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Synthesis of Group 13 Sesquialkoxides and Their Application as Precursors to Crystalline Oxide Films

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The reaction of Me_3Ga with an excess of 4-methylbenzyl alcohol ($4\text{-}MeC_6H_4CH_2OH$) in toluene, under reflux conditions, resulted in the formation of the sesquialkoxide $[Ga\{MeGa(OCH_2C_6H_4Me\text{-}4)_3\}_3]$ (**1**). In contrast, reaction of Me_3In with excess of 4-methylbenzyl alcohol ($4\text{-}MeC_6H_4CH_2OH$) under the same conditions afforded another type of sesquialkoxide, $[In\{Me_2In(OCH_2C_6H_4Me\text{-}4)_2\}_3]$ (**2**). Compounds **1** and **2** have been characterized by NMR, FTIR, and elemental analysis, and the structure of **1** was determined by X-ray crystallography. The structure of **1** consists of a central Ga^{3+} ion coordinated by three $[MeGa(OCH_2C_6H_4Me\text{-}4)(\mu\text{-}OCH_2C_6H_4Me\text{-}4)_2]^-$ units such that it has a coordination number of six. The surrounding metal ions are four coordinate. ^1H NMR data for **1** indicate that in solution two isomers (1:1) are present, namely, the C_1- and C_3-symmetrical isomers, but in the solid state **1** exists as the C_3-symmetrical isomer. Compound **1** possesses the correct ratio of Ga:O atoms (2:3) for that found in gallium oxide (Ga_2O_3), and LPCVD of **1** afforded crystalline Ga_2O_3 films at 600 °C. These results are surprising, as Ga_2O_3 films are typically only crystalline above 700 °C.

Introduction

Gallium oxide (Ga_2O_3) is thermally stable, an electrical insulator at room temperature, and semiconducting above 400 °C. It is considered to be one of the most ideal materials for application as thin-film gas sensors at high temperatures.[1,2] At temperatures above 900 °C the electric conductivity changes depend on the concentration of oxygen; hence the oxygen concentration can be detected.[3] Above 400 °C, gallium oxide thin film operates as a surface-control-type sensor to reducing gases, e.g., CO and EtOH.[4] Therefore, it may be possible to switch the function of the sensor with temperature.[5] Indium oxide films are both transparent to visible light and conductive and find application as transparent conductive oxide (TCO) coatings. Dopants (e.g., tin or fluorine) can be used to increase the conductivity of the films and to make them more suitable for applications such as in solid-state optoelectronic devices.[6]

The versatility of metal alkoxides as convenient precursors to metal oxides via chemical vapor deposition (CVD) processes is widely recognized;[7−9] they are easy to prepare and purify and are intrinsically noncorrosive so can be stored almost indefinitely when kept in a dry atmosphere. Furthermore, metal alkoxides are ideal for use in aerosol-assisted (AA)CVD due to their solubility in a wide range of organic solvents and in low pressure (LP)CVD as a result of their high volatility.[10] Precursors previously employed for the CVD of Ga_2O_3 and In_2O_3 have either contained an excess of oxygen (e.g., gallium or indium tris(alkoxides)[11]) or been used in the presence of an oxygen source (e.g., O_2 or H_2O). Gallium tris(alkoxides), $[Ga(OR)_3]_n$, were first reported in 1964 in separate papers by Mehrotra and Mehrotra[12] and Funk and Paul.[13] Gallium tris(ethoxide) and gallium tris(isopropoxide) were isolated from the reaction of $GaCl_3$ with 3 equiv of NaOR. An extensive series of gallium and indium tris(alkoxides) were subsequently published and prepared via alkoxide/alcohol exchange reactions.[14−16] This series of compounds provided the first information regarding possible structures of the gallium tris(alkoxides). However, Oliver and Worrall also demonstrated that $[Ga(O^iPr)_3]$ existed in solution as an equilibrium mixture of tetramer and dimer.[17,18]

