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Structural Aspects of Chlorine-Aluminium Alkoxides

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In Memory of Professor Hans Georg von Schnering

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Abstract. $LiAlH_4$ and $AlCl_3$ reacted in a ratio 1:3 to obtain Cl_2AlH, which is stabilised by the addition of two equivalents of N-methylpiperidine (nmp) to form dichloroalane (**1**) as bis adduct of nmp. Compound **1** was allowed to react with 2,6-*t*Bu-4-MeC_6H_2OH and HO^cHex in a 1:1 ratio to get compounds **2** and **3**, respectively. Cl_2Al(2,6-*t*Bu-4-MeC_6H_2O)(nmp) (**2**) is a monomer in which the central aluminium atom is tetracoordinate. Contrary to the parent compound **1**, compound **2** is stabilised by only one nmp molecule. The larger bulk of the alkoxide in **2** prevents the second nmp molecule to reach the aluminium atom. Compound **3** crystallises as unique anionic tri-nuclear aluminium entity $[Al_3Cl_6(OR)_4]^-$ $[nmp_2H]^+$ with a protonated nmp as counter-cation. The lesser bulk of the cyclohexanolate leads to a higher oligomerisation of $ROAlCl_2$ (R = cyclohexyl). When a relatively bulkier alcohol, 1-methylcyclohexanol, was allowed to react with mixtures of $LiAlH_4$ and $AlCl_3$ prepared in 1:1 and 1:3 ratios in solution, compounds **4** and **5**, respectively, were obtained. Both compounds ($(HClAlOR)_2$ (**4**) and $(Cl_2AlOR)_2$ (**5**), R = ^{c}HexMe-1)) are dimers with oxygen as bridging atom in the Al_2O_2 rings. All compounds **2**, **3**, **4**, and **5** were structurally characterised by X-ray diffraction on single crystals.

Introduction

Alkoxy-aluminium chlorides of the general formula $Cl_x(OR)_{3-x}Al$ are of general interest due to their role in organic synthesis. The high Lewis-acidic aluminium center is believed to be responsible for catalytic activity in organic reactions, for example in ring opening polymerisations.[1,2] On the other hand, compounds containing Al–Cl and Al–O*R* bonds are of high interest as precursors for the synthesis of alumina through non-aqueous sol-gel processes.[3] Hydrid-modified alkoxyaluminium chloride has been used successfully as single source precursor for preparation of metastable $H_x(X)_{1-x}AlO$ material.[4] The hydride ligand leads to a significant decrease in the decomposition temperature of the precursor upon a substrate in a CVD (chemical vapour deposition) process.

The molecular structures for alkoxy-aluminium chlorides are primarily dominated by intermolecular oligomerisation through Lewis acid-base interactions leading to dimers and trimers. Very few examples of monomeric alkoxy-aluminium chlorides have been reported so far, in which the electron-deficient aluminium metal atom is stabilised by electron donating ligand(s) (bases) and the intermolecular interaction is hindered by the high bulk of the alkoxy group.[5,6] In the oligomers the oxygen of the alkoxy group acts as stabilising base towards aluminium putting the chlorine ligands into terminal bonding positions. The degree of oligomerisation/polymerisation depends upon the steric bulk of the alkyl moiety. The most common structural motif of aluminium chloride alkoxides are dimers and trimers. The dimeric alkoxy-aluminium chloride displaying a central four-membered Al_2O_2 ring also exists in solution.[7,8] The trinuclear alkoxy-aluminium chlorides exhibit three different types of structures (Scheme 1). One of them has a central six-membered cyclic skeleton which is puckered due to the repulsion among the exocyclic chlorine and alkyl moieties (Scheme 1; **A**).[9] The other tri-nuclear alkoxy-aluminium chlorides have bicyclic four-membered Al_2O_2 structures in which the central aluminium atoms are penta- (Scheme 1; **B**) and hexacoordinate (Scheme 1; **C**) alongside with tetracoordinate terminal aluminium atoms.[7,10,11] These types of molecular structures of alkoxy-aluminium chlorides may differ in their Cl/Al/O*R* ratio to that of the starting compounds.[11] This peculiarity is often ascribed to ligand scrambling and redistribution.

Here we report upon the synthesis and single crystal analysis of different alkoxy-aluminium chlorides as well as hydride-modified alkoxy-aluminium chlorides. The alkoxy groups carry alkyl moieties of different steric bulk. Therefore, the molecular structures found are monomeric or oligomeric with the aluminium metal atoms displaying coordination numbers of 4, 5, and even 6.

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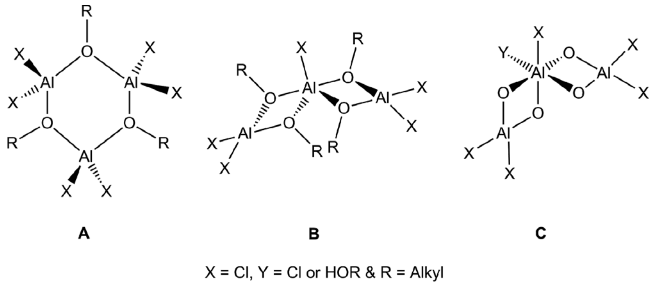


Scheme 1. Different structures exhibited by the tri-nuclear alkoxy-aluminium chlorides.[7,10–11]

Results and Discussion

Synthesis and Spectroscopic Analysis

The title compounds (**2**–**5**) were synthesised under nitrogen using different synthetic routes. The precursor compound dichloroalane **1** is obtained as a monomeric bis adduct of N-methylpiperidine (nmp). Following routes for similar reactions,[12,13] $AlCl_3$ and $LiAlH_4$ in diethylether are mixed together in a 3:1 ratio to which nmp is added as stabilising base (Equation (1)).

