



Synthesis and characterization of three new amido-phosphate salts with a $C(O)NHP(O)(O)^-[N]$ skeleton

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SUMMARY: The structural features of three new $[XC(O)NHP(O)(O)Y]^{-}[H_2Y]^{+}$ amido-phosphate salts [$X = CCl_3$ and $Y = NHC_6H_4(2-F)$ (1); $X = CCl_3$ and $Y = N(C_2H_5)(C_6H_{11})$ (2); $X = C_6H_5$ and $Y = (NHC_6H_4(3-Cl))$ (3)] are studied. For each of structures (1) and (2), the asymmetric unit is composed of one cation-anion pair; while for (3), it consists of two symmetrically independent cation-anion pairs. In both structures (1) and (2), the anions and cations are linked via $-H_2N^{+}-H...O^{\delta-}$ hydrogen bonds into linear arrangements; parallel to the b axis for (1) and parallel to the a axis for (2). In structure (3), the cations and anions are hydrogen-bonded to each other forming a linear arrangement along the b axis; so that in this aggregation, the hydrogen-bonded dimers of anions, built from $N-H...O=C$ hydrogen bonds, are connected to the neighbouring cations *via* $-HN^{+}-H...O^{\delta-}$ hydrogen bonds. For the $N-H...O$ hydrogen bonds, the donor...acceptor ($N...O$) distances of cation-anion compounds (1) – (3) and six analogous phosphate salts found in the Cambridge Structural Database (CSD) are compared with the values related to neutral $C(O)NHP(O)$ -based structures.

Keywords: Structural feature, Amido-phosphate salt, Hydrogen bond.

1. INTRODUCTION

Phosphate derivatives ($XYP(O)O^{-}$, where $X, Y = O^{-}, OH, OR, OAr, NRR',$ halide ion, ...) have attracted significant attention due to their utility in supramolecular chemistry and crystal engineering and their ability as the metal complexing agents (Wisser & Janiak, 2007; Selpokura & Lis, 2006). In previous works, some phosphate salts were studied structurally, such as containing $PO_2Cl_2^{-}$ (Gholivand & Pourayoubi, 2004) and $CF_3C(O)N(H)P(O)(O)[NH(tert-C_4H_9)]^{-}$ anions (Gholivand *et al.*, 2005). In this paper we present the synthesis, characterization and X-ray crystallography investigation of three new amido-phosphate salts. Then, the $-HN^{+}-H...O^{\delta-}$ hydrogen bonds in structures (1) – (3) are compared with the $-HN^{+}-H...O^{\delta-}$ hydrogen bonds in cation-anion compounds found in the Cambridge Structural Database (CSD) and the $N-H...O$ hydrogen bond in neutral deposited $C(O)NHP(O)$ -based compounds.

2. EXPERIMENTAL

2.1. Syntheses

The reagents $C_6H_5C(O)NHP(O)Cl_2$ and $CCl_3C(O)NHP(O)Cl_2$ were prepared according to the respective descriptions given by Narula *et al.* (1999) and Raissi Shabari *et al.* (2012).

