

Synthesis and structure of tris (acetylacetonato) aluminum(III)

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Tris(acetylacetonato)aluminium(III), [Al(C₂H₇O₂)₃], a precursor in vapor deposition of aluminum oxide, has been prepared starting from industrial alum, Al₂(SO₄)₃.16H₂O and characterized by chemical, IR, thermal (TG-DSC) and single crystal X-ray diffraction analyses. The compound crystallizes in the monoclinic space group P2₁/c and all atoms are located in general positions. The central metal is hexacoordinated to three bidentate acetylacetonate ligands.

Keywords: Inorganic chemistry, Aluminum acetylacetonate, Alumina, Alum, Crystal structure, X-ray diffraction

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Alumina, Al₂O₃, is an important ceramic material widely used in catalysis and in refractories due to its mechanical strength, thermal stability over a wide temperature range and high specific area¹⁻⁶. Due to the widespread utility, synthetic routes of this oxide has been studied well over many decades and continuous efforts are being made to develop new processes to yield high quality alumina-based materials. It has been reported⁷ that tris(acetylacetonato)-aluminium(III), [Al(C₂H₇O₂)₃], also called as aluminium acetylacetonate, [Al(acac)₃], (**1**), has been used as a precursor in vapor deposition of aluminum oxide. It is a useful precursor for the formation of alumina at a low temperatures, i.e., ~200 °C. Crystalline aluminum oxide films have been grown on Si (100) by low-pressure metal organic chemical vapor deposition, using (**1**) as a precursor⁷. It has also been used in chemical vapor deposition due to its low boiling property. However, organometallic sol-gel approach is one of the most widely utilized industrial techniques for alumina synthesis as gelation technology enables flexibility in tailoring the final material for the desired applicability. The crucial

point in gelation is the initiation of hydrolysis and control of condensation. The use of chelating agents such as acetylacetone (acac), ethylacetoacetate, monoethanolamine, long chain carboxylic acid, etc. have been tried. It has been observed that a transparent gel is obtained at optimal acacH/ASB (Al-tri-sec-butoxide) mole ratios⁸ of 0.3–0.4. During chelation either one of the alkoxy bonds of [Al(OR)₃] is replaced by acac, or there can be a polymeric form such as [Al(OR)₂(acac)]_n (ref. 9). Spray pyrolysis of metal alkoxides dissolved in volatile organic solvents is yet another well tried route to manufacture of metal oxides¹⁰ (US Pat 595836). However, in spray pyrolysis of metal alkoxides trace amount of moisture leads to hydrolysis of metal to give a precipitate, which blocked the nozzles of the aerosolizer. The same was observed by us while screening different precursors for spray pyrolysis and hence, we resorted to simple metal salts for synthesizing iron oxide¹¹, aluminum oxide¹² and TiO₂.

To investigate the role of acetylacetone in arresting hydrolysis, it is of interest to first prepare the [Al(acac)₃] and then replace the ligands stepwise with butoxide, and, also try an alternate route of preparing first Al-butoxide and exchange the ligand with acacH. Towards this goal we have investigated the chemistry and crystal structure of acetylacetonates of aluminum. The present novel synthesis of acetylacetonate complex of aluminum involves the treatment of an acidic solution of aluminum with ammoniacal solution of acetylacetonate.

Although the known synthetic routes enable the synthesis of (**1**), one of the objectives in the present method is to use industrial alum, Al₂(SO₄)₃.16H₂O, as a starting material in order to give alternate usage of this important industrial byproduct in the production of alumina. The use of an alternate source stems from a recent X-ray structure report showing that [Al(acac)₃] exists in a polymorphic δ-modification^{13,14} at around 110 K. Accordingly, in this study the tris complex was prepared using alum as starting material and its properties investigated by chemical, FTIR, TG-DSC and X-ray analysis.

Experimental

[Al(acac)₃] (**1**) was prepared using alum, an industrial byproduct, which was obtained from

Hindalco Industries Ltd, India. A solution of alum $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ (0.1M) was prepared using doubly distilled water. The solution was acidic. To this solution, an ammoniacal solution of acetylacetonone was added in small proportions with continuous swirling till the solution became neutral or slightly basic (pH 7-8). The reaction mixture was allowed to stand for 15 minutes. The pale yellow precipitate formed, was filtered, washed with doubly distilled water and dried under vacuum. The complex was recrystallized using dimethyl formamide as solvent. The resulting crystals formed were isolated by suction filtration. Aluminum content of the complex (**1**) was estimated titrimetrically using EDTA. The crystals were suitable for single crystal X-ray study.

IR spectra were recorded on a Shimadzu (IR Prestige 21) FTIR spectrophotometer. The sample was diluted with KBr for the spectral analysis. IR spectra of the complex were also recorded after heating at 200 °C and 300 °C.

