

Face-to-face stacking of quinoid rings of alkali salts of bromanilic acid

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A series of alkali salts of hydrogen bromanilic acid trihydrates (K^+ , Rb^+ and Cs^+ , potassium, rubidium and caesium 2,5-dibromo-4-hydroxy-3,6-dioxocyclohexa-1,4-dien-1-olate trihydrate), bromanilic acid tetrahydrate (Na^+ , disodium 2,5-dibromo-3,6-dioxocyclohexa-1,4-diene-1,4-diolate tetrahydrate) and bromanilic acid dihydrates (K^+ , Rb^+ and Cs^+ , dipotassium, dirubidium and dicaesium 2,5-dibromo-3,6-dioxocyclohexa-1,4-diene-1,4-diolate dihydrate) were prepared and studied by single-crystal X-ray diffraction. Their crystal packings are dominated by quinoid ring stacking. The monoanionic quinoid rings pack face-to-face without offset and with short centroid separations (3.25–3.30 Å), while the dianionic rings form offset stacks (1.4–1.8 Å) with a larger centroid separation (3.8–4.1 Å).

1. Introduction

Aromatic $\pi \cdot \cdot \pi$ interactions are well known and have been extensively studied (Hunter & Sanders, 1990; Hunter, 1993, 1994; Głowka *et al.*, 1999; Janiak, 2000; Hunter *et al.*, 2001; Mayer *et al.*, 2003; Salonen *et al.*, 2011) having already found their way into supramolecular chemistry textbooks (Steed & Atwood, 2009). However, the stacking of quinoid rings has been documented for the first time only recently in crystals of some simple alkali salts of chloranilic acid (3,6-dichloro-2,5-dihydroxyquinone; Molčanov *et al.*, 2009*a,b*, 2011). The electronic structure of the quinoid compounds is entirely different to that of the aromatics: in quinoid rings there is almost no electron delocalization and the single and double bonds are well separated (Fig. 1). Since delocalized π electrons play the most important role in $\pi \cdot \cdot \pi$ interactions of aromatic rings, it is logical to assume that quinoid rings without delocalized electrons form different kinds of intermolecular interactions.

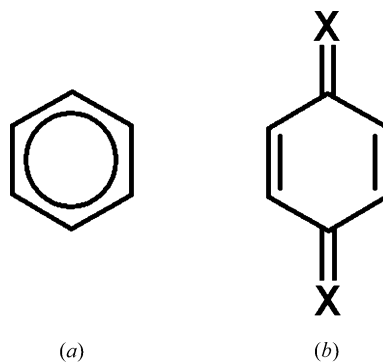
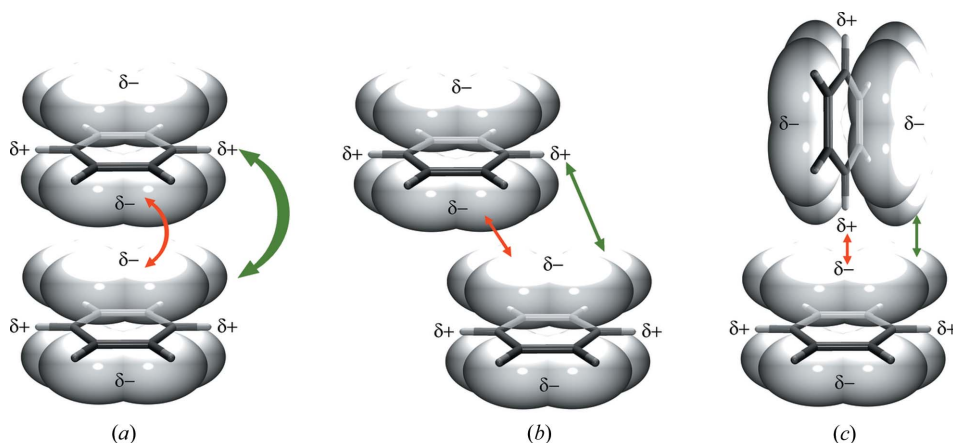


Figure 1

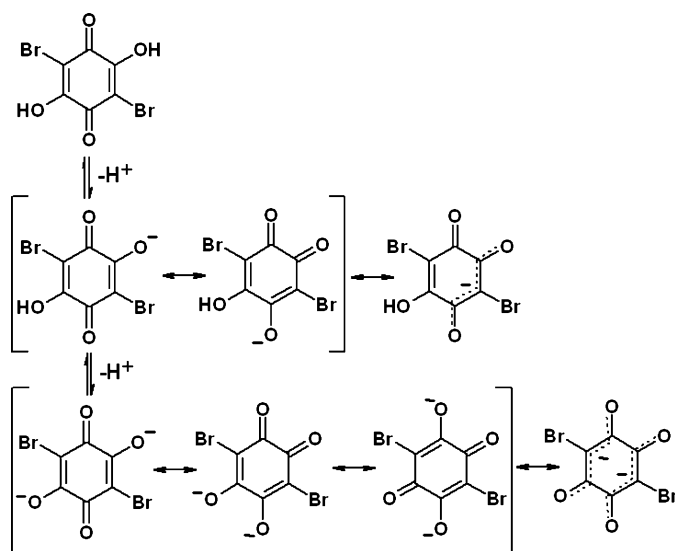
Schematic representation of the electronic structure of (a) aromatic rings with delocalized π electrons and conjugated C–C bonds, and (b) quinoid rings with well separated single and double bonds.


Figure 2

Attractive $\sigma \cdots \pi$ (green) and repulsive $\pi \cdots \pi$ (red) interactions between two aromatic rings in three different arrangements: (a) parallel face-to-face, (b) parallel, offset and (c) T-shaped. For aromatic ring arrangements (b) and (c) are energetically favourable (the resultant force is weak attraction), while (a) is unfavourable (strong repulsion).

The two energetically most favoured arrangements of aromatic rings are offset parallel and T-shaped (Hunter *et al.*, 2001; Mayer *et al.*, 2003; Salonen *et al.*, 2011; Fig. 2), where attractions $\sigma \cdots \pi$ (between the partially positive σ -skeleton and the partially negative delocalized π -electron cloud) outperform $\pi \cdots \pi$ repulsion. However, some quinoid rings favour face-to-face parallel arrangement (Molčanov *et al.*, 2009a, 2011): because of their electronic structure, the $\sigma \cdots \pi$ attraction outperforms $\pi \cdots \pi$ repulsion in the parallel face-to-face geometry (Fig. 2a).

