigma(I)$]	0.0399	0.0519	0.0528	0.0436
wR_2 (all data)	0.0909	0.1356	0.1247	0.1138
Largest difference peak and hole ($e\text{\AA}^{-3}$)	1.741 and -1.045	1.473 and -1.869	2.021 and -1.218	2.382 and -1.717

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

	1		2		1		2	
As(1)–Se(1)	2.4827(12)	2.4274(16)	As(1)–Se(2)	2.4274(10)	2.2924(18)			
As(1)–Se(3)	2.2950(13)	2.4821(17)	As(2)–Se(2)	2.3938(11)	2.3875(15)			
As(2)–Se(4)	2.5059(10)	2.5105(15)	As(2)–Se(6)	2.4081(12)	2.4110(17)			
As(3)–Se(1)#1	2.3696(10)	2.3867(16)	As(3)–Se(4)	2.3893(11)	2.4320(18)			
As(3)–Se(5)	2.4363(12)	2.3718(15)	As(4)–Se(5)	2.4325(12)	2.4225(18)			
As(4)–Se(6)	2.4236(11)	2.4313(17)	As(4)–Se(7)	2.3004(13)	2.2958(18)			
TM(1)–N(1)	2.095(6)	2.078(8)	TM(1)–N(2)	2.099(5)	2.094(8)			
TM(1)–N(3)	2.093(6)	2.096(8)	TM(1)–N(4)	2.085(6)	2.096(9)			
TM(1)–N(5)	2.090(5)	2.079(8)	TM(1)–N(6)	2.084(6)	2.075(8)			
Se(1)–As(1)–Se(2)	98.70(4)	98.74(6)	Se(1)–As(1)–Se(3)	107.92(4)	98.90(6)			
Se(2)–As(1)–Se(3)	98.50(4)	107.75(6)	Se(2)–As(2)–Se(4)	86.51(4)	86.64(5)			
Se(2)–As(2)–Se(6)	105.25(4)	105.20(6)	Se(4)–As(2)–Se(6)	98.63(4)	98.65(6)			
Se(1)#1–As(3)–Se(4)	102.51(4)	101.63(6)	Se(1)#1–As(3)–Se(5)	95.13(4)	102.36(6)			
Se(4)–As(3)–Se(5)	101.63(4)	95.19(6)	Se(5)–As(4)–Se(6)	101.91(4)	101.91(6)			
Se(5)–As(4)–Se(7)	98.18(5)	99.65(7)	Se(6)–As(4)–Se(7)	99.68(5)	98.44(7)			
As(1)–Se(1)–As(3)#1	102.54(4)	93.28(5)	As(1)–Se(2)–As(2)	93.31(4)	102.63(6)			
As(2)–Se(4)–As(3)	87.03(4)	87.05(5)	As(3)–Se(5)–As(4)	98.27(4)	104.26(6)			
As(2)–Se(6)–As(4)	104.25(4)	98.47(6)						
N(1)–TM(1)–N(2)	79.5(2)	79.6(3)	N(1)–TM(1)–N(3)	93.2(2)	93.3(3)			
N(1)–TM(1)–N(4)	169.9(2)	169.7(3)	N(1)–TM(1)–N(5)	92.3(2)	94.8(3)			
N(1)–TM(1)–N(6)	93.5(2)	95.3(3)	N(2)–TM(1)–N(3)	93.0(2)	93.1(3)			
N(2)–TM(1)–N(4)	93.5(2)	93.3(3)	N(2)–TM(1)–N(5)	169.5(2)	170.8(3)			
N(2)–TM(1)–N(6)	94.1(2)	94.6(3)	N(3)–TM(1)–N(4)	79.8(2)	79.5(3)			
N(3)–TM(1)–N(5)	93.9(2)	94.4(3)	N(3)–TM(1)–N(6)	171.0(2)	169.4(3)			
N(4)–TM(1)–N(5)	95.4(2)	93.2(3)	N(4)–TM(1)–N(6)	94.2(2)	92.8(3)			
N(5)–TM(1)–N(6)	79.9(2)	78.6(3)						

Symmetry transformations used to generate equivalent atoms: For **1**: (#1) $-x+1, -y+1, -z+1$. For **2**: (#1) $-x+1, -y+1, -z$.

