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## Introduction

Gallium sulfides are refractory materials which are produced by traditional synthetic routes due to their existence in four stoichiometric forms: gallium monosulfide (GaS), gallium sesquisulfide (Ga<sub>2</sub>S<sub>3</sub>), Ga<sub>2</sub>S and Ga<sub>4</sub>S<sub>5</sub>. Additionally, both GaS and Ga<sub>2</sub>S<sub>3</sub> exhibit polymorphism.<sup>1–4</sup> In contrast, aluminium sulfides possess only one stoichiometric form, Al<sub>2</sub>S<sub>3</sub>, with four polymorphs, whilst gallium selenides and tellurides are known to form only three and four phases, respectively.<sup>3,5</sup> However, gallium sulfides possess wide band gaps in the range of 3.05–2.85 eV and have potential for use in photovoltaics and optoelectronics and as passivating layers in III–V group semiconductor devices.<sup>6–9</sup> Thus, low temperature 'soft' processing routes that produce well-defined phases and stoichiometries of these materials would potentially be of tremendous utility.

# Accessing $\gamma$ -Ga<sub>2</sub>S<sub>3</sub> by solventless thermolysis of gallium xanthates: a low-temperature limit for crystalline products<sup>†</sup>

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Alkyl-xanthato gallium(III) complexes of the form  $[Ga(S_2COR)_3]$ , where R = Me(1), Et (2), <sup>i</sup>Pr (3), <sup>n</sup>Pr (4), <sup>n</sup>Bu (5), <sup>s</sup>Bu (6) and <sup>i</sup>Bu (7), have been synthesized and fully characterised. The crystal structures for 1 and 3–7 have been solved and examined to elucidate if these structures are related to their decomposition. Thermogravimetric analysis was used to gain insight into the decomposition temperatures for each 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  $R \ge Et$  these complexes did not produce crystalline gallium sulfides until heated to 500 °C, where  $\gamma$ -Ga<sub>2</sub>S<sub>3</sub> was the sole product formed. In the case of R = Me, Chugaev elimination did not occur and amorphous Ga<sub>x</sub>S<sub>y</sub> 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.

Molecular precursor routes towards gallium sulfides in particular present an excellent opportunity 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 of 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 the literature. For example, Barron et al. used gallium-chalcogen cubanes to deposit cubic GaS using MOCVD. The cubic [<sup>t</sup>BuGaS]<sub>4</sub> clusters act as seeds for oriented nucleation followed by the growth of cubic GaS.<sup>10</sup> By using  $[Cp^*Ga(\mu-S)]_4$ , where  $Cp^*$  is  $(C_5Me_5)$  or (C<sub>5</sub>Me<sub>4</sub>Et), Barron et al. prepared γ-Ga<sub>2</sub>S<sub>3</sub>.<sup>10,11</sup> In contrast, [Ga(S<sup>i</sup>Pr)<sub>2</sub>(µ-S<sup>i</sup>Pr)]<sub>2</sub> has been used as a molecular precursor in LP-MOCVD experiments to produce different phases of gallium sulfides depending on the substrate used; y-Ga<sub>2</sub>S<sub>3</sub> is produced on glass,  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> on silicon (100), and highly oriented y-Ga<sub>2</sub>S<sub>3</sub> on YSZ (111), suggesting that an epitaxial cases.12 growth mechanism in these occurs  $[MeGa(SCH_2CH_2S)]_3$  was used to synthesize nanometric  $\beta$ -Ga<sub>2</sub>S<sub>3</sub> when pyrolysed between 300 and 500 °C.<sup>13</sup> Ramalingam et al. prepared  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> nanoparticles from tris (cyclo-hexylmethyldithiocarbamato) gallium(III) and tris(cyclohexyl-ethyldithiocarbamato) gallium(III), using a solvothermal method.<sup>14</sup> Malik et al. synthesised monodisperse cubic GaS nanoparticles using [Ga(S2CNEt2)3] in 4-ethylpyridine at



