Solvothermal Syntheses and Crystal Structures of New One-dimensional Selenogallates [bappH$_2$][Ga$_2$Se$_4$] (bapp = 1,4-Bis-(3-aminopropyl)piperazine) and [Mn(en)$_3$][Ga$_2$Se$_5$] (en = Ethylenediamine)

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Two new selenogallates, [bappH$_2$][Ga$_2$Se$_4$] (**1**) (bapp = 1,4-bis(3-aminopropyl)-piperazine) and [Mn(en)$_3$][Ga$_2$Se$_5$] (**2**) (en = ethylenediamine), have been synthesized under solvothermal conditions and structurally characterized by single-crystal X-ray diffraction. Compounds **1** and **2** contain one-dimensional polymeric chains $\{[\mathrm{Ga_2Se_4}]^{2-}\}_\infty$ and $\{[\mathrm{Ga_2Se_5}]^{2-}\}_\infty$, respectively. The negative charges of the polymeric chains are balanced by a protonated 1,4-bis(3-aminopropyl)piperazine cation in **1** and by the metal-amine complex cations [Mn(en)$_3$]$^{2+}$ in **2**. TGA analyses have shown that compound **2** is thermally more stable than compound **1**.

Key words: Selenogallate, Organic Amine, Polyselenide, Solvothermal Synthesis, Crystal Structure

Introduction

Microporous materials have attracted a great deal of attention because of their applications in areas ranging from catalysis to molecular sieves and ion exchange [1]. To develop traditional applications of microporous materials, great efforts have been employed to expand oxide open frameworks to their chalcogenide analogs. Since Bedard first reported microporous sulfido compounds by replacing O^{2-} by S^{2-} in an oxide framework in 1989 [2], a number of microporous chalcogenide open frameworks containing elements of Group 13 (*e. g.* gallium and indium) have been synthesized and characterized [3 – 7]. These compounds have applications similar to zeolites because gallium and indium are in the same group as aluminum that is a key element in zeolite frameworks. In addition, they may find applications in catalysis and semiconductor technologies due to their novel properties as electrocatalysts, photocatalysts, semiconductors and fast ion conductors [8 – 12].

Solvothermal synthesis is the most efficient method for the preparation of metal chalcogeno (chalcogenido) frameworks of main group elements templated by organo-ammonium or metal cations as counterions [13, 14]. Meanwhile, organic amines with different C/N ratios and molecular structures play a key role in the formation of various architectures. More recently, Feng and co-workers reported gallium and indium chalcogenide frameworks with protonated organic amines or alkali/alkaline earth metal cations (Li$^+$, Na$^+$, Ka$^+$, Ca^{2+}) [15, 16]. The structures of these materials are based on various building blocks of supertetrahedral (T_n) units, such as [InS$_2$]$^-$, [Ga$_4$Se$_8$]$^{4-}$, [Ga$_{10}$S$_{18}$]$^{6-}$, and [M_4In$_{16}$S$_{33}$]$^{10-}$ (M = Mn, Co, Zn, Cd), [Cu$_5$In$_{30}$S$_{54}$]$^{13-}$, [Cu$_7$In$_{28}$S$_{53}$]$^{15-}$ [17 – 22]. These building blocks are often organized to open frameworks by corner-sharing chalcogen elements. It is very interesting that [Ga$_{10}$S$_{16}$]$^{2-}$ and [Ga$_{10}$S$_{18}$]$^{6-}$ units may be organized by organic linkers such as dipyridine ligands to one- or two-dimensional inorganic-organic hybrid materials as reported by Vaqueiro *et al.* [23 – 25]. Dai and co-workers reported similar structures templated by metal-amine complexes of the type [M(L)$_\mathrm{n}$]$^{2+}$ (M = Mn, Fe, Co, Ni, Zn; L = ethylenediamine, 1,10-phenanthroline, 1,2-diaminopropane, diethylenetriamine, and 1,2-diaminocyclohexane; n = 2 ∼ 3) [18, 26 – 30]. On the other hand, chalcogen anions can be linked together to form polychalcogen anions under solvothermal conditions [31 – 34], such as chelating $(Se\text{-}Se)^{2-}$ anions in the compound $[Ga(en)_3][Ga_3Se_7(en)]$ (en = ethylenediamine) [35]. As an extension of our previous research of main group chalcogenometallates [36 – 39], we herein report on the solvothermal synthesis and structural characterization of a new polymeric selenogallate $[bappH_2][Ga_2Se_4]$ (bapp = 1,4-bis(3-aminopropyl)piperazine) and a novel polyselenogallate anion $[Ga_2Se_5]^{2-}$ templated by the metal-amine complex cation $[Mn(en)_3]^{2+}$.