ZnCl₂ in water produced selenidoarsenates [Ni(phen)₃]₂[As₈Se₁₄] (**1**) and [Zn(phen)₃]₂[As₈Se₁₄] (**2**). Reactions with CoCl₂ and NiCl₂ in 45% CH₃OH aqueous solution afforded polyselenidoarsenates [Co(phen)₃]₂[As₂Se₆] (**3**) and [Ni(phen)₃]₂[As₂Se₆] (**4**). In our previous work, reactions with CoCl₂ and NiCl₂ in CH₃OH solvent gave [Co(phen)₃][As₂Se₂(μ-Se₃)(μ-Se₅)] and [Ni(phen)₃][As₂Se₂(μ-Se₃)(μ-Se₅)], which contain helical [As₂Se₂(μ-Se₃)(μ-Se₅)²⁻]_n chain [34, 35]. During solvothermal reactions, TM ions are coordinated by three phen, forming [TM(phen)₃]²⁺ cationic counter ions to the selenidoarsenate and polyselenidoarsenate anions, but reaction solvents exert influence on the selenidoarsenate anions.

3.2. Crystal structures

Compounds **1** and **2** are isostructural with a cobalt analog [Co(phen)₃]₂[As₈Se₁₄] [34]. The Ni²⁺ and Zn²⁺ ions are coordinated with three phen ligands, forming octahedral complex cations [TM(phen)₃]²⁺ (TM = Ni, Zn) with *trans* N–TM–N angles in the range of 169.5(2)–171.0(2)° for [Ni(phen)₃]²⁺ and 169.4(3)–170.8(3)° for [Zn(phen)₃]²⁺ (table 2). The Ni–N and Zn–N bond lengths are 2.084(6)–2.099(5) Å and 2.075(8)–2.096(9) Å, respectively, which match well with those reported [39, 40]. The discrete [As₈Se₁₄]⁴⁻ anion in **1** and **2** contains four crystallographically distinct As(III) centers, each coordinated by three Se²⁻ anions at 2.2924(18)–2.5105(15) Å in a pyramidal

geometry with Se–As–Se angles of 86.51(4)–107.92(4)° (table 2). Three AsSe₃ (As(2), As(3), and As(4)) trigonal pyramids are vertex-linked to form a cyclic As₃Se₅ unit (figure 1). The As₃Se₅ unit is corner-linked to As(1)Se₃ trigonal pyramid forming the asymmetric structural unit As₄Se₇. Two As₄Se₇ units are further coupled by sharing Se(1) and Se(1a) yielding the isolated [As₈Se₁₄]^{4−} (figure 1). The binding mode leads to formation of two As₃Se₃ and one As₆Se₆ heterocycles within the [As₈Se₁₄]^{4−} anion. With the exception of Se(3) and Se(7) which are terminal ligands, all Se join two As in the [As₈Se₁₄]^{4−} anion as μ -Se ligands. The terminal As–Se₁ bond lengths [2.2950(13) and 2.3004(13) Å in **1**, 2.2924(18) and 2.2958(18) Å in **2**] are shorter than those of bridging As–Se₆ bonds [2.3696(10)–2.5059(10) Å in **1**, 2.3718(15)–2.5105(15) Å in **2**] (table 2). Secondary As···Se interactions are observed in [As₈Se₁₄]^{4−}. As shown in figure 1, As(2) and As(3) in As₃Se₅ interact with Se(4) and Se(2) in the other As₃Se₅ unit with As···Se secondary bond lengths of 3.404 and 3.517 Å in **1** and 3.416 and 3.524 Å in **2**, shorter than the sum of the van der Waals radii of 4.0 Å for As and Se [25, 41]. Taking into account the secondary interaction, As(2) and As(3) form ψ -AsSe₄ trigonal bipyramids (figure 1).