2.1.1 Synthesis of (1):

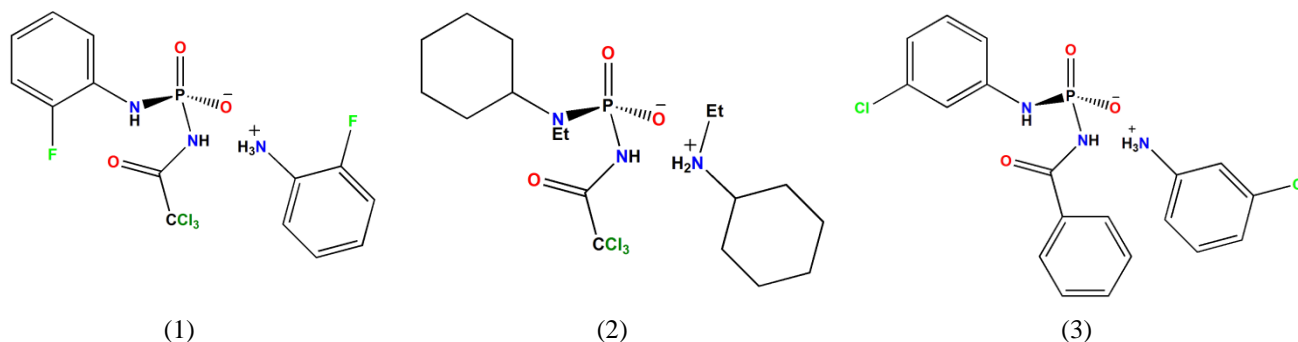
To a solution of $\text{CCl}_3\text{C(O)NHP(O)Cl}_2$ (2 mmol) in dry chloroform, a solution of 2-fluoroaniline (8 mmol) in the same solvent was added at 273 K under stirring. After 4 h, the solvent was evaporated and the solid product was washed with distilled water. Colorless single crystals were obtained from a mixture of $\text{CH}_3\text{OH}/\text{CH}_3\text{CN}$ (4:1 v/v) by slow evaporation at room temperature. IR (KBr, cm^{-1}): 3412, 3317, 3288, 2933, 2855, 1618, 1540, 1431, 1336, 1236, 1107, 1012, 931, 859, 755, 669. Selected Crystal data: Monoclinic, $P2_1/c$, $a = 16.1769$ (14) Å, $b = 5.5121$ (3) Å, $c = 20.8083$ (16) Å, $\beta = 108.730$ (7)°, $Z = 4$, $V = 1757.2$ (2) Å³, Mo K α Radiation, $\mu = 0.65$ mm⁻¹, $T = 120$ K, $0.68 \times 0.50 \times 0.16$ mm, $R_{\text{int}} = 0$, $R[F^2 > 2\sigma(F^2)] = 0.030$, $wR(F^2) = 0.084$, $S = 1.17$, Reflections = 6182, Parameters = 261, Restraints = 0, $\Delta\rho_{\text{max}} = 0.23$ e Å⁻³, $\Delta\rho_{\text{min}} = -0.21$ e Å⁻³.

2.1.2. Synthesis of (2):

Compound (2) was obtained in a similar procedure to (1), but by using N-ethylcyclohexylamine instead of 2-fluoroaniline. Colorless single crystals were obtained from a mixture of $\text{CH}_3\text{OH}/\text{CH}_3\text{CN}$ (4:1 v/v) by slow evaporation at room temperature. IR (KBr, cm^{-1}): 3381, 3328, 3042, 2861, 1701, 1582, 1491, 1462, 1372, 1257, 1229, 952, 871, 832. Selected Crystal data: Triclinic, $P\bar{1}$, $a = 10.1460$ (7) Å, $b = 10.9540$ (7) Å, $c = 12.2501$ (6) Å, $\alpha = 105.846$ (5)°, $\beta = 109.545$ (5)°, $\gamma = 99.075$ (5)°, $Z = 2$, $V = 4754.53$ (8) Å³, Mo K α Radiation, $\mu = 4.33$ mm⁻¹, $T = 120$ K, $0.07 \times 0.07 \times 0.03$ mm, $R_{\text{int}} = 0.045$, $R[F^2 > 2\sigma(F^2)] = 0.036$, $wR(F^2) = 0.046$, $S = 1.15$, Reflections = 4101, Parameters = 262, Restraints = 0, $\Delta\rho_{\text{max}} = 0.22$ e Å⁻³, $\Delta\rho_{\text{min}} = -0.22$ e Å⁻³.

