

Structure and Motion of Tetrakis(trichlorophosphazeno)phosphonium Hexachlorophosphate, $[P(NPCl_3)_4]^+PCl_6^-$, at 93 K

FERDINAND BELAJ

Institut für Anorganische Chemie, Universität Graz, Schubertstrasse 1, A-8010 Graz, Austria.

E-mail: ferdinand.belaj@kfunigraz.ac.at

(Received 13 November 1996; accepted 8 April 1997)

Abstract

$[P(NPCl_3)_4]^+PCl_6^-$, $M_r = 880.02$, monoclinic, $P2_1/m$, $a = 7.720$ (2), $b = 21.235$ (5), $c = 8.248$ (2) Å, $\beta = 91.12$ (2)°, $V = 1351.9$ (6) Å³, $Z = 2$, $D_x = 2.162$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $T = 93$ K, $R = 0.0497$, $S = 1.007$ for 4536 unique observed reflections and 140 parameters. The cations and anions show site symmetries of $C_s(m)$ and $C_i(\bar{1})$, respectively. The P—N bond lengths in the $NPCl_3$ groups are distinctly shorter [1.515 (4)–1.532 (4) Å] than those attached to the central P atom [1.595 (2)–1.611 (4) Å], the P—Cl bond lengths are 1.961 (1)–1.975 (1) Å in the cations and 2.132 (1)–2.142 (1) Å in the anions; the P—N—P angles lie in the range 132.5 (2)–142.9 (3)°. The structure is a derivative of the CsCl structure type showing interionic distances of 3.314 (1)–3.414 (1) Å between the Cl atoms. The differences between the angles $P-Cl_{\text{cation}} \cdots Cl_{\text{anion}}$ [153.38 (5)–168.28 (5)°] and $P-Cl_{\text{anion}} \cdots Cl_{\text{cation}}$ [102.30 (3)–116.35 (4)°] are very probably caused by the arrangement of the lone pairs at the Cl atoms. The thermal motion analysis showed that the anion behaves as a rigid body $\{R_u = [\Sigma w(\Delta U)^2 / \Sigma w(U_{\text{obs}})^2]^{1/2} = 0.024\}$, whereas the cation does not ($R_u = 0.347$). Allowing three intramolecular torsions the residual index R_u for the cation could be lowered to 0.184.

1. Introduction

At the crystal structure determination of $[P(NPCl_3)_4]^+[ICl_2]^- \cdot 2[(CCl_4)_x(CHCl_3)_{1-x}]$, $x = 0.67$ (2) [P5I (Belaj, 1995a)], the cation could not be described without any difficulties: At room temperature the N and Cl atoms especially showed unusually large displacement parameters, the P—N distances were extremely short [1.45 (2) and 1.48 (2) Å] and a correlation of the P—N—P bond angles with the P \cdots P distances found in the Cambridge Structural Database (CSD; Allen *et al.*, 1991) suggested a P—N—P bond angle of *ca* 136° rather than the 173.3 (11)° observed. An accurate low-temperature structure determination of P5I was defeated by a phase transition from tetragonal ($I4_1/acd$) to orthorhombic ($Ibca$).

In order to study the structure of this cation more precisely, particularly at low temperature, the structure

determination of the salt with the Cl^- anion or the larger PCl_6^- anion was planned. Since no suitable single crystals could be obtained from the chloride $[P(NPCl_3)_4]Cl$ (Schmidpeter & Weingand, 1969a,b), the structure of the hitherto unknown title compound $[P(NPCl_3)_4]PCl_6$ (P5P) was determined.

