

The Synthesis and X-Ray Structural Characterisation of the First Mixed Alkali Metal Organonitrogen Molecular Cluster $\text{LiNa}_3[\text{O}=\text{P}(\text{NMe}_2)_3]_3[\text{N}=\text{C}(\text{NMe}_2)_2]_4$

William Clegg,^a Robert E. Mulvey,^{*b,c} Ronald Snaith,^{c,d} Gerald E. Toogood,^b and Kenneth Wade^{*b}

^a Department of Inorganic Chemistry, The University, Newcastle-upon-Tyne NE1 7RU, U.K.

^b Department of Chemistry, Durham University Science Laboratories, South Road, Durham DH1 3LE, U.K.

^c Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, U.K.

^d University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

A mixed alkali metal guanidino complex $\text{LiNa}_3[\text{O}=\text{P}(\text{NMe}_2)_3]_3[\text{N}=\text{C}(\text{NMe}_2)_2]_4$ (**1**), the first compound of its type, has been synthesised from Bu^nLi , Bu^nNa , $\text{O}=\text{P}(\text{NMe}_2)_3$, and $\text{HN}=\text{C}(\text{NMe}_2)_2$; an X-ray crystallographic study shows it to be a cubane-type cluster built up of novel $\mu_3\text{-N-LiNa}_2$ and $\mu_3\text{-N-Na}_3$ pyramids though additional $\text{Li} \cdots \text{H-C}$ interactions are indicated.

The metal-nitrogen distances and ligand orientations in iminolithium hexamers $(\text{LiN}=\text{CR}^1\text{R}^2)_6$ ^{1,2} and in the tetramer $(\text{pyridine} \cdot \text{LiN}=\text{CPh}_2)_4$ ^{2,3} are readily explained in terms of a 'stacked-ring' approach in which 6-membered $(\text{LiN})_3$ ring systems or 4-membered $(\text{LiN})_2$ ring systems form the fun-

damental units from which these molecules are built. $(\text{Li-C})_n$ ⁴ or $(\text{Li-O})_n$ ⁵ ring and stacked-ring structures feature widely in organolithium or lithium alkoxide chemistry. Seeking to extend our knowledge of such systems, we attempted the synthesis of the mixed alkali metal system

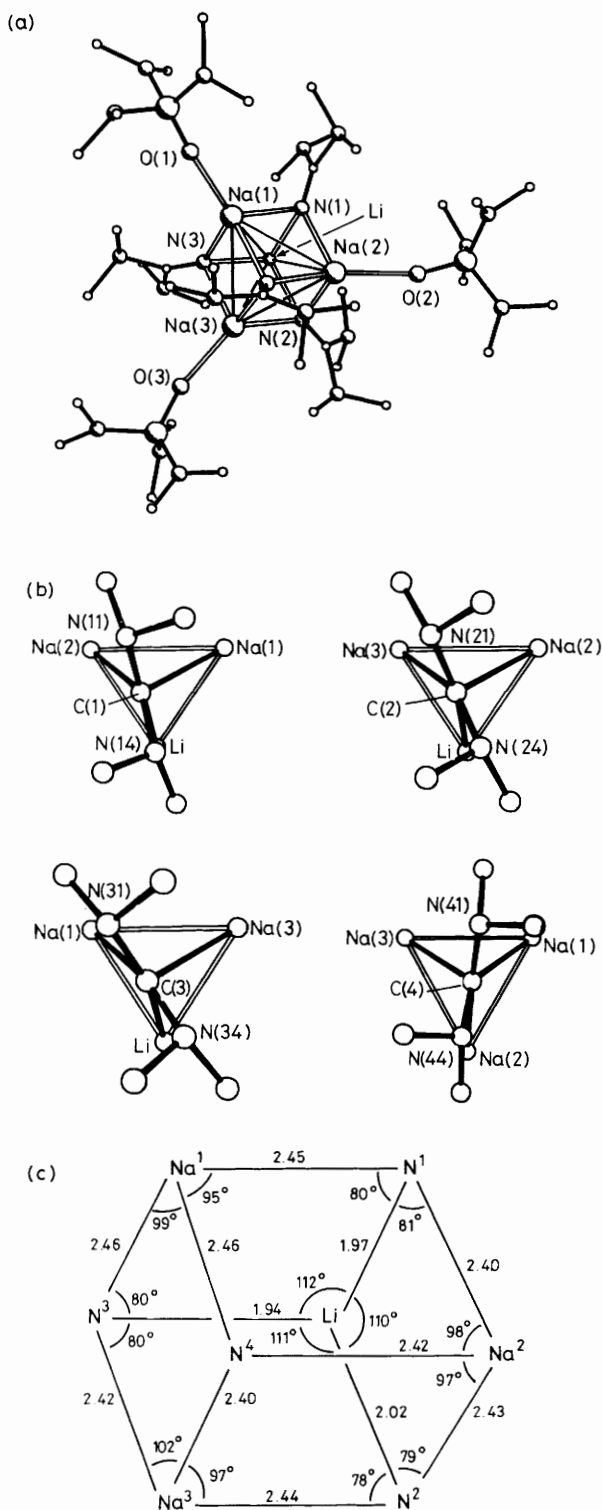


Figure 1. (a) The molecular structure of (1). (b) Guanidino ligand orientations over LiNa_2 and Na_3 faces of LiNa_3 tetrahedron. (c) Selected bond lengths (in Å) and bond angles in (1).

