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Acta Cryst. (1980). **B36**, 1014–1017

Bis(trichlorophosphine)iminium Hexachlorophosphate*

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(Received 17 July 1979; accepted 19 November 1979)

Abstract

[Cl₃PNPCl₃][PCl₆] is monoclinic, *P*2₁/*c*, with *a* = 11·692 (5), *b* = 20·898 (9), *c* = 15·872 (6) Å, β = 119·00 (3)°, *Z* = 8 (two independent molecules), *D*_c = 2·08 Mg m⁻³. The structure was solved by direct methods and refined by least squares to a final *R*₁ = 0·052 for 1575 observed reflections. The cations in the structure have *cisoid* configurations with P–N distances of 1·51–1·56 Å and PNP angles of 135·7 (8) and 139·0 (8)°. The P–Cl distances (uncorrected for thermal effects) are in the range 2·101 (7)–2·146 (6) Å in the anion and 1·924 (7)–1·962 (7) Å in the cation.

Introduction

As part of a continuing study of the reactions of sulphur–nitrogen compounds with Lewis acids, the reaction of S₇NH with SbCl₅ has recently been shown to produce the dithionitronium cation NS₂⁺ (Faggiani, Gillespie, Lock & Tyrer, 1978), whilst reactions of S₇NH (and S₄N₄H₄) with the oxidant PF₅ have so far been observed to produce only NH₄⁺PF₆⁻ and sulphur. However, the analogous reaction of S₇NH with PCl₅ in a 1:2 molar ratio in CH₂Cl₂ gave a complex mixture of solid products, one of which has been identified in this study as the title compound. A small approximately spherical crystal of radius 0·1 mm

was selected from the reaction products and sealed in a Lindemann capillary. Accurate unit-cell dimensions were obtained by least-squares refinement with 15 high-angle reflections measured on a Syntex *P*2₁ diffractometer using Mo *K*α radiation (λ = 0·71069 Å). Data were collected to a maximum 2θ of 35° using θ–2θ scans over a 2θ scan range (*K*α₁ – 1·0°) to (*K*α₂ + 1·0°) with the variable scan rate of 8·0–29·3° min⁻¹ depending on the intensity of a preliminary count. The crystal was recentred several times during the data collection. 2000 data were collected and corrections for Lorentz and polarization effects were applied. No absorption corrections were considered necessary (μ = 2·2 mm⁻¹ and μ*R* = 0·22). No experimental density was measured due to the moisture sensitivity of the crystal and because it was isolated from a mixture of products.

Although the composition of the crystal was initially unknown, a suitable number of S and N atoms in the unit cell was assumed for the calculation of normalized structure factors and the structure solution was attempted using the direct-method routines of the program *SHELX* (Sheldrick, 1976). Two octahedral PCl₆⁻ groups found in one of the several *E* maps calculated were sufficient to phase a subsequent Fourier map which revealed the two [Cl₆P₂N]⁺ cations. Atomic assignments in these cations were made on the basis of other data. The single-crystal Raman spectrum of the cation is comparable to that previously published (Baumgaertner, Sawodny & Goubeau, 1965) although more bands were observed (Table 1), presumably due to solid-state crystal effects. The ³¹P NMR spectrum of

* Alternative name: Trichlorol(trichlorophosphoranylidene)iminio]phosphorus(V) hexachlorophosphate.

the product mixture contains a large singlet at -20.3 p.p.m. (relative to H_3PO_4) due to the $[\text{Cl}_3\text{PNPCl}_3]^+$ cation. (It should also be noted that the crystal is

Table 1. Raman frequencies for $[\text{Cl}_3\text{PNPCl}_3][\text{PCl}_6]$

$\Delta\nu$ (cm^{-1})	$\Delta\nu$ (cm^{-1}) ^a	$\Delta\nu$ (cm^{-1})	$\Delta\nu$ (cm^{-1}) ^a	
87 (4)		249 (14)	247 (7)	$\nu_3 \text{PCl}_6^-$
116 (4)		266 sh		$\left\{ \begin{array}{l} \nu_2 \text{ and } \nu_3 \\ \text{PCl}_6^- \end{array} \right.$
154 (12)	163 (2)	276 (21)	276 (3)	
160 (11)		288 (9)		$\nu_1 \text{PCl}_6^-$
169 (14)		357 (100)	358 (10)	
206 (7)	210 (0)	467 (11)	468 (4)	Broad
213 (9)		629 < 1	495 (0)	
216 (9)		637 < 1	611 (0)	
240 (18)		647 < 1	632 (1)	
		661 < 1	648 (0)	
		836 < 1	820 (1)	

(a) Baumgaertner, Sawodny & Goubeau (1965).

