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Article

Mixed-Valent Selenidoantimonates(III,V) with Transition-Metal Complexes as Counterions: Solvothermal Syntheses and Characterization of $[M(dien)_2]_2Sb_4Se_9$ (M = Mn, Fe), $[Co(dien)_2]_2Sb_2Se_6$, and $[Ni(dien)_2]_2Sb_2Se_5$

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Novel selenidoantimonate compounds $[M(dien)_2]_2Sb_4Se_9$ [M = Mn (**1**), Fe (**2**)], $[Co(dien)_2]_2Sb_2Se_6$ (**3**), and $[Ni(dien)_2]_2Sb_2Se_5$ (**4**) (dien = diethylenetriamine) were solvothermally synthesized and characterized. The unique features of compounds **1**–**3** are the mixed-valent anionic structures constructed by the $Sb^{III}Se_3$ trigonal pyramid and $Sb^{V}Se_4$ tetrahedron. Three $Sb^{III}Se_3$ pyramids share common corners, forming a heterocyclic Sb_3Se_6 moiety, and the Sb_3Se_6 moieties are further connected with $Sb^{V}Se_4$ tetrahedra to form the novel one-dimensional $[Sb_4Se_9{}^{4-}]_n$ anionic chain in **1** and **2**. The discrete $[Sb_2Se_6]^{4-}$ anion in **3** is formed by an $Sb^{III}Se_3$ trigonal pyramid and an $Sb^{V}Se_4$ tetrahedron sharing a common corner. The $[Sb_2Se_5]^{4-}$ anion in **4** is composed of two $Sb^{III}Se_3$ trigonal pyramids connected in the same manner as the $[Sb_2Se_6]^{4-}$ anion. The mixed-valent $[Sb_4Se_9{}^{4-}]_n$ and $[Sb_2Se_6]^{4-}$ anions were not observed before. The synthesis and solid-state structural studies of the title compounds show that the transition-metal complexes exhibit different structure-directing effects on the formation of selenidoantimonates in dien. Extensive N–H···Se hydrogen bonds are observed between cations and anions in compounds **1**–**4**, resulting in three-dimensional network structures. Optical and thermal properties of the compounds are reported.

Introduction

Since the microporous thiogermanates and thiostannates were prepared by a hydrothermal method in solution in 1989,[1] the number of new chalcogenidometalates synthesized under hydro- or solvothermal conditions has increased dramatically. The mild solvothermal reaction in amine has proven to be a versatile route for the synthesis of heavy-metal chalcogenides containing main-group elements Ge, Sn, As, and Sb.[2] In the case of chalcogenidoantimonates, since the cobalt antimony sulfide $[Co(en)_3]CoSb_4S_8$ (en = ethylenediamine)[3] was prepared, a large number of new and exciting thioantimonates(III) containing transition metals have been synthesized using transition-metal amino complexes as structure-directing agents through the solvothermal route.[4] The structures of these thioantimonates(III) are characterized by the condensation of the $Sb^{III}S_m$ ($m = 3-6$)[2b] building units to form a series of $Sb^{III}{}_xS_y{}^{z-}$ polyanions. It is believed that the rich structural diversity of thioantimonates(III) is due to the stereochemically active lone pair.[5] We note that the similar architectural feature is observed in thiosalts of As.[2a−d] However, the thioantimonates(V) are seldom interconnected to form a polyanion and always exist as an isolated tetrahedral $[Sb^{V}S_4]^{3-}$ anion[6] except that in some cases $[Sb^{V}S_4]^{3-}$ is bound to metal cations.[7] Compound $[Ni(dien)_2]_2Sb_4S_9$[8] is the only example of the thioantimonates containing Sb^{III} and Sb^{V}.

On the other hand, compared with the overwhelming thioantimonates, the selenidoantimonates containing transition metals are less explored under mild solvothermal

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conditions. The limited examples include selenidoantimonates(III) $[Fe(en)_3]_2Sb_2Se_5$,[9] $Cs_2Cu_2Sb_2Se_5$,[10] $Cu_2SbSe_3{\cdot}0.5en$,[11] and $Cu_2SbSe_3{\cdot}en$[11] and selenidoantimonates(V) $[M(en)_3(Hen)]SbSe_4$ (M = Ge, Mn, Fe),[12] $[Ga(en)_3]SbSe_4$,[13] $[Mn(en)_3]_2[Mn_4(en)_9(SbSe_4)_4]{\cdot}2H_2O$,[14] $[Mn(en)_3][Mn_2(SbSe_4)_2(en)_4(H_2O)]$,[15] and $[Ln(en)_4(SbSe_4)]$ (Ln = La, Nd).[16] However, the coexistence of Sb^{III} and Sb^{V} within a polymeric selenidoantimonate anion has not been observed yet. We now report the solvothermal preparation of four novel selenidoantimonates $[Mn(dien)_2]_2Sb_4Se_9$ (**1**), $[Fe(dien)_2]_2Sb_4Se_9$ (**2**), $[Co(dien)_2]_2Sb_2Se_6$ (**3**), and $[Ni(dien)_2]_2Sb_2Se_5$ (**4**). To the best of our knowledge, the mixed-valent anions $[Sb_4Se_9]^{4-}$ and $[Sb_2Se_6]^{4-}$ are the first two examples of selenidoantimonates with coexisting trivalent and pentavalent Sb atoms.

