

Three-dimensional networks in the 1:2 organic salts 2,2'-biimidazolium bis(3-carboxy-4-hydroxybenzene-sulfonate) and 2,2'-bibenzimidazolium bis(3-carboxy-4-hydroxybenzene-sulfonate) trihydrate

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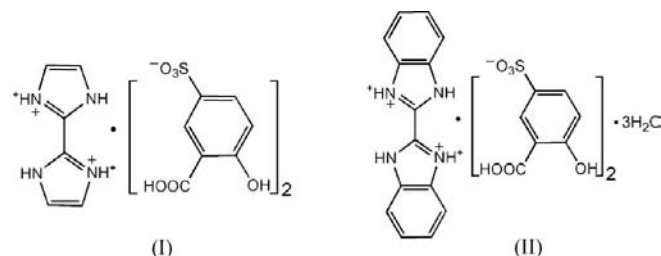
The two title compounds of 2,2'-biimidazole (Bim) with 5-sulfosalicylic acid (5-H₂SSA) and 2,2'-bibenzimidazole (Bbim) with 5-H₂SSA are 1:2 organic salts, viz. C₆H₈N₄²⁺·2C₇H₅O₆S⁻, (I), and C₁₄H₁₂N₄²⁺·2C₇H₅O₆S⁻·3H₂O, (II). The cation of compound (I) lies on a centre of inversion, whereas that of (II) lies on a twofold axis. Whilst compound (I) is anhydrous, three water molecules are incorporated into the crystal structure of (II). The substitution of imidazole H atoms by other chemical groups may favour the incorporation of water molecules into the crystal structure. In both compounds, the component cations and anions adopt a homogeneous arrangement, forming alternating cation and anion layers which run parallel to the (001) plane in (I) and to the (100) plane in (II). By a combination of N—H···O, O—H···O and C—H···O hydrogen bonds, the ions in both compounds are linked into three-dimensional networks. In addition, π–π interactions are observed between symmetry-related benzene rings of Bbim²⁺ cations in (II).

Comment

In a continuation of our studies (Meng *et al.*, 2007, 2008) of the molecular and supramolecular structures of organic salts formed by 5-sulfosalicylic acid (5-H₂SSA) and N-containing Lewis bases, viz. 2,2'-biimidazole (Bim) and 2,2'-bibenzimidazole (Bbim), we report here the title salts, H₂Bim²⁺·2(5-HSSA⁻), (I), and H₂Bbim²⁺·2(5-HSSA⁻)·3H₂O, (II).

In both (I) and (II), the H atoms are transferred from the sulfonic acid group to the imidazole N atom, forming 1:2 organic salts (Lewis base to acid). However, there are some

apparent differences between their crystallization behaviours. Firstly, compound (I) is anhydrous and crystallizes in the space group *P* $\bar{1}$. The planar Bim²⁺ cation sits about an inversion centre at (1, 0, $\frac{1}{2}$). The asymmetric unit thus consists of half a Bim²⁺ cation and a 5-HSSA⁻ anion (Fig. 1). In comparison,



compound (II) crystallizes in the monoclinic system, space group *C*2/*c*. There is a twofold screw axis lying at (0, *y*, $\frac{1}{4}$) relating the two halves of the Bbim²⁺ cation, with a dihedral angle of 36.5 (1)° between them. There are also one and a half water molecules in the asymmetric unit (Fig. 2). Secondly, the conformations of the sulfonate groups with respect to their respective benzene rings are different in the two compounds. In (I), the perpendicular distances of each O atom to the benzene plane are *ca* 0.074 (1), 1.155 (1) and 1.219 (1) Å; however, the corresponding distances in (II) are *ca* 0.439 (1), 0.841 (1) and 1.398 (1) Å.

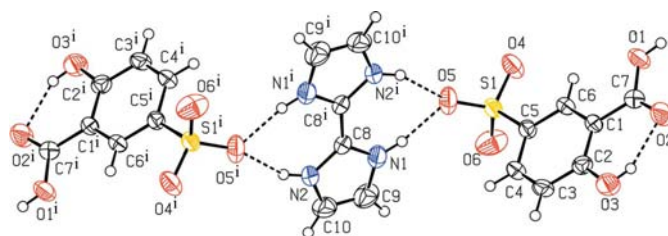


Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines. [Symmetry code: (i) $2 - x, -y, 1 - z$.]

