



An unusual reaction of Me_3Al with the macrobicyclic ligand
 $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3$ ($\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3=1,15\text{-diazas-}3,4:12,13\text{-dibenzo-}5,8,11\text{-trioxabicyclo}[13,3,1]\text{nonadecane}$)
Synthesis and crystal structure of a novel μ_3 -oxygen-bridged
tetranuclear organoaluminum complex
 $(\text{Me}_3\text{Al})(\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3)(\text{AlMe}_2)_2(\text{AlMe}_3)(\mu_3\text{-O})$

Qun Zhao, Hong-Sui Sun *, Xiao-Zeng You

State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, Nanjing 210093, PR China

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Abstract

The reaction of AlMe_3 with the macrobicyclic ligand 1,15-diaza-3,4:12,13-dibenzo-5,8,11-trioxabicyclo[13,3,1]nonadecane ($\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3$) in a 4:1 ratio in the presence of a trace of water resulted in the formation of a novel tetranuclear organoaluminum complex $(\text{Me}_3\text{Al})(\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3)(\text{AlMe}_2)_2(\text{AlMe}_3)(\mu_3\text{-O})$ in a nearly quantitative yield. The complex has been characterized by $^1\text{H-NMR}$, EI mass spectra and elemental analyses. A single crystal X-ray diffraction study reveals a μ_3 -oxygen atom bridging three different alkyl aluminum centers in a trigonal planar geometry, and the fourth aluminum center is bonded to the ether oxygen of the macrobicyclic ligand with a dative bond length. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Aluminum; μ_3 -Oxo-bridged; Macrobicyclic; Tetranuclear complex; Crystal structure

1. Introduction

The syntheses and characterizations of organometallic compounds which contain both Group 13 and 15 elements have been a subject of interest for many years [1–3]. The compounds have the potential to serve as intermediates to ceramic, semiconductor, or electronic materials [4–8].

Investigations concerning the organoaluminum chemistry of macrocyclic azacrown ethers has attracted much attention on account of their rich structural and bonding features and potential applications. Macro-

cyclic azacrown ethers affected Lewis base sites in addition to the possibility of condensation products. Moreover, the coordination chemistry of aluminum could also be affected by the macrocyclic effect.

Recently, we have synthesized a novel macrobicyclic ligand 1,15-diaza-3,4:12,13-dibenzo-5,8,11-trioxabicyclo[13,3,1]nonadecane ($\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3$) (Fig. 1). In this paper, we present the synthesis and solid-state structural determination of the novel tetranuclear organoaluminum complex $(\text{Me}_3\text{Al})(\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3)(\text{AlMe}_2)_2(\text{AlMe}_3)(\mu_3\text{-O})$ derived from this ligand. To our knowledge, the title complex represents the first structurally characterized organoaluminum complex containing a μ_3 -oxygen atom bridging three different alkyl aluminum centers in a trigonal planar geometry, and

* Corresponding author. Fax: +86 025 3314502; e-mail: ccinu@netra.nju.edu.cn

which differs greatly from those organoaluminum-macrocyclic amine complexes reported previously by Robinson and co-workers [9–11].

2. Experimental details

2.1. General procedures

All experiments were performed in a HE-493 Dri-Train Drybox under a nitrogen atmosphere, solvents were carefully dried by distillation from sodium and diphenyl ketone under nitrogen prior to use. $^1\text{H-NMR}$ spectra were obtained on a Bruker AM500 spectrometer in C_6D_6 using SiMe_4 as internal reference. Mass spectra were obtained on a ZAB-MS instrument. Microanalyses (C, H, N) were performed on a Perkin-Elmer 240C elemental analyzer. Trimethylaluminum was provided by the Special Gas Institute of Nanjing University. 1,4-Bis(2'-formylphenyl)-1,4-dioxabutane (Odien) was synthesized according to the literature method [12].

