DALTON
COMMUNICATION

The first *catena*-trihydrogen triphosphide: synthesis and crystal structure of $[Na(NH_3)_5][Na(NH_3)_3(P_3H_3)]$

Nikolaus Korber * and Jürgen Aschenbrenner

Institut für Anorganische Chemie der Universität Regensburg, Universitätsstraße 31, 93053 Regensburg, Germany. E-mail: nikolaus.korber@chemie.uni-regensburg.de

Received 16th February 2001, Accepted 13th March 2001
First published as an Advance Article on the web 23rd March 2001

The reaction of P_4 with sodium in liquid ammonia (P : Na ratio 3 : 5) yields crystalline $NaNH_2$ and $[Na(NH_3)_5]$-$[Na(NH_3)_3(P_3H_3)]$, which contains all-*trans* *catena*-$P_3H_3^{2-}$ stabilised in the ion complex $[Na(NH_3)_3(P_3H_3)]^-$.

In contrast to the intensively studied polyphosphanes P_mH_n[1] and polyphosphides P_m^{n-},[2] much less is known about hydrogen polyphosphides $P_mH_{n-x}^{x-}$, which can be interpreted as intermediates between polyphosphanes and polyphosphides in Brønsted protonation–deprotonation processes. Due to their generally low thermal stability, several hydrogen polyphosphides had been identified exclusively by ^{31}P solution NMR,[3] until recently directed synthetic routes to stable, crystalline compounds containing $P_7H_2^-$ and $P_{11}H^{2-}$ were developed.[4] In these reactions, the polyphosphide cages P_7^{3-} and P_{11}^{3-}, which are generated by dissolving the corresponding binary alkali metal polyphosphides, are protonated under very controlled conditions in liquid ammonia in the presence of voluminous counter ions. Although this protonation of polyphosphides introduced the first rational access to stable hydrogen polyphosphides, it is clearly restricted to those polyphosphorus species for which dissolvable polyphosphides are known, which is mainly the case for cage species like P_{11}^{3-}, P_{16}^{2-} or P_{21}^{3-} [2] with a low charge-per-atom ratio. The higher charged ring and chain polyanions also known from solid polyphosphides are unlikely candidates for congruent dissolution in any solvent.

The alternative we present now is the *in situ* generation of small polyphosphide anions by reductive cleavage of P_4 with alkali metal solutions in liquid ammonia, which results in hydrogen polyphosphides by parallel deprotonation of ammonia. The reaction of an excess of sodium with white phosphorus (P : Na ratio 3 : 5, *ca.* 0.05 mol) in liquid ammonia (*ca.* 20 ml) at 238 K yields colourless crystals of $NaNH_2$ and yellow crystals of $[Na(NH_3)_5][Na(NH_3)_3(P_3H_3)]$; both products were identified by single crystal X-ray crystallography. The following equation applies:

$$5\,Na + 0.75\,P_4 + 11\,NH_3 \longrightarrow [Na(NH_3)_5][Na(NH_3)_3P_3H_3] + 3\,NaNH_2 \quad (1)$$

As is the case for other previously investigated similar ammoniates,[5] $[Na(NH_3)_5][Na(NH_3)_3P_3H_3]$ is thermally very unstable and decomposes to a red, X-ray amorphous solid even below 273 K. Its crystal structure[6] is built from sodium pentaammine complexes $Na(NH_3)_5^+$ and ion complexes $[Na(NH_3)_3(P_3H_3)]^-$ (Fig. 1). In the ion complex, the terminal phosphorus atoms of the new trihydrogen triphosphide $P_3H_3^{2-}$ have close contacts to a sodium cation (Na–P 3.081(1) Å) in an η^2-like arrangement, the co-ordination sphere of the cation is completed by three ammonia ligands (Fig. 2). The hydrogen atoms of the $P_3H_3^{2-}$ anion are in the all-*trans* configuration, the P–H distances (average 1.27 Å) agree well with the previously determined value for $P_{11}H^{2-}$.[7] The P–P distances of 2.1977(6) Å are longer than expected for a bond between a phosphorus atom with two covalent bonds and a phosphorus atom with three covalent bonds (*ca.* 2.16 Å[2]), which is probably due to the Na–P contacts. The P–P–P angle of 113.1(4)° is larger than both the values for unprotonated P_3^{5-} (107.5°[2]) and triphosphane(5) P_3H_5 (*ca.* 104.5[1]), which again is probably caused by the formation of the ion complex.

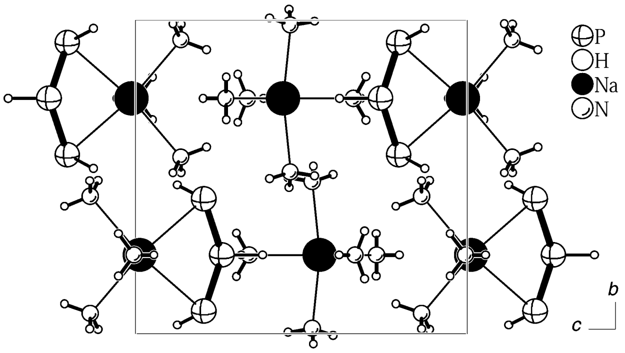

Fig. 1 Section of the structure of $[Na(NH_3)_5][Na(NH_3)_3P_3H_3]$ projected on the *b–c* plane.

