The Tetrabromophosphite, PBr_4^- Ion

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Summary The preparation and properties of salts of the PBr_4^- ion, the first examples of negative halogeno-ions of the very weak Lewis acids, the phosphorus trihalides, are reported.

THE acceptor properties of the phosphorus(III) halides in general, and of phosphorus(III) bromide in particular, have been little investigated.[1] The P–N bond in the trimethylamine–phosphorus tribromide complex has been estimated to have a bond energy of only 3·1 kcal./mole, compared with 4·6 kcal./mole for the corresponding chloro-compound.[2] There is also some evidence for a dioxan complex of phosphorus(III) bromide,[3] and the order of acceptor ability $PCl_3 > PBr_3 \sim MePCl_2 > Me_3P$ has been suggested.[4] We report the preparation of a series of new compounds $R_4N^+PBr_4^-$ (R = Et, Pr^n, Bu^n) where phosphorus(III) bromide acts as an acceptor to the bromide ion.

Addition of a saturated solution of a tetra-alkylammonium bromide (R = Pr^n, Bu^n in 1,2-dichloroethane to a solution of phosphorus(III) bromide in the same solvent produces a lime-green coloration. A new peak is observed in the ^{31}P n.m.r. spectrum at -150 ± 2 p.p.m. relative to 85% phosphoric acid, the shift value depending slightly on the cation used. The intensity of this peak is always much lower (*ca.* 1 : 200) than that of unchanged PBr_3 at -229 p.p.m.[5] When this mixed solution is cooled in ice, pale yellow crystals are deposited. The crystals are separated in a dry-box and washed with low-boiling petroleum to remove solvent and unchanged phosphorus tribromide. The $(n\text{-}C_3H_7)_4NPBr_4$ salt analysed satisfactorily for C,H,N,Br,P, and the cation. The i.r. (Nujol mull) and Raman spectra of the solid salt were recorded, care being taken to exclude moisture since the compound fumes readily in the air. The results (cm.$^{-1}$) are

I.r. (to 200 cm.$^{-1}$)	384vs, 307w, 283w.
Raman	383s, 356s, 307s, 280vw, 182 broad sh, 149ms, ~128vvw, ~100sh.w.

The number of lines in the spectra, particularly in the Raman, indicate that the PBr_4^- ion cannot be a regular tetrahedron, and probably has C_{2v} symmetry, like SF_4.

A little of the compound was dissolved in nitrobenzene and the ^{31}P n.m.r. spectrum run. The main peak observed was that of phosphorus(III) bromide, confirming that the equilibrium

$$PBr_3 + Br^- \rightleftarrows PBr_4^-$$

lies well to the left, and that the PBr_4^- ion is stabilized by the limited solubility of its tetra-alkylammonium salts.

Attempts to prepare solid compounds containing the PCl_4^- ion, which might be expected to be more stable,[4] have so far been unsuccessful.

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[1] D. S. Payne, "The Chemistry of Phosphorus Halides" in "Topics in Phosphorus Chemistry," vol. 4, Interscience, New York, 1967.
[2] P. A. McCuster and B. C. Curran, *J. Amer. Chem. Soc.*, 1942, **64**, 614.
[3] K. Suenga and A. Kotera, *J. Chem. Soc. Japan*, 1949, **70**, 116.
[4] R. R. Holmes and R. P. Wagner, *Inorg. Chem.*, 1963, **2**, 384.
[5] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," vol. 2, Pergamon, Oxford, 1966.