

Tetrachloro-phosphonium Salts of Hexachloro Antimonate and Niobate and their Solvates. Preparation and Structure by Vibrational Spectroscopy and X-ray Crystallography

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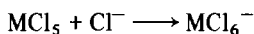
Abstract

Four ionic compounds were isolated and identified: $[\text{PCl}_4][\text{SbCl}_6]$, **1**; $[\text{PCl}_4][\text{SbCl}_6] \cdot 1/2\text{POCl}_3$, **2**; $[\text{PCl}_4][\text{NbCl}_6]$, **3**; and $[\text{PCl}_4][\text{NbCl}_6] \cdot \text{SOCl}_2$, **4**. Vibrational spectra were obtained for all these substances and compound **2** was also characterized by X-ray crystallography. This compound crystallizes in the tetragonal space group $P4_2/\text{mbc}$ with $a = 14.658(2)$ Å, $c = 14.915(2)$ Å and $Z = 8$. The structure was refined by least-squares methods using 1154 reflections to a conventional R factor of 2.8%.

Introduction

Phosphorus pentachloride can react as a Lewis base, transferring a chloride anion to a covalent halide, reacting as a Lewis acid. Thus an ionic compound is formed with the PCl_4^+ cation. Recent studies dealt with reactions of PCl_5 with various trichlorides [1] and tin tetrachloride [2]. In the latter system, several compounds were isolated. Complete vibrational spectra were reported for all these compounds [1, 2] and in some cases X-ray analyses were also reported [2].

It is the purpose of this paper to report the extension of these studies to reactions taking place between PCl_5 and some pentachlorides. Similarly to trichlorides which form tetracoordinated anions, pentachlorides also behave as Lewis acids forming hexacoordinated anions, according to:



Indeed, in reacting PCl_5 with antimony and niobium pentachlorides, reactions take place in accordance with:



However, more complexed compounds have also been isolated, namely solvates of the above men-

tioned salts. These contain in the crystal molecules of the solvents in which the reactions took place, namely phosphoryl chloride and thionyl chloride.

Altogether, four compounds were isolated and their structures verified, namely: $[\text{PCl}_4][\text{SbCl}_6]$, **1**; $[\text{PCl}_4][\text{SbCl}_6] \cdot 1/2\text{POCl}_3$, **2**; $[\text{PCl}_4][\text{NbCl}_6]$, **3**; and $[\text{PCl}_4][\text{NbCl}_6] \cdot \text{SOCl}_2$, **4**. Vibrational spectra were obtained for all four compounds and assigned properly. Compound **2** was also studied by X-ray crystallography. Vibrational spectra have been reported in the literature [3-5] for compound **1** and for compounds related to **2** and **4**, but as different solvates, namely with AsCl_3 [6]. Although X-ray analysis [7] has been reported for compound **3**, no vibrational spectra has been reported until now. Thus the compounds **2** and **4** are newly reported and identified.

Experimental

Preparation

All the compounds, including the reactants, are extremely hydrolysable and were therefore handled under the exclusion of moisture. All operations, such as the preparation of solutions, mixing, filtering the solid products and the sampling for the spectroscopic studies, were performed in a dry box. Only the refluxing of the solutions was done in the open, with a drying tube connected to the top of the condenser.

The anhydrous reacting materials were commercially available and were used without further purification. Solutions were prepared in different non-aqueous solvents such as dichloromethane, POCl_3 and SOCl_2 . The CH_2Cl_2 was dried prior to use, with molecular sieves (3A). Solutions of appropriate concentrations of the reactants were mixed and in some cases refluxed, allowing the solid products to precipitate. These were washed with the pure solvent and then stored for sampling.

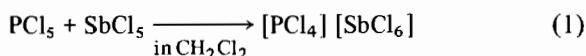
Single crystals of **2** and **4** were obtained from solutions of POCl_3 or SOCl_2 . These solvents provided

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a larger liquid range between their boiling points and room temperature than did CH_2Cl_2 . The solutions were refluxed, dissolving all the reacting materials forming clear solutions from which the single crystals precipitated out when allowed to cool to room temperature.

