

Intramolecularly stabilized organoaluminium and organogallium compounds: synthesis and X-ray crystal structures of some dimethylaluminium and -gallium alkoxides $\text{Me}_2\text{M}-\text{O}-\text{R}-\text{OR}'$ and amides $\text{Me}_2\text{M}-\text{NH}-\text{R}-\text{OR}'$

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Abstract

The intramolecularly stabilized dimeric organoaluminium and organogallium alkoxide complexes $[(\text{CH}_3)_2\text{Al}(\mu\text{-O}-\text{R}-\text{OR}')_2]$ ($\text{R}/\text{R}' = \text{CH}_2\text{CH}_2/\text{C}_6\text{H}_5$ (**1a**), $\text{CH}(\text{CH}_3)\text{CH}_2/\text{CH}_3$ (**2a**), $\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_2/\text{CH}_3$ (**3a**), $\text{CH}_2\text{C}_6\text{H}_4\text{-2}/\text{CH}_3$ (**4a**), $\text{C}_6\text{H}_4\text{-2}/\text{CH}_3$ (**5a**), $\text{C}_6\text{H}_4\text{-2}/\text{C}_2\text{H}_5$ (**6a**), $\text{C}_6\text{H}_3\text{-4-CH}_3\text{-2}/\text{CH}_3$ (**7a**)), $[(\text{CH}_3)_2\text{Ga}(\mu\text{-O}-\text{R}-\text{OR}')_2]$ ($\text{R}/\text{R}' = \text{CH}(\text{CH}_3)\text{CH}_2/\text{CH}_3$ (**2b**), $\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_2/\text{CH}_3$ (**3b**), $\text{CH}_2\text{C}_6\text{H}_4\text{-2}/\text{CH}_3$ (**4b**), $\text{C}_6\text{H}_4\text{-2}/\text{CH}_3$ (**5b**), $\text{C}_6\text{H}_4\text{-2}/\text{C}_2\text{H}_5$ (**6b**), $\text{CH}_2\text{CH}_2/\text{CH}_3$ (**8b**)), $[(\text{CH}_3)_2\text{Al}(\mu\text{-NH}-\text{R}-\text{OR}')_2]$ ($\text{R}/\text{R}' = \text{CH}_2\text{CH}_2/\text{CH}_3$ (**9a**) and $\text{CH}_2\text{CH}_2\text{CH}_2/\text{CH}_3$ (**10a**)) have been synthesized from trimethylaluminium or trimethylgallium and the corresponding alkoxy alcohols. Trimethylgallium reacts with $\text{CH}_3\text{OCH}_2\text{CH}_2\text{NH}_2$ and $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ with formation of the 1:1 adducts **11b** and **12b**, which decompose above 110 °C to yield CH_4 as well as $[(\text{CH}_3)_2\text{Ga}(\mu\text{-NH}-(\text{CH}_2)_2\text{-OCH}_3)_2]$ (**9b**) and $[(\text{CH}_3)_2\text{Ga}(\mu\text{-NH}-(\text{CH}_2)_3\text{-OCH}_3)_2]$ (**10b**) respectively. The ^1H -, ^{13}C -NMR and mass spectra of the new compounds, as well as the X-ray crystal structure analyses of **2b**, **4a**, **5a**, **5b**, **8b**, and **12b**, are reported and discussed.

Keywords: Gallium; Aluminium; Alkoxides; Amides

1. Introduction

Organometallic compounds of aluminium, gallium and indium have found increasing interest in recent years because of a wide range of possible uses, e.g. as volatile precursor compounds for metal-organic chemical vapour deposition (MOCVD) of Group III/V (13/15) semi-conducting materials [1], as precursors for ceramic materials [2], as reagents in organic synthesis [3], or as highly active cocatalysts for the metathesis of alkenes and alkynes as well as the polymerization of olefins [4–8]. As part of our program to develop novel organometallic compounds for industrial use which are less air- and moisture-sensitive and therefore easier to handle than the compounds commonly used today, we transferred the principle of intramolecular base-stabilization, which was very successful for MOCVD precursors

[1], to the development of new cocatalysts, which could be a very important alternative to methyl alumoxane (MAO) [4], and prepared and tested the first organoaluminium and organogallium compounds containing bidentate, intramolecularly coordinating ligands with oxygen or nitrogen as coordinating atom [9].

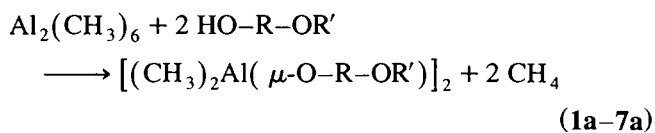
A few organoaluminium compounds of this type are known [2b,10–17]. They are mainly dimeric with coordination number 5 for aluminium, for example $[(\text{CH}_3)_2\text{AlOCH}_2\text{CH}_2\text{OCH}_3]_2$ [11], $[(\text{CH}_3)_2\text{AlOCH}(\text{C}_6\text{H}_5)\text{CH}(\text{CH}_3)\text{NHCH}_3]_2$ [12], $[(\text{CH}_3)_2\text{AlOC}_6\text{H}_4\text{-SCH}_3]_2$ [13], $[(^i\text{C}_4\text{H}_9)_2\text{AlOC}_6\text{H}_4\text{SCH}_3]_2$ [13], $[(\text{C}_2\text{H}_5)_2\text{AlOC}_6\text{H}_4\text{OCH}_3]_2$ [13], $[(^i\text{C}_4\text{H}_9)_2\text{AlOC}_6\text{H}_4\text{-OCH}_3]_2$ [13], $[(\text{CH}_3)_2\text{GaOC}_6\text{H}_4\text{OCH}_3]_2$ [13] or $[(\text{C}_2\text{H}_5)_2\text{AlNC}_4\text{H}_8\text{S}]_2$ [14]. In this paper we report on the synthesis of some new dimethylaluminium and dimethylgallium compounds with various types of difunctional ligand. Owing to the lower reactivity of trimethylgallium it was also possible to isolate two adducts of trimethylgallium with $\text{CH}_3\text{OCH}_2\text{CH}_2\text{NH}_2$ and $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$. Such adducts were known for

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trimethylaluminium, but a proof by X-ray structural analysis was possible only in case of a hindered intramolecular stabilization [14].

2. Synthesis and properties

Trimethylaluminium reacts in pentane at $-78\text{ }^{\circ}\text{C}$ with equivalent amounts of ethylene glycol monophenyl ether, 1-methoxy-2-propanol, 3-methoxy-3-methylbutanol, 2-methoxy benzylalcohol, 2-methoxyphenol, 2-ethoxyphenol, and 2-methoxy-4-methylphenol, with vigorous evolution of methane and formation of the dimeric dimethylaluminium alkoxides **1a–4a** and aryloxides **5a–7a**, which are isolated in high yields as colourless solids after crystallization from toluene or sublimation in vacuum:



R = $-\text{CH}_2\text{CH}_2-$	R' = C_6H_5	1a
R = $-\text{CH}(\text{CH}_3)\text{CH}_2-$	R' = CH_3	2a
R = $-\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_2-$	R' = CH_3	3a
R = $-\text{CH}_2\text{C}_6\text{H}_4-2-$	R' = CH_3	4a
R = $-\text{C}_6\text{H}_4-2-$	R' = CH_3	5a
R = $-\text{C}_6\text{H}_4-2-$	R' = C_2H_5	6a
R = $-\text{C}_6\text{H}_3(\text{CH}_3-4)-2-$	R' = CH_3	7a

The reactions of trimethylgallium with 1-methoxy-2-propanol, 3-methoxy-3-methyl butanol, 2-methoxybenzylalcohol, 2-methoxyphenol, 2-ethoxyphenol and ethylene glycol monomethyl ether under the same conditions result in the formation of the dimeric dimethylgallium alkoxides and -aryloxides **2b–6b** and **8b**. The mass spectrum of **6b** showed no masses heavier than the monomeric unit. Cryoscopic molecular weight investigations, as well as our attempts to isolate single crystals of this compound for an X-ray structural analysis, failed.

