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Novel Polyselenidoarsenate and Selenidoarsenate: Solvothermal Synthesis and Characterization of $[Co(phen)_3][As_2Se_2(\mu\text{-}Se_3)(\mu\text{-}Se_5)]$ and $[Co(phen)_3]_2[As_8Se_{14}]$

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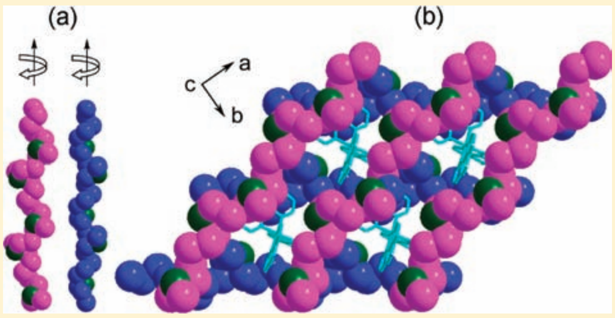
S *Supporting Information*

ABSTRACT: Novel cobalt polyselenidoarsenate $[Co(phen)_3]$-$[As_2Se_2(\mu\text{-}Se_3)(\mu\text{-}Se_5)]$ (**1**; phen = 1,10-phenanthroline) was methanolothermally synthesized by the reaction of $CoCl_2$, As_2O_3, and Se templated by phen in a CH_3OH solvent at 130 °C. The same reaction in a H_2O solvent yielded cobalt selenidoarsenate $[Co(phen)_3]_2[As_8Se_{14}]$ (**2**). In **1**, the $AsSe^+$ units are alternately joined by the $\mu\text{-}Se_3{}^{2-}$ and $\mu\text{-}Se_5{}^{2-}$ bridging ligands to form a novel helical polyselenidoarsenate chain $[As_2Se_2(\mu\text{-}Se_3)(\mu\text{-}Se_5)^{2-}]_\infty$. In **2**, eight pyramidal $AsSe_3$ units are connected via corner sharing into the new member of the selenidoarsenate aggregate $[As_8Se_{14}]^{4-}$ with a condensation grade of 0.571, which represents the first discrete selenidoarsenate(III) with a condensation grade of above 0.50. The octahedral complex $[Co(phen)_3]^{2+}$ is formed in situ to act as a countercation in compounds **1** and **2**. **1** and **2** exhibit steep absorption band gaps at 2.09 and 2.16 eV, respectively.



INTRODUCTION

Main-group chalcogenometalates have attracted increasing attention because of their potential applications as optical, electrical, and ion-exchange materials[1] and chemical sensors,[2] and a large member of these chalcogenides have been synthesized and characterized.[3,4] In the case of chalcogenoarsenates, a variety of binary isolated polyselenidoarsenates and selenidoarsenates have been prepared by the extraction method at room temperature or the solvothermal method in moderate temperature range. The cyclic discrete polyselenidoarsenates $[As_2Se_6]^{2-}$, $[AsSe_6]^-$, and $[AsSe_8]^-$ were prepared by extraction of arsenic selenides from en (en = ethylenediamine) or CH_3CN solutions templated by Et_4N^+, enH^+, or Ph_4P^+.[5,6] These polyselenidoarsenate anions are constructed by a $[AsSe_3]^{3-}$ trigonal pyramid linked through the Se−Se bond. On the other hand, the fundamental building units $[AsSe_3]^{3-}$ are readily condensed by corner or edge sharing in the presence of suitable counterions, resulting in the formation of a series of selenidoarsenate anions. The examples include $[As_2Se_4]^{2-}$,[7,8] $[As_2Se_5]^{4-}$,[9] $[As_3Se_6]^{3-}$,[10] and $[As_4Se_8]^{4-}$.[11] In addition, the $AsSe_3$ units can be connected by the As−As bond besides the As−Se linkage to give mixed-valent selenidoarsenate(II,III) $[As_4Se_6]^{2-}$.[5,8,12] On the other hand, the $[AsSe_3]^{3-}$ units are prone to condensation via Ag^+ or Hg^{2+} ions, leading to extended ternary selenidoarsenates(III).[13] Recently, the Sheldrick group had solvothermally prepared coordinative selenidoarsenates using a tridentate N-donor ligand of terpy (terpy = 2,2′;6′,2″-terpyridine) or a tetradentate N-donor ligand of tren [tren = tris(2-aminoethyl)amine] as templates in the presence of transition-metal Mn^{II}. The bridging ligands $\mu\text{-}As_2Se_4$, $\mu\text{-}As_2Se_5$, $\mu\text{-}As_4Se_7$, and $\mu\text{-}As_4Se_8$ are observed to coordinate to $[Mn(tren)]^{2+}$ or $[Mn(terpy)]^{2+}$ complexes.[14] Polyselenidoarsenate ligands to the Mn^{II} center are also obtained in $[\{Mn(terpy)\}_3(\mu\text{-}AsSe_2(Se_2))_2]$ and $[\{Mn(cyclam)\}_2(\mu\text{-}As_2Se_6)]$ (cyclam = 1,4,8,11-tetraazacyclotetradecane).[15]