Experimental Section

Materials and Methods. All analytical-grade chemicals were obtained commercially and were used without further purification. Elemental analysis was conducted on a MOD 1106 elemental analyzer. Fourier transform IR 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 $\alpha/S = (1 - R)^2/2R$.[17] Thermoanalytical measurements was performed using a thermogravimetric analysis−differential scanning calorimetry (TGA−DSC) microanalyzer of SDT 2960, and all of the samples were heated under a N_2 stream of 100 mL min^{-1} with a heating rate of 5 °C min^{-1}. Powder X-ray diffraction (XRD) patterns were collected on a D/MAX-3C diffractometer using graphite-monochromatized Cu Kα radiation ($\lambda = 1.5406$ Å).

Syntheses. All compounds were synthesized in diethylenetriamine (dien) by the solvothermal method. In a typical synthetic procedure, reactants in a certain molar ratio were dispersed in dien under stirring, and then the mixture was loaded into a Teflon-lined stainless steel autoclave with an inner volume of 15 mL. The sealed autoclave was heated at 140 °C for 7 days. After cooling to ambient temperature, crystals were filtered off, washed with ethanol and ether, and stored under vacuum.

$[Mn(dien)_2]_2Sb_4Se_9$ (1). The red platelet crystals of **1** were obtained by the reaction of $MnCl_2$ (0.126 g, 1 mmol), Sb (0.122 g, 1.0 mmol), and Se (0.237 g, 3 mmol) in 2 mL of dien with a yield of about 50% based on Sb. Besides the title compound, an unknown amorphous phase was obtained. Anal. Calcd for $C_{16}H_{52}N_{12}Se_9Mn_2Sb_4$: C, 11.17; H, 3.05; N, 9.77. Found: C, 10.95; H, 3.24; N, 9.52. IR bands (KBr, cm^{-1}): 3419 (s), 3296 (s), 3203 (vs), 3110 (vs), 2886 (s), 1582 (m), 1565 (m), 1459 (m), 1326 (m), 1226 (w), 1151 (m), 108o (m), 1027 (m), 972 (m), 894 (w), 818 (w), 771 (w), 687 (w), 562 (m), 463 (m).

$[Fe(dien)_2]_2Sb_4Se_9$ (2). Red platelet crystals of **2** were obtained by the reaction of $FeCl_2$ (0.127 g, 1 mmol), Sb (0.122 g, 1.0 mmol), and Se (0.237 g, 3 mmol) in 2 mL of dien with a yield of about 45% based on Sb. Colorless $[Fe(dien)_2]Cl_2$ was identified as the byproduct. Anal. Calcd for $C_{16}H_{52}N_{12}Se_9Fe_2Sb_4$: C, 11.16; H, 3.04; N, 9.76. Found: C, 10.87; H, 3.22; N, 9.56. IR bands (KBr, cm^{-1}): 3404 (s), 3325 (vs), 3195 (vs), 3087 (s), 2886 (vs), 1652 (m), 1574 (m), 1459 (m), 1219 (m), 1212 (m), 1135 (w), 1081 (m), 972 (m), 895 (w), 818 (w), 764 (w), 695 (w), 563 (m), 465 (m).

$[Co(dien)_2]_2Sb_2Se_6$ (3). Orange-red block crystals of **3** were obtained by the reaction of $CoCl_2$ (0.130 g, 1 mmol), Sb (0.122 g, 1.0 mmol), and Se (0.237 g, 3 mmol) in 2 mL of dien with a yield of about 65% based on Sb. Anal. Calcd for $C_{16}H_{52}N_{12}Se_6Co_2Sb_2$: C, 15.40; H, 4.20; N, 13.47. Found: C, 15.32; H, 4.12; N, 13.34. IR bands (KBr, cm^{-1}): 3427 (s), 3296 (m), 3203 (vs), 3110 (vs), 2917 (m), 2871 (s), 1582 (s), 1459 (s), 1327 (m), 1296 (w), 1269 (w), 1229 (w), 1145 (m), 1071 (s), 1025 (s), 979 (s), 946 (s), 895 (w), 894 (m), 828 (w), 676 (s), 564 (m), 469 (m).

