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# Tetraethylammonium Bromo(1,3-dithiol-2-one-4,5-dithiolato)diethylstannate(1−)

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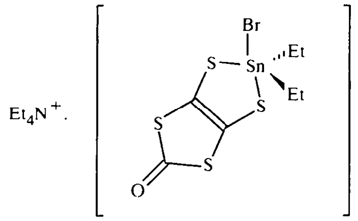
## Abstract

In the title compound, tetraethylammonium bromo-[4,5-dimercapto-1,3-dithiol-2-onato(2−)-$S^4$,$S^5$]diethylstannate(1−), $[N(C_2H_5)_4][SnBr(C_2H_5)_2(C_3OS_4)]$, the anion lies about a mirror plane and the Sn atom has distorted trigonal-bipyramidal geometry, with axial distances Sn—Br 2.8776 (16) and Sn—S 2.562 (2) Å, and equatorial distances Sn—S 2.458 (2) and Sn—C 2.111 (7) Å. The $[NEt_4]^+$ cation is disordered about an inversion centre.

## Comment

Various tin complexes of the dithiolato ligand 1,3-dithiole-2-thione-4,5-dithiolato [$C_3S_5^{2-}$, (I)] have been studied (Doidge-Harrison *et al.*, 1991, 1996; Doidge-Harrison, Howie, Irvine, Spencer & Wardell, 1992; Doidge-Harrison, Howie, Irvine & Wardell, 1992; Buchanan *et al.*, 1996; Aupers *et al.*, 1998; Khan *et al.*, 1998). These include complexes of the type $[Q][R_2SnX(C_3S_5)]$ [(II); $Q$ is an onium cation; $R$ = alkyl or aryl; $X$ = halide or pseudohalide], which contain near trigonal-bipyramidal Sn centres (Doidge-Harrison *et al.*, 1991; Aupers *et al.*, 1998; Khan *et al.*, 1998).

Compounds of the related dithiolato ligand 1,3-dithiol-2-one-4,5-dithiolato [(III), dmio, $C_3OS_4^{2-}$] have attracted much less study. A search of the October 1997 release of the Cambridge Structural Database (Allen & Kennard, 1993) yielded only six hits for such complexes [with Ti (Zeltner *et al.*, 1994), Ni (Olk *et al.*, 1988; Vicente *et al.*, 1988; Sun *et al.*, 1997), Cu (Vicente *et al.*, 1987) and W (Yang *et al.*, 1991)]. We report here the structure of the title compound, $[NEt_4]^+.[Et_2SnBr(C_3OS_4)]^-$, (IV), which exists as an ionic species, with negligible interactions between the cations and anions.



(IV)

The anion has the Sn, Br and dmio ligand atoms lying on a mirror plane and the geometry about tin (Fig. 1) is slightly distorted trigonal bipyramidal, with the Br and a dithiolato S atom in axial sites [Br1—Sn1—S2 167.07 (7)°]; the equatorial sites are occupied by the ethyl ligands and the other dithiolate S atom. As expected, the axial Sn—S bond is longer than the equatorial one [Sn1—S2 2.562 (2) and Sn1—S1 2.458 (2) Å]. The Sn—Br bond length in (IV) [2.8776 (16) Å] is considerably longer than the sum of the covalent radii

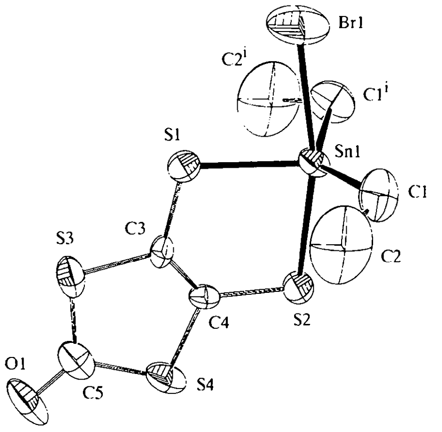


Fig. 1. A view of (IV) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The symmetry code is as in Table 2.

(2.39 Å), but well within the sum of the van der Waals radii (4.0–4.2 Å; Huheey *et al.*, 1993). The Sn—Br bond length in $[1,4\text{-}Me_2\text{-pyridinium}][Ph_2SnBr(C_3S_5)]$ [2.7139 (10) Å; Aupers *et al.*, 1998] is considerably shorter than that determined here for (IV), but still longer than the sum of the covalent radii.

The bite angle (S1—Sn1—S2) of the dmio ligand in (IV) is 87.15 (7)°. While the sum of the equatorial bond angles [357.6 (5)°] is near 360°, the C—Sn—C bond angle is surprising large at 135.4 (5)°. In related complexes such as $[Q][R_2SnX(C_3S_5)]$, which also contain trigonal-bipyramidal anions, the C—Sn—C equatorial angles are all less than that found in (IV), being in the range 110.5 (3)–120.9 (6)° (Doidge-Harrison *et al.*, 1991; Aupers *et al.*, 1998; Khan *et al.*, 1998). The bite angles of the dmit ligands in (II) are in the range 84.5 (1)–86.55 (6)° and hence are only slightly smaller than that in (IV).

