CRYSTAL STRUCTURES OF TWO PHOSPHONATE SALTS: MONOCYCLOHEXYLAMMONIUM HYDROGEN PHOSPHONATE AND MONOCYCLOHEXYLAMMONIUM PHENYL PHOSPHONATE

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Abstract: Hydrogen phosphonate anions and monocyclohexylammonium cations interacting through hydrogen bonds conduct to the formation of a salt namely monocyclohexylammonium hydrogen phosphonate. In this structure, hydrogen phosphonate anions are linked by pairs through O—H···O hydrogen bonds leading to anionic dimers. Each dimer is connected to its two neighbours through cations via N—H···O hydrogen bonds leading to infinite chains which are then connected by N—H···O hydrogen bonds giving rise to a layered structure. The phenyl phosphonates form dimers that are connected through an expended hydrogen bonding network involving the cations into a layer.

Keywords: crystal structure, monocyclohexylammonium, hydrogen phosphonate, phenyl phosphonate, layered structure

1. INTRODUCTION

Interest in phosphonate chemistry is owed to the applications they display [1, 2] as well as their properties such as proton conductivity [3, 4], optical [5] and catalyst properties [6]. A search of the Cambridge Structural Database (CSD version 5.40) [7] returned 61 different structures containing hydrogen phosphonate anion. 42 of these structures are hydrogen phosphonate ammonium salts and 19 are metallic compounds. Among the 42 ammonium salts, 3 structures contain both hydrogen phosphonate and, fluorophosphonate (FPOH₂⁻), phosphonic acid or phosphonate. The CSD shows 20 structures containing hydrogen phenyl phosphonates with an alkaline or an organic counter cation. Five (5) of these hydrogen phenyl phosphonate compounds contain phenyl phosphonic acid molecules. To date, hundreds and hundreds structures of monocyclohexyl ammonium have been deposited in the CSD. The Dakar group focusing in phosphonate characterization has reported several works [8-10]. Recently, we published the crystalline structures of two triorganotin phosphonate polymers among with the first PH₃⁻ bridged trioorganotin phosphonate polymer [11]. Thus, continuing to focus in phosphonato organotin(IV), compound 2 was first isolated by serendipitous by mixing trimethyltin chloride with monocyclohexyl amine in the presence of phenyl phosphonic acid, PhPO(OH)₂⁻. Seeking phosphonate salts soluble in organic solvents usable for further organotin syntheses, we have targeted the interactions between
monocyclohexyl amine and hydrogen phosphonic acid, HPO(OH)$_2$ leading to the isolation of compound 1 (Figure 1). The reaction between monocyclohexyl amine and phenyl phosphonic acid also has been took out yielding crystals of compound 2 (Figure 1). We report herein the two structures.

![Molecular representations of monocyclohexylammonium hydrogen phosphonate (1) and monocyclohexylammonium phenyl phosphonate (2) related to this study.](image)

**2. EXPERIMENTAL SETUP**

**Synthesis of compounds 1 and 2:**

All chemicals were purchased from Aldrich Company and were used without any further purification. To 20 mL hydrogen phosphonic acid, H$_3$PO$_3$ was added slowly 10 mL equimolar aqueous solution of monocyclohexyl amine, CyNH$_2$. The resulting clear solution was stirred 2h at room temperature (300 K) in the opened atmosphere then submitted to a forced evaporation at 333 K. After some days, colourless block-shaped like crystals of the salt 1 suitable for an X-ray crystallographic analysis were obtained. The salt 2 was first isolated serendipitously by reacting equimolar amounts of a 5 mL ethanol solution of monocyclohexyl amine, a 10 mL ethanol solution of phenylphosphonic acid, and a 15 mL ethanol solution of trimethyltin chloride. The clear obtained mixture was stirred 2h at room temperature (300 K) in the opened atmosphere. A slow solvent evaporation afforded colourless crystals of salt 2 suitable for an X-ray crystallographic study. After its serendipitous synthesis, the salt 2 has also been prepared, similarly to salt 1, from reaction between phenyl phosphonic acid, PhPO(OH)$_3$ and monocyclohexyl amine, CyNH$_2$ in a 1:1 molar ratio.

