

Syntheses and crystal structures of the homoleptic $[\text{Et}_4\text{N}][\text{M}(\text{SC}_6\text{H}_4\text{Me-}p)_4]$ ($\text{M} = \text{Ga}, \text{In}$) and $[\text{Et}_4\text{N}][\text{Ga}(\text{SePh})_4]$

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ABSTRACT

Treatment of $[\text{Et}_4\text{N}][\text{GaCl}_4]$ with four equivalents of NaQR in methanol afforded the substitution complexes $[\text{Et}_4\text{N}][\text{Ga}(\text{QR})_4]$ (QR = $\text{SC}_6\text{H}_4\text{Me-}p$ **1**, QR = SePh **3**), while the indium analogues $[\text{Et}_4\text{N}][\text{In}(\text{SC}_6\text{H}_4\text{Me-}p)_4]$ (**2**) was prepared by the reaction of $\text{InCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{NaSC}_6\text{H}_4\text{Me-}p$ in the presence of $[\text{Et}_4\text{N}]\text{Cl} \cdot x\text{H}_2\text{O}$. The structures of these three complexes, as determined by single-crystal X-ray diffraction, feature well-separated cations and anions with the metal centers of the anions tetrahedrally coordinated to four thiolate or selenolate ligands. The thermal stability of the three complexes was studied by thermal gravimetric analysis.

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1. Introduction

Many indium thiolates and selenolates have been synthesized, owing to their potential application for materials as single-source precursors [1–3]. However, the analogues of gallium complexes with thiolate and selenolate ligands have not been well explored [4,5]. Although solid-state gallium chalcogenide compounds have come under increasing investigation in the past two decades [6–8], the reactivities and structures of soluble gallium compounds have not been extensively studied. There are several literatures concerning neutral homoleptic gallium alkylthiolate and arylthiolate compounds, for examples, a series of $\text{Ga}(\text{SR})_3$ compounds were obtained from reactions of GaCl_3 and Me_3SiSR , or from GaPh_3 with RSH (R = Me, Et, *n*-Pr, *i*-Pr, Ph, CH_2Ph) [9,10]. Monomeric three-coordinate gallium $\text{Ga}[\text{Q}(2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2)_3]$ (Q = S, Se) were formed mainly due to the bulky thiolate and selenolate [11]. The four-coordinate gallium anions $[\text{Ga}(\text{SR})_4]^-$ (R = Me, Et, *i*-Pr, Ph, 2,3,5,6-Me₄C₆H₂, 2,4,6-*i*-Pr₃C₆H₂) were isolated from the reactions of $(\text{NH}_4)[\text{GaCl}_4]$ with four equivalents of the corresponding thiolate ligands [12,13]. Likewise, the anionic indium selenolates $[\text{In}(\text{SePh})_4]^-$ and $[\text{In}(\text{SePh})_3(\text{SeH})]^-$ were synthesized from the above similar reactions of gallium complexes and structurally characterized by Ibers [14]. However, no analogue of gallium-tetraselenolates $[\text{Ga}(\text{SeR})_4]^-$ has been reported to date. Herein we report the synthesis and molecular structures of the homoleptic compounds with tetrahedral gallium coordination, $[\text{Et}_4\text{N}][\text{Ga}(\text{SC}_6\text{H}_4\text{Me-}p)_4]$ and $[\text{Et}_4\text{N}][\text{Ga}(\text{SePh})_4]$.

2. Experimental

2.1. Materials and measurements

All syntheses were performed in oven-dried glassware under a purified nitrogen atmosphere using standard Schlenk techniques. Ga_2O_3 , $\text{InCl}_3 \cdot 3\text{H}_2\text{O}$, *p*-thiocresol ($\text{HSC}_6\text{H}_4\text{Me-}p$), and PhSeSePh were purchased from Alfa Chemical Company and were used as supplied. All other reagents and solvents were used without further purification. $[\text{NH}_4][\text{GaCl}_4]$ was prepared according to the literature method [15]. All elemental analyses were performed using a Perkin-Elmer 2400 CHN analyzer. Infrared spectra were recorded on a Digilab FTS-40 spectrophotometer with the use of pressed KBr pellets. Positive FAB mass spectra were recorded on a Finnigan TSQ 7000 spectrometer. ¹H NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300 MHz and with reference to SiMe_4 (¹H). Thermogravimetric analysis (TGA) was performed by using a Delta TGA instrument.

