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Crystal and Molecular Structure of the Methyl Iodide Adduct of Tetraphosphorus Hexakis(*N*-methylimide), $P_4(NCH_3)_6CH_3I$

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The adamantane-like cage molecule $P_4(NCH_3)_6$ reacts with CH_3I to form a cationic methylated cage, with the methyl group attached to a phosphorus atom. Crystals of $P_4(NCH_3)_6CH_3I$ are monoclinic (space group $P2_1/c$) with $a = 11.383$ (2) Å, $b = 11.558$ (4) Å, $c = 14.584$ (3) Å, $\beta = 119.62$ (5)°, and $Z = 4$. Full-matrix least-squares refinement of 593 manual diffractometer data yielded a final R of 0.049. The P-C bond distance is 1.84 (1) Å, the P-N bonds of the methylated P are shorter than the other P-N bonds (1.65 (1) *vs.* 1.71 (3) Å), and the N-P-N bond angles of the unique P are larger than the others (107 (3) *vs.* 101 (1)°).

Introduction

The methylimide analog of P_4O_6, $P_4(NCH_3)_6$, was first prepared by Holmes and Forstner in 1960;[1,2] also reported was the 1:1 adduct of the imide cage with methyl iodide. Because of our general interest in the structural features of inorganic cage molecules and their derivatives, the molecular structure of the methyl iodide adduct has been determined and is the subject of this report.

Experimental Section

Preparation and X-Ray Data. The subject adduct was prepared by the reaction of $P_4(NCH_3)_6$ with CH_3I as described by Holmes.[2] Suitable crystals are obtained by adding 0.1 g of $P_4(NCH_3)_6$ to 10 ml of dry methyl iodide and holding the solution at −20° for 24 hr. Higher temperatures gave crystals too small for X-ray purposes, lower temperatures slowed the reaction to impractical times, and use of polar solvents led to decomposition of the product.

The approximately parallelepiped crystal used for data collection measured 0.045 × 0.225 × 0.360 mm (all ±0.002 mm) in the [100], [$10\bar{1}$], and [010] directions. The crystal was mounted on a glass fiber with the b axis roughly parallel to the ϕ axis of the diffractometer.

The diffractometer used was a GE XRD-5 manually operated quarter-circle system, with Mo Kα (λ 0.71069 Å) radiation filtered by a 1-mil thickness of Zr foil. A scintillation counter was used with a pulse height analyzer set for a 90% window. Least-squares refinement of the setting angles of 22 carefully centered reflections gave, at 23°, $a = 11.383$ (2) Å, $b = 11.558$ (4) Å, $c = 14.584$ (3) Å, and $\beta = 119.62$ (5)°. The crystal density, measured by suspension in a mixture of ethyl iodide and tetrachloroethylene, is 1.74 (2) g/cm³, which compares with 1.75 g/cm³ calculated for four formula units per unit cell. Systematic absences indicated the space group to be $P2_1/c$ (No. 14). Four molecules per unit cell in $P2_1/c$ imposes no crystallographic symmetry on the molecules.

The absorption coefficient of $[P_4(NCH_3)_6CH_3^+][I^-]$ for Mo Kα radiation is 13.2 cm^{-1}; no correction was made for absorption. No general corrections were made for extinction; however, the 002 reflection was omitted from the final refinement because of apparent extinction effects.

For intensity data collection a θ-2θ scan of 1.5° in 2θ was made at a speed of 2°/min with a takeoff angle of 3°. Stationary-crystal, stationary-counter background readings were taken for 10 sec at each end of the scans. All reflections with $0° < 2\theta < 40°$ were examined (1557). Of these, 593 reflections had $I \geqslant 1.8\sigma(I)$; these were used for the solution and refinement of the structure. Four reflections, measured periodically during the 5-day data collection, indicated there was reasonable crystal and electronic stability while the data were collected ($\Delta I < 2\sigma$).

The standard deviations for I were calculated by $\sigma(I) = (S + BT^2 + 0.0016I^2)^{1/2}$ [where S is the total scan count, B is the sum of the background counts, T = (scan time)/(total background time), and $I = S - BT$], except for a small number of reflections for which the two background readings differed by more than twice the calculated σ due to tailing of the reflection peak. For the latter reflections the standard deviations were set equal to the deviation of the background readings from the mean background value.

