The Structures of Hypervalent Phosphorus(III) Anions $P(CN)_{4-n}Br_n^-$. Transition from ψ-Trigonal-bipyramidal to ψ-Octahedral Co-ordination and Deviation from Valence Shell Electron Pair Repulsion Theory

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Salts of the title anion series have been prepared with the sodium–[18]crown-6 cation (n = 1 and 2) ([18]crown-6 = 1,4,7,10,13,16-hexaoxacyclo-octadecane) or tetra-alkylammonium cations (n = 4) by addition of Br^- to $P(CN)_3$ or PBr_3, or by Br_2 or BrCN oxidation of $P(CN)_2^-$. Contrary to this, CN^- addition to $P(CN)_3$, in a reductive elimination, gives $P(CN)_2^-$. *X*-Ray crystal-structure determinations of the above mentioned three salts are reported and their anion structures are discussed. The $P(CN)_2Br_2^-$ anion shows the ψ-trigonal-bipyramidal co-ordination expected on the basis of Valence Shell Electron Pair Repulsion Theory (V.S.E.P.R.), $P(CN)_3Br^-$ has ψ-octahedral co-ordination in a dimeric, bromide double-bridge structure, and PBr_4^- a structure intermediate between the two. Here the trigonal-bipyramidal co-ordination is distorted towards a tetrahedral geometry. This is in contradiction to V.S.E.P.R. and presumably the result of ligand–ligand repulsion. The structures are of interest as transition-state models of phosphorus(III) nucleophilic substitution.

PHOSPHORUS(III) halides, phosphites, and aminophosphanes, PX_3 (X = halogen, OR, or NR_2 respectively), undergo nucleophilic substitution rather easily.[1] Obviously it takes relatively little extra energy to reach the transition state involving four-co-ordinate phosphorus(III). Its geometry is proposed to be ψ-trigonal bipyramidal with the lone pair equatorial and the entering nucleophile and leaving X opposite each other in apical positions.[2,3] No structure determination of a hypervalent,[†] four-co-ordinate phosphorus(III) species has so far been made, however, to provide a model for this transition-state geometry. It is thus still open to discussion to what extent the lone pair is in fact stereochemically effective.[4] The octahedral hypervalent anion $SbBr_6^{3-}$ represents a well known exception to the lone-pair effect, which normally dominates over ligand–ligand repulsion. For the smaller phosphorus centre, four ligands may be sufficient to reduce the stereochemical effectiveness of the lone pair.

Although the kinetic evidence [1] appears to imply that relatively little energy is necessary to expand the co-ordination round trivalent phosphorus, known hypervalent phosphorus(III) compounds are very rare. The only examples other than the tetrahalogenophosphates(III) [‡] PX_4^- (X = Cl [5] or Br [6]) and cyanohalogenophosphates(III) $P(CN)_{4-n}X_n^-$ (n = 1 or 2; X = Cl, Br, or I [4,5]) from our work are the thermally unstable trimethylamine adducts of phosphorus trihalides $PX_3N(CH_3)_3$ (X = Cl or Br),[7] adducts of PCl_3 and PBr_3 with pyridines or amides, where no structural information is known,[8] and more recently the anion obtained from deprotonating a hydrido-spirophosphorane.[9]

RESULTS AND DISCUSSION

Preparation.—Anions of the series $P(CN)_{4-n}Br_n^-$ can be prepared with bulky counter ions such as tetra-alkylammonium or crown ether–sodium cations. The members with $n = 1$ [4] and $n = 4$ [6] were obtained by the addition of bromide to phosphorus(III) cyanide and phosphorus(III) bromide respectively, equations (1) and (2). While the addition equilibrium for $P(CN)_3Br^-$

$$P(CN)_3 + Br^- \rightleftharpoons P(CN)_3Br^- \quad (1)$$

$$PBr_3 + Br^- \rightleftharpoons PBr_4^- \quad (2)$$

(with crown ether–sodium or NR_4^+ cations) is mobile on the n.m.r. time scale and lies very far to the right,[4] it is immobile for PBr_4^- (with the tetra-alkylammonium cation) and lies well to the left.[6] The former anion was also prepared by BrCN oxidation of the dicyanophosphide ion [10,11] and the compound where $n = 2$ by its Br_2 oxidation, equations (3) and (4).[4] The missing

$$P(CN)_2^- + BrCN \longrightarrow P(CN)_3Br^- \quad (3)$$

$$P(CN)_2^- + Br_2 \longrightarrow P(CN)_2Br_2^- \quad (4)$$

member, $n = 3$, was expected to result from the addition of cyanide to phosphorus(III) bromide. Instead, only the products of its dismutation could be detected by ^{31}P n.m.r. spectroscopy, equation (5). Finally, the tetra-

$$PBr_3 + CN^- \longrightarrow [P(CN)Br_3^-] \longrightarrow \tfrac{1}{2}P(CN)_2Br_2^- + \tfrac{1}{2}PBr_4^- \quad (5)$$

cyanophosphate(III) ion, $n = 0$, should have been accessible by either cyanide addition to phosphorus(III)

[†] Atoms having more bonds than expected from the octet rule are termed hypervalent.

