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ARTICLE

Accessing γ -Ga₂S₃ by solventless thermolysis of gallium xanthates: A low temperature limit for crystalline products?

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Alkyl-xanthato gallium(III) complexes of the form [Ga(S₂COR)₃] where R = Me (**1**), Et (**2**), ⁱPr (**3**), ⁿPr (**4**), ⁿBu (**5**), ^sBu (**6**) and ^tBu (**7**) have been synthesized and fully characterised. Crystal structures for **1** and **3–7** have been solved and their structures examined to elucidate if their structure is related to their decomposition. Thermogravimetric analysis was used to give insight into the decomposition temperatures for every complex. Unlike previously explored metal xanthate complexes which break down at low temperatures (< 250 °C), to form crystalline metal chalcogenides, powder X-ray diffraction measurements suggest that when R ≥ Et these complexes did not produce crystalline gallium sulfide until heated to 500 °C, where the γ -Ga₂S₃ was the sole product formed. In the case of R = Me Chugaev elimination is unable to occur and amorphous Ga_xS_y products were formed. We conclude therefore that the low temperature synthesis route offered by the thermal decomposition of metal xanthate precursors, which has been reported for many metal sulfide systems prior to this, may not be appropriate in the case of gallium sulfides.

Introduction

Gallium sulfides are refractory materials to produce by traditional synthetic routes due to their existence in four stoichiometric forms: gallium monosulfide (GaS), gallium sesquisulfide (Ga₂S₃), Ga₂S and Ga₄S₅. Additionally, both GaS and Ga₂S₃ exhibit polymorphism.^{1–4} In contrast, aluminium sulfides possess only one stoichiometric form, Al₂S₃, with four polymorphs, whilst gallium selenides and tellurides are known to form only three and four phases respectively.^{3,5} However, gallium sulfides possess wide band gaps in the range 3.05 – 2.85 eV and have potential for use in photovoltaics, optoelectronics and as passivating layers in III–V group semiconductor devices.^{6–9} Thus, low temperature ‘soft’ processing routes that produce well-defined phases and stoichiometries of these materials would potentially be of tremendous utility.

Molecular precursor routes towards gallium sulfides in particular present an excellent opportunity by which to control the phase and stoichiometry of the materials produced. As

there are seven potential phases that can be formed the control of the phase achieved is a greater concern as compared to other metal chalcogenides with fewer potential phases, *e.g.* PbS, CdS and ZnS and this therefore remains a challenge, which is reflected in the range of materials produced in literature. For example, Barron *et al.* used gallium-chalcogen cubanes to deposit cubic GaS using MOCVD. The cubic [tBuGaS]₄ clusters act as seeds for oriented nucleation followed by the growth of cubic GaS.¹⁰ When using [Cp*Ga(μ -S)]₄, where Cp* is (C₅Me₅) or (C₅Me₄Et), Barron *et al.* prepared γ -Ga₂S₃.^{10,11} In contrast, [Ga(SⁱPr)₂(μ -SⁱPr)]₂ has been used as a molecular precursor in LP-MOCVD experiments to produce different phases of gallium sulfide depending on the substrate used; γ -Ga₂S₃ is produced on glass, α -Ga₂S₃ on silicon (100), and highly oriented γ -Ga₂S₃ on YSZ (111) suggesting an epitaxial growth mechanism occurs in these cases.¹² [MeGa(SCH₂CH₂S)]₃ was used to synthesize nanometric β -Ga₂S₃ when pyrolysed between 300 and 500 °C.¹³ Ramalingam *et al.* have prepared α -Ga₂S₃ nanoparticles from tris(cyclo-hexylmethylthiocarbamate) gallium(III) and tris(cyclohexyl-ethylthiocarbamate) gallium(III), using a solvothermal method.¹⁴ Malik *et al.* synthesised mono-dispersed cubic GaS nanoparticles using [Ga(S₂CNEt₂)₃] in 4-ethylpyridine at 167 °C.¹⁵ [Ga(S₂CNMeⁿHex)₃], made from an asymmetrical amine, yielded α -Ga₂S₃ when using LP-MOCVD at 500 °C.¹⁶ The tris-monothiocarbamate complex, [Ga(SOCNEt)₃], produced cubic GaS at 350 °C by AACVD.¹⁷ Barron *et al.* studied the preparation of di-*tert*-butyl gallium dithiocarbamate precursors [(^tBu)₂Ga(S₂CNR₂)] where R = Me or Et. Both precursors formed hexagonal GaS by AP-MOCVD at relatively

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low temperatures.¹⁸ Guihua Shang *et al.* used the thiocarboxy complexes of the form $[\text{Ga}(\text{SCOMe})_2\text{Me}(\text{dmpy})]$ (where $\text{dmpy} = 3,5\text{-dimethylpyridine}$) to deposit hexagonal $\alpha\text{-Ga}_2\text{S}_3$ by AACVD.¹⁹ However, despite these reports, the use of molecular precursor routes to produce gallium sulfides is relatively unexplored compared with other routes towards these materials.

