



## Synthesis and structural characterisation of gallium and indium fluoroalkoxide 'ate' complexes

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### ARTICLE INFO

#### Article history:

Received 10 October 2008

Received in revised form 31 October 2008

Accepted 3 November 2008

Available online 7 November 2008

#### Keywords:

Indium

Gallium

Fluorinated alkoxides

Group 1

Heterobimetallic

### ABSTRACT

The treatment of  $\text{InCl}_3$  with  $\text{MOCH}(\text{CF}_3)_2$  ( $M = \text{Li, Na, K}$ ) in a 1:6 stoichiometry, followed by recrystallisation results in the formation of the bimetallic "ate" complexes  $[\text{Na}_3\text{In}(\text{OCH}(\text{CF}_3)_2)_6(\text{THF})_3]$  (**2**) and  $[\text{Li}_3\text{In}(\text{OCH}(\text{CF}_3)_2)_6(\text{THF})_3]$  (**5**) from hexane, and  $[\text{K}_3\text{In}(\text{OCH}(\text{CF}_3)_2)_6]$  (**4**) from a THF and toluene mixture. If a 1:3 stoichiometry is used chloride containing compounds  $[\text{Na}_2\text{InCl}(\text{OCH}(\text{CF}_3)_2)_4(\text{THF})_4]$  (**1**) and  $[\text{KInCl}_2(\text{OCH}(\text{CF}_3)_2)_2(\text{THF})_3] \cdot \text{THF}$  (**3**) are obtained on recrystallisation from hexane. Treatment of  $\text{GaCl}_3$  with 6 equivalents of  $\text{LiOC}(\text{CH}_3)_2\text{CF}_3$  gives  $[\text{LiGa}(\text{OC}(\text{CH}_3)_2\text{CF}_3)_4(\text{THF})_2]$  (**6**) on recrystallisation from hexane. The protolysis reaction between  $\text{In}(\text{N}(\text{SiMe}_3)_2)_3$ , formed *in situ* from  $(\text{Me}_3\text{Si})_2\text{NH}$ ,  $^t\text{BuLi}$  and  $\text{InCl}_3$ , and  $\text{HOCH}(\text{CH}_3)_2\text{CF}_3$  results in isolation of  $[\text{LiIn}(\text{OCH}(\text{CH}_3)_2\text{CF}_3)_3\text{Bu}]_2$  (**7**) from hexane. The structures of **2**, **4**, and **5** all contain the tetranuclear core  $\text{InO}_6\text{M}_3$ . 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  $\text{GaO}_2\text{Li}$  four-membered parallelogram at its core. Complex **7** has a tetranuclear  $\text{In}_2\text{O}_6\text{Li}_2$  core and an unexpected  $^t\text{Bu}$  group on the In atoms. The coordination spheres of the alkali metals in **1–6** include solvated THF while **1–5** display additional close  $M \cdots F$  interactions.

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### 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  $\text{BiAr}_3$  ( $\text{Ar} = \text{Ph, } p\text{-Tol}$ ) with  $(\text{CF}_3)_2\text{CHOH}$  [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;  $\text{Al}(\text{OCH}(\text{CF}_3)_2)_3$  was synthesised from  $\text{AlCl}_3$  and

$\text{Na}(\text{OCH}(\text{CF}_3)_2)$  using reflux conditions and an excess of hexafluoroisopropanol [12] while a series of  $\text{In}(\text{OR})_3$  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  $\text{GaCl}_3$  [22].

In this paper we now report that we have found the salt metathesis reactions of alkali metal fluoroalkoxides with  $\text{InCl}_3$  and  $\text{GaCl}_3$  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  $\text{LiGaO}_2$  and  $\text{LiAlO}_2$  are promising substrates for the epitaxial growth of GaN [24,25] and that volatile heterobimetallic complexes of lithium aluminate or gallate,  $[\text{Li}(\text{OCH}_2\text{CH}_2\text{O-Me})_2\text{MMe}_2]$  ( $M = \text{Al, Ga}$ ), are suitable precursors for the formation of  $\text{LiMO}_2$  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:  $[\text{Na}_2\text{InCl}(\text{OCH}(\text{CF}_3)_2)_4(\text{THF})_4]$  (**1**),  $[\text{Na}_3\text{In}(\text{OCH}(\text{CF}_3)_2)_6(\text{THF})_3]$  (**2**),  $[\text{KInCl}_2(\text{OCH}(\text{CF}_3)_2)_2(\text{THF})_3]_n \cdot \text{THF}$  (**3**),  $[\text{K}_3\text{In}(\text{OCH}(\text{CF}_3)_2)_6]_n$  (**4**),  $[\text{Li}_3\text{In}(\text{OCH}(\text{CF}_3)_2)_6(\text{THF})_3]$  (**5**),  $[\text{LiGa}(\text{OC}(\text{CH}_3)_2\text{CF}_3)_4(\text{THF})_2]$  (**6**),  $[\text{LiIn}(\text{OCH}(\text{CH}_3)_2\text{CF}_3)_3\text{Bu}]_2$  (**7**).

## 2. Results and discussion

### 2.1. Synthesis

The indium “ate” complexes **1–5** were synthesised by treating  $\text{InCl}_3$  with  $\text{MOCH}(\text{CF}_3)_2$  ( $M = \text{Li}, \text{Na}, \text{K}$ ) in THF at  $-78^\circ\text{C}$  under an  $\text{N}_2$  atmosphere. The reaction of  $\text{InCl}_3$  with 3 equivalents of  $\text{NaOCH}(\text{CF}_3)_2$  resulted in the formation and isolation of yellow crystals of the chloride containing bimetallic compound **1**,  $[\text{Na}_2\text{InCl}(\text{OCH}(\text{CF}_3)_2)_4(\text{THF})_4]$ , in a 33% yield. When the stoichiometry of the reaction was changed to 1:6 for  $\text{InCl}_3$  and  $\text{NaOCH}(\text{CF}_3)_2$ , respectively, the colourless bimetallic compound **2**,  $[\text{Na}_3\text{In}(\text{OCH}(\text{CF}_3)_2)_6(\text{THF})_3]$ , 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  $[\text{KInCl}_2(\text{OCH}(\text{CF}_3)_2)_2(\text{THF})_3]_n \cdot \text{THF}$  (**3**) in a 34% yield. The analogous 1:6 stoichiometric reaction produced colourless crystals of  $[\text{K}_3\text{In}(\text{OCH}(\text{CF}_3)_2)_6]_n$  (**4**) in a 48% yield. After the reactions with Na and K, inclusion of the smaller  $\text{Li}^+$  cation was explored. Reaction of  $\text{LiOCH}(\text{CF}_3)_2$  with  $\text{InCl}_3$  in a stoichiometry of 6:1, resulted in isolation of crystals of compound **5**,  $[\text{Li}_3\text{In}(\text{OCH}(\text{CF}_3)_2)_6(\text{THF})_3]$ , in a 49% yield. Replacing  $\text{InCl}_3$  with  $\text{GaCl}_3$  resulted in the formation and isolation of crystals of  $[\text{LiGa}(\text{OC}(\text{CH}_3)_2\text{CF}_3)_4(\text{THF})_2]$  (**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  $\text{In}(\text{N}(\text{SiMe}_3)_2)_3$  was carried out by the sequential lithiation of  $(\text{Me}_3\text{Si})_2\text{NH}$  by  $n\text{BuLi}$ , and subsequent salt elimination reaction with  $\text{InCl}_3$ . The addition of  $\text{CF}_3(\text{CH}_2)\text{CHOH}$  to this solution produced crystals of  $[\text{LiIn}(\text{OCH}(\text{CH}_3)_2\text{CF}_3)_3\text{Bu}]_2$  (**7**) in a 28% yield after cooling the hexane solution to  $-30^\circ\text{C}$ . Presumably, the Bu groups result from the incomplete formation of  $\text{In}(\text{N}(\text{SiMe}_3)_2)_3$  and the high solubility of  $n\text{BuLi}$  in hexane.

### 2.2. Analysis

Compounds **1–7** were characterised by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  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  $49\text{--}51^\circ\text{C}$ . Compounds **3–7** melt at  $120\text{--}121^\circ\text{C}$ ,  $121\text{--}123^\circ\text{C}$ ,  $110\text{--}112^\circ\text{C}$ ,  $116\text{--}118^\circ\text{C}$  and  $67\text{--}69^\circ\text{C}$ , respectively.

NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ ) data were determined in  $\text{C}_6\text{D}_6$  for compounds **1**, **2**, **5**, **6** and **7**. Due to a lack of solubility in benzene, spectra for **4** were obtained in  $d_8\text{-THF}$  and in  $d_6\text{-DMSO}$  for compound **3**.  $^1\text{H}$  NMR and  $^{13}\text{C}$  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  $30^\circ\text{C}$  the  $(\text{CF}_3)_2\text{CHO}$  ligands are all fluxional and the spectra largely unremarkable, revealing expected chemical shifts and coupling constants. These are detailed in Section 4.

