Soluble Pyridine Complexes of the Ternary Gallium(III) Chalcogenide Halides (GaEX)_3, with E = S, Se and X = Cl, Br

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Pyridine Complexes, Ternary Gallium(III) Chalcogenide Halides

The four ternary gallium(III) chalcogenide halides GaEX with E = S, Se and X = Cl, Br can be prepared a) from the binary gallium(III) chalcogenides Ga_2E_3 and halides Ga_X_3, b) from gallium(I) tetrahalogallates(III) Ga(GaX)_4 and the chalcogen E, and c) from gallium metal and the dichalcogen dihalides E_2X_2. The new method c) was shown to be the most convenient preparation. The products are readily soluble in pyridine to give trinuclear molecular complexes [GaEX•Py]_3, which are not volatile without decomposition, but can be purified by crystallization. The structures have been determined by single crystal X-ray diffraction techniques. The two chlorides are isostructural and show twisted tub-form six-membered ring molecules with the pyridine donors in axial positions. The two bromides are also isostructural, but with the pyridine ligands in two axial and one equatorial positions.

Introduction

There is considerable current interest in binary and ternary compounds of gallium with elements of Group 15 and 16 owing to the extensive usage of these systems in semiconductor technology [1, 2]. High-performance microelectronic and photovoltaic devices of the III/V e. g. I/III/VI type (e. g. CuGaSe_2) [2], respectively, are just two typical examples of existing and potential applications. The preparation of the solid phases required as bulk materials or as thin, epitaxial films relies heavily on the availability of volatile and/or soluble precursors which can be readily purified by standard methods. The halides are useful intermediates for further derivatization.

While simple gallium halides and alkyls are compounds which are volatile in an acceptable range of temperatures, the binary gallium chalcogenides Ga_2E_3 (E = S, Se) are high-melting solids which decompose with disproportionation on heating [1]. Their structures are two- (GaS) [3] or three-dimensional networks (Ga_2S_3) [4] which cannot be degraded into low-molecular units thermally or by solvents.

The phase diagrams of the ternary systems gallium / chalcogen / halogen have been determined [5, 6] and show several incongruently melting individual phases of various stoichiometries, the most obvious of which are those of the type GaEX. The structures of the tellurides GaTeCl and GaTeBr have been determined [5, 7] and were shown to feature puckered layers with three-coordinate tellurium, four-coordinate gallium and terminally bound halogen atoms. The sulfur and selenium analogues may be assumed to have similar structures, but no final conclusion has been reached.

During earlier work in this Laboratory [8] it was observed that gallium(III) sulfide chloride GaSCl is readily soluble in pyridine, and that from the resulting colourless solutions a pure crystalline product can be isolated. Very surprisingly, this compound was shown to be a tris-pyridine complex of the trimer [GaSCl]_3 with a six-membered ring structure.

The present account shows that this finding could be generalized including the bromides and selenides of the same type. Improved convenient methods for the preparation are given and details of the structures are discussed.

Preparations

Gallium sulfide chloride, GaSCl, can be prepared as an incongruently melting stoichiometric ternary phase (peritectic decomposition 580 °C) [6, 9].
However, because this phase tolerates excess halogen \([\text{GaS}_{1-x}\text{Cl}_{x+1}]\) to quite significant values of \(x\), the compound is difficult to obtain pure, e.g. from GaCl\(_3\) and Ga\(_2\)S\(_3\) (eq. (1)).

\[
\text{(GaCl}_3\text{)}_2 + 2 \text{Ga}_2\text{S}_3 \rightarrow 6 \text{GaCl} \\
\]

An alternative synthetic route [8] uses Ga[GaCl\(_4\)] and elemental sulfur. The reaction can be carried out in dry aromatic hydrocarbons like benzene or toluene, in which Ga[GaCl\(_4\)] is soluble with formation of discrete arené complexes (eq. (2c)) [10]. Anhydrous GaCl\(_3\) is generated as a by-product, and therefore the yields are not in excess of 50% based on gallium. The GaCl\(_3\) produced can be readily recycled, however, employing a new method of preparation for Ga[GaCl\(_4\)] recently published from this Laboratory [11]; (GaCl\(_3\))\(_2\) is converted into (HGaCl\(_2\))\(_2\) in quantitative yield on reaction with trimethyl- or triethylsilane (eq. (2a)). Thermolysis of (HGaCl\(_2\))\(_2\) gives hydrogen gas and Ga[GaCl\(_4\)], again in quantitative yield (eq. (2b)).