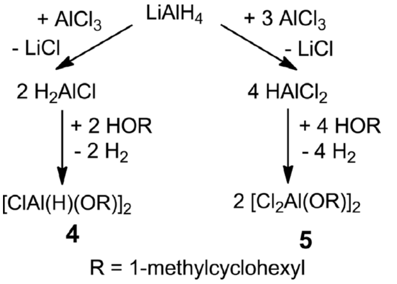
$$LiAlH_4 + 3\ AlCl_3 + 8\ C_6H_{13}N \longrightarrow \underset{\mathbf{1}}{4\ [HAlCl_2{\cdot}2C_6H_{13}N]} + LiCl \qquad (1)$$

The ^1H and ^{13}C NMR spectra clearly show the nmp ligand in **1** and the Al–H bond is confirmed by a characteristic band at 1785 cm^{-1} in the IR spectrum.[14] Compounds **2** and **3** can be obtained from **1** by reaction of the corresponding alcohols, HO*R* (*R* = 2,6-*t*Bu-4-MeC_6H_2,**2**, and ^{c}Hex,**3**) with elimination of dihydrogen in a simple 1:1 ratio according to equation (2). The hydrogen evolution is expressed by bubbles produced in the reaction mixture after addition of alcohols to **1**. Addition of 2,6-*t*Bu-4-MeC_6H_2OH to **1** gives rise to precipitation of colourless crystals after reducing the volume of the soles which are characterised as $[Cl_2Al(2,6\text{-}t\text{Bu-4-}MeC_6H_2O)]$ with nmp as further ligand on aluminium (**2**). Crystals of **3** are obtained at room temperature as soon as the solution is concentrated by pumping off the solvent. The obtained product **3** has a stoichiometry, which deviates from the starting 1:1:2 ratio of Al/O*R*/Cl. It indicates that some excess alcohol has reacted. The organic moieties in **2** and **3** are confirmed by ^1H and ^{13}C NMR spectroscopy.

$$\mathbf{1} + HOR \longrightarrow \underset{\mathbf{2}}{[Cl_2Al(OR){\cdot}nmp]} / \underset{\mathbf{3}}{[(Cl_2Al)_3(\mu\text{-}OR)_4][H(nmp)_2]{\cdot}Et_2O} \qquad (2)$$

$$R = 2,6\text{-}^tBu\text{-}4\text{-}MeC_6H_2\ \mathbf{2},\ ^cHex\ \mathbf{3}$$

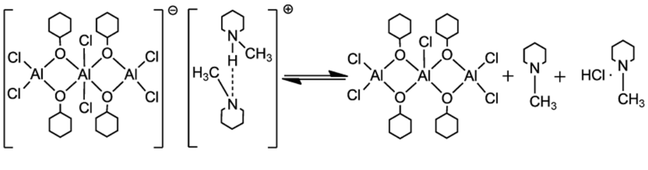
Compounds **4** and **5** are obtained following a two step reaction route (Scheme 2).[15] In a first step, appropriate amounts of $LiAlH_4$ and $AlCl_3$ are mixed in diethyl ether followed by the addition of alcohol in required stoichiometric amounts in the second step. Hydrogen evolution is indicated by the bubbles produced in the reaction mixtures. After storage, colourless crystals of **4** and **5** formed from the concentrated diethylether solutions at +4 °C. X-ray analyses reveal dimeric structures for **4** and **5** both displaying a central four-membered Al_2O_2 ring (following section). The organic pendant groups are confirmed by ^1H and ^{13}C NMR spectroscopy. From the numbers of resonances in the NMR spectrum of **4** it can be deduced that it exists in two isomeric forms in solution with *cis*- and *trans*-orientations of hydrogen and chlorine with respect to the four-membered Al_2O_2 cycle. The Al–H bond in **4** is confirmed by characteristic stretching vibration at 1905 cm^{-1} in its IR spectrum.[4]



Scheme 2. Two step reactions for synthesis of **4** and **5**.

In the ^{27}Al NMR spectrum of **1** appears a single peak at 118 ppm in deutrated benzene; the peak does not fall into the characteristic region of pentacoordinate aluminium atoms with oxygen and halides as ligands. Therefore, we recorded the spectrum in different solvents like e.g. diethylether as a potential base, but obtained almost the same δ-value. We attribute this unusual shift (far from the usual value of 50 ± 20 ppm) to the double nitrogen coordination following arguments and findings of *Benn* et al.[16] who described several pentacoordinate complexes with nitrogen on the aluminium atom in the range of more than 100 ppm. Of course, we cannot exclude another explanation: the two nmp ligands may be in fast exchange so that the aluminium atom in **1** is tetracoordinate in solution in contrast to the solid (see below).