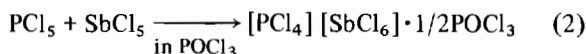
[PCl₄]/[SbCl₆]/ (1)

PCl_5 (0.7 g) and SbCl_5 (0.33 ml), at molar ratio of 1:1 were dissolved in 30 ml of CH_2Cl_2 . The white precipitate was filtered and dried under vacuum. The reaction is in accordance with:



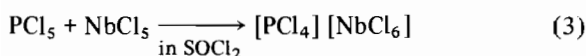
[PCl₄]/[SbCl₆]/1/2POCl₃ (2)

PCl_5 (0.7 g) and SbCl_5 (0.33 ml) were dissolved in 35 ml of POCl_3 . The solution was refluxed for 15 min, and allowed to cool to room temperature. The white crystalline product which formed upon cooling was filtered and dried under vacuum. The reaction is in accordance with:



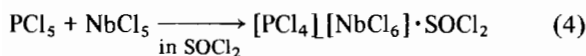
[PCl₄]/[NbCl₆]/ (3)

PCl_5 (0.7 g) and NbCl_5 (0.91 g) at molar ratio of 1:1 were dissolved in 40 ml of SOCl_2 , reacting at room temperature. The yellowish product was filtered and dried under vacuum. The reaction is in accordance with:



[PCl₄]/[NbCl₆]/SOCl₂ (4)

PCl_5 (0.7 g) and NbCl_5 (0.91 g) were dissolved in 30 ml of SOCl_2 . The solution was refluxed for 20 min. The yellowish product which formed upon cooling was filtered and dried under vacuum. The reaction is in accordance with:



X-ray Crystallography

Single crystals of **2** 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 **2** at 22 ± 2 °C on a PW 1100 Philips four-circle computer-controlled diffractor, Mo-K α ($\lambda = 0.71069$ 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 $12^\circ < \theta < 16^\circ$. 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 ψ -scan method. The structure was solved

TABLE I. Crystallographic Data.

Formula	$\text{Cl}_{11.5}\text{O}_{0.5}\text{P}_{1.5}\text{Sb}$
FW	583.92
Space group	$P4_2/\text{mbc}$
<i>a</i> (Å)	14.658(2)
<i>c</i> (Å)	14.915(2)
<i>V</i>	3205(1)
<i>Z</i>	8
Crystal size (mm)	0.5 × 0.5 × 0.1
<i>d</i> (calcd) (g cm ⁻³)	2.420
μ (cm ⁻¹)	35.14
2 θ range (deg)	3 → 50
No. of unique data	1472
Data with $F_o^2 > 3\sigma(F_o^2)$	1154
No. of variables	74
<i>R</i>	0.028
<i>R_w</i>	0.032

using the results of MULTAN direct method analysis and refined* in space group $P4_2/\text{mbc}$ to convergence using anisotropic thermal parameters for all atoms. The phosphorus atom of the POCl_3 molecule resides on a $\bar{4}$ crystallographic site at 0, 0, 1/4. This means that the chlorine and oxygen atoms are statistically disordered. The parameters of the disordered atoms (Cl, O) were therefore refined using occupancy factors of 0.75 for Cl and 0.25 for O.

The discrepancy indices $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [(\sum w|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ are listed in Table I.

Raman Spectra

The Raman spectra were recorded on a Spex double monochromator, model 1401, fitted with a model 164 Spectra Physics argon ion laser, using the 514.5 nm line for excitation [7]. The spectra were also rechecked using the 488.0 nm line for excitation, which resulted in exactly the same spectra.

The spectral slits were equal to 2 cm^{-1} . 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.

*All crystallographic computing was done on a CYBER 74 computer at the Hebrew University of Jerusalem, using the SHELX (1977) structure determination package [8].

TABLE II. Raman Frequencies in cm^{-1} of PCl_4^+ in Various Compounds and their Relative Intensities.

Vibration	Compounds							
	1		2		3		4	
	R	I	R	I	R	I	R	I
$\nu_1(A_1)$	460	100	456	87	455	92	457	100
$\nu_2(E)$	190	33	195	30	{ 180 206	100	180	sh
$\nu_3(F_2)$	{ 653 658	7	{ 645 675	{ 7 3	{ 642 655 665	4	{ 652 665	10
$\nu_4(F_2)$	252	78	252	100	{ 249 255	{ 50 sh	252	90

Infrared Spectra

The infrared spectra were recorded on a Perkin-Elmer instrument, model 180. Polyethylene discs were pressed for the far IR region, where most fundamentals were observed. Silver chloride discs were used for the higher frequency region in the medium IR range, where mostly overtones and combination bands were observed.

