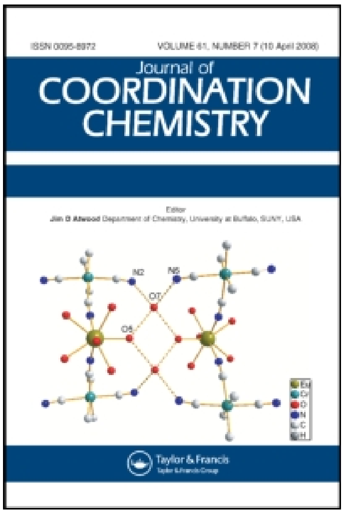

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Three 1-D selenidogallates $[GaSe_2^-]_n$, displaying conformational variations

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Three new 1-D selenidogallates $[Co(en)_3]Ga_2Se_4$ (**1**), $[(dienH_2)(dienH)_3]Ga_5Se_{10}$ (**2**) and $[(tetaH_2)_3(teta)]Ga_6Se_{12}$ (**3**) (en = ethylenediamine, dien = diethylenetriamine, teta = triethylenetetramine) were prepared under mild solvothermal conditions and structurally characterized. Although 1-D $[GaSe_2^-]_n$ chains in **1**–**3** are all built of $GaSe_4$ tetrahedra sharing opposite edges, these chains were classified as three types according to the period of the repeating unit. The crystal structure of type I (**2**) consists of 1-D common straight chains with $[Ga_2Se_4]^{2-}$ periodic units, while the crystal structures of type II (**1**) and type III (**3**) contain 1-D sinusoidal chains with $[Ga_4Se_8]^{4-}$ and $[Ga_8Se_{16}]^{8-}$ periodic units, respectively. The band gaps of 3.27 eV for **1**, 3.26 for **2** and 3.17 eV for **3** have been derived from optical absorptions.

Keywords: Solvothermal synthesis; Crystal structure; Selenidogallates; One-dimension

1. Introduction

Low-dimensional chalcogenides have been a major focus of research in new solid-state materials because of their intriguing structural motifs coupled with inherent anisotropic physical or chemical properties [1]. Among the various families of these materials, binary (or ternary) chalcogenidiometalates of Group 13 (Ga and In), which are characterized by the 1-D $[MQ_2^-]_n$ backbone (M = Ga, In; Q = S, Se, Te) built from MQ_4 tetrahedra sharing opposite edges, is important. Examples of 1-D $[InQ_2^-]_n$ chains are observed in $MInQ_2$ (M = Na[2], K[2,3], Rb[4], Tl[5]; Q = Te, and M = Tl[5], Q = Se), and AIn_2Te_4 (A = Ca[6], Ba[2], Sr[2]); these compounds are generally synthesized by a flux growth technique at intermediate or higher temperatures. Low temperature techniques of cathodic dissolution and solventothermal reactions have been employed to prepare similar compounds $[C_{10}N_4H_{26}]_{0.5}[InS_2]$ [7], $[(C_4H_9)_4N]_2In_2Te_4$ [8] and $[La(en)_4Cl]In_2Te_4$ [9]. More recently, we have investigated the synthetic systems of $In_2S_3/Ni/S_8$/amine and $InCl_3/MCl_2$(or Fe)/Te/amine under milder solvothermal