Indium oxide precursors incorporating alkoxide ligands include $[In(OCMe(CF_3)_2)_3(H_2N^tBu)]$ and $[Me_2In(OC(CF_3)_2$-

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$\mathrm{CH_2NHMe)]_2}$.[19,20] The precursors $\mathrm{[Ga(hfac)_3]}$ (hfac = hexafluoroacetoacetonate), $\mathrm{[Ga(O^tBu)_3]_2}$, and $\mathrm{[Ga(OCH(CF_3)_2)_3(HNMe_2)]}$ have been used to deposit $\mathrm{Ga_2O_3}$ films via LPCVD in the presence of $\mathrm{O_2}$ at 450 °C.[21−23] However, the formation of $\mathrm{GaF_3}$ was observed in the mass spectrum of $\mathrm{[Ga(hfac)_3]}$, and the presence of fluorine in $\mathrm{Ga_2O_3}$ films could induce problems for gas sensor applications, due to changes in baseline resistance and sensor drift. Thus, there is a real need for new $\mathrm{Ga_2O_3}$ and $\mathrm{In_2O_3}$ CVD precursors.

Group 13 sesquialkoxides[24−27] are tetrameric compounds, which possess a M:O ratio of 2:3, the desired ratio for $\mathrm{M_2O_3}$. Thus, complexes of this type are ideal precursors to group 13 oxides. Indeed, the formation of $\mathrm{Al_2O_3}$ using an aluminum sesquialkoxide has been indicated, although no details were reported.[27] Although a number of aluminum sesquialkoxides have been reported, analogous examples for Ga and In are limited and no deposition studies have been reported.[24,27,28] The synthesis of sesquialkoxides usually involves a ligand redistribution reaction between metallanes and earth metal alkoxides. We have investigated the reaction of metallanes ($\mathrm{Me_3Ga}$ and $\mathrm{Me_3In}$) with ROH ($\mathrm{R = OCH_2C_6H_4Me\text{-}4}$) in a 4:9 ratio, which afforded two different types of sesquialkoxides. The complexes possess a 2:3 ratio of M:O, and preliminary CVD reactions are also reported.

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in an MBraun Unilab glove box. All solvents were distilled from appropriate drying agents prior to use (sodium for toluene; sodium benzophenone for THF). Trimethylgallium and trimethylindium were obtained from Epichem Ltd. All other reagents were procured commercially from Aldrich and used without further purification. Microanalytical data were obtained at University College London (UCL). NMR spectra were recorded on a Bruker AMX400 spectrometer at UCL, referenced to $\mathrm{CD_2Cl_2}$, which was dried and degassed over molecular sieves prior to use; ^{1}H and ^{13}C chemical shifts are reported relative to $\mathrm{SiMe_4}$ (δ 0.00). FT-IR spectra were obtained on a Shimadzu FTIR-8200 instrument. Thermal gravimetric analysis (TGA) was performed under a dinitrogen atmosphere with a heating rate of 10 °C min^{-1} and on a Netzsch STA 449C instrument. Raman spectra were acquired on a Renishaw Raman System 1000 using a helium-neon laser of wavelength 632.8 nm. The Raman system was calibrated against the emission lines of neon. X-ray powder diffraction patterns were measured on a Siemens D5000 diffractometer using monochromated Cu Kα_1 radiation (λ_1 = 1.5406 Å). The diffractometer used glancing incident radiation (1.5°). Samples were indexed using Unit Cell and compared to database standards. EDXA was obtained on a JEOL 25, and SEM was obtained on a Hitachi S570 instrument using the KEVEX system. UV−vis spectra were recorded in the range 200−1100 nm using a Helios double-beam instrument. Film solubility was assessed by immersing a 1 cm × 0.6 cm piece of glass into solvent (water, dichloromethane, ether, toluene, acetone, and concentrated nitric and hydrochloric acids). Hardness scratch tests were conducted using a brass stylus and a stainless steel scalpel.