Intermolecular distances shorter than the sum of the van der Waals radii do not necessarily indicate a strong attraction; interactions may actually be repulsive but stabilized by a large number of stronger attractive interactions (Dance, 2003). However, strong attractive interactions are expected in the


Figure 3

Dissociation of bromanilic acid (H_2BA) showing its monoanion (HBA^-) with a delocalized system in half of the ring, and its dianion (BA^{2-}) with two delocalized systems separated by two single C–C bonds.

vicinity of strong Lewis-acidic or Lewis-basic groups, and in such cases (for example, hydrogen bonding) shorter intermolecular distances are expected, and the interactions might have a partial covalent character (Miller & Novoa, 2007). The close face-to-face contacts of the aromatic rings, although energetically unfavourable, can be enforced by hydrogen bonds (Sokolov *et al.*, 2006). Such a type of stacking has a potential role in the design of organic semiconducting materials (Bendikov *et al.*, 2004; Sokolov *et al.*, 2006), however, it is difficult to engineer enforced stacking. On the other hand, quinoid rings tend to self-assemble into face-to-face

stacks (Molčanov *et al.*, 2011). Their crystals are stable and easy to prepare (Molčanov *et al.*, 2009a,b, 2011). Thus, salts of 2,5-dihydroxyquinones have a promising role in the design of functional materials.

In this study we have prepared a series of alkali salts of bromanilic acid (2,5-dihydroxy-3,6-dibromoquinone, Fig. 3), a bromo analogue of chloranilic acid. In contrast to chloranilic acid, in bromanilic acid and its salts somewhat different packing effects can be expected due to the different sizes of chlorine and bromine. Different polarizability of the substituents might also have an effect on interactions between the molecules. Two (de)protonation states of the acid are present; the salts comprise either a hydrogen bromanilate monoanion or bromanilate dianion (Fig. 3). Bromanilic acid and its salts are hardly studied, although a few of their crystal structures are deposited in the Cambridge Structural Database (Allen, 2002).

2. Experimental

2.1. Preparation

Bromanilic acid was prepared according to a modified Gräbe's procedure (Vanino, 1937): 1.00 g of tetrabromoquinone (bromanil) was added to a solution of sodium hydroxide (0.9 g in 30 ml of water) and heated at 353 K for 2 h. The colour of the solution turned dark purple. Purple sodium bromanilate was precipitated upon addition of 2 g NaCl; the precipitate was washed with 10% aqueous NaOH until the filtrate turned colourless. The neutral bromanilic acid was obtained by dissolution of sodium bromanilate in 10% hydrochloric acid; red crystals were precipitated. Anhydrous bromanilic acid was obtained (0.55 g; $\eta = 78\%$).

A single-crystal X-ray diffraction experiment confirmed that the bromanilic acid, although crystallized from aqueous solution, was indeed anhydrous (Robl, 1987) rather than a

Table 1

Experimental details.

Experiments were carried out at 293 K with Cu $K\alpha$ radiation using an Oxford Xcalibur Nova diffractometer.

	KHBA·3H ₂ O	RbHBA·3H ₂ O	CsHBA·3H ₂ O
Crystal data			
Chemical formula	C ₆ H ₇ Br ₂ O ₇ K	C ₆ H ₇ Br ₂ O ₇ Rb	C ₆ H ₅ Br ₂ CsO ₆ ·H ₂ O
M_r	390.02	436.39	483.83
Crystal system, space group	Tetragonal, $P4_2/n$	Tetragonal, $P4_2/n$	Tetragonal, $P4_2/n$
a, b, c (Å)	18.3890 (7), 18.3890 (7), 6.4262 (8)	18.6351 (1), 18.6351 (1), 6.528 (1)	18.9442 (1), 18.9442 (1), 6.6730 (1)
α, β, γ (°)	90, 90, 90	90, 90, 90	90, 90, 90
V (Å ³)	2173.05 (2)	2266.96 (2)	2394.82 (4)
Z	–	8	8
D_x (Mg m ⁻³)	–	2.557	2.684
μ (mm ⁻¹)	–	14.50	32.16
Crystal size (mm)	0.12 × 0.05 × 0.03	0.23 × 0.20 × 0.09	0.15 × 0.06 × 0.03
Data collection			
Absorption correction	–	Multi-scan	Multi-scan
T_{\min}, T_{\max}	–	0.488, 1	0.207, 1
No. of measured, independent and observed parameters	–	20 373, 2330, 2232	6509, 2425, 2129
R_{int}	–	0.026	0.028
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	–	0.044, 0.136, 1.21	0.046, 0.139, 1.15
No. of reflections	–	2330	2425
No. of parameters	–	167	161
No. of restraints	–	13	19
H-atom treatment	–	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	–	1.00, –0.95	1.42, –0.94