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conditions giving a series of 1-D indium chalcogenidiometalates $[Ni(dien)_2]_{0.5}[InS_2]$ (dien =diethylenetriamine) [10], $[Ni(dap)_3]_{0.5}[InS_2]$ (dap = 1,2-diaminopropane) [10], $[Zn(tren)(\mu\text{-teta})_{0.5}][InTe_2]Cl$ (tren = *N*,*N*,*N*-tris(2-aminoethyl)amine) [11], $[M(en)_3]In_2Te_4 \cdot en$ (M = Ni and Co) [11], and $[M(en)_3]_2In_4Te_8 \cdot (en)_{0.5}$ (M = Mn, Fe, and Zn) [11]. Though these 1-D $[InQ_2^-]_n$ chains are all built from InQ_4 tetrahedra sharing opposite edges, the chains display three types of conformations [11], demonstrating that the different cations have different influence on the formation of 1-D $[InQ_2^-]_n$ anionic chains. However, compared with these 1-D indium chalcogenidiometalates, similar gallium chalcogenidiometalates are less explored under mild solvothermal conditions; the limited examples include $[C_{10}N_4H_{26}]_{0.5}[GaS_2]$ [7], $[M(en)_3]_{0.5}[GaS_2]$ (M = Mn, Co, Ni) [12] and $(C_4H_{11}N_2)GaSe_2$ [13]. As an extension of our previous study of 1-D indium chalcogenidiometalates, we used a solvothermal method to prepare three 1-D selenidogallates $[Co(en)_3]Ga_2Se_4$ (**1**), $[(dienH_2)(dienH)_3]Ga_5Se_{10}$ (**2**) and $[(tetaH_2)_3(teta)]Ga_6Se_{12}$ (**3**). Similar conformational variations of 1-D $[GaSe_2^-]_n$ chains as found for 1-D $[InQ_2^-]_n$ chains are discussed herein.

2. Experimental

2.1. *Materials and physical measurements*

Analytically pure starting materials were purchased and used without additional purification. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer in dry KBr pellets. Elemental analysis was carried out on an EA 1110 elemental analyzer. Room-temperature optical diffuse reflectance spectra of the powdered samples were obtained with a Shimadzu UV-3150 spectrometer. The absorption (α/S) data were calculated according to the procedure reported in the literature [14].

2.2. *Synthesis of $[Co(en)_3]Ga_2Se_4$ (1)*

A mixture of Ga (0.0139 g, 0.2 mmol), Co (0.0059 g, 0.1 mmol), Se (0.0316 g, 0.4 mmol), en (2 mL) and H_2O (0.5 mL) was transferred into a thick-walled Pyrex tube. The sealed tube was heated at 180°C for 10d to yield red block-shaped crystals (18% yield based on Ga). C, H, N analysis: found: C: 10.23%, H: 3.61%, N: 12.23%; Calcd: C: 10.38%, H: 3.48%, N: 12.10%. IR(cm^{-1}): 3735(m), 3419(m), 3364(m), 3328(m), 2935(w), 2871(w), 1628(m), 1458(vw), 1382(w), 1289(m), 1250(s), 1196(s), 1142(w), 1057(m), 1006(w), 903(w), 787(w), 594(vs), 571(vs), 509(s).

2.3. *Synthesis of $[(dienH_2)(dienH)_3]Ga_5Se_{10}$ (2)*

A mixture of $GaCl_3$ (0.0352 g, 0.2 mmol), Se (0.0254 g, 0.4 mmol), dien (2 mL) and H_2O (0.4 mL) was transferred into a thick-walled Pyrex tube. The sealed tube was heated at 160°C for 4d to yield colorless block-shaped crystals (23% yield based on Ga). C, H, N analysis: found: C: 12.14%, H: 3.93%, N: 10.65%; Calcd: C: 12.35%, H: 3.69%, N: 10.80%. IR(cm^{-1}): 3357(s), 2932(m), 2855(m), 1605(vs), 1458(s), 1381(m), 1289(w), 1250(m), 1196(m), 1057(m), 1011(m), 949(m), 801(w), 696(m), 637(vs), 571(s), 433(m).