2.2. Preparation of $[\text{Et}_4\text{N}][\text{Ga}(\text{SC}_6\text{H}_4\text{Me-}p)_4]$ (**1**)

To a solution of $[\text{Et}_4\text{N}][\text{GaCl}_4]$ (171 mg, 0.50 mmol) in methanol (10 ml) was added dropwise $\text{NaSC}_6\text{H}_4\text{Me-}p$ (292 mg, 2.00 mmol) in 10 ml of methanol with stirring. The mixture was stirred at room temperature for 30 min. Fine white solids were observed. The precipitates were collected by suction filtration and washed twice with 10 ml portions of diethyl ether. White air-stable solids were obtained and further recrystallized from DMF/diethyl ether to give colorless block crystals of **1** in five days. Yield: 301 mg, 87%. IR

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(KBr, cm^{-1}): $\nu(\text{C-S})$ 648 (m). ^1H NMR (DMSO- d_6 , ppm): δ 1.01 (s, 12H, CH_3 in Et_4N), 2.14 (s, 12H, CH_3), 2.93 (t, 8H, CH_2 in Et_4N), 6.72–7.16 (m, 16H, Ph). MS (FAB): m/z 562 ($\text{M}^+ - [\text{Et}_4\text{N}]$). Anal. Calcd. for $\text{C}_{36}\text{H}_{48}\text{NS}_4\text{Ga}$: C, 62.4; H, 6.98; N, 2.02. Found: C, 62.2; H, 6.94; N, 1.99%.

2.3. Preparation of $[\text{Et}_4\text{N}][\text{In}(\text{SC}_6\text{H}_4\text{Me-p})_4]$ (**2**)

To a slurry solution of $\text{InCl}_3 \cdot 3\text{H}_2\text{O}$ (138 mg, 0.50 mmol) and $[\text{Et}_4\text{N}]\text{Cl} \cdot x\text{H}_2\text{O}$ (86 mg, 0.50 mmol) in methanol (15 ml) was added dropwise $\text{NaSC}_6\text{H}_4\text{Me-p}$ (292 mg, 2.00 mmol) in 10 ml of methanol with stirring. The mixture was stirred at room temperature for 15 min, during which time a fine white solid gradually separated from the solution. The precipitates were collected by suction filtration and washed twice with 10 ml portions of diethyl ether. White air-stable solids were obtained and further recrystallized from DMF/diethyl ether to give colorless block crystals of **2** in three days. Yield: 283 mg, 78%. IR (KBr, cm^{-1}): $\nu(\text{C-S})$ 641 (m). ^1H NMR (DMSO- d_6 , ppm): δ 1.05 (s, 12H, CH_3 in Et_4N), 2.12 (s, 12H, CH_3), 2.90 (t, 8H, CH_2 in Et_4N), 6.71–7.25 (m, 16H, Ph). MS (FAB): m/z 607 ($\text{M}^+ - \text{Et}_4\text{N}$). Anal. Calcd. for $\text{C}_{36}\text{H}_{48}\text{NS}_4\text{In}$: C, 58.6; H, 6.56; N, 1.90. Found: C, 58.4; H, 6.52; N, 1.87%.

2.4. Preparation of $[\text{Et}_4\text{N}][\text{Ga}(\text{SeC}_6\text{H}_5)_4]$ (**3**)

To a slurry of $[\text{Et}_4\text{N}][\text{GaCl}_4]$ (171 mg, 0.50 mmol) in methanol (10 ml) was added dropwise NaSePh (358 mg, 2.00 mmol) (prepared *in situ* by the reaction of PhSeSePh and NaBH_4 in a 1:2 mol ratio) in 10 ml of methanol with stirring. The mixture was stirred at room temperature for 30 min. Fine white solids were observed. The solution was cooled to 0 °C and the precipitates were collected by filtration and then washed twice with 10 ml portions of diethyl ether. White air-stable solids were obtained and further recrystallized from DMF/diethyl ether to give colorless block crystals of **3** in a week. Yield: 297 mg, 63%. IR (KBr, cm^{-1}): $\nu(\text{C-Se})$ 562 (m). ^1H NMR (DMSO- d_6 , ppm): δ 1.03 (s, 12H, CH_3 in Et_4N), 2.94 (t, 8H, CH_2 in Et_4N), 6.91–7.35 (m, 20H, Ph). MS (FAB): m/z 694 ($\text{M}^+ - [\text{Et}_4\text{N}]$). Anal. Calcd. for $\text{C}_{32}\text{H}_{40}\text{NSe}_4\text{Ga}$: C, 46.6; H, 4.89; N, 1.70. Found: C, 46.2; H, 4.85; N, 1.66%.

