

Tetrathiafulvalenium 4-oxo-2,2,6,6-tetramethylpiperidin-1-sulfate

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Key indicators

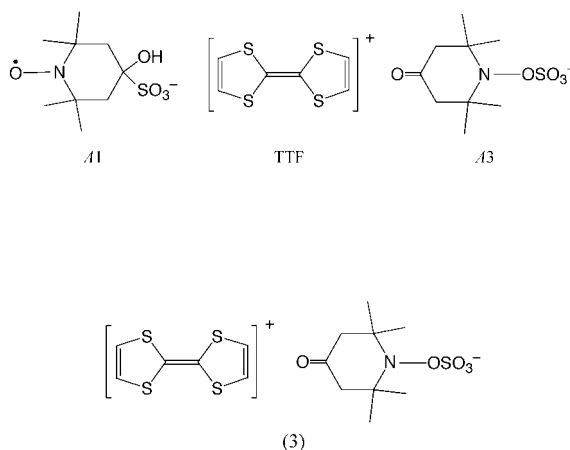
Single-crystal X-ray study
 $T = 296$ K
Mean $\sigma(\text{C}-\text{C}) = 0.007$ Å
 R factor = 0.067
 wR factor = 0.042
Data-to-parameter ratio = 10.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $\text{C}_6\text{H}_4\text{S}_4^+\cdot\text{C}_9\text{H}_{16}\text{NO}_5\text{S}^-$, which includes an organic diamagnetic anion, was obtained unexpectedly by metathesis of the tetraphenylphosphonium salt of an organic free-radical anion, 2,2,6,6-tetramethylpiperidinyloxy-4-hydroxy-4-sulfonate, with $(\text{TTF})_3(\text{BF}_4)_2$ (TTF = tetrathiafulvalene).

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Comment

Recently we prepared the first crystalline tetraphenylphosphonium salt (1) of a stable organic radical anion 2,2,6,6-tetramethylpiperidinyloxy-4-hydroxy-4-sulfonate (A1), which is the bisulfite-adduct of 4-oxo-TEMPO (TEMPO = 2,2,6,6-tetramethylpiperidin-1-oxyl) (Akutsu *et al.*, 2003). The salt (1) is a paramagnet due to the magnetic moment on the TEMPO group. Our aim is to prepare a salt of this anion with an organic electron donor to obtain a potential organic magnetic conductor (Akutsu *et al.*, 2001*a,b*). To this end, we attempted to obtain crystals of a TTF salt by metathesis. A solution of (1) and $(\text{TTF})_3(\text{BF}_4)_2$ (2) (TTF = tetrathiafulvalene), in acetonitrile, was prepared and the solvent allowed to evaporate slowly, giving black crystals. Single crystal X-ray diffraction revealed that the crystal is a TTF salt including a diamagnetic anion 4-oxo-2,2,6,6-tetramethylpiperidin-1-sulfate (A3) instead of the expected paramagnetic anion (A1). We report here the structure of the TTF salt of A3, compound (3). The origin of A3 in (3) is not clear, and we found no evidence for its presence in the starting sample.



The title compound, (3), consists of a TTF cation and an A3 anion (Fig. 1 and Table 1). A view of the crystal structure along the c axis is shown in Fig. 2. Almost planar cations form a stair-like stack with two alternating kinds of overlaps: (i) between

