

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

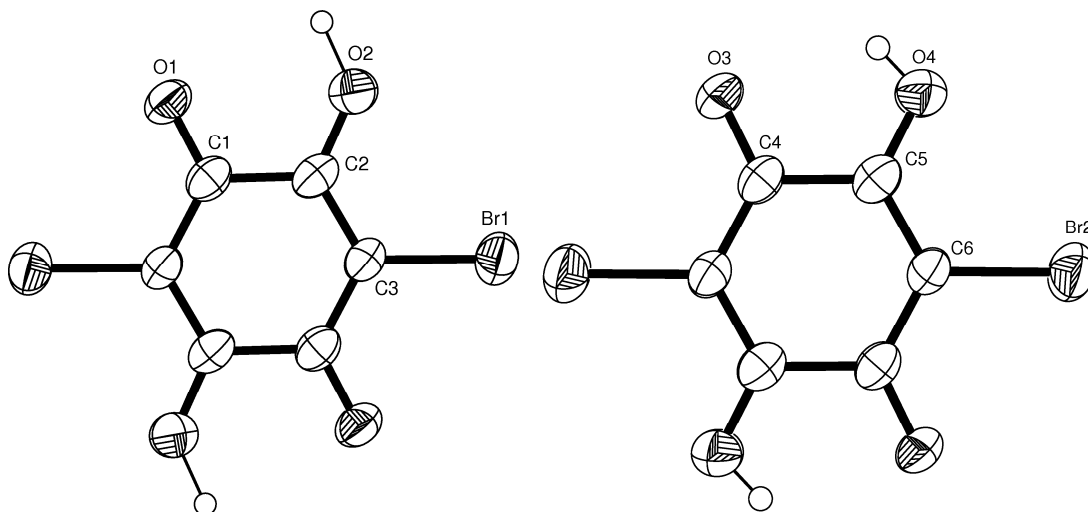
**Supporting Information**

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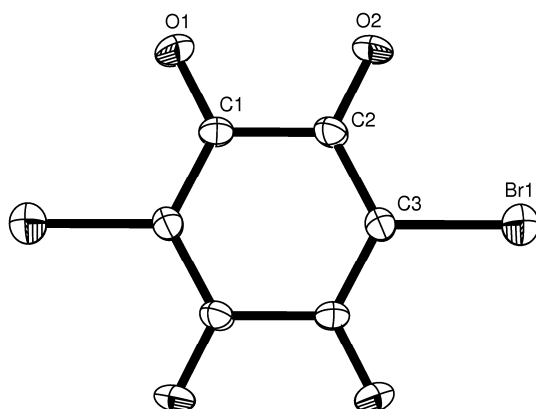
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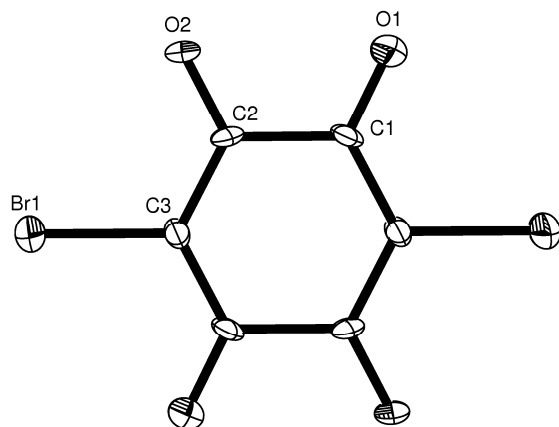
## S1 ORTEP drawings of bromanilate and hydrogen bromanilate anions



**Figure S1** ORTEP (Farrugia, 1997) drawing of two symmetry-independent hydrogen bromanilate anions in **CsHBA·3H<sub>2</sub>O**. Displacement ellipsoids are drawn at the probability of 50 % and hydrogen atoms are depicted as spheres of arbitrary radii. In hydrogenbromanilate structures, a hydrogen atom is disordered between O2 and O4 atoms with  $pp=0.5$  at each oxygen atom.