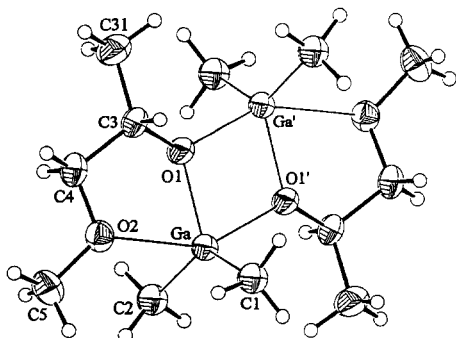


Fig. 1. ZORTEP [20] diagram with atom-labelling scheme for $[(\text{CH}_3)_2\text{Ga}(\mu\text{-OCH}(\text{CH}_3)\text{CH}_2\text{OCH}_3)]_2$ (**2b**).

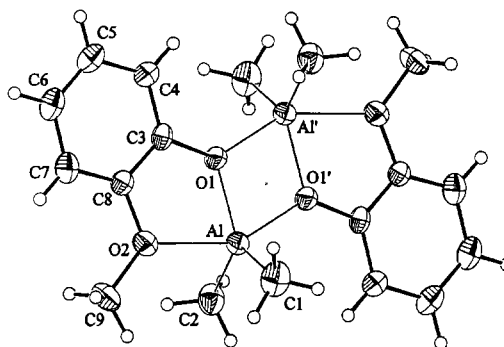
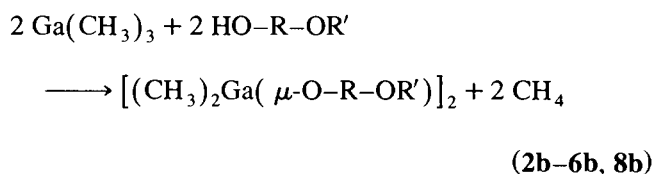


Fig. 2. ZORTEP [20] diagram with atom-labelling scheme for $[(\text{CH}_3)_2\text{Al}(\mu\text{-OC}_6\text{H}_4\text{-2-OCH}_3)]_2$ (**5a**).

Therefore, we cannot exclude a monomeric formula for **6b**.

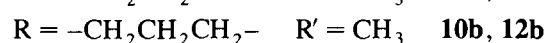
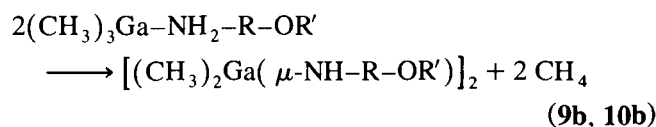
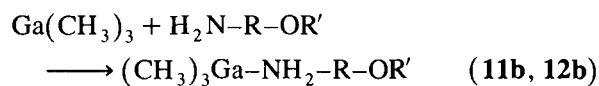
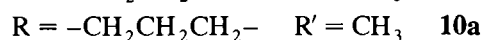
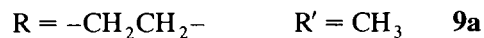
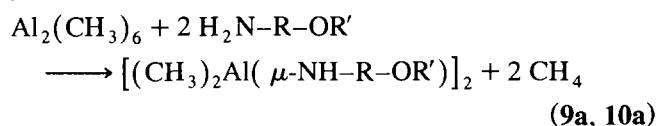


R = $-\text{CH}(\text{CH}_3)\text{CH}_2-$	R' = CH_3	2b
R = $-\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_2-$	R' = CH_3	3b
R = $-\text{CH}_2\text{C}_6\text{H}_4-2-$	R' = CH_3	4b
R = $-\text{C}_6\text{H}_4-2-$	R' = CH_3	5b
R = $-\text{C}_6\text{H}_4-2-$	R' = C_2H_5	6b
R = $-\text{CH}_2\text{CH}_2-$	R' = CH_3	8b

The new aluminium and gallium complexes are both air- and moisture-sensitive, decomposing over a period of minutes in the solid state on exposure to air. They are nearly insoluble in saturated hydrocarbons such as pentane and slightly soluble in unsaturated hydrocarbons such as benzene or toluene. All compounds are very soluble in donor solvents such as diethyl ether and tetrahydrofuran.

Trimethylaluminium reacts with the alkoxy amines 2-methoxy ethylamine and 3-methoxy propylamine with evolution of methane to give the dimeric dimethylaluminium amides **9a** and **10a**. In contrast, trimethylgallium reacts with the same alkoxy amines at room temperature with formation of the 1:1 adducts **11b** and **12b** respectively, which are purified by vacuum distillation at $60\text{ }^{\circ}\text{C}$ without decomposition. Heating to $110\text{ }^{\circ}\text{C}$ is necessary to start methane evolution. The dimethylgallium amides **9b** and **10b** resulted after heating **11b** and **12b** for 24 h. This is in agreement with previous investigations which demonstrated that alkane elimination from trimethylgallium amine adducts with forma-

tion of a gallium–nitrogen bond requires elevated temperatures [18,19].



The new dimethylaluminium and dimethylgallium amides show the same chemical and physical properties

as the alkoxide complexes described above. They are dimers in the gas phase, as demonstrated by their mass spectra. Their ^1H - and ^{13}C -NMR spectra recorded in benzene show the expected chemical shifts and coupling patterns.

3. Molecular structure of 2b, 4a, 5a, 5b, 8b and 12b

Single crystal X-ray structures were determined for the aluminium complexes **4a** and **5a**, the gallium complexes **2b**, **5b** and **8b** and the intermediate 1:1 complex **12b**. The crystal data and refinement parameters are given in Table 1. A structure solution was also attempted for **3a**, but it was not possible to get a satisfactory refinement.

In the crystal of **2b** (Fig. 1) the molecules are disordered statistically around a crystallographic mirror plane. Since the geometrical combination of the disordered methyl groups with the rest of the molecule is somewhat ambiguous, the corresponding bond angles in

Table 1
Crystal data and structure refinement

	2b	4a	5a	5b	8b	12b
Empirical formula	$\text{C}_{12}\text{H}_{30}\text{Ga}_2\text{O}_4$	$\text{C}_{20}\text{H}_{30}\text{Al}_2\text{O}_4$	$\text{C}_{18}\text{H}_{26}\text{Al}_2\text{O}_4 \cdot \text{C}_7\text{H}_8$	$\text{C}_{18}\text{H}_{26}\text{Ga}_2\text{O}_4 \cdot \text{C}_7\text{H}_8$	$\text{C}_{10}\text{H}_{26}\text{Ga}_2\text{O}_4$	$\text{C}_7\text{H}_{20}\text{GaNO}$
Formula weight (g mol^{-1})	377.80	388.40	452.48	537.96	349.75	203.96
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$C2/m$ (No. 12)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
Unit cell dimensions						
a (Å)	12.255(13)	9.523(2)	8.569(5)	8.711(4)	7.163(2)	6.1994(10)
b (Å)	9.220(10)	7.7444(13)	9.169(2)	9.161(3)	14.311(4)	15.207(3)
c (Å)	8.040(13)	15.153(5)	9.287(5)	9.276(3)	8.203(4)	11.658(3)
α (°)	90	90	82.49(3)	82.23(3)	90	90
β (°)	104.59(10)	100.77(2)	66.70(4)	67.72(4)	104.12(3)	91.07(2)
γ (°)	90	90	70.61(3)	70.03(3)	90	90
Unit cell volume (Å ³)	879(2)	1097.9(5)	632.1(5)	643.8(4)	815.4(5)	1098.8(4)
Z	2	2	1	1	2	4
Calculated density (Mg m^{-3})	1.427	1.175	1.189	1.388	1.424	1.233
Absorption coefficient (mm^{-1})	3.068	0.152	0.142	2.119	3.302	2.455
$F(000)$	392	416	242	278	360	432
Crystal size (mm^3)	0.24 × 0.48 × 0.48	0.24 × 0.36 × 0.36	0.06 × 0.21 × 0.36	0.60 × 0.60 × 1.20	0.21 × 0.42 × 0.50	0.12 × 0.30 × 0.36
θ range for data collection (°)	2.62–27.44	2.34–27.42	2.35–27.48	2.37–27.66	2.85–27.40	2.20–27.40
Index ranges	$-15 \leq h \leq 15$ $-11 \leq k \leq 11$ $0 \leq l \leq 10$	$0 \leq h \leq 12$ $0 \leq k \leq 10$ $-19 \leq l \leq 19$	$0 \leq h \leq 11$ $-11 \leq k \leq 11$ $-11 \leq l \leq 12$	$0 \leq h \leq 11$ $-11 \leq k \leq 11$ $-11 \leq l \leq 12$	$0 \leq h \leq 9$ $0 \leq k \leq 18$ $-10 \leq l \leq 10$	$0 \leq h \leq 8$ $0 \leq k \leq 19$ $-15 \leq l \leq 15$
Number of reflections						
collected	2123	2641	3088	3120	1997	2712
independent	1062	2496	2886	2923	1852	2486
(after DIFABS)	(991)	(2033)	(2026)		(1398)	
observed ($I > 2\sigma(I)$)	984	1663	1725	2758	1357	2260
Number of parameters	61	121	164	164	76	95
Goodness-of-fit on F^2	1.094	0.590	0.670	0.981	0.982	1.067
Final R indices						
R_1 ($I > 2\sigma(I)$)	0.0383	0.0354	0.0470	0.0320	0.0802	0.0643
wR_2 (all data)	0.1085	0.0801	0.1063	0.0930	0.2928	0.2086
Final difference Fourier map						
max. (e Å^{-3})	0.480	0.242	0.191	0.890	1.141	1.436
min. (e Å^{-3})	-0.552	-0.259	-0.232	-1.015	-1.912	-1.636

