Structures of the potassium aluminates $[\{K_2(Me_3AlOBu^t)_2\cdot pmdeta\}_\infty]$ and $[\{K(pmdeta)_2\}^+(AlMe_4)^-]$: how the nature of the alane reagent determines which of these products form from alkoxide-containing reaction mixtures

Fiona J. Craig, Alan R. Kennedy, Robert E.Mulvey* and Mark D. Spicer

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK G1 1XL

Equimolar mixtures of $AlMe_3$, Bu^tOK and pmdeta produce either title compound depending on whether solvent-free, dimeric $[(AlMe_3)_2]$ or the amine-solvated monomer $[Me_3Al\cdot(H)N(CH_2Ph)_2]$ is used as the source of the alane.

Potassium aluminates have recently attracted attention due to their interesting structural and bonding features. Notable landmark discoveries include the presence of an Al–Al bond in $[K_2(Al_2Bu^i{}_6)]$,[1] and of an Al_{12} borane-type icosahedral cluster which obeys Wade's rules[2] in $[K_2(Al_{12}Bu^i{}_{12})]$.[3] Generally, this area is dominated by solvent-separated ion pair (SSIP) arrangements; while contacted ion pair structures (CIP) are rare. Reported here are the novel CIP structure of the alkoxide derivative $[\{K_2(Me_3AlOBu^t)_2\cdot pmdeta\}_\infty]$, **1**, which exhibits two distinct K environments in an intricate, sheet network, and the simple SSIP structure of alkoxide-free $[\{K(pmdeta)_2\}^+(AlMe_4)^-]$ **2**, with its single K environment. Remarkably, the controlling factor in determining which product (**1** or **2**) crystallises from a 1 : 1 : 1, $AlMe_3$–Bu^tOK–pmdeta† mixture appears to be the form in which the alane is delivered: the amine adduct $[Me_3Al\cdot(H)N(CH_2Ph)_2]$ **3** produces **1**; solvent-free $[(AlMe_3)_2]$ **4** produces **2**.

In the synthetic procedure performed under argon, a chilled hexane solution of **3** or **4** (5 mmol) was added to Bu^tOK (5 mmol, suspended in toluene), then mixed with pmdeta (5 mmol) and warmed to effect dissolution. Freezer-cooling of these solutions afforded colourless crystals of **1** or **2** respectively.‡ Repeating each reaction in triplicate always produced the same, solitary crystalline product, *i.e.* either **1** or **2**, with no hint of contamination by the other product. Changing the molar ratio of pmdeta in the reaction mixtures to match that in the formulae of **1** and **2** (*i.e.* 0.5 and 2.0 equiv. respectively) produced solutions which also deposited the same crystalline products. Significantly, however, despite prolonged heating, complete dissolution could not be achieved on treating a 1 : 1 $[(AlMe_3)_2]$–Bu^tOK mixture with 0.5 equiv. of pmdeta.

The crystal structure of **1**§ consists of $K_2(Me_3AlOBu^t)_2$(pmdeta) units interconnected by K···Me–Al interactions to give the overall infinite lattice structure. Although both K(1) and K(2) attain seven-coordination they are chemically distinct, as are the two (Me_3AlOBu^t) fragments (Fig. 1). The dimeric substructure (Fig. 1) arises from the bridging behaviour of the C(11) and C(12) methyl groups and further similar K···Me–Al interactions involving the methyl groups of C(10), C(17) and C(19) expand the structure into a polymeric chain [range of K···C lengths, 3.091(4)–3.270(4) Å]. Longer range interactions,