Table 2. Final atomic positional parameters ($\times 10^4$) and thermal parameters (\AA^2) with standard deviations in parentheses for $[\text{Cl}_3\text{PNPCl}_3][\text{PCl}_6]$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^* ($\times 10^3$)
Anion 1				
P(1)	5188 (4)	2193 (2)	4289 (3)	41 (3)
Cl(1)	3911 (5)	1392 (2)	3768 (4)	87 (4)
Cl(2)	3580 (4)	2813 (2)	3541 (4)	80 (4)
Cl(3)	6475 (5)	2997 (2)	4839 (4)	81 (4)
Cl(4)	6797 (4)	1580 (2)	5067 (4)	85 (4)
Cl(5)	5496 (5)	2166 (3)	3078 (3)	101 (4)
Cl(6)	4875 (5)	2238 (2)	5512 (3)	87 (4)
Anion 2				
P(2)	387 (4)	4693 (2)	2838 (3)	40 (3)
Cl(7)	222 (5)	4776 (2)	4106 (3)	74 (3)
Cl(8)	-1136 (4)	5383 (2)	2156 (3)	58 (3)
Cl(9)	566 (5)	4632 (2)	1558 (3)	88 (4)
Cl(10)	1778 (4)	5462 (2)	3331 (4)	78 (4)
Cl(11)	1909 (5)	4025 (3)	3513 (4)	94 (4)
Cl(12)	-1007 (5)	3952 (2)	2324 (4)	91 (4)
Cation 1				
N(1)	5683 (11)	158 (5)	2754 (8)	42 (9)
P(11)	4651 (4)	277 (2)	1678 (3)	44 (3)
P(12)	5904 (4)	-350 (2)	3504 (3)	49 (3)
Cl(13)	4561 (6)	-406 (2)	835 (3)	104 (5)
Cl(14)	5057 (4)	1052 (2)	1198 (3)	70 (3)
Cl(15)	2894 (4)	388 (3)	1498 (3)	98 (4)
Cl(16)	6268 (5)	-1195 (2)	3160 (4)	91 (4)
Cl(17)	4443 (5)	-462 (3)	3755 (4)	102 (4)
Cl(18)	7422 (5)	-121 (3)	4712 (3)	80 (4)
Cation 2				
N(2)	504 (11)	7614 (5)	616 (8)	39 (9)
P(21)	632 (4)	7096 (2)	1356 (3)	50 (3)
P(22)	-360 (4)	7767 (2)	-440 (3)	44 (3)
Cl(19)	1051 (5)	6256 (2)	1050 (4)	94 (4)
Cl(20)	2002 (5)	7313 (2)	2635 (3)	75 (4)
Cl(21)	-978 (5)	6994 (3)	1432 (4)	98 (4)
Cl(22)	175 (5)	8559 (2)	-775 (3)	79 (4)
Cl(23)	-328 (5)	7106 (2)	-1293 (3)	77 (4)
Cl(24)	-2212 (4)	7872 (3)	-809 (4)	87 (4)

* $U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

Table 3. Bond lengths (\AA) and bond angles ($^\circ$) with standard deviations in parentheses

Values in square brackets are interatomic distances corrected for thermal motion assuming a riding model.

Anions					
P(1)—Cl(1)	2.126 (6)	[2.126]	P(2)—Cl(7)	2.120 (8)	[2.143]
—Cl(2)	2.112 (6)	[2.140]	—Cl(8)	2.134 (6)	[2.149]
—Cl(3)	2.139 (6)	[2.166]	—Cl(9)	2.145 (8)	[2.171]
—Cl(4)	2.110 (6)	[2.140]	—Cl(10)	2.146 (6)	[2.174]
—Cl(5)	2.121 (8)	[2.160]	—Cl(11)	2.101 (7)	[2.141]
—Cl(6)	2.145 (8)	[2.171]	—Cl(12)	2.105 (6)	[2.141]
Average P ^v —Cl			2.125		
Cations					
N(1)—P(11)	1.561 (10)		N(2)—P(21)	1.550 (11)	
—P(12)	1.521 (13)		—P(22)	1.513 (13)	
P(11)—Cl(13)	1.924 (7)	[1.969]	P(21)—Cl(19)	1.946 (7)	[1.976]
—Cl(14)	1.944 (7)	[1.963]	—Cl(20)	1.934 (5)	[1.958]
—Cl(15)	1.946 (7)	[1.990]	—Cl(21)	1.955 (9)	[1.988]
P(12)—Cl(16)	1.955 (7)	[1.986]	P(22)—Cl(22)	1.933 (7)	[1.958]
—Cl(17)	1.947 (9)	[1.981]	—Cl(23)	1.947 (7)	[1.973]
—Cl(18)	1.938 (5)	[1.973]	—Cl(24)	1.962 (7)	[1.997]
Average P—Cl			1.944		

