

Synthesis and Structure of an Aluminum Bis(3-chloropentanedionate) Isopropoxide: $[\text{Al}(\mu\text{-O}^i\text{Pr})(3\text{-Clacac})_2]_2$

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$[\text{Al}(\text{O}^i\text{Pr})_3]_4$ was reacted at ambient temperature with 3-chloropentanedione (3-ClacacH) in 1 : 1 molar ratio in toluene, to obtain the mono-substituted product. However, the bis-substituted dinuclear tetrakis(3-chloropentanedionato)-di- μ -isopropoxy-dialuminum(III) $[\text{Al}(\mu\text{-O}^i\text{Pr})(3\text{-Clacac})_2]_2$ (**1A**) was isolated in 46% yield upon aging of the reaction mixture at -10°C . The supernatant upon aging yielded a crop of tris-3-chloroacetylacetonate $\text{Al}(3\text{-Clacac})_3\cdot\text{H}_2\text{O}$ (**1**) in 13% yield. Complexes **1A** (monoclinic, space group $P2_1/c$ with $Z = 2$) and **1** (cubic, space group $P4\bar{3}n$ with $Z = 8$) were characterized by elemental analyses, NMR and IR spectroscopy and single-crystal X-ray crystallography.

Key words: Aluminum, 3-Chloropentanedione, Isopropoxy, Single-crystal X-Ray Crystallography

Introduction

Nano-dimensional alumina (Al_2O_3) is an insulator, chemically non-reactive and used in computer components. Due to its large band gap energy of $\sim 8.8\text{ eV}$ and thermal stability, it is considered to be one of the most attractive dielectric materials. γ -Alumina is an important component of the mixed metal oxides acting as catalyst supports for Pt, Rh and/or Pd for conversion of toxic gases to inert ones [1]. The sol-gel process is an important way to produce metal-organic hybrid polymers. The properties of sol-gel products depend on (a) the precursors such as metal alkoxides, (b) the processing pH, (c) the complexing ligands, and (d) the processing temperature. Aluminum alkoxides are used as chief precursors for the synthesis of alumina. Carboxylic acids as well as β -diketones are extensively used to modify metal alkoxides for generating new precursors for the production of the corresponding metal oxides. The sturdy chelating tendency of β -diketones has led to the synthesis of a number of neutral complexes with covalent characteristics such as solubility in organic solvents only. This property has comprehensively been used in solvent extraction and chromatographic tech-

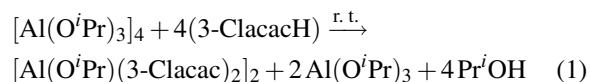
niques [2]. In 1988, Mehrotra discussed the chemistry of metal β -diketonates based on oxygen bonding, carbon bonding and by both oxygen and carbon bonding [3]. Bi- or even multidentate ligands bound strongly to the metal as a corollary of the chelate effect give rise to lesser reactivity with regard to the hydrolysis-condensation reactions, in comparison to the parent metal alkoxides, in the sol-gel process [4]. Often the metal centers in alkoxides are bridged *via* alkoxy groups. Freshly prepared aluminium tri-*iso*-propoxide was proposed to be a trimer, but it rearranges to a tetramer after aging for a few weeks, whereas aluminium tri-*tert*-butoxide exists as a dimer with tetrahedral environment around the metal centers. $[\text{Al}(\text{O}^i\text{Pr})_3]_4$ is used as a Lewis acid, but successive substitution with chelating ligands reduces the Lewis acidity of the resulting complex. Wengrovius and coworkers investigated the changes in structure and coordination behavior of $[\text{Al}(\text{O}^i\text{Pr})_3]_4$ after modification with β -diketones and found a dinuclear complex with tetrahedral and octahedral coordination around the aluminum atoms [5]. The authors also studied the kinetics of formation and disproportionation of $\text{Al}(\text{OR})(\text{acac})_2$ complexes in solution at higher temperatures and found that such complexes are unstable

and disproportionate to give Al(acac)₃ [5]. The stability of the aluminum alkoxy β -diketonates has been linked both to the bridging OR groups as well as to the extent of coordination of the Al centers [6]. The molecular structures of Al(acac)₃ and Al(C₅H₂F₆O₂)₃ have been published very recently [7, 8]. Our previous work was mainly focused on the isopropoxy/*n*-butoxy carboxylate clusters [9–11] of Ti(IV) and Zr(IV) [12]. A hexanuclear Gd(III) compound [13] Gd₆(μ_3 -OH)₆(acac)₁₂·1.25 CHCl₃ was also reported out of the reaction of gadolinium isopropoxide and acetylacetone.

