DOI: 10.1002/ejic.201001235

Gallium and Indium β-Diketonate Complexes: AACVD of [In(thd)$_3$] and the Attempted Synthesis of Gallium and Indium Bis(β-diketonates)

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Keywords: Gallium / Indium / Chemical vapor deposition / Thin films

Aerosol-assisted chemical vapour deposition (AACVD) of a suspension of [In(thd)$_3$] (thd = 2,2,6,6-tetramethylheptane-3,5-dionate) in CH_2Cl_2 at 450 °C afforded thin crystalline films of indium oxide. The films were analyzed by scanning electron microscopy (SEM), glancing angle X-ray diffraction (XRD) and energy dispersive analysis of X-rays (EDX). Efforts to grow thicker films were hampered by the poor solubility of [In(thd)$_3$], so the synthesis of heteroleptic compounds of the type [M(bdk)$_2$X] (M = Ga, In; bdk = β-diketonate; X = chloride, hydride, methyl) was attempted such that the solubility could be improved by tuning the ligands surrounding the metal centre. Reaction of stoichiometric amounts of β-diketones [Hthd and 2,4-pentanedione (acetylacetone, Hacac)] with Lewis base-stabilized adducts of GaH_3 resulted only in the isolation of the homoleptic gallium tris(β-diketonate) compounds [Ga(bdk)$_3$], instead of the expected heteroleptic gallium bis(β-diketonate) hydride, [GaH(bdk)$_2$]. An unexpected reduction of Hthd to 2,2,6,6-tetramethylheptane-3,5-diol was also observed. Other attempted syntheses of gallium bis(β-diketonate) compounds also resulted in the isolation of homoleptic [Ga(bdk)$_3$] complexes and similar results were obtained for indium. The compounds were characterised by ^1H NMR spectroscopy, mass spectrometry and elemental analysis and the structures of [In(thd)$_3$] and 2,2,6,6-tetramethylheptane-3,5-diol were determined by X-ray crystallography.

Introduction

There is currently a significant interest in thin films of gallium oxide (Ga_2O_3) and indium oxide (In_2O_3). For example, Ga_2O_3 is an electrical insulator at room temperature but becomes semiconducting above 450 °C with its electrical resistivity varying according to the concentration of reducing gases in the atmosphere.[1] Above 900 °C its resistivity changes with the atmospheric concentration of oxygen, therefore it can act as an oxygen gas sensor.[2] In_2O_3 is a transparent conducting oxide (TCO) material which finds applications in solid state optoelectronics.[3] Despite this interest, until recently there were relatively few reports of the use of CVD (chemical vapour deposition) to synthesise thin films of gallium or indium oxide due to the lack of precursor materials with high vapor pressure and low decomposition temperatures.[4]

A number of gallium and indium precursors have been investigated, including metal diketonate, carboxylate, alkyl hydroxide, and halide complexes; however, none of these precursors are entirely satisfactory.[4] Indium carboxylate complexes, for example, are solids at moderate temperatures, a property that can produce variable precursor delivery to the substrate. Metal alkoxides are often chosen as molecular precursors for the CVD of metal oxides.[5,6] We have recently investigated the use of donor-functionalized alkoxides as potential precursors to gallium and indium oxide, since these complexes are not especially air- or moisture-sensitive and have increased solubility.[7–10] Complexes of the type [$R_2M(OR')]_2$ {R = Me, Et; M = Ga, In; R′ = $CH_2CH_2NMe_2$, CH_2CH_2OMe, $CH(CH_3)CH_2NMe_2$}, have been used as precursors via both low pressure and aerosol-assisted CVD (LPCVD and AACVD).[11,12] The gallium and indium oxide films produced from these precursors were oxygen deficient as-deposited. However, after annealing in air, stoichiometric crystalline Ga_2O_3 and In_2O_3 films resulted. The oxygen deficiency was not unexpected since the ratio of M/O in the precursor is only 1:1 vs. 2:3 in the metal oxide (M_2O_3) and the deposition was conducted under an inert atmosphere.

Homoleptic gallium β-diketonates are a class of compound which have previously been used as precursors for the CVD of gallium oxide. The complexes [Ga(acac)$_3$],[13] [Ga(dbm)$_3$],[14] [Ga(thd)$_3$][15] and [Ga(hfac)$_3$][16] (acac = acetylacetonate, dbm = dibenzoylmethanoate, thd = 2,2,6,6-tetramethylheptane-3,5-dionate, hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate, Figure 1) are all six-coordinate, octahedral species which contain a Ga/O coordination ratio of 1:6. [Ga(acac)$_3$], which is commercially available, is not an ideal precursor owing to its high melting point and low volatility.[13,17–19] Fluorine substitution on the diketonate significantly increased the volatility of the precursor, but the decomposition pathway of [Ga(hfac)$_3$] contains GaF_3 as

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one possible end product; a compound which could contaminate the gallium oxide film which would adversely affect its gas sensing properties.[16]

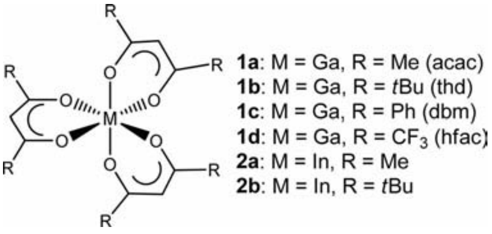
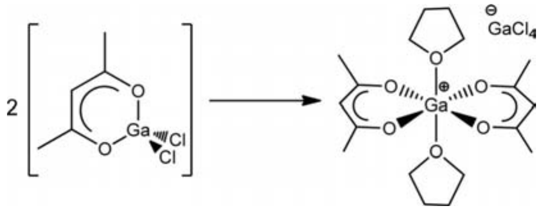


Figure 1. Homoleptic gallium and indium tris(β-diketonates) referred to in this article.

