

Synthesis and Crystal Structure of a New Hydrated Phosphinate Salt, $[(C_6H_5CH_2)_2NH_2]^+[(C_6H_5)_2P(O)(O)]^- \cdot H_2O$

Pari MARANDI,* Akbar RAISSI SHABARI,* Morteza KHOSRAVI,* and Mehrdad POURAYOUBI**†

*Faculty of Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran

**Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran

The asymmetric unit of the title hydrated salt contains one $[(C_6H_5CH_2)_2NH_2]^+$ cation, one $[(C_6H_5)_2P(O)(O)]^-$ anion and one solvent water molecule. In the anion, the P atom is in a distorted tetrahedral $[C]_2P[O][O]$ environment with the highest angle of $116.38(9)^\circ$ for the O-P-O angle and the lowest angle of $102.74(10)^\circ$ for the C-P-C angle. The most characteristic feature of the cation is the open C-N-C angle (of $113.50(17)^\circ$). In the crystal structure, the cations, anions and water molecules are hydrogen-bonded to each other, through O-H...O (O...O = $2.904(3)\text{Å}$ and $2.921(2)\text{Å}$) and N-H...O (N...O = $2.731(2)\text{Å}$ and $2.766(3)\text{Å}$) hydrogen bonds, building a linear arrangement along the *b* axis. In this hydrogen-bond pattern, the PO groups act as a double hydrogen-bond acceptor.

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Recently, the structural features were investigated for some phosphorus-nitrogen and phosphorus-oxygen compounds, such as with $P(O)[N]_3$,¹⁻³ $P(O)[O]_2[N]$,³ $P(S)[N]_3$ ⁴ and $P(S)[O]_2[N]$ ⁴ segments. We report here on the title structure (with a $[C]_2P[O][O]$ segment), Fig. 1. For the synthesis of the title compound, a solution of $(C_6H_5CH_2)_2NH$ (8 mmol) in $CHCl_3$ (10 ml) was added to a solution of $(C_6H_5)_2P(O)Cl$ (4 mmol) in the same solvent (10 ml) at ice-bath temperature. After stirring for 4 h, and allowing the mixture to come to room temperature within the procedure, the solid that formed was filtered off. The filtered solution was evaporated *in vacuo* to obtain a crude product as a solid, which was washed with distilled water. Single crystals suitable for X-ray crystallography were obtained from a solution of the product in $CHCl_3$ by slow evaporation at room temperature. IR (KBr, cm^{-1}): 3465, 3059, 2984, 2902, 2790, 2397, 1641, 1591, 1496, 1485, 1453, 1439, 1391, 1364, 1308, 1227, 1130, 1115, 1032, 998, 951, 848, 786, 751, 730, 697, 561, 534, 487.

The crystallographic data are summarized in Table 1, and selected bond lengths and angles are given in Table 2. The asymmetric unit of the title hydrated salt is composed of one $[(C_6H_5CH_2)_2NH_2]^+$ cation, one $[(C_6H_5)_2P(O)(O)]^-$ anion and one solvent water molecule (Fig. 2). In general, all bond distances are within the values characteristic according the atoms involved. The P-O bond lengths of anion (P1-O1 $1.5145(17)\text{Å}$,

P1-O2 $1.5175(16)\text{Å}$) are relatively similar (due to the delocalization of negative charge over two oxygen atoms), similar to such bonds for a previously reported structure $[(C_2H_5)_2NH_2][[(C_6H_5)_2P(O)(O)]]$.⁶ In the cation, the C19-N1-C20 angle is relatively open (of $113.50(17)^\circ$), which is in accordance with a similar angle in the structure of $[(C_6H_5CH_2)_2NH_2]Cl$ salt (of $112.2(2)^\circ$).⁷ The dihedral angle between the mean planes (C13/C14/C15/C16/C17/C18 and C21/C22/C23/C24/C25/C26) of the phenyl rings is 85.9° .