The solvents and templates are thought to play an important role in the solvothermal synthesis of chalcogenidometalates.[16] There has been substantial precedent for aminothermal and hydrothermal syntheses of the transition-metal-containing chalcogenidometalates.[3,4] However, the methanolothermal synthesis of these chalcogenidometalates is limited, although the method was applied to prepare alkali chalcogenidometalates in the methanol solvent many years ago.[13,17] Now our investigation of the ternary Co/As/Se system in a CH_3OH solvent in the presence of coordinative template phen under solvothermal conditions yields novel polyselenidoarsenate $[Co(phen)_3][As_2Se_2(\mu\text{-}Se_3)$-$(\mu\text{-}Se_5)]$ (**1**). By comparison, the same reaction in H_2O gives selenidoarsenate $[Co(phen)_3]_2[As_8Se_{14}]$ (**2**). Novel polyselenidoarsenate chain $[As_2Se_2(\mu\text{-}Se_3)(\mu\text{-}Se_5)^{2-}]_\infty$ and selenidoarsenate aggregate $[As_8Se_{14}]^{4-}$ with a condensation grade of above 0.50 are observed in **1** and **2**, respectively.

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

	1	2
empirical formula	$C_{36}H_{24}N_6CoAs_2Se_{10}$	$C_{72}H_{48}N_{12}Co_2As_8Se_{14}$
fw	1538.98	2903.88
cryst color	black	dark red
cryst syst	monoclinic	triclinic
space group	$C2$ (No. 5)	$P\bar{1}$ (No. 2)
a, Å	24.461(6)	10.3519(5)
b, Å	11.2937(19)	12.7439(4)
c, Å	19.454(5)	17.4740(12)
α, deg	90.00	76.602(6)
β, deg	127.736(4)	88.032(7)
γ, deg	90.00	66.677(5)
V, $Å^3$	4250.1(16)	2055.00(18)
Z	4	1
T, K	293(2)	223(2)
calcd density, Mg m^{-3}	2.405	2.346
$F(000)$	2860	1358
2θ(max), deg	50.70	50.70
Flack value	0.05(3)	
total reflns collected	20 984	17 576
unique reflns	7627 (R_{int} = 0.0729)	7463 (R_{int} = 0.0609)
no. of param	445	488
R1 [$I > 2\sigma(I)$]	0.0482	0.0436
wR2 (all data)	0.1487	0.1074
GOF on F^2	1.071	0.958

EXPERIMENTAL SECTION

Materials and Methods. All starting chemicals were of analytical grade and used as purchased. Elemental analyses were conducted on a EA1110-CHNS-O elemental analyzer. Fourier transform infrared spectra were recorded with a Nicolet Magna-IR 550 spectrometer in dry KBr disks in the 4000−400 cm^{-1} range. Room temperature optical diffuse-reflectance spectra of the powdered sample were obtained with a Shimadzu UV-3150 spectrometer. The absorption (α/S) data were calculated from the reflectance using the Kubelka−Munk function $\alpha/S = (1 - R)^2/2R$.[18] Thermoanalytical measurements were performed using a thermogravimetric differential scanning calorimetry (TG-DSC) microanalyzer of SDT 2960, and all of the samples were heated under a nitrogen stream of 100 mL min^{-1} with a heating rate of 5 °C min^{-1}.