2.2. Preparation of $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3$

Propane-1,3-diamine (0.8 g) in methanol (20 ml) was added slowly to a well stirred, warm solution of Odien (3.7 g) in methanol (400 ml). The solution was stirred for 5 min, and sodium borohydride (2.5 g), together with a small amount of borax, was added slowly to the stirred solution. After the reaction had ceased, the solution was cooled and then filtered. On addition of ice to the filtrate, an oil separated, which was extracted over chloroform (three times). The extracts were dried over anhydrous sodium sulfate. The chloroform was removed by using a rotary evaporator to yield an oil that eventually crystallized to form a white solid. The solid was recrystallized from dichloromethane to afford the macrobicyclic compound as a crystalline product. Yield: 2.0 g, 58%. m.p., 204–205°C. Anal. Calc. for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3$: C, 71.64; H, 7.60; N, 7.60%. Found: C, 71.38; H, 7.52; N, 7.14%. $^1\text{H-NMR}$ (DMSO): 1.52(2H, m, CCH_2C); 2.43(4H, m, NCH_2CH_2); 3.36(2H, s, NCH_2N); 3.54(4H, s, ArCH_2); 3.78, 4.08 (m, OCH_2CH_2); 6.83–7.21 (m, Ar). Mass spectrum: parent peak, m/e 367.2.

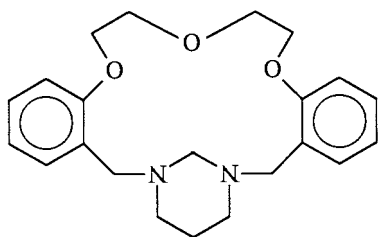


Fig. 1. Structural formula of the ligand $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3$.

Table 1

Crystal data and structure refinement for $(\text{Me}_3\text{Al})(\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3)(\text{AlMe}_2)_2(\text{AlMe}_3)(\mu_3\text{-O})$

Empirical formula	$\text{C}_{39}\text{H}_{66}\text{Al}_4\text{N}_2\text{O}_4$
Formula weight	734.86
Temperature (K)	295(2)
Radiation (wavelength, Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> (Å)	12.837(2)
<i>b</i> (Å)	13.480(2)
<i>c</i> (Å)	14.219(3)
α (°)	71.59(2)
β (°)	83.92(2)
γ (°)	75.692(14)
<i>V</i> (Å ³)	2261.2(7)
<i>D</i> _{calc.} (g cm ⁻³)	1.079
<i>Z</i>	2
Absorption coefficient (mm ⁻¹)	0.139
<i>F</i> (000)	796
Crystal dimensions (mm)	0.45 × 0.28 × 0.35
Crystal habit	Colorless columnar
θ range for data collected (°)	1.86–22.50
No. of reflections collected	5886
Independent reflections	5575 ($R_{\text{int}} = 0.1148$)
Observed reflections [$I > 2\sigma(I)$]	3340
Data/restraints/parameters	5558/28/482
Goodness-of-fit on F^2	1.045
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0699$; $wR_2 = 0.1472$
<i>R</i> indices (all data)	$R_1 = 0.1548$; $wR_2 = 0.2260$
Extinction coefficient	0.0027(11)
Greatest difference peak and hole (e Å ⁻³)	0.271, -0.270

2.3. Preparation of

$(\text{Me}_3\text{Al})(\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3)(\text{AlMe}_2)_2(\text{AlMe}_3)(\mu_3\text{-O})$