2.5. X-ray crystallographic study

The structures of $[\text{Et}_4\text{N}][\text{Ga}(\text{SC}_6\text{H}_4\text{Me-p})_4]$ (**1**), $[\text{Et}_4\text{N}][\text{In}(\text{SC}_6\text{H}_4\text{Me-p})_4]$ (**2**), and $[\text{Et}_4\text{N}][\text{Ga}(\text{SePh})_4]$ (**3**) were determined by the single-crystal X-ray diffraction technique. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer with Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 296 K using an ω scan mode. The collected frames were processed with the software Saint [16]. The data was corrected for absorption using the program Sadabs [17]. Structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 using the Shelxtl software package [18]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically ($\text{C}_{\text{sp}3}\text{-H} = 0.96$, $\text{C}_{\text{sp}2}\text{-H} = 0.93 \text{ \AA}$) and included in the structure factor calculations with assigned isotropic displacement parameters but were not refined. The Flack parameter values of **1** and **2** indicate that the correct enantiomorphs have been selected in both structures. Further details of the data determination, crystal data and structure refinement parameters are summarized in Table 1.

3. Results and discussion

Treatment of $[\text{Et}_4\text{N}][\text{GaCl}_4]$ with four equivalents of $\text{NaSC}_6\text{H}_4\text{Me-p}$ in methanol afforded the substitution complex $[\text{Et}_4\text{N}][\text{Ga}(\text{SC}_6\text{H}_4\text{Me-p})_4]$ (**1**) in a yield of 87%. The indium analogues $[\text{Et}_4\text{N}][\text{In}(\text{SC}_6\text{H}_4\text{Me-p})_4]$ (**2**) was prepared similarly by the

Table 1

Crystal data and structure refinement for complexes $[\text{Et}_4\text{N}][\text{Ga}(\text{SC}_6\text{H}_4\text{Me-p})_4]$ (**1**), $[\text{Et}_4\text{N}][\text{In}(\text{SC}_6\text{H}_4\text{Me-p})_4]$ (**2**), $[\text{Et}_4\text{N}][\text{Ga}(\text{SePh})_4]$ (**3**).

Complex	1	2	3
Formula	$\text{C}_{36}\text{H}_{48}\text{NS}_4\text{Ga}$	$\text{C}_{36}\text{H}_{48}\text{NS}_4\text{In}$	$\text{C}_{32}\text{H}_{40}\text{NSe}_4\text{Ga}$
Formula weight	692.71	737.81	824.21
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	Cc	Cc	$P2_1/c$
a (Å)	22.5014(4)	22.6647(4)	12.1527(3)
b (Å)	10.6150(2)	10.5550(2)	12.9180(3)
c (Å)	15.8714(3)	16.0707(3)	21.4221(4)
β (°)	103.614(1)	103.399(1)	93.679(1)
V (Å ³)	3684.41(12)	3739.88(12)	3356.09(11)
Z	4	4	4
$D_{\text{calcd.}}$ g cm ⁻³	1.249	1.310	1.631
Temperature, K	296(2)	296(2)	296(2)
$F(000)$	1464	1536	1624
μ (Mo $K\alpha$) mm ⁻¹	0.998	0.879	5.179
No. reflections measured	17534	17796	33377
No. unique reflections	6078	7408	7689
No. observed reflections	3471	6400	5199
No. parameters	379	379	344
R_{int}	0.0428	0.0155	0.0370
$R1^a$, $wR2^b$ ($I > 2\sigma(I)$)	0.0468, 0.1019	0.0268, 0.0664	0.0292, 0.0663
$R1^a$, $wR2^b$ (all data)	0.0979, 0.1209	0.0335, 0.0703	0.0590, 0.0766
GoF ^c	1.019	1.017	0.941
Flack value	0.00(0)	0.00(0)	–
Final diff. peaks (e Å ⁻³)	+0.307, –0.210	+0.354, –0.244	+0.368, –0.391