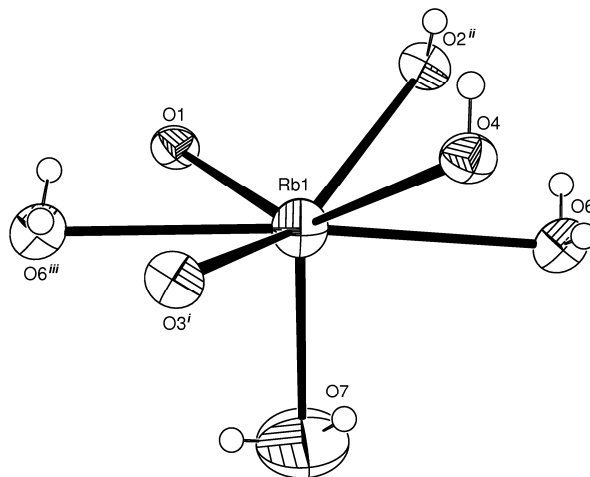


**Figure S2** ORTEP (Farrugia, 1997) drawing of a bromanilate anion in **Rb<sub>2</sub>BA·2H<sub>2</sub>O**. Displacement ellipsoids are drawn at the probability of 50 % and hydrogen atoms are depicted as spheres of arbitrary radii.

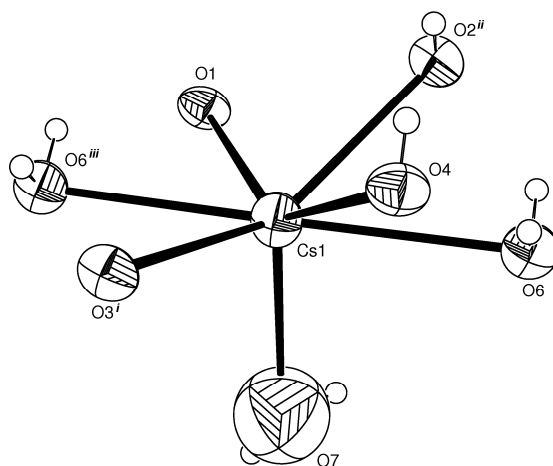


**Figure S3** ORTEP (Farrugia, 1997) drawing of a bromanilate anion in  $\text{Cs}_2\text{BA}\cdot 2\text{H}_2\text{O}$ . Displacement ellipsoids are drawn at the probability of 50 % and hydrogen atoms are depicted as spheres of arbitrary radii.