Synthesis of 1. A solution of 4-methylbenzyl alcohol (1.78 g, 14.6 mmol) in toluene (5 mL) was added dropwise to a stirred solution of $\mathrm{Me_3Ga}$ (0.75 g, 6.5 mmol) in toluene (5 mL) at room temperature. After refluxing the resulting solution for 24 h, the solvent was removed in vacuo to yield a brown, viscous liquid. THF (8 mL) was added, and after 48 h at −20 °C colorless crystals of **1** were formed (1.2 g, 52%), mp 102 °C. ^{1}H NMR (400.14 MHz, $\mathrm{CD_2Cl_2}$): δ −1.24, (s, 9H, $\mathrm{GaC}\mathit{H}_3$, C_3-symmetric isomer), −1.09, −0.91, −0.89 (s, 3 × 3H, $\mathrm{GaC}\mathit{H}_3$, C_1-symmetric isomer), 2.28−2.34 (m, 2 × 27H, $\mathrm{OCH_2C_6H_4C}\mathit{H}_3$, C_3- and C_1-symmetric isomer), 4.39−5.59 (m, 2 × 18H, $\mathrm{OC}\mathit{H}_2\mathrm{C_6H_4CH_3}$, C_3- and C_1-symmetric isomer), 7.02−7.49 (m, 2 × 36H, $\mathrm{OCH_2C_6}\mathit{H}_4\mathrm{CH_3}$). ^{13}C{^{1}H} NMR (100.61 MHz, $\mathrm{CD_2Cl_2}$): δ −11.6, −11.0 ($\mathrm{Ga}\mathit{C}\mathrm{H_3}$), 22.6. 27.4 ($\mathrm{OCH_2C_6H_4}\mathit{C}\mathrm{H_3}$), 67.8, 68.7, 69.2, 69.6 ($\mathrm{OCH_2}\mathit{C}_6\mathrm{H_4CH_3}$), 128.0, 128.6, 128.7, 130.2, 130.7, 130.9, 131.0, 131.5, 132.0, 137.3, 138.9, 139.4 ($\mathrm{OCH_2}\mathit{C}_6\mathrm{H_4CH_3}$). FTIR (cm^{-1}): 2358 m, 2341 m, 1652 w, 1558 w, 1456 s, 1377 s, 1261 m, 1010 m, 804 m. Anal. Calc for $\mathrm{C_{75}H_{90}O_9Ga_4}$: C, 63.69; H, 6.41. Found: C, 63.93; H, 6.75.

Synthesis of 2. A solution of 4-methylbenzyl alcohol (0.85 g, 7.03 mmol) in toluene (5 mL) was added dropwise to a stirred solution of $\mathrm{Me_3In}$ (0.5 g, 3.12 mmol) in toluene (5 mL) at room temperature. After refluxing the resulting solution for 24 h, the solvent was removed in vacuo to yield a white solid. THF (8 mL) was added, and after 48 h at −20 °C colorless crystalline **2** was isolated (0.7 g, 70%), mp 210 °C. ^{1}H NMR (400.14 MHz, $\mathrm{CD_2Cl_2}$): δ −0.52, (s, 18H, $\mathrm{InC}\mathit{H}_3$), 2.32 (s, 18H, $\mathrm{OCH_2C_6H_4C}\mathit{H}_3$), 5.07 (d, AB J = 11.2 Hz, 6H, $\mathrm{OC}\mathit{H}_2\mathrm{C_6H_4CH_3}$), 5.20 (d, AB J = 11.2 Hz, 6H, $\mathrm{OC}\mathit{H}_2\mathrm{C_6H_4CH_3}$), 7.13 (m, 12H, $\mathrm{OCH_2C_6}\mathit{H}_4\mathrm{CH_3}$), 7.27 (m, 12H, $\mathrm{OCH_2C_6}\mathit{H}_4\mathrm{CH_3}$). ^{13}C{^{1}H} NMR (100.61 MHz, $\mathrm{CD_2Cl_2}$): δ −1.1 ($\mathrm{In}\mathit{C}\mathrm{H_3}$), 21.1 ($\mathrm{OCH_2C_6H_4}\mathit{C}\mathrm{H_3}$), 64.6 ($\mathrm{O}\mathit{C}\mathrm{H_2C_6H_4CH_3}$), 127.9 ($\mathrm{C^4}$, $\mathrm{OCH_2}\mathit{C}_6\mathrm{H_4CH_3}$), 128.6 ($\mathrm{C^{2/6}}$, $\mathrm{OCH_2}\mathit{C}_6\mathrm{H_4CH_3}$), 137.6 ($\mathrm{C^{3/5}}$, $\mathrm{OCH_2}\mathit{C}_6\mathrm{H_4CH_3}$), 141.0 ($\mathrm{C^1}$, $\mathrm{OCH_2}\mathit{C}_6\mathrm{H_4CH_3}$). FTIR (cm^{-1}): 2682 w, 1463 s, 1377 s, 1261 w, 1085 m, 1073 m, 1012 m, 997 m, 798 m, 721 w. Anal. Calc for $\mathrm{C_{72}H_{54}O_6In_4}$: C, 50.81; H, 5.68. Found: C, 50.11; H, 5.32.