$[Ni(dien)_2]_2Sb_2Se_5$ (4). Orange-red block crystals of **3** were obtained by the reaction of $NiCl_2$ (0.130 g, 1 mmol), Sb (0.122 g, 1.0 mmol), and Se (0.237 g, 3 mmol) in 2 mL of dien with a yield of about 70% based on Sb. Anal. Calcd for $C_{16}H_{52}N_{12}Se_5Ni_2Sb_2$: C, 16.45; H, 4.48; N, 14.38. Found: C, 16.34; H, 4.25; N, 14.16. IR bands (KBr, cm^{-1}): 3416 (s), 3326 (m), 3201 (vs), 3098 (vs), 2885 (s), 1576 (s), 1459 (s), 1327 (m), 1269 (w), 1149 (m), 1078 (s), 1026 (s), 974 (s), 895 (w), 894 (m), 828 (w), 676 (s), 566 (m), 466 (m).

X-ray Crystal Structure Determinations. The intensity data were collected on a Rigaku Mercury CCD diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å) at 193(2) K. The crystal structures were solved by direct methods

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

	1	**2**	**3**	**4**
empirical formula	$C_{16}H_{52}N_{12}Se_9Mn_2Sb_4$	$C_{16}H_{52}N_{12}Se_9Fe_2Sb_4$	$C_{16}H_{52}N_{12}Se_6Co_2Sb_2$	$C_{16}H_{52}N_{12}Se_5Ni_2Sb_2$
fw	1720.22	1722.04	1247.82	1168.42
color of cryst	red	red	orange-red	orange
cryst dimens, mm^3	0.30 × 0.22 × 0.07	0.30 × 0.19 × 0.07	0.30 × 0.16 × 0.14	0.24 × 0.20 × 0.18
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$	$P2_1$	$P2_1/n$
a, Å	11.8398(10)	11.8107(8)	9.8063(12)	9.2322(16)
b, Å	11.8284(7)	11.6077(8)	14.4563(18)	14.604(2)
c, Å	31.099(3)	31.955(2)	12.8319(12)	12.989(2)
β, deg	90.00	95.420(2)	90.585(4)	90.00
V, Å^3	4355.2(6)	4361.3(5)	1819.0(4)	1751.1(5)
Z	4	4	2	2
T, K	193(2)	193(2)	193(2)	193(2)
calcd density, Mg m^{-3}	2.623	2.623	2.278	2.216
abs coeff, mm^{-1}	10.558	10.630	8.397	7.810
F(000)	3168	3176	1184	1120
2θ(max), deg	50.70	54.96	50.70	54.96
total reflns collected	42 888	46 412	18 179	19 369
unique reflns	7962 ($R_{int} = 0.0644$)	9979 ($R_{int} = 0.0550$)	6343 ($R_{int} = 0.0389$)	3999 ($R_{int} = 0.0390$)
no. of param	390	387	345	182
R1 [$I > 2\sigma(I)$]	0.0406	0.0497	0.0317	0.0403
wR2 (all data)	0.0915	0.1032	0.0675	0.0834
GOF on F^2	1.116	1.149	1.072	1.121

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[M(dien)_2]^{2+}$ Anions in **1**−**4**

	1 (M = Mn)	**2** (M = Fe)	**3** (M = Co)	**4** (M = Ni)
M1−N	2.244(9)−2.308(9)	2.215(6)−2.263(6)	2.133(7)−2.178(7)	2.085(4)−2.133(4)
M2−N	2.259(9)−2.373(8)	2.205(6)−2.262(6)	2.143(6)−2.195(6)	
N−M1−N (cis)	75.2(3)−124.0(3)	77.2(2)−111.7(2)	80.7(3)−102.9(3)	82.10(16)−97.93(15)
N−M1−N (trans)	145.7(3)−156.2(3)	158.5(3)−165.8(3)	174.0(3)−177.3(3)	178.45(16)−179.74(18)
N−M2−N (cis)	74.7(3)−131.7(3)	76.3(2)−109.9(2)	81.2(2)−100.5(2)	
N−M2−N (trans)	145.0(3)−150.9(3)	161.5(3)−169.1(3)	177.2(2)−179.2(2)	

using the *SHELXS-97* program[18] and refined structures by a full-matrix least-squares procedure using the *SHELXL-97* program.[19] All of the non-H atoms were refined anisotropically. The atoms C15 and C16 in compound **2** are disordered, and the occupancies of the disordered atoms are assigned as 52% and 48% for C/C′. In **4**, the Sb1 and Se1 atoms are also disordered with the occupancies of 50% and 50% for both Sb/Sb′ and Se/Se′. The H atoms were added geometrically and refined using the riding model. Crystallographic, experimental, and analytical data for the title compounds are listed in Table 1.

