A Unique Lithium Halide Complex, [$(LiBr)_2$·3HMPA·Toluene]: Synthesis from Reaction of Solid NH_4Br with Bu^{n}Li in HMPA (Hexamethylphosphoramide)/Toluene Media, Crystal Structure showing Two Li–Br Units Linked by Three μ_2-HMPA Ligands, and Detection of $^7Li \cdots {}^{31}P$ Coupling in Solutions of the Complex

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Reaction of solid NH_4Br with Bu^{n}Li and HMPA (hexamethylphosphoramide) (1 : 1 : 2 ratio) in toluene produces $(LiBr)_2$·3HMPA·toluene, (**1**), shown by *X*-ray crystallography to contain $(LiBr)_2$·3HMPA molecules whose two terminal Li–Br units are linked by three μ_2-HMPA ligands and with toluene molecules lying between these units in the lattice; in arene solutions, the $(LiBr)_2$·3HMPA units remain intact, giving rise in ^7Li n.m.r. spectra to 1 : 3 : 3 : 1 quartets caused by through-bond (O=P) coupling of each ^7Li nucleus to three ^{31}P(HMPA) centres.

We recently reported[1,2] a novel *in situ* route to anhydrous lithium complexes, $(LiX \cdot xL)_n$ {X = Cl, Br, I, SCN, Lewis base L = HMPA [O : $P(NMe_2)_3$], TMEDA (tetramethylethylenediamine), PMDETA (pentamethyldiethylenetriamine)} by reaction of solid ammonium salts NH_4X with Bu^{n}Li or solid LiH in the presence of L.[3] This route has advantages over direct ones [attempted dissolution of $(LiX)_\infty$ salts in L [4]] and over earlier *in situ* ones using organic or metal halides as X^- sources, *e.g.*, Bu^{n}Li + Bu^{n}Br/PMDETA giving $(LiBr \cdot PMDETA)_2$,[5] and $Bu^t_2C{=}NLi$ + $AlCl_3$/HMPA giving $(LiCl \cdot HMPA)_4$[4]: in particular, ammonium salts have low lattice energies, so giving rapid and high-yield reactions, and they are not prone to prior hydration. One complex described,[1] tentatively formulated as $(LiBr \cdot 2HMPA)_n$ (though possible incorporation of toluene, used as solvent for these reactions, was implied) has now been further investigated: it is in fact, as freshly isolated, (LiBr·1.5HMPA·0.5 toluene)$_n$, (**1**). Its crystal structure contains a discrete binuclear species (n = 2) with two LiBr 'monomers' being bridged by the O atoms of three HMPA ligands. In solutions, cryoscopic and ^7Li n.m.r. spectroscopic studies prove that, on dissolution, toluene is released but that the Br–Li·(μ_2-HMPA)$_3$·Li–Br unit remains intact; in particular, a quartet is observed in ^7Li n.m.r. spectra, attributed to coupling to three ^{31}P centres of three μ_2-HMPA ligands.

A red solution of Bu^{n}Li (5 mmol) in toluene (5 ml) and HMPA (1.79 g, 10 mmol) was frozen, then solid NH_4Br (0.49 g, 5 mmol) was added. On warming to 50 °C, the mixture turned violet (with vigorous gas evolution), then sepia, and finally, after *ca.* 15 min, to a colourless solution with no remaining solid. Addition of hexane (5 ml) and toluene (7 ml) caused separation of a yellow oil, cooling of the whole providing colourless crystals. If these are merely filtered off, analytical and ^1H n.m.r. spectroscopic data show them to be (LiBr·1.5 HMPA·0.5 toluene)$_n$,(**1**).† However, some of the toluene is quite easily lost, so that, if separately prepared batches of (**1**) are washed with hexane, then vacuum pumped

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† For (LiBr·1.5HMPA·0.5 toluene)$_n$, (**1**): yield, 60%, first batch of crystals, m.p. 56—58 °C; ^1H n.m.r. spectrum ([$^2H_6$]benzene): δ 2.58/2.47 (d, 27H of HMPA), δ 2.11 (s, 1.5H of toluene-Me). Analyses $(C_{12.5}H_{31}BrLiN_{4.5}O_{1.5}P_{1.5})_n$: Calcd., C, 37.4; H, 7.7; Br, 19.9; Li, 1.7; N, 15.7. Found, C, 36.0; H, 7.7; Br, 19.7; Li, 1.8; N, 16.5%.

