



# Isostructural behaviour in ammonium and potassium salt forms of sulfonated azo dyes

Alan R. Kennedy,\* Jennifer B. A. Kirkhouse, Karen M. McCarney and Olivier Puissegur

Department of Pure & Applied Chemistry, University of Strathclyde, Glasgow, G1 1XQ, United Kingdom. \*Correspondence e-mail: a.r.kennedy@strath.ac.uk

Received 11 January 2024

Accepted 8 February 2024

Edited by R. Diniz, Universidade Federal de Minas Gerais, Brazil

**Keywords:** single-crystal X-ray diffraction; dye; salt selection; sulfonated azo; pseudo-alkali metal; alkali metal; crystal structure; isostructural.

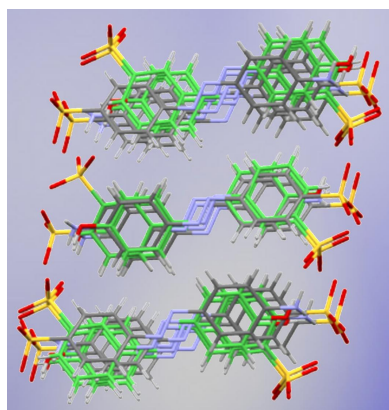
**CCDC references:** 2331925; 2331924; 2331923; 2331922; 2331921; 2331920; 2331919; 2331918; 2331917

**Supporting information:** this article has supporting information at journals.iucr.org/c

The structures of five ammonium salt forms of monosulfonated azo dyes, derivatives of 4-(2-phenyldiazen-1-yl)benzenesulfonate, with the general formula  $[\text{NH}_4][\text{O}_3\text{S}(\text{C}_6\text{H}_4)\text{NN}(\text{C}_6\text{H}_5)\text{RR}']\cdot\text{XH}_2\text{O}$  [ $R = \text{OH}, \text{NH}_2$  or  $\text{N}(\text{C}_2\text{H}_4\text{OH})_2$ ;  $R' = \text{H}$  or  $\text{OH}$ ] are presented. All form simple layered structures with alternating hydrophobic (organic) and hydrophilic (cation, solvent and polar groups) layers. To assess for isostructural behaviour of the ammonium cation with  $M^+$  ions, the packing of these structures is compared with literature examples. To aid this comparison, the corresponding structures of four potassium salt forms of the monosulfonated azo dyes are also presented herein. Of the five ammonium salts it is found that three have isostructural equivalents. In two cases this equivalent is a potassium salt form and in one case it is a rubidium salt form. The isostructurality of ion packing and of unit-cell symmetry and dimensions tolerates cases where the ammonium ions form somewhat different interaction types with cofomer species than do the potassium or rubidium ions. No sodium salt forms are found to be isostructural with any ammonium equivalent. However, similarities in the anion packing within a single hydrophobic layer are found for a group that consists of the ammonium and rubidium salt forms of one azo anion species and the sodium and silver salt forms of a different azo species.

## 1. Introduction

The process of salt selection aims to choose the form of an active organic material that has the best properties for effectiveness and for commercialization. Salt selection is well studied in the area of pharmaceuticals (Stahl & Wermuth, 2008; Mahmood *et al.*, 2023; Bharate, 2021; Arlin *et al.*, 2011; Black *et al.*, 2007), but it is perhaps less well known that similar processes are used to select for material properties in other areas too. One example is the process of laking sulfonated azo colourants. A typical process here involves the substitution of an  $M^+$  cation with an  $M^{2+}$  cation, such as Ca or Ba, to switch from an aqueous-soluble dyestuff to an insoluble pigment (Christie & Mackay, 2008; Schmidt *et al.*, 2009; Kennedy *et al.*, 2012). As with pharmaceuticals, the material properties of pigments are dependant upon their crystal structures, and upon the intermolecular interactions present within the crystal (Hao & Iqbal, 1997). However, in the field of sulfonated azo colourants relatively few pigment structures are known due to the insoluble nature of the materials and to the highly anisotropic habits of many species. This means that a high percentage of the crystal structures that are known are derived from less common methods than standard single-crystal X-ray diffraction (*e.g.* structure from powder diffraction, from electron diffraction or through use of synchrotron radiation – see Schmidt *et al.*, 2009; Gorelik *et al.*, 2009; Kennedy *et al.*, 2000; Grzesiak-Nowak *et al.*, 2019). One strategy for understanding



**Table 1**  
Experimental details.

H atoms were treated by a mixture of independent and constrained refinement. The absorption correction was multi-scan for NH<sub>4</sub>**1** (*CrysAlis PRO*; Rigaku OD, 2019) and K**1** (*SADABS*; Bruker, 2012).

	NH <sub>4</sub> <b>1</b>	NH <sub>4</sub> <b>2</b>	NH <sub>4</sub> <b>3</b>
<b>Crystal data</b>			
Chemical formula	NH <sub>4</sub> <sup>+</sup> ·C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> O <sub>4</sub> S <sup>-</sup>	NH <sub>4</sub> <sup>+</sup> ·C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> O <sub>5</sub> S <sup>-</sup> ·2H <sub>2</sub> O	NH <sub>4</sub> <sup>+</sup> ·C <sub>12</sub> H <sub>10</sub> N <sub>3</sub> O <sub>3</sub> S <sup>-</sup> ·1.5H <sub>2</sub> O
<i>M<sub>r</sub></i>	295.31	347.34	321.35
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub>	Triclinic, <i>P</i> $\bar{1}$	Monoclinic, <i>C</i> 2/ <i>c</i>
Temperature (K)	100	123	123
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.8163 (1), 6.9218 (1), 15.6295 (2)	8.2876 (1), 10.6404 (1), 17.4834 (3)	35.1636 (15), 7.8905 (3), 10.4972 (5)
$\alpha$ , $\beta$ , $\gamma$ (°)	90, 93.354 (1), 90	89.734 (1), 84.793 (1), 86.146 (1)	90, 100.091 (2), 90
<i>V</i> (Å <sup>3</sup> )	628.15 (2)	1531.91 (4)	2867.5 (2)
<i>Z</i>	2	4	8
Radiation type	Cu <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	2.48	0.25	0.25
Crystal size (mm)	0.22 × 0.12 × 0.06	0.42 × 0.40 × 0.10	0.35 × 0.30 × 0.05
<b>Data collection</b>			
Diffractometer	Rigaku Synergy-i	Enraf–Nonius KappaCCD	Enraf–Nonius KappaCCD
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.859, 1.000	–	–
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	10144, 2345, 2336	15978, 8209, 6704	6133, 3271, 1857
<i>R</i> <sub>int</sub>	0.054	0.021	0.074
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.616	0.685	0.649
<b>Refinement</b>			
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.029, 0.084, 1.08	0.036, 0.094, 1.02	0.049, 0.105, 1.02
No. of reflections	2345	8209	3271
No. of parameters	203	495	231
No. of restraints	1	1	1
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.26, -0.33	0.58, -0.41	0.26, -0.46
Absolute structure	Refined as an inversion twin.	–	–
Absolute structure parameter	0.00 (2)	–	–
	NH <sub>4</sub> <b>4</b>	NH <sub>4</sub> <b>5</b>	K <b>1</b>
<b>Crystal data</b>			
Chemical formula	NH <sub>4</sub> <sup>+</sup> ·C <sub>16</sub> H <sub>18</sub> N <sub>3</sub> O <sub>5</sub> S <sup>-</sup> ·H <sub>2</sub> O	NH <sub>4</sub> <sup>+</sup> ·C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> O <sub>4</sub> S <sup>-</sup>	[K(C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> O <sub>4</sub> S)(H <sub>2</sub> O)]
<i>M<sub>r</sub></i>	400.45	295.31	334.39
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Orthorhombic, <i>Pccn</i>	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	123	123	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.4933 (1), 13.0977 (2), 17.1657 (3)	12.6592 (3), 28.3597 (7), 7.1268 (2)	5.9620 (7), 7.2033 (11), 31.929 (5)
$\alpha$ , $\beta$ , $\gamma$ (°)	90.970 (1), 103.180 (1), 95.132 (1)	90, 90, 90	83.852 (14), 86.361 (15), 88.868 (15)
<i>V</i> (Å <sup>3</sup> )	1850.43 (5)	2558.60 (11)	1360.5 (3)
<i>Z</i>	4	8	4
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Synchrotron, $\lambda$ = 0.689 Å
$\mu$ (mm <sup>-1</sup> )	0.22	0.27	0.51
Crystal size (mm)	0.5 × 0.5 × 0.15	0.30 × 0.10 × 0.05	0.20 × 0.14 × 0.03
<b>Data collection</b>			
Diffractometer	Enraf–Nonius KappaCCD	Enraf–Nonius KappaCCD	Bruker APEXII CCD
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	–	–	0.751, 1.000
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	16736, 8841, 5911	5346, 2923, 1850	10143, 5691, 4405
<i>R</i> <sub>int</sub>	0.043	0.069	0.032
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.660	0.649	0.636
<b>Refinement</b>			
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.047, 0.118, 1.04	0.051, 0.118, 1.03	0.060, 0.180, 1.02
No. of reflections	8841	2923	5691
No. of parameters	550	201	403
No. of restraints	8	0	6
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.57, -0.42	0.29, -0.45	0.59, -0.67
	K <b>3</b>	K <b>4</b>	K <b>5</b>
<b>Crystal data</b>			
Chemical formula	[K(C <sub>12</sub> H <sub>10</sub> N <sub>3</sub> O <sub>3</sub> S)(H <sub>2</sub> O) <sub>2</sub> ]	[K(C <sub>16</sub> H <sub>18</sub> N <sub>3</sub> O <sub>5</sub> S)(H <sub>2</sub> O) <sub>2</sub> ]	[K(C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> O <sub>4</sub> S)]
<i>M<sub>r</sub></i>	351.42	439.52	316.37
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>	Orthorhombic, <i>Pccn</i>

Table 1 (continued)

	K3	K4	K5
Temperature (K)	123	123	123
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.3058 (2), 13.6247 (2), 18.4664 (3)	9.4006 (2), 12.1583 (3), 34.4743 (9)	12.5535 (2), 27.9698 (5), 6.9982 (1)
$\alpha$ , $\beta$ , $\gamma$ (°)	88.373 (1), 73.971 (1), 66.313 (1)	90, 95.496 (1), 90	90, 90, 90
<i>V</i> (Å <sup>3</sup> )	2933.52 (8)	3922.14 (16)	2457.20 (7)
<i>Z</i>	8	8	8
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
$\mu$ (mm <sup>-1</sup> )	0.53	0.42	0.62
Crystal size (mm)	0.7 × 0.3 × 0.02	0.20 × 0.18 × 0.08	0.70 × 0.08 × 0.04
Data collection			
Diffraction	Enraf–Nonius KappaCCD	Enraf–Nonius KappaCCD	Enraf–Nonius KappaCCD
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	26000, 13392, 10848	14501, 7971, 4387	5174, 2802, 1971
<i>R</i> <sub>int</sub>	0.023	0.084	0.056
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.649	0.628	0.648
Refinement			
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.036, 0.098, 1.03	0.060, 0.102, 1.01	0.042, 0.092, 1.05
No. of reflections	13392	7971	2802
No. of parameters	895	560	185
No. of restraints	24	112	1
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.80, -0.79	0.37, -0.34	0.39, -0.41

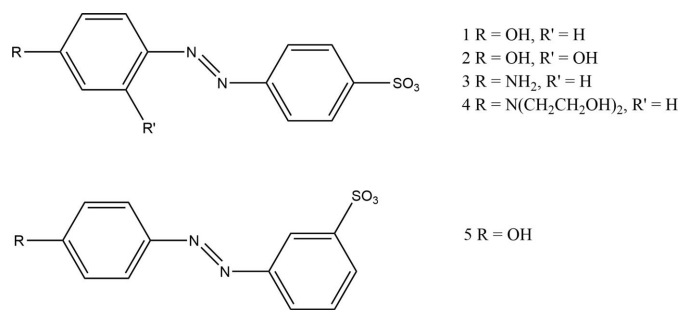
Computer programs: *CrysAlis PRO* (Rigaku OD, 2019), *DENZO* and *COLLECT* (Otwinowski & Minor, 1997), *APEX2*, *SAINT* and *SADABS* (Bruker, 2012), *SHELXT* (Sheldrick, 2015a), *SIR92* (Altomare *et al.*, 1994) and *SHELXL2018* (Sheldrick, 2015b) in *WinGX* (Farrugia, 2012).

the structure of sulfonated azo pigments has been to study systematically the structures of similarly functionalized, but easier to manipulate, dyes and then to cross-check any structure-to-property relationships identified against those pigment structures that are known (Kennedy *et al.*, 2004, 2009, 2012).

Ammonium salt forms of sulfonated azo colourants are sometimes used in preference to alkali-metal salts, either in the finished product or as an intermediate prior to laking (Christie & Mackay, 2008; Al Isawi *et al.*, 2021; Gonzalez & Miksovská, 2014). Despite this, only two structures of ammonium salts of sulfonated azo colourants appear to have been determined, namely, those of diammonium Orange G tetrahydrate and of the nitrile-substituted [NH<sub>4</sub>][O<sub>3</sub>S(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>NN(C<sub>6</sub>H<sub>4</sub>)NHCH<sub>2</sub>CH<sub>2</sub>CN]·H<sub>2</sub>O (Ojala *et al.*, 1994; Astbury *et al.*, 2013). The NH<sub>4</sub><sup>+</sup> ion is sometimes known as a pseudo-alkali metal due to its propensity to act in an isostructural manner with the heavier Group 1 metal ions. Its effective ionic radius has been estimated at 1.40 to 1.67 Å, depending on the coordination number (Sidey, 2016). Thus, as well as having the same charge as an alkali metal, it also has an ionic radius similar to those of K<sup>+</sup> and Rb<sup>+</sup>. An obvious difference is that bonds from an alkali-metal ion to, for example, an O-atom donor are typically described as ionic *M*–O interactions, whereas NH<sub>4</sub><sup>+</sup> will interact with O *via* N–H···O hydrogen bonds. As there are four H-atom donors per ammonium ion this may limit NH<sub>4</sub><sup>+</sup> to lower coordination numbers than those typically seen for K or Rb. It seems to be this feature that is responsible for ammonium forming isostructural pairs with Na compounds, as well as with K and Rb compounds, despite the smaller ionic radius of Na<sup>+</sup> (*e.g.* Khan & Baur, 1972; Christov, 2003; Emerson *et al.*, 2014). Many examples of isostructurality between ammonium and Group 1 metal ions are for inorganic systems, but organic examples are also known. Of particular relevance to sulfonated azo species is the sweetener cyclamic

acid. This is an RSO<sub>3</sub><sup>-</sup>-containing organic species and its ammonium, Na, K and Rb salt forms are known to form an isostructural series (Leban *et al.*, 2007).

In order to investigate the structural relationships between ammonium salt forms of sulfonated azo dyes and their alkali-metal congeners, we herein present the crystal structures of ammonium salts of five azo anion species (Scheme 1). The structures of their Na-salt equivalents have already been reported (Kennedy *et al.*, 2001, 2020; Dodds *et al.*, 2017), as has the structure of one of their K equivalents (Kennedy *et al.*, 2004). In order to complete the comparison we report herein the crystal structures of the remaining four K-salt equivalents.



Scheme 1

## 2. Experimental

The Na salt of dye **3** was obtained from Fujifilm. The other dyes were synthesized as their Na salts using the well-known azo-coupling method (Alsantali *et al.*, 2022; Kennedy *et al.*, 2001). Na salts were converted to NH<sub>4</sub> or K salts by reaction with a slight excess of either NH<sub>4</sub>Cl or KCl in warm water. Solutions were filtered to give clear aqueous solutions and then allowed to evaporate for 2 to 7 d. This gave yellow or

yellow–orange crystals of the desired salt forms that were suitable for single-crystal diffraction analysis. FT–IR spectra were measured as KBr discs using a Nicolet Avatar 380 spectrometer. Raman data were measured from solids using a Reinshaw Ramascope with excitation at 785 nm. Aqueous UV–Vis spectra were measured using a Cary 300 Bio spectrophotometer and solid-state UV–Vis spectra were measured using a Phillips PU8749 spectrophotometer. Measurements on **K1** were made at Station 9.8 of the Daresbury SRS. All other measurements were made using standard Rigaku Synergy-i (**NH<sub>4</sub>1**) or Enraf–Nonius KappaCCD (all other structures) laboratory diffractometers equipped with CCD detectors.

### 2.1. Spectroscopic data

**NH<sub>4</sub>1**, FT–IR ( $\text{cm}^{-1}$ ): 3421, 3267, 3088, 1598, 1501, 1280, 1193, 1040. Raman ( $\text{cm}^{-1}$ ): 1120, 1147, 1185, 1435, 1459, 1594. UV–Vis ( $\lambda_{\text{max}}$ , nm): 348 (aq), 346 (solid).

**NH<sub>4</sub>2**, FT–IR ( $\text{cm}^{-1}$ ): 1629, 1588, 1419, 1337, 1198, 1116, 1034, 999, 840, 804. Raman ( $\text{cm}^{-1}$ ): 239, 317, 348, 446, 836, 1036, 1122, 1161, 1197, 1324, 1375, 1419, 1591. UV–Vis ( $\lambda_{\text{max}}$ , nm): 417 (aq), 334 (solid).

**NH<sub>4</sub>3**, FT–IR ( $\text{cm}^{-1}$ ): 1634, 1603, 1501, 1398, 1383, 1275, 1193, 1116, 1034, 1004, 835. Raman ( $\text{cm}^{-1}$ ): peaks masked by fluorescence. UV–Vis ( $\lambda_{\text{max}}$ , nm): 386 (aq), 332 (solid).

**NH<sub>4</sub>4**, FT–IR ( $\text{cm}^{-1}$ ): 1598, 1511, 1403, 1213, 1116, 1075, 1024, 844, 814, 691. Raman ( $\text{cm}^{-1}$ ): 1034, 1115, 1143, 1197, 1315, 1356, 1387, 1419, 1441, 1589. UV–Vis ( $\lambda_{\text{max}}$ , nm): 459 (aq), 418 (solid).

**NH<sub>4</sub>5**, FT–IR ( $\text{cm}^{-1}$ ): 3405, 3190, 2366, 1597, 1495, 1423, 1177, 1136, 1034. Raman ( $\text{cm}^{-1}$ ): 1138, 1183, 1422, 1452 (somewhat masked by fluorescence). UV–Vis ( $\lambda_{\text{max}}$ , nm): 348 (aq), 351 (solid).

**K1**, FT–IR ( $\text{cm}^{-1}$ ): 1593, 1460, 1372, 1178, 850, 717. Raman ( $\text{cm}^{-1}$ ): 628, 794, 922, 1102, 1121, 1147, 1158, 1309, 1396, 1435, 1590, 1607. UV–Vis ( $\lambda_{\text{max}}$ , nm): 348 (aq), 334 (solid).

**K2**, FT–IR ( $\text{cm}^{-1}$ ): 3472, 3390, 1593, 1469, 1372, 1198, 1121, 1039, 839, 803. Raman ( $\text{cm}^{-1}$ ): 1033, 1122, 1161, 1198, 1326, 1374, 1418, 1592. UV–Vis ( $\lambda_{\text{max}}$ , nm): 430 (aq), 336 (solid).

**K3**, FT–IR ( $\text{cm}^{-1}$ ): 1644, 1460, 1372, 1193, 1116, 1029, 839, 716. Raman ( $\text{cm}^{-1}$ ): 780, 921, 1036, 1120, 1152, 1427, 1588. UV–Vis ( $\lambda_{\text{max}}$ , nm): 387 (aq), 345 (solid).

**K4**, FT–IR ( $\text{cm}^{-1}$ ): 1597, 1515, 1382, 1351, 1316, 1259, 1223, 1182, 1116, 1049, 1003. Raman ( $\text{cm}^{-1}$ ): 739, 1032, 1117, 1143, 1195, 1315, 1355, 1392, 1421, 1440. UV–Vis ( $\lambda_{\text{max}}$ , nm): 458 (aq), 413 (solid).

**K5**, FT–IR ( $\text{cm}^{-1}$ ): 3390, 3078, 1603, 1501, 1383, 1188, 1034, 845. Raman ( $\text{cm}^{-1}$ ): 1136, 1169, 1185, 1424, 1454 (somewhat masked by fluorescence). UV–Vis ( $\lambda_{\text{max}}$ , nm): 347 (aq), 348 (solid).

### 2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. For **K4**, the azobenzene core of one of the two crystallographically independent dye anions was treated as disordered over two sites. In a similar way, one of the four independent  $\text{SO}_3$  groups of **K3** was also

treated as disordered over two sites, a rotation about the C–S bond giving alternative positions for the three O atoms. In both cases, appropriate restraints and constraints on the displacement parameters were added so as to ensure that the structures approximated normal behaviour. Finally, one water molecule of **NH<sub>4</sub>4** was modelled as rotationally disordered about atom O2W so that the water molecule has three independent H-atom sites. Where possible, H atoms attached to O or to N atoms were positioned as found in difference syntheses and refined freely and isotropically. Where riding models were required, X–H bond lengths were set at 0.88 (1) Å. All H atoms bound to C atoms were included in riding models, with C–H = 0.95 or 0.99 Å for CH and  $\text{CH}_2$  groups, respectively. For all H atoms in riding models,  $U_{\text{iso}}(\text{H})$  values were set to  $1.2U_{\text{eq}}$  of the parent atom.

### 3. Results and discussion

All structures discussed are of crystal samples obtained from aqueous recrystallizations. Aqueous conditions were chosen to best reflect normal synthesis and usage of sulfonated azo dyes. It is possible to dry the hydrate structures described to give anhydrous materials. However, no polymorph screen has been attempted and so the existence of other forms is entirely likely. Selected crystallographic and refinement parameters are given in Table 1 and selected geometric parameters are given in Tables 2 to 14. Representations of the crystal structures of the ammonium salt forms **NH<sub>4</sub>1**, **NH<sub>4</sub>2**, **NH<sub>4</sub>3**, **NH<sub>4</sub>4** and **NH<sub>4</sub>5** are given in Figs. 1 to 5. Both the phenol derivatives **NH<sub>4</sub>1** and **NH<sub>4</sub>5** are simple anhydrous salts with an  $\text{NH}_4^+$  cation and an azo anion in the asymmetric unit. The other species are all hydrated forms as shown in Table 15. Additionally, both **NH<sub>4</sub>2** and **NH<sub>4</sub>4** are  $Z' = 2$  structures with two cation/anion pairs per asymmetric unit, as well as their accompanying water molecules. The bond lengths about the azo chromophores are in good agreement with those described for *s*-block metal salts of similar azo anions (Kennedy *et al.*, 2001, 2020). The N=N bonds range from 1.254 (3) to 1.275 (2) Å, whilst the C–N bonds show ranges of 1.423 (2)–1.439 (2) and 1.396 (2)–1.425 (3) Å for the bonds

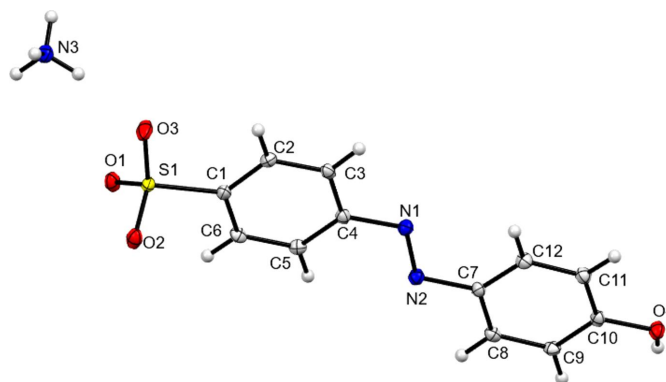
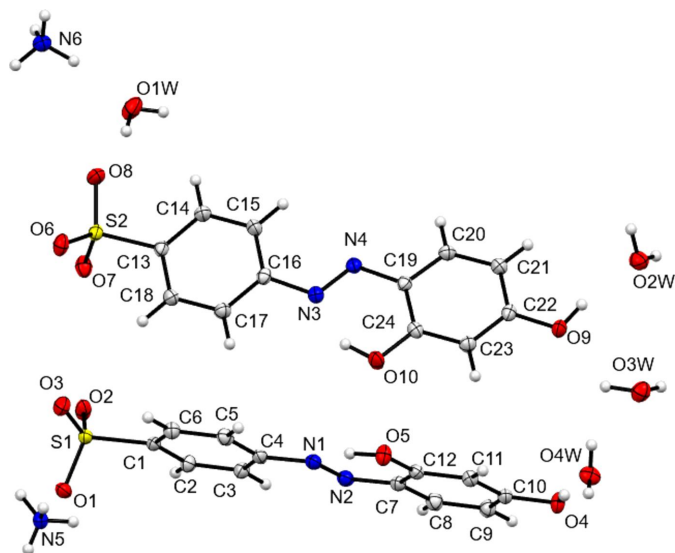


Figure 1

The asymmetric unit contents of **NH<sub>4</sub>1**. Here and elsewhere displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small spheres of arbitrary size.





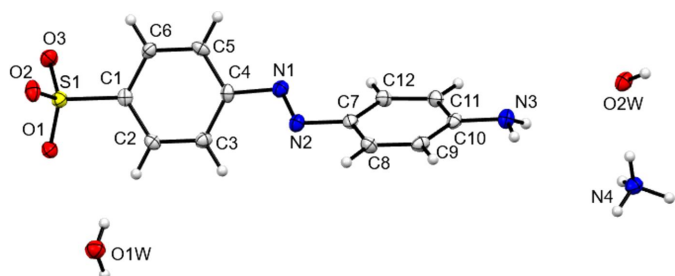
**Figure 2**  
The asymmetric unit contents of NH<sub>4</sub>2.

**Table 2**  
Hydrogen-bond geometry (Å, °) for NH<sub>4</sub>1.

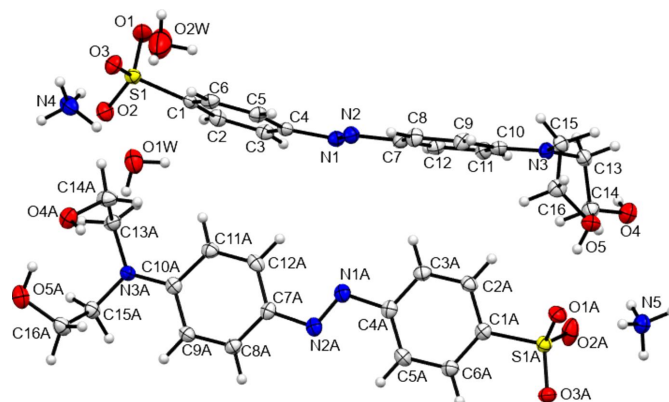
<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H4N...O2 <sup>i</sup>	0.91 (5)	2.30 (5)	2.940 (4)	127 (4)
N3—H4N...O1 <sup>ii</sup>	0.91 (5)	2.21 (5)	2.969 (3)	141 (4)
N3—H3N...O3	0.86 (5)	1.96 (5)	2.808 (3)	170 (4)
N3—H1N...O1 <sup>iii</sup>	0.86 (4)	2.03 (5)	2.889 (4)	176 (4)
N3—H2N...O4 <sup>iv</sup>	0.88 (4)	2.10 (4)	2.946 (3)	159 (4)
O4—H1H...O2 <sup>v</sup>	0.87 (5)	1.95 (5)	2.802 (3)	167 (4)

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

involving the C atoms of the sulfonated and nonsulfonated rings, respectively. The generally shorter bonds of the latter are due to resonance with the OH and amine substituents. It is noteworthy that it is NH<sub>4</sub>2 that displays both the longest N=N bond and the shortest N—C bond. The intramolecular O—H...N hydrogen bonding of NH<sub>4</sub>2 raises the possibility of tautomerism in this species and, although the electron density shows that the compound clearly exists largely as the azo tautomer, the bond lengths observed tend to reflect a small contribution from the alternative hydrazone tautomer. [See Kennedy *et al.* (2020) for a detailed discussion of factors that influence bond lengths and hence colour in similar azo dyes,



**Figure 3**  
The asymmetric unit contents of NH<sub>4</sub>3. A twofold rotation axis passes through atom O2W.



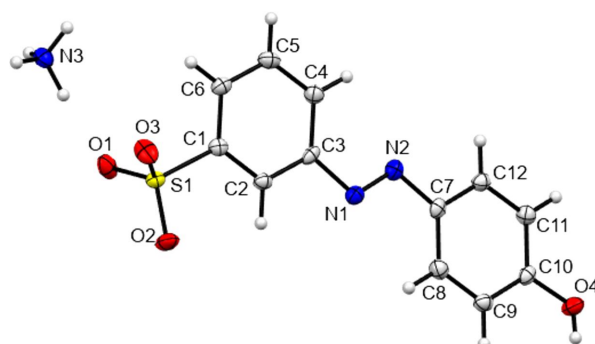
**Figure 4**  
The asymmetric unit contents of NH<sub>4</sub>4. The water molecule labelled O2W is disordered so as to give three independent H-atom sites.

**Table 3**  
Hydrogen-bond geometry (Å, °) for NH<sub>4</sub>2.

<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>
O4—H1H...O4W	0.84 (2)	1.81 (2)	2.6357 (17)	170 (2)
O5—H2H...N1	0.98 (3)	1.65 (3)	2.5535 (16)	151 (2)
O9—H3H...O2W	0.85 (2)	1.83 (2)	2.6673 (16)	168 (2)
O10—H4H...N3	0.93 (3)	1.69 (3)	2.5420 (16)	149 (2)
N5—H1N...O1 <sup>i</sup>	0.80 (2)	2.16 (2)	2.8858 (17)	151.1 (18)
N5—H1N...O1W <sup>ii</sup>	0.80 (2)	2.627 (19)	3.034 (2)	113.3 (15)
N5—H2N...O1	0.92 (2)	1.94 (2)	2.8403 (18)	168 (2)
N5—H3N...O3W <sup>iii</sup>	0.94 (2)	1.91 (2)	2.8488 (17)	172 (2)
N5—H4N...O6 <sup>iv</sup>	0.89 (2)	2.01 (2)	2.8425 (16)	156 (2)
N6—H5N...S2 <sup>v</sup>	0.90 (2)	2.99 (2)	3.7547 (15)	143.5 (17)
N6—H5N...O7 <sup>v</sup>	0.90 (2)	1.99 (2)	2.8804 (18)	168 (2)
N6—H6N...O1W	0.92 (2)	1.90 (2)	2.8027 (18)	169.7 (19)
N6—H7N...O3W <sup>vi</sup>	0.92 (2)	1.96 (2)	2.8733 (19)	170.4 (19)
N6—H8N...O2 <sup>vii</sup>	0.84 (2)	2.42 (2)	2.9090 (18)	117.8 (18)
N6—H8N...O3 <sup>v</sup>	0.84 (2)	2.36 (2)	2.9153 (17)	123.8 (19)
O1W—H2W...O4 <sup>viii</sup>	0.84 (3)	2.01 (3)	2.8150 (16)	162 (2)
O1W—H1W...O8	0.82 (3)	1.98 (3)	2.7858 (17)	166 (2)
O2W—H3W...O3 <sup>viii</sup>	0.83 (3)	2.04 (3)	2.8639 (16)	171 (2)
O2W—H4W...O8 <sup>vi</sup>	0.87 (1)	1.94 (1)	2.7918 (17)	169 (2)
O3W—H5W...O7 <sup>viii</sup>	0.88 (3)	1.83 (3)	2.7106 (16)	179 (2)
O3W—H6W...O9	0.95 (3)	2.04 (3)	2.8347 (15)	140 (2)
O4W—H7W...O2 <sup>ix</sup>	0.81 (2)	1.94 (2)	2.7482 (17)	175 (2)
O4W—H8W...O6 <sup>ix</sup>	0.81 (3)	2.01 (3)	2.8128 (16)	171 (2)

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

and Yatsenko *et al.* (2024) for a discussion on azo/hydrazone tautomerization in solid-state arylazo compounds.] Most of



**Figure 5**  
The asymmetric unit contents of NH<sub>4</sub>5.

**Table 4**  
Hydrogen-bond geometry (Å, °) for NH<sub>4</sub>3.

<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>
N4—H1N...O2W	0.90 (3)	2.00 (3)	2.850 (3)	157 (2)
N4—H2N...O1 <sup>i</sup>	0.94 (3)	1.93 (3)	2.862 (3)	167 (3)
N4—H2N...O1W <sup>i</sup>	0.94 (3)	2.57 (3)	3.039 (3)	111 (2)
N4—H3N...O2 <sup>ii</sup>	0.86 (3)	2.14 (3)	2.963 (3)	161 (3)
N4—H3N...O3 <sup>ii</sup>	0.86 (3)	2.66 (3)	3.351 (3)	139 (3)
N4—H4N...O3 <sup>iii</sup>	0.98 (4)	2.07 (4)	2.987 (3)	155 (3)
N3—H5N...O1W <sup>i</sup>	0.85 (3)	2.23 (3)	3.067 (3)	168 (2)
N3—H6N...O2 <sup>ii</sup>	0.86 (3)	2.17 (3)	3.015 (3)	165 (2)
O1W—H1W...N3 <sup>ii</sup>	0.83 (3)	2.21 (3)	3.011 (3)	162 (3)
O1W—H2W...O3 <sup>iv</sup>	0.88 (3)	1.99 (3)	2.861 (3)	169 (3)
O2W—H3W...O1 <sup>v</sup>	0.87 (1)	1.97 (1)	2.792 (3)	159 (3)

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

**Table 5**  
Hydrogen-bond geometry (Å, °) for NH<sub>4</sub>4.

<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...O1 <sup>i</sup>	0.88 (1)	1.93 (1)	2.802 (2)	176 (3)
O1W—H2W...O5 <sup>ii</sup>	0.88 (1)	1.84 (1)	2.711 (2)	168 (2)
O2W—H3W...O1A <sup>ii</sup>	0.91 (1)	2.05 (1)	2.945 (2)	172 (3)
O2W—H4W...O2W <sup>iii</sup>	0.89 (1)	2.29 (4)	3.031 (5)	141 (6)
O4—H1H...O3A <sup>iv</sup>	0.84 (3)	2.05 (3)	2.885 (2)	169 (3)
O5—H2H...O1A	0.81 (3)	1.90 (3)	2.698 (2)	169 (3)
O4A—H3H...O1 <sup>i</sup>	0.80 (3)	1.96 (3)	2.756 (2)	177 (3)
O5A—H4H...O4A	0.97 (3)	1.79 (3)	2.734 (2)	165 (3)
N4—H1N...O3	0.87 (3)	2.09 (3)	2.957 (3)	176 (2)
N4—H2N...O2 <sup>v</sup>	0.95 (3)	1.92 (3)	2.841 (3)	163 (2)
N4—H3N...O3A <sup>vi</sup>	0.89 (3)	2.05 (3)	2.923 (3)	167 (2)
N4—H4N...O1W	1.13 (4)	1.69 (4)	2.818 (3)	176 (3)
N5—H5N...O2A	0.91 (3)	1.89 (3)	2.784 (3)	164 (2)
N5—H6N...O5A <sup>vii</sup>	0.89 (4)	2.21 (4)	2.935 (3)	138 (3)
N5—H6N...O1W <sup>viii</sup>	0.89 (4)	2.51 (4)	3.094 (3)	123 (3)
N5—H7N...O3 <sup>ix</sup>	0.96 (4)	2.03 (4)	2.952 (3)	159 (3)
N5—H8N...O4 <sup>x</sup>	0.96 (3)	2.00 (3)	2.943 (3)	168 (3)

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

the azo anions have planar conformations, with angles between the planes of the aromatic rings ranging from 2.23 (9) to 12.32 (11)°. Despite this, the azo group does form a small step between the two parallel ring planes [e.g. in NH<sub>4</sub>1, atom N2 lies 0.473 (5) Å out of the plane defined by atoms C1–C6]. The exception is the anion of NH<sub>4</sub>3, which adopts a twisted conformation with an angle of 58.76 (11)° between the planes of its two aromatic rings. This out-of-plane twist in the solid

**Table 6**  
Hydrogen-bond geometry (Å, °) for NH<sub>4</sub>5.

<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 <sup>i</sup>	0.90 (4)	2.48 (3)	3.002 (4)	118 (3)
N3—H1N...O4 <sup>ii</sup>	0.90 (4)	2.35 (3)	2.913 (4)	121 (3)
N3—H1N...O4 <sup>iii</sup>	0.90 (4)	2.50 (4)	3.162 (4)	131 (3)
N3—H2N...O1	0.96 (4)	1.94 (4)	2.893 (3)	171 (3)
N3—H3N...O1 <sup>iv</sup>	0.89 (3)	1.97 (3)	2.822 (3)	159 (3)
N3—H4N...O3 <sup>v</sup>	0.90 (4)	1.97 (4)	2.831 (3)	160 (3)
O4—H1H...O2 <sup>vi</sup>	0.82 (4)	2.00 (4)	2.707 (3)	144 (4)

Symmetry codes: (i)  $x - \frac{1}{2}, -y + 1, -z + \frac{1}{2}$ ; (ii)  $x - \frac{1}{2}, y - \frac{1}{2}, -z$ ; (iii)  $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (iv)  $-x + \frac{3}{2}, y, z + \frac{1}{2}$ ; (v)  $-x + \frac{3}{2}, y, z - \frac{1}{2}$ ; (vi)  $-x + \frac{5}{2}, -y + \frac{3}{2}, z$ .

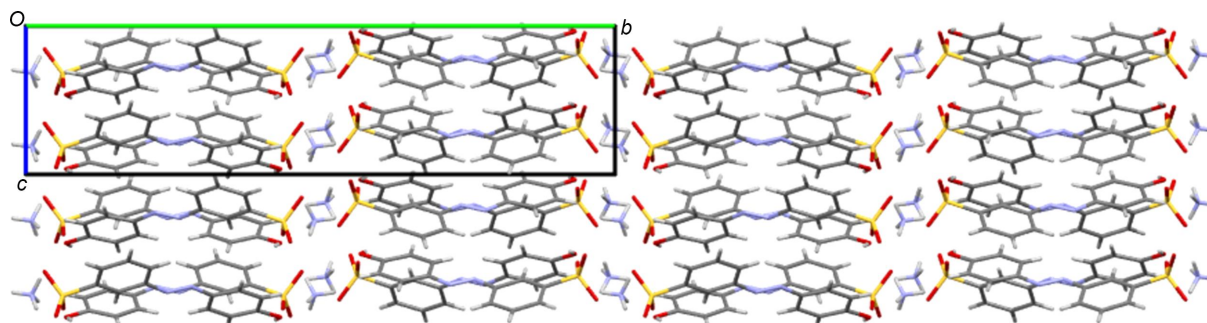
**Table 7**  
Selected bond lengths (Å) for K1.

K1—O1	2.642 (2)	K2—O5	2.625 (2)
K1—O2W <sup>i</sup>	2.688 (3)	K2—O2W	2.713 (2)
K1—O2 <sup>ii</sup>	2.728 (2)	K2—O7 <sup>ii</sup>	2.736 (2)
K1—O6	2.829 (3)	K2—O1 <sup>ii</sup>	2.769 (2)
K1—O8 <sup>iii</sup>	2.957 (2)	K2—O8 <sup>v</sup>	2.904 (2)
K1—O7	3.027 (2)	K2—O3 <sup>ii</sup>	3.020 (2)
K1—O4 <sup>iv</sup>	3.116 (2)	K2—O1W	3.050 (3)
K1—O1W <sup>i</sup>	3.149 (2)		

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

state should alter the resonance through the azobenzene fragment and may contribute to the relatively large difference found between the solution-state and solid-state  $\lambda_{\max}$  values (386 versus 332 nm). It has previously been shown for *s*-block metal salt forms that the planar or twisted conformation of *ortho*-sulfonated azo anions correlates with the packing motifs observed. Thus, twisted azo species gave structures with a simple alternating layer structure, *i.e.* layers of organic anions alternating with hydrophilic layers containing the cations and water molecules. In contrast, planar azo anions gave structures with organic bilayers (Kennedy *et al.*, 2009). This is not observed here; all the ammonium salts of the *para*- and *meta*-sulfonated anions **1** to **5** give simple layering structures with no bilayers, irrespective of the planarity of the anion (see Figs. 6 and 7 for examples).

Each H atom of every NH<sub>4</sub><sup>+</sup> cation acts as a hydrogen-bond donor to at least one O atom. There are no NH<sub>4</sub>-to-N hydrogen-bonding interactions. From Tables 2 to 6 and the summary Table 15, it can be seen that of the 28 independent N—H donors of the ammonium groups, 10 form bifurcated



**Figure 6**  
Packed structure of NH<sub>4</sub>5 viewed along the *a* axis. Note the simple layering structure with alternating hydrophobic (arylazo) and hydrophilic (cation) layers parallel to the *ac* plane.

**Table 8**  
Hydrogen-bond geometry (Å, °) for K1.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O4-H4H\cdots O1W^{vi}$	0.88 (1)	1.83 (2)	2.676 (3)	160 (3)
$O8-H8H\cdots O6^{vii}$	0.88 (1)	1.93 (3)	2.748 (3)	155 (5)
$O1W-H1W\cdots O3^{iii}$	0.87 (1)	1.95 (2)	2.801 (3)	165 (4)
$O1W-H2W\cdots O2^{viii}$	0.88 (1)	1.93 (1)	2.803 (4)	177 (5)
$O2W-H3W\cdots O3^{ix}$	0.88 (1)	2.20 (3)	2.866 (3)	133 (4)
$O2W-H3W\cdots O4^{vi}$	0.88 (1)	2.29 (3)	2.905 (3)	127 (3)
$O2W-H4W\cdots O5^{ii}$	0.88 (1)	1.92 (2)	2.778 (3)	165 (4)

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

**Table 9**  
Selected bond lengths (Å) for K3.

K1—O2	2.6531 (14)	K3—O3C	2.649 (2)
K1—O1A <sup>i</sup>	2.6570 (14)	K3—O1B	2.7285 (16)
K1—O6W <sup>ii</sup>	2.7388 (15)	K3—O5W <sup>iv</sup>	2.8713 (16)
K1—O7W <sup>ii</sup>	2.7669 (15)	K3—O4W	2.8932 (16)
K1—O1W	2.7806 (15)	K3—O5W	2.9166 (15)
K1—O1A	2.8284 (14)	K3—O3B	3.2009 (19)
K1—O2A	2.9928 (15)	K3—O4W <sup>iv</sup>	3.2971 (17)
K2—O3	2.7462 (14)	K4—O2B <sup>v</sup>	2.6854 (15)
K2—O1C	2.7536 (17)	K4—O6W	2.7164 (15)
K2—O2A	2.7929 (14)	K4—O2B	2.7701 (15)
K2—O2W	2.8559 (16)	K4—O8W	2.8338 (16)
K2—O3W <sup>iii</sup>	2.8666 (15)	K4—O7W	2.8395 (16)
K2—O3W	2.8901 (16)	K4—O3C	2.954 (2)
K2—O2	3.0708 (15)	K4—O2C	3.097 (2)
K2—O3A	3.1446 (16)	K4—O1B	3.1503 (16)
K3—O3	2.6206 (14)		

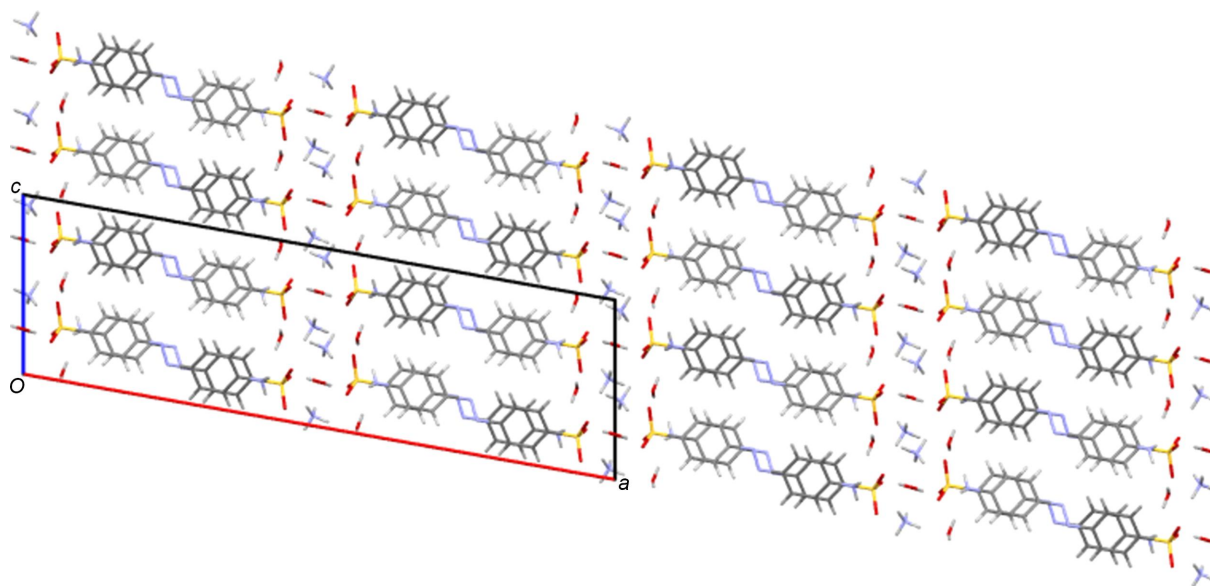
Symmetry codes: (i)  $-x+1, -y, -z$ ; (ii)  $x-1, y, z$ ; (iii)  $-x+1, -y+1, -z$ ; (iv)  $-x+2, -y, -z$ ; (v)  $-x+2, -y+1, -z$ .

hydrogen bonds and two (atoms H8N of NH<sub>4</sub>2 and H1N of NH<sub>4</sub>5) interact with three separate O-atom acceptors. Most ammonium cations interact with six O atoms, but one (that containing atom N4 of structure NH<sub>4</sub>4) has a coordination number of 5 and one (containing atom N3 of NH<sub>4</sub>5) has a coordination number of 7. In all five structures, the majority of

the ammonium cation hydrogen-bond interactions are with the O atoms of the formally negatively charged SO<sub>3</sub> groups. For the anhydrous species NH<sub>4</sub>1 and NH<sub>4</sub>5, the ammonium ions also donate hydrogen bonds to the phenol OH groups; thus, hydrogen bonding from ammonium to both the SO<sub>3</sub> head and the OH tail of the azo anions leads to the anions bridging between the inorganic/hydrophilic layers of the packing structures (Fig. 6). The hydrates NH<sub>4</sub>2 and NH<sub>4</sub>3 have no direct ammonium-to-tail-group hydrogen-bond interactions; instead, the water molecules act as intermediaries or bridges and accept/donate hydrogen bonds from both ammonium and tail groups. Thus, for these hydrate species, interactions between the hydrophobic and hydrophilic layers of the packing structure is *via* the water molecules. Despite featuring a lower cation coordination number, in hydrate NH<sub>4</sub>4, the cations donate hydrogen bonds to all of the different types of acceptor groups available, *i.e.* to the SO<sub>3</sub> heads, to the OH groups of the tail and to bridging water molecules.

As they are situated at the centre of the hydrophobic layers, none of the  $-N=N-$  chromophore units take part in intermolecular hydrogen bonding. Indeed, the azo groups of NH<sub>4</sub>1, NH<sub>4</sub>3 and NH<sub>4</sub>4 have no intermolecular contacts less than the sum of the van der Waals radii. NH<sub>4</sub>5 is the only species of the five to show face-to-face  $\pi$ -contacts between the azobenzene units, with closest N2 $\cdots$ C4 and C7 $\cdots$ C3 contact distances of 3.160 (4) and 3.352 (4) Å, respectively. This forms the stacking motif seen extending parallel to the *c* axis in Fig. 8. In NH<sub>4</sub>2, the *ortho*-OH substituent of one of the independent azo anions of the asymmetric unit approaches the azo group of the other anion [O10 $\cdots$ N1 = 3.052 (2) Å], creating dimeric pairs of anions (Fig. 9).

The structure of K2 was reported by Kennedy *et al.* (2004). Here, we report the remaining K-salt structures of azo anions 1 to 5. Figs. 9 to 13 show the fundamental features of these structures and selected geometric parameters are given in



**Figure 7**  
Packed structure of NH<sub>4</sub>3 viewed along the *b* axis. Despite the twisted nature of the azo anion, this structure has a similar simple layering structure with alternating hydrophobic (arylazo) and hydrophilic (cation and water) layers as the planar species. Here the layers lie parallel to the *bc* plane.