The ligand $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3$ (0.30 g, 0.82 mmol) was suspended in 10 ml of toluene and stirred, while a solution of trimethylaluminum (0.30 ml, 3.2 mmol) in 10 ml toluene was added at room temperature (r.t.). A homogeneous solution resulted gradually within 30 min, and then the solution was heated at 50°C for 5 h. The concentration of the reaction mixture yielded colorless single crystals suitable for X-ray analysis. Yield: 0.45 g, 90%. Anal. Calc. for $\text{C}_{32}\text{H}_{58}\text{Al}_4\text{N}_2\text{O}_4$: C, 59.73; H, 9.02; N, 4.35%. Found: C, 58.62; H, 8.56; N, 4.14%. $^1\text{H-NMR}$ (500 MHz, C_6D_6): -0.57(18H, s, AlMe_3); -0.33(12H, s, AlMe_2); 1.63(2H, m, CCH_2C); 2.50(4H, NCH_2CH_2); 3.25(2H, m, NCH_2N); 3.46(4H, s, ArCH_2); 3.61, 3.81(8H, m, OCH_2CH_2); 6.59–7.29(8H, m, Ar). MS (% intensity, m/e): 367.1(36.22, $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3$), 57.0(100, AlMe_2).

2.4. X-ray structure determination of

$(\text{Me}_3\text{Al})(\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3)(\text{AlMe}_2)_2(\text{AlMe}_3)(\mu_3\text{-O})$

A transparent colorless single crystal was mounted in a Lindemann glass capillary and then flame-sealed

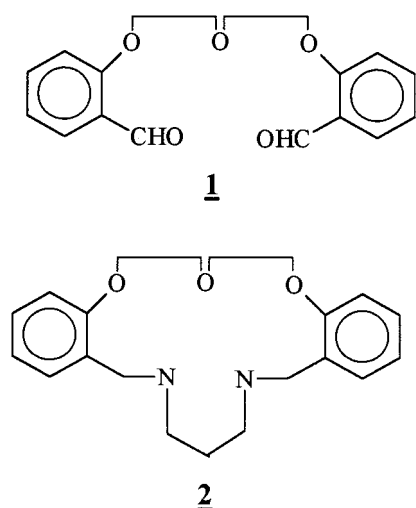


Fig. 2. Structural formula of Odien (**1**) and OdienNtnH₄ (**2**).

under a nitrogen atmosphere. Data were collected at 294 K on a Siemens P₄ four-circle diffractometer with monochromated Mo-K_α ($\lambda = 0.71703 \text{ \AA}$) radiation using a $\theta/2\theta$ scan mode with a variable scan speed, 5.0–50.0 min⁻¹ in ω . The data were corrected for Lorentz and polarization effects during data reduction using XSCANS [13]. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL version 5.0 [14]. Out of a total of 5886 reflections measured 5575 independent reflections were used in the refinement. Final R_1 and wR_2 values were 0.0699 and 0.1472, respectively, for 482 parameters and goodness-of-fit = 1.045 [$I > 2\sigma(I)$], and $wR2 = 0.2260$ (all data). The weighting scheme was $w^{-1} = \sigma^2(F_0^2)$, $wR = [\sum w(F_0^2 - F_c^2) / \sum w(F_0^2)^2]^{1/2}$. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms in compound **2** except for those in toluene were added at calculated positions using a C–H

bond length of 0.95 Å, and were included in the structure-factor calculation. All computations were carried out on a PC-586 computer using the SHELXTL-PC Program Package [14]. Analytical expressions of neutral-atom scattering factors employed and anomalous dispersion corrections were incorporated [15]. Crystal data and details of refinement are presented in Table 1. Additional data, including complete listing of bond distances and angles, anisotropic displacement coefficients and hydrogen atom coordinates, packing diagram and a list of observed and calculated structure factors are available from the authors.

3. Results and discussion

3.1. Synthesis and characterization

The reaction of Odien (Fig. 2) with propane-1,3-diamine in methanol resulted in a new macrobicyclic C₂₂H₂₈N₂O₃ (compound **1**), rather than the expected macrocycle 1,15-diaza-3,4:12,13-dibenzo-5,8,11-trioxacyclooctadecane (OdienNtnH₄) (Fig. 2) as reported in the literature [12]. The possible reaction pathway could include the formation of the expected macrocycle OdienNtnH₄, followed by the recrystallization from dichloromethane to afford compound **1**. The structure of compound **1** in the solid state has been further determined by single crystal X-ray diffraction analysis (Fig. 3) [16], which is just consistent with the elemental analyses and the spectroscopic studies.

