metal-organic papers

Potassium (4-methyl-2-oxo-2*H*-chromen-7-yl-oxy)sulfate

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In the title compound, $K^+ \cdot C_{10}H_7O_6S^-$, the sulfate S atom is located in the plane defined by the rest of the anion. This uncommon geometry is accompanied by the existence of a bifurcated three-centered intramolecular C—H···O interaction involving two of the sulfate O atoms. The combination of intra- and intermolecular contacts gives rise to $R_4^5(24)$ rings and folded layers parallel to (010), in which one of the sulfate O atoms and the carbonyl O atom act as acceptors. The stabilization of the crystal structure along the *b* axis comes from the coordination of the anions to the potassium cations and is assisted by π–π stacking interactions between layers.

Comment

Compound (I), also named potassium 4-methylumbelliferone sulfate or potassium 7-hydroxy-4-methylcoumarin sulfate, is commonly used as a substrate in various biochemical pathways in living cells involving sulfate esters (Tan & Pang, 2001; Anundi *et al.*, 1986; el-Mouelhi & Kauffman, 1986). Sulfate transfer is an important process in biological systems and some sulfate esters have become the subject of a number of mechanistic studies (Lopez *et al.*, 2001; Hopkins *et al.*, 1983), but only a few have been characterized by X-ray diffraction.


(I)
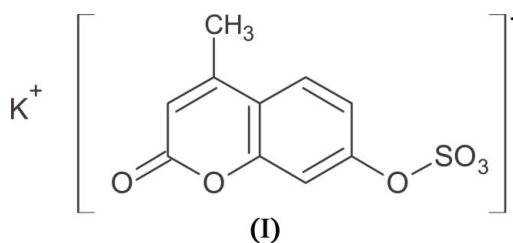
A search of the Cambridge Structural Database (Version 5.27 of November 2005; Allen, 2002) revealed only 16 examples of aryl sulfate monoesters. The common feature observed in all of them is the significant tendency of the sulfate group to be located synclinal (or anticlinal) in relation to the rest of the anion. The most commonly observed S—O—C—C torsion angle values range from 80 to 100°, but they have never been reported to be smaller than 54° (or larger than 128°). To the best of our knowledge, the only exceptions are the unpublished results of Popek (1998), who found the sulfate group to be located nearly in the plane of the aromatic system [the S—O—C—C angles in two of the three crystallographically independent anions in potassium 8-hydroxyquinoline-*O*-sulfate are 4.5 (6) and 17.5 (6)°] or even exactly in that plane [the whole anion in sodium 8-hydroxyquinoline-*O*-sulfate pentahydrate lies on the crystallographic mirror plane]. We report here the results of a study of (I), in which the S atom
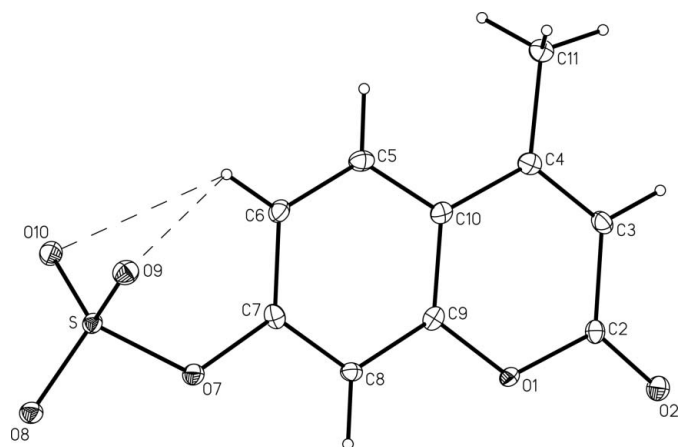
Figure 1
The molecular structure of the 7-hydroxy-4-methylcoumarin sulfate anion in (I), showing the atom numbering scheme and the intramolecular C—H···O interactions (dashed lines). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.
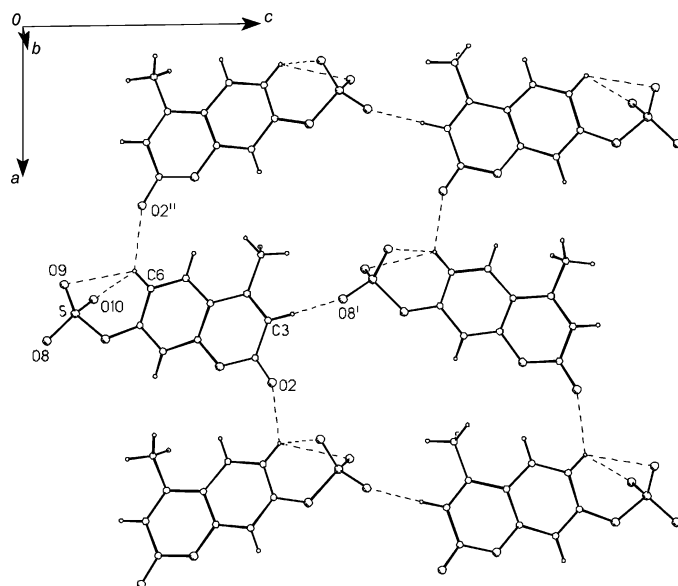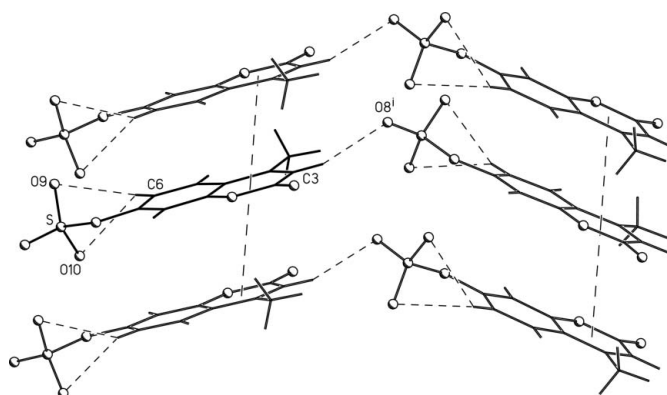