2. Experimental

2.1. Preparation

Reaction of $P(NH_2)_4Cl$ (0.44 g, 3.37 mmol) with PCl_5 (3.51 g, 16.8 mmol) in 150 ml of $CHCl_3$ for 5 h at 333 K under an N_2 atmosphere gave a microcrystalline yellowish precipitate of P5P. Removal of the solvent, addition of $C_2H_4Cl_2$ until a clear solution was obtained at 333 K, removal of excess solvent by a cooling trap until crystallization started, slowly cooling to room temperature over several hours and completing the precipitation overnight in a refrigerator gave crystals too small for structure determination. Suitable single crystals were obtained from this product by repeatedly careful heating to a maximum of 333 K until the majority of the small crystals were dissolved, followed by slow cooling. $F_p = 542$ K; FT-Raman (Nicolet Raman spectrometer 910, crystal powder, cm^{-1}): 1411w, 1310vw, 1288vw, 1230vw, 843w, 825w, 613w, 590w, 502m, 486w, 465m, 440s, 420w, 390w, 356vs, 341m, 318m, 281w, 271s, 244vs, 229w, 212m, 200w, 158s.

2.2. Crystal structure determination

A single-crystal was immersed in oil and immediately cooled to 93 K. All the measurements were performed on a modified Stoe four-circle diffractometer with a Nonius low-temperature device. The 15 strongest peaks in the structure solution corresponded to the P and Cl atoms, the next three peaks to the N atoms. The experimental details and final agreement factors are summarized in Table 1.

The cations and anions show site symmetries of $C_s(m)$ and $C_i(\bar{1})$, respectively. After full-matrix least-squares refinements of all the atoms with anisotropic displacement parameters, the final difference electron-density map contained three rather high peaks (0.74–1.31 e Å⁻³),

Table 1. *Experimental details*

Crystal data	
Chemical formula	$Cl_{12}N_4P_5^+PCl_6^-$
Chemical formula weight	880.02
Cell setting	Monoclinic
Space group	$P2_1/m$
a (Å)	7.720 (2)
b (Å)	21.235 (5)
c (Å)	8.248 (2)
β (°)	91.12 (2)
V (Å ³)	1351.9 (6)
Z	2
D_x (Mg m ⁻³)	2.162
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.71069
No. of reflections for cell parameters	71
θ range (°)	12.5–15.0
μ (mm ⁻¹)	2.181
Temperature (K)	93 (2)
Crystal form	Block
Crystal size (mm)	0.35 × 0.30 × 0.15
Crystal colour	Pale yellow
Data collection	
Diffractometer	Stoe four-circle diffractometer
Data collection method	Profile data from ω scans
Absorption correction	Empirical (Parkin, Moezzi & Hope, 1995)
T_{\min}	0.583
T_{\max}	0.871
No. of measured reflections	7690
No. of independent reflections	6427
No. of observed reflections	4536
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.0329
θ_{\max} (°)	36.00
Range of h, k, l	–12 → h → 12 –1 → k → 35 –1 → l → 13
No. of standard reflections	3
Frequency of standard reflections	Every 100 reflections
Intensity decay (%)	1.5
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0497
$wR(F^2)$	0.1091
S	1.058
No. of reflections used in refinement	6415
No. of parameters used	140
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0530P)^2 + 0.5323P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.001
$\Delta\rho_{\max}$ (e Å ⁻³)	1.307
$\Delta\rho_{\min}$ (e Å ⁻³)	–0.793
Extinction method	<i>SHELXL93</i> (Sheldrick, 1993)
Extinction coefficient	0.0019 (6)
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C)
Computer programs	
Data collection	Local program
Cell refinement	Local program
Data reduction	Local program
Structure solution	<i>SHELXS86</i> (Sheldrick, 1985)

Table 1 (cont.)

Structure refinement	<i>SHELXL93</i> (Sheldrick, 1993)
Preparation of material for publication	<i>SHELXL93</i> (Sheldrick, 1993)
Plot Programs	<i>ORTEP</i> (Johnson, 1965)
Motion analysis	<i>TMA14</i> (Schomaker & Trueblood, 1968; Dunitz & White, 1973; Trueblood, 1978; Dunitz, Maverick & Trueblood, 1988a,b)

showing distances 1.77–1.99 Å to P3 and 0.67–0.86 Å to the Cl atoms Cl31–Cl33. These peak positions suggest that they are due to an unresolved torsional disorder around the N3–P3 bond involving the PCl₃ group which is not on the mirror plane. Refinement with an isotropic displacement parameter common to these three Cl atoms [$U_{\text{iso}} = 0.042$ (8) Å²], and a common occupancy factor constrained to total one with the common occupancy factor of the atoms Cl31–Cl33, resulted in a very low occupancy [0.027 (4)] of these disordered Cl atoms and it did not seem worthwhile to include their positions in Table 2.†