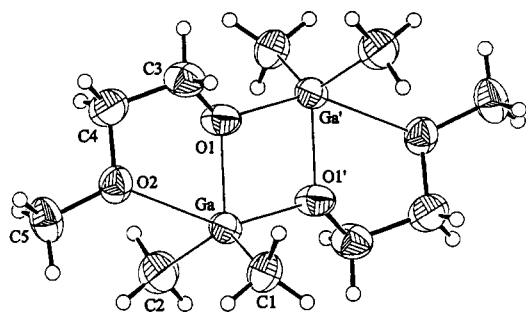


Fig. 3. ZORTEP [20] diagram with atom-labelling scheme for $[(\text{CH}_3)_2\text{Ga}(\mu\text{-OCH}_2\text{CH}_2\text{OCH}_3)]_2$ (**8b**).

Table 2 might be less accurate than indicated by their standard deviations. **5a** and **5b** are isostructural. Both compounds crystallize with one disordered molecule of toluene per unit cell. Fig. 2 shows a ZORTEP-plot [20] of the aluminium derivative **5a**. An X-ray structural analysis of a solvent-free crystal of the gallium complex **5b** was published recently by Oliver and coworkers [13]. Fig. 3 shows a ZORTEP-plot of **8b**. It is isostructural to its aluminium homologue, published a couple of years ago by Krüger and coworkers [11]. All compounds mentioned so far, as well as **4a** (Fig. 4), share the same structural motif: they all crystallize as centrosymmetric dimers. The four-membered ring $\text{M}-\text{O}1-\text{M}'-\text{O}1'$ ($\text{M} = \text{Al}, \text{Ga}$) is absolutely planar because of its symmetry. The coordinating oxygen atoms $\text{O}2$ and $\text{O}2'$ also fit well into this plane. The coordination spheres around the metal centres are compared in Table 2. In all these complexes, the distances $\text{M}-\text{O}1$ and $\text{M}-\text{O}1'$ are of the same order of magnitude, with the second one systematically longer than the first (by about 0.1 Å). The coordinative bond $\text{M}-\text{O}2$ is, of course, much longer.

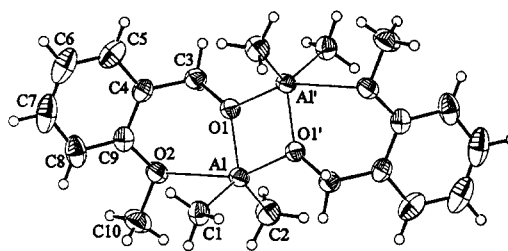


Fig. 4. ZORTEP [20] diagram with atom-labelling scheme for $[(\text{CH}_3)_2\text{Al}(\mu\text{-OCH}_2\text{C}_6\text{H}_4\text{-2-OCH}_3)]_2$ (**4a**).

The metal atom and these three oxygen atoms lie within one plane. A second plane, defined by the metal centre and the two methyl carbon atoms $\text{C}1$ and $\text{C}2$, is always approximately perpendicular to the first one. It would be interesting to compare the bond lengths and angles of **5b** with the corresponding values found by Oliver and coworkers [13] to learn more about the influence of intermolecular forces on the intramolecular geometry. Unfortunately, the crystal structures were determined at different temperatures, and consequently the differences observed should be attributed mainly to the temperature effect. Particularly, the bond lengths $\text{Ga}-\text{O}$ in the molecular core should be influenced exclusively by the latter, and indeed all these distances are smaller in our analysis than in the structure of Oliver and coworkers, carried out at room temperature.

The systematic absences for **3a** (monoclinic, $a = 13.744(8)$ Å, $b = 11.071(9)$ Å, $c = 14.67(2)$ Å, $\beta = 111.64(7)^\circ$) could not be determined unambiguously. After several attempts to resolve the structure in different space groups, it became obvious that problems arose from the coupled effects of disorder and pseudosymmetry. The best approximation was achieved in the space

Table 2
Selected bond lengths (Å) and angles ($^\circ$) for **2b**, **4a**, **5a**, **5b** and **8b**

	2b (M = Ga)	4a (M = Al)	5a (M = Al)	5b (M = Ga)	8b (M = Ga)
<i>Bond lengths</i>					
M–C1	1.972(9)	1.959(2)	1.950(4)	1.959(2)	1.939(9)
M–C2	1.943(9)	1.952(2)	1.956(3)	1.959(3)	1.944(11)
M–O1	1.914(4)	1.8215(14)	1.858(2)	1.936(2)	1.934(6)
M–O1'	1.999(4)	1.8802(13)	1.938(2)	2.039(2)	2.012(7)
M–O2	2.568(5)	2.572(2)	2.198(3)	2.442(2)	2.624(6)
M...M'	3.042(5)	2.8719(11)	3.015(2)	3.1445(13)	3.055(2)
O1...O1'	2.464(7)	2.336(2)	2.308(4)	2.434(3)	2.499(14)
<i>Bond angles</i>					
C1–M–C2	130.9(4)	122.29(9)	120.5(2)	129.83(13)	127.9(5)
C1–M–O1	109.6(3)	117.47(8)	116.86(14)	111.67(11)	114.3(4)
C1–M–O1'	99.1(3)	105.03(7)	101.94(14)	102.17(10)	103.9(4)
C1–M–O2	82.6(3)	84.38(6)	92.20(13)	91.48(10)	86.2(3)
C2–M–O1	115.3(3)	116.19(9)	121.77(13)	116.41(10)	113.0(4)
C2–M–O1'	108.4(3)	105.01(7)	101.77(12)	102.79(11)	105.7(4)
C2–M–O2	93.5(3)	87.30(7)	92.62(12)	90.92(9)	90.1(4)
O1–M–O1'	78.0(2)	78.25(6)	74.86(10)	75.46(8)	78.5(3)
O1–M–O2	71.4(2)	77.95(5)	75.83(9)	71.08(7)	70.3(2)
O1'–M–O2	147.87(14)	156.12(6)	150.67(9)	146.51(6)	148.6(2)
M–O1–M'	102.0(2)	101.75(6)	105.14(10)	104.54(8)	101.5(3)

Symmetry transformations used to generate equivalent atoms M' and $\text{O}1'$: $1-x, 1-y, 1-z$.

