Synthesis and Crystal Structure of a New Hydrated Phosphinate Salt, 
[(C₆H₅CH₂)₂NH][(C₆H₅)₂P(O)(O)]·H₂O

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The asymmetric unit of the title hydrated salt contains one [(C₆H₅CH₂)₂NH₂]+ cation, one [(C₆H₅)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)° for the O–P–O angle and the lowest angle of 102.74(10)° for the C–P–C angle. The most characteristic feature of the cation is the open C–N–C angle (of 113.50(17)°). 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)Å and 2.921(2)Å) and N–H···O (N–O = 2.731(2)Å and 2.766(3)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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Table 1 Crystal and experimental data

- P1-O1 1.5145(17)Å, P1-O2 1.5175(16)Å are relatively similar (due to the delocalization of negative charge over two oxygen atoms), similar to such bonds for a previously reported structure [(C₆H₅CH₂)₂NH][(C₆H₅)₂P(O)(O)]⁻. In the cation, the C19-N1-C20 angle is relatively open (of 112.2(2)°), which is in accordance with a similar angle in the structure of [(C₆H₅CH₂)₂NH]Cl salt (of 112.2(2)°). 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] segment, the PO groups acting as double hydrogen-bond acceptors.

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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, P(O)[O][N]₄ and P(S)[O][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 (C₆H₅CH₂)₂NH (8 mmol) in CHCl₃ (10 ml) was added to a solution of (C₆H₅)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 CHCl₃ by slow evaporation at room temperature. IR (KBr, cm⁻¹): 3465, 3059, 2984, 2902, 2799, 2397, 1641, 1496, 1485, 1439, 1391, 1364, 1308, 1227, 1130, 1115, 1032, 951, 848, 786, 751, 730, 697, 561, 534, 487.

Fig. 1 Chemical structure of the title hydrated salt.

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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 [(C2H5)2NH2][(C6H5)2P(O)(O)] salt, and also in the non-coordinated [(C6H5)2P(O)(O)]– anion in the structure C80H112Mn2N4O8P11+, C12H10O2P11–, H2O1.8

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(–H–N)–(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–O and N–H–O hydrogen bonds are given in Table 3. The O–O and N–O distances

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

<table>
<thead>
<tr>
<th></th>
<th>P1-O1</th>
<th>P1-C7</th>
<th>O1-P1-C7</th>
<th>C7-C8</th>
<th>C20-C21</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1-O2</td>
<td>1.5145(17)</td>
<td>1.798(2)</td>
<td>1.5175(16)</td>
<td>1.458(3)</td>
<td>1.547(3)</td>
</tr>
<tr>
<td>O1-P1-C7</td>
<td>116.38(9)</td>
<td>109.61(9)</td>
<td>108.93(9)</td>
<td>113.50(17)</td>
<td>121.57(16)</td>
</tr>
<tr>
<td>P1-C4</td>
<td>1.813(2)</td>
<td>1.401(3)</td>
<td>1.374(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C7-C12</td>
<td>119.59(17)</td>
<td></td>
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Fig. 2 Displacement ellipsoid plot (50% probability level) and atom-numbering scheme for the title hydrated salt.

(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.

References