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Synthesis, and Structural Characterization of $[[\text{CH}_3(\text{C}_5\text{H}_4\text{N})\text{Ga}(\text{SCH}_2(\text{CO})\text{O})_2]^-][(\text{4-MepyH})]^+$, A Novel Ga(III) Five-Coordinate Complex

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SYNTHESIS, AND STRUCTURAL CHARACTERIZATION OF [$\{\text{CH}_3(\text{C}_5\text{H}_4\text{N})\}\text{Ga}(\text{SCH}_2(\text{CO})\text{O})_2\}^-\text{[(4-MepyH)}]^+$, A NOVEL Ga(III) FIVE-COORDINATE COMPLEX

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The synthesis and structural characterization of a novel ionic Ga(III) five-coordinate complex [$\{\text{CH}_3(\text{C}_5\text{H}_4\text{N})\}\text{Ga}(\text{SCH}_2(\text{CO})\text{O})_2\}^-\text{[(4-MepyH)}]^+$, (4-Mepy = $\text{CH}_3(\text{C}_5\text{H}_5\text{N})$) from the reaction between Ga_2Cl_4 with sodium mercapto-acetic acid in 4-methylpyridine is described. Under basic reaction conditions the mercapto ligand is found to behave as a $2e^-$ bidentate ligand. Single crystal X-ray diffraction studies show the complex to have a distorted square-pyramidal geometry with the [$^-\text{SCH}_2(\text{CO})\text{CO}^-$] ligands *trans*. The compound crystallizes in the $P2_1/c$ (No. 14) space group with $a = 7.7413(6)$ Å, $b = 16.744(2)$ Å, $c = 14.459(2)$ Å, $V = 1987.1(6)$ Å³, $R(F_o) = 0.032$ and $R_w = 0.038$.

INTRODUCTION

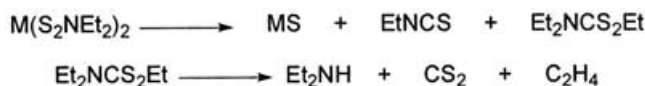
Metal chalcogenide semiconductors display very high radiation tolerance and high optical absorption coefficient [1], consequently Metal Organic Chemical Vapor Deposition (MOCVD) precursors to III/VI materials have received considerable interest for fabrication of optoelectronic devices and thin-film solar cell arrays [2]. One major advantage of metal chalcogenide complexes is their ability to behave as binary single-source precursors [3–6]. The decomposition yields metal sulfide moieties, which can be incorporated into thin-film coatings during fabrication, e.g. dithiocarbamates (Scheme 1) [7]. More recently, O'Brien *et al.* have demonstrated the case in which binary, single-source precursors can serve as excellent reagents for the preparation of semiconducting nanoparticles [8].

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SCHEME 1 Suggested decomposition pathway of metal chalcogenides.

Therefore, the facile syntheses of single-source precursors, which readily decompose to afford the desired semiconductors with the correct stoichiometry, are highly desirable. Previously we reported the preparation of a number of novel gallium(III) dithiocarbamate complexes and recently an indium(III) thioglycolic derivative [9]. Further to this series, we now report the facile preparation of $[\{\text{CH}_3(\text{C}_5\text{H}_4\text{N})\}\text{Ga}(\text{SCH}_2(\text{CO})\text{O})_2]^-[(4\text{-MepyH})]^+$ **1** as a possible precursor to the semiconductor GaS, or Ga₂S₃.

EXPERIMENTAL

General

Air and moisture-sensitive materials were handled under anaerobic conditions using standard Schlenk-line techniques, in flame-dried glassware. Solids were manipulated in a Vacuum Atmospheres dry box equipped with a HE-493 dri-train. Heptane and 4-methylpyridine were distilled from CaH₂ under a dinitrogen atmosphere prior to use. Anhydrous gallium(III) chloride and [NaSCH₂(CO)OH] were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification.

Preparation of $[\{\text{CH}_3(\text{C}_5\text{H}_4\text{N})\}\text{Ga}(\text{SCH}_2(\text{CO})\text{O})_2]^-[(4\text{-MepyH})]^+$

Sodium mercapto-acetic acid (NaSCH₂(CO)OH) (0.25 mmol) and a small excess of Ga₂Cl₄ (0.30 mmol), were reacted in 25 mL of 4-methylpyridine at 0°C with subsequent warming to room temperature, under argon. The solution was allowed to react for 7 days, filtered and then layered with 25 mL of heptane, which afforded colorless white needles suitable for single crystal analysis after 3 days (yield 35%).