The P1 atom is in a distorted tetrahedral $[C]_2P[O][O]$

Table 1 Crystal and experimental data

Chemical formula: $C_{26}H_{28}NO_3P$	
Formula weight = 433.46	
$T = 120(2)\text{K}$	
Crystal system: Monoclinic	Space group: $P2_1/c$
$a = 13.273(3)\text{Å}$	
$b = 9.7015(19)\text{Å}$	$\beta = 109.50(3)^\circ$
$c = 18.444(7)\text{Å}$	
$V = 2238.8(12)\text{Å}^3$	$Z = 4$
$D_x = 1.286\text{ g/cm}^3$	
Radiation: Mo $K\alpha$ ($\lambda = 0.71073\text{ Å}$)	
$\mu(\text{Mo } K\alpha) = 0.151\text{ mm}^{-1}$	$F(0\ 0\ 0) = 920$
Crystal size = $0.50 \times 0.47 \times 0.40\text{ mm}^3$	
No. of reflections collected = 11752	
Unique = 3927 [$R(\text{int}) = 0.0490$]	
θ range for data collection: 2.40 to 25.00°	
Data/restraints/parameters = 3927/1/283	
Goodness-of-fit on $F^2 = 1.040$	
Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0458$, $wR_2 = 0.0961$	
R indices (all data): $R_1 = 0.0669$, $wR_2 = 0.1019$	
$(\Delta/\sigma)_{\text{max}} = 0.001$	
$(\Delta\rho)_{\text{max}} = 0.341\text{ e.Å}^{-3}$	$(\Delta\rho)_{\text{min}} = -0.323\text{ e.Å}^{-3}$
Measurement: STOE IPDS 2T	
Program system: SHELXS-97 ⁵	
Structure determination: SHELXL-97 ⁵	
Refinement: Full-matrix least-squares on F^2	
CCDC deposition number: 1050016	

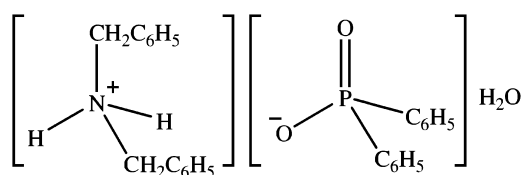


Fig. 1 Chemical structure of the title hydrated salt.

† To whom correspondence should be addressed.
 E-mail: pourayoubi@um.ac.ir

Table 2 Selected bond lengths [Å] and angles [°]

P1-O1	1.5145(17)	P1-O2	1.5175(16)
P1-C7	1.798(2)	P1-C4	1.813(2)
N1-C19	1.458(3)	N1-C20	1.499(3)
C7-C8	1.375(3)	C7-C12	1.401(3)
C20-C21	1.547(3)	C21-C22	1.374(3)
O1-P1-O2	116.38(9)	O1-P1-C7	109.35(10)
O2-P1-C7	109.61(9)	O1-P1-C4	108.95(9)
O2-P1-C4	108.93(9)	C7-P1-C4	102.74(10)
C19-N1-C20	113.50(17)	C5-C4-P1	119.59(17)
C3-C4-P1	121.57(16)	N1-C20-C21	113.58(17)

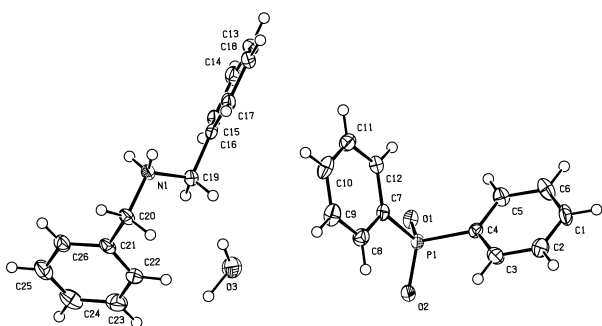


Fig. 2 Displacement ellipsoid plot (50% probability level) and atom-numbering scheme for the title hydrated salt.