2.4. *Synthesis of [(tetaH$_2$)$_3$(teta)]Ga$_6$Se$_{12}$ (3)*

Colorless block-shaped crystals of **3** were prepared by a similar method used in the synthesis of **2** except that dien was replaced by teta (yield, 31%, based on Ga). C, H, N analysis: found: C: 14.61%, H: 4.33%, N: 11.52%; Calcd: C: 14.73%, H: 4.02%, N: 11.45%. IR(cm^{-1}): 3218(m), 2963(m), 2847(m), 1589(s), 1520(w), 1450(s), 1389(m), 1288(m), 1250(m), 1196(s), 1135(m), 1057(s), 1003(m), 949(m), 872(s), 802(vw), 764(vs), 687(vw), 563(s), 524(m), 478(w), 439(w).

2.5. *X-ray structure determination*

The intensity data were collected on a Rigaku Mercury CCD diffractometer at 193(2) K using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) with ω-scan to a maximum 2θ value of 50.70° for **1**–**3**. A red $0.30 \times 0.11 \times 0.09$ mm block crystal of **1**, a colorless $0.41 \times 0.15 \times 0.10$ mm block crystal of **2**, and a colorless $0.30 \times 0.25 \times 0.20$ mm block crystal of **3** were used for data collection. The structures were solved with direct methods using the SHELXS-97 program [15] and refinement was performed against F^2 using SHELXL-97 [16]. All non-hydrogen atoms were refined anisotropically. The H atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters using a riding model. The H atoms of **1** were not dealt with due to disorder of en. The H atoms of C9, C10, C11, C12, N7 and N8 in **2** and C13 and N9 in **3** were not dealt with because of the disorder of C10, C11 and N7 atoms in **2** and N9 atom in **3**. For **2** and **3**, high displacement parameters result from disorder in C10, C11 and N7 of dien and N9 of teta, but these could not be resolved. Technical details of data collections and refinement are summarized in table 1. Selected bond distances (Å) and angles (°) are listed in table 2. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 687528-687530. These data can be obtained free of charge via www.ccdc.cam.ac.uk.

3. Results and discussion

3.1. *Synthesis of the compounds*

Single crystals of [Co(en)$_3$]Ga$_2$Se$_4$ (**1**) were conveniently obtained by reaction of Ga, Co and Se in aqueous solution of en under solvothermal conditions; no single crystal was obtained in pure en. It is likely that Se underwent disproportionation reactions to give SeO$_3$ and Se^{2-} in aqueous solution [13, 17] and Se^{2-} is used to form the 1D polymeric anion $[\mathrm{GaSe}_2^-]_n$. Compounds [(tetaH$_2$)$_3$(teta)]Ga$_6$Se$_{12}$ (**2**) and [(dienH$_2$)(dienH)$_3$]Ga$_5$Se$_{10}$ (**3**) were synthesized by solvothermal reaction from GaCl$_3$/Se/teta (or dien)/H$_2$O mixture at 160°C. When GaCl$_3$ was replaced by Ga as the source for Ga^{3+} under similar solvothermal conditions, however, no single crystals were obtained, demonstrating that Cl$^-$ could function as a mineralizer [17, 18].

3.2. *Description of the structures*

Compound **1** crystallizes in the orthorhombic space group Cmcm with four formula units in the unit cell and **2** crystallizes in the monoclinic space group $P2_1/c$ with four

Table 1. Crystal data and structure refinement for **1**, **2**, and **3**.

