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Solvothermal Synthesis and Crystal Structure of A Supramolecular Compound *Tris*(*tert*-butylamino)chlorophosphonium Chloride

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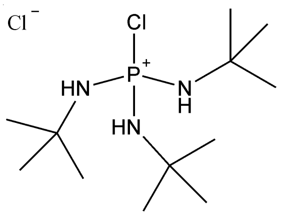
During the research of the reaction of $OP(NHt\text{-}Bu)_3$ and $ZnCl_2$ with hydrochloric acid in toluene, the crystal of the *tris*(*tert*-butylamino)chlorophosphonium chloride $[ClP(NHt\text{-}Bu)_3](Cl)$ (**1**) was obtained under solvothermal reaction condition. The single-crystal X-ray diffraction reveals the title compound crystallizes in space group $P2_1/c$ (No. 14) with a = 15.280(3) Å, b = 9.2100(18) Å, c = 12.790(3) Å, $\alpha = 90°$, $\beta = 93.19(3)°$, $\gamma = 90°$, V = 1797.1(6) $Å^3$, Z = 4, $D_c = 1.176$ g cm^{-3}, $F_{(000)} = 688$, $\mu = 0.44$ mm^{-1}. The phosphorus atom of cation is located in the center of a tetrahedron constructed of a chloride atom and three N atoms of three NHt-Bu groups. The anion of Cl^- is connected with a cation and adjacent cation through three N-H···Cl hydrogen bonds. And through these hydrogen bonds, a zig-zag supramolecular chain is formed, which array all along the c axis.

Key Words: Solvothermal synthesis, Hydrogen bonds, Supramolecular structure.

INTRODUCTION

The preparation and structural characterization of imido analogues of common phosphorus oxoanions is an active area of main group chemistry[1-4]. Chivers *et al.*[5] found that $OP(NHt\text{-}Bu)_3$ could be protonated and converted to a cation under hydrothermal condition with $CuCl_2$[5]. Armstrong *et al.*[6] had also investigated the reaction of $OP(NHt\text{-}Bu)_3$ and $ZnMe_2$ and successfully synthesized some novel zinc cluster compounds exhibited interesting molecular structure. Being motivated these researches, we employed $OP(NHt\text{-}Bu)_3$, $ZnCl_2$ and hydrochloric acid as reactor to synthesize novel zinc coordinated compound, but a new organic phosphorous cation compound featured as a supramolecular structure was obtained (**Scheme-I**). During the past decades, a large number of supramolecular structures have been assembled and characterized due to their interesting structure and many respected applications in sensors, catalysis, optical/optoelectronic and magnetic materials *etc.*[7-13]. Here, we report the solvothermal synthesis and crystal structure of a supramolecular compound $[ClP(NHt\text{-}Bu)_3](Cl)$ (**1**).



Scheme-I

EXPERIMENTAL

Synthesis of $[ClP(NHt\text{-}Bu)_3](Cl)$ (1): All chemicals were obtained from commercial sources and used as received. The title compound was synthesized by a solvothermal reaction from toluene. The solvothermal treatment of $ZnCl_2$ (1 mmol) with $OP(NHt\text{-}Bu)_3$ (1 mmol) in HCl (1 mL) and toluene (10 mL) at 353 K for 2 days produces $[ClP(NHt\text{-}Bu)_3](Cl)$ crystals after cooling down to room temperature, yield 25 % (based on $OP(NHt\text{-}Bu)_3$).

Single crystal structure determination: X-Ray intensity data for **1** were collected on a black prism crystal (0.20 mm × 0.10 mm × 0.10 mm) at 153(2) K on a Bruker P4 CCD area detector diffractometer using graphite monochromated MoK_α radiation ($\lambda = 0.071073$ nm). The structure was solved using direct methods and refined by full-matrix least-squares techniques. All non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. All hydrogen atoms were added at calculated positions and refined using a riding model. The structure was refined on F^2 using SHELXTL-97 software package without any unusual events[14]. The crystal and refinement details for compound **1** are listed in Table-1. The selected bond lengths and bond angles are gathered in Table-2.

TABLE- 1
CRYSTAL DATA, COLLECTION AND STRUCTURE REFINEMENT PARAMETERS FOR COMPOUND **1**

	$C_{12}H_{30}ClN_3PCl$ (**1**)
Empirical formula	$C_{12}H_{30}Cl_2N_3P$
Formula weight	318.26
Temperature (K)	153(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Crystal size (mm^3)	0.20 × 0.10 × 0.10
Crystal description	Chunk, colorless
a (Å)	15.280(3)
b (Å)	9.2100(18)
c (Å)	12.790(3)
β (°)	93.19(3)
Volume V(Å^3)	1797.1(6)
Z	4
D_{calc} (Mg m^3)	1.176
μ (mm^{-1})	0.44
$F_{(000)}$	688
$2\theta_{max}$ (deg.)	54.82
Final R indices [$I > 2\sigma(I)$]$^{\#}$	$R_1 = 0.0547$, $wR_2 = 0.1582$
R indices (all data)$^{\#}$	$R_1 = 0.0627$, $wR_2 = 0.1632$
Goodness-of-fit on F^2	1.037

$$^{\#}R_1 = \sum\left(\left\|Fo\right| - \left|Fc\right\|\right) / \sum\left|Fo\right| ; \quad wR_2 = \left\{\frac{\sum w[(Fo^2 - Fc^2)]}{\sum w[(Fo^2)^2]}\right\}^{0.5}$$

