

An Aluminium-Oxide-Isopropoxide Cluster with Peripheral Ammonia Ligands

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The reaction of toluene solutions of aluminium isopropoxide with ammonia gas, without exclusion of moisture, affords high yields of a decanuclear aluminium-oxide-isopropoxide-ammonia cluster of the composition $[\text{Al}_{10}\text{O}_6(\text{OiPr})_{18}(\text{NH}_3)_8]$. The compact centrosymmetric cluster units feature tetra-, penta- and hexa-coordinate aluminium atoms, tri- and tetra-coordinate interstitial oxygen atoms, and bridging and terminal isopropoxide groups. The ammonia molecules occupy peripheral positions at two types of aluminium atoms.

There is currently considerable interest in the formation, structure and properties of aluminium alkoxide clusters, and their partial hydrolysis products. These compounds are important precursors for the preparation of oxide-based inorganic materials *via* sol-gel and CVD processes [1 - 3].

While the *hydrolysis* of aluminium alkoxides and aryloxides has been studied in detail for many homologues of the series [1], there has never been a systematic study of analogous *ammonolysis* reactions using primary or secondary amines [4], which can lead to mixed alkoxide/amide compounds. Likewise, degradation of alkoxide clusters by tertiary amines or ammonia has rarely been probed [5].

During a study of aluminium alkoxide solvolysis we observed the formation of large colourless, transparent crystals whenever ammonia gas was allowed to enter solutions of aluminium isopropoxide in toluene. A closer investigation of this reaction has shown that moisture does not have to be excluded, but that it is required to obtain the product in satisfactory quantities. An investigation of the composition of the new compound has shown an intriguing polynary stoichiometry, and the structural study has revealed an exceedingly complicated molecular geometry.

Results

For a controlled synthesis of the title compound, freshly distilled aluminium triisopropoxide is

dissolved in toluene and a stream of ammonia gas is passed slowly through this solution at ambient temperature for several hours. The product crystallizes and the crop can be isolated by decantation (75% yield, m.p. 164°C).

The room temperature ^1H and ^{13}C NMR spectra of the compound in di- or trichloromethane solution show poorly resolved sets of signals for different types of isopropoxide groups, while the ^{27}Al NMR spectrum (20°C) has three very broad humps (Fig. 1). None of these spectra is sufficiently resolved to allow assignments of the peaks to individual structural units. There is also a noticeable temperature dependence of the number and shapes of the resonances suggesting dynamic phenomena in solution. FAB mass spectra show fragments with $m/z = 1166.3$ and 1064.0 , which cannot be assigned to meaningful parent groups.

Structure elucidation, therefore, relied mainly on the elemental analysis and the single crystal X-ray diffraction study. However, the elemental analysis suffers from a loss of ammonia during drying of the compound in a vacuum and some solvent inclusion into the crystal (below).

Crystals of the product are triclinic, space group $P\bar{1}$, with one molecule in the unit cell. The asymmetric unit consists of one half of this molecule which is related to the second half by a center of inversion (Fig. 2). The cluster has five crystallographically independent types of aluminium atoms (Al1 - Al5), two of them with a similar environment of oxygen atoms (Al3, Al5) and three with a very

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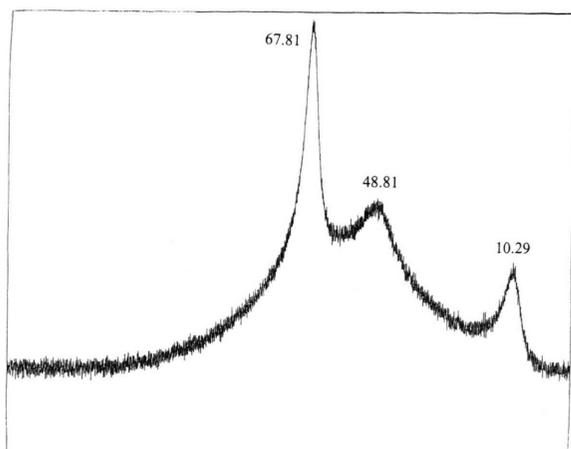


Fig. 1. ^{27}Al NMR spectrum of the title compound (in CD_2Cl_2 , δ rel. aqueous $[\text{Al}(\text{OH})_2]^{3+}$).

different environment of oxygen and nitrogen atoms (Al1, Al2 and Al4). The aluminium atoms in the periphery of the cluster, Al3 and Al5, are in a tetrahedral coordination sphere of three isopropoxide groups and one three-coordinate (μ^3) oxygen atom (O2 and O3, respectively). By contrast, the internal aluminium atoms have either coordination number 5 (Al1 and Al2) or 6 (Al4). Al1 carries two terminal (η^1) and one μ^2 *i*PrO groups together with one μ^4 oxygen atom (O41) and one NH_3 molecule (N11), Al2 has one bridging *i*PrO group, two μ^3 oxygen atoms, one μ^4 oxygen atom (O41), and again one NH_3 molecule (N21), and the coordination polyhedra for both Al1 and Al2 may be described as distorted trigonal bipyramidal. Hexacoordinate Al4 is surrounded by two μ^3 and two μ^4 oxygen atoms and two ammonia molecules in the form of an octahedron with the NH_3 units in *cis*-positions.

