Abstract: To date, aluminyl anions have been exclusively isolated as their potassium salts. We report herein synthesis of the lithium and sodium aluminyls, $\text{M[Al(NON)}\text{2}]$ ($\text{M} = \text{Li, Na. NON}_2^{\text{2}} = \text{D(SiMe}_3\text{)Dipp}_2^{\text{2}}$). Both compounds crystallize from non-coordinating solvent as slipped contacted dimeric pairs with strong $\text{M} - \text{Si}(\text{arene})$ interactions. Isolation from Et$_2$O solution affords the monomeric ion pairs (NON)$_2^{\text{2}}\text{Al-MEt}_2\text{O}$, which contain discrete Al–Li and Al–Na bonds. The ability of the full series of Li, Na and K aluminyls to activate dihydrogen is reported.

In 2018 aluminyl compounds entered the arena of low-valent main group chemistry as a new class of aluminium(I) anion.\textsuperscript{11} The first aluminyl anion consisted of a three-coordinate Al(i) cæter supported by a xanthene-based diamido ligand, [NON$_2^{\text{2}}\text{Al}]$\textsuperscript{2}.\textsuperscript{2} The crystal structure showed a contacted dimeric pair (CDP) in which the potassium cations were involved in $\text{K} - \text{Si}(\text{arene})$ interactions (Figure 1, $\text{K}_2[\text{III}]$). Shortly thereafter we reported the two-coordinate aluminyl anion $\text{K}[$III$]$, that also crystallized as a CDP,\textsuperscript{2} a motif that is common in aluminyl chemistry where $\text{K} - \text{Si}(\text{arene})$ contacts are possible (e.g. $\text{K}[$III$]$,\textsuperscript{3,4} and $\text{K}[$IV$]$).\textsuperscript{5}

In the absence of ligand substrates available for $\text{K} - \text{Si}(\text{arene})$ interactions, other aluminyl structures are observed.\textsuperscript{6} The dialkyl aluminyl [K($\text{tBu}_2$)]\textsuperscript{[II]}($\text{tBu} = \text{tBu}$)\textsuperscript{6} exists as a monomeric ion pair (MIP) with an Al–K bond considerably shorter than the Al–K contacts in the CDPs. Furthermore, compounds in which the potassium ion is segregated have been reported.\textsuperscript{2} The addition of [2.2.2]cryptand to $\text{K}[$III$]$ afforded the separated ion pair (SIP) [K(2.2.2)-crypt][NON$_2^{\text{2}}\text{Al}]$\textsuperscript{2}.\textsuperscript{2} and the two-coordinate SIP [K(12-crown-4)][NON$_2^{\text{2}}\text{Al}]$\textsuperscript{2} was isolated from reduction of the dialane precursor in the presence of [2.2.2]-crown-4 (12-c-4).\textsuperscript{2}

Despite the chemistry of the aluminyl anions being governed by reactivity at aluminium,\textsuperscript{7} the potassium cation may also influence the reactivity through synergic interactions in a protocol that is established for many bimetallic compounds incorporating group 1 metals.\textsuperscript{8} This is illustrated by the contrasting reactivity of $\text{K}[$III$]$ and [K(12-crown-4)]\textsuperscript{[III]} with benzene, where the CDP showed the thermally promoted oxidative addition of a C–H bond to $\text{Al}^{\text{III}}$, whereas SIP [K(12-crown-4)]\textsuperscript{[III]} underwent a reversible C–H bond activation at room temperature.\textsuperscript{9} In addition, computational analysis showed that activation of substituted arenes with [K(12-crown-4)]\textsuperscript{[III]} involves coordination of the aromatic ring to $\text{K}$, which lowered the $\sigma^*$-orbital energy facilitating nucleophilic attack of $\text{Al}$ in a meta-selective $\text{S}_{\text{n}}\text{Ar}$ reaction.\textsuperscript{10}

