

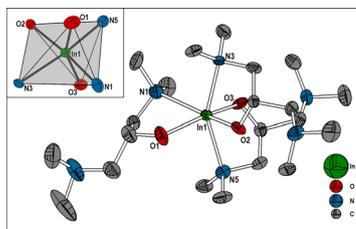
Monomeric aminoalcoholates of aluminium(III), gallium(III), and indium(III)

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Abstract The synthesis of novel, homoleptic group 13 alkoxides is presented. $M(\text{OCH}(\text{CH}_2\text{NR}_2)_2)_3$, where $M=\text{Al}$, Ga, In and $\text{R}=\text{Me}$, Et, are characterised by room temperature NMR spectroscopy and single-crystal XRD showing the monomeric nature of all aminoalcoholates.

Graphical abstract



Keywords Aluminium alkoxides · Gallium alkoxides · Indium alkoxides · Aminoalcohols · Coordination chemistry

Introduction

Metal alkoxides have been successfully used as molecular precursors for the synthesis of oxide materials via chemical vapour deposition (CVD) [1–3] or sol–gel processing [4–

6]. The well-known tendency to form oligomeric derivatives by the formation of alkoxo-bridges and the sensitivity towards hydrolysis require modifications of the alkoxides to tailor their applicability in materials synthesis [7]. Monomeric alkoxide derivatives could be used in metal oxide synthesis via sol–gel processing, because the individual metallic species should allow the doping and incorporation of individual group 13 metals in an oxide matrix.

Effective ways to alter the physico-chemical properties by changing the degree of oligomerisation in alkoxide derivatives are (1) sterical crowding to shield the metal centre with sterically demanding ligands and (2) the addition of donor molecules or the incorporation of additional donor functionalities for an efficient chelating effect leading to coordinative saturation of the metal centre [8]. Different donor functionalised alcohols have been employed to form metal alkoxides with low degree of oligomerisation, including amines [9], ethers [10], and also very recently thioethers [11].

The structural features of Al, Ga, and In alkoxides have been reviewed and describe their usually obtained dimeric/oligomeric structures [6, 12]. A convenient way to reduce the degree of oligomerisation is the addition of donor molecules, e.g. Lewis bases such as amines, to synthesise heteroleptic alkoxide monomers $[\text{M}(\text{OR})_3(\text{D})_x]$ with $x = 1$ for $M=\text{Al}$; $x = 1, 2$ for $M=\text{Ga}$; and $x = 1, 2, 3$ for $M=\text{In}$ [1, 13, 14]. Homoleptic, monomeric structures of group 13 alkoxides have only been observed in salts containing anionic moieties formed by Lewis acid–base reaction in the presence of larger organic/organometallic cations [15, 16] and in structurally related aryloxides, such as hydroxyquinoline derivatives, containing a secondary coordinating donor functionality [17, 18]. While the ligand systems presented in this paper have been used before in

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Table 1 Compound names and abbreviations

Compound	Abbrev.
Aluminium tris[1,3-bis(dimethylamino)propan-2-olate]	1
Gallium tris[1,3-bis(dimethylamino)propan-2-olate]	2
Indium tris[1,3-bis(dimethylamino)propan-2-olate]	3
Aluminium tris[1,3-bis(diethylamino)propan-2-olate]	4
Gallium tris[1,3-bis(diethylamino)propan-2-olate]	5
Indium tris[1,3-bis(diethylamino)propan-2-olate]	6

the synthesis of heteroleptic group 13 alkoxides, all reported species $R_2'M(OR)$ with $R'=Cl, CH_3, C_2H_5$ have been dimeric [19–21]. An unusual homoleptic, monomeric copper(II) alkoxide has been described in the literature for the dimethylaminoalcoholate ligand also used in this study [22].

Herein, we describe the synthesis of rare homoleptic, monomeric group 13 alkoxides using aminoalcoholate ligands. The formation of monomeric derivatives is supported by the steric demand of the ligands used in this study. The new alkoxides are summarised in Table 1.

Results and discussion

All metal alkoxides described in this study have been synthesised in high yields via alcohol exchange reactions starting from aluminium or gallium *tert*-butoxide or alcoholysis of indium tris(bis(trimethylsilyl)amide), respectively (Scheme 1).