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|;$$

$$^b wR2 = \left[\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^4 \right]^{1/2};$$

$$^c \text{GoF} = \left[\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{param}}) \right]^{1/2}.$$

reaction of $\text{InCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{NaSC}_6\text{H}_4\text{Me-p}$ in the presence of $[\text{Et}_4\text{N}]\text{Cl} \cdot x\text{H}_2\text{O}$. The analogous selenolate derivative of gallium $[\text{Et}_4\text{N}][\text{Ga}(\text{SePh})_4]$ (**3**) was prepared from similar reaction of $[\text{Et}_4\text{N}][\text{GaCl}_4]$ with four equivalents of NaSePh . White crystalline thiolate and selenolate complexes $[\text{M}(\text{SR})_4]^-$ ($\text{M} = \text{Ga}, \text{In}$) were stable in both solid-state and solution. Both complexes were soluble in DMSO and DMF, and slight soluble THF and MeCN, but poorly soluble in common solvents. The infrared spectra of complexes **1** and **2** display the characteristic C–S stretching vibration of the coordinated thiolate ligands at 648 and 641 cm^{-1} . The C–Se stretching vibration at 562 cm^{-1} in the IR spectrum indicated the presence of selenolate ligands in complex **3**. The ^1H NMR spectra of three complexes display the typical multiple peaks in the ranges δ 6.70–7.40 ppm, which were assigned to the protons of the phenyl moiety. The molecular ions corresponding to $[\text{Ga}(\text{SC}_6\text{H}_4\text{Me-p})_4]^-$, $[\text{In}(\text{SC}_6\text{H}_4\text{Me-p})_4]^-$ and $[\text{Ga}(\text{SePh})_4]^-$ can be observed at m/z 562, 607 and 694 in the mass spectra of **1**, **2** and **3**, with their characteristic isotopic distribution patterns.

Crystal structures of **1**, **2**, and **3** have been determined by X-ray diffraction study. All crystal structures consist of discrete $[\text{Et}_4\text{N}]^+$ cations and its corresponding complex anions. In all structures, the $[\text{Et}_4\text{N}]^+$ cations exhibit normal bond distances and angles. The structures of the anions, $[\text{Ga}(\text{SC}_6\text{H}_4\text{Me-p})_4]^-$ in **1** and $[\text{In}(\text{SC}_6\text{H}_4\text{Me-p})_4]^-$ in **2**, are shown in Figs. 1 and 2, respectively. The anions in **1** and **2** have a distorted tetrahedral geometry which were similar to those the gallium-thiolate anions $[\text{i-Pr}_4\text{N}][\text{Ga}(\text{SET})_4]$ [12], and $[\text{Et}_4\text{N}][\text{Ga}(\text{SPh})_4]$ [12] and indium-thiolate anions $[\text{Ph}_4\text{P}][\text{In}(\text{S-t-Bu})_4]$ [19] and $[\text{Me}_4\text{N}][\text{In}(\text{SC}_6\text{H}_3\text{Me}_2\text{-2,6})_4]$ [20]. The Ga–S bond lengths in **1** range from 2.254(2) to 2.291(2) Å (av. 2.273(2) Å), which are in good agreement with those in $[\text{i-Pr}_2\text{NH}_2][\text{Ga}(\text{S-i-Pr})_4]$ (av. 2.2678(6) Å) [13], $[\text{i-Pr}_4\text{N}][\text{Ga}(\text{SET})_4]$ (av. 2.264(3) Å) [12], and $[\text{Et}_4\text{N}][\text{Ga}(\text{SPh})_4]$ (av. 2.257(3) Å) [12]. The S–Ga–S bond angles in **1** vary from 97.06(7) to 117.31(9)°, which were expected for distorted tetrahedral coordination environment, which are comparable to those in $[\text{i-Pr}_2\text{NH}_2][\text{Ga}(\text{S-i-Pr})_4]$ (from 97.10(2) to 118.22(2)°) [13] and $[\text{Et}_4\text{N}][\text{Ga}(\text{S-Ph})_4]$ (from 101.6(1) to 114.2(1)°) [12]. Similarly, the In–S bond lengths in **2** range from

