Monatsh Chem (2011) 142:1203–1209
DOI 10.1007/s00706-011-0561-z

ORIGINAL PAPER

New polyselenidoarsenate salts with transition metal complexes as counterions: solvothermal synthesis, crystal structures, and properties of $[M(dien)_2]As_2Se_6$ (M = Co, Ni) and $[Mn(dap)_3]As_2Se_6$

Jing Zhao · Jingjing Liang · Yingli Pan ·
Yong Zhang · Dingxian Jia

Received: 9 February 2011 / Accepted: 26 June 2011 / Published online: 16 July 2011

Abstract New polyselenidoarsenates $[Co(dien)_2]As_2Se_6$, $[Ni(dien)_2]As_2Se_6$ (dien = diethylenetriamine), and $[Mn(dap)_3]As_2Se_6$ (dap = 1,2-diaminopropane) were synthesized by the reaction of As_2O_3, Se, and transition metal chloride in dien or dap solvent under solvothermal conditions. The compounds consist of a polyselenidoarsenate anion $[As_2Se_6]^{2-}$ and an octahedral complex cation $[M(dien)_2]^{2+}$ (M = Co, Ni) or $[Mn(dap)_3]^{2+}$. Two trigonal–pyramidal $AsSe_3$ units are joined through two Se–Se bonds forming the dimeric $[As_2Se_6]^{2-}$ anion with a six-membered ring As_2Se_4 in chair conformation. In the crystal structures the anion and cations are connected into extended structures via weak N–H···Se hydrogen bonds. Thermogravimetric analyses show that the dien-containing compounds decompose in one step under nitrogen stream, whereas the Mn compound exhibits a two-step decomposition process.

Keywords Chalcogenides · Metal complexes · Solvothermal synthesis · X-ray structure determination

Introduction

Since Bedard et al. [1, 2] hydrothermally prepared microporous tin and germanium sulfides in amine aqueous solution in the late 1980s, templating syntheses under mild solvothermal conditions in the presence of a structure-directing agent have been widely used in the preparation of binary chalcogenides of main group metals [3]. In 1996, Stephan and Kanatzidis solvothermally synthesized the first ternary cobalt thioantimonate $[Co(en)_3]CoSb_4S_8$ by introducing the transition metal ion Co^{2+} into the reaction of $SbS_3{}^{3-}$ and S with coordinative en (ethylenediamine) as the solvent [4]. The en molecule coordinates to the Co^{2+} ion as a chelating ligand to form the complex cation $[Co(en)_3]^{2+}$, which acts as structure-directing agent in the solvothermal synthesis. So far, a large number of chalcogenidoantimonate salts with transition metal complex cations as the counterions have been prepared by the solvothermal method in different coordinative ethylene polyamines, e.g., $[M(en)_3]Sb_2S_4$ (M = Co, Ni) [5], $Mn_2(en)Sb_2S_5$ [6], $[Co(en)_3]Sb_{12}S_{19}$ [7], $[Ni(dien)_2]_3(Sb_3S_6)_2$ [8], $[Ni(dien)_2]Sb_4S_8$ [9], $[Ni(dien)_2]Sb_4S_9$ [10], $[Fe(dien)_2]Sb_6S_{10}\cdot 0.5H_2O$ [11], $[Fe(dien)_2]Fe_2Sb_4S_{10}$ (dien = diethylenediamine) [12], $[M(tren)]_2Sb_2S_4$ (M = Co, Ni) [13], $[Mn(tren)]_2Sb_2S_5$ (tren = tris(2-aminoethyl)-amine) [14], $[Fe(chxn)_2]Sb_6S_{10}$, $[Co(chxn)_3]_3(SbS_4)_2\cdot 4H_2O$ (chxn = *trans*-1,2-diaminocyclohexane) [15], $[Co(dien)_2][Co(tren)SbS_4]_2\cdot 4H_2O$ [16], $[Co(dien)_2][Co(tren)SbS_4]_2\cdot 0.5H_2O$, $\{[Co(tren)]_2[CoSb_2S_6]\}\cdot H_2O$ [17], $[Fe(en)_3]_2Sb_2Se_5$ [18], $[M(dien)_2]_2Sb_4Se_9$ (M = Fe, Mn), $[Co(dien)_2]_2Sb_2Se_6$, and $[Ni(dien)_2]_2Sb_2Se_5$ [19].

However, compared with the bewildering array of chalcogenidoantimonates, the solvothermal syntheses of the chalcogenidoarsenate analogues in ethylene polyamine solvents have been less explored, and only limited examples of

---

Electronic supplementary material The online version of this article (doi:10.1007/s00706-011-0561-z) contains supplementary material, which is available to authorized users.