Homoleptic indium β-diketonates such as [In(acac)$_3$] and [In(thd)$_3$] (Figure 1) are potential molecular precursors for In$_2$O$_3$ thin films. However, they are high-melting solids {melting point of [In(acac)$_3$]: 190 °C} hence they are far from ideal for conventional CVD experiments. However, [In(thd)$_3$] is sufficiently soluble that it can be employed in solution-based CVD experiments, albeit at very low concentrations of ca. 0.05 mol L^{-1} in a non-polar solvent (hexane).[20] [In(thd)$_3$] has also been used in plasma enhanced chemical vapour deposition (PECVD) as a precursor to thin films of In$_2$O$_3$.[21]

The use of heteroleptic gallium and indium β-diketonates as CVD precursors should improve upon the poor volatility of the non-fluorinated homoleptic tris(β-diketonates). Gallium mono(β-diketonate) complexes have been known since 1953 when the synthesis of [Me$_2$Ga(acac)] was reported[22] but surprisingly, we could find only one example of a gallium bis(β-diketonate) in the literature.[23] It was isolated from a ligand redistribution reaction of [Cl$_2$Ga(acac)] in THF, which crystallised as the involatile ion pair [Ga(acac)$_2$(THF)$_2$]$^+$[GaCl$_4$]$^-$ (Scheme 1) and is therefore unsuitable for conventional CVD purposes. Similarly, an indium mono(β-diketonate) has previously been reported and used as a precursor for the CVD of Cu-In thin films,[24] but no indium bis(β-diketonates) have been reported.



Scheme 1. Isolation of the only known gallium bis(β-diketonate).

The synthesis of gallium and indium bis(β-diketonates) is desirable primarily for their potential as highly volatile and soluble precursors for CVD. They may also lead to gallium and indium compounds with interesting and/or unusual coordination modes, as well as heteroleptic gallium and indium compounds, which would also be good potential CVD precursors. AACVD is a useful solution-based method when conventional precursors prove involatile or thermally stable. Herein, we report the formation of pure, crystalline indium oxide films via AACVD of [In(thd)$_3$]. Furthermore, our attempts at the synthesis of gallium and indium bis(β-diketonate) compounds, the solid state X-ray structures of [In(thd)$_3$] and the unexpected reduction product obtained from the reaction of [(quin)GaH$_3$] and Hthd (quin = quinuclidine) are also reported.

Results and Discussion

Although the low solubility of [In(thd)$_3$] in non-polar solvents had previously been noted, it was thought that sufficient material could be dissolved in a suitable solvent (e.g. THF, CH$_2$Cl$_2$) to enable AACVD to take place. Following a literature procedure, the synthesis of [In(thd)$_3$] was accomplished in good yield.[25] Recrystallisation of the crude reaction mixture from ethanol led to the formation of colourless crystals. Upon checking the CCDC (August 2010 update), it was discovered that the solid-state structure of [In(thd)$_3$] had not previously been determined, hence a single-crystal X-ray diffraction study was carried out (Figure 2).

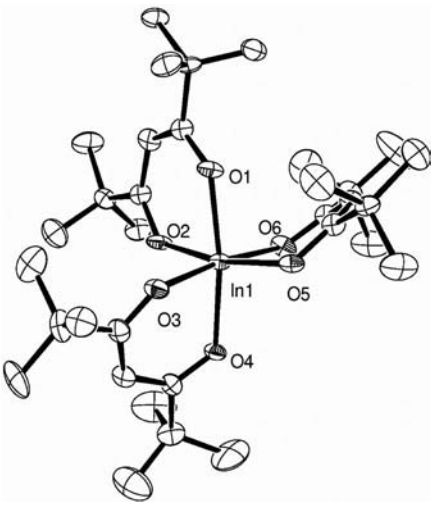


Figure 2. ORTEP representation of [In(thd)$_3$], showing one of two symmetry-independent molecules in the asymmetric unit. Thermal ellipsoids at 50 % probability, hydrogen atoms and positional disorder at one of the *tert*-butyl groups omitted for clarity.

The crystal structure of [In(thd)$_3$] shows the expected slightly distorted octahedral coordination geometry at indium. It crystallised in the triclinic space group $P\bar{1}$ with two symmetry-independent molecules in the asymmetric unit, hence a Z value of four. The range of In–O bond lengths [2.114(7)–2.147(8) Å] was consistent with previously reported homoleptic indium β-diketonates [2.110(5)–2.141(5) Å] found in [In(acac)$_3$] and [In(dbm)$_3$].[14,26] A small amount of positional disorder was found at one of the *tert*-butyl groups of a thd ligand, which was modelled over two positions with the occupancy factors allowed to refine freely.

Thermogravimetric analysis of [In(thd)$_3$] confirmed that it had a high melting point (ca. 160 °C, first spike in the DSC trace) and also a high volatilisation temperature (ca.