Contrary to **1**, the aluminium atom in **2** is tetracoordinate deduced from the appearance of a single broad signal at 82.5 ppm in the ^{27}Al NMR spectrum.[17] The bulky alkoxy group (2,6-*t*Bu-4-MeC_6H_2O) hinders the aluminium atom to be accessed by a second stabilising base. Owing to the facile ligand scrambling in aluminium chloride alkoxides,[18] the solution NMR spectra of **3** are quite complex and difficult to correlate with the solid state data obtained from X-ray diffraction. The ^{27}Al NMR spectrum of **3** gives four signals at 4 ppm, 43 ppm, 92 ppm and 109 ppm. The signals at 92 ppm and 4 ppm correspond to that of tetracoordinate and hexacoordinate aluminium atoms, respectively.[19] The third signal at 43 ppm is in the region of pentacoordinate aluminium atoms.[19] It seems reasonable that **3** undergoes ligand scrambling in solution giving two different products which are in equilibrium to each other (Scheme 3). The fourth signal at 109 ppm is quite sharp and is thought to be due to the presence of highly symmetrical $[AlCl_4]^-$ (not shown in Scheme 3).[20] The ^{27}Al NMR spectrum recorded for compound **4** in deuterated benzene is unusual but matches well with the ^{27}Al NMR spectra reported for structurally similar compounds.[17] Two signals at 89 ppm and 100 ppm indicate two different aluminium atoms of coordination number 4. The signal at 100 ppm is due to the tetracoordinate aluminium atom of compound **4**.[17] The signal at 89 ppm could be due to the other *cis*/*trans* isomer but more likely seems to be compatible with the compound $[Cl_2Al(O^cHex\mathit{Me}\text{-}1)]_2$, which may be present in the solution as a result of ligand exchange; as it is well-known, aluminium chloride alkoxides are susceptible to rapid ligand exchange in solution.[18] Unfortunately, we could not obtain well-dissolved temperature dependent NMR spectra for **4**. Contrary to that of **4**, the ^{27}Al NMR spectrum of **5** has a single broad signal at 89 ppm, which corresponds to that of structurally identical compounds, $[Cl_2Al(OR)]_2$ also having tetracoordinate aluminium atoms.[11,17].



Scheme 3. Proposed equilibrium in solution between the two compounds, $[(Cl_2Al)_2(Cl_2Al(O^cHex)_4)]^-[H(NMP)_2]^+$ and $[(Cl_2Al)_2(ClAl(O^cHex)_4)]\cdot nmp\cdot HCl$.

Single X-ray Structure Analyses

Single crystals of **1** and the title compounds (**2–5**) were isolated and analysed by the single-crystal X-ray diffraction method. The most relevant data for compounds **1**–**5** are summarised in Table 1.

The pertinent bond angles and lengths of compounds **1**–**3** are presented in Table 2 and those of compounds **4** and **5** are given in Table 3.

The structure of compound **1** is new in the sense that there is no reported example of the type, $[Cl_2AlH\cdot 2nmp]$. The double Lewis base adduct of Cl_2AlH (Figure 1) has a crystallographic symmetry plane running through the Al–H an Al–N bonds and in approximation a C_{2v} point symmetry. The molecular structure of **1** has resemblance to that of the earlier reported monochloroalane.[14,21] The central aluminium atom is pentacoordinate having distorted trigonal bipyramidal arrangement. The nitrogen atoms are at the apical positions whereas the chlorine atoms and hydrogen occupy the equatorial positions. Contrary to the monochloroalane,[14] the N–Al–N entity of **1** has a remarkable deviation from linearity (8.49(1)°). The relatively higher degree of deviation from linearity could be related to the presence of two chlorine atoms against one chlorine atom in case of the monochloroalane.[14] The Al–Cl(1) bond length is 2.196(1) Å, which is shorter by 0.03 Å to that in $H_2AlCl\cdot 2nmp$. The Al–N(1) and Al–N(2) bond lengths of 2.163(1) Å and 2.175(1) Å, respectively are long for donor bonds and are even longer than those observed in $H_2AlCl\cdot 2nmp$. This may be due to the second chlorine atom which increases the steric demand around the aluminium atom and repels the amine groups.

The asymmetric compound **2,** which is the derivative of compound **1** by exchange of hydrogen through alkoxy, is a monomer in which the aluminium atom is tetracoordinate (Figure 2). The central aluminium atom has highly distorted tetrahedral arrangement. Substituting hydrogen by a bulky alkoxy group, $OC_6H_2Bu^t\text{-}2,6\text{-}Me\text{-}4$, in **1** reduces the coordination number from five (**1**) to four in **2** by expelling one of the nmp ligands. Only very few examples of monomeric dichloroaluminium aryloxides can be found in the literature.[5,6] Compound **2** has a similar structure to that of $Cl_2Al(OR)\cdot Et_2O$ ($R = C_6H_2Bu^t\text{-}2,6\text{-}Me\text{-}4$),[5] the only difference being the stabilising base. The Al–Cl bond lengths are in the range reported for terminal Al–Cl bonds.[5] The Al–Cl and Al–O bond lengths are longer by approximately 0.011(1) Å and 0.013(1) Å, respectively, compared to those in $Cl_2Al(OR)\cdot Et_2O$ ($R = C_6H_2Bu^t\text{-}2,6\text{-}Me\text{-}4$). This may be due to the relatively bulky stabilising base nmp.