The reduction of Al[NON$_2^{\text{2}}\text{Al}]$ with lithium in Et$_2$O afforded pale yellow crystals of Li$_2$[NON$_2^{\text{2}}\text{Al}]$\textsuperscript{2}.\textsuperscript{1} The reduction of Al[NON$_2^{\text{2}}\text{Al}]$ with lithium in Et$_2$O afforded pale yellow crystals of Li$_2$[NON$_2^{\text{2}}\text{Al}]$\textsuperscript{2}.\textsuperscript{1} Although no identifiable peak was observed in the $^{27}$Li NMR spectra for either compound,\textsuperscript{11} a singlet at $\delta = -2.93$ was observed in the $^7$Li NMR spectrum of [1], with a high field chemical shift consistent with the shielding effect of an aromatic ring current (vide infra). The diffusion coefficients $D$ of [1] ($5.32 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) and [2] ($4.60 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) measured by $^1$H diffusion-ordered NMR spectroscopy (DOSY, toluene-D$_8$ 298 K) are lower than the monomeric iodide $\text{Al}^{\text{III}}$ ($D = 6.14 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$), indicating retention of the CDP in aromatic solvents.\textsuperscript{11}
X-ray diffraction data show that \([1]_1\) and \([2]_1\) are best described as ‘slipped’ CDPs (Figure 2). Within each structure the shortest Al–M distance (Al–Li 2.746(3) Å and Al–Na 3.030(6) Å) is greater than the sum of the covalent radii \([\sum_{\text{cov}}(\text{Al, Li})] = 2.49 \text{ Å}\) and \([\sum_{\text{cov}}(\text{Al, Na})] = 2.87 \text{ Å}\). The remaining Al–M distances are considerably longer (Al–Li 3.364(3) Å; Al–Na 3.560(6) Å) generating a pronounced asymmetry within the dimer and contrasting with the symmetrical bonding in the potassium aluminyls. Such slippage has been observed in a Mg(0) compound and was attributed to Na–Li(CD3)2 interactions.17 This is supported by analogous contacts in \([1]_2\) and \([2]_2\), where short Li–Ct and Na–Ct distances\(^1\text{H}\) suggest strongly held CDPs.

The reduced number of contacts between the monomeric \([\text{M(NON}^{\text{en}})]\) units in \([1]_1\) and \([2]_1\), and the observed colour change of lithium aluminyl from colourless in Et2O to pale yellow for the isolated CDP suggested a solvated form may be accessible in coordinating solvent. Accordingly, the relative energies of the CDPs were calculated and compared with the hypothetical \([\text{M(NON}^{\text{en}})]\) monomers and the Et2O solvated MIP forms \([\text{ON}^{\text{en}}](\text{Al–M}+ \text{M}^{+})\text{Et}_{2}\text{O}\) (Table S1). For \([\text{M} = \text{Li and Na}\), breaking the dimer into monomeric units results in a loss of stability amounting to 25.4 kcal mol\(^{-1}\) and 15.9 kcal mol\(^{-1}\), respectively. However, solvating the alkali metal with two equivalents of Et2O stabilizes the MIPs, with overall energies of \(-7.0 \text{ kcal mol}^{-1}\) (Al–Li) and \(-3.2 \text{ kcal mol}^{-1}\) (Al–Na) relative to the respective CDPs. When \(\text{M} = \text{K}\), a similar loss of stability is noted on monomer formation (24.6 kcal mol\(^{-1}\)). However, compensation of this energy loss is not achieved on solvation by ether and \([\text{ON}^{\text{en}}](\text{Al–M}+ \text{M}^{+})\text{Et}_{2}\text{O}\) is less stable than \([\text{K}][\text{II}]\) by 7.7 kcal mol\(^{-1}\).

