# Structures of the Phosphazenes [ClC(NPCl₃)₂]⁺PCl₆⁻ and [CH₃C(NPCl₃)₂]⁺SbCl₆⁻ at 90 K

FERDINAND BELAJ

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

## Abstract

The asymmetric units of both ionic compounds [*N*-(chloroformimidoyl)phosphorimidic trichloridato]trichlorophosphorus hexachlorophosphate, [ClC(NPCl₃)₂]⁺PCl₆⁻ (1), and [*N*-(acetimidoyl)phosphorimidic trichloridato]trichlorophosphorus hexachloroantimonate, [CH₃C(NPCl₃)₂]⁺SbCl₆⁻ (2), contain two formula units with the atoms located on general positions. All the cations show *cis–trans* conformations with respect to their *X*—C—N—P torsion angles [*X* = Cl for (1), C for (2)], but quite different conformations with respect to their C—N—P—Cl torsion angles. Therefore, the two NPCl₃ groups of a cation are inequivalent, even though they are equivalent in solution. The very flexible C—N—P angles ranging from 120.6 (3) to 140.9 (3)° can be attributed to the intramolecular Cl···Cl and Cl···N contacts. A widening of the C—N—P angles correlates with a shortening of the P—N distances. The rigid-body motion analysis shows that the non-rigid intramolecular motions in the cations cannot be explained by allowance for intramolecular torsion of the three rigid subunits about specific bonds.

## 1. Introduction

After the structural investigations of open-chained compounds in which the NPCl₃ group is attached to phosphorus [Cl₃PNP(O)Cl₂ (Belaj, 1993), ClP(NPCl₃)₃⁺*X*⁻ (Belaj, 1992), P(NPCl₃)₄⁺*X*⁻ (Belaj, 1997)] or sulfur [SO₂(NPCl₃)₂ (Belaj, 1995)], the first structure determinations of two ionic compounds in which two NPCl₃ groups are bonded to a C atom were described in this work. Hitherto, only a few structures with a single NPCl₃ group [(CCl₃)₂C(Cl)NPCl₃ (Antipin, Struchkov, Yurchenko & Kozlov, 1982), (CF₃)₃CNPCl₃ (Antipin, Struchkov & Kozlov, 1985), (2,4,6-Buₜ³C₆H₂)NPCl₃ (Burford, Clyburne, Gates, Schriver & Richardson, 1994), (C₂N₃PCl₃)NPCl₃ (Belaj, 1996)] or with three NPCl₃ groups bonded to a C atom [C(NPCl₃)₃]⁺SbCl₆⁻ (Müller, Lorenz & Schmock, 1979; Müller, 1980)] have been reported in the literature [Inorganic Crystal Structure Database (Bergerhoff & Brown, 1987), Cambridge Structural Database (Allen *et*

*al.*, 1991)]. The very similar title compounds have quite different crystallographic symmetries (monoclinic non-centrosymmetric *versus* triclinic centrosymmetric). The equivalent geometric parameters and the conformational variability of the cations can be studied well since the asymmetric unit consists of two formula units in both compounds.

## 2. Experimental

Slight yellow single crystals of (1) could be synthesized by reaction of NH₂CN with PCl₅ (1:3) in C₂H₄Cl₂ (Becke-Goehring & Jung, 1970) and single crystals of (2) were obtained by reaction of [CH₃C(NH₂)₂]⁺SbCl₆⁻ and PCl₅ (1:2) in CH₃NO₂ (Schmidpeter, Düll & Böhm, 1968). The crystals were immersed in oil and immediately cooled to 90 K. All the following measurements were carried out with graphite-monochromatized Mo *Kα* radiation on a modified Stoe four-circle diffractometer with modified Nonius low-temperature equipment. The unit cells were checked for the presence of higher lattice symmetry (Le Page, 1982). The experimental details and final agreement factors are summarized in Table 1.

The structure of (1) was solved by direct methods. In the course of refinement the structure of (1) was inverted, leading to a smaller Flack parameter *x* [*x* = 0 for correct and *x* = 1 for inverted absolute structure (Flack, 1983)] of 0.12 (6), indicating the correct absolute structure.

The structure of (2) could not be solved by direct methods in the correct space group *P*Ī, but in the non-centrosymmetric space group *P*1 the positions of all non-H atoms of four formula units could be located in the Fourier map. Afterwards, the structure was checked for centrosymmetry and transformed to the space group *P*Ī. Refinements in both space groups indicate *P*Ī to be correct. The methyl groups were refined as rigid groups, the H atoms were refined with common isotropic temperature factors for all the atoms of the same methyl group. In one SbCl₆⁻ group a low-grade disorder in a plane normal to a Sb—Cl bond was detected. One site occupation factor (s.o.f.) common to the four Cl atoms in that plane (Cl43–Cl46) was refined [0.955 (5)], the s.o.f.'s of the four corresponding atoms (Cl53–Cl56) were constrained to add up to one. The strongest peaks of