Compound **3** crystallises at room temperature by concentration of the mother liquor. As result of X-ray structure determination, **3** (Figure 3) is found to be composed of a cation-anion pair and a diethylether molecule in its crystal lattice. The resulting stoichiometry of OR/Al/Cl differs from the starting 1:1:2 ratios. The anion has the composition $[(Cl_2Al)_3(O^cHex)_4]^-$ and is electronically neutralised by the cation $[H(nmp)_2]^+$. The tri-nuclear anionic part of the compound has almost C_2 point symmetry with the pseudo twofold axis running through Al(1). The hexacoordinate central atom Al(1) has highly distorted octahedral arrangement composed of two terminal chlorine atoms and four bridging oxygen atoms of the cyclohexoxy group. The bridging Al(1)–O bond lengths are longer than the bridging Al(2)–O and Al(3)–O bond lengths reflecting the higher coordination number at Al(1) compared to Al(2) and Al(3). Another interesting feature is the *trans* effect of the chlorine ligands at Al(1) on the Al–O bond lengths, as we find longer distances for the alkoxy groups which are *trans*-oriented to the terminal chlorine atoms. As also found for Al–O, the Al–Cl bond lengths for the chlorine atoms attached to the hexacoordinate aluminium atom are longer than those attached to the tetra-coordinated aluminium atoms. As usual, the most acute angles in the Al_2O_2 rings are found at the bigger aluminium atoms (compared to oxygen). The sum of angles around oxygen atoms are in the range of 359.8(2)–359.9(2)° indicating that all the oxygen atoms have trigonal planar arrangement (sp^2 hybridisation).[22] The anionic molecule has a counterpart cation formed by the interaction of a proton, which is split off the alcohol, with nmp. The so formed ammonium type $Hnmp^+$ is bonded to a second nmp molecule through hydrogen bonding ($N\cdots N = 2.82$ Å).

The molecular structures of **4** and **5** obtained from single crystal analyses are depicted in Figure 4 and Figure 5, respectively. Both molecules are centrosymmetric dimers with central four-membered Al_2O_2 rings. The aluminium atoms are tetracoordinated in **4** and **5** having distorted tetrahedral geometries. The bridging Al–O and terminal Al–Cl bond distances are in their characteristic ranges.[4,11] Whereas the aluminium atom in **4** has three different ligands (H, Cl, O*R*), the aluminium atom in **5** only has two (Cl, O*R*). In both compounds the Al–O distances within the ring are almost identical. The sum of angles at oxygen atoms in **4** and **5** approaches 360°, which indicates sp^2 hybridisation for the oxygen atoms.[22] The higher

Table 1. Crystallographic data for compounds **1**–**5**.

compound number	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_{12}H_{27}AlCl_2N_2$	$C_{21}H_{36}AlCl_2NO$	$C_{40}H_{81}Al_3Cl_6N_2O_5$	$C_{14}H_{28}Al_2Cl_2O_2$	$C_{14}H_{26}Al_2Cl_4O_2$
Formula weight	297.24	416.39	963.71	353.22	422.11
Temp /K	130(2) K	152(2)	142(2)	152(2)	152(2)
Wavelength /Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*Pnma*	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a /Å	10.9807(9)	10.1847(6)	11.9289(9)	8.9335(6)	9.0178(4)
b /Å	10.4692(8)	15.817(1)	17.069(1)	8.2062(6)	8.6817(4)
c /Å	14.132(1)	14.824(1)	25.110(2)	13.052(1)	13.1491(5)
β /deg	90	106.80(1)	94.975(4)	105.054(3)	104.821(2)
V /Å^3	1624.6(2)	2286.0(3)	5093.5(7)	924.0(1)	995.19(7)
Z	4	4	4	2	2
Density calcd. /Mg·m^{-3}	1.215	1.210	1.257	1.270	1.409
Abs coefficient /mm^{-1}	0.438	0.333	0.429	0.445	0.686
F(000)	640	896	2064	376	440
Crystal size /mm	0.59 × 0.41 × 0.20	0.50 × 0.32 × 0.30	0.40 × 0.10 × 0.09	0.29 × 0.26 × 0.06	0.47 × 0.37 × 0.31
θ-range for data collection /°	2.35 to 36.79	1.93 to 27.94°	1.44 to 27.14°	2.36 to 27.83°	2.34 to 34.95°
Index ranges	$-18 \le h \le 18$ $-17 \le k \le 17$ $-23 \le l \le 11$	$-13 \le h \le 13$ $-13 \le k \le 20$ $-19 \le l \le 19$	$-15 \le h \le 15$ $-21 \le k \le 20$ $-32 \le l \le 32$	$-11 \le h \le 10$ $-10 \le k \le 7$ $-16 \le l \le 17$	$-9 \le h \le 14$ $-13 \le k \le 10$ $-21 \le l \le 21$
Reflections collected	17621	21609	43139	7751	16344
Independent reflections [$I > 2\sigma(I)$] (R_{int})	4237 [0.0237]	5472[0.0451]	11234[0.0820]	2190[0.0464]	4356[0.0491]
Completeness to θ /%	99.9	99.8	99.5	99.9	99.8
Absorption correction	Multiscan	Multiscan	Multiscan	Multiscan	Multiscan
Max. and min. Transmission	0.9183 and 0.7815	0.9056 and 0.8521	0.9624 and 0.8480	0.9755 and 0.8802	0.8166 and 0.7406
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	4237 / 0 / 149	5472 / 0 / 379	11234 / 0 / 513	2190 / 0 / 147	4356 / 0 / 152
GOF in F^2	1.028	1.061	1.003	1.066	1.051
R_1, wR_2 [$I > 2\sigma(I)$]	0.0331, 0.0916	0.0519, 0.1323	0.0501, 0.0908	0.0459, 0.1156	0.0313, 0.0835
R_1, wR_2 (all data),	0.0456, 0.0999	0.0715, 0.1447	0.1073, 0.1076	0.0719, 0.1288	0.0394, 0.0880
largest diff peak and hole /e·Å^{-3}	0.377 and –0.547	0.784 and –0.629	0.666 and –0.671	0.474 and –0.415	0.413 and –0.296

chlorine content in **5** compared to **4** is reflected by a shorter Al–O distance (difference: 0.016(1) Å).

