REACTION OF $MeAlCl_2$ WITH ETHYL ALCOHOL (1:1) LEADING TO $[(Cl_2Al)_3(\mu\text{-}OEt)_6Al]$

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Abstract

The reaction of $MeAlCl_2$ with EtOH (1:1) yields $[(Cl_2Al)_3(\mu\text{-}OEt)_6Al]$ via $EtOAlCl_2$ as an intermediate. The aluminum compound containing a six-coordinated aluminum atom was characterized by NMR and its structure was determined by X-ray analysis.

1. Introduction

Alkylaluminum dichlorides are an interesting group of compounds due to the large relative Lewis acidity of aluminum and the presence of two different types of substituents at the aluminum atom. However, the chemistry of these compounds and of their reaction products with organic compounds are less known than with, e.g. trialkylaluminum compounds. The reason for this is the often low solubility of the products formed in these reactions, e.g. $MeOAlCl_2$, successive reactions leading to a mixture of products and non-selectivity of the reaction resulting from the presence of different substituents at the aluminum atom [1–3].

In this paper the reaction of methylaluminum dichloride and ethyl alcohol (1:1) is described. The novel ethoxychloroaluminum complex $[(Cl_2Al)_3(\mu\text{-}OEt)_6Al]$ obtained from this reaction is characterized by NMR and X-ray analysis. The expected $EtOAlCl_2$ is the intermediate in this reaction,

2. Results and Discussion

2.1. Reaction of $MeAlCl_2$ with EtOH

In the first step of the reaction of $MeAlCl_2$ with ethyl alcohol (1:1) carried out in hexane (20 °C) $EtOAlCl_2$ (**I**) is formed and methane evolves (1).

$$MeAlCl_2 + EtOH \longrightarrow \underset{\mathbf{I}}{EtOAlCl_2} + MeH \qquad (1)$$

On the basis of ^1H NMR studies it was found that the conversion of methyl groups after 24 h of reaction was 95 %. The spectrum shows a signal of MeAl protons at -0.41 ppm, two CH_3 triplets at 1.07 and 0.83 ppm, and two CH_2 quartets at 4.06 and 3.34 ppm of the ethoxy groups. The 1.07:0.83 signals area ratio of 6:1 was found. The same ratio was found for the 4.06:3.34 quartets. This suggests that the 1.07 and 4.06 ppm signals correspond to $EtOAlCl_2$ **I** (eq. 1), and the 3.34; 0.83; −0.41 ppm signals to the aluminum compound containing MeAl groups besides EtOAl ones.The ^{27}Al NMR spectrum of the reaction mixture studied displays the signal of four coordinative aluminum at 94.05 ppm.

When the reaction time was prolonged to 48 hours, a decay of the 3.34; 0.83; −0.41 ppm signals was observed in the ^1H NMR spectrum of the post-reaction mixture (eg. 1). However, new signals of very weak intensity appeared, indicating the formation of the compound $[(Cl_2Al)_3(\mu\text{-}OEt)_6Al]$ **II**. The Al:Cl molar ratio in the post-reaction mixture was found to be 1:2.

The products of the reaction of $MeAlCl_2$ and EtOH carried out in hexane are well soluble in the reaction solvent. Partial distillation of hexane, and then lowering of the temperature results crystals of $[(Cl_2Al)_3(\mu\text{-}OEt)_6Al]$ in a 60.7 % yield. The aluminum compound **II** containing four- and six-coordinated aluminum is formed as a result of disproportionation of $EtOAlCl_2$. The solution after crystallization of **II** contains aluminum compounds of unidentified composition.

The formation of $[(Cl_2Al)_3(\mu\text{-}OEt)_6Al]$ is confirmed by elemental analysis, NMR studies, molecular weight determination and the structure of the compound determined by X-ray analysis. Elemental analysis showed that in the compound studied, the aluminum to chlorine molar ratio is 4:6. In the ^1H NMR spectrum of compound **II** the CH_3 triplet at 1.23 ppm and two CH_2 multiplets at 3.56 and 4.02 ppm of the ethoxy groups were found. Each of the multiplets is composed of eight lines. This indicates that the methylene protons are diastereotopic The reason for this is the chirality of the six-coordinated aluminum center of compound **II**. The ^{13}C NMR spectrum shows a CH_3 resonance at 17.47 and CH_2 one at 60.98 ppm. In the ^{27}Al NMR spectrum signals of four- and six-coordinated aluminum atoms at 93.31 and 6.20 ppm, respectively, were found. The molecular weight of compound **II** was determined cryoscopically in benzene (found 586, calculated 591).