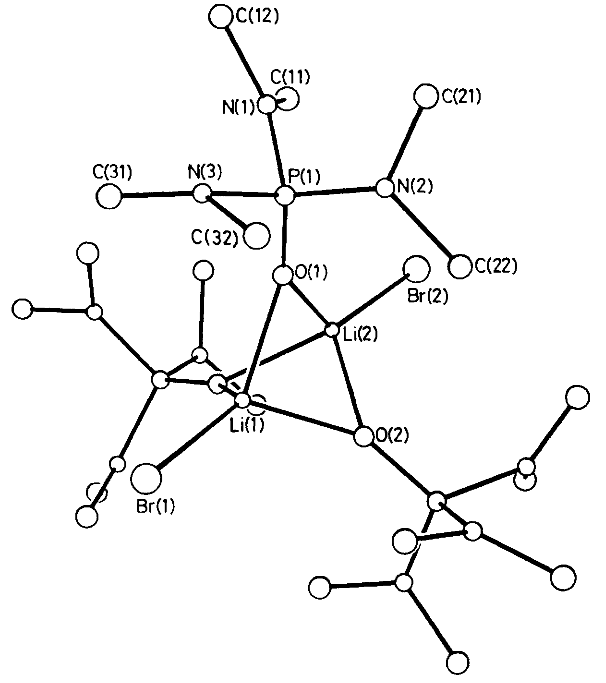

Figure 1. A PLUTO plot of one of the [LiBr·1.5HMPA]$_2$ dimers showing the atom numbering scheme. Methyl hydrogen atoms have been omitted for clarity.

(0.3 mmHg, 30 min), analyses and ^{1}H n.m.r. spectra imply consistently a formula (LiBr·1.5HMPA·0.35 toluene)$_n$, (**1**)′.‡

Crystals of (**1**), mounted wet with toluene, were investigated by X-ray diffraction.§ The structure found (whose essential unit is shown in Figure 1) is indeed that of (LiBr·1.5 HMPA·0.5 toluene)$_n$, with n = 2: there are two crystallographically independent (LiBr·1.5 HMPA)$_2$ molecules within the asymmetric unit, the two toluene molecules (disordered) lying between these but not interacting with them. The two LiBr units within each molecule [Li–Br distance averaged over the independent molecules, 2.40 Å, range 2.39(2) Å—2.42(2) Å] are linked by three μ_2-HMPA ligands [average Li–O distance, 2.01 Å, range 1.97(3)—2.07(2) Å]. The observation of two such donor-connected LiHal 'monomers' is unusual (perhaps unprecedented), and the Li–Br distances in (**1**) are particularly short: association *via* halide bridges is the norm, *e.g.*, (LiBr·2L)$_2$, L = 2-MeC$_5$H$_4$N, obtained by direct dissolution, with an average Li–Br distance of 2.56 Å,[6] while in a LiBr tris-complexed monomer, LiBr·(3,5-Me$_2$C$_5$H$_3$N)$_3$, this distance is 2.51 Å.[6] The observation of three μ_2-HMPA ligands is certainly unprecedented. Two such have occurred, *e.g.*, in the cation of [Li(HMPA)(H$_2$O)$_2$]$_2$$^{2+}$ 2Cl$^-$,[7] but the closest analogy is with (LiClO$_4$)$_2$·(Me·CO·NH$_2$)$_3$·(Me-CO·NH·CO·Me)$_2$,[8] which has three μ_2-acetamide ligands; however the Li–O bridge bonds are long (av. 2.10 Å) and the ClO$_4$$^-$ ions are essentially separated [Li–O, 2.77(2) Å] from Li$^+$. It is also noteworthy that (**1**) displays an especially short cross-bridge Li · · · Li distance [av. 2.36(3) Å, *cf.* 2.74(2) Å in the above acetamide complex]. Furthermore, its isolation cements our view (simplistic) of how these *in situ* routes work, *viz.* breakdown of an (NH$_4$X)$_\infty$ lattice, low-temperature production of single LiX units, and then their capture by bases, L, present.