Results and Discussion

Structures of Cations. The counterions to balance the charge of binary selenidoantimonate anions in compounds **1**−**4** are transition-metal complex cations with tridentate dien ligands. In **1**−**3**, there are two crystallographically independent $[M(dien)_2]^{2+}$ (M = Mn, Fe, Co) cations in the asymmetric unit, respectively. Both $[Mn(dien)_2]^{2+}$ and $[Fe(dien)_2]^{2+}$ exhibit the same conformation of *u-fac*, whereas the $[Co(dien)_2]^{2+}$ ion is in a *s-fac* conformation. The conformation of the $[Ni(dien)_2]^{2+}$ ion in **4** is the same as that of the $[Co(dien)_2]^{2+}$ ion. The geometric isomers of transition-metal complexes with dien ligands have been intensively studied before.[20] All of these transition-metal ions are coordinated by six N atoms of two dien ligands and are in a distorted octahedral environment, as is evidenced by the axial N−M−N angles deviating from 180° (Table 2). The coordination octahedron of *u-fac* is more distorted than that of *s-fac* (Table 2). We noted that the $[Co(dien)_2]^{2+}$ ion has not been reported until now although dien complexes of transition-metal ions have been known for a long time. The Co−N distances of $[Co(dien)_2]^{2+}$ ranging from 2.133(7) to 2.195(6) Å are, as expected, longer than those of the $[Co(dien)_2]^{3+}$ ions, for example, Co−N distances 1.956(8)−1.987(7) Å in $[Co(dien)_2]Al_3P_4O_{16}{\cdot}3H_2O$[21] and 1.9498(19)−1.969(2) Å in $[Co(dien)_2](VO_3)_3{\cdot}H_2O$.[22] The M−N distances of Mn−N, Fe−N, and Ni−N are similar to the literature values for $[M(dien)_2]^{2+}$ complexes, respectively.[4h,i,m,n,23] Variation of the M−N (M = Mn, Fe, Co, Ni) bond distances in **1**−**4** (Table 2) is in accordance with the evolution of the ionic radii going from Mn^{2+} to Ni^{2+}.[24]

Structures of Anions. The new compound **1** crystallizes in the orthorhombic space group $P2_12_12_1$, and **2** crystallizes in the monoclinic space group $P2_1/c$. However, they exhibit very similar molecular structures. The one-dimensional polymeric structures of **1** and **2** are composed of unusual

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Table 3. Selected Bond Distances (Å) and Angles (deg) for Anions in **1**−**4**

	1	**2**	**3**	**4**
$Sb^{III}-Se$	2.4696(12)−3.0002(11)	2.4679(9)−2.9349(9)	2.4951(9)−2.6627(9)	2.4722(8)−2.6181(11)
$Sb^{V}-Se$	2.4413(12)−2.5114(11)	2.4232(9)−2.5154(9)	2.4266(9)−2.5517(8)	
$Se-Sb-Se^{a}$	96.50(4)−100.53(4)	93.66(3)−102.43(3)	95.27(3)−103.20(3)	98.34(3)−104.89(3)
$Se-Sb-Se^{b}$	104.84(4)−112.43(4)	105.63(3)−113.59(3)	105.50(3)−112.99(4)	
$Se-Sb-Se^{c}$	90.02(3)−174.61(4)	87.85(2)−175.27(3)		
Sb−Se1−Sb	94.59(4)	94.98(3)	103.71(3)	95.53(4)

[a] Angles for $Sb^{III}Se_3$ trigonal pyramids. [b] Angles for $Sb^{V}Se_4$ tetrahedra in **1**−**3**. [c] Angles for ψ-$Sb^{III}Se_4$ trigonal bipyramids in **1** and **2**.

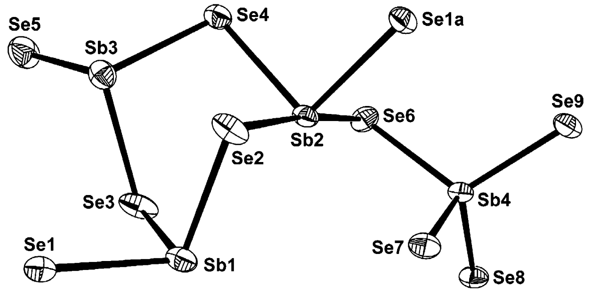

Figure 1. Structure of the $[Sb_4Se_9]^{4-}$ anion in **1** with labeling. Displacement ellipsoids are shown at the 50% level.

