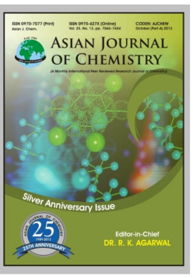
Estd. 1989
Asian Journal of Chemistry; Vol. 25, No. 15 (2013), 8361-8367

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14744



Linking Nitrate and Dihydrogenphosphate Motifs with N,N',N''-Triisopropylguanidinium Cation: Syntheses and Structures of NO_3^- and $H_2PO_4^-$ Salts

FAROUQ F. SAID

Department of Chemistry, Al al-Bayt University, Mafraq 25113, Jordan

Corresponding author: E-mail: fjuqqa@aabu.edu.jo

(*Received*: 25 October 2012; *Accepted*: 21 August 2013) AJC-13951

The trisubstituted guanidine N,N',N''-triisopropylguanidine (TPG) reacts with ammonium nitrate in water and with phosphoric acid in THF to produce $(TPGH)_2(NO_3)_2(H_2O)$ (**1**) and $(TPGH)_2(H_2PO_4)_2(H_3PO_4)$ (**2**) salts. Compounds **1** and **2** were characterized by X-ray diffraction analysis and the two structures displayed two crystallographically unique cations. A complex hydrogen-bonding scheme operates in **1** between the guanidinium cation and nitrate anion *via* N–H···O and O–H···O synthons. The primary structure of **2** is the formation of dihydrogenphosphate anion chains along the c-axis direction through O–H···O synthon, which are triply-crossed by the 3-fold cations consolidating a 3-D structure. Compound **1** crystallized in the monoclinic space group P2(1)/n, where a = 16.841(5) Å, b = 9.122(3) Å, c = 19.926(6) Å, β = 95.041(6)° and compound **2** crystallized in the monoclinic system space group P2(1)/c with a = 16.542(2) Å, β = 10.8515(16) Å, c = 18.702(3) Å, β = 91.888º(3).

Key Words: N,N',N''-Triisopropylguanidinium cation, Nitrate and (di)hydrogenphosphate anions, Synthon and motif.

INTRODUCTION

In the field of molecular recognition, the guanidinium group has been established as a highly effective functional group for the binding of anionic guests. This moiety has been proven to form a strong interaction with anions such as carboxylates, phosphates, sulfates and nitrates through hydrogen-bonding and charge pairing in competitive solvent systems. The ability of the guanidinium group to bind to anions arises from the geometrical orientation of this functional group in such that it aligns well with the previously mentioned anionic groups, leading to a strong interaction[1]. The guanidinium group is of interest due to its biological activity, hydrogen bonding capabilities, stability and positive charge integrity over a wide pH range[2]. The guanidinium functional group occurs naturally in guanine and arginine and the guanidiniums have been used to study the mechanism of phosphodiester hydrolysis, as anion receptors in synthetic sensors and in the formation of novel secondary structure elements[3-7].

We are interested in analyzing the hydrogen bonding schemes offered by the extended structures of N-substituted guanidinium compounds[8-12]. In this paper and in keeping with the ultimate goal of employing these interactions in future crystal design, we focus on the ability of N,N',N''-triisopropylguanidinium cation to form a new supramolecular motif with the nitrate and (di)hydrogen phosphate anions. The symmetrical substitution pattern in N,N',N''-triisopropylguanidinium retains the C_3-symmetry in the cation, as in the parent guanidinium and preserving the potential for three-fold, hydrogen bonding arrays.

EXPERIMENTAL

N,N',N''-Triisopropylguanidine (TPG) was prepared according to literature methods[13]. All other reagents were purchased from Aldrich Chemical Company and used without further purification. Elemental analyses were run on a Perkin-Elmer PE CHN 4000 elemental analysis system.

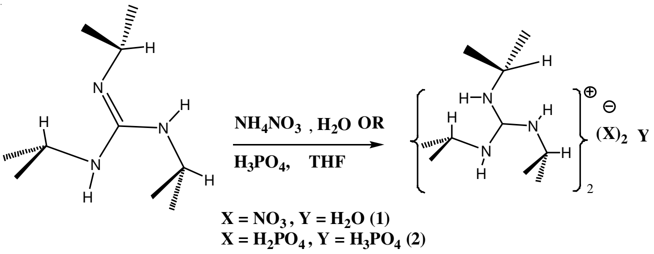
Synthesis and crystallization of $(TPGH)_2(NO_3)_2(H_2O)$ (1): In a round bottom flask, a combination of 0.072 g (0.389 mmol) N,N',N''-triisopropylguanidine and 0.031 g (0.389) mmol) ammonium nitrate were dissolved in 10 mL of distilled water and boiled for 5 min. White tubular crystals of $(TPGH)_2(NO_3)_2(H_2O)$ (**1**) were deposited upon slow evaporation of the solution at ambient temperature (92.1 % yield). In addition to confirming the molecular formula through elemental analysis, the solid obtained was examined by single crystal X-ray analysis. Anal. (calcd.) for $C_{20}H_{50}N_8O_7$ C, 46.67; H, 9.72; N, 21.76. Found C, 46.12 ; H, 9.81; N, 21.34.

Synthesis and crystallization of $(TPGH)_2(H_2PO_4)_2H_3PO_4\}$ (2): In a round bottom flask, 0.072 g (0.389 mmol) N,N',N''-triisopropylguanidine was dissolved in 10 mL THF and orthophosphoric acid was added drop wise. A colourless precipitate of $(TPGH)_2^{2+}\{(H_2PO_4)_2{\cdot}H_3PO_4\}^{2-}$ (**2**) deposited immediately which was crystallized from THF and methanol in 1/2 ratio (94.5 % yield). In addition to confirming the molecular formula through elemental analysis, the solid obtained was examined by single crystal X-ray analysis. Anal. calculated for $C_{20}H_{55}N_6O_{12}P_3$; C, 36.14; H, 8.34; N, 12.65. Found C, 36.42; H, 8.50; N, 12.64.