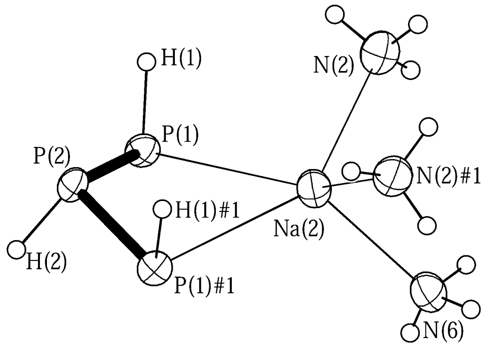

Fig. 2 ORTEP[10] plot of $[Na(NH_3)_3(P_3H_3)]^-$. Selected interatomic distances [Å] and angles [°]: P(1)–P(2) 2.1977(6), P(1)–H(1) 1.26(3), P(2)–H(2) 1.28(4), P(1)–Na(2) 3.081(1), Na(2)–N(2) 2.519(2), Na(2)–N(6) 2.486(3); P(1)–P(2)–P(1)#1 113.1(4), P(2)–P(1)–H(1) 95(1), P(1)–P(2)–H(2) 97.5(9). Symmetry operation used to generate equivalent atoms: #1 = $-x, y + 0.5, -z$.

$[Na(NH_3)_5][Na(NH_3)_3P_3H_3]$ crystallises in the space group $P2_1/m$, which is rare for molecular compounds. In this case the mirror plane *m* is compatible with the molecular symmetries of the sodium pentaammine cation and the ion complex; both of the central sodium ions reside on special positions, as well as N(6), P(2), H(2), N(3), N(4) and N(5).

Further analogous experiments show that this very simple preparative approach is a general route to hydrogen triphosphides: an excess of lithium instead of sodium leads to an ammonia-rich crystalline phase which contains $P_3H_3^{2-}$ and PH_2^-, and the reductive cleavage of P_{11}^{3-} with lithium yields $P_3H_2^{3-}$ (both compounds were identified by crystallography on single crystals).[8] The reaction of P_4 with Na with the P : Na

DOI: 10.1039/b101533h

ratio of 2 : 1 in liquid ammonia was reported to result in a mixture of $NaPH_2$, Na_2P_7H and the unstable 1,3-diaminotriphosphane(5) $H_2N–(PH)_3–NH_2$,[9] which was identified by ^{31}P NMR spectroscopy. This further derivative of P_3H_5 detected in liquid ammonia substantiates the hypothesis that reductive cleavage of P_4 or other polyphosphorus cages in this solvent may provide an easy and useful access to open-chain triphosphorus species.

Notes and references

1 M. Baudler and K. Glinka, *Chem. Rev.*, 1993, 1623; M. Baudler and K. Glinka, *Chem. Rev.*, 1994, 1273.

2 H.-G. von Schnering and W. Hönle, *Chem. Rev.*, 1988, 243; H.-G. von Schnering and W. Hönle, *Phosphides: Solid State Chemistry*, in *Encyclopedia of inorganic chemistry*, ed. R. B. King, John Wiley & Sons, Chichester, 1994, pp. 3106–3143.

3 M. Baudler, R. Riekehof-Böhmer, *Z. Naturforsch.*, *Teil B*, 1985, **40**, 1424.

4 N. Korber and H.-G. von Schnering, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 1713; N. Korber, J. Daniels and H.-G. von Schnering, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 1107.

5 N. Korber, *Phosphorus*, *Sulfur*, *Silicon Relat. Elem.*, 1997, **124/125**, 339.

6 Crystal data and structure refinement for $[Na(NH_3)_5][Na(NH_3)_3P_3H_3]$: $M = 278.17$, monoclinic, space group $P2_1/m$ (no. 11), $a = 7.3400(7)$, $b = 10.2514(8)$, $c = 10.873(1)$ Å, $\beta = 96.50(1)°$, $V = 812(1)$ Å^3, $Z = 2$, μ(Mo-K_α) = 0.39 mm^{-1}, no. of reflections measured 11494, no. of independent reflections 1660 ($R_{int} = 0.059$), $T = 123(2)$ K. The H-atoms were located by difference Fourier synthesis and refined free with isotropic displacement parameters. The final wR_2 value was 0.079 [corresponds to a conventional R value of 0.032 using only reflections with $I > 2\sigma(I)$]. CCDC reference number 158623. See http://www.rsc.org/suppdata/dt/b1/b101533h/ for crystallographic data in CIF or other electronic format.

7 N. Korber and J. Daniels, *Inorg. Chem.*, 1997, **36**, 4906.

8 N. Korber, J. Daniels and J. Aschenbrenner, unpublished results.

9 M. Baudler and D. Düster, *Z. Naturforsch.*, *Teil B*, 1987, **42**, 330.

10 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.