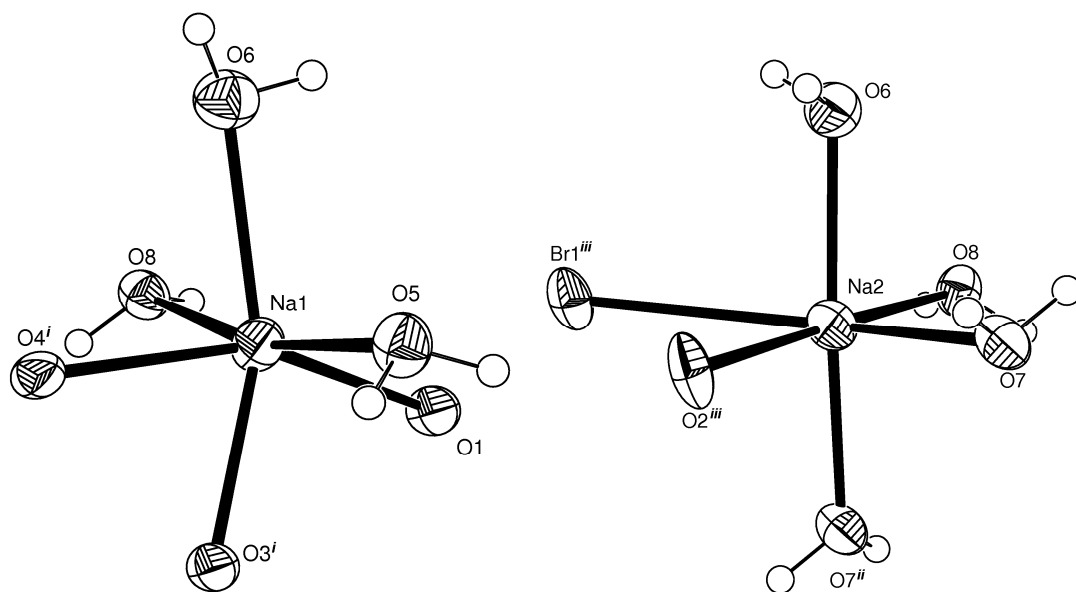
## S2 Details on cation coordination



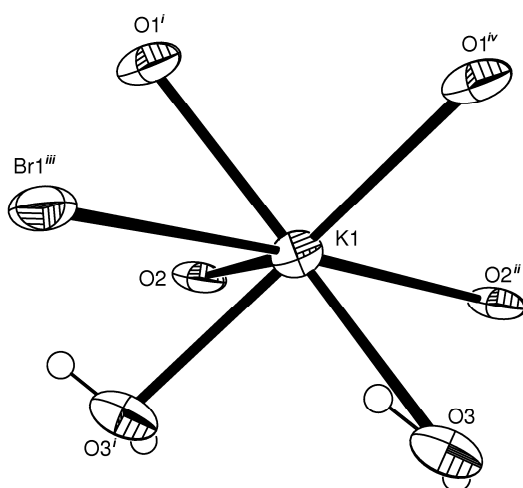
**Figure S4** ORTEP (Farrugia, 1997) drawing of the alkali cation coordination sphere in **RbHBA·3H<sub>2</sub>O**. Displacement ellipsoids are drawn at the probability of 50 % and hydrogen atoms are depicted as spheres of arbitrary radii. Symmetry operators: *i*)  $3/2-y, x, 5/2-z$ ; *ii*)  $1/2+y, 1-x, 1/2+z$ ; *iii*)  $x, y, -1+z$ .



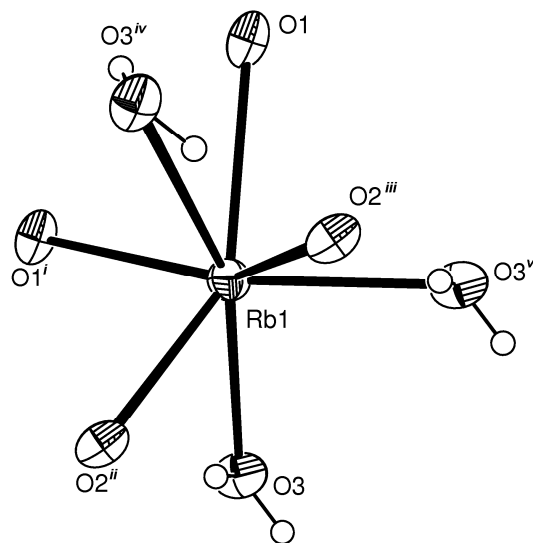
**Figure S5** ORTEP (Farrugia, 1997) drawing of the alkali cation coordination sphere in **CsHBA·3H<sub>2</sub>O**. Displacement ellipsoids are drawn at the probability of 50 % and hydrogen atoms are depicted as spheres of arbitrary radii. Symmetry operators: *i*)  $3/2-y, x, 5/2-z$ ; *ii*)  $1/2+y, 1-x, 1/2+z$ ; *iii*)  $x, y, -1+z$ .



