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Isolation of new polynuclear aluminium amides; trinuclear $[AlCl(MeNCH_2CH_2NMe)_2(Al(NMe_2)Cl)(Al(NMe_2)_2)]$ and fluxional adamantane-like $[Al_4Cl_2(NMe_2)_6(NMe)O]$

Graham Leggett, Majid Motevalli, Alice C. Sullivan *

Department of Chemistry, Queen Mary and Westfield College, Mile End Road, London E1 4NS, UK

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Abstract

In attempted transamination reactions involving $[Al_2(NMe_2)_6]$ and the amines, *N*,*N*′-dimethylethylenediamine, DMEDA, or diethylenetriamine, DETA, insoluble white powders were formed. Two unexpected compounds, trinuclear $[AlCl(MeNCH_2CH_2NMe)_2(Al(NMe_2)Cl)(Al(NMe_2)_2)]$ (**1**) and adamantane-like $[Al_4Cl_2(NMe_2)_6(NMe)O]$ (**2**) were isolated in similar reactions where the aluminium amide sample $[Al_2(NMe_2)_6]$ contained some 1% residual chloride. Compound **2** was also identified (by NMR and mass spectroscopy) as the major product from the reaction between Al_2Cl_6 and $LiNMe_2$ (1:5) in the presence of traces of water. The compounds **1** and **2** have been characterized by X-ray crystallography, mass spectroscopy and NMR. Variable temperature solution phase proton NMR shows that there is inversion at nitrogen in the bridging amides in adamantanoid structure **2**.

Keywords: Aluminium; Amides; Fluxional; Polynuclear

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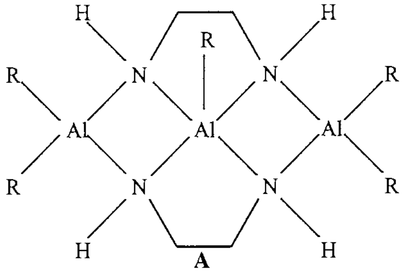
1. Introduction

Transamination represents one possible route to aluminium amide compounds [1,2]. In this reaction the more volatile amine is eliminated, yields are generally quantitative and purification simple.

$$L_nMNR_2 + HNR'_2 \rightarrow L_nMNR'_2 + HNR_2.$$

Transaminations involving elimination of dimethylamine, $HNMe_2$, have been reported for relatively few examples. In contrast reactions of organoaluminium compounds with amines involving elimination of alkane are well documented. Amido aluminium compounds exhibit variable degrees of association [3]. The reactions of ethylenediamine with trimethylaluminium and triethylaluminium in a 2:3 molar ratio give the trinuclear compounds $MeAl[(HN(CH_2)_2NH)AlMe_2]_2$ and $EtAl[(HN(CH_2)_2NH)AlEt_2]_2$, respectively, with structure A [4].



A

The same compounds are formed from the reaction of ethylenediamine with the dimers $[Al_2R'_4(NEt_2)_2]$ ($R' = Me$, Et) demonstrating the variety of approaches that can be employed to produce a particular compound [5].

$$3Al_2(NEt_2)_2R'_4 + 4H_2NCH_2CH_2NH_2$$
$$\rightarrow 2[AlR'][HNCH_2CH_2NHAlR'_2]_2 + 6Et_2NH + 2R'H$$

Tetranuclear amido aluminium complexes $[Al(CH_3)]_2[HN(CH_2)_3N(CH_2)_3NH]_2[Al(CH_3)_2]_2$ and $[Al(CH_3)]_2[HN(CH_2)_2N(CH_2)_2NH]_2[Al(CH_3)_2]_2$ containing tridentate amido ligands may be obtained from trimethylaluminium and the tridentate amines, 3,3′-iminobispropylamide and DETA [6].

We were originally interested in carrying out similar reactions between DMEDA or DETA and

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* Corresponding author.

