The Isolation and Crystal Structure of $\{Li\cdot(H_2O)_2\cdot[O{=}P(NMe_2)_3]\}_2^{2+}\cdot 2Cl^-$: a $(LiO)_2$ Ring Compound with Bridging Neutral Oxygen (Hexamethylphosphoramide) Ligands

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The low melting-point, hydrocarbon-soluble, and moisture-sensitive crystalline material isolated from the reaction of hydrated lithium chloride with $O{=}P(NMe_2)_3$ (HMPA) has been shown by *X*-ray crystallography to be the discrete, internally-ionic complex, $[Li\cdot(H_2O)_2\cdot HMPA]_2^{2+}\cdot 2Cl^-$; the chloride ions are hydrogen bonded to the cation's water molecules, which are terminally bonded to the lithium atoms, while the centre of the cation consists of a planar $(LiO)_2$ ring provided by bridging, yet formally neutral, HMPA ligands.

We report the isolation and crystal structure of $[Li\cdot(H_2O)_2\cdot HMPA]_2^{2+}\cdot 2Cl^-$, (**1**), [HMPA = $O{=}P(NMe_2)_3$]. An earlier study[1] on the seemingly-related lithium chloride complex, $[ClLi\cdot HMPA]_4$, (**2**), which was shown to have a pseudo-cubane structure with Cl atoms triply-bridging Li_3 faces and with HMPA ligands terminally attached to each lithium, prompted a simple investigation of the behaviour of deliberately *hydrated* lithium chloride in the presence of HMPA. The so obtained crystalline material, (**1**), has a markedly different stoicheiometry and structure (Figure 1) from that of (**2**) noted above. It consists of a dimeric, doubly-charged lithium cation with *no* Li–Cl bonds, the

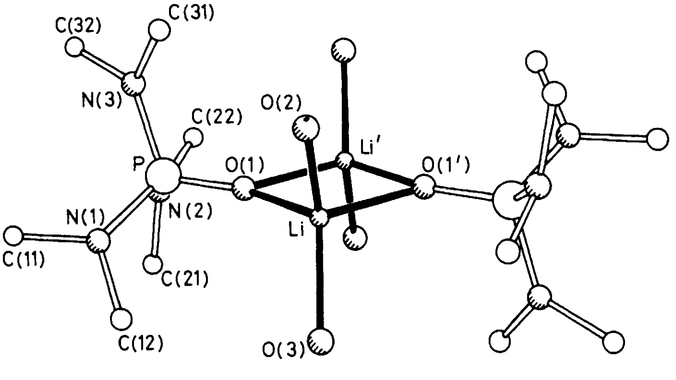

Figure 1. Structure of the cation of $\{Li\cdot(H_2O)_2\cdot[O{=}P(NMe_2)_3]\}_2^{2+}\cdot 2Cl^-$, (**1**). *Crystal data* for (**1**): $C_{12}H_{44}Li_2N_6O_6P_2$, M = 515.3, triclinic, space group $P\bar{1}$, a = 8.560(2), b = 8.825(2), c = 9.921(2) Å, α = 98.37(1), β = 91.42(1), γ = 115.35(1)°, U = 666.9 Å^3, Z = 1, D_c = 1.283 g cm^{-3}, $F(000)$ = 276, μ = 3.95 cm^{-1}, R = 0.038 for 2576 reflections with $F > 4\sigma(F)$ using Mo-K_α radiation (λ = 0.71069 Å). Key dimensions: Li–O(1) 1.984(3), Li–O(1′) 2.013(3), Li–O(2) 1.940(4), Li–O(3) 1.936(4), O(1)–P 1.496(1) Å; Li–O(1)–Li′ 82.3(1), O(1)–Li–O(1′) 97.7(1), Li–O(1)–P 152.0(1), Li′–O(1)–P 125.2(1), O(2)–Li–O(3) 127.1(2)°.

chlorides acting as counter-ions hydrogen bonded to water ligands of the cations; further, within the cation, each Li has four bonds to oxygen atoms [*cf.* in (**2**), 3 bonds to Cl atoms, 1 to an O atom] provided by two terminally-attached H_2O molecules, and by two formally *neutral,* yet *bridging,* HMPA ligands, which thus help form a planar $(LiO)_2$ ring.

$$[ClLi\cdot HMPA]_4$$
(**2**)

