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Synthesis and Structure of the Bis(amido)sodate Salt $Na[Na\{N(SiMe_3)_2AlMe_3\}_2]$: An Na^+ Ion Complexed Solely by Na^+---H_3C- Interactions

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Summary: The synthesis and structural characterization of the sodium amide salt $Na[Na\{N(SiMe_3)_2AlMe_3\}_2]$ *are described. The structure is composed of an infinite array of bis(amido)sodate* $[Na\{N(SiMe_3)_2AlMe_3\}_2]^-$ *anions and* Na^+ *cations, the latter being "solvated" by* Na^+---H_3C- *interactions alone.*

Although the structures of isoelectronic molecules are often very similar, the structures of the isoelectronic alkyl and amide species $[LiC(SiMe_3)_3]_2$[1] and $[LiN(SiMe_3)_2AlMe_3]_\infty$[2] are quite different. This difference was attributed[2] to the strength of Li---CH_3-Al interactions in $[LiN(SiMe_3)_2AlMe_3]_\infty$ which could not be easily accommodated geometrically in the dimeric structure found for the alkyl. Furthermore, it was suggested that in sterically less restricted $-N(SiMe_3)_2AlMe_3$ derivatives of larger metal ions, similar M---CH_3 interactions could occur in both the alkyl and amide derivatives and the same type structures should be observed. This argument was justified on the basis of the similar structures found for $Yb[N(SiMe_3)_2AlMe_3]_2$[3] and $Yb[C(SiMe_3)_3]_2$.[4] By this criterion the structures of the sodium derivatives $NaN(SiMe_3)_2AlMe_3$ and $NaC(SiMe_3)_3$ should be similar, since the Na^+ ion is almost equal in size to Yb^{2+}.[5] Although the solid-state structure of uncomplexed $NaC(SiMe_3)_3$ is not currently known, the structure[6] of $[Na(TMEDA)_2OEt_2][Na\{C(SiMe_3)_3\}_2]$ has shown that the organosodium moiety exists as the unique dialkylsodate ion $[Na\{C(SiMe_3)_3\}_2]^-$. In this paper, it is shown that the uncomplexed amide analogue $NaN(SiMe_3)_2AlMe_3$ incorporates bis(amido)sodate, i.e. $[Na\{N(SiMe_3)_2AlMe_3\}_2]^-$ ions, as part of a structure in which the Na^+ countercations are complexed exclusively by Na---H_3C-Al interactions.

The compound **1** was synthesized[7] by treatment of $NaN(SiMe_3)_2$ with an equimolar amount of $AlMe_3$ in toluene. It crystallizes in the space group $P\bar{1}$. The structure[8] of the asymmetric unit consists of an ion pair of formula $Na[Na\{N(SiMe_3)_2AlMe_3\}_2]$, which is related to an identical species via an inversion center to afford the unit cell (Figure 1). This incorporates two ion pairs

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(7) All manipulations were carried out under anaerobic and anhydrous conditions. With stirring at room temperature a 2 M solution of $AlMe_3$ (3.7 mL, 7.4 mmol) in toluene was added dropwise via a syringe to a solution of $NaN(SiMe_3)_2$ (1.36 g, 7.42 mmol) in toluene (30 mL). A white precipitate formed, and stirring was continued for 30 min, after which time the precipitate was allowed to settle. The supernatant liquid was removed by cannula, and the precipitate was then washed with hexane (10 mL). Drying under reduced pressure (0.01 mmHg) afforded the product as a white microcrystalline material. Crystals of **1** that were suitable for X-ray crystallographic studies were obtained from a saturated solution in hot toluene: yield 1.20 g (87%); mp 187 °C dec. Anal. Calcd for $C_9H_{27}AlNNaSi_2$: C, 42.31; H, 10.66; N, 5.48. Found: C, 42.82; H, 10.41; N, 5.41. ^1H NMR (C_6D_6): δ 0.25 ($SiMe_3$, 18H), -0.52 ($AlMe_3$, 9H). IR (Nujol, cm^{-1}): 2205 w, 1915 w, 1855 w, 1610 w, 1400 w, 1287 w, 1262 sh, 1248 vs, 1180 m, 1138 s, 1020 sh, 912 vs, 874 vs, 835 vs br, 780 sh, 755 vs br, 670 vs, 613 s, 598 sh, 555 s, 441 m, 364 mw, 300 w.