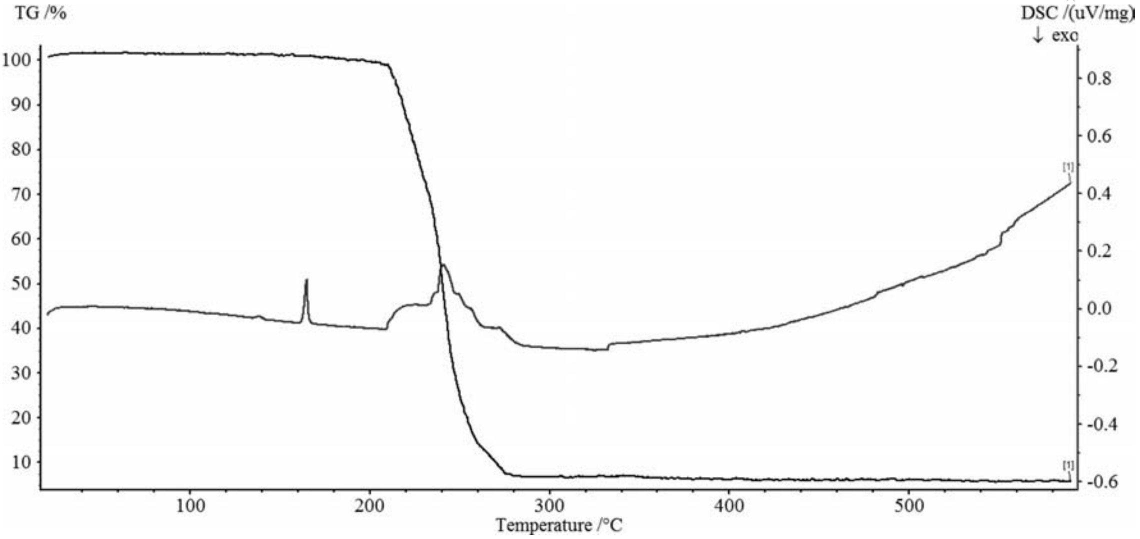


Figure 3. TGA/DSC graph for [In(thd)$_3$].

210 °C). The expected residual mass for complete decomposition to In_2O_3 is 21%, but the low observed residual mass of ca. 5% indicated that the vast majority of the compound sublimed before decomposition took place. This is borne out by the TGA trace, which shows a steady, smooth, one-step loss of mass between 210–260 °C, characteristic of sublimation of the sample. This was somewhat surprising and indicated that [In(thd)$_3$] might also be a viable CVD precursor for LPCVD (Figure 3).

Initial attempts at growing thin films of In_2O_3 from [In(thd)$_3$] on glass microscope slides were undertaken using LPCVD in a tube furnace heated to 500 °C. A small amount of white powder was deposited on the glass slide nearest the precursor, but the majority of the material sublimed through the tube furnace and condensed on the glass slide immediately outside the hot zone of the furnace. The white powder was not adhesive to the glass substrate (it was easily wiped off with a tissue) and glancing angle X-ray diffraction (XRD) analysis revealed it was amorphous. Energy dispersive X-ray (EDX) analysis did, however, reveal the presence of indium in the powder. Lowering the furnace temperature resulted in no precursor being transported into the hot zone whilst increasing the temperature did not increase the amount of decomposition occurring within the hot zone of the furnace.

To circumvent this issue, a bespoke LPCVD reactor which allowed fine control of the system pressure via both a throttle valve attached to the vacuum pump and a low flow of nitrogen carrier gas was utilised.[27] Running the reactor at ca. 5 mbar pressure, with the precursor heated to 175 °C and a substrate temperature of 500 °C, resulted in the deposition of a very thin, greyish film. The coverage of the borosilicate glass substrate was good, but the film was too thin for XRD analysis. EDX analysis indicated that indium was present, albeit in very small amounts: 25 atom-% was the highest observed value, with significant breakthrough to the underlying glass substrate occurring.

One possible explanation for the poor quality of films formed is the high thermodynamic stability of the precursor (vide infra) coupled with the short time that the precursor spends inside the deposition chamber of the reactor. At low pressures, insufficient quantities of the precursor decompose in the deposition chamber of the CVD reactor, with most of the [In(thd)$_3$] passing straight through the deposition chamber, solidifying on the first cool surface it meets. Because of this thermodynamic stability, very thin films were formed using LPCVD hence other methods of getting the precursor into the CVD reactor, leading to longer retention times in the deposition chamber, were investigated.

As mentioned above, [In(thd)$_3$] was synthesised to investigate solution-based methods (AACVD) of getting the precursor into the reaction chamber. In order to find a suitable solvent, [In(thd)$_3$] (ca. 200 mg) was added to CH_2Cl_2, toluene and THF (ca. 30 mL); in all cases a fine suspension formed which, upon standing for 1 hour, settled at the bottom of the flask. Initial attempts concentrated on passing an aerosol derived from the toluene suspension into a CVD reactor heated to 450 °C. However, no deposition was observed on the glass substrate and the majority of the precursor was not transported into the reactor.

Owing to the volatility of the solvent, aerosols derived from CH_2Cl_2 can be passed through a CVD reactor very quickly. Suspending [In(thd)$_3$] in CH_2Cl_2, atomising it and quickly running the aerosol into the reactor (deposition time ca. 30 min) resulted in almost all of the precursor being transported across. The resulting transparent film, formed exclusively on the bottom plate at a substrate temperature of 450 °C, was thicker and analysis by XRD and scanning electron microscopy (SEM) was possible. The film was adherent, passing the scotch tape test, although it was scratched with a stainless steel stylus.

