

Supramolecular Assemblies in Salts of 2,2'-Biimidazole with 5-Sulfosalicylic Acid and 3,4,5-Trihydroxybenzoic Acid

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Supramolecular assemblies of 2,2'-biimidazole with 5-sulfosalicylic acid and 3,4,5-trihydroxybenzoic acid, have been synthesized and characterized by single-crystal X-ray diffraction methods. Both the two proton-transfer compounds of 2,2'-biimidazole with 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid, 5-SSA) [namely bis(2-(2-1*H*-imidazolyl)-1*H*-imidazolium) 4-hydroxybenzene-3-carboxylate-1-sulfonate monohydrate, $2(\text{C}_6\text{H}_7\text{N}_4)^+ \cdot \text{C}_7\text{H}_4\text{O}_6\text{S}^{2-} \cdot \text{H}_2\text{O}$, (**I**)] and 3,4,5-trihydroxybenzoic acid [namely 2,2'-bi-1*H*-imidazolium bis(3,4,5-trihydroxybenzoate) tetrahydrate, $\text{C}_6\text{H}_8\text{N}_4^{2+} \cdot 2(\text{C}_7\text{H}_5\text{O}_5)^- \cdot 4(\text{H}_2\text{O})$, (**II**)] feature extensively hydrogen-bonded three-dimensional network structures having significant interlayer π - π interactions between the cation and anion species. In **I**, a 5-SSA²⁻ dianionic species results from deprotonation of both the sulfonic and the carboxylic acid groups, all available O-atom acceptors interact with all cation and water molecule donors by hydrogen bonds. In **II**, the formula unit displays a crystallographic inversion symmetry. The structural information about the two complexes between 2,2'-biimidazole compound and benzenecarboxylic acids obtained in this work will be particularly important for the rational design of supramolecular organic functional materials.

Keywords 2,2'-biimidazole, 5-sulfosalicylic acid, 3,4,5-trihydroxybenzoic acid, hydrogen bonding, supramolecular

Introduction

Molecular assembly is a vital aspect of crystal engineering, an area of considerable and widespread attention.¹⁻⁷ The primary goal in this field is to control the way in which individual molecules are brought together into extended architectures in the solid state, allowing us to affect solid state reactivity, and to design new functional materials. The synthetic tools available for the construction of such assemblies are non-covalent forces, many of which are poorly understood and difficult to calculate and measure. Consequently, controlling the chemical reactivity and properties of a solid through precise control over its crystal structure is a formidable task. The good news is that many assemblies and structural patterns have been constructed through intermolecular interactions, and the use of molecules or ions as building blocks of ordered networks has become an important synthetic strategy in chemistry and materials sciences.⁸⁻¹⁰ However, crystal engineering is still in its infancy and thus it is necessary to assemble structural information, to identify recurring packing motifs and to correlate these with intermolecular interactions.¹¹ Many intermolecular connectors rely on the complementarity of various hydrogen-bonding moieties. Examples of such connectors include carboxylic acid/2-aminopyridine,¹² carboxylic acid/urea,¹³

amide/acid,¹⁴ carboxylic acid/oxime, and hydroxyl/amino.¹⁵

In this context, the neutral molecule 2,2'-biimidazole (H_2biim) appears as an interesting molecular building block for the design of new multidimensional supramolecular arrangements, owing to its capacity to act as a donor or acceptor in the formation of hydrogen bonds.¹⁶ Furthermore, H_2biim forms, with relative ease, cationic (H_3biim^+ and $\text{H}_4\text{biim}^{2+}$) and anionic (Hbiim^- and biim^{2-}) species by means of the reversible protonation or deprotonation of the molecule.¹⁷ In the field of crystal engineering,¹ it has recently been reported that monoanionic moieties can also be used to design new inorganic supramolecular architectures in the solid state, based on the double property of this anion to coordinate to metal centres and at the same time to form intermolecular hydrogen bonds.¹⁸ On the other hand, the cationic entities could also represent potential molecular building blocks for the self-assembly of new arrangements via hydrogen bonds, owing to the augmented number of donor groups of these moieties in relation to the neutral molecule. Furthermore, because of the positive charge, these molecular species are very attractive to be considered in the context of modular self-assembly.¹⁹ In this sense, a second component with a complementary functional group could be assembled

