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Anion Guided Self-Assembling of Guaninium Cations

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Abstract

Anions guide self-assemblies of ribbons or end-capped dimers of guaninium cations. Self-assemblies of several salts of guanine are compared with related guanine salts from literature. End-capped dimers of guaninium cations self-assembled by perchlorate or by dihydrogen-phosphate anions whereas sulphate-bisulphate anions stabilizes infinite ribbon-like assemblies of cations. Formation of discrete, dimer, or ribbons of cations in guaninium salts depends on anions and water has less dominant role other than to modify environments of anions. This result is a contrast effect caused by aquation on self-assembilies of neutral guanine molecules.

Keywords: Guaninium cations; Self-assembly; Anion-assisted assembly; End-capped structures; Ribbon-like assembly

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Background

Aquated or free anions are found to guide self-assemblies of guaninium cations. End capped dimeric sub-assemblies are held by perchlorate or dihydrogen-phosphate to form self-assemblies; whereas sulphate-bisulphate guides guaninium cations to form ribbon-like assemblies of cations. Though hydration causes large variation of self-assembling of guanine, self-assembling of guaninium cations is invariant of aquation of anions.

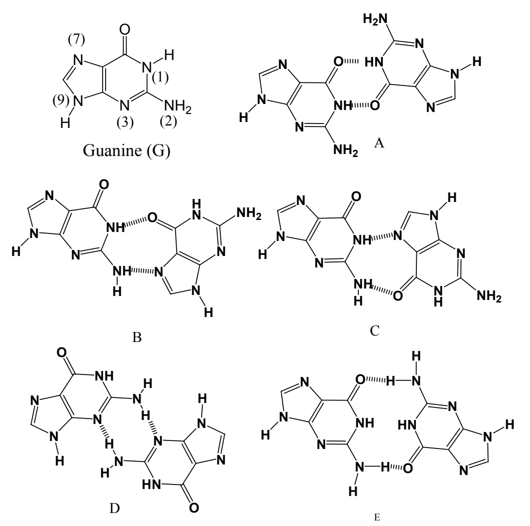
Introduction

Self-complementary multiple hydrogen bond sites present in guanine and derivatives, help them to self-assemble into various supramolecular assemblies such as dimers, ribbons, tapes or macrocycles [1,2]. These assemblies have shown potential to develop sensors, nano-materials [3-5]. Famous G-quartet (G = guanine) assemblies find applications as hydrogels [6-9]. These GG pairs mainly assemble as ribbon or as part of cyclic G quartet in solid-state have applications in molecular electronics [10,11]. In addition, guanine derivatives form metal complexes [12-14]. Guanine nucleobases self-assemble to form four different type guanine-guanine pairs in DNA or RNA [15-18] which are shown in **Scheme 1**. Compartively, guanine has more numbers of ways to form self-assemblies than N-substituted guanines. However, poor solubility of guanine in common solvent stands as an obstacle to carry out structural study unsubstituted guanine, hence comparatively lesser structural study as compared to other base counterparts such as adenine have been carried out [19-21]. Broomhead [22] established structure of guanine hydrochloride monohydrate by X-ray in 1951, which followed structural study on salts such as nitrate [23] and phosphate and dihydrogen-phosphate [24]. These **(Scheme 1)** reports are available in literature as segmented structural report and have not been made systematic; hence we set to study supramolecular architectures of structures of salts with various oxyanions. Lattice water molecules seldom participate in base pairing [25] but presence of single water molecule considerably influences guanine-guanine pairing patterns [26]. Keeping in mind the importance of such systems in crystal engineering [27] our focus in this study is on (i) protonation of guanine by varying tetrahedral anion from monobasic to tribasic acids, (ii) different self-assemblies of guanine or anion assisted assemblies in their protonated form, and (iii) role of lattice hydrates in assemblies.

