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Synthesis and structural characterisation of gallium and indium fluoroalkoxide ‘ate’ complexes

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The treatment of $InCl_3$ with $MOCH(CF_3)_2$ (M = Li, Na, K) in a 1:6 stoichiometry, followed by recrystallisation results in the formation of the bimetallic “ate” complexes $[Na_3In(OCH(CF_3)_2)_6(THF)_3]$ (**2**) and $[Li_3In(OCH(CF_3)_2)_6(THF)_3]$ (**5**) from hexane, and $[K_3In(OCH(CF_3)_2)_6]_n$ (**4**) from a THF and toluene mixture. If a 1:3 stoichiometry is used chloride containing compounds $[Na_2InCl(OCH(CF_3)_2)_4(THF)_4]$ (**1**) and $[KInCl_2\ (OCH(CF_3)_2)_2(THF)_3]_n \cdot \mathit{THF}$ (**3**) are obtained on recrystallisation from hexane. Treatment of $GaCl_3$ with 6 equivalents of $LiOC(CH_3)_2CF_3$ gives $[LiGa(OC(CH_3)_2CF_3)_4(THF)_2]$ (**6**) on recrystallisation from hexane. The protolysis reaction between $In(N(SiMe_3)_2)_3$, formed *in situ* from $(Me_3Si)_2NH$, ^{n}BuLi and Incl$_3$, and $HOCH(CH_3)CF_3$ results in isolation of $[LiIn(OCH(CH_3)CF_3)_3Bu]_2$ (**7**) from hexane. The structures of **2**, **4**, and **5** all contain the tetranuclear core InO_6M_3. Compounds **1** and **3** have residual chloride; **1** is a trinuclear species with two THF ligands per Na, while **3** is a linear polymer. Compound **6** has a GaO_2Li four-membered parallelogram at its core. Complex **7** has a tetranuclear $In_2O_6Li_2$ core and an unexpected ^{n}Bu group on the In atoms. The coordination spheres of the alkali metals in **1**–**6** include solvated THF while **1**–**5** display additional close M···F interactions.

1. Introduction

Due to their reactivity, hydrolytic instability and molecular diversity, metal alkoxides are important and versatile precursors for oxide based materials [1–5]. While their synthetic and structural chemistry has been well researched they remain both fascinating and challenging, particularly when considering the design of precursors for materials which have particular properties and of known and consistent composition. Optimising volatility, decomposition temperatures and pathways [4,6], and solubility [7] relies primarily on appropriate ligand choice or design, as well as the nature of the metal itself. This is exemplified by recent reports on the use of donor-functionalized ligands such as aminoalkoxides [8,9]. Fluorinated alcohols are another alternative source of ligand which have the potential to impart favourable properties when compared with their non-fluorinated analogues [10]. Recently, we described the synthesis and structural characterisation of a rich variety of bismuth fluoroalkoxides and oxo-clusters obtained from the treatment of $BiAr_3$ (Ar = Ph, *p*-Tol) with $(CF_3)_2CHOH$ [11]. On seeking to explore the related synthetic chemistry of the fluoroalkoxides of gallium and indium, a salt elimination approach was adopted as this had previously been reported to be successful in the synthesis of fluorinated and non-fluorinated alkoxides; $Al(OCH(CF_3)_2)_3$ was synthesised from $AlCl_3$ and $Na(OCH(CF_3)_2)$ using reflux conditions and an excess of hexafluoroisopropanol [12] while a series of $In(OR)_3$ compounds have been prepared from the reactions of Gp 13 metal halides with non-fluorinated alkali metal alkoxides [13–15]. Another alternative route to indium fluoroalkoxides using an amide-alcohol exchange route has been exploited by Hoffman and co-workers [16–21], however, Carmalt and co-workers have recently described problems of halide incorporation in gallium alkoxides founded on incomplete amide formation from $GaCl_3$ [22].

In this paper we now report that we have found the salt metathesis reactions of alkali metal fluoroalkoxides with $InCl_3$ and $GaCl_3$ to be also problematic. Only a series of heterobimetallic gallate and indate complexes have been isolated from the reaction mixtures.

Due to the possible undesirable incorporation of alkali metals into the oxide film, where they will act as *p*-type dopants [23] such ‘ate’ complexes are not suitable for homo-metallic semiconductor thin films. However, it has been previously reported that single crystals of $LiGaO_2$ and $LiAlO_2$ are promising substrates for the epitaxial growth of GaN [24,25] and that volatile heterobimetallic complexes of lithium aluminate or gallate, $[Li(OCH_2CH_2OMe)_2MMe_2]$ (M = Al, Ga), are suitable precursors for the formation of $LiMO_2$ films by MOCVD [26]. In addition, bimetallic Gp 1/13 complexes are of some interest in synthetic organic chemistry because of their application as catalysts [27] and as initiators in polymerisation reactions [28]. These heterobimetallic alkoxides can also be readily compared with Gp 1/13 BINOLate complexes

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[27] (BINOL = 1,1′-binaphthyl-2,2′-diol) and with lanthanoid based Shibasaki catalysts, which have been used extensively in asymmetric synthesis [29–32].

