A new type of alumoxane obtained by controlled hydrolysis of *N*,*N*-dialkylcarbamato complexes of aluminium; crystal and molecular structure of $[Al_4(\mu_3\text{-}O)_2(O_2CNPr^i_2)_8]$

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The aluminium(III) *N*,*N*-diisopropylcarbamato derivative $[Al_2(O_2CNPr^i_2)_6]$ undergoes hydrolysis with a stoichiometric amount of water giving the μ_3-oxo derivative $[Al_4(\mu_3\text{-}O)_2(O_2CNPr^i_2)_8]$, which is analytically, spectroscopically and structurally characterized.

Hydrolysis of aluminium derivatives is an area of considerable interest, the ultimate goal being a better understanding of the processes leading to aluminium oxides[1] or aluminosilicates[2] from appropriate precursors. In this connection, halo-,[3] alkoxo,[1a,2] and alkyl derivatives[1d,4] of aluminium have been studied extensively. Some alkylalumoxanes[4] have been characterized crystallographically by Barron and coworkers, who obtained them by partial hydrolysis of aluminium alkyls; thus, hydrolysis of $AlBu^i_3$ gave[4b,c] the tetranuclear $[Al_4(\mu_3\text{-}O)_2Bu^i_8]$ together with the octanuclear $[Al_8(\mu_3\text{-}O)_8Bu^i_8]$.

Our earlier work on homoleptic *N*,*N*-dialkylcarbamato complexes of aluminium[5] prompted us to study the hydrolysis of these compounds, and to verify their aptitude as alumoxane precursors. This paper reports the first case of a hydrolytic process involving an aluminium-bonded *N*,*N*-dialkylcarbamato group, and the first member of a new type of alumoxane.

The dinuclear[5] *N*,*N*-diisopropylcarbamato derivative $[Al_2(O_2CNPr^i_2)_6]$ undergoes hydrolysis with a stoichiometric amount of water [eqn. (1)] giving the μ_3-oxo derivative $[Al_4(\mu_3\text{-}O)_2(O_2CNPr^i_2)_8]$.† An alternative, less satisfactory preparative procedure, consists of treating anhydrous $AlCl_3$ and $AlCl_3{\cdot}6H_2O$ in the appropriate molar ratio, with $Pr^i_2NH{-}CO_2$, [eqn. (2)].

$$2[Al_2(O_2CNPr^i_2)_6] + 2H_2O \longrightarrow [Al_4(\mu_3\text{-}O)_2(O_2CNPr^i_2)_8] + 4Pr^i_2NH + 4CO_2 \qquad (1)$$

$$11\ AlCl_3 + AlCl_3{\cdot}6H_2O + 24\ CO_2 + 60\ Pr^i_2NH \longrightarrow 3[Al_4(\mu_3\text{-}O)_2(O_2CNPr^i_2)_8] + 36\ [NH_2Pr^i_2]\ Cl \qquad (2)$$

In the latter case, the toluene soluble μ-oxo derivative is separated by filtration from the substantially insoluble dialkylammonium chloride. X-Ray diffraction‡ has established the molecular structure of the title compound, as the heptane solvated product, to consist of a tetranuclear assembly of aluminium atoms joined together by μ_3-oxo ligands and by carbamato bridges (Fig. 1). The structure contains two $Al_2(\mu_3\text{-}O)(O_2CNPr^i_2)_4$ fragments with the Al(1)–O(1)–Al(2) and the Al(3)–O(2)–Al(4) sequences joined together by bridging carbamato groups and by the third coordination site of the μ_3-oxo ligand. Bridging carbamato groups have also been found in the homoleptic dinuclear precursor $[Al_2(O_2CNPr^i_2)_6]$[5] and in the recently reported alkylcarbamato complexes $[(Me_2Al)_2\{\mu\text{-}O_2CNPr^i_2\}_2]$ and $[(Me_2Al)_2\{(\mu\text{-}O_2CNPr^i_2)_2\}_2Mg]$.[8] The present molecule contains five- [Al(1), Al(3)] and six-coordinate [Al(2), Al(4)] aluminium atoms with distorted trigonal-bipyramidal and octahedral geometries, respectively. It is worth noting that five-coordination to oxygen-containing ligands is uncommon for aluminium; known cases are found in andalusite, Al_2SiO_5[9a] and in an aluminium–barium glycolate.[9b] Drying *in vacuo* at room temp. converts the heptane solvated tetranuclear substance into the desolvated species, through a presumably topotactic process[9c,d] which maintains an elevated degree of crystallinity, as shown by X-ray powder diagrams.§

