

Syntheses, properties and crystal structures of ionic $[Al_2(\mu, \eta^2\text{-thffo})_2(\text{EtOH})_4Cl_2]Cl_2$, $[Al_3(\mu, \eta^2\text{-thffo})_4Cl_4][AlEtCl_3]$ and tetranuclear $[Al_4(\mu, \eta^2\text{-thffo})_4(\mu\text{-OEt})_2Cl_6]$ (thffo = $OCH_2CH(CH_2)_3O$) compounds¹

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Abstract

The bis- μ -(2-tetrahydrofuryloxo-*O, O'*)tetraethanoldichlorodialuminium(III) dichlorate $[Al_2(\mu, \eta^2\text{-thffo})_2(\text{EtOH})_4Cl_2]Cl_2$ (**1**), tetra- μ -(2-tetrahydrofuryloxo-*O, O'*)tetrachlorotrialuminium(III) trichloroethoxyaluminate(III) dichloromethane(1/1), $[Al_3(\mu, \eta^2\text{-thffo})_4Cl_4][AlEtCl_3] \cdot CH_2Cl_2$ (**2**) salts are synthesized in direct reaction of $AlCl_3(\text{THF})_2$ with Nathffo and $AlEtCl_2$ with thffo in THF or benzene, respectively. The addition of $AlCl_3(\text{THF})_2$ to the $Mg(\text{thffo})_2$ results in the formation of tetrakis- μ -(2-tetrahydrofuryloxo-*O, O'*)di- μ -ethoxy-hexachlorotetraaluminium(III) tetrahydrofuran (1/1) $[Al_4(\mu, \eta^2\text{-thffo})_4(\mu\text{-OEt})_2Cl_6] \cdot \text{THF}$ (**3**) species. Compound **1** crystallized in the space group $P2_1/n$, with $a = 8.615(2)$, $b = 16.445(3)$, $c = 10.052(2)$ Å and $\beta = 90.53(3)^\circ$. Compound **2** belongs to the $C2/c$ space group with $a = 32.046(5)$, $b = 14.255(3)$, $c = 15.443(3)$ Å and $\beta = 123.85(3)^\circ$. Crystals of **3** are triclinic, space group $P\bar{1}$, $a = 10.365(2)$, $b = 10.854(2)$, $c = 11.880(3)$ Å and $\alpha = 70.40(2)$, $\beta = 65.19(2)$, $\gamma = 80.18(2)^\circ$. The centrosymmetric cation of the salt **1**, in the crystalline state is a dimer composed of two octahedra related by a crystallographic inversion centre and sharing an edge. The $[Al_3(\mu, \eta^2\text{-thffo})_4Cl_4]^+$ cation of the species **2** is a centrosymmetrical with an aluminium–oxygen framework, which consists of the central octahedral atom linked to two five-coordinate aluminium sites by μ -alkoxy bridges. The structure of **3** includes two five-coordinate and two six-coordinate Al atoms linked by μ -alkoxy bridges to form tetranuclear chains with a symmetry center. © 1998 Elsevier Science S.A.

Keywords: Aluminium(III); Alumoxanes; Alkoxides; Crystal structure; Chelate

1. Introduction

The controlled hydrolysis of $AlMe_3$ yields oligomeric compounds of the general formula $(CH_3AlO)_n$ called alumoxanes. Methylalumoxane is a poorly characterized species which consists of linear, cyclic and cross-linked compounds, probably containing predominately four-coordinate Al centres [1–3]. These species are of tremendous importance for Ziegler/Natta and Kaminsky olefin polymerization catalysts [1–6]. Aluminium alkoxides are generally not included in the group of alumoxanes because they do not contain at least one

bridging oxo group between two aluminium centers [7]. However, their properties should be of importance for solving structural problems and providing information upon degrees of association of aluminium–oxygen centers. This work is a part of our systematic study on complexes with O-donor functions in bidentate alkoxy ligand such as 2-tetrahydrofurfuryl alcohol ($O(CH_2)_3CHCH_2OH = \text{thffoH}$). Previously, the structures and properties of $[Mg_4(\mu_3, \eta^2\text{-thffo})_2(\mu, \eta^2\text{-thffo})_4Cl_2]$ and $[V_2Mg_2(\mu_3, \eta^2\text{-thffo})_2(\mu, \eta^2\text{-thffo})_4Cl_4]$ procatalysts for the alkene polymerization process, have been reported [8,9].