TG-DSC thermograms were recorded on a NETZSCH STA-409PC simultaneous thermal analyzer in flowing air using Al_2O_3 crucibles. Heating rate of 10 °C/min was maintained for all measurements. The melting point was also determined using Thiel's tube. Isothermal weight loss studies were carried out by heating the sample in a temperature-controlled furnace for two hours at 200 °C and 300 °C. Additionally, weighed amounts of sample was taken in a silica crucible and heated on a Bunsen burner.

The recrystallised (**1**) was studied using single crystal X-ray diffractometry on a Stoe IPDS 1 diffractometer using graphite monochromated Mo- K_α radiation. X-ray studies were carried out at Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel, Kiel, Germany.

The intensity data were collected at 170 K. The raw intensities were corrected for Lorentz polarization effects. The structure was solved with direct method using SHELXS-97 and refinement was done against F^2 using SHELXL-97¹⁶. All non-hydrogen atoms were refined using anisotropic displacement parameters. Crystal data and some selected refinement results for (**1**) are summarized in Table 1.

Results and discussion

The IR spectrum of the tris complex exhibits several signals in the IR region (400 cm^{-1} - 4000 cm^{-1}) indicating the presence of the organic ligand. The anhydrous nature of the complex is evident

Table 1—Crystal data and structure refinement for aluminium acetylacetonate

Empirical formula	$\text{C}_{15}\text{H}_{21}\text{AlO}_6$
Formula weight	324.30
Temperature	170(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 13.8475(11)$ Å; $\alpha = 90^\circ$ $b = 7.4649(4)$ Å; $\beta = 98.993(9)^\circ$ $c = 16.2019(13)$ Å; $\gamma = 90^\circ$
Volume	$1654.2(2)$ Å ³
Z	4
Density (calc.)	1.302 mg/m ³
Absorption coefficient	0.147 mm ⁻¹
$F(000)$	688
Crystal size	0.4 x 0.3 x 0.3 mm ³
θ range for data collection	2.74° to 28.06°
Index ranges	$-18 \leq h \leq 15$; $-9 \leq k \leq 9$; $-21 \leq l \leq 21$
Reflections collected	12768
Independent reflections	3961 [$R(\text{int}) = 0.0288$]
Completeness to $\theta = 28.06^\circ$	98.7 %
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3961/0/205
Goodness-of-fit on F^2	1.044
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0373$, $wR2 = 0.1016$
R indices (all data)	$R1 = 0.0491$, $wR2 = 0.1083$
Largest diff. peak and hole	0.214 and -0.242 e.Å ⁻³

from the absence of O-H vibration as no signals are observed beyond 3000 cm^{-1} . The signals observed at 410 , 484 cm^{-1} may be assigned to the bending mode of Al-O vibration, while those at 576 , 659 , 687 , 776 and 935 cm^{-1} are due to $\nu_{\text{Al-O}}$ vibrations^{5,15}. On heating the complex at 200 °C, all the IR peaks are retained. However, in the IR of samples heated at 300 °C only the peaks at 510 cm^{-1} due to $\nu_{\text{Al-O}}$, at 1560 cm^{-1} due to $\delta_{\text{H-O-H}}$ and at 1450 cm^{-1} due to ν_{OCO} are observed. The sample was found to be black in color. On heating at 300 °C, some carbonaceous material was found in the sample.

The melting point of complex (**1**) using Thiel's tube was found to be 192 °C. The TG-DSC thermogram of (**1**) (Fig. 1) exhibits two endothermic events at 195 °C and 257 °C, followed by a complex exothermic process at 340-500 °C with a peak at 444 °C. The TG curve does not show any change till 200 °C. A mass loss of about 91 % is observed till ~250 °C and decomposition continues resulting in total pyrolysis. From these observations and the recorded melting point, the first endotherm at 195 °C can be attributed to the melting of (**1**). The sharp endotherm accompanied by a total weight loss at

257 °C, indicates its decomposition to alumina, which may be the γ modification as seen in IR spectrum at 300 °C. It has been reported⁵ that γ -alumina can be synthesized at 200 °C from $[\text{Al}(\text{acac})_3]$. Here, the endothermic peak with weight loss in TG, endotherm in DSC and the peaks in the IR spectrum indicate formation of alumina. However, the weight loss is higher than expected. Above this temperature, there is continuous weight loss till 418 °C and the DSC shows a broad exotherm. This may be due to continuous vaporization of the molten mass of **(1)**. Hence, at the earlier stage also the higher weight loss may be because of some molten **(1)** vaporizing even at low temperature.

