Formation and Crystal Structure of 2,3,5-Triphenyltetrazolium Hexachlorophosphate and Dichlorophosphate(V), $[TPT]^+[PCl_6]^-$ and $[TPT]^+[PO_2Cl_2]^-$

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2,3,5-Triphenyltetrazolium hexachlorophosphate, $[C_{19}H_{15}N_4]^+[PCl_6]^-$, $[TPT]^+[PCl_6]^-$ (**1**), and 2,3,5-triphenyltetrazolium dichlorophosphate(V), $[C_{19}H_{15}N_4]^+[PO_2Cl_2]^-$, $[TPT]^+[PO_2Cl_2]^-$ (**2**), were synthesized by reactions of anhydrous 2,3,5-triphenyltetrazolium chloride, $[TPT]^+Cl^-$, and 2,3,5-triphenyltetrazolium chloride monohydrate $[TPT]^+Cl^- \cdot H_2O$, with PCl_5 in dry acetonitrile, and their crystal structures were determined by single-crystal X-ray diffraction analysis. In the title compounds, the $[TPT]^+$ cations show a face-to-face stacked orientation between the phenyl rings of neighboring molecules, which is caused by intermolecular $\pi \cdots \pi$ interactions. The crystal structure of compound **1** consists of layers of 2,3,5-triphenyltetrazolium cations and hexachlorophosphate anions. In compound **2** the tetrahedral $[PO_2Cl_2]^-$ anions exhibit approximate C_{2v} symmetry with P–O bond lengths from 1.454 to 1.463 Å and P–Cl bond lengths from 2.038 to 2.050 Å. The Raman spectrum of compound **1** was recorded, and the assignment of the $[PCl_6]^-$ Raman modes is proposed.

Key words: 2,3,5-Triphenyltetrazolium Hexachlorophosphate(V), 2,3,5-Triphenyltetrazolium Dichlorophosphate(V), $[PCl_6]^-$, $[PO_2Cl_2]^-$, Crystal Structure, Raman Spectroscopy

Introduction

2,3,5-Triphenyltetrazolium chloride, TTC (a commercial product), and other tetrazolium salts are mainly used as color indicators for the determination of reduction equivalents in diagnostic applications as well as in clinical research and cell biology [1]. Otherwise, TTC acts as an excellent chloride ion donor for Lewis acidic metal chlorides as, *e. g.*, $SbCl_5$, $CdCl_2$, $CoCl_2$, or $CuCl_2$ leading to the respective chlorometallates [2 – 5]. With other anions also stable compounds as for example $[TPT]^+[ReO_4]^-$ (triphenyltetrazolium perrhenate), or solvates like $TTC \cdot H_2O$ (triphenyltetrazolium chloride hydrate), are formed [1, 6]. TTC might also be used for studies of salt syntheses where the size of the cationic group is related to the kind and structure of the corresponding anionic units.

Usually, phosphorus pentachloride behaves as strong chloride ion donor giving $[PCl_4]^+$ as an indicative unit in vibrational spectroscopic investigations [7 – 9]. On the other hand, the examples of phosphorus pentachloride acting as chloride ion acceptor resulting in $[PCl_6]^-$ are scarce. Only CsCl, the strongest chloride ion donor among the alkali chlorides, is able to form the unique $Cs^+[PCl_6]^-$ [10]. Furthermore and until now, hexachlorophosphates are only known with large polyatomic cations as, *e. g.*, $[Ph_4P]^+$ [11], $[N(PCl_3)_2]^+$ [12, 13], and $[P(NPCl_3)_4]^+$ [14].

Otherwise, general structural informations of dichlorophosphates(V) are scarce, too. From vibrational spectra it has been concluded that $[PO_2Cl_2]^-$ acts mainly as a bridging unit in main group and transition metal compounds [15 – 18]. The complete vibrational spectrum of $[(CH_3)_4Sb]$ $[PO_2Cl_2]$ is known allowing the conclusion that it is built up ionically [19], as well as its homolog $[(CH_3)_4As]^+$ $[PO_2Cl_2]^-$ [20], referenced in [19]. The first X-ray crystal structure determination of the $[PO_2Cl_2]^-$ anion in 2-chloro-1,3-diisopropyl-4,5-dimethyl-imidazolium dichlorophosphate(V) was published 2002 by Kuhn *et al.* [21]. Furthermore, the crystal structure of cyclohexyl *tert*-butyl ammonium dichlorophosphate(V) was published recently [22]. The fortuitous encounter of single crystals of the title compound **2** now gave the opportunity to determine its structure.

