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# Preparation, Crystal Structure and Raman Spectrum of Tetrachloro Phosphonium Tetrachloro-iodate $[PCl_4][ICl_4]$

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## Abstract

The preparation of $[PtCl_4][ICl_4]$ is described. Its structure was determined by both X-ray analysis and Raman spectroscopy. This compound is orthorhombic, space group *Imma* with $a = 12.315(1)$, $b = 16.302(2)$, $c = 12.215(1)$ Å, $V = 2452(1)$ Å$^3$ and $Z = 8$. The structure was refined by least squares to $R = 3.2\%$ using 753 observed reflections. The $PtCl_4^+$ cation is tetrahedral with $T_d$ symmetry, whereas the two crystallographically independent $ICl_4^-$ anions are square planar – one with an almost ideal $D_{4h}$ symmetry and the other slightly distorted to a $C_{2v}$ symmetry. The I–Cl distances are in the range of 2.461(4)–2.508(3) Å.

## Introduction

Phosphorus pentachloride can react as a Lewis base transferring a chloride anion to a covalent chloride which behaves as a Lewis acid, thus forming ionic compounds. A variety of such solid complexes with a $PCl_4^+$ cation have been prepared and identified. In recent studies, several new compounds of this type have been isolated and their structures were determined using various physical methods, such as X-ray analysis and vibrational spectroscopy [1–4].

All these compounds were prepared in non-aqueous solvents, dissolving the reactants and precipitating out pure ionic compounds, in accordance with the general formula:

$$PCl_5 + MCl_x \longrightarrow [PCl_4][MCl_{x+1}] \quad (x = 3, 4 \text{ and } 5)$$

Such a reaction is not very suitable for attempting to prepare $[PCl_4][ICl_4]$ by reacting $PCl_5$ in a solvent with $I_2Cl_6$. The iodine trichloride is only stable in the solid state. Attempted melting of $I_2Cl_6$ or dissolution leads to partial decomposition [5] according to:

$$(I_2Cl_6) \rightarrow 2ICl + 2Cl_2$$

As a result, standard preparation in solution cannot assure the precipitation of a pure compound. Instead, a mixture of $[PCl_4][ICl_2]$ and $[PCl_4][ICl_4]$ might separate out.

A brief report [6] described the preparation of $[PCl_4][ICl_4]$, **1**, by addition of solid $I_2Cl_6$ to a heated suspension of $PCl_5$ in nitromethane. This report also quotes the fact that a similar experiment resulted in a different compound, namely $PCl_5 \cdot ICl$; no additional experimental evidence was provided in order to substantiate the structure as $[PCl_4][ICl_4]$.

It is the purpose of this paper to report a reliable preparative method for compound **1** and experimental results to elucidate its structure. The compound **1** was prepared, while the parent compound $I_2Cl_6$ has been prepared *in situ* in the presence of $PCl_5$. A pure and well-crystallized product was obtained, and both its Raman spectrum and its single-crystal X-ray analysis have provided proof for its ionic structure as assumed.

## Experimental

### *Preparation*

The reaction was performed in a solution of $CH_2Cl_2$ at room temperature or in $POCl_3$, just below its boiling point, around 90 °C. In a solution of $CH_2Cl_2$, a fine polycrystalline product was obtained, suitable for Raman studies but not for single-crystal X-ray analysis. In order to obtain well-defined single crystals for X-ray analysis, the second solvent, $POCl_3$, which had been kept at 90 °C, was used.

In both cases, 2.5 g of $PCl_5$ and 1 g of iodine were dissolved in 50 ml of the appropriate solvent, in a bubble reactor. A slight excess of $PCl_5$ was used to prevent the presence of an excess of iodine after completion of the reaction. As already mentioned, the solutions were kept at room temperature and at 90 °C, in the cases of $CH_2Cl_2$ or $POCl_3$, respectively.

