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Crystal structures of sodium-, lithium-, and ammonium 4,5-dihydroxybenzene-1,3-disulfonate (tiron) hydrates

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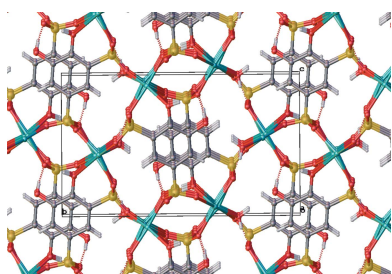
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The solid-state structures of the Na⁺, Li⁺, and NH₄⁺ salts of the 4,5-dihydroxybenzene-1,3-disulfonate (tiron) dianion are reported, namely disodium 4,5-dihydroxybenzene-1,3-disulfonate, 2Na⁺·C₆H₄O₈S₂²⁻, μ -4,5-dihydroxybenzene-1,3-disulfonato-bis[aqualithium(I)] hemihydrate, [Li₂(C₆H₄O₈S₂)(H₂O)₂].0.5H₂O, and diammonium 4,5-dihydroxybenzene-1,3-disulfonate monohydrate, 2NH₄⁺·C₆H₄O₈S₂²⁻·H₂O. Intermolecular interactions vary with the size of the cation, and the asymmetric unit cell, and the macromolecular features are also affected. The sodium in Na₂(tiron) is coordinated in a distorted octahedral environment through the sulfonate oxygen and hydroxyl oxygen donors on tiron, as well as an interstitial water molecule. Lithium, with its smaller ionic radius, is coordinated in a distorted tetrahedral environment by sulfonic and phenolic O atoms, as well as water in Li₂(tiron). The surrounding tiron anions coordinating to sodium or lithium in Na₂(tiron) and Li₂(tiron), respectively, result in a three-dimensional network held together by the coordinate bonds to the alkali metal cations. The formation of such a three-dimensional network for tiron salts is relatively rare and has not been observed with monovalent cations. Finally, (NH₄)₂(tiron) exhibits extensive hydrogen-bonding arrays between NH₄⁺ and the surrounding tiron anions and interstitial water molecules. This series of structures may be valuable for understanding charge transfer in a putative solid-state fuel cell utilizing tiron.

1. Chemical context

Catechols play important roles across many areas of chemistry and biology. Their rich coordination chemistry with metal ions (Pierpont & Lange, 1994; Sever & Wilker, 2004) emerges for example in siderophores (Boukhalfa & Crumbliss, 2002; Raymond *et al.*, 2015; Springer & Butler, 2016). One catechol-containing siderophore, enterobactin (ent) has the strongest characterized Fe^{III} complex to date ($K_a = 10^{49}$) (Loomis & Raymond, 1991). Catechols are also key to the function of some marine bioadhesives (Lee *et al.*, 2011); in one recent example, a protein in sessile marine organisms uses a cooperation between surface residues containing 3,4-dihydroxyphenylalanine (DOPA) and lysine to bind strongly to mineral surfaces (Rapp *et al.*, 2016). Some species of ascidians produce a polyphenol-containing molecule called tunichrome that has been implicated in metal binding and/or metal function (Sugumaran & Robinson, 2012).



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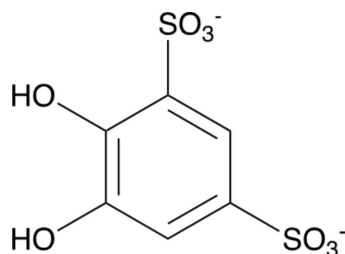


Figure 1
Tiron dianion (4,5-dihydroxy-1,3-benzenedisulfonate).

Upon binding to metal cations such as Fe^{III} and Ti^{IV} , catechols typically form brightly colored complexes (Sever & Wilker, 2004; Pierpont & Lange, 1994). In solution, however, some catechols can oxidize and form polymers, thus forming metal complexes that are more difficult to characterize. Compared to unsubstituted catechol, tiron (4,5-dihydroxy-1,3-benzenedisulfonic acid, Fig. 1) allows for improved water solubility as well as reduced polymerization by substituting electron-withdrawing sulfonic acid moieties (Sommer, 1963*a,b*). Tiron has long been used for colorimetric determination of both Ti^{IV} and Fe^{III} (Yoe & Armstrong, 1945, 1947), hence its name.

The free acid of tiron has been used in an aqueous flow battery because of its two-electron redox couple within range of an aqueous system, high water solubility, and low cost (Yang *et al.*, 2014). When crystallized, tiron molecules can form a network through coordination of the counter-cation to the sulfonate or protonated or deprotonated hydroxide of the tiron (Côté & Shimizu, 2001, 2003; Sheriff *et al.*, 2003; Guan & Wang, 2016, 2017). These networks can range from one-dimensional networks, which form a linear polymer (Côté & Shimizu, 2003; Sheriff *et al.*, 2003), to three-dimensional networks in which each tiron anion is coordinated to a metal cation and forms an interconnected lattice among all tiron anions in the crystal (Côté & Shimizu, 2001, 2003; Guan & Wang, 2016). Many of these tiron-containing crystal structures exhibit counter-cation-dependent luminescent properties (Guan & Wang, 2016, 2017). The three-dimensional networks with tiron can absorb H_2S gas after interstitial and coordinated H_2O are liberated with heat (Côté & Shimizu, 2003). Currently, examples of three-dimensional networks formed by tiron and cations are relatively rare. Presented here are the first two examples of the preparation and characterization of the Li^+ tiron salt and Na^+ tiron salt, which forms a three-dimensional network. In addition to $\text{Li}_2(\text{tiron})$ and $\text{Na}_2(\text{tiron})$, the preparation and crystallization of the NH_4^+ tiron salt is reported. This species is the first tiron salt which utilizes a counter-cation capable of hydrogen bond (H-bond) donation to allow for a complex H-bonding network.

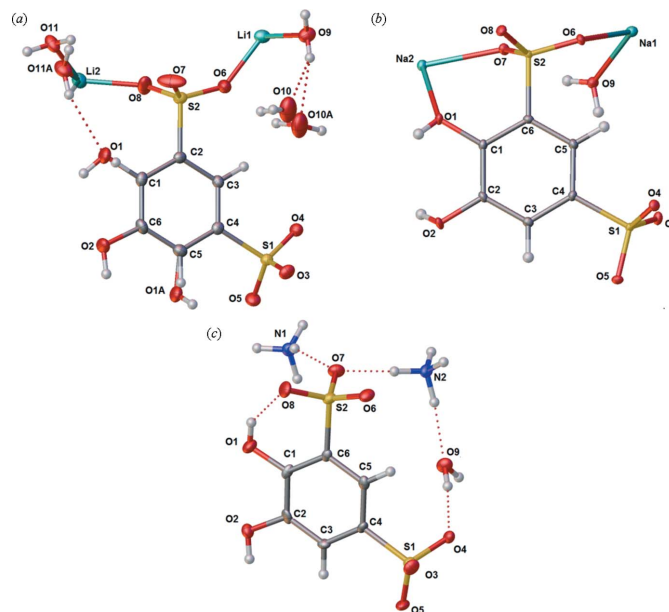
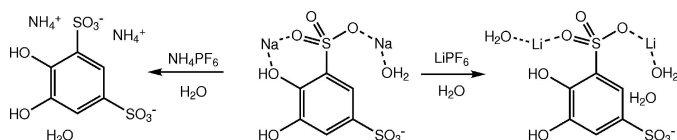


Figure 2
Displacement ellipsoid plots of the asymmetric unit contents for the crystal structures of tiron salts characterized in this study: (a) $\text{Li}_2(\text{tiron}) \cdot 2.5\text{H}_2\text{O}$, (b) $\text{Na}_2(\text{tiron}) \cdot \text{H}_2\text{O}$ and (c) $(\text{NH}_4)_2(\text{tiron}) \cdot \text{H}_2\text{O}$. Ellipsoids are shown at the 50% probability. Hydrogen atoms shown as spheres.

2. Structural commentary

Three tiron salts of different monovalent cations were crystallized. $\text{Li}_2(\text{tiron})$ and $(\text{NH}_4)_2(\text{tiron})$ were both prepared from commercially available $\text{Na}_2(\text{tiron})$ by salt metathesis. In each case, the Na^+ cation was removed by 15-crown-5 ether.

All asymmetric units (Fig. 2) contain two of their respective cations on general positions. Water is included in all asymmetric units, however in different amounts. Both sodium and ammonium tiron have one water molecule in the asymmetric unit, whereas lithium tiron has 2.5 water molecules in the asymmetric unit. The lithium tiron also exhibits rotational whole-molecule disorder leading to two possible placements of O1 on the phenyl, and representing a major and minor orientation [89.2 (3) and 10.8 (3)% occupancy, respectively].

The structure of $\text{Li}_2(\text{tiron})$ is presented in the $P2_1/n$ space group. The lithium ion is coordinated by phenolic, sulfonate and water oxygen atoms. Lithium is bonded to only three sulfonate moieties, and one water molecule in a distorted tetrahedral geometry. An extensive H-bonding network with three types of solvate water molecules stabilizes the crystal structure (Table 1, Fig. 3). The geometrically frustrated water molecule containing O10 sits in a pocket surrounded by H-bond donors and acceptors from sulfonate (O6, O4), and water (O9), and phenol (O2). As a result of the frustration, O10 is highly disordered, modeled with a two-site split-atom model that additionally exhibits special-position disorder about the inversion element at Wyckoff position *d*. The result is a four-site disorder model for the water molecule containing O10. The lithium-bound water molecule containing O11 H-bonds with sulfonate oxygen atoms O4 and O8, but the oxygen

Table 1

Hydrogen-bond geometry (Å, °) for Li₂(tiron)·2.5H₂O.

<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>
O1—H1···O2	0.84	2.22	2.685 (3)	115
O1—H1···O9 ⁱ	0.84	1.93	2.693 (3)	150
O1A—H1A···O8 ⁱⁱ	0.84	2.31	2.978 (17)	136
O2—H2···O1A	0.84	2.29	2.693 (16)	110
O2—H2···O7 ⁱⁱⁱ	0.84	2.60	3.082 (3)	117
O2—H2···O11 ⁱⁱ	0.84	2.13	2.952 (6)	166
O9—H9A···O3 ^{iv}	0.8323 (17)	1.9961 (16)	2.821 (2)	170.86 (13)
O9—H9B···O10 ^{iv}	0.8033 (17)	2.19 (6)	2.96 (6)	160.0 (18)
O9—H9B···O10	0.8033 (17)	1.98 (6)	2.73 (6)	155.0 (16)
O9—H9B···O10A ^{iv}	0.8033 (17)	2.02 (4)	2.80 (4)	164.8 (14)
O9—H9B···O10A	0.8033 (17)	2.08 (4)	2.83 (4)	156.2 (12)
O11—H11A···O4 ^v	0.840 (2)	2.1244 (16)	2.957 (3)	171.19 (17)
O11—H11B···O8 ^{vi}	0.829 (3)	2.0583 (19)	2.873 (3)	167.4 (4)
O11A—H11C···O6 ^{vi}	0.843 (8)	2.5753 (18)	3.290 (8)	143.3 (5)
O11A—H11C···O8 ^{vi}	0.843 (8)	1.9964 (18)	2.776 (8)	153.2 (8)
O11A—H11D···O1	0.862 (18)	2.1019 (19)	2.851 (17)	145.0 (5)
O10—H10A···O2 ⁱⁱⁱ	0.81 (6)	2.2562 (16)	2.93 (6)	141 (4)
O10—H10B···O6	1.02 (6)	2.2175 (18)	3.14 (6)	150 (3)
O10A—H10C···O2 ^{vii}	0.90 (5)	2.3694 (16)	3.13 (5)	142 (3)
O10A—H10D···O6	0.86 (4)	2.3000 (17)	3.10 (5)	155 (3)

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

atom is disordered, pyramidalized predominantly toward the phenolic O—H hydrogen atom of O2 due to H-bonding, but with a minor component pyramidalized toward O1, which is less available as an H-bond acceptor since the phenolic hydrogen of O1 is already involved in an intramolecular *ortho*-H-bond with its own O2 (Fig. 2). The water molecule containing O9 is also lithium bound, but not disordered, and interacts with O10/10A of the disordered water and with sulfonate oxygen O3 and the phenolic hydrogen atom of O1.

