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Dipotassium biphenyl-4,4′-disulfonate dihydrate: a coordination polymer

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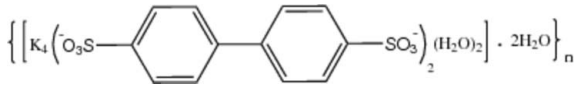
Key indicators: single-crystal X-ray study; T = 297 K; mean σ(C–C) = 0.006 Å; R factor = 0.031; wR factor = 0.083; data-to-parameter ratio = 10.1.

The polymeric structure of the title compound, poly-[[diaquabis(μ-biphenyl-4,4′-disulfonato)tetrapotassium(I)] dihydrate], $\{[K_2(C_{12}H_8O_6S_2)(H_2O)]\cdot H_2O\}_n$, is based on an asymmetric unit comprising three independent and different potassium centres, one six-coordinate [K—O = 2.657 (3)–2.866 (5) Å], one seven-coordinate [K—O = 2.703 (3)–3.040 (4) Å], and the third ten-coordinate [K—O = 2.751 (3)–3.079 (4) Å], with two of these lying on crystallographic mirror planes. The four half-occupancy water molecules also lie on the mirror planes with two coordinated (one monodentate, the other bidentate bridging) and two as molecules of solvation. The interlinked coordination polyhedra form chains which are joined laterally through the biphenyl residues as well as through head-to-tail water hydrogen-bonding interactions, giving a two-dimensional structure.

Related literature

For other 4,4′-biphenyldisulfonate crystal structures, see: Swift *et al.* (1998); Liao *et al.* (2001); Cai *et al.* (2001); Usuki *et al.* (2002). For related literature, see: Pivovar *et al.* (2002). For synthesis, see: Feldmann (1931).



Experimental

Crystal data

$[K_2(C_{12}H_8O_6S_2)(H_2O)]\cdot H_2O$
M_r = 426.56
Monoclinic, *Cm*
a = 5.8316 (10) Å
b = 19.691 (7) Å
c = 14.623 (2) Å
β = 98.953 (13)°
V = 1658.7 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.86 mm^{-1}
T = 297 (2) K
0.32 × 0.25 × 0.20 mm

Data collection

Rigaku AFC 7R diffractometer
Absorption correction: ψ scan (*TEXSAN for Windows*; Molecular Structure Corporation, 1999)
T_{min} = 0.774, T_{max} = 0.849
2295 measured reflections
2295 independent reflections
2196 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
3 standard reflections
frequency: 150 min
intensity decay: 0.6%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.083
S = 0.88
2295 reflections
227 parameters
2 restraints
H-atom parameters not refined
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}
Absolute structure: Flack (1983), 322 Friedel pairs
Flack parameter: 0.02 (8)

Table 1
Selected bond lengths (Å).

K1—O43*B*	2.850 (4)	K2—O42*A*^{vii}	2.741 (3)
K1—O41*B*^{i}	2.703 (3)	K3—O2*W*	3.079 (4)
K1—O41*A*^{ii}	3.040 (4)	K3—O41*B*	2.751 (3)
K1—O43*A*^{ii}	3.058 (3)	K3—O42*B*	3.076 (4)
K1—O42*A*^{iii}	2.866 (3)	K3—O42*A*^{iii}	2.938 (3)
K1—O43*B*^{iv}	2.739 (3)	K3—O43*A*^{iii}	3.027 (3)
K1—O41*A*^{v}	2.681 (3)	K3—O2*W*^{viii}	2.793 (4)
K2—O1*W*	2.703 (6)	K3—O41*B*^{ix}	2.751 (3)
K2—O2*W*	2.866 (5)	K3—O42*B*^{ix}	3.076 (4)
K2—O43*A*^{ii}	2.657 (3)	K3—O42*A*^{vii}	2.938 (3)
K2—O42*A*^{iii}	2.741 (3)	K3—O43*A*^{vii}	3.027 (3)
K2—O43*A*^{vi}	2.657 (3)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H11*W*···O4*W*^{iii}	0.97	2.18	2.778 (9)	119
O2*W*—H2*W*···O42*B*	0.96	1.91	2.840 (5)	162
O3*W*—H3*W*···O42*B*	0.96	1.95	2.884 (5)	162
O4*W*—H41*W*···O3*W*	0.90	1.82	2.715 (9)	180
O4*W*—H41*W*···O3*W*	0.90	1.82	2.715 (9)	180
C5*A*—H5*A*···O43*A*	0.95	2.50	2.916 (5)	106
C5*B*—H5*B*···O41*B*	0.94	2.47	2.873 (5)	106

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

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2210).

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Cai, J., Hu, X.-P., Yao, J.-H. & Ji, L.-N. (2001). *Inorg. Chem. Commun.* **4**, 478–482.

Feldmann, J. (1931). *Helv. Chim. Acta*, **14**, 751–778.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Liao, C.-Z., Feng, X.-L., Yao, J.-H. & Cai, J.-W. (2001). *Acta Cryst.* C**57**, 1215–1216.

Molecular Structure Corporation (1999). *MSC/AFC Diffractometer Control Software* and *TEXSAN for Windows* (Version 1.06). MSC, The Woodlands, Texas, USA.

Pivovar, A. M., Ward, M. D., Brown, C. M. & Neumann, D. A. (2002). *J. Phys. Chem.* **106**, 4916–4924.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Swift, J. A., Pivovar, A. M., Reynolds, A. M. & Ward, M. D. (1998). *J. Am. Chem. Soc.* **120**, 5887–5894.

Usuki, N., Ohba, M. & Okawa, H. (2002). *J. Chem. Soc. Jpn*, **75**, 1693–1698.

supplementary materials

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Dipotassium biphenyl-4,4'-disulfonate dihydrate: a coordination polymer

G. Smith, U. D. Wermuth and P. C. Healy

Comment

Compounds of 4,4'-biphenyldisulfonic acid (BPDS) are not numerous in the crystallographic literature. The guanidinium salts have been used for the generation of 2-D structures for the formation of crystalline clathrates with aromatic hydrocarbons (Swift *et al.*, 1998; Pivovar *et al.*, 2002). The bis(alaninium) salt is also known (Liao *et al.*, 2001). With coordination compounds, BDPDS is generally found as a dianionic counter ion (Cai *et al.*, 2001; Usuki *et al.*, 2002). We obtained X-ray diffraction quality crystals of the hydrated dipotassium salt of BPDS as an intermediate in the synthesis of BPDS, when recrystallized from water. The structure of this compound, $K_2^{2+}\cdot C_{12}H_8O_6S_2^{2-}\cdot 2H_2O$ (I) is reported here.

