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Tetraphenylphosphonium 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy-4-sulfonate

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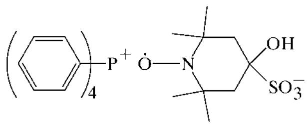
The title compound, $C_{24}H_{20}P^+\cdot C_9H_{17}NO_5S^-$, consists of an organic monovalent cation and an organic monovalent anion, the latter being derived from the TEMPO radical (TEMPO is 2,2,6,6-tetramethylpiperidin-1-oxyl). Two inversion-related anions interact *via* two –O—H···O—S– hydrogen bonds, forming a dimer in which there are no short contacts between the spin centres (–N—O) of the $TEMPO(OH)SO_3^-$ anions. Furthermore, no significant magnetic interaction is observed between the dimers because the dimer is surrounded by cations. These results are consistent with the paramagnetic behaviour of the title salt.

Comment

In recent decades, many stable organic radicals and their derivatives have been synthesized because they are suitable for use in studying the magnetic properties of molecular materials (Kahn, 1993). Our current interests are in the preparation, structure elucidation and characterization of stable organic radical anions that are useful not only as components of magnetic materials but also as counter-ions of organic conductors (Akutsu *et al.*, 2001*a*,*b*). We have examined the anion that is the bisulfide adduct of 4-oxo-TEMPO (TEMPO is 2,2,6,6-tetramethylpiperidin-1-oxyl), and we report here the structure of the tetraphenylphosphonium salt, (I).



(I)

The crystal structure consists of the tetraphenylphosphonium cation and the anion. A view of the anion is shown in Fig. 1 and selected bond lengths are presented in Table 1. The anion forms a dimer about the centre of symmetry, with hydrogen bonds between sulfonate atom O1 and hydroxy atom O4 in the centrosymmetrically related molecule (Fig. 1 and Table 2). Similar hydrogen bonds are observed in another dimeric bisulfide adduct, namely potassium hydroxymethanesulfonate (Cameron & Chute, 1979).

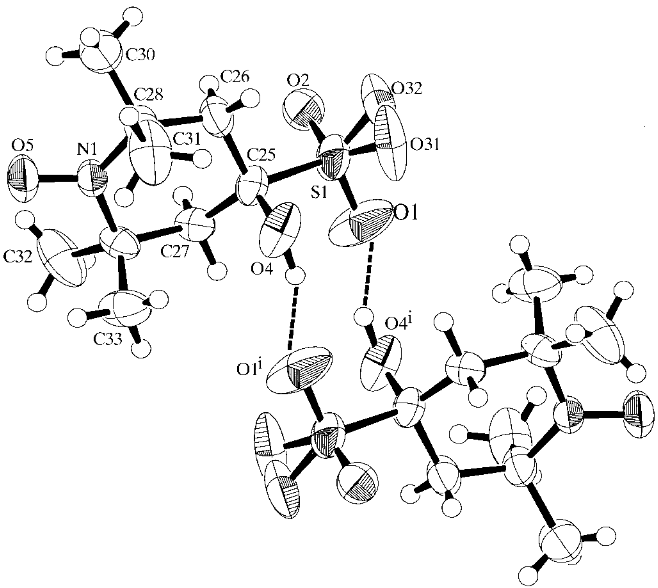


Figure 1
A view of the anions in (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate the hydrogen bonds between anions. [Symmetry code: (i) $-x, 1-y, 2-z$.]

The O5···O5($-x, 1-y, 2-z$) distance between the spin centres of the TEMPO anions in the dimer is 12.192 (5) Å, indicating that magnetic interactions are unlikely *via* this intradimer route. Each dimer is also surrounded by tetraphenylphosphonium cations, which add to the magnetic isolation. In fact, the nearest distance, O5···O5($1-x, -y, 1-z$), is 6.678 (5) Å, which is too large to allow any significant magnetic interactions in the crystal. These results are consistent with the bulk magnetic properties of this salt (Currie–Weiss behaviour from 2–300 K with $\theta = -0.137$ K and $C = 0.391$ e.m.u. mol^{-1} K^{-1}).

Experimental

For the preparation of (I), the corresponding sodium salt was prepared by reacting 4-oxo-TEMPO (1.0 g, 5.9 mmol) with $NaHSO_3$ (1.8 g, 18 mmol) in a mixed solvent of tetrahydrofuran (10 ml), water (10 ml) and H_2SO_4 (30%, 1.7 g) at 278–280 K, with stirring, for 1–2 min. Exchange of the counter-cation with tetraphenylphosphonium chloride gave the title salt, (I), as orange needle-like crystals after recrystallization from CH_2Cl_2/toluene (yield 62%).

Crystal data

$C_{24}H_{20}P^+\cdot C_9H_{17}NO_5S^-$
$M_r = 590.69$
Triclinic, $P\overline{1}$
$a = 11.733$ (2) Å
$b = 12.212$ (3) Å
$c = 11.501$ (3) Å
$\alpha = 103.79$ (2)°
$\beta = 96.89$ (2)°
$\gamma = 70.82$ (1)°
$V = 1510.1$ (6) Å^3

$Z = 2$
$D_x = 1.299$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 14.9$–15.0°
$\mu = 0.20$ mm^{-1}
$T = 296.2$ K
Block, orange
0.50 × 0.50 × 0.30 mm

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Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.888$, $T_{\max} = 0.941$
7269 measured reflections
6933 independent reflections
4180 reflections with $I > 3\sigma(I)$

$R_{\rm int} = 0.032$
$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 15$
$k = -14 \rightarrow 15$
$l = -14 \rightarrow 14$
3 standard reflections every 150 reflections intensity decay: 0.5%

Refinement

Refinement on F
$R = 0.058$
$wR = 0.051$
$S = 1.19$
4185 reflections
379 parameters
H-atom parameters not refined

Weighting method: Chebychev polynomial within 3 parameters: 399, −1.74 and 2.77 (Carruthers & Watkin, 1999)
$W = [\text{weight}] \times \{1 - [(\delta F/6)\sigma F]^2\}^2$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.56$ e Å^{-3}
$\Delta\rho_{\min} = -0.46$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

S1—O1	1.413 (3)	C25—C26	1.517 (4)
S1—O2	1.437 (3)	C25—C27	1.507 (4)
S1—O31	1.392 (16)	C26—C28	1.529 (4)
S1—O32	1.536 (13)	C27—C29	1.538 (4)
S1—C25	1.846 (3)	C28—C30	1.536 (5)
O4—C25	1.412 (4)	C28—C31	1.542 (6)
O5—N1	1.281 (3)	C29—C32	1.523 (5)
N1—C28	1.471 (4)	C29—C33	1.528 (5)
N1—C29	1.481 (4)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4—H1$\cdots$O1$^{\rm i}$	0.95	1.83	2.754 (5)	165

Symmetry code: (i) $-x, 1-y, 2-z$.

There is positional disorder of one of the sulfonate O atoms, and this atom was refined over two possible positions (O31 and O32), each with an occupancy of 50%. The elongated displacement ellipsoids of the sulfonate O atoms suggest rotational disorder of the SO_3 group. All H atoms were located from difference density maps and were assigned fixed distances and $U_{\rm iso}$ values of 0.0507 Å^2.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997–1999); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 2001); software used to prepare material for publication: *TEXSAN for Windows*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1128). Services for accessing these data are described at the back of the journal.

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