[‡] Because of its greater generality we prefer (σ^4-)phosphite or phosphate(III) as the name for PX_4^- type anions rather than the alternative phosphoranide.[9]

cyanide, or cyanogen oxidation of dicyanophosphide. It is in fact produced in the former reaction at low temperature, but decomposes in a reductive elimination to give the dicyanophosphide, equation (6). The details

$$P(CN)_3 + CN^- \longrightarrow P(CN)_4^- \longrightarrow P(CN)_2^- + [(CN)_2] \quad (6)$$

of this reaction are still under investigation. The suggested second alternative would be a reversal of the decomposition, but is clearly not practicable under the experimental conditions so far employed.

A high-field ^{31}P chemical shift [$\delta(^{31}P)$] relative to the three-co-ordinate phosphorus compound is characteristic for all the anions of the series: $[Na(C_{12}H_{24}O_6)][P(CN)_{4-n}Br_n]$ (solvent thf), −242 ($n = 0$), −182 ($n = 1$),[4] −165 ($n = 2$);[4] $[NR_4][P(CN)_{4-n}Br_n]$(solvent CH_2Cl_2), −239 ($n = 0$), −179 ($n = 1$), 150 ($n = 4$);[6] $P(CN)_{3-n}Br_n$ (solvent CH_3CN) (ref. 12), −137 ($n = 0$), −64 ($n = 1$), 62 ($n = 2$), 227 ($n = 3$).

We now report and compare the *X*-ray crystal and molecular structures of three members of the series: $P(CN)_3Br^-$, $P(CN)_2Br_2^-$, and PBr_4^-. In accordance with the above discussion of the transition-state geometry of nucleophilic displacement at phosphorus(III) derivatives and on the basis of V.S.E.P.R. rules, a ψ-trigonal-bipyramidal ligand arrangement would be predicted for them. Points of interest were the tendency and degree of distortion of the idealised geometry and the distribution of CN and Br between apical and equatorial positions. The relative apicophilicity (the change in energy when two groups exchange apical and equatorial positions in a trigonal bipyramid) of these two ligands is not known; on a tentative scale they fall in the same range.[13]

$P(CN)_2Br_2^-$.—The structure was determined for a crystal of the $[Na(C_{12}H_{24}O_6)(thf)_2]^+$ ($C_{12}H_{24}O_6$ = [18]-crown-6 = 1,4,7,10,13,16-hexaoxacyclo-octadecane, thf = tetrahydrofuran) salt. The anion which lies on a crystallographic C_2 axis clearly shows the expected ψ-trigonal-bipyramidal co-ordination of phosphorus with the bromide ligands in apical position (Figure 1). This distribution with a bent equatorial $P(CN)_2$ arrangement has already been deduced from the two CN bands in the i.r. spectrum.[4] The (almost) linear arrangement Br^-–$P(CN)_2$–Br^- resembles the linear structure of a trihalide * and thus fits well with the concept of the pseudohalide character of $P(CN)_2^-$.[9] The bond lengths and angles are given in Table 1.

TABLE 1

Bond lengths (pm) and angles (°) in $P(CN)_2Br_2^-$

P–Br	249.6(1)	Br–P–Br′	171.4(1)
		C(1)–P–C(1′)	101.4(6)
P–C(1)	177.5(9)	Br–P–C(1)	86.3(2)
C(1)–N(1)	114.3(11)	Br–P–C(1′)	88.3(2)
		P–C(1)–N(1)	169.9(8)

The axial BrPBr angle [171.4(1)°] and especially the equatorial CPC angle [101.4(6)°] are considerably smaller than the 180° and 120° respectively of the ideal geometry, showing a definite lone-pair stereochemical effect. The PBr_2 plane is almost but not exactly perpendicular (dihedral angle 88.7°) to the equatorial PC_2 plane, their intersection coinciding with the crystallographic two-fold axis. The anion thus deviated somewhat from C_{2v} symmetry.