Scattering factors for neutral P, N, C, and H atoms and the iodide ion were calculated from the analytical functions of Cromer and Waber,[3] and real and imaginary anomalous dispersion corrections were made for P and I using the values given by Cromer.[4] All calculations were done with the IBM 360/50 computer at the University of Arkansas Computer Center using programs described previously.[5]

Solution and Refinement of the Structure. The structure was solved using a three-dimensional sharpened Patterson map. Fourier and full-matrix least-squares refinement of all nonhydrogen atoms with isotropic temperature factors led to an unweighted R_1 ($\Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.062 and a weighted residual R_2 ($[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where $w = 1/\sigma(F)$, of 0.071.

In the least-squares refinement the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. When the hydrogen atoms were located in idealized positions suggested by a difference Fourier map and the iodine and phosphorus atoms were refined with anisotropic thermal parameters, R_1 and R_2 became 0.049 and 0.056, respectively. This final refinement consisted of 98 parameters and 593 reflections. In the final cycle of refinement no parameter shifted by more than 0.05σ. The standard deviation of an observation of unit weight is 0.85. A final difference map did not have any peaks which were interpretable chemically. The largest value was 0.5 e/Å³, which is equal to 10% of the maximum electron density of a carbon atom on a regular electron density map. Inspection of the reflection list of the final least squares did not reveal any $\Delta F/\sigma$ dependence on either F or θ values.

The final positional and isotropic thermal parameters are given in Table I, and Table II gives the final anisotropic thermal parameters. Table III gives the rms amplitudes of vibration of the phosphorus and iodine atoms. Table IV lists the intramolecular distances and angles. Figure 1 shows the anisotropic ellipsoids and the atom-numbering scheme used; Figure 2 shows the crystal packing.

Results and Discussion

The reaction of $P_4(NCH_3)_6$ with CH_3I produces a cationic cage unit with the seventh methyl group attached to a phosphorus atom. The insolubility of the adduct in methyl iodide is probably the main barrier to methylation of the other phosphorus atoms. The average 1.71 (3) Å P-N bond distances and the 101 (1)° N-P-N bond angles which do not involve the four-bonded phosphorus atom, as well as the 1.51 (2) Å N-C bond distances and 115 (2)° P-N-C angles, are equal to the values found in $P(NCH_3NCH_3)_3P$.[6] This P-N distance is shorter than the 1.77-1.80 Å usually[7,8] considered

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(1) R. R. Holmes and J. A. Forstner, *J. Amer. Chem. Soc.*, **82**, 5509 (1960).

(2) R. R. Holmes, *J. Amer. Chem. Soc.*, 83, 1334 (1961).

(3) D. T. Cromer and J. T. Waber, private communication, Los Alamos Scientific Laboratory.

(4) D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

(5) J. E. Stuckey, A. W. Cordes, L. B. Handy, R. W. Perry, and C. K. Fair, *Inorg. Chem.*, 11, 1846 (1972).

(6) W. vanDoorne, G. W. Hunt, R. W. Perry, and A. W. Cordes, *Inorg. Chem.*, 10, 2591 (1971).

(7) E. Hobbs, D. E. C. Corbridge, and B. Raistrick, *Acta Crystallogr.*, 6, 621 (1953).

Table I.[a] Positional Parameters and Isotropic Thermal Parameters in $[P_4(NCH_3)_6CH_3^+][I^-]$

	x	*y*	*z*	*B*, Å²
I	0.1045 (2)	0.2020 (2)	0.1781 (2)	
P(1)	0.697 (1)	0.0730 (8)	0.3115 (7)	
P(2)	0.6078 (7)	0.1998 (9)	0.1054 (5)	
P(3)	0.5447 (8)	0.3001 (9)	0.2675 (5)	
P(4)	0.8210 (8)	0.2892 (9)	0.3057 (5)	
N(1)	0.634 (2)	0.077 (2)	0.175 (2)	4 (1)
N(2)	0.588 (2)	0.165 (2)	0.323 (2)	2.8 (9)
N(3)	0.840 (2)	0.159 (2)	0.357 (2)	4 (1)
N(4)	0.508 (2)	0.274 (2)	0.139 (2)	3.1 (8)
N(5)	0.754 (2)	0.273 (2)	0.176 (2)	2.7 (8)
N(6)	0.705 (2)	0.358 (2)	0.320 (2)	3 (1)
C(1)	0.692 (3)	−0.022 (3)	0.139 (2)	5 (2)
C(2)	0.482 (3)	0.106 (3)	0.340 (2)	4 (1)
C(3)	0.968 (3)	0.098 (3)	0.387 (2)	4 (1)
C(4)	0.359 (3)	0.278 (3)	0.058 (2)	4 (1)
C(5)	0.775 (3)	0.379 (3)	0.122 (2)	4 (1)
C(6)	0.748 (3)	0.420 (3)	0.423 (2)	5 (1)
C(7)	0.978 (3)	0.361 (3)	0.365 (2)	4 (1)
H(1)[b]	0.793	−0.018	0.180	9
H(2)	0.660	−0.013	0.062	9
H(3)	0.661	−0.097	0.153	9
H(4)	0.427	0.166	0.350	9
H(5)	0.528	0.055	0.403	9
H(6)	0.427	0.059	0.276	9
H(7)	0.987	0.100	0.327	9
H(8)	0.960	0.016	0.405	9
H(9)	1.043	0.137	0.450	9
H(10)	0.308	0.308	0.092	9
H(11)	0.328	0.199	0.030	9
H(12)	0.346	0.331	−0.001	9
H(13)	0.806	0.446	0.171	9
H(14)	0.689	0.398	0.057	9
H(15)	0.846	0.360	0.102	9
H(16)	0.680	0.405	0.447	9
H(17)	0.754	0.505	0.413	9
H(18)	0.838	0.390	0.478	9
H(19)	1.050	0.306	0.371	9
H(20)	1.001	0.389	0.436	9
H(21)	0.973	0.429	0.320	9