Complex (**1**) is extremely soluble in arene solvents (>2 g per ml of benzene or toluene at 20 °C). On dissolution, (**1**) appears simply to shed its toluene, leaving the (LiBr)$_2$·3HMPA unit intact. Firstly, cryoscopic relative molecular mass (c.r.m.m.) measurements on benzene solutions of (**1**)′ (r.m.m., 775.4) of concentrations 1.1—4.4 × 10^{-2} mol dm^{-3} [relative to the empirical formula of (**1**), mass 401.5] give remarkably constant values of 452—458(±15): freeing of lattice-bound toluene from (**1**)′, giving (LiBr·1.5 HMPA)$_2$ and 0.70 toluene, would produce an (apparent) r.m.m. value of 456. Secondly, and more significantly, 139.96 MHz ^{7}Li n.m.r. spectra of (**1**) or (**1**)′ {in [^{2}H$_8$]toluene, 25 to −95 °C, 1.6 × 10^{-2} to 8.7 × 10^{-1} mol dm^{-3} solutions} each display one signal (δ −0.95 to −1.10 p.p.m., relative to external Ph^{7}Li), indicating the presence of just one type of Li-containing species. That this is indeed (LiBr)$_2$·3HMPA is shown by observation (in −95 °C spectra of more concentrated solutions) of a 1 : 3 : 3 : 1 quartet, attributable to through (O=P)-bond coupling of ^{7}Li with three HMPA-^{31}P atoms [^2J(^{7}Li-^{31}P) = 3.84 Hz]. Direct ^{7}Li-^{31}P coupling has been observed in several lithium phosphide complexes (J = 36 −122 Hz),[9] but, to our knowledge, two-bond coupling has not, and certainly not to Li from P centres in neutral ligands as opposed to anionic ones.

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‡ For (LiBr·1.5HMPA·0.35 toluene)$_n$, (**1**)′: m.p. 70—72 °C; ^{1}H n.m.r. spectrum ([^{2}H$_6$]benzene): δ 2.56/2.44 (d, 27H of HMPA), δ 2.12 (s, ~1.1H of toluene-Me). Analyses ($C_{11.45}H_{29.8}BrLiN_{4.5}O_{1.5}P_{1.5}$)$_n$: Calcd., C, 35.4; H, 7.7; Br, 20.6; Li, 1.8; N, 16.2. Found, C, 35.0; H, 7.7; Br, 21.0; Li, 1.8; N, 16.5%.

§ *Crystal data* for (**1**): [LiBr·1.5HMPA·0.5toluene]$_2$, $C_{25}H_{62}Br_2Li_2N_9O_3P_3$, M = 803.43, transparent block, 0.30 × 0.45 × 0.50 mm, triclinic, $P\bar{1}$ (No. 2), a = 15.183(2), b = 16.082(2), c = 19.523(3) Å, α = 113.17(1), β = 100.45(1), γ = 90.47(1)°, U = 4293(1) Å^3, Z = 4 (dimer units), D_c = 1.243 g cm^{-3}, F(000) = 1680, λ(Cu-K_α) = 1.54178 Å, μ(Cu-K_α) = 41.40 cm^{-1}; 13 651 measured intensities ($2\theta_{max}$ = 116°), averaged to give 4989 unique reflections with $F > 5\sigma(F)$; structure solved by direct methods and refined by blocked-cascade least-square to R = 0.078 and R_w = 0.085. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.

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3 The route is under preliminary patent (Br. Pat. Appl. No. 8724662), filed by the Associated Octel Co. Ltd., U.K.; likely applications of these complexes were noted in reference 1.

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