# Base free lithium-organoaluminate and the gallium congener: potential precursors to heterometallic assemblies†

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**The first examples of base free lithium-organoaluminate and the corresponding gallium compound [LM(Me)OLi]$_3$ (M = Al (3), Ga (4); L = HC{C(Me)N-2,6-*i*Pr$_2$C$_6$H$_3$}$_2$) have been prepared by the reaction of Li[N(SiMe$_3$)$_2$] with the corresponding metal hydroxides LM(Me)OH (M = Al (1), Ga(2)); the oxygen atom in the M–O–Li fragment exists as oxide ion and is involved in the central Li$_3$O$_3$ six-membered ring formation.**

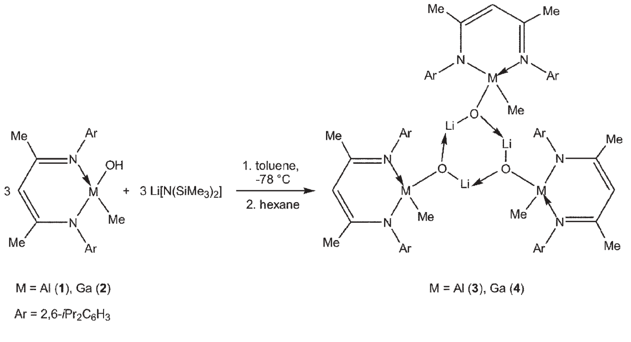
The reactions of trialkylaluminium with alkali metal hydroxides have been reported in 1960 by Ziegler.[1] They result in the formation of metallate compounds. The importance of metallates such as Na[Et$_2$AlOAlEt$_3$] has been demonstrated in the synthesis of stereoregular polymers.[1] The products in the reaction of R$_3$Al compounds with LiOH or NaOH were isolated as [R$_2$AlOM′][AlR$_3$] (M′ = Li, Na)[2–4] and were useful in polymerization of acetaldehyde to polyacetals. In spite of the potential activity of lithium aluminates in polymerization reactions no detailed structural studies have been made on such simple compounds.

The structurally characterized lithium aluminate, [Me$_2$AlN(2-C$_5$H$_4$N)Ph]$_2$(O)Li$_2$·2THF[5] is the only example where the oxygen atom was found in the form of an oxide. We have reported on the synthesis and structural elucidation of monolithium salts of the type [Mes$_3$M(μ-OHLi)]·3THF which undergoes further deprotonation with *n*BuLi to afford [Mes$_2$M(μ-OLi)]$_2$·4THF[6] (M = Al, Ga). It can be noted that lithium aluminates which have been structurally characterized contain the oxygen atom as alkoxide rather than oxide. The lithium atoms have a coordination number higher than two and they are often found to coordinate with the *N*-donor ligands in addition to the *O*–coordinating sites *e.g.*, pyridine,[7] amines,[7] amino alcohols[8] or methylthio ethanol.[9] Chelated anionic aluminates, reported by Hill and Atwood, fall in this category.[10] Nöth and co-workers reported on organyloxy-hydridoaluminates[11,12] with Al–H–Li and Al–Li–O bridges for lithium cations. However, the stability of these compounds is affected due to their dismutation reactions.[11]

The examples of lithium-gallate compounds are even rarer compared to those of aluminium, and in fact no gallium lithium compounds containing oxides are known. The reported examples are only those of alkyl- or aryloxometallates. Thus the compounds [Ga$_3$Li$_4$(*t*Bu)$_6$(neol)$_3$(OH)(THF)][13] (neol = 2,2-dimethylpropane-1,3-diol), [(2,4,6-tris((dimethylamino)methyl)phenoxy)$_2$GaCl$_2$]Li,[14] {[GaI(C(SiMe$_3$)$_3$)(OCMe$_3$)(OH)]Li}$_2$,[15] {Li(THF)}$_2${Ga((*S*)-BINOLate)$_3$}],[16] and [{Li(DME)}$_3${Ga((*S*)-BINOLate)$_3$}]·1.5THF[16] [(*S*)-BINOL = (*S*)-(−)-2,2′-dihydroxy-1,1′-binaphthyl] contain alkyl- or aryloxolithium moieties.