Experimental Section

Materials and measurements

1,4-Bis-(3-aminopropyl)piperazine (bapp) and ethylenediamine (en) were purchased from Alfa Aesar and used without further purification. All other reagents and solvents were used without further purification. Infrared spectra were recorded on a Nicolet 170sx FT-IR spectrophotometer with use of pressed KBr pellets. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. Thermogravimetric analysis was performed by using a Delta TGA instrument. The samples were heated under a nitrogen stream of 100 mL min^{-1} with a heating rate of 5 °C min^{-1}.

*Preparation of $[bappH_2][Ga_2Se_4]$ (**1**)*

Gallium metal (69.7 mg, 1.0 mmol) and selenium powder (197 mg, 2.5 mmol) were mixed with 1,4-bis-(3-aminopropyl)piperazine (2.112 g, 16 mmol) and distilled water (2 mL) in a 23 mL Teflon-lined stainless-steel autoclave and stirred for 20 min. The vessel was sealed and heated to 170 °C for 6 d. Then the autoclave was cooled to r. t. Yellow prism-shaped crystals of $[bappH_2][Ga_2Se_4]$ (**1**) were obtained and air dried. The yield based on Ga was *ca.* 46 %. – Elemental analysis for $C_{10}H_{26}N_4Ga_2Se_4$ (657.63): calcd. C 18.3, H 4.0, N 8.5; found C 18.2, H 3.9, N 8.5.

*Preparation of $[Mn(en)_3][Ga_2Se_5]$ (**2**)*

Gallium metal (69.7 mg, 1.0 mmol), selenium powder (237.0 mg, 3.0 mmol) and $Mn(CH_3COO)_2 \cdot 4H_2O$ (147.0 mg, 0.6 mmol) were mixed with ethylenediamine (2.404 g, 40 mmol) and distilled water (2 mL) in a 23 mL Teflon-lined stainlesssteel autoclave and stirred for 20 min. The vessel was sealed and heated to 190 °C for 6 d. Then the autoclave was cooled to r. t. Red bar-shaped crystals of $[Mn(en)_3][Ga_2Se_5]$ (**2**) were obtained and air dried. The yield based on Ga was *ca.* 53 %. – Elemental analysis for $C_6H_{24}N_6MnGa_2Se_5$ (771.51): calcd. C 9.4, H 3.1, N 10.9; found C 9.3, H 3.1, N 10.8.