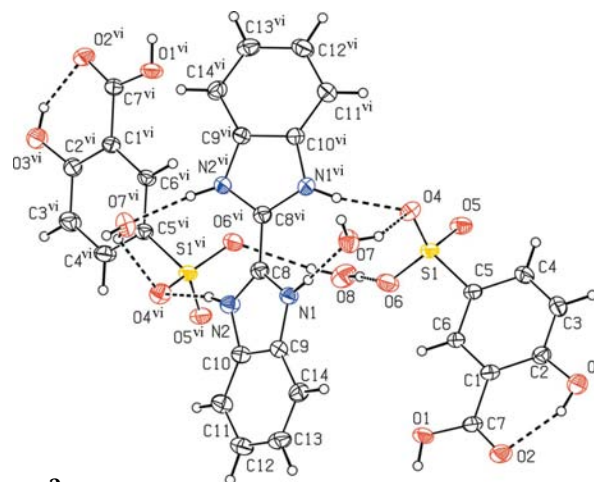


Figure 2

The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines. [Symmetry code: (vi) $-x, y, \frac{1}{2} - z$.]

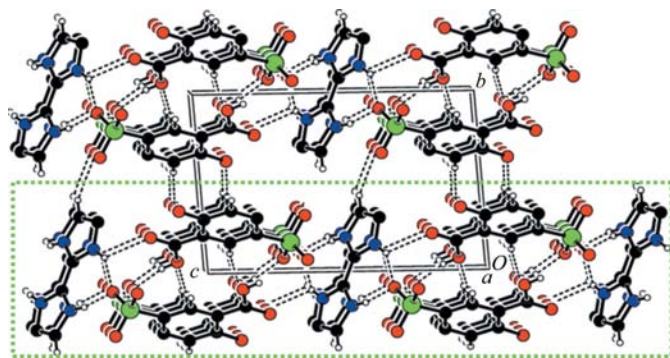


Figure 3
Part of the crystal structure of (I), showing the formation of the three-dimensional network. Hydrogen bonds are shown as dashed lines. For the sake of clarity, H atoms not involved in the motif have been omitted. The bottom outlined area shows the (010) framework.

In the packing structures of the title compounds, the ionic components are linked into three-dimensional networks by a combination of N—H \cdots O, O—H \cdots O and C—H \cdots O hydrogen bonds. In (I), the supramolecular structure can be analysed in terms of two substructures. Firstly, *via* the intermolecular hydrogen bonds N1—H1 \cdots O5, N2—H2 \cdots O5(2 - x, -y, 1 - z), N2—H2 \cdots O2(1 + x, y, -1 + z), O1—H1A \cdots O4(-x, -y, 2 - z) and C6—H6 \cdots O1(-x, -y, 2 - z), the dications and anions are linked into two-dimensional layers running parallel to the (010) plane (Fig. 3). Secondly, the (010) layers are joined together by the combinatory actions of the hydrogen bonds C3—H3 \cdots O3(2 - x, 1 - y, 2 - z) and C9—H9 \cdots O6(1 - x, 1 - y, 1 - z), forming a three-dimensional network (Fig. 3). Although no π - π interactions are observed between the imidazole and benzene rings of (I), the cations and anions each adopt an alternating homogeneous arrangement, *i.e.* the Bim $^{2+}$ cations stack only on top of Bim $^{2+}$ cations and 5-HSSA $^{-}$ anions stack only on top of 5-HSSA $^{-}$ anions.

Similar to the packing pattern in (I), the components in (II) are linked into a three-dimensional network by means of extensive hydrogen bonding (Table 1), and the Bbim $^{2+}$ dications and 5-HSSA $^{-}$ anions also form a homogeneous arrangement (Fig. 4). However, analysis using *PLATON* (Spek, 2003) indicates that strong π - π interactions exist between symmetry-related benzene rings in these layers [centroid-to-centroid separations = 3.572 (2) and 3.835 (2) Å, interplanar spacings = 3.421 (2) and 3.520 (2) Å; symmetry codes: (-x, 1 - y, 1 - z) and (-x, 2 - y, 1 - z)]. A search of the Cambridge Structural Database (CSD, Version 5.29; Allen, 2002) for organic compounds containing at least one 5-HSSA $^{-}$ anion and one imidazole cation was conducted to determine the effect of the substitution of imidazole H atoms on the incorporation of water molecules into the crystal structure. Only one 1:1 salt formed by 5-sulfosalicylic acid and imidazole was found to be anhydrous [CSD refcode HILNEW (Yang, 2007)]. The other three hits, consisting of substituted imidazole cations and 5-HSSA $^{-}$ anions, all incorporated one to three water molecules [refcodes CIKRUK (Hou, 2007),

