Synthesis and Crystal Structure of the Mixed Alkali Metal Imide $Li_{4-x}Na_{2+x}[N{=}C(Ph)Bu^t]_6$: Three (Metal–Nitrogen)$_2$ Ring Dimers in a Triple-layered Stack

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The first uncomplexed mixed alkali metal molecular species to be synthesised and structurally characterised, $Li_{4-x}Na_{2+x}[N{=}C(Ph)Bu^t]_6$, has been shown by *X*-ray diffraction to exist as a complicated series of discrete isostructural molecules, each with six metal centres, arranged in a triple-stack of (metal–nitrogen)$_2$ cyclic rings.

Our recent synthesis and *X*-ray structural determination of the cubane-type complex, $LiNa_3(HMPA)_3[N{=}C(NMe_2)_2]_4$ [HMPA = $O{=}P(NMe_2)_3$], pinpointed for the first time an organo(alkali metal) molecular cluster with both lithium and sodium constituent atoms.[1] The only other such mixed metal system characterised since, $[Na(TMEDA)]_3[Li(Ph)_4]$ (TMEDA = $Me_2NCH_2CH_2NMe_2$), has a rather different structure, being interpreted as an 'ate complex, though with the same 1Li : 3Na composition.[2] In marked contrast, we now report the preparation and crystal structure of an imido-compound of lithium and sodium, free of a Lewis base complexing agent, (**1**), of molecular formula $Li_{4-x}Na_{2+x}$-$[N{=}C(Ph)Bu^t]_6$, with *x* approximately 0.3 for the single crystal actually examined. Its fractional stoicheiometry stems from the presence of a complicated series of isostructural molecules with mutual substitution disorder of Li and Na. In addition, n.m.r. (^{1}H, ^{6}Li, ^{7}Li) spectroscopic studies show that [^{2}H$_8$]toluene solutions of (**1**) exhibit a wealth of lithium-containing species.

Under an atmosphere of dry argon, a freshly standardised solution of PhLi (10 mmol in ether–cyclohexane) was added to a stirred suspension of PhNa (10 mmol in hexane) at 25 °C.[3] Neat $Bu^tC{\equiv}N$ (1.66 g, 20 mmol) was delivered to this mixture, initially giving a yellow, but ultimately pale red, solution. Standing the solution overnight afforded a crop of yellow crystals of the bimetallic imide, $Li_{4-x}Na_{2+x}[N{=}C(Ph)Bu^t]_6$, (**1**).†

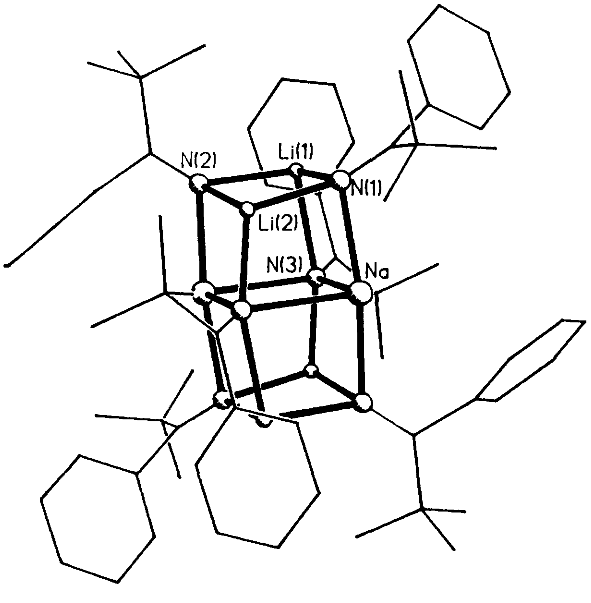

Figure 1. The centrosymmetric molecule of $Li_4Na_2[N{=}C(Ph)Bu^t]_6$ showing the atom numbering scheme for the metal–nitrogen core. Hydrogen atoms have been omitted for clarity.