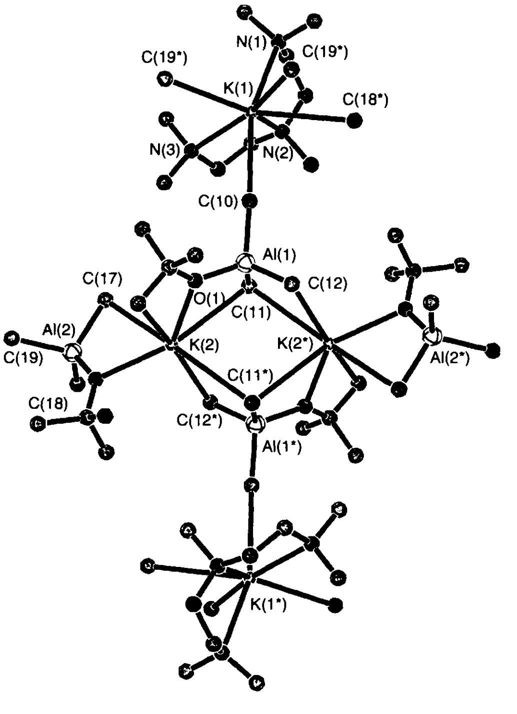

Fig. 1 Dimeric fragment of the crystal structure of **1** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected distances (Å): K(1)–N(1) 2.869(3), K(1)–N(2) 2.852(3), K(1)–N(3) 3.034(3), K(2)–O(1) 2.630(2), Al(1)–O(1) 1.779(2), K(2)–O(2) 2.652(2), Al(2)–O(2) 1.778(2), K(2)–C(16) 3.346(5).

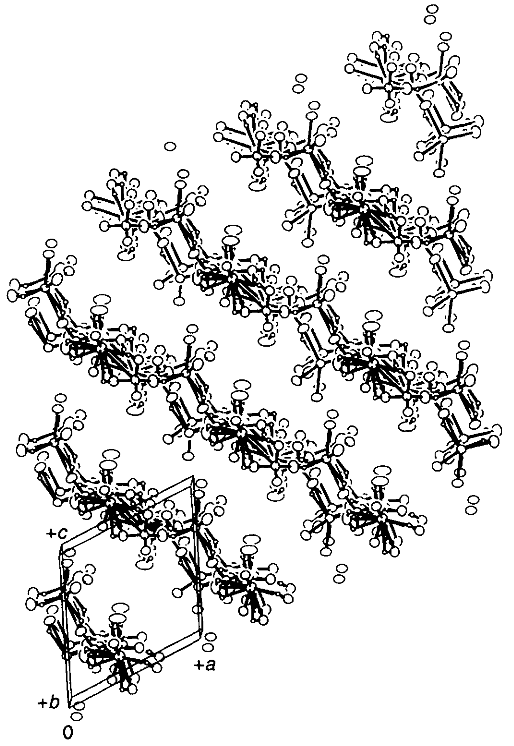

Fig. 2 Extended structure of **1**. All hydrogen atoms and pmdeta carbon atoms are omitted. Direction of view is approximately along the *b*-axis.

K(1)···C(18′)–Al(2′) and K(1)···C(19′)–Al(2′) [K···C lengths, 3.433(3), 3.582(4) Å where primed atoms are related by the translation *x*, *y* + 1, *z*], complete the coordination shell of pmdeta-complexed K(1) and link the chains into sheets (Fig. 2). The local coordination geometries about Al(1) and Al(2) are essentially equivalent (four-coordinate, distorted tetrahedral; mean bond lengths Al–C 1.999 Å, Al–O 1.778 Å). There is no precedent for this structure in the literature. The closest analogy is the dimethoxyethane adduct $[\{[(Me_3Si)_2CH]_2AlMe(OC_2H_4OMe)K(dme)\}_\infty]$[4] which forms a one-dimensional polymeric chain arrangement (*cf.* two-dimensional sheet here) through intermolecular K···Me–Al bridges (K···C bond length 3.269 Å).

By comparison, the crystal structure of **2**§ is simple, consisting of the discrete ions $[\{K(pmdeta)_2\}^+]$ and $[AlMe_4^-]$. Though mono K-pmdeta complexes are known,[5] the former is believed to be the first structurally characterised bis example. Its cation sits in an irregular coordination polyhedron of six N atoms (Fig. 3). Al–C bond lengths within the distorted tetrahedral anion span 1.986(7)–2.014(6) Å (mean 2.002 Å). Note that the shortest K···C(Me) distance is 4.587(4) Å, compared to 3.15 Å in the solvent-free analogue $[K^+(AlMe_4)^-]$.[6]

Why should the Al reagents **3** and **4** give different products with the Bu^tOK–pmdeta mixture? Intriguingly, the explanation could lie in the preorganisation of their respective Al centres. Existing as a dimer, **4** offers the possibility of dividing asymmetrically (Scheme 1) to yield $[Me_2Al(OBu^t)]$ and $[K^+(AlMe_4)^-]$ respectively. Further reactions on adding the second alkoxide equivalent are likely to involve only the former product on account of its more δ+ Al centre. In contrast, **3** offers a monomeric 'Me_3Al' unit which is ultimately retained after reaction.