A comparison with the $P(CN)_2^-$ anion structure[10] reveals that in the oxidative Br_2 addition the CPC angle opens by 6.4° (somewhat less than expected for the change from ψ-tetrahedral to diequatorial ψ-trigonal bipyramidal), and the PC bond lengthens 3.5 pm (on average). In general the parameters of the (equatorial) $P(CN)_2$ unit do not differ greatly from ' normal ' ones as in $P(CN)_3$.[14] In contrast, the (axial) PBr bond distance of 249.6(1) pm is very much (12%) longer than in PBr_3[15] or in any other known structure (206—223 pm).[16] The observed $P(CN)_2Br_2^-$ structure is thus in good agreement with the proposed geometrical concept of the transition state of phosphorus(III) nucleophilic substitution, *i.e.* almost collinear, long and equal bonds from P to Br (the latter representing entering and leaving groups), and with the other two ligands (CN) almost not involved.

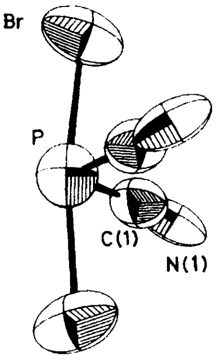

FIGURE 1 ORTEP plot of $P(CN)_2Br_2^-$

In view of the structures of the other anions of the series it should be pointed out that no short intermolecular contacts between the $P(CN)_2Br_2^-$ anions are observed in the crystal.

The cation consists of a sodium centre at a crystallographic centre of symmetry (0.5, 0.5, 0, and 0.5, 0.5, 0.5), surrounded almost symmetrically by the crown ether and perpendicular to its ring by two tetrahydrofuran molecules. The sodium co-ordination is approximately that of an obtuse hexagonal bipyramid. The array is very similar to the cation of crown ether complexed $NaP(CN)_2$,[11] except for a three-fold disordering of the thf molecules. The details of the cation structures will be more fully discussed in a different context in a subsequent paper.

$P(CN)_3Br^-$.—In this case too a crystal of the $[Na(C_{12}H_{24}O_6)(thf)_2]^+$ salt was used for structure determination. At first sight little structural change would be expected for just one Br in $P(CN)_2Br_2^-$ being replaced by CN. But now there are no longer two sets of different ligands available for apical and equatorial positions and

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* There is one other trihalide analogue known with a pseudohalide centre: $NCSe$–$Se(CN)$–$SeCN^-$ (S. Hauge, *Acta Chem. Scand.*, 1971, **25**, 3081).

CN would have to adopt an apical position. In fact the structure turns out to be drastically different.[17] The $P(CN)_3Br^-$ anion forms a dimer with crystallographic C_{2h} symmetry, two identical $P(CN)_3$ units being held together by a symmetric bromide double bridge (Figure 2). The co-ordination of the phosphorus is now ψ-octahedral. As expected from lone-pair repulsion, the phosphorus atom lies somewhat *below* the basal plane (8.1 pm) towards the lone pair. That the position *trans* to the lone pair is taken up by CN is consistent * with its being less apicophilic than Br. The bond lengths and angles are given in Table 2.

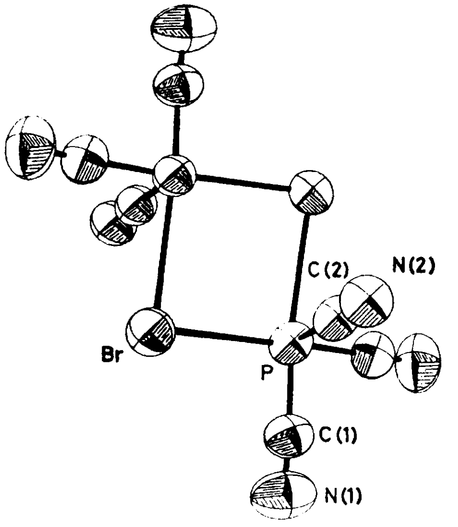

FIGURE 2 ORTEP plot of $[P(CN)_3Br^-]_2$

The parameters of the $P(CN)_3$ unit compare well with those of neutral $P(CN)_3$,[14] the CPC angle being 1.2° smaller, the PC bond 3.1 pm longer, and the CN bond 2.3 pm shorter (on average). Remarkably, there is no significant difference between the basal and the apical CN groups. The PBr bond is again much longer than in the structure discussed before and now 40% longer than the normal single bond.

TABLE 2

Bond lengths (pm) and angles (°) in $[P(CN)_3Br^-]_2$

P–Br	305.8(1)	Br–P–Br	99.9(1)
P–C(1)	182.3(6)	Br–P–C(1)	84.4(2)
P–C(2)	181.0(8)	Br–P–C(2)	83.5(1)
C(1)–N(1)	112.5(8)	C(1)–P–C(1)	91.0(4)
C(2)–N(2)	112.8(10)	C(1)–P–C(2)	92.9(2)
		P–C(1)–N(1)	173.5(5)
		P–C(2)–N(2)	179.8(2)
		P–Br–P	80.1(1)

Obviously the original phosphorus tricyanide geometry is much better preserved in the octahedral dimeric structure of the anion with three almost equal CN ligands than would be possible in the monomeric trigonal-bipyramidal structure with two equatorial and one apical, and necessarily rather unlike, CN group. This saving in reorganization is apparently sufficient to favour dimerisation. The iodine analogue $P_2(CN)_6I_2^{2-}$ shows the same structure,[17] its salt being isomorphous to the one described here.