XRD analysis of the resulting film revealed that a single phase of cubic indium oxide had been deposited (Figure 4). The film morphology was studied by SEM, revealing tri-

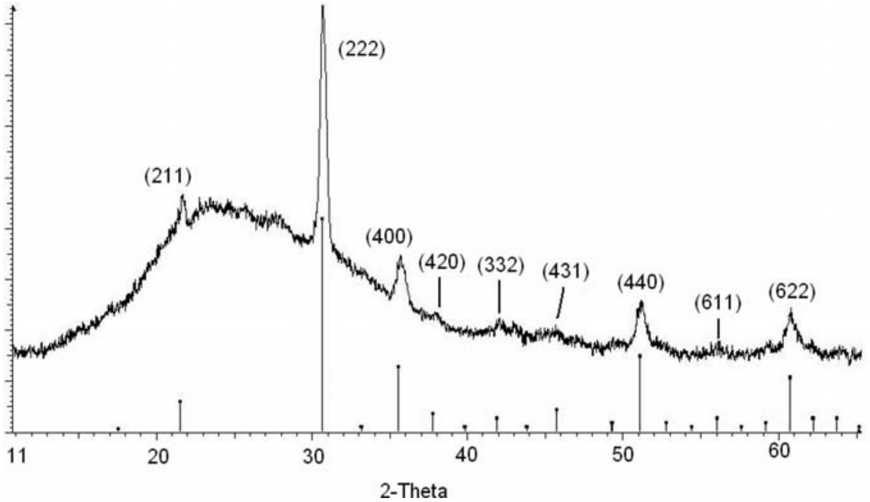


Figure 4. XRD spectrum of the In_2O_3 film deposited on glass by AACVD from [In(thd)$_3$].

angular crystals of size ca. 500 nm (Figure 5). EDX analysis of the film confirmed that a significant amount of indium was present in the film, but accurate determination of the In/O ratio was not possible owing to the fact that breakthrough to the underlying glass substrate was observed. The film was too thin for accurate wavelength dispersive X-ray (WDX) analysis to be performed.

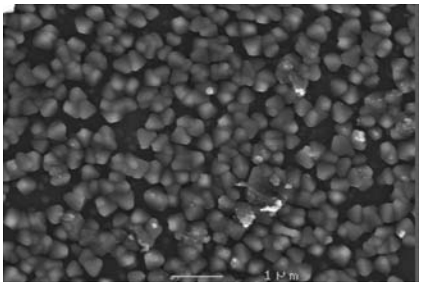
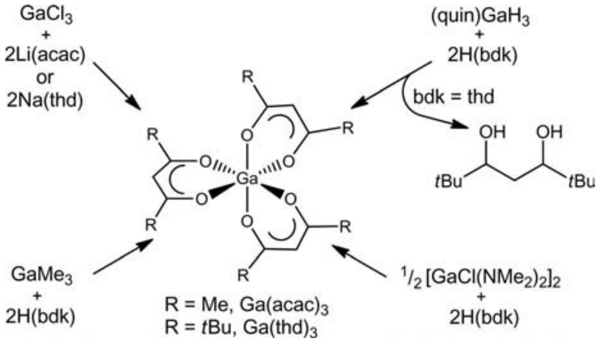


Figure 5. SEM image of the In_2O_3 film deposited from [In(thd)$_3$] via AACVD.

Unfortunately, thicker films of In_2O_3 could not be obtained by varying the CVD conditions (amount of precursor, deposition time, N_2 flow rate etc.). Attempts at using [In(acac)$_3$] as a precursor were futile because no suitable solvent could be found. Even the use of suspensions of [In(acac)$_3$] in CH_2Cl_2 were unsuccessful because the precursor settled at the bottom of the flask too quickly, hence insufficient amounts of precursor were transported into the reactor to form a film of In_2O_3. Instead, efforts were concentrated on the synthesis of a more soluble/volatile β-diketonate-based precursor, specifically gallium and indium bis(β-diketonates). It was thought that by removing one of the β-diketonate ligands and replacing it with a smaller ligand (e.g. alkoxide), a more volatile, more soluble and less thermodynamically stable precursor than the homoleptic tris(β-diketonates) would be obtained. This would enable more precursor to be transported into the deposition chamber of a CVD reactor which would decompose more readily, affording thicker films of gallium and indium oxide.

As previously reported, the reaction of Na(acac) with $GaCl_3$ in a 1:1 ratio affords [Cl_2Ga(acac)] in excellent yield.[23] We investigated the reaction, in toluene, of Na(acac) with $GaCl_3$ in a 2:1 ratio in order to isolate a gallium bis(β-diketonate), [Ga(acac)$_2$Cl], which could also be employed in future reactions to yield heteroleptic gallium complexes. After filtering the reaction mixture and cooling the filtrate to –18 °C, a colourless crystalline compound was obtained (Scheme 2). Analytical and spectroscopic data (^{1}H NMR spectroscopy, mass spectrometry, elemental analysis) for the crystalline compound was consistent with the formation of the gallium tris(β-diketonate) [Ga(acac)$_3$] rather than the expected gallium bis(β-diketonate). The unit cell of the crystalline compound, determined by a single-crystal X-ray diffraction study, was consistent with [Ga(acac)$_3$]. No other products could be isolated from the reaction and the results were reproducible with the reaction being repeated a number of times. Attempts at repeating the reaction with the bulkier β-diketonate Li(thd) only led to the isolation of [Ga(thd)$_3$].



Scheme 2. Synthetic routes towards gallium bis(β-diketonates) attempted in this paper.

Since the salt elimination route only afforded the gallium tris(β-diketonate), an alternative route involving the reaction of the quinuclidine adduct of gallane [(quin)GaH$_3$][28] with Hacac was investigated. Treatment of [(quin)GaH$_3$]

with two equivalents of Hacac in diethyl ether resulted in the vigorous evolution of hydrogen gas and the formation of a small amount of grey powder, thought to be metallic gallium. After filtration and workup, a white solid was isolated in 41% yield. Spectroscopic and analytical data of the white solid revealed the homoleptic β-diketonate [Ga(acac)$_3$] had again been formed. The ^{1}H NMR spectrum contained only two peaks at δ = 1.99 and 5.40 ppm, consistent with literature values for [Ga(acac)$_3$], which integrated to a 1:6 ratio.[29] No peak corresponding to the Ga–H group was present.