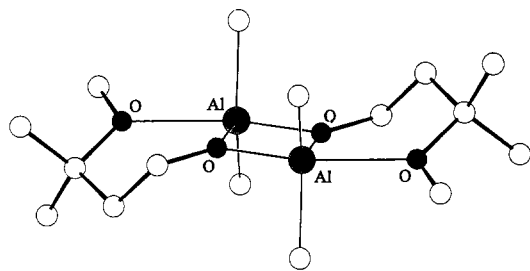


Fig. 5. Approximate molecular structure of $[(\text{CH}_3)_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{OCH}_3)]_2$ (**3a**).

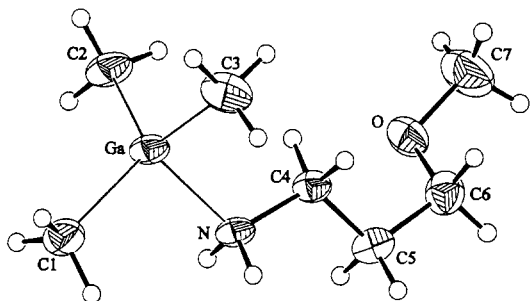


Fig. 6. ZORTEP [20] diagram with atom-labelling scheme for $(\text{CH}_3)_3\text{Ga}(\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_3)$ (**12b**).

group $P2_1/a$ (No. 14) with two independent centrosymmetric dimer molecules, one “proper”, and one disordered. The parameters of these two molecules were strongly correlated by pseudosymmetry, yielding no reliable detailed geometry. However, the picture was clear enough to get a view of the overall conformation (Fig. 5), which is in accordance with the general scheme discussed above.

The molecular structure of $(\text{CH}_3)_3\text{Ga-NH}_2\text{CH}_2\text{CH}_2\text{-CH}_2\text{OCH}_3$ (**12b**) is depicted in Fig. 6. The coordination sphere around gallium can be discussed as a moderately distorted tetrahedron (Table 3). The most interesting feature of this crystal structure is the fact that gallium retains a four-fold coordination despite the presence of a methoxy group, which should be a good potential donor. This behaviour can be explained by the observation that the oxygen atom instead is involved in a hydrogen bond

Table 3
Selected bond lengths (Å) and angles (°) for **12b**

Bond lengths	
Ga–C1	1.981(4)
Ga–C2	1.997(4)
Ga–C3	1.979(4)
Ga–N	2.097(3)
Bond angles	
C1–Ga–C2	116.6(2)
C1–Ga–C3	117.3(2)
C2–Ga–C3	114.9(2)
C1–Ga–N	100.9(2)
C2–Ga–N	101.37(14)
C3–Ga–N	101.4(2)

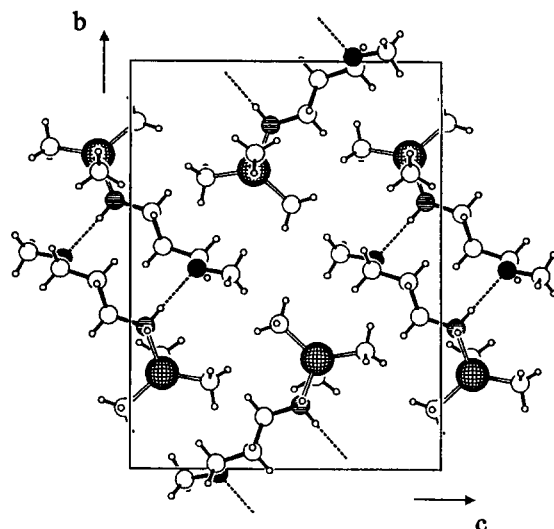


Fig. 7. PLUTONN [24] plot of the molecular arrangement of $(\text{CH}_3)_3\text{Ga}(\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_3)$ (**12b**) in the unit cell showing the hydrogen bonds. The viewing direction is a projection along the crystallographic a -axis.

interaction with one of the N–H bonds, connecting the molecules to centric H-bonded dimers (Fig. 7). Obviously, this is the energetically more favourable choice for the oxygen atom, at least in the solid state. Similar hydrogen bonds have been observed in the crystal structure of $(\text{CH}_3)_2\text{GaOCH}_2\text{CH}_2\text{NH}_2$, where they are also responsible for monomeric units [21].

4. Experimental details

4.1. General comments

All reactions were carried out in an atmosphere of dry, oxygen-free argon. CHN analyses were performed on a Perkin-Elmer 240 C elemental analyzer. Some unacceptable analyses are caused by partial hydrolysis, which could not be avoided. Mass spectra (electron impact ionization) were obtained on the instrument Varian MAT 311 A (70 eV). NMR spectra were recorded on the spectrometer Bruker ARX 200 (^1H -NMR at 200 MHz in C_6D_6 ; $^{13}\text{C}\{^1\text{H}\}$ -NMR at 50.32 MHz in C_6D_6) unless stated otherwise; chemical shifts are referenced to $(\text{CH}_3)_4\text{Si}$ with positive shifts referring to lower field.

4.2. $[(\text{CH}_3)_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OC}_6\text{H}_5)]_2$ (**1a**)

Pentane (150 ml) was cooled to -78°C and $\text{Al}(\text{CH}_3)_3$ (19.1 ml, 14.4 g, 200 mmol) was added carefully. Freshly distilled ethylene glycol monophenyl ether (24.89 ml, 200 mmol) was added dropwise. During the addition a violent evolution of gas was observed. The resulting white suspension was stirred for an additional 2 h, and after that the reaction mixture

was allowed to warm to 20 °C. After 12 h of further stirring at room temperature the solvent was removed by vacuum evaporation to give **1a** as white powder. The product was purified by vacuum sublimation at 0.1 mbar per 100 °C bath temperature. Yield 33.02 g (85%). M.p. (sealed) 144–146 °C. Anal. Found: C, 61.11; H, 7.89. $C_{20}H_{30}Al_2O_4$ (**1a**). Calc.: C, 61.85; H, 7.78%. 1H -NMR: 7.07–7.15 (m, 2H, aromatic H), 6.81–6.87 (m, 3H, aromatic H), 3.50 (m, 2H, OCH_2), 3.35 (m, 2H, $PhOCH_2$), –0.41 (s, 6H, $AlCH_3$) ppm. $^{13}C\{^1H\}$ -NMR: 157.9, 129.8, 121.9, 115.0 (aromatic C), 67.5 ($PhOCH_2$), 60.4 (OCH_2), –10.5 ($AlCH_3$) ppm. MS (160 °C, m/z (%)): 373 (100) $[M-CH_3]^+$, 343 (8.4) $[M-3CH_3]^+$, 267 (15.3) $[M-(CH_2CH_2OC_6H_5)]^+$, 194 (16.6) $[(CH_3)_2Al(\mu-OCH_2CH_2OC_6H_5)]^+$, 179 (19.9) $[(CH_3)Al(\mu-OCH_2CH_2OC_6H_5)]^+$, 164 (20.3) $[AlOCH_2CH_2OC_6H_5]^+$.

4.3. $[(CH_3)_2Al(\mu-OCH(CH_3)CH_2OCH_3)]_2$ (**2a**)

This compound was prepared, analogously to **1a**, from 19.1 ml (200 mmol) of $Al(CH_3)_3$ and 19.59 ml (200 mmol) of freshly distilled 1-methoxy-2-propanol in 150 ml of pentane. The product was purified by vacuum distillation at 0.1 mbar per 110 °C bath temperature to give pure white solid **2a**. Yield 27.46 g (94%). M.p. (sealed) 110–112 °C. Anal. Found: C, 48.76; H, 10.72. $C_{12}H_{30}Al_2O_4$ (**2a**). Calc.: C, 49.30; H, 10.34%. 1H -NMR: 3.87 (m, 1H, OCH), 2.95 (s, 3H, OCH_3), 2.82 (m, 1H, OCH_2), 2.68 (m, 1H, OCH_2), 1.05 (t, 3H, $C(CH_3)$), –0.63 (s, 6H, $AlCH_3$) ppm. $^{13}C\{^1H\}$ -NMR: 75.6, 75.9 (OCH), 64.9, 65.3 (OCH_2), 56.9 (OCH_3), 19.0, 19.2 ($(H_3C)CH$), –9.8 ($AlCH_3$) ppm. MS (40 °C, m/z (%)): 277 (100) $[M-CH_3]^+$, 247 (1.9) $[M-3CH_3]^+$, 219 (34.8) $[M-(CH_3)_2AlO]^+$, 147 (16.4) $[(H_3C)_2Al(\mu-OCH(CH_3)CH_2OCH_3)]^+$, 131 (34.5) $[(H_3C)Al(\mu-OCH(CH_3)CH_2OCH_3)]^+$, 117 (8.4) $[AlOCH(CH_3)CH_2OCH_3]^+$.

