

Probing the supramolecular interaction synthons of 1-benzofuran-2,3-dicarboxylic acid in its monoanionic form

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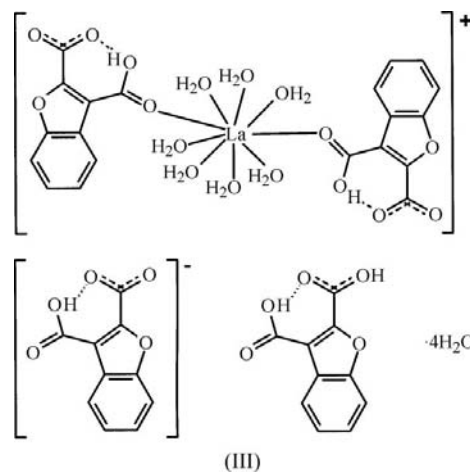
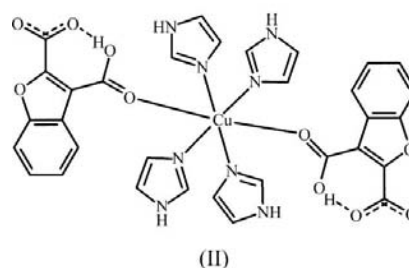
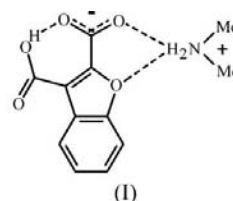
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1-Benzofuran-2,3-dicarboxylic acid ($C_{10}H_6O_5$) is a dicarboxylic acid ligand which can readily engage in organometallic complexes with various metal ions. This ligand is characterized by an intramolecular hydrogen bond between the two carboxyl residues, and, as a monoanionic species, readily forms supramolecular adducts with different organic and inorganic cations. These are a 1:1 adduct with the dimethylammonium cation, namely dimethylammonium 3-carboxy-1-benzofuran-2-carboxylate, $C_2H_8N^+ \cdot C_{10}H_5O_5^-$, (I), a 2:1 complex with Cu^{2+} ions in which four neutral imidazole molecules also coordinate the metal atom, namely bis(3-carboxy-1-benzofuran-2-carboxylato- κO^3)tetrakis(1*H*-imidazole- κN^3)-copper(II), $[Cu(C_{10}H_5O_5)_2(C_3H_4N_2)_4]$, (II), and a 4:1 adduct with $[La(H_2O)_7]^{3+}$ ions, namely heptaaquabis(3-carboxy-1-benzofuran-2-carboxylato- κO^3)lanthanum 3-carboxy-1-benzofuran-2-carboxylate 1-benzofuran-2,3-dicarboxylic acid solvate tetrahydrate, $[La(C_{10}H_5O_5)_2(H_2O)_7](C_{10}H_5O_5) \cdot C_{10}H_6O_5 \cdot 4H_2O$, (III). In the crystal structure, complex (II) resides on inversion centres, while complex (III) resides on axes of twofold rotation. The crystal packing in all three structures reveals π - π stacking interactions between the planar aromatic benzofuran residues, as well as hydrogen bonding between the components. The significance of this study lies in the first crystallographic characterization of the title framework, which consistently exhibits the presence of an intramolecular hydrogen bond and a consequent monoanionic-only nature. It shows further that the anion can coordinate readily to metal cations as a ligand, as well as acting as a monovalent counterion. Finally, the aromaticity of the flat benzofuran residue provides an additional supramolecular synthon that directs and facilitates the crystal packing of compounds (I)–(III).

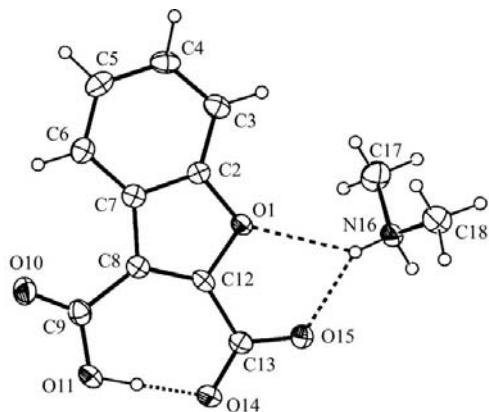
Comment

Organic polycarboxylic acids can be considered as attractive building blocks for the construction of supramolecular archi-

