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Poly[(μ -5,7-dihydroxy-4-oxo-2-phenyl-4H-chromene-8-sulfonato)potassium(I)]Bin Liu^{a,b,*} and Bo-Lun Yang^a

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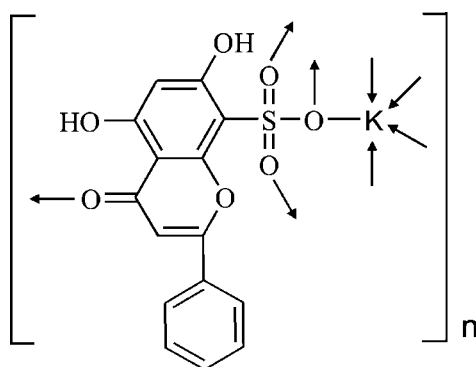
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.044; wR factor = 0.152; data-to-parameter ratio = 12.0.

In the polymeric title compound, $[\text{K}(\text{C}_{15}\text{H}_9\text{O}_7\text{S})]_n$, the potassium cation is five-coordinated by four sulfonate O atoms and one carbonyl O atom. Two intramolecular O—H...O hydrogen bonds stabilize the conformation of the anion. The polymeric three-dimensional supramolecular architecture is formed *via* coordination interactions and π - π stacking interactions involving centrosymmetrically related pyrone rings, with a centroid-centroid separation of 3.513 (2) Å.

Related literature

For biological activities of flavonoids, see: Aljancic *et al.* (1999); Habtemariam (1997); Knekt *et al.* (1997); Ko *et al.* (1998); Nkengfack *et al.* (1994); Sakaguchi *et al.* (1992). For related structures, see: Benedict *et al.* (2004); Li & Zhang (2008); Wang & Zhang (2005*a,b*); Zhang & Wang (2005*a,b*).



Experimental

Crystal data

 $[\text{K}(\text{C}_{15}\text{H}_9\text{O}_7\text{S})]$ $M_r = 372.38$ Orthorhombic, *Pccn* $a = 19.0846$ (19) Å $b = 20.6555$ (19) Å $c = 7.5148$ (7) Å $V = 2962.3$ (5) Å³ $Z = 8$ Mo $K\alpha$ radiation $\mu = 0.54$ mm⁻¹ $T = 296$ (2) K $0.37 \times 0.20 \times 0.13$ mm

Data collection

Bruker SMART-1000 CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 1999)
 $T_{\min} = 0.825$, $T_{\max} = 0.933$

13998 measured reflections
2637 independent reflections
1746 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.044$ $wR(F^2) = 0.152$ $S = 1.02$

2637 reflections

220 parameters

H-atom parameters constrained

 $\Delta\rho_{\max} = 0.26$ e Å⁻³ $\Delta\rho_{\min} = -0.29$ e Å⁻³

Table 1

Selected bond lengths (Å).

| | | | |
|----------------------|-----------|---------------------|-----------|
| K1—O5 ⁱ | 2.674 (2) | K1—O3 ^{iv} | 2.642 (2) |
| K1—O6 ⁱⁱ | 2.754 (2) | K1—O6 | 2.756 (3) |
| K1—O7 ⁱⁱⁱ | 2.655 (3) | | |

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

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------|-------|-------------|-------------|---------------|
| O1—H1 \cdots O7 | 0.82 | 1.84 | 2.588 (4) | 152 |
| O2—H2 \cdots O3 | 0.82 | 1.87 | 2.604 (4) | 148 |

Symmetry codes: .

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2268).

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supplementary materials

Acta Cryst. (2009). E65, m66-m67 [doi:10.1107/S1600536808041779]

Poly[(μ -5,7-dihydroxy-4-oxo-2-phenyl-4*H*-chromene-8-sulfonato)potassium(I)]

B. Liu and B.-L. Yang

Comment

The biological properties of flavonoids (2-phenylbenzo- γ -pyrone derivatives) are well known (Sakaguchi *et al.*, 1992; Nkengfack *et al.*, 1994; Habtemariam, 1997; Knekt *et al.*, 1997; Ko *et al.*, 1998; Aljancic *et al.*, 1999). The main problem that these compounds present for their use in biological experiments is their poor solubility in water. To overcome this problem, many flavonoidsulfonate derivatives have been synthesized, for example [Ni(H₂O)₆](C₁₇H₁₃O₇S)₂.8H₂O (Zhang & Wang, 2005*a*), [Sr(H₂O)₇(C₁₆H₁₁O₄SO₃)](C₁₆H₁₁O₄SO₃).6H₂O (Zhang & Wang, 2005*b*), [Mg(H₂O)₆](C₁₉H₁₇O₄SO₃)₂.8H₂O and [Zn(H₂O)₆](C₁₉H₁₇O₄SO₃)₂.8H₂O (Wang & Zhang, 2005*a*) and [Co(H₂O)₆](C₁₉H₁₇O₄SO₃)₂.8H₂O (Wang & Zhang, 2005*b*). Against this background, we report here the solid-state characterization of the potassium salt of 5,7-dihydroxyflavone-8-sulfonate.