The alkanols, 1,3-bis(dimethylamino)propan-2-ol and 1,3-bis(diethylamino)propan-2-ol, have been prepared according to a procedure described in the literature [23]. The alkoxides were characterised by room temperature 1H and ^{13}C NMR spectroscopy as well as single-crystal X-ray diffraction (1–5). 1H NMR spectra clearly show a coordination of the amino donors indicated by a pronounced

down-field shift of the groups in the vicinity of the nitrogen atom (Fig. 1). For instance, the methyl groups of the amino functionality in 1,3-bis(dimethylamino)-2-propanolates of Al, Ga, and In are shifted by ~ 0.2 ppm upon coordination to the metal centre. Since there are more donors available than coordination sites on the central atom, there should be coordinated and pendant NMe_2 moieties of the 1,3-bis(dimethylamino)-2-propanolate and NEt_2 groups of the 1,3-bis(diethylamino)-2-propanolate ligands. For instance, the single signals in the 1H NMR spectra of compound **3** for the groups in the vicinity of the amino functionality, the protons bound to C_β and the methyl groups (Fig. 1a, b) therefore indicate a fast exchange of coordinated and uncoordinated amino functionalities at room temperature. Similar shifts in the 1H NMR spectra are also observed for the five other alkoxides described herein. Room temperature 1H NMR cannot provide reliable data on the presence of monomers or dimers even though for some stable dimers it is possible to observe signals for both the terminal and bridging alkoxy ligands [24, 25]. The here described metal alkoxide derivatives do not show separate signals for bridging and terminal alcoholate ligands; however, the quick exchange in binding modes makes it more difficult to assign a nuclearity, and the possibility of a dimer formation cannot be ruled out at RT in solution.

More evidence for the monomeric nature of the alkoxides was obtained by single-crystal XRD analysis. Suitable crystals of 1–5 either formed from the highly viscous metal alkoxides or from *n*-hexane solutions. Detailed crystallographic and refinement data are listed in Table 2. Aluminium and gallium species (**1**, **2**, **4**, and **5**) exhibit very similar structures featuring a distorted trigonal bipyramidal arrangement consisting of three equatorial alkoxy oxygen atoms and two nitrogen donors in the apical positions (Fig. 2a, b). Figure 2 only contains two of the four structures due to their structural similarity. In both structures, two of the three ligands have one coordinating

Scheme 1

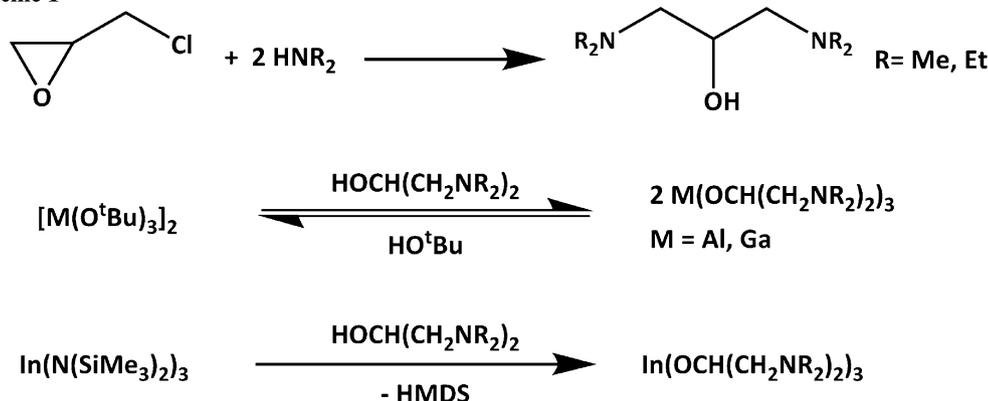


Fig. 1 ^1H NMR of the free alcohol and **3**, clearly showing coordination of the nitrogen donor. Also notice the ABX pattern of protons *b* and *c*

