

$\omega/2\theta$ scans
 Absorption correction:
 ψ scan (NRCVAX; Gabe,
 LePage, Charland, Lee &
 White, 1989)
 $T_{\min} = 0.804$, $T_{\max} = 0.932$
 15 186 measured reflections
 7558 independent reflections

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.069$
 $wR(F^2) = 0.108$
 $S = 0.918$
 7558 reflections
 542 parameters
 H atoms riding, C—H =
 0.93 Å
 $w = 1/[\sigma^2(F_o^2)]$
 $(\Delta/\sigma)_{\max} = -0.008$

$R_{\text{int}} = 0.071$
 $\theta_{\max} = 25.0^\circ$
 $h = -13 \rightarrow 13$
 $k = -13 \rightarrow 13$
 $l = -20 \rightarrow 19$
 3 standard reflections
 every 200 reflections
 intensity decay: 1.2%

$\Delta\rho_{\max} = 0.36 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.30 \text{ e } \text{Å}^{-3}$
 Extinction correction:
 SHELXL93 (Sheldrick,
 1993)
 Extinction coefficient:
 0.0009 (2)
 Scattering factors from
 International Tables for
 Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Mn1—C5	1.827 (6)	Mn2—C7	1.834 (7)
Mn1—C1	1.839 (6)	Mn2—C8	1.835 (6)
Mn1—C4	1.846 (6)	Mn2—C10	1.837 (6)
Mn1—C3	1.850 (6)	Mn2—C6	1.844 (6)
Mn1—C2	1.852 (6)	Mn2—C9	1.846 (6)
Mn1—Si1	2.509 (2)	Mn2—Si2	2.498 (2)
Si1—C21	1.882 (5)	Si2—C61	1.879 (5)
Si1—C11	1.890 (5)	Si2—C41	1.880 (5)
Si1—C31	1.898 (5)	Si2—C51	1.892 (5)
Mn1—Si1—C11—C16	59.2 (4)	Mn2—Si2—C41—C42	64.9 (4)
Mn1—Si1—C21—C22	68.9 (4)	Mn2—Si2—C51—C56	20.7 (5)
Mn1—Si1—C31—C32	45.5 (5)	Mn2—Si2—C61—C66	71.5 (5)

Table 2. Carbonyl stretching frequencies (cm⁻¹) for the pentacarbonyl(triphenylsilyl)manganese(I) and triphenyltin(pentacarbonyl)manganese(I) complexes

Assignment	Mn(CO) ₅ (SiPh ₃)		Mn(CO) ₅ (SnPh ₃)	
	IR	Raman	IR	Raman
a_1 (equatorial)	2095 (m)	2096 (m)	2092 (ms)	2093 (m)
b_1	2030 (mw)	2029 (s)	2029 (sh)	2024 (ms, sh)
e	2010 (br)	2010 (mw)	2013 (ms)	2014 (s)
			1998 (ms)	1991 (mw)
a_1 (axial)	1988 (s)	1992 (ms)	1983 (s)	1975 (mw)
	1970 (s)	1980 (s)	1976 (s)	

IR spectra were recorded for Nujol mulls on KBr plates, Raman spectra were measured on powders packed into a 2 mm diameter sampling cup.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1985). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: modified versions of *NRC2* and *NRC2A* (Ahmed, Hall, Pippy & Huber, 1966). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* in *NRCVAX94* (Johnson, 1976) and *PLATON96* (Spek, 1990). Software used to prepare material for publication: *SHELXL93* and *NRCVAX94*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1256). Services for accessing these data are described at the back of the journal.

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5-(*o*-Chlorophenyl)-1,3-dithia-2,4-diazolylum Hexafluoroarsenate

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Abstract

The structure of the title compound, (C₇H₄ClN₂S₂)[AsF₆], has four crystallographically independent cations, in each of which, attractive S···Cl interactions enhance the intrinsic electronic tendency of the two rings to coplanarity. The C—C—S torsion angles about the bond joining the rings are 1.4 (11), 9.0 (11), 9.5 (11) and 5.0 (12)°, and in each cation the S···Cl distance is close to 2.9 Å.