	Na ₂ BA·4H ₂ O	K ₂ BA·2H ₂ O	Rb ₂ BA·2H ₂ O	Cs ₂ BA·2H ₂ O
Crystal data				
Chemical formula	C ₆ H ₈ Br ₂ Na ₂ O ₈	C ₆ H ₄ Br ₂ K ₂ O ₆	C ₆ H ₄ Br ₂ O ₆ Rb ₂	C ₆ H ₄ Br ₂ Cs ₂ O ₆
M_r	413.90	410.11	502.85	597.73
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
a, b, c (Å)	8.0223 (6), 8.6764 (6), 9.9131 (6)	3.8441 (2), 9.4171 (4), 15.1001 (6)	4.0228 (1), 9.5488 (3), 15.1307 (4)	4.3380 (1), 9.7036 (3), 15.1253 (5)
α, β, γ (°)	108.113 (6), 110.543 (6), 91.991 (6)	90, 96.813 (4), 90	90, 96.521 (2), 90	90, 95.793 (3), 90
V (Å ³)	606.03 (7)	542.77 (4)	577.45 (3)	633.44 (3)
Z	2	2	2	2
D_x (Mg m ⁻³)	2.268	2.509	2.892	3.134
μ (mm ⁻¹)	9.52	16.50	19.25	52.40
Crystal size (mm)	0.25 × 0.05 × 0.05	0.20 × 0.15 × 0.05	0.30 × 0.16 × 0.03	0.15 × 0.10 × 0.05
Data collection				
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
T_{\min}, T_{\max}	0.194, 1	0.242, 1	0.151, 1	0.118, 1
No. of measured, independent and observed parameters	4617, 2459, 1989	2213, 1112, 956	3568, 1181, 1159	2628, 1315, 1226
R_{int}	0.033	0.034	0.032	0.073
Refinement				
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.030, 0.094, 1.03	0.041, 0.122, 1.07	0.047, 0.128, 1.12	0.074, 0.204, 1.05
No. of reflections	2459	1112	1181	1315
No. of parameters	196	80	81	81
No. of restraints	15	3	3	4
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.58, –0.51	0.80, –0.6	0.77, –2.03	2.24, –2.70

Computer programs used: *CrysAlis Pro* (Oxford Diffraction Ltd, 2007), *SHELXS97*, *SHELXL97* (Sheldrick, 2008), *ORTEP3* (Farrugia, 1997), *WinGX* (Farrugia, 1999).

dihydrate obtained by crystallization of chloranilic acid (Vanino, 1937; Andersen, 1967).

The alkali salts of bromanilic acid were prepared by the addition of a half-equivalent or equivalent amount of alkali

Table 2

The two possible settings of the unit cells for three isostructural alkali hydrogen bromanilates and ammonium chloranilate dihydrate (Herbstein & Kaftory, 1972).

	$P4_2/mnm$ cell (incorrect)		$P4_2/n$ cell (correct)	
	a', b'	c	a', b'	c
$(\text{NH}_4)_2\text{CA}\cdot 2\text{H}_2\text{O}^\dagger$	12.96	6.70	18.33	6.70
$\text{KHBA}\cdot 3\text{H}_2\text{O}$	13.0030 (7)	6.4262 (8)	18.3890 (7)	6.4262 (8)
$\text{RbHBA}\cdot 3\text{H}_2\text{O}$	13.1770 (1)	6.5278 (1)	18.6351 (1)	6.5278 (1)
$\text{CsHBA}\cdot 3\text{H}_2\text{O}$	13.3956 (1)	6.6730 (1)	18.9442 (1)	6.6730 (1)

[†] The unit cell determined by Herbstein & Kaftory (1972); no atomic coordinates reported.

carbonate (Merck and Kemika, p.a. grade) into an aqueous solution of bromanilic acid. The crystals were grown by slow evaporation of the solution at room temperature.

2.2. X-ray diffraction

Single-crystal measurements were performed on an Oxford Diffraction Xcalibur Nova R diffractometer (microfocus Cu tube) at room temperature. The program package *CrysAlis PRO* (Oxford Diffraction Ltd, 2007) was used for data reduction. The structures were solved using *SHELXS97* (Sheldrick, 2008) and refined with *SHELXL97* (Sheldrick, 2008). The models were refined using full-matrix least-squares refinement; all non-H atoms were refined anisotropically. H atoms were located in a difference-Fourier map and refined using the following restraints: $d(\text{O}_{\text{hydroxyl}}-\text{H}) = 0.82 \text{ \AA}$, $d(\text{O}_{\text{water}}-\text{H}) = 0.95 \text{ \AA}$; $d(\text{H}\cdots\text{H}) = 1.50 \text{ \AA}$. Molecular geometry calculations were performed using *PLATON* (Spek, 2003), and molecular graphics were prepared using *ORTEP3* (Farrugia, 1997). Crystallographic and refinement data for the structures reported in this paper are shown in Table 1.¹

2.3. Pseudosymmetry and disorder in crystals of hydrogen bromanilate salts

The choice of unit cell and space group for three isostructural hydrogen bromanilate salts was not straightforward because of the pseudosymmetry. In the cell initially found (Table 1) systematically absent reflections indicated the space group $P4_2/n$. However, an extra set of systematically absent reflections was found: hhl reflections with $h + l$ odd have zero intensity. Such an extinction would indicate a set of n glide planes parallel to (110) and $(\bar{1}\bar{1}0)$, but they are inconsistent with any space group. The program *PLATON* (Spek, 2003) also reported disagreement for the space group $P4_2/n$.

Another unit cell with a' and b' axes parallel to the directions $[110]$ and $[\bar{1}\bar{1}0]$ of the initial cell can be chosen, using the transformation matrix

$$\begin{pmatrix} 1/2 & 1/2 & 0 \\ 1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (1)$$

Its parameters are listed in Table 2, and systematic absences are consistent with the space group $P4_2/mnm$. *PLATON* (Spek, 2003) could not find any additional symmetry elements for this cell. However, refinement in the unit cell $P4_2/mnm$ yielded a poor structure with $R \simeq 0.13$ and unrealistic geometry: disordered water molecules and distances between alkali cations which are too short (3.16 Å in the case of the caesium salt, while the sum of van der Waals radii is 6.86 Å; distances which were too short were also observed for the other two salts). Clearly, such a structure can only be an artefact of incorrect symmetry.