The  $^1\text{H}$  NMR spectrum of compound **6**,  $[\text{LiGa}(\text{OC}(\text{CH}_3)_2\text{CF}_3)_4(\text{THF})_2]$ , showed only one type of fluoroalkoxide ligand in

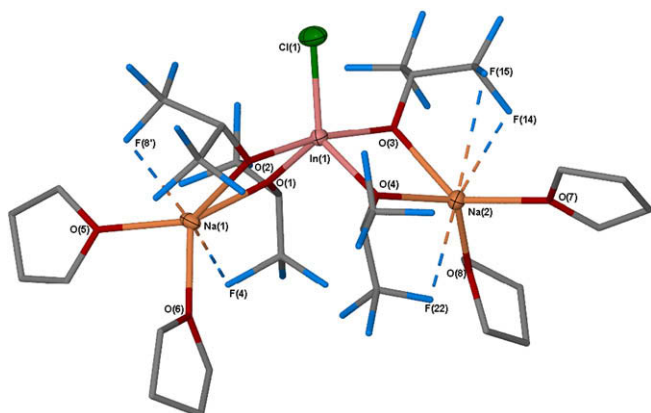
$\text{C}_6\text{D}_6$  and in  $d_6\text{-DMSO}$ , despite the presence of two different modes (bridging and terminal) in the solid-state structure. The proton corresponding to the methyl groups on the fluoroalkoxide ligands,  $-\text{OC}(\text{CH}_3)_2\text{CF}_3$ , appear at 1.58 ppm in  $\text{C}_6\text{D}_6$  and at 1.30 ppm in  $d_6\text{-DMSO}$  in the  $^1\text{H}$  NMR spectra. This can be explained by an averaging of the signals in solution at room temperature. In the  $^{19}\text{F}$  NMR spectrum in  $d_6\text{-DMSO}$  one singlet was observed at  $-82.3$  ppm. The  $^{13}\text{C}$  NMR spectrum obtained in  $d_6\text{-DMSO}$ , in addition to the THF signals, shows a resonance at 24.2 ppm corresponding to the Me carbons of the  $\text{OC}(\text{CH}_3)_2\text{CF}_3$  ligand and a multiplet at 71.1 ppm for the quaternary carbon C–O on  $\text{OC}(\text{CH}_3)_2\text{CF}_3$ . However, no signal is observed for the carbon bearing fluorine ( $\text{CF}_3$ ).

In compound **7**,  $[\text{LiIn}(\text{OCH}(\text{CH}_3)_2\text{CF}_3)_3\text{Bu}]_2$ , the fluoroalkoxide ligands also exist in two different coordination environments. However, in the  $^1\text{H}$  NMR spectrum in  $\text{C}_6\text{D}_6$  at room temperature fluxional behaviour gives rise to only one signal for each of the CH (4.29 ppm) and  $\text{CH}_3$  protons (1.17 ppm,  $J(\text{H}, \text{H}) = 6.46$  Hz). The methyl protons from the *n*Bu group are observed as a triplet at 0.88 ppm with a coupling constant of  $J(\text{H}, \text{H}) = 7.29$  Hz. The  $\text{CH}_2$  protons from the *n*-butyl group were detected at 1.65 ppm as a multiplet for  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ , and as a septet at 1.28 ppm for  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  with  $J(\text{H}, \text{H}) = 7.27$  Hz). In the  $^{19}\text{F}$  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  $-30^\circ\text{C}$ . Crystals of **4** were grown in a more polar toluene/THF solvent mixture, again at  $-30^\circ\text{C}$ . The high solubility of the majority of the complexes in relatively non-polar solvents at ambient and refrigeration temperatures ( $4^\circ\text{C}$ ) 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.

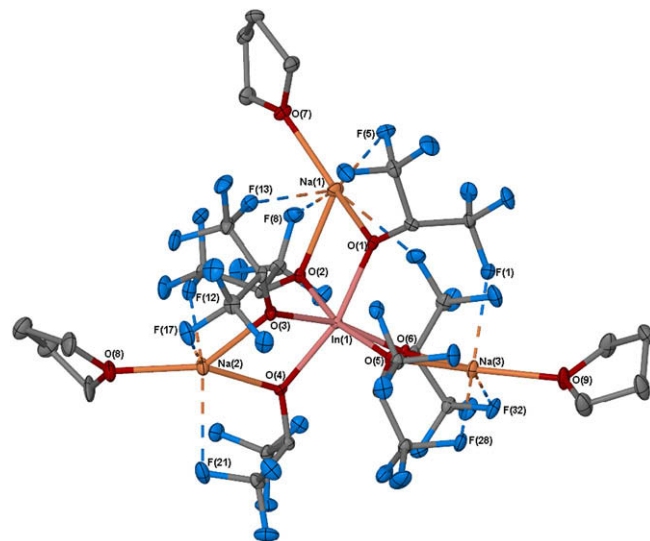
Compound **1**  $[\text{Na}_2\text{InCl}(\text{OCH}(\text{CF}_3)_2)_4(\text{THF})_4]$  crystallises in the monoclinic crystal system, and chiral space group  $P2_1$  (refined as a racemic twin). The asymmetric unit consists of a five-coordinate indium centre, chloride ion, two sodium ions, four hexafluoroisopropoxide 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  $81.4(4)\text{--}170.8(4)^\circ$ . The average In–O<sub>alk</sub> bond distance is 2.1 Å. Similar bond distances were observed for indium complexes with  $\text{In}_2\text{O}_2$  frameworks, for example, in the dimers  $[\text{Me}(\text{Cl})\text{InO}^t\text{Bu}]_2$ ,  $[\text{Me}(\text{Br})\text{InO}^t\text{Bu}]_2$ , and  $\{[(\text{Me}_3\text{Si})_2\text{N}]\text{MeInO}^t\text{Bu}\}_2$  the average In–O<sub>alk</sub> bond distances are 2.115(7), 2.121(7), and 2.145(7) Å, respectively [33]. Also, the indium fluoroalkoxide  $[\text{In}\{\mu\text{-OCMe}_2(\text{CF}_3)\}\{\text{OCMe}_2(\text{CF}_3)\}_2]$  has analogous bridging In–O<sub>alk</sub> bond distance of 2.129(5) Å [16]. The In–O<sub>alk</sub> bond distances in **1** are comparable with that of 2.136(4) Å in the indate complex  $\text{Li}[(\text{Ar}^n\text{O})_2\text{InCl}_2]$  ( $\text{Ar}^n\text{O}^- = 2,4,6\text{-tris}[(\text{dimethylamino})\text{methyl}]\text{phenoxy}$  ligand) [34]. Each Na ion adopts a distorted quasi-tetrahedral geometry with angles in the range of  $71.4(3)\text{--}141.0(5)^\circ$  for Na(1) and  $72.6(3)\text{--}135.6(5)^\circ$  for Na(2). The average bond distance for Na–O<sub>THF</sub> is 2.27 Å and for Na–O<sub>alk</sub> is 2.33 Å. These bond distances are comparable to those observed



**Fig. 1.** Crystal structure of **1** (hydrogen atoms are omitted for clarity). Thermal ellipsoids given at 30% probability. Selected bond lengths (Å) and angles (°): In1–O1 2.043(8), In1–O2 2.153(9), In1–O3 2.130(9), In1–O4 2.083(11), In1–Cl1 2.355(4), Na1–O1 2.321(14), Na1–O2 2.395(11), Na1–O5 2.272(13), Na1–O6 2.311(13), Na2–O3 2.350(11), Na2–O4 2.289(12), Na2–O7 2.280(10), Na2–O8 2.234(14), Na1–F8 2.85(3), O1–In1–O2 81.9(4), O1–In1–O3 95.6(4), O2–In1–O3 170.8(4), O4–In1–O1 109.8(4), O4–In1–O2 91.2(4), O4–In1–O3 81.4(4), O1–In1–Cl1 127.1(3), O2–In1–Cl1 93.1(3), O3–In1–Cl1 95.4(3), O4–In1–Cl1 123.0(3). Symmetry operators:  $x, y, z; -x, \frac{1}{2} + y, -z$ .

in  $[\text{Na}_3\text{Y}(\text{OCH}(\text{CF}_3)_2)_6(\text{THF})_3]$  (2.238(9)–2.308(7) Å) [8]. The  $\text{Na}^+$  coordination environment is completed by two THF molecules and secondary contacts with the fluorine atoms from neighbouring hexafluoroalkoxide ligands. The average  $\text{Na} \cdots \text{F}$  distance is 3.31 Å, which is longer than the sum of corresponding covalent radii (2.27 Å) and shorter than the sum of van der Waals radii (3.80 Å) [35]. Two  $\text{In}(\mu\text{-O})_2\text{Na}$  units are twisted relative to the indium centre and have torsion angles  $\text{O}(4)\text{--In}(1)\text{--O}(2)\text{--Na}(1)$  of ca.  $-105^\circ$ ,  $\text{Na}(2)\text{--O}(3)\text{--In}(1)\text{--O}(1)$  of ca.  $-103^\circ$ ,  $\text{Na}(2)\text{--O}(4)\text{--In}(1)\text{--O}(2)$  of ca.  $169^\circ$ , and  $\text{Na}(1)\text{--O}(1)\text{--In}(1)\text{--O}(3)$  of ca.  $166^\circ$ .

