

The authors would like to thank the National Natural Science Foundation of China for a grant (No. 29401003). S-HG is grateful to the State Department of Education for a special grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1054). Services for accessing these data are described at the back of the journal.

References

- Alcock, N. W., Cook, D. F., McKenzie, E. D. & Worthington, J. M. (1980). *Inorg. Chim. Acta*, **38**, 107–112.
- Deroche, A., Morgenstern-Badarau, I., Keita, B., Cesario, M., Guilhem, J., Keita, B., Nadjo, L. & Houée-Levin, C. (1996). *J. Am. Chem. Soc.* **118**, 4567–4573.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Gou, S.-H., You, X.-Z., Yu, K.-B. & Lu, J.-P. (1993). *Inorg. Chem.* **32**, 1883–1887.
- Kirchner, R. M., Mealli, C., Bailey, M., Howe, N., Torre, L. P., Wilson, L. J., Andrews, L. C., Rose, N. J. & Lingafelter, E. C. (1987). *Coord. Chem. Rev.* **77**, 89–163.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Riley, D. P., Rivers, W. J. & Weiss, R. H. (1991). *Anal. Biochem.* **196**, 344–349.
- Sanyal, I., Ghosh, P. & Karlin, K. D. (1995). *Inorg. Chem.* **34**, 3050–3056.
- Sheldrick, G. M. (1995). *SHELXTL*. Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1994). *XSCANS User's Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sim, P. G. & Sinn, E. (1978). *Inorg. Chem.* **17**, 1288–1294.

Acta Cryst. (1999). **C55**, 744–748

catena-Poly[triphenyltin- μ -(*N,N*-diethylthiocarbamoylthioacetato-*O:O'*)], catena-poly[triphenyltin- μ -(*N*-methyl-*N*-phenylthiocarbamoylthioacetato-*O:O'*)] and triphenyl(*N,N*-tetramethylenethiocarbamoylthioacetato-*O*)tin

KONG MUN LO,^a V. G. KUMAR DAS,^a SEIK WENG NG^b AND JAMES M. HOOK^c

^aDepartment of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia, ^bInstitute of Postgraduate Studies and Research, University of Malaya, 50603 Kuala Lumpur, Malaysia, and ^cNMR Facility, School of Chemistry, University of New South Wales, Sydney 2052, Australia.
E-mail: h1nswen@umcsd.um.edu.my

(Received 29 July 1998; accepted 11 January 1999)

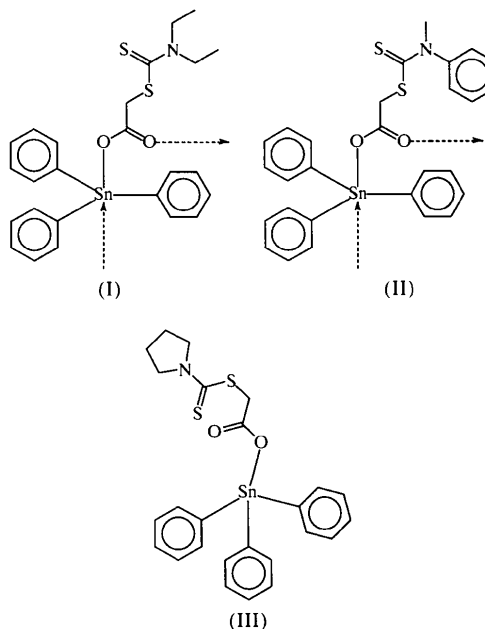
Abstract

Carboxylate bridges link the two independent molecules of triphenyltin *N,N*-diethylthiocarbamoylthioacetate, (I), and the four independent molecules

of triphenyltin *N*-methyl-*N*-phenylthiocarbamoylthioacetate, (II), into linear chains whose Sn atoms show *trans*-trigonal-bipyramidal coordination, *i.e.* (I) is *catena*-poly[triphenyltin- μ -(*N,N*-diethylthiocarbamoylthioacetato-*O:O'*)], [Sn(C₆H₅)₃(μ -C₇H₁₂NO₂S₂)]_n, and (II) is *catena*-poly[triphenyltin- μ -(*N*-methyl-*N*-phenylthiocarbamoylthioacetato-*O:O'*)], [Sn(C₆H₅)₃(μ -C₁₀H₁₀NO₂S₂)]_n. Triphenyltin *N,N*-tetramethylenethiocarbamoylthioacetate {or triphenyl(*N,N*-tetramethylenethiocarbamoylthioacetato-*O*)tin, [Sn(C₆H₅)₃(C₇H₁₀-NO₂S₂)]} exists as a monomeric tetrahedral molecule.