Experimental Section

Synthesis and characterisation

Solution of guanine (G, 1 mmol) in water (5 ml) was reacted independently with 1 ml of acid, perchloric (70%) or sulphuric (98%) or phosphoric (85%) acid, respectively which afforded their salt 1, 2 or 3. Colorless solution obtained in each case was allowed to evaporate slowly at ambient temperature. After one week, single crystals suitable for X-ray crystallography were



Scheme 1 Structure of guanine and assembling of guanine-guanine pairs.

harvested. Salt $[(HG)(ClO_4)]1.5H_2O$ 1: Yield, 48%. Elemental analysis calculated for $C_5H_9ClN_5O_{7.5}$, C, 20.37; H, 3.05; N, 23.76%; found C, 20.31; H, 3.04; N, 23.84%. IR (KBr, cm^{-1}): 3436 (w), 3377 (m), 3167 (m), 3102 (m), 2922 (m), 1711 (s), 1654 (s), 1607 (w), 1388 (s), 1144 (w), 1111 (m), 1084 (s). Molar conductance: 307.0 Scm^2mol^{-1} in water. Salt $[(HG)_2(HSO_4)_2(SO_4)]2H_2O$ (2): Yield, 45%. Elemental analysis calculated for $C_{20}H_{30}N_{20}O_{18}S_3$, C, 25.67; H, 3.21; N, 29.95%; found C, 25.60; H, 3.14; N, 30.02%. IR (KBr, cm^{-1}): 3336 (bs), 3104 (bs), 2907 (w), 1697 (s), 1654 (m), 1615 (m), 1375 (s), 1073 (s). Molar conductance: 524.0 Scm^2mol^{-1} in water. Thermal analysis: decomposition range ~ 80-175 °C (loss of two water molecules of crystallization). Salt $[(HG)(H_2PO_4)]H_2O$ (3): Yield, 52%. Elemental analysis calculated for $C_5H_{10}N_5O_6P$, C, 22.46; H, 3.74; N, 26.20%; found C, 22.33; H, 3.69; N, 25.95%. Selected IR data (KBr, cm^{-1}): 3473 (w), 3333 (w), 3178 (w), 3139 (s), 2922 (w), 1672 (s), 1615 (s), 1382 (m), 1099 (m), 1047 (s), 965 (m). Molar conductance: 168.0 Scm^2mol^{-1} in water. Thermal analysis: decomposition range: ~70-135 °C (loss of water molecules).

Physical measurements

Infrared spectra (KBr pellets) of salts 1-3 were recorded with a Thermo iS10 FTIR spectrophotometer in 4000-400 cm^{-1} spectral region. Elemental analyses were performed with a Perkin Elmer 2400 series micro analytical analyzer. Elico conductivity meter, model CM 180, was used to determine molar conductance.

X-ray structural studies

Single crystal diffraction data for 1-3 were collected at 296 K with Mo Kα radiation (λ = 0.71073 Å) using a Bruker Nonius SMART APEX diffractometer equipped with graphite monochromator and Apex CCD camera. SMART software (v 2.1-4) was used for indexing and unit cell parameters. Data reduction and cell refinement were performed using SAINT software and the space groups of these crystals were determined from systematic absences by XPREP. The structures were solved by direct methods and refined by full-matrix least-square calculations using SHELXTL software [35]. All the non-hydrogen atoms were refined in anisotropic approximation against F^2 of all reflections. Hydrogen atoms attached to nitrogen atoms of guanine were located in difference Fourier synthesis maps, and refined with isotropic displacement coefficients. Crystal parameters are summarized in **Table 1.**