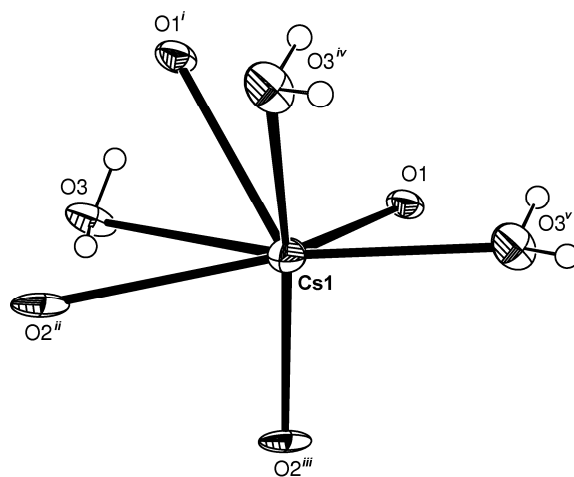
**Figure S6** ORTEP (Farrugia, 1997) drawing of the alkali cation coordination spheres in  $\text{Na}_2\text{BA}\cdot 4\text{H}_2\text{O}$ . Displacement ellipsoids are drawn at the probability of 50 % and hydrogen atoms are depicted as spheres of arbitrary radii. Symmetry operators: *i*)  $x, -1+y, z$ ; *ii*)  $1-x, 1-y, 2-z$ ; *iii*)  $x, y, 1+z$ .



**Figure S7** ORTEP (Farrugia, 1997) drawing of the alkali cation coordination sphere in  $\text{K}_2\text{BA}\cdot 2\text{H}_2\text{O}$ . Displacement ellipsoids are drawn at the probability of 50 % and hydrogen atoms are depicted as spheres of arbitrary radii. Symmetry operators: *i*)  $2-x, 1/2+y, 1/2-z$ ; *ii*)  $1+x, y, z$ ; *iii*)  $1+x, y, z$ ; *iv*)  $1-x, 1/2+y, 1/2-z$ .



**Figure S8** ORTEP (Farrugia, 1997) drawing of the alkali cation coordination sphere in **Rb<sub>2</sub>BA·2H<sub>2</sub>O**. Displacement ellipsoids are drawn at the probability of 50 % and hydrogen atoms are depicted as spheres of arbitrary radii. Symmetry operators: *i*)  $1+x, y, z$ ; *ii*)  $-1/2+x, 1/2-y, -1/2+z$ ; *iii*)  $1/2+x, 1/2-y, -1/2+z$ ; *iv*)  $-1+x, y, z$ .



**Figure S9** ORTEP (Farrugia, 1997) drawing of the alkali cation coordination sphere in **Cs<sub>2</sub>BA·2H<sub>2</sub>O**. Displacement ellipsoids are drawn at the probability of 50 % and hydrogen atoms are depicted as spheres of arbitrary radii. Symmetry operators: *i*)  $1+x, y, z$ ; *ii*)  $-1/2+x, 1/2-y, -1/2+z$ ; *iii*)  $1/2+x, 1/2-y, -1/2+z$ ; *iv*)  $-1+x, y, z$ .