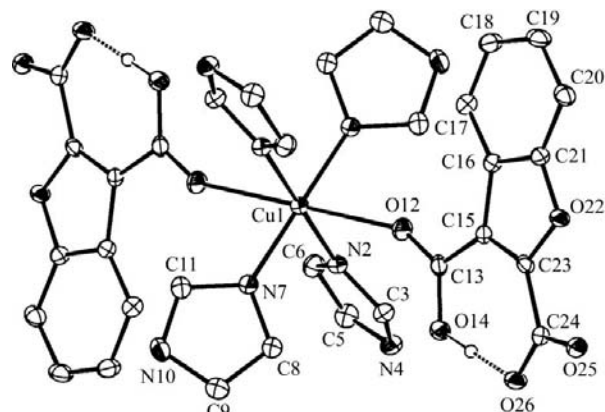
tectures, because of their ability to link to metal centres in a variety of coordination modes simultaneously and generate extended networks. Moreover, such ligands can be readily deprotonated to balance the charge of the metal ions they interact with (and thus enjoy electrostatic attraction to the metal centres), without the need to incorporate foreign ions into the product. Several examples of materials with bifunctional anions, such as benzene-1,4-dicarboxylate (Guilera & Steed, 1999), trifunctional anions, such as benzene-1,3,5-tricarboxylate (Liu *et al.*, 2007) or cyclohexane-1,3,5-tricarboxylate (Fang *et al.*, 2006), tetrafunctional anions, such as benzene-1,2,4,5-tetracarboxylate (Ghosh & Bharadwaj, 2004) or naphthalene-1,4,5,8-tetracarboxylate (Koner & Goldberg, 2009), and hexafunctional anions, such as benzenehexacarboxylate (Yang *et al.*, 2004), have been studied extensively in recent years. The tetra(carboxyphenyl)porphyrin ligand provides a particularly fascinating example of a tetracarboxylic acid prone to forming rigid open-framework solids



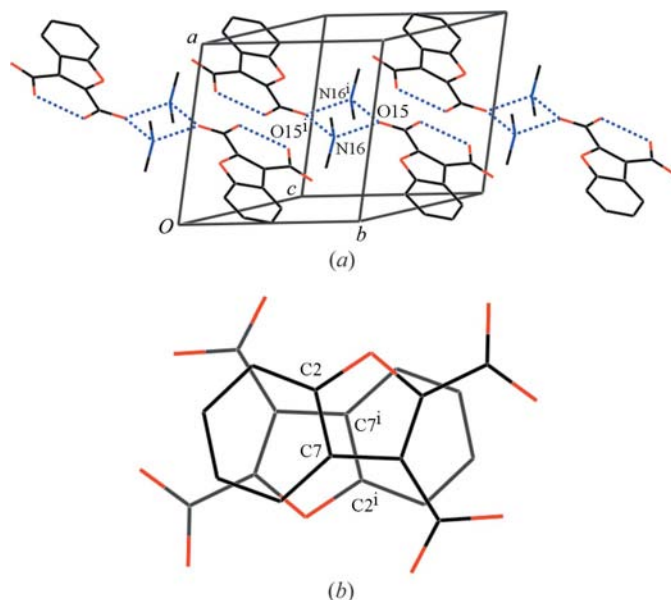
via coordination polymerization through metal ions (Goldberg, 2005). In the above context, we focus in this study on the 1-benzofuran-2,3-dicarboxylic acid (BFDC) building block, aiming to explore for the first time (structures of neither the carboxylic acid form nor the carboxylate form of this


Figure 1

The molecular structure of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level at *ca* 110 K, and H atoms are shown as small spheres of arbitrary radii. Intra- and intermolecular hydrogen bonds are indicated by dashed lines.


Figure 3

The molecular structure of compound (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level at *ca* 110 K. H atoms have been omitted, except for those involved in intramolecular hydrogen bonding (dashed lines). The octahedral complex is located on a centre of inversion at (0, 0, 0), and only atoms of the asymmetric unit are labelled.