J. Zhao · J. Liang · Y. Pan · Y. Zhang · D. Jia (✉)
Key Laboratory of Organic Synthesis of Jiangsu Province,
College of Chemistry, Chemical Engineering and Materials
Science, Soochow University, Suzhou 215123,
People's Republic of China
e-mail: jiadingxian@suda.edu.cn

these transition metal-containing chalcogenidoarsenates are reported. The solvothermal reaction of As_2O_3 and Se in the presence of transition metal in en gave selenidoarsenates $[Co(en)_3]_2As_2Se_5$ and $[Mn(en)_3]_2As_2Se_5$ [20, 21]. The same reaction with arsenic and selenium as starting materials produced polyselenidoarsenates $[Fe(en)_3]As_2Se_6$ and $[Mn(en)_3]As_2Se_6$ [22]. In addition, coordinative selenidoarsenate units μ-As_2Se_4, μ-As_2Se_5, μ-As_4Se_7, and μ-As_4Se_8 are observed in the manganese complexes with tridentate N-donor terpy (terpy = 2,2′;6′,2″-terpyridine) or tetradentate N-donor tren as the coligands [23–25].

In this paper we report the preparation of polyselenidoarsenates $[Co(dien)_2]As_2Se_6$ (**1**), $[Ni(dien)_2]As_2Se_6$ (**2**), and $[Mn(dap)_3]As_2Se_6$ (**3**) in dien and dap solvents with As_2O_3 and Se as the starting materials. The influences of starting materials and ethylene polyamines on the solvothermal synthesis are discussed.

Results and discussion

Syntheses of the compounds and infrared spectra

The polyselenidoarsenates $[Co(dien)_2]As_2Se_6$ (**1**), $[Ni(dien)_2]As_2Se_6$ (**2**), and $[Mn(dap)_3]As_2Se_6$ (**3**) were prepared by the solvothermal reaction of As_2O_3 and Se in dien or dap solvent in the presence of transition metal ions Co^{2+}, Ni^{2+}, or Mn^{2+}, respectively. The dien and dap act as chelating ligands to coordinate to the transition metal ions, forming octahedral $[M(dien)_2]^{2+}$ (M = Co, Ni) or $[Mn(dap)_3]^{2+}$ complex cations, which serve as the counterions to the polyselenidoarsenate $[As_2Se_6]^{2-}$ anion. The same reaction in en solvent gave selenidoarsenates $[Co(en)_3]_2As_2Se_5$ and $[Mn(en)_3]_2As_2Se_5$ [20, 21]. The similar reaction in en solvent with arsenic and selenium as starting materials produced polyselenidoarsenate compounds $[Fe(en)_3]As_2Se_6$ and $[Mn(en)_3]As_2Se_6$ [22]. These observations imply that the starting materials and ethylene polyamine solvents have an intriguing influence on the condensation manner of the trigonal–pyramidal $AsSe_3$ units under solvothermal conditions. In the IR spectra of **1**–**3**, there are broad absorption bands in the frequency range 3,516–3,106 cm^{-1}, which are assigned to the N–H stretching modes of en or dap ligands. The broad absorption band feature is due to the presence of hydrogen bonds which are confirmed by the crystal structure determination below. Other absorption bands of en or dap are observed between 700 and 1,600 cm^{-1}.

Description of the structures

Compounds **1** and **2** are isostructural. They crystallize in the monoclinic space group $P2_1/n$ with two formula units in the unit cell. Compound **3** crystallizes in the monoclinic space group $C2/c$ with four formula units in the unit cell. Compounds **1**–**3** are composed of $[As_2Se_6]^{2-}$ anion and transition metal amino complex cations $[M(dien)_2]^{2+}$ (M = Co, Ni) or $[Mn(dap)_3]^{2+}$. The $[As_2Se_6]^{2-}$ anion is constructed from two trigonal–pyramidal $AsSe_3$ units joined through two Se–Se bonds. It contains a six-membered ring As_2Se_4 in chair conformation with a centrosymmetric structure (Fig. 1). In the $[As_2Se_6]^{2-}$ anion, the terminal As(1)–Se(3) bond length (2.2940(12) Å in **1**, 2.2905(14) Å in **2**, 2.2820(12) Å in **3**) is obviously shorter than those of the bridging As(1)–Se(1) and As(1)–Se(2) bond lengths (av. 2.4264(12) Å in **1**, 2.4215(15) Å in **2**, 2.4296(13) Å in **3**, Table 1). The Se–Se bond lengths are 2.3537(12) Å in **1**, 2.3550(13) Å in **2**, and 2.3595(12) Å in **3**, which agree with twice the covalent radius of selenium (1.17 Å) [26]. The bond lengths and angles of the $[As_2Se_6]^{2-}$ anion are in agreement with the corresponding values observed in other compounds containing the $[As_2Se_6]^{2-}$ anion [22, 27–31].

