

REGULAR ARTICLE

Solvothermal syntheses, crystal structures, optical and thermal properties of new selenidogermanate and polyselenidogermanate

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Abstract. New selenidogermanate salts $[\text{NH}_4]_2[\text{H}_2\text{N}(\text{CH}_3)_2]_2\text{Ge}_2\text{Se}_6$ (**1**) and $[\text{Ni}(\text{dien})_2]_2\text{Ge}_2\text{Se}_5(\text{Se}_2)$ (**2**) (dien = diethylenetriamine), and a selenidogermanate complex $[\{\text{Ni}(\text{tepa})\}_2(\mu\text{-Ge}_2\text{Se}_6)]$ (**3**) (tepa = tetraethylenepentamine) were prepared by solvothermal reactions. Compounds **1** and **2** consist of discrete $[\text{Ge}_2\text{Se}_6]^{4-}$ and $[\text{Ge}_2\text{Se}_7]^{4-}$ anions, and NH_4^+ , $[\text{H}_2\text{N}(\text{CH}_3)_2]^+$ and $[\text{Ni}(\text{dien})_2]^{2+}$ counter cations, respectively. The $[\text{Ge}_2\text{Se}_6]^{4-}$ anion is constructed by two tetrahedral GeSe_4 building units *via* edge-sharing. In **2**, two tetrahedral GeSe_4 units are linked by a corner and a Se–Se bond to form a polyselenidogermanate anion $[\text{Ge}_2\text{Se}_7]^{4-}$ containing a five-membered ring Ge_2Se_3 . The dimeric $[\text{Ge}_2\text{Se}_6]^{4-}$ anion acts as a bridging ligand *via* the *trans* terminal Se atoms to link two $[\text{Ni}(\text{tepa})]^{2+}$ cations, resulting in neutral complex **3**. The Ni^{2+} ion in **2** is coordinated by two tridentate *dien* ligands, while it is coordinated by a pentadentate *tepa* ligand and a selenidogermanate anion in **3**. The different coordination environments of Ni^{2+} ions indicate the influence of the denticity of ethylene polyamines on the formation of selenidogermanates in the presence of transition metal ions. The compounds **1–3** exhibit optical band gaps between 2.06 and 2.35 eV.

Keywords. Selenidogermanates; nickel; solvothermal syntheses; crystal structures; optical properties

1. Introduction

The design and syntheses of new crystalline inorganic–organic hybrid chalcogenide materials have become an increasingly active area due to their structural diversity and potential applications in the fields such as photocatalysis, fast ion conductivity, ion exchange, magnetism and thermoelectrics.^{1–6} During the last decade, a great many of chalcogenidogermanates have been prepared by solvothermal method, which has proven to be a fruitful route to chalcogenide materials.^{7–11} From a structural point of view, the cations used to compensate the negative charges of the chalcogenidogermanate anions can be classified as metal cations,^{12–18} and organic quaternary ammonium or protonated amine cations.^{19–29} Recently, a number of chalcogenidogermanates were synthesized in the presence of transition metal (TM) or lanthanide (Ln) ions in polyamine solutions,^{30–41} giving $[\text{Mn}(\text{en})_3]\text{GeSb}_2\text{S}_6$ (en = ethylenediamine),³² $[\text{Co}(\text{dien})_2]_2\text{GeSb}_4\text{S}_{10}$,³² $[\text{Ni}(\text{dien})_2]_3[\text{Ge}_3\text{Sb}_8\text{S}_{21}] \cdot 0.5\text{H}_2\text{O}$ (dien = diethylenetriamine),³³ $[\text{Ni}_2(\text{teta})_3]\text{Ge}_4\text{S}_{10} \cdot \text{H}_2\text{O}$ (teta = triethylenetetramine),³⁴ $[\{\text{Mn}(\text{en})_3\}_2$

$(\text{Ge}_5\text{Te}_{10})\}_n$,³⁵ and $[\{\text{Ln}(\text{tepa})(\mu\text{-OH})\}_2(\mu\text{-Ge}_2\text{Se}_8)]_n$ (Ln = Eu, Gd, Dy) (tepa = tetraethylenepentamine),⁴⁰ for example. The ethylene polyamines play an important role on the formation of thiogermanates in the presence of transition metal ion. The ethylene polyamine serves not only as reaction medium, but also as chelating ligand to the TM centers to form a complex cation. In *en* and *dien* solutions, the TM^{2+} complex cations were employed to prepare discrete chalcogenidogermanates in superheated polyamines. Because, the coordination sites of TM^{2+} ions are prone to be saturated by three bidentate *en* or two tridentate *dien* ligands. The incorporation of TM to chalcogenidogermanates is well produced by choosing the tetradentate or pentadentate amino ligands, such as 1,4,8,11-tetraazacyclotetradecane (cyclam) and tetraethylenepentamine (tepa). The TM^{2+} ion is coordinated by the amino ligand and leaves one or more potential binding site(s) which is fully occupied by a terminal S or Se atom of the chalcogenidogermanate anion. As a result, TM–chalcogenidogermanate complexes $[\{\text{Mn}(\text{cyclam})\}_2(\mu\text{-Ge}_2\text{Se}_7)] \cdot \text{CH}_3\text{OH} \cdot 1.5\text{H}_2\text{O}$, $[\{\text{TM}(\text{tepa})\}_2(\mu\text{-Ge}_2\text{S}_6)]$ (M = Co, Ni, Mn), and $[\{\text{M}(\text{tepa})\}_2(\mu\text{-Ge}_2\text{Se}_6)]$ (TM = Mn, Fe) were obtained.^{42–45}