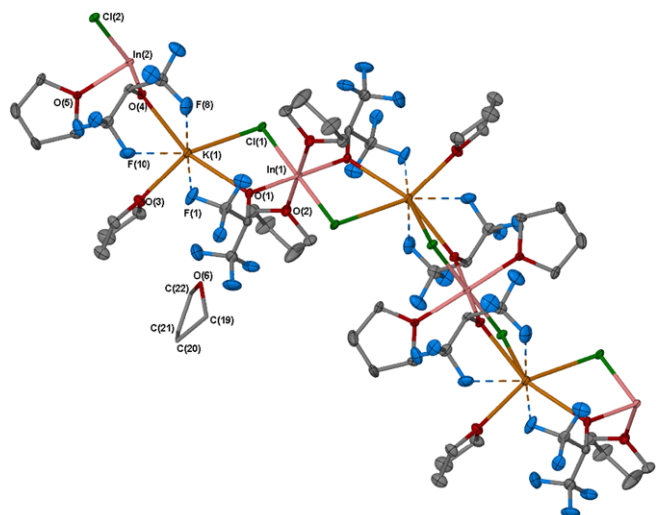
Compound **2**,  $[\text{Na}_3\text{In}(\text{OCH}(\text{CF}_3)_2)_6(\text{THF})_3]$ , crystallises in the triclinic crystal system, and space group  $P\bar{1}$ . The asymmetric unit consists of an indium atom, three sodium ions, six hexafluoroisopropoxide ligands, and three THF molecules (Fig. 2). The indium atom is in a distorted octahedral geometry ( $\text{O--In--O}$  bond angles from  $166.04(13)^\circ$  to  $76.94(12)^\circ$ ) created by six alkoxide ligands. The  $\text{In--O}$  distances in (**2**) are in the range 2.126(3)–2.160(3) Å. Each sodium ion is capped by two hexafluoroisopropoxide ligands and has one coordinated THF molecule. The coordination geometry around Na(1) is quasi-planar with the sum of the three angles being  $337.0^\circ$ , while Na(2) and Na(3) have planar geometry with sums of the angles of  $356.7^\circ$  and  $359.3^\circ$ , respectively. The average bond distances for  $\text{Na--O}_{\text{THF}}$  and for  $\text{Na--O}_{\text{alk}}$  are equal at 2.27 Å. Saturation of the Na cation coordination environment is completed by contacts with the fluorine atoms from neighbouring hexafluoroalkoxide ligands. For Na(1) there are four contacts with fluorine atoms with an average bond distance of 2.87 Å. Na(2) and Na(3) have only three contacts with fluorine ions with shorter bond distances (av. 2.57 Å and 2.49 Å, respectively). Na(1) also has an additional longer, weaker interaction (2.924(4) Å) with the F atom of a second neighbouring molecule. A very similar coordination environment for Na ions was observed in  $[\text{Na}_3\text{Y}(\text{OCH}(\text{CF}_3)_2)_6(\text{THF})_3]$  [8]. All  $\text{Na} \cdots \text{F}$  interactions in **2** fall within the range of the sum of the corresponding covalent radii (2.27 Å) and sum of the van der Waals radii (3.80 Å) [35]. One of the bridged heterobimetallic units,  $\text{In}(\mu\text{-O})_2\text{Na}$ , is flat, while two others are slightly bent with torsion angles of ca.  $-14.2^\circ$  for  $\text{In}(1)\text{--O}(5)\text{--Na}(3)\text{--O}(6)$  and ca.  $13.5^\circ$  for  $\text{In}(1)\text{--O}(3)\text{--Na}(2)\text{--O}(4)$ . Each sodium ion has only one coordinated molecule of THF in contrast with two THF molecules on each sodium ion in **1**. This can be explained by saturation of the coordination environment around Na in **2** with



**Fig. 2.** Crystal structure of **2** (hydrogen atoms are omitted for clarity). Thermal ellipsoids at 30% probability. Selected bond lengths (Å) and angles (°): In1–O1 2.141(3), In1–O2 2.126(3), In1–O3 2.160(3), In1–O4 2.155(3), In1–O5 2.142(3), In1–O6 2.145(3), Na1–O1 2.279(4), Na1–O2 2.258(4), Na1–O7 2.286(4), Na2–O3 2.234(4), Na2–O4 2.293(4), Na2–O8 2.240(4), Na3–O5 2.277(4), Na3–O6 2.265(4), Na3–O9 2.277(4), O1–In1–O3 95.01(13), O1–In1–O4 164.51(12), O1–In1–O6 95.01(13), O2–In1–O5 166.04(13), O2–In1–O6 94.95(13), O2–In1–O1 79.59(13), O2–In1–O4 88.12(13), O2–In1–O3 97.60(13), O4–In1–O3 77.17(13), O5–In1–O1 89.71(13), O5–In1–O4, 103.80(13), O5–In1–O3 92.19(13), O5–In1–O6 76.94(12), O6–In1–O3 165.16(12), O6–In1–O4 95.42(13). Symmetry operators:  $x, y, z; -x, -y, -z$ .

$\text{Na} \cdots \text{F}$  interactions from two neighbouring hexafluoroalkoxide ligands. While in compound **1** saturation is achieved by an additional THF ligand per sodium ion.

Compound **3**,  $[\text{KInCl}_2(\text{OCH}(\text{CF}_3)_2)_2(\text{THF})_3] \cdot \text{THF}$ , crystallises in the triclinic crystal system, and space group  $P\bar{1}$ . The X-ray structure shows that **3** is a mono-dimensional polymer with zig-zag chains of alternating K and In, which are joined by hexafluoroalkoxide ligands and Cl ions forming repetitive flat  $\text{In}(\mu\text{-O})(\mu\text{-Cl})\text{K}$  units (Fig. 3). Each Indium atom has additionally two *trans*-THF ligands. The asymmetric unit consists of one central K cation flanked by two In atoms, lying on crystallographic inversion centres, with bridging chloride and hexafluoroisopropoxide ligands, and an additional THF molecule is present in the crystal lattice. There is no evidence of strong inter-chain interactions, such as hydrogen bonding or  $\text{K} \cdots \text{F}$  interactions. Around the K ion there is a highly distorted square pyramidal geometry ( $\text{O--K--O}$  and  $\text{O--K--Cl}$  are in a range  $63.57(7)\text{--}150.40(11)^\circ$ ) created by having a THF molecule in an apical position, and two Cl atoms and two hexafluoroisopropoxide ligands in terminal positions. The average  $\text{K--O}_{\text{alk}}$  bond distance in **3**, 2.75 Å, is comparable with those in the heterobimetallic Sb and Sn complexes  $[\text{KSb}(\text{O}^t\text{Bu})_4]$ , 2.650(2)–2.967(2) Å [36],  $[\text{K}_2\text{Sb}(\text{O}^t\text{Bu})_5\text{dioxane}]$ , 2.592(3)–2.778(2) Å [36], and  $[\text{KSn}(\text{O}^t\text{Bu})_5]_n$ , 2.643(8)–2.814(7) Å [37]. The terminal bond distance  $\text{K}(1)\text{--O}(3)_{\text{THF}}$ , 2.651(4) Å, as expected, is shorter than the bridging  $\text{K--O}_{\text{alk}}$  (av. 2.75 Å). The bond length for  $\text{K}(1)\text{--Cl}(1)\#2$  is 3.1427(16) Å which is only marginally shorter than that found in crystalline KCl, 3.1476(4) Å [38]. Saturation of the  $\text{K}^+$  coordination sphere is completed by three secondary interactions with F atoms of hexafluoroisopropoxide ligands. The average  $\text{K} \cdots \text{F}$  interaction is 3.03 Å, which is longer than the sum of K and F covalent radii (2.69 Å) [39], but shorter than the sum of van der Waals radii of corresponding elements (4.25 Å) [35]. Each indium centre is six-coordinate and has almost perfect octahedral geometry formed by two THF molecules two chlorine atoms and two hexafluoroisopropoxide ligands. A

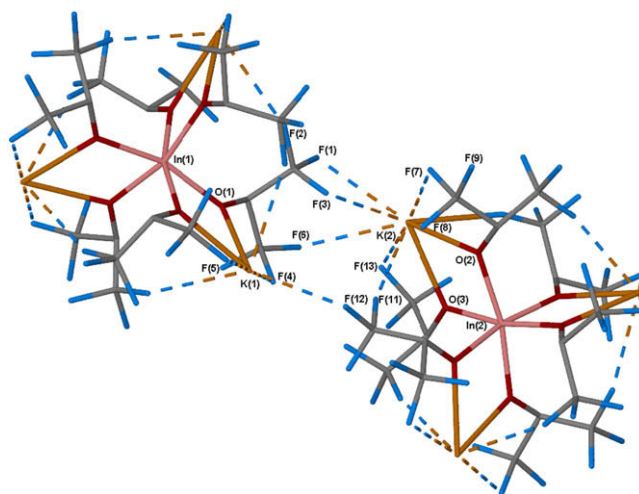


**Fig. 3.** Crystal structure of **3** (hydrogen atoms are omitted for clarity). Thermal ellipsoids given at 30% probability. Selected bond lengths (Å) and angles (°): In1–O1 2.101(3), In1–O2 2.269(3), In2–O4 2.097(3), In2–O5 2.272(3), In1–Cl1 2.4494(13), In2–Cl2 2.4562(12), K1–O3 2.651(4), K1–O4 2.726(4), K1–Cl1 3.1167(17), K1–F1 2.915(4), K1–F8 3.139(4), K1–F10 3.050(4), In1...K1 4.1263(11), O1–In1–O2 90.42(13), O1–In1–Cl1 86.29(10), O2–In1–Cl1 91.26(11), O4–In2–O5 89.89(12), O5–In2–Cl2 90.07(9), O4–In2–Cl2 85.84(9), O1–K1–Cl1 63.72(7), O3–K1–Cl1 129.77(9), O4–K1–Cl1 110.82(8), O3–K1–O1 105.44(12), O3–K1–O4 99.58(12), O4–K1–O1 150.40(11). Symmetry operators:  $x, y, z$  and  $-x, -y, -z$ .

slight deviation from 90° (86.29(10)–94.16(9)°) in angles around the In centres is caused by formation of In( $\mu$ -O)( $\mu$ -Cl)K units.