	1	**2**	**3**
Empirical formula	$C_6H_{24}CoGa_2N_6Se_4$	$C_{16}H_{57}Ga_5N_{12}Se_{10}$	$C_{24}H_{78}Ga_6N_{16}Se_{12}$
Fw	694.52	1555.91	1956.83
Color of cryst.	red	colorless	colorless
Cryst. dimens., mm^3	$0.30 \times 0.11 \times 0.09$	$0.41 \times 0.15 \times 0.10$	$0.30 \times 0.25 \times 0.20$
Cryst. syst.	Orthorhombic	Monoclinic	Monoclinic
Space group	Cmcm	$P2_1/c$	Cc
a (Å)	9.692(3)	6.3116(9)	20.566(4)
b (Å)	15.631(5)	13.7484(18)	25.896(5)
c (Å)	12.698(4)	47.890(6)	12.785(3)
β (°)	90	90.6400(10)	125.568(4)
V (Å^3)	1923.7(10)	4155.4(10)	5538.5(19)
Z	4	4	4
T, K	193(2)	173(2)	193(2)
Calcd density, $Mg \cdot m^{-3}$	2.398	2.469	2.342
Abs. coeff., mm^{-1}	11.197	11.989	10.800
$F(000)$	1308	2884	1252
2θ(max), (°)	50.70	50.70	50.70
Total reflns. collected	9283	28503	24203
Unique reflns.	977	7296	8884
No. of param.	73	419	535
$R_1[I > 2\sigma(I)]$	0.0449	0.0988	0.0660
wR_2 (all data)	0.1021	0.2279	0.1517
GOF on F^2	1.158	1.075	1.026
Largest diff. peak and hole ($e \cdot Å^{-3}$)	0.917 and −0.633	1.290 and −1.305	2.904 and −0.910

formula units in the unit cell. The structure of **1** contains $GaSe_4$ tetrahedra linked by sharing opposite edges to form a 1-D sinusoidal $[GaSe_2^-]_n$ chain [figure 1(a), figure 2(b)]. All central Ga atoms in **1** are arranged in a sinusoidal line and the $Ga \cdots Ga \cdots Ga$ angle is 176.13(4)°. There are two kinds of $Ga \cdots Ga$ distances along the $[GaSe_2^-]_n$ chain, 3.1877(16) Å for $Ga1 \cdots Ga1a$ and 3.1685 Å for $Ga1 \cdots Ga1b$ (symmetry operation: (a) $1 - x, y, 1.5 - z$; (b) $x, 1 - y, 1 - z$). The repeating unit consists of four $GaSe_4$ tetrahedra with a period of 12.6980 Å, which is slightly less than the sum of the four $Ga \cdots Ga$ distances (12.7124 Å). Such chains are observed in transition metal thiogallates $[M(en)_3]_{0.5}[GaS_2]$ (M = Mn, Co, Ni) [12], but compound **1** contains a 1-D sinusoidal $[GaSe_2^-]_n$ chain.

The 1-D $[GaSe_2^-]_n$ chains in **2** are composed of $[Ga_2Se_4^{2-}]$ periodic units formed by two $GaSe_4$ tetrahedra sharing opposite edges, propagating along the crystallographic a-axis [type I, figure 1(b)]. The period of the repeating unit is 6.3116(28) Å, equal to the sum of two adjacent $Ga \cdots Ga$ distances or the unit cell length a [6.3116(9) Å]. All central Ga atoms are in a straight line, $Ga \cdots Ga \cdots Ga$ angle 180° [figure 2(a)]. Similar chains are also found in gallium chalcogenidiometalates $[C_{10}N_4H_{26}]_{0.5}[GaS_2]$ [7] and $(C_4H_{11}N_2)GaSe_2$ [13]. The variations in $Ga \cdots Ga \cdots Ga$ angles appear to be a consequence of a combination of crystallographic-imposed symmetry and packing effects arising from the presence of different size cations.

Compound **3** crystallizes in the monoclinic space group Cc with four formula units in the unit cell. The 1-D polymeric structure of **3** consists of rare sinusoidal $[Ga_8Se_{16}^{8-}]_n$ chains propagating along the crystallographic c-axis [figure 1(c), figure 2(c)]. The repeating unit contains eight edge-sharing tetrahedra with a period in the range 22.365(7)–22.384(7) Å. All Ga_2Se_2 four-membered rings take a butterfly

Table 2. Selected bond lengths (Å) and angles (deg) for **1**, **2**, and **3**.