Figure 2

The crystal packing in (I). H atoms have been omitted for clarity. (a) A view of the crystal structure and the centrosymmetric hydrogen bonding of two anions and two cations around an inversion centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The secondary N16—H16A...O1 hydrogen bond has been omitted. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.] (b) The parallel overlap of the anions related by inversion at $(0, 1, \frac{1}{2})$. [Symmetry code: (i) $-x, 2 - y, 1 - z$.]

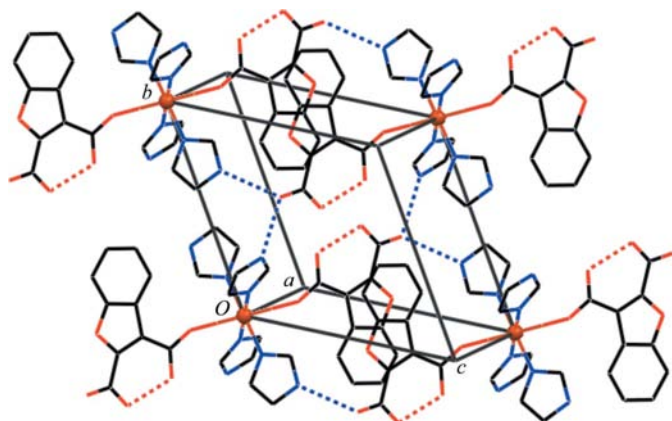
compound have been reported previously) its structural features and possible synthons of supramolecular interaction with other components.

Compounds (I)–(III) were obtained in the mildly basic reaction environments used to promote the formation of metal–carboxylate coordination bonds. Although we failed to formulate coordination polymers at this stage, the present characterization of the crystalline products provided useful information. Thus, when the title dicarboxylic acid was reacted with a lanthanum nitrate salt (see *Experimental*) in the presence of *N,N*-dimethylformamide (DMF) under hydro-

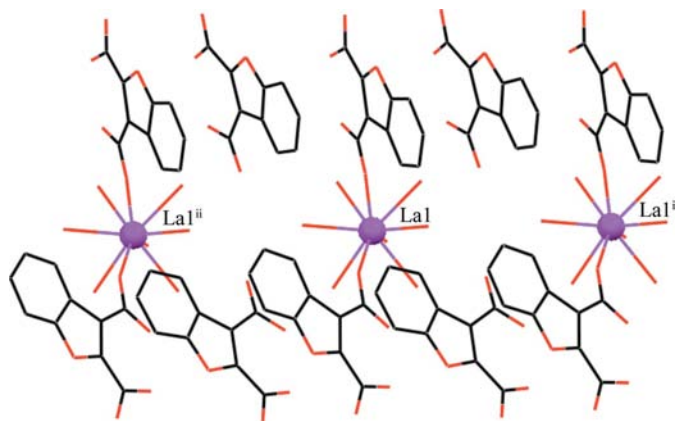
thermal conditions, no metal ions were incorporated into the structure. Instead, the 1:1 salt, (I), formed between the mono-deprotonated benzofuran component (BFDC[−]) and a dimethylammonium cation (a product resulting from hydrolysis of DMF). The observed molecular structure of BFDC[−] in (I) throws light on the preferred form of this species in the other crystal structures as well, and deserves particular attention. Fig. 1 reveals that the spatial proximity of the two *ortho*-substituted carboxylic acid functions is favourable to the formation of an intramolecular O11—H11...O14 hydrogen bond (Table 1). Moreover, deprotonation occurs favourably on the carboxylic acid group (C13/O14/O15) which is closer to the electron-withdrawing etheral site. These features explain the preferred behaviour of this ligand. Although it bears two carboxylic acid functions, it tends to act as a monoprotic acid, the H atoms of the second acid group being engaged in an effective intramolecular hydrogen bond. In addition, hydrogen bonding also occurs between the ammonium cation and BFDC[−] (Table 1).