The three broad ^{27}Al NMR resonances of solutions of the title compound may thus be assigned to tetra-, penta- and hexa-coordinate aluminium atoms. The relative intensities are in agreement with this assignment, but no further discrimination is possible.

All μ^3 -coordinated oxygen atoms (O2, O3) are coordinated solely to aluminium atoms and have a trigonal planar geometry. This configuration is quite common in aluminium oxide or aluminium silicate structures [6], and the range of bond lengths covered in the present structure is in good agreement with previous data. μ^4 and μ^5 oxygen atoms are less common in molecular oxide chemistry, and

the peculiar coordination geometry of O4 (pseudo-trigonal bipyramidal with one apical position vacant) is particularly rare [7, 8]. However, the structure of an aluminium oxide ethoxide cluster [9] does also contain oxide units in a similar environment, and this agreement supports the structural assignments proposed in the present work.

The ammonia molecules have been identified 1) through a localization and isotropic refinement of the three hydrogen atoms in the structure calculations, and 2) by the rather long Al-N distances as compared to Al-O distances (Caption to Fig. 2). Hydrogen bonding of the ammonia ligands is ruled out by the long distances to all neighbouring units.

There is significant residual electron density in the crystal lattice, which must be ascribed to solvent molecules (toluene, isopropanol) trapped in the lattice. All attempts to corroborate this assumption through the application of various models of disorder have not been successful.

Experimental

Preparation of the compound: Aluminium triisopropoxide (5.0 g, 24.5 mmol) was dissolved in dry toluene (30 ml) and ammonia gas was passed (without drying) through this solution at room temperature for 4 h. The solution was then kept over night at 20°C. The crystals formed were separated by decantation and dried in a vacuum for 5 h [yield 2.90 g (75.6%), m.p. 164°C].

$\text{C}_{54}\text{H}_{150}\text{N}_8\text{Al}_{10}\text{O}_{24}$ (1565.62)

Calcd C 41.43 H 9.66 Al 17.23 N 7.16 %,

Found C 43.15 H 9.50 Al 17.60 N 6.34 %.

^1H NMR (CD_2Cl_2 , 20°C): δ 1.76, 18H, m, Me; 4.00–4.30, 3H, three m, CH; 3.97, 4H, br. s, NH_3 . ^{27}Al NMR (v.s., rel. ext. $[\text{Al}(\text{OH})_2]^{3+}$): δ 10.3, 48.8 and 67.8, three broad resonances (Fig. 1). IR (Nujol): 3166.6 cm^{-1} , $\nu(\text{NH}_3)$.

Structure determination: A specimen of suitable quality and size was mounted in a glass capillary and used for measurements of precise cell constants and intensity data collection. The measurements were made on an Enraf-Nonius CAD-4 diffractometer, using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) with ω scan mode at -91°C. Lp correction was applied, but data were not corrected for absorption [μ ($\text{MoK}\alpha$) = 1.65 cm^{-1}]. The structure was solved by direct methods and completed by full-matrix least-squares techniques against F^2 .

Data for compound $\text{C}_{54}\text{H}_{150}\text{N}_8\text{Al}_{10}\text{O}_{24}$, $M_r = 1565.62$, triclinic, $a = 14.079(1)$, $b = 14.580(1)$, $c = 14.971(2) \text{ \AA}$, $\alpha = 101.24(1)$, $\beta = 101.36(1)$, $\gamma = 111.09(1)^\circ$, space group

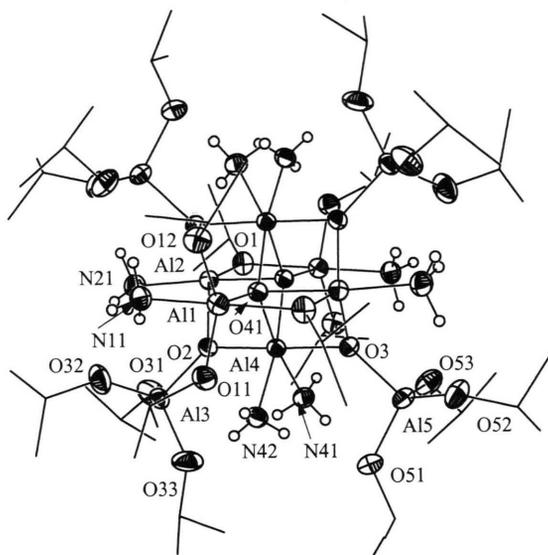


Fig. 2. Molecular structure of the title compound (ORTEP drawing with 50% probability ellipsoids, CH-atoms omitted for clarity). The two halves of the cluster are related by a center of inversion. Selected bond lengths [Å] and angles [°]: Al1-O1 1.999 (2), Al1-O11 1.753 (2), Al1-O12 1.750 (2), Al1-O41 1.837 (2), Al1-N11 2.035 (3), Al2-O1 1.803 (2), Al2-O2 1.797 (2), Al2-O3' 1.780 (2), Al2-O41' 1.961 (2), Al2-N21 1.980 (3), Al3-O2 1.894 (2), Al3-O31 1.732 (3), Al3-O32 1.735 (3), Al3-O33 1.728 (3), Al4-O2 1.778 (2), Al4-O3 1.917 (2), Al4-O41 1.970 (2),