$[Sb_4Se_9{}^{4-}]_n$ anionic chains, which are constructed by Sb_3Se_6 and $SbSe_4$ units (Figure 1). The heterocyclic Sb_3Se_6 moiety is formed by three $Sb^{III}Se_3$ trigonal pyramids (Sb1, Sb2, and Sb3) sharing common corners. The interconnection of the $Sb^{V}Se_4$ tetrahedron with the Sb_3Se_6 unit through coordination of Se(6) to Sb(2) yields the one-dimensional $[Sb_4Se_9{}^{4-}]_n$ anionic chain. In the Sb_3Se_6 unit, the coordination number of the Sb1 and Sb3 atoms is 3, with $Sb^{III}-Se$ bond lengths ranging from 2.4696(12) to 2.6177(12) Å for **1** and from 2.4679(9) to 2.6381(9) Å for **2**. The interatomic distances and angles (Table 3) are in the typical range of those for the well-known $SbSe_3$ trigonal pyramid reported in the literature.[9,25] The connection of the $Sb^{V}Se_4$ unit enhances the coordination number of Sb2 from 3 to 4, leading to the formation of a ψ trigonal bipyramid (ψ-$SbSe_4$) with two short [2.6203(11) and 2.6314(11) Å for **1** and 2.5860(8) and 2.6187(9) Å for **2**] and two longer [2.8087(11) and 3.0002(11) Å for **1** and 2.8424(9) and 2.9349(9) Å for **2**] Sb−Se bonds. We note that the two long Sb−Se bonds (Sb2−Se2 and Sb2−Se6) are nearly trans to each other in the distorted ψ-$SbSe_4$ trigonal bipyramid (Figure 1), as is evidenced by the Se2−Sb2−Se6 angle [174.61(4)° for **1** and 175.27(3)° for **2**]. In the $Sb4^{V}Se_4$ tetrahedron, the $Sb^{V}-Se$ distances scattering from 2.4413(12) to 2.5114(11) Å in **1** and from 2.4232(9) to 2.5144(9) Å in **2** are significantly shorter than those of the $Sb^{III}-Se$ bonds (Table 3). The $Sb^{V}-Se$ interatomic distances and Se−Sb−Se angles (Table 3) are in good agreement with those observed in other compounds containing tetrahedral $Sb^{V}Se_4{}^{3-}$ anions.[12a,b,13−15]

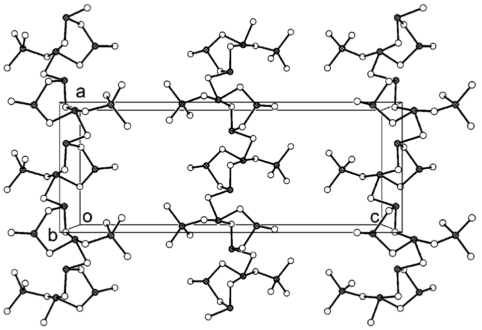

Figure 2. Crystal structure of $[Sb_4Se_9{}^{4-}]_n$ anionic chains in **1** viewed along the *b* axis.

The $[Sb_4Se_9{}^{4-}]_n$ anionic chains in **1** are stacked parallel to each other along the *a* axis (Figure 2). The $Sb^{V}Se_4$ tetrahedra are located at the exterior of the central Sb_3Se_6 backbone of the chain. Between the $[Sb_4Se_9{}^{4-}]_n$ chains, large pockets are created by the dangling $SbSe_4$ groups (Figure 2) that host the cations (see Figure S1 in the Supporting Information), showing the structure-directing effect of the $[Mn(dien)_2]^{2+}$ complex cations. Between the $[Sb_4Se_9]^{4-}$ unit and the $[Mn(dien)_2]^{2+}$ cations, 16 short intermolecular N−H···Se distances, with H···Se distances varying from 2.61 to 3.00 Å and N−H···Se angles between 131.7 and 170.3°, are observed, indicating weak hydrogen bonding (see Figure S1 in the Supporting Information). The H···Se lengths and N−H···Se angles are consistent with the values in the literature.[16,26] Similar hydrogen bonds are observed in compound **2**. Although hydrogen-bonding interactions are generally weak, they contribute to the stability of the structures and are important for the determination of the crystal packing.

As mentioned above, in the presence of transition-metal complex ions as structure-directing agents, the $Sb^{III}S_m$ units exhibit excellent flexibility in the condensation reactions to form a series of $[Sb_xS_y]^{z-}$ polymeric anions under the solvothermal conditions. The examples of thioantimonate polymeric anions include one-dimensional anions $[Sb_2S_4{}^{2-}]_n$,[4a−c] and $[Sb_4S_7{}^{2-}]_n$,[4c−f] two-dimensional anions $[Sb_2S_4{}^{2-}]_n$,[4a] $[Sb_4S_7{}^{2-}]_n$,[4g] $[Sb_6S_{10}{}^{2-}]_n$,[4h] and $[Sb_{22}S_{42}{}^{18-}]_n$,[4i] and three-dimensional anions $[Sb_{12}S_{21}{}^{6-}]_n$[4g] and $[Sb_{12}S_{19}{}^{2-}]_n$.[4j] However, the $Sb^{III}Se_x$ units seem to be less facile in the formation of a binary $[Sb_xSe_y]^{z-}$ polymeric anion in the presence of transition-metal complexes. The $[Sb_4Se_9{}^{4-}]_n$ ions in **1** and **2** are rare examples of polymeric selenidoantimonate containing transition-metal complexes. We note that the polymeric $[Sb_xSe_y]^{z-}$ anions prepared in the presence of alkali (and alkaline-earth) and organic cations have been known

