Solvothermal synthesis of three new dimeric thiogermanates (enH)$_4$Ge$_2$S$_6$, [Mn(en)$_3$]$_2$Ge$_2$S$_6$ and [Ni(en)$_3$]$_2$Ge$_2$S$_6$ from germanium dioxide and sulfur powder

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Abstract

Three new thiogermanates (enH)$_4$Ge$_2$S$_6$ (**1**) and [M(en)$_3$]$_2$Ge$_2$S$_6$ (M = Mn (**2**), Ni (**3**); en = ethylenediamine) were synthesized using GeO$_2$ and S$_8$ as starting materials in molar ratio of 1:0.5 under solvothermal conditions. These compounds suggest that the dimeric [Ge$_2$S$_6$]$^{4-}$ anion is likely to be the main germanium-containing species in en system and it also might be preferred as counter anions by the transition metal complex cations in crystallization. The cations of [Mn(en)$_3$]$^{2+}$ and [Ni(en)$_3$]$^{2+}$ are even better mineralizers than the protonated amine of [enH]$^+$. The crystal systems of [Ge$_2$S$_6$]$^{4-}$ compounds are related to entities of cations and intermolecular reactions between cations and [Ge$_2$S$_6$]$^{4-}$ anions. The compounds remove ethylenediamine and H$_2$S molecules in multi steps when being heated under nitrogen stream.

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1. Introduction

Since Bedard reported microporous compound of germanium(IV) sulfide synthesized by hydrothermal technique in the presence of organic amine in 1989 [1,2], lots of mesostructured metal germanium sulfides have been synthesized and documented [3–15]. Except for [(Hdabco)$_2$(H$_3$O)(H$_2$O)][AgGe$_4$S$_{10}$] [3] and [(H$_2$dabco)$_2$][MnGe$_4$S$_{10}$]·3H$_2$O (dabco = 1,4-diazabicyclo[2,2,2]octane) [4], which were prepared in one step using GeS$_2$ and Ag(CH$_3$CO$_2$)·3H$_2$O or MnCl$_2$·4H$_2$O as source materials in 1,4-diazabicyclo[2,2,2]octane solution, most of these mesostructured materials were derived from supermolecular self-assembling of adamantane

[Ge$_4$S$_{10}$]$^{4-}$ anionic cluster precursors. The adamantane precursors of K$_4$Ge$_4$S$_{10}$/Na$_4$Ge$_4$S$_{10}$ [6–12] and (Me$_4$N)$_4$Ge$_4$S$_{10}$ [12–15] were previously prepared by high-temperatured molten salt (flux) method and mild hydrothermal method in tetra-alkylammonium hydroxide solution respectively. Then, the [Ge$_4$S$_{10}$]$^{4-}$ building blocks are interconnected by transition metal ions in the presence of surfactant molecules as the structure-directing agents to form mesostructured germanium(IV) sulfides.

The solvothermal reaction in superheated ethylenediamine has proved to be a versatile route for the syntheses of chalcogenometalates [16]. Recently, we unexpectedly isolated dimeric thiogermanate compound of [Ge$_2$S$_6$]$^{4-}$ in an attempt to prepare the mesostructured germanium(IV) sulfide directly from GeO$_2$/S$_8$/ethylenediamine system under mild solvothermal conditions. The dimeric [Ge$_2$S$_6$]$^{4-}$ anion might equilibrate with the adamantane [Ge$_4$S$_{10}$]$^{4-}$ anionic cluster and, if so, help people to understand the formation mechanism

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of mesostructured thiogermanate framework. Therefore, the synthesis and characterization of dimeric $[Ge_2S_6]^{4-}$ compounds are of both theoretical and practical significance. We report here the syntheses, crystal structures and thermal behaviors of three new thiogermanates of $(Hen)_4Ge_2S_6$ (**1**), $[Mn(en)_3]_2Ge_2S_6$ (**2**) and $[Ni(en)_3]_2Ge_2S_6$ (**3**). To our knowledge, **2** and **3** are the first examples of $[Ge_2S_6]^{4-}$ compounds with transition metal complex cations acting as charge balancing ions.

2. Experimental

2.1. Physical measurements

All chemicals were analytically pure and were used without further purification. Elemental analysis was conducted on an EA-1110 elemental analyzer. Thermoanalytical measurements were performed using a DSC-TGA microanalyzer of SDT 2960 and all the samples were heated under a nitrogen stream of 100 mL/min with a heating rate of 5 °C/min.