2.1.3. Synthesis of (3):

To a solution of $\text{C}_6\text{H}_5\text{C(O)NHP(O)Cl}_2$ (2 mmol) in chloroform, a solution of 3-chloroaniline (8 mmol) in the same solvent was added at 273 K under stirring. After 4 h, the solvent was evaporated and the product was washed with distilled water. Colorless single crystals suitable for X-ray crystallography were obtained from a mixture of $\text{CH}_3\text{OH}/\text{CH}_3\text{CN}$ (4:1 v/v) by slow evaporation at room temperature. IR (KBr, cm^{-1}): 3042, 2931, 2787, 1709, 1605, 1502, 1457, 1386, 1324, 1205, 1160, 1124, 1072, 1032, 994, 938, 875, 779. Selected Crystal data: Monoclinic, $P2_1/n$, $a = 19.1706$ (2) Å, $b = 13.2601$ (1) Å, $c = 20.2643$ (2) Å, $\beta = 112.6340$ (5)°, $Z = 8$, $V = 4754.53$ (8) Å³, Mo K α Radiation, $\mu = 0.36$ mm⁻¹, $T = 295$ K, $0.43 \times 0.29 \times 0.19$ mm, $R_{\text{int}} = 0.021$, $R[F^2 > 2\sigma(F^2)] = 0.065$, $wR(F^2) = 0.222$, $S = 1.08$, Reflections = 11998, Parameters = 537, Restraints = 8, $\Delta\rho_{\text{max}} = 0.54$ e Å⁻³, $\Delta\rho_{\text{min}} = -0.55$ e Å⁻³.



Scheme 1:
Chemical structures of 1 – 3

3. DISCUSSION

Each of the asymmetric units of (1) and (2) consists of one cation-anion pair; whereas, for (3), it consists of two symmetrically independent cation-anion pairs. The chemical structures of (1) – (3) are shown in Scheme 1. Selected bond distances and angles are given in Table 1.

In all anionic components of structures (1) – (3), the P atoms display a distorted tetrahedral configuration with the largest range of bond angles around the P atom for (2) (104.83(12)° to 119.06(11)°). The phosphorus-oxygen bond lengths are comparable to those in the similar proton transfer compounds (Yazdanbakhsh *et al.*, 2009) and the phosphorus-oxygen bond lengths are longer than the P=O double bond length (Corbridge, 1995). Moreover, as the phosphorous-oxygen bond lengths of $[\text{P(O)(O)}]^-$ segment (in all structures) have no significant differences, it may be concluded that the negative charge is delocalized over two oxygen atoms. In each anion, the P—N_{CP} bond lengths [N_{CP} is introduced as the nitrogen atom of the C(O)—NH—P(O) fragment] is longer than the other P—N bond.

In (1), the anions and cations are linked via $-\text{H}_2\text{N}^+-\text{H}\dots\text{O}^{\delta-}$ hydrogen bonds into linear arrangements parallel to [010]. In (2), the centrosymmetric dimers of anions, formed through $\text{N}_{\text{CP}}-\text{H}\dots\text{O}^{\delta-}$ hydrogen bonds, are hydrogen bonded to the centrosymmetric hydrogen-bonded dimer of cations *via* charge-assisted $-\text{HN}^+-\text{H}\dots\text{O}=\text{C}$ and $-\text{HN}^+-\text{H}\dots\text{O}^{\delta-}$ hydrogen bonds. These hydrogen bonds lead to a linear arrangement along [100]. Structure (3) exists as a hydrogen-bonded linear arrangement along the [010] axis including two independent cation-anion pairs. In this arrangement, the non-centrosymmetric dimers of anions formed through $\text{N}-\text{H}\dots\text{O}=\text{C}$ hydrogen bonds are hydrogen bonded to neighboring cations *via* charge-assisted $-\text{HN}^{\delta+}-\text{H}\dots\text{O}^{\delta-}-\text{P}$ hydrogen bonds.

The short N...O distances are found in the range of 2.66 Å to 2.88 Å for the set including cation-anion structures 1, 2 and 3 and six similar structures found in the Cambridge Structural Database (CSD, Version 5.35, Feb 2014 update; Allen, 2002). On the other hand, for neutral structures with a C(O)NHP(O)[N]₂ segment, the N...O distances were reported within 2.75 Å to 3.05 Å (Pourayoubi & Tarahhomi *et al.*, 2011). The short N...O distances in cation-anion compounds are related to the charge-assisted mechanism.

