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New Selenidogermanates with Transition-Metal Complexes as Counterions: Solvothermal Synthesis, Crystal Structures, and Properties of $[Mn(en)_3]_2Ge_2Se_6$ and $[Fe(dien)_2]_2Ge_2Se_6$

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Summary. New selenidogermanates $[Mn(en)_3]_2Ge_2Se_6$ (*en* = ethylenediamine) and $[Fe(dien)_2]_2Ge_2Se_6$ (*dien* = diethylenetriamine) were synthesized by the reaction of germanium dioxide, elemental selenium, and transition metal chlorides in respectively *en* and *dien*. Both compounds crystallize in the monoclinic space group $P2_1/n$ with two formula units in the unit cell, and consist of discrete $[Ge_2Se_6]^{4-}$ anions with transition metal complex cations as counter ions. The $[Ge_2Se_6]^{4-}$ anion is formed by two $GeSe_4$ tetrahedra sharing a common edge to form a planar Ge_2Se_2 four-membered ring. The $[Mn(en)_3]^{2+}$ and $[Ni(dien)_2]^{2+}$ complex cations are in distorted octahedral geometry. In both selenidogermanates extensive N–H···Se hydrogen bonding contacts lead to 3-dimensional network structures. The band gaps of 2.36 and 2.25 eV were derived from optical absorption spectra. Thermogravimetric analysis shows that the first compound decomposes in two steps under the nitrogen stream, while the second exhibits a one-step decomposition process.

Keywords. Solvothermal synthesis; X-Ray structure determination; Selenidogermanates; Metal complexes.

Introduction

The solvothermal synthesis of selenidogermanates has attracted increasing attention because of the structural diversity based on the condensation of tetrahedral $[GeSe_4]^{4-}$ anions [1, 2]. The $[GeSe_4]^{4-}$ anions connect by corner- or edge-sharing to form discrete anions, such as dimeric $[Ge_2Se_6]^{4-}$ [3–6] and $[Ge_2Se_7]^{6-}$ [7], and adamantane-like $[Ge_4Se_{10}]^{4-}$ [8–13] species. The condensation of $[GeSe_4]^{4-}$ building units through corner-bridging also gives polymeric anions, for example one-dimensional $[GeSe_3{}^{2-}]_n$ chains in Na_2GeSe_3 [14] and two-dimensional $[Ge_2Se_5{}^{2-}]_n$ layers in $Na_2Ge_2Se_5$ [15]. The Se–Se bonding linkage between $[GeSe_4]^{4-}$ units is observed in compounds $Cs_4Ge_2Se_8$ [16] and M_2GeSe_4 (M = K, Rb) [17]. The counter ions to compensate the charge of these selenidogermanate anions can be classified as alkali metal cations [3–5, 7–9, 14–17] and organic cations [6, 10–12]. Recently, selenidogermanates with transition-metal complexes as counter ions, $(enH_2)[\{Mn(en)_2(enH)\}_2(\mu\text{-}en)][Ge_2Se_7]_2$ [18], $[Mn(dien)_2]_2Ge_2Se_7$ [18], and ternary selenidogermanate $[Ba(H_2O)_{10}][\{Cr(en)\}_2(GeSe_4)_2]$ [19], have been prepared in amine. The combination of transition metals should lead to new properties, such as characteristic optical and magnetic properties of transition metals, for selenidogermanates.

Although binuclear anions of the type $[M_2E_6]^{4-}$ (M = Ge, Sn; E = S, Se, Te) with transition metal complex cations have been known for $[Ge_2S_6]^{4-}$ [20] and $[Sn_2E_6]^{4-}$ [21–25], analogous anions have not previously been characterised for $[Ge_2Se_6]^{4-}$ anion. In our systematic synthesis of chalcogenidometalates containing transition metals in superheated amine [24–29], two new selenidogermanates $[Mn(en)_3]_2Ge_2Se_6$ (**1**) and $[Fe(dien)_2]_2Ge_2Se_6$ (**2**) were directly synthesized using GeO_2 and Se as source materials in the presence of transition metal ion in amine. We report here

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the syntheses, crystal structures, optical property, and thermal stability of the chalcogenometalates. To the best of our knowledge, compounds **1** and **2** are the first two examples of dimeric $[Ge_2Se_6]^{4-}$ selenidogermanate anions with transition metal complex cations acting as charge compensating ions.