Conclusions

Either intermediate chloroalanes from the reaction of $LiAlH_4$ and $AlCl_3$ or the base stabilised chloroalane $Cl_2HAl{\cdot}2nmp$ (**1**) may be used to introduce alcohol groups by hydrogen elimination. As the chloroalanes are prone to ligand scrambling and interconversion, not only simple chloro alkoxyalanes may be obtained as exemplified by compound **3**. The electronic deficiency at the aluminium atom and the bulk of the stabilising base and/or alkoxide control the degree of polymerisation of the alkoxyalanes.

Compounds **1** and **2** are base-stabilised monomers in solution as well as in solid state. The lower coordination number of aluminium in **2** is due to the higher bulk of the alkoxy group.

When a stoichiometric amount of 1-methylcyclohexanol is added into the stoichiometric solutions of $LiAlH_4$ and $AlCl_3$, dimeric compounds **4** and **5** are obtained. The steric bulk of the alkoxide moiety is sufficient to prevent from the formation of higher coordination oligomers. To satisfy the electronic deficiency at the aluminium atoms, the oxygen atom of the alkoxide group behaves as a bridging base. Contrarily, when a sterically less bulky alkoxide, cyclohexanol, is used, the resulting molecule **3** is a "trimer", which had trapped a further alcohol, split into RO^- and H^+ with the base nmp.

Experimental Section

All reactions were carried out under dry nitrogen using modified Schlenk vacuum line techniques. $LiAlH_4$ and 2,6-di-*tert*-butyl-4-methylphenol were purchased from Aldrich and used as such while $AlCl_3$ from Aldrich was sublimed before use. Cyclohexanol and 1-methylcyclohexanol were distilled from magnesium turnings and kept over molecular sieves. Diethylether, benzene and all other hydrocarbon solvents were freshly distilled from Na/benzophenone under N_2 and kept under N_2/Na wires. NMR spectra (^1H and ^{13}C) were recorded with a Bruker AC200 NMR spectrometer with TMS (0.00 ppm) as internal standard. The ^1H and ^{13}C NMR spectra were referenced to the proton signals and carbon resonances of [D_6]benzene, 7.16 and 128.0 ppm, respectively. The ^{27}Al NMR spectra were recorded with a multinuclear Bruker ACP 200 NMR spectrometer at 52.1 MHz. IR spectra (4000–

Table 2. Pertinent Bond Lengths /Å and Angles /deg of Compounds **1**–**3**.

compound **1**				compound **2**			
Bond Length				Bond Length			
Al_1-N_1	2.163(1)	Al_1-Cl_1	2.1963(3)	Al_1-O_1	1.713(1)	Al1–Cl1	2.1258(9)
Al_1-N_2	2.175(1)	Al_1-H_1	1.535(1)	Al_1-N_1	1.998(2)	Al1–Cl2	2.1422(9)
Angle				Angle			
$N_1-Al_1-N_2$	171.51(4)			$O_1-Al_1-N_1$	107.74(8)	$O_1-Al_1-Cl_2$	118.45(6)
$N_1-Al_1-Cl_1$	92.61(2)			$O_1-Al_1-Cl_1$	111.66(6)	$N_1-Al_1-Cl_2$	97.40(7)
$N_2-Al_1-Cl_1$	92.09(2)	$Cl_{1a}-Al_1-Cl_1$	112.72(2)	$N_1-Al_1-Cl_1$	113.00(7)	$Cl_1-Al_1-Cl_2$	107.91(4)
compound **3**							
Bond Length							
Al_1-O_3	1.928(2)	Al_1-Cl_1	2.265(2)	Al_2-Cl_3	2.117(1)	Al_3-Cl_5	2.117(1)
Al_1-O_1	1.930(2)	Al_1-Cl_2	2.286(2)	Al_2-Cl_4	2.128(1)	Al_3-Cl_6	2.131(1)
Al_1-O_2	1.976(2)	Al_2-O_2	1.761(1)	Al_3-O_4	1.764(2)	$N_1 \cdots H_1$	1.93(3)
Al_1-O_4	1.991(2)	Al_2-O_1	1.778(1)	Al_3-O_3	1.774(2)	N_2-H_1	0.89(3)
Angle							
$O_3-Al_1-O_1$	160.46(8)	$O_2-Al_1-Cl_1$	90.79(6)	$O_2-Al_2-Cl_3$	115.63(7)	$O_4-Al_3-Cl_6$	115.90(7)
$O_3-Al_1-O_2$	90.93(8)	$O_4-Al_1-Cl_1$	171.79(6)	$O_1-Al_2-Cl_3$	116.43(7)	$O_3-Al_3-Cl_6$	114.09(7)
$O_1-Al_1-O_2$	75.19(8)	$O_3-Al_1-Cl_2$	96.63(6)	$O_2-Al_2-Cl_4$	115.91(7)	$Cl_5-Al_3-Cl_6$	107.87(4)
$O_3-Al_1-O_4$	74.76(7)	$O_1-Al_1-Cl_2$	96.85(6)	$O_1-Al_2-Cl_4$	114.29(7)	$Al_2-O_1-Al_1$	100.60(9)
$O_1-Al_1-O_4$	91.00(8)	$O_2-Al_1-Cl_2$	172.01(7)	$Cl_3-Al_2-Cl_4$	108.57(4)	$Al_2-O_2-Al_1$	99.48(9)
$O_2-Al_1-O_4$	88.81(8)	$O_4-Al_1-Cl_2$	90.69(6)	$O_4-Al_3-O_3$	84.53(8)	$Al_3-O_3-Al_1$	101.38(9)
$O_3-Al_1-Cl_1$	96.95(6)	$Cl_1-Al_1-Cl_2$	90.84(4)	$O_4-Al_3-Cl_5$	116.47(7)	$Al_3-O_4-Al_1$	99.33(8)
$O_1-Al_1-Cl_1$	96.92(6)	$O_2-Al_2-O_1$	84.66(8)	$O_3-Al_3-Cl_5$	116.84(7)		