E-mail address: a.c.sullivan@qmw.ac.uk (A.C. Sullivan)

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$[Al_2(NMe_2)_6]$. We report here on two unexpected amidoaluminium compounds $[AlCl(MeNCH_2CH_2NMe)_2(Al(NMe_2)Cl)(Al(NMe_2)_2)]$ (**1**) and $[Al_4Cl_2(NMe_2)_6(NMe)O]$ (**2**) which we isolated in the course of this work. In several attempts to prepare the unknown amidoaluminium chloride compound $[Al_2Cl(NMe_2)_5]$ (from Al_2Cl_6 and $LiNMe_2$ (1:5)) as a potential precursor for compounds like **1** and **2**, the adamantanoid compound **2** was identified as a major product. We report on the structural characterization of both **1** and **2** and on the unusual fluxional behavior of **2**. The structural features of both compounds give an indication of their origin and possibilities for rational syntheses of a series of similar compounds.

2. Isolation of compounds $[AlCl(MeNCH_2CH_2NMe)_2(Al(NMe_2)Cl)(Al(NMe_2)_2)]$ (1) and $[Al_4Cl_2[N(CH_3)_2]_2[N(CH_3)_2]_4(NCH_3)O]$ (2)

The starting material $[Al_2(NMe_2)_6]$ used in this work was prepared as described in the literature via the reaction of aluminium trichloride with lithium dimethylamide [7]. Transamination reactions were carried out in petroleum ether using $[Al_2(NMe_2)_6]$ (recrystallized and sublimed prior to use) and DMEDA, or DETA in 2:3 and 1:1 molar ratio, respectively. The target product compounds were trinuclear $[AlNMe_2(MeNCH_2CH_2NMeAl(NMe_2)_2)_2]$ and tertranuclear $[AlNMe_2]_2[HN(CH_2)_2N(CH_2)_2NH]_2[Al(NMe_2)_2]_2$ analogues of the reported organoaluminium compounds mentioned above. In the event insoluble white powders (m.p. > 300°C) were deposited from these reactions and no hydrocarbon soluble products could be isolated. These white powders were not investigated further. Similar transamination reactions with DMEDA in petroleum ether, but where the aluminium amide used had been recrystallized and not sublimed prior to use and which was subsequently found to contain 1% Cl, also resulted in deposition of an intractable white solid (m.p. > 300°C) as the major product. However the filtered petroleum ether mother liquor gave a small quantity of clear, colorless, plate-like crystals at room temperature. The reaction was repeated several times with the same result. X-ray crystallography revealed the trinuclear structure $[AlCl(MeNCH_2CH_2NMe)_2(Al(NMe_2)Cl)(Al(NMe_2)_2)]$ (**1**) shown in Fig. 1 similar to that of $MeAl[(HN(CH_2)_2NH)AlMe_2]_2$. We did not attempt a specific rational synthesis for compound **1**. However the structural composition of **1** suggests reactions between amidoaluminium chlorides and polydentate amines can be a source of chloride containing polynuclear compounds.

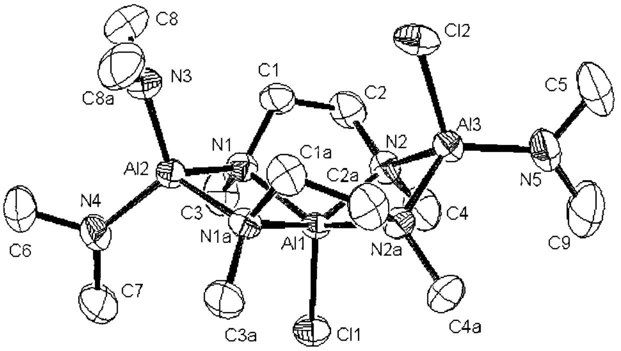

Fig. 1. Molecular structure of compound **1**. Thermal ellipsoids show 30% probability levels; hydrogen atoms have been omitted.

