ORIGINAL PAPER

# Three Dimensional Framework Structures of N, N', N''-Tricyclohexylguanidinium Halides

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Received: 3 February 2012/Accepted: 4 August 2012/Published online: 23 August 2012 © Springer Science+Business Media, LLC 2012

Abstract The structures of two salts of N,N',N''-tricyclohexylguanidinium with chloride (1) and bromide (2) have been determined at 201 K. Crystals of both 1 and 2 are in the cubic space group  $P2_13$ , with Z = 4 and cell dimensions a = 12.5940(18) Å (1) and a = 12.7352(8) Å (2). In the isomorphous structures of 1 and 2, the orientation of the cyclohexyl rings around the planar  $CN_3^+$  unit produces steric hindrance. As a consequence of this particular orientation of the tricyclohexylguanidinium cation (hereafter denoted CHGH<sup>+</sup>), hydrogen bonding is restricted to classical N–H···X and non-classical (cyclohexyl) C–H···X hydrogen bonds. Consequently, each guanidinium cation (CHGH<sup>+</sup>) is connected to three surrounding X<sup>-</sup> anions and each X<sup>-</sup> anion is connected with three surrounding cations to form three-dimensional structures.

Keywords N–H…X and C–H…X hydrogen bonding  $\cdot$  Trisubstituted guanidinium cation  $\cdot$  Supramolecular structure

## Introduction

Non-covalent interactions play an important role in organizing structural units in both natural and artificial systems [1]. They exercise important effects on the organization and properties of many materials in areas such as biology

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D. S. Richeson · T. Kell Department of Chemistry, University of Ottawa, Ottawa, ON KIN 6N5, Canada [2, 3], crystal engineering [4, 5] and material science [6, 7]. The interactions governing the crystal organization are expected to affect the packing and ultimately the specific properties of solids.

On the other hand, guanidines are of special interest due to their possible application in medicine [8, 9]. They are considered super bases that readily accept a proton to generate guanidinium cations [10]. The structural features and hydrogen bonding array provided by these cations suggest that they are good building blocks for the formation of supramolecular entities. However, their significance in the generation of multi-dimensional networks has only recently been appreciated [11-14]. Some of these studies were focused on guanidinium derivatives, which are attempting to analyze the influence of the different substituents of guanidinium and the variation of anion on the packing interactions that govern the crystal organization and as consequence, the properties of the resulting salts [15–17]. It remains a difficult task to predict and control the crystal structures of such compounds. Intermolecular interactions are at the heart of supramolecular chemistry [1], and the field of crystal supramolecularity seeks to understand intermolecular interactions by analyses of crystal packing. Intermolecular interactions includes both classical and nonclassical hydrogen bonding (see for example references [18, 19]), halogen...halogen interactions (see for example references [20, 21]), aryl---aryl interactions [22], X---aryl [23] and C–H…aryl interactions [24].

In connection with ongoing studies [15-17, 25] of the structural aspects of N,N',N''-trisubstituted guanidinium salts containing different anions, we herein report the crystal structures of the compounds, N,N',N''-tricy-clohexylguanidinium with chloride (1) and bromide (2), along with an analysis of the supramolecular aspects of these crystal structures.

It is noteworthy that Cai and Hu [26] have reported the structure of N,N',N''-tricyclohexylguanidinium chloride at 298 K. While these researchers determined the chloride structure at a higher temperature, they did not interpret the crystal packing in terms of intermolecular interactions or with respect to the supramolecular aspects of these crystals, as is done in this work.

#### Experimental

#### Synthesis

Synthesis and crystallization of N,N',N''-tricyclohexylguanidinium chloride, (CHGH<sup>+</sup>)Cl<sup>-</sup> **1**. In a round bottom flask, a combination of 0.071 g (1.34 mmol) ammonium chloride and 0.41 g (1.34 mmol) N,N',N''-tricyclohexylguanidine were dissolved in 10 mL of distilled water. A white precipitate of (CHGH<sup>+</sup>)Cl<sup>-</sup> was deposited immediately from the solution (0.43 g, 94.1 % yield). The product was crystallized from a mixture of methanol and distilled water to give white cubic crystals. Anal. Calcd for C<sub>19</sub>H<sub>36</sub>ClN<sub>3</sub>: C, 66.73; H, 10.61; N, 12.29. Found: C, 66.49; H, 10.33; N, 11.97.