Results and Discussion

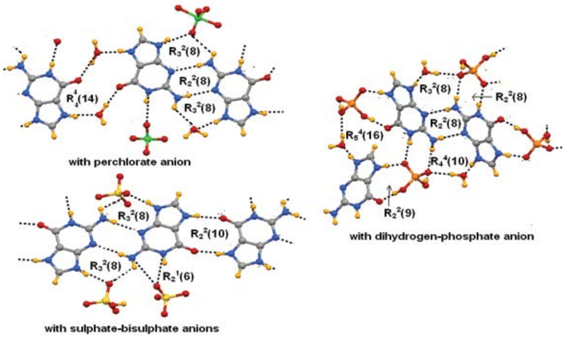
Guanine was treated with different oxy-acids possessing tetrahedral anion in aqueous medium with an anticipation to generate hydrated assemblies of salts. Treatment of guanine (G) with perchloric, sulphuric or phosphoric acid in water afforded respective salt $(HG)(ClO_4)\cdot 1.5H_2O$ (1), $(HG)_4(HSO_4)_2(SO_4)\cdot 2H_2O$ (2) or $(HG)(H_2PO_4)\cdot H_2O$ (3). It may be noticed that the hydration in each salt is different. The dihydrogen-phosphate salt was reported earlier [24] but we have redone the structure so as to make a comparison on crystals obtained from three different acids under similar conditions. Crystal structure of guaninium-perchlorate (1) consists of two units of guaninium cation $[HG]^+$ and perchlorate anion, and four lattice water molecules. In the perchlorate salt 1, protonation by perchloric acid took place at conventional site as observed earlier [28]. In the crystal structure, one oxygen atom of perchlorate is found to be disordered. The electron density of disordered atom is distributed over two crystallographically equivalent positions. Due to flexible interacting ability among supramolecular components possibly allowed the crystallographic disorder in perchlorate anion [29]. Guaninium cations form dimer through Watson-Crick edge by interacting through N-H···N interactions between two symmetry independent cations form $R_2^2(8)$ motif [30,31] **(Figure 1a).** Due to interaction of such sub-assemblies of cations two lattice water molecules results in an extended one-dimensional ribbon along crystallographic *c*-axis cations which posseses $R_4^4(14)$ motif as illustrated in **Figure 1a.** The perchlorate anions and lattice water molecules form one-dimensional chain as shown in **Figure 1b.** In lattice, adjacent guanine-perchlorate ribbons reside in a parallel manner, holding perchlorate anions from either side **(Figure 1c)**. Distances between such planes are ~ 3.2 Å. These chains provide connecting points to keep the dimeric pairs of cations at two ends to form grid like arrangements of cations. On the other hand depending on host, aquated perchlorate anions were shown form hexameric cyclic hydrogen bonded assembly having appearance of open-book [32,33]. Hence, present example shows stabilisation of aquated assemblies of perchlorate anions by dimeric guaninium cations. The structure may be also describe alternatively as assemly of end capped dimeric cations capped by perchlorate ions through a $R_3^2(8)$ motif on one side and water molecules froming on other sides and such units held by $R_4^4(14)$ motifs (**Table 2**). Single crystals obtained from reaction of guanine with sulphuric acid in water, had a composition $(HG)_4(HSO_4)_2(SO_4)\cdot 2H_2O$ (2). This result is different from earlier report as heating aqueous solution of guanine with sulpuric acid gave the guaninium salt $(HG)_2SO_4.2.5H_2O$ [31]. Hence, it clearly points out that variation of recation conditions significantly affects the deprotonation of the acid. The salt 2 is comprised of both sulphate and bisulphate anion. The asymmetric unit has four $[HG]^+$ cations, two bisulphate anions, one sulphate anion and two lattice water molecules. Anhydrous form of guanine salt having sulphate and bisulphate

Table 1 Crystal parameters for the structures 1-3.

Compound No.	Salt 1	Salt 2	Salt 3 (reported earlier[31])
Formula	$C_{10}H_{18}Cl_2N_{10}O_{15}$	$C_{20}H_{30}N_{20}O_{18}S_3$	$C_5H_{10}N_5O_6P$
Mr	589.24	934.82	267.15
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	Cc	P-1	$P2_1/n$
a (Å)	4.9051(3)	6.4530(5)	4.5542(2)
b (Å)	46.567(3)	13.3515(9)	12.5955(5)
c (Å)	9.7185(6)	20.9920(14)	18.2991(7)
α (deg)	90.00	77.048(4)	90.00
β (deg)	96.646(4)	81.672(4)	92.606(2)
γ (deg)	90.00	86.203(4)	90.00
V (Å^3)	2204.9(2)	1742.9(2)	1048.60(7)
Z	4	2	4
D_{calc} (gcm^{-3})	1.775	1.781	1.692
μ (mm^{-1})	0.393	0.324	0.292
F(000)	1208	964	552
Total no. of reflns	15906	19714	10860
Independent reflns	3676	5853	1833
ϑ_{range}	0.87 – 24.98	1.00 – 25.00	1.96 - 25.00
Ranges (h, k, l)	$-5 \le h \le 5$ $-54 \le k \le 54$ $-11 \le l \le 11$	$-7 \le h \le 7$ $-15 \le k \le 14$ $-24 \le l \le 22$	$-5 \le h \le 5$ $-14 \le k \le 14$ $-21 \le l \le 21$
Completeness to 2θ (%)	99.2	95.1	98.9
Data /restraints/ parameters	3676 / 6 / 358	5853 / 0 / 562	1833 / 0 / 182
GOF (F^2)	0.820	1.195	1.070
R_1, wR_2 [$I > 2\sigma(I)$]	0.0612, 0.1648	0.0769, 0.1925	0.0328, 0.0899
R_1, wR_2 (all data)	0.0862, 0.1956	0.1112, 0.2138	0.0389, 0.0944
Largest diff peak / hole (e Å^{-3})	0.392 / -0.650	0.907 / -0.587	0.272 / -0.422