X-Ray Crystal Data Collection

Single crystal X-ray diffraction data were collected on an Enraf-Nonius CAD4 computer-controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator. A colorless needle of GaS₂O₄N₂C₁₆H₁₉ (*M* = 437.19), having approximate dimensions of 0.19 × 0.11 × 0.11 mm was mounted on a glass fiber. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range 20 < θ < 22°, measured by the computer-controlled diagonal slit method of centering. The monoclinic cell parameters, calculated volume and density are shown in Table I. Crystal quality was determined by measuring several intense omega reflections, which displayed a half height width of 0.57° with a take off angle of 3.0°, indicating moderate crystal quality. There were no systematic absences; the space group was determined to be P2₁/c (No. 14). A total of 2562 reflections were collected, of which 2562 were unique [10].

TABLE I Crystallographic data for GaS₂O₄N₂C₁₆H₁₉, (CCDC 170557)

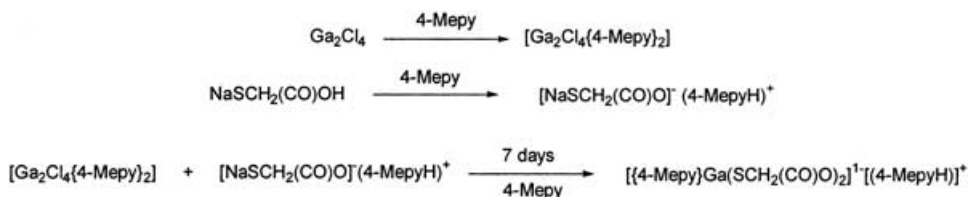
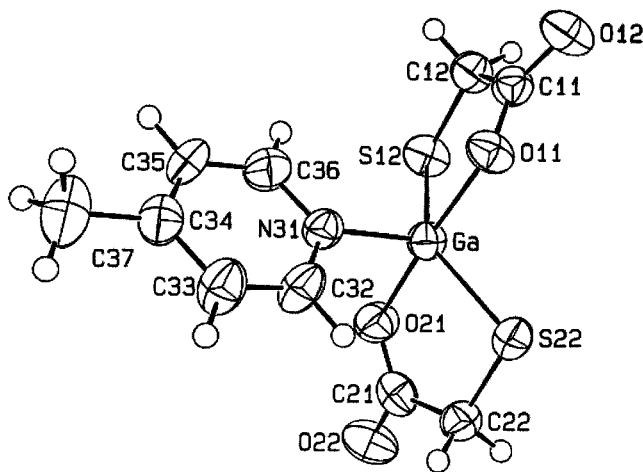
Formula weight	437.19
Crystal size (mm)	0.50 × 0.17 × 0.13
Space group (No.)	P2 ₁ /c (No. 14)
<i>a</i> (Å)	7.7413(6)
<i>b</i> (Å)	16.744(2)
<i>c</i> (Å)	14.459(2)
β (°)	90.763(9)
γ (°)	98.983(9)
<i>V</i> (Å ³)	1874.1(6)
<i>Z</i>	4
ρ_{calc} (g cm ⁻³)	1.549
Temperature (K)	293
λ Radiation (wavelength)	Mo-K α (0.71073 Å)
μ (cm ⁻¹)	16.98
Transmission coefficient	1.000–0.769
Scan method	ω - 2θ
<i>h</i> , <i>k</i> , <i>l</i>	– 8 to 8, 0 to 18, 0 to 15
No. observed data	2562
No. unique data	2562
Largest shift/esd in final cycle	0.19
<i>R</i> (<i>F</i> _o)	0.032
<i>R</i> _w	0.038
<i>F</i> ₀₀₀	896.0
Goodness of fit	0.874

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 17.0 cm⁻¹ for Mo-K α radiation. An empirical absorption correction based on the method of Walker and Stuart was applied [11]. Relative transmission coefficients ranged from 0.769 to 1.000 with an average of 0.916.

The structure was solved using the solution program MoLEN on a VAX computer [12]. Interpretation of a Patterson heavy atom method revealed the position of the In atom. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculations but not refined. The structure was refined in full-matrix least-squares where *w* is defined as per the Killean and Lawrence method with terms of 0.020 and 1.0 [13].