Structural determination and refinement of the crystal structures: A single colourless crystal suitable for X-ray diffraction measurements was mounted on a glass fibre. Unit cell measurements and intensity data collections were performed on a Bruker-AXS SMART 1 k CCD diffractometer at 203 K using graphite monochromatized MoK_α radiation (λ = 0.71073 Å). The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS). The crystal structures were solved and refined using the SHELXTL program suite. Direct methods yielded all non-hydrogen atoms. All hydrogen atom positions either were located from the difference Fourier Map or were calculated geometrically and were riding on their respective atoms.

RESULTS AND DISCUSSION

The guanidine employed in this study, N,N',N''-triisopropylguanidine, reacts readily and in near quantitative yields with ammonium nitrate or phosphoric acid as summarized in **Scheme-I** below to yield $(TPGH)_2(NO_3)_2(H_2O)$ (**1**) or $(TPGH)_2(H_2PO_4)_2(H_3PO_4)$ (**2**).



Scheme-I

Molecular structure of $(TPGH)_2(NO_3)_2(H_2O)$ (1): Compound (**1**) was grown from an aqueous solution. It crystallized in the monoclinic space group P2(1)/n, where a = 16.841(5) Å, b = 9.122(3) Å, c = 19.926(6) Å, $\alpha = \gamma$ = 90°, β = 95.041(6)° (Table-1).

A diagram of the asymmetric unit and the numbering scheme is presented in (Fig. 1).

The crystallographic asymmetric unit comprises two independent guanidinium cations with no remarkable differences between their structural parameters, residing on pseudo C_3 propeller-like orientation of N^iPr groups for the planar guanidinium cations; two nitrate anions and one molecule of water. Selected values of bond distances and angles are given in Table-2. The guanidinium cations can be labeled G-C1 and G-C11. Similarly the nitrate anions are conveniently labeled N7-O and N8-O.

The nearly equivalent C-N bond lengths of 1.325(6) and1.333(4) Å for G-C1 and G-C11 respectively are in good agreement with those seen in related structures[14-27] and as expected for a central carbon with sp^2 hybridization taking

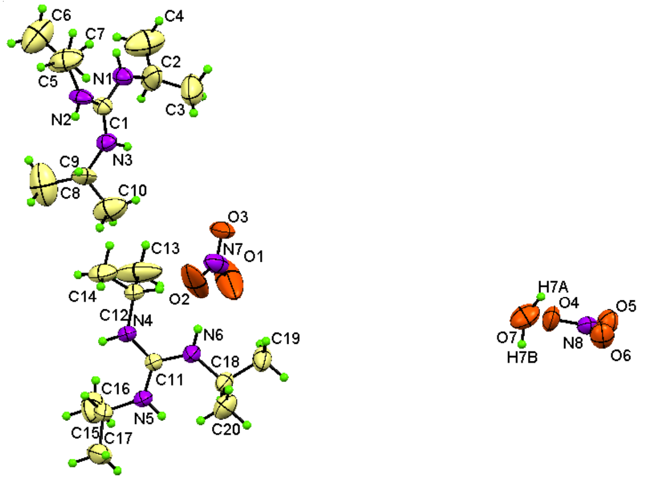


Fig. 1. ORTEP diagram showing the molecular structure and numbering scheme for $(TPGH)_2(NO_3)_2(H_2O)$ (**1**)

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR $(TPGH)_2(NO_3)_2(H_2O)$ (**1**)

Empirical formula	$C_{20}H_{50}N_8O_7$
Formula weight	514.68
Temperature	207(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 16.841(5); Å, α = 90º;
	b = 9.122(3) Å; β = 95.041(6)º
	c = 19.926(6) Å; γ = 90º
Volume	3049.1(16) $Å^3$
Z, Calculated density	4, 1.121 Mg/m^3
Absorption coefficient	0.085 mm^{-1}
F(000)	1128
Crystal size	0.35 × 0.25 × 0.20 mm
Theta range for data collection	1.66 to 23.25 º
Limiting indices	-18<=h<=18, -10<=k<=10, -22<=l<=22
Reflections collected/unique	18247/4324 [R(int) = 0.0579]
Completeness to theta = 23.25	98.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9833 and 0.9710
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4324/0/371
Goodness-of-fit on F^2	1.007
Final R indices [I>2σ(I)]	R1 = 0.0746, wR2 = 0.1806
R indices (all data)	R1 = 0.1201, wR2 = 0.2085
Largest diff. peak and hole	0.273 and -0.233 $e.A^{-3}$

TABLE-2
SELECTED BOND LENGTHS [Å] AND ANGLES [°] FOR $(TPGH)_2(NO_3)_2(H_2O)$ (**1**)