The bulkier β-diketone 2,2,6,6-tetramethylheptane-3,5-dione (Hthd) was then used as it was expected that this ligand would cause more steric crowding at the gallium centre, enabling the gallium bis(β-diketonate) to be isolated. Thus, reaction of [(quin)GaH$_3$] with two equivalents of Hthd in diethyl ether also resulted in the formation of hydrogen gas and a small amount of grey powder. After filtration, cooling the filtrate to 4 °C for 16 h resulted in the formation of colourless crystals in two different morphologies: plates and sheets. Spectroscopic and analytical data showed that the homoleptic gallium tris(β-diketonate) [Ga(thd)$_3$] had been synthesised and isolated. No evidence for the formation of [GaH(thd)$_2$] was observed; for example no peak corresponding to Ga–H was seen in the ^{1}H NMR spectrum. Again, only two peaks were observed in positions corresponding to literature values for [Ga(thd)$_3$]: 1.19 and 5.82 ppm, integrating to a ratio of 1:18.[15]

A single-crystal X-ray diffraction study of the plates confirmed that [Ga(thd)$_3$] had been formed. However, the dataset quality was poor, and merely sufficient to show the connectivity of the non-hydrogen atoms. Similarly to the analogous [Ga(acac)$_3$], [Ga(dbm)$_3$] and [Ga(hfac)$_3$] complexes, [Ga(thd)$_3$] is a six-coordinate octahedral species where each β-diketonate is bound to a single gallium centre through the two oxygen atoms.

Structural characterisation of the sheets (Figure 6) revealed the unexpected formation of 2,2,6,6-tetramethylheptane-3,5-diol, the doubly reduced form of Hthd. This could not be chemically separated from [Ga(thd)$_3$], hence spectroscopic characterisation was not possible. However, the identity of the compound was confirmed by the molecular geometry at C(3) and C(5), which was consistent with sp^3-hybridised carbon; the C–O bond lengths [1.439(2) and 1.440(2) Å], which were characteristic of a C–O single bond rather than a C=O double bond; and the presence of Q-peaks in the Fourier difference map in the expected locations for the methine and alcohol protons.

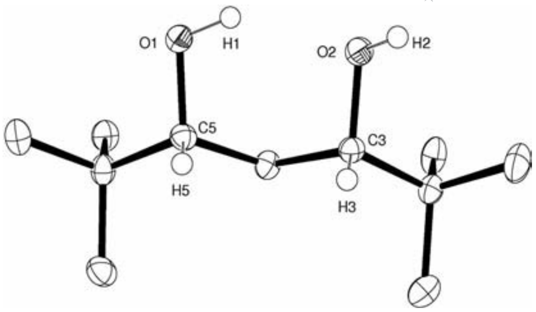


Figure 6. ORTEP representation of 2,2,6,6-tetramethylheptane-3,5-diol. Thermal ellipsoids at 50% probability, *tert*-butyl and methylene hydrogen atoms omitted for clarity.

The crystal packing involved both intermolecular and intramolecular hydrogen-bonding interactions. The intermolecular interactions (2.89 Å) result in the formation of an infinite 1D chain of molecules, parallel to the direction of the *b*-axis of the unit cell. The intramolecular interaction (2.74 Å) is between O(1) and O(2) and, as expected, is slightly shorter than the intermolecular interaction (Figure 7).

Because the use of hydride-containing reagents led to the unexpected isolation of a β-diol after reduction of Hthd, the H$_2$ elimination route was abandoned in favour of methane elimination. It was previously discovered that reacting GaMe$_3$ with a large excess of donor-functionalized alcohol only resulted in the formation of a mixture of the mono- and bis-substituted gallium alkoxides [GaMe$_x$(OR)$_{3-x}$] (x = 1, 2) with no evidence for the formation of the tris(alkoxide), even at reaction temperatures of 110 °C.[11] To this end, two equivalents of Hacac were added to a toluene solution of GaMe$_3$ at –78 °C, warmed to room temp. and refluxed for 16 hours. ^{1}H NMR spectroscopy of the yellow oil which was isolated after removal of all volatiles revealed the formation of [GaMe$_2$(acac)] as the major product: the peak for the acac methyl groups integrated to the same value as the peak around 0 ppm corresponding to the gallium methyl groups.

A yellow oil was also obtained when an excess of Hacac was used. This, upon analysis by ^{1}H NMR spectroscopy, only indicated the presence of one Ga–Me environment which integrated to the same value as the acac methyl groups, consistent with the formation of [GaMe$_2$(acac)]. Signals corresponding to [Ga(acac)$_3$] were also observed, the presence of which was confirmed by mass spectrometric analysis of the oil which contained an ion at m/z 267, con-