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167 °C.<sup>15</sup> [Ga(S<sub>2</sub>CNMe<sup>*n*</sup>Hex)<sub>3</sub>], prepared from an asymmetrical amine, yielded α-Ga<sub>2</sub>S<sub>3</sub> when using LP-MOCVD at 500 °C.<sup>16</sup> The tris-monothiocarbamate complex, [Ga(SOCNEt)<sub>3</sub>], produced cubic GaS at 350 °C by AACVD.<sup>17</sup> Barron *et al.* studied the preparation of di-*tert*-butyl gallium dithiocarbamate precursors [(<sup>t</sup>Bu)<sub>2</sub>Ga(S<sub>2</sub>CNR<sub>2</sub>)], where R = Me or Et. Both precursors formed hexagonal GaS by AP-MOCVD at relatively low temperatures.<sup>18</sup> Guihua Shang *et al.* used thiocarboxy complexes of the form [Ga(SCOMe)<sub>2</sub>Me(dmpy)] (where dmpy = 3,5dimethylpyridine) to deposit hexagonal α-Ga<sub>2</sub>S<sub>3</sub> by AACVD.<sup>19</sup> 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.<sup>20–22</sup> These properties have been exploited by us and others for solventless thermolysis of metal xanthate precursors to form the corresponding metal chalcogenides, *e.g.* CdS, FeS,<sup>23</sup> CuS,<sup>21,24</sup> PbS,<sup>25</sup> ZnS,<sup>26</sup> and SnS,<sup>27</sup> chalcogenide spinels ( $A^{II}B_2^{III}X_4$ )<sup>28</sup> and Cu<sub>2</sub>ZnSnS<sub>4</sub>.<sup>29</sup> 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.<sup>30–35</sup>

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

### **Experimental section**

Anhydrous toluene ( $\geq$ 99.8%, Sigma-Aldrich), anhydrous chloride (99.9%, Sigma-Aldrich), gallium(III) methanol (≥99.8%, Sigma-Aldrich), ethanol (≥99.8%, Sigma-Aldrich), 2-propanol (≥99.5%, Sigma-Aldrich), 1-propanol (99%, Sigma-Aldrich), 1-butanol (99%, Sigma-Aldrich), 2-butanol (99%, Sigma-Aldrich), isobutanol (99%, Sigma-Aldrich), carbon disulfide (99%, Sigma-Aldrich), hexane (≥97%, Sigma-Aldrich) and potassium ethyl xanthogenate (96%, Sigma-Aldrich) were used as received. All syntheses were performed under an N<sub>2</sub> environment using the Schlenk technique unless otherwise stated. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using a Bruker AC400 FT-NMR spectrometer. Melting points were determined using melting point apparatus (Stuart; Cole-Palmer, UK); infrared spectra were recorded via ATR (4000-400 cm<sup>-1</sup>, resolution 4 cm<sup>-1</sup>); and elemental analysis was performed with a Carlo Erba EA 1108. Thermogravimetric analyses (TGA) were performed using a Seiko SSC/S200 at a heating rate of 10 °C

min<sup>-1</sup> under N<sub>2</sub>. Powder X-ray diffraction (PXRD) patterns were obtained using an X'Pert diffractometer with a Cu-K $\alpha$  source, and scanning electron microscopy (SEM) was performed 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 a Mo-K $\alpha$  wavelength source at 150 K for precursors **1**, **2**, **3**, **4**, **5**, and 7 and with a 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) with a monochromatic Al K\_alpha X-ray source (1486 eV, 10 mA emission, and 150 W). Survey spectra were measured with a pass energy of 80 eV and high-resolution 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 C 1s peak at 284.8 eV associated with adventitious hydrocarbons.