3. Structural results

The conformation of the cation and the labelling scheme for both ions in P5P are shown in Fig. 1, and selected geometric parameters are reported in Table 3. In the cation the P–N bond lengths to the central P atom are slightly larger than the equivalent ones in $[ClP(NPCl_3)_3]^+X^-$ [$X^- = Cl^-, PCl_6^-$; 1.575 (2)–1.590 (3) Å (Belaj, 1992)] or in $Cl_2P(O)NPCl_3$ [1.583 (3)–1.593 (3) Å (Belaj, 1993)]. The P–N bond

† A list of structure factors has been deposited with the IUCr (Reference: SE0209). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

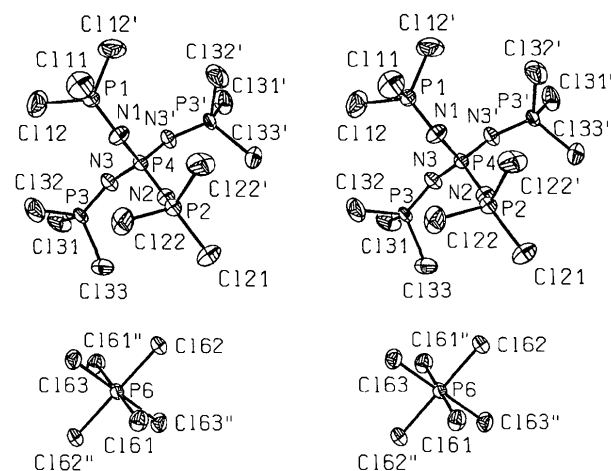


Fig. 1. Stereoscopic plot of the two ions showing the atomic numbering scheme. The ellipsoids are drawn at the 90% probability level. Symmetry codes: (i) $x, \frac{1}{2} - y, z$; (ii) $1 - x, 1 - y, -z$.