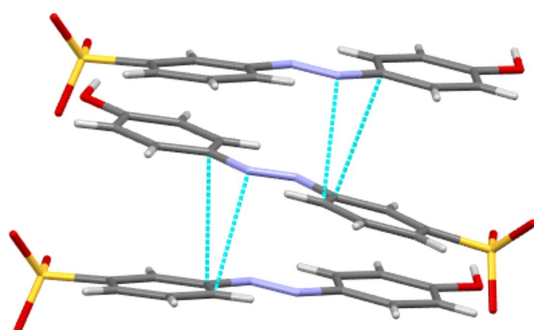


**Table 10**  
 Hydrogen-bond geometry (Å, °) for **K3**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H1N $\cdots$ O3B <sup>vi</sup>	0.92 (3)	2.35 (3)	3.210 (2)	155 (2)
N3—H2N $\cdots$ O2W <sup>vi</sup>	0.81 (3)	2.40 (3)	3.147 (2)	154 (2)
N3A—H3N $\cdots$ O8W <sup>vii</sup>	0.82 (3)	2.27 (3)	3.016 (2)	153 (3)
N3A—H4N $\cdots$ O1 <sup>viii</sup>	0.88 (3)	2.27 (3)	3.115 (2)	161 (2)
N3B—H5N $\cdots$ O2C <sup>ix</sup>	0.90 (3)	2.50 (3)	3.384 (3)	167 (2)
N3B—H5N $\cdots$ O5C <sup>ix</sup>	0.90 (3)	2.26 (3)	3.078 (14)	151 (2)
N3B—H6N $\cdots$ O1W <sup>vi</sup>	0.88 (3)	2.21 (3)	3.065 (2)	164 (2)
N3C—H7N $\cdots$ O4W <sup>viii</sup>	0.86 (3)	2.38 (3)	3.149 (2)	149 (2)
N3C—H8N $\cdots$ O3A <sup>vii</sup>	0.87 (3)	2.53 (3)	3.330 (2)	154 (2)
O1W—H1W $\cdots$ N3C <sup>x</sup>	0.87 (1)	2.62 (2)	3.428 (2)	156 (2)
O1W—H2W $\cdots$ O1B <sup>ii</sup>	0.87 (1)	1.94 (1)	2.808 (2)	174 (2)
O2W—H3W $\cdots$ O1C <sup>iii</sup>	0.87 (1)	2.14 (1)	2.963 (3)	160 (3)
O2W—H3W $\cdots$ O5C <sup>iii</sup>	0.87 (1)	2.24 (3)	2.973 (18)	143 (2)
O2W—H4W $\cdots$ N3B <sup>vi</sup>	0.87 (1)	2.56 (2)	3.322 (2)	148 (2)
O3W—H5W $\cdots$ N3 <sup>vi</sup>	0.87 (1)	2.25 (2)	3.036 (2)	151 (3)
O3W—H6W $\cdots$ O3B	0.87 (1)	2.15 (2)	2.906 (2)	145 (2)
O4W—H7W $\cdots$ O1	0.87 (1)	2.03 (1)	2.879 (2)	166 (3)
O4W—H8W $\cdots$ O3C <sup>iv</sup>	0.87 (1)	2.02 (1)	2.837 (2)	156 (2)
O4W—H8W $\cdots$ O6C <sup>iv</sup>	0.87 (1)	2.27 (2)	3.126 (16)	170 (3)
O5W—H9W $\cdots$ O3 <sup>iv</sup>	0.87 (1)	2.66 (2)	3.376 (2)	141 (2)
O5W—H10W $\cdots$ O3A <sup>iv</sup>	0.89 (1)	1.93 (1)	2.807 (2)	169 (2)
O6W—H11W $\cdots$ O5W	0.87 (1)	2.11 (1)	2.924 (2)	158 (2)
O6W—H12W $\cdots$ O1 <sup>iv</sup>	0.86 (1)	1.95 (1)	2.7885 (19)	164 (3)
O7W—H13W $\cdots$ O2C <sup>v</sup>	0.87 (1)	2.02 (1)	2.896 (2)	177 (3)
O7W—H13W $\cdots$ O5C <sup>v</sup>	0.87 (1)	1.88 (2)	2.698 (12)	156 (3)
O7W—H14W $\cdots$ O3W <sup>v</sup>	0.88 (1)	2.22 (1)	3.085 (2)	169 (2)
O8W—H15W $\cdots$ O2A <sup>xi</sup>	0.88 (1)	1.94 (1)	2.808 (2)	168 (2)

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

Table 7 to 14. **K5** is anhydrous and a  $Z' = 1$  structure, but all other K salts were isolated as hydrates and have  $Z' = 2$  (or 4 for **K3**); see Table 15 for a summary of these and other structural features. Values for the disordered anion of **K4** have been excluded from the geometric discussion below. The azo N=N bond lengths range from 1.258 (3) to 1.276 (3) Å, with the long value again found for the salt of **2** with its intramolecular O—H $\cdots$ N hydrogen bond and the possibility of tautomerization. The C—N bonds range from 1.420 (3) to 1.442 (4) and from 1.397 (3) to 1.432 (4) Å for the bonds to the sulfonated heads and to the phenol/amine tails, respectively. Again, it is **K2** that presents the most different bond lengths. All these bond lengths are similar to those found for the NH<sub>4</sub> salts, above, and for related sulfonated azo salt forms (Kennedy *et al.*, 2020). Most azo anions have planar geome-


**Figure 8**  
 Part of azo stack propagating parallel to the  $c$  axis in the structure of NH<sub>4</sub>**5**.

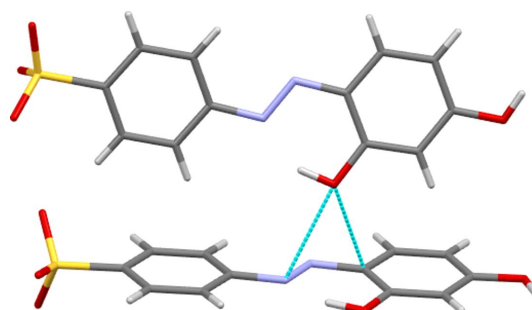
**Table 11**  
 Selected bond lengths (Å) for **K4**.

K1—O2W <sup>i</sup>	2.738 (3)	K2—O5 <sup>v</sup>	2.794 (3)
K1—O1A <sup>ii</sup>	2.771 (3)	K2—O1A	2.800 (2)
K1—O1W	2.772 (3)	K2—O2A <sup>ii</sup>	2.821 (2)
K1—O2A	2.786 (2)	K2—O1	2.862 (2)
K1—O3W <sup>iii</sup>	2.798 (3)	K2—O1W <sup>iii</sup>	2.898 (3)
K1—O4A <sup>iv</sup>	2.820 (3)	K2—O3A	2.947 (2)
K1—O3A	2.919 (2)	K2—O2	3.073 (3)
K2—O2W <sup>i</sup>	2.753 (3)		

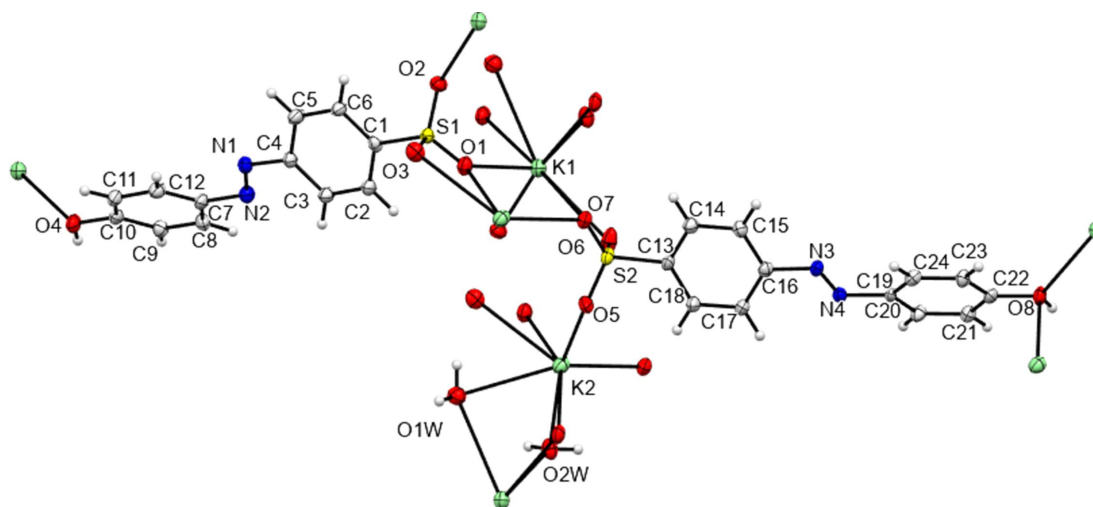
Symmetry codes: (i)  $-x+2, -y+1, -z$ ; (ii)  $-x+1, -y+1, -z$ ; (iii)  $x+\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$ ; (iv)  $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$ ; (v)  $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$ .

tries [angles between ring planes = 0.93 (7) to 8.15 (22)°], with the exception of **K1**, where the two independent azo anions are both twisted [angles between ring planes = 43.15 (7) and 40.48 (8)°]. This contrasts with the ammonium salt structures, where all species were planar except for the twisted NH<sub>4</sub>**3**. As with the NH<sub>4</sub> species, all five K structures both planar and twisted have simple layered packing systems with layers of hydrophilic/inorganic species (K and water) alternating with layers of a hydrophobic/organic nature (azobenzene) (see Fig. 14 for an example).

Each K centre has a coordination number of 7 or 8 (see Table 15), with all bonds from K being to O atoms. All K centres interact with SO<sub>3</sub> groups and, where present, with water molecules. In **K1**, **K4** and the anhydrous **K5**, there are also bonds formed between K and the OH groups of the tails of the azo anions. No such K-to-tail bonds are formed to the OH groups of **K2** or to the NH<sub>2</sub> groups of **K3**, instead these form only hydrogen bonds (Table 10). This throws up a similarity to the NH<sub>4</sub> structures, where no direct NH<sub>4</sub>-to-tail hydrogen bond was found for NH<sub>4</sub>**2** or NH<sub>4</sub>**3**, despite such bonds existing in all other compounds. As would be expected from the positions of the sulfonate groups and the nature of the cation, all five potassium salts form structures described elsewhere as class three ‘higher connectivity’ azo colourant structures (Kennedy *et al.*, 2004). Structures **K1** and **K5** both form three-dimensional coordination polymers, with K—O bonds (K-to-SO<sub>3</sub> in **K5** and both K-to-SO<sub>3</sub> and K-to-OH<sub>2</sub> in **K1**) forming bridges between K centres and allowing propagation of the polymer in two dimensions, whilst the third dimension features bridging between K centres through the body of the azo ion and hence utilizing both the head and tail functional groups of the azo anions (Fig. 14). Despite also


**Figure 9**  
 Dimeric close contact between the two azo anions of the asymmetric unit of NH<sub>4</sub>**2**.





**Figure 10**  
The contents of the asymmetric unit of **K1** extended so as to show the coordination geometry about each independent K centre.

**Table 12**  
Hydrogen-bond geometry (Å, °) for **K4**.

<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>
O4—H1 <i>H</i> ...O4 <i>W</i>	0.87 (1)	1.84 (1)	2.703 (4)	171 (4)
O5—H2 <i>H</i> ...O4	0.88 (1)	1.85 (1)	2.719 (3)	173 (4)
O4 <i>A</i> —H3 <i>H</i> ...O5 <i>A</i>	0.87 (1)	1.86 (2)	2.695 (3)	161 (3)
O5 <i>A</i> —H4 <i>H</i> ...O3 <i>W</i>	0.88 (1)	1.93 (2)	2.738 (3)	154 (3)
O1 <i>W</i> —H1 <i>W</i> ...O5 <i>A</i> <sup>iii</sup>	0.87 (1)	2.22 (2)	3.017 (3)	151 (3)
O1 <i>W</i> —H2 <i>W</i> ...O4 <sup>iv</sup>	0.87 (1)	2.08 (1)	2.906 (3)	158 (3)
O2 <i>W</i> —H3 <i>W</i> ...O5 <sup>v</sup>	0.87 (1)	1.93 (1)	2.791 (4)	170 (4)
O2 <i>W</i> —H4 <i>W</i> ...O2	0.87 (1)	1.99 (2)	2.795 (3)	153 (3)
O3 <i>W</i> —H5 <i>W</i> ...O3 <sup>vi</sup>	0.87 (1)	1.93 (1)	2.786 (3)	167 (3)
O3 <i>W</i> —H6 <i>W</i> ...O4 <sup>vii</sup>	0.88 (1)	1.99 (1)	2.821 (4)	158 (3)
O4 <i>W</i> —H7 <i>W</i> ...O4 <sup>viii</sup>	0.88 (1)	1.94 (1)	2.789 (3)	163 (3)
O4 <i>W</i> —H8 <i>W</i> ...O1 <sup>vi</sup>	0.88 (1)	1.86 (1)	2.738 (3)	180 (4)

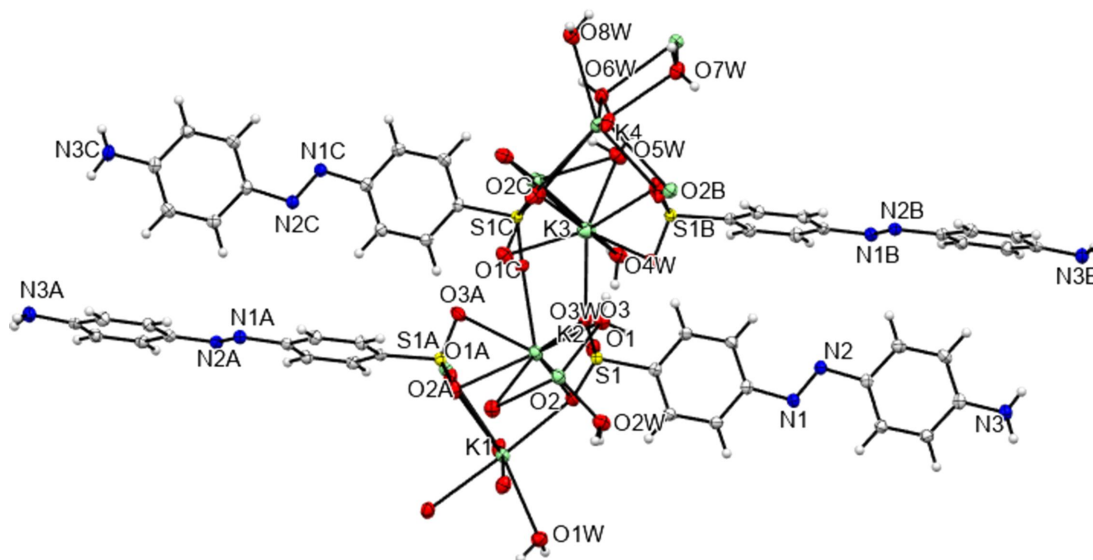
Symmetry codes: (iii)  $x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$ ; (iv)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (v)  $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (vi)  $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (vii)  $-x + 1, -y + 1, -z + 1$ ; (viii)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

**Table 13**  
Selected bond lengths (Å) for **K5**.

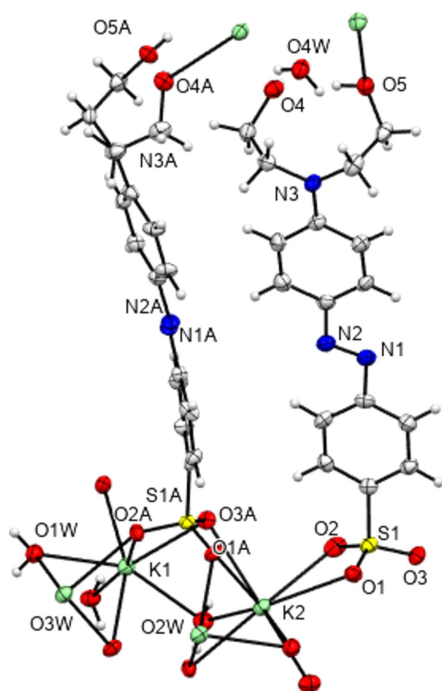
K1—O2 <sup>i</sup>	2.7117 (18)	K1—O1	2.863 (2)
K1—O3 <sup>ii</sup>	2.7511 (18)	K1—O2	2.970 (2)
K1—O4 <sup>iii</sup>	2.7954 (19)	K1—O4 <sup>v</sup>	3.0023 (19)
K1—O3 <sup>iv</sup>	2.815 (2)		

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

featuring bridges between K centres *via* head-to-tail contacts with the azo anion, **K4** is only a two-dimensional coordination polymer. Here, SO<sub>3</sub> and OH<sub>2</sub> bridges between K centres lead only to discrete K<sub>4</sub> tetramers and it is only the through-azo head-to-tail interactions that allow the coordination polymer to propagate parallel to the *b* and *c* directions (Fig. 15). With



**Figure 11**  
The contents of the asymmetric unit of **K3** extended so as to show the coordination geometry about each independent K centre. Disorder in the SO<sub>3</sub> group of atom S1C is not shown for clarity.

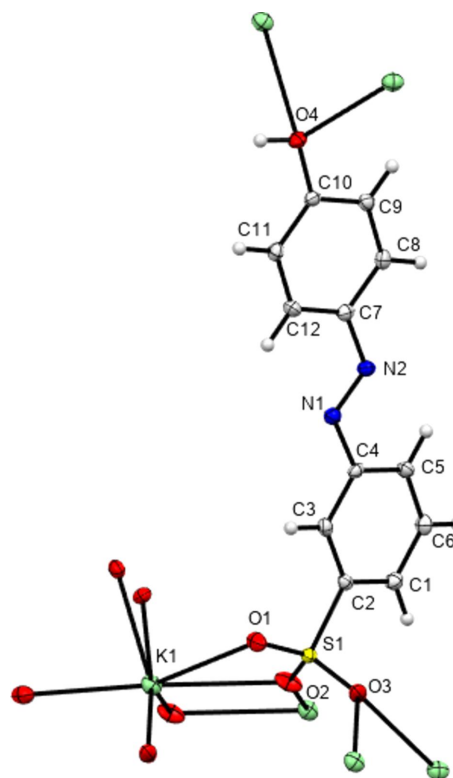


**Figure 12**

The contents of the asymmetric unit of **K4** extended so as to show the coordination geometry about each independent K centre. Disorder in the azo ion of atom **N1A** is not shown for clarity.

no interaction with the amine tail of the azo anion, **K3** displays a two-dimensional coordination polymer structure based solely on  $\text{SO}_3$  and  $\text{OH}_2$  bridges between K centres. Here, the polymeric structure propagates parallel to the  $a$  and  $b$  directions (Fig. 16). **K2** also does not feature any K-to-tail interactions and here only a one-dimensional coordination polymer is formed.  $\text{SO}_3$  and  $\text{OH}_2$  bridges between K centres leads to a polymer that propagates parallel to the crystallographic  $a$  direction (Fig. 17).

The structures of the five Na salt equivalents of **1** to **5** crystallized from water solutions are all available from the



**Figure 13**

The contents of the asymmetric unit of **K5** extended so as to show the coordination geometry about the K centre.

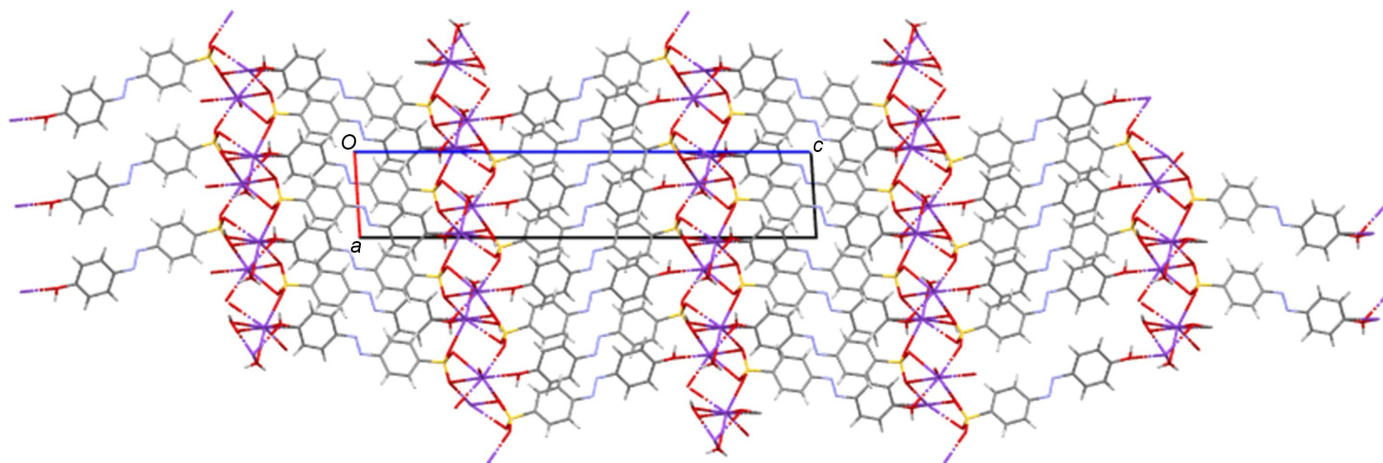
**Table 14**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for **K5**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O4-H1H\cdots O1^v$	0.87 (1)	2.02 (3)	2.732 (3)	139 (3)

Symmetry code:  $(v) -x + \frac{3}{2}, -y + \frac{1}{2}, z$ .

literature (Kennedy *et al.*, 2001, 2020; Dodds *et al.*, 2017). As summarized in Table 15, **Na1** forms a one-dimensional coordination polymer, whilst the other four Na structures all form



**Figure 14**

Packing diagram of **K1** as viewed along the  $b$  axis. Note the alternating hydrophobic and hydrophilic layers that propagate parallel to the  $ab$  plane. The three-dimensional coordination polymer propagates parallel to  $a$  and  $b$  (and throughout the hydrophilic layers) via sulfonate and water bridges between the K centres. The coordination polymer propagates parallel to  $c$  via K bonding to both the sulfonate head and the OH tail of the azo anions.

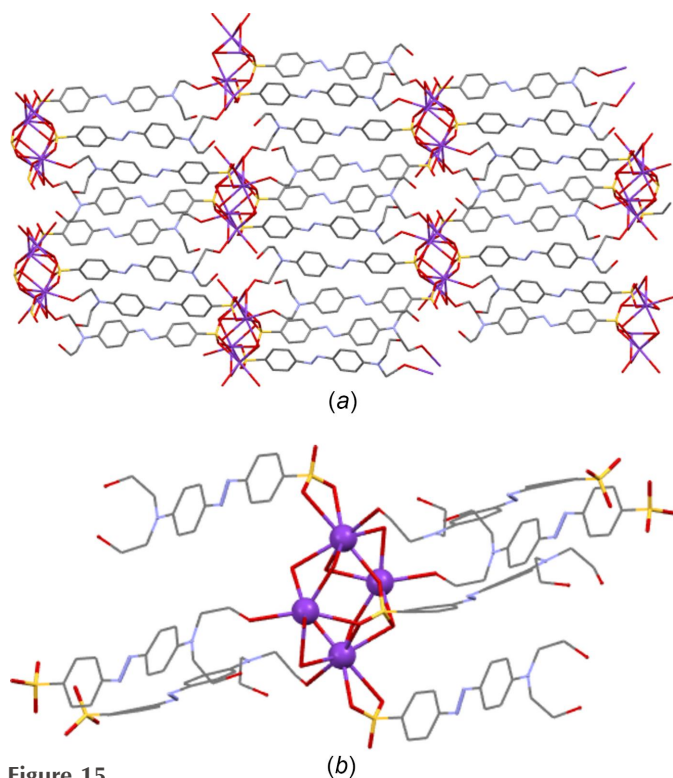
**Table 15**  
Selected crystallographic parameters and bonding characteristics.

	NH <sub>4</sub> 1	Na1	K1	NH <sub>4</sub> 2	Na2	K2	NH <sub>4</sub> 3	Na3	K3
CN	6	6	8, 7	6, 6	6	7, 7	6	6	7,8,8,8
CPD		1	3		2	1		2	2
H <sub>2</sub> O	0	2	1	2	2.5	2	1.5	2	2
Cation-to-SO <sub>3</sub> interaction	yes	yes	yes	yes	yes	yes	yes	yes	yes
Cation-to-tail interaction	yes	no	yes	no	no	no	no	yes	no
Cation-to-water interaction	no	yes	yes	yes	yes	yes	yes	yes	yes
Space group	<i>P2</i> <sub>1</sub>	<i>Pbcn</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C2/c</i>	<i>P</i> $\bar{1}$	<i>C2/c</i>	<i>P2</i> <sub>1</sub>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	5.8163 (1)	14.383	5.9620 (7)	8.2876 (1)	35.036	8.177	35.1636 (15)	7.829	13.3058 (2)
<i>b</i> (Å)	6.9218 (1)	5.813	7.2033 (11)	10.6404 (1)	5.410	10.529	7.8905 (3)	5.784	13.6247 (2)
<i>c</i> (Å)	15.6295 (2)	32.891	31.929 (5)	17.4834 (3)	15.978	17.483	10.4972 (5)	16.486	18.4664 (3)
$\alpha$ (°)	90	90	83.852 (14)	89.734 (1)	90	89.82	90	90	88.373 (1)
$\beta$ (°)	93.354 (1)	90	86.361 (15)	84.793 (1)	98.05	85.49	100.091 (2)	98.62	73.971 (1)
$\gamma$ (°)	90	90	88.868 (15)	86.146 (1)	90	86.81	90	90	66.313 (1)
<i>V/Z</i> (Å <sup>3</sup> )	314.07	343.75	340.12	382.98	374.85	374.57	358.43	369.05	366.69

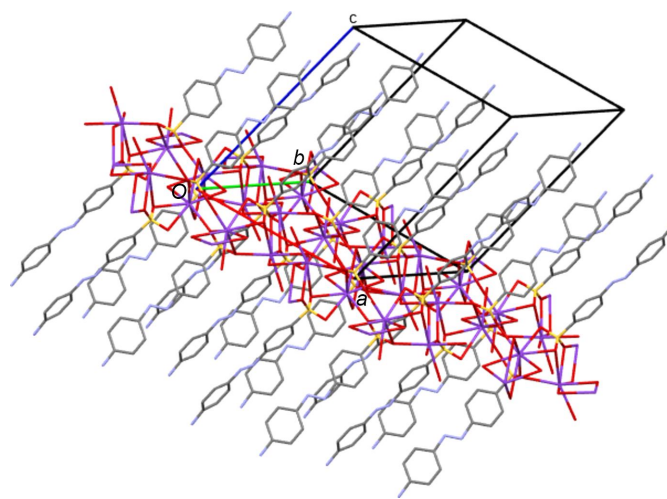
	NH <sub>4</sub> 4	Na4	K4	NH <sub>4</sub> 5	Na5	K5
CN	5, 6	7,7	7, 8	7	6	7
CPD		2	2		2	3
H <sub>2</sub> O	1	1.5	2	0	2	0
Cation-to-SO <sub>3</sub> interaction	yes	yes	yes	yes	yes	yes
Cation-to-tail interaction	yes	yes	yes	yes	yes	yes
Cation-to-water interaction	yes	yes	yes	no	yes	no
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P2</i> <sub>1</sub> / <i>n</i>	<i>Pccn</i>	<i>Pbca</i>	<i>Pccn</i>
<i>a</i> (Å)	8.4930 (1)	9.691	9.4006 (2)	12.6590 (2)	7.123	12.5535 (2)
<i>b</i> (Å)	13.0980 (2)	11.487	12.1583 (3)	28.3600 (3)	11.940	27.9698 (5)
<i>c</i> (Å)	17.1660 (3)	16.605	34.4743 (9)	7.1270 (7)	32.561	6.9982 (1)
$\alpha$ (°)	90.970 (1)	93.73	90	90	90	90
$\beta$ (°)	103.180 (1)	92.76	95.496 (1)	90	90	90
$\gamma$ (°)	95.132 (1)	95.37	90	90	90	90
<i>V/Z</i> (Å <sup>3</sup> )	462.61	458.04	490.27	319.82	346.14	307.15

Notes: CN = coordination number; CPD = coordination polymer dimensionality; *V/Z* = unit-cell volume divided by *Z*.



**Figure 15**  
(a) View of K4 illustrating that here K tetramers link into a two-dimensional coordination polymer only *via* through-azo interactions with the head and tail groups of the azo anions. (b) Detail of one K<sub>4</sub> tetrameric unit.

two-dimensional coordination polymers. All Na centres are six-coordinate, except for those in Na<sub>4</sub>, which are seven-coordinate. All Na centres bond to O atoms of the sulfonate groups and to water ligands. Na<sub>1</sub> and Na<sub>2</sub> do not form bonds from Na to the tail phenol groups, but the other three structures do form Na-to-tail bonds to N or to O atoms. The azo anions that form bonds to Na with their tail groups are thus



**Figure 16**  
The two-dimensional coordination polymer of K<sub>3</sub> propagates only *via* sulfonate groups and water groups that bridge between K centres – there is no head-to-tail through-azo bridge.

**Table 16**

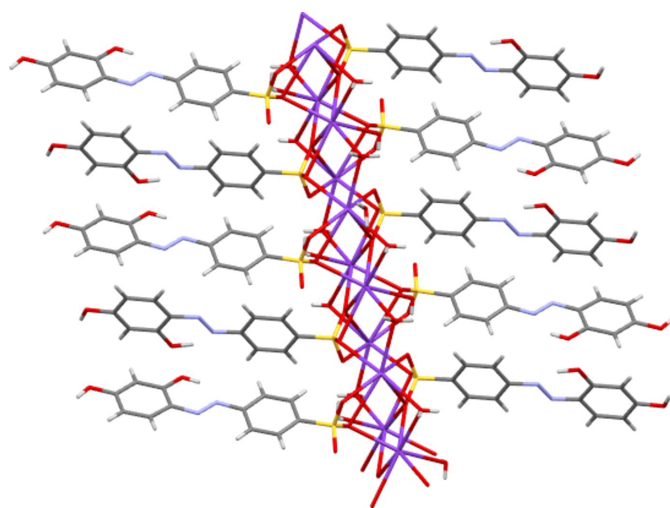
Unit-cell dimensions of selected salt forms of Orange G (OG).

Data taken from Ojala *et al.* (1994) and from Kennedy *et al.* (2006).

	NH <sub>4</sub> OG	AgOG	NaOG	Na/KOG	Na/RbOG
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	9.165	8.870	8.900	8.991	9.025
<i>b</i> (Å)	10.149	10.678	10.470	10.401	10.654
<i>c</i> (Å)	12.623	13.273	13.735	14.996	15.077
$\alpha$ (°)	87.43	73.56	73.49	83.35	82.30
$\beta$ (°)	88.07	77.19	79.29	85.05	84.92
$\gamma$ (°)	71.00	71.66	69.50	70.23	69.39

different from those that interact with K or with NH<sub>4</sub>, as described above. The generally lower coordination numbers of the Na salts (6 or 7) as compared to the K salts (7 or 8) seems to be reflected in a similarly generally lower dimensionality of coordination polymers (one- or two-dimensional for Na, and one- to three-dimensional for K), but this is not a hard and fast rule. This is shown by comparing Na2 with K2, where Na has a coordination number of 6 *versus* 7 for K, but where the Na compound is a two-dimensional coordination polymer and the K compound only one-dimensional.

Comparing the unit-cell dimensions given in Table 15, it can clearly be seen that there are two isostructural pairs. The space group and unit-cell dimensions of NH<sub>4</sub>2 match those of K2 and there is a similar match between NH<sub>4</sub>5 and K5. Based on the unit-cell dimensions, none of the Na species are isostructural with any NH<sub>4</sub> or K salt form. For the NH<sub>4</sub>5 and K5 pair, all generalized structural descriptors (such as *Z'*, hydration state and the coordination number of the cation) are identical, as would be expected for a truly isostructural pair. However, the descriptors given for the NH<sub>4</sub>2 and K2 pair in Table 15, whilst mostly identical, do differ with respect to the coordination number of the cation. The NH<sub>4</sub> ions are given as making six interactions each, whilst the K centres are given as each making seven interactions. Investigation shows that this

**Figure 17**

The one-dimensional coordination polymer structure of K2, with the coordination chain propagating parallel to the *a* direction (Kennedy *et al.*, 2004).

difference is not just a case of an inappropriate cut-off distance being used to calculate potential hydrogen-bonding interactions. For example, the ‘extra’ seventh bond for atom K1 is an interaction with a sulfonate O atom. The closest sulfonate O atom to the equivalent ammonium ion in NH<sub>4</sub>2, that has not already been accounted for as a hydrogen-bonding interaction, gives an N···O distance of over 4.2 Å, which is clearly too long for a hydrogen bond; see Table 3 for genuine N···O hydrogen-bond distances. Thus, although NH<sub>4</sub>2 and K2 have similar unit-cell dimensions and similar compositions, small changes in the orientations of the sulfonate groups and the cations allow the ammonium and potassium cations to make somewhat different interactions from each other. The ability of isostructural structures to tolerate small changes within a given packing motif has been discussed recently by Bombicz (2024).

Expanding from the 15 structures of Table 15 to other literature structures, of the five azo anions studied here, only 3 has had the structure of its Rb salt form reported (Kennedy *et al.*, 2004). The structure of Rb3 is found to be isostructural with that of NH<sub>4</sub>3 (compare *C2/c*, 35.256, 7.738, 10.674 Å and 99.88° with the values given for NH<sub>4</sub>3 in Table 1). As with NH<sub>4</sub>2 and K2 above, all structural descriptors match, except for the Rb cation having a higher coordination number than the ammonium cation (8 *versus* 6). Other sulfonated monoazo NH<sub>4</sub> salt form structures available are those of diammonium Orange G tetrahydrate and of the nitrile-substituted [NH<sub>4</sub>][O<sub>3</sub>S(C<sub>6</sub>H<sub>4</sub>)NN(C<sub>6</sub>H<sub>4</sub>)NHCH<sub>2</sub>CH<sub>2</sub>CN]·H<sub>2</sub>O (Ojala *et al.*, 1994; Astbury *et al.*, 2013). For these azo anions, the only available comparisons for the ammonium salts are the Na and mixed Na/K and Na/Rb salt forms of Orange G and the Na salt of the nitrile (Kennedy *et al.*, 2006; Astbury *et al.*, 2013). Based on unit-cell dimensions, the nitrile shows no isostructurality. There are however similarities, if not exact matches, between the unit cells of the Orange G structures of Table 16; see comments below for a fuller discussion of these features.

The ‘crystal packing similarity’ tool available within *Mercury* (Macrae *et al.*, 2020) can be used to find packing similarity regardless of any matches in the unit-cell dimension. For instance, it has been used to find similarities in the packing behaviour of dopamine and tyramine fragments in the salt and hydrate forms of these active pharmaceutical ingredients (APIs), regardless of counter-ions, solvents and the identity and protonation state of the phenylethylamine fragment itself (Kennedy *et al.*, 2023). This tool was applied to the 15 structures of Table 15 and to the other relevant NH<sub>4</sub>, Na, K, Rb, Cs and Ag salt structures found in the Cambridge Structural Database (CSD; Groom *et al.*, 2016). The packing analysis was set up to examine packed fragments consisting of 15 sulfonated azo molecular units. Other components (cations and solvent molecules) were ignored. Indeed, in order to simplify the definition of a ‘molecular fragment’, all metal ions were deleted from the CIF files used for these analyses. Only the three pairs previously identified as being isostructural from their unit-cell dimensions (*i.e.* NH<sub>4</sub>2 and K2, NH<sub>4</sub>5 and K5, and NH<sub>4</sub>3 and Rb3) had azo anion packing that matched at a 15/15 level with a 20% tolerance allowed. However, it was

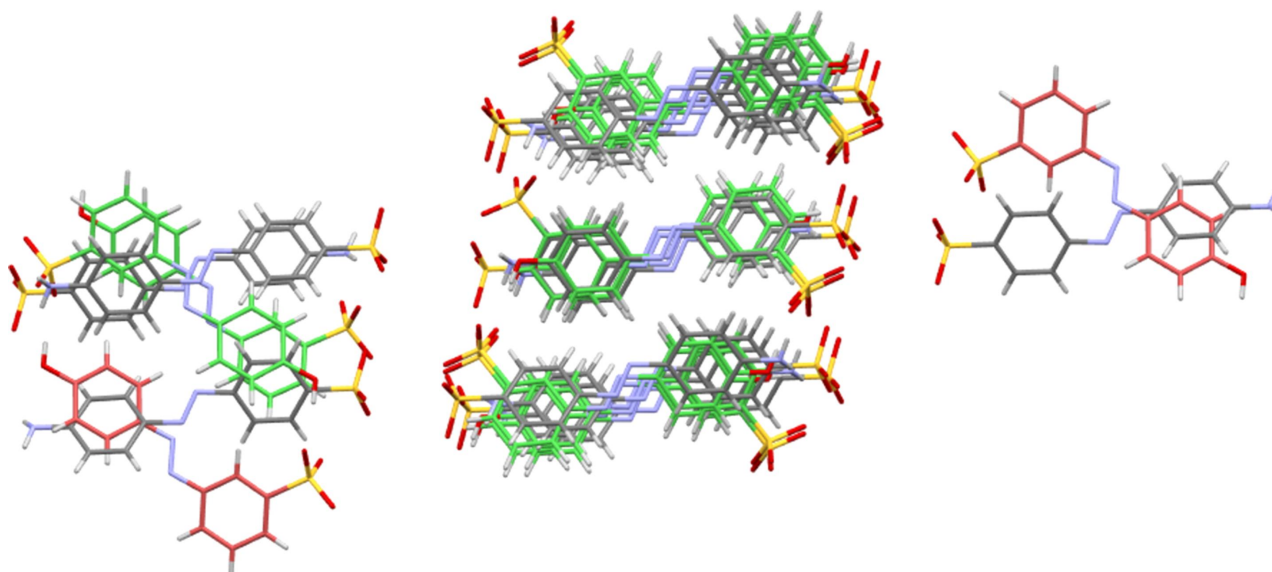


found that  $\text{NH}_4\mathbf{3}$  also matched at a 13/15 level with the isostructural pair of structures having CSD refcodes BAHNAC and BAHNIK (Dodds *et al.*, 2017). Surprisingly, these two structures are not forms of the *para*- $\text{NH}_2$ -substituted anion  $\mathbf{3}$ , but correspond to the Na and Ag salt forms of the *meta*-OH-substituted anion  $\mathbf{5}$ . Further investigation of these structures reveals that it is their layered natures that lead to this partial match. Those azo fragments that lie within a single hydrophobic layer of  $\text{NH}_4\mathbf{3}$  match well with their equivalents in Na $\mathbf{5}$  and Ag $\mathbf{5}$ , despite the differences in  $\text{SO}_3$  position and the different chemical natures of the  $\text{NH}_2/\text{OH}$  tail groups. However, the azo fragments within the neighbouring hydrophobic layers do not match, being rotated with respect to one another (Fig. 18). A similar situation was found for the Orange G salts of Table 16. As is perhaps suggested by the differences in the unit-cell parameters, none of the metal salt forms were truly isostructural with the ammonium salt of Orange G. However, both the mixed Na/K and Na/Rb species matched the ammonium salt at a 12/15 level and the pure Na species matched at a 9/15 level. As with the case for  $\mathbf{3}$  above, the matches within one organic layer are reasonable, but the structures do not match well when neighbouring layers are considered. Finally, examining the structures of Table 15 it can be seen that  $\text{NH}_4\mathbf{1}$  and K $\mathbf{1}$  have somewhat similar *a* and *b* dimensions, whilst *c* is approximately doubled. Despite this, investigations showed that these structures did not show any significant similarity in the packing for the azo anions.

#### 4. Summary

Five new structures of ammonium salt forms of sulfonated azo dyes have been presented and compared to the equivalent Na and K salt structures. Despite being based on ammonium-to-sulfonate hydrogen bonds rather than metal-ion-to-sulfonate bonds, the ammonium salt forms are found to have structural

types that are in many ways similar to those found for heavier alkali-metal ions (Na, K and Rb). The ammonium structures have the same simple alternating hydrophobic/hydrophilic layer structures described earlier for *s*-block metal salt forms of *para*- and *meta*-sulfonated azo dyes (Kennedy *et al.*, 2004) and do not show the more complicated layering motifs seen elsewhere (Kennedy *et al.*, 2009). Two of the five ammonium structures ( $\text{NH}_4\mathbf{2}$  and  $\text{NH}_4\mathbf{5}$ ) show isostructurality with their equivalent potassium structures. For anion  $\mathbf{3}$ , the ammonium and Rb salt forms are also found to be isostructural, although unfortunately no other Rb salt structures are available for comparison. For the isostructural pair of  $\mathbf{5}$ , all structural descriptors are very similar, but for the  $\mathbf{2}$  and  $\mathbf{3}$  pairs there are small differences in, for example, the rotation of the sulfonate groups that allow the ammonium cations to make less formal contacts than do the K or Rb ions. No sodium salt is found to be isostructural with an ammonium salt, but use of the ‘crystal packing similarity’ tool within *Mercury* did highlight that the azo anions of  $\text{NH}_4\mathbf{3}$  do adopt similar packing to the chemically different azo anions of both Na $\mathbf{5}$  and Ag $\mathbf{5}$ , although this similarity only holds within a single hydrophobic layer, with neighbouring layers behaving differently. The ammonium salt of Orange G shows similar single-layer-matching behaviour with its Na and mixed Na/K and Na/Rb salt forms. Overall there is thus a high propensity for ammonium salt forms of sulfonated azo dyes to be isostructural with the equivalent K or Rb forms, a propensity which is aided by small amounts of flexibility in the structures that allows for the different coordinating abilities of the cations. Little evidence is found for isostructural relationships between the salt forms of sulfonated azo dyes of ammonium salts and the equivalent sodium salts. Here, the smaller radius of the  $\text{Na}^+$  ion is perhaps hard to offset against the lower coordination number of sodium. However, the similarity of anion packing found, for instance, within single layers for  $\text{NH}_4\mathbf{3}$  (and hence Rb $\mathbf{3}$ ) with Na $\mathbf{5}$  and



**Figure 18**

15-fragment overlay of the structure of  $\text{NH}_4\mathbf{3}$  (multicoloured) with that of BAHNIK (Ag $\mathbf{5}$ , green and red; Dodds *et al.*, 2017). The anionic azo fragments in the central layer give reasonable packing matches for the azobenzene units, but the anions of the neighbouring layers do not match well.

Ag5 may indicate that isostructurality is possible and may be found if a larger sample of structures was available.

## References

- Al Isawi, W. A., Jianrattanasawat, S., Tripodanos, E., Demadis, K. D., Kirillov, A. M., Zeller, M. & Mezei, G. (2021). *Cryst. Growth Des.* **21**, 5421–5439.
- Alsantali, R. I., Raja, Q. A., Alzahrani, A. Y. A., Sadiq, A., Naeem, N., Mughal, E. U., Al-Rooqi, M. M., El Guesmi, N., Moussa, Z. & Ahmed, S. A. (2022). *Dyes Pigments*, **199**, 110050.
- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Arlin, J.-B., Florence, A. J., Johnston, A., Kennedy, A. R., Miller, G. J. & Patterson, K. (2011). *Cryst. Growth Des.* **11**, 1318–1327.
- Astbury, C., Conway, L. K., Gillespie, C., Hodge, K., Innes, E. & Kennedy, A. R. (2013). *Dyes Pigments*, **97**, 100–104.
- Bharate, S. S. (2021). *Pharm. Res.* **38**, 1307–1326.
- Black, S. N., Collier, E. A., Davey, R. J. & Roberts, R. J. (2007). *J. Pharm. Sci.* **96**, 1053–1068.
- Bombicz, P. (2024). *IUCrJ*, **11**, 3–6.
- Bruker (2012). *APEX2, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Christie, R. M. & Mackay, J. L. (2008). *Coloration Technol.* **124**, 133–144.
- Christov, C. (2003). *Calphad*, **27**, 153–160.
- Dodds, C. A., Hobday, C. L., Kennedy, A. R., McKellar, S. C., Smillie, K. & Walls, A. (2017). *New J. Chem.* **41**, 1574–1581.
- Emerson, A. J., Edwards, A. J., Batten, S. R. & Turner, D. R. (2014). *CrystEngComm*, **16**, 1625–1631.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Gonzalez, W. G. & Miksovska, J. (2014). *Biochim. Biophys. Acta*, **1844**, 1472–1480.
- Gorelik, T., Schmidt, M. U., Brüning, J., Bekó, S. & Kolb, U. (2009). *Cryst. Growth Des.* **9**, 3898–3903.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Grzesiak-Nowak, M., Oszejca, M., Rafalska-Łasocha, A., Goszczycki, P., Ostrowska, K. & Łasocha, W. (2019). *Dyes Pigments*, **160**, 252–258.
- Hao, Z. & Iqbal, A. (1997). *Coord. Chem. Rev.* **26**, 203–213.
- Kennedy, A. R., Andrikopoulos, P. C., Arlin, J.-A., Armstrong, D. R., Duxbury, N., Graham, D. V. & Kirkhouse, J. B. (2009). *Chem. Eur. J.* **15**, 9494–9504.
- Kennedy, A. R., Conway, L. K., Kirkhouse, J. B. A., McCarney, K. M., Puissegur, O., Staunton, E., Teat, S. J. & Warren, J. E. (2020). *Crystals*, **10**, 662–678.
- Kennedy, A. R., Cruickshank, L., Maher, P. & McKinnon, Z. (2023). *Acta Cryst.* **C79**, 386–394.
- Kennedy, A. R., Hughes, M. P., Monaghan, M. L., Staunton, E., Teat, S. J. & Smith, W. E. (2001). *J. Chem. Soc. Dalton Trans.* pp. 2199–2205.
- Kennedy, A. R., Kirkhouse, J. A. B., McCarney, K. M., Puissegur, O., Smith, W. E., Staunton, E., Teat, S. J., Cherryman, J. C. & James, R. (2004). *Chem. Eur. J.* **10**, 4606–4615.
- Kennedy, A. R., Kirkhouse, J. B. A. & Whyte, L. (2006). *Inorg. Chem.* **45**, 2965–2971.
- Kennedy, A. R., McNair, C., Smith, W. E., Chisholm, G. & Teat, S. J. (2000). *Angew. Chem. Int. Ed.* **39**, 638–640.
- Kennedy, A. R., Stewart, H., Eremin, K. & Stenger, J. (2012). *Chem. Eur. J.* **18**, 3064–3069.
- Khan, A. A. & Baur, W. H. (1972). *Acta Cryst.* **B28**, 683–693.
- Leban, I., Rudan-Tasić, D., Lah, N. & Klofutar, C. (2007). *Acta Cryst.* **B63**, 418–425.
- Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
- Mahmood, T., Sarfraz, R. M., Ismail, A., Ali, M. & Khan, A. R. (2023). *Assay Drug Dev. Technol.* **21**, 65–79.
- Ojala, W. H., Lu, L. K., Albers, K. E., Gleason, W. B., Richardson, T. I., Lovrien, R. E. & Sudbeck, E. A. (1994). *Acta Cryst.* **B50**, 684–694.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Rigaku OD (2019). *CrysAlis PRO*. Rigaku Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
- Schmidt, M. U., van de Streek, J. & Ivashevskaya, S. N. (2009). *Chem. Eur. J.* **15**, 338–341.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Sidey, V. (2016). *Acta Cryst.* **B72**, 626–633.
- Stahl, P. H. & Wermuth, C. G. (2008). Editors. *Handbook of Pharmaceutical Salts: Properties, Selection and Use*. VHCA: Zurich.
- Yatsenko, A. V., Kultin, D. Y. & Paseshnikchenko, K. A. (2024). *Dyes Pigments*, **222**, 111883.

## supporting information

*Acta Cryst.* (2024). C80, 66-79 [https://doi.org/10.1107/S2053229624001293]

## Isostructural behaviour in ammonium and potassium salt forms of sulfonated azo dyes

**Alan R. Kennedy, Jennifer B. A. Kirkhouse, Karen M. McCarney and Olivier Puissegur**

### Computing details

#### Ammonium 4-[2-(4-hydroxyphenyl)diazen-1-yl]benzenesulfonate (NH41)

##### Crystal data

$\text{NH}_4^+ \cdot \text{C}_{12}\text{H}_9\text{N}_2\text{O}_4\text{S}^-$   
 $M_r = 295.31$   
 Monoclinic,  $P2_1$   
 $a = 5.8163$  (1) Å  
 $b = 6.9218$  (1) Å  
 $c = 15.6295$  (2) Å  
 $\beta = 93.354$  (1)°  
 $V = 628.15$  (2) Å<sup>3</sup>  
 $Z = 2$

$F(000) = 308$   
 $D_x = 1.561$  Mg m<sup>-3</sup>  
 Cu  $K\alpha$  radiation,  $\lambda = 1.54184$  Å  
 Cell parameters from 12251 reflections  
 $\theta = 2.8$ – $71.4$ °  
 $\mu = 2.48$  mm<sup>-1</sup>  
 $T = 100$  K  
 Broken tablet, yellow  
 $0.22 \times 0.12 \times 0.06$  mm

##### Data collection

Rigaku Synergy-i  
 diffractometer  
 Radiation source: microsource tube  
 $\omega$  scans  
 Absorption correction: multi-scan  
 (*CrysAlis PRO*; Rigaku OD, 2019)  
 $T_{\min} = 0.859$ ,  $T_{\max} = 1.000$   
 10144 measured reflections

2345 independent reflections  
 2336 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.054$   
 $\theta_{\max} = 71.8$ °,  $\theta_{\min} = 2.8$ °  
 $h = -7 \rightarrow 7$   
 $k = -8 \rightarrow 8$   
 $l = -18 \rightarrow 19$

##### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.029$   
 $wR(F^2) = 0.084$   
 $S = 1.08$   
 2345 reflections  
 203 parameters  
 1 restraint  
 Hydrogen site location: mixed  
 H atoms treated by a mixture of independent  
 and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 0.3416P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.26$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.33$  e Å<sup>-3</sup>  
 Extinction correction: SHELXL2018  
 (Sheldrick, 2015b),  
 $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.0059 (10)  
 Absolute structure: Refined as an inversion  
 twin.  
 Absolute structure parameter: 0.00 (2)

*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.