The Co^{2+} and Ni^{2+} ions are coordinated by two tridentate dien ligands to form the sixfold complexes $[M(dien)_2]^{2+}$ (M = Co, Ni), whereas the Mn^{2+} ion is coordinated by three bidentate dap ligands to form the sixfold complexes $[Mn(dap)_3]^{2+}$. The crystal structures of $[Co(dien)_2]^{2+}$ and $[Mn(dap)_3]^{2+}$ complexes are shown in Fig. 2. The coordination polyhedron of $[M(dien)_2]^{2+}$ can be described as a slightly distorted octahedron with *cis*-N–M–N angles of 81.1(2)–98.9(2)° for $[Co(dien)_2]^{2+}$ and 82.1(3)–97.9(3)° for $[Ni(dien)_2]^{2+}$ (Table 1). The $[Co(dien)_2]^{2+}$ and $[Ni(dien)_2]^{2+}$ complexes exhibit the conformation of *s-fac*. It is well known that the octahedral transition metal complexes $[M(dien)_2]^{2+}$ exist as *s-fac*, *u-fac*, and *mer* geometric isomers, and their geometry has been intensively studied before [32–36]. The $[Mn(dap)_3]^{2+}$ complex forms a more distorted octahedron with *cis*-N–Mn–N angles of 77.0(2)–95.6(2)°. The M–N bond lengths (av. 2.165(5) Å for Co–N, 2.117(6) Å for Ni–N, 2.274(6) Å for Mn–N, Table 1) are in the normal ranges observed in other compounds containing Co^{2+} [7, 16, 17], Ni^{2+} [8–10], and Mn^{2+} [6, 19] complexes with ethylene polyamine ligands.

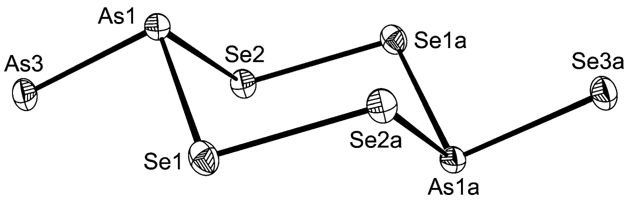

Fig. 1 Crystal structure of the $[As_2Se_6]^{2-}$ anion in **1** with labeling scheme (50% probability ellipsoids)

Table 1 Selected bond lengths/Å and angles/° for **1**–**3**

	1 (M = Co)	**2** (M = Ni)	**3** (M = Mn)
As(1)–Se(1)#1	2.4277(11)	2.4190(15)	2.4274(13)
As(1)–Se(2)	2.4251(12)	2.4220(14)	2.4319(12)
As(1)–Se(3)	2.2940(12)	2.2905(14)	2.2820(12)
Se(1)–Se(2)#1	2.3537(12)	2.3550(13)	2.3595(12)
M(1)–N(1)	2.178(5)	2.127(6)	2.241(6)
M(1)–N(2)	2.147(5)	2.096(6)	2.275(5)
M(1)–N(3)	2.169(5)	2.128(6)	2.306(7)
Se(2)–As(1)–Se(1)#1	99.41(4)	99.57(5)	100.06(4)
Se(3)–As(1)–Se(1)#1	88.96(4)	100.04(5)	91.45(4)
Se(2)–As(1)–Se(3)	100.27(4)	89.02(5)	98.26(5)
Se(2)–Se(1)–As(1)#1	107.72(4)	96.88(4)	105.36(4)
Se(1)–Se(2)–As(1)	96.91(4)	107.72(5)	99.76(4)
N(1)–M(1)–N(2)	81.1(2)	82.1(3)	77.0(2)
N(1)–M(1)–N(3)	90.9(2)	89.3(3)	94.8(3)
N(1)–M(1)–N(1)#2	180.0	180.0	92.4(3)
N(1)–M(1)–N(2)#2	98.9(2)	97.9(3)	95.6(2)
N(1)–M(1)–N(3)#2	89.1(2)	90.7(2)	170.1(2)
N(2)–M(1)–N(3)	81.4(2)	97.0(3)	92.7(2)
N(2)–M(1)–N(2)#2	180.0	180.0	169.4(3)
N(2)–M(1)–N(3)#2	98.6(2)	83.0(3)	95.5(2)
N(3)–M(1)–N(3)#2	180.0	180.0	78.8(4)