Low-Pressure CVD of 1. Compound **1** (0.1 g) was loaded into the sealed end of a quartz tube (50 cm length × 25 mm diameter) in the glovebox. Glass (70 mm × 6 mm × 2 mm) substrates were placed carefully along the inside of the tube. The tube was then placed in a furnace such that 35 cm was inside the furnace and the end containing the sample protruded by 5 cm. The tube was heated to a temperature of 600 °C under dynamic vacuum (3.0 kPa). The tube was slowly drawn into the furnace, ca. 1 cm/30 min, until the sample started to melt. Once the compound had decomposed, the furnace was allowed to cool to room temperature. Translucent light gray films were deposited on the glass substrates.

Crystal Structure Determination and Refinement. Crystals of **1** were obtained at −20 °C from a concentrated solution of THF. A single crystal was mounted on a glass fiber, and all geometric and intensity data were taken from this sample on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 150 ± 2 K. Data reduction and integration was carried out with SAINT+,[29] and absorption corrections were applied using the program SADABS.[30] The structure was solved by direct methods using SHELXS-97[31] and

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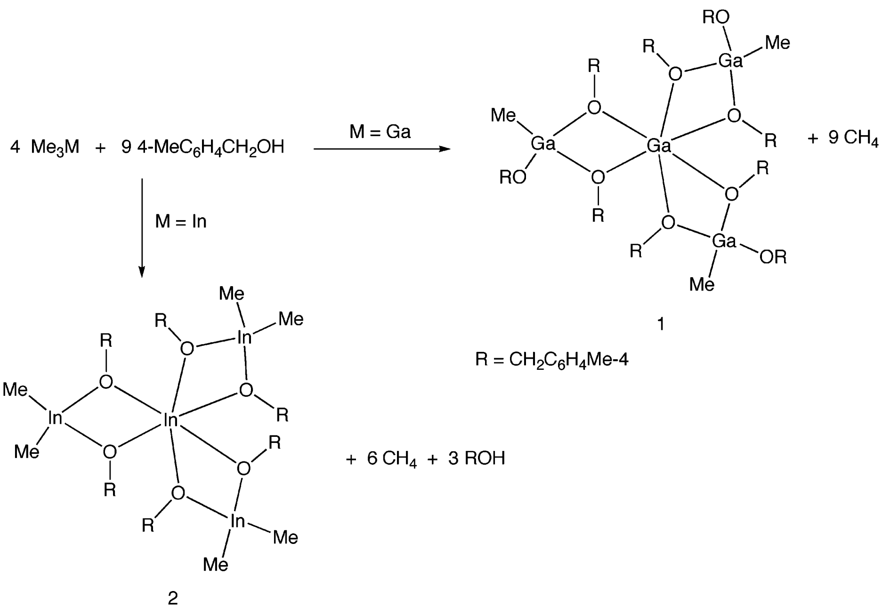
Scheme 1



