

Plus (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL93*.

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Bis(trichlorophosphine)iminium Hexachlorophosphate

FERDINAND BELAJ

Institut für Anorganische Chemie, Karl-Franzens-Universität Graz, Schubertstraße 1, A-8010 Graz, Austria. E-mail: belaj@kfunigraz.ac.at

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Abstract

The structure of the title compound, trichloro[(trichlorophosphoranylidene)iminio]phosphorus(V) hexachlorophosphate, $(\text{NP}_2\text{Cl}_6)\text{PCl}_6$ or $[\text{N}(\text{PCl}_3)_2]^+\cdot\text{PCl}_6^-$, contains two formula units in the asymmetric unit. The cations show slightly distorted C_{2v} symmetry. The P—N dis-

tances range from 1.556 (3) to 1.562 (3) Å and the P—N—P bonding angles are 133.3 (2) and 135.8 (2)°.

Comment

The crystal structure of the title compound, (I), was previously determined by Faggiani *et al.* (1980). They isolated the compound from a complex mixture of solid products of the reaction of S_7NH with PCl_5 . Since they collected reflection data at room temperature using $\text{Mo K}\alpha$ radiation only to a maximum θ of 17.5°, the P—N distances in the two cations of the asymmetric unit range from 1.513 (13) to 1.561 (10) Å. In the course of our work on trichlorophosphazenes, more accurate structural data of this fundamental substance were desirable.

In principle, the structure determination of (I) performed at 95 K confirmed the earlier structure analysis. The atomic labelling scheme was retained. The P—N distances in the two cations of the asymmetric unit are now much more reliable; as expected, the P—N distances within a cation are equal. According to the correlation between the P—N distance and the P—N—P bonding angle in acyclic compounds (Belaj, 1995a), the mean value of these distances is larger by about two standard deviations in the cation which is more bent by packing forces. Both cations show only slightly distorted *trans-trans* conformations [the groupings of Cl—P—N—P—Cl display a 'W' form, with torsion angles Cl—P—N—P ≥ 174.0 (2)°], as observed in $\text{Cl}_3\text{PNP}(\text{O})\text{Cl}_2$ (Belaj, 1993) or in $\text{SO}_2(\text{NPCl}_3)_2$ (Belaj, 1995b). As discussed in the latter work, the N—P—Cl angles including a Cl atom of the 'W' fragment (namely Cl14, Cl18, Cl20 and Cl22) are significantly smaller [109.36 (12)–110.04 (12)°] than the others [112.76 (12)–113.97 (12)°], whereas the opposite is true for the Cl—P—Cl angles [106.80 (6)–107.64 (6) versus 105.60 (6)–106.20 (6)°].

In the PCl_6^- anions, the P—Cl distances range from 2.1212 (12) to 2.1624 (12) Å, the *cis* Cl—P—Cl angles range from 89.32 (5) to 90.85 (5)° and no *trans* angle is smaller than 179.0 (6)°.

There are two remarkably short inter-ionic Cl \cdots Cl distances between the anions [Cl2 \cdots Cl11 3.182 (2) and Cl7 \cdots Cl17 3.194 (2) Å, compared with the sum of the van der Waals radii of 3.50 Å (Bondi, 1964)]. They are also present but not mentioned in the room-temperature structure determination of Faggiani *et al.* (1980) [3.186 (8) and 3.260 (7) Å, respectively]. In contrast, the shortest inter-ionic Cl \cdots Cl distances are 3.335 (1) Å between a cation and an anion, and 3.630 (2) Å between two cations. This strange situation, in which contacts between counter-ions are larger than between anions, shows that a simple inspection of short interionic Cl \cdots Cl contacts is not sufficient, and that an examination of the arrangement of the P atoms at the centre of the anions and in the NPCl_3 groups of the cations is necessary.

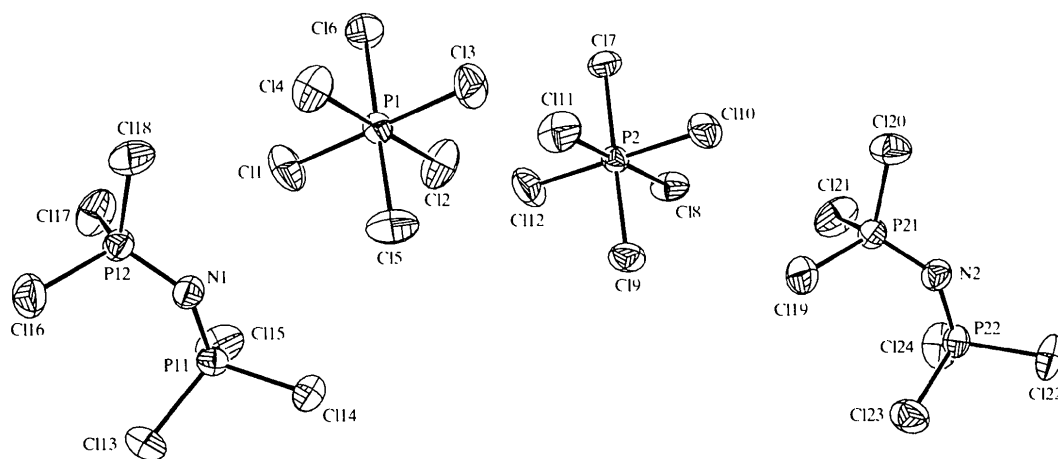


Fig. 1. The asymmetric unit of (I) showing 90% probability displacement ellipsoids.