The asymmetric unit of title compound consists of one potassium(I) cation and one 5,7-dihydroxyflavone-8-sulfonate anion (Fig. 1). The cation has a distorted coordination geometry and is coordinated by four sulfonate O atoms (O5ⁱ, O6, O6ⁱⁱ, and O7ⁱⁱⁱ; symmetry codes: (i) $x, y, z + 1$; (ii) $x, -y + 1/2, z + 1/2$; (iii) $-x + 1/2, y, z + 1/2$) and one carbonyl O atom (O3^{iv}; symmetry code: (iv) $-x, -y + 1, -z + 1$). The K—O bond distances (Table 1) are in agreement with those found in K⁺.C₁₆H₁₁O₈⁻.2H₂O (Benedict *et al.*, 2004). The flavone skeleton presents the same structure of a corresponding flavonesulfonate ligand reported previously (Li & Zhang, 2008) and is stabilized by intramolecular hydrogen bonds, with O1—H1 \cdots O7 = 2.588 (4) Å and O2—H2 \cdots O3 = 2.640 (4) Å (Table 2).

As shown in Fig. 2, K1^{vi} (symmetry code: (vi) $x, -y + 1/2, z - 1/2$) and K1^{vii} (symmetry code: (vii) $-x + 1/2, y, z - 1/2$) coordinate with O6 and O7^{viii} (symmetry code: (viii) $-x + 1/2, -y + 1/2, z$) and O6^{viii} and O7, respectively, resulting in a centrosymmetric eight-membered chelate ring that is non-planar. Coordination bonds K1^{vi}—O3^{ix} (symmetry code: (ix) $-x, y - 1/2, -z + 1/2$) and K1^{vii}—O3^x (symmetry code: (x) $x + 1/2, -y + 1, -z + 1/2$) link the flavone skeletons [C1—C15/O4]^{ix} and [C1—C15/O4]^x and the eight-membered ring together to form a two-dimensional sheet-like structure in the *ab* plane. Another eight-membered chelate ring is built up by O6ⁱⁱ, S1ⁱⁱ, O7ⁱⁱ, K1^{viii}, O6ⁱⁱⁱ, S1ⁱⁱⁱ, O7ⁱⁱⁱ and K1. Two adjacent eight-membered rings are further linked into a one-dimensional polyion chain along the *c* axis by the coordination bonds K1—O6, K1^{vii}—O5ⁱⁱⁱ, K1^{viii}—O6^{viii} and K1^{vi}—O5ⁱⁱ (Fig. 3). Additionally, $\pi\cdots\pi$ stacking interactions (Fig. 2) between centrosymmetrically related pyrone rings may be effective in the stabilization of the three-dimensional polymeric structure, with a centroid-centroid distance of 3.513 (2) Å, a perpendicular interplanar distance of 3.342 (3) Å and a centroid \cdots centroid offset of 1.084 (2) Å.

Experimental

5,7-dihydroxyflavone (1.0 g, 3.9 mmol) was added slowly to concentrated sulfuric acid (6 ml) with stirring. The reaction was maintained at room temperature for 12 h. Then, the mixture was poured into a KCl saturated aqueous solution (50 ml) and a yellow precipitate appeared. After 5 h, the precipitate was filtered and washed with a KCl saturated aqueous solution until

supplementary materials

the pH value of the filtrate was 7. The solid product was recrystallized from an ethanol-water (1:1 v/v) solution. Colourless plate-shaped crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent for about 4 d at room temperature (yield 83%).

Refinement

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å, O—H = 0.82 Å, and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ or $1.5 U_{\text{eq}}(\text{O})$.

Figures

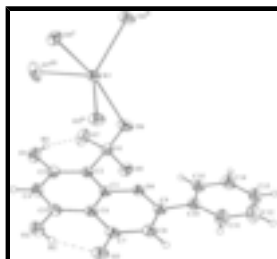


Fig. 1. The coordination environment of the potassium(I) cation in the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Intramolecular hydrogen bonds are shown as dashed lines. Symmetry codes: (i) $x, y, z + 1$; (ii) $x, -y + 1/2, z + 1/2$; (iii) $-x + 1/2, y, z + 1/2$; (iv) $-x, -y + 1, -z + 1$.

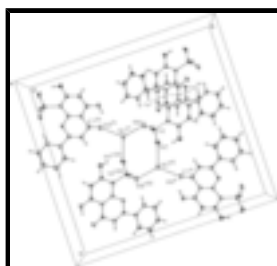


Fig. 2. Packing diagram of the title compound viewed along the c axis, showing the sheet-like structure in the ab plane. The dashed line indicates the π - π stacking interaction. $Cg1$ is the centroid of the pyrone ring. Symmetry codes: (vi) $x, -y + 1/2, z - 1/2$; (vii) $-x + 1/2, y, z - 1/2$; (viii) $-x + 1/2, -y + 1/2, z$; (ix) $-x, y - 1/2, -z + 1/2$; (x) $x + 1/2, -y + 1, -z + 1/2$; (xi) $-x, -y + 1, -z$.



Fig. 3. The one-dimensional polyion chain along the c axis in the title compound. Symmetry codes: (ii) $x, -y + 1/2, z + 1/2$; (iii) $-x + 1/2, y, z + 1/2$; (vi) $x, -y + 1/2, z - 1/2$; (vii) $-y + 1/2, y, z - 1/2$; (viii) $-x + 1/2, -y + 1/2, z$.

