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The products formed in the reaction of MeAlCl_2 with alcohols (1:1)

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Abstract

The products formed in the reaction (1:1) of MeAlCl_2 with alcohols ROH, where R = Et, ⁱPr, ⁿBu, ⁱBu, ^sBu, ^tBu, ^tBuCH₂ were investigated. Depends on the alcohol used the formation of $[\text{Cl}_2\text{Al}(\mu\text{-OR})_2]_2\text{AlCl}$ or/and $[\text{Cl}_2\text{Al}(\mu\text{-OR})_2]_3\text{Al}$ except dimeric or/and trimeric ROAlCl_2 were found. The products have been characterized by NMR and cryoscopically in benzene. The crystal structures of $[\text{Cl}_2\text{Al}(\mu\text{-O}^n\text{Bu})_2]_3\text{Al}$ and $[\text{Cl}_2\text{Al}(\mu\text{-OCH}_2^t\text{Bu})_2]$ were determined by X-ray diffraction studies.

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1. Introduction

Although the compounds of general formulae ROAlCl_2 are known since many years, their chemistry and structure still remain unexplored [1]. The structure of MeOAlCl_2 has been determined in solid state by X-ray method only just few years ago [2]. The methoxy-aluminum species was found to be a trimer with non-planar six-membered Al_3O_3 ring structure. On the other hand compound PhOAlCl_2 directly after synthesis is a dimer what was established from spectroscopic and cryoscopic measurements [3]. After 24 h a trimeric form was found as well. The presence of methyl groups in *ortho* positions of the aromatic ring in 2,6- $\text{Me}_2\text{-C}_6\text{H}_3\text{OAlCl}_2$ leads to the formation of a dimer only with bridging oxygen atom [4], while the substitution of phenyl ring by *tert*-butyl groups in *ortho* positions in 2,6-^tBu₂-4-MeC₆H₃OAl(Cl)Me results in dimer with bridging chlorine atoms [5].

The common method to synthesize (alkoxy)dichloroaluminum derivatives is the controlled reaction of appropriate alcohol with organoaluminum compounds of the general formulae RAlCl_2 . However, due to

unselectivity of the reaction a mixture of products can be formed [6]. We have reported earlier that the tetrametallic complex $[\text{Cl}_2\text{Al}(\mu\text{-OEt})_2]_3\text{Al}$ is a main product isolated by crystallization from the reaction of MeAlCl_2 and EtOH (1:1) [7], while the expected EtOAlCl_2 appears as an intermediate only. It is worth noting that the tetrametallic aluminum compounds can be used as precursors to Al_2O_3 [8].

In this paper we described the results of our systematic studies of the products formed in the reaction of MeAlCl_2 with primary, secondary and tertiary alcohols at 1:1 molar ratio. We undertook attempts to recognize the influence of the nature of the alcohols on the products of the studied reactions. The products were characterized by NMR studies, cryoscopic molecular weight measurements in solution and elemental analysis. The structures of two obtained compounds have been analyzed by X-ray method.

2. Results and discussion

The reaction of MeAlCl_2 with equimolar amount of alcohols ROH, where R = Et, ⁱPr, ⁿBu, ⁱBu, ^sBu, ^tBu, CH_2^tBu results in the evolution of a gas, presumably methane and formation of the appropriate (alkoxy)dichloroaluminum compound (Eq. (1)).

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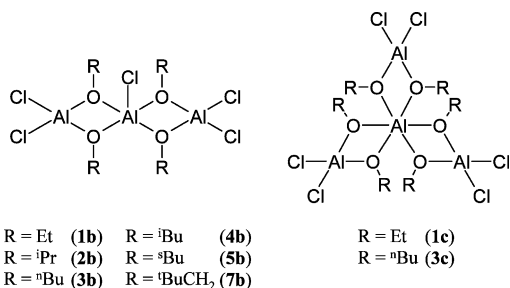
$n = 2$ or 3

R = Et	1a
R = ⁱ Pr	2a
R = ⁿ Bu	3a
R = ⁱ Bu	4a
R = ^s Bu	5a
R = ^t Bu	6a
R = CH ₂ Bu	7a

The formed compounds ROAlCl₂ can undergo conversion reaction to trimetallic aluminum compound [Cl₂Al(μ-OR)₂]₂AlCl (b) or/and tetrametallic aluminum one [Cl₂Al(μ-OR)₂]₃Al (c) (Scheme 1). On the contrary to the chloroalkoxypolymetallic aluminum compounds the trimetallic and tetrametallic alkyl derivatives of aluminum only are well structurally characterized in literature [9,10].

2.1. Products of reaction MeAlCl₂ with EtOH

¹H-NMR studies of the reaction mixture Eq. (1) just after synthesis show that it contains compound **1a** and tetrametallic aluminum compound [Cl₂Al(μ-OEt)₂]₃Al (**1c**), with the molar ratio 20:1, respectively. Additionally, the spectra imply the presence of dimeric and trimeric forms of EtOAlCl₂ (**1a**). Solution molecular weight measurements allowed to determine **1a** association degree ($n = 2.8$) and to assign the proton resonance lines in ¹H-NMR spectra to dimer and trimer. The ²⁷Al-NMR spectra show signals at 93 ppm assigned to four-coordinate aluminum atoms in **1a** and **1c** while the signal at 6 ppm corresponds to six-coordinate aluminum center in **1c**. Attempts to isolate pure products by crystallization resulted in conversion of **1a** to **1c**, and compound **1c** was separated with 60% yield. The crystal structure of **1c** was determined by X-ray method earlier [7]. After crystallization of **1c** ²⁷Al-NMR spectra of the lye showed the new third signal of aluminum atom at 44 ppm. It suggests the chloroethoxy compound **1b** with five coordinate aluminum atom is formed as well. We could not however isolate this compound.



Scheme 1.