The NMR studies and the molecular weight determination confirm that compound **II** isolated as a result of crystallization is stable after dissolving in the solvents used.

The possibility of obtaining ethoxychloroaluminum compounds **I** and **II** from the reaction of $MeAlCl_2$ and EtOH (1:1) in other solvents - THF and toluene was also studied.

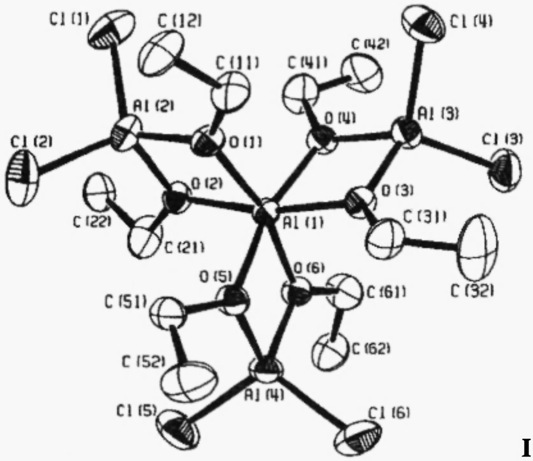
A mixture of products is formed, however, in the reaction carried out in THF. The ^1H NMR spectra show THF signals and several signals of the EtOAl groups. Tetrahydrofuran forms stable complexes with the products. No decay of THF signals was observed in the ^1H NMR spectrum recorded after attempts of its removal by distillation (6 h) under reduced pressure. The ^{27}Al NMR spectra of the mixture show signals of four- and five-coordinated aluminum at 89.12 and 48.07 ppm, respectively.

In the reaction carried out in toluene an insoluble yellow precipitate is formed. The products obtained from the reactions in THF and toluene were not studied further.

2.2. *Molecular structure of $[(CH_2Al)_3(\mu\text{-}OEt)_6Al]$* **II**

The structure of aluminum compounds containing four- and six-coordinated aluminum centers, e.g.: $\{[Al(OPr^i)_2]_3(\mu\text{-}OPr^i)_6Al\}$ [4, 5], $[(AlMe_2)_3(\mu\text{-}OCH_2\text{-}2\text{-}C_4H_3S)_6Al]$ [6] are known in the literature.

A perspective view of a molecule of compound **II** with the atom numbering system is shown below.



II

Thermal ellipsoids are drawn at the 30% level. Hydrogen atoms have been omitted for clarity.

The X-ray crystal structure analysis revealed that the molecules of **II** contain a central aluminum atom bridged with three Cl_2Al units by six ethoxy groups. The ethoxy groups oxygen atoms are the bridging atoms. The Al_4O_6 core of the compound is composed of one six- and three four-coordinate aluminum atoms. The core of the complex has an idealized D_3 symmetry, which indicates that two optical isomers are present in the crystal. The selected bond lengths and angles in compound **II** are shown in Tables 1 and 2. The average length of the six-coordinated Al–O bonds is 1.907 Å. They are longer by 0.135 Å than the average length of the four-coordinated aluminum atom - oxygen atom bonds. The geometry of three four-coordinated peripheral aluminum atoms corresponds to a distorted tetrahedron. The chlorine atoms of Cl_2Al units lie in a plane perpendicular to the plane of the Al_2O_2 four-membered ring. The obtained lengths of the Cl-Al bonds lie in the 2.094(2)–2.105(2) Å range typical for terminal bonds in aluminum chloride compounds [7–9].

Table 1. Selected bond lengths [Å] for **II**.

Al(1)-O(6)	1.898(2)	Al(2)-Cl(2)	2.105(2)
Al(1)-O(4)	1.902(2)	Al(3)-O(4)	1.770(2)
Al(1)-O(1)	1.906(2)	Al(3)-O(3)	1.770(2)
Al(1)-O(2)	1.906(2)	Al(3)-Cl(3)	2.1002(14)
Al(1)-O(5)	1.912(2)	Al(3)-Cl(4)	2.1019(14)
Al(1)-O(3)	1.918(2)	Al(4)-O(6)	1.766(2)
Al(2)-O(2)	1.770(2)	Al(4)-O(5)	1.773(2)
Al(2)-O(1)	1.774(2)	Al(4)-Cl(6)	2.1016(15)
Al(2)-Cl(1)	2.094(2)	Al(4)-Cl(5)	2.105(2)

Table 2. Selected bond angles [°] for **II**.