Anions			
Cl(1)—P(1)—Cl(2)	89.9 (2)	Cl(7)—P(2)—Cl(8)	89.4 (3)
—Cl(3)	178.9 (4)	—Cl(9)	178.7 (3)
—Cl(4)	90.4 (2)	—Cl(10)	89.7 (3)
—Cl(5)	91.3 (3)	—Cl(11)	90.9 (3)
—Cl(6)	89.5 (3)	—Cl(12)	91.1 (3)
Cl(2)—P(1)—Cl(3)	90.4 (2)	Cl(8)—P(2)—Cl(9)	90.0 (2)
—Cl(4)	178.7 (4)	—Cl(10)	88.7 (2)
—Cl(5)	90.2 (3)	—Cl(11)	179.1 (3)
—Cl(6)	89.2 (3)	—Cl(12)	90.1 (2)
Cl(3)—P(1)—Cl(4)	89.2 (2)	Cl(9)—P(2)—Cl(10)	89.2 (3)
—Cl(5)	89.8 (3)	—Cl(11)	89.8 (3)
—Cl(6)	89.5 (3)	—Cl(12)	90.1 (3)
Cl(4)—P(1)—Cl(5)	91.1 (3)	Cl(10)—P(2)—Cl(11)	90.4 (2)
—Cl(6)	89.5 (3)	—Cl(12)	178.6 (3)
Cl(5)—P(1)—Cl(6)	179.1 (3)	Cl(11)—P(2)—Cl(12)	90.8 (3)
Cations			
P(11)—N(1)—P(12)	135.7 (8)	P(21)—N(2)—P(22)	139.0 (8)
N(1)—P(11)—Cl(13)	113.2 (5)	N(2)—P(21)—Cl(19)	112.6 (6)
—Cl(14)	110.9 (5)	—Cl(20)	111.1 (5)
—Cl(15)	112.4 (7)	—Cl(21)	112.4 (6)
Cl(13)—P(11)—Cl(14)	106.7 (4)	Cl(19)—P(21)—Cl(20)	107.0 (3)
—Cl(15)	106.8 (3)	—Cl(21)	106.5 (3)
Cl(14)—P(11)—Cl(15)	106.5 (3)	Cl(20)—P(21)—Cl(21)	107.0 (4)
N(1)—P(12)—Cl(16)	112.9 (6)	N(2)—P(22)—Cl(22)	110.8 (5)
—Cl(17)	114.3 (6)	—Cl(23)	113.1 (5)
—Cl(18)	109.2 (5)	—Cl(24)	113.7 (7)
Cl(16)—P(12)—Cl(17)	106.3 (3)	Cl(22)—P(22)—Cl(23)	107.4 (4)
—Cl(18)	106.3 (3)	—Cl(24)	106.2 (3)
Cl(17)—P(12)—Cl(18)	107.5 (4)	Cl(23)—P(22)—Cl(24)	105.2 (3)

colourless whereas all S—N cations with the exception of SN^+ are coloured.) Block-diagonal least-squares refinement on $\sum w(F_o - F_c)^2$ using anisotropic thermal parameters for all atoms converged (maximum shift/error < 0.2) to give a final R_1 of 0.052 and R_2 of 0.049 for 1575 observed $[I/\sigma(I) > 3.0]$ data $\{R_1 = \sum |F_o| - |F_c| / \sum F_o; R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}\}$. The weights used were given by the expressions $w = xy$ where: (1) $x = F/60$ if $F < 60$, or $x = 160/F$ if $F > 160$, otherwise $x = 1.0$ and (2) $y = \sin \theta / 0.16$ if $\sin \theta < 0.16$, or $y = 0.26 / \sin \theta$ if $\sin \theta > 0.26$, otherwise $y = 1.0$. A final comparison of $\langle w|F_o| - |F_c|^2 \rangle$ as a function of F_o and $\sin \theta$ showed

no systematic trends and a final difference Fourier map was featureless. Computing was carried out using the XRAY system (1972) and SHELX (Sheldrick, 1976) on a CDC 6400 computer. The final atomic coordinates and temperature factors are included in Table 2 and bond lengths and bond angles are given in Table 3. Figs. 1 and 2 give views of the two $[\text{Cl}_3\text{PNPCl}_3]^+$ cations and the crystal packing respectively.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34906 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