4.4. $[(CH_3)_2Al(\mu-OCH_2CH_2C(CH_3)_2OCH_3)]_2$ (**3a**)

This compound was prepared, analogously to **1a**, from 19.1 ml (200 mmol) of $Al(CH_3)_3$ and 25.42 ml (200 mmol) of freshly distilled 3-methoxy-3-methylbutanol in 150 ml of pentane. The resulting white product (2 g) was dissolved in 20 ml of toluene. This solution was cooled to –30 °C, affording **3a** as a transparent crystalline product. Total yield 32.25 g (91%). M.p. (sealed) 77–79 °C. Anal. Found: C, 54.60; H, 10.83. $C_{16}H_{38}Al_2O_4$ (**3a**). Calc.: C, 55.15; H, 10.99%. 1H -NMR: 4.12 (m, 1H, OCH_2), 3.73 (t, 1H, OCH_2), 2.92 (s, 3H, OCH_3), 1.89 (m, 1H, CH_2), 1.55 (t, 1H, CH_2), 0.92 (s, 3H, CCH_3), 0.83 (s, 3H, CCH_3), –0.39 (s, 3H, $AlCH_3$), –0.47 (s, 3H, $AlCH_3$) ppm. $^{13}C\{^1H\}$ -NMR: 76.6, 73.1 ($C(CH_3)_2$), 61.8, 58.0 (OCH_2), 49.1 (OCH_3), 44.1, 42.8 (CH_2), 24.9, 24.2

(H_3CC), –8.9 ($AlCH_3$) ppm. MS (70 °C, m/z (%)): 333 (12.8) $[M-CH_3]^+$, 301 (31.4) $[M-CH_3-CH_3OH]^+$, 247 (55.6) $[M-H_3COC(CH_3)_2CH_2CH_2]^+$, 231 (100) $[M-OCH_2CH_2C(CH_3)_2OCH_3]^+$, 174 (1.1) $[(H_3C)_2Al(\mu-OCH_2CH_2C(CH_3)_2OCH_3)]^+$, 73 (54.0) $[(H_3C)_2AlO]^+$.

4.5. $[(CH_3)_2Al(\mu-OCH_2C_6H_4-2-OCH_3)]_2$ (**4a**)

This compound was prepared, analogously to **1a**, by addition of freshly distilled 2-methoxy benzylalcohol (25 ml, 200 mmol) to 19.1 ml of $Al(CH_3)_3$ (200 mmol) in 150 ml of pentane. Colourless crystals of **4a** were obtained by vacuum sublimation at 0.1 mbar per 90 °C bath temperature. Yield 32.24 g (83%). M.p. (sealed) 109–111 °C. Anal. Found: C, 61.35; H, 7.85. $C_{20}H_{30}Al_2O_4$ (**4a**). Calc.: C, 61.85; H, 7.78%. 1H -NMR: 6.97–7.03 (m, 2H, aromatic H), 6.71–6.75 (m, 1H, aromatic H), 6.38–6.43 (m, 1H, aromatic H), 4.61 (s, 2H, OCH_2), 3.33 (s, 3H, OCH_3), –0.54 (s, 6H, $AlCH_3$) ppm. $^{13}C\{^1H\}$ -NMR: 157.7, 130.3, 129.4, 127.3, 121.1, 110.6 (aromatic C), 61.2 (OCH_2), 54.6 (OCH_3), –10.7 ($AlCH_3$) ppm. MS (120 °C, m/z (%)): 373 (66.8) $[M-CH_3]^+$, 343 (1.1) $[M-3CH_3]^+$, 267 (4.6) $[M-OCH_2C_6H_4]^+$, 179 (1.5) $[(H_3C)Al(\mu-OCH_2C_6H_4OCH_3)]^+$, 121 (100) $[CH_2C_6H_4OCH_3]^+$, 91 (42.8) $[CH_2C_6H_5]^+$.

4.6. $[(CH_3)_2Al(\mu-OC_6H_4-2-OCH_3)]_2$ (**5a**)

This compound was prepared, analogously to **1a**, from 19.1 ml (200 mmol) of $Al(CH_3)_3$ and 21.97 ml (24.83 g, 200 mmol) of freshly distilled 2-methoxyphenol in 150 ml of pentane. The resulting **5a** was purified by vacuum sublimation at 0.1 mbar per 90 °C bath temperature. Three grams of the product were dissolved in toluene (ca. 20 ml). The toluene solution was cooled to –30 °C, affording a transparent crystalline product. Total yield 30.63 g (85%). M.p. (sealed) 182–184 °C. Anal. Found: C, 59.77; H, 7.06. $C_{18}H_{26}Al_2O_4$ (**5a**). Calc.: C, 59.99; H, 7.27%. 1H -NMR: 7.29–7.33 (m, 1H, aromatic H), 6.60–6.80 (m, 2H, aromatic H), 6.23–6.26 (m, 1H, aromatic H), 3.20 (s, 3H, OCH_3), –0.29 (s, 6H, $AlCH_3$) ppm. $^{13}C\{^1H\}$ -NMR: 146.5, 144.2, 122.9, 120.7, 116.4, 110.1 (aromatic C), 54.0 (OCH_3), –9.5 ($AlCH_3$) ppm. MS (140 °C, m/z (%)): 345 (22.8) $[M-CH_3]^+$, 315 (9.5) $[M-3CH_3]^+$, 180 (13.4) $[(H_3C)_2Al(\mu-OC_6H_4-2-OCH_3)]^+$, 165 (60.5) $[(H_3C)Al(\mu-OC_6H_4-2-OCH_3)]^+$, 150 (100) $[AlOC_6H_4-2-OCH_3]^+$, 124 (7.1) $[HOC_6H_4-2-OCH_3]^+$, 109 (9.0) $[OC_6H_4OH]^+$.

4.7. $[(CH_3)_2Al(\mu-OC_6H_4-2-OC_2H_5)]_2$ (**6a**)

This compound was prepared, analogously to **1a**, from 19.1 ml (200 mmol) of $Al(CH_3)_3$ and 25.1 ml

(200 mmol) of freshly distilled pyrocatechol monoethylether in 150 ml of pentane. The resulting **6a** was purified by vacuum sublimation at 0.1 mbar per 160 °C bath temperature to give a transparent crystalline product. Yield 33.69 g (87%). M.p. (sealed) 86–88 °C. Anal. Found: C, 61.69; H, 7.65. $C_{20}H_{30}Al_2O_4$ (**6a**). Calc.: C, 61.85; H, 7.78%. 1H -NMR: 7.33 (dd, 1H, aromatic H), 6.71 (m, 2H, aromatic H), 6.34 (dd, 1H, aromatic H), 3.80 (q, 2H, OCH_2), 0.97 (t, 3H, CCH_3), -0.24 (s, 6H, $AlCH_3$) ppm. $^{13}C\{^1H\}$ -NMR: 145.0, 144.3, 122.3, 120.5, 116.7, 110.6 (aromatic C), 63.6 (OCH_2), 13.3 (CCH_3), -8.5 ($AlCH_3$) ppm. MS (140 °C, m/z (%)): 373 (28.7) $[M-CH_3]^+$, 343 (1.1) $[M-3CH_3]^+$, 329 (14.9) $[M-Al(CH_3)_3]^+$, 285 (17.3) $[M-(H_3C)_2AlOC_2H_5]^+$, 194 (17.9) $[(H_3C)_2Al(\mu-OC_6H_4-2-OC_2H_5)]^+$, 179 (49.0) $[(H_3C)Al(\mu-OC_6H_4-2-OC_2H_5)]^+$, 151 (100) $[(H_3C)Al(\mu-OC_6H_4-2-OH)]^+$.