The structure of (I) is based on an asymmetric unit comprising three independent and different potassium centres, one six-coordinate (K2) [K–O range, 2.657 (3)–2.866 (5) Å], one seven- coordinate (K1) [K–O range, 2.703 (3)–3.040 (4) Å] and the third ten-coordinate (K3) [K–O range, 2.751 (3)–3.079 (4) Å], with two of these (K2 and K3) lying on crystallographic mirror planes (Fig. 1). The four half-occupancy water molecules also lie on the mirror planes with two coordinated [one monodentate (O1W on K2), and one bidentate (O2W, bridging K2 and K3)], and the other two (OW3, OW4) as molecules of solvation. The structure has pseudo 2/m symmetry, the 2-fold rotational symmetry along the *b* axis being upset largely by the differing roles of the water molecules in the structure. This was also consistent with the failure to obtain a solution of the structure in the space group *C*2/*m*.

The interlinked potassium coordination polyhedra form chains which extend down the *b* axix and are linked laterally across the *c* cell direction through the biphenyl residues of the BPDS ligands, giving a 2-D structure (Fig. 2). This is somewhat analogous to the 2-D but hydrogen-bonded guanidinium-BPDS open framework structures (Swift *et al.*, 1998; Pivovar *et al.*, 2002) which accommodate interstitial inert aromatic molecules. With (I), the water molecules are similarly accommodated in the interstitial spaces along the crystallographic mirror planes in linear head-to-tail interactions (Table 1) and also link the coordination polymer chains. In addition, the coordinated water molecules give lateral $O–H\cdots O_{sulfonate}$ interactions within the polymer chains.

Within the BPDS anion, the two phenyl rings (A and B) are close to co-planar [torsion angle C2A–C1A–C1B–C6B, −178.3 (5) °], which is similar to that found in the alaninium salt where the two residues are inversion related (Liao *et al.*, 2001).

Experimental

The title compound was obtained as colourless crystals from the room temperature evaporation of an aqueous solution of dipotassium 4,4-biphenyldisulfonate, an intermediate product in the synthesis of 4,4'-biphenyldisulfonic acid by the sulfonation of biphenyl using the procedure of Feldmann (1931).

Refinement

Hydrogen atoms on the water molecules were located by difference methods but their positional and isotropic displacement parameters were fixed as located and $U_{iso}(H) = 1.2U_{eq}(O)$, respectively; see Table 1 for distances. The aromatic H atoms were included in the refinement in their calculated positions (C–H = 0.94–0.95 Å) using a riding model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

Fig. 1. Molecular configuration and atom naming scheme for the BPDS ligand, the three independent potassium coordination polyhedra and the water molecules in the asymmetric unit of (I). Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen-bonding interactions associated with the water molecules. The two potassium ions (K2, K3) and the four water molecules (O1W–O4W) lie on a crystallographic mirror plane. Symmetry codes: (i) *x* − 1, *y*, *z*; (ii) *x* − 1, *y*, *z* + 1; (iii) *x*, *y*, *z* + 1; (iv) *x* − 1/2, −*y* + 1/2, *z*; (v) *x* − 1/2, −*y* + 1/2, *z* + 1; (vi) *x* − 1, −*y*, *z* + 1; (vii) *x*, −*y*, *z* + 1; (viii) *x* + 1, *y*, *z*; (ix) *x*, −*y*, *z*.

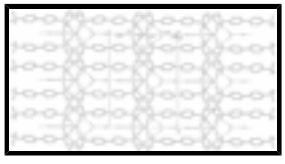


Fig. 2. The 2-D hydrogen-bonded structure of (I) viewed down the *a* axis, showing *K*–$O_{sulfonate}$ coordination-polymer chains with the biphenyl step linkages, together with the water mediated hydrogen-bonding associations lying on the mirror planes at *y* = 0, 1/2.

dipotassium biphenyl-4,4'-disulfonate dihydrate

Crystal data

$2K^+ \cdot C_{12}H_8O_6S_2^{2-} \cdot 2H_2O$	$F_{000} = 872$
$M_r = 426.56$	$D_x = 1.708$ Mg m^{-3}
Monoclinic, *Cm*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: C -2y	Cell parameters from 25 reflections
a = 5.8316 (10) Å	θ = 12.9–17.1º
b = 19.691 (7) Å	μ = 0.86 mm^{-1}
c = 14.623 (2) Å	*T* = 297 (2) K
β = 98.953 (13)º	Block, colourless
V = 1658.7 (7) Å^3	0.32 × 0.25 × 0.20 mm
Z = 4	

Data collection

Rigaku AFC 7R diffractometer	$R_{int} = 0.016$
Radiation source: rotating anode	$\theta_{max} = 27.5$º
Monochromator: graphite	$\theta_{min} = 2.5$º
T = 297(2) K	*h* = −3→7
ω–2θ scans	*k* = 0→25
Absorption correction: ψ scan	*l* = −18→18

(TEXSAN for Windows; Molecular Structure Corporation, 1999)

T_{min} = 0.774, T_{max} = 0.849

2295 measured reflections

2295 independent reflections

2196 reflections with $I > 2\sigma(I)$

3 standard reflections

every 150 min

intensity decay: 0.6%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.083$

$S = 0.88$

2295 reflections

227 parameters

2 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 15.7726P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.40$ e Å^{-3}

$\Delta\rho_{min} = -0.39$ e Å^{-3}

Extinction correction: none

Absolute structure: Flack (1983)

Flack parameter: 0.02 (8)