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with biimidazolium units to generate unique supramolecular arrangements. So far, to the best of our knowledge, only anionic species have been considered in the crystal engineering context, whereas very few crystal structures from cationic units are known, *i.e.* $[(\text{H}_3\text{biim}^+)(\text{I}^-)(\text{H}_2\text{biim})]^{20}$, $[(\text{H}_3\text{biim}^+)_2(\text{TCNQ}^-)(\text{TCNQ}^0)]^{20}$ where $\text{TCNQ} = 7,7,8,8\text{-tetracyanoquinodimethane}$, $[(\text{H}_4\text{biim}^{2+})(\text{picrate}^-)_2]^{20}$, $[(\text{H}_4\text{biim}^{2+})(\text{Cl}^-)_2]^{21}$ and $[(\text{H}_3\text{biim}^+)(\text{Cl}^-)(\text{PABA})]^{22}$ where $\text{PABA} = p\text{-aminobenzoic acid}$.

As part of our efforts to investigate the utilization of biimidazolium derivatives as a modular tool for the generation of solid state architectures, in this contribution we have undertaken the study of the crystal structure and hydrogen bonding motifs of bis[2-(2-1*H*-imidazolyl)-1*H*-imidazolium] 4-hydroxybenzene-3-carboxylate-1-sulfonate monohydrate (**I**), 2,2'-bi-1*H*-imidazolium bis(3,4,5-trihydroxybenzoate) tetrahydrate (**II**).

Experimental

General methods

All reagents were commercially available and used as received. 2,2'-Biimidazole was synthesized in accordance with a published procedure.²³ Elemental analysis was performed on a Perkin-Elmer 240C instrument. IR spectra were recorded on a Shimadzu FT-IR-8300 spectrometer with KBr as discs.

General procedure

Bis(2-(2-1*H*-imidazolyl)-1*H*-imidazolium) 4-hydroxybenzene-3-carboxylate-1-sulfonate monohydrate (I**):** To a solution of 0.5 mmol of 2,2'-biimidazole in 30 mL of H_2O was added a solution of 0.5 mmol of 5-sulfosalicylic acid (5-SSA). The resulting solution was refluxed for about 2 h, filtered, and the filtrate allowed to stand at room temperature. Colorless crystals of **I** appeared after one month by slow evaporation of the aqueous solution.

2,2'-Bi-1*H*-imidazolium bis(3,4,5-trihydroxybenzoate) tetrahydrate (II**):** It was prepared by a procedure similar to that for **I**, using 3,4,5-trihydroxybenzoic acid (THBA) instead of 5-SSA. After one month, yellow crystals of **II** appeared.

I: Yield 82%; *m.p.* > 300 °C; Anal. calcd for $\text{C}_{19}\text{H}_{20}\text{N}_8\text{O}_7\text{S}$: C 45.24, H 3.97, N 22.22; found C 45.26, H 3.40, N 22.32. IR (KBr) ν : 3537, 3460 (O—H), 3181, 3115 (N—H), 3042, 2953 (aromatic C—H), 1651 (C=N), 1587 (asymm. CO_2^-), 1475, 1373 (symm. CO_2^-), 1176 (SO_3^-), 1123, 1076 (C—O), 1028 (SO_3^-), 875, 830 (aromatic C—H), 675 (SO_3^-) cm^{-1} .

II: Yield 76%; *m.p.* > 300 °C; Anal. calcd for $\text{C}_{20}\text{H}_{26}\text{N}_4\text{O}_{14}$: C 43.96, H 4.76, N 10.26; found C 43.53, H 4.41, N 10.39. IR (KBr) ν : 3448, 3320 (O—H), 3101 (N—H), 3018, 2905 (aromatic C—H), 1620 (C=N), 1560 (asymm. CO_2^-), 1398 (symm. CO_2^-), 1020 (C—O), 849 (aromatic C—H) cm^{-1} .