Here we describe syntheses leading to the $[Al_2(\mu, \eta^2\text{-thffo})_2(\text{EtOH})_4Cl_2]Cl_2$ (**1**), $[Al_3(\mu, \eta^2\text{-thffo})_4Cl_4][AlEtCl_3] \cdot CH_2Cl_2$ (**2**) salts and tetranuclear $[Al_4(\mu, \eta^2\text{-thffo})_4(\mu\text{-OEt})_2Cl_6] \cdot \text{THF}$ (**3**) compound

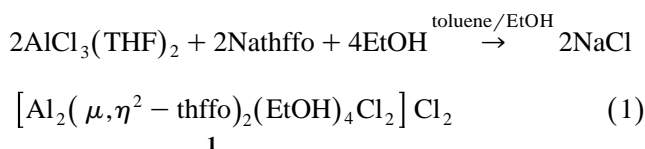
^{*} Corresponding author.

¹ Dedicated to Professor P. Royo on the occasion of his 60th birthday.

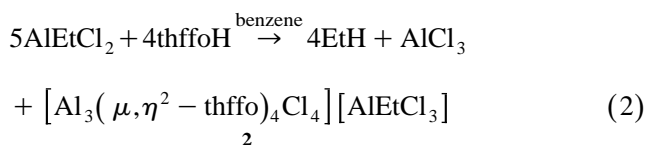
(THF = tetrahydrofuran), and report the details of their crystal structures.

2. Result and discussion

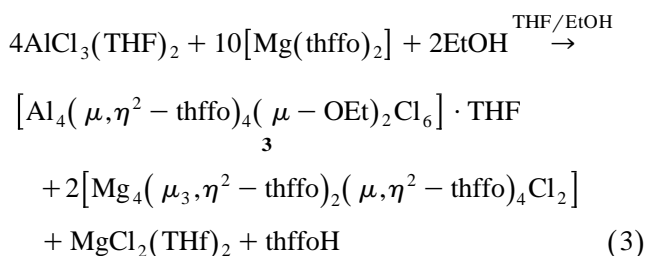
As stated in Section 1, we were interested in determination of the degree of association of aluminium–oxygen centres formed by aluminium alkoxides. We found that the reaction of $\text{AlCl}_3(\text{THF})_2$ with Nathffo in a 1:1 molar ratio in THF and addition of toluene/ethanol (2:1) solution gives colourless air-sensitive needle-shaped crystals of $[\text{Al}_2(\mu, \eta^2\text{-thffo})_2(\text{EtOH})_4\text{Cl}_2]\text{Cl}_2$ **1**, which can be stored under N_2 . The crystalline species has good solubility in THF and ethanol, but unstable, undergoing decomposition, on exposure either to air or moisture to give unidentified products:



The salt **2** was obtained by the straightforward reaction of AlEtCl_2 with tetrahydrofurfuryl alcohol in benzene.



The alkoxo magnesium species is used as a suitable component for preparation of the modern high-activity polyalkene catalysts [10]. Therefore, the interaction of $[\text{Mg}(\text{thffo})_2]$ with aluminium catalyst component was also the subject of our studies. The addition of $\text{AlCl}_3(\text{THF})_2$ to the $[\text{Mg}(\text{thffo})_2]$ at 1:4 molar ratio in THF/EtOH (2:1) results in the formation of the colourless $[\text{Al}_4(\mu, \eta^2\text{-thffo})_4(\mu\text{-OEt})_2\text{Cl}_6] \cdot \text{THF}$ **3** and $[\text{Mg}_4(\mu_3, \eta^2\text{-thffo})_2(\mu, \eta^2\text{-thffo})_4\text{Cl}_2]$ compound [8].



In order to confirm the nature of the compound $[\text{Al}_4(\mu, \eta^2\text{-thffo})_4(\mu\text{-OEt})_2\text{Cl}_6] \cdot \text{THF}$ the mass spectrum was recorded. The liquid matrix ion mass spectrum of **3** shows peak due to the tetranuclear species at $(m+1)/z = 814$. This formulation was confirmed by an X-ray structural study. Unfortunately, reactions of AlEt_2Cl , AlEt_3 and AlMe_3 with thffoH and $[\text{Mg}(\text{thffo})_2]$ lead to untractable oily products.