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TABLE I. Crystallographic Data

| | |
|---|---|
| Formula | $Cl_8IP$ |
| Formula weight | 441.50 |
| Space group | *Imma* |
| $a$ (Å) | 12.315(1) |
| $b$ (Å) | 16.302(2) |
| $c$ (Å) | 12.215(1) |
| $V$ (Å$^3$) | 2452(1) |
| $Z$ | 8 |
| Crystal dimensions (mm) | 0.5 × 0.5 × 0.5 |
| $d$(calc) (g cm$^{-3}$) | 2.401 |
| $\mu$ (cm$^{-1}$) | 41.47 |
| $2\theta$ range (deg) | 3–50 |
| Number of unique data | 1160 |
| Data with $F_o^2 > 3\sigma(F_o^2)$ | 753 |
| Number of variables | 59 |
| $R$ | 0.032 |
| $R_w$ | 0.049 |

A stream of dried chlorine gas was bubbled through the dark-colored solution, which slowly brightened up, turning yellowish, followed by the appearance of a yellow precipitate. When the $POCl_3$ solution was used, well-defined crystals precipitated on cooling to room temperature. The product was filtered in a dry box and dried under vacuum. Sampling of the product also took place in the dry box.

*X-ray Crystallography*

Single crystals of **1** were transferred in the dry box from their mother liquor into a Petri dish and were covered with an inert silicone oil (Dow Corning 704) to prevent contact with the air. A crystal was selected and checked under a microscope, pushed into a thin-walled glass capillary with the aid of a glass fiber, and sealed off with epoxy glue.

Data were collected for compound **1** at 22 ± 2 °C on a PW 1100 Philips four-circle computer-controlled diffractometer; Mo K$\alpha$ ($\lambda$ = 0.71069 Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 20 reflections in the range $12° < \theta < 16°$. Data were measured by using a $\omega$–$2\theta$ motion. Crystallographic data and other pertinent information are given in Table I. Lorentz and polarization corrections were applied. Intensity data were corrected for absorption by the empirical $\psi$-scan method. The structure was solved using the results of MULTAN direct method analysis and refined* in space group *Imma* to convergence using anisotropic thermal parameters for all atoms. The discrepancy indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [(\Sigma w|F| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ are listed in Table I.

*Raman Spectra*

The Raman spectra were recorded on a Spex double monochromator, model 1401, fitted with a Spectra Physics, Krypton ion laser, model 164 using the 647.1 nm excitation, as described elsewhere [7]. The spectral slits were equal to 2 cm$^{-1}$ and in recording the isotope splitting, spectral slits were reduced to 1 cm$^{-1}$. The samples were kept in glass capillaries, sealed off in a flame.

## Results and Discussion

*$[PCl_4][ICl_4]$, Structural Results*

The atomic positional parameters are listed in Table II. Table III presents the bond lengths, contact distances and angles. The latter Table also includes, in square brackets, lengths and distances after correction for thermal motion. Figure 1 gives a stereoscopic view of a complete unit cell, which is actually of a stacked structure with alternating planes of $PCl_4^+$ cations and $ICl_4^-$ anions. The $PCl_4^+$ cation resides on a crystallographic two-fold axis (eight fold) with typical P–Cl distances and Cl–P–Cl tetrahedral angles. There are, however, two crystallographically distinct $ICl_4^-$ anions in the cell, which are stacked together at alternating positions. Figure 2 illustrates the $ICl_4^-$ anion mirror plane at $y = ¼$, including numbering scheme and dimensions.

TABLE II. Positional Parameters and Estimated Standard Deviations for $[PCl_4][ICl_4]$

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| I(1) | 0.00000 | 0.25000 | 0.06276(6) |
| I(2) | 0.00000 | 0.25000 | 0.57135(6) |
| P | 0.25000 | 0.0034(2) | 0.25000 |
| Cl(1) | 0.00000 | 0.0972(2) | 0.0618(2) |
| Cl(2) | 0.2016(3)[a] | 0.25000 | 0.0574(4) |
| Cl(3) | 0.00000 | 0.4027(2) | 0.5697(2) |
| Cl(4) | 0.00000 | 0.25000 | 0.3660(3) |
| Cl(5) | 0.00000 | 0.25000 | 0.7728(3) |
| Cl(6) | 0.3466(2) | 0.0726(2) | 0.1690(2) |
| Cl(7) | 0.1701(2) | −0.0654(2) | 0.1511(2) |