### S3 Geometric parameters of hydrogen bonding

**Table S1** Geometric parameters of hydrogen bonds.

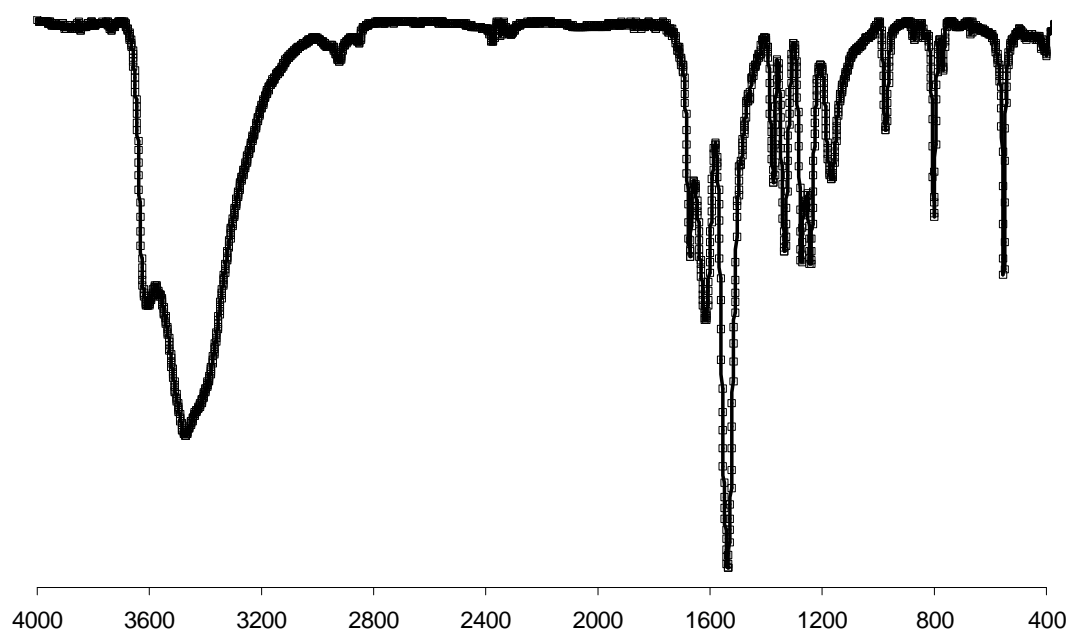
	$D-H / \text{\AA}$	$H \cdots A / \text{\AA}$	$D \cdots A / \text{\AA}$	$D-H \cdots A / ^\circ$	Symm. op. on $A$
<b>RbHBA·3H<sub>2</sub>O</b>					
O2–H2···O5	1.01	1.81	2.823(5)	177	$x, y, z$
O4–H4···O3	0.82	2.19	2.659(5)	117	$3/2 - x, 3/2 - y, z$
O4–H4···O5	0.82	2.15	2.873(5)	148	$1/2 + y, 1 - x, 1/2 + z$
O5–H5A···O7	0.94(8)	2.56(9)	3.212(12)	128(7)	$1 - x, 2 - y, 1 - z$
O5–H5B···Br2	0.95(7)	2.83(7)	3.730(4)	158(8)	$1 - x, 1 - y, 3 - z$
O6–H6A···O4	0.93(5)	2.40(5)	3.052(5)	127(2)	$x, y, z$
O6–H6A···O3	0.93(5)	2.26(3)	2.970(5)	133(4)	$3/2 - y, x, 7/2 - z$
O6–H6B···O2	0.92(7)	2.40(6)	3.058(5)	129(2)	$1/2 + y, 1 - x, 1/2 + z$
<b>CsHBA·3H<sub>2</sub>O</b>					
O2–H2···O5	1.07	1.80	2.873(8)	176	$x, y, z$
O4–H4···O3	0.82	2.17	2.642(8)	117	$3/2 - x, 3/2 - y, z$
O4–H4···O5	0.82	2.24	2.972(8)	149	$1/2 + y, 1 - x, 1/2 + z$
O5–H5A···O7	0.94(4)	2.56(9)	3.33(2)	139(10)	$x, y, z$
O5–H5A···O7	0.94(4)	2.57(10)	3.24(2)	128(9)	$1 - x, 2 - y, 1 - z$
O5–H5B···O4	0.95(6)	2.13(8)	2.972(8)	148(8)	$1 - y, -1/2 + x, -1/2 + z$
O5–H5B···O3	0.95(6)	2.50(6)	3.237(8)	148(8)	$-1/2 + y, 1 - x, -1/2 + z$
O6–H6A···O3	0.95(12)	2.54(9)	3.069(8)	115(6)	$3/2 - y, x, 7/2 - z$
<b>Na<sub>2</sub>BA·4H<sub>2</sub>O</b>					
O5–H5A···O3	0.92(4)	2.11(4)	3.004(3)	164(4)	$2 - x, 2 - y, 1 - z$
O5–H5B···O1	0.92(4)	2.55(5)	3.271(4)	136(3)	$2 - x, 1 - y, 1 - z$
O5–H5B···O2	0.92(4)	2.00(4)	2.818(4)	147(4)	$2 - x, 2 - y, 1 - z$
O6–H6A···O4	0.94(5)	2.02(5)	2.909(3)	157(5)	$2 - x, 2 - y, 1 - z$
O6–H6B···Br2	0.94(5)	2.86(5)	3.460(3)	123(5)	$x, y, z$
O6–H6B···Br2	0.94(5)	2.74(6)	3.508(3)	140(5)	$2 - x, 2 - y, 2 - z$
O7–H7A···O4	0.91(3)	2.09(3)	2.930(3)	155(3)	$x, -1 + y, z$
O7–H7B···O5	0.93(3)	1.92(3)	2.819(4)	163(3)	$2 - x, 2 - y, 2 - z$
O7–H8A···O3	0.94(4)	2.01(5)	2.868(3)	151(4)	$1 - x, 2 - y, 1 - z$
O7–H8B···O1	0.93(4)	2.16(4)	2.964(3)	144(3)	$1 - x, 1 - y, 1 - z$
O7–H8B···O2	0.93(4)	2.50(4)	3.301(4)	145(3)	$1 - x, 1 - y, 1 - z$
<b>K<sub>2</sub>BA·2H<sub>2</sub>O</b>					
O3–H3A···O1	0.93(3)	1.85(4)	2.722(4)	154(6)	$1 + x, y, z$