In **1** and **2**, two [TM(phen)₃]²⁺ are coupled by face-to-face π ··· π stacking interactions between two parallel aromatic planes (containing N3 and N4 in **1**; N1 and N2 in **2**) of phen (figure 2a). The interplane distance between the centroids of the two phen ligands is 3.297 Å in **1** and 3.303 Å in **2**, in the range of those for phen complexes reported [42, 43]. The coupled [Ni(phen)₃]²⁺ are arranged into a parallel array along the *a*-axis (figure 2a). Each [As₈Se₁₄]^{4−} contacts two neighboring [As₈Se₁₄]^{4−} via As(1)···Se(2a) interactions with As···Se separation of 3.957 Å in **1** and 3.978 Å in **2** (figure 2b), indicating weaker secondary As···Se interactions than those within [As₈Se₁₄]^{4−}. The secondary As···Se interactions connect [As₈Se₁₄]^{4−} anions into a chain along the *a*-axis (figure 2b). This anionic chain locates between two arrays of [TM(phen)₃]²⁺ cations (figure 3).

Compounds **3** and **4** crystallize in the triclinic crystal system and contain two formula units in the unit cell (table 1). They consist of [TM(phen)₃]²⁺ (TM = Co, Ni) and

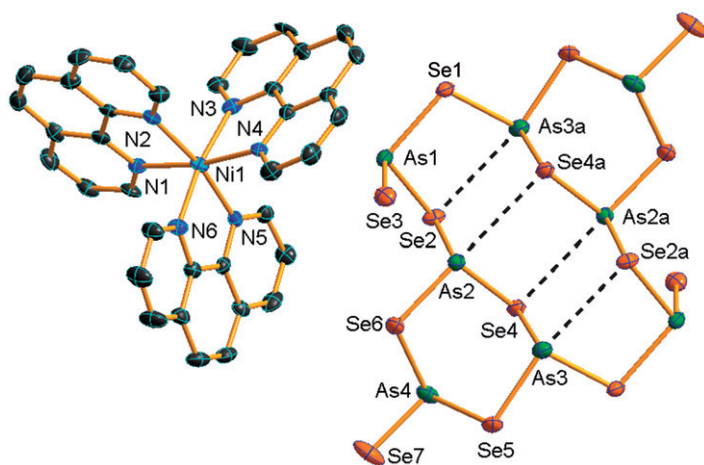


Figure 1. Crystal structure of **1** with the labeling scheme (thermal ellipsoids are drawn at 50% probability). Hydrogen atoms are omitted for clarity.

$[\text{As}_2\text{Se}_6]^{2-}$ ions. Like TM^{2+} in **1** and **2**, the Co^{2+} and Ni^{2+} ions are also coordinated by three phen in a slightly distorted octahedral geometry with axial N–TM–N angles in the range of $168.6(8)$ – $172.7(7)^\circ$ in **3** and $173.6(4)$ – $176.6(4)^\circ$ in **4** (table 3). There are two crystallographically distinct As in **3** and **4**, and both As(1) and As(2) are coordinated by three Se, yielding AsSe_3 trigonal pyramids. Two $\text{As}(1)\text{Se}_3$ trigonal pyramids are joined by two Se–Se bonds to form a dimeric anion $[\text{As}(1)_2\text{Se}_6]^{2-}$ (figure 4); As is coordinated by one Se^{2-} and two Se_2^{2-} ions, forming the polyselenidoarsenate anion $[\text{As}_2\text{Se}_2(\text{Se}_2)_2]^{2-}$, which contains a six-membered As_2Se_4 ring in the chair conformation with a centrosymmetric structure. The $[\text{As}(2)_2\text{Se}_6]^{2-}$ anion is similarly formed from two $\text{As}(2)\text{Se}_3$ trigonal pyramids (figure 4). $[\text{As}_2\text{Se}_6]^{2-}$ contains a six-membered As_2Se_4 ring in the chair conformation with a centrosymmetric structure and has two sets of As–Se bond lengths. Terminal As– Se_t bonds are shorter than bridging As– Se_b bonds (table 3). As–Se and Se–Se bond lengths of $[\text{As}_2\text{Se}_6]^{2-}$ are similar to corresponding values observed in other compounds containing dimeric $[\text{As}_2\text{Se}_6]^{2-}$ [44–48]. In **3**, each $[\text{Co}(\text{phen})_3]^{2+}$ contacts with two neighboring cations *via* face-to-face $\pi \cdots \pi$ stacking interactions with $\pi \cdots \pi$ separations 3.204 and 3.329 Å. The $[\text{Co}(\text{phen})_3]^{2+}$ are assembled in chains along the *b*-axis by $\pi \cdots \pi$ stacking interactions (figure 5). $[\text{As}_2\text{Se}_6]^{2-}$ locate between the chains (figure 6).