TABLE- 2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) FOR **1**

Cl1-P1	2.0378(11)	P1-N1	1.609(3)
P1-N2	1.614(3)	P1-N3	1.602(3)
N1-C1	1.496(4)	N2-C5	1.501(4)
N3-C9	1.498(4)	–	–
N1-P1-Cl1	110.41(11)	N2-P1-Cl1	110.51(11)
N3-P1-Cl1	100.30(10)	N1-P1-N2	102.28(14)
N3-P1-N1	115.80(15)	N3-P1-N2	117.71(15)
C1-N1-P1	130.1(2)	C5-N2-P1	130.5(2)
C9-N3-P1	130.1(2)	–	–

RESULTS AND DISCUSSION

We have synthesized the supramolecular compound [ClP(NHt-Bu)$_3$](Cl) (**1**) (Figs. 1 and 2), which crystallizes in a monoclinic system and adopts a centrosymmetric space group of $P2_1/c$. In the cation of compound **1**, the central phosphorus atom has tetrahedral coordination sphere. The coordination environment of P atom is constituted of a chloride atom and three N atoms of three NHt-Bu groups (Fig. 1). Three big *t*-Bu groups of the exterior of the cation surround the centre of the PN_3Cl tetrahedron and the cation look like a tripod structure on the whole. The anion is a Cl^- and it is connected with the cation and adjacent cation with three N-H···Cl hydrogen bonding interactions. One is N1-H1A···Cl2 bond with D···A distance of 3.220 (3) Å, the second one is N2-H2A···Cl2 bond with D···A distance of 3.224 (3) Å and the third one is N3-H3A···Cl2 bond with D···A distance of 3.199(3) Å. Then through these hydrogen bonding interactions, all adjacent cations and anions connect each other along c axis to give out of a supramolecular zig-zag like infinite chain (Fig. 2). The hydrogen bonding data of lengths and angles are in the range of ordinary examples and have been examined by the PLATON program[15,16]. The details of hydrogen bonding interactions are shown in Table-3.

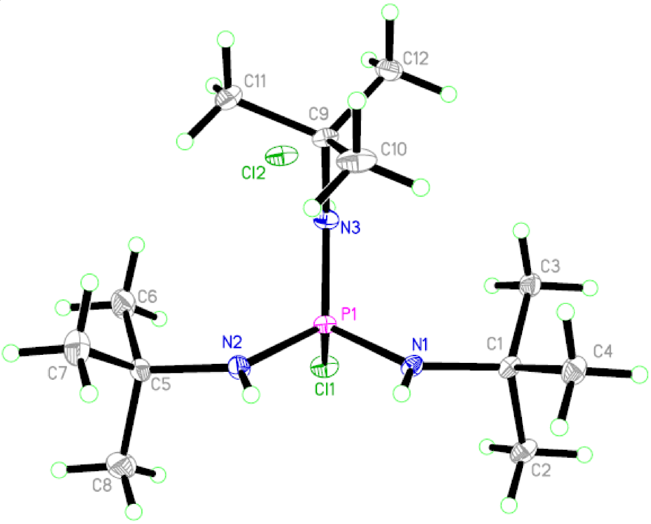


Fig. 1. Structure and labeling of the compound **1**, with displacement ellipsoids drawn at the 30 % probability level and H atoms shown as small spheres of arbitrary radii

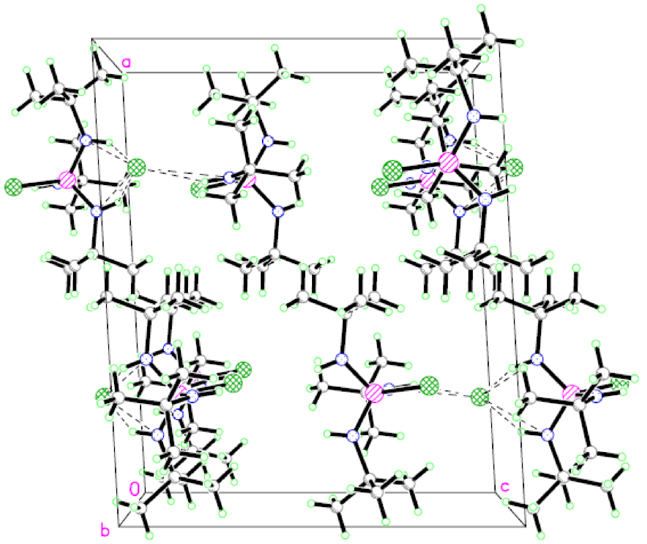


Fig. 2. Packing diagram viewed along the b-direction, the dash lines present as the hydrogen bonds. (Cl, green; P, purple; N, blue; C, gray; H, white)

TABLE- 3
HYDROGEN-BOND GEOMETRY (Å, °) FOR **1**

D-H···A	D-H	H···A	D···A	D-H···A
N1-1A···Cl2^{i}	0.86(3)	2.58(3)	3.220(3)	132(3)
N2-2A···Cl2^{i}	0.86(3)	2.59(3)	3.224(3)	132(3)
N3-3A···Cl2	0.86(2)	2.39(2)	3.199(3)	158(2)
C6-6A···Cl1	0.96(4)	2.76(4)	3.488(4)	133(4)

Symmetry codes: (i) x, -y + 1/2, z + 1/2.

Conclusion

The supramolecular compound [ClP(NHt-Bu)$_3$](Cl) has been synthesized and characterized as a supramolecular zig-zag chain structure constructed by three type of N-H···Cl hydrogen bonding interactions.

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