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Lewis-Acid-Base Synthesis of $[\text{Se}_3\text{Cl}_3]_2[\text{SnCl}_6]$ and $[\text{BMIm}]_2[\text{Ga}_8\text{As}_6\text{Cl}_{16}\text{O}_{14}]$

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$[\text{Se}_3\text{Cl}_3]_2[\text{SnCl}_6]$ (**1**) and $[\text{BMIm}]_2[\text{Ga}_8\text{As}_6\text{Cl}_{16}\text{O}_{14}]$ (**2**) are prepared by Lewis-acid-base reaction of SnCl_2 with SeCl_4 and As_2O_3 with $\text{GaCl}_3/[\text{BMIm}]\text{Cl}$ at room temperature and at 60°C . **1** contains $[\text{ClSe-Se-SeCl}_2]^+$ cations with an Se_3 unit and isolated octahedral $[\text{SnCl}_6]^{2-}$ anions. The cation was yet only obtainable via $\text{Se}^0/\text{Se}^{4+}$ synproportionation in liquid SO_2 with AsF_5 . The $[\text{Ga}_8\text{As}_6\text{Cl}_{16}\text{O}_{14}]^{2-}$ anion in **2** consists of two central edge-sharing

GaO_6 octahedra, surrounded by pseudo-tetrahedral AsO_3 units and tetrahedral GaCl_3O and GaCl_2O_2 units. Moreover, an almost planar central Ga_4O_4 ring surrounded by six GaAs_2O_3 rings is characteristic, which was not described before. The title compounds are characterized by X-ray diffraction based on single crystals and powders, infrared spectroscopy, thermogravimetry, and optical spectroscopy.

Introduction

Liquid-phase syntheses with metal halides or metal oxides at moderate temperatures ($\leq 100^\circ\text{C}$) are often limited by an insufficient solubility of the starting materials or of solvents that support a dissolution only upon formation by solvato complexes. Such coordinated solvent molecules, however, often remain as ligands in the product after the synthesis and influence or even dominate the products' chemistry and material properties.^[1] Moreover, solvents and coordinated solvent molecules can initiate acid-base reactions or redox reactions with the starting materials, which reduce the pH range and/or the electrochemical window for certain chemical reaction.^[2] In this regard, ionic liquids turned out to be very interesting as they offer a combination of sufficient solubility, weakly coordinating properties, and good redox stability.^[3]

Specifically for metal halides, ionic liquids give the opportunity to fine-tune reactions and to adjust the respective conditions to obtain metastable products with comparable composition and structure and similar thermodynamic stability.^[4] In this regard, different compounds with unusual binding situation and/or spectacular building units were already described, including cluster compounds, polyhalides, or even new element modifications.^[5] Systematic studies regarding the influence of small changes of the synthesis conditions (e.g.,

temperature, concentration) on the resulting product are rare until now. Examples comprise the formation of polybromides,^[6] low-valent halides in the system Te-Bi/Al-Cl ,^[7] the connectivity of (ZnBr_4) tetrahedra in bromido zincates,^[8] the structure of hexanuclear niobium clusters,^[9] or the composition of chalcogenidometallates.^[10] These reports mainly focus on the behavior of metal halides in ionic liquids, whereas studies on metal oxides are limited and predominately focused on the solubility in ionic liquids as such to realize nanoparticles and/or thinfilms of the respective metal oxide.^[11]

Aiming at an ionic-liquid-based synthesis of novel compounds with non-linear optical (NLO) effects such as second-harmonic generation (SHG),^[12] we recently obtained examples like the ionic $[\text{SeCl}_3]^+[\text{GaCl}_4]^-$, $[\text{TeCl}_3]^+[\text{GaCl}_4]^-$, $[\text{TeCl}_3]^+[\text{TiCl}_6]^{2-}$, or the molecular $\text{Cl}_2\text{SeOGaCl}_3$,^[13] which show promising SHG intensities up to $10\times\text{KDP}$ (KDP: potassium dihydrogenphosphate used as a reference with already strong SHG intensity).^[14] A key-feature of these compounds is the absence of any center of inversion, which often occurs in the presence of tetrahedral or pseudo-tetrahedral building units such as $\text{Se}^{\text{IV}}\text{O}_3$, $\text{Te}^{\text{IV}}\text{O}_3$, $\text{I}^{\text{V}}\text{O}_3$, $[\text{SeCl}_3]^+$, $[\text{TeCl}_3]^+$, $[\text{GaCl}_4]^-$, $(\text{Cl}_2\text{SeO})^-$ or $(-\text{OGaCl}_3)$.^[13,15] In difference to many SHG materials, the above compounds were prepared via simple Lewis-acid-base reactions in ionic liquids at moderate temperature ($\leq 100^\circ\text{C}$) with quantitative yield. Based on our preliminary work, we here specifically focus on Lewis-acid-base reactions with SnCl_2 and As_2O_3 , for which tetrahedral and/or pseudo-tetrahedral building units are also to be expected.