The crystal structure of (I) is shown in Fig. 2(a). It reveals that centrosymmetric hydrogen-bonded dimers are formed with an $R_4^2(8)$ ring motif (Bernstein *et al.*, 1995) involving two cations and two anions. The rigid benzofuran group (O1/C2—C8/C12) is essentially planar with delocalized π -electron density. Not surprisingly, therefore, its intermolecular organization in the crystal structure involves π – π interactions between partially overlapping anions located at (x, y, z) and $(-x, 2 - y, 1 - z)$ (Fig. 2b). The mean interplanar distance between the inversion-related O1/C2—C8/C12 fragments of these two species is 3.388 (7) Å, while the distance between the centres of the corresponding C2—C7 bonds is 3.492 (3) Å. Only minimal overlap occurs, however, between subsequent (along the *a* axis) parallel aromatic species related by inversion at $(\frac{1}{2}, 1, \frac{1}{2})$.

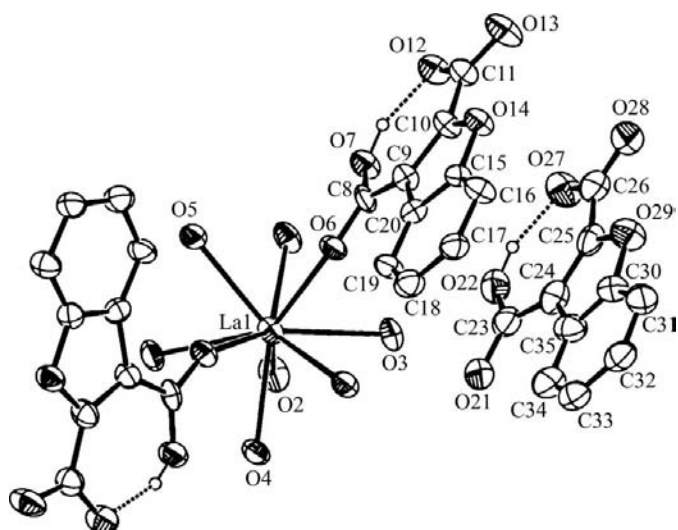
Reaction of the dicarboxylic acid ligand with Cu^{II} ions, in the presence of imidazole, yielded compound (II), which represents an octahedral complex (Fig. 3) with four imidazole

**Figure 4**

The crystal packing in (II). The Cu^{II} ions of the octahedral coordination complexes are denoted by small spheres. Note the pairing (via partial π - π overlap) of the benzofuran units around inversion centres at $(\frac{1}{2}, 0, \frac{1}{2})$, as well as the intermolecular hydrogen bonding (intra- and intermolecular hydrogen bonds are denoted by dashed lines) in the $(10\bar{1})$ plane of the crystal. H atoms have been omitted for clarity.

**Figure 6**

Molecules displaced along the b axis in (III), illustrating the dominant π - π stacking arrangement of the benzofuran fragments in the crystal structure. H atoms have been omitted for clarity. [Symmetry codes: (i) $x, y + 1, z$; (ii) $x, y - 1, z$.]

**Figure 5**

The molecular structure of compound (III), showing the atom-labelling scheme. The lanthanide ion La1 and coordinated water atom O2 reside on an axis of twofold rotation at $(\frac{1}{4}, \frac{1}{4}, z)$, and only atoms of the asymmetric unit are labelled. Displacement ellipsoids are drawn at the 50% probability level at *ca* 110 K. H atoms have been omitted, except for those involved in the intramolecular hydrogen bond (dashed lines). The disordered noncoordinated water solvent has also been omitted.

ligands occupying the equatorial positions and two BFDC^- anions coordinating to the axial positions. It resides on centres of inversion. The reaction of BFDC with the Cu^{II} ions has not affected the features observed in (I), namely the presence of an intramolecular hydrogen bond associated with mono-deprotonation only. Correspondingly, the two BFDC^- ligating species balance the 2+ charge of the central metal ion. As commonly observed in the literature, the octahedral geometry of (II) is axially distorted due to the Jahn-Teller effect. The equatorial $\text{Cu1}-\text{N2}$ and $\text{Cu1}-\text{N7}$ bond lengths are 2.009 (2) and 2.015 (2) Å, respectively, while the axial $\text{Cu1}-\text{O12}$ bond

lengths are 2.451 (2) Å. The stacking interactions between the aromatic benzofuran fragments are also evident in the crystal structure of (II) (Fig. 4). Adjacent inversion-related [at $(\frac{1}{2}, 0, \frac{1}{2})$] $\text{C15}-\text{C21}/\text{O22}/\text{C23}$ benzofuran fragments overlap one another at a mean interplanar distance of 3.424 (13) Å. Neighbouring units of the octahedral complex are also linked via hydrogen bonds between the NH sites of the imidazoles of one unit and the carboxylic acid fragment of adjacent anions (Table 2). The $\text{N}-\text{H}\cdots\text{O}$ bonds develop sheets of hydrogen-bonded molecules in the $(10\bar{1})$ plane (Fig. 4).