**X-ray crystallography of [(CyNH$_3$)(HPO$_3$H)] (1):**

A crystal of approximate dimensions 0.073×0.059×0.011 mm was used for data collection. The X-ray crystallographic data were collected using a Bruker Kappa ApexII diffractometer, at $T = 150$ K. Data were measured using $\phi$ and $\omega$ scans using MoKα radiation ($\lambda = 0.71073$ Å) using a collection strategy to obtain a hemisphere of unique data determined by Apex2 [12]. Cell parameters were determined and refined using the SAINT program [13]. Data were corrected for absorption by multi-scan absorption correction using SADABS2012/1 [14]. The structure was solved using SHELXT [15] and the structure refined using least-squares minimization SHELXL [16].

Program used for the representation of the molecular and crystal structures: Olex2 [17]. The Crystallographic data and experimental details for structural analyses are summarized in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3, respectively.

CCDC 1978308 (1) contains 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, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

**X-ray crystallography of [(CyNH$_3$)(PhPO$_3$H)] (2):**

A crystal of approximate dimensions 0.35×0.25×0.007 mm was used for data collection. The X-ray crystallographic data were collected using a Bruker Kappa ApexII diffractometer, at $T = 150$ K. Data were measured using $\phi$ and $\omega$ scans using MoKα radiation ($\lambda = 0.71073$ Å) using a collection strategy to obtain a hemisphere of unique data determined by Apex2 [12]. Cell parameters were determined and refined using the SAINT program [13]. Data were corrected for absorption by multi-scan absorption correction using SADABS2012/1 [14]. The structure was solved using SHELXT [15] and the structure refined using least-squares minimization SHELXL [16].
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CCDC 1978309 (2) contains 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, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

Table 1. Crystal data and structure refinement for compounds (1) and (2).

| Parameters          | Compound (1) | Compound (2) |
|---------------------|--------------|--------------|
| Empirical formula   | H₂O₂·P·CH₃CN | C₆H₄O₂·P·CH₃CN |
| Formula weight      | 181.17       | 257.26       |
| Temperature         | 150 (2) K    | 150 (2) K    |
| Wavelength          | 0.71073 Å    | 1.34139 Å    |
| Crystal system      | Monoclinic   | Monoclinic   |
| Space group         | P₂₁/c        | P₂₁/c        |
| Unit cell dimensions| a = 8.378 (11) Å | a = 13.0297 (5) Å |
|                     | α = 90°      | α = 90°      |
|                     | b = 6.623 (9) Å | b = 6.2169 (2) Å |
|                     | β = 95.195 (17)° | β = 103.043 (2)° |
|                     | c = 16.99 (2) Å | c = 17.3831 (7) Å |
|                     | γ = 90°      | γ = 90°      |
| Volume              | 939 (2) Å³   | 1371.78 (9) Å³ |
| Z                   | 4            | 4            |
| Calculated density  | 1.282 g cm⁻³ | 1.246 g cm⁻³ |
| Absorption coefficient | 0.258 mm⁻¹   | 0.198 mm⁻¹   |
| F(000)              | 392          | 552          |
| Crystal size        | 0.07 × 0.06 × 0.01 mm³ | 0.35 × 0.25 × 0.01 mm³ |
| Theta range for data collection | 2.408°–27.102° | 2.405–30.647° |
| Limiting indices   | -10 ≤ h ≤ 10, -8 ≤ k ≤ 8, | -18 ≤ h ≤ 18, -8 ≤ k ≤ 8, |
|                     | -21 ≤ l ≤ 21 | -24 ≤ l ≤ 24 |
| Reflections collected/unique | 19681/2069 | 44955/4217 |
| R₁, wR₂, S       | 0.0671       | 0.0272       |
| Absorption correction | Multi-scan  | Multi-scan |
| Max. and min. transmission | 0.7455 and 0.6720 | 0.7461 and 0.7119 |
| Refinement method  | Full-matrix least-squares on F² | Full-matrix least-squares on F² |
| Data/restraints/parameters | 20690/0/153 | 42170/0/234 |
| Goodness-of-fit on F² | 1.035 | 1.154 |
| Final R indices (I/σ(I)) | R₁ = 0.0377, wR₂ = 0.0832 | R₁ = 0.0406, wR₂ = 0.1037 |
| R indices (all data) | R₁ = 0.0667, wR₂ = 0.0742 | R₁ = 0.0481, wR₂ = 0.0976 |
| Largest diff. peak and hole | 0.275 and -0.337 e Å⁻³ | 0.549 and -0.298 e Å⁻³ |

For compound (2), U = 1/[σ²(Fc)² + (0.039P)² + 0.1817P] for I and U = 1/[σ²(Fc)² + (0.039P)² + 0.8112P] for 2, where P = (Fc)² + 2(Fc)²)/3.