Allowing Et2O solutions of \([1]_1\) and \([2]_1\) to evaporate gave colourless crystals \([\text{NON}^{\text{en}}](\text{Al–Li}+ \text{Li}^{+})\text{Et}_{2}\text{O}\) (8) and \([\text{NON}^{\text{en}}](\text{Al–Na}+ \text{Na}^{+})\text{Et}_{2}\text{O}\) (4), respectively (Scheme 1). Performing the procedure with \([\text{K}][\text{III}]\) did not give the analogous potassium compound, in agreement with the calculated CDP and MIP energies. The \(^{1}H\) NMR spectrum of 3 (CD3OH, 298 K) shows peaks for a new ligand environment and confirms the presence of 2 equivalents of Et2O. Intriguingly, resonances for the dimer \([1]_1\), were consistently observed in the \(^{1}H\), \(^{13}C\), Li and DOSY NMR spectra of isolated 3. A \(\Delta \nu\) Li NMR resonance at \(\Delta \nu_1 2.68\), congruent with disruption of the \(\text{Li}–\text{H}(\text{ar}^\text{en})\) interactions, and a low molecular weight species \((D = 6.21 \times 10^{-3} \text{ kg m}^{-3})\) in the DOSY were assigned to \([\text{NON}^{\text{en}}](\text{Al}–\text{Li}+ \text{Li}^{+})\text{Et}_{2}\text{O}\). In contrast, the \(^{1}H\) and \(^{13}C\) NMR spectra of 4 showed only peaks for \([2]_1\) and non-coordinated Et2O at 298 K. These data indicate an equilibrium between the CDPs and the solvated MIPs with the CDPs dominating at high temperature. This was confirmed by a van’t Hoff analysis of variable temperature NMR data, giving \(\Delta = -34 \text{ kJ mol}^{-1}\) and \(\Delta S = -78 \text{ J K}^{-1}\text{mol}^{-1}\) (Al–Li), \(\Delta = -141 \text{ kJ mol}^{-1}\) (M = Na). These data correspond to \(\Delta G(253 \text{ K})\) values of \(-15.2 \text{ kJ mol}^{-1}\) and \(-1.5 \text{ kJ mol}^{-1}\).
mol$^1$ for Li and Na, respectively, consistent with a smaller energy difference between the CDP and MIP forms for the sodium aluminyls in agreement with results from DFT studies.

The crystal structures of 3 and 4 confirmed formation of the monomeric ion pair (NON$^2$H)Al{Et$_2$O}$_2$ (Figure 4), containing unsupported Al–Li and Al–Na bonds. In both cases the aluminium is distorted trigonal planar defined by the chelating NON$^2$H ligand and a solvated alkali metal atom. The Al–Li bond length in 3 is 2.767(2) Å slightly longer than that in [1], and 11.1 % greater than ΣAl(Li). The corresponding Al–Na bond in 4 (0.0137(8) Å) is shorter than in [2], and only 5.0 % greater than ΣAl(Na).

Natural Bond Order (NBO) analysis of 3 and 4 located no covalent bonds between aluminium and the alkali metals, although substantial ‘donor–acceptor’ interactions were found (stabilisation energies of 3.405 kcal mol$^{-1}$ and 4.252 kcal mol$^{-1}$). In both cases the HOMO depicts lone pair character retained at Al, composed of 80.2 % s and 19.8 % p for 3 and 79.3 % s and 20.7 % p for 4. The orbital lobes are directed towards Li/Na, with the extension less pronounced for 4 (Figures S4S–S61).

Comparison of the Al–M bonds in the CDP and MIP structure types was performed by analysis of the Wiberg bond indices (WBI, Table S4). The WBI for the Al–Li bond in 3 is 0.2209, denoting less electron sharing between the two atoms than the major interactions in the CDP (WBI = 0.2681 / 0.2664). However, considering the sum of the major and minor Al–Li interactions in [1], (0.3626 / 0.3706), we note a greater overall sharing in the dimer. Comparing these values with the sodium species, the Al–Na WBI in 4 (0.2506) is greater than the stronger interaction in [2], (0.1712) but less than the sum (0.2638). This trend is also reflected in the delocalisation indices (DI$s$) for each structure, with [1], (0.1114 > 3 (0.1085) and [2], (0.1684 > 4 (0.1873), consistent with greater overall WBI in the CDP for M = Li, whereas for M = Na this occurs for the MIP.