Table 1. *Experimental details*

| | (1) | (2) |
|---|---|---|
| **Crystal data** | | |
| Chemical formula | $[CCl_7N_2P_2]^+PCl_6^-$ | $[C_2H_3Cl_6N_2P_2]^+SbCl_6^-$ |
| Chemical formula weight | 593.83 | 664.19 |
| Cell setting | Monoclinic | Triclinic |
| Space group | $P2_1$ | $P\bar{1}$ |
| $a$ (Å) | 9.958 (2) | 12.133 (1) |
| $b$ (Å) | 11.546 (2) | 12.229 (1) |
| $c$ (Å) | 15.726 (2) | 13.975 (2) |
| $\alpha$ (°) | | 90.09 (1) |
| $\beta$ (°) | 96.90 (1) | 91.17 (1) |
| $\gamma$ (°) | | 108.86 (1) |
| $V$ (Å$^3$) | 1795.0 (5) | 1961.7 (4) |
| $Z$ | 4 | 4 |
| $D_x$ (Mg m$^{-3}$) | 2.197 | 2.249 |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ |
| Wavelength (Å) | 0.71069 | 0.71069 |
| No. of reflections for cell parameters | 53 | 70 |
| $\theta$ range (°) | 15.0–19.5 | 15.6–18.4 |
| $\mu$ (mm$^{-1}$) | 2.250 | 3.189 |
| Temperature (K) | 90 (2) | 90 (2) |
| Crystal form | Block | Block |
| Crystal size (mm) | 0.40 × 0.35 × 0.30 | 0.35 × 0.30 × 0.20 |
| Crystal colour | Pale yellow | Pale yellow |
| | | |
| **Data collection** | | |
| Diffractometer | Stoe four-circle diffractometer | Stoe four-circle diffractometer |
| Data collection method | Profile data from $\omega$ scans | Profile data from $\omega$ scans |
| Absorption correction | Empirical (Parkin, Moezzi & Hope, 1995) | Empirical (Parkin, Moezzi & Hope, 1995) |
| $T_{min}$ | 0.630 | 0.563 |
| $T_{max}$ | 0.844 | 0.876 |
| No. of measured reflections | 12 747 | 12 700 |
| No. of independent reflections | 12 281 | 11 420 |
| No. of observed reflections | 10 519 | 9316 |
| Criterion for observed reflections | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ |
| $R_{int}$ | 0.0274 | 0.0263 |
| $\theta_{max}$ (°) | 40.00 | 30.02 |
| Range of $h$, $k$, $l$ | $-18 \rightarrow h \rightarrow 17$ | $-17 \rightarrow h \rightarrow 17$ |
| | $-1 \rightarrow k \rightarrow 20$ | $-17 \rightarrow k \rightarrow 17$ |
| | $0 \rightarrow l \rightarrow 28$ | $0 \rightarrow l \rightarrow 19$ |
| No. of standard reflections | 3 | 3 |
| Frequency of standard reflections | Every 100 reflections | Every 100 reflections |
| Intensity decay (%) | 1.02 | 1.48 |
| | | |
| **Refinement** | | |
| Refinement on | $F^2$ | $F^2$ |
| $R[F > 4\sigma(F)]$ | 0.0313 | 0.0357 |
| $wR(F^2)$ | 0.0854 | 0.0932 |
| $S$ | 1.063 | 1.033 |
| No. of reflections used in refinement | 12 231 | 11 416 |
| No. of parameters used | 343 | 365 |
| H-atom treatment | – | Common $U_{iso}$ for each rigid $CH_3$ group (AFIX 35) |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.0398P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.0422P)^2 + 2.0943P]$, where $P = (F_o^2 + 2F_c^2)/3$ |
| $(\Delta/\sigma)_{max}$ | −0.001 | −0.002 |
| $\Delta\rho_{max}$ (e Å$^{-3}$) | 0.629 | 1.045 |
| $\Delta\rho_{min}$ (e Å$^{-3}$) | −0.738 | −1.270 |
| Extinction method | None | None |
| Source of atomic scattering factors | *International Tables for Crystallography* (1992, Vol. C) | *International Tables for Crystallography* (1992, Vol. C) |
| | | |
| **Computer programs** | | |
| Data collection | Local program | Local program |
| Cell refinement | Local program | Local program |
| Data reduction | Local program | Local program |
| Structure solution | *SHELXS*86 (Sheldrick, 1985) | *SHELXS*86 (Sheldrick, 1985) |
| Structure refinement | *SHELXL*93 (Sheldrick, 1993) | *SHELXL*93 (Sheldrick, 1993) |
| Preparation of material for publication | *SHELXL*93 (Sheldrick, 1993) | *SHELXL*93 (Sheldrick, 1993) |

