

## Three-dimensional hydrogen-bonded structures in the guanidinium salts of the monocyclic dicarboxylic acids *rac-trans*-cyclohexane-1,2-dicarboxylic acid (2:1, anhydrous), isophthalic acid (1:1, monohydrate) and terephthalic acid (2:1, trihydrate)

Graham Smith<sup>a\*</sup> and Urs D. Wermuth<sup>b</sup>

<sup>a</sup>Faculty of Science and Technology, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia, and <sup>b</sup>School of Biomolecular and Physical Sciences, Griffith University, Nathan, Queensland 4111, Australia  
Correspondence e-mail: g.smith@qut.edu.au

Received 19 August 2010

Accepted 19 October 2010

Online 6 November 2010

The structures of bis(guanidinium) *rac-trans*-cyclohexane-1,2-dicarboxylate,  $2\text{CH}_6\text{N}_3^+ \cdot \text{C}_8\text{H}_{10}\text{O}_4^{2-}$ , (I), guanidinium 3-carboxybenzoate monohydrate,  $\text{CH}_6\text{N}_3^+ \cdot \text{C}_8\text{H}_5\text{O}_4^- \cdot \text{H}_2\text{O}$ , (II), and bis(guanidinium) benzene-1,4-dicarboxylate trihydrate,  $2\text{CH}_6\text{N}_3^+ \cdot \text{C}_8\text{H}_4\text{O}_4^{2-} \cdot 3\text{H}_2\text{O}$ , (III), all reveal three-dimensional hydrogen-bonded framework structures. In anhydrous (I), both guanidinium cations form classic cyclic  $R_2^2(8)$  N—H...O, O'carboxylate and asymmetric cyclic  $R_1^1(6)$  hydrogen-bonding interactions, while one cation forms an unusual enlarged cyclic interaction with O-atom acceptors of separate *ortho*-related carboxylate groups [graph set  $R_2^2(11)$ ]. Cations and anions also associate across inversion centres, giving cyclic  $R_4^2(8)$  motifs. In the 1:1 guanidinium salt, (II), the cation forms two separate cyclic  $R_2^1(6)$  interactions, one with a carboxyl O-atom acceptor and the other with the solvent water molecule. The structure is unusual in that both carboxyl groups form short interanion O...H...O contacts, one across a crystallographic inversion centre [ $\text{O} \cdots \text{O} = 2.483(2) \text{ \AA}$ ] and the other about a twofold axis of rotation [ $\text{O} \cdots \text{O} = 2.462(2) \text{ \AA}$ ], representing shared sites on these elements for the single acid H atom. The water molecule links the cation–anion ribbon structures into a three-dimensional framework. In (III), the repeating molecular unit comprises a benzene-1,4-dicarboxylate dianion which lies across a crystallographic inversion centre, two guanidinium cations and two solvent water molecules (each set related by twofold rotational symmetry), and a single water molecule which lies on a twofold axis. Each guanidinium cation forms three types of cyclic interaction with the dianions: one  $R_1^1(6)$ , the others  $R_2^2(8)$  and  $R_3^3(10)$  (both of these involving the water molecules), giving a three-dimen-

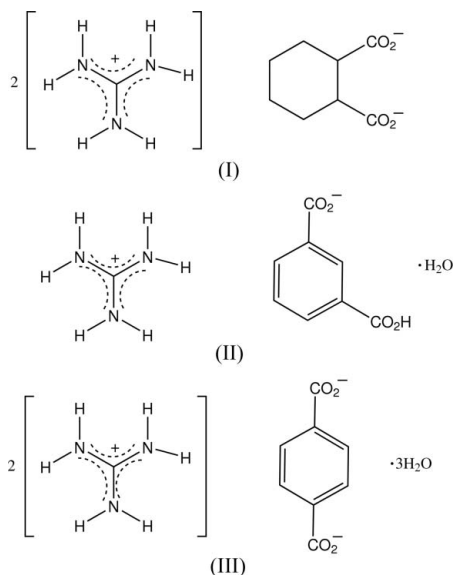
sional structure through bridges down the *b*-cell direction. The water molecule at the general site also forms an unusual cyclic  $R_2^2(4)$  homodimeric association across an inversion centre [ $\text{O} \cdots \text{O} = 2.875(2) \text{ \AA}$ ]. The work described here provides further examples of the common cyclic guanidinium–carboxylate hydrogen-bonding associations, as well as featuring other less common cyclic motifs.