The inter-ionic P...P distances below 7.3 Å are as follows: each P atom of an anion (henceforth P_{an}) is surrounded by 12 P atoms of a cation (henceforth P_{cat}), with distances in the range 5.3471 (18)–7.0531 (18) Å, but only by two P_{an} atoms [7.0081 (18) and 7.1530 (19) Å]. Each P_{cat} atom is surrounded by six P_{an} atoms but only by three or four P_{cat} atoms in the range 5.6458 (17)–6.3236 (18) Å. In addition, the P—Cl distances of the Cl atoms involved in the short inter-ionic Cl...Cl distances between the anions are shorter [2.1230 (14)–2.1302 (13) Å] than the others [mean 2.145 (4) Å]. This suggests that these Cl atoms are less negatively charged than the others of the PCl₆[−] anions, thus enabling the short inter-ionic contacts. I surmise that these anions are able to distribute the charge unequally among the Cl atoms in order to optimize the packing arrangement.

Data collection

Stoe four-circle diffractometer
 ω scans
 Absorption correction: none
 8889 measured reflections
 7490 independent reflections
 6243 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -14 \rightarrow 14$
 $k = -1 \rightarrow 26$
 $l = -1 \rightarrow 20$
 3 standard reflections
 every 100 reflections
 intensity decay: 1.96%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.092$
 $S = 1.115$
 7490 reflections
 290 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0391P)^2 + 2.3302P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.637 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.531 \text{ e } \text{Å}^{-3}$
 Extinction correction:
 SHELXL97 (Sheldrick, 1997)
 Extinction coefficient:
 0.00084 (10)
 Scattering factors from
 International Tables for
 Crystallography (Vol. C)

Experimental

The synthesis was carried out by the reaction of NH₄Cl and PCl₅ in a C₂H₂Cl₄/C₆H₅NO₂ mixture (Becke-Goehring & Lehr, 1961). Recrystallization was from C₂H₂Cl₄.

Crystal data

(NP₂Cl₆)PCl₆

$M_r = 532.36$

Monoclinic

$P2_1/c$

$a = 11.483 (2) \text{ Å}$

$b = 20.709 (4) \text{ Å}$

$c = 15.652 (3) \text{ Å}$

$\beta = 118.71 (1)^\circ$

$V = 3264.5 (11) \text{ Å}^3$

$Z = 8$

$D_x = 2.166 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ Å}$

Cell parameters from 50 reflections

$\theta = 15.05\text{--}19.65^\circ$

$\mu = 2.300 \text{ mm}^{-1}$

$T = 95 (2) \text{ K}$

Block

$0.30 \times 0.25 \times 0.22 \text{ mm}$

Pale yellow

Table 1. Selected geometric parameters (Å, °)

P1—C11	2.1457 (13)	P11—C113	1.9591 (13)
P1—C12	2.1293 (12)	P11—C114	1.9586 (13)
P1—C13	2.1558 (13)	P11—C115	1.9582 (12)
P1—C14	2.1212 (12)	P12—C116	1.9648 (13)
P1—C15	2.1343 (13)	P12—C117	1.9603 (13)
P1—C16	2.1568 (12)	P12—C118	1.9536 (13)
P2—C17	2.1302 (12)	N2—P22	1.556 (3)
P2—C18	2.1455 (12)	N2—P21	1.557 (3)
P2—C19	2.1624 (12)	P21—C119	1.9599 (13)
P2—C10	2.1509 (12)	P21—C120	1.9499 (13)
P2—C111	2.1230 (12)	P21—C121	1.9622 (13)
P2—C112	2.1323 (13)	P22—C122	1.9495 (13)
N1—P11	1.560 (3)	P22—C123	1.9596 (13)
N1—P12	1.562 (3)	P22—C124	1.9715 (12)
P11—N1—P12	133.3 (2)	N2—P22—C124	113.34 (12)
P22—N2—P21	135.8 (2)	C115—P11—C113	105.63 (6)
N1—P11—C114	110.04 (12)	C117—P12—C116	105.86 (6)
N1—P12—C118	109.36 (12)	C119—P21—C121	106.20 (6)
N2—P21—C120	109.51 (12)	C123—P22—C124	105.60 (6)
N2—P22—C122	109.47 (12)	C114—P11—C113	107.23 (6)

N1—P11—C113	113.59 (12)	C115—P11—C114	107.09 (6)
N1—P11—C115	112.87 (12)	C118—P12—C116	107.34 (6)
N1—P12—C116	112.81 (12)	C118—P12—C117	107.13 (6)
N1—P12—C117	113.97 (12)	C120—P21—C119	107.64 (6)
N2—P21—C119	113.34 (12)	C120—P21—C121	107.06 (6)
N2—P21—C121	112.76 (12)	C122—P22—C123	107.57 (6)
N2—P22—C123	113.68 (12)	C122—P22—C124	106.80 (6)
P12—N1—P11—C114	−178.3 (2)	P22—N2—P21—C120	−176.0 (2)
P11—N1—P12—C118	−174.0 (2)	P21—N2—P22—C122	178.3 (2)

All atoms were refined with anisotropic displacement parameters without any constraints.