4.8. $[(CH_3)_2Al(\mu-OC_6H_3-2-OCH_3-4-CH_3)]_2$ (**7a**)

This compound was prepared, analogously to **1a**, from 7.6 ml (79 mmol) of $Al(CH_3)_3$ and 10 ml (79 mmol) of freshly distilled 2-methoxy-4-methylphenol in 50 ml of pentane. White crystals of **7a** were obtained by vacuum sublimation at 0.1 mbar per 100 °C bath temperature. Yield 11.62 g (75%). M.p. (sealed) 242–244 °C. Anal. Found: C, 61.04; H, 7.85. $C_{20}H_{30}Al_2O_4$ (**7a**). Calc.: C, 61.85; H, 7.78%. 1H -NMR (C_6D_6 , 400 MHz): 7.20 (d, 1H, aromatic H), 6.57 (dd, 1H, aromatic H), 6.17 (d, 1H, aromatic H), 3.21 (s, 3H, OCH_3), 2.06 (s, 3H, CH_3), -0.27 (s, 6H, $AlCH_3$) ppm. $^{13}C\{^1H\}$ -NMR: 146.2, 142.0, 130.1, 123.0, 116.0, 111.0 (aromatic C), 54.0 (OCH_3), 21.0 (CH_3), -9.4 ($AlCH_3$) ppm. MS (100 °C, m/z (%)): 373 (28.1) $[M-CH_3]^+$, 343 (12.5) $[M-3CH_3]^+$, 194 (13.4) $[(H_3C)_2Al(\mu-OC_6H_3-2-OCH_3-4-CH_3)]^+$, 179 (47.0) $[(H_3C)Al(\mu-OC_6H_3-2-OCH_3-4-CH_3)]^+$, 164 (100) $[AlOC_6H_3-2-OCH_3-4-CH_3]^+$, 138 (7.1) $[HOC_6H_3-2-OCH_3-4-CH_3]^+$.

4.9. $[(CH_3)_2Ga(\mu-OCH(CH_3)CH_2OCH_3)]_2$ (**2b**)

Freshly distilled 1-methoxy-2-propanol (6.82 ml, 6.28 g, 70 mmol) was added at room temperature to a stirred solution of $Ga(CH_3)_3$ (8.00 g, 70 mmol) in 150 ml of pentane. An evolution of gas was observed. The resulting solution was then stirred overnight; the solvent was removed by distillation and the white residue was purified by vacuum sublimation at 0.1 mbar per 74 °C bath temperature. Colourless crystals of **2b** could be isolated after a vacuum distillation at 50 °C per 0.1 mbar and standing for 1 h at -30 °C. Total yield 11.81 g (89%). M.p. (sealed) 70–71 °C. Anal. Found: C, 37.90; H, 7.60. $C_{12}H_{30}Ga_2O_4$ (**2b**). Calc.: C, 38.15; H, 8.00%. 1H -NMR: 3.78 (m, 1H, OCH), 2.93 (s, 3H, OCH_3), 2.84 (m, 2H, OCH_2), 0.99 (m, 3H, $C(CH_3)_2$), 0.05 (s, 6H, $GaCH_3$) ppm. $^{13}C\{^1H\}$ -NMR: 78.52, 78.69 (OCH),

67.15, 67.32 (OCH_2), 57.82 (OCH_3), 20.18 ($(H_3C)CH$), -4.82 ($GaCH_3$). MS (60 °C, m/z (%)): 361/363/365 (38.6) $[M-CH_3]^+$, 188/190 (0.4) $[(H_3C)_2Ga(\mu-OCH(CH_3)CH_2OCH_3)]^+$, 173/175 (100.0) $[(H_3C)Ga(\mu-OCH(CH_3)CH_2OCH_3)]^+$, 99/101 (20.3) $[Ga(CH_3)_2]^+$, 69/71 (6.4) $[Ga]^+$, 45 (11.1) $[C_2H_5O]^+$.

4.10. $[(CH_3)_2Ga(\mu-OCH_2CH_2C(CH_3)_2OCH_3)]_2$ (**3b**)

This compound was prepared from 13.29 ml (12.29 g, 104 mmol) of freshly distilled 3-methoxy-3-methylbutanol and $Ga(CH_3)_3$ (11.90 g, 104 mmol) in 50 ml of pentane by the same method described for **2b**. The resulting **3b** was purified by vacuum distillation at 67 °C per 0.1 mbar to give a pure colourless crystalline solid using the same method as described for **2b**. Total yield 19.96 g (89%). M.p. (sealed) 45–46 °C. Anal. Found: C, 43.88; H, 8.52. $C_{16}H_{38}Ga_2O_4$ (**2b**). Calc.: C, 44.32; H, 8.82%. 1H -NMR: 4.03 (m, 1H, OCH_2), 3.83 (m, 1H, OCH_2), 2.97 (s, 3H, OCH_3), 1.79 (m, 1H, CH_2), 1.65 (m, 1H, CH_2), 0.98 (s, 3H, $C(CH_3)_2$), 0.94 (s, 3H, $C(CH_3)_2$), 0.06 (s, 3H, $GaCH_3$) 0.02 (s, 3H, $GaCH_3$) ppm. $^{13}C\{^1H\}$ -NMR: 73.21 ($C(CH_3)_2$), 61.62, 60.44 (OCH_2), 49.01, 48.79 (OCH_3), 44.21 (CH_2) 25.09 ($(H_3C)_2C$), -5.52 , -6.35 ($GaCH_3$) ppm. MS (40 °C, m/z (%)): 417/419/421 (25.4) $[M-CH_3]^+$, 99/101 (43.7) $[Ga(CH_3)_2]^+$, 73 (100.0) $[C_4H_9O]^+$, 69/71 (12.3) $[Ga]^+$.

4.11. $[(CH_3)_2Ga(\mu-OCH_2C_6H_4-2-OCH_3)]_2$ (**4b**)

This compound was prepared from 8.28 ml (67 mmol) of freshly distilled 2-methoxy benzylalcohol and $Ga(CH_3)_3$ (7.72 g, 67 mmol) in 50 ml of pentane by the same method described for **2b**. Colourless crystals of **4b** were obtained by vacuum sublimation at 0.1 mbar per 70 °C bath temperature. Yield 14.13 g (89%). M.p. (sealed) 66–68 °C. Anal. Found: C, 50.81; H, 6.63. $C_{20}H_{30}Ga_2O_4$ (**4b**). Calc.: C, 50.69; H, 6.38%. 1H -NMR: 7.00–7.04 (m, 2H, aromatic H), 6.78–6.93 (m, 1H, aromatic H), 6.50–6.58 (m, 1H, aromatic H), 4.77 (s, 2H, OCH_2), 3.29 (s, 3H, OCH_3), -0.05 (m, 6H, $GaCH_3$) ppm. $^{13}C\{^1H\}$ -NMR: 157.43, 157.13, 129.70, 128.68, 120.78, 110.18 (aromatic C), 54.36 (OCH_2), -6.47 ($GaCH_3$) ppm. MS (80 °C, m/z (%)): 472/474/476 (0.1) $[M]^+$, 457/459/461 (100.0) $[M-CH_3]^+$, 236/238 (0.4) $[(H_3C)_2Ga(\mu-OCH_2C_6H_4-OCH_3)]^+$, 221/223 (16.4) $[(H_3C)Ga(\mu-OCH_2C_6H_4-OCH_3)]^+$, 121 (86.6) $[C_8H_9O]^+$, 99/101 (4.2) $[Ga(CH_3)_2]^+$, 91 (30.8) $[C_7H_7]^+$, 69/71 (2.7) $[Ga]^+$.