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Now, reaction of GeO_2 and Se was investigated under different solvothermal conditions. A new selenidogermanate with mixed cations, $[\text{NH}_4]_2[\text{H}_2\text{N}(\text{CH}_3)_2]_2\text{Ge}_2\text{Se}_6$ (**1**) was prepared by the reaction with NH_4Cl in $(\text{CH}_3)_2\text{NH}$ solution. The reaction with NiCl_2 in methanol solution of *dien* produced a polyselenidogermanate $[\text{Ni}(\text{dien})_2]_2\text{Ge}_2\text{Se}_5(\text{Se}_2)$ (**2**) with Ni(II) complex cation for the first time. The same reaction with *tepa* instead of *dien* afforded a Ni(II) complex with a selenidogermanate ligand $[\{\text{Ni}(\text{tepa})\}_2(\mu\text{-Ge}_2\text{Se}_6)]$ (**3**). Herein, we present the syntheses, crystal structures, and characterization of optical and thermal properties of compounds **1–3**.

2. Experimental

2.1 Synthesis

2.1a Synthesis of $[\text{NH}_4]_2[\text{H}_2\text{N}(\text{CH}_3)_2]_2\text{Ge}_2\text{Se}_6$ (1**):** GeO_2 (52 mg, 0.5 mmol), Se (156 mg, 2 mmol), NH_4Cl (53 mg, 1.0 mmol), were dispersed in $(\text{CH}_3)_2\text{NH}$ (3.0 mL) and H_2O (1.0 mL) by stirring for 15 min. Then, the dispersion was loaded into a teflon-lined stainless steel autoclave of 10 mL volume. The sealed autoclave was heated under autogenous pressure at 150°C for 6 days. Upon cooling to room temperature, yellow block crystals of **1** were filtered off, washed with ethanol, and dried under a vacuum at room temperature (46% yield based on GeO_2). Elemental analysis for $\text{C}_4\text{H}_{24}\text{N}_4\text{Ge}_2\text{Se}_6$ (**1**) (747.21): Anal. Calc.: C, 6.43; H, 3.24; N, 7.50 (%). Found: C, 6.31; H, 3.19; N, 7.38 (%). IR (KBr disk, cm^{-1}): 3301 (s), 3074 (w), 2925 (s), 2850 (s), 2652 (w), 1550 (s), 1504 (s), 1149 (s), 1341 (s), 1281 (s), 1222 (s), 1181 (s), 1106 (m), 983 (m), 886 (m), 849 (m), 771 (m), 551 (m).

2.1b Synthesis of $[\text{Ni}(\text{dien})_2]_2\text{Ge}_2\text{Se}_5(\text{Se}_2)$ (2**):** GeO_2 (52 mg, 0.5 mmol), Se (156 mg, 2 mmol), and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (119 mg, 0.5 mmol) were dispersed in diethylenetriamine (*dien*) (2.0 mL) and CH_3OH (1.0 mL) by stirring for 15 min. Then, the dispersion was loaded into a teflon-lined stainless steel autoclave of 10 mL volume. The sealed autoclave was heated under autogenous pressure at 170°C for 6 days. Upon cooling to room temperature, orange-red block crystals of **2** were filtered off, washed with ethanol, and dried under a vacuum at room temperature (58% yield based on GeO_2). Elemental analysis for $\text{C}_{16}\text{H}_{52}\text{N}_{12}\text{Ni}_2\text{Ge}_2\text{Se}_7$ (**2**) (1228.02): Anal. Calc.: C, 15.65; H, 4.27; N, 13.69 (%). Found: C, 15.42; H, 4.09; N, 13.55 (%). IR (KBr disk, cm^{-1}): 3248 (s), 2928 (s), 1572 (s), 1504 (s), 1378 (m), 1326 (s), 1214 (w), 1154 (w), 1009 (m), 957 (m), 815 (w), 614 (m), 584 (m), 484 (w), 435 (w).

2.1c Synthesis of $[\{\text{Ni}(\text{tepa})\}_2(\mu\text{-Ge}_2\text{Se}_6)]$ (3**):** Purple crystals of compound **3** (62% yield based on GeO_2) were prepared by a procedure similar to that of the synthesis of **2**, except that tetraethylenepentamine (*tepa*) was used instead of *dien*. Elemental analysis for $\text{C}_{16}\text{H}_{46}\text{N}_{10}\text{Ni}_2\text{Ge}_2\text{Se}_6$ (**3**) (1114.99): Anal. Calc.: C, 17.24; H, 4.16; N, 12.56 (%). Found: C, 17.11; H, 3.95; N, 12.41 (%). IR (KBr disk, cm^{-1}): 3241 (s), 3115 (s), 2939 (m), 2868 (m), 2212 (w), 1598 (s), 1492 (m), 1348 (m), 1318 (m), 1154 (w), 1080 (m), 1027 (s), 823 (w), 778 (w), 636 (s), 517 (w), 435 (m).