Comment

Triphenyltin alkanoates adopt linear carboxylate-bridged polymeric structures that usually propagate by twofold screw-axial translations; these polymers display a repeat distance of 5.2 Å, this distance being generally insensitive to the nature of the substituent on the carboxylate anion (Ng *et al.*, 1988). Triphenyltin *N,N*-dimethylthiocarbamoylthioacetate, which crystallizes with two symmetry-independent molecules in the unit cell, propagates by a twofold screw axis, but its repeat distance of 4.3 Å represents an anomaly (Ng & Kumar Das, 1995). The shorter repeat distance implies a more helical conformation of the polymeric chain. The repeat distance contrasts with a length of 4.9 Å for trimethyltin *N,N*-dimethylthiocarbamoylthioacetate, whose two symmetry-independent molecules propagate by mere translations, so that the architecture approaches a zigzag arrangement (Ng & Kumar Das, 1996). The rigidities of the polymeric backbone in the two carboxylates can be distinguished by the slope of the variable-temperature Sn^{119m} Mössbauer plot (Ng & Kumar Das, 1991).



The title *N,N*-diethylthiocarbamoylthioacetate polymer, (I), displays a three-line Mössbauer spectrum that has been interpreted in terms of two Sn sites, one in a five-coordinate environment and the other in a four-coordinate environment (Ng & Kumar Das, 1991). This assignment is, however, not supported by crystal structure analysis. The compound crystallizes with cell constants that match those of the *N,N*-dimethylthiocarbamoylthioacetate polymer; the two structures also show matching atomic coordinates, so that the origin

of the three-line Mössbauer spectrum remains obscure. On the other hand, tricyclohexyltin *N,N*-diethylthiocarbamoylthioacetate exists as a tetrahedral compound (Ng & Kumar Das, 1997), in agreement with the spectroscopic assignment.

The title *N*-methyl-*N*-phenylthiocarbamoylthioacetate polymer, (II), crystallizes with four independent molecules; the bond dimensions involving the Sn atom are similar in the four molecules. The chain propagates on the *b*-*c* face of the unit cell, and its repeat distance