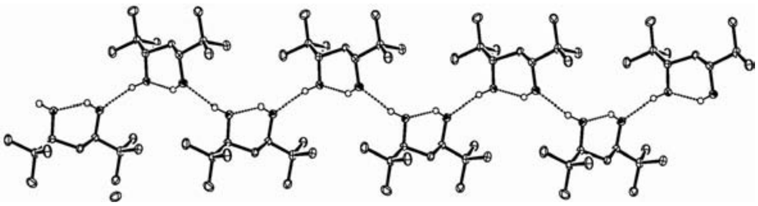


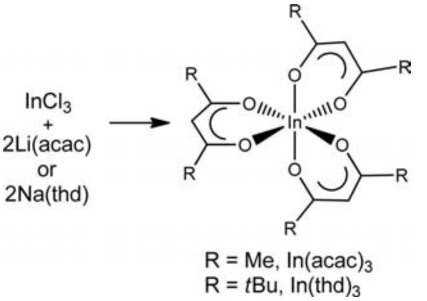
Figure 7. ORTEP representation showing the hydrogen-bonding interactions of 2,2,6,6-tetramethylheptane-3,5-diol (zig-zag line). Thermal ellipsoids at 50% probability, hydrogen atoms (bar OH) omitted for clarity.

sistent with the $[Ga(acac)_2]^+$ ion. It also contained an ion at *m*/*z* 283, consistent with the formation of $[Ga(CH_4)(acac)_2]^+$. This is a result of the chemical ionisation method which used methane as an ionising gas, which reacted with the $[Ga(acac)_2]^+$ ion forming an adduct with *m*/*z* 283. The presence of an ion at *m*/*z* 366 corresponding to $[Ga(acac)_3]^+$ indicated that the homoleptic tris(β-diketonate) had again been formed.

Using an excess of the bulkier ligand Hthd in the reaction with $GaMe_3$ led to the formation of a colourless oil which solidified upon cooling to –18 °C. The ^1H NMR spectrum of the solid revealed no peaks in the region associated with Ga–Me groups but mass spectrometric analysis showed the presence of ions at *m*/*z* 435 and 451, corresponding to $[Ga(thd)_2]^+$ and $[Ga(CH_4)(thd)_2]^+$, respectively. The lack of Ga–Me resonances in the ^1H NMR spectrum confirmed that the peak at *m*/*z* 451 was due to a reaction between the methane ionisation gas and the $[Ga(thd)_2]^+$ ion, something borne out by the presence of a peak at *m*/*z* 618, consistent with $[Ga(thd)_3]^+$.

The hydride and methane elimination routes described above mainly resulted in the formation of the homoleptic gallium tris(β-diketonates), with the mono(β-diketonate) $[GaMe_2(acac)]$ isolated from the reaction of two equivalents of Hacac with $GaMe_3$. Therefore, a further alternative route was investigated involving amine elimination. Starting from a gallium compound with only two amide ligands, the expectation was that, upon elimination of amine, a gallium bis(β-diketonate) would be isolated. Thus, the reaction of dimeric $[GaCl(NMe_2)_2]_2$ with four equivalents of β-diketones (Hacac, Hthd) in diethyl ether resulted in the formation of a white solid after removal of all volatiles. Analytical and spectroscopic data again showed that the homoleptic complexes $[Ga(bdk)_3]$ had been formed and isolated. The tris(β-diketonates) were presumably isolated from a ligand redistribution occurring after the intermediate $[GaCl(bdk)_2]$ is initially formed. Finally, the ligand redistribution reaction of $GaCl_3$ and two equivalents of $[Ga(acac)_3]$ in Et_2O was attempted, but no reaction was observed.

Attempts to synthesise indium bis(β-diketonate) compounds followed similar routes to those described above for gallium (Scheme 3). The reaction of $InCl_3$ and Na(acac) in a 1:2 ratio resulted in the formation of a colourless solid after workup, which was consistent with $[In(acac)_3]$ upon analysis: the ^1H NMR spectrum exhibited two peaks at δ = 2.02 and 5.42 ppm which integrated to a 1:6 ratio, consistent with literature values for $[In(acac)_3]$.[30] Similarly, the related reaction of $InCl_3$ with two equivalents of the bulkier Li(thd) resulted in the isolation of colourless crystals of $[In(thd)_3]$ rather than the expected indium bis(β-diketonate) $[InCl(thd)_2]$. The unit cell obtained by single-crystal X-ray analysis of the crystals was consistent with that obtained for $[In(thd)_3]$.



Scheme 3. Attempted syntheses of indium bis(β-diketonates).

Conclusions

$[In(thd)_3]$ has been used as a molecular precursor to thin films of indium oxide using AACVD, affording transparent, crystalline films. However, its poor solubility and high thermal stability led to the attempted synthesis of bis(β-diketonate) complexes of gallium and indium. This failed for two reasons: (i) the high kinetic and thermodynamic stability of $[M(bdk)_3]$ (M = Ga, In) and (ii) a facile rearrangement of the intermediate $[GaCl(bdk)_2]$ to the extremely stable homoleptic gallium β-diketonates. The synthesis of gallium bis[benzoyl(thiobenzoyl)methanoate] chloride has been previously reported, although it was thought that steric crowding at the gallium centre due to the size of the sulfur atoms was the reason for the stability of the five-coordinate product.[31] However, it was not possible to isolate $[Ga(bdk)_2X]$ complexes even when massively increasing the size of the diketonate ligand. The high stability of $[Ga(bdk)_3]$ compounds is borne out by the fact that diketones are capable of removing all three methyl groups of $GaMe_3$, reactivity which had not previously been observed for alcohols even under extremely forcing conditions.

The compound $[(quin)GaH_3]$ can also act as a reducing agent towards carbonyl groups, resulting in the formation of a β-diol as a byproduct from the reaction of $[(quin)GaH_3]$ with Hthd.