2.1. X-ray crystal structure determination of **1**–**3**

The crystal structure of **1** consists of $[\text{Al}_2(\mu, \eta^2\text{-thffo})_2(\text{EtOH})_4\text{Cl}_2]^{2+}$ cations and Cl^- anions in a 1:2 ratio. The geometry of the $[\text{Al}_2(\mu, \eta^2\text{-thffo})_2(\text{EtOH})_4\text{Cl}_2]^{2+}$ cation in **1** is presented in Fig. 1 and selected bond distances and angles are given in Table 1. The centrosymmetric cation of the salt **1**, in the crystalline state is a dimer composed of two octahedra related by a crystallographic inversion centre and sharing an edge. Each aluminium atom is octahedrally coordinated by μ -alkoxo O(11) and O(11') atoms and the ether oxygen atom O(10) of thffo ligands as well as two O(21) and O(31) oxygen atoms of coordinated ethanol molecules and one chlorine atom. The coordinated ethanol molecules are in *trans* orientation. The ether O(10) atom of the tetrahydrofurfuryl ring is situated *trans* to the bridging μ -alkoxo O(11) oxygen atom whereas Cl(1) chlorine atom is *cis* oriented to the O(11') oxygen atom. The Al–Cl(1) bond length of 2.213(2) Å is similar to Al–Cl distances in $[\text{AlCl}(\text{CH}_3\text{CN})_5]^{2+}$ and in $[\text{AlCl}_2(\text{THF})_4]^{2+}$ cations [11,12]. The Al–O_(alkoxo) distances (see Table 1) are close to the corresponding values in many aluminium complexes, e.g., in $[\text{Al}(\text{O}-i\text{Pr})(3,5\text{-heptanedione})_2]_2$ [13] and in $[\text{Al}_3(\mu\text{-O})(\mu\text{-OEt})_2(\text{py})_3\text{Cl}_5]$ [14]. The Al–O_(eter) bond length of 1.928(2) Å is typical for six-coordinated aluminium compounds [11]. The non-coordinated Cl^- anions contributes to packing by forming strong hydrogen bonds involving hydroxyl group of the ethanol molecules: O(21)–H(21) ... Cl(2)ⁱ [O(21) ... Cl(2)⁽ⁱ⁾ 2.957(3) Å, $\angle\text{O}(21)\text{--H}(21)\text{...Cl}(2)^{(i)}$ 166(4)°] and

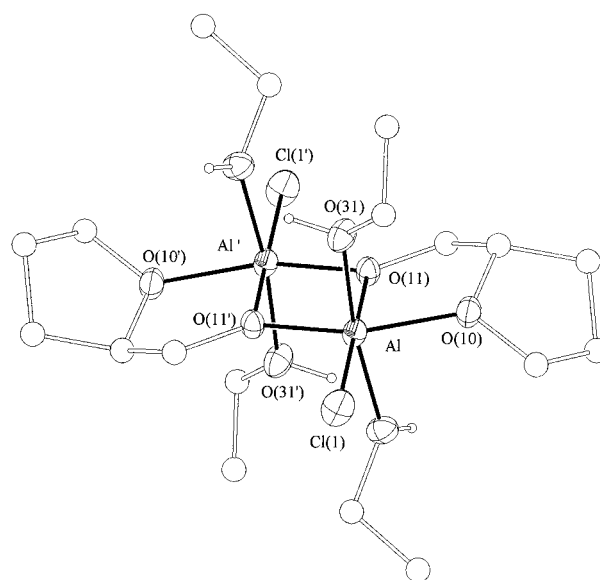


Fig. 1. The molecular structure of **1** with atom numbering scheme. The displacement ellipsoids are drawn at the 30% probability level. The C bonded H atoms are excluded for clarity. The C and H atoms are represented by circles of an arbitrary radii.

O(31)–H(31) ... Cl(2)ⁱⁱ [O(31) ... Cl(2)⁽ⁱⁱ⁾ 3.012(3) Å, ∠O(31)–H(31) ... Cl(2)⁽ⁱⁱ⁾ 175(4)°] where (i) = x – 0.5, y – 1.5, 0.5 – z, and (ii) = 0.5 – x, 1.5 – y, 0.5 + x.