X-ray crystallography

The raw data of compounds **I** and **II** were obtained on a Bruker SMART APEX CCD automatic diffractometer. Reflection data were collected at 293 K using $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The collected data were reduced using the program SAINT²⁴ and empirical absorption correction was carried out using an SADABS²⁵ program. The structure was solved by direct methods (SHELXS97)²⁶ and then refined on F^2 by full-matrix least-squares procedure using anisotropic displacement parameters.²⁷ H atoms involved in hydrogen-bonding interactions were initially placed in geometric positions using a riding model, and then their coordinates were freely refined. In the structure of **I**, two disordered H atoms (H1A, H3A) were refined with 50% occupancy. All other hydrogen atoms were placed in the geometrical positions using a riding model. U_{iso} was constrained to be 1.2 times (1.5 for OH) U_{eq} of the carrier atom. Atomic scattering factors are from International Tables for X-ray crystallography²⁸ and molecular graphics from SHELXTL.²⁹ The main crystallographic data are given in Table 1. The final positional parameters are listed in Table 2. Primary intermolecular hydrogen bonds are listed in Table 3.

Results and discussion

Within a unit cell of **I**, there are two H_3biim^+ ($\text{H}_3\text{biim}^+ \text{-1}$ involving N(1), N(2), N(3), N(4) and $\text{H}_3\text{biim}^+ \text{-2}$ involving N(5), N(6), N(7), N(8), one 5-SSA²⁻ and one water molecule (Figure 1 and Scheme 1). The two imidazole rings of each H_3biim^+ in **I** are conformed with a dihedral of $11.4(2)^\circ$ ($\text{H}_3\text{biim}^+ \text{-1}$) and $5.0(3)^\circ$ ($\text{H}_3\text{biim}^+ \text{-2}$), respectively. In the 5-SSA²⁻ anion species, similar structural and conformational features to those previously observed were found.³⁰⁻³² The most unusual feature is the presence of dianionic 5-SSA²⁻ species. An usual intramolecular S(6) cyclic hydrogen bond³³ was found between phenol OH group and a carboxyl O atom [O(1)—H(1B)⋯O(3) 2.512(4) Å], which is well comparable with the value [O(2)—H(2)⋯O(72) 2.558(2) Å] in 1,4-phenylenediaminium 4-hydroxybenzene-3-carboxylate-1-sulfonate,³⁴ where the carboxylic acid group is also deprotonated. Two adjacent $\text{H}_3\text{biim}^+ \text{-2}$ species connect each other by a direct side-by-side interaction yielding a centrosymmetrical [$\text{H}_3\text{biim}^+ \cdots \text{H}_3\text{biim}^+$] dimer, in which two symmetrical N—H⋯N hydrogen bonds are involved [N(6)—H(6A)⋯N(8C) = 2.806(4) Å; symmetry codes:

Scheme 1

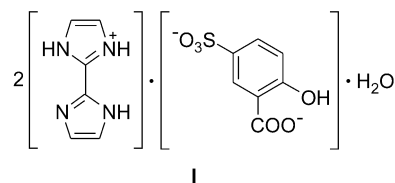


Table 1 Crystallographic data and structural refinement parameters

Complex	I	II
Empirical formula	C ₁₉ H ₂₀ N ₈ O ₇ S	C ₂₀ H ₂₆ N ₄ O ₁₄
Formula weight	504.49	546.45
Temperature/K	298(2)	298(2)
Wavelength ($\lambda/\text{\AA}$)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	<i>C2/c</i>	<i>P-1</i>
<i>a</i> / \AA	18.205(3)	8.341(2)
<i>b</i> / \AA	9.4616(16)	8.439(2)
<i>c</i> / \AA	25.496(4)	10.171(3)
$\alpha/^\circ$	90	95.022(3)
$\beta/^\circ$	92.183(2)	113.431(3)
$\gamma/^\circ$	90	111.950(3)
<i>Z</i>	8	1
$D_{\text{calc}}/(\text{g}\cdot\text{cm}^{-3})$	1.527	1.550
Volume/ \AA^3	4388.4(13)	585.4(3)
μ/mm^{-1}	0.209	0.133
<i>F</i> (000)	2096	286
Crystal size/mm	0.40 \times 0.40 \times 0.30	0.40 \times 0.30 \times 0.10
θ range for data collection/ $^\circ$	1.60—25.00	2.27—25.01
	$-21 \leq h \leq 20$	$-9 \leq h \leq 8$
Index range	$-11 \leq k \leq 10$	$-9 \leq k \leq 10$
	$-15 \leq l \leq 30$	$-7 \leq l \leq 12$
Unique data	3856	2016
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restraints/parameters	3856/0/317	2016/9/173
Goodness-of-fit on F^2	1.271	1.126
Final <i>R</i> indices [$I > 2\sigma(I)$]: R_1, wR_2	0.0793, 0.1588	0.0471, 0.1143
<i>R</i> indices (all data): R_1, wR_2	0.0891, 0.1632	0.0526, 0.1181
Largest diffraction peak and hole/($\text{e}\cdot\text{\AA}^{-3}$)	0.362 and -0.361	0.169 and -0.222

