PPh$_4$$^+H_2P_7$$^-$—the First Stable Hydrogen Polyphosphide Salt

Nikolaus Korber and Hans-Georg von Schnering*

Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany

The tetraphenylphosphonium salt of the hydrogen polyphosphide H$_2$P$_7$$^-$ is synthesized from K$_3$P$_{11}$ and PPh$_4$Cl in liquid ammonia and the nortricyclene topology of the anion is proven by X-ray crystal structure analysis.

The homoatomic polyphosphorus species in both solid state metal polyphosphides and polyphosphanes often closely resemble each other.[1,2,3] A well known example is the heptaphosphanortricyclene cage (Fig. 1) which has been observed for isolated P$_7$$^{3-}$ anions in Ba$_3$P$_{14}$ and M^I$_3$P$_7$(M^I = Li–Cs) and the heptaphosphane(3) P$_7$H$_3$, the only polycyclic phosphane isolated in the pure state up to the present.[2] The sole difference between the two phosphorus species is the presence or absence of protons, their formal chemical relationship might be discussed in terms of the Brønsted acid–base concept. The validity of this formal relationship is difficult to prove experimentally because of numerous side reactions leading to the formation of higher phosphanes upon the protonation of phosphides as well as upon the abstraction of protons from phosphanes. Consequently, any intermediate hydrogen polyphosphides which would form the missing link between polyphosphanes and polyphospides are almost completely unknown. An exception is the study of the reaction between diphosphane(4) P$_2$H$_4$ and n-butyllithium at low temperatures by NMR techniques, during which several partially lithiated polyphosphanes, e.g. Li$_2$HP$_7$ and LiH$_2$P$_7$, seem to form as highly reactive intermediates.[4]

We now report the serendipitous synthesis of PPh$_4$$^+H_2P_7$$^-$ 1, the first stable hydrogen polyphosphide. Compound 1 forms by slow diffusion of a solution of K$_3$P$_{11}$ in liquid NH$_3$ into a suspension of PPh$_4$Cl in the same solvent at −40 °C, the PPh$_4$Cl having been diluted with water in the molar ratio of 1:2. Compound 1 crystallizes from the reaction mixture in the form of large (0.2–1 mm), honey-coloured octahedra, which are separated mechanically from the residue consisting of KCl, KOH and higher phosphanes, after the removal of the solvent. Surprisingly, 1 is quite stable to air and moisture. Compound 1 dissolves readily in dry Me$_2$SO and MeCN (under standard inert conditions) but cannot be recovered from these solutions, the rapidly deepening red colour of which suggests the formation of increasingly larger polyphosphorus species.

The single crystal structure analysis† of 1 shows an arrangement of cations and anions resembling that in CsCl (Fig. 2). The cavity formed by eight PPh$_4$$^+$ cations is rather large for the H$_2$P$_7$$^-$ anion, which may account for a certain amount of orientational disorder on the part of this species. After the structure refined well in the initial stages, four distinct peaks in the difference fourier synthesis in the vicinity of the anion indicated the presence of a second orientation of the nortricyclene cage. The two different orientations are positioned in such a way that three atoms of each very nearly coincide [P(#1)

and P(3), P(#3) and P(6), P(#2) and P(5)] (Fig. 3). Refinement of an improved structural model resulted in an occupancy of 25% for the second orientation. The disorder, while leaving the nortricyclene cage clearly discernible, prevents the localisation of the hydrogen atoms bonded to phosphorus. The height h of the cage (Fig. 1), however, is known to differ significantly depending on the number of bonds formed by the equatorial P atoms. h is 300 pm for P$_7$$^{3-}$ (Na$_3$P$_7$^{5}) and 315 pm for P$_7$$^{±0}$ (P$_7$R$_3$^{6}). Thus, the expected value for P$_7$$^-$ in H$_2$P$_7$$^-$ is the weighted mean,‡ 310 pm. The observed height in 1 is 309(1) pm (higher occupancy orientation).

Independent evidence for the presence of P–H bonds in 1 is provided by the FTIR spectrum, which shows a very strong, sharp band at 2250 cm^{-1} corresponding to the P–H stretching frequency.