2.2 Materials, instruments, and analytical methods

All solvents and reagents for synthesis were of analytical grade and were used as received. Elemental analyses (C, H, N) were performed using an EA1110-CHNS-O elemental analyzer. Fourier transform infrared (FT-IR) spectra were recorded with a Nicolet Magna-IR 550 spectrometer using dry KBr discs over the $4000\text{--}400\text{ cm}^{-1}$ range. Optical diffuse reflectance spectra of powder samples were obtained with a Shimadzu UV-3150 spectrometer at room temperature. Absorption (α/S) data were calculated from the reflectance using the Kubelka-Munk function $\alpha/S = (1-R)^2/2R$.⁴⁶ Thermogravimetric analysis (TGA) was conducted on a TG 3600 micro-analyzer and the samples were heated at a rate of 5°C min^{-1} under a nitrogen stream of 100 mL min^{-1} .

2.3 X-ray diffraction

Single-crystal X-ray diffraction data for compounds **1–3** were collected on a Rigaku Saturn (**1** and **3**) or Rigaku Mercury (**2**) CCD diffractometer at 223(2) K. Data were collected using graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) with a ω -scan method to a maximum 2θ value of 50.70° for **1–2**, and 50° for **3** and were corrected for radiation absorption by methods incorporated in the diffractometer software. The structures were solved with direct methods using the program of SHELXS-97,⁴⁷ and the refinement was performed against F^2 using the program of SHELXL-97.⁴⁸ All non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of hydrogen atoms were calculated theoretically. X-ray collection data and selected refinement results are summarized in Table 1.

3. Results and Discussion

3.1 Syntheses and Infrared Spectra

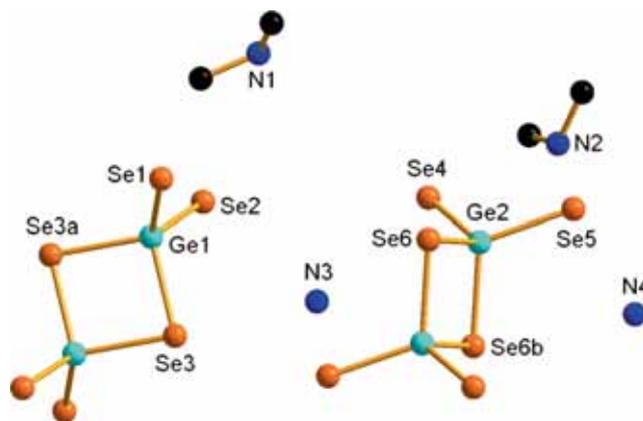
Title compounds were prepared under solvothermal conditions. Reaction of GeO_2 , Se and NH_4Cl in a 1:4:2

Table 1. Crystal data and structure refinement for 1–3.

Compounds	1	2	3
Formula	C ₄ H ₂₄ N ₄ Ge ₂ Se ₆	C ₁₆ H ₅₂ N ₁₂ Ni ₂ Ge ₂ Se ₇	C ₁₆ H ₄₆ N ₁₀ Ni ₂ Ge ₂ Se ₆
<i>M</i> r	747.21	1228.02	1114.99
Crystal system	Monoclinic	Monoclinic	Tetragonal
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>I</i> 4 ₁ / <i>a</i>
<i>a</i> (Å)	13.503(3)	15.741(3)	26.001(3)
<i>b</i> (Å)	7.7775(16)	14.463(3)	26.001(3)
<i>c</i> (Å)	19.583(4)	16.390(3)	9.7079(12)
α (°)	90	90	90
β (°)	106.03(3)	103.03(3)	90
γ (°)	90	90	90
<i>V</i> (Å ³)	1976.6(7)	3635.2(13)	6562.9(14)
<i>Z</i>	4	4	8
<i>D</i> _{calcd} (g cm ⁻³)	2.511	2.244	2.257
<i>F</i> (000)	1376	2360	4288
Goodness-of-fit on <i>F</i> ²	1.124	1.153	1.115
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0460 <i>wR</i> ₂ = 0.1049	<i>R</i> ₁ = 0.0490 <i>wR</i> ₂ = 0.0937	<i>R</i> ₁ = 0.0497 <i>wR</i> ₂ = 0.0953
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0507 <i>wR</i> ₂ = 0.1168	<i>R</i> ₁ = 0.066 <i>wR</i> ₂ = 0.1113	<i>R</i> ₁ = 0.0543 <i>wR</i> ₂ = 0.1010

molar ratio in (CH₃)₂NH (70%) aqueous solution at 150°C for 6 days produced yellow crystals of **1**. The reaction without NH₄Cl produced amorphous phase of black powder and no crystalline compound was obtained. Similar synthesis using CH₃NH₂ instead of (CH₃)₂NH failed to give crystalline compound. The NH₄⁺ ion may maintain an appropriate pH value of the solution in the reaction. In addition, it acts as a counter cation in the final product. CH₃OH was necessary for the synthesis of polyselenidogermanate [Ni(dien)₂]₂Ge₂Se₅(Se₂) (**2**). The reaction without addition of CH₃OH produced amorphous powder. However, the reaction GeO₂, Se, and FeCl₂·4H₂O in *dien* without CH₃OH afforded selenidogermanate compound [Fe(dien)₂]₂Ge₂Se₆.³¹ Compound **3** was prepared in a *tepa*/CH₃OH mixed solution. The reaction without CH₃OH also produced the same compound **3**, but the yield decreased to 32%. The purity of bulk phases of compounds **1–3** were investigated using powder X-ray diffraction (PXRD). The PXRD patterns of the bulk phases are consistent with the simulated PXRD patterns based on single-crystal XRD data (Figures S1–S3 in the Supplementary Information), respectively.