	Distance		
C(1)-N(3)	1.289(6)	N(7)-O(3)	1.149(8)
C(1)-N(2)	1.321(6)	N(7)-O(1)	1.227(14)
C(1)-N(1)	1.364(6)	N(7)-O(2)	1.171(12)
C(11)-N(4)	1.324(4)	N(8)-O(5)	1.242(4)
C(11)-N(5)	1.332(4)	N(8)-O(6)	1.242(4)
C(11)-N(6)	1.342(4)	N(8)-O(4)	1.246(4)
	Angles		
N(3)-C(1)-N(2)	121.4(5)	O(3)-N(7)-O(1)	114.8(13)
N(3)-C(1)-N(1)	121.6(5)	O(3)-N(7)-O(2)	125.9(13)
N(2)-C(1)-N(1)	116.8(4)	O(1)-N(7)-O(2)	118.3(13)
N(4)-C(11)-N(5)	121.1(3)	O(5)-N(8)-O(6)	120.0(3)
N(4)-C(11)-N(6)	119.6(3)	O(5)-N(8)-O(4)	119.9(3)
N(5)-C(11)-N(6)	119.3(3)	O(6)-N(8)-O(4)	120.1(4)

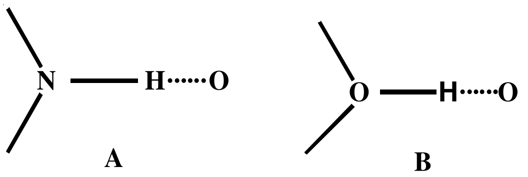
into account the charge delocalization over the three C-N bonds; and the planarity of the CN_3 core (Σ of angles = 360º) suggests an electron delocalized, Y-conjugated species[28]. Also, the nitrate N8-O bond lengths of 1.246(4), 1.242(4) and 1.242(4) respectively are nearly equivalent indicating a delocalized π-bonding arrangement of these bonds and as expected for a central nitrogen with sp^2 hybridization taking into account the charge delocalization over the three N-O bonds. However, the N-O distances for N7-O of 1.227(14),1.171(12) and 1.149(8) Å respectively are not equivalent indicating different environments for the three oxygen terminals of this anion. The N7-O angles are also different indicating again different environments of this anion, while the 120º average of the N8-O is as expected for a delocalized π-bonding arrangement of these bonds and for a central nitrogen with sp^2 hybridization taking into account the charge delocalization over the three N-O bonds.

Supramolecular hydrogen-bonding synthons for $(TPGH)_2(NO_3)_2(H_2O)$ (1): A complex hydrogen-bonding schemes operate between the guanidinium cations, nitrate anions and the water molecule *via* N–H···O (synthon A) and O–H···O (synthon B) **Scheme-II**. The N-H groups of the cations act as donors to the oxygen's terminals of the nitrates and to the oxygen atom of the water molecule *via* N–H···O hydrogen bonding. The water molecule acts as an acceptor from one of the cations or a donor to the nitrate anions through O–H···O hydrogen bonding. A summary of the metrical parameters of the hydrogen-bonding is presented in Table-3.

TABLE-3
HYDROGEN BONDS [Å AND º] for $(TPGH)_2(NO_3)_2(H_2O)$ (**1**)
AND $(TPGH)_2(H_2PO_4)_2(H_3PO_4)$ (**2**)

D–H···A	d(D-H)	d(H···A)	d(D···A)	∠(DHA)
Compound **1**				
N(1)-H(1A)...O(3)	0.870	2.520	3.149	129.8
N(2)-H(2A)...O(6)	0.871	2.439	3.099	133.0
N(3)-H(3A)...O(7)	0.870	2.181	2.994	155.5
N(4)-H(4A)...O(5)	0.871	2.279	3.044	146.6
N(5)-H(5A)...O(2)	0.870	2.203	2.999	152.1
N(6)-H(6A)...O(1)	0.871	2.233	3.045	155.1
O(7)-H(7A)...O(4)	0.927	2.559	2.866	99.80
O(7)-H(7B)...O(3)	0.937	2.876	3.507	125.7
Compound **2**				
N(1)-H(1A)...O(9)#1	0.87	2.29	3.106(6)	156.0
N(2)-H(2A)...O(1)#2	0.87	2.39	3.137(6)	143.6
N(3)-H(3A)...O(8)#3	0.87	2.24	2.987(6)	143.5
N(4)-H(4A)...O(2)	0.87	2.18	3.007(6)	159.4
N(5)-H(5A)...O(11)#4	0.87	2.43	3.267(5)	160.8
N(6)-H(6A)...O(12)	0.87	2.15	3.011(5)	168.0
O(3)-H(3E)...O(6)	0.83	1.87	2.704(6)	179.4
O(4)-H(4C)...O(12)#1	0.83	1.81	2.640(5)	172.9
O(5)-H(5E)...O(1)	0.83	1.71	2.536(6)	175.2
O(7)-H(7B)...O(4)	0.83	2.16	2.978(6)	170.8
O(9)-H(9D)...O(8)	0.83	1.73	2.544(5)	164.8
O(10)-H(10A)...O(2)#5	0.83	1.73	2.551(5)	169.4
O(11)-H(11B)...O(6)	0.83	1.70	2.512(5)	165.0

Symmetry transformations used to generate equivalent atoms: #1 x,y+1,z; #2 -x+1,y+1/2,-z+1/; #3 -x+1,-y+1,-z; #4 -x,y+1/2,-z+1/2; #5 x,y-1,z; van der Walls radii taken from Bondi, A.J. Phys. Chem., 1964, 68, 441. Pertinent radii; C = 1.70, Å H = 1.2 , Å O = 1.52 Å, N = 1.55 Å



Scheme-II

A particularly significant feature of synthons (**A**) and (**B**), is the fact that the multiple N–H···O and O–H···O hydrogen-bonding form significant contacts to support the overall connectivity of the crystal lattice and ensures the planarity of the guanidinium CN_3 core.

