



Structures of five salt forms of disulfonated monoazo dyes

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Received 15 August 2020

Accepted 18 September 2020

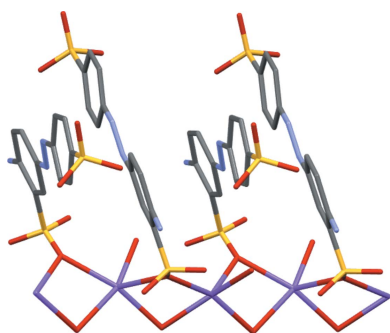
Edited by D. S. Yufit, University of Durham, United Kingdom

Keywords: dyes; salt forms; sulfonates; monoazo; coordination polymers; crystal structure.**CCDC references:** 2032738; 2032737; 2032736; 2032735; 2032734**Supporting information:** this article has supporting information at journals.iucr.org/c

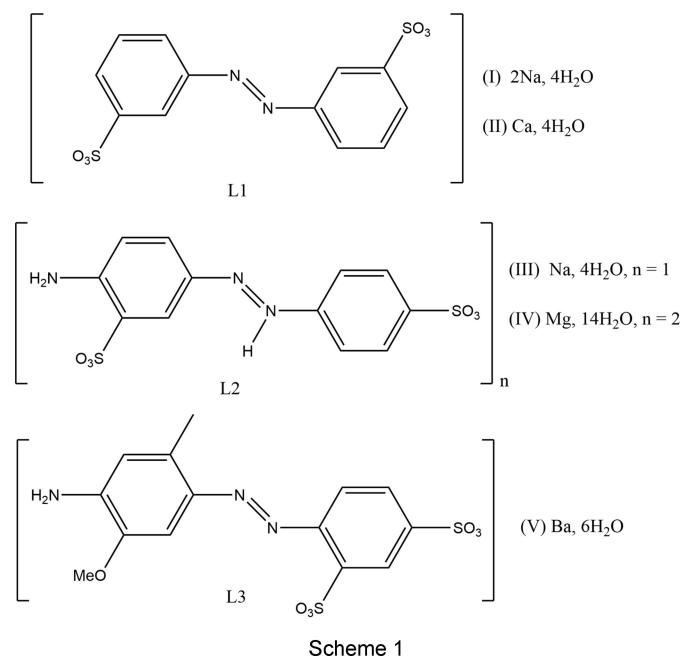
The structures of five *s*-block metal salt forms of three disulfonated monoazo dyes are presented. These are poly[di- μ -aqua-diaqua[μ_4 -3,3'-(diazane-1,2-diyl)-bis(benzenesulfonato)]disodium(I)], [Na₂(C₁₂H₈N₂O₆S₂)(H₂O)₄]_n, (I), *catena*-poly[[tetraaquacalcium(II)]- μ -3,3'-(diazane-1,2-diyl)bis(benzenesulfonato)], [Ca(C₁₂H₈N₂O₆S₂)(H₂O)₄]_n, (II), *catena*-poly[[[diaquacalcium(II)]- μ -2-(4-amino-3-sulfonatophenyl)-1-(4-sulfonatophenyl)diazenium] dihydrate], {[Na(C₁₂H₁₀N₃O₆S₂)(H₂O)₂·2H₂O]_n, (III), hexaaquamagnesium bis[2-(4-amino-3-sulfonatophenyl)-1-(4-sulfonatophenyl)diazenium] octahydrate, [Mg(H₂O)₆](C₁₂H₁₀N₃O₆S₂)₂·8H₂O, (IV), and poly[[[μ_2 -4-[2-(4-amino-2-methyl-5-methoxyphenyl)diazen-1-yl]benzene-1,3-disulfonato]di- μ -aqua-diaquabarium(II)] dihydrate], {[Ba(C₁₄H₁₃N₃O₇S₂)(H₂O)₄·2H₂O]_n, (V). Compound (III) is that obtained on crystallizing the commercial dyestuff Acid Yellow 9 [74543-21-8]. The Mg species is a solvent-separated ion-pair structure and the others are all coordination polymers with bonds from the metal atoms to sulfonate groups. Compound (I) is a three-dimensional coordination polymer, (V) is a two-dimensional coordination polymer and both (II) and (III) are one-dimensional coordination polymers. The coordination behaviour of the azo ligands and the water ligands, the dimensionality of the coordination polymers and the overall packing motifs of these five structures are contrasted to those of monosulfonate monoazo congeners. It is found that (I) and (II) adopt similar structural types to those of monosulfonate species but that the other three structures do not.

1. Introduction

Azo compounds have a long history of use as both dyes and pigments. One of the commonest subclasses is that of sulfonated azo species, where the sulfonate group is typically added to aid water solubility and/or to decrease toxicity (Hunger *et al.*, 2003). Despite being widely referred to as organic colourants, the commercial products of sulfonated azo species are commonly metal complexes and often *s*-block metal salt forms (Christie & Mackay, 2008). Even before large-scale crystallographic studies were available, it was recognized that small structural changes systematically changed the colour and material properties of such dyestuffs (Greenwood *et al.*, 1986). These structure–property relationships led to an interest in more detailed structural investigations. A reasonable number of crystal structures of the salt forms of monosulfonated azo dyes and even pigments are now known (*e.g.* Kennedy *et al.*, 2000, 2004, 2009; Tapmeyer *et al.*, 2020; Aiken *et al.*, 2013). However, far fewer relevant structures of disulfonated azo species are known, despite these being commercially commonplace. The only azobenzene-based disulfonate structures that we are aware of are those of azobenzene-4,4'-disulfonate (Soegiarto & Ward, 2009; Soegiarto *et al.*, 2010,



2011). In these structures, the disulfonate ions are utilized as framework hosts for a series of functional organic guests and thus they are not of particular relevance to commercial colourant materials. Some *s*-block metal salt structures of more complicated disulfonated dyes, with naphthalene- rather than azobenzene-based azo fragments, are also known (*e.g.* Black *et al.*, 2019; Kennedy *et al.*, 2006; Ojala *et al.*, 1994). The azo moiety in all these examples exists in the hydrazone tautomeric form and in all cases both sulfonate groups lie on only one ring system at one end of the azo bond. The only colourant relevant disulfonate structures with sulfonate groups on both the ring systems, at either end of an azo bond, are the Ca lake structures of Pigment Yellow 183 and Pigment Yellow 191 determined by Schmidt and co-workers (Ivashevskaya *et al.*, 2009; Schmidt *et al.*, 2009). These are relatively complex materials with pyrazolone groups between the two sulfonated aryl rings. Herein we present five new structures of *s*-block metal salt forms of azobenzene disulfonate derivatives (Scheme 1), namely, $[\text{Na}_2\text{L1}(\text{OH}_2)_4]_n$, (I), and $[\text{CaL1}(\text{OH}_2)_4]_n$, (II), where L1 is azobenzene-3,3'-disulfonate; $\{[\text{NaL2}(\text{OH}_2)_2] \cdot 2\text{H}_2\text{O}\}_n$, (III), and $[\text{Mg}(\text{OH}_2)_6] \cdot [\text{L2}]_2 \cdot 8\text{H}_2\text{O}$, (IV), where L2 is 4-aminodiazoniumylbenzene-3,4'-disulfonate; and $\{[\text{BaL3}(\text{OH}_2)_4] \cdot 2\text{H}_2\text{O}\}_n$ (V), where L3 is 4-amino-2-methyl-5-methoxyazobenzene-2',4'-disulfonate. Structure (III) is notable as it was obtained from recrystallizing the commercial dyestuff Acid Yellow 9 [74543-21-8].



Scheme 1

2. Experimental

2.1. Synthesis and crystallization

The Raman spectra of solid samples were measured using a Reinshaw Ramascope 2000 instrument with excitation at 785 nm. IR samples were prepared as KBr discs and spectra were measured using a Nicolet Avatar 360 FT-IR.

The Na salt of azobenzene-3,3'-disulfonate, (I), was produced by the alkaline reduction of 3-nitrobenzenesulfonic acid by glucose (Galbraith *et al.*, 1951). Yellow crystals suitable for analysis were obtained directly from the aqueous reaction mixture. IR (KBr): 1645 (*br*), 1470, 1419, 1235, 1199, 1107, 1081, 1045, 999, 902, 810, 712, 685, 620, 569, 528 cm^{-1} . Raman: 1477, 1413, 1183, 1163, 1104, 995, 283 cm^{-1} . Microanalysis found (expected) (%): C 31.57 (31.44), H 3.56 (3.53), N 5.90 (6.11), S 13.66 (13.99).

The Ca salt (II) was prepared by adding excess CaCl_2 to an aqueous solution of (I). After filtration, the resulting solution deposited yellow–orange crystals of (II) after slow evaporation (four weeks). IR (KBr): 1629, 1465, 1204, 1102, 1076, 1050, 999, 794, 712, 682, 615 cm^{-1} . Raman: 1592, 1420, 1376, 1325, 1198, 1162, 1124, 978, 822, 602, 381, 350, 277 cm^{-1} . The crystals were somewhat hygroscopic and an acceptable microanalysis was not obtained.

The monosodium salt of Acid Yellow 9 was purchased from Sigma–Aldrich and recrystallized from water to give fibrous red crystals of (III). The Mg salt (IV) was prepared by adding an equimolar amount of MgCl_2 to an aqueous solution of the monosodium salt of Acid Yellow 9. After filtering off the initial dark precipitate, allowing the remaining solution to evaporate to dryness gave red crystals of (IV). IR (KBr): 1625, 1574, 1528, 1392, 1162, 1008, 879 cm^{-1} .

The free acid equivalent of (V) was provided by Dystar UK. Treatment of an aqueous solution with $\text{Ba}(\text{OH})_2$ gave an orange solution. After several attempts, a simple slow evaporation (approximately four weeks) from water gave a few suitable orange crystals of (V).

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Data for (III) were measured at the Daresbury SRS Station 9.8 (Cernik *et al.*, 1997) and for (V), data were measured by the UK National Crystallography Service (Cole & Gale, 2012).

Disorder models were used for one non-metal-bound water molecule of both (III) and (IV), and also for one SO_3 group of (IV). In all cases, a two-site model was used and site-occupancy factors were refined. Suitable restraints and constraints were applied to the bond lengths and displacement parameters of the disordered units to ensure that they displayed approximately normal behaviour.

For all structures, H atoms bound to C atoms were placed in the expected geometric positions and treated in riding mode, with $\text{C}–\text{H} = 0.95 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for $\text{C}–\text{H}$ groups, and $\text{C}–\text{H} = 0.98 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for CH_3 groups. H atoms bound to N or O atoms were located by difference synthesis and placed accordingly. For (III) and (IV), H atoms bound to N atoms were refined freely and isotropically. For (V), the $\text{N}–\text{H}$ distances were restrained to 0.88 (1) \AA . All water H atoms were restrained such that $\text{O}–\text{H} = 0.88$ (1) \AA and $\text{H} \cdots \text{H} = 1.33$ (2) \AA . For the water H atoms of (V) and the H atoms of the disordered groups, U_{iso} values were allowed to

Table 1
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	[Na ₂ (C ₁₂ H ₈ N ₂ O ₆ S ₂)(H ₂ O) ₄]	[Ca(C ₁₂ H ₈ N ₂ O ₆ S ₂)(H ₂ O) ₄]	[Na(C ₁₂ H ₁₀ N ₃ O ₆ S ₂)(H ₂ O) ₂]-2H ₂ O
<i>M_r</i>	458.37	452.47	451.40
Crystal system, space group	Monoclinic, <i>C2/c</i>	Triclinic, <i>P</i> $\bar{1}$	Monoclinic, <i>P2₁/c</i>
Temperature (K)	130	123	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	21.2141 (9), 5.5370 (3), 15.3045 (8)	6.3875 (2), 6.7470 (2), 11.3030 (5)	13.9454 (18), 19.517 (3), 6.9014 (9)
α , β , γ (°)	90, 90.310 (2), 90	94.289 (2), 103.160 (2), 108.456 (2)	90, 93.838 (2), 90
<i>V</i> (Å ³)	1797.68 (16)	444.21 (3)	1874.2 (4)
<i>Z</i>	4	1	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Synchrotron, $\lambda = 0.6775$ Å
μ (mm ⁻¹)	0.40	0.65	0.32
Crystal size (mm)	0.50 × 0.32 × 0.08	0.50 × 0.25 × 0.05	0.50 × 0.01 × 0.01
Data collection			
Diffractometer	Nonius KappaCCD	Nonius Kappa CCD	Bruker APEXII
Absorption correction	–	–	Multi-scan (<i>SADABS</i> ; Bruker, 2012)
<i>T_{min}</i> , <i>T_{max}</i>	–	–	0.676, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	3500, 1865, 1414	3837, 2038, 1775	15360, 3531, 2772
<i>R_{int}</i>	0.035	0.020	0.049
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.629	0.651	0.608
Refinement			
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> [<i>F</i> ²], <i>S</i>	0.038, 0.090, 1.04	0.027, 0.070, 1.05	0.040, 0.107, 1.04
No. of reflections	1865	2038	3531
No. of parameters	145	140	311
No. of restraints	6	6	15
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	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)	0.43, -0.32	0.40, -0.46	0.35, -0.44
	(IV)	(V)	
Crystal data			
Chemical formula	[Mg(H ₂ O) ₆](C ₁₂ H ₁₀ N ₃ O ₆ S ₂) ₂ ·8H ₂ O	[Ba(C ₁₄ H ₁₃ N ₃ O ₇ S ₂)(H ₂ O) ₄]-2H ₂ O	
<i>M_r</i>	989.23	644.83	
Crystal system, space group	Monoclinic, <i>C2/c</i>	Orthorhombic, <i>Pbca</i>	
Temperature (K)	123	123	
<i>a</i> , <i>b</i> , <i>c</i> (Å)	36.896 (3), 6.7806 (4), 17.9140 (12)	7.1293 (4), 18.8368 (11), 34.752 (2)	
α , β , γ (°)	90, 111.178 (9), 90	90, 90, 90	
<i>V</i> (Å ³)	4179.0 (6)	4667.0 (5)	
<i>Z</i>	4	8	
Radiation type	Cu <i>K</i> α	Mo <i>K</i> α	
μ (mm ⁻¹)	3.12	1.95	
Crystal size (mm)	0.5 × 0.05 × 0.03	0.25 × 0.10 × 0.04	
Data collection			
Diffractometer	Oxford Diffraction Gemini S	Nonius KappaCCD	
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2019)	Multi-scan (<i>SADABS</i> ; Bruker, 2012)	
<i>T_{min}</i> , <i>T_{max}</i>	0.572, 1.000	0.448, 0.743	
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	7541, 4093, 3287	7914, 4489, 3554	
<i>R_{int}</i>	0.039	0.037	
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.621	0.616	
Refinement			
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> [<i>F</i> ²], <i>S</i>	0.050, 0.143, 1.06	0.042, 0.096, 1.15	
No. of reflections	4093	4489	
No. of parameters	359	344	
No. of restraints	110	20	
H-atom treatment	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)	0.80, -0.38	1.65, -1.23	

Computer programs: *COLLECT* (Hoof, 1998), *SAINT* (Bruker, 2012), *CrysAlis PRO* (Rigaku OD, 2019), *DENZO* (Otwinowski & Minor, 1997), *SHELXS* (Sheldrick, 2015), *SIR92* (Altomare *et al.*, 1994), *WinGX* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2020), *ORTEP-3* (Farrugia, 2012) and *SHELXL2014* (Sheldrick, 2015).

ride on the parent O atom and for all other water H atoms, U_{iso} values were allowed to refine freely.

3. Results and discussion

Previous work on the salt forms of monosulfonated dyes and pigments has shown that many structural features can be predicted from knowledge of the cation identity and the position of the sulfonate group (Kennedy *et al.*, 2009, 2012). With respect to *L1* and the metal cations used herein, relevant observations on monosulfonated species with a similar *meta* relationship between the azo and SO_3 groups are as follows. Na structures are expected to feature high-dimensionality coordination polymers with both SO_3 and H_2O groups bridging between Na centres. However, if metal-to-sulfonate bonds exist at all, then Ca structures should either be nonpolymeric entities or simple one-dimensional polymers with H_2O ligands adopting only terminal positions. *L2* has both *meta* and *para* relationships between its azo and SO_3 groups. Again extrapolation from what is known of monosulfonated azo salt forms would suggest that for *L2* an Mg species should be a solvent-separated ion-pair structure with no $\text{Mg}-\text{O}_3\text{S}$ bonds, whilst Na species should have a high-dimensional coordination polymer structure similar to those predicted for an Na salt of *L1* above (Kennedy *et al.*, 2004). In all cases, the overall packing should feature simple alternating layers of hydrophilic groups (*e.g.* cations, SO_3 and H_2O) and hydrophobic groups (the aryl azo body of the anions) (Kennedy *et al.*, 2009).

The structure of disulfonate (I) fits well with these predictions from monosulfonates. It is indeed a three-dimensional coordination polymer with both SO_3 and H_2O groups bridging between metal centres, and it forms a simple layered structure as expected. In more detail, the asymmetric unit of (I) contains two separate Na sites, both of which occupy special positions (Na1 sits on a twofold axis and Na2 on a centre of symmetry in the space group $C2/c$). It also contains two water ligands and

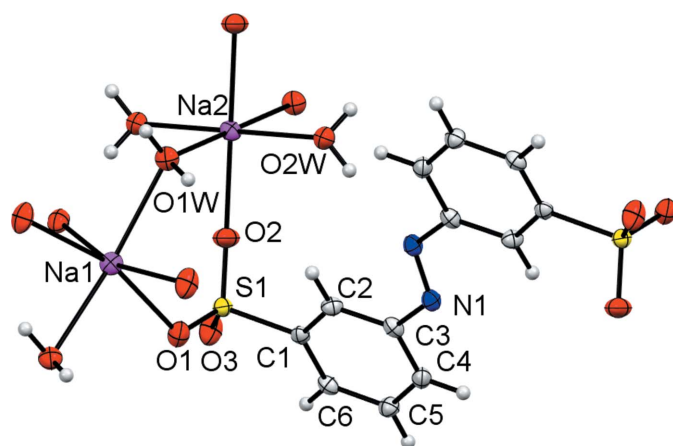


Figure 1
The asymmetric unit of (I) expanded to show the coordination shell about Na1 and Na2, and the conformation of *L1*. Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms are drawn as small spheres of arbitrary size.

Table 2
Selected geometric parameters (\AA , $^\circ$) for (I).