Metal xanthate precursors offer an attractive route to metal sulfides due to their low decomposition temperatures and formation of volatile bi-products upon decomposition, *i.e.* SCO , H_2S and an alkyl-ene.^{20–22} These properties have been exploited by us and others for solventless thermolysis of metal xanthate precursors, to form corresponding metal chalcogenides, *e.g.* CdS , FeS ,²³ CuS ,^{21,24} PbS ,²⁵ ZnS ,²⁶ SnS ,²⁷ and chalcogenide spinels ($\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{X}_4$).²⁸ $\text{Cu}_2\text{ZnSnS}_4$.²⁹ Metal xanthate complexes have also been proven to be successful precursors for a wide range of nanometric binary, ternary and quaternary target metal sulphides in other media, *e.g.* in solution or within polymers.^{30–35}

In this work we report the synthesis of a series of linear and branched alkylxanthato gallium(III) complexes and examine the influence of alkyl chain length on their breakdown profiles. We determine the suitability of the gallium(III) xanthates as precursors for gallium sulphides by low temperature thermolysis. It should be noted that whilst the complexes *tris*(*O*-ethylxanthato)gallium(III) and dimethylpentan-3-yl xanthato gallium(III) have been previously reported but their thermal decomposition was not studied in detail – we also report these aspects here.^{36,37}

Experimental Section

Anhydrous toluene ($\geq 99.8\%$, Sigma-Aldrich), anhydrous gallium(III) chloride (99.9% , Sigma-Aldrich), methanol ($\geq 99.8\%$, Sigma-Aldrich), ethanol ($\geq 99.8\%$, Sigma-Aldrich), 2-propanol ($\geq 99.5\%$, Sigma-Aldrich), 1-propanol (99% , Sigma-Aldrich), 1-butanol (99% , Sigma-Aldrich), 2-butanol (99% , Sigma-Aldrich), iso-butanol (99% , Sigma-Aldrich), carbon disulfide (99% , Sigma-Aldrich), hexane ($\geq 97\%$, Sigma-Aldrich) and potassium ethyl xanthogenate (96% , Sigma-Aldrich) were used as received. All syntheses were performed under an N_2 environment using Schleck technique unless stated. ^1H and ^{13}C NMR spectra were obtained using a Bruker AC400 FT-NMR. Melting points were determined using a melting point apparatus (Stuart; Cole-Palmer, UK); infrared spectra were recorded *via* ATR ($4000\text{--}400\text{ cm}^{-1}$, resolution 4 cm^{-1}); and elemental analysis was performed with a Carlo Erba EA 1108. Thermo-gravimetric analyses (TGA) were performed using a Seiko SSC/S200 at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under N_2 . Powder X-ray diffraction (pXRD) patterns were obtained using an X'Pert diffractometer with $\text{Cu-K}\alpha$ source, and scanning electronic microscopy (SEM), using a Tescan Mira 3 FEG scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) spectrometer. Single-crystal X-ray diffraction data for all precursors were collected on a dual source Rigaku FR-X rotating anode diffractometer with using a $\text{Mo-K}\alpha$ wavelength source at 150 K for precursors (**1**, **2**, **3**, **4**, **5**, and **7**) and with using $\text{Cu-K}\alpha$

wavelength source at 200 K for precursor (**6**), and reduced using a CrysAlisPro 171.39.30c. The structure was solved and refined using SHELXTL 2016, implemented through Olex2 v1.2.9.

XPS was performed using a Kratos Axis Ultra spectrometer (Kratos Analytical, UK) using a monochromated Al K_α X-ray source (1486 eV , 10 mA emission, 150 W). Survey spectra were measured with a pass energy of 80 eV and high-res spectra with a pass energy of 20 eV . A charge neutraliser was used to remove differential charging often exhibited by powders. Binding energy calibration was performed using the $\text{C } 1\text{ s}$ peak to 284.8 eV associated with adventitious hydrocarbon.