Results and Discussion

Syntheses of the Compounds

The selenidogermanates are traditionally prepared using binary germanium selenides or ternary alkali or alkaline earth germanium selenides as precursors, such as Ge_2Se_3 [6], $K_4Ge_4Se_{10}$ [10–13], and Ba_2GeSe_4 [19]. In this work, selenidogermanate anion $[Ge_2Se_6]^{4-}$ was directly synthesized using GeO_2 and Se as starting materials. The selenide ions involved in the formation of the selenidogermanate anion are produced by the disproportionation of selenium in *en* under solvothermal condition, and this method has been widely used in the preparation of selenidometalates [30]. Comparably, the solvothermal reaction of elemental Ge and Se in *en* and *dien* produces $[Ge_2Se_7]^{4-}$ anion [18].

Description of the Structures

Compounds **1** and **2** crystallize in the monoclinic space group $P2_1/n$ with two formula units in the unit cell. The counter ions to balance the negative charge of $[Ge_2Se_6]^{4-}$ ions in compounds **1** and **2** are transition metal amino complexes. The Mn^{2+} and Fe^{2+} cations are coordinated by three bidentate *en* ligands and two tridentate *dien* ligands to form the sixfold coordination of N atoms. Both coordination polyhedra can be described as distorted octahedra, which are manifested by the axial *trans*-N–*M*–N angles deviating from 180° (Table 1). The octahedral cation $[Mn(en)_3]^{2+}$ is in ether of $\Lambda(\delta\delta\delta)$ or $\Delta(\lambda\lambda\lambda)$ conformation, as found for the $[Co(en)_3]^{2+}$ cation in $[Co(en)_3]CoSb_4S_8$ [31]. The $[Fe(dien)_2]^{2+}$ cation in **2** exhibits the conformation of *u-fac*. We note that the geometric isomers of transition metal complexes with *dien* ligands have been intensively studied before [32–34]. The Mn–N bond distances between 2.222(5) and 2.296(5) Å, and Fe–N bond distances between 2.192(3) and 2.306(2) Å are in the normal ranges as found in other compounds containing $[Mn(en)_3]^{2+}$ [24, 35] and $[Fe(dien)_2]^{2+}$ [36, 37] complex cations, respectively.

The dimeric anion in compounds **1** and **2** is constructed by two $GeSe_4$ tetrahedra sharing a common edge to form a planar Ge_2Se_2 four-membered ring. The Ge–Se$_t$ (terminal) bond distances are 2.3034(8)–2.3080(8) Å for **1** and 2.2958(5)–2.2971(5) for **2**, and are shorter than those of Ge–Se$_b$ (bridging) bonds (2.4089(8)–2.4161(8) Å for **1**, 2.4170(5)–2.4312(5) Å for **2**) (Table 1). The distances of the two kinds of bonds are in good agreement

Table 1. Selected distances/Å and angles/° for **1** and **2**

	1 ($M=$ Mn)	**2** ($M=$ Fe)		**1** ($M=$ Mn)	**2** ($M=$ Fe)
Ge–Se(1)	2.4161(8)	2.4170(5)	Ge–Se(2)	2.3080(8)	2.2958(5)
Ge–Se(3)	2.3034(8)	2.2971(5)	Ge–Se(1)^a	2.4089(8)	2.4312(5)
M–N(1)	2.222(5)	2.275(3)	M–N(2)	2.296(5)	2.200(3)
M–N(3)	2.262(5)	2.216(3)	M–N(4)	2.288(5)	2.306(2)
M–N(5)	2.267(5)	2.192(3)	M–N(6)	2.296(5)	2.161(2)
Se(1)–Ge–Se(2)	112.94(3)	112.183(18)	Se(1)–Ge–Se(3)	114.01(3)	112.859(19)
Se(2)–Ge–Se(3)	110.15(3)	112.38(2)	Se(2)–Ge–Se(1)^a	114.94(3)	114.688(19)
Se(3)–Ge–Se(1)^a	111.42(3)	111.821(19)	Se(1)–Ge–Se(1)^a	92.46(3)	91.312(17)
Ge–Se(1)–Ge^a	87.54(3)	88.688(17)			
N(1)–M–N(2)	77.16(17)	78.05(10)	N(1)–M–N(3)	92.84(18)	77.26(10)
N(1)–M–N(4)	100.20(18)	111.89(9)	N(1)–M–N(5)	163.75(18)	164.28(9)
N(1)–M–N(6)	92.84(18)	90.40(10)	N(2)–M–N(3)	93.55(17)	95.50(11)
N(2)–M–N(4)	170.87(18)	167.13(10)	N(2)–M–N(5)	90.02(18)	95.85(10)
N(2)–M–N(6)	97.45(18)	94.29(10)	N(3)–M–N(4)	77.77(17)	94.75(10)
N(3)–M–N(5)	97.95(18)	89.06(10)	N(3)–M–N(6)	168.50(18)	162.28(11)
N(4)–M–N(5)	93.95(19)	76.55(9)	N(4)–M–N(6)	91.38(18)	77.93(9)
N(5)–M–N(6)	78.79(18)	104.59(10)			