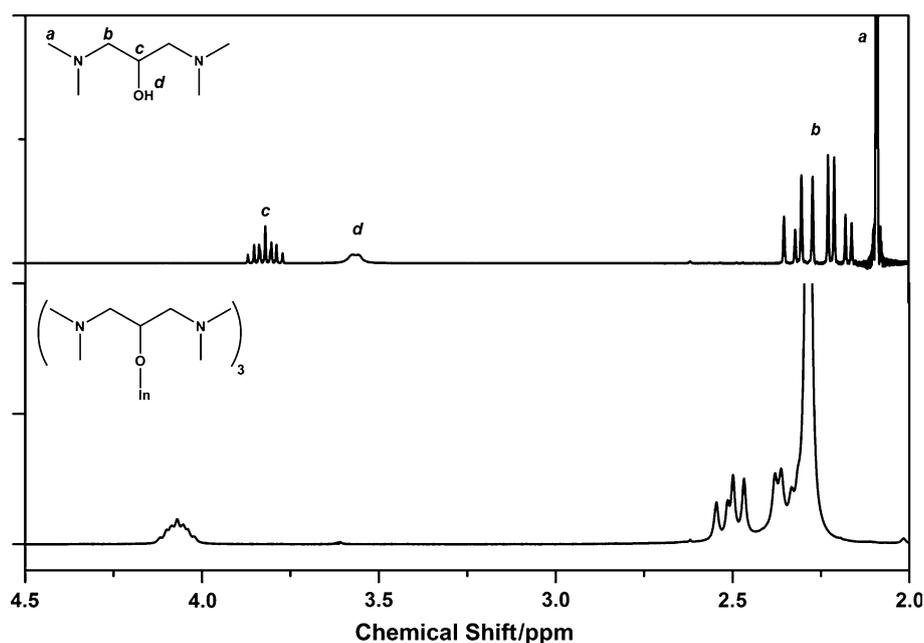


Table 2 Crystal data and structure refinement details

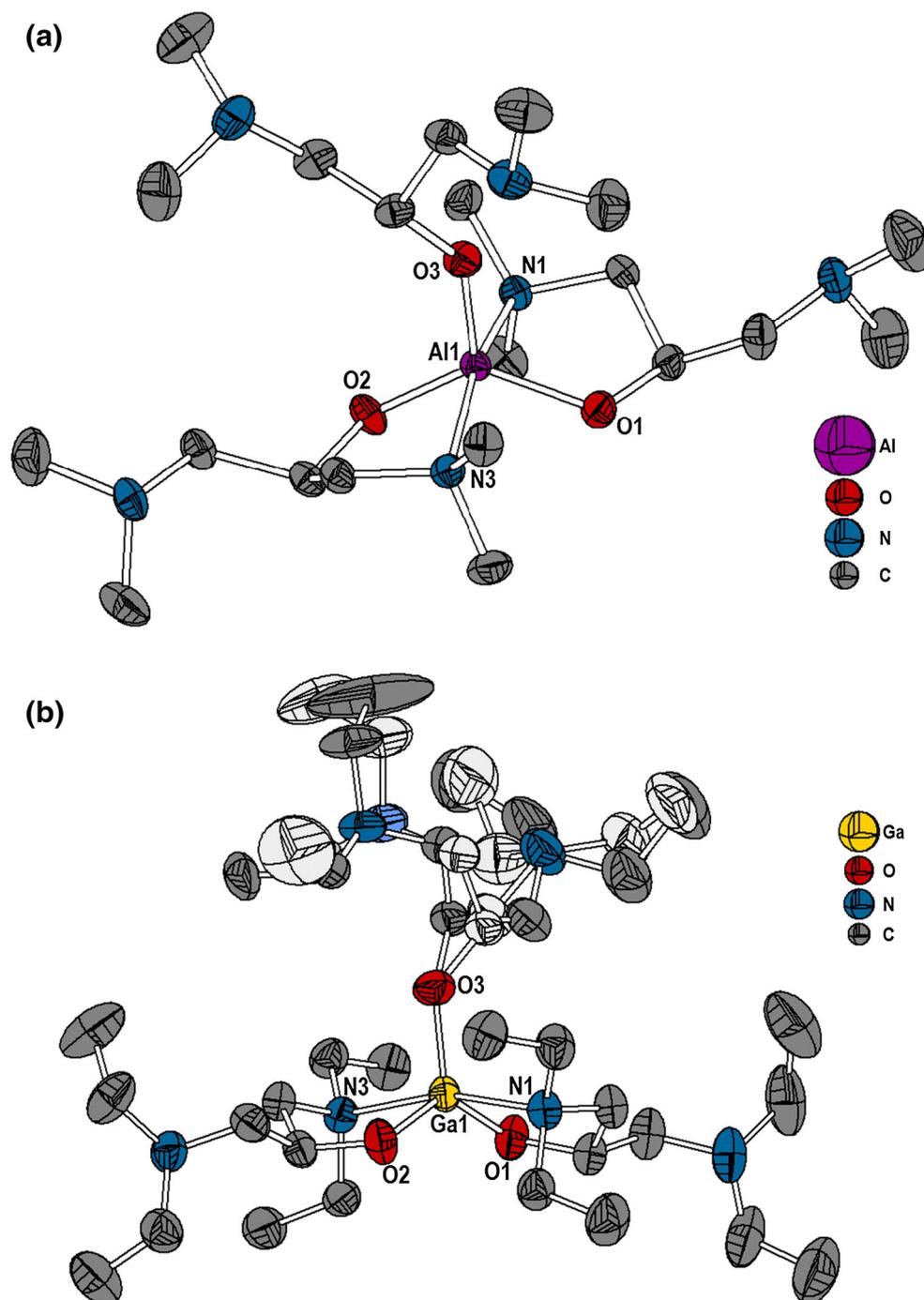
Compound	1	2	3	4	5
Emp. Formula	$\text{C}_{21}\text{H}_{51}\text{AlN}_6\text{O}_3$	$\text{C}_{21}\text{H}_{51}\text{GaN}_6\text{O}_3$	$\text{C}_{21}\text{H}_{51}\text{InN}_6\text{O}_3$	$\text{C}_{33}\text{H}_{75}\text{AlN}_6\text{O}_3$	$\text{C}_{33}\text{H}_{75}\text{GaN}_6\text{O}_3$
M_r	462.66	505.39	550.49	630.97	673.71
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
<i>a</i> /pm	871.43(5)	880.72(1)	1174.8(2)	918.09(6)	903.00(2)
<i>b</i> /pm	1025.91(6)	1019.61(1)	878.47(18)	1266.26(8)	1280.97(3)
<i>c</i> /pm	1600.34(8)	1607.70(2)	2790.8(6)	1713.88(11)	1754.25(4)
$\alpha/^\circ$	76.570(2)	75.8008(6)	90.00	97.919(2)	98.5460(10)
$\beta/^\circ$	81.588(2)	82.0703(6)	99.14(3)	92.143(2)	93.6160(10)
$\gamma/^\circ$	84.368(2)	84.4410(6)	90.00	96.908(2)	96.7740(10)
$V/\text{pm}^3 \times 10^6$	1373.56(13)	1383.22(3)	2843.7(10)	1956.2(2)	1985.91(8)
<i>Z</i>	2	2	4	2	2
$D_x/\text{g cm}^{-3}$	1.119	1.213	1.286	1.071	1.127
μ/mm^{-1}	0.10	1.03	0.86	0.09	0.73
Crystal size/mm	$0.6 \times 0.6 \times 0.6$	$0.40 \times 0.40 \times 0.20$	$0.2 \times 0.36 \times 0.4$	$0.3 \times 0.4 \times 0.6$	$0.4 \times 0.5 \times 0.7$
No. measured refl.	79178	14117	64160	83378	32246
Obs. Refl. [$I > 2\sigma(I)$]	7436	6229	9397	9413	11274
$\theta_{\text{max}}/^\circ$	32.6	28.3	33.4	30.234	31.1
$R [F^2 > 2\sigma(F)]$, wR (F^2), S	0.042, 0.111, 1.02	0.029, 0.076, 1.06	0.076, 0.212, 1.28	0.076, 0.232, 1.05	0.035, 0.098, 1.07
Ref./param.	10024/280	6836/292	10300/293	12165/557	12569/491
Weighting scheme ^a	$a = 0.0516$ $b = 0.3731$	$a = 0.0436$, $b = 0.3702$	$a = 0.037$, $b = 41.8488$	$a = 0.1211$, $b = 1.3942$	$a = 0.0583$, $b = 0.3702$