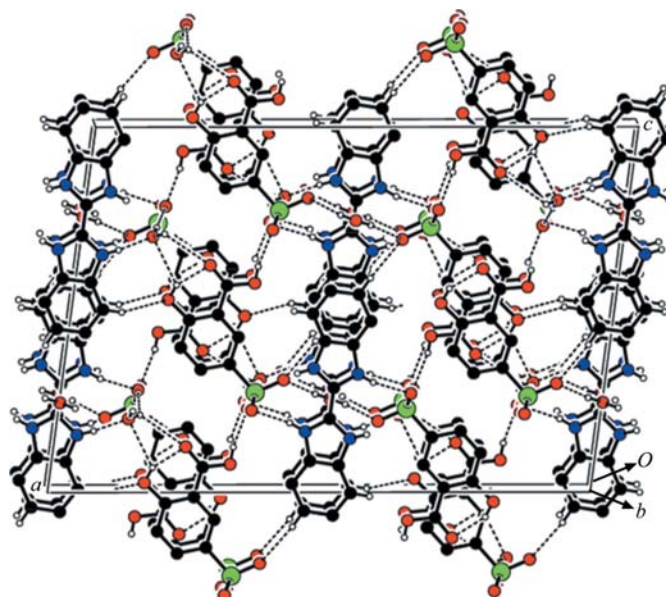


Figure 4
Part of the crystal structure of (II), showing the formation of the three-dimensional network. For the sake of clarity, H atoms not involved in the motif have been omitted.

XEYZUX (Wang & Wei, 2007) and WUYRUD (Madarasz *et al.*, 2002). Although no systematic rules can be drawn from the above, it can be speculated that the substitution of the imidazole H atoms by methyl, phenyl, *etc.*, may be in favour of water molecules being incorporated into these organic salts. We will study this potential correlation further.

In conclusion, two 1:2 organic salts formed by 5-H $_2$ SSA and imidazole derivatives are reported in this paper. In both compounds, the cations and anions adopt a homogeneous arrangement, forming alternating cation and anion layers. It was also found that substitution of imidazole H atoms by other groups may favour the cocrystallization of water molecules into the crystal structure.

Experimental

2,2'-Biimidazole and 2,2'-bibenzimidazole were synthesized according to the methods of Cromer *et al.* (1987) and Sakamoto *et al.* (2000). All other reagents and solvents were used as obtained. For (I), 1:2 molar quantities of 2,2'-biimidazole (0.2 mmol, 26.8 mg) and 5-sulfosalicylic acid dihydrate (0.4 mmol, 101.6 mg) were dissolved in 95% methanol (20 ml). The mixture was stirred for 10 min at ambient temperature and then filtered. The resulting colourless solution was kept in air for 3 d, yielding colourless plate-shaped crystals. The crystals were filtered off carefully, washed with distilled water and dried in air (yield: 40%, 46.0 mg, based on the 1:2 organic salt). In a similar manner, crystals of (II) were obtained by dissolving 1:2 molar quantities of 2,2'-bibenzimidazole (0.2 mmol, 46.8 mg) and 5-sulfosalicylic acid dihydrate (0.4 mmol, 101.6 mg) in 95% methanol (20 ml). The mixture was stirred for 30 min at room temperature and then filtered. The resulting colourless solution was kept in air for one week, yielding colourless plate-shaped crystals. The crystals were filtered off carefully, washed with distilled water and dried in air (yield: 55%, 145.0 mg, based on the 1:2 organic salt).