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

Table 2 Hydrogen bond lengths/Å and angles/° for **1**–**3**

D–H···A	*d*(H···A)	*d*(D···A)	<(DHA)
1			
N(1)-H(1A)···Se(2)#1	2.97	3.648(6)	133.0
N(1)-H(1B)···Se(3)#2	2.81	3.714(6)	172.3
N(2)-H(2)···Se(3)	2.84	3.677(6)	151.1
N(3)-H(3A)···Se(3)#3	2.71	3.502(6)	146.1
N(3)-H(3B)···Se(1)#1	3.03	3.787(6)	141.4
2			
N(1)-H(1A)···Se(1)#1	2.93	3.736(7)	150.3
N(1)-H(1B)···Se(3)#2	2.83	3.720(7)	170.5
N(2)-H(2)···Se(3)	2.84	3.668(7)	151.9
N(3)-H(3A)···Se(1)	3.04	3.796(6)	142.6
N(3)-H(3B)···Se(3)#2	2.73	3.505(6)	145.2
3			
N(1)-H(1A)···Se(3)	2.92	3.709(6)	145.6
N(1)-H(1B)···Se(3)#1	2.83	3.605(6)	144.6
N(2)-H(2A)···Se(3)#2	2.71	3.579(6)	160.8

Symmetry transformations used to generate equivalent atoms: For **1**: #1) −*x*, −*y*, −*z* + 1; #2) −*x* + 1, −*y*, −*z* + 1; #3) *x*−1, *y*, *z*. For **2**: #1) −*x*, −*y* + 1, −*z* + 1; #2) −*x* + 1, −*y* + 1, −*z* + 1. For **3**: #1) −*x* + 1/2, −*y* + 1/2, −*z* + 1; #2) −*x*, *y*, −*z* + 1/2

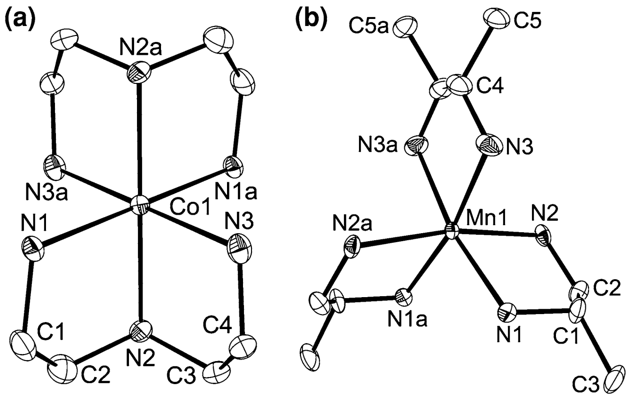

Fig. 2 Crystal structures of complexes $[Co(dien)_2]^{2+}$ (**a**) in **1** and $[Mn(dap)_3]^{2+}$ (**b**) in **3** with labeling scheme (50% probability ellipsoids). The hydrogen atoms are omitted for clarity

In **1**, all Se atoms of $[As_2Se_6]^{2-}$ are involved in intermolecular N–H···Se hydrogen bonding with adjacent $[Co(dien)_2]^{2+}$ cations. Each $[As_2Se_6]^{2-}$ anion contacts with four $[Co(dien)_2]^{2+}$ cations via hydrogen bonds, with N···Se distances of 3.502(6)–3.787(6) Å and N–H···Se angles of 133.0–172.3° (Table 2), which are consistent with the values reported in the literature [19, 21]. Through the N–H···Se hydrogen bonds, the $[As_2Se_6]^{2-}$ and $[Co(dien)_2]^{2+}$ ions are connected into a layer perpendicular to the *b* axis (Fig. 3). The layers are parallel to each other in the crystal structure (Fig. 4). A similar intermolecular hydrogen bonding structure is observed in compound **2** (Table 2). In **3**, the terminal Se(3) atom of $[As_2Se_6]^{2-}$ takes part in hydrogen bonding interaction with four adjacent $[Mn(dap)_3]^{2+}$ cations with N···Se distances of 3.579(6)–3.709(6) Å and N–H···Se angles of 144.6–160.8° (Table 2). The $[As_2Se_6]^{2-}$ and $[Mn(dap)_3]^{2+}$ ions are also connected into a layer perpendicular to the *b* axis trough the N–H···Se hydrogen bonds (Fig. 5). The layers are further connected into a 3-D network via the N–H···Se bonds. In the same layer, the neighboring $[As_2Se_6]^{2-}$ anions are linked into a chain via weak As···As secondary interaction. The As···As distance of 3.564 Å is shorter than twice the covalent radius of arsenic (2.0 Å) [26].

Several $[As_2Se_6]^{2-}$ salts have been prepared by the extraction method at room temperature with arsenic polyselenides as starting materials in the presence of different metal or organic cations. When $NaAs_2Se_3$ is extracted with 2.2.2-cryptand (1,10-diaza-4,7,13,16,21,24-hexaoxabicyclo[8.8.8] hexacosane) in en solvent, $[Na(2.2.2\text{-cryptand})]_2As_2Se_6$ was obtained [27]. The extraction of $AsSe_4$ in a saturated en solution of Et_4NBr gave $[Et_4N]_2As_2Se_6$ [28]. $[Ph_4P]_2As_2Se_6$ was obtained by the reaction of As_4Se_4 and Ph_4PCl in en/DMF (*N*,*N*-dimethylformamide) mixed solution [29]. The similar reaction in CH_3CN produced $[Ph_4P]_2As_2Se_6\cdot 2CH_3CN$ [30].