^a $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$

and one dangling amino donor, while the third ligand exhibits no further nitrogen coordination to the metal centre. This coordination is rare for Al and Ga alkoxides

and aminoalcoholates, which tend to form dimers or higher oligomers with two bridging oxygen atoms from alcoholate ligands [6, 7, 12]. A similar trigonal bipyramidal

Fig. 2 Crystal structure of **a 1** and **b 5** with 75 % probability ellipsoids. Disordered parts in **(b)** are depicted in *pale colours*. Hydrogen atoms were omitted for clarity



coordination sphere was observed in heteroleptic aminoalcoholate complexes of the form $[\text{Ga}(\text{OR})_2\text{L}]$ with $\text{L}=\text{Cl}$, Et, etc. [26, 27]. The only trigonal bipyramidal coordination in $\text{Ga}(\text{OR})_3$ subunits is observed for crystals of $[\text{Ga}(\text{OC}_2\text{H}_4\text{N}(\text{CH}_3)_2)_3\text{LiCl}]_2$, where the dangling amine and the respective oxygen are chelating a Li from LiCl and form a bridge between the two alkoxide units [28]. An alternative synthesis route yields the compound without LiCl; however, the crystal quality was too poor to provide a

full dataset and only the connectivity of the core atoms in the tris(alkoxide) complex was confirmed. The here described structural arrangement is unusual, because to date all evidence on tris-aminoalcoholate group 13 complexes had pointed towards complexes being oxygen-bridged dimers [26].