In the IR spectra of title compounds (Figures S4–S6, in SI), the absorption peaks located in the frequency range 3074–3301 cm⁻¹ could be assigned to the asymmetric and symmetric N–H stretching vibrations of the amino groups of [H₂N(CH₃)₂]⁺, *dien* or *tepa*. The C–H stretching vibrations occur between 2850 and 2939 cm⁻¹. The N–H and C–H deformation modes occur in the range 1550–1598 cm⁻¹ and 1492–1504 cm⁻¹,

**Figure 1.** Crystal structure of **1** with the labeling scheme. Hydrogen atoms are omitted for clarity.

respectively. The strong bands in 1009–1027 cm⁻¹ could be assigned to C–N stretching vibrations.

3.2 Structure description

3.2a [NH₄]₂[H₂N(CH₃)₂]₂Ge₂Se₆ (**1**): Compound **1** crystallizes in the monoclinic crystal system with space group *P*2₁/*n* with four formula units in the unit cell (Table 1). The crystal structure consists of discrete dimeric [Ge₂Se₆]⁴⁻ anions with charge compensating cations [NH₄]⁺ and [H₂N(CH₃)₂]⁺ (Figure 1). There are two crystallographically independent Ge⁴⁺, and six Se²⁻ ions in **1**. Both Ge(1)⁴⁺ and Ge(2)⁴⁺ ions are coordinated to four Se²⁻ anions forming GeSe₄ tetrahedra. Two tetrahedral Ge(1)Se₄ units are joined

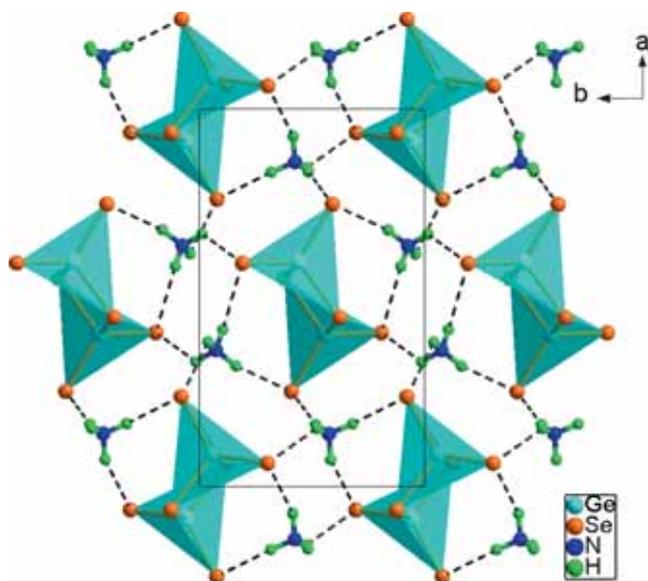


Figure 2. A view of the layer assembled by $[\text{Ge}_2\text{Se}_6]^{4-}$ and $[\text{NH}_4]^+$ ions *via* $\text{N}-\text{H}\cdots\text{Se}$ H-bonding (shown in dashed lines) in **1**. Cyan tetrahedron: GeSe_4 .

Table 2. Selected bond lengths (Å) and angles ($^\circ$) for **1**.

${}^a\text{Ge}-\text{Se}_b$	2.3935(17)–2.4051(16)
${}^b\text{Ge}-\text{Se}_t$	2.2929(17)–2.3121(18)
$\text{Se}_t-\text{Ge}-\text{Se}_t$	113.37(7), 113.96(7)
$\text{Se}_t-\text{Ge}-\text{Se}_b$	109.00(6)–113.62(7)
$\text{Se}_b-\text{Ge}-\text{Se}_b$	95.07(6), 95.45(6)
$\text{Ge}-\text{Se}-\text{Ge}$	84.55(6), 84.93(6)

a Terminal and b bridging Ge–Se bond lengths of $[\text{Ge}_2\text{Se}_6]^{4-}$ unit.

via edge-sharing, forming a dimeric $[\text{Ge}_2\text{Se}_6]^{4-}$ anion (Figure 1). Another $[\text{Ge}_2\text{Se}_6]^{4-}$ anion is formed by two $\text{Ge}(2)\text{Se}_4$ units with the same connection modes. In the $[\text{Ge}_2\text{Se}_6]^{4-}$ anions, the $\text{Ge}-\text{Se}_b$ bridging bond lengths vary range from 2.3935(17) to 2.4051(16) Å, which are longer than the $\text{Ge}-\text{Se}_t$ terminal bond lengths [$\text{Ge}-\text{Se}_t$: 2.2929(17)–2.3121(18) Å] (Table 2 and Table S1 in SI). The distances of the two kinds of bonds are consistent with the corresponding values in other compounds containing the $[\text{Ge}_2\text{Se}_6]^{4-}$ anions.^{19,31,32,49} The $\text{Se}-\text{Ge}-\text{Se}$ angles range from 95.07(6) to 113.96(7) $^\circ$, indicating the distorted tetrahedral geometry for the GeSe_4 units. The $\text{Se}-\text{Ge}-\text{Se}$ angles increase in the order: $\text{Se}_b-\text{Ge}-\text{Se}_b > \text{Se}_t-\text{Ge}-\text{Se}_b > \text{Se}_t-\text{Ge}-\text{Se}_t$ (Table 2).