Supporting information: Crystallographic Information files of the salts 1-3 are deposited to Cambridge Crystallographic database and they have CCDC Nos. 1014792-1014794.

was prepared earlier by dehydration of corresponding hydrated salt [31]. Anhydrous salt had a similar ribbon-like assembly of cations as observed in the hydrated salt. In hydrated anions hold the ribbons, whereas in anhydrous form they are held directly by the anions. Thus, role of water in presence of sulphate-bisulphate anion has little to do to change the assembling of cations. Among the four $[HG]^+$ cations present in the asymmetric unit, two are symmetry independent, the symmetry equivalent pair form one-dimensional planar ribbon through $R_2^2(10)$ motifs along crystallographic *a*-axis as shown in **Figure 2a**. Hydrogen bond parameters are listed in **Table 2**. Close look at crystal structure of 2 shows that cationic guaninium ribbons are aligned parallel separated by a distance of 3.24 Å **(Figure 2b)**. Sulphate and bisulphate anions lie on two sides of ribbons. Sulphate anions are held by bifurcated hydrogen bonds with two N-H bonds, forming a $R_2^1(6)$ motifs on one side and $R_3^2(8)$ on another side. On the other hand bisulphate are held to cations by $R_3^2(8)$ motif on one side and by N-H···O interactions **(Figure 2a)** on another side. Anions and lattice water molecules form infinite anion-water cluster as shown in **Figure 2c**. Common feature between the guaninium sulphate salts reported by others and us is guaninium cations showed same type of cationic ribbon based on cyclic hydrogen bonded $R_2^2(8)$ and $R_2^2(10)$ motifs. Phosphoric acid reacted with guanine to form a salt with a composition $(HG)(H_2PO_4)\cdot H_2O$ (3), structure of which was reported earlier [24]. It posses end capped cationic dimeric assemblies bound to dihydrogen phosphate anions and water molecules through $R_2^2(8)$ and $R_4^4(10)$ hydrogen bonded motifs **(Figure 2c)**. These end capped structures are linked to each other through $R_2^2(9)$ and $R_5^4(16)$ type hydrogen bond motifs. On the other hand, nitrate salt of guanine $(H_2G)(NO_3)_2\cdot 2H_2O$ (4) reported [23] earlier was also confirmed by us that same is also formed under ordinary condition on reaction of guanine with nitric acid. It is comprised of diprotonated guanine forming planar sheet like assembly with nitrate anions and lattice water molecules help in stacking. Infra-red spectra of salts **1-4** show stretching vibrations appearing in the range of 3436-3472 cm^{-1} **(Figure 3)** from hydrogen bonded water molecules [34]. The N-H stretching vibrations appear in range 3100-3377 cm^{-1} but stretching frequencies differ with anion; suggests different hydrogen bonding environment for the cationic part in each case. In these regions, guanine salts containing perchlorate and dihydrogen-phosphate anions exhibit sharp stretching