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Table 1. Crystal and structure refinement data of $[TPT]^+[PCl_6]^-$ (**1**) and $[TPT]^+[PO_2Cl_2]^-$ (**2**).

Formula	$C_{19}H_{15}Cl_6N_4P$	$C_{19}H_{15}Cl_2N_4O_2P$
M_r, g mol^{-1}	543.02	433.22
Crystal size, mm^3	$0.29 \times 0.27 \times 0.26$	$0.28 \times 0.25 \times 0.24$
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a, Å	9.288(2)	15.791(3)
b, Å	10.291(2)	16.124(2)
c, Å	13.959(3)	17.476(2)
α, deg	87.05(1)	90
β, deg	78.75(1)	114.70(1)
γ, deg	63.38(1)	90
V, Å^3	1168.9(3)	4042.4(9)
Z	2	8
D_{calc}, g cm^{-3}	1.54	1.42
μ (MoK_α), mm^{-1}	0.8	0.4
$F(000)$, e	548	1776
T, K	223(2)	223(2)
2θ range, deg	1.00 – 25.68	1.00 – 25.00
hkl ranges	$-11 \le h \le 11$, $-12 \le k \le 12$, $-15 \le l \le 17$	$-18 \le h \le 18$, $-18 \le k \le 18$, $-20 \le l \le 20$
Refl. measured / unique	18955 / 4394	17783 / 6745
R_{int}	0.0487	0.0565
Param. refined	331	625
R_1 $[I \ge 2\sigma(I)]$[a]	0.0406	0.0435
wR_2 $[I \ge 2\sigma(I)]$[a]	0.0790	0.0963
R_1 (all data)[a]	0.0652	0.0516
wR_2 (all data)[a]	0.0869	0.1011
Parameters A / B (weighting scheme)[b]	0.0352 / 0.3339	0.0437 / 2.8713
GoF (F^2)[c]	1.059	1.045
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.34 / −0.29	0.75 / −0.63

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$;
[b] $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$;
[c] GoF = $[\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

Results and Discussion

Direct treatment of anhydrous 2,3,5-triphenyltetrazolium chloride, $[TPT]^+Cl^-$, or 2,3,5-triphenyltetrazolium chloride monohydrate, $[TPT]^+Cl^- \cdot H_2O$, with PCl_5 in dry acetonitrile provided the colorless crystalline solids of compounds **1** and **2**, respectively. The products are extremely sensitive to air and moisture, but can be stored safely under an atmosphere of dry nitrogen.

The $[TPT]^+$ cation is common to both salts. This presents an opportunity to compare its structure in different compounds. The C–N and N–N bond lengths in the tetrazolium ring do not vary significantly between both structures (Table 2). Comparison with other crystal structures of 2,3,5-triphenyltetrazolium salts reveals that the internal dimensions of the $[TPT]^+$ cation are largely insensitive to the local environment [2, 23].

Table 2. Interatomic distances (Å) and angles (deg) for the $[TPT]^+$ cation in **1** and **2** with estimated standard deviations in parentheses.