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

In the first $ICl_4^-$ ion, the central iodine atom, I(1), resides on an *mm* axis at 0, ¼, 0.06276; and the two chlorine atoms, Cl(1) and Cl(2), reside on the mirror planes at 0, $y$, $z$ and $x$, ¼, $z$, respectively. In the second $ICl_4^-$ ion, I(2), Cl(4) and Cl(5) reside on the *mm* axis at 0, ¼, $z$ and Cl(3) in the mirror plane at

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*All crystallographic computing was done on a CYBER 74 computer at the Hebrew University of Jerusalem, using the SHELX (1977) structure determination package.

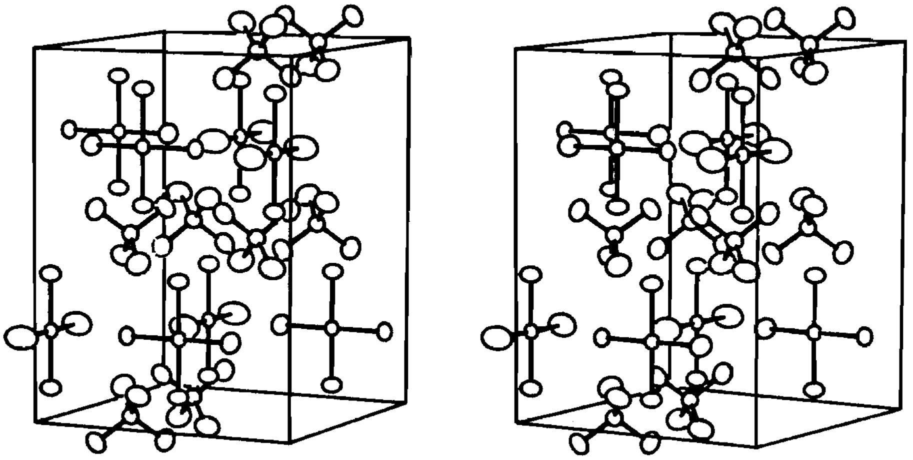

Fig. 1. A stereogram showing the unit cell contents of [PCl$_4$] [ICl$_4$].

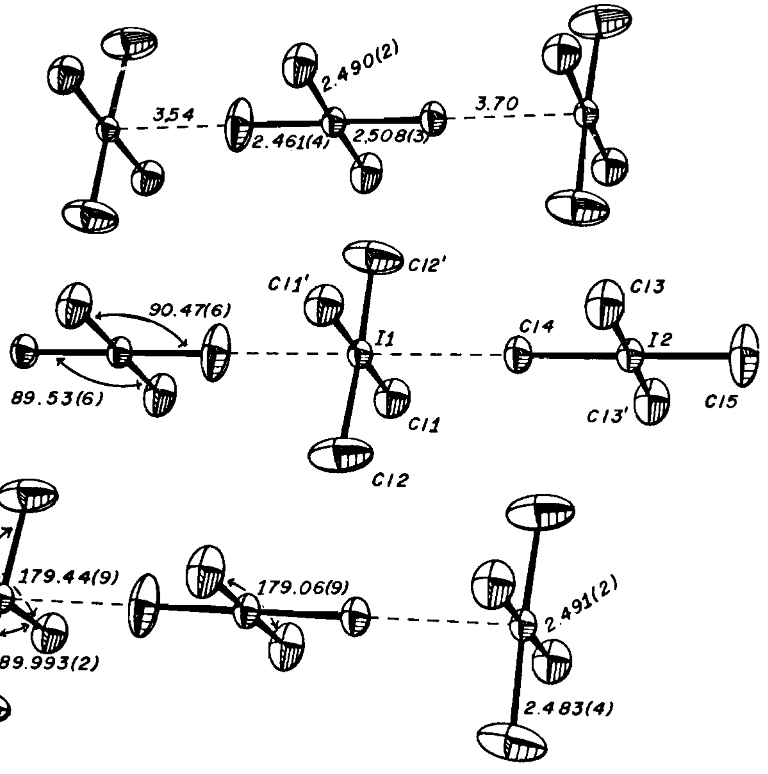

Fig. 2. The ICl$_4^-$ anions in the mirror plane at $y = \frac{1}{4}$. Thermal ellipsoids are scaled to enclose 50% probability.