The reaction of AlMe₃ with the macrobicyclic C₂₂H₂₈N₂O₃ in a 4:1 ratio resulted in the formation of (Me₃Al)(C₂₂H₂₈N₂O₃)(AlMe₂)₂(AlMe₃)(μ_3 -O) in nearly quantitative yield. Compound **2** forms colorless crystals which are liable to lose solvent of crystallization when exposed to air and moisture. Compound **2** crystallized

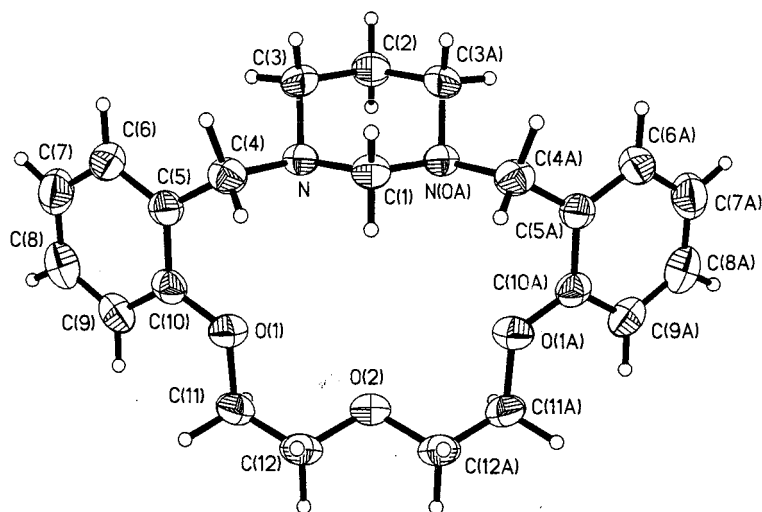


Fig. 3. Molecular structure of C₂₂H₂₈N₂O₃ showing 30% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