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
K1	0.27341 (18)	0.18494 (4)	0.50427 (7)	0.0306 (2)
K2	0.3806 (2)	0.00000	0.66340 (8)	0.0322 (3)
K3	0.8140 (2)	0.00000	0.48912 (8)	0.0331 (3)
S4A	0.85074 (12)	0.13645 (4)	−0.35496 (5)	0.0216 (2)
S4B	0.67991 (14)	0.14568 (5)	0.35851 (6)	0.0255 (2)
O1W	0.4854 (11)	0.00000	0.8501 (4)	0.080 (3)
O2W	0.2800 (7)	0.00000	0.4652 (3)	0.0354 (12)
O41A	0.8714 (6)	0.20502 (15)	−0.3888 (2)	0.0431 (9)
O41B	0.9000 (5)	0.12170 (17)	0.40854 (18)	0.0370 (9)
O42A	0.6357 (5)	0.10358 (17)	−0.39554 (19)	0.0374 (9)
O42B	0.4950 (6)	0.09558 (17)	0.3603 (2)	0.0404 (10)

O43A	1.0527 (5)	0.09479 (17)	−0.3630 (2)	0.0403 (10)
O43B	0.6088 (6)	0.21186 (17)	0.3865 (2)	0.0389 (9)
C1A	0.7952 (7)	0.15078 (19)	−0.0464 (3)	0.0274 (10)
C1B	0.7699 (7)	0.1525 (2)	0.0539 (3)	0.0285 (10)
C2A	0.6400 (8)	0.1846 (3)	−0.1132 (3)	0.0459 (15)
C2B	0.5868 (9)	0.1849 (2)	0.0848 (3)	0.0427 (14)
C3A	0.6591 (9)	0.1809 (2)	−0.2069 (3)	0.0424 (15)
C3B	0.5603 (8)	0.1853 (2)	0.1778 (3)	0.0429 (15)
C4A	0.8342 (7)	0.14383 (19)	−0.2346 (2)	0.0253 (10)
C4B	0.7182 (7)	0.1511 (2)	0.2407 (3)	0.0273 (10)
C5A	0.9927 (8)	0.1114 (3)	−0.1700 (3)	0.0497 (16)
C5B	0.9036 (10)	0.1196 (4)	0.2123 (3)	0.065 (2)
C6A	0.9716 (9)	0.1150 (3)	−0.0765 (3)	0.0533 (18)
C6B	0.9281 (9)	0.1203 (4)	0.1193 (3)	0.066 (2)
O3W	0.3491 (11)	0.00000	0.2133 (3)	0.0608 (19)
O4W	0.4275 (14)	0.00000	0.0351 (5)	0.083 (2)
H2A	0.51870	0.20980	−0.09300	0.0550*
H2B	0.47780	0.20740	0.04090	0.0510*
H2W	0.34800	0.03900	0.44000	0.0420*
H3A	0.55160	0.20360	−0.25180	0.0500*
H3B	0.43380	0.20770	0.19790	0.0510*
H5A	1.11400	0.08620	−0.19020	0.0600*
H5B	1.01260	0.09710	0.25620	0.0780*
H6A	1.07910	0.09230	−0.03160	0.0640*
H6B	1.05460	0.09790	0.09920	0.0790*
H11W	0.35600	0.00000	0.88400	0.0960*
H12W	0.61400	0.00000	0.88400	0.0960*
H3W	0.39700	0.03850	0.25200	0.0730*
H41W	0.40200	0.00000	0.09400	0.0970*
H42W	0.57940	0.00000	0.03750	0.0970*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K1	0.0334 (4)	0.0286 (4)	0.0307 (3)	−0.0007 (4)	0.0082 (3)	0.0001 (4)
K2	0.0286 (6)	0.0346 (6)	0.0344 (6)	0.0000	0.0083 (5)	0.0000
K3	0.0357 (6)	0.0317 (5)	0.0325 (6)	0.0000	0.0076 (5)	0.0000
S4A	0.0243 (4)	0.0239 (4)	0.0174 (4)	0.0011 (3)	0.0058 (3)	0.0000 (3)
S4B	0.0310 (4)	0.0297 (4)	0.0166 (4)	−0.0042 (4)	0.0062 (3)	−0.0006 (3)
O1W	0.073 (4)	0.116 (6)	0.045 (3)	0.0000	−0.005 (3)	0.0000
O2W	0.038 (2)	0.036 (2)	0.035 (2)	0.0000	0.0147 (17)	0.0000
O41A	0.076 (2)	0.0276 (14)	0.0285 (14)	−0.0031 (16)	0.0174 (15)	0.0044 (11)
O41B	0.0383 (16)	0.0489 (17)	0.0230 (13)	0.0000 (14)	0.0020 (11)	0.0051 (12)
O42A	0.0328 (14)	0.0533 (18)	0.0267 (14)	−0.0133 (14)	0.0063 (11)	−0.0078 (12)
O42B	0.0453 (17)	0.0468 (19)	0.0302 (14)	−0.0183 (15)	0.0095 (13)	0.0004 (13)
O43A	0.0370 (16)	0.057 (2)	0.0279 (14)	0.0217 (15)	0.0085 (12)	0.0012 (13)
O43B	0.0518 (17)	0.0391 (16)	0.0277 (14)	0.0023 (14)	0.0120 (13)	−0.0056 (12)
C1A	0.0342 (19)	0.0320 (18)	0.0168 (15)	0.0031 (16)	0.0068 (14)	0.0009 (13)

C1B	0.0317 (19)	0.0359 (19)	0.0181 (16)	0.0004 (16)	0.0041 (14)	−0.0003 (14)
C2A	0.051 (3)	0.069 (3)	0.0196 (17)	0.030 (2)	0.0114 (18)	0.0024 (18)
C2B	0.049 (2)	0.058 (3)	0.0222 (19)	0.024 (2)	0.0086 (17)	0.0073 (19)
C3A	0.049 (3)	0.059 (3)	0.0196 (18)	0.025 (2)	0.0071 (17)	0.0072 (17)
C3B	0.050 (3)	0.056 (3)	0.0252 (19)	0.025 (2)	0.0140 (18)	0.0019 (17)
C4A	0.0306 (18)	0.0305 (17)	0.0154 (15)	−0.0001 (15)	0.0057 (14)	−0.0018 (13)
C4B	0.0318 (19)	0.0332 (19)	0.0170 (16)	−0.0034 (15)	0.0041 (14)	−0.0016 (13)
C5A	0.044 (2)	0.084 (4)	0.0220 (18)	0.036 (3)	0.0079 (17)	0.001 (2)
C5B	0.061 (3)	0.116 (5)	0.0188 (19)	0.048 (3)	0.012 (2)	0.016 (2)
C6A	0.052 (3)	0.085 (4)	0.0229 (18)	0.037 (3)	0.0059 (18)	0.006 (2)
C6B	0.054 (3)	0.122 (5)	0.023 (2)	0.053 (3)	0.014 (2)	0.016 (3)
O3W	0.080 (4)	0.057 (3)	0.040 (3)	0.0000	−0.008 (3)	0.0000
O4W	0.091 (5)	0.104 (6)	0.055 (4)	0.0000	0.003 (4)	0.0000