2.2. Products of reaction MeAlCl₂ with ⁱPrOH

The reaction of MeAlCl₂ with ⁱPrOH Eq. (1) proceeds with the formation of dimeric ⁱPrOAlCl₂ (**2a**) and [Cl₂Al(μ-OⁱPr)₂]₂AlCl (**2b**). The integration of the signals in ¹H-NMR spectra of the post-reaction mixture shows 2:3 molar ratio of **2a** to **2b**. ²⁷Al-NMR spectra proof the presence of both four- and five-coordinate aluminum atoms in the mixture. The compound **2b** was isolated by crystallization with 43% yield and spectrally characterized. It should be noted, that **2b** was synthesized before in the reaction of AlCl₃ with Al(OⁱPr)₃ and its structure determined by X-ray method [11].

2.3. Products of reaction MeAlCl₂ with ⁿBuOH

The reaction of MeAlCl₂ with ⁿBuOH Eq. (1) leads initially to the formation of dimeric and trimeric forms of ⁿBuOAlCl₂ (**3a**) and of tetrametallic aluminum complex [Cl₂Al(μ-OⁿBu)₂]₃Al (**3c**), with the molar ratio 24:1, respectively. The relative intensity of proton signals in ¹H-NMR spectra shows 3:10 molar ratio of dimer to trimer **3a**, respectively. No changes in the reaction mixture stored for 70 days at room temperature were observed. Similarly to ethoxy derivative **1a**, the crystallization at -15 °C proceeds with conversion reaction of ⁿBuOAlCl₂ giving compound **3c** with 47% yield.

The compound **3c** was characterized spectroscopically and by X-ray methods. The molecular structure with atom numbering scheme is shown in Fig. 1. The selected bonds lengths and angles are collected in Table 1. The molecule of **3c** shows C₂ symmetry and resides on the crystallographic twofold axis with two aluminum centers Al(1) and Al(2) located in special positions (4e according Wyckoff notation). The studied compound contains the central six-coordinate aluminum atom with three four-coordinate aluminum atoms occupying the

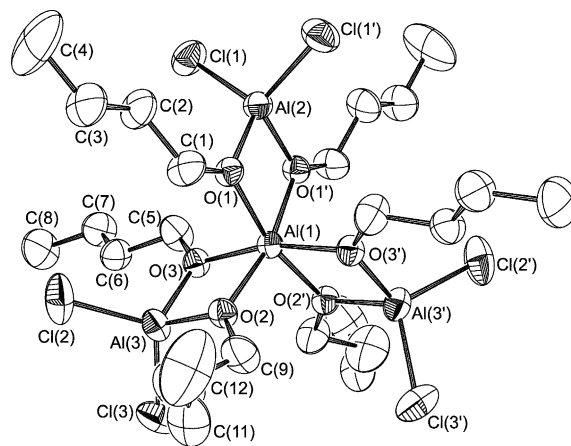


Fig. 1. An ORTEP diagram of [Cl₂Al(μ-OⁿBu)₂]₃Al (**3c**). Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and bond angles (°) for $[(\text{Cl}_2\text{Al})_3(\mu\text{-O}^n\text{Bu})_6]\text{Al}$ (**3c**)^a

Bond lengths			
Al(1)–O(2)	1.906(2)	Al(1)–O(1)	1.907(2)
Al(1)–O(3)	1.910(2)	Al(2)–O(1)	1.767(2)
Al(2)–Cl(1)	2.1000(14)	Al(3)–O(2)	1.772(2)
Al(3)–O(3)	1.775(2)	Al(3)–Cl(2)	2.0973(17)
Al(3)–Cl(3)	2.1062(17)	O(1)–C(1)	1.452(4)
Bond angles			
O(1')–Al(2)–O(1)	83.25(14)	Cl(1')–Al(2)–Cl(1)	111.24(10)
O(2)–Al(3)–O(3)	83.25(10)	Cl(2)–Al(3)–Cl(3)	112.80(7)
Al(2)–O(1)–Al(1)	100.38(10)	Al(3)–O(2)–Al(1)	100.38(10)
Al(3)–O(3)–Al(1)	100.11(10)		

^a Symmetry transformation used to generate equivalent atoms labeled with prime: $-x, y, -z+1/2$.

periphery. The geometry at the central aluminum Al(1) atom can be described as distorted octahedral with Al–O(bridging) distances almost equal [1.906(2)–1.910(2) Å]. The four-coordinate aluminum Al(2) and Al(3) atoms form much shorter Al–O bonds ranging from 1.767(2) to 1.775(2) Å. The $\text{Al}_2(\mu\text{-O})_2$ rings feature O–Al(1)–O angles of ca. 76°. The angles formed by four-coordinate aluminum and two bridging oxygen atoms are somewhat more obtuse and are equal to 83.3(1)°. Detailed analysis of the remaining bond distances and angles indicates that the central $(\text{Cl}_2\text{AlO}_2)_3\text{Al}$ core displays approximate D_3 point group symmetry. The observed geometry of **3c** is in very good agreement with the ones found for analogous previously reported tetrametallic ethoxy complex **1c** [7].

Lowering quickly the temperature of the mixture obtained from the reaction of MeAlCl_2 with $^n\text{BuOH}$ Eq. (1) results in precipitation of a solid. ^1H -NMR spectra show, that the solid contains compounds **3a**, **3c** and **3b** in molar ratio 16:3:1, respectively. The ^{27}Al -NMR spectra provide the evidence for existing not only the trimetallic aluminum complex $[\text{Cl}_2\text{Al}(\mu\text{-O}^n\text{Bu})_2]_2\text{AlCl}$ (**3b**) but also $[\text{Cl}_2\text{Al}(\mu\text{-O}^n\text{Bu})_2]_2\text{AlO}^n\text{Bu}$. The resonance lines of five coordinate aluminum atoms at 40 and 43 ppm were found.