The trigonal pyramids $[\text{AsE}_3]^{3-}$ ($\text{E} = \text{S}, \text{Se}$) are readily condensed to form oligomeric or polymeric chalcogenidoarsenate(III) anions $[\text{As}_x\text{E}_y]^{n-}$. Their grades *c* ($c = x/y$) lie in the range of $0.333 < c < 0.667$ depending upon the size and shape of their counter ions [8]. In the case of selenidoarsenate, discrete $[\text{As}_x\text{Se}_y]^{n-}$ aggregates with *c* values of 0.500

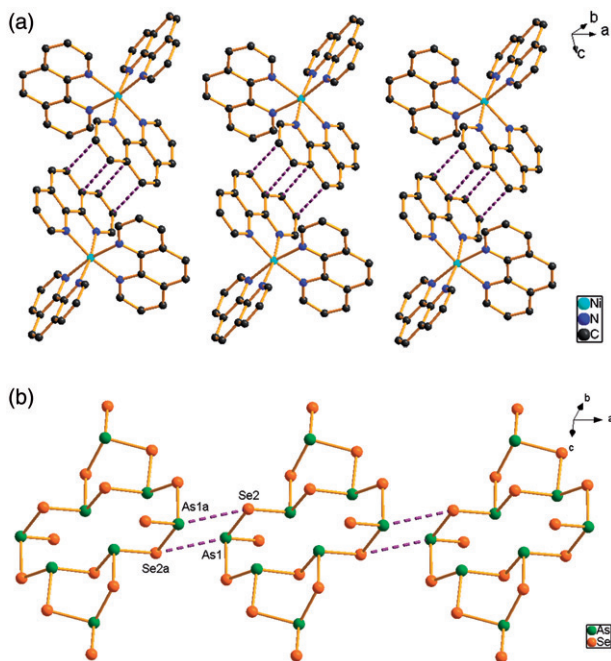
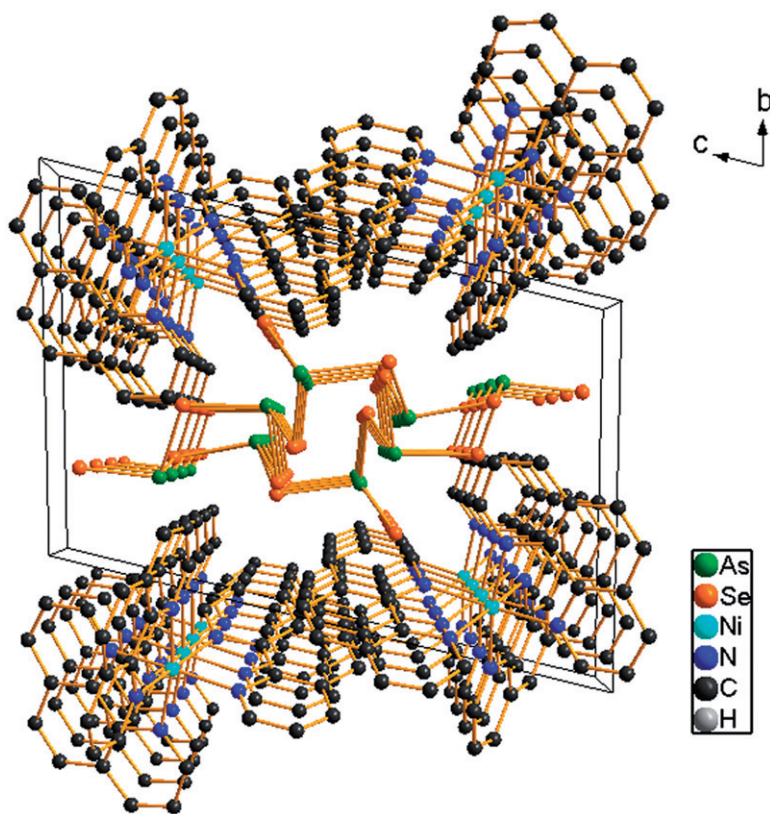