$\text{LiNa}[\text{N}=\text{C}(\text{NMe}_2)_2]$ by adding tetramethylguanidine, $\text{HN}=\text{C}(\text{NMe}_2)_2$ (2 equiv.), to a mixture of *n*-butyl-lithium (1 equiv.) and *n*-butyl-sodium (1 equiv.) in chilled *n*-hexane. The resulting cloudy solution was warmed to 18 °C and an excess of hexamethylphosphoramide [HMPA , $\text{O}=\text{P}(\text{NMe}_2)_3$; *ca.* 5

equiv.] was added. Cooling to 0 °C afforded pale yellow, extremely moisture-sensitive crystals of the title compound $\text{LiNa}_3[\text{O}=\text{P}(\text{NMe}_2)_3[\text{N}=\text{C}(\text{NMe}_2)_2]_4$ (1), which were recrystallised from hexane-toluene, m.p. 98 °C. This same product, consistently showing an $\text{Li}:\text{Na}$ ratio of 1:3 [and analysing satisfactorily for (1)] was obtained from subsequent reactions in which the $\text{LiBu}^n:\text{NaBu}^n$ ratio was varied within the range 1:1 to 1:3. Yields were high (*ca.* 70% based on the quantity of LiBu^n used).

An X-ray crystallographic study of (1) established the LiNa_3N_4 cubane-type structure shown in Figure 1,[†] which shows views of (a) the complete molecule, (b) the guanidino ligand orientations over the LiNa_2 or Na_3 triangles they triply-bridge, and (c) selected bond distances and angles in the LiNa_3N_4 core. Each HMPA ligand occupies an *exo* site, terminally attached through its oxygen atom to a sodium atom [$\text{Na}-\text{O}$ distances 2.249(6), 2.275(5), and 2.219(6) Å; $\text{Na}-\text{O}-\text{P}$ angles 173.9(3), 150.1(3), and 164.7(5)°]. The $\text{C}=\text{N}$ bonds of all four guanidino ligands have lengths [1.254(9), 1.223(9), 1.254(8), and 1.235(8) Å] that are normal for carbon-nitrogen double bonds. Clearly, the LiNa_3N_4 cubane skeletal bonding is highly polar, essentially involving alkali metal cations Li^+ and Na^+ and guanidinate anions $[\text{N}=\text{C}(\text{NMe}_2)_2]^-$. Nevertheless, the two lone pairs of electrons on the azomethine nitrogen atoms of such anions, which lie in their $\text{N}_2\text{C}=\text{N}$ planes, are formally available to form 2- or 3-centre bonds to neighbouring metal atoms, and use of such bonds helps to rationalize the structure of (1).

From Figure 1(b), we see that the guanidino groups that bridge the LiNa_2 faces of the LiNa_3 tetrahedron are aligned roughly so as to eclipse the lithium atom and one each of the sodium atoms. Such alignments, only slightly distorted from those that would give each guanidino group a μ_2 -bridging role over a particular $\text{Li}-\text{Na}$ edge, allow each $\text{Li}-\text{N}$ link to be regarded as a 2-centre 2-electron bond using one of the guanidinate lone pairs, the other forming an unsymmetrical 3-centre 2-electron bond to the two sodium atoms. The fourth guanidino ligand has an orientation compatible with a 2-centre bond to $\text{Na}(2)$ and a symmetrical 3-centre bond to $\text{Na}(1)$ and $\text{Na}(3)$. The $\text{N}-\text{Li}-\text{N}$ bond angles, all *ca.* 111°, appear consistent with this bonding picture which, however, does not explain the spread of $\text{N}-\text{Li}$ bond lengths (1.942–2.020 Å), although the mean length (1.98 Å) is appropriate for the expected single bonds. The greater length of the $\text{Na}-\text{N}$ bonds (mean 2.43 Å) reflects the larger radius of sodium than lithium atoms⁶ more than it reflects any difference in bond orders.

The suggested assignment of metal-nitrogen bonds to the LiNa_3N_4 core of (1) is incidentally incompatible with a 'ring-stacking' description^{1,2} of this molecule, which would require each metal atom to participate in one 2-centre and two 3-centre bonds. The departure from the pattern previously found for the all-lithium imido systems^{1,3} is believed to reflect the difference in the polarising powers of lithium and sodium.

Another manifestation of the strong polarising power of lithium is provided by the guanidino groups bridging the LiNa_2 triangles. Each has one methyl group leaning perceptibly towards the lithium atom, as if involved in $\text{Li} \cdots \text{H}-\text{C}$

[†] Crystal data for (1): $\text{C}_{38}\text{H}_{102}\text{LiN}_{21}\text{Na}_3\text{O}_3\text{P}_3$, $M = 1070$, monoclinic, $a = 12.482(1)$, $b = 35.152(3)$, $c = 15.641(2)$ Å, $\beta = 106.070(8)^\circ$, $U = 6594.6$ Å³, $Z = 4$, $D_c = 1.078$ g cm⁻³, $F(000) = 2328$, $\mu = 1.40$ mm⁻¹ for $\text{Cu}-K_\alpha$ radiation ($\lambda = 1.54184$ Å), space group *Cc*. $R = 0.062$ for 3980 diffractometer-measured reflections with $F > 3\sigma(F)$, anisotropic thermal parameters, and H atoms in calculated positions. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

bonding interactions of the type familiar in organo and related lithium systems containing co-ordinatively unsaturated metal atoms^{4c,7} (the Li ··· C distances involved, 2.9—3.1 Å, imply Li ··· H distances of *ca.* 2.5 Å). Such interactions may explain why the lithium atom in (1), unlike the sodium atoms, does not accommodate an HMPA molecule.

A final feature of (1) worthy of comment concerns the guanidino Me₂N groups. Their lone pairs are consistently orientated in an anti-clockwise manner as viewed in Figure 1(b).

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