Geometric parameters (Å, °)

K1—O43B	2.850 (4)	S4B—C4B	1.775 (4)
K1—O41B^{i}	2.703 (3)	O1W—H12W	0.8300
K1—O41A^{ii}	3.040 (4)	O1W—H11W	0.9700
K1—O43A^{ii}	3.058 (3)	O2W—H2W^{ix}	0.9600
K1—O42A^{iii}	2.866 (3)	O2W—H2W	0.9600
K1—O43B^{iv}	2.739 (3)	O3W—H3W	0.9600
K1—O41A^{v}	2.681 (3)	O3W—H3W^{ix}	0.9600
K2—O1W	2.703 (6)	O4W—H41W	0.9000
K2—O2W	2.866 (5)	O4W—H42W	0.8800
K2—O43A^{ii}	2.657 (3)	C1A—C6A	1.375 (7)
K2—O42A^{iii}	2.741 (3)	C1A—C2A	1.393 (6)
K2—O43A^{vi}	2.657 (3)	C1A—C1B	1.497 (6)
K2—O42A^{vii}	2.741 (3)	C1B—C2B	1.379 (6)
K3—O2W	3.079 (4)	C1B—C6B	1.376 (7)
K3—O41B	2.751 (3)	C2A—C3A	1.394 (6)
K3—O42B	3.076 (4)	C2B—C3B	1.392 (6)
K3—O42A^{iii}	2.938 (3)	C3A—C4A	1.367 (6)
K3—O43A^{iii}	3.027 (3)	C3B—C4B	1.373 (6)
K3—O2W^{viii}	2.793 (4)	C4A—C5A	1.372 (6)
K3—O41B^{ix}	2.751 (3)	C4B—C5B	1.366 (7)
K3—O42B^{ix}	3.076 (4)	C5A—C6A	1.394 (6)
K3—O42A^{vii}	2.938 (3)	C5B—C6B	1.389 (6)
K3—O43A^{vii}	3.027 (3)	C2A—H2A	0.9500
S4A—O41A	1.450 (3)	C2B—H2B	0.9400
S4A—O42A	1.453 (3)	C3A—H3A	0.9500
S4A—O43A	1.455 (3)	C3B—H3B	0.9400
S4A—C4A	1.784 (3)	C5A—H5A	0.9500
S4B—O41B	1.454 (3)	C5B—H5B	0.9400
S4B—O42B	1.465 (4)	C6A—H6A	0.9500
S4B—O43B	1.446 (4)	C6B—H6B	0.9400

O41B^{i}—K1—O43B	110.25 (9)	O41B^{ix}—K3—O42B^{ix}	48.53 (9)
O41A^{ii}—K1—O43B	160.66 (9)	O41B^{ix}—K3—O42A^{vii}	75.26 (9)
O43A^{ii}—K1—O43B	152.59 (10)	O41B^{ix}—K3—O43A^{vii}	71.01 (8)
O42A^{iii}—K1—O43B	83.81 (9)	O42A^{vii}—K3—O42B^{ix}	72.09 (8)
O43B—K1—O43B^{iv}	71.84 (10)	O42B^{ix}—K3—O43A^{vii}	103.14 (9)
O41A^{v}—K1—O43B	95.63 (10)	O42A^{vii}—K3—O43A^{vii}	47.64 (8)
O41A^{ii}—K1—O41B^{i}	72.70 (9)	O41A—S4A—O42A	112.82 (19)
O41B^{i}—K1—O43A^{ii}	71.13 (9)	O41A—S4A—O43A	112.72 (19)
O41B^{i}—K1—O42A^{iii}	118.54 (10)	O41A—S4A—C4A	106.33 (17)
O41B^{i}—K1—O43B^{iv}	80.84 (10)	O42A—S4A—O43A	111.95 (18)
O41A^{v}—K1—O41B^{i}	139.11 (11)	O42A—S4A—C4A	105.28 (17)
O41A^{ii}—K1—O43A^{ii}	46.73 (8)	O43A—S4A—C4A	107.12 (18)
O41A^{ii}—K1—O42A^{iii}	112.09 (9)	K3—S4B—O41B	49.33 (13)
O41A^{ii}—K1—O43B^{iv}	90.23 (10)	K3—S4B—O42B	62.39 (13)
O41A^{ii}—K1—O41A^{v}	72.92 (10)	K3—S4B—O43B	129.77 (13)
O42A^{iii}—K1—O43A^{ii}	72.58 (9)	K3—S4B—C4B	122.20 (14)
O43A^{ii}—K1—O43B^{iv}	133.53 (10)	O41B—S4B—O42B	111.53 (19)
O41A^{v}—K1—O43A^{ii}	99.88 (9)	O41B—S4B—O43B	114.83 (19)
O42A^{iii}—K1—O43B^{iv}	153.45 (10)	O41B—S4B—C4B	105.87 (18)
O41A^{v}—K1—O42A^{iii}	94.61 (10)	O42B—S4B—O43B	111.0 (2)
O41A^{v}—K1—O43B^{iv}	77.83 (9)	O42B—S4B—C4B	105.19 (18)
O1W—K2—O2W	178.76 (17)	O43B—S4B—C4B	107.79 (18)
O1W—K2—O43A^{ii}	101.02 (12)	K2—O2W—K3	80.85 (11)
O1W—K2—O42A^{iii}	105.61 (11)	K2—O2W—K3^{i}	85.61 (12)
O1W—K2—O43A^{vi}	101.02 (12)	K3—O2W—K3^{i}	166.45 (17)
O1W—K2—O42A^{vii}	105.61 (11)	K1^{x}—O41A—S4A	99.57 (16)
O2W—K2—O43A^{ii}	79.84 (9)	K1^{xi}—O41A—S4A	158.5 (2)
O2W—K2—O42A^{iii}	73.61 (8)	K1^{x}—O41A—K1^{xi}	85.21 (9)
O2W—K2—O43A^{vi}	79.84 (9)	K3—O41B—S4B	107.04 (16)
O2W—K2—O42A^{vii}	73.61 (8)	K1^{viii}—O41B—K3	111.44 (10)
O42A^{iii}—K2—O43A^{ii}	81.09 (9)	K1^{viii}—O41B—S4B	133.48 (19)
O43A^{ii}—K2—O43A^{vi}	89.26 (10)	K1^{xii}—O42A—S4A	118.71 (18)
O42A^{vii}—K2—O43A^{ii}	152.93 (10)	K2^{xii}—O42A—S4A	132.77 (17)
O42A^{iii}—K2—O43A^{vi}	152.93 (10)	K3^{xii}—O42A—S4A	100.58 (15)
O42A^{iii}—K2—O42A^{vii}	96.15 (10)	K1^{xii}—O42A—K2^{xii}	100.58 (10)
O42A^{vii}—K2—O43A^{vi}	81.09 (9)	K1^{xii}—O42A—K3^{xii}	113.15 (10)
S4B—K3—O2W	78.47 (5)	K2^{xii}—O42A—K3^{xii}	85.52 (10)
S4B—K3—O41B	23.63 (6)	K3—O42B—S4B	92.65 (15)
S4B—K3—O42B	24.96 (7)	K3^{xii}—O43A—S4A	96.74 (14)
S4B—K3—O42A^{iii}	70.87 (6)	K1^{x}—O43A—S4A	98.62 (15)
S4B—K3—O43A^{iii}	85.56 (6)	K2^{x}—O43A—S4A	163.26 (19)