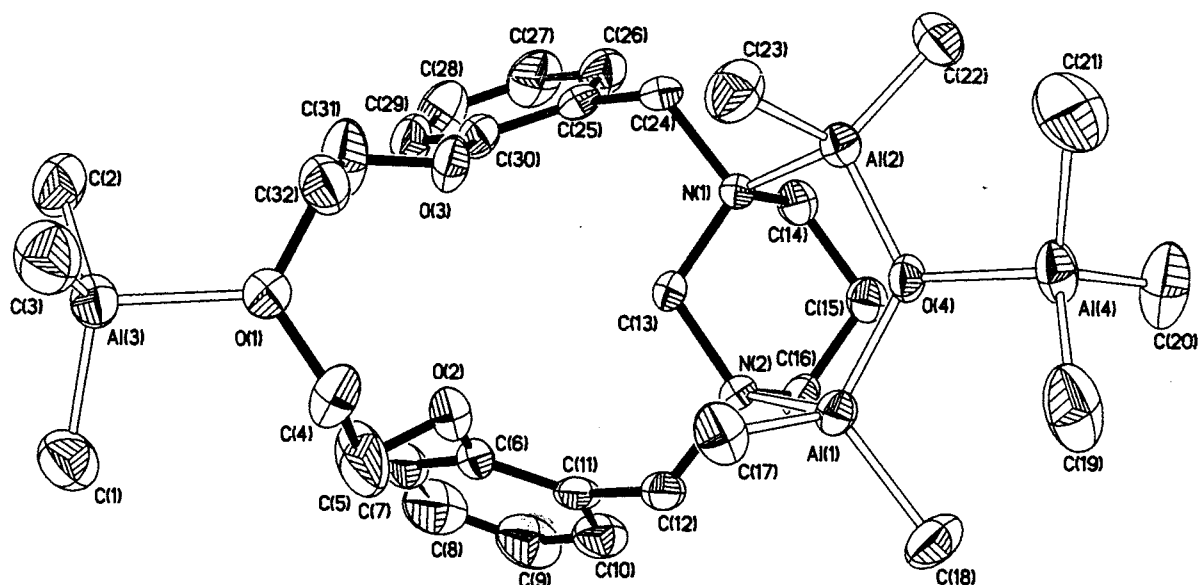


Fig. 4. Molecular structure of $(\text{Me}_3\text{Al})(\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3)(\text{AlMe}_2)_2(\text{AlMe}_3)(\mu_3\text{-O})$ showing 30% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

from toluene but showed very little solubility in toluene, once crystallized.

Compound **2** was insoluble in benzene; thus the $^1\text{H-NMR}$ spectra of **2** was obtained from a very dilute C_6D_6 solution. The $^1\text{H-NMR}$ spectrum of compound **2** displayed significant peaks in comparison with that of the free macrobicyclic ligand. The singlets at -0.57 and -0.33 ppm were assigned to the methyl groups attached to AlMe_3 and AlMe_2 , respectively, indicative of the formation of the alkylaluminum complex.

Compound **2** showed no parent molecular ion $[\text{M}]^+$. Two fragments $[\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3]^+$ and $[\text{AlMe}_2]^+$ were found with strong intensity in the EI mass spectra.

3.2. X-ray crystal structure of $(\text{Me}_3\text{Al})(\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3)(\text{AlMe}_2)_2(\text{AlMe}_3)(\mu_3\text{-O})$

The asymmetric structure of compound **2** was confirmed by single-crystal X-ray diffraction analysis. The molecular structure of **2** is shown in Fig. 4. Selected bond distances and angles are listed in Table 2. Compound **2** belongs to the triclinic system $P\bar{1}$. There are two molecules as well as two molecules of toluene as solvents of crystallization in the unit cell.

The four atoms Al(1), Al(2), Al(4) and O(4) are nearly coplanar with the mean deviation from the best squares plane of 0.054 Å. The near-coplanarity is also confirmed by the fact that the sum of the appropriate angles is about 360° ($\Sigma \text{X-O-Y} = 358.1(6)^\circ$), and consequently, the O(4) atom has a nearly trigonal planar geometry. The average $\text{Al}\cdots\text{Al}'$ contacts of 3.13 Å is not indicative of metal–metal interaction between the three aluminum centers. The $\text{Al}\cdots\text{Al}'$ separation in compound **2** is different from those observed previously in the

molecule of $[\text{Al}_4(\mu_3\text{-8-quinolyimide})_2(\text{CH}_3)_7(\mu\text{-OCH}_3)]$ (Fig. 5) [17]. In the latter, the shortest separation ($2.801(3)$ Å) is between Al1 and Al2 which is apparently caused by the two imido nitrogen bridges, and the longest separation ($3.460(3)$ Å) is between Al3 and Al4 which are bridged by the methoxy ligand.

The Al(1)–O(4) bond distance ($1.770(4)$ Å) is essentially the same as the Al(2)–O(4) distance ($1.782(4)$ Å). These values are slightly longer than the reference values for normal Al–O bond distance to four-coordinate aluminum estimated from the modified Schomaker–Stevensen rule (1.69 Å) [18]. The Al(4)–O(4) bond distance ($1.891(3)$ Å) is close to the mean of the reference values for normal and dative bond from oxygen to four-coordinate aluminum [2]. Similar Al–O bond distances have been reported in dimeric four-coordinate bridged organoaluminum alkoxides such as $[\text{Me}_2\text{Al}(\text{OC}_6\text{H}_3\text{-2-allyl-6-Me})_2]$ (1.861 Å) [19] and $[\text{Me}_2\text{Al}(\text{OSiMe}_3)_2]$ (1.843 Å) [20]. Another aluminum center Al(3) is bonded to the oxygen O(1) with a normal dative bond length ($1.992(4)$ Å). This is close to the reference value for a dative bond from an ether O to an Al atom bonded to three alkyl groups [21,22]. Each amino nitrogen atom coordinates one aluminum atom, thus attaining tetrahedral geometry. The bond distances of Al(2)–N(1) ($2.093(4)$ Å) and Al(1)–N(2) ($2.086(4)$ Å) are nearly equal. The Al–N bond distances are somewhat longer than values reported in the literature [23–25].