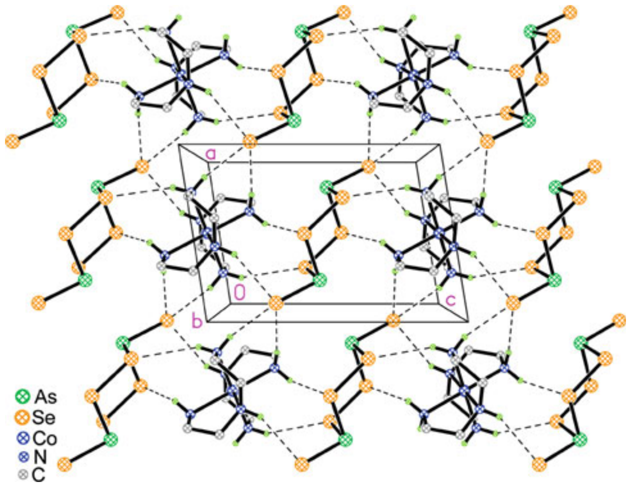

Fig. 3 A view of the layer constructed from $[As_2Se_6]^{2-}$ and $[Co(dien)_2]^{2+}$ ions via N–H···Se interactions (shown in *dashed lines*) in **1**. Hydrogen atoms of CH_2 groups are omitted for clarity

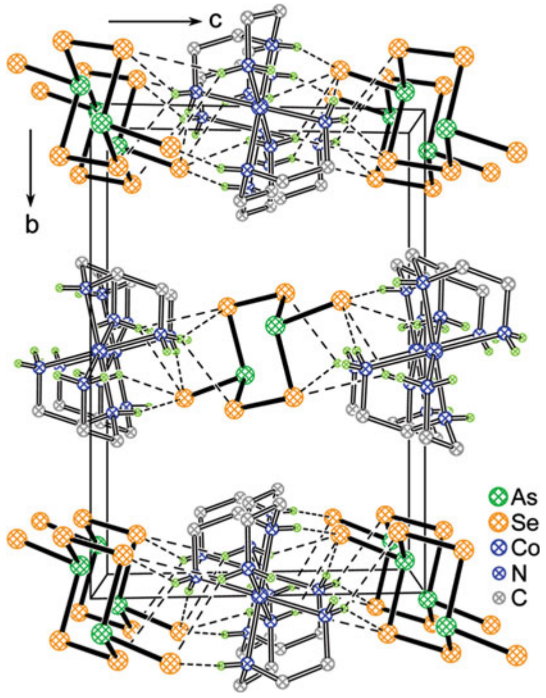

Fig. 4 Crystal packing of **1** viewed along *a* axis. Hydrogen atoms of CH_2 groups are omitted for clarity

In this work, three $[As_2Se_6]^{2-}$ compounds with transition metal complex cations as counterions, $[Co(dien)_2]As_2Se_6$, $[Ni(dien)_2]As_2Se_6$, and $[Mn(dap)_3]As_2Se_6$, were prepared by a solvothermal method with arsenic oxide, selenium, and transition metal chloride as starting materials in dien and dap solvents. The transition metal complex cations formed in the solvothermal reactions act as the counter cations to the $[As_2Se_6]^{2-}$ anion. The only examples of these transition metal polyselenidoarsenates reported before are $[Fe(en)_3]As_2Se_6$ and $[Mn(en)_3]As_2Se_6$ [22].

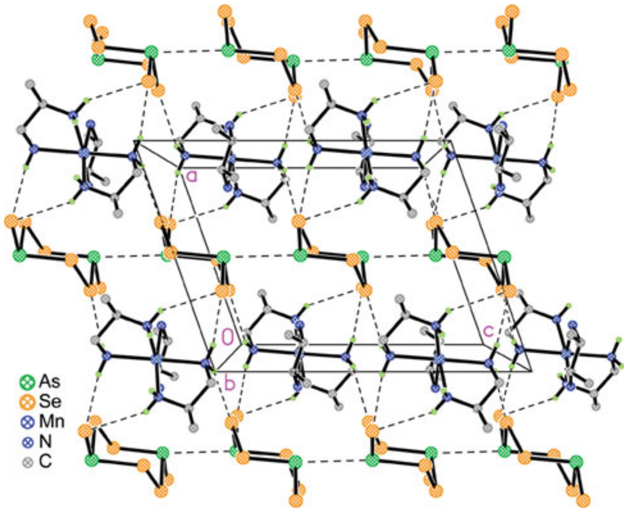

Fig. 5 A view of the layer constructed from $[As_2Se_6]^{2-}$ and $[Mn(dpa)_3]^{2+}$ ions via N–H···Se interactions (shown in *dashed lines*) in **3**. Hydrogen atoms of CH_2 groups are omitted for clarity