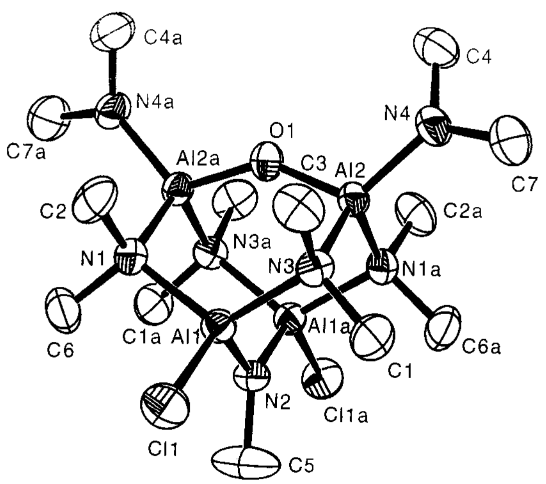

Fig. 2. Molecular structure of compound **2**. Thermal ellipsoids show 30% probability levels; hydrogen atoms have been omitted.

In reactions with DETA where the aluminium amide sample used had 1% Cl the bulk product was again an intractable white powder. However the filtered diethyl ether washings from this solid gave a small quantity of colorless needles of a single compound subsequently identified as the adamantanoid compound $[Al_4Cl_2(NMe_2)_6(NMe)O]$ (**2**) with structure shown in Fig. 2.

The amidoaluminium chloride precursors for chlorinated compounds **1** and **2** above are not immediately obvious. The compounds $[AlCl(NMe_2)_2]_2$ [8] and $[AlCl_2(NMe_2)]$ [9] have been reported. We carried out the reaction between $[Al_2Cl_6]$ and $LiNMe_2$ in a 1:5 molar ratio in order to synthesize the unknown chlorinated compound $[Al_2Cl(NMe_2)_5]$, as a potential precursor to compounds like **1** and **2**. Aluminium trichloride was added to a cooled (−20°C) slurry of lithium dimethylamide in petroleum spirit (b.p. 60–80°C). The mixture was refluxed for ca. 12 h and a white solid was obtained from the cooled concentrated solution. ^1H-NMR indicated a mixture of compounds had formed but clearly showed that the adamantanoid compound $[Al_4Cl_2(NMe_2)_6(NMe)O]$ (**2**) was present among these products and its presence and identity was confirmed by mass spectroscopy, molecular ion $[C_{13}H_{39}Al_4Cl_2N_7O]^+$ *m/e* 487.1890. A molecular ion associated

Table 1
Bond lengths (Å) and angles (°) for compound **1** [a]