The discovery of the first isolated hydrogen phosphide anion, even if prepared by a reaction which is not easily understandable, may be the first hint that some polyphosphides and
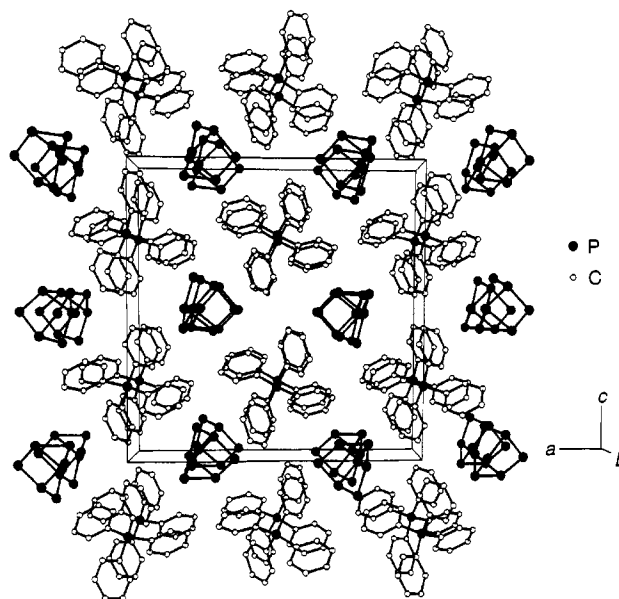
Fig. 2 Crystal structure of PPh$_4$$^+H_2P_7$$^-$ viewed along (010). Only the main orientation (occupancy $ca.$ 75%) of the H$_2$P$_7$$^-$ anion is shown
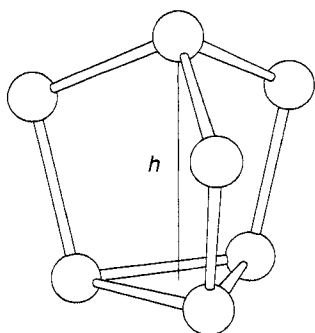
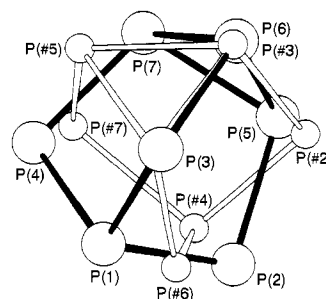Fig. 1 Topology of the heptaphosphanortricyclene cage

Fig. 3 The two orientations of H$_2$P$_7$$^-$ in the crystal. Smaller circles and # indicate the less occupied orientation

their corresponding polyphosphanes are linked by an unbroken *chain of increasingly* protonated anions, which can be trapped using large cations.

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Footnotes

† *Crystal data* for **1**: $C_{24}H_{22}P_8$, $M = 558.17$, monoclinic, space group $P2/c$, $a = 1866.25(9)$, $b = 748.17(3)$, $c = 1906.6(1)$ pm, $\beta = 90.881(5)°$, $V = 2.6618(2)$ nm^3, $Z = 4$, $D_c = 1.388$ g cm^{-3}, μ(Mo-Kα) = 0.536 mm^{-1}. No. of reflections measured 10113, no. of independent reflections 4693 ($R_{int} = 0.021$), no. of observed reflections with $I > 2\sigma(I)$ 3649, no. of parameters 355. The lattice constants were determined by a STOE indexing program and refined by a least-squares routine with the angular settings of 136 reflections ($27 < \theta < 30$). Diffraction data were collected on a STOE-STADI 4 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 71.073$ pm) at 293(2) K to $\theta_{max} = 25°$ using a learned profile routine. Three intensity control reflections were measured every hour, showing a total decay of 0.7%. Intensity data were corrected for linear isotropic decay, Lorentz and polarisation effects. The structure was solved by a combination of direct methods (SHELXS-86[7]) and Fourier techniques, and refined on F^2 using all 4693 independent reflections (SHELXL-93[8]). Non-hydrogen atoms were refined anisotropically, with the hydrogen atoms at calculated positions riding on the carbon atoms. The occupancy factors for all phosphorus atoms were constrained to one parameter for each of the two orientations of the cage, and the sum of both parameters was constrained to be unity. The final wR_2 value was 0.1734 [corresponds to a conventional R value of 0.058 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.

‡ $h(P_7{}^-) = 1/3 [h(P_7{}^{3-}) + 2 h(P_7{}^{\pm0})]$.

References

1 H.-G. von Schnering and W. Hönle, *Chem. Rev.*, 1988, 243.
2 M. Baudler and K. Glinka, *Chem. Rev.*, 1993, 1623.
3 M. Baudler and K. Glinka, *Chem. Rev.*, 1994, 1273.
4 M. Baudler and R. Heumüller, *Z. Naturforsch., Teil B*, 1984, **39**, 1306; M. Baudler, R. Heumüller, J. Germershausen and J. Hahn, *Z. Anorg. Allg. Chem.*, 1985, **526**, 7; M. Baudler and R. Heumüller, *Z. Anorg. Allg. Chem.*, 1988, **559**, 49; M. Baudler, R. Heumüller and D. Düster, *Z. Anorg. Allg. Chem.*, 1993, **619**, 1007.
5 H.-G. von Schnering, W. Hönle, V. Marinquez, T. Meyer, Ch. Mensing and W. Giering, *2nd Int. Conf. Solid State Chem.*, Collect. Abstr. FV54, Eindhoven, 1982.
6 C. Mujica, D. Weber and H.-G. von Schnering, *Z. Naturforsch., Teil B*, 1986, **41**, 991.
7 G. M. Sheldrick, SHELXS-86, A Program for Crystal Structure Determination, University of Göttingen, 1986.
8 G. M. Sheldrick, SHELXL-93, University of Göttingen, 1993.