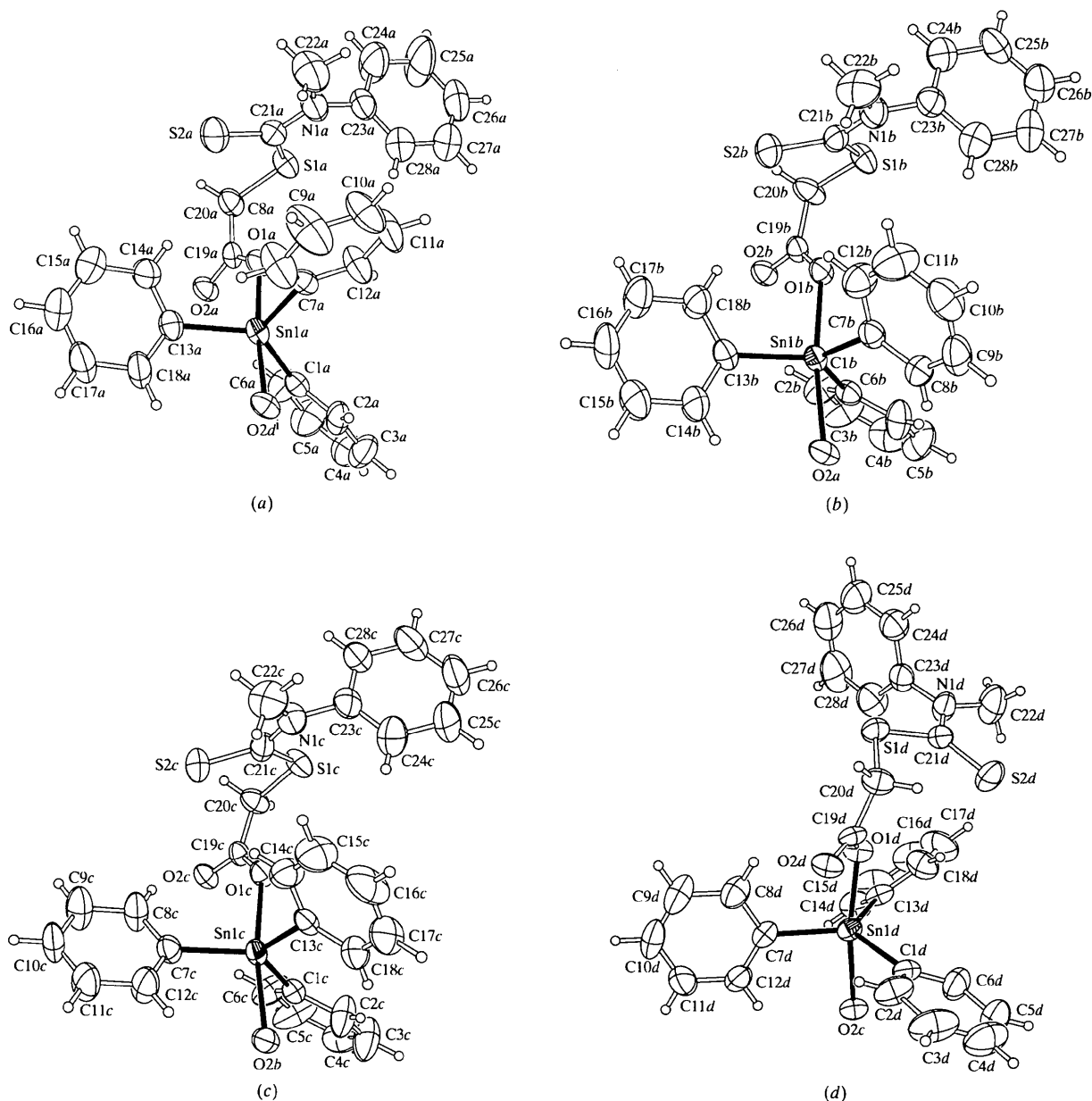


Fig. 1. ORTEP (Johnson, 1976) plot of (a) molecule a, (b) molecule b, (c) molecule c and (d) molecule d of triphenyltin *N*-methyl-*N*-phenylthiocarbamoylthioacetate, (II), with ellipsoids at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

is 22.04 = 5.5 Å. The molecules are packed in such a manner that voids exist (Spek, 1990), so that the packing can be regarded as being more compact compared with that of the *N,N*-diethylthiocarbamoylthioacetate.

Triphenyltin *N,N*-tetramethylenethiocarbamoylthioacetate, (III), exists as a monomeric tetrahedral molecule.