\[
\begin{align*}
\text{(GaCl}_3\text{)}_2 + 2 \text{Et}_3\text{SiH} & \rightarrow \text{(HGaCl}_2\text{)}_2 + 2 \text{Et}_3\text{SiCl} \\
\text{(HGaCl}_2\text{)}_2 & \rightarrow \text{Ga}[\text{GaCl}_4] + \text{H}_2 \\
\text{Ga}[\text{GaCl}_4] + \text{S} & \rightarrow \text{GaSCl} + \text{GaCl}_3
\end{align*}
\]

A new method starts with gallium metal and commercial disulfur dichloride S\(_2\)Cl\(_2\) (Eq. (3)).

\[
2 \text{Ga} + \text{S}_2\text{Cl}_2 \rightarrow 2 \text{GaSCl}
\]

On heating in the absence of a solvent, the two components undergo an exothermic reaction as soon as the melting point of the gallium metal is reached (30 °C). The reaction can be brought to completion by refluxing a slurry in toluene. An excess of S\(_2\)Cl\(_2\) does not alter the composition of the product. The yield of crude, grey material with significant deviations from the theoretical 1:1:1 stoichiometry is ca. 90% based on gallium metal. For purification, the ternary compound obtained from any of the three methods (eq. (1 - 3)) can be dissolved in anhydrous pyridine and crystallized as the colourless trinuclear pyridine adduct 1 (eq. (4)).

\[
3 \text{GaSCl} + 3 \text{Py} \rightarrow \text{[GaSCl} \cdot \text{Py}]_3
\]

**Gallium sulfide bromide**, GaSBr, was also detected in the phase diagram GaBr\(_3\) / Ga\(_2\)S\(_3\) as an incongruently melting phase (peritectic decomposition 645 °C) (eq. (5)) [6, 9]. In the present study it was found that GaSBr can also be prepared from Ga[GaBr\(_4\)] and elemental sulfur in toluene at 60 °C (eq. (7)). In contrast to the chloro analogue (above) there is no appreciable reaction at room temperature. The colourless product precipitates from the reaction mixture in 73% yield. Suspended in toluene, GaSBr reacts with anhydrous pyridine to give the colourless crystalline adduct [GaSBr·Py]\(_3\), 2 (eq. (8)).

\[
\begin{align*}
\text{(GaBr}_3\text{)}_2 + 2 \text{Ga}_2\text{S}_3 & \rightarrow 6 \text{GaSBr} \\
2 \text{Ga} + 2 \text{HgBr}_2 & \rightarrow \text{Ga}[\text{GaBr}_4] + 2 \text{Hg} \\
\text{Ga}[\text{GaBr}_4] + \text{S} & \rightarrow \text{GaSBr} + \text{GaBr}_3 \\
3 \text{GaSBr} + 3 \text{Py} & \rightarrow \text{[GaSBr} \cdot \text{Py}]_3
\end{align*}
\]

2 Gallium(I) tetrabromogallate(III) is best prepared from gallium metal and mercuric bromide [12] in toluene as the arene complex (eq. (6)). The GaBr\(_3\) by-product cannot be recycled via HGaBr\(_2\) because this hydride is too unstable. The reaction of gallium metal with disulfur dibromide is also an unattractive pathway owing the low stability of S\(_2\)Br\(_2\).

**Gallium selenide chloride and bromide**, GaSeCl and GaSeBr, are also components in the phase diagrams [5, 9] GaCl\(_3\) / Ga\(_2\)Se\(_3\) (melting incongruently at 511 °C) and GaBr\(_3\) / Ga\(_2\)Se\(_3\) (594 °C). The methods of choice for their preparation are the reactions of gallium metal with diselenide dichloride and dibromide, respectively, in boiling carbon disulfide (eq. (9)). Extraction of the crude products with pyridine and crystallization from pyridine / acetonitrile or pyridine / hexane afford the colourless trinuclear pyridine adducts 3 and 4, respectively (eq. (10)).