O(6)-Al(1)-O(4)	94.65(9)	Cl(1)-Al(2)-Cl(2)	112.54(7)
O(6)-Al(1)-O(1)	164.96(10)	O(4)-Al(3)-O(3)	83.53(10)
O(4)-Al(1)-O(1)	96.60(10)	O(4)-Al(3)-Cl(3)	115.97(8)
O(6)-Al(1)-O(2)	93.16(9)	O(3)-Al(3)-Cl(3)	114.70(9)
O(4)-Al(1)-O(2)	94.94(9)	O(4)-Al(3)-Cl(4)	113.25(8)
O(1)-Al(1)-O(2)	75.99(9)	O(3)-Al(3)-Cl(4)	114.96(9)
O(6)-Al(1)-O(5)	76.20(9)	Cl(3)-Al(3)-Cl(4)	111.79(6)
O(4)-Al(1)-O(5)	165.23(10)	O(6)-Al(4)-O(5)	83.25(10)
O(1)-Al(1)-O(5)	94.59(9)	O(6)-Al(4)-Cl(6)	111.90(9)
O(2)-Al(1)-O(5)	97.10(10)	O(5)-Al(4)-Cl(6)	116.58(9)
O(6)-Al(1)-O(3)	97.03(9)	O(6)-Al(4)-Cl(5)	117.15(9)
O(4)-Al(1)-O(3)	76.23(9)	O(5)-Al(4)-Cl(5)	111.96(9)
O(1)-Al(1)-O(3)	95.31(9)	Cl(6)-Al(4)-Cl(5)	112.98(7)
O(2)-Al(1)-O(3)	166.99(10)	Al(3)-O(4)-Al(1)	100.43(10)
O(5)-Al(1)-O(3)	93.19(9)	Al(4)-O(6)-Al(1)	100.67(10)
O(2)-Al(2)-O(1)	82.91(10)	Al(2)-O(1)-Al(1)	100.48(10)
O(2)-Al(2)-Cl(1)	114.95(9)	Al(2)-O(2)-Al(1)	100.61(10)
O(1)-Al(2)-Cl(1)	115.19(10)	Al(3)-O(3)-Al(1)	99.80(10)
O(2)-Al(2)-Cl(2)	113.34(10)	Al(4)-O(5)-Al(1)	99.87(10)
O(1)-Al(2)-Cl(2)	114.87(9)		

3. Experimental Details

3.1. General comments

All the reactions were carried out under dry argon using Schlenk techniques. Solvents were dried by standard methods. NMR spectra (^{1}H, ^{13}C and ^{27}Al) were run on a Varian VXR-300 spectrometer. ^{27}Al chemical shifts are reported relative to external Al(acac)$_3$.

3.2. Synthesis of $[(Cl_2Al)_3(\mu\text{-}OEt)_6Al]$

EtOH (2 ml, 34 mmol) in hexane was slowly added (2 h) to a stirred solution of Cl_2AlMe (3.84 g, 34 mmol) in hexane (120 ml) cooled to -15 °C. Methane slowly evolved during the reaction. The mixture was allowed to warm up to ambient temperature (1 h) and the reaction was carried out for 48 h, then the solvent was removed (80 ml) in vacuo. The solution thus prepared was left for 2 days at 8 °C to give white crystals of **II** (yield 2.01 g, 60.7%).

Anal. Found: Cl, 36.04; Al, 18.27; Mw: (cryoscopically in benzene): 586. $C_{12}H_{30}Cl_6O_6Al_4$. Calc.: Cl, 35.99; Al, 18.26; Mw: 591. ^{1}H NMR (C_6D_6): δ 1.23 (t, $J = 7.2$ Hz, 3H, $C\mathit{H}_3CH_2$), 3.56 (dq, $J = 7.2$ Hz, 1H, $CH_3C\mathit{H}_2$), 4.02 (dq, $J = 7.2$, 1H, $CH_3C\mathit{H}_2$) ppm. ^{13}C NMR (C_6D_6): δ 17.47 ($\mathit{C}H_3CH_2$), 62.98 ($CH_3\mathit{C}H_2$) ppm. ^{27}Al NMR (C_6D_6): δ 93.31, 6.20 ppm.