Table 2 The final atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for non-hydrogen atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Complex I									
S(1)	2119(1)	3751(1)	3328(1)	41(1)	C(3)	178(2)	3444(4)	1562(2)	37(1)
S(1)	2119(1)	3751(1)	3328(1)	41(1)	C(3)	178(2)	3444(4)	1562(2)	37(1)
O(1)	450(2)	8305(3)	4309(1)	56(1)	C(4)	424(2)	4884(4)	1611(1)	36(1)
O(2)	1074(2)	4878(3)	5226(1)	49(1)	C(5)	946(2)	6907(4)	1445(2)	48(1)
O(3)	465(2)	6895(3)	5144(1)	60(1)	C(6)	739(2)	6908(4)	1942(2)	49(1)
O(4)	2097(2)	2521(3)	3666(1)	59(1)	C(7)	2168(2)	3692(4)	1604(2)	43(1)
O(5)	2853(2)	4316(3)	3303(1)	54(1)	C(8)	2004(2)	2595(4)	1295(1)	40(1)
O(6)	1776(2)	3498(3)	2818(1)	63(1)	C(9)	2572(2)	4149(4)	822(1)	34(1)
O(1W)	1598(2)	364(4)	2653(2)	107(2)	C(10)	2920(2)	4839(4)	390(1)	38(1)
N(1)	$-1(2)$	2645(4)	1960(1)	54(1)	C(11)	3501(3)	6442(5)	$-45(2)$	64(1)
N(2)	126(2)	2689(3)	1120(1)	43(1)	C(12)	3387(3)	5286(5)	$-341(2)$	59(1)
N(3)	417(2)	5641(3)	2046(1)	44(1)	C(13)	1595(2)	5068(4)	3638(1)	35(1)
N(4)	744(2)	5634(3)	1235(1)	40(1)	C(14)	1423(2)	4968(4)	4157(1)	35(1)
N(5)	2518(2)	4658(3)	1305(1)	39(1)	C(15)	1035(2)	6029(4)	4398(1)	35(1)

Continued

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
N(6)	2260(2)	2888(3)	810(1)	36(1)	C(16)	825(2)	7234(4)	4104(2)	38(1)
N(7)	3196(2)	6148(3)	421(1)	51(1)	C(17)	1022(2)	7337(4)	3582(2)	43(1)
N(8)	3020(2)	4271(3)	-75(1)	46(1)	C(18)	1397(2)	6266(4)	3351(2)	40(1)
C(1)	-171(3)	1345(5)	1762(2)	67(1)	C(19)	849(2)	5900(4)	4962(2)	40(1)
C(2)	-96(3)	1363(5)	1245(2)	56(1)					
Complex II									
C(1)	1218(3)	464(3)	7644(2)	33(1)	N(1)	6729(3)	4300(2)	9741(2)	37(1)
C(2)	737(3)	1743(3)	7065(2)	31(1)	N(2)	5710(3)	6073(2)	8684(2)	37(1)
C(3)	1517(3)	2543(3)	6181(2)	32(1)	O(1)	2308(3)	-2086(2)	8795(2)	50(1)
C(4)	2800(3)	2076(3)	5897(2)	31(1)	O(2)	4119(2)	-1835(2)	7650(2)	40(1)
C(5)	3289(3)	809(3)	6485(2)	33(1)	O(3)	3483(2)	2933(2)	5014(2)	43(1)
C(6)	2498(3)	-5(3)	7360(2)	31(1)	O(4)	990(2)	3781(2)	5636(2)	45(1)
C(7)	2990(3)	-1396(3)	7975(2)	34(1)	O(5)	-492(2)	2282(2)	7320(2)	45(1)
C(8)	6951(3)	5905(3)	8191(3)	41(1)	O(1W)	6942(2)	3336(2)	5282(2)	45(1)
C(9)	7582(3)	4796(3)	8848(2)	41(1)	O(2W)	8009(3)	570(2)	8866(2)	58(1)
C(10)	5581(3)	5086(3)	9621(2)	31(1)					