Synthesis and crystallization of N,N',N''-tricyclohexylguanidinium bromide, (CHGH)<sup>+</sup>Br<sup>-</sup>, 2. In a round bottom flask, a combination of 0.131 g (1.34 mmol) ammonium bromide and 0.41 g (1.34 mmol) N,N',N''-tricyclohexylguanidine were dissolved in 10 mL of distilled water. A white precipitate of (CHGH)<sup>+</sup>Br<sup>-</sup> was deposited immediately from the solution (0.48 g, 92.3 % yield). The product was crystallized from a mixture of methanol and distilled water to give white cubic crystals. Anal. Calcd for C<sub>19</sub>H<sub>36</sub>BrN<sub>3</sub>: C, 59.05; H, 9.39; N, 10.87. Found: C, 59.21; H, 9.17; N, 10.67.

## X-Ray Crystallography

Crystals of compounds **1** and **2** were grown from a solution of methanol and water. Single colorless blocks of **1** and **2** suitable for X-ray diffraction measurements were each mounted on individual glass fibres. Unit cell measurements and intensity data collections were performed on a Bruker-AXS SMART 1 k CCD diffractometer [27] at 202 K using graphite monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$ Å). The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction *SADABS* [27]. The crystal data and refinement parameters for **1** and **2** are listed in Table 1. Interatomic distances and angles are listed in Table 2. The reflection data were consistent with a cubic system; *P*2<sub>1</sub>3.

The crystal structures were solved and refined using the *SHELXTL* program suite [28]. Direct methods yielded all

non-hydrogen atoms. All hydrogen atom positions were either located from the difference Fourier Map or were calculated geometrically and were riding on their respective carbon atoms. In **1**, three atoms in the cyclohexyl group were disordered and modeled over two positions with relative occupancies of 85:15 %. In **2**, two atoms in the cyclohexyl group were disordered and modeled over two positions with relative occupancies of 87:13 %.

With the exception of the minor component of the cyclohexyl disorder, all non-hydrogen atoms were refined with anisotropic thermal parameters. In **1**, the largest residual electron density peak (0.156 e/Å<sup>3</sup>) was associated with the disordered portion of the cyclohexyl ring, whereas, the largest residual electron density peak in **2** (0.322 e/Å<sup>3</sup>) was associated with the Br1 atom. Full-matrix least-squares refinement on  $F^2$  gave  $R_1 = 0.0481$  and  $wR_2 = 0.1081$  and  $R_1 = 0.0417$  and  $wR_2 = 0.1025$  at convergence for **1** and **2**, respectively.

#### **Results and Discussion**

#### Molecular Structure

Structures of the title compounds 1 and 2, are presented in Fig. 1 and are typical N, N', N'' trisubstituted guanidinium halide salts with normal geometric parameters [15-17, 25]. The central guanidinium fragment of the cation in both salts is planar [sum of NCN angles is 360°] with bond lengths and angles as expected for a central  $Csp^2$  hybridization, accounting for charge delocalization between the three C-N bonds. The bond length C1-N1 [in the range 1.337(3)-1.340(4) Å] is comparable with literature averages for trisubstituted guanidinium salts, for example, triphenylguanidinium bromide (1.328(3), 1.330(3) and 1.336(3) Å [29]), *N*-benzoyl-N', N''-diphenylguanidinium chloride [1.379(2), 1.321(2), 1.326(2) Å], bis(N,N',N''-triisopropylguanidinium) fumarate-fumaric acid (1/1) (1.331 (3), 1.334(3) and 1.335(3) Å [30]) and unsubstituted guanidinium cations (1.321 and 1.328 Å, respectively [31]). The cyclohexyl ring has the normal chair conformation with conventional bond lengths and angles. Selected geometrical parameters for both salts are listed in Table 2.