S4B—K3—O2W^{viii}	94.10 (6)	K1^{x}—O43A—K3^{xii}	95.55 (9)
S4B—K3—S4B^{ix}	111.64 (4)	K2^{x}—O43A—K3^{xii}	84.90 (9)
S4B—K3—O41B^{ix}	121.69 (7)	K1^{x}—O43A—K2^{x}	97.79 (9)
S4B—K3—O42B^{ix}	96.07 (7)	K1—O43B—S4B	104.92 (17)
S4B—K3—O42A^{vii}	145.18 (7)	K1—O43B—K1^{xiii}	87.96 (9)
S4B—K3—O43A^{vii}	160.55 (7)	K1^{xiii}—O43B—S4B	139.4 (2)
O2W—K3—O41B	101.53 (8)	H11W—O1W—H12W	113.00
O2W—K3—O42B	54.96 (9)	K2—O1W—H11W	117.00
O2W—K3—O42A^{iii}	67.86 (8)	K2—O1W—H12W	130.00
O2W—K3—O43A^{iii}	115.20 (9)	K2—O2W—H2W	111.00
O2W—K3—O2W^{viii}	166.45 (13)	K3—O2W—H2W^{ix}	65.00
S4B^{ix}—K3—O2W	78.47 (5)	K2—O2W—H2W^{ix}	111.00
O2W—K3—O41B^{ix}	101.53 (8)	K3—O2W—H2W	65.00
O2W—K3—O42B^{ix}	54.96 (9)	K3^{i}—O2W—H2W^{ix}	121.00
O2W—K3—O42A^{vii}	67.86 (8)	K3^{i}—O2W—H2W	121.00
O2W—K3—O43A^{vii}	115.20 (9)	H2W—O2W—H2W^{ix}	106.00
O41B—K3—O42B	48.53 (9)	H3W—O3W—H3W^{ix}	104.00
O41B—K3—O42A^{iii}	75.26 (9)	H41W—O4W—H42W	106.00
O41B—K3—O43A^{iii}	71.01 (8)	C2A—C1A—C6A	117.2 (4)
O2W^{viii}—K3—O41B	72.58 (8)	C1B—C1A—C6A	121.2 (4)
S4B^{ix}—K3—O41B	121.69 (7)	C1B—C1A—C2A	121.6 (4)
O41B—K3—O41B^{ix}	121.19 (10)	C1A—C1B—C6B	120.9 (4)
O41B—K3—O42B^{ix}	113.82 (9)	C1A—C1B—C2B	122.1 (4)
O41B—K3—O42A^{vii}	162.77 (10)	C2B—C1B—C6B	117.1 (4)
O41B—K3—O43A^{vii}	138.51 (9)	C1A—C2A—C3A	121.4 (4)
O42A^{iii}—K3—O42B	72.09 (8)	C1B—C2B—C3B	122.1 (4)
O42B—K3—O43A^{iii}	103.14 (9)	C2A—C3A—C4A	119.8 (4)
O2W^{viii}—K3—O42B	115.52 (10)	C2B—C3B—C4B	119.1 (4)
S4B^{ix}—K3—O42B	96.07 (7)	S4A—C4A—C3A	119.6 (3)
O41B^{ix}—K3—O42B	113.82 (9)	S4A—C4A—C5A	120.5 (3)
O42B—K3—O42B^{ix}	75.45 (9)	C3A—C4A—C5A	119.9 (3)
O42A^{vii}—K3—O42B	122.82 (10)	S4B—C4B—C3B	120.5 (3)
O42B—K3—O43A^{vii}	169.11 (9)	S4B—C4B—C5B	119.5 (3)
O42A^{iii}—K3—O43A^{iii}	47.64 (8)	C3B—C4B—C5B	120.0 (4)
O2W^{viii}—K3—O42A^{iii}	120.66 (8)	C4A—C5A—C6A	119.9 (4)
S4B^{ix}—K3—O42A^{iii}	145.18 (7)	C4B—C5B—C6B	120.0 (5)
O41B^{ix}—K3—O42A^{iii}	162.77 (10)	C1A—C6A—C5A	121.7 (5)
O42A^{iii}—K3—O42B^{ix}	122.82 (10)	C1B—C6B—C5B	121.7 (5)
O42A^{iii}—K3—O42A^{vii}	87.93 (9)	C1A—C2A—H2A	118.00
O42A^{iii}—K3—O43A^{vii}	100.51 (9)	C3A—C2A—H2A	121.00
O2W^{viii}—K3—O43A^{iii}	75.00 (9)	C1B—C2B—H2B	118.00