Thermal properties

Compounds **1** and **2** decompose in one step upon heating under nitrogen stream. The observed mass losses of 22.7% for **1** (Fig. 6a) and 22.5% for **2** are in accordance with the complete removal of all dien ligands (theoretical value 23.2% for **1** and **2**). Compound **3** decomposes in two steps with total mass loss of 24.2% (Fig. 6b), which matches with the removal of the dap ligands (theoretical value 24.7%).

Experimental

All chemicals for syntheses were commercially obtained from Aldrich and used as purchased. Elemental analyses (C, H, and N) were performed on a EA1110-CHNS-O elemental analyzer. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer in dry KBr discs in the 4,000–400 cm^{-1} range. Thermogravimetric analysis (TGA) was performed on a SDT 2960 apparatus and all the samples were heated under a nitrogen stream of 100 cm^3/min with a heating rate of 5 °C/min. The micropobe analysis by energy dispersive X-ray spectroscopy (EDXS) was performed on an Hitachi S-4700 spectrometer.

Bis(diethylenetriamine)cobalt(II) hexaselenidoarsenate (**1**, $C_8H_{26}As_2CoN_6Se_6$)

A mixture of 119 mg $CoCl_2 \cdot 6H_2O$ (0.5 mmol), 99 mg As_2O_3 (0.5 mmol), 237 mg Se (3 mmol), and 6 cm^3 diethylenetriamine was stirred for 30 min, then the mixture was sealed in a Teflon-lined autoclave with inner volume of 15 cm^3. The autoclave was heated at 140 °C for 4 days and then cooled to room temperature. The resulting yellow platelet crystals of **1** were filtered off, washed with ethanol, and dried at ambient temperature (42% yield based on As_2O_3). Elemental analysis results of the crystals are consistent with the stoichiometry of $C_8H_{26}As_2CoN_6Se_6$. EDXS analysis gave the heavy atom component of $CoAs_{2.12}Se_{6.18}$. IR (KBr): $\bar{\nu} = 3{,}378$ (s), 3,288 (s), 3,185 (s), 3,106 (s), 2,918 (s), 2,852 (s), 1,570 (s), 1,517 (s), 1,456 (s), 1,432 (m), 1,325 (m), 1,150 (w), 1,061 (m), 992 (w), 952 (m), 893 (m), 863 (w), 769 (w), 626 (w), 485 (m), 444 (m) cm^{-1}.

Bis(diethylenetriamine)nickel(II) hexaselenidoarsenate (**2**, $C_8H_{26}As_2N_6NiSe_6$)

A mixture of 119 mg $NiCl_2{\cdot}6H_2O$ (0.5 mmol), 99 mg As_2O_3 (0.5 mmol), 237 mg Se (3 mmol), and 6 cm^3 diethylenetriamine was stirred for 30 min, then the mixture was sealed in a Teflon-lined autoclave with inner volume of 15 cm^3. The autoclave was heated at 140 °C for 4 days and then cooled to room temperature. The resulting red block crystals of **2** were filtered off, washed with ethanol, and dried at ambient temperature (49% yield based on As_2O_3). Elemental analysis results of the crystals are consistent with the stoichiometry of $C_8H_{26}As_2N_6NiSe_6$. EDXS analysis gave the heavy atom component of $NiAs_{2.14}Se_{6.25}$. IR (KBr): $\bar{\nu} = 3{,}374$ (s), 3,298 (s), 3,195 (s), 3,112 (s), 2,928 (s), 2,861 (s), 1,567 (s), 1,512 (s), 1,388 (s), 1,322 (m), 1,265 (m), 1,148 (m), 1,071 (s), 1,022 (m), 971 (m), 952 (m), 942 (m), 895 (w), 810 (w), 671 (s), 591 (w), 563 (w), 493 (w), 466 (w) cm^{-1}.