In light of the above, we were tempted to examine the reactions of substituted acetylacetones with [Al(O^{*i*}Pr)₃]₄. In the present case, [Al(O^{*i*}Pr)₃]₄ has been reacted with 3-chloro acetylacetone in 1 : 1 molar ratio at room temperature to finally give the tris-complex Al(3-Clacac)₃·H₂O (**1**) along with an intermediate **1A** with composition [Al(μ -O^{*i*}Pr)(3-Clacac)₂]₂ which have octahedral environments around Al centers.

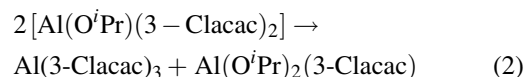
Results and Discussion

The facile interactions of aluminum alkoxides with ligands having protic hydrogen atoms, in desired stoichiometric ratio, in organic solvents, has proved to be of great importance in the synthesis of organic derivatives of aluminum. Reportedly, the chemistry of β -diketonate derivatives of main group elements is subjugated by formation of stable chelated derivatives with 1,3-diketonate anions [14]. Substitution of alkoxy groups in aluminum alkoxides with β -diketones [5] and β -diketo esters [15] has previously been investigated. Mono- and bis-substituted products could be isolated [5] from the reactions of Al(O^{*i*}Pr)₃ both with acetylacetone and 3,5-heptanedione at ambient temperature in 1 : 1 and 1 : 2 molar ratios, respectively. However, in our case the reaction of aluminum tri-*iso*-propoxide and 3-ClacacH in 1 : 1 molar ratio did not yield the mono-substituted product. Instead, a bis-substituted intermediate precursor [Al(μ -O^{*i*}Pr)(3-Clacac)₂]₂ was crystallized (yield 46%), the formation of which may be schematized by Eq. 1.



The supernatant of the reaction mixture upon aging at low temperature finally yielded 13% of the tris-

substituted Al(3-Clacac)₃·H₂O (Eq. 2).



Under the given conditions, it appears that two molecules of the bis-substituted product **1A** have combined to form the tris- along with the mono-substituted product (Eq. 2). Wengrovius *et al.* [5] have obtained the bis-substituted product by further addition of one mole of β -diketone to the mono-substituted product, and the mechanism has been explained on the basis of disproportionation. The thermal stabilities of bis-substituted products were also studied [5], and the compounds were found to be less stable and to change to the corresponding tris-substituted products in the temperature range 43.9 to 86.3 °C. In contrast, we have obtained the bis-substituted **1A** by the reaction of [Al(O^{*i*}Pr)₃]₄ with 3-ClacacH in 1 : 1 molar ratio in toluene which subsequently converted to the tris-substituted complex **1** even at low temperature. Obviously, the presence of a chlorine atom in 3-ClacacH, due to its –I effect, increases the amount of the enol form to 92% [16] and imparts enhanced reactivity in comparison to acacH. This may be the reason of the formation of bis/tris-substituted complexes in place of the mono-substituted one.

The ¹H NMR spectrum of compound **1A** showed the shifting of the signal of the bridging isopropoxy group to lower field in comparison to the tetrameric [Al(O^{*i*}Pr)₃]₄ [15]. The resonance of the methine group in [Al(O^{*i*}Pr)₃]₄ appeared at 4.7 ppm whereas in complex **1A** the peak was shifted to 3.9 ppm. The doublet at 1.12 in the spectrum of **1A** for the methyl groups for [Al(O^{*i*}Pr)₃]₄ was found at 1.32 ppm. The singlet present at 2.12 ppm corresponds to the methyl groups of the 3-Clacac ligand. In the ¹³C NMR spectrum of **1A** peaks at 189.3 and 87.3 ppm, respectively, correspond to (CO) and methyl of the 3-Clacac ligand. In the FT-IR spectrum of compound **1A** bands observed at 765, 831, 905, and 943 cm⁻¹ are due to $\nu(\text{Al-O})$ vibrations. The peak at 1023 cm⁻¹ corresponds to $\nu(\text{C-O})$ of the bridging isopropoxy group. The ¹H NMR spectrum of compound **1** showed a single resonance peak at $\delta = 2.14$ ppm for the methyl protons of the ligand. The ¹³C NMR spectrum also confirmed the presence of only β -diketonate ligands.