Table 3. Pertinent bond lengths /Å and angles /deg of compounds **4** and **5**.

compound **4**				compound **5**			
Bond Length				Bond Length			
Al–Cl	2.1197(9)	$Al-O_a$	1.823(2)	Al_1-O_{1a}	1.8043(7)	Al_1-Cl_1	2.0919(4)
Al–H	1.640(3)	$Al\ldots Al_a$	2.766(1)	Al_1-O_1	1.8083(7)	Al_1-Cl_2	2.0968(4)
Al–O	1.822(2)						
Angle				Angle			
$O-Al-O_a$	81.30(8)	C_1-O-Al	130.1(1)	$O_{1a}-Al_1-O_1$	82.34(3)	$Cl_1-Al_1-Cl_2$	113.47(2)
O–Al–Cl	111.35(6)	C_1-O-Al_a	130.0(1)	$O_{1a}-Al_1-Cl_1$	113.21(2)	$C_1-O_1-Al_{1a}$	131.62(5)
$O_a-Al-Cl$	112.81(6)	$Al-O-Al_a$	98.70(8)	$O_1-Al_1-Cl_1$	114.90(3)	$C_1-O_1-Al_1$	130.27(5)
H–Al–Cl	109.67(5)			$O_{1a}-Al_1-Cl_2$	115.71(3)	$Al_{1a}-O_1-Al_1$	97.76(3)
H–Al–O	119.19(5)			$O_1-Al_1-Cl_2$	113.72(3)		

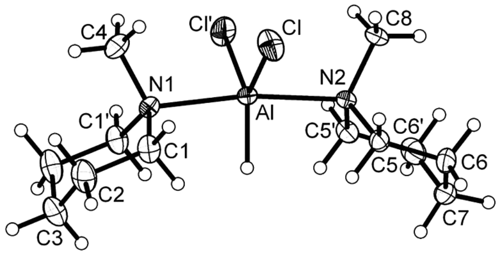


Figure 1. Molecular structure of $[Cl_2Al(H)\cdot 2nmp]$ (**1**) with 50 % thermal ellipsoids.

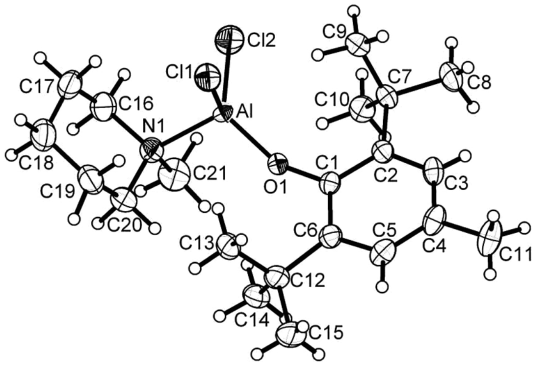


Figure 2. Molecular structure of $[Cl_2Al(2,6\text{-}t\text{Bu-4-MeC}_6H_2O)]\cdot$nmp (**2**) with 50 % thermal ellipsoids.

400 cm^{-1}) were collected with a Varian 2000 FT-IR spectrometer. Elemental (C, H and N) analyses were carried out using a LECO CHN 900 elemental analyser. The Al and Cl contents were determined by complexometric and titrimetric techniques.[23,24]

The single-crystal X-ray diffraction analyses were performed with a BrukerAXS X8 Apex II diffractometer at –150 °C using graphite-monochromated Mo-K_α X-ray radiation (λ = 0.711 Å). The crystal structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX software package for crystal structure

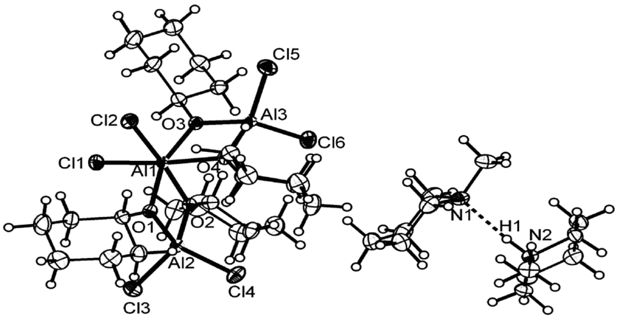


Figure 3. Molecular structure of $[(Cl_2Al)_3(O^cHex)_4)]^-[H(nmp)_2]^+\cdot Et_2O$ (**3**) with 50 % thermal ellipsoids.