The cation has a similar structure to that of the foregoing salt, the co-ordination of the sodium being approximately that of an obtuse hexagonal bipyramid. In this case, however, the cation displays crystallographic mirror symmetry with one of the axial thf ligands disordered with respect to the mirror plane.

The solid-state ^{31}P n.m.r. spectrum of the compound $[NPr^n_4][P(CN)_3Br]$ consisted of a well defined single peak at −182 p.p.m., in excellent agreement with the solution data given earlier. These results suggest that the dimeric structure occurs in solution as well as in the solid.

PBr_4^-.—Infrared and particularly Raman spectra already indicated that the PBr_4^- ion is not a regular tetrahedron but probably has C_{2v} symmetry.[6] A crystal of the tetra-n-propylammonium salt was used for the *X*-ray structure determination. Unexpectedly, PBr_4^-, the only anion of this series with a uniform set of ligands, shows the least symmetric structure, and is therefore discussed last. At first sight it approximates to the expected trigonal-bipyramidal C_{2v} structure (Figure 3) and resembles $P(CN)_2Br_2^-$. It has two sets of Br ligands, *viz.* equatorial ones with normal PBr bond lengths (*ca.* 220 pm) and axial ones with bond lengths as in $P(CN)_2Br_2^-$ (*ca.* 250 pm), but there are significant differences within these sets. The different equatorial lengths certainly originate from the pairing of two PBr_4^- anions around a crystallographic inversion centre, the longer PBr bond being *trans*, the shorter *cis* to the secondary bond to the Br of the neighbouring anion. The pairing is in the direction of the dimeric structure as in $[P(CN)_3Br^-]_2$ but the bromide double bridge is very asymmetric here. The PBr distance between neighbouring anions is 56% longer than the PBr bond in PBr_3, but still 10% shorter than the sum of the van der Waals radii (385 pm). This distance and the axial PBr bond which constitute the asymmetric bridge average to 299 pm, which is close to the 306 pm for the PBr distance of the symmetric bridge in $[P(CN)_3Br^-]_2$. The molecular dimensions are listed in Table 3.

TABLE 3

Bond lengths (pm) and angles (°) in PBr_4^-

P–Br(1)	252.7(4)	Br(1)–P–Br(2)	170.0(1)
P–Br(2)	262.0(4)	Br(1)–P–Br(3)	93.9(1)
P–Br(3)	222.1(3)	Br(1)–P–Br(4)	93.3(1)
P–Br(4)	225.5(3)	Br(2)–P–Br(3)	92.9(1)
P · · · Br(1′)	346.0(4)	Br(2)–P–Br(4)	92.8(1)
		Br(3)–P–Br(4)	99.4(1)
		Br(1′) · · · P–Br(1)	83.9(1)
		Br(1′) · · · P–Br(2)	88.5(1)
		Br(1′) · · · P–Br(3)	92.5(1)
		Br(1′) · · · P–Br(4)	167.9(1)

In striking contrast with the $P(CN)_2Br_2^-$ structure, where the angles between axial and equatorial bonds were all <90° (86.3—88.3°), they are all >90° (92.8—93.9°) in the PBr_4^- structure, clearly in opposition to the

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* According to V.S.E.P.R. rules the equatorial positions of a trigonal bipyramid and the position *trans* to the lone pair in a ψ-octahedron are the ones less affected by electron-pair repulsion.

V.S.E.P.R. prediction of dominating lone-pair repulsion. This must be due to the ψ-trigonal bipyramid being distorted toward the tetrahedron with a stereochemically inactive lone pair. The equatorial angle of 99.4°, even smaller than the tetrahedral angle, may be explained by a simultaneous distortion towards the ψ-octahedron of the dimer. In fact a weighted superposition of the three ideal geometries simulates all observed angles (°) to within one degree (see below).