An *X*-ray diffraction study shows that (**1**) crystallises as discrete molecules each having six metal sites incorporated in a triple-layered stack of three (metal–nitrogen)$_2$ rings. Basically the outer rings contain lithium and the central one sodium, giving the centrosymmetric molecule, $Li_4Na_2[N{=}C(Ph)Bu^t]_6$, shown in Figure 1.‡ However, each Na site is 13.1(6)% occupied by lithium and *one* of the Li sites, Li(1), (and its equivalent opposite) is 27.7(6)% occupied by sodium, making the actual Li : Na ratio 1.6 : 1.0 and not 2.0 : 1.0. The Li(2) site appears to be essentially 'pure' [99.7(5)% occupation by Li on attempted refinement]. In the macroscopic crystal, the net effect is a random mixture of molecules of the same gross geometrical structure, the basic building block of which is a four-membered (MN)$_2$ ring (where M = 2 Na's *or* 2 Li's *or* 1 Na and 1 Li). A stacking arrangement of rings, thereby increasing the co-ordination numbers of their metal atoms (*i.e.*, from 2, to 3 in outer rings, and to 4 in any inner ones), has many precedents in lithium cluster chemistry.[4] However, the all-lithium analogue of (**1**), $[LiN{=}C(Ph)Bu^t]_6$, is itself a stack of two (LiN)$_3$ *six*-membered rings in the crystal and indeed uncomplexed imidolithiums adopt six-membered ring arrangements as a rule;[4a,b] that such are not observed in the heterometallic structure of (**1**), possibly suggests that association of a (LiN)$_3$ ring with a (NaN)$_3$ one is prevented by the marked difference in their sizes, and that inherently smaller four-membered rings provide a better fit for stacking. On the other hand, many lithium *complexes* contain four-membered rings; a good example loosely related to (**1**) is $(LiC{\equiv}CBu^t)_{12}(THF)_4$ (THF = tetrahydrofuran) with six stacked (LiC)$_2$ ring dimers.[5]

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† Satisfactory analyses (H,Li,N,Na) were obtained for (**1**); C analysis was slightly low (found 74.4, required 76.2%). The extremely air- and moisture-sensitive crystals do not have a distinct melting point, but on heating go through a series of colour changes from tan, to orange, to deep red, and finally, to black at *ca.* 180—185 °C. Yield of (**1**) based on the amount of PhLi consumed was 34%. Although the stoicheiometry suggests other products, no further solid materials were isolated.

‡ *Crystal data* for (**1**): $C_{66}H_{84}Li_{3.7}N_6Na_{2.3}$, M = 1040.0, triclinic, space group $P\bar{1}$, a = 12.277(2), b = 12.336(2), c = 12.504(2) Å, α = 96.71(1), β = 110.51(1), γ = 108.32(1)°, U = 1628.0 Å^3, Z = 1, D_c = 1.056 g cm^{-3}. 4390 Unique reflections were measured on a Siemens AED2 diffractometer using graphite monochromated Cu-K_α radiation (λ = 1.54184 Å), μ (Cu-K_α) = 0.57 mm^{-1}, with ω/θ scans, of which 2636 were observed [$F > 4\sigma_c(F)$], $F(000)$ = 558. Structure solution by direct methods (SHELXTL, G. M. Sheldrick, University of Göttingen, 1985), refinement by blocked-cascade least-squares; R = 0.064, R_w = 0.046. 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.

Unfortunately, a detailed discussion of the bond lengths and bond angles involving the metals in (**1**) is negated by the observed substitutional disorder of Li and Na (*i.e.*, values determined represent the *mean* over all the molecules for metal–nitrogen links in certain positions; in some molecules the metal could be Na, in others the same metal site could be occupied by Li). Notwithstanding, the core bonding is highly polar, essentially consisting of Li^+ and Na^+ cations and $Bu^t(Ph)C=N^-$ anions. The organic periphery of (**1**) is straightforward, with normal C=N bonds of lengths (1.25—1.27 Å).

Finally, n.m.r. spectroscopic experiments on $[^2H_8]$toluene solutions of (**1**) intimate that there are many Li-containing solution species present and that these retain their integrity over the concentration and temperature ranges studied.§ For example, the ^7Li n.m.r. spectra of solutions of concentration 35 mg/ml, 70 mg/ml, and 130 mg/ml recorded at −97 °C are identical and making allowances for broadening due to temperature effects, they concur with the spectra at 25 °C. The four principal resonances and one shoulder cover a small chemical shift range (1.06 to −0.07 p.p.m.); five distinct Bu^t environments, again four major and one minor, are also observed in the ^1H n.m.r. spectra. In conclusion, qualitatively these results reflect the mixture of molecules noted for solid (**1**), probably with these ring-stacked molecules remaining intact in solution. Certainly, given the restricted chemical shift range common for ^7Li nuclei it is likely that these would give similar cluttered signals.

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§ *N.m.r. spectroscopic data* for (**1**) (solvent $[^2H_8]$toluene): ^7Li (139.9 MHz, 25 °C, conc. 130 mg/ml) δ 1.06, 0.59, 0.31, 0.13 (all s), and −0.07 (sh) ppm (Ξ value, 38.863 882 MHz); ^6Li (52.9 MHz, 25 °C, conc. 130 mg/ml) δ 1.06 (7Li), 0.60 (30Li), 0.31 (38Li), 0.13 (23Li), and −0.07 (2Li) (all s) p.p.m. (Ξ value, 14.716 12 MHz); ^1H (360.1 MHz, 25 °C, conc. 35 mg/ml) Ph (5H total) m centred at δ 7.00, 6.92 and 6.72, Bu^t (9H total) s at δ 0.93 (11H), 0.91 (29H), 0.90 (24H), 0.87 (9H), and 0.82 (1H).