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$) for (1)*

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Cl1 | 0.53199 (6) | 1.24441 (5) | 0.25740 (4) | 0.01903 (10) |
| C1 | 0.5051 (2) | 1.0979 (2) | 0.24699 (14) | 0.0126 (3) |
| N11 | 0.5975 (2) | 1.0243 (2) | 0.27980 (13) | 0.0136 (3) |
| P11 | 0.73182 (6) | 1.04059 (6) | 0.34260 (4) | 0.01343 (10) |
| Cl11 | 0.70514 (7) | 1.11551 (7) | 0.45124 (4) | 0.02254 (12) |
| Cl12 | 0.87603 (7) | 1.12809 (8) | 0.29632 (4) | 0.02428 (13) |
| Cl13 | 0.80194 (7) | 0.88474 (7) | 0.36810 (5) | 0.02390 (13) |
| N12 | 0.3876 (2) | 1.0687 (2) | 0.20553 (13) | 0.0129 (3) |
| P12 | 0.34316 (6) | 0.93696 (6) | 0.18780 (4) | 0.01082 (9) |
| Cl14 | 0.38755 (6) | 0.82529 (5) | 0.28178 (4) | 0.01480 (9) |
| Cl15 | 0.41889 (7) | 0.87519 (6) | 0.08785 (4) | 0.01770 (10) |
| Cl16 | 0.14654 (6) | 0.93690 (6) | 0.16220 (4) | 0.02032 (11) |
| Cl2 | 1.08105 (6) | 0.69334 (5) | 0.30438 (4) | 0.01545 (9) |
| C2 | 0.9859 (2) | 0.5903 (2) | 0.24426 (14) | 0.0119 (3) |
| N21 | 1.0256 (2) | 0.4823 (2) | 0.24390 (13) | 0.0130 (3) |
| P21 | 1.14655 (6) | 0.41275 (6) | 0.29259 (4) | 0.01191 (9) |
| Cl21 | 1.10943 (7) | 0.36404 (7) | 0.40682 (4) | 0.02108 (11) |
| Cl22 | 1.32607 (6) | 0.48615 (6) | 0.30869 (5) | 0.02076 (11) |
| Cl23 | 1.16720 (6) | 0.27059 (6) | 0.22724 (4) | 0.01630 (9) |
| N22 | 0.8755 (2) | 0.6322 (2) | 0.20229 (13) | 0.0152 (3) |
| P22 | 0.76032 (6) | 0.57345 (6) | 0.13917 (4) | 0.01178 (9) |
| Cl24 | 0.58566 (6) | 0.61927 (7) | 0.17434 (4) | 0.01954 (11) |
| Cl25 | 0.76518 (7) | 0.63486 (6) | 0.02368 (4) | 0.01856 (10) |
| Cl26 | 0.75505 (6) | 0.40310 (5) | 0.12867 (4) | 0.01535 (9) |
| P3 | 0.21999 (6) | 0.52612 (6) | −0.00741 (4) | 0.01087 (9) |
| Cl31 | 0.36201 (6) | 0.40660 (5) | 0.05873 (4) | 0.01499 (9) |
| Cl32 | 0.08027 (6) | 0.64744 (5) | −0.07212 (4) | 0.01563 (9) |
| Cl33 | 0.22502 (6) | 0.62744 (6) | 0.10759 (4) | 0.01572 (9) |
| Cl34 | 0.21351 (6) | 0.42394 (5) | −0.12185 (3) | 0.01533 (9) |
| Cl35 | 0.38497 (5) | 0.62605 (5) | −0.04604 (4) | 0.01433 (9) |
| Cl36 | 0.05697 (5) | 0.42691 (5) | 0.03091 (4) | 0.01479 (9) |
| P4 | 1.27898 (6) | 1.01168 (6) | 0.51989 (4) | 0.01130 (9) |
| Cl41 | 1.29908 (7) | 1.08890 (6) | 0.39858 (4) | 0.02062 (11) |
| Cl42 | 1.25637 (6) | 0.93616 (6) | 0.64213 (4) | 0.01705 (9) |
| Cl43 | 1.14682 (6) | 0.88231 (6) | 0.45786 (4) | 0.01896 (10) |
| Cl44 | 1.41002 (6) | 1.14176 (6) | 0.58192 (4) | 0.01973 (11) |
| Cl45 | 1.44809 (6) | 0.90177 (6) | 0.50817 (4) | 0.01611 (9) |
| Cl46 | 1.10644 (6) | 1.11973 (6) | 0.53215 (4) | 0.01643 (9) |

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$) for (2)*

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.7548 (3) | 0.9871 (3) | 0.7678 (3) | 0.0166 (6) |
| Cl1 | 0.6778 (4) | 0.8978 (4) | 0.8311 (3) | 0.0244 (8) |
| N11 | 0.8346 (3) | 1.0833 (3) | 0.7997 (2) | 0.0184 (6) |
| P11 | 0.88569 (8) | 1.14786 (8) | 0.89489 (7) | 0.0157 (2) |
| Cl11 | 1.04960 (9) | 1.15647 (10) | 0.91171 (8) | 0.0297 (2) |
| Cl12 | 0.88755 (12) | 1.30841 (9) | 0.88474 (8) | 0.0327 (2) |
| Cl13 | 0.80992 (9) | 1.08770 (9) | 1.01604 (7) | 0.0249 (2) |
| N12 | 0.7413 (3) | 0.9668 (3) | 0.6740 (2) | 0.0184 (6) |
| P12 | 0.82344 (9) | 1.05355 (8) | 0.60066 (7) | 0.0159 (2) |
| Cl14 | 0.99027 (8) | 1.07111 (8) | 0.61428 (7) | 0.0198 (2) |
| Cl15 | 0.81637 (9) | 1.21276 (8) | 0.60062 (7) | 0.0244 (2) |
| Cl16 | 0.77148 (10) | 0.99091 (9) | 0.47241 (7) | 0.0263 (2) |
| C2 | 0.7357 (3) | 0.4782 (3) | 0.3052 (3) | 0.0162 (6) |
| C21 | 0.8206 (3) | 0.5485 (3) | 0.3794 (3) | 0.0207 (7) |
| N21 | 0.6378 (3) | 0.3955 (3) | 0.3273 (2) | 0.0176 (6) |
| P21 | 0.57601 (8) | 0.33022 (8) | 0.41642 (7) | 0.0141 (2) |
| Cl21 | 0.41256 (8) | 0.32505 (9) | 0.41366 (7) | 0.0230 (2) |
| Cl22 | 0.57100 (9) | 0.16753 (8) | 0.40933 (7) | 0.0221 (2) |
| Cl23 | 0.63810 (8) | 0.38722 (8) | 0.54559 (6) | 0.0200 (2) |
| N22 | 0.7628 (3) | 0.5020 (3) | 0.2143 (2) | 0.0179 (6) |
| P22 | 0.68147 (8) | 0.43436 (8) | 0.12795 (7) | 0.0160 (2) |
| Cl24 | 0.52221 (8) | 0.44415 (9) | 0.12420 (7) | 0.0222 (2) |
| Cl25 | 0.66168 (9) | 0.26782 (8) | 0.11832 (7) | 0.0241 (2) |
| Cl26 | 0.75566 (9) | 0.50495 (9) | 0.01023 (7) | 0.0258 (2) |
| Sb3 | 0.94051 (2) | 0.67946 (2) | 0.73025 (2) | 0.01185 (5) |
| Cl31 | 0.97105 (8) | 0.86296 (7) | 0.80099 (6) | 0.0176 (2) |
| Cl32 | 0.90485 (9) | 0.49386 (8) | 0.66073 (8) | 0.0234 (2) |
| Cl33 | 1.00265 (8) | 0.61345 (8) | 0.87518 (6) | 0.0187 (2) |
| Cl34 | 0.87952 (8) | 0.74541 (8) | 0.58465 (6) | 0.0183 (2) |
| Cl35 | 1.13389 (7) | 0.73721 (8) | 0.67535 (7) | 0.0185 (2) |
| Cl36 | 0.74646 (8) | 0.62061 (8) | 0.78400 (7) | 0.0217 (2) |
| Sb4 | 0.57068 (2) | 0.82082 (2) | 0.21030 (2) | 0.01386 (5) |
| Cl41 | 0.48964 (10) | 0.89506 (9) | 0.33859 (8) | 0.0279 (2) |
| Cl42 | 0.65313 (9) | 0.74978 (9) | 0.08062 (7) | 0.0259 (2) |
| Cl43† | 0.64405 (14) | 0.71327 (15) | 0.32135 (9) | 0.0323 (4) |
| Cl44† | 0.5009 (2) | 0.9299 (2) | 0.09891 (11) | 0.0415 (4) |
| Cl45† | 0.39759 (11) | 0.66487 (13) | 0.19384 (10) | 0.0330 (4) |
| Cl46† | 0.74530 (15) | 0.97682 (15) | 0.23042 (10) | 0.0381 (4) |
| Cl53‡ | 0.5969 (23) | 0.6683 (21) | 0.3016 (17) | 0.018 (4) |
| Cl54‡ | 0.5309 (20) | 0.9693 (22) | 0.1264 (19) | 0.018 (4) |
| Cl55‡ | 0.3746 (20) | 0.7045 (23) | 0.1920 (16) | 0.018 (4) |
| Cl56‡ | 0.7513 (27) | 0.9416 (25) | 0.2428 (22) | 0.018 (4) |