O3-H3B...Br1	0.94(6)	2.88(6)	3.608(3)	136(5)	$2 - x, -1/2 + y, 1/2 - z$
O3-H3B...O2	0.94(6)	2.19(6)	3.034(5)	150(5)	$2 - x, -1/2 + y, 1/2 - z$
<b>Rb<sub>2</sub>BA·2H<sub>2</sub>O</b>					
O3-H3A...O1	0.96(6)	2.15(11)	2.732(4)	118(10)	$2 - x, -1/2 + y, 1/2 - z$
O3-H3A...O2	0.96(6)	2.18(8)	3.080(4)	155(7)	$2 - x, -1/2 + y, 1/2 - z$
O3-H3B...O2	0.96(3)	2.14(4)	2.972(5)	144(6)	$1-x,-y,1-z$
<b>Cs<sub>2</sub>BA·2H<sub>2</sub>O</b>					
O3-H3A...Br1	0.95(6)	2.92(7)	3.673(7)	137(5)	$1 - x, -y, 1 - z$
O3-H3A...O2	0.95(6)	2.17(6)	2.946(11)	138(5)	$1 - x, -y, 1 - z$

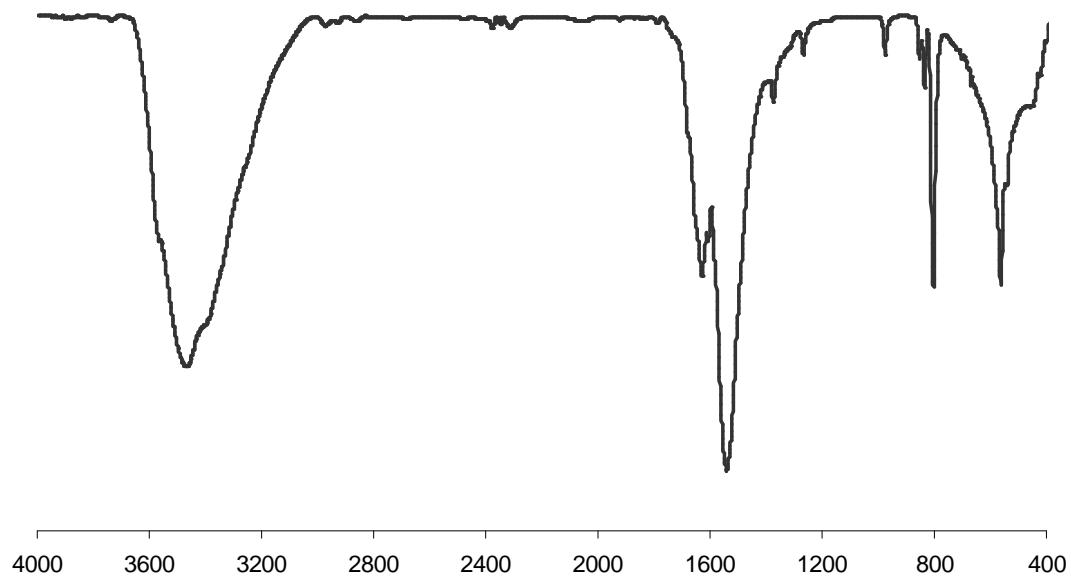


## S4 IR spectra

Infrared spectra were recorded by using KBr pellets on a Bruker Alpha-T spectrometer, in the 4000–400  $\text{cm}^{-1}$  region. Spectra of hydrogen bromanilates are virtually identical (Table S2), which is no surprise, since the compounds are isostructural. An example, **CsHBA·3H<sub>2</sub>O**, is shown in Fig. S10. Bromanilates also yielded almost identical spectra (Fig. S11, Table S2). The spectra were assigned in analogy to a detailed study of similar chloranilate salts (Biliškov *et al.*, 2011).



**Figure S10** An example of a hydrogen bromanilate: IR spectrum of **CsHBA·3H<sub>2</sub>O**.



**Figure S11** An example of a bromanilate: IR spectrum of  $\text{Na}_2\text{BA}\cdot 4\text{H}_2\text{O}$ .

**Table S2** Characteristic infrared bands (wavenumbers in  $\text{cm}^{-1}$ ) in the 4000 – 400  $\text{cm}^{-1}$  region. Assignment of the spectra according to Biliškov *et al.* (2011).

Wavenumber						Assignment
<b>Na<sub>2</sub>BA·4H<sub>2</sub>O</b>	<b>K<sub>2</sub>BA·2H<sub>2</sub>O</b>	<b>Rb<sub>2</sub>BA·2H<sub>2</sub>O</b>	<b>Cs<sub>2</sub>BA·2H<sub>2</sub>O</b>	<b>KHBA·3H<sub>2</sub>O</b>	<b>CsHBA·3H<sub>2</sub>O</b>	