Local hydrogen-bonding scheme for $(TPGH)_2(NO_3)_2(H_2O)$ (1): A view of the local hydrogen bonding network of this solid is presented in Fig. 2. Each of the guanidinium cations experiences an unsymmetrical use of the three N-H groups in hydrogen bonding. Guanidinium G-C1 links one N7-O and one N8-O through N–H···O interactions forming two hydrogen bonds and the third N-H group interacts with the (O7) terminal of a H_2O moiety leading to a third N–H···O hydrogen bond. While guanidinium G-C11 undergoes hydrogen-bonding interactions with two N7-O and one N8-O anions leading to three N–H···O hydrogen bonds. Each of the NO_3^- anions also experiences different local hydrogen-bonding interactions. Nitrate N7-O interacts with two G-C11 cations forming two N–H···O hydrogen bonds and the remaining oxygen center interacts with the O7 center of a water molecule constituting a third O–H···O hydrogen bond, which in turn links with another independent G-C1 cation. On the other hand the nitrate N8-O connects one G-C1, one G-C11 and one H_2O molecule. Then H_2O links with the O3 center of another N7-O anion through O–H···O hydrogen bonding. Thus, the water molecule acts as a multi hydrogen-bonding entity that leads to the supramolecular structure of compound (**1**).

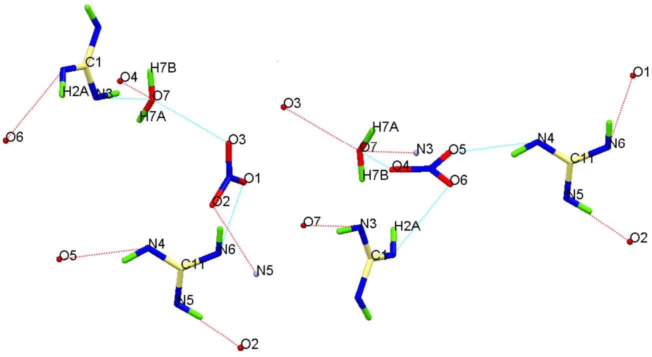


Fig. 2. A representation of the local interactions for $(TPGH)_2(NO_3)_2(H_2O)$ (**1**). The isopropyl groups and hydrogen atoms have been omitted for clarity

Extended structure for $(TPGH)_2(NO_3)_2(H_2O)$ (1): These local interactions generate a set of extended interactions. Fig. 3 displays a view of the extended hydrogen-bonding scheme for $(TPGH)_2(NO_3)_2(H_2O)$ (**1**) along the b-axis direction. Within the structure, the guanidinium cations, the N8-O anions and the water entities exist in the form of 1-D curly chains that extend along the b-axis direction. N–H···O and O–O···H hydrogen bonds link the chains to form different cyclic motifs that dominate the structure. Individual chains are connected by the bridging alternately oriented 3-fold N7-O anions yielding sheets and exhibiting large rings of an open 3-D net structure (Fig. 3). Intra-sheet hydrogen-bonding between the terminal oxygen atoms of the anions and the guanidinium cations strengthens the connections between the chains within a sheet.

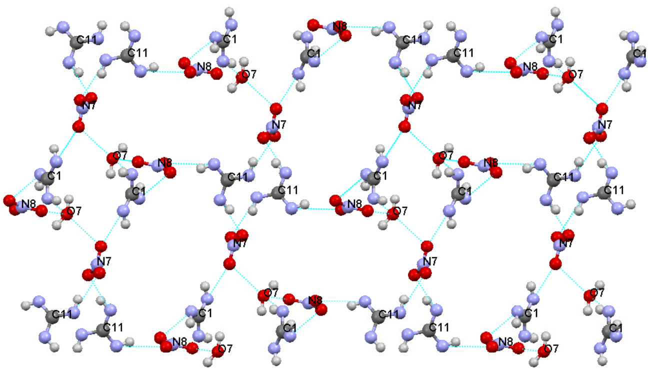


Fig. 3. A representation of the expanded structure of $(TPGH)_2(NO_3)_2(H_2O)$ (**1**) along the b-axis direction showing the interconnection of the chains through N–H···O hydrogen-bonding leading to a 2-D corrugated supramolecular sheets. The isopropyl groups and hydrogen atoms have been omitted for clarity

Molecular structure of $(TPGH)_2(H_2PO_4)_2(H_3PO_4)$ (2): The crystallographic asymmetric unit of $(TPGH)_2(H_2PO_4)_2(H_3PO_4)$ (**2**) comprises two independent guanidinium cations, residing on pseudo C_3 propeller-like orientation of N^iPr groups for the planar guanidinium cations, two dihydrogenphosphate anions and one equivalent of phosphoric acid. The crystal data and structure refinement are presented in (Table-4) and a diagram of the unit cell and the numbering scheme is presented in Fig. 4. The structure of this colourless solid is consistent with the monoclinic system, space group P2(1)/c with a = 16.542(2) Å, b = 10.8515(16) Å, c = 18.702(3) Å, a = γ = 90º, β = 91.888º(3).