Compound 1			
N(1)–N(5)	1.312(3)	N(3)–C(4)	1.448(3)
N(1)–N(2)	1.341(3)	N(5)–C(4)	1.349(4)
N(2)–N(3)	1.305(3)	N(2)–C(12)	1.448(3)
N(1)–C(6)	1.449(3)	C(4)–C(18)	1.460(4)
N(2)–N(1)–N(5)	110.2(2)	N(1)–N(2)–C(12)	123.2(2)
N(2)–N(1)–C(6)	124.3(2)	N(2)–N(3)–C(4)	103.8(2)
N(5)–N(1)–C(6)	125.5(2)	N(1)–N(5)–C(4)	103.4(2)
N(1)–N(2)–N(3)	110.1(2)	N(3)–C(4)–N(5)	112.4(2)
N(3)–N(2)–C(12)	126.7(2)	N(3)–C(4)–C(18)	123.9(3)
Compound 2			
N(1)–N(5)	1.309(3)	N(24)–N(28)	1.314(2)
N(1)–N(2)	1.328(3)	N(24)–N(25)	1.326(3)
N(2)–N(3)	1.314(2)	N(25)–N(26)	1.315(3)
N(1)–C(6)	1.444(3)	N(24)–C(29)	1.447(3)
N(3)–C(4)	1.333(3)	N(26)–C(27)	1.345(3)
N(5)–C(4)	1.347(3)	N(26)–C(27)	1.333(3)
N(2)–N(1)–N(5)	109.9(2)	N(25)–N(24)–N(28)	110.0(2)
N(2)–N(1)–C(6)	126.2(2)	N(28)–N(24)–N(29)	123.5(2)
N(5)–N(1)–C(6)	123.8(2)	N(25)–N(24)–C(29)	126.4(2)
N(1)–N(2)–N(3)	110.3(2)	N(26)–N(25)–C(24)	110.2(2)
N(3)–N(2)–C(12)	122.9(2)	N(26)–N(25)–C(35)	124.2(2)
N(1)–N(2)–C(12)	126.8(2)	N(24)–N(25)–C(35)	125.6(2)
N(2)–N(3)–C(4)	103.6(2)	N(25)–N(26)–C(27)	103.3(2)
N(1)–N(5)–C(4)	103.7(2)	N(24)–N(28)–C(27)	103.8(2)
N(3)–C(4)–N(5)	112.5(2)	N(24)–N(28)–C(27)	112.7(2)

Crystal and molecular structures

*2,3,5-Triphenyltetrazolium hexachlorophosphate, $[TPT]^+[PCl_6]^-$ (**1**)*

$[TPT]^+[PCl_6]^-$ crystallizes in the triclinic space group $P\bar{1}$ (no. 2) with two formula units in the unit cell (Table 1). The crystal structure of compound **1** consists of layers of 2,3,5-triphenyltetrazolium cations and hexachlorophosphate anions. The closest interaction contact C(10)···Cl–PCl_5 (3.389 Å) is slightly shorter than the analogous closest contact taken from the crystal structure of $[TPT]^+[SbCl_6]^-$ (3.538 Å) [2] (Fig. 1). However, in both cases, the contacts are close to the van der Waals distance, and the interactions appear to be largely of a Coulomb type. No hydrogen bonds are found.

The packing diagram of compound **1** shows the face-to-face stacked orientation between the phenyl rings of neighboring molecules, which is caused by intermolecular $\pi \cdots \pi$ interactions (Fig. 2). The closest contact between the neighboring phenyl rings is 3.68 Å, which is in excellent agreement with the values determined for the simplest pro-

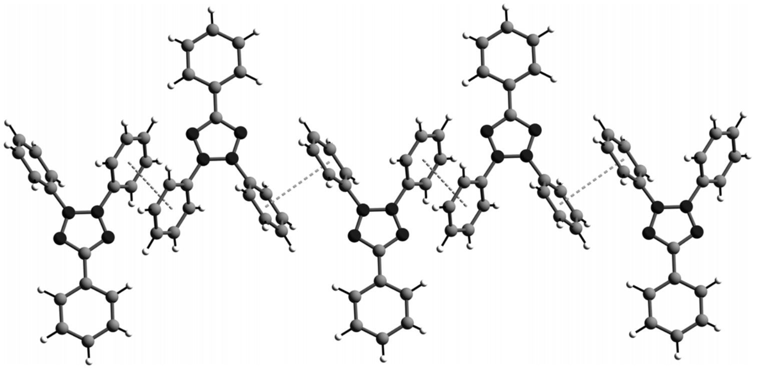

Fig. 2. Face-to-face stacking of the phenyl rings in crystals of compound **1**.