0, $y$, $z$. The crystallographic symmetry of the first ICl$_4^-$ with I(1) is very nearly square-planar with $D_{4h}$ symmetry, whereas the second one with I(2) is slightly distorted into $C_{2v}$ symmetry.

The I(1)–Cl bond distances are 2.491–2.483 Å and are to be considered as terminal chlorines. In the second type of ICl$_4^-$ with I(2), two chlorines in *trans* positions, namely Cl(4) and Cl(5), act as bridging to I(1) along the *mm* axis. The intermolecular contact distances are 3.54 (after thermal motion correction 3.50 Å) and 3.70 Å. These are shorter than the sum of the van der Waal's radii of I and Cl of 3.84 Å [8]. These could, therefore, be considered as secondary bonding to non-metallic elements as described by Alcock [9], which, together with the covalent bonds, create an octahedral environment around I(1).

The existence of such bonding is rather exceptional. First of all, in this case the secondary bondings are not linear to the primary bonds as usually expect-

TABLE III. Bond Lengths, Contact Distances and Bond Angles for [$PCl_4$] [$ICl_4$]

| | |
|---|---|
| I(1)–Cl(1) | 2.491(2) [2.512(6)][a] |
| I(1)–Cl(2) | 2.483(4) [2.53(1)] |
| I(2)–Cl(3) | 2.490(2) [2.511(7)] |
| I(2)–Cl(4) | 2.508(3) [2.515(8)] |
| I(2)–Cl(5) | 2.461(4) [2.50(1)] |
| P–Cl(6) | 1.916(2) [1.943(9)] |
| P–Cl(7) | 1.920(3) [1.955(9)] |
| Contact distances (Å) | |
| I(1)–Cl(4) | 3.70(1) [3.70(1)] |
| I(1)–Cl(5) | 3.54(1) [3.50(1)] |
| Angles (deg) | |
| Cl(1) I(1)–Cl(1)′ | 179.44(9) |
| Cl(1)–I(1)–Cl(2) | 89.99(1) |
| Cl(2)–I(1)–Cl(2)′ | 177.0(2) |
| Cl(3)–I(2)–Cl(3)′ | 179.06(9) |
| Cl(3)–I(2)–Cl(4) | 89.53(6) |
| Cl(3)–I(2)–Cl(5) | 90.47(6) |
| Cl(6)–P–Cl(6)′ | 107.8(2) |
| Cl(6)–P–Cl(7) | 109.7(1) |
| Cl(6)–P–Cl(7)′ | 110.5(1) |
| Cl(7)–P–Cl(7)′ | 108.5(2) |

[a] All square bracket values after correction for thermal motion.

ed, but are right-angled interactions. Secondly, they are in the same direction as the non-bonding lone pair electrons on the central atom I(1). Similar exceptions do exist and have been discussed by Alcock [9]. The $TeCl_6^{2-}$ and $TeBr_6^{2-}$ also have a regular octahedral geometry, but formally have seven electron pairs. The rather large size of the central atoms, Te and I, may be the reason for such exceptions.

Whereas the I(1) is in an octahedral environment, including both intra- and intermolecular bonding, the I(2) remains only a tetracoordinated atom. The closest intermolecular contact, I(2)–Cl(2), is about 4.00 Å, larger than the sum of the van der Waals radii of I and Cl. Similarly, the angles differ considerably. Whereas the Cl(5)–I(1)–Cl(4) is exactly 180°, the related angle Cl(2)–I(2)–Cl(2) is about 134°.

The I–Cl distances in the two ions vary in the range of 2.461(4)–2.508(3) Å, probably due to packing forces in the crystal. These variations are much smaller than those reported for the structures of $KICl_4 \cdot H_2O$ (2.42, 2.47, 2.53, 2.60 Å) [10] and of [$SCl_3$] [$ICl_4$] (2.437–2.603 Å) [11].