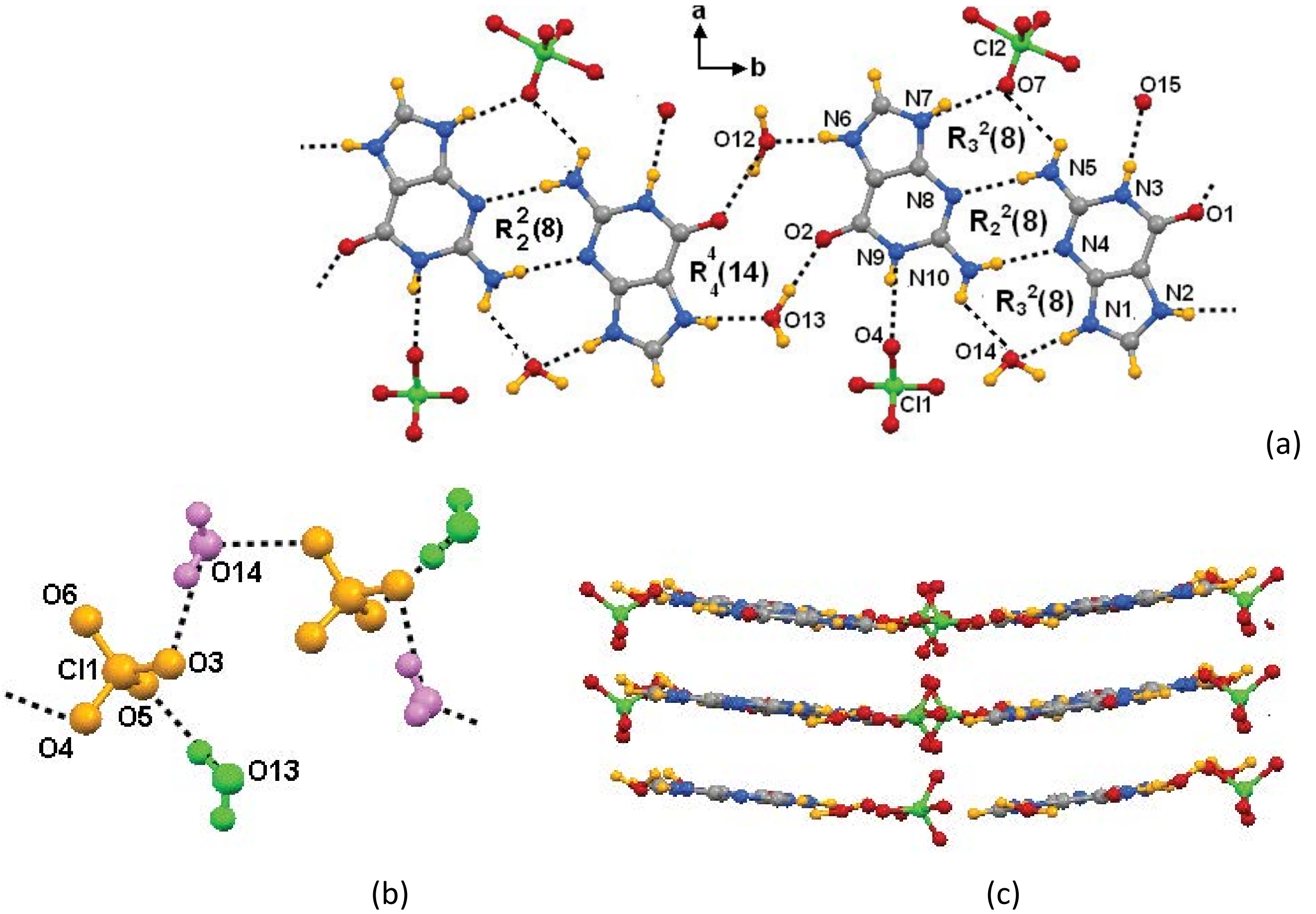


Figure 1 (a) Hydrogen-bonded 1D-ribbon of protonated guanine; (b) Interactions among perchlorates and water molecules in the salt and (c) Layers of cations threaded by anions, in lattice of salt 1.