Results and Discussion

Synthesis

Based on our preliminary data,^[13] we intended to use SnCl_2 and As_2O_3 to establish tetrahedral and/or pseudo-tetrahedral building units in order to realize novel NLO materials via simple

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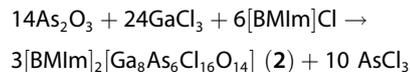
Lewis-acid-base reactions. In the case of SnCl_2 , a reaction with SeCl_4 as a mild Lewis acid was intended – similar to $[\text{SeCl}_3]^+ [\text{GaCl}_4]^{-[13b]}$ – to potentially obtain a composition $[\text{SeCl}_3]^+ [\text{SnCl}_3]^-$. For As_2O_3 , we intended to use GaCl_3 as a strong Lewis acid to activate and to dissolve As_2O_3 .

In contrast to our expectation, the reaction of SnCl_2 and SeCl_4 at room temperature resulted in a brownish liquid (Figure 1a). After cooling to 3°C for one week, orange-red crystals of $[\text{Se}_3\text{Cl}_3]_2^+ [\text{SnCl}_6]^{2-}$ (**1**) were obtained according to the following reaction:



Thus, Sn^{2+} was oxidized to Sn^{4+} , and Se^{4+} was reduced to Se_3^{4+} . Thereafter, SnCl_4 acts as Lewis acid with formation of $[\text{SnCl}_6]^{2-}$. Since the by-product SnCl_4 is liquid (m.p. -33°C), **1** remains dissolved in liquid SnCl_4 and requires crystallization at 3°C . Attempts to purify **1** by evaporation of SnCl_4 only lead to a decomposition of the title compound.

As a second example, we intended to react As_2O_3 as a Lewis base with GaCl_3 as a Lewis acid, following our previous reactions of SeCl_4 or SeOCl_2 with GaCl_3 .^[13a] The synthesis was performed at 60°C with addition of $[\text{BMIm}]\text{Cl}$, which together with GaCl_3 forms an ionic liquid as fluid phase. With these conditions, rhombohedral, colorless crystals of $[\text{BMIm}]_2[\text{Ga}_8\text{As}_6\text{Cl}_{16}\text{O}_{14}]$ were obtained at 60°C after one week according to the following reaction (Figure 1b):



Both compounds **1** and **2** are highly sensitive to moisture and, therefore, need to be handled and stored with inert conditions (e.g., nitrogen or argon atmosphere).

Structural Characterization

According to X-ray structure analysis based on single crystals, $[\text{Se}_3\text{Cl}_3]_2^+ [\text{SnCl}_6]^{2-}$ (**1**) crystallizes in the triclinic space group $P\bar{1}$ (Figure 2a; *SI*: Table S1, Figure S1) and consists of isolated $[\text{ClSe-Se-SeCl}_2]^+$ cations with a Se_3 unit (Figure 2b) and isolated octahedral $[\text{SnCl}_6]^{2-}$ anions (Figure 2c). Although **1** is a new compound as such, the $[\text{SnCl}_6]^{2-}$ anion is of course well-known (e.g., $[\text{CH}_3\text{NH}_3]_2[\text{SnCl}_6]$, $[\text{C}_5\text{NH}_5\text{Cl}]_2[\text{SnCl}_6]$).^[16] The $[\text{Se}_3\text{Cl}_3]^+$ cation has been reported only once until now by Sutherland *et al.* with the compound $[\text{Se}_3\text{Cl}_3][\text{AsF}_6]$.^[17] Here, the formation of the $[\text{Se}_3\text{Cl}_3]^+$ cation required quite harsh conditions with a synproportionation of Se and SeCl_4 in liquid SO_2 as the solvent and AsF_5 as highly reactive Lewis acid. The $[\text{SnCl}_6]^{2-}$ anion in **1** exhibits Sn–Cl distances of 236.3(2)–242.3(2) pm and Cl–Sn–Cl angles of 89.6(1)–90.2(1) $^\circ$, which are in good agreement with the literature (Sn–Cl: 241.1(1)–243.4(1) pm; Cl–Sn–Cl: 89.6(4)–91.3(3) $^\circ$).^[16b] The $[\text{Se}_3\text{Cl}_3]^+$ cation shows Se–Se distances of 220.8(1) and 246.4(2) pm, an Se–Se–Se angle of 102.0(1) $^\circ$, and Se–Cl distances of 209.7(2)–215.4(3) pm. Hereof, the shorter Se–Se distance belongs to the Se–SeCl unit. As expected, distances and angles are similar to $[\text{Se}_3\text{Cl}_3]^+$ in $[\text{Se}_3\text{Cl}_3][\text{AsF}_6]$ (Se–Se: 219.1(3), 255.1(3) pm; Se–Cl: 208.8(5)–218.2(5) pm; Se–Se–Se: 102.9(1) $^\circ$).^[17] The $[\text{Se}_3\text{Cl}_3]^+$ cation, in fact, can be considered as a pseudo-tetrahedral building unit according to the designation $\text{Se}(\text{SeCl})(\text{SeCl}_2)$ with two lone-electron pairs at the central Se atom.