4.12. $[(CH_3)_2Ga(\mu-OC_6H_4-2-OCH_3)]_2$ (**5b**)

This compound was prepared from 12.54 g (101 mmol) of freshly distilled 2-methoxyphenol and $Ga(CH_3)_3$ (11.60 g, 101 mmol) in 150 ml of pentane by

the same method described for **2b**. Colourless crystals of **5b** were obtained by vacuum sublimation at 0.1 mbar per 150 °C bath temperature using the same method as for **2b**. Total yield 20.11 g (89%). M.p. (sealed) 179–180 °C. Anal. Found: C, 47.91; H, 5.50. $C_{18}H_{26}Ga_2O_4$ (**5b**). Calc.: C, 48.49; H, 5.88%. 1H -NMR: 6.99 (dd, 1H, aromatic H), 6.82 (ddd, 1H, aromatic H), 6.68 (ddd, 1H, aromatic H), 6.42 (dd, 1H, aromatic H), 3.14 (s, 3H, OCH₃), 0.19 (s, 6H, GaCH₃) ppm. $^{13}C\{^1H\}$ -NMR: 148.43, 142.48, 122.40, 119.22, 116.67, 111.27 (aromatic C), 54.05 (s, OCH₃), -4.52 (s, GaCH₃) ppm. MS (120 °C, m/z (%)): 444/446/448 (0.8) $[M]^+$, 222/224 (31.6) $[(H_3C)_2Ga(\mu-OC_6H_4-2-OCH_3)]^+$, 207/209 (64.8) $[H_3CGa(\mu-OC_6H_4-2-OCH_3)]^+$, 192/194 (100.0) $[Ga(\mu-OC_6H_4-2-OCH_3-2CH_3)]^+$, 124 (10.5) $[HOC_6H_4-2-OCH_3]^+$, 99/101 (27.0) $[Ga(CH_3)_2]^+$, 69/71 (29.6) $[Ga]^+$.

4.13. $(CH_3)_2Ga(\mu-OC_6H_4-2-OCH_2H_5)$ (**6b**)

This compound was prepared from 10.55 ml of freshly distilled pyrocatechol monoethyl ether (11.61 g, 84 mmol) and $Ga(CH_3)_3$ (9.65 g, 84 mmol) in 150 ml of pentane by the same method as described for **2b**. The resulting **6b** was purified by vacuum sublimation at 0.1 mbar per 115 °C bath temperature to give a white powder. Yield 17.30 g (87%). M.p. (sealed) 155–157 °C. Anal. Found: C, 50.30; H, 5.91. $C_{10}H_{15}GaO_2$ (**6b**). Calc.: C, 50.69; H, 6.38%. 1H -NMR: 6.98–7.02 (m, 1H, aromatic H), 6.68–6.87 (m, 2H, aromatic H), 6.45–6.51 (m, 1H, aromatic H), 3.59, 3.42 (q, 2H, OCH₂), 1.04, 0.87 (t, 3H, CCH₃), -0.27 (s, 6H, GaCH₃) ppm. $^{13}C\{^1H\}$ -NMR: 147.61, 146.92, 121.95, 119.16, 117.05, 111.78 (aromatic C) 63.50, 64.00, (CH₂), 14.33, 14.51 (CCH₃), -3.14 (GaCH₃) ppm. MS (130 °C, m/z (%)): 236/238 (42.0) $[M]^+$, 221/223 (51.8) $[M-CH_3]^+$, 192/194 (100.0) $[M-C_2H_5, CH_3]^+$, 177/179 (22.6) $[M-C_2H_5, 2CH_3]^+$, 99/101 (12.3) $[Ga(CH_3)_2]^+$, 69/71 (16.4) $[Ga]^+$.

4.14. $[(CH_3)_2Ga(\mu-OCH_2CH_2OCH_3)]_2$ (**8b**)

This compound was prepared from 8.43 ml of freshly distilled ethylene glycol monomethylether (8.11 g, 107 mmol) and $Ga(CH_3)_3$ (12.25 g, 107 mmol) in 50 ml of pentane by the same method as described for **2b**. A vacuum distillation at 50 °C per 0.1 mbar gave a colourless liquid and after standing for 1 h at -30 °C colourless crystalline solid **8b** was formed. Yield 16.61 g (89%). M.p. (sealed) 31–33 °C. Anal. Found: C, 33.99; H, 7.33. $C_{10}H_{26}Ga_2O_4$ (**8b**). Calc.: C, 34.34; H, 7.49%. 1H -NMR: 3.47 (t, 2H, H₂COGa), 2.99 (t, 2H, OCH₂), 2.96 (s, 3H, OCH₃), -0.03 (s, 6H, GaCH₃) ppm. $^{13}C\{^1H\}$ -NMR: 74.21 (OCH₂), 61.12 (H₂COGa), 57.92 (OCH₃), -7.08 (GaCH₃) ppm. MS (25 °C, m/z (%)): 333/335/337 (32.8) $[M-CH_3]^+$, 159/161 (80.4)

$[(H_3C)Ga(\mu-O(CH_2)_2OCH_3)]^+$, 99/101 (50.8) $[Ga(CH_3)_2]^+$, 45 (100.0) $[C_2H_5O]^+$.

4.15. $[(CH_3)_2Al(\mu-NHCH_2CH_2OCH_3)]_2$ (**9a**)

This compound was prepared using the method described for **1a**, by addition of freshly distilled 2-methoxyethylamine (17.3 ml, 200 mmol) to 19.1 ml (200 mmol) of $Al(CH_3)_3$ in 150 ml of pentane. The product was purified by vacuum distillation at 73–77 °C per 0.1 mbar to give **9a** as an oily light yellow liquid. Yield 18.91 g (72%). Anal. Found: C, 45.19; H, 10.43; N, 11.12. $C_{10}H_{28}Al_2N_2O_2$ (**9a**). Calc.: C, 45.79; H, 10.76; N, 10.68%. 1H -NMR: 3.02 (s, 3H, OCH₃), 2.94 (m, 2H, OCH₂), 2.56 (m, 2H, NCH₂), 1.05 (s, br, 1H, NH), -0.68 (s, 6H, AlCH₃) ppm. $^{13}C\{^1H\}$ -NMR: 73.8 (OCH₂), 58.3 (OCH₃), 42.5 (NCH₂), -10.5 (AlCH₃) ppm. MS (80 °C, m/z (%)): 262 (4.1) $[M]^+$, 246 (54.7) $[M-CH_3]^+$, 131 (100) $[(H_3C)_2Al(\mu-NHCH_2CH_2OCH_3)]^+$, 116 (61.5) $[(H_3C)Al(\mu-NHCH_2CH_2OCH_3)]^+$, 57 (55.4) $[C_3H_7N]^+$.

4.16. $[(CH_3)_2Al(\mu-NHCH_2CH_2CH_2OCH_3)]_2$ (**10a**)

This compound was prepared using the method described for **1a**, by addition of freshly distilled 3-methoxypropylamine (18.30 ml, 200 mmol) to 19.1 ml (200 mmol) of $Al(CH_3)_3$ in 150 ml of pentane. The product was purified by vacuum distillation at 89–92 °C per 0.1 mbar resulting in white solid **10a**. Yield 14.02 g (48%). M.p. (sealed) 42–44 °C. Anal. Found: C, 49.14; H, 10.99; N, 10.30. $C_{12}H_{32}Al_2N_2O_2$ (**10a**). Calc.: C, 49.64; H, 11.11; N, 9.65%. 1H -NMR: 3.05 (m, 2H, OCH₂), 3.01 (s, 3H, OCH₃), 2.69 (m, 2H, NCH₂), 1.48 (m, 2H, CH₂), 1.00 (s, br, 1H, NH), -0.56 (s, 6H, AlCH₃) ppm. $^{13}C\{^1H\}$ -NMR: 72.9 (OCH₂), 58.6 (OCH₃), 42.3 (NCH₂), 31.6 (CH₂), -9.52 (AlCH₃) ppm. MS (20 °C, m/z (%)): 275 (84.8) $[M-CH_3]^+$, 130 (45.6) $[(H_3C)Al(\mu-NH(CH_2)_3OCH_3)]^+$, 73 (7.7) $[(H_3C)_2AlO]^+$, 57 (10.8) $[C_3H_7N]^+$.