2.2. Synthesis

2.2.1. (Hen)₄Ge₂S₆ (1)

$(Hen)_4Ge_2S_6$ was prepared by reacting GeO_2 with S_8 in an aqueous solution of ethylenediamine. GeO_2 (104.6 mg, 1.0 mmol) and S_8 (128.4 mg, 0.5 mmol) were mixed in 80% ethylenediamine (6 mL) under stirring, and then the mixture was loaded into a Teflon-lined stainless-steel autoclave with inner volume of 15 mL. The sealed autoclave was heated to 150 °C for 4 days. A clear yellow solution was obtained after the autoclave was cooled to room temperature. The solution was transferred to a flask, covered and laid aside. After about 2 weeks, colorless block crystals of **1** appeared at the bottom of the flask. The crystals were isolated by filtration, washed with ethanol and ether. The yield based on GeO_2 is about 40%. **1** is stable in air. C, H, N analysis: found: C 16.48%; H 6.20%; N 19.16%; calcd.: C 16.51%; H 6.23%; N 19.25%.

2.2.2. [Mn(en)₃]₂Ge₂S₆ (2) and [Ni(en)₃]₂Ge₂S₆ (3)

$[Mn(en)_3]_2Ge_2S_6$ and $[Ni(en)_3]_2Ge_2S_6$ were prepared with similar methods. In a typical synthetic procedure, the reactants of $MCl_2 \cdot xH_2O$ ($MnCl_2 \cdot 4H_2O$ for **2**, $NiCl_2 \cdot 6H_2O$ for **3**), GeO_2 and S_8 in molar ratio of 1:1:0.5 were dissolved in 6 mL ethylenediamine under stirring, then the mixture was loaded into a Teflon-lined stainless-steel autoclave. The sealed autoclave was heated to 150 °C for 4 days. After being cooled to ambient temperature, colorless platelet crystals of **2** and purple chiplike crystals of **3** were obtained. The crystals were washed with ethanol and ether, stored under

vacuum. The yields based on GeO_2 are about 55% and 60%, for **2** and **3**, respectively. C, H, N analysis for **2**: found: C 17.82%; H 6.06%; N 20.74%; calcd.: C 17.84%; H 5.99%; N 20.80%. **3**: found: C 17.62%; H 6.01%; N 20.58%; calcd.: C 17.67%; H 5.93%; N 20.61%.

2.3. Structure determination

Intensities were collected on a Rigaku Mercury CCD diffractometer using ω-scan method with graphite monochromated Mo$K\alpha$ radiation ($\lambda = 0.071070$ nm) at $-80 + 1$ °C to a maximum 2θ value of 55.0° and 50.0°, respectively, for **1–2** and **3**. An absorption correction was applied for all the compounds using multi-scan. The structures were solved with direct methods using the program of SHELXS-97 [17]. All the compounds were refined against F^2. The refinement of **1** and **2** were made using SHELXL-97 [18], but that of **3** was made using CRYSTALS [19]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by calculation except that H atoms of NH_2 groups in **1** were located by difference Fourier maps. The N atoms in **3** are disordered and the occupation ratio of disordered N:N′ is refined to 0.60: 0.40. Technical details of data acquisition and refinement results are summarized in Table 1.

3. Results and discussion

3.1. Syntheses of the compounds

Under solvothermal conditions, the dimeric $[Ge_2S_6]^{4-}$ thiogermanates of $(enH)_4Ge_2S_6$ (**1**) and $[M(en)_3]_2Ge_2S_6$ ($M = $ Mn (**2**), Ni (**3**)) were conveniently obtained using GeO_2 and S_8 as starting materials instead of GeS_2, which is usually used to prepare germanium sulfides, and this is a new route to dimeric $[Ge_2S_6]^{4-}$ anions. The first dimeric compound $Na_4Ge_2S_6 \cdot 14H_2O$ was obtained by dissolving GeS_2 in Na_2S aqueous solution at constant pH of 7–8 [20]. In the GeO_2/S_8/ethylenediamine system, when transition metal ions, such as Mn^{2+} and Ni^{2+}, were added, the compounds **2** and **3** were obtained immediately at the end of the solvothermal reaction. But in the absence of the transition metal ions, only a clear yellow solution was obtained and the protonated compound of $(enH)_4Ge_2S_6$ (**1**) was isolated after the resulted reaction solution was laid aside for 2 weeks at room temperature. The transition metal complex cations of $[Mn(en)_3]^{2+}$ and $[Ni(en)_3]^{2+}$ exhibit better mineralizers than the protonated cation of $[enH]^+$ due to their larger ion radii. Although the dimeric thiogermanates of $Na_4Ge_2S_6 \cdot 14H_2O$ [20,21], $Tl_4Ge_2S_6$ [22], $K_2Au_2Ge_2S_6$ [23] and $[(C_4H_9)_2NH_2]_4Ge_2S_6$ [24] have been known for many years, the dimeric $[Ge_2S_6]^{4-}$ anions with transition