Results and Discussion

All the observed data support a structure of ionic nature of all the four compounds studied. All of these contain the PCl_4^+ cation with the appropriate hexachloride anion.

The various observed data, vibrational spectra and X-ray analysis will be discussed separately for compounds with differing anions. However, an examination of the spectral part of the PCl_4^+ cation, common to all four compounds, will be presented first.

PCl_4^+

This tetrahedral cation with a T_d symmetry is expected to show four Raman active vibrations, two of them also being infrared-active. All of these have indeed been observed and their frequencies, as listed in Table II, are in good agreement with earlier ones reported in the literature [1]. Earlier reported and assigned spectra [3-5] of compound 1 are incomplete and include different assignments for $\nu_2(E)$ of PCl_4^+ .

The expected isotope splitting of the Raman active totally symmetric stretching vibration $\nu_1(A_1)$, resulting from the natural abundance of the isotopes of atomic mass 35 and 37 of chlorine, have also been observed in these compounds. The separation of 3 cm^{-1} and the relative intensities of the observed lines

are in good agreement with the calculated values, as listed in Table III. These isotopic effects provide additional proof for the presence of the PCl_4^+ cation.

TABLE III. Relative Intensities of Isotopic Splittings in the ν_1 of PCl_4^+ in Various Compounds.

Species	Compound 1		Compound 2		Calculated $I_{\text{calc.}}$
	cm^{-1}	I_{obs}	cm^{-1}	I_{obs}	
P^{35}Cl_4	461.5	78	458	86	81
$\text{P}^{35}\text{Cl}_3\text{}^{37}\text{Cl}$	458.5	108	455	108	108
$\text{P}^{35}\text{Cl}_2\text{}^{37}\text{Cl}_2$	456.5	68	452	57	54
$\text{P}^{35}\text{Cl}^{37}\text{Cl}_3$	454	20	449	11	12
P^{37}Cl_4	451	4	--	--	1

$[\text{PCl}_4]/[\text{SbCl}_6^-]$, 1 and $[\text{PCl}_4]/[\text{SbCl}_6^-] \cdot 1/2\text{POCl}_3$, 2

The Raman and infrared spectra of these compounds are presented in Figs. 1 and 2, respectively. Table IV summarizes the numerical frequencies and their assignments, which agree with reported values [3-5].

In addition to the four observed Raman frequencies attributed to the PCl_4^+ cation, three additional lines are assigned to the SbCl_6^- anion. In such an octahedral species of O_h symmetry, three Raman active vibrations are expected, mutually exclusive with two infrared ones. The three observed frequencies are assigned as $\nu_1(A_{1g})$, $\nu_2(E_g)$ and $\nu_5(F_{2g})$ of the octahedral SbCl_6^- anion, displaying the characteristic strong-weak-medium intensity pattern for an MX_6 species. The additional observed frequency at 705 cm^{-1} is most likely an overtone or combination band of the SbCl_6^- , whose spectral part is more intense than that of the PCl_4^+ .

In compound 2, which is the POCl_3 solvate of compound 1, five additional lines were observed and attributed to the POCl_3 vibrations. Most of the

TABLE IV. Vibrational Frequencies of $\text{PCl}_4\text{SbCl}_6^-$ and its Solvates.