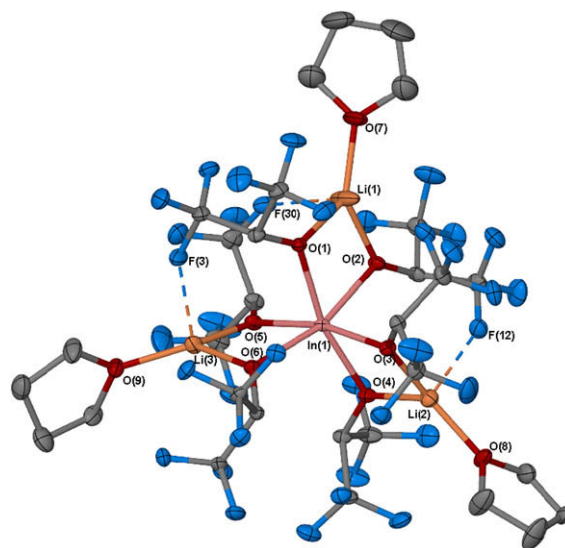
Compound **4**,  $[\text{K}_3\text{In}(\text{OCH}(\text{CF}_3)_2)_6]_n$ , crystallises in the hexagonal space group  $P\bar{3}c1$ . The asymmetric unit is comprised of two unique In atoms (In(1) resides on 3-fold and 2-fold rotation axes; In(2) resides on a 3-fold axis), two K atoms (K(2) has full occupancy and K(1) residing on a 2-fold rotation axis) and three isopropoxide ligands; one bound to In(1) and two bound to In(2). The six-coordinate In atoms have distorted octahedral geometry formed by six alkoxide ligands (Fig. 4). The O–In(1)–O and O–In(2)–O bond angle ranges are 79.4(5)–164.0(5)° and 81.1(3)–169.2(3)°, respectively. Each of the three potassium ions in the  $\text{K}_3\text{In}(\text{OCH}(\text{CF}_3)_2)_6$  unit is capped by two hexafluoroisopropoxide ligands, creating flat In( $\mu$ -O) $_2$ K parallelograms. All In(1)–O and In(2)–O distances in compound **4** are *ca* 2.16 Å. The K–O bond distances are close to 2.60 Å. The values for In–O and K–O bond distances are comparable with those observed in the BINOLate complex  $[\text{K}_3\text{In}((S)\text{-BINOLate})_3(\text{C}_7\text{H}_8)_2]\cdot 2\text{C}_7\text{H}_8$  (av. 2.15 Å and 2.61 Å, respectively) [27]. In the coordination sphere of each K ion are two hexafluoroalkoxide ligands and multiple K...F interactions. Four K...F contacts from the neighbouring ligands, and five K...F contacts from neighbouring molecules create a high coordination number of 11 for K atom. The K...F bond distances range from 2.71 Å to 3.23 Å. These distances are in the range of the sum of K and F covalent radii (2.69 Å) [39] and the sum of van der Waals radii of corresponding elements (4.25 Å) [35]. In contrast to compounds **2** and **5**, there are no solvent molecules coordinated to the K ions. Their coordination spheres are completed by numerous K...F inter- and intramolecular interactions. Compound **4** is organised in a hybrid three dimensional metal organic framework via K...F interactions from neighbouring molecules.

Compound **5**,  $[\text{Li}_3\text{In}(\text{OCH}(\text{CF}_3)_2)_6(\text{THF})_3]$ , crystallises in the monoclinic crystal system, and space group  $C2/c$ . The asymmetric unit consists of one indium atom, three lithium atoms, six hexafluoroisopropoxide ligands, and three THF molecules (Fig. 5). The six-coordinate In atom has a distorted octahedral geometry created by six alkoxide ligands. The O–In–O bond angles vary from 75.57(9) Å



**Fig. 4.** Crystal structure of **4** (hydrogen atoms are omitted for clarity). Inter- and intramolecular M...F bonds shown by hashed lines. Selected bond lengths (Å) and angles (°): In1–O1 2.162(9), In2–O2 2.154(9), In2–O3 2.154(9), K1–O1 2.609(10), K1–F4 2.708(9), K1–F12 2.820(11), K2–O3 2.626(10), K2–F1 3.052(12), K2–F3 3.080(11), K2–F6 3.110(10), K2–F11 2.792(10), K2–F13 2.770(9), In1–K1 3.876(6), In2–K2 3.841(3), O1–In1–O1#7 164.0(5), O1–In1–O1#8 79.4(5), O1#5–In1–O1 101.9(5), O1#6–In1–O1 90.4(3), O2–In2–O2#1 91.5(3), O2–In2–O3 96.5(3), In1–O1–K1 108.3(4), In2–O3–K2 106.5(3). Symmetry operators:  $x, y, z$ ;  $-x, -y, -z$ ;  $-x+y, -x, z$ ;  $x-y, -y, \frac{1}{2}-z$ ;  $-x, -x+y, \frac{1}{2}-z$ ;  $y, x, \frac{1}{2}-z$ ;  $-x, -y, -z$ ;  $x-y, x, -z$ ;  $-x+y, y, \frac{1}{2}+z, x, x-y, \frac{1}{2}+z, -y, -x, \frac{1}{2}+z$ .

to 166.96(9) Å. In–O<sub>alk</sub> distances in **5** are in the range 2.140(2)–2.163(2) Å. Each Li atom is capped by two alkoxide ligands (Li–O<sub>alk</sub> av. 1.89 Å) and has one-coordinated THF molecule (Li–O<sub>THF</sub>, av. 1.87 Å) and one secondary contact with a fluorine atom from a neighbouring alkoxide ligand. The Li(2)...F(12) and Li(3)...F(3)



**Fig. 5.** Crystal structure of **5** (hydrogen atoms are omitted for clarity). Thermal ellipsoids given at 30% probability. Selected bond lengths (Å) and angles (°): In1–O1 2.144(2), In1–O2 2.163(2), In1–O3 2.151(2), In1–O4 2.140(2), In1–O5 2.161(2), In1–O6 2.145(2), Li1–O1 1.862(9), Li1–O2 1.882(9), Li1–O7 1.862(9), Li2–O3 1.884(7), Li2–O4 1.912(8), Li3–O5 1.887(7), Li3–O6 1.903(7), Li2–O8 1.865(7), Li3–O9 1.891(7), O1–In1–O2 77.51(9), O1–In1–O3 95.78(9), O1–In1–O6 89.98(9), O1–In1–O5 94.69(10), O3–In1–O5 166.96(9), O3–In1–O2 94.31(10), O4–In1–O3 76.29(9), O4–In1–O1 165.48(9), O4–In1–O6, 102.88(9), O4–In1–O5 95.02(10), O4–In1–O2 90.83(9), O5–In1–O2 95.54(10), O6–In1–O2 164.13(10), O6–In1–O3 96.66(9), O6–In1–O5 75.57(9), O1–Li1–O2 92.1(4), O3–Li2–O4 88.5(3), O5–Li3–O6 88.2(3). Symmetry operators:  $x, y, z$ ;  $-x, y, \frac{1}{2}-z$ ;  $\frac{1}{2}+x, \frac{1}{2}+y, z$ ;  $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ ;  $-x, -y, -z$ ;  $x, -y, \frac{1}{2}+z$ ;  $\frac{1}{2}-x, \frac{1}{2}-y, -z$ ;  $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$ .

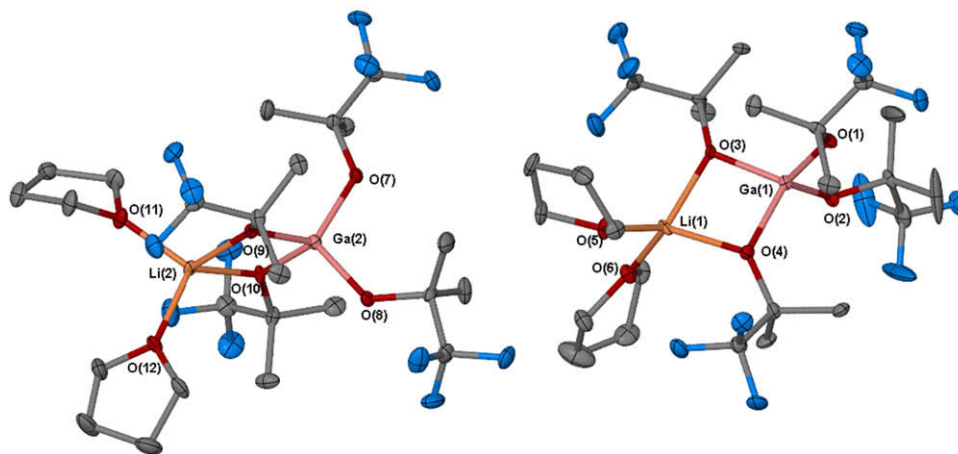
contacts have an average bond distance of 2.180(8) Å, while the Li(1)⋯F(30) is significantly longer at 2.652(15) Å. The length of F⋯Li contacts is within the sphere of the sum of covalent radii (2.07 Å) [39] and the sum of van der Waals radii (3.32 Å) [35]. The presence of Li⋯F contacts explains the distortion around the In centre. One of the In(μ-O)<sub>2</sub>Li units is reasonably flat with a torsion angle of ca. −4.3° for In(1)–O(1)–Li(1)–O(2), while two others are slightly bent with torsion angles of ca. 13.7° for In(1)–O(6)–Li(3)–O(5), and ca. −11.5° for In(1)–O(3)–Li(2)–O(4). The coordination geometry around the Li atoms is quasi-planar with the sums of the three angles around Li(1), Li(2), and Li(3) of ca. 360°, 352.6°, 355.5°, respectively.