Data collection: local program. Cell refinement: local program. Data reduction: local program. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL97*.

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Tricaesium Tetraiodozincate(II) Iodide, Cs₃ZnI₅

K. FRIESE, G. MADARIAGA AND T. BREZEWski

*Departamento de Física de la Materia Condensada,
 Universidad del País Vasco, Apartado 644, 48080 Bilbao,
 Spain. E-mail: wmbfrxxk@lg.ehu.es*

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Abstract

Cs₃ZnI₅ is isotypic with Cs₃CoI₅, (NH₄)₃ZnCl₅ and Cs₃HgCl₅. The structure consists of distorted [ZnI₄]^{2−} tetrahedra and chains of face-sharing [Cs₆I]⁵⁺ octahedra parallel to the *x* axis. The ninefold coordination around one Cs⁺ ion is best described as a quadratic antiprism with one of the basal faces centred. The other Cs⁺ ion

is coordinated by eight I[−] ions in the form of a strongly truncated 'bisdisphenoid'.

Comment

For halogenides of type A₃BX₅ (A = Cs, NH₃; B = Co, Zn, Hg; X = Cl, Br, I), two different structure types are known. Cs₃CoCl₅ (Powell & Wells, 1935; Figgis *et al.*, 1964, 1980; Williams *et al.*, 1980; Reynolds *et al.*, 1981) and Cs₃CoBr₅ (Figgis & Reynolds, 1981) crystallize with tetragonal symmetry in space group *I4/mcm*, whereas (NH₄)₃ZnCl₅ (Klug & Alexander, 1944; Schmitz, 1981), Cs₃HgCl₅ (Clegg *et al.*, 1976) and Cs₃CoI₅ (Stäudel & Seifert, 1978) have orthorhombic symmetry with space group *Pnam* (see Table 3). In both structure types, the B cation is tetrahedrally coordinated by the X[−] anions; additionally, isolated X[−] ions are surrounded by six A cations in the form of a slightly distorted octahedron.

A detailed comparison between (NH₄)₃ZnCl₅ and Ba₃SiS₅ has been given by Schmitz (1981), who pointed out the close relationship between orthorhombic A₃BX₅ compounds and Ge₃Rh₅.

During our investigations on A₂BX₄ compounds of the β-K₂SO₄ type, we obtained crystals of Cs₃ZnI₅. Their existence was first reported by Billesbach & Ullman (1992, 1993), who confirmed the orthorhombic symmetry and gave a brief description of the structure. Since no coordinates or further details were given by the authors, we decided to refine the crystal structure.

The structure of Cs₃ZnI₅ is isotypic with (NH₄)₃ZnCl₅ (Klug & Alexander, 1944; Schmitz, 1981), Cs₃HgCl₅ (Clegg *et al.*, 1976) and Cs₃CoI₅ (Stäudel & Seifert, 1978). The *ab* projection of the structure of Cs₃ZnI₅ is shown in Fig. 1, with the *bc* projection shown in Fig. 2. Apart from Cs1 and I4, all ions lie on the mirror plane perpendicular to *c*.

The Zn²⁺ ions are coordinated by four I[−] ions in the form of slightly distorted tetrahedra, with symmetry *m* and Zn—I distances ranging from 2.594 (1) to 2.620 (2) Å (see Table 2). The average Zn—I distance (2.602 Å) is significantly shorter than the sum of the ionic radii (2.800 Å; Shannon, 1976) indicating the covalent character of the Zn—I bonds. The average separation of the I[−] ions within the tetrahedra is 4.246 Å, which corresponds well to the sum of the ionic radii (4.120 Å).

Around the isolated I3 ion, which does not form part of the tetrahedra, the Cs²⁺ ions form a slightly distorted octahedron (Fig. 2 and Table 2). Neighbouring [Cs₆I]⁵⁺ octahedra share common faces and thus form chains of composition [I₂Cs₆]_∞⁴⁺ parallel to the *x* axis (Fig. 1).

The Cs1 ion is coordinated by 7+2 I[−] ions in the form of a strongly distorted quadratic antiprism with one of the basal planes centred. The Cs1—I distances range from 3.798 (1) to 4.312 (2) Å; the Zn²⁺ ion is nearer to the Cs1 ion than the two most weakly