Cage Compounds

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Inverse Coordination of an Ionic Lattice by a Metal Host**

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There is considerable interest in the effects of modifying the structures of ionic compounds into molecular arrangements, to give materials with unusual properties such as low melting points and solubility in organic solvents.[1] Fragmentation of

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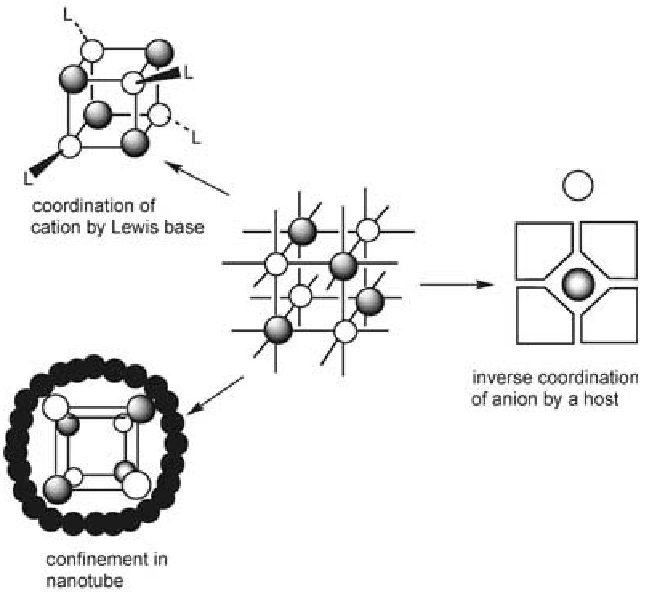
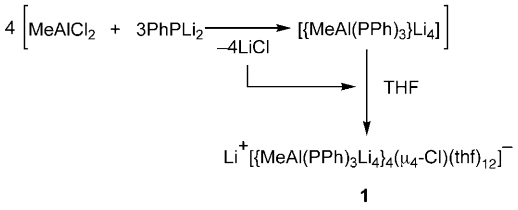
an ionic lattice can be achieved by replacing some or all of the cation–anion bonding with Lewis base coordination (Scheme 1).[1] In notable cases, the molecular species produced have a close resemblance to the parent lattice.[2] A further strategy is the confinement of a salt lattice within another framework. Recent research has focused on the growth of salt lattices within carbon nanotubes (Scheme 1).[3] Remarkably, novel lattice arrangements can be formed which are different to the bulk materials. A third way by which alkali metal salt lattices can, in theory, be modified is by coordination of the anion (Scheme 1).

This approach is the opposite to the conventional coordination of the cation using a Lewis base and thus can be termed as "inverse coordination".[4] Although there are many examples of anion receptors based on organic frameworks, in these anion receptors interactions are relatively weak compared to the lattice energies of simple metal salts.[5] The obvious candidates for strong anion receptors are inorganic metal hosts. Recent studies by Mulvey[4] and Hawthorne and Zheng[6] have illustrated the power of inverse coordination of this type using macrocyclic hosts.



Scheme 1. Modification of ionic lattices, as illustrated for the fragmentation of the NaCl-type lattice.

As part of our studies into the structural and materials properties of p-block-metal phosphides,[7–9] we recently investigated the synthesis of Group 13 anions $[RE(PR)_3]^{4-}$ (E = Al, Ga, In).[10] From the reaction of "$PhPLi_2$"[11] with $MeAlCl_2$ in tetrahydrofuran (THF) the ion-separated compound $Li^+[\{MeAl(PPh)_3Li_4\}_4(\mu_4\text{-}Cl)(thf)_{12}]^-$ (**1**) was obtained as a crystalline product in 43% yield (first batch; see Scheme 2 and Experimental Section).



Scheme 2. Synthesis of **1**.

Although **1** was characterized by spectroscopic and analytical investigations, its elaborate structure was not fully apparent until a later low-temperature X-ray study.[12] This study showed that the heterometallic cage anion of **1** has a $[Al_4P_{12}Li_{16}(\mu_4\text{-}Cl)]$ core (Figure 1 a), in which an interstitial Cl^- anion is effectively coordinated by four of the anticipated $[MeAl(PPh)_3Li_4]$ units. Although templating of inorganic cages by halide ions has been seen before,[13] to our knowledge **1** is the first example in which a lattice of a simple binary salt is modified by inverse coordination exclusively of one ion.