2.4. Products of reaction MeAlCl_2 with $^i\text{BuOH}$

The formation of $^i\text{BuOAlCl}_2$ (**4a**) quantitatively was observed just after reaction of MeAlCl_2 with $^i\text{BuOH}$ Eq. (1). The solution molecular weight measurements ($n = 2.14$) and ^1H -NMR spectra indicate an equilibrium between dimeric and trimeric forms of **4a**, whereas after 7 days the ^1H -NMR spectra do not show the presence of the dimer. Additionally in the spectra we have found the compound $[\text{Cl}_2\text{Al}(\mu\text{-O}^i\text{Bu})_2]_2\text{AlCl}$ (**4b**) (molar ratio **4b**:**4a** equal to 1:13), as well. The ^{27}Al -NMR spectrum

confirmed the presence of five-coordinate aluminum atom with the signal at 45 ppm.

2.5. Products of reaction MeAlCl_2 with $^s\text{BuOH}$

The evidence for formation of dimer $^s\text{BuOAlCl}_2$ (**5a**) in reaction of MeAlCl_2 with $^s\text{BuOH}$ was found from ^1H - and ^{13}C -NMR spectra and solution molecular weight measurements. The degree of association of **5a** was found to be 2.0 and did not change after 7 days. ^1H -NMR spectrum recorded however 50 days later show very low intensities set of resonance lines which can be attributed to $[\text{Cl}_2\text{Al}(\mu\text{-O}^s\text{Bu})_2]_2\text{AlCl}$ (**5b**). The spectrum is complex and not very informative due to chiral carbon of *sec*-butyl group and possibilities of the formation of **5b** diastereoisomers. ^{27}Al -NMR spectra show resonance lines at 93 and 44 ppm indicating the existence of **5b** in the solution.

2.6. Products of reaction MeAlCl_2 with $^t\text{BuOH}$

In the reaction of MeAlCl_2 and $^t\text{BuOH}$ the $^t\text{BuOAlCl}_2$ (**6a**) was formed Eq. (1). At room temperature the compound **6a** is unstable both in the solution and the solid state. It decomposes slowly with gas evolution forming insoluble in common solvents solid. Compound **6a** was isolated in 45% yield by crystallization and characterized by NMR (^1H , ^{13}C , ^{27}Al) spectroscopy. The ^1H - and ^{13}C -NMR spectra of the compound show a one signal of ^tBuO group. The ^{27}Al -NMR spectra display signal of four coordinate aluminum atom at 90 ppm implying the presence of the oligomeric, probably dimeric form.

2.7. Products of reaction MeAlCl_2 with $^t\text{BuCH}_2\text{OH}$

The ^1H -NMR spectra of the post-reaction mixture show that $^t\text{BuCH}_2\text{OAlCl}_2$ (**7a**) is the only product formed directly after mixing of $^t\text{BuCH}_2\text{OH}$ with MeAlCl_2 (1:1). The compound **7a** was isolated by crystallization. After 50 days of storing the post-reaction mixture at room temperature the NMR spectroscopy provided evidence of formation of trimetallic aluminum complex $[\text{Cl}_2\text{Al}(\mu\text{-O}^t\text{Bu})_2]_2\text{AlCl}$ (**7b**) as well. Calculations based on the integration of the proton signals in ^1H -NMR reveal the molar ratio of **7a** to **7b** to be equal 50:1. ^{27}Al -NMR spectra show new signal at 43 ppm attributed to five coordinate aluminum atom of **7b**.

We have tried to separate by crystallization **7b** but crystals of **7a** precipitated only. The X-ray crystallographic analysis of **7a** reveals that the compound crystallizes in the monoclinic space group $P2_1/c$. The structure consists of a discrete centrosymmetric $^t\text{BuCH}_2\text{O}$ bridged dimers. Selected bond distances and angles are presented in Table 2. The molecular structure of the $[\text{Cl}_2\text{Al}(\mu\text{-OCH}_2^t\text{Bu})_2]$ (**7a**) is shown in Fig. 2.

Table 2
Selected bond lengths (Å) and bond angles (°) for $[(\mu\text{-O}^t\text{Bu-CH}_2)\text{AlCl}_2]_2$ (**7a**)^a

Bond lengths			
Al(1)–Cl(1)	2.0556(19)	Al(1)–Cl(2)	2.0488(19)
Al(1)–O(1)	1.772(3)	Al(1)–O(1')	1.776(3)
O(1)–C(1)	1.453(4)	Al(1)–Al(1')	2.668(3)
Bond angles			
Cl(2)–Al(1)–Cl(1)	117.00(9)	O(1)–Al(1)–O(1')	82.50(13)
C(1)–O(1)–Al(1)	124.8(2)	C(1)–O(1)–Al(1')	131.1(2)
Al(1)–O(1)–Al(1')	97.50(13)		

^a Atoms labeled with prime belong to the centrosymmetric counterpart of the dimer.

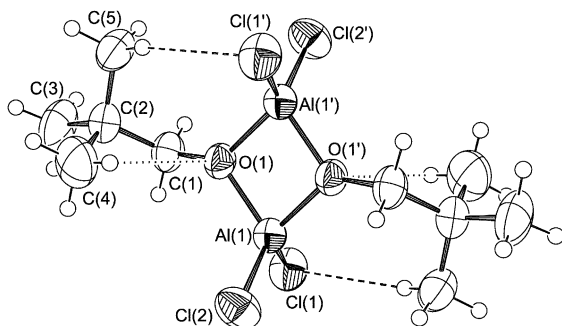


Fig. 2. An ORTEP view of $[\text{Cl}_2\text{Al}(\mu\text{-O}^t\text{BuCH}_2)]_2$ (**7a**) showing the intermolecular C–H···Cl (dashed lines) and C–H···O (dotted lines) hydrogen bonds. Thermal ellipsoids are drawn at 50% probability.