Poly[(μ -5,7-dihydroxy-4-oxo-2-phenyl-4H-chromene-8-yl)sulfonato]potassium(I)]

Crystal data

[K(C₁₅H₉O₇S)]

$M_r = 372.38$

Orthorhombic, $Pccn$

Hall symbol: -P 2ab 2ac

$a = 19.0846$ (19) Å

$b = 20.6555$ (19) Å

$c = 7.5148$ (7) Å

$V = 2962.3$ (5) Å³

$Z = 8$

$F_{000} = 1520$

$D_x = 1.670$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 2056 reflections

$\theta = 2.9$ – 20.9°

$\mu = 0.54$ mm⁻¹

$T = 296$ (2) K

Plate, colourless

$0.37 \times 0.20 \times 0.13$ mm

Data collection

| | |
|--|--|
| Bruker SMART-1000 CCD area-detector diffractometer | 2637 independent reflections |
| Radiation source: fine-focus sealed tube | 1746 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{\text{int}} = 0.049$ |
| $T = 296(2)$ K | $\theta_{\text{max}} = 25.1^\circ$ |
| φ and ω scans | $\theta_{\text{min}} = 1.5^\circ$ |
| Absorption correction: multi-scan (SADABS; Bruker, 1999) | $h = -21 \rightarrow 22$ |
| $T_{\text{min}} = 0.825$, $T_{\text{max}} = 0.933$ | $k = -24 \rightarrow 22$ |
| 13998 measured reflections | $l = -7 \rightarrow 8$ |

Refinement

| | |
|--|---|
| Refinement on F^2 | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.044$ | $w = 1/[\sigma^2(F_o^2) + (0.091P)^2]$ |
| $wR(F^2) = 0.152$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.02$ | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| 2637 reflections | $\Delta\rho_{\text{max}} = 0.26 \text{ e } \text{\AA}^{-3}$ |
| 220 parameters | $\Delta\rho_{\text{min}} = -0.28 \text{ e } \text{\AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$ |
| Secondary atom site location: difference Fourier map | Extinction coefficient: none |

Special details

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. 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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|--------------|--------------|--------------|----------------------------------|
| K1 | 0.13853 (4) | 0.30967 (3) | 0.70530 (10) | 0.0614 (3) |
| S1 | 0.15766 (5) | 0.35454 (4) | 0.23290 (12) | 0.0609 (3) |
| O1 | 0.24816 (13) | 0.46137 (12) | 0.4226 (4) | 0.0808 (8) |