Table 1
Crystal data and structure refinement for $(Hen)_4Ge_2S_6$ (**1**), $Mn(en)_3]_2Ge_2S_6$ (**2**) and $[Ni(en)_3]_2Ge_2S_6$ (**3**)

Compound	1	2	3
Formula	$C_8H_{36}N_8Ge_2S_6$	$C_{12}H_{48}N_{12}Mn_2Ge_2S_6$	$C_{12}H_{48}N_{12}Ni_2Ge_2S_6$
Formula weight ($g\,mol^{-1}$)	581.99	808.04	815.53
Color, habit	Colorless, block	Colorless, platelet	Purple, chip
Dimensions (mm)	$0.22 \times 0.19 \times 0.10$	$0.30 \times 0.25 \times 0.06$	$0.15 \times 0.12 \times 0.11$
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$ (No.2)	$C2/c$ (No. 15)	$Pbca$ (No.61)
D_{calc} ($g\,cm^{-3}$)	1.614	1.680	1.715
a (Å)	7.8594(16)	15.115(4)	15.562(10)
b (Å)	9.5138(18)	10.530(3)	11.226(7)
c (Å)	9.7266(12)	22.897(6)	18.074(12)
α (deg)	64.206(13)	90	90
β (deg)	66.798(14)	118.777(4)	90
γ (deg)	84.916(18)	90	90
V (Å^3)	598.84(18)	3194.3(15)	3157.6(36)
T (K)	193.1	193.1	193.1
Z	1	4	4
μ (mm^{-1})	3.043	3.055	3.482
Scane range (deg)	$6.50 \leqslant 2\theta \leqslant 54.96$	$6.16 \leqslant 2\theta \leqslant 54.96$	$6.4 \leqslant 2\theta \leqslant 50.06$
Index range	$-10 \leqslant h \leqslant 9$	$-19 \leqslant h \leqslant 16$	$-15 \leqslant h \leqslant 18$
	$-12 \leqslant k \leqslant 11$	$-13 \leqslant k \leqslant 13$	$-13 \leqslant k \leqslant 13$
	$-12 \leqslant l \leqslant 12$	$-28 \leqslant l \leqslant 29$	$-20 \leqslant l \leqslant 21$
Measured reflections	6803	17494	42836
Independent reflections	2709	3648	3161
Reflections with $[I > 2\sigma]$	2383	3406	1608
R_{int}	0.0364	0.0466	0.120
Variables	151	154	208
$R_1[I > 2\sigma(I)]$	0.0414	0.0472	0.0710
$wR_2[I > 2\sigma(I)]$	0.0593	0.0699	0.1560
Goodness of fit	1.169	1.302	1.000

metal complex cations acting as charge balancing ions were prepared for the first time in this work. We note that, besides $[Ge_2S_6]^{4-}$, the $[Ge_2S_6]^{6-}$ compounds have also been known for a long time [25–27].

Recently, thiogermanates with different degrees of condensation ($[Ge_xS_y]^{n-}$) have been prepared from different amine solutions under solvothermal conditions. The adamantane $[Ge_4S_{10}]^{4-}$ anion was obtained from GeS_2 in an aqueous solution of $(CH_3)_4NHS$ at 150 °C [13], and from Ge and S in a tetramethylammonium hydroxide solution at the same temperature [14]. In the dipropylammonium hydrogen chloride and $NaHCO_3$ mixed solution, the freshly prepared GeS_2 condensed to one-dimensional $[Ge_4S_9]^{2-}$ polyanion at 125 °C [28]. In ethylenediamine solution, the dimeric $[Ge_2S_6]^{4-}$ anion was obtained by reacting GeO_2 with S_8 at 150 °C (this work). The degree of condensation of the $[Ge_xS_y]^{n-}$ anion is predominantly influenced by the pH of solution [29]. In high pH range, such as in en system, the dimeric $[Ge_2S_6]^{4-}$ anion is likely to be the main germanium-containing species, but at low pH, $[Ge_4S_{10}]^{4-}$ and $[Ge_4S_9]^{2-}$, etc. high condensed species might be predominant. The size and charge of the counter cation will also play a role (in addition to pH) in

directing crystallization, so it is also possible that $[Ge_2S_6]^{4-}$ anions are preferred as counter anions by $[M(en)_3]^{2+}$.

3.2. Description of the structures

Compounds **1–3** crystallize in triclinic space group of $P\bar{1}$, monoclinic space group of $C2/c$ and orthorhombic space group of $Pbca$, respectively. The three compounds are composed of discrete $[Ge_2S_6]^{4-}$ anions with protonated amines or transition metal complex cations acting as counter ions.