The coordination sphere of the Li and Na ions in compounds **1**, **2**, and **5** is completed by THF molecules and secondary F contacts. These 'saturate' the Li (CN = 4) and Na (CN = 6–7) coordination spheres and prevent polymerization. In contrast, despite the presence of K⋯F interactions compounds **3** and **4** are organised in linear and three dimensional polymers, respectively, most likely due to the larger ionic radius of K<sup>+</sup>. Structural similarities are observed in compounds **2**, **4**, and **5**. They are also comparable to those of the sesquialkoxides [40] [Al((μ-O<sup>i</sup>Pr)<sub>2</sub>Al(μ-O<sup>i</sup>Pr)<sub>2</sub>)<sub>3</sub>] [41], [Ga(Me-Ga(OCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me-4)<sub>3</sub>)<sub>3</sub>] [42], [In(Me<sub>2</sub>In(OCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me-4)<sub>2</sub>)<sub>3</sub>] [42], [In{(μ-OCH<sub>2</sub>Et)<sub>2</sub>In(OCH<sub>2</sub>Et)<sub>2</sub>)<sub>3</sub>] [20], [Ga{(μ-O<sup>i</sup>Pr)<sub>2</sub>Ga(O<sup>i</sup>Pr)<sub>2</sub>)<sub>3</sub>] [19]; bimetallic Y–Al complexes [Na<sub>3</sub>Y(OCH(CF<sub>3</sub>)<sub>2</sub>)<sub>6</sub>(THF)<sub>3</sub>] [8], [Y((μ-O<sup>t</sup>Bu)(μ-OMe)AlMe<sub>2</sub>)<sub>3</sub>] [43]; BINOL compounds of indium [Li<sub>3</sub>In((S)-BINOLate)<sub>3</sub>(DME)<sub>3</sub> · 2DME] [27] and [K<sub>3</sub>In((S)-BINOLate)<sub>3</sub>(C<sub>7</sub>H<sub>8</sub>)<sub>3</sub> · 2C<sub>7</sub>H<sub>8</sub>] [27]. In general, all of them have a six-coordinate central atom coordinated via O bridges with three other metal atoms.

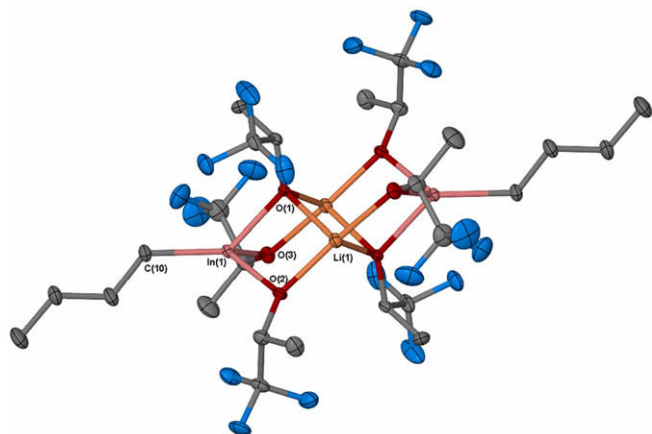
Compound **6**, [LiGa(OC(CH<sub>3</sub>)<sub>2</sub>CF<sub>3</sub>)<sub>4</sub>(THF)<sub>2</sub>], crystallises in the monoclinic crystal system, and space group *P*2<sub>1</sub> (refined as racemic twin). The asymmetric unit has two molecules, each consisting of four-coordinate gallium and lithium ions, four 2-trifluoromethyl-2-propoxide ligands, and two THF molecules (Fig. 6). The gallium atoms adopt a slightly distorted tetrahedral geometry created by four alkoxide ligands with angles in a range of 88.3(2)–109.7(2)°. The average Ga–O bond lengths for the terminal alkoxides is 1.81 Å and for the bridging alkoxides is slightly longer at 1.86 Å. The presence of the more electropositive Li ion in the Ga(μ-O)<sub>2</sub>Li unit exerts an influence on the bond distance Ga–O<sub>bridging</sub>, which is shorter than for the other reported gallium compounds with

Ga(μ-O)<sub>2</sub>Ga units (range for Ga–O<sub>bridging</sub>, 1.91 Å–2.10 Å) [44,45]. A similar observation is made for the Li–O bond lengths. The average Li–O<sub>alk</sub> bond length is 1.99 Å, while Li–O<sub>THF</sub> average bond length is at 1.95 Å. The longer length of the M–O<sub>bridging</sub> (M = Li, Ga) bond distances are expected and can be explained by the sharing of the electron density between two metals centres in the unit Ga(μ-O)<sub>2</sub>Li, while for terminal ligands the electron density is only shared between the ligands and the metal resulting in shorter M–O<sub>terminal</sub> bond distances. The Li–O<sub>THF</sub> bond distances in **6** are comparable with those observed in solvated lithium aryloxides, such as [Li(OPh)(THF)<sub>4</sub>] (av. 1.91 Å) and in [Li(Dip)(THF)<sub>3</sub>] (Dip = OC<sub>6</sub>H<sub>3</sub>(2,6-<sup>t</sup>Pr)<sub>2</sub>) (av. 1.94 Å) [46]. The lithium ions also have a slightly distorted tetrahedral geometry, formed by two alkoxide ligands and two-coordinated terminal THF molecules. The angles around the Li ions are in the range 81.0(4)–121.0(6)°. The distortion of tetrahedral geometry around the Li and Ga centres is caused by the formation of Ga(μ-O)<sub>2</sub>Li units. The average Li⋯Ga distance is 2.83 Å, which is slightly longer than the sum of covalent radii of corresponding atoms (2.6 Å) [39]. The Ga(μ-O)<sub>2</sub>Li parallelograms of both molecules show slight differences in the degree of bending; one is almost flat and has a torsion angle of ca. 2.2° for O(9)–Li(2)–O(10)–Ga(2), while the other is more bent and has a torsion angle of ca. −5.9° for Li(1)–O(3)–Ga(1)–O(4).

Compound **7**, [LiIn(OCH(CH<sub>3</sub>)CF<sub>3</sub>)<sub>3</sub>Bu]<sub>2</sub>, crystallises in the triclinic crystal system, and space group *P*1̄. The asymmetric unit consists of one indium and one lithium atom, three 1,1,1-trifluoro-2-propoxide ligands, and a *n*-butyl group. The four-coordinate In atoms have distorted tetrahedral geometry created by three alkoxide ligands, and a *n*-butyl group (Fig. 7). The angles around the In centre are in the range of 81.36(9)–132.07(15)°. The average In–O<sub>alk</sub> bond distance is 2.09 Å. The In(1)–C(10) bond distance is 2.131(4) Å and it is within the range reported for terminal In–C bonds in [MeInCl(O<sup>t</sup>Bu)<sub>2</sub>] and [MeInBr(O<sup>t</sup>Bu)<sub>2</sub>] [33]. The coordination geometry around the lithium ions is highly distorted formed by four alkoxide ligands, where the range of O–Li–O angles is from 86.3(3)° to 167.1(4)°. The average Li–O bond length in the Li<sub>2</sub>(μ-O)<sub>2</sub> unit is 2.01 Å, while in the In(μ-O)<sub>2</sub>Li unit, the average Li–O bond length is 1.96 Å. Similar bond distances have been observed in lithium phenolates such as [Li(OPh)(THF)<sub>4</sub>], [Li(OC<sub>6</sub>H<sub>4</sub>(2-Me))(THF)<sub>4</sub>], [Li(OC<sub>6</sub>H<sub>3</sub>(2,6-Me)<sub>2</sub>)(THF)<sub>4</sub>], and [Li(OC<sub>6</sub>H<sub>4</sub>(2-<sup>t</sup>Pr))<sub>2</sub>(THF)<sub>4</sub>] [46].



**Fig. 6.** Crystal structure of **6** (hydrogen atoms are omitted for clarity). Thermal ellipsoids given at 30% probability. Selected bond lengths (Å) and angles (°): Ga1–O1 1.809(5), Ga1–O2 1.808(5), Ga1–O3 1.864(4), Ga1–O4 1.864(5), Ga2–O7 1.821(5), Ga2–O8 1.813(5), Ga2–O9 1.872(5), Ga2–O10 1.850(4), Li1–O3 1.982(12), Li1–O4 2.016(12), Li1–O5 1.935(12), Li1–O6 1.941(12), Li2–O9 1.976(12), Li2–O10 1.985(13), Li2–O11 1.974(12), Li2–O12 1.939(13), O1–Ga1–O3 117.6(2), O1–Ga1–O4 117.13(19), O2–Ga1–O1 109.7(2), O2–Ga1–O3 111.2(2), O2–Ga1–O4 111.4(2), O4–Ga1–O3 88.3(2), O7–Ga2–O9 117.7(2), O7–Ga2–O10 116.9(2), O8–Ga2–O7 109.2(2), O8–Ga2–O9 111.6(2), O8–Ga2–O10 111.4(2), O10–Ga2–O9 88.8(2), Ga1–O4–Li1 94.5(4), Ga1–O3–Li1 95.6(4), Ga2–O9–Li2 94.3(4), Ga2–O10–Li2 94.7(4). Symmetry operators: *x*, *y*, *z*;  $-x$ ,  $\frac{1}{2} + y$ ,  $-z$ .



**Fig. 7.** Crystal structure of **7** (hydrogen atoms are omitted for clarity). Thermal ellipsoids given at 30% probability. Selected bond lengths (Å) and angles (°): In1–O1 2.108(2), In1–O2 2.083(2), In1–O3 2.071(3), Li1–O1 2.011(7), Li1–O2 1.950(6), In1–C10 2.131(4), O2–In1–O1 81.38(9), O3–In1–O2 100.04(10), O3–In1–O1 81.36(9), O3–In1–C10 132.07(15), O2–In1–C10 118.08(15), O1–In1–C10 129.55(13), Li1–O1–In1 93.83(19), Li1–O2–In1 96.4(2), O2–Li1–O1 87.2(3). Symmetry operators:  $x, y, z; -x, -y, -z$ .

#### 2.4. Discussion

The formation of ‘ate’ complexes with highly Lewis acidic metals, such as those of group 13 and the lanthanoids, can be difficult to prevent, particularly when the reaction medium does not immediately support precipitation, and hence complete separation of any alkali metal halide salts resulting from metathesis reactions. As such numerous examples exist as both solvent separated ion-pairs, and as contact ion-pairs with various bridging modes [47].