[a] In all of the tables the numbers in parentheses are estimated standard deviations in the least significant digit(s) of the preceding parameter. [b] The H atom positions were calculated from the C positions as described above, and the isotropic temperature factors were assigned values of 9.0. None of these H atom parameters was included in the least-squares refinement.

Table II. Anisotropic Thermal Parameters $\times 10^4$ for the Iodine and Phosphorus Atoms in $[P_4(NCH_3)_6CH_3^+][I^-]$[a]

	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
I	124 (3)	87 (2)	71 (2)	−3 (4)	52 (2)	−12 (3)
P(1)	124 (16)	58 (9)	63 (7)	10 (10)	54 (9)	9 (7)
P(2)	120 (12)	51 (8)	44 (6)	11 (12)	41 (7)	−3 (8)
P(3)	111 (13)	57 (8)	49 (6)	14 (12)	43 (8)	−6 (8)
P(4)	92 (12)	55 (8)	47 (7)	4 (12)	31 (8)	2 (8)

[a] The form of the thermal correction is $\exp[-(h^2\beta(1,1) + k^2\beta(2,2) + l^2\beta(3,3) + 2hk\beta(1,2) + 2hl\beta(1,3) + 2kl\beta(2,3))]$.

Table III. Root-Mean-Square Amplitudes of Vibration of the Iodine and Phosphorus Atoms in $[P_4(NCH_3)_6CH_3^+][I^-]$

	Min	Intermed	Max
I	0.216 (5)	0.244 (4)	0.260 (4)
P(1)	0.19 (2)	0.21 (2)	0.25 (2)
P(2)	0.16 (2)	0.19 (2)	0.25 (1)
P(3)	0.16 (2)	0.21 (2)	0.24 (2)
P(4)	0.18 (2)	0.20 (2)	0.22 (2)

Table IV. Selected Bond Distances (Å) and Angles (deg) in $[P_4(NCH_3)^+][I^-]$

Distances			
P(1)-N(1)	1.75 (2)	P(4)-N(5)	1.66 (2)
P(1)-N(2)	1.71 (2)	P(4)-N(6)	1.65 (2)
P(1)-N(3)	1.74 (2)	P(4)-N (av)[a]	1.65 (1)
P(2)-N(1)	1.68 (2)	P(4)-C(7)	1.77 (3)
P(2)-N(4)	1.68 (2)	N(1)-C(1)	1.54 (3)
P(2)-N(5)	1.69 (2)	N(2)-C(2)	1.49 (3)
P(3)-N(2)	1.72 (2)	N(3)-C(3)	1.48 (3)
P(3)-N(4)	1.73 (2)	N(4)-C(4)	1.51 (3)
P(3)-N(6)	1.72 (2)	N(5)-C(5)	1.54 (3)
P-N (av)[a]	1.71 (3)	N(6)-C(6)	1.51 (3)
P(4)-N(3)	1.64 (2)	N-C (av)[a]	1.51 (2)