Assignment ^a	$[\text{PCl}_4][\text{SbCl}_6]$		$[\text{PCl}_4][\text{SbCl}_6][1/2\text{POCl}_2]$		POCl_3		I (ref. 3)		I (ref. 5)		I (ref. 4)		$[\text{PCl}_4][\text{SbCl}_6][\text{AsCl}_3]$ (ref. 6)	
	R	IR	R	I	R	I	R	I	R	IR	R	I	R	I
$\nu_5(\text{F}_{2g})-\text{SbCl}_6^-$	{ 173 178	41 sh	{ 174 181	57 sh	171	45	172br	168	30	175	60			
$\nu_4(\text{F}_{1u})-\text{SbCl}_6^-$		175s								185vs				180vs
$\nu_2(\text{E})-\text{PCl}_4^+$	190	9	195	9	171	45	172br	143	20	158	20			
$\nu_4(\text{F}_2)-\text{PCl}_4^+$			195	9	192	28								
$\nu_4(\text{F}_2)\text{PCl}_4^+$	252	21	248m	30	252	40	250m	248	10	252m	20	252m		
$\nu_3(\text{A}_1)-\text{POCl}_3$			271	2	269	16								
$\nu_2(\text{Eg})-\text{SbCl}_6^-$	{ 277 288	7 23	{ 285 295	16 23			289m	{ 281 290	10 10	288	30			
$\nu_1(\text{A}_{1g})-\text{SbCl}_6^-$	330	100	332	100	331	70	331vs	334	100	334	100			
$\nu_3(\text{F}_{1u})-\text{SbCl}_6^-$		340vs					345s			336vs				331vs
$\nu_6(\text{E})-\text{POCl}_3$			348	17	339	17								
$\nu_1(\text{A}_1)-\text{PCl}_4^+$	460	27	456	26	455	30	454s	459	30	463	30			
$\nu_2(\text{A}_1)-\text{POCl}_3$			482	8	485	100								
$\nu_4(\text{E})-\text{POCl}_3$			580	0.5	582	br,3								
$\nu_3(\text{F}_2)-\text{PCl}_4^+$	{ 653 658	2	{ 615s 648s	2 1	653	10	643m	652w		{ 644vs 666vs	10	{ 632m 646m		
$2\nu_3$ or $(\nu_1 + \nu_3)-\text{SbCl}_6^-$	705	3												
$\nu_1(\text{A}_1)-\text{POCl}_3$			1300	2	1292	8								

^aR: Raman; IR: infrared; I: relative intensities of Raman frequencies; vs: very strong; m: medium; br: broad.

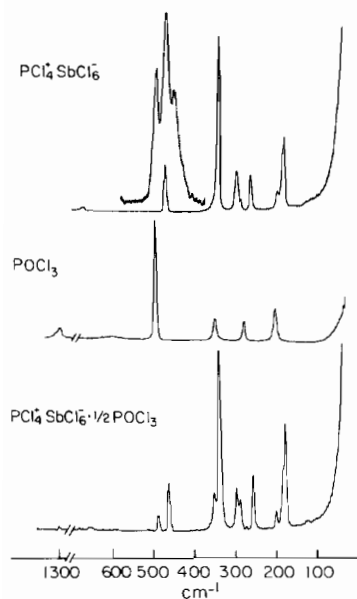


Fig. 1. Raman spectra of $[\text{PCl}_4][\text{SbCl}_6]$, POCl_3 and $[\text{PCl}_4][\text{SbCl}_6] \cdot 1/2\text{POCl}_3$.

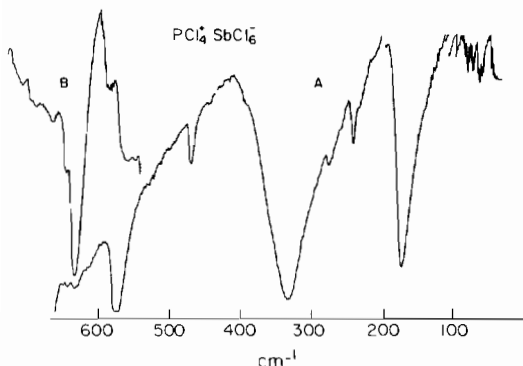


Fig. 2. Infrared spectrum of $[\text{PCl}_4][\text{SbCl}_6]$. (A) polyethylene disc; (B) silver chloride disc.

solvate frequencies are slightly higher than those observed in pure liquid POCl_3 . Such a slight change of frequencies in different phases, namely liquid and solid, is not unexpected. Similarly the vibrations of the ionic species are also slightly different and are in the solvate mostly shifted to higher frequencies. A similar effect is reported for the AsCl_3 solvate of compound 1 [4, 6].

The major difference between our assignments and earlier data relates to $\nu_2(\text{E})$ of PCl_4^+ . The assignment of this vibration at frequencies at 143 cm^{-1} [4] or 158 cm^{-1} [6] is rather low. Similarly the assignment around $171\text{--}172 \text{ cm}^{-1}$ [3, 5], while coinciding with the $\nu_5(\text{F}_{2g})$ of SbCl_6^- , stems probably from failing to resolve the weak (but pronounced) shoulder at 190 cm^{-1} , which we assign as ν_2 of PCl_4^+ in agreement with spectral data of related compounds [1, 2].