On heating the complex at 200 °C, the observed mass loss was 54 %. The IR spectrum shows peaks with diminished intensity while the DSC thermogram shows an endotherm, indicating that the sample melts and a part of it vaporizes. When heated at 300 °C isothermally, a mass loss of ~97 % is observed. IR spectrum shows peaks due to alumina (510 cm^{-1}) and some adsorbed moisture content (1560 cm^{-1}) and carbonaceous material (1450 cm^{-1}). It is thus very clear that although alumina is formed, the particles are fine and so do not remain in the crucible.

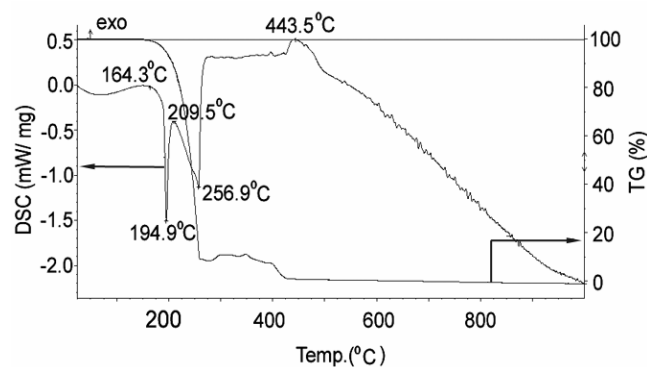


Fig. 1—TG -DSC curves of $[\text{Al}(\text{acac})_3]$ (**1**).

To confirm the vaporization, the sample (~500 mg) was heated in crucible on a flame. It was observed that no residue remained in the crucible, indicating that the present method of synthesis helps in vaporizing the complex totally. Thus the material can be used in chemical vapor deposition of alumina.

X-ray diffraction studies shows that **(1)** crystallises in the monoclinic space group $P2_1/c$ with all atoms located in general positions (Fig. 2). The unit cell dimensions of **(1)** are consistent with the data at 180 K for the earlier reported α -modification¹⁶. The bond lengths and bond angles of the organic ligand are in the expected range. (Table 2). The central metal atom is hexa-coordinated and is linked to six oxygen atoms from three bidentate acetylacetonate ligands.

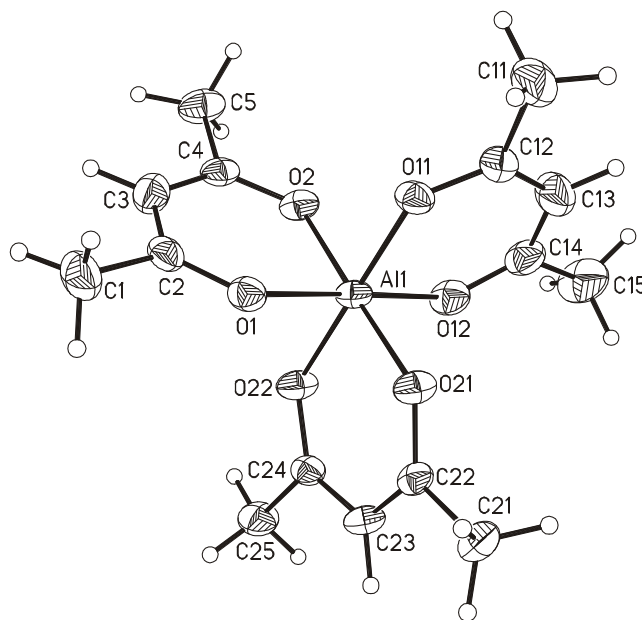


Fig. 2—Crystal structure of $[\text{Al}(\text{acac})_3]$ (**1**) showing the atom labeling scheme. [Displacement ellipsoids are drawn at 50 % probability level, except for the H atoms which are shown as circles of arbitrary radius].

Table 2—Selected bond lengths and bond angles in $[\text{Al}(\text{acac})_3]$ (**1**)

Bond lengths (Å)

Al(1)-O(12)	1.8764(10)	Al(1)-O(21)	1.8859(10)
Al(1)-O(11)	1.8820(10)	Al(1)-O(1)	1.8870(10)
Al(1)-O(2)	1.8855(10)	Al(1)-O(22)	1.8916(10)

Bond angles (°)

O(12)-Al(1)-O(11)	91.82(4)	O(2)-Al(1)-O(1)	91.21(4)
O(12)-Al(1)-O(2)	88.85(5)	O(21)-Al(1)-O(1)	89.00(4)
O(11)-Al(1)-O(2)	90.40(4)	O(12)-Al(1)-O(22)	88.33(5)
O(12)-Al(1)-O(21)	91.00(5)	O(11)-Al(1)-O(22)	179.55(5)
O(11)-Al(1)-O(21)	88.13(4)	O(2)-Al(1)-O(22)	90.03(4)
O(2)-Al(1)-O(21)	178.52(4)	O(21)-Al(1)-O(22)	91.44(4)
O(12)-Al(1)-O(1)	177.96(5)	O(1)-Al(1)-O(22)	89.64(5)
O(11)-Al(1)-O(1)	90.22(4)		

