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 $\text{OP}(\text{NHt-Bu})_3$ and ZnCl_2 with hydrochloric acid in toluene, the crystal of the *tris(tert-butylamino)chlorophosphonium chloride* $[\text{CIP}(\text{NHt-Bu})_3](\text{Cl})$ (**1**) was obtained under solvothermal reaction condition. The single-crystal X-ray diffraction reveals the title compound crystallizes in space group $\text{P2}_1/\text{c}$ (No. 14) with $a = 15.280(3) \text{ \AA}$, $b = 9.2100(18) \text{ \AA}$, $c = 12.790(3) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 93.19(3)^\circ$, $\gamma = 90^\circ$, $V = 1797.1(6) \text{ \AA}^3$, $Z = 4$, $D_c = 1.176 \text{ g cm}^{-3}$, $F_{(000)} = 688$, $\mu = 0.44 \text{ mm}^{-1}$. 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 $\text{N-H}\cdots\text{Cl}$ 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 chemistry¹⁻⁴. Chivers *et al.*⁵ found that $\text{OP}(\text{NHt-Bu})_3$ 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 $\text{OP}(\text{NHt-Bu})_3$ and ZnMe_2 and successfully synthesized some novel zinc cluster compounds exhibited interesting molecular structure. Being motivated these researches, we employed $\text{OP}(\text{NHt-Bu})_3$, 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 $[\text{CIP}(\text{NHt-Bu})_3](\text{Cl})$ (**1**).

EXPERIMENTAL

Synthesis of $[\text{CIP}(\text{NHt-Bu})_3](\text{Cl})$ (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)

Scheme-I

with $\text{OP}(\text{NHt-Bu})_3$ (1 mmol) in HCl (1 mL) and toluene (10 mL) at 353 K for 2 days produces $[\text{CIP}(\text{NHt-Bu})_3](\text{Cl})$ crystals after cooling down to room temperature, yield 25 % (based on $\text{OP}(\text{NHt-Bu})_3$).

Single crystal structure determination: X-Ray intensity data for **1** were collected on a black prism crystal ($0.20 \text{ mm} \times 0.10 \text{ mm} \times 0.10 \text{ mm}$) at 153(2) K on a Bruker P4 CCD area detector diffractometer using graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.071073 \text{ nm}$). 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 events¹⁴. 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 Cl ₂ N ₃ P (1)	
Empirical formula	C ₁₂ H ₃₀ Cl ₂ N ₃ P
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
2θ _{max} (deg.)	54.82
Final R indices [I > 2σ(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

$$^{\#} R_1 = \sum \left(\frac{|F_o| - |F_c|}{\sum |F_o|} \right); wR_2 = \left\{ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right\}^{0.5}$$

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 [CIP(NHt-Bu)₃](Cl) (**1**) (Figs. 1 and 2), which crystallizes in a monoclinic system and adopts a centrosymmetric space group of P2₁/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 center of the PN₃Cl 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 [CIP(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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