However the 195 cm^{-1} line in compound 2 seems to result from the collapse of ν_2 of PCl_4^+ and ν_5 of POCl_3 .

$[\text{PCl}_4][\text{SbCl}_6] \cdot 1/2\text{POCl}_3$, 2, Structural Results

The atomic positional parameters are listed in Table V, while Table VI presents the bond lengths and angles.

The SbCl_6^- anion resides on a crystallographic mirror plane (eight fold) which bisects the antimony atoms and four chlorine atoms Cl(2), Cl(3), Cl(4) and Cl(5). The average Sb–Cl distance is $2.366(7) \text{ \AA}$, similar to that found in many other compounds containing this octahedral ion.

The PCl_4^+ cation resides on a crystallographic two-fold axis (eight fold) with an average P–Cl distance of $1.932(9) \text{ \AA}$ and bond angles of a tetrahedron [2].

As mentioned in the experimental section, the POCl_3 molecule resides on a crystallographic 4 site (four-fold). The distance P–X (X = Cl, O) is $1.881(2)$,

TABLE V. Positional Parameters and e.s.d.s for Compound 2^a.

Atom	x	y	z
Sb	0.62435(3)	0.23659(3)	0.00000
Cl(1)	0.6243(1)	0.2336(1)	–0.15869(9)
Cl(2)	0.4996(2)	0.3373(1)	0.00000
Cl(3)	0.5222(2)	0.1107(1)	0.00000
Cl(4)	0.7270(2)	0.3609(2)	0.00000
Cl(5)	0.7485(2)	0.1329(2)	0.00000
P	0.1327(1)	0.6327	0.25000
Cl(6)	0.1298(1)	0.7408(1)	0.1769(1)
Cl(7)	0.1310(1)	0.5259(1)	0.1730(1)
P(2)	0.00000	0.00000	0.25000
Cl, O	–0.1011(1)	0.0117(2)	0.1731(2)

^aE.s.d.s in the least significant digits are shown in parentheses.

TABLE VI. Bond Lengths (Å) and Angles (deg.) for Compound 2.

Lengths			
Sb–Cl(1)	2.367(1)	Sb–Cl(5)	2.371(2)
Sb–Cl(2)	2.350(2)	P–Cl(6)	1.923(1)
Sb–Cl(3)	2.377(2)	P–Cl(7)	1.942(2)
Sb–Cl(4)	2.363(2)	P(2)–Cl, O	1.881(2)
Angles			
Cl(1)–Sb–Cl(2)	90.65(4)	Cl(3)–Sb–Cl(4)	179.51(8)
Cl(1)–Sb–Cl(3)	89.17(4)	Cl(3)–Sb–Cl(5)	89.17(8)
Cl(1)–Sb–Cl(4)	90.82(4)	Cl(4)–Sb–Cl(5)	90.34(8)
Cl(1)–Sb–Cl(5)	89.34(4)	Cl(6)–P–Cl(7)	109.20(7)
Cl(2)–Sb–Cl(3)	89.86(8)	Cl(6)–P–Cl(6)'	110.92(1)
Cl(2)–Sb–Cl(4)	90.63(8)	Cl(6)–P–Cl(7)'	109.15(1)
Cl(2)–Sb–Cl(5)	179.03(8)	Cl(7)–P–Cl(7)'	109.2(1)

which is near to the average between three P-Cl distances (1.98 Å) and one P=O distance (1.46 Å), as found in the structure of POCl₃ [9].

[PCl₄][NbCl₆], 3 and [PCl₄][NbCl₆]SOCl₂, 4

The Raman spectra of these compounds are presented in Fig. 3. Table VII summarizes the numerical frequencies and their assignments.