Table 1. Crystal data, data collection parameters and details of the structure refinement of compounds **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{10}H_{26}Ga_2N_4Se_4$	$C_6H_{24}N_6MnGa_2Se_5$
Formula weight	657.63	771.51
Color, habit	yellow, prism	red, bar
Crystal size, mm^3	$0.20 \times 0.13 \times 0.1$	$0.25 \times 0.12 \times 0.11$
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	*Pbcn*
a, Å	6.3517(3)	9.7717(12)
b, Å	7.8498(4)	15.2971(19)
c, Å	10.7818(5)	13.7494(17)
α, deg	71.457(2)	90
β, deg	84.925(2)	90
γ, deg	72.084(3)	90
Volume, Å^3	484.93(4)	2055.2(4)
Z	1	4
Density (calcd.), g cm^{-3}	2.30	2.50
Absorption coeff., mm^{-1}	10.3	12.1
Temperature, K	296(2)	296(2)
F(000), e	312	1444
Radiation; λ Å	MoK_α; 0.71073	MoK_α; 0.71073
Reflections collected	8593	11900
Unique reflections / R_{int}	2157 / 0.30	2339 / 0.037
Parameters refined	100	104
Final $R1$ / $wR2$ $[I \ge 2\sigma(I)]^{a,b}$	0.027 / 0.75	0.033 / 0.070
Final $R1$ / $wR2$ (all data)^{a,b}	0.031 / 0.76	0.052 / 0.077
Weighting scheme A / B^b	0.0290 / 0.0761	0.0700 / 0.
Goodness of fit (GoF)^c	1.03	1.02
Final difference peaks, e Å^{-3}	+0.75 / −0.86	+1.42 / −0.58

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [c] $\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

X-Ray crystallography

Single crystals of compounds **1** and **2** were mounted in random orientation on glass fibers. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer with MoK_α radiation using an ω scan mode. The collected frames were processed with the software SAINT [40]. The dataset was corrected for absorption using the program SADABS [41]. Structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [42, 43]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms except the hydrogen atoms of the NH_2 groups were generated geometrically (C_{sp^3}-H = 0.97 Å), assigned isotropic displacement parameters, and allowed to ride on their respective parent carbon atoms before the final cycle of least-squares refinement. Crystal data, data collection parameters and details of the structure refinement are given in Table 1.

CCDC 830581 and 830582 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Solvothermal reaction of gallium metal with selenium powder 1,4-bis-(3-aminopropyl)piperazine and water in a molar ratio of 1 : 3 : 16 : 125 at 170 ℃ produced the new compound [bappH_2][Ga_2Se_4] (**1**). When the magnesium salt and ethylenediamine were employed in a similar reaction at 190 ℃, a novel polyselenide compound [Mn(en)$_3$][Ga_2Se_5] (**2**) was obtained. However, no crystals were obtained in the absence of water. Selenium powder served as the source for the Se^{2-} anion by reaction between selenium and amine or OH^- under solvothermal conditions. Typically, the molar ratio of the chalcogen and the metal element employed should be more than 2.5 in similar reactions. The IR absorption bands with variable intensities in the frequency range of 2910 – 3150 cm^{-1} for $\nu(NH_3)$ indicate the presence of the protonated amine in compound **1** while the strong bands in the range of 3220 – 3440 cm^{-1} in the IR spectrum of compound **2** correspond to the stretching vibrations of NH_2 from ethylenediamine [44].

X-Ray structural analyses revealed that compound **1** crystallizes in the triclinic space group $P\bar{1}$ and consists of one-dimensional polymeric gallium selenide $\{[Ga_2Se_5]^{2-}\}_\infty$ anions and protonated 1,4-bis-(3-aminopropyl)piperazine cations. The chain can be described as $GaSe_4$ tetrahedra sharing opposite edges. The Ga atom is coordinated to four Se atoms with an average bond length of 2.4158(4) Å, forming a slightly distorted tetrahedron with bond angles Se-Ga-Se ranging from 96.543(15) to 120.446(18)° (Figs. 1 and 2). The bond lengths and angles in **1** are similar to those found in a similar compound [Co(en)$_3$][Ga_2Se_4] [28]. Two terminal NH_2 groups in 1,4-bis-(3-aminopropyl)-piperazine were protonated and function as charge-compensating cations and templates for the direct formation of the framework. The average distance between two adjacent gallium atoms is 3.177(1) Å. In addition, the polymeric anions and the protonated amine cations are organized to an extended three-dimensional network by weak N-H···Se hydrogen bonds between terminal nitrogen atoms of the bapp ligands and selenium atoms of the polymeric anions, with the distances varying from 3.405(4) to 3.477(4) Å. The cations occupy the space between polymeric anions, as shown in Fig. 3.