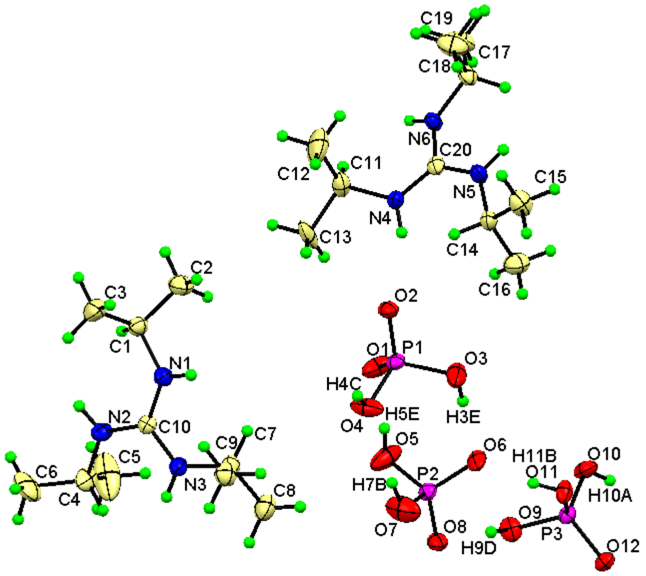


Fig. 4. ORTEP diagram showing the molecular structure and numbering scheme for $(TPGH)_2(H_2PO_4)_2(H_3PO_4)$ (**2**)

TABLE-4
CRYSTAL DATA AND STRUCTURE
REFINEMENT FOR $(TPGH)_2(H_2PO_4)_2(H_3PO_4)$ (**2**)

Empirical formula	$C_{20}H_{55}N_6O_{12}P_3$
Formula weight	664.61
Temperature	203(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 16.542(2) Å; α = 90º b = 10.8515(16) Å; β = 91.888(3)º c = 18.702(3) Å; γ = 90º
Volume	3355.4(8) $Å^3$
Z, Calculated density	4, 1.316 Mg/m^3
Absorption coefficient	0.239 mm^{-1}
F(000)	1432
Crystal size	0.20 × 0.10 × 0.10 mm
Theta range for data collection	1.23 to 26.37 º
Limiting indices	-20<=h<=20, -13<=k<=13, -23<=l<=21
Reflections collected/unique	22651/6671 [R(int) = 0.0748]
Completeness to theta = 26.37	97.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9765 and 0.9538
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6671/0/370
Goodness-of-fit on F^2	1.002
Final R indices [I>2σ(I)]	R1 = 0.0820, wR2 = 0.1849
R indices (all data)	R1 = 0.1330, wR2 = 0.2067
Largest diff. peak and hole	0.622 and -0.430 e.A^{-3}

The two guanidinium cations display no remarkable differences between their structural geometrical parameters, as seen from the values of bond distances and angles (Table-5).

TABLE-5
SELECTED BOND LENGTHS [Å] AND
ANGLES [º] FOR $(TPGH)_2(H_2PO_4)_2(H_3PO_4)$ (**2**)

Distance			
P(1)-O(1)	1.486(4)	P(3)-O(11)	1.551(4)
P(1)-O(2)	1.498(4)	P(3)-O(9)	1.551(4)
P(1)-O(3)	1.569(4)	P(3)-O(10)	1.554(4)
P(1)-O(4)	1.585(4)	N(1)-C(10)	1.328(6)
P(2)-O(6)	1.494(4)	N(2)-C(10)	1.330(6)
P(2)-O(8)	1.505(4)	N(3)-C(10)	1.345(7)
P(2)-O(5)	1.531(4)	N(5)-C(20)	1.329(6)
P(2)-O(7)	1.573(5)	N(6)-C(20)	1.359(7)
P(3)-O(12)	1.497(4)		
Angles			
O(1)-P(1)-O(2)	117.9(2)	O(1)-P(1)-O(3)	109.9(3)
O(2)-P(1)-O(3)	107.0(2)	O(1)-P(1)-O(4)	105.5(3)
O(2)-P(1)-O(4)	110.8(2)	O(3)-P(1)-O(4)	105.0(3)
O(6)-P(2)-O(8)	114.2(2)	O(6)-P(2)-O(5)	111.3(3)
O(8)-P(2)-O(5)	110.2(2)	O(6)-P(2)-O(7)	107.5(3)
O(8)-P(2)-O(7)	106.7(2)	O(5)-P(2)-O(7)	106.5(3)
O(12)-P(3)-O(11)	111.7(2)	O(12)-P(3)-O(9)	112.4(2)
O(11)-P(3)-O(9)	108.6(2)	O(12)-P(3)-O(10)	111.3(2)
O(11)-P(3)-O(10)	107.3(2)	O(9)-P(3)-O(10)	105.2(2)
C(10)-N(1)-C(1)	125.4(4)	C(10)-N(2)-C(4)	125.8(5)
C(10)-N(3)-C(7)	126.7(4)	C(20)-N(4)-C(11)	123.4(5)
C(9)-C(7)-C(8)	112.0(5)	N(1)-C(10)-N(2)	121.9(5)
N(1)-C(10)-N(3)	119.1(5)	N(2)-C(10)-N(3)	118.9(4)
C(19)-C(17)-C(18)	111.2(5)	N(5)-C(20)-N(4)	122.0(5)
N(5)-C(20)-N(6)	119.1(4)	N(4)-C(20)-N(6)	118.9(5)

For the purpose of dissecting the extended structure of this salt, the two independent guanidinium cations can be conveniently labeled by their central carbon atoms and labeled

G-C10 and G-C20. Similarly the two dihydrogen phosphate anions and phosphoric acid are conveniently labeled by their central phosphorous atoms and labeled P1-O, P2-O and P3-O.