3466 s		3521 s	3486 s	3606 m	3608 s	v(OH)
				3467 s	3472 s	v(OH)
	3297s			3299 s		Hydrogen-bonded v(OH)
	3254 s			3247 s		Hydrogen-bonded v(OH)
1628 m	1657 s	1632 m	1628 m	1656 m	1672 m	v(C=C)
1606 m	1626 s	1612 s		1625 s	1617 s	v(C=O)
1541 s	1537 s	1542 s	1531 s	1536 s	1536 s	Hydrogen-bonded v(C=O)
1675 w*		1374 w*		1354 m	1373 m	v(C-O)
1267 w*	1274 s**	1262 w*	1256 w*		1333 m	Hydrogen bonded v(C-O)
				1274 s	1274 s	$\delta(\text{COH})$
					1260 m	$\delta(\text{COH})$
				1242 m	1241 m	$\delta(\text{CCH})$
				1180 m	1167 m	$\delta(\text{COH})$
975 w	967 m	969 w	963 w	968 m	974 m	v(C-C)
852 w	851 w	850 w	836 w	890 w	873 w	v(C-Br)
834 w	811 m	832 w	821 w	804 m	801 s	v(C-Br)
803 m	754 m	798 s	792 s	754 w	769 w	C=O wagging
				688 w	713 w	$\tau(\text{CCOH})$
668 w	687 m	669 w	668 w	669 w	669 w	$\delta(\text{CC=O})$
562 s	556 m	560 m	557 m	555 m	552 s	C-Br wagging

\* Very weak bands are attributed to impurities.

\*\* Unable to assign.

## S5 Thermal stability of the compounds

Since the compounds decompose before melting, their thermal stability was checked by TG/DTA measurements. The samples were heated to 800°C (rate of 10°C min<sup>-1</sup>). Hydrate salts are stable to 50°C, and begin to decompose at higher temperature. They are fully dehydrated above 200°C. The organic part - quinoid anion - decomposes at temperatures 270 - 350°C; the colourless residue was identified as alkali oxide.

## S6 References

Farrugia, L. J. (1997). *J. Appl. Cryst.*, **30**, 565.

Biliškov, N, Kojic-Prodic, B., Mali, G., Molcanov, K. & Stare, J. (2011). *J. Phys. Chem. A.*, **115**, 3154-3166.