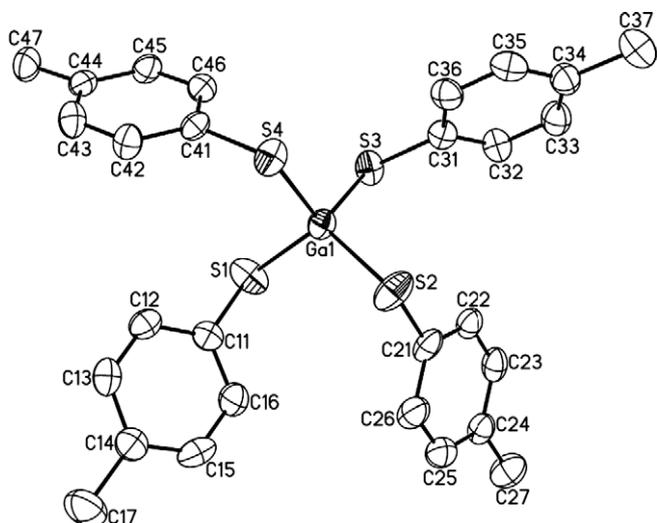


Fig. 1. View of the $[\text{Ga}(\text{SC}_6\text{H}_4\text{Me-}p)_4]^-$ anion in **1** showing the atom numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes, with hydrogen atoms omitted. Selected bond lengths (Å) and angles ($^\circ$): Ga(1)–S(1) 2.262(2), Ga(1)–S(2) 2.2544(18), Ga(1)–S(3) 2.2830(17), Ga(1)–S(4) 2.2913(17); S(2)–Ga(1)–S(1) 117.31(9), S(2)–Ga(1)–S(3) 115.65(8), S(1)–Ga(1)–S(3) 97.06(7), S(2)–Ga(1)–S(4) 98.84(7), S(1)–Ga(1)–S(4) 113.15(8), S(3)–Ga(1)–S(4) 115.95(7).

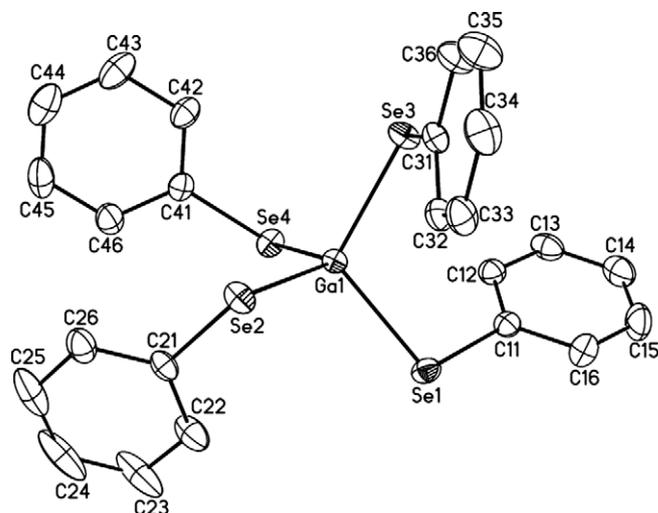


Fig. 3. View of the $[\text{Ga}(\text{SePh})_4]^-$ anion in **3** showing the atom numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes, with hydrogen atoms omitted. Selected bond lengths (Å) and angles ($^\circ$): Ga(1)–Se(1) 2.4052(4), Ga(1)–Se(2) 2.4069(4), Ga(1)–Se(3) 2.4013(4), Ga(1)–Se(4) 2.3963(4); Se(1)–Ga(1)–Se(2) 106.126(15), Se(3)–Ga(1)–Se(1) 111.855(15), Se(3)–Ga(1)–Se(2) 110.610(14), Se(4)–Ga(1)–Se(3) 106.221(15), Se(4)–Ga(1)–Se(1) 109.127(14), Se(4)–Ga(1)–Se(2) 112.992(15).

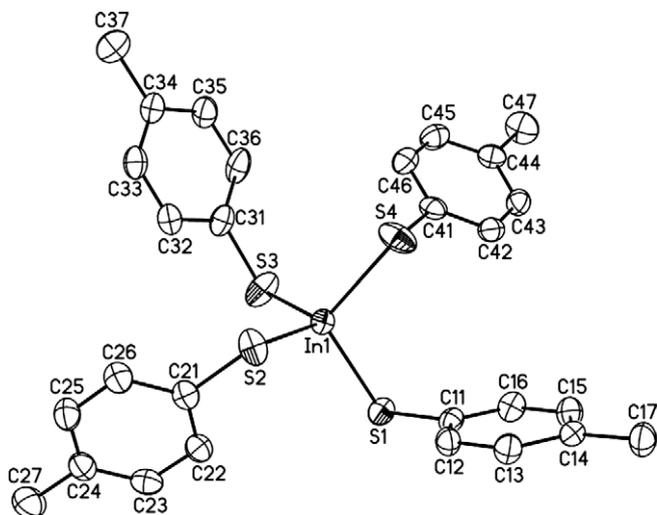


Fig. 2. View of the $[\text{In}(\text{SC}_6\text{H}_4\text{Me-}p)_4]^-$ anion in **2** showing the atom numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes, with hydrogen atoms omitted. Selected bond lengths (Å) and angles ($^\circ$): In(1)–S(1) 2.4593(9), In(1)–S(2) 2.4536(9), In(1)–S(3) 2.4484(10), In(1)–S(4) 2.4445(12); S(2)–In(1)–S(1) 116.12(4), S(3)–In(1)–S(1) 100.51(3), S(4)–In(1)–S(1) 111.95(4), S(3)–In(1)–S(2) 113.95(4), S(4)–In(1)–S(3) 116.75(5), S(4)–In(1)–S(2) 98.44(3).