The K$_2$[M] aluminium system reacted with dihydrogen under ambient conditions (2.0 bar, 5 days, room temperature) to afford K$_2$[Al(NON$^2$H)$_2$]$_2$. Using this reaction as a benchmark, we examined the hydrogenation of the series of M$_2$[Al(NON$^2$H)$_2$]$_2$ aluminyls for M = Li, Na, K. All reactions require heating to proceed, and data were collected for 0.063 M solutions in C$_2$D$_5$ with 1.5 bar H$_2$ at 100 °C. Using the time taken for 50% conversion (t=0) as an approximate measure of the rate of the reaction, we observe that the hydrogenation proceeds in the order Li (t=5 = 1.5 days) > Na (t=6 = 6 days) > K (t=12 = 12 days). Allowing reaction to go to completion allowed isolation of the dihydroidaluminate M$_2$[Al(NON$^2$H)$_2$]$_2$(H)$_2$(Scheme 2. M = Li [5], M = Na [6], M = K [7]). The low solubility of [5] in non-coordinating solvents prevented spectroscopic analysis, and the crude solid was therefore crystallized from Et$_2$O, affording [NON$^2$H]$_4$[M(μ-H)$_2$Li(OEt)$_2$] (8).

Although the Al/H resonances of the dihydroidaluminate salts are not observed in the $^1$H NMR spectra, resolved peaks in $^{27}$Al NMR spectra of [5], [6], and [7] indicate a change in the coordination environment at aluminium compared with [1] and [2], for which no $^{27}$Al NMR signals were observed. The full-width half-maximum (FWHM) of these peaks are significantly reduced in the $^{27}$Al($^1$H) spectra, indicating the presence of $^{27}$Al/H interactions. Furthermore, the infrared spectra show stretches between 1714 and 1645 cm$^{-1}$, characteristic for Al–H bonds. Compound 8 shows an analogous $^{27}$Al($^1$H) resonance at $\delta_{Al}$ 117, which relates into a broad triplet in the proton-coupled $^{27}$Al NMR spectrum (Figure S51).

X-ray crystallographic analysis of [6] and [7] confirm their structures as the M$_2$[Al(NON$^2$H)$_2$]$_2$ dimers (M = Na, [6]; M = K, [7]). Evidence for the formation of the Al/H$_2$ groups is inferred from changes to the gross structural features of the dimer compared with the aluminyl starting materials (Figure 5).

Comparison of the crystal structure of 8 (Figure S54) with that of 3 also shows significant changes to the overall structure, with a reduction in the interplanar N$_2$/Al–Li angle from 26.30(4)° in 3 to 11.10(6)° in 8. We note that the incorporation of two hydride ligands decreases the Al–Li distance from 2.767(2) Å in 3 to 2.640(3) Å in 8, resulting in a value similar to that in the structurally related compound, (Me$_2$Si)$_2$N$_2$[Al(μ-H)$_2$Li(OEt)$_2$] (2.621(5) Å).$^{11}$

In summary we have demonstrated that the aluminyl anion [Al(NON$^2$H)$_2$]$^-$ is not exclusive to its potassium salt but can be accessed as the lithium and sodium complexes via standard reduction procedures. All three members of the series activate
dihydrogen to form the corresponding dihydroaluminate salts with the rate of conversion Li > Na > K.

Figure 5. Displacement ellipsoid plots (30 %, C-atoms reduced for clarity) of the core structures of (a) [6], (inset: core [2]) and (b) [7], (inset: core K[6]). Selected bond lengths (Å) and angles (°): (a) Al1···Al2 4.5357(4), Na1···Na2 5.5749(8). (b) Al1···Al2 5.4512(6), K1···K2 6.514(2) Å.

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Keywords: aluminium anion • sodium aluminyl • lithium aluminyl • dihydrogen activation
Entry for the Table of Contents

It turns out there is nothing special about potassium after all. Sodium and lithium reduce Al(III) iodide precursors to the M$_2$(Al(NON$_2$Dipp)$_2$)$_2$ aluminyls (M = Li, Na). The crystal structures show non-symmetrical dimers held by M···π(arene) interactions. Addition of Et$_2$O afforded the monomeric ion pairs (NON$_2$Dipp)Al–M(Et$_2$O)$_2$ containing unsupported Al–Li and Al–Na bonds. All species activate dihydrogen, albeit at significantly different rates of reaction.

Twitter usernames: @Coles_lab, @DrAnker15, @clairemcmulin, @evansinorganic, @SamENeale