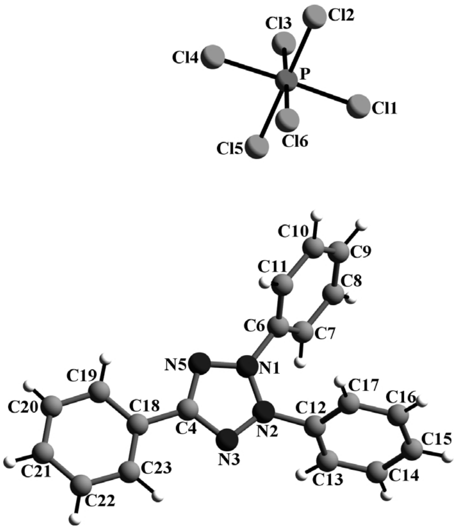

Fig. 1. Perspective view of the [TPT]$^+$ cation and the [PCl$_6$]$^-$ anion in compound **1**.

totype of $\pi\cdots\pi$ interactions, the benzene dimer [24, 25].

The five atoms in the tetrazolium ring [N(1), N(2), N(3), C(4) and N(5)] are coplanar. N(1)–N(5) and N(2)–N(3) are almost equivalent (1.305 and 1.312 Å) (Table 2). The N(1)–N(2) bond (1.341 Å) is longer than the former two bonds. This may be ascribed to the repulsion between the relevant phenyl groups. The torsion angles of the phenyl rings are 116.00, 117.83 and 176.27°. These values agree well with those reported for $\{[\mathrm{TPT}]^+\}_2[\mathrm{CdCl_4}]^{2-}$ [26], $[\mathrm{TPT}]^+[\mathrm{CoCl_2(NPh{=}N{-}CPh{=}N{-}NPh]^-}$ [27] and $[\mathrm{TPT}]^+[\mathrm{SbCl_6}]^-$ [2].

The anionic unit is placed in an approximately octahedral O_h symmetry with *cis*-Cl–P–Cl angles all within a 1.19° deviation from 90°, and *trans*-Cl–P–Cl angles of 177.6 and 178.1° in the equatorial positions, and 178.0° in the axial positions. The average P–Cl$_{\mathrm{ax}}$ and P–Cl$_{\mathrm{eq}}$ bond lengths are 2.127 and 2.146 Å (Table 3). These data correspond very well with those found in $[\mathrm{NP_2Cl_6}]^+[\mathrm{PCl_6}]^-$ and $[\mathrm{N(PCl_3)_2}]^+[\mathrm{PCl_6}]^-$ [13].

Table 3. Selected interatomic distances (Å) and angles (deg) for [TPT]$^+$[PCl$_6$]$^-$ (**1**) and [TPT]$^+$[PO$_2$Cl$_2$]$^-$ (**2**).

Compound 1			
P–Cl(1)	2.114(1)	P–Cl(4)	2.140(1)
P–Cl(2)	2.118(1)	P–Cl(5)	2.161(1)
P–Cl(3)	2.122(1)	P–Cl(6)	2.182(1)
Cl(1)–P–Cl(2)	91.19(5)	Cl(2)–P–Cl(5)	177.63(5)
Cl(1)–P–Cl(3)	91.18(5)	Cl(3)–P–Cl(5)	90.58(4)
Cl(2)–P–Cl(3)	91.70(5)	Cl(4)–P–Cl(5)	89.15(4)
Cl(1)–P–Cl(4)	178.00(5)	Cl(1)–P–Cl(6)	89.40(5)
Cl(2)–P–Cl(4)	90.17(5)	Cl(2)–P–Cl(6)	90.13(5)
Cl(3)–P–Cl(4)	90.26(5)	Cl(3)–P–Cl(6)	178.07(5)
Cl(1)–P–Cl(5)	89.44(5)	Cl(4)–P–Cl(6)	89.13(5)
Compound 2			
P(1)–O(1)	1.454(2)	P(2)–O(3)	1.456(2)
P(1)–O(2)	1.463(2)	P(2)–O(4)	1.463(2)
P(1)–Cl(1)	2.038(1)	P(2)–Cl(3)	2.046(1)
P(1)–Cl(2)	2.050(1)	P(2)–Cl(4)	2.050(1)
O(1)–P(1)–O(2)	124.27(8)	O(3)–P(2)–O(4)	123.97(9)
O(1)–P(1)–Cl(1)	107.51(9)	O(3)–P(2)–Cl(3)	108.57(9)
O(1)–P(1)–Cl(2)	108.56(9)	O(3)–P(2)–Cl(4)	106.66(8)
O(2)–P(1)–Cl(1)	108.05(9)	O(4)–P(2)–Cl(3)	107.11(8)
O(2)–P(1)–Cl(2)	105.89(8)	O(4)–P(2)–Cl(4)	107.81(8)
Cl(1)–P(1)–Cl(2)	99.89(5)	Cl(3)–P(2)–Cl(4)	100.19(5)

*2,3,5-Triphenyltetrazolium dichlorophosphate, [TPT]$^+$[PO$_2$Cl$_2$]$^-$ (**2**)*

Title compound **2** crystallizes in the monoclinic space group $P2_1/n$ (no. 14) with eight formula units per unit cell. The asymmetric unit of the structure contains two independent [TPT]$^+$ cations and [PO$_2$Cl$_2$]$^-$ anions (Table 1).