Bond distances for M–O, where M=Al, Ga, are all in agreement with bond lengths of terminal alkoxo ligands, which are shorter than those of bridging alkoxo moieties

Table 3 Selected bond length and angles

1		2		3		4		5	
Bond	Distance/pm								
Al1–O1	176.5(1)	Ga1–O1	184.9(1)	In1–O1	205.5(6)	Al1–O1	176.2(2)	Ga1–O1	184.4(1)
Al1–O2	176.8(7)	Ga1–O2	184.9(1)	In1–O2	209.7(6)	Al1–O2	176.3(1)	Ga1–O2	184.7(1)
Al1–O3	173.7(9)	Ga1–O3	183.4(1)	In1–O3	207.0(5)	Al1–O3	172.3(1)	Ga1–O3	182.1(1)
Al1–N1	209.9(8)	Ga1–N1	215.2(1)	In1–N1	256.7(7)	Al1–N1	216.1(2)	Ga1–N1	221.7(1)
Al1–N3	211.9(8)	Ga1–N3	218.0(1)	In1–N3	234.4(6)	Al1–N3	215.7(2)	Ga1–N3	221.5(1)
				In1–N5	243.2(6)				
Angle	/°								
O1–Al1–O2	128.55(4)	O1–Ga1–O2	128.78(5)	O1–In1–O2	95.7(2)	O1–Al1–O2	126.62(6)	O1–Ga1–O2	130.04(4)
O1–Al1–O3	113.62(4)	O1–Ga1–O3	111.74(5)	O1–In1–O3	153.9(2)	O1–Al1–O3	119.59(7)	O1–Ga1–O3	119.57(4)
O2–Al1–O3	117.83(4)	O2–Ga1–O3	119.47(5)	O2–In1–O3	105.2(2)	O2–Al1–O3	113.79(6)	O2–Ga1–O3	110.39(4)
O1–Al1–N1	83.87(4)	O1–Ga1–N1	83.22(5)	O1–In1–N1	74.7(2)	O1–Al1–N1	84.15(6)	O1–Ga1–N1	83.85(4)
O1–Al1–N3	87.59(4)	O1–Ga1–N3	87.65(5)	O2–In1–N3	77.6(2)	O1–Al1–N3	90.61(6)	O1–Ga1–N3	97.97(4)
O2–Al1–N3	84.11(4)	O2–Ga1–N3	83.67(4)	O3–In1–N5	76.6(2)	O2–Al1–N3	83.52(6)	O2–Ga1–N3	82.42(4)
N1–Al1–N3	165.26(4)	N1–Ga1–N3	164.26(4)	O1–In1–N3	111.8(2)	N1–Al1–N3	165.82(6)	N1–Ga1–N3	163.42(4)
				O1–In1–N5	90.5(2)				

reported in the literature [7, 27]. While the M–O bond distances for the ligands with coordinating donor sites are almost identical, the M–O distance for the ligand with only dangling nitrogen donors is significantly smaller, i.e. 176.5(1)/176.8(7) vs. 173.7(9) pm for **1**. This shorter bond length is typical for non-chelating, terminal alcoholate ligands [9]. The apical coordinating nitrogen atoms N1 and N3 are tilted away from the non-chelating ligand leading to N1–M–N3 bond angles of 163.42(4)°–165.82(6)°, which are much smaller than the expected 180° for an ideal trigonal bipyramid. This also leads to highly anisotropic angles in the equatorial plane featuring wider O1–M–O2 angles ranging from 126.62(6)° to 130.04(4)°, while O1–M–O3 and O2–M–O3 exhibit values from 110.39(4)° to 119.59(7)°. For a detailed list of selected bond lengths and angles, see Table 3.