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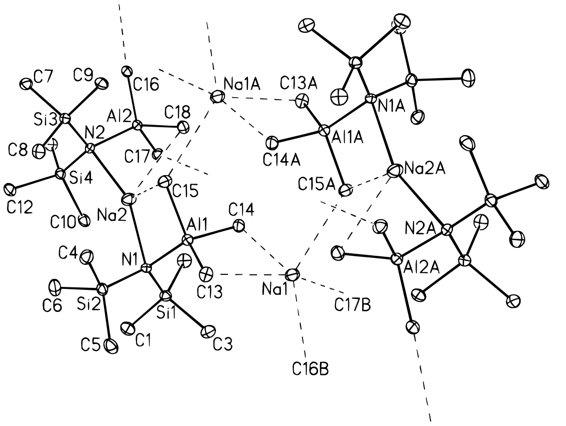

Figure 1. Thermal ellipsoid plot (30%) of **1** illustrating the structure of the unit cell. Some important interatomic distances (Å) and angles (deg) for the bis(amido)sodate anion: Na(2)−N(1) = 2.513(3), Na(2)−N(2) = 2.483(3), Na(2)- - -C(15) = 2.885(5), Na(2)- - -C(18) = 3.085(5); N(1)−Na(2)−N(2) = 159.37(11), N(1)−Na(2)- - -C(15) = 72.07(13), N(2)−Na(2)- - -C(18) = 69.61(12), C(15)- - -Na(2)- - -C(18) = 80.58(14). See also the text.

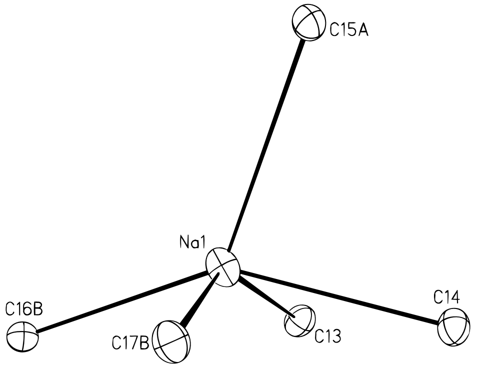

Figure 2. Thermal ellipsoid plot of the coordination environment at Na(1). Important distances (Å) and angles (deg): Na(1)- - -C(13) = 2.859(5), Na(1)- - -C(14) = 2.795(5), Na(1)- - -C(15a) = 3.109(5), Na−C(16b) = 2.733(5), Na- - -C(17b) = 2.803(4); C(13)- - -Na(1)- - -C(17b) = 148.1(2), C(14)- - -Na(1)- - -C(16b) = 144.8(2), C(13)- - -Na(1)- - -C(14) = 69.24(13), C(14)- - -Na(1)- - -C(17b) = 92.8(2), C(13)- - -Na(1)−C(16b) = 89.50(14), C(16b)- - -Na(1)- - -C(17b) = 91.46(14), C(14)- - -Na(1)- - -C(15a) = 84.07(14), C(15a)- - -Na(1)- - -C(16b) = 131.1(2).

which are linked by Na- - -CH_3−Al interactions involving two of the four sodium ions (i.e. Na(1) and Na(1a)) in the unit cell. These dimeric motifs are linked to neighboring "dimers" through further Na(1) and Na(1a)- - -CH_3−Al interactions to form a polymeric "double layer" structure. In effect, sodium cations are each complexed, with varying strength, by five aluminum methyl groups (Figure 2) which feature Na(1)−C distances of 2.733(5) Å (C(16b)), 2.795(5) Å (C(14)), 2.803(4) Å (C(17b)), 2.859(5) Å (C(13)), and 3.109(5) Å (C(15a)).

In the bis(amido)sodate anion Na(2) is bound to two $-N(SiMe_3)_2AlMe_3$ amide ligands, which coordinate primarily through nitrogen. This arrangement affords an interligand N(1)−Na(2)−N(2) angle of 159.37(13)° at the metal and Na−N bond lengths which average 2.50(2) Å. Further Na(2)−ligand interactions are apparent from the Na(2)- - -C(15) and Na(1)- - -C(18) distances of 2.885(5) and 3.085(5) Å. The Al−N bond lengths are 1.917(3) and 1.936(3) Å, and the Al−C distances fall within the narrow range 1.984(5)−2.015(4) Å. The N−Si bond lengths and Si−N−Si angles average 1.747(3) Å and 117.6(4)°.