Na1—O3 ⁱ	2.4174 (19)	Na2—O2	2.3340 (18)
Na1—O3 ⁱⁱ	2.4175 (19)	Na2—O1W	2.3688 (17)
Na1—O1	2.419 (2)	Na2—O1W ^{iv}	2.3688 (17)
Na1—O1 ⁱⁱⁱ	2.419 (2)	Na2—O2W ^{iv}	2.4480 (17)
Na1—O1W ⁱⁱⁱ	2.5019 (18)	Na2—O2W	2.4480 (17)
Na1—O1W	2.5019 (18)	N1—N1 ^v	1.262 (4)
Na2—O2 ^{iv}	2.3340 (18)	N1—C3	1.431 (3)
O3 ⁱ —Na1—O3 ⁱⁱ	100.81 (10)	O2 ^{iv} —Na2—O2	180.0
O3 ⁱ —Na1—O1	85.49 (6)	O2 ^{iv} —Na2—O1W	91.49 (7)
O3 ⁱⁱ —Na1—O1	163.62 (6)	O2—Na2—O1W	88.51 (7)
O1—Na1—O1 ⁱⁱⁱ	92.59 (9)	O1W—Na2—O1W ^{iv}	180.0
O3 ⁱ —Na1—O1W ⁱⁱⁱ	86.52 (7)	O2—Na2—O2W ^{iv}	98.30 (6)
O3 ⁱⁱ —Na1—O1W ⁱⁱⁱ	75.28 (6)	O1W—Na2—O2W ^{iv}	87.42 (6)
O1—Na1—O1W ⁱⁱⁱ	90.17 (6)	O2—Na2—O2W	81.70 (6)
O1—Na1—O1W	109.77 (6)	O1W—Na2—O2W	92.58 (6)
O1W ⁱⁱⁱ —Na1—O1W	151.40 (10)		

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

Table 3
Hydrogen-bond geometry (\AA , $^\circ$) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H2W \cdots O2W ⁱ	0.87 (1)	2.07 (2)	2.919 (3)	163 (3)
O1W—H1W \cdots O2 ⁱ	0.87 (1)	2.29 (2)	3.044 (3)	145 (3)
O1W—H1W \cdots O3 ⁱ	0.87 (1)	2.32 (3)	3.005 (3)	136 (3)
O2W—H3W \cdots O1 ⁱⁱⁱ	0.87 (1)	1.94 (1)	2.807 (2)	175 (3)
O2W—H4W \cdots N1 ^{vi}	0.87 (1)	2.22 (1)	3.076 (3)	168 (3)

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

half of an *L1* dianion. A crystallographic centre of symmetry is located at the centre of the azo bond, giving a planar dianion with mutually *anti* SO_3 groups (Fig. 1). As can be seen from Table 2, each Na centre is approximately octahedral, with Na1

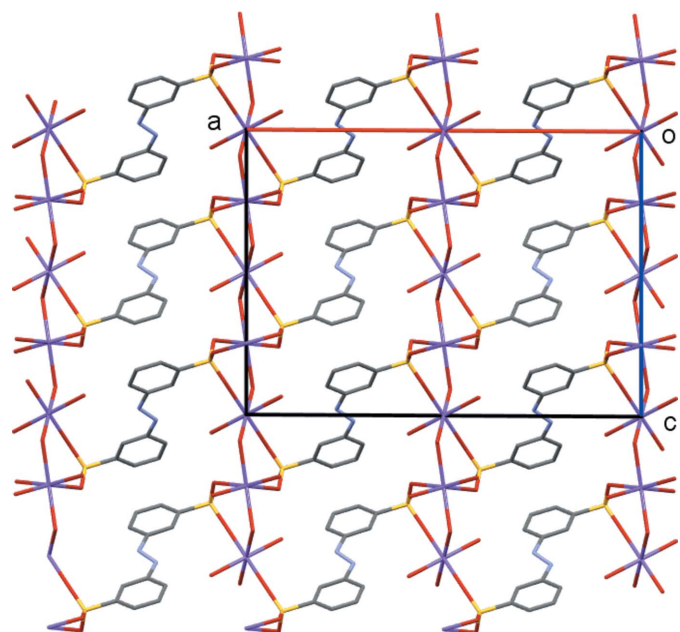
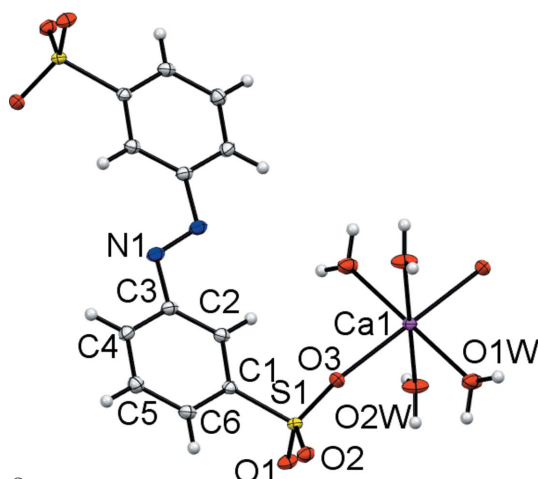


Figure 2
Packing diagram of (I), viewed down the *b* axis. Note the alternating hydrophobic and hydrophilic layers that lie parallel to the *bc* plane.


Figure 3

The asymmetric unit of (II) expanded to show the coordination shell about Ca1 and the conformation of L1. Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms are drawn as small spheres of arbitrary size.

bonding to two bridging water molecules and to four O atoms of four different L1 dianions. Na2 bonds to two O atoms of two L1 dianions and to four water ligands, two of which form terminal bonds and two of which bridge to Na1 centres. Note that the bond lengths involving Na1 are systematically longer than those of Na2 [ranges 2.4174 (19)–2.5019 (18) and 2.3340 (18)–2.4480 (17) Å for Na1 and Na2, respectively]. The SO₃ units each form three bonds to Na centres, one from each O atom. Within the hydrophilic layers, pairs of Na1 centres are linked by eight-membered [NaOSO]₂ rings, whilst the Na1 and Na2 centres are linked by six-membered [NaOSONaO] rings, with both bridging sulfonate and water ligands. As can be seen from Fig. 2, the layers expand parallel to the *bc* plane, with the disulfonate dianions bridging between neighbouring hydrophilic layers to give the overall three-dimensional coordination polymer. The hydrogen-bond details for (I) are given in Table 3.

The asymmetric unit of (II) contains half of an L1 dianion, two water ligands and a Ca site. Both the Ca1 site and the centre of the azo N=N bond occupy crystallographic inversion centres. As with (I), this gives a planar dianion with *anti* SO₃ groups and an octahedral metal centre (Fig. 3 and Table 4). Ca1 forms bonds to O atoms from two *trans* SO₃ groups and to four terminal water ligands. Each SO₃ group makes a single Ca–O bond and thus the disulfonate dianion

Table 4

Selected geometric parameters (Å, °) for (II).

Ca1–O3	2.3050 (11)	Ca1–O2W ⁱ	2.3385 (12)
Ca1–O3 ⁱ	2.3051 (11)	Ca1–O2W	2.3385 (12)
Ca1–O1W	2.3235 (12)	N1–N1 ⁱⁱ	1.256 (3)
Ca1–O1W ⁱ	2.3236 (12)	N1–C3	1.432 (2)
O3–Ca1–O3 ⁱ	180.0	O1W–Ca1–O2W ⁱ	90.52 (5)
O3–Ca1–O1W	87.66 (4)	O3–Ca1–O2W	86.93 (5)
O3–Ca1–O1W ⁱ	92.34 (4)	O1W–Ca1–O2W	89.48 (5)
O1W–Ca1–O1W ⁱ	180.00 (6)	O2W ⁱ –Ca1–O2W	180.0
O3–Ca1–O2W ⁱ	93.07 (4)		

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

Table 5

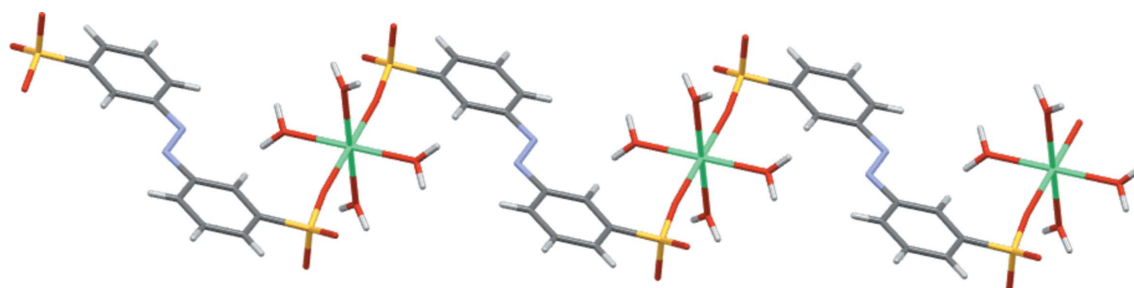
Hydrogen-bond geometry (Å, °) for (II).

<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>
O1W–H1W···O2 ⁱⁱⁱ	0.87 (1)	2.01 (1)	2.8521 (17)	162 (2)
O1W–H2W···O1 ^{iv}	0.86 (1)	2.00 (1)	2.8454 (17)	165 (2)
O2W–H3W···O2 ^{iv}	0.86 (1)	1.95 (1)	2.8119 (16)	174 (2)
O2W–H4W···O1 ^v	0.86 (1)	1.94 (1)	2.7907 (16)	168 (2)

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

links Ca centres into a one-dimensional coordination polymer (Fig. 4). These features combine to give the layered structure shown in Fig. 5. Within the hydrophilic layers, hydrogen bonding between the water ligands and the two noncoordinating O atoms of SO₃ link neighbouring coordination chains (Table 5). Thus, structure (II) also follows the rules proposed for monosulfonated azo dye salts. There are Ca–O₃S bonds, but these are relatively few in number and, even with the two-headed nature of the disulfonate ligand, they combine to give only a one-dimensional coordination polymer. The H₂O ligands take no part in bridging between metal centres and the overall packing motif is one of simple alternating hydrophobic and hydrophilic layers.

Structure (III) was obtained from aqueous recrystallization of the commercial product called ‘Acid Yellow 9, monosodium salt’. An interesting problem here was to discover the protonation site. The crystal structures of three acidic sulfonated azobenzene-based dyes with amino substituents are known. 4-Aminoazobenzene-4'-sulfonic acid crystallizes with protonation of the amino group, giving an –NH₃⁺-bearing zwitterion, whilst the other two known structures crystallize with protonation of the azo N atom furthest from the neutral –NH₂ group (Lu *et al.*, 2009; Miyano *et al.*, 2016; Kennedy *et al.*,


Figure 4

Part of the one-dimensional coordination polymer of (II).

Table 6
Selected geometric parameters (Å, °) for (III).

Na1—O1W	2.275 (2)	N1—N2	1.294 (3)
Na1—O2W ⁱ	2.335 (2)	N1—C4	1.411 (3)
Na1—O2W	2.369 (2)	N2—C7	1.341 (3)
Na1—O6	2.409 (2)	N3—C10	1.316 (3)
Na1—O6 ⁱ	2.425 (2)		
O1W—Na1—O2W ⁱ	154.18 (9)	O2W—Na1—O6	75.46 (7)
O1W—Na1—O2W	96.67 (9)	O1W—Na1—O6 ⁱ	85.06 (8)
O2W ⁱ —Na1—O2W	95.44 (7)	O2W ⁱ —Na1—O6 ⁱ	75.79 (7)
O1W—Na1—O6	88.23 (8)	O2W—Na1—O6 ⁱ	159.34 (8)
O2W ⁱ —Na1—O6	116.93 (8)	O6—Na1—O6 ⁱ	125.20 (8)

Symmetry code: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

Table 7
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>
N1—H1N···O3W ⁱⁱ	0.84 (3)	2.10 (3)	2.878 (3)	153 (3)
N3—H2N···O4W	0.82 (3)	2.04 (3)	2.847 (5)	170 (3)
N3—H2N···O5W	0.82 (3)	2.05 (4)	2.843 (11)	163 (3)
N3—H3N···O4	0.81 (3)	2.60 (3)	3.084 (3)	120 (3)
N3—H3N···O4 ⁱⁱⁱ	0.81 (3)	2.20 (3)	2.923 (3)	150 (3)
N3—H3N···O5	0.81 (3)	2.61 (3)	3.095 (3)	120 (3)
O1W—H1W···O5 ^{iv}	0.88 (1)	1.93 (2)	2.773 (3)	160 (4)
O1W—H2W···O4 ⁱ	0.88 (1)	1.93 (2)	2.756 (3)	157 (4)
O2W—H3W···O3 ^v	0.88 (1)	1.90 (1)	2.774 (2)	176 (4)
O2W—H4W···O1 ^{vi}	0.88 (1)	1.88 (1)	2.746 (3)	171 (3)
O3W—H5W···O2 ^{vii}	0.86 (1)	2.03 (1)	2.866 (3)	164 (3)
O3W—H6W···O3 ^{vi}	0.87 (1)	2.22 (1)	3.081 (3)	171 (3)
O4W—H7W···O3 ^z	0.88 (1)	2.02 (1)	2.887 (5)	175 (4)
O4W—H8W···O1 ^{iv}	0.88 (1)	1.97 (1)	2.846 (5)	173 (5)
O5W—H9W···O3 ^z	0.88 (1)	2.08 (2)	2.947 (13)	170 (10)
O5W—H10W···O1 ^{iv}	0.88 (1)	1.89 (2)	2.765 (9)	171 (10)

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

2020). The azo group is the commonest protonation site for the free acid forms of sulfonated azo dyes that do not bear a more basic substituent (Kennedy *et al.*, 2001, 2020). The asymmetric unit of (III) was found to contain an Na centre, a monoanionic *L2* ligand with protonation at azo atom N1, two

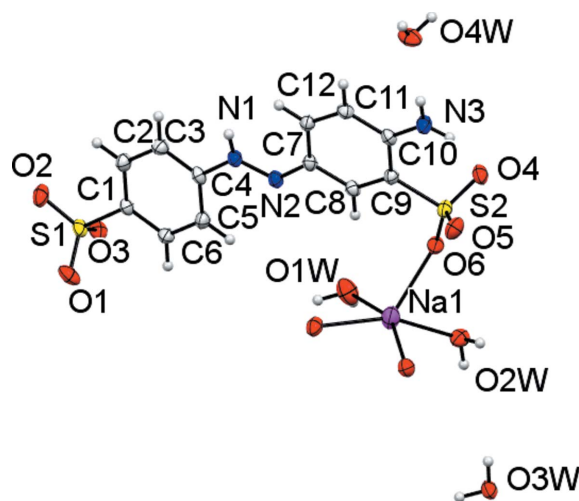


Figure 6

The asymmetric unit of (III) expanded to show the coordination shell about Na1. The minor-disorder component at O4W is not shown. Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms are drawn as small spheres of arbitrary size.

metal-coordinated water ligands and two non-bound water molecules, one of which is disordered (Fig. 6). Unusually for an Na salt of an aryl sulfonate, only one of the six independent SO₃ O atoms is involved in bonding to Na. This Na1—O6 interaction involves the SO₃ group *meta* to the azo bond. Na1 exists in a distorted square-pyramidal and hence five-coordinate environment, where one bond is to a terminal water ligand and the other four bonds (from two water ligands and two SO₃ groups) all bridge to neighbouring Na centres (see Table 6 for geometric details). The Na—O bond lengths of (III) [range 2.275 (2)–2.425 (2) Å] are understandably shorter than those of the six-coordinate Na centres of (I). An interesting detail is that in (III) the Na-to-OH₂ distances are shorter than the Na-to-SO₃ distances. This is the opposite of the case in (I). The one-dimensional coordination polymers in (III) are formed by chains of [Na1—O2W—Na1—O6] rings

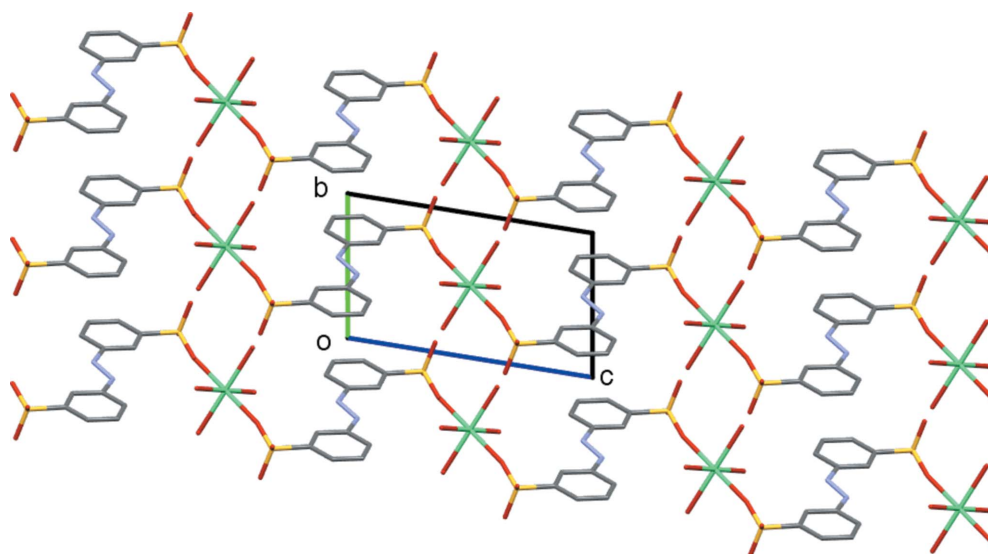


Figure 5

Packing diagram of (II), viewed down the *a* axis. Note the alternating hydrophobic and hydrophilic layers that lie parallel to the *ab* plane.

Table 8
Selected geometric parameters (Å, °) for (IV).

Mg1—O2W	2.0322 (19)	N1—C4	1.413 (3)
Mg1—O1W	2.0472 (18)	N2—C7	1.342 (4)
Mg1—O3W	2.0769 (19)	N3—C10	1.309 (4)
N1—N2	1.294 (4)		
O2W ⁱ —Mg1—O2W	180.0	O1W—Mg1—O3W ⁱ	88.07 (8)
O2W ⁱ —Mg1—O1W	88.72 (8)	O2W—Mg1—O3W	91.69 (8)
O2W—Mg1—O1W	91.28 (8)	O1W—Mg1—O3W	91.93 (8)
O1W—Mg1—O1W ⁱ	180.0	O3W ⁱ —Mg1—O3W	180.0
O2W—Mg1—O3W ⁱ	88.31 (8)		

Symmetry code: (i) $-x - \frac{1}{2}, -y + \frac{1}{2}, -z$.

Table 9
Hydrogen-bond geometry (Å, °) for (IV).

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1N...O7W	0.84 (4)	1.99 (5)	2.80 (2)	164 (4)
N1—H1N...O8W	0.84 (4)	2.00 (6)	2.83 (4)	170 (4)
N3—H2N...O5W ⁱⁱ	0.87 (4)	2.02 (4)	2.881 (3)	174 (4)
N3—H3N...O6	0.84 (5)	2.03 (5)	2.700 (7)	137 (4)
N3—H3N...O6A	0.84 (5)	2.10 (5)	2.763 (14)	136 (4)
O1W—H1W...O3	0.87 (1)	1.92 (1)	2.769 (3)	167 (3)
O1W—H2W...O1 ⁱⁱⁱ	0.87 (1)	1.84 (1)	2.714 (3)	177 (4)
O2W—H3W...O4W	0.87 (1)	1.88 (1)	2.727 (3)	165 (3)
O2W—H4W...O2 ^{iv}	0.87 (1)	1.95 (1)	2.812 (3)	173 (4)
O3W—H5W...O4W ^v	0.87 (1)	1.85 (1)	2.707 (3)	169 (4)
O3W—H6W...O6 ^{vi}	0.87 (1)	2.04 (2)	2.897 (6)	169 (4)
O3W—H6W...O6A ^{vi}	0.87 (1)	2.18 (2)	2.983 (11)	153 (3)
O4W—H8W...O5W	0.87 (1)	1.95 (2)	2.803 (3)	166 (4)
O4W—H7W...O6W	0.87 (1)	1.86 (1)	2.706 (3)	162 (3)
O5W—H10W...O2 ⁱ	0.87 (1)	2.16 (3)	2.829 (3)	133 (3)
O5W—H9W...O3 ^{vii}	0.87 (1)	1.99 (1)	2.820 (3)	160 (3)
O5W—H10W...O3 ^{viii}	0.87 (1)	2.52 (3)	3.251 (3)	141 (3)
O6W—H11W...O4 ^{vi}	0.87 (1)	2.18 (2)	3.028 (13)	167 (4)
O6W—H11W...O4A ^{vi}	0.87 (1)	1.94 (3)	2.81 (2)	174 (4)
O6W—H12W...O5 ^{ix}	0.87 (1)	2.02 (2)	2.878 (8)	170 (5)
O6W—H12W...O5A ^{ix}	0.87 (1)	2.43 (2)	3.276 (14)	163 (4)
O6W—H12W...O6A ^{ix}	0.87 (1)	2.52 (3)	3.220 (17)	139 (4)
O7W—H13W...O5 ^x	0.89 (1)	2.35 (6)	2.89 (2)	119 (5)
O7W—H14W...O6W ⁱⁱ	0.88 (1)	2.52 (3)	3.354 (18)	159 (5)
O7W—H14W...O4 ^{xi}	0.88 (1)	2.35 (5)	2.92 (2)	123 (4)
O8W—H16W...O5A ^x	0.89	2.01	2.87 (4)	163
O8W—H15W...O4A ^{xi}	0.88	2.18	2.81 (4)	128

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

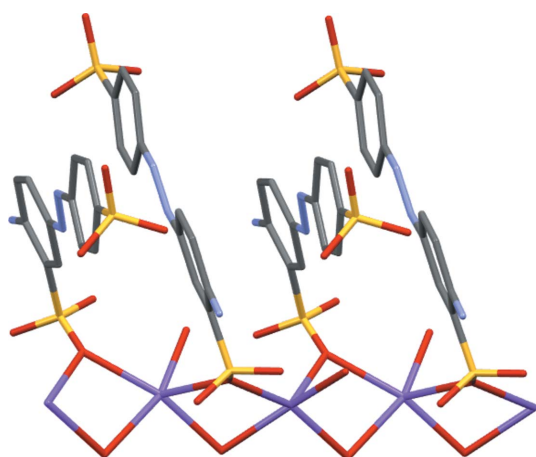


Figure 7
Part of the one-dimensional coordination polymer of (III).

