Potassium 4-nitrophenylsulfonate monohydrate

Alexandrea J. Blatch,[a]
Judith A. K. Howard,[a]
Michael R. Probert,[a]
Christian A. Smethurst[b] **and**
Andrew Whiting[a]*

[a]Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England, and [b]GlaxoSmithKline Pharmaceuticals, New Frontiers Science Park, Third Avenue, Harlow, Essex CM19 5AW, England

Correspondence e-mail:
a.s.batsanov@durham.ac.uk

The title compound, $K^+ \cdot C_6H_4NO_5S^- \cdot H_2O$, forms a three-dimensional polymeric structure with an O_8 coordination environment of the K^+ cation.

Comment

As part of a programme aimed at developing new aza-Baeyer–Villiger reactions, we have examined the use of N-alkyl-O-arylsulfonylhydroxylamines as potential nitrene equivalents (Hoffman & Buntain, 1988; Hoffman & Salvador, 1989a, 1991). Attempts have therefore been made to prepare a range of N-alkyl-O-arylsulfonylhydroxylamines p-XC$_6$H$_4$SO$_2$NHR by reacting RNH$_2$ with sulfonyl peroxides p-XC$_6$H$_4$SO$_2$OO-SO$_2$C$_6$H$_4$-p-X, which in turn are accessible from sulfonyl chlorides p-XC$_6$H$_4$SO$_2$Cl by reaction with t-BuOOH (Hoffman & Cadena, 1977; Hoffman & Belfoure, 1983; Hoffman & Salvador, 1989b). The title compound, (I), was isolated as a by-product during this synthesis.

(I)
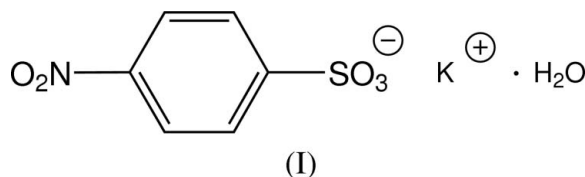
Numerous esters of 4-nitrophenylsulfonic acid have been structurally characterized, as well as some salts with organic cations (Russell *et al.*, 1994; Chan & Wong, 2002; Tamura *et al.*, 2002). However, no salt or complex of any metal with this anion has been studied previously.

(I) has a three-dimensional polymeric (*catena*) crystal structure (Fig. 1). The asymmetric unit comprises one formula unit. The potassium cation is coordinated by eight O atoms, *viz.* five from the sulfonate groups of four different anions, one from a nitro group of another anion, and two μ_2-bridging water molecules. The coordination polyhedron can be described as a distorted monocapped pentagonal bipyramid. The anion links five K^+ cations, four of them *via* one O atom each. There is only one case of chelation, the sulfonate atoms O1 and O2 coordinated to the same potassium ion, and even this one is highly asymmmetric. The K—O2 distance is 0.33 Å longer than K—O1 and is by far the longest in the structure.

The aqua bridge is highly asymmetric: the K—O distances differ by 0.176 Å and the stronger-bound potassium ion is practically coplanar with the H$_2$O plane. The weakly coordinated O2 atom and the uncoordinated O5 atom of the nitro group act as acceptors of hydrogen bonds donated by the water molecules. Notwithstanding these differences, both N—
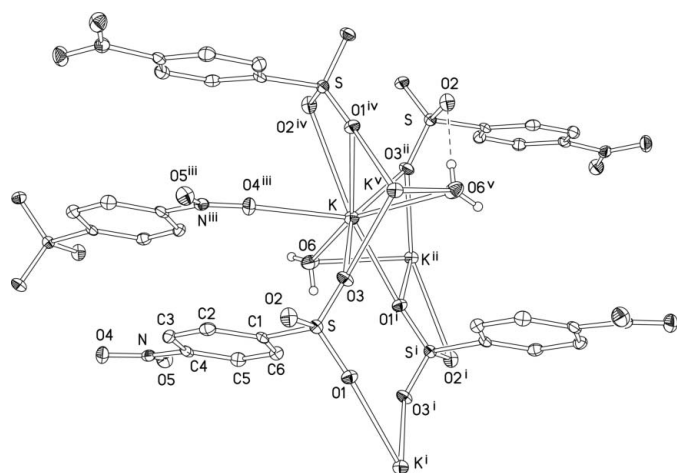
Figure 1
The environment of a K$^+$ cation in the structure of (I) (50% displacement ellipsoids). [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$, (ii) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$, (iii) $-x, 1 - y, 1 - z$, (iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$, (v) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$.]