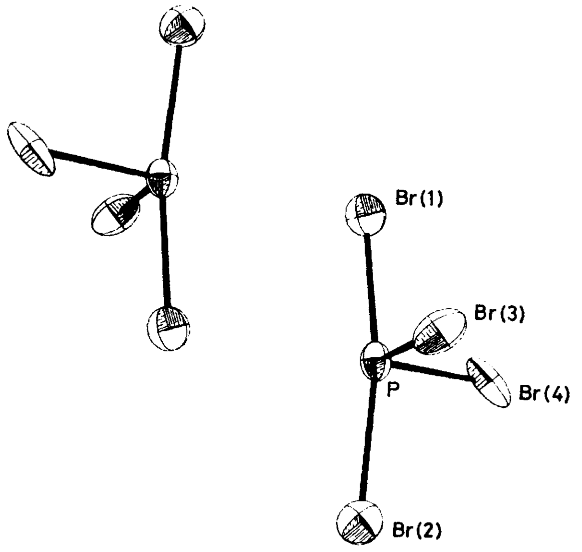

FIGURE 3 ORTEP plot of PBr_4^-

	Trigonal bipyramid	Octahedron	Tetrahedron	Weighted average	Obs.
Axial–equatorial	90	90	109.5	93.1	92.8—93.9
Equatorial–equatorial	120	90	109.5	99.4	99.4
Axial–axial	180	180	109.5	168.7	170.0
Weighting for best fit	63% + 21% + 16%				

The reduced lone-pair stereochemical effect can also be seen when the phosphorus is considered as being five-co-ordinate. The Br ligands constitute a distorted ψ-octahedral co-ordination in which the phosphorus atom lies *above* the basal plane Br(1)Br(2)Br(4)Br(1′) (22.0 pm) towards the apical bromine atom and *away from* the lone pair, in contrast to the situation in $[P(CN)_3Br^-]_2$. The distances of the bromine atoms from the plane of best fit are Br(1) 6.3, Br(1′) −5.1, Br(2) 5.8, Br(4) −7.0, and Br(3) 243.5 pm.

Still unexplained remains the fact that the axial PBr bond involved in the bridge to the neighbouring anion is shorter and its angles are somewhat larger than the corresponding bond parameters of the terminal apical Br. Recalling the reaction by which PBr_4^- forms, this can be rationalized in terms of a ' not fully completed addition ' of the entering Br^-, *i.e.* Br(2), to the PBr_3 molecule, *i.e.* Br(1)Br(3)Br(4), in which the BrPBr angle was originally 101°.[15] This argument applies to the monomeric species, but may be modified by the occurrence of dimerisation. The $NPr^n{}_4^+$ cation displays an approximately T_d geometry.

The solid-state ^{31}P n.m.r. spectrum of $[NPr^n{}_4][PBr_4]$ consisted of a broad peak at *ca.* 217 p.p.m., with a sharp weak peak superposed at 225.7 p.p.m., the latter possibly arising from some slight decomposition to PBr_3. In this instance there is a considerable difference in shift between the solid and solution, so the asymmetric dimeric structure may well break up in solution to give monomeric PBr_4^- units.

Conclusions and Comparisons.—The CN group proves to be definitely less apicophilic than Br. In the case of $P(CN)_3Br^-$, dimerization prevents the CN from being forced into an apical position.

While the PCN group turns out to be virtually invariant in the anions studied, the PBr bond lengths extend over an unexpectedly wide range (Table 4). The axial–equatorial angles in PBr_4^- are the smallest BrPBr angles yet observed and seem to indicate their limiting value set up by sharply increasing (presumably Pauli force based) ligand–ligand repulsion.* This repulsion induces a slight but definite distortion towards tetrahedral co-ordination for PBr_4^- and makes it deviate from the V.S.E.P.R. prediction, to our knowledge the only example for a third period element centre. The BrP(CN) angles on the other hand can easily decrease below 90°.

TABLE 4

Comparison of bond lengths (pm) and angles (°)

	$P(CN)_3$ [a]	PBr_3 [b]	$P(CN)_{4-n}Br_n^-$
d(P–CN)	177—180		178—182
d(P–Br) terminal		222	222—262
d(P–Br) bridge			306—346
NC–P–CN	93—94		91—101
Br–P–Br		101	93—99
Br–P–CN			84—88

[a] Ref. 13. [b] Ref. 14.

Judged from their structures, the hypervalent anions PX_4^- gain their stability from the small PX_3 reorganization necessary, rather than from the strength of the additional bond. This accounts for the long and weak PBr bonds found.† If the anions are taken as transition-state models for phosphorus(III) nucleophilic substitution, again the small degree of reorganization required should be important. In certain cases a further decrease in reorganization and thus in activation energy seems possible to adding another donor and turning the ψ-trigonal-bipyramidal array into a ψ-octahedral one. The assistance of a donor base should therefore be taken into consideration when explaining the substitution mechanism.