Experimental Section

General: All reactions were carried out under nitrogen using standard Schlenk and glove-box techniques. $GaCl_3$ (10 mesh beads, 99.99 %) and Hacac were bought from Sigma Aldrich, Hthd and $InCl_3$ from Alfa Aesar and all were used without further purification. $GaMe_3$ was supplied by SAFC Hitech Ltd. Alkali metal β-diketonate salts were prepared by adding a slight excess of the diketone to a hexane solution of *n*BuLi (or hexane suspension of NaH), filtering and drying the resulting white solid. Solvents were dried using alumina columns such that the water concentration was 5–10 ppm. $[(quin)GaH_3]$[28] and $[ClGa(NMe_2)_2]_2$[32] were synthesised according to literature methods.

^1H NMR spectra were obtained on a Bruker AMX-400 spectrometer, operating at 295 K and 400.12 MHz. Spectra were recorded using $CDCl_3$ and C_6D_6, which were dried and degassed over molecular sieves prior to use. Mass spectra were obtained using a Micromass 70-SE spectrometer using chemical ionization (CI) with methane reagent gas. Elemental analyses were obtained at UCL.

General Procedures

Salt Metathesis: A suspension of the alkali metal diketonate (2.0 mmol) in toluene (10 mL) at –78 °C was added slowly to the metal chloride (1.0 mmol) dissolved in toluene (10 mL) at –78 °C and stirred for 15 min, before warming to room temp. and stirring for 5 h. After this time the reaction was filtered, concentrated to ca. 5 mL in vacuo and cooled to –18° for one week where colourless crystals were deposited.

Hydride Elimination: [(Quin)GaH_3] (184 mg, 1.0 mmol) was dissolved in Et_2O (20 mL) and cooled to –78 °C. The diketone (2.0 mmol) was added via syringe, resulting in vigorous evolution of H_2. The reaction was stirred for 15 min, then warmed to room temp. and stirred for 16 h. After this time, the solution was filtered and concentrated, then cooled to –18 °C where colourless crystals deposited.

Methane Elimination: $GaMe_3$ (500 mg, 4.4 mmol) was cooled to –78 °C and dissolved in toluene (20 mL). The diketone (17.4 mmol) was added via syringe, the solution was stirred at –78 °C for 15 min, warmed to room temp. then refluxed for 16 h. After cooling and removal of solvents, the residue was dissolved in Et_2O and cooled to –18 °C where a white crystalline solid precipitated.

Amine Elimination: $[ClGa(NMe_2)_2]_2$ (193 mg, 0.5 mmol) was dissolved in Et_2O (20 mL) and cooled to –78 °C. The diketone (2.0 mmol) was added via syringe; the reaction was stirred for 15 min then warmed to room temp. and stirred for 5 h. After this time, removal of volatiles in vacuo afforded a white solid.

[Ga(acac)$_3$]: The salt metathesis route with 176 mg of $GaCl_3$ and 244 mg of Na(acac) resulted in the formation of the title compound in 37% yield. The hydride elimination route with 0.20 mL of Hacac afforded the title compound in 41% yield. The methane elimination route with 1.79 mL of Hacac led to the isolation of the title compound in 77% yield. Finally, the amine metathesis route with 0.20 mL of Hacac afforded the title compound in 36% yield. All products gave spectroscopic data consistent with known literature values.[29] NMR (400.0 MHz, $CDCl_3$): δ_H = 1.99 (s, 3 H, CH), 5.40 (s, 18 H, CH_3) ppm. LRMS (CI^+, CH_4): *m*/*z* = 183/185 [Ga(acac)(CH_4)]$^+$ (100%), 267/269 [Ga(acac)$_2$]$^+$, 283/285 [Ga(acac)$_2$(CH_4)]$^+$, 366/368 [Ga(acac)$_3$]$^+$. $C_{15}H_{21}GaO_6$ (367.05): calcd. C 49.08, H 5.77; found C 49.10, H 5.65 {calcd. for [Ga(acac)$_2$Me]: C 46.69, H 6.06}.

[Ga(thd)$_3$]: Using the hydride elimination route with 0.42 mL of Hthd, the title compound was formed in 59% yield. The methane elimination route with 3.63 mL of Hthd resulted in the formation of the title compound in 82% yield. The amine metathesis route with 0.42 mL of Hthd afforded the title compound in 43% yield. All products gave spectroscopic data consistent with known literature values.[15] NMR (400.0 MHz, $CDCl_3$): δ_H = 5.82 (s, 3 H, CH), 1.19 (s, 54 H, CH_3) ppm. LRMS (CI^+, CH_4): *m*/*z* = 435/437 [Ga(thd)$_2$]$^+$, 451/453 [Ga(thd)$_2$(CH_4)]$^+$ (100%), 618/620 [Ga(thd)$_3$]$^+$. $C_{33}H_{57}GaO_6$ (619.53): calcd. C 63.98, H 9.27; found C 64.10, H 9.35 {calcd. for [Ga(thd)$_2$Me]: C 61.21, H 9.16}.

2,2,6,6-Tetramethylheptane-3,5-diol: X-ray quality single crystals were obtained from the synthesis of [Ga(thd)$_3$] via the hydride elimination route. They could not be chemically separated from [Ga(thd)$_3$], hence no spectroscopic data was obtained.

[In(acac)$_3$]: Using the salt metathesis route with 221 mg of $InCl_3$ and 244 mg of Na(acac), the title compound was formed in 44% yield. Spectroscopic data were consistent with known literature values.[30] NMR (400.0 MHz, $CDCl_3$): δ_H = 5.42 (s, 3 H, CH), 2.02 (s, 15 H, CH_3) ppm.

[In(thd)$_3$]: Using the salt metathesis route with 221 mg of $InCl_3$ and 380 mg of Li(thd), the title compound was formed in 56% yield. Spectroscopic data were consistent with known literature values.[25] NMR (400.0 MHz, $CDCl_3$): δ_H = 5.85 (s, 3 H, CH), 1.17 (s, 54 H, CH_3) ppm.