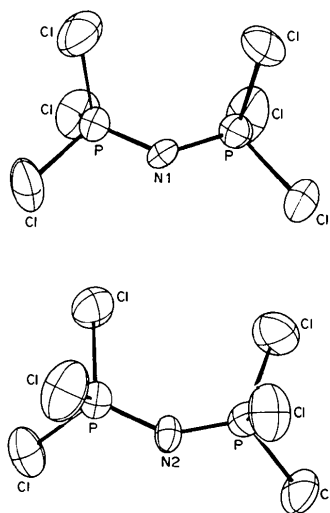


Fig. 1. ORTEP views of the two independent $[\text{Cl}_3\text{PNPCl}_3]^+$ cations in the asymmetric unit.

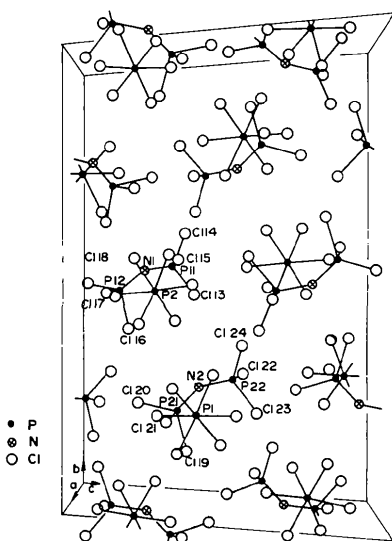


Fig. 2. Packing diagram for $[\text{Cl}_3\text{PNPCl}_3][\text{PCl}_6]^-$, viewed almost down *a*.

Discussion

The two $[\text{Cl}_3\text{PNPCl}_3]^+$ cations in the asymmetric unit both have *cisoid* configurations (Handy, Ruff & Dahl, 1970) with an average P–N bond length of 1.54 Å. The P–Cl distances in the two cations are in the range 1.924 (7)–1.962 (7) Å (1.958–1.997 Å after applying a riding correction to the bond lengths) and individual deviations from the average of 1.94 Å are probably not significant. The environment around the P atoms in the cations is essentially tetrahedral with average Cl–P–N and Cl–P–Cl bond angles for the two cations of 112 and 107° respectively. In the octahedral PCl_6^- the P–Cl bond lengths are in the range 2.101 (7)–2.146 (6) Å and *cis* and *trans* Cl–P–Cl angles are not significantly different from 90 and 180°. The significant differences between some of the P–Cl distances may be attributed to thermal motion of the chlorines since the range of P–Cl distances after applying riding motion corrections is 2.140–2.174 Å.

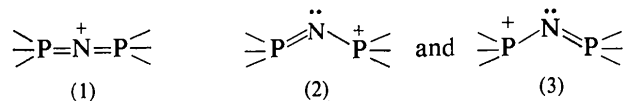
The observed P–Cl bond length in the cation compares well with P–Cl distances of 1.90–1.96 Å found in several structures containing the tetrahedral PCl_4^+ ion (Collins & Webster, 1972; Preiss, 1971; Kistenmacher & Stucky, 1971) and is considerably shorter than the average P–Cl bond length in the PCl_6^- anions.

The length of a P–N single bond has been assumed to be in the region of 1.77–1.78 Å as observed in $(\text{CH}_3\text{NPCl}_3)_2$ and $[\text{CH}_3\text{NPF}_2(\text{C}_6\text{H}_5)]_2$ (Allcock, 1972). The observed P–N distance is considerably shorter than these lengths and is comparable to the P–N bond lengths in cyclo- and polyphosphazenes which are in the range 1.47–1.62 Å and are known to have some multiple-bond character (Allcock, 1972).