In **1**, the $[\text{NH}_4]^+$ and $[\text{H}_2\text{N}(\text{CH}_3)_2]^+$ counter ions contact $[\text{Ge}_2\text{Se}_6]^{4-}$ anion *via* $\text{N}-\text{H}\cdots\text{Se}$ with $\text{N}\cdots\text{Se}$ separation varying in the range of 3.438(12)–3.502(12) Å (Table S4 in SI), indicating intermolecular $\text{N}-\text{H}\cdots\text{Se}$ hydrogen bond interactions, which result in a 3-D H-bonding network. Each $[\text{NH}_4]^+$ cation contacts three $[\text{Ge}_2\text{Se}_6]^{4-}$ anions *via* $\text{N}-\text{H}\cdots\text{Se}$ bonding, whereas

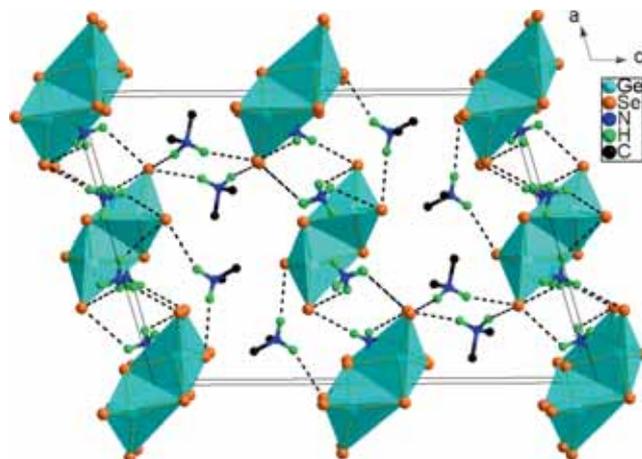


Figure 3. Crystal packing diagram of **1**, showing intermolecular $\text{N}-\text{H}\cdots\text{Se}$ hydrogen bonds. Hydrogen atoms of CH_3 are omitted for clarity. Cyan tetrahedron: GeSe_4 .

each $[\text{Ge}_2\text{Se}_6]^{4-}$ anion interacts six $[\text{NH}_4]^+$ cations. As a result, the $[\text{NH}_4]^+$ and $[\text{Ge}_2\text{Se}_6]^{4-}$ ions form a $\{([\text{NH}_4]^+)_2/[\text{Ge}_2\text{Se}_6]^{4-}\}$ anionic layer perpendicular to the c axis *via* these $\text{N}-\text{H}\cdots\text{Se}$ hydrogen bonds (Figure 2). Two protonated $[\text{H}_2\text{N}(\text{CH}_3)_2]^+$ ions are located between the $\{([\text{NH}_4]^+)_2/[\text{Ge}_2\text{Se}_6]^{4-}\}$ anionic layers. They interact with the layers through $\text{N}-\text{H}\cdots\text{Se}$ H-bonds, resulting in a 3-D H-bonding network (Figure 3). All terminal Se atoms of $[\text{Ge}_2\text{Se}_6]^{4-}$ are involved in the H-bonding interaction, and each $[\text{Ge}_2\text{Se}_6]^{4-}$ anion contacts six $[\text{NH}_4]^+$ and two $[\text{H}_2\text{N}(\text{CH}_3)_2]^+$ cations (Figure S7 in SI).

3.2b $[\text{Ni}(\text{dien})_2]_2\text{Ge}_2\text{Se}_5(\text{Se}_2)$ (**2**): Compound **2** crystallizes in the monoclinic crystal system with space group $P2_1/c$ with four formula units in the unit cell (Table 1). It consists of a dimeric polyselenidogermanate $[\text{Ge}_2\text{Se}_7]^{4-}$ anion and two $[\text{Ni}(\text{dien})_2]^{2+}$ cations (Figure 4). $\text{Ge}(1)^{4+}$ and $\text{Ge}(2)^{4+}$ ions both coordinate with four Se^{2-} atoms to form two tetrahedral GeSe_4 units. The two GeSe_4 units are connected sharing a corner and a $\text{Se}-\text{Se}$ bond (Figure 4), forming a $[\text{Ge}_2\text{Se}_5(\text{Se}_2)]^{4-}$ dimeric anion (Figure 4a). As a result, a five-membered ring Ge_2Se_3 is formed in the anion. The $\text{Ge}-\text{Se}-\text{Ge}$ bond angle [$106.33(9)^\circ$] of $[\text{Ge}_2\text{Se}_5(\text{Se}_2)]^{4-}$ is much larger than the corresponding angle of the dimeric $[\text{Ge}_2\text{Se}_6]^{4-}$ [$84.55(6)^\circ$ and $84.93(6)^\circ$] anion in **1**, because the $[\text{Ge}_2\text{Se}_6]^{4-}$ anion contains a four-membered straining ring Ge_2Se_2 . The terminal and bridging $\text{Ge}-\text{Se}$ bond lengths are 2.283(3)–2.306(3) Å and 2.399(3)–2.421(3) Å (Table 3), respectively, and the $\text{Se}-\text{Se}$ bond distance is 2.325(3) Å. Both $\text{Ge}-\text{Se}$ and $\text{Se}-\text{Se}$ bond lengths are consistent with the corresponding values found in the compounds (enH₂)