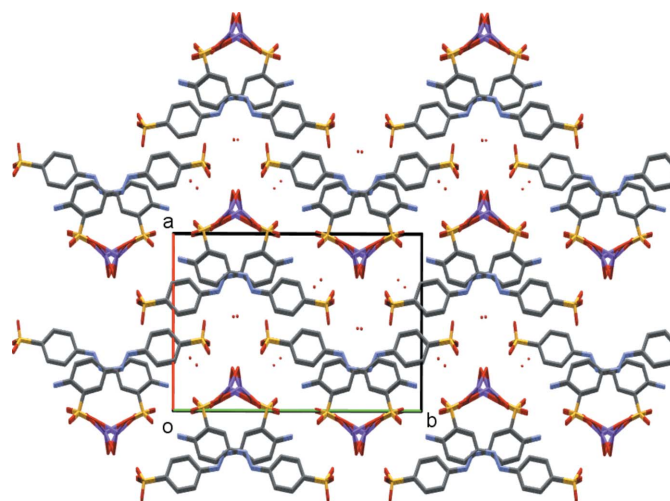


Figure 8
Packing diagram of (III), viewed down the *c* axis. H atoms have been omitted for clarity. Note the hydrate channels that extend parallel to the *c* axis.

and propagate parallel to the crystallographic *c* direction. Each chain is asymmetric, with the *L2* anions on one side and the water ligands on the other (Fig. 7). This structure is thus unlike those of the monosulfonated azo Na salts as, despite having an extra potential metal-bonding group in the form of the second SO₃ substituent, it does not form a higher-dimensional coordination polymer. A further difference is highlighted by Fig. 8, which shows that (III) is not a simple alternating layer structure. Note the hydrate channels running parallel to *c*. A reason for this may be that the simple alternate layering seen elsewhere is a function of the azo anions' approximation to linear spacers, with hydrophilic head and tail groups separated by a hydrophobic central region (Kennedy *et al.*, 2009). As *L2* is protonated on the azo group, this introduces a hydrophilic group and strong hydrogen-bond donor to the centre of the azo anion. It may be that the need to provide a hydrogen-bond acceptor to this formally charged N—H group is what breaks the otherwise common simple layering

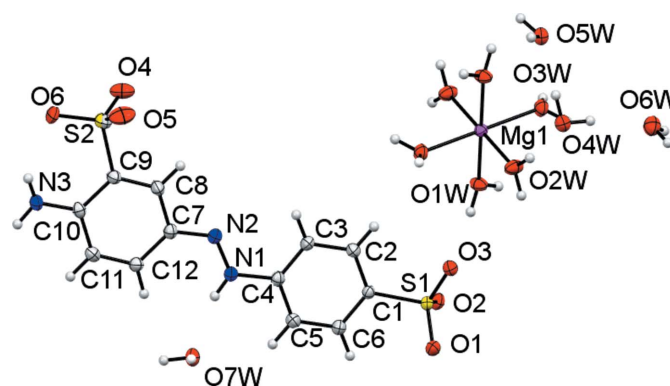


Figure 9
The asymmetric unit of (IV) expanded to show the coordination shell about Mg1. The minor-disorder components of the sulfonate groups of S2 and the O7W water molecule are not shown. Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms are drawn as small spheres of arbitrary size.

Table 10
Selected geometric parameters (Å, °) for (V).

Ba1—O2W	2.704 (4)	Ba1—O3W	2.911 (4)
Ba1—O1W	2.747 (4)	Ba1—O3W ⁱⁱⁱ	3.105 (4)
Ba1—O4 ⁱ	2.753 (4)	N1—N2	1.277 (6)
Ba1—O1	2.759 (4)	N1—C4	1.426 (6)
Ba1—O5 ⁱⁱ	2.788 (4)	N2—C7	1.393 (6)
Ba1—O4W	2.819 (4)	N3—C10	1.354 (7)
O2W—Ba1—O1W	72.69 (14)	O1—Ba1—O3W	85.63 (11)
O2W—Ba1—O4 ⁱ	68.74 (12)	O5 ⁱⁱ —Ba1—O3W	87.04 (11)
O1W—Ba1—O4 ⁱ	83.39 (12)	O4W—Ba1—O3W	76.65 (11)
O2W—Ba1—O1	73.66 (13)	O2W—Ba1—O3W ⁱⁱⁱ	124.26 (12)
O1W—Ba1—O1	146.32 (12)	O1W—Ba1—O3W ⁱⁱⁱ	126.70 (12)
O4 ⁱ —Ba1—O1	85.75 (11)	O4 ⁱ —Ba1—O3W ⁱⁱⁱ	64.01 (10)
O2W—Ba1—O5 ⁱⁱ	63.22 (12)	O1—Ba1—O3W ⁱⁱⁱ	75.02 (10)
O1W—Ba1—O5 ⁱⁱ	85.47 (12)	O5 ⁱⁱ —Ba1—O3W ⁱⁱⁱ	147.67 (10)
O4 ⁱ —Ba1—O5 ⁱⁱ	131.85 (10)	O4W—Ba1—O3W ⁱⁱⁱ	60.15 (10)
O1—Ba1—O5 ⁱⁱ	78.35 (11)	O3W—Ba1—O3W ⁱⁱⁱ	73.06 (5)
O2W—Ba1—O4W	136.43 (13)	O2W—Ba1—O4W ^{iv}	115.49 (11)
O1W—Ba1—O4W	74.19 (12)	O1W—Ba1—O4W ^{iv}	67.73 (11)
O4 ⁱ —Ba1—O4W	80.10 (11)	O4 ⁱ —Ba1—O4W ^{iv}	146.32 (10)
O1—Ba1—O4W	134.80 (11)	O1—Ba1—O4W ^{iv}	127.91 (11)
O5 ⁱⁱ —Ba1—O4W	140.16 (11)	O5 ⁱⁱ —Ba1—O4W ^{iv}	64.82 (10)
O2W—Ba1—O3W	146.29 (13)	O4W—Ba1—O4W ^{iv}	75.76 (7)
O1W—Ba1—O3W	123.10 (12)	O3W—Ba1—O4W ^{iv}	58.23 (10)
O4 ⁱ —Ba1—O3W	136.99 (11)	O3W ⁱⁱⁱ —Ba1—O4W ^{iv}	120.18 (10)

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

motif (Table 7). In this respect, the packing of (III) is more similar to the packing of free acid sulfonated azo structures than it is to the packing of equivalent salt forms (Kennedy *et al.*, 2020).

All known Mg salt forms of sulfonated azo dyes and pigments are solvent-separated ion pairs, with no direct bond between Mg and SO₃ (Kennedy *et al.*, 2006, 2009, 2012). As is shown in Fig. 9, the structure of (IV) is also of this type. Its asymmetric unit contains an L2 anion that is protonated at the azo N1 atom, half of an octahedral [Mg(OH₂)₆] dication (with Mg1 situated at a crystallographic inversion centre) and four noncoordinated water molecules (Table 8). One of the water molecules and the SO₃ group *ortho* to NH₂ are disordered. As shown in the packing diagram (Fig. 10), there are hydrophilic layers that extend parallel to the *bc* plane. The organic anions

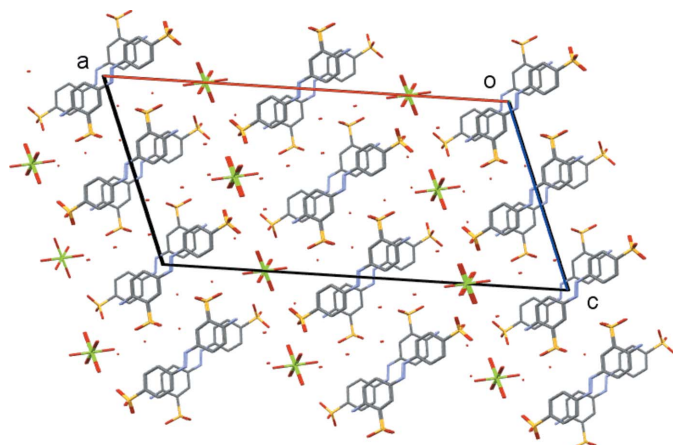


Figure 10
Packing diagram of (IV), viewed down the *b* axis. H atoms have been omitted for clarity. Note the solvent water molecules lying within the layers of azo dianions that lie parallel to the *bc* plane.

lie between these but their azobenzene cores do not form continuous hydrophobic layers – instead water molecules are dispersed within these layers. Thus, rather than true two-dimensional layers, the hydrophobic azobenzene units form stacks parallel to the *b* direction surrounded by [Mg(OH₂)₆]²⁺ ions and water molecules. As with (III) above, the protonation of the azo unit at the centre of the anion appears to mitigate against the simple alternating layer structures seen elsewhere. In both (III) and (IV), the protonated azo group acts as a hydrogen-bond donor to water molecules (see Tables 7 and 9).

Fig. 11 shows the contents of the asymmetric unit of (V) extended to give the complete coordination geometry (Table 10). The asymmetric unit consists of an azo dianion, a Ba^{II} cation with four coordinated water ligands and two non-bound water molecules. The Ba centre is nonacoordinated, with three bonds to O atoms of SO₃ groups and six bonds to water ligands. The Ba—O—Ba bridges all involve water O atoms. Both SO₃ groups interact with the Ba atom, with the group *ortho* to the azo group making two Ba—O bonds and the *para* SO₃ group making one bond. This is notable as *ortho* SO₃ groups are generally unfavourable coordination sites compared to *para* SO₃ groups (Kennedy *et al.*, 2009). As with both L2 structures, here the amino group of L3 takes no part in coordination to the metal atom.

Complex (V) forms a two-dimensional coordination polymer. Ba—O—Ba bridges involving the water molecules extend the polymer parallel to the *a* direction, whilst parallel to the *b* direction, the polymer propagates through the coordination of the two SO₃ groups to give the large [Ba(OH₂)₄-Ba(L3)]₂ cyclic structures shown in Fig. 12. The overall packing (Fig. 13) shows a layered structure with hydrophobic and hydrophilic layers parallel to the *ab* plane. As with (III) and (IV), the amine group of (V) is essentially planar rather than pyramidal. However, it differs by acting as a hydrogen-bond donor to only SO₃ groups (Table 11), whilst the amine groups of (III) and (IV) donate hydrogen bonds to both SO₃ and water groups. None of the amine groups act as hydrogen-

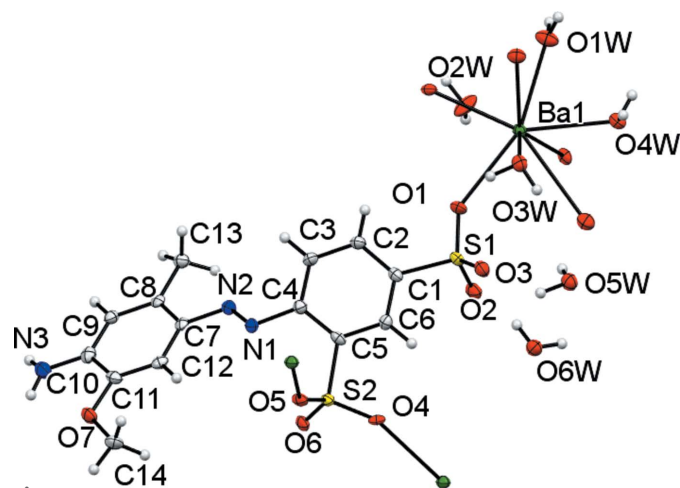


Figure 11
The asymmetric unit of (V) expanded to show the coordination shell about Ba1 and all dative bonds originating from the modelled dianion. Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms are drawn as small spheres of arbitrary size.

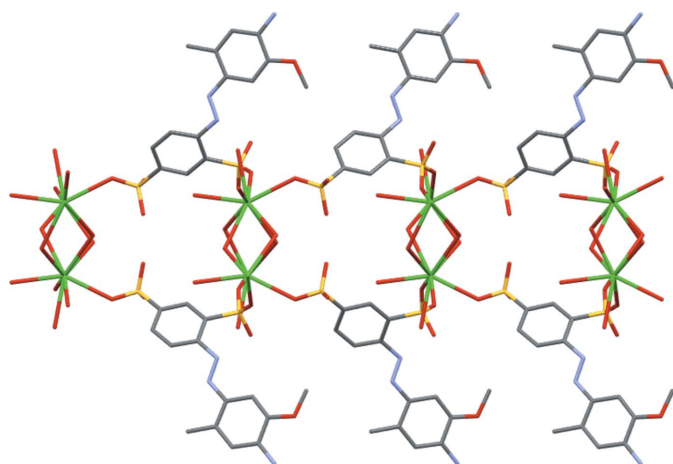


Figure 12
Part of the two-dimensional coordination polymer of (V), viewed down the *a* axis, showing the coordination polymer extending by SO₃ coordination parallel to the *b* direction.

bond acceptors. Azo atom N1 of (V) does act as a hydrogen-bond acceptor from water, as do both azo N atoms of (I), but this is not the case for any of the other azo N atoms, see hydrogen-bond tables for details.

The literature on the Ba salt forms of monosulfonated azo dyes predicts structures with no bridging water ligands and with discrete coordination complexes or simple one-dimensional coordination polymers (Kennedy *et al.*, 2004, 2009). Neither prediction is true for disulfonate (V).

For L2, with its protonated azo group, the N=N bond lengths of (III) and (IV) are 1.294 (3) and 1.294 (4) Å, respectively. The N2–C7 bond lengths are also equivalent at

Table 11
Hydrogen-bond geometry (Å, °) for (V).

<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>
N3–H1N···O2 ^v	0.88 (1)	2.27 (2)	3.144 (6)	172 (6)
N3–H2N···O6 ^{vi}	0.88 (1)	2.28 (5)	2.984 (6)	138 (6)
O1W–H1W···O2 ⁱ	0.87 (1)	2.21 (3)	2.987 (5)	148 (5)
O1W–H2W···O6W ^{vii}	0.87 (1)	1.92 (2)	2.766 (6)	161 (6)
O2W–H3W···O6 ⁱ	0.88 (1)	2.03 (3)	2.772 (6)	141 (5)
O2W–H4W···N1 ⁱⁱ	0.88 (1)	2.10 (2)	2.948 (6)	162 (5)
O3W–H5W···O5W ^{viii}	0.88 (1)	2.04 (3)	2.805 (5)	145 (4)
O3W–H6W···O5W ^{iv}	0.88 (1)	1.97 (1)	2.833 (6)	168 (5)
O4W–H7W···O4 ^{vii}	0.88 (1)	2.06 (2)	2.901 (5)	160 (4)
O4W–H8W···O6W ⁱ	0.88 (1)	1.87 (2)	2.741 (5)	171 (5)
O5W–H9W···O2	0.88 (1)	1.97 (3)	2.805 (5)	158 (6)
O5W–H10W···O5 ⁱ	0.88 (1)	2.17 (3)	2.917 (5)	143 (5)
O6W–H11W···O3	0.88 (1)	1.88 (2)	2.737 (5)	166 (6)
O6W–H12W···O3 ⁱⁱⁱ	0.88 (1)	1.93 (1)	2.800 (6)	174 (5)

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

1.341 (3) and 1.342 (4) Å. These values are as expected for a protonated azo unit bound to an aniline fragment and, despite being for an anionic ligand, are close matches to those found for the overall neutral but zwitterionic free acid forms of those monosulfonated azo dyes which also feature protonated azo groups (Kennedy *et al.*, 2020). At 1.256 (3) and 1.432 (2) Å, the N=N and N2–C7 bond lengths of L1 in (II) are clearly much shorter and longer, respectively, than their equivalents in L2. They fit well with the ranges found for the 4,4' isomer and with those found for monosulfonated azo species with no strong electron-donating ring substituents (Soegiarto *et al.*, 2009, 2010, 2011; Kennedy *et al.*, 2001, 2020). The N=N bond in (I) is 1.262 (4) Å and is thus outside the ranges of the literature

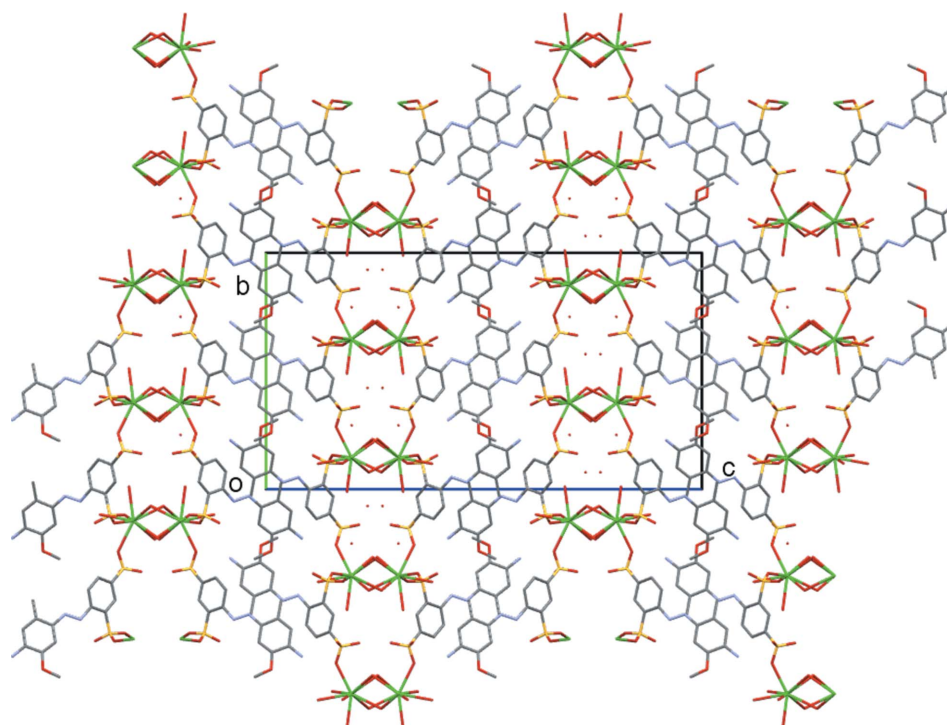


Figure 13
Packing diagram of (V), viewed down the *a* axis. H atoms have been omitted for clarity.

structures above; however, the difference is not statistically significant. For (V), the N=N and N2–C7 bond lengths of L3 are intermediate between the lengths reported for L1 and L2 above at 1.277 (6) and 1.393 (6) Å. Such distortions from the expected geometry of azobenzene (Harada & Ogawa, 2004) can be explained by the resonance electron-donating ability of the NH₂ group *para* to the azo group (Kennedy *et al.*, 2020). The values found for dianion L3 are, however, slightly more distorted from the azobenzene base than has been found for metal complexes of related monoanions, such as 4-aminoazobenzene-4'-sulfonate (Kennedy *et al.*, 2004; Lu *et al.*, 2009). A final point about the geometries of the azo species herein is that in (I)–(IV), the azo moiety is essentially planar [range of dihedral angles between ring planes = 0.00 (6)–14.13 (6)°]. In comparison, the dianion of (V) is distinctly twisted [dihedral angle between the ring planes = 34.0 (2)°] and stepped [*e.g.* atom N2 lies 0.905 (9) Å out of the plane defined by atoms C1–C6].