Here we now report the synthesis and characterisation of seven new heterobimetallic Gp 1/13 fluoroalkoxides: $[Na_2InCl(OCH(CF_3)_2)_4(THF)_4]$ (**1**), $[Na_3In(OCH(CF_3)_2)_6(THF)_3]$ (**2**), $[KInCl_2(OCH(CF_3)_2)_2(THF)_3]_n \cdot$ *THF* (**3**), $[K_3In(OCH(CF_3)_2)_6]_n$ (**4**), $[Li_3In(OCH(CF_3)_2)_6(THF)_3]$ (**5**), $[LiGa(OC(CH_3)_2CF_3)_4(THF)_2]$ (**6**), $[LiIn(OCHCH_3CF_3)_3Bu]_2$ (**7**).

2. Results and discussion

2.1. Synthesis

The indium "ate" complexes **1**–**5** were synthesised by treating $InCl_3$ with $MOCH(CF_3)_2$ (M = Li, Na, K) in THF at −78 °C under an N_2 atmosphere. The reaction of $InCl_3$ with 3 equivalents of $NaOCH(CF_3)_2$ resulted in the formation and isolation of yellow crystals of the chloride containing bimetallic compound **1**, $[Na_2InCl(OCH(CF_3)_2)_4(THF)_4]$, in a 33% yield. When the stoichiometry of the reaction was changed to 1:6 for $InCl_3$ and $NaOCH(CF_3)_2$, respectively, the colourless bimetallic compound **2**, $[Na_3In(OCH(CF_3)_2)_6(THF)_3]$, was isolated in a 47% yield. The replacement of sodium with potassium resulted in the isolation of colourless crystals of the bimetallic chloride containing polymer $[KInCl_2(OCH(CF_3)_2)_2(THF)_3]_n \cdot$ *THF* (**3**) in a 34% yield. The analogous 1:6 stoichiometric reaction produced colourless crystals of $[K_3In(OCH(CF_3)_2)_6]_n$ (**4**) in a 48% yield. After the reactions with Na and K, inclusion of the smaller Li^+ cation was explored. Reaction of $LiOCH(CF_3)_2$ with $InCl_3$ in a stoichiometry of 6:1, resulted in isolation of crystals of compound **5**, $[Li_3In(OCH(CF_3)_2)_6(THF)_3]$, in a 49% yield. Replacing $InCl_3$ with $GaCl_3$ resulted in the formation and isolation of crystals of $[LiGa(OC(CH_3)_2CF_3)_4(THF)_2]$ (**6**) in a yield of 46%.

Another commonly used approach for the synthesis of indium alkoxides is *via* amine/alcohol exchange (protolysis) reactions. The *in situ* synthesis of a hexane solution of $In(N(SiMe_3)_2)_3$ was carried out by the sequential lithiation of $(Me_3Si)_2NH$ by *n*BuLi, and subsequent salt elimination reaction with $InCl_3$. The addition of $CF_3(CH_3)CHOH$ to this solution produced crystals of $[LiIn(OCHCH_3CF_3)_3Bu]_2$ (**7**) in a 28% yield after cooling the hexane solution to −30 °C. Presumably, the Bu groups result from the incomplete formation of $In(N(SiMe_3)_2)_3$ and the high solubility of *n*BuLi in hexane.

2.2. Analysis

Compounds **1**–**7** were characterised by ^1H, ^{13}C and ^{19}F NMR spectroscopy, elemental analysis, melting point, and single crystal X-ray diffraction. For compounds **2**–**7** microanalytical data were in agreement with the solid-state structures. However, for compound **1** the partial loss of THF was observed. All compounds show reasonably low melting points with compound **2** having the lowest of 49–51 °C. Compounds **3**–**7** melt at 120–121 °C, 121–123 °C, 110–112 °C, 116–118 °C and 67–69 °C, respectively.

NMR (^1H, ^{13}C, ^{19}F) data were determined in C_6D_6 for compounds **1**, **2**, **5**, **6** and **7**. Due to a lack of solubility in benzene, spectra for **4** were obtained in d_8-THF and in d_6-DMSO for compound **3**. ^1H NMR and ^{13}C NMR spectra for compounds **1**, **2**, **3** and **5** verified the presence of THF ligands in the coordination sphere of the alkali metals, consistent with the solid-state structures. Despite a variation in ligand binding modes for **1, 2, 4** and **5** with **3**, at 30 °C the $(CF_3)_2CHO$ ligands are all fluxional and the spectra largely unremarkable, revealing expected chemical shifts and coupling constants. These are detailed in Section 4.