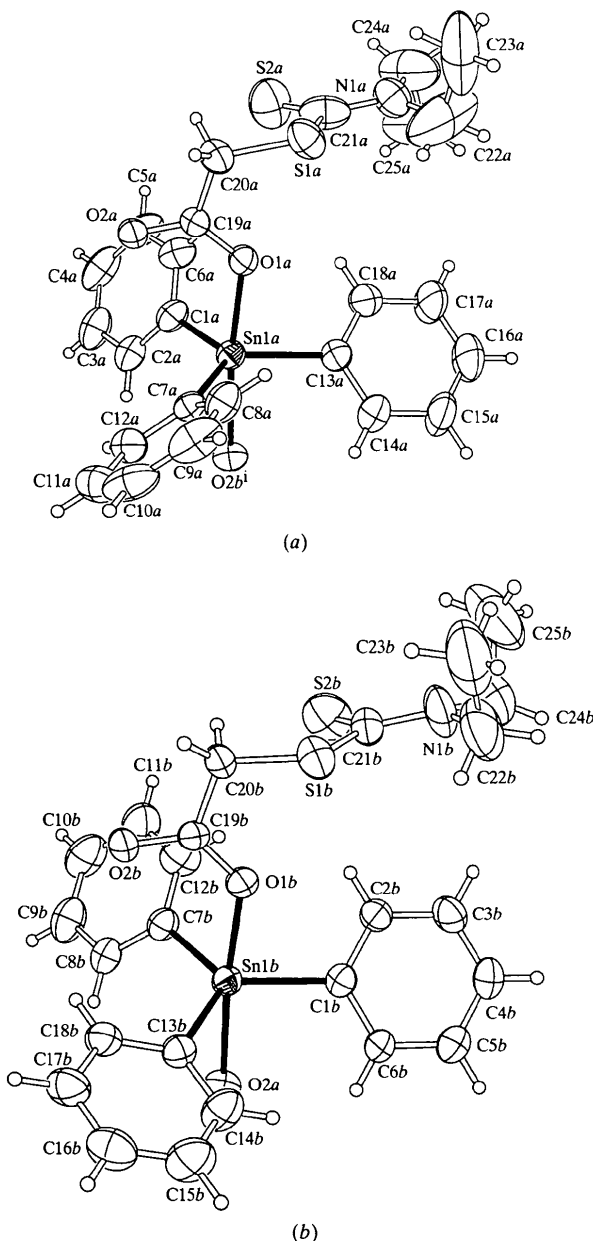


Fig. 2. ORTEP (Johnson, 1976) plot of (a) molecule *a* and (b) molecule *b* of triphenyltin *N,N*-diethylthiocarbamoylthioacetate, (I), with ellipsoids at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

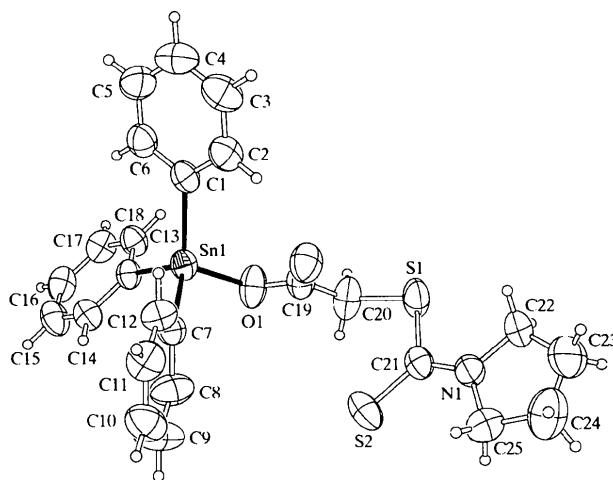


Fig. 3. ORTEP (Johnson, 1976) plot of triphenyltin *N,N*-tetramethylenethiocarbamoylthioacetate, (III), with ellipsoids at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

Experimental

The thiocarbamoylthioacetic acids were synthesized from chloroacetic acid, carbon disulfide and the secondary amine (Nachmias, 1952), and were recrystallized from ethanol. Equimolar quantities of diethylthiocarbamoylthioacetic acid and triphenyltin hydroxide were heated in a small volume of ethanol; the crystalline organotin carboxylate (I) separated on cooling the filtered solution. The analogous reaction with *N*-methyl-*N*-phenylthiocarbamoylthioacetic acid and triphenyltin hydroxide, and with *N,N*-tetramethylenethiocarbamoylthioacetic acid yielded (II) and (III), respectively. The solid-state ¹¹⁹Sn NMR spectrum of (II) shows a cluster of three sites at -257/-266/-278 p.p.m. (relative to tetramethyltin). The spectrum of (III) also shows a cluster of sites at -218 to -297 p.p.m.

Compound (I)

Crystal data

[Sn(C₆H₅)₃(C₇H₁₂NO₂S₂)]

M_r = 556.29

Monoclinic

*P*2₁/*c*

a = 12.900 (2) Å

b = 18.135 (2) Å

c = 21.822 (4) Å

β = 97.42 (1)°

V = 5062 (1) Å³

Z = 8

D_x = 1.460 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25

reflections

θ = 12.0–13.0°

μ = 1.195 mm⁻¹

T = 298 (2) K

Block

0.55 × 0.50 × 0.45 mm

Colorless

Data collection

Enraf–Nonius CAD-4

diffractometer

ω scans

Absorption correction:

ψ scan (North *et al.*, 1968)

T_{min} = 0.493, *T_{max}* = 0.584

5739 reflections with

I > 2σ(*I*)

R_{int} = 0.029

θ_{max} = 25°

h = -15 → 15

k = 0 → 21

l = 0 → 25

9167 measured reflections
8911 independent reflections

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.058$
 $wR(F^2) = 0.166$
 $S = 1.009$
8911 reflections
487 parameters
H-atom parameters
constrained, with $U(H) = 1.5U_{eq}(C)$

3 standard reflections
frequency: 60 min
intensity decay: 4%

$w = 1/[\sigma^2(F_o^2) + (0.0818P)^2 + 7.1495P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.198 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.598 \text{ e } \text{\AA}^{-3}$
Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.124$
 $S = 1.002$
18 499 reflections
931 parameters
H-atom parameters
constrained, with $U(H) = 1.5U_{eq}(C)$