The C-N bond lengths for G-C10 averages 1.334 Å and for G-C20 averages 1.340 Å. The N-C-N angles for G-C10 averages 119.9º and for G-C20 averages 120º. These geometrical parameters are in good accord with those seen in related structures[14-27] and indicate planarity of the CN_3 core (sum of angles = 360º); and suggest an electron delocalized Y-conjugated species[28] as expected for sp^2 hybridization of a central carbon atom. However, the P-O bond lengths for $H_2PO_4^-$ anions are not equivalent. P1-O distances are 1.486(4), 1.498(4), 1.569(4), 1.585(4) Å, respectively. P1-O1 and P1-O2 bond lengths are significantly shorter than P1-O3 and P1-O4 bonds indicating a delocalized π-bonding arrangement of these two bonds; and P1-O3 and P1-O4 bond lengths are as expected for a protonated phosphate anion. On the other hand the P2-O bond lengths are 1.531(4), 1.494(4), 1.573(5),1.505(4) Å, respectively. The P2-O6 and P2-O8 bond lengths are also significantly shorter than P2-O5 and P2-O7 bonds indicating a delocalized π-bonding for these bonds, while P2-O5 and P2-O7 bond lengths are as expected for protonated phosphate anion. The P3-O bond lengths for the H_3PO_4 acid moiety are 1.551(4), 1.554(4), 1.551(4) and 1.497(4) respectively, having P3-O12 shorter than the other three bonds indicating a P=O π-bond for this bond and the other three bonds are as expected for protonated phosphoric acid. The O-P-O angles for P1-O, P2-O and P3-O each averages 109.4º. These averages are consistent with a T_d geometry and sp^3 hybridization of the central phosphorous atom.

Supramolecular hydrogen-bonding synthons for $(TPGH)_2(H_2PO_4)_2(H_3PO_4)$ (2): Again, a complex hydrogen-bonding schemes operate between the guanidinium cations, (di)hydrogen phosphate anions and phosphoric acid entities *via* N–H···O and P–O–H···O interactions. The guanidiniun N-H groups act as donors to the P-O groups. The P-O and P-O-(H) groups act either as donors or acceptors in interactions between and among the three phosphates.

Local hydrogen-bonding scheme for $(TPGH)_2(H_2PO_4)_2(H_3PO_4)$ (2): The N-H groups of G-C10 makes three links through N–H···O hydrogen bonding interactions to nearby oxygen atoms. One with P1-O, the second with P2-O and the third with P3-O of three independent phosphates; also the N-H groups of G-C20 undergo three interactions with three nearby oxygen terminals. Two of the hydrogen bonds with two independent P3-O phosphoric acids and the third with P1-O anion. Thus, all the N-H groups of both cations are involved in hydrogen-bonding interactions with the phosphates as donors forming six N–H···O hydrogen bonds (Figs. 5 and 6). The P=O and P-O-H groups of the three phosphates are also involved in hydrogen bonding interactions with each other in a complex hydrogen-bonding scheme leading to generation of trimers constructed from two anions and one phosphoric acid moiety $(H_2PO_4)_2(H_3PO_4)^{2-}$. These connectivity's result in cyclic topologies based on a complex network of 3,4,5,6 and 8-membered rings. Thus, all the P=O and P-O-H groups are involved in hydrogen-bonding interactions as donors or acceptors.

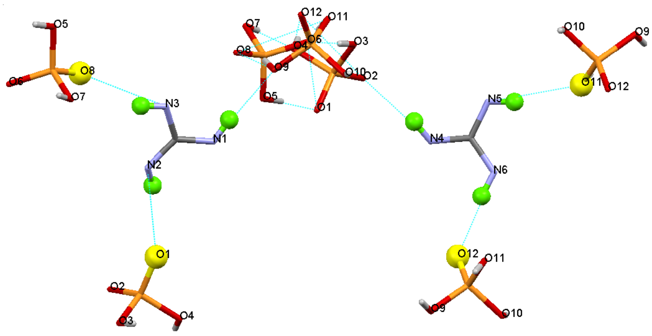


Fig. 5. A diagram emphasizing the local interactions for $(TPGH)_2(H_2PO_4)_2(H_3PO_4)$ (**2**). The isopropyl groups and hydrogen atoms have been omitted for clarity

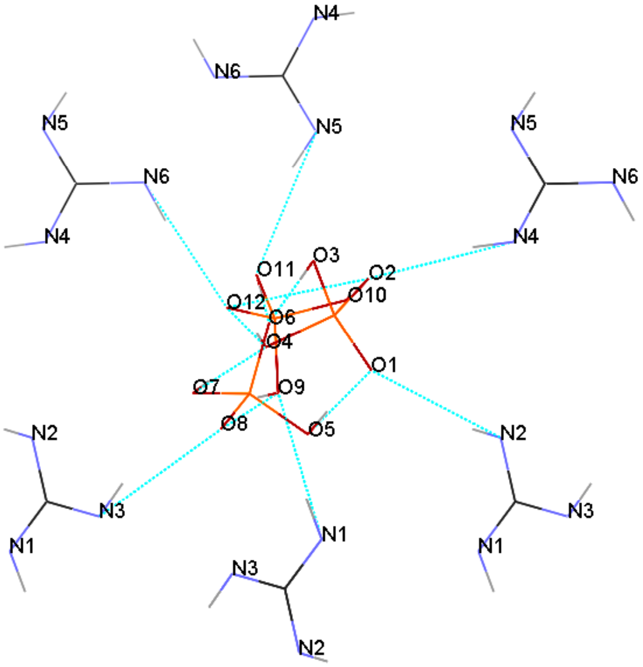


Fig. 6. A presentation emphasizing the six hydrogen N–H···O bonds formed from the local interactions in $(TPGH)_2(H_2PO_4)_2(H_3PO_4)$ (**2**). The isopropyl groups and hydrogen atoms have been omitted for clarity

Extended structure for $(TPGH)_2(H_2PO_4)_2(H_3PO_4)$ (2): These local interactions generate a set of extended interactions structure for $(TPGH)_2(H_2PO_4)_2(H_3PO_4)$ (**2**). The local interactions between P1-O, P2-O and P3-O through O–H···O hydrogen-bonding propagate along the c-axis direction leading to chains along this axis (Fig. 7). The individual chains are further linked by the 3-fold bridging cations *via* N–H···O hydrogen bonding yielding 2-D sheets and exhibiting large rings of an open 3-D net structure. Fig. 8 displays the extended structure of this compound along the b-axis direction.