The sodium salt of tiron is also presented in the $P2_1/n$ space group. Each sodium atom is bonded to four sulfonate moieties, one hydroxide, and one water oxygen atom to give a distorted octahedral geometry (Fig. 4). The two types of Na atoms are

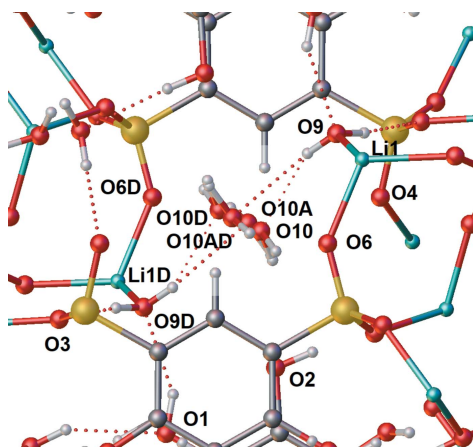


Figure 3

Ball and stick representation of Li₂(tiron)·2.5H₂O, including the H-bonding environment of neighboring tiron anions and water showing all disorder components. Atom labels with the suffix D are generated *via* inversion through the center of symmetry at Wyckoff position *d*. Atom labels with the suffix A represent minor components of two-site disorder models.

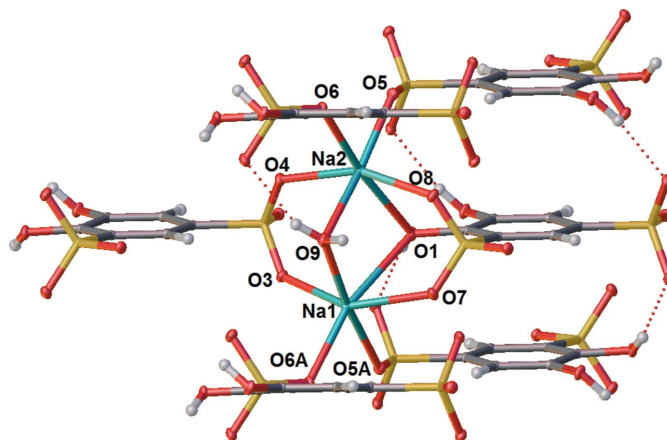


Table 2

Hydrogen-bond geometry (Å, °) for Na₂(tiron)·H₂O.

<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>
O1—H1...O3 ⁱ	0.82 (2)	2.05 (2)	2.8256 (15)	156 (2)
O2—H2...O4 ⁱⁱ	0.84	1.98	2.8145 (14)	169
O9—H9A...O2 ⁱⁱ	0.82 (3)	2.18 (3)	2.9904 (15)	173 (3)
O9—H9B...O7 ⁱⁱⁱ	0.80 (3)	2.14 (3)	2.8975 (15)	158 (3)

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $-x+1, -y+1, -z+1$; (iii) $x-1, y, z$.

which π -stack with one another about a crystallographic inversion center (Wyckoff position *b*), hence the rings are perfectly parallel. The other lithium ion, Li2, links through a sulfonate group (S1) of one tiron to the other sulfonate group S(2) of a third tiron, generating a 'square' assembly of tiron anions and two Li2 ions around a crystallographic inversion element (Wyckoff position *a*, Fig. 6). The distance of 3.718 (10) Å between the centroids of neighboring arene rings is consistent with a strong π -stacking interaction, and suggests the interaction is augmented by the array of H-bonding interactions among phenolic hydroxyl and sulfonate groups and water (Table 1, Fig. 3).

The H-bonding in the sodium complex is entirely intermolecular (Table 2, Fig. 7). Both hydroxyl moieties H-bond to a sulfonate moiety on an adjacent tiron anion. The hydroxyl O1 H-bonds to the sulfonate based O3 [O—H...O—S 2.05 (2) Å]. The other hydroxyl O4 H-bonds to O2 of the same sulfonate with a slightly shorter H-bond [O—H...O—S 1.98 Å]. These two H-bonds decrease hyperconjugation to the π -system from the oxygen atom in the hydroxyls by reducing the torsion angle by 32.08 and 46.16° for O1 and O2, respec-

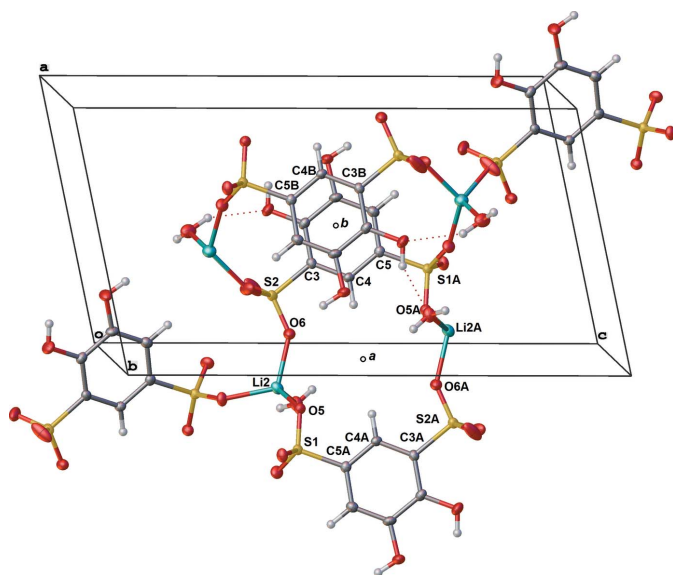


Figure 6

Illustration of selected nearest neighbor lithium linkages of neighboring tiron anions in Li₂(tiron)·2.5H₂O. Atom labels with the suffix B are generated *via* inversion through the center of symmetry at the center of the cell (Wyckoff *b*) and those with the suffix A are generated *via* inversion through the center of symmetry in the *a*-face (Wyckoff *b*). Ellipsoids shown at the 50% probability level. Hydrogen atoms are shown as spheres.

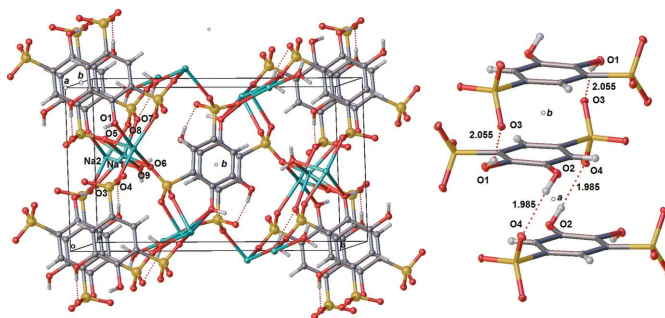


Figure 7

Packed structures of Na₂(tiron)·H₂O. Left: packing arrangement in the unit cell. Right: displacement ellipsoid plot showing alternating units in a π -stacked arrangement in the crystallographic *a*-axis direction. Ellipsoids are shown at the 50% probability level, hydrogen atoms are shown as spheres.

tively. This deviation from a fully hyperconjugated hydroxyl exemplifies the importance of the formation of the H-bond. An H-bond not shown exists between a proton in water bound by Na⁺ and a tiron-based hydroxyl O2 position as well as a sulfonate in the first position [O—H...O—H 2.18 (3) Å, O—H...O—S 2.14 (3) Å].

Two types of sodium atoms arrange in channels along the crystallographic *a*-axis direction, and are bridged by sulfonyl oxygen atoms O3, O4, O5, and O6, by phenolic oxygen atom O1, and by water oxygen atom O9 (Fig. 7). Neighboring tiron arenes π -stack along the crystallographic *a*-axis direction, related by crystallographic inversion centers (Wyckoff letters *a* and *b*), also requiring the arene rings to be parallel, as in the lithium salt. The π -stacking interactions are further augmented by H-bonding interactions between the phenolic hydrogens of O1 and O2 with sulfonate oxygens O3 and O4 respectively. The π -stacking distance of 3.753 (18) Å is similar to that observed in the lithium salt with its corresponding dense array of H-bonding interactions, but slightly shorter due to the more acute O—Na—O bond angles in octahedrally coordinated sodium atoms, in contrast to tetrahedrally coordinated lithium atoms in the lithium salt. This arrangement of Na⁺ and tiron ions results in an ordered array of sodium channels interspersed between columns of strongly

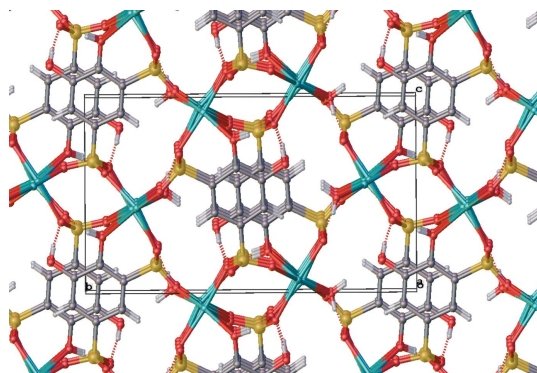


Figure 8

Extended packing diagram of Na₂(tiron)·H₂O, showing the columnar arrangement of tiron aryl groups and parallel sodium ion channels.

Table 3

Hydrogen-bond geometry (Å, °) for (NH₄)₂(tiron)·H₂O.

<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>
O1—H1...O5 ⁱ	0.84	2.47	2.974 (4)	119
O1—H1...O8	0.84	2.06	2.790 (4)	146
O2—H2...O9 ⁱⁱ	0.84	1.99	2.830 (5)	174
O9—H9A...O3 ⁱⁱⁱ	0.85 (2)	2.03 (2)	2.871 (5)	171 (5)
O9—H9B...O4	0.86 (2)	1.97 (2)	2.831 (4)	174 (5)
N1—H1A...O4 ^{iv}	0.95 (2)	2.13 (3)	2.980 (5)	148 (3)
N1—H1A...O8 ⁱⁱⁱ	0.95 (2)	2.30 (4)	2.907 (5)	121 (3)
N1—H1B...O5 ^v	0.95 (2)	2.11 (2)	2.996 (5)	155 (3)
N1—H1C...O1 ^{vi}	0.95 (2)	2.03 (3)	2.850 (5)	143 (3)
N1—H1C...O2 ^{vi}	0.95 (2)	2.63 (3)	3.470 (5)	147 (3)
N1—H1D...O3 ⁱ	0.96 (2)	2.41 (4)	2.891 (5)	111 (3)
N1—H1D...O7	0.96 (2)	2.02 (3)	2.847 (5)	143 (3)
N2—H2A...O9	0.97 (2)	1.95 (2)	2.917 (5)	174 (3)
N2—H2B...O7	0.97 (2)	1.87 (2)	2.834 (5)	171 (3)
N2—H2C...O6 ⁱⁱⁱ	0.95 (2)	2.03 (3)	2.901 (5)	152 (3)
N2—H2C...O7 ^{vii}	0.95 (2)	2.60 (3)	3.215 (5)	123 (3)
N2—H2D...O3 ^{viii}	0.96 (2)	2.45 (4)	3.025 (5)	119 (3)
N2—H2D...O4 ^{viii}	0.96 (2)	1.99 (2)	2.916 (5)	161 (3)
N2—H2D...O8 ^{vii}	0.96 (2)	2.60 (4)	3.113 (5)	114 (3)

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

interacting π -stacked tiron aryl groups, all in the crystallographic *a*-axis direction (Fig. 8).