The structure of the [Al₃(μ, η²-thffo)₄Cl₄]⁺ cation is shown in Fig. 2 and selected geometrical parameters are listed in Table 1. The crystals of **2** consists of the

Table 1
Selected bond distances (Å) and angles (deg) for **1**, **2** and **3**

Complex 1							
Al Cl(1)			2.213(2)	Al O(21)			1.933(2)
Al O(11')			1.839(2)	Al O(31)			1.953(2)
Al O(11)			1.886(2)	Al Al'			2.930(2)
Al O(10)			1.928(2)				
O(11)	Al	Cl(1)	178.7(1)	O(11')	Al	Cl(1)	103.0(1)
O(11)	Al	O(10)	81.4(1)	O(21)	Al	Cl(1)	89.1(1)
O(11)	Al	O(21)	89.9(1)	O(21)	Al	O(31)	172.0(1)
O(11)	Al	O(31)	91.5(1)	O(31)	Al	Cl(1)	89.7(1)
O(11')	Al	O(11)	76.3(1)	O(10)	Al	Cl(1)	99.4(1)
O(11')	Al	O(10)	157.5(1)	O(10)	Al	O(21)	87.3(1)
O(11')	Al	O(21)	95.5(1)	O(10)	Al	O(31)	85.1(1)
O(11')	Al	O(31)	92.4(1)				
Complex 2							
Al(1) O(11)			1.815(7)	Al(2) O(21')			1.821(6)
Al(1) O(21')			1.842(7)	Al(2) O(21)			1.821(6)
Al(1) O(10)			1.959(8)	Al(2) O(11')			1.881(7)
Al(1) Cl(2)			2.122(5)	Al(2) O(11)			1.881(7)
Al(1) Cl(1)			2.132(4)	Al(2) O(20)			1.929(8)
Al(1) Al(2)			2.902(4)	Al(2) O(20')			1.929(8)
Al(2) Al(1')			2.902(4)				
O(11)	Al(1)	Cl(2)	126.8(3)	O(21)	Al(2)	O(11)	104.2(3)
O(21')	Al(1)	Cl(2)	98.9(3)	O(11')	Al(2)	O(11)	96.9(5)
O(10)	Al(1)	Cl(2)	94.0(3)	O(21')	Al(2)	O(20)	99.0(3)
O(11)	Al(1)	Cl(1)	121.0(3)	O(21)	Al(2)	O(20)	81.6(3)
O(21')	Al(1)	Cl(1)	100.3(3)	O(11')	Al(2)	O(20)	156.5(3)
O(10)	Al(1)	Cl(1)	94.6(3)	O(11)	Al(2)	O(20)	92.3(3)
Cl(2)	Al(1)	Cl(1)	112.0(2)	O(21')	Al(2)	O(20')	81.6(3)
O(11)	Al(1)	O(21')	76.4(3)	O(21)	Al(2)	O(20')	99.0(3)
O(11)	Al(1)	O(10)	78.6(3)	O(11')	Al(2)	O(20')	92.3(3)
O(21')	Al(1)	O(10)	154.9(4)	O(11)	Al(2)	O(20')	156.5(3)
O(21')	Al(2)	O(21)	179.2(5)	O(20)	Al(2)	O(20')	87.7(5)
O(21')	Al(2)	O(11')	104.2(3)	O(21')	Al(2)	O(11)	75.3(3)
O(21)	Al(2)	O(11')	75.3(3)				
Complex 3							
Al(1) Cl(1)			2.157(2)	Al(1) Cl(2)			2.160(2)
Al(2) Cl(3)			2.279(2)	Al(1) O(10)			1.979(3)
Al(1) O(11)			1.804(2)	Al(2) O(11)			1.914(2)
Al(1) O(31)			1.841(2)	Al(2) O(31)			1.863(2)
Al(2) O(20)			2.018(2)	Al(2) O(21')			1.868(2)
Al(2) O(21)			1.871(2)	Al(2) Al(2')			2.919(2)
Al(1) Al(2)			2.918(2)				
O(11)	Al(1)	Cl(1)	117.9(1)	O(11)	Al(1)	Cl(2)	130.3(1)
O(31)	Al(1)	Cl(1)	100.5(1)	O(31)	Al(1)	Cl(2)	99.6(1)
O(10)	Al(1)	Cl(1)	94.3(1)	O(10)	Al(1)	Cl(2)	90.7(1)
O(11)	Al(1)	O(31)	77.9(1)	O(11)	Al(1)	O(10)	80.0(1)
O(31)	Al(1)	O(10)	157.3(1)	Cl(1)	Al(1)	Cl(2)	111.4(1)
O(31)	Al(2)	O(21')	102.5(1)	O(31)	Al(2)	O(11)	74.7(1)
O(31)	Al(2)	O(21)	169.5(1)	O(21')	Al(2)	O(11)	95.2(1)
O(21')	Al(2)	O(21)	77.3(1)	O(21')	Al(2)	O(20)	157.8(1)
O(21)	Al(2)	O(11)	94.8(1)	O(21)	Al(2)	O(20)	80.5(1)
O(31)	Al(2)	O(20)	99.2(1)	O(31)	Al(2)	Cl(3)	93.9(1)
O(11)	Al(2)	O(20)	85.8(1)	O(11)	Al(2)	Cl(3)	165.5(1)
O(21')	Al(2)	Cl(3)	96.1(1)	O(20)	Al(2)	Cl(3)	87.2(1)
O(21)	Al(2)	Cl(3)	96.5(1)				

Primed atoms are related to unprimed by: –x, –y + 1, –z + 1 for **1**; –x, y, 3/2 – z for **2**; 1 – x, –y + 1, –z + 2 for **3**.