2.446(1) to 2.459(1) Å and the S–In–S bond angles in **2** vary from 98.44(3) to 116.12(4) $^\circ$, which are compared with those in the related tetrahedral $[\text{In}(\text{SR})_4]^-$ complexes such as $[\text{Ph}_4\text{P}][\text{In}(\text{S-}t\text{-Bu})_4]$ (In–S 2.451(3)–2.489(3) Å and S–In–S 103.8(1)–114.6(1) $^\circ$) [19] and $[\text{Me}_4\text{N}][\text{In}(\text{SC}_6\text{H}_3\text{Me}_2\text{-}2,6)_4]$ (In–S 2.450(2)–2.473(2) Å and S–In–S 107.34(4)–111.49(4) $^\circ$) [20].

The structure of the anion, $[\text{Ga}(\text{SePh})_4]^-$, of **3** is shown in Fig. 3. The $[\text{Ga}(\text{SePh})_4]^-$ anion is isostructural to the indium analogue $[\text{In}(\text{SePh})_4]^-$. Examples of the homoleptic gallium-selenolate complexes with tetrahedral coordination geometry are $[\text{Ga}\{(\text{SeP-Ph}_2)_2\text{N}\}_2][\text{GaCl}_4]$ [21] and $[\text{Ga}(\text{Se}_2\text{P}^i\text{Pr}_2)_2(\eta\text{-Se}_2\text{P}^i\text{Pr}_2)_2]$ [22]. The gallium(III) center is tetrahedrally coordinated to four PhSe $^-$ ligands. The Se–Ga–Se bond angles in **3** are in the range of 106.22(2)–112.99(2) $^\circ$, slightly distorted from tetrahedral which

are probably due to the steric crowding of the bulky phenyl rings. The Ga–Se bond lengths ranging from 2.3963(4) to 2.4069(4) Å (av. 2.4024(4) Å) in **3** are comparable with those in $[\text{Ga}\{(\text{SeP-Ph}_2)_2\text{N}\}_2][\text{GaCl}_4]$ (av. 2.4059(8) Å) [21], but slightly shorter than those in $[\text{Ga}(\text{Se}_2\text{P}^i\text{Pr}_2)_2(\eta\text{-Se}_2\text{P}^i\text{Pr}_2)_2]$ (av. 2.4200(4) Å) with chelating GaSe_2 bite angle [22].

In order to examine the thermal stability of the homoleptic complexes, thermal gravimetric analyses (TGA) were carried out between 30 and 600 $^\circ\text{C}$ in static atmosphere of air. Complexes **1** and **2** were stable at 148 $^\circ\text{C}$. Further increasing in temperature caused decomposition of the complexes. The loss of the organic cations occurred simultaneously. For **1**, a single-step weight loss was observed between 155 and 325 $^\circ\text{C}$, which is attributed to the release of the thiolate ligands and leaving Ga_2S_3 as a yellow powder (observed 16.8%, calculated 17.0%). The decomposition temperature of **2** is almost the same as that of **1**. A weight loss of 49.8% (calculated 51.0%) was observed from 160 to 315 $^\circ\text{C}$ corresponding to the loss of one organic cation and two *p*-MeC $_6$ H $_4$ S $^-$ ligands per formula unit. Further weight loss was observed at 320 $^\circ\text{C}$, and the remaining yellow powdery product was In_2S_3 (observed 22.2%, calculated 22.1%). The selenolate complex **3** lost ca. 77% of its mass from 175 to 330 $^\circ\text{C}$, leaving yellow powder residue which was microanalyzed to show an average ratio of Ga:Se of 2:3. The three homoleptic complexes proved to be potentially a single-source precursor for nano-crystalline gallium(indium)–sulfur(selenium) materials [23]. Further study of this aspect will be carried out.

4. Supplementary material

Crystal data (excluding structure factors) for the structure analyses have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-738145 (**1**), CCDC-731846 (**2**) and CCDC-731847 (**3**). 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 deposit@ccdc.cam.ac.uk).

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