$[\text{BMIm}]_2[\text{Ga}_8\text{As}_6\text{Cl}_{16}\text{O}_{14}]$ (**2**) crystallizes in the triclinic space group $P\bar{1}$ and consists of complex $[\text{Ga}_8\text{As}_6\text{Cl}_{16}\text{O}_{14}]^{2-}$ anions and $[\text{BMIm}]^+$ cations (Figure 3; *SI*: Table S1, Figure S2). Beside single-crystal structure analysis, structure and purity of **2** were confirmed by X-ray powder diffraction analysis with Rietveld refinement (*SI*: Figure S3). Owing to comparable electron numbers (i.e. Ga^{3+} with 28 e^- ; As^{3+} with 30 e^-), and thus, comparable scattering power, both elements cannot be differentiated by X-ray diffraction. However, the $[\text{Ga}_8\text{As}_6\text{Cl}_{16}\text{O}_{14}]^{2-}$ anion clearly shows six obvious

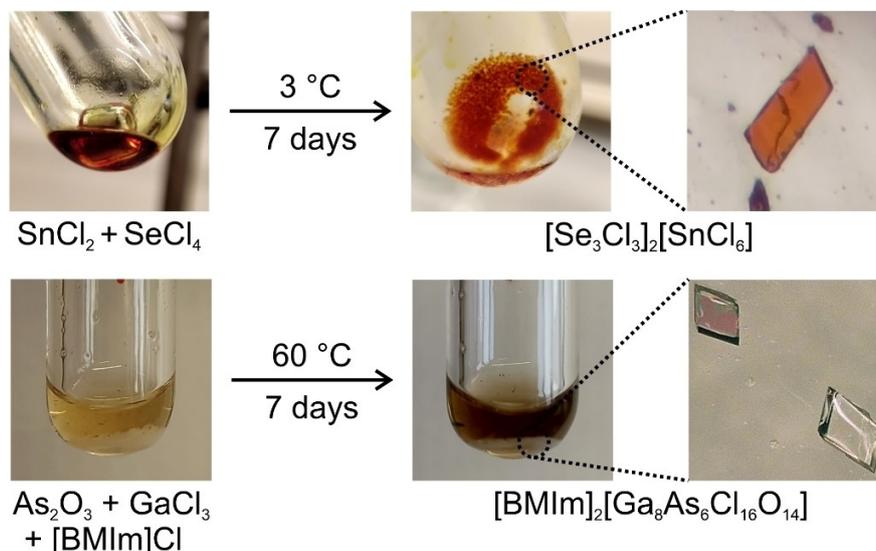


Figure 1. Scheme illustrating the synthesis of $[\text{Se}_3\text{Cl}_3]_2 [\text{SnCl}_6]$ and $[\text{BMIm}]_2 [\text{Ga}_8\text{As}_6\text{Cl}_{16}\text{O}_{14}]$.

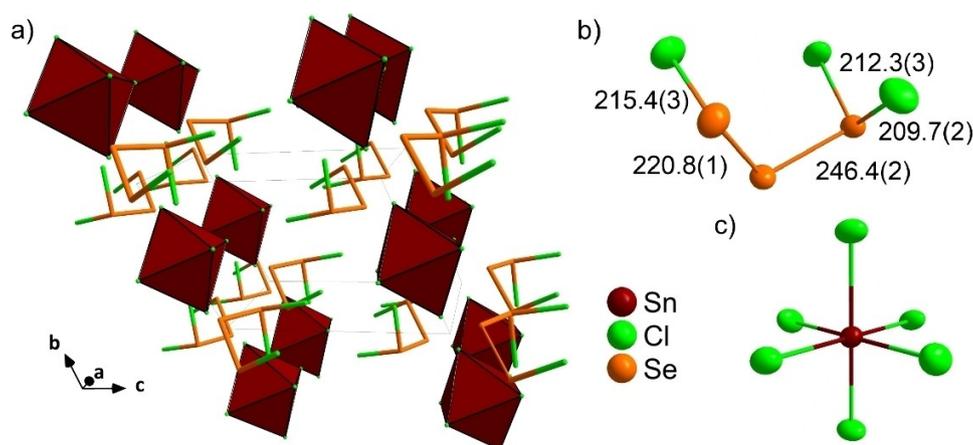


Figure 2. Crystal structure of 1: a) $(2 \times 2 \times 2)$ supercell showing the alternating orientation of the $[\text{Se}_3\text{Cl}_3]^+$ cations and the identical orientation of the $[\text{SnCl}_6]^{2-}$ octahedra, b) isolated $[\text{Se}_3\text{Cl}_3]^+$ cation, c) isolated $[\text{SnCl}_6]^{2-}$ anion.