The conformation of the macrobicyclic ligand in the compound **2** is significantly different from that observed in the free ligand. The corresponding O–C and N–C bond distances in the free ligand $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3$ (**1**) and $(\text{Me}_3\text{Al})(\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3)(\text{AlMe}_2)_2(\text{AlMe}_3)(\mu_3\text{-O})$ (**2**)

Table 2

Selected bond lengths (Å) and angles (°) for $(\text{Me}_3\text{Al})(\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3)$ $(\text{AlMe}_3)_2(\text{AlMe}_3)(\mu_3\text{-O})$ with estimated S.D. in parentheses

Bond length (Å)			
Al(1)–O(4)	1.770(4)	Al(1)–C(17)	1.995(6)
Al(1)–C(18)	1.962(6)	Al(1)–N(2)	2.086(4)
Al(2)–O(4)	1.782(4)	Al(2)–C(22)	1.949(6)
Al(2)–C(23)	1.943(6)	Al(2)–N(1)	2.093(4)
Al(3)–C(1)	1.950(7)	Al(3)–C(2)	1.961(7)
Al(3)–C(3)	1.964(7)	Al(3)–O(1)	1.992(4)
Al(4)–O(4)	1.891(3)	Al(4)–C(20)	1.945(7)
Al(4)–C(21)	1.989(8)	Al(4)–C(19)	1.993(7)
Bond angle (°)			
O(4)–Al(1)–C(17)	111.8(2)	O(4)–Al(1)–C(18)	114.4(2)
C(17)–Al(1)–C(18)	119.4(3)	O(4)–Al(1)–N(2)	102.4(2)
C(17)–Al(1)–N(2)	103.6(2)	C(18)–Al(1)–N(2)	102.6(2)
O(4)–Al(2)–C(22)	114.0(2)	O(4)–Al(2)–C(23)	111.3(3)
C(22)–Al(2)–C(23)	120.6(3)	O(4)–Al(2)–N(1)	102.0(2)
C(22)–Al(2)–N(1)	101.5(2)	C(23)–Al(2)–N(1)	104.6(2)
C(1)–Al(3)–C(2)	116.1(3)	C(1)–Al(3)–C(3)	117.1(3)
C(2)–Al(3)–C(3)	114.2(3)	C(1)–Al(3)–O(1)	101.9(3)
C(2)–Al(3)–O(1)	101.5(2)	C(3)–Al(3)–O(1)	102.5(3)
O(4)–Al(4)–C(20)	106.2(3)	O(4)–Al(4)–C(21)	106.9(3)
C(20)–Al(4)–C(21)	113.0(4)	O(4)–Al(4)–C(19)	108.6(2)
C(20)–Al(4)–C(19)	113.2(4)	C(21)–Al(4)–C(19)	108.8(4)
C(4)–O(1)–Al(3)	120.0(4)	Al(1)–O(4)–Al(2)	124.6(2)
Al(1)–O(4)–Al(4)	117.1(2)	Al(2)–O(4)–Al(4)	116.4(2)

are listed in Table 3. In the free ligand, the N_2O_3 donor set is very nearly planar with the mean deviation from the best plane of 0.058 Å, and the macrobicyclic shows approximate mirror symmetry about a plane containing the O(3) atom, the methylene group, and the central atom of the trimethylene bridge [19]. By comparison, the N_2O_3 donor set in compound **2** has a completely non-planar arrangement with the mean deviation from the best squares plane of 0.43 Å, and the structure of the complexed macrobicyclic is asymmetric.