Bond lengths			
Al(1)–N(1) # 1	1.994(2)	Al(3)–N(2)	1.911(2)
Al(1)–N(1)	1.994(2)	Al(3)–Cl(2)	2.1403(17)
Al(1)–N(2)	2.021(2)	N(1)–C(1)	1.479(3)
Al(1)–N(2) # 1	2.021(2)	N(1)–C(3)	1.488(4)
Al(1)–Cl(1)	2.1413(14)	N(2)–C(2)	1.490(4)
Al(1)–Al(3)	2.8717(16)	N(2)–C(4)	1.494(4)
Al(1)–Al(2)	2.8772(17)	N(3)–C(8)	1.439(4)
Al(2)–N(3)	1.797(3)	N(3)–C(8) # 1	1.439(4)
Al(2)–N(4)	1.800(3)	N(4)–C(7)	1.434(6)
Al(2)–N(1)	1.933(2)	N(4)–C(6)	1.446(6)
Al(2)–N(1) # 1	1.933(2)	N(5)–C(9)	1.437(7)
Al(3)–N(5)	1.775(4)	N(5)–C(5)	1.454(7)
Al(3)–N(2) # 1	1.911(2)	C(1)–C(2)	1.515(4)
Bond angles			
N(1) # 1–Al(1)–N(1)	83.80(13)	C(1)–N(1)–C(3)	109.5(2)
N(1) # 1–Al(1)–N(2)	143.34(10)	C(1)–N(1)–Al(2)	116.48(18)
N(1)–Al(1)–N(2)	85.98(9)	C(3)–N(1)–Al(2)	116.42(18)
N(1) # 1–Al(1)–N(2) # 1	85.98(9)	C(1)–N(1)–Al(1)	102.53(16)
N(1)–Al(1)–N(2) # 1	143.34(10)	C(3)–N(1)–Al(1)	116.20(18)
N(2)–Al(1)–N(2) # 1	81.55(13)	Al(2)–N(1)–Al(1)	94.22(10)
N(1) # 1–Al(1)–Cl(1)	108.10(7)	C(2)–N(2)–C(4)	109.2(3)
N(1)–Al(1)–Cl(1)	108.10(7)	C(2)–N(2)–Al(3)	118.47(18)
N(2)–Al(1)–Cl(1)	108.54(7)	C(4)–N(2)–Al(3)	110.84(19)
N(2) # 1–Al(1)–Cl(1)	108.54(7)	C(2)–N(2)–Al(1)	109.37(17)
Al(3)–Al(1)–Al(2)	125.54(5)	C(4)–N(2)–Al(1)	114.60(19)
N(3)–Al(2)–N(4)	114.92(17)	Al(3)–N(2)–Al(1)	93.79(10)
N(3)–Al(2)–N(1)	112.51(10)	C(8)–N(3)–C(8) # 1	111.9(4)
N(4)–Al(2)–N(1)	113.38(10)	C(8)–N(3)–Al(2)	123.43(19)
N(3)–Al(2)–N(1) # 1	112.51(10)	C(8) # 1–N(3)–Al(2)	123.4(2)
N(4)–Al(2)–N(1) # 1	113.38(10)	C(7)–N(4)–C(6)	110.3(4)
N(1)–Al(2)–N(1) # 1	87.08(13)	C(7)–N(4)–Al(2)	129.0(3)
N(5)–Al(3)–N(2) # 1	120.01(11)	C(6)–N(4)–Al(2)	120.7(3)
N(5)–Al(3)–N(2)	120.01(11)	C(9)–N(5)–C(5)	109.3(4)
N(2) # 1–Al(3)–N(2)	87.36(14)	C(9)–N(5)–Al(3)	128.4(4)
N(5)–Al(3)–Cl(2)	111.32(15)	C(5)–N(5)–Al(3)	122.3(4)
N(2) # 1–Al(3)–Cl(2)	107.75(8)	N(1)–C(1)–C(2)	110.6(2)
N(2)–Al(3)–Cl(2)	107.75(8)	N(2)–C(2)–C(1)	108.8(2)

[a] Symmetry transformations used to generate equivalent atoms: # 1 *x*, −*y*+1/2, *z*.

with the target compound [$Al_2Cl(NMe_2)_5$] was not seen. In related work Noth and Konrad recovered starting material but also isolated the adamantane-like compound [$Al_4Cl_4[N(CH_3)_2]_4(NCH_3)_2$] (in 9% yield) following the pyrolysis of [$AlCl(NMe_2)_2]_2$ at 250°C [10]. They proposed a mechanism involving elimination of the amine, NMe_3, from the intermediate [$(Me_2NAlCl)_2$-μ-NMe]. It is possible that a similar process starting from [$Al_2Cl(NMe_2)_5$] could give an adamantane-like compound [$Al_4Cl_2(NMe_2)_6(NMe)_2$] which closely resembles [$Al_4Cl_2(NMe_2)_6(NMe)O$] (**2**). However this does not account for the origin of the oxo-bridge in **2** and at this point we can only speculate that its presence is due to adventitious traces of water or oxygen. Its likely that a series of oxo-bridged cage structures like **2** may be available at relatively low temperature by deliberate addition of stoichiometric quantities of water to amidoaluminium chloride precursors and this will form the basis of some further work.

The new adamantane-like compound **2** was characterized using single-crystal X-ray diffraction, high-resolution mass spectrometry and was further studied using variable temperature ^{1}H-NMR.