Symmetry transformations used to generate equivalent atoms: ^{a} $-x+1, -y+1, -z+1$

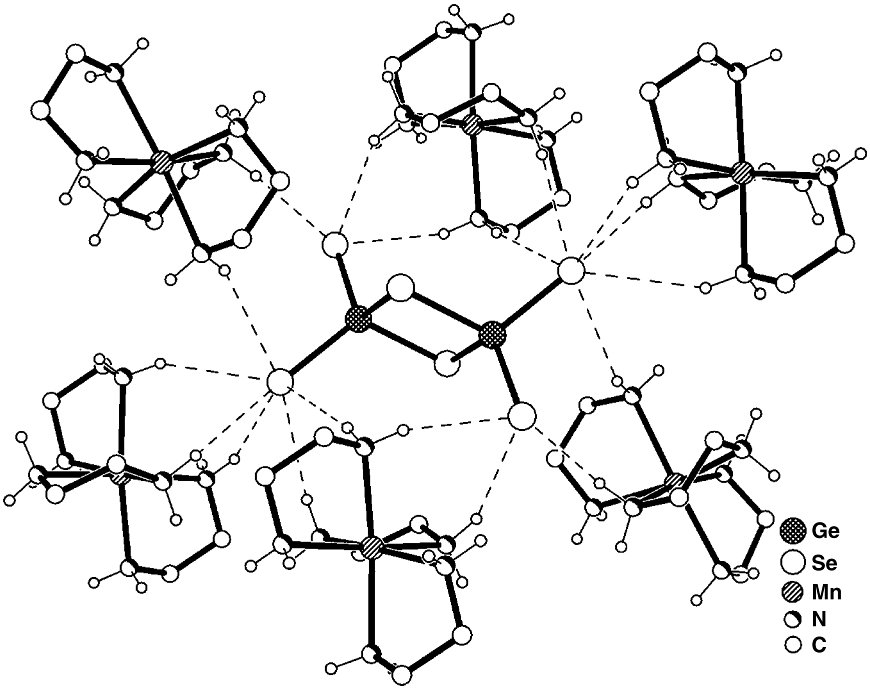

Fig. 1. View of surrounding of a $[Ge_2Se_6]^{4-}$ anion in **1**, showing the N–H$\cdots$Se hydrogen bonds (dashed lines). Hydrogen atoms of CH_2 groups are omitted for clarity

with those in the compounds containing $[Ge_2Se_6]^{4-}$ ions [5, 6], but are longer than those of discrete adamantane $[Ge_4Se_{10}]^{4-}$ anion [12]. The Se–Ge–Se angles range from 92.46(3) to 114.94(3)° for **1**, and from 91.312(17) to 114.688(19)° for **2**, indicating the distorted tetrahedral geometry for $GeSe_4$ units. The angles (Table 1) match well with those of other analogous dimeric anions $[M_2E_6]^{4-}$ (M = Ge, Sn; E = S, Se, Te) [20–25], whose angles are always in the order of $E_t{-}M{-}E_t > E_b{-}M{-}E_b > M{-}E{-}M'$.

In **1**, all the terminal Se atoms of $[Ge_2Se_6]^{4-}$ are involved in intermolecular N–H$\cdots$Se hydrogen bonding with adjacent $[Mn(en)_3]^{2+}$ cations. The environment of a $[Ge_2Se_6]^{4-}$ anion showing hydrogen bonding is depicted in Fig. 1. Every $[Ge_2Se_6]^{4-}$ anion contacts with six $[Mn(en)_3]^{2+}$ cations *via* hydrogen bonds with N$\cdots$Se distances varying from 3.492(5) to 3.820(5) Å and the N–H$\cdots$Se angles varying from 143.2 to 173.4° (Table 2), which are consistent with the values reported in the literature [38]. The intermolecular hydrogen bonding contacts lead to a three-dimensional network of $[Mn(en)_3]^{2+}$ and $[Ge_2Se_6]^{4-}$ ions (Fig. 2). Similar intermolecular hydrogen bonding is observed in compound **2** (Table 2 and Fig. 3).