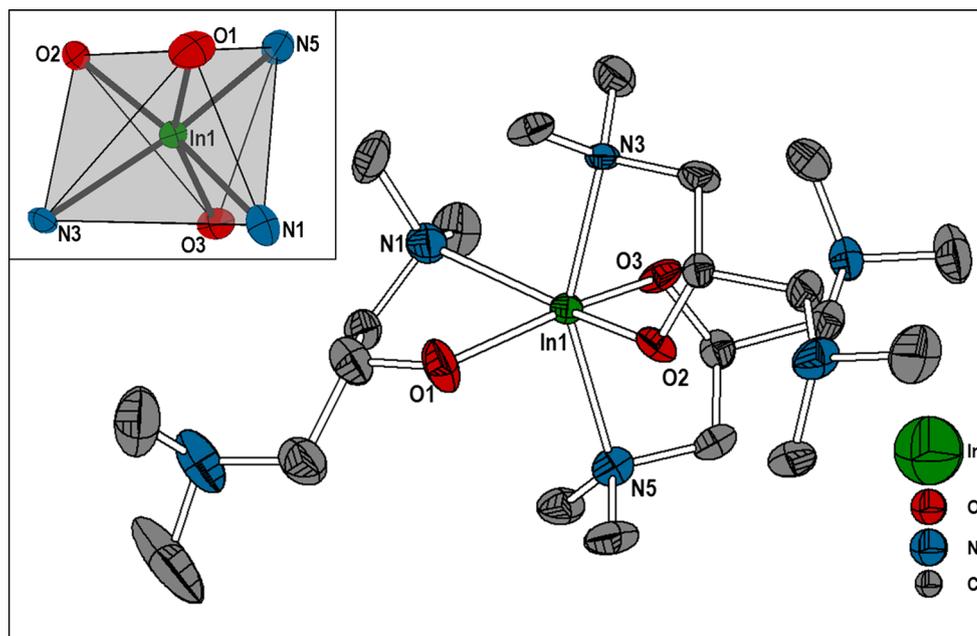
While the dimethylamino derivatives **1** and **2** did not feature any disorder in the crystal structure, both diethylamino derivatives **4** and **5** exhibit very similar positional disorder on the organic backbone of the non-chelating ligand (Fig. 2b). This is most likely the result of packing effects within the unit cell coupled with increased degrees of freedom due to the non-chelating aminoalcoholate moiety. The structures were refined using the split-atom model, leading to occupational densities of approximately 50:50 and 60:40 % for compounds **4** and **5**, respectively.

In contrast to the fivefold coordination of Al and Ga species, the dimethylamino indium derivative **3** exhibits a

distorted trigonal antiprismatic arrangement of the coordinating alcoholate oxygen and amine donors (Fig. 3). The higher coordination number of the indium derivatives is caused by the larger cation radius of the metal centre. The homoleptic In alkoxide **3** constitutes three sets of coordinating oxygen and nitrogen atoms, leaving each ligand with an additional pendant donor site. The trigonal planes of the antiprismatic coordination sphere consist of O1–O2–N5 as well as O3–N1–N3 and are slightly tilted by 3.65° with respect to each other (inset Fig. 3). In addition, these trigonal planes of the antiprism are distorted. Their edge lengths range from 303.0(8) to 319.7(8) pm and 308.4(8) to 359.5(9) pm, while angles range from 57.7(2)° to 63.1(2)° and 57.4(2) to 69.3(2)° for the triangles O1–O2–N5 and O3–N1–N3, respectively.

The In–O bond distances (205.5(6)–209.7(6) pm) are well within the reported ranges for terminal alkoxo ligands, and the In–N bond lengths (234.4(6)–256.7(7) pm) are consistent with literature data for coordinating amino groups in aminoalcoholates, respectively [9, 20]. The In–N and In–O bond lengths within the individual chelating ligands correlate inversely with each other. The longest In–N bond (In1–N1) and the shortest In–O bond (In1–O1) belong to the same chelating ligand, while the reverse order is found in another chelating aminoalcoholate (In1–N3 and In1–O2). O–In1–N bond angles for atoms forming a five-membered InOCCN ring, i.e. belonging to the same ligand (O1–In1–N1, O2–In1–N3 and O3–In1–N5, respectively), feature values from 74.7(2)° to 77.6(2)°. These values are

Fig. 3 Crystal structure of **3** with 75 % thermal ellipsoids. *Inset* shows the coordination polyhedron. Hydrogen atoms were omitted for clarity



well within the ranges for terminal five-membered In metallacycles [9]. O–In–N angles between different ligands on the other hand exhibit larger values between 83.6(2)° and 111.8(2)°.

Conclusions

Six homoleptic, monomeric amino-functionalised Al, Ga, and In alkoxides have been synthesised and characterised. The Al and Ga derivatives exhibit a distorted trigonal bipyramidal arrangement with two amino donors coordinating to the metal centre. In contrast, the In centre of the aminoalcoholate is sixfold coordinated forming a trigonal antiprism. These homoleptic group 13 aminoalcoholates are the first examples of structurally characterised monomers of this structurally rich class of coordination compounds.

Experimental

All alkoxide derivatives were synthesised and manipulated under dry, oxygen-free nitrogen applying standard Schlenk techniques. All solvents were dried and desiccated prior to use and stored over Na wire or molecular sieve.

¹H and ¹³C solution NMR spectra were recorded on a Bruker AVANCE 250 spectrometer (250.13 MHz {¹H}, 62.86 MHz {¹³C}) equipped with a 5-mm inverse-broadband probe head and a z-gradient unit. Deuterated solvents were purchased from Sigma-Aldrich and stored over Na.