Conclusion

In this report we have further elucidated the intermolecular interactions that influence the fundamental structural features of solids designed around novel N,N',N"-trisubstituted guanidinium cations.

The solid state structures of the two new compounds $(TPGH)_2(NO_3)_2(H_2O)$ (**1**) and $(TPGH)_2(H_2PO_4)_2(H_3PO_4)$ (**2**) reported here exhibit common features. Both compounds

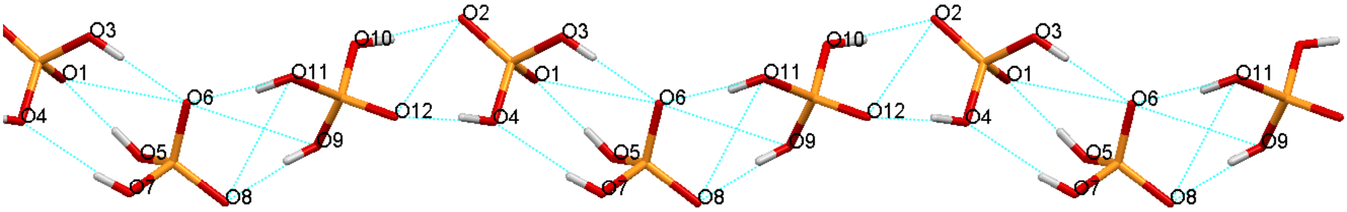


Fig. 7. A diagram emphasizing the formation of the phosphate chain along the c-axis direction for $(TPGH)_2(H_2PO_4)_2(H_3PO_4)$ (**2**). The isopropyl groups and hydrogen atoms have been omitted for clarity

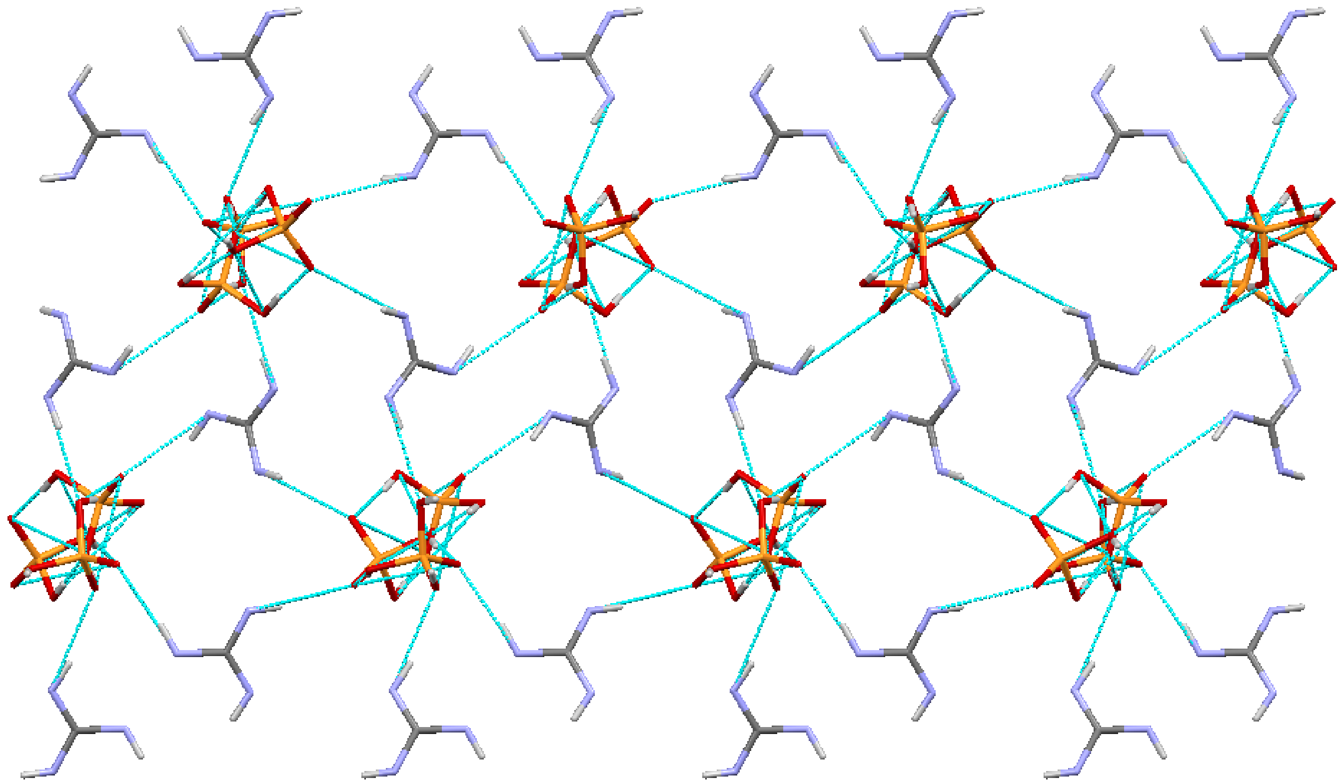


Fig. 8. A diagram representing the expanded hydrogen-bonding interactions for $(TPGH)_2(H_2PO_4)_2(H_3PO_4)$ (**2**) along the b-axis direction. The isopropyl groups and hydrogen atoms have been omitted for clarity

crystallized in the monoclinic space group and the crystallographic asymmetric unit of each comprises two independent guanidinium cations and two anions; and both are solvated. The presence of water in compound **1** and phosphoric acid in compound **2** seems to be important to support the overall connectivity's and the supramolecular structural lattices of the these compounds. The trisubstituted guanidinium cation, the nitrate and phosphate anions used in this study have been proven to form strong interactions through hydrogen bonding and charge pairing in competitive solvent systems and could be utilized as receptors in synthetic sensors designs. Trisubstituted guanidinium cations certainly represent interesting three-fold, hydrogen bonding moieties for crystal design and our continuing efforts are attempting to unravel the influence of substituents and identity of the acceptors in their extended structures.