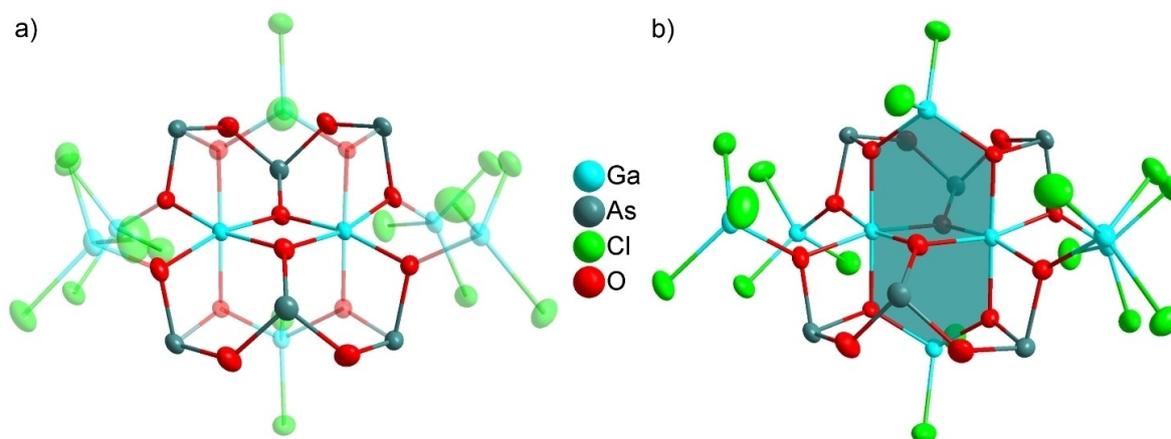


Figure 3. $[\text{Ga}_8\text{As}_6\text{Cl}_{16}\text{O}_{14}]^{2-}$ anion in 2 with specific view on a) the tetrahedral and octahedral coordination of Ga^{3+} and the pseudo-tetrahedral coordination of As^{3+} , b) the central eight-membered Ga_4O_4 ring with attached six-membered GaAs_2O_3 rings.

pseudo-tetrahedral positions, which can be assigned to As^{3+} with its lone-electron pair (Figure 3). In addition, six slightly distorted tetrahedral positions and two distorted octahedral positions are observed and can be assigned to Ga^{3+} . The resulting As:Ga ratio of 6:8 was confirmed by electron-dispersive X-ray spectroscopy (EDXS) with contents of 56 at-% Cl, 26 at-% Ga, 18 at-% As (heavy elements As, Ga, Cl summed up to 100%), which agree with the calculated values (53 at-% Cl, 27 at-% Ga, 20 at-% As). In sum, the $[\text{Ga}_8\text{As}_6\text{Cl}_{16}\text{O}_{14}]^{2-}$ anion consists of two central edge-sharing GaO_6 octahedra, connected via edge- or corner-sharing pseudo-tetrahedral AsO_3 units that are additionally surrounded by six tetrahedral GaCl_3O (4 \times) or GaCl_2O_2 (2 \times) units (Figure 3a). Moreover, an almost planar central Ga_4O_4 eight-membered ring should be noticed (Figure 3b). In addition, 6 six-membered GaAs_2O_3 rings are attached to the central Ga_4O_4 ring. Although both structural motives, Ga_4O_6 rings^[18] and GaAs_2O_3 rings,^[19] were observed before, a combination of both in one complex anion is here observed for the first time.

The Ga–O distances in 1 are 188.1(4)–189.3(5) pm for tetrahedral coordination as well as 195.3(4)–197.6(4) pm for octahedral