The complexes  $[\text{Na}_2\text{InCl}(\text{OCH}(\text{CF}_3)_2)_4(\text{THF})_4]$  (**1**),  $[\text{Na}_3\text{In}(\text{OCH}(\text{CF}_3)_2)_6(\text{THF})_3]$  (**2**),  $[\text{K}_3\text{In}(\text{OCH}(\text{CF}_3)_2)_6]_n$  (**4**) and  $[\text{Li}_3\text{In}_3(\text{OCH}(\text{CF}_3)_2)_6(\text{THF})_3]$  (**5**), all show similarities to the formation of ‘ate’ complexes of the lanthanoid metals [47,48]. For example, sodium yttrium fluoroalkoxide,  $[\text{Na}_3\text{Y}(\text{OCH}(\text{CF}_3)_2)_6(\text{THF})_3]$ , was synthesised via the metathesis reaction of  $\text{YCl}_3$  and  $\text{NaOCH}(\text{CF}_3)_2$  in a 1:6 molar ratio [8,48]. Veith et al. have commented on the fact that the problem of alkali metal or halide ion retention is more common for the smaller Li and Na ions, and that the use of the larger K ion can, in some cases, overcome the problem, supposedly because of lower solubility of KCl salt in common organic solvents in comparison with LiCl and NaCl [49]. They also noticed, however, that using the heavier alkali metals does not always solve the problem of salt retention [49]. For example, bimetallic lanthanide complexes,  $[\text{KLn}(\text{OAr})_4]$  (Ln = Nd, Er, Lu), were isolated from the reaction of  $\text{LnCl}_3$  (anhydrous) with  $\text{KOAr}$  in either 1:3 or 1:4 molar ratios [49–51]. Also, Labrize et al., pointed out that the retention of alkali metals in alkoxide complexes only occurs if bulky OR ligands and/or small alkali metals were used, as well as through poor stoichiometry control [48]. In the present work three different alkali metals were used, Li, Na and K, to synthesise a range of indium alkoxides. Also, reactions with different stoichiometries (1:3 and 1:6) of  $\text{InCl}_3$  and  $\text{MOCH}(\text{CF}_3)_2$  were performed. In the case of indium the size of the alkali metal and the stoichiometry did not influence the retention of alkali metals in the structure, since in the reactions with a 1:3 stoichiometry the isolated products still contained group 1 metal ions and halide ions. When Li and Na alkoxides were used, the isolated compounds **1**, **2**, and **5** shared the presence of THF ligands in the coordination sphere of the alkali metals. If the K alkoxide was employed in the reaction with 1:6 stoichiometry the isolated compound **4** had no solvent in the lattice and behaves as a polymer in the solid-state due to intermolec-

ular  $\text{K} \cdots \text{F}$  interactions. In contrast, the reaction with a 1:3 stoichiometry produced the polymeric compound **3**,  $[\text{KInCl}_2(\text{OCH}(\text{CF}_3)_2)_2(\text{THF})_3]_n \cdot \text{THF}$ . In an attempt to synthesise a gallium alkoxide via the reaction of  $\text{GaCl}_3$  with  $\text{LiOC}(\text{CH}_3)_2\text{CF}_3$ , a bimetallic complex  $[\text{LiGa}(\text{OC}(\text{CH}_3)_2\text{CF}_3)_4(\text{THF})_2]$  (**6**) was isolated. Compound  $[\text{LiIn}(\text{OCHCH}_3\text{CF}_3)_3\text{Bu}]_2$  (**7**) retains Li in the structure. The presence of a Bu group on the indium atom can be attributed to the retention of excess or unreacted  $^n\text{BuLi}$  in the reaction mixture. A possible explanation for the formation of the discrete molecular compounds **6** and **7** is that the  $\text{OC}(\text{CH}_3)_2\text{CF}_3$  and  $\text{OCHCH}_3\text{CF}_3$  ligands have only one fluorinated Me group and minimise the possibility of close  $\text{M} \cdots \text{F}$  interactions in comparison with  $\text{OCH}(\text{CF}_3)_2$ .

Is it possible to avoid the formation of ‘ate’ complexes completely by avoiding metal salts in the formation of Gp 13 alkoxides? Perhaps not. Hoffman has previously described the formation and isolation of the monometallic ammonium indium ‘ate’ complexes, for example  $[\text{H}_2\text{tmp}][\text{In}\{\text{OCMe}(\text{CF}_3)_2\}_4]$ , even in metathesis reactions using indium *tris*-amides and fluorinated alcohols [16].

### 3. Conclusions

In this work the synthesis and characterisation of seven new heterobimetallic alkoxide complexes with groups 1/13 metals are reported;  $[\text{Na}_2\text{InCl}(\text{OCH}(\text{CF}_3)_2)_4(\text{THF})_4]$ ,  $[\text{Na}_3\text{In}(\text{OCH}(\text{CF}_3)_2)_6(\text{THF})_3]$ ,  $[\text{KInCl}_2(\text{OCH}(\text{CF}_3)_2)_2(\text{THF})_3]_n \cdot \text{THF}$ ,  $[\text{K}_3\text{In}(\text{OCH}(\text{CF}_3)_2)_6]_n$ ,  $[\text{Li}_3\text{In}(\text{OCH}(\text{CF}_3)_2)_6(\text{THF})_3]$ ,  $[\text{LiGa}(\text{OC}(\text{CH}_3)_2\text{CF}_3)_4(\text{THF})_2]$ , and  $[\text{LiIn}(\text{OCHCH}_3\text{CF}_3)_3\text{Bu}]_2$ . The structural motif  $\text{M}'(\mu\text{-O})_2\text{M}$  (where  $\text{M}' = \text{Ga, In}$ ;  $\text{M} = \text{Li, Na, K}$ ) is a dominant part of the solid-state structures of the heterobimetallic alkoxides. Indium and gallium centres have tetrahedral or octahedral molecular geometry. The size of alkali metal determines the presence of THF ligands in the coordination sphere. Although, synthesised compounds **1–7** are volatile solids, they may not be useful precursors for oxide materials. However, compounds **1–7** can be potential catalysts or ligand transfer reagents in organic synthesis due to presence of the active mixed metal  $\text{M–Ga/In}$  ( $\text{M} = \text{Li, Na, K}$ ) system.

### 4. Experimental

#### 4.1. General details

All syntheses and compound manipulations were carried out using inert atmosphere techniques under a dry  $\text{N}_2$  atmosphere and a recirculating Ar gas glove box. All solvents were dried using a MBraun SPS-800 and stored over molecular sieves (4A). All reagents were purchased from Sigma Aldrich and used without further purification. 1,1,1,3,3,3-hexafluoro-2-propanol was dried under reflux with Mg and stored over molecular sieves (4A). NaH was obtained in 60% oil and washed prior use with hexane. NMR spectra were obtained with Bruker AV200 and DPX-300 spectrometers with chemical shifts referenced  $d_6$ -DMSO,  $\text{C}_6\text{D}_6$ , or  $d_8$ -THF where appropriate. Elemental analysis was carried out by CMAS, Melbourne, Australia and the Campbell Microanalytical Laboratory, New Zealand.

#### 4.2. Synthesis of $[\text{Na}_2\text{InCl}(\text{OCH}(\text{CF}_3)_2)_4(\text{THF})_4]$ (**1**)

To a suspension of NaH (0.50 g, 20 mmol) in THF a solution of  $\text{HOCH}(\text{CF}_3)_2$  (2.10 ml, 20 mmol) in THF was slowly added at  $0^\circ\text{C}$ . The reaction was stirred for 1 h at room temperature. The resulting  $\text{NaOCH}(\text{CF}_3)_2$  was added slowly to  $\text{InCl}_3$  (1.46 g, 6.60 mmol) in THF at  $-78^\circ\text{C}$ . The reaction was left overnight at room temperature. After evaporation of THF an oily yellowish solid remained which was then dissolved in hexane and filtered. Upon cooling at

–30 °C yellow crystals of **1** were obtained. Yield 2.50 g, 33%. <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>, 30 °C): δ 1.26 (m, 2H, THF), 3.31 (m, 2H, THF), 5.01 (m, 1H, OCH(CF<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>, 30 °C): δ 23.2 (s, C, THF), 68.5 (s, C, THF), 72.9 (p, OCH(CF<sub>3</sub>)<sub>2</sub>, J(C, F) = 30.9 Hz), 122.9 (q, CF<sub>3</sub>, J(C, F) = 282.6 Hz). <sup>19</sup>F NMR (300 MHz, d<sub>6</sub>-DMSO, 30 °C): δ –74.6 (m). Elemental Anal. Calc. (%) for C<sub>28</sub>H<sub>36</sub>ClF<sub>24</sub>InNa<sub>2</sub>O<sub>8</sub>: C, 29.17; H, 3.15. Elemental Anal. Calc. (%) for C<sub>24</sub>H<sub>28</sub>ClF<sub>24</sub>InNa<sub>2</sub>O<sub>7</sub> (loss of THF): C, 26.67; H, 2.61. Found: C, 27.40; H, 2.67%.

#### 4.3. Synthesis of [Na<sub>3</sub>In(OCH(CF<sub>3</sub>)<sub>2</sub>)<sub>6</sub>(THF)<sub>3</sub>] (**2**)

To a suspension of NaH (0.50 g, 20.0 mmol) in THF, a solution of HOCH(CF<sub>3</sub>)<sub>2</sub> (2.10 ml, 20 mmol) in THF was slowly added at 0 °C. The reaction was stirred for 1 h at room temperature. The resulting NaOCH(CF<sub>3</sub>)<sub>2</sub> was added slowly to InCl<sub>3</sub> (0.74 g, 3.30 mmol) in THF at –78 °C. The reaction was left overnight at room temperature. After evaporation of THF an oily yellowish solid was dissolved in hexane and filtered. Upon cooling at –30 °C colourless crystals of **2** were obtained from hexane. Yield 2.10 g, 47%. M.p. 49–51 °C. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 30 °C): δ 1.26 (m, 2H, THF), 3.34 (m, 2H, THF), 5.14 (m, 1H, OCH(CF<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 30 °C): δ 25.6 (s, C, THF), 68.5 (s, C, THF), 72.9 (m, CH). <sup>13</sup>C NMR (300 MHz, d<sub>6</sub>-DMSO, 30 °C): δ 24.3 (s, C, THF), 66.2 (s, C, THF), 71.6 (p, CH, J(C, H) = 30.55 Hz), 121.9 (q, CF<sub>3</sub>, J(C, F) = 284.25 Hz). Elemental Anal. Calc. (%) for C<sub>30</sub>H<sub>30</sub>F<sub>36</sub>InNa<sub>3</sub>O<sub>9</sub>: C, 25.70; H, 2.16. Found: C, 25.59; H, 2.25%.