### Comment

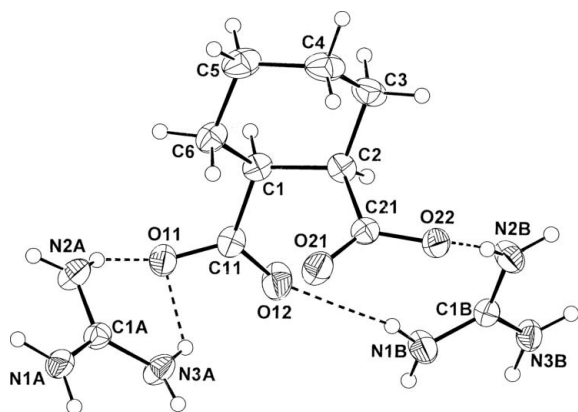
The structures of the guanidinium salts of aromatic and heteroaromatic polyfunctional carboxylic acids are not numerous in the crystallographic literature, but they are of interest because of the capacity of the guanidinium cation to generate stable supramolecular framework structures through hydrogen-bonding associations, largely cyclic, such as those found in the structures of guanidinium carbonate (Adams & Small, 1974) and guanidinium bicarbonate (Baldwin *et al.*, 1986). Among the known aromatic and heteroaromatic carboxylate examples are the monoguanidinium salts of the dicarboxylic acids 4-hydroxypyridine-2,6-dicarboxylic acid (an unusual anhydrous compound in which the pyridine N atom and one of the carboxylic acid groups exist as a zwitterion; Moghimi *et al.*, 2005) and 3-nitrophthalic acid (a monohydrate; Smith, Wermuth & Healy, 2007). Other bifunctional acid salts are those with 4-chloro-3-nitrobenzoic acid (a monohydrate; Najafpour *et al.*, 2007), 4-amino-2,4,6-trichloropicolinic acid (Parthasarathi *et al.*, 1984), 4-nitroanthranilic acid (Smith, Wermuth, Healy & White, 2007), 3-nitrobenzoic acid (Smith & Wermuth, 2010), 4-nitrobenzoic acid (Kleb *et al.*, 1998), 4-aminobenzoic acid (Pereira Silva *et al.*, 2010), 3,5-dinitrobenzoic acid (Smith, Wermuth & White, 2007) and 3,5-dinitrosalicylic acid (Smith *et al.*, 2001) (all anhydrous). The known bis(guanidinium) salts are those with phthalic acid (anhydrous; Krumbe & Haussuhl, 1987) and pyrazine-2,3-dicarboxylic acid (a trihydrate; Smith *et al.*, 2006). Another bis(guanidinium) example but with a tetracarboxylic acid is that with benzene-1,2,4,5-tetracarboxylic acid (pyromellitic acid; Sun *et al.*, 2002). However, the most spectacular examples have been found in the supramolecular ribbon structures of the guanidinium bicarbonate *tert*-butylammonium salts of terephthalic acid (Mak & Xue, 2000). Among these examples, high-dimensional hydrogen-bonded structures are predominant, with the guanidinium cation forming multiple cyclic hydrogen-bonding associations with carboxylate O-atom acceptors, most commonly those defined by graph sets  $R_2^2(8)$  and  $R_1^1(6)$  and, to a lesser extent,  $R_1^1(4)$  (Etter *et al.*, 1990). In the hydrated examples, the water molecules are usually incorporated in expanded cyclic associations.

Our 1:1 stoichiometric reactions of a number of monocyclic dicarboxylic acids, including *rac-trans*-cyclohexane-1,2-dicarboxylic acid, isophthalic acid and terephthalic acid, with guanidinium carbonate in aqueous propan-2-ol gave relatively hard chemically stable crystals of the anhydrous salt bis(guanidinium) *rac-trans*-cyclohexane-1,2-dicarboxylate, (I), guanidinium 3-carboxybenzoate monohydrate, (II), and bis(guanidinium) benzene-1,4-dicarboxylate trihydrate, (III),

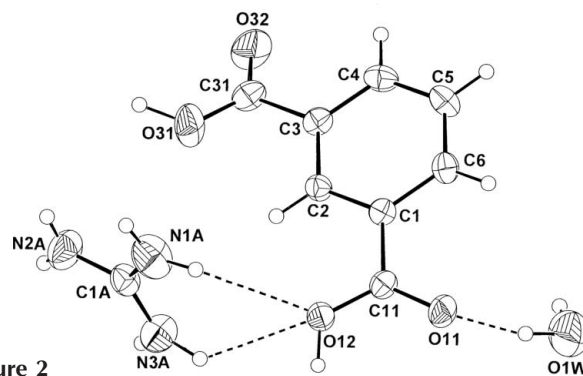
respectively. The structures and hydrogen-bonding patterns for (I)–(III) are reported here. The molecular contents of the asymmetric units of these three compounds and their atom-numbering schemes are shown in Figs. 1–3.