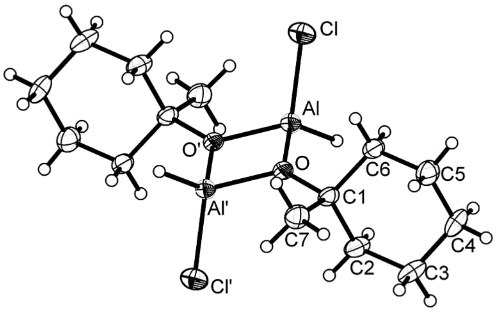


Figure 4. Molecular structure of $[ClAl(H)(O^cHex\text{-}Me)]_2$ (**4**) with 50 % thermal ellipsoids.

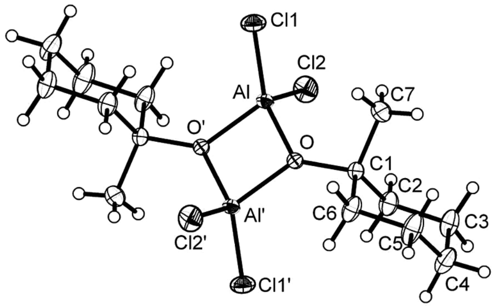


Figure 5. Molecular structure of $[Cl_2Al(O^cHex\text{-}Me)]_2$ (**5**) with 50 % thermal ellipsoids.

solution and refinement.[25] All non-hydrogen atoms were refined with anisotropic thermal parameters in the later cycles of refinement. Further details of crystal structure determination are available from CCDC.[26]

Syntheses

$[Cl_2AlH\cdot 2nmp]$ (nmp = N-methylpiperidine) (1): To a suspension of lithium aluminium hydride (0.198 g, 5.22 mmol) in diethyl ether (50 mL) was added a solution of aluminium trichloride (2.086 g, 15.7 mmol) in diethyl ether (50 mL). After 1 h stirring, an excess of N-methylpiperidine (nmp) (5.07 mL, 41.7 mmol) was added drop by drop to the mixture with cooling (ice bath) and stirred for additional 1 h. Hexane (ca. 100 mL) was added to the resulting mixture to complete the precipitation of lithium chloride salt, which was separated by filtration and the volume of the solvents was reduced at low pressure to allow the formation of 4.34 g (70 %) of colourless crystals of $Cl_2AlH\cdot 2nmp$ (**1**).

NMR (C_6D_6, TMS): **^{1}H NMR** (200 MHz): δ = 2.42–2.37 (m, α-CH_2–, nmp), 2.08 (s, –CH_3, nmp), 1.25–1.14 (m, β-CH_2–, nmp), 1.08–1.00 (m, γ-CH_2–, nmp). **^{13}C NMR** (50.3 MHz): δ = 54.17 (s, α-CH_2–, nmp), 42.59 (s, –CH_3, nmp), 23.14 (s, β-CH_2–, nmp), 22.14 (s, γ-CH_2–, nmp). **^{27}Al NMR:** δ = 118 ($w_{1/2}$ = 810 Hz). **IR:** (Al–H) ν = 1785 cm^{-1}. **Elemental Analysis**: Calcd. C 48.49; H 9.16; N 9.42; Al 9.08; Cl 23.85. Found C 48.66; H 10.01; N 9.00; Al 8.90; Cl 24.20 %.

$[Cl_2Al(2,6\text{-}t\text{Bu-4-Me}C_6H_2O)\cdot nmp]$ (2): **C**ompound **1** ($Cl_2AlH\cdot 2nmp$) (0.55 g, 1.85 mmol) was dissolved in diethyl ether (30 mL) and the solution was added to 2,6-*t*Bu-4MeC_6H_2OH (0.407 g, 1.85 mmol) in diethyl ether (30 mL). Evolution of hydrogen was observed and the reaction was completed by stirring for 6 hours at room temperature. The solution was concentrated by removing the solvent under reduced pressure. Fine crystals of **2** were obtained with a yield of 0.67 g (88 %) after storing the concentrated solution for approximately 12 hours in a refrigerator at +4 °C.

NMR (C_6D_6, TMS): **^{1}H NMR** (200 MHz): δ = 6.89 (s, γ-CH, aryl ring), 2.24 (m, α-CH_2–, nmp), 2.11 (s, –CH_3, nmp), 2.10 (s, –CH_3, aryl ring), 1.35 (s, –CH_3, *tert*-butyl), 1.88–1.42 (m, β- & γ-CH_2–, nmp), **^{13}C NMR** (50.3 MHz): δ = 151.67 (s, α-C, alkoxy), 139.03 (s, β-C, alkoxy), 125.76 (s, γ-C, alkoxy), 130.00 (s, δ-C, alkoxy), 53.61 (s, α-CH_2-, nmp), 39.16 (s, –CH_3, alkoxy), 35.40 (s, –CH_3, nmp), 34.05 (s, **C**$(CH_3)_3$, alkoxy), 30.30 (s, C(**C**$H_3)_3$, alkoxy), 21.13 (s, β-CH_2–, nmp), 17.97 (s, γ-CH_2–, nmp). **^{27}Al NMR:** δ = 82.5 ($w_{1/2}$ = 1550 Hz). **Elemental Analysis**: Calcd. C 60.57; H 8.71; N 3.36; Al 6.48. Found C 61.79; H 8.67; N 2.34; Al 6.35 %.