#### Synthesis of potassium alkyl xanthates

Potassium alkyl xanthate (KS<sub>2</sub>COR) ligands with various alkyl groups (methyl, ethyl, isopropyl, *n*-propyl, *n*-butyl, *s*-butyl and i-butyl) were prepared according to the method of McNaughter *et al.*<sup>25</sup> A typical ligand synthesis is as follows for K(S<sub>2</sub>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 °C. Carbon disulfide (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*-methyl xanthato)gallium(m), [Ga(S<sub>2</sub>COMe)<sub>3</sub>] (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 to the solution of GaCl<sub>3</sub> and it was stirred for two hours. The precipitate of KCl formed was separated by filtration under air and the solvent from the mother liquor was 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 °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 °C. Yield: 51%. FT-IR (solid)  $\nu_{\rm max}/{\rm cm}^{-1}$ : 2938 (w), 1436 (w), 1236 (s), 1170 (s), 1027 (s) and 945 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ/ppm: 4.18 (s, 3H; OMe). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ /ppm: 45.0 (OMe); 202.7 (S<sub>2</sub>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-ethyl xanthato)gallium(III), [Ga(S<sub>2</sub>COEt)<sub>3</sub>] (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 °C. Yield: 65% (1.21 g). FT-IR (solid)  $\nu_{max}/cm^{-1}$ : 2987 (w), 1433 (w), 1244 (s), 1117 (s), 1023 (s) and 860 (m). <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>, 400 MHz): 1.45–1.47 ppm (t, 8 Hz, 3H; OCH<sub>2</sub><u>Me</u>); 5.18–5.27 ppm (q, 2H; OC<u>H</u><sub>2</sub>–). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ /ppm: 14.0 (OCH<sub>2</sub><u>C</u>H<sub>3</sub>); 74.7 ppm (O<u>C</u>H<sub>2</sub>–); 226 (S2<u>C</u>–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*-isopropyl xanthato)gallium(III), [Ga(S<sub>2</sub>CO<sup>i</sup>Pr)<sub>3</sub>] (3)

The procedure was the same as for (1) using gallium(III) chloride (1.51 g, 8.6 mmol) and K(S<sub>2</sub>CO<sup>i</sup>Pr) (4.48 g, 25.8 mmol), resulting in off-white shiny crystals of gallium(III) isopropyl xanthate. M.p. 87–88 °C. Yield: 41% (1.75 g). FT-IR (solid)  $\nu_{max}/cm^{-1}$ : 2978 (w), 1447 (w), 1240 (s), 1084 (s), 1020 (s) and 899 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ /ppm: 1.46 (d, *J* = 8 Hz, 6H; OCH(Me)<sub>2</sub>); 5.18–5.27 ppm (sep, 1H; OCH–). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 400 MHz), 21.44 (OCH(CH<sub>3</sub>)2); 83.9 ppm (s, NCH–); 225.06 ppm (s, S<sub>2</sub>C–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*-propyl xanthato)gallium(III), [Ga(S<sub>2</sub>CO<sup>*n*</sup>Pr)<sub>3</sub>] (4)

The procedure was the same as for precursor (1), using  $K(S_2CO^nPr)$  (4.48 g, 25.8 mmol) and GaCl<sub>3</sub> (1.51 g, 8.6 mmol). M.p. 58–60 °C. Yield: 41%. FT-IR (solid)  $\nu_{max}/cm^{-1}$ : 2969 (w), 1455 (w), 1248 (s), 1138 (s), 1033 (s) and 939 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 1.04 ppm (t, 8 Hz, 3H; OCH<sub>2</sub>CH<sub>2</sub>Me); 1.83–1.92 ppm (m, 2H; OCH<sub>2</sub>CH<sub>2</sub>Me); 4.40–4.44 ppm (t, 2H; OCH<sub>2</sub>CH<sub>2</sub>Me). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ /ppm: 10.3 (s, OCH<sub>2</sub>CH<sub>2</sub>Me); 21.8 (s, NCH<sub>2</sub>CH<sub>2</sub>); 80.3 (s, OCH<sub>2</sub>-); 227 (s, S<sub>2</sub>C–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*-butyl xanthato)gallium(m), [Ga(S<sub>2</sub>CO<sup>*n*</sup>Bu)<sub>3</sub>] (5)