supplementary materials

| | | | | |
|-----|---------------|--------------|-------------|-------------|
| H1 | 0.2561 | 0.4241 | 0.3913 | 0.121* |
| O2 | 0.07320 (14) | 0.61774 (10) | 0.4594 (4) | 0.0757 (8) |
| H2 | 0.0318 | 0.6235 | 0.4351 | 0.114* |
| O3 | -0.04849 (13) | 0.59352 (11) | 0.3174 (3) | 0.0681 (7) |
| O4 | 0.02313 (11) | 0.41527 (10) | 0.1793 (3) | 0.0518 (6) |
| O5 | 0.14317 (13) | 0.34558 (12) | 0.0469 (3) | 0.0711 (7) |
| O6 | 0.11604 (17) | 0.31214 (11) | 0.3432 (3) | 0.0830 (8) |
| O7 | 0.23185 (16) | 0.34965 (14) | 0.2716 (4) | 0.1005 (11) |
| C1 | 0.06796 (17) | 0.45769 (15) | 0.2611 (4) | 0.0483 (8) |
| C2 | 0.13557 (17) | 0.43436 (15) | 0.2928 (4) | 0.0510 (8) |
| C3 | 0.18152 (19) | 0.47689 (16) | 0.3815 (4) | 0.0587 (8) |
| C4 | 0.15971 (19) | 0.53813 (16) | 0.4343 (5) | 0.0637 (9) |
| H4 | 0.1910 | 0.5653 | 0.4928 | 0.076* |
| C5 | 0.09334 (19) | 0.55884 (15) | 0.4016 (4) | 0.0574 (8) |
| C6 | 0.04475 (17) | 0.51880 (14) | 0.3107 (4) | 0.0494 (8) |
| C7 | -0.02559 (19) | 0.53857 (15) | 0.2717 (4) | 0.0555 (9) |
| C8 | -0.06835 (18) | 0.49192 (16) | 0.1810 (4) | 0.0563 (8) |
| H8 | -0.1140 | 0.5029 | 0.1495 | 0.068* |
| C9 | -0.04401 (17) | 0.43304 (15) | 0.1409 (4) | 0.0515 (8) |
| C10 | -0.08112 (18) | 0.38009 (16) | 0.0517 (4) | 0.0571 (8) |
| C11 | -0.1517 (2) | 0.3838 (2) | 0.0188 (6) | 0.0862 (13) |
| H11 | -0.1761 | 0.4205 | 0.0549 | 0.103* |
| C12 | -0.1872 (3) | 0.3350 (2) | -0.0658 (8) | 0.1055 (16) |
| H12 | -0.2352 | 0.3384 | -0.0857 | 0.127* |
| C13 | -0.1515 (3) | 0.2812 (2) | -0.1205 (6) | 0.0930 (14) |
| H13 | -0.1751 | 0.2485 | -0.1806 | 0.112* |
| C14 | -0.0811 (3) | 0.27500 (18) | -0.0878 (6) | 0.0805 (12) |
| H14 | -0.0572 | 0.2380 | -0.1237 | 0.097* |
| C15 | -0.0457 (2) | 0.32438 (16) | -0.0007 (4) | 0.0654 (9) |
| H15 | 0.0019 | 0.3202 | 0.0229 | 0.079* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|-------------|-------------|-------------|--------------|--------------|--------------|
| K1 | 0.0902 (6) | 0.0465 (5) | 0.0474 (5) | 0.0031 (3) | -0.0002 (4) | -0.0003 (3) |
| S1 | 0.0824 (7) | 0.0503 (5) | 0.0499 (6) | 0.0108 (4) | -0.0088 (4) | -0.0111 (4) |
| O1 | 0.0802 (18) | 0.0717 (17) | 0.0906 (19) | 0.0055 (13) | -0.0169 (15) | -0.0260 (15) |
| O2 | 0.110 (2) | 0.0437 (13) | 0.0731 (18) | 0.0056 (13) | -0.0029 (16) | -0.0139 (12) |
| O3 | 0.0923 (18) | 0.0503 (14) | 0.0618 (15) | 0.0184 (12) | 0.0040 (12) | -0.0021 (11) |
| O4 | 0.0652 (14) | 0.0425 (12) | 0.0477 (13) | -0.0009 (10) | 0.0000 (10) | -0.0024 (10) |
| O5 | 0.0899 (17) | 0.0801 (17) | 0.0432 (15) | 0.0097 (13) | -0.0021 (11) | -0.0177 (12) |
| O6 | 0.144 (2) | 0.0461 (14) | 0.0583 (15) | 0.0019 (14) | 0.0097 (16) | 0.0017 (12) |
| O7 | 0.089 (2) | 0.089 (2) | 0.124 (3) | 0.0313 (16) | -0.0417 (18) | -0.0468 (17) |
| C1 | 0.065 (2) | 0.0459 (18) | 0.0340 (17) | -0.0041 (14) | 0.0040 (14) | 0.0003 (13) |
| C2 | 0.068 (2) | 0.0476 (18) | 0.0368 (17) | 0.0016 (15) | -0.0004 (15) | -0.0012 (14) |
| C3 | 0.074 (2) | 0.0527 (19) | 0.050 (2) | -0.0003 (17) | -0.0002 (17) | -0.0027 (16) |
| C4 | 0.082 (3) | 0.050 (2) | 0.059 (2) | -0.0092 (17) | -0.0038 (18) | -0.0100 (17) |
| C5 | 0.084 (2) | 0.0445 (18) | 0.0434 (19) | -0.0014 (16) | 0.0025 (17) | -0.0013 (15) |

| | | | | | | |
|-----|-----------|-------------|-------------|--------------|--------------|--------------|
| C6 | 0.069 (2) | 0.0425 (17) | 0.0366 (17) | 0.0021 (15) | 0.0032 (15) | 0.0009 (13) |
| C7 | 0.083 (2) | 0.0437 (18) | 0.0395 (17) | 0.0045 (16) | 0.0111 (16) | 0.0056 (14) |
| C8 | 0.067 (2) | 0.055 (2) | 0.047 (2) | 0.0026 (16) | 0.0066 (16) | 0.0026 (15) |
| C9 | 0.063 (2) | 0.0546 (19) | 0.0368 (17) | -0.0023 (16) | 0.0067 (15) | 0.0058 (14) |
| C10 | 0.067 (2) | 0.056 (2) | 0.048 (2) | -0.0070 (16) | 0.0021 (16) | 0.0012 (16) |
| C11 | 0.080 (3) | 0.080 (3) | 0.099 (3) | -0.005 (2) | -0.006 (2) | -0.021 (3) |
| C12 | 0.081 (3) | 0.096 (3) | 0.139 (5) | -0.013 (3) | -0.012 (3) | -0.021 (3) |
| C13 | 0.106 (4) | 0.088 (3) | 0.085 (3) | -0.039 (3) | -0.015 (3) | -0.006 (3) |
| C14 | 0.116 (4) | 0.057 (2) | 0.069 (3) | -0.015 (2) | 0.002 (2) | -0.0078 (19) |
| C15 | 0.085 (3) | 0.059 (2) | 0.052 (2) | -0.0076 (19) | -0.0020 (18) | 0.0029 (17) |

