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S-[4-(Trimethylammonio)phenyl] thiosulfate, an aromatic organic thiosulfate

Jin-Xiang Chen,[a] Qing-Feng Xu,[a] Yong Zhang,[a] Sharifuddin M. Zain,[b] Seik Weng Ng[b] and Jian-Ping Lang[a,c]*

[a]School of Chemistry and Chemical Engineering, Suzhou University, 1 Shizi Street, Suzhou 215006, Jiangsu, People's Republic of China, [b]Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia, and [c]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, Jiangsu, People's Republic of China
Correspondence e-mail: jplang@suda.edu.cn

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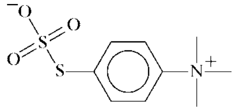
The title compound, $C_9H_{13}NO_3S_2$, exists as a zwitterion with crystallographic mirror symmetry. The central S atom of the S_2O_3 group adopts a slightly distorted tetrahedral coordination geometry. The S—S bond length is 2.1137 (7) Å, while the S—O bond lengths are in the range 1.4417 (12)–1.457 (2) Å. The zwitterions in the crystal adopt a head-to-tail arrangement, which leads to the formation of a three-dimensional network through C—H···O hydrogen bonds.

Comment

Zwitterionic organic compounds having a negatively charged thiolate end readily coordinate to metal ions to form metal thiolates (Ahmed *et al.*, 1998). One such reactant, 4-(trimethylammonio)benzenethiol hexafluorophosphate, reacts with metal ions to form cluster complexes (Chen *et al.*, 2004). The ready synthesis of such cluster complexes prompted an attempt at preparing a silver cluster complex, but the reaction with silver bromide in the presence of 4,4′-bipyridyl disulfide furnished instead the title compound, (I) (Fig. 1), which is yet another zwitterionic compound. The structure of (I) is a rare example of an organic thiosulfate, these being limited to one aromatic (Boese *et al.*, 1999) and six aliphatic examples (Cruz *et al.*, 1995; Foust & Janickis, 1980; Keefe & Stewart, 1972; Okaya, 1966; Steudel *et al.*, 1993; Zhang *et al.*, 1985). In all of these, an ammonium ($-NH_3$ or $>NH_2$) group interacts with the thiosulfate group through hydrogen bonds, and the S—O distances in the thiosulfate unit are similar to one another, in agreement with the delocalized nature of this group; for example, in $CH_3NH_2CH(CH_3)CH(C_6H_5)S_2O_3$, the three S—O distances are essentially identical [1.445 (2), 1.448 (2) and 1.456 (2) Å; Cruz *et al.*, 1995]. The simple thiosulfate ion has been isolated in ammonium salts, for example, bis(adamantanium) thiosulfate (Jiang *et al.*, 1998) and bis(tetraethylammonium) thiosulfate dihydrate (Leyten *et al.*, 1988).



(I)

The compound that is most closely comparable to (I) is zwitterionic 4-(trimethylammonio)benzenesulfonate, (II) (Even *et al.*, 1999), which is obtained from the thermally induced rearrangement of methyl 4-(dimethylamino)benzenesulfonate (Kusto *et al.*, 1999). The rearrangement has been investigated theoretically (Oda & Sato, 1998) and the driving force has been attributed to the large electric dipolar interactions among the zwitterions in the resulting product (Oda & Sato, 1997). Compound (II) exhibits three phases, *viz.* *Pcn*2 at low temperature, *Pca*2$_1$ at room temperature and *P*4$_2$/*ncm* at high temperature (Boese *et al.*, 1999). For the low-temperature phase, the S—O distances in the two independent molecules [1.448 (3)–1.458 (3) Å; Boese *et al.*, 1999] suggest delocalization of the negative charge over the SO_3 unit.

Compound (I), which crystallizes with imposed mirror symmetry, may be viewed as an arylated thiosulfate product. Atom S1 in the S_2O_3 group has a slightly distorted tetrahedral coordination geometry; the mean O—S—O angle (113.98°; Table 1) is consistent with those reported for the thiosulfate complexes $[CoCl_2(en)_2](HOCH_2)S_2O_3$ (en is ethylenediamine; 112.8°; Foust & Janickis, 1980) and $Me_2HN(CH_2S_2O_3)_2Na$ (113.6°; Zhang *et al.*, 1985), and slightly greater than those in the $(Me_4N)_2[Co(S_2O_3)_2(H_2O)_4]$ complex (110.8°; Alan & Michael, 1999). The S1—S2 distance in (I) [2.1137 (7) Å] is appreciably longer than those of coordinated thiosulfate ions that exhibit monodentate bonding through the S atoms only, such as in $(Me_4N)_2[Co(S_2O_3)_2(H_2O)_4]$ [2.011 (2) Å] and *trans*-$(Me_4N)_2[Ni(S_2O_3)_2(H_2O)_4]$ [2.014 (1) Å; Alan & Michael, 1999], but slightly shorter than the S—S bond distance (2.155 Å) of $HSSO_3^-$ (Karol & Ralf, 1992) and similar to the values for free alkyl thiosulfate ions, such as $Me_2HN(CH_2S_2O_3)_2Na$ [2.082 (1) Å; Zhang *et al.*, 1985] and $[CoCl_2(en)_2]HOCH_2S_2O_3$ [2.0779 (15) Å; Foust &

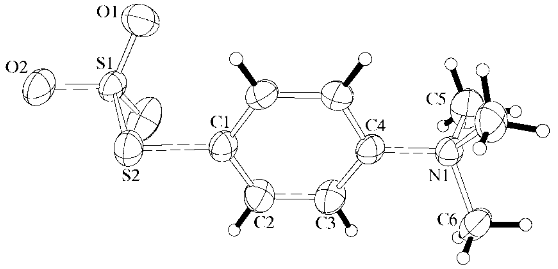


Figure 1
An *ORTEP*II (Johnson, 1976) plot of (I), with displacement ellipsoids at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