In compound **1**, the dimeric $[Ge_2S_6]^{4-}$ ion is constructed by two edge-linked tetrahedral GeS_4 units forming a planar Ge_2S_2 four-membered ring (Fig. 1). The average distance of $Ge–S_t$ (terminal bond) is shorter than that of $Ge–S_b$ (bridging bond) by 0.113 Å (Table 2). Both kinds of bond distances are in good agreement with corresponding distances in the compounds containing $[Ge_2S_6]^{4-}$ ions [21,24], but are longer than those of discrete adamantane $[Ge_4S_{10}]^{4-}$ anion [30]. Compared with bonds distances and angles of **1**, the anionic structures of **2** and **3** are very similar to that of **1** (Table 2). The angles of $[Ge_2S_6]^{4-}$ anions of **1–3** match well

with those of other analogues of dimeric $[M_2Q_6]^{4-}$ anions (M = Ge [21–24,31], Sn [33–34,38–42]; Q = S, Se, Te), whose angles are always in the order of $Q_t–M–Q_t > Q_b–M–Q_b > M–Q–M'$.

A number of main group chalcogenidometalate anions with counter ions of protonated amine cations
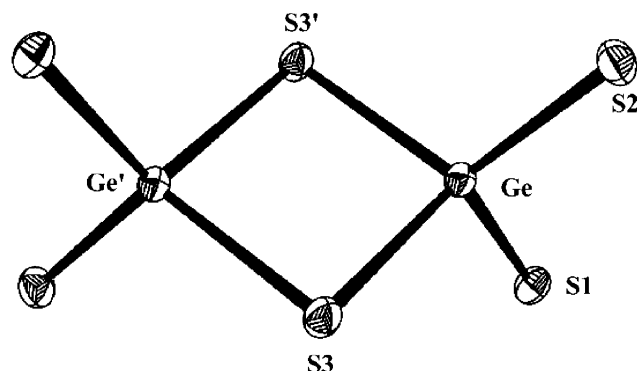

Fig. 1. Structure of the $[Ge_2S_6]^{4-}$ anion drawn from compound **1** with labeling and displacement ellipsoids drawn at the 50% probability level.

have been synthesized in recent years [24,28,31–37], in which three compounds concern chalcogenidogermi-nates, i.e., $[(C_4H_9)_2NH_2]_4Ge_2S_6$ [24], $[(Pr^n{}_2NH_2)][(Pr^n)(Et)NH_2]Ge_4S_9$ [28] and $[(Et_4N)_2(enH)_2]Ge_2Se_6$ [31]. In crystal structure of **1**, there are two independent mono-protonated units of $[H_3N(1)–CH_2CH_2–N(2)H_2]^+$ and $[H_3N(3)–CH_2CH_2–N(4)H_2]^+$. The two $[enH]^+$ units exhibit *trans* and *cis* conformations with torsion angles $-168.0(3)°$ (N(1)–C(1)–C(2)–N(2)) and $-61.9(4)°$ (N(3)–C(3)–C(4)–N(4)), respectively (Fig. 2). These two mono-protonated amines are head to tail linked by N(3)–H(3C)···N(2) hydrogen bonds with N···N distance of 2.857(4) Å and N–H···N angle of 164(3)°. The ammonium group of $[H_3N(1)–CH_2CH_2–N(2)H_2]^+$ interacts with terminal S atoms of $[Ge_2S_6]^{4-}$ via N–H···S hydrogen bonds with N–H···S angles ranging from 172(3)° to 177(3)° (Fig. 3a). The N···S distances varying from 3.241 to 3.284 Å are comparable to corresponding distances observed in analogue of $(Hen)_4Sn_2S_6$ [34]. It is interesting that compound **1** is not isostructural to $(Hen)_4Sn_2S_6$. The ionic size match-ing and hydrogen bonds might play influence on