The tetrahedral $[GeSe_4]^{4-}$ anion is the primary building unit for selenidogermanates. The tetrameric

Table 2. Selected hydrogen bond distances/Å and N–H$\cdots$Se angles/° for **1** and **2**

D–H$\cdots A$	d(H$\cdots A$)	d($D\cdots A$)	$<$(DHA)
1			
N(1)–H(1A) $\cdots$Se(2)^{a}	2.77	3.679(5)	169.4
N(1)–H(1B) $\cdots$Se(3)	2.63	3.492(5)	156.3
N(2)–H(2A) $\cdots$Se(3)^{b}	2.64	3.491(5)	154.2
N(2)–H(2B) $\cdots$Se(2)^{c}	2.79	3.651(5)	155.4
N(3)–H(3A) $\cdots$Se(2)^{a}	2.76	3.679(5)	173.4
N(3)–H(3B) $\cdots$Se(2)^{c}	2.68	3.556(5)	159.3
N(4)–H(4A) $\cdots$Se(3)^{d}	3.04	3.820(5)	143.2
N(4)–H(4B) $\cdots$Se(3)	2.87	3.696(5)	150.9
N(5)–H(5A) $\cdots$Se(3)^{d}	2.84	3.750(5)	169.9
2			
N(1)–H(1)$\cdots$Se(3)^{a}	2.75	3.670(2)	168.4
N(2)–H(2A) $\cdots$Se(1)^{a}	2.90	3.567(2)	130.1
N(2)–H(2B)$\cdots$Se(2)	2.69	3.588(3)	167.1
N(3)–H(3A)$\cdots$Se(3)^{b}	2.81	3.706(3)	165.9
N(4)–H(4)$\cdots$Se(3)^{b}	2.71	3.490(3)	142.2
N(5)–H(5A)$\cdots$Se(1)^{c}	2.78	3.587(3)	147.3
N(5)–H(5B)$\cdots$Se(2)^{d}	2.52	3.434(2)	174.0
N(6)–H(6A)$\cdots$Se(3)^{e}	2.81	3.631(3)	149.7
N(6)–H(6B)$\cdots$Se(2)	2.75	3.576(3)	149.6

Symmetry transformations used to generate equivalent atoms: For **1**: ^{a} $-x+1$, $-y+1$, $-z+1$; ^{b} $x-1/2$, $-y+1/2$, $z+1/2$; ^{c} x, y, $z+1$; ^{d} $x+1/2$, $-y+1/2$, $z+1/2$. For **2**: ^{a} $x-1/2$, $-y+1/2$, $z-1/2$; ^{b} $x+1/2$, $-y+1/2$, $z-1/2$; ^{c} $-x+1$, $-y$, $-z+1$; ^{d} $-x+1/2$, $y-1/2$, $-z+1/2$; ^{e} $-x+1$, $-y+1$, $-z+1$

adamantane-like $[Ge_4Se_{10}]^{4-}$ anion is produced as the predominant condensation product of $[GeSe_4]^{4-}$ units in the solution of lower *pH*-values [1]. The preparation of compounds **1** and **2** shows that the $[Ge_2Se_6]^{4-}$ anion exists in the basic solvents of *en* and *dien*. The condensation of $[GeSe_4]^{4-}$ primary unit