It is noteworthy that the disorder of three atoms in the cyclohexyl group in **1** (relative occupancies of 85:15 %) and three atoms in **2** (relative occupancies of 87:13 %). This might be related to the size of the anion and how efficient the packing is. With the chloride and bromide anions the size is much smaller as compared to the iodide anion (no disorder observed) [25]. Therefore, the bigger the size the more efficient the packing as it well fill more space, and well also interact more closely with the N–H and C–H donors without lose in the packing preventing any

Identification code	CCDC 865452	CCDC 865451
Empirical formula; Formula weight	C <sub>19</sub> H <sub>36</sub> ClN <sub>3</sub> ; 341.45	C <sub>19</sub> H <sub>36</sub> BrN <sub>3</sub> ; 386.42
Temperature/(K)	201(2)	201(2)
$\lambda/(\text{\AA})$	0.71073	0.71073
Crystal system; Space group	Cubic, P2 <sub>1</sub> 3	Cubic, P2 <sub>1</sub> 3
Unit cell dimensions		
a/(Å)	12.5940 (18)	12.7352(8)
Volume/(Å <sup>3</sup> )	1997.5 (5)	2065.5(2)
Z	4	4
Density (calculated)/(Mg/m <sup>3</sup> )	1.135	1.243
$\mu/(\mathrm{mm}^{-1})$	0.196	1.995
<i>F</i> (000)	750	824
Crystal size/(mm <sup>3</sup> )	$0.10\times0.10\times0.10$	$0.10\times0.10\times0.08$
Theta range for data collection	2.29 to 26.27	3.20 to 25.67
Index ranges	$-15 \leq h \leq 15,  -15 \leq k \leq 15,  -15 \leq l \leq 15$	$-15 \le h \le 15,  -15 \le k \le 15,  -15 \le l \le 13$
Reflections collected	14889	17009
Independent reflections	1364 [R(int) = $0.1032$ ]	1309 [R(int) = $0.0582$ ]
Completeness to theta = $25.0^{\circ}$	99.6 %	99.3 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9807 and 0.9807	0.8567 and 0.8255
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data/restraints/parameters	1364/36/91	1309/59/87
Goodness-of-fit on $F^2$	1.041	1.100
Final R indices $[I > 2$ sigma $(I)]$	R1 = 0.0481, wR2 = 0.1081	R1 = 0.0417, wR2 = 0.1025
R indices (all data)	R1 = 0.1054, wR2 = 0.1367	R1 = 0.0585, wR2 = 0.1137
Absolute structure parameter	0.01(17)	0.03(3)
Largest diff. peak and hole/(e.Å $^{-3}$ )	0.156 and -0.171	0.322 and -0.220

 Table 1 Crystal data and structure refinement for 1 and 2

disorder of cyclohexyl groups. The size of the counter anion and consequently the efficiency of intermolecular N/C–H…N interactions in the structures allows for different thermal motion of the molecules, most visible by the thermal ellipsoids of the terminal cyclohexyl rings.

Supramolecular Hydrogen-Bonding Synthons in  $[CHGH]^+X^-$ ; X = Cl, Br

The supramolecular hydrogen-bonding synthons (Scheme 1) in [CHGH<sup>+</sup>]X<sup>-</sup>; X = Cl, Br are shown in Fig. 2. The structural data for those contacts which are considered to be viable hydrogen-bonds are listed in Table 3. A particularly significant feature of the synthons (**a** and **b**) shown in Fig. 2 is the fact that one of the cyclohexyl (1-positioned) C–H hydrogens form weak C–H···X contacts [2.767 and 2.887 Å in **1** and **2**, respectively] to support the N–H···X [2.585 and 2.797 Å in **1** and **2**, respectively] hydrogen-bonds. When compared to the *N*,*N'*,*N''*-tricyclohexylguanidinium iodide derivative [25], similar features were observed with the interactions being with comparable geometrical parameters [C/N···H distances of 3.027 and 2.856 Å, respectively]. This supporting interaction ensures planarity of the guanidine  $CN_3$  moiety and the hydrogen-bonded halide atoms as illustrated by the low values for the C–N–H···X torsion angles. These angles, together with other pertinent inter-atomic distances and angles are summarized in Table 3. The C–H···X interaction (Fig. 2) forms a classical C–H···X contact with a single halide atom (Scheme 1; synthon **b**).