Synthesis of $[Co(phen)_3][As_2Se_2(\mu\text{-}Se_3)(\mu\text{-}Se_5)]$ (1). $CoCl_2 \cdot 6H_2O$ (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), en (180 mg, 3 mmol), and 6 mL of CH_3OH were loaded into a Teflon-lined stainless steel autoclave with an inner volume of 10 mL. The reaction was run at 130 °C for 5 days and then cooled to ambient temperature. Black block crystals of **1** were filtered off, washed with methanol, and stored under a vacuum (62% yield based on As_2O_3). Elem Anal. Calcd for $C_{36}H_{24}N_6CoAs_2Se_{10}$: C, 28.10; H, 1.57; N, 5.46. Found: C, 27.91; H, 1.52; N, 5.38. IR data (KBr, cm^{-1}): 3732 (w), 3560 (w), 3453 (w), 3067 (w), 1645 (w), 1597 (s), 1468 (m), 1440 (s), 1309 (m), 1250 (w), 1157 (m), 1102 (w), 1007 (s), 768 (s), 731 (m), 648 (w), 478 (m), 411 (w).

Synthesis of $[Co(phen)_3]_2[As_8Se_{14}]$ (2). Compound **2** was prepared with a procedure similar to that for the synthesis of **1**, except that a H_2O solvent was used instead of a CH_3OH solvent. Dark-red prism crystals of **2** were filtered off, washed with methanol, and stored under vacuum (38% yield based on As_2O_3). Elem Anal. Calcd for $C_{72}H_{48}N_{12}Co_2As_8Se_{14}$: C, 29.78; H, 1.67; N, 5.79. Found: C, 29.62; H, 1.61; N, 5.65. IR data (KBr, cm^{-1}): 3736 (w), 3657 (w), 3021 (w), 1591 (s), 1563 (m), 1466 (m), 1429 (s), 1308 (m), 1243 (w), 1154 (s), 1103 (w), 1006 (s), 811 (w),761 (s), 732 (m), 644 (m), 617 (w), 454 (w), 412 (s).

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

$As-Se_t$[a]	2.258(3), 2.266(3)	2.2954(12), 2.2978(13)
$As-Se_b$[b]	2.381(3)−2.494(3)	2.3722(10)−2.5075(10)
Se−Se	2.311(3)−2.338(4)	
Co−N	2.081(15)−2.126(13)	2.077(6)−2.106(6)
Se−As−Se	89.31(10)−109.46(11)	86.50(3)−107.77(4)
As−Se−As	101.62(14)−110.99(12)	87.06(3)−104.22(4)
N−Co−N (cis)	79.8(8)−98.0(5)	79.2(2)−95.0(2)
N−Co−N (trans)	168.7(5)−176.9(7)	169.7(2)−171.3(2)

[a] Terminal bond lengths. [b] Bridging bond lengths.

X-ray Crystal Structure Determinations. Data were collected on a Rigaku Mercury CCD diffractometer at 293(2) K using graphite-monochromated Mo Kα radiation with a ω-scan method to a maximum 2θ value of 50.70° for **1** and **2**. An absorption correction was applied for all of the compounds using multiscan. The structures were solved with direct methods using the program *SHELXS-97*,[19] and the refinement was performed against F^2 using *SHELXL-97*.[19] All of the non-H atoms were refined anisotropically. The H atoms were added geometrically and refined using the riding model. **1** has a Flack parameter of 0.05(3) refined with a twin crystal. Crystallographic, experimental, and analytical data for the title compounds are listed in Table 1.