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* The PBr_5 molecule which inevitably involves BrPBr angles of 90° is thus expected to be unstable. In fact it has not yet been inequivocally demonstrated to exist.[18] The same applies to PBr_6^-. The ^{31}P n.m.r. spectra of solutions of ' PBr_5 ' in organic solvents such as CH_2Cl_2 or MeCN show the presence of PBr_3 only, whereas in liquid bromine only the PBr_4^+ ion is found.

† Cyanide ligands alone cannot form such a structure equally well and $P(CN)_4^-$ is hence unstable (see preparation).

There are two other examples of edge-sharing pairs of ψ-octahedra known: $[BiCl_4^-]_2$ parallels the symmetric bridge case [19] of $[P(CN)_3Br^-]_2$ and $[AsCl_3$(1,3-dimethylimidazole-2-thione)$]_2$ [20] the more loosely linked and unsymmetrical case of $[PBr_4^-]_2$. Most recently a face-sharing pair of ψ-octahedra was reported to describe the structure [21] of $Sb_2OCl_6^{2-}$.

EXPERIMENTAL

[18]*Crown-6–Sodium Dibromodicyanophosphate*(III), (1).—Bromine (2.59 g, 16.2 mmol) in thf (20 cm^3) was added to a solution of $[Na(C_{12}H_{24}O_6)][P(CN)_2]$ (6.00 g, 16.2 mmol) in thf (30 cm^3). After evaporating the almost colourless solution *in vacuo* to half its volume and cooling to −20 °C colourless crystals deposited. At room temperature *in vacuo* they lose the sodium-co-ordinated thf and become opaque (3.50 g, 41%) {Found: C, 31.1; H, 5.1; N, 3.9. $[C_{12}H_{24}NaO_6][C_2Br_2N_2P]$ (M = 530.1) requires C, 31.7; H, 4.6; N, 5.3%}.

[18]*Crown-6–Sodium Bromotricyanophosphate*(III), (2).—*Preparation from* $P(CN)_2^-$ *and* BrCN. BrCN (6.8 g, 62.4 mmol) in thf (10 cm^3) was added to a solution of $[Na(C_{12}H_{24}O_6)][P(CN)_2]$ (23.8 g, 64.3 mmol) in thf (70 cm^3). The resulting deep brown solution was evaporated *in vacuo* to three quarters of its volume, diluted with diethyl ether until the first turbidity appeared, and cooled to −20 °C. The colourless crystals were separated and dried *in vacuo*, becoming opaque from the loss of thf (8.8 g, 29%).

Preparation from $P(CN)_3$ *and* Br^-. Solutions of $P(CN)_3$ (1.24 g, 11.4 mmol) in thf (25 cm^3) and $[Na(C_{12}H_{24}O_6)]Br$ (4.17 g, 11.4 mmol) in acetonitrile (30 cm^3) were mixed and evaporated. The residue was dissolved in thf (50 cm^3) and the solution diluted with diethyl ether (30 cm^3) and filtered. Cooling to −20 °C yielded colourless crystals, which were dried as above (2.02 g, 37%) {Found: C, 38.2; H, 5.1; N, 8.9. $[C_{12}H_{24}NaO_6][C_3BrN_3P]$ (M = 476.3) requires C, 37.8; H, 5.1; N, 8.8%}.

TABLE 5

Crystal and refinement data

Compound	(1)	(2)	(3)
Space group	*P*2/*c*	*Cmca*	*Pbca*
a/pm	940.7(4)	1 367.9(1)	1 970.1(4)
b/pm	903.7(3)	2 063.5(1)	1 520.3(2)
c/pm	1 863.4(6)	2 227.6(2)	1 344.2(2)
β/°	93.19(4)	90	90
U/Å^3	1 581.7(10)	6 287.8(7)	4 026.6(11)
Z	2	4	8
M	674.3	1 241.0	537.0
D_c/g cm^{-3}	1.42	1.31	1.77
Radiation	Cu-K_α	Cu-K_α	Cu-K_α
μ/cm^{-1}	44.4	26.1	98.2
2θ range/°	3.5—125.0	3.5—135.0	3.5—125.0
F^2 rejection criterion d [a]	2.0	2.0	2.5
Number of observed reflections	1 766	1 853	1 783
R	0.071	0.064	0.064
$R' = (\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}F_o)$	0.074	0.063	0.063
g [b]	0.0002	0.0002	0.0005

[a] Reflections with $F^2 < d\sigma(F^2)$ were not included in the structure refinement. [b] The weights were given by $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$.

Tetra-n-propylammonium Tetrabromophosphate(III), (3).—Phosphorus tribromide was added to a concentrated solution of $[NPr^n_4]Br$ in CH_2Cl_2. The mixture was allowed to cool carefully in a freezer, and crystals of the tetrabromophosphate(III) were deposited [Found: C, 27.0; H, 6.2; N, 2.6. $C_{12}H_{28}Br_4NP$ (M = 537.0) requires C, 26.8; H, 5.2; N, 2.6%].