The Extended Structure of **1** and **2**. Crystal Packing and Supramolecular Structures

The 3-D network architecture of both 1 and 2 salts, can be described in a number of ways. We consider the following to be the most appropriate. The crystallographically independent CHGH<sup>+</sup> cations occur in chains, with the  $X^-$  anions arranged parallel to the cation chains. The cations and anions occur in a threefold array: three anions surround each cation (via its three N–H···X and C–H···X interactions, Fig. 3; Table 3), and three cations surround each anion resulting in the formation of three-dimensional supramolecular structure. This packing is similar to that observed in the iodide derivative [25], where The CHGH<sup>+</sup>

Table 2 S	Selected	geometrical	parameters	(Å,°)	for 1	and 2
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Bond distances		Bond angles	Bond angles		
Compound 1	a				
N1-C1	1.337 (3)	C1-N1-C2	125.6(3)		
N1-C2	1.461 (4)	N1-C2-C7	111.0(3)		
C2C7	1.519 (5)	N1 <sup>i</sup> -C1-N1 <sup>ii</sup>	119.984(9)		
C2–C3	1.525 (6)	N1 <sup>i</sup> -C1-N1	119.991(10)		
C3–C4	1.590 (7)	N1 <sup>ii</sup> -C1-N1	119.989(10)		
C4–C5	1.542 (8)	N1-C2-C3	110.2(4)		
C5–C6	1.490 (7)	C7-C2-C3	108.3(4)		
C6–C7	1.520 (5)	C2-C3-C4	106.2(5)		
Compound 2	b				
N1C1	1.340(4)	C1-N1-C2	126.1(4)		
N1-C2	1.463(7)	N1 <sup>i</sup> -C1-N1	119.984(17)		
C2–C7	1.502(8)	N1 <sup>i</sup> -C1-N1 <sup>ii</sup>	119.986(17)		
C2–C3	1.549(8)	N1-C1-N1 <sup>ii</sup>	119.983(17)		
C3–C4	1.571(9)	N1-C2-C7	110.9(5)		
C4–C5	1.518(9)	C2-C3-C4	106.3(6)		
C5-C6	1.506(8)	C5-C4-C3	108.8(6)		
C6–C7	1.525(7)	C6-C5-C4	110.1(6)		

<sup>a</sup> Symmetry codes (i) z + 1, x - 1, y; (ii)y + 1, z, x - 1

<sup>b</sup> Symmetry codes (i) z + 1/2, -x + 1/2, -y; (ii)-y + 1/2, -z, x - 1/2

ions occur in chains, with the I<sup>-</sup> anions arranged parallel to the cation chains in a threefold array: three anions surround each cation [via its three N–H···I, 2.856 Å; (165°) and C–H···I (3.027 Å; 158°) interactions, Fig. 2], and three cations surround each anion. These interactions and the symmetry related ones in the structures of **1**, **2** and the iodide derivative [25], will result in the three-dimensional overall packing diagram, Fig. 4, in which tetrameric [(CHGH<sup>+</sup>)<sub>3</sub>X<sup>-</sup>]<sub>4</sub> units translates in the three directions *a*, *b* and *c* crystallographic axes to form the cubic lattice. In such arrangement, the cation forms arrays, where the anions are imprisoned in the cavities, and surrounded by three cations in a six coordination arrangement, Fig. 5.

The guanidinium CHGH<sup>+</sup> cations in compounds 1 and 2 display hydrogen bonds to the halide anion through both the N–H and the 1-position cyclohexyl C–H moieties to form a supramolecular hydrogen-bonded network to the halide anions. Although the supramolecular synthons based on C–H donors are longer, and by inference, less strong, than those based on N–H donors, they are nonetheless, structure determining. These types of supramolecular synthons have been observed in other related compounds. The stability of this crystal lattice is evidenced by the crystallization of a whole series of isomorphous compounds of this type, in addition to the title compounds, the derivative N,N',N''-tricyclohexylguanidinium iodide derivative [25], even with



Fig. 1 Molecular structures of: a  $[CHGH^+]Cl^-$  (1); b  $[CHGH^+]Br^-$  (2). Thermal ellipsoids drown at the 50 % probability level. Only one orientation of the disordered cyclohexyl groups is displayed in the figures



Scheme 1 Hydrogen-bonding synthons found in (1) and (2)

different substituents like N,N',N''-triisopropylguanidinium chloride [17]. When using another symmetrical derivative, namely the N,N',N''-triisopropylguanidinium chloride [17], a similar highly symmetric lattice is reproduced, while the less symmetric N,N'-diisopropyl-N''-2,6-dimethylguanidinium