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Janickis, 1980]. The S—O distances in the S_2O_3 group in (I) range from 1.4417 (12) to 1.457 (2) Å, which indicates some S—O multiple-bond character [*cf*. 1.433–1.455 Å in $Me_2HN(CH_2S_2O_3)_2Na$; Zhang *et al.*, 1985], with the bonding delocalized between atom S1 and the three O atoms. The mean S—O distance in (I) (1.446 Å) is comparable to those found in $[CoCl_2(en)_2]HOCH_2S_2O_3$ (1.449 Å) and $Me_2HN(CH_2S_2O_3)_2Na$ (1.444 Å). The S2—C1 bond distance [1.776 (2) Å] is slightly shorter than those reported in other thiosulfate complexes, such as $[CoCl_2(en)_2]HOCH_2S_2O_3$ [1.829 (4) Å] and $Me_2HN(CH_2S_2O_3)_2Na$ [1.814 (3) Å and 1.816 Å]. Ammonium atom N1 is sp^3 hybridized, forming a cationic charge center, and all N—C bond lengths and C—N—C angles are normal.

The zwitterions in the crystal stack in a head-to-tail manner, parallel to the polar *c* axis, *via* hydrogen bonds from the methyl H atoms to the O atoms of the S_2O_3 group (Table 2), thereby forming a three-dimensional network.

The dipole moment lies approximately along the vector from the N atom to the single-bonded O atom (dipole moment = 26.78 D) but is not parallel to the *c* axis. In contrast, the dipole moment of the α phase of 4-(trimethylammonio)benzenesulfonate is aligned along a crystallographic axis (calculated dipole moment = 24.97 D; Sarma & Dunitz, 1990).

Experimental

4-(Trimethylammonio)benzenethiol hexafluorophosphate was synthesized according to the procedure of DePamphilis *et al.* (1974). The resulting compound (0.125 g, 0.4 mmol) in methanol (5 ml) was neutralized with excess triethylamine (0.25 ml); the solution was then reacted with silver bromide powder (0.038 g, 0.2 mmol). The clear colorless solution that formed after the mixture had been stirred briefly was treated with 4,4′-dipyridyl disulfide (0.044 g, 0.2 mmol) in acetonitrile (2 ml). Prismatic colorless crystals were separated from the orange solution after several days in about 20% yield. The crystals were washed with ether. Analysis found: C 43.52, H 5.18, N 5.32%; calculated for $C_9H_{13}NO_3S_2$: C 43.70, H 5.28, N 5.66%. IR (KBr, cm^{-1}): 1488 (*s*), 1217 (*s*), 1190 (*s*), 1024 (*s*), 1009 (*s*), 609 (*s*), 525 (*m*). Although the compound is not the intended product, the reaction is reproducible. The dipole moments of 4-(trimethylammonio)benzenesulfonate and (I) were computed at the PM3 level using *HyperChem* (Hypercube, 2001).

Crystal data

$C_9H_{13}NO_3S_2$
$M_r = 247.32$
Orthorhombic, $Pmn2_1$
$a = 9.0937$ (11) Å
$b = 5.6809$ (6) Å
$c = 10.3830$ (11) Å
$V = 536.39$ (10) Å^3
$Z = 2$
$D_x = 1.531$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 2404 reflections
$\theta = 3.6$–27.5°
$\mu = 0.48$ mm^{-1}
$T = 193$ (2) K
Prism, colorless
0.30 × 0.30 × 0.25 mm

Data collection

Rigaku Mercury diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
$T_{\min} = 0.869$, $T_{\max} = 0.889$
5598 measured reflections
1291 independent reflections

1263 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.020$
$\theta_{\max} = 27.5°$
$h = -11 \rightarrow 10$
$k = -7 \rightarrow 7$
$l = -13 \rightarrow 13$

Table 1
Selected geometric parameters (Å, °).

S1—O1	1.4417 (12)	N1—C6	1.5027 (19)
S1—O2	1.457 (2)	N1—C5	1.509 (3)
S1—S2	2.1137 (7)	C1—C2	1.388 (2)
S2—C1	1.776 (2)	C2—C3	1.382 (2)
N1—C4	1.496 (3)	C3—C4	1.387 (2)
O1—S1—O2	113.99 (7)	C6—N1—C5	108.23 (12)
O1—S1—S2	106.64 (6)	C2—C1—S2	120.37 (11)
O2—S1—S2	100.06 (9)	C3—C2—C1	120.66 (16)
C1—S2—S1	99.55 (8)	C2—C3—C4	119.66 (15)
C4—N1—C6	111.92 (11)	C3—C4—N1	119.90 (11)
C4—N1—C5	109.26 (17)		

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C5—H5B⋯O2$^{\rm i}$	0.97 (4)	2.42 (4)	3.363 (3)	165 (3)
C6—H6A⋯O1$^{\rm ii}$	0.91 (2)	2.55 (2)	3.406 (2)	158.0 (16)
C2—H2⋯O2$^{\rm iii}$	0.93 (3)	2.69 (3)	3.4244 (17)	136.5 (17)

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.060$
$S = 1.06$
1291 reflections
107 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 0.1062P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}
Absolute structure: Flack (1983), 604 Friedel pairs
Flack parameter = −0.02 (8)

H atoms were located from a difference Fourier map and their positions were refined freely [C—H = 0.90 (2)–0.97 (4) Å], along with their isotropic displacement parameters.

Data collection: *CrystalClear* (Molecular Structure Corporation and Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1631). Services for accessing these data are described at the back of the journal.

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