**Refinement.** Refined as a 2-component inversion twin.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.35361 (10)	0.29158 (10)	0.12661 (3)	0.0123 (2)
O1	0.4130 (4)	0.4665 (3)	0.08089 (13)	0.0173 (5)
O2	0.4932 (4)	0.1276 (3)	0.10136 (13)	0.0182 (5)
O3	0.1084 (3)	0.2481 (4)	0.12008 (12)	0.0230 (6)
O4	1.1582 (3)	0.3583 (3)	0.85733 (13)	0.0162 (5)
N1	0.6429 (4)	0.3448 (4)	0.49689 (15)	0.0138 (5)
N2	0.8571 (4)	0.3609 (4)	0.51273 (15)	0.0138 (5)
N3	−0.2044 (4)	0.3231 (4)	−0.01967 (16)	0.0159 (6)
C1	0.4303 (5)	0.3311 (4)	0.23627 (17)	0.0134 (6)
C2	0.2832 (4)	0.2720 (5)	0.29837 (16)	0.0127 (5)
H2	0.134187	0.223460	0.282173	0.015*
C3	0.3571 (4)	0.2850 (5)	0.38439 (15)	0.0127 (5)
H3	0.256899	0.248354	0.427438	0.015*
C4	0.5780 (5)	0.3516 (4)	0.40746 (18)	0.0130 (6)
C5	0.7218 (5)	0.4191 (4)	0.34458 (17)	0.0126 (6)
H5	0.868874	0.471605	0.360730	0.015*
C6	0.6473 (5)	0.4084 (4)	0.25935 (18)	0.0130 (6)
H6	0.743184	0.453318	0.216382	0.016*
C7	0.9258 (5)	0.3512 (4)	0.60152 (17)	0.0123 (6)
C8	1.1468 (5)	0.4181 (4)	0.62395 (17)	0.0132 (6)
H8	1.243125	0.460308	0.580605	0.016*
C9	1.2272 (5)	0.4236 (4)	0.70920 (17)	0.0135 (6)
H9	1.376389	0.472961	0.724518	0.016*
C10	1.0875 (5)	0.3560 (4)	0.77230 (17)	0.0127 (6)
C11	0.8704 (4)	0.2800 (5)	0.74958 (16)	0.0142 (5)
H11	0.778425	0.229619	0.792613	0.017*
C12	0.7882 (4)	0.2777 (5)	0.66469 (16)	0.0139 (5)
H12	0.639877	0.226653	0.649335	0.017*
H1H	1.268 (8)	0.444 (8)	0.861 (3)	0.037 (12)*
H1N	−0.260 (7)	0.214 (7)	−0.038 (2)	0.018 (9)*
H2N	−0.114 (7)	0.362 (6)	−0.060 (3)	0.025 (10)*
H3N	−0.122 (8)	0.301 (8)	0.027 (3)	0.043 (12)*
H4N	−0.312 (9)	0.414 (8)	−0.008 (3)	0.051 (14)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0123 (3)	0.0150 (3)	0.0093 (3)	0.0001 (3)	−0.0010 (2)	0.0009 (3)



O1	0.0233 (10)	0.0151 (11)	0.0137 (9)	0.0022 (9)	0.0038 (8)	0.0041 (8)
O2	0.0259 (11)	0.0153 (11)	0.0131 (10)	0.0039 (9)	-0.0018 (8)	-0.0026 (8)
O3	0.0152 (10)	0.0391 (16)	0.0142 (9)	-0.0059 (10)	-0.0029 (7)	0.0036 (10)
O4	0.0157 (10)	0.0205 (11)	0.0121 (9)	-0.0028 (9)	-0.0014 (7)	-0.0014 (8)
N1	0.0132 (11)	0.0146 (13)	0.0133 (11)	-0.0003 (9)	-0.0003 (9)	-0.0014 (9)
N2	0.0137 (11)	0.0146 (11)	0.0130 (11)	-0.0006 (10)	-0.0003 (9)	-0.0005 (9)
N3	0.0156 (11)	0.0176 (16)	0.0142 (12)	-0.0015 (10)	-0.0007 (10)	0.0003 (10)
C1	0.0140 (12)	0.0154 (16)	0.0108 (12)	0.0033 (10)	0.0000 (9)	-0.0001 (10)
C2	0.0114 (11)	0.0126 (14)	0.0139 (12)	0.0005 (12)	-0.0011 (9)	-0.0001 (12)
C3	0.0139 (11)	0.0117 (12)	0.0128 (11)	0.0023 (13)	0.0034 (9)	0.0006 (12)
C4	0.0151 (13)	0.0130 (13)	0.0109 (12)	0.0015 (11)	0.0014 (10)	-0.0009 (10)
C5	0.0118 (12)	0.0107 (14)	0.0154 (13)	-0.0002 (11)	0.0006 (10)	-0.0009 (11)
C6	0.0124 (12)	0.0119 (14)	0.0150 (13)	-0.0017 (11)	0.0036 (10)	0.0010 (11)
C7	0.0130 (12)	0.0127 (14)	0.0112 (12)	0.0012 (11)	0.0002 (10)	-0.0019 (10)
C8	0.0131 (12)	0.0122 (14)	0.0144 (13)	0.0007 (11)	0.0026 (10)	-0.0006 (11)
C9	0.0094 (12)	0.0152 (15)	0.0158 (13)	-0.0012 (11)	0.0002 (10)	-0.0016 (12)
C10	0.0162 (13)	0.0114 (13)	0.0105 (12)	0.0017 (11)	-0.0001 (10)	-0.0021 (10)
C11	0.0144 (12)	0.0151 (14)	0.0135 (11)	-0.0001 (13)	0.0025 (9)	0.0008 (13)
C12	0.0132 (12)	0.0137 (14)	0.0147 (12)	-0.0017 (13)	0.0007 (9)	-0.0017 (13)

*Geometric parameters (Å, °)*

S1—O3	1.456 (2)	C3—C4	1.392 (4)
S1—O1	1.457 (2)	C3—H3	0.9500
S1—O2	1.463 (2)	C4—C5	1.407 (4)
S1—C1	1.767 (3)	C5—C6	1.379 (4)
O4—C10	1.368 (3)	C5—H5	0.9500
O4—H1H	0.87 (5)	C6—H6	0.9500
N1—N2	1.261 (3)	C7—C8	1.392 (4)
N1—C4	1.427 (4)	C7—C12	1.402 (4)
N2—C7	1.423 (4)	C8—C9	1.386 (4)
N3—H1N	0.86 (4)	C8—H8	0.9500
N3—H2N	0.88 (4)	C9—C10	1.395 (4)
N3—H3N	0.86 (5)	C9—H9	0.9500
N3—H4N	0.91 (5)	C10—C11	1.394 (4)
C1—C2	1.392 (4)	C11—C12	1.384 (3)
C1—C6	1.399 (4)	C11—H11	0.9500
C2—C3	1.390 (3)	C12—H12	0.9500
C2—H2	0.9500		
O3—S1—O1	113.38 (13)	C5—C4—N1	124.1 (3)
O3—S1—O2	112.19 (14)	C6—C5—C4	119.4 (3)
O1—S1—O2	111.15 (12)	C6—C5—H5	120.3
O3—S1—C1	106.90 (12)	C4—C5—H5	120.3
O1—S1—C1	107.07 (13)	C5—C6—C1	119.8 (3)
O2—S1—C1	105.62 (12)	C5—C6—H6	120.1
C10—O4—H1H	105 (3)	C1—C6—H6	120.1
N2—N1—C4	113.0 (2)	C8—C7—C12	120.0 (2)

N1—N2—C7	113.9 (2)	C8—C7—N2	115.6 (2)
H1N—N3—H2N	105 (4)	C12—C7—N2	124.4 (2)
H1N—N3—H3N	108 (4)	C9—C8—C7	120.4 (2)
H2N—N3—H3N	109 (4)	C9—C8—H8	119.8
H1N—N3—H4N	115 (4)	C7—C8—H8	119.8
H2N—N3—H4N	112 (4)	C8—C9—C10	119.5 (3)
H3N—N3—H4N	107 (4)	C8—C9—H9	120.2
C2—C1—C6	121.0 (2)	C10—C9—H9	120.2
C2—C1—S1	120.0 (2)	O4—C10—C11	117.9 (2)
C6—C1—S1	118.8 (2)	O4—C10—C9	121.9 (3)
C3—C2—C1	119.2 (2)	C11—C10—C9	120.2 (2)
C3—C2—H2	120.4	C12—C11—C10	120.4 (2)
C1—C2—H2	120.4	C12—C11—H11	119.8
C2—C3—C4	120.0 (2)	C10—C11—H11	119.8
C2—C3—H3	120.0	C11—C12—C7	119.4 (2)
C4—C3—H3	120.0	C11—C12—H12	120.3
C3—C4—C5	120.4 (3)	C7—C12—H12	120.3
C3—C4—N1	115.5 (2)		
C4—N1—N2—C7	-179.0 (2)	C4—C5—C6—C1	0.1 (4)
O3—S1—C1—C2	15.9 (3)	C2—C1—C6—C5	2.8 (4)
O1—S1—C1—C2	137.7 (2)	S1—C1—C6—C5	-172.3 (2)
O2—S1—C1—C2	-103.8 (2)	N1—N2—C7—C8	-163.7 (3)
O3—S1—C1—C6	-169.0 (2)	N1—N2—C7—C12	17.3 (4)
O1—S1—C1—C6	-47.2 (3)	C12—C7—C8—C9	-3.9 (4)
O2—S1—C1—C6	71.3 (3)	N2—C7—C8—C9	177.0 (3)
C6—C1—C2—C3	-2.0 (4)	C7—C8—C9—C10	1.9 (4)
S1—C1—C2—C3	173.0 (2)	C8—C9—C10—O4	-179.9 (3)
C1—C2—C3—C4	-1.7 (5)	C8—C9—C10—C11	1.3 (4)
C2—C3—C4—C5	4.5 (5)	O4—C10—C11—C12	178.7 (3)
C2—C3—C4—N1	-175.2 (3)	C9—C10—C11—C12	-2.4 (5)
N2—N1—C4—C3	163.8 (3)	C10—C11—C12—C7	0.4 (5)
N2—N1—C4—C5	-16.0 (4)	C8—C7—C12—C11	2.7 (4)
C3—C4—C5—C6	-3.8 (4)	N2—C7—C12—C11	-178.3 (3)
N1—C4—C5—C6	176.0 (3)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H4N $\cdots$ O2 <sup>i</sup>	0.91 (5)	2.30 (5)	2.940 (4)	127 (4)
N3—H4N $\cdots$ O1 <sup>ii</sup>	0.91 (5)	2.21 (5)	2.969 (3)	141 (4)
N3—H3N $\cdots$ O3	0.86 (5)	1.96 (5)	2.808 (3)	170 (4)
N3—H1N $\cdots$ O1 <sup>iii</sup>	0.86 (4)	2.03 (5)	2.889 (4)	176 (4)
N3—H2N $\cdots$ O4 <sup>iv</sup>	0.88 (4)	2.10 (4)	2.946 (3)	159 (4)
O4—H1H $\cdots$ O2 <sup>v</sup>	0.87 (5)	1.95 (5)	2.802 (3)	167 (4)

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

Ammonium 4-[2-(2,4-dihydroxyphenyl)diazen-1-yl]benzenesulfonate dihydrate (NH42)

Crystal data

$\text{NH}_4^+ \cdot \text{C}_{12}\text{H}_9\text{N}_2\text{O}_5\text{S}^- \cdot 2\text{H}_2\text{O}$

$M_r = 347.34$

Triclinic,  $P\bar{1}$

$a = 8.2876$  (1) Å

$b = 10.6404$  (1) Å

$c = 17.4834$  (3) Å

$\alpha = 89.734$  (1)°

$\beta = 84.793$  (1)°

$\gamma = 86.146$  (1)°

$V = 1531.91$  (4) Å<sup>3</sup>

$Z = 4$

$F(000) = 728$

$D_x = 1.506$  Mg m<sup>-3</sup>

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

Cell parameters from 8081 reflections

$\theta = 1.0\text{--}29.1^\circ$

$\mu = 0.25$  mm<sup>-1</sup>

$T = 123$  K

Rhomb, yellow-orange

$0.42 \times 0.40 \times 0.10$  mm

Data collection

Enraf–Nonius KappaCCD  
diffractometer

Radiation source: sealed tube  
phi and  $\omega$  scans

15978 measured reflections

8209 independent reflections

6704 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\text{max}} = 29.1^\circ$ ,  $\theta_{\text{min}} = 1.2^\circ$

$h = -11 \rightarrow 11$

$k = -14 \rightarrow 14$

$l = -23 \rightarrow 23$

Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.094$

$S = 1.02$

8209 reflections

495 parameters

1 restraint

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2 + 0.8626P]$

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

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

$\Delta\rho_{\text{max}} = 0.58$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.41$  e Å<sup>-3</sup>

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 (Å<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.62192 (4)	0.04619 (3)	0.10240 (2)	0.01709 (8)
S2	0.09636 (4)	0.38246 (3)	0.12364 (2)	0.01713 (8)
O1	0.76850 (13)	-0.01171 (10)	0.06027 (6)	0.0214 (2)
O2	0.48499 (13)	-0.03156 (11)	0.09970 (6)	0.0271 (2)
O3	0.58719 (14)	0.17567 (10)	0.07836 (6)	0.0260 (2)
O4	0.98516 (14)	0.14681 (10)	0.75672 (6)	0.0219 (2)
O5	0.71395 (13)	-0.04078 (10)	0.56317 (6)	0.0222 (2)
O6	0.07572 (14)	0.25449 (10)	0.09790 (6)	0.0242 (2)
O7	0.22672 (14)	0.43876 (10)	0.07644 (6)	0.0250 (2)
O8	-0.05487 (13)	0.46083 (11)	0.12893 (6)	0.0270 (2)
O9	0.52842 (13)	0.41871 (10)	0.76776 (6)	0.0218 (2)

O10	0.51487 (14)	0.23392 (10)	0.52554 (6)	0.0245 (2)
O1W	−0.16671 (16)	0.71210 (13)	0.15040 (8)	0.0322 (3)
O2W	0.38515 (14)	0.56714 (12)	0.88010 (7)	0.0275 (2)
O3W	0.71337 (14)	0.32285 (11)	0.88635 (7)	0.0260 (2)
O4W	0.84097 (16)	−0.00710 (11)	0.85537 (7)	0.0255 (2)
N1	0.76041 (15)	0.05814 (11)	0.43032 (7)	0.0187 (2)
N2	0.85430 (15)	0.13819 (11)	0.45120 (7)	0.0193 (2)
N3	0.33504 (14)	0.35053 (11)	0.43444 (7)	0.0176 (2)
N4	0.28336 (14)	0.43660 (11)	0.48284 (7)	0.0174 (2)
N5	0.93365 (17)	0.16781 (13)	−0.03240 (7)	0.0194 (2)
N6	−0.39612 (17)	0.72023 (14)	0.04186 (8)	0.0233 (3)
C1	0.66330 (17)	0.05333 (13)	0.19978 (7)	0.0162 (3)
C2	0.77120 (17)	0.13898 (13)	0.22148 (8)	0.0192 (3)
H1	0.819914	0.193701	0.184416	0.023*
C3	0.80712 (18)	0.14393 (13)	0.29746 (8)	0.0193 (3)
H2	0.880801	0.201593	0.312773	0.023*
C4	0.73336 (17)	0.06287 (13)	0.35112 (8)	0.0179 (3)
C5	0.62652 (18)	−0.02228 (14)	0.32902 (8)	0.0201 (3)
H3	0.577284	−0.076857	0.366013	0.024*
C6	0.59143 (18)	−0.02792 (14)	0.25305 (8)	0.0196 (3)
4H	0.519150	−0.086608	0.237650	0.023*
C7	0.88081 (17)	0.13237 (13)	0.52941 (8)	0.0181 (3)
C8	0.98383 (18)	0.21938 (14)	0.55419 (8)	0.0213 (3)
H5	1.030580	0.276831	0.518260	0.026*
C9	1.01927 (18)	0.22375 (14)	0.62985 (8)	0.0207 (3)
H6	1.090060	0.283074	0.645886	0.025*
C10	0.94882 (17)	0.13902 (13)	0.68248 (8)	0.0180 (3)
C11	0.84685 (17)	0.05103 (13)	0.65983 (8)	0.0184 (3)
H8	0.800804	−0.005918	0.696292	0.022*
C12	0.81178 (17)	0.04618 (13)	0.58317 (8)	0.0175 (3)
C13	0.15837 (16)	0.37139 (13)	0.21753 (8)	0.0166 (3)
C14	0.08726 (18)	0.45338 (14)	0.27459 (8)	0.0219 (3)
H10	0.001186	0.512467	0.263835	0.026*
C15	0.14229 (18)	0.44866 (14)	0.34716 (8)	0.0221 (3)
H11	0.094605	0.504738	0.386260	0.027*
C16	0.26783 (17)	0.36126 (13)	0.36236 (8)	0.0169 (3)
C17	0.33736 (18)	0.27771 (13)	0.30555 (8)	0.0195 (3)
H12	0.421320	0.217035	0.316760	0.023*
C18	0.28372 (17)	0.28334 (13)	0.23264 (8)	0.0195 (3)
H13	0.331939	0.227749	0.193401	0.023*
C19	0.34935 (16)	0.42642 (13)	0.55348 (8)	0.0162 (3)
C20	0.29766 (17)	0.52133 (13)	0.60747 (8)	0.0188 (3)
H14	0.222998	0.587727	0.594106	0.023*
C21	0.35318 (18)	0.52007 (14)	0.67955 (8)	0.0196 (3)
H15	0.314923	0.583618	0.716005	0.023*
C22	0.46707 (17)	0.42355 (13)	0.69833 (8)	0.0172 (3)
C23	0.52292 (18)	0.32983 (13)	0.64569 (8)	0.0189 (3)
H17	0.601645	0.266207	0.658768	0.023*



C24	0.46361 (17)	0.32899 (13)	0.57373 (8)	0.0172 (3)
H1H	0.939 (3)	0.092 (2)	0.7835 (12)	0.037 (6)*
H2H	0.708 (3)	-0.022 (2)	0.5086 (15)	0.062 (7)*
H3H	0.477 (3)	0.473 (2)	0.7984 (13)	0.042 (6)*
H4H	0.464 (3)	0.254 (2)	0.4811 (15)	0.060 (7)*
H1N	1.013 (2)	0.1347 (18)	-0.0556 (11)	0.023 (5)*
H2N	0.871 (3)	0.109 (2)	-0.0084 (13)	0.042 (6)*
H3N	0.868 (3)	0.218 (2)	-0.0635 (13)	0.045 (6)*
H4N	0.966 (3)	0.216 (2)	0.0036 (14)	0.047 (6)*
H5N	-0.354 (3)	0.663 (2)	0.0065 (13)	0.040 (6)*
H6N	-0.329 (3)	0.7249 (19)	0.0805 (13)	0.040 (6)*
H7N	-0.495 (3)	0.697 (2)	0.0640 (13)	0.042 (6)*
H8N	-0.412 (3)	0.790 (2)	0.0202 (13)	0.043 (6)*
H1W	-0.123 (3)	0.640 (3)	0.1495 (14)	0.055 (7)*
H2W	-0.131 (3)	0.754 (2)	0.1849 (15)	0.055 (7)*
H3W	0.403 (3)	0.641 (2)	0.8893 (14)	0.050 (7)*
H4W	0.2803 (12)	0.566 (2)	0.8824 (13)	0.048 (6)*
H5W	0.733 (3)	0.400 (2)	0.8992 (14)	0.055 (7)*
H6W	0.691 (3)	0.330 (3)	0.8338 (17)	0.078 (9)*
H7W	0.744 (3)	0.0001 (19)	0.8695 (12)	0.031 (5)*
H8W	0.868 (3)	-0.080 (2)	0.8637 (13)	0.048 (7)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.01834 (17)	0.01888 (16)	0.01370 (15)	0.00414 (13)	-0.00344 (12)	-0.00218 (12)
S2	0.01813 (17)	0.01791 (16)	0.01587 (16)	-0.00119 (12)	-0.00427 (12)	-0.00132 (12)
O1	0.0217 (5)	0.0244 (5)	0.0167 (5)	0.0061 (4)	0.0000 (4)	-0.0011 (4)
O2	0.0231 (6)	0.0357 (6)	0.0236 (5)	-0.0038 (5)	-0.0060 (4)	-0.0062 (5)
O3	0.0384 (6)	0.0202 (5)	0.0191 (5)	0.0095 (5)	-0.0100 (5)	-0.0017 (4)
O4	0.0276 (6)	0.0249 (5)	0.0145 (5)	-0.0060 (4)	-0.0055 (4)	-0.0014 (4)
O5	0.0265 (6)	0.0235 (5)	0.0178 (5)	-0.0075 (4)	-0.0045 (4)	0.0006 (4)
O6	0.0331 (6)	0.0195 (5)	0.0216 (5)	-0.0045 (4)	-0.0096 (4)	-0.0020 (4)
O7	0.0296 (6)	0.0279 (6)	0.0180 (5)	-0.0084 (5)	-0.0002 (4)	0.0000 (4)
O8	0.0236 (6)	0.0316 (6)	0.0261 (6)	0.0074 (5)	-0.0099 (4)	-0.0045 (5)
O9	0.0244 (5)	0.0248 (5)	0.0166 (5)	0.0030 (4)	-0.0066 (4)	-0.0026 (4)
O10	0.0310 (6)	0.0225 (5)	0.0192 (5)	0.0092 (4)	-0.0058 (4)	-0.0052 (4)
O1W	0.0351 (7)	0.0257 (6)	0.0388 (7)	-0.0025 (5)	-0.0192 (6)	-0.0029 (5)
O2W	0.0237 (6)	0.0269 (6)	0.0318 (6)	-0.0001 (5)	-0.0027 (5)	-0.0081 (5)
O3W	0.0290 (6)	0.0232 (6)	0.0265 (6)	-0.0016 (5)	-0.0067 (5)	0.0022 (4)
O4W	0.0249 (6)	0.0235 (6)	0.0275 (6)	-0.0009 (5)	0.0009 (5)	0.0017 (4)
N1	0.0186 (6)	0.0194 (6)	0.0173 (6)	0.0027 (5)	-0.0010 (5)	-0.0013 (4)
N2	0.0188 (6)	0.0196 (6)	0.0189 (6)	0.0018 (5)	-0.0002 (5)	0.0001 (4)
N3	0.0187 (6)	0.0179 (6)	0.0162 (5)	-0.0015 (5)	-0.0015 (4)	-0.0005 (4)
N4	0.0164 (6)	0.0188 (6)	0.0172 (5)	-0.0022 (4)	-0.0011 (4)	-0.0008 (4)
N5	0.0207 (6)	0.0213 (6)	0.0163 (6)	-0.0015 (5)	-0.0026 (5)	-0.0031 (5)
N6	0.0210 (7)	0.0251 (7)	0.0237 (7)	0.0024 (5)	-0.0043 (5)	-0.0014 (6)
C1	0.0167 (6)	0.0186 (6)	0.0129 (6)	0.0039 (5)	-0.0027 (5)	-0.0013 (5)

C2	0.0205 (7)	0.0207 (7)	0.0162 (6)	0.0001 (5)	-0.0024 (5)	0.0014 (5)
C3	0.0196 (7)	0.0202 (7)	0.0184 (6)	0.0009 (5)	-0.0043 (5)	-0.0015 (5)
C4	0.0193 (7)	0.0198 (7)	0.0137 (6)	0.0069 (5)	-0.0024 (5)	-0.0001 (5)
C5	0.0209 (7)	0.0213 (7)	0.0172 (6)	0.0013 (6)	0.0004 (5)	0.0025 (5)
C6	0.0200 (7)	0.0203 (7)	0.0185 (7)	-0.0007 (5)	-0.0022 (5)	-0.0007 (5)
C7	0.0179 (7)	0.0200 (7)	0.0158 (6)	0.0041 (5)	-0.0016 (5)	-0.0012 (5)
C8	0.0221 (7)	0.0219 (7)	0.0196 (7)	-0.0006 (6)	-0.0011 (5)	0.0003 (5)
C9	0.0222 (7)	0.0201 (7)	0.0202 (7)	-0.0014 (6)	-0.0045 (6)	-0.0021 (5)
C10	0.0181 (7)	0.0200 (7)	0.0158 (6)	0.0031 (5)	-0.0041 (5)	-0.0037 (5)
C11	0.0187 (7)	0.0196 (7)	0.0167 (6)	0.0001 (5)	-0.0015 (5)	-0.0016 (5)
C12	0.0156 (6)	0.0176 (6)	0.0190 (6)	0.0018 (5)	-0.0020 (5)	-0.0047 (5)
C13	0.0158 (6)	0.0196 (6)	0.0150 (6)	-0.0034 (5)	-0.0025 (5)	-0.0011 (5)
C14	0.0207 (7)	0.0253 (7)	0.0192 (7)	0.0051 (6)	-0.0040 (5)	-0.0027 (6)
C15	0.0234 (7)	0.0254 (7)	0.0169 (6)	0.0043 (6)	-0.0022 (6)	-0.0052 (5)
C16	0.0169 (6)	0.0179 (6)	0.0163 (6)	-0.0038 (5)	-0.0026 (5)	0.0005 (5)
C17	0.0191 (7)	0.0186 (7)	0.0210 (7)	0.0021 (5)	-0.0048 (5)	-0.0015 (5)
C18	0.0191 (7)	0.0196 (7)	0.0197 (7)	0.0008 (5)	-0.0029 (5)	-0.0045 (5)
C19	0.0152 (6)	0.0181 (6)	0.0157 (6)	-0.0022 (5)	-0.0022 (5)	0.0004 (5)
C20	0.0173 (7)	0.0187 (7)	0.0202 (7)	0.0015 (5)	-0.0027 (5)	-0.0004 (5)
C21	0.0197 (7)	0.0204 (7)	0.0183 (6)	0.0009 (5)	-0.0016 (5)	-0.0028 (5)
C22	0.0174 (6)	0.0197 (6)	0.0151 (6)	-0.0042 (5)	-0.0028 (5)	0.0010 (5)
C23	0.0205 (7)	0.0172 (6)	0.0190 (6)	0.0020 (5)	-0.0039 (5)	0.0003 (5)
C24	0.0188 (7)	0.0162 (6)	0.0164 (6)	-0.0017 (5)	0.0002 (5)	-0.0015 (5)

*Geometric parameters (Å, °)*

S1—O2	1.4529 (12)	C1—C6	1.389 (2)
S1—O3	1.4564 (11)	C1—C2	1.396 (2)
S1—O1	1.4624 (10)	C2—C3	1.3896 (19)
S1—C1	1.7700 (13)	C2—H1	0.9500
S2—O8	1.4539 (11)	C3—C4	1.399 (2)
S2—O7	1.4586 (11)	C3—H2	0.9500
S2—O6	1.4617 (11)	C4—C5	1.388 (2)
S2—C13	1.7653 (14)	C5—C6	1.3875 (19)
O4—C10	1.3629 (16)	C5—H3	0.9500
O4—H1H	0.84 (2)	C6—4H	0.9500
O5—C12	1.3383 (17)	C7—C8	1.397 (2)
O5—H2H	0.98 (3)	C7—C12	1.420 (2)
O9—C22	1.3574 (16)	C8—C9	1.382 (2)
O9—H3H	0.85 (2)	C8—H5	0.9500
O10—C24	1.3413 (16)	C9—C10	1.402 (2)
O10—H4H	0.93 (3)	C9—H6	0.9500
O1W—H1W	0.82 (3)	C10—C11	1.385 (2)
O1W—H2W	0.84 (3)	C11—C12	1.3990 (19)
O2W—H3W	0.83 (3)	C11—H8	0.9500
O2W—H4W	0.867 (10)	C13—C14	1.3913 (19)
O3W—H5W	0.88 (3)	C13—C18	1.3940 (19)
O3W—H6W	0.95 (3)	C14—C15	1.3863 (19)

O4W—H7W	0.81 (2)	C14—H10	0.9500
O4W—H8W	0.81 (3)	C15—C16	1.391 (2)
N1—N2	1.2680 (17)	C15—H11	0.9500
N1—C4	1.4227 (17)	C16—C17	1.3943 (19)
N2—C7	1.4050 (17)	C17—C18	1.3874 (19)
N3—N4	1.2756 (16)	C17—H12	0.9500
N3—C16	1.4244 (17)	C18—H13	0.9500
N4—C19	1.3963 (17)	C19—C20	1.4041 (19)
N5—H1N	0.80 (2)	C19—C24	1.4221 (19)
N5—H2N	0.92 (2)	C20—C21	1.3799 (19)
N5—H3N	0.94 (2)	C20—H14	0.9500
N5—H4N	0.89 (2)	C21—C22	1.4059 (19)
N6—H5N	0.90 (2)	C21—H15	0.9500
N6—H6N	0.92 (2)	C22—C23	1.3874 (19)
N6—H7N	0.92 (2)	C23—C24	1.3919 (19)
N6—H8N	0.84 (2)	C23—H17	0.9500
O2—S1—O3	113.29 (7)	C8—C7—N2	115.77 (13)
O2—S1—O1	111.57 (6)	C8—C7—C12	119.15 (13)
O3—S1—O1	111.92 (7)	N2—C7—C12	125.08 (13)
O2—S1—C1	106.74 (7)	C9—C8—C7	121.46 (14)
O3—S1—C1	106.36 (6)	C9—C8—H5	119.3
O1—S1—C1	106.44 (6)	C7—C8—H5	119.3
O8—S2—O7	112.77 (7)	C8—C9—C10	118.78 (14)
O8—S2—O6	112.41 (7)	C8—C9—H6	120.6
O7—S2—O6	110.95 (7)	C10—C9—H6	120.6
O8—S2—C13	106.48 (6)	O4—C10—C11	121.49 (13)
O7—S2—C13	106.47 (6)	O4—C10—C9	117.21 (13)
O6—S2—C13	107.32 (6)	C11—C10—C9	121.31 (13)
C10—O4—H1H	110.2 (15)	C10—C11—C12	119.88 (13)
C12—O5—H2H	101.5 (15)	C10—C11—H8	120.1
C22—O9—H3H	110.6 (15)	C12—C11—H8	120.1
C24—O10—H4H	103.8 (15)	O5—C12—C11	118.27 (13)
H1W—O1W—H2W	109 (2)	O5—C12—C7	122.31 (12)
H3W—O2W—H4W	105 (2)	C11—C12—C7	119.42 (13)
H5W—O3W—H6W	104 (2)	C14—C13—C18	120.74 (13)
H7W—O4W—H8W	104 (2)	C14—C13—S2	120.09 (11)
N2—N1—C4	114.84 (12)	C18—C13—S2	119.11 (10)
N1—N2—C7	114.40 (12)	C15—C14—C13	119.86 (13)
N4—N3—C16	114.71 (11)	C15—C14—H10	120.1
N3—N4—C19	114.81 (11)	C13—C14—H10	120.1
H1N—N5—H2N	111.0 (18)	C14—C15—C16	119.56 (13)
H1N—N5—H3N	113.3 (19)	C14—C15—H11	120.2
H2N—N5—H3N	108.3 (19)	C16—C15—H11	120.2
H1N—N5—H4N	108.0 (19)	C15—C16—C17	120.60 (13)
H2N—N5—H4N	107.7 (19)	C15—C16—N3	123.87 (12)
H3N—N5—H4N	108.4 (19)	C17—C16—N3	115.52 (12)
H5N—N6—H6N	110.5 (18)	C18—C17—C16	119.88 (13)

H5N—N6—H7N	110.3 (19)	C18—C17—H12	120.1
H6N—N6—H7N	107.0 (18)	C16—C17—H12	120.1
H5N—N6—H8N	109 (2)	C17—C18—C13	119.34 (13)
H6N—N6—H8N	112 (2)	C17—C18—H13	120.3
H7N—N6—H8N	108 (2)	C13—C18—H13	120.3
C6—C1—C2	120.97 (12)	N4—C19—C20	116.23 (12)
C6—C1—S1	119.83 (11)	N4—C19—C24	125.04 (12)
C2—C1—S1	119.18 (11)	C20—C19—C24	118.73 (12)
C3—C2—C1	119.78 (13)	C21—C20—C19	121.30 (13)
C3—C2—H1	120.1	C21—C20—H14	119.3
C1—C2—H1	120.1	C19—C20—H14	119.3
C2—C3—C4	119.12 (13)	C20—C21—C22	119.15 (13)
C2—C3—H2	120.4	C20—C21—H15	120.4
C4—C3—H2	120.4	C22—C21—H15	120.4
C5—C4—C3	120.73 (13)	O9—C22—C23	117.27 (12)
C5—C4—N1	114.64 (13)	O9—C22—C21	121.83 (12)
C3—C4—N1	124.62 (13)	C23—C22—C21	120.89 (12)
C6—C5—C4	120.20 (13)	C22—C23—C24	120.02 (13)
C6—C5—H3	119.9	C22—C23—H17	120.0
C4—C5—H3	119.9	C24—C23—H17	120.0
C5—C6—C1	119.19 (13)	O10—C24—C23	118.42 (12)
C5—C6—4H	120.4	O10—C24—C19	121.70 (12)
C1—C6—4H	120.4	C23—C24—C19	119.87 (12)
C4—N1—N2—C7	-179.73 (11)	N2—C7—C12—C11	-179.40 (12)
C16—N3—N4—C19	-179.87 (11)	O8—S2—C13—C14	-14.43 (14)
O2—S1—C1—C6	12.29 (13)	O7—S2—C13—C14	106.13 (13)
O3—S1—C1—C6	133.52 (11)	O6—S2—C13—C14	-135.01 (12)
O1—S1—C1—C6	-106.99 (12)	O8—S2—C13—C18	168.28 (12)
O2—S1—C1—C2	-169.23 (11)	O7—S2—C13—C18	-71.16 (13)
O3—S1—C1—C2	-47.99 (13)	O6—S2—C13—C18	47.70 (13)
O1—S1—C1—C2	71.50 (12)	C18—C13—C14—C15	0.6 (2)
C6—C1—C2—C3	-0.3 (2)	S2—C13—C14—C15	-176.62 (12)
S1—C1—C2—C3	-178.79 (10)	C13—C14—C15—C16	-0.4 (2)
C1—C2—C3—C4	-0.3 (2)	C14—C15—C16—C17	-0.7 (2)
C2—C3—C4—C5	0.5 (2)	C14—C15—C16—N3	178.73 (14)
C2—C3—C4—N1	179.66 (12)	N4—N3—C16—C15	-7.1 (2)
N2—N1—C4—C5	-178.08 (12)	N4—N3—C16—C17	172.30 (13)
N2—N1—C4—C3	2.70 (19)	C15—C16—C17—C18	1.5 (2)
C3—C4—C5—C6	0.0 (2)	N3—C16—C17—C18	-178.00 (13)
N1—C4—C5—C6	-179.29 (12)	C16—C17—C18—C13	-1.2 (2)
C4—C5—C6—C1	-0.6 (2)	C14—C13—C18—C17	0.1 (2)
C2—C1—C6—C5	0.8 (2)	S2—C13—C18—C17	177.42 (11)
S1—C1—C6—C5	179.23 (11)	N3—N4—C19—C20	178.63 (12)
N1—N2—C7—C8	179.98 (12)	N3—N4—C19—C24	-0.9 (2)
N1—N2—C7—C12	0.06 (19)	N4—C19—C20—C21	179.16 (13)
N2—C7—C8—C9	179.75 (13)	C24—C19—C20—C21	-1.2 (2)
C12—C7—C8—C9	-0.3 (2)	C19—C20—C21—C22	1.7 (2)

C7—C8—C9—C10	−0.4 (2)	C20—C21—C22—O9	178.72 (13)
C8—C9—C10—O4	−179.37 (13)	C20—C21—C22—C23	−0.4 (2)
C8—C9—C10—C11	0.7 (2)	O9—C22—C23—C24	179.45 (13)
O4—C10—C11—C12	179.74 (12)	C21—C22—C23—C24	−1.4 (2)
C9—C10—C11—C12	−0.4 (2)	C22—C23—C24—O10	−177.09 (13)
C10—C11—C12—O5	179.41 (12)	C22—C23—C24—C19	1.9 (2)
C10—C11—C12—C7	−0.3 (2)	N4—C19—C24—O10	−2.1 (2)
C8—C7—C12—O5	−179.05 (13)	C20—C19—C24—O10	178.33 (13)
N2—C7—C12—O5	0.9 (2)	N4—C19—C24—C23	178.99 (13)
C8—C7—C12—C11	0.7 (2)	C20—C19—C24—C23	−0.6 (2)

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>
O4—H1H···O4W	0.84 (2)	1.81 (2)	2.6357 (17)	170 (2)
O5—H2H···N1	0.98 (3)	1.65 (3)	2.5535 (16)	151 (2)
O9—H3H···O2W	0.85 (2)	1.83 (2)	2.6673 (16)	168 (2)
O10—H4H···N3	0.93 (3)	1.69 (3)	2.5420 (16)	149 (2)
N5—H1N···O1 <sup>i</sup>	0.80 (2)	2.16 (2)	2.8858 (17)	151.1 (18)
N5—H1N···O1W <sup>ii</sup>	0.80 (2)	2.627 (19)	3.034 (2)	113.3 (15)
N5—H2N···O1	0.92 (2)	1.94 (2)	2.8403 (18)	168 (2)
N5—H3N···O3W <sup>iii</sup>	0.94 (2)	1.91 (2)	2.8488 (17)	172 (2)
N5—H4N···O6 <sup>iv</sup>	0.89 (2)	2.01 (2)	2.8425 (16)	156 (2)
N6—H5N···S2 <sup>v</sup>	0.90 (2)	2.99 (2)	3.7547 (15)	143.5 (17)
N6—H5N···O7 <sup>v</sup>	0.90 (2)	1.99 (2)	2.8804 (18)	168 (2)
N6—H6N···O1W	0.92 (2)	1.90 (2)	2.8027 (18)	169.7 (19)
N6—H7N···O3W <sup>vi</sup>	0.92 (2)	1.96 (2)	2.8733 (19)	170.4 (19)
N6—H8N···O2 <sup>vii</sup>	0.84 (2)	2.42 (2)	2.9090 (18)	117.8 (18)
N6—H8N···O3 <sup>v</sup>	0.84 (2)	2.36 (2)	2.9153 (17)	123.8 (19)
O1W—H2W···O4 <sup>viii</sup>	0.84 (3)	2.01 (3)	2.8150 (16)	162 (2)
O1W—H1W···O8	0.82 (3)	1.98 (3)	2.7858 (17)	166 (2)
O2W—H3W···O3 <sup>viii</sup>	0.83 (3)	2.04 (3)	2.8639 (16)	171 (2)
O2W—H4W···O8 <sup>vi</sup>	0.87 (1)	1.94 (1)	2.7918 (17)	169 (2)
O3W—H5W···O7 <sup>viii</sup>	0.88 (3)	1.83 (3)	2.7106 (16)	179 (2)
O3W—H6W···O9	0.95 (3)	2.04 (3)	2.8347 (15)	140 (2)
O4W—H7W···O2 <sup>ix</sup>	0.81 (2)	1.94 (2)	2.7482 (17)	175 (2)
O4W—H8W···O6 <sup>ix</sup>	0.81 (3)	2.01 (3)	2.8128 (16)	171 (2)

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

Ammonium 4-[2-(4-aminophenyl)diazen-1-yl]benzenesulfonate sesquihydrate (NH43)

Crystal data

$\text{NH}_4^+\cdot\text{C}_{12}\text{H}_{10}\text{N}_3\text{O}_3\text{S}^- \cdot 1.5(\text{H}_2\text{O})$

$M_r = 321.35$

Monoclinic,  $C2/c$

$a = 35.1636 (15) \text{ \AA}$

$b = 7.8905 (3) \text{ \AA}$

$c = 10.4972 (5) \text{ \AA}$

$\beta = 100.091 (2)^\circ$

$V = 2867.5 (2) \text{ \AA}^3$

$Z = 8$

$F(000) = 1352$

$D_x = 1.489 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.7107 \text{ \AA}$



Cell parameters from 3419 reflections  
 $\theta = 1.0\text{--}27.5^\circ$   
 $\mu = 0.25\text{ mm}^{-1}$

$T = 123\text{ K}$   
 Plate, yellow  
 $0.35 \times 0.30 \times 0.05\text{ mm}$

*Data collection*

Enraf–Nonius KappaCCD  
 diffractometer  
 Radiation source: sealed tube  
 phi and  $\omega$  scans  
 6133 measured reflections  
 3271 independent reflections

1857 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.074$   
 $\theta_{\text{max}} = 27.5^\circ$ ,  $\theta_{\text{min}} = 2.4^\circ$   
 $h = -45 \rightarrow 45$   
 $k = -10 \rightarrow 10$   
 $l = -13 \rightarrow 13$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.049$   
 $wR(F^2) = 0.105$   
 $S = 1.02$   
 3271 reflections  
 231 parameters  
 1 restraint

Hydrogen site location: mixed  
 H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0404P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.26\text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.46\text{ e \AA}^{-3}$

*Special details*

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.43663 (2)	0.11499 (8)	0.70251 (6)	0.01953 (19)
O1	0.45304 (4)	0.2492 (2)	0.79049 (15)	0.0232 (4)
O2	0.45060 (5)	−0.0525 (2)	0.74823 (16)	0.0254 (4)
O3	0.44203 (5)	0.1429 (2)	0.56905 (15)	0.0258 (4)
O1W	0.43599 (5)	0.5179 (3)	0.9712 (2)	0.0288 (5)
O2W	0.000000	0.0222 (3)	0.750000	0.0255 (6)
N1	0.26669 (5)	0.1179 (2)	0.69356 (18)	0.0206 (5)
N2	0.25653 (6)	0.1029 (2)	0.80233 (19)	0.0209 (5)
N3	0.09692 (6)	0.1286 (3)	0.8002 (2)	0.0229 (5)
N4	0.01011 (8)	0.2779 (3)	0.9447 (2)	0.0231 (5)
C1	0.38640 (6)	0.1194 (3)	0.7015 (2)	0.0158 (5)
C2	0.37175 (7)	0.1937 (3)	0.8030 (2)	0.0178 (6)
H3	0.388827	0.245602	0.872118	0.021*
C3	0.33251 (7)	0.1922 (3)	0.8037 (2)	0.0199 (6)
H4	0.322609	0.241477	0.873737	0.024*
C4	0.30749 (7)	0.1180 (3)	0.7009 (2)	0.0182 (6)
C5	0.32184 (7)	0.0481 (3)	0.5976 (2)	0.0193 (6)
H1	0.304641	0.001030	0.526474	0.023*
C6	0.36131 (7)	0.0470 (3)	0.5983 (2)	0.0189 (6)
H2	0.371235	−0.002996	0.528569	0.023*

C7	0.21591 (7)	0.1143 (3)	0.7977 (2)	0.0189 (6)
C8	0.20127 (7)	0.0432 (3)	0.9007 (2)	0.0217 (6)
H7	0.218270	-0.007777	0.970567	0.026*
C9	0.16185 (7)	0.0469 (3)	0.9011 (2)	0.0204 (6)
H8	0.151853	-0.005480	0.969770	0.024*
C10	0.13691 (7)	0.1264 (3)	0.8022 (2)	0.0177 (6)
C11	0.15198 (7)	0.2021 (3)	0.7018 (2)	0.0211 (6)
H6	0.135167	0.259073	0.634717	0.025*
C12	0.19107 (7)	0.1952 (3)	0.6988 (2)	0.0197 (6)
H5	0.200951	0.245721	0.629153	0.024*
H1N	0.0074 (8)	0.178 (4)	0.902 (3)	0.046 (9)*
H2N	0.0243 (9)	0.255 (4)	1.028 (3)	0.068 (11)*
H3N	0.0210 (9)	0.348 (4)	0.900 (3)	0.065 (12)*
H4N	-0.0141 (10)	0.327 (4)	0.963 (3)	0.081 (12)*
H5N	0.0911 (8)	0.092 (3)	0.870 (3)	0.036 (9)*
H6N	0.0856 (7)	0.223 (4)	0.775 (2)	0.038 (9)*
H1W	0.4271 (8)	0.525 (4)	0.892 (3)	0.040 (10)*
H2W	0.4346 (9)	0.622 (4)	1.000 (3)	0.065 (12)*
H3W	-0.0192 (6)	-0.044 (3)	0.757 (3)	0.049 (10)*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0178 (3)	0.0194 (3)	0.0217 (4)	-0.0012 (3)	0.0044 (3)	-0.0010 (3)
O1	0.0187 (10)	0.0243 (10)	0.0269 (10)	-0.0035 (8)	0.0046 (7)	-0.0055 (9)
O2	0.0190 (10)	0.0197 (10)	0.0370 (11)	0.0025 (8)	0.0038 (8)	0.0025 (8)
O3	0.0229 (10)	0.0360 (12)	0.0202 (9)	-0.0035 (9)	0.0087 (7)	0.0004 (8)
O1W	0.0314 (12)	0.0306 (13)	0.0240 (13)	0.0036 (10)	0.0038 (9)	0.0001 (10)
O2W	0.0249 (17)	0.0245 (16)	0.0294 (15)	0.000	0.0109 (13)	0.000
N1	0.0201 (12)	0.0199 (12)	0.0226 (12)	-0.0003 (10)	0.0058 (9)	-0.0003 (11)
N2	0.0186 (12)	0.0218 (12)	0.0234 (12)	-0.0003 (10)	0.0066 (9)	0.0005 (10)
N3	0.0201 (13)	0.0218 (14)	0.0276 (14)	0.0016 (12)	0.0064 (10)	0.0020 (12)
N4	0.0245 (14)	0.0216 (15)	0.0237 (15)	-0.0005 (12)	0.0058 (12)	-0.0015 (13)
C1	0.0166 (13)	0.0121 (13)	0.0188 (13)	0.0001 (12)	0.0039 (10)	0.0060 (12)
C2	0.0186 (14)	0.0163 (13)	0.0178 (13)	-0.0021 (12)	0.0011 (10)	0.0012 (11)
C3	0.0213 (14)	0.0211 (14)	0.0186 (13)	-0.0011 (12)	0.0068 (11)	-0.0005 (12)
C4	0.0158 (13)	0.0173 (13)	0.0215 (14)	0.0019 (12)	0.0037 (10)	0.0048 (12)
C5	0.0225 (15)	0.0195 (14)	0.0140 (13)	-0.0016 (12)	-0.0022 (11)	0.0027 (11)
C6	0.0199 (14)	0.0205 (14)	0.0173 (14)	0.0022 (12)	0.0064 (11)	-0.0002 (12)
C7	0.0168 (14)	0.0176 (13)	0.0219 (14)	0.0007 (12)	0.0023 (11)	-0.0041 (12)
C8	0.0214 (15)	0.0242 (14)	0.0184 (14)	0.0013 (12)	0.0008 (11)	0.0004 (12)
C9	0.0246 (15)	0.0199 (14)	0.0184 (14)	-0.0031 (12)	0.0085 (11)	-0.0006 (12)
C10	0.0185 (14)	0.0141 (13)	0.0214 (14)	0.0002 (12)	0.0057 (11)	-0.0016 (12)
C11	0.0217 (14)	0.0199 (14)	0.0204 (14)	0.0044 (12)	0.0004 (11)	-0.0009 (12)
C12	0.0204 (14)	0.0197 (14)	0.0195 (14)	-0.0026 (12)	0.0043 (11)	-0.0001 (12)

*Geometric parameters (Å, °)*

S1—O1	1.4564 (17)	C1—C6	1.394 (3)
S1—O2	1.4612 (17)	C2—C3	1.381 (3)
S1—O3	1.4630 (16)	C2—H3	0.9500
S1—C1	1.765 (2)	C3—C4	1.396 (3)
O1W—H1W	0.83 (3)	C3—H4	0.9500
O1W—H2W	0.88 (3)	C4—C5	1.389 (3)
O2W—H3W	0.867 (10)	C5—C6	1.387 (3)
O2W—H3W <sup>i</sup>	0.867 (10)	C5—H1	0.9500
N1—N2	1.260 (2)	C6—H2	0.9500
N1—C4	1.423 (3)	C7—C12	1.390 (3)
N2—C7	1.423 (3)	C7—C8	1.394 (3)
N3—C10	1.403 (3)	C8—C9	1.387 (3)
N3—H5N	0.85 (3)	C8—H7	0.9500
N3—H6N	0.86 (3)	C9—C10	1.387 (3)
N4—H1N	0.90 (3)	C9—H8	0.9500
N4—H2N	0.94 (3)	C10—C11	1.394 (3)
N4—H3N	0.86 (3)	C11—C12	1.382 (3)
N4—H4N	0.98 (4)	C11—H6	0.9500
C1—C2	1.391 (3)	C12—H5	0.9500
O1—S1—O2	112.10 (10)	C5—C4—C3	120.3 (2)
O1—S1—O3	113.23 (10)	C5—C4—N1	117.3 (2)
O2—S1—O3	110.97 (10)	C3—C4—N1	122.4 (2)
O1—S1—C1	105.93 (10)	C6—C5—C4	119.9 (2)
O2—S1—C1	107.36 (10)	C6—C5—H1	120.0
O3—S1—C1	106.79 (10)	C4—C5—H1	120.0
H1W—O1W—H2W	104 (3)	C5—C6—C1	119.9 (2)
H3W—O2W—H3W <sup>i</sup>	106 (4)	C5—C6—H2	120.1
N2—N1—C4	113.20 (18)	C1—C6—H2	120.1
N1—N2—C7	113.92 (19)	C12—C7—C8	119.7 (2)
C10—N3—H5N	112.2 (18)	C12—C7—N2	123.3 (2)
C10—N3—H6N	114.9 (18)	C8—C7—N2	116.9 (2)
H5N—N3—H6N	113 (3)	C9—C8—C7	119.9 (2)
H1N—N4—H2N	106 (3)	C9—C8—H7	120.0
H1N—N4—H3N	108 (3)	C7—C8—H7	120.0
H2N—N4—H3N	115 (3)	C10—C9—C8	120.6 (2)
H1N—N4—H4N	115 (3)	C10—C9—H8	119.7
H2N—N4—H4N	103 (2)	C8—C9—H8	119.7
H3N—N4—H4N	110 (3)	C9—C10—C11	119.0 (2)
C2—C1—C6	119.9 (2)	C9—C10—N3	121.1 (2)
C2—C1—S1	120.53 (17)	C11—C10—N3	119.8 (2)
C6—C1—S1	119.54 (18)	C12—C11—C10	120.8 (2)
C3—C2—C1	120.3 (2)	C12—C11—H6	119.6
C3—C2—H3	119.8	C10—C11—H6	119.6
C1—C2—H3	119.8	C11—C12—C7	119.9 (2)
C2—C3—C4	119.6 (2)	C11—C12—H5	120.1

C2—C3—H4	120.2	C7—C12—H5	120.1
C4—C3—H4	120.2		
C4—N1—N2—C7	175.90 (19)	C4—C5—C6—C1	-1.4 (4)
O1—S1—C1—C2	-21.1 (2)	C2—C1—C6—C5	-0.5 (3)
O2—S1—C1—C2	98.82 (19)	S1—C1—C6—C5	179.20 (18)
O3—S1—C1—C2	-142.10 (19)	N1—N2—C7—C12	-23.1 (3)
O1—S1—C1—C6	159.19 (18)	N1—N2—C7—C8	158.6 (2)
O2—S1—C1—C6	-80.9 (2)	C12—C7—C8—C9	2.9 (4)
O3—S1—C1—C6	38.2 (2)	N2—C7—C8—C9	-178.7 (2)
C6—C1—C2—C3	1.7 (3)	C7—C8—C9—C10	-2.4 (4)
S1—C1—C2—C3	-178.02 (18)	C8—C9—C10—C11	0.3 (4)
C1—C2—C3—C4	-1.0 (4)	C8—C9—C10—N3	178.9 (2)
C2—C3—C4—C5	-0.9 (4)	C9—C10—C11—C12	1.4 (3)
C2—C3—C4—N1	-177.6 (2)	N3—C10—C11—C12	-177.2 (2)
N2—N1—C4—C5	147.6 (2)	C10—C11—C12—C7	-1.0 (3)
N2—N1—C4—C3	-35.6 (3)	C8—C7—C12—C11	-1.2 (3)
C3—C4—C5—C6	2.1 (4)	N2—C7—C12—C11	-179.5 (2)
N1—C4—C5—C6	179.0 (2)		

Symmetry code: (i)  $-x, y, -z+3/2$ .