Synthesis of potassium alkyl xanthates. Potassium alkyl xanthate (KS_2COR) ligands with various alkyl groups (methyl, ethyl, isopropyl, *n*-propyl, *n*-butyl, *s*-butyl and *i*-butyl) were prepared according to the method of McNaughten *et al.*²⁵ A typical ligand synthesis is as follows for $\text{K}(\text{S}_2\text{COMe})$, potassium hydroxide was dissolved (3.5 g , 62.3 mmol) in excess methanol by stirring for one hour and was subsequently cooled to $0\text{ }^\circ\text{C}$. Carbon disulphide (4.7 g , 3.7 ml , 62.3 mmol) was added dropwise with stirring for one hour. The yellow precipitate was filtered, recrystallized from acetone and dried in air to obtain fine yellow crystals of potassium methyl xanthate.

Synthesis of tris(*O*-methylxanthato)gallium(III), $[\text{Ga}(\text{S}_2\text{COMe})_3]$ (1**).** Gallium(III) chloride (1.51 g , 8.6 mmol) was dissolved in dry toluene (40 ml) resulting in a colourless solution. Potassium methyl xanthate (3.76 g , 25.8 mmol) was added the solution of GaCl_3 and it was stirred for two hours. The precipitate of KCl formed was separated by filtration under air and the solvent from the mother liquors removed *in vacuo* to produce a slightly opaque viscous liquid. Hexane (8 ml) was added to the liquid and the mixture was stored at $4\text{ }^\circ\text{C}$ for 12 hours, which resulted in the formation of off-white shiny crystals. The crystals were collected by filtration and washed with cold hexane. M.p. $59 - 60\text{ }^\circ\text{C}$. Yield: 51% . FT-IR (solid) $\nu_{\text{max}}/\text{cm}^{-1}$: 2938 (w) , 1436 (w) , 1236 (s) , 1170 (s) , 1027 (s) and 945 (m) . ^1H NMR (CDCl_3 , 400 MHz) δ /ppm: 4.18 (s, 3H; OMe) . ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 400 MHz) δ /ppm: 45.0 (OMe) ; $202.7\text{ (S}_2\text{C-O)}$. Elemental analysis: Found (Calc). C, 18.91 (18.43) ; H, 2.31 (2.32) ; S, 48.38 (49.11) ; Ga, 14.12 (17.85) .

Synthesis of tris(*O*-ethylxanthato)gallium(III), $[\text{Ga}(\text{S}_2\text{COEt})_3]$ (2**).** The procedure was the same as for (**1**) with gallium (III) chloride (1.51 g , 8.6 mmol) and potassium ethyl xanthate (4.12 g , 25.8 mmol) being used. Off-white shiny crystals were collected and washed with cold hexane. M.p. $82 - 83\text{ }^\circ\text{C}$. Yield: 65% (1.21 g). FT-IR (solid) $\nu_{\text{max}}/\text{cm}^{-1}$: 2987 (w) , 1433 (w) , 1244 (s) , 1117 (s) , 1023 (s) and 860 (m) . ^1H NMR spectra (CDCl_3 , 400 MHz), $1.45\text{--}1.47\text{ ppm (t, 8 Hz, 3H; OCH}_2\text{Me)}$; $5.18\text{--}5.27\text{ ppm (q, 2H; OCH}_2\text{--)}$. ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 400 MHz) δ /ppm: $14.0\text{ (OCH}_2\text{CH}_3)$; $74.7\text{ ppm (OCH}_2\text{--)}$; $226\text{ (S}_2\text{C-O)}$. Elemental analysis: Found (Calc). C, 24.96 (25.19) ; H, 3.49 (3.75) ; S, 44.34 (43.55) ; Ga, 16.12 (16.09) .

Synthesis of tris(*O*-isopropylxanthato)gallium(III), $[\text{Ga}(\text{S}_2\text{CO}^i\text{Pr})_3]$ (3**).** The procedure was the same as for (**1**) with the quantities using gallium (III) chloride (1.51 g , 8.6 mmol) and $\text{K}(\text{S}_2\text{CO}^i\text{Pr})$ (4.48 g , 25.8 mmol) resulting in an off-white shiny crystals of gallium(III) isopropyl xanthate. M.p. $87\text{--}88\text{ }^\circ\text{C}$. Yield: 41% (1.75 g). FT-IR (solid) $\nu_{\text{max}}/\text{cm}^{-1}$: 2978 (w) , 1447 (w) , 1240

(s), 1084 (s), 1020 (s) and 899 (m). ^1H NMR (CDCl_3 , 400 MHz) δ /ppm: 1.46 (d, $J = 8$ Hz, 6H; $\text{OCH}(\text{Me})_2$); 5.18–5.27 ppm (sep, 1H; $\text{OCH}-$). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 400 MHz), 21.44 ($\text{OCH}(\text{CH}_3)_2$); 83.9 ppm (s, $\text{NCH}-$); 225.06 ppm (s, $\text{S}_2\text{C}-\text{O}$). Elemental analysis: Found (Calc). C, 30.33 (30.69); H, 4.46 (4.65); S, 40.41 (39.23); Ga, 14.96 (14.52).