Geometric parameters (Å, °)

| | | | |
|--|-------------|--------------------------------------|-------------|
| K1—O5 ⁱ | 2.674 (2) | C1—C2 | 1.398 (4) |
| K1—O6 ⁱⁱ | 2.754 (2) | C2—C3 | 1.409 (5) |
| K1—O7 ⁱⁱⁱ | 2.655 (3) | C3—C4 | 1.389 (5) |
| K1—O3 ^{iv} | 2.642 (2) | C4—C5 | 1.359 (5) |
| K1—O6 | 2.756 (3) | C4—H4 | 0.9300 |
| K1—S1 ⁱⁱ | 3.4177 (12) | C5—C6 | 1.418 (4) |
| S1—O5 | 1.437 (2) | C6—C7 | 1.433 (5) |
| S1—O6 | 1.444 (3) | C7—C8 | 1.435 (5) |
| S1—O7 | 1.449 (3) | C8—C9 | 1.336 (4) |
| S1—C2 | 1.760 (3) | C8—H8 | 0.9300 |
| O1—C3 | 1.347 (4) | C9—C10 | 1.466 (4) |
| O1—H1 | 0.8200 | C10—C11 | 1.371 (5) |
| O2—C5 | 1.348 (4) | C10—C15 | 1.391 (5) |
| O2—H2 | 0.8200 | C11—C12 | 1.372 (6) |
| O3—C7 | 1.264 (4) | C11—H11 | 0.9300 |
| O3—K1 ^{iv} | 2.642 (2) | C12—C13 | 1.366 (6) |
| O4—C9 | 1.364 (4) | C12—H12 | 0.9300 |
| O4—C1 | 1.370 (4) | C13—C14 | 1.372 (6) |
| O5—K1 ^v | 2.674 (2) | C13—H13 | 0.9300 |
| O6—K1 ^{vi} | 2.754 (2) | C14—C15 | 1.387 (5) |
| O7—K1 ^{vii} | 2.655 (3) | C14—H14 | 0.9300 |
| C1—C6 | 1.389 (4) | C15—H15 | 0.9300 |
| O3 ^{iv} —K1—O7 ⁱⁱⁱ | 112.50 (9) | C5—O2—H2 | 109.5 |
| O3 ^{iv} —K1—O5 ⁱ | 82.73 (7) | C7—O3—K1 ^{iv} | 152.5 (2) |
| O7 ⁱⁱⁱ —K1—O5 ⁱ | 72.70 (8) | C9—O4—C1 | 120.6 (2) |
| O3 ^{iv} —K1—O6 ⁱⁱ | 127.89 (9) | S1—O5—K1 ^v | 167.47 (15) |
| O7 ⁱⁱⁱ —K1—O6 ⁱⁱ | 111.02 (10) | S1—O5—K1 ^{vi} | 77.73 (11) |
| O5 ⁱ —K1—O6 ⁱⁱ | 84.11 (8) | K1 ^v —O5—K1 ^{vi} | 94.19 (7) |
| O3 ^{iv} —K1—O6 | 79.69 (8) | S1—O6—K1 ^{vi} | 104.63 (13) |
| O7 ⁱⁱⁱ —K1—O6 | 108.95 (10) | S1—O6—K1 | 119.49 (16) |
| O5 ⁱ —K1—O6 | 161.50 (8) | K1 ^{vi} —O6—K1 | 109.29 (8) |
| O6 ⁱⁱ —K1—O6 | 111.35 (7) | S1—O7—K1 ^{vii} | 153.43 (16) |