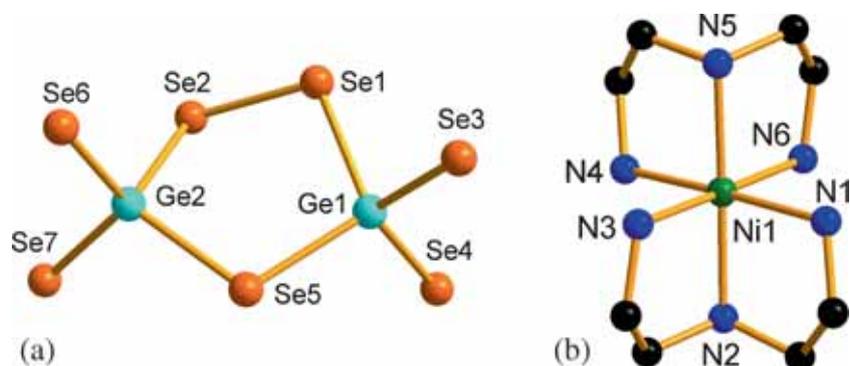


Figure 4. Crystal structures of the $[\text{Ge}_2\text{Se}_7]^{4-}$ anion (a), and $[\text{Ni}(1)(\text{dien})_2]^{2+}$ cation (b) in **2**. Hydrogen atoms are omitted for clarity.

Table 3. Selected bond lengths (\AA) and angles ($^\circ$) for **2** and **3**.

	2	3
${}^a\text{Ge}-\text{Se}_b$	2.399(3)–2.421(3)	2.335(3)–2.338(3)
${}^b\text{Ge}-\text{Se}_t$	2.283(3)–2.306(3)	2.259(2)–2.288(2)
Se–Se	2.325(3)	
Ni–Se		2.666(2)
Ni–N	2.076(14)–2.149(15)	2.118(11)–2.169(11)
Se–Ge–Se	97.65(10)–116.43(11)	95.38(9)–114.78(8)
Ge–Se–Ge	106.33(9)	84.62(9)
Ge–Se–Ni		111.02(8)
N–Ni–N(Se)	82.2(6)–178.4(7)	77.1(5)–166.8(5)

a Terminal and b bridging Ge–Se bond lengths of $[\text{Ge}_2\text{Se}_7]^{4-}$ in **2** and $[\text{Ge}_2\text{Se}_6]^{4-}$ in **3**.

$[\{\text{Mn}(\text{en})_2(\text{enH})\}_2(\mu\text{-en})](\text{Ge}_2\text{Se}_7)$,³⁷ $(1,2\text{-dapH})_2\{[\text{Mn}(1,2\text{-dap})_2]\text{Ge}_2\text{Se}_7\}$, and $[\{\text{Mn}(\text{cyclam})\}_2(\mu\text{-Ge}_2\text{Se}_7)]\cdot\text{CH}_3\text{OH}\cdot 1.5\text{H}_2\text{O}$.⁴²

The $\text{Ni}(1)^{2+}$ ion is 6-fold coordinated by two tridentate *dien* ligands to form a distorted octahedral $[\text{Ni}(\text{dien})_2]^{2+}$ cation (Figure 4b). The $[\text{Ni}(1)(\text{dien})_2]^{2+}$ cation shows the symmetrical facial (*sfac*) geometry. The $\text{Ni}(2)^{2+}$ ion also forms an octahedral $[\text{Ni}(\text{dien})_2]^{2+}$ cation in *sfac* configuration with two *dien* ligands (Figure S8 in SI). The Ni–N bond lengths are in the range of 2.076(14)–2.149(15) \AA (Table 3), which are comparable to the Ni–N bond lengths observed in compounds containing $[\text{Ni}(\text{dien})_2]^{2+}$ complex.^{34,43} The $[\text{Ni}(\text{dien})_2]^{2+}$ cation contacts $[\text{Ge}_2\text{Se}_7]^{4-}$ anions via $\text{N}-\text{H}\cdots\text{Se}$ H-bonds, forming a layer perpendicular to the *a* axis (Figure 5). The layers are further connected to a 3-D network via $\text{N}-\text{H}\cdots\text{Se}$ H-bonds between the layers (Figure S9 in SI). The $\text{N}\cdots\text{Se}$ distances and $\text{N}-\text{H}\cdots\text{Se}$ angles vary in the range of 3.434(17)–3.754(15) \AA and 136.6–174.0 $^\circ$, respectively (Table S4 in SI).

The ternary system TM/Ge/E (E = S, Se) has been investigated in different ethylene polyamines under solvothermal conditions, and a number of TM(II)-con-

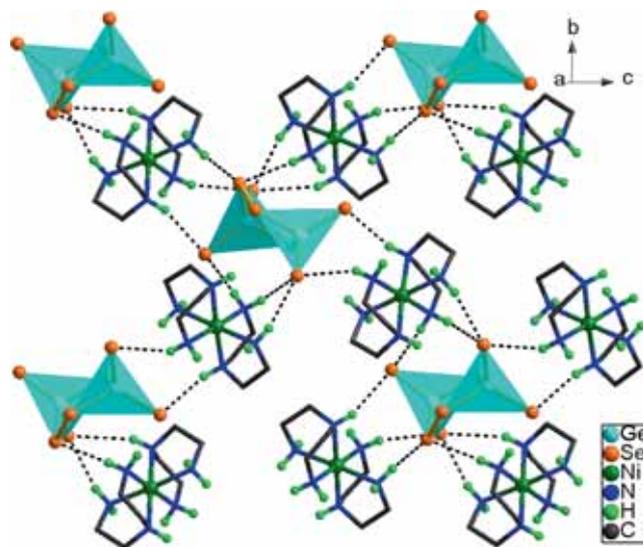


Figure 5. A sectional crystal packing diagram of **2**, showing intermolecular $\text{N}-\text{H}\cdots\text{Se}$ hydrogen bonds. Hydrogen atoms of CH_2 are omitted for clarity. Cyan tetrahedron: GeSe_4 .