Table 3 Primary hydrogen bonds in complexes I and II

D—H···A	<i>d</i> (D—H)/Å	<i>d</i> (H···A)/Å	∠DHA/(°)	<i>d</i> (D···A)/Å
Complex I				
N(7)—H(7A)···O(4)	0.86	1.91	161.3	2.734(4)
N(6)—H(6A)···N(8)	0.86	1.97	162.5	2.806(4)
N(5)—H(5A)···O(4)	0.86	2.00	154.5	2.798(4)
N(4)—H(4A)···O(2)	0.86	1.86	167.6	2.710(4)
N(3)—H(3A)···N(3)	0.86	2.02	152.8	2.815(6)
N(2)—H(2A)···O(3)	0.86	1.78	164.0	2.617(4)
N(1)—H(1A)···N(1)	0.86	1.94	156.9	2.755(7)
O(1W)—H(1WB)···O(6)	0.82	2.49	122.4	3.011(5)
O(1W)—H(1WA)···O(5)	0.83	2.05	163.8	2.847(4)
O(1)—H(1B)···O(3)	0.82	1.79	146.8	2.512(4)
C(1)—H(1)···O(1W)	0.93	2.58	123.0	3.184(6)
C(5)—H(5)···O(5)	0.93	2.57	126.0	3.206(5)
C(8)—H(8)···O(5)	0.93	2.55	135.0	3.275(5)
C(2)—H(2)···O(1)	0.93	2.38	161.0	3.273(6)
C(7)—H(7)···O(6)	0.93	2.29	168.0	3.209(5)
C(11)—H(11)···O(2)	0.93	2.50	157.0	3.377(6)
Complex II				
O(2W)—H(2WA)···O(2)	0.89	1.89	165.5	2.761(2)
O(2W)—H(2WB)···O(1)	0.86	1.97	150.9	2.754(2)
O(1W)—H(1WB)···O(5)	0.88	1.94	170.4	2.808(2)
O(1W)—H(1WA)···O(2)	0.90	1.87	172.4	2.772(2)
N(2)—H(2A)···O(2)	0.86	1.79	167.2	2.637(2)
N(1)—H(1A)···O(1)	0.86	1.81	164.0	2.648(2)
O(5)—H(5B)···O(2W)	0.82	1.78	173.3	2.595(2)
O(4)—H(4B)···O(1W)	0.82	2.15	148.7	2.882(2)
O(3)—H(3B)···O(1W)	0.82	1.87	165.8	2.672(2)
C(8)—H(8)···O(3)	0.93	2.55	153.0	3.406(2)

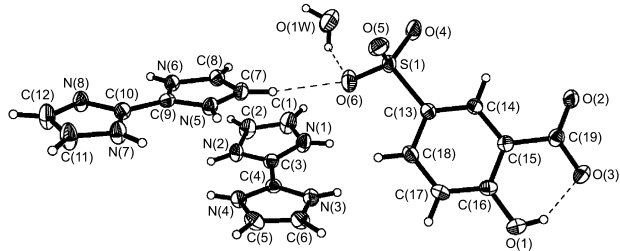


Figure 1 The atom-numbering scheme for the two H_3biim^+ cations, the 5-SSA^{2-} anion and the water molecule in **I**. Non-H atoms are shown as 30% probability displacement ellipsoids and hydrogen bonds are shown as dashed lines.