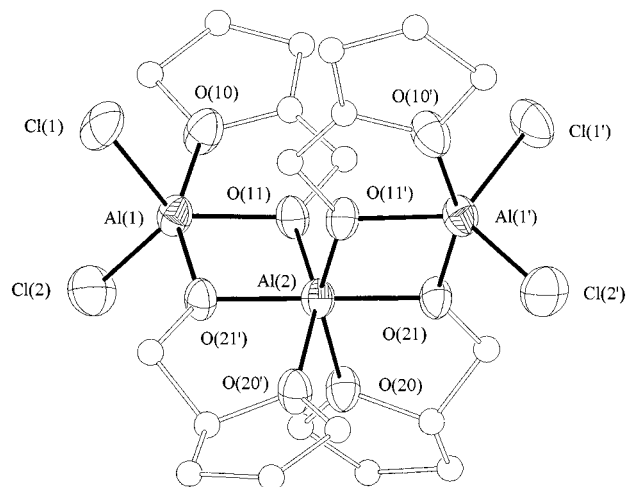


Fig. 2. The molecular structure of **2** with atom numbering scheme. The displacement ellipsoids are drawn at the 30% probability level. The C bonded H atoms are excluded for clarity. The C atoms are represented by circles of an arbitrary radii.

$[\text{Al}_3(\mu, \eta^2\text{-thffo})_4\text{Cl}_4]^+$ cations and $[\text{AlEtCl}_3]^-$ anions in 1:1 ratio. The cation is a centrosymmetric trinuclear complex with an aluminium–oxygen framework, which consists of the central octahedral aluminium Al(2) atom linked to two five-coordinate Al(1) and Al(1') aluminium sites by μ -alkoxo bridges. The octahedral coordination sphere of central Al(2) is filled up by two ether oxygen atoms of the thffo ligand which are in a *cis* orientation. The coordination of the terminal Al(1) and Al(1') atoms are completed by two chlorine and one

ether oxygen atom of the tetrahydrofurfuryl ring. In the cation of **2**, the Al(μ -O) $_2$ Al bridges are asymmetric [Al(2)–O(11) 1.881(7), Al(1)–O(21') 1.821(6) Å and Al(1)–O(21') 1.861(7), Al(2)–O(2) 1.818(6) Å]. This structure feature is characteristic for oxygen bridges in aluminium compounds such as $[\text{Al}(\text{O}-i\text{Pr})(3,5\text{-heptanedione})_2]_2$ [13] and $[\text{Al}_3(\mu\text{-O})(\mu\text{-OEt})_2(\text{py})_3\text{Cl}_5]$ [14]. The Al(1)–Cl(1,2) distances of 2.115(5) and 2.134(4) Å, are comparable to those found in five-coordinate aluminium atom $[\text{Al}_2\text{Cl}_2(\text{acac})_3]$ [15]. The Al(1)–O(10) and Al(2)–O(20) bond distances of 1.959(8) and 1.929(8) Å, respectively, are similar to the corresponding Al–O bond lengths in $[(\text{AlEt})_2\text{diazacrown-6}]^{2+}$ which are in range 1.950(5)–1.959(5) Å [16].

Molecule of **3** is shown in Fig. 3 and some important molecular geometry parameters are given in Table 1. The structure of **3** includes two five-coordinate Al and two six-coordinate Al atoms linked by μ -alkoxo bridges to form tetranuclear chains with a symmetry center. The ether oxygen atom O(20) of the chelating ligand and one chlorine Cl(3) atom complete the octahedral coordination sphere of internal aluminium Al(2) atoms and are in a *cis* orientation. On the periphery of the cation, Al(1) atoms are coordinated additionally by two chlorine Cl(1,2) atoms and one ether oxygen O(10) atom of the tetrahydrofurfuryl ring. The Al(1) \cdots Al(2) and Al(2) \cdots Al(2') distances and Al–O bond lengths are close to those found in **1** and **2** (see Table 1). The Al–Al–Al–Al backbone is not linear as evidenced by the angle of Al(1)–Al(2)–Al(2') of 124.5(9)°.