$w = 1/[\sigma^2(F_o^2) + (0.0538P)^2 + 1.1698P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.759 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.775 \text{ e } \text{\AA}^{-3}$
Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters ($\text{\AA}$, $^\circ$) for (I)

Sn1a—C1a	2.125 (4)	Sn1b—C1b	2.134 (3)
Sn1a—C7a	2.113 (4)	Sn1b—C7b	2.115 (4)
Sn1a—C13a	2.144 (4)	Sn1b—C13b	2.115 (4)
Sn1a—O1a	2.186 (5)	Sn1b—O1b	2.206 (5)
Sn1a—O2b'	2.326 (5)	Sn1b—O2a	2.343 (5)
C1a—Sn1a—C7a	122.8 (2)	C1b—Sn1b—C7b	119.0 (2)
C1a—Sn1a—C13a	118.3 (2)	C1b—Sn1b—C13b	119.9 (2)
C1a—Sn1a—O1a	95.4 (2)	C1b—Sn1b—O1b	86.4 (2)
C1a—Sn1a—O2b'	91.8 (2)	C1b—Sn1b—O2a	88.8 (2)
C7a—Sn1a—C13a	118.5 (2)	C7b—Sn1b—C13b	120.8 (2)
C7a—Sn1a—O1a	93.2 (2)	C7b—Sn1b—O1b	92.9 (2)
C7a—Sn1a—O2b'	84.8 (2)	C7b—Sn1b—O2a	92.1 (2)
C13a—Sn1a—O1a	86.9 (2)	C13b—Sn1b—O1b	95.9 (2)
C13a—Sn1a—O2b'	87.7 (2)	C13b—Sn1b—O2a	83.9 (2)
O1a—Sn1a—O2b'	172.4 (2)	O1b—Sn1b—O2a	174.4 (2)
C19a—O1a—Sn1a	126.2 (5)	C19b—O1b—Sn1b	129.3 (5)
C19a—O2a—Sn1b	140.6 (5)	C19b—O2b—Sn1a ⁱⁱ	131.3 (5)

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

Compound (II)

Crystal data

$[\text{Sn}(\text{C}_6\text{H}_5)_3(\text{C}_{10}\text{H}_{10}\text{NO}_2\text{S}_2)]$
 $M_r = 590.30$
Triclinic
 $P\bar{1}$
 $a = 17.019 (2) \text{ \AA}$
 $b = 18.466 (2) \text{ \AA}$
 $c = 18.921 (2) \text{ \AA}$
 $\alpha = 71.952 (7)^\circ$
 $\beta = 72.482 (8)^\circ$
 $\gamma = 73.333 (9)^\circ$
 $V = 5267.1 (9) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.489 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Enraf–Nonius CAD-4
diffractometer
 ω scans
Absorption correction:
 ψ scan (North *et al.*,
1968)
 $T_{\min} = 0.512$, $T_{\max} = 0.881$
19 187 measured reflections
18 499 independent
reflections

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
Cell parameters from 25
reflections
 $\theta = 12.25\text{--}12.75^\circ$
 $\mu = 1.154 \text{ mm}^{-1}$
 $T = 298 (2) \text{ K}$
Plate
 $0.44 \times 0.44 \times 0.11 \text{ mm}$
Colorless

Table 2. Selected geometric parameters ($\text{\AA}$, $^\circ$) for (II)