RESULTS AND DISCUSSION

Synthesis and IR Spectra. Cobalt polyselenidoarsenate(III) (**1**) was prepared by the reaction of $CoCl_2$, As_2O_3, Se, and phen in a CH_3OH solvent at 130 °C. When the reaction was conducted in a H_2O solvent at the same temperature, a new cobalt selenidoarsenate(III) (**2**) was obtained. The amine en is needed in the reactions. The basic en may play an important role in the conversion of selenium to polyselenide or selenide anions, which react with As_2O_3 to form polyselenidoarsenate or selenidoarsenate during the solvothermal reactions. In our previous work, the reaction of $CoCl_2$, As_2O_3, and Se in an en solvent gave selenidoarsenate(III) $[Co(en)_3]_2As_2Se_5$.[9a] The syntheses of **1**, **2**, and $[Co(en)_3]_2As_2Se_5$ show influence of the reaction solvents on the condensation manner of the trigonal-pyramidal $AsSe_3$ units under solvothermal conditions. In the IR spectra of **1** and **2**, the relatively weak absorption bands in the frequency range 3736−3067 cm^{-1} are due to the C−H vibrations of the aromatic ring H atoms. The absorption bands in the range 1671−1440 cm^{-1} correspond to ring vibrations of the phen ligand.

Crystal Structures. Compound **1** crystallizes in the monoclinic space group $C2$ with four formula units in the unit cell (Table 1). It consisits of the $[Co(phen)_3]^{2+}$ complex cation and $[As_2Se_2(\mu\text{-}Se_3)(\mu\text{-}Se_5)^{2-}]_\infty$ chain. Two crystallographically distinct Co^{2+} ions are coordinated by six N atoms of three phen ligands at distances between 2.081(15) and 2.126(13) Å in a distorted octahedral geometry with cis N−Co−N angles in the range of 79.8(8)−98.0(5)° and trans N−Co−N angles in the range of 168.7(5)−176.9(7)° (Table 2). The Co−N bond lengths match well with those of the reported cobalt complexes with the phen ligand.[20] The $[As_2Se_2(\mu\text{-}Se_3)(\mu\text{-}Se_5)]^{2-}$ anion contains two crystallographically As^{3+} centers, and each is coordinated by a terminal Se^{2-} to give $AsSe^+$ units. The $AsSe^+$ units are joined together by $\mu\text{-}Se_3{}^{2-}$ and $\mu\text{-}Se_5{}^{2-}$ bridging ligands to give rise to a one-dimensional chain $[As_2Se_2(\mu\text{-}Se_3)(\mu\text{-}Se_5)^{2-}]_\infty$,

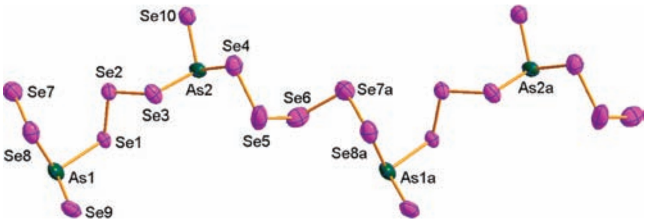

Figure 1. Crystal structure of the helical $[As_2Se_2(\mu\text{-}Se_3)(\mu\text{-}Se_5)^{2-}]_\infty$ chain in **1** with the labeling scheme (thermal ellipsoids are drawn at 50% probability).

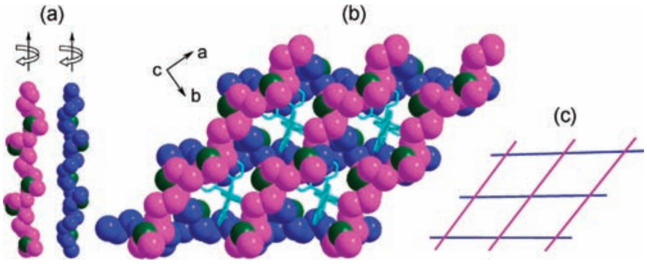

Figure 2. (a) Right-handed helices A (purple) and B (blue) in **1**. (b) Perspective view of the cross-stacking of helices A (purple) and B (blue) in **1**. (c) Topological structure of the $[As_2Se_2(\mu\text{-}Se_3)(\mu\text{-}Se_5)^{2-}]_\infty$ chains in **1**.