RESULTS AND DISCUSSION

The use of GaCl₂ as a starting material for novel main group complexes has renewed interest. Gallium dichloride is more correctly represented as a Ga(I) and Ga(III) complex ([Ga⁺][GaCl₄]). The salt comprises a reducing gallium(I) species with the Lewis acidic, tetrahedral GaCl₄⁻ ion. The preparation of **1** can be presumed to occur via the formation of the intermediate, chlorogallium 4-methylpyridine [Ga₂Cl₄(4-Mepy)₂] **2** [9]. The subsequent addition of sodium mercapto-acetic acid (NaSCH₂(CO)OH) to the basic solution of **2** at 0°C, followed by warming to room temperature results in the initial deprotonation of the acidic hydrogen to yield the intermediate 2e⁻ bidentate donor ligand (S⁻CH₂(CO)O⁻) [14–17]. The reaction then proceeds by the concomitant cleavage of the Ga–Ga bond via disproportionation to Ga metal and Ga(III) cation due to the basic reactions conditions [18], followed by ligation of S⁻CH₂(CO)O⁻ to yield the novel gallium(III) moiety (Scheme 2).

SCHEME 2 Preparation of $[(\text{CH}_3(\text{C}_5\text{H}_4\text{N}))\text{Ga}(\text{SCH}_2(\text{CO})\text{O})_2]^-[(\text{4-MepyH})_2]^+ \mathbf{1}$.FIGURE 1 X-ray single crystal structure for $[(\text{CH}_3(\text{C}_5\text{H}_4\text{N}))\text{Ga}(\text{SCH}_2(\text{CO})\text{O})_2]^-[(\text{4-MepyH})]^+ \mathbf{1}$. The $[(\text{4-MepyH})]^+$ cation has been omitted for clarity.

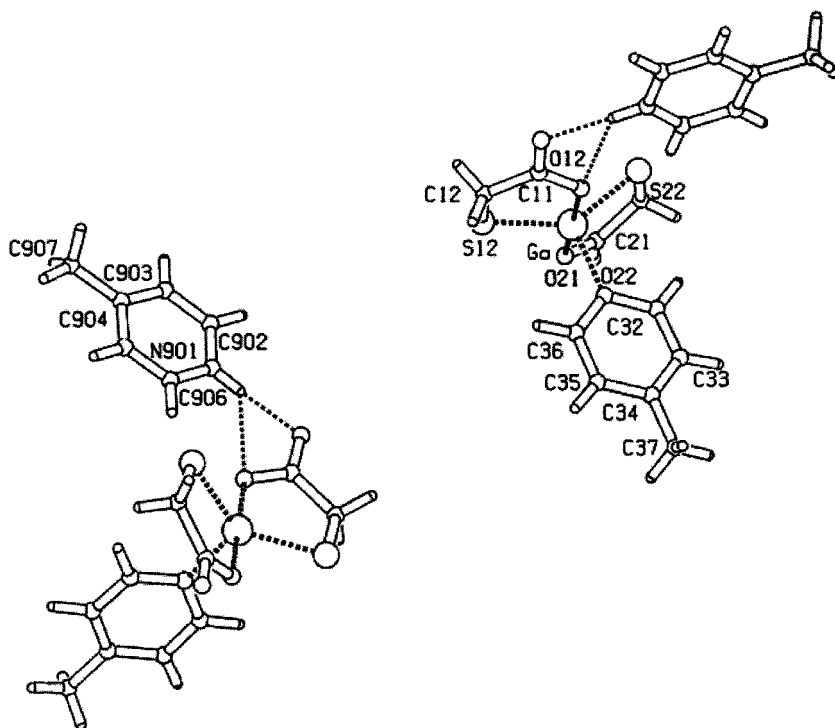
The reaction is then filtered to remove elemental Ga and the filtrate carefully layered with freshly distilled heptane. Controlled evaporation at room temperature under inert conditions produced a large quantity of colorless crystals, from which one was selected for analysis by single crystal X-ray diffraction. The product was elucidated as the unexpected ionic species $[(\text{CH}_3(\text{C}_5\text{H}_4\text{N}))\text{Ga}(\text{SCH}_2(\text{CO})\text{O})_2]^-[(\text{4-MepyH})]^+ \mathbf{1}$ (Fig. 1, Table II).

The thioglycolic ligands are arranged in the expected *trans* geometry, binding through both sulfur and oxygen. In addition, Ga having an underlying d^{10} configuration allows it to take part in $d_\pi-d_\pi$ and $d_\pi-p_\pi$ back bonding with the auxiliary sulfur and oxygen atoms of the bidentate ligand, respectively [19].