The four-membered central $\text{Al}_2(\mu\text{-O})_2$ ring is planar and the Al–O bond lengths are, within experimental error, the same [1.772(3) and 1.776(3) Å], and within the range expected for the four-coordinate aluminum in

$\text{Cl}_2\text{Al}(\mu\text{-OR})_2\text{Al}$ cores, cf. for example, those found for **1c** and **3c**. The aluminum atoms display a distorted tetrahedral coordination sphere. The distortion is mainly caused by the constraints in the four-membered $\text{Al}_2(\mu\text{-O})_2$ bridging ring and the most acute angle, O(1)–Al(1)–O(1'), is equal $82.50(13)^\circ$. The alkyl group of the alkoxy ligand adopts asymmetrical conformations with respect to the central ring, with the C(1) atom significantly moved [0.520(4) Å] out of the Al_2O_2 plane. A detailed inspection of intra- and intermolecular contacts does reveal that two hydrogen atoms of the ^tBu group are involved in the weak intramolecular hydrogen bonding interactions with Cl(1) and O(1) atoms (dashed and dotted lines in Fig. 2). The uncorrected C(5)–H(52)···Cl(1') and C(4)–H(42)···O(1) distances and angles are equal 2.85, 2.54 Å, and 163 and 101° , respectively. Taking into account the orientation of the ^tBu group and relatively low anisotropic thermal parameters U_{ij} of both C(4) and C(5) carbon atoms, there is evidence that dimeric structure is additionally stabilized by a pair of weak intramolecular hydrogen bonds.

3. Conclusions

The obtained results indicate that the tri- and tetrametallic aluminum compounds appear in the reaction of MeAlCl_2 with studied alcohols via conversion of ROAlCl_2 probably in the sequence of reactions Eqs. (2)–(5).

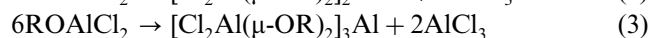
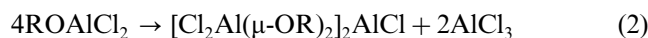
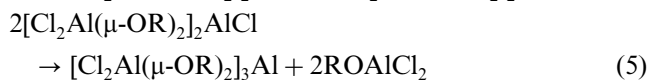


Table 3
The products identified in the studied reactions of MeAlCl_2 with various alcohols

ROH	dimer	trimer	trimetallic comp.	tetrametallic comp.
	$[\text{Cl}_2\text{Al}(\mu\text{-OR})_2]$	$[\text{Cl}_2\text{Al}(\mu\text{-OR})_3]$	$[\text{Cl}_2\text{Al}(\mu\text{-OR})_2]_2\text{AlCl}$	$[\text{Cl}_2\text{Al}(\mu\text{-OR})_2]_3\text{Al}$
	X	X	X	X
	X	X	X	X
	X	X	X	
	X		X	
	X		X	
	X		X	
	X			



Based on the obtained results we have found that the character of RO group is a key feature in the conversion to oligometallic complexes as well as in association forms of ROAlCl_2 . It was shown schematically in Table 3.

The alkoxyaluminum compounds derived from primary alcohols with straight-chain alkyls (Et, ⁿBu) convert to tri- and tetrametallic aluminum compounds. For (alkoxy)chloroaluminum derivatives obtained from secondary alcohols (ⁱPr, ^sBu) and primary ones with branched β carbon (^tBu, CH_2^iBu) a trimetallic aluminum form is favored. ^tBuOAlCl₂ derived from tertiary alcohol does not transform to oligoaluminum complexes but decomposes slowly at room temperature.

A degree of association of studied ROAlCl_2 compounds depends on the hindering effect of alkoxy RO group. For compounds derived from primary alcohols (Et, ⁿBu, and ⁱBu) dimer–trimer equilibrium was observed. For alkoxyaluminum derivatives obtained from secondary (ⁱPr, ^sBu), and tertiary (^tBu) alcohols as well as primary ones with branched β carbon (CH_2^iBu) a dimeric form is favored. The influence of steric effect of substituents bonded to oxygen atom in ROAlMe_2 on association degree was studied widely by Barron and co-workers earlier [12].

4. Experimental

4.1. General remarks

All compounds were prepared and manipulated under an argon atmosphere using standard Schlenk techniques. All solvent used (hexane, benzene, toluene) were dried over benzophenone ketyl. Dichloromethylaluminum were purchased from Aldrich as 1.0 M solution in hexane and used without further purification. Ethyl alcohol was dried by refluxing over magnesium promoted with iodine. Other alcohols were distilled under Ar over Na before use.

¹H-, ¹³C- and ²⁷Al-NMR measurements were performed on Varian–VXR 300 (300 MHz) or Varian–Gemini (¹H, 199.971; ¹³C, 50.283; ²⁷Al, 52.106 MHz). The proton chemical shifts were referenced to $\text{C}_6\text{D}_5\text{H}$ ($\delta = 7.15$ ppm), the carbon resonances to C_6D_6 ($\delta = 128$ ppm) and the ²⁷Al-NMR spectra to $\text{Al}(\text{H}_2\text{O})_6^{3+}$ in benzene. Molecular weight was determined by cryoscopic measurements in benzene solution.

4.2. The reaction of MeAlCl_2 with EtOH

To solution of MeAlCl_2 (1.920 g, 17 mmol) in 80 ml of hexane cooled to 0 °C, ethyl alcohol (0.785 g, 17 mmol) in 60 ml of hexane was slowly added from funnel. During addition the gas evolution was observed. The reaction mixture was allowed to warm up to room temperature (r.t.) and stirred 24 h to give light-yellow solution. After decantation and solvent evaporation in vacuo, clear, viscous liquid (2.299 g, yield 95%) was obtained. The viscous liquid contained mainly EtOAlCl_2 .

Anal. for $\text{C}_2\text{H}_5\text{AlCl}_2\text{O}$, Calc. (Found): C, 16.80 (16.49); H, 3.53 (3.59); Al, 18.88 (18.21); Cl, 49.60 (48.25)%. M_w (cryoscopically in benzene): 402, Calc. for $\text{C}_4\text{H}_{10}\text{Al}_2\text{Cl}_4\text{O}_2$ (**1a** dimer) 285.89, Calc. for $\text{C}_6\text{H}_{15}\text{Al}_3\text{Cl}_6\text{O}_3$ (**1a** trimer) 428.84, Calc. for tetrametallic aluminum compound $\text{C}_{12}\text{H}_{30}\text{Al}_4\text{Cl}_6\text{O}_6$ (**1c**) 591.00.