Angles			
N(1)-P(1)-N(2)	101 (1)	P(1)-N(2)-C(2)	115 (2)
N(1)-P(1)-N(3)	101 (1)	P(1)-N(3)-C(3)	115 (2)
N(2)-P(1)-N(3)	101 (1)	P(2)-N(1)-C(1)	114 (2)
N(1)-P(2)-N(4)	101 (1)	P(2)-N(4)-C(4)	116 (2)
N(1)-P(2)-N(5)	103 (1)	P(2)-N(5)-C(5)	116 (2)
N(4)-P(2)-N(5)	99 (1)	P(3)-N(2)-C(2)	115 (2)
N(2)-P(3)-N(4)	103 (1)	P(3)-N(4)-C(4)	115 (2)
N(2)-P(3)-N(6)	99 (1)	P(3)-N(6)-C(6)	112 (2)
N(4)-P(3)-N(6)	101 (1)	P(4)-N(3)-C(3)	118 (2)
N-P-N (av)[a]	101 (1)	P(4)-N(5)-C(5)	113 (2)
N(3)-P(4)-N(5)	107 (1)	P(4)-N(6)-C(6)	118 (2)
N(3)-P(4)-N(6)	109 (1)	P-N-C (av)[a]	115 (2)
N(5)-P(4)-N(6)	104 (1)	P(1)-N(1)-P(2)	124 (1)
N-P(4)-N (av)[a]	107 (3)	P(3)-N(4)-P(2)	125 (1)
N(3)-P(4)-C(7)	110 (1)	P(3)-N(2)-P(1)	124 (1)
N(5)-P(4)-C(7)	113 (1)	P(4)-N(3)-P(1)	118 (1)
N(6)-P(4)-C(7)	113 (1)	P(4)-N(5)-P(2)	121 (1)
N-P(4)-C (av)[a]	112 (2)	P(4)-N(6)-P(3)	119 (1)
P(1)-N(1)-C(1)	111 (2)	P-N-P (av)[a]	122 (3)

[a] Weighted average and rms deviation.

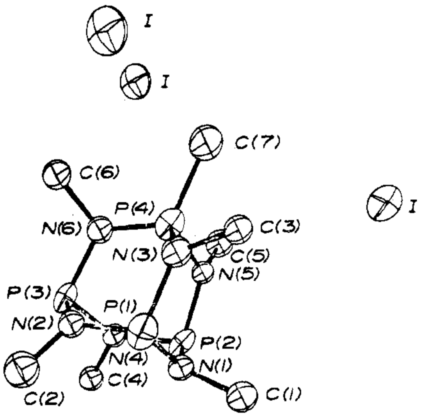

Figure 1. The thermal ellipsoids and atom numbering for $P_4(NCH_3)_6CH_3I$.

for a single P-N bond but is not as short as the 1.57-1.60 Å P-N bonds characteristic of the phosphonitrilic ring molecules. The short P-N bond lengths and the 352° sum-of-the-angles at the nitrogen atoms suggest a P-N bond order of greater than unity, as proposed by Gilge and Seff for $OP(NCH_3NCH_3)_3PO$.[9]

The methylated phosphorus atom has significantly larger N-P-N bond angles (107 (3)° *vs.* 101 (1)°) and shorter P-N distances (1.65 (1) Å *vs.* 1.71 (3) Å). These differences are similar to the P-N bond shortening (1.71 (3) to 1.66 (3) Å) and N-P-N bond angle opening (101 (1) to 104 (2)°) which take place when an oxygen is added to the phosphorus in the change from $P(NCH_3NCH_3)_3P$ to $OP(NCH_3NCH_3)_3PO$. If there is π character in the P-N linkages of these compounds as a result of participation of the d orbitals of phosphorus, the shortening of the P-N bonds upon addition of a methyl cation or an oxygen atom is consistent with the familiar rea-

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(8) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(9) J. W. Gilge and K. Seff, *Inorg. Chem.*, 11, 1643 (1972).

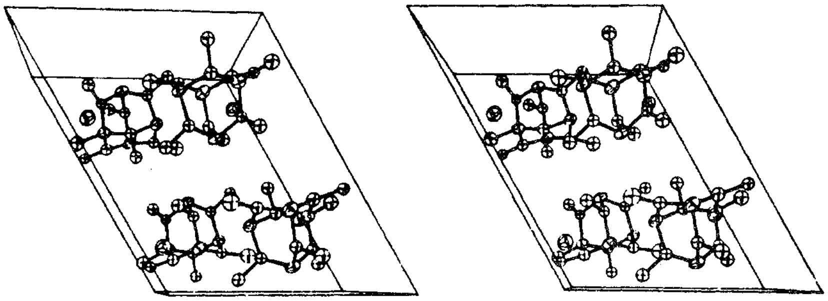

Figure 2. Stereoview of the packing of $P_4(NCH_3)_6CH_3I$ in the unit cell, as viewed along the *b* axis.

soning that electronegative substituents decrease the size of the d orbitals and allow for more favorable overlap.