The heavy atoms caesium, rubidium and bromine, located at special positions in the space group $P4_2/mnm$, cause additional extinctions. However, the extinctions observed are not compatible with the extinctions of the real space groups. Refinement in the space group $P4_2/n$ yielded agreeable R values (Table 1) and no unrealistically short interatomic distances. Therefore, we conclude that the correct symmetry is $P4_2/n$. Additional extinctions (hhl reflections with $h + l$ odd) are a result of pseudosymmetry: coordinates of both alkali cations and hydrogen bromanilate anions correspond to special positions in the space group $P4_2/mnm$, generating pseudo- n glide planes parallel to (110) and $(\bar{1}\bar{1}0)$. The relation between correct and incorrect unit cells and crystallographic and pseudosymmetry elements is shown in Fig. 4. Atomic coordinates in $P4_2/mnm$ form two sets: one corresponds to the atomic positions in the $P4_2/n$ cell, while the other is its mirror image, obtained by a 180° rotation about the c axis. Thus, the $P4_2/mnm$ structure is obtained by merohedral twinning. In both space groups the centroids of hydrogen bromanilate rings are located on symmetry axes (4_2 and $\bar{4}$ in the case of $P4_2/n$)

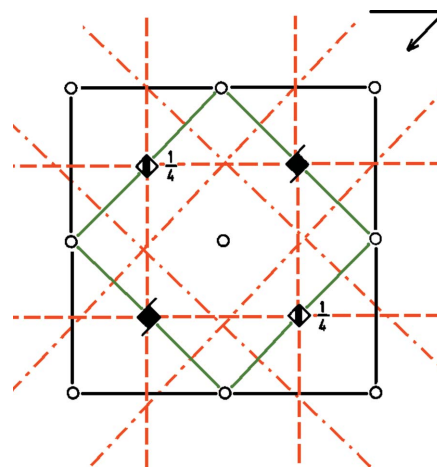


Figure 4 Relation of the correct cell $P4_2/n$ (black outline) and the incorrect $P4_2/mnm$ (green outline). Pseudo- n glide planes in $P4_2/n$ coincide with the crystallographic glide planes in the space group $P4_2/mnm$ (in red). All symbols are drawn in accordance with *International Tables for Crystallography* (Hahn, 1984).

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: GP5046). Services for accessing these data are described at the back of the journal.

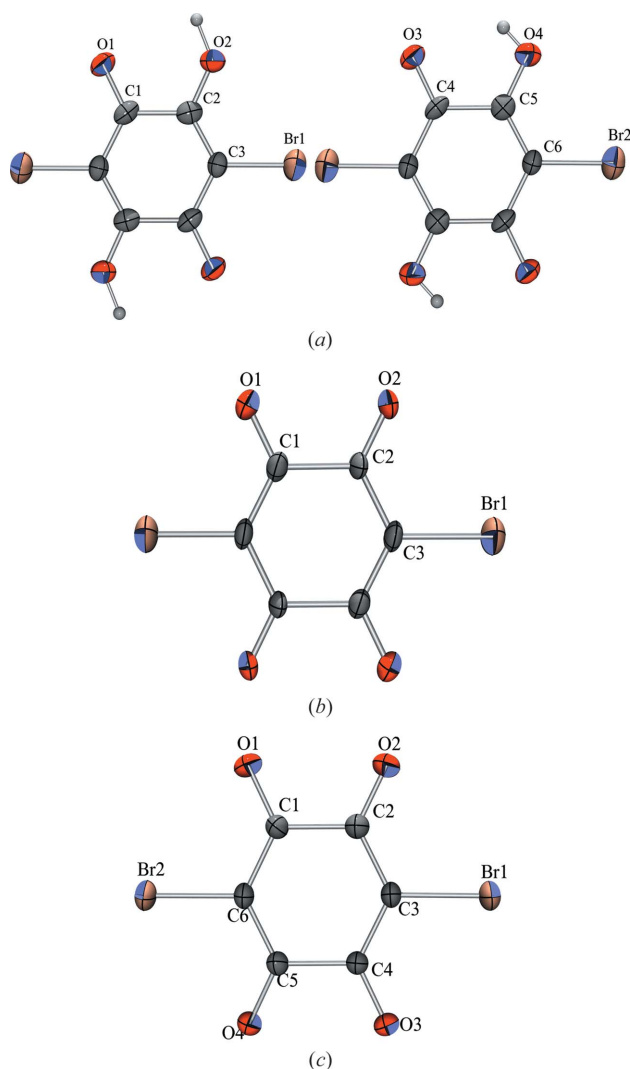
Table 3

A list of compounds discussed in this paper.

	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
HBA ⁻	–	KHBA·3H ₂ O	RbHBA·3H ₂ O	CsHBA·3H ₂ O
BA ²⁻	Na ₂ BA·4H ₂ O	K ₂ BA·2H ₂ O	Rb ₂ BA·2H ₂ O	Cs ₂ BA·2H ₂ O

and are disordered in order to conform to the required symmetry. The disorder was modelled with H atoms populated 0.5 at both O atoms in the *para* position; the C–C and C–O bond lengths agree with such a model.

It is interesting to note that the unit-cell parameters of ammonium chloranilate dihydrate determined in 1972 by Herbstein & Kaftory (1972) are very close to the unit cell setting observed for hydrogen bromanilates described herein

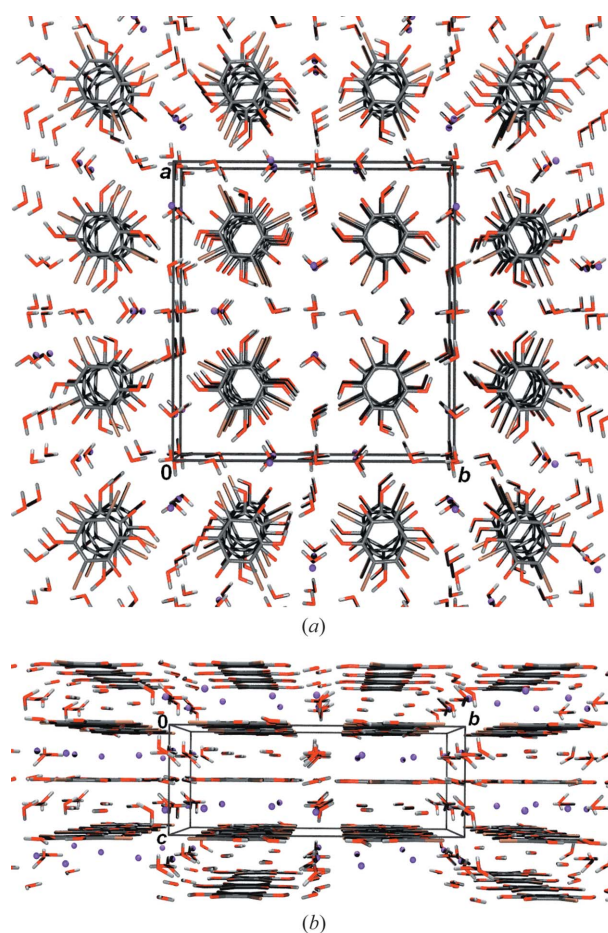

Figure 5

ORTEP3 (Farrugia, 1997) drawings of (a) two symmetry-independent hydrogen bromanilate monoanions of RbHBA·3H₂O, (b) bromanilate dianion of K₂BA·2H₂O and (c) bromanilate dianion of NaBA·4H₂O. Atom-numbering schemes are applied to all the structures discussed. Displacement ellipsoids are drawn at a probability of 50% and H atoms are depicted as spheres of arbitrary radii. In hydrogen bromanilate structures, a H atom of the OH group is disordered (H pp = 0.5, each) between *para*-positioned O2 and O2ⁱ, and O4 and O4ⁱ atoms.