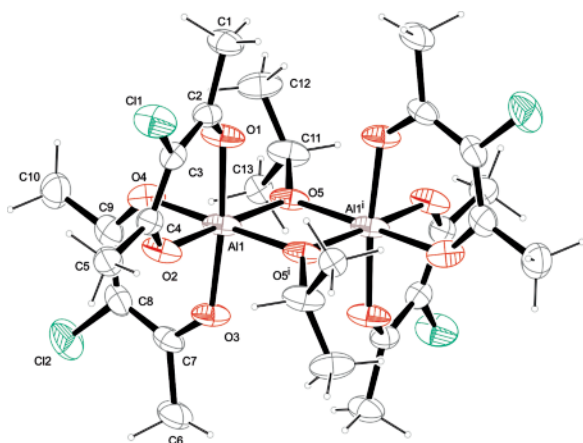


Fig. 1. ORTEP representation of the molecular structure of **1A** in the crystal (displacement ellipsoids at the 50% probability level; H atoms as spheres with arbitrary radius; see Table 1 for symmetry operation of equivalent atoms).

Crystal and molecular structures

Compound **1A** crystallizes in the monoclinic space group $P2_1/c$ with $Z = 2$. The molecular structure of complex **1A** is shown in Fig. 1. The molecule is a centrosymmetric dimer with half of the molecule in the asymmetric unit. The aluminum atoms have octahedral coordination with bridging isopropoxide groups. The μ -O^{*i*}Pr groups result in an asymmetric bridging [Al1–O5 = 1.883(2) and Al1–O^{*i*}5 = 1.869(2) Å]. Interestingly, the Al–O (O of 3-Clacac) bond length Al1–O2 = 1.907(2) Å is slightly longer than Al1–O4 = 1.882(3) Å. The bond angle O3–Al–O4 [88.71(11)°] is a little larger than O1–Al–O2 [87.3(10)°] (Table 1). All Al–O–C bond angles are different [Al1–O2–C4 = 130.7(2)°, Al1–O1–C2 = 131.2(2)°, Al1–O3–C7 = 131.5(2)°, Al1–O4–C9 = 131.3(2)°] (Table 2).

X-Ray diffraction also revealed that compound **1** has a similar composition as the recently reported tris-(3-chloropentane-2,4-dionato)-aluminium [17] but with a water molecule which is located close to a three-fold axis and has C5- and C1-bound hydrogen atoms as closest neighbors in distances of 3.10 and 3.15 Å, re-

Table 1. Selected bond lengths (Å) of compound **1A**^a.

Al1–O5 ^{<i>i</i>}	1.869(2)	Al1–O4	1.882(3)
Al1–O5	1.883(2)	Al1–O1	1.889(2)
Al1–O3	1.894(2)	Al1–O2	1.907(2)
Al1···Al ^{<i>i</i>}	2.923(2)		

^a Symmetry operation: ^{*i*} 1 – *x*, 1 – *y*, –*z*.

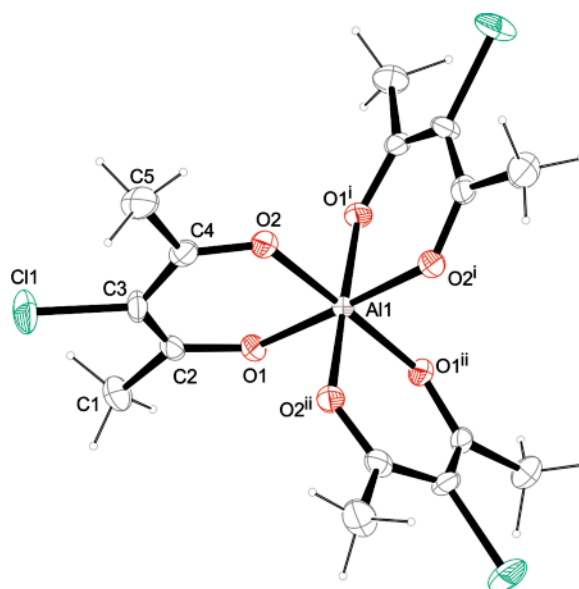


Fig. 2. ORTEP representation of the molecular structure of **1** in the crystal (displacement ellipsoids at the 50% probability level; H atoms as spheres with arbitrary radius; see Table 4 for symmetry operations of equivalent atoms).

Table 2. Selected bond angles (deg) of compound **1A**^a.