in which $\mu\text{-}Se_3{}^{2-}$ and $\mu\text{-}Se_5{}^{2-}$ units occur alternately. In other words, the chain $[As_2Se_2(\mu\text{-}Se_3)(\mu\text{-}Se_5)^{2-}]_\infty$ is based on repeated $[AsSe{-}Se_5{-}AsSe{-}Se_3{-}AsSe]_\infty$ units (Figure 1). Each As atom is surrounded by three Se atoms to form the trigonal pyramid $AsSe_3$ with As−Se bonds in the range of 2.266(3)−2.494(3) Å and Se−As−Se angles in the range of 89.31(10)−109.46(11)° (Table 2). The $[As_2Se_2(\mu\text{-}Se_3)(\mu\text{-}Se_5)^{2-}]_\infty$ anion has two sets of As−Se bond lengths (Table 2). The terminal As−Se_t bond lengths [2.258(3) and 2.266(3) Å], as expected, are shorter than those of the bridging As−Se_b bonds [2.381(3)−2.494(3) Å] (Table 2). The As−Se lengths are in the range of those reported for the anion $[As_2Se_6]^{2-}$ [As−Se = 2.268(4)−2.438(3) Å].[5−7] However, the Se−As−Se angles scatter in a wider range compared to the angles of the cyclic anion $[As_2Se_6]^{2-}$ [Se−As−Se = 93.81(12)−102.87(11)°]. The Se−Se bond lengths in the triselenide unit $Se_3{}^{2-}$ [2.311(3) and 2.324(3) Å] are slightly shorter than those in the pentaselenide unit $Se_5{}^{2-}$ [Se−Se = 2.315(4)−2.338(4) Å], and both compare well to those found in other polyselenides, e.g., $[NEt_4][AsSe_8]$ [Se−Se = 2.320(5) and 2.350(5) Å],[6] $KPdCu(Se_2)(Se_3)$ [Se−Se = 2.338(2) and 2.390(1) Å],[21] and $[V_2(Se_2)_2(\mu\text{-}Se_2)_2(\mu\text{-}Se_5)]^{2-}$ [Se−Se = 2.339(3)−2.453(3) Å].[22]

The $[As_2Se_2(\mu\text{-}Se_3)(\mu\text{-}Se_5)^{2-}]_\infty$ polymeric anion contains $\mu\text{-}Se_3$ and $\mu\text{-}Se_5$ bridging ligands. As a common structural unit of polyselenides, the triselenide unit $Se_3{}^{2-}$ has been observed as a terminal,[23] a $\mu\text{-}Se_3$,[21] or a μ-cyclo-Se_3[24] brigding ligand in transition-metal polyselenides. However, the bidentate bridging $\mu\text{-}Se_5$ coordination mode is rare for the pentaselenide $Se_5{}^{2-}$ unit. The $Se_5{}^{2-}$ unit has been observed to coordinate to a single As^{3+} center as a bidentate chelating ligand $\eta^2\text{-}Se_5$ to form six-membered ring $AsSe_5$ in the $[AsSe_6]^-$ anion.[6] Chelating transition-metal centers Mn,[25] Fe,[26] Cu,[27] Zn,[28] and Pd[29] have also been observed as the $\eta^2\text{-}Se_5$ ligand. However, the only example of the bidentate bridging coordination mode $\mu\text{-}Se_5$ is observed in the anion $[V_2(Se_2)_2(\mu\text{-}Se_2)_2(\mu\text{-}Se_5)]^{2-}$.[22] The only polyselenidoarsenate(III) chains reported before are observed in alkalizelenoarsenates $KAsSe_3 \cdot H_2O$, $RbAsSe_3 \cdot 0.5H_2O$, and $CsAsSe_3 \cdot 0.5H_2O$.[30] These compounds contain polyselenoarsenate(III) anions $(AsSe_3{}^-)_\infty$, in which the $\psi\text{-}AsSe_3$ tetrahedral units are linked together through $\mu\text{-}Se_2{}^{2-}$ units into an infinite zweier single chain. The helical $[As_2Se_2(\mu\text{-}Se_3)(\mu\text{-}Se_5)^{2-}]_\infty$ anion in **1** is the first example of polyselenoarsenate(III) chains with $\mu\text{-}Se_3{}^{2-}$ and $\mu\text{-}Se_5{}^{2-}$ units as the linkages. The striking feature of **1** is the existence of the one-dimensional helical $[As_2Se_2(\mu\text{-}Se_3)(\mu\text{-}Se_5)^{2-}]_\infty$ chain and its unique stacking. There are two different directional helical chains in the crystal lattice, hereafter referred to as helices A and B (Figure 2). Both helices A and B exhibit a right-handed screw sense, which cross at an angle of 52.7°. In the crystal of **1**, helices A run parallel to each other to form a layer (referred to as layer A). The layer B is similarly formed by helices B. Both A and B layers propagate parallel to the (001) lattice plane and alternately stack in a crossed manner, creating pseudoparallelogram channels with a size of ca. 7.5 Å × 12.5 Å to accommodate the $[Co(phen)_3]^{2+}$ cations (Figures 2 and 3). The $[Co(phen)_3]^{2+}$ cations in **1** are in either in the Δ or Λ conformation in the inversion position, so they are a racemic mixture in the crystals. The helical $[As_2Se_2(\mu\text{-}Se_3)(\mu\text{-}Se_5)^{2-}]_\infty$ chain leads to a chiral space group of **1**.