Tris(1,2-diaminopropane)manganese(II)-hexaselenidoarsenate (**3**, $C_9H_{30}As_2MnN_6Se_6$)

A mixture of 99 mg $MnCl_2{\cdot}4H_2O$ (0.5 mmol), 99 mg As_2O_3 (0.5 mmol), 237 mg Se (3 mmol), and 6 cm^3 1,2-diaminopropane was stirred for 30 min, then the mixture was sealed in a Teflon-lined autoclave with inner volume of 15 cm^3. The autoclave was heated at 140 °C for 4 days and then cooled to room temperature. The resulting yellow block crystals of **3** were filtered off, washed with ethanol, and dried at ambient temperature (51% yield based on As_2O_3). Elemental analysis results of the crystals are consistent with the stoichiometry of $C_9H_{30}As_2MnN_6Se_6$. EDXS analysis gave the heavy atom component of $MnAs_{2.09}Se_{6.21}$. IR (KBr): $\bar{\nu} = 3{,}516$ (s), 3,452 (s), 3,280 (s), 3,273 (s), 3,180 (s), 2,922 (s), 2,880 (s), 1,634 (s), 1,568 (s), 1,477 (m), 1,447 (m), 1,383 (w), 1,319 (m), 1,283 (w), 1,246 (w), 1,133 (m), 1,089 (s), 1,011 (s), 975 (s), 971 (m), 889 (w), 789 (m), 675 (s), 640 (s), 618 (s), 517 (m), 446 (m) cm^{-1}.

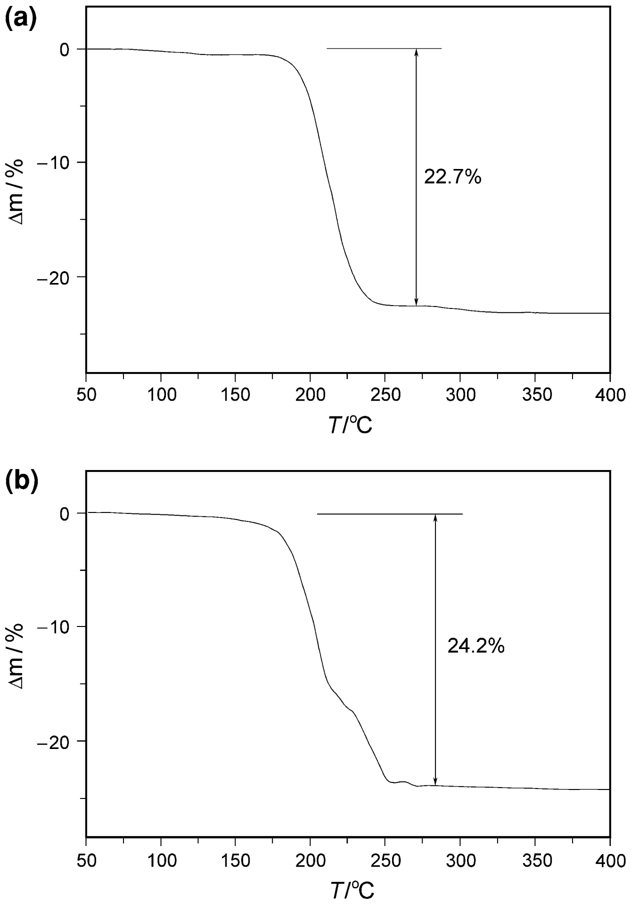

Fig. 6 Thermogravimetric analysis curves of compounds **1** (**a**) and **3** (**b**)

Structure determination

Intensities were collected on a Rigaku Saturn CCD diffractometer using ω-scan method with graphite monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71075$ Å) at −50(2) °C to a maximum 2θ value of 50.70° for **1** and **2** and 49.00° for **3**. An absorption correction was applied for all the compounds using multiscan. The structures were solved with direct methods using the program SHELXS-97 [37], and the refinement was performed against F^2 using the program SHELXL-97 [38]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters. Technical details of data acquisition and refinement results are summarized in Table 3.

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 807576, 807577, and 807578. These 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

Table 3 Crystallographic data and structure refinements for **1–3**

	1	**2**	**3**
Formula	$C_8H_{26}As_2CoN_6Se_6$	$C_8H_{26}As_2N_6NiSe_6$	$C_9H_{30}As_2MnN_6Se_6$
Formula weight	888.87	888.63	900.92
Dimensions/mm^3	0.45 × 0.16 × 0.12	0.25 × 0.20 × 0.17	0.22 × 0.20 × 0.20
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)
a/Å	7.2128(18)	7.226(2)	10.047(4)
b/Å	15.111(4)	14.993(5)	20.396(7)
c/Å	10.445(3)	10.468(3)	12.980(5)
$\beta/°$	99.110(8)	99.585(7)	109.373(4)
V/Å^3	1,124.1(5)	1,118.3(6)	2,509.2(15)
Z	2	2	4
T/K	223(2)	223(2)	223(2)
D_{calc}/g cm^{-3}	2.626	2.639	2.385
$F(000)$	826	828	1,684
μ/mm^{-1}	13.404	13.574	11.854
Max $2\theta/°$	50.70	50.70	50.00
Reflections collected	5,444	10,501	5,112
Independent reflections	2,043	2,042	2,210
R_{int}	0.0536	0.0600	0.0352
Parameters	107	107	110
R_1 and wR_2 [$I > 2\sigma(I)$]	0.0327, 0.0616	0.0343, 0.0705	0.0435, 0.1051
R_1 and wR_2 (all data)	0.0489, 0.0770	0.0569, 0.0855	0.0571, 0.1118
$\Delta\rho$/e Å^{-3}	−0.331/1.112	−0.951/0.714	−0.941/0.804
Goodness-of-fit	1.062	1.023	1.084

1EZ, UK; fax: +44-1223-336033, or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments We are grateful to the National Natural Science Foundation of P. R. China (NSFC, No. 20771077), and the Key Laboratory of Organic Synthesis of Jiangsu Province, Soochow University financial support.