LPCVD: For tube furnace experiments, the precursor (250 mg) was placed in a small sample vial at the end of a quartz tube 500 mm long and 15 mm diameter with six borosilicate glass slides (75 mm × 12 mm × 1 mm) placed along the tube end-to-end. The tube was sealed with a Schlenk gas adaptor and placed in a tube furnace such that the precursor was not directly in contact with the heater. The furnace was allowed to reach 500 °C before the tube was opened to vacuum (typically 0.1 mbar) and left to run for 3 h.

Experiments were also performed using a horizontal cold-wall reactor comprising a stainless steel reaction chamber (100 mm long, 40 mm diameter) housing a resistively heated aluminium substrate holder.[27] The reactor was connected to a resistively heated stainless steel precursor holder, containing 150 mg of [In(thd)$_3$], with standard Swagelock fittings. The system was evacuated and the pressure of the reactor and inlet gas flow (nitrogen) were regulated using mechanical throttle valves. The substrate temperature was varied between 400–600 °C while the precursor bubbler temperature was maintained at 175 °C. Depositions were carried out for 4 h at a total pressure of 5 mbar on 30 × 15 mm borosilicate glass.

AACVD: Nitrogen (99.99%) was obtained from BOC and used as supplied. Depositions were obtained on SiCO coated float-glass of ca. 90 × 45 × 4 mm. Prior to use the glass substrates were cleaned using petroleum ether (60–80 °C) and *i*PrOH, then dried in air. [In(thd)$_3$] (0.20 g, 0.32 mmol) was suspended in CH_2Cl_2 (ca. 30 mL) and vaporized at room temperature by use of a PIFCO ultrasonic humidifier. Two-way taps were used to divert the nitrogen carrier gas through the bubbler and the aerosol was carried into the reactor in a stream of nitrogen gas at a rate of 1 L min^{-1} through a brass baffle to obtain a laminar flow.

A graphite block containing a Whatman cartridge heater was used to heat the glass substrate. The temperature of the substrate was monitored by a Pt-Rh thermocouple. Depositions were carried out by heating the horizontal bed reactor to 450 °C before diverting the nitrogen line through the aerosol and hence to the reactor. The total time for the deposition process was 30 min. Large pieces of glass (ca. 4 × 2 cm) were used for X-ray powder diffraction. The coated glass substrate was cut into ca. 1 × 1 cm squares for subsequent analysis by scanning electron microscopy (SEM).

Film Analysis Methods: X-ray powder diffraction patterns were measured on a Siemens D5000 diffractometer using monochromated Cu-K_α radiation (λ = 1.5400 Å) radiation. The diffractometer used glancing incident radiation (1.5°). The films on the glass substrates were indexed using Unit Cell and compared to database standards. SEM was carried out on a JEOL 6301 filament scanning electron microscope.

Crystallography: A summary of the crystal data, data collection and refinement for crystallographically characterized compounds are given in Table 1. Datasets were collected on a Enraf–Nonius Kappa CCD area detector diffractometer with an FR591 rotating anode (Mo-K_α radiation) and an Oxford Cryosystems low temperature device operating in ω scanning mode with ψ and ω scans to fill the Ewald sphere. The programs used for control and integration were Collect,[33] Scalepack and Denzo.[34] The crystals were mounted on a glass fibre with silicon grease from paraffin oil. All solutions and refinements were performed using the WinGX package[35] and all software packages within. All non-hydrogen atoms were refined using anisotropic thermal parameters and hydrogen atoms were added using a riding model. One of the *tert*-butyl groups in [In(thd)$_3$] was disordered over two positions and the occupancy factors of the modelled disorder were not fixed during refinement cycles.

Table 1. Crystallographic data for compounds reported in this paper.

	2,2,6,6-Tetramethylheptanediol	In(thd)$_3$
Formula	$C_{11}H_{24}O_2$	$C_{33}H_{57}InO_6$
Mass	188.30	664.61
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a [Å]	10.5060(4)	12.3455(9)
b [Å]	9.2079(3)	13.7464(10)
c [Å]	12.0689(5)	23.4551(18)
α [°]		106.809(2)
β [°]	93.438(2)	99.520(3)
γ [°]		96.598(3)
Volume [Å^3]	1165.42(8)	3701.7(5)
Z	4	4
$D_{calcd.}$ [Mg/m^3]	1.073	1.193
T [K]	120(2)	120(2)
μ [mm^{-1}]	0.071	0.674
Data collected	10948	16888
Unique data	2664	16888
Goodness of fit on F^2	1.062	1.220
R_{int}	0.0577	0.0000
Final $R(\|F\|)$ [$F_o > 2\sigma(F_o)$]	$R_1 = 0.0632$, $wR_2 = 0.1260$	$R_1 = 0.1260$, $wR_2 = 0.2528$
Final $R(F^2)$ (all data)	$R_1 = 0.0873$, $wR_2 = 0.1386$	$R_1 = 0.1692$, $wR_2 = 0.2908$

CCDC-801518 (for In(thd)$_3$) and -801519 (for 2,2,6,6-tetramethylheptanediol) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We would like to thank the Engineering and Physical Sciences Research Council (EPSRC) for funding (grant number EP/F035675/1) and Dr. Peter Horton at the EPSRC National Crystallography Service at the University of Southampton for dataset collection. We would also like to thank Dr. Chris Blackman at UCL for advice and use of the cold wall LPCVD reactor.

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Received: November 24, 2010