

In situ complexation of lithium chloride by amphiprotic cyclophosphazenes

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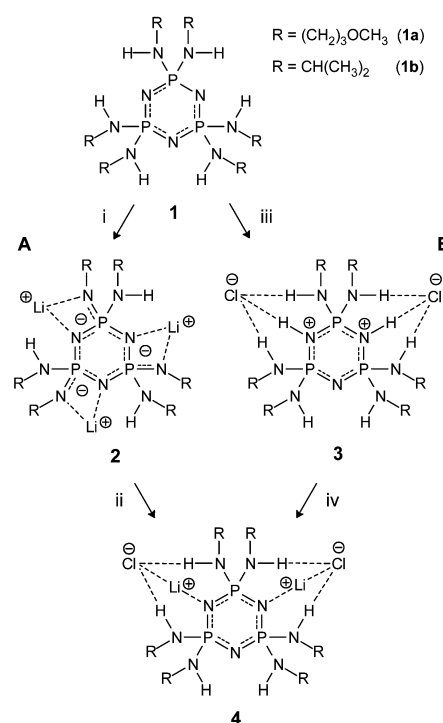
The amphiprotic cyclophosphazene $\{\text{CH}_3\text{O}(\text{CH}_2)_3\text{NH}\}_6\text{P}_3\text{N}_3$ (**1**) incorporates lithium chloride *via* successive protonation with HCl and deprotonation with $\text{Bu}^\text{n}\text{Li}$ (or *vice versa*) to generate the coordination polymer $1\cdot 2\text{LiCl}$, a molecular model compound for lithium ion containing solid polymer electrolytes.

Solid polymers hosting highly mobile lithium ions are promising materials as thin film electrolytes for secondary lithium batteries.¹ Polyphosphazenes have been thoroughly investigated as electrolyte polymers, since the ease of side chain derivatisation in phosphazenes enables fine-tuning of the properties of the polymer matrix. In particular, polyphosphazenes carrying polyether groups form stable films and exhibit high ion conductivities.² In recent years we have been studying the deprotonation behaviour of hexakis(organoamino)cyclo-triphosphazenes $(\text{RNH})_6\text{P}_3\text{N}_3$ (**1**).³ Organolithium compounds, such as $\text{Bu}^\text{n}\text{Li}$, deprotonate **1** to give lithium salts of trianionic and hexaanionic phosphazenes, $[(\text{RNH})_3(\text{RN})_3\text{P}_3\text{N}_3]^{3-}$ (**2**) and $[(\text{RN})_6\text{P}_3\text{N}_3]^{6-}$, respectively.⁴ Conversely, Brønsted acids protonate **1** to form phosphazanium ions $[(\text{RNH})_6\text{P}_3\text{N}_3\text{H}]^+$ and $[(\text{RNH})_6\text{P}_3\text{N}_3\text{H}_2]^{2+}$ (**3**).⁵ This extensive amphiprotic behaviour involving eight protic functions and the large array of potential binding sites for both cations (*via* N centres) and anions (*via* NH groups) gave us the concept to introduce lithium salts into neutral phosphazenes *in situ* by successive acid–base reactions in order to obtain molecular model compounds for lithium ion containing polyphosphazene electrolytes. A number of *in situ* methods have been reported, which generate molecular complexes of inorganic lithium salts.⁶ A prominent example is the ammonium salt route, where NH_4X is deprotonated by $\text{Bu}^\text{n}\text{Li}$ in the presence of an organic donor ligand L to yield complexes of composition $(\text{LiX})_m\text{L}_n$. The usually oligomeric $(\text{LiX})_m$ core is stabilised within the lipophilic ligand sphere L_n , which also provides solubility in organic solvents.⁶