Unlike Na⁺ and Li⁺, NH₄⁺ cannot be coordinated by any atoms on tiron or water. Because of this inability, NH₄⁺ interactions with the surrounding molecules are primarily H-bond based. Both ammonium ions H-bond to three sulfonate moieties and an oxygen atom from a phenolic hydroxyl or a water molecule (Tables 3 and 4, Fig. 9). The ammonium ion

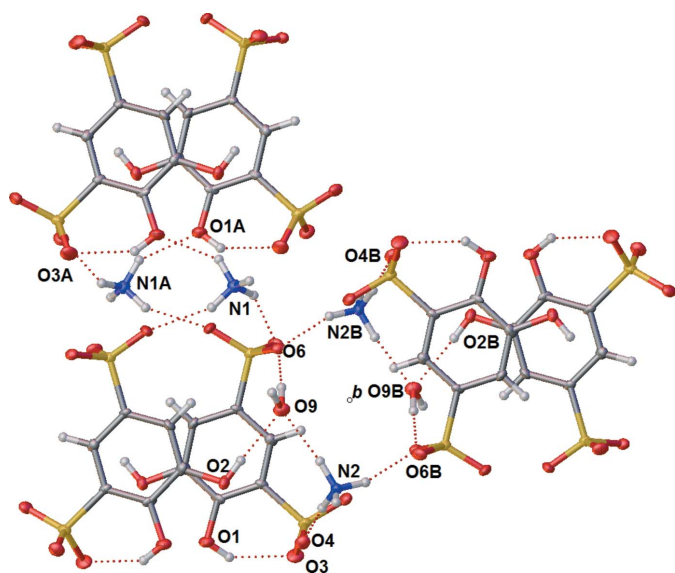


Figure 9

Displacement ellipsoid plot of (NH₄)₂(tiron)·H₂O showing neighboring H-bonding interactions among six tiron anions, four ammonium ions, and two water solvate molecules. Ellipsoids are shown at the 50% probability level and hydrogen atoms are shown as open spheres. Atom labels with the suffix B are generated by symmetry about a crystallographic center of inversion (Wyckoff position *b*), and atom labels with the suffix A are generated by one or more glide operation.

Table 4

H-bonding to all NH₄⁺ based protons in (NH₄)₂(tiron)·H₂O.

Proton on NH ₄	Acceptor/moiety	H-bond distance (Å)
N ₁ H _{1a}	O4/sulfonate	2.13 (3)
N ₁ H _{1b}	O5/sulfonate	2.10 (2)
N ₁ H _{1c}	O1/phenolic	2.04 (3)
N ₁ H _{1d}	O7/sulfonate	2.02 (3)
N ₂ H _{2a}	O9/water	1.95 (2)
N ₂ H _{2b}	O7/sulfonate	1.87 (2)
N ₂ H _{2c}	O6/sulfonate	2.03 (3)
N ₂ H _{2d}	O4/sulfonate	1.99 (2)

containing N1 forms H-bonds with two tiron molecules that are horizontally next to each other in the unit cell as well as a tiron above and a tiron below. The ammonium ion containing N2 also forms a similar H-bonding network with the tiron molecules but also stabilizes an interstitial water. This water H-bonds to two first position sulfonate moieties in alternating layers of tiron molecules [O—H...O—S 1.97 (2) Å, O—H...O—S 2.03 (2) Å]. Finally, O5 of a phenolic hydroxyl is H-bonded to this interstitial water [O—H...OH₂ 1.99 Å] (Fig. 9). Regarding intramolecular H-bonding, because the protons on the hydroxyls are pointed away from each other to allow for H-bonding to N1, the phenolic hydroxyl containing O1 is directed to H-bond with O3 of the sulfonate (Fig. 9).

The (NH₄)₂(tiron) packs such that the tiron units connect to one another along the crystallographic *c*-axis direction *via* a six-membered H-bonding array of two lattice water molecules, two ammonium ions (containing N2), and two sulfonate oxygen atoms (Fig. 9). The ammonium ions containing N1 further serve to link tiron units along the crystallographic *b*-axis direction by H-bonding with sulfonate oxygen O8 and phenolic oxygen atom O1. Further, the arene π -stacking

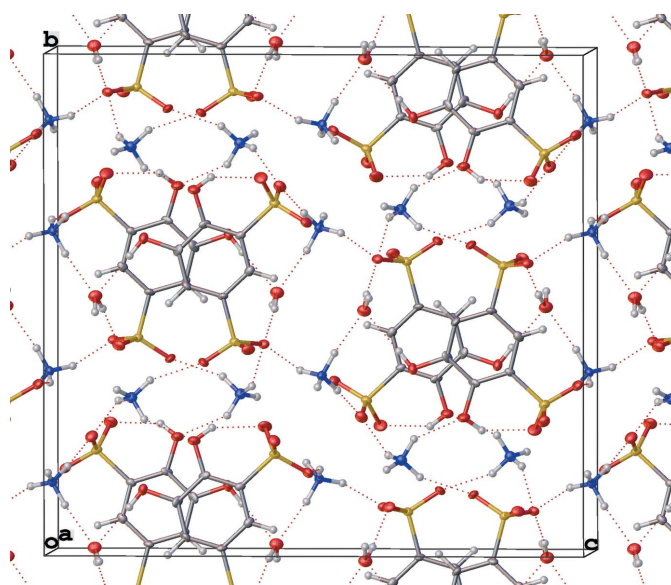


Figure 10

Extended packing view of (NH₄)₂(tiron) structure showing the three-dimensional H-bond network.

Table 5
Crystallographically characterized tiron salts.

CSD code	Counter-cation	Observed coordination number	Charge of tiron	Intercentroid distance (Å)	Reference
CAZZEI	Na ⁺	2, 1, 1	3 [−]	3.857	(Riley <i>et al.</i> , 1983)
HUCMOH	Ba ²⁺	9	2 [−]	3.520	(Côté & Shimizu, 2003)
OMARAV	Ca ²⁺	8	2 [−]	3.598	(Côté & Shimizu, 2003)
OMAREZ	Sr ²⁺	9	2 [−]	3.654	(Côté & Shimizu, 2003)
OMARID	Mg ²⁺	6 (all water)	2 [−]	4.180	(Côté & Shimizu, 2003)
FIMBEJ	Zn ²⁺	6 (no tiron)	2 [−]	N/A	(Wang <i>et al.</i> , 2005)
NIWKUA	Cd ²⁺	6 (one sulfonate)	2 [−]	N/A	(Zhang <i>et al.</i> , 2008)
FIRMEA	Cu ²⁺	6 (one sulfonate)	2 [−]	N/A	(Lu <i>et al.</i> , 2014)
TUYNUY	Mg ²⁺	6 (no tiron)	2 [−]	N/A	(Guan, 2016)
ADOXUP	La ³⁺	9	3 [−]	3.530	(Guan & Wang, 2016)
HUCMOH02	Ba ²⁺	9	2 [−]	3.516	(Guan & Wang, 2016)

interactions and additional H-bonding interactions between sulfonate oxygen atoms and both ammonium ions link these strands to one another in the crystallographic *a*-axis direction to give the three-dimensional H-bonding network (Fig. 10), although the π -stacking distance is greatest in the ammonium salt [4.006 (3) Å] in comparison to the Li⁺ and Na⁺ salts. This result is possibly due to the lower strength of N—H H-bonds in comparison to O—H H-bonds. Unlike the Li⁺ and Na⁺ salts, the planes of the arene rings of tiron in the NH₄⁺ tiron are canted at an angle of 2.08°, related to one another by the crystallographic glide operations.

4. Database survey

In the reported structures, interactions with sulfonate moieties and the protonated hydroxyl moieties together create a complex network formed through coordinate bonds or H-bonds. A search of the Cambridge Structural Database (Version 5.39, February 2018; Groom *et al.*, 2016) yielded several structures that included tiron (Table 5). Of the structures reported, seven exhibited π -stacking interactions between at least two tiron molecules as represented by their intercentroid distances. A rarer structural feature of these complexes is the formation of networks between tiron molecules and their corresponding counter-cations in which only HUCMOH, ADOXUP, and HUCMOH02 form three-dimensional networks by eliciting multiple bonds to the cations (Côté & Shimizu, 2003; Guan & Wang, 2016). Both presented Li⁺ and Na⁺ tiron salts are the first examples of tiron-containing structures with monovalent cations that form three-dimensional networks. Furthermore, the NH₄⁺ tiron salt presented is the first example of a tiron complex in which the counter-cation H-bonds to the tiron.

5. Synthesis and crystallization

Na₂(tiron)·H₂O

Na₂(tiron)·H₂O was used as received from the commercial source (97%, Sigma Aldrich) and added to water until it was saturated. The slurry was filtered into a 1 dram scintillation vial and covered with a Kimwipe. The solution was allowed to sit undisturbed at room temperature until the water evaporated. The crystals which developed were off-white needles.

Li₂(tiron)·2.5H₂O

In 2.00 mL of water, 0.100 g of Na₂(tiron)·H₂O was dissolved. To this solution, 0.94 g of LiPF₆ was added. Once the lithium salt dissolved, 0.120 mL 15-crown-5 was added which immediately resulted in a white precipitate. The slurry was stirred while adding 1 mL of dichloromethane (DCM), then the DCM layer was removed by pipette. The aqueous solution was extracted twice more with DCM for a total of three times. The water was then evaporated by gentle heating. A white powder was obtained and triturated with 1 mL of diethyl ether three times. The resulting solid was dried, partially dissolved in ethanol, filtered, and allowed to sit undisturbed in a 1 dram scintillation vial at room temperature. The resulting crystals were off-white needles.

(NH₄)₂(tiron)·H₂O

Na₂(tiron)·H₂O (0.100 g) was added and dissolved in 2.00 mL of water. After the Na₂(tiron) had dissolved, 0.098 g of NH₄PF₆ was added and dissolved. Upon adding NH₄PF₆, the solution turned rose pink. To this solution, 0.120 mL of 15-crown-5 was added and a white precipitate formed. The slurry was extracted three times total with 1 mL of DCM each time. The aqueous solution was gently heated to dryness. The solid was then triturated with three separate 1 mL portions of diethyl ether. The solid was dried and dissolved in methanol, filtered, and allowed to sit undisturbed in a 1 dram vial at room temperature. The crystals which formed were off-white needles with a purple/rose-colored oily residue coating them.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 6. Water hydrogens were located in difference maps and refined wherever possible. H atoms bonded to C were placed in geometrically idealized positions based on *sp*² hybridization with C—H bond lengths of 0.95 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C). A combination of calculated H atoms and H atoms found in the difference map was utilized for phenolic O—H and H₂O molecules. For phenolic OH, H atoms were either located and freely refined, or placed in idealized *sp*³ positions with bond lengths of 0.84 Å and *U*_{iso}(H) = 1.5*U*_{eq}(O), and permitted to rotate about the O—C bond. For water molecules, hydrogen atoms were either located in the difference-Fourier map and refined with restraints

Table 6
Experimental details.