Table 2. Fractional atomic coordinates and equivalent isotropic and anisotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (4/3)\Sigma_i \Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P4	0.94742 (12)	1/4	0.57615 (12)	0.00986 (15)	0.0112 (3)	0.0084 (3)	0.0100 (4)	0	0.0013 (3)	0
N1	0.9091 (5)	1/4	0.7675 (4)	0.0165 (6)	0.0170 (14)	0.022 (2)	0.0103 (13)	0	-0.0003 (11)	0
P1	0.99678 (14)	1/4	0.93339 (13)	0.0135 (2)	0. (4)	0.0125 (4)	0.0092 (4)	0	0.0008 (3)	0
Cl11	0.8228 (2)	1/4	1.10443 (15)	0.0278 (2)	0.0361 (6)	0.0323 (6)	0.0156 (4)	0	0.0126 (4)	0
Cl12	1.14578 (14)	0.32321 (5)	0.98453 (12)	0.0319 (2)	0.0413 (5)	0.0281 (4)	0.0261 (4)	-0.0003 (3)	-0.0070 (3)	-0.0176 (4)
N2	0.7651 (4)	1/4	0.4795 (4)	0.0130 (5)	0.0130 (12)	0.0143 (13)	0.0118 (12)	0	0.0022 (10)	0
P2	0.57732 (13)	1/4	0.53610 (13)	0.0118 (2)	0.0117 (4)	0.0117 (4)	0.0118 (4)	0	0.0019 (3)	0
Cl21	0.42270 (13)	1/4	0.34385 (13)	0.0197 (2)	0.0146 (4)	0.0285 (5)	0.0159 (4)	0	-0.0025 (3)	0
Cl22	0.50874 (11)	0.32322 (4)	0.66692 (11)	0.0269 (2)	0.0253 (3)	0.0281 (4)	0.0273 (4)	-0.0147 (3)	-0.0003 (3)	0.0104 (3)
N3	1.0604 (3)	0.30944 (11)	0.5252 (3)	0.0139 (4)	0.0135 (8)	0.0089 (8)	0.0192 (10)	0.0009 (8)	0.0011 (7)	0.0005 (7)
P3	1.02555 (9)	0.37933 (3)	0.49364 (9)	0.01183 (12)	0.0164 (3)	0.0062 (2)	0.0129 (3)	0.0007 (2)	0.0002 (2)	0.0006 (2)
Cl31	1.23347 (10)	0.41919 (4)	0.40710 (11)	0.0228 (2)	0.0216 (3)	0.0169 (3)	0.0301 (4)	0.0100 (3)	0.0031 (3)	-0.0047 (2)
Cl32	0.96417 (14)	0.42922 (4)	0.68578 (11)	0.0283 (2)	0.0495 (5)	0.0160 (3)	0.0196 (3)	-0.0054 (3)	0.0046 (3)	0.0068 (3)
Cl33	0.84030 (11)	0.39925 (4)	0.33394 (11)	0.0237 (2)	0.0256 (3)	0.0183 (3)	0.0267 (4)	0.0052 (3)	-0.0106 (3)	0.0019 (2)
P6	1/2	1/2	0	0.0114 (2)	0.0135 (4)	0.0090 (3)	0.0118 (4)	-0.0010 (3)	0.0003 (3)	-0.0008 (3)
Cl61	0.22557 (9)	0.49140 (3)	0.01352 (9)	0.01662 (12)	0.0133 (2)	0.0186 (3)	0.0179 (3)	-0.0027 (2)	0.0003 (2)	-0.0010 (2)
Cl62	0.52737 (10)	0.40139 (3)	0.04882 (9)	0.01726 (12)	0.0229 (3)	0.0096 (2)	0.0192 (3)	-0.0003 (2)	-0.0026 (2)	-0.0003 (2)
Cl63	0.51610 (9)	0.51936 (3)	0.25433 (8)	0.01593 (12)	0.0203 (3)	0.0154 (3)	0.0121 (2)	-0.0025 (2)	0.0003 (2)	-0.0014 (2)

Table 3. Selected geometric parameters (\AA^2)

P4—N3	1.595 (5)	P2—Cl22	1.9709 (10)
P4—N2	1.604 (4)	N3—P3	1.530 (2)
P4—N1	1.611 (4)	P3—Cl31	1.9614 (11)
N1—P1	1.515 (4)	P3—Cl33	1.9713 (11)
P1—Cl11	1.967 (2)	P3—Cl32	1.9718 (11)
P1—Cl12 ¹	1.9746 (11)	P6—Cl61	2.1316 (9)
N2—P2	1.532 (3)	P6—Cl63	2.1389 (8)
P2—Cl21	1.9660 (15)	P6—Cl62	2.1421 (8)
N3—P4—N3 ¹	104.6 (2)	N2—P2—Cl22	115.64 (8)
N3—P4—N2	110.37 (12)	Cl21—P2—Cl22	106.03 (5)
N3—P4—N1	111.70 (12)	Cl22 ¹ —P2—Cl22	104.16 (8)
N2—P4—N1	108.1 (2)	P3—N3—P4	135.8 (2)
P1—N1—P4	142.9 (3)	N3—P3—Cl31	109.77 (10)
N1—P1—Cl11	110.4 (2)	N3—P3—Cl33	116.41 (10)
N1—P1—Cl12	116.18 (8)	Cl31—P3—Cl33	104.62 (5)
Cl11—P1—Cl12	104.48 (6)	N3—P3—Cl32	115.38 (11)
Cl12—P1—Cl12 ¹	103.87 (8)	Cl31—P3—Cl32	105.77 (5)
P2—N2—P4	132.5 (2)	Cl33—P3—Cl32	103.83 (5)
N2—P2—Cl21	108.52 (15)		
N3—P4—N1—P1	-58.39 (11)	P4—N2—P2—Cl22	-61.05 (8)
N2—P4—N1—P1	180.0	N3 ¹ —P4—N3—P3	160.90 (13)
P4—N1—P1—Cl11	180.0	N2—P4—N3—P3	42.2 (3)
P4—N1—P1—Cl12	61.32 (9)	N1—P4—N3—P3	-78.1 (3)
N3—P4—N2—P2	-122.42 (11)	P4—N3—P3—Cl31	-172.6 (2)
N1—P4—N2—P2	0.0	P4—N3—P3—Cl33	-54.0 (3)
P4—N2—P2—Cl21	180.0	P4—N3—P3—Cl32	68.1 (3)