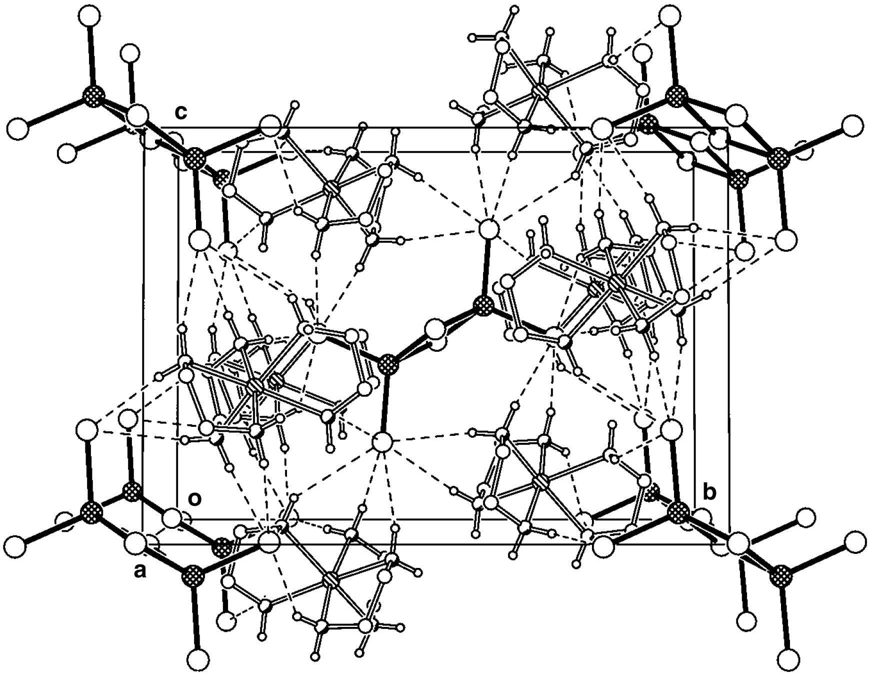

Fig. 2. Packing of the molecules of **1** with view along *a*-axis. Hydrogen atoms of CH_2 groups are omitted for clarity

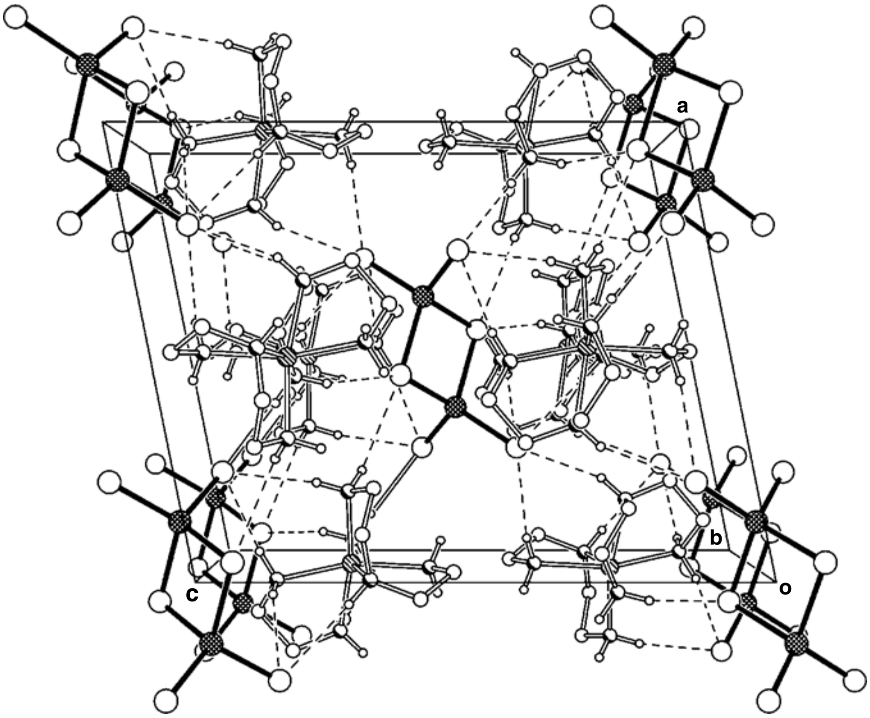

Fig. 3. Packing of the molecules of **2** with view along *b*-axis. Hydrogen atoms of CH_2 groups are omitted for clarity

is influenced by *pH* of the solution, and the solution with lower *pH*-values is beneficial to a higher condensation degree of $[GeSe_4]^{4-}$ anions.

Optical Property and Thermal Analysis

The optical absorption spectra of compounds **1** and **2** (Fig. 4) show well-defined abrupt absorption edges from which the band gaps can be estimated 2.36 eV for **1**, and 2.25 eV for **2**. Both band gaps are comparable with those of organic-inorganic hybrid selenidogermanates $[C_nH_{2n+1}N(CH_3)_3]_2ZnGe_4Se_{10}$ and $[C_nH_{2n+1}N(CH_3)_3]_2CdGe_4Se_{10}$ ($n = 12$, 14, 16, 18) [11], whose band gaps lie in the range of 2.3–2.6 eV and 2.1–2.4 eV.