Our long standing interest towards the synthesis of hetero-bimetallic oxides containing Al or Ga has gained a considerable shape during the recent past. The successful synthesis of terminal hydroxides of Al and Ga, LAl(Me)OH (**1**)[17–19] and LGa(Me)OH (**2**),[20] respectively allowed a rational design to assemble novel hetero-bimetallic systems with predictable composition and properties.[17–27] Herein we describe the reactions of **1** and **2** with Li[N(SiMe$_3$)$_2$] to afford the novel trimeric lithium-organoaluminate [LAl(Me)OLi]$_3$ (**3**) and the corresponding gallium congener [LGa(Me)OLi]$_3$ (**4**). The utility of **3** and **4** can be envisaged as alternative precursors, to those of LAl(Me)OH (**1**) and LGa(Me)OH (**2**), towards the assembly of soluble heterometallic oxides in reactions with metal halides. Compounds **3** and **4** represent the first examples of base free lithium-organoaluminate and lithium-organogallate species.

The reaction of LM(Me)OH with Li[N(SiMe$_3$)$_2$] leads to deprotonation of the metal hydroxide to afford [LM(Me)OLi]$_3$ (M = Al (**3**), Ga (**4**)) as depicted in Scheme 1.‡ Compound **3** melts at 250 °C whereas **4** melts with decomposition at 280 °C. In the IR spectrum of **3** and **4** no band corresponding to the MO–H stretching mode was found, indicating complete deprotonation of the metal hydroxides. The EI mass spectrum of **3** shows the base peak at *m*/*z* 459 attributed to [$M^+$–Me–Li], whereas the corresponding ion for **4** appears at *m*/*z* 503. The $^7$Li NMR for compound **3** exhibits the lithium atom to resonate at 1.97 ppm, and at 1.92 ppm for compound **4**. The $^1$H NMR spectrum of **3** shows the Al–*Me* to resonate at −1.07 ppm and the γ-C*H* at 4.98 ppm whereas the Ga–*Me* in **4** appears at −0.60 ppm and the γ-C*H* at 4.82 ppm.



**Scheme 1** Synthesis of the lithium-organoaluminate and the gallium congener.

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† Electronic supplementary information (ESI) available: Figures for the molecular structure of **3** and **4**. See DOI: 10.1039/b712240c

The unambiguous molecular structures of **3** and **4** were determined by single crystal X-ray structural analysis.[28,29] Single crystals of **3** and **4** suitable for X-ray structural analysis were obtained from *n*-hexane solutions. Compounds **3** and **4** crystallize in the hexagonal system, space group $P6_3$ with a *n*-hexane molecule as solvent of crystallization.§ Compounds **3** and **4** exist as a trimer in the solid state. The molecular structure of **3** is shown in Fig. 1 and the perspective view of the packing in **3** and *n*-hexane molecules filling the channels is shown in Fig. 2. The structure of **4** is isomorphous to that of **3** (see ESI†). The metric parameters of **3** and **4** have been listed in Table 1.

Compounds **3** and **4** form the trimer of the LM(Me)OLi unit with a central six-membered $Li_3O_3$ ring, centered on a three fold axis. The terminal metal atoms in the chelated ligand rings are arranged in an almost perpendicular manner with respect to the central $Li_3O_3$ ring.

The Al(1)–O(1) distance of 1.698(1) Å in **3** is shorter than the distance in its parent compound LAl(Me)OH (**1**)[17,18] (1.731(3) Å). The Li–O bond lengths (1.791(3) and 1.808(3) Å) observed in the central $Li_3O_3$ ring are in general considerably shorter than those found in $[Me_2AlN(2\text{-}C_5H_4N)Ph]_2(O)Li_2\cdot 2THF$ (1.89 Å),[5] $[Li(THF)_2(\mu\text{-O-}(-)\text{-menthol})_2Al(H)_2]\cdot THF$ (av. 1.944 Å),[11] $(2,6\text{-}tBu_2C_6H_3O)_2Al(O\text{-}nBu)_2Li\cdot 2THF$ (av. 1.960 Å),[11] $[(2,6\text{-}iPr_2C_6H_3O)Al(H)(\mu\text{-}OC_6H_3\text{-}2,6\text{-}iPr_2)_2Li(Et_2O)]$ (1.912 Å),[11] $[\{2,4\text{-}(H)_2\text{-}6\text{-}(CH_2NH\text{-}(2,6\text{-}iPr_2C_6H_3))C_6H_2O\}_2Al]Li\cdot THF$ (1.962 Å),[10] and $[\{(2,4\text{-}(tBu)_2\text{-}6\text{-}(CH_2NH\text{-}tBu)C_6H_2O\}_2Al]Li\cdot THF$ (1.98 Å).[10] The Li···Li separation within the $Li_3O_3$ ring is 2.712(4) Å. The exocyclic Al(1)–O(1)–Li(1) and C(6)–Al(1)–O(1) bond angles are 137.4(1) and 117.1(1)° respectively, whereas the endocyclic Li(1A)–O(1)–Li(1) bond angle is 97.8(2)°. The *n*-hexane molecules in the crystal lattice occupy six positions due to the $6_3$ axis in the space group $P6_3$ (**4**) and twelve positions in the case of **3**, respectively, due to the additional disorder. The *n*-hexane molecules are located within the channels generated by the arrangement of the peripheral β-diketiminate ligands in the crystal lattice of **3** and **4** (Fig. 2).