Support for this 'preorganisation' idea comes from an examination of the corresponding tmeda† reaction systems (under the same equimolar conditions). An identical pattern emerges: **3** produces alkoxide-containing $[\{K(Me_3AlOBu^t)\cdot tmeda\}_n]$; **4** produces alkoxide-free $[\{K(tmeda)_2\}^+(AlMe_4)^-]$.[7]

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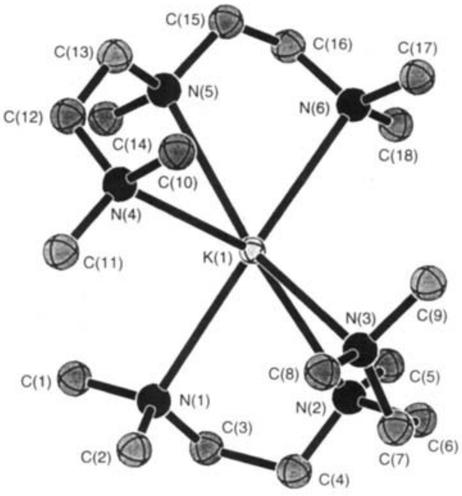
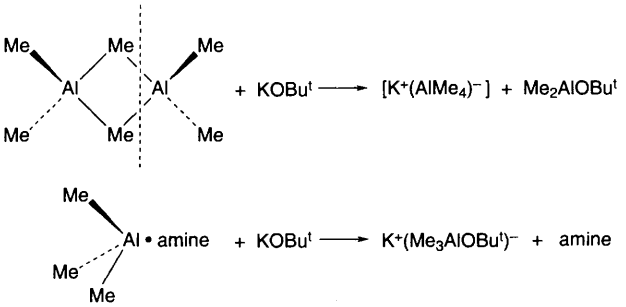


Fig. 3 View of the cation moiety of **2** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected distances (Å): K–N(1) 2.929(4), K–N(2) 2.904(4), K–N(3) 3.045(4), K–N(4) 2.994(5), K–N(5) 2.914(5), K–N(6) 3.066(5).



Scheme 1

Footnotes

† pmdeta = *N,N′,N′,N″,N″*-pentamethyldiethylenetriamine, tmeda = *N,N,N′,N′*-tetramethylethylenediamine.

‡ **1**: mp 106–110 °C; yield (based on alkoxide consumption), 76%.

2: mp 53–56 °C; yield (maximum possible = 50% due to insufficient pmdeta present), 37% (when correct stoichiometry used, increased to 68%). Satisfactory analyses (Al, C, H, K, N) and ^1H NMR spectroscopic data for both compounds. No other solids were obtained on further cooling of the filtrates from which **1** or **2** crystallised.

§ *Crystal data*: **1**, $C_{23}H_{59}Al_2K_2N_3O_2$; M = 541.90, triclinic, space group $P\bar{1}$, a = 12.225(2), b = 12.842(3), c = 12.989(2) Å, α = 74.15(1), β = 64.50(1), γ = 79.64(2)°, U = 1765.9(6) Å^3, 8901 collected reflections, 8507 unique (R_m = 0.015). One Bu^t group 50 : 50 disordered over two sites, other H atoms included but not refined. Full-matrix, least-squares refinement on F converged at R = 0.047, R_w = 0.067, S = 2.25 based on 4803 observations [$I > 2\sigma(I)$] and 316 parameters, $|\Delta\rho|_{max}$ = 0.48 e Å^{-3}.

2, $C_{22}H_{58}AlKN_6$; M = 472.82, orthorhombic, space group $P2_12_12_1$, a = 15.561(3), b = 19.571(2), c = 10.703(1) Å, U = 3259.7(8) Å^3, 5188 collected reflections, 4549 unique (R_m = 0.021). Disorder in ligand backbone modelled as 2/3 present C_2H_4 fragment and 1/3 present C_2 fragment—the latter modelled isotropically. H atoms included but not refined. Full-matrix, least-squares refinement on F converged at R = 0.045, R_w = 0.053, S = 1.65 based on 2588 observations [$I > 2\sigma(I)$] and 279 parameters.

For both structures data collected at room temp. on a Rigaku AFC7S diffractometer, λ = 0.71069 Å. Data corrected for Lorentz polarisation and, in the case of **2**, decay effects. Solution by direct methods. All calculations used the TeXsan package. TeXsan, Crystal Structure Analysis Package, Molecular Structure Corp., 1985 and 1992. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/166.

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