Synthesis of tris(*O*-*n*-propylxanthato)gallium(III), $[\text{Ga}(\text{S}_2\text{CO}^n\text{Pr})_3]$ (4). The procedure was synthesised using the same method as for the precursor (1); using $\text{K}(\text{S}_2\text{CO}^n\text{Pr})$ (4.48 g, 25.8 mmol), GaCl_3 (1.51 g, 8.6 mmol). M.p. 58–60 °C. Yield: 41 %. FT-IR (solid) $\nu_{\text{max}}/\text{cm}^{-1}$: 2969 (w), 1455 (w), 1248 (s), 1138 (s), 1033 (s) and 939 (m). ^1H NMR (CDCl_3 , 400 MHz), 1.04 ppm (t, 8 Hz, 3H; $\text{OCH}_2\text{CH}_2\text{Me}$); 1.83–1.92 ppm (m, 2H; $\text{OCH}_2\text{CH}_2\text{Me}$) 4.40–4.44 ppm (t, 2H; $\text{OCH}_2\text{CH}_2\text{Me}$). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 400 MHz) δ /ppm: 10.3 (s, $\text{OCH}_2\text{CH}_2\text{Me}$); 21.8 (s, NCH_2CH_2); 80.3 (s, OCH_2-); 227 (s, $\text{S}_2\text{C}-\text{O}$). Elemental analysis: Found (Calc). C, 30.33 (30.57); H, 4.46 (4.35); S, 40.41 (40.38); Ga, 14.96 (14.70).

Synthesis of tris(*O*-*n*-butylxanthato)gallium(III), $[\text{Ga}(\text{S}_2\text{CO}^n\text{Bu})_3]$ (5). The procedure was synthesised using the same method as for the precursor (1); using $\text{K}(\text{S}_2\text{CO}^n\text{Bu})$ (4.84 g, 25.6 mmol), GaCl_3 (1.51 g, 8.6 mmol). M.p. 40–42 °C. Yield: 40 %. FT-IR (solid) $\nu_{\text{max}}/\text{cm}^{-1}$: 2952 (w), 1452 (w), 1214(s), 1140 (m), 1036 (s) and 917 (m). ^1H NMR spectra (CDCl_3 , 400 MHz), 0.96–0.99 ppm (8 Hz, t, 3H; $\text{OCH}_2\text{CH}_2\text{CH}_2\text{Me}$); 1.43–1.52 ppm (sex, 2H; $\text{OCH}_2\text{CH}_2\text{CH}_2\text{Me}$); 1.79–1.86 ppm (m, 2H; OCH_2CH_2-); 4.44–4.48 ppm (t, 2H; OCH_2-). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 400 MHz) δ /ppm: 13.7 (s, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{Me}$); 19.0 ($\text{OCH}_2\text{CH}_2\text{CH}_2$); 30.35 ppm (OCH_2CH_2-); 78.7 (OCH_2-); 227 ($\text{S}_2\text{C}-\text{O}$). Element analysis: Found (Calc). C, 34.83(35.01); H, 5.27(5.24); S, 37.12(37.17); Ga, 13.49(13.22).