Compound (I)

Crystal data

$C_6H_8N_4^{2+} \cdot 2C_7H_5O_6S^-$	$\gamma = 89.573 (1)^\circ$
$M_r = 570.5$	$V = 571.13 (9) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 5.4296 (5) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 8.2995 (7) \text{ \AA}$	$\mu = 0.31 \text{ mm}^{-1}$
$c = 12.7083 (11) \text{ \AA}$	$T = 297 (2) \text{ K}$
$\alpha = 85.961 (2)^\circ$	$0.20 \times 0.16 \times 0.04 \text{ mm}$
$\beta = 88.895 (2)^\circ$	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	6501 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1997)	2451 independent reflections
$T_{\min} = 0.931$, $T_{\max} = 0.988$	1758 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.146$	$\Delta\rho_{\text{max}} = 0.41 \text{ e \AA}^{-3}$
$S = 1.10$	$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$
2451 reflections	
184 parameters	

Compound (II)

Crystal data

$C_{14}H_{12}N_4^{2+} \cdot 2C_7H_5O_6S^- \cdot 3H_2O$	$V = 3094.3 (2) \text{ \AA}^3$
$M_r = 724.66$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 25.0519 (9) \text{ \AA}$	$\mu = 0.26 \text{ mm}^{-1}$
$b = 7.3158 (3) \text{ \AA}$	$T = 295 (2) \text{ K}$
$c = 17.0309 (6) \text{ \AA}$	$0.30 \times 0.20 \times 0.04 \text{ mm}$
$\beta = 97.553 (3)^\circ$	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	14378 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1997)	3008 independent reflections
$T_{\min} = 0.918$, $T_{\max} = 0.990$	2489 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.118$	$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
$S = 1.07$	$\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$
3008 reflections	
243 parameters	

For both compounds, H atoms bonded to aromatic C atoms were positioned geometrically, with $C-H = 0.93 \text{ \AA}$, and refined in a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{aromatic C})$. H atoms bonded to N and O atoms were found in difference maps and the N-H and O-H distances were refined freely [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ and $1.5U_{\text{eq}}(\text{O})$].

For both compounds, data collection: SMART (Bruker, 2001); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick,

Table 1

Hydrogen-bond geometry of the two title compounds (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
(I)				
N1-H1 \cdots O5	0.86 (4)	1.82 (4)	2.660 (3)	167 (3)
N2-H2 \cdots O5 ⁱ	0.83 (3)	2.10 (3)	2.849 (3)	150 (3)
N2-H2 \cdots O2 ⁱⁱ	0.83 (3)	2.40 (4)	2.934 (3)	123 (3)
O1-H1A \cdots O4 ⁱⁱⁱ	0.83 (4)	1.87 (4)	2.681 (3)	166 (4)
O3-H3A \cdots O3	0.83 (4)	1.89 (4)	2.624 (3)	148 (4)
C3-H3 \cdots O3 ^{iv}	0.93	2.50	3.424 (4)	171
C6-H6 \cdots O1 ⁱⁱⁱ	0.93	2.47	3.382 (4)	168
C9-H9 \cdots O6 ^v	0.93	2.28	3.061 (4)	141
(II)				
N1-H1 \cdots O7	0.862 (19)	1.805 (19)	2.664 (2)	174 (2)
N2-H2 \cdots O4 ^{vi}	0.846 (19)	1.940 (19)	2.775 (2)	169 (2)
O1-H1A \cdots O5 ^{vii}	0.82 (2)	1.92 (2)	2.723 (2)	167 (3)
O3-H3A \cdots O2	0.83 (3)	1.87 (3)	2.632 (2)	152 (3)
O3-H3A \cdots O7 ^{viii}	0.83 (3)	2.51 (3)	3.055 (3)	124 (3)
O7-H7A \cdots O5 ^{ix}	0.82 (2)	1.99 (2)	2.805 (2)	178 (4)
O7-H7B \cdots O4	0.82 (3)	2.21 (2)	2.836 (2)	134 (3)
O7-H7B \cdots O2 ^{viii}	0.82 (3)	2.57 (3)	2.967 (2)	112 (2)
O8-H8A \cdots O6 ^{vi}	0.85 (3)	2.11 (3)	2.950 (2)	171 (3)
C12-H12 \cdots O6 ^x	0.93	2.48	3.402 (3)	169
C14-H14 \cdots O3 ^{viii}	0.93	2.58	3.454 (3)	156

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

2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: PLATON.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR3049). Services for accessing these data are described at the back of the journal.

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