Table 2
Selected distances (Å) and angles (deg) for **1**, **2** and **3**

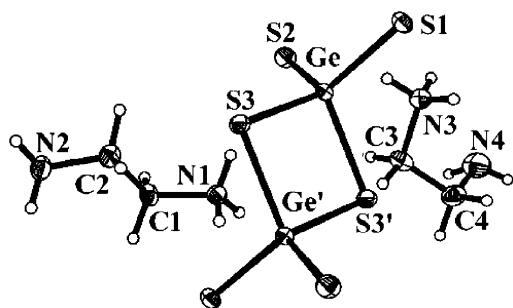|	$(Hen)_4Ge_2S_6$ (**1**)	$[Mn(en)_3]_2Ge_2S_6$ (**2**)	$[Ni(en)_3]_2Ge_2S_6$ (**3**)
Ge–S(1)	2.1581(9)	2.1668(9)	2.164(3)
Ge–S(2)	2.1691(8)	2.1596(10)	2.170(4)
Ge–S(3)	2.2697(9)	2.2760(9)	2.267(4)
Ge–(S3′)	2.2843(11)	2.2807(9)	2.274(4)
S(1)–Ge–S(2)	114.18(4)	113.26(4)	111.1(2)
S(1)–Ge–S(3)	110.98(3)	112.15(4)	114.8(2)
S(2)–Ge–S(3)	113.74(4)	110.75(4)	112.4(1)
S(1)–Ge–S(3′)	110.20(3)	113.79(4)	112.0(1)
S(2)–Ge–S(3′)	112.65(4)	112.91(3)	114.0(1)
S(3)–Ge–S(3′)	93.27(3)	92.22(4)	91.3(1)
Ge–S(3)–Ge′	86.73(3)	87.78(4)	88.7(1)
		M = Mn	M = Ni
M–N(1)		2.283(3)	2.13(2)
M–N(2)		2.284(3)	2.22(2)
M–N(3)		2.287(3)	2.09(2)
M–N(4)		2.267(3)	2.14(2)
M–N(5)		2.261(3)	2.07(2)
M–N(6)		2.287(3)	2.13(2)
N(1)–M–N(2)		76.11(10)	81.0(8)
N(1)–M–N(3)		95.05(10)	168.2(8)
N(1)–M–N(4)		171.23(10)	89.8(7)
N(1)–M–N(5)		102.07(11)	95.9(8)
N(1)–M–N(6)		88.13(10)	94.9(8)
N(2)–M–N(3)		94.61(11)	90.0(8)
N(2)–M–N(4)		100.99(10)	92.6(7)
N(2)–M–N(5)		104.42(12)	172.7(7)
N(2)–M–N(6)		164.20(10)	90.3(7)
N(3)–M–N(4)		76.83(9)	83.0(7)
N(3)–M–N(5)		156.90(12)	93.9(8)
N(3)–M–N(6)		87.72(10)	92.7(8)
N(4)–M–N(5)		86.65(11)	94.0(7)
N(4)–M–N(6)		94.76(10)	174.8(7)
N(5)–M–N(6)		77.55(12)	83.3(7)

Fig. 2. The structure of **1** with labeling and displacement ellipsoids drawn at the 50% probability level.
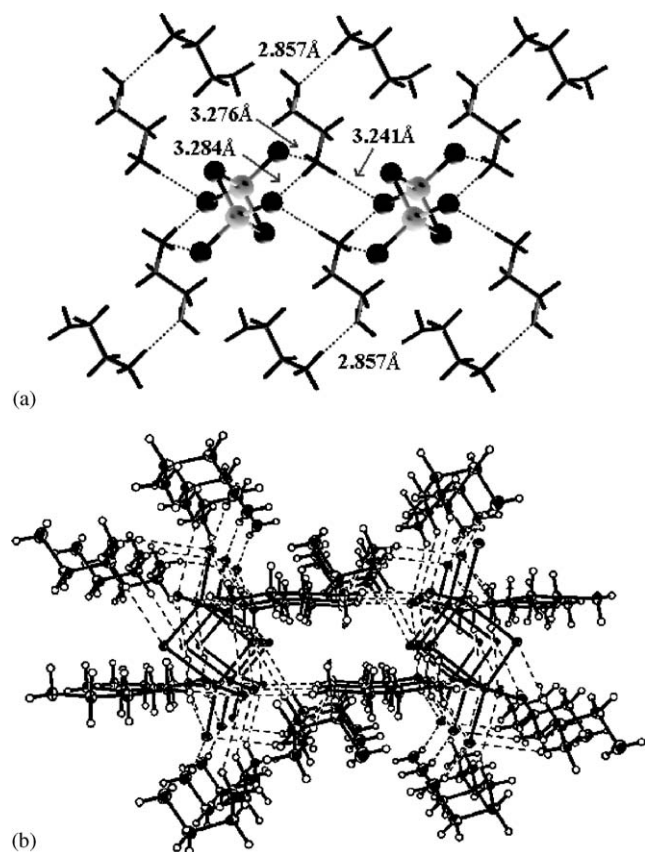

Fig. 3. (a) View of the hydrogen bonds (shown in dashed lines) in **1**; (b) view of the three-dimensional arrangement of the anions and cations in **1** (view along *c*-axis) resulted by hydrogen bonds, displacement ellipsoids are drawn at the 20% probability level.

structural parameters. The hydrogen bond interactions lead to a three-dimensional arrangement of the $[Ge_2S_6]^{4-}$ anions and $[enH]^+$ cations in **1** (Fig. 3b).