4. Conclusion

Compounds (I) and (II) both contain the simple disulfonate L1 and both have structures that fit with the structural types seen for equivalent monosulfonate salt species – they give the expected dimensionality coordination polymers in which the bonding roles of water ligands are predictable and their packing structures have the expected alternating layer motifs (Kennedy *et al.*, 2004). However, the other three structures presented herein do not have the same structural features as their monosulfonate cognates. Structures (III) and (IV) both contain the monoanion L2. Neither adopts the expected simple alternating layer structure and Na salt (III) is a one-dimensional coordination polymer rather than the expected two- or three-dimensional coordination polymer. The strong hydrogen-bonding N–H group at the centre of L2 is a feature not seen in other salt structures. This difference gives a rational explanation for the difference in packing behaviour. Finally, the Ba salt of L3, *i.e.* (V), does give the expected layered packing, but has metal-centre-bridging water ligands and an unexpected two-dimensional rather than a one-dimensional coordination polymer structure. The extra dimensionality of the coordination polymer may simply be related to the extra SO₃ group in L3 compared to literature structures, but it is less clear why the coordination role of the water ligands should also change.

Acknowledgements

The authors thank the UK National Crystallography Service (University of Southampton) for the data collection on (V) and Mrs Margaret Adams (University of Strathclyde) for microanalysis. The CCLRC is thanked for providing a beam-time award at Daresbury SRS and Dystar UK are thanked for providing L3 as the free acid form.

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supporting information

Acta Cryst. (2020). C76, 972-981 [https://doi.org/10.1107/S2053229620012735]

Structures of five salt forms of disulfonated monoazo dyes

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Computing details

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hoof, 1998) for (I), (II), (V); *SAINT* (Bruker, 2012) for (III); *CrysAlis PRO* (Rigaku OD, 2019) for (IV). Cell refinement: *DENZO* (Otwinowski & Minor, 1997) for (I), (II), (V); *SAINT* (Bruker, 2012) for (III); *CrysAlis PRO* (Rigaku OD, 2019) for (IV). Data reduction: *DENZO* (Otwinowski & Minor, 1997) for (I), (II), (V); *SAINT* (Bruker, 2012) for (III); *CrysAlis PRO* (Rigaku OD, 2019) for (IV). Program(s) used to solve structure: *SHELXS* (Sheldrick, 2015) for (I), (III); *SIR92* (Altomare *et al.*, 1994) for (II), (IV), (V). For all structures, program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015) and *WinGX* (Farrugia, 2012); molecular graphics: *Mercury* (Macrae *et al.*, 2020) and *ORTEP-3* (Farrugia, 2012). Software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) for (I), (II), (IV), (V).

Poly[di- μ -aqua-diaqua[μ_4 -3,3'-(diazane-1,2-diyl)bis(benzenesulfonato)]disodium(I)] (I)

Crystal data

[Na₂(C₁₂H₈N₂O₆S₂)(H₂O)₄]
 $M_r = 458.37$
 Monoclinic, *C2/c*
 $a = 21.2141$ (9) Å
 $b = 5.5370$ (3) Å
 $c = 15.3045$ (8) Å
 $\beta = 90.310$ (2)°
 $V = 1797.68$ (16) Å³
 $Z = 4$

$F(000) = 944$
 $D_x = 1.694$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 2025 reflections
 $\theta = 1.0$ – 26.4 °
 $\mu = 0.40$ mm⁻¹
 $T = 130$ K
 Plate, yellow
 $0.50 \times 0.32 \times 0.08$ mm

Data collection

Nonius KappaCCD
 diffractometer
 Radiation source: sealed tube
 ω and phi scans
 3500 measured reflections
 1865 independent reflections

1414 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$
 $\theta_{\text{max}} = 26.6$ °, $\theta_{\text{min}} = 1.9$ °
 $h = 0 \rightarrow 26$
 $k = -6 \rightarrow 6$
 $l = -19 \rightarrow 19$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.090$
 $S = 1.04$
 1865 reflections

145 parameters
 6 restraints
 Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0342P)^2 + 3.0179P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

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

$$\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.09144 (3)	0.74864 (11)	0.31076 (4)	0.01712 (16)
Na1	0.0000	0.2759 (2)	0.2500	0.0219 (3)
Na2	0.0000	0.5000	0.5000	0.0195 (3)
O1	0.08204 (8)	0.5777 (3)	0.23944 (11)	0.0253 (4)
O2	0.05412 (8)	0.6889 (4)	0.38656 (11)	0.0351 (5)
O3	0.08455 (8)	0.9976 (3)	0.28351 (12)	0.0293 (4)
O1W	-0.01637 (9)	0.1643 (3)	0.40666 (11)	0.0237 (4)
O2W	-0.08853 (8)	0.7231 (3)	0.43599 (11)	0.0256 (4)
N1	0.27167 (9)	0.3035 (3)	0.47962 (12)	0.0186 (4)
C1	0.17132 (11)	0.7150 (4)	0.34449 (14)	0.0157 (5)
C2	0.18751 (11)	0.5193 (4)	0.39621 (15)	0.0180 (5)
H2	0.1567	0.4030	0.4121	0.022*
C3	0.24990 (11)	0.4954 (4)	0.42461 (14)	0.0182 (5)
C4	0.29542 (11)	0.6610 (4)	0.39847 (15)	0.0196 (5)
H4	0.3380	0.6416	0.4168	0.023*
C5	0.27865 (11)	0.8541 (5)	0.34576 (15)	0.0205 (5)
H5	0.3098	0.9664	0.3275	0.025*
C6	0.21610 (11)	0.8837 (4)	0.31940 (15)	0.0182 (5)
H6	0.2042	1.0183	0.2845	0.022*
H1W	0.0172 (9)	0.076 (5)	0.399 (2)	0.066 (12)*
H2W	-0.0447 (11)	0.052 (5)	0.415 (2)	0.076 (13)*
H3W	-0.0888 (13)	0.676 (6)	0.3820 (9)	0.053 (11)*
H4W	-0.1281 (6)	0.723 (6)	0.4498 (18)	0.053 (10)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0161 (3)	0.0178 (3)	0.0175 (3)	0.0025 (3)	0.0005 (2)	0.0031 (3)
Na1	0.0230 (7)	0.0185 (7)	0.0242 (7)	0.000	0.0003 (5)	0.000
Na2	0.0220 (7)	0.0179 (7)	0.0185 (7)	0.0000 (6)	0.0002 (5)	0.0003 (6)
O1	0.0213 (9)	0.0257 (10)	0.0291 (10)	0.0017 (8)	-0.0031 (7)	-0.0061 (8)
O2	0.0229 (10)	0.0565 (14)	0.0259 (10)	0.0079 (9)	0.0063 (8)	0.0157 (9)
O3	0.0258 (10)	0.0193 (9)	0.0425 (11)	0.0045 (8)	-0.0077 (8)	0.0058 (8)
O1W	0.0255 (10)	0.0207 (9)	0.0250 (10)	0.0017 (8)	0.0000 (8)	-0.0023 (8)
O2W	0.0201 (10)	0.0336 (11)	0.0230 (10)	0.0017 (8)	-0.0005 (7)	0.0021 (9)
N1	0.0194 (10)	0.0184 (11)	0.0181 (10)	0.0028 (8)	-0.0014 (8)	-0.0002 (8)

C1	0.0161 (11)	0.0174 (12)	0.0135 (11)	0.0023 (10)	0.0009 (9)	-0.0020 (9)
C2	0.0189 (13)	0.0157 (12)	0.0194 (12)	0.0003 (10)	0.0022 (9)	0.0015 (10)
C3	0.0225 (13)	0.0166 (12)	0.0155 (11)	0.0024 (10)	-0.0010 (9)	-0.0001 (10)
C4	0.0170 (12)	0.0230 (13)	0.0188 (12)	0.0011 (10)	-0.0013 (9)	-0.0031 (10)
C5	0.0215 (13)	0.0201 (12)	0.0200 (12)	-0.0053 (10)	0.0015 (10)	-0.0012 (11)
C6	0.0245 (13)	0.0152 (12)	0.0149 (11)	0.0003 (10)	0.0002 (9)	0.0006 (10)

Geometric parameters (\AA , $^\circ$)

S1—O2	1.4464 (18)	Na2—O2W	2.4480 (17)
S1—O3	1.4474 (18)	Na2—Na1 ^{iv}	4.0223 (4)
S1—O1	1.4575 (18)	O3—Na1 ^v	2.4174 (19)
S1—C1	1.779 (2)	O1W—H1W	0.871 (10)
S1—Na1	3.3852 (12)	O1W—H2W	0.872 (10)
Na1—O3 ⁱ	2.4174 (19)	O2W—H3W	0.867 (10)
Na1—O3 ⁱⁱ	2.4175 (19)	O2W—H4W	0.866 (10)
Na1—O1	2.419 (2)	N1—N1 ^{vi}	1.262 (4)
Na1—O1 ⁱⁱⁱ	2.419 (2)	N1—C3	1.431 (3)
Na1—O1W ⁱⁱⁱ	2.5019 (18)	C1—C2	1.384 (3)
Na1—O1W	2.5019 (18)	C1—C6	1.388 (3)
Na1—S1 ⁱⁱⁱ	3.3853 (12)	C2—C3	1.397 (3)
Na1—Na2	4.0223 (5)	C2—H2	0.9500
Na1—Na2 ⁱⁱⁱ	4.0223 (5)	C3—C4	1.392 (3)
Na1—H1W	2.56 (3)	C4—C5	1.384 (3)
Na2—O2 ^{iv}	2.3340 (18)	C4—H4	0.9500
Na2—O2	2.3340 (18)	C5—C6	1.395 (3)
Na2—O1W	2.3688 (17)	C5—H5	0.9500
Na2—O1W ^{iv}	2.3688 (17)	C6—H6	0.9500
Na2—O2W ^{iv}	2.4480 (17)		
O2—S1—O3	113.21 (12)	S1 ⁱⁱⁱ —Na1—H1W	131.1 (4)
O2—S1—O1	112.26 (12)	Na2—Na1—H1W	44.4 (6)
O3—S1—O1	112.92 (11)	Na2 ⁱⁱⁱ —Na1—H1W	168.6 (3)
O2—S1—C1	105.55 (10)	O2 ^{iv} —Na2—O2	180.0
O3—S1—C1	106.13 (11)	O2 ^{iv} —Na2—O1W	91.49 (7)
O1—S1—C1	106.00 (10)	O2—Na2—O1W	88.51 (7)
O2—S1—Na1	74.22 (9)	O2 ^{iv} —Na2—O1W ^{iv}	88.51 (7)
O3—S1—Na1	126.91 (8)	O2—Na2—O1W ^{iv}	91.49 (7)
O1—S1—Na1	38.41 (7)	O1W—Na2—O1W ^{iv}	180.0
C1—S1—Na1	122.85 (8)	O2 ^{iv} —Na2—O2W ^{iv}	81.69 (6)
O3 ⁱ —Na1—O3 ⁱⁱ	100.81 (10)	O2—Na2—O2W ^{iv}	98.30 (6)
O3 ⁱ —Na1—O1	85.49 (6)	O1W—Na2—O2W ^{iv}	87.42 (6)
O3 ⁱⁱ —Na1—O1	163.62 (6)	O1W ^{iv} —Na2—O2W ^{iv}	92.58 (6)
O3 ⁱ —Na1—O1 ⁱⁱⁱ	163.62 (6)	O2 ^{iv} —Na2—O2W	98.31 (6)
O3 ⁱⁱ —Na1—O1 ⁱⁱⁱ	85.49 (6)	O2—Na2—O2W	81.70 (6)
O1—Na1—O1 ⁱⁱⁱ	92.59 (9)	O1W—Na2—O2W	92.58 (6)
O3 ⁱ —Na1—O1W ⁱⁱⁱ	86.52 (7)	O1W ^{iv} —Na2—O2W	87.42 (6)
O3 ⁱⁱ —Na1—O1W ⁱⁱⁱ	75.28 (6)	O2W ^{iv} —Na2—O2W	180.0

O1—Na1—O1W ⁱⁱⁱ	90.17 (6)	O2 ^{iv} —Na2—Na1	124.88 (5)
O1 ⁱⁱⁱ —Na1—O1W ⁱⁱⁱ	109.77 (6)	O2—Na2—Na1	55.12 (5)
O3 ⁱ —Na1—O1W	75.28 (6)	O1W—Na2—Na1	35.41 (5)
O3 ⁱⁱ —Na1—O1W	86.52 (7)	O1W ^{iv} —Na2—Na1	144.59 (5)
O1—Na1—O1W	109.77 (6)	O2W ^{iv} —Na2—Na1	102.77 (4)
O1 ⁱⁱⁱ —Na1—O1W	90.17 (6)	O2W—Na2—Na1	77.23 (4)
O1W ⁱⁱⁱ —Na1—O1W	151.40 (10)	O2 ^{iv} —Na2—Na1 ^{iv}	55.12 (5)
O3 ⁱ —Na1—S1	90.64 (4)	O2—Na2—Na1 ^{iv}	124.88 (5)
O3 ⁱⁱ —Na1—S1	167.03 (6)	O1W—Na2—Na1 ^{iv}	144.59 (5)
O1—Na1—S1	21.98 (4)	O1W ^{iv} —Na2—Na1 ^{iv}	35.41 (5)
O1 ⁱⁱⁱ —Na1—S1	81.88 (5)	O2W ^{iv} —Na2—Na1 ^{iv}	77.23 (4)
O1W ⁱⁱⁱ —Na1—S1	111.83 (5)	O2W—Na2—Na1 ^{iv}	102.77 (4)
O1W—Na1—S1	90.57 (5)	Na1—Na2—Na1 ^{iv}	180.0
O3 ⁱ —Na1—S1 ⁱⁱⁱ	167.03 (6)	S1—O1—Na1	119.61 (10)
O3 ⁱⁱ —Na1—S1 ⁱⁱⁱ	90.64 (4)	S1—O2—Na2	166.59 (14)
O1—Na1—S1 ⁱⁱⁱ	81.88 (5)	S1—O3—Na1 ^v	137.88 (11)
O1 ⁱⁱⁱ —Na1—S1 ⁱⁱⁱ	21.98 (4)	Na2—O1W—Na1	111.31 (8)
O1W ⁱⁱⁱ —Na1—S1 ⁱⁱⁱ	90.58 (5)	Na2—O1W—H1W	114 (2)
O1W—Na1—S1 ⁱⁱⁱ	111.83 (5)	Na1—O1W—H1W	84 (2)
S1—Na1—S1 ⁱⁱⁱ	78.70 (3)	Na2—O1W—H2W	125 (2)
O3 ⁱ —Na1—Na2	89.92 (4)	Na1—O1W—H2W	114 (3)
O3 ⁱⁱ —Na1—Na2	113.24 (5)	H1W—O1W—H2W	101 (2)
O1—Na1—Na2	81.61 (4)	Na2—O2W—H3W	103 (2)
O1 ⁱⁱⁱ —Na1—Na2	73.71 (4)	Na2—O2W—H4W	130 (2)
O1W ⁱⁱⁱ —Na1—Na2	171.28 (5)	H3W—O2W—H4W	103.3 (19)
O1W—Na1—Na2	33.27 (4)	N1 ^{vi} —N1—C3	113.9 (2)
S1—Na1—Na2	60.206 (15)	C2—C1—C6	121.1 (2)
S1 ⁱⁱⁱ —Na1—Na2	91.13 (2)	C2—C1—S1	118.74 (18)
O3 ⁱ —Na1—Na2 ⁱⁱⁱ	113.24 (5)	C6—C1—S1	120.12 (17)
O3 ⁱⁱ —Na1—Na2 ⁱⁱⁱ	89.92 (4)	C1—C2—C3	118.9 (2)
O1—Na1—Na2 ⁱⁱⁱ	73.71 (4)	C1—C2—H2	120.5
O1 ⁱⁱⁱ —Na1—Na2 ⁱⁱⁱ	81.61 (4)	C3—C2—H2	120.5
O1W ⁱⁱⁱ —Na1—Na2 ⁱⁱⁱ	33.27 (4)	C4—C3—C2	120.4 (2)
O1W—Na1—Na2 ⁱⁱⁱ	171.28 (5)	C4—C3—N1	115.9 (2)
S1—Na1—Na2 ⁱⁱⁱ	91.13 (2)	C2—C3—N1	123.7 (2)
S1 ⁱⁱⁱ —Na1—Na2 ⁱⁱⁱ	60.207 (15)	C5—C4—C3	120.0 (2)
Na2—Na1—Na2 ⁱⁱⁱ	144.06 (4)	C5—C4—H4	120.0
O3 ⁱ —Na1—H1W	55.5 (3)	C3—C4—H4	120.0
O3 ⁱⁱ —Na1—H1W	90.9 (7)	C4—C5—C6	120.0 (2)
O1—Na1—H1W	105.0 (7)	C4—C5—H5	120.0
O1 ⁱⁱⁱ —Na1—H1W	109.8 (3)	C6—C5—H5	120.0
O1W ⁱⁱⁱ —Na1—H1W	136.7 (5)	C1—C6—C5	119.5 (2)
O1W—Na1—H1W	19.8 (3)	C1—C6—H6	120.2
S1—Na1—H1W	90.6 (7)	C5—C6—H6	120.2
O2—S1—O1—Na1	8.38 (15)	O3—S1—C1—C6	-17.6 (2)
O3—S1—O1—Na1	-121.08 (12)	O1—S1—C1—C6	102.7 (2)
C1—S1—O1—Na1	123.13 (11)	Na1—S1—C1—C6	140.94 (16)

O3—S1—O2—Na2	167.7 (5)	C6—C1—C2—C3	1.2 (3)
O1—S1—O2—Na2	38.4 (5)	S1—C1—C2—C3	-178.45 (17)
C1—S1—O2—Na2	-76.6 (5)	C1—C2—C3—C4	-2.4 (3)
Na1—S1—O2—Na2	43.8 (5)	C1—C2—C3—N1	178.7 (2)
O2—S1—O3—Na1 ^v	-51.3 (2)	N1 ^{vi} —N1—C3—C4	162.2 (2)
O1—S1—O3—Na1 ^v	77.64 (18)	N1 ^{vi} —N1—C3—C2	-18.9 (4)
C1—S1—O3—Na1 ^v	-166.65 (15)	C2—C3—C4—C5	1.6 (3)
Na1—S1—O3—Na1 ^v	35.9 (2)	N1—C3—C4—C5	-179.4 (2)
O2—S1—C1—C2	41.6 (2)	C3—C4—C5—C6	0.5 (3)
O3—S1—C1—C2	162.04 (18)	C2—C1—C6—C5	0.8 (3)
O1—S1—C1—C2	-77.7 (2)	S1—C1—C6—C5	-179.51 (18)
Na1—S1—C1—C2	-39.4 (2)	C4—C5—C6—C1	-1.7 (3)
O2—S1—C1—C6	-138.1 (2)		

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

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1 W —H2 W ···O2 W ^{iv}	0.87 (1)	2.07 (2)	2.919 (3)	163 (3)
O1 W —H1 W ···O2 ⁱ	0.87 (1)	2.29 (2)	3.044 (3)	145 (3)
O1 W —H1 W ···O3 ⁱ	0.87 (1)	2.32 (3)	3.005 (3)	136 (3)
O2 W —H3 W ···O1 ⁱⁱⁱ	0.87 (1)	1.94 (1)	2.807 (2)	175 (3)
O2 W —H4 W ···N1 ^{vii}	0.87 (1)	2.22 (1)	3.076 (3)	168 (3)

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

catena-Poly[[tetraaquacalcium(II)]- μ -3,3'-(diazane-1,2-diyl)bis(benzenesulfonato)] (II)

Crystal data

[Ca(C₁₂H₈N₂O₆S₂)(H₂O)₄]