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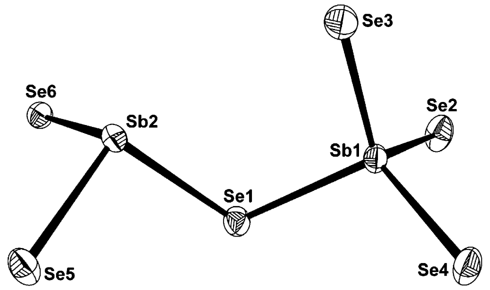

Figure 3. Structure of the $[Sb_2Se_6]^{4-}$ anion in **3** with labeling. Displacement ellipsoids are shown at the 50% level.

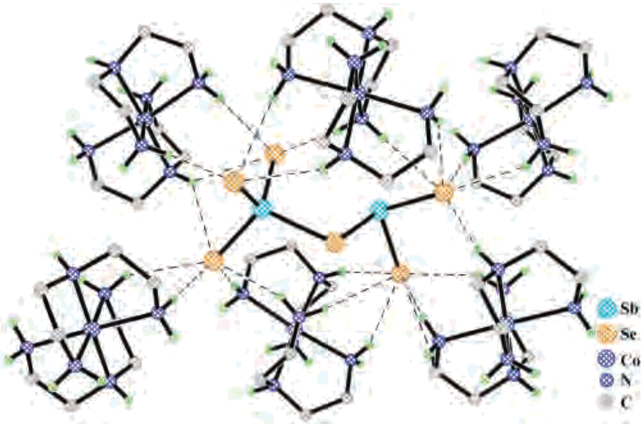

Figure 4. View of intermolecular N−H···Se hydrogen-bonding interactions in **3**. H atoms of C−H are omitted for clarity.

for a long time, such as $[Sb_3Se_5^{-}]_n$,[27] $[Sb_4Se_8^{2-}]_n$,[28] $[Sb_5Se_9^{3-}]_n$,[29] and $[Sb_{12}Se_{20}]^{4-}$.[25c] The polymeric selenidoantimonate structures are also observed in the multinary selenidoantimonate compounds, such as $Cs_2Cu_2Sb_2Se_5$,[10] Cu_2SbSe_3·0.5en,[11] and Cu_2SbSe_3·en.[11]

In **3**, the anionic dimer $[Sb_2Se_6]^{4-}$ is formed by an $Sb^{III}Se_3$ trigonal pyramid and an $Sb^{V}Se_4$ tetrahedron sharing a common corner (Figure 3). The Sb−Se bond lengths in the $Sb^{III}Se_3$ unit range from 2.4951(9) (Sb2−Se5) to 2.6627(9) (Sb2−Se1) Å, with Se−Sb−Se angles ranging from 95.27(3) to 103.20(3)° (Table 3). The Sb^{III}−Se distances, as well as the angles, are comparable with those of $Sb^{III}Se_3$ trigonal pyramids in **1** and **2**, respectively. The Sb^{V}−Se interatomic distances ranging from 2.4266(9) to 2.5517(8) Å and the Se−Sb−Se angles varying from 105.50(3) to 112.99(4)° (Table 3) are in good agreement with those of the $Sb^{V}Se_4$ unit in compounds **1** and **2**, and again the Sb^{V}−Se distances are shorter than those of the Sb^{III}−Se bonds. In the crystal structure of **3**, all five terminal Se atoms of the $[Sb_2Se_6]^{4-}$ anion are involved in hydrogen bonds to H atoms with six $[Co(dien)_2]^{2+}$ cations (Figure 4), with H···Se distances between 2.49 and 3.03 Å and N−H···Se angles between 139.3 and 178.2°. The intermolecular hydrogen-bonding contacts lead to a three-dimensional arrangement of cations and anions (see Figure S2 in the Supporting Information).

Several dimeric anions of selenidoantimonate(III) have been isolated and characterized so far. The $[Sb_2Se_4]^{2-}$ [25d] anion is formed by two edge-sharing $Sb^{III}Se_3$ trigonal pyramids, while the $[Sb_2Se_5]^{4-}$ [9] anion is composed of two corner-sharing $Sb^{III}Se_3$ trigonal pyramids. However, the dimeric $[Sb_2Se_6]^{4-}$ anion, which is built up by a $Sb^{III}Se_3$ trigonal pyramid and a $Sb^{V}Se_4$ tetrahedron, has never been observed before. It is a new species of binary selenidoantimonate anions. It is very different from the known Sb_2Se_6 species in compound $[K(2.2.2\text{-cryptand})]_2[Sb_2Se_6]$,[25e] in which the $[Sb_2Se_6]^{2-}$ anion contains two Sb^{III} centers and is constructed by two trigonal-pyramidal $Sb^{III}Se_3$ units joined through two Se−Se bonds forming a six-membered Sb_2Se_4 ring.