X-*Ray Crystal-structure Determination*.—Crystals of (1) and (2) were grown from thf or thf–diethyl ether and kept in contact with the mother-liquor. In order to obtain crystals suitable for X-ray analyses it was necessary to cut fragments out of the larger crystals of (1)—(3) grown from solution. These were sealed in glass capillary tubes under a nitrogen atmosphere. It proved impossible to obtain crystals of very good quality for an X-ray analysis. In particular, crystals of (1) and (2) displayed a wide mosaic spread.

Intensity data were collected for (1)—(3) on a Syntex $P2_1$ four-circle diffractometer in the θ—2θ mode with graphite-monochromated Cu-K_α radiation. The crystal and refinement data are summarized in Table 5. Empirical absorption corrections using azimuthal scan data were applied to the intensity data for all three derivatives.

The thf molecule in (1) is severely disordered. It was found that this could best be described in terms of a three-fold disorder with molecules comprised of the following atoms: molecule 1, O(11), C(11), C(12), C(13), C(14); molecule 2, O(11), C(11′), C(12), C(13), C(14′); and molecule 3, O(11), C(21), C(22), C(23), C(24). The atom O(11) has hereby a site occupation factor of 1.0, C(11), C(11′), C(14), and C(14′) of 0.3, C(12) and C(13) of 0.6, and C(21)—C(24) of 0.4. The atoms of the disordered thf molecules were refined under the following bond-length restraints: d(C–O) = 145 ± 2 and d(C–C) = 151 ± 2 pm. The atoms C(11), C(11′), C(14), and C(14′) were refined isotropically, the remaining non-hydrogen atoms anisotropically. The positions of the methylene hydrogens of the crown ether were calculated geometrically.

TABLE 6

Positional parameters of $[Na(C_{12}H_{24}O_6)(thf)_2][P(CN)_2Br_2]$, (1)

Atom *	x/a	y/b	z/c
P	0.000 0(0)	0.142 5(3)	0.750 0(0)
Br	0.021 6(1)	0.121 9(1)	0.617 5(1)
Na	0.500 0(0)	0.500 0(0)	0.000 0(0)
C(1)	0.146 0(9)	0.018 1(9)	0.758 5(4)
N(1)	0.252 0(7)	−0.043 6(8)	0.764 7(3)
O(1)	0.336 1(4)	0.365 8(5)	1.097 7(2)
C(2)	0.316 0(8)	0.160 1(8)	1.018 4(4)
C(3)	0.342 0(8)	0.210 0(9)	1.094 6(4)
O(4)	0.430 4(4)	0.208 3(5)	0.978 8(2)
C(5)	0.416 8(8)	0.159 3(8)	0.907 2(4)
C(6)	0.540 5(8)	0.206 5(8)	0.868 7(4)
O(7)	0.543 5(5)	0.363 8(5)	0.865 9(2)
C(8)	0.660 9(8)	0.419 1(10)	0.830 9(3)
C(9)	0.651 5(8)	0.582 9(9)	0.831 1(3)
O(11)	0.290 4(4)	0.583 2(5)	0.939 9(2)
C(12)	0.075 5(14)	0.708 3(16)	0.921 4(9)
C(13)	0.082 2(14)	0.589 1(18)	0.865 4(7)
C(21)	0.162 7(14)	0.602 9(26)	0.977 4(8)
C(22)	0.047 3(18)	0.617 5(28)	0.918 6(11)
C(23)	0.115 3(19)	0.636 8(28)	0.847 9(11)
C(24)	0.272 5(18)	0.638 4(28)	0.868 3(8)
C(11)	0.203 6(19)	0.692 3(23)	0.972 2(10)
C(11′)	0.232 1(26)	0.731 9(18)	0.942 5(15)
C(14)	0.235 0(16)	0.539 0(23)	0.869 3(8)
C(14′)	0.195 6(20)	0.486 1(18)	0.897 1(12)

* The atom sequence O(1)—C(9) represents the [18]crown ether, O(11)—C(14′) the atoms of the disordered thf molecule (see text).