(Table 2). The space group $P4_2/nm$ (for the cell with $a = 12.96 \text{ \AA}$) was reported. However, its cell can easily be transformed to be consistent with the space group $P4_2/n$ ($a = 18.33 \text{ \AA}$) determined for hydrogen bromanilate homologues presented in this work (Table 2). Unfortunately, atomic coordinates were not determined and our attempts to prepare ammonium chloranilate dihydrate were unsuccessful (Molčanov *et al.*, 2009b).

3. Results and discussion

The structures of salts of alkali mono- and dianion bromanilate hydrates (Table 3, Fig. 5) were determined. Unlike hydrogen chloranilate rings, which are located in the general position (Molčanov *et al.*, 2009a,b, 2011; Molčanov & Kojić-Prodić, 2010), centroids of hydrogen bromanilate rings in RbHBA·3H₂O and CsHBA·3H₂O are located on 4₂ and $\bar{4}$ axes, leading to a disorder over two orientations (Fig. 5a). Therefore, their geometric parameters suffer from disorder. However, two crystal structures of organic hydrogen bromanilate salts (Zaman *et al.*, 2001a,b) have already been deposited in the CSD (Version 5.32, November 2010; Allen, 2002) and their geometric parameters are similar to hydrogen


Figure 6

Packing of CsHBA·3H₂O viewed in the directions: (a) [001] and (b) [100]. Hydrogen bonds are omitted for clarity and alkali cations are depicted as spheres of arbitrary radii. The packing of KHBA·3H₂O and RbHBA·3H₂O reveals an isostructural relationship.

Table 4
Geometric parameters of $\pi \cdots \pi$ interactions.

$\pi \cdots \pi$	Cg...Cg (Å) [†]	α [‡]	β [§]	Cg...plane(Cg2) (Å)	Offset (Å)
RbHBA·3H₂O					
C1→C3...C1→C3 ⁱ	3.264 (2)	0.00	0.00	3.264 (2)	0.00
C4→C5'...C4→C5' ⁱⁱⁱ	3.276 (2)	0.00	0.00	3.276 (2)	0.00
C4→C5''...C4→C5'' ⁱⁱⁱ	3.252 (2)	0.00	0.00	3.252 (2)	0.00
CsHBA·3H₂O					
C1→C3...C1→C3 ⁱ	3.336 (4)	0.00	0.00	3.336 (4)	0.00
C4→C5'...C4→C5' ⁱⁱⁱ	3.404 (4)	0.00	0.00	3.404 (4)	0.00
C4→C5''...C4→C5'' ⁱⁱⁱ	3.269 (4)	0.00	0.00	3.269 (4)	0.00
Na₂BA·4H₂O					
C1→C6...C1→C6 ^{iv}	4.015 (2)	0.00	21.06	3.7470 (13)	1.443
C1→C6'...C1→C6' ^v	4.007 (2)	0.00	21.26	3.7344 (13)	1.453
K₂BA·2H₂O					
C1→C3''...C1→C3'' ^{vi}	3.844 (2)	0.00	24.43	3.500 (1)	1.590
Rb₂BA·2H₂O					
C1→C2''...C1→C2'' ^{vii}	4.023 (2)	0.00	26.61	3.5967 (16)	1.802
Cs₂BA·2H₂O					
C1→C2''...C1→C2'' ^{viii}	4.338 (5)	0.00	30.23	3.748 (3)	2.184

Symmetry codes: (i) $1-x, -\frac{1}{2}+y, -\frac{1}{2}+z$; (ii) $x, \frac{3}{2}-y, \frac{5}{2}-z$; (iii) $x, \frac{3}{2}-y, \frac{7}{2}-z$; (iv) $1-x, 2-y, 1-z$; (v) $2-x, 2-y, 1-z$; (vi) $-x, 1-y, 1-z$; (vii) $1-x, 1-y, 1-z$. [†] Cg = centre of gravity of the quinoid ring. [‡] α = angle between planes of two quinoid rings. [§] β = angle between Cg...Cg line and normal to the plane of the first quinoid ring.

chloranilates (Molčanov *et al.*, 2009a, 2011; Molčanov & Kojić-Prodić, 2010; Biliškov *et al.*, 2011). The possibility of a dynamic proton disorder (*i.e.* proton transfer) was ruled out by IR spectroscopy. The IR spectrum of CsHBA·3H₂O showed no Zundel-like continuum typical of proton transfer (Biliškov *et al.*, 2011; for details see the supplementary material). Crystals of KHBA·3H₂O were poor and their structure could not be properly refined, but cell parameters (Tables 1 and 2) and systematic absences indicate an isostructural relationship to RbHBA·3H₂O and CsHBA·3H₂O. Geometries of the dianions, which are not disordered, agree well with those of their chloranilate analogues (Molčanov *et al.*, 2009a,b; Molčanov & Kojić-Prodić, 2010; see Figs. 5b and c). In NaBA·4H₂O the dianion is located in a general position (Fig. 5c; in other bromanilate structures it reveals a crystallographic symmetry C_i (Fig. 5b).