Synthesis of tris(*O*-*s*-butylxanthato)gallium(III), $[\text{Ga}(\text{S}_2\text{CO}^s\text{Bu})_3]$ (6). The procedure was synthesised using the same method as for the precursor (1); using $\text{K}(\text{S}_2\text{CO}^s\text{Bu})$ (4.84 g, 25.8 mmol), GaCl_3 (1.51 g, 8.6 mmol). M.p. 70–71 °C. Yield: 35 %. FT-IR (solid) $\nu_{\text{max}}/\text{cm}^{-1}$: 2971 (w), 1453 (w), 1233 (s), 1098 (s), 1030 (s) and 869 (m). ^1H NMR (CDCl_3 , 400 MHz) δ / ppm, 1.00 (t, $J = 8$ Hz, 3H; $\text{OCH}(\text{Me})\text{CH}_2\text{Me}$); 1.42 (d, 3H; $\text{OCH}(\text{Me})-$); 1.70–1.93 (m, 2H; $\text{OCH}(\text{Me})\text{CH}_2$); 5.02–5.10 (m, 1H; $\text{OCH}(\text{Me})-$). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 400 MHz), 9.57 ($\text{OCH}(\text{Me})\text{CH}_2\text{Me}$); 18.8 ($\text{OCH}(\text{Me})\text{CH}_2$); 28.7 ($\text{OCH}(\text{Me})-$); 88.8 ($\text{OCH}(\text{Me})-$); 226 (s, $\text{S}_2\text{C}-\text{O}$). Element analysis: Found (Calc). C, 34.83 (34.80); H, 5.27 (5.17); S, 37.12 (36.90); Ga, 13.49(13.43).

Synthesis of tris(*O*-*i*-butylxanthato)gallium(III), $[\text{Ga}(\text{S}_2\text{CO}^i\text{Bu})_3]$ (7). The procedure was synthesised using the same method as for the precursor (1); using $\text{K}(\text{S}_2\text{CO}^i\text{Bu})$ (4.84 g, 25.8 mmol), GaCl_3 (1.51 g, 8.6 mmol). Yield: 50 %. M.p. 55–57 °C. FT-IR (solid) $\nu_{\text{max}}/\text{cm}^{-1}$: 2961 (w), 1448 (w), 1205 (s), 1177 (s), 1036 (s) and 975 (m). ^1H NMR (CDCl_3 , 400 MHz) δ / ppm, 1.02 (t, 6H; $\text{OCH}_2\text{CH}(\text{Me})_2$); 2.11–2.25 (m, 1H; $\text{OCH}_2\text{CH}(\text{Me})_2$); 4.23 (t, $J = 8$ Hz, 2H; $\text{OCH}_2\text{CH}(\text{Me})_2$). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 400 MHz) δ / ppm: 19.0 (s, $\text{OCH}_2\text{CH}(\text{Me})_2$); 19.0 ppm (s, $\text{OCH}_2\text{CH}(\text{Me})_2$); 27.9 ppm ($\text{OCH}_2\text{CH}(\text{Me})_2$); 84.7 ppm (s, OCH_2-); 227 (s, $\text{S}_2\text{C}-\text{O}$). Elemental analysis: Found (Calc). C, 34.83 (34.19); H, 5.27 (5.12); S, 37.12 (35.51); Ga, 13.49 (13.15).

Pyrolysis of Precursors by melt reaction method

Pyrolysis was conducted in a ceramic boat by heating 0.2 g of each precursor to 500 °C for one hour in a tube furnace (carbolite GERO 30–3000 °C) under N_2 gas. Upon cooling, the black powders were collected.

Results and discussion

Seven alkyl xanthato gallium(III) complexes with different alkyl groups, $[\text{Ga}(\text{S}_2\text{COMe})_3]$ (1), $[\text{Ga}(\text{S}_2\text{COEt})_3]$ (2), $[\text{Ga}(\text{S}_2\text{CO}^i\text{Pr})_3]$ (3), $[\text{Ga}(\text{S}_2\text{CO}^n\text{Pr})_3]$ (4), $[\text{Ga}(\text{S}_2\text{CO}^n\text{Bu})_3]$ (5), $[\text{Ga}(\text{S}_2\text{CO}^s\text{Bu})_3]$ (6) and $[\text{Ga}(\text{S}_2\text{CO}^i\text{Bu})_3]$ (7) were prepared by metathesis of gallium(III) chloride with the relevant potassium alkylxanthate in dry toluene. Products were characterised by their FTIR and NMR spectra (SI Figure 1.1, SI Figure 2.1–S2.7) as well as elemental analysis. All complexes were powders with an off-white shiny appearance and were stored at –20 °C. All seven complexes readily dissolved in chloroform, toluene and DCM.