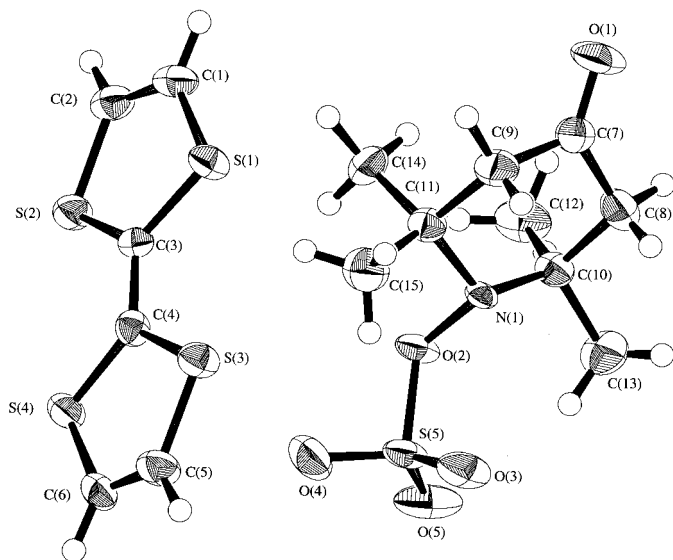


Figure 1
The tetrathiafulvalene cation and the 4-oxo-2,2,6,6-tetramethylpiperidine-1-sulfate anion in the title salt. Displacement ellipsoids are drawn at the 50% probability level.

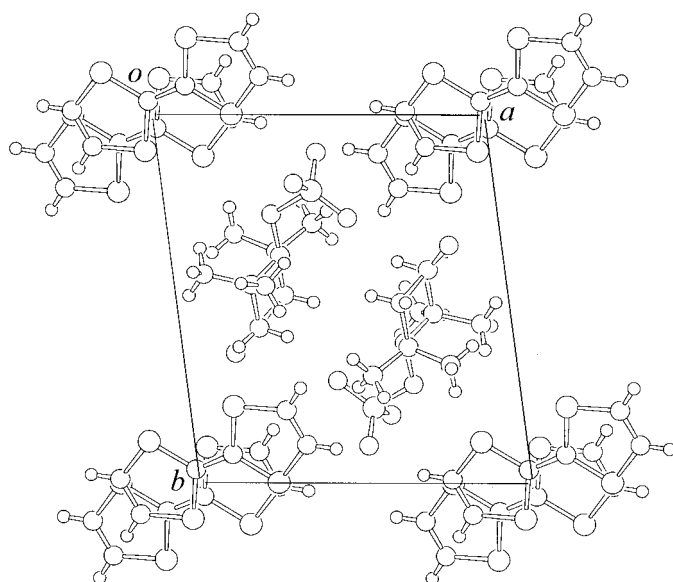


Figure 2
The crystal packing, viewed along the *c* axis.

two TTF moieties with no lateral shift, and (ii) between halves of dithiole rings only (Fig. 3); the interplanar separations are 3.38 (3) Å (TTFⁱ...TTFⁱ) and 3.54 (3) Å (TTFⁱ...TTFⁱⁱ), respectively [Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, -y, 1 - z$]. The central C=C bond is 1.398 (7) Å, which corresponds to the distances in TTF cation salts (1.39–1.40 Å; Batsanov *et al.*, 1997 and references therein). There are two intrastack S...S contacts [S1ⁱ...S4ⁱ = 3.329 (3) Å and S2ⁱ...S3ⁱ = 3.416 (3) Å] shorter than the sum of their van der Waals radii. There are no shorter interstack S...S contacts because the stacks are separated by the relatively large anions. No hydrogen bonds are observed between the anions.