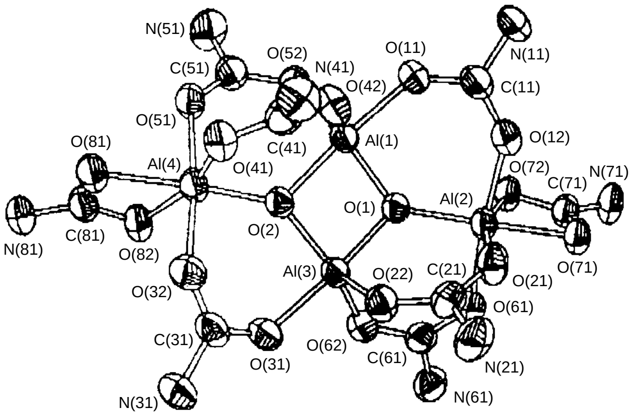
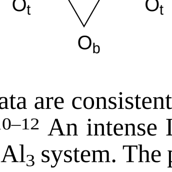


Fig. 1 ZORTEP drawing of $[Al_4(\mu_3\text{-}O)_2(O_2CNPr^i_2)_8]{\cdot}0.5C_7H_{16}$ with the atom numbering scheme. Ellipsoids are at 50% probability, dialkyl groups and solvent are omitted for clarity. Relevant bond distances (Å) and angles (°). Five-coordinate aluminium: Al(1)–O(11) 1.863(2), Al(1)–O(42) 1.836(2), Al(1)–O(52) 1.811(2), Al(1)–O(1) 1.781(2) Al(1)–O(2) 1.832(2), O(42)–Al(1)–O(52) 106.4(1), O(1)–Al(1)–O(42) 119.3(9), O(1)–Al(1)–O(52), 134.3(1). Six-coordinate aluminium: Al(2)–O(12) 1.899(2), Al(2)–O(61) 1.935(2), Al(2)–O(72) 1.958(2), Al(2)–O(71) 1.937(2), Al(2)–O(1) 1.775(2); O(12)–Al(2)–O(72) 89.9(9), O(61)–Al(2)–O(72) 88.1(1), O(21)–Al(2)–O(61) 89.9(1), O(12)–Al(2)–O(21) 90.2(1), O(1)–Al(2)–O(71) 171.3(1). μ_3-Oxygen; Al(1)–O(1)–Al(2) 134.0(1), Al(1)–O(1)–Al(3) 97.2(1), Al(2)–O(1)–Al(3) 120.9(1), Al(1)–O(2)–Al(3) 97.7(1), Al(1)–O(2)–Al(4) 120.9(1), Al(3)–O(2)–Al(4) 134.3(1).

To a first approximation, the six-coordinate aluminium can be regarded as asymmetric, as shown below in a view along two opposite triangular faces of the octahedron [O_b, O_t and O_μ are the oxygen atoms belonging to bridging and terminal carbamato groups, and to the triply bridging oxo group, respectively]. As the tetranuclear aluminium compound crystallizes in the centrosymmetric space group $P\bar{1}$, the two enantiomers in the crystal are related by an inversion centre.



The spectroscopic data are consistent with the literature data for μ-oxo derivatives.[10–12] An intense IR band at 772 cm^{-1} is attributed to the $(\mu_3\text{-}O)Al_3$ system. The presence of a single Al–

O stretching vibration in the tetranuclear aluminium compound suggests either accidental degeneracy or an almost planar $(\mu_3\text{-O})Al_3$ system; the latter hypothesis is consistent with the solid-state data showing that the triply bridging oxides O(1) and O(2) are 0.28 and 0.27 Å, respectively, away from the plane of the three aluminium atoms to which they are connected. On the other hand, the $Al_4(\mu_4\text{-O})_2$ system is also almost planar, the dihedral angle between the Al(1)–Al(2)–Al(3) and Al(1)–Al(3)–Al(4) planes being only 8°. The Al_4O_2 frame closely resembles the tetranuclear alkylalumoxane $[Al_4(\mu_3\text{-O})_2Bu^i{}_8]$ with two μ_3-oxo ligands and a substantially planar Al_4O_2 core. The Al_4O_2 frame is also known in a few cases, namely the anionic $[Al_4O_2Me_{10}]^{2-}$ [4a] and $[Al_4O_2Cl_{10}]^{2-}$ [3c] or the alkylalumoxane $[Al_4(\mu_3\text{-O})_2Bu^i{}_8]$.[4b] The $Al_3(\mu_3\text{-O})$ moieties in $[Al_5(Bu^t)_5(\mu_3\text{-O})_2(\mu_3\text{-OH})_2(\mu\text{-OH})_2(\mu\text{-O}_2CPh)_2]\cdot MeCN$,[1d] containing five-coordinate aluminium, show Al–O distances in the range 1.785(4)–1.827(3) Å, similar to those observed in our case; the Al–O–Al angles are 106.1(2), 107.1(2) and 130.0(2)°, corresponding to a greater deviation from planarity.

Despite the low symmetry of the aluminium environment, the NMR data are relatively simple. The broad ^{27}Al NMR resonance at δ 4.0 with a shoulder at δ *ca*. 50 is suggestive of non-equivalent aluminium centres[13a] broadened by the large quadrupole moment of the metal.[13b] The ^{13}C NMR spectrum shows three main O_2CNR_2 resonances due to non-equivalent carbamato groups. The ^1H NMR spectra indicate the presence of non-equivalent alkyl groups within the tetranuclear compound; fast rotation around the C–N bond, on the NMR timescale, is further suggested by the observation of two main CH (multiplets) and four main CH_3 (doublets) resonances.