The procedure was the same as for precursor (1), using K(S<sub>2</sub>CO<sup>n</sup>Bu) (4.84 g, 25.6 mmol) and GaCl<sub>3</sub> (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). <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>, 400 MHz): 0.96-0.99 ppm (8 Hz, t, 3H; OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me); 1.43-1.52 ppm (sex, 2H; OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me); 1.79-1.86 ppm (m, 2H; OCH<sub>2</sub>CH<sub>2</sub>-); 4.44-4.48 ppm (t, 2H; OCH<sub>2</sub>-). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ /ppm: 13.7 (s, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me); 19.0  $(OCH_2CH_2CH_2);$ 30.35 ppm (OCH<sub>2</sub>CH<sub>2</sub>-); 78.7 (OCH<sub>2</sub>-); 227 (S2C-O). Elemental 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*-butyl xanthato)gallium(III), [Ga(S<sub>2</sub>CO<sup>s</sup>Bu)<sub>3</sub>] (6)

The procedure was the same as for precursor (1), using  $K(S_2CO^sBu)$  (4.84 g, 25.8 mmol) and  $GaCl_3$  (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). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ /ppm, 1.00 (t, J = 8 Hz, 3H; OCH(Me) CH<sub>2</sub>Me); 1.42 (d, 3H; OCH(Me)–); 1.70–1.93 (m, 2H; OCH(Me) CH<sub>2</sub>); 5.02–5.10 (m, 1H; OCH(Me)–). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 400 MHz), 9.57 (OCH(Me)CH<sub>2</sub>Me); 18.8 (OCH(Me)CH<sub>2</sub>); 28.7 (OCH(Me)–); 88.8 (OCH(Me)–); 226 (s, S<sub>2</sub>C–O). Elemental 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-butyl xanthato)gallium(m), [Ga(S<sub>2</sub>CO<sup>i</sup>Bu)<sub>3</sub>] (7)

The procedure was the same as for precursor (1), using  $K(S_2CO^{i}Bu)$  (4.84 g, 25.8 mmol) and  $GaCl_3$  (1.51 g, 8.6 mmol). Yield: 50%. M.p. 55–57 °C. FT-IR (solid)  $\nu_{max}/cm^{-1}$ : 2961 (w), 1448 (w), 1205 (s), 1177 (s), 1036 (s) and 975 (m). <sup>1</sup>H NMR (CDCl\_3, 400 MHz)  $\delta$ /ppm, 1.02 (t, 6H; OCH<sub>2</sub>CH(Me)<sub>2</sub>); 2.11–2.25 (m, 1H; OCH<sub>2</sub>CH(Me)<sub>2</sub>); 4.23 (t, *J* = 8 Hz, 2H; OCH<sub>2</sub>CH(Me)<sub>2</sub>. <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl\_3, 400 MHz)  $\delta$ /ppm: 19.0 (s, OCH<sub>2</sub>CH(Me)<sub>2</sub>); 19.0 ppm (s, OCH<sub>2</sub>CH(Me~)); 27.9 ppm (OCH<sub>2</sub>CH(Me)); 84.7 ppm (s, OCH<sub>2</sub>-); 227 (s, S2C–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 the melt reaction method

Pyrolysis was conducted in a ceramic boat by heating 0.2 g of each precursor to 500  $^{\circ}$ C for one hour in a tube furnace (Carbolite Gero 30–3000  $^{\circ}$ C) under N<sub>2</sub> gas. Upon cooling, black powders were collected.

#### **Results and discussion**

Seven alkyl xanthato gallium(III) complexes with different alkyl groups,  $[Ga(S_2COMe)_3]$  (1),  $[Ga(S_2COEt)_3]$  (2),  $[Ga(S_2CO<sup>3</sup>Pr)_3]$  (3),  $[Ga(S_2CO<sup>n</sup>Pr)_3]$  (4),  $[Ga(S_2CO<sup>n</sup>Bu)_3]$  (5),  $[Ga(S_2CO<sup>s</sup>Bu)_3]$  (6) and  $[Ga(S_2CO<sup>3</sup>Bu)_3]$  (7), were prepared by metathesis of gallium(III) chloride with the relevant potassium alkyl xanthate in dry toluene. The products were characterised using their FTIR and NMR spectra (ESI Fig. 1.1, 2.1–2.7†), and 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; while complex **2** has been reported previously, our data are included for completeness (Fig. 1). The crystal data and refinement parameters associated with these structures are shown in ESI Tables 3.1-3.3;<sup>36</sup>