¹H-NMR (C_6D_6 , ppm): (EtOAlCl_2)₂ δ 1.07 (t, ³J = 7.2 Hz, 3H, CH₃), 3.62 (q, ³J = 7.2 Hz, 2H, CH₂); (EtOAlCl_2)₃ δ 1.12 (t, ³J = 7.0 Hz, 3H, CH₃), 4.10 (q, ³J = 7.0 Hz, 2H, CH₂). ²⁷Al-NMR: 93 ppm ($\omega_{1/2} = 260$ Hz).

Crystallization from the reaction mixture at –15 °C leads to precipitation of $[\text{Cl}_2\text{Al}(\mu\text{-OEt})_2]_3\text{Al}$ (**1c**) as white crystals with 60% yield (1.005 g).

Anal. for $\text{C}_{12}\text{H}_{30}\text{Al}_4\text{Cl}_6\text{O}_6$, Calc. (Found): C, 24.39 (24.42); H, 5.12 (5.01); Al, 18.26 (18.33); Cl, 35.99 (36.14)%. M_w (cryoscopically in benzene): 587, Calc. 591.00. ¹H-NMR (C_6D_6): δ 1.23 (t, ³J = 7.2 Hz, 3H, CH_3CH_2), 3.52 (dq, ²J = 10.8 Hz, ³J = 7.2 Hz, 1H, HCH), 4.04 (dq, ²J = 10.8 Hz, ³J = 7.2 Hz, 1H, HCH). ¹³C-NMR (C_6D_6): δ 17.47 (CH_3CH_2), 62.98 (CH_3CH_2). ²⁷Al-NMR (C_6D_6): δ 93 ($\omega_{1/2} = 260$ Hz), 5 ($\omega_{1/2} = 60$ Hz) ppm.

4.3. The reaction of MeAlCl_2 with ⁱPrOH

ⁱPrOH (0.781 g, 13.0 mmol) in 60 ml of toluene was added slowly to hexane solution (20 ml) of MeAlCl_2 (1.468 g, 13.0 mmol) cooled to 0 °C. The addition was followed by gas evolution. The reaction mixture was allowed to warm up to r.t. and stirred 24 h. The decantation and evaporation of the solvents in vacuo give white waxy solid (3.57 g) with 96% yield.

Anal. for $\text{C}_3\text{H}_7\text{AlCl}_2\text{O}$, Calc. (Found): C, 22.95 (26.33); H, 4.49 (5.02); Al, 17.19 (16.56); Cl, 45.17 (38.06)%. M_w (cryoscopically in benzene): 442, Calc. for $\text{C}_6\text{H}_{14}\text{Al}_2\text{Cl}_4\text{O}_2$ (**2a** dimer) 313.95, Calc. for trimetallic aluminum compound $\text{C}_{12}\text{H}_{28}\text{Al}_3\text{Cl}_5\text{O}_4$ (**2b**) 494.56.

(ⁱPrOAlCl₂)₂: ¹H-NMR (C_6D_6): δ 1.02 (d, ³J = 5.8 Hz, 6H, OCH(CH₃)), 4.07 (sept, ³J = 5.8 Hz, 1H, CH). ¹³C-NMR (C_6D_6): δ 23.19 (OCH(CH₃)), 72.17 (OCH(CH₃)) ppm. ²⁷Al-NMR (C_6D_6): 91 ppm ($\omega_{1/2} = 825$ Hz). Crystallization from hexane at –15 °C give

white crystalline solid of $[\text{Cl}_2\text{Al}(\mu\text{-O}^i\text{Pr})_2]_2\text{AlCl}$ (**2b**) with 43% yield.

Anal. for $\text{C}_{12}\text{H}_{28}\text{Al}_3\text{Cl}_5\text{O}_4$, Calc. (Found): C, 29.14 (28.93); H, 5.71 (5.80); Al, 16.37 (16.23); Cl, 35.84 (35.96)%. M_w (cryoscopically in benzene): 501, Calc. 494.56.

$^1\text{H-NMR}$ (C_6D_6): δ 1.27 (d, $^3J = 6.3$ Hz, 6H, $\text{OCH}(\text{CH}_3)_2$), 4.31 (sept, $^3J = 6.3$ Hz, 1H, $\text{OCH}(\text{CH}_3)_2$). $^{13}\text{C-NMR}$ (C_6D_6): δ 24.77 [$\text{OCH}(\text{CH}_3)$], 72.42 [$\text{OCH}(\text{CH}_3)_2$]. $^{27}\text{Al-NMR}$ (C_6D_6): δ 91 ($\omega_{1/2} = 825$ Hz), 43 ($\omega_{1/2} = 332$ Hz) ppm.

4.4. Reaction of MeAlCl_2 with $^n\text{BuOH}$

A solution of $^n\text{BuOH}$ (1.622 g, 21.9 mmol) in 60 ml of hexane was added to cooled to 0°C solution of MeAlCl_2 (2.473 g, 21.9 mmol) in 80 ml of hexane. The reaction mixture was allowed to warm up to ambient temperature and stirred for 24 h to give after decantation and solvent evaporation in vacuo colorless oil (3.62 g), yield 97%. The oil contained mainly dimer and trimer of $^n\text{BuOAlCl}_2$ (**3a**).

Anal. for $\text{C}_4\text{H}_9\text{AlCl}_2\text{O}$, Calc. (Found): C, 28.10 (28.91); H, 5.30 (5.37); Al, 15.78 (15.03); Cl, 41.46 (40.99)%. M_w (cryoscopically in benzene): 499, Calc. 171.00 (monomer).