The crystal packings of three isostructural hydrogen bromanilate salts, KHBA·3H₂O, RbHBA·3H₂O and CsHBA·3H₂O, are dominated by face-to-face stacks of the mono anions (Fig. 6, Table 4). Unlike hydrogen chloranilates (Molčanov *et al.*, 2009a,b) which stack with a small offset (~ 0.2 Å), hydrogen bromanilate rings are not offset at all, offsets being strictly zero due to the symmetry. Centroid distances and interatomic distances between contiguous rings are shorter than 3.3 Å, which is substantially shorter than the sum of the van der Waals radii (for carbon it is 3.5 Å).

The steric effect of bulky bromine substituents can be illustrated by two contiguous rings in a stack (Fig. 7). While hydrogen chloranilate rings (Molčanov *et al.*, 2009a,b, 2011) pack in an almost eclipsed arrangement (Fig. 7a) where one ring is rotated by less than 10° relative to the other, hydrogen

bromanilate rings are rotated by 30°, and stack in a staggered fashion (Fig. 7b).

In the structures of dianion bromanilate salts, Na₂BA·4H₂O, K₂BA·2H₂O, Rb₂BA·2H₂O and Cs₂BA·2H₂O (Figs. 8–10), no face-to-face stacking was observed. The dianions form offset stacks with geometries similar to aromatic stacking (Table 4). However, the rings in those stacks remain strictly parallel (Table 4), even when not fixed by symmetry. Our search of the Cambridge Structural Database (Allen, 2002) reveals that the stacked quinoid rings tend to be perfectly parallel (Molčanov *et al.*, 2011). Apparently, face-to-face stacking of dianionic quinoid (at least chloranilate and bromanilate) rings is not energetically favourable due to:

(i) the strong repulsion of double negative charges and

(ii) the lack of $\sigma \cdots \pi$ attractions due to a significant delocalization of π electrons.

Differences in the stacks of mono- and dianions against aromatics is due to their different electronic structures (Figs. 1–3). The aromatic $\pi \cdots \pi$ interactions are a consequence of electron delocalization, whereas molecules with localized or only partially delocalized π -electrons

will necessarily develop $\pi \cdots \pi$ interactions in stacks of geometrically different architecture. The unusually short $\pi \cdots \pi$ interactions can be explained by the electron-density distribution in quinoid rings, which involve recognisable single and double bonds rather than completely delocalized π -systems (Fig. 3). Therefore, molecules can stack in such a way

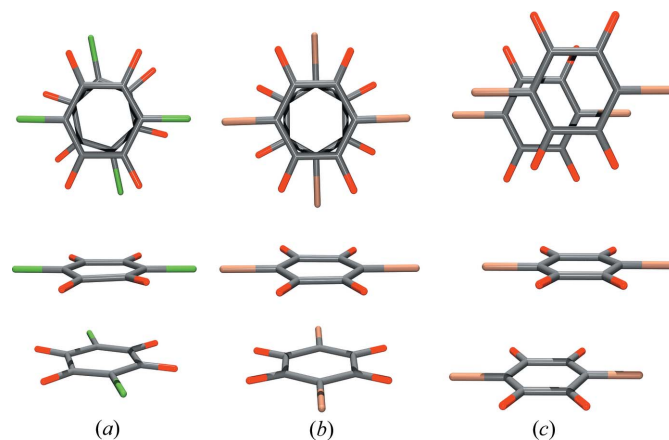


Figure 7

Top-down (upper row) and side-view of a pair of contiguous rings in a stack: (a) hydrogen chloranilate anions in potassium hydrogen chloranilate dihydrate (Molčanov *et al.*, 2009a) stack in a nearly eclipsed fashion; (b) hydrogen bromanilate anions in RbHBA·3H₂O form a staggered arrangement; (c) bromanilate dianions in K₂BA·2H₂O form offset stacks with a geometry similar to aromatic π -interactions. The hydrogen bromanilate rings are not offset at all, whereas a very small offset (~ 0.2 Å) occurred in hydrogen chloranilate stacks. Offset of bromanilate dianions is necessary to prevent $\pi \cdots \pi$ repulsions between π bonds from contiguous rings (*e.g.* C–O). H atoms of OH groups are not shown due to a disorder.

that single bonds are sandwiched between double ones and *vice versa*. Such an arrangement minimizes repulsions of π -electrons, while maximizing σ - π (Janiak, 2000; Steed & Atwood, 2009) and dipolar attraction – because of the many electronegative substituents the quinoid rings possess strong local dipoles; even C–C bonds are quite polar (Fig. 3). In the π -stack the monoanions also involve strong repulsions (negatively charged monoanions and a significant portion of the ring has delocalized π -electrons, Fig. 3), however, the repulsion can be minimized by optimal orientation of dipoles in the two contiguous rings (Figs. 7*b*). It can be deduced that the total charge of the stacks and degree of electron delocalization have a crucial impact over the type of stacks that can be formed. Thus, dianions with double negative charges and *two* delocalized systems (Fig. 3) will necessarily be arranged in a geometrically different fashion (Fig. 7*c*). Electrostatic repulsions do not allow close contacts (as in the orientation in Fig. 7*b*). Therefore, the only solution to minimize repulsion is to increase both centroid separation distances and offset contiguous rings (as revealed in the database search described by Molčanov *et al.*, 2011 and Fig. 7*c*).

The unit-cell dimensions and space-group symmetry of the salts $\text{K}_2\text{BA}\cdot 2\text{H}_2\text{O}$ (Fig. 9), $\text{Rb}_2\text{BA}\cdot 2\text{H}_2\text{O}$ and $\text{Cs}_2\text{BA}\cdot 2\text{H}_2\text{O}$