But the structures of **2** and **3** are isostructural to the analogous thiostannates of $[Mn(en)_3]_2Sn_2S_6$ [39] and $[Ni(en)_3]_2Sn_2S_6$ [38], respectively. In **2** and **3**, both Mn^{2+} and Ni^{2+} cations are in similar octahedral coordination geometry coordinated by three bidentate ligands of ethylenediamine (Fig. 4). The Mn–N bond distances

varying from 2.261(3) to 2.287(3) Å are within the range of other compounds containing the $[Mn(en)_3]^{2+}$ cations [39,43]. The coordination octahedron of $[Mn(en)_3]^{2+}$, whose three axial N–Mn–N angles range from 156.90(12)° to 171.23(10)°, is apparently distorted. The $[Ni(en)_3]^{2+}$ cation is also a distorted octahedron with the octahedral axial N–Ni–N angles varying from 168.2(8)° to 174.8(7)° (Table 2). The Ni–N bond distances (2.07(2)–2.22(2)) are in agreement with those of the similar compound reported in the literature [38]. The $[Mn(en)_3]^{2+}$ cation exhibits two conformations of $\Delta(\lambda\lambda\lambda)$ (Fig. 4a1) and $\Lambda(\delta\delta\delta)$ (Fig. 4a2). In **3**, the N atoms of ethylenediamine ligands is disordered with $\Lambda(\delta\delta\delta)$: $\Delta(\lambda\lambda\lambda)$ (or $\Delta(\lambda\lambda\lambda)$: $\Lambda(\delta\delta\delta)$ in inversion position) occupation ratio of 0.60:0.40 (Fig. 4b).

Hydrogen bond interactions between $[Ge_2S_6]^{4-}$ anions and $[M(en)_3]^{2+}$ cations are found in **2** and **3**. All the $[Ge_2S_6]^{4-}$ anions interact with –NH$_2$ group of en through N–H···S hydrogen bonds. In **2** every $[Ge_2S_6]^{4-}$ anion is surrounded by six $[Mn(en)_3]^{2+}$ cations (Fig. 5a) forming interactions of N–H···S hydrogen bonds, which lead to a three-dimensional arrangement of $[Ge_2S_6]^{4-}$ and $[Mn(en)_3]^{2+}$. In **3**, there are fewer hydrogen bonds between anions and cations (Fig. 5b). One $[Ge_2S_6]^{4-}$ anion forms six hydrogen bonds to four $[Ni(en)_3]^{2+}$ cations resulting in a layered arrangement of anions and cations.

The crystal system of $A_xGe_2S_6$ (*A* = cation) family is related to entities of A^+ cations (Table 3). The smaller metal ions result in triclinic crystal system. The Tl(I) ion in $Tl_4Ge_2S_6$ is covalent bonded to the anion and therefore the radii is similar to that of Na$^+$. The larger metal ions of K$^+$ and Au$^+$ lead to monoclinic. Owing to the flexibility of protonated amines, $(enH)_4Ge_2S_6$ and $[(C_4H_9)_2NH_2]_4Ge_2S_6$ still crystallize in crystal system of triclinic. When A^+ ion becomes much larger spherical cation of $[Ni(en)_3]^{2+}$, $[Ni(en)_3]_2Ge_2S_6$ is in orthorhombic crystal system. Ion of $[Mn(en)_3]^{2+}$ is slight larger than $[Ni(en)_3]^{2+}$, due to more N–H···S interactions between $[Mn(en)_3]^{2+}$ and $[Ge_2S_6]^{4-}$, $[Mn(en)_3]_2Ge_2S_6$ takes different crystal system from the Ni compound.