Although no spectral data has been reported for compound 3, partial spectral data for a related AsCl₃ solvate has been reported [6]. As in the compounds 1 and 2, seven fundamentals are expected, four of the tetrahedral PCl₄⁺ cation and three of the octahedral anion. Similarly to the former compounds, the anionic vibrations result in more intense lines than the cationic ones and as a result some overtones or combination bands were also observed and assigned. The observed frequencies of the solid solvate are slightly different from those observed in the pure SOCl₂ liquid. The ν₂(E_g) of NbCl₆⁻ in the solvate spectrum seems to collapse with the 284 cm⁻¹ frequency of SOCl₂ and thus its relative intensity in the solvate is higher than in

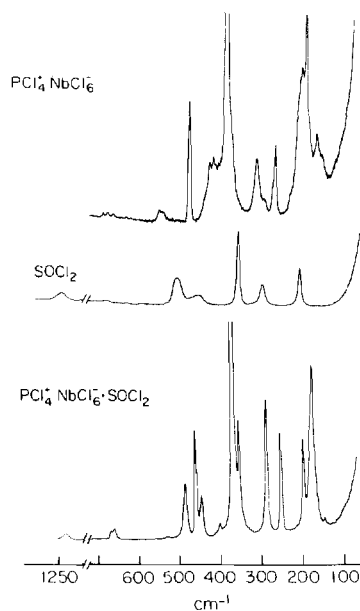


Fig. 3. Raman Spectra of [PCl₄][NbCl₆], SOCl₂ and [PCl₄][NbCl₆]·SOCl₂.

TABLE VII. Vibrational Frequencies of PCl₄⁺NbCl₆⁻ and its Solvates.

Assignment	[PCl ₄][NbCl ₆]			[PCl ₄][NbCl ₆][SOCl ₂]		SOCl ₂		[PCl ₄][NbCl ₆]AsCl ₃ (ref. 6)		
	R	I	IR	R	I	R	I	R	I	IR
ν ₄ (F _{1u})-NbCl ₆ ⁻	144	2	160s	144	1.6					166vs, br
ν ₅ (F _{2g})-NbCl ₆ ⁻	173	21		173	32			176	40	
ν ₂ (E)-PCl ₄ ⁺	{ 180 206	{ 14 sh		180	sh			176	40	
ν ₃ (A')-SOCl ₂				196	18	192	49			
ν ₄ (F ₂)-PCl ₄ ⁺	{ 249 255	{ 7 sh	244m	252	19			253	20	251 S
ν ₂ (E _g)-NbCl ₆ ⁻	{ 275 295	{ 1 6		284	27					
ν ₆ (A'')-SOCl ₂				284	27	284	27			
ν ₃ (F _{1u})-NbCl ₆ ⁻			{ 300vs 360vs							308vs, br
ν ₄ (A')-SOCl ₂				352	22	341	100			
ν ₁ (A _{1g})-NbCl ₆ ⁻	{ 367 400	{ 100 6		{ 366 398	{ 100 2			368	100	
ν ₅ (A'')-SOCl ₂				440	8	438	11			
ν ₁ (A ₁)-PCl ₄ ⁺	455	13		457	21			458	20	
ν ₂ (A')-SOCl ₂				482	10	490	35			
(ν ₁ + ν ₅)-NbCl ₆ ⁻	525	1		525	0.2					
ν ₃ (F ₂)-PCl ₄ ⁺	{ 642 655 665	{ 0.5 0.5 0.5	{ 630vs 655m	{ 652 665	{ 2 2					648vs
ν ₁ (A')-SOCl ₂				1230	5	1229	8			

the pure compound **3**. The observed Raman frequencies of NbCl_6^- are in good agreement with earlier reported values [10].

The attempt to obtain single crystals of compound **3** or **4**, when preparation took place in SOCl_2 , was successful and X-ray data were collected. However, with time the crystals desintegrated and no structural data were available, whereas the structure of compound **3** has been reported [7] when single crystals were grown by sublimation.

All the studies of PCl_5 reactions with covalent halides have yielded compounds in which PCl_5 behaves as a Lewis base forming the PCl_4^+ cation. In no case was the counter anion PCl_6^- identified, which would result from acidic behavior of PCl_5 . Even a rather weak Lewis acid such as NbCl_5 is still more acidic than PCl_5 .

The PCl_6^- anion has been formed only by reacting PCl_5 with ionic salts such as tetra-alkyl ammonium chlorides.

Supplementary Material Available

Tables of structure factors and thermal parameters for compound **2** (6 pages). Copies are available on request from A.B.

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