Fig. 2 The diagram showing one guanidium cation and three anions in order to emphasize the orientation of the supramolecular synthon that results from hydrogen bonding array of three N–H···X and three C–H···X interactions. The N/C···X distances are shown to aid the visualization of H-bonding interactions. Similar arrangement is applied for the iodide derivative (C/N···X distances of 3.950 and 3.694 Å, respectively)

Fig. 3 A partial packing diagram of 2, showing the CHGH<sup>+</sup> cations and anions occur in a threefold array: three anions surround each cation and three cations surround each anion. Different molecular rendering is used to clarify the arrangement

Table 3 Hydrogen bond parameters (Å, °) for 1 and 2

D–H···A	D–H	$H \cdots A$	$D \cdots A$	$D-\mathrm{H}\cdots A$
Compound 1 <sup>a</sup>				
N1-H1…Cl1	0.94(3)	2.585	3.515(4)	171
C2-H2···Cl1 <sup>i</sup>	0.99(4)	2.767	3.728(4)	164
Compound 2 <sup>b</sup>				
$N1-H1\cdots Br1^i$	0.78(4)	2.797	3.572(5)	170
C2-H2···Br1 <sup>ii</sup>	0.93(6)	2.887	3.800(6)	168

<sup>a</sup> Symmetry codes (i) 2 - x, -1/2 + y, -1/2 + z

<sup>b</sup> Symmetry codes (i) 3/2 - x, 1 - y, -1/2 + z; (ii)x, -1 + y, -1 + z

chloride or bromide [17] produced a less symmetric lattice as the cation has reduced symmetry and therefore produces a less symmetric lattice [17]. Similar concepts apply whenever less symmetric cations or anions are used [15, 16].

On the other hand, the moderate increase in the size of the anions and most importantly the retention of spherically symmetric Cl<sup>-</sup> and Br<sup>-</sup> anions did not lead to much change in space group symmetry. This is consistent with the arrangement of hydrogen bonding motifs discussed previously, Fig. 2. This preserved the orientation of the cations and anions and favors formation of similar space groups.



Fig. 4 Overall packing diagram of 2. Halide ions appear as *black* spheres. Similar packing is observed for (1). The first carbon (of the cyclohexyl group) involved in attraction is presented, the other omitted for clarity. Hydrogen atoms not involved in hydrogen bonding deleted for clarity



Fig. 5 The anion is surrounded by three cations in a six coordination arrangement (view for 2)

The formation of this high symmetry lattice may be understood in terms of the spherical shape and size of the halide anion used in this study, as compared to the other anionic salts that form the other lower symmetry lattices [15-17]. Further, the less than spherical symmetry of other anions will make it very unlikely to fit in such cubic lattice. Moreover, the 1:1, cation:anion charge ratio in this lattice type is another factor in the formation of such lattices.

#### **Concluding Remarks**

The crystal and molecular structures of the guanidinium halides, [CHGH<sup>+</sup>]Cl (1) and [CHGH<sup>+</sup>]Br (2), have been determined and compared with the iodide derivative [25] and those of other derivatives. Some common features are:

- 1. The compounds  $[CHGH^+]X^-$ ; X = Cl, Br, I and the different substituted N,N',N''-triisopropylguanidinium chloride crystallize in cubic crystal structures.
- Similar hydrogen bonding arrays are observed with each cation in these structures having two hydrogen bonding (classical N-H…X and non-classical C-H…X).
- 3. Each anion in these structures has two hydrogen bonding and another four symmetrically related ones in a total six intermolecular interactions leading to a coordination number of six around each anion.
- 4. The stability of such lattice is evident by the crystallization of an isomorphous series of [CHGH<sup>+</sup>]X<sup>-</sup>;

X = Cl, Br, I and the N, N', N''-triisopropylguanidinium chloride, which show the possibility of using such supramolecular motifs as a crystal engineering tools.

### **Supplementary Material**

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 865451 & 865452 Copies of this information may be obtained from the director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Tel.: +44 1223 762910; fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or on the web www: http// www.ccdc.cam.ac.uk/deposit.

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