The phosphorus atoms P(1) and P(2) have slightly distorted tetrahedral coordination, with P–O bond

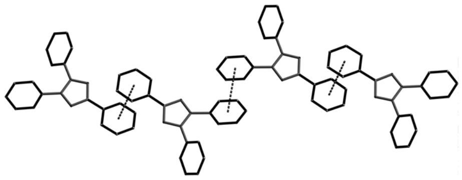

Fig. 3. Face-to-face stacking of the phenyl rings forming compound **2**. (Hydrogen atoms have been omitted for clarity).

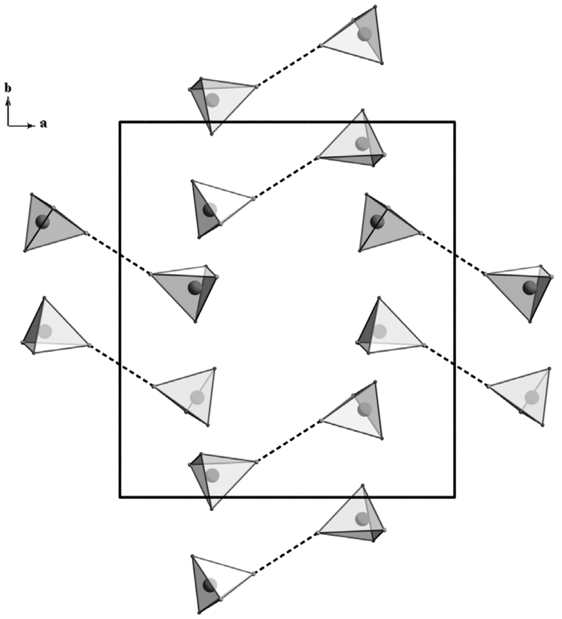

Fig. 4. Cl···Cl interactions in the crystal structure of $[TPT]^+[PO_2Cl_2]^-$ (**2**).

lengths from 1.454 to 1.463 Å (Table 3), in agreement with a normal double bond length (1.45 Å) [28]. The P–Cl bond lengths range from 2.038 to 2.050(1) Å. The bond angles around P(1) range from 99.9 to 124.3°. The minimum and maximum values of angles are observed for Cl(1)–P(1)–Cl(2) and O(1)–P(1)–O(2), respectively. For P(2), bond angles are in the region of 100.2 – 124.4°, with the smallest angle Cl(3)–P(2)–Cl(4) and the largest O(3)–P(2)–O(4) (Table 3).

There is a $\pi \cdots \pi$ stacking interaction between parallel aromatic phenyl rings, as shown in Fig. 3. The interplanar distance of the phenyl ligands is 3.799 Å, again close to the values found for the benzene dimer [24, 25].

The chlorine atoms of the $[PO_2Cl_2]^-$ ions play an important role in the packing of the tetrahedral units, with a Cl(2)···Cl(3) distance of 3.769 Å. This value indicates slight van der Waals attraction [29, 30] (Fig. 4).

Table 4. Raman frequencies (cm^{-1}) of crystalline $[TPT]^+$ $[PCl_6]^-$ (**1**) below 500 cm^{-1} along with their estimated intensities and proposed assignment[a].

$[TPT]^+[PCl_6]^-$ Raman	$[PCl_6]^-$ in crystalline $[PCl_4]^+[PCl_6]^-$ [b]	Assignment / O_h mode description
354 vvs	360	ν_1 / A_{1g} : ν_s
	444	ν_3 / F_{1u} : ν_{as}
270 sh / 262 m	283	ν_2 / E_g : ν
240 sh	238	ν_5 / F_{2g} : δ
	285	ν_4 / F_{1u} : δ
	[168][c]	[ν_6 / F_{2u} : (i. a.)]?
100 sh, 81 vs		Lattice vibration

[a] Estimated intensities: s: strong, m: medium, w: weak, v: very, sh: shoulder. ν: stretching, δ: bending; [b] ref. [31]; [c] estimated value [32].