These molecular characteristics of $\text{BFDC}/\text{BFDC}^-$ are also preserved in the reaction of BFDC with trivalent metal ions such as La^{3+} . The molecular structure of the resulting $[\text{La}(\text{BFDC}^-)_2(\text{H}_2\text{O})_7](\text{BFDC}^-)(\text{BFDC})\cdot 4\text{H}_2\text{O}$ adduct, (III), is shown in Fig. 5. In spite of the high coordination number of this metal (*i.e.* 9), only two monoanionic ligand species coordinate to it, possibly due to steric constraints. The coordination environment is completed by seven molecules of water. Units of the complex are positioned on twofold rotation axes $(\frac{1}{4}, \frac{1}{4}, z)$. The coordination distances are $\text{La1}-\text{O6}(\text{BFDC}^-) = 2.508$ (4) Å and $\text{La1}-\text{O}(\text{water}) = 2.567$ (4)–2.599 (4) Å. Additional noncoordinated BFDC and BFDC^- (to balance the charge of the trivalent cation) moieties are incorporated into the structure between the aromatic fragments of adjacent entities of the lanthanum complex aligned along the b axis. Correspondingly, the noncoordinated ligand in the asymmetric unit represents 50% a neutral species and 50% a monoanion. Fig. 6 nicely illustrates the parallel alignment of the ligands along the b axis of the crystal structure. Partial but significant overlap occurs between the $\text{C9}/\text{C10}/\text{O14}/\text{C15}-\text{C25}$ and $\text{C24}/\text{C25}/\text{O29}/\text{C30}-\text{C35}$ benzofuran fragments of the asymmetric unit, with a mean interplanar distance between them of 3.387 (9) Å. Minimal parallel overlap exists between the $\text{C24}/\text{C25}/\text{O29}/\text{C30}-\text{C35}$ framework at (x, y, z) and the adjacent $\text{C9}/\text{C10}/\text{O14}/\text{C15}-\text{C25}$ residue at $(x, y - 1, z)$, the corresponding mean perpendicular distance between these planes being 3.124 (17) Å. Additional noncoordinated solvent (most probably water) was found incorporated within the

intermolecular voids, but it could not be reliably identified. The water ligands coordinated to La are involved in numerous hydrogen-bonding interactions with neighbouring entities, yielding an extended supramolecular pattern of three-dimensional connectivity (Table 3).

In summary, this study characterizes the molecular structure of the benzofurandicarboxylic acid ligand, elucidating its high propensity to react as a monoanion, while maintaining an intramolecular hydrogen bond between the two carboxylic acid substituents. Consistent occurrence of the latter makes a second deprotonation of BFDC⁻ less probable. The aromatic nature of BFDC⁻ is widely reflected in the intermolecular π - π stacking interactions observed in the three crystal structures presented here, with a nearly constant spacing of 3.37–3.42 Å between the overlapping benzofurans. Application of the BFDC ligand, as a bidentate or polydentate bridging ligand, in the synthesis of extended coordination polymers may require more extreme experimental conditions.