1			
Ga1–Se1	2.3811(16)	Ga1–Se2	2.4175(15)
Ga1–Se3	2.4145(11)	Co1–N3	2.171(8)
Co1–N1	2.185(10)	Co1–N2	2.195(8)
Se1–Ga1–Se3	113.90(4)	Se3#1–Ga1–Se3	97.99(5)
Se1–Ga1–Se2	96.74(5)	Se3–Ga1–Se2	117.71(3)
N2#3–Co1–N2	170.5(5)	N3–Co1–N1#2	169.5(3)
2			
Ga2–Se1	2.419(2)	Ga1–Se1	2.422(2)
Ga2–Se4	2.410(2)	Ga1–Se2	2.415(2)
Ga2–Se3	2.411(2)	Ga1–Se3#7	2.413(2)
Ga2–Se2	2.403(2)	Ga1–Se4#7	2.409(2)
Ga5–Se10	2.409(2)	Ga3–Se8	2.402(3)
Ga5–Se9#6	2.410(2)	Ga3–Se5	2.412(2)
Ga5–Se9	2.418(2)	Ga3–Se7	2.411(2)
Ga5–Se10#5	2.411(2)	Ga3–Se6	2.402(3)
Ga4–Se8	2.401(3)		
Ga4–Se6#4	2.413(3)		
Ga4–Se7	2.425(3)		
Ga4–Se5#4	2.425(3)		
Se4#7–Ga1–Se3#7	98.06(8)	Se2–Ga1–Se1	98.23(8)
Se4–Ga2–Se3	98.19(8)	Se2–Ga2–Se1	98.63(8)
Se8–Ga3–Se7	98.67(9)	Se5–Ga3–Se6	97.71(8)
Se8–Ga4–Se7	98.76(9)	Se6#4–Ga4–Se5#4	97.34(8)
Se9#6–Ga5–Se9	98.70(8)	Se10–Ga5–Se10#5	97.82(8)
3			
Ga6–Se11	2.395(4)	Ga6–Se12	2.415(3)
Ga6–Se10	2.408(3)	Ga5–Se10	2.414(3)
Ga2–Se4	2.418(3)	Ga3–Se4	2.437(4)
Ga2–Se2	2.414(3)	Ga1–Se2	2.418(3)
Ga5–Se9	2.410(3)	Ga4–Se7	2.450(4)
Ga4–Se8	2.412(3)	Ga6–Se9	2.414(3)
Ga4–Se6	2.410(3)	Ga3–Se6	2.426(3)
Ga2–Se1	2.412(3)	Ga1–Se1	2.422(3)
Ga4–Se5	2.409(3)	Ga3–Se5	2.420(3)
Ga3–Se3	2.403(3)	Ga2–Se3	2.423(4)
Ga5–Se12#10	2.404(4)	Ga5–Se11#10	2.409(3)
Ga1–Se7#11	2.399(3)	Ga1–Se8#11	2.411(4)
Se10–Ga6–Se9	96.56(13)	Se11–Ga6–Se12	97.04(13)
Se12#10–Ga5–Se11#10	96.97(13)	Se9–Ga5–Se10	96.49(12)
Se8–Ga4–Se7	96.53(14)	Se5–Ga4–Se6	97.88(15)
Se5–Ga3–Se6	97.16(14)	Se3–Ga3–Se4	96.97(13)
Se1–Ga2–Se2	96.58(13)	Se4–Ga2–Se3	96.92(14)
Se7#11–Ga1–Se8#11	97.94(13)	Se2–Ga1–Se1	96.22(13)

Symmetry transformations used to generate equivalent atoms: (#1) $-x+1, -y+1, -z+1$; (#2) $-x+2, y, z$; (#3) $-x+2, y, -z+3/2$; (#4) $x+1, y, z$; (#5) $-x+1, -y+1, -z+1$; (#6) $-x, -y+1, -z+1$; (#7) $x-1, y, z$; (#8) $x, -y+2, z-1/2$; (#9) $x, y, z-1$; (#10) $x, -y+2, z+1/2$; (#11) $x, y, z+1$.

structure, and the dihedral angles between the wing planes Ga2/Ga3/Se3 and Ga2/Ga3/Se4 is 175.7°. The Ga $\cdots$ Ga $\cdots$ Ga angles vary from 175.06(11) to 177.86(12)°. When viewed down the [001] direction, the 1-D $[GaSe_2^-]_n$ chains of **3** are significantly different from those of **1** and **2** (figure 2) and represent a new type for selenidogallates.