\[
\begin{align*}
2 \text{Ga} + \text{Se}_2\text{X}_2 & \rightarrow 2 \text{GaSeX} \\
3 \text{GaSeX} + 3 \text{Py} & \rightarrow \text{[GaSeX} \cdot \text{Py}]_3
\end{align*}
\]

Compounds 1 - 4 were characterized by elemental analysis. The \(^1\)H NMR spectra (in acetonitrile-d\(_3\)) show the resonances of the \(\alpha\), \(m\) and \(p\)-hydrogen atoms which are shifted to lower field by 0.3 - 0.5 ppm as compared to the signals of free pyridine. The pyridine ligands are thus virtually equivalent in acetonitrile solution at room temperature. Owing to the limited solubility no low temperature studies could be carried out. The NMR-equivalence of the pyridine ligands can arise from rapid dissociation-association (ligand exchange) processes or – less likely – from rapid intramolecular scrambling.
In the IR spectra (KBr) the ring deformation vibrations of the ligands appear at ca. 650 and 430 cm$^{-1}$, and are thus shifted significantly from the values 604 and 405 cm$^{-1}$ of free pyridine. All other pyridine bands show only minor displacements. The mass spectra (Cl) show only fragments of the trimers.

Crystal Structures

Crystals of the two chlorides 1 and 3 are isomorphous (monoclinic, space group $P\overline{2}_1/c$, $Z = 4$). The structures contain discrete trimeric units with no sub-van der Waals contacts. The structures of the molecules are based on distorted boat-formed six-membered rings $Ga_3E_3$ ($E = S, Se$) (Fig. 1) which are superimposable (Fig. 2). The atoms $Ga_1, Se_1, Se_2$ and $Ga_3$ are almost coplanar, while $Ga_2$ and $Se_3$ are both below this reference plane. The molecules have no crystallographically imposed symmetry, but approach quite closely the requirements of point group $C_s$ (the virtual mirror plane passing through $Cl_2, Ga_2$ and $Se_3$ in Fig. 1, bottom). Two pyridine rings are mutually cis while the third one is in a trans position, giving a sequence trans, trans, cis circling the ring. Referring to the boat (tub) conformation, all three pyridine ligands are in axial positions ($N_1 - N_3$). The corresponding N-Ga bonds are almost perpendicular to the reference plane ($Ga_1, Se_1, Se_2, Ga_3$).

Crystals of the two bromides 2 and 4 are also isomorphous (monoclinic, space group $C2/c$, $Z = 8$), but not isomorphous with 1 and 3. The structures also contain isolated trimeric units with a conformation based on a boat-formed six-membered ring (Fig. 3). However, the distribution of the pyridine ligands is different from that in 1 and 3. The struc-
Fig. 3. Molecular structure of compound 2 (top) and 3 (bottom) (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity).

Figures do not approach mirror symmetry because in both cases one of the pyridine molecules is bound equatorial (N2 at Ga2 in Fig. 3). A superposition of the two structures 2 and 4 (Fig. 4) shows the close similarity. The relative disposition of the pyridine ligands at the six-membered ring is also trans, trans, cis circling the ring, but with a different distribution over the three gallium atoms at the boat framework. This conformation requires point group C1 for both structures, 2 and 4. Two pyridine ligands are in axial positions (N1 and N3) while the third one is equatorial (N2).

If the rings of compounds 1 - 4 are flattened out to give planar hexagons, the distribution of the ligands is identical (trans-trans-cis circling the ring, Scheme 1). This flat model has mirror symmetry. Differences for 1 / 3 (C₃ symmetry) and 2 / 4 (C₁ symmetry) arise because of different foldings of these hexagons to give the boat conformations:

a) For 1 and 3 one of the two foldings occurs at a transannular line connecting two gallium atoms with the pyridine rings cis to each other. This folding leads to a retention of the mirror symmetry (point group C₃, Scheme 1). Note that folding is possible in two different directions (up or down). The resulting conformers have the same symmetry, but the ligands change their axial or equatorial positions, respectively.

b) For 2 and 4 the folding occurs at a transannular line connecting two gallium atoms with the pyridine ligands trans to each other. This folding destroys the mirror symmetry and yields chiral molecules (point group C₁). Depending on the direction of the folding, the two enantiomers are generated (Scheme 1).

The structures of the two types of compounds are thus based on the same substitution pattern at a common six-membered ring system, but with a different ring folding when generating the boat conformations.