† Site occupancy = 0.955 (5).    ‡ Site occupancy = 0.045 (5).

the final difference-Fourier map ($0.75$–$1.05$ e $\mathring{A}^{-3}$) are situated $0.8$–$1.5$ $\mathring{A}$ from the Sb atoms.

The fractional atomic coordinates and equivalent isotropic displacement parameters for the two structures are reported in Tables 2 and 3†

## 3. Results and discussion

The atomic numbering of the two crystallographically independent cations and anions is shown in Fig. 1 for (1) and in Fig. 2 for (2). Selected bond lengths and angles are listed in Table 4.

The structure analyses confirm the ionic nature of the two compounds. All the cations show *cis–trans* conformations with respect to their $X$—C—N—P torsion angles [here and in the following $X$ = Cl for (1), C for (2)]

† Lists of anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: SE0217). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

instead of the most symmetric ($C_{2v}$-$mm2$) *cis–cis* conformation; a *trans–trans* conformation is unfavourable due to steric hindrance of the two NPCl$_3$ groups. Semi-empirical MNDO (modified neglect of diatomic overlap) calculations (Dewar & Thiel, 1977; Boyd, 1993) performed for both cations yielded two local energy minima, confirmed by the calculated complete set of harmonic vibrational frequencies: In accordance with structural data the *cis–trans* conformation ($C_s$-$m$ symmetry) was computed to be more stable [by $25.46$ kJ mol$^{-1}$ for (1) and $46.01$ kJ mol$^{-1}$ for (2)] than the *cis–cis* conformation ($C_{2v}$-$mm2$ symmetry). For both cations the minima show C—N—P—Cl torsion angles of 180 or $\pm63.2°$ within a tolerance of $0.5°$; *cis* geometries with C—N—P—Cl torsion angles of 0 and $\pm120°$ are no minima and refine to the *trans* structures. Fig. 3 shows

the differences of the conformations of the four crystallographically independent cations observed in the two crystal structures in comparison with the geometries obtained from the MNDO calculations for the lower minima. Whereas the geometry of the $X$—C(NP)₂ fragment is almost invariable, the orientations of the PCl₃ groups, although being almost the same for the two independent cations of (2), are quite different in (1). Evidently, packing effects have some importance for the orientation of these groups. Therefore, the agreement with the calculated orientations is rather poor.

In five of the eight NPCl₃ groups the C—N—P—Cl torsion angles observed deviate up to 19.4 (2)° from 180°. The three other NPCl₃ groups show unusual *cis* geometries with C—N—P—Cl torsion angles of −7.5 (5) to 10.6 (5)° as hitherto observed only in (Cl₃C)₂C(Cl)—NPCl₃ (Antipin, Struchkov, Yurchenko & Kozlov, 1982), (C₄H₉)₃C₆H₂—NPCl₃ (Burford,

Clyburne, Gates, Schriver & Richardson, 1994) and [Cl—P(NPCl₃)₃]⁺PCl₆⁻.0.5C₂H₂Cl₄ (Belaj, 1992) for compounds containing an NPCl₃ group. As observed and discussed in the structure analysis of SO₂(NPCl₃)₂ (Belaj, 1995), the N—P—Cl bond angles and, to a lesser degree, the P—Cl distances depend on the C—N—P—Cl torsion angles.