References

1. Bedard RL, Vail LD, Milson ST, Flanigen EM (1988) US Patent 4,880,761
2. Bedard RL, Milson ST, Vail LD, Bennett JM, Flanigen EM (1989) Zeolite: facts, figures, future. Proceedings of 8th international zeolite conference. Elsevier, Amsterdam, p 375
3. Sheldrick WS, Wachhold M (1998) Coord Chem Rev 176:211
4. Stephan HO, Kanatzidis MG (1996) J Am Chem Soc 118: 12226
5. Stephan HO, Kanatzidis MG (1997) Inorg Chem 36:6050
6. Schur M, Bensch W (2002) Z Naturforsch B 57:1
7. Vaqueiro P, Chippindale AM, Powell AV (2004) Inorg Chem 43:7963
8. Kiebach R, Studt F, Näther C, Bensch W (2004) Eur J Inorg Chem 2553
9. Bensch W, Näther C, Stähler R (2001) Chem Commun 477
10. Stähler R, Mosel BD, Eckert H, Bensch W (2002) Angew Chem Int Ed 41:4487
11. Stähler R, Näther C, Bensch W (2001) Eur J Inorg Chem 1835
12. Kiebach R, Bensch W, Hoffmann RD, Pöttgen R (2003) Z Anorg Allg Chem 629:532
13. Stähler R, Bensch W (2001) Eur J Inorg Chem 3073
14. Schaefer M, Näther C, Lehnert N, Bensch W (2004) Inorg Chem 43:2914
15. Kiebach R, Warratz R, Näther C, Bensch W (2009) Z Anorg Allg Chem 635:988
16. Engelke L, Näther C, Leisner P, Bensch W (2008) Z Anorg Allg Chem 634:2959
17. Lichte J, Lühmann H, Näther C, Bensch W (2009) Z Anorg Allg Chem 635:2021
18. Chen Z, Wang RJ, Huang XY, Li J (2000) Acta Crystallogr C56:1100
19. Jia DX, Zhang Y, Zhao QX, Deng J (2006) Inorg Chem 45:9812
20. Jia DX, Zhao QX, Song LF, Zhang Y, Dai J (2006) Chinese J Struct Chem 25:1110
21. Jia DX, Zhao QX, Dai J, Zhang Y, Zhu QY (2006) Z Anorg Allg Chem 632:349
22. Fu ML, Guo GC, Liu X, Liu B, Cai LZ, Huang JS (2005) Inorg Chem Commun 8:18
23. Kromm A, Sheldrick WS (2008) Z Anorg Allg Chem 634:225
24. Kromm A, Sheldrick WS (2008) Z Anorg Allg Chem 634:121
25. Kromm A, Sheldrick WS (2008) Z Anorg Allg Chem 634:2948
26. Dean JA (1973) Lange's handbook of chemistry, 11th edn. McGraw-Hill, New York, p 3
27. Belin CHE, Charbonnel MM (1982) Inorg Chem 21:2504
28. Smith DM, Pell MA, Ibers JA (1998) Inorg Chem 37:2340
29. Ansari MA, Ibers JA, O'Neal SC, Pennington WT, Kolis JW (1992) Polyhedron 11:1877

30. Czado W, Müller U (1998) Z Anorg Allg Chem 624:239
31. Kromm A, Sheldrick WS (2007) Acta Cryst E63:m581
32. Keene FR, Searle GH (1972) Inorg Chem 11:148
33. Yoshikawa Y, Yamasaki K (1972) Bull Chem Soc Jpn 45:179
34. Mukherjee AK, Koner S, Ghosh A, Chaudhuri NR, Mukherjee M, Welch AJ (1994) J Chem Soc Dalton Trans 2367
35. Tatehata A, Muraida A (1998) Inorg Chem Commun 1:392
36. Rodríguez V, Gutiérrez-Zorrilla JM, Vitoria P, Luque A, Román P, Martínez-Ripoll M (1999) Inorg Chim Acta 290:57
37. Sheldrick GM (1997) SHELXS-97 Program for structure solution. University of Göttingen, Germany
38. Sheldrick GM (1997) SHELXL-97 Program for structure refinement. University of Göttingen, Germany