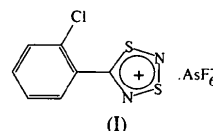
Comment

Dithiadiazole systems (five-membered rings containing CNSSN or CNSNS) are studied for a variety of reasons, including their potential uses as organic magnets (Banister & Rawson, 1992; Genin & Hoffmann, 1997) and non-linear optic materials (Banister, Luke, Rawson, Whitehead & Singer, 1997). A number of structures have been reported, with a variety of substituents on the ring C atom; for the CNSSN ring system there are 43 entries in the latest release of the Cambridge Structural Database (Allen & Kennard, 1993), while the CNSNS system is less well represented with 15 entries. One of the features of interest in the structures with an aromatic substituent is the degree to which the substituent and heterocyclic rings are coplanar, providing for delocalization over the two rings. Such coplanarity is to be expected when it is not prevented by steric or other constraints and, indeed, for the 30 structures with an aromatic or substituted aromatic ring attached to the CNSSN ring system, N—C—C—C torsion angles about the bond joining the two rings are, with very few exceptions, under 20°; two compounds with *ortho*-fluoro substituents on the phenyl or pyridyl ring (Banister *et al.*, 1995) both have torsion angles close to 32°.

Only two structures have been reported which have a phenyl substituent attached to the CNSNS 1,3,2,4-dithiadiazolium ring. With a simple phenyl group, the torsion angle for the hexafluoroarsenate salt of the cation is 23.4° (Ayes *et al.*, 1992). The dication in which a central benzene ring is *para*-substituted by one CNSNS and one CNSSN ring (also as its hexafluoroarsenate

salt) has a torsion angle of 25.1° for the CNSNS ring and 16.7° for the CNSSN ring (Banister *et al.*, 1993). These results suggest that coplanarity of the rings is intrinsically less likely in the CNSNS case, probably because of greater steric interaction between the *ortho*-H atom and a neighbouring ring S atom.

We were interested, therefore, in investigating the effect of an *ortho*-halo substituent on the phenyl ring of a CNSNS compound; steric interactions might dictate a higher degree of twist from coplanarity, or alternatively there could be attractive S···Hal interactions to pull the two rings towards coplanarity. We have prepared the *ortho*-chloro and *ortho*-bromo derivatives (both as hexafluoroarsenate salts) and determined their crystal structures. The bromo derivative was obtained as rather poor quality crystals and the structure is of low precision. The chloro derivative, (I), has four independent cations (Fig. 1) and four anions in the asymmetric unit. Twofold disorder of orientation was resolved and refined for two of the anions; the anions are of unremarkable geometry.



The internal geometry of the CNSNS ring is comparable to those previously reported. In all four independent cations, the *ortho*-chloro substituent is directed towards the neighbouring sulfur rather than nitrogen of the heterocycle. Cl···S distances are 2.910(3), 2.895(3),