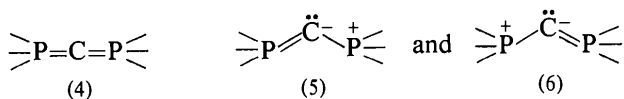
As with sulphur–nitrogen compounds the angle at the N atom, whether in an acyclic or cyclic phosphorus–nitrogen compound, has been observed to vary quite widely depending on ring size, conformation and charge. The average P–N–P angle in the present cation (137.5°) may be compared to the analogous angle in the related bis(triphenylphosphine)iminium cation $[\text{Ph}_3\text{PNPPh}_3]^+$, which usually has a value of ~140° (Handy, Ruff & Dahl, 1970), although it has been found in one case with crystallographically linear geometry for the PNP system (Wilson & Bau, 1974). In the related compound $[(\text{Ph}_2\text{PNH}_2)_2\text{N}]^+\text{Cl}^-$ the cation has P–N distances of 1.57 and 1.58 (1) Å and the PNP angle is 136 (1)° (Cox & Corey, 1969). It is also instructive to compare the $(\geq\text{PNP}\leq)^+$ system with the isoelectronic $(\geq\text{PCP}\leq)$ system. In one form of bis(triphenylphosphoranylidene)methane, there are two independent molecules in the asymmetric unit with different PCP bond angles of 130.1 (6) and 143.8 (6)° (Vincent & Wheatley, 1972), while in another form of the same compound the bond angle is 131.7 (3)° (Hardy, Zink, Kaska & Baldwin, 1978). Furthermore,

in the recently reported structure of bis(diphenylmethylphosphoranylidene)methane the PCP angle is as small as $121.8(3)^\circ$ (Schmidbauer, Hasslberger, Deschler, Schubert, Kappenstein & Frank, 1979).

In compounds containing the $(\geq\text{PNP}\leq)^+$ group the frequently observed PNP angle of approximately 140° can be rationalized on the basis of contributions from the three valence-bond structures

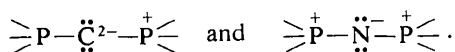


with (2) and (3) implying a bond angle of 120° being somewhat more important. The three corresponding structures



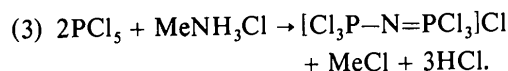
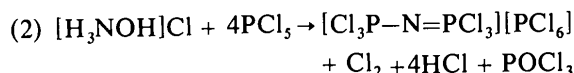
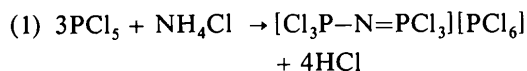
are necessary to account for the average bond angle of *ca* 137° in $\text{Ph}_3\text{PCPPh}_3$. The variability of the PNP and PCP angles from one compound to another and the substantial differences in the PNP and PCP bond angles in crystallographically non-equivalent forms of the same molecule clearly indicate that the PCP and PNP bond angles are highly flexible and are probably more strongly influenced by steric and packing factors than by electronic factors. It would seem reasonable to suppose, therefore, that the three principal resonance forms (1), (2) and (3) or (4), (5) and (6) have very similar energies and thus other factors can cause large variations in the bond angle between 120 and 180° . The bond lengths in all the cases considered above indicate considerable double-bond character and do not show much variation with bond angle.

As the above rationalization in terms of varying contributions of the structures (1)–(6) implies a significant increase in bond length with decreasing bond angle, which is not observed, it has to be concluded that our understanding of the bonding in these systems is still rather rudimentary. Although it has been proposed that the non-linearity of $\text{Ph}_3\text{PCPPh}_3$ is due to the participation of phosphorus *d* orbitals in the bonding (Vincent & Wheatley, 1972), it has also been shown that the participation of these orbitals leads to lowering of the energy of the linear form (Carroll & Titus, 1977). Certainly all the valence-bond structures (1) to (6) imply the use of phosphorus *3d* orbitals. Indeed if the use of such orbitals is avoided this can only be expressed in valence-bond terms by assuming that the major contributing structures are



Neither of these structures seems very satisfactory and they are certainly not consistent with the rather short PN and PC bonds.

The $[\text{Cl}_3\text{PNP}\text{Cl}_3]^+$ cation has previously been prepared by the following routes (Fluck, Schmid & Haubold, 1977; Allcock, 1972; Armitage, 1972):



The reaction of S_4N_4 with PCl_3 has also been shown to give the $[\text{Cl}_6\text{P}_2\text{N}]^+$ cation as a chloride salt (Becke-Goehring & Lehr, 1963; Glemser & Wyszomeirski, 1961).

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