Footnote 1. Raman (cm^{-1} / intensity) of crystalline $[TPT]^+$-$[PCl_6]^-$: 3098 vw, 3072 s, 3048 sh, 1607 vvs, 1585 s, 1526 vs, 1487 m, 1454 s, 1415 w, 1372 s, 1329 w, 1225 w-m, 1160 w, 1077 w, 1026 w, 1003 vs, 679 w, 618 vw, 405 vw, 354 vvs, 270 sh, 240 sh, 100 sh, 81 vs.

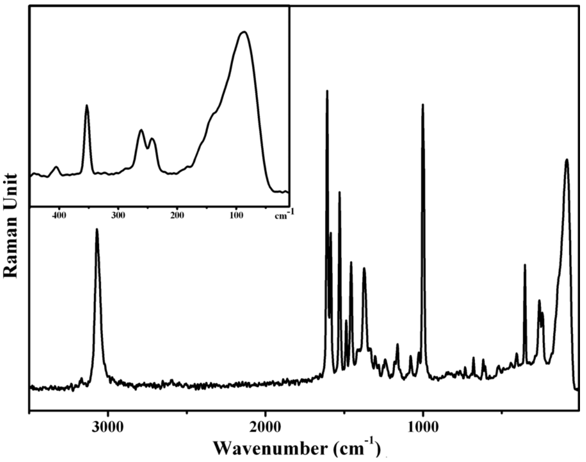

Fig. 5. FT-Raman spectrum ($\lambda_{exc.}$ = 1064 nm) of crystalline $[TPT]^+[PCl_6]^-$ (**1**). Insert: $[PCl_6]^-$-relevant frequency region below 450 cm^{-1}. (Raman intensity in arbitrary units).

Raman spectrum of [TPT] [PCl₆] and band assignment for 2,3,5-triphenyltetrazolium hexachlorophosphate, $[TPT]^+[PCl_6]^-$ (1)

Compound **1** does consist of $[TPT]^+$ cations and $[PCl_6]^-$ anions. Both units can be clearly detected by Raman spectroscopy (Fig. 5). In this contribution the vibrational behavior of $[PCl_6]^-$ is the more interesting part, therefore the Raman spectrum of crystalline $[TPT]^+[PCl_6]^-$ is considered only in the relevant range below 500 cm^{-1}.

The vibrational frequencies of the $[PCl_6]^-$ unit of **1** are presented in Table 4 along with the proposed assignments and in comparison to literature data [31, 32].

The $[TPT]^+$ frequencies are very similar to those of $[TPT]^+Cl^-$ [33] and $[TPT]^+[SbCl_6]^-$ [2], and they are only given in footnote 1 below Table 4.

A vibrational analysis for the octahedral $[PCl_6]^-$ unit delivers [31]:

$$\Gamma_{\text{vib}}([\text{PCl}_6]^-/O_h) = \text{A}_{1g}\ (\text{RE}) + \text{E}_g\ (\text{RE}) + 2\ \text{F}_{1u}\ (\text{IR}) + \text{F}_{2g}\ (\text{RE}) + \text{F}_{2u}\ (\text{i.a.}),$$

with RE = Raman, IR = Infrared and i. a. = inactive, and with $A_{1g} + E_g + F_{1u}$ as stretching and $F_{1u} + F_{2g}$ as bending modes.

The assignment given for the $[PCl_6]^-$ modes of **1** is made in analogy to the measured $[PCl_6]^-$ frequencies of solid phosphorus pentachloride consisting of $[PCl_4]^+[PCl_6]^-$ ions (*c.f.* Table 4). The vibrational frequencies of $[PCl_6]^-$ are all consistent with the octahedral structure and in agreement with other experimental values [10, 12, 32]. The strongest Raman band at 354 cm^{-1} belongs to ν_1 / A_{1g}, the medium Raman mode at 262 cm^{-1} to ν_2 / E_g and the one at 240 cm^{-1} to ν_5 / F_{2g}. The modes below 100 cm^{-1} are ascribed to lattice vibrations.