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N4—H1N $\cdots$ O2W	0.90 (3)	2.00 (3)	2.850 (3)	157 (2)
N4—H2N $\cdots$ O1 <sup>ii</sup>	0.94 (3)	1.93 (3)	2.862 (3)	167 (3)
N4—H2N $\cdots$ O1W <sup>ii</sup>	0.94 (3)	2.57 (3)	3.039 (3)	111 (2)
N4—H3N $\cdots$ O2 <sup>iii</sup>	0.86 (3)	2.14 (3)	2.963 (3)	161 (3)
N4—H3N $\cdots$ O3 <sup>iii</sup>	0.86 (3)	2.66 (3)	3.351 (3)	139 (3)
N4—H4N $\cdots$ O3 <sup>iv</sup>	0.98 (4)	2.07 (4)	2.987 (3)	155 (3)
N3—H5N $\cdots$ O1W <sup>ii</sup>	0.85 (3)	2.23 (3)	3.067 (3)	168 (2)
N3—H6N $\cdots$ O2 <sup>iii</sup>	0.86 (3)	2.17 (3)	3.015 (3)	165 (2)
O1W—H1W $\cdots$ N3 <sup>iii</sup>	0.83 (3)	2.21 (3)	3.011 (3)	162 (3)
O1W—H2W $\cdots$ O3 <sup>v</sup>	0.88 (3)	1.99 (3)	2.861 (3)	169 (3)
O2W—H3W $\cdots$ O1 <sup>vi</sup>	0.87 (1)	1.97 (1)	2.792 (3)	159 (3)

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

#### Ammonium 4-(2-{4-[bis(2-hydroxyethyl)amino]phenyl}diazen-1-yl)benzenesulfonate monohydrate (NH44)

##### Crystal data

$\text{NH}_4^+\cdot\text{C}_{16}\text{H}_{18}\text{N}_3\text{O}_5\text{S}^-\cdot\text{H}_2\text{O}$

$M_r = 400.45$

Triclinic,  $P\bar{1}$

$a = 8.4933$  (1)  $\text{\AA}$

$b = 13.0977$  (2)  $\text{\AA}$

$c = 17.1657$  (3)  $\text{\AA}$

$\alpha = 90.970$  (1) $^\circ$

$\beta = 103.180$  (1) $^\circ$

$\gamma = 95.132$  (1) $^\circ$

$V = 1850.43$  (5)  $\text{\AA}^3$

$Z = 4$

$F(000) = 848$

$D_x = 1.437$   $\text{Mg m}^{-3}$

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

Cell parameters from 8751 reflections

$\theta = 1.0\text{--}27.9^\circ$

$\mu = 0.22 \text{ mm}^{-1}$   
 $T = 123 \text{ K}$

Cut plate, yellow orange  
 $0.5 \times 0.5 \times 0.15 \text{ mm}$

*Data collection*

Enraf–Nonius KappaCCD  
 diffractometer  
 Radiation source: sealed tube  
 phi and  $\omega$  scans  
 16736 measured reflections  
 8841 independent reflections

5911 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.043$   
 $\theta_{\text{max}} = 28.0^\circ$ ,  $\theta_{\text{min}} = 1.2^\circ$   
 $h = -11 \rightarrow 11$   
 $k = -17 \rightarrow 17$   
 $l = -22 \rightarrow 22$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.047$   
 $wR(F^2) = 0.118$   
 $S = 1.04$   
 8841 reflections  
 550 parameters  
 8 restraints

Hydrogen site location: mixed  
 H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0528P)^2 + 0.4114P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.57 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.42 \text{ e } \text{Å}^{-3}$

*Special details*

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
S1	-0.17962 (6)	0.40832 (4)	0.11851 (3)	0.02084 (13)	
S1A	0.89947 (6)	0.10864 (4)	0.81730 (3)	0.02110 (13)	
O1	-0.35205 (17)	0.38875 (12)	0.11656 (9)	0.0329 (4)	
O1A	0.88697 (18)	-0.00026 (10)	0.79522 (9)	0.0297 (4)	
O2	-0.12780 (18)	0.51596 (10)	0.11604 (9)	0.0303 (4)	
O2A	0.7922 (2)	0.13162 (13)	0.86831 (9)	0.0399 (4)	
O3	-0.13347 (18)	0.34429 (11)	0.05857 (8)	0.0275 (3)	
O3A	1.06745 (17)	0.14814 (11)	0.85103 (9)	0.0270 (3)	
O4	0.3424 (2)	0.03149 (12)	0.90342 (9)	0.0310 (4)	
O4A	0.3842 (2)	0.50130 (13)	0.07514 (9)	0.0298 (4)	
O5	0.6302 (2)	-0.14218 (13)	0.77988 (9)	0.0299 (4)	
O5A	0.5451 (2)	0.69228 (13)	0.07851 (9)	0.0338 (4)	
N1	0.0781 (2)	0.23905 (13)	0.43773 (10)	0.0220 (4)	
N1A	0.6312 (2)	0.32623 (13)	0.52115 (10)	0.0239 (4)	
N2	0.1444 (2)	0.15696 (13)	0.43423 (10)	0.0236 (4)	
N2A	0.7053 (2)	0.41022 (13)	0.50930 (10)	0.0230 (4)	
N3	0.3017 (2)	-0.08822 (12)	0.69994 (10)	0.0213 (4)	
N3A	0.4234 (2)	0.61579 (12)	0.23547 (10)	0.0204 (4)	
N4	0.1309 (3)	0.30779 (17)	-0.02165 (13)	0.0305 (5)	
N5	0.6587 (3)	0.15278 (17)	1.00084 (13)	0.0289 (4)	
C1	-0.0800 (2)	0.36624 (14)	0.21287 (12)	0.0187 (4)	



---

C1A	0.8318 (2)	0.17296 (15)	0.72803 (12)	0.0200 (4)
C2	−0.0972 (3)	0.41491 (15)	0.28276 (12)	0.0228 (5)
H2	−0.149957	0.476152	0.279943	0.027*
C2A	0.6835 (3)	0.13752 (15)	0.67789 (12)	0.0227 (5)
H2A	0.624361	0.077229	0.690080	0.027*
C3	−0.0375 (2)	0.37424 (15)	0.35638 (12)	0.0222 (5)
H3	−0.047185	0.408354	0.404098	0.027*
C3A	0.6224 (3)	0.19002 (15)	0.61039 (12)	0.0235 (5)
H3A	0.520852	0.165819	0.576214	0.028*
C4	0.0369 (2)	0.28326 (15)	0.36042 (12)	0.0198 (4)
C4A	0.7085 (3)	0.27817 (15)	0.59206 (12)	0.0219 (5)
C5	0.0585 (2)	0.23671 (15)	0.29092 (12)	0.0214 (4)
H5	0.112535	0.175969	0.293915	0.026*
C5A	0.8571 (3)	0.31410 (16)	0.64225 (13)	0.0248 (5)
H5A	0.915888	0.374439	0.629883	0.030*
C6	0.0020 (2)	0.27789 (15)	0.21743 (12)	0.0220 (4)
H6	0.018872	0.246300	0.170152	0.026*
C6A	0.9192 (3)	0.26163 (15)	0.71037 (12)	0.0239 (5)
H6A	1.020451	0.285888	0.744758	0.029*
C7	0.1810 (2)	0.10273 (15)	0.50505 (12)	0.0223 (5)
C7A	0.6255 (3)	0.45964 (15)	0.44071 (12)	0.0215 (4)
C8	0.2579 (3)	0.01469 (16)	0.49867 (13)	0.0253 (5)
H8	0.281847	−0.002980	0.448998	0.030*
C8A	0.7089 (3)	0.54725 (15)	0.41917 (12)	0.0226 (5)
H8A	0.811905	0.572131	0.451636	0.027*
C9	0.3005 (3)	−0.04780 (16)	0.56259 (12)	0.0245 (5)
H9	0.355253	−0.106573	0.556626	0.029*
C9A	0.6442 (2)	0.59843 (15)	0.35140 (12)	0.0217 (4)
H9A	0.704469	0.657026	0.337306	0.026*
C10	0.2635 (2)	−0.02522 (15)	0.63652 (12)	0.0205 (4)
C10A	0.4899 (2)	0.56516 (14)	0.30270 (12)	0.0195 (4)
C11	0.1840 (2)	0.06468 (15)	0.64191 (12)	0.0231 (5)
H11	0.158480	0.082624	0.691148	0.028*
C11A	0.4039 (3)	0.47813 (15)	0.32746 (12)	0.0221 (4)
H11A	0.298707	0.454379	0.296832	0.026*
C12	0.1430 (2)	0.12635 (15)	0.57798 (12)	0.0225 (5)
H12	0.088398	0.185410	0.583295	0.027*
C12A	0.4703 (3)	0.42788 (15)	0.39475 (12)	0.0233 (5)
H12A	0.409623	0.370507	0.410364	0.028*
C13	0.2643 (3)	−0.06521 (16)	0.77689 (12)	0.0240 (5)
H13A	0.258991	−0.129575	0.805996	0.029*
H13B	0.155624	−0.039534	0.766994	0.029*
C13A	0.2716 (3)	0.57465 (16)	0.18036 (12)	0.0241 (5)
H13C	0.231958	0.628891	0.143451	0.029*
H13D	0.189095	0.557588	0.211785	0.029*
C14	0.3863 (3)	0.01328 (16)	0.82977 (12)	0.0257 (5)
H14A	0.495397	−0.011879	0.840483	0.031*
H14B	0.391470	0.078372	0.801570	0.031*

C14A	0.2853 (3)	0.48032 (17)	0.13115 (13)	0.0300 (5)	
H14C	0.332100	0.427377	0.167557	0.036*	
H14D	0.175268	0.452262	0.101761	0.036*	
C15	0.3707 (3)	-0.18485 (15)	0.69021 (13)	0.0237 (5)	
H15A	0.318931	-0.215719	0.636409	0.028*	
H15B	0.343701	-0.232829	0.730219	0.028*	
C15A	0.5049 (3)	0.71091 (15)	0.21544 (12)	0.0232 (5)	
H15C	0.565540	0.747437	0.265797	0.028*	
H15D	0.421297	0.754838	0.188657	0.028*	
C16	0.5525 (3)	-0.17382 (16)	0.69951 (13)	0.0262 (5)	
H16A	0.588976	-0.240219	0.686007	0.031*	
H16B	0.582318	-0.122439	0.662418	0.031*	
C16A	0.6218 (3)	0.69837 (17)	0.16185 (13)	0.0277 (5)	
H16C	0.706454	0.757198	0.172350	0.033*	
H16D	0.676385	0.635262	0.175844	0.033*	
O1W	0.3971 (2)	0.22906 (13)	0.08102 (10)	0.0413 (4)	
H1W	0.473 (2)	0.2803 (14)	0.0933 (14)	0.050*	
H2W	0.393 (3)	0.2095 (18)	0.1295 (8)	0.050*	
O2W	0.0195 (3)	0.09867 (17)	0.05014 (14)	0.0781 (7)	
H3W	0.043 (4)	0.073 (3)	0.0998 (10)	0.094*	
H4W	-0.040 (7)	0.043 (3)	0.025 (2)	0.094*	0.5
H5W	0.114 (5)	0.085 (6)	0.038 (3)	0.094*	0.5
H1H	0.260 (4)	0.065 (2)	0.8945 (19)	0.074 (11)*	
H2H	0.704 (4)	-0.099 (2)	0.7780 (17)	0.053 (9)*	
H3H	0.461 (4)	0.469 (2)	0.0886 (18)	0.068 (11)*	
H4H	0.482 (4)	0.626 (2)	0.0679 (17)	0.062 (9)*	
H1N	0.050 (3)	0.3194 (18)	-0.0005 (15)	0.035 (7)*	
H2N	0.145 (3)	0.373 (2)	-0.0441 (15)	0.047 (8)*	
H3N	0.095 (3)	0.260 (2)	-0.0613 (17)	0.046 (8)*	
H4N	0.234 (5)	0.274 (3)	0.021 (2)	0.104 (12)*	
H5N	0.703 (3)	0.133 (2)	0.9597 (17)	0.051 (8)*	
H6N	0.561 (5)	0.176 (3)	0.985 (2)	0.089 (12)*	
H7N	0.724 (4)	0.209 (3)	1.0321 (19)	0.076 (10)*	
H8N	0.642 (4)	0.094 (2)	1.0311 (18)	0.068 (9)*	

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0168 (3)	0.0223 (3)	0.0236 (3)	0.0022 (2)	0.0046 (2)	0.0025 (2)
S1A	0.0208 (3)	0.0229 (3)	0.0204 (3)	0.0026 (2)	0.0060 (2)	0.0013 (2)
O1	0.0154 (8)	0.0475 (10)	0.0362 (9)	0.0040 (7)	0.0054 (7)	0.0123 (7)
O1A	0.0321 (9)	0.0203 (8)	0.0336 (9)	-0.0030 (6)	0.0027 (7)	0.0030 (6)
O2	0.0352 (9)	0.0209 (8)	0.0338 (9)	0.0033 (7)	0.0052 (7)	0.0063 (6)
O2A	0.0398 (10)	0.0631 (12)	0.0252 (9)	0.0237 (9)	0.0168 (8)	0.0112 (8)
O3	0.0302 (9)	0.0301 (8)	0.0225 (8)	0.0062 (7)	0.0054 (7)	-0.0005 (6)
O3A	0.0230 (8)	0.0249 (8)	0.0293 (8)	-0.0019 (6)	-0.0002 (6)	0.0015 (6)
O4	0.0336 (10)	0.0337 (9)	0.0266 (9)	0.0067 (8)	0.0072 (7)	0.0019 (7)
O4A	0.0287 (9)	0.0379 (9)	0.0254 (9)	0.0094 (8)	0.0091 (7)	0.0008 (7)

---

O5	0.0239 (9)	0.0340 (9)	0.0295 (9)	-0.0038 (7)	0.0041 (7)	0.0016 (7)
O5A	0.0416 (10)	0.0343 (10)	0.0299 (9)	0.0067 (8)	0.0155 (8)	0.0070 (7)
N1	0.0200 (9)	0.0224 (9)	0.0235 (9)	0.0030 (7)	0.0042 (7)	0.0002 (7)
N1A	0.0293 (11)	0.0220 (9)	0.0219 (9)	0.0034 (8)	0.0084 (8)	-0.0004 (7)
N2	0.0241 (10)	0.0210 (9)	0.0248 (10)	0.0033 (8)	0.0036 (8)	0.0017 (7)
N2A	0.0285 (10)	0.0212 (9)	0.0216 (9)	0.0043 (8)	0.0098 (8)	-0.0005 (7)
N3	0.0216 (10)	0.0212 (9)	0.0217 (9)	0.0042 (7)	0.0051 (7)	0.0028 (7)
N3A	0.0193 (9)	0.0204 (9)	0.0209 (9)	-0.0010 (7)	0.0047 (7)	0.0007 (7)
N4	0.0379 (13)	0.0289 (12)	0.0270 (11)	-0.0040 (10)	0.0154 (10)	-0.0051 (10)
N5	0.0321 (13)	0.0323 (12)	0.0232 (11)	0.0018 (10)	0.0088 (9)	0.0012 (9)
C1	0.0148 (10)	0.0180 (10)	0.0231 (11)	-0.0012 (8)	0.0050 (8)	0.0019 (8)
C1A	0.0208 (11)	0.0208 (10)	0.0201 (11)	0.0046 (8)	0.0076 (9)	-0.0018 (8)
C2	0.0229 (12)	0.0175 (10)	0.0286 (12)	0.0041 (8)	0.0061 (9)	0.0003 (9)
C2A	0.0249 (12)	0.0192 (10)	0.0240 (11)	-0.0007 (9)	0.0071 (9)	-0.0014 (8)
C3	0.0227 (11)	0.0202 (11)	0.0243 (11)	0.0002 (9)	0.0078 (9)	-0.0038 (8)
C3A	0.0236 (12)	0.0227 (11)	0.0234 (11)	0.0013 (9)	0.0044 (9)	-0.0026 (9)
C4	0.0160 (10)	0.0201 (10)	0.0223 (11)	-0.0017 (8)	0.0037 (8)	0.0003 (8)
C4A	0.0254 (12)	0.0216 (11)	0.0200 (11)	0.0055 (9)	0.0073 (9)	-0.0012 (8)
C5	0.0168 (11)	0.0217 (11)	0.0257 (11)	0.0054 (8)	0.0038 (9)	0.0004 (9)
C5A	0.0258 (12)	0.0215 (11)	0.0287 (12)	0.0004 (9)	0.0101 (9)	0.0030 (9)
C6	0.0170 (11)	0.0249 (11)	0.0246 (11)	0.0030 (9)	0.0053 (9)	-0.0027 (9)
C6A	0.0215 (11)	0.0252 (11)	0.0249 (11)	0.0005 (9)	0.0056 (9)	-0.0008 (9)
C7	0.0211 (11)	0.0233 (11)	0.0208 (11)	0.0024 (9)	0.0015 (9)	0.0007 (8)
C7A	0.0248 (12)	0.0219 (11)	0.0185 (11)	0.0055 (9)	0.0055 (9)	-0.0011 (8)
C8	0.0299 (13)	0.0243 (11)	0.0224 (11)	0.0040 (9)	0.0074 (9)	-0.0016 (9)
C8A	0.0212 (11)	0.0238 (11)	0.0224 (11)	0.0031 (9)	0.0042 (9)	-0.0008 (9)
C9	0.0276 (12)	0.0218 (11)	0.0240 (11)	0.0051 (9)	0.0049 (9)	-0.0024 (9)
C9A	0.0225 (11)	0.0195 (10)	0.0237 (11)	-0.0010 (8)	0.0078 (9)	-0.0006 (8)
C10	0.0160 (11)	0.0218 (11)	0.0222 (11)	-0.0002 (8)	0.0022 (8)	-0.0010 (8)
C10A	0.0218 (11)	0.0189 (10)	0.0201 (11)	0.0041 (8)	0.0091 (9)	-0.0021 (8)
C11	0.0219 (11)	0.0276 (11)	0.0210 (11)	0.0029 (9)	0.0073 (9)	-0.0019 (9)
C11A	0.0224 (11)	0.0215 (11)	0.0222 (11)	0.0002 (9)	0.0058 (9)	-0.0026 (8)
C12	0.0198 (11)	0.0222 (11)	0.0249 (11)	0.0040 (9)	0.0031 (9)	-0.0014 (9)
C12A	0.0296 (13)	0.0178 (10)	0.0253 (11)	-0.0003 (9)	0.0132 (9)	-0.0013 (8)
C13	0.0253 (12)	0.0234 (11)	0.0237 (11)	0.0000 (9)	0.0077 (9)	0.0031 (9)
C13A	0.0209 (11)	0.0288 (12)	0.0218 (11)	0.0010 (9)	0.0044 (9)	-0.0014 (9)
C14	0.0289 (13)	0.0244 (11)	0.0233 (12)	0.0011 (9)	0.0056 (9)	-0.0009 (9)
C14A	0.0258 (13)	0.0357 (13)	0.0278 (12)	-0.0045 (10)	0.0081 (10)	-0.0087 (10)
C15	0.0260 (12)	0.0177 (10)	0.0266 (12)	0.0018 (9)	0.0046 (9)	0.0022 (8)
C15A	0.0233 (12)	0.0209 (11)	0.0257 (12)	0.0041 (9)	0.0055 (9)	0.0031 (9)
C16	0.0278 (13)	0.0239 (11)	0.0271 (12)	0.0039 (9)	0.0064 (10)	-0.0012 (9)
C16A	0.0239 (12)	0.0262 (12)	0.0343 (13)	0.0024 (9)	0.0091 (10)	0.0046 (10)
O1W	0.0530 (12)	0.0355 (10)	0.0374 (10)	0.0040 (8)	0.0141 (9)	0.0100 (8)
O2W	0.114 (2)	0.0569 (14)	0.0507 (14)	-0.0083 (15)	-0.0009 (13)	0.0128 (11)

---

*Geometric parameters (Å, °)*

S1—O2	1.4431 (15)	C5—H5	0.9500
S1—O1	1.4566 (15)	C5A—C6A	1.389 (3)
S1—O3	1.4592 (15)	C5A—H5A	0.9500
S1—C1	1.770 (2)	C6—H6	0.9500
S1A—O2A	1.4462 (16)	C6A—H6A	0.9500
S1A—O3A	1.4559 (15)	C7—C8	1.390 (3)
S1A—O1A	1.4579 (15)	C7—C12	1.399 (3)
S1A—C1A	1.765 (2)	C7A—C8A	1.394 (3)
O4—C14	1.420 (3)	C7A—C12A	1.397 (3)
O4—H1H	0.84 (3)	C8—C9	1.381 (3)
O4A—C14A	1.429 (3)	C8—H8	0.9500
O4A—H3H	0.80 (3)	C8A—C9A	1.380 (3)
O5—C16	1.424 (3)	C8A—H8A	0.9500
O5—H2H	0.81 (3)	C9—C10	1.408 (3)
O5A—C16A	1.428 (3)	C9—H9	0.9500
O5A—H4H	0.97 (3)	C9A—C10A	1.411 (3)
N1—N2	1.264 (2)	C9A—H9A	0.9500
N1—C4	1.439 (2)	C10—C11	1.421 (3)
N1A—N2A	1.261 (2)	C10A—C11A	1.422 (3)
N1A—C4A	1.430 (3)	C11—C12	1.373 (3)
N2—C7	1.405 (2)	C11—H11	0.9500
N2A—C7A	1.416 (3)	C11A—C12A	1.371 (3)
N3—C10	1.374 (2)	C11A—H11A	0.9500
N3—C13	1.460 (3)	C12—H12	0.9500
N3—C15	1.464 (3)	C12A—H12A	0.9500
N3A—C10A	1.373 (2)	C13—C14	1.518 (3)
N3A—C15A	1.455 (2)	C13—H13A	0.9900
N3A—C13A	1.467 (3)	C13—H13B	0.9900
N4—H1N	0.87 (3)	C13A—C14A	1.513 (3)
N4—H2N	0.95 (3)	C13A—H13C	0.9900
N4—H3N	0.89 (3)	C13A—H13D	0.9900
N4—H4N	1.13 (4)	C14—H14A	0.9900
N5—H5N	0.91 (3)	C14—H14B	0.9900
N5—H6N	0.89 (4)	C14A—H14C	0.9900
N5—H7N	0.96 (4)	C14A—H14D	0.9900
N5—H8N	0.96 (3)	C15—C16	1.509 (3)
C1—C2	1.392 (3)	C15—H15A	0.9900
C1—C6	1.397 (3)	C15—H15B	0.9900
C1A—C2A	1.389 (3)	C15A—C16A	1.516 (3)
C1A—C6A	1.397 (3)	C15A—H15C	0.9900
C2—C3	1.384 (3)	C15A—H15D	0.9900
C2—H2	0.9500	C16—H16A	0.9900
C2A—C3A	1.379 (3)	C16—H16B	0.9900
C2A—H2A	0.9500	C16A—H16C	0.9900
C3—C4	1.393 (3)	C16A—H16D	0.9900
C3—H3	0.9500	O1W—H1W	0.875 (10)

C3A—C4A	1.390 (3)	O1W—H2W	0.882 (9)
C3A—H3A	0.9500	O2W—H3W	0.907 (10)
C4—C5	1.387 (3)	O2W—H4W	0.889 (10)
C4A—C5A	1.393 (3)	O2W—H5W	0.899 (10)
C5—C6	1.380 (3)		
O2—S1—O1	112.96 (9)	C9—C8—H8	119.1
O2—S1—O3	113.85 (9)	C7—C8—H8	119.1
O1—S1—O3	111.27 (9)	C9A—C8A—C7A	121.04 (19)
O2—S1—C1	107.12 (9)	C9A—C8A—H8A	119.5
O1—S1—C1	104.63 (9)	C7A—C8A—H8A	119.5
O3—S1—C1	106.25 (9)	C8—C9—C10	120.62 (19)
O2A—S1A—O3A	112.58 (10)	C8—C9—H9	119.7
O2A—S1A—O1A	112.66 (10)	C10—C9—H9	119.7
O3A—S1A—O1A	111.19 (9)	C8A—C9A—C10A	121.12 (18)
O2A—S1A—C1A	105.65 (9)	C8A—C9A—H9A	119.4
O3A—S1A—C1A	107.50 (9)	C10A—C9A—H9A	119.4
O1A—S1A—C1A	106.79 (9)	N3—C10—C9	121.13 (18)
C14—O4—H1H	109 (2)	N3—C10—C11	121.97 (18)
C14A—O4A—H3H	106 (2)	C9—C10—C11	116.90 (18)
C16—O5—H2H	107 (2)	N3A—C10A—C9A	121.74 (17)
C16A—O5A—H4H	106.9 (17)	N3A—C10A—C11A	121.25 (18)
N2—N1—C4	111.31 (16)	C9A—C10A—C11A	116.99 (18)
N2A—N1A—C4A	113.71 (17)	C12—C11—C10	121.86 (19)
N1—N2—C7	116.79 (17)	C12—C11—H11	119.1
N1A—N2A—C7A	113.68 (17)	C10—C11—H11	119.1
C10—N3—C13	121.50 (17)	C12A—C11A—C10A	121.17 (19)
C10—N3—C15	120.47 (17)	C12A—C11A—H11A	119.4
C13—N3—C15	117.88 (16)	C10A—C11A—H11A	119.4
C10A—N3A—C15A	120.69 (17)	C11—C12—C7	120.38 (19)
C10A—N3A—C13A	121.44 (16)	C11—C12—H12	119.8
C15A—N3A—C13A	117.84 (16)	C7—C12—H12	119.8
H1N—N4—H2N	98 (2)	C11A—C12A—C7A	121.10 (19)
H1N—N4—H3N	108 (2)	C11A—C12A—H12A	119.5
H2N—N4—H3N	109 (2)	C7A—C12A—H12A	119.5
H1N—N4—H4N	114 (2)	N3—C13—C14	114.18 (17)
H2N—N4—H4N	122 (2)	N3—C13—H13A	108.7
H3N—N4—H4N	105 (2)	C14—C13—H13A	108.7
H5N—N5—H6N	114 (3)	N3—C13—H13B	108.7
H5N—N5—H7N	111 (3)	C14—C13—H13B	108.7
H6N—N5—H7N	104 (3)	H13A—C13—H13B	107.6
H5N—N5—H8N	108 (2)	N3A—C13A—C14A	114.69 (17)
H6N—N5—H8N	106 (3)	N3A—C13A—H13C	108.6
H7N—N5—H8N	114 (3)	C14A—C13A—H13C	108.6
C2—C1—C6	119.76 (18)	N3A—C13A—H13D	108.6
C2—C1—S1	119.93 (15)	C14A—C13A—H13D	108.6
C6—C1—S1	119.99 (16)	H13C—C13A—H13D	107.6
C2A—C1A—C6A	120.26 (18)	O4—C14—C13	110.98 (17)



C2A—C1A—S1A	118.50 (15)	O4—C14—H14A	109.4
C6A—C1A—S1A	121.11 (16)	C13—C14—H14A	109.4
C3—C2—C1	120.12 (18)	O4—C14—H14B	109.4
C3—C2—H2	119.9	C13—C14—H14B	109.4
C1—C2—H2	119.9	H14A—C14—H14B	108.0
C3A—C2A—C1A	119.88 (19)	O4A—C14A—C13A	112.62 (18)
C3A—C2A—H2A	120.1	O4A—C14A—H14C	109.1
C1A—C2A—H2A	120.1	C13A—C14A—H14C	109.1
C2—C3—C4	119.95 (19)	O4A—C14A—H14D	109.1
C2—C3—H3	120.0	C13A—C14A—H14D	109.1
C4—C3—H3	120.0	H14C—C14A—H14D	107.8
C2A—C3A—C4A	120.4 (2)	N3—C15—C16	114.16 (17)
C2A—C3A—H3A	119.8	N3—C15—H15A	108.7
C4A—C3A—H3A	119.8	C16—C15—H15A	108.7
C5—C4—C3	119.75 (18)	N3—C15—H15B	108.7
C5—C4—N1	123.30 (17)	C16—C15—H15B	108.7
C3—C4—N1	116.82 (18)	H15A—C15—H15B	107.6
C3A—C4A—C5A	119.94 (18)	N3A—C15A—C16A	115.20 (17)
C3A—C4A—N1A	114.97 (18)	N3A—C15A—H15C	108.5
C5A—C4A—N1A	125.08 (18)	C16A—C15A—H15C	108.5
C6—C5—C4	120.56 (18)	N3A—C15A—H15D	108.5
C6—C5—H5	119.7	C16A—C15A—H15D	108.5
C4—C5—H5	119.7	H15C—C15A—H15D	107.5
C6A—C5A—C4A	119.94 (19)	O5—C16—C15	109.56 (18)
C6A—C5A—H5A	120.0	O5—C16—H16A	109.8
C4A—C5A—H5A	120.0	C15—C16—H16A	109.8
C5—C6—C1	119.72 (19)	O5—C16—H16B	109.8
C5—C6—H6	120.1	C15—C16—H16B	109.8
C1—C6—H6	120.1	H16A—C16—H16B	108.2
C5A—C6A—C1A	119.6 (2)	O5A—C16A—C15A	113.46 (18)
C5A—C6A—H6A	120.2	O5A—C16A—H16C	108.9
C1A—C6A—H6A	120.2	C15A—C16A—H16C	108.9
C8—C7—C12	118.44 (18)	O5A—C16A—H16D	108.9
C8—C7—N2	114.54 (18)	C15A—C16A—H16D	108.9
C12—C7—N2	126.97 (18)	H16C—C16A—H16D	107.7
C8A—C7A—C12A	118.49 (18)	H1W—O1W—H2W	99.8 (17)
C8A—C7A—N2A	116.70 (18)	H3W—O2W—H4W	97 (2)
C12A—C7A—N2A	124.81 (18)	H3W—O2W—H5W	95 (2)
C9—C8—C7	121.8 (2)	H4W—O2W—H5W	97 (7)
C4—N1—N2—C7	-176.00 (16)	N1A—N2A—C7A—C12A	7.7 (3)
C4A—N1A—N2A—C7A	-177.76 (16)	C12—C7—C8—C9	-1.6 (3)
O2—S1—C1—C2	56.35 (18)	N2—C7—C8—C9	-179.29 (19)
O1—S1—C1—C2	-63.79 (18)	C12A—C7A—C8A—C9A	-3.7 (3)
O3—S1—C1—C2	178.39 (16)	N2A—C7A—C8A—C9A	177.34 (18)
O2—S1—C1—C6	-130.20 (16)	C7—C8—C9—C10	1.5 (3)
O1—S1—C1—C6	109.65 (17)	C7A—C8A—C9A—C10A	1.5 (3)
O3—S1—C1—C6	-8.16 (19)	C13—N3—C10—C9	179.78 (19)

O2A—S1A—C1A—C2A	-69.61 (18)	C15—N3—C10—C9	-4.7 (3)
O3A—S1A—C1A—C2A	169.97 (15)	C13—N3—C10—C11	-0.8 (3)
O1A—S1A—C1A—C2A	50.56 (18)	C15—N3—C10—C11	174.65 (18)
O2A—S1A—C1A—C6A	106.12 (18)	C8—C9—C10—N3	178.38 (19)
O3A—S1A—C1A—C6A	-14.30 (19)	C8—C9—C10—C11	-1.0 (3)
O1A—S1A—C1A—C6A	-133.71 (17)	C15A—N3A—C10A—C9A	-4.9 (3)
C6—C1—C2—C3	-1.9 (3)	C13A—N3A—C10A—C9A	173.20 (18)
S1—C1—C2—C3	171.55 (15)	C15A—N3A—C10A—C11A	173.48 (18)
C6A—C1A—C2A—C3A	0.0 (3)	C13A—N3A—C10A—C11A	-8.4 (3)
S1A—C1A—C2A—C3A	175.81 (16)	C8A—C9A—C10A—N3A	179.49 (18)
C1—C2—C3—C4	-1.4 (3)	C8A—C9A—C10A—C11A	1.1 (3)
C1A—C2A—C3A—C4A	0.2 (3)	N3—C10—C11—C12	-178.63 (19)
C2—C3—C4—C5	3.4 (3)	C9—C10—C11—C12	0.8 (3)
C2—C3—C4—N1	-172.66 (18)	N3A—C10A—C11A—C12A	-179.79 (18)
N2—N1—C4—C5	4.0 (3)	C9A—C10A—C11A—C12A	-1.4 (3)
N2—N1—C4—C3	179.91 (18)	C10—C11—C12—C7	-0.9 (3)
C2A—C3A—C4A—C5A	-0.3 (3)	C8—C7—C12—C11	1.3 (3)
C2A—C3A—C4A—N1A	-179.21 (18)	N2—C7—C12—C11	178.69 (19)
N2A—N1A—C4A—C3A	174.69 (17)	C10A—C11A—C12A—C7A	-0.9 (3)
N2A—N1A—C4A—C5A	-4.2 (3)	C8A—C7A—C12A—C11A	3.4 (3)
C3—C4—C5—C6	-2.2 (3)	N2A—C7A—C12A—C11A	-177.73 (19)
N1—C4—C5—C6	173.63 (18)	C10—N3—C13—C14	-81.0 (2)
C3A—C4A—C5A—C6A	0.2 (3)	C15—N3—C13—C14	103.4 (2)
N1A—C4A—C5A—C6A	179.01 (19)	C10A—N3A—C13A—C14A	-71.0 (2)
C4—C5—C6—C1	-1.1 (3)	C15A—N3A—C13A—C14A	107.2 (2)
C2—C1—C6—C5	3.2 (3)	N3—C13—C14—O4	-179.84 (16)
S1—C1—C6—C5	-170.31 (15)	N3A—C13A—C14A—O4A	-66.8 (2)
C4A—C5A—C6A—C1A	0.0 (3)	C10—N3—C15—C16	84.3 (2)
C2A—C1A—C6A—C5A	-0.1 (3)	C13—N3—C15—C16	-100.0 (2)
S1A—C1A—C6A—C5A	-175.79 (16)	C10A—N3A—C15A—C16A	90.8 (2)
N1—N2—C7—C8	-178.25 (18)	C13A—N3A—C15A—C16A	-87.4 (2)
N1—N2—C7—C12	4.3 (3)	N3—C15—C16—O5	66.0 (2)
N1A—N2A—C7A—C8A	-173.40 (18)	N3A—C15A—C16A—O5A	85.7 (2)

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>
O1 <i>W</i> —H1 <i>W</i> ...O1 <sup>i</sup>	0.88 (1)	1.93 (1)	2.802 (2)	176 (3)
O1 <i>W</i> —H2 <i>W</i> ...O5 <sup>ii</sup>	0.88 (1)	1.84 (1)	2.711 (2)	168 (2)
O2 <i>W</i> —H3 <i>W</i> ...O1 <i>A</i> <sup>iii</sup>	0.91 (1)	2.05 (1)	2.945 (2)	172 (3)
O2 <i>W</i> —H4 <i>W</i> ...O2 <i>W</i> <sup>iii</sup>	0.89 (1)	2.29 (4)	3.031 (5)	141 (6)
O4—H1 <i>H</i> ...O3 <i>A</i> <sup>iv</sup>	0.84 (3)	2.05 (3)	2.885 (2)	169 (3)
O5—H2 <i>H</i> ...O1 <i>A</i>	0.81 (3)	1.90 (3)	2.698 (2)	169 (3)
O4 <i>A</i> —H3 <i>H</i> ...O1 <sup>i</sup>	0.80 (3)	1.96 (3)	2.756 (2)	177 (3)
O5 <i>A</i> —H4 <i>H</i> ...O4 <i>A</i>	0.97 (3)	1.79 (3)	2.734 (2)	165 (3)
N4—H1 <i>N</i> ...O3	0.87 (3)	2.09 (3)	2.957 (3)	176 (2)
N4—H2 <i>N</i> ...O2 <sup>v</sup>	0.95 (3)	1.92 (3)	2.841 (3)	163 (2)
N4—H3 <i>N</i> ...O3 <i>A</i> <sup>vi</sup>	0.89 (3)	2.05 (3)	2.923 (3)	167 (2)

N4—H4N···O1W	1.13 (4)	1.69 (4)	2.818 (3)	176 (3)
N5—H5N···O2A	0.91 (3)	1.89 (3)	2.784 (3)	164 (2)
N5—H6N···O5A <sup>vii</sup>	0.89 (4)	2.21 (4)	2.935 (3)	138 (3)
N5—H6N···O1W <sup>iii</sup>	0.89 (4)	2.51 (4)	3.094 (3)	123 (3)
N5—H7N···O3 <sup>ix</sup>	0.96 (4)	2.03 (4)	2.952 (3)	159 (3)
N5—H8N···O4 <sup>x</sup>	0.96 (3)	2.00 (3)	2.943 (3)	168 (3)

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

### Ammonium 3-[2-(4-hydroxyphenyl)diazen-1-yl]benzenesulfonate (NH45)

#### Crystal data

$\text{NH}_4^+ \cdot \text{C}_{12}\text{H}_9\text{N}_2\text{O}_4\text{S}^-$

$M_r = 295.31$

Orthorhombic, *Pccn*

$a = 12.6592$  (3) Å

$b = 28.3597$  (7) Å

$c = 7.1268$  (2) Å

$V = 2558.60$  (11) Å<sup>3</sup>

$Z = 8$

$F(000) = 1232$

$D_x = 1.533$  Mg m<sup>-3</sup>

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

Cell parameters from 3229 reflections

$\theta = 1.0$ – $27.5^\circ$

$\mu = 0.27$  mm<sup>-1</sup>

$T = 123$  K

Cut needle, yellow-orange

$0.30 \times 0.10 \times 0.05$  mm

#### Data collection

Enraf–Nonius KappaCCD  
diffractometer

Radiation source: sealed tube  
phi and  $\omega$  scans

5346 measured reflections

2923 independent reflections

1850 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.069$

$\theta_{\text{max}} = 27.5^\circ$ ,  $\theta_{\text{min}} = 1.8^\circ$

$h = -16 \rightarrow 16$

$k = -36 \rightarrow 36$

$l = -9 \rightarrow 9$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.051$

$wR(F^2) = 0.118$

$S = 1.03$

2923 reflections

201 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2 + 2.7325P]$

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

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

$\Delta\rho_{\text{max}} = 0.29$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.45$  e Å<sup>-3</sup>

#### 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 (Å<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.94027 (5)	0.56239 (2)	0.18127 (9)	0.01749 (18)
O1	0.85668 (15)	0.55115 (7)	0.0463 (3)	0.0287 (5)
O2	1.04360 (14)	0.56367 (7)	0.0953 (3)	0.0278 (5)
O3	0.93547 (16)	0.53174 (7)	0.3437 (3)	0.0301 (5)

O4	1.24530 (16)	0.93197 (7)	0.0369 (3)	0.0255 (5)
N1	1.02393 (17)	0.73916 (8)	0.2062 (3)	0.0203 (5)
N2	0.99241 (18)	0.78005 (9)	0.2434 (3)	0.0203 (5)
N3	0.6639 (2)	0.50958 (11)	0.1885 (4)	0.0229 (6)
C1	0.9119 (2)	0.62035 (10)	0.2584 (3)	0.0168 (6)
C2	0.9772 (2)	0.65733 (10)	0.2101 (4)	0.0180 (6)
H2	1.039750	0.651624	0.139888	0.022*
C3	0.9512 (2)	0.70309 (10)	0.2644 (4)	0.0176 (6)
C4	0.8602 (2)	0.71133 (10)	0.3688 (4)	0.0206 (6)
H4	0.842341	0.742487	0.406115	0.025*
C5	0.7955 (2)	0.67381 (10)	0.4181 (4)	0.0222 (7)
H5	0.733423	0.679368	0.489583	0.027*
C6	0.8209 (2)	0.62841 (10)	0.3640 (4)	0.0202 (6)
H6	0.776597	0.602809	0.398488	0.024*
C7	1.0619 (2)	0.81667 (10)	0.1844 (4)	0.0181 (6)
C8	1.1588 (2)	0.80929 (10)	0.0944 (4)	0.0220 (6)
H8	1.181883	0.778107	0.068094	0.026*
C9	1.2208 (2)	0.84727 (10)	0.0436 (4)	0.0208 (6)
H9	1.286594	0.842325	−0.017454	0.025*
C10	1.1862 (2)	0.89298 (10)	0.0825 (4)	0.0182 (6)
C11	1.0895 (2)	0.90081 (10)	0.1682 (4)	0.0200 (6)
H11	1.065732	0.932015	0.191929	0.024*
C12	1.0278 (2)	0.86232 (10)	0.2188 (4)	0.0191 (6)
H12	0.961388	0.867354	0.277683	0.023*
H1N	0.673 (3)	0.4784 (13)	0.204 (5)	0.042 (10)*
H2N	0.731 (3)	0.5206 (11)	0.146 (5)	0.046 (10)*
H3N	0.641 (2)	0.5235 (11)	0.292 (4)	0.026 (8)*
H4N	0.619 (3)	0.5176 (12)	0.096 (5)	0.048 (11)*
H1H	1.306 (3)	0.9239 (14)	0.020 (6)	0.063 (13)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0153 (3)	0.0193 (3)	0.0179 (3)	0.0001 (3)	0.0004 (3)	0.0010 (3)
O1	0.0239 (11)	0.0337 (13)	0.0287 (11)	0.0064 (9)	−0.0101 (9)	−0.0126 (10)
O2	0.0172 (10)	0.0255 (11)	0.0407 (12)	0.0015 (9)	0.0095 (9)	0.0013 (10)
O3	0.0488 (13)	0.0207 (11)	0.0208 (10)	0.0014 (10)	0.0054 (10)	0.0055 (9)
O4	0.0188 (10)	0.0256 (12)	0.0319 (11)	−0.0016 (10)	0.0045 (10)	0.0032 (10)
N1	0.0191 (11)	0.0208 (13)	0.0211 (12)	−0.0016 (10)	−0.0006 (10)	−0.0001 (11)
N2	0.0211 (13)	0.0203 (13)	0.0194 (12)	−0.0017 (11)	−0.0025 (9)	0.0018 (10)
N3	0.0259 (14)	0.0243 (15)	0.0185 (13)	0.0008 (12)	0.0015 (13)	−0.0021 (13)
C1	0.0166 (14)	0.0197 (15)	0.0141 (13)	0.0011 (12)	−0.0008 (11)	0.0025 (12)
C2	0.0138 (13)	0.0220 (15)	0.0182 (14)	0.0010 (12)	−0.0001 (11)	−0.0002 (12)
C3	0.0135 (13)	0.0231 (15)	0.0163 (13)	−0.0053 (12)	−0.0040 (11)	0.0036 (12)
C4	0.0185 (13)	0.0198 (16)	0.0235 (14)	0.0025 (12)	−0.0007 (12)	−0.0006 (13)
C5	0.0168 (14)	0.0278 (18)	0.0218 (15)	0.0033 (12)	0.0023 (12)	0.0002 (13)
C6	0.0165 (13)	0.0239 (16)	0.0200 (14)	−0.0017 (12)	−0.0003 (12)	0.0025 (13)
C7	0.0173 (12)	0.0212 (14)	0.0156 (13)	−0.0023 (12)	−0.0055 (12)	−0.0001 (12)

C8	0.0217 (14)	0.0219 (16)	0.0225 (15)	0.0016 (12)	-0.0022 (12)	-0.0031 (13)
C9	0.0162 (14)	0.0270 (17)	0.0193 (14)	0.0004 (12)	0.0000 (11)	-0.0023 (13)
C10	0.0172 (14)	0.0211 (16)	0.0163 (14)	-0.0034 (12)	-0.0031 (11)	0.0014 (12)
C11	0.0193 (13)	0.0186 (15)	0.0222 (14)	0.0020 (11)	-0.0021 (12)	0.0007 (13)
C12	0.0158 (13)	0.0241 (16)	0.0174 (13)	-0.0008 (12)	-0.0015 (11)	-0.0007 (13)

*Geometric parameters (Å, °)*

S1—O2	1.4449 (19)	C3—C4	1.392 (4)
S1—O3	1.449 (2)	C4—C5	1.387 (4)
S1—O1	1.4648 (19)	C4—H4	0.9500
S1—C1	1.770 (3)	C5—C6	1.382 (4)
O4—C10	1.374 (3)	C5—H5	0.9500
O4—H1H	0.82 (4)	C6—H6	0.9500
N1—N2	1.254 (3)	C7—C12	1.387 (4)
N1—C3	1.437 (3)	C7—C8	1.400 (4)
N2—C7	1.425 (3)	C8—C9	1.381 (4)
N3—H1N	0.90 (4)	C8—H8	0.9500
N3—H2N	0.96 (4)	C9—C10	1.396 (4)
N3—H3N	0.89 (3)	C9—H9	0.9500
N3—H4N	0.90 (4)	C10—C11	1.386 (4)
C1—C2	1.379 (4)	C11—C12	1.390 (4)
C1—C6	1.395 (4)	C11—H11	0.9500
C2—C3	1.394 (4)	C12—H12	0.9500
C2—H2	0.9500		
O2—S1—O3	113.06 (12)	C3—C4—H4	120.2
O2—S1—O1	112.41 (12)	C6—C5—C4	120.4 (3)
O3—S1—O1	111.33 (12)	C6—C5—H5	119.8
O2—S1—C1	106.97 (12)	C4—C5—H5	119.8
O3—S1—C1	107.48 (12)	C5—C6—C1	119.7 (3)
O1—S1—C1	105.04 (12)	C5—C6—H6	120.2
C10—O4—H1H	109 (3)	C1—C6—H6	120.2
N2—N1—C3	113.2 (2)	C12—C7—C8	119.6 (3)
N1—N2—C7	114.5 (2)	C12—C7—N2	115.9 (2)
H1N—N3—H2N	105 (3)	C8—C7—N2	124.6 (2)
H1N—N3—H3N	112 (3)	C9—C8—C7	120.1 (3)
H2N—N3—H3N	114 (3)	C9—C8—H8	120.0
H1N—N3—H4N	114 (3)	C7—C8—H8	120.0
H2N—N3—H4N	105 (3)	C8—C9—C10	119.6 (3)
H3N—N3—H4N	107 (3)	C8—C9—H9	120.2
C2—C1—C6	120.4 (3)	C10—C9—H9	120.2
C2—C1—S1	120.5 (2)	O4—C10—C11	117.1 (2)
C6—C1—S1	119.2 (2)	O4—C10—C9	122.0 (2)
C1—C2—C3	119.8 (2)	C11—C10—C9	120.9 (3)
C1—C2—H2	120.1	C10—C11—C12	119.0 (3)
C3—C2—H2	120.1	C10—C11—H11	120.5
C4—C3—C2	120.0 (2)	C12—C11—H11	120.5



C4—C3—N1	124.4 (3)	C7—C12—C11	120.8 (3)
C2—C3—N1	115.6 (2)	C7—C12—H12	119.6
C5—C4—C3	119.7 (3)	C11—C12—H12	119.6
C5—C4—H4	120.2		
C3—N1—N2—C7	-178.9 (2)	C4—C5—C6—C1	-0.3 (4)
O2—S1—C1—C2	8.3 (3)	C2—C1—C6—C5	0.8 (4)
O3—S1—C1—C2	130.0 (2)	S1—C1—C6—C5	-177.2 (2)
O1—S1—C1—C2	-111.3 (2)	N1—N2—C7—C12	178.2 (2)
O2—S1—C1—C6	-173.6 (2)	N1—N2—C7—C8	-0.8 (4)
O3—S1—C1—C6	-51.9 (2)	C12—C7—C8—C9	1.3 (4)
O1—S1—C1—C6	66.7 (2)	N2—C7—C8—C9	-179.7 (2)
C6—C1—C2—C3	-1.0 (4)	C7—C8—C9—C10	-0.1 (4)
S1—C1—C2—C3	177.0 (2)	C8—C9—C10—O4	179.3 (2)
C1—C2—C3—C4	0.6 (4)	C8—C9—C10—C11	-1.3 (4)
C1—C2—C3—N1	-179.6 (2)	O4—C10—C11—C12	-179.2 (2)
N2—N1—C3—C4	-6.4 (4)	C9—C10—C11—C12	1.3 (4)
N2—N1—C3—C2	173.9 (2)	C8—C7—C12—C11	-1.3 (4)
C2—C3—C4—C5	-0.1 (4)	N2—C7—C12—C11	179.6 (2)
N1—C3—C4—C5	-179.8 (2)	C10—C11—C12—C7	-0.1 (4)
C3—C4—C5—C6	-0.1 (4)		

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>
N3—H1N...O2 <sup>i</sup>	0.90 (4)	2.48 (3)	3.002 (4)	118 (3)
N3—H1N...O4 <sup>ii</sup>	0.90 (4)	2.35 (3)	2.913 (4)	121 (3)
N3—H1N...O4 <sup>iii</sup>	0.90 (4)	2.50 (4)	3.162 (4)	131 (3)
N3—H2N...O1	0.96 (4)	1.94 (4)	2.893 (3)	171 (3)
N3—H3N...O1 <sup>iv</sup>	0.89 (3)	1.97 (3)	2.822 (3)	159 (3)
N3—H4N...O3 <sup>v</sup>	0.90 (4)	1.97 (4)	2.831 (3)	160 (3)
O4—H1H...O2 <sup>vi</sup>	0.82 (4)	2.00 (4)	2.707 (3)	144 (4)

Symmetry codes: (i)  $x-1/2, -y+1, -z+1/2$ ; (ii)  $x-1/2, y-1/2, -z$ ; (iii)  $-x+2, y-1/2, -z+1/2$ ; (iv)  $-x+3/2, y, z+1/2$ ; (v)  $-x+3/2, y, z-1/2$ ; (vi)  $-x+5/2, -y+3/2, z$ .