Experimental

The dicarboxylic acid BFDC, as well as all the other reactants and solvents used, were obtained commercially. Compound (I) was obtained by heating a mixture of La(NO₃)₃·6H₂O (0.130 g, 0.3 mmol), BFDC (0.124 g, 0.6 mmol) and dimethylformamide (DMF; 3 ml) in a sealed 5 ml reactor at 433 K for 48 h, followed by gradual cooling to ambient temperature. Colourless needles of (I) were collected by filtration and air-dried; there was no incorporation of lanthanum ions. Needle-shaped crystals of (III) were obtained by a similar procedure, omitting the DMF component from the reaction mixture. Blue crystals of (II) were obtained by adding a solution of Cu(NO₃)₂·2.5H₂O (0.058 g, 0.25 mmol) in H₂O (4 ml) to a suspension of BFDC (0.052 g, 0.25 mmol) in H₂O (7 ml), followed by dropwise addition of imidazole (0.068 g, 1 mmol) in DMF (2 ml) under continuous stirring at about 333 K. The resulting blue mixture was cooled to room temperature and filtered. Crystals of (II) were obtained by allowing the filtrate to stand at room temperature for 3 d.

Compound (I)

Crystal data

C ₂ H ₈ N ⁺ ·C ₁₀ H ₅ O ₅ ⁻	$\gamma = 81.035 (4)^\circ$
$M_r = 251.23$	$V = 582.17 (5) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.3381 (4) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 8.6806 (3) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$c = 8.8521 (5) \text{ \AA}$	$T = 110 (2) \text{ K}$
$\alpha = 68.4693 (17)^\circ$	$0.40 \times 0.20 \times 0.20 \text{ mm}$
$\beta = 78.8197 (17)^\circ$	

Data collection

Nonius KappaCCD area-detector diffractometer	2385 independent reflections
7187 measured reflections	1822 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.116$	$\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$
$S = 1.04$	$\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$
2385 reflections	
174 parameters	

Table 1
Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O11–H11 \cdots O14	0.97 (2)	1.51 (2)	2.4817 (19)	178 (2)
N16–H16A \cdots O15	0.87 (2)	2.02 (2)	2.7798 (19)	145.2 (18)
N16–H16A \cdots O1	0.87 (2)	2.45 (2)	3.185 (2)	142.9 (17)
N16–H16B \cdots O15 ⁱ	0.96 (2)	1.80 (2)	2.750 (2)	171.0 (18)

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Compound (II)

Crystal data

[Cu(C ₁₀ H ₅ O ₅) ₂ (C ₃ H ₄ N ₂) ₄]	$\gamma = 99.4472 (9)^\circ$
$M_r = 746.15$	$V = 796.68 (4) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 8.1383 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.9782 (3) \text{ \AA}$	$\mu = 0.76 \text{ mm}^{-1}$
$c = 11.3225 (2) \text{ \AA}$	$T = 110 (2) \text{ K}$
$\alpha = 107.5049 (12)^\circ$	$0.45 \times 0.30 \times 0.25 \text{ mm}$
$\beta = 108.4826 (14)^\circ$	

Data collection

Nonius KappaCCD area-detector diffractometer	8773 measured reflections
Absorption correction: multi-scan (Blessing, 1995)	3753 independent reflections
$T_{\text{min}} = 0.726, T_{\text{max}} = 0.833$	3386 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	232 parameters
$wR(F^2) = 0.097$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
3753 reflections	$\Delta\rho_{\text{min}} = -0.62 \text{ e \AA}^{-3}$

Compound (III)

Crystal data

[La(C ₁₀ H ₅ O ₅) ₂ (H ₂ O) ₇]- (C ₁₀ H ₅ O ₅)·C ₁₀ H ₆ O ₅ ·4H ₂ O]	$V = 9542.0 (6) \text{ \AA}^3$
$M_r = 1156.64$	$Z = 8$
Orthorhombic, $Fdd2$	Mo $K\alpha$ radiation
$a = 38.9250 (16) \text{ \AA}$	$\mu = 1.00 \text{ mm}^{-1}$
$b = 8.6186 (3) \text{ \AA}$	$T = 110 (2) \text{ K}$
$c = 28.4430 (9) \text{ \AA}$	$0.30 \times 0.25 \times 0.15 \text{ mm}$

Data collection

Nonius KappaCCD area-detector diffractometer	16083 measured reflections
Absorption correction: multi-scan (Blessing, 1995)	4497 independent reflections
$T_{\text{min}} = 0.755, T_{\text{max}} = 0.866$	3667 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.083$

Table 2
Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O14–H14 \cdots O26	0.95	1.49	2.4380 (17)	174
N4–H4 \cdots O25 ⁱ	0.88	1.98	2.779 (2)	150
N10–H10 \cdots O25 ⁱⁱ	0.88	1.99	2.799 (2)	153

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x - 1, y, z - 1$.