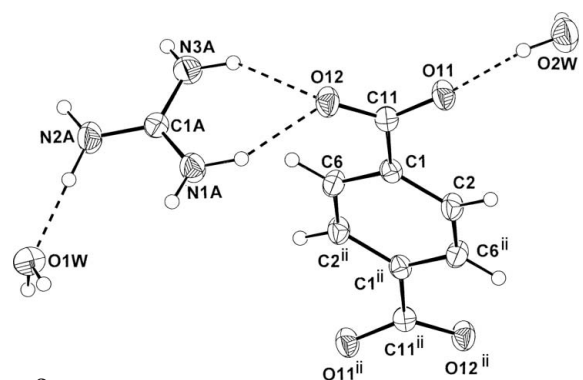
In the anhydrous 2:1 guanidinium salt, (I), both cations (*A* and *B*) form classic cyclic  $R_2^2(8)$   $N-H \cdots O_{\text{carboxylate}}$  hydrogen-bonding interactions with, respectively,  $O21^{ii}/O22^{ii}$  and  $O11^{iii}/O12^{iii}$  (Fig. 4) (for symmetry codes, see Table 1). Each cation is also involved in asymmetric cyclic  $R_2^1(6)$  interactions with carboxylate O-atom acceptors. Additionally, cation *B* forms an unusual enlarged cyclic interaction [graph set  $R_2^2(11)$ ] with acceptors  $O12$  and  $O22$  of the two adjacent *cis*-related carboxylate groups. Further hydrogen-bonding extensions, including a centrosymmetric cyclic bis(cation–anion) association [graph set  $R_2^2(8)$ ] (Fig. 4), produce the three-dimensional framework structure. The structure also contains a relatively long intermolecular  $N2B-H \cdots N3B^v$  interaction [ $N \cdots N = 3.3191(18)$  Å; for symmetry code, see Table 1], and there is



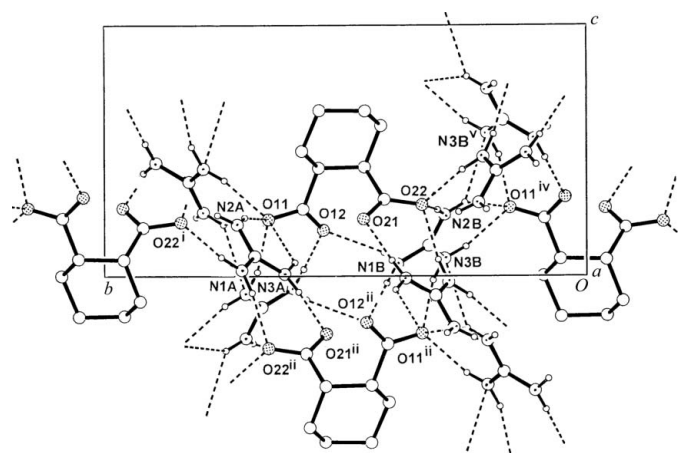
**Figure 1**  
The molecular configuration and atom-numbering scheme for the two guanidinium cations (*A* and *B*) and the cyclohexane-1,2-dicarboxylate anion in (I). Interspecies hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 40% probability level.



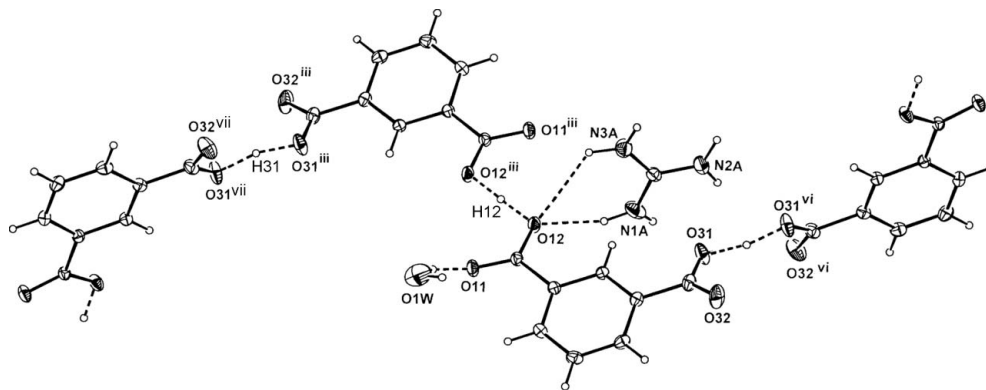
**Figure 2**  
The molecular configuration and atom-numbering scheme for the guanidinium cation, hydrogen isophthalate anion and solvent water molecule in (II). The two acid H atoms shown lie on half-occupancy sites on an inversion centre and a twofold axis. Interspecies hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 40% probability level.