The bonding within the novel sodate anion $[Na\{N(SiMe_3)_2AlMe_3\}_2]^-$ can be compared to the structures of other sodium amides and the closely related dialkylsodate anion. The average Na−N distance of 2.50(2) Å in **1** is slightly longer than (but within 1 standard deviation of) the Na−C bond length of 2.479(6) Å in the isoelectronic dialkylsodate anion $[Na\{C(SiMe_3)_3\}_2]^-$.[6] This is surprising, in view of the fact that M−N bonds in amides[9] are usually shorter than M−C bonds in related metal alkyls. This is due to the smaller size[10] of nitrogen and an ionic contribution[11] to bond strength arising from the greater polarity of the M−N bond. It is also notable that the Na−N distance is considerably longer than the average Na−N bond lengths of 2.355(3) and 2.399(5) Å, observed in the compounds $\{NaN(SiMe_3)_2\}_\infty$[12] and $\{NaN(SiMe_3)SiMe_2O(t\text{-}Bu)\}_2$,[13] both of which feature two-coordinate Na^+ ions. However, the Na−N bond length is essentially equal to those observed in the structure of $NaN(t\text{-}Bu)AlMe_2N(t\text{-}Bu)SiMeN(H)\text{-}t\text{-}Bu$,[14] which also has a two-coordinate Na^+ ion coordinated to two nitrogens (one amide, Na−N = 2.48(1) Å; one amine, Na−N = 2.52(1) Å) and which interacts further with methyl groups, with the closest Na- - -C interactions being 2.89(2) and 3.06(2) Å. In a wider context it may be noted that most Na−N(amide) distances in which the sodium ion is four-coordinate appear to fall in the range of ca. 2.35−2.45 Å.[15,16] In essence, the Na−N distances in compound **1** are long in comparison to those in other sodium amides. This may be attributed to a number of factors, which include (a) the anionic nature of the $[Na\{N(SiMe_3)_2AlMe_3\}_2]^-$ moiety, which increases interelectronic repulsion and reduces the ionic contribution to bond strength, (b) the presence of secondary interactions between sodium and the aluminum methyl groups, which increases the effective coordination number of sodium, and (c) the strong competitive interaction between aluminum and the amide nitrogen, which results in short[17] Al−N distances of 1.917(3) and 1.936(3) Å. These N−Al distances are

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[8] Crystal data at 130 K with Cu Kα (λ = 1.541 84 Å) radiation for **1**: $C_{18}H_{54}Al_2N_2Na_2Si_4$, fw 510.93, a = 8.812(2) Å, b = 12.642(2) Å, c = 15.436(3) Å, α = 74.89(1)°, β = 86.92(1)°, γ = 71.17(1)°, triclinic, space group $P1$, Z = 2, R = 0.059 for 3319 ($I > 2\sigma(I)$) data, refinement on F^2 with SHELXL-93 (G. M. Sheldrick, Göttingen, Germany, 1993).

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marginally shorter than the 1.944(3) Å observed in the structure of $\{LiN(SiMe_3)_2AlMe_3\}_\infty$.[2]

Other structural features of the $[Na\{N(SiMe_3)_2AlMe_3\}_2]^-$ anion also merit comment. The Al–C bond lengths in **1** are fairly uniform, in comparison with the large variation observed in $\{LiN(SiMe_3)_2AlMe_3\}_\infty$. This is probably due to the fact that all Al–CH_3 groups in **1** are involved in secondary interactions to the sodium countercation, whereas in $\{LiN(SiMe_3)_2AlMe_3\}_\infty$[2] one of the three Al–$CH_3$ moieties does not participate in such bonding and a shorter Al–C bond, 1.974(4) Å in length, is the result. Other aspects of the structure of some interest are the Na–N–Al angles, which at 88.67(13) and 93.29(13)° are considerably wider than the Li–N–Al angle of 82.4(2)° in $\{LiN(SiMe_3)_2AlMe_3\}_\infty$. The wider angles in **1** are consistent with the Na(2)- - -H_3C–Al interactions and are weaker than the corresponding Li- - -C–Al interactions.

An unique feature of the structure of **1** is the complexation of the Na(1) cation. In essence, Na(1) is surrounded by five methyl groups, as illustrated in Figure 2. The coordination is very distorted from any of the regular five-coordinate geometries. The longest Na(1)- - -C distance (3.109(5) Å) concerns C(15), which interacts much more strongly with Na(2) of the anion (Na(2)- - -C(15) = 2.885(5) Å). The remaining Na- - -C interactions fall within the range 2.733(5)–2.859(2) Å. These distances are somewhat shorter than the 2.963(7) Å observed in $\{NaN(SiMe_3)SiMe_2O(t\text{-}Bu)\}_2$[13] or the Na- - -C interactions of 2.89(2) and 2.306(2) Å in NaN(*t*-Bu)$AlMe_2$N(*t*-Bu)SiMeN(H)-*t*-Bu.[14] The Na- - -H(Me) interactions in **1** (2.46(5)–2.64(4) Å) seem to be very similar to those observed in $\{NaCH(SiMe_3)_2\}_\infty$,[18] whose Na- - -H interactions are in the range of 2.40–2.65 Å. These strong interactions are also consistent with the long average Na–$CH(SiMe_3)_2$ bond distance of 2.555(10) Å in $\{NaCH(SiMe_3)_2\}_\infty$.[18] Attempts to crystallize K, Rb, or Cs derivatives of the $^-N(SiMe_3)_2AlMe_3$ ion in the absence of Lewis bases have not been successful, owing primarily to very low solubility in hydrocarbons. Further experiments to achieve this objective are in progress.

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Supporting Information Available: Tables of data collection parameters, complete atom coordinates and *U* values, distances and angles, and anisotropic thermal parameters (12 pages). Ordering information is given on any current masthead page.

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