S4B^{ix}—K3—O43A^{iii}	160.55 (7)	C3B—C2B—H2B	120.00
O41B^{ix}—K3—O43A^{iii}	138.51 (9)	C4A—C3A—H3A	119.00
O42B^{ix}—K3—O43A^{iii}	169.11 (9)	C2A—C3A—H3A	121.00
O42A^{vii}—K3—O43A^{iii}	100.51 (9)	C2B—C3B—H3B	121.00
O43A^{iii}—K3—O43A^{vii}	76.15 (9)	C4B—C3B—H3B	120.00
S4B^{ix}—K3—O2W^{viii}	94.10 (6)	C4A—C5A—H5A	119.00
O2W^{viii}—K3—O41B^{ix}	72.58 (8)	C6A—C5A—H5A	121.00
O2W^{viii}—K3—O42B^{ix}	115.52 (10)	C6B—C5B—H5B	121.00
O2W^{viii}—K3—O42A^{vii}	120.66 (8)	C4B—C5B—H5B	119.00
O2W^{viii}—K3—O43A^{vii}	75.00 (9)	C1A—C6A—H6A	118.00
S4B^{ix}—K3—O41B^{ix}	23.63 (6)	C5A—C6A—H6A	120.00
S4B^{ix}—K3—O42B^{ix}	24.96 (7)	C5B—C6B—H6B	120.00
S4B^{ix}—K3—O42A^{vii}	70.87 (6)	C1B—C6B—H6B	118.00
S4B^{ix}—K3—O43A^{vii}	85.56 (6)		
O41B^{i}—K1—O43B—S4B	−63.28 (18)	S4B—K3—O42A^{iii}—K1	36.28 (8)
O41B^{i}—K1—O43B—K1^{xiii}	155.80 (9)	S4B—K3—O42A^{iii}—K2	135.88 (8)
O43A^{ii}—K1—O43B—S4B	24.6 (3)	O2W—K3—O42A^{iii}—K1	−48.71 (11)
O43A^{ii}—K1—O43B—K1^{xiii}	−116.35 (19)	O41B—K3—O42A^{iii}—K1	60.57 (11)
O42A^{iii}—K1—O43B—S4B	54.89 (16)	O41B—K3—O42A^{iii}—K2	160.18 (10)
O42A^{iii}—K1—O43B—K1^{xiii}	−86.03 (10)	O42B—K3—O42A^{iii}—K1	9.96 (11)
O43B^{iv}—K1—O43B—S4B	−135.85 (18)	O42B—K3—O42A^{iii}—K2	109.57 (10)
O43B^{iv}—K1—O43B—K1^{xiii}	83.23 (10)	S4B—K3—O42A^{vii}—K2	−35.22 (15)
O41A^{v}—K1—O43B—S4B	148.94 (16)	O42B—K3—O42A^{vii}—K2	−51.07 (12)
O41A^{v}—K1—O43B—K1^{xiii}	8.02 (10)	O42A—S4A—O41A—K1^{x}	−112.87 (16)
O43B—K1—O41B^{i}—S4B^{i}	−92.7 (2)	O42A—S4A—O41A—K1^{xi}	−11.5 (6)
O43B—K1—O43A^{ii}—K2	10.8 (2)	O43A—S4A—O41A—K1^{x}	15.15 (19)
O43B—K1—O43A^{ii}—S4A^{ii}	−172.48 (16)	O43A—S4A—O41A—K1^{xi}	116.5 (5)
O43B—K1—O42A^{iii}—K2	−145.49 (11)	C4A—S4A—O41A—K1^{x}	132.23 (15)
O43B—K1—O42A^{iii}—K3	−55.87 (11)	C4A—S4A—O41A—K1^{xi}	−126.4 (5)
O43B—K1—O42A^{iii}—S4A^{iii}	61.65 (17)	O41A—S4A—O42A—K1^{xii}	−13.0 (2)
O43B—K1—O43B^{iv}—K1^{iv}	−165.58 (11)	O41A—S4A—O42A—K2^{xii}	−155.4 (2)
O43B—K1—O43B^{iv}—S4B^{iv}	−54.9 (3)	O41A—S4A—O42A—K3^{xii}	110.94 (17)
O43B—K1—O41A^{v}—S4A^{v}	96.8 (5)	O43A—S4A—O42A—K1^{xii}	−141.42 (17)
O43B—K1—O41A^{v}—K1^{xiii}	−7.24 (9)	O43A—S4A—O42A—K2^{xii}	76.2 (3)
O1W—K2—O43A^{ii}—K1	125.43 (12)	O43A—S4A—O42A—K3^{xii}	−17.47 (19)
O2W—K2—O43A^{ii}—K1	−53.67 (9)	C4A—S4A—O42A—K1^{xii}	102.53 (18)
O1W—K2—O42A^{iii}—K1	−121.86 (13)	C4A—S4A—O42A—K2^{xii}	−39.8 (3)
O2W—K2—O42A^{iii}—K1	59.14 (10)	C4A—S4A—O42A—K3^{xii}	−133.52 (14)
O2W—K3—S4B—O41B	167.29 (17)	O41A—S4A—O43A—K3^{xii}	−111.70 (15)
O2W—K3—S4B—O42B	−18.15 (16)	O41A—S4A—O43A—K1^{x}	−15.01 (18)