The negative charge of the 1-D $[GaSe_2^-]_n$ chains in **1**–**3** is balanced by the $[Co(en)_3]^{2+}$ complex cation or protonated organic amine. The Co^{2+} ion in **1** is coordinated by six N atoms of three bidentate en ligands with Co–N distances ranging from 2.171(8) to 2.195(8) Å. The conformation of $[Co(en)_3]^{2+}$ is difficult to determine due to the disorder of the en ligands. There are numerous N–H $\cdots$ Se weak H-bonds between the $[GaSe_2^-]_n$

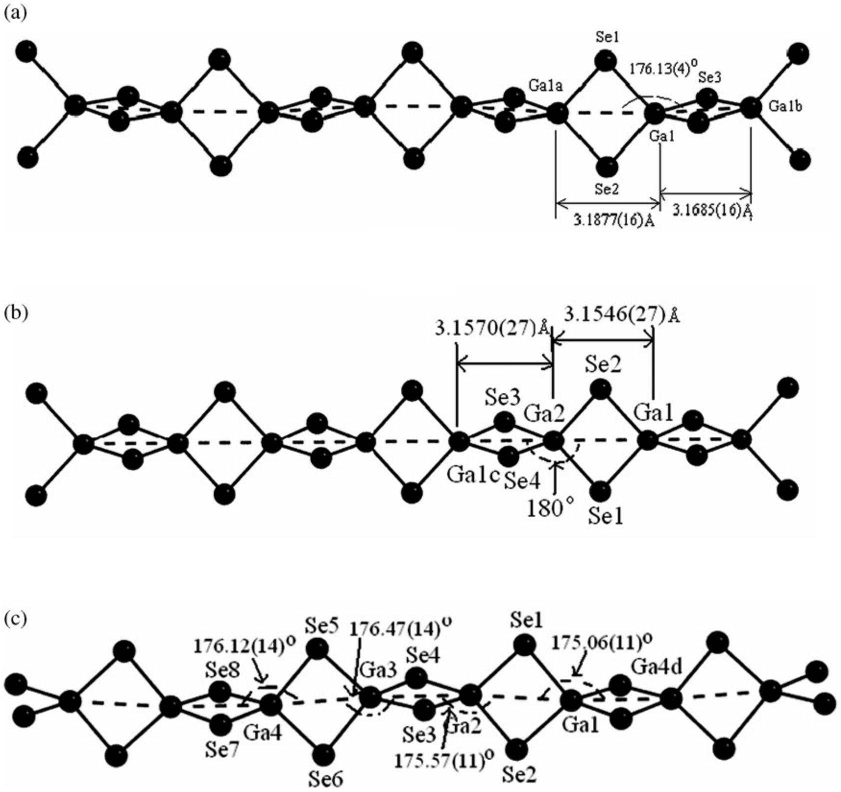

Figure 1. The 1-D $[GaSe_2^-]_n$ anionic chains in **1**(a), **2**(b) and **3**(c) [symmetry operation: (a) $1-x$, y, $1.5-z$; (b) x, $1-y$, $1-z$; (c) $1+x$, y, z; (d) x, y, $1+z$].