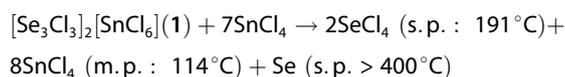
coordination, which is in accordance with reference data (GaO_4 : 187.8(5)–188.1(6) pm; GaO_6 : 193.6(5)–197.6(6) pm).^[18] Cl/O–Ga–Cl/O angles of 102.4(1)–115.2(1) $^\circ$ confirm the distorted tetrahedral coordination of Ga^{3+} . For the GaO_6 octahedra, O–Ga–O angles of 83.0(2) to 94.9(2) $^\circ$ are observed. Only those O–Ga–O angles with oxygen atoms being bridged by AsO_3 units (O1, O2 and O6, O7) are significantly smaller (two-times 76.1(2) $^\circ$), resulting in significantly larger O–Ga–O angles of non-bridged oxygen atoms (101.9(2) and 104.2(2) $^\circ$). The Ga–Cl distances (213.2(2)–216.5(2) pm) are as well in agreement with the literature (213.1(2)–216.8(2) pm). Finally, the As–O distances (176.8(5)–182.1(4) pm) compare to As_2O_3 (172.3–180.9 pm).^[20] The O–As–O angles of 84.0(2)–101.7(2) $^\circ$ reflect the pseudo-tetrahedral coordination.

Material Properties

In addition to the structural characterization, the title compounds were examined by Fourier-transform infrared (FT-IR) spectroscopy,

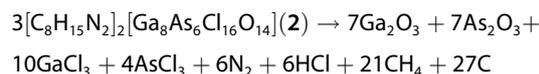
thermogravimetry (TG), and optical spectroscopy (UV-Vis). For **1**, FT-IR spectra only show less-specific, broad $\nu(\text{Se}-\text{Cl})$ and $\nu(\text{Sn}-\text{Cl})$ vibrations ($1500\text{--}500\text{ cm}^{-1}$), which are comparable to SeCl_4 and SnCl_2 as references (Figure 4a). FT-IR spectra of **2** are dominated by $\nu(\text{C}-\text{H})$ ($3200\text{--}2800\text{ cm}^{-1}$) and the fingerprint area ($1700\text{--}500\text{ cm}^{-1}$) of the $[\text{BmIm}]^+$ cation (Figure 4b). Moreover, a broad $\nu(\text{As}-\text{O})$ and a sharp $\nu(\text{Ga}-\text{Cl})$ vibration are observed at $900\text{--}600\text{ cm}^{-1}$ and 495 cm^{-1} and comparable to As_2O_3 and GaCl_3 as references. Finally, the absence of any $\nu(\text{O}-\text{H})$ or $\nu(\text{C}=\text{O})$ vibration indicates the absence of moisture or carbonates.

TG shows the complete decomposition and evaporation of **1** up to 200°C (Figure 5a). The evaporation can be ascribed to the following reaction:



Here, it needs to be noticed that the formation of **1** is accompanied by the formation of seven equivalents of liquid SnCl_4 . Since a separation of SnCl_4 without decomposition of **1** is difficult, TG was performed with the as-obtained solution of **1** in liquid SnCl_4 .

Taking the presence of SnCl_4 into account, a mass loss of 96% with 4% Se remaining up to 400°C is to be expected, which is in good agreement with the experiment, showing a mass loss of 95% ($< 200^\circ\text{C}$) and additional 3% ($> 200^\circ\text{C}$). **2** decomposes in four steps with mass losses of 14% ($100\text{--}300^\circ\text{C}$), 9% ($300\text{--}400^\circ\text{C}$), 48% ($400\text{--}550^\circ\text{C}$), and 6% ($550\text{--}1100^\circ\text{C}$) (Figure 5b), which can be ascribed to the following reaction:



Based on this reaction, mass losses of 12% (N_2 , HCl , CH_4), 12% (AsCl_3), 50% (GaCl_3 , As_2O_3), 5% (C) and a solid remain of 21% (Ga_2O_3) are calculated and well in agreement with the experimental data. The solid residue of 21% was indeed identified via XRD as Ga_2O_3 , which remains as the most stable oxide compound in the system (*SI: Figure S4*). In sum, TG and the quantification of the mass losses also confirm the composition of both title compounds.

Finally, the optical properties of **1** were analyzed by UV-Vis spectroscopy (Figure 6a). Here, a strong absorption below 500 nm occurs, which is in accordance with the orange-red color of single