frequencies, while marked broadening peaks appeared for the nitrate and sulphate-bisulphate containing guanine salts. This is attributed to difference in hydrogen bonds associated with dimer or infinite ribbon of protonated guanine molecules surrounded by anions. Each salt also exhibits characteristic sharp stretching vibrations for corresponding anion. Generally IR-stretching of perchlorate ions is guided by environment around it, perchlorate anion in symmetric environment or free anion shows one single stretching around 1150 cm^{-1}, however we observed three symmetric shows signals at 1143 cm^{-1}, 1111 cm^{-1} and 1083 cm^{-1}. This supports that the perchlorate is under influence of strong hydrogen bond as illustrated in **Figure 2a.** In case of sulphate absorption due to S=O appears at 1073 cm^{-1}. Whereas, biphosphate shows strong absorptions due to P=O stretching at 1099 cm^{-1}, 1047 cm^{-1} and 965 cm^{-1} respectively whereas the nitrate salts shows N=O stretching at 1384 cm^{-1}.

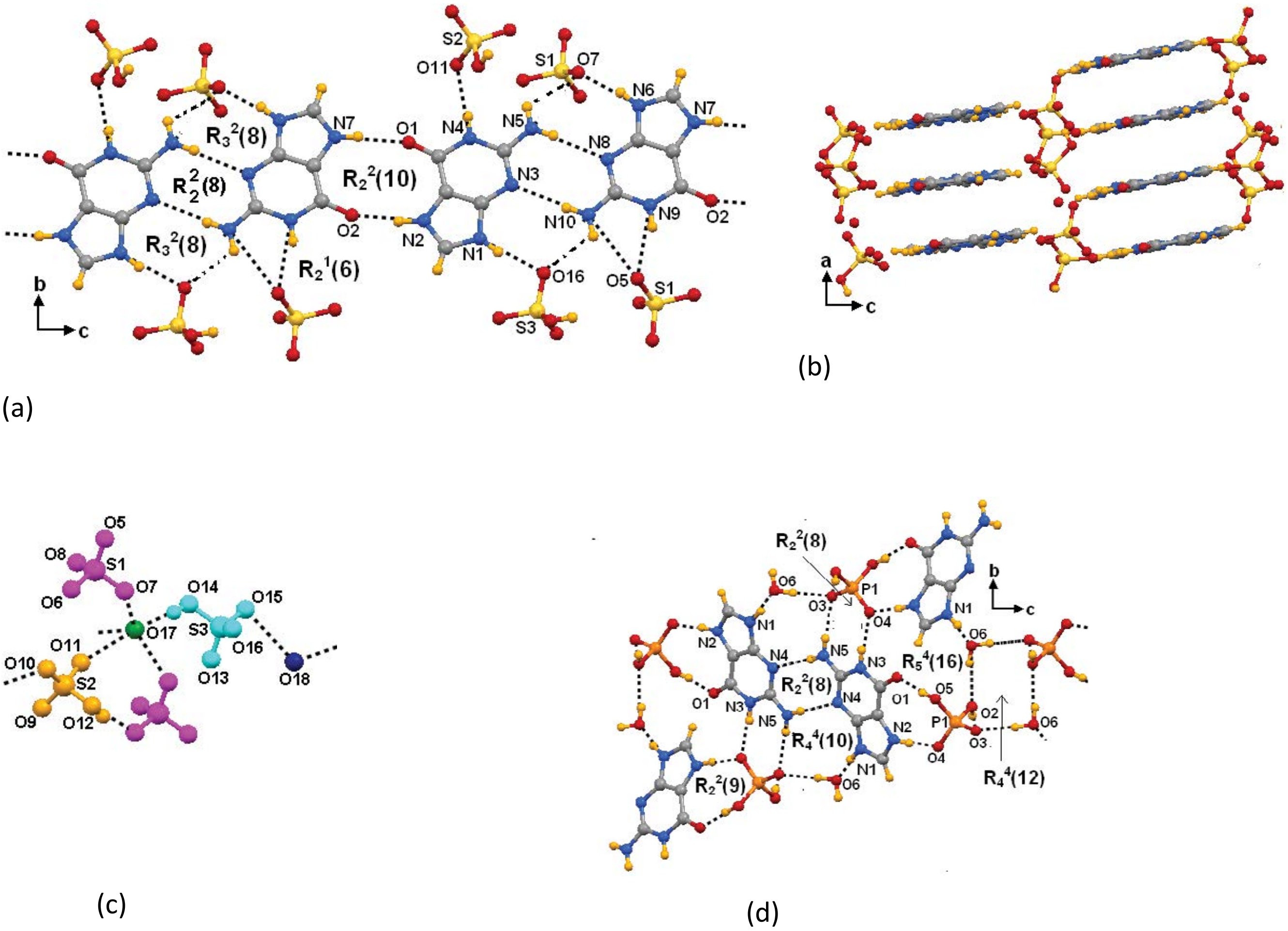
Table 2 Selected hydrogen-bond parameters for the salts 1-2.