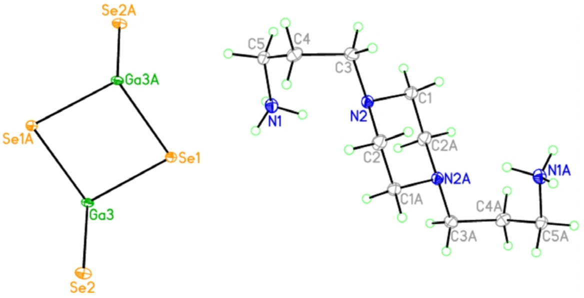

Fig. 1. The structure of **1** with atom labeling and displacement ellipsoids drawn at the 40 % probability level.

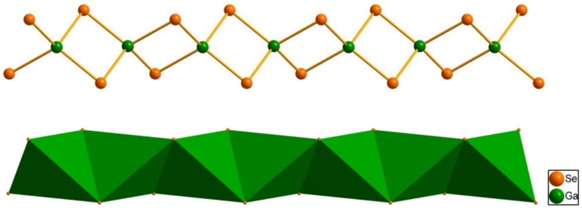

Fig. 2. View of the chain built by tetrahedral $GaSe_4$ units sharing opposite edges (top) and its polyhedral connection (bottom) in complex **1** as shown along the crystallographic *b* axis.

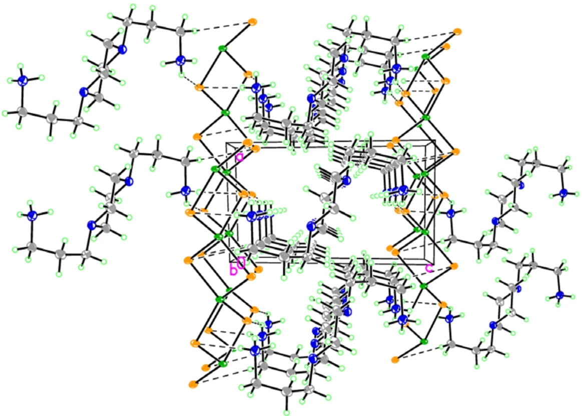

Fig. 3. View of the three-dimensional arrangement of the anions and cations in **1** (view along the *b* axis) as resulting from weak N-H···Se hydrogen bonds.

Compound **2** crystallizes in the orthorhombic space group *Pbcn* with four formula units in the unit cell. It consists of a polymeric gallium polyselenide chain of $\{[Ga_2Se_5]^{2-}\}_\infty$ with the metal-amine complex $[Mn(en)_3]^{2+}$ as charge-compensating cations. The $\{[Ga_2Se_5]^{2-}\}_\infty$ chain can be described as tetrahedral $GaSe_4$ units sharing three edges and chelating another edge to form alternating four-membered rings Ga_2Se_2 and five-membered rings Ga_2Se_3 (Figs. 4 and 5). The bond length of chelating Se-Se is 2.3334(10) Å. The Ga^{3+} ion is coordinated to four Se atoms with an average bond length of 2.4056(7) Å, forming

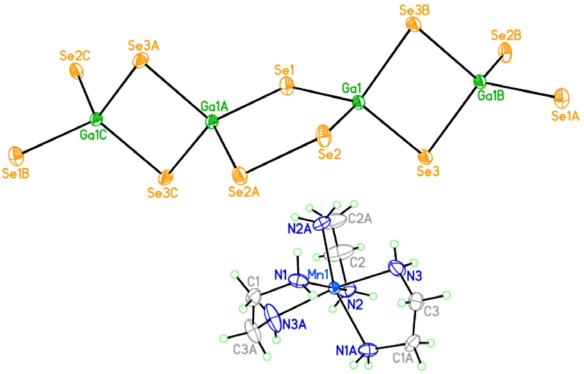

Fig. 4. The structure of **2** with atom labeling and displacement ellipsoids drawn at the 40 % probability level.