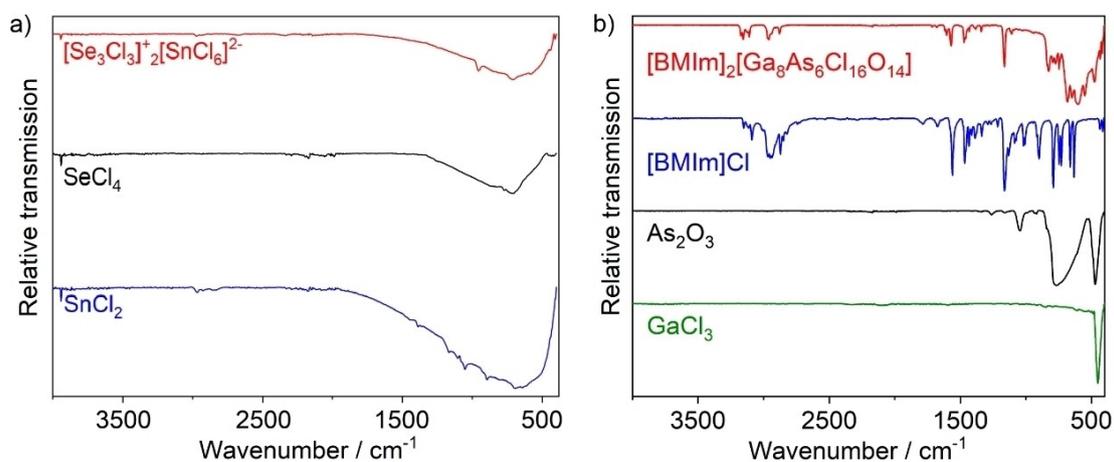


Figure 4. FT-IR spectra of a) $[\text{Se}_3\text{Cl}_3]_2[\text{SnCl}_6]$ (SnCl_2 , SeCl_4 as references), b) $[\text{BmIm}]_2[\text{Ga}_8\text{As}_6\text{Cl}_{16}\text{O}_{14}]$ (As_2O_3 , GaCl_3 , $[\text{BmIm}]\text{Cl}$ as references).

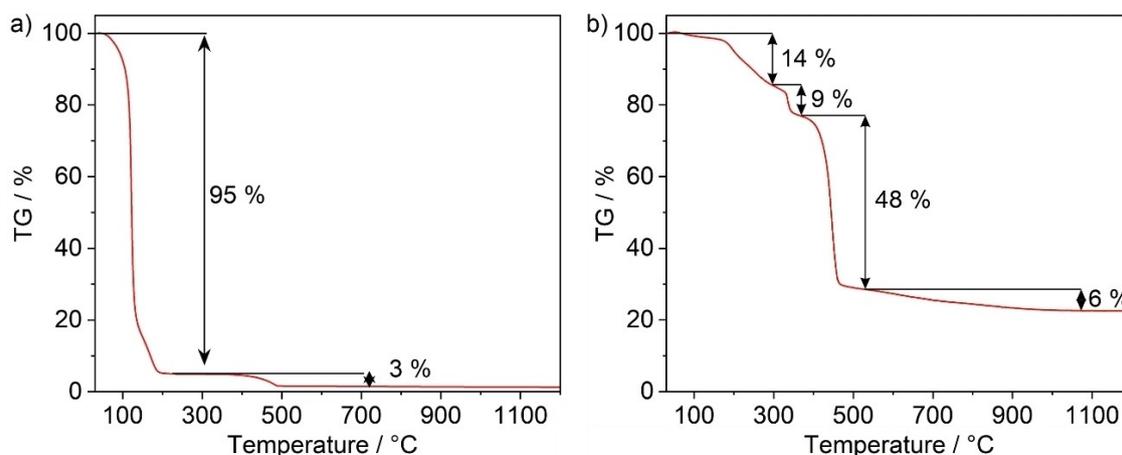


Figure 5. TG of a) $[\text{Se}_3\text{Cl}_3]_2[\text{SnCl}_6]$ and b) $[\text{BmIm}]_2[\text{Ga}_8\text{As}_6\text{Cl}_{16}\text{O}_{14}]$ (performed in nitrogen atmosphere).

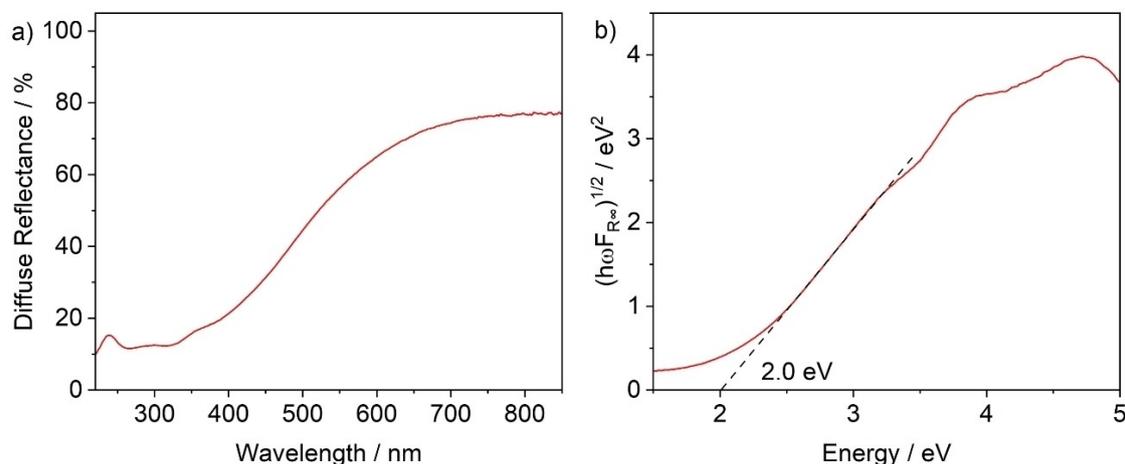


Figure 6. Optical properties of $[\text{Se}_3\text{Cl}_3]_2[\text{SnCl}_6]$: a) UV-Vis spectrum, b) Tauc plot.