Herein, we report that lithium chloride can be accommodated into cyclophosphazenes, **1**, by routes **A** and **B** (Scheme 1). Route **A** introduces the lithium ions first by deprotonation of **1** with $\text{Bu}^\text{n}\text{Li}$ leading to the trianionic species **2**.⁴ The chloride ions are then inserted by protonation of **2** with Et_3NHCl . Route **B** introduces the chloride ions first by protonating **1** with HCl to give the dicationic species **3**. This is then deprotonated with $\text{Bu}^\text{n}\text{Li}$ to yield the lithium chloride adduct **4**. We have equipped the R groups in **1** with ether functions to increase the number of potential donor sites for lithium ions. $\{\text{CH}_3\text{O}(\text{CH}_2)_3\text{NH}\}_6\text{P}_3\text{N}_3$ (**1a**) exists as a viscous oil at room temperature. The deprotonation and protonation behaviour of **1a** was monitored by ^{31}P NMR spectroscopy showing that **1a** (18.9 ppm) is deprotonated by three equivalents of $\text{Bu}^\text{n}\text{Li}$ in a similar fashion as the previously reported anilino derivatives, $(\text{PhNH})_6\text{P}_3\text{N}_3$,⁴ giving trianionic **2a** (24.4 ppm). Protonation of **1a** with HCl causes the ^{31}P NMR signal to shift to 12.7 ppm, indicating the presence of **3a** which, like **1a**, is an oily substance at room temperature. Structural information about the location of protons and the interaction of chloride ions in **3** was gained from the isopropyl derivative **1b**, which shows a similar signal shift (**1b**: 15.7 ppm, **3b**: 7.1 ppm) in the ^{31}P NMR spectra upon reaction with HCl and gives suitable crystals of the phosphazeni-

um dichloride salt **3b**. The crystal structure reveals that two N(ring) centres are protonated.[†] The four P–N(ring) bonds associated with protonated N(ring) atoms are considerably longer (av. 1.65 Å) than those of the two non-protonated P–N(ring) units (av. 1.56 Å). Chloride ions interact with both endocyclic and exocyclic NH functions *via* hydrogen bonds. N...Cl distances of endocyclic NH...Cl bonds are shorter (av. 3.10 Å) than those of exocyclic NH...Cl bonds (av. 3.23 Å). The phosphazanium dicationic species are bridged by pairs of chloride ions resulting in a supramolecular 1-D chain (Fig. 1).

Both reaction of **2a** with Et_3NHCl (route **A**) and treatment of **3a** with $\text{Bu}^\text{n}\text{Li}$ (route **B**) yield the lithium chloride adduct **4a**, which exhibits a similar ^{31}P NMR chemical shift as **1a**. The LiCl adduct **4a** precipitates from THF solution upon addition of hexane as a hygroscopic white powder, which melts at 65 °C.⁷ Microanalytical data of this material correspond to the composition $[(\text{LiCl})_2\{\text{CH}_3\text{O}(\text{CH}_2)_3\text{NH}\}_6\text{P}_3\text{N}_3]$. Crystals of **4a** suitable for X-ray structure analysis were obtained by slow diffusion of hexane into a solution of **4a** in THF.[†] Two equivalents of LiCl per phosphazene molecule are incorporated into the crystal structure (Fig. 1). Each phosphazene molecule binds two lithium ions *via* two N(ring) centres, whilst the exocyclic NH groups are not interacting with lithium ions. The Li–N interaction has no marked impact on the P–N(ring) bond lengths. All P–N(ring) distances in **4a** are within a close range (1.594(2) to 1.617(2) Å) and comparable to those found in



Scheme 1 Reagents and conditions: (i) 3 $\text{Bu}^\text{n}\text{Li}$ (1.6 M in hexane), THF; (ii) 3 Et_3NHCl , THF, then filtration and precipitation of **4a** with hexane; (iii) anhydrous HCl, THF; (iv) 2 $\text{Bu}^\text{n}\text{Li}$ (1.6 M in hexane), THF, then precipitation of **4a** with hexane (86% yield).