The cubane complex, (**2**),[1] had been isolated from an *in situ* reaction of the imidolithium complex, $(Bu^t_2C{=}NLi\cdot HMPA)_2$, with $AlCl_3$ in diethyl ether–hexane, while the direct route using anhydrous LiCl with the donor proved less successful. In contrast here, simple addition of HMPA to a mixture of *hydrated* LiCl and toluene under nitrogen readily caused dissolution, and subsequent cooling at −10 °C afforded fine colourless needles of (**1**). The i.r. spectrum of the product had sharp ν(O–H) bands indicative of bound, stoicheiometric amounts of water ligands rather than of entrapped solvate, and characterisation (by elemental analysis and n.m.r. spectroscopy) proved (**1**) to be of the formula $[LiCl\cdot(H_2O)_2\cdot HMPA]_n$. The structural formulation subsequently provided by *X*-ray diffraction is $[Li(H_2O)_2\cdot HMPA]_2^{2+}\cdot 2Cl^-$. The water ligands and chloride ions are involved in hydrogen bonding, each Cl^- forming four hydrogen bonds with Cl · · · O between 3.18 and 3.26 Å, these being approximately colinear with the O–H bonds. The hydrogen bond network forms sheets parallel to the *ab* plane. Between the sheets normal van der Waal's contacts are observed between HMPA methyl groups. This sheet structure is easily broken down on heating [hence the low m.p. of 63 °C; *cf.* complex (**2**), 142 °C, and anhydrous LiCl, 605 °C] or by dissolution [hence (**1**)'s high solubility in hydrocarbon solvents].

The structure of the cation of (**1**) is shown in Figure 1, whose legend notes key dimensions.† While simple lithium salts have long been studied in numerous donor media, and conclusions drawn about ion-pairing behaviour,[2] relatively few solid-state structures of isolated crystalline materials have been reported. The best available for analogy with the terminal $Li{-}OH_2$ bonds in (**1**), (Li–O, 1.936 and 1.940 Å) are those of $[LiClO_4\cdot(18\text{-crown-}6)\cdot 2H_2O]$,[3] where each Li is bound to two ether and two water oxygen atoms (Li–O av. 2.01 Å), and of $[LiCl\cdot(C_5H_5N)_2\cdot(H_2O)_2]$,[4] with lithium contacts to one Cl, two pyridine N, and one water oxygen at 1.94 Å. In this context of the $Li{-}OH_2$ bonds, a particularly interesting feature of complex (**1**), aside from the previously noted drastic structural amendment brought about by such ligands, *cf.* the non-aquo cubane (**2**), is their very presence. Thus, (**1**) is exceedingly moisture-sensitive, *i.e.,* it contains clearly highly reactive, yet, anomalously, unreacted, ligands.

A final intriguing, aspect of the structure of (**1**) is the presence of bridging, yet neutral, HMPA ligands, with Li–μ-O bonds of length 1.984 and 2.013 Å. Such an unusual bonding mode in a discrete, oligomeric complex had previously only been noted in the μ_2-O isomer of the seemingly remotely-related phenyl(pyridyl)amidolithium (Pyr = pyridyl), [Ph(2-Pyr)NLi·HMPA]$_2$,[5] Li–O av. 1.924 Å, though carbonyl groups effect association in ionic polymers $LiI\cdot 2[(NH_2)_2C{=}O]$,[6] Li–O 1.92 Å, and $(LiClO_4)_2\cdot[\mu\text{-}\{MeC(O)NH_2\}]_3\cdot[MeC(O)\cdot NH\cdot C(O)Me]$,[7] Li–μ-O 2.14 Å. The Li–HMPA bridge bonds in (**1**) are expectedly longer than the usual Li–HMPA terminal bonds, *e.g.* in cubane (**2**), 1.858—1.877 Å, and in the μ_2-N isomer of the phenyl(pyridyl)amidolithium, 1.870 Å. While there are many examples of *anionic* oxygen ligands bridging metal atoms, *e.g.*, the alkoxide, $[(\mu\text{-}ArO)Li\cdot OEt_2]_2$,[8] with μ_2-O–Li 1.86 Å, and the enolate, $\{[\mu\text{-}(H_2C{=}C(Bu^t)O)]Li\cdot THF\}_4$ (THF = tetrahydrofuran),[9] with μ_3-O–Li 1.97 Å, the tempting isoelectronic analogy between $R_3C{-}O^-$ and HMPA viewed as $(Me_2N)_3\text{-}\overset{+}{P}{-}O^-$ does not seem to be valid. Thus, P–O distances in the terminal HMPA complexes, the μ_2-N isomer of [Ph(2-Pyr)NLi·HMPA]$_2$ and cubane (**2**), are 1.469 and 1.465 Å, respectively, and these do not significantly lengthen in the μ_2-O isomer of the former or now in (**1**), being 1.488 and 1.496 Å, respectively.

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† Atomic co-ordinates are available from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.