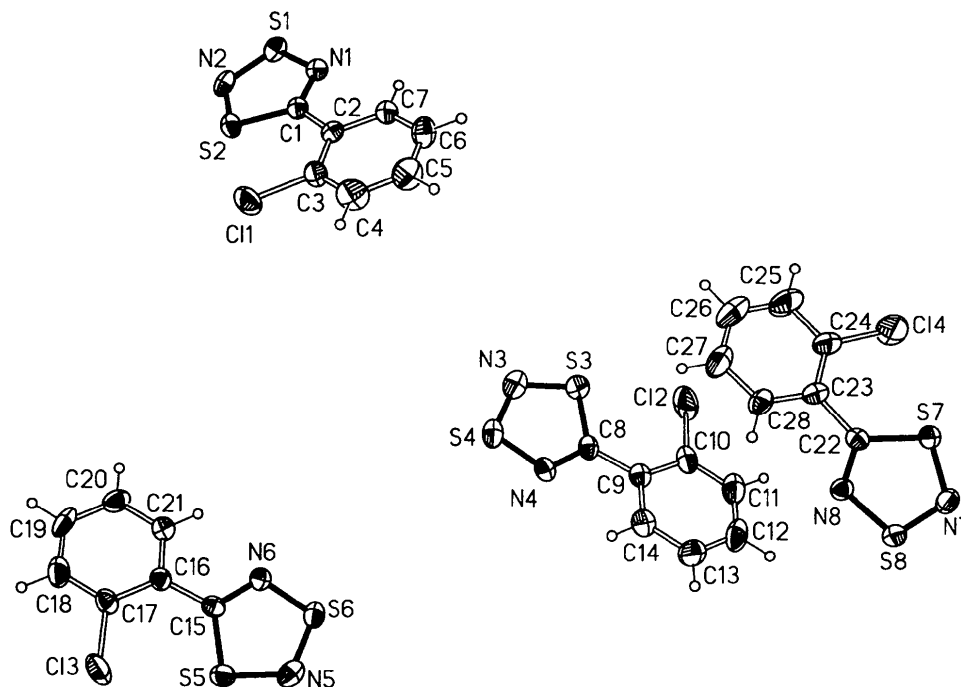


Fig. 1. The structure of the four cations with atom labels and 50% probability ellipsoids for non-H atoms.

2.908 (3) and 2.896 (3) Å, and the C—C—S torsion angles (ignoring the sign, since each cation appears as both enantiomers in this space group) are 1.4 (11), 9.0 (11), 9.5 (11) and 5.0 (12)°. We conclude that attractive S...Cl interactions enhance the electronic tendency of the rings to coplanarity. The corresponding torsion angles in the two independent cations of the structurally less well characterized *ortho*-bromo derivative are also under 10°, in support of this conclusion.

Experimental

SO₂ (10 ml) was condensed into a vessel containing [SNS][AsF₆] (0.180 g, 0.67 mmol) and *o*-chlorobenzonitrile (0.105 g, 0.69 mmol). The reagents dissolved to give a deep red solution. After 18 h stirring, the solvent was evaporated and excess *o*-chlorobenzonitrile removed by washing with hexane (3 × 10 ml) to give the crude product in 75% yield as a yellow moisture-sensitive solid. Crystals were obtained from solution in SO₂ by cycling the temperature between 293 and 253 K over 7 d. Satisfactory chemical analyses were obtained.

Crystal data

(C₇H₄ClN₂S₂)[AsF₆]

M_r = 404.61

Monoclinic

*P*₂/n

a = 25.760 (4) Å

b = 8.1590 (18) Å

c = 27.156 (4) Å

β = 116.257 (12)°

V = 5118.6 (16) Å³

Z = 16

D_x = 2.100 Mg m⁻³

D_m not measured

Data collection

Stoe–Siemens diffractometer with Cryostream cooler (Cosier & Glazer, 1986)

ω/θ scans with on-line profile fitting (Clegg, 1981)

Absorption correction:

empirical from ψ scans (Sheldrick, 1994)

T_{min} = 0.404, *T_{max}* = 0.570

7376 measured reflections

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 28 reflections

θ = 11.03–12.47°

μ = 3.249 mm⁻¹

T = 160 (2) K

Block

0.44 × 0.26 × 0.20 mm

Pale yellow

6660 independent reflections

5057 reflections with

I > 2σ(*I*)