supplementary materials

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| O3 ^{iv} —K1—S1 ⁱⁱ | 145.54 (6) | O4—C1—C6 | 120.2 (3) |
| O7 ⁱⁱⁱ —K1—S1 ⁱⁱ | 101.41 (7) | O4—C1—C2 | 115.6 (3) |
| O5 ⁱ —K1—S1 ⁱⁱ | 102.33 (6) | C6—C1—C2 | 124.2 (3) |
| O6 ⁱⁱ —K1—S1 ⁱⁱ | 24.13 (6) | C1—C2—C3 | 116.1 (3) |
| O6—K1—S1 ⁱⁱ | 95.45 (5) | C1—C2—S1 | 120.0 (2) |
| O3 ^{iv} —K1—O5 ⁱⁱ | 134.72 (7) | C3—C2—S1 | 123.8 (3) |
| O7 ⁱⁱⁱ —K1—O5 ⁱⁱ | 109.43 (8) | O1—C3—C4 | 115.7 (3) |
| O5 ⁱ —K1—O5 ⁱⁱ | 126.38 (7) | O1—C3—C2 | 123.2 (3) |
| O6 ⁱⁱ —K1—O5 ⁱⁱ | 43.85 (7) | C4—C3—C2 | 121.1 (3) |
| O6—K1—O5 ⁱⁱ | 71.21 (6) | C5—C4—C3 | 120.9 (3) |
| S1 ⁱⁱ —K1—O5 ⁱⁱ | 24.25 (4) | C5—C4—H4 | 119.5 |
| O3 ^{iv} —K1—K1 ^{vi} | 111.17 (5) | C3—C4—H4 | 119.5 |
| O7 ⁱⁱⁱ —K1—K1 ^{vi} | 109.12 (6) | O2—C5—C4 | 119.4 (3) |
| O5 ⁱ —K1—K1 ^{vi} | 162.75 (6) | O2—C5—C6 | 119.7 (3) |
| O6 ⁱⁱ —K1—K1 ^{vi} | 79.25 (6) | C4—C5—C6 | 120.9 (3) |
| O6—K1—K1 ^{vi} | 35.35 (5) | C1—C6—C5 | 116.8 (3) |
| S1 ⁱⁱ —K1—K1 ^{vi} | 60.42 (2) | C1—C6—C7 | 120.2 (3) |
| O5 ⁱⁱ —K1—K1 ^{vi} | 36.40 (4) | C5—C6—C7 | 123.0 (3) |
| O3 ^{iv} —K1—K1 ⁱⁱ | 117.97 (5) | O3—C7—C8 | 122.4 (3) |
| O7 ⁱⁱⁱ —K1—K1 ⁱⁱ | 90.78 (8) | O3—C7—C6 | 121.6 (3) |
| O5 ⁱ —K1—K1 ⁱⁱ | 49.41 (6) | C8—C7—C6 | 116.0 (3) |
| O6 ⁱⁱ —K1—K1 ⁱⁱ | 35.37 (6) | C9—C8—C7 | 121.4 (3) |
| O6—K1—K1 ⁱⁱ | 146.71 (6) | C9—C8—H8 | 119.3 |
| S1 ⁱⁱ —K1—K1 ⁱⁱ | 53.48 (2) | C7—C8—H8 | 119.3 |
| O5 ⁱⁱ —K1—K1 ⁱⁱ | 77.10 (4) | C8—C9—O4 | 121.6 (3) |
| K1 ^{vi} —K1—K1 ⁱⁱ | 113.47 (3) | C8—C9—C10 | 127.9 (3) |
| O3 ^{iv} —K1—K1 ^{viii} | 160.42 (6) | O4—C9—C10 | 110.5 (3) |
| O7 ⁱⁱⁱ —K1—K1 ^{viii} | 49.44 (7) | C11—C10—C15 | 118.2 (3) |
| O5 ⁱ —K1—K1 ^{viii} | 96.34 (5) | C11—C10—C9 | 121.0 (3) |
| O6 ⁱⁱ —K1—K1 ^{viii} | 71.15 (7) | C15—C10—C9 | 120.8 (3) |
| O6—K1—K1 ^{viii} | 98.28 (6) | C10—C11—C12 | 121.9 (4) |
| S1 ⁱⁱ —K1—K1 ^{viii} | 53.85 (2) | C10—C11—H11 | 119.1 |
| O5 ⁱⁱ —K1—K1 ^{viii} | 60.52 (4) | C12—C11—H11 | 119.1 |
| K1 ^{vi} —K1—K1 ^{viii} | 74.040 (15) | C13—C12—C11 | 119.4 (4) |
| K1 ⁱⁱ —K1—K1 ^{viii} | 74.040 (15) | C13—C12—H12 | 120.3 |
| O5—S1—O6 | 111.97 (16) | C11—C12—H12 | 120.3 |
| O5—S1—O7 | 111.99 (17) | C12—C13—C14 | 120.7 (4) |
| O6—S1—O7 | 112.33 (19) | C12—C13—H13 | 119.6 |
| O5—S1—C2 | 108.86 (15) | C14—C13—H13 | 119.6 |
| O6—S1—C2 | 106.85 (15) | C13—C14—C15 | 119.5 (4) |
| O7—S1—C2 | 104.36 (16) | C13—C14—H14 | 120.3 |
| O5—S1—K1 ^{vi} | 78.02 (11) | C15—C14—H14 | 120.3 |