Al4-O41' 1.954 (2), Al4-N41 2.027 (3), Al4-N42 1.997 (3), Al5-O3 1.779 (2), Al5-O51 1.742 (3), Al5-O52 1.738 (3);

Al1-O1-Al2 100.17 (10), Al1-O1-C11 121.3 (2), Al2-O1-C11 135.7 (2), Al2-O2-Al3 124.71 (12), Al2-O2-A4 100.78 (10), Al3-O2-Al4 133.67 (12), Al2'-O3-Al4 99.02 (9), Al2'-O3-Al5 132.28 (12), Al4-O3-Al5 127.00 (11), Al1-O41-Al2' 100.42 (9), Al1-O41-Al4 127.46 (11), Al1-O41-Al4' 128.44 (11), Al4-O41-Al4' 101.32 (9), Al4-O41-Al2' 91.38 (8), Al4'-O41-Al2' 93.20 (9), O11-Al1-O12 121.17 (11), O11-Al1-O41 120.75 (1), O11-Al1-O1' 90.21 (10), O11-Al1-N11 94.06 (12), O12-Al1-O41 117.93 (11), O12-Al1-O1' 97.24 (11), O12-Al1-N11 89.68 (12), O1'-Al1-O41 78.59 (9), O1'-Al1-N11 168.50 (11), O41-Al1-N11 90.07 (10), O2-Al2-O3' 114.08 (10), O2-Al2-O41' 83.50 (9), O2-Al2-O1 124.51 (10), O2-Al2-N21 93.71 (11), O1-Al2-O3' 117.43 (11), O1-Al2-O41' 80.41 (9), O1-Al2-N21 99.52 (12), O3'-Al2-O41' 86.53 (9), O3'-Al2-N21 96.58 (11), O41'-Al2-N21 176.48 (11), O2-Al3-O31 107.15 (12), O2-Al3-O32 102.17 (11), O2-Al2-O33 106.48 (12), O31-Al3-O32 112.8 (2), O31-Al3-O33 112.1 (2), O32-Al3-O33 115.1 (2), O2-Al4-O3 177.25 (9), O2-Al4-O41 98.10 (9), O2-Al4-O41' 81.23 (9), O2-Al4-N41 87.68 (11), O2-Al4-N42 93.43 (11), O3-Al4-O41 82.66 (8), O3-Al4-O41' 96.36 (9), O3-Al4-N41 91.34 (11), O3-Al4-N42 89.12 (11), O41-Al4-O41' 78.68 (9), O41-Al4-N41 172.42 (11), O41-Al4-N42 95.41 (10), O41'-Al4-N41 97.48 (11), O41'-Al4-N42 171.31 (11), N41-Al4-N42 89.10 (12), O3-Al5-O51 105.95 (11), O3-Al5-O52 110.84 (11), O3-Al5-O53 104.39 (11), O51-Al5-O52 111.03 (14), O51-Al5-O53 111.62 (14), O52-Al5-O53 112.61 (14).

$P\bar{1}$ [No. 2], $Z = 1$, $D_{\text{calc}} = 1.088 \text{ g cm}^{-3}$, $F(000) = 852$ e. 9337 intensity data were measured up to $(\sin\theta/\lambda)_{\text{max}} = 0.62 \text{ \AA}^{-1}$, of which 8690 independent structure factors were used for refinement. All non-H atoms were refined with anisotropic displacement parameters. Isopropyl H-atoms were placed in idealized calculated positions and allowed to ride on their carbon atoms. The ammonia H-atoms were located and refined with isotropic contributions. The function minimized was $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$, with $w = 1/\sigma^2(F_o^2) + (ap)^2 + bp$, and $p = (F_o^2 + 2F_c^2)/3$; $a = 0.1440$, $b = 2.91$. The final R and R_w values were 0.0678 [based on $I \geq 2\sigma(I)$] and 0.2120, respectively, for 481 refined parameters; residual electron densities: $+2.827 / -0.479 \text{ e \AA}^{-3}$, which could not be

assigned to a meaningful model. Important interatomic distances and angles are summarized in the corresponding figure caption. Anisotropic thermal parameters, tables of distances and angles, and atomic coordinates have been deposited with Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting CSD No. 408275.

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