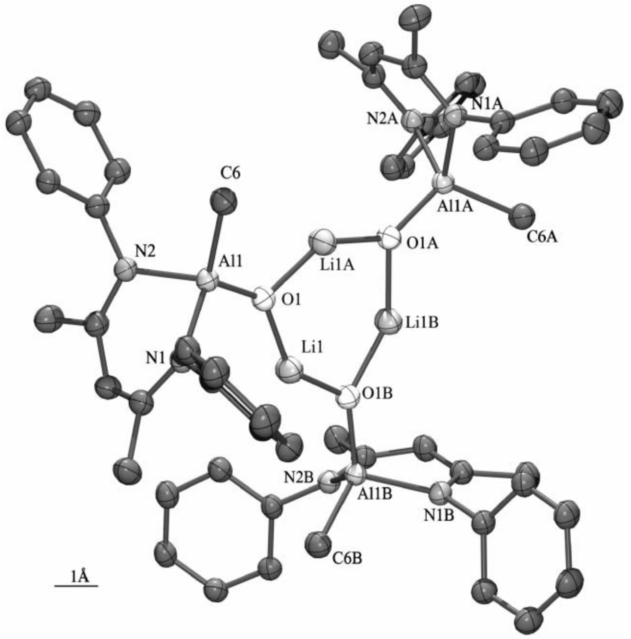

**Fig. 1** Molecular crystal structure of $[LAl(Me)OLi]_3$ (**3**). Thermal ellipsoids are shown with 50% probability. All hydrogen atoms, *i*Pr groups on N–Ph, and *n*-hexane molecule are omitted for clarity. Symmetry operations: A = (1 − *y*, *x* − *y*, *z*) and B = (−*x* + *y* + 1, 1 − *x*, *z*).

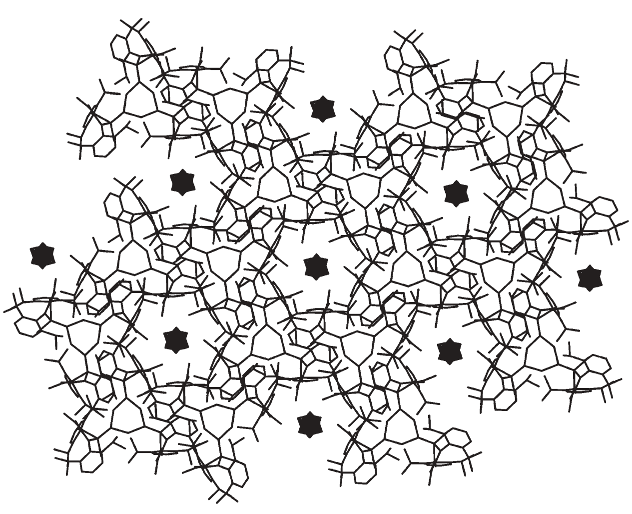

**Fig. 2** Perspective view of the packing in $[LAl(Me)OLi]_3$ (**3**). The *n*-hexane molecules fill the channels between the molecules of **3** and are disordered about the $6_3$ symmetry axes.