	Li ₂ (tiron)·2.5H ₂ O	Na ₂ (tiron)·H ₂	(NH ₄) ₂ (tiron)·H ₂ O
Crystal data			
Chemical formula	[Li ₂ (C ₆ H ₄ O ₈ S ₂)(H ₂ O) ₂] ₂ ·H ₂ O	2Na ⁺ ·C ₆ H ₆ O ₉ S ₂ ^{2−}	2NH ₄ ⁺ ·C ₆ H ₄ O ₈ S ₂ ^{2−} ·H ₂ O
<i>M_r</i>	654.26	332.21	322.31
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>	Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>	Orthorhombic, <i>Pbca</i>
Temperature (K)	100	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.5847 (18), 7.4498 (15), 17.599 (4)	6.8156 (7), 16.1449 (15), 9.5870 (9)	6.5023 (15), 18.779 (4), 20.236 (4)
α , β , γ (°)	90, 102.997 (4), 90	90, 92.727 (2), 90	90, 90, 90
<i>V</i> (Å ³)	1224.5 (4)	1053.73 (18)	2470.9 (9)
<i>Z</i>	2	4	8
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ^{−1})	0.49	0.63	0.48
Crystal size (mm)	0.24 × 0.09 × 0.04	0.45 × 0.16 × 0.13	0.10 × 0.05 × 0.04
Data collection			
Diffractometer	Bruker APEXII	Bruker APEXII	Bruker APEXII
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2014)	Multi-scan (<i>SADABS</i> ; Bruker, 2014)	Multi-scan (<i>SADABS</i> ; Bruker, 2014)
<i>T</i> _{min} , <i>T</i> _{max}	0.670, 0.746	0.676, 0.746	0.663, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	15864, 2851, 2313	9573, 2485, 2340	12544, 2255, 1354
<i>R</i> _{int}	0.049	0.025	0.147
Refinement			
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.041, 0.100, 1.02	0.023, 0.071, 1.08	0.055, 0.127, 1.01
No. of reflections	2851	2485	2255
No. of parameters	217	185	204
No. of restraints	18	0	23
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ^{−3})	0.44, −0.48	0.44, −0.43	0.42, −0.53

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SAINT* (Bruker, 2016), *SHELXS97* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

(detailed below), or added and refined with restraints according to the most likely hydrogen-bonding interactions. For disordered water molecules, restraints (SIMU, DFIX, DANG, ISOR) and constraints (EADP) were employed to improve displacement parameters as well as allow for convergence of H-atom locations. For SIMU restraints on the disordered O10 of Li₂(tiron)·2.5H₂O, the restraint was set at *s* = 0.005 Å, *st* = 0.02 Å, and the default cutoff of 1.7 Å. These atoms were further restrained with ISOR 0.01 0.02. The disordered O—H phenoxyl group on the tiron ligand for the Li₂(tiron) crystal structure was located from a difference map and refined to a 0.892 (3)/0.108 (3) site occupancy. The lithium-bound water molecule was refined to a 0.751 (12)/0.249 (12) site occupancy. The disordered solvate water molecule on Wyckoff position *d* containing O10 was refined to a 0.30 (5)/0.20 (5) site occupancy. H atoms bonded to N were located in the difference-Fourier maps and restrained using DFIX and DANG to idealized *sp*³ hybridization with N—H bond lengths of 1.00 (2) Å and *U*_{iso}(H) = 1.5*U*_{eq}(N). EADP was used to constrain the ellipsoids of the disordered O1 to be equivalent for accurate refinement of occupancies.

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Crystal structures of sodium-, lithium-, and ammonium 4,5-dihydroxybenzene-1,3-disulfonate (tiron) hydrates

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Computing details

For all structures, data collection: *APEX2* (Bruker, 2014). Cell refinement: *SAINT* (Bruker, 2014) for NaTiron, NH4Tiron; *SAINT* (Bruker, 2016) for LiTiron. Data reduction: *SAINT* (Bruker, 2014) for NaTiron, NH4Tiron; *SAINT* (Bruker, 2016) for LiTiron. For all structures, program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Disodium 4,5-dihydroxybenzene-1,3-disulfonate (NaTiron)

Crystal data



$M_r = 332.21$

Monoclinic, $P2_1/n$

$a = 6.8156$ (7) Å

$b = 16.1449$ (15) Å

$c = 9.5870$ (9) Å

$\beta = 92.727$ (2)°

$V = 1053.73$ (18) Å³

$Z = 4$

$F(000) = 672$

$D_x = 2.094$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 6900 reflections

$\theta = 2.5\text{--}27.9^\circ$

$\mu = 0.63$ mm⁻¹

$T = 100$ K

Plank, colorless

$0.45 \times 0.16 \times 0.13$ mm

Data collection

Bruker APEXII

diffractometer

Radiation source: sealed tube

Graphite monochromator

Detector resolution: 8.333 pixels mm⁻¹

ω and φ scans

Absorption correction: multi-scan

(SADABS; Bruker, 2014)

$T_{\min} = 0.676$, $T_{\max} = 0.746$

9573 measured reflections

2485 independent reflections

2340 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

$\theta_{\max} = 27.9^\circ$, $\theta_{\min} = 2.5^\circ$

$h = -8 \rightarrow 8$

$k = -17 \rightarrow 21$

$l = -11 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.071$

$S = 1.08$

2485 reflections

185 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 0.6133P]$

where $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.74934 (5)	0.47581 (2)	0.82422 (3)	0.00662 (9)
S2	0.78290 (5)	0.28628 (2)	0.35605 (3)	0.00666 (9)
Na1	0.52212 (8)	0.15609 (3)	0.55730 (6)	0.01024 (13)
Na2	0.52978 (8)	0.35866 (3)	0.07130 (6)	0.00904 (13)
O1	0.77862 (15)	0.44913 (6)	0.21044 (10)	0.0095 (2)
H1	0.834 (3)	0.4913 (15)	0.184 (2)	0.026 (6)*
O2	0.72832 (15)	0.60443 (6)	0.33613 (10)	0.0103 (2)
H2	0.646843	0.597179	0.268721	0.015*
O3	0.93352 (15)	0.43988 (6)	0.88058 (10)	0.0102 (2)
O4	0.57824 (15)	0.42796 (6)	0.86349 (10)	0.0104 (2)
O5	0.73253 (14)	0.56359 (6)	0.85674 (10)	0.0094 (2)
O6	0.78663 (15)	0.22645 (6)	0.47032 (10)	0.0089 (2)
O7	0.96390 (15)	0.28408 (6)	0.27946 (10)	0.0104 (2)
O8	0.60507 (15)	0.28136 (6)	0.26724 (10)	0.0102 (2)
O9	0.26274 (16)	0.24089 (7)	0.49210 (11)	0.0115 (2)
H9A	0.256 (4)	0.2814 (17)	0.542 (3)	0.042 (7)*
H9B	0.205 (4)	0.2515 (16)	0.419 (3)	0.037 (7)*
C1	0.76633 (19)	0.45634 (8)	0.35261 (13)	0.0074 (2)
C2	0.74189 (19)	0.53371 (8)	0.41504 (14)	0.0078 (3)
C3	0.73789 (19)	0.53988 (8)	0.55936 (14)	0.0082 (2)
H3	0.723889	0.592459	0.602256	0.010*
C4	0.75445 (19)	0.46884 (8)	0.64062 (13)	0.0073 (2)
C5	0.77038 (19)	0.39085 (8)	0.58031 (13)	0.0082 (3)
H5	0.778109	0.342517	0.636828	0.010*
C6	0.77476 (19)	0.38501 (8)	0.43624 (14)	0.0072 (2)

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.00802 (17)	0.00652 (17)	0.00529 (15)	−0.00008 (11)	−0.00004 (11)	−0.00033 (10)
S2	0.00871 (17)	0.00549 (16)	0.00574 (16)	0.00048 (11)	−0.00007 (12)	0.00022 (11)
Na1	0.0092 (3)	0.0105 (3)	0.0109 (3)	0.0003 (2)	−0.0001 (2)	−0.0014 (2)
Na2	0.0093 (3)	0.0099 (3)	0.0079 (3)	0.0004 (2)	−0.0002 (2)	0.0004 (2)
O1	0.0137 (5)	0.0090 (5)	0.0060 (4)	−0.0021 (4)	0.0006 (3)	0.0014 (4)
O2	0.0152 (5)	0.0072 (5)	0.0081 (4)	−0.0012 (4)	−0.0029 (4)	0.0030 (4)
O3	0.0105 (5)	0.0108 (5)	0.0091 (4)	0.0022 (4)	−0.0018 (3)	0.0007 (4)
O4	0.0111 (5)	0.0121 (5)	0.0079 (4)	−0.0035 (4)	0.0009 (3)	0.0017 (4)

O5	0.0110 (5)	0.0071 (5)	0.0100 (4)	0.0005 (4)	0.0007 (3)	−0.0018 (3)
O6	0.0113 (5)	0.0073 (4)	0.0081 (4)	0.0008 (4)	0.0003 (4)	0.0024 (3)
O7	0.0116 (5)	0.0111 (5)	0.0087 (5)	0.0022 (4)	0.0031 (4)	0.0003 (3)
O8	0.0118 (5)	0.0095 (5)	0.0091 (5)	−0.0010 (4)	−0.0029 (4)	0.0005 (3)
O9	0.0135 (5)	0.0114 (5)	0.0095 (5)	0.0012 (4)	−0.0007 (4)	−0.0003 (4)
C1	0.0066 (6)	0.0090 (6)	0.0065 (6)	−0.0009 (5)	0.0000 (4)	0.0007 (5)
C2	0.0072 (6)	0.0069 (6)	0.0093 (6)	−0.0006 (5)	−0.0003 (5)	0.0021 (5)
C3	0.0073 (6)	0.0074 (6)	0.0100 (6)	−0.0008 (5)	0.0003 (5)	0.0000 (5)
C4	0.0068 (6)	0.0091 (6)	0.0059 (6)	−0.0007 (5)	−0.0001 (4)	0.0003 (5)
C5	0.0079 (6)	0.0080 (6)	0.0086 (6)	−0.0002 (5)	0.0004 (5)	0.0013 (5)
C6	0.0065 (6)	0.0064 (6)	0.0087 (6)	0.0004 (5)	0.0002 (4)	−0.0007 (5)

Geometric parameters (Å, °)