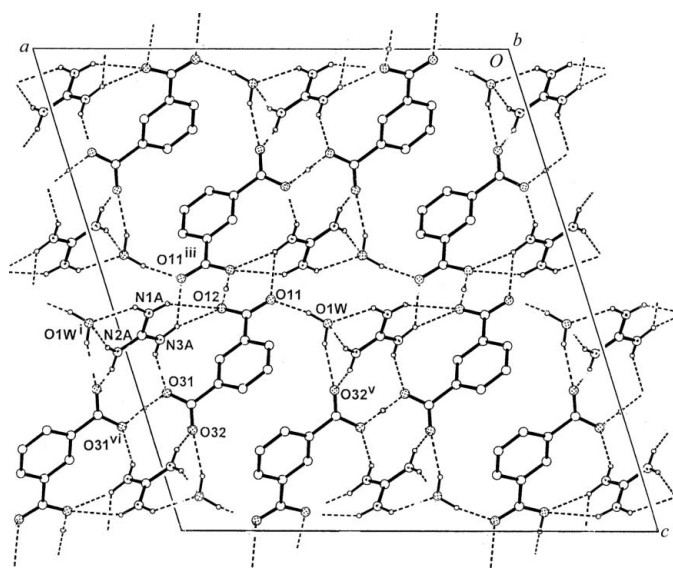
**Figure 3**  
The molecular configuration and atom-numbering scheme for the guanidinium cation (*A*), the benzene-1,4-dicarboxylate dianion and the two solvent water molecules in the asymmetric unit of (III). The dianion lies across an inversion centre [symmetry code: (ii)  $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + 1$ ], while water molecule *O1W* lies on the twofold rotation axis at  $(\frac{1}{2}, y, \frac{3}{4})$ . Displacement ellipsoids are drawn at the 40% probability level. Dashed lines indicate hydrogen bonds.



**Figure 4**  
The three-dimensional framework structure of (I), viewed down the approximate *a*-axis direction in the unit cell, showing hydrogen-bonding associations as dashed lines. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. (For symmetry codes, see Table 1.)

**Figure 5**

The head-to-tail hydrogen-bonding extensions of the hydrogen isophthalate anions with the attached guanidinium cation and water species in the structure of (II), showing the shared acid H atoms H12 [located on an inversion centre at  $(\frac{3}{4}, \frac{3}{4}, \frac{1}{2})$ ] and H31 [located on the twofold axis at  $(1, y, \frac{3}{2})$ ]. Dashed lines indicate hydrogen bonds. [For symmetry codes, see Table 2; additionally, (vii)  $x - \frac{3}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ]

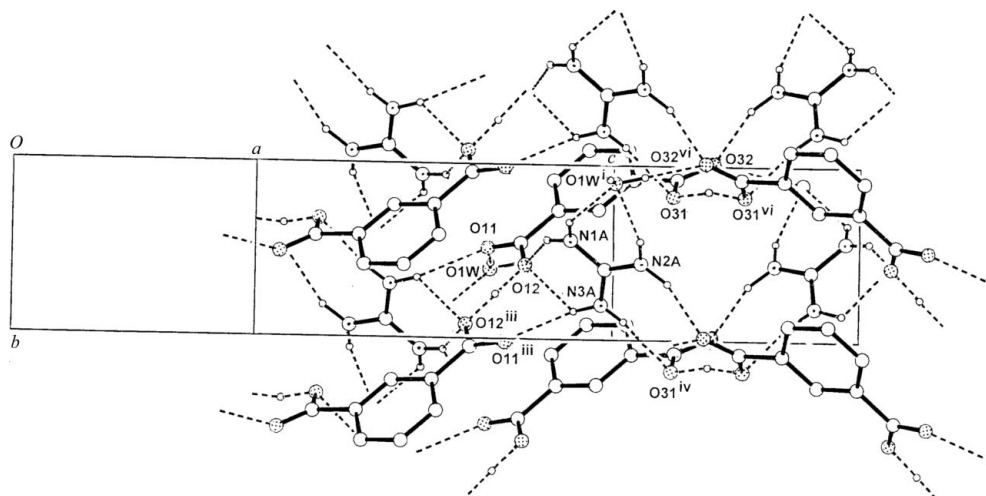
**Figure 6**

The hydrogen-bonded framework structure of (II), viewed down the *b*-axis direction of the unit cell, showing hydrogen-bonding associations as dashed lines. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. For symmetry codes, see Table 2.