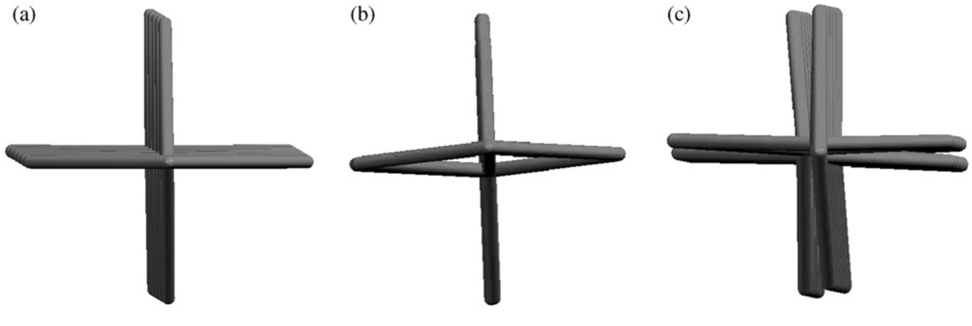

Figure 2. View of the 1-D chains along the axial direction, showing different types (a) straight. (b) sinusoidal chain with planar Ga_2Se_2 ring. (c) sinusoidal chain with butterfly Ga_2Se_2 ring.

anion and $[Co(en)_3]^{2+}$ cations in **1**. The $[Co(en)_3]^{2+}$ complex cations assemble to form pseudo-channels via these H-bonds, which not only induces formation of the 1-D sinusoidal $[GaSe_2^-]_n$ chain, but also stabilizes the whole crystal structure [figure 3(a)]. In **2** and **3**, the position of the additional proton can be located from single-crystal diffraction data, suggesting that protonation occurs on a particular N atom instead of being statistically distributed over N atoms. The 1-D $[GaSe_2^-]_n$ chains in **2** and **3** are separated by protonated amines or free amine molecules via N–H$\cdots$N and

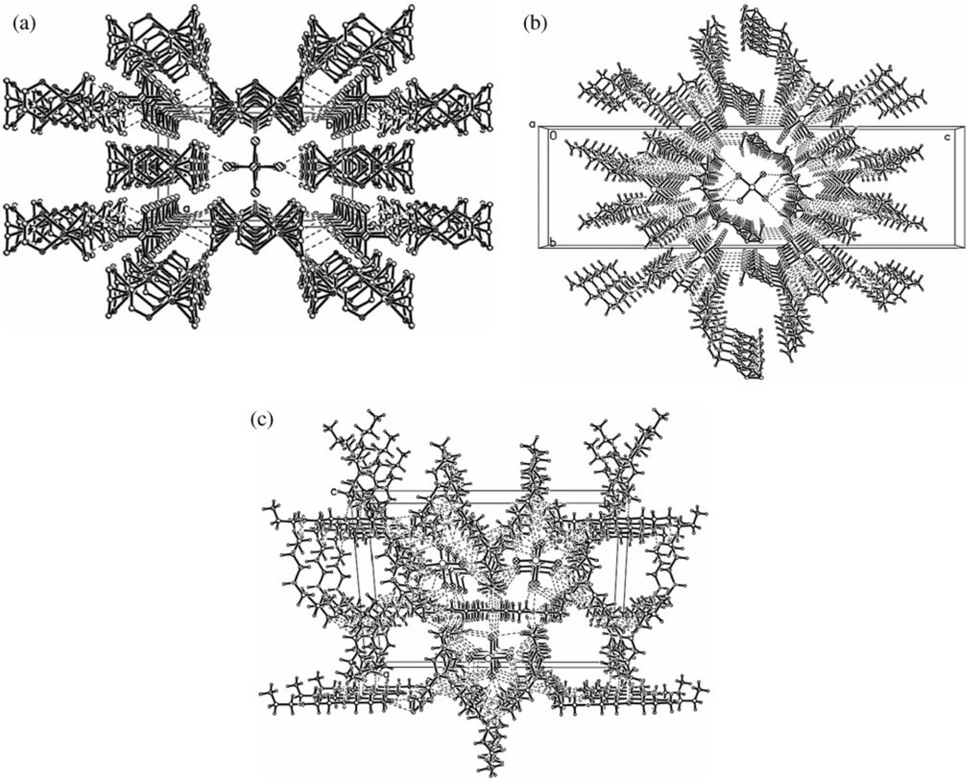

Figure 3. The packing diagrams of **1**(a), **2**(b) and **3**(c), showing channels along the axial direction.