In the crystal structures the central C atoms have three coplanar bonds, but the deviations of the four cations from $C_s$-$m$ symmetry, mainly for (1), are rather large: The P atoms lie up to 0.218 (3) Å, and the *cis*/*trans* Cl atoms of the NPCl₃ groups up to 0.615 (5) Å above/below the $X$CN₂ planes. For the cations of (1) – the analogous is valid for (2) – the mesomeric limiting formulae (I)–(IV) are of different importance: In the crystal structure of chloro-(2-chlorophenyl)phenylcarbenium hexafluoroantimonate (Laube, Bannwart & Hollenstein, 1993) the short C—Cl bond of 1.668 (8) Å is attributed to a partial $\pi$-
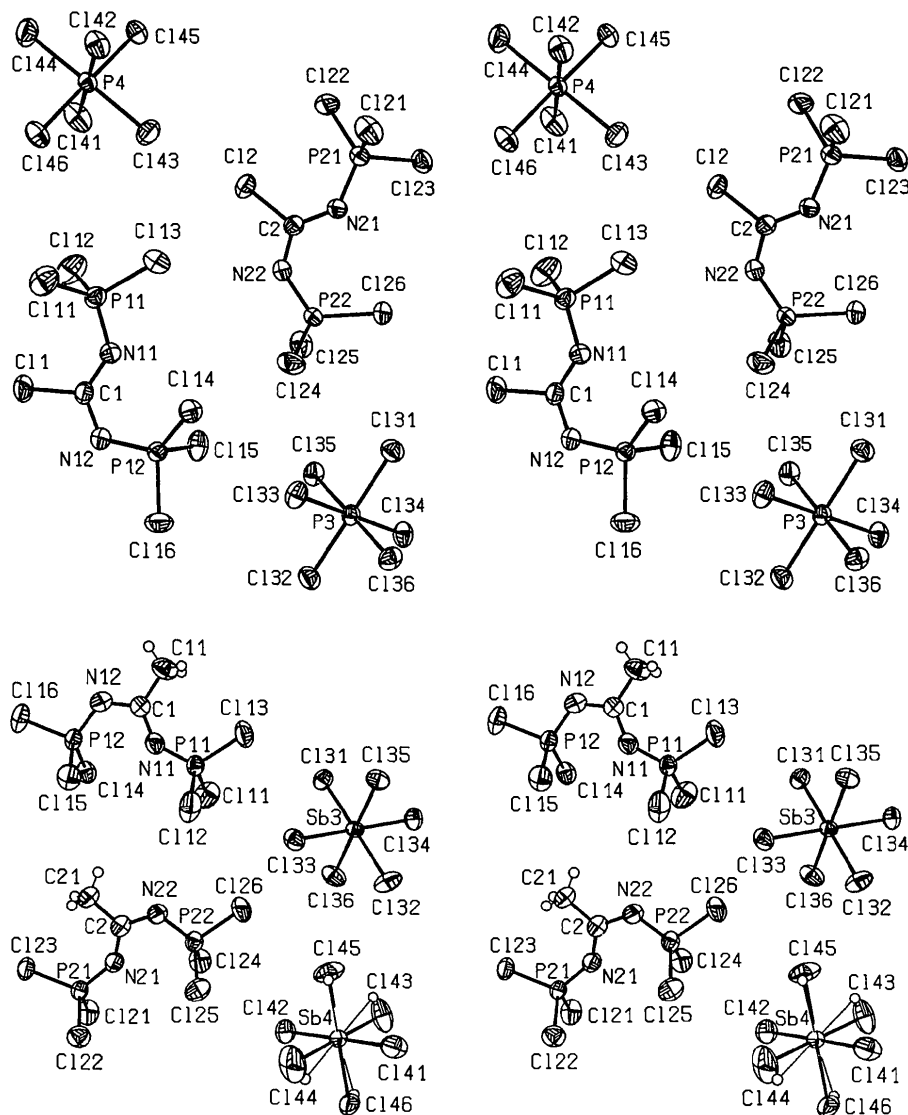


Fig. 1. Stereoscopic *ORTEP* (Johnson, 1965) plot showing the atomic numbering scheme of the two cations and the two anions in the asymmetric unit of (1). The probability ellipsoids are drawn at the 90% probability level.



Fig. 2. Stereoscopic *ORTEP* (Johnson, 1965) plot showing the atomic numbering scheme of the two cations and the two anions in the asymmetric unit of (2). The probability ellipsoids are drawn at the 90% probability level, the four disordered Cl atoms of one SbCl₆⁻ anion are drawn with arbitrary radii.