Figure 2. (a) A view of $[\text{Ni}(\text{phen})_3]^{2+}$ cations showing $\pi \cdots \pi$ stacking interactions in **1**. Hydrogen atoms are omitted for clarity. (b) A view of anionic chain assembled by $[\text{As}_8\text{Se}_{14}]^{4-}$ *via* secondary As \cdots Se interactions in **1**.

Figure 3. Crystal packing of **1**. Hydrogen atoms are omitted for clarity.Table 3. Selected bond lengths (Å) and angles (°) for **3** and **4**.

	3	4		3	4
As(1)–Se(1)	2.413(4)	2.506(3)	As(1)–Se(2)#1	2.441(5)	2.386(4)
As(1)–Se(3)	2.262(4)	2.289(2)	As(2)–Se(4)	2.387(8)	2.4174(19)
As(2)–Se(5)#2	2.532(8)	2.4122(17)	As(2)–Se(6)	2.273(7)	2.2761(18)
Se(1)–Se(2)	2.352(4)	2.339(2)	Se(4)–Se(5)	2.336(7)	2.3569(18)
TM(1)–N(1)	2.08(2)	2.036(8)	TM(1)–N(2)	2.110(18)	2.027(9)
TM(1)–N(3)	2.099(16)	2.038(8)	TM(1)–N(4)	2.10(2)	2.016(8)
TM(1)–N(5)	2.093(17)	2.011(8)	TM(1)–N(6)	2.04(2)	2.013(9)
Se(1)–As(1)–Se(2)#1	99.77(16)	97.20(12)	Se(1)–As(1)–Se(3)	96.81(17)	99.84(9)
Se(2)#1–As(1)–Se(3)	94.61(16)	95.30(10)	Se(4)–As(2)–Se(5)#1	96.9(3)	99.67(7)
Se(1)–As(2)–Se(6)	95.3(3)	93.62(7)	Se(5)#2–As(2)–Se(6)	99.5(2)	97.31(6)
As(1)–Se(1)–Se(2)	101.34(17)	101.83(10)	As(1)#1–Se(2)–Se(1)	101.41(15)	100.29(11)
As(2)–Se(4)–Se(5)	100.8(3)	101.96(7)	As(2)#2–Se(5)–Se(4)	101.6(2)	100.72(6)
N(1)–TM(1)–N(2)	78.6(7)	83.0(4)	N(1)–TM(1)–N(3)	92.5(8)	176.6(4)
N(1)–TM(1)–N(4)	95.2(7)	94.9(4)	N(1)–TM(1)–N(5)	93.8(8)	89.7(3)
N(1)–TM(1)–N(6)	168.6(8)	92.2(4)	N(2)–TM(1)–N(3)	94.9(8)	94.4(4)
N(2)–TM(1)–N(4)	169.7(8)	91.0(4)	N(2)–TM(1)–N(5)	89.8(8)	93.9(4)
N(2)–TM(1)–N(6)	94.1(8)	174.2(3)	N(3)–TM(1)–N(4)	77.0(7)	82.9(4)
N(3)–TM(1)–N(5)	172.7(7)	92.6(4)	N(3)–TM(1)–N(6)	96.8(8)	90.5(4)
N(4)–TM(1)–N(5)	98.9(7)	173.6(4)	N(4)–TM(1)–N(6)	93.2(8)	92.7(4)
N(5)–TM(1)–N(6)	77.3(8)	82.8(4)			

Symmetry transformations used to generate equivalent atoms: For **3**: (#1) $-x+1, -y, -z+1$; (#2) $-x+2, -y+1, -z+2$. For **4**: (#1) $-x+1, -y+1, -z$; (#2) $-x, -y+1, -z+1$.