The N atom of the $[NEt_4]^+$ cation lies at the inversion centre at (0,0,0), which requires that the ethyl groups be disordered (see *Experimental*). Examination of the structure with *PLATON* (Spek, 1998) showed that there were no solvent-accessible voids in the crystal lattice.

## Experimental

A solution of $Et_2SnBr_2$ (0.52 g, 2.0 mmol) in MeOH (20 ml) was added to a stirred suspension of bis(tetraethylammonium) bis(1,3-dithiol-2-one-4,5-dithiolato)zincate(2−) (0.69 g, 1.0 mmol; Chohan *et al.*, 1997) in MeOH (20 ml). The reaction mixture was stirred for 3 h and filtered. The precipitate was recrystallized from MeOH (yield 0.75 g, 76%; m.p. 415–416 K). Analysis found: C 31.9, H 5.1, N 2.6%; calculated for $C_{15}H_{30}BrNOS_4Sn$: C 31.5, H 5.2, N 2.4%; IR (KBr, $cm^{-1}$): 3055, 3002, 2986, 1665, 1612, 1590, 1475, 1451, 1414, 1395, 1302, 1177, 1020, 998, 892, 690, 492, 466; $^1H$ NMR (250 MHz, $Me_2SO\text{-}d_6$) $\delta$: 1.20 [*t*, 6H, $J$(H-H) = 8.1 Hz, $J(^{119}Sn\text{-}1H)$ = 120 Hz, $CH_3$ of the anion], 1.41 [*tt*, 12H, $J$(H-H) = 7.2 Hz, $CH_3$ of the cation], 1.59 [*q*, 4H, $J$(H-H) = 8.1 Hz, $CH_2$ of the anion], 3.32 [*q*, 8H, $J$(H-H) = 7.2 Hz, $CH_2$ of the cation]; $^{13}C$ NMR (63 MHz, $Me_2SO\text{-}d_6$) $\delta$: 7.5 ($CH_3$ of the cation), 11.8 [$J(^{119}Sn\text{-}^{13}C)$ = 40.5 Hz, $CH_3$ of the anion], 23.5 [$J(^{119}Sn\text{-}^{13}C)$ = 535 Hz, $CH_2$ of the anion], 52.7 ($CH_2$ of the cation), 119.4 (C═C), 192.5 (C═O); $^{119}Sn$ NMR (93 MHz, $Me_2SO\text{-}d_6$) $\delta$: −169.7.

*Crystal data*

$(C_8H_{20}N)[SnBr(C_2H_5)_2\text{-}(C_3OS_4)]$
$M_r = 567.24$
Orthorhombic
*Pnma*
$a = 11.0167\ (10)$ Å
$b = 13.6197\ (8)$ Å
$c = 15.4733\ (11)$ Å
$V = 2321.7\ (3)$ Å$^3$
$Z = 4$
$D_x = 1.623$ Mg m$^{-3}$
$D_m$ not measured
Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 10.04\text{–}15.27°$
$\mu = 3.184$ mm$^{-1}$
$T = 294\ (1)$ K
Block
0.40 × 0.40 × 0.20 mm
Colourless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical *via* $\psi$ scans at 4° steps (North *et al.*, 1968)
$T_{min} = 0.320$, $T_{max} = 0.529$
5777 measured reflections
2771 independent reflections
1606 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 27.90°$
$h = 0 \rightarrow 14$
$k = -17 \rightarrow 17$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 120 min
intensity variation: 0.7%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.153$
$S = 1.021$
2771 reflections
123 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0931P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.677$ e Å$^{-3}$
$\Delta\rho_{min} = -0.480$ e Å$^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0032 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Br1 | 0.24897 (16) | 1/4 | 0.72431 (14) | 0.1751 (9) |
| Sn1 | 0.02077 (5) | 1/4 | 0.63382 (3) | 0.0563 (3) |
| S1 | 0.16176 (18) | 1/4 | 0.51072 (15) | 0.0700 (6) |
| S2 | −0.15191 (18) | 1/4 | 0.52294 (15) | 0.0721 (6) |
| S3 | 0.1217 (3) | 1/4 | 0.32209 (15) | 0.0814 (7) |
| S4 | −0.1405 (3) | 1/4 | 0.33163 (15) | 0.0799 (7) |
| C1 | −0.0046 (8) | 0.3934 (6) | 0.6823 (6) | 0.115 (3) |
| C2 | 0.0171 (12) | 0.4734 (8) | 0.6180 (10) | 0.238 (10) |
| C3 | 0.0564 (6) | 1/4 | 0.4247 (5) | 0.0500 (17) |
| C4 | −0.0604 (6) | 1/4 | 0.4293 (5) | 0.0473 (16) |
| C5 | −0.0123 (10) | 1/4 | 0.2628 (6) | 0.079 (3) |
| O1 | −0.0197 (9) | 1/4 | 0.1859 (4) | 0.118 (3) |
| N1 | 0 | 0 | 0 | 0.0567 (16) |
| C11† | −0.0779 (11) | −0.0558 (8) | 0.0621 (8) | 0.116 (3) |
| C12‡ | −0.171 (2) | 0.0070 (16) | 0.1055 (18) | 0.091 (4) |
| C13† | 0.0685 (12) | 0.0777 (8) | 0.0471 (8) | 0.116 (3) |
| C14† | 0.143 (2) | 0.0385 (14) | 0.1206 (13) | 0.129 (5) |
| C21† | 0.0820 (11) | −0.0683 (8) | −0.0426 (8) | 0.116 (3) |
| C22† | 0.1603 (15) | −0.0298 (12) | −0.1134 (11) | 0.091 (4) |
| C23† | −0.0786 (11) | 0.0540 (8) | −0.0630 (8) | 0.116 (3) |
| C24‡ | −0.163 (3) | −0.0141 (18) | −0.110 (2) | 0.129 (5) |
| C15§ | −0.039 (3) | −0.1633 (10) | 0.060 (2) | 0.097 (11) |
| C25§ | −0.035 (3) | 0.1614 (10) | −0.063 (2) | 0.097 (11) |

