References

Bell, C. F. & Theocharis, C. R. (1987). *Acta Cryst.* C**43**, 26–27.

Biyuskin, V. N., Samus, Y. M., Samus, N. M. & Bake, I. O. (1987). *J. Struct. Chem.* (*Engl. Transl.*), **28**, 119–121.

Brown, J. N. & Agrawal, K. C. (1977). *Acta Cryst.* B**33**, 980–981.

Brown, J. N. & Agrawal, K. C. (1978*a*). *Acta Cryst.* B**34**, 1002–1011.

Brown, J. N. & Agrawal, K. C. (1978*b*). *Acta Cryst.* B**34**, 2078–2081.

Duan, C.-Y., Wu, B.-M. & Mak, T. C. W. (1996). *J. Chem. Soc. Dalton Trans.* pp. 3485–3490.

Farrarri, M. B., Fava, G. G., Tarasconi, P. & Pelizzi, C. (1989). *J. Chem. Soc. Dalton Trans.* pp. 361–365.

Garcia-Tojal, J., Urtiaga, M. K., Cortes, R., Lezama, L., Arriortua, M. I. & Rojo, T. J. (1994). *J. Chem. Soc. Dalton Trans*, pp. 2233–2238.

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Krause, K. L. & Phillips, G. N. (1992). *J. Appl. Cryst.* **25**, 146–164.

Liberta, A. E. & West, D. X. (1992). *Biometal*, **5**, 121–126.

Liu, M. C., Lin, T. S., Penketh, P. & Sartorelli, A. C. (1995). *J. Med. Chem.* **38**, 4234–4241.

Podhye, S. & Kauffman, G. B. (1985). *Coord. Chem. Res.* **63**, 127–164.

Siemens (1995). *SHELXTL Reference Manual*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Tanner, J. & Krause, K. (1994). *Rigaku J.* **11**, 4–7.

West, D. X., Liberta, A. E., Rajendran, K. G. & Hall, I. H. (1993). *Anticancer Drugs*, **4**, 241–246.

Acta Cryst. (1998). C**54**, 1399–1401

1,4-Dimethylpyridinium (1,3-Dithiole-2-thione-4,5-dithiolato)(isothiocyanato)diphenylstannate(1−)

Abdullah Khan,[a] John N. Low,[b] James L. Wardell[a] and George Ferguson[c]

[a]*Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, Aberdeen AB9 2UE, Scotland,* [b]*NCR Advanced Mechatronics Research Centre, Department of Applied Physics and Electronic & Mechanical Engineering, University of Dundee, Dundee DD1 4HN, Scotland, and* [c]*Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1. E-mail: j.n.low@dundee.ac.uk*

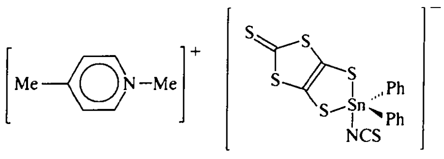
(*Received 23 March 1998; accepted 14 April 1998*)

Abstract

In the title compound, 1,4-dimethylpyridinium [4,5-dimercapto-1,3-dithiole-2-thionato(2−)-S^4,S^5](isothiocyanato)diphenylstannate(1−), $(C_7H_{10}N)[Sn(NCS)(C_6H_5)_2(C_3S_5)]$, the anion has distorted trigonal-bipyramidal coordination at the Sn atom, with the thiocyanato N and a thiolato S atom axial [Sn—N 2.262 (3), Sn—S 2.5917 (10) Å and N—Sn—S 164.58 (8)°]. The remaining thiolato S and two phenyl C atoms complete the equatorial coordination at Sn [Sn—S 2.4399 (10), and Sn—C 2.137 (4) and 2.139 (4) Å].

Comment

The 1,3-dithiole-2-thione-4,5-dithiolate (dmit) ligand, (1), forms complexes with various metals, including tin (Buchanan *et al.*, 1996; Doidge-Harrison *et al.*, 1991, 1992, 1996). As part of our ongoing research into such complexes, the title compound, $[1,4\text{-}Me_2\text{-pyridinium}]^+.[Ph_2Sn(dmit)(NCS)]^-$, (2), was prepared (see *Experimental*).



(2)

Our analysis shows that the asymmetric unit of (2) contains two $[1,4\text{-}Me_2\text{-pyridinium}]^+$ cations, each of which lies about independent inversion centres (with consequent disorder of *para*-C and *para*-N atoms), and a $[Ph_2Sn(dmit)(NCS)]^-$ anion (Fig. 1) in a general position.