In summary, the difference between the structure types of 1, 2 and 3, 4 is therefore purely conformational. The orientation of the pyridine ligands in the C₃ structures of 1 and 2 resembles that of [MeGaS-Py]₃ [13], [EtGaSPy]₃ [13] and [tBuGaS-Py]₃ [14] but the boat frameworks are more strongly distorted in all three cases. The trianion [15] [(GaCl₂S)₃]³⁻ with six equivalent chlorine
ligands has a distorted boat conformation approaching mirror symmetry.

The mean bond distances Ga-S and Ga-Se and the angles S-Ga-S, Ga-S-Ga and Se-Ga-Se, Ga-Se-Ga of the rings agree quite closely in compounds 1 and 3 or 2 and 4, respectively, and the exocyclic distances Ga-Cl in 1 and 2, and GaBr in 3 and 4, are also very similar, with minor variations for axial and equatorial positions (Table 1). The ring angles are generally smaller than the tetrahedral reference at the chalcogen atoms (average over all four structures: 99.76°) and larger at the gallium atoms (average: 122.59°).

**Conclusions**

The present work has shown that the ternary compounds GaEX (E = S, Se; X = Cl, Br) can be prepared in a crude form via a series of synthetic pathways from convenient starting materials and in acceptable yields. The products are assumed to
have imperfect two-dimensional structures as suggested by the known framework pattern of the analogous tellurium compounds GaTeCl and GaTeBr. The ternary sulfides and seleniums were found to dissolve in anhydrous pyridine with degradation of the lattices to give trinuclear molecular complexes which can be crystallized from organic solvents. Their structures are based on boat-form six-membered rings with a different ligand distribution over the axial and equatorial positions. The two isomorphous chlorides approach closely an arrangement of the axial and equatorial positions. The two isomorphous bromides have chiral conformations (point group C$_1$). The pyridine ligands can not be removed on heating in a vacuum. Extensive redistribution of halogen, chalcogen and pyridine groups occurs instead leaving ill-defined residues after removing the volatile by-products, mainly Py and PyGaCl$_3$.

**Experimental Section**

All manipulations were carried out under an atmosphere of dry nitrogen. All solvents were dried using standard methods. Ga[GaBr$_3$] [12], Se$_2$Cl$_2$ [16] and Se$_2$Br$_2$ [16] were prepared following literature procedures.

$[\text{GaCl} \cdot \text{Py}]_3$ (1): To gallium metal (1.00 g, 14.3 mmol) disulfur dichloride (0.97 g, 7.15 mmol) is added. The mixture is carefully warmed to 30 °C with stirring (melting point of gallium: 29.78 °C). In a violent reaction a grey product is formed. When after several minutes the reaction has subsided, dry toluene (10 ml) is added together with more disulfur dichloride (0.20 g, 1.48 mmol). Further heating under reflux for 5 h results in a light grey product which is filtered off and washed with dry toluene (3 × 7 ml). After treatment with pyridine (10 ml), filtration of the resulting solution and addition of hexane (10 ml), a colourless precipitate is formed. The product is filtered off, washed with hexane (2 × 8 ml) and recrystallized from acetonitrile / pyridine. Yield: 2.26 g (73%) [8].

IR (KBr): 3062(w), 1608(s), 1483(m), 1450(s), 1044(m), 1014(m), 1063(m), 769(m), 756(m), 689(s), 647(m), 427(m). $^1$H NMR in CD$_3$CN: 8.90 [br s, 2H, o-H], 7.66 [m, 2H, m-H], 8.13 [t, 1H, $^3$J = 6.8 Hz, m-H].

$\text{GaSBr}$: Ga[GaBr$_3$] (6.46 g, 14.67 mmol) and sulfur (0.40 g, 12.67 mmol) are dissolved in toluene (150 ml). The solution is stirred for 4 h at 60 °C. A colourless precipitate forms which, after cooling, is filtered off, washed with toluene (2 × 15 ml) and dried in vacuo. Yield: 1.95 g (73%).

Anal. for GaSBr: calcd. S 17.65, Br 43.98; found: S 16.51, Br 44.78.