Salt	Bond (symmetry)	d_{D-H} (Å)	$d_{H\cdots A}$ (Å)	$d_{D\cdots A}$ (Å)	<D-H···(Å)
1	N(1)-H(1A)···O(14)	0.86	1.89	2.745(8)	171
	N(2)-H(2)···O(13)^{i}	0.86	1.85	2.700(8)	167
	N(3)-H(3)···O(15)	0.86	1.97	2.834(9)	177
	N(5)-H(5A)···N(8)^{ii}	0.86	2.24	3.102(8)	175
	N(6)-H(6A)···O(12)	0.86	1.80	2.656(9)	170
	N(7)-H(7)···O(7)^{iii}	0.86	1.99	2.827(12)	163
	N(9)-H(9)···O(4)	0.86	2.08	2.912(7)	161
	N(10)-H(10A)···N(4)^{iii}	0.86	2.16	3.015(8)	177
	O(12)-H(12A)···O(1)^{iv}	0.97(12)	1.84(15)	2.741(8)	154(18)
	O(13)-H(13B)···O(2)	0.97(5)	1.83(5)	2.799(7)	179(7)
2	N(1)-H(1N)···O(16)^{v}	0.86	1.89	2.735(5)	168
	N(2)-H(2N)···O(2)^{vi}	0.95(5)	1.75(5)	2.694(5)	171(4)
	N(4)-H(4N)···O(11)	0.86	1.99	2.827(5)	164
	N(5)-H(5NB)···N(9)	0.86	2.21	3.060(6)	173
	N(6)-H(6N)···O(7)	0.86	1.83	2.675(5)	168
	N(7)-H(7N)···O(1)^{vii}	0.86	1.90	2.757(5)	172
	N(8)-H(8N)···O(5)^{v}	0.86	2.04	2.840(5)	155
	N(10)-H(10A)···N(3)	0.86	2.22	3.079(6)	175
	N(11)-H(11N)···O(8)^{ix}	0.86	1.82	2.659(5)	166
	N(12)-H(12N)···O(4)^{viii}	0.99(8)	1.78(8)	2.762(5)	174(9)
	N(13)-H(13N)···O(17)	0.86	2.03	2.873(5)	168
	N(15)-H(15A)···N(19)^{ix}	0.86	2.27	3.125(6)	172
	N(15)-H(15B)···O10	0.86	2.12	2.949(5)	163
	N(16)-H(16N)···O(9)^{ix}	0.86	1.78	2.610(6)	163
	N(17)-H(17N)···O(3)^{viii}	0.95(4)	1.70(4)	2.655(5)	177(4)
	N(18)-H(18N)···O13	0.86	1.99	2.819(5)	160
	N(20)-H(20A)···N(14)^{ix}	0.86	2.21	3.066(6)	174

Symmetry codes: (i) 1+x, y, -1+z; (ii) -1+x, y, z; (iii) 1+x, y, z; (iv) -1+x, y, 1+z; (v) 1-x, 1-y, -z; (vi) x, 1+y, z; (vii) x, -1+y, z; (viii) 1-x, -y, 1-z; (ix) 1-x, 1-y, 1-z.

Conclusion

Hydrated salts of guanine salts of mono-, di-, tri-basic acids have shown highly anion dependent self-assemblies to provide scope for formation of ribbon or end capped or discrete self-assemblies of guaninium cations. On the other hand, planar nitrate ion acts as a template to stabilize discrete guaninium di-cations. Triple hydrogen bonded assemblies which generally contribute to insoluble nature of guanine, are absent in any of these structures of the salt studied. It is also observed that water molecules do not change the arrangements of cationic assemblies of guanine in hydrated or anhydrous form of salt, this result is advantageous over the structural changes caused by hydration in self-assemblies of neutral guanine molecules.