taining selenidogermanates decorated with polyamines at TM center have been prepared. Dimeric $[\text{Ge}_2\text{E}_6]^{4-}$ and tetrameric $[\text{Ge}_4\text{E}_{10}]^{4-}$ anions are the dominant selenidogermanate aggregates in the solvothermal syntheses.^{30–32,36,43,44} It is notable that polyselenidogermanate $[\text{Ge}_2\text{Se}_7]^{4-}$ anion is only obtained using Mn(II)-polyamine complex as the structure-directing agent. Free $[\text{Ge}_2\text{Se}_7]^{4-}$ anion is observed in compounds $(\text{enH}_2)[\{\text{Mn}(\text{en})_2(\text{enH})\}_2(\mu\text{-en})](\text{Ge}_2\text{Se}_7)_2$ and $[\text{Mn}(\text{dien})_2]_2\text{Ge}_2\text{Se}_7$.³⁷ But the $[\text{Ge}_2\text{Se}_7]^{4-}$ anion is distorted with $[\text{Ge}_2\text{Se}_6]^{4-}$ unit in the former, and with $[\text{Ge}_2\text{Se}_8]^{4-}$ unit in the latter. Using 1,4,8,11-tetraazacyclotetradecane (cyclam) and 1,2-propanediamine (1,2-dap) as ligands to Mn(II) centers, Mn– Ge_2Se_7 complexes are obtained.^{38,42} Compound **2** is the first example of $[\text{Ge}_2\text{Se}_7]^{4-}$ anion with counter cation other than the Mn(II)-complex.

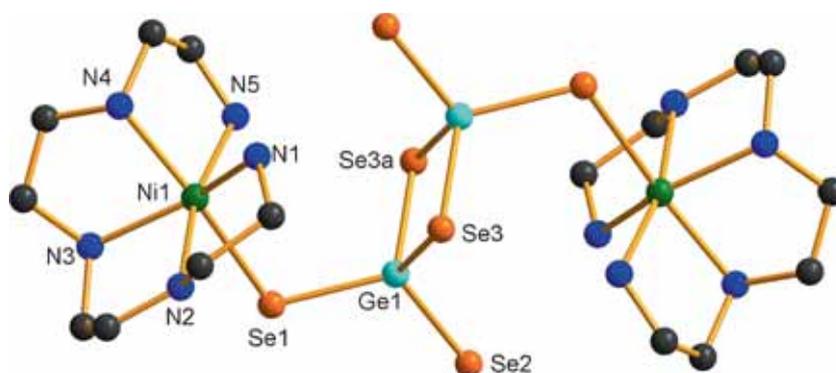


Figure 6. Crystal structure of **3** with the labeling scheme. Hydrogen atoms are omitted for clarity.

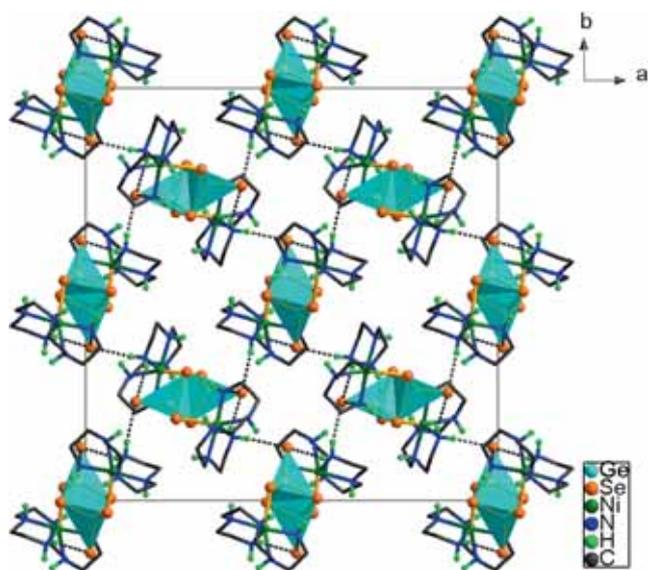


Figure 7. Crystal packing diagram of **3**, showing intermolecular N–H···Se hydrogen bonds. Hydrogen atoms of CH₂ are omitted for clarity. Cyan tetrahedron: GeSe₄.