Symmetry code: (i) x, 1/2 - y, z.

lengths in the NPCl_3 groups are distinctly shorter and virtually equal to those observed in $[\text{ClP}(\text{NPCl}_3)_3]^+ \text{X}^-$ or $\text{Cl}_3\text{PNP}(\text{O})\text{Cl}_2$. The very flexible P—N—P angles in P5P [132.5 (2)—142.9 (3)°] are comparable to those in the above cited compounds. As frequently observed (Belaj, 1996), all three NPCl_3 groups are oriented in a way that the P—N—P—Cl torsion angles to the Cl atoms $\text{Cl}n1$ ($n = 1-3$) are close to 180°, if not constrained to 180° by

symmetry. As observed and discussed in the structure analysis of $\text{SO}_2(\text{NPCl}_3)_2$ (Belaj, 1995b), the N—P—Cl bond angles and, to a lesser degree, the P—Cl distances for these *trans*-Cl atoms in the NPCl_3 groups are smaller than for the others [108.5 (2)—110.4 (2) versus 115.4 (1)—116.4 (1)°; 1.961 (1)—1.967 (2) versus 1.971 (1)—1.975 (1) Å].

If all the NPCl_3 groups are *trans* oriented, as observed in P5P, the conformation of the cation can be described by the four torsion angles P1—N1—P_c—N2, N1—P_c—N2—P2, P3—N3—P_c—N4 and N3—P_c—N4—P4 of the central P_c(NP)₄ fragment. If they are restricted to 0° = *cis* (C) or 180° = *trans* (T), the symmetrical conformations *CCCC* [$D_{2d}(\bar{4}2m)$], *CCCT* [$C_s(m)$], *CCTT* [$C_{2v}(mm2)$], *CTCT* [$C_2(2)$], *CTTT* [$C_s(m)$] and *TTTT* [$D_{2d}(\bar{4}2m)$] may be distinguished. Furthermore, a *gauche* conformation of $S_4(\bar{4})$ symmetry, *GGGG*, in which the four torsion angles cited above have values of φ , φ , $-\varphi$, $-\varphi$ (φ ca 90°), must be taken into account. Semi-empirical MNDO [modified neglect of diatomic overlap (Dewar & Thiel, 1977)] calculations resulted in the following: The only energy minimum confirmed by the calculated complete set of harmonic vibrational frequencies which could be found for the cation was for the *GGGG* ($\varphi = 84.5^\circ$; P—N 1.632, 1.576; P—Cl 1.994, 2.002 Å; P—N—P 131.0; P—N—P—Cl $\pm 165.5^\circ$; $\Delta H_f^\circ = 149.9 \text{ kJ mol}^{-1}$); the *CCCC* ($\Delta H_f^\circ = 259.7 \text{ kJ mol}^{-1}$) and *TTTT* conformations ($\Delta H_f^\circ = 231.7 \text{ kJ mol}^{-1}$) are fifth-order saddle points in the hypersphere; the *CCCT*, *CCTT*, *CTCT* and *CTTT* conformations ($\Delta H_f^\circ = 226.3, 247.1, 190.9$ and $161.8 \text{ kJ mol}^{-1}$, respectively) all converge to the *GGGG* conformation when the symmetry constraints are released. In the crystalline state tetraphenylmethane, tetraphenylsilane, tetraphenylgermanium and tetraphenyltin adopt conformations with $S_4(\bar{4})$ symmetry, the tetraphenylphosphonium ion with almost $S_4(\bar{4})$ symme-