#### 4.4. Synthesis of [KInCl<sub>2</sub>(OCH(CF<sub>3</sub>)<sub>2</sub>)<sub>2</sub>(THF)<sub>3</sub>]<sub>n</sub> · THF (**3**)

Potassium metal (0.78 g, 20.0 mmol) was placed in THF (20 mL) and a solution of HOCH(CF<sub>3</sub>)<sub>2</sub> (2.1 ml, 20 mmol) in THF (20 mL) slowly added at 0 °C. The reaction was left for 1 h at room temperature. The resulting KOCH(CF<sub>3</sub>)<sub>2</sub> was added to a solution of InCl<sub>3</sub> (0.25 g, 6.60 mmol) in THF at –78 °C. The reaction mixture was left overnight to react at room temperature. The volatile compounds were removed under vacuum to give a white oily solid which was dissolved in hexane. The single crystals of compound **3** grew at –30 °C. Yield 1.80 g, 34%. M.p. 120–121 °C. <sup>1</sup>H NMR (300 MHz, d<sub>6</sub>-DMSO, 30 °C): δ 1.75 (m, 3H, THF), 3.57 (m, 3H, THF), 4.88 (m, 1H, OCH(CF<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (300 MHz, d<sub>6</sub>-DMSO, 30 °C): 24.5 (s, CH<sub>2</sub>, THF), 66.4 (s, CH<sub>2</sub>, THF), 71.6 (m, CH), 121.7 (q, CF<sub>3</sub>, J(C, F) = 285.5 Hz). <sup>19</sup>F NMR (376 MHz, d<sub>6</sub>-DMSO, 30 °C): δ –73.1 (m). Elemental Anal. Calc. (%) for C<sub>18</sub>H<sub>26</sub>Cl<sub>2</sub>F<sub>12</sub>In<sub>2</sub>KO<sub>5</sub> (without lattice THF molecule): C, 24.29; H, 2.94. Found: C, 23.27; H, 2.72%.

#### 4.5. Synthesis of [K<sub>3</sub>In(OCH(CF<sub>3</sub>)<sub>2</sub>)<sub>6</sub>]<sub>n</sub> (**4**)

Potassium metal (0.78 g, 20.0 mmol) was placed in THF (20 mL) and a solution of HOCH(CF<sub>3</sub>)<sub>2</sub> (2.10 ml, 20.0 mmol) in THF (20 mL) slowly added at 0 °C. The reaction was left for 1 h at room temperature. The resulting KOCH(CF<sub>3</sub>)<sub>2</sub> was added to a solution of InCl<sub>3</sub> (0.74 g, 3.30 mmol) in THF at –78 °C. The reaction mixture was left overnight to react at room temperature. The volatile compounds were removed under vacuum and the resulted white oily solid was dissolved in toluene and THF mixture. Single crystals of compound **4** grew at –30 °C. Yield 1.90 g, 48%. M.p. 121–123 °C. <sup>1</sup>H NMR (300 MHz, d<sub>8</sub>-THF, 30 °C): δ 4.59 (p, OCH(CF<sub>3</sub>)<sub>2</sub>, J(H, F) = 6.4 Hz). <sup>13</sup>C NMR (300 MHz, d<sub>8</sub>-THF, 30 °C): 70.4 (m, CH), 122.2 (q, CF<sub>3</sub>, J(C, F) = 281.6 Hz). <sup>1</sup>H NMR (300 MHz, d<sub>6</sub>-DMSO, 30 °C): δ 5.04 (bs, OCH(CF<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (300 MHz, d<sub>6</sub>-DMSO, 30 °C): 67.0 (p, CH, J(C, H) = 31.7 Hz), 119.9 (q, CF<sub>3</sub>, J(C, F) = 284.5 Hz). <sup>19</sup>F NMR (376 MHz, d<sub>6</sub>-DMSO, 30 °C): δ –73.4 (d, CF<sub>3</sub>, J(F, H) = 7.5 Hz). Elemental Anal. Calc. (%) for C<sub>18</sub>H<sub>6</sub>F<sub>36</sub>InK<sub>3</sub>O<sub>6</sub>: C, 17.52; H, 0.49. Found: C, 17.50; H, 0.50%.

#### 4.6. Synthesis of [Li<sub>3</sub>In(OCH(CF<sub>3</sub>)<sub>2</sub>)<sub>6</sub>(THF)<sub>3</sub>] (**5**)

A solution of HOCH(CF<sub>3</sub>)<sub>2</sub> (2.60 ml, 25.0 mmol) in THF (40 mL) was slowly added at 0 °C to a solution of <sup>n</sup>BuLi (1.3 M in hexane, 19 ml, 25 mmol). The reaction was left for 1 h at room temperature. The resulting LiOCH(CF<sub>3</sub>)<sub>2</sub> was added to a solution of InCl<sub>3</sub> (0.89 g, 4.00 mmol) in THF at –78 °C and left overnight to react at room temperature. After evaporation of volatile compounds under vacuum an oily liquid was obtained. This was dissolved in hexane and filtered. Colourless crystals of compound **5** grew at –30 °C. Yield: 2.60 g, 49%. M.p. 110–112 °C. <sup>1</sup>H NMR (300 MHz, d<sub>6</sub>-C<sub>6</sub>D<sub>6</sub>, 30 °C): δ 1.24 (m, 2H, THF), 3.46 (m, 2H, THF), 5.16 (bs, 1H, OCH(CF<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (300 MHz, d<sub>6</sub>-C<sub>6</sub>D<sub>6</sub>, 30 °C): 23.8 (s, CH), 67.1 (s, CH), 71.4 (m, CH), 121.4 (q, CF<sub>3</sub>, J(C, F) = 282.45 Hz). <sup>19</sup>F NMR (300 MHz, d<sub>6</sub>-C<sub>6</sub>D<sub>6</sub>, 30 °C): δ –74.8 (s, CF<sub>3</sub>). IR (cm<sup>–1</sup>): 1371 (w), 1284 (m), 1174 (s), 1086 (s), 1041 (m), 885 (w), 852 (m), 743 (w), 685 (m). Elemental Anal. Calc. (%) for C<sub>30</sub>H<sub>30</sub>F<sub>36</sub>InLi<sub>3</sub>O<sub>9</sub>: C, 26.61; H, 2.23. Found: C, 26.67; H, 2.32%.

#### 4.7. Synthesis of [LiGa(OC(CH<sub>3</sub>)<sub>2</sub>CF<sub>3</sub>)<sub>4</sub>(THF)<sub>2</sub>] (**6**)

A solution of HOC(CH<sub>3</sub>)<sub>2</sub>CF<sub>3</sub> (1.80 ml, 20.0 mmol) in THF (40 mL) was slowly added at 0 °C to a solution of <sup>n</sup>BuLi (1.6 M in hexane, 12.5 ml, 20 mmol). The reaction was left for 1 h at room temperature. The resulting solution of LiOC(CH<sub>3</sub>)<sub>2</sub>CF<sub>3</sub> was added to a solution of GaCl<sub>3</sub> (0.50 M in pentane, 6.70 ml, 3.00 mmol) in hexane at –78 °C and left stirring overnight at room temperature. After evaporation of volatile compounds under vacuum an oily liquid was obtained which was taken up in hexane and filtered. Yellow crystals of compound **6** grew at –30 °C from hexane. Yield 1.00 g, 46%. M.p. 116–118 °C. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 30 °C): δ 1.58 (s, 3H, CH<sub>3</sub>), 1.38 (m, 1H, THF), 3.50 (m, 1H, THF). <sup>13</sup>C NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 30 °C): δ 25.8 (s, OC(CH<sub>3</sub>)<sub>2</sub>CF<sub>3</sub>), 25.6 (s, THF), 68.6 (s, THF), 74.3 (m, OC(CH<sub>3</sub>)<sub>2</sub>CF<sub>3</sub>), 126.8 (q, CF<sub>3</sub>, J(C, F) = 284.0 Hz). <sup>1</sup>H NMR (300 MHz, d<sub>6</sub>-DMSO, 30 °C): δ 1.30 (s, 3H, CH<sub>3</sub>), 1.77 (m, 1H, THF), 3.60 (m, 1H, THF). <sup>13</sup>C NMR (300 MHz, d<sub>6</sub>-DMSO, 30 °C): δ 24.2 (s, OC(CH<sub>3</sub>)<sub>2</sub>CF<sub>3</sub>), 24.6 (s, THF), 66.5 (s, THF), 71.1 (m, OC(CH<sub>3</sub>)<sub>2</sub>CF<sub>3</sub>). <sup>19</sup>F NMR (376 MHz, d<sub>6</sub>-DMSO, 30 °C): δ –82.3 (s). Elemental Anal. Calc. (%) for C<sub>24</sub>H<sub>40</sub>F<sub>12</sub>GaLiO<sub>6</sub>: C, 39.53; H, 5.53. Found: C 39.05; H 5.51%.