Table 4. *Selected geometric parameters (Å, °) for (1) and (2) at 90 K*

|  | (1), $n = 1$ | (1), $n = 2$ | (2), $n = 1$ | (2), $n = 2$ |
|---|---|---|---|---|
| $Cn$—$Cln$ | 1.718 (2) | 1.730 (2) | — | — |
| $Cn$—$Cn1$ | — | — | 1.492 (5) | 1.502 (5) |
| $Cn$—$Nn1$ | 1.312 (3) | 1.308 (3) | 1.328 (5) | 1.330 (5) |
| $Cn$—$Nn2$ | 1.312 (3) | 1.305 (3) | 1.331 (5) | 1.328 (5) |
| $Nn1$—$Pn1$ | 1.576 (2) | 1.568 (2) | 1.557 (3) | 1.551 (3) |
| $Pn1$—$Cln1$ | 1.9613 (9) | 1.9593 (9) | 1.9665 (14) | 1.9632 (13) |
| $Pn1$—$Cln2$ | 1.9657 (9) | 1.9670 (9) | 1.9616 (14) | 1.9731 (13) |
| $Pn1$—$Cln3$ | 1.9542 (10) | 1.9605 (9) | 1.9706 (13) | 1.9781 (13) |
| $Nn2$—$Pn2$ | 1.600 (2) | 1.578 (2) | 1.591 (3) | 1.591 (3) |
| $Pn2$—$Cln4$ | 1.9710 (8) | 1.9601 (9) | 1.9705 (14) | 1.9740 (13) |
| $Pn2$—$Cln5$ | 1.9578 (9) | 1.9557 (9) | 1.9764 (13) | 1.9762 (14) |
| $Pn2$—$Cln6$ | 1.9509 (9) | 1.9739 (9) | 1.9581 (13) | 1.9556 (14) |
|  |  |  |  |  |
| $Cln$—$Cn$—$Nn1$ | 120.4 (2) | 120.8 (2) | — | — |
| $Cln$—$Cn$—$Nn2$ | 114.8 (2) | 113.2 (2) | — | — |
| $Cn1$—$Cn$—$Nn1$ | — | — | 124.0 (4) | 122.9 (3) |
| $Cn1$—$Cn$—$Nn2$ | — | — | 116.7 (3) | 116.8 (3) |
| $Nn1$—$Cn$—$Nn2$ | 124.8 (2) | 126.0 (2) | 119.3 (3) | 120.3 (3) |
| $Cn$—$Nn1$—$Pn1$ | 132.2 (2) | 134.5 (2) | 140.9 (3) | 139.5 (3) |
| $Cn$—$Nn2$—$Pn2$ | 122.8 (2) | 131.5 (2) | 120.6 (3) | 122.3 (3) |
| $Nn1$—$Pn1$—$Cln1$ | 113.90 (8) | 112.09 (8) | 109.91 (14) | 109.42 (13) |
| $Nn1$—$Pn1$—$Cln2$ | 115.61 (9) | 118.36 (9) | 108.60 (14) | 109.40 (13) |
| $Nn1$—$Pn1$—$Cln3$ | 105.90 (9) | 107.18 (9) | 118.97 (13) | 119.26 (13) |
| $Nn2$—$Pn2$—$Cln4$ | 117.32 (8) | 108.01 (9) | 115.01 (13) | 115.33 (13) |
| $Nn2$—$Pn2$—$Cln5$ | 111.17 (8) | 109.33 (9) | 116.13 (13) | 115.55 (13) |
| $Nn2$—$Pn2$—$Cln6$ | 106.64 (8) | 119.43 (9) | 106.48 (13) | 106.56 (13) |
| $Cln1$—$Pn1$—$Cln2$ | 106.10 (4) | 105.92 (4) | 105.64 (7) | 105.43 (6) |
| $Cln1$—$Pn1$—$Cln3$ | 108.05 (5) | 106.47 (4) | 106.00 (6) | 106.02 (6) |
| $Cln2$—$Pn1$—$Cln3$ | 106.88 (5) | 106.10 (4) | 106.92 (7) | 106.43 (6) |
| $Cln4$—$Pn2$—$Cln5$ | 106.88 (4) | 106.62 (4) | 105.24 (6) | 105.48 (6) |
| $Cln4$—$Pn2$—$Cln6$ | 106.48 (4) | 106.08 (4) | 107.48 (6) | 106.70 (6) |
| $Cln5$—$Pn2$—$Cln6$ | 107.94 (4) | 106.67 (4) | 105.87 (6) | 106.60 (6) |
|  |  |  |  |  |
| $Cln$—$Cn$—$Nn1$—$Pn1$ | 10.3 (3) | 4.1 (3) | — | — |
| $Cln$—$Cn$—$Nn2$—$Pn2$ | 179.2 (1) | 178.9 (2) | — | — |
| $Cn1$—$Cn$—$Nn1$—$Pn1$ | — | — | −0.1 (7) | −7.3 (7) |
| $Cn1$—$Cn$—$Nn2$—$Pn2$ | — | — | −176.9 (3) | 179.8 (3) |
| $Nn2$—$Cn$—$Nn1$—$Pn1$ | −169.1 (2) | −175.5 (2) | −179.8 (3) | 172.5 (3) |
| $Nn1$—$Cn$—$Nn2$—$Pn2$ | −1.4 (3) | −1.4 (4) | 2.8 (5) | 0.0 (5) |
| $Cn$—$Nn1$—$Pn1$—$Cln1$ | 56.1 (3) | 82.7 (2) | 114.9 (4) | 132.8 (4) |
| $Cn$—$Nn1$—$Pn1$—$Cln2$ | −67.1 (2) | −41.1 (3) | −130.0 (4) | −112.2 (4) |
| $Cn$—$Nn1$—$Pn1$—$Cln3$ | 174.7 (2) | −160.9 (2) | −7.5 (5) | 10.6 (5) |
| $Cn$—$Nn2$—$Pn2$—$Cln4$ | 41.4 (2) | 131.8 (2) | 61.7 (3) | 59.6 (3) |
| $Cn$—$Nn2$—$Pn2$—$Cln5$ | −82.0 (2) | −112.6 (2) | −61.8 (3) | −64.1 (3) |
| $Cn$—$Nn2$—$Pn2$—$Cln6$ | 160.6 (2) | 10.6 (3) | −179.4 (3) | 177.7 (3) |



(I)       (II)       (III)       (IV)
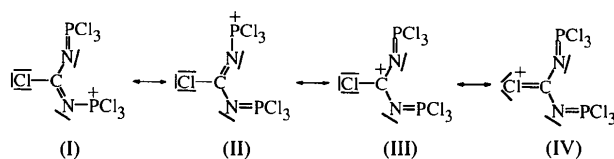
bond resulting from Cl back-donation [resonance formula equivalent to (IV) in addition to the carbenium formula equivalent to (III)]. A similar bonding situation with some importance of carbenium [equivalent to (III)] and chloronium [equivalent to (IV)] limiting formulae must be assumed for the compounds $[Cl_2C{=}NH_2]^+SbCl_6^-$ [C—Cl 1.663 (6)–1.680 (6) Å (Minkwitz, Meckstroth & Preut, 1992)] and $[Cl_2C{=}NH{-}CCl_3]^+SbCl_6^-$ [C—Cl 1.651 (6), 1.651 (5) Å (Minkwitz, Lamek & Preut, 1993)] also. In

(1) the chloronium formula (IV) is less important since the observed C—Cl bond lengths of 1.718 (2) and 1.730 (2) Å do not deviate substantially from the average length of 1.734 Å obtained for $Csp^2$—Cl bonds (Allen *et al.*, 1992).