The ^1H NMR spectrum of compound **6**, $[LiGa(OC(CH_3)_2CF_3)_4(THF)_2]$, showed only one type of fluoroalkoxide ligand in C_6D_6 and in d_6-DMSO, despite the presence of two different modes (bridging and terminal) in the solid-state structure. The proton corresponding to the methyl groups on the fluoroalkoxide ligands, $-OC(CH_3)_2CF_3$, appear at 1.58 ppm in C_6D_6 and at 1.30 ppm at d_6-DMSO in the ^1H NMR spectra. This can be explained by an averaging of the signals in solution at room temperature. In the ^{19}F NMR spectrum in d_6-DMSO one singlet was observed at −82.3 ppm. The ^{13}C NMR spectrum obtained in d_6-DMSO, in addition to the THF signals, shows a resonance at 24.2 ppm corresponding to the Me carbons of the $OC(CH_3)_2CF_3$ ligand and a multiplet at 71.1 ppm for the quaternary carbon *C*–O on $OC(CH_3)_2CF_3$. However, no signal is observed for the carbon bearing fluorine (CF_3).

In compound **7**, $[LiIn(OCH(CH_3)CF_3)_3Bu]_2$, the fluoroalkoxide ligands also exist in two different coordination environments. However, in the ^1H NMR spectrum in C_6D_6 at room temperature fluxional behaviour gives rise to only one signal for each of the C*H* (4.29 ppm) and CH_3 protons (1.17 ppm, *J*(H, H) = 6.46 Hz). The methyl protons from the *n*Bu group are observed as a triplet at 0.88 ppm with a coupling constant of *J*(H, H) = 7.29 Hz. The CH_2 protons from the *n*-butyl group were detected at 1.65 ppm as a multiplet for $-CH_2CH_2CH_2CH_3$, and as a septet at 1.28 ppm for $-CH_2CH_2CH_2CH_3$ with *J*(H, H) = 7.27 Hz). In the ^{19}F NMR spectrum one broad singlet was observed at −78.1 ppm.

2.3. Molecular structures

With the exception of **4** crystals of all the complexes were obtained from hexane solution stored at −30 °C. Crystals of **4** were grown in a more polar toluene/THF solvent mixture, again at −30 °C. The high solubility of the majority of the complexes in relatively non-polar solvents at ambient and refrigeration temperatures (4 °C) provided a significant challenge in obtaining good quality single crystals. In particular, crystals of **1** and **4** good enough to support full non-isotropic refinement were difficult to obtain, and the crystals were typically twinned. For these compounds, the structures presented derive from the best quality data we have collected to date. Since a majority of atoms could not be refined anisotropically detailed discussions on accurate bond lengths and angles is not appropriate. However, as presented the observed distances and geometries accord well with those found in analogous compounds and general comparisons can be made. Complex **6** is a racemic twin, however, a full refinement and accurate structure determination was obtained.

Compound **1** $[Na_2InCl(OCH(CF_3)_2)_4(THF)_4]$ crystallises in the monoclinic crystal system, and chiral space group $P2_1$ (refined as a racemic twin). The asymmetric unit consists of a five-coordinate indium centre, chloride ion, two sodium ions, four hexafluoroisopropoxide ligands, and four THF molecules (Fig. 1). The indium atom is in a highly distorted square pyramidal geometry formed by the single chloride ion in an apical position and four oxygen atoms from the hexafluoroisopropoxide ligands in basal positions. The range of angles around the In atoms is 81.4(4)–170.8(4)°. The average In-O_{alk} bond distance is 2.1 Å. Similar bond distances were observed for indium complexes with In_2O_2 frameworks, for example, in the dimers $[Me(Cl)InO^tBu]_2$, $[Me(Br)InO^tBu]_2$, and $[\{(Me_3Si)_2N\}MeInO^tBu]_2$ the average In–O_{alk} bond distances are 2.115(7), 2.121(7), and 2.145(7) Å, respectively [33]. Also, the indium fluoroalkoxide $[In\{\mu\text{-}OCMe_2(CF_3)\}\{OCMe_2(CF_3)\}_2]_2$ has analogous bridging In–O_{alk} bond distance of 2.129(5) Å [16]. The In–O_{alk} bond distances in **1** are comparable with that of 2.136(4) Å in the indate complex $Li[(Ar^nO)_2InCl_2]$ (Ar^nO^- = 2,4,6-tris((dimethylamino)methyl)phenoxy ligand) [34]. Each Na ion adopts a distorted quasi-tetrahedral geometry with angles in the range of 71.4(3)–141.0(5)° for Na(1) and 72.6(3)–135.6(5)° for Na(2). The average bond distance for Na–O_{THF} is 2.27 Å and for Na–O_{alk} is 2.33 Å. These bond distances are comparable to those observed