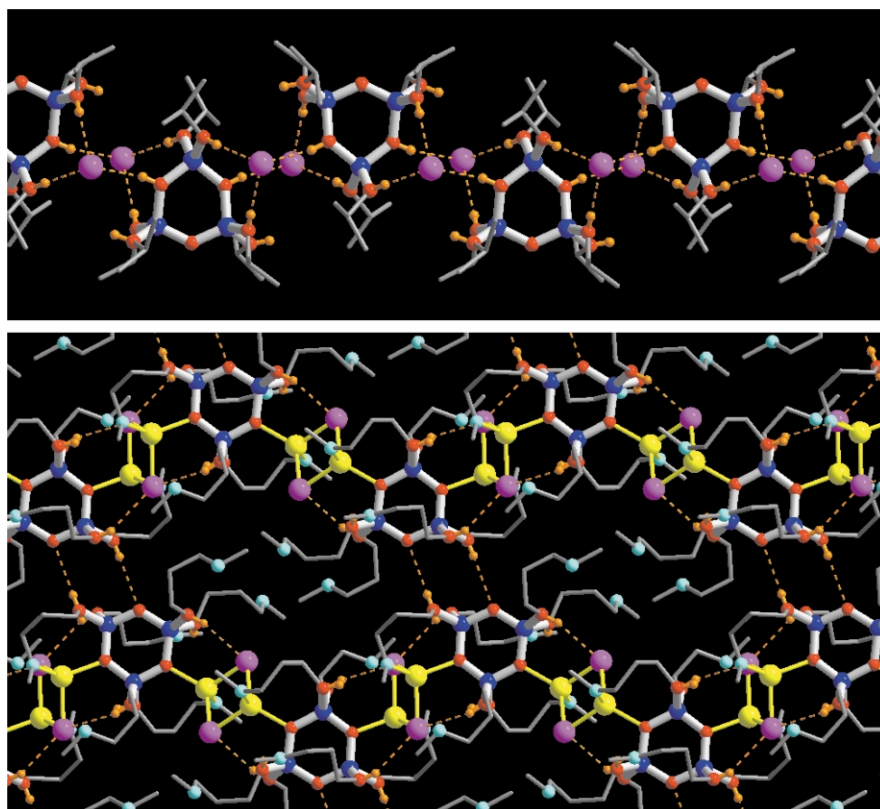


Fig. 1 Crystal structures of **3b** (top) and **4a** (bottom); P, blue; N, red; Li, yellow; H, orange; Cl, purple; O, turquoise.

derivatives of **1**.⁸ Two chloride ions and one ether function complete the tetrahedral coordination sphere of the lithium ions. The two crystallographically unique Li–N bonds are 2.047(5) and 2.094(5) Å long, Li–Cl interactions range between 2.337(5) and 2.350(5) Å and the two unique Li–O bonds measure 1.978(5) and 1.995(6) Å, respectively. These bond lengths are comparable with corresponding bond lengths of LiCl adducts of organic ethers and amines.⁶ Chloride ions form hydrogen bonds with exocyclic NH groups. N...Cl distances (3.350(2) and 3.431(2) Å) are slightly longer than in **3b**. Other hydrogen bonds in **4a** include an intramolecular NH...O bond (N...O 3.126(3) Å) and an intermolecular NH...N(ring) bond (N...N 3.304(3) Å). The supramolecular structure is dominated by the interaction of dimeric (LiCl)₂ units with phosphazene molecules resulting in a 1-D coordination polymer. In addition, pairs of NH...N(ring) bonds between phosphazene molecules from neighbouring chains extend the supramolecular structure into a 2-D architecture.

Cyclophosphazene–LiCl adducts such as **4a** can serve as valuable molecular models for polyphosphazene electrolytes by providing detailed structural data of ion–phosphazene interactions. Until now it was unclear whether the phosphazene backbone interacts with lithium ions. This study shows that such coordination can occur. Another interesting feature of **4a** is the ability of the phosphazene ligand to bind cations and anions simultaneously. The ligand–anion interaction is established via N–H...X bonds, which might support anion immobilisation in the polyphosphazene matrix. It should be noted that NH-functions in **1a** are inert towards elemental lithium,⁹ a necessity for components used in lithium fuel cells. Also, the *in situ* introduction of LiCl into the cyclophosphazene matrix promises interesting applications for molecular cyclophosphazenes in solid electrolyte materials, considering the high ionic conductivity of some solid ‘molecular’ electrolytes such as Li(CH₃OH)₄I.¹⁰

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Notes and references

† Crystal data. **3b**: C₁₈H₅₀Cl₂N₉P₃, *M* = 556.48, *T* = 100 K, *P*2₁/*c*, *a* = 14.017(2), *b* = 17.140(2), *c* = 13.128(2) Å, β = 100.420(2)°, *V* = 3102.0(7) Å³, *Z* = 4, μ(MoK_α) = 0.387, 5471 independent reflections (*R*_{int} = 0.072), *R*1 = 0.046, *wR*2 = 0.118; **4a**: C₂₄H₆₀Cl₂Li₂N₉O₆P₃, *M* = 748.50, *T* = 150 K, *P*1, *a* = 11.049(2), *b* = 11.709(2), *c* = 16.158(2) Å, α = 70.746(2), β = 85.124(2), γ = 80.226(2)°, *V* = 1943.9(4) Å³, *Z* = 2, μ(MoK_α) = 0.337, 5529 independent reflections (*R*_{int} = 0.061), *R*1 = 0.038, *wR*2 = 0.085. NH hydrogens were located in difference maps and were refined using similar distance restraints for N–H bonds. CCDC reference numbers 203806 and 203807. See <http://www.rsc.org/suppdata/cc/b3/b301725g/> for crystallographic data in .cif format.

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