4.17. $(CH_3)_3Ga-NH_2(CH_2)_2OCH_3$ (**11b**)

This compound was prepared from 10.90 ml (9.50 g, 127 mmol) of freshly distilled 2-methoxyethylamine and $Ga(CH_3)_3$ (14.53 g, 127 mmol) in 100 ml of pentane by the method described for the synthesis of **1b**. There was no evolution of methane during the reaction at room temperature. The product was purified by vacuum distillation at 60 °C per 0.1 mbar to give a pure colourless liquid. Yield 20.50 g (85%) of **11b**. 1H -NMR: 2.89 (s, 3H, OCH₃), 2.67 (t, 2H, OCH₂), 2.15 (m, 2H, NCH₂), 1.47 (s, br, 2H, NH₂), -0.29 (s, 9H, GaCH₃) ppm. $^{13}C\{^1H\}$ -NMR: 70.59 (OCH₂), 57.58 (OCH₃), 40.71 (NCH₂), -6.20 (GaCH₃) ppm. MS (30 °C, m/z (%)): 174/176 (10.0) $[M-CH_3]^+$, 99/101.

(100.0) $[\text{Ga}(\text{CH}_3)_2]^+$, 84/86. (7.4) $[\text{GaCH}_3]^+$, 69/71 (15.6) $[\text{Ga}]^+$, 45 (15.5) $[\text{C}_2\text{H}_5\text{O}]^+$.

4.18. $(\text{CH}_3)_3\text{Ga}-\text{NH}_2(\text{CH}_2)_3\text{OCH}_3$ (**12b**)

This compound was prepared from 4.57 ml (5.17 g, 50 mmol) of freshly distilled 3-methoxypropylamine and $\text{Ga}(\text{CH}_3)_3$ (5.74 g, 50 mmol) in 50 ml of pentane by the method described for the synthesis of **11b**. The resulting **12b** was purified by vacuum distillation at 67 °C per 0.1 mbar followed by the procedure described for **8b**. Yield 9.59 g (94%). M.p. (sealed) 28–29 °C. $^1\text{H-NMR}$: 3.04 (t, 2H, OCH_2), 2.98 (s, 3H, OCH_3), 2.44 (t, 2H, NCH_2), 1.30 (m, 2H, CH_2), 0.92 (s, br, 2H, NH_2), –0.13 (s, 9H, GaCH_3) ppm. $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$: 71.94 (OCH_2), 58.46 (OCH_3), 40.47 (NCH_2), 30.79 (CH_2), –5.91 (GaCH_3).

4.19. $[(\text{CH}_3)_2\text{Ga}(\mu\text{-NH}(\text{CH}_2)_2\text{OCH}_3)]_2$ (**9b**)

20 g (105 mmol) of **11b** were heated for 24 h to 110 °C. The oily residue was purified by vacuum distillation at 90 °C per 0.1 mbar to give **9b** as a colourless liquid. Yield 14.21 g (78%). Anal. Found: C, 34.11; H, 8.18; N, 8.41. $\text{C}_{10}\text{H}_{28}\text{Ga}_2\text{N}_2\text{O}_2$ (**9b**). Calc.: C, 34.54; H, 8.11; N, 8.05%. $^1\text{H-NMR}$: 2.98 (s, 3H, OCH_3), 2.93 (m, 2H, OCH_2), 2.64 (m, 2H, NCH_2), 1.31 (s, br, 1H, NH), –0.21 (s, 6H, GaCH_3) ppm. $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$: 74.32 (OCH_2), 58.50 (OCH_3), 44.45 (NCH_2), –8.30 (GaCH_3) ppm. MS (30 °C, m/z (%)): 331/333/335 (19.2) $[\text{M}-\text{CH}_3]^+$, 256/258/260 (13.5) $[\text{M}-2(\text{C}_2\text{H}_5\text{O})]^+$, 158/160 (36.6) $[(\text{H}_3\text{C})\text{Ga}(\mu\text{-NHCH}_2\text{-CH}_2\text{OCH}_3)]^+$, 99/101 (100.0) $[\text{Ga}(\text{CH}_3)_2]^+$, 84/86 (8, 6) $[\text{GaCH}_3]^+$, 69/71 (20.4) $[\text{Ga}]^+$.

4.20. $[(\text{CH}_3)_2\text{Ga}(\mu\text{-NH}(\text{CH}_2)_3\text{OCH}_3)]_2$ (**10b**)

9.00 g (44 mmol) of **12b** were heated for 24 h to 110 °C. The oily residue was purified by vacuum distillation at 67 °C per 0.1 mbar to give **10b** as a colourless crystalline solid which was further purified as described for **8b**. Yield 7.37 g (89%). M.p. (sealed) 33–35 °C. Anal. Found: C, 38.21; H, 8.48; N, 7.92. $\text{C}_{12}\text{H}_{32}\text{Ga}_2\text{N}_2\text{O}_2$ (**10b**). Calc.: C, 38.63; H, 8.58; N, 7.45%. $^1\text{H-NMR}$: 2.91 (s, 3H, OCH_3), 2.87 (t, 2H, OCH_2), 2.25 (m, 2H, NCH_2), 1.53 (s, br, 1H, NH), 1.04 (m, 2H, CH_2), –0.10 (s, 6H, GaCH_3) ppm. $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$: 72.02 (OCH_2), 58.52 (OCH_3), 40.85 (NCH_2), 30.83 (CH_2), –5.81 (GaCH_3) ppm. MS (40 °C, m/z (%)): 315/317/319 (76.3) $[\text{M}-\text{C}_3\text{H}_7\text{O}]^+$, 199/201/203 (100.0) $[\text{M}-2\text{C}_4\text{H}_8\text{NO}]^+$, 187/189 (6.8) $[(\text{H}_3\text{C})_2\text{Ga}(\mu\text{-NH}(\text{CH}_2)_3\text{OCH}_3)]$, 99/101 (86.1) $[\text{Ga}(\text{CH}_3)_2]^+$, 84/86 (8.7) $[\text{GaCH}_3]^+$, 69/71 (5.4) $[\text{Ga}]^+$.

4.21. X-ray crystallographic analyses

The X-ray data were collected on an Enraf-Nonius CAD4 diffractometer (ω - 2θ scan, $\lambda = 0.71069 \text{ \AA}$) equipped with a low temperature device. Cell parameters were determined from 25 reflexes in the range $16^\circ \leq 2\theta \leq 25^\circ$ by least-squares refinement. The crystal orientation was checked during measurement every 200 reflexes and the orientation matrix was redetermined when the deviation of one of the three monitor reflexes exceeded a given limit. Intensity changes were also monitored on three standard reflexes that were rescanned every 2 h. The raw data were corrected for Lorentz and polarization effects. Intensity scaling according to the periodically checked standard reflexes was applied to the data of **2b** and **4a**. Absorption correction was carried out using ψ -scan data (**5b**, **12b**) or the empirical method DIFABS [22] (**2b**, **4a**, **5a**, **8b**). Structure solution and refinement was carried out with the SHELXS-86 [23] and SHELXL-93 [24] software respectively. The refinement method was full-matrix least-squares on F^2 . The older SHELX-76 [25] program was also used to prepare the data for DIFABS. The input files for the SHELX programs were prepared with the program UTILITY [26]. All non-hydrogen atoms were refined with anisotropic temperature factors, with the exception of the disordered methyl carbon atoms of **2b**. The positions of the hydrogen atoms were calculated with fixed isotropic temperature factors ($U_{\text{iso}} = 0.08 \text{ \AA}^2$), only the rotation of methyl groups was refined. Molecular plots were obtained with the programs ZORTEP [20] and PLUTON [27]. Details of the crystal data and structure refinement are shown in Table 1. Full information on the crystal structures can be ordered from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbh, D-76344 Eggenstein-Leopoldshafen, Germany by giving the authors, journal citation and corresponding CSD-number (401855 (**2b**), 401853 (**4a**), 401851 (**5a**), 401852 (**5b**), 401854 (**8b**), 401856 (**12b**)).

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