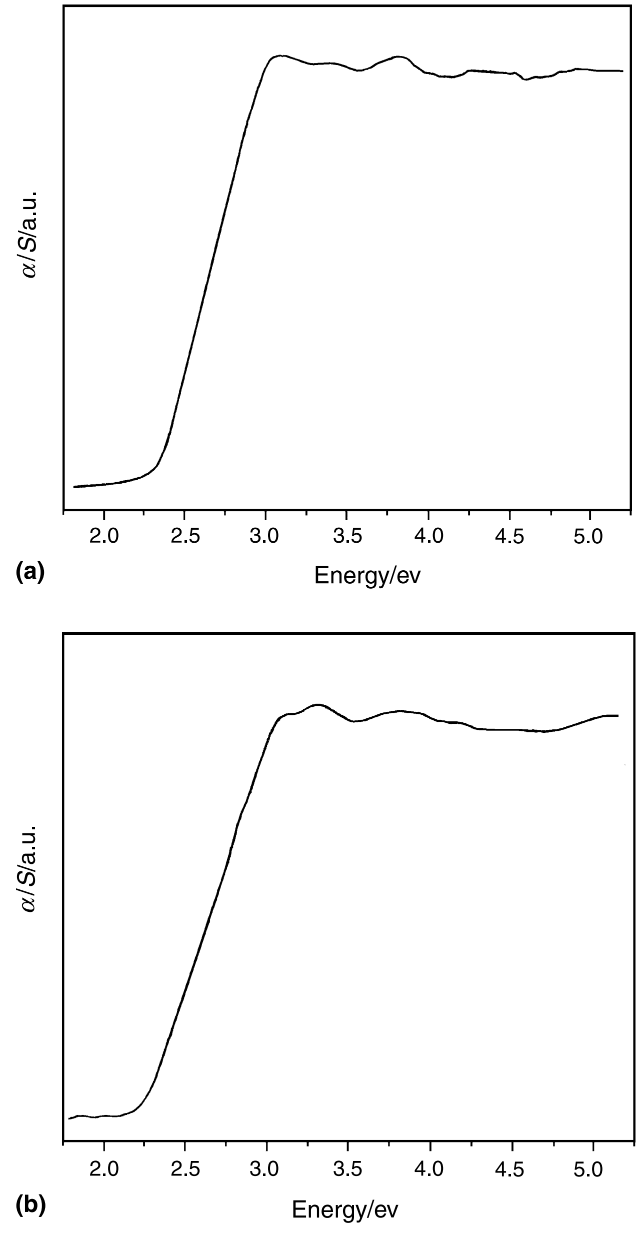

Fig. 4. Optical absorption spectra of **1** (a) and **2** (b)

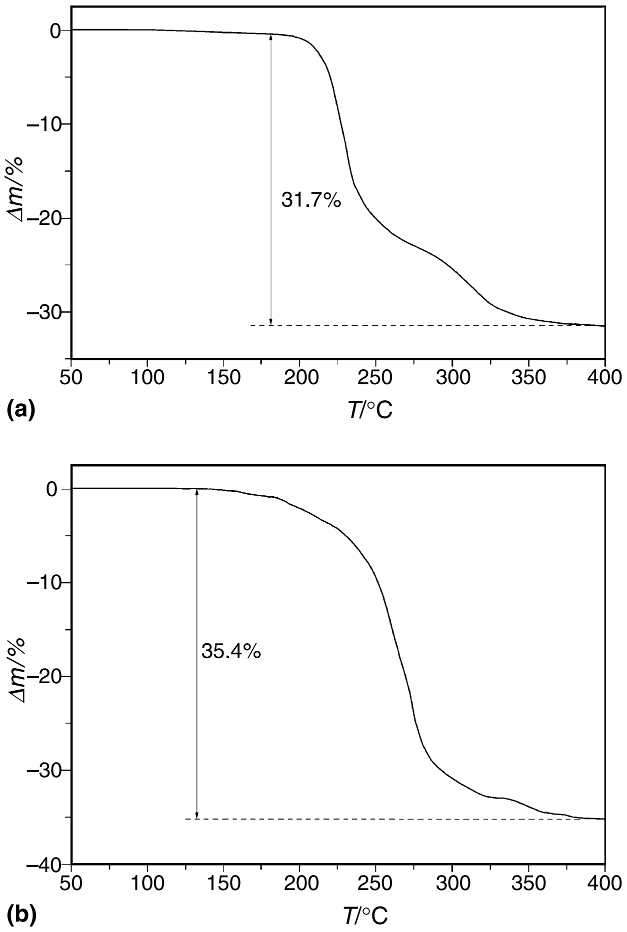

Fig. 5. TGA curves of compounds **1** (a) and **2** (b)

The two compounds are stable up to 190–210°C on heating. Compound **1** decomposes in two steps (Fig. 5a) between 210 and 350°C, and the overall weight change of 31.7% is approximately in accordance with the complete removal of the six *en* lgands (calcd.: 33.1%). A one-step mass loss procedure in the range 190–375°C is observed for compound **2** with the mass loss of 35.4% (Fig. 5b), which is in agreement with the complete removal of all *dien* ligands (calcd.: 36.1%).