The crystal structures of complexes (1), (3), (4), (5), (6) and (7) are novel structures while complex (2) has been reported previously but our data is included for completeness (Figure 1). The crystal data and refinement parameters associated with these structures are presented in the SI Tables 3.1–3.3.³⁶

Examination of the crystal structures revealed intermolecular S–S distances below the sum of the van der Waals radii, *i.e.* below 3.78 Å, suggesting possible S–S interactions in the solid state for (6), (5) and (2) structures with distances of 3.6852(19) Å, 3.475(2) Å and 3.535(1) Å respectively. This was also observed by Hoskins *et al.* for the complex (2) with a slightly different S–S distance of 3.598(4) Å with the difference attributed to greater errors with the earlier measurement.³⁶

It has been suggested by Harcourt and Winter that a feature exhibited by many metal xanthate complexes is the presence of an asymmetric binding mode by the xanthate to the metal centre.³³ To determine if this is an intrinsic property of the molecule or as a consequence of the observation of the structure as a crystalline solid the possible intermolecular interactions, such S–S van der Waals interactions, were examined and the consequences this would have for the decomposition.³⁸

Complex (5) possesses the shortest S–S intermolecular distance of $\text{S}(1)-\text{S}(5) = 3.4749(24)$ Å. S(5) and S(1) reside in adjacent xanthate ligands within the complex which both show a large Ga–S bond difference of 0.1013(7) and 0.1194(8) Å (Figure 2(b)). The remaining ligand with no S–S interactions has a Ga–S bond difference of 0.0021(7) suggesting that in Ga xanthate complexes that the primary contributor to asymmetric Ga–S bonding is from intermolecular S–S interactions in the solid state. This is in contrast to the observations of the binding of xanthates to groups 14 and 15 elements where large M–S bond differences of approximately 0.5 Å are seen.^{25,38}

Figure 1: X-ray crystal structures of gallium xanthates. $[\text{Ga}(\text{S}_2\text{COMe})_3]$ (**1**), $[\text{Ga}(\text{S}_2\text{COEt})_3]$ (**2**), $[\text{Ga}(\text{S}_2\text{CO}^i\text{Pr})_3]$ (**3**), $[\text{Ga}(\text{S}_2\text{CO}^n\text{Pr})_3]$ (**4**), $[\text{Ga}(\text{S}_2\text{CO}^i\text{Bu})_3]$ (**5**), $[\text{Ga}(\text{S}_2\text{CO}^n\text{Bu})_3]$ (**6**) and $[\text{Ga}(\text{S}_2\text{CO}^t\text{Bu})_3]$ (**7**). Green = Ga, red = O, black = C, yellow = S. Thermal ellipsoids at 50% probability. CCDC range 1900046-1900052.

The clearest example of a complex with no intermolecular S-S interactions is complex (**7**) with the closest S-S distance above the sum of the van der Waals radii at 4.286(26) Å. This complex possesses a distorted octahedral shape presumably caused by coordination of the xanthate ligand (Figure 2(a)). The distorted octahedron consists of two parallel near-equilateral triangles and six isosceles triangles created from the bite of the xanthate ligands each having vdW interactions with two other xanthate ligands. The differences in the Ga-S bonds from within the same xanthate are small, all beneath 0.031 Å, suggesting the complex with no intermolecular S-S interactions has little asymmetric bonding between the S donor sites caused by intramolecular interactions. The careful examination of S-S contacts is required to distinguish between M-S differences internal to the molecule and M-S differences caused in the crystal packing. The intrinsic bond length differences may influence the breakdown of the precursor and potentially the phase created when breaking down within the solid or liquid states. In the case of gallium xanthates the large Ga-S bond differences can be attributed to intermolecular S-S interactions and consequentially a relationship between Ga-S bond differences of $[\text{Ga}(\text{S}_2\text{COR})_3]$ in the solid state and breakdown temperatures cannot be drawn.

Figure 2: Coordination spheres of complexes (a) $[\text{Ga}(\text{S}_2\text{CO}^t\text{Bu})_3]$, (**7**), displaying no intermolecular S-S interactions and (b) $[\text{Ga}(\text{S}_2\text{CO}^i\text{Bu})_3]$, (**5**), showing the intermolecular S-S interactions (dashed lines) occurring between metal xanthate complexes. Gallium (green), sulphur (yellow) and oxygen (red) with carbons and hydrogens from the alkyl groups omitted for clarity.