The highly negative chemical shifts [−38.5 p.p.m. in (1) (Becke-Goehring & Jung, 1970), −32.7 p.p.m. in (2) (Schmidpeter, Düll & Böhm, 1968)] in the $^{31}P$ NMR spectra indicate that the positive charge must be mainly attributed to the P atoms [formulae (I) and (II)] rather than to the more electronegative C atom. The MNDO calculation for (1) resulted in atomic charges of +0.817 (*cis*-P), +0.803 (*trans*-P), +0.348 (C), +0.049 (Cl bonded to C), −0.485 (*cis*-N), −0.356 (*trans*-N), +0.027 (*trans*-Cl bonded to P), −0.064 to −0.051 (other Cl's bonded to P).
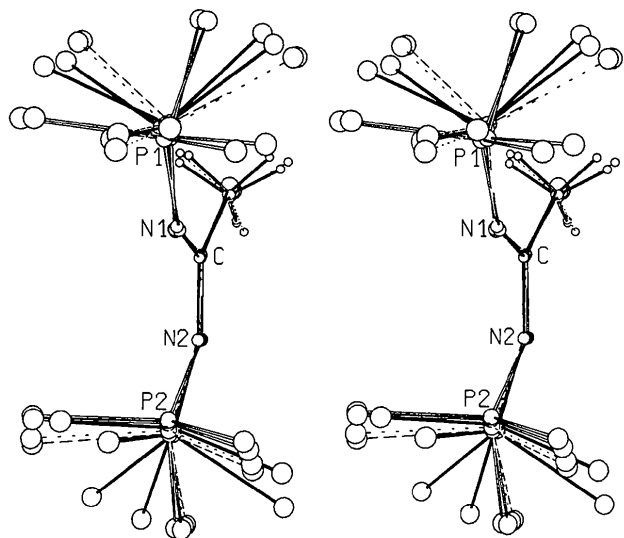
Fig. 3. Comparison of the conformations of the cations determined by crystal structure analyses [(1) plotted with filled bonds, (2) plotted with open bonds] with the minimum geometries obtained from MNDO calculations [(1) plotted with dashed bonds, (2) plotted with dotted bonds]. The least-squares fit was performed for the equivalent atomic positions of $Cn$, $Nn1$, $Pn1$, $Nn2$, $Pn2$ and $X$ [$X = Cln$ for (1), $Cn1$ for (2)].

According to the singlet in the $^{31}$P NMR spectra of (1) (Becke-Goehring & Jung, 1970; Haubold & Fluck, 1972) and (2) (Schmidpeter, Düll & Böhm, 1968), the two P atoms are chemically equivalent in solution by rotation around the C—N bonds. This does not hold true in the crystal for the adopted *cis–trans* conformation. The fact that in all four cations the $Pn1$—$Nn1$ distances are significantly shorter than the distances $Pn2$—$Nn2$ (see Table 4), that all the $Cn$—$Nn1$—$Pn1$ angles are larger than the $Cn$—$Nn2$—$Pn2$ angles, and that the calculated bond order (MNDO) is larger for $Cn$—$Nn2$ (1.43) than for $Cn$—$Nn1$ (1.34) points to more contribution from the *s-trans* limiting formula (I) than from the *s-cis* formula (II). On the other hand, the observed $X$—$Cn$—$Nn2$ angles as well as the calculated (MNDO) ones are the smallest around $Cn$, indicating a higher multiple-bond character of the $Cn$—$Nn1$ bonds [*s-cis* formula (II)]. However, the C—N distances are the same within a cation, even though they are distinctly shorter in (1) than in (2).

The substitution of one $NPCl_3$ group in $[C(NPCl_3)_3]^+SbCl_6^-$ (3) (Müller, Lorenz & Schmock, 1979; Müller, 1980) by the Cl atom in (1) or the methyl group in (2) cancels the equivalence of the $NPCl_3$ groups, shortens the C—N bonds and lengthens the N—P bonds
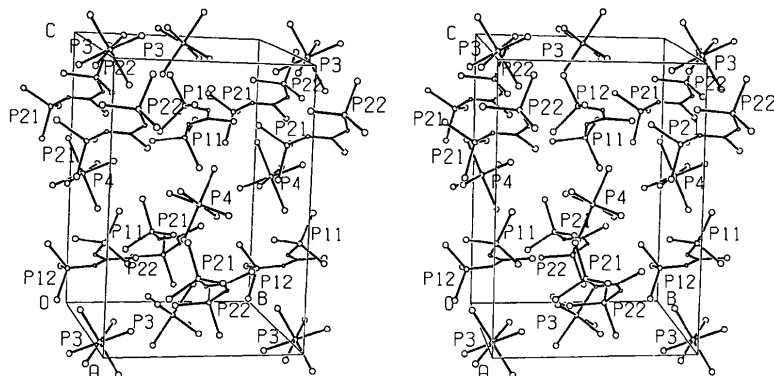


Fig. 4. Stereoscopic view of the packing in the crystal structure of (1). The atoms are drawn as spheres with arbitrary radii.
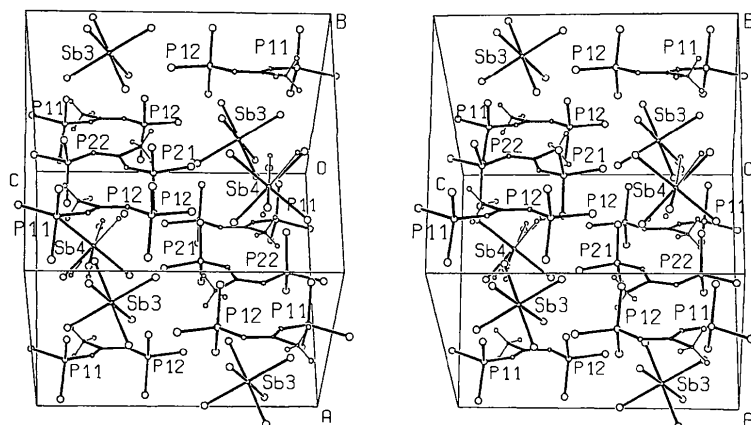


Fig. 5. Stereoscopic view of the packing in the crystal structure of (2). The atoms are drawn as spheres with arbitrary radii.