S1—O3	1.4628 (10)	Na2—O5 ^{vi}	2.3163 (11)
S1—O4	1.4630 (10)	Na2—O6 ⁱⁱⁱ	2.3278 (11)
S1—O5	1.4567 (10)	Na2—O8	2.2929 (11)
S1—C4	1.7657 (13)	Na2—O9 ^{vii}	2.4073 (12)
S2—Na2	3.3683 (7)	O1—H1	0.82 (2)
S2—O6	1.4599 (10)	O1—C1	1.3746 (16)
S2—O7	1.4658 (10)	O2—H2	0.8400
S2—O8	1.4499 (10)	O2—C2	1.3704 (16)
S2—C6	1.7717 (14)	O9—H9A	0.82 (3)
Na1—Na2 ⁱ	3.3731 (8)	O9—H9B	0.80 (3)
Na1—Na2 ⁱⁱ	3.4644 (8)	C1—C2	1.3984 (18)
Na1—O1 ⁱ	2.8332 (12)	C1—C6	1.4028 (18)
Na1—O3 ⁱⁱⁱ	2.3534 (11)	C2—C3	1.3888 (19)
Na1—O5 ^{iv}	2.3611 (11)	C3—H3	0.9500
Na1—O6	2.3192 (12)	C3—C4	1.3881 (18)
Na1—O7 ⁱ	2.3890 (11)	C4—C5	1.3920 (19)
Na1—O9	2.2988 (12)	C5—H5	0.9500
Na2—O1	2.5640 (12)	C5—C6	1.3862 (18)
Na2—O4 ^v	2.3223 (11)		
O3—S1—O4	112.09 (6)	O5 ^{vi} —Na2—O9 ^{vii}	170.31 (4)
O3—S1—C4	106.60 (6)	O6 ⁱⁱⁱ —Na2—O1	173.13 (4)
O4—S1—C4	106.06 (6)	O6 ⁱⁱⁱ —Na2—O9 ^{vii}	86.67 (4)
O5—S1—O3	112.43 (6)	O8—Na2—O1	76.54 (4)
O5—S1—O4	112.76 (6)	O8—Na2—O4 ^v	158.38 (4)
O5—S1—C4	106.31 (6)	O8—Na2—O5 ^{vi}	101.35 (4)
O6—S2—Na2	145.86 (4)	O8—Na2—O6 ⁱⁱⁱ	98.43 (4)
O6—S2—O7	112.01 (6)	O8—Na2—O9 ^{vii}	76.69 (4)
O6—S2—C6	105.63 (6)	O9 ^{vii} —Na2—O1	96.58 (4)
O7—S2—Na2	90.76 (4)	Na1 ^{vii} —O1—H1	92.7 (16)
O7—S2—C6	106.48 (6)	Na2—O1—Na1 ^{vii}	77.18 (3)
O8—S2—Na2	33.02 (4)	Na2—O1—H1	127.7 (15)
O8—S2—O6	112.87 (6)	C1—O1—Na1 ^{vii}	129.01 (8)
O8—S2—O7	113.86 (6)	C1—O1—Na2	119.61 (8)

O8—S2—C6	105.17 (6)	C1—O1—H1	106.6 (15)
C6—S2—Na2	90.81 (5)	C2—O2—H2	109.5
Na2 ⁱ —Na1—Na2 ⁱⁱ	170.83 (3)	S1—O3—Na1 ⁱⁱ	135.50 (6)
O1 ⁱ —Na1—Na2 ⁱ	47.83 (2)	S1—O4—Na2 ^{viii}	128.53 (6)
O1 ⁱ —Na1—Na2 ⁱⁱ	123.18 (3)	S1—O5—Na1 ^{ix}	128.93 (6)
O3 ⁱⁱⁱ —Na1—Na2 ⁱⁱ	101.78 (3)	S1—O5—Na2 ^{vi}	131.35 (6)
O3 ⁱⁱⁱ —Na1—Na2 ⁱ	76.14 (3)	Na2 ^{vi} —O5—Na1 ^{ix}	95.57 (4)
O3 ⁱⁱⁱ —Na1—O1 ⁱ	80.89 (4)	S2—O6—Na1	127.43 (6)
O3 ⁱⁱⁱ —Na1—O5 ^{iv}	89.31 (4)	S2—O6—Na2 ⁱⁱ	133.57 (6)
O3 ⁱⁱⁱ —Na1—O7 ⁱ	149.34 (4)	Na1—O6—Na2 ⁱⁱ	96.41 (4)
O5 ^{iv} —Na1—Na2 ⁱ	129.11 (3)	S2—O7—Na1 ^{vii}	128.04 (6)
O5 ^{iv} —Na1—Na2 ⁱⁱ	41.72 (3)	S2—O8—Na2	126.83 (6)
O5 ^{iv} —Na1—O1 ⁱ	82.09 (4)	Na1—O9—Na2 ⁱ	91.54 (4)
O5 ^{iv} —Na1—O7 ⁱ	95.13 (4)	Na1—O9—H9A	112.4 (19)
O6—Na1—Na2 ⁱⁱ	41.89 (3)	Na1—O9—H9B	134.7 (18)
O6—Na1—Na2 ⁱ	147.21 (3)	Na2 ⁱ —O9—H9A	107.1 (19)
O6—Na1—O1 ⁱ	164.68 (4)	Na2 ⁱ —O9—H9B	96.3 (19)
O6—Na1—O3 ⁱⁱⁱ	103.94 (4)	H9A—O9—H9B	108 (2)
O6—Na1—O5 ^{iv}	83.43 (4)	O1—C1—C2	120.94 (12)
O6—Na1—O7 ⁱ	106.70 (4)	O1—C1—C6	119.63 (12)
O7 ⁱ —Na1—Na2 ⁱⁱ	101.61 (3)	C2—C1—C6	119.42 (12)
O7 ⁱ —Na1—Na2 ⁱ	77.60 (3)	O2—C2—C1	120.95 (12)
O7 ⁱ —Na1—O1 ⁱ	69.77 (3)	O2—C2—C3	119.09 (12)
O9—Na1—Na2 ⁱⁱ	143.62 (4)	C3—C2—C1	119.93 (12)
O9—Na1—Na2 ⁱ	45.51 (3)	C2—C3—H3	120.2
O9—Na1—O1 ⁱ	92.07 (4)	C4—C3—C2	119.66 (12)
O9—Na1—O3 ⁱⁱⁱ	91.64 (4)	C4—C3—H3	120.2
O9—Na1—O5 ^{iv}	173.87 (4)	C3—C4—S1	120.12 (10)
O9—Na1—O6	102.21 (4)	C3—C4—C5	121.34 (12)
O9—Na1—O7 ⁱ	80.99 (4)	C5—C4—S1	118.52 (10)
O4 ^v —Na2—O1	93.11 (4)	C4—C5—H5	120.6
O4 ^v —Na2—O6 ⁱⁱⁱ	93.16 (4)	C6—C5—C4	118.76 (12)
O4 ^v —Na2—O9 ^{vii}	85.88 (4)	C6—C5—H5	120.6
O5 ^{vi} —Na2—O1	92.13 (4)	C1—C6—S2	119.47 (10)
O5 ^{vi} —Na2—O4 ^v	97.91 (4)	C5—C6—S2	119.74 (10)
O5 ^{vi} —Na2—O6 ⁱⁱⁱ	84.23 (4)	C5—C6—C1	120.76 (12)
S1—C4—C5—C6	−179.90 (10)	O6—S2—C6—C1	−178.85 (11)
Na1 ^{vii} —O1—C1—C2	141.05 (10)	O6—S2—C6—C5	−0.93 (12)
Na1 ^{vii} —O1—C1—C6	−40.13 (17)	O7—S2—O6—Na1	−148.47 (7)
Na2—S2—O6—Na1	−20.03 (12)	O7—S2—O6—Na2 ⁱⁱ	8.76 (10)
Na2—S2—O6—Na2 ⁱⁱ	137.20 (6)	O7—S2—O8—Na2	−49.16 (9)
Na2—S2—O7—Na1 ^{vii}	11.89 (7)	O7—S2—C6—C1	61.90 (12)
Na2—S2—C6—C1	−29.14 (11)	O7—S2—C6—C5	−120.18 (11)
Na2—S2—C6—C5	148.78 (11)	O8—S2—O6—Na1	−18.39 (9)
Na2—O1—C1—C2	−121.37 (12)	O8—S2—O6—Na2 ⁱⁱ	138.85 (8)
Na2—O1—C1—C6	57.45 (15)	O8—S2—O7—Na1 ^{vii}	36.24 (9)
O1—C1—C2—O2	0.4 (2)	O8—S2—C6—C1	−59.25 (12)

O1—C1—C2—C3	−177.37 (12)	O8—S2—C6—C5	118.67 (11)
O1—C1—C6—S2	−4.63 (17)	C1—C2—C3—C4	−1.2 (2)
O1—C1—C6—C5	177.47 (12)	C2—C1—C6—S2	174.21 (10)
O2—C2—C3—C4	−179.04 (12)	C2—C1—C6—C5	−3.7 (2)
O3—S1—O4—Na2 ^{viii}	35.85 (9)	C2—C3—C4—S1	−179.94 (10)
O3—S1—O5—Na1 ^{ix}	13.55 (9)	C2—C3—C4—C5	−1.6 (2)
O3—S1—O5—Na2 ^{vi}	−137.77 (7)	C3—C4—C5—C6	1.7 (2)
O3—S1—C4—C3	−121.82 (11)	C4—S1—O3—Na1 ⁱⁱ	−132.68 (8)
O3—S1—C4—C5	59.75 (12)	C4—S1—O4—Na2 ^{viii}	151.80 (7)
O4—S1—O3—Na1 ⁱⁱ	−17.06 (10)	C4—S1—O5—Na1 ^{ix}	−102.73 (8)
O4—S1—O5—Na1 ^{ix}	141.46 (7)	C4—S1—O5—Na2 ^{vi}	105.95 (8)
O4—S1—O5—Na2 ^{vi}	−9.86 (10)	C4—C5—C6—S2	−176.94 (10)
O4—S1—C4—C3	118.57 (11)	C4—C5—C6—C1	1.0 (2)
O4—S1—C4—C5	−59.86 (12)	C6—S2—O6—Na1	96.00 (8)
O5—S1—O3—Na1 ⁱⁱ	111.21 (9)	C6—S2—O6—Na2 ⁱⁱ	−106.76 (8)
O5—S1—O4—Na2 ^{viii}	−92.24 (8)	C6—S2—O7—Na1 ^{vii}	−79.18 (8)
O5—S1—C4—C3	−1.68 (13)	C6—S2—O8—Na2	67.03 (8)
O5—S1—C4—C5	179.89 (10)	C6—C1—C2—O2	−178.42 (12)
O6—S2—O7—Na1 ^{vii}	165.81 (6)	C6—C1—C2—C3	3.8 (2)
O6—S2—O8—Na2	−178.30 (6)		

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 $\cdots$ O3 ^x	0.82 (2)	2.05 (2)	2.8256 (15)	156 (2)
O2—H2 $\cdots$ O4 ^{vi}	0.84	1.98	2.8145 (14)	169
O9—H9A $\cdots$ O2 ^{vi}	0.82 (3)	2.18 (3)	2.9904 (15)	173 (3)
O9—H9B $\cdots$ O7 ^{xi}	0.80 (3)	2.14 (3)	2.8975 (15)	158 (3)

Symmetry codes: (vi) $-x+1, -y+1, -z+1$; (x) $-x+2, -y+1, -z+1$; (xi) $x-1, y, z$.