try, whereas the tetraphenylborate anion has $D_{2d}(\bar{4}2m)$ symmetry in its K^+ salt and almost $D_{2d}(\bar{4}2m)$ symmetry in its $(CH_3)_4N^+$ salt (Dunitz, 1979). The less-symmetrical *CTTT* conformation observed in the structure of P5P is only slightly higher in energy (11.9 kJ mol^{-1}) than the more stable *GGGG* conformation and is presumably forced by packing effects. It is remarkable that the geometry parameters of the $P_c(\cdots P)_4$ fragment for the *GGGG* conformation are equal to those observed in P5I [$P \cdots P_4 \times 4.689, 2 \times 4.922 \text{ \AA}$, $P \cdots P_c \cdots P_4 \times 106.8, 2 \times 114.9^\circ$ compared with $4 \times 4.721 (5), 2 \times 4.902 (5) \text{ \AA}$ and $4 \times 107.4 (1), 2 \times 113.6 (1)^\circ$, respectively], which of course are quite different from those in P5P [$2 \times 4.437 (2), 2 \times 4.558 (2), 4.562 (2), 5.141 (2) \text{ \AA}$; $2 \times 100.63 (3), 2 \times 102.14 (3), 102.87 (5)$ and $143.03 (5)^\circ$, respectively] by the different *CTTT* conformations. Consequently, a re-refinement of the room-temperature data of P5I was performed in the space group $I4_1/acd$, where the cation has crystallographic $S_4(\bar{4})$ symmetry with an appropriate model of two disordered cations, but this model could not be reconciled with the data: The *R* factors increased despite the larger number of parameters.

In contrast to the exceptional geometry parameters determined in the cation of P5I (see the *Introduction*), the cation in P5P shows bond lengths and angles as expected from similar compounds and the peculiarities found in the structure of P5I are evidently not an intrinsic property of the cation, but rather depend on the packing. Obviously, the packing with the linear ICl_2^- anion, including solvent molecules, allows the cation a larger freedom of movement than packing with the PCl_6^- anion (see Fig. 2). The structure of P5I is a derivative of the NaCl structure (CN = 6): the smaller ICl_2^- anions are located in the octahedral holes as a closest-packed lattice of the cations [$P1 \cdots I1 6.944 (2) - 8.057 (2) \text{ \AA}$]. On the contrary, the structure type of P5P is a derivative of the

CsCl structure (CN = 8), which is the most stable packing of ions of comparable size: each ion in P5P is surrounded by eight counterions [$P4 \cdots P6 7.267 (2) - 8.352 (2) \text{ \AA}$].

There are only a few interionic contacts with distances less than the sum of the van der Waals radii [$Cl \cdots Cl 3.50, N \cdots Cl 3.30 \text{ \AA}$ (Bondi, 1964)]. Each Cl atom of the cation, except Cl11 and Cl21 which are located at the mirror planes, shows exactly one short interionic distance to a Cl atom of the anion, being slightly shorter for the Cl atoms of the $NPCl_3$ group around P3 [$3.314 (1) - 3.359 (1) \text{ \AA}$] than for the others [$3.411 (1)$ and $3.414 (1) \text{ \AA}$]. All the $P-Cl_{\text{cation}} \cdots Cl_{\text{anion}}$ angles lie in the range $153.38 (5) - 168.28 (5)^\circ$, whereas the $P-Cl_{\text{anion}} \cdots Cl_{\text{cation}}$ angles lie in the quite different range $102.30 (3) - 116.35 (4)^\circ$. Very probably this difference is not forced by packing requirements, but reflects the distribution of electronic charge at the Cl atoms. Evidently, by the tetrahedral arrangement of the lone pairs the most negative region of the Cl atoms in the anion makes an angle of $\sim 109^\circ$, the most positive region of the Cl atoms in the cation an angle of $\sim 160^\circ$ with the Cl—P bond. An investigation of the geometries of all known structures containing the tetrachlorophosphonium cation and/or hexachlorophosphate anion found in the ICSD (Inorganic Crystal Structural Database) showed that these angles observed in P5P are typical of these ions and can be expected for other complex ions also bearing electronegative halogen ligands. In addition, one short interionic distance [$N2 \cdots Cl11 3.134 (4) \text{ \AA}$] is observed between the cations (see Fig. 2).