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Footnotes and References

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† Anhydrous $AlCl_3$ (7.65 g, 57.37 mmol) was added to a toluene solution (400 ml) of diisopropylamine (60.3 ml, 430 mmol) presaturated with CO_2. The mixture was stirred for 3 d under carbon dioxide at room temp. The dialkylammonium chloride was filtered off and washed with toluene (3 × 50 ml) and the colourless filtrate was hydrolyzed under a dinitrogen atmosphere by dropwise addition of water (0.5 ml, 27.78 mmol) dissolved in thf (350 ml), corresponding to a Al/H_2O molar ratio of 2.07. Vacuum–dinitrogen cycles were repeated several times during the hydrolysis. The volatiles were then removed *in vacuo*; the solid residue was dried for 6 h at 50 °C and heptane (250 ml) was then added. The resulting suspension was filtered and the colourless μ-oxo derivative was dried *in vacuo* at room temp. for several hours. Yield 12.29 g, 66%. Anal. Calc. for $C_{56}H_{112}Al_4N_8O_{18}$: Al, 8.3; CO_2, 27.2. Found: Al, 8.0; CO_2, 26.7%. Samples of the vacuum-dried polycrystalline substance gave an X-ray diffraction diagram (dry argon, Siemens D5000 diffractometer) with the following parameters [spacings *d*/Å, intensities (%) in parentheses]: 14.091(21), 13.156(3), 12.079(75), 11.842(100), 10.659(44), 9.240(4), 8.634(12), 8.085(6), 7.352(3), 7.011(12), 6.429(9), 6.239(3), 5.894(6), 5.581(10), 5.412(8), 5.300(17), 5.143(8), 4.634(9), 4.530(4), 4.395(6), 4.316(5), 4.191(3), 4.040(4), 3.948(3), 3.790(3), 3.659(4), 3.605(3), 3.531(3), 3.119(3). *Selected spectroscopic data*, NMR (benzene, δ); ^1H: 1.09 (d), 1.27 (d), 1.34 (d), 1.45 (d), 3.86 (m), 4.40 (m); ^{27}Al: 3.5 (s), *ca*. 50(sh), with respect to $[Al(H_2O)_6]Cl_3$; ^{13}C: 160.2, 161.4, 167.1 (O_2CNR_2). IR (cm^{-1}, Nujol, PCTFE): 1613s, 1580s (br), 1520s (br), 1460s, 1391s, 1380s, 1361s, 1319m, 1262w, 1216s, 1164s, 1136s, 1075s, 1062m, 1038m, 922m, 902m, 873m, 817m, 805s, 772s $(\mu_3\text{-O})_3$, 689m, 629s, 564s, 540m, 514m, 476s, 438m.

‡ X-Ray quality single crystals of the heptane-solvated substance were obtained from hot dry heptane by slow cooling to room temp.; the crystals were not subjected to drying *in vacuo* in order to prevent loss of heptane and formation of the microcrystalline unsolvated product (*vide infra*). *Crystal data* for $[Al_4(\mu_3\text{-O})_2(O_2CNPr^i{}_2)_8]\cdot 0.5C_7H_{16}$: $C_{59.5}H_{120}Al_4N_8O_{18}$, M = 1343.6, triclinic, space group $P\bar{1}$, a = 14.937(3), b = 16.534(3), c = 18.039(4) Å; α = 89.23(1); β = 71.83(2); γ = 82.39(1)°; Z = 2; U = 4193(2) Å^3; D_c = 1.064 g cm^{-3}; Cu-Kα radiation (λ = 1.541 84 Å). Colourless blocks, 0.8 × 0.5 × 0.5 mm, T = 203 K, 15576 reflections collected, θ range 5.12–65.05°, 13 868 independent reflections, 11639 observed $[I \geqslant 2\sigma(I)]$, ω-scans. Structure calculation: data reduction SDP,[7a] solution SHELXS86,[7b] refinement SHELXL93[7c] molecular graphics ZORTEP,[7d] 1215 parameters, R_1 = 0.064, wR_2 = 0.209 for all independent reflections, GOF = 1.060, μ = 1.009 mm^{-1}, absorption correction: ψ-scans (T_{min} = 0.970, T_{max} = 1.000). CCDC 182/555. Further details of the crystal structure investigations may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, by quoting the depository number CSD 406324.

§ A single crystal of the solvated product, after drying *in vacuo* at room temp. was converted to the polycrystalline solid, and gave the following X-ray powder diagram [Debye–Scherrer camera, spacings *d*/Å, intensities (%) in parentheses]: 13.9(78), 12.1(86), 11.7(61), 10.4(100), 8.52(53), 6.97(61), 6.33(46), 6.26(25), 5.86(3.6), 5.55(43), 5.39(21), 5.27(82), 4.78(3.6), 4.66(39), 4.56(14), 4.434(18), 4.318(32), 4.186(7). The diagram is consistent with that reported above for the unsolvated product, and different from that calculated[6] on the basis of the single-crystal parameters.

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