(a)

(b)

(c)

(d)

Figure 2 (a) 1D-ribbon of guaninium cations in salt 2, (b) View showing parallel ribbons in 2, (c) Sulphate-bisulphate-water cluster. (d) Assembly of guaninium cations with dihydrogen phosphate and lattice water molecules [24].

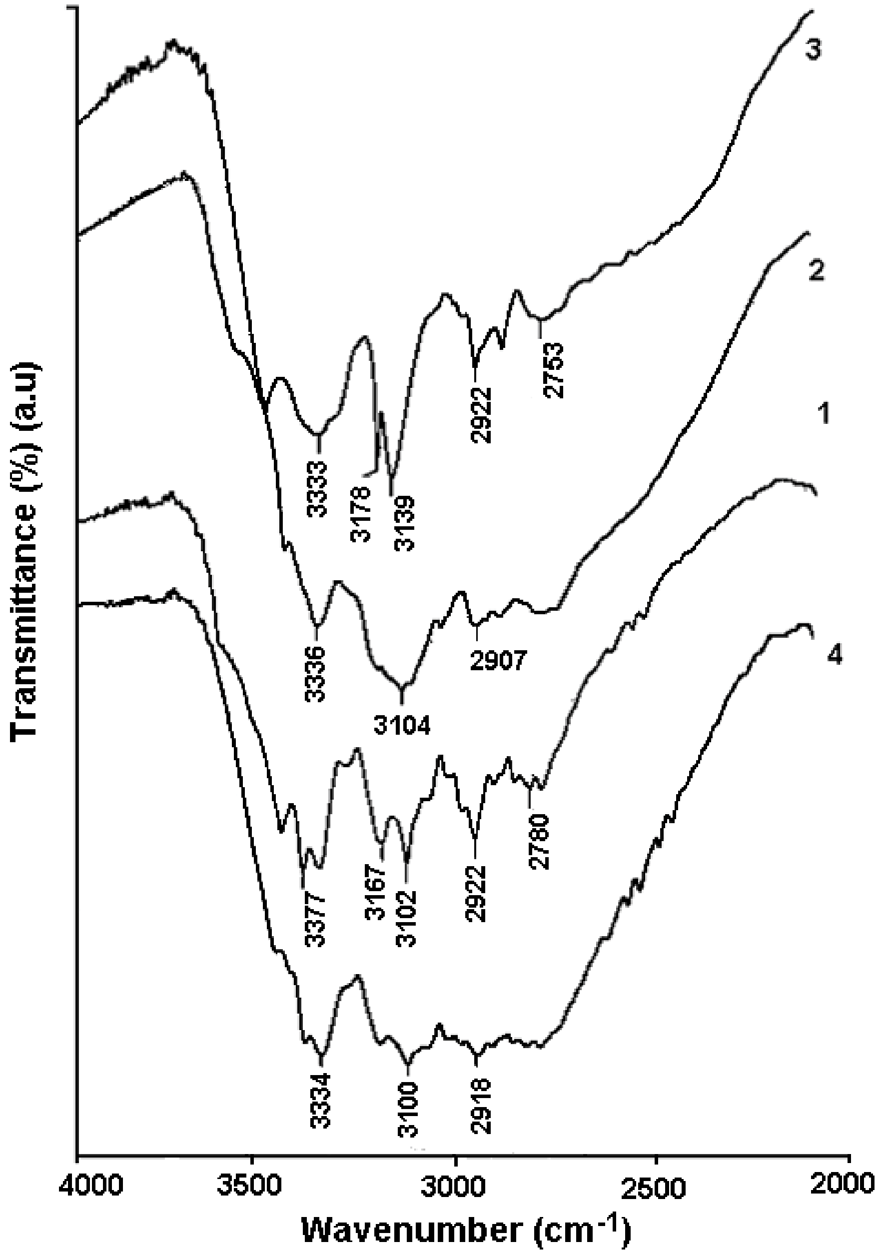


Figure 3 FT-IR spectra showing N-H and O-H stretching vibrations of 1-4.

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