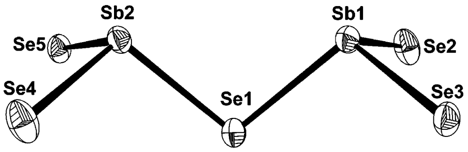

Figure 5. Structure of the $[Sb_2Se_5]^{4-}$ anion in **4** with labeling. Displacement ellipsoids are shown at the 50% level.

Because there are no polyselenide units in compounds **1**−**3**, formal bond valence sums[30] are consistent with an oxidation state of 3+ for three Sb atoms (Sb1, Sb2, and Sb3) and an oxidation state of 5+ for one Sb atom (Sb4) for the $[Sb_4Se_9]^{4-}$ anion in compounds **1** and **2** and an oxidation state of 3+ for one Sb atom and an oxidation state of 5+ for another Sb atom for the $[Sb_2Se_6]^{4-}$ anion in compound **3**. Mixed-valent Sb atoms similar to those of the $[Sb_4Se_9]^{4-}$ anion have been observed in the thio analogue $[Sb_4S_9]^{4-}$.[8] The selenidoantimonate anions composed of mixed-valent $[Sb^{III}Se_3]^{3-}$ and $[Sb^{V}Se_4]^{3-}$ units are rare. Compounds **1**−**3** are the only phases synthesized by the solvothermal method that exhibit such mixed oxidation states of the Sb atoms.

The structure of the anionic dimer $[Sb_2Se_5]^{4-}$ in **4** is depicted in Figure 5. It is composed of two $Sb^{III}Se_3$ trigonal pyramids sharing a common corner. The Sb1 and Se1 atoms are disordered with occupancies of 50% and 50% for both Sb/Sb′ and Se/Se′. The Sb−Se bond distances spread from 2.4722(8) to 2.6181(11) Å, and the Se−Sb−Se angles range from 98.34(3) to 104.89(3)° (Table 3). The Sb−Se_t(terminal) bond distances [av Sb−Se_t: 2.4984(8) Å] are, as expected, shorter than those of Sb−Se_b(bridging) [av Sb−Se_b: 2.6152(11) Å]. The Sb−Se bond distances and Se−Sb−Se angles are in good agreement with those of the literature.[9,25] The arrangement of the **4** molecules within the crystal structure is shown in Figure 6. The $[Sb_2Se_5]^{4-}$ anions are stacked in columns parallel to the *a* axis. Every four $[Sb_2Se_5]^{4-}$ columns form a one-dimensional channel in which $[Ni(dien)_2]^{2+}$ cations are located. Extensive N−H···Se hydrogen bonds are also observed between cations and anions.

Compounds **1**−**4** are synthesized under conditions similar to those in the dien solvent but have different anionic structures of $[Sb_4Se_9]^{4-}$, $[Sb_2Se_6]^{4-}$, and $[Sb_2Se_5]^{4-}$. This implies that the transition-metal complex cations $[M(dien)_2]^{2+}$ (M = Mn, Fe, Co, Ni), which are formed in situ, exhibit different structure-directing effects on the formation of

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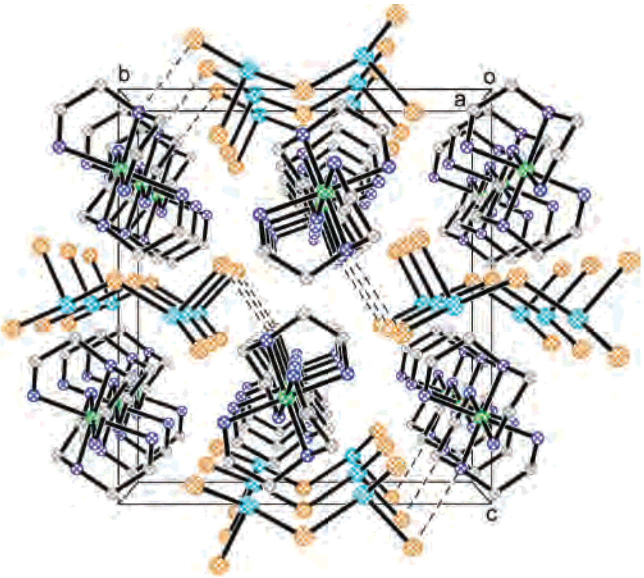

Figure 6. Packing of the molecules of **4** with a view along the *a* axis. H atoms are omitted for clarity.