Supplementary material

CCDC 864197 contains the supplementary crystallographic data for compound (**1**) and CCDC 869283 contains the supplementary crystallographic data for compound (**2**). These data can be obtained free of charge from The Cambridge Data Centre via www.ccdc.cam.ac.uk/data.request/cif.

ACKNOWLEDGEMENTS

The author thanks Dr. Glenn Yap and Dr. Ilia Korobkov for their help in the X-ray analysis of the titled structures. My appreciation is extended to Professor Darrin Richeson for his support.

REFERENCES

1. M.D. Best, S.L. Tobey and E.V. Anslyn, *Coord. Chem. Rev.*, **240**, 3 (2003).
2. C.L. Hanon and E.V. Anslyn, *Bioorg. Chem. Frontiers*, **3**, 193 (1993).
3. D.M. Perrault, L.A. Cabell and E.V. Anslyn, *Bioorg. Med. Chem.*, **5**, 1209 (1997).
4. A. Metzger, V.M. Lynch and E.V. Anslyn, *Angew. Chem. Int. Ed. Engl.*, **36**, 862 (1997).
5. K.A. Schung and W. Lindner, *Chem. Rev.*, **105**, 67 (2005).
6. M. Dincer, N. Ozdemir, E. Saripinar, L. Kulak and O. Buyukgungor, *Acta Cryst. C*, **C61**, o722 (2005).
7. F.A. Cotton, V.W. Day, E.E. Hazen and S. Larsen, *J. Am. Chem. Soc.*, **95**, 4834 (1973).

8. F.F. Said, P. Bazinet, T.-G. Ong, G.P.A. Yap and D. Richeson, *Cryst. Growth Des.*, **5**, 1881 (2005).
9. F.F. Said, P. Bazinet, T.-G. Ong, G.P.A. Yap and D. Richeson, *Cryst. Growth Des.*, **6**, 258 (2006).
10. F.F. Said, P. Bazinet, G.P.A. Yap and D. Richeson, *Cryst. Growth Des.*, **6**, 1848 (2006).
11. F.F. Said, B.F. Ali and D. Richeson, *Acta Cryst.*, **E67**, O3467 (2011).
12. F.F. Said, B.F. Ali, D. Richeson and I. Korobkov, *Acta Cryst.*, **E68**, o1906 (2012).
13. T.G. Ong, G.P.A. Yap and D.S. Richeson, *J. Am. Chem. Soc.*, **125**, 8100 (2003); T.G. Ong, G.P.A. Yap and D.S. Richeson, *Organometallics*, **22**, 387 (2003); N. Thirupathi, G.P.A. Yap and D.S. Richeson, *Chem. Commun.*, 2483 (1999); M.K.T. Tin, N. Thirupathi, G.P.A. Yap and D.S. Richeson, *J. Chem. Soc., Dalton Trans.*, 2947 (1999); M.K.T. Tin, G.P.A. Yap and D.S. Richeson, *Inorg. Chem.*, **37**, 6728 (1998).
14. B.F. Abrahams, M.G. Haywood, T.A. Hudson and R. Robson, *Angew. Chem. Int. Ed.*, **43**, 6157 (2004).
15. B.F. Abrahams, M.G. Haywood, T. A. Hudson and R. Robson, *J. Am. Chem. Soc.*, **127**, 816 (2005).
16. K.T. Holman, A.M. Pivovar and M.D. Ward, *Science*, **294**, 1907 (2001).
17. K.T. Holman, A.M. Pivovar, A.M. Swift, J.A. and M.D. Ward, *Acc. Chem. Res.*, **34**, 107 (2001).
18. W.T.A. Harrison, M.L.F. Phillips, W. Clegg and S.J Teat, *J. Solid State Chem.*, **148**, 433 (1999).
19. T. Steiner, *Angew. Chem. Int. Ed.*, **41**, 48 (2002).
20. D.R. Trivedi, A. Ballabh and P. Dastidar, *CrystEngComm.*, **5**, 358 (2003).
21. A. Ballabh, D.R. Trivedi, P. Dastidar and E. Suresh, *CrystEngComm.*, **4**, 135 (2002).
22. J.C. MacDonald, P.C. Dorrestein and M.M. Pilley, *Cryst. Growth Des.*, **1**, 29 (2001).
23. C.B. Aakeroy and M. Nieuwenhuyzen, *J. Am. Chem. Soc.*, **116**, 10983 (1994).
24. C.B. Aakeroy, P.B. Hitchcock and K.R. Seddon, *Chem. Commun.*, 553 (1992).
25. J. Emsley, *Chem. Soc. Rev.*, **9**, 91 (1980).
26. J.C. Speakman, *Struct. Bond.*, **12**, 141 (1972).
27. T. Steiner, *Acta Crystallogr.*, **B57**, 103 (2001).
28. A. Gobbi and G. Frenking, *J. Am. Chem. Soc.*, **115**, 2362 (1993).