$[Li(NH_3)_4]_3P_{11}\cdot 5NH_3$: preparation and crystal structure of a Zintl compound ammoniate with a very high ammonia content

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The ammoniate $[Li(NH_3)_4]_3P_{11}\cdot 5NH_3$, prepared from Cs_3P_{11} and an exchange resin loaded with Li^+ in liquid ammonia, forms a three-dimensional network of lithium tetraamine complexes and free ammonia molecules of crystallisation linked by N–H···N hydrogen bonds, with undecaphosphatrishomocubane anions $P_{11}{}^{3-}$ sitting in large cavities.

The early history of Zintl anion chemistry is inseparably connected with the use of liquid ammonia as a solvent.[1] Already Johannis observed the change of colour associated with the formation of homoatomic polyanions upon reaction of solutions of sodium in liquid ammonia with a variety of post-transition elements,[2] and the breakthrough work of Zintl *et al.* on the characterisation of these species relied to a large extent on potentiometric titrations in ammonia.[3] They demonstrated that the solutions resulting from the extraction of binary intermetallic compounds in the Na–Pb or Na–Sb system contain anions of the composition $Pb_9{}^{4-}$ or $Sb_7{}^{3-}$. Upon evaporation of these solutions, however, highly unstable ammoniates precipitated, which quickly reverted to the intermetallic compounds due to loss of ammonia. Similarly, several polyphosphides were synthesised from alkali metals and P_4 in liquid ammonia,[4] which could only be obtained as finely divided, amorphous powders because of the decomposition of the initially formed ammoniates.

The thermal instability of these ammoniates, which is caused by the low stability of ammine complexes of the alkali-metal cations, has been the most serious obstacle to the structural characterisation of Zintl anions. Consequently, later investigations abandoned the solvent ammonia and turned to chelating amines like ethylenediamine (en), which permitted crystal structure determinations of compounds like $[Rb(en)]_3P_7$[5] and $Na_4(en)_7Sn_9$.[6] Finally, the ingenious use of cryptands by Corbett has produced a wealth of structural information on Zintl anions.[7]

Modern low-temperature techniques, however, make unnecessary the avoidance of liquid ammonia, which still has several advantages, especially for the work with thermally unstable compounds. To demonstrate this, we set out to prepare an ammoniate of the as yet unknown polyphosphide Li_3P_{11}, which, in contrast to the other alkali-metal phases $M^I{}_3P_{11}$ (M^I = Na–Cs) containing the 'ufosane' anion $P_{11}{}^{3-}$,[8] can not be synthesised from the elements.[5]

Another advantage of liquid ammonia is its similarity to water, which can be exploited by simply imitating well known techniques from aqueous chemistry like the application of solid ion-exchange resins, the preparative use of which in liquid ammonia has been reported recently.[9] Thus, when a solution of Cs_3P_{11} in liquid ammonia was allowed to react with an approximately 20-fold excess of a thoroughly dried exchange resin in its Li^+ form at 230 K, large red crystals precipitated after 6 h. These were separated from the resin by extraction using an H-type glass vessel with a glass frit. Subsequent analysis of the product showed that caesium had been completely exchanged for lithium. If ammonia was distilled of at low temperatures, however, the crystalline material decomposed to a glassy red solid, which indicated that an ammoniate had formed as expected. If crystals were removed from the mother-liquor into an atmosphere of dry argon, complete decomposition under evolution of ammonia took place immediately and spectacularly. Nevertheless, a single-crystal structure analysis could be performed by adapting the crystal selection and mounting technique of Kottke and Stalke[10] to the special needs of liquid ammonia.[11] The analysis† revealed the composition of the ammoniate to be $Li_3P_{11}\cdot 17NH_3$. All lithium cations are coordinated by four ammonia molecules of solvation each, forming roughly tetrahedral ammine complexes (Fig. 1), which makes the formula $[Li(NH_3)_4]_3P_{11}\cdot 5NH_3$ more appropriate. The Li–N distances within the three crystallographically inequivalent lithium tetraammine complexes range from 2.016 to 2.098 Å with an average of 2.059 Å. Most of the N–Li–N angles are close to the 109.47° angle of an ideal tetrahedron. The tetraammine complexes are connected to each other by a complicated network of N–H···N hydrogen bonds involving the remaining ammonia molecules of crystallisation which do not coordinate to lithium cations. Four of these 'free' ammonia