Table 1: TGA final residues and matched phase

Precursor	Final residue, %	Calculated, %	
		GaS	Ga ₂ S ₃
[Ga(S ₂ COMe) ₃]	26.4	26.0	-
[Ga(S ₂ COEt) ₃]	26.4	-	27.2
[Ga(S ₂ CO ^{<i>n</i>} Pr) ₃]	25.3	-	24.8
[Ga(S ₂ CO ^{<i>n</i>} Bu) ₃]	24.2	-	24.8
[Ga(S ₂ CO ^{<i>i</i>} Pr) ₃]	22.4	-	22.8
[Ga(S ₂ CO ^{<i>i</i>} Bu) ₃]	22.5	-	22.8
[Ga(S ₂ CO ^{<i>t</i>} Bu) ₃]	23.2	-	22.8

Examination of the TGA profiles revealed a variety of multistep breakdowns for both the linear alkyl chains, Figure 3, and the branched alkyl chains, Figure 4. The residual mass of 26.4 % for [Ga(S₂COMe)₃] (**1**) corresponds closely to the expected mass of GaS 26.0 %, (Table 1). The TGA profile step sizes revealed the loss of two potential species for each step, *i.e.* SCOR-H (SCO and the alkene) or multiples of H₂S, (SI Figure 4.1–4.3 and SI Table 4.2). In the cases of [Ga(S₂COEt)₃] and longer alkyl chains regardless of branching all lost three equivalents of SCO and corresponding alkene followed by the loss of half an H₂S. The Et, ^{*i*}Pr and ^{*t*}Bu show a clean two-step process where the first step corresponds to the loss of three equivalents of SCO and alkene with the second step corresponding to loss of half an equivalent of H₂S as expected for a Chugaev elimination based decomposition. For ^{*n*}Pr, ^{*n*}Bu and ^{*i*}Bu the initial step involving the loss of three equivalents of alkene and SCO display two features, as highlighted by the first derivative (SI Figure 4.1–4.3), although the total weight loss of the step corresponds to the correct amount for a Chugaev elimination of all three ligands, SI Table 4.2. The deconvolution of these features and the elucidation of the products formed requires further study to fully understand the mechanistic differences between chains.

Figure 3: TGA profiles for the *n*-alkyl series of [Ga(S₂COR)₃] precursors where R = Me, Et, ^{*n*}Pr and ^{*n*}Bu. **Figure 4:** TGA profiles for the branched alkyl series of [Ga(S₂COR)₃] precursors where R = ^{*i*}Pr, ^{*s*}Bu and ^{*t*}Bu.

The ¹³C NMR shifts of the xanthate *ipso* carbon were compared to the temperature of the first breakdown step of the complexes from TGA. The Me-Et-^{*n*}Pr-^{*t*}Bu series showed a decrease in shift from Me to ^{*i*}Pr and an increase for ^{*t*}Bu, SI Figure 5.1(a). This is in contrast to the expected result if the position of the shift was governed purely by the inductive influence the alkyl group, *i.e.* the same trend as the pK_a values of the corresponding alcohols. A deviation from the expected order was also observed for the Me-Et-^{*n*}Pr-^{*n*}Bu series, SI Figure 5.1(b). When plotted against the temperature of the first breakdown step the ¹³C shifts show a negative correlation between the electron density at the *ipso* carbon as reflected by the ¹³C shift increasing with a decrease in the temperature of the first breakdown step, SI Figure 5.2.

XPS of the powders produced allowed examination of the composition of the film and any contamination. Examination of the Ga 2p profile showed a major contribution from a sulfur bound species at 1117.8 eV with a minor contribution from an oxygen bound species at 1119 eV resulting in between 0.9 and 4.9 % of binding to oxygen, SI Table 6.1 and SI Figure 6.1. The S 2p 3/2 peak shows only one species at approx. 161.5 eV with no intensity at the predicted location for sulfur bound to oxygen at 168–170 eV, SI Figure 6.2. For the Et complexes and greater Ga/S was in the region of 1.3 to 1.8 indicating likely formation of a Ga₂S₃ phase whereas for Me the S/Ga was 2.0. A S/Ga of two gives a stoichiometry of GaS₂ which is not observed as a crystalline phase and is likely to contain both the +1 and +3 oxidation states of Ga, *e.g.* Ga^IGa^{III}S₄.

Initial thermolysis of [Ga(S₂COEt)₃] at 250 °C, (*i.e.* the temperature where full decomposition was observed by TGA) for one hour resulted in an amorphous material that showed no Bragg reflections in its powder X-ray diffraction (PXRD) pattern (Figure 5, top). The thermolysis was repeated at 350, 450 and 500 °C and with temperatures held for 1 h to assist formation of a crystalline phase. It was found that despite being well in excess of the predicted temperature for the molecular breakdown, as-observed by TGA, only temperatures of 500 °C produced crystalline γ-Ga₂S₃ powders.