C: $-x + 1/2, -y + 1/2, -z$]. While two adjacent $\text{H}_3\text{biim}^+ - 1$ species connect each other yielding an unsymmetrical [$\text{H}_3\text{biim}^+ \cdots \text{H}_3\text{biim}^+$] dimer, in which two $\text{N}-\text{H} \cdots \text{N}$ hydrogen bonds are involved [$\text{N}(1)-\text{H}(1\text{A}) \cdots \text{N}(1\text{A})$ 2.755(7) Å, $\text{N}(3)-\text{H}(3\text{A}) \cdots \text{N}(3\text{A})$ 2.815(6) Å, symmetry codes: A: $-x, y, -z + 1/2$], which may be the result of the more contorted H_3biim^+ in $\text{H}_3\text{biim}^+ - 1$ than in $\text{H}_3\text{biim}^+ - 2$. This intermolecular interaction between two biimidazolic species can be designated as an $R_2^2(10)$ hydrogen bonds. In contrast, these contacts are shorter than those in the self-complementary $R_2^2(10)$ hydrogen bond [2.87(1) Å] found in the neutral H_2biim molecule,³⁵ maybe as a consequence of the charge located in both cations. In addition, the $\text{H}_3\text{biim}^+ - 1$ cation and 5-SSA^{2-} anion species connect each other through cyclic $R_2^2(9)$ interactions [$\text{N}(2)-\text{H}(2\text{A}) \cdots \text{O}(3\text{D})$ 2.617(4) Å, $\text{N}(4)-\text{H}(4\text{A}) \cdots \text{O}(2\text{D})$ 2.710(4) Å; symmetry codes: D: $x, -y + 1, z - 1/2$] due to deprotonation of the acid by the H_2biim . Similarly, the $\text{H}_3\text{biim}^+ - 2$ cation and 5-SSA^{2-} anion species connect each other through cyclic $R_2^1(7)$ interactions [$\text{N}(5)-\text{H}(5\text{A}) \cdots \text{O}(4\text{E})$ 2.798(4) Å, $\text{N}(7)-\text{H}(7\text{A}) \cdots \text{O}(4\text{E})$ 2.734(4) Å; symmetry codes: E: $-x + 1/2, y + 1/2, -z + 1/2$] (Figure 2).

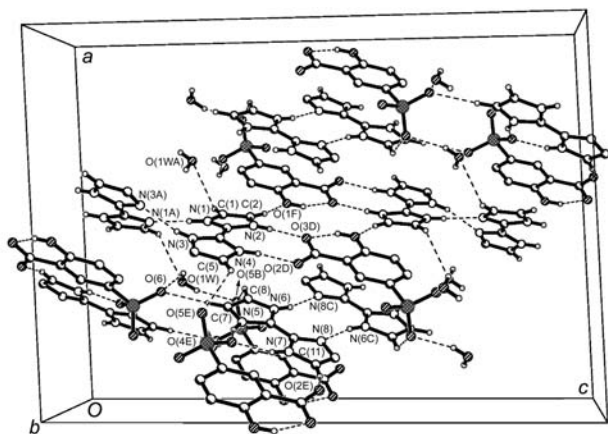


Figure 2 Structure extension through hydrogen-bonding interactions in **I**. Hydrogen bonds are shown as dashed lines [symmetry code: (A) $-x, y, -z + 1/2$. (B) $-x + 1/2, y - 1/2, -z + 1/2$. (C) $-x + 1/2, -y + 1/2, -z$. (D) $x, -y + 1, z - 1/2$. (E) $-x + 1/2, y + 1/2, -z + 1/2$. (F) $-x, y - 1, -z + 1/2$].

There are some $\text{O}-\text{H} \cdots \text{O}$ hydrogen-bond interactions [$\text{O}(1\text{W})-\text{H}(1\text{WB}) \cdots \text{O}(6)$ 3.011(5) Å, $\text{O}(1\text{W})-\text{H}(1\text{WA}) \cdots \text{O}(5\text{B})$ 2.847(4) Å; symmetry codes: B: $-x + 1/2, y - 1/2, -z + 1/2$] between the water molecules and O atoms of 5-SSA sulfonate groups, weak $\text{C}-\text{H} \cdots \text{O}$ hydrogen-bond interactions [$\text{C}(7)-\text{H}(7) \cdots \text{O}(6)$ 3.209(5) Å, $\text{C}(1)-\text{H}(1) \cdots \text{O}(1\text{WA})$ 3.184(6) Å, $\text{C}(8)-\text{H}(8) \cdots \text{O}(5\text{B})$ 3.275(5) Å, $\text{C}(5)-\text{H}(5) \cdots \text{O}(5\text{E})$ 3.206(5) Å, $\text{C}(11)-\text{H}(11) \cdots \text{O}(2\text{E})$ 3.377(6) Å, $\text{C}(2)-\text{H}(2) \cdots \text{O}(1\text{F})$ 3.273(6) Å; symmetry codes: A: $-x, y, -z + 1/2$; B: $-x + 1/2, y - 1/2, -z + 1/2$; E: $-x + 1/2, y + 1/2, -z + 1/2$; F: $-x, y - 1, -z + 1/2$] and cation-anion $\pi-\pi$ ring-stacking interactions [the inter-ring centroid distances are the benzene ring [$\text{C}(13)-\text{C}(14)-\text{C}(15)-\text{C}(16)-\text{C}(17)-\text{C}(18)$]-imidazole ring [$\text{N}(3\text{G})-\text{C}(4\text{G})-\text{N}(4\text{G})-\text{C}(5\text{G})-\text{C}(6\text{G})$]; symmetry codes: G: $-x, -y, -z$] 3.62(1) Å and benzene ring [$\text{C}(13)-\text{C}(14)-\text{C}(15)-\text{C}(16)-\text{C}(17)-\text{C}(18)$]-imidazole ring [$\text{N}(5\text{H})-\text{C}(7\text{H})-\text{C}(8\text{H})-\text{N}(6\text{H})-\text{C}(9\text{H})$]; symmetry codes: H: $x, -y, z - 1/2$] 3.56(1) Å and interplanar dihedral angle 3.93(1)° and 1.77(1)°, respectively]. The overall result is an infinite three-dimensional network structure (Figure 2).