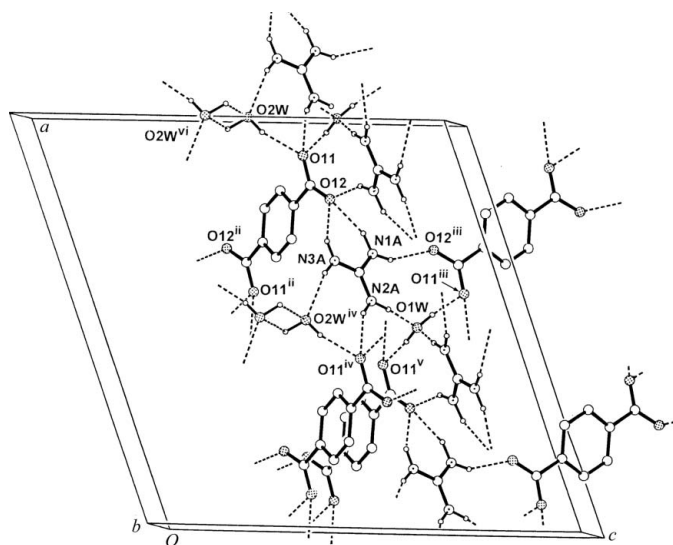
one potential guanidinium donor (H22A) for which there is no reasonable acceptor.

The structure of the hydrated 1:1 guanidinium hydrogen isophthalate salt, (II) (Fig. 2), is unusual in that each of the carboxyl groups forms short inter-anion O...H...O contacts, one across a crystallographic inversion centre [O12...O12<sup>iii</sup> = 2.483 (2) Å] and the other about a twofold axis of rotation [O31...O31<sup>vi</sup> = 2.462 (2) Å] (Fig. 5) (for symmetry codes, see Table 2). H atoms were located on these symmetry elements and therefore represent shared sites on these elements for the single acid H atom. These interactions effectively give anion-anion associated ribbon structures, which extend across the approximate *ac* diagonal in the unit cell (Fig. 6) and accommodate both the cations and the water molecules. The cation forms two separate cyclic  $R_2^1(6)$  interactions, one with a carboxyl O-atom acceptor (involving atoms N1A and N3A) and the other with the solvent water molecule (involving atoms N1A and N2A), and these substructures are interlinked by the water molecules and further expanded down the *b* axis into a three-dimensional framework structure (Fig. 7).

In guanidinium terephthalate trihydrate, (III), the formula unit comprises a benzene-1,4-dicarboxylate dianion which lies

**Figure 7**

A second view of the hydrogen-bonding (dashed lines) in the framework structure of (II), viewed down the approximate *a* direction of the unit cell, showing extensions down *b*. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. (For symmetry codes, see Table 2.)

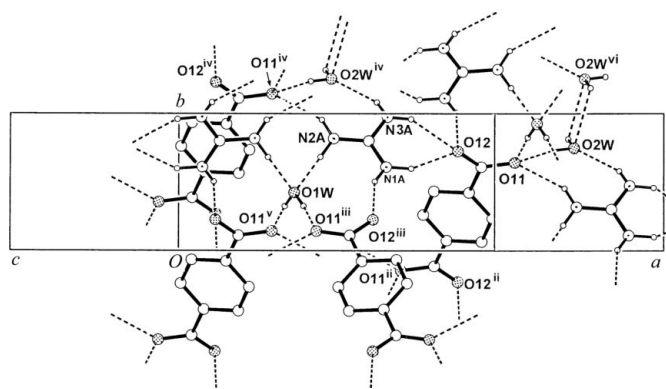


**Figure 8**  
The hydrogen-bonding in the structure of (III), viewed down the *b* axis in the unit cell, showing associations as dashed lines. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. [Symmetry code: (vi)  $-x + 2, -y + 2, -z + 1$ ; for other symmetry codes, see Table 3 and Fig. 3.]

across a crystallographic inversion centre, two guanidinium cations and two solvent water molecules (both pairs related by twofold rotational symmetry), and a third water molecule (O1W) lying on a crystallographic twofold axis (Fig. 3). The guanidinium cations and the dianion form two types of cyclic hydrogen-bonding motifs, one the common guanidinium  $R_2^1(6)$  association (with atoms N1A and N3A) and the others incorporating the two water molecules: (a) atom O1W with atoms N1A and N2A [graph set  $R_3^3(10)$ ] and (b) atom O2W with atoms N2A and N3A [graph set  $R_3^2(8)$ ] (Table 3; Figs. 8 and 9), giving the three-dimensional framework structure. Present also in the structure of (III) are unusual inversion-related water–water interactions involving atoms O2W and O2W<sup>vi</sup> [ $O \cdots O = 2.875(2) \text{ \AA}$ ; symmetry code: (vi)  $-x + 2, -y + 2, -z + 1$ ], giving discrete cyclic dimers. Although the O2W–H22W<sup>vi</sup>··O2W<sup>vi</sup> ‘bond’ angle ( $113^\circ$ ) is less than would normally be accepted for a conventional hydrogen bond, this unusual  $R_2^2(4)$  association must be recognized as such in the assembly of the structure of (III).