3. Characterization of [$AlCl(MeNCH_2CH_2NMe)_2$-($Al(NMe_2)Cl$)($Al(NMe_2)_2$)] (1)

The X-ray crystal structure of **1** is shown in Fig. 1 and bond distances and angles are given in Table 1. Similar structures have been reported for MeAl[(HN-$(CH_2)_2$NH)$AlMe_2]_2$, EtAl[(HN$(CH_2)_2$NH)$AlEt_2]_2$ [4] and HAl[(EtN$(CH_2)_2$NEt)$AlH_2]_2$ [11]. The molecule **1** contains two four-membered Al_2N_2 rings and two five-membered AlC_2N_2 rings. In the related compound MeAl[(HN$(CH_2)_2$NH)$AlMe_2]_2$ the central aluminium with coordination $AlCN_4$ is in a distorted trigonal bipyramidal environment where the axial coordination sites are occupied by the nitrogen atoms of one of the chelating amide groups and the equatorial sites by nitrogens from the other chelating amide and the terminal methyl group [4]. Within this fragment N–Al–N angles are 125.4(1) and 149.2(1)°. The central Al(1) in **1** however adopts a distorted square pyramidal geometry with Al(1) sitting below the plane of the nitrogen donor atoms. The comparable bond angles N(1) # 1–Al(1)–N(2) and N(1)–Al(1)–N(2) # 1 are identical in **1** with a value of 143.34(10)°. The polyhedral framework in **1** is considerably more symmetrical than in MeAl[(HN$(CH_2)_2$NH)$AlMe_2]_2$ despite the unsymmetrical substitution at the edge-bridging aluminiums (there are two terminal NMe_2 groups coordinated to Al(2) with one NMe_2 group and one chloride group on Al(3)). The angles subtended by Al(2) and Al(3) are almost identical. The terminal methyl groups of the chelating amide ligands are proximal to the terminal chloride on the central aluminium atom while the ethylene bridges extend above the central N4 plane producing the cradle shaped core observed. The bond lengths of Al(1)–N(1) # 1 and Al(1)–N(1) are 1.994(2) Å while Al(1)–N(2) and Al(1)–N(2) # 1 are 2.021(2) Å which are close to the Al–N distances in MeAl-[(HN$(CH_2)_2$NH)$AlMe_2]_2$.

It is not possible to unambiguously assign either the ^{13}C-NMR (consisting of two distinct groups of sharp peaks, six peaks between δ 37 and 44 ppm and a further three peaks between 50 and 52 ppm) or proton NMR spectrum (at least seven peaks, some overlap ping, between δ 2.3–2.8ppm) recorded for **1**. The complex peak patterns in both spectra may indicate that there are distinct magnetic environments associated with the CH_2 groups in the ethylene bridges and methyl groups attached to both terminal and bridging nitrogens, in-keeping with the solid-state structure.

The solid-state structure is retained in the gas phase. The most intense peak observed in the spectrum at m/e 455.1981 (100%), can be assigned to the molecular ion with the formula $[C_{14}H_{38}Al_3Cl_2N_7]^+$.

3.1. Characterization of $[Al_4Cl_2(NMe_2)_6(NMe)O]$ (**2**)

There are many stable inorganic compounds with adamantane-like skeletons containing a wide range of elements positioned at both the bridgehead and in bridging positions and these have been reviewed [12]. The X-ray crystal structure of **2** is shown in Fig. 2 with bond lengths and angles in Table 2. The structure is similar to that reported by Thewalt and Kawada [13] for $[Al_4Cl_4(NMe_2)_4(NMe)_2]$. Compound **2** belongs to point group C_{2v} where the symmetry is crystallographically imposed; two dimethylamido and the two chloride groups are terminal while the oxo-, an imido, and two amido groups take up bridging coordination modes such that the oxo and imido groups each bridge a different pair of aluminium atoms. The imido bridge Al–N–Al bond angles in the compound $[Al_4Cl_4(NMe_2)_4(NMe)_2]$ are 121.2° compared to 119.52(13)° in the compound **2**. The presence of an Al–O–Al oxo bridge in **2** with the angle 143.20(14)° may have the effect of reducing strain in the framework. The Al–N–Al bridging amido bond angles in **2** Al(1)–N(3)–Al(2) (105.82(8)°) and Al(1)–N(2)–Al(1) # 1 (106.38(8)°) are very similar to those in $[Al_4Cl_4[NMe_2]_4(NMe)_2]$ (107.2°).