O2W—K3—S4B—O43B	77.0 (2)
O2W—K3—S4B—C4B	−109.31 (18)
O41B—K3—S4B—O42B	174.6 (2)
O41B—K3—S4B—O43B	−90.3 (2)
O41B—K3—S4B—C4B	83.4 (2)
O42B—K3—S4B—O41B	−174.6 (2)
O42B—K3—S4B—O43B	95.2 (2)
O42B—K3—S4B—C4B	−91.2 (2)
O42A^{iii}—K3—S4B—O41B	96.94 (16)
O42A^{iii}—K3—S4B—O42B	−88.50 (16)
O42A^{iii}—K3—S4B—O43B	6.6 (2)
O42A^{iii}—K3—S4B—C4B	−179.66 (18)
O43A^{iii}—K3—S4B—O41B	50.45 (16)
O43A^{iii}—K3—S4B—O42B	−135.00 (15)
O43A^{iii}—K3—S4B—O43B	−39.9 (2)
O43A^{iii}—K3—S4B—C4B	133.85 (17)
O2W^{viii}—K3—S4B—O41B	−24.14 (17)
O2W^{viii}—K3—S4B—O42B	150.41 (16)
O2W^{viii}—K3—S4B—O43B	−114.4 (2)
O2W^{viii}—K3—S4B—C4B	59.26 (18)
S4B^{ix}—K3—S4B—O41B	−120.20 (16)
S4B^{ix}—K3—S4B—O42B	54.36 (14)
S4B^{ix}—K3—S4B—O43B	149.50 (19)
S4B^{ix}—K3—S4B—C4B	−36.80 (17)
O41B^{ix}—K3—S4B—O41B	−96.17 (17)
O41B^{ix}—K3—S4B—O42B	78.38 (16)
O41B^{ix}—K3—S4B—O43B	173.5 (2)
O41B^{ix}—K3—S4B—C4B	−12.77 (19)
O42B^{ix}—K3—S4B—O41B	−140.37 (17)
O42B^{ix}—K3—S4B—O42B	34.19 (16)
O42B^{ix}—K3—S4B—O43B	129.3 (2)
O42B^{ix}—K3—S4B—C4B	−56.97 (18)
O42A^{vii}—K3—S4B—O41B	152.50 (19)
O42A^{vii}—K3—S4B—O42B	−32.95 (18)
O42A^{vii}—K3—S4B—O43B	62.2 (2)
O42A^{vii}—K3—S4B—C4B	−124.1 (2)
S4B—K3—O2W—K2	−122.40 (3)
O41B—K3—O2W—K2	−117.24 (7)
O42B—K3—O2W—K2	−131.64 (8)
S4B—K3—O41B—K1^{viii}	153.3 (2)
O2W—K3—O41B—S4B	−12.71 (17)
O2W—K3—O41B—K1^{viii}	140.62 (11)
O42A—S4A—O43A—K3^{xii}	16.77 (18)
O42A—S4A—O43A—K1^{x}	113.45 (15)
C4A—S4A—O43A—K3^{xii}	131.69 (15)
C4A—S4A—O43A—K1^{x}	−131.62 (15)
O41A—S4A—C4A—C3A	59.0 (4)
O41A—S4A—C4A—C5A	−122.4 (4)
O42A—S4A—C4A—C3A	−60.9 (4)
O42A—S4A—C4A—C5A	117.7 (4)
O43A—S4A—C4A—C3A	179.8 (3)
O43A—S4A—C4A—C5A	−1.6 (4)
K3—S4B—O41B—K1^{viii}	−144.8 (3)
O42B—S4B—O41B—K3	−5.2 (2)
O42B—S4B—O41B—K1^{viii}	−150.0 (2)
O43B—S4B—O41B—K3	122.13 (18)
O43B—S4B—O41B—K1^{viii}	−22.7 (3)
C4B—S4B—O41B—K3	−119.08 (16)
C4B—S4B—O41B—K1^{viii}	96.1 (2)
O41B—S4B—O42B—K3	4.44 (17)
O43B—S4B—O42B—K3	−124.95 (15)
C4B—S4B—O42B—K3	118.76 (15)
K3—S4B—O43B—K1	−44.0 (2)
K3—S4B—O43B—K1^{xiii}	60.7 (3)
O41B—S4B—O43B—K1	−100.68 (18)
O41B—S4B—O43B—K1^{xiii}	4.0 (3)
O42B—S4B—O43B—K1	26.9 (2)
O42B—S4B—O43B—K1^{xiii}	131.6 (3)
C4B—S4B—O43B—K1	141.61 (16)
C4B—S4B—O43B—K1^{xiii}	−113.7 (3)
K3—S4B—C4B—C3B	142.0 (3)
K3—S4B—C4B—C5B	−36.5 (5)
O41B—S4B—C4B—C3B	−166.4 (3)
O41B—S4B—C4B—C5B	15.1 (5)
O42B—S4B—C4B—C3B	75.4 (4)
O42B—S4B—C4B—C5B	−103.1 (5)
O43B—S4B—C4B—C3B	−43.0 (4)
O43B—S4B—C4B—C5B	138.5 (4)
C2A—C1A—C1B—C2B	3.0 (6)
C2A—C1A—C1B—C6B	−178.3 (5)
C6A—C1A—C1B—C2B	−176.3 (4)
C6A—C1A—C1B—C6B	2.5 (7)
C1B—C1A—C2A—C3A	−177.7 (4)
C6A—C1A—C2A—C3A	1.6 (7)