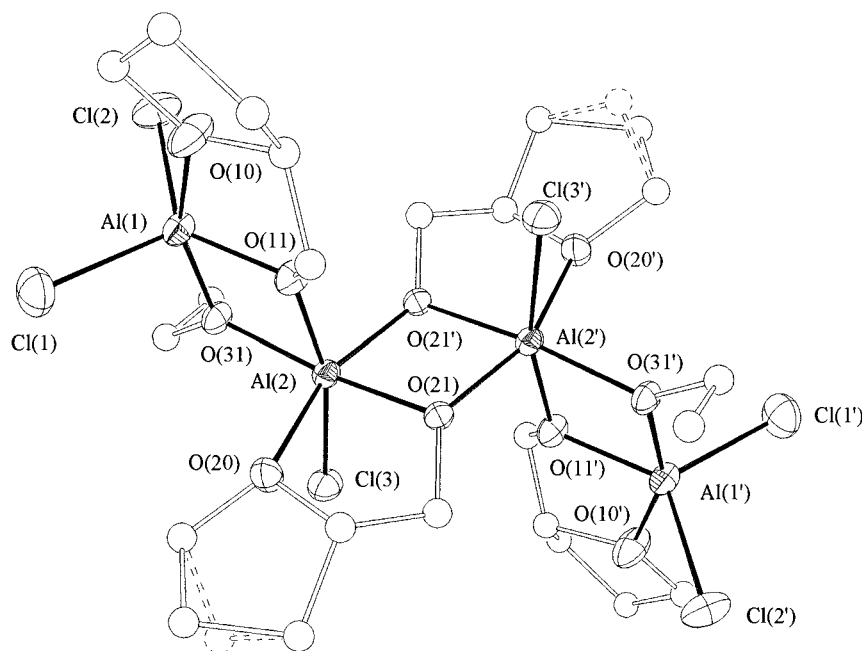


Fig. 3. The molecular structure of **3** with atom numbering scheme. The displacement ellipsoids are drawn at the 30% probability level. The C bonded H atoms are excluded for clarity. The C atoms are represented by circles of an arbitrary radii.

3. Conclusions

During reaction (1) in toluene probably $[Al_2(\mu, \eta^2\text{-thffo})_2Cl_4]$ species (similar to $[Al_2(\mu, \eta^2\text{-OCH}_2\text{CH}_2\text{OCH}_3)_2(\text{CH}_3)_4]$ [17]) is formed which could be easily transformed into **1** in the presence of ethanol. The tendency of aluminium alkoxide compounds to maximize their coordination number by associating ligands is well-documented [18–23].

The corresponding reaction with $AlEtCl_2$ in benzene (Eq. (2)) led to the formation of $[Al_3(\mu, \eta^2\text{-thffo})_4Cl_4][AlEtCl_3]$ salt because dichloroethylaluminium behaves as a halide-abstracting reagent. It follows that the $[AlEtCl_3]^-$ anion gives the least soluble salt **2** which precipitate preferentially so driving the equilibrium to their formation. The $[Al_3(\mu, \eta^2\text{-thffo})_4Cl_4]^+$ cation displays a trinuclear nature with six-coordinate Al(III) centre linked by double μ -alkoxo bridges with two five-coordinate aluminium atoms.

Two different tetranuclear compounds $[Al_4(\mu, \eta^2\text{-thffo})_4(\mu\text{-OEt})_2Cl_6] \cdot \text{THF}$ and $[Mg_4(\mu_3, \eta^2\text{-thffo})_2(\mu, \eta^2\text{-thffo})_4Cl_2]^4$ are produced from the reaction of $AlCl_3$ and $[Mg(\text{thffo})_2]$. The compound $[Al_4(\mu, \eta^2\text{-thffo})_4(\mu\text{-OEt})_2Cl_6]$ displays a tetranuclear nature with two internal six-coordinated and two peripheral five-coordinated aluminium atoms. In contrast to **1** the compound **3** did not undergo ionization. This fact can be explained only by further studies.