Diammonium 4,5-dihydroxybenzene-1,3-disulfonate monohydrate (NH₄Tiron)

Crystal data

$2\text{NH}_4^+\cdot\text{C}_6\text{H}_4\text{O}_8\text{S}_2^{2-}\cdot\text{H}_2\text{O}$

$M_r = 322.31$

Orthorhombic, $Pbca$

$a = 6.5023$ (15) $\text{\AA}$

$b = 18.779$ (4) $\text{\AA}$

$c = 20.236$ (4) $\text{\AA}$

$V = 2470.9$ (9) $\text{\AA}^3$

$Z = 8$

$F(000) = 1344$

$D_x = 1.733$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ $\text{\AA}$

Cell parameters from 511 reflections

$\theta = 3.0\text{--}21.0^\circ$

$\mu = 0.48$ mm^{-1}

$T = 100$ K

Plank, colorless

$0.10 \times 0.05 \times 0.04$ mm

Data collection

Bruker APEXII

diffractometer

Radiation source: sealed tube

Graphite monochromator

Detector resolution: 8.333 pixels mm^{-1}

ω and ϕ scans

Absorption correction: multi-scan

(SADABS; Bruker, 2014)

$T_{\min} = 0.663$, $T_{\max} = 0.746$
 12544 measured reflections
 2255 independent reflections
 1354 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.147$

$\theta_{\max} = 25.3^\circ$, $\theta_{\min} = 2.0^\circ$
 $h = -7 \rightarrow 7$
 $k = -22 \rightarrow 22$
 $l = -15 \rightarrow 24$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.127$
 $S = 1.01$
 2255 reflections
 204 parameters
 23 restraints

Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0411P)^2 + 0.6346P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.42 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.53 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.29066 (17)	0.42273 (6)	0.34618 (5)	0.0132 (3)
S2	0.26230 (17)	0.69952 (6)	0.42150 (6)	0.0154 (3)
O1	0.2580 (5)	0.72630 (16)	0.27192 (15)	0.0216 (8)
H1	0.224751	0.751861	0.304271	0.032*
O2	0.2771 (5)	0.62901 (17)	0.17777 (13)	0.0175 (7)
H2	0.270116	0.594058	0.151957	0.026*
O3	0.0895 (5)	0.41015 (16)	0.37651 (14)	0.0184 (8)
O4	0.4555 (5)	0.41571 (16)	0.39574 (14)	0.0152 (7)
O5	0.3278 (5)	0.38099 (17)	0.28738 (14)	0.0199 (8)
O6	0.2038 (5)	0.66240 (16)	0.48126 (15)	0.0193 (8)
O7	0.4689 (5)	0.72999 (17)	0.42551 (15)	0.0209 (8)
O8	0.1134 (5)	0.75262 (17)	0.39943 (16)	0.0234 (8)
C1	0.2691 (7)	0.6571 (2)	0.2915 (2)	0.0127 (10)
C2	0.2800 (7)	0.6052 (3)	0.2418 (2)	0.0152 (11)
C3	0.2921 (7)	0.5343 (2)	0.2580 (2)	0.0129 (10)
H3	0.301928	0.499446	0.224165	0.015*
C4	0.2901 (7)	0.5134 (2)	0.3242 (2)	0.0119 (10)
C5	0.2797 (7)	0.5640 (2)	0.3741 (2)	0.0138 (10)
H5	0.279726	0.549780	0.419125	0.017*
C6	0.2694 (6)	0.6352 (2)	0.3576 (2)	0.0115 (9)
O9	0.7831 (5)	0.51345 (17)	0.41197 (17)	0.0209 (8)
H9A	0.883 (5)	0.487 (2)	0.401 (2)	0.031*
H9B	0.684 (5)	0.483 (2)	0.410 (2)	0.031*
N1	0.7375 (6)	0.8117 (2)	0.34433 (18)	0.0172 (9)
H1A	0.853 (4)	0.829 (2)	0.3686 (17)	0.026*

H1B	0.707 (6)	0.8458 (17)	0.3109 (15)	0.026*
H1C	0.762 (6)	0.7691 (14)	0.3204 (17)	0.026*
H1D	0.620 (4)	0.804 (2)	0.3718 (16)	0.026*
N2	0.7621 (6)	0.6433 (2)	0.49080 (17)	0.0159 (9)
H2A	0.767 (6)	0.5981 (13)	0.4675 (17)	0.024*
H2B	0.673 (5)	0.6738 (18)	0.4648 (16)	0.024*
H2C	0.895 (4)	0.664 (2)	0.4954 (19)	0.024*
H2D	0.698 (6)	0.634 (2)	0.5323 (12)	0.024*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0118 (5)	0.0115 (6)	0.0162 (6)	0.0002 (5)	−0.0002 (5)	−0.0014 (5)
S2	0.0156 (6)	0.0120 (6)	0.0186 (6)	0.0004 (5)	−0.0001 (5)	−0.0024 (5)
O1	0.028 (2)	0.0126 (18)	0.0244 (18)	0.0027 (16)	0.0000 (17)	−0.0008 (14)
O2	0.0188 (18)	0.0202 (19)	0.0135 (15)	0.0027 (16)	0.0001 (15)	0.0018 (14)
O3	0.0134 (18)	0.016 (2)	0.0258 (18)	−0.0042 (14)	0.0062 (14)	0.0024 (15)
O4	0.0136 (17)	0.0127 (19)	0.0194 (16)	0.0014 (14)	−0.0035 (13)	0.0004 (14)
O5	0.032 (2)	0.0115 (18)	0.0158 (17)	0.0028 (15)	−0.0010 (15)	−0.0042 (14)
O6	0.024 (2)	0.0156 (19)	0.0185 (17)	0.0012 (15)	0.0059 (15)	−0.0035 (14)
O7	0.0184 (18)	0.020 (2)	0.0239 (18)	−0.0051 (14)	0.0004 (15)	−0.0033 (15)
O8	0.022 (2)	0.019 (2)	0.0291 (18)	0.0111 (16)	−0.0067 (17)	0.0004 (16)
C1	0.006 (2)	0.011 (2)	0.021 (2)	0.0002 (19)	0.005 (2)	0.0040 (19)
C2	0.008 (2)	0.021 (3)	0.016 (2)	−0.002 (2)	−0.006 (2)	0.005 (2)
C3	0.011 (2)	0.013 (2)	0.014 (2)	0.002 (2)	0.0008 (19)	−0.005 (2)
C4	0.009 (2)	0.008 (3)	0.018 (2)	−0.0018 (19)	−0.002 (2)	0.0014 (19)
C5	0.008 (2)	0.017 (3)	0.017 (2)	−0.001 (2)	−0.0017 (19)	0.004 (2)
C6	0.006 (2)	0.011 (2)	0.017 (2)	−0.0003 (18)	−0.001 (2)	0.0023 (19)
O9	0.0136 (18)	0.020 (2)	0.0290 (19)	−0.0020 (15)	−0.0015 (16)	−0.0015 (16)
N1	0.014 (2)	0.018 (2)	0.019 (2)	−0.0015 (18)	−0.0003 (19)	−0.0002 (18)
N2	0.019 (2)	0.015 (2)	0.014 (2)	0.0006 (19)	0.0029 (19)	0.0010 (17)

Geometric parameters ($\text{\AA}$, $^\circ$)

S1—O3	1.464 (3)	C3—H3	0.9500
S1—O4	1.474 (3)	C3—C4	1.396 (6)
S1—O5	1.445 (3)	C4—C5	1.388 (6)
S1—C4	1.760 (4)	C5—H5	0.9500
S2—O6	1.447 (3)	C5—C6	1.378 (6)
S2—O7	1.462 (3)	O9—H9A	0.849 (19)
S2—O8	1.460 (3)	O9—H9B	0.861 (19)
S2—C6	1.770 (4)	N1—H1A	0.951 (18)
O1—H1	0.8400	N1—H1B	0.954 (17)
O1—C1	1.361 (5)	N1—H1C	0.949 (17)
O2—H2	0.8400	N1—H1D	0.956 (17)
O2—C2	1.370 (5)	N2—H2A	0.972 (17)
C1—C2	1.402 (6)	N2—H2B	0.969 (17)
C1—C6	1.401 (6)	N2—H2C	0.948 (17)

C2—C3	1.373 (6)	N2—H2D	0.955 (17)
O3—S1—O4	110.49 (18)	C3—C4—S1	121.0 (3)
O3—S1—C4	105.1 (2)	C5—C4—S1	118.6 (3)
O4—S1—C4	105.1 (2)	C5—C4—C3	120.4 (4)
O5—S1—O3	114.01 (19)	C4—C5—H5	120.3
O5—S1—O4	112.96 (19)	C6—C5—C4	119.4 (4)
O5—S1—C4	108.5 (2)	C6—C5—H5	120.3
O6—S2—O7	112.6 (2)	C1—C6—S2	119.8 (3)
O6—S2—O8	114.2 (2)	C5—C6—S2	119.1 (3)
O6—S2—C6	106.75 (19)	C5—C6—C1	121.0 (4)
O7—S2—C6	106.47 (19)	H9A—O9—H9B	100 (3)
O8—S2—O7	111.0 (2)	H1A—N1—H1B	108 (3)
O8—S2—C6	105.1 (2)	H1A—N1—H1C	114 (3)
C1—O1—H1	109.5	H1A—N1—H1D	112 (3)
C2—O2—H2	109.5	H1B—N1—H1C	104 (3)
O1—C1—C2	117.3 (4)	H1B—N1—H1D	110 (3)
O1—C1—C6	123.9 (4)	H1C—N1—H1D	108 (3)
C6—C1—C2	118.8 (4)	H2A—N2—H2B	106 (3)
O2—C2—C1	116.8 (4)	H2A—N2—H2C	112 (3)
O2—C2—C3	122.9 (4)	H2A—N2—H2D	106 (3)
C3—C2—C1	120.3 (4)	H2B—N2—H2C	111 (3)
C2—C3—H3	119.9	H2B—N2—H2D	109 (3)
C2—C3—C4	120.1 (4)	H2C—N2—H2D	113 (3)
C4—C3—H3	119.9		
S1—C4—C5—C6	−177.0 (3)	O7—S2—C6—C1	−76.0 (4)
O1—C1—C2—O2	−0.4 (6)	O7—S2—C6—C5	102.6 (4)
O1—C1—C2—C3	179.8 (4)	O8—S2—C6—C1	41.9 (4)
O1—C1—C6—S2	−1.8 (6)	O8—S2—C6—C5	−139.5 (4)
O1—C1—C6—C5	179.6 (4)	C1—C2—C3—C4	1.1 (6)
O2—C2—C3—C4	−178.6 (4)	C2—C1—C6—S2	178.4 (3)
O3—S1—C4—C3	−112.9 (4)	C2—C1—C6—C5	−0.2 (6)
O3—S1—C4—C5	64.7 (4)	C2—C3—C4—S1	176.4 (4)
O4—S1—C4—C3	130.5 (4)	C2—C3—C4—C5	−1.2 (7)
O4—S1—C4—C5	−51.9 (4)	C3—C4—C5—C6	0.6 (6)
O5—S1—C4—C3	9.4 (4)	C4—C5—C6—S2	−178.5 (3)
O5—S1—C4—C5	−173.0 (3)	C4—C5—C6—C1	0.1 (6)
O6—S2—C6—C1	163.6 (3)	C6—C1—C2—O2	179.3 (4)
O6—S2—C6—C5	−17.8 (4)	C6—C1—C2—C3	−0.4 (6)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O1—H1 $\cdots$ O5 ⁱ	0.84	2.47	2.974 (4)	119
O1—H1 $\cdots$ O8	0.84	2.06	2.790 (4)	146
O2—H2 $\cdots$ O9 ⁱⁱ	0.84	1.99	2.830 (5)	174
O9—H9A $\cdots$ O3 ⁱⁱⁱ	0.85 (2)	2.03 (2)	2.871 (5)	171 (5)