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| O6—S1—K1 ^{vi} | 51.24 (10) | C14—C15—C10 | 120.3 (4) |
| O7—S1—K1 ^{vi} | 92.71 (12) | C14—C15—H15 | 119.8 |
| C2—S1—K1 ^{vi} | 156.86 (12) | C10—C15—H15 | 119.8 |
| C3—O1—H1 | 109.5 | | |
| O6—S1—O5—K1 ^v | -89.8 (8) | O5—S1—C2—C3 | -127.7 (3) |
| O7—S1—O5—K1 ^v | 37.4 (8) | O6—S1—C2—C3 | 111.2 (3) |
| C2—S1—O5—K1 ^v | 152.3 (7) | O7—S1—C2—C3 | -8.0 (3) |
| K1 ^{vi} —S1—O5—K1 ^v | -50.7 (7) | K1 ^{vi} —S1—C2—C3 | 128.4 (3) |
| O6—S1—O5—K1 ^{vi} | -39.14 (14) | C1—C2—C3—O1 | 179.6 (3) |
| O7—S1—O5—K1 ^{vi} | 88.08 (15) | S1—C2—C3—O1 | 2.9 (5) |
| C2—S1—O5—K1 ^{vi} | -157.05 (13) | C1—C2—C3—C4 | 0.4 (5) |
| O5—S1—O6—K1 ^{vi} | 52.35 (18) | S1—C2—C3—C4 | -176.3 (3) |
| O7—S1—O6—K1 ^{vi} | -74.68 (17) | O1—C3—C4—C5 | -179.4 (3) |
| C2—S1—O6—K1 ^{vi} | 171.45 (13) | C2—C3—C4—C5 | -0.1 (5) |
| O5—S1—O6—K1 | 175.02 (14) | C3—C4—C5—O2 | 178.0 (3) |
| O7—S1—O6—K1 | 48.0 (2) | C3—C4—C5—C6 | -0.8 (5) |
| C2—S1—O6—K1 | -65.88 (19) | O4—C1—C6—C5 | 177.3 (3) |
| K1 ^{vi} —S1—O6—K1 | 122.7 (2) | C2—C1—C6—C5 | -1.0 (4) |
| O3 ^{iv} —K1—O6—S1 | 86.63 (17) | O4—C1—C6—C7 | -1.9 (4) |
| O7 ⁱⁱⁱ —K1—O6—S1 | -23.78 (19) | C2—C1—C6—C7 | 179.7 (3) |
| O5 ⁱ —K1—O6—S1 | 68.3 (4) | O2—C5—C6—C1 | -177.4 (3) |
| O6 ⁱⁱ —K1—O6—S1 | -146.56 (11) | C4—C5—C6—C1 | 1.3 (5) |
| S1 ⁱⁱ —K1—O6—S1 | -127.83 (16) | O2—C5—C6—C7 | 1.8 (5) |
| O5 ⁱⁱ —K1—O6—S1 | -128.54 (18) | C4—C5—C6—C7 | -179.5 (3) |
| K1 ^{vi} —K1—O6—S1 | -120.4 (2) | K1 ^{iv} —O3—C7—C8 | -19.5 (6) |
| K1 ⁱⁱ —K1—O6—S1 | -147.10 (9) | K1 ^{iv} —O3—C7—C6 | 161.6 (3) |
| K1 ^{viii} —K1—O6—S1 | -73.63 (16) | C1—C6—C7—O3 | 179.0 (3) |
| O3 ^{iv} —K1—O6—K1 ^{vi} | -153.01 (12) | C5—C6—C7—O3 | -0.2 (5) |
| O7 ⁱⁱⁱ —K1—O6—K1 ^{vi} | 96.58 (12) | C1—C6—C7—C8 | 0.0 (4) |
| O5 ⁱ —K1—O6—K1 ^{vi} | -171.4 (2) | C5—C6—C7—C8 | -179.2 (3) |
| O6 ⁱⁱ —K1—O6—K1 ^{vi} | -26.21 (19) | O3—C7—C8—C9 | -177.0 (3) |
| S1 ⁱⁱ —K1—O6—K1 ^{vi} | -7.48 (11) | C6—C7—C8—C9 | 1.9 (5) |
| O5 ⁱⁱ —K1—O6—K1 ^{vi} | -8.18 (9) | C7—C8—C9—O4 | -2.0 (5) |
| K1 ⁱⁱ —K1—O6—K1 ^{vi} | -26.7 (2) | C7—C8—C9—C10 | 179.1 (3) |
| K1 ^{viii} —K1—O6—K1 ^{vi} | 46.72 (11) | C1—O4—C9—C8 | 0.1 (4) |
| O5—S1—O7—K1 ^{vii} | -24.2 (5) | C1—O4—C9—C10 | 179.1 (2) |
| O6—S1—O7—K1 ^{vii} | 102.8 (5) | C8—C9—C10—C11 | -8.7 (5) |
| C2—S1—O7—K1 ^{vii} | -141.8 (4) | O4—C9—C10—C11 | 172.3 (3) |
| K1 ^{vi} —S1—O7—K1 ^{vii} | 54.0 (5) | C8—C9—C10—C15 | 171.8 (3) |
| C9—O4—C1—C6 | 1.9 (4) | O4—C9—C10—C15 | -7.2 (4) |
| C9—O4—C1—C2 | -179.6 (2) | C15—C10—C11—C12 | -1.1 (6) |
| O4—C1—C2—C3 | -178.2 (3) | C9—C10—C11—C12 | 179.5 (4) |

supplementary materials

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| C6—C1—C2—C3 | 0.2 (5) | C10—C11—C12—C13 | -0.5 (8) |
| O4—C1—C2—S1 | -1.4 (4) | C11—C12—C13—C14 | 1.6 (8) |
| C6—C1—C2—S1 | 177.0 (2) | C12—C13—C14—C15 | -1.0 (7) |
| O5—S1—C2—C1 | 55.8 (3) | C13—C14—C15—C10 | -0.6 (6) |
| O6—S1—C2—C1 | -65.3 (3) | C11—C10—C15—C14 | 1.7 (5) |
| O7—S1—C2—C1 | 175.5 (3) | C9—C10—C15—C14 | -178.9 (3) |
| K1 ^{vi} —S1—C2—C1 | -48.2 (4) | | |

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

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------|-------|-------------|-------------|---------------|
| O1—H1 \cdots O7 | 0.82 | 1.84 | 2.588 (4) | 152 |
| O2—H2 \cdots O3 | 0.82 | 1.87 | 2.604 (4) | 148 |