O bond lengths are equal within experimental error (mean 1.233 (3) Å), as are the three S—O bond lengths (mean 1.453 (3) Å). The benzene ring and the nitro group of the anion form a dihedral angle of 11.2 (1)°, whereas the S—O2 bond is nearly coplanar with the ring: the dihedral angle C2—C1—S—O2 is 9.0 (3)°.

Experimental

4-Nitrobenzenesulfonyl peroxide p-O$_2$NC$_6$H$_4$SO$_2$OOSO$_2$C$_6$H$_4$NO$_2$-p (II) was prepared according to Dannley *et al.* (1970). To a solution of K$_2$CO$_3$ (5.10 g, 36.9 mmol) in water (76 ml), ethanol (38 ml) and hydrogen peroxide (35%, 8.75 g) at 253 K a cooled (253 K) solution of 4-nitrobenzenesulfonyl chloride (7.88 g, 35.6 mmol) in chloroform (10 ml) was added and the suspension was mixed at full power for 1 min using a Breville Classique^{TM} blender. Ethanol (80 ml) was added and the solution was mixed for 4 min at low power. The precipitate formed was filtered off, washed with distilled water and recrystallized from acetone to give (II) as a yellow solid (2.22 g, 31%). The filtrate was cooled at 253 K for 24 h, yielding (I) as yellow crystals (0.160 g, 1.2%), m.p. >593 K, IR, v, cm^{-1}: 3065 (CH aromatic stretch), 1529 (NO$_2$), 1461 (SO$_2$) 819 (p-disubstituted aromatic). ^{1}H NMR (200 MHz, CDCl$_3$): 8.20 (d, 2H, CH aromatic, J 8.6 Hz), 8.49 (d, 2H, CH aromatic, J = 8.4 Hz). ^{13}C NMR (100 MHz, CDCl3): 123.5 (2 × PhCNO$_2$), 126.0 (4 × CH aromatic), 140.0 (4 × CH aromatic), 148.0 (2 × PhCSO$_2$). The properties of (I) agree with those reported by Kozlov & Davydov (1965) or Dietze *et al.* (1989).

Crystal data

K$^+$·C$_6$H$_4$NO$_5$S$^-$·H$_2$O
M_r = 259.28
Monoclinic, $P2_1/c$
a = 10.794 (1) Å
b = 7.1516 (6) Å
c = 12.417 (1) Å
β = 106.15 (1)°
V = 920.70 (14) Å^3
Z = 4
D_x = 1.871 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2733 reflections
θ = 3.3–27.5°
μ = 0.81 mm^{-1}
T = 120 (2) K
Block, yellow
0.3 × 0.2 × 0.15 mm

Data collection

Siemens SMART 1K CCD area detector diffractometer
ω scans
Absorption correction: none
9859 measured reflections
2117 independent reflections
1596 reflections with $I > 2\sigma(I)$
R_{int} = 0.067
θ_{max} = 27.5°
$h = -14 \rightarrow 13$
$k = -9 \rightarrow 9$
$l = -16 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.095
S = 1.05
2117 reflections
144 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2 + 0.9635P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

K—O1^i	2.712 (2)	K—O4^{iii}	2.802 (2)
K—O3^{ii}	2.765 (2)	K—O1^{iv}	2.819 (2)
K—O3	2.775 (2)	K—O6^v	2.955 (3)
K—O6	2.779 (2)	K—O2^{iv}	3.148 (2)
O1^i—K—O3^{ii}	87.93 (6)	O4^{iii}—K—O1^{iv}	72.37 (6)
O1^i—K—O3	78.99 (6)	O1^i—K—O6^v	85.46 (7)
O3^{ii}—K—O3	151.04 (3)	O3^{ii}—K—O6^v	74.70 (7)
O1^i—K—O6	66.46 (7)	O3—K—O6^v	78.56 (7)
O3^{ii}—K—O6	81.82 (7)	O6—K—O6^v	143.93 (7)
O3—K—O6	115.27 (7)	O4^{iii}—K—O6^v	127.38 (7)
O1^i—K—O4^{iii}	128.10 (7)	O1^{iv}—K—O6^v	62.76 (7)
O3^{ii}—K—O4^{iii}	134.60 (7)	O1^i—K—O2^{iv}	156.06 (6)
O3—K—O4^{iii}	71.80 (7)	O3^{ii}—K—O2^{iv}	70.29 (6)
O6—K—O4^{iii}	88.53 (7)	O3—K—O2^{iv}	124.93 (6)
O1^i—K—O1^{iv}	146.95 (5)	O6—K—O2^{iv}	99.66 (7)
O3^{ii}—K—O1^{iv}	91.85 (6)	O4^{iii}—K—O2^{iv}	67.84 (6)
O3—K—O1^{iv}	85.63 (6)	O1^{iv}—K—O2^{iv}	47.52 (6)
O6—K—O1^{iv}	146.11 (7)	O6^v—K—O2^{iv}	97.73 (7)