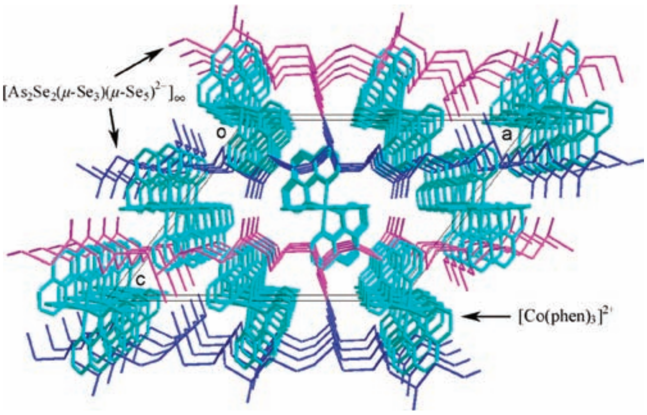

Figure 3. Crystal packing diagram of **1** viewed down the crystallographic *b* axis, showing layers A (purple) and B (blue) formed by helices A and B, respectively.

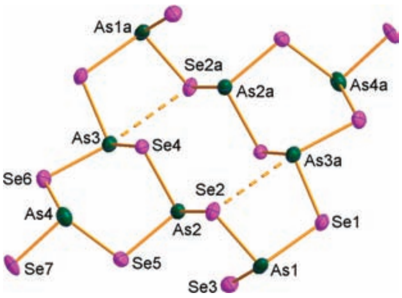

Figure 4. Crystal structure of the $[As_8Se_{14}]^{4-}$ anion in **2** with the labeling scheme (thermal ellipsoids are drawn at 50% probability).

Compound **2** consists of $[Co(phen)_3]^{2+}$ and $[As_8Se_{14}]^{4-}$ ions. Like the Co^{2+} ion in **1**, the Co^{2+} in **2** also forms octahedral complex $[Co(phen)_3]^{2+}$. The $[As_8Se_{14}]^{4-}$ anion contains four crystallographically distinct As^{3+} centers, and each is pyramidally coordinated by three Se^{2-} anions. Three $AsSe_3$ (As2, As3, and As4) trigonal pyramids are vertex-linked to form a cyclic As_3Se_5

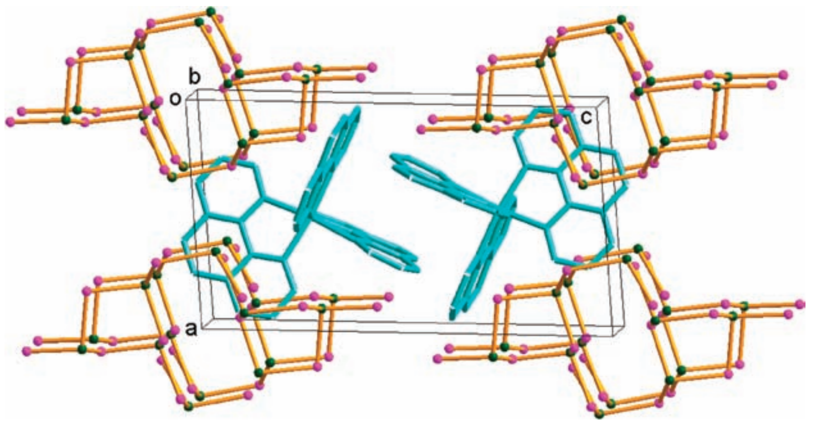

Figure 5. Crystal packing of **2**.