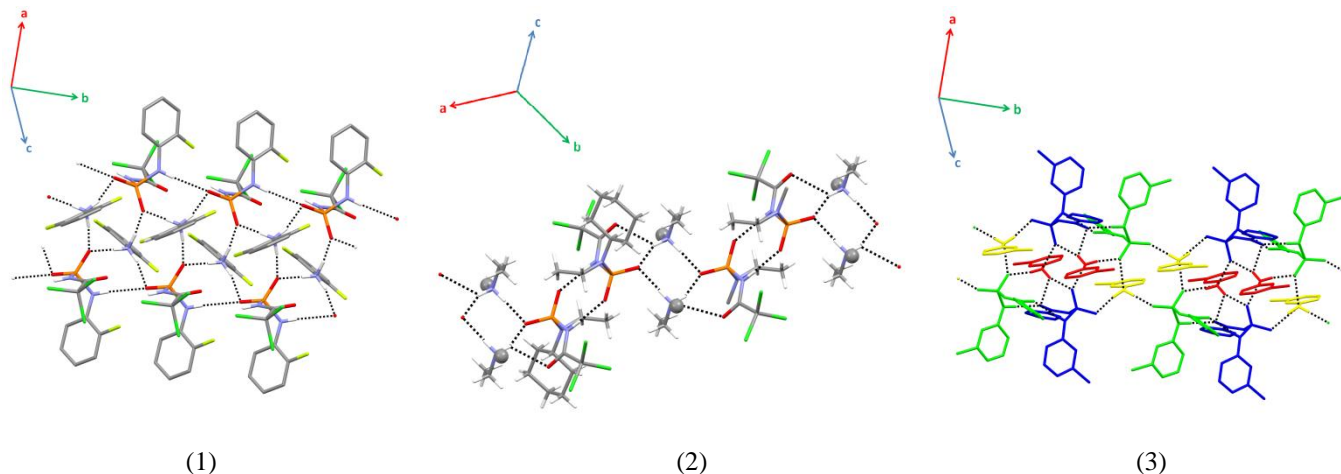


Figure 1: Views of the crystal packing diagrams for (1) – (3), showing the hydrogen-bonded chains (H atoms not involved in hydrogen bonding have been omitted for the sake of clarity). For (2), the cyclohexyl rings in cation components are shown as balls for more clarity. For (3), the symmetrically independent components are shown as different colors.

4. ACKNOWLEDGMENTS

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Table 1 Selected geometric parameters (Å, °) for 1–3.

(1)			
P1—O1	1.4925(12)	P1—O2	1.4826(11)
P1—N1	1.6561(14)	P1—N8	1.7087(12)
O1—P1—O2	118.92(6)	O1—P1—N1	105.68(7)
O1—P1—N8	109.56(7)	O2—P1—N1	112.44(7)
O2—P1—N8	103.81(6)	N1—P1—N8	105.73(6)
(2)			
P1—O1	1.498(2)	P1—O2	1.4796(19)
P1—N1	1.737(2)	P1—N2	1.649(2)
O1—P1—O2	119.06(11)	O1—P1—N1	106.03(9)
O1—P1—N2	109.13(12)	O2—P1—N1	104.83(12)
O2—P1—N2	109.93(10)	N1—P1—N2	107.10(11)
(3)			
P1A—O2A	4821(16)	P1A—O1A	1.4925(17)
P1A—N1A	1.6521(19)	P1A—N2A	1.698(2)
P1B—O2B	1.4861(15)	P1B—O1B	1.4929(15)
P1B—N1B	1.6596(18)	P1B—N2B	1.7030(18)
O2A—P1A—O1A	119.21(10)	O2A—P1A—N1A	112.56(10)
O1A—P1A—N1A	105.75(9)	O2A—P1A—N2A	102.50(10)
O1A—P1A—N2A	109.51(10)	N1A—P1A—N2A	106.71(10)
O2B—P1B—O1B	118.31(9)	O2B—P1B—N1B	112.28(9)
O1B—P1B—N1B	105.74(9)	O2B—P1B—N2B	104.41(9)
O1B—P1B—N2B	108.85(9)	N1B—P1B—N2B	106.71(9)