R_{int} = 0.058

θ_{max} = 22.51°

h = -27 → 27

k = -5 → 8

l = -26 → 29

4 standard reflections

frequency: 60 min

intensity decay: none

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.041

wR(*F*²) = 0.115

S = 1.075

6660 reflections

735 parameters

H atoms: see below

w = 1/[σ²(*F_o*²) + (0.0346*P*)²

+ 35.511*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.071

Δρ_{max} = 0.549 e Å⁻³

Δρ_{min} = -0.647 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

S1—N2	1.576 (6)	S5—N5	1.620 (6)
S1—N1	1.602 (6)	S5—C15	1.744 (7)
S2—N2	1.621 (6)	S6—N5	1.580 (7)
S2—C1	1.753 (6)	S6—N6	1.598 (6)
N1—C1	1.333 (8)	N6—C15	1.326 (8)
C1—C2	1.459 (9)	C15—C16	1.463 (9)
S3—N3	1.615 (6)	S7—N7	1.609 (6)
S3—C8	1.751 (7)	S7—C22	1.747 (7)
S4—N3	1.580 (7)	S8—N7	1.577 (6)
S4—N4	1.591 (6)	S8—N8	1.596 (5)
N4—C8	1.315 (8)	N8—C22	1.332 (8)
C8—C9	1.465 (9)	C22—C23	1.471 (10)
N2—S1—N1	103.6 (3)	N5—S5—C15	96.8 (3)
N2—S2—C1	96.9 (3)	N5—S6—N6	104.0 (3)
C1—N1—S1	113.7 (4)	S6—N5—S5	112.3 (4)
S1—N2—S2	112.8 (3)	C15—N6—S6	113.0 (5)
N1—C1—C2	119.9 (6)	N6—C15—C16	119.0 (6)
N1—C1—S2	112.9 (5)	N6—C15—S5	113.9 (5)
C2—C1—S2	127.2 (5)	C16—C15—S5	127.1 (5)
N3—S3—C8	96.2 (3)	N7—S7—C22	97.1 (3)
N3—S4—N4	103.3 (3)	N7—S8—N8	103.9 (3)
S4—N3—S3	113.0 (4)	S8—N7—S7	112.6 (3)
C8—N4—S4	113.7 (5)	C22—N8—S8	113.1 (5)
N4—C8—C9	119.7 (6)	N8—C22—C23	119.7 (6)
N4—C8—S3	113.7 (5)	N8—C22—S7	113.2 (5)
C9—C8—S3	126.5 (5)	C23—C22—S7	127.1 (5)

Reflection intensities decreased rapidly at higher angle and were considered too weak for effective measurement above 22.5° in θ; this is presumably a consequence of the anion disorder. Twofold disorder of orientation was resolved for two of the four anions; for these, the major component was refined with anisotropic displacement parameters and the minor component was refined with isotropic displacement parameters. Refined occupancy factors were 0.840:0.160 (7) and 0.918:0.082 (7). A high degree of anisotropy in some of the F atoms indicates that this disorder model, while satisfactory, is only approximate. H atoms were placed geometrically and refined with a riding model, and with *U*_{iso} constrained to be 1.2*U*_{eq} of the carrier atom.

Data collection: *DIF4* (Stoe & Cie, 1988). Cell refinement: *DIF4*. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and local programs.

We thank EPSRC and the Royal Society for financial support.

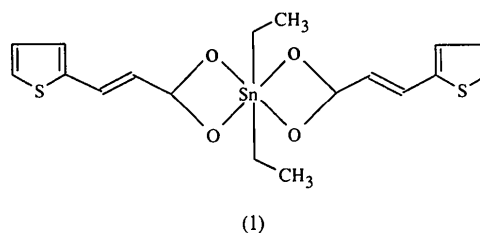
Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1156). Services for accessing these data are described at the back of the journal.

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In this paper, we wish to report the crystal structure of the title compound, (1).



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Diethylbis[3-(2-thienyl)-2-propenoato-*O, O'*]-tin(IV)

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Abstract

The crystal structure of $[\text{Sn}(\text{C}_2\text{H}_5)_2(\text{C}_7\text{H}_5\text{O}_2\text{S})_2]$ contains discrete molecules in which hexa-coordinated Sn atoms lie on twofold axes. The Sn atom is coordinated asymmetrically to two symmetry-related propenoates, with Sn—O distances of 2.105 (5) and 2.538 (6) Å, and to two ethyl groups, with Sn—C distances of 2.155 (2) Å.