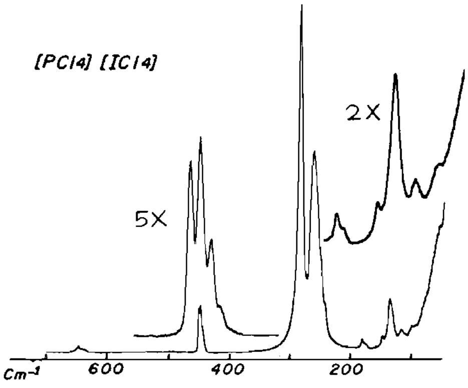

Fig. 3. Raman spectrum of [$PCl_4$] [$ICl_4$].

TABLE IV. Raman Frequencies ($cm^{-1}$) of [$PCl_4$] [$ICl_4$] Fundamentals and their Relative Intensities

| Assignments | [$PCl_4$] [$ICl_4$][a] Raman | [$PCl_4$] [$ICl_4$][a] $I$ | [$ICl_4$][b] Raman |
|---|---|---|---|
| $\nu_3(F_2)$–$PCl_4^+$ | 651 | 2 | |
| | 645 | 1 | |
| $\nu_1(A_1)$–$PCl_4^+$ | 454 | | |
| | 451 | 15 | |
| | 448 | | |
| | 445 | | |
| | 442 | | |
| $\nu_1(A_{1g})$–$ICl_4^-$ | 284 | 100 | 284vs |
| $\nu_4(B_{2g})$–$ICl_4^-$ | 260 | 56 | 260s |
| $\nu_4(F_2)$–$PCl_4^+$ | 250 | sh | |
| $\nu_6(E_u)$–$ICl_4^-$ | 243 | sh | 250w |
| | 225 | sh | 228w |
| $\nu_2(E)$–$PCl_4^+$ | 179 | 3 | |
| | 172 | 1 | |
| $\nu_3(A_{2u})$–$ICl_4^-$ | 144 | 3 | 155w |
| $\nu_2(B_{1g})$–$ICl_4^-$ | 132 | 13 | 144mw |
| $\nu_7(E_u)$–$ICl_4^-$ | 116 | 3 | 130w |
| | 95 | 1 | 114w |

[a] This work. [b] Ref. 12, form II

TABLE V. Relative Intensities of Isotopic Splittings in $\nu_1$ of $PCl_4^+$

| Species | $cm^{-1}$ | $I_{obs}$ | $I_{calc}$ |
|---|---|---|---|
| $P^{35}Cl_4$ | 454.2 | 95 | 81 |
| $P^{35}Cl_3{}^{37}Cl$ | 451.2 | 108 | 108 |
| $P^{35}Cl_2{}^{37}Cl_2$ | 448.0 | 52 | 54 |
| $P^{35}Cl^{37}Cl_3$ | 445.0 | 12 | 12 |
| $P^{37}Cl_4$ | 442.0 | 2 | 1 |

### *Raman Spectrum*

The Raman spectrum of compound **1** is presented in Fig. 3, and the numerical frequencies are summarized in Table IV. Four Raman active vibrations are expected for the tetrahedral $PCl_4^+$ cation with $T_d$ symmetry, and three Raman active vibrations are expected for the square-planar $ICl_4^-$ anion with $D_{4h}$ symmetry. The slight distortion of the second $ICl_4^-$ to $C_{2v}$ symmetry is not noticed in the spectrum.

Three of the cationic vibrations have been observed clearly; their frequencies are in good agreement with those observed in similar compounds with the $PCl_4^+$ cation [1–4]. The asymmetric bending mode $\nu_4(F_2)$ is usually observed around 250 cm$^{-1}$, with an average intensity of about 50% of that of the totally symmetric stretching $\nu_1(A_1)$ of $PCl_4^+$. Since the stretching vibrations of the $ICl_4^-$ anion show up with much stronger intensities than those of the $PCl_4^+$ cation, it is quite reasonable to assume that the $\nu_4$ of $PCl_4^+$ is covered up by the very intense $ICl_4^-$ vibration at 260 cm$^{-1}$. The $\nu_4$ of $PCl_4^+$ can alternatively be assigned to the very weak shoulder on the low frequency side of $ICl_4^-$ vibration at 260 cm$^{-1}$.