3.4. X-ray structure determination

A transparent colorless well-shaped crystal of **II** was placed in a thin-walled capillary tube (Lindemann glass) in an inert atmosphere. The tube was plugged with grease, flame sealed and then mounted on a goniometer head of a four-circle P3 (Siemens AG) diffractometer. The crystallographic data, a summary of data collection and the refinement procedure are presented in Table 3.

Table 3. Crystal data and structure refinement for **II**.

Empirical formula		$C_{12}H_{30}Al_4Cl_6O_6$
Formula weight		590.98
Temperature (K)		293(2)
Wavelength (e)		0.71073
Crystal system		Monoclinic
Space group		$P2_1/c$
Unit cell dimensions		
a (Å)		17.017(2)
b (Å)		11.2249(15)
c (Å)		14.783(2)
β(°)		91.390(12)
Volume (Å^3)		2822.9(7)
Z		4
Density (calc.) (Mgxm^{-3})		1.391
Absorption coefficient (mm^{-1})		0.756
F(000)		1216
Crystal size (mm^3)		0.76 x 0.28 x 0.16
Θ range for data collection		2.17 to 24.05
Index ranges		$-19 \leq h \leq 19, -12 \leq k \leq 0, 0 \leq l \leq 16$
Reflections collected		4535
Independent reflections		4345
R_{int}		0.0151
Absorption correction		Gaussian, based on the crystal shape
Max. and min. transmission		0.8883 and 0.8085
Refinement method		Full-matrix least-squares on F^2
Data/restraints/parameters		4345 / 60 / 328
Goodness-of-fit on F^2		1.028
Final R indices [$I>2\sigma(I)$]	R_1	0.0397
	wR_2	0.0965
R indices (all data)	R_1	0.0651
	wR_2	0.1055
Largest diff. peak/hole (exÅ^{-3})		0.286 / -0.174

The crystal system, the orientation matrix and the unit-cell parameters were obtained from the least-squares refinement of the angular positions measured for 30 reflections randomly found in the 2θ range between 14 and 29°. The intensities were collected up to $2\theta = 50°$ [maximum $(\sin \theta)/\lambda = 0.60$] in the θ-2θ mode with the scan range 1.9° plus the Kα_1-Kα_2 separation at various scan speeds. Two check reflections and (013), repeated every 70 reflections, showed a decay of 0.5 %. The intensities were adjusted accordingly and corrected for the Lorentz-polarization effect. No absorption correction was applied. The phase problem was solved by direct methods using the SHELXS-86 program [10].

Table 4. Atomic coordinates and equivalent isotropic displacement parameters [Å^2] for II. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Al(1)	0.24811(5)	0.02279(8)	0.24461(6)	0.0415(2)
Al(2)	0.10947(6)	0.12178(10)	0.31521(7)	0.0642(3)
Al(3)	0.24046(6)	-0.17064(9)	0.12265(6)	0.0538(3)
Al(4)	0.39574(6)	0.11848(9)	0.29659(7)	0.0599(3)
Cl(1)	0.00642(6)	0.02595(13)	0.33905(8)	0.1052(4)
Cl(2)	0.10046(8)	0.30217(11)	0.35251(9)	0.1141(4)
Cl(3)	0.32694(6)	-0.30272(9)	0.11017(7)	0.0847(3)
Cl(4)	0.14445(7)	-0.19959(11)	0.03324(7)	0.0898(3)
Cl(5)	0.41786(7)	0.21101(11)	0.41843(8)	0.1058(4)
Cl(6)	0.49553(6)	0.10439(10)	0.21626(9)	0.0971(4)
O(4)	0.21226(11)	-0.1373(2)	0.23430(12)	0.0479(5)
O(6)	0.34470(11)	-0.0181(2)	0.30355(13)	0.0485(5)
O(1)	0.15156(11)	0.0965(2)	0.20825(13)	0.0529(5)
C(11)	0.1146(8)	0.106(2)	0.1195(5)	0.081(5)
C(12)	0.0485(6)	0.1898(11)	0.1164(7)	0.088(3)
C(11A)	0.1224(9)	0.129(3)	0.1188(8)	0.079(6)
C(12A)	0.0379(8)	0.109(2)	0.1062(12)	0.130(7)
O(2)	0.19712(12)	0.0532(2)	0.35568(13)	0.0522(5)
C(21)	0.2238(10)	0.056(2)	0.4502(5)	0.083(6)
C(22)	0.1611(14)	0.036(2)	0.5131(5)	0.072(4)
C(21A)	0.2256(13)	0.016(3)	0.4455(6)	0.067(6)
C(22A)	0.177(2)	0.060(3)	0.5173(8)	0.112(11)
O(3)	0.27680(12)	-0.0229(2)	0.12480(13)	0.0510(5)
C(31)	0.3119(12)	0.0474(14)	0.0543(9)	0.071(5)
C(32)	0.3602(10)	-0.0311(11)	-0.0066(9)	0.136(6)
C(31A)	0.3330(15)	0.027(2)	0.0627(9)	0.066(6)
C(32A)	0.3074(10)	-0.0006(15)	-0.0340(5)	0.093(5)
C(41)	0.1614(2)	-0.2072(3)	0.2911(3)	0.0801(12)
C(42)	0.1738(3)	-0.3363(3)	0.2815(3)	0.0896(13)
O(5)	0.30780(11)	0.1670(2)	0.24135(14)	0.0512(5)
C(51)	0.2840(8)	0.2916(6)	0.2336(9)	0.062(3)
C(52)	0.3462(12)	0.3605(11)	0.188(2)	0.108(6)
C(51A)	0.2843(13)	0.2781(9)	0.1967(14)	0.075(6)
C(52A)	0.3451(19)	0.3708(14)	0.215(3)	0.133(12)
C(61)	0.3768(2)	-0.1331(3)	0.3305(3)	0.0764(11)
C(62)	0.4372(2)	-0.1223(3)	0.4029(2)	0.0790(11)