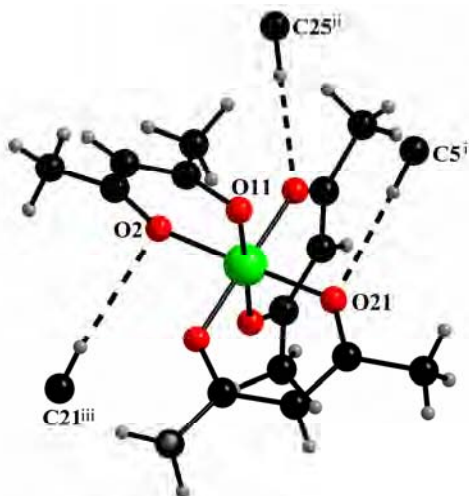


Fig. 3—A view of the surroundings of (1) showing its link with three different molecules via weak C-H...O interactions (dotted line). [Symmetry code: (i) $x, y+1, z$; (ii) $x, -y+1.5, z-0.5$; (iii) $x, y-1, z$]

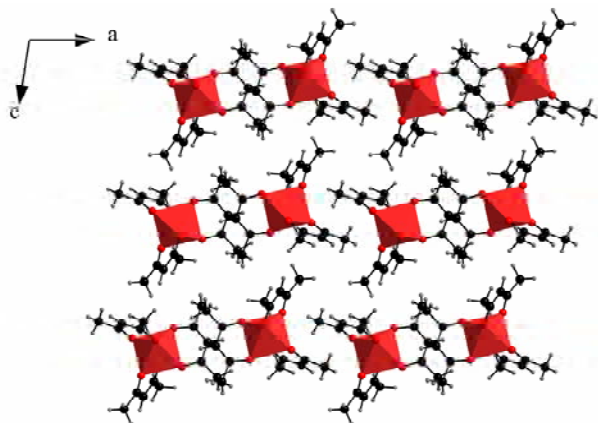


Fig. 4—The crystallographic packing of (1) viewed along b axis. [$\{AlO_6\}$ units are shown as octahedra].

The Al-O bond lengths are scattered over a very narrow range and vary between 1.8764 and 1.8855 Å and are in excellent agreement with reported values. The *cis* O-Al-O angles range from 88.13° to 91.82° while the *trans* O-Al-O angles vary from 177.96° to 179.56°, indicating very little distortion of the AlO_6 octahedron. A scrutiny of the structure reveals that each $[Al(acac)_3]$ molecule is linked to three other symmetry related molecule with the aid of C-H...O interactions. The H atoms attracted to C5, C25 and C21 function as H donors while the one O atom of each acac ligand O2, O11 and O21 function as H acceptors. In all three C-H...O interactions ranging from 2.56 to 2.71 Å and accompanied by DHA in the range 158 to 178° are observed (Fig. 3). The geometrical parameters of these H-bonds are summarised in Table 3. A view of the crystallographic packing along b axis is depicted in Fig. 4.

Table 3—Hydrogen bonding geometry for $[Al(acac)_3]$ (1)

D-H...A	$d(D-H)$ (Å)	$d(H...A)$ (Å)	$d(D...A)$ (Å)	<DHA (°)
C5-H5C...O21 ⁱ	0.98	2.56	3.54	178
C25-H25B...O11 ⁱⁱ	0.98	2.52	3.50	172
C21-H21C...O2 ⁱⁱⁱ	0.98	2.71	3.64	158

Symmetry code: (i) $x, y+1, z$; (ii) $x, -y+1.5, z-0.5$; (iii) $x, y-1, z$.

The structure indicates that each aluminum ion is bonded to three molecules of acetylacetonate (Fig. 2). Aluminum content was found to be 8% from the chemical analysis of (1). The metal content is in agreement with the calculated value of 9.2% for the above structure. Considering the structure and aluminum content, formula can be fixed as $[Al(C_2H_7O_2)_3]$.

The above results show that the title complex prepared from alum, an industrial byproduct, crystallizes as the a -modification in the monoclinic space group $P2_1/c$ and the structure is in accordance with reported observations. The complex volatilizes at 300 °C and hence is useful for chemical vapor deposition of alumina.

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Supplementary data

Crystallographic data (excluding structure factors) for the structure reported for $[Al(acac)_3]$ have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 801839. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK. (Fax: +44-(0)1223-33-6033; Email: deposit@ccdc.cam.ac.uk).

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