Poly[aqua{4-[2-(4-hydroxyphenyl)diazen-1-yl]benzenesulfonato}potassium] (K1)

Crystal data

[K(C<sub>12</sub>H<sub>9</sub>N<sub>2</sub>O<sub>4</sub>S)(H<sub>2</sub>O)]

*M<sub>r</sub>* = 334.39

Triclinic, *P*1̄

*a* = 5.9620 (7) Å

*b* = 7.2033 (11) Å

*c* = 31.929 (5) Å

α = 83.852 (14)°

β = 86.361 (15)°

γ = 88.868 (15)°

*V* = 1360.5 (3) Å<sup>3</sup>

*Z* = 4

*F*(000) = 688

*D<sub>x</sub>* = 1.633 Mg m<sup>-3</sup>

Synchrotron radiation, λ = 0.689 Å

Cell parameters from 10143 reflections

θ = 2.5–26.0°

μ = 0.51 mm<sup>-1</sup>

*T* = 150 K

Plate, yellow

0.20 × 0.14 × 0.03 mm

Data collection

Bruker APEXII CCD  
diffractometer

Radiation source: Daresbury SRS Station 9.8

$\omega$  scans

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

$T_{\min} = 0.751$ ,  $T_{\max} = 1.000$

10143 measured reflections

5691 independent reflections

4405 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 26.0^\circ$ ,  $\theta_{\min} = 2.5^\circ$

$h = -7 \rightarrow 7$

$k = -9 \rightarrow 9$

$l = -40 \rightarrow 39$

Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.060$

$wR(F^2) = 0.180$

$S = 1.02$

5691 reflections

403 parameters

6 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent

and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1366P)^2]$

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

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

$\Delta\rho_{\max} = 0.59 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.67 \text{ e } \text{\AA}^{-3}$

Special details

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
K1	0.36696 (11)	-0.01827 (9)	0.75009 (2)	0.02505 (19)
K2	1.04941 (11)	-0.53233 (10)	0.77938 (2)	0.02465 (19)
S1	-0.11322 (12)	-0.24184 (10)	0.69389 (2)	0.01926 (19)
S2	0.54537 (12)	-0.32684 (11)	0.83209 (2)	0.0213 (2)
O1	0.0904 (4)	-0.2355 (3)	0.71678 (6)	0.0268 (5)
O2	-0.2642 (4)	-0.0810 (3)	0.69821 (6)	0.0277 (5)
O3	-0.2304 (4)	-0.4194 (3)	0.70500 (7)	0.0281 (5)
O4	0.5925 (4)	-0.2727 (3)	0.32948 (6)	0.0285 (5)
O5	0.6597 (4)	-0.4995 (3)	0.82126 (7)	0.0306 (5)
O6	0.6621 (4)	-0.1604 (4)	0.81212 (7)	0.0371 (6)
O7	0.3080 (4)	-0.3207 (3)	0.82324 (6)	0.0254 (5)
O8	0.9857 (4)	-0.0787 (3)	1.18624 (6)	0.0246 (5)
O1W	0.9915 (4)	-0.7663 (3)	0.70673 (7)	0.0294 (5)
O2W	1.4663 (4)	-0.6612 (3)	0.75731 (7)	0.0267 (5)
N1	0.1526 (4)	-0.2478 (4)	0.51080 (8)	0.0241 (6)
N2	0.3607 (4)	-0.2444 (4)	0.50057 (8)	0.0244 (6)
N3	0.6433 (4)	-0.2553 (3)	1.01425 (7)	0.0211 (5)
N4	0.8446 (4)	-0.2370 (3)	1.02266 (8)	0.0219 (5)
C1	-0.0256 (5)	-0.2344 (4)	0.63988 (8)	0.0188 (6)
C2	0.1890 (5)	-0.3011 (4)	0.62818 (9)	0.0224 (6)
H2	0.289784	-0.343168	0.649169	0.027*
C3	0.2539 (5)	-0.3054 (4)	0.58561 (9)	0.0229 (6)

H3	0.399776	-0.348997	0.577331	0.027*
C4	0.1017 (5)	-0.2448 (4)	0.55507 (9)	0.0210 (6)
C5	-0.1142 (5)	-0.1801 (5)	0.56692 (9)	0.0261 (7)
H5	-0.216726	-0.140838	0.546051	0.031*
C6	-0.1768 (5)	-0.1740 (4)	0.60948 (9)	0.0221 (6)
H6	-0.321876	-0.128863	0.617822	0.027*
C7	0.4134 (5)	-0.2564 (4)	0.45656 (9)	0.0223 (6)
C8	0.6279 (5)	-0.2012 (4)	0.44089 (9)	0.0240 (6)
H8	0.731988	-0.162898	0.459482	0.029*
C9	0.6902 (5)	-0.2017 (4)	0.39842 (9)	0.0223 (6)
H9	0.834366	-0.158982	0.387603	0.027*
C10	0.5398 (5)	-0.2654 (4)	0.37162 (9)	0.0214 (6)
C11	0.3261 (5)	-0.3279 (5)	0.38736 (9)	0.0250 (6)
H11	0.225448	-0.374106	0.369166	0.030*
C12	0.2637 (5)	-0.3213 (5)	0.42974 (9)	0.0251 (7)
H12	0.118444	-0.361226	0.440581	0.030*
C13	0.5661 (5)	-0.3265 (4)	0.88708 (9)	0.0201 (6)
C14	0.3888 (5)	-0.2573 (4)	0.91189 (9)	0.0239 (6)
H14	0.250402	-0.221333	0.899981	0.029*
C15	0.4177 (5)	-0.2415 (4)	0.95442 (9)	0.0227 (6)
H15	0.297484	-0.197564	0.971870	0.027*
C16	0.6237 (5)	-0.2906 (4)	0.97118 (9)	0.0192 (6)
C17	0.7970 (5)	-0.3667 (4)	0.94658 (9)	0.0219 (6)
H17	0.934209	-0.405492	0.958599	0.026*
C18	0.7675 (5)	-0.3852 (4)	0.90454 (9)	0.0235 (6)
H18	0.884138	-0.437672	0.887653	0.028*
C19	0.8724 (5)	-0.2009 (4)	1.06517 (8)	0.0199 (6)
C20	1.0813 (5)	-0.1333 (4)	1.07323 (9)	0.0216 (6)
H20	1.196039	-0.116093	1.051188	0.026*
C21	1.1211 (5)	-0.0912 (4)	1.11342 (9)	0.0214 (6)
H21	1.263161	-0.044719	1.118899	0.026*
C22	0.9530 (5)	-0.1169 (4)	1.14585 (9)	0.0209 (6)
C23	0.7465 (5)	-0.1886 (4)	1.13802 (9)	0.0222 (6)
H23	0.633336	-0.207817	1.160321	0.027*
C24	0.7039 (5)	-0.2324 (4)	1.09797 (9)	0.0214 (6)
H24	0.563378	-0.282682	1.092802	0.026*
H4H	0.736 (2)	-0.251 (5)	0.3235 (11)	0.025 (9)*
H8H	1.121 (4)	-0.034 (7)	1.1861 (17)	0.075 (17)*
H1W	0.909 (6)	-0.666 (3)	0.7025 (12)	0.040 (11)*
H2W	0.908 (7)	-0.862 (5)	0.7037 (16)	0.060 (15)*
H3W	1.510 (7)	-0.619 (6)	0.7314 (6)	0.043 (11)*
H4W	1.541 (7)	-0.598 (6)	0.7737 (12)	0.051 (13)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
K1	0.0278 (4)	0.0274 (4)	0.0203 (3)	0.0015 (3)	-0.0027 (3)	-0.0038 (3)
K2	0.0222 (4)	0.0303 (4)	0.0206 (3)	0.0020 (3)	-0.0018 (2)	0.0010 (3)

S1	0.0225 (4)	0.0210 (4)	0.0138 (3)	0.0025 (3)	0.0000 (3)	-0.0006 (3)
S2	0.0225 (4)	0.0284 (4)	0.0133 (3)	-0.0015 (3)	-0.0034 (3)	-0.0025 (3)
O1	0.0307 (12)	0.0315 (12)	0.0184 (10)	0.0001 (9)	-0.0038 (8)	-0.0022 (9)
O2	0.0298 (12)	0.0324 (12)	0.0202 (11)	0.0116 (9)	0.0018 (8)	-0.0032 (9)
O3	0.0328 (12)	0.0253 (12)	0.0248 (11)	-0.0031 (9)	0.0047 (9)	0.0007 (9)
O4	0.0298 (12)	0.0408 (14)	0.0146 (10)	0.0061 (10)	-0.0013 (8)	-0.0032 (9)
O5	0.0295 (12)	0.0425 (14)	0.0223 (11)	0.0108 (10)	-0.0040 (9)	-0.0148 (10)
O6	0.0503 (15)	0.0400 (15)	0.0209 (11)	-0.0217 (12)	-0.0086 (10)	0.0043 (10)
O7	0.0260 (11)	0.0308 (12)	0.0206 (10)	0.0020 (9)	-0.0076 (8)	-0.0054 (9)
O8	0.0288 (12)	0.0326 (12)	0.0127 (9)	-0.0007 (9)	-0.0031 (8)	-0.0034 (8)
O1W	0.0303 (13)	0.0298 (13)	0.0277 (12)	0.0033 (10)	-0.0002 (9)	-0.0034 (10)
O2W	0.0299 (12)	0.0301 (12)	0.0201 (11)	-0.0065 (9)	0.0039 (9)	-0.0046 (9)
N1	0.0303 (14)	0.0253 (14)	0.0169 (12)	0.0039 (10)	-0.0013 (10)	-0.0038 (10)
N2	0.0268 (13)	0.0285 (14)	0.0173 (12)	0.0021 (10)	0.0004 (10)	-0.0011 (10)
N3	0.0247 (13)	0.0244 (13)	0.0145 (11)	0.0036 (10)	-0.0051 (9)	-0.0027 (9)
N4	0.0292 (14)	0.0206 (13)	0.0162 (11)	0.0042 (10)	-0.0030 (9)	-0.0037 (9)
C1	0.0262 (15)	0.0155 (13)	0.0146 (13)	-0.0017 (11)	0.0016 (10)	-0.0020 (10)
C2	0.0247 (15)	0.0246 (15)	0.0174 (13)	0.0030 (11)	-0.0010 (11)	-0.0007 (11)
C3	0.0207 (14)	0.0276 (16)	0.0195 (14)	0.0047 (11)	-0.0004 (11)	-0.0007 (11)
C4	0.0218 (14)	0.0246 (15)	0.0163 (13)	0.0020 (11)	-0.0007 (10)	-0.0014 (11)
C5	0.0242 (15)	0.0342 (18)	0.0187 (14)	0.0072 (12)	-0.0029 (11)	0.0018 (12)
C6	0.0190 (14)	0.0270 (16)	0.0200 (14)	0.0043 (11)	-0.0036 (11)	-0.0004 (11)
C7	0.0264 (15)	0.0251 (15)	0.0147 (13)	0.0057 (11)	-0.0021 (11)	0.0010 (11)
C8	0.0267 (15)	0.0255 (16)	0.0210 (15)	0.0001 (12)	-0.0020 (11)	-0.0080 (12)
C9	0.0228 (14)	0.0226 (15)	0.0213 (14)	-0.0006 (11)	-0.0003 (11)	-0.0017 (11)
C10	0.0247 (15)	0.0240 (15)	0.0149 (13)	0.0057 (11)	-0.0025 (10)	0.0005 (11)
C11	0.0235 (15)	0.0318 (17)	0.0201 (14)	0.0042 (12)	-0.0055 (11)	-0.0037 (12)
C12	0.0216 (15)	0.0320 (17)	0.0207 (14)	0.0034 (12)	-0.0008 (11)	-0.0001 (12)
C13	0.0255 (15)	0.0218 (14)	0.0131 (12)	0.0022 (11)	-0.0056 (10)	-0.0007 (10)
C14	0.0230 (15)	0.0292 (16)	0.0189 (14)	0.0035 (11)	-0.0007 (11)	-0.0005 (11)
C15	0.0250 (15)	0.0252 (16)	0.0182 (13)	0.0028 (11)	-0.0003 (11)	-0.0039 (11)
C16	0.0233 (14)	0.0170 (14)	0.0172 (13)	-0.0010 (10)	-0.0024 (10)	0.0004 (10)
C17	0.0227 (14)	0.0252 (15)	0.0187 (14)	0.0033 (11)	-0.0071 (11)	-0.0040 (11)
C18	0.0240 (15)	0.0307 (16)	0.0161 (13)	0.0067 (12)	-0.0029 (11)	-0.0040 (11)
C19	0.0282 (15)	0.0212 (14)	0.0110 (12)	0.0085 (11)	-0.0057 (10)	-0.0042 (10)
C20	0.0164 (13)	0.0290 (16)	0.0192 (14)	-0.0004 (11)	-0.0012 (10)	-0.0019 (11)
C21	0.0222 (14)	0.0228 (15)	0.0193 (14)	-0.0012 (11)	-0.0039 (11)	-0.0012 (11)
C22	0.0274 (15)	0.0201 (14)	0.0148 (13)	0.0041 (11)	-0.0040 (11)	0.0012 (10)
C23	0.0263 (15)	0.0248 (15)	0.0147 (13)	0.0000 (11)	0.0000 (11)	0.0002 (11)
C24	0.0201 (14)	0.0225 (15)	0.0213 (14)	0.0001 (11)	-0.0044 (11)	0.0009 (11)

---

*Geometric parameters (Å, °)*

K1—O1	2.642 (2)	N3—N4	1.258 (4)
K1—O2W <sup>i</sup>	2.688 (3)	N3—C16	1.437 (4)
K1—O2 <sup>ii</sup>	2.728 (2)	N4—C19	1.429 (4)
K1—O6	2.829 (3)	C1—C6	1.396 (4)
K1—O8 <sup>iii</sup>	2.957 (2)	C1—C2	1.400 (4)

---

K1—O7	3.027 (2)	C2—C3	1.393 (4)
K1—O4 <sup>iv</sup>	3.116 (2)	C2—H2	0.9500
K1—O1W <sup>i</sup>	3.149 (2)	C3—C4	1.404 (4)
K1—S2	3.4555 (11)	C3—H3	0.9500
K1—K2 <sup>i</sup>	4.1142 (12)	C4—C5	1.403 (4)
K1—K2 <sup>v</sup>	4.1810 (12)	C5—C6	1.391 (4)
K2—O5	2.625 (2)	C5—H5	0.9500
K2—O2W	2.713 (2)	C6—H6	0.9500
K2—O7 <sup>ii</sup>	2.736 (2)	C7—C8	1.393 (4)
K2—O1 <sup>ii</sup>	2.769 (2)	C7—C12	1.396 (4)
K2—O8 <sup>vi</sup>	2.904 (2)	C8—C9	1.383 (4)
K2—O3 <sup>ii</sup>	3.020 (2)	C8—H8	0.9500
K2—O1W	3.050 (3)	C9—C10	1.395 (4)
K2—C22 <sup>vi</sup>	3.285 (3)	C9—H9	0.9500
K2—C23 <sup>vi</sup>	3.414 (3)	C10—C11	1.404 (4)
K2—S1 <sup>ii</sup>	3.4353 (11)	C11—C12	1.386 (4)
K2—S2	3.7108 (11)	C11—H11	0.9500
K2—H1W	2.91 (4)	C12—H12	0.9500
K2—H4W	2.96 (4)	C13—C18	1.395 (4)
S1—O1	1.460 (2)	C13—C14	1.397 (4)
S1—O2	1.466 (2)	C14—C15	1.396 (4)
S1—O3	1.469 (2)	C14—H14	0.9500
S1—C1	1.765 (3)	C15—C16	1.395 (4)
S2—O7	1.460 (2)	C15—H15	0.9500
S2—O6	1.464 (2)	C16—C17	1.397 (4)
S2—O5	1.470 (2)	C17—C18	1.385 (4)
S2—C13	1.768 (3)	C17—H17	0.9500
O4—C10	1.368 (3)	C18—H18	0.9500
O4—H4H	0.880 (10)	C19—C20	1.395 (4)
O8—C22	1.374 (4)	C19—C24	1.408 (4)
O8—H8H	0.876 (11)	C20—C21	1.386 (4)
O1W—H1W	0.872 (10)	C20—H20	0.9500
O1W—H2W	0.877 (10)	C21—C22	1.395 (4)
O2W—H3W	0.875 (10)	C21—H21	0.9500
O2W—H4W	0.878 (10)	C22—C23	1.392 (4)
N1—N2	1.262 (4)	C23—C24	1.389 (4)
N1—C4	1.429 (4)	C23—H23	0.9500
N2—C7	1.432 (4)	C24—H24	0.9500
O1—K1—O2W <sup>i</sup>	143.99 (8)	S1 <sup>ii</sup> —K2—H4W	110.8 (9)
O1—K1—O2 <sup>ii</sup>	96.82 (7)	S2—K2—H4W	149.6 (4)
O2W <sup>i</sup> —K1—O2 <sup>ii</sup>	94.96 (7)	K1 <sup>vii</sup> —K2—H4W	54.5 (6)
O1—K1—O6	122.07 (7)	H1W—K2—H4W	102.9 (8)
O2W <sup>i</sup> —K1—O6	93.29 (8)	O1—S1—O2	113.45 (14)
O2 <sup>ii</sup> —K1—O6	81.29 (7)	O1—S1—O3	111.38 (13)
O1—K1—O8 <sup>iii</sup>	91.74 (7)	O2—S1—O3	111.79 (13)
O2W <sup>i</sup> —K1—O8 <sup>iii</sup>	78.80 (7)	O1—S1—C1	106.56 (13)
O2 <sup>ii</sup> —K1—O8 <sup>iii</sup>	171.32 (7)	O2—S1—C1	106.74 (13)

O6—K1—O8 <sup>iii</sup>	92.97 (7)	O3—S1—C1	106.42 (13)
O1—K1—O7	81.20 (7)	O1—S1—K2 <sup>v</sup>	51.36 (9)
O2W <sup>i</sup> —K1—O7	124.81 (7)	O2—S1—K2 <sup>v</sup>	122.43 (9)
O2 <sup>ii</sup> —K1—O7	112.15 (7)	O3—S1—K2 <sup>v</sup>	61.34 (10)
O6—K1—O7	48.56 (6)	C1—S1—K2 <sup>v</sup>	130.60 (10)
O8 <sup>iii</sup> —K1—O7	67.71 (6)	O7—S2—O6	111.40 (15)
O1—K1—O4 <sup>iv</sup>	94.29 (7)	O7—S2—O5	112.83 (14)
O2W <sup>i</sup> —K1—O4 <sup>iv</sup>	59.54 (7)	O6—S2—O5	111.82 (15)
O2 <sup>ii</sup> —K1—O4 <sup>iv</sup>	67.50 (6)	O7—S2—C13	108.58 (13)
O6—K1—O4 <sup>iv</sup>	134.83 (7)	O6—S2—C13	106.38 (14)
O8 <sup>iii</sup> —K1—O4 <sup>iv</sup>	113.39 (6)	O5—S2—C13	105.38 (13)
O7—K1—O4 <sup>iv</sup>	175.43 (7)	O7—S2—K1	60.88 (9)
O1—K1—O1W <sup>i</sup>	71.39 (7)	O6—S2—K1	53.06 (10)
O2W <sup>i</sup> —K1—O1W <sup>i</sup>	72.75 (7)	O5—S2—K1	117.59 (9)
O2 <sup>ii</sup> —K1—O1W <sup>i</sup>	114.51 (7)	C13—S2—K1	136.61 (10)
O6—K1—O1W <sup>i</sup>	159.23 (7)	O7—S2—K2	132.58 (9)
O8 <sup>iii</sup> —K1—O1W <sup>i</sup>	69.63 (6)	O6—S2—K2	77.99 (12)
O7—K1—O1W <sup>i</sup>	127.79 (6)	O5—S2—K2	34.05 (10)
O4 <sup>iv</sup> —K1—O1W <sup>i</sup>	50.58 (6)	C13—S2—K2	112.84 (10)
O1—K1—S2	99.79 (5)	K1—S2—K2	100.28 (2)
O2W <sup>i</sup> —K1—S2	113.31 (6)	S1—O1—K1	145.40 (14)
O2 <sup>ii</sup> —K1—S2	93.51 (5)	S1—O1—K2 <sup>v</sup>	104.32 (11)
O6—K1—S2	24.42 (5)	K1—O1—K2 <sup>v</sup>	101.16 (7)
O8 <sup>iii</sup> —K1—S2	83.59 (5)	S1—O2—K1 <sup>v</sup>	133.87 (12)
O7—K1—S2	24.92 (4)	S1—O3—K2 <sup>v</sup>	93.40 (11)
O4 <sup>iv</sup> —K1—S2	157.67 (5)	C10—O4—K1 <sup>iv</sup>	135.45 (18)
O1W <sup>i</sup> —K1—S2	151.14 (5)	C10—O4—H4H	110 (2)
O1—K1—K2 <sup>i</sup>	111.21 (5)	K1 <sup>iv</sup> —O4—H4H	72 (2)
O2W <sup>i</sup> —K1—K2 <sup>i</sup>	40.61 (5)	S2—O5—K2	127.68 (14)
O2 <sup>ii</sup> —K1—K2 <sup>i</sup>	131.67 (5)	S2—O6—K1	102.52 (12)
O6—K1—K2 <sup>i</sup>	112.19 (6)	S2—O7—K2 <sup>v</sup>	133.41 (13)
O8 <sup>iii</sup> —K1—K2 <sup>i</sup>	44.90 (5)	S2—O7—K1	94.20 (10)
O7—K1—K2 <sup>i</sup>	110.51 (5)	K2 <sup>v</sup> —O7—K1	92.89 (6)
O4 <sup>iv</sup> —K1—K2 <sup>i</sup>	71.74 (5)	C22—O8—K2 <sup>vi</sup>	93.35 (16)
O1W <sup>i</sup> —K1—K2 <sup>i</sup>	47.40 (5)	C22—O8—K1 <sup>iii</sup>	126.30 (17)
S2—K1—K2 <sup>i</sup>	118.03 (2)	K2 <sup>vi</sup> —O8—K1 <sup>iii</sup>	89.15 (6)
O1—K1—K2 <sup>v</sup>	40.53 (5)	C22—O8—H8H	107 (4)
O2W <sup>i</sup> —K1—K2 <sup>v</sup>	157.68 (5)	K2 <sup>vi</sup> —O8—H8H	114 (4)
O2 <sup>ii</sup> —K1—K2 <sup>v</sup>	106.51 (6)	K1 <sup>iii</sup> —O8—H8H	120 (4)
O6—K1—K2 <sup>v</sup>	84.18 (5)	K2—O1W—K1 <sup>vii</sup>	83.14 (6)
O8 <sup>iii</sup> —K1—K2 <sup>v</sup>	79.19 (5)	K2—O1W—H1W	72 (3)
O7—K1—K2 <sup>v</sup>	40.81 (4)	K1 <sup>vii</sup> —O1W—H1W	155 (3)
O4 <sup>iv</sup> —K1—K2 <sup>v</sup>	134.64 (5)	K2—O1W—H2W	134 (3)
O1W <sup>i</sup> —K1—K2 <sup>v</sup>	102.80 (5)	K1 <sup>vii</sup> —O1W—H2W	93 (3)
S2—K1—K2 <sup>v</sup>	60.30 (2)	H1W—O1W—H2W	108 (4)
K2 <sup>i</sup> —K1—K2 <sup>v</sup>	120.54 (2)	K1 <sup>vii</sup> —O2W—K2	99.23 (7)
O5—K2—O2W	160.56 (7)	K1 <sup>vii</sup> —O2W—H3W	103 (3)
O5—K2—O7 <sup>ii</sup>	99.88 (7)	K2—O2W—H3W	112 (3)



O2W—K2—O7 <sup>ii</sup>	79.33 (7)	K1 <sup>vii</sup> —O2W—H4W	139 (3)
O5—K2—O1 <sup>ii</sup>	108.12 (7)	K2—O2W—H4W	97 (3)
O2W—K2—O1 <sup>ii</sup>	91.20 (7)	H3W—O2W—H4W	106 (4)
O7 <sup>ii</sup> —K2—O1 <sup>ii</sup>	84.47 (7)	N2—N1—C4	113.4 (3)
O5—K2—O8 <sup>vi</sup>	83.48 (7)	N1—N2—C7	113.7 (3)
O2W—K2—O8 <sup>vi</sup>	79.34 (7)	N4—N3—C16	112.2 (2)
O7 <sup>ii</sup> —K2—O8 <sup>vi</sup>	114.54 (7)	N3—N4—C19	114.2 (2)
O1 <sup>ii</sup> —K2—O8 <sup>vi</sup>	156.28 (7)	C6—C1—C2	121.0 (3)
O5—K2—O3 <sup>ii</sup>	81.94 (7)	C6—C1—S1	119.4 (2)
O2W—K2—O3 <sup>ii</sup>	113.62 (7)	C2—C1—S1	119.5 (2)
O7 <sup>ii</sup> —K2—O3 <sup>ii</sup>	130.17 (7)	C3—C2—C1	119.7 (3)
O1 <sup>ii</sup> —K2—O3 <sup>ii</sup>	49.17 (6)	C3—C2—H2	120.2
O8 <sup>vi</sup> —K2—O3 <sup>ii</sup>	115.13 (7)	C1—C2—H2	120.2
O5—K2—O1W	109.02 (7)	C2—C3—C4	119.4 (3)
O2W—K2—O1W	74.07 (7)	C2—C3—H3	120.3
O7 <sup>ii</sup> —K2—O1W	151.04 (7)	C4—C3—H3	120.3
O1 <sup>ii</sup> —K2—O1W	84.82 (7)	C5—C4—C3	120.8 (3)
O8 <sup>vi</sup> —K2—O1W	71.71 (6)	C5—C4—N1	116.1 (3)
O3 <sup>ii</sup> —K2—O1W	54.96 (6)	C3—C4—N1	123.1 (3)
O5—K2—C22 <sup>vi</sup>	75.97 (8)	C6—C5—C4	119.5 (3)
O2W—K2—C22 <sup>vi</sup>	84.63 (7)	C6—C5—H5	120.3
O7 <sup>ii</sup> —K2—C22 <sup>vi</sup>	92.32 (7)	C4—C5—H5	120.3
O1 <sup>ii</sup> —K2—C22 <sup>vi</sup>	175.16 (7)	C5—C6—C1	119.7 (3)
O8 <sup>vi</sup> —K2—C22 <sup>vi</sup>	24.68 (7)	C5—C6—H6	120.1
O3 <sup>ii</sup> —K2—C22 <sup>vi</sup>	135.03 (7)	C1—C6—H6	120.1
O1W—K2—C22 <sup>vi</sup>	96.36 (7)	C8—C7—C12	120.0 (3)
O5—K2—C23 <sup>vi</sup>	91.18 (7)	C8—C7—N2	116.5 (3)
O2W—K2—C23 <sup>vi</sup>	70.03 (7)	C12—C7—N2	123.5 (3)
O7 <sup>ii</sup> —K2—C23 <sup>vi</sup>	71.42 (7)	C9—C8—C7	120.4 (3)
O1 <sup>ii</sup> —K2—C23 <sup>vi</sup>	151.52 (7)	C9—C8—H8	119.8
O8 <sup>vi</sup> —K2—C23 <sup>vi</sup>	43.13 (7)	C7—C8—H8	119.8
O3 <sup>ii</sup> —K2—C23 <sup>vi</sup>	158.09 (7)	C8—C9—C10	119.5 (3)
O1W—K2—C23 <sup>vi</sup>	109.00 (7)	C8—C9—H9	120.3
C22 <sup>vi</sup> —K2—C23 <sup>vi</sup>	23.89 (7)	C10—C9—H9	120.3
O5—K2—S1 <sup>ii</sup>	92.88 (6)	O4—C10—C9	122.4 (3)
O2W—K2—S1 <sup>ii</sup>	106.08 (5)	O4—C10—C11	117.1 (3)
O7 <sup>ii</sup> —K2—S1 <sup>ii</sup>	105.92 (5)	C9—C10—C11	120.6 (3)
O1 <sup>ii</sup> —K2—S1 <sup>ii</sup>	24.32 (5)	C12—C11—C10	119.3 (3)
O8 <sup>vi</sup> —K2—S1 <sup>ii</sup>	139.42 (5)	C12—C11—H11	120.4
O3 <sup>ii</sup> —K2—S1 <sup>ii</sup>	25.26 (4)	C10—C11—H11	120.4
O1W—K2—S1 <sup>ii</sup>	71.45 (5)	C11—C12—C7	120.2 (3)
C22 <sup>vi</sup> —K2—S1 <sup>ii</sup>	160.14 (6)	C11—C12—H12	119.9
C23 <sup>vi</sup> —K2—S1 <sup>ii</sup>	175.50 (5)	C7—C12—H12	119.9
O5—K2—S2	18.27 (6)	C18—C13—C14	120.9 (3)
O2W—K2—S2	166.25 (6)	C18—C13—S2	118.7 (2)
O7 <sup>ii</sup> —K2—S2	88.14 (5)	C14—C13—S2	120.3 (2)
O1 <sup>ii</sup> —K2—S2	93.22 (5)	C15—C14—C13	119.1 (3)
O8 <sup>vi</sup> —K2—S2	101.09 (5)	C15—C14—H14	120.4

O3 <sup>ii</sup> —K2—S2	78.85 (4)	C13—C14—H14	120.4
O1W—K2—S2	119.29 (5)	C16—C15—C14	119.8 (3)
C22 <sup>vi</sup> —K2—S2	90.29 (5)	C16—C15—H15	120.1
C23 <sup>vi</sup> —K2—S2	100.72 (5)	C14—C15—H15	120.1
S1 <sup>ii</sup> —K2—S2	82.67 (2)	C15—C16—C17	120.7 (3)
O5—K2—K1 <sup>vii</sup>	127.22 (6)	C15—C16—N3	115.7 (2)
O2W—K2—K1 <sup>vii</sup>	40.16 (5)	C17—C16—N3	123.6 (3)
O7 <sup>ii</sup> —K2—K1 <sup>vii</sup>	112.89 (5)	C18—C17—C16	119.6 (3)
O1 <sup>ii</sup> —K2—K1 <sup>vii</sup>	114.97 (5)	C18—C17—H17	120.2
O8 <sup>vi</sup> —K2—K1 <sup>vii</sup>	45.95 (4)	C16—C17—H17	120.2
O3 <sup>ii</sup> —K2—K1 <sup>vii</sup>	104.05 (5)	C17—C18—C13	119.8 (3)
O1W—K2—K1 <sup>vii</sup>	49.46 (5)	C17—C18—H18	120.1
C22 <sup>vi</sup> —K2—K1 <sup>vii</sup>	62.99 (5)	C13—C18—H18	120.1
C23 <sup>vi</sup> —K2—K1 <sup>vii</sup>	63.93 (5)	C20—C19—C24	120.4 (3)
S1 <sup>ii</sup> —K2—K1 <sup>vii</sup>	114.76 (2)	C20—C19—N4	116.1 (2)
S2—K2—K1 <sup>vii</sup>	145.49 (3)	C24—C19—N4	123.5 (3)
O5—K2—H1W	100.8 (7)	C21—C20—C19	119.9 (3)
O2W—K2—H1W	86.6 (5)	C21—C20—H20	120.0
O7 <sup>ii</sup> —K2—H1W	153.4 (8)	C19—C20—H20	120.0
O1 <sup>ii</sup> —K2—H1W	73.3 (6)	C20—C21—C22	120.1 (3)
O8 <sup>vi</sup> —K2—H1W	84.4 (5)	C20—C21—H21	119.9
O3 <sup>ii</sup> —K2—H1W	38.4 (2)	C22—C21—H21	119.9
O1W—K2—H1W	16.6 (2)	O8—C22—C23	117.9 (2)
C22 <sup>vi</sup> —K2—H1W	108.8 (6)	O8—C22—C21	122.1 (3)
C23 <sup>vi</sup> —K2—H1W	124.5 (4)	C23—C22—C21	119.9 (3)
S1 <sup>ii</sup> —K2—H1W	56.5 (4)	O8—C22—K2 <sup>vi</sup>	61.97 (14)
S2—K2—H1W	107.2 (5)	C23—C22—K2 <sup>vi</sup>	83.25 (17)
K1 <sup>vii</sup> —K2—H1W	66.0 (2)	C21—C22—K2 <sup>vi</sup>	123.43 (19)
O5—K2—H4W	153.1 (7)	C24—C23—C22	120.7 (3)
O2W—K2—H4W	17.1 (4)	C24—C23—K2 <sup>vi</sup>	129.2 (2)
O7 <sup>ii</sup> —K2—H4W	62.3 (4)	C22—C23—K2 <sup>vi</sup>	72.86 (16)
O1 <sup>ii</sup> —K2—H4W	90.9 (9)	C24—C23—H23	119.6
O8 <sup>vi</sup> —K2—H4W	86.3 (8)	C22—C23—H23	119.6
O3 <sup>ii</sup> —K2—H4W	124.8 (7)	K2 <sup>vi</sup> —C23—H23	70.0
O1W—K2—H4W	91.1 (4)	C23—C24—C19	118.9 (3)
C22 <sup>vi</sup> —K2—H4W	84.4 (9)	C23—C24—H24	120.6
C23 <sup>vi</sup> —K2—H4W	64.8 (9)	C19—C24—H24	120.6
O2—S1—O1—K1	-22.5 (2)	N2—C7—C8—C9	-177.6 (3)
O3—S1—O1—K1	-149.71 (19)	C7—C8—C9—C10	-2.7 (5)
C1—S1—O1—K1	94.6 (2)	K1 <sup>iv</sup> —O4—C10—C9	-75.6 (4)
K2 <sup>v</sup> —S1—O1—K1	-136.2 (2)	K1 <sup>iv</sup> —O4—C10—C11	105.2 (3)
O2—S1—O1—K2 <sup>v</sup>	113.68 (12)	C8—C9—C10—O4	-178.8 (3)
O3—S1—O1—K2 <sup>v</sup>	-13.50 (14)	C8—C9—C10—C11	0.3 (4)
C1—S1—O1—K2 <sup>v</sup>	-129.16 (11)	O4—C10—C11—C12	-179.3 (3)
O1—S1—O2—K1 <sup>v</sup>	-95.7 (2)	C9—C10—C11—C12	1.6 (4)
O3—S1—O2—K1 <sup>v</sup>	31.2 (2)	C10—C11—C12—C7	-1.1 (5)
C1—S1—O2—K1 <sup>v</sup>	147.23 (17)	C8—C7—C12—C11	-1.2 (5)

K2 <sup>v</sup> —S1—O2—K1 <sup>v</sup>	-37.8 (2)	N2—C7—C12—C11	179.6 (3)
O1—S1—O3—K2 <sup>v</sup>	11.99 (12)	O7—S2—C13—C18	161.7 (2)
O2—S1—O3—K2 <sup>v</sup>	-116.08 (11)	O6—S2—C13—C18	-78.3 (3)
C1—S1—O3—K2 <sup>v</sup>	127.74 (11)	O5—S2—C13—C18	40.6 (3)
O7—S2—O5—K2	133.50 (15)	K1—S2—C13—C18	-131.3 (2)
O6—S2—O5—K2	7.0 (2)	K2—S2—C13—C18	5.3 (3)
C13—S2—O5—K2	-108.19 (16)	O7—S2—C13—C14	-22.4 (3)
K1—S2—O5—K2	65.57 (17)	O6—S2—C13—C14	97.6 (3)
O7—S2—O6—K1	-18.44 (16)	O5—S2—C13—C14	-143.5 (3)
O5—S2—O6—K1	108.85 (13)	K1—S2—C13—C14	44.6 (3)
C13—S2—O6—K1	-136.60 (12)	K2—S2—C13—C14	-178.8 (2)
K2—S2—O6—K1	112.84 (9)	C18—C13—C14—C15	2.0 (5)
O6—S2—O7—K2 <sup>v</sup>	114.81 (18)	S2—C13—C14—C15	-173.8 (2)
O5—S2—O7—K2 <sup>v</sup>	-11.9 (2)	C13—C14—C15—C16	1.6 (4)
C13—S2—O7—K2 <sup>v</sup>	-128.36 (16)	C14—C15—C16—C17	-4.2 (4)
K1—S2—O7—K2 <sup>v</sup>	97.99 (15)	C14—C15—C16—N3	175.1 (3)
K2—S2—O7—K2 <sup>v</sup>	21.6 (2)	N4—N3—C16—C15	-155.9 (3)
O6—S2—O7—K1	16.82 (14)	N4—N3—C16—C17	23.3 (4)
O5—S2—O7—K1	-109.92 (12)	C15—C16—C17—C18	3.1 (4)
C13—S2—O7—K1	133.65 (11)	N3—C16—C17—C18	-176.1 (3)
K2—S2—O7—K1	-76.44 (11)	C16—C17—C18—C13	0.5 (5)
C4—N1—N2—C7	177.2 (2)	C14—C13—C18—C17	-3.1 (5)
C16—N3—N4—C19	179.8 (2)	S2—C13—C18—C17	172.8 (2)
O1—S1—C1—C6	-157.8 (2)	N3—N4—C19—C20	-164.3 (3)
O2—S1—C1—C6	-36.3 (3)	N3—N4—C19—C24	16.5 (4)
O3—S1—C1—C6	83.2 (3)	C24—C19—C20—C21	-2.0 (4)
K2 <sup>v</sup> —S1—C1—C6	149.3 (2)	N4—C19—C20—C21	178.8 (3)
O1—S1—C1—C2	26.5 (3)	C19—C20—C21—C22	0.2 (4)
O2—S1—C1—C2	148.1 (2)	K2 <sup>vi</sup> —O8—C22—C23	64.3 (3)
O3—S1—C1—C2	-92.4 (3)	K1 <sup>iii</sup> —O8—C22—C23	-27.1 (4)
K2 <sup>v</sup> —S1—C1—C2	-26.4 (3)	K2 <sup>vi</sup> —O8—C22—C21	-113.8 (3)
C6—C1—C2—C3	0.7 (5)	K1 <sup>iii</sup> —O8—C22—C21	154.8 (2)
S1—C1—C2—C3	176.3 (2)	K1 <sup>iii</sup> —O8—C22—K2 <sup>vi</sup>	-91.41 (16)
C1—C2—C3—C4	-0.8 (5)	C20—C21—C22—O8	179.4 (3)
C2—C3—C4—C5	0.0 (5)	C20—C21—C22—C23	1.3 (4)
C2—C3—C4—N1	-178.8 (3)	C20—C21—C22—K2 <sup>vi</sup>	103.9 (3)
N2—N1—C4—C5	157.3 (3)	O8—C22—C23—C24	-179.2 (3)
N2—N1—C4—C3	-23.8 (4)	C21—C22—C23—C24	-1.0 (4)
C3—C4—C5—C6	0.8 (5)	K2 <sup>vi</sup> —C22—C23—C24	-125.9 (3)
N1—C4—C5—C6	179.7 (3)	O8—C22—C23—K2 <sup>vi</sup>	-53.2 (2)
C4—C5—C6—C1	-0.8 (5)	C21—C22—C23—K2 <sup>vi</sup>	124.9 (3)
C2—C1—C6—C5	0.1 (5)	C22—C23—C24—C19	-0.7 (4)
S1—C1—C6—C5	-175.5 (2)	K2 <sup>vi</sup> —C23—C24—C19	-93.2 (3)
N1—N2—C7—C8	162.4 (3)	C20—C19—C24—C23	2.3 (4)
N1—N2—C7—C12	-18.4 (4)	N4—C19—C24—C23	-178.5 (3)
C12—C7—C8—C9	3.1 (5)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H4H $\cdots$ O1W <sup>viii</sup>	0.88 (1)	1.83 (2)	2.676 (3)	160 (3)
O8—H8H $\cdots$ O6 <sup>ix</sup>	0.88 (1)	1.93 (3)	2.748 (3)	155 (5)
O1W—H1W $\cdots$ O3 <sup>ii</sup>	0.87 (1)	1.95 (2)	2.801 (3)	165 (4)
O1W—H2W $\cdots$ O2 <sup>vii</sup>	0.88 (1)	1.93 (1)	2.803 (4)	177 (5)
O2W—H3W $\cdots$ O3 <sup>x</sup>	0.88 (1)	2.20 (3)	2.866 (3)	133 (4)
O2W—H3W $\cdots$ O4 <sup>viii</sup>	0.88 (1)	2.29 (3)	2.905 (3)	127 (3)
O2W—H4W $\cdots$ O5 <sup>ii</sup>	0.88 (1)	1.92 (2)	2.778 (3)	165 (4)

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

Poly[*diaqua*{4-[2-(4-aminophenyl)diazen-1-yl]benzenesulfonato}potassium] (K3)

## Crystal data

$[\text{K}(\text{C}_{12}\text{H}_{10}\text{N}_3\text{O}_3\text{S})(\text{H}_2\text{O})_2]$

$M_r = 351.42$

Triclinic,  $P\bar{1}$

$a = 13.3058$  (2)  $\text{\AA}$

$b = 13.6247$  (2)  $\text{\AA}$

$c = 18.4664$  (3)  $\text{\AA}$

$\alpha = 88.373$  (1) $^\circ$

$\beta = 73.971$  (1) $^\circ$

$\gamma = 66.313$  (1) $^\circ$

$V = 2933.52$  (8)  $\text{\AA}^3$

$Z = 8$

$F(000) = 1456$

$D_x = 1.591$   $\text{Mg m}^{-3}$

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

Cell parameters from 13626 reflections

$\theta = 0.4\text{--}27.5^\circ$

$\mu = 0.53$   $\text{mm}^{-1}$

$T = 123$  K

Sheet, yellow

$0.7 \times 0.3 \times 0.02$  mm

## Data collection

Enraf–Nonius KappaCCD  
diffractometer

Radiation source: sealed tube

$\omega$  and  $\phi$  scans

26000 measured reflections

13392 independent reflections

10848 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\text{max}} = 27.5^\circ$ ,  $\theta_{\text{min}} = 1.6^\circ$

$h = -17 \rightarrow 17$

$k = -17 \rightarrow 17$

$l = -23 \rightarrow 23$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.098$

$S = 1.03$

13392 reflections

895 parameters

24 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2 + 2.5026P]$

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

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

$\Delta\rho_{\text{max}} = 0.80$   $\text{e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.79$   $\text{e \AA}^{-3}$

## Special details

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
K1	0.36432 (3)	0.16149 (3)	0.04727 (2)	0.01821 (9)	
K2	0.56585 (4)	0.34009 (3)	0.00078 (2)	0.02089 (10)	
K3	0.91040 (4)	0.14309 (4)	0.03328 (3)	0.03042 (11)	
K4	1.11003 (4)	0.34080 (3)	-0.05349 (2)	0.02172 (10)	
S1	0.60885 (4)	0.15844 (4)	0.13423 (2)	0.01617 (10)	
S1A	0.58680 (4)	0.12938 (4)	-0.11362 (2)	0.01558 (10)	
S1B	0.90352 (4)	0.37392 (4)	0.11946 (2)	0.01655 (10)	
S1C	0.88336 (4)	0.33155 (4)	-0.12057 (2)	0.01540 (10)	
O1	0.66126 (12)	0.04249 (11)	0.14108 (8)	0.0230 (3)	
O1A	0.56604 (12)	0.04564 (11)	-0.07064 (7)	0.0224 (3)	
O1B	0.99145 (14)	0.26429 (11)	0.09571 (8)	0.0291 (3)	
O2	0.50128 (12)	0.19267 (11)	0.11594 (8)	0.0235 (3)	
O1W	0.17161 (13)	0.17402 (12)	0.16143 (8)	0.0256 (3)	
O2A	0.49160 (12)	0.23543 (11)	-0.08722 (8)	0.0234 (3)	
O2B	0.93443 (13)	0.45183 (11)	0.07491 (8)	0.0268 (3)	
O3	0.68945 (12)	0.19462 (11)	0.08320 (7)	0.0225 (3)	
O2W	0.38778 (13)	0.44516 (13)	0.13668 (9)	0.0281 (3)	
O3A	0.69498 (12)	0.13426 (13)	-0.11593 (8)	0.0279 (3)	
O3B	0.79182 (13)	0.37860 (15)	0.12144 (9)	0.0365 (4)	
O3W	0.60988 (13)	0.50992 (12)	0.05734 (8)	0.0257 (3)	
O4W	0.90005 (13)	-0.02527 (12)	0.13023 (9)	0.0282 (3)	
O5W	1.12711 (13)	-0.00124 (12)	0.05792 (9)	0.0293 (3)	
H9W	1.1620 (18)	-0.0209 (19)	0.0100 (6)	0.035*	
H10W	1.1896 (14)	-0.0422 (17)	0.0707 (12)	0.035*	
O6W	1.22994 (13)	0.13309 (11)	-0.03169 (8)	0.0233 (3)	
O7W	1.24230 (13)	0.37602 (11)	0.03183 (8)	0.0255 (3)	
O8W	1.31574 (13)	0.33491 (12)	-0.15548 (9)	0.0275 (3)	
H15W	1.3758 (15)	0.3093 (17)	-0.1379 (13)	0.033*	
H16W	1.324 (2)	0.3912 (13)	-0.1745 (13)	0.033*	
O1C	0.76263 (16)	0.35833 (19)	-0.08326 (10)	0.0220 (4)	0.878 (4)
O2C	0.91077 (19)	0.42551 (14)	-0.12630 (9)	0.0228 (4)	0.878 (4)
O3C	0.95984 (17)	0.24694 (16)	-0.08543 (11)	0.0239 (4)	0.878 (4)
O4C	0.7885 (13)	0.3113 (13)	-0.0773 (8)	0.0220 (4)	0.122 (4)
O5C	0.8522 (14)	0.4454 (11)	-0.1293 (7)	0.0228 (4)	0.122 (4)
O6C	0.9823 (14)	0.2762 (13)	-0.1002 (9)	0.0239 (4)	0.122 (4)
N1	0.49955 (13)	0.33938 (12)	0.44977 (9)	0.0172 (3)	
N1A	0.62709 (13)	0.03685 (12)	-0.43692 (9)	0.0173 (3)	
N1B	0.87099 (13)	0.46335 (12)	0.44147 (9)	0.0176 (3)	
N1C	1.00015 (13)	0.16488 (12)	-0.44137 (9)	0.0168 (3)	
N2	0.58070 (13)	0.34190 (12)	0.47114 (9)	0.0171 (3)	
N2A	0.63343 (13)	-0.05449 (12)	-0.45571 (9)	0.0176 (3)	
N2B	0.86504 (13)	0.55398 (12)	0.46122 (9)	0.0173 (3)	
N2C	0.92154 (13)	0.15932 (12)	-0.46417 (9)	0.0174 (3)	
N3	0.46770 (17)	0.50272 (14)	0.77320 (9)	0.0212 (3)	
N3A	0.69006 (15)	-0.15131 (16)	-0.76079 (10)	0.0226 (4)	

