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Key indicators

Single-crystal X-ray study
 $T = 120$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.042
 wR factor = 0.095
Data-to-parameter ratio = 14.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

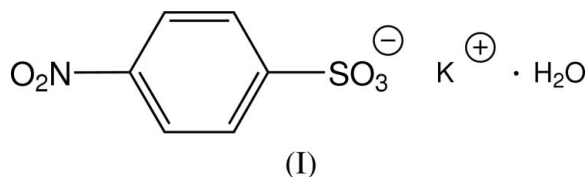
Potassium 4-nitrophenylsulfonate monohydrate

The title compound, $\text{K}^+\cdot\text{C}_6\text{H}_4\text{NO}_3\text{S}^-\cdot\text{H}_2\text{O}$, forms a three-dimensional polymeric structure with an O_8 coordination environment of the K^+ cation.

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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, 1989*a*, 1991). Attempts have therefore been made to prepare a range of *N*-alkyl-*O*-arylsulfonylhydroxylamines *p*- $\text{XC}_6\text{H}_4\text{SO}_2\text{NHR}$ by reacting RNH_2 with sulfonyl peroxides *p*- $\text{XC}_6\text{H}_4\text{SO}_2\text{OO}-\text{SO}_2\text{C}_6\text{H}_4$ -*p*- X , which in turn are accessible from sulfonyl chlorides *p*- $\text{XC}_6\text{H}_4\text{SO}_2\text{Cl}$ by reaction with *t*-BuOOH (Hoffman & Cadena, 1977; Hoffman & Belfoure, 1983; Hoffman & Salvador, 1989*b*). The title compound, (I), was isolated as a by-product during this synthesis.



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 asymmetric. The $\text{K}-\text{O}2$ distance is 0.33 Å longer than $\text{K}-\text{O}1$ and is by far the longest in the structure.

The aqua bridge is highly asymmetric: the $\text{K}-\text{O}$ distances differ by 0.176 Å and the stronger-bound potassium ion is practically coplanar with the H_2O 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—

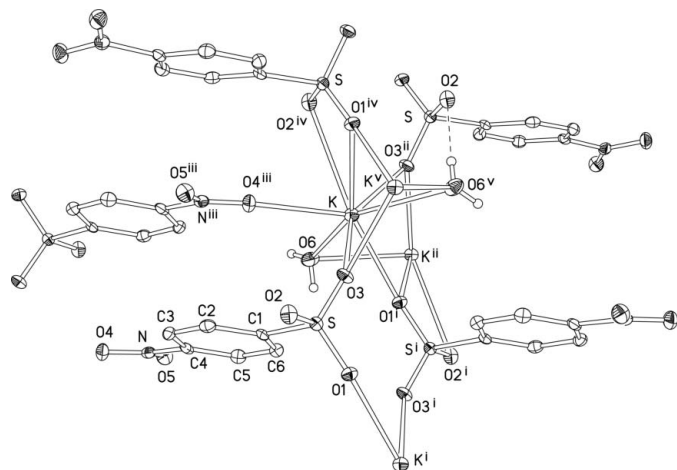


Figure 1
The environment of a K^+ cation in the structure of (I) (50% displacement ellipsoids). [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$, (ii) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$, (iii) $-x, 1 - y, 1 - z$, (iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$, (v) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$.]

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 $p\text{-O}_2\text{NC}_6\text{H}_4\text{SO}_2\text{OOSO}_2\text{C}_6\text{H}_4\text{NO}_2 \cdot p$ (II) was prepared according to Dannley *et al.* (1970). To a solution of K_2CO_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™ 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, ν, cm^{-1} : 3065 (CH aromatic stretch), 1529 (NO_2), 1461 (SO_2) 819 (p -disubstituted aromatic). ^1H 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, CDCl_3): 123.5 (2 \times PhCNO₂), 126.0 (4 \times CH aromatic), 140.0 (4 \times CH aromatic), 148.0 (2 \times PhCSO₂). The properties of (I) agree with those reported by Kozlov & Davydov (1965) or Dietze *et al.* (1989).

Crystal data

$\text{K}^+ \cdot \text{C}_6\text{H}_4\text{NO}_5\text{S}^- \cdot \text{H}_2\text{O}$
 $M_r = 259.28$
Monoclinic, $P2_1/c$
 $a = 10.794$ (1) Å
 $b = 7.1516$ (6) Å
 $c = 12.417$ (1) Å
 $\beta = 106.15$ (1)°
 $V = 920.70$ (14) Å³
 $Z = 4$

$D_x = 1.871$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 2733 reflections
 $\theta = 3.3\text{--}27.5^\circ$
 $\mu = 0.81$ mm⁻¹
 $T = 120$ (2) K
Block, yellow
 $0.3 \times 0.2 \times 0.15$ mm

Data collection

Siemens SMART 1K CCD area detector diffractometer
 ω scans
Absorption correction: none
9859 measured reflections
2117 independent reflections

1596 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.067$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -14 \rightarrow 13$
 $k = -9 \rightarrow 9$
 $l = -16 \rightarrow 15$

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 $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.46 \text{ e \AA}^{-3}$

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, °).

$D\text{—}H \cdots A$	$D\text{—}H$	$H \cdots A$	$D \cdots A$	$D\text{—}H \cdots A$
O6—H01 \cdots O2 ^{vi}	0.78 (4)	2.15 (4)	2.922 (3)	172 (4)
O6—H02 \cdots 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, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

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.

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