The infrared spectrum of **I** confirms a deprotonation has occurred, with strong asymmetric and symmetric carboxylate absorptions at 1587 and 1373 cm^{-1} , respectively, which is similar to those previously reported.³⁶

Within a unit cell of **II**, there is one symmetry independent THBA^- , half an $\text{H}_4\text{biim}^{2+}$, and two water molecules (Figure 3 and Scheme 2). The two imidazole rings are coplanar in $\text{H}_4\text{biim}^{2+}$, which is different from those in **I**. The $\text{H}_4\text{biim}^{2+}$ is centrosymmetric. The formula unit displays a crystallographic inversion symmetry. The inversion center lies at the center of the bond $\text{C}(10)-\text{C}(10\text{A})$ (A: $-x + 1, -y + 1, -z + 2$). A fundamental unit of crystal structure consists of a hydrogen-bonded trimer: $\text{THBA}^- \cdots \text{H}_4\text{biim}^{2+} \cdots \text{THBA}^-$, through $R_2^2(9)$ cyclic hydrogen bonds [$\text{N}(2)-\text{H}(2\text{A}) \cdots \text{O}(2\text{C})$ 2.637(2) Å, $\text{N}(1)-\text{H}(1\text{A}) \cdots \text{O}(1\text{G})$ 2.648(2) Å; symmetry codes: C: $x, y + 1, z$; G: $-x + 1, -y, -z + 2$] due to deprotonation of the acid by the H_2biim , with $\text{N}-\text{H} \cdots \text{O}$ hydrogen bond interactions in place of $\text{O}-\text{H} \cdots \text{N}$ interactions.²² The synthon $R_2^2(9)$ is similar to that previously reported.³⁷ The trimer unit was bonded forming three dimensional networks by $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds [$\text{O}(2\text{W})-\text{H}(2\text{WA}) \cdots \text{O}(2)$ 2.761(2) Å, $\text{O}(2\text{W})-\text{H}(2\text{WB}) \cdots \text{O}(1\text{G})$ 2.754(2) Å, $\text{O}(1\text{W})-\text{H}(1\text{WB}) \cdots \text{O}(5\text{D})$ 2.808(2) Å, $\text{O}(1\text{W})-\text{H}(1\text{WA}) \cdots \text{O}(2\text{F})$ 2.772(2) Å, $\text{O}(5)-\text{H}(5\text{B}) \cdots \text{O}(2\text{WE})$ 2.595(2) Å, $\text{O}(4)-\text{H}(4\text{B}) \cdots \text{O}(1\text{WB})$ 2.882(2) Å, $\text{O}(3)-\text{H}(3\text{B}) \cdots \text{O}(1\text{W})$ 2.672(2) Å; symmetry codes: B: $-x + 1, -y + 1, -z + 1$, D: $x + 1, y, z$, E: $x - 1, y, z$, F: $-x + 1, -y, -z + 1$] interactions between the water molecules and O atoms of THBA^- and weak $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds [$\text{C}(8)-\text{H}(8) \cdots \text{O}(3\text{B})$ (symmetry codes: B: $-x + 1, -y + 1, -z + 1$) 3.406(2) Å] (Figure 4 and Table 3). Two other different $\pi-\pi$ interactions [the inter-ring centroid distances are the imidazole ring [$\text{N}(1)-\text{C}(9)-\text{C}(8)-\text{N}(2)-\text{C}(10)$]-benzene ring [$\text{C}(1)-\text{C}(2)-\text{C}(3)-\text{C}(4)-\text{C}(5)-\text{C}(6)$] 3.60(1) Å and benzene ring