Concluding Remarks

A further member in the very exclusive group of salt-like dichlorophosphates(V) could be obtained and structurally characterized. $[TPT]^+[PO_2Cl_2]^-$ exhibits a combination of interactions, namely ionic combined with weak π-π stacking interactions between parallel packed phenyl rings of the [TPT] cations. Compound **2** is soluble in CH_3CN, and it could be used for the preparation of further unknown dichlorophosphates(V) by salt metathesis reactions, as *e. g.* for the synthesis of alkali compounds $M^IPO_2Cl_2$.

Experimental Section

Materials and methods

All manipulations and chemical reactions were performed in a dry argon atmosphere using standard Schlenk, vacuum-line and glove-box techniques. Phosphorus pentachloride (p. a. $\geq$ 98.0 %, Fluka) and 2,3,5-triphenyltetrazolium chloride (p. a. $\geq$ 99.0 %, Fluka) were used without additional purification. CH_3CN was distilled and dried over P_4O_{10}. The melting temperatures were determined on a Büchi 520 apparatus, and the given temperatures are uncorrected values. The FT-Raman spectrum of the solid compound **1** was recorded with a Raman module FRA 106 (Nd:YAG laser, 1064 nm) attached to a Bruker IFS 66v interferometer.

2,3,5-Triphenyltetrazolium hexachlorophosphate (1)

Anhydrous 2,3,5-triphenyltetrazolium chloride (TTC) was synthesized according to the literature [34]. A mixture of 335 mg (1 mmol) TTC (dried for 2 h at 120 °C) and of 208.5 mg (1 mmol) PCl_5 was gently heated until a homogenous melt was formed (150 °C, 10 min). After cooling to r. t. 10 mL of dry CH_3CN was added giving a clear solution on warming up. After one week colorless single crystals (0.293 mg) of the title compound grew in the solution. The melting temperature was found to be 150 – 152 °C. Yield: 54 %. $C_{19}H_{15}Cl_6N_4P$ (543.04): calcd. C 42.02, H 2.78, N 10.32; found C 41.68, H 2.97, N 10.01.

2,3,5-Triphenyltetrazolium dichlorophosphate(V) (2)

A mixture of 352.5 mg (1 mmol) $TTC \cdot H_2O$ and of 208.5 mg PCl_5 (1 mmol) was gently heated until a homogeneous melt was formed. After cooling to r. t. 10 mL of dry CH_3CN was added giving a clear solution on warming up. After several days colorless crystals (112 mg) of the title compound were formed. The melting temperature was found to be 170 – 175 °C. Yield: 25.6 %. $C_{19}H_{15}Cl_2N_4O_2P$ (433.22): calcd. C 52.68, H 3.49, N 12.93; found C 52.31, H 3.67, N 12.57.

The formation of $[PO_2Cl_2]^-$ in this preparation of $[TPT]^+[PCl_6]^-$ is due to the presence of water in the reaction mixture (*c.f.* ref. [6]). Formation of $[PO_2Cl_2]^-$ *respective* $[TPT]^+[PO_2Cl_2]^-$ is possible by partial hydrolysis of PCl_5 *via* $POCl_3$ and its primary hydrolysis product HPO_2Cl_2 [35] in the presence of Cl^- according to: $PCl_5 + 2\ H_2O + [TPT]^+[Cl]^- = [TPT]^+[PO_2Cl_2]^- + 4\ HCl$.

X-Ray crystallography

Suitable single crystals of the title compounds were selected under oil protection with the help of a polarization microscope and transferred to 0.3 mm quartz capillaries. The X-ray reflection data were collected on a Stoe-II single-crystal X-ray diffractometer with MoK_α radiation (λ = 0.71073 Å) at a temperature of 223 K. Structure solution and refinements were carried out by Direct Methods using the programs SHELXS-97 and SHELXL-97 [36]. All non-H atom positions were refined anisotropically. Hydrogen atom positions were determined by final Difference Fourier Synthesis. Details of crystal data and structure refinement parameters are summarized in Table 1. For producing the structure drawings the programs DIAMOND [37] and POV-RAY [38] were used.

CCDC 734856 (**1**), and CCDC 734857 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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