environment with a difference of about 13.6° between the highest angle (O1-P1-O2) and the lowest angle (C7-P1-C4); for the angles, see Table 2. This is similar to that observed for the $[(C_2H_5)_2NH_2][(C_6H_5)_2P(O)(O)]$ salt,⁶ and also in the non-coordinated $[(C_6H_5)_2P(O)(O)]^-$ anion in the structure $C_{80}H_{112}Mn_2N_4O_8P_1^{1+}$, $C_{12}H_{10}O_2P_1^{1-}$, H_2O_1 .⁸

In the crystal structure, each water molecule is hydrogen bonded to two neighboring phosphinate anions, and each cation is also hydrogen bonded to two neighboring phosphinate anions; thus, the two O-H units of the water molecule and two N-H units of the cation participate in the hydrogen-bond pattern as H-bond donors. On the other hand, the two oxygen atoms of the P(O)(O)⁻ segment of the anion take part in the hydrogen-bonding interaction. Thus, the cyclic hydrogen-bonded motifs are built in the crystal structure including four H-atom donors and two H-atom acceptors (where the H-bond acceptors, PO groups, act as a double hydrogen-bond acceptor, forming PO(\cdots H-N)(\cdots H-O) grouping). The overall pattern based on the hydrogen bonds discussed is a linear arrangement, including cations, anions and water molecules, along the *b* axis, Fig. 3. The geometry values of the O-H \cdots O and N-H \cdots O hydrogen bonds are given in Table 3. The O \cdots O and N \cdots O distances

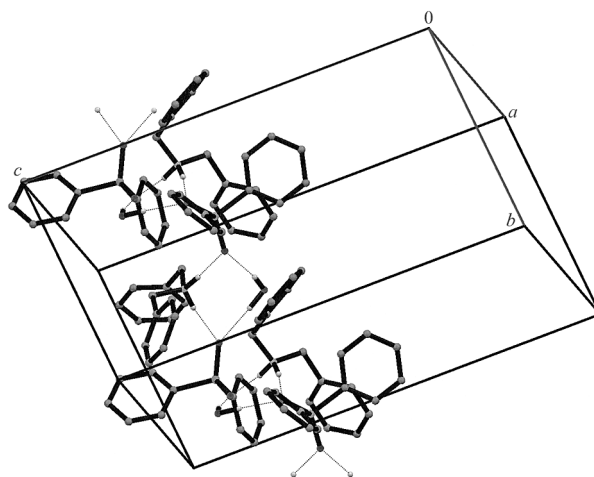


Fig. 3 View of the crystal packing of the title hydrated salt, showing a linear aggregation of $[(C_6H_5CH_2)_2NH_2]^+$ cations, $[(C_6H_5)_2P(O)(O)]^-$ anions and water molecules along the *b* axis, mediated by N-H \cdots O and O-H \cdots O hydrogen bonds. Hydrogen bonds are drawn as dotted lines and only N- and O-bound H atoms are shown.

Table 3 Hydrogen-bonding geometry (e.s.d.'s are given in parentheses)

D-H \cdots A	D-H(Å)	H \cdots A(Å)	D \cdots A(Å)	\angle D-H \cdots A(°)
N1-H1A \cdots O2 ⁱ	0.96	1.81	2.766(3)	172
N1-H1B \cdots O1 ⁱⁱ	0.86	1.88	2.731(2)	171
O3-H3A \cdots O2 ⁱⁱⁱ	0.78(2)	2.15(2)	2.921(2)	169(3)
O3-H3B \cdots O1 ⁱ	0.98	1.93	2.904(3)	172

Symmetry codes: (i) $x, -y+3/2, z+1/2$; (ii) $-x+1, -y+2, -z+1$; (iii) $-x+1, -y+1, -z+1$.

(2.904(3)/2.921(2)Å and 2.731(2)/2.766(3)Å) suggest relatively strong hydrogen bonds due to the effect of negative and positive charges.

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