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

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O6—H01⋯O2^{vi}	0.78 (4)	2.15 (4)	2.922 (3)	172 (4)
O6—H02⋯O5^{vii}	0.85 (4)	2.23 (4)	3.050 (3)	161 (4)

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

Water atoms H01 and H02 were located in a difference map and refined isotropically. Benzene H atoms were treated as riding on the C atoms, C—H 0.95 Å, U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

References

Bruker (2001). *SMART* (Version 5.625), *SAINT* (Version 6.02A) and *SHELXTL* (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.

Chan, K. W. Y. & Wong, W. T. (2002). *Acta Cryst.* E**58**, o1048–o1050.

Dannley, R. L., Gagen, J. E. & Stewart, O. J. (1970). *J. Org. Chem.* **35**, 3076–3079.

Dietze, P. E.; Hariri R. & Khattak, J. (1989). *J. Org. Chem.* **54**, 3317–3320.

Hoffman, R. V. & Belfoure, E. L. (1983). *Synthesis*, pp. 34–35.

Hoffman, R. V. & Buntain, G. A. (1988). *J. Org. Chem.* **53**, 3316–3321.

Hoffman, R. V. & Cadena, R. (1977). *J. Am. Chem. Soc.* **99**, 8226–8232.

Hoffman, R. V. & Salvador, J. (1989*a*). *Tetrahedron Lett.* **30**, 4207–4210.

Hoffman, R. V. & Salvador, J. (1989*b*). *J. Chem. Soc. Perkin Trans. 1*, pp. 1375–1380.

Hoffman, R. V. & Salvador, J. (1991). *Tetrahedron Lett.* **32**, 2429–2432.

Kozlov V. V. & Davydov, A. A. (1965). *Zh. Org. Khim.* **1**, 559–562. (In Russian.)

Russell, V. A., Etter, M. C. & Ward, M. D. (1994). *Chem. Mater.* **6**, 1206–1217.

Tamura, R., Fujimoto, D., Lepp, Z., Misaki, K., Miura, H., Takahashi, H., Ushio, T., Nakai, T. & Hirotsu, K. (2002). *J. Am. Chem. Soc.* **124**, 13139–13153.

Potassium 4-nitrophenylsulfonate monohydrate

Alexandrea J. Blatch, Judith A. K. Howard, Michael R. Probert, Christian A. Smethurst and Andrew Whiting

Potassium 4-nitrophenylsulfonate monohydrate

Crystal data

$K^+ \cdot C_6H_4NO_5S^- \cdot H_2O$	$F(000) = 528$
$M_r = 259.28$	$D_x = 1.871$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 2733 reflections
$a = 10.794$ (1) Å	$\theta = 3.3–27.5°$
$b = 7.1516$ (6) Å	$\mu = 0.81$ mm^{-1}
$c = 12.417$ (1) Å	$T = 120$ K
$\beta = 106.15$ (1)°	Block, colourless
$V = 920.70$ (14) Å^3	$0.3 \times 0.2 \times 0.15$ mm
$Z = 4$	

Data collection

Siemens SMART 1K CCD area detector diffractometer	2117 independent reflections
	1596 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.067$
Graphite monochromator	$\theta_{max} = 27.5°$, $\theta_{min} = 2.0°$
Detector resolution: 8 pixels mm^{-1}	$h = -14 \rightarrow 13$
ω scans	$k = -9 \rightarrow 9$
9859 measured reflections	$l = -16 \rightarrow 15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.042$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.095$	
$S = 1.05$	H atoms treated by a mixture of independent and constrained refinement
2117 reflections	
144 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2 + 0.9635P]$
0 restraints	where $P = (F_o^2 + 2F_c^2)/3$
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.39$ e Å^{-3}
	$\Delta\rho_{min} = -0.46$ e Å^{-3}

Special details

Experimental. The data collection nominally covered full sphere of reciprocal Space, by a combination of 5 sets of ω scans each set at different φ and/or 2θ angles and each scan (10 s exposure) covering 0.3° in ω. Crystal to detector distance 4.51 cm.