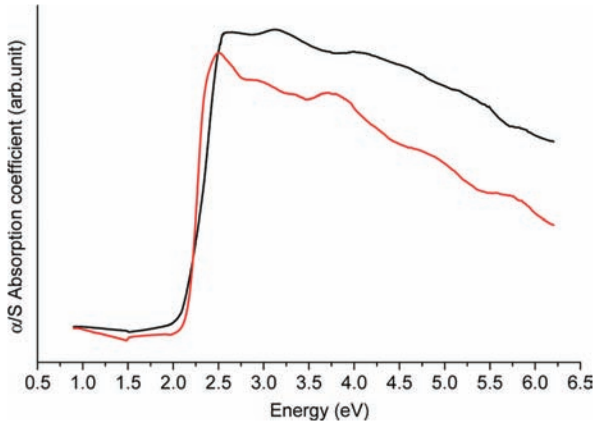

Figure 6. Solid-state optical absorption spectra of **1** (black) and **2** (red).

unit (Figure 4). The As_3Se_5 unit is corner-linked to the $As1Se_3$ trigonal pyramid, forming the asymmetric structural unit As_4Se_7. Two As_4Se_7 units are further coupled by sharing Se1 and Se1a atoms, yielding the isolated $[As_8Se_{14}]^{4-}$ anion (Figure 4). The binding mode leads to the formation of two As_3Se_3 and one As_6Se_6 heterocycles within the $[As_8Se_{14}]^{4-}$ anion. The terminal $As-Se_t$ bond lengths [2.2954(12) and 2.2978(13) Å] are slightly shorter than those of the bridging $As-Se_b$ bonds [2.3722(10)−2.5075(10) Å] (Table 2). The Se−As−Se angles are in the range of 86.50(3)−107.77(4)°. In the $[As_8Se_{14}]^{4-}$ anion, secondary Se···As interaction is observed between Se2a and As3 with a secondary bond length of 3.403 Å, which is shorter than the sum of the van der Waals radii of 4.0 Å for As and Se atoms.[12,14b] The secondary Se2a···As3 interaction leads to a lengthening of the opposite primary bond As3−Se6 [2.4351(13) Å], which is the longest bond among the As−Se bonds. Taking into account secondary interaction, the As3 atom forms a ψ-$AsSe_4$ trigonal bipyramid. In the crystal structure, the $[As_8Se_{14}]^{4-}$ anion locates at every corner of the unit cell. Two $[Co(phen)_3]^{2+}$ cations are enclosed in the unit cell by the eight $[As_8Se_{14}]^{4-}$ anions at the corners (Figure 5).

The condensation grades c ($c = x/y$) for the oligomeric or polymeric chalcogenidoarsenate anions $[As_xE_y]^{n-}$ (E = S, Se) lie in the range of $0.333 < c < 0.667$ depending upon the sizes of their counterions.[4] In the case of selenidoarsenates, the discreted $[As_xSe_y]^{n-}$ aggregates with c values of 0.333 ($[As_2Se_6]^{2-}$)[5,6] and 0.500 ($[As_2Se_4]^{2-}$, $[As_3Se_6]^{3-}$, and $[As_4Se_8]^{4-}$)[7,8,10,11] had been obtained with alkali (and alkaline-earth) metal cations and organic ammonium or phosphonium cations as the counterions. The $[As_2Se_5]^{4-}$ anion with c of 0.400 was isolated with counterion $[Co(en)_3]^{2+}$ or $[Mn(en)_3]^{2+}$.[9] Now the bulky $[Co(phen)_3]^{2+}$ complex cation leads to the formation of a new member of the selenidoarsenate aggregate $[As_8Se_{14}]^{4-}$ with a condensation grade of 0.571. As far as we know, the $[As_8Se_{14}]^{4-}$ anion is the first discrete selenidoarsenate(III) to exhibit a condensation grade of above 0.50. We note that the first coordinative polymeric selenidoarsenate(III) with a condensation grade of 0.571 is observed in $[\{Mn(tren)\}(As_4Se_7)]$.[14a]