N3B	0.81564 (15)	0.63159 (16)	0.76852 (10)	0.0238 (4)
N3C	1.04330 (17)	0.00391 (14)	−0.76838 (9)	0.0221 (4)
C1	0.57751 (15)	0.21914 (14)	0.22572 (10)	0.0147 (3)
C1A	0.59373 (15)	0.10016 (14)	−0.20806 (10)	0.0146 (3)
C1B	0.89745 (15)	0.40302 (14)	0.21380 (10)	0.0152 (3)
C1C	0.91372 (15)	0.27882 (14)	−0.21423 (10)	0.0149 (3)
C2	0.46687 (16)	0.25495 (14)	0.27370 (10)	0.0174 (4)
H2	0.406898	0.252756	0.256284	0.021*
C2A	0.59565 (16)	0.00262 (15)	−0.23074 (10)	0.0173 (4)
H2A	0.589860	−0.047690	−0.194892	0.021*
C2B	0.89368 (16)	0.50142 (15)	0.23675 (10)	0.0174 (4)
H2B	0.897118	0.552580	0.201182	0.021*
C2C	0.82832 (15)	0.27106 (14)	−0.24037 (10)	0.0166 (4)
H2C	0.753033	0.291570	−0.207218	0.020*
C3	0.44475 (16)	0.29419 (15)	0.34773 (11)	0.0184 (4)
H3	0.369302	0.318596	0.381298	0.022*
C3A	0.60606 (15)	−0.02100 (15)	−0.30590 (10)	0.0169 (4)
H3A	0.607199	−0.087354	−0.321551	0.020*
C3B	0.88492 (15)	0.52458 (15)	0.31145 (10)	0.0169 (4)
H3B	0.882456	0.591479	0.327216	0.020*
C3C	0.85370 (16)	0.23313 (14)	−0.31523 (10)	0.0166 (4)
H3C	0.796056	0.226894	−0.333317	0.020*
C4	0.53297 (16)	0.29782 (14)	0.37283 (10)	0.0156 (4)
C4A	0.61481 (15)	0.05321 (14)	−0.35826 (10)	0.0158 (4)
C4B	0.87976 (15)	0.44910 (15)	0.36324 (10)	0.0162 (4)
C4C	0.96408 (15)	0.20436 (14)	−0.36353 (10)	0.0154 (3)
C5	0.64367 (15)	0.26369 (14)	0.32360 (10)	0.0168 (4)
H5	0.703310	0.267634	0.340529	0.020*
C5A	0.61020 (16)	0.15177 (15)	−0.33499 (10)	0.0179 (4)
H5A	0.614125	0.202845	−0.370557	0.022*
C5B	0.88510 (16)	0.35028 (15)	0.34002 (10)	0.0179 (4)
H5B	0.882686	0.298779	0.375479	0.022*
C5C	1.04950 (16)	0.21144 (15)	−0.33698 (10)	0.0179 (4)
H5C	1.124708	0.191197	−0.370185	0.022*
C6	0.66621 (16)	0.22407 (15)	0.24999 (11)	0.0180 (4)
H6	0.741426	0.200389	0.216181	0.022*
C6A	0.59988 (16)	0.17544 (14)	−0.25996 (10)	0.0167 (4)
H6A	0.597033	0.242455	−0.244075	0.020*
C6B	0.89394 (16)	0.32676 (15)	0.26520 (10)	0.0176 (4)
H6B	0.897544	0.259428	0.249272	0.021*
C6C	1.02495 (16)	0.24797 (15)	−0.26216 (10)	0.0173 (4)
H6C	1.083268	0.251967	−0.243697	0.021*
C7	0.54673 (16)	0.38451 (14)	0.54765 (10)	0.0157 (4)
C7A	0.64460 (15)	−0.07259 (14)	−0.53316 (10)	0.0158 (4)
C7B	0.85779 (15)	0.56769 (15)	0.53871 (10)	0.0162 (4)
C7C	0.95806 (16)	0.11810 (14)	−0.54119 (10)	0.0155 (4)
C8	0.43404 (16)	0.42187 (15)	0.59522 (10)	0.0173 (4)
H8	0.374791	0.420291	0.576679	0.021*



C8A	0.65069 (15)	-0.17206 (15)	-0.55619 (11)	0.0178 (4)
H8A	0.646107	-0.222375	-0.520123	0.021*
C8B	0.84642 (16)	0.66756 (15)	0.56518 (11)	0.0182 (4)
H8B	0.846841	0.721222	0.531250	0.022*
C8C	0.87466 (16)	0.11037 (15)	-0.56976 (10)	0.0177 (4)
H8C	0.798442	0.131704	-0.537895	0.021*
C9	0.40933 (16)	0.46096 (15)	0.66906 (11)	0.0186 (4)
H9	0.332944	0.485441	0.701215	0.022*
C9A	0.66334 (16)	-0.19812 (15)	-0.63115 (11)	0.0180 (4)
H9A	0.667436	-0.266082	-0.646125	0.022*
C9B	0.83449 (16)	0.68896 (15)	0.64097 (11)	0.0190 (4)
H9B	0.826049	0.757445	0.658631	0.023*
C9C	0.90248 (16)	0.07160 (15)	-0.64467 (11)	0.0185 (4)
H9C	0.845055	0.066993	-0.663857	0.022*
C10	0.49517 (16)	0.46511 (14)	0.69734 (10)	0.0168 (4)
C10A	0.67011 (15)	-0.12459 (15)	-0.68493 (10)	0.0175 (4)
C10B	0.83482 (15)	0.61027 (15)	0.69145 (10)	0.0177 (4)
C10C	1.01397 (16)	0.03949 (14)	-0.69172 (10)	0.0167 (4)
C11	0.60659 (16)	0.42965 (15)	0.64948 (11)	0.0181 (4)
H11	0.665465	0.432619	0.667803	0.022*
C11A	0.66057 (16)	-0.02318 (15)	-0.66082 (11)	0.0197 (4)
H11A	0.663013	0.028064	-0.696478	0.024*
C11B	0.85061 (16)	0.50880 (15)	0.66346 (11)	0.0192 (4)
H11B	0.853477	0.453906	0.696747	0.023*
C11C	1.09807 (16)	0.04553 (15)	-0.66239 (11)	0.0187 (4)
H11C	1.174597	0.022944	-0.694008	0.022*
C12	0.63237 (16)	0.38987 (15)	0.57499 (11)	0.0186 (4)
H12	0.708552	0.366292	0.542639	0.022*
C12A	0.64776 (16)	0.00269 (15)	-0.58628 (11)	0.0179 (4)
H12A	0.641058	0.071506	-0.570813	0.021*
C12B	0.86200 (16)	0.48764 (15)	0.58844 (11)	0.0181 (4)
H12B	0.872754	0.418489	0.570389	0.022*
C12C	1.07081 (16)	0.08399 (15)	-0.58800 (10)	0.0175 (4)
H12C	1.128572	0.087303	-0.568568	0.021*
H1N	0.395 (2)	0.554 (2)	0.7950 (14)	0.031 (6)*
H2N	0.516 (2)	0.518 (2)	0.7822 (15)	0.033 (7)*
H3N	0.673 (2)	-0.200 (2)	-0.7689 (15)	0.039 (8)*
H4N	0.666 (2)	-0.097 (2)	-0.7876 (15)	0.036 (7)*
H5N	0.852 (2)	0.576 (2)	0.7920 (15)	0.037 (7)*
H6N	0.831 (2)	0.685 (2)	0.7808 (15)	0.035 (7)*
H7N	0.991 (2)	-0.009 (2)	-0.7789 (16)	0.043 (8)*
H8N	1.111 (2)	-0.047 (2)	-0.7869 (14)	0.031 (7)*
H1W	0.155 (2)	0.1254 (19)	0.1873 (15)	0.064 (10)*
H2W	0.1166 (15)	0.1971 (18)	0.1402 (12)	0.031 (7)*
H3W	0.3304 (17)	0.4996 (15)	0.1291 (17)	0.056 (9)*
H4W	0.358 (2)	0.3993 (17)	0.1527 (17)	0.063 (10)*
H5W	0.581 (2)	0.531 (3)	0.1053 (7)	0.082 (12)*
H6W	0.6785 (12)	0.4633 (18)	0.0554 (15)	0.049 (8)*

H7W	0.8265 (9)	−0.0080 (19)	0.1414 (16)	0.047 (8)*
H8W	0.9269 (19)	−0.0950 (8)	0.1270 (16)	0.045 (8)*
H11W	1.187 (2)	0.110 (2)	0.0020 (12)	0.050 (9)*
H12W	1.275 (2)	0.0765 (15)	−0.0625 (13)	0.057 (9)*
H13W	1.1940 (18)	0.4350 (14)	0.0606 (13)	0.052 (9)*
H14W	1.2900 (18)	0.400 (2)	0.0029 (13)	0.049 (8)*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
K1	0.01762 (19)	0.0189 (2)	0.01943 (19)	−0.00785 (16)	−0.00678 (15)	0.00224 (15)
K2	0.0220 (2)	0.0183 (2)	0.0234 (2)	−0.00772 (16)	−0.00867 (17)	0.00016 (16)
K3	0.0264 (2)	0.0278 (2)	0.0359 (3)	−0.0133 (2)	−0.0032 (2)	−0.00333 (19)
K4	0.0225 (2)	0.0200 (2)	0.0208 (2)	−0.00755 (17)	−0.00514 (17)	0.00190 (16)
S1	0.0161 (2)	0.0179 (2)	0.0145 (2)	−0.00651 (17)	−0.00479 (17)	−0.00092 (16)
S1A	0.0172 (2)	0.0162 (2)	0.0146 (2)	−0.00747 (17)	−0.00571 (17)	0.00230 (16)
S1B	0.0171 (2)	0.0197 (2)	0.0143 (2)	−0.00834 (18)	−0.00570 (17)	0.00287 (17)
S1C	0.0157 (2)	0.0162 (2)	0.0139 (2)	−0.00658 (17)	−0.00328 (17)	−0.00098 (16)
O1	0.0270 (7)	0.0178 (7)	0.0206 (7)	−0.0065 (6)	−0.0051 (6)	−0.0022 (5)
O1A	0.0317 (8)	0.0200 (7)	0.0152 (6)	−0.0124 (6)	−0.0034 (6)	0.0026 (5)
O1B	0.0400 (9)	0.0211 (7)	0.0234 (7)	−0.0050 (6)	−0.0159 (7)	−0.0036 (6)
O2	0.0198 (7)	0.0300 (8)	0.0218 (7)	−0.0090 (6)	−0.0092 (6)	−0.0023 (6)
O1W	0.0237 (7)	0.0269 (8)	0.0246 (7)	−0.0088 (6)	−0.0068 (6)	0.0037 (6)
O2A	0.0293 (8)	0.0171 (7)	0.0213 (7)	−0.0045 (6)	−0.0112 (6)	−0.0021 (5)
O2B	0.0412 (9)	0.0249 (7)	0.0153 (7)	−0.0181 (7)	−0.0031 (6)	0.0030 (6)
O3	0.0229 (7)	0.0296 (8)	0.0167 (7)	−0.0136 (6)	−0.0045 (6)	0.0044 (6)
O2W	0.0238 (8)	0.0273 (8)	0.0330 (8)	−0.0092 (7)	−0.0102 (7)	0.0027 (7)
O3A	0.0242 (7)	0.0443 (9)	0.0244 (7)	−0.0199 (7)	−0.0127 (6)	0.0090 (7)
O3B	0.0242 (8)	0.0722 (12)	0.0224 (8)	−0.0264 (8)	−0.0114 (6)	0.0106 (8)
O3W	0.0290 (8)	0.0219 (7)	0.0251 (8)	−0.0075 (6)	−0.0105 (6)	0.0018 (6)
O4W	0.0220 (8)	0.0272 (8)	0.0359 (9)	−0.0093 (6)	−0.0101 (7)	0.0025 (7)
O5W	0.0285 (8)	0.0292 (8)	0.0333 (8)	−0.0107 (7)	−0.0159 (7)	0.0064 (7)
O6W	0.0253 (8)	0.0214 (7)	0.0206 (7)	−0.0071 (6)	−0.0060 (6)	−0.0036 (6)
O7W	0.0297 (8)	0.0208 (7)	0.0230 (7)	−0.0084 (6)	−0.0059 (6)	0.0009 (6)
O8W	0.0272 (8)	0.0265 (8)	0.0303 (8)	−0.0103 (6)	−0.0122 (7)	0.0040 (6)
O1C	0.0169 (9)	0.0284 (12)	0.0186 (7)	−0.0099 (9)	−0.0004 (6)	−0.0047 (8)
O2C	0.0276 (12)	0.0219 (8)	0.0209 (8)	−0.0156 (8)	−0.0011 (8)	−0.0036 (6)
O3C	0.0296 (10)	0.0208 (10)	0.0174 (9)	−0.0041 (7)	−0.0102 (8)	0.0018 (7)
O4C	0.0169 (9)	0.0284 (12)	0.0186 (7)	−0.0099 (9)	−0.0004 (6)	−0.0047 (8)
O5C	0.0276 (12)	0.0219 (8)	0.0209 (8)	−0.0156 (8)	−0.0011 (8)	−0.0036 (6)
O6C	0.0296 (10)	0.0208 (10)	0.0174 (9)	−0.0041 (7)	−0.0102 (8)	0.0018 (7)
N1	0.0179 (8)	0.0182 (8)	0.0163 (7)	−0.0079 (6)	−0.0054 (6)	0.0003 (6)
N1A	0.0177 (8)	0.0191 (8)	0.0155 (7)	−0.0076 (6)	−0.0052 (6)	0.0009 (6)
N1B	0.0176 (8)	0.0194 (8)	0.0169 (8)	−0.0079 (6)	−0.0059 (6)	0.0013 (6)
N1C	0.0181 (8)	0.0173 (7)	0.0156 (7)	−0.0076 (6)	−0.0049 (6)	0.0001 (6)
N2	0.0182 (8)	0.0168 (8)	0.0168 (7)	−0.0074 (6)	−0.0052 (6)	0.0003 (6)
N2A	0.0163 (8)	0.0198 (8)	0.0160 (8)	−0.0066 (6)	−0.0046 (6)	0.0010 (6)
N2B	0.0152 (7)	0.0193 (8)	0.0163 (8)	−0.0060 (6)	−0.0043 (6)	0.0008 (6)

N2C	0.0182 (8)	0.0175 (8)	0.0163 (7)	-0.0067 (6)	-0.0054 (6)	0.0005 (6)
N3	0.0243 (9)	0.0227 (9)	0.0179 (8)	-0.0096 (8)	-0.0079 (7)	0.0004 (7)
N3A	0.0252 (9)	0.0265 (9)	0.0183 (8)	-0.0116 (8)	-0.0081 (7)	0.0016 (7)
N3B	0.0217 (9)	0.0293 (10)	0.0182 (8)	-0.0073 (8)	-0.0069 (7)	-0.0027 (7)
N3C	0.0244 (9)	0.0233 (9)	0.0165 (8)	-0.0070 (8)	-0.0064 (7)	-0.0016 (7)
C1	0.0159 (8)	0.0132 (8)	0.0147 (8)	-0.0058 (7)	-0.0045 (7)	0.0018 (7)
C1A	0.0121 (8)	0.0167 (8)	0.0137 (8)	-0.0052 (7)	-0.0030 (7)	0.0009 (7)
C1B	0.0128 (8)	0.0182 (9)	0.0138 (8)	-0.0059 (7)	-0.0035 (7)	0.0010 (7)
C1C	0.0173 (9)	0.0136 (8)	0.0138 (8)	-0.0064 (7)	-0.0044 (7)	0.0006 (6)
C2	0.0152 (9)	0.0183 (9)	0.0195 (9)	-0.0070 (7)	-0.0061 (7)	0.0013 (7)
C2A	0.0177 (9)	0.0176 (9)	0.0181 (9)	-0.0084 (7)	-0.0058 (7)	0.0039 (7)
C2B	0.0180 (9)	0.0178 (9)	0.0172 (9)	-0.0081 (7)	-0.0055 (7)	0.0045 (7)
C2C	0.0146 (8)	0.0173 (9)	0.0172 (9)	-0.0065 (7)	-0.0034 (7)	0.0011 (7)
C3	0.0142 (9)	0.0198 (9)	0.0199 (9)	-0.0067 (7)	-0.0034 (7)	0.0000 (7)
C3A	0.0177 (9)	0.0157 (9)	0.0182 (9)	-0.0077 (7)	-0.0051 (7)	0.0009 (7)
C3B	0.0168 (9)	0.0157 (9)	0.0190 (9)	-0.0078 (7)	-0.0046 (7)	0.0018 (7)
C3C	0.0173 (9)	0.0166 (9)	0.0174 (9)	-0.0080 (7)	-0.0057 (7)	0.0012 (7)
C4	0.0187 (9)	0.0127 (8)	0.0158 (8)	-0.0064 (7)	-0.0053 (7)	0.0011 (7)
C4A	0.0130 (8)	0.0186 (9)	0.0161 (9)	-0.0064 (7)	-0.0048 (7)	0.0021 (7)
C4B	0.0128 (8)	0.0202 (9)	0.0147 (8)	-0.0057 (7)	-0.0044 (7)	0.0020 (7)
C4C	0.0171 (9)	0.0126 (8)	0.0153 (8)	-0.0057 (7)	-0.0036 (7)	0.0010 (7)
C5	0.0151 (8)	0.0179 (9)	0.0191 (9)	-0.0075 (7)	-0.0066 (7)	0.0009 (7)
C5A	0.0193 (9)	0.0178 (9)	0.0178 (9)	-0.0083 (7)	-0.0064 (7)	0.0051 (7)
C5B	0.0203 (9)	0.0172 (9)	0.0172 (9)	-0.0084 (7)	-0.0059 (7)	0.0045 (7)
C5C	0.0150 (9)	0.0200 (9)	0.0174 (9)	-0.0067 (7)	-0.0030 (7)	-0.0004 (7)
C6	0.0153 (9)	0.0193 (9)	0.0187 (9)	-0.0069 (7)	-0.0039 (7)	-0.0007 (7)
C6A	0.0187 (9)	0.0151 (8)	0.0173 (9)	-0.0077 (7)	-0.0058 (7)	0.0019 (7)
C6B	0.0183 (9)	0.0165 (9)	0.0181 (9)	-0.0079 (7)	-0.0043 (7)	0.0009 (7)
C6C	0.0156 (9)	0.0198 (9)	0.0182 (9)	-0.0078 (7)	-0.0066 (7)	0.0012 (7)
C7	0.0181 (9)	0.0137 (8)	0.0161 (8)	-0.0072 (7)	-0.0054 (7)	0.0018 (7)
C7A	0.0145 (8)	0.0179 (9)	0.0152 (8)	-0.0068 (7)	-0.0045 (7)	0.0006 (7)
C7B	0.0131 (8)	0.0193 (9)	0.0150 (8)	-0.0061 (7)	-0.0029 (7)	0.0005 (7)
C7C	0.0185 (9)	0.0138 (8)	0.0137 (8)	-0.0059 (7)	-0.0052 (7)	0.0020 (7)
C8	0.0168 (9)	0.0184 (9)	0.0179 (9)	-0.0082 (7)	-0.0055 (7)	0.0027 (7)
C8A	0.0156 (9)	0.0189 (9)	0.0197 (9)	-0.0071 (7)	-0.0065 (7)	0.0038 (7)
C8B	0.0168 (9)	0.0182 (9)	0.0205 (9)	-0.0073 (7)	-0.0067 (7)	0.0023 (7)
C8C	0.0169 (9)	0.0175 (9)	0.0184 (9)	-0.0069 (7)	-0.0050 (7)	0.0021 (7)
C9	0.0169 (9)	0.0202 (9)	0.0176 (9)	-0.0075 (7)	-0.0033 (7)	0.0021 (7)
C9A	0.0166 (9)	0.0170 (9)	0.0205 (9)	-0.0067 (7)	-0.0055 (7)	-0.0003 (7)
C9B	0.0163 (9)	0.0189 (9)	0.0218 (9)	-0.0067 (7)	-0.0060 (7)	-0.0029 (7)
C9C	0.0190 (9)	0.0185 (9)	0.0207 (9)	-0.0081 (7)	-0.0095 (8)	0.0029 (7)
C10	0.0229 (9)	0.0134 (8)	0.0157 (8)	-0.0081 (7)	-0.0073 (7)	0.0039 (7)
C10A	0.0118 (8)	0.0216 (9)	0.0179 (9)	-0.0054 (7)	-0.0045 (7)	-0.0009 (7)
C10B	0.0113 (8)	0.0235 (9)	0.0171 (9)	-0.0057 (7)	-0.0041 (7)	-0.0012 (7)
C10C	0.0223 (9)	0.0123 (8)	0.0150 (8)	-0.0057 (7)	-0.0067 (7)	0.0023 (7)
C11	0.0175 (9)	0.0176 (9)	0.0226 (9)	-0.0079 (7)	-0.0101 (8)	0.0019 (7)
C11A	0.0213 (9)	0.0214 (9)	0.0192 (9)	-0.0109 (8)	-0.0073 (8)	0.0060 (7)
C11B	0.0196 (9)	0.0219 (9)	0.0182 (9)	-0.0096 (8)	-0.0072 (7)	0.0051 (7)

C11C	0.0182 (9)	0.0197 (9)	0.0181 (9)	-0.0083 (7)	-0.0042 (7)	0.0023 (7)
C12	0.0169 (9)	0.0172 (9)	0.0213 (9)	-0.0069 (7)	-0.0048 (7)	0.0010 (7)
C12A	0.0191 (9)	0.0174 (9)	0.0195 (9)	-0.0089 (7)	-0.0072 (7)	0.0023 (7)
C12B	0.0175 (9)	0.0186 (9)	0.0190 (9)	-0.0081 (7)	-0.0053 (7)	0.0005 (7)
C12C	0.0156 (9)	0.0196 (9)	0.0185 (9)	-0.0073 (7)	-0.0066 (7)	0.0018 (7)

*Geometric parameters (Å, °)*

K1—O2	2.6531 (14)	N2C—C7C	1.421 (2)
K1—O1A <sup>i</sup>	2.6570 (14)	N3—C10	1.402 (2)
K1—O6W <sup>ii</sup>	2.7388 (15)	N3—H1N	0.92 (3)
K1—O7W <sup>ii</sup>	2.7669 (15)	N3—H2N	0.81 (3)
K1—O1W	2.7806 (15)	N3A—C10A	1.382 (2)
K1—O1A	2.8284 (14)	N3A—H3N	0.82 (3)
K1—O2A	2.9928 (15)	N3A—H4N	0.88 (3)
K1—S1A	3.4580 (6)	N3B—C10B	1.392 (2)
K1—K4 <sup>ii</sup>	4.1781 (6)	N3B—H5N	0.90 (3)
K1—K2	4.2073 (6)	N3B—H6N	0.88 (3)
K1—K1 <sup>i</sup>	4.4315 (8)	N3C—C10C	1.405 (2)
K2—O3	2.7462 (14)	N3C—H7N	0.86 (3)
K2—O1C	2.7536 (17)	N3C—H8N	0.87 (3)
K2—O4C	2.784 (14)	C1—C2	1.385 (2)
K2—O2A	2.7929 (14)	C1—C6	1.399 (3)
K2—O2W	2.8559 (16)	C1A—C2A	1.393 (3)
K2—O3W <sup>iii</sup>	2.8666 (15)	C1A—C6A	1.395 (2)
K2—O3W	2.8901 (16)	C1B—C6B	1.393 (3)
K2—O2	3.0708 (15)	C1B—C2B	1.395 (3)
K2—O3A	3.1446 (16)	C1C—C2C	1.392 (3)
K2—S1	3.4381 (6)	C1C—C6C	1.396 (3)
K2—S1A	3.4869 (6)	C2—C3	1.391 (3)
K2—K2 <sup>iii</sup>	3.9929 (8)	C2—H2	0.9500
K2—H6W	3.00 (3)	C2A—C3A	1.390 (3)
K3—O3	2.6206 (14)	C2A—H2A	0.9500
K3—O3C	2.649 (2)	C2B—C3B	1.386 (3)
K3—O1B	2.7285 (16)	C2B—H2B	0.9500
K3—O5W <sup>iv</sup>	2.8713 (16)	C2C—C3C	1.391 (2)
K3—O4W	2.8932 (16)	C2C—H2C	0.9500
K3—O5W	2.9166 (15)	C3—C4	1.394 (3)
K3—O6C	3.181 (17)	C3—H3	0.9500
K3—O3B	3.2009 (19)	C3A—C4A	1.396 (3)
K3—O4C	3.261 (16)	C3A—H3A	0.9500
K3—O4W <sup>iv</sup>	3.2971 (17)	C3B—C4B	1.393 (3)
K3—S1B	3.5219 (7)	C3B—H3B	0.9500
K3—K3 <sup>iv</sup>	3.6855 (9)	C3C—C4C	1.393 (3)
K3—H9W <sup>iv</sup>	2.48 (2)	C3C—H3C	0.9500
K4—O6C	2.542 (17)	C4—C5	1.395 (3)
K4—O2B <sup>v</sup>	2.6854 (15)	C4A—C5A	1.394 (3)
K4—O6W	2.7164 (15)	C4B—C5B	1.393 (3)

K4—O2B	2.7701 (15)	C4C—C5C	1.393 (3)
K4—O8W	2.8338 (16)	C5—C6	1.384 (3)
K4—O7W	2.8395 (16)	C5—H5	0.9500
K4—O3C	2.954 (2)	C5A—C6A	1.388 (3)
K4—O2C	3.097 (2)	C5A—H5A	0.9500
K4—O1B	3.1503 (16)	C5B—C6B	1.389 (3)
K4—S1B	3.4918 (6)	C5B—H5B	0.9500
K4—S1C	3.6089 (6)	C5C—C6C	1.387 (2)
S1—O2	1.4497 (14)	C5C—H5C	0.9500
S1—O3	1.4565 (14)	C6—H6	0.9500
S1—O1	1.4664 (14)	C6A—H6A	0.9500
S1—C1	1.7680 (18)	C6B—H6B	0.9500
S1A—O1A	1.4452 (14)	C6C—H6C	0.9500
S1A—O3A	1.4564 (14)	C7—C12	1.395 (3)
S1A—O2A	1.4691 (14)	C7—C8	1.401 (3)
S1A—C1A	1.7690 (18)	C7A—C8A	1.396 (3)
S1B—O2B	1.4447 (14)	C7A—C12A	1.404 (3)
S1B—O3B	1.4519 (15)	C7B—C8B	1.395 (3)
S1B—O1B	1.4635 (15)	C7B—C12B	1.399 (3)
S1B—C1B	1.7706 (18)	C7C—C8C	1.393 (3)
S1C—O6C	1.380 (16)	C7C—C12C	1.400 (3)
S1C—O4C	1.421 (15)	C8—C9	1.380 (3)
S1C—O5C	1.453 (13)	C8—H8	0.9500
S1C—O1C	1.4562 (18)	C8A—C9A	1.386 (3)
S1C—O2C	1.4592 (17)	C8A—H8A	0.9500
S1C—O3C	1.4715 (18)	C8B—C9B	1.390 (3)
S1C—C1C	1.7670 (18)	C8B—H8B	0.9500
O1W—H1W	0.871 (10)	C8C—C9C	1.390 (3)
O1W—H2W	0.869 (9)	C8C—H8C	0.9500
O2W—H3W	0.866 (10)	C9—C10	1.401 (3)
O2W—H4W	0.869 (10)	C9—H9	0.9500
O3W—H5W	0.867 (10)	C9A—C10A	1.402 (3)
O3W—H6W	0.869 (10)	C9A—H9A	0.9500
O4W—H7W	0.873 (10)	C9B—C10B	1.400 (3)
O4W—H8W	0.867 (10)	C9B—H9B	0.9500
O5W—H9W	0.870 (9)	C9C—C10C	1.391 (3)
O5W—H10W	0.888 (9)	C9C—H9C	0.9500
O6W—H11W	0.866 (10)	C10—C11	1.392 (3)
O6W—H12W	0.862 (10)	C10A—C11A	1.409 (3)
O7W—H13W	0.873 (10)	C10B—C11B	1.404 (3)
O7W—H14W	0.876 (10)	C10C—C11C	1.401 (3)
O8W—H15W	0.882 (9)	C11—C12	1.391 (3)
O8W—H16W	0.870 (9)	C11—H11	0.9500
N1—N2	1.260 (2)	C11A—C12A	1.378 (3)
N1—C4	1.425 (2)	C11A—H11A	0.9500
N1A—N2A	1.265 (2)	C11B—C12B	1.377 (3)
N1A—C4A	1.430 (2)	C11B—H11B	0.9500
N1B—N2B	1.263 (2)	C11C—C12C	1.381 (3)

N1B—C4B	1.429 (2)	C11C—H11C	0.9500
N1C—N2C	1.259 (2)	C12—H12	0.9500
N1C—C4C	1.429 (2)	C12A—H12A	0.9500
N2—C7	1.421 (2)	C12B—H12B	0.9500
N2A—C7A	1.415 (2)	C12C—H12C	0.9500
N2B—C7B	1.420 (2)		
O2—K1—O1A <sup>i</sup>	93.46 (5)	O1A—S1A—K2	112.62 (6)
O2—K1—O6W <sup>ii</sup>	176.42 (5)	O3A—S1A—K2	64.38 (6)
O1A <sup>i</sup> —K1—O6W <sup>ii</sup>	88.31 (4)	O2A—S1A—K2	50.50 (6)
O2—K1—O7W <sup>ii</sup>	96.46 (5)	C1A—S1A—K2	139.34 (6)
O1A <sup>i</sup> —K1—O7W <sup>ii</sup>	166.72 (5)	K1—S1A—K2	74.573 (13)
O6W <sup>ii</sup> —K1—O7W <sup>ii</sup>	82.29 (4)	O2B—S1B—O3B	114.07 (10)
O2—K1—O1W	106.10 (5)	O2B—S1B—O1B	111.81 (9)
O1A <sup>i</sup> —K1—O1W	81.52 (4)	O3B—S1B—O1B	110.35 (10)
O6W <sup>ii</sup> —K1—O1W	77.24 (5)	O2B—S1B—C1B	107.17 (9)
O7W <sup>ii</sup> —K1—O1W	87.25 (5)	O3B—S1B—C1B	106.78 (9)
O2—K1—O1A	86.00 (4)	O1B—S1B—C1B	106.18 (8)
O1A <sup>i</sup> —K1—O1A	72.27 (5)	O2B—S1B—K4	49.10 (6)
O6W <sup>ii</sup> —K1—O1A	91.58 (4)	O3B—S1B—K4	120.29 (6)
O7W <sup>ii</sup> —K1—O1A	117.16 (4)	O1B—S1B—K4	64.44 (6)
O1W—K1—O1A	151.82 (4)	C1B—S1B—K4	132.51 (6)
O2—K1—O2A	84.65 (4)	O2B—S1B—K3	121.36 (6)
O1A <sup>i</sup> —K1—O2A	121.15 (4)	O3B—S1B—K3	65.35 (8)
O6W <sup>ii</sup> —K1—O2A	91.77 (4)	O1B—S1B—K3	46.46 (6)
O7W <sup>ii</sup> —K1—O2A	68.76 (4)	C1B—S1B—K3	129.95 (6)
O1W—K1—O2A	154.89 (4)	K4—S1B—K3	79.306 (14)
O1A—K1—O2A	48.89 (4)	O6C—S1C—O4C	113.4 (8)
O2—K1—S1A	83.01 (3)	O6C—S1C—O5C	117.1 (8)
O1A <sup>i</sup> —K1—S1A	96.24 (3)	O4C—S1C—O5C	112.0 (8)
O6W <sup>ii</sup> —K1—S1A	93.70 (3)	O1C—S1C—O2C	112.83 (10)
O7W <sup>ii</sup> —K1—S1A	93.72 (3)	O1C—S1C—O3C	112.65 (11)
O1W—K1—S1A	170.69 (4)	O2C—S1C—O3C	110.62 (11)
O1A—K1—S1A	24.01 (3)	O6C—S1C—C1C	105.1 (6)
O2A—K1—S1A	25.02 (3)	O4C—S1C—C1C	105.8 (6)
O2—K1—K4 <sup>ii</sup>	138.74 (3)	O5C—S1C—C1C	101.8 (5)
O1A <sup>i</sup> —K1—K4 <sup>ii</sup>	127.69 (3)	O1C—S1C—C1C	107.36 (9)
O6W <sup>ii</sup> —K1—K4 <sup>ii</sup>	39.82 (3)	O2C—S1C—C1C	106.53 (9)
O7W <sup>ii</sup> —K1—K4 <sup>ii</sup>	42.49 (3)	O3C—S1C—C1C	106.40 (9)
O1W—K1—K4 <sup>ii</sup>	80.55 (3)	O6C—S1C—K4	31.8 (7)
O1A—K1—K4 <sup>ii</sup>	107.32 (3)	O4C—S1C—K4	126.2 (6)
O2A—K1—K4 <sup>ii</sup>	76.73 (3)	O5C—S1C—K4	85.8 (7)
S1A—K1—K4 <sup>ii</sup>	93.909 (13)	O1C—S1C—K4	132.42 (7)
O2—K1—K2	46.70 (3)	O2C—S1C—K4	58.12 (9)
O1A <sup>i</sup> —K1—K2	126.75 (3)	O3C—S1C—K4	52.50 (9)
O6W <sup>ii</sup> —K1—K2	129.93 (3)	C1C—S1C—K4	120.10 (6)
O7W <sup>ii</sup> —K1—K2	66.47 (3)	O6C—S1C—K3	54.9 (7)
O1W—K1—K2	135.07 (3)	O4C—S1C—K3	58.5 (7)



O1A—K1—K2	71.44 (3)	O5C—S1C—K3	139.2 (5)
O2A—K1—K2	41.51 (3)	O1C—S1C—K3	80.14 (9)
S1A—K1—K2	53.027 (11)	O2C—S1C—K3	126.37 (8)
K4 <sup>ii</sup> —K1—K2	99.729 (12)	O3C—S1C—K3	32.52 (9)
O2—K1—K1 <sup>i</sup>	89.53 (3)	C1C—S1C—K3	119.03 (6)
O1A <sup>i</sup> —K1—K1 <sup>i</sup>	37.44 (3)	K4—S1C—K3	74.665 (13)
O6W <sup>ii</sup> —K1—K1 <sup>i</sup>	89.99 (3)	S1A—O1A—K1 <sup>i</sup>	148.88 (8)
O7W <sup>ii</sup> —K1—K1 <sup>i</sup>	151.03 (4)	S1A—O1A—K1	103.22 (7)
O1W—K1—K1 <sup>i</sup>	118.31 (3)	K1 <sup>i</sup> —O1A—K1	107.73 (5)
O1A—K1—K1 <sup>i</sup>	34.83 (3)	S1B—O1B—K3	110.66 (8)
O2A—K1—K1 <sup>i</sup>	83.71 (3)	S1B—O1B—K4	90.78 (7)
S1A—K1—K1 <sup>i</sup>	58.808 (12)	K3—O1B—K4	98.91 (4)
K4 <sup>ii</sup> —K1—K1 <sup>i</sup>	123.824 (16)	S1—O2—K1	152.11 (8)
K2—K1—K1 <sup>i</sup>	98.949 (14)	S1—O2—K2	91.86 (7)
O3—K2—O1C	89.81 (6)	K1—O2—K2	94.34 (4)
O3—K2—O4C	78.8 (3)	K1—O1W—H1W	132 (2)
O3—K2—O2A	109.42 (4)	K1—O1W—H2W	104.3 (16)
O1C—K2—O2A	110.70 (5)	H1W—O1W—H2W	99.6 (18)
O4C—K2—O2A	108.2 (3)	S1A—O2A—K2	105.55 (7)
O3—K2—O2W	90.13 (4)	S1A—O2A—K1	95.50 (7)
O1C—K2—O2W	136.34 (5)	K2—O2A—K1	93.24 (4)
O4C—K2—O2W	141.4 (3)	S1B—O2B—K4 <sup>v</sup>	148.49 (9)
O2A—K2—O2W	110.39 (5)	S1B—O2B—K4	107.69 (7)
O3—K2—O3W <sup>iii</sup>	166.01 (5)	K4 <sup>v</sup> —O2B—K4	103.59 (5)
O1C—K2—O3W <sup>iii</sup>	103.96 (6)	S1—O3—K3	139.98 (8)
O2A—K2—O3W <sup>iii</sup>	68.31 (4)	S1—O3—K2	105.64 (7)
O2W—K2—O3W <sup>iii</sup>	78.26 (4)	K3—O3—K2	113.39 (5)
O3—K2—O3W	91.51 (4)	K2—O2W—H3W	113 (2)
O1C—K2—O3W	64.79 (5)	K2—O2W—H4W	105 (2)
O4C—K2—O3W	71.9 (3)	H3W—O2W—H4W	102.9 (19)
O2A—K2—O3W	158.82 (4)	S1A—O3A—K2	90.93 (7)
O2W—K2—O3W	71.57 (5)	S1B—O3B—K3	90.31 (8)
O3W <sup>iii</sup> —K2—O3W	92.17 (4)	K2 <sup>iii</sup> —O3W—K2	87.83 (4)
O3—K2—O2	48.75 (4)	K2 <sup>iii</sup> —O3W—H5W	101 (2)
O1C—K2—O2	137.53 (6)	K2—O3W—H5W	118 (2)
O4C—K2—O2	125.3 (3)	K2 <sup>iii</sup> —O3W—H6W	156.1 (18)
O2A—K2—O2	80.89 (4)	K2—O3W—H6W	89.1 (19)
O2W—K2—O2	63.80 (4)	H5W—O3W—H6W	101.7 (19)
O3W <sup>iii</sup> —K2—O2	117.99 (4)	K3—O4W—K3 <sup>iv</sup>	72.75 (4)
O3W—K2—O2	116.97 (4)	K3—O4W—H7W	98.2 (17)
O3—K2—O3A	79.15 (4)	K3 <sup>iv</sup> —O4W—H7W	125.5 (19)
O1C—K2—O3A	75.40 (5)	K3—O4W—H8W	138.6 (18)
O4C—K2—O3A	67.3 (3)	K3 <sup>iv</sup> —O4W—H8W	66.2 (18)
O2A—K2—O3A	47.21 (4)	H7W—O4W—H8W	101.3 (18)
O2W—K2—O3A	146.90 (4)	K3 <sup>iv</sup> —O5W—K3	79.10 (4)
O3W <sup>iii</sup> —K2—O3A	106.42 (4)	K3 <sup>iv</sup> —O5W—H9W	54.9 (17)
O3W—K2—O3A	139.15 (4)	K3—O5W—H9W	94.2 (15)
O2—K2—O3A	86.27 (4)	K3 <sup>iv</sup> —O5W—H10W	105.4 (16)

O3—K2—S1	24.08 (3)	K3—O5W—H10W	173.6 (15)
O1C—K2—S1	113.82 (5)	H9W—O5W—H10W	92.1 (15)
O4C—K2—S1	102.4 (3)	K4—O6W—K1 <sup>vi</sup>	99.97 (5)
O2A—K2—S1	97.78 (3)	K4—O6W—H11W	110.5 (18)
O2W—K2—S1	74.17 (3)	K1 <sup>vi</sup> —O6W—H11W	102 (2)
O3W <sup>iii</sup> —K2—S1	142.21 (4)	K4—O6W—H12W	132.8 (19)
O3W—K2—S1	102.89 (3)	K1 <sup>vi</sup> —O6W—H12W	104 (2)
O2—K2—S1	24.93 (3)	H11W—O6W—H12W	103.3 (18)
O3A—K2—S1	84.46 (3)	K1 <sup>vi</sup> —O7W—K4	96.35 (5)
O3—K2—S1A	90.20 (3)	K1 <sup>vi</sup> —O7W—H13W	138.7 (18)
O1C—K2—S1A	97.37 (4)	K4—O7W—H13W	103.0 (19)
O4C—K2—S1A	90.9 (3)	K1 <sup>vi</sup> —O7W—H14W	108.2 (17)
O2A—K2—S1A	23.95 (3)	K4—O7W—H14W	109.1 (19)
O2W—K2—S1A	126.29 (4)	H13W—O7W—H14W	99.4 (17)
O3W <sup>iii</sup> —K2—S1A	90.46 (3)	K4—O8W—H15W	114.6 (16)
O3W—K2—S1A	162.07 (4)	K4—O8W—H16W	124.1 (16)
O2—K2—S1A	76.98 (3)	H15W—O8W—H16W	98.9 (16)
O3A—K2—S1A	24.68 (3)	S1C—O1C—K2	160.77 (14)
S1—K2—S1A	85.573 (14)	S1C—O2C—K4	98.29 (10)
O3—K2—K2 <sup>iii</sup>	135.69 (3)	S1C—O3C—K3	130.10 (12)
O1C—K2—K2 <sup>iii</sup>	82.24 (5)	S1C—O3C—K4	104.22 (11)
O2A—K2—K2 <sup>iii</sup>	114.18 (3)	K3—O3C—K4	105.93 (6)
O2W—K2—K2 <sup>iii</sup>	67.98 (3)	S1C—O4C—K2	161.7 (10)
O3W <sup>iii</sup> —K2—K2 <sup>iii</sup>	46.33 (3)	S1C—O4C—K3	99.6 (7)
O3W—K2—K2 <sup>iii</sup>	45.84 (3)	K2—O4C—K3	95.5 (4)
O2—K2—K2 <sup>iii</sup>	131.69 (3)	S1C—O6C—K4	131.6 (9)
O3A—K2—K2 <sup>iii</sup>	138.62 (3)	S1C—O6C—K3	104.4 (9)
S1—K2—K2 <sup>iii</sup>	136.779 (19)	K4—O6C—K3	102.3 (5)
S1A—K2—K2 <sup>iii</sup>	133.976 (19)	N2—N1—C4	113.70 (15)
O3—K2—H6W	78.2 (4)	N2A—N1A—C4A	113.11 (15)
O1C—K2—H6W	55.3 (4)	N2B—N1B—C4B	113.55 (15)
O4C—K2—H6W	59.6 (5)	N2C—N1C—C4C	113.74 (15)
O2A—K2—H6W	164.9 (5)	N1—N2—C7	113.51 (15)
O2W—K2—H6W	82.1 (4)	N1A—N2A—C7A	114.38 (15)
O3W <sup>iii</sup> —K2—H6W	107.5 (3)	N1B—N2B—C7B	113.58 (15)
O3W—K2—H6W	16.8 (2)	N1C—N2C—C7C	113.67 (15)
O2—K2—H6W	113.1 (5)	C10—N3—H1N	117.5 (15)
O3A—K2—H6W	125.1 (3)	C10—N3—H2N	113.3 (19)
S1—K2—H6W	93.8 (5)	H1N—N3—H2N	111 (2)
S1A—K2—H6W	149.7 (3)	C10A—N3A—H3N	114.1 (19)
K2 <sup>iii</sup> —K2—H6W	61.5 (3)	C10A—N3A—H4N	115.9 (17)
O3—K3—O3C	111.17 (5)	H3N—N3A—H4N	112 (3)
O3—K3—O1B	116.49 (5)	C10B—N3B—H5N	115.7 (17)
O3C—K3—O1B	81.50 (6)	C10B—N3B—H6N	115.6 (17)
O3—K3—O5W <sup>iv</sup>	75.72 (5)	H5N—N3B—H6N	106 (2)
O3C—K3—O5W <sup>iv</sup>	90.88 (6)	C10C—N3C—H7N	112.5 (19)
O1B—K3—O5W <sup>iv</sup>	167.29 (5)	C10C—N3C—H8N	115.8 (16)
O3—K3—O4W	77.80 (4)	H7N—N3C—H8N	113 (2)

O3C—K3—O4W	162.84 (5)	C2—C1—C6	121.15 (17)
O1B—K3—O4W	108.15 (5)	C2—C1—S1	119.32 (14)
O5W <sup>iv</sup> —K3—O4W	76.90 (5)	C6—C1—S1	119.41 (14)
O3—K3—O5W	141.48 (5)	C2A—C1A—C6A	120.45 (16)
O3C—K3—O5W	107.21 (5)	C2A—C1A—S1A	120.64 (14)
O1B—K3—O5W	72.00 (4)	C6A—C1A—S1A	118.89 (14)
O5W <sup>iv</sup> —K3—O5W	100.90 (4)	C6B—C1B—C2B	120.54 (17)
O4W—K3—O5W	64.31 (4)	C6B—C1B—S1B	118.77 (14)
O3—K3—O6C	114.4 (3)	C2B—C1B—S1B	120.67 (14)
O1B—K3—O6C	75.9 (3)	C2C—C1C—C6C	120.71 (17)
O5W <sup>iv</sup> —K3—O6C	96.3 (3)	C2C—C1C—S1C	120.99 (14)
O4W—K3—O6C	164.5 (3)	C6C—C1C—S1C	118.28 (14)
O5W—K3—O6C	104.1 (3)	C1—C2—C3	119.08 (17)
O3—K3—O3B	72.30 (4)	C1—C2—H2	120.5
O3C—K3—O3B	83.22 (5)	C3—C2—H2	120.5
O1B—K3—O3B	46.78 (4)	C3A—C2A—C1A	119.91 (17)
O5W <sup>iv</sup> —K3—O3B	142.66 (4)	C3A—C2A—H2A	120.0
O4W—K3—O3B	113.80 (5)	C1A—C2A—H2A	120.0
O5W—K3—O3B	116.10 (4)	C3B—C2B—C1B	120.03 (17)
O6C—K3—O3B	80.1 (3)	C3B—C2B—H2B	120.0
O3—K3—O4C	72.3 (3)	C1B—C2B—H2B	120.0
O1B—K3—O4C	100.0 (3)	C3C—C2C—C1C	119.71 (17)
O5W <sup>iv</sup> —K3—O4C	79.8 (3)	C3C—C2C—H2C	120.1
O4W—K3—O4C	145.7 (3)	C1C—C2C—H2C	120.1
O5W—K3—O4C	145.8 (3)	C2—C3—C4	120.20 (17)
O6C—K3—O4C	42.6 (4)	C2—C3—H3	119.9
O3B—K3—O4C	72.6 (3)	C4—C3—H3	119.9
O3—K3—O4W <sup>iv</sup>	131.51 (4)	C2A—C3A—C4A	119.70 (17)
O3C—K3—O4W <sup>iv</sup>	55.72 (5)	C2A—C3A—H3A	120.1
O1B—K3—O4W <sup>iv</sup>	107.63 (4)	C4A—C3A—H3A	120.1
O5W <sup>iv</sup> —K3—O4W <sup>iv</sup>	59.69 (4)	C2B—C3B—C4B	119.58 (17)
O4W—K3—O4W <sup>iv</sup>	107.25 (4)	C2B—C3B—H3B	120.2
O5W—K3—O4W <sup>iv</sup>	70.16 (4)	C4B—C3B—H3B	120.2
O3B—K3—O4W <sup>iv</sup>	136.67 (4)	C2C—C3C—C4C	119.64 (17)
O3—K3—S1B	96.20 (3)	C2C—C3C—H3C	120.2
O3C—K3—S1B	78.29 (4)	C4C—C3C—H3C	120.2
O1B—K3—S1B	22.88 (3)	C3—C4—C5	120.29 (17)
O5W <sup>iv</sup> —K3—S1B	163.31 (4)	C3—C4—N1	114.87 (16)
O4W—K3—S1B	116.15 (4)	C5—C4—N1	124.83 (16)
O5W—K3—S1B	94.47 (3)	C5A—C4A—C3A	120.20 (17)
O6C—K3—S1B	73.5 (3)	C5A—C4A—N1A	115.36 (16)
O3B—K3—S1B	24.35 (3)	C3A—C4A—N1A	124.43 (17)
O4C—K3—S1B	83.8 (3)	C5B—C4B—C3B	120.33 (17)
O4W <sup>iv</sup> —K3—S1B	121.09 (3)	C5B—C4B—N1B	114.82 (16)
O3—K3—K3 <sup>iv</sup>	115.28 (4)	C3B—C4B—N1B	124.84 (17)
O3C—K3—K3 <sup>iv</sup>	104.25 (4)	C5C—C4C—C3C	120.44 (17)
O1B—K3—K3 <sup>iv</sup>	121.03 (4)	C5C—C4C—N1C	114.83 (16)
O5W <sup>iv</sup> —K3—K3 <sup>iv</sup>	50.99 (3)	C3C—C4C—N1C	124.72 (16)

O4W—K3—K3 <sup>iv</sup>	58.69 (3)	C6—C5—C4	119.71 (17)
O5W—K3—K3 <sup>iv</sup>	49.91 (3)	C6—C5—H5	120.1
O3B—K3—K3 <sup>iv</sup>	165.36 (4)	C4—C5—H5	120.1
O4W <sup>iv</sup> —K3—K3 <sup>iv</sup>	48.56 (3)	C6A—C5A—C4A	120.13 (17)
S1B—K3—K3 <sup>iv</sup>	143.90 (2)	C6A—C5A—H5A	119.9
O3—K3—H9W <sup>iv</sup>	62.8 (4)	C4A—C5A—H5A	119.9
O3C—K3—H9W <sup>iv</sup>	105.2 (4)	C6B—C5B—C4B	120.25 (17)
O1B—K3—H9W <sup>iv</sup>	173.2 (4)	C6B—C5B—H5B	119.9
O5W <sup>iv</sup> —K3—H9W <sup>iv</sup>	16.7 (3)	C4B—C5B—H5B	119.9
O4W—K3—H9W <sup>iv</sup>	65.0 (4)	C6C—C5C—C4C	120.11 (17)
O5W—K3—H9W <sup>iv</sup>	104.2 (5)	C6C—C5C—H5C	119.9
O3B—K3—H9W <sup>iv</sup>	134.4 (5)	C4C—C5C—H5C	119.9
O4W <sup>iv</sup> —K3—H9W <sup>iv</sup>	75.7 (3)	C5—C6—C1	119.55 (17)
S1B—K3—H9W <sup>iv</sup>	158.7 (4)	C5—C6—H6	120.2
K3 <sup>iv</sup> —K3—H9W <sup>iv</sup>	56.5 (5)	C1—C6—H6	120.2
O6C—K4—O6W	87.6 (3)	C5A—C6A—C1A	119.56 (17)
O2B <sup>v</sup> —K4—O6W	158.58 (5)	C5A—C6A—H6A	120.2
O6C—K4—O2B	92.2 (4)	C1A—C6A—H6A	120.2
O2B <sup>v</sup> —K4—O2B	76.41 (5)	C5B—C6B—C1B	119.26 (17)
O6W—K4—O2B	111.99 (4)	C5B—C6B—H6B	120.4
O6C—K4—O8W	119.9 (4)	C1B—C6B—H6B	120.4
O2B <sup>v</sup> —K4—O8W	75.67 (5)	C5C—C6C—C1C	119.36 (17)
O6W—K4—O8W	87.78 (5)	C5C—C6C—H6C	120.3
O2B—K4—O8W	143.65 (5)	C1C—C6C—H6C	120.3
O6C—K4—O7W	163.8 (4)	C12—C7—C8	119.49 (17)
O2B <sup>v</sup> —K4—O7W	80.59 (5)	C12—C7—N2	116.54 (16)
O6W—K4—O7W	81.35 (4)	C8—C7—N2	123.96 (16)
O2B—K4—O7W	81.20 (5)	C8A—C7A—C12A	119.35 (17)
O8W—K4—O7W	71.68 (4)	C8A—C7A—N2A	116.26 (16)
O2B <sup>v</sup> —K4—O3C	119.29 (5)	C12A—C7A—N2A	124.38 (16)
O6W—K4—O3C	81.43 (5)	C8B—C7B—C12B	119.37 (17)
O2B—K4—O3C	88.02 (5)	C8B—C7B—N2B	116.68 (16)
O8W—K4—O3C	126.13 (5)	C12B—C7B—N2B	123.95 (17)
O7W—K4—O3C	154.52 (5)	C8C—C7C—C12C	119.49 (17)
O2B <sup>v</sup> —K4—O2C	72.75 (5)	C8C—C7C—N2C	116.32 (16)
O6W—K4—O2C	126.89 (4)	C12C—C7C—N2C	124.18 (16)
O2B—K4—O2C	81.89 (5)	C9—C8—C7	119.86 (17)
O8W—K4—O2C	111.10 (5)	C9—C8—H8	120.1
O7W—K4—O2C	151.11 (4)	C7—C8—H8	120.1
O3C—K4—O2C	46.87 (5)	C9A—C8A—C7A	120.66 (17)
O6C—K4—O1B	79.0 (4)	C9A—C8A—H8A	119.7
O2B <sup>v</sup> —K4—O1B	123.67 (4)	C7A—C8A—H8A	119.7
O6W—K4—O1B	66.06 (4)	C9B—C8B—C7B	120.32 (17)
O2B—K4—O1B	47.47 (4)	C9B—C8B—H8B	119.8
O8W—K4—O1B	147.95 (4)	C7B—C8B—H8B	119.8
O7W—K4—O1B	85.73 (4)	C9C—C8C—C7C	120.29 (17)
O3C—K4—O1B	70.13 (5)	C9C—C8C—H8C	119.9
O2C—K4—O1B	99.72 (4)	C7C—C8C—H8C	119.9