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

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 $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement.

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

	x	y	z	U_{iso}*/U_{eq}
K	0.43521 (6)	0.53657 (9)	0.74392 (5)	0.01343 (16)
S	0.37624 (7)	0.22064 (10)	0.46669 (6)	0.01054 (17)
O1	0.4524 (2)	0.2686 (3)	0.39107 (17)	0.0140 (5)
O2	0.3285 (2)	0.0291 (3)	0.45242 (18)	0.0159 (5)
O3	0.4386 (2)	0.2697 (3)	0.58251 (17)	0.0149 (5)
O4	−0.1962 (2)	0.6461 (3)	0.31470 (18)	0.0192 (5)
O5	−0.0704 (2)	0.8883 (3)	0.35935 (18)	0.0188 (5)
O6	0.3076 (2)	0.8669 (3)	0.6626 (2)	0.0207 (5)
H01	0.315 (4)	0.900 (5)	0.605 (3)	0.026 (11)*
H02	0.252 (4)	0.945 (6)	0.672 (3)	0.039 (12)*
N	−0.0886 (2)	0.7181 (4)	0.3463 (2)	0.0147 (5)
C1	0.2366 (3)	0.3660 (4)	0.4267 (2)	0.0108 (6)
C2	0.1131 (3)	0.2881 (4)	0.4060 (2)	0.0132 (6)
H2	0.1032	0.1568	0.4118	0.016*
C3	0.0058 (3)	0.4025 (4)	0.3772 (2)	0.0136 (6)
H3	−0.0787	0.3518	0.3622	0.016*
C4	0.0250 (3)	0.5950 (4)	0.3708 (2)	0.0122 (6)
C5	0.1463 (3)	0.6745 (4)	0.3908 (2)	0.0144 (6)
H5	0.1559	0.8060	0.3859	0.017*
C6	0.2534 (3)	0.5582 (4)	0.4183 (2)	0.0139 (6)
H6	0.3376	0.6092	0.4312	0.017*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K	0.0157 (3)	0.0116 (3)	0.0132 (3)	−0.0007 (3)	0.0043 (2)	0.0000 (2)
S	0.0110 (4)	0.0094 (3)	0.0109 (4)	0.0007 (3)	0.0023 (3)	−0.0001 (3)
O1	0.0159 (11)	0.0149 (11)	0.0126 (11)	0.0009 (8)	0.0063 (9)	0.0003 (8)
O2	0.0161 (11)	0.0095 (10)	0.0212 (12)	0.0010 (9)	0.0036 (9)	0.0014 (9)
O3	0.0169 (11)	0.0159 (11)	0.0097 (10)	0.0022 (9)	0.0000 (8)	−0.0016 (8)
O4	0.0121 (12)	0.0241 (12)	0.0207 (12)	−0.0035 (9)	0.0032 (9)	0.0018 (9)
O5	0.0191 (12)	0.0150 (11)	0.0217 (12)	0.0042 (9)	0.0046 (10)	0.0011 (9)
O6	0.0237 (14)	0.0214 (13)	0.0197 (13)	0.0069 (10)	0.0106 (11)	0.0055 (10)
N	0.0137 (14)	0.0205 (14)	0.0107 (13)	0.0018 (11)	0.0047 (10)	0.0033 (10)
C1	0.0109 (14)	0.0142 (15)	0.0061 (14)	−0.0007 (12)	0.0003 (11)	−0.0015 (11)
C2	0.0177 (16)	0.0117 (14)	0.0110 (14)	−0.0015 (12)	0.0055 (12)	−0.0023 (11)
C3	0.0127 (15)	0.0168 (15)	0.0115 (15)	−0.0049 (12)	0.0039 (12)	−0.0005 (11)
C4	0.0126 (15)	0.0154 (15)	0.0070 (14)	0.0023 (12)	0.0002 (11)	0.0002 (11)

C5	0.0175 (16)	0.0120 (14)	0.0137 (15)	0.0002 (12)	0.0045 (12)	−0.0010 (11)
C6	0.0129 (15)	0.0164 (16)	0.0128 (15)	0.0002 (12)	0.0041 (12)	0.0009 (11)

Geometric parameters (Å, º)