[cf. 1.340 (9)–1.351 (9) and 1.539 (6)–1.571 (6) Å, respectively, in (3)], since there are only two limiting formulae of positively charged P atoms instead of three in (3). In (1) and (2) both bond orders are thereby estimated as 3/2 instead of 4/3 and 5/3 for the C—N bonds and the N—P bonds in (3), respectively. In the cation [P(NPCl₃)₄]⁺ (Belaj, 1997) P—N bond lengths of 1.595 (2)–1.611 (4) and 1.515 (4)–1.532 (4) Å, according to the rough bond orders of 5/4 and 7/4, respectively, were observed. Furthermore, a shortening of the P—N distances in (1) and (2) correlates with a widening of the C—N—P angles.

The very flexible C—N—P angles in (1) and (2) depend on the intramolecular Cl···Cl and Cl···N distances (see Table 4) resulting from the different orientations of the NPCl₃ groups: If there are no short interactions, as in three of the four NPCl₃ groups around Pn2, C—N—P angles of 120.6 (3)–122.8 (2)° are observed [cf. 121.0 (6)–127.8 (6)° in (3); 121.5 (2)–125.3 (2)° in the exocyclic NPCl₃ groups of C₂N₃PCl₃–NPCl₃ (Belaj, 1996)]; the Cl···N contact in the fourth cis group [C2—N22—P22—Cl26 = 10.6 (3)° in (1)] widens the C2—N22—P22 angle to 131.5 (2)° and thereby shortens N22—P22 to 1.578 (2) Å. The Cn—Nn1—Pn1 angles are larger than the Cn—Nn2—Pn2 angles due to the X···Cl interactions resulting from the cis—X—Cn—Nn1—Pn1 arrangements. These interactions are largest for the two cis-NPCl₃ groups in (2) [139.5 (3) and 140.9 (3)° in (2) versus 132.2 (2) and 134.5 (2)° in (1)].

In the octahedral anions of (1) and (2) the mean P—Cl and Sb—Cl distances are 2.145 (2) and 2.369 (3) Å, respectively. A search of the Inorganic Crystal Structure Database (Bergerhoff & Brown, 1987) for PCl₆⁻ anions [five hits; the disordered compounds (PCl₄)₃TiCl₆PCl₆ (Shamir, Schneider, Bino & Cohen, 1986) and (PCl₄)₃SnCl₆PCl₆ (Shamir, Luski, Bino, Cohen & Gibson, 1985) were ignored] and SbCl₆⁻ anions [38 hits; the wrong cell constant b = 56.72 (1) Å in S₅N₅SbCl₆ (Gillespie, Sawyer, Slim & Tyrer, 1982) was corrected to b = 46.72 (1) Å] yielded mean distances of 2.127 (4) and 2.365 (1) Å, respectively. The Cl—P—Cl and Cl—Sb—Cl angles show deviations from 90° (or 180°) not larger than 1.03 (4) and 1.51 (5)°, respectively.

In the crystal structures of (1) and (2) the cations and anions individually show distorted cubic closest packings (Figs. 4 and 5). Besides some intermolecular distances less than the sum of the van der Waals radii [1.75 Å for Cl (Bondi, 1964)] between the counterions there is one short Cl44···Cl44 contact of 3.259 (2) Å between two SbCl₆⁻ anions related by an inversion centre. Possibly, this forced proximity gives cause for the low-grade disorder detected in this anion. No short contact is observed between the smaller PCl₆⁻ anions in (1).

An analysis of the nuclear anisotropic displacement parameters $U^{ij}$ showed that the rigid-bond test (Hirshfeld, 1976) according to which the differences $\Delta = z^2_{A,B} - z^2_{B,A}$ for atoms at least as heavy as carbon should vanish for every covalently bonded pair of atoms A and B ($z^2_{A,B}$ denotes the observed mean-square amplitude of the vibration of atom A along the direction of the A—B bond) is fulfilled with a single exception [N11—P11 in (2): $\Delta = 0.0043$ (15) Å²]. For P—Cl bonds the values of $|\Delta|$ are ≤ 0.0005 (4) Å² in (1) and ≤ 0.0008 (6) Å² in (2); for other bonds ≤ 0.0014 (8) Å² in (1) and ≤ 0.0029 (21) Å² in (2), disregarding the cited exception. The mean values of $\Delta$ are 0.0003 Å² for (1) and 0.0010 Å² for (2). The higher precision in the displacement parameters of (1) is a result of the more extensive data collection until $2\theta = 80°$ instead of 60° at (2).

The rigid-body motion analysis (Schomaker & Trueblood, 1968) shows that the anions as well as all the NPCl₃ groups of the cations behave as rigid bodies: the residual indices $R_u$, defined as $R_u = \{\Sigma w(\Delta U)^2 / \Sigma w(U_{obs})^2\}^{1/2}$, with $w = 1/\sigma^2$, are ≤ 0.025 in (1) and ≤ 0.027 in (2), except for the slightly disordered anion around Sb4 ($R_u = 0.042$). As stated for the cation [P(NPCl₃)₄]⁺ (Belaj, 1997), all the four cations in (1) and (2) show the presence of non-rigid intramolecular motions ($R_u = 0.138$–0.181 assuming the rigid-body model), which cannot be explained by allowance for intramolecular torsion (Dunitz & White, 1973; Trueblood, 1978) about the C—N or N—P bonds by including terms for the correlations of the internal and overall motions (Dunitz, Maverick & Trueblood, 1988a,b): the residual indices $R_u$ did not drop below 0.081. To all appearances the internal librations in the cations can be better described by somewhat independent motions of the three rigid subunits coupled by the highly flexible N atoms as 'ball joints'.

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