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 complex **2** with a slightly different S–S distance of 3.598(4) Å and the difference is attributed to greater errors with the earlier measurement.<sup>36</sup>



Fig. 1 X-ray crystal structures of gallium xanthates. (a)  $[Ga(S_2COMe)_3]$  (1), (b)  $[Ga(S_2COEt)_3]$  (2), (c)  $[Ga(S_2CO^{I}Pr)_3]$  (3), (d)  $[Ga(S_2CO^{P}Pr)_3]$  (4), (e)  $[Ga(S_2CO^{P}Bu)_3]$  (5), (f)  $[Ga(S_2CO^{S}Bu)_3]$  (6) and (g)  $[Ga(S_2CO^{I}Bu)_3]$  (7). Green = Ga, red = O, black = C, and yellow = S. Thermal ellipsoids at 50% probability. CCDC range is 1900046–1900052.†

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.<sup>38</sup> 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, *e.g.* S–S van der Waals interactions, were examined and compared to the decomposition temperatures and products.

Complex 5 possesses the shortest S–S intermolecular distance of S(1)–S(5) = 3.4749(24) Å. S(5) and S(1) reside in adjacent xanthate ligands within the complex, and show large Ga–S bond differences of 0.1013(7) and 0.1194(8) Å (Fig. 2(b)). The remaining ligand with no S–S interactions has a Ga–S bond difference of 0.0021(7) Å, suggesting that in Ga xanthate complexes the primary contribution to the 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 group 14 and 15 elements where large M–S bond differences of approximately 0.5 Å are seen.<sup>25,38</sup>

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 the coordination of the xanthate ligand (Fig. 2(a)). The distorted octahedron consists of two parallel near-equilateral triangles and six isosceles triangles created from the S–Ga–S bite angles 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 below 0.031 Å, suggesting that the complex with no intermolecular S–S

interactions has little asymmetric bonding between the S donor sites caused by intramolecular interactions. 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 the breakdown occurs 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  $[Ga(S_2COR)_3]$  in the solid state and breakdown temperatures cannot be drawn.

Examination of the TGA profiles revealed a variety of multistep breakdowns for both the linear alkyl chains (Fig. 3) and the branched alkyl chains (Fig. 4). The residual mass of 26.4% for  $[Ga(S_2COMe)_3]$  (1) corresponds closely to the expected mass of GaS of 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 H<sub>2</sub>S (ESI Fig. 4.1-4.3 and ESI Table 4.2<sup>†</sup>). In the cases of  $[Ga(S_2COEt)_3]$  and longer alkyl chains regardless of branching, all lost three equivalents of SCO and the corresponding alkene followed by the loss of half an H<sub>2</sub>S. The Et, <sup>i</sup>Pr and <sup>s</sup>Bu show a clean two-step process, where the first step corresponds to the loss of three equivalents of SCO and the alkene, and the second step corresponds to the loss of half an equivalent of H2S as expected for Chugaev elimination-based decomposition. For "Pr, "Bu and <sup>1</sup>Bu, the initial step involving the loss of three equivalents of the alkene and SCO shows two features, as highlighted by the first derivative (ESI Fig. 4.1-4.3<sup>†</sup>), although the total weight



**Fig. 2** Coordination spheres of complexes. (a)  $[Ga(S_2CO^iBu)_3]$ , (7), showing no intermolecular S–S interactions and (b)  $[Ga(S_2CO^nBu)_3]$ , (5), showing the intermolecular S–S interactions (dashed lines) occurring between metal xanthate complexes. Gallium (green), sulfur (yellow) and oxygen (red) with carbons and hydrogens from the alkyl groups are omitted for clarity.

loss of the step corresponds to the correct amount for the Chugaev elimination of all three ligands (ESI Table 4.2).† The deconvolution of these features and the elucidation of the products formed require further study to fully understand the mechanistic differences between chains.