Experimental

Physical Measurements

Elemental analyses (C, H, and N) were performed on a MOD 1106 elemental analyzer; their results agreed with calculated values. UV-Vis spectra were measured with a Shimadzu UV-3150 spectrometer at room temperature. The absorption (α/S)

data were calculated from the reflectance using the *Kubelka-Munk* function $\alpha/S=(1\text{-}R)^2/2R$ [39], where R is the reflectance at a given energy, α the absorption, and S the scattering coefficient. Thermogravimetric analysis (TGA) was performed on a SDT 2960 apparatus and all the samples were heated under a N_2 stream of 100 cm^3/min with a heating rate of 5°C/min.

[Mn(en)$_3$]$_2$Ge$_2$Se$_6$ (**1**, $C_{12}H_{48}N_{12}Se_6Mn_2Ge_2$)

A mixture of 198 mg $MnCl_2 \cdot 4H_2O$ (1 mmol), 104.6 mg GeO_2 (1.0 mmol), and 237 mg Se (3 mmol) in 6 cm^3 *en* was stirred for 30 min, then the mixture was sealed in a Teflon-lined autoclave with an inner volume of 15 cm^3. The autoclave was heated at 160°C for 7 days and then cooled to room temperature. The resulting yellow block crystals **1** were filtered off, washed with ethanol, and dried at ambient temperature (yield 52%).

[Fe(dien)$_2$]$_2$Ge$_2$Se$_6$ (**2**, $C_{16}H_{52}N_{12}Se_6Fe_2Ge_2$)

A mixture of 199 mg $FeCl_2 \cdot 4H_2O$ (1 mmol), 104.6 mg GeO_2 (1.0 mmol), and 237 mg Se (3 mmol) in 6 cm^3 *dien* 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 160°C for 7 days and then cooled to room temperature. The resulting orange-yellow block crystals **2** were filtered off, washed with ethanol, and dried at ambient temperature (yield 48%).

Structure Determination

Intensities were collected on a Rigaku Mercury CCD diffractometer using ω-scan method with graphite monochromated Mo-Kα radiation ($\lambda = 0.071073$ nm) at −80(2)°C to a maximum 2θ value of 54.94 for **1**, and 50.68 for **2**. An absorption correction was applied for all the compounds using multiscan. The structures were solved with direct methods using the program SHELXS-97 [40], and the refinement was performed against F^2 using the program SHELXL-97 [41]. 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. 622790 and 622791. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html

Table 3. Crystallographic data for [Mn(*en*)$_3$]$_2$Ge$_2$Se$_6$ (**1**) and [Fe(*dien*)$_2$]$_2$Ge$_2$Se$_6$ (**2**)

	1	**2**
Formula	$C_{12}H_{48}N_{12}Se_6Mn_2Ge_2$	$C_{16}H_{52}N_{12}Se_6Fe_2Ge_2$
Formula weight	1089.44	1143.34
Dimensions/mm^3	0.25 × 0.15 × 0.15	0.50 × 0.45 × 0.10
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	9.0583(11)	12.4257(19)
b/Å	16.3189(19)	9.3122(14)
c/Å	11.6281(13)	15.385(3)
β/°	92.264(3)	101.422(4)
V/Å^3	1717.5(3)	1745.0(5)
Z	2	2
T/K	193(2)	193(2)
D_{calc}/g · cm^{-3}	2.107	2.176
F(000)	1044	1104
μ/mm^{-1}	8.834	8.808
Scan range/°	$6.10 \le 2\theta \le 54.94$	$6.42 \le 2\theta \le 50.68$
Index range	$-11 \le h \le 11$ $-16 \le k \le 21$ $-13 \le l \le 15$	$-14 \le h \le 14$ $-11 \le k \le 11$ $-18 \le l \le 17$
Measured reflections	18960	16651
Independent	3908	3177
R_{int}	0.0437	0.0505
Reflections with ($I > 2\sigma(I)$)	3404	2849
Parameters	155	173
$R1$ ($I > 2\sigma(I)$)	0.0470	0.0239
$R1$ (for all reflections)	0.0575	0.0288
$wR2$ ($I > 2\sigma(I)$)	0.0848	0.0503
$wR2$ (for all reflections)	0.0887	0.0524
$\Delta\rho$/e Å^{-3}	−0.798/1.240	−0.645/0.538
Goodness of fit	1.139	1.029

or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk.