Figure 5: Powder X-ray diffraction of thermolysis products. Top: PXRD patterns of γ -Ga₂S₃ powder obtained from pyrolysis of [Ga(S₂COEt)₃] at different temperatures (a) 250 °C, (b) 350 °C, (c) 450 °C and (d) 500 °C for one hour under N₂. Bottom: PXRD patterns of γ -Ga₂S₃ powders obtained from pyrolysis of precursors (1–7) at 500 °C for one hour under N₂. The stick pattern below corresponds to cubic γ -Ga₂S₃ (ICDD no. 00-043-0916; F-43m, $a = 5.210$ Å)

The observed difference between the crystallinity of the powders resulting from the furnace experiments and that of the TGA may be attributable to the difference in heating profile used in both experiments. In the case of the TGA the sample was heated from room temperature to 600 °C at a heating rate of 10 °C min⁻¹, whereas, the sample heated in the furnace was heated rapidly to the target temperature at 85 °C min⁻¹ and was held at this temperature for one hour. Only at 500 °C were reflections corresponding to the crystalline phase of γ -Ga₂S₃ were observed when breaking down [Ga(S₂COEt)₃]. We must conclude that the TGA experiments did not put enough energy into the sample to cause a crystalline phase of gallium sulphide to be formed. Subsequently (1) to (7) were all heated at 500 °C. The products of thermolysis from precursors (2) – (7) have PXRD patterns corresponding to γ -Ga₂S₃ with (1) clearly amorphous despite the same heating profile (Figure 5, bottom). These low intensity reflections correspond to the (111), (220) and (311) planes of the defect zinc-blende γ -Ga₂S₃ (ICDD no. 00-043-0916; F-43m, $a = 5.210$ Å) and are significantly broadened indicating small, possibly nanoscale, crystalline domains.

The breakdown products from [Ga(S₂COMe)₃] when examined by XPS and TGA have provided contrasting results with respect to the stoichiometry of the Ga_xS_y powder produced. XRD has also demonstrated that unlike the longer chain complexes that the heating profile used does not produce

a crystalline phase unlike the longer chains which produce γ -Ga₂S₃. As the Me complex does not possess a β -hydrogen required for the six membered cyclic transition state the *syn*-elimination cannot occur. An alternative pathway is for the ligands to react as a free xanthic acid which is unstable and reforms CS₂ and the free alcohol. The TGA profile for [Ga(S₂COMe)₃] shows a single step whereby the ligands are lost rapidly and indicates that the all the ligands are lost by the same mechanism although a complete understanding of this cannot be concluded from our data.

Figure 6: Secondary electron SEM image of a crystallite of γ -Ga₂S₃ produced from the decomposition of [Ga(S₂COEt)₃] at 500 °C (a) with corresponding EDX elemental maps for S K α (b) and Ga L α (c).

SEM images of (2-7) showed randomly shaped aggregated crystals of γ -Ga₂S₃, (SI Figure 7.1). EDX spectroscopy analysis showed that the γ -Ga₂S₃ powders were gallium rich by between ca. 0.3 - 3.2 % away from the expected value (SI Table 7.1). Ga rich γ -Ga₂S₃ powders are an unexpected result from the perspective of each precursor containing six sulphur atoms and one gallium, but reports by O'Brien *et al.* suggest that this has been observed when using metal dithiocarbamate precursors at high temperatures metal rich phases are observed.³⁹ EDX elemental mapping of gallium sulfide powders showed a uniform distribution of gallium and sulfur (Figure 6).

Conclusions

In this work we have reported the synthesis and full characterization of seven gallium xanthate complexes with low breakdown temperatures. Despite their low breakdown temperatures in the region of 250 °C it was found that heating at temperatures lower than 500 °C did not result in any crystalline phases of Ga_xS_y . Performing the breakdown at 500 °C for one hour yielded γ - Ga_2S_3 for all $[Ga(S_2COR)_3]$ precursors where $R \geq Et$. When $R = Me$ the complex is unable to undergo a Chugaev elimination and the resulting powders displayed varying Ga_xS_y stoichiometries and produced an amorphous material. Previous reports using metal xanthate complexes with increasing linear alkyl chain length show the TGA profiles changing from a single step to a two-step breakdown process.²⁵ At the comparatively high temperatures between 300 and 500 °C required for the formation of Ga_2S_3 the subtleties of the molecular breakdown below 250 °C have a reduced influence on the morphology of the material made unlike PbS which requires far lower temperatures to form. Hence, the gallium sulfide system offers an insight into the balance of precursor breakdown characteristics versus the temperature required for the formation of the target phase. These findings suggest that metal xanthate complexes with low temperature breakdown requirements are best suited for target phases that readily form at low temperatures.

Conflicts of interest

There are no conflicts of interest to declare.

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