The Li–O bond lengths observed in **4** (1.776(3) and 1.806(3) Å) are comparable to those of the aluminium analogue **3** (1.791(3) and 1.808(3) Å) but significantly shorter than those found in $[Ga_3Li_4(tBu)_6(neol)_3(OH)(THF)]$ (1.80(4) to 1.99(4) Å),[13] $[Ga_2Li(tBu)_4(OH)_2(neol\text{-}H)]$ (1.82(1) to 1.90(1) Å),[13] and $\{[GaI(C(SiMe_3)_3)(OCMe_3)(OH)]Li\}_2$ (1.923(7) to 1.956(7) Å).[15] The Ga(1)–O(1) bond length (1.784(1) Å) in **4** is shorter than that in the corresponding hydroxide LGa(Me)OH (**2**) (1.831(1) Å).[20] The exocyclic Ga(1)–O(1)–Li(1) and C(6)–Ga(1)–O(1) bond angles are 135.3(1) and 119.4(1)° respectively, whereas the endocyclic Li(1A)–O(1)–Li(1) bond angle is 99.5(2)°.

**Table 1** Selected bond distances (Å) and angles (deg) of complexes **3** and **4**[a]

| | 3 | 4 |
|---|---|---|
| M(1)–O(1) | 1.698(1) | 1.784(1) |
| M(1)–C(6) | 1.974(2) | 1.973(2) |
| Li(1)–O(1) | 1.791(3) | 1.776(3) |
| Li(1A)–O(1) | 1.808(3) | 1.806(3) |
| M(1)–N(1) | 1.953(1) | 2.018(2) |
| M(1)–N(2) | 1.936(1) | 1.998(2) |
| Li(1)···Li(1A) | 2.712(4) | 2.734(5) |
| N(1)–M(1)–N(2) | 93.7(1) | 92.24(1) |
| M(1)–O(1)–Li(1) | 137.4(1) | 135.3(1) |
| M(1)–O(1)–Li(1A) | 124.7(1) | 124.9(1) |
| C(6)–M(1)–O(1) | 117.1(1) | 119.4(1) |
| N(1)–M(1)–C(6) | 111.5(1) | 112.8(1) |
| N(2)–M(1)–C(6) | 109.0(1) | 110.5(1) |
| N(1)–M(1)–O(1) | 111.3(1) | 109.5(1) |
| N(2)–M(1)–O(1) | 111.9(1) | 109.0(1) |
| Li(1A)–O(1)–Li(1) | 97.8(2) | 99.5(2) |
| O(1)–Li(1)–O(1B) | 142.2(2) | 140.5(2) |

[a] M = Al (**3**); Ga (**4**).

In summary, we have described the syntheses and single crystal X-ray structures of the first base free lithium-organoaluminate and lithium-organogallate supported by β-diketiminate ligand. The hydroxides LAl(Me)OH and LGa(Me)OH could easily be deprotonated by using $\mathrm{Li[N(SiMe_3)_2]}$ to afford the title compounds. In absence of a coordinating agent or base the compounds tend to trimerize. The lithium compounds are potential starting materials to assemble new homo- or heterometallic species by reaction with metal halides. Such studies are currently being pursued.