#### 4.8. Synthesis of [LiIn(OCHCH<sub>3</sub>CF<sub>3</sub>)<sub>3</sub>Bu]<sub>2</sub> (**7**)

<sup>n</sup>BuLi (1.60 M in hexane, 24.4 ml, 39.0 mmol) was added to (Me<sub>3</sub>Si)<sub>2</sub>NH (8.10 ml, 39.0 mmol) at room temperature and left for 1 h to react. The reaction mixture was then added to a solution of InCl<sub>3</sub> (2.90 g, 13.0 mmol) in THF at –10 °C and left stirring for 3 h at room temperature. THF was then evaporated and replaced by hexane, forming a precipitate which was filtered off. To this solution of In(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub> in hexane was added HOCHCH<sub>3</sub>CF<sub>3</sub> (3.5 ml, 39 mmol) at –78 °C. No precipitation was observed. The reaction mixture was left overnight at room temperature. After evaporation of the volatile compounds under vacuum an oily product was isolated and redissolved in hexane. Colourless crystals of compound **7** grew at –30 °C from hexane. Yield 1.90 g, 28%. M.p. 67–69 °C. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 30 °C): δ 0.88 (t, 3H, InCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, J(H, H) = 7.3 Hz), 1.17 (d, 9H, J(H, H) = 6.5 Hz, OCHCH<sub>3</sub>CF<sub>3</sub>), 1.28 (sep, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, J(H, H) = 7.3 Hz), 1.65 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.29 (bs, 3H, OCHCH<sub>3</sub>CF<sub>3</sub>). <sup>13</sup>C NMR (300 MHz, d<sub>6</sub>-C<sub>6</sub>D<sub>6</sub>, 30 °C): 12.2 (s, OCHCH<sub>3</sub>CF<sub>3</sub>), 18.3 (s, CH<sub>3</sub>), 27.0 (s, CH<sub>2</sub>), 27.7 (s, CH<sub>2</sub>), 67.2 (m, CH), 124.5 (q, CF<sub>3</sub>, J(C, F) = 281.2 Hz). <sup>19</sup>F NMR (376 MHz, d<sub>6</sub>-C<sub>6</sub>D<sub>6</sub>, 30 °C): δ –78.1 (bs). Elemental Anal. Calc. (%) for C<sub>13</sub>H<sub>21</sub>F<sub>9</sub>InLiO<sub>3</sub>: C, 30.14; H, 4.09. Found: C, 30.48; H, 4.38%.

**Table 1**  
Crystal data and experimental parameters for compounds 1–7.

Compound	1 <sup>a</sup>	2 <sup>b</sup>	3 <sup>c</sup>	4 <sup>d</sup>	5 <sup>e</sup>	6 <sup>f</sup>	7
Formula	C <sub>28</sub> H <sub>36</sub> ClF <sub>24</sub> InNa <sub>2</sub> O <sub>8</sub>	C <sub>30</sub> H <sub>30</sub> F <sub>36</sub> InNa <sub>3</sub> O <sub>9</sub>	C <sub>22</sub> H <sub>34</sub> Cl <sub>2</sub> F <sub>12</sub> InK <sub>2</sub> O <sub>6</sub>	C <sub>18</sub> H <sub>6</sub> F <sub>36</sub> InK <sub>3</sub> O <sub>6</sub>	C <sub>30</sub> H <sub>30</sub> F <sub>36</sub> InLi <sub>3</sub> O <sub>9</sub>	C <sub>24</sub> H <sub>40</sub> F <sub>12</sub> GaLiO <sub>6</sub>	C <sub>36</sub> H <sub>42</sub> F <sub>18</sub> In <sub>2</sub> Li <sub>2</sub> O <sub>6</sub>
Formula weight	1152.82	1402.33	847.31	1234.35	1354.18	729.22	1036.12
Temperature (K)	123(2)	123(2)	123(2)	123(2)	123(2)	123(2)	123(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Hexagonal	Monoclinic	Monoclinic	Triclinic
Space group	P2 <sub>1</sub> (No. 4)	P1 (No. 2)	P1 (No. 2)	P3c1 (No. 165)	C2/c (No. 15)	P2 <sub>1</sub> (No. 4)	P1 (No. 2)
a (Å)	10.0016(4)	11.0935(4)	10.730(2)	16.7980(3)	34.5278(7)	10.9967(2)	9.4747(3)
b (Å)	12.1828(5)	14.0412(5)	13.5271(4)	16.7980(3)	17.3171(3)	18.3135(4)	10.6675(4)
c (Å)	18.0762(7)	16.8661(6)	13.9758(4)	20.9058(5)	17.8588(3)	16.3899(3)	11.4166(3)
α (°)	90	84.033(2)	108.833(1)	90	90	90	65.810(2)
β (°)	93.179(3)	79.390(2)	106.683(1)	90	117.685(1)	103.774(1)	79.652(2)
γ (°)	90	69.565(2)	106.488(1)	120	90	90	68.412(2)
V (Å <sup>3</sup> )	2199.15(15)	2417.50(15)	1673.20(8)	5108.72(18)	9455.7(3)	3205.81(11)	978.17(6)
Z	2	2	2	6	8	4	1
D <sub>calcd.</sub> (g cm <sup>-3</sup> )	1.741	1.926	1.682	2.407	1.902	1.511	1.759
μ (mm <sup>-1</sup> )	0.762	0.702	1.091	1.297	0.689	0.960	1.300
Size (mm)	0.07 × 0.07 × 0.06	0.09 × 0.07 × 0.07	0.08 × 0.07 × 0.07	0.07 × 0.06 × 0.06	0.07 × 0.07 × 0.05	0.09 × 0.08 × 0.08	0.07 × 0.07 × 0.06
2θ <sub>max</sub> (°)	50	52	55	50	52.5	50	55
No. of reflections, collected	37319	37951	21436	43989	87659	29363	22173
No. of unique reflections/[R <sub>int</sub> ]	7667/0.099	9295/0.078	7573/0.093	3003/0.124	9510/0.0821	11135/0.117	4476/0.037
Data with I > 2σ(I)	5404	6104	4868	2778	7803	6811	4137
Goodness-of-fit (GOF)	1.016	1.086	1.037	1.251	1.060	1.012	1.142
R	0.097	0.054	0.059	0.135	0.047	0.067	0.042
wR <sub>2</sub>	0.243	0.089	0.128	0.240	0.097	0.92	0.084
Diffraction	Bruker X8 APEX CCD	Bruker X8 APEX CCD	Nonius Kappa CCD	Bruker X8 APEX CCD	Bruker X8 APEX CCD	Nonius Kappa CCD	Bruker X8 APEX CCD

<sup>a</sup> Connectivity structure only as data supported anisotropic refinement of In, Na and Cl only; the largest residual electron density peak was 1.94 e Å<sup>-3</sup> located 0.896 Å from In(1). The choice of space group was confirmed by PLATON [53] the structure was refined as a racemic TWIN with fractional contributions 0.55:0.45. The alkoxy ligands O(2)C(4)–C(6) and O(4)C(10)–C(12) were refined with the CF<sub>3</sub> groups disordered over two positions having refined occupancies of 0.64:0.36 and 0.55:0.45, respectively. The geometry of the CF<sub>3</sub> groups was restrained to reasonable values. The THF molecule was also modelled with the 4 C atoms disordered over two positions having refined occupancies of 0.52:0.48 and restrained geometry.

<sup>b</sup> THF molecules O(7)C(19)–C(22) and O(9)C(23)–C(26) were modelled with 3 C atoms as disordered over two positions having occupancies set at 0.60:0.40 and 0.50:0.50, respectively after trial refinement. Disorder components were refined with geometries and anisotropic thermal parameters restrained to be similar.

<sup>c</sup> After location of the primary molecule, residual electron density was modelled as a lattice THF, disordered over two positions having refined occupancies 0.55:0.45 and isotropic thermal parameter forms.

<sup>d</sup> Full sphere of data collected. Connectivity structure only as data would not support anisotropic refinement of non-hydrogen atoms; the highest residual electron density peak 3.38 e Å<sup>-3</sup> was 0.574 Å from K(1). Space group choice confirmed by PLATON; attempts to refine as a merohedral TWIN in the lower symmetry Laue group (space group P(3)) with the 2-fold axis as the TWIN law were unsatisfactory.

<sup>e</sup> A THF molecule O(8)C(23)–C(26) was modelled with the β-C atoms as disordered over two positions; occupancies set at 0.50 after trial refinement.

<sup>f</sup> Space group choice confirmed by PLATON. Model refined as a racemic TWIN with the fractional contribution 0.50. Some thermal ellipsoids e.g. C(22) (THF) and in the ligand O(2)C(5)–C(7) are somewhat elongated, plausibly indicating disorder. Attempts to model disorder in these atoms were unsatisfactory.

#### 4.9. X-ray crystallography

Crystalline samples were mounted on glass fibres in viscous hydrocarbon oil. Crystal data were collected using either an Enraf-Nonius Kappa CCD or a Bruker X8 APEX CCD instrument with monochromated MoKα radiation, λ = 0.71073 Å. All data were collected at 123 K, maintained using an open flow of nitrogen from an Oxford Cryostreams cryostat. X-ray data were processed using the DENZO program or Bruker Apex2 v2.0 [52]. Structural solution and refinement was carried out using the graphical interface X-Seed [53] and SHELXS-97 [54]. Unless otherwise indicated all non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions (riding model) and were not refined. Crystal data and refinement parameters for all complexes are shown in Table 1.

#### 5. Supplementary material

CCDC 702316, 702317, 702318, 702319, 702320, 702321 and 702322 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](http://www.ccdc.cam.ac.uk/data_request/cif).

#### Acknowledgments

The authors would like to thank the Australian Research Council and the CRC Smartprint for financial support, and the Faculty of Science at Monash University for a Postgraduate Publication Award (for I.N.).

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