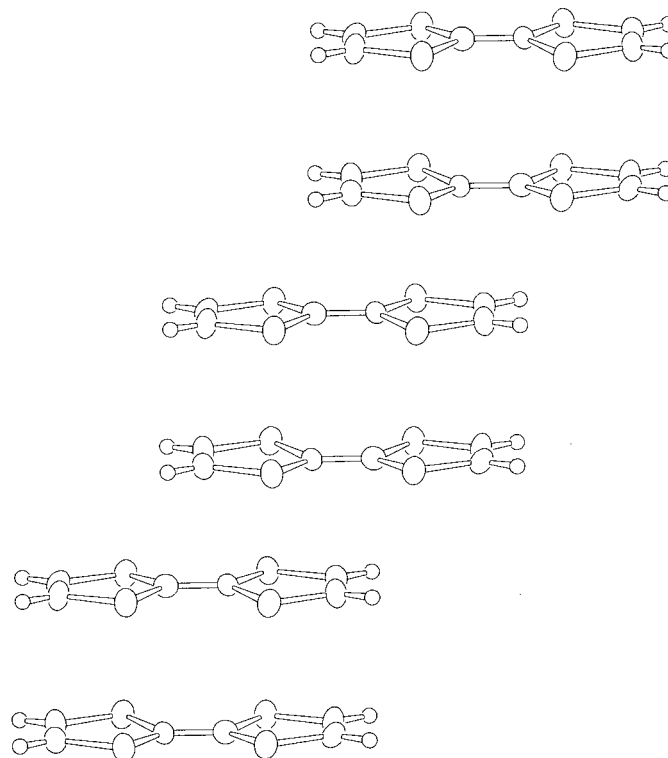


Figure 3
The TTF stacking pattern.

Experimental

Salt (1) (14.6 mg, 0.025 mmol) was dissolved in acetonitrile (20 ml) and an acetonitrile solution (20 ml) of (2) (9.4 mg, 0.012 mmol) was added. The mixture was left to stand in a jar at room temperature, allowing very slow evaporation of the solvent for several weeks, resulting in black plate-like crystals of the title compound.

Crystal data

$C_6H_4S_4^+ \cdot C_9H_{16}NO_5S^-$
 $M_r = 454.63$
 Triclinic, $P\bar{1}$
 $a = 10.884$ (1) Å
 $b = 12.132$ (2) Å
 $c = 7.948$ (1) Å
 $\alpha = 102.78$ (1)°
 $\beta = 106.02$ (1)°
 $\gamma = 79.52$ (1)°
 $V = 975.5$ (3) Å³

$Z = 2$
 $D_x = 1.548$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 14.1$ – 15.0 °
 $\mu = 0.62$ mm⁻¹
 $T = 296.2$ K
 Plate, black
 0.18 × 0.15 × 0.05 mm

Data collection

Rigaku AFC-7R diffractometer
 ω -2 θ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{min} = 0.950$, $T_{max} = 0.970$
 4709 measured reflections
 4476 independent reflections
 2479 reflections with $I > 2\sigma(I)$

$R_{int} = 0.028$
 $\theta_{max} = 27.5$ °
 $h = 0 \rightarrow 14$
 $k = -15 \rightarrow 15$
 $l = -10 \rightarrow 9$
 3 standard reflections
 every 150 reflections
 intensity decay: 0.4%

Refinement

Refinement on F
 $R = 0.067$
 $wR = 0.042$
 $S = 1.71$
 2479 reflections
 235 parameters

H-atom parameters not refined
 $w = 1/[\sigma^2(F_o)]$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.55$ e Å⁻³
 $\Delta\rho_{min} = -0.55$ e Å⁻³

Table 1
Selected geometric parameters (Å).

S1—C1	1.718 (6)	S5—O4	1.437 (5)
S1—C3	1.716 (5)	S5—O5	1.430 (5)
S2—C2	1.730 (6)	O1—C7	1.201 (6)
S2—C3	1.724 (5)	O2—N1	1.456 (5)
S3—C4	1.717 (5)	N1—C10	1.484 (7)
S3—C5	1.723 (6)	N1—C11	1.485 (7)
S4—C4	1.719 (5)	C1—C2	1.334 (8)
S4—C6	1.726 (6)	C3—C4	1.398 (7)
S5—O2	1.659 (4)	C5—C6	1.318 (8)
S5—O3	1.430 (4)		

All the H atoms were located in a difference Fourier map and fixed, with $U_{\text{iso}} = 0.0507 \text{ \AA}^2$.

Data collection: *MSC/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1994); cell refinement: *MSC/AFD Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997–1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s)

used to refine structure: *TEXSAN for Windows*; software used to prepare material for publication: *TEXSAN for Windows*.

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