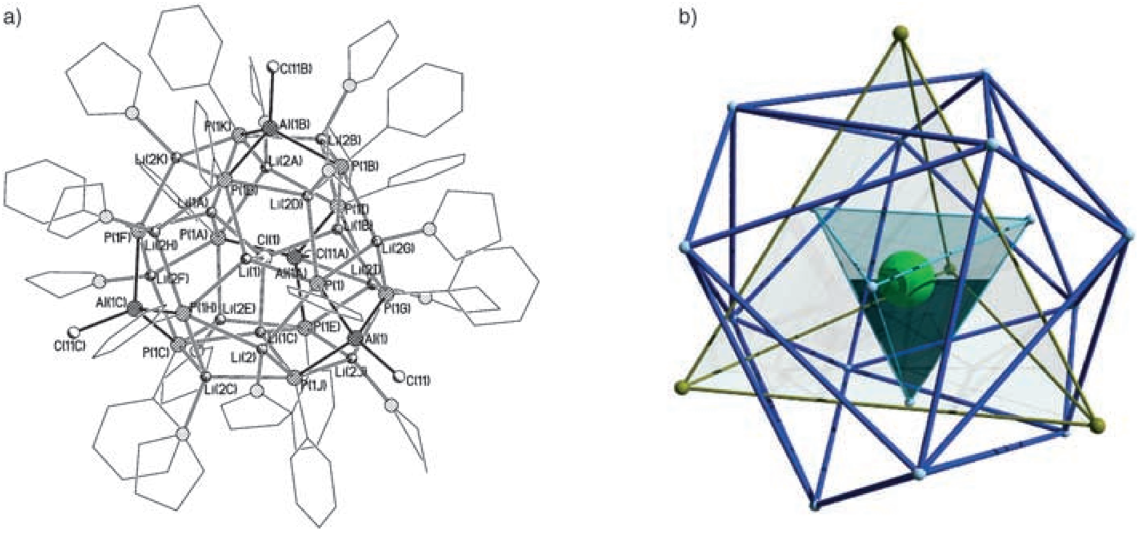


Figure 1. a) Structure of the heterometallic anion of **1**. Selected bond lengths [Å] and angles [°]: Al(1)–C(10) 2.01(2), Al(1)–P(1) 2.461(3), P(1)–Li(1) 2.530(5), P(1)–Li(2) 2.63(1), P(1)–Li(2D) 2.47(2), P(1)–Li(2G) 2.71(2), Li(1)–Cl(1) 2.45(2); P(1)-Al(1)-P(1G) 103.0(1), C(10)-Al(1)-P(1) 115.33(9), Li-Cl(1)-Li(mean) 109.5. Symmetry transformations used to generate equivalent atoms: **A** $x, -y+1, -z+1$; **B** $-x+1, -y+1, z$; **C** $-x+1, y, -z+1$; **D** $-z+1, x, -y+1$; **E** $y, -z+1, -x+1$; **F** z, x, y; G y, z, x; **H** $-x+{}^3/_2, -z+1, y+0$; **I** $-x+{}^3/_2, z+0, -y+1$; b) Polyhedral Li (outer shell: blue), Al (gold), Li (inner shell: light blue).

Interestingly, lithium complexes containing the related nitrogen anions $[R'Al(NAr)_3]^{4-}$ (R′ = Et, *n*Bu; Ar = 2-MeO-C_6H_4) adopt the ion-separated arrangements $[Li(thf)_4]^+{}_2$-$[\{R'Al(NR)_3\}_2Li_6]^{2-}$, in which no encapsulation of Cl^- ion occurs even though LiCl was also present as a byproduct in their formation.[10] This difference may reflect the lower ligand bite angle of the $[RAl(NAr)_3]^{4-}$ anions (average N···N distance 2.91 Å) compared to the $[MeAl(PPh)_3]^{4-}$ analogue (P···P 3.85 Å).[14] The tetrahedral $[MeAl(PPh)_3]^{4-}$ anions of **1** are arranged in a supramolecular tetrahedron (gold, Figure 1b), which defines the polyhedral arrangement of Li^+ cations. The twelve phosphorus atoms of the cage are all six-coordinate, each being bonded to four Li^+ cations within the core (Li–P 2.47(2)–2.71(2) Å). The twelve symmetry-related ions Li(1) to Li(1K) (dark blue, Figure 1b) form an outer shell of ions that are each bonded to three phosphorus centers and to the oxygen atom of a thf ligand. The inner sphere of Li ions Li(1) to Li(1C) (light blue, Figure 1b) have a similar tetrahedral environment, but their fourth coordination site is occupied by the central Cl^- anion (Li(1–1C)–Cl(1) 2.45(2) Å) rather than an O atom from thf.