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References

[1] Krebs B (1983) Angew Chem Int Ed **22**: 113
[2] Sheldrick WS, Wachhold M (1998) Coord Chem Rev **176**: 211
[3] Eulenberger G (1982) Monatsh Chem **113**: 859
[4] Krebs B, Muller H (1983) Z Anorg Allg Chem **496**: 47
[5] Eisenmann B, Hansa J (1993) Z Kristallogr **203**: 301
[6] Park C-W, Pell MA, Ibers JA (1996) Inorg Chem **35**: 4555
[7] Eisenmann B, Hansa J, Schäfer H (1986) Rev Chim Minér **23**: 8
[8] Eulenberger G (1981) Z Naturforsch Teil B **36**: 523
[9] Eisenmann B, Hansa J (1993) Z Kristallogr **205**: 325
[10] Wachhold M, Kanatzidis MG (2000) Chem Mater **12**: 2914
[11] Wachhold M, Rangan KK, Lei M, Thorpe MF, Billinge SJL, Petkov V, Heising J, Kanatzidis MG (2000) J Solid State Chem **152**: 21
[12] Wachhold M, Rangan KK, Billinge SJL, Petkov V, Heising J, Kanatzidis MG (2000) Adv Mater **12**: 85
[13] Coucouvanis D, Kanatzidis MG, Simhon E, Baenziger NC (1982) J Am Chem Soc **104**: 1874
[14] Eisenmann B, Hansa J, Schäfer H (1985) Z Naturforsch Teil B **40**: 450
[15] Eisenmann B, Hansa J, Schäfer H (1984) Rev Chim Minér **21**: 817
[16] Sheldrick WS, Schaaf B (1994) Z Naturforsch Teil B **49**: 655
[17] Sheldrick WS, Schaaf B (1995) Z Naturforsch Teil B **50**: 1469
[18] Almsick T, Loose A, Sheldrick WS (2005) Z Anorg Allg Chem **631**: 21
[19] Melullis M, Brandmayer MK, Dehnen S (2006) Z Anorg Allg Chem **632**: 64
[20] Jia DX, Dai J, Zhu QY, Cao LH, Lin HH (2005) J Solid State Chem **178**: 874
[21] Shreeve-Keyer JL, Warren CJ, Dhingra SS, Haushalter RC (1997) Polyhedron **16**: 1193
[22] Li J, Chen Z, Emge TJ, Yuen T, Proserpio DM (1998) Inorg Chim Acta **273**: 310
[23] Behrens M, Scherb S, Näther C, Bensch W (2003) Z Anorg Allg Chem **629**: 1367
[24] Jia DX, Zhang Y, Dai J, Zhu QY, Gu XM (2004) Z Anorg Allg Chem **630**: 313
[25] Jia DX, Dai J, Zhu QY, Zhang Y, Gu XM (2004) Polyhedron **23**: 937
[26] Jia DX, Zhang Y, Dai J, Zhu QY, Gu XM (2004) J Solid State Chem **177**: 2477
[27] Jia DX, Zhu QY, Dai J, Lu W, Guo WJ (2005) Inorg Chem **44**: 819
[28] Jia DX, Zhao QX, Zhang Y, Dai J, Zou JL (2005) Inorg Chem **44**: 8861
[29] Jia DX, Zhao QX, Zhang Y, Dai J, Zhou J (2006) Eur J Inorg Chem 2760
[30] Li J, Chen Z, Wang RJ, Proserpio DM (1999) Coord Chem Rev **190–192**: 707
[31] Stephan H-O, Kanatzidis MG (1996) J Am Chem Soc **118**: 12226
[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] Bensch W, Schur M (1997) Z Naturforsch Teil B **52**: 405
[36] Stähler R, Näther C, Bensch W (2001) Eur J Inorg Chem 1835
[37] Kiebach R, Bensch W, Hoffmann RD, Pöttgen R (2003) Z Anorg Allg Chem **629**: 532
[38] Dehnen S, Zimmermann C (2002) Z Anorg Allg Chem **628**: 2463
[39] Wendlandt WW, Hecht HG (1966) Reflectance Spectroscopy, Interscience Publishers, New York
[40] Sheldrick GM (1997) SHELXS-97, Program for structure solution, Universität of Göttingen, Germany
[41] Sheldrick GM (1997) SHELXL-97, Program for structure refinement, Universität of Göttingen, Germany