$^1\text{H-NMR}$ (C_6D_6): dimer δ 0.68 (t, $^3J = 7.4$ Hz, 3H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.12 (m, $^3J = 7.5$, δ , 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.64 (m, $^3J = 7.5$ Hz, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.79 (t, $^3J = 7.5$ Hz, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); trimer δ 0.63 (t, $^3J = 7.4$ Hz, 3H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.01 (m, $^3J = 7.5$ Hz, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.72 (m, $^3J = 7.6$ Hz, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.23 (t, $^3J = 7.6$ Hz, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C-NMR}$ (C_6D_6): dimer δ 13.53 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 18.83 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 34.02 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 67.37 ($\text{OCH}_2\text{CH}_2\text{C}_2\text{CH}_3$); trimer δ 13.36 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 18.19 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 33.35 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 72.59 ($\text{OCH}_2\text{CH}_2\text{C}_2\text{CH}_3$). $^{27}\text{Al-NMR}$ (C_6D_6): δ 94 ($\omega_{1/2} = 560$ Hz) ppm. Crystallization from hexane leads to precipitation of white crystals of $[\text{Cl}_2\text{Al}(\mu\text{-O}^n\text{Bu})_2]_3\text{Al}$ (**3c**) with 47% yield (1.30 g).

Anal. for $\text{C}_{24}\text{H}_{54}\text{Al}_4\text{Cl}_6\text{O}_6$, Calc. (Found): C, 37.96 (38.08); H, 7.17 (7.02); Al, 14.21 (14.51); Cl, 28.01 (27.66)%. M_w (cryoscopically in benzene): 745, Calc. 759.32.

$^1\text{H-NMR}$ (C_6D_6): δ 0.76 (t, $^3J = 7.6$ Hz, 3H; $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.16 (m, $^3J = 7.6$ Hz, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.93 (m, $^3J = 7.6$ Hz, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.92 (dt, $^2J = 10.5$ Hz, $^3J = 5.9$ Hz, 1H, $\text{OCH}_2\text{CH}_2\text{C}_2\text{CH}_3$), 4.27 (dt, $^2J = 10.5$ Hz, $^3J = 5.9$ Hz, 1H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C-NMR}$ (C_6D_6): δ 13.53 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 19.03 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 34.51 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 66.89 (OCH_2CH_2

CH_2CH_3) ppm. $^{27}\text{Al-NMR}$ (C_6D_6): δ 94 ($\omega_{1/2} = 560$ Hz), 6 ($\omega_{1/2} = 103$ Hz) ppm.

4.5. Reaction of MeAlCl_2 with $^i\text{BuOH}$

To the solution of MeAlCl_2 (2.43 g, 21.5 mmol) in 80 ml of hexane cooled to 0°C a $^i\text{BuOH}$ (1.59 g, 21.5 mmol) in 50 ml of hexane was added. The reaction mixture was warm up to r.t. and stirred for 24 h. The solution was decanted and solvent evaporated in vacuo giving white solid of $^i\text{BuOAlCl}_2$ (**4a**) (3.57g) in 97% yield.

Anal. for $\text{C}_4\text{H}_9\text{AlCl}_2\text{O}$, Calc. (Found): C, 28.10 (28.51); H, 5.30 (5.11); Al, 15.78 (15.94); Cl, 41.46 (40.97)%. M_w just after synthesis (cryoscopically in benzene): 366 ($n = 2.14$), 7 days later 515 ($n = 3.01$), Calc. 171.00.

$^1\text{H-NMR}$ (C_6H_6): dimer δ 0.62 (d, $^3J = 6.6$ Hz, 6H; $\text{OCH}_2\text{CH}(\text{CH}_3)_2$), 1.62 (m, $^3J = 6.6$ Hz, 1H, $\text{OCH}_2\text{CH}(\text{CH}_3)_2$), 3.41 (d, $^3J = 6.9$ Hz, 2H, $\text{OCH}_2\text{CH}(\text{CH}_3)_2$). $^{27}\text{Al-NMR}$ (C_6H_6): δ 94 ($\omega_{1/2} = 844$ Hz).

$^1\text{H-NMR}$ (C_6H_6): trimer δ 0.73 (d, $^3J = 6.6$ Hz, 6H, $\text{OCH}_2\text{CH}(\text{CH}_3)_2$), 2.16 (m, $^3J = 6.6$ Hz, 1H, $\text{OCH}_2\text{CH}(\text{CH}_3)_2$), 4.18 (d, $^3J = 7.6$ Hz, 2H, $\text{OCH}_2\text{CH}(\text{CH}_3)_2$). $^{13}\text{C-NMR}$ (C_6D_6): trimer δ 18.2 ($\text{OCH}_2\text{CH}(\text{CH}_3)_2$), 30.33 ($\text{OCH}_2\text{CH}(\text{CH}_3)_2$), 78.34 ($\text{OCH}_2\text{CH}(\text{CH}_3)_2$). $^{27}\text{Al-NMR}$ (C_6H_6): δ 94 ($\omega_{1/2} = 720$ Hz).

Seven days later in ^1H - and $^{27}\text{Al-NMR}$ spectra signals of $[\text{Cl}_2\text{Al}(\mu\text{-O}^i\text{Bu})_2]_2\text{AlCl}$ (**4b**) appeared. $^1\text{H-NMR}$ (C_6D_6): δ 0.74 (d, $^3J = 6.6$ Hz, 6H, $\text{OCH}_2\text{CH}(\text{CH}_3)_2$), 1.95 (m, $^3J = 6.6$ Hz, 1H, $\text{OCH}_2\text{CH}(\text{CH}_3)_2$), 3.70 (d, $^3J = 7.2$ Hz, 2H, $\text{OCH}_2\text{CH}(\text{CH}_3)_2$). $^{27}\text{Al-NMR}$ (C_6D_6): δ 94 ($\omega_{1/2} = 720$ Hz), 45 ($\omega_{1/2} = 300$ Hz).

4.6. Reaction of MeAlCl_2 with $^s\text{BuOH}$

$^s\text{BuOH}$ (1.62 g, 21.8 mmol) in 50 ml of hexane was added to cooled solution to 0°C of MeAlCl_2 (2.46, 21.8 mmol) in 80 ml of hexane. The reaction mixture was allowed to warm up to ambient temperature and stirred for 24 h. A solvent was removed in vacuo giving white solid (3.59 g) of $^s\text{BuOAlCl}_2$ (**5a**), yield 96%.