([As₂Se₄]²⁻, [As₃Se₆]³⁻ and [As₄Se₈]⁴⁻) [10–12, 14, 22, 49] have been obtained with alkali and alkaline earth metal cations, ammonium or phosphonium cations as the counter ions. The [As₂Se₃]⁴⁻ anion with *c* of 0.400 was isolated in en with [Mn(en)₃]²⁺ [21]. However, discrete selenidoarsenates with condensation grade more than 0.500 is scarce. Now, a new selenidoarsenate [As₈Se₁₄]⁴⁻ with condensation grade of 0.571 was prepared with [Ni(phen)₃]²⁺ and [Zn(phen)₃]²⁺. The only example of [As₈Se₁₄]⁴⁻ before is [Co(phen)₃]₂[As₈Se₁₄] [34]; the first coordinative polymeric selenidoarsenate(III) with condensation grade of 0.571 is observed in [{Mn(tren)}(As₄Se₇)] [24]. [As₂Se₆]²⁻, which is formed by two AsSe₃ trigonal pyramids *via* two Se–Se bonds, is the most common polyselenidoarsenate. Beside [As₂Se₆]²⁻ compounds with organic counter cations [44–48], the [As₂Se₆]²⁻ anions were also obtained with TM complex cations, exemplified by [Fe(en)₃][As₂Se₆], [Mn(en)₃][As₂Se₆] [22], [Co(dien)₂][As₂Se₆,

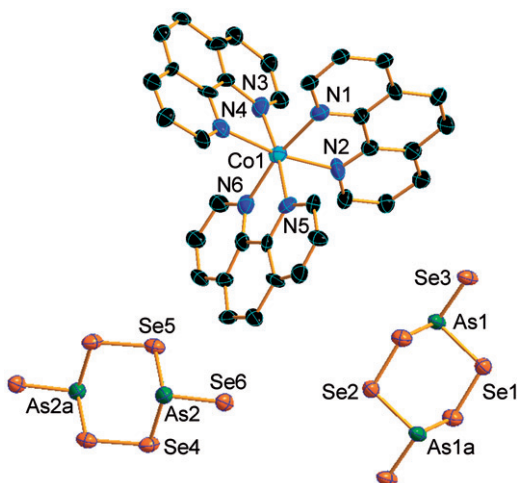


Figure 4. Crystal structure of **3** with the labeling scheme (thermal ellipsoids are drawn at 50% probability). Hydrogen atoms are omitted for clarity.

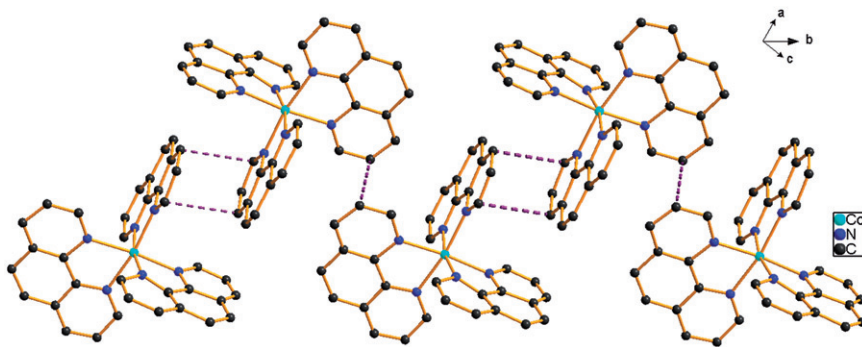


Figure 5. (a) A view of the array of [Co(phen)₃]²⁺ cations assembled by $\pi \cdots \pi$ stacking interactions in **3**. Hydrogen atoms are omitted for clarity.