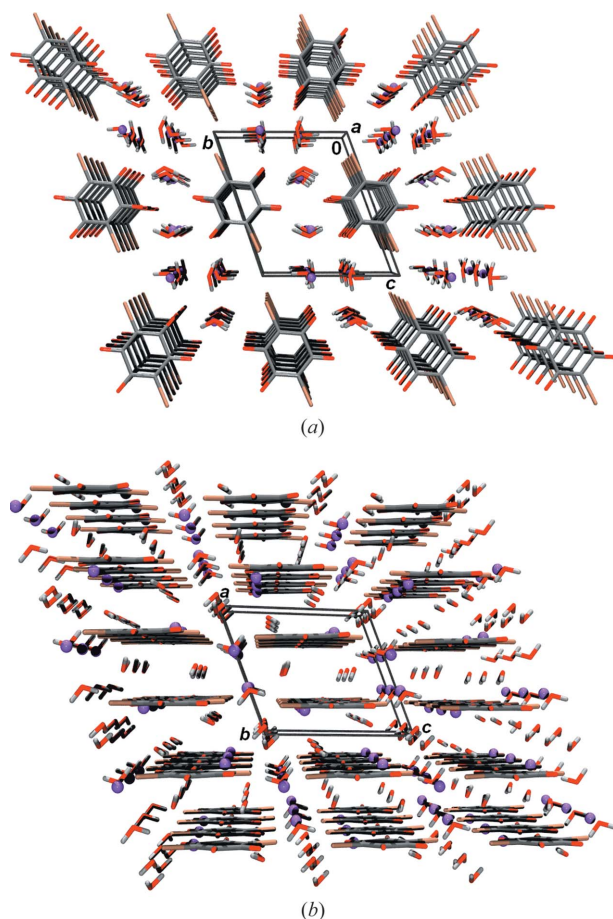


Figure 8
Crystal packing of $\text{Na}_2\text{BA}\cdot 4\text{H}_2\text{O}$ viewed in the directions: (a) [100] and (b) [010] showing stacks of parallel offset dianions. Hydrogen bonds are omitted for clarity and sodium cations are depicted as spheres of arbitrary radii.

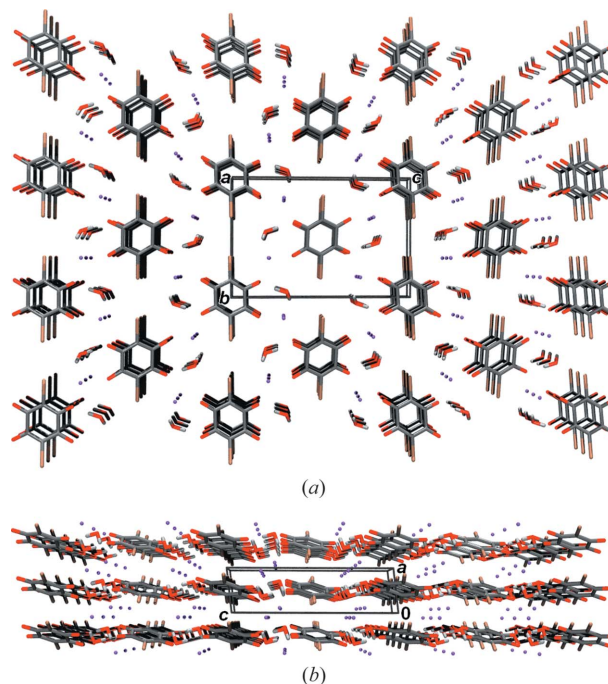


Figure 9
Crystal packing of $\text{K}_2\text{BA}\cdot 2\text{H}_2\text{O}$ viewed in the directions: (a) [100] and (b) [010] showing stacks of parallel offset dianions. Hydrogen bonds are omitted for clarity and potassium cations are depicted as spheres of arbitrary radii.

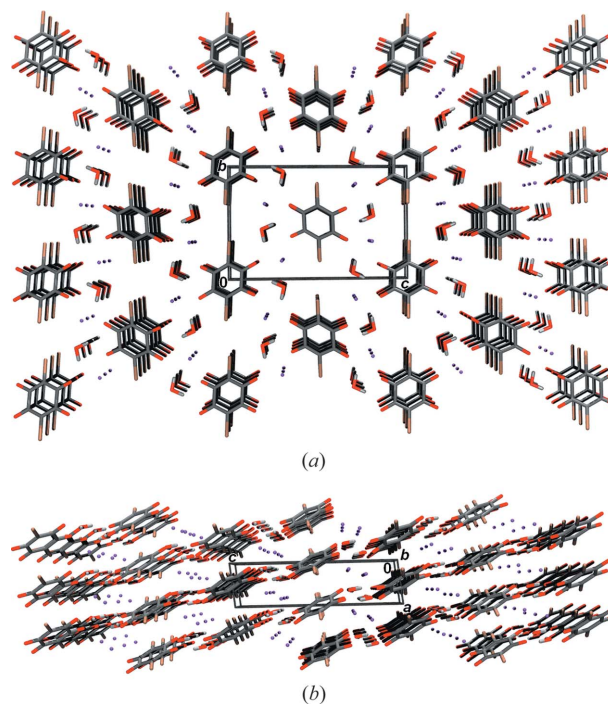


Figure 10
Crystal packing of $\text{Rb}_2\text{BA}\cdot 2\text{H}_2\text{O}$ viewed in the directions: (a) [100] and (b) [010] showing stacks of parallel offset dianions. Hydrogen bonds are omitted for clarity and alkali cations are depicted as spheres of arbitrary radii. The crystal packing of $\text{Cs}_2\text{BA}\cdot 2\text{H}_2\text{O}$ is isostructural to $\text{Rb}_2\text{BA}\cdot 2\text{H}_2\text{O}$.

(Fig. 10) suggest an isostructural relationship. However, the direction of the glide plane is different: in $K_2BA \cdot 2H_2O$ it is along c , whereas in the other two (which are also isostructural) it is the diagonal glide plane n . A very small difference in the crystal packing due to a different direction of gliding can be seen in Figs. 9*b* and 10*b*.

In the crystal packings of monohydrogen bromanilate trihydrates the crystal water molecules are involved in an intensive three-dimensional-network (Fig. 11, supplementary material, Table S1). The hydrogen bromanilates are not directly connected by hydrogen bonds, however, they are hydrogen-bonded through water molecules between stacks. Intrastack hydrogen bonds do not occur owing to steric reasons. The hydroxy groups of both monoanions (*A* and *B*) act as proton donors to the water molecule O5, which donates its protons to the water molecule O7 and Br2. The water molecule O6 is the proton donor to all O atoms of monoanions (except a carbonyl O1). There is no explicit evidence that hydrogen bonding is responsible for certain stacking architecture. Whether monoanionic rings will stack with or without offset is apparently a matter of their environment – hydrogen bonds and polarization by cations may or may not stabilize π -stacking depending on steric conditions.