crystals (cf. Figure 1a). Based on the shape of the absorption, a band gap transition can be expected as the origin. Via a Tauc plot, an indirect band gap of 2.0 eV was determined (Figure 6b), which is again in agreement with the orange-red color of **1**. Finally, it should be noticed that – against our intention – an SHG effect is not expected as both title compounds crystallize in the inversion-symmetric space group $P\bar{1}$. Beside the formation of two novel compounds via Lewis-acid-base reaction and despite the intended formation of tetrahedral ($\text{GaCl}_3\text{O}/\text{GaCl}_2\text{O}_2$ units in **2**) or pseudo-tetrahedral ($[\text{Se}_3\text{Cl}_3]^+$ cation in **1**, AsO_3 units in **2**) building units, the space-group symmetry unfortunately is against any NLO effect of the title compounds.

Conclusions

The novel compounds $[\text{Se}_3\text{Cl}_3]_2[\text{SnCl}_6]$ (**1**) and $[\text{BMIm}]_2[\text{Ga}_8\text{As}_6\text{Cl}_{16}\text{O}_{14}]$ (**2**) were obtained by Lewis-acid-base reaction at 20 and 60 °C by reaction of the Lewis bases SnCl_2 and As_2O_3 with the Lewis acids SeCl_4 or $\text{GaCl}_3/[\text{BMIm}]\text{Cl}$. **1** consists of isolated $[\text{ClSe-Se-SeCl}_2]^+$ cations and isolated octahedral $[\text{SnCl}_6]^{2-}$ anions. The cation was realized until now only by $\text{Se}^0/\text{Se}^{4+}$ synproportionation in liquid SO_2 with AsF_5 . **2** contains $[\text{Ga}_8\text{As}_6\text{Cl}_{16}\text{O}_{14}]^{2-}$ anions with two central edge-sharing GaO_6 octahedra, surrounded by pseudo-tetrahedral AsO_3 units and tetrahedral GaCl_3O and GaCl_2O_2 units. An additional structural feature is an almost planar central Ga_4O_4 eight-membered ring, surrounded by six GaAs_2O_3 rings. Although both title compounds exhibit tetrahedral building units ($\text{GaCl}_3\text{O}/\text{GaCl}_2\text{O}_2$ units in **2**) or pseudo-tetrahedral building units ($[\text{Se}_3\text{Cl}_3]^+$ cation in **1**, AsO_3 units in **2**), our initial aim to realize compounds with nonlinear optical (NLO) effects was not achieved as the space-group symmetry of both compounds includes inversion centers. The novel compounds **1** and **2**, nevertheless, show that Lewis-acid-base reactions can result in novel structural building units as well as an activation of oxides such as As_2O_3 in absence of conventional solvents.

Experimental Section

General considerations. The starting materials SeCl_4 (35–36.5% Se content, Sigma-Aldrich), SnCl_2 (98%, Sigma-Aldrich), and GaCl_3 (99.999%, ABCR) were commercially available and used as received. As_2O_3 (99.995%, Sigma-Aldrich) and 1-butyl-3-methylimidazolium chloride ($[\text{BMIm}]\text{Cl}$, 99.0%, Iolitec) were dried three days under reduced pressure ($< 10^{-3}$ mbar) at 120 °C before use. All reactants were filled and stored in argon-filled gloveboxes (MBraun Unilab, $\text{O}_2/\text{H}_2\text{O} < 1$ ppm). The reactions were performed using standard Schlenk techniques and glass ampoules. All glass ware was evacuated three times to $< 10^{-3}$ mbar, heated, and flushed with argon to remove all moisture.

$[\text{Se}_3\text{Cl}_3]_2[\text{SnCl}_6]$. 265.0 mg (1.2 mmol) of SeCl_4 and 304.2 mg (1.6 mmol) of SnCl_2 were reacted under argon in a glass ampoule at room temperature, resulting in an orange liquid. After cooling to 3 °C for one week, orange-brownish crystals of $[\text{Se}_3\text{Cl}_3]_2[\text{SnCl}_6]$ were obtained with quantitative yield.