Table 2. Selected bond lengths (Å) for compounds (1) and (2).

| Atom—Atom          | Bond length (Å) | Atom—Atom          | Bond length (Å) |
|--------------------|-----------------|--------------------|-----------------|
| P₁—O₂              | 1.510 (2)       | P₁—O₃              | 1.5033 (9)      |
| P₁—O₃              | 1.505 (2)       | P₁—O₁              | 1.5063 (10)     |
| P₁—O₁              | 1.579 (2)       | P₁—O₂              | 1.5762 (9)      |
| P₁—H₁D             | 1.320 (17)      | P₁—C₁              | 1.8005 (13)     |
| N₁—C₁              | 1.505 (3)       | N₁—C₇              | 1.4931 (15)     |
| C₁—C₂              | 1.528 (3)       | C₁—C₆              | 1.3898 (19)     |
| C₁—C₆              | 1.528 (3)       | C₁—C₂              | 1.3936 (19)     |
| C₂—C₃              | 1.534 (3)       | C₁₂—C₇             | 1.5221 (17)     |
| C₆—C₅              | 1.536 (3)       | C₁₂—C₁₁            | 1.5252 (19)     |
| C₃—C₄              | 1.531 (3)       | C₇—C₈              | 1.5240 (17)     |
| C₅—C₄              | 1.531 (3)       | C₈—C₉              | 1.530 (2)       |
| C₁—C₆              | 1.528 (3)       | C₆—C₅              | 1.396 (2)       |
| C₂—C₃              | 1.534 (3)       | C₂—C₃              | 1.394 (2)       |
| C₃—C₄              | 1.531 (3)       | C₁₁—C₁₀            | 1.524 (2)       |
| C₅—C₄              | 1.531 (3)       | C₉—C₁₀             | 1.526 (2)       |
| N₁—C₁              | 1.505 (3)       | C₃—C₄              | 1.378 (3)       |
| C₁—C₂              | 1.528 (3)       | C₄—C₅              | 1.380 (3)       |
| C₁—C₆              | 1.528 (3)       | | |
Table 3. Selected angles (°) for compounds (1) and (2).

| Atom-atom-atom | Compound (I) | Angle value | Atom-atom-atom | Compound (2) | Angle value |
|-----------------|--------------|-------------|----------------|--------------|-------------|
| O2—P1—O1       |              | 111.10 (8)  | O3—P1—O2      |              | 116.85 (6)  |
| O2—P1—H1D      | 105.4 (7)    |             | O3—P1—O2      | 107.09 (6)   |
| O3—P1—O2       | 116.65 (9)   |             | O3—P1—C1      | 107.22 (6)   |
| O3—P1—O1       | 108.03 (10)  |             | O1—P1—O2      | 110.33 (5)   |
| O3—P1—H1D      | 109.1 (7)    |             | O1—P1—C1      | 108.40 (6)   |
| O1—P1—H1D      | 106.0 (7)    |             | O2—P1—C1      | 106.43 (6)   |
| N1—C1—C2       | 109.93 (16)  |             | C6—C1—P1      | 121.21 (10)  |
| N1—C1—C6       | 110.44 (16)  |             | C6—C1—C2      | 118.75 (13)  |
| C6—C1—C2       | 111.52 (18)  |             | C2—C1—P1      | 120.02 (11)  |
| C1—C2—C3       | 110.27 (17)  |             | C7—C12—C11    | 110.32 (11)  |
| C1—C6—C5       | 110.41 (17)  |             | N1—C7—C12     | 109.63 (10)  |
| C4—C3—C2       | 111.26 (18)  |             | N1—C7—C8      | 109.24 (10)  |
| C4—C5—C6       | 111.68 (19)  |             | C12—C7—C8     | 111.74 (10)  |
| C5—C4—C3       | 111.6 (2)    |             | C7—C8—C9      | 110.80 (12)  |

3. RESULTS AND DISCUSSION

Salt 1 crystallizes in the monoclinic space group P2(1)/c. Its asymmetric unit depicted in Figure 2 is comprised of one hydrogen phosphonate anion and one monocyclohexyl ammonium cation. The hydrogen phosphonate anion with P—O distances ranging from 1.505 (2) Å to 1.579 (2) Å and angles comprised between 105.04 (7) and 116.65 (9)° describes a distorted tetrahedral geometry and are in the range of those previously reported [18-20]. The O atoms of the longer P—O bond are both involved in a very strong hydrogen bonding interaction [9, 10, 21], the significantly longer one being involved in a second strong hydrogen bond. The shortest P—O bond is that whose O atom act as acceptor of two symmetric hydrogen bonds. Bonds and angles within the monocyclohexyl ammonium are otherwise comparable to those recorded in the literature [22-24].