O42B—K3—O41B—S4B	3.06 (12)	C1B—C1A—C6A—C5A	178.1 (5)
O42B—K3—O41B—K1^{viii}	156.39 (16)	C2A—C1A—C6A—C5A	−1.2 (8)
O42A^{iii}—K3—O41B—S4B	−75.87 (15)	C1A—C1B—C2B—C3B	178.6 (4)
O43A^{iii}—K3—O41B—S4B	−125.62 (17)	C6B—C1B—C2B—C3B	−0.2 (7)
O2W^{viii}—K3—O41B—S4B	154.69 (18)	C1A—C1B—C6B—C5B	−178.0 (6)
S4B^{ix}—K3—O41B—S4B	70.76 (16)	C2B—C1B—C6B—C5B	0.8 (9)
O41B^{ix}—K3—O41B—S4B	98.52 (16)	C1A—C2A—C3A—C4A	−0.5 (7)
O42B^{ix}—K3—O41B—S4B	43.89 (18)	C1B—C2B—C3B—C4B	−1.5 (6)
O43A^{vii}—K3—O41B—S4B	−165.15 (13)	C2A—C3A—C4A—S4A	177.5 (4)
O2W—K3—O42B—S4B	158.11 (18)	C2A—C3A—C4A—C5A	−1.1 (7)
O41B—K3—O42B—S4B	−2.91 (11)	C2B—C3B—C4B—S4B	−175.8 (3)
O42A^{iii}—K3—O42B—S4B	83.00 (14)	C2B—C3B—C4B—C5B	2.7 (7)
O43A^{iii}—K3—O42B—S4B	46.38 (15)	S4A—C4A—C5A—C6A	−177.1 (4)
O2W^{viii}—K3—O42B—S4B	−33.08 (17)	C3A—C4A—C5A—C6A	1.5 (7)
S4B^{ix}—K3—O42B—S4B	−130.57 (13)	S4B—C4B—C5B—C6B	176.4 (5)
O41B^{ix}—K3—O42B—S4B	−114.34 (14)	C3B—C4B—C5B—C6B	−2.1 (9)
O42B^{ix}—K3—O42B—S4B	−144.75 (16)	C4A—C5A—C6A—C1A	−0.3 (8)
O42A^{vii}—K3—O42B—S4B	158.31 (12)	C4B—C5B—C6B—C1B	0.4 (10)

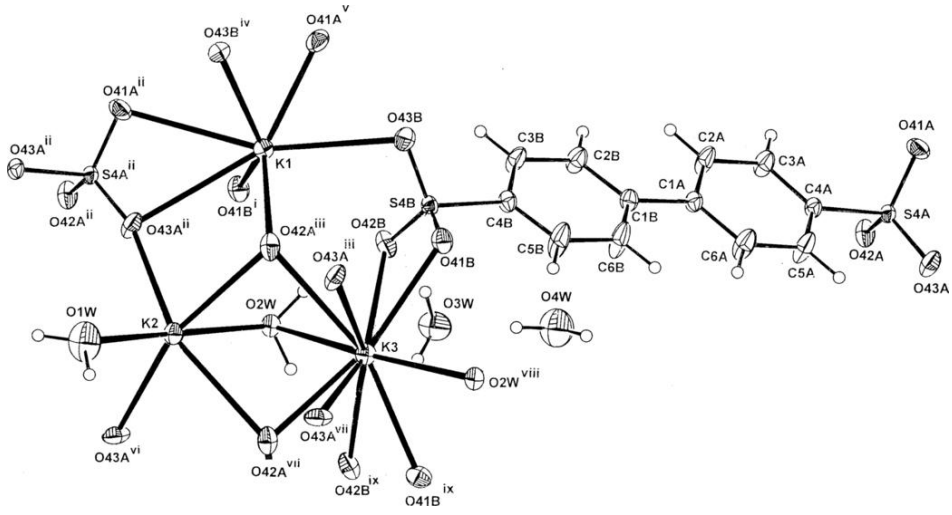
Symmetry codes: (i) *x*−1, *y*, *z*; (ii) *x*−1, *y*, *z*+1; (iii) *x*, *y*, *z*+1; (iv) *x*−1/2, −*y*+1/2, *z*; (v) *x*−1/2, −*y*+1/2, *z*+1; (vi) *x*−1, −*y*, *z*+1; (vii) *x*, −*y*, *z*+1; (viii) *x*+1, *y*, *z*; (ix) *x*, −*y*, *z*; (x) *x*+1, *y*, *z*−1; (xi) *x*+1/2, −*y*+1/2, *z*−1; (xii) *x*, *y*, *z*−1; (xiii) *x*+1/2, −*y*+1/2, *z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H11W···O4W^{iii}	0.97	2.18	2.778 (9)	119
O2W—H2W···O42B	0.96	1.91	2.840 (5)	162
O3W—H3W···O42B	0.96	1.95	2.884 (5)	162
O4W—H41W···O3W	0.90	1.82	2.715 (9)	180
O4W—H41W···O3W	0.90	1.82	2.715 (9)	180
C5A—H5A···O43A	0.95	2.50	2.916 (5)	106
C5B—H5B···O41B	0.94	2.47	2.873 (5)	106

Symmetry codes: (iii) *x*, *y*, *z*+1.

Fig. 1


O43B iv
O41A v
O41A ii
O43A ii
S4A ii
O42A ii
O43A ii
K1
O41B i
O43B
S4B
O42A iii
O42B
O43A iii
O41B
C3B
C2B
C4B
C1B
C5B
C6B
C2A
C3A
C1A
C4A
C6A
C5A
O41A
S4A
O42A
O43A
O1W
K2
O2W
K3
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O4W
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O43A vi
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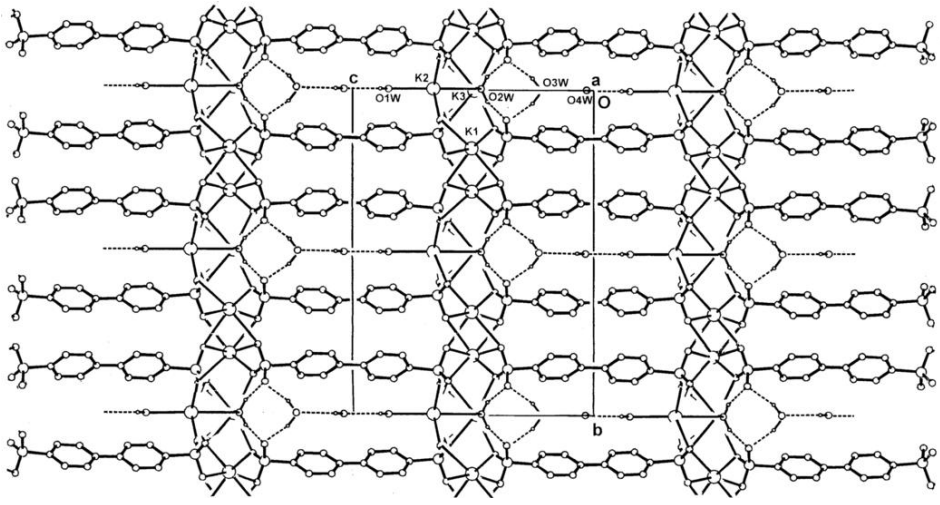
Fig. 2