Table 2
Bond lengths (Å) and angles (°) for **2** [a]

Bond lengths			
Al(1)–N(2)	1.7920(13)	N(1)–C(2)	1.495(3)
Al(1)–N(1)	1.9281(18)	N(1)–Al(2) # 1	1.9565(18)
Al(1)–N(3)	1.9423(18)	N(2)–C(5)	1.456(4)
Al(1)–Cl(1)	2.1557(8)	N(2)–Al(1) # 1	1.7920(13)
Al(2)–O(1)	1.6979(9)	N(3)–C(3)	1.496(3)
Al(2)–N(4)	1.7906(18)	N(3)–C(1)	1.501(3)
Al(2)–N(3)	1.9515(17)	N(4)–C(7)	1.436(3)
Al(2)–N(1) # 1	1.9565(18)	N(4)–C(4)	1.452(3)
N(1)–C(6)	1.492(3)	O(1)–Al(2) # 1	1.6979(9)
Bond angles			
N(2)–Al(1)–N(1)	106.44(6)	C(2)–N(1)–Al(2) # 1	106.01(14)
N(2)–Al(1)–N(3)	107.29(7)	Al(1)–N(1)–Al(2) # 1	106.38(8)
N(1)–Al(1)–N(3)	115.38(7)	C(5)–N(2)–Al(1)	120.24(6)
N(2)–Al(1)–Cl(1)	117.31(7)	C(5)–N(2)–Al(1) # 1	120.24(6)
N(1)–Al(1)–Cl(1)	105.36(6)	Al(1)–N(2)–Al(1) # 1	119.52(13)
N(3)–Al(1)–Cl(1)	105.46(6)	C(3)–N(3)–C(1)	107.12(18)
O(1)–Al(2)–N(4)	117.87(10)	C(3)–N(3)–Al(1)	115.03(14)
O(1)–Al(2)–N(3)	101.18(7)	C(1)–N(3)–Al(1)	105.48(14)
N(4)–Al(2)–N(3)	113.94(8)	C(3)–N(3)–Al(2)	105.68(13)
O(1)–Al(2)–N(1) # 1	101.18(7)	C(1)–N(3)–Al(2)	118.14(15)
N(4)–Al(2)–N(1) # 1	111.94(8)	Al(1)–N(3)–Al(2)	105.82(8)
N(3)–Al(2)–N(1) # 1	109.52(8)	C(7)–N(4)–C(4)	111.2(2)
C(6)–N(1)–C(2)	106.69(19)	C(7)–N(4)–Al(2)	127.82(17)
C(6)–N(1)–Al(1)	107.82(15)	C(4)–N(4)–Al(2)	119.94(16)
C(2)–N(1)–Al(1)	114.77(14)	Al(2)–O(1)–Al(2) # 1	143.20(14)
C(6)–N(1)–Al(2) # 1	115.44(14)		

[a] Symmetry transformations used to generate equivalent atoms: # 1 y, x, $-z$.

The assignment of peaks for the molecular ion isotopic cluster in the mass spectrum of $[Al_4Cl_2(NMe_2)_6(NMe)O]$ (**2**) is summarized in Table 3. Additional peaks observed for the measured masses 452.1928, 445.0068 and 399.0765 correspond to the loss of a terminal chlorine, one NMe_2 group and two NMe_2 groups, respectively

4. Variable temperature ^{1}H-NMR of $[Al_4Cl_2(NMe_2)_6(NMe)O]$

It is clear from the solid state structure of **2**, that the two methyls in each of the bridging amide groups are non-equivalent and that there are two equivalent sets of methyls with approximate *cis* or *trans* relationships to neighboring terminal Al–Cl groups. A broad peak is observed in the spectrum recorded at 303 K at 2.53 ppm for the bridging dimethylamido ligands (instead of two sharp singlets for two magnetically distinct methyl environments defined above). On cooling the sample to room temperature (270 K) the broad resonance splits into two sharp singlets of equal intensity. Coalescence occurred at 297 K giving $\Delta G^{\neq} = 88$ kJ mol^{-1}. The most likely exchange mechanism is a reversible bridge cleavage incorporating classic nitrogen inversion. A similar process is probably operating in the related compound $[Al_4Cl_4(NMe)_2)_4(NMe)_2]$, but would not be detected by NMR because the bridging amido methyls are magnetically equivalent in the frozen structure.