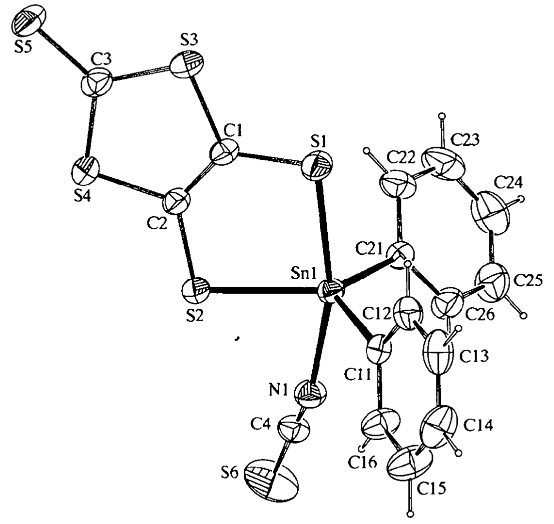


Fig. 1. A view of the anion in (2) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The anion contains a pentacoordinate Sn atom, with a distorted trigonal-bipyramidal geometry. The chelating dmit ligand is bonded to Sn *via* the dithiolate S atoms in axial [Sn1—S1 2.5917 (10) Å] and equatorial [Sn1—S2 2.4399 (10) Å] sites, with a bite angle of 86.37 (3)°; the corresponding values in $[NBu_4][Me_2Sn(dmit)Cl]$, (3), are 2.662 (3), 2.451 (3) Å and 84.5 (1)°, respectively (Doidge-Harrison *et al.*, 1991). The bite angles of the dmit ligand in (2) and (3) can be compared with those in other organotin–dmit complexes, *e.g.* 85.7 (2) and 85.8 (1)° in pentacoordinate $[NBu_4][R Sn(dmit)_2]$ (R = Bu and Ph, respectively) (Doidge-Harrison *et al.*, 1992), 89.93 (5)° in pentacoordinate $[PhMeSn(dmit)]_n$ (Doidge-Harrison *et al.*, 1996) and 88.42 (8)° in hexacoordinate $[(MeO_2CCH_2CH_2CO)_2Sn(dmit)]$ (Buchanan *et al.*, 1996). A search of the October 1997 release of the Cambridge Structural Database (Allen & Kennard, 1993) showed that there were no Sn(dmit) complexes listed other than those mentioned above.

The remaining axial site in (2) is occupied by the N atom of the NCS group, with Sn1—N1 2.262 (3) Å, S1—Sn1—N1 164.58 (8) and Sn1—N1—C4 156.8 (3)°. The Sn1—N1 bond length in (2) is comparable with that [2.268 (5) Å] found in $[NEt_4][Ph_3Sn(NCS)_2]$ (Cox & Wardell, 1996). The NCS group is essentially linear [S6—C4—N1 178.5 (4)°].

As noted above, two 1,4-dimethylpyridinium cations lie about independent inversion centres, resulting in disorder of the *para*-N and *para*-C atoms. Examination of the structure with *PLATON* (Spek, 1998) showed that there were no solvent-accessible voids in the crystal lattice.

Experimental

The compound $[1,4\text{-}Me_2\text{-pyridinium}][Ph_2SnCl(dmit)]$ was obtained from Ph_2SnCl_2 and $[1,4\text{-}Me_2\text{-pyridinium}]_2[Zn(dmit)_2]$ following a general procedure (Doidge-Harrison *et al.*, 1991). To a solution of this compound (1.53 g, 2.5 mmol) in Me_2CO (50 ml) was added a solution of NaSCN (0.41 g, 5.0 mmol) in MeOH (10 ml). The reaction mixture was left for 3 h, filtered and the filtrate rotary evaporated to leave an orange solid residue. This was washed successively with water, propan-2-ol and petrol (313–333 K), and was recrystallized from Me_2CO/MeOH to give an orange crystalline solid (yield 77%, m.p. 407–408 K). Analysis found: C 43.0, H 3.1, N 4.2%; calculated for $C_{23}H_{20}N_3S_6Sn$: C 43.5, H 3.2, N 4.4%; IR (KBr, cm^{-1}): 3044, 2046 (NCS), 1477, 1429, 1055 (C=S), 735; ^1H NMR (Cd_3COCD_3, 250 MHz) δ: 2.70 (*s*, 3H, Me), 4.54 (*s*, 3H, Me), 7.44 (*m*, 6H, *m*/*p*-aryl-H), 7.97 (*m*, 4H, *o*-aryl-H), 8.00 (*d*, J = 8.3 Hz, 2H) and 8.89 (*d*, J = 8.3 Hz, 2H, aryl-H of cation).