Anal. for $\text{C}_4\text{H}_9\text{AlCl}_2\text{O}$, Calc. (Found): C, 28.10 (28.33); H, 5.30 (5.14); Al, 15.78 (16.01); Cl, 41.46 (40.99)%. M_w (cryoscopically in benzene): 340, Calc. 171.00. $^1\text{H-NMR}$ (C_6D_6): δ 0.56 (t, $^3J = 7.4$ Hz, 3H, $\text{OCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$), 1.09 (d, $^3J = 6.3$ Hz, 3H, $\text{OCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$), 1.31 (m, $^3J = 7.4$ Hz, 1H, $\text{OCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$), 1.59 (m, $^3J = 7.4$ Hz, 1H, $\text{OCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$), 3.87 (m, $^3J = 6.3$ Hz, 1H, $\text{OCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$). $^{13}\text{C-NMR}$ (C_6D_6): δ 9.50 ($\text{OCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$), 21.60 ($\text{OCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$), 31.64 ($\text{OCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$), 79.23 ($\text{OCH}(\text{CH}_3)_2\text{CH}_3$). $^{27}\text{Al-NMR}$ (C_6D_6): δ 93 ($\omega_{1/2} = 507$ Hz).

4.7. Reactions of MeAlCl₂ with ^tBuOH

To the cooled to 0 °C solution of MeAlCl₂ (5.82 g, 51.5 mmol) in 100 ml of hexane ^tBuOH (3.81 g, 51.5 mmol) in 50 ml of hexane was added. The reaction mixture was allowed to warm up to r.t. and stirred for 24 h. The solution was decanted and solvent removed in vacuo giving light-yellow solid (3.96g) of ^tBuOAlCl₂ (**6a**), yield 45%.

Anal. for C₄H₉AlCl₂O, Calc. (Found): C, 28.10 (28.41); H, 5.30 (5.50); Al, 15.78 (15.55); Cl, 41.46 (41.10)%. ¹H-NMR (C₆D₆): δ 1.25 (C(CH₃)₃). ¹³C-NMR (C₆D₆): δ 30.78 (C(CH₃)), 84.25 (C(CH₃)₃). ²⁷Al-NMR (C₆D₆): δ 90 (ω_{1/2} = 150 Hz).

4.8. Reactions of MeAlCl₂ with ^tBuCH₂OH

To solution of MeAlCl₂ (2.26 g, 20.0 mmol) in 60 ml of hexane cooled to 0 °C ^tBuCH₂OH (1.76 g, 20.0 mmol) was added. The reaction mixture was allowed to warm up to r.t. and stirred for 24 h. The solvent was evaporated to give white solid of ^tBuCH₂OAlCl₂ (**7a**) with 94% yield (3.47 g).

Anal. for C₅H₁₁AlCl₂O, Calc. (Found): C, 32.46 (32.41); H, 5.99 (6.09); Al, 14.58 (14.41); Cl, 38.32 (37.61)%. *M_w* (cryoscopically in benzene): 381, Calc. 185.03.

¹H-NMR (C₆D₆): δ 0.70 (s, 9H, (OCH₂C(CH₃)₃), 3.60 (s, 2H, OCH₂C(CH₃)₃). ¹³C-NMR (C₆D₆): δ 25.68 (OCH₂C(CH₃)₃), 32.03 (OCH₂C(CH₃)₃), 79.01 (OCH₂C(CH₃)₃). ²⁷Al-NMR (C₆D₆): 93 (ω_{1/2} = 1220 Hz).

After 10 days in NMR spectra signal of [Cl₂Al(μ-OCH₂Bu^t)₂AlCl (**7b**) appeared.

¹H-NMR (C₆D₆): δ 0.96 (s, 9H OCH₂C(CH₃)₃), 3.87 (s, 2H, OCH₂C(CH₃)₃). ¹³C-NMR (C₆D₆): δ 27.11 (OCH₂C(CH₃)₃), 32.90 (OCH₂C(CH₃)₃), 78.20 (OCH₂C(CH₃)₃). ²⁷Al-NMR (C₆D₆): δ 93 (ω_{1/2} = 1220 Hz), 43 (ω_{1/2} = 300 Hz).

4.9. X-ray structure determination

Single crystals of **3c** and **7a** suitable for X-ray diffraction studies were placed in a thin walled capillary tubes (Lindemann glass) in an inert atmosphere, plugged with grease and flame sealed. X-ray diffraction data for compound **3c** was collected at r.t. on a Siemens P3 diffractometer and for compound **7a** on a Kuma KM4 diffractometer. The intensities were recorded in the ω–2θ scan mode and corrected for Lorentz-polarization effects. Crystal data, data collection and refinement parameters are given in Table 4. The structures were solved by direct methods using the SHELXS-97 program [13]. Full-matrix least-squares refinement method against *F*² values was carried out by using the SHELXL-97 [14]. Neutral-atom complex scattering factors were

Table 4

Crystal data, data collection, structure solution, and refinement parameters for compounds **3c** and **7a**.

	3c	7a
Empirical formula	C ₂₄ H ₅₄ Al ₄ Cl ₆ O ₆	C ₁₀ H ₂₂ Al ₂ Cl ₄ O ₂
Formula weight	759.29	370.04
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group, number	<i>C</i> 2/ <i>c</i> , 15	<i>P</i> 2 ₁ / <i>c</i> , 14
<i>a</i> (Å)	13.582(5)	7.183(5)
<i>b</i> (Å)	13.811(4)	6.551(6)
<i>c</i> (Å)	21.578(8)	18.783(16)
β (°)	90.69(3)	93.49(7)
<i>V</i> (Å ³)	4047(2)	882.2(13)
<i>Z</i>	4	2
<i>D</i> _{calc} (g cm ⁻³)	1.246	1.393
Absorption coefficient (mm ⁻¹)	0.542	0.763
<i>F</i> (000)	1600	384
Crystal size (mm)	0.80 × 0.40 × 0.20	0.68 × 0.36 × 0.12
2θ Range (°)	2.1–25.0	2.2–25.0
Radiation	Mo–K _α (λ = 0.71073 Å)	
Measured reflections	3739	1531
Unique reflections	3578 (<i>R</i> _{int} = 0.019)	1494 (<i>R</i> _{int} = 0.066)
Data/parameters/restraints	3578/204/26	1494/96/0
Reflections with <i>I</i> > 2σ(<i>I</i>)	2299	1155
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0498, 0.1330	0.0636, 0.1803
<i>R</i> ₁ , <i>wR</i> ₂ (all data) ^a	0.0826, 0.1501	0.0796, 0.1991
Goodness-of-fit (<i>S</i>) ^b	1.051	1.081
Weights <i>a</i> , <i>b</i> ^c	0.080, 1.17	0.156, 0.068
Largest difference peak and hole (e Å ⁻³)	+0.35 and –0.28	+0.67 and –0.55