O6C—K4—S1B	81.9 (4)	C8—C9—C10	121.02 (17)
O2B <sup>v</sup> —K4—S1B	99.57 (3)	C8—C9—H9	119.5
O6W—K4—S1B	90.68 (3)	C10—C9—H9	119.5
O2B—K4—S1B	23.22 (3)	C8A—C9A—C10A	120.26 (17)
O8W—K4—S1B	158.02 (4)	C8A—C9A—H9A	119.9
O7W—K4—S1B	86.41 (3)	C10A—C9A—H9A	119.9
O3C—K4—S1B	75.16 (4)	C8B—C9B—C10B	120.45 (17)
O2C—K4—S1B	87.21 (3)	C8B—C9B—H9B	119.8
O1B—K4—S1B	24.78 (3)	C10B—C9B—H9B	119.8
O6C—K4—S1C	16.6 (3)	C8C—C9C—C10C	120.35 (17)
O2B <sup>v</sup> —K4—S1C	96.17 (4)	C8C—C9C—H9C	119.8
O6W—K4—S1C	104.10 (3)	C10C—C9C—H9C	119.8
O2B—K4—S1C	84.45 (3)	C11—C10—C9	118.90 (17)
O8W—K4—S1C	121.29 (3)	C11—C10—N3	121.55 (17)
O7W—K4—S1C	165.64 (3)	C9—C10—N3	119.54 (18)
O3C—K4—S1C	23.28 (4)	N3A—C10A—C9A	121.31 (18)
O2C—K4—S1C	23.58 (3)	N3A—C10A—C11A	119.94 (18)
O1B—K4—S1C	84.49 (3)	C9A—C10A—C11A	118.71 (17)
S1B—K4—S1C	80.317 (14)	N3B—C10B—C9B	121.73 (18)
O2B <sup>v</sup> —K4—K1 <sup>vi</sup>	120.62 (4)	N3B—C10B—C11B	119.62 (18)
O6W—K4—K1 <sup>vi</sup>	40.21 (3)	C9B—C10B—C11B	118.61 (17)
O2B—K4—K1 <sup>vi</sup>	99.50 (3)	C9C—C10C—C11C	119.19 (17)
O8W—K4—K1 <sup>vi</sup>	75.67 (3)	C9C—C10C—N3C	121.44 (18)
O7W—K4—K1 <sup>vi</sup>	41.16 (3)	C11C—C10C—N3C	119.35 (18)
O3C—K4—K1 <sup>vi</sup>	119.71 (4)	C12—C11—C10	120.48 (17)
O2C—K4—K1 <sup>vi</sup>	166.57 (3)	C12—C11—H11	119.8
O1B—K4—K1 <sup>vi</sup>	72.38 (3)	C10—C11—H11	119.8
S1B—K4—K1 <sup>vi</sup>	89.108 (13)	C12A—C11A—C10A	120.94 (17)
S1C—K4—K1 <sup>vi</sup>	142.993 (15)	C12A—C11A—H11A	119.5
O2—S1—O3	112.68 (8)	C10A—C11A—H11A	119.5
O2—S1—O1	113.18 (9)	C12B—C11B—C10B	120.96 (17)
O3—S1—O1	111.78 (8)	C12B—C11B—H11B	119.5
O2—S1—C1	107.16 (8)	C10B—C11B—H11B	119.5
O3—S1—C1	106.88 (8)	C12C—C11C—C10C	120.65 (17)
O1—S1—C1	104.50 (8)	C12C—C11C—H11C	119.7
O2—S1—K2	63.22 (6)	C10C—C11C—H11C	119.7
O3—S1—K2	50.28 (6)	C11—C12—C7	120.23 (17)
O1—S1—K2	141.39 (6)	C11—C12—H12	119.9
C1—S1—K2	113.31 (6)	C7—C12—H12	119.9
O1A—S1A—O3A	113.91 (9)	C11A—C12A—C7A	120.02 (17)
O1A—S1A—O2A	111.82 (8)	C11A—C12A—H12A	120.0
O3A—S1A—O2A	110.19 (9)	C7A—C12A—H12A	120.0
O1A—S1A—C1A	107.12 (8)	C11B—C12B—C7B	120.22 (17)
O3A—S1A—C1A	106.79 (8)	C11B—C12B—H12B	119.9
O2A—S1A—C1A	106.56 (8)	C7B—C12B—H12B	119.9
O1A—S1A—K1	52.78 (6)	C11C—C12C—C7C	120.01 (17)
O3A—S1A—K1	126.06 (6)	C11C—C12C—H12C	120.0
O2A—S1A—K1	59.48 (6)	C7C—C12C—H12C	120.0

C1A—S1A—K1	127.14 (6)		
O3A—S1A—O1A—K1 <sup>i</sup>	-55.79 (18)	O2B—S1B—C1B—C2B	15.16 (17)
O2A—S1A—O1A—K1 <sup>i</sup>	178.46 (14)	O3B—S1B—C1B—C2B	-107.45 (16)
C1A—S1A—O1A—K1 <sup>i</sup>	62.06 (18)	O1B—S1B—C1B—C2B	134.79 (15)
K1—S1A—O1A—K1 <sup>i</sup>	-173.9 (2)	K4—S1B—C1B—C2B	64.89 (17)
K2—S1A—O1A—K1 <sup>i</sup>	-126.67 (14)	K3—S1B—C1B—C2B	-179.04 (11)
O3A—S1A—O1A—K1	118.15 (8)	O6C—S1C—C1C—C2C	147.2 (8)
O2A—S1A—O1A—K1	-7.61 (9)	O4C—S1C—C1C—C2C	26.9 (7)
C1A—S1A—O1A—K1	-124.01 (7)	O5C—S1C—C1C—C2C	-90.2 (7)
K2—S1A—O1A—K1	47.27 (7)	O1C—S1C—C1C—C2C	1.15 (19)
O2B—S1B—O1B—K3	-113.15 (9)	O2C—S1C—C1C—C2C	-119.97 (17)
O3B—S1B—O1B—K3	14.94 (11)	O3C—S1C—C1C—C2C	121.98 (17)
C1B—S1B—O1B—K3	130.29 (8)	K4—S1C—C1C—C2C	177.73 (12)
K4—S1B—O1B—K3	-99.83 (7)	K3—S1C—C1C—C2C	89.32 (15)
O2B—S1B—O1B—K4	-13.32 (9)	O6C—S1C—C1C—C6C	-34.6 (8)
O3B—S1B—O1B—K4	114.77 (7)	O4C—S1C—C1C—C6C	-154.9 (7)
C1B—S1B—O1B—K4	-129.88 (7)	O5C—S1C—C1C—C6C	87.9 (7)
K3—S1B—O1B—K4	99.83 (7)	O1C—S1C—C1C—C6C	179.31 (16)
O3—S1—O2—K1	93.56 (19)	O2C—S1C—C1C—C6C	58.20 (18)
O1—S1—O2—K1	-34.5 (2)	O3C—S1C—C1C—C6C	-59.85 (18)
C1—S1—O2—K1	-149.16 (17)	K4—S1C—C1C—C6C	-4.11 (17)
K2—S1—O2—K1	102.90 (19)	K3—S1C—C1C—C6C	-92.51 (15)
O3—S1—O2—K2	-9.33 (8)	C6—C1—C2—C3	-1.4 (3)
O1—S1—O2—K2	-137.39 (7)	S1—C1—C2—C3	174.55 (14)
C1—S1—O2—K2	107.94 (7)	C6A—C1A—C2A—C3A	1.3 (3)
O1A—S1A—O2A—K2	101.94 (8)	S1A—C1A—C2A—C3A	-177.25 (14)
O3A—S1A—O2A—K2	-25.82 (9)	C6B—C1B—C2B—C3B	-0.8 (3)
C1A—S1A—O2A—K2	-141.32 (7)	S1B—C1B—C2B—C3B	177.75 (14)
K1—S1A—O2A—K2	94.92 (6)	C6C—C1C—C2C—C3C	-0.6 (3)
O1A—S1A—O2A—K1	7.03 (9)	S1C—C1C—C2C—C3C	177.50 (13)
O3A—S1A—O2A—K1	-120.74 (7)	C1—C2—C3—C4	0.4 (3)
C1A—S1A—O2A—K1	123.77 (7)	C1A—C2A—C3A—C4A	0.2 (3)
K2—S1A—O2A—K1	-94.92 (6)	C1B—C2B—C3B—C4B	-0.1 (3)
O3B—S1B—O2B—K4 <sup>v</sup>	62.58 (19)	C1C—C2C—C3C—C4C	-0.7 (3)
O1B—S1B—O2B—K4 <sup>v</sup>	-171.33 (15)	C2—C3—C4—C5	1.0 (3)
C1B—S1B—O2B—K4 <sup>v</sup>	-55.38 (19)	C2—C3—C4—N1	-179.85 (16)
K4—S1B—O2B—K4 <sup>v</sup>	172.7 (2)	N2—N1—C4—C3	-179.97 (16)
K3—S1B—O2B—K4 <sup>v</sup>	137.35 (14)	N2—N1—C4—C5	-0.9 (3)
O3B—S1B—O2B—K4	-110.12 (10)	C2A—C3A—C4A—C5A	-1.6 (3)
O1B—S1B—O2B—K4	15.96 (10)	C2A—C3A—C4A—N1A	179.28 (17)
C1B—S1B—O2B—K4	131.92 (7)	N2A—N1A—C4A—C5A	178.53 (16)
K3—S1B—O2B—K4	-35.35 (9)	N2A—N1A—C4A—C3A	-2.4 (3)
O2—S1—O3—K3	-156.23 (11)	C2B—C3B—C4B—C5B	1.0 (3)
O1—S1—O3—K3	-27.45 (15)	C2B—C3B—C4B—N1B	179.82 (17)
C1—S1—O3—K3	86.33 (13)	N2B—N1B—C4B—C5B	-179.28 (16)
K2—S1—O3—K3	-167.08 (16)	N2B—N1B—C4B—C3B	1.8 (3)
O2—S1—O3—K2	10.85 (9)	C2C—C3C—C4C—C5C	1.2 (3)



O1—S1—O3—K2	139.64 (7)	C2C—C3C—C4C—N1C	-179.76 (16)
C1—S1—O3—K2	-106.59 (8)	N2C—N1C—C4C—C5C	-179.89 (16)
O1A—S1A—O3A—K2	-104.72 (7)	N2C—N1C—C4C—C3C	1.0 (3)
O2A—S1A—O3A—K2	21.89 (8)	C3—C4—C5—C6	-1.3 (3)
C1A—S1A—O3A—K2	137.24 (7)	N1—C4—C5—C6	179.62 (17)
K1—S1A—O3A—K2	-44.44 (7)	C3A—C4A—C5A—C6A	1.7 (3)
O2B—S1B—O3B—K3	114.97 (8)	N1A—C4A—C5A—C6A	-179.15 (16)
O1B—S1B—O3B—K3	-11.87 (8)	C3B—C4B—C5B—C6B	-0.9 (3)
C1B—S1B—O3B—K3	-126.84 (7)	N1B—C4B—C5B—C6B	-179.90 (16)
K4—S1B—O3B—K3	59.70 (7)	C3C—C4C—C5C—C6C	-0.4 (3)
O2C—S1C—O1C—K2	-150.2 (3)	N1C—C4C—C5C—C6C	-179.56 (16)
O3C—S1C—O1C—K2	-24.1 (3)	C4—C5—C6—C1	0.3 (3)
C1C—S1C—O1C—K2	92.7 (3)	C2—C1—C6—C5	1.1 (3)
K4—S1C—O1C—K2	-83.3 (3)	S1—C1—C6—C5	-174.87 (14)
K3—S1C—O1C—K2	-24.8 (3)	C4A—C5A—C6A—C1A	-0.2 (3)
O1C—S1C—O2C—K4	126.88 (9)	C2A—C1A—C6A—C5A	-1.2 (3)
O3C—S1C—O2C—K4	-0.33 (10)	S1A—C1A—C6A—C5A	177.32 (14)
C1C—S1C—O2C—K4	-115.57 (7)	C4B—C5B—C6B—C1B	0.0 (3)
K3—S1C—O2C—K4	32.34 (10)	C2B—C1B—C6B—C5B	0.8 (3)
O1C—S1C—O3C—K3	-1.26 (17)	S1B—C1B—C6B—C5B	-177.75 (14)
O2C—S1C—O3C—K3	126.05 (13)	C4C—C5C—C6C—C1C	-0.9 (3)
C1C—S1C—O3C—K3	-118.63 (12)	C2C—C1C—C6C—C5C	1.4 (3)
K4—S1C—O3C—K3	125.70 (15)	S1C—C1C—C6C—C5C	-176.79 (14)
O1C—S1C—O3C—K4	-126.95 (9)	N1—N2—C7—C12	-179.85 (16)
O2C—S1C—O3C—K4	0.35 (11)	N1—N2—C7—C8	-0.9 (2)
C1C—S1C—O3C—K4	115.67 (8)	N1A—N2A—C7A—C8A	-179.35 (16)
K3—S1C—O3C—K4	-125.70 (15)	N1A—N2A—C7A—C12A	-0.5 (3)
O6C—S1C—O4C—K2	145 (3)	N1B—N2B—C7B—C8B	-177.56 (16)
O5C—S1C—O4C—K2	10 (3)	N1B—N2B—C7B—C12B	2.8 (3)
C1C—S1C—O4C—K2	-100 (3)	N1C—N2C—C7C—C8C	-179.80 (16)
K4—S1C—O4C—K2	112 (3)	N1C—N2C—C7C—C12C	1.4 (3)
K3—S1C—O4C—K2	145 (3)	C12—C7—C8—C9	-1.7 (3)
O6C—S1C—O4C—K3	0.0 (9)	N2—C7—C8—C9	179.36 (16)
O5C—S1C—O4C—K3	-135.2 (6)	C12A—C7A—C8A—C9A	2.0 (3)
C1C—S1C—O4C—K3	114.7 (3)	N2A—C7A—C8A—C9A	-179.08 (16)
K4—S1C—O4C—K3	-33.8 (8)	C12B—C7B—C8B—C9B	-2.7 (3)
O4C—S1C—O6C—K4	-121.5 (11)	N2B—C7B—C8B—C9B	177.61 (16)
O5C—S1C—O6C—K4	11.3 (15)	C12C—C7C—C8C—C9C	-1.6 (3)
C1C—S1C—O6C—K4	123.4 (10)	N2C—C7C—C8C—C9C	179.58 (16)
K3—S1C—O6C—K4	-121.5 (13)	C7—C8—C9—C10	0.7 (3)
O4C—S1C—O6C—K3	0.0 (10)	C7A—C8A—C9A—C10A	-0.1 (3)
O5C—S1C—O6C—K3	132.8 (6)	C7B—C8B—C9B—C10B	0.6 (3)
C1C—S1C—O6C—K3	-115.1 (4)	C7C—C8C—C9C—C10C	0.4 (3)
K4—S1C—O6C—K3	121.5 (13)	C8—C9—C10—C11	0.4 (3)
C4—N1—N2—C7	179.35 (14)	C8—C9—C10—N3	-178.37 (17)
C4A—N1A—N2A—C7A	179.46 (15)	C8A—C9A—C10A—N3A	175.81 (17)
C4B—N1B—N2B—C7B	-179.25 (14)	C8A—C9A—C10A—C11A	-1.8 (3)
C4C—N1C—N2C—C7C	-178.85 (14)	C8B—C9B—C10B—N3B	-175.77 (17)

O2—S1—C1—C2	20.81 (17)	C8B—C9B—C10B—C11B	1.7 (3)
O3—S1—C1—C2	141.83 (15)	C8C—C9C—C10C—C11C	0.8 (3)
O1—S1—C1—C2	-99.54 (15)	C8C—C9C—C10C—N3C	-177.53 (17)
K2—S1—C1—C2	88.45 (15)	C9—C10—C11—C12	-0.6 (3)
O2—S1—C1—C6	-163.12 (14)	N3—C10—C11—C12	178.20 (17)
O3—S1—C1—C6	-42.11 (17)	N3A—C10A—C11A—C12A	-175.97 (17)
O1—S1—C1—C6	76.52 (16)	C9A—C10A—C11A—C12A	1.6 (3)
K2—S1—C1—C6	-95.49 (14)	N3B—C10B—C11B—C12B	175.56 (17)
O1A—S1A—C1A—C2A	-8.81 (17)	C9B—C10B—C11B—C12B	-2.0 (3)
O3A—S1A—C1A—C2A	113.60 (16)	C9C—C10C—C11C—C12C	-0.7 (3)
O2A—S1A—C1A—C2A	-128.64 (15)	N3C—C10C—C11C—C12C	177.57 (17)
K1—S1A—C1A—C2A	-64.70 (16)	C10—C11—C12—C7	-0.4 (3)
K2—S1A—C1A—C2A	-176.40 (10)	C8—C7—C12—C11	1.5 (3)
O1A—S1A—C1A—C6A	172.63 (14)	N2—C7—C12—C11	-179.43 (16)
O3A—S1A—C1A—C6A	-64.96 (16)	C10A—C11A—C12A—C7A	0.3 (3)
O2A—S1A—C1A—C6A	52.80 (16)	C8A—C7A—C12A—C11A	-2.1 (3)
K1—S1A—C1A—C6A	116.74 (14)	N2A—C7A—C12A—C11A	179.05 (17)
K2—S1A—C1A—C6A	5.0 (2)	C10B—C11B—C12B—C7B	-0.1 (3)
O2B—S1B—C1B—C6B	-166.25 (15)	C8B—C7B—C12B—C11B	2.5 (3)
O3B—S1B—C1B—C6B	71.14 (17)	N2B—C7B—C12B—C11B	-177.89 (17)
O1B—S1B—C1B—C6B	-46.61 (17)	C10C—C11C—C12C—C7C	-0.4 (3)
K4—S1B—C1B—C6B	-116.52 (14)	C8C—C7C—C12C—C11C	1.6 (3)
K3—S1B—C1B—C6B	-0.45 (18)	N2C—C7C—C12C—C11C	-179.67 (17)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H1N $\cdots$ O3B <sup>vii</sup>	0.92 (3)	2.35 (3)	3.210 (2)	155 (2)
N3—H2N $\cdots$ O2W <sup>vii</sup>	0.81 (3)	2.40 (3)	3.147 (2)	154 (2)
N3A—H3N $\cdots$ O8W <sup>viii</sup>	0.82 (3)	2.27 (3)	3.016 (2)	153 (3)
N3A—H4N $\cdots$ O1 <sup>ix</sup>	0.88 (3)	2.27 (3)	3.115 (2)	161 (2)
N3B—H5N $\cdots$ O2C <sup>x</sup>	0.90 (3)	2.50 (3)	3.384 (3)	167 (2)
N3B—H5N $\cdots$ O5C <sup>x</sup>	0.90 (3)	2.26 (3)	3.078 (14)	151 (2)
N3B—H6N $\cdots$ O1W <sup>vii</sup>	0.88 (3)	2.21 (3)	3.065 (2)	164 (2)
N3C—H7N $\cdots$ O4W <sup>ix</sup>	0.86 (3)	2.38 (3)	3.149 (2)	149 (2)
N3C—H8N $\cdots$ O3A <sup>viii</sup>	0.87 (3)	2.53 (3)	3.330 (2)	154 (2)
O1W—H1W $\cdots$ N3C <sup>xi</sup>	0.87 (1)	2.62 (2)	3.428 (2)	156 (2)
O1W—H2W $\cdots$ O1B <sup>ii</sup>	0.87 (1)	1.94 (1)	2.808 (2)	174 (2)
O2W—H3W $\cdots$ O1C <sup>iii</sup>	0.87 (1)	2.13 (1)	2.963 (3)	160 (3)
O2W—H3W $\cdots$ O5C <sup>iii</sup>	0.87 (1)	2.24 (3)	2.973 (18)	143 (2)
O2W—H4W $\cdots$ N3B <sup>vii</sup>	0.87 (1)	2.56 (2)	3.322 (2)	148 (2)
O3W—H5W $\cdots$ N3 <sup>vii</sup>	0.87 (1)	2.25 (2)	3.036 (2)	151 (3)
O3W—H6W $\cdots$ O3B	0.87 (1)	2.15 (2)	2.906 (2)	145 (2)
O4W—H7W $\cdots$ O1	0.87 (1)	2.03 (1)	2.879 (2)	166 (3)
O4W—H8W $\cdots$ O3C <sup>iv</sup>	0.87 (1)	2.02 (1)	2.837 (2)	156 (2)
O4W—H8W $\cdots$ O6C <sup>iv</sup>	0.87 (1)	2.27 (2)	3.126 (16)	170 (3)

O5W—H9W···O3 <sup>iv</sup>	0.87 (1)	2.66 (2)	3.376 (2)	141 (2)
O5W—H10W···O3A <sup>iv</sup>	0.89 (1)	1.93 (1)	2.807 (2)	169 (2)
O6W—H11W···O5W	0.87 (1)	2.11 (1)	2.924 (2)	158 (2)
O6W—H12W···O1 <sup>iv</sup>	0.86 (1)	1.95 (1)	2.7885 (19)	164 (3)
O7W—H13W···O2C <sup>v</sup>	0.87 (1)	2.02 (1)	2.896 (2)	177 (3)
O7W—H13W···O5C <sup>v</sup>	0.87 (1)	1.88 (2)	2.698 (12)	156 (3)
O7W—H14W···O3W <sup>n</sup>	0.88 (1)	2.22 (1)	3.085 (2)	169 (2)
O8W—H15W···O2A <sup>vi</sup>	0.88 (1)	1.94 (1)	2.808 (2)	168 (2)

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

### Poly[*diaqua*[4-(2-{4-[bis(2-hydroxyethyl)amino]phenyl}diazene-1-yl)benzenesulfonato]potassium] (K4)

#### Crystal data

[K(C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>O<sub>5</sub>S)(H<sub>2</sub>O)<sub>2</sub>]

$M_r = 439.52$

Monoclinic,  $P2_1/n$

$a = 9.4006$  (2) Å

$b = 12.1583$  (3) Å

$c = 34.4743$  (9) Å

$\beta = 95.496$  (1)°

$V = 3922.14$  (16) Å<sup>3</sup>

$Z = 8$

$F(000) = 1840$

$D_x = 1.489$  Mg m<sup>-3</sup>

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

Cell parameters from 4144 reflections

$\theta = 1.0$ – $27.5$ °

$\mu = 0.42$  mm<sup>-1</sup>

$T = 123$  K

Fragment, yellow-orange

$0.20 \times 0.18 \times 0.08$  mm

#### Data collection

Enraf–Nonius KappaCCD  
diffractometer

Radiation source: sealed tube

$\omega$  and  $\phi$  scans

14501 measured reflections

7971 independent reflections

4387 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.084$

$\theta_{\text{max}} = 26.5$ °,  $\theta_{\text{min}} = 1.8$ °

$h = -11$ → $11$

$k = -15$ → $14$

$l = -43$ → $43$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.060$

$wR(F^2) = 0.102$

$S = 1.01$

7971 reflections

560 parameters

112 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0208P)^2 + 3.3444P]$

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

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

$\Delta\rho_{\text{max}} = 0.37$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.34$  e Å<sup>-3</sup>

#### 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 (Å<sup>2</sup>)

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
K1	0.62092 (8)	0.71226 (6)	0.01530 (2)	0.0258 (2)	

K2	0.77029 (8)	0.37647 (7)	0.01526 (2)	0.0271 (2)	
S1	1.00862 (10)	0.25029 (7)	0.08760 (3)	0.0245 (2)	
S1A	0.52799 (9)	0.49509 (7)	0.06827 (3)	0.0199 (2)	
O1	0.8908 (2)	0.20077 (19)	0.06291 (7)	0.0278 (6)	
O1A	0.5147 (2)	0.38622 (18)	0.05067 (7)	0.0266 (6)	
O2	1.0283 (3)	0.36445 (19)	0.07699 (7)	0.0353 (7)	
O2A	0.4295 (2)	0.57474 (18)	0.04875 (7)	0.0249 (6)	
O3	1.1377 (2)	0.1841 (2)	0.08914 (7)	0.0318 (7)	
O3A	0.6749 (2)	0.53511 (18)	0.07197 (7)	0.0249 (6)	
O4	0.3408 (3)	0.3821 (2)	0.43887 (8)	0.0303 (6)	
H1H	0.419 (2)	0.421 (2)	0.4435 (10)	0.036*	
O4A	-0.1792 (2)	0.37386 (19)	0.42667 (7)	0.0280 (6)	
H3H	-0.109 (2)	0.420 (2)	0.4311 (10)	0.034*	
O5	0.4632 (3)	0.1879 (2)	0.46276 (8)	0.0331 (7)	
H2H	0.429 (4)	0.2534 (15)	0.4564 (10)	0.040*	
O5A	-0.0092 (2)	0.5506 (2)	0.44089 (7)	0.0282 (6)	
H4H	0.066 (2)	0.554 (3)	0.4579 (7)	0.034*	
O1W	0.3676 (3)	0.8304 (2)	0.00680 (7)	0.0318 (7)	
H1W	0.373 (4)	0.876 (2)	-0.0126 (7)	0.038*	
H2W	0.305 (3)	0.863 (2)	0.0197 (8)	0.038*	
O2W	1.1728 (3)	0.4172 (2)	0.01231 (8)	0.0382 (7)	
H3W	1.109 (3)	0.378 (3)	-0.0014 (8)	0.046*	
H4W	1.156 (4)	0.403 (3)	0.0361 (4)	0.046*	
O3W	0.2480 (2)	0.6137 (2)	0.47825 (7)	0.0295 (6)	
H5W	0.296 (3)	0.630 (3)	0.4587 (6)	0.035*	
H6W	0.316 (2)	0.586 (3)	0.4947 (7)	0.035*	
O4W	0.5948 (3)	0.4831 (2)	0.45676 (8)	0.0341 (7)	
H7W	0.659 (3)	0.455 (2)	0.4428 (9)	0.041*	
H8W	0.599 (3)	0.5528 (10)	0.4505 (10)	0.041*	
N1	0.7690 (3)	0.2169 (3)	0.24068 (8)	0.0308 (8)	
N2	0.6618 (3)	0.2771 (3)	0.24382 (8)	0.0308 (8)	
N1A	0.3029 (6)	0.5236 (5)	0.22279 (16)	0.0262 (14)	0.661 (7)
N2A	0.2019 (7)	0.4551 (5)	0.22954 (17)	0.0274 (13)	0.661 (7)
N2B	0.2462 (13)	0.5338 (11)	0.2346 (3)	0.0274 (13)	0.339 (7)
N1B	0.2353 (13)	0.4540 (12)	0.2145 (4)	0.0262 (14)	0.339 (7)
N3	0.3547 (3)	0.2138 (2)	0.37386 (8)	0.0259 (7)	
N3A	-0.1168 (3)	0.5177 (2)	0.35650 (8)	0.0265 (7)	
C1	0.9529 (3)	0.2518 (3)	0.13522 (10)	0.0211 (8)	
C1A	0.4756 (19)	0.4898 (12)	0.1160 (4)	0.0164 (17)	0.661 (7)
C2	0.8560 (4)	0.3317 (3)	0.14473 (10)	0.0263 (9)	
H1	0.831089	0.390539	0.127249	0.032*	
C3	0.7963 (4)	0.3250 (3)	0.17975 (11)	0.0290 (10)	
H2	0.731465	0.379860	0.186724	0.035*	
C4	0.8321 (4)	0.2369 (3)	0.20482 (10)	0.0255 (9)	
C5	0.9339 (4)	0.1616 (3)	0.19610 (11)	0.0303 (10)	
H3	0.963122	0.105188	0.214192	0.036*	
C6	0.9934 (4)	0.1681 (3)	0.16106 (10)	0.0264 (9)	
H4	1.061896	0.115256	0.154753	0.032*	

C7	0.5910 (4)	0.2558 (3)	0.27774 (10)	0.0268 (9)	
C8	0.4826 (4)	0.3286 (3)	0.28460 (11)	0.0325 (10)	
H5	0.460671	0.387794	0.267050	0.039*	
C9	0.4060 (4)	0.3164 (3)	0.31657 (10)	0.0298 (10)	
H6	0.334356	0.368631	0.321110	0.036*	
C10	0.4322 (4)	0.2281 (3)	0.34243 (10)	0.0237 (9)	
C10A	−0.0325 (18)	0.5018 (10)	0.3265 (4)	0.0260 (16)	0.661 (7)
C11	0.5412 (4)	0.1540 (3)	0.33454 (11)	0.0292 (10)	
H7	0.561914	0.093513	0.351601	0.035*	
C12	0.6185 (4)	0.1666 (3)	0.30281 (11)	0.0292 (10)	
H8	0.690395	0.114777	0.298035	0.035*	
C2A	0.3749 (17)	0.4139 (10)	0.1248 (3)	0.0236 (15)	0.661 (7)
H2A	0.343592	0.358075	0.106681	0.028*	0.661 (7)
C3A	0.3191 (10)	0.4205 (7)	0.1612 (3)	0.0233 (16)	0.661 (7)
H3A	0.250484	0.368325	0.167921	0.028*	0.661 (7)
C4A	0.3642 (8)	0.5029 (6)	0.1871 (2)	0.0196 (17)	0.661 (7)
C5A	0.4737 (9)	0.5739 (6)	0.1789 (3)	0.0230 (16)	0.661 (7)
H5A	0.509392	0.627066	0.197539	0.028*	0.661 (7)
C6A	0.5301 (15)	0.5663 (10)	0.1434 (4)	0.0250 (14)	0.661 (7)
H6A	0.606084	0.613376	0.137698	0.030*	0.661 (7)
C7A	0.1305 (8)	0.4756 (6)	0.2625 (2)	0.0213 (16)	0.661 (7)
C8A	0.0395 (9)	0.3926 (6)	0.2724 (3)	0.0262 (16)	0.661 (7)
H8A	0.031325	0.327123	0.257344	0.031*	0.661 (7)
C9A	−0.0391 (15)	0.4038 (9)	0.3039 (4)	0.0292 (16)	0.661 (7)
H9A	−0.098664	0.345127	0.310670	0.035*	0.661 (7)
C11A	0.0654 (15)	0.5837 (7)	0.3162 (3)	0.0263 (16)	0.661 (7)
H11A	0.077171	0.648604	0.331527	0.032*	0.661 (7)
C12A	0.1434 (9)	0.5712 (6)	0.2847 (2)	0.0244 (16)	0.661 (7)
H12A	0.206264	0.628024	0.278124	0.029*	0.661 (7)
C1B	0.470 (4)	0.470 (3)	0.1158 (7)	0.0164 (17)	0.339 (7)
C2B	0.367 (3)	0.391 (2)	0.1201 (6)	0.0236 (15)	0.339 (7)
H2B	0.344024	0.338534	0.099962	0.028*	0.339 (7)
C3B	0.297 (2)	0.3878 (13)	0.1538 (6)	0.0233 (16)	0.339 (7)
H3B	0.226149	0.333454	0.156719	0.028*	0.339 (7)
C4B	0.3303 (16)	0.4644 (11)	0.1832 (5)	0.0196 (17)	0.339 (7)
C5B	0.4338 (19)	0.5440 (12)	0.1789 (5)	0.0230 (16)	0.339 (7)
H5B	0.456688	0.596294	0.198977	0.028*	0.339 (7)
C6B	0.504 (3)	0.5470 (19)	0.1452 (7)	0.0250 (14)	0.339 (7)
H6B	0.574565	0.601377	0.142220	0.030*	0.339 (7)
C7B	0.1512 (15)	0.5240 (11)	0.2660 (4)	0.0213 (16)	0.339 (7)
C8B	0.1485 (19)	0.6142 (9)	0.2907 (5)	0.0244 (16)	0.339 (7)
H8B	0.207002	0.676301	0.286941	0.029*	0.339 (7)
C9B	0.060 (3)	0.6136 (15)	0.3208 (7)	0.0263 (16)	0.339 (7)
H9B	0.058397	0.675243	0.337650	0.032*	0.339 (7)
C10B	−0.025 (4)	0.523 (2)	0.3262 (8)	0.0260 (16)	0.339 (7)
C11B	−0.023 (3)	0.4325 (16)	0.3016 (8)	0.0292 (16)	0.339 (7)
H11B	−0.081131	0.370347	0.305289	0.035*	0.339 (7)
C12B	0.066 (2)	0.4331 (10)	0.2714 (5)	0.0262 (16)	0.339 (7)

H12B	0.067473	0.371403	0.254579	0.031*	0.339 (7)
C13	0.2378 (4)	0.2887 (3)	0.38086 (11)	0.0293 (9)	
H10	0.174460	0.251538	0.398096	0.035*	
H9	0.180883	0.303336	0.355723	0.035*	
C13A	-0.2335 (4)	0.4395 (3)	0.35967 (11)	0.0340 (10)	
H10Z	-0.265121	0.410732	0.333383	0.041*	
H9Z	-0.315305	0.478847	0.369322	0.041*	
C14	0.2845 (4)	0.3974 (3)	0.39906 (11)	0.0337 (10)	
H11	0.358573	0.430807	0.384207	0.040*	
H12	0.201974	0.448291	0.397926	0.040*	
C14A	-0.1938 (4)	0.3438 (3)	0.38641 (11)	0.0325 (10)	
H12Z	-0.268054	0.286201	0.382158	0.039*	
H11Z	-0.102392	0.312115	0.379608	0.039*	
C15	0.3763 (4)	0.1161 (3)	0.39830 (11)	0.0321 (10)	
H14	0.394140	0.052405	0.381567	0.038*	
H13	0.287528	0.101129	0.410683	0.038*	
C15A	-0.1184 (4)	0.6188 (3)	0.37928 (11)	0.0299 (10)	
H13A	-0.209267	0.621970	0.391553	0.036*	
H14A	-0.117071	0.682160	0.361280	0.036*	
C16	0.4991 (4)	0.1263 (3)	0.42982 (11)	0.0306 (10)	
H15	0.530215	0.051774	0.438510	0.037*	
H16	0.580613	0.162388	0.418761	0.037*	
C16A	0.0029 (4)	0.6315 (3)	0.41055 (10)	0.0282 (9)	
H16A	0.094903	0.621735	0.399200	0.034*	
H15A	0.001225	0.706329	0.421790	0.034*	

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
K1	0.0291 (5)	0.0211 (4)	0.0282 (5)	-0.0024 (4)	0.0077 (4)	0.0004 (4)
K2	0.0232 (5)	0.0295 (5)	0.0295 (5)	0.0007 (4)	0.0064 (4)	-0.0018 (4)
S1	0.0244 (5)	0.0240 (5)	0.0260 (5)	-0.0008 (5)	0.0076 (4)	-0.0009 (5)
S1A	0.0197 (5)	0.0203 (5)	0.0203 (5)	-0.0010 (4)	0.0056 (4)	0.0007 (4)
O1	0.0256 (14)	0.0323 (15)	0.0250 (14)	0.0007 (12)	0.0007 (12)	-0.0023 (12)
O1A	0.0300 (15)	0.0207 (14)	0.0306 (15)	-0.0009 (12)	0.0101 (12)	-0.0049 (12)
O2	0.0450 (17)	0.0240 (15)	0.0401 (17)	-0.0071 (13)	0.0209 (14)	0.0016 (13)
O2A	0.0234 (14)	0.0267 (14)	0.0251 (14)	0.0049 (12)	0.0052 (12)	0.0081 (12)
O3	0.0207 (14)	0.0421 (16)	0.0336 (16)	0.0089 (13)	0.0081 (12)	-0.0010 (13)
O3A	0.0154 (13)	0.0298 (14)	0.0300 (15)	-0.0050 (11)	0.0046 (12)	0.0003 (12)
O4	0.0344 (16)	0.0262 (15)	0.0310 (16)	-0.0023 (13)	0.0069 (14)	-0.0022 (13)
O4A	0.0284 (16)	0.0260 (15)	0.0295 (15)	-0.0067 (12)	0.0025 (13)	0.0020 (13)
O5	0.0378 (17)	0.0300 (16)	0.0320 (16)	0.0080 (14)	0.0055 (13)	0.0038 (14)
O5A	0.0282 (16)	0.0307 (15)	0.0251 (16)	-0.0026 (13)	-0.0010 (12)	0.0011 (13)
O1W	0.0376 (17)	0.0276 (15)	0.0312 (17)	0.0063 (13)	0.0085 (13)	0.0033 (13)
O2W	0.0408 (19)	0.0425 (18)	0.0330 (17)	0.0056 (14)	0.0128 (15)	0.0074 (15)
O3W	0.0272 (16)	0.0347 (16)	0.0272 (16)	0.0041 (13)	0.0055 (13)	0.0020 (14)
O4W	0.0358 (17)	0.0297 (15)	0.0384 (17)	0.0063 (14)	0.0115 (13)	0.0041 (14)
N1	0.033 (2)	0.034 (2)	0.0251 (18)	0.0018 (17)	0.0030 (16)	-0.0051 (16)



N2	0.0289 (19)	0.037 (2)	0.0264 (19)	0.0022 (17)	0.0031 (16)	-0.0059 (16)
N1A	0.020 (3)	0.039 (3)	0.021 (3)	0.003 (2)	0.012 (2)	0.006 (3)
N2A	0.027 (3)	0.035 (3)	0.021 (3)	0.002 (3)	0.011 (2)	0.005 (3)
N2B	0.027 (3)	0.035 (3)	0.021 (3)	0.002 (3)	0.011 (2)	0.005 (3)
N1B	0.020 (3)	0.039 (3)	0.021 (3)	0.003 (2)	0.012 (2)	0.006 (3)
N3	0.0232 (17)	0.0275 (18)	0.0279 (18)	0.0015 (15)	0.0073 (15)	-0.0004 (16)
N3A	0.0232 (17)	0.0360 (19)	0.0214 (17)	0.0012 (16)	0.0074 (14)	-0.0003 (16)
C1	0.016 (2)	0.025 (2)	0.023 (2)	-0.0074 (17)	0.0021 (17)	-0.0016 (18)
C1A	0.021 (2)	0.011 (5)	0.0182 (19)	0.006 (3)	0.0058 (17)	0.005 (3)
C2	0.026 (2)	0.024 (2)	0.028 (2)	-0.0015 (18)	-0.0011 (19)	0.0027 (18)
C3	0.029 (2)	0.027 (2)	0.031 (2)	0.0012 (19)	0.010 (2)	-0.007 (2)
C4	0.027 (2)	0.031 (2)	0.019 (2)	-0.0059 (19)	0.0023 (18)	-0.0030 (18)
C5	0.036 (2)	0.031 (2)	0.024 (2)	0.002 (2)	0.003 (2)	0.0025 (19)
C6	0.022 (2)	0.031 (2)	0.027 (2)	0.0009 (18)	0.0048 (18)	-0.0038 (19)
C7	0.024 (2)	0.035 (2)	0.021 (2)	-0.0002 (19)	0.0003 (18)	-0.0058 (19)
C8	0.030 (2)	0.038 (2)	0.029 (2)	0.004 (2)	0.000 (2)	0.002 (2)
C9	0.023 (2)	0.038 (2)	0.028 (2)	0.0078 (19)	0.0002 (19)	0.002 (2)
C10	0.019 (2)	0.027 (2)	0.026 (2)	-0.0025 (18)	0.0041 (17)	-0.0030 (18)
C10A	0.018 (3)	0.040 (5)	0.020 (2)	0.002 (3)	0.0011 (18)	0.004 (3)
C11	0.031 (2)	0.027 (2)	0.030 (2)	0.0007 (19)	0.0064 (19)	-0.0032 (18)
C12	0.027 (2)	0.030 (2)	0.031 (2)	0.0053 (19)	0.0056 (19)	-0.010 (2)
C2A	0.023 (3)	0.021 (5)	0.027 (3)	-0.001 (4)	0.008 (3)	0.000 (2)
C3A	0.010 (4)	0.034 (5)	0.026 (5)	-0.014 (3)	-0.002 (3)	0.007 (4)
C4A	0.019 (4)	0.016 (5)	0.024 (3)	-0.004 (3)	0.003 (3)	0.004 (3)
C5A	0.033 (5)	0.014 (4)	0.022 (2)	-0.010 (3)	0.003 (3)	0.000 (3)
C6A	0.037 (5)	0.015 (4)	0.024 (2)	-0.009 (3)	0.008 (3)	0.003 (3)
C7A	0.019 (3)	0.026 (5)	0.019 (3)	-0.005 (4)	0.001 (2)	-0.001 (3)
C8A	0.024 (4)	0.031 (5)	0.023 (2)	-0.013 (3)	0.003 (3)	-0.009 (4)
C9A	0.026 (4)	0.042 (5)	0.021 (3)	-0.008 (4)	0.006 (2)	-0.002 (4)
C11A	0.029 (3)	0.025 (5)	0.026 (3)	0.004 (4)	0.007 (2)	0.000 (3)
C12A	0.023 (2)	0.023 (5)	0.028 (4)	-0.003 (4)	0.004 (2)	0.004 (4)
C1B	0.021 (2)	0.011 (5)	0.0182 (19)	0.006 (3)	0.0058 (17)	0.005 (3)
C2B	0.023 (3)	0.021 (5)	0.027 (3)	-0.001 (4)	0.008 (3)	0.000 (2)
C3B	0.010 (4)	0.034 (5)	0.026 (5)	-0.014 (3)	-0.002 (3)	0.007 (4)
C4B	0.019 (4)	0.016 (5)	0.024 (3)	-0.004 (3)	0.003 (3)	0.004 (3)
C5B	0.033 (5)	0.014 (4)	0.022 (2)	-0.010 (3)	0.003 (3)	0.000 (3)
C6B	0.037 (5)	0.015 (4)	0.024 (2)	-0.009 (3)	0.008 (3)	0.003 (3)
C7B	0.019 (3)	0.026 (5)	0.019 (3)	-0.005 (4)	0.001 (2)	-0.001 (3)
C8B	0.023 (2)	0.023 (5)	0.028 (4)	-0.003 (4)	0.004 (2)	0.004 (4)
C9B	0.029 (3)	0.025 (5)	0.026 (3)	0.004 (4)	0.007 (2)	0.000 (3)
C10B	0.018 (3)	0.040 (5)	0.020 (2)	0.002 (3)	0.0011 (18)	0.004 (3)
C11B	0.026 (4)	0.042 (5)	0.021 (3)	-0.008 (4)	0.006 (2)	-0.002 (4)
C12B	0.024 (4)	0.031 (5)	0.023 (2)	-0.013 (3)	0.003 (3)	-0.009 (4)
C13	0.018 (2)	0.042 (2)	0.027 (2)	0.0008 (19)	0.0033 (18)	0.000 (2)
C13A	0.025 (2)	0.048 (3)	0.030 (2)	0.000 (2)	0.007 (2)	-0.009 (2)
C14	0.037 (2)	0.030 (2)	0.035 (2)	0.011 (2)	0.009 (2)	0.004 (2)
C14A	0.027 (2)	0.033 (2)	0.038 (3)	-0.0094 (19)	0.005 (2)	-0.010 (2)
C15	0.026 (2)	0.027 (2)	0.044 (3)	-0.0039 (19)	0.011 (2)	-0.002 (2)

C15A	0.026 (2)	0.033 (2)	0.032 (2)	0.0114 (19)	0.0073 (19)	0.010 (2)
C16	0.032 (2)	0.025 (2)	0.038 (2)	0.0038 (19)	0.016 (2)	0.004 (2)
C16A	0.034 (2)	0.020 (2)	0.031 (2)	-0.0014 (18)	0.0087 (19)	0.0006 (19)

*Geometric parameters (Å, °)*

K1—O2W <sup>i</sup>	2.738 (3)	C5—H3	0.9500
K1—O1A <sup>ii</sup>	2.771 (3)	C6—H4	0.9500
K1—O1W	2.772 (3)	C7—C8	1.388 (5)
K1—O2A	2.786 (2)	C7—C12	1.395 (5)
K1—O3W <sup>iii</sup>	2.798 (3)	C8—C9	1.381 (5)
K1—O4A <sup>iv</sup>	2.820 (3)	C8—H5	0.9500
K1—O3A	2.919 (2)	C9—C10	1.401 (5)
K1—S1A	3.3728 (11)	C9—H6	0.9500
K1—K2 <sup>ii</sup>	3.8802 (11)	C10—C11	1.411 (5)
K1—K2	4.3173 (11)	C10A—C9A	1.420 (8)
K2—O2W <sup>i</sup>	2.753 (3)	C10A—C11A	1.423 (7)
K2—O5 <sup>v</sup>	2.794 (3)	C11—C12	1.379 (5)
K2—O1A	2.800 (2)	C11—H7	0.9500
K2—O2A <sup>ii</sup>	2.821 (2)	C12—H8	0.9500
K2—O1	2.862 (2)	C2A—C3A	1.406 (7)
K2—O1W <sup>ii</sup>	2.898 (3)	C2A—H2A	0.9500
K2—O3A	2.947 (2)	C3A—C4A	1.381 (8)
K2—O2	3.073 (3)	C3A—H3A	0.9500
K2—S1A	3.3773 (11)	C4A—C5A	1.393 (8)
K2—S1	3.5388 (13)	C5A—C6A	1.384 (8)
S1—O2	1.452 (2)	C5A—H5A	0.9500
S1—O3	1.453 (2)	C6A—H6A	0.9500
S1—O1	1.461 (2)	C7A—C8A	1.387 (8)
S1—C1	1.770 (3)	C7A—C12A	1.391 (8)
S1A—O1A	1.457 (2)	C8A—C9A	1.377 (8)
S1A—O3A	1.458 (2)	C8A—H8A	0.9500
S1A—O2A	1.459 (2)	C9A—H9A	0.9500
S1A—C1A	1.764 (9)	C11A—C12A	1.376 (7)
S1A—C1B	1.798 (17)	C11A—H11A	0.9500
O4—C14	1.435 (4)	C12A—H12A	0.9500
O4—H1H	0.873 (10)	C1B—C2B	1.3900
O4A—C14A	1.429 (4)	C1B—C6B	1.3900
O4A—H3H	0.870 (10)	C2B—C3B	1.3900
O5—C16	1.428 (4)	C2B—H2B	0.9500
O5—H2H	0.878 (10)	C3B—C4B	1.3900
O5A—C16A	1.448 (4)	C3B—H3B	0.9500
O5A—H4H	0.876 (10)	C4B—C5B	1.3900
O1W—H1W	0.874 (10)	C5B—C6B	1.3900
O1W—H2W	0.869 (10)	C5B—H5B	0.9500
O2W—H3W	0.871 (10)	C6B—H6B	0.9500
O2W—H4W	0.869 (10)	C7B—C8B	1.3900
O3W—H5W	0.871 (10)	C7B—C12B	1.3900