The crystal packing consists of sheets of iodide ions lying in the *yz* plane with $P_4(NCH_3)_6CH_3^+$ cations on each side arranged so that the charged phosphorus atom in each cation points almost directly into the center of a triangle of iodide ions (the distances from this phosphorus to the three nearest iodide ions are 4.57, 4.76, and 4.83 Å). The packing is such that only half of the triangular faces have associated cations. A triangular face of iodide ions is illustrated in the ORTEP drawing of the cation in Figure 1. There are no unusually short intermolecular forces in the molecule.

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Registry No. $[P_4(NCH_3)_6CH_3^+][I^-]$, 36919-57-0; $P_4(NCH_3)_6$-CH_3I, 51329-59-0.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1688.

Contribution from the Department of Chemistry,
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Crystal Structure of $XeF_3^+SbF_6^-$

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The crystal structure of $XeF_3^+SbF_6^-$ has been accurately determined from three-dimensional X-ray counter data. Crystals are monoclinic with $a = 5.394$ (1) Å, $b = 15.559$ (2) Å, $c = 8.782$ (1) Å, $\beta = 103.10$ (1)°, $V = 717.84$ Å^3, $Z = 4$, and $d_c = 3.92$ g cm^{-3}. The structure has been refined in space group $P2_1/n$ to a final conventional R factor of 0.048 for 1264 independent reflections with $I \geq 3\sigma(I)$. The structure consists of $XeF_3^+SbF_6^-$ units with a close contact of 2.485 (10) Å between the Xe atom of the T-shaped cation and an F atom of the octahedral anion. The bridging F atom is coplanar with the cation with a bridge angle of 140.8 (4)°.

Introduction

The preparation of the compound $XeF_3^+Sb_2F_{11}^-$ and its characterization by ^{19}F nmr and Raman spectroscopy was first reported from this laboratory[1] and it was shown that the spectroscopic evidence was in complete accord with the expected T-shape geometry for the XeF_3^+ cation. Subsequently we prepared the crystalline compound $XeF_3^+SbF_6^-$ and had made considerable progress in the determination of its structure by X-ray crystallography when Bartlett, *et al.*, gave a preliminary report[2] of the structure of $XeF_3^+Sb_2F_{11}^-$. We have since completed the refinement of the structure of $XeF_3^+SbF_6^-$ and we now report the results and compare them in detail with those obtained by Bartlett, *et al.*, for XeF_3^+-$Sb_2F_{11}^-$, the full details of which have been published[3] since the completion of our work. At the same time McKee, Adams, and Bartlett[4] published the unit cell parameters of $XeF_3^+SbF_6^-$.

Experimental Section

Details of the techniques used for the preparation of $XeF_4 \cdot SbF_5$ and related complexes are described elsewhere.[5] The complex was prepared by dissolving XeF_4 and SbF_5 in the ratio 3.4:1 in anhydrous HF. Crystals were grown by slowly pumping the HF off at room temperature, giving a mixture of XeF_4 and $XeF_3^+SbF_6^-$ crystals. Excess XeF_4 was then pumped off at room temperature and pumping continued for several hours to give dry crystals. A Raman spectrum of the single crystal used for the X-ray structure determination showed it to be identical with the bulk material.

Crystal Data. $XeF_3^+SbF_6^-$ is monoclinic with $a = 5.394$ (1) Å, $b = 15.559$ (2) Å, $c = 8.782$ (1) Å, $\beta = 103.10$ (1)°, $V = 717.85$ Å^3, $Z = 4$, $d_c = 3.92$ g cm^{-3}, FW = 424.04, $F(000) = 744$, and μ(Mo Kα) = 87.6 cm^{-1}. The unit cell parameters were obtained from a least-squares refinement of 15 reflections in the region $35 < 2\theta < 45°$ and we believe that they are more accurate than those of McKee, Adams,

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(1) R. J. Gillespie, B. Landa, and G. J. Schrobilgen, *Chem. Commun.*, 1543 (1971).

(2) D. E. McKee, C. J. Adams, A. Zalkin, and N. Bartlett, *J. Chem. Soc., Chem. Commun.*, 26 (1973).

(3) D. E. McKee, A. Zalkin, and N. Bartlett, *Inorg. Chem.*, 12, 1713 (1973).

(4) D. E. McKee, C. J. Adams, and N. Bartlett, *Inorg. Chem.*, 12, 1722 (1973).

(5) R. J. Gillespie and G. J. Schrobilgen, *Inorg. Chem.*, in press.