3.3. Thermal analysis

The thermal behaviors of compounds **1–3** were conducted on a DSC-TGA microanalyzer under nitrogen between temperature 20 and 450 °C. Compound **1** decomposes in four steps (Fig. 6a). In the first step, the mass loss of 11.1% corresponds with removal one en ligand (calc.: 10.3% for 1 en). In the following two steps, total mass loss of 26.0% is in agreement with removing two en ligands and one H$_2$S molecule (calc.: 20.6% for 2 en and 5.9% for 1 H$_2$S). **1** loses its last amine and second H$_2$S with mass loss of 15.7% (calc.: 10.3% for 1 en and 5.9% for 1 H$_2$S) in the fourth step. The total mass loss of 52.7% is in good agreement with theoretical value of
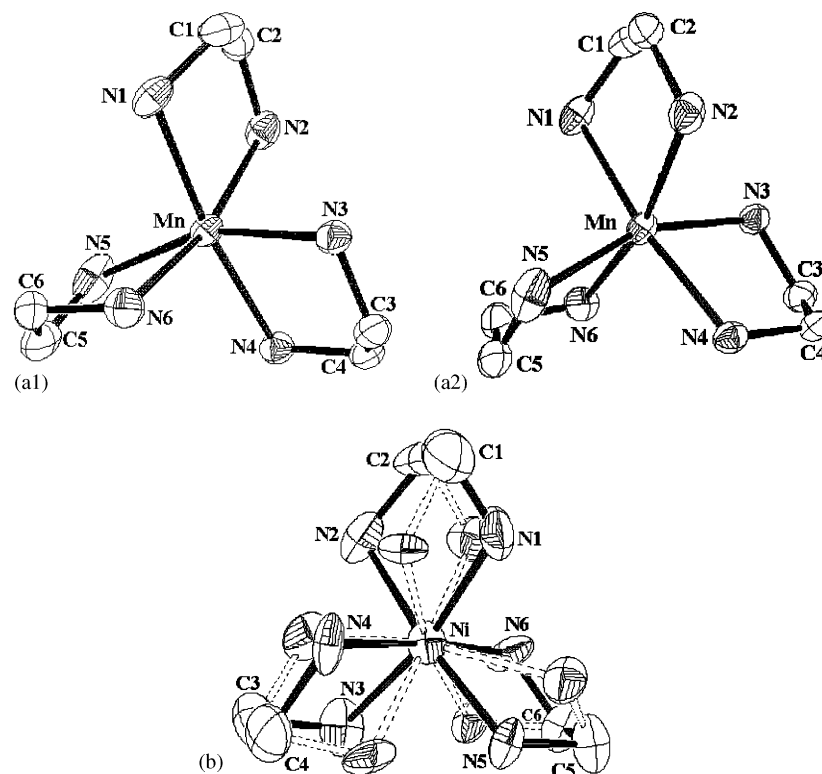
Fig. 4. ORTEP representation of the transition metal complex cations in **2** (a1 and a2) and **3** (b) with labeling and displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.
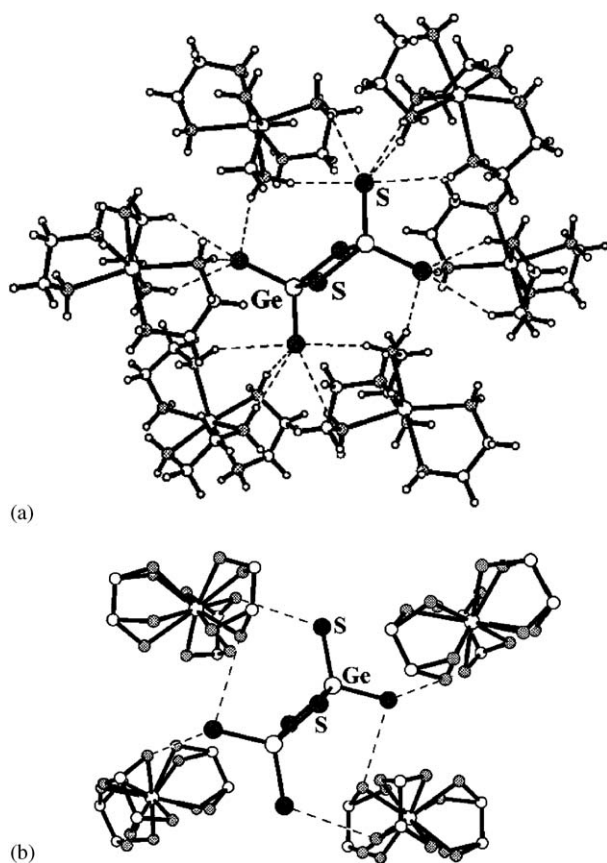

(a)

(b)

Table 3
Crystal system and space group for family of $A_x Ge_2 S_6$

A	Crystal system	Space group	References
Na^+	Triclinic	$P\bar{1}$	[21]
Tl^+	Triclinic	$P\bar{1}$	[22]
$[enH]^+$	Triclinic	$P\bar{1}$	This paper
$[(C_4H_9)_2NH_2]^+$	Triclinic	$P\bar{1}$	[24]
K^+	Monoclinic	$P2_1/n$	[23]
Au^+	Monoclinic	$P2_1/n$	[23]
$[Mn(en)_3]^{2+}$	Monoclinic	$C2/c$	This paper
$[Ni(en)_3]^{2+}$	Orthorhombic	$Pbca$	This paper

53.0% involving complete removing four en and two H_2S molecules and GeS_2 remains as residue. The four-step mass losses concur with four endothermic peaks at 92, 133, 160 and 250 °C, respectively on DSC curve (Fig. 6a).