$M_r = 452.47$

Triclinic, $P\bar{1}$

$a = 6.3875$ (2) Å

$b = 6.7470$ (2) Å

$c = 11.3030$ (5) Å

$\alpha = 94.289$ (2)°

$\beta = 103.160$ (2)°

$\gamma = 108.456$ (2)°

$V = 444.21$ (3) Å³

$Z = 1$

$F(000) = 234$

$D_x = 1.691$ Mg m⁻³

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

Cell parameters from 1934 reflections

$\theta = 1.0$ – 27.5 °

$\mu = 0.65$ mm⁻¹

$T = 123$ K

Plate, yellow-orange

$0.50 \times 0.25 \times 0.05$ mm

Data collection

Nonius Kappa CCD

diffractometer

Radiation source: sealed tube

phi and ω scans

3837 measured reflections

2038 independent reflections

1775 reflections with $I > 2\sigma(I)$

$R_{int} = 0.020$

$\theta_{max} = 27.6$ °, $\theta_{min} = 1.9$ °

$h = -8$ → 8

$k = -8$ → 8

$l = -14$ → 14

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.070$

$S = 1.05$
 2038 reflections
 140 parameters
 6 restraints
 Hydrogen site location: mixed

H atoms treated by a mixture of independent
 and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0253P)^2 + 0.2861P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.46 \text{ e } \text{\AA}^{-3}$$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ca1	0.5000	0.5000	0.5000	0.01202 (12)
S1	0.81011 (6)	0.85257 (6)	0.30913 (3)	0.01227 (11)
O1	0.82484 (19)	1.06481 (17)	0.35704 (11)	0.0180 (3)
O2	1.03284 (18)	0.83889 (18)	0.30803 (10)	0.0167 (2)
O3	0.6843 (2)	0.69091 (18)	0.37004 (11)	0.0202 (3)
O1W	0.8574 (2)	0.5188 (2)	0.61733 (12)	0.0230 (3)
O2W	0.5467 (2)	0.82518 (18)	0.61047 (12)	0.0229 (3)
N1	0.0426 (2)	0.5479 (2)	-0.03915 (13)	0.0170 (3)
C1	0.6455 (3)	0.7956 (2)	0.15386 (14)	0.0125 (3)
C2	0.4105 (3)	0.6926 (2)	0.12544 (15)	0.0143 (3)
H2	0.3369	0.6498	0.1881	0.017*
C3	0.2852 (3)	0.6534 (2)	0.00261 (15)	0.0147 (3)
C4	0.3926 (3)	0.7176 (2)	-0.08881 (15)	0.0165 (3)
H4	0.3047	0.6926	-0.1719	0.020*
C5	0.6283 (3)	0.8181 (3)	-0.05911 (15)	0.0173 (3)
H5	0.7019	0.8592	-0.1220	0.021*
C6	0.7562 (3)	0.8584 (2)	0.06276 (15)	0.0157 (3)
H6	0.9173	0.9280	0.0839	0.019*
H1W	0.922 (4)	0.429 (3)	0.644 (2)	0.045 (7)*
H2W	0.973 (3)	0.635 (2)	0.630 (2)	0.057 (8)*
H3W	0.671 (2)	0.933 (3)	0.632 (2)	0.048 (7)*
H4W	0.442 (3)	0.877 (3)	0.618 (2)	0.040 (7)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca1	0.0106 (2)	0.0102 (2)	0.0134 (2)	0.00197 (16)	0.00191 (16)	0.00172 (16)
S1	0.00967 (19)	0.01111 (19)	0.01310 (19)	0.00092 (14)	0.00129 (14)	0.00152 (14)
O1	0.0153 (6)	0.0142 (6)	0.0206 (6)	0.0038 (4)	0.0011 (5)	-0.0032 (5)
O2	0.0114 (5)	0.0185 (6)	0.0182 (6)	0.0048 (4)	0.0008 (4)	0.0020 (5)
O3	0.0173 (6)	0.0215 (6)	0.0152 (6)	-0.0019 (5)	0.0021 (5)	0.0072 (5)
O1W	0.0130 (6)	0.0183 (6)	0.0330 (7)	0.0039 (5)	-0.0018 (5)	0.0069 (5)

O2W	0.0156 (6)	0.0147 (6)	0.0348 (7)	0.0022 (5)	0.0067 (5)	-0.0055 (5)
N1	0.0120 (7)	0.0160 (7)	0.0189 (7)	0.0020 (5)	0.0006 (5)	0.0007 (5)
C1	0.0123 (7)	0.0093 (7)	0.0142 (7)	0.0027 (6)	0.0016 (6)	0.0014 (6)
C2	0.0126 (7)	0.0120 (7)	0.0175 (8)	0.0036 (6)	0.0036 (6)	0.0027 (6)
C3	0.0113 (7)	0.0120 (7)	0.0184 (8)	0.0030 (6)	0.0012 (6)	0.0013 (6)
C4	0.0173 (8)	0.0141 (8)	0.0143 (8)	0.0038 (6)	-0.0003 (6)	0.0004 (6)
C5	0.0176 (8)	0.0174 (8)	0.0163 (8)	0.0044 (6)	0.0058 (6)	0.0031 (6)
C6	0.0124 (7)	0.0128 (7)	0.0196 (8)	0.0018 (6)	0.0035 (6)	0.0017 (6)

Geometric parameters (Å, °)

Ca1—O3	2.3050 (11)	O2W—H4W	0.863 (9)
Ca1—O3 ⁱ	2.3051 (11)	N1—N1 ⁱⁱ	1.256 (3)
Ca1—O1W	2.3235 (12)	N1—C3	1.432 (2)
Ca1—O1W ⁱ	2.3236 (12)	C1—C2	1.388 (2)
Ca1—O2W ⁱ	2.3385 (12)	C1—C6	1.395 (2)
Ca1—O2W	2.3385 (12)	C2—C3	1.394 (2)
S1—O3	1.4556 (11)	C2—H2	0.9500
S1—O2	1.4573 (12)	C3—C4	1.388 (2)
S1—O1	1.4588 (12)	C4—C5	1.388 (2)
S1—C1	1.7711 (16)	C4—H4	0.9500
O1W—H1W	0.870 (9)	C5—C6	1.389 (2)
O1W—H2W	0.864 (10)	C5—H5	0.9500
O2W—H3W	0.862 (10)	C6—H6	0.9500
O3—Ca1—O3 ⁱ	180.0	H1W—O1W—H2W	102.3 (17)
O3—Ca1—O1W	87.66 (4)	Ca1—O2W—H3W	125.5 (15)
O3 ⁱ —Ca1—O1W	92.34 (4)	Ca1—O2W—H4W	127.9 (15)
O3—Ca1—O1W ⁱ	92.34 (4)	H3W—O2W—H4W	103.9 (17)
O3 ⁱ —Ca1—O1W ⁱ	87.66 (4)	N1 ⁱⁱ —N1—C3	113.72 (17)
O1W—Ca1—O1W ⁱ	180.00 (6)	C2—C1—C6	121.50 (14)
O3—Ca1—O2W ⁱ	93.07 (4)	C2—C1—S1	119.72 (12)
O3 ⁱ —Ca1—O2W ⁱ	86.93 (5)	C6—C1—S1	118.78 (12)
O1W—Ca1—O2W ⁱ	90.52 (5)	C1—C2—C3	118.31 (15)
O1W ⁱ —Ca1—O2W ⁱ	89.48 (5)	C1—C2—H2	120.8
O3—Ca1—O2W	86.93 (5)	C3—C2—H2	120.8
O3 ⁱ —Ca1—O2W	93.07 (4)	C4—C3—C2	120.82 (14)
O1W—Ca1—O2W	89.48 (5)	C4—C3—N1	115.24 (14)
O1W ⁱ —Ca1—O2W	90.52 (5)	C2—C3—N1	123.94 (15)
O2W ⁱ —Ca1—O2W	180.0	C3—C4—C5	120.17 (15)
O3—S1—O2	112.30 (7)	C3—C4—H4	119.9
O3—S1—O1	112.52 (7)	C5—C4—H4	119.9
O2—S1—O1	112.61 (7)	C4—C5—C6	119.87 (15)
O3—S1—C1	105.40 (7)	C4—C5—H5	120.1
O2—S1—C1	106.74 (7)	C6—C5—H5	120.1
O1—S1—C1	106.66 (7)	C5—C6—C1	119.31 (14)
S1—O3—Ca1	166.87 (8)	C5—C6—H6	120.3
Ca1—O1W—H1W	136.4 (15)	C1—C6—H6	120.3

Ca1—O1W—H2W	120.0 (16)		
O2—S1—O3—Ca1	111.4 (3)	C1—C2—C3—C4	-0.6 (2)
O1—S1—O3—Ca1	-16.9 (4)	C1—C2—C3—N1	179.69 (14)
C1—S1—O3—Ca1	-132.8 (3)	N1 ⁱⁱ —N1—C3—C4	165.42 (17)
O3—S1—C1—C2	27.51 (14)	N1 ⁱⁱ —N1—C3—C2	-14.8 (3)
O2—S1—C1—C2	147.11 (12)	C2—C3—C4—C5	1.4 (2)
O1—S1—C1—C2	-92.29 (13)	N1—C3—C4—C5	-178.84 (14)
O3—S1—C1—C6	-153.27 (13)	C3—C4—C5—C6	-1.3 (2)
O2—S1—C1—C6	-33.67 (14)	C4—C5—C6—C1	0.4 (2)
O1—S1—C1—C6	86.93 (13)	C2—C1—C6—C5	0.4 (2)
C6—C1—C2—C3	-0.3 (2)	S1—C1—C6—C5	-178.82 (12)
S1—C1—C2—C3	178.88 (11)		

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

Hydrogen-bond geometry (Å, °)

<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>
O1W—H1W...O2 ⁱⁱⁱ	0.87 (1)	2.01 (1)	2.8521 (17)	162 (2)
O1W—H2W...O1 ^{iv}	0.86 (1)	2.00 (1)	2.8454 (17)	165 (2)
O2W—H3W...O2 ^{iv}	0.86 (1)	1.95 (1)	2.8119 (16)	174 (2)
O2W—H4W...O1 ^v	0.86 (1)	1.94 (1)	2.7907 (16)	168 (2)

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

catena-Poly[[[diaquacalcium(II)]- μ -2-(4-amino-3-sulfonatophenyl)-\ 1-(4-sulfonatophenyl)diazenium] dihydrate] (III)

Crystal data

[Na(C₁₂H₁₀N₃O₆S₂)(H₂O)₂] \cdot 2H₂O

M_r = 451.40

Monoclinic, *P*2₁/*c*

a = 13.9454 (18) Å

b = 19.517 (3) Å

c = 6.9014 (9) Å

β = 93.838 (2)°

V = 1874.2 (4) Å³

Z = 4

F(000) = 936

D_x = 1.600 Mg m⁻³

Synchrotron radiation, λ = 0.6775 Å

Cell parameters from 8092 reflections

θ = 1.4–24.3°

μ = 0.32 mm⁻¹

T = 150 K

Fibre, red

0.50 × 0.01 × 0.01 mm

Data collection

APEXII

diffractometer

Radiation source: Station 9.8 Daresbury SRS

ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2012)

T_{min} = 0.676, *T_{max}* = 1.000

15360 measured reflections

3531 independent reflections

2772 reflections with *I* > 2 σ (*I*)

R_{int} = 0.049

θ_{\max} = 24.3°, θ_{\min} = 1.4°

h = -16→16

k = -23→23

l = -8→8

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.107$
 $S = 1.04$
 3531 reflections
 311 parameters
 15 restraints

Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0583P)^2 + 0.7405P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.35 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.44 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Na1	0.12675 (8)	0.22691 (6)	0.23165 (16)	0.0383 (3)	
S1	-0.39901 (4)	-0.11626 (3)	0.25342 (9)	0.02313 (17)	
S2	0.01324 (4)	0.38021 (3)	0.06796 (9)	0.02399 (17)	
O1	-0.33121 (14)	-0.14369 (9)	0.4031 (3)	0.0352 (5)	
O2	-0.49783 (13)	-0.12523 (9)	0.2974 (3)	0.0348 (5)	
O3	-0.38045 (12)	-0.14348 (8)	0.0621 (3)	0.0276 (4)	
O4	-0.00470 (13)	0.42439 (8)	-0.1002 (3)	0.0295 (4)	
O5	0.06200 (12)	0.41576 (10)	0.2293 (3)	0.0344 (5)	
O6	0.05796 (12)	0.31539 (9)	0.0222 (3)	0.0291 (4)	
O1W	0.02623 (18)	0.15088 (11)	0.0719 (3)	0.0463 (5)	
O2W	0.23561 (13)	0.23836 (9)	-0.0156 (3)	0.0301 (4)	
O3W	0.53321 (13)	0.24230 (9)	0.4670 (3)	0.0319 (4)	
O4W	-0.2986 (10)	0.5679 (6)	0.2536 (7)	0.036 (2)	0.67 (4)
H7W	-0.322 (3)	0.593 (2)	0.344 (5)	0.043*	0.6659
H8W	-0.308 (4)	0.594 (2)	0.152 (4)	0.043*	0.6659
O5W	-0.258 (2)	0.5945 (15)	0.2586 (13)	0.043 (6)	0.33 (4)
H9W	-0.294 (6)	0.614 (5)	0.343 (11)	0.052*	0.3341
H10W	-0.287 (7)	0.611 (5)	0.151 (8)	0.052*	0.3341
N1	-0.32011 (15)	0.18160 (10)	0.2481 (3)	0.0226 (4)	
N2	-0.23798 (14)	0.20549 (10)	0.2029 (3)	0.0228 (5)	
N3	-0.14295 (18)	0.47735 (11)	0.1967 (3)	0.0271 (5)	
C1	-0.37563 (17)	-0.02746 (12)	0.2466 (3)	0.0210 (5)	
C2	-0.45031 (17)	0.01909 (12)	0.2548 (4)	0.0254 (5)	
H2	-0.5145	0.0034	0.2609	0.030*	
C3	-0.43073 (17)	0.08833 (12)	0.2541 (4)	0.0255 (5)	
H3	-0.4813	0.1207	0.2599	0.031*	
C4	-0.33685 (18)	0.11031 (11)	0.2448 (4)	0.0222 (5)	
C5	-0.26117 (18)	0.06385 (12)	0.2347 (4)	0.0244 (5)	
H5	-0.1971	0.0796	0.2271	0.029*	
C6	-0.28139 (17)	-0.00534 (12)	0.2358 (4)	0.0238 (5)	

H6	-0.2310	-0.0378	0.2293	0.029*
C7	-0.22223 (17)	0.27328 (12)	0.2046 (3)	0.0205 (5)
C8	-0.12979 (17)	0.29210 (12)	0.1488 (3)	0.0206 (5)
H8	-0.0862	0.2573	0.1151	0.025*
C9	-0.10223 (16)	0.35880 (12)	0.1425 (3)	0.0212 (5)
C10	-0.16655 (17)	0.41207 (12)	0.1950 (3)	0.0215 (5)
C11	-0.26021 (17)	0.39255 (12)	0.2479 (4)	0.0229 (5)
H11	-0.3045	0.4271	0.2796	0.027*
C12	-0.28719 (17)	0.32635 (12)	0.2540 (3)	0.0217 (5)
H12	-0.3496	0.3148	0.2911	0.026*
H3N	-0.092 (2)	0.4909 (17)	0.164 (5)	0.047 (10)*
H1N	-0.365 (2)	0.2073 (15)	0.279 (4)	0.027 (7)*
H2N	-0.184 (2)	0.5049 (16)	0.224 (4)	0.037 (9)*
H2W	0.006 (3)	0.1202 (15)	0.153 (5)	0.103 (17)*
H5W	0.511 (2)	0.2091 (11)	0.534 (4)	0.059 (11)*
H3W	0.2823 (16)	0.2095 (12)	-0.036 (5)	0.064 (11)*
H4W	0.2700 (19)	0.2733 (10)	0.028 (5)	0.056 (11)*
H6W	0.4863 (17)	0.2716 (13)	0.466 (5)	0.066 (12)*
H1W	0.046 (3)	0.1233 (15)	-0.019 (4)	0.077 (14)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Na1	0.0349 (6)	0.0465 (7)	0.0334 (6)	-0.0113 (5)	0.0016 (5)	0.0046 (5)
S1	0.0273 (3)	0.0131 (3)	0.0294 (4)	-0.0020 (2)	0.0045 (3)	0.0000 (2)
S2	0.0222 (3)	0.0193 (3)	0.0313 (4)	-0.0031 (2)	0.0076 (2)	-0.0007 (3)
O1	0.0504 (12)	0.0183 (9)	0.0358 (11)	0.0020 (8)	-0.0061 (9)	0.0040 (8)
O2	0.0329 (10)	0.0202 (9)	0.0530 (12)	-0.0064 (8)	0.0160 (9)	-0.0027 (9)
O3	0.0337 (10)	0.0185 (9)	0.0312 (10)	0.0008 (7)	0.0060 (8)	-0.0034 (7)
O4	0.0341 (10)	0.0196 (9)	0.0358 (10)	-0.0010 (7)	0.0108 (8)	0.0047 (8)
O5	0.0276 (10)	0.0366 (11)	0.0392 (11)	-0.0094 (8)	0.0042 (8)	-0.0066 (9)
O6	0.0257 (9)	0.0207 (9)	0.0418 (11)	0.0020 (7)	0.0100 (8)	0.0018 (8)
O1W	0.0674 (16)	0.0345 (12)	0.0368 (12)	-0.0072 (11)	0.0022 (11)	0.0001 (10)
O2W	0.0280 (10)	0.0235 (10)	0.0390 (11)	0.0017 (8)	0.0034 (8)	-0.0046 (8)
O3W	0.0327 (11)	0.0221 (9)	0.0421 (11)	0.0030 (8)	0.0123 (9)	0.0091 (9)
O4W	0.044 (5)	0.032 (4)	0.032 (2)	0.015 (3)	0.0048 (19)	-0.0011 (18)
O5W	0.048 (9)	0.045 (9)	0.036 (4)	0.020 (8)	-0.003 (4)	-0.006 (4)
N1	0.0237 (11)	0.0151 (10)	0.0294 (12)	-0.0020 (9)	0.0046 (9)	0.0010 (9)
N2	0.0252 (11)	0.0179 (10)	0.0252 (11)	-0.0033 (8)	0.0014 (9)	0.0011 (8)
N3	0.0262 (12)	0.0159 (11)	0.0401 (14)	-0.0010 (10)	0.0099 (10)	-0.0005 (10)
C1	0.0246 (12)	0.0139 (11)	0.0244 (12)	-0.0020 (9)	0.0017 (10)	0.0000 (9)
C2	0.0234 (12)	0.0196 (12)	0.0331 (14)	-0.0043 (10)	0.0020 (10)	-0.0012 (10)
C3	0.0240 (13)	0.0199 (12)	0.0328 (14)	0.0020 (10)	0.0021 (11)	0.0000 (11)
C4	0.0288 (13)	0.0139 (11)	0.0241 (13)	-0.0021 (10)	0.0023 (10)	0.0006 (10)
C5	0.0211 (12)	0.0215 (13)	0.0309 (14)	-0.0035 (10)	0.0034 (10)	0.0011 (11)
C6	0.0224 (12)	0.0184 (12)	0.0308 (13)	0.0023 (9)	0.0029 (10)	0.0013 (10)
C7	0.0219 (12)	0.0161 (12)	0.0234 (12)	-0.0024 (9)	0.0005 (10)	-0.0005 (9)
C8	0.0230 (12)	0.0163 (12)	0.0225 (12)	0.0003 (9)	0.0018 (10)	-0.0006 (9)

C9	0.0202 (12)	0.0182 (12)	0.0253 (13)	-0.0015 (9)	0.0028 (10)	0.0003 (10)
C10	0.0255 (12)	0.0165 (12)	0.0226 (12)	-0.0011 (10)	0.0013 (10)	0.0022 (10)
C11	0.0245 (12)	0.0182 (12)	0.0264 (13)	0.0028 (9)	0.0044 (10)	0.0006 (10)
C12	0.0204 (12)	0.0206 (12)	0.0244 (13)	-0.0013 (9)	0.0035 (10)	0.0008 (10)

Geometric parameters (Å, °)