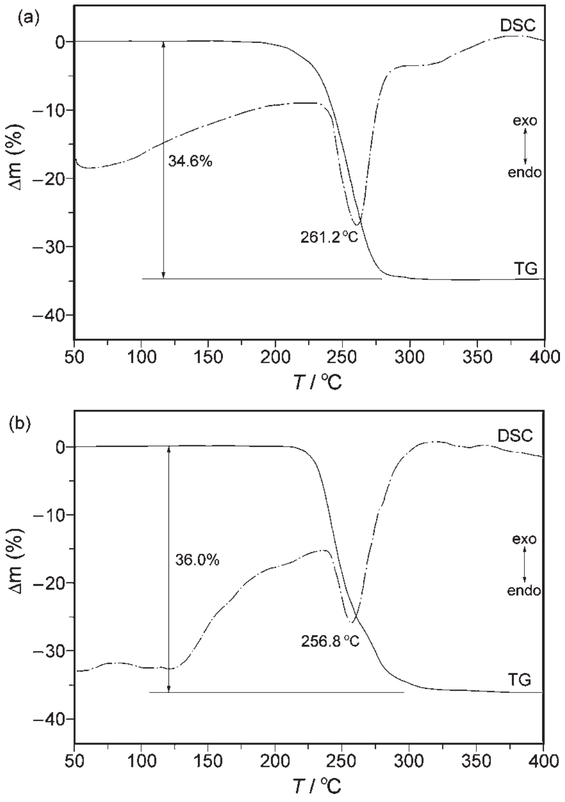

Figure 7. TG-DSC curves of compounds **1** (a) and **2** (b).

Optical Properties and Thermogravimetric Analyses. The UV−vis reflectance spectroscopies of **1** and **2** were measured on powder samples at room temperature. The absorption data from the reflectance spectroscopy by the Kubelka—Munk function demonstrate that compound **1** exhibits a steep absorption edge with a corresponding band gap at 2.09 (Figure 6), whereas compound **2** shows a band gap at 2.16 eV. These intense absorptions are likely the result of charge-transfer transitions from the selenium-dominated filled valence band to the transition-metal-dominated empty conduction band.[31]

The thermal stabilities of compounds **1** and **2** are investigated under a nitrogen atmosphere, and the TG-DSC curves are shown in Figure 7. Compounds **1** and **2** decompose in one step at $T_{\mathrm{onset}} = 202.7$ and 210.3 °C with mass losses of 34.6% and 36.0%, respectively. The mass losses are in good accordance with removal of all of their phen ligands (theoretical values: 35.1% for **1** and 37.2% for **2**). Decomposition is accompanied by strong endothermic signals in the DSC curve with peak temperatures of 261.2 and 256.8 °C for **1** and **2**, respectively.

■ CONCLUSION

In summary, we have shown the solvent effect on the solvothermal synthesis of arsenic selenides by methanolothermal and hydrothermal preparations of polyselenidoarsenate **1** and selenidoarsenate **2** via the same reaction of $CoCl_2$, As_2O_3, Se, and phen in CH_3OH and H_2O solvents, respectively. **1** contains the novel helical polyselenidoarsenate chain $[As_2Se_2(\mu\text{-}Se_3)(\mu\text{-}Se_5)^{2-}]_\infty$. The cross-stacking of the helical $[As_2Se_2(\mu\text{-}Se_3)(\mu\text{-}Se_5)^{2-}]_\infty$ chains leads to pseudoparallelogram channels to accommodate $[Co(phen)_3]^{2+}$ cations in the crystal structure of **1**. Compound **2** contains the oligomeric $[As_8Se_{14}]^{4-}$ anion with a condensation grade of 0.571, which represents the first discrete selenidoarsenate(III) with a condensation grade of above 0.50.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Crystallographic data in CIF format of **1** and **2**, selected bond lengths and angles, and IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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