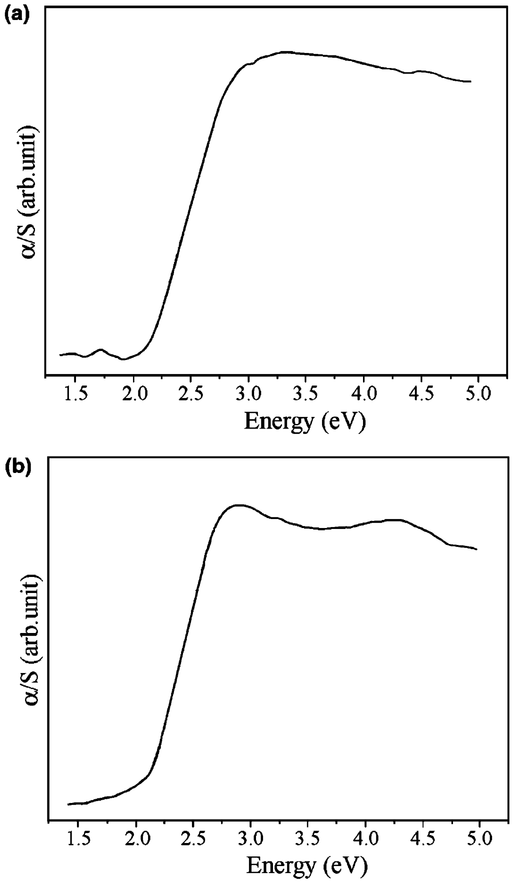

Figure 7. Optical absorption spectra of **1** (a) and **2** (b).

selenidoantimonates under solvothermal conditions. The size matching and N−H···Se hydrogen bonding with $[M(dien)_2]^{2+}$ complexes might play important roles in the formation and stabilization of the binary selenidoantimonate anions. The intriguing structure-directing effects of transition-metal complexes are commonly observed in the solvothermal synthesis of thioantimonates in amine solutions. Templated by transition-metal complexes, a large number of oligomeric or polymeric $[Sb_xS_y]^{z-}$ anions have been obtained.[4]

Optical Properties. The optical absorption spectra of compounds **1** and **2** show well-defined abrupt absorption edges from which the band gaps can be estimated: 2.08 eV for **1** and 2.14 eV for **2** (Figure 7). The band gaps suggested that compounds **1** and **2** are semiconductors. Both band gaps are larger than those of layered selenidoantimonate(III) compounds $Cs_2Cu_2Sb_2Se_5$ (1.2−1.3 eV),[10] Cu_2SbSe_3·0.5en (1.58 eV),[11] and Cu_2SbSe_3·en (1.61 eV).[11]

Thermal Properties. Thermal stabilities of compounds **1**−**3** are measured in the 50−400 °C range by the TGA−DSC method under a N_2 atmosphere. TGA curves show that all of the compounds decompose in a single step with mass losses of 23.5% for **1**, 23.6% for **2**, and 32.6% for **3**, which roughly corresponds with the loss of four dien ligands (theoretical values: 24.0% for **1**, 24.0% for **2**, and 33.1% for **3**) (see Figures S3−S5 in the Supporting Information). Decomposition is accompanied by strong endothermic peaks at temperatures of 228, 231, and 237 °C in the DSC curves for compounds **1**−**3**, respectively. An unknown phase and crystalline Sb_2Se_3 (JCPDS No. 15-861) were observed by the XRD pattern in the dark-gray sample of **1** obtained after heating to 400 °C (Figure S6 in the Supporting Information). In the XRD pattern of the residue of compound **3**, crystalline $CoSb_2Se_4$ (JCPDS No. 38-990) can be identified (Figure S7 in the Supporting Information).

Conclusion

In summary, novel binary selenidoantimonate anions, $[Sb_4Se_9]^{4-}$, $[Sb_2Se_6]^{4-}$, and $[Sb_2Se_5]^{4-}$, have been isolated from the dien solvent in the presence of transition metals by the solvothermal method. The synthesis and solid-state structural studies of **1**−**4** in the paper show that the transition-metal complex cations, $[M(dien)_2]^{2+}$ (M = Mn, Fe, Co, Ni), exhibit different influences on the formation of selenidoantimonates under solvothermal conditions. The special features of the structures of compounds **1**−**3** are the coexistence of Sb^{III} and Sb^{V} within a selenidoantimonate anion. The three compounds are the first examples of selenidoantimonates containing mixed-valent Sb atoms.

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Supporting Information Available: X-ray crystallographic files in CIF format for **1**−**4**, figures of hydrogen bonding, tables of fractional atomic coordinates, TGA−DSC curves, and powder XRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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