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Synthesis and molecular structure of $AlMe[O{=}C(OMe)C_6H_4\text{-}o\text{-}O]_2$. The first structurally characterized five-coordinated simple alkylaluminium chelate complex *,**

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Abstract

The interaction of $AlMe_3$ with 2 equiv. of $O{=}C(OMe)C_6H_4\text{-}o\text{-}OH$ leads to the formation of the mononuclear, five-coordinated aluminium compound $AlMe[O{=}C(OMe)C_6H_4\text{-}o\text{-}O]_2$. The title compound has been characterized by IR, ^1H and ^{27}Al NMR spectroscopies and its structure has been confirmed by X-ray crystallography. The compound crystallizes in the monoclinic space group $C2/c$ with the unit cell parameters $a = 16.144(2)$, $b = 7.703(1)$, $c = 14.792(2)$ Å, $\beta = 112.76(1)°$, $Z = 4$, observed data = 1060, $R = 0.0380$, $R_w = 0.0378$.

Organoaluminium compounds are often used as reagents in organic synthesis and as catalysts or components of catalysts in many catalytical processes. For a better understanding of their role in synthesis and catalysis it is essential to know the coordination ability of aluminium and to study the properties of organoaluminium compounds with coordination other than four. Recently there has been increased interest in three-coordinated sterically crowded aluminium compounds [1]. Several compounds with a higher coordination number have been synthesized and structurally characterized. Besides six- [2] and seven-coordinated [3] compounds special interest has been shown towards five-coordinated species. Of the latter, the most numerous groups are the dimeric organoaluminium compounds [1a,4] (where the two monomeric units, consisting of dialkylaluminium species chelated by a bidentate ligand, are connected by oxygen bridges) and multinuclear aluminium compounds with open and close-chain ligands [5]. Two crystal structures of monomeric monoalkylaluminium complexes with macrocycle ligands containing a five-coordinated aluminium atom in square pyramidal environments have been published so far [5g,h]. Here, we report the synthesis and molecular structure of what is to our knowledge the first five-coordinated simple alkylaluminium chelate complex.

The reaction of $AlMe_3$ with methyl salicylate (mesal H) in 1:2 stoichiometry results in the formation of $AlMe(mesal)_2$ [6*], whose structure has been confirmed by X-ray crystallography [7*] and which is consistent with spectroscopic data [8*]. The molecular structure of $AlMe(mesal)_2$ is shown in Fig. 1. The structure consists of discrete monomeric units with a five-coordinated aluminium atom. The coordination geometry around the Al atom can be described as a distorted trigonal bipyramid. The two mesal anions act as bidentate chelating ligand, forming planar six-membered AlOCCCO rings.

The aluminium atom lies well within the equatorial plane that is defined by methyl carbon C(0) and aryloxide oxygens, O(2) and O(2′). All the bond angles involving Al in this plane are close to 120° (118.28(10)–120.86(7)°). The apical positions are occupied by the

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* Reference number with an asterisk indicates a note in the list of references.

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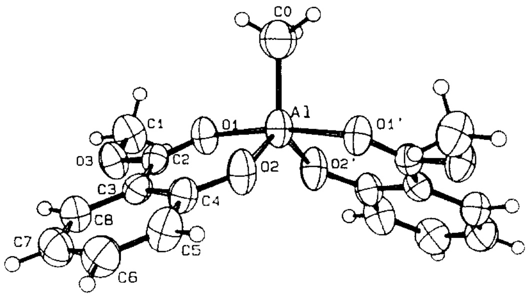

Fig. 1. A view of the AlMe[O=C(OMe)C_6H_4-*o*-O]$_2$ molecule showing the atom labelling scheme. Thermal ellipsoids show 50% probability levels. Selected bond distances (Å) and angles (°): Al–C0, 1.941(5), Al–O1, 1.968(1); Al–O2, 1.773(2); C2–O1, 1.235(2); C4–O2, 1.326(2); O1–Al–O1′, 170.09(9); C0–Al–O2, 120.86(7); C0–Al–O2′, 120.86(7); O2–Al–O2′, 118.28(10).

carbonyl oxygen of ester groups. The angle defined by the two apical substituents, O(1)–Al–O(1′), is 170.05(9)°. The Al–C(0) distance of 1.941(5) Å is at the short end of the range of Al–C lengths 1.942(3)–1.988(6) Å, for five-coordinated monoalkylaluminium species in multinuclear aluminium compounds or in complexes with macrocycle ligands [9]. The covalent aryloxide Al–O distance (1.773(2) Å) is quite short and may be compared to the aryloxide Al–O distance (1.765(5) Å) in the four-coordinated aluminium 0,0′-chelate complex with deprotonated 3-tert-butyl-2-hydroxy-5-methylacetophenone, AlMe(dbmp)[O=C(Me)-C_6H_3(^{t}Bu)O], dbmp = [OC_6H_3(Me)(^{t}Bu)$_2$] [9]. The dative ester Al–O distance (1.968(1) Å) is significantly longer than those observed for the four-coordinated ketone analogue [AlMe(dbmp)O=C(Me)C_6H_3(^{t}Bu)O; 1.836(4) Å] [9] or ester complexes [AlMe(BHT)$_2$O=C-(OMe)Ph; 1.851(7) Å] and AlEt$_2$(BHT)[O=C(OMe)C_6-H_4-*p*-Me] [10] however it is significantly shorter than those we have observed for the five-coordinated ketone complex [AlEt$_2$(O=C(Ph)C(Ph)O]$_2$; 2.145(6) Å] [11].