developed using alternating cycles of least-squares refinement and difference Fourier synthesis.[32] All non-hydrogen atoms were refined anisotropically. One of the methylbenzoxo groups (C22−C28) was found to be disordered and was modeled over three sites with ratios 80.6:3.8:5.6. The benzyl rings were restrained to be flat, and the bond lengths and angles of each part were restrained to be the same. Additionally, the thermal parameters for equivalent atoms were constrained. Hydrogen atoms were placed in calculated positions and their thermal parameters linked to those of the atoms to which they were attached (riding model) except for the methyl groups of C8 and C10, which were treated with a rigid rotor model, and C18, which was treated with an idealized disordered methyl model. Nine regions of highly disordered THF in the unit cell were accounted for using SQUEEZE,[33] which calculated 309 electrons, giving an average of 34 electrons per THF (THF has 40 electrons). See Table 1 for selected crystal data.

Crystal data in CIF format, CCDC 618654, for **1** have been deposited with the Cambridge Crystallographic Data Centre.

Results and Discussion

In an attempt to isolate a molecular precursor to Ga_2O_3, with the correct Ga:O ratio (2:3), the reaction between Me_3Ga and excess 4-$MeC_6H_4CH_2OH$ was carried out. After workup of the reaction mixture and recrystallization from THF at −20 °C, colorless crystals of **1** were obtained (Scheme 1). Analytical and spectroscopic data for **1** were consistent with the formation of the sesquialkoxide $[Ga\{MeGa(OCH_2C_6H_4Me\text{-}4)_3\}_3]$ (**1**). The ^1H NMR of **1** shows the presence of two species, the C_3-symmetrical and C_1-symmetrical isomers, in a 1:1 ratio. An AB spin system was observed in the NMR of **1** due to the chirality of the complexes (diastereotopic H atoms). The structure of **1** was determined by single-crystal X-ray crystallography (Figure 1) and can be described as a Ga^{3+} ion coordinated with three metallate $[MeGa(OCH_2C_6H_4Me\text{-}4)(\mu\text{-}OCH_2C_6H_4Me\text{-}4)_2]^-$ units. The central Ga atom in **1** is six-coordinate with three four-coordinate gallium atoms occupying the periphery. Thus, the central Ga atom is chelated in a bidentate fashion through two oxygen atoms of the three $[MeGa(OCH_2C_6H_4Me\text{-}4)(\mu\text{-}OCH_2C_6H_4Me\text{-}4)_2]^-$ units. The Ga−O distances (Table 1) are slightly longer around the central Ga atom (1.962(1) and 1.973(1) Å) than the bridging Ga−μO bond lengths for the terminal four-coordinate gallium atoms (1.916(1) and 1.912(1) Å). This is due to the increase in atomic radii with increasing coordination number. As expected, the terminal Ga−O bond distances are the shortest (1.812(1) Å). The Ga_2O_2 rings in **1** are planar with small inner ring angles at Ga (75.96(5) and

Table 1. Crystallographic Data for Compound 1[a]

chemical formula	$C_{81}H_{102}Ga_4O_{10}$.
CCDC deposit no.	618654
fw	1522.51
T (K)	150(2)
space group	$R\bar{3}$
a (Å)	15.6095(19)
b (Å)	15.6095
c (Å)	55.392(7)
γ (deg)	120
V (Å^3)	11688(2)
Z	6
ρ_{calcd} (g cm^{-3})	1.298
λ (Å)	0.71073
μ (mm^{-1})	1.424
R_1[b]	0.0352
wR_2[c]	0.0930