† Site occupancy = 0.50. ‡ Site occupancy = 0.317 (9). § Site occupancy = 0.183 (9).

Table 2. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Br1—Sn1 | 2.8776 (16) | S2—C4 | 1.765 (8) |
| Sn1—S1 | 2.458 (2) | S3—C3 | 1.744 (7) |
| Sn1—S2 | 2.562 (2) | S3—C5 | 1.739 (10) |
| Sn1—C1 | 2.111 (7) | S4—C4 | 1.750 (7) |
| S1—C3 | 1.765 (8) | S4—C5 | 1.770 (10) |
| Br1—Sn1—S1 | 79.92 (7) | S1—Sn1—S2 | 87.15 (7) |
| Br1—Sn1—S2 | 167.07 (7) | S1—Sn1—C1 | 111.1 (2) |
| Br1—Sn1—C1 | 86.7 (2) | C1—Sn1—C1$^i$ | 135.4 (5) |

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

Molecule (IV) crystallized in the orthorhombic system; space group *Pnma* or *Pn*$2_1$*a* from the systematic absences. Both possibilities were examined in considerable detail and *Pnma* eventually selected after refinement in *Pn*$2_1$*a* led to various non-sensible parameters. The anion lies on a mirror plane; the N atom of the $[NEt_4]^+$ cation is on a crystallographic centre of symmetry which requires that the ethyl groups be disordered equally over two sites with 0.5 occupancy. Detailed inspection of successive difference-map plots showed clearly that two of the terminal methyl groups of the cation were each further disordered unequally over at least two sites. Sites for these groups were located from a difference Fourier plot and restrained to maintain sensible geometry using appropriate *DFIX* instructions during the *SHELXL*97 (Sheldrick, 1997) refinement. Site occupancies for these disordered methyl C atoms refined to 0.317 (9) (for C12 and C24) and 0.183 (9) (for C15 and C25). All non-H atoms of the anion and the N atom of the cation were allowed anisotropic displacement parameters. The partial-occupancy C atoms of the cation were only allowed isotropic motion. A view of the conformation of the cation is deposited. H atoms were treated as riding atoms (C—H 0.96–0.97 Å), but no allowance was made for the H atoms of the minor components of the cation.

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* in *CAD*-4-*PC*. Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989). Program(s) used to solve structure: *NRCVAX*96 *via* Patterson heavy-atom method. Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*97. Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1998). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*97 and *WordPerfect* macro *PRPCIF*97 (Ferguson, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1200). Services for accessing these data are described at the back of the journal. A simplistic view of the cation which does not show the disorder introduced by the inversion centre at the N atom has also been deposited.

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*Acta Cryst.* (1998). C54, 1403–1406

# Deca-$\mu$-acetato-di-$\mu_4$-oxo-tetra(pyridine-*N*)-dimanganese(III)tetramanganese(II) Pyridine Solvate

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## Abstract

The title compound, $[Mn_6O_2(C_2H_3O_2)_{10}(C_5H_5N)_4].C_5H_5N$, consists of well separated $[Mn_6O_2(OAc)_{10}py_4]$ complex units (OAc is acetate and py is pyridine) and pyridine solvent molecules. Six Mn atoms with distorted octahedral coordination spheres are connected by bridging oxo and acetato ligands. The Mn—O distances are between 1.892 (2) and 2.318 (3) Å, and the Mn—N distances are 2.287 (3) and 2.302 (4) Å. The magnetic moment at 300 K amounts to $\mu_{exp} = 5.66\ \mu_B$.

## Comment

The complex $[Mn_6O_2(OAc)_{10}py_4].py$ (OAc is acetate and py is pyridine), (I), was obtained as a by-product in

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