Table 3
Hydrogen-bond geometry (Å, °) for (III).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H2...O28 ⁱ	0.90	2.24	2.791 (5)	119
O3—H3A...O28 ⁱ	0.90	2.01	2.838 (7)	152
O3—H3B...O22	0.90	2.06	2.932 (6)	162
O4—H4A...O13 ⁱⁱ	0.90	1.92	2.760 (6)	154
O4—H4B...O7 ⁱⁱⁱ	0.90	1.92	2.793 (6)	162
O5—H5A...O21 ⁱⁱⁱ	0.90	1.91	2.779 (6)	160
O5—H5B...O21 ^{iv}	0.90	2.13	2.906 (6)	144
O7—H7...O12	0.90	1.57	2.438 (6)	160
O22—H22...O27	0.90	1.58	2.447 (7)	161

Symmetry codes: (i) $-x + \frac{3}{4}, y + \frac{1}{4}, z - \frac{1}{4}$; (ii) $x - \frac{1}{4}, -y + \frac{1}{4}, z - \frac{1}{4}$; (iii) $-x + \frac{1}{2}, -y + \frac{1}{2}, z$; (iv) $x, y + 1, z$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.114$

$S = 1.00$

4497 reflections

309 parameters

1 restraint

H-atom parameters constrained

$\Delta\rho_{\max} = 0.64 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -0.78 \text{ e } \text{Å}^{-3}$

Absolute structure: Flack (1983),
with 2093 Friedel pairs

Flack parameter: 0.49 (3)

C-bound H atoms were located in calculated positions and constrained to ride on their parent atoms, with C—H = 0.95 or 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5U_{\text{eq}}(\text{C})$. In (I), H atoms bound to O and N atoms were located in a difference Fourier map. Their coordinates were included in the refinement but assigned $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O,N})$. In (II), the imidazole N-bound H atom was placed in a calculated position at N—H = 0.88 Å, while the carboxyl O-bound H atom was located in a difference Fourier map. The two atoms were assigned $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O,N})$, but their atomic parameters were not refined. In (III), the H atoms bound to atoms O3, O4 and O5 were located in a difference Fourier map. Those attached to atoms O2, O7 and O22 could not be located reliably; they were placed in calculated positions to optimize the O2...O28 ($-x + \frac{3}{4}, y + \frac{1}{4}, z - \frac{1}{4}$), O7...O12 and O22...O27 hydrogen bonds, respectively. Charge-balance considerations and the symmetry features of this structure required that the noncoordinated BFDC moiety is only partially deprotonated (*i.e.* deprotonation occurs in 50% of these fragments). The additional H atom (with 50% occupancy) bound to either O27 or O28 of the noncoordinated ligand could not be clearly located (though most probably it should be there) in difference Fourier maps. The corresponding O—H distances were then restrained to O—H = 0.90 (2) Å and assigned $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. Their atomic parameters were not refined in the final least-squares calculations. Nevertheless, the presence of weak peaks of residual density between O7 and O12, and between O22 and O27 may indicate that the hydrogen bond in these two species is partially delocalized. Compound (III) crystallized as a hydrate in the space group *Fdd2* and represents a racemic twin. The water solvent incorporated into the crystal lattice could not be reli-

ably characterized by discrete atoms (possibly due to its location on, and apparent disorder about, special positions). Conventional refinement with the solvent excluded converged at $R1 = 0.071$, the difference Fourier electron-density map revealing four significant peaks within $1.9\text{--}2.6 \text{ e } \text{Å}^3$ related to the solvent. This relatively low R factor attests to the essential correctness of the main structural model in (III). The contribution of the water solvent was thus subtracted from the diffraction data by the SQUEEZE procedure in *PLATON* (Spek, 2003), which led to $R1 = 0.049$. These calculations showed that there are eight voids per cell of 200 Å^3 each. The residual electron count was assessed to be 304 e per cell, which corresponds nicely with four water molecules per void (two water species per asymmetric unit).

For all three compounds, data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3067). Services for accessing these data are described at the back of the journal.

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