In the crystal packings of dianion bromanilate hydrates dianions can exhibit an acceptor function only in the hydrogen-bond network (Fig. 12). Thus, dianion interactions are realised *via* hydrogen bonds with water molecules, which play a significant role in the hydrogen-bonding network exhibiting different crystal packings of bromanilate dianion

salts. Details on hydrogen bonding are included in the supplementary material.

4. Conclusions

A series of alkali salts of hydrogen bromanilic acid trihydrates (K^+ , Rb^+ and Cs^+), bromanilic acid tetrahydrate (Na^+), and bromanilic acid dihydrates (K^+ , Rb^+ and Cs^+) were prepared and their structures determined and analysed. In their crystals the stacking of quinoid rings is a dominant motif. The salts of hydrogen bromanilic acid show face-to-face stacking arrangements with no offset revealing short separation distances of the ring centroids (3.25–3.30 Å). However, dianion salts of bromanilic acid are stacked in the same way as aromatic rings. The interactions within stacks involving monoanions of bromanilic acid are different to those of its dianions. These differences are due to their different electron distributions within rings (Fig. 3). The pronounced repulsion of stacked dianions, having more delocalized negative charge, can be optimized by increasing the ring-separation distances.

These interactions can be exploited in crystal engineering to generate two- and three-dimensional molecular assemblies for functional materials (Kitagawa & Kawata, 2002; Kitagawa & Matsuda, 2007).

Within the crystal packing of $KHBA \cdot 3H_2O$, $RbHBA \cdot 3H_2O$ and $CsHBA \cdot 3H_2O$ salts an isostructural relationship is observed. The series of $K_2BA \cdot 2H_2O$, $Rb_2BA \cdot 2H_2O$ and $Cs_2BA \cdot 2H_2O$ salts also reveals an isostructural relationship.

By comparison of bromanilate and hydrogen bromanilate salts with their chloranilate and hydrogen chloranilate analogues (Herbstein & Kaftory, 1972; Molčanov *et al.*, 2009*a,b*, 2011), it is obvious that the steric effect of the large Br atom plays a major role in their crystal packing. No isostructural relationship was observed between chloranilate

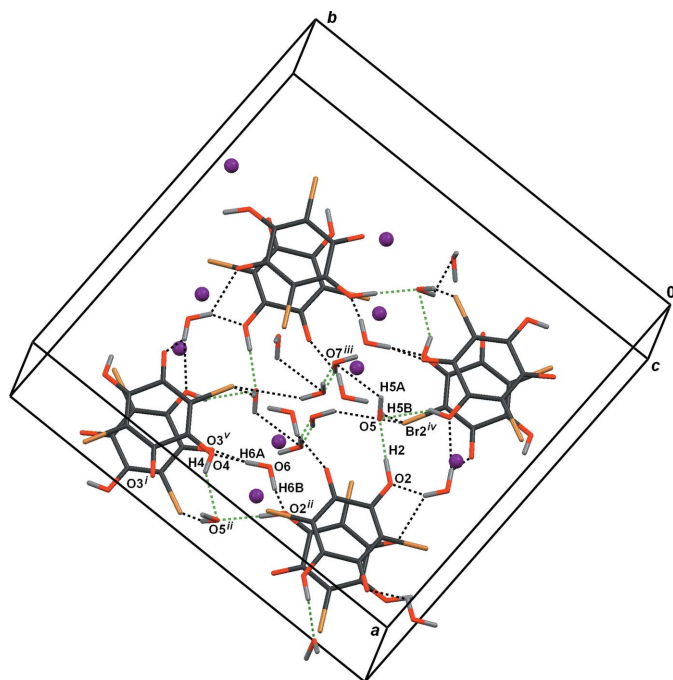


Figure 11
Hydrogen-bonding scheme of $RbHBA \cdot 3H_2O$. Hydrogen bonds with disordered protons are shown as green dotted lines; those with ordered protons are shown as black dotted lines. Alkali cations are depicted as spheres of arbitrary radii. Symmetry codes: (i) $\frac{3}{2} - x, \frac{3}{2} - y, z$; (ii) $\frac{1}{2} + y, 1 - x, \frac{1}{2} + z$; (iii) $1 - x, 2 - y, 1 - z$; (iv) $1 - x, 1 - y, 3 - z$; (v) $\frac{3}{2} - y, x, \frac{7}{2} - z$.

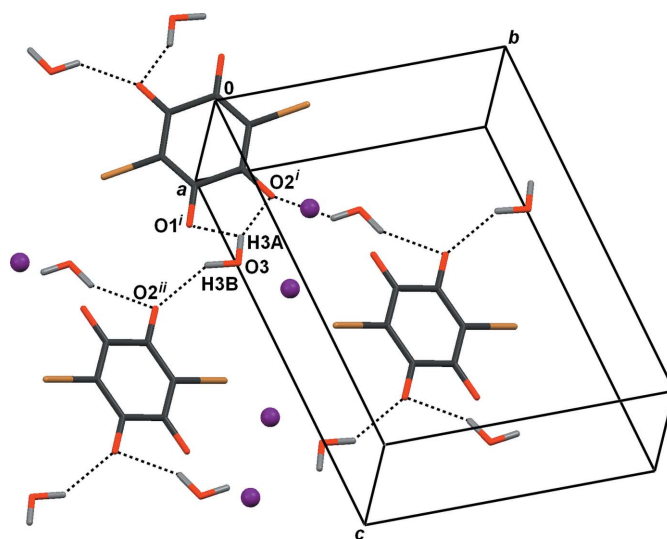


Figure 12
Hydrogen-bonding scheme of $Rb_2BA \cdot 2H_2O$. Hydrogen bonds are shown as black dotted lines and alkali cations are depicted as spheres of arbitrary radii. Symmetry operators: (i) $2 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, -y, 1 - z$.

and bromanilate salts. The quinoid rings stack in all the hydrogen bromanilate salts, while crystal water molecules and hydrogen bonds act as 'glue', holding the stacks together and stabilizing the crystal packing. Generally, the size and polarity of the cations and solvent molecules should be optimized to stabilize a crystal with no obstruction to the anions stacking.

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