The <sup>13</sup>C NMR shifts of the xanthate *ipso* carbon were compared to the temperature at the first breakdown step of the complexes from TGA. The Me–Et–<sup>i</sup>Pr–<sup>i</sup>Bu series showed a decrease in shift from Me to <sup>i</sup>Pr and an increase for <sup>i</sup>Bu (ESI Fig. 5.1(a)).† This is in contrast to the expected result if the position of the shift was governed purely by the inductive influence of 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–<sup>n</sup>Pr–<sup>n</sup>Bu series (ESI Fig. 5.1(b)).† When plotted against the temperature at the first breakdown step, the <sup>13</sup>C shifts show a negative correlation between the electron density at the *ipso* carbon as reflected by the <sup>13</sup>C shift increasing with a decrease in the temperature of the first breakdown step (ESI Fig. 5.2).†



Fig. 3 TGA profiles for the *n*-alkyl series of  $[Ga(S_2COR)_3]$  precursors, where R = Me, Et, <sup>*n*</sup>Pr and <sup>*n*</sup>Bu.



Fig. 4 TGA profiles for the branched alkyl series of  $[Ga(S_2COR)_3]$  precursors, where R =  $^i Pr,\,^s Bu$  and  $^i Bu.$ 

Table 1 TGA final residues and matched phases

Precursor	Final residue, %	Calculated, %	
		GaS	Ga <sub>2</sub> S <sub>3</sub>
[Ga(S <sub>2</sub> COMe) <sub>3</sub> ]	26.4	26.0	_
[Ga(S <sub>2</sub> COEt) <sub>3</sub> ]	26.4	_	27.2
[Ga(S <sub>2</sub> CO <sup>i</sup> Pr) <sub>3</sub> ]	25.3	_	24.8
$[Ga(S_2CO^nPr)_3]$	24.2	_	24.8
$[Ga(S_2CO^nBu)_3]$	22.4	_	22.8
Ga(S <sub>2</sub> CO <sup>s</sup> Bu) <sub>3</sub>	22.5	_	22.8
Ga(S <sub>2</sub> CO <sup>i</sup> Bu) <sub>3</sub>	23.2	_	22.8

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XPS of the powders produced allowed the 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 and a minor contribution from an oxygen-bound species at 1119 eV resulting in between 0.9 and 4.9% of binding to oxygen (ESI Table 6.1 and ESI Fig. 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 (ESI Fig. 6.2).† For the complexes of alkyl group Et or greater the Ga/S value was in the region of 1.3 to 1.8 indicating likely formation of a Ga<sub>2</sub>S<sub>3</sub> phase whereas for Me the S/Ga was 2.0. A S/Ga of two gives a stoichiometry of GaS<sub>2</sub>, 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<sup>I</sup>Ga<sup>III</sup>S<sub>4</sub>.

Initial thermolysis of  $[Ga(S_2COEt)_3]$  at 250 °C (*i.e.* the temperature at which full decomposition was observed by TGA) for one hour resulted in an amorphous material which showed no Bragg reflections in its powder X-ray diffraction (PXRD) pattern (Fig. 5, top). The thermolysis was repeated at 350, 450 and 500 °C, with these temperatures held for 1 h to assist in the 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 a temperature of 500 °C produced crystalline  $\gamma$ -Ga<sub>2</sub>S<sub>3</sub> powders.

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 the heating profiles used in both experiments. In the case of TGA, the sample was heated from room temperature to 600 °C at a heating rate of 10 °C min<sup>-1</sup>, whereas the sample in the furnace was heated rapidly to the target temperature of 85 °C min<sup>-1</sup> and was held at this temperature for one hour. Only at 500 °C the reflections corresponding to the crystalline phase of y-Ga<sub>2</sub>S<sub>3</sub> were observed when breaking down  $[Ga(S_2COEt)_3]$ . We must conclude that the TGA experiments did not provide sufficient energy to the sample to enable the formation of a crystalline phase of gallium sulfide. Subsequently 1 to 7 were all heated at 500 °C. The products of thermolysis from precursors 2 to 7 have PXRD patterns corresponding to  $\gamma$ -Ga<sub>2</sub>S<sub>3</sub> with 1 being clearly amorphous despite the same heating profile (Fig. 5, bottom). These lowintensity reflections correspond to the (111), (220) and (311) planes of the defect of zinc blende y-Ga2S3 (ICDD no. 00-043-0916;  $F\bar{4}3m$ , a = 5.210 Å) and are significantly broadened indicating small, possibly nanoscale, crystalline domains.