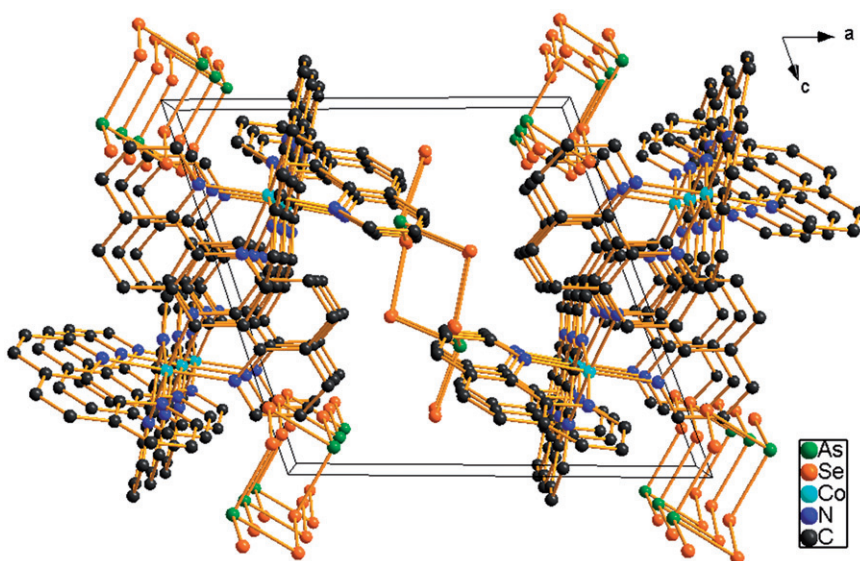


Figure 6. Crystal packing of **3**. Hydrogen atoms are omitted for clarity.

$[\text{Ni}(\text{dien})_2]\text{As}_2\text{Se}_6$, and $[\text{Mn}(\text{dap})_3]\text{As}_2\text{Se}_6$ [23]. Now it is isolated from CH_3OH aqueous solution with $[\text{Co}(\text{phen})_3]^{2+}$ and $[\text{Ni}(\text{phen})_3]^{2+}$ counter cations in **3** and **4**.

3.3. Optical properties

The UV-Vis reflectance spectroscopies of **1** and **2** were measured on powder samples at room temperature. Absorption data from reflectance spectroscopy by the Kubelka-Munk function demonstrate that **1** and **2** exhibit steep absorption edge with corresponding bandgap at 1.71 and 2.33 eV, respectively (figure 7), indicating that **1** and **2** have semiconducting properties, and band gaps are in accord with the compounds color.

4. Conclusion

Solvothermal reactions of As_2O_3 , Se, dien and phen in the presence of TMCl_2 are investigated in different solvents. The solvothermal reactions in water produced selenidoarsenates $[\text{Ni}(\text{phen})_3]_2[\text{As}_8\text{Se}_{14}]$ (**1**) and $[\text{Zn}(\text{phen})_3]_2[\text{As}_8\text{Se}_{14}]$ (**2**), respectively, which contain $[\text{As}_8\text{Se}_{14}]^{4-}$ with condensation grade more than 0.50. Reactions in CH_3OH aqueous solution afforded polyselenidoarsenates $[\text{Co}(\text{phen})_3]_2[\text{As}_2\text{Se}_6]$ (**3**) and $[\text{Ni}(\text{phen})_3]_2[\text{As}_2\text{Se}_6]$ (**4**) containing $[\text{As}_2\text{Se}_6]^{2-}$ with condensation grade of 0.333. The syntheses of **1–4** show the solvent effect on the $\text{TM}^{2+}/\text{As}_2\text{O}_3/\text{Se}/\text{phen}$ solvothermal system.