K—O1^i	2.712 (2)	O6—H01	0.78 (4)
K—O3^{ii}	2.765 (2)	O6—H02	0.85 (4)
K—O3	2.775 (2)	N—C4	1.471 (4)
K—O6	2.779 (2)	C1—C6	1.395 (4)
K—O4^{iii}	2.802 (2)	C1—C2	1.401 (4)
K—O1^{iv}	2.819 (2)	C2—C3	1.382 (4)
K—O6^v	2.955 (3)	C2—H2	0.9500
K—O2^{iv}	3.148 (2)	C3—C4	1.398 (4)
S—O1	1.451 (2)	C3—H3	0.9500
S—O3	1.451 (2)	C4—C5	1.384 (4)
S—O2	1.457 (2)	C5—C6	1.388 (4)
S—C1	1.784 (3)	C5—H5	0.9500
O4—N	1.230 (3)	C6—H6	0.9500
O5—N	1.236 (3)		
O1^i—K—O3^{ii}	87.93 (6)	S—O1—K^{vi}	106.82 (10)
O1^i—K—O3	78.99 (6)	K^i—O1—K^{vi}	87.55 (6)
O3^{ii}—K—O3	151.04 (3)	S—O2—K^{vi}	92.42 (10)
O1^i—K—O6	66.46 (7)	S—O3—K^v	128.22 (11)
O3^{ii}—K—O6	81.82 (7)	S—O3—K	141.86 (12)
O3—K—O6	115.27 (7)	K^v—O3—K	87.38 (6)
O1^i—K—O4^{iii}	128.10 (7)	N—O4—K^{iii}	175.69 (19)
O3^{ii}—K—O4^{iii}	134.60 (7)	K—O6—K^{ii}	83.67 (7)
O3—K—O4^{iii}	71.80 (7)	K—O6—H01	115 (3)
O6—K—O4^{iii}	88.53 (7)	K^{ii}—O6—H01	85 (3)
O1^i—K—O1^{iv}	146.95 (5)	K—O6—H02	144 (3)
O3^{ii}—K—O1^{iv}	91.85 (6)	K^{ii}—O6—H02	108 (3)
O3—K—O1^{iv}	85.63 (6)	H01—O6—H02	100 (4)
O6—K—O1^{iv}	146.11 (7)	O4—N—O5	123.7 (3)
O4^{iii}—K—O1^{iv}	72.37 (6)	O4—N—C4	118.3 (2)
O1^i—K—O6^v	85.46 (7)	O5—N—C4	118.0 (2)
O3^{ii}—K—O6^v	74.70 (7)	C6—C1—C2	121.0 (3)
O3—K—O6^v	78.56 (7)	C6—C1—S	118.5 (2)
O6—K—O6^v	143.93 (7)	C2—C1—S	120.4 (2)
O4^{iii}—K—O6^v	127.38 (7)	C3—C2—C1	119.9 (3)
O1^{iv}—K—O6^v	62.76 (7)	C3—C2—H2	120.0
O1^i—K—O2^{iv}	156.06 (6)	C1—C2—H2	120.0
O3^{ii}—K—O2^{iv}	70.29 (6)	C2—C3—C4	118.1 (3)
O3—K—O2^{iv}	124.93 (6)	C2—C3—H3	121.0
O6—K—O2^{iv}	99.66 (7)	C4—C3—H3	121.0
O4^{iii}—K—O2^{iv}	67.84 (6)	C5—C4—C3	122.8 (3)
O1^{iv}—K—O2^{iv}	47.52 (6)	C5—C4—N	118.9 (3)
O6^v—K—O2^{iv}	97.73 (7)	C3—C4—N	118.2 (3)

O1—S—O3	113.22 (12)	C4—C5—C6	118.7 (3)
O1—S—O2	112.87 (12)	C4—C5—H5	120.7
O3—S—O2	113.49 (13)	C6—C5—H5	120.7
O1—S—C1	105.61 (13)	C5—C6—C1	119.5 (3)
O3—S—C1	104.94 (12)	C5—C6—H6	120.3
O2—S—C1	105.73 (13)	C1—C6—H6	120.3
S—O1—K^{i}	162.38 (12)		
C2—C1—S—O2	9.0 (3)	C5—C4—N—O5	−9.6 (4)
C3—C4—N—O4	−11.6 (4)		

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

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O6—H01···O2^{vii}	0.78 (4)	2.15 (4)	2.922 (3)	172 (4)
O6—H02···O5^{viii}	0.85 (4)	2.23 (4)	3.050 (3)	161 (4)

Symmetry codes: (vii) x, y+1, z; (viii) −x, −y+2, −z+1.