The breakdown products from  $[Ga(S_2COMe)_3]$  when examined by XPS and TGA provided contrasting results with respect



**Fig. 5** Powder X-ray diffraction of thermolysis products. Top: PXRD patterns of  $\gamma$ -Ga<sub>2</sub>S<sub>3</sub> powders obtained from pyrolysis of [Ga(S<sub>2</sub>COEt)<sub>3</sub>] at different temperatures (a) 250 °C, (b) 350 °C, (c) 450 °C and (d) 500 °C for one hour under N<sub>2</sub>. Bottom: PXRD patterns of  $\gamma$ -Ga<sub>2</sub>S<sub>3</sub> powders obtained from pyrolysis of precursors **1–7** at 500 °C for one hour under N<sub>2</sub>. The stick pattern below corresponds to cubic  $\gamma$ -Ga<sub>2</sub>S<sub>3</sub> (ICDD no. 00-043-0916; F43*m*, *a* = 5.210 Å).



Fig. 6 Secondary electron SEM image of a crystallite of  $\gamma$ -Ga<sub>2</sub>S<sub>3</sub> produced from the decomposition of [Ga(S<sub>2</sub>COEt)<sub>3</sub>] at 500 °C (a) with corresponding EDX elemental maps for S K $\alpha$  (b) and Ga L $\alpha$  (c).

to the stoichiometry of the  $Ga_xS_y$  powder produced. XRD has demonstrated that  $[Ga(S_2COMe)_3]$  does not produce a crystalline phase unlike all longer alkyl chain complexes which produce  $\gamma$ -Ga<sub>2</sub>S<sub>3</sub>. As the Me complex does not possess a  $\beta$ -hydrogen required for the six-membered cyclic transition state, the *syn*-elimination cannot occur. An alternative pathway for the ligands is to react as a free xanthic acid which is unstable and reform CS<sub>2</sub> and the free alcohol. The TGA profile for  $[Ga(S_2COMe)_3]$  shows a single step whereby the ligands are lost rapidly and indicates that all the ligands are lost by the same mechanism, although a complete understanding of this cannot be attained from our data.

SEM images of 2–7 showed randomly shaped aggregated crystals of  $\gamma$ -Ga<sub>2</sub>S<sub>3</sub> (ESI Fig. 7.1†). EDX spectroscopic analysis showed that the  $\gamma$ -Ga<sub>2</sub>S<sub>3</sub> powders were gallium rich by between *ca.* 0.3–3.2% away from the expected value (ESI Table 7.1†). Garich  $\gamma$ -Ga<sub>2</sub>S<sub>3</sub> 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 on using metal dithiocarbamate precursors at high temperatures, metalrich phases are observed.<sup>39</sup> EDX elemental mapping of gallium sulfide powders showed uniform distribution of gallium and sulfur (Fig. 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<sub>x</sub>S<sub>y</sub>. Performing the breakdown at 500 °C for one hour yielded  $\gamma$ -Ga<sub>2</sub>S<sub>3</sub> for all [Ga(S<sub>2</sub>COR)<sub>3</sub>] precursors, where R  $\geq$  Et. When R = Me, the complex is unable to undergo Chugaev elimination and the resulting powders showed various Ga<sub>x</sub>S<sub>v</sub> stoichiometries and produced an amorphous material. Previous reports using metal xanthate complexes with increasing linear alkyl chain lengths show TGA profiles changing from a singlestep to a two-step breakdown process.<sup>25</sup> At comparatively high temperatures between 300 and 500 °C required for the formation of Ga<sub>2</sub>S<sub>3</sub>, the subtleties of the molecular breakdown below 250 °C have a reduced influence on the morphology of the material prepared unlike PbS which requires far lower temperatures to form. Hence, the gallium sulfide system offers an insight into the balance of the 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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