In the hydrogen isophthalate anion of (II), one of the carboxyl groups is close to coplanar with the benzene ring [torsion angle C2–C1–C11–O11 =  $-170.30(19)^\circ$ ], while the other is twisted out of the plane [torsion angle C2–C3–C31–O32 =  $159.9(2)^\circ$ ]. This latter value is comparable with that for the C2–C1–C11–O12 torsion angle in both carboxyl groups in (III) [ $-159.86(15)^\circ$ ].

The three-dimensional structures of (I)–(III) reported here show not only classic guanidinium cyclic  $R_2^2(8)$  N–H··O<sub>carboxyl</sub> and  $R_2^1(6)$  hydrogen-bonding motifs but, in addition, various expanded cyclic associations involving the solvent water molecules, and in the case of anhydrous (I), an unusual  $R_2^2(11)$  cyclic guanidinium–carboxylate interaction. In addition, with (II), the 1:1 guanidinium salt appears to be preferred over the 2:1 salt as expected and found in (I) and (III),



**Figure 9**  
The hydrogen-bonded framework structure of (III), viewed perpendicular to *b*, showing the role of the unusual centrosymmetric associated water dimers in the structure extension. Dashed lines indicate hydrogen bonds. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. For symmetry codes, see Table 3 and Fig. 8.

considering the identical 1:1 stoichiometric acid/guanidinium carbonate reaction conditions employed in all three preparations.

## Experimental

The title compounds, (I)–(III), were synthesized by heating together under reflux for 10 min 1 mmol quantities of, respectively, *rac-trans*-cyclohexane-1,2-dicarboxylic acid [for (I)], benzene-1,3-dicarboxylic acid (isophthalic acid) [for (II)] and benzene-1,4-dicarboxylic acid (terephthalic acid) [for (III)], with guanidinium carbonate (1 mmol) in 50% aqueous propan-2-ol (50 ml). After concentration to *ca* 30 ml, partial room-temperature evaporation of the hot-filtered solutions gave large colourless plates [for (I) and (III)] or small colourless flat platelets [for (II)] [m.p.: 525 K for (I), 474 K for (II) and 505 K for (III)]. For (I) and (III), specimens suitable for X-ray analysis were cleaved from larger crystals.

## Compound (I)

### Crystal data

$2\text{CH}_6\text{N}_3^+ \cdot \text{C}_8\text{H}_{10}\text{O}_4^{2-}$	$V = 1455.4(2) \text{ \AA}^3$
$M_r = 290.34$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.7425(10) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$b = 16.0538(15) \text{ \AA}$	$T = 200 \text{ K}$
$c = 8.5067(8) \text{ \AA}$	$0.50 \times 0.50 \times 0.45 \text{ mm}$
$\beta = 97.224(9)^\circ$	

### Data collection

Oxford Gemini-S CCD area-detector diffractometer	10102 measured reflections
Absorption correction: multi-scan ( <i>CrysAlis Pro</i> ; Oxford Diffraction, 2009)	2858 independent reflections
$T_{\min} = 0.956, T_{\max} = 0.980$	2222 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.026$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.089$	$\Delta\rho_{\text{max}} = 0.21 \text{ e \AA}^{-3}$
$S = 1.05$	$\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$
2858 reflections	
229 parameters	



## Compound (II)

## Crystal data

CH <sub>6</sub> N <sub>3</sub> <sup>+</sup> ·C <sub>8</sub> H <sub>5</sub> O <sub>4</sub> <sup>-</sup> ·H <sub>2</sub> O	$V = 2286.3 (5) \text{ \AA}^3$
$M_r = 243.22$	$Z = 8$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 20.970 (3) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$b = 5.1421 (6) \text{ \AA}$	$T = 297 \text{ K}$
$c = 22.241 (2) \text{ \AA}$	$0.40 \times 0.30 \times 0.16 \text{ mm}$
$\beta = 107.577 (14)^\circ$	

## Data collection

Oxford Gemini-S CCD area-detector diffractometer	3906 measured reflections
Absorption correction: multi-scan ( <i>CrysAlis Pro</i> ; Oxford Diffraction, 2009)	2239 independent reflections
$T_{\min} = 0.907$ , $T_{\max} = 0.987$	1694 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.013$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.156$	$\Delta\rho_{\text{max}} = 0.58 \text{ e \AA}^{-3}$
$S = 1.06$	$\Delta\rho_{\text{min}} = -0.50 \text{ e \AA}^{-3}$
2239 reflections	
181 parameters	

## Compound (III)

## Crystal data

2CH <sub>6</sub> N <sub>3</sub> <sup>+</sup> ·C <sub>8</sub> H <sub>4</sub> O <sub>4</sub> <sup>2-</sup> ·3H <sub>2</sub> O	$V = 1579.07 (11) \text{ \AA}^3$
$M_r = 338.34$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 18.0402 (7) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$b = 5.1420 (2) \text{ \AA}$	$T = 297 \text{ K}$
$c = 18.1496 (7) \text{ \AA}$	$0.25 \times 0.25 \times 0.25 \text{ mm}$
$\beta = 110.297 (4)^\circ$	