$[(Cl_2Al)_3(\mu\text{-}O^cHex)_4]^-$ $[H(nmp)_2]^+\cdot Et_2O$ (3): The alcohol HO^cHex (0.72 mL, 6.88 mmol) was dissolved in diethyl ether (30 mL) and the solution was added to a solution of compound **1** (2.051 g, 6.88 mmol) in diethyl ether (30 mL) under evolution of hydrogen. The reaction was completed by stirring for 6 hours at room temperature. The solution was concentrated by removing the solvent under reduced pressure. Fine crystals of **3** were obtained after storing the solution for approximately 12 hours in a refrigerator at +4 °C with a yield of 1.96 g (89 %).

NMR (C_6D_6, TMS): **^{1}H NMR** (200 MHz): δ = 3.31–3.18 (q, –CH_2–, diethyl ether), 3.17 (m, α-CH, ^{c}Hex), 2.21–2.17 (m, α-CH_2–, nmp), 2.10–1.37 (m, –CH_2–, ^{c}Hex), 2.06 (s, –CH_3, nmp), 1.49–1.40 (m, β-CH_2–, nmp), 1.27–1.21 (m, γ-CH_2–, nmp), 1.01–0.95 (t, –CH_3, diethyl ether). **^{13}C NMR** (50.3 MHz): δ = 66.28 (s, –CH_3, diethyl ether), 78.68 (s, α-CH, alkoxy), 36.30 (s, β-CH_2–, alkoxy), 25.62 (s, δ-CH_2–, alkoxy), 22.56 (s, γ-CH_2–, alkoxy), 53.89 (s, α-CH_2–, nmp), 34.94 (s, –CH_3, nmp), 24.92 (s, β-CH_2–, nmp), 21.41 (s, γ-CH_2–, nmp), 15.92 (s, –CH_2–, diethyl ether). **^{27}Al NMR:** δ = 4.5 ($w_{1/2}$ = 150 Hz), 43.7 ($w_{1/2}$ = 450 Hz), 92.3 ($w_{1/2}$ = 890 Hz), 109.6 ($w_{1/2}$ = 40 Hz). **Elemental Analysis**: Calcd. C 49.85; H 8.47; N 2.93; Al 8.40. Found C 50.79; H 7.67; N 2.34; Al 8.69 %.

$[ClAl(H)(O^cHex\textit{Me}\text{-}1)]_2$ (4): To a suspension of lithium aluminium hydride (0.268 g, 7.06 mmol) in diethyl ether (75 mL) was added a solution of aluminium trichloride (0.940 g, 7.06 mmol) prepared in diethyl ether (75 mL) under cooling. After 1 h stirring, 1-methylcyclohexanol (1.76 mL, 14.12 mmol) was added drop by drop to the reaction mixture and stirred for additional 3 h. The volume of this solution was reduced to its half by removing the solvent under low pressure and afterwards hexane (50 mL) was added to the resulting mixture to complete the precipitation of lithium chloride. The lithium chloride salt was separated by filtration and the volume of the filtrate was reduced under reduced pressure to allow the formation of 2.15 g (86.34 %) of colourless crystals of $[ClAl(H)(OR)]_2$ (**4**) at +4 °C.

NMR (C_6D_6, TMS): **^{1}H NMR** (C_6D_6): δ = 1.34 (s, $-CH_3$), 1.36 (s, $-CH_3$), 1.7–0.9 (m, $-CH_2$–ring). **^{13}C NMR** (C_6D_6): δ = 82.25 (s, α-CH, ring), 82.27 (s, α-CH_2–), 39.74 (s, β-CH_2–, ring), 39.56 (s, β-CH_2–, ring), 24.31 (s, $-CH_3$), 22.78 (s, $-CH_3$). **^{27}Al NMR:** δ = 100.9. **IR:** (Al–H) ν = 1905 cm^{-1}; **Elemental Analysis**: Calcd. C 47.60; H 7.99; Al 15.28; Cl 20.07. Found C 42.45; H 7.29; Al 15.36; Cl 19.72 %.

$[Cl_2Al(O^cHexMe\text{-}1)]_2$ (5): To a suspension of lithium aluminium hydride (0.104 g, 2.77 mmol) in diethyl ether (75 mL) was added a solution of aluminium trichloride (1.099 g, 8.24 mmol) in diethyl ether (75 mL) under cooling. After 1 h stirring, 1-methylcyclohexanol (1.36 mL, 10.95 mmol) was added drop by drop to the above mixture and stirred for additional 3 h. The volume of the solution mixture was reduced to its half by removing diethylether under reduced pressure and afterwards hexane (50 mL) was added to the resulting mixture to complete the precipitation of lithium chloride. The lithium chloride salt was separated by filtration and the volume of the filtrate was reduced under low pressure to allow the formation 1.75 g (75.75 %) of colourless crystals of $[Cl_2Al(OR)]_2$ (**5**).

NMR (C_6D_6, TMS): **^{1}H NMR** (C_6D_6): δ = 1.47 (s, $-CH_3$), 1.87–1.41 (m, ring-CH_2–). **^{13}C NMR:** δ = 87.44 (s, α-CH), 40.62 (s, β-CH_2–), 25.21 (s, γ-CH_2–), 24.17 (s, δ-CH_2–). **^{27}Al NMR:** δ = 89. **IR:** (C–H) ν = 2936 cm^{-1}. **Elemental Analysis**: Calcd. C 39.83; H 6.21; Al 12.78; Cl 33.59. Found C 38.46; H 5.40; Al 11.99; Cl 34.05 %.

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[26] Full data of the X-ray structure determinations can be obtained by the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-12233-36066; E-Mail: deposit@ccdc.cam.ac.uk): **1**: 808694, **2**: 808695, **3**: 808696, **4**: 808697, **5**: 808698.

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