O3W—H6W	0.879 (10)	C8B—C9B	1.3900
O4W—H7W	0.875 (10)	C8B—H8B	0.9500
O4W—H8W	0.876 (10)	C9B—C10B	1.3900
N1—N2	1.259 (4)	C9B—H9B	0.9500
N1—C4	1.442 (4)	C10B—C11B	1.3900
N2—C7	1.423 (4)	C11B—C12B	1.3900
N1A—N2A	1.301 (11)	C11B—H11B	0.9500
N1A—C4A	1.431 (9)	C12B—H12B	0.9500
N2A—C7A	1.396 (9)	C13—C14	1.510 (5)
N2B—N1B	1.19 (2)	C13—H10	0.9900
N2B—C7B	1.472 (17)	C13—H9	0.9900
N1B—C4B	1.471 (18)	C13A—C14A	1.509 (5)
N3—C10	1.373 (4)	C13A—H10Z	0.9900
N3—C15	1.459 (4)	C13A—H9Z	0.9900
N3—C13	1.465 (4)	C14—H11	0.9900
N3A—C10A	1.376 (9)	C14—H12	0.9900
N3A—C10B	1.415 (13)	C14A—H12Z	0.9900
N3A—C15A	1.459 (4)	C14A—H11Z	0.9900
N3A—C13A	1.465 (4)	C15—C16	1.513 (5)
C1—C6	1.382 (5)	C15—H14	0.9900
C1—C2	1.392 (5)	C15—H13	0.9900
C1A—C2A	1.377 (7)	C15A—C16A	1.500 (5)
C1A—C6A	1.387 (7)	C15A—H13A	0.9900
C2—C3	1.381 (5)	C15A—H14A	0.9900
C2—H1	0.9500	C16—H15	0.9900
C3—C4	1.397 (5)	C16—H16	0.9900
C3—H2	0.9500	C16A—H16A	0.9900
C4—C5	1.378 (5)	C16A—H15A	0.9900
C5—C6	1.381 (5)		
O2W <sup>i</sup> —K1—O1A <sup>ii</sup>	75.62 (8)	K1 <sup>viii</sup> —O3W—H6W	108 (2)
O2W <sup>i</sup> —K1—O1W	152.98 (9)	H5W—O3W—H6W	101.2 (19)
O1A <sup>ii</sup> —K1—O1W	79.29 (8)	H7W—O4W—H8W	101.1 (19)
O2W <sup>i</sup> —K1—O2A	107.81 (7)	N2—N1—C4	112.0 (3)
O1A <sup>ii</sup> —K1—O2A	79.38 (7)	N1—N2—C7	113.9 (3)
O1W—K1—O2A	76.85 (7)	N2A—N1A—C4A	113.7 (7)
O2W <sup>i</sup> —K1—O3W <sup>iii</sup>	85.91 (7)	N1A—N2A—C7A	116.5 (7)
O1A <sup>ii</sup> —K1—O3W <sup>iii</sup>	97.77 (7)	N1B—N2B—C7B	109.7 (13)
O1W—K1—O3W <sup>iii</sup>	87.69 (7)	N2B—N1B—C4B	109.5 (14)
O2A—K1—O3W <sup>iii</sup>	164.54 (7)	C10—N3—C15	120.3 (3)
O2W <sup>i</sup> —K1—O4A <sup>iv</sup>	123.44 (8)	C10—N3—C13	120.9 (3)
O1A <sup>ii</sup> —K1—O4A <sup>iv</sup>	157.87 (7)	C15—N3—C13	118.4 (3)
O1W—K1—O4A <sup>iv</sup>	79.66 (8)	C10A—N3A—C15A	124.0 (5)
O2A—K1—O4A <sup>iv</sup>	102.35 (7)	C10B—N3A—C15A	113.5 (10)
O3W <sup>iii</sup> —K1—O4A <sup>iv</sup>	74.59 (7)	C10A—N3A—C13A	117.0 (6)
O2W <sup>i</sup> —K1—O3A	74.04 (7)	C10B—N3A—C13A	126.5 (11)
O1A <sup>ii</sup> —K1—O3A	105.50 (7)	C15A—N3A—C13A	117.4 (3)
O1W—K1—O3A	123.06 (7)	C6—C1—C2	120.5 (3)

O2A—K1—O3A	50.05 (6)	C6—C1—S1	120.2 (3)
O3W <sup>iii</sup> —K1—O3A	144.00 (7)	C2—C1—S1	119.0 (3)
O4A <sup>iv</sup> —K1—O3A	91.71 (7)	C2A—C1A—C6A	121.1 (5)
O2W <sup>i</sup> —K1—S1A	88.10 (6)	C2A—C1A—S1A	119.3 (8)
O1A <sup>ii</sup> —K1—S1A	89.05 (5)	C6A—C1A—S1A	119.4 (7)
O1W—K1—S1A	101.45 (6)	C3—C2—C1	119.6 (3)
O2A—K1—S1A	25.17 (5)	C3—C2—H1	120.2
O3W <sup>iii</sup> —K1—S1A	169.52 (6)	C1—C2—H1	120.2
O4A <sup>iv</sup> —K1—S1A	101.78 (6)	C2—C3—C4	119.5 (3)
O3A—K1—S1A	25.51 (4)	C2—C3—H2	120.3
O2W <sup>i</sup> —K1—K2 <sup>ii</sup>	115.47 (6)	C4—C3—H2	120.3
O1A <sup>ii</sup> —K1—K2 <sup>ii</sup>	46.16 (5)	C5—C4—C3	120.3 (3)
O1W—K1—K2 <sup>ii</sup>	48.19 (6)	C5—C4—N1	115.2 (3)
O2A—K1—K2 <sup>ii</sup>	46.57 (5)	C3—C4—N1	124.4 (3)
O3W <sup>iii</sup> —K1—K2 <sup>ii</sup>	121.42 (6)	C4—C5—C6	120.0 (4)
O4A <sup>iv</sup> —K1—K2 <sup>ii</sup>	120.07 (5)	C4—C5—H3	120.0
O3A—K1—K2 <sup>ii</sup>	94.36 (5)	C6—C5—H3	120.0
S1A—K1—K2 <sup>ii</sup>	68.99 (2)	C5—C6—C1	119.8 (3)
O2W <sup>i</sup> —K1—K2	38.29 (5)	C5—C6—H4	120.1
O1A <sup>ii</sup> —K1—K2	73.45 (5)	C1—C6—H4	120.1
O1W—K1—K2	140.00 (6)	C8—C7—C12	119.1 (3)
O2A—K1—K2	69.85 (5)	C8—C7—N2	115.6 (3)
O3W <sup>iii</sup> —K1—K2	124.19 (5)	C12—C7—N2	125.3 (3)
O4A <sup>iv</sup> —K1—K2	128.17 (6)	C9—C8—C7	121.0 (4)
O3A—K1—K2	42.86 (5)	C9—C8—H5	119.5
S1A—K1—K2	50.28 (2)	C7—C8—H5	119.5
K2 <sup>ii</sup> —K1—K2	92.11 (2)	C8—C9—C10	121.2 (3)
O2W <sup>i</sup> —K2—O5 <sup>v</sup>	82.66 (8)	C8—C9—H6	119.4
O2W <sup>i</sup> —K2—O1A	108.37 (7)	C10—C9—H6	119.4
O5 <sup>v</sup> —K2—O1A	158.69 (8)	N3—C10—C9	121.7 (3)
O2W <sup>i</sup> —K2—O2A <sup>ii</sup>	71.04 (8)	N3—C10—C11	121.4 (3)
O5 <sup>v</sup> —K2—O2A <sup>ii</sup>	88.68 (7)	C9—C10—C11	116.9 (3)
O1A—K2—O2A <sup>ii</sup>	78.30 (7)	N3A—C10A—C9A	122.1 (8)
O2W <sup>i</sup> —K2—O1	143.04 (8)	N3A—C10A—C11A	121.4 (8)
O5 <sup>v</sup> —K2—O1	85.24 (7)	C9A—C10A—C11A	116.5 (5)
O1A—K2—O1	95.18 (7)	C12—C11—C10	122.0 (4)
O2A <sup>ii</sup> —K2—O1	143.46 (7)	C12—C11—H7	119.0
O2W <sup>i</sup> —K2—O1W <sup>ii</sup>	142.86 (9)	C10—C11—H7	119.0
O5 <sup>v</sup> —K2—O1W <sup>ii</sup>	83.60 (7)	C11—C12—C7	119.9 (3)
O1A—K2—O1W <sup>ii</sup>	76.71 (7)	C11—C12—H8	120.1
O2A <sup>ii</sup> —K2—O1W <sup>ii</sup>	74.31 (7)	C7—C12—H8	120.1
O1—K2—O1W <sup>ii</sup>	69.22 (7)	C1A—C2A—C3A	118.7 (5)
O2W <sup>i</sup> —K2—O3A	73.39 (7)	C1A—C2A—H2A	120.6
O5 <sup>v</sup> —K2—O3A	150.57 (7)	C3A—C2A—H2A	120.6
O1A—K2—O3A	49.80 (6)	C4A—C3A—C2A	120.1 (5)
O2A <sup>ii</sup> —K2—O3A	99.16 (7)	C4A—C3A—H3A	120.0
O1—K2—O3A	103.69 (7)	C2A—C3A—H3A	120.0
O1W <sup>ii</sup> —K2—O3A	125.83 (7)	C3A—C4A—C5A	120.3 (5)

O2W <sup>i</sup> —K2—O2	96.65 (8)	C3A—C4A—N1A	124.1 (6)
O5 <sup>v</sup> —K2—O2	85.25 (7)	C5A—C4A—N1A	115.6 (6)
O1A—K2—O2	110.70 (7)	C6A—C5A—C4A	119.4 (5)
O2A <sup>ii</sup> —K2—O2	166.92 (7)	C6A—C5A—H5A	120.3
O1—K2—O2	47.48 (6)	C4A—C5A—H5A	120.3
O1W <sup>ii</sup> —K2—O2	116.36 (7)	C5A—C6A—C1A	119.9 (5)
O3A—K2—O2	80.90 (6)	C5A—C6A—H6A	120.1
O2W <sup>i</sup> —K2—S1A	87.77 (6)	C1A—C6A—H6A	120.1
O5 <sup>v</sup> —K2—S1A	169.57 (6)	C8A—C7A—C12A	119.7 (5)
O1A—K2—S1A	25.12 (5)	C8A—C7A—N2A	115.2 (6)
O2A <sup>ii</sup> —K2—S1A	84.29 (5)	C12A—C7A—N2A	125.0 (6)
O1—K2—S1A	104.98 (5)	C9A—C8A—C7A	120.8 (5)
O1W <sup>ii</sup> —K2—S1A	101.81 (5)	C9A—C8A—H8A	119.6
O3A—K2—S1A	25.51 (4)	C7A—C8A—H8A	119.6
O2—K2—S1A	100.02 (5)	C8A—C9A—C10A	121.1 (6)
O2W <sup>i</sup> —K2—S1	120.50 (7)	C8A—C9A—H9A	119.5
O5 <sup>v</sup> —K2—S1	85.91 (6)	C10A—C9A—H9A	119.5
O1A—K2—S1	102.88 (6)	C12A—C11A—C10A	121.7 (6)
O2A <sup>ii</sup> —K2—S1	166.36 (6)	C12A—C11A—H11A	119.1
O1—K2—S1	23.47 (5)	C10A—C11A—H11A	119.1
O1W <sup>ii</sup> —K2—S1	92.63 (6)	C11A—C12A—C7A	120.1 (5)
O3A—K2—S1	91.63 (5)	C11A—C12A—H12A	120.0
O2—K2—S1	24.07 (4)	C7A—C12A—H12A	120.0
S1A—K2—S1	102.59 (3)	C2B—C1B—C6B	120.0
O2W <sup>i</sup> —K2—K1 <sup>ii</sup>	111.72 (6)	C2B—C1B—S1A	119.2 (15)
O5 <sup>v</sup> —K2—K1 <sup>ii</sup>	113.78 (6)	C6B—C1B—S1A	119.0 (14)
O1A—K2—K1 <sup>ii</sup>	45.54 (5)	C1B—C2B—C3B	120.0
O2A <sup>ii</sup> —K2—K1 <sup>ii</sup>	45.83 (5)	C1B—C2B—H2B	120.0
O1—K2—K1 <sup>ii</sup>	105.13 (5)	C3B—C2B—H2B	120.0
O1W <sup>ii</sup> —K2—K1 <sup>ii</sup>	45.48 (5)	C4B—C3B—C2B	120.0
O3A—K2—K1 <sup>ii</sup>	91.22 (5)	C4B—C3B—H3B	120.0
O2—K2—K1 <sup>ii</sup>	147.08 (5)	C2B—C3B—H3B	120.0
S1A—K2—K1 <sup>ii</sup>	66.10 (2)	C5B—C4B—C3B	120.0
S1—K2—K1 <sup>ii</sup>	126.19 (3)	C5B—C4B—N1B	128.2 (12)
O2W <sup>i</sup> —K2—K1	38.04 (5)	C3B—C4B—N1B	111.5 (12)
O5 <sup>v</sup> —K2—K1	119.77 (6)	C6B—C5B—C4B	120.0
O1A—K2—K1	70.56 (5)	C6B—C5B—H5B	120.0
O2A <sup>ii</sup> —K2—K1	66.99 (5)	C4B—C5B—H5B	120.0
O1—K2—K1	144.74 (5)	C5B—C6B—C1B	120.0
O1W <sup>ii</sup> —K2—K1	133.12 (6)	C5B—C6B—H6B	120.0
O3A—K2—K1	42.37 (5)	C1B—C6B—H6B	120.0
O2—K2—K1	106.25 (5)	C8B—C7B—C12B	120.0
S1A—K2—K1	50.19 (2)	C8B—C7B—N2B	115.7 (11)
S1—K2—K1	126.42 (3)	C12B—C7B—N2B	124.3 (11)
K1 <sup>ii</sup> —K2—K1	87.89 (2)	C7B—C8B—C9B	120.0
O2—S1—O3	114.37 (15)	C7B—C8B—H8B	120.0
O2—S1—O1	110.80 (15)	C9B—C8B—H8B	120.0
O3—S1—O1	112.16 (14)	C8B—C9B—C10B	120.0

O2—S1—C1	106.26 (15)	C8B—C9B—H9B	120.0
O3—S1—C1	107.00 (16)	C10B—C9B—H9B	120.0
O1—S1—C1	105.62 (14)	C9B—C10B—C11B	120.0
O2—S1—K2	59.68 (11)	C9B—C10B—N3A	122.3 (15)
O3—S1—K2	137.40 (11)	C11B—C10B—N3A	117.7 (15)
O1—S1—K2	51.27 (10)	C10B—C11B—C12B	120.0
C1—S1—K2	115.17 (12)	C10B—C11B—H11B	120.0
O1A—S1A—O3A	112.48 (14)	C12B—C11B—H11B	120.0
O1A—S1A—O2A	112.69 (15)	C11B—C12B—C7B	120.0
O3A—S1A—O2A	111.87 (14)	C11B—C12B—H12B	120.0
O1A—S1A—C1A	109.6 (4)	C7B—C12B—H12B	120.0
O3A—S1A—C1A	106.1 (6)	N3—C13—C14	114.8 (3)
O2A—S1A—C1A	103.5 (7)	N3—C13—H10	108.6
O1A—S1A—C1B	101.9 (9)	C14—C13—H10	108.6
O3A—S1A—C1B	110.0 (11)	N3—C13—H9	108.6
O2A—S1A—C1B	107.3 (13)	C14—C13—H9	108.6
O1A—S1A—K1	120.14 (10)	H10—C13—H9	107.5
O3A—S1A—K1	59.59 (10)	N3A—C13A—C14A	113.8 (3)
O2A—S1A—K1	54.29 (9)	N3A—C13A—H10Z	108.8
C1A—S1A—K1	130.1 (4)	C14A—C13A—H10Z	108.8
C1B—S1A—K1	137.7 (9)	N3A—C13A—H9Z	108.8
O1A—S1A—K2	54.68 (9)	C14A—C13A—H9Z	108.8
O3A—S1A—K2	60.50 (9)	H10Z—C13A—H9Z	107.7
O2A—S1A—K2	117.69 (10)	O4—C14—C13	110.5 (3)
C1A—S1A—K2	138.8 (7)	O4—C14—H11	109.6
C1B—S1A—K2	134.4 (13)	C13—C14—H11	109.6
K1—S1A—K2	79.52 (3)	O4—C14—H12	109.6
S1—O1—K2	105.26 (12)	C13—C14—H12	109.6
S1A—O1A—K1 <sup>ii</sup>	138.52 (14)	H11—C14—H12	108.1
S1A—O1A—K2	100.21 (11)	O4A—C14A—C13A	113.0 (3)
K1 <sup>ii</sup> —O1A—K2	88.30 (7)	O4A—C14A—H12Z	109.0
S1—O2—K2	96.25 (12)	C13A—C14A—H12Z	109.0
S1A—O2A—K1	100.55 (11)	O4A—C14A—H11Z	109.0
S1A—O2A—K2 <sup>ii</sup>	147.79 (14)	C13A—C14A—H11Z	109.0
K1—O2A—K2 <sup>ii</sup>	87.60 (7)	H12Z—C14A—H11Z	107.8
S1A—O3A—K1	94.89 (11)	N3—C15—C16	113.7 (3)
S1A—O3A—K2	93.98 (11)	N3—C15—H14	108.8
K1—O3A—K2	94.78 (7)	C16—C15—H14	108.8
C14—O4—H1H	109 (2)	N3—C15—H13	108.8
C14A—O4A—K1 <sup>vi</sup>	120.3 (2)	C16—C15—H13	108.8
C14A—O4A—H3H	110 (2)	H14—C15—H13	107.7
K1 <sup>vi</sup> —O4A—H3H	103 (2)	N3A—C15A—C16A	115.3 (3)
C16—O5—K2 <sup>vii</sup>	125.9 (2)	N3A—C15A—H13A	108.5
C16—O5—H2H	113 (2)	C16A—C15A—H13A	108.5
K2 <sup>vii</sup> —O5—H2H	100 (2)	N3A—C15A—H14A	108.5
C16A—O5A—H4H	110 (2)	C16A—C15A—H14A	108.5
K1—O1W—K2 <sup>ii</sup>	86.33 (7)	H13A—C15A—H14A	107.5
K1—O1W—H1W	107 (2)	O5—C16—C15	113.0 (3)

K2 <sup>ii</sup> —O1W—H1W	114 (2)	O5—C16—H15	109.0
K1—O1W—H2W	143 (2)	C15—C16—H15	109.0
K2 <sup>ii</sup> —O1W—H2W	103 (2)	O5—C16—H16	109.0
H1W—O1W—H2W	102 (2)	C15—C16—H16	109.0
K1 <sup>i</sup> —O2W—K2 <sup>i</sup>	103.67 (8)	H15—C16—H16	107.8
K1 <sup>i</sup> —O2W—H3W	88 (3)	O5A—C16A—C15A	110.0 (3)
K2 <sup>i</sup> —O2W—H3W	117 (2)	O5A—C16A—H16A	109.7
K1 <sup>i</sup> —O2W—H4W	114 (3)	C15A—C16A—H16A	109.7
K2 <sup>i</sup> —O2W—H4W	125 (2)	O5A—C16A—H15A	109.7
H3W—O2W—H4W	103 (2)	C15A—C16A—H15A	109.7
K1 <sup>viii</sup> —O3W—H5W	117 (2)	H16A—C16A—H15A	108.2
O2—S1—O1—K2	-4.66 (15)	C13A—N3A—C10A—C11A	167.9 (7)
O3—S1—O1—K2	-133.81 (12)	N3—C10—C11—C12	179.2 (3)
C1—S1—O1—K2	109.99 (14)	C9—C10—C11—C12	-0.3 (5)
O3A—S1A—O1A—K1 <sup>ii</sup>	-117.96 (19)	C10—C11—C12—C7	0.9 (6)
O2A—S1A—O1A—K1 <sup>ii</sup>	9.6 (2)	C8—C7—C12—C11	-2.0 (5)
C1A—S1A—O1A—K1 <sup>ii</sup>	124.3 (7)	N2—C7—C12—C11	-179.1 (3)
C1B—S1A—O1A—K1 <sup>ii</sup>	124.3 (13)	C6A—C1A—C2A—C3A	5.0 (8)
K1—S1A—O1A—K1 <sup>ii</sup>	-51.1 (2)	S1A—C1A—C2A—C3A	-171.1 (14)
K2—S1A—O1A—K1 <sup>ii</sup>	-99.11 (19)	C1A—C2A—C3A—C4A	0.8 (8)
O3A—S1A—O1A—K2	-18.85 (16)	C2A—C3A—C4A—C5A	-5.6 (9)
O2A—S1A—O1A—K2	108.73 (12)	C2A—C3A—C4A—N1A	173.0 (9)
C1A—S1A—O1A—K2	-136.6 (7)	N2A—N1A—C4A—C3A	1.9 (10)
C1B—S1A—O1A—K2	-136.6 (13)	N2A—N1A—C4A—C5A	-179.4 (6)
K1—S1A—O1A—K2	48.00 (13)	C3A—C4A—C5A—C6A	4.6 (9)
O3—S1—O2—K2	132.16 (13)	N1A—C4A—C5A—C6A	-174.1 (9)
O1—S1—O2—K2	4.21 (13)	C4A—C5A—C6A—C1A	1.2 (8)
C1—S1—O2—K2	-110.04 (13)	C2A—C1A—C6A—C5A	-6.1 (8)
O1A—S1A—O2A—K1	-111.70 (12)	S1A—C1A—C6A—C5A	170.0 (14)
O3A—S1A—O2A—K1	16.21 (15)	N1A—N2A—C7A—C8A	-170.3 (7)
C1A—S1A—O2A—K1	130.0 (4)	N1A—N2A—C7A—C12A	10.5 (10)
C1B—S1A—O2A—K1	136.9 (9)	C12A—C7A—C8A—C9A	0.5 (9)
K2—S1A—O2A—K1	-50.93 (11)	N2A—C7A—C8A—C9A	-178.8 (9)
O1A—S1A—O2A—K2 <sup>ii</sup>	-9.3 (3)	C7A—C8A—C9A—C10A	1.8 (9)
O3A—S1A—O2A—K2 <sup>ii</sup>	118.7 (2)	N3A—C10A—C9A—C8A	175.8 (17)
C1A—S1A—O2A—K2 <sup>ii</sup>	-127.5 (5)	C11A—C10A—C9A—C8A	-3.7 (8)
C1B—S1A—O2A—K2 <sup>ii</sup>	-120.7 (9)	N3A—C10A—C11A—C12A	-175.8 (16)
K1—S1A—O2A—K2 <sup>ii</sup>	102.4 (2)	C9A—C10A—C11A—C12A	3.7 (8)
K2—S1A—O2A—K2 <sup>ii</sup>	51.5 (3)	C10A—C11A—C12A—C7A	-1.6 (9)
O1A—S1A—O3A—K1	112.78 (13)	C8A—C7A—C12A—C11A	-0.6 (9)
O2A—S1A—O3A—K1	-15.23 (14)	N2A—C7A—C12A—C11A	178.6 (9)
C1A—S1A—O3A—K1	-127.4 (6)	O1A—S1A—C1B—C2B	-32.3 (17)
C1B—S1A—O3A—K1	-134.4 (12)	O3A—S1A—C1B—C2B	-151.8 (11)
K2—S1A—O3A—K1	95.15 (8)	O2A—S1A—C1B—C2B	86.3 (15)
O1A—S1A—O3A—K2	17.63 (15)	K1—S1A—C1B—C2B	141.8 (10)
O2A—S1A—O3A—K2	-110.38 (12)	K2—S1A—C1B—C2B	-84.0 (19)
C1A—S1A—O3A—K2	137.4 (6)	O1A—S1A—C1B—C6B	162.7 (14)



C1B—S1A—O3A—K2	130.5 (12)	O3A—S1A—C1B—C6B	43 (2)
K1—S1A—O3A—K2	-95.15 (8)	O2A—S1A—C1B—C6B	-78.7 (17)
C4—N1—N2—C7	176.5 (3)	K1—S1A—C1B—C6B	-23 (3)
C4A—N1A—N2A—C7A	-175.4 (6)	K2—S1A—C1B—C6B	111.0 (14)
C7B—N2B—N1B—C4B	179.9 (11)	C6B—C1B—C2B—C3B	0.0
O2—S1—C1—C6	-146.5 (3)	S1A—C1B—C2B—C3B	-165 (3)
O3—S1—C1—C6	-23.9 (3)	C1B—C2B—C3B—C4B	0.0
O1—S1—C1—C6	95.8 (3)	C2B—C3B—C4B—C5B	0.0
K2—S1—C1—C6	149.9 (2)	C2B—C3B—C4B—N1B	174.5 (17)
O2—S1—C1—C2	40.2 (3)	N2B—N1B—C4B—C5B	9 (2)
O3—S1—C1—C2	162.8 (3)	N2B—N1B—C4B—C3B	-165.3 (14)
O1—S1—C1—C2	-77.5 (3)	C3B—C4B—C5B—C6B	0.0
K2—S1—C1—C2	-23.4 (3)	N1B—C4B—C5B—C6B	-174 (2)
O1A—S1A—C1A—C2A	-29.6 (10)	C4B—C5B—C6B—C1B	0.0
O3A—S1A—C1A—C2A	-151.2 (7)	C2B—C1B—C6B—C5B	0.0
O2A—S1A—C1A—C2A	90.9 (8)	S1A—C1B—C6B—C5B	165 (3)
K1—S1A—C1A—C2A	145.2 (6)	N1B—N2B—C7B—C8B	-177.2 (13)
K2—S1A—C1A—C2A	-87.9 (10)	N1B—N2B—C7B—C12B	1.6 (19)
O1A—S1A—C1A—C6A	154.3 (7)	C12B—C7B—C8B—C9B	0.0
O3A—S1A—C1A—C6A	32.6 (10)	N2B—C7B—C8B—C9B	178.9 (17)
O2A—S1A—C1A—C6A	-85.3 (9)	C7B—C8B—C9B—C10B	0.0
K1—S1A—C1A—C6A	-30.9 (14)	C8B—C9B—C10B—C11B	0.0
K2—S1A—C1A—C6A	96.0 (9)	C8B—C9B—C10B—N3A	180 (3)
C6—C1—C2—C3	-2.2 (5)	C15A—N3A—C10B—C9B	4 (3)
S1—C1—C2—C3	171.0 (3)	C13A—N3A—C10B—C9B	165.0 (9)
C1—C2—C3—C4	-1.2 (5)	C15A—N3A—C10B—C11B	-176.5 (10)
C2—C3—C4—C5	4.7 (5)	C13A—N3A—C10B—C11B	-15 (3)
C2—C3—C4—N1	-175.3 (3)	C9B—C10B—C11B—C12B	0.0
N2—N1—C4—C5	-169.2 (3)	N3A—C10B—C11B—C12B	-180 (3)
N2—N1—C4—C3	10.8 (5)	C10B—C11B—C12B—C7B	0.0
C3—C4—C5—C6	-4.9 (5)	C8B—C7B—C12B—C11B	0.0
N1—C4—C5—C6	175.1 (3)	N2B—C7B—C12B—C11B	-178.8 (19)
C4—C5—C6—C1	1.5 (5)	C10—N3—C13—C14	-78.6 (4)
C2—C1—C6—C5	2.1 (5)	C15—N3—C13—C14	108.5 (4)
S1—C1—C6—C5	-171.1 (3)	C10A—N3A—C13A—C14A	92.9 (10)
N1—N2—C7—C8	172.8 (3)	C10B—N3A—C13A—C14A	99 (2)
N1—N2—C7—C12	-9.9 (5)	C15A—N3A—C13A—C14A	-100.6 (4)
C12—C7—C8—C9	2.5 (6)	N3—C13—C14—O4	-70.5 (4)
N2—C7—C8—C9	179.9 (3)	K1 <sup>vi</sup> —O4A—C14A—C13A	176.5 (2)
C7—C8—C9—C10	-2.0 (6)	N3A—C13A—C14A—O4A	72.4 (4)
C15—N3—C10—C9	174.8 (3)	C10—N3—C15—C16	84.7 (4)
C13—N3—C10—C9	2.0 (5)	C13—N3—C15—C16	-102.3 (4)
C15—N3—C10—C11	-4.7 (5)	C10A—N3A—C15A—C16A	-79.5 (11)
C13—N3—C10—C11	-177.5 (3)	C10B—N3A—C15A—C16A	-81.8 (19)
C8—C9—C10—N3	-178.6 (3)	C13A—N3A—C15A—C16A	115.0 (3)
C8—C9—C10—C11	0.9 (5)	K2 <sup>vii</sup> —O5—C16—C15	67.5 (4)
C15A—N3A—C10A—C9A	-177.1 (6)	N3—C15—C16—O5	79.4 (4)

C13A—N3A—C10A—C9A	-11.6 (14)	N3A—C15A—C16A—O5A	-67.6 (4)
C15A—N3A—C10A—C11A	2.4 (16)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H1H $\cdots$ O4W	0.87 (1)	1.84 (1)	2.703 (4)	171 (4)
O5—H2H $\cdots$ O4	0.88 (1)	1.85 (1)	2.719 (3)	173 (4)
O4A—H3H $\cdots$ O5A	0.87 (1)	1.86 (2)	2.695 (3)	161 (3)
O5A—H4H $\cdots$ O3W	0.88 (1)	1.93 (2)	2.738 (3)	154 (3)
O1W—H1W $\cdots$ O5A <sup>iii</sup>	0.87 (1)	2.22 (2)	3.017 (3)	151 (3)
O1W—H2W $\cdots$ O4 <sup>iv</sup>	0.87 (1)	2.08 (1)	2.906 (3)	158 (3)
O2W—H3W $\cdots$ O5 <sup>v</sup>	0.87 (1)	1.93 (1)	2.791 (4)	170 (4)
O2W—H4W $\cdots$ O2	0.87 (1)	1.99 (2)	2.795 (3)	153 (3)
O3W—H5W $\cdots$ O3 <sup>ix</sup>	0.87 (1)	1.93 (1)	2.786 (3)	167 (3)
O3W—H6W $\cdots$ O4W <sup>x</sup>	0.88 (1)	1.99 (1)	2.821 (4)	158 (3)
O4W—H7W $\cdots$ O4A <sup>xi</sup>	0.88 (1)	1.94 (1)	2.789 (3)	163 (3)
O4W—H8W $\cdots$ O1 <sup>ix</sup>	0.88 (1)	1.86 (1)	2.738 (3)	180 (4)

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

Poly[(3-{2-(4-hydroxyphenyl)diazen-1-yl}benzenesulfonato)potassium] (K5)

Crystal data

$[\text{K}(\text{C}_{12}\text{H}_9\text{N}_2\text{O}_4\text{S})]$

$M_r = 316.37$

Orthorhombic, *Pccn*

$a = 12.5535$  (2)  $\text{\AA}$

$b = 27.9698$  (5)  $\text{\AA}$

$c = 6.9982$  (1)  $\text{\AA}$

$V = 2457.20$  (7)  $\text{\AA}^3$

$Z = 8$

$F(000) = 1296$

$D_x = 1.710$   $\text{Mg m}^{-3}$

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

Cell parameters from 3222 reflections

$\theta = 1.0\text{--}27.5^\circ$

$\mu = 0.62$   $\text{mm}^{-1}$

$T = 123$  K

Needle, yellow

$0.70 \times 0.08 \times 0.04$  mm

Data collection

Enraf–Nonius KappaCCD  
diffractometer

Radiation source: sealed tube

$\omega$  and  $\phi$  scans

5174 measured reflections

2802 independent reflections

1971 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.056$

$\theta_{\text{max}} = 27.4^\circ$ ,  $\theta_{\text{min}} = 1.5^\circ$

$h = -16 \rightarrow 16$

$k = -35 \rightarrow 36$

$l = -9 \rightarrow 9$

Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.092$

$S = 1.05$

2802 reflections

185 parameters

1 restraint

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2 + 2.2145P]$

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

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

$\Delta\rho_{\text{max}} = 0.39$   $\text{e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.41$   $\text{e \AA}^{-3}$

*Special details*

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
K1	0.65356 (5)	0.50424 (2)	0.18594 (8)	0.01900 (15)
S1	0.42945 (5)	0.44186 (2)	0.33020 (9)	0.01226 (15)
O1	0.53205 (14)	0.44178 (6)	0.4257 (3)	0.0221 (4)
O2	0.42970 (16)	0.47067 (6)	0.1573 (2)	0.0232 (5)
O3	0.34195 (15)	0.45457 (6)	0.4572 (3)	0.0219 (4)
O4	0.75203 (15)	0.06592 (6)	0.4630 (3)	0.0176 (4)
N1	0.52435 (16)	0.26259 (7)	0.3155 (3)	0.0151 (5)
N2	0.49261 (17)	0.22095 (7)	0.2784 (3)	0.0151 (5)
C1	0.3142 (2)	0.37266 (9)	0.1500 (4)	0.0154 (6)
H1	0.268119	0.397996	0.113452	0.018*
C2	0.4042 (2)	0.38193 (8)	0.2578 (3)	0.0119 (5)
C3	0.4732 (2)	0.34535 (8)	0.3090 (4)	0.0138 (5)
H3	0.535957	0.352124	0.379793	0.017*
C4	0.4493 (2)	0.29836 (8)	0.2554 (4)	0.0128 (5)
C5	0.3585 (2)	0.28883 (9)	0.1480 (4)	0.0149 (6)
H5	0.342403	0.256992	0.110563	0.018*
C6	0.2919 (2)	0.32598 (9)	0.0959 (4)	0.0169 (6)
H6	0.229995	0.319477	0.022130	0.020*
C7	0.5637 (2)	0.18368 (8)	0.3358 (4)	0.0144 (5)
C8	0.5289 (2)	0.13728 (9)	0.2979 (4)	0.0158 (6)
H8	0.461027	0.132318	0.241007	0.019*
C9	0.59238 (19)	0.09843 (9)	0.3426 (4)	0.0152 (5)
H9	0.568711	0.066853	0.316210	0.018*
C10	0.6911 (2)	0.10615 (8)	0.4263 (4)	0.0137 (5)
C11	0.7258 (2)	0.15214 (9)	0.4697 (4)	0.0154 (6)
H11	0.792806	0.156931	0.529763	0.019*
C12	0.6618 (2)	0.19088 (9)	0.4247 (4)	0.0158 (6)
H12	0.684753	0.222373	0.454440	0.019*
H1H	0.8159 (13)	0.0744 (12)	0.495 (5)	0.055 (12)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
K1	0.0221 (3)	0.0181 (3)	0.0168 (3)	−0.0013 (2)	0.0001 (3)	0.0007 (2)
S1	0.0124 (3)	0.0102 (3)	0.0142 (3)	−0.0002 (2)	−0.0006 (3)	0.0008 (3)
O1	0.0169 (10)	0.0165 (9)	0.0330 (11)	−0.0001 (8)	−0.0122 (9)	−0.0002 (9)
O2	0.0394 (12)	0.0155 (9)	0.0146 (10)	−0.0021 (9)	−0.0034 (9)	0.0049 (8)
O3	0.0197 (11)	0.0184 (9)	0.0278 (11)	−0.0036 (8)	0.0121 (9)	−0.0083 (8)
O4	0.0144 (10)	0.0147 (8)	0.0238 (10)	0.0036 (8)	−0.0036 (9)	0.0008 (8)

N1	0.0159 (11)	0.0137 (10)	0.0158 (11)	0.0004 (8)	0.0033 (10)	-0.0003 (9)
N2	0.0168 (12)	0.0124 (10)	0.0161 (12)	0.0016 (9)	0.0019 (9)	-0.0006 (9)
C1	0.0146 (14)	0.0151 (12)	0.0165 (14)	0.0018 (10)	-0.0010 (11)	0.0005 (11)
C2	0.0134 (13)	0.0114 (11)	0.0109 (12)	-0.0015 (10)	0.0014 (10)	-0.0005 (10)
C3	0.0124 (13)	0.0157 (12)	0.0134 (13)	-0.0022 (10)	0.0013 (11)	-0.0004 (11)
C4	0.0121 (13)	0.0134 (12)	0.0130 (12)	0.0024 (10)	0.0040 (10)	0.0021 (10)
C5	0.0155 (14)	0.0130 (11)	0.0161 (14)	-0.0015 (10)	0.0009 (11)	-0.0022 (10)
C6	0.0149 (14)	0.0203 (13)	0.0154 (14)	-0.0016 (11)	-0.0036 (12)	-0.0008 (11)
C7	0.0156 (13)	0.0137 (12)	0.0138 (13)	0.0020 (10)	0.0025 (11)	0.0016 (11)
C8	0.0125 (13)	0.0185 (13)	0.0164 (14)	-0.0019 (10)	0.0016 (11)	0.0005 (11)
C9	0.0162 (14)	0.0128 (12)	0.0164 (13)	-0.0005 (10)	0.0034 (11)	0.0000 (11)
C10	0.0135 (13)	0.0124 (12)	0.0153 (13)	0.0023 (10)	0.0025 (11)	0.0007 (10)
C11	0.0115 (14)	0.0171 (12)	0.0177 (14)	-0.0005 (10)	-0.0022 (11)	0.0003 (11)
C12	0.0165 (14)	0.0113 (11)	0.0197 (14)	-0.0017 (10)	0.0010 (12)	-0.0015 (11)

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

K1—O2 <sup>i</sup>	2.7117 (18)	C1—C2	1.383 (3)
K1—O3 <sup>ii</sup>	2.7511 (18)	C1—C6	1.388 (3)
K1—O4 <sup>iii</sup>	2.7954 (19)	C1—H1	0.9500
K1—O3 <sup>iv</sup>	2.815 (2)	C2—C3	1.387 (3)
K1—O1	2.863 (2)	C3—C4	1.399 (3)
K1—O2	2.970 (2)	C3—H3	0.9500
K1—O4 <sup>v</sup>	3.0023 (19)	C4—C5	1.391 (3)
K1—S1	3.4611 (8)	C5—C6	1.383 (3)
K1—S1 <sup>iv</sup>	3.7788 (9)	C5—H5	0.9500
K1—K1 <sup>vi</sup>	4.2551 (7)	C6—H6	0.9500
K1—K1 <sup>vii</sup>	4.2551 (7)	C7—C12	1.394 (3)
K1—K1 <sup>i</sup>	4.6577 (12)	C7—C8	1.395 (3)
S1—O1	1.4510 (18)	C8—C9	1.384 (3)
S1—O2	1.4539 (18)	C8—H8	0.9500
S1—O3	1.4568 (18)	C9—C10	1.387 (3)
S1—C2	1.779 (2)	C9—H9	0.9500
O4—C10	1.385 (3)	C10—C11	1.392 (3)
O4—H1H	0.866 (10)	C11—C12	1.385 (3)
N1—N2	1.258 (3)	C11—H11	0.9500
N1—C4	1.437 (3)	C12—H12	0.9500
N2—C7	1.430 (3)		
O2 <sup>i</sup> —K1—O3 <sup>ii</sup>	134.72 (6)	O1—S1—O2	112.48 (12)
O2 <sup>i</sup> —K1—O4 <sup>iii</sup>	81.82 (6)	O1—S1—O3	112.88 (11)
O3 <sup>ii</sup> —K1—O4 <sup>iii</sup>	142.35 (6)	O2—S1—O3	111.97 (11)
O2 <sup>i</sup> —K1—O3 <sup>iv</sup>	84.43 (6)	O1—S1—C2	106.71 (11)
O3 <sup>ii</sup> —K1—O3 <sup>iv</sup>	97.73 (5)	O2—S1—C2	106.57 (11)
O4 <sup>iii</sup> —K1—O3 <sup>iv</sup>	73.57 (5)	O3—S1—C2	105.63 (11)
O2 <sup>i</sup> —K1—O1	118.14 (6)	O1—S1—K1	54.10 (8)
O3 <sup>ii</sup> —K1—O1	74.59 (5)	O2—S1—K1	58.40 (8)
O4 <sup>iii</sup> —K1—O1	97.72 (5)	O3—S1—K1	131.90 (7)

O3 <sup>iv</sup> —K1—O1	154.96 (5)	C2—S1—K1	122.44 (8)
O2 <sup>i</sup> —K1—O2	69.95 (6)	O1—S1—K1 <sup>viii</sup>	145.89 (8)
O3 <sup>ii</sup> —K1—O2	102.30 (5)	O2—S1—K1 <sup>viii</sup>	75.88 (8)
O4 <sup>iii</sup> —K1—O2	99.13 (5)	O3—S1—K1 <sup>viii</sup>	39.63 (8)
O3 <sup>iv</sup> —K1—O2	154.22 (5)	C2—S1—K1 <sup>viii</sup>	101.78 (8)
O1—K1—O2	48.88 (5)	K1—S1—K1 <sup>viii</sup>	122.356 (16)
O2 <sup>i</sup> —K1—O4 <sup>v</sup>	153.28 (5)	S1—O1—K1	101.66 (9)
O3 <sup>ii</sup> —K1—O4 <sup>v</sup>	71.30 (5)	S1—O2—K1 <sup>i</sup>	151.62 (11)
O4 <sup>iii</sup> —K1—O4 <sup>v</sup>	74.16 (4)	S1—O2—K1	96.95 (9)
O3 <sup>iv</sup> —K1—O4 <sup>v</sup>	99.53 (5)	K1 <sup>i</sup> —O2—K1	110.05 (6)
O1—K1—O4 <sup>v</sup>	55.46 (5)	S1—O3—K1 <sup>ii</sup>	129.83 (11)
O2—K1—O4 <sup>v</sup>	102.15 (5)	S1—O3—K1 <sup>viii</sup>	121.09 (10)
O2 <sup>i</sup> —K1—S1	94.33 (4)	K1 <sup>ii</sup> —O3—K1 <sup>viii</sup>	99.72 (6)
O3 <sup>ii</sup> —K1—S1	87.87 (4)	C10—O4—K1 <sup>ix</sup>	115.43 (15)
O4 <sup>iii</sup> —K1—S1	99.69 (4)	C10—O4—K1 <sup>v</sup>	129.03 (15)
O3 <sup>iv</sup> —K1—S1	173.25 (4)	K1 <sup>ix</sup> —O4—K1 <sup>v</sup>	94.37 (5)
O1—K1—S1	24.24 (4)	C10—O4—H1H	110 (2)
O2—K1—S1	24.64 (3)	K1 <sup>ix</sup> —O4—H1H	117 (2)
O4 <sup>v</sup> —K1—S1	78.64 (4)	K1 <sup>v</sup> —O4—H1H	89 (2)
O2 <sup>i</sup> —K1—S1 <sup>iv</sup>	102.92 (4)	N2—N1—C4	112.1 (2)
O3 <sup>ii</sup> —K1—S1 <sup>iv</sup>	80.87 (4)	N1—N2—C7	114.8 (2)
O4 <sup>iii</sup> —K1—S1 <sup>iv</sup>	81.84 (4)	C2—C1—C6	119.4 (2)
O3 <sup>iv</sup> —K1—S1 <sup>iv</sup>	19.28 (4)	C2—C1—H1	120.3
O1—K1—S1 <sup>iv</sup>	138.53 (4)	C6—C1—H1	120.3
O2—K1—S1 <sup>iv</sup>	172.48 (4)	C1—C2—C3	120.8 (2)
O4 <sup>v</sup> —K1—S1 <sup>iv</sup>	85.31 (4)	C1—C2—S1	118.51 (19)
S1—K1—S1 <sup>iv</sup>	162.711 (19)	C3—C2—S1	120.68 (19)
O2 <sup>i</sup> —K1—K1 <sup>vi</sup>	59.40 (4)	C2—C3—C4	119.3 (2)
O3 <sup>ii</sup> —K1—K1 <sup>vi</sup>	137.30 (4)	C2—C3—H3	120.3
O4 <sup>iii</sup> —K1—K1 <sup>vi</sup>	44.71 (4)	C4—C3—H3	120.3
O3 <sup>iv</sup> —K1—K1 <sup>vi</sup>	39.59 (4)	C5—C4—C3	120.0 (2)
O1—K1—K1 <sup>vi</sup>	141.74 (4)	C5—C4—N1	124.2 (2)
O2—K1—K1 <sup>vi</sup>	118.87 (4)	C3—C4—N1	115.8 (2)
O4 <sup>v</sup> —K1—K1 <sup>vi</sup>	107.84 (4)	C6—C5—C4	119.6 (2)
S1—K1—K1 <sup>vi</sup>	134.620 (17)	C6—C5—H5	120.2
S1 <sup>iv</sup> —K1—K1 <sup>vi</sup>	56.903 (18)	C4—C5—H5	120.2
O2 <sup>i</sup> —K1—K1 <sup>vii</sup>	161.38 (4)	C5—C6—C1	120.8 (2)
O3 <sup>ii</sup> —K1—K1 <sup>vii</sup>	40.69 (4)	C5—C6—H6	119.6
O4 <sup>iii</sup> —K1—K1 <sup>vii</sup>	101.97 (4)	C1—C6—H6	119.6
O3 <sup>iv</sup> —K1—K1 <sup>vii</sup>	79.31 (4)	C12—C7—C8	119.8 (2)
O1—K1—K1 <sup>vii</sup>	79.70 (4)	C12—C7—N2	124.9 (2)
O2—K1—K1 <sup>vii</sup>	126.44 (4)	C8—C7—N2	115.4 (2)
O4 <sup>v</sup> —K1—K1 <sup>vii</sup>	40.92 (4)	C9—C8—C7	120.4 (2)
S1—K1—K1 <sup>vii</sup>	102.865 (15)	C9—C8—H8	119.8
S1 <sup>iv</sup> —K1—K1 <sup>vii</sup>	60.202 (18)	C7—C8—H8	119.8
K1 <sup>vi</sup> —K1—K1 <sup>vii</sup>	110.64 (3)	C8—C9—C10	119.2 (2)
O2 <sup>i</sup> —K1—K1 <sup>i</sup>	36.80 (4)	C8—C9—H9	120.4
O3 <sup>ii</sup> —K1—K1 <sup>i</sup>	123.06 (5)	C10—C9—H9	120.4

O4 <sup>iii</sup> —K1—K1 <sup>i</sup>	91.05 (4)	O4—C10—C9	116.4 (2)
O3 <sup>iv</sup> —K1—K1 <sup>i</sup>	121.17 (4)	O4—C10—C11	122.5 (2)
O1—K1—K1 <sup>i</sup>	81.68 (4)	C9—C10—C11	121.0 (2)
O2—K1—K1 <sup>i</sup>	33.16 (3)	C12—C11—C10	119.5 (2)
O4 <sup>v</sup> —K1—K1 <sup>i</sup>	130.86 (4)	C12—C11—H11	120.3
S1—K1—K1 <sup>i</sup>	57.616 (16)	C10—C11—H11	120.3
S1 <sup>iv</sup> —K1—K1 <sup>i</sup>	139.67 (2)	C11—C12—C7	120.1 (2)
K1 <sup>vi</sup> —K1—K1 <sup>i</sup>	90.662 (13)	C11—C12—H12	120.0
K1 <sup>vii</sup> —K1—K1 <sup>i</sup>	158.51 (2)	C7—C12—H12	120.0
O2—S1—O1—K1	1.78 (12)	O2—S1—C2—C3	125.4 (2)
O3—S1—O1—K1	-126.11 (9)	O3—S1—C2—C3	-115.4 (2)
C2—S1—O1—K1	118.29 (10)	K1—S1—C2—C3	62.7 (2)
K1 <sup>viii</sup> —S1—O1—K1	-96.28 (13)	K1 <sup>viii</sup> —S1—C2—C3	-156.05 (19)
O1—S1—O2—K1 <sup>i</sup>	160.5 (2)	C1—C2—C3—C4	-1.9 (4)
O3—S1—O2—K1 <sup>i</sup>	-71.1 (2)	S1—C2—C3—C4	177.85 (19)
C2—S1—O2—K1 <sup>i</sup>	43.9 (3)	C2—C3—C4—C5	1.5 (4)
K1—S1—O2—K1 <sup>i</sup>	162.2 (3)	C2—C3—C4—N1	-179.5 (2)
K1 <sup>viii</sup> —S1—O2—K1 <sup>i</sup>	-54.4 (2)	N2—N1—C4—C5	-7.4 (3)
O1—S1—O2—K1	-1.69 (11)	N2—N1—C4—C3	173.6 (2)
O3—S1—O2—K1	126.67 (9)	C3—C4—C5—C6	-0.5 (4)
C2—S1—O2—K1	-118.29 (10)	N1—C4—C5—C6	-179.4 (2)
K1 <sup>viii</sup> —S1—O2—K1	143.38 (6)	C4—C5—C6—C1	-0.2 (4)
O1—S1—O3—K1 <sup>ii</sup>	14.64 (16)	C2—C1—C6—C5	-0.1 (4)
O2—S1—O3—K1 <sup>ii</sup>	-113.50 (13)	N1—N2—C7—C12	-0.6 (4)
C2—S1—O3—K1 <sup>ii</sup>	130.89 (13)	N1—N2—C7—C8	179.1 (2)
K1—S1—O3—K1 <sup>ii</sup>	-46.90 (17)	C12—C7—C8—C9	-2.0 (4)
K1 <sup>viii</sup> —S1—O3—K1 <sup>ii</sup>	-139.42 (18)	N2—C7—C8—C9	178.3 (2)
O1—S1—O3—K1 <sup>viii</sup>	154.06 (10)	C7—C8—C9—C10	0.3 (4)
O2—S1—O3—K1 <sup>viii</sup>	25.92 (14)	K1 <sup>ix</sup> —O4—C10—C9	-55.4 (3)
C2—S1—O3—K1 <sup>viii</sup>	-89.69 (12)	K1 <sup>v</sup> —O4—C10—C9	64.2 (3)
K1—S1—O3—K1 <sup>viii</sup>	92.52 (11)	K1 <sup>ix</sup> —O4—C10—C11	124.8 (2)
C4—N1—N2—C7	-179.7 (2)	K1 <sup>v</sup> —O4—C10—C11	-115.6 (2)
C6—C1—C2—C3	1.2 (4)	C8—C9—C10—O4	-178.3 (2)
C6—C1—C2—S1	-178.5 (2)	C8—C9—C10—C11	1.5 (4)
O1—S1—C2—C1	-175.3 (2)	O4—C10—C11—C12	178.4 (2)
O2—S1—C2—C1	-54.9 (2)	C9—C10—C11—C12	-1.5 (4)
O3—S1—C2—C1	64.3 (2)	C10—C11—C12—C7	-0.3 (4)
K1—S1—C2—C1	-117.61 (19)	C8—C7—C12—C11	2.0 (4)
K1 <sup>viii</sup> —S1—C2—C1	23.7 (2)	N2—C7—C12—C11	-178.3 (2)
O1—S1—C2—C3	5.0 (2)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
---------------	-------	-------------	-------------	---------------

---

O4—H1H···O1 <sup>v</sup>	0.87 (1)	2.02 (3)	2.732 (3)	139 (3)
--------------------------	----------	----------	-----------	---------

---

Symmetry code: (v)  $-x+3/2, -y+1/2, z$ .