## Data collection

Oxford Gemini-S Ultra CCD area-detector diffractometer	3988 measured reflections
Absorption correction: multi-scan ( <i>CrysAlis RED</i> ; Oxford Diffraction, 2008)	1546 independent reflections
$T_{\min} = 0.98$ , $T_{\max} = 0.99$	1177 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.020$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.114$	$\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$
$S = 1.04$	$\Delta\rho_{\text{min}} = -0.48 \text{ e \AA}^{-3}$
1546 reflections	
130 parameters	

H atoms involved in hydrogen-bonding interactions were located by difference methods and their positional and isotropic displacement parameters were refined, with the exception of the water H atoms of (II) and (III) which were constrained to ride on their parent atom, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ . Aromatic H atoms were included in the refinement in calculated positions using a riding-model approximation, with  $\text{C}-\text{H} = 0.95 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: *CrysAlis Pro* (Oxford Diffraction, 2009) for (I) and (II); *CrysAlis CCD* (Oxford Diffraction, 2008) for (III). Cell refinement: *CrysAlis Pro* for (I) and (II); *CrysAlis RED* (Oxford Diffraction, 2008) for (III). Data reduction: *CrysAlis Pro* for (I) and (II); *CrysAlis RED* for (III). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994) for (I) and (III); *SHELXS97* (Sheldrick, 2008) for (II). For all compounds, program(s) used to refine structure:

Table 1

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (I).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
N1A—H11A $\cdots$ O22 <sup>i</sup>	0.910 (16)	1.946 (15)	2.8492 (16)	171.2 (13)
N1A—H12A $\cdots$ O22 <sup>ii</sup>	0.878 (16)	1.960 (16)	2.8255 (15)	168.6 (14)
N2A—H21A $\cdots$ O11	0.844 (18)	2.065 (18)	2.8780 (18)	161.6 (15)
N3A—H31A $\cdots$ O21 <sup>iii</sup>	0.865 (15)	1.963 (15)	2.8270 (16)	176.4 (16)
N3A—H32A $\cdots$ O11	0.817 (17)	2.593 (17)	3.2299 (16)	135.9 (14)
N1B—H11B $\cdots$ O12 <sup>iii</sup>	0.890 (15)	1.899 (15)	2.7863 (17)	175.0 (15)
N1B—H12B $\cdots$ O12	0.810 (17)	2.204 (18)	2.9097 (17)	145.9 (16)
N2B—H21B $\cdots$ O22	0.850 (18)	1.999 (18)	2.8447 (18)	173.8 (16)
N2B—H22B $\cdots$ O11 <sup>iv</sup>	0.871 (16)	2.579 (16)	3.2913 (17)	139.6 (13)
N2B—H22B $\cdots$ N3B <sup>v</sup>	0.871 (16)	2.593 (15)	3.3191 (18)	141.5 (13)
N3B—H31B $\cdots$ O11 <sup>iv</sup>	0.856 (17)	2.011 (17)	2.8468 (15)	165.1 (15)
N3B—H32B $\cdots$ O11 <sup>iii</sup>	0.948 (16)	1.975 (15)	2.8981 (15)	164.2 (14)

Symmetry codes: (i)  $-x, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $-x, -y + 1, -z$ ; (iii)  $-x + 1, -y + 1, -z$ ; (iv)  $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (v)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ .

Table 2

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (II).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
N1A—H11A $\cdots$ O12	0.92 (4)	2.50 (4)	3.284 (4)	144 (3)
N1A—H12A $\cdots$ O1W <sup>i</sup>	0.85 (5)	2.44 (5)	3.156 (5)	144 (4)
N2A—H21A $\cdots$ O1W <sup>i</sup>	0.82 (4)	2.19 (4)	2.972 (4)	161 (4)
N2A—H22A $\cdots$ O32 <sup>ii</sup>	0.98 (4)	1.92 (4)	2.854 (3)	158 (3)
N3A—H31A $\cdots$ O12	0.96 (6)	2.52 (6)	3.253 (3)	133 (4)
N3A—H31A $\cdots$ O11 <sup>iii</sup>	0.96 (6)	2.31 (6)	3.050 (3)	134 (5)
N3A—H32A $\cdots$ O31 <sup>iv</sup>	0.83 (3)	2.28 (3)	3.034 (3)	153 (3)
O1W—H11W $\cdots$ O32 <sup>v</sup>	0.90	2.12	2.982 (4)	160
O1W—H12W $\cdots$ O11	0.98	1.84	2.806 (4)	166
O12—H12 $\cdots$ O12 <sup>iii</sup>	1.24	1.24	2.483 (2)	180
O31—H31 $\cdots$ O31 <sup>vi</sup>	1.241 (6)	1.241 (6)	2.462 (2)	165 (5)

Symmetry codes: (i)  $x + \frac{1}{2}, y - \frac{1}{2}, z$ ; (ii)  $-x + 2, y + 1, -z + \frac{3}{2}$ ; (iii)  $-x + \frac{3}{2}, -y + \frac{3}{2}, -z + 1$ ; (iv)  $x, y + 1, z$ ; (v)  $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (vi)  $-x + 2, y, -z + \frac{3}{2}$ .