[a] Bruker SMART APEX diffractometer ω rotation with narrow frames, graphite monochromated Mo Kα radiation, refinement based on F^2. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Ga\{MeGa(OCH_2C_6H_4Me\text{-}4)\}_3]$ (1)[a]

	Bond Lengths		
Ga(1)−O(2a)	1.962(1)	Ga(1)−O(1)	1.973(1)
Ga(2)−O(3)	1.812(1)	Ga(2)−O(1)	1.912(1)
Ga(2)−O(2)	1.916(1)	Ga(2)−C(10)	1.940(1)
	Bond Angles		
O(2b)−Ga(1)−O(2)	95.93(5)	O(2b)−Ga(1)−O(1)	95.60(5)
O(2)−Ga(1)−O(1)	75.96(5)	O(2a)−Ga(1)−O(1)	166.54(5)
O(2)−Ga(1)−O(1)	93.92(5)	O(3)−Ga(2)−O(1)	104.41(6)
O(3)−Ga(2)−O(2)	107.30(6)	O(1)−Ga(2)−O(2)	78.48(5)
O(3)−Ga(2)−C(10)	121.83(8)	O(1)−Ga(2)−C(10)	117.01(8)
O(2)−Ga(2)−C(10)	119.10(7)		

[a] Symmetry operations for equivalent atoms: *a* = −*x*+*y*, −*x*, *z*; *b* = −*y*, *x*−*y*, *z*.

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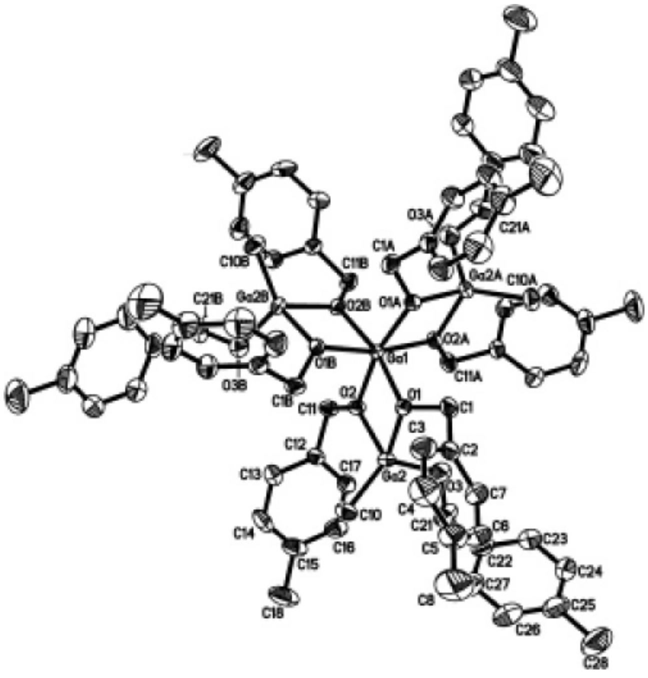

Figure 1. Molecular structure of **1** (hydrogen atoms and minor disorder components are omitted for clarity) showing thermal ellipsoids at the 50% probability level.

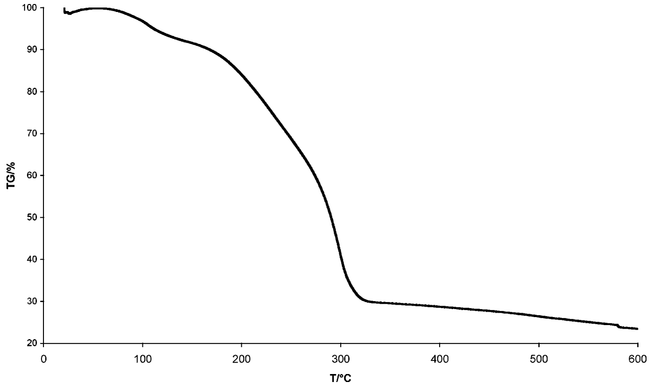

Figure 2. TGA of **1**.