Single-crystal X-ray diffraction experiments were performed at low temperature (100–130 K) on a BRUKER AXS SMART APEX II diffractometer with a CCD area detector using graphite-monochromated Mo-K_α radiation ($\lambda = 71.073$ pm). Data were collected with ω - and φ -scans and 0.5° frame width. Data were corrected for polarisation and Lorentz effects, and an empirical absorption correction (SADABS) was applied. The cell dimensions were refined with all unique reflections. The structures were solved with direct methods (SHELXS97) or dual-space algorithms (compound **3**) as implemented in SHELXT [29], and refinement to convergence was carried out with the full-matrix least-squares method based on F^2 (SHELXL97/SHELXL14) with anisotropic structure parameters for all non-hydrogen atoms. The hydrogen atoms were placed on calculated positions and refined riding on their parent atoms.

Twinning was observed for compound **3** consistent with a (001) mirror plane as twin operation. Therefore, reflections were manually analysed using the RLATT tool (Bruker 2014), and refinement was conducted using HKL5 map.

CCDC 1430667 (**1**), CCDC 1430668 (**2**), CCDC 1430669 (**3**), CCDC 1430670 (**4**), and CCDC 1430671 (**5**) contain supplementary crystallographic data. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

General synthesis procedure for alkoxides

Approximately 250 mg of aluminium *tert*-butoxide [Al(O^tBu)₃]₂, gallium *tert*-butoxide [Ga(O^tBu)₃]₂ or

indium tris(bis(trimethylsilyl)amide) $\text{In}(\text{N}(\text{SiMe}_3)_2)_3$, was dissolved in 5 cm^3 of toluene and 3.05 equiv. of the aminoalcohol was added. After stirring at RT overnight, the volatile alcohols and solvent were removed under reduced pressure at elevated temperature. The reaction progress was monitored via ^1H NMR spectroscopy. If applicable, the reaction was completed by adding a few drops of the aminoalcohol to a concentrated solution. After removal of volatile by-products and solvents, all compounds were obtained as colourless oils at room temperature.

Aluminium tris[1,3-bis(dimethylamino)propan-2-olate] (1), $\text{AlC}_{21}\text{H}_{51}\text{N}_6\text{O}_3$

$[\text{Al}(\text{O}^t\text{Bu})_3]_2$ (345 mg, 1.4 mmol) in 5 cm^3 toluene was reacted with 618 mg 1,3-bis(dimethylamino)propan-2-ol (4.22 mmol) at room temperature. After stirring overnight, removal of volatile residues yielded 622 mg (1.3 mmol, 96 %) of **1** as clear, colourless, viscous oil. The compound solidified/crystallised overnight, the quickest of all the aminoalcoholates described in this study. ^1H NMR (C_6D_6 , 250.13 MHz): $\delta = 2.32$ (s, 30H, CH_3), 2.35–2.60 (m, 18H, CH_3 , CH_2), 4.12 (quint, $J = 6.15$ Hz, CH) ppm; ^{13}C $\{^1\text{H}\}$ NMR (C_6D_6 , 62.86 MHz): $\delta = 46.8$ (s, CH_3), 66.4 (s, CH_2), 67.2 (s, CH) ppm.

Gallium tris[1,3-bis(dimethylamino)propan-2-olate] (2), $\text{GaC}_{21}\text{H}_{51}\text{N}_6\text{O}_3$

$[\text{Ga}(\text{O}^t\text{Bu})_3]_2$ (213 mg, 0.74 mmol) and 334 mg 1,3-bis(dimethylamino)propan-2-ol (2.28 mmol) were stirred in 5 cm^3 toluene overnight. After removing all volatile substances, 374 mg (7.4 mmol, 96 %) of **2** was obtained as colourless viscous oil. Crystals formed in this oil after a few days and were separated before the whole substance crystallised. ^1H NMR (C_6D_6 , 250.13 MHz): $\delta = 2.35$ (s, 33H, CH_3), 2.39 (s, 3H, CH_3), 2.42 (dd, $J = 5.27$ Hz, 11.78 Hz, 6H, CH_2), 2.51 (dd, $J = 7.18$ Hz, 11.78 Hz, 6H, CH_2), 4.12 (tt, $J = 5.30$ Hz, 7.13 Hz, 3H, CH) ppm; ^{13}C $\{^1\text{H}\}$ NMR (C_6D_6 , 62.86 MHz): $\delta = 46.8$ (s, CH_3), 67.1 (s, CH_2), 68.3 (s, CH) ppm.