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## Notes and references

‡ *Synthesis* of $\mathrm{[LAl(Me)OLi]_3}$ (**3**): Toluene (20 ml) was added to the mixture of LAl(Me)OH (0.48 g, 1.00 mmol) and $\mathrm{Li[N(SiMe_3)_2]}$ (0.17 g, 1.00 mmol) at −78 °C. The resulting solution was stirred at room temperature for 12 h. After removal of all volatiles *in vacuo* the crude product was extracted with *n*-hexane (20 ml). The filtrate was kept at room temperature for 3 d to give colourless crystals. The crystals were collected by filtration and the filtrate was concentrated (*ca.* 10 ml) and kept at 4 °C for 4 d to give another crop. Total yield: 0.21 g, 43%. Mp 250 °C. Anal. found: C, 74.42; H, 9.34; N, 5.38%. Calcd. for $\mathrm{C_{90}H_{132}Al_3Li_3N_6O_3}$: C, 74.66; H, 9.19; N, 5.80%. $^1$H NMR (200 MHz, $\mathrm{C_7D_8}$): $\delta = -1.07$ (s, 9H, Al*Me*), 1.12, 1.26, 1.37, 1.49 (d, $^3J_{\mathrm{H–H}} = 6.8$ Hz, 12 × 6H, $\mathrm{CH}Me_2$), 1.64 (s, 3 × 6H, $\mathrm{CH}(CMe)_2$), 3.69, 3.28 (sept, $^3J_{\mathrm{H–H}} = 6.8$ Hz, 12 × 1H, $\mathrm{C}H\mathrm{Me_2}$), 4.98 (s, 3 × 1H, γ-C*H*), 6.91–7.22 (m, 6 × 3H, $\mathrm{C_6}H_3$). $^7$Li NMR (116.6 MHz, $\mathrm{C_7D_8}$): $\delta$ 1.97. EI-MS: *m*/*z* (%): 459 (100) [$M^+$ − Me–Li], 444 (20) [$M^+$ − 2Me–Li]. IR (Nujol, cm$^{-1}$): 1624, 1587, 1552, 1527, 1395, 1320, 1261, 1222, 1100, 1058, 1021, 937, 858, 799, 759, 722, 703, 686, 637, 598, 448. *Synthesis* of $\mathrm{[LGa(Me)OLi]_3}$ (**4**): $\mathrm{[LGa(Me)OLi]_3}$ (**4**) was prepared in a manner analogous to that of $\mathrm{[LAl(Me)OLi]_3}$ (**3**). The quantities of reactants used were LGa(Me)OH (0.77 g, 1.50 mmol) and $\mathrm{Li[N(SiMe_3)_2]}$ (0.27 g, 1.60 mmol). Yield: 0.46 g, 58%. Mp 280 °C (decomp.). Anal. found: C, 68.62; H, 8.38; N, 5.38%. Calcd. for $\mathrm{C_{90}H_{132}Ga_3Li_3N_6O_3}$: C, 68.59; H, 8.44; N, 5.33%. $^1$H NMR (500 MHz, $\mathrm{C_6D_6}$): $\delta = -0.60$ (s, 9 H, Ga*Me*), 1.14, 1.30, 1.34, 1.49 (d, $^3J_{\mathrm{H–H}} = 6.8$ Hz, 12 × 6H, $\mathrm{CH}Me_2$), 1.64 (s, 3 × 6H, $\mathrm{CH}(CMe)_2$), 3.36, 3.78 (sept, $^3J_{\mathrm{H–H}} = 6.8$ Hz, 12 × 1H, $\mathrm{C}H\mathrm{Me_2}$), 4.82 (s, 3 × 1H, γ-C*H*), 7.11–7.16 (m, 6 × 3H, $\mathrm{C_6}H_3$). $^7$Li NMR (116.6 MHz, $\mathrm{C_6D_6}$): $\delta$ 1.92. EI-MS: *m*/*z* (%): 503 (100) [$M^+$ − Me–Li], 487 (40) [$M^+$ − Me–OLi]. IR (Nujol, cm$^{-1}$): 1623, 1554, 1523, 1320, 1260, 1196, 1177, 1106, 1057, 1021, 937, 858, 797, 760, 728, 638, 583, 556, 441.

§ *Crystal data* for **3**·*n*-hexane: $\mathrm{C_{96}H_{146}Al_3Li_3N_6O_3}$, $M = 1533.95$ g mol$^{-1}$, hexagonal, space group $P6_3$, $a = b = 15.847(2)$, $c = 21.396(4)$ Å, $U = 4653(1)$ Å$^3$, $\rho_{\mathrm{calcd}} = 1.095$ Mg m$^{-3}$, $T = 100(2)$ K, $Z = 2$, $\mu$[Cu-Kα] = 0.746 mm$^{-1}$, 26482 reflections measured, 4395 unique ($R_{\mathrm{int}} = 0.0275$) which were used in all calculations; $R_1 = 0.0249$ and w$R_2 = 0.0661$ for $I > 2\sigma(I)$. *Crystal data* for **4**·*n*-hexane: $\mathrm{C_{96}H_{146}Ga_3Li_3N_6O_3}$, $M = 1662.18$ g mol$^{-1}$, hexagonal, space group $P6_3$, $a = b = 15.902(2)$, $c = 21.419(3)$ Å, $U = 4690.7(11)$ Å$^3$, $\rho_{\mathrm{calcd}} = 1.177$ Mg m$^{-3}$, $T = 100(2)$ K, $Z = 2$, $\mu$[Cu-Kα] = 1.376 mm$^{-1}$, 33693 reflections measured, 4490 unique ($R_{\mathrm{int}} = 0.0330$) which were used in all calculations; $R_1 = 0.0218$ and w$R_2 = 0.0601$ for $I > 2\sigma(I)$. CCDC 654337 (**3**) and 654338 (**4**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b712240c

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