Na1—O1W	2.275 (2)	O5W—H10W	0.879 (10)
Na1—O2W ⁱ	2.335 (2)	N1—N2	1.294 (3)
Na1—O2W	2.369 (2)	N1—C4	1.411 (3)
Na1—O6	2.409 (2)	N1—H1N	0.84 (3)
Na1—O6 ⁱ	2.425 (2)	N2—C7	1.341 (3)
Na1—Na1 ⁱⁱ	3.5664 (7)	N3—C10	1.316 (3)
Na1—Na1 ⁱ	3.5665 (7)	N3—H3N	0.81 (3)
Na1—H4W	2.68 (3)	N3—H2N	0.82 (3)
S1—O2	1.4415 (18)	C1—C2	1.386 (3)
S1—O1	1.4552 (19)	C1—C6	1.390 (3)
S1—O3	1.4623 (18)	C2—C3	1.379 (3)
S1—C1	1.765 (2)	C2—H2	0.9500
S2—O5	1.4430 (19)	C3—C4	1.383 (3)
S2—O4	1.4541 (18)	C3—H3	0.9500
S2—O6	1.4545 (18)	C4—C5	1.397 (3)
S2—C9	1.773 (2)	C5—C6	1.380 (3)
O6—Na1 ⁱⁱ	2.425 (2)	C5—H5	0.9500
O1W—H2W	0.878 (10)	C6—H6	0.9500
O1W—H1W	0.883 (10)	C7—C8	1.418 (3)
O2W—Na1 ⁱⁱ	2.335 (2)	C7—C12	1.432 (3)
O2W—H3W	0.879 (10)	C8—C9	1.359 (3)
O2W—H4W	0.876 (10)	C8—H8	0.9500
O3W—H5W	0.863 (10)	C9—C10	1.435 (3)
O3W—H6W	0.869 (10)	C10—C11	1.431 (3)
O4W—H7W	0.875 (10)	C11—C12	1.347 (3)
O4W—H8W	0.876 (10)	C11—H11	0.9500
O5W—H9W	0.878 (10)	C12—H12	0.9500
O1W—Na1—O2W ⁱ	154.18 (9)	Na1 ⁱⁱ —O2W—H4W	110 (2)
O1W—Na1—O2W	96.67 (9)	Na1—O2W—H4W	101 (2)
O2W ⁱ —Na1—O2W	95.44 (7)	H3W—O2W—H4W	99.1 (19)
O1W—Na1—O6	88.23 (8)	H5W—O3W—H6W	102 (2)
O2W ⁱ —Na1—O6	116.93 (8)	H7W—O4W—H8W	101 (2)
O2W—Na1—O6	75.46 (7)	H9W—O5W—H10W	99 (2)
O1W—Na1—O6 ⁱ	85.06 (8)	N2—N1—C4	120.0 (2)
O2W ⁱ —Na1—O6 ⁱ	75.79 (7)	N2—N1—H1N	122.2 (19)
O2W—Na1—O6 ⁱ	159.34 (8)	C4—N1—H1N	117.8 (19)
O6—Na1—O6 ⁱ	125.20 (8)	N1—N2—C7	120.0 (2)
O1W—Na1—Na1 ⁱⁱ	74.68 (6)	C10—N3—H3N	123 (2)
O2W ⁱ —Na1—Na1 ⁱⁱ	127.39 (6)	C10—N3—H2N	118 (2)
O2W—Na1—Na1 ⁱⁱ	40.34 (5)	H3N—N3—H2N	120 (3)

O6—Na1—Na1 ⁱⁱ	42.63 (5)	C2—C1—C6	120.9 (2)
O6 ⁱ —Na1—Na1 ⁱⁱ	155.75 (5)	C2—C1—S1	120.13 (18)
O1W—Na1—Na1 ⁱ	126.43 (7)	C6—C1—S1	118.91 (18)
O2W ⁱ —Na1—Na1 ⁱ	41.06 (5)	C3—C2—C1	119.5 (2)
O2W—Na1—Na1 ⁱ	135.61 (6)	C3—C2—H2	120.2
O6—Na1—Na1 ⁱ	111.93 (7)	C1—C2—H2	120.2
O6 ⁱ —Na1—Na1 ⁱ	42.29 (5)	C2—C3—C4	119.5 (2)
Na1 ⁱⁱ —Na1—Na1 ⁱ	150.73 (7)	C2—C3—H3	120.2
O1W—Na1—H4W	115.1 (4)	C4—C3—H3	120.2
O2W ⁱ —Na1—H4W	79.8 (5)	C3—C4—C5	121.4 (2)
O2W—Na1—H4W	18.8 (4)	C3—C4—N1	117.5 (2)
O6—Na1—H4W	74.0 (7)	C5—C4—N1	121.1 (2)
O6 ⁱ —Na1—H4W	154.1 (6)	C6—C5—C4	118.7 (2)
Na1 ⁱⁱ —Na1—H4W	50.1 (6)	C6—C5—H5	120.7
Na1 ⁱ —Na1—H4W	118.1 (5)	C4—C5—H5	120.7
O2—S1—O1	113.00 (12)	C5—C6—C1	119.9 (2)
O2—S1—O3	112.05 (11)	C5—C6—H6	120.0
O1—S1—O3	111.19 (11)	C1—C6—H6	120.0
O2—S1—C1	107.81 (11)	N2—C7—C8	113.9 (2)
O1—S1—C1	105.53 (11)	N2—C7—C12	127.6 (2)
O3—S1—C1	106.78 (11)	C8—C7—C12	118.6 (2)
O5—S2—O4	112.19 (11)	C9—C8—C7	121.4 (2)
O5—S2—O6	113.51 (11)	C9—C8—H8	119.3
O4—S2—O6	113.34 (11)	C7—C8—H8	119.3
O5—S2—C9	106.24 (11)	C8—C9—C10	120.2 (2)
O4—S2—C9	105.09 (11)	C8—C9—S2	119.96 (18)
O6—S2—C9	105.60 (11)	C10—C9—S2	119.84 (17)
S2—O6—Na1	130.74 (11)	N3—C10—C11	119.2 (2)
S2—O6—Na1 ⁱⁱ	132.42 (11)	N3—C10—C9	122.9 (2)
Na1—O6—Na1 ⁱⁱ	95.07 (6)	C11—C10—C9	117.9 (2)
Na1—O1W—H2W	110 (3)	C12—C11—C10	121.6 (2)
Na1—O1W—H1W	122 (3)	C12—C11—H11	119.2
H2W—O1W—H1W	99 (2)	C10—C11—H11	119.2
Na1 ⁱⁱ —O2W—Na1	98.59 (8)	C11—C12—C7	120.3 (2)
Na1 ⁱⁱ —O2W—H3W	121 (2)	C11—C12—H12	119.9
Na1—O2W—H3W	125 (2)	C7—C12—H12	119.9
O5—S2—O6—Na1	40.72 (16)	C2—C1—C6—C5	0.5 (4)
O4—S2—O6—Na1	170.23 (12)	S1—C1—C6—C5	-178.6 (2)
C9—S2—O6—Na1	-75.26 (15)	N1—N2—C7—C8	-179.0 (2)
O5—S2—O6—Na1 ⁱⁱ	-120.22 (14)	N1—N2—C7—C12	0.6 (4)
O4—S2—O6—Na1 ⁱⁱ	9.30 (18)	N2—C7—C8—C9	179.9 (2)
C9—S2—O6—Na1 ⁱⁱ	123.80 (14)	C12—C7—C8—C9	0.3 (4)
C4—N1—N2—C7	179.5 (2)	C7—C8—C9—C10	0.7 (4)
O2—S1—C1—C2	-8.7 (2)	C7—C8—C9—S2	-178.92 (18)
O1—S1—C1—C2	-129.7 (2)	O5—S2—C9—C8	-120.0 (2)
O3—S1—C1—C2	111.9 (2)	O4—S2—C9—C8	120.9 (2)
O2—S1—C1—C6	170.41 (19)	O6—S2—C9—C8	0.8 (2)

O1—S1—C1—C6	49.4 (2)	O5—S2—C9—C10	60.4 (2)
O3—S1—C1—C6	-69.0 (2)	O4—S2—C9—C10	-58.7 (2)
C6—C1—C2—C3	-0.6 (4)	O6—S2—C9—C10	-178.80 (19)
S1—C1—C2—C3	178.45 (19)	C8—C9—C10—N3	178.1 (2)
C1—C2—C3—C4	0.1 (4)	S2—C9—C10—N3	-2.2 (3)
C2—C3—C4—C5	0.5 (4)	C8—C9—C10—C11	-1.7 (3)
C2—C3—C4—N1	-178.8 (2)	S2—C9—C10—C11	177.93 (18)
N2—N1—C4—C3	-166.8 (2)	N3—C10—C11—C12	-178.1 (2)
N2—N1—C4—C5	13.9 (4)	C9—C10—C11—C12	1.7 (4)
C3—C4—C5—C6	-0.6 (4)	C10—C11—C12—C7	-0.8 (4)
N1—C4—C5—C6	178.7 (2)	N2—C7—C12—C11	-179.8 (2)
C4—C5—C6—C1	0.1 (4)	C8—C7—C12—C11	-0.3 (4)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N \cdots O3W ⁱⁱⁱ	0.84 (3)	2.10 (3)	2.878 (3)	153 (3)
N3—H2N \cdots O4W	0.82 (3)	2.04 (3)	2.847 (5)	170 (3)
N3—H2N \cdots O5W	0.82 (3)	2.05 (4)	2.843 (11)	163 (3)
N3—H3N \cdots O4	0.81 (3)	2.60 (3)	3.084 (3)	120 (3)
N3—H3N \cdots O4 ^{iv}	0.81 (3)	2.20 (3)	2.923 (3)	150 (3)
N3—H3N \cdots O5	0.81 (3)	2.61 (3)	3.095 (3)	120 (3)
O1W—H1W \cdots O5 ⁱⁱ	0.88 (1)	1.93 (2)	2.773 (3)	160 (4)
O1W—H2W \cdots O4 ⁱ	0.88 (1)	1.93 (2)	2.756 (3)	157 (4)
O2W—H3W \cdots O3 ^v	0.88 (1)	1.90 (1)	2.774 (2)	176 (4)
O2W—H4W \cdots O1 ^{vi}	0.88 (1)	1.88 (1)	2.746 (3)	171 (3)
O3W—H5W \cdots O2 ^{vii}	0.86 (1)	2.03 (1)	2.866 (3)	164 (3)
O3W—H6W \cdots O3 ^{vi}	0.87 (1)	2.22 (1)	3.081 (3)	171 (3)
O4W—H7W \cdots O3 ⁱ	0.88 (1)	2.02 (1)	2.887 (5)	175 (4)
O4W—H8W \cdots O1 ⁱⁱ	0.88 (1)	1.97 (1)	2.846 (5)	173 (5)
O5W—H9W \cdots O3 ⁱ	0.88 (1)	2.08 (2)	2.947 (13)	170 (10)
O5W—H10W \cdots O1 ⁱⁱ	0.88 (1)	1.89 (2)	2.765 (9)	171 (10)

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

Hexaaquamagnesium bis{2-(4-amino-3-sulfonatophenyl)-1-(4-sulfonatophenyl)diazonium} octahydrate (IV)

Crystal data

$[\text{Mg}(\text{H}_2\text{O})_6](\text{C}_{12}\text{H}_{10}\text{N}_3\text{O}_6\text{S}_2)_2 \cdot 8\text{H}_2\text{O}$

$M_r = 989.23$

Monoclinic, $C2/c$

$a = 36.896$ (3) \AA

$b = 6.7806$ (4) \AA

$c = 17.9140$ (12) \AA

$\beta = 111.178$ (9) $^\circ$

$V = 4179.0$ (6) \AA^3

$Z = 4$

$F(000) = 2072$

$D_x = 1.572$ Mg m^{-3}

$\text{Cu K}\alpha$ radiation, $\lambda = 1.5418$ \AA

Cell parameters from 1905 reflections

$\theta = 4.3\text{--}73.1^\circ$

$\mu = 3.12$ mm^{-1}

$T = 123$ K

Long needle, red

$0.5 \times 0.05 \times 0.03$ mm

Data collection

Oxford Diffraction Gemini S diffractometer	4093 independent reflections
Radiation source: sealed tube	3287 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.039$
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2019)	$\theta_{\text{max}} = 73.2^\circ$, $\theta_{\text{min}} = 5.0^\circ$
$T_{\text{min}} = 0.572$, $T_{\text{max}} = 1.000$	$h = -38 \rightarrow 45$
7541 measured reflections	$k = -6 \rightarrow 8$
	$l = -21 \rightarrow 15$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.050$	$w = 1/[\sigma^2(F_o^2) + (0.0813P)^2 + 0.7784P]$
$wR(F^2) = 0.143$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{\text{max}} < 0.001$
4093 reflections	$\Delta\rho_{\text{max}} = 0.80 \text{ e } \text{\AA}^{-3}$
359 parameters	$\Delta\rho_{\text{min}} = -0.38 \text{ e } \text{\AA}^{-3}$
110 restraints	

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Mg1	-0.2500	0.2500	0.0000	0.0176 (3)	
S1	-0.19426 (2)	0.24840 (8)	-0.24675 (4)	0.01688 (17)	
O1	-0.19535 (5)	0.3776 (3)	-0.31234 (11)	0.0241 (4)	
O2	-0.20622 (5)	0.0469 (3)	-0.27349 (11)	0.0228 (4)	
O3	-0.21518 (5)	0.3271 (3)	-0.19768 (11)	0.0229 (4)	
O1W	-0.24688 (6)	0.1251 (3)	-0.10154 (11)	0.0251 (4)	
O2W	-0.27304 (6)	0.5014 (3)	-0.06023 (12)	0.0281 (4)	
O3W	-0.30486 (6)	0.1320 (3)	-0.02226 (12)	0.0246 (4)	
O4W	-0.31418 (6)	0.7439 (3)	0.00138 (13)	0.0266 (4)	
O5W	-0.29954 (6)	0.7674 (3)	0.16593 (12)	0.0236 (4)	
O6W	-0.39177 (7)	0.7067 (3)	-0.07645 (14)	0.0334 (5)	
O7W	0.0109 (5)	0.219 (3)	-0.1575 (12)	0.0307 (19)	0.638 (12)
H13W	0.0139 (17)	0.346 (4)	-0.146 (4)	0.046*	0.6377
H14W	0.0355 (7)	0.186 (8)	-0.144 (4)	0.046*	0.6377
N1	-0.02640 (7)	0.2391 (3)	-0.04636 (14)	0.0204 (5)	
N2	-0.01425 (7)	0.2547 (3)	0.03076 (14)	0.0213 (5)	
N3	0.13859 (7)	0.2773 (4)	0.22824 (16)	0.0233 (5)	
C1	-0.14448 (8)	0.2379 (3)	-0.18386 (15)	0.0168 (5)	
C2	-0.13333 (8)	0.2471 (4)	-0.10121 (16)	0.0206 (5)	
H2	-0.1524	0.2538	-0.0771	0.025*	
C3	-0.09400 (8)	0.2462 (4)	-0.05389 (16)	0.0214 (5)	
H3	-0.0858	0.2528	0.0028	0.026*	

C4	-0.06672 (8)	0.2355 (4)	-0.09123 (16)	0.0196 (5)	
C5	-0.07798 (8)	0.2241 (4)	-0.17404 (17)	0.0214 (5)	
H5	-0.0590	0.2161	-0.1982	0.026*	
C6	-0.11712 (8)	0.2245 (4)	-0.22083 (16)	0.0213 (5)	
H6	-0.1253	0.2158	-0.2775	0.026*	
C7	0.02395 (8)	0.2602 (4)	0.07415 (17)	0.0204 (5)	
C8	0.03296 (8)	0.2748 (4)	0.15798 (17)	0.0236 (6)	
H8	0.0123	0.2806	0.1778	0.028*	
C9	0.07028 (8)	0.2807 (4)	0.21070 (16)	0.0213 (5)	
C10	0.10190 (8)	0.2726 (3)	0.18162 (17)	0.0191 (5)	
C11	0.09238 (8)	0.2577 (4)	0.09611 (17)	0.0208 (5)	
H11	0.1128	0.2518	0.0758	0.025*	
C12	0.05534 (8)	0.2519 (4)	0.04459 (16)	0.0209 (5)	
H12	0.0499	0.2424	-0.0113	0.025*	
S2	0.0782 (2)	0.2875 (14)	0.3153 (3)	0.0256 (5)	0.638 (12)
O4	0.0564 (3)	0.1246 (16)	0.3309 (10)	0.0390 (19)	0.638 (12)
O5	0.0628 (3)	0.4763 (12)	0.3280 (5)	0.0439 (16)	0.638 (12)
O6	0.11985 (18)	0.2653 (15)	0.3606 (4)	0.0542 (18)	0.638 (12)
S2A	0.0753 (4)	0.300 (3)	0.3128 (5)	0.0256 (5)	0.362 (12)
O4A	0.0650 (7)	0.105 (3)	0.3300 (19)	0.0390 (19)	0.362 (12)
O5A	0.0488 (4)	0.454 (2)	0.3169 (10)	0.0439 (16)	0.362 (12)
O6A	0.1150 (3)	0.362 (3)	0.3546 (7)	0.0542 (18)	0.362 (12)
O8W	0.0158 (10)	0.189 (5)	-0.149 (2)	0.0307 (19)	0.362 (12)
H16W	0.0210	0.3101	-0.1623	0.046*	0.362 (12)
H15W	0.0203	0.1197	-0.1863	0.046*	0.362 (12)
H2N	0.1562 (12)	0.280 (5)	0.207 (2)	0.029 (9)*	
H1N	-0.0114 (12)	0.226 (5)	-0.072 (3)	0.034 (10)*	
H3N	0.1447 (14)	0.299 (6)	0.277 (3)	0.049 (13)*	
H3W	-0.2859 (8)	0.594 (4)	-0.0471 (17)	0.024 (8)*	
H1W	-0.2378 (11)	0.172 (5)	-0.1364 (17)	0.044 (11)*	
H9W	-0.2895 (10)	0.882 (3)	0.184 (2)	0.043 (11)*	
H8W	-0.3098 (11)	0.729 (6)	0.0521 (7)	0.051 (13)*	
H11W	-0.4034 (11)	0.606 (3)	-0.105 (2)	0.052 (13)*	
H7W	-0.3385 (4)	0.707 (5)	-0.0197 (19)	0.033 (10)*	
H5W	-0.3086 (11)	0.0055 (18)	-0.021 (2)	0.046 (11)*	
H4W	-0.2777 (11)	0.523 (6)	-0.1107 (9)	0.051 (12)*	
H12W	-0.4031 (12)	0.806 (4)	-0.106 (2)	0.063 (15)*	
H6W	-0.3258 (7)	0.173 (5)	-0.0602 (19)	0.049 (12)*	
H2W	-0.2649 (8)	0.043 (4)	-0.1293 (18)	0.037 (10)*	
H10W	-0.2840 (9)	0.691 (4)	0.2032 (18)	0.046 (12)*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg1	0.0180 (6)	0.0191 (5)	0.0148 (6)	-0.0012 (4)	0.0050 (5)	-0.0003 (4)
S1	0.0136 (3)	0.0195 (3)	0.0170 (3)	0.0002 (2)	0.0048 (2)	0.0011 (2)
O1	0.0195 (9)	0.0282 (9)	0.0237 (9)	0.0023 (8)	0.0066 (7)	0.0069 (8)
O2	0.0192 (9)	0.0236 (9)	0.0221 (9)	-0.0023 (7)	0.0036 (7)	-0.0017 (7)