O5–Al1–O4 ^{<i>i</i>}	173.50(11)	O5–Al1–O5 ^{<i>i</i>}	77.68(10)
O4–Al1–O5	96.40(10)	O5–Al1–O1 ^{<i>i</i>}	94.55(11)
O4–Al1–O1	88.19(11)	O5–Al1–O3 ^{<i>i</i>}	89.21(10)
O4–Al1–O3	88.71(11)	O5–Al1–O3	95.61(10)
O1–Al1–O3	173.52(12)	O5–Al1–O2 ^{<i>i</i>}	96.05(10)
O1–Al1–O2	87.30(10)	O5–Al1–Al1 ^{<i>i</i>}	39.01(7)
O1–Al1–Al1 ^{<i>i</i>}	93.14(9)	C2–O1–Al1	131.2(2)
C4–O2–Al1	130.7(2)	C11–O5–Al1 ^{<i>i</i>}	123.5(2)
C11–O5–Al1	132.2(2)	Al1–O5–Al1 ^{<i>i</i>}	102.32(10)

^a Symmetry operation: ^{*i*} 1 – *x*, 1 – *y*, –*z*.

Table 3. Selected bond lengths (Å) of compound **1**.

Al1–O1	1.8724(17)	Al1–O2	1.8788(18)
C11–C3	1.758(3)	C1–C2	1.502(4)
O1–C2	1.277(3)	C2–C3	1.384(4)
O2–C4	1.261(3)	C3–C4	1.404(4)
C4–C5	1.503(4)		

spectively. The disordered water molecule is not shown in Fig. 2. Notably, the crystal systems and molecular formulae are not the same. While **1** crystallized in the cubic space group $P4\bar{3}n$ with $Z = 8$ (Fig. 2), the reported complex [17] crystallized monoclinically in space group $C2/c$ with $Z = 4$. The metal atom is hexacoordinated and linked to six oxygen atoms from three

Table 4. Selected bond angles (deg) of compound **1**^a.

O1–Al1–O2	90.30(7)	O1–Al1–O1 ⁱ	89.27(8)
O1–Al1–O2 ⁱ	178.61(8)	O1–Al1–O2 ⁱⁱ	92.05(7)
O2–Al1–O2 ⁱⁱ	88.40(9)		

^a Symmetry operations: ⁱ y, z, x; ⁱⁱ z, x, y.

3-chloroacetylacetonate ligands. The important bond lengths and angles for complex **1** are listed in Tables 3 and 4, respectively. The average Al–O bond length in **1** is 1.887 Å, in good accordance with the reported [17] value (1.875 Å).

It is noteworthy that the chelation ability of 3-Clacac increases the stability of the molecule, and the products may be used as precursors for metal-organic chemical vapor deposition (MOCVD) [18, 19].

Experimental Section

All the reactions were carried out under stringently anhydrous conditions using Schlenk and vacuum line techniques

under dry argon. [Al(OⁱPr)₃]₄ (Aldrich Chemicals) was purified by vacuum distillation and aged to be converted to a solid before carrying out the reactions. Toluene and CDCl₃ were dried by standard procedures. ¹H NMR spectra were recorded in CDCl₃ on a Bruker Biospin ARX 300 spectrometer with tetramethylsilane (TMS) as internal reference. A Jasco FT-IR-5300 spectrometer was used for recording the infrared spectra of the compounds as Nujol mulls between NaCl plates. Aluminum was gravimetrically determined as Al₂O₃. Isopropoxy analysis (for **1A**) was done by the method of Bradley and Mehrotra [20].

Synthesis of **1A**

A solution of 3-ClacacH (0.932 g, 6.92 mmol) in toluene (≈ 20 mL) was added dropwise to a stirred solution of aluminum *iso*-propoxide (1.415 g, 1.73 mmol) in toluene (20 mL) over 30 min at room temperature. After complete addition, stirring of the reaction mixture was continued for 18 h followed by reducing the volume of the solution under vacuum to half. Then the reaction mixture was left for crystallization at –10 °C to give compound **1A** after 5 h (1.13 g,