4. Experimental details

4.1. General

Syntheses were carried out under dry dinitrogen following standard Schlenk techniques. All solvents, were distilled under dinitrogen from the appropriate drying agents prior to use. The complexes $AlCl_3(\text{THF})_2$ [11] and $[MgCl_2(\text{THF})_2]$ [24] were prepared according to literature methods. Infrared spectra were recorded on a Perkin-Elmer 180 instrument in Nujol mulls. Mass spectra were recorded on an Finnigan MaT TSQ 700 spectrometer.

4.2. Synthesis of $[Al_2(\mu, \eta^2\text{-thffo})_2(\text{EtOH})_4Cl_2]Cl_2$ (**1**)

A solution of $AlCl_3(\text{THF})_2$ (5.55 g; 20 mmol) and $Nathffo$ (2.48 g; 20 mmol) in 80 cm^3 THF was stirred at room temperature for 1 h. Then the volume of the filtrate was reduced in vacuo to ca. 50 cm^3 and a mixture of 40 cm^3 toluene and 20 cm^3 of ethanol was added and left to crystallize at 273 K. After two weeks, the colourless crystals of compound **1** were collected, washed with *n*-hexane ($3 \times 5\text{ cm}^3$) and dried in vacuo. Yield: 2.16 g (74%). Anal. Calcd. for $C_{18}H_{42}Cl_4O_8Al_2$: Cl, 37.13; Al, 9.27. Anal. Found: Cl, 37.20; Al, 9.30. IR

(Nujol, cm^{-3}): 218 (w), 232 (w), 265 (w), 315 (m), 349 (s), 372 (vs), 398 (s), 480 (s), 530 (s, br), 575 (s), 655 (s) 710 (vs), 805 (vs), 875 (s), 946 (vs), 997 (s), 1020 (vs), 1045 (vs), 1072 (s), 1088 (s), 1133 (m), 1182 (w).

4.3. Synthesis of $[Al_3(\mu, \eta^2\text{-thffo})_4Cl_4][AlEtCl_3] \cdot CH_2Cl_2$ (**2**)

A mixture of 15.5 cm^3 (16.3 g; 160 mmol) of tetrahydrofurfuryl alcohol and 30 cm^3 benzene was added dropwise to a solution of $AlEtCl_2$ (20.3 g; 160 mmol) at 273 K, stirred for 3 h and then slowly warmed to room temperature. The solvent was pumped off in vacuo. To obtain crystals suitable for X-ray analysis, 8 g of the solid was dissolved in 50 cm^3 of CH_2Cl_2 and placed in a refrigerator. After 2 days, the colourless needle-shaped crystals were filtered off and washed with hexane ($3 \times 5\text{ cm}^3$). Yield 4 g, (50%). Anal. Calcd. for $C_{23}H_{43}Cl_9O_9Al_4$: Cl, 30.80; Al, 13.40. Anal. Found: Cl, 30.71; Al, 13.46. IR (Nujol, cm^{-3}): 292 (m), 340 (m), 383 (s), 485 (vs, br), 570 (vs), 610 (w), 665 (s), 703 (vs), 736 (s), 802 (s), 830 (s), 874 (w), 920 (w), 935 (s), 1002 (s), 1045 (vs, br), 1141 (w), 1180 (w), 1192 (w).

4.4. Synthesis of $[Al_4(\mu, \eta^2\text{-thffo})_4(\mu\text{-OEt})_2Cl_6] \cdot \text{THF}$ (**3**)

To $AlCl_3(\text{THF})_2$ (1.33 g; 10 mmol) in THF (50 cm^3) was added $Mg(\text{thffo})_2$ (9.04 g; 40 mmol) and stirred at room temperature for 4 h. Next the volume was reduced in vacuo to ca. 20 cm^3 , filtered and a mixture of 10 cm^3 toluene and 4 cm^3 of ethanol was added and left to crystallize at 273 K. After one week, needle-shaped crystals together with white solid were obtained. Elementary analysis showed the presence of Mg, Al and Cl atoms. The liquid matrix ion mass spectrum showed the peaks $(m+1)/z$ at 939 and 814 due to the known tetranuclear $[Mg_4(\mu_3, \eta^2\text{-thffo})_2(\mu, \eta^2\text{-thffo})_4Cl_2]$ species [8] and the compound **3**, respectively. Good-quality crystal for X-ray examination were taken directly from the postreaction mixture.