O9—H9B···O4	0.86 (2)	1.97 (2)	2.831 (4)	174 (5)
N1—H1A···O4 ^{iv}	0.95 (2)	2.13 (3)	2.980 (5)	148 (3)
N1—H1A···O8 ⁱⁱⁱ	0.95 (2)	2.30 (4)	2.907 (5)	121 (3)
N1—H1B···O5 ^v	0.95 (2)	2.11 (2)	2.996 (5)	155 (3)
N1—H1C···O1 ^{vi}	0.95 (2)	2.03 (3)	2.850 (5)	143 (3)
N1—H1C···O2 ^{vi}	0.95 (2)	2.63 (3)	3.470 (5)	147 (3)
N1—H1D···O3 ⁱ	0.96 (2)	2.41 (4)	2.891 (5)	111 (3)
N1—H1D···O7	0.96 (2)	2.02 (3)	2.847 (5)	143 (3)
N2—H2A···O9	0.97 (2)	1.95 (2)	2.917 (5)	174 (3)
N2—H2B···O7	0.97 (2)	1.87 (2)	2.834 (5)	171 (3)
N2—H2C···O6 ⁱⁱⁱ	0.95 (2)	2.03 (3)	2.901 (5)	152 (3)
N2—H2C···O7 ^{vii}	0.95 (2)	2.60 (3)	3.215 (5)	123 (3)
N2—H2D···O3 ^{viii}	0.96 (2)	2.45 (4)	3.025 (5)	119 (3)
N2—H2D···O4 ^{viii}	0.96 (2)	1.99 (2)	2.916 (5)	161 (3)
N2—H2D···O8 ^{vii}	0.96 (2)	2.60 (4)	3.113 (5)	114 (3)

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

μ -4,5-Dihydroxybenzene-1,3-disulfonato-bis[aqualithium(I)] hemihydrate (LiTiron)

Crystal data

[Li₂(C₆H₄O₈S₂)(H₂O)₂]₂·H₂O

$M_r = 654.26$

Monoclinic, $P2_1/n$

$a = 9.5847$ (18) Å

$b = 7.4498$ (15) Å

$c = 17.599$ (4) Å

$\beta = 102.997$ (4)°

$V = 1224.5$ (4) Å³

$Z = 2$

$F(000) = 668$

$D_x = 1.775$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3529 reflections

$\theta = 2.2\text{--}27.8^\circ$

$\mu = 0.49$ mm⁻¹

$T = 100$ K

Plank, colourless

$0.24 \times 0.09 \times 0.04$ mm

Data collection

Bruker APEXII

diffractometer

Radiation source: sealed tube

Graphite monochromator

Detector resolution: 8.333 pixels mm⁻¹

ω and φ scans

Absorption correction: multi-scan

(SADABS; Bruker, 2014)

$T_{\min} = 0.670$, $T_{\max} = 0.746$

15864 measured reflections

2851 independent reflections

2313 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.049$

$\theta_{\max} = 27.9^\circ$, $\theta_{\min} = 2.2^\circ$

$h = -12 \rightarrow 12$

$k = -9 \rightarrow 9$

$l = -23 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.100$

$S = 1.02$

2851 reflections

217 parameters

18 restraints

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 1.2637P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.44$ e Å⁻³

$\Delta\rho_{\min} = -0.48$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
S1	0.32410 (6)	0.37552 (7)	0.67254 (3)	0.01367 (14)	
S2	0.20642 (6)	0.24170 (8)	0.35997 (3)	0.01575 (15)	
O1	0.5203 (2)	0.1795 (3)	0.38983 (11)	0.0257 (5)	0.892 (3)
H1	0.610071	0.172739	0.400448	0.039*	0.892 (3)
O1A	0.6234 (16)	0.305 (2)	0.6540 (9)	0.0257 (5)	0.108 (3)
H1A	0.616503	0.223206	0.685965	0.039*	0.108 (3)
O2	0.71321 (17)	0.2031 (3)	0.52616 (10)	0.0267 (4)	
H2	0.763939	0.215385	0.571438	0.040*	
O3	0.32479 (17)	0.2061 (2)	0.71493 (9)	0.0185 (4)	
O4	0.17924 (16)	0.4482 (2)	0.64770 (9)	0.0173 (3)	
O5	0.42396 (17)	0.5036 (2)	0.71657 (9)	0.0215 (4)	
O6	0.06889 (17)	0.2875 (2)	0.37599 (10)	0.0221 (4)	
O7	0.2162 (2)	0.0587 (3)	0.33493 (11)	0.0390 (5)	
O8	0.24746 (18)	0.3710 (3)	0.30624 (10)	0.0309 (5)	
O9	−0.21479 (18)	0.1015 (2)	0.37158 (10)	0.0233 (4)	
H9A	−0.241410	0.013821	0.342640	0.044*	
H9B	−0.166840	0.058560	0.410700	0.044*	
O11	0.4064 (3)	0.1930 (4)	0.1751 (3)	0.0238 (11)	0.751 (12)
H11A	0.487329	0.164550	0.168051	0.025*	0.751 (12)
H11B	0.366160	0.103101	0.187910	0.025*	0.751 (12)
O11A	0.4377 (10)	0.1619 (13)	0.2239 (10)	0.028 (3)	0.249 (12)
H11C	0.396660	0.068010	0.203321	0.034*	0.249 (12)
H11D	0.483500	0.127750	0.269549	0.034*	0.249 (12)
C1	0.4755 (2)	0.2263 (3)	0.45422 (13)	0.0154 (5)	
H1B	0.506816	0.192678	0.408715	0.018*	0.108 (3)
C2	0.5738 (2)	0.2393 (3)	0.52645 (14)	0.0175 (5)	
C3	0.5268 (2)	0.2844 (3)	0.59252 (14)	0.0169 (5)	
H3	0.592517	0.288774	0.641732	0.020*	0.892 (3)
C4	0.3821 (2)	0.3237 (3)	0.58686 (13)	0.0138 (4)	
C5	0.2839 (2)	0.3139 (3)	0.51595 (13)	0.0134 (4)	
H5	0.185883	0.341503	0.512466	0.016*	
C6	0.3312 (2)	0.2633 (3)	0.45013 (13)	0.0136 (4)	
Li1	−0.1315 (4)	0.3045 (5)	0.3289 (2)	0.0188 (8)	
Li2	0.3913 (4)	0.3966 (6)	0.2447 (2)	0.0224 (9)	
O10	0.011 (6)	−0.038 (9)	0.478 (3)	0.045 (5)	0.20 (5)
H10A	0.057700	−0.123691	0.468720	0.068*	0.20 (5)
H10B	0.066210	0.054340	0.453980	0.068*	0.20 (5)
O10A	0.005 (4)	0.042 (6)	0.507 (3)	0.043 (5)	0.30 (5)
H10C	−0.047541	0.116070	0.529981	0.065*	0.30 (5)

H10D	0.045200	0.118550	0.481750	0.065*	0.30 (5)
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Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0148 (3)	0.0123 (3)	0.0136 (3)	−0.0003 (2)	0.00248 (19)	−0.0012 (2)
S2	0.0166 (3)	0.0155 (3)	0.0143 (3)	0.0031 (2)	0.0016 (2)	−0.0006 (2)
O1	0.0209 (10)	0.0374 (12)	0.0215 (10)	0.0025 (8)	0.0105 (8)	−0.0048 (9)
O1A	0.0209 (10)	0.0374 (12)	0.0215 (10)	0.0025 (8)	0.0105 (8)	−0.0048 (9)
O2	0.0141 (8)	0.0442 (12)	0.0219 (9)	0.0071 (7)	0.0043 (7)	−0.0002 (8)
O3	0.0265 (9)	0.0134 (8)	0.0154 (8)	0.0007 (6)	0.0044 (6)	0.0024 (6)
O4	0.0166 (8)	0.0183 (8)	0.0169 (8)	0.0014 (6)	0.0035 (6)	−0.0019 (7)
O5	0.0208 (9)	0.0214 (9)	0.0218 (9)	−0.0054 (7)	0.0035 (7)	−0.0074 (7)
O6	0.0158 (8)	0.0316 (10)	0.0187 (9)	−0.0009 (7)	0.0034 (6)	−0.0021 (7)
O7	0.0451 (12)	0.0210 (10)	0.0378 (12)	0.0131 (8)	−0.0185 (9)	−0.0163 (9)
O8	0.0236 (9)	0.0469 (12)	0.0239 (10)	0.0088 (8)	0.0085 (7)	0.0187 (9)
O9	0.0293 (9)	0.0184 (9)	0.0220 (9)	−0.0009 (7)	0.0051 (7)	0.0004 (7)
O11	0.0168 (13)	0.0183 (13)	0.037 (3)	−0.0016 (9)	0.0070 (14)	−0.0075 (14)
O11A	0.023 (4)	0.025 (4)	0.036 (8)	−0.004 (3)	0.007 (4)	−0.011 (4)
C1	0.0183 (11)	0.0116 (11)	0.0182 (12)	0.0011 (8)	0.0082 (9)	0.0009 (9)
C2	0.0121 (10)	0.0165 (11)	0.0245 (13)	0.0023 (8)	0.0052 (9)	0.0012 (10)
C3	0.0157 (11)	0.0151 (12)	0.0188 (12)	−0.0001 (8)	0.0014 (9)	0.0005 (9)
C4	0.0172 (11)	0.0092 (10)	0.0154 (11)	−0.0010 (8)	0.0046 (8)	0.0009 (8)
C5	0.0130 (10)	0.0107 (10)	0.0168 (11)	0.0003 (8)	0.0042 (8)	−0.0009 (9)
C6	0.0160 (11)	0.0110 (10)	0.0134 (11)	−0.0017 (8)	0.0023 (8)	0.0009 (8)
Li1	0.021 (2)	0.0144 (19)	0.019 (2)	−0.0001 (15)	0.0005 (15)	0.0006 (16)
Li2	0.020 (2)	0.022 (2)	0.025 (2)	−0.0026 (16)	0.0045 (16)	0.0007 (17)
O10	0.042 (8)	0.050 (6)	0.049 (13)	0.010 (7)	0.023 (8)	0.020 (10)
O10A	0.040 (7)	0.050 (6)	0.047 (12)	0.008 (6)	0.024 (7)	0.020 (9)

Geometric parameters ($\text{\AA}$, $^\circ$)

S1—O3	1.4655 (17)	O9—H9B	0.8033 (17)
S1—O4	1.4626 (16)	O9—Li1	1.939 (4)
S1—O5	1.4466 (16)	O11—H11A	0.840 (2)
S1—C4	1.764 (2)	O11—H11B	0.829 (3)
S1—Li1 ⁱ	3.012 (4)	O11—Li2	1.975 (5)
S1—Li1 ⁱⁱ	3.005 (4)	O11A—H11C	0.843 (8)
S2—O6	1.4493 (17)	O11A—H11D	0.862 (18)
S2—O7	1.4422 (19)	O11A—Li2	1.861 (9)
S2—O8	1.4642 (19)	C1—H1B	0.9500
S2—C6	1.766 (2)	C1—C2	1.405 (3)
O1—H1	0.8400	C1—C6	1.396 (3)
O1—C1	1.345 (3)	C2—C3	1.380 (3)
O1A—H1A	0.8400	C3—H3	0.9500
O1A—C3	1.265 (16)	C3—C4	1.398 (3)
O2—H2	0.8400	C4—C5	1.386 (3)
O2—C2	1.364 (3)	C5—H5	0.9500