O3	0.0194 (9)	0.0272 (9)	0.0224 (9)	0.0016 (8)	0.0079 (7)	0.0002 (7)
O1W	0.0291 (10)	0.0299 (10)	0.0183 (9)	-0.0098 (8)	0.0111 (8)	-0.0059 (8)
O2W	0.0354 (11)	0.0270 (10)	0.0223 (9)	0.0094 (9)	0.0108 (8)	0.0063 (8)
O3W	0.0183 (9)	0.0268 (9)	0.0254 (9)	-0.0036 (8)	0.0038 (7)	-0.0002 (7)
O4W	0.0221 (10)	0.0314 (10)	0.0263 (10)	-0.0012 (8)	0.0088 (8)	0.0004 (8)
O5W	0.0195 (9)	0.0237 (9)	0.0266 (10)	0.0000 (7)	0.0070 (8)	-0.0002 (7)
O6W	0.0271 (11)	0.0371 (11)	0.0323 (12)	-0.0032 (9)	0.0064 (9)	-0.0008 (9)
O7W	0.020 (5)	0.042 (6)	0.029 (4)	0.008 (3)	0.008 (3)	0.006 (3)
N1	0.0168 (11)	0.0244 (11)	0.0193 (11)	0.0004 (8)	0.0056 (9)	-0.0003 (8)
N2	0.0181 (11)	0.0248 (10)	0.0192 (11)	0.0000 (8)	0.0048 (9)	-0.0001 (8)
N3	0.0158 (11)	0.0311 (12)	0.0223 (12)	-0.0035 (9)	0.0062 (9)	-0.0025 (9)
C1	0.0151 (12)	0.0170 (10)	0.0167 (12)	0.0009 (9)	0.0040 (9)	0.0020 (9)
C2	0.0178 (13)	0.0255 (12)	0.0193 (13)	0.0012 (10)	0.0077 (10)	0.0000 (9)
C3	0.0185 (13)	0.0280 (12)	0.0161 (12)	-0.0013 (10)	0.0042 (10)	0.0007 (9)
C4	0.0175 (12)	0.0188 (11)	0.0211 (13)	-0.0007 (9)	0.0054 (10)	0.0007 (9)
C5	0.0190 (13)	0.0239 (12)	0.0222 (13)	-0.0002 (10)	0.0087 (11)	0.0013 (10)
C6	0.0182 (13)	0.0257 (12)	0.0193 (12)	0.0000 (10)	0.0061 (10)	0.0003 (9)
C7	0.0178 (13)	0.0219 (12)	0.0208 (13)	-0.0016 (10)	0.0062 (10)	-0.0008 (9)
C8	0.0168 (12)	0.0324 (13)	0.0227 (13)	-0.0021 (11)	0.0086 (10)	-0.0028 (10)
C9	0.0199 (13)	0.0268 (13)	0.0185 (12)	-0.0026 (10)	0.0086 (10)	-0.0021 (9)
C10	0.0167 (12)	0.0166 (11)	0.0244 (13)	-0.0013 (9)	0.0078 (10)	-0.0009 (9)
C11	0.0206 (13)	0.0201 (11)	0.0241 (13)	-0.0003 (10)	0.0111 (11)	0.0005 (9)
C12	0.0217 (13)	0.0229 (12)	0.0188 (12)	-0.0015 (10)	0.0080 (10)	0.0001 (9)
S2	0.0164 (10)	0.0416 (12)	0.0181 (4)	-0.0034 (8)	0.0056 (5)	-0.0033 (5)
O4	0.055 (5)	0.041 (2)	0.0269 (12)	-0.002 (3)	0.022 (4)	0.001 (2)
O5	0.067 (5)	0.040 (2)	0.026 (3)	0.002 (3)	0.019 (4)	-0.0086 (17)
O6	0.0169 (19)	0.121 (6)	0.0188 (15)	0.003 (3)	-0.0002 (14)	0.004 (3)
S2A	0.0164 (10)	0.0416 (12)	0.0181 (4)	-0.0034 (8)	0.0056 (5)	-0.0033 (5)
O4A	0.055 (5)	0.041 (2)	0.0269 (12)	-0.002 (3)	0.022 (4)	0.001 (2)
O5A	0.067 (5)	0.040 (2)	0.026 (3)	0.002 (3)	0.019 (4)	-0.0086 (17)
O6A	0.0169 (19)	0.121 (6)	0.0188 (15)	0.003 (3)	-0.0002 (14)	0.004 (3)
O8W	0.020 (5)	0.042 (6)	0.029 (4)	0.008 (3)	0.008 (3)	0.006 (3)

Geometric parameters (Å, °)

Mg1—O2W ⁱ	2.0322 (19)	N3—H3N	0.84 (5)
Mg1—O2W	2.0322 (19)	C1—C2	1.388 (4)
Mg1—O1W	2.0472 (18)	C1—C6	1.396 (4)
Mg1—O1W ⁱ	2.0472 (18)	C2—C3	1.391 (4)
Mg1—O3W ⁱ	2.0769 (19)	C2—H2	0.9500
Mg1—O3W	2.0769 (19)	C3—C4	1.397 (4)
S1—O1	1.4544 (19)	C3—H3	0.9500
S1—O2	1.4624 (19)	C4—C5	1.391 (4)
S1—O3	1.464 (2)	C5—C6	1.383 (4)
S1—C1	1.776 (3)	C5—H5	0.9500
O1W—H1W	0.867 (10)	C6—H6	0.9500
O1W—H2W	0.873 (10)	C7—C8	1.419 (4)
O2W—H3W	0.868 (10)	C7—C12	1.438 (4)

O2W—H4W	0.869 (10)	C8—C9	1.360 (4)
O3W—H5W	0.870 (10)	C8—H8	0.9500
O3W—H6W	0.871 (10)	C9—C10	1.441 (4)
O4W—H8W	0.870 (10)	C9—S2A	1.775 (9)
O4W—H7W	0.874 (10)	C9—S2	1.789 (6)
O5W—H9W	0.872 (10)	C10—C11	1.446 (4)
O5W—H10W	0.874 (10)	C11—C12	1.345 (4)
O6W—H11W	0.868 (10)	C11—H11	0.9500
O6W—H12W	0.871 (10)	C12—H12	0.9500
O7W—H13W	0.887 (10)	S2—O5	1.451 (6)
O7W—H14W	0.879 (10)	S2—O4	1.452 (6)
N1—N2	1.294 (4)	S2—O6	1.465 (6)
N1—C4	1.413 (3)	S2A—O4A	1.444 (9)
N1—H1N	0.84 (4)	S2A—O5A	1.445 (9)
N2—C7	1.342 (4)	S2A—O6A	1.445 (9)
N3—C10	1.309 (4)	O8W—H16W	0.8927
N3—H2N	0.87 (4)	O8W—H15W	0.8807
O2W ⁱ —Mg1—O2W	180.0	C3—C2—H2	120.3
O2W ⁱ —Mg1—O1W	88.72 (8)	C2—C3—C4	118.8 (3)
O2W—Mg1—O1W	91.28 (8)	C2—C3—H3	120.6
O2W ⁱ —Mg1—O1W ⁱ	91.28 (8)	C4—C3—H3	120.6
O2W—Mg1—O1W ⁱ	88.72 (8)	C5—C4—C3	121.6 (3)
O1W—Mg1—O1W ⁱ	180.0	C5—C4—N1	117.1 (3)
O2W ⁱ —Mg1—O3W ⁱ	91.69 (8)	C3—C4—N1	121.3 (2)
O2W—Mg1—O3W ⁱ	88.31 (8)	C6—C5—C4	119.4 (3)
O1W—Mg1—O3W ⁱ	88.07 (8)	C6—C5—H5	120.3
O1W ⁱ —Mg1—O3W ⁱ	91.93 (8)	C4—C5—H5	120.3
O2W ⁱ —Mg1—O3W	88.31 (8)	C5—C6—C1	119.2 (3)
O2W—Mg1—O3W	91.69 (8)	C5—C6—H6	120.4
O1W—Mg1—O3W	91.93 (8)	C1—C6—H6	120.4
O1W ⁱ —Mg1—O3W	88.07 (8)	N2—C7—C8	114.2 (2)
O3W ⁱ —Mg1—O3W	180.0	N2—C7—C12	127.1 (3)
O1—S1—O2	112.39 (12)	C8—C7—C12	118.7 (3)
O1—S1—O3	113.50 (12)	C9—C8—C7	121.9 (3)
O2—S1—O3	112.04 (12)	C9—C8—H8	119.1
O1—S1—C1	104.89 (11)	C7—C8—H8	119.1
O2—S1—C1	106.91 (11)	C8—C9—C10	119.8 (2)
O3—S1—C1	106.42 (12)	C8—C9—S2A	114.8 (5)
Mg1—O1W—H1W	130 (2)	C10—C9—S2A	125.4 (5)
Mg1—O1W—H2W	120 (2)	C8—C9—S2	117.9 (3)
H1W—O1W—H2W	104 (2)	C10—C9—S2	122.2 (3)
Mg1—O2W—H3W	129 (2)	N3—C10—C9	123.7 (3)
Mg1—O2W—H4W	125 (2)	N3—C10—C11	118.5 (3)
H3W—O2W—H4W	104 (2)	C9—C10—C11	117.8 (2)
Mg1—O3W—H5W	122 (3)	C12—C11—C10	121.8 (3)
Mg1—O3W—H6W	124 (3)	C12—C11—H11	119.1
H5W—O3W—H6W	103 (2)	C10—C11—H11	119.1

H8W—O4W—H7W	101 (2)	C11—C12—C7	120.0 (3)
H9W—O5W—H10W	100 (2)	C11—C12—H12	120.0
H11W—O6W—H12W	103 (2)	C7—C12—H12	120.0
H13W—O7W—H14W	99 (2)	O5—S2—O4	111.5 (7)
N2—N1—C4	119.8 (2)	O5—S2—O6	113.3 (6)
N2—N1—H1N	123 (3)	O4—S2—O6	111.0 (7)
C4—N1—H1N	117 (3)	O5—S2—C9	105.2 (6)
N1—N2—C7	120.5 (2)	O4—S2—C9	106.9 (8)
C10—N3—H2N	119 (3)	O6—S2—C9	108.6 (5)
C10—N3—H3N	120 (3)	O4A—S2A—O5A	114.5 (14)
H2N—N3—H3N	120 (4)	O4A—S2A—O6A	116.7 (15)
C2—C1—C6	121.5 (2)	O5A—S2A—O6A	110.1 (11)
C2—C1—S1	121.0 (2)	O4A—S2A—C9	102.3 (15)
C6—C1—S1	117.5 (2)	O5A—S2A—C9	106.6 (10)
C1—C2—C3	119.4 (3)	O6A—S2A—C9	105.3 (9)
C1—C2—H2	120.3	H16W—O8W—H15W	100.0
C4—N1—N2—C7	-179.3 (2)	C7—C8—C9—S2	-177.1 (4)
O1—S1—C1—C2	137.8 (2)	C8—C9—C10—N3	-179.9 (3)
O2—S1—C1—C2	-102.7 (2)	S2A—C9—C10—N3	0.6 (8)
O3—S1—C1—C2	17.3 (2)	S2—C9—C10—N3	-2.8 (5)
O1—S1—C1—C6	-40.8 (2)	C8—C9—C10—C11	-0.2 (4)
O2—S1—C1—C6	78.7 (2)	S2A—C9—C10—C11	-179.6 (7)
O3—S1—C1—C6	-161.37 (19)	S2—C9—C10—C11	177.0 (4)
C6—C1—C2—C3	1.1 (4)	N3—C10—C11—C12	180.0 (3)
S1—C1—C2—C3	-177.5 (2)	C9—C10—C11—C12	0.2 (4)
C1—C2—C3—C4	-0.2 (4)	C10—C11—C12—C7	-0.1 (4)
C2—C3—C4—C5	-0.5 (4)	N2—C7—C12—C11	-179.5 (3)
C2—C3—C4—N1	178.4 (2)	C8—C7—C12—C11	0.1 (4)
N2—N1—C4—C5	178.2 (2)	C8—C9—S2—O5	-66.3 (6)
N2—N1—C4—C3	-0.8 (4)	C10—C9—S2—O5	116.5 (5)
C3—C4—C5—C6	0.4 (4)	C8—C9—S2—O4	52.3 (7)
N1—C4—C5—C6	-178.6 (2)	C10—C9—S2—O4	-124.9 (6)
C4—C5—C6—C1	0.5 (4)	C8—C9—S2—O6	172.1 (5)
C2—C1—C6—C5	-1.2 (4)	C10—C9—S2—O6	-5.1 (8)
S1—C1—C6—C5	177.4 (2)	C8—C9—S2A—O4A	73.9 (12)
N1—N2—C7—C8	-179.2 (2)	C10—C9—S2A—O4A	-106.6 (11)
N1—N2—C7—C12	0.5 (4)	C8—C9—S2A—O5A	-46.7 (12)
N2—C7—C8—C9	179.6 (3)	C10—C9—S2A—O5A	132.8 (9)
C12—C7—C8—C9	-0.1 (4)	C8—C9—S2A—O6A	-163.7 (9)
C7—C8—C9—C10	0.1 (4)	C10—C9—S2A—O6A	15.8 (13)
C7—C8—C9—S2A	179.7 (7)		

Symmetry code: (i) $-x-1/2, -y+1/2, -z$.

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>
N1—H1N \cdots O7W	0.84 (4)	1.99 (5)	2.80 (2)	164 (4)

N1—H1N...O8W	0.84 (4)	2.00 (6)	2.83 (4)	170 (4)
N3—H2N...O5W ⁱⁱ	0.87 (4)	2.02 (4)	2.881 (3)	174 (4)
N3—H3N...O6	0.84 (5)	2.03 (5)	2.700 (7)	137 (4)
N3—H3N...O6A	0.84 (5)	2.10 (5)	2.763 (14)	136 (4)
O1W—H1W...O3	0.87 (1)	1.92 (1)	2.769 (3)	167 (3)
O1W—H2W...O1 ⁱⁱⁱ	0.87 (1)	1.84 (1)	2.714 (3)	177 (4)
O2W—H3W...O4W	0.87 (1)	1.88 (1)	2.727 (3)	165 (3)
O2W—H4W...O2 ^{iv}	0.87 (1)	1.95 (1)	2.812 (3)	173 (4)
O3W—H5W...O4W ^v	0.87 (1)	1.85 (1)	2.707 (3)	169 (4)
O3W—H6W...O6 ^{vi}	0.87 (1)	2.04 (2)	2.897 (6)	169 (4)
O3W—H6W...O6A ^{vi}	0.87 (1)	2.18 (2)	2.983 (11)	153 (3)
O4W—H8W...O5W	0.87 (1)	1.95 (2)	2.803 (3)	166 (4)
O4W—H7W...O6W	0.87 (1)	1.86 (1)	2.706 (3)	162 (3)
O5W—H10W...O2 ⁱ	0.87 (1)	2.16 (3)	2.829 (3)	133 (3)
O5W—H9W...O3 ^{vii}	0.87 (1)	1.99 (1)	2.820 (3)	160 (3)
O5W—H10W...O3 ^{viii}	0.87 (1)	2.52 (3)	3.251 (3)	141 (3)
O6W—H11W...O4 ^{vi}	0.87 (1)	2.17 (2)	3.028 (13)	167 (4)
O6W—H11W...O4A ^{vi}	0.87 (1)	1.94 (3)	2.81 (2)	174 (4)
O6W—H12W...O5 ^{ix}	0.87 (1)	2.02 (2)	2.878 (8)	170 (5)
O6W—H12W...O5A ^{ix}	0.87 (1)	2.43 (2)	3.276 (14)	163 (4)
O6W—H12W...O6A ^{ix}	0.87 (1)	2.52 (3)	3.220 (17)	139 (4)
O7W—H13W...O5 ^x	0.89 (1)	2.35 (6)	2.89 (2)	119 (5)
O7W—H14W...O6W ^{xi}	0.88 (1)	2.52 (3)	3.354 (18)	159 (5)
O7W—H14W...O4 ^{xi}	0.88 (1)	2.35 (5)	2.92 (2)	123 (4)
O8W—H16W...O5A ^x	0.89	2.01	2.87 (4)	163
O8W—H15W...O4A ^{xi}	0.88	2.18	2.81 (4)	128

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

Poly[[[μ_2 -4-[2-(4-amino-2-methyl-5-methoxyphenyl)diazen-1-yl]benzene-1,3-disulfonato]di- μ -aqua-diaquabarium(II)] dihydrate] (V)

Crystal data

[Ba(C₁₄H₁₃N₃O₇S₂)(H₂O)₄] \cdot 2H₂O

$M_r = 644.83$

Orthorhombic, *Pbca*

$a = 7.1293$ (4) Å

$b = 18.8368$ (11) Å

$c = 34.752$ (2) Å

$V = 4667.0$ (5) Å³

$Z = 8$

$F(000) = 2576$

Data collection

Nonius KappaCCD
diffractometer

Radiation source: rotating anode

ω and phi scans

Absorption correction: multi-scan
(SADABS; Bruker, 2012)

$D_x = 1.835$ Mg m⁻³

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

Cell parameters from 4623 reflections

$\theta = 1.0$ – 26.0°

$\mu = 1.95$ mm⁻¹

$T = 123$ K

Elongated rhomb, orange

$0.25 \times 0.10 \times 0.04$ mm

$T_{\min} = 0.448$, $T_{\max} = 0.743$

7914 measured reflections

4489 independent reflections

3554 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$

$\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 2.2^\circ$

$h = -8 \rightarrow 8$
 $k = -23 \rightarrow 23$

$l = -42 \rightarrow 42$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.096$
 $S = 1.15$
 4489 reflections
 344 parameters
 20 restraints

Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0229P)^2 + 26.8527P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.65 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.23 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ba1	0.46936 (4)	0.13398 (2)	0.19569 (2)	0.01523 (10)
S1	0.3700 (2)	0.33522 (7)	0.17263 (4)	0.0177 (3)
S2	0.52454 (19)	0.61085 (6)	0.14177 (4)	0.0142 (3)
O1	0.4242 (6)	0.26422 (18)	0.16056 (11)	0.0235 (9)
O2	0.1747 (6)	0.35234 (19)	0.16343 (11)	0.0229 (9)
O3	0.4127 (6)	0.34897 (18)	0.21305 (10)	0.0225 (9)
O4	0.3983 (5)	0.60937 (18)	0.17551 (10)	0.0178 (8)
O5	0.7040 (5)	0.64361 (18)	0.15189 (10)	0.0174 (8)
O6	0.4375 (5)	0.64224 (18)	0.10819 (10)	0.0183 (8)
O7	0.9268 (6)	0.76192 (18)	-0.01184 (10)	0.0229 (9)
O1W	0.5033 (6)	-0.0101 (2)	0.18560 (12)	0.0291 (10)
H1W	0.457 (8)	-0.042 (2)	0.1701 (13)	0.035*
H2W	0.569 (8)	-0.037 (2)	0.2011 (13)	0.035*
O2W	0.4366 (6)	0.1078 (3)	0.11948 (12)	0.0328 (10)
H3W	0.338 (5)	0.115 (3)	0.1049 (13)	0.039*
H4W	0.510 (6)	0.086 (3)	0.1030 (13)	0.039*
O3W	0.6687 (6)	0.21189 (19)	0.25537 (11)	0.0227 (9)
H5W	0.710 (7)	0.2458 (19)	0.2404 (13)	0.027*
H6W	0.588 (6)	0.236 (2)	0.2692 (13)	0.027*
O4W	0.3374 (6)	0.0719 (2)	0.26436 (11)	0.0225 (9)
H7W	0.415 (7)	0.072 (3)	0.2841 (11)	0.027*
H8W	0.320 (8)	0.0258 (8)	0.2628 (14)	0.027*
O5W	-0.1119 (6)	0.2702 (2)	0.19632 (11)	0.0238 (9)
H9W	-0.046 (7)	0.305 (2)	0.1861 (13)	0.029*
H10W	-0.145 (8)	0.248 (2)	0.1752 (8)	0.029*
O6W	0.2298 (6)	0.42869 (19)	0.26713 (11)	0.0238 (9)
H11W	0.274 (7)	0.405 (2)	0.2472 (11)	0.029*
H12W	0.136 (6)	0.401 (2)	0.2733 (15)	0.029*