4.5. Crystal structure solution and refinement

The crystals were sealed in a glass capillaries under nitrogen stream. Preliminary examination and intensities data collections were carried out on a KUMA KM-4 four-circle diffractometer [25] using graphite-monochromated $Mo-K_\alpha$ radiation (0.71073 Å). Cell parameters were obtained from a least-squares fit of the setting angles of 25 reflections in the ranges: $19.1^\circ < 2\theta < 27.5^\circ$ for **1**, $18.5^\circ < 2\theta < 30.7^\circ$ for **2** and $17.3^\circ < 2\theta < 29.9^\circ$ for **3**. Intensities were collected with ω - 2θ scan mode up to $2\theta = 46^\circ$, 50° , 46° for **1**, **2**, **3** respectively. After each group of 100 reflections three standard intensities

Table 2
Crystal data and structure refinement details for complexes **1**, **2** and **3**

	1	2	3
Formula	C ₁₈ H ₄₂ Al ₂ Cl ₄ O ₈	C ₂₃ H ₄₃ Al ₃ Cl ₉ O ₈	C ₂₈ H ₅₄ Al ₄ Cl ₆ O ₁₁
<i>f</i> _w	582.30	847.61	887.37
<i>T</i> , K	298(2)	300(2)	299(2)
Cryst system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	$\bar{P}1$
<i>a</i> (Å)	8.615(2)	23.046(5)	10.365(2)
<i>b</i> (Å)	16.445(3)	14.255(3)	10.854(2)
<i>c</i> (Å)	10.052(2)	15.443(3)	11.880(3)
α (°)			70.40(2)
β (°)	90.53(3)	123.85(3)	65.19(2)
γ (°)			80.18(2)
<i>V</i> (Å ³)	1424.0(5)	4213.4(15)	1142.2(4)
<i>Z</i>	4	4	2
<i>D</i> _c (g/cm ³)	1.358	1.371	1.395
μ (mm ⁻¹)	0.514	0.718	0.506
<i>F</i> (000)	616	1780	504
Cryst size (mm)	0.9 × 0.4 × 0.4	0.9 × 0.4 × 0.4	0.7 × 0.6 × 0.5
No. of data collected	2159	3364	3657
No. of data with <i>I</i> > 2σ(<i>I</i>)	1769	1061	2108
No. of parameters varied	153	235	254
<i>R</i> ₁ ^a	0.0338	0.0768	0.0324
<i>wR</i> ₂ ^b	0.0906	0.2069	0.0930

$$^a R_1 = \sum(F_o - F_c) / \sum F_o$$

$$^b wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$$

were monitored and no evidence of crystal decay was observed for **1**. In the cases of **2** and **3**, the intensities of the standard reflections decreased by 9.5 and 19.3%, respectively, and the recorded data for **2** and **3** were rescaled according to the intensities of the control reflections. For all data, Lorentz and polarization corrections were applied. The crystal data and some features of the structure refinement are summarized in Table 2. The structures were solved by direct methods (SHELXS86) [26] and refined on *F*² by full-matrix least-squares program (SHELXL93) [27]. The carbon bonded H-atoms were included in calculated the positions and refined using a riding model with isotropic displacement parameters equal to 1.2 *U*_{eq} of the attached C atom. In structure **1**, the H atoms of hydroxyl groups were located from difference Fourier map and refined without any restraints. In structure **2**, the Al(3) atom of AlEtCl₃⁻ anion is placed on a 2-fold axis. The ethyl group and two Cl atoms of this anion are disordered between two sets of symmetry related positions. The third Cl atom is distributed between four positions (two symmetry-related pair; the positions within a pair are symmetrically independent). It was necessary to impose one restraint an Al–Cl bond length to avoid too short a contact. In structure **2**, CH₂Cl₂ molecule is disordered and solvent atoms were refined with a 0.5 occupancy. In structure **3**, one C atom of thffo ring is split over two sites—occupancy factors for these two positions were refined as 0.67 and 0.33. A weighing

scheme of the form: $w = 1/\sigma^2(F_o^2) + (0.2097P)^2$, $w = 1/\sigma^2(F_o^2) + (0.0413P)^2 + 1.49P$ and $w = 1/\sigma^2(F_o^2) + (0.1214P)^2 + 1.95P$ (where *P* is defined as $(F_o^2 + 2F_c^2)/3$) were applied for **1**, **2** and **3**, respectively. For the last cycle of the refinement the maximum value of the ratio Δ/σ was below 0.005 Å for **1**, **2** and **3**. The final difference map showed a generally featureless background within -0.25 and 0.59 eÅ⁻³ for **1**, -0.34 and 0.51 eÅ⁻³ for **2**, -0.19 and 0.31 eÅ⁻³ for **3**.

5. Supplementary material

Complete crystallographic data of complexes **1–3** are available from the authors.

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