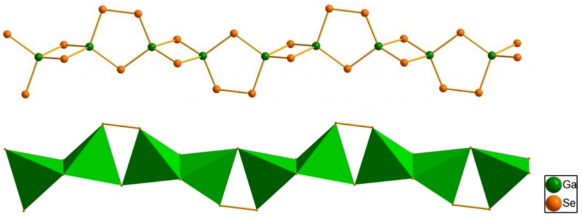

Fig. 5. View of the gallium polyselenide chain built from Ga_2Se_2 and Ga_2Se_3 rings (top) and its polyhedral connection (bottom) in complex **2** as viewed along the crystallographic *a* axis.

a slightly distorted tetrahedron with bond angles Se-Ga-Se ranging from 98.16(2) to 116.34(2)°. The Ga-Ga distances in the Ga_2Se_2 and Ga_2Se_3 rings are 3.156(1) and 3.783(1) Å, respectively. The bond angle Ga-Se-Ga in the Ga_2Se_2 ring is 81.84(2)°, while the angles Ga-Se-Ga and Ga-Se-Se in the Ga_2Se_3 ring are 105.01(4) and 104.627(19)°, respectively. These values are comparable with those in the related compound $[Ga(en)_3][Ga_3Se_7(en)]$ [29]. In the cation $[Mn(en)_3]^{2+}$, the Mn^{2+} ion is octahedrally coordinated by six nitrogen atoms of three bidentate en ligands with Mn-N distances from 2.240(5) to 2.298(6) Å. In addition, weak N-H···Se hydrogen bonds connect the polymeric anions and complex cations into a three-dimensional framework, as shown in Fig. 6.

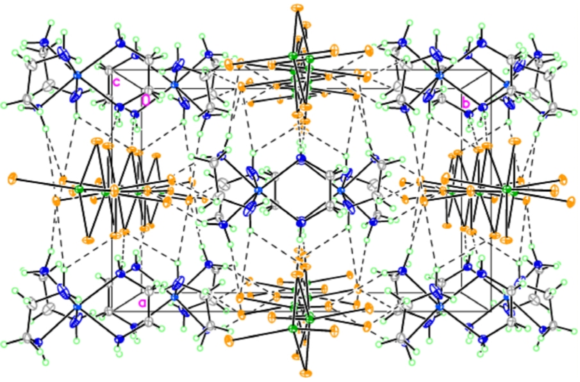

Fig. 6. View of the three-dimensional arrangement of the anions and cations in **2** (view along the *c* axis) as resulting from weak N-H···Se hydrogen bonds (displacement ellipsoids drawn at the 30 % probability level)

In order to examine the thermal stability of the two compounds, thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 20 and 500 ℃ in a static atmosphere of nitrogen. Compound **1** releases one bapp ligand with a mass loss of 31.2 % at 95 ℃ (calcd: 30.7 %), and then loses 1 mole of Se with mass a loss of 12.4 % between 250 and 450 ℃ (calcd: 12.0 %). Compound **2** is stable up to 280 ℃ at which temperature decomposition starts by the loss of three en ligands in one step with a mass loss of 24.3 % (calcd: 23.4 %), followed by the loss of one selenium equivalent with a mass loss of 9.6 % (calcd: 10.3 %) between 330 and 500 ℃. Thus, compound **2** is thermally more stable than compound **1**.

In summary, we have synthesized under solvothermal conditions and structurally characterized two new gallium selenides $[bappH_2][Ga_2Se_4]$ (**1**) and $[Mn(en)_3][Ga_2Se_5]$ (**2**) which contain one-dimensional polymeric chains. The negative charges of the polymeric chains were balanced by a protonated 1,4-bis-(3-aminopropyl)piperazine cation in **1** and the metal-amine complex cations $[Mn(en)_3]^{2+}$ in **2**. Weak hydrogen bonds N-H···Se play an important role in the formation of three-dimensional supramolecular architectures which are assembled from the polymeric anions and organic amine or metal complex cations. TGA analysis shows that compound **2** is thermally more stable than compound **1**.

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