$[\text{BMIm}]_2[\text{Ga}_8\text{As}_6\text{Cl}_{16}\text{O}_{14}]$. 58.9 mg (0.30 mmol) of As_2O_3 , 209.7 mg (1.20 mmol) of GaCl_3 and 104.0 mg (0.60 mmol) of $[\text{BMIm}]\text{Cl}$ were reacted under argon in a glass ampoule at 60 °C for one week. After cooling to room temperature with a rate of 1 K/h, colorless crystals of $[\text{BMIm}]_2[\text{Ga}_8\text{As}_6\text{Cl}_{16}\text{O}_{14}]$ were obtained with a yield of 30%.

X-ray data collection and structure solution. Selected single crystals of $[\text{Se}_3\text{Cl}_3]_2[\text{SnCl}_6]$ and $[\text{BMIm}]_2[\text{Ga}_8\text{As}_6\text{Cl}_{16}\text{O}_{14}]$ were covered with inert oil (perfluoropolyalkylether, ABCR) and deposited on a microgripper (MiTeGen). For $[\text{Se}_3\text{Cl}_3]_2[\text{SnCl}_6]$, a transfer of selected crystals to the diffractometer in a low-temperature N_2 atmosphere was required. Data collection for both compounds was performed at 210 K on an IPDS II image plate diffractometer (Stoe) using $\text{Mo-K}\alpha$ radiation ($\lambda = 71.073$ pm, graphite monochromator). Data reduction and absorption correction were performed with the X-AREA software package (version 1.75, Stoe) and Stoe LANA (Version 1.63.1, Stoe).^[21] For structure solution and refinement, SHELXT and SHELXL were used.^[22] All atomic displacement parameters were refined anisotropically. Images were generated with DIAMOND.^[23] Further details related to the crystal structure may also be obtained from the joint CCDC/FIZ Karlsruhe deposition service on quoting the CCDC numbers 2355834 for **1** and 2355835 for **2**.

X-ray powder diffraction (XRD). X-ray powder diffraction analysis (XRD) was performed on a Stoe Stadi-P diffractometer (Stoe, Germany) using $\text{Cu-K}\alpha$ radiation ($\lambda = 154.06$ pm) with a Ge-monochromator. Rietveld refinements were performed with the program TOPAS-Academic

(version 5), using the *cif*-data to confirm the phase purity of the title compound.

Energy-dispersive X-ray spectroscopy (EDXS) was carried out using an AMETEC EDAX mounted on a Zeiss SEM Supra 35 VP scanning electron microscope. For measurement, the sample was fixed with conductive carbon pads on aluminum sample holders. The experimental data of the heavy elements are well in agreement with the expected values.

Fourier-transform infrared (FT-IR) spectra were recorded on a Bruker Vertex 70 FT-IR spectrometer (Bruker, Germany). The samples were measured in reflection with a Platinum A 225 ATR unit.

Thermogravimetry (TG) was carried out on a Netzsch STA 449 F3 Jupiter device (Netzsch, Germany), using α -Al₂O₃ as a crucible material and reference. Buoyancy effects were corrected by baseline subtraction based on a blank measurement. The samples were measured under dried nitrogen up to 1200 °C with a heating rate of 5 K/min. The Netzsch software PROTEUS Thermal Analysis (Version 5.2.1) was used for graphical illustration.

Optical spectra (UV-Vis) of powder samples were recorded on a Shimadzu UV-2700 spectrometer (Shimadzu, Japan), equipped with an integrating sphere, in a wavelength interval of 250–800 nm against BaSO₄ as reference.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

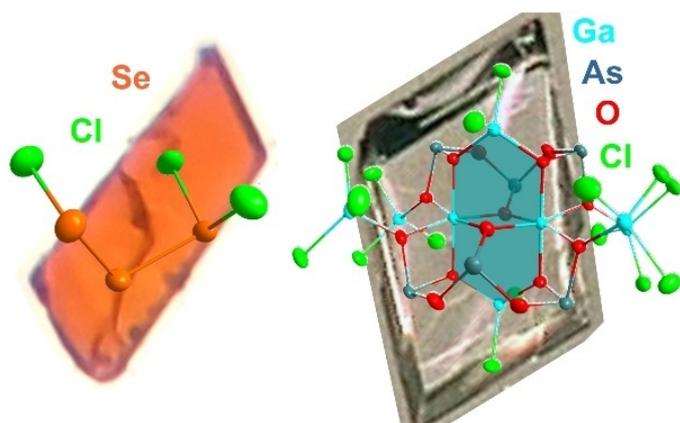
Keywords: crystal structure · gallium arsenic oxychloride · synthesis · Selenium chloride · tin chloride

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Lewis-Acid-Base Synthesis of
[Se₃Cl₃]₂[SnCl₆] and
[BMIm]₂[Ga₈As₆Cl₁₆O₁₄]