78.48(5)°) and angles greater than 90° at O. The structure of **1** is similar to the related Ga complex [Ga{MeGa(OCH$_2$Ph)$_3$}$_3$], and all bond lengths and angles are comparable.[25]

The reaction of Me$_3$In and an excess of 4-MeC$_6$H$_4$CH$_2$OH afforded, after workup, colorless crystalline **2** (Scheme 1). Spectroscopic and analytical data for **2** indicated that the indium sesquialkoxide [In{Me$_2$In(OCH$_2$C$_6$H$_4$Me-4)$_2$}$_3$] had formed. Unfortunately, X-ray-quality crystals of **2** could not be obtained. However, the ^{1}H NMR of **2** shows the presence of only one set of resonances for the In−Me group and one for the aromatic protons in OCH$_2$C$_6$*H*$_4$Me-4 and the methyl group in OCH$_2$C$_6$H$_4$*Me*-4. These data are consistent with the formation of a symmetrical structure rather than the same type of sesquialkoxide as observed for **1** (Scheme 1). The OC*H*$_2$ moieties are diastereotopic, as shown by the presence of two closely spaced doublets in the ^{1}H NMR of **2**. Therefore, it is likely that compound **2** possesses D_3 symmetry similar to those of related indium and aluminum complexes, of the type [M{Me$_2$M(OR)$_2$}$_3$] structurally characterized.[25,26,28] Formation of the two different sesquialkoxides for gallium and indium (compounds **1** and **2**) is due to differences in the reactivity of Me$_3$Ga versus Me$_3$In. Thus, the more reactive Me$_3$Ga gives with 4-MeC$_6$H$_4$CH$_2$OH the unsymmetrical sesquialkoxide [Ga{MeGa(OCH$_2$C$_6$H$_4$Me-4)$_3$}$_3$], whereas the less reactive Me$_3$In yields the symmetrical sesquialkoxide [In{Me$_2$In(OCH$_2$C$_6$H$_4$Me-4)$_2$}$_3$].

In order to study the decomposition pathway of compounds **1** and **2**, thermal analyses were carried out. The TGA (thermal gravimetric analysis) of **1** (10 °C/min from 20 to 600 °C) shows a weight loss of 72% (calculated weight loss 73% for Ga$_2$O$_3$ formation from **1**). This behavior indicates that compound **1** may be a suitable single-source precursor for the deposition of Ga$_2$O$_3$ thin films. The TGA of **1** (Figure 2) is clean, although the decomposition of **1** does not occur in clean, discrete stages but is continuous from the onset at ca. 110 °C throughout the temperature range studied. The decomposition of **1** begins at a higher temperature than the melting point, suggesting that transport of the intact molecule to the substrate could be successfully achieved. The TGA of **2** shows an overall weight loss of 55% between 20 and 600 °C, which corresponds well with the calculated weight loss of 56% for In$_2$O$_3$ formation. It is worth noting that TGA at atmospheric pressure gives only an indication of the potential of the precursors to form bulk metal oxides.

LPCVD of **1** was investigated, the details of which are described in the Experimental Section. Compound **1** deposited gray-colored films on glass substrates at 600 °C. The film produced was analyzed by WDX (wavelength dispersive X-ray analysis), powder XRD, Raman, and UV−vis measurements. The WDX data showed the presence of gallium and oxygen in the film. Significant breakthrough of the excitation volume through the coating to the underlying glass was observed, and so accurate quantitative analysis by WDX was difficult. However, WDX data showed that carbon contamination was 1−2%. By scanning electron microscopy (SEM) the gallium oxide films show the formation of agglomerates of approximately 0.1 μm. All the films were investigated using Raman microscopy. In all cases no Raman scattering was observed, and it is thought that gallium oxide is a poor Raman scatterer. However, Raman spectroscopy indicated the absence of graphitic carbon in the films. The gallium oxide films passed the Scotch tape test and could not be abraded with a brass stylus but could be marked with a stainless steel scalpel; this is typical of Ga$_2$O$_3$.[10]