Positional and thermal parameters of the non-hydrogen atoms (first isotropic and then anisotropic) were adjusted by means of several rounds of full matrix least-squares calculation [11]. The hydrogen atoms were included in the idealized positions and not refined. A disorder was found of ethyl groups in the molecule studied. Four ethyl groups from six exhibited a disordering over two sites and were modeled in terms of two sets of atoms with the sum of their occupation factors equal 1. Final difference Fourier synthesis contained no unusual features. The structure was refined against F^2 with $w^{-1} = \sigma^2(F_0^2) = (0.0587\ P)^2$ where $P = (F_0^2 + 2F_c^2)/3$. The R values presented in Table 3 are defined as $wR_2=(\Sigma w(F_0^2 + 2F_c^2)^2/\Sigma w\ F_0^4)'$ and $R_1=\Sigma||F_0|-|F_c||/\Sigma|F_0|$.

Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 4.

Tables of hydrogen atom coordinates and anisotropic thermal parameter and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

References

1. M.D. Headly, J.W. Ziller, A.R. Barron, *Organometallics* **11** (1992) 3041.
2. W. Kosinska, K. Zardecka, A. Kunicki, M. Bolesławski, S. Pasynkiewicz, *J. Organomet. Chem.* **153** (1978) 281.
3. W. Kosinska, A. Kunicki, M. Bolesławski, S. Pasynkiewicz, *J. Organomet. Chem.* **161** (1978) 289.
4. K. Folting, W.E. Streib, K.G. Caulton, O. Poncelet, L.G. Hubert-Pfalzgraf, *Polyhedron* **10** (1991) 1639.
5. N.Ya. Turova, V.A. Kozunov, A.I. Yanovskii, N.G. Bokii, Yu.T. Struchkov, B.L. Tarnopolskii, *J. Inorg. Nucl. Chem.* **41** (1979) 5.
6. R. Kumar, V.S.J. de Mel, M.L. Sierra, D.G. Hendershot, J.P. Oliver, *Organometallics* **13** (1994) 2079.
7. A.R. Barron, G. Wilkinson, M. Motevalli, M. Hursthouse, *J. Chem. Soc., Dalton Trans.* **1987**, 837.
8. P. Sobota, M.O. Mustafa, J. Utko, T. Lis, *J. Organomet. Chem.* **368** (1989) 257.
9. C.M. Means, S.G. Bott, J.L. Atwood, *Polyhedron* **9** (1990) 309.
10. G.M. Sheldrick, *Acta Crystallogr., Sect. A* **46** (1990) 467.
11. G.M. Sheldrick, SHELXL-93, Universität Göttingen, Göttingen, 1993.

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