[C(1)-C(2)-C(3)-C(4)-C(5)-C(6)]-benzene ring [C(1H)-C(2H)-C(3H)-C(4H)-C(5H)-C(6H)]; symmetry codes: H: $-x, -y, -z+1$] 3.54(1) Å and interplanar dihedral angles are 5.6(5)° and 0°, respectively] help to sustain the stacking arrangement (Figure 4).

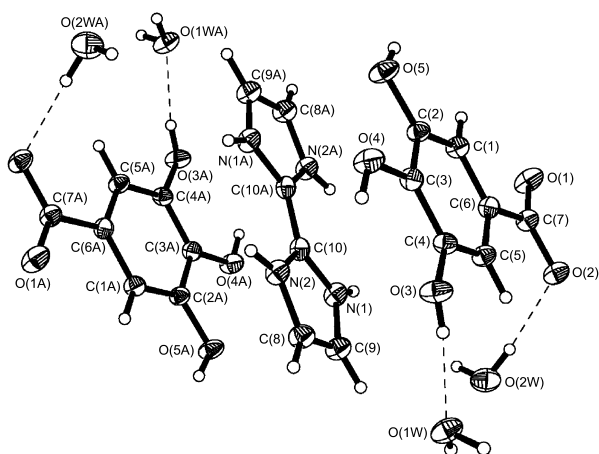


Figure 3 The atom-numbering scheme for the H_4biim^{2+} cation, the two $THBA^-$ anions and four water molecules in **II**. Non-H atoms are shown as 30% probability displacement ellipsoids and hydrogen bonds are shown as dashed lines [symmetry code: (A) $-x+1, -y+1, -z+2$].

Scheme 2

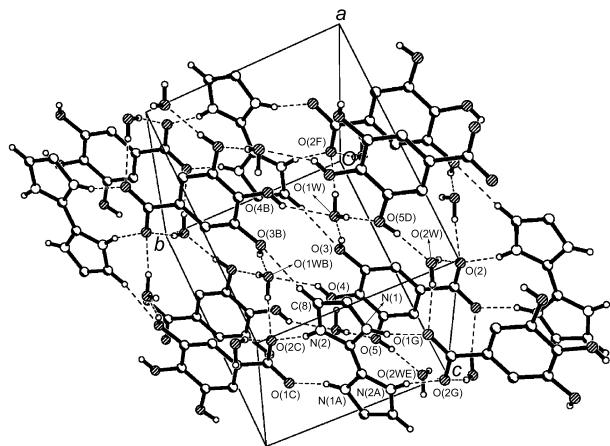
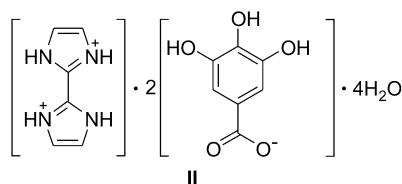


Figure 4 Structure extension through hydrogen-bonding interactions in **II**. Hydrogen bonds are shown as dashed lines [symmetry code: (A) $-x+1, -y+1, -z+2$. (B) $-x+1, -y+1, -z+1$. (C) $x, y+1, z$. (D) $x+1, y, z$. (E) $x-1, y, z$. (F) $-x+1, y, -z+1$. (G) $-x+1, -y, -z+2$].

The infrared spectrum of **II** confirms also a depro-

tonation has occurred, with strong asymmetric and symmetric carboxylate absorptions at 1560 and 1398 cm^{-1} , respectively, which is similar to **I** and those previously reported.³⁶

In conclusion, it was found that 2,2'-biimidazole could spontaneously form supramolecular assemblies with benzoic acids, such as 5-sulfosalicylic acid and 3,4,5-trihydroxybenzoic acid by proton-transfer. Besides the hydrogen bonding interactions between the host and guest molecules, π - π stacking interactions also play an important role in the solid-state packing of these two complexes. The structural information about the complexes between 2,2'-biimidazole compound and benzoic acids obtained in this work will be particularly important for the rational design of supramolecular organic functional materials.

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