$[\text{GaSBr} \cdot \text{Py}]_3$ (2): Gallium sulfide bromide (0.44 g, 2.42 mmol) is dispersed in toluene (9 ml) and treated with pyridine (2 ml). An oil is formed, which soon resolidifies to give a colourless precipitate. The product is filtered off, washed with toluene and dried in vacuo. It is recrystallized from pyridine / hexane. Yield: 0.47 g (74%).

Anal. for C$_{15}$H$_{25}$Br$_3$Ga$_3$N$_3$: calcd. C 23.03, H 1.93, Br 30.64, N 5.37, S 12.30; found: C 23.21, H 1.97, Br 30.25, N 5.45, S 11.56. IR (KBr): 3062(w), 1608(s), 1483(m), 1450(s), 1042(m), 1013(m), 1210(m), 1064(s), 758(m), 689(s), 648(m), 427(m). $^1$H NMR in CD$_3$CN: 8.90 [br s, 2H, o-H], 7.66 [m, 2H, m-H], 8.13 [t, 1H, $^3$J = 7.4 Hz, p-H].

$[\text{GaSeCl} \cdot \text{Py}]_3$ (3): Gallium (0.70 g, 1.0 mmol) is added to a solution of diselenium dichloride (1.15 g, 0.50 mmol) in carbon disulfide (10 ml) and the mixture is refluxed for 12 h. The resulting grey solid is filtered off and washed with carbon disulfide (7 ml) and toluene (7 ml). Extraction of the solid with pyridine (5 ml) and treatment of the filtrate with acetonitrile (30 ml) leads to the formation of a light yellow precipitate. After filtration and washing with toluene until the supernatant solution remains colourless the product is recrystallized from acetonitrile / pyridine. Yield: 0.24 g (30%).

Anal. for C$_{15}$H$_{25}$Cl$_3$Ga$_3$N$_3$: calcd. C 22.81, H 1.91, Cl 13.47, N 5.32, Se 30.00; found: C 22.76, H 1.96, Cl 13.09, N 5.45, Se 29.24. IR (KBr): 3062(w), 1607(s), 1484(m), 1446(s), 1043(m), 1012(m), 1210(m), 1063(s), 759(s), 691(s), 646(s), 427(m). $^1$H NMR in CD$_3$CN: 8.87 [br s, 2H, o-H], 7.69 [m, 2H, m-H], 8.15 [t, 2H, $^3$J = 7.0 Hz, p-H].

$[\text{GaSeBr} \cdot \text{Py}]_3$ (4): Gallium (0.89 g, 1.3 mmol) is added to a solution of diselenium dichloride (2.03 g, 0.64 mmol) in carbon disulfide (10 ml) and the mixture is refluxed for 12 h. The resulting grey solid is filtered off and washed with carbon disulfide (7 ml) and toluene (7 ml). Extraction of the solid with pyridine (5 ml) and treatment of the filtrate with hexane (15 ml) leads to the formation of a light yellow precipitate. After filtration and washing with toluene until the supernatant solution remains colourless the product is recrystallized from pyridine / hexane. Yield: 0.54 g (45%).

Anal. for C$_{15}$H$_{25}$Br$_3$Ga$_3$N$_3$: calcd. C 19.52, H 1.64, Br 25.97, N 4.55, Se 25.66; found: C 20.37, H 1.79, Br 25.76, N 4.73, Se 25.00. IR (KBr): 3050(w), 1610(s), 1484(m), 1449(s), 1046(w), 1016(w), 1210(w), 1065(s), 758(m), 689(s), 650(m), 427(m). $^1$H NMR in CD$_3$CN: 8.90 [br s, 2H, o-H], 7.70 [m, 2H, m-H], 8.15 [t, 2H, $^3$J = 10.6 Hz, p-H].

X-ray crystallography: Specimens of suitable quality and size of compounds 2, 3, and 4 were mounted on...
Table 2. Crystal data, data collection, and structure refinement of compounds 2 - 4.

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\(^a\) wR2 = \([\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\)^{1/2}; w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]; p = (F_o^2 + 2F_c^2)/3.

the ends of quartz fibers in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo-K\(\alpha\) radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix least-squares calculations on F\textsuperscript{2} (SHELXL-97). The thermal motion was treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were calculated and allowed to ride on their parent atoms with fixed isotropic contributions. Important interatomic distances and angles are shown in Table 1, and further information on crystal data, data collection and structure refinement are summarized in Table 2. Thermal parameters and tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDS 164154 - 164156.