N–H $\cdots$ Se weak H-bonds [figures 3(b)–(c)]. Although the structures are affected by these hydrogen bonds, the presence of conformational disorder of the amines suggests that the hydrogen bonding network within these lattices is not so strong to influence the 1-D chain structures.

3.3. *Optical properties*

The optical absorption spectrum of **1** in figure 4 show an absorption band at *ca.* 2.56 eV, attributed to a d-d transition of Co(II). From the well-defined abrupt absorption edges, the band gaps can be estimated as 3.27 eV for **1**, 3.26 for **2** and 3.17 eV for **3**, which can be assigned to the electronic excitation located at the anion. These results confirm that these materials are semiconductors with large exciting energy-gap. Compared with the value of 2.1 eV reported for bulk Ga_2Se_3 [19], there is a blue shift of the absorption edge. Similar blue shifts have also been observed in other solvothermally prepared thiogallates [20].

4. Conclusions

Single crystals of three 1-D selenidogallates $[Co(en)_3]Ga_2Se_4$ (**1**), $[(dienH_2)(dienH)_3]Ga_5Se_{10}$ (**2**) and $[(tetaH_2)_3(teta)]Ga_6Se_{12}$ (**3**) were obtained under mild

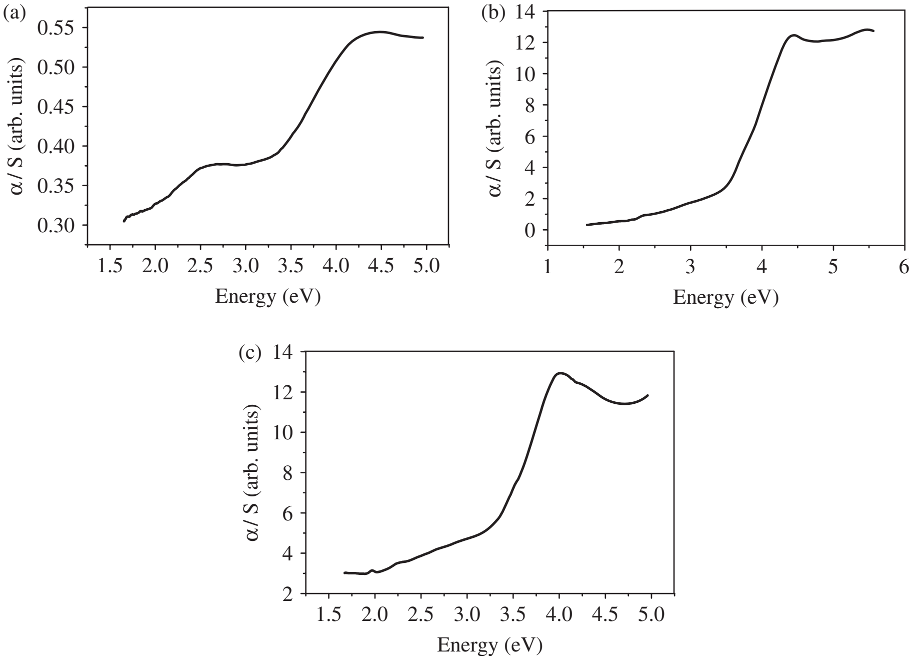

Figure 4. Optical absorption spectra of **1**(a), **2**(b) and **3**(c).

solvothermal conditions. Although Cl^- in **2** and **3** was not incorporated into the final structures, it was likely an effective mineralizer. The 1-D polymeric structure in **2** is linear, while 1-D infinite sinusoidal chains in **1** and **3** display conformational variations arising from the presence of different counter cations.

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