Fig. 2. The molecular structure of compound 1, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

Salt 2 crystallizes in the monoclinic space group P2(1)/c. Its asymmetric unit depicted in Figure 3 consists of one phenyl phosphonate anion and one monocyclohexyl ammonium cation. The geometric parameters within the anion with P—O lengths varying from 1.5033 (9) Å to 1.5762 (9) Å and angles from 106.43 (6)° to 116.85 (6)° are in accordance with those in salt 1. The geometric parameters within the cation are otherwise not exceptional compared to those in compound 1.
Fig. 3. The molecular structure of compound 2, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

In a supramolecular viewing, in the crystal of compounds 1 and 2, phosphonate anions form dianionic dimers through a very strong O—H···O hydrogen bonding interactions. These dimers are connected to each other through two monocylohexyl ammonium cations via N—H···O hydrogen bonds growing an hydrogen bonded chain depicted in Figure 4. These chains are then connected, through the remaining nitrogen H atom of the cation, by N—H···O hydrogen bonds giving rise to a layered structure (Tables 4, 5 and Figure 4). The layer morphologies exhibit two types of self- assemblies describing a 10-membered and a 16-membered hydrogen bonded macrocycles involving both cations and anions, and a 8-membered hydrogen bonded ring involving only anions. The 16-membered and 8-membered hydrogen bonded self- assemblies alternate into the expending chain while the encountered 10-membered hydrogen bonded macrocycle come from linkage of chains that grows the layer. Thus, each cation is surrounded by three different dimers and each dimer is surrounded by six different cations. All the hydrogen bonded macrocycles are both fused (Figure 4).

Table 4. Hydrogen-bond geometry (Å, °) for compound (1).

| Bond         | D—H (Å) | H···A (Å) | D···A (Å) | H···A (°) |
|--------------|---------|-----------|-----------|-----------|
| N1—H1A···O2  | 0.91    | 1.89      | 2.799 (3) | 173       |
| N1—H1B···O3  | 0.91    | 1.87      | 2.781 (4) | 175       |
| N1—H1C···O3b | 0.91    | 1.88      | 2.787 (4) | 173       |
| O1—H1E···O2  | 0.76 (2)| 1.88 (2)  | 2.635 (3) | 173 (2)   |

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

Table 5. Hydrogen-bond geometry (Å, °) for compound (2).

| Bond         | D—H (Å) | H···A (Å) | D···A (Å) | H···A (°) |
|--------------|---------|-----------|-----------|-----------|
| N1—H1A···O3  | 0.884 (19)| 1.867 (19)| 2.7497 (13)| 176.3 (18) |
| N1—H1B···O3  | 0.94 (2) | 1.82 (2)  | 2.7511 (14)| 172.8 (18) |
| N1—H1C···O1  | 0.90 (2) | 1.85 (2)  | 2.7470 (13)| 173.2 (18) |
| O2—H2···O1   | 0.83 (2) | 1.76 (2)  | 2.5870 (13)| 173 (2)    |

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

Fig. 4. The molecular structure of salt 1, showing the 16-membered (pink buckle), 10-membered (blue buckle) and 8-membered hydrogen (green buckle) bonded macrocycles within a two-dimensional layer-like arrangement through N—H···O and O—H···O interactions.
Moreover, in compound 2, the two phenyl groups of the anionic dimers are oriented in such way that they lay in almost coplanar planes so that the former positioned on one side of the 8-membered hydrogen bonded ring plane while the latter occupy the over side. Therefore, all dimers are oriented in an isotactic fashion. Similarly, cyclohexyl groups within compounds 1 and 2 are also disposed, between dimers, in an up-down sequence that can be described as isotactic (Figure 5).

![Fig. 5. The crystal packing of salts 1 [a)] and 2 [b)]. Displacement ellipsoids are drawn at the 50% probability level.](image)

4. CONCLUSIONS

The studied phosphonates salts 1 and 2 both describe a dianionic dimer in which two phosphonate anions are linked through strong H-bonds. In all structures concerning this work, a hydrogen bonded infinite chain grew from hydrogen bonding interactions between dimers and monocycohexyl ammonium. In spite of the formula difference, compounds 1 and 2 are isosctructural. Further attempts investigating the isolation of various metal phosphonate compounds are in progress.

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