4. Motion analysis

Analysis of the nuclear anisotropic displacement parameters U^{ij} started with the rigid-bond test (Hirshfeld, 1976). For atoms at least as heavy as carbon, the

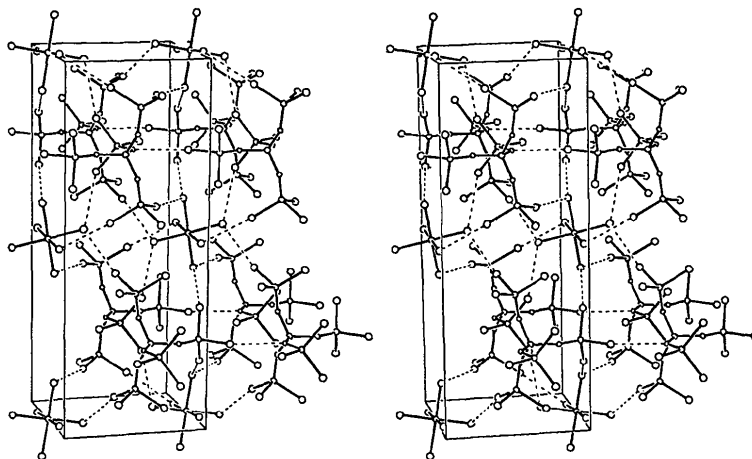


Fig. 2. Stereoscopic drawing of the packing of the ions in P5P (*b* up, *c* to the right). The atoms are drawn as spheres with arbitrary radii. Interionic contacts with distances less than the sum of the van der Waals radii are drawn with dashed lines.

difference $\Delta = z_{A,B}^2 - z_{B,A}^2$ should vanish for every covalently bonded pair of atoms A and B , where $z_{A,B}^2$ denotes the observed mean-square amplitude of vibration of atom A along the direction of the bond $A-B$. In P5P the values of $|\Delta|$ are ≤ 0.0004 (4) \AA^2 in the anion and ≤ 0.0007 (5) \AA^2 in the cation for the P—Cl bonds. At the P—N bonds the $|\Delta|$ values are $\leq 2\sigma(\Delta)$, except for the P3—N3 bond [0.0027 (9) \AA^2]. Whereas at the P—Cl bonds the mean of the differences Δ is close to zero [$\bar{\Delta} = 0.0003$ (2) \AA^2], at the P—N bonds the vibrational mean-square amplitudes of the N atoms along the directions of the bonds on average are slightly larger than those of the P atoms [$\bar{\Delta} = 0.0015$ (4) \AA^2].

The analysis in terms of rigid-body motion (Schomaker & Trueblood, 1968) shows that the PCl_6^- anion behaves as a rigid body: the residual index R_u , defined as $R_u = [\sum w(\Delta U)^2 / \sum w(U_{\text{obs}})^2]^{1/2}$, with $w = 1/\sigma^2$, is 0.024, the maximum difference Δ between non-bonded pairs of atoms being 0.0012 (4) \AA^2 . In contrast to this, but very similar to the situation in P5I, the cation clearly shows the presence of non-rigid intramolecular motions [$R_u = 0.347$ for 70 observations and 12 parameters, $\Delta_{\text{max}} = 0.0213$ (6) \AA^2 for the non-bonded pair of atoms P2...Cl32]. Since the four different tetrahedral sub-units P4(—N)₄ and Nn—Pn(—Cl)₃ ($n = 1-3$) of the cation in a first approximation can be described as rigid bodies [$R_u = 0.046, 0.004, 0.019$ and 0.027 , respectively], the question arises how the non-rigid motion of the cation can be composed of motions of these almost rigid tetrahedra. Omission of the N atoms [$R_u = 0.348$ for the P4(...PCl₃)₄ fragment] shows that the non-rigidity is not an artifact caused by ill-defined displacement parameters of the lighter N atoms.