	1A	1
Empirical formula	C ₂₆ H ₃₈ Al ₂ Cl ₄ O ₁₀	C ₁₅ H ₂₀ AlCl ₃ O ₇
<i>M_r</i>	706.348	445.655
Crystal size, mm ³	0.12 × 0.05 × 0.03	0.12 × 0.10 × 0.08
<i>T</i> , K	123(2)	123(2)
Radiation; wavelength, Å		MoK α ; 0.71073
Diffractionmeter		Bruker D8Venture
Crystal System	monoclinic	cubic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 4̄3 <i>n</i>
<i>a</i> , Å	10.6313(9)	16.3934(1)
<i>b</i> , Å	17.7208(15)	16.3934(1)
<i>c</i> , Å	9.5567(7)	16.3934(1)
β , deg	115.306(2)	90
<i>V</i> , Å ³	1627.7(2)	4405.62(5)
<i>Z</i>	2	8
<i>D</i> _{calcd.} , g m ^{–3}	1.44	1.34
μ , mm ^{–1}	0.5	0.5
Transmission factor range	0.6764–0.7452	0.7127–0.7452
Absorption correction		multiscan
Refls. measured	26 890	68 904
Refls. unique/ <i>R</i> _{int}	2995/0.0546	1356/0.0440
Mean $\sigma(I)/I$	0.0351	0.0082
θ range	3.13–25.39	3.51–25.34
Observed refls. (<i>I</i> > 2 $\sigma(I)$)	2259	1312
Hydrogen refinement	constr.	mixed
Refined parameters	196	82
<i>R</i> 1 (<i>F</i> _{obs})/ <i>wR</i> 2 (all <i>F</i> ²) ^{a,b}	0.0515/0.1266	0.0405/0.1218
<i>a</i> / <i>b</i> (weighting scheme) ^b	0.0419/3.2410	0.0846/0.9266
<i>S</i> ^c	1.027	1.233
(shift/error) _{max}	0.001	0.001
$\Delta\rho_{\text{fin}}$ (max/min), e Å ^{–3}	0.84/–0.50	0.72/–0.58

Table 5. Crystallographic data of compounds **1A** and **1**.

^a $R1(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $wR2(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$; ^c $S = \text{GoF} = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$; $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$.

46%). – C₂₆H₃₈Al₂Cl₄O₁₀ (706.348): calcd. Al 7.61, OⁱPr 16.61; found Al 7.54, OⁱPr 16.80. – ¹H NMR (25 °C): δ = 3.94 (m, CH of OⁱPr), 1.23 (d, CH₃ of OⁱPr) 1.69 ppm (s, CH₃ of the β -ketone). – ¹³C NMR (25 °C): δ = 189.34 (s, CO of the β -ketone), 75.56 (s, CH₃ of the β -ketone), 87.3 (s, α -carbon of the ligand), 55.2 (s, CH₃ of OⁱPr), 29.4 ppm (s, CH of OⁱPr). – ²⁷Al NMR (25 °C): δ = 3.2 ppm(s). – FT-IR (Nujol): ν = 765, 831, 905, 943 (Al–O) stretching, 1023 cm⁻¹ (C–O of bridging isopropoxy).

Synthesis of **1**

The crystalline compound **1A** was separated by decantation, and the remaining supernatant was again kept for crystallization to give crystals of compound **1** (0.401 g, 13%). – C₁₅H₂₀AlCl₃O₇ (445.655): calcd. Al 6.04, C 40.38, H 4.48; found Al 6.12, C 40.26, H 4.32. – ¹H NMR (25 °C): δ = 2.25 ppm (s, CH₃ of the β -ketone). – ¹³C NMR (25 °C): δ = 185.34 (s, CO of the β -ketone), 62.56 (s, CH₃ of the β -ketone), δ = 84.24 ppm (s, α -carbon of the ligand). – ²⁷Al NMR (25 °C): δ = 3.2 ppm (s). – FT-IR (Nujol): ν = 410, 464 (Al–O) bending, 765, 810, 945, 943 cm⁻¹ (Al–O) stretching.

Crystal structure determinations of **1A** and **1**

Crystals suitable for X-ray crystallography were selected by means of a polarization microscope, mounted on the tip of a glass fiber, and investigated on a Nonius Kappa CCD diffractometer using MoK α radiation (graded multilayer X-ray optics). Crystal data for compounds **1A** and **1** are given in Table 5. The measurement temperature was 200 K. The structure was solved by Direct Methods with the program SIR97 [21] and refined by full-matrix least-squares calculations [22] on F² (SHELXL-97). The water molecule O3 of **1A** is disordered over three sites close to a threefold axis. Its hydrogen atoms have not been considered in the refinement. All other hydrogen atoms were positioned geometrically and treated as riding on their parent atoms.

CCDC 956693 (**1A**) and 956694 (**1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

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