N1	0.7484 (6)	0.5510 (2)	0.07400 (12)	0.0155 (9)
N2	0.7400 (6)	0.5290 (2)	0.03926 (12)	0.0168 (10)
N3	0.9314 (8)	0.7070 (3)	-0.08174 (14)	0.0250 (11)
C1	0.5036 (7)	0.3964 (3)	0.14543 (14)	0.0158 (11)
C2	0.6185 (8)	0.3746 (3)	0.11551 (15)	0.0182 (12)
H2	0.6392	0.3255	0.1108	0.022*
C3	0.7031 (8)	0.4258 (3)	0.09250 (15)	0.0183 (12)
H3	0.7817	0.4113	0.0719	0.022*
C4	0.6745 (8)	0.4981 (3)	0.09918 (15)	0.0158 (11)
C5	0.5678 (8)	0.5194 (3)	0.13124 (15)	0.0161 (11)
C6	0.4806 (8)	0.4688 (3)	0.15396 (14)	0.0155 (11)
H6	0.4055	0.4830	0.1752	0.019*
C7	0.7944 (7)	0.5760 (3)	0.01038 (14)	0.0146 (11)
C8	0.7904 (7)	0.5476 (3)	-0.02719 (15)	0.0152 (11)
C9	0.8361 (8)	0.5924 (3)	-0.05756 (15)	0.0175 (11)
H9	0.8346	0.5738	-0.0830	0.021*
C10	0.8843 (8)	0.6637 (3)	-0.05219 (15)	0.0195 (12)
C11	0.8853 (8)	0.6905 (3)	-0.01369 (16)	0.0182 (11)
C12	0.8409 (7)	0.6479 (3)	0.01663 (15)	0.0167 (11)
H12	0.8412	0.6666	0.0420	0.020*
C13	0.7344 (8)	0.4715 (3)	-0.03471 (16)	0.0202 (12)
H13A	0.7096	0.4651	-0.0622	0.030*
H13B	0.6210	0.4602	-0.0200	0.030*
H13C	0.8364	0.4398	-0.0268	0.030*
C14	0.9168 (9)	0.7942 (3)	0.02544 (16)	0.0244 (13)
H14A	0.7913	0.7869	0.0363	0.037*
H14B	0.9418	0.8452	0.0232	0.037*
H14C	1.0105	0.7725	0.0424	0.037*
H1N	0.911 (9)	0.693 (3)	-0.1055 (7)	0.033 (18)*
H2N	0.955 (10)	0.7519 (12)	-0.077 (2)	0.05 (2)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba1	0.01377 (17)	0.01302 (15)	0.01890 (16)	-0.00088 (13)	-0.00011 (13)	0.00011 (12)
S1	0.0207 (7)	0.0111 (6)	0.0214 (7)	-0.0017 (5)	0.0025 (6)	0.0020 (5)
S2	0.0126 (6)	0.0110 (6)	0.0189 (6)	-0.0004 (5)	0.0005 (5)	0.0001 (5)
O1	0.032 (2)	0.0110 (18)	0.028 (2)	0.0017 (17)	0.0066 (18)	0.0012 (15)
O2	0.020 (2)	0.0161 (19)	0.033 (2)	-0.0035 (16)	0.0008 (17)	0.0027 (16)
O3	0.029 (2)	0.0173 (19)	0.021 (2)	-0.0021 (17)	0.0030 (18)	0.0021 (15)
O4	0.0154 (19)	0.0146 (17)	0.023 (2)	0.0081 (15)	0.0013 (16)	-0.0002 (15)
O5	0.015 (2)	0.0111 (17)	0.026 (2)	-0.0021 (15)	-0.0007 (16)	-0.0024 (15)
O6	0.017 (2)	0.0131 (18)	0.0248 (19)	-0.0044 (16)	0.0016 (16)	0.0037 (14)
O7	0.030 (2)	0.0142 (18)	0.025 (2)	-0.0047 (17)	0.0030 (18)	0.0011 (15)
O1W	0.033 (3)	0.018 (2)	0.036 (2)	0.0001 (19)	-0.010 (2)	-0.0025 (16)
O2W	0.016 (2)	0.056 (3)	0.026 (2)	0.007 (2)	-0.0030 (18)	-0.015 (2)
O3W	0.023 (2)	0.0203 (19)	0.025 (2)	-0.0029 (18)	0.0034 (18)	0.0010 (16)
O4W	0.025 (2)	0.0181 (19)	0.024 (2)	0.0009 (18)	0.0006 (18)	0.0034 (16)

O5W	0.025 (2)	0.020 (2)	0.026 (2)	-0.0054 (17)	0.003 (2)	-0.0012 (17)
O6W	0.024 (2)	0.0178 (19)	0.029 (2)	-0.0046 (18)	0.0048 (18)	-0.0031 (16)
N1	0.014 (2)	0.015 (2)	0.018 (2)	-0.0014 (18)	0.0011 (19)	0.0009 (17)
N2	0.015 (2)	0.016 (2)	0.019 (2)	-0.0005 (19)	-0.0007 (19)	0.0003 (18)
N3	0.032 (3)	0.019 (2)	0.024 (3)	-0.002 (2)	0.002 (2)	0.001 (2)
C1	0.015 (3)	0.013 (2)	0.020 (3)	-0.001 (2)	-0.003 (2)	0.003 (2)
C2	0.022 (3)	0.013 (3)	0.020 (3)	0.002 (2)	0.001 (2)	-0.001 (2)
C3	0.020 (3)	0.016 (3)	0.018 (3)	0.003 (2)	0.003 (2)	-0.002 (2)
C4	0.015 (3)	0.015 (3)	0.018 (3)	-0.001 (2)	0.000 (2)	-0.001 (2)
C5	0.018 (3)	0.011 (2)	0.019 (3)	-0.003 (2)	-0.004 (2)	0.0013 (19)
C6	0.014 (3)	0.017 (3)	0.015 (2)	-0.002 (2)	0.000 (2)	-0.0015 (19)
C7	0.009 (3)	0.018 (3)	0.017 (3)	0.004 (2)	0.001 (2)	0.002 (2)
C8	0.007 (3)	0.016 (3)	0.023 (3)	0.002 (2)	0.001 (2)	0.000 (2)
C9	0.016 (3)	0.018 (3)	0.018 (3)	0.004 (2)	0.001 (2)	-0.001 (2)
C10	0.013 (3)	0.025 (3)	0.021 (3)	0.001 (2)	0.000 (2)	0.002 (2)
C11	0.016 (3)	0.013 (2)	0.026 (3)	0.002 (2)	-0.002 (2)	0.001 (2)
C12	0.012 (3)	0.019 (3)	0.019 (3)	0.003 (2)	-0.002 (2)	-0.004 (2)
C13	0.019 (3)	0.016 (3)	0.025 (3)	0.001 (2)	0.000 (2)	-0.002 (2)
C14	0.030 (4)	0.014 (3)	0.029 (3)	0.001 (2)	0.003 (3)	-0.003 (2)

Geometric parameters (Å, °)

Ba1—O2W	2.704 (4)	O6W—H11W	0.878 (10)
Ba1—O1W	2.747 (4)	O6W—H12W	0.876 (10)
Ba1—O4 ⁱ	2.753 (4)	N1—N2	1.277 (6)
Ba1—O1	2.759 (4)	N1—C4	1.426 (6)
Ba1—O5 ⁱⁱ	2.788 (4)	N2—C7	1.393 (6)
Ba1—O4W	2.819 (4)	N3—C10	1.354 (7)
Ba1—O3W	2.911 (4)	N3—H1N	0.879 (10)
Ba1—O3W ⁱⁱⁱ	3.105 (4)	N3—H2N	0.877 (10)
Ba1—O4W ^{iv}	3.191 (4)	C1—C2	1.386 (7)
S1—O1	1.454 (4)	C1—C6	1.406 (7)
S1—O3	1.460 (4)	C2—C3	1.391 (7)
S1—O2	1.465 (4)	C2—H2	0.9500
S1—C1	1.768 (5)	C3—C4	1.397 (7)
S2—O6	1.448 (4)	C3—H3	0.9500
S2—O5	1.463 (4)	C4—C5	1.408 (7)
S2—O4	1.478 (4)	C5—C6	1.385 (7)
S2—C5	1.788 (5)	C6—H6	0.9500
O4—Ba1 ^v	2.753 (4)	C7—C8	1.411 (7)
O5—Ba1 ^{vi}	2.788 (4)	C7—C12	1.412 (7)
O7—C11	1.379 (6)	C8—C9	1.390 (7)
O7—C14	1.433 (6)	C8—C13	1.511 (7)
O1W—H1W	0.873 (10)	C9—C10	1.400 (7)
O1W—H2W	0.873 (10)	C9—H9	0.9500
O2W—H3W	0.877 (10)	C10—C11	1.430 (7)
O2W—H4W	0.875 (10)	C11—C12	1.361 (7)
O3W—Ba1 ^{iv}	3.105 (4)	C12—H12	0.9500

O3W—H5W	0.875 (10)	C13—H13A	0.9800
O3W—H6W	0.876 (10)	C13—H13B	0.9800
O4W—Ba1 ⁱⁱⁱ	3.191 (4)	C13—H13C	0.9800
O4W—H7W	0.879 (10)	C14—H14A	0.9800
O4W—H8W	0.878 (10)	C14—H14B	0.9800
O5W—H9W	0.877 (10)	C14—H14C	0.9800
O5W—H10W	0.876 (10)		
O2W—Ba1—O1W	72.69 (14)	H5W—O3W—H6W	100 (2)
O2W—Ba1—O4 ⁱ	68.74 (12)	Ba1—O4W—Ba1 ⁱⁱⁱ	119.37 (12)
O1W—Ba1—O4 ⁱ	83.39 (12)	Ba1—O4W—H7W	116 (4)
O2W—Ba1—O1	73.66 (13)	Ba1 ⁱⁱⁱ —O4W—H7W	100 (4)
O1W—Ba1—O1	146.32 (12)	Ba1—O4W—H8W	114 (4)
O4 ⁱ —Ba1—O1	85.75 (11)	Ba1 ⁱⁱⁱ —O4W—H8W	106 (4)
O2W—Ba1—O5 ⁱⁱ	63.22 (12)	H7W—O4W—H8W	99 (2)
O1W—Ba1—O5 ⁱⁱ	85.47 (12)	H9W—O5W—H10W	99 (2)
O4 ⁱ —Ba1—O5 ⁱⁱ	131.85 (10)	H11W—O6W—H12W	100 (2)
O1—Ba1—O5 ⁱⁱ	78.35 (11)	N2—N1—C4	109.7 (4)
O2W—Ba1—O4W	136.43 (13)	N1—N2—C7	117.5 (4)
O1W—Ba1—O4W	74.19 (12)	C10—N3—H1N	119 (4)
O4 ⁱ —Ba1—O4W	80.10 (11)	C10—N3—H2N	119 (5)
O1—Ba1—O4W	134.80 (11)	H1N—N3—H2N	120 (6)
O5 ⁱⁱ —Ba1—O4W	140.16 (11)	C2—C1—C6	121.0 (5)
O2W—Ba1—O3W	146.29 (13)	C2—C1—S1	121.8 (4)
O1W—Ba1—O3W	123.10 (12)	C6—C1—S1	117.2 (4)
O4 ⁱ —Ba1—O3W	136.99 (11)	C1—C2—C3	118.8 (5)
O1—Ba1—O3W	85.63 (11)	C1—C2—H2	120.6
O5 ⁱⁱ —Ba1—O3W	87.04 (11)	C3—C2—H2	120.6
O4W—Ba1—O3W	76.65 (11)	C2—C3—C4	121.2 (5)
O2W—Ba1—O3W ⁱⁱⁱ	124.26 (12)	C2—C3—H3	119.4
O1W—Ba1—O3W ⁱⁱⁱ	126.70 (12)	C4—C3—H3	119.4
O4 ⁱ —Ba1—O3W ⁱⁱⁱ	64.01 (10)	C3—C4—C5	119.2 (5)
O1—Ba1—O3W ⁱⁱⁱ	75.02 (10)	C3—C4—N1	121.7 (5)
O5 ⁱⁱ —Ba1—O3W ⁱⁱⁱ	147.67 (10)	C5—C4—N1	119.1 (4)
O4W—Ba1—O3W ⁱⁱⁱ	60.15 (10)	C6—C5—C4	119.9 (5)
O3W—Ba1—O3W ⁱⁱⁱ	73.06 (5)	C6—C5—S2	118.0 (4)
O2W—Ba1—O4W ^{iv}	115.49 (11)	C4—C5—S2	122.0 (4)
O1W—Ba1—O4W ^{iv}	67.73 (11)	C5—C6—C1	119.7 (5)
O4 ⁱ —Ba1—O4W ^{iv}	146.32 (10)	C5—C6—H6	120.2
O1—Ba1—O4W ^{iv}	127.91 (11)	C1—C6—H6	120.2
O5 ⁱⁱ —Ba1—O4W ^{iv}	64.82 (10)	N2—C7—C8	114.9 (4)
O4W—Ba1—O4W ^{iv}	75.76 (7)	N2—C7—C12	124.3 (5)
O3W—Ba1—O4W ^{iv}	58.23 (10)	C8—C7—C12	120.7 (5)
O3W ⁱⁱⁱ —Ba1—O4W ^{iv}	120.18 (10)	C9—C8—C7	117.9 (5)
O1—S1—O3	112.7 (2)	C9—C8—C13	120.4 (5)
O1—S1—O2	113.1 (2)	C7—C8—C13	121.6 (5)
O3—S1—O2	111.7 (2)	C8—C9—C10	122.6 (5)
O1—S1—C1	107.6 (2)	C8—C9—H9	118.7

O3—S1—C1	106.7 (2)	C10—C9—H9	118.7
O2—S1—C1	104.6 (2)	N3—C10—C9	122.6 (5)
O6—S2—O5	113.3 (2)	N3—C10—C11	119.7 (5)
O6—S2—O4	112.7 (2)	C9—C10—C11	117.7 (5)
O5—S2—O4	110.5 (2)	C12—C11—O7	126.0 (5)
O6—S2—C5	107.6 (2)	C12—C11—C10	121.0 (5)
O5—S2—C5	107.7 (2)	O7—C11—C10	112.9 (4)
O4—S2—C5	104.4 (2)	C11—C12—C7	120.1 (5)
S1—O1—Ba1	136.2 (2)	C11—C12—H12	120.0
S2—O4—Ba1 ^v	141.1 (2)	C7—C12—H12	120.0
S2—O5—Ba1 ^{vi}	146.5 (2)	C8—C13—H13A	109.5
C11—O7—C14	116.4 (4)	C8—C13—H13B	109.5
Ba1—O1W—H1W	137 (3)	H13A—C13—H13B	109.5
Ba1—O1W—H2W	123 (3)	C8—C13—H13C	109.5
H1W—O1W—H2W	101 (2)	H13A—C13—H13C	109.5
Ba1—O2W—H3W	127 (4)	H13B—C13—H13C	109.5
Ba1—O2W—H4W	132 (4)	O7—C14—H14A	109.5
H3W—O2W—H4W	100 (2)	O7—C14—H14B	109.5
Ba1—O3W—Ba1 ^{iv}	119.27 (12)	H14A—C14—H14B	109.5
Ba1—O3W—H5W	96 (4)	O7—C14—H14C	109.5
Ba1 ^{iv} —O3W—H5W	116 (4)	H14A—C14—H14C	109.5
Ba1—O3W—H6W	109 (4)	H14B—C14—H14C	109.5
Ba1 ^{iv} —O3W—H6W	114 (4)		
O3—S1—O1—Ba1	26.9 (4)	O4—S2—C5—C6	1.2 (5)
O2—S1—O1—Ba1	-100.9 (3)	O6—S2—C5—C4	56.1 (5)
C1—S1—O1—Ba1	144.1 (3)	O5—S2—C5—C4	-66.4 (5)
O6—S2—O4—Ba1 ^v	8.8 (4)	O4—S2—C5—C4	176.1 (4)
O5—S2—O4—Ba1 ^v	136.7 (3)	C4—C5—C6—C1	1.8 (8)
C5—S2—O4—Ba1 ^v	-107.7 (3)	S2—C5—C6—C1	176.9 (4)
O6—S2—O5—Ba1 ^{vi}	-167.3 (3)	C2—C1—C6—C5	2.6 (8)
O4—S2—O5—Ba1 ^{vi}	65.1 (4)	S1—C1—C6—C5	-173.9 (4)
C5—S2—O5—Ba1 ^{vi}	-48.3 (4)	N1—N2—C7—C8	177.2 (5)
C4—N1—N2—C7	175.6 (4)	N1—N2—C7—C12	-6.2 (8)
O1—S1—C1—C2	6.8 (5)	N2—C7—C8—C9	177.6 (5)
O3—S1—C1—C2	127.9 (4)	C12—C7—C8—C9	0.9 (8)
O2—S1—C1—C2	-113.7 (5)	N2—C7—C8—C13	-1.1 (7)
O1—S1—C1—C6	-176.7 (4)	C12—C7—C8—C13	-177.8 (5)
O3—S1—C1—C6	-55.6 (5)	C7—C8—C9—C10	-0.4 (8)
O2—S1—C1—C6	62.8 (4)	C13—C8—C9—C10	178.4 (5)
C6—C1—C2—C3	-3.6 (8)	C8—C9—C10—N3	179.0 (5)
S1—C1—C2—C3	172.8 (4)	C8—C9—C10—C11	-0.1 (8)
C1—C2—C3—C4	0.3 (8)	C14—O7—C11—C12	-1.8 (8)
C2—C3—C4—C5	4.0 (8)	C14—O7—C11—C10	175.4 (5)
C2—C3—C4—N1	-175.0 (5)	N3—C10—C11—C12	-179.2 (5)
N2—N1—C4—C3	36.7 (7)	C9—C10—C11—C12	0.0 (8)
N2—N1—C4—C5	-142.4 (5)	N3—C10—C11—O7	3.4 (8)
C3—C4—C5—C6	-5.0 (8)	C9—C10—C11—O7	-177.4 (5)

N1—C4—C5—C6	174.0 (5)	O7—C11—C12—C7	177.6 (5)
C3—C4—C5—S2	-179.9 (4)	C10—C11—C12—C7	0.5 (8)
N1—C4—C5—S2	-0.8 (7)	N2—C7—C12—C11	-177.4 (5)
O6—S2—C5—C6	-118.8 (4)	C8—C7—C12—C11	-1.0 (8)
O5—S2—C5—C6	118.6 (4)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H1N \cdots O2 ^{vii}	0.88 (1)	2.27 (2)	3.144 (6)	172 (6)
N3—H2N \cdots O6 ^{viii}	0.88 (1)	2.28 (5)	2.984 (6)	138 (6)
O1W—H1W \cdots O2 ⁱ	0.87 (1)	2.21 (3)	2.987 (5)	148 (5)
O1W—H2W \cdots O6W ^{ix}	0.87 (1)	1.92 (2)	2.766 (6)	161 (6)
O2W—H3W \cdots O6 ⁱ	0.88 (1)	2.03 (3)	2.772 (6)	141 (5)
O2W—H4W \cdots N1 ⁱⁱ	0.88 (1)	2.10 (2)	2.948 (6)	162 (5)
O3W—H5W \cdots O5W ^x	0.88 (1)	2.04 (3)	2.805 (5)	145 (4)
O3W—H6W \cdots O5W ^{xv}	0.88 (1)	1.97 (1)	2.833 (6)	168 (5)
O4W—H7W \cdots O4 ^{ix}	0.88 (1)	2.06 (2)	2.901 (5)	160 (4)
O4W—H8W \cdots O6W ^l	0.88 (1)	1.87 (2)	2.741 (5)	171 (5)
O5W—H9W \cdots O2	0.88 (1)	1.97 (3)	2.805 (5)	158 (6)
O5W—H10W \cdots O5 ⁱ	0.88 (1)	2.17 (3)	2.917 (5)	143 (5)
O6W—H11W \cdots O3	0.88 (1)	1.88 (2)	2.737 (5)	166 (6)
O6W—H12W \cdots O3 ⁱⁱⁱ	0.88 (1)	1.93 (1)	2.800 (6)	174 (5)

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