O3—Li1 ⁱⁱ	1.957 (4)	C5—C6	1.388 (3)
O4—Li1 ⁱ	1.964 (4)	Li2—H11D	2.193 (4)
O5—Li2 ⁱⁱⁱ	1.900 (4)	O10—H10A	0.81 (6)
O6—Li1	1.917 (4)	O10—H10B	1.02 (6)
O7—Li2 ^{iv}	1.958 (5)	O10A—H10C	0.90 (5)
O8—Li2	1.945 (5)	O10A—H10D	0.86 (4)
O9—H9A	0.8323 (17)		
O3—S1—C4	106.28 (10)	O2—C2—C3	123.8 (2)
O3—S1—Li1 ⁱ	128.22 (11)	C3—C2—C1	120.0 (2)
O4—S1—O3	111.49 (10)	O1A—C3—C2	115.8 (7)
O4—S1—C4	106.64 (10)	O1A—C3—C4	124.0 (7)
O4—S1—Li1 ⁱⁱ	111.62 (10)	C2—C3—H3	120.1
O5—S1—O3	111.63 (10)	C2—C3—C4	119.8 (2)
O5—S1—O4	112.66 (10)	C4—C3—H3	120.1
O5—S1—C4	107.73 (10)	C3—C4—S1	118.89 (17)
C4—S1—Li1 ⁱ	118.47 (11)	C5—C4—S1	120.01 (16)
C4—S1—Li1 ⁱⁱ	132.73 (11)	C5—C4—C3	121.0 (2)
Li1 ⁱⁱ —S1—Li1 ⁱ	108.75 (7)	C4—C5—H5	120.6
O6—S2—O8	111.04 (10)	C4—C5—C6	118.8 (2)
O6—S2—C6	105.40 (10)	C6—C5—H5	120.6
O7—S2—O6	113.98 (12)	C1—C6—S2	119.42 (17)
O7—S2—O8	112.28 (13)	C5—C6—S2	119.48 (17)
O7—S2—C6	106.44 (10)	C5—C6—C1	121.1 (2)
O8—S2—C6	107.11 (11)	S1 ^v —Li1—S1 ⁱ	112.65 (12)
C1—O1—H1	109.5	O3 ^v —Li1—S1 ⁱ	91.92 (14)
C3—O1A—H1A	109.5	O3 ^v —Li1—O4 ⁱ	104.25 (19)
C2—O2—H2	109.5	O4 ⁱ —Li1—S1 ^v	128.23 (18)
S1—O3—Li1 ⁱⁱⁱ	122.14 (15)	O6—Li1—S1 ⁱ	127.50 (18)
S1—O4—Li1 ⁱ	122.34 (15)	O6—Li1—S1 ^v	106.74 (17)
S1—O5—Li2 ⁱⁱⁱ	154.32 (17)	O6—Li1—O3 ^v	113.8 (2)
S2—O6—Li1	142.95 (17)	O6—Li1—O4 ⁱ	103.28 (19)
S2—O7—Li2 ^{iv}	137.88 (16)	O6—Li1—O9	103.95 (19)
S2—O8—Li2	138.70 (17)	O9—Li1—S1 ⁱ	108.40 (17)
H9A—O9—H9B	104.44 (18)	O9—Li1—S1 ^v	91.18 (15)
Li1—O9—H9A	118.14 (19)	O9—Li1—O3 ^v	110.7 (2)
Li1—O9—H9B	115.87 (18)	O9—Li1—O4 ⁱ	121.0 (2)
H11A—O11—H11B	109.7 (3)	O5 ⁱⁱⁱ —Li2—O7 ^{vi}	108.3 (2)
Li2—O11—H11A	119.0 (3)	O5 ⁱⁱⁱ —Li2—O8	124.0 (2)
Li2—O11—H11B	110.4 (4)	O5 ⁱⁱⁱ —Li2—O11	109.3 (2)
H11C—O11A—H11D	104.3 (14)	O7 ^{vi} —Li2—O11	97.5 (2)
Li2—O11A—H11C	139.0 (10)	O8—Li2—O7 ^{vi}	97.7 (2)
Li2—O11A—H11D	100.9 (8)	O8—Li2—O11	115.5 (2)
O1—C1—C2	120.3 (2)	O11A—Li2—O5 ⁱⁱⁱ	101.2 (3)
O1—C1—C6	120.5 (2)	O11A—Li2—O7 ^{vi}	123.3 (6)
C2—C1—H1B	120.4	O11A—Li2—O8	104.4 (4)
C6—C1—H1B	120.4	H10A—O10—H10B	95 (5)
C6—C1—C2	119.2 (2)	H10C—O10A—H10D	101 (4)

O2—C2—C1	116.2 (2)		
S1—C4—C5—C6	−176.51 (16)	O8—S2—O6—Li1	66.9 (3)
O1—C1—C2—O2	0.3 (3)	O8—S2—O7—Li2 ^{iv}	−74.8 (3)
O1—C1—C2—C3	−178.9 (2)	O8—S2—C6—C1	−62.2 (2)
O1—C1—C6—S2	1.9 (3)	O8—S2—C6—C5	118.80 (18)
O1—C1—C6—C5	−179.2 (2)	C1—C2—C3—O1A	−175.5 (9)
O1A—C3—C4—S1	−9.0 (10)	C1—C2—C3—C4	−2.4 (3)
O1A—C3—C4—C5	174.0 (10)	C2—C1—C6—S2	−178.43 (17)
O2—C2—C3—O1A	5.3 (10)	C2—C1—C6—C5	0.5 (3)
O2—C2—C3—C4	178.4 (2)	C2—C3—C4—S1	178.46 (17)
O3—S1—O4—Li1 ⁱ	127.63 (18)	C2—C3—C4—C5	1.5 (3)
O3—S1—O5—Li2 ⁱⁱⁱ	79.3 (4)	C3—C4—C5—C6	0.4 (3)
O3—S1—C4—C3	−73.21 (19)	C4—S1—O3—Li1 ⁱⁱ	147.14 (17)
O3—S1—C4—C5	103.75 (19)	C4—S1—O4—Li1 ⁱ	−116.77 (18)
O4—S1—O3—Li1 ⁱⁱ	−97.05 (18)	C4—S1—O5—Li2 ⁱⁱⁱ	−37.0 (4)
O4—S1—O5—Li2 ⁱⁱⁱ	−154.4 (4)	C4—C5—C6—S2	177.56 (17)
O4—S1—C4—C3	167.74 (17)	C4—C5—C6—C1	−1.4 (3)
O4—S1—C4—C5	−15.3 (2)	C6—S2—O6—Li1	−177.4 (3)
O5—S1—O3—Li1 ⁱⁱ	29.9 (2)	C6—S2—O7—Li2 ^{iv}	168.3 (3)
O5—S1—O4—Li1 ⁱ	1.2 (2)	C6—S2—O8—Li2	76.1 (3)
O5—S1—C4—C3	46.6 (2)	C6—C1—C2—O2	−179.4 (2)
O5—S1—C4—C5	−136.48 (18)	C6—C1—C2—C3	1.4 (3)
O6—S2—O7—Li2 ^{iv}	52.6 (3)	Li1 ⁱ —S1—O3—Li1 ⁱⁱ	−63.3 (2)
O6—S2—O8—Li2	−169.3 (2)	Li1 ⁱⁱ —S1—O4—Li1 ⁱ	91.57 (15)
O6—S2—C6—C1	179.47 (17)	Li1 ⁱⁱ —S1—O5—Li2 ⁱⁱⁱ	95.4 (4)
O6—S2—C6—C5	0.5 (2)	Li1 ⁱ —S1—O5—Li2 ⁱⁱⁱ	−153.7 (4)
O7—S2—O6—Li1	−61.1 (3)	Li1 ⁱ —S1—C4—C3	133.71 (18)
O7—S2—O8—Li2	−40.4 (3)	Li1 ⁱⁱ —S1—C4—C3	−49.2 (2)
O7—S2—C6—C1	58.1 (2)	Li1 ⁱ —S1—C4—C5	−49.3 (2)
O7—S2—C6—C5	−120.90 (19)	Li1 ⁱⁱ —S1—C4—C5	127.79 (19)

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $x+1/2, -y+1/2, z+1/2$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1/2, y-1/2, -z+1/2$; (v) $x-1/2, -y+1/2, z-1/2$; (vi) $-x+1/2, y+1/2, -z+1/2$.

Hydrogen-bond geometry ($\text{\AA}$, $^\circ$)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O1—H1 $\cdots$ O2	0.84	2.22	2.685 (3)	115
O1—H1 $\cdots$ O9 ^{vii}	0.84	1.93	2.693 (3)	150
O1A—H1A $\cdots$ O8 ⁱⁱ	0.84	2.31	2.978 (17)	136
O2—H2 $\cdots$ O1A	0.84	2.29	2.693 (16)	110
O2—H2 $\cdots$ O7 ^{viii}	0.84	2.60	3.082 (3)	117
O2—H2 $\cdots$ O11 ⁱⁱ	0.84	2.13	2.952 (6)	166
O9—H9A $\cdots$ O3 ^{ix}	0.8323 (17)	1.9961 (16)	2.821 (2)	170.86 (13)
O9—H9B $\cdots$ O10 ^{ix}	0.8033 (17)	2.19 (6)	2.96 (6)	160.0 (18)
O9—H9B $\cdots$ O10	0.8033 (17)	1.98 (6)	2.73 (6)	155.0 (16)
O9—H9B $\cdots$ O10A ^{ix}	0.8033 (17)	2.02 (4)	2.80 (4)	164.8 (14)
O9—H9B $\cdots$ O10A	0.8033 (17)	2.08 (4)	2.83 (4)	156.2 (12)

O11—H11A···O4 ^x	0.840 (2)	2.1244 (16)	2.957 (3)	171.19 (17)
O11—H11B···O8 ^{iv}	0.829 (3)	2.0583 (19)	2.873 (3)	167.4 (4)
O11A—H11C···O6 ^{iv}	0.843 (8)	2.5753 (18)	3.290 (8)	143.3 (5)
O11A—H11C···O8 ^{iv}	0.843 (8)	1.9964 (18)	2.776 (8)	153.2 (8)
O11A—H11D···O1	0.862 (18)	2.1019 (19)	2.851 (17)	145.0 (5)
O10—H10A···O2 ^{viii}	0.81 (6)	2.2562 (16)	2.93 (6)	141 (4)
O10—H10B···O6	1.02 (6)	2.2175 (18)	3.14 (6)	150 (3)
O10A—H10C···O2 ^{xi}	0.90 (5)	2.3694 (16)	3.13 (5)	142 (3)
O10A—H10D···O6	0.86 (4)	2.3000 (17)	3.10 (5)	155 (3)

Symmetry codes: (ii) $x+1/2, -y+1/2, z+1/2$; (iv) $-x+1/2, y-1/2, -z+1/2$; (vii) $x+1, y, z$; (viii) $-x+1, -y, -z+1$; (ix) $-x, -y, -z+1$; (x) $x+1/2, -y+1/2, z-1/2$; (xi) $x-1, y, z$.