^a *R*₁ = Σ ||*F*_o| – |*F*_c|| / Σ |*F*_c|, *wR*₂ = {Σ [*w*(*F*_o² – *F*_c²)] / Σ [*w*(*F*_o²)]^{1/2}.

^b Gof = *S* = {Σ [*w*(*F*_o² – *F*_c²)] / (n – *p*)^{1/2} where *n* is the number of reflections and *p* is the total number of parameters refined.

^c *w*⁻¹ = σ²(*F*_o²) + (*a*·*P*)² + *b*·*P*; where *P* = (*F*_o² + 2*F*_c²)/3.

employed [15]. As resulted from the refinement process of **3c**, the terminal ethyl group [–C(11)–C(12)] in one of the *n*-butoxy ligand was disordered over two sites. The disorder was modeled in terms of two sets of atoms with similarity restraints concerning chemically equivalent C–C distances. The refined final occupancy factor for the major conformer was equal to 0.744(9). In both structures, all non-hydrogen atoms were refined with anisotropic displacement parameters, including the partial occupancy atoms of the disordered part of the molecule **3c**. Hydrogen atoms were introduced at geometrically idealized coordinates and allowed to ride on their parent C atoms. ORTEP drawings were made using ORTEP3 for Windows [16].

5. Supplementary material

Listings of crystal and refinement data, atomic coordinates, bond distances and angles, thermal parameters are available from Cambridge Crystallographic

Data Centre, CCDC nos. 208950 and 208951 for compounds **3c** and **7a**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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References

- [1] (a) H. Schmidbaur, H. Hussek, F. Schindler, *Chem. Ber.* 97 (1964) 255;
 (b) H. Schmidbaur, *Angew. Chem.* 77 (1965) 169;
 (c) W.G. Joung, W.H. Hartung, F.S. Krossley, *J. Am. Chem. Soc.* 58 (1936) 100;
 (d) V. Sharman, M. Simard, J.D. Wuest, *Inorg. Chem.* 30 (1991) 579;
 (e) M.D. Healy, J.W. Ziller, A.R. Barron, *Organometallics* 11 (1992) 3041;
 (f) S. Schulz, H.W. Roesky, M. Noltemeyer, H.G. Schmidt, *J. Chem. Soc., Dalton Trans.* (1995) 177;
 (g) A. Pietrzykowski, T. Skrok, S. Pasynkiewicz, M. Brzoska-Mizgalski, J. Zachara, R. Anulewicz-Ostrowska, K. Suwińska, L.B. Jerzykiewicz, *Inorg. Chim. Acta* 334 (2002) 385;
 (h) W. Ziemkowska, S. Pasynkiewicz, R. Anulewicz-Ostrowska, M. Fraczak, *Main Group Met. Chem.* 23 (2000) 169;
 (i) P. Sobota, P.J. Utko, A.I. Brusilovets, L.B. Jerzykiewicz, *J. Organomet. Chem.* 553 (2000) 379.
- [2] T. Gelbrich, U. Dümchen, P. Jörchel, *Acta Crystallogr C* 55 (1999) 856.
- [3] K.B. Starowieyski, S. Pasynkiewicz, M. Skowrońska, *J. Organomet. Chem.* 31 (1971) 149.
- [4] S. Pasynkiewicz, K.B. Starowieyski, M. Skowrońska-Ptasińska, *J. Organomet. Chem.* 52 (1973) 269.
- [5] (a) M. Skowrońska-Ptasińska, K.B. Starowieyski, S. Pasynkiewicz, *J. Organomet. Chem.* 160 (1978) 403;
 (b) J.A. Jegier, D.A. Atwood, *Bull. Soc. Chim. Fr.* 133 (1996) 965.
- [6] W. Kosińska, K. Żardecka, A. Kunicki, M. Boleslawski, S. Pasynkiewicz, *J. Organomet. Chem.* 153 (1978) 281.
- [7] A.R. Kunicki, A. Orechin, J. Zachara, *Main Group Met. Chem.* 21 (1998) 365.
- [8] D.A. Atwood, J.A. Jegier, S. Liu, D. Rutherford, P. Wei, R.C. Tucker, *Organometallics* 18 (1999) 976.
- [9] M.-A. Munoz-Hernandez, P. Wei, S. Liu, D.A. Atwood, *Coord. Chem. Rev.* 210 (2000) 1 (and references therein).
- [10] B. Neumüller, *Chem. Soc. Rev.* 32 (2003) 30 (and references therein).
- [11] A.I. Yanovsky, V.A. Kozunov, N.Y. Turova, N.G. Furmanova, Y.T. Struchkov, *Dokl. Akad. Nauk SSSR* 244 (1979) 119.
- [12] J.H. Rogers, A.W. Apblett, W.M. Cleaver, A.N. Tyler, A.R. Barron, *J. Chem. Soc., Dalton Trans.* (1992) 3179.
- [13] G.M. Sheldrick, *Acta Crystallogr., Sect. A* 46 (1990) 467.
- [14] G.M. Sheldrick, *SHELXL-97*, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.
- [15] A.J.C. Wilson (Ed.), *International Tables for Crystallography*, vol. C, Kluwer Academic Publisher, Dordrecht, 1992.
- [16] L.J. Farrugia, *ORTEP-3*, *J. Appl. Crystallogr.* 30 (1997) 565.