One of the thf molecules in (2) is disordered with respect to the crystallographic mirror plane. Atoms O(21)—C(24) (Table 7) were assigned site occupation factors of 0.5 and their O–O and C–C distances refined under the same constraint as

TABLE 7

Positional parameters of $[Na(C_{12}H_{24}O_6)(thf)_2][P(CN)_3Br]$, (2)

Atom *	*x*/*a*	*y*/*b*	*z*/*c*
Br	0.671 2(1)	0.500 0(0)	1.000 0(0)
P	0.500 0(0)	0.533 6(1)	0.917 3(1)
C(1)	0.595 1(5)	0.549 2(2)	0.861 9(3)
N(1)	0.653 8(4)	0.564 6(2)	0.829 6(2)
C(2)	0.500 0(0)	0.447 3(4)	0.902 5(3)
N(2)	0.500 0(0)	0.393 5(3)	0.893 4(3)
Na	0.000 0(0)	0.171 3(1)	0.379 2(1)
O(1)	0.000 0(0)	0.298 9(3)	0.438 6(3)
C(1′)	0.088 1(8)	0.304 7(3)	0.473 9(4)
C(2′)	0.170 3(7)	0.295 9(4)	0.434 3(5)
O(2)	0.172 8(4)	0.229 1(2)	0.418 5(2)
C(3)	0.251 5(7)	0.215 5(5)	0.378 8(4)
C(4)	0.257 4(7)	0.144 2(6)	0.369 4(4)
O(4)	0.170 2(4)	0.122 7(3)	0.340 3(2)
C(5)	0.171 0(8)	0.055 2(5)	0.333 7(5)
C(6)	0.088 1(10)	0.038 2(5)	0.297 4(4)
O(6)	0.000 0(0)	0.054 8(3)	0.328 8(3)
O(21)	0.006 2(16)	0.235 6(3)	0.291 8(2)
O(31)	0.000 0(0)	0.122 0(3)	0.473 4(2)
C(31)	0.085 2(5)	0.104 2(3)	0.504 8(3)
C(32)	0.053 6(6)	0.094 2(5)	0.568 7(2)
C(21)	0.038 3(10)	0.211 9(6)	0.235 3(5)
C(22)	0.030 4(10)	0.270 0(5)	0.193 7(5)
C(23)	−0.034 3(8)	0.319 7(5)	0.225 4(4)
C(24)	−0.037 6(10)	0.297 6(6)	0.290 0(5)

* The atom sequence O(1)—O(6) represents the [18]crown ether, and O(31), C(31), C(32) the thf molecule with crystallographic mirror symmetry. Atoms O(21) and C(21)—C(24) belong to the thf molecule which is disordered with respect to the crystallographic mirror plane with $x = 0$.

for the disordered thf molecule in (1). The atoms C(21)—C(24) were refined isotropically, the remaining atoms anisotropically. Inclusion of the hydrogen atoms at geometrically calculated positions led to unrealistically high isotropic temperature factors and their consideration was, therefore, abandoned.

TABLE 8

Positional parameters of $[N(C_3H_7)_4][PBr_4]$, (3)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Br(1)	0.560 6(1)	0.402 7(1)	0.553 3(1)
Br(2)	0.300 4(1)	0.400 6(1)	0.549 7(1)
Br(3)	0.433 4(1)	0.325 3(1)	0.397 1(1)
Br(4)	0.432 6(1)	0.265 7(1)	0.641 9(1)
P	0.433 0(2)	0.387 6(2)	0.546 4(2)
N	0.182 9(5)	0.311 7(5)	0.247 6(7)
C(11)	0.239 6(6)	0.364 7(9)	0.201 4(8)
C(12)	0.276 3(8)	0.425 4(9)	0.271 1(12)
C(13)	0.335 4(8)	0.468 0(11)	0.216 0(15)
C(21)	0.128 4(6)	0.369 3(8)	0.294 1(9)
C(22)	0.095 1(7)	0.435 5(9)	0.227 1(10)
C(23)	0.043 0(8)	0.485 2(10)	0.290 5(12)
C(31)	0.156 3(7)	0.259 1(9)	0.161 0(9)
C(32)	0.095 3(7)	0.201 0(9)	0.179 1(10)
C(33)	0.078 9(8)	0.152 4(10)	0.081 4(11)
C(41)	0.208 7(6)	0.253 4(8)	0.331 9(8)
C(42)	0.262 6(8)	0.191 3(9)	0.309 4(10)
C(43)	0.283 3(9)	0.140 1(10)	0.404 8(11)

The positions of the methylene hydrogens in (3) were geometrically calculated and the methyl groups refined as rigid groups. Group isotropic temperature factors were assigned to the hydrogen atoms and the remaining atoms refined anisotropically. Atomic positional parameters for (1)—(3) are listed in Tables 6—8. All thermal parameters, bond lengths and angles, hydrogen-atom positional parameters, and structure factor tables are deposited in Supplementary Publication No. SUP 22927 (40 pp.).*

Phosphorus-31 n.m.r. spectra were recorded as described previously[10,22] chemical shifts are expressed relative to 85% H_3PO_4 with the downfield direction taken as positive.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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