A single, unsolvated Li^+ countercation is present in the lattice of **1** for each of the cage anions (the charge of each anion being −1). Owing to the cubic space group there is inherent uncertainty as to the location of these Li^+ cations, however, their most likely location is midway between cluster anions (along the edges of the cubic unit cell and the central face-to-face diagonals), that is, $\frac{1}{3}$ Li^+ occupancy in each of these 24 symmetry-related sites balancing the −8 charge of the 8 anions. Eight anions are depicted in Figure 2.[12] The Li^+ cations loosely bind two cluster anions together through agostic C–H···Li interactions with two pairs of symmetry-related thf molecules (C···Li 2.82–2.84 Å).[15] The resulting zeolite-like structure contains large voids (ca. 17 Å in diameter) and has nearest neighbor Li^+ and encapsulated Cl^- ions separated by 8.76 Å. The absence of further disordered thf molecules or $[Li(thf)_4]^+$ cations in these voids was shown by elemental analysis and ^1H NMR spectroscopic studies of bulk samples of **1** (analyzed both before and after exposure to a vacuum). We assume that **1** adopts this open arrangement in order to minimize anion–anion repulsion, while allowing efficient anion–cation interactions between the polyhedra. Clearly, anion–anion repulsion would be significantly greater in the close-packed structure of the original LiCl lattice.

Solid-state ^6Li and ^7Li magic-angle-spinning (MAS) NMR studies of **1** are consistent with the X-ray study,[16] showing the expected presence of a highly mobile Li^+ cation as a result of its weak coordination. Two resonances are found in the ^6Li NMR spectrum at $\delta = 3.8$ ($w_{1/2} = 50$ Hz, 10 Hz line broadening) and 2.2 ppm (very broad). At least two overlapping resonances are apparent in the ^7Li NMR spectrum at $\delta = 3.6$ and 0.4 ppm.[17] The ^7Li relaxation-assisted separation (2D-RAS) spectrum[18] shows that the peak at $\delta = 0.4$ ppm has a longitudinal relaxation time constant $t_1 = 107$ s, which is consistent with a mobile lithium ion without strong interactions to other nuclei (Li(3)), while the peak at $\delta = 3.6$ ppm has $t_1 = 6$ s. The peak at $\delta = 0.4$ ppm does not appear in a $^7Li\{^1H\}$ CPMAS NMR spectrum, confirming that lithium is not bound strongly to any protons in the crystal. Furthermore, the peak at $\delta = 3.6$ ppm is very broad and likely contains the peaks appearing at $\delta = 3.8$ and 2.2 ppm observed in the ^6Li NMR spectrum which are assigned to the cage lithium atoms Li(1) and Li(2). It can be noted that all three Li environments are observed for **1** in solution in THF.

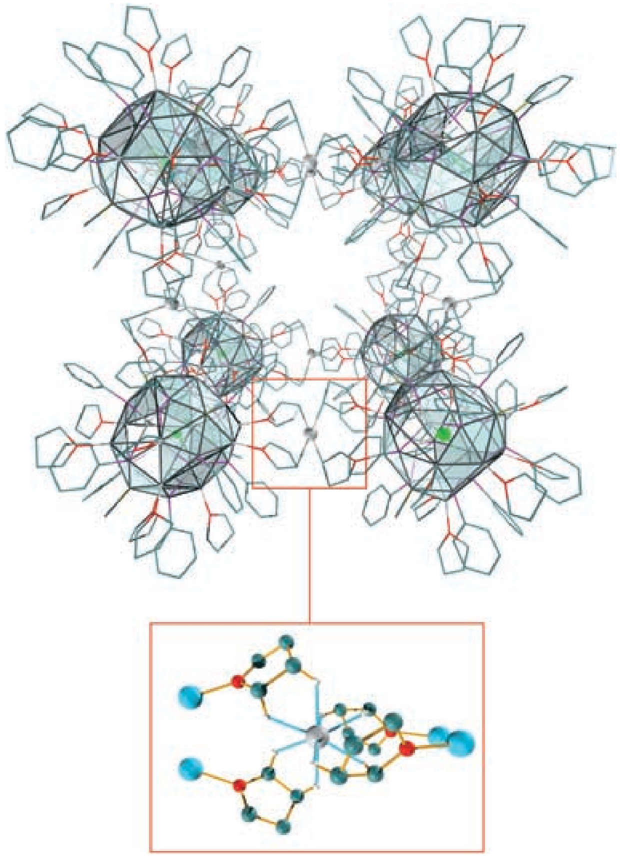


Figure 2. Formation of cube-shaped cavities within the structure of **1**, showing the partial occupancy Li(3) sites between adjacent cluster anions. The insert shows the thf C–H···Li^+ interactions that anchor the Li^+ counterions in the lattice: C···Li 2.81–2.84 Å (H···Li 2.09–2.16 Å).