Comment

Diorganotin carboxylates of general formula $R_2\text{SnL}_2$ (where R = alkyl or aryl, and L = carboxylate anion) usually exist in an octahedral state in the solid phase (Tiekink, 1991; Gielen, Buoualam, Mahieu & Tiekink, 1992; Piret, Buoualam, Willem & Gielen, 1993). However, their geometry in solution cannot be defined with certainty because of the dynamic processes involved with carboxylate O atoms, due to competition in their coordination behaviour with the Sn atom (Danish, Alt *et al.*, 1995; Danish, Ali *et al.*, 1995). We wanted to investigate the contribution of a heteroatom, as part of a five-membered ring, on the geometry of the central Sn atom. In this regard, we have prepared several compounds and have studied their geometry in the solid as well as in the solution phase. It has been observed that a heteroatom which is an integral part of a five-membered ring has no substantial effect on the geometry of the central metal atom either in the solid or the solution phase.

The structure of (1) (Fig. 1) is composed of discrete monomeric molecules in which Sn atoms lie on a crystallographic twofold axis such that only half of the molecule represents the asymmetric unit.

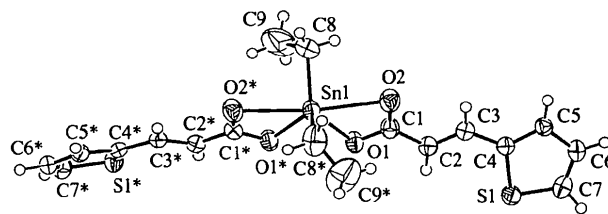


Fig. 1. ORTEP (Johnson, 1976) drawing of (1) with the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level and H atoms have been assigned arbitrary radii; the minor fraction of disordered C9 has been ignored. Symmetry operation for starred atoms: $2 - x, y, \frac{3}{2} - z$.

The hexa-coordinated Sn atom is surrounded by four O atoms of the propenoate ligands forming an almost planar base, and the ethyl groups occupy the two remaining positions resulting in a highly distorted octahedral geometry which may best be described as based on a skew-trapezoidal planar geometry. The terminal C atom of the methyl group is disordered over two sites, C9 and C9', with site occupancies 0.78 (2) and 0.22 (2), respectively. The symmetry-related propenoates are asymmetrically coordinated to the Sn atom, with Sn—O bond distances of 2.105 (5) and 2.538 (6) Å; the Sn—C bond distances are 2.155 (2) Å. The angle between the Et_2Sn and SnCO_2 planes is $73.0(2)^\circ$, while the SnCO_2 and thienyl (S1, C4–C7) rings are inclined at $24.2(3)^\circ$ with respect to each other; both the rings are individually planar, the maximum deviations being 0.024 (5) and 0.019 (4) Å, respectively. The molecules are separated by normal van der Waals contacts in the crystal with no Sn...S interactions. The structures exhibiting similar geometry as found in (1) include $\text{Me}_2\text{Sn}(\text{OAc})_2$ (Lockhart, Calabrese & Davidson, 1987), $\text{Bu}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{SC}_6\text{H}_5)_2$ (Sandhu, Sharma & Tiekink, 1989), $^n\text{Bu}_2\text{Sn}[\text{O}_2\text{C}(\text{CH}_2\text{Ph})\text{C}(\text{H})\text{N}(\text{H})\text{C}(\text{O})\text{CH}_2\text{Cl}]_2$ (Sandhu, Hundal & Tiekink, 1991), $\text{Me}_2\text{Sn}(\text{O}_2\text{CPh})_2$ (Tiekink, 1991), $\text{Et}_2\text{Sn}(\text{O}_2\text{CC}_4\text{H}_3\text{S})_2$ (Vatsa, Jain, Das & Tiekink, 1991) and $\text{Et}_2\text{Sn}(\text{O}_2\text{CC}_5\text{H}_3\text{NSMe})_2$ (Gie-