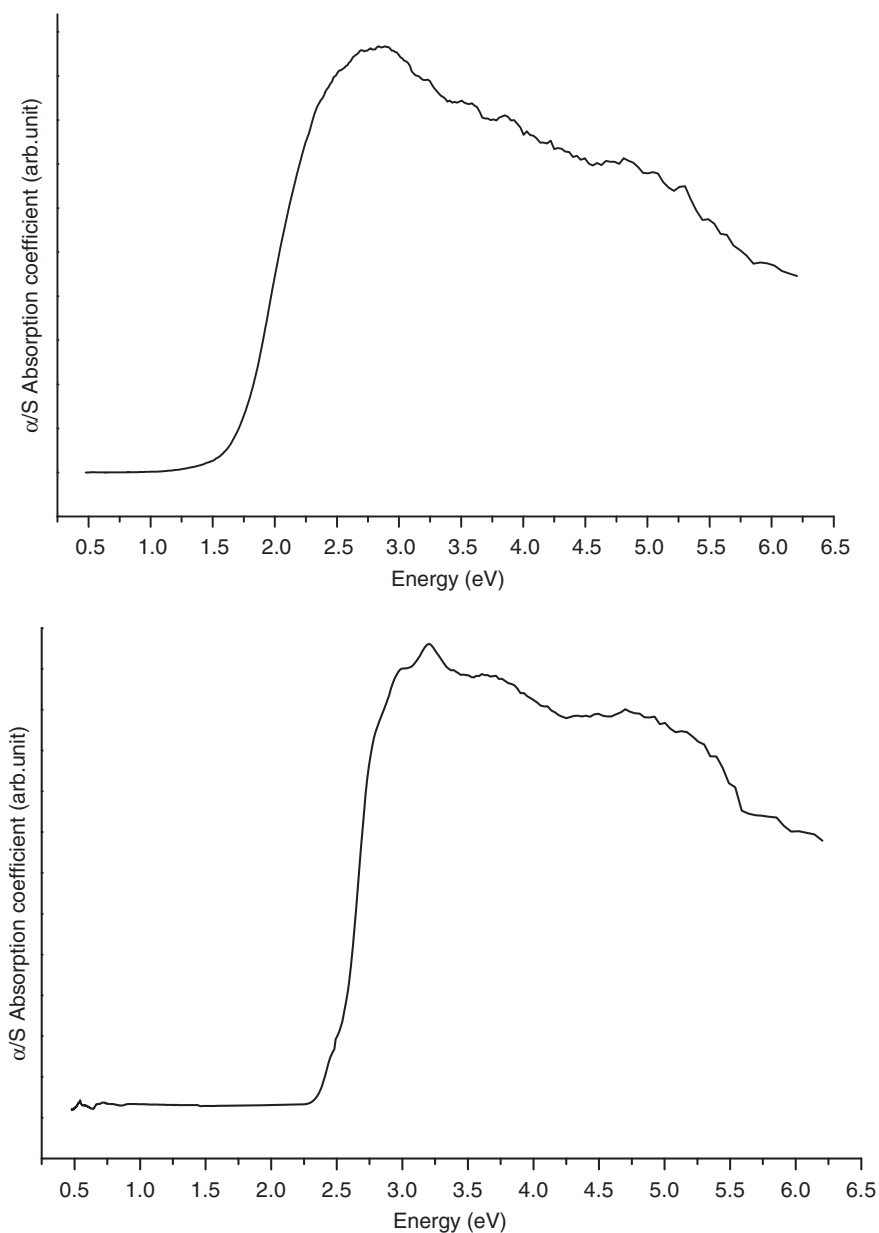


Figure 7. Optical absorption spectra of **1** (top) and **2** (bottom).

Supplementary material

Crystallographic data for the structures reported in the paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary data, CCDC Nos. 880 841 (**1**), 880 842 (**2**), 880 843 (**3**), and 880 844 (**4**). Copies of the data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge

Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033 or E-mail: deposit@ccdc.cam.ac.uk

Acknowledgments

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