Only relatively recently have a few organoaluminum complexes with N/O mixed-donor crown ethers been reported. Generally speaking, the reaction types between the N/O mixed-donor crown ethers and the aluminum trialkyls are either forming dative $\text{N} \rightarrow \text{M}$ (or $\text{O} \rightarrow \text{M}$) bonds or resulting extensive covalent $\text{N} \rightarrow \text{M}$ interaction by alkane elimination. However, to our

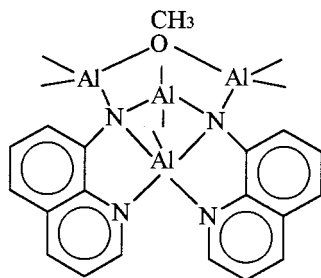


Fig. 5. Structural formula of $\text{Al}_4(\mu_3\text{-8-quinolyimide})_2(\text{CH}_3)_7(\mu\text{-OCH}_3)$.

Table 3

The corresponding O–C and N–C bond distances (Å) in $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3$ (**1**) and $(\text{Me}_3\text{Al})(\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3)(\text{AlMe}_3)_2(\text{AlMe}_3)(\mu_3\text{-O})$ (**2**)

Compound 1		Compound 2	
O(1)–C(10)	1.360(2)	O(1)–C(32)	1.434(7)
O(1)–C(11)	1.431(2)	O(1)–C(4)	1.445(8)
O(2)–C(12) ^a	1.412(2)	O(2)–C(6)	1.365(8)
O(2)–C(12)	1.412(2)	O(2)–C(5)	1.373(9)
		O(3)–C(31)	1.364(7)
		O(3)–C(30)	1.372(7)
N–C(1)	1.451(2)	N(1)–C(14)	1.484(6)
N–C(3)	1.465(2)	N(1)–C(13)	1.484(6)
N–C(4)	1.471(2)	N(1)–C(24)	1.530(6)
C(1)–N ^a	1.451(2)	N(2)–C(16)	1.481(6)
		N(2)–C(13)	1.496(6)
		N(2)–C(12)	1.512(6)

^a Symmetry codes in compound **1**: 1 – x, y, z.

surprise, the reaction of the macrobicyclic $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_3$ with Me_3Al resulted in a quite different type of product—a novel μ_3 -oxygen-bridged tetranuclear organoaluminum complex rather than the expected adduct or condensation product, as we found in the organoaluminum chemistry of the N/O mixed-donor crown ethers.

Structural evidence for μ_3 -oxygen atom as a bridging ligand, i.e. an oxygen capping a triangle of metal atoms, is not very common in organoaluminum amido and imido complexes. We postulate that the μ_3 -oxygen atom was produced by the reaction of trimethylaluminum with a trace amount of H_2O present in the reaction medium. Each of the two AlMe_3 might eliminate one methyl group due to the hydrolysis. To our knowledge, there are only a few main group organometallic oxo compounds containing an oxo bridging ligand which have been recently structurally characterized in the solid state. One such is the hexamer $[\text{Me}_4\text{Zn}_6\text{O}_2(\text{MeN}(\text{CH}_2)_3\text{NMe}_2)_4]$ or $[\text{Et}_4\text{Zn}_6\text{O}_2(\text{MeN}(\text{CH}_2)_2\text{NMe}_2)_4]$ from the reaction of dimethyl- or diethylzinc with *N,N,N*-trimethylethylene or propylenediamine in the presence of traces of moisture [26]. The other is the tetranuclear organoindium complex $(\text{InEt})_4(\text{di-2-pyridylamido})_2(\mu_4\text{-O})$, which possesses a μ_4 -oxygen atom bridging two unusual five-coordinate and usual four-coordinate indium atoms in distorted trigonal bipyramidal and tetrahedral environments, respectively [27]. Further investigations of the reaction mechanism are in progress.

Acknowledgements

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