5. Conclusions

The formation of $[AlCl(MeNCH_2CH_2NMe)_2(Al(NMe_2)Cl)(Al(NMe_2)_2)]$ (**1**) above indicates that an interesting range of chlorinated polynuclear compounds may be available from reactions between amidoaluminium chlorides and polydentate amines. The oxo-bridged adamantanoid compound **2** was identified (by NMR and mass spectroscopy) among the products from the reaction between Al_2Cl_6 and $LiNMe_2$ (1:5). The target compound $[Al_2Cl(NMe_2)_5]$ was not isolated. Compound **2** is apparently formed under much milder conditions than the related $[Al_4Cl_4(NMe_2)_4(NMe)_2]$, which requires pyrolysis of $[AlCl(NMe_2)_2]_2$ at 250°C. In future work we will investigate products from reactions between amidoaluminium chlorides and chelating

Table 3
Molecular ion isotopic cluster from compound **2**

Measured mass	Assignment	Possible formulae	Calculated intensity (%)	Observed intensity (%)
487.1907	Molecular ion	$C_{13}H_{39}Al_4Cl_2N_7O$	100	100
488.1883	Molecular ion + 1 au	$^{12}C_{12}^{13}CH_{39}Al_4Cl_2N_7O$ $C_{13}H_{39}Al_4Cl_2^{14}N_6^{15}NO$	16.82	18.3
489.1910	Molecular ion + 2 au	$C_{13}H_{39}Al_4^{35}Cl^{37}N_7O$	64.5	65
490.1912	Molecular ion + 3 au	$^{12}C_{12}^{13}CH_{39}Al_4^{35}Cl^{37}ClN_7O$ $C_{13}H_{39}Al_4^{35}Cl^{37}Cl^{14}N_6^{15}NO$	10.93	10.97
491.1758	Molecular ion + 4 au	$C_{13}H_{39}Al_4^{37}Cl_2N_7O$	10.55	10.56

amines and the possible synthesis of oxo-bridged cage compounds by deliberate addition of stoichiometric quantities of water to appropriate amidoaluminium chlorides.

6. Experimental

All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques and a conventional nitrogen filled glove box. The DMEDA and DETA were dried over molecular sieves (4 Å) prior to use. Melting points were recorded on samples sealed in capillaries under nitrogen. ^1H- and ^{13}C-NMR spectra were obtained at ambient temperature on a Bruker WH250 (^1H operating frequency 250 MHz) spectrometer. Mass spectral data were obtained on a Kratos MS-50-TC spectrometer. Single-crystal X-ray intensity data were collected on an Enraf–Nonius CAD-4 diffractometer operating in the $\omega/2\theta$ mode.

6.1. *Attempted preparation of [Al(NMe)$_2$(MeNCH$_2$-CH$_2$NMeAl(NMe$_2$))$_2$]: isolation of [AlCl(MeNCH$_2$-CH$_2$NMe)$_2$(Al(NMe$_2$)Cl)(Al(NMe$_2$)$_2$)]*

A sample of $[Al_2(NMe_2)_6]$ (2.21 g) prepared as described [1], but omitting the sublimation step, was dissolved in petroleum spirits (ca. 50 cm^3) and treated dropwise with *N*,*N′*-dimethylethylenediamine (0.009 mol) in petroleum spirits (ca. 20cm^3). A heavy white precipitate was formed and heat was evolved. The reaction mixture was stirred for 12 h. The suspended solid was allowed to settle and the straw-yellow supernatant solution was transferred into a second flask. A small quantity of plate-like, colorless, crystals (0.25 g, m.p. 153–155°C) almost immediately formed in the decanted solution. MS: m/e 455.1981 (100%) [M$^+$]. The residual white solid (m.p. > 300°C) failed to dissolve in a range of solvents.