Figure 2
A fragment of the layer built up from the anions linked by C—H···O interactions (dashed lines), viewed down the *b* axis. Symmetry codes are given in Table 2.

Figure 3
A diagram showing the π–π interactions (dashed lines) in (I).

Figure 4
The packing mode for (I) showing the coordination sphere of the K^+ ion. K···O and K···K distances (Å): K···O8 = 3.082 (2), K···O10 = 2.757 (2), K···O2^A = 2.773 (2), K···O7^B = 3.280 (2), K···O8^B = 2.792 (2), K···O9^C = 2.672 (2), K···O9^D = 2.971 (2), K···O10^D = 3.122 (2), K···K^{D,E} = 4.648 (2). [Symmetry codes: (A) $\frac{1}{2} - x$, $1 - y$, $z - \frac{1}{2}$; (B) $\frac{1}{2} - x$, $\frac{1}{2} + y$, z; (C) x, $1 + y$, z; (D) $-x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$; (E) $-x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$.]
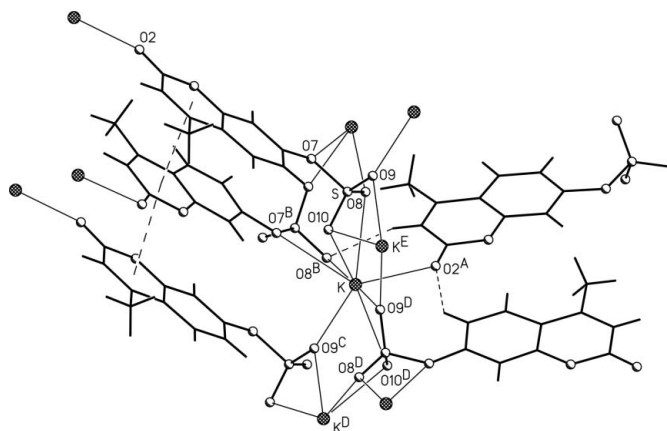
along with one of the sulfate O atoms are coplanar with the plane defined by the rest of the anion.

The crystal structure of (I) is built up from potassium cations and 7-hydroxy-4-methylcoumarin sulfate anions (Fig. 1). The 7-hydroxy-4-methylcoumarin unit is planar with normal bond lengths and angles. The S—O7—C7—C6 torsion angle (Table 1) reveals that the sulfate group lies in the plane of the coumarin group, which has very rarely been observed in this class of compounds. Additionally, one of the sulfate O atoms (O8) is antiperiplanar to C7, making it coplanar with the plane defined by the coumarin group and the S atom. Two other sulfate O atoms (O9 and O10) are synclinal with respect to C7, which is a common feature found in most of the sulfate esters studied to date (Allen, 2002). In (I) the uncommon

orientation of the sulfate group is accompanied by the existence of a bifurcated three-centered intramolecular C—H···O interaction between C6 from the coumarin group and both the sulfate synclinal O atoms (O9 and O10; Fig. 1). The observed value for the ester S—O7 bond length corresponds well to the average found for other aromatic sulfate esters (Popek, 1998). The terminal S—O distances range from 1.440 (2) to 1.447 (2) Å, and are almost 0.2 Å shorter than that for the ester S—O7 (Table 1), which is also in agreement with the previous observations for this class of compounds. In the sulfate group of (I), a deviation from ideal tetrahedral geometry is observed, especially in the O7—S—O8$_{ap}$ and O8$_{ap}$—S—O9$_{sc}$ angles. It is of note that the O7—S—O8 angle is one of the smallest O—S—O angles that have been reported for related compounds. The only exception is potassium *p*-nitrophenyl sulfate with an O—S—O$_{ap}$ angle of 99.91 (9)° (Sierosławski *et al.*, 2004).