Crystal data

$(C_7H_{10}N)[Sn(NCS)(C_6H_5)_2\text{-}(C_3S_5)]$
$M_r = 635.46$
Monoclinic
$P2_1/a$
$a = 8.9189\ (11)$ Å
$b = 18.2124\ (14)$ Å
$c = 16.813\ (2)$ Å
$\beta = 103.134\ (11)°$
$V = 2659.6\ (5)\ Å^3$
$Z = 4$
$D_x = 1.587\ Mg\ m^{-3}$
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 9.95\text{–}18.30°$
$\mu = 1.447\ mm^{-1}$
$T = 294\ (1)$ K
Block
0.42 × 0.42 × 0.31 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical *via* ψ scans at 4° steps (North *et al.*, 1968)
$T_{min} = 0.534$, $T_{max} = 0.666$
6456 measured reflections
6086 independent reflections
4120 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 27.42°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 23$
$l = 0 \rightarrow 21$
3 standard reflections
frequency: 120 min
intensity variation: 0.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.096$
$S = 1.004$
6086 reflections
289 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.717\ e\ Å^{-3}$
$\Delta\rho_{min} = -0.801\ e\ Å^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Sn1—S1	2.5917 (10)	S3—C1	1.753 (3)
Sn1—S2	2.4399 (10)	S3—C3	1.719 (4)
Sn1—N1	2.262 (3)	S4—C2	1.746 (4)
Sn1—C11	2.139 (4)	S4—C3	1.715 (4)
Sn1—C21	2.137 (4)	S5—C3	1.654 (4)
S1—C1	1.735 (4)	S6—C4	1.608 (4)
S2—C2	1.740 (4)		
S1—Sn1—S2	86.37 (3)	S2—Sn1—C11	117.42 (10)
S1—Sn1—N1	164.58 (8)	S2—Sn1—C21	121.92 (10)
S1—Sn1—C11	98.32 (10)	N1—Sn1—C11	91.45 (13)
S1—Sn1—C21	96.71 (10)	N1—Sn1—C21	88.75 (12)
S2—Sn1—N1	78.53 (8)	C11 Sn1—C21	119.36 (13)

Molecule (2) crystallized in the monoclinic system; space group $P2_1/a$ from the systematic absences. The disorder in the cations was allowed for by treating each of the disordered N/C sites as being composed of equal contributions of N and C atoms and using the *SHELXL97 EXYZ* and *EADP* instructions (Sheldrick, 1997). H atoms were treated as riding atoms (C—H 0.93–0.96 Å).

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).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1198). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Buchanan, H., Howie, R. A., Khan, A., Spencer, G. M., Wardell, J. L. & Aupers, J. H. (1996). *J. Chem. Soc. Dalton Trans.* pp. 541–548.

Cox, P. J. & Wardell, J. L. (1996). *Acta Cryst.* **C52**, 317–319.

Doidge-Harrison, M. S. V., Howie, R. A., Irvine, J. T. S., Spencer, G. M. & Wardell, J. L. (1991). *J. Organomet. Chem.* **414**, C5–8.

Doidge-Harrison, M. S. V., Howie, R. A., Irvine, J. T. S., Spencer, G. M. & Wardell, J. L. (1992). *J. Organomet. Chem.* **436**, 23–33.
Doidge-Harrison, M. S. V., Irvine, J. T. S., Khan, A., Spencer, G. M., Wardell, J. L. & Aupers, J. H. (1996). *J. Organomet. Chem.* **516**, 199–205.
Enraf–Nonius (1992). *CAD-4-PC Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Ferguson, G. (1997). *PRPCIF97. A WordPerfect-5.1 Macro to Merge and Polish CIF Format Files from NRCVAX and SHELXL97 Programs*. University of Guelph, Canada.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Spek, A. L. (1998). *PLATON. Molecular Geometry Program*. Version of March 1998. University of Utrecht, The Netherlands.

Acta Cryst. (1998). C**54**, 1401–1403

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

ZAHID H. CHOHAN,[a] JAMES L. WARDELL,[a] JOHN N. LOW,[b] PAUL R. MEEHAN[c] AND GEORGE FERGUSON[c]

[a]*Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland,* [b]*AMRC, Department of Applied Physics and Electronic & Mechanical Engineering, University of Dundee, Dundee DD1 4HN, Scotland, and* [c]*Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1. E-mail: j.n.low@dundee.ac.uk*

(*Received 26 March 1998; accepted 23 April 1998*)

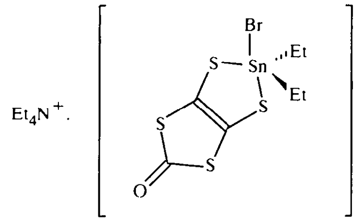
Abstract

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

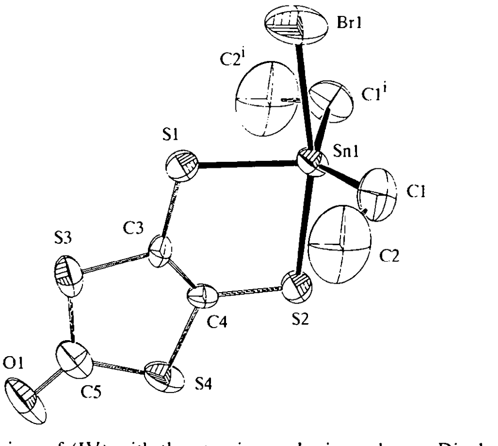


Fig. 1. A view of (IV) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The symmetry code is as in Table 2.