3.2c $[\{Ni(tepa)\}_2(\mu-Ge_2Se_6)]$ (**3**): Complex **3** crystallizes in the tetragonal space group $I4_1/a$ with eight formula units in the unit cell. It is isostructural to the compounds $[\{TM(tepa)\}_2(\mu-Ge_2Se_6)]$ (TM = Mn, Fe).⁴⁵ **3** is composed from $[Ge_2Se_6]^{4-}$ and $[Ni(tepa)]^{2+}$ fragments (Figure 6). The Ni²⁺ ion is coordinated to a *tepa* molecule to form a $[Ni(tepa)]^{2+}$ unit. Acting as bidentate bridging ligand $\mu-Ge_2Se_6$, the $[Ge_2Se_6]^{4-}$ anion links two $[Ni(tepa)]^{2+}$ units *via* two *trans* terminal Se atoms, forming neutral binuclear complex **3**. Because of the coordination, the tetrahedral GeSe₄ units of $\mu-Ge_2Se_6$ in **3** are more distorted than the GeSe₄ units of the discrete $[Ge_2Se_6]^{4-}$ anions in **1**, manifested by the Se–Ge–Se bond angles (Tables 2 and 3). The Ni²⁺ ion is in a 6-fold coordinated environment involving five nitrogen atoms of a *tepa* ligand and one Se atom of the Ge_2Se_6 unit, resulting in an octahedron NiN₅Se. The NiN₅Se octahedron is more distorted than the NiN₆ octahedron in compound **2**, as exhibited by

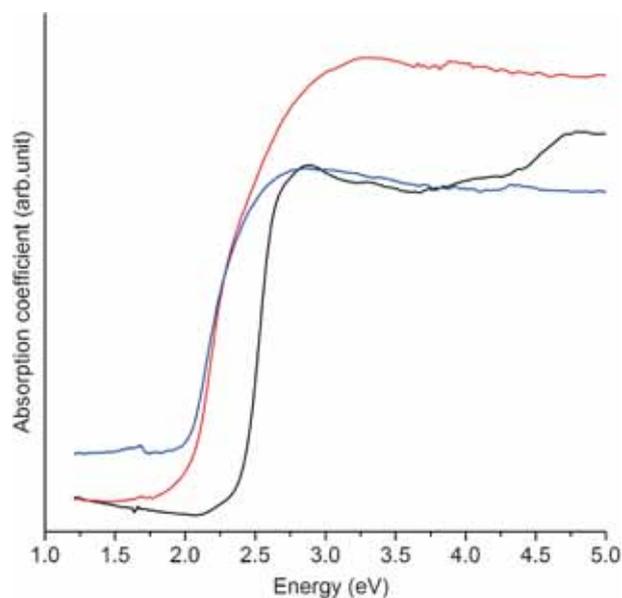


Figure 8. Solid state optical absorption spectra of compounds **1** (black), **2** (red), and **3** (blue).

their bond angles around the Ni(II) centers (Tables S2 and S3 in SI). In **3**, all terminal Se atoms of Ge_2Se_6 unit are involved in weak N–H···Se [3.401(12)–3.654(12) Å and 149.5–168.3°] (Table S4 in SI) hydrogen bond interactions with four neighbor $[\{Ni(tepa)\}_2(\mu-Ge_2Se_6)]$ molecules (Figure 7). The N–H···Se hydrogen bonds connect the $[\{Ni(tepa)\}_2(\mu-Ge_2Se_6)]$ molecules into a three-dimensional network (Figure S10 in SI).

3.3 Optical Properties

Solid-state optical absorption spectra of compounds **1–3** were recorded using powder samples at room temperature. The absorption data were converted from the diffuse-reflectance spectra by the Kubelka-Munk function.⁴⁶ The complexes exhibit well-defined steep absorption edges from which the optical band gaps (E_g) can be estimated at 2.35, 2.10 and 2.06

eV for **1–3** (Figure 8), respectively, which indicate that these compounds exhibit possible semiconducting properties. Blue shift occurs from organic-hybrid selenidogermanate **1** to Ni-selenidogermanates **2** and **3**. The band gap of **3** is higher than that of S-analog $[\text{Ni}(\text{tepa})]_2(\mu\text{-Ge}_2\text{S}_6)$ ($E_g = 2.48$ eV).⁴⁴

3.4 Thermal properties

Thermal stabilities of compounds **1–3** were investigated using thermogravimetric analysis (TGA) method under a nitrogen atmosphere (Figure S11 in SI). TGA curve shows that compound **1** exhibits a multi-step decomposition process with the total weight loss of 37.2% between 170°C and 310°C. The total weight loss is in accordance with the release of two NH_3 , H_2Se , and $\text{HN}(\text{CH}_3)_2$ molecules. Compound **2** exhibits two overlapped decomposition processes between 210°C and 350°C with a total weight loss of 32.8%, which corresponds to the losses of four *dien* (33.6%) ligands. Compound **3** decomposes in one step with the weight loss of 32.5%. The weight loss is in agreement with the loss of two *tepa* (33.9%) molecules.

4. Conclusions

In summary, three new H-bond-based supramolecular selenidogermanates compounds (**1–3**) have been synthesized under solvothermal conditions and characterized. The formation of binary selenidogermanate units is influenced by the reaction media and counter cations. Compound **2** represents the first polyselenidogermanate anion of $[\text{Ge}_2\text{Se}_7]^{4-}$ with counter cations other than the Mn-complexes. The crystal structures of **2** and **3** indicate that complexation between the selenidogermanate anion and transition metal cations are related to the denticity of ethylene polyamines. Furthermore, the optical and thermal properties of the compounds **1–3** were also investigated.

Supplementary Information (SI)

Crystallographic data for the crystal structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC Numbers: CCDC-1490346 (**1**), CCDC-1490347 (**2**), and CCDC-1490348 (**3**), which contain supplementary crystallographic data for this paper. Other supplementary data associated with this article can be found in the online version. Supplementary information is available at www.ias.ac.in/chemsci.

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