Fig. 1

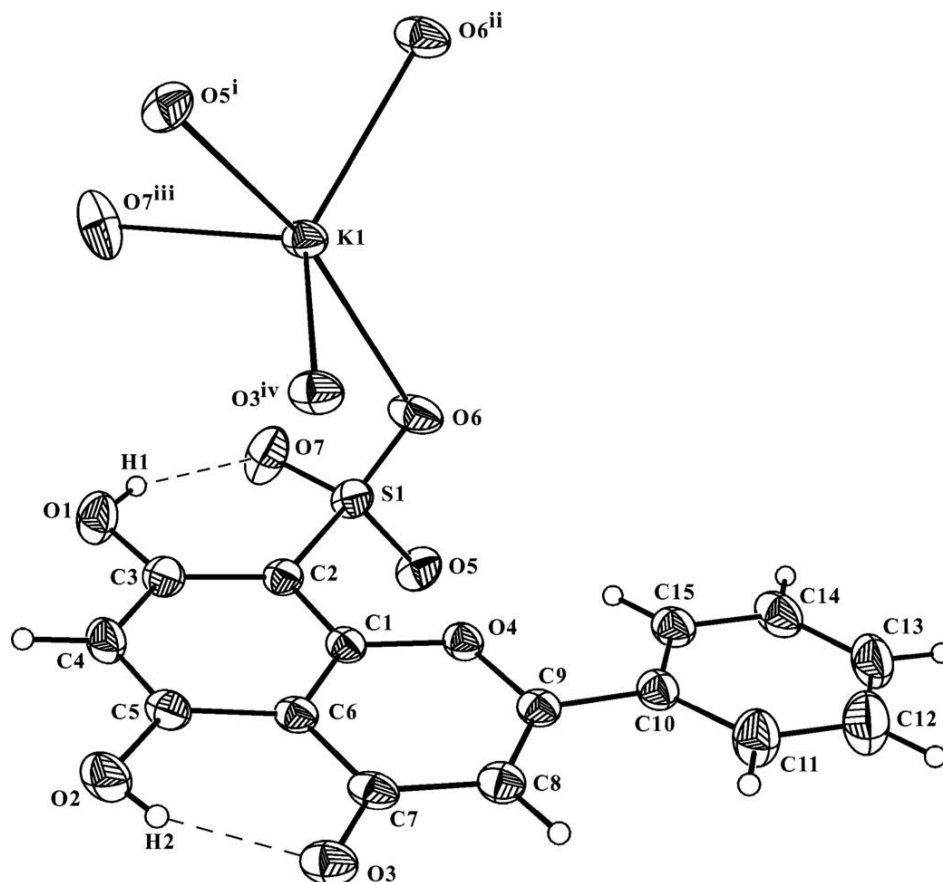


Fig. 2

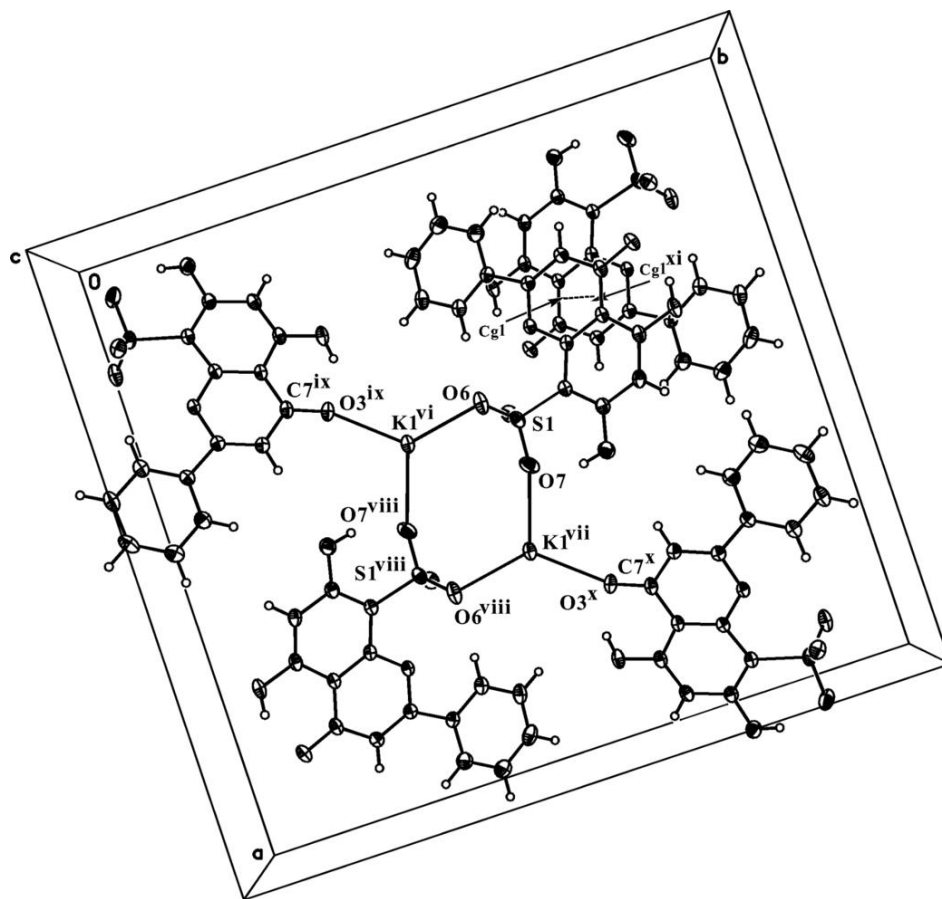


Fig. 3