Compound **1** is significant as it represents a novel thioglycolic five-coordinate Ga(III) ionic complex and the first structurally characterized. The unit cell contains two unique ionic molecules, which show a distorted trigonal pyramidal geometry around the gallium atom. Comparison of the Ga–N bond length of 2.017(4) Å shows it is consistent with that reported for $[\text{Ga}_2\text{Cl}_4(\text{4-Mepy})_2]$ (2.005(6) Å) [9]. The Ga–O(11) bond length of 2.039(3) Å is longer than the Ga–O(21) bond length of 1.969(3). The variation in bond lengths may be attributed to the presence of hydrogen bonding observed between both oxygen's and the protonated amine $\text{O}(12)\cdots\text{H}(+)$, $\text{O}(11)\cdots\text{H}(+)$ 1.85(7) and 2.53(7) Å, respectively, thus resulting in elongation of the Ga–O(11) (Fig. 2). With the absence of hydrogen bonding for the second thioglycolic ligand a Ga–O(21) bond length of 1.969(3) is determined, which is similar to those found in gallium

TABLE II Selected bond distances (Å) and angles (°) for GaS₂O₄N₂C₁₆H₁₉

Bond	Distance/Å	Atoms	Angle/°
Ga–S(12)	2.243(1)	S(12)–Ga–S(22)	138.18(6)
Ga–S(22)	2.242(1)	S(12)–Ga–O(11)	86.8(1)
Ga–O(11)	2.039(3)	S(12)–Ga–O(21)	93.8(1)
Ga–O(21)	1.969(3)	S(12)–Ga–N(31)	111.6(1)
Ga–N(31)	2.017(4)	S(22)–Ga–O(11)	88.3(1)
S(12)–C(12)	1.804(5)	S(22)–Ga–O(21)	88.9(1)
S(22)–C(22)	1.805(5)	S(22)–Ga–N(31)	110.1(1)
O(11)–C(11)	1.273(5)	O(11)–Ga–O(21)	176.5(2)
O(11)–H(+)	2.53(7)	O(11)–Ga–N(31)	91.9(1)
O(12)–C(11)	1.239(6)	O(21)–Ga–N(31)	91.1(2)
O(12)–H(+)	1.85(7)	Ga–S(12)–C(12)	97.5(2)
O(21)–C(21)	1.280(6)	Ga–S(22)–C(22)	95.8(2)
O(22)–C(21)	1.217(6)	Ga–O(11)–C(11)	120.0(3)
N(31)–C(32)	1.329(6)	Ga–O(21)–C(21)	121.0(4)
N(31)–C(36)	1.324(6)	Ga–N(31)–C(32)	120.5(3)
N(901)–H(+)	0.88(7)	Ga–N(31)–C(36)	122.8(4)

FIGURE 2 The crystal structure of $[\{\text{CH}_3(\text{C}_3\text{H}_4\text{N})\}\text{Ga}(\text{SCH}_2(\text{CO})\text{O})]^{-}[(4\text{-MepyH})^+]^+$ **1**; two molecules are represented displaying ionic interactions.

carboxylates, (Ga–O = 1.958(5) to 1.984(5) Å) [20]. In addition, the Ga–S bond lengths of 2.243(1) and 2.242(1) Å are typical for this family of ligands [9]. Long distance interactions are also observed between the adjacent carbonyl group and the cation of 2.53(7) Å, which would account for the relatively close geometric arrangement of the cation.

Comparison of O(11)–C(11) and C(11)–O(12) bond lengths of 1.273(5) and 1.239(6) Å show that they are comparable to those reported in the literature for C–O and C=O, respectively, thus further suggesting that the ligand is acting as a 2e[−] donor with the carbonyl group directed away from the metal coordination sphere.

SUMMARY

The thioglycolic ligand represents a bidentate ligand comprised of both auxiliary soft (S) and hard donor (O) atoms. Metal thioglycolic complexes reported in the literature demonstrate the ligand's ability to serve as either a 1e[−] and/or 2e[−] donor ligand. Reactions reported in neutral conditions illustrate the ligand preferentially behaves as a 1e[−] donor. In addition, the use of sterically demanding groups on the ligand has been shown to reduce ligand to metal association [14]. In basic reaction conditions the acidic proton is readily removed, affording the 2e[−] bidentate donor ligand. In this work we demonstrate that 4-methylpyridine can serve as a reaction solvent, in addition to a base and dative ligand by the isolation and characterization of **1**. In conclusion, a novel array of coordination chemistry can be invoked by manipulation of the pH of the reaction medium and the steric bulk of peripheral groups of these types of ligands.

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