6.2. *Isolation of [Al$_4$Cl$_2$(NMe$_2$)$_6$(NMe)O]*

A sample of $[Al_2(NMe_2)_6]$ prepared as described [1], but omitting the sublimation step, (0.26 g, 0.8 mmol) was dissolved in petroleum spirits (50 cm^3) and diethylenetriamine (0.8 mmol) added. A white solid was formed and a white vapor was generated. The reaction mixture was refluxed for 2 h. The solvent was removed in vacuo to leave a white solid. The solid was washed with diethyl ether and the straw-yellow washings filtered from the insoluble material. The solution was cooled to 5°C overnight to give colorless, needle-like crystals (0.05 g) of **2**. M.p. = 160°C. MS: m/e 487.1907 [M$^+$].^1H-NMR ($CDCl_3$, 250 MHz): δ 2.5 (s, 24H, bridging *NMe$_2$*), 2.6 (s, 12H, terminal *NMe$_2$*), 3.00 (3H, s, bridging *NMe*).

Both the above procedures were repeated with samples of $[Al_2(NMe_2)_6]$ purified by recrystallization followed by sublimation and containing no chlorinated species. In both cases insoluble white solids were deposited and no hydrocarbon soluble products could be isolated.

6.3. *Attempted preparation of [Al$_2$Cl(NMe$_2$)$_5$]; evidence for formation of [Al$_4$Cl$_2$(NMe$_2$)$_6$(NMe)O]*

$[Al_2Cl_6]$ (2.09 g, 8 mmol) was added to a suspension of $LiNMe_2$ (2.00, 40 mmol) in petroleum ether. The reaction mixture was refluxed for 2 h. The solvent was reduced in vacuo and the remaining solution cooled at − 25°C overnight to leave a white solid (1.7 g). ^1H-NMR ($CDCl_3$, 250 MHz): peaks due to compound **2** present. MS: m/e 487.1907 [M$^+$].

7. Crystallography

Data were collected on a CAD4 diffractometer using Mo–K$_\alpha$ ($\lambda = 0.71069$ Å) radiation and corrected for absorption using ψ-scans [14] (see Table 4 for details of data collection and refinement). The structures were

Table 4
Crystallographic data for compounds **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{14}H_{38}Al_3Cl_2N_7$	$C_{13}H_{39}Al_4Cl_2N_7O$
Formula weight	456.35	488.33
Temperature (K)	293(2)	293(2)
Crystal system	Orthorhombic	Tetragonal
Space group	P_{nma}	$P4_32_12$
Unit cell dimensions		
a (Å)	13.777(3)	11.2960(10)
b (Å)	8.807(2)	11.2960(10)
c (Å)	20.220(4)	19.8230(10)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V (Å^3)	2453.4(9)	2529.4(3)
Z	4	4
$D_{calc.}$ (Mg m^{-3})	1.236	1.282
Absorption coefficient (mm^{-1})	0.386	0.414
F(000)	976	1040
Crystal size (mm^3)	$0.2\times0.2\times0.18$	$0.3\times0.3\times0.2$
Theta range for data collection (°)	1.79–24.97	2.08–24.97
Index ranges	$-16\leq h\leq 0$, $-10\leq k\leq 0$, $0\leq l\leq 24$	$0\leq h\leq 13$, $0\leq k\leq 13$, $0\leq l\leq 23$
Reflections collected	2311	2520
Completeness to theta (%)	100	100
Independent reflections	2311 [$R_{int}=0.0204$]	2224 [$R_{int}=0.0184$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2311/0/153	2224/0/138
Goodness-of-fit on F	0.982	0.609
Final R indices [$I>2\sigma(I)$]	$R_1=0.0431$, $wR_2=0.1122$	$R_1=0.0248$, $wR_2=0.0708$
R indices (all data)	$R_1=0.0683$, $wR_2=0.1219$	$R_1=0.0309$, $wR_2=0.0765$
Largest diff. peak and hole (e Å^{-3})	0.278 and −0.213	0.225 and −0.119

solved by direct methods (SHELXS-97) [15] and refined by full-matrix least-squares on F^2 (SHELXL-97) [15]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were put in geometrically ideal positions (riding model) and refined.

8. Supplementary material

Supplementary data (atomic coordinates, bond lengths and angles and thermal parameters) have been deposited at the Cambridge Crystallographic Data Centre, CCDC Nos. 134364 and 134365. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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