Compound **2** also decomposes in four steps (Fig. 6b). The mass loss of 29.6% in the first and second steps is in accordance with the removal of four en ligands (calc.:

Fig. 5. Views of the N–H···S hydrogen bonds (shown in dashed lines) between anions and cations for **2** (a) and **3** (b) (at 50% probability level).
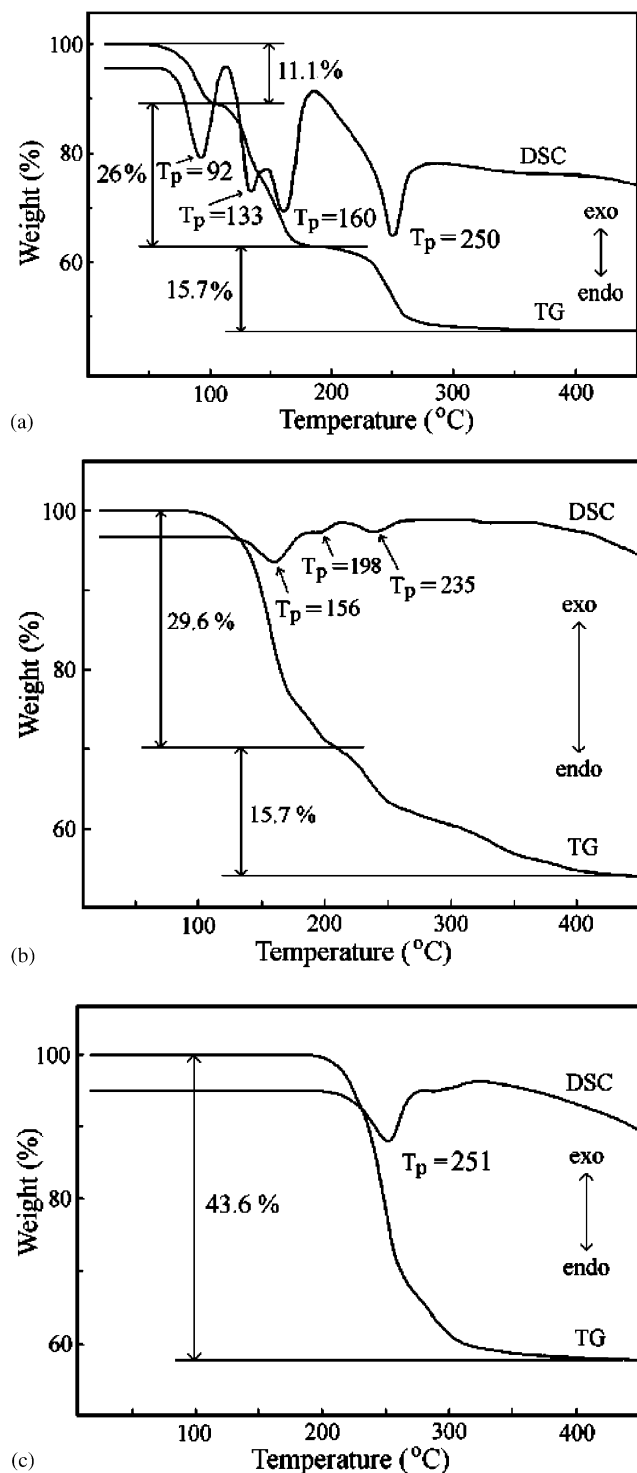
Fig. 6. TGA-DSC curves for compounds **1** (a), **2** (b) and **3** (c).

is observed for compound **3** with peak temperature of decomposition at 251 °C (Fig. 6c) and a weak nodal at about 300 °C on DSC curve. The corresponding total mass loss of 43.6% is in agreement with the complete removal all en ligands (calc.: 44.1% for 6 en). The decomposition mechanisms of the compounds are complex and some steps are overlapped. Therefore, one of the assignment steps in the TG curves might include multi decomposition steps.

4. Supplementary data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 239977-239979. 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 1EZ, UK; fax: +44-1223-336-033, or mailto: deposit@ccdc.cam.ac.uk.

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29.8% for 4 en). The third and fourth steps are overlapped with the total mass loss of 15.7% (calc.: 14.9% for 2 en). The mass losses are accompanied by three endothermic signals at 156, 198 and 235 °C on DSC curve, but the endothermic peak in the fourth step is very weak. (Fig. 5b). A two-step mass loss procedure

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