The analysis was continued with an allowance for intramolecular torsion about libration axes (Dunitz & White, 1973; Trueblood, 1978), including terms for the correlations of the internal and overall motions (Dunitz, Maverick & Trueblood, 1988a,b). If non-rigid body librations about all the three different P—N bonds of the NPCl₃ groups are allowed, the R_u value dropped from 0.347 only to 0.212 (30 parameters). An even better agreement with the data is obtained if the second NPCl₃ group is allowed to librate about the P2...N1 connecting line instead of the P2—N2 bond (R_u value of 0.184): The overall libration and translational motions are rather isotropic [eigenvalues of **L** (deg²): 2.93, 2.15, 1.74 and of **T** ($\text{\AA}^2 \times 10^{-4}$): 146, 100, 79], and the overall mean-square amplitudes of the three rigid groups are almost equal [values of $\langle \varphi^2 \rangle + 2\langle \varphi\lambda' \rangle$ (Dunitz, Maverick & Trueblood, 1988a,b) in deg²: 20.7, 25.4, 26.4] and much larger than the parallel components of **L**. The calculated correlation terms between the internal and overall motions were less than 0.51σ , except one trifling value of 1.44σ .

The introduction of additional libration axes, e.g. the three P—N bonds to the central P atom, resulted in severe correlations. Furthermore, the largest differences between U_{obs} and U_{calc} were found for the N atoms, mainly in the directions normal to the P—N—P planes. The N atoms show larger displacement parameters than those produced by the overall motion of the cation. Evidently, they cannot be explained by allowance for intramolecular torsion about the P—N bonds.

The author thanks Professor Dr W. Schnick, Laboratory of Inorganic Chemistry, University of Bayreuth, for 0.81 g of $[\text{P}(\text{NH}_2)_4]\text{Cl}$ and Professor Dr Ch. Kratky, Institute of Physical Chemistry, University of Graz, for the use of the diffractometer.

References

- Allen, F. H., Davies, J. E., Galloy, J. J., Johnson, O., Kennard, O., Macrae, C. F., Mitchell, E. M., Mitchell, G. F., Smith, J. M. & Watson, D. G. (1991). *J. Chem. Inf. Comput. Sci.* **31**, 187–204.
- Belaj, F. (1992). *Acta Cryst.* **B48**, 598–604.
- Belaj, F. (1993). *Acta Cryst.* **B49**, 254–258.
- Belaj, F. (1995a). *Acta Cryst.* **B51**, 65–71.
- Belaj, F. (1995b). *Acta Cryst.* **B51**, 161–166.
- Belaj, F. (1996). *Phosphorus Sulfur Silicon* **109–110**, 71–74.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Dewar, M. J. S. & Thiel, W. (1977). *J. Am. Chem. Soc.* **99**, 4899–4917.
- Dunitz, J. D. (1979). *X-ray Analysis and the Structure of Organic Molecules*, pp. 484–491. London: Cornell University Press.
- Dunitz, J. D., Maverick, E. F. & Trueblood, K. N. (1988a). *Angew. Chem.* **100**, 910–926.
- Dunitz, J. D., Maverick, E. F. & Trueblood, K. N. (1988b). *Angew. Chem. Int. Ed. Engl.* **27**, 880–895.
- Dunitz, J. D. & White, D. N. J. (1973). *Acta Cryst.* **A29**, 93–94.
- Hirshfeld, F. L. (1976). *Acta Cryst.* **A32**, 239–244.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Parkin, A., Moezzi, B. & Hope, H. (1995). *J. Appl. Cryst.* **28**, 53–56.
- Schmidpeter, P. & Weingand, C. (1969a). *Angew. Chem.* **81**, 573–574.
- Schmidpeter, P. & Weingand, C. (1969b). *Angew. Chem. Int. Ed. Engl.* **8**, 615–616.
- Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Trueblood, K. N. (1978). *Acta Cryst.* **A34**, 950–954.