The totally symmetric stretching vibration $\nu_1(A_1)$ of $PCl_4^+$ shows the expected isotopic splitting with a separation of 3 cm$^{-1}$. This splitting results from the natural abundance of the two chlorine isotopes of mass 35 and 37. The relative intensities of the various frequencies are listed in Table V and are in good agreement with the calculated values.

If the $ICl_4^-$ anion were of a pure square planar structure with $D_{4h}$ symmetry, only three Raman active vibrations would be expected, namely two stretching vibrations, $A_{1g}$ and $B_{2g}$, and one bending mode, $B_{1g}$; these are mutually exclusive with three infrared active vibrations. Actually, all three of the Raman active vibrations have indeed been observed as rather intense lines, but, in addition, three very weak lines are noticed, which are assigned to the infrared active vibrations. In other Raman spectra reported for compounds with the $ICl_4^-$ anion [12–14], similar observations have been made. This is explained on the basis of the fact that some distortion of the $D_{4h}$ symmetry occurs in the solid, thus causing the breakdown of the mutually exclusive selection rules. However, as usual, the asymmetric vibrations are weak in the Raman, and the $\nu_6(E_u)$ asymmetric stretch can hardly be seen as a shoulder on the very intense symmetric stretching. This IR active vibration can possibly be assigned as a doublet [11] to the weak shoulders at 243 and 225 cm$^{-1}$, whereas the shoulder at 250 cm$^{-1}$ has been assigned to the $\nu_4(F_2)$ of the $PCl_4^+$ cation.

In an earlier study [1], the structures of [PCl$_4$]-[MCl$_4$] compounds have been reported in which both ions are tetrahedral, whereas, in this study, a square-planar structure is reported for the anion in [PCl$_4$] [ICl$_4$]. An additional study is underway of $PCl_4^+$ salts with $SbCl_4^-$ and $BiCl_4^-$ anions, which are expected to be of $C_{2v}$ symmetry.

## Supplementary Material

Tables of structure factors and thermal parameters (6 pages) are available from the authors.

## References

1 J. Shamir, B. J. van der Veken, M. A. Herman and R. Rafaeloff, *J. Raman Spectrosc., 11,* 215 (1981).
2 J. Shamir, S. Luski, A. Bino, S. Cohen and D. Gibson, *Inorg. Chem., 24,* 2301 (1985).
3 J. Shamir, S. Luski, A. Bino, S. Cohen and D. Gibson, *Inorg. Chim. Acta, 104,* 91 (1985).
4 J. Shamir, S. Schneider, A. Bino and S. Cohen, *Inorg. Chim. Acta, 111,* 141 (1986).
5 A. J. Downs and C. J. Adams, in A. F. Trotman-Dickenson (ed.), 'Comprehensive Inorganic Chemistry', Vol. 2, Pergamon, 1973, p. 1482, 1523.
6 M. Becke-Goehring and P. B. Hermuth, *Z. Anorg. Allg. Chem., 369,* 105 (1969).
7 A. Loewenschuss, J. Shamir and M.Ardon, *Inorg. Chem., 15,* 238 (1976).
8 J. E. Huheey, 'Inorganic Chemistry, Principles of Structure and Reactivity', Harper and Row, London, 1978, p. 232–233.
9 N. W. Alcock, *Adv. Inorg. Chem. Radiochem., 15,* 1 (1972).
10 R. J. Elema, J. L. De Boer and Auf je Vos, *Acta Crystallogr., 16,* 243 (1963).
11 A. J. Edwards, *J. Chem. Soc., Dalton Trans.,* 1723 (1978).
12 J. P. Huvenne, B. Boniface, F. Wallart and P. Legrand, *Spectrochim. Acta, Part A, 31,* 1937 (1975).
13 A. Finch, P. N. Gates and T. H. Page, *Inorg. Chim. Acta, 25,* L49 (1977).
14 A. Finch, P. N. Gates, T. H. Page, K. B.Dillon and T. C. Waddington, *J. Chem. Soc., Dalton Trans.,* 2401 (1980).