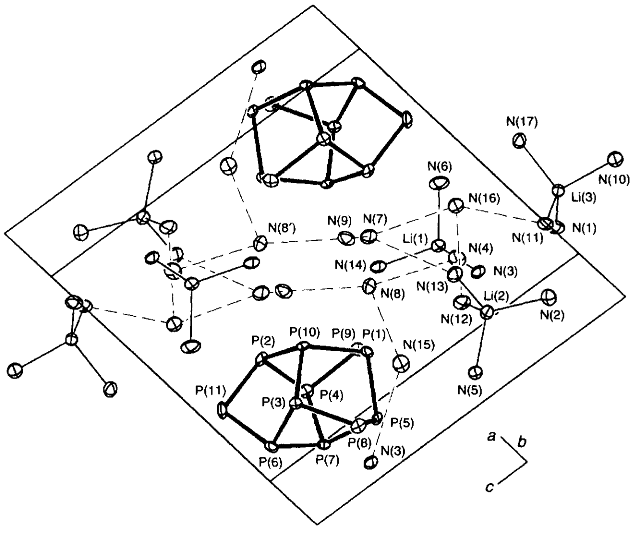

Fig. 1 ORTEP plot of a section of the structure of $[Li(NH_3)_4]_3P_{11}\cdot 5NH_3$ (50% probability ellipsoids). Possible hydrogen bonds are shown by dashed lines. Selected interatomic distances (Å) and angles (°): P(1)–P(9) 2.146(2), P(1)–P(5) 2.192(2), P(1)–P(10) 2.266(2), P(2)–P(11) 2.163(2), P(2)–P(4) 2.220(2), P(2)–P(10) 2.233(2), P(3)–P(8) 2.172(2), P(3)–P(6) 2.196(2), P(3)–P(10) 2.227(2), P(4)–P(9) 2.163(2), P(4)–P(7) 2.220(2), P(5)–P(8) 2.154(2), P(5)–P(7) 2.241(2), P(6)–P(11) 2.151(2), P(6)–P(7) 2.259(2), Li(1)–N(6) 2.053(8), Li(1)–N(14) 2.057(8), Li(1)–N(4) 2.058(8), Li(1)–N(3) 2.074(9), Li(2)–N(5) 2.016(8), Li(2)–N(12) 2.022(9), Li(2)–N(2) 2.064(8), Li(2)–N(13) 2.086(8), Li(3)–N(11) 2.039(8), Li(3)–N(1) 2.043(9), Li(3)–N(17) 2.069(8), Li(3)–N(10) 2.098(8), N(3)···N(15) 3.369(6), N(4)···N(8) 3.346(6), N(5)···N(15) 3.119(6), N(11)···N(16) 3.201(6), N(12)···N(16) 3.171(6), N(13)···N(7) 3.402(6), N(7)···N(16) 3.261(6), N(7)···N(9) 3.288(7), N(8′)···N(9) 3.341(6), N(8)···N(15) 3.346(7); N(6)–Li(1)–N(14) 109.5(4), N(6)–Li(1)–N(4) 107.4(4), N(14)–Li(1)–N(4) 106.1(4), N(6)–Li(1)–N(3) 109.1(4), N(14)–Li(1)–N(3) 113.5(4), N(4)–Li(1)–N(3) 111.1(4).

molecules have three nearest neighbours, one only two. The corresponding N···N distances range from 3.14 to 3.41 Å. These N···N distances are in accordance with those observed for the hydrogen bonds in cubic solid ammonia itself, in which each nitrogen atom has a distance of 3.38 Å to six nearest neighbours.[12] In the cavities within the network of lithium-coordinating and free solvent molecules lies the pentacyclic Zintl anion P_{11}^{3-}, which has the trishomocubane ('ufosane') cage structure reported previously.[8,13] Free P_{11}^{3-} cages which are not coordinated by alkali-metal cations are a novel feature, however, and have only been observed for $(NEtMe_3)_3P_{11}$[14] and $(NEt_4)_3P_{11}$.[15]

Surprisingly, although the lithium tetraammine complex has been considered the prevailing ammine complex of the lithium cation in liquid ammonia solutions as well as in several solid ammoniates,[16] no diffraction study of its structure seems to be available, as was revealed by a search in the ICSD.[17]‡ Evidence for this species, however, was provided by Raman spectra of liquid ammonia solutions of $LiNO_3$.[19]. It should be noted that $Li(NH_3)_4^+$ is isoelectronic to the prototypical quarternary ammonium cation NMe_4^+, and serves as a voluminous non-coordinating cation in the title compound in perfect analogy to the quaternary ammonium cations in the compounds containing 'naked' P_{11}^{3-} listed above. The relative stability of $Li(NH_3)_4^+$, which is indicated by the symmetric stretching vibration of 249 cm^{-1} as compared to much lower values for the ammine complexes of the remaining alkali-metal cations,[19] led to our choice of lithium for a first structural study of a heavily ammoniated alkali-metal Zintl compound. It should be noted, however, that structure determinations on caesium-containing polyphosphides in which up to five ammonia molecules coordinate directly to the alkali-metal cation[20] suggest that our approach can be extended to the ammoniates of the heavier alkali metals as well.

As structure determinations of ammonia-rich ammoniates are now made possible by advanced methods of crystal preparation, liquid ammonia can be reclaimed as a solvent for the study of Zintl anions. Due to good solubilities as well as high stabilities of the solutions, this is especially advantageous for exploring the chemistry of those Zintl anions which decompose in water.

Footnotes

† *Crystal data* for $[Li(NH_3)_4]_3P_{11}\cdot 5NH_3 : H_{51}Li_3N_{17}P_{11}$, $M = 651.07$, red prisms, triclinic, space group $P\bar{1}$ (no. 2), $a = 1177.0(7)$, $b = 1229.9(9)$, $c = 1237.6(7)$ pm, $\alpha = 89.36(5)$, $\beta = 79.46(5)$, $\gamma = 80.33(5)°$, $U = 1.736(2)$ nm^3, $Z = 2$, $D_c = 1.246$ g cm^{-3}, μ(Mo-Kα) = 0.56 mm^{-1}. No. of measured reflections 5758, no. of independent reflections 5467, no. of observed reflections with $I > 2\sigma(I)$ 4924, no. of parameters 434, no. of restraints 2550. Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 71.073$ pm) at 123(2) K to $\theta_{max} = 24°$. Three intensity control reflections were measured every hour, showing a total decay of 24%. The structure was solved by direct methods and refined on F^2 using all independent reflections. The hydrogen atoms of the ammonia molecules were located by difference Fourier synthesis and were restrained in such a way that all H···H distances in all the molecules were taken to be equal within standard deviations, as well as all N–H distances. The final wR_2 value was 0.287 [corresponding to a conventional R value of 0.098 by using only reflections with $I > 2\sigma(I)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/177.

‡ The very precise structural study of the tetraammine of elemental lithium itself by neutron powder data which was reported recently[18] is not relevant in this case, as the additional electron causes the coordination of the metal to be decidedly non-tetrahedral.

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