The coordination of the mesal ligand to the aluminium atom results in the formation of a nearly planar system containing two six-membered rings. The largest deviation from this plane is 0.040(2) Å for the O(1) atom. Within the mesal ligand the carbonyl C(O)–O(2) distance and other C–O and C–C bond distances agree with related bond distances in the ketone and ester adducts of four-coordinated organoaluminium compounds [9,10]. NMR and IR spectroscopies [8] indicate that the structure found for AlMe(mesal)$_2$ in the solid state remains unchanged in solution. The ^{27}Al NMR spectrum shows one resonance at 66 ppm ($W_{1/2}$ = 1740 Hz), consistent with a five-coordinated aluminium atom. The ^{1}H NMR spectrum shows single resonances of the H_3C–Al and H_3C–O protons and four well separated multiplets of the aromatic protons. The IR spectrum shows a ν(C=O) band at 1638 and 1657 cm^{-1}. The decrease in the carbonyl stretching frequency when compared to that of the free ester is consistent with the coordination of the carbonyl group of the ester to aluminium.

AlMe(mesal)$_2$ represents the first five-coordinated simple monomeric alkylaluminium chelate complex containing an aluminium atom in a trigonal bipyramidal environment.

Supplementary material available

Tables of atomic positional and anisotropic thermal parameters, isotropic equivalent parameters, and bond distances and angles (5 pages), and a listing of observed and calculated structure factors (4 pages) can be obtained from the Cambridge Crystallographic Data Centre.

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6 Standard Schlenk techniques were employed, under an atmosphere of nitrogen. To a solution of trimethylaluminium (1.01 g, 14 mmol) in toluene (20 cm^3) was slowly added methyl salicylate (4.25 g, 28 mmol) at −78°C. The solution was warmed to room

temperature in 2 h. The solvent was evaporated *in vacuo* at ambient temperature. The resulting white product was recrystallized from a dichloromethane/diethylether solution at −5°C.

7 Crystal data for $AlO_6C_{17}H_{17}$: monoclinic, space group $C2/c$, unit cell: $a = 16.1441(24)$, $b = 7.7034(10)$, $c = 14.7923(21)$ Å, $\beta = 112.756(11)°$, $V = 1696.4(4)$ Å^3, $Z = 4$, D(calcd) = 1.348 g/cm^3, λ(Mo Kα) = 0.71073 Å (graphite monochromator), $\mu = 1.416$ cm^{-1}, T = 25°C. A colourless crystal (0.52 × 0.14 × 0.28 mm) was sealed under argon in a Lindemann capillary and measured on a P3 (Siemens AG) diffractometer. The intensities were collected up to $2\theta = 50°$ (max $\sin\theta/\lambda = 0.60$) in the ω-2θ mode (scan range 2.0° + Kα_1 − Kα_2 sep.) and various scan speeds between 4.2 and 29.3° min^{-1}. Two check reflections ($20\bar{6}$) and (130) repeated every 70 reflections showed only random ±1.0% variation of net intensity. In total 1660 reflections were measured, of which 1478 were unique ($R_{int} = 0.0155$, $R(\sigma) = 0.0353$) and 1060 observed ($F_o > 3\sigma$). The phase problem was solved by direct methods (G.M. Sheldrick, SHELXS-86, Program for Crystal Structure Determination, University of Göttingen, Germany, 1986). All nonhydrogen atoms were found on the most appropriate E-map, and were anisotropically refined (G.M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, Cambridge, Eng. 1976), $R = 0.066$. The compound showed C_2 point symmetry with the Al–Me bond located on the two-fold axis. Standard difference map techniques were used to locate all H atoms (assuming s.o.f. for H atoms in Me group equal to 1/2). Final $R = 0.0380$, $R_w = 0.0378$ ($w(F) = 0.9186[\sigma^2(F) + 0.00050F^2]^{-1}$), and residual = +0.15/−0.21 eÅ^{-3}.

8 ^{1}H NMR (CH_2Cl_2/C_6D_6,δ): 7.61 (2H,d,6-CH), 7.18 (2H,t,5-CH), 6.82 (2H,d,3-CH), 6.50 (2H,t,4-CH), 3.64 (6H,s,OCH_3), −0.66 (3H,s,Al–CH_3); ^{27}Al NMR [δ in ppm relative to external Al(acac)$_3$]: 66 ($W_{1/2} = 1740$ Hz); IR (in CH_2Cl_2, KBr plates): 1655m, 1638s, 1604w, 1554w, 1476s, 1462s, 1444s, 1420s, 1360s, 1344m, 1200w, 1160m, 1144w, 1110m, 1032w, 960w, 844w, 572w, 532w, 454w, 362w.

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