Indium tris[1,3-bis(dimethylamino)propan-2-olate] (3), $\text{InC}_{21}\text{H}_{51}\text{N}_6\text{O}_3$

$\text{In}(\text{HMDS})_3$ (456 mg, 0.77 mmol) was mixed with 350 mg of 1,3-bis(dimethylamino)propan-2-ol (2.39 mmol) in 7 cm^3 toluene. After stirring for 3 h at room temperature, volatiles were removed under reduced pressure to yield 415 mg (0.75 mmol, 98 %) of **3** as colourless, viscous oil. Crystals have been grown from a hexane solution at -5°C . ^1H NMR (C_6D_6 , 250.13 MHz): $\delta = 2.30$ (s, 36H, CH_3), 2.35 (dd, $J = 4.23$ Hz, 11.61 Hz, 6H, CH_2), 2.51 (dd, $J = 7.9$ Hz, 11.61 Hz, 6H, CH_2), 4.07 (m, 3H, CH) ppm; ^{13}C $\{^1\text{H}\}$ NMR (C_6D_6 , 62.86 MHz): $\delta = 47.1$ (s, CH_3), 67.3 (s, CH_2), 68.6 (s, CH) ppm.

Aluminium tris[1,3-bis(diethylamino)propan-2-olate] (4), $\text{AlC}_{33}\text{H}_{75}\text{N}_6\text{O}_3$

$[\text{Al}(\text{OtBu})_3]_2$ (328 mg, 1.33 mmol) and 821 mg 1,3-bis(diethylamino)propan-2-ol (4.06 mmol) were stirred in 5 cm^3 toluene overnight. Removal of the solvent and by-products under reduced pressure yielded 797 mg (1.26 mmol, 95 %) of **4** as colourless, viscous oil. Crystals have been grown from a hexane solution at -5°C . ^1H NMR (C_6D_6 , 250.13 MHz): $\delta = 1.07$ (t, $J = 6.99$ Hz, 36H, CH_3), 2.53–2.99 (m, 36H, CH_2CH_3 , CHCH_2), 4.14 (quint, $J = 6.26$ Hz, 3H, CH) ppm; ^{13}C $\{^1\text{H}\}$ NMR (C_6D_6 , 62.86 MHz): $\delta = 11.2$ (s, CH_3), 46.9 (s, CH_2CH_3), 61.2 (s, CHCH_2), 67.9 (s, CH) ppm.

Gallium tris[1,3-bis(diethylamino)propan-2-olate] (5), $\text{GaC}_{33}\text{H}_{75}\text{N}_6\text{O}_3$

$[\text{Ga}(\text{OtBu})_3]_2$ (233 mg, 0.81 mmol) was mixed with 500 mg 1,3-bis(diethylamino)propan-2-ol (2.46 mmol) in 6 cm^3 toluene. After stirring overnight, all volatile substances were removed to obtain 526 mg (781 mmol, 97 %) of **5** as colourless, viscous oil. Crystals formed in this oil after a few days and were separated before the whole substance crystallised. ^1H NMR (C_6D_6 , 250.13 MHz): $\delta = 1.07$ (t, $J = 7.10$ Hz, 36H, CH_3), 2.56–2.95 (m, 36H, CH_2CH_3 , CHCH_2), 4.13 (quint, $J = 6.26$ Hz, 3H, CH) ppm; ^{13}C $\{^1\text{H}\}$ NMR (C_6D_6 , 62.86 MHz): $\delta = 11.3$ (s, CH_3), 47.0 (s, CH_2CH_3), 61.0 (s, CHCH_2), 68.9 (s, CH) ppm.

Indium tris[1,3-bis(diethylamino)propan-2-olate] (6), $\text{InC}_{33}\text{H}_{75}\text{N}_6\text{O}_3$

$\text{In}(\text{HMDS})_3$ (306 mg, 0.51 mmol) and 308 mg 1,3-bis(diethylamino)propan-2-ol (1.55 mmol) were stirred in 8 cm^3 toluene overnight. Removal of solvent and by-products yielded 355 mg (0.49 mmol, 97 %) of **6** as colourless, viscous oil. ^1H NMR (C_6D_6 , 250.13 MHz): $\delta = 1.07$ (t, $J = 7.06$ Hz, 36H, CH_3), 2.58 (dd, $J = 7.04$ Hz, 12.36 Hz, 6H, CHCH_2), 2.64–2.95 (m, 30H, CH_2CH_3 , CHCH_2), 4.18 (quin, $J = 6.48$ Hz, 3H, CH) ppm; ^{13}C $\{^1\text{H}\}$ NMR (C_6D_6 , 62.86 MHz): $\delta = 11.3$ (s, CH_3), 47.3 (s, CH_2CH_3), 62.3 (s, CHCH_2), 69.3 (s, CH) ppm.

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