X-ray powder diffraction of the film obtained from **1** showed a diffraction pattern consistent with the monocline β-Ga$_2$O$_3$ structure (Figure 3). Determination of the lattice constants gave $a = 12.26(2)$ Å, $b = 3.038$ Å, and $c = 5.81(1)$ Å, which are in agreement with those reported previously for Ga$_2$O$_3$ thin films.[10] Conducting a Tauc plot[34] of the UV/visible data indicated that the films had a indirect band gap of 4.3 eV, comparable to other values for Ga$_2$O$_3$ of 4.2−4.9 eV.[4]

Given the successful formation of Ga$_2$O$_3$ films from **1**, LPCVD of **2** was investigated. In contrast to **1**, compound **2** afforded black films at 600 °C. Powder XRD of these films indicated that decomposition had occurred, and rather than forming In$_2$O$_3$, indium metal was deposited. These results are in contrast to the TGA of **2**, which indicated clean decomposition of **2** to In$_2$O$_3$. However, the melting point of **2** is significantly higher than the gallium complex **1**, suggesting that decomposition of **2** has occurred before the melting point. Thus, transporting the precursor intact to the substrate without decomposition would not be possible.

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(34) Tauc, J., Ed. *Proceedings of the International School of Physics*; Enrico Fermi, Course XXXIV, The Optical Properties of Solids, 1966.

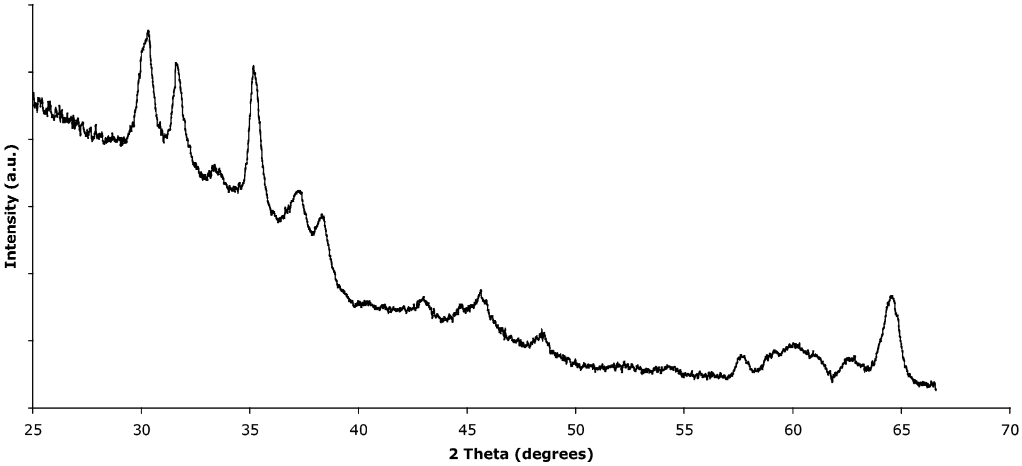

Figure 3. XRD of Ga_2O_3 thin films deposited from **1** by LPCVD at 600 °C.

Conclusions

The synthesis and characterization of two different group 13 sesquialkoxides, $[Ga\{MeGa(OCH_2C_6H_4Me\text{-}4)_3\}_3]$ and $[In\{Me_2In(OCH_2C_6H_4Me\text{-}4)_2\}_3]$, have been described. The structure of the gallium derivative, $[Ga\{MeGa(OCH_2C_6H_4Me\text{-}4)_3\}_3]$, has also been reported. The formation of crystalline Ga_2O_3 films from this complex was achieved. The formation of crystalline Ga_2O_3 films from **1** at the temperature of deposition (600 °C) is significant since all previous reports have found that only amorphous Ga_2O_3 films are obtained below 700 °C.[10−13]

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