The structure of **1** dramatically illustrates the concept of lattice modification using inverse coordination of a simple ionic salt. A large expansion of the NaCl-type lattice of LiCl results from the encapsulation of the Cl^- ions within the cages, with a loss of the original close packing of the chloride ion array. This type of structural modification provides a potentially general new strategy for crystal engineering. Such a strategy should lead to a novel approach to fast-ion conductors.[19,20] The generalization of this synthetic approach using inorganic frameworks with building blocks related to the $[MeAl(PPh)_3]^{4-}$ anions in **1** is therefore an exciting prospect both from a theoretical and technological standpoint.[21]

Experimental Section

1: All manipulations were performed under dry, O_2-free argon. *n*BuLi (8.25 mL, 1.60 M in hexane, 13.2 mmol) was added to a stirred solution of $PhPH_2$ (0.66 mL, 6.00 mmol) in diethyl ether (50.0 mL) at −78 °C.

The reaction mixture was allowed to warm to room temperature and stirred for a further 1 h, producing a yellow precipitate, then the reaction mixture was heated at reflux (14 h). The resulting suspension was cooled to −78 °C, and $MeAlCl_2$ (2.00 mL, 1.00 M in hexane, 2.00 mmol) was added. The mixture was allowed to warm to room temperature and then heated at reflux (14 h) to give a yellow solution and white precipitate. After replacing the solvent by toluene (50.0 mL) and filtration (Celite, P4) to remove LiCl, the solvent was removed under vacuum and a yellow precipitate was obtained. Crystallization from THF at room temperature (14 h) led to light yellow cube-shaped crystals of **1** (0.54 g yield, 43 % first batch of crystals); decomp. ca. 210 °C (red) to ca. 270 °C (black solid); IR (Nujol, NaCl), $\tilde{\nu} = 3030$(w) (C−H aryl stretch), 1570(w) (C$\overset{...}{=}$C stretch), 1022(s) cm^{-1}; no P−H stretching band was observed; ^1H NMR (500.2 MHz, 298 K, C_6D_6): $\delta = 8.3$ (m, *m*-CH Ph), 7.22 (q, *p*-CHPh), 0.40 ppm (br s, Me-Al); ^{31}P NMR (202.5 MHz, 298 K, THF/[D_6]acetone capillary, 85 % H_3PO_4/D_2O): $\delta = -161.8$ ppm; ^7Li NMR (194.4 MHz, 298 K, THF/[D_6]acetone capillary, sat. $LiCl/D_2O$): $\delta = 2.25$ (br s, $w_{1/2} = 29$ Hz, Li(3)), 1.82 (br s, $w_{1/2} = 29$ Hz, Li(1)), 0.36 ppm (s, $w_{1/2} = 10$ Hz, Li(2)); assignments were made solely on the basis of the approximate integration of the spectrum, 1:4:8 ratio of the resonances (theoretical 1:4:12). The ^{31}P and ^7Li NMR solution spectra do not change with concentration or temperature (180–298 K), proving that no fragmentation of the anion of **1** occurs in solution. Solid state MAS-NMR, ^7Li (155.406 MHz, 32 scans, 15-s recycle delay): $\delta = 3.6$ (Li(1) and Li(2)), 0.4 ppm (Li(3)); $^7Li\{^1H\}$ CPMAS (399.87 MHz for ^1H, 4-ms contact time, 8 scans): $\delta = 3.6$ ppm; $^6Li\{^1H\}$ CPMAS (58.89 MHz/399.87 MHz for ^1H, 3-ms contact time, 4096 scans): $\delta = 3.8$ (Li(1)), 2.2 ppm (Li(2)); assignments made on the basis of approximate 2:1 integration. Sixty logarithmically spaced τ values were collected between 0.01 s and 160 s for the RAS spectrum; twenty-four transients were collected for each τ value;[22] elemental analysis (%) calcd for **1**: C 60.0, H 6.8, P 15.0; found (typical): C 59.0, H 7.6, P 12.7.

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