Table 3

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (III).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
N1A—H11A $\cdots$ O12	0.95 (2)	2.00 (2)	2.868 (2)	151.3 (19)
N1A—H12A $\cdots$ O12 <sup>iii</sup>	0.88 (2)	2.15 (2)	2.963 (2)	153 (2)
N2A—H21A $\cdots$ O1W	0.96 (3)	1.79 (3)	2.752 (2)	174 (2)
N2A—H22A $\cdots$ O11 <sup>iv</sup>	0.90 (3)	2.17 (3)	2.988 (2)	151 (2)
N3A—H31A $\cdots$ O2W <sup>iv</sup>	0.82 (2)	2.27 (3)	3.043 (2)	157 (2)
N3A—H32A $\cdots$ O12	0.89 (2)	2.16 (2)	2.947 (2)	146.6 (18)
O1W—H11W $\cdots$ O11 <sup>v</sup>	0.92	1.73	2.6542 (14)	174
O2W—H21W $\cdots$ O11	0.85	1.93	2.7591 (19)	162

Symmetry codes: (iii)  $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (iv)  $x - \frac{1}{2}, y + \frac{1}{2}, z$ ; (v)  $x - \frac{1}{2}, y - \frac{1}{2}, z$ .

*SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 1999); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

The authors acknowledge financial support from the Australian Research Council, the Faculty of Science and Technology, Queensland University of Technology, and the School of Biomolecular and Physical Sciences, Griffith University.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3361). Services for accessing these data are described at the back of the journal.

## References

- Adams, J. M. & Small, R. W. H. (1974). *Acta Cryst.* **B30**, 2191–2193.
- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Baldwin, D. A., Denner, L., Egan, T. J. & Markwell, A. J. (1986). *Acta Cryst.* **C42**, 1197–1199.
- Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* **B46**, 256–262.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Kleb, D.-C., Schürmann, M., Preut, H. & Bleckmann, P. (1998). *Z. Krist. New Cryst. Struct.* **213**, 581–582.
- Krumbe, W. & Haussuhl, S. (1987). *Z. Kristallogr.* **179**, 267–269.
- Mak, T. C. W. & Xue, F. (2000). *J. Am. Chem. Soc.* **122**, 9860–9861.
- Moghimi, A., Aghabozorg, H., Soleimannejad, J. & Ramezanipour, F. (2005). *Acta Cryst.* **E61**, o442–o444.
- Najafpour, M. M., Holyńska, M. & Lis, T. (2007). *Acta Cryst.* **E63**, o3727.
- Oxford Diffraction (2008). *CrysAlis CCD* (Version 1.171.32.24) and *CrysAlis RED* (Version 1.171.32.15). Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
- Oxford Diffraction (2009). *CrysAlis Pro*. Version 1.171.33.41. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
- Parthasarathi, V., Wolfrum, S., Noordik, J. H., Buerskins, P. T., Kennard, C. H. L., Smith, G. & O'Reilly, E. J. (1984). *Cryst. Struct. Commun.* **11**, 1519–1524.
- Pereira Silva, P. S., Ramos Silva, M., Paixão, J. A. & Matos Beja, A. (2010). *Acta Cryst.* **E66**, o524.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Smith, G., Bott, R. C. & Wermuth, U. D. (2001). *Acta Cryst.* **E57**, o640–o642.
- Smith, G. & Wermuth, U. D. (2010). *Acta Cryst.* **E66**, o1946.
- Smith, G., Wermuth, U. D. & Healy, P. C. (2007). *Acta Cryst.* **E63**, o3527–o3528.
- Smith, G., Wermuth, U. D., Healy, P. C. & White, J. M. (2007). *Acta Cryst.* **E63**, o7–o9.
- Smith, G., Wermuth, U. D. & White, J. M. (2007). *Acta Cryst.* **E63**, o867–o868.
- Smith, G., Wermuth, U. D., Young, D. J. & White, J. M. (2006). *Acta Cryst.* **E62**, o3912–o3914.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Sun, Y.-Q., Zhang, J. & Yang, G.-Y. (2002). *Acta Cryst.* **E58**, o904–o906.