Besides the bifurcated conformation–stabilizing intramolecular C—H···O contacts, the C6 atom is also involved in an intermolecular C6—H6—O2^{ii} interaction to the carbonyl O atom from an adjacent symmetry-related anion (symmetry

code as in Table 2). In this way atom C6 acts in a trifurcated four-centered contact to three different acceptors (Fig. 2). On the other hand, atom C3 is also involved in an intermolecular contact to the sulfate O8 atom from another adjacent anion. The combination of these intra- and intermolecular contacts gives rise to $R_4^5(24)$ rings and folded layers parallel to (010) (Fig. 2). Proposed C—H···O interactions are listed in Table 2.

The stabilization of the crystal packing in (I) along the b axis comes from the coordination of the anions to the potassium cations and from π–π stacking interactions between the aromatic O1/C2/C3/C4/C10/C9 rings from adjacent layers, located at $y = \frac{1}{4}, \frac{3}{4}, \cdots$ (Fig. 3). The distance between the centers of adjacent rings is approximately 3.48 Å. The potassium cations are located within the layers, in the voids between the anions, with each cation coordinating by five anions. The K···O distances range from 2.672 (2) to 3.280 (2) Å (see Fig. 4 caption). The anions coordinating to the same metal cation are involved in forming three different adjacent layers, which can be seen in Fig. 4. The eight-coordinate potassium polyhedron is composed of six terminal O atoms from four different sulfate groups, one ester O7 atom and one carbonyl O2 atom (Fig. 4). Thus, every metal cation is chelated by three anions via two sulfate O atoms each, while the two other anions are monodentate ligands for this cation. In this way, atoms O9 and O10 from two different sulfate groups serve as bridges between two adjacent K$^+$ ions to form $-[\text{K}\cdots\text{O9(O10)}]_n-$ chains with K···K^{D,E} distances of 4.648 (2) Å (for symmetry codes see Fig. 4 caption). Additionally, sulfate atom O7 coordinates to a potassium cation from an adjacent chain, and atom O8 acts as the bridging atom between the metal centers from these two chains. Thus, every sulfate group is coordinated to four different K$^+$ ions: three from one chain and one from another, which gives rise to layers parallel to the (001) plane.

Experimental

The crystal used for data collection was taken directly from the bottle supplied by Fluka. Recrystallization was attempted, but was unsuccessful; the compound is almost insoluble in most solvents and, additionally, is not stable in some of them.

Crystal data

K$^+$·C$_{10}$H$_7$O$_6$S$^-$
$M_r = 294.32$
Orthorhombic, $Pbca$
$a = 14.230$ (3) Å
$b = 6.945$ (2) Å
$c = 21.808$ (9) Å
$V = 2155$ (2) Å^3
$Z = 8$
$D_x = 1.814$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 12730 reflections
$\theta = 4.5$–$28.1°$
$\mu = 0.70$ mm^{-1}
$T = 100$ (2) K
Needle, colourless
$0.54 \times 0.05 \times 0.05$ mm

Data collection

Oxford Diffraction Xcalibur diffractometer
ω and φ scans
Absorption correction: analytical (CrysAlis RED; Oxford Diffraction, 2003)
$T_{min} = 0.775$, $T_{max} = 0.968$
26394 measured reflections

1995 independent reflections
1831 reflections with $I > 2\sigma(I)$
$R_{int} = 0.065$
$\theta_{max} = 25.5°$
$h = -17 \rightarrow 17$
$k = -8 \rightarrow 8$
$l = -26 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.105$
$S = 1.24$
1995 reflections
164 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0439P)^2 + 1.5833P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S—O7	1.629 (2)	O1—C2	1.385 (3)
S—O8	1.440 (2)	O1—C9	1.388 (4)
S—O9	1.440 (2)	O2—C2	1.206 (4)
S—O10	1.447 (2)	O7—C7	1.399 (3)
O7—S—O8	100.23 (12)	O8—S—O10	113.86 (13)
O7—S—O9	106.49 (12)	O9—S—O10	112.52 (13)
O7—S—O10	107.08 (12)	C7—O7—S	122.6 (2)
O8—S—O9	115.26 (13)		
O8—S—O7—C7	175.4 (2)	O10—S—O7—C7	56.4 (2)
O9—S—O7—C7	−64.2 (2)	S—O7—C7—C6	3.4 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···O8^i	0.95	2.40	3.312 (4)	161
C6—H6···O2^{ii}	0.95	2.40	3.106 (4)	131
C6—H6···O9	0.95	2.58	3.119 (4)	116
C6—H6···O10	0.95	2.56	3.054 (4)	113

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

All H atoms were found in difference Fourier maps. In the final refinement cycles, the H atoms were treated as riding atoms, with C—H distances of 0.95 or 0.98 Å, and with U_{iso}(H) values of $1.2U_{eq}$(C) for aromatic and $1.5U_{eq}$(C) for methyl H atoms.

Data collection: CrysAlis CCD (Oxford Diffraction, 2003); cell refinement: CrysAlis RED (Oxford Diffraction, 2003); data reduction: CrysAlis RED; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXL97.

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