Sn1a—C1a	2.145 (3)	Sn1c—C1c	2.131 (3)
Sn1a—C7a	2.125 (3)	Sn1c—C7c	2.159 (3)
Sn1a—C13a	2.161 (3)	Sn1c—C13c	2.145 (3)
Sn1a—O1a	2.187 (4)	Sn1c—O1c	2.190 (2)
Sn1a—O2d'	2.359 (2)	Sn1c—O2b	2.354 (2)
Sn1b—C1b	2.136 (3)	Sn1d—C1d	2.130 (3)
Sn1b—C7b	2.143 (3)	Sn1d—C7d	2.151 (3)
Sn1b—C13b	2.169 (3)	Sn1d—C13d	2.123 (3)
Sn1b—O1b	2.197 (2)	Sn1d—O1d	2.188 (2)
Sn1b—O2a	2.317 (4)	Sn1d—O2c	2.396 (2)
C1a—Sn1a—C7a	120.0 (2)	C1c—Sn1c—C7c	128.1 (2)
C1a—Sn1a—C13a	129.3 (1)	C1c—Sn1c—C13c	119.9 (1)
C1a—Sn1a—O1a	95.2 (2)	C1c—Sn1c—O1c	91.7 (1)
C1a—Sn1a—O2d'	86.6 (2)	C1c—Sn1c—O2b	86.4 (1)
C7a—Sn1a—C13a	109.8 (1)	C7c—Sn1c—C13c	111.0 (1)
C7a—Sn1a—O1a	87.0 (2)	C7c—Sn1c—O1c	97.8 (1)
C7a—Sn1a—O2d'	85.7 (2)	C7c—Sn1c—O2b	90.4 (1)
C13a—Sn1a—O1a	96.0 (1)	C13c—Sn1c—O1c	90.5 (1)
C13a—Sn1a—O2d'	88.7 (2)	C13c—Sn1c—O2b	82.7 (1)
O1a—Sn1a—O2d'	172.3 (2)	C19c—O1c—Sn1c	135.0 (2)
C19a—O1a—Sn1a	129.0 (3)	C19b—O2b—Sn1c	137.2 (1)
C19d—O2d—Sn1a ⁱⁱ	141.3 (1)	C1d—Sn1d—C13d	116.2 (1)
C1b—Sn1b—C7b	119.8 (2)	C1d—Sn1d—C7d	125.7 (2)
C1b—Sn1b—C13b	126.5 (1)	C1d—Sn1d—O1d	94.8 (1)
C1b—Sn1b—O1b	94.2 (1)	C1d—Sn1d—O2c	84.3 (1)
C1b—Sn1b—O2a	84.8 (2)	C7d—Sn1d—C13d	117.2 (1)
C7b—Sn1b—C13b	112.8 (1)	C7d—Sn1d—O1d	97.4 (1)
C7b—Sn1b—O1b	87.8 (1)	C7d—Sn1d—O2c	91.3 (1)
C7b—Sn1b—O2a	84.9 (2)	C13d—Sn1d—O1d	86.9 (1)
C13b—Sn1b—O1b	96.7 (1)	C13d—Sn1d—O2c	84.6 (1)
C13b—Sn1b—O2a	91.1 (1)	O1d—Sn1d—O2c	169.9 (1)
O1b—Sn1b—O2a	171.0 (1)	C19d—O1d—Sn1d	128.0 (1)
C19b—O1b—Sn1b	130.5 (1)	C19c—O2c—Sn1d	140.6 (2)
C19a—O2a—Sn1b	140.3 (3)		

Symmetry codes: (i) $x, y - 1, 1 + z$; (ii) $x, 1 + y, z - 1$.

Compound (III)

Crystal data

$[\text{Sn}(\text{C}_6\text{H}_5)_3(\text{C}_7\text{H}_{10}\text{NO}_2\text{S}_2)]$
 $M_r = 554.27$
Triclinic
 $P\bar{1}$
 $a = 9.7442 (3) \text{ \AA}$
 $b = 9.8923 (5) \text{ \AA}$
 $c = 13.3187 (4) \text{ \AA}$
 $\alpha = 107.064 (4)^\circ$
 $\beta = 95.246 (3)^\circ$
 $\gamma = 97.153 (4)^\circ$
 $V = 1206.62 (8) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.526 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
Cell parameters from 25
reflections
 $\theta = 14.0\text{--}16.0^\circ$
 $\mu = 1.253 \text{ mm}^{-1}$
 $T = 298 (2) \text{ K}$
Block
 $0.43 \times 0.22 \times 0.22 \text{ mm}$
Colorless

Data collection

Enraf–Nonius CAD-4
diffractometer
 ω – 2θ scans
Absorption correction:
 ψ scan (North *et al.*,
1968)
 $T_{\min} = 0.677$, $T_{\max} = 0.738$
4532 measured reflections
4259 independent reflections

3971 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.009$
 $\theta_{\max} = 25.06^\circ$
 $h = 0 \rightarrow 11$
 $k = -11 \rightarrow 11$
 $l = -15 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.057$
 $S = 1.003$
4259 reflections
280 parameters
H-atom parameters
constrained, with $U(\text{H}) =$
 $1.5U_{\text{eq}}(\text{C})$

$w = 1/[\sigma^2(F_o^2) + (0.0340P)^2$
 $+ 0.4226P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.320 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.281 \text{ e } \text{\AA}^{-3}$
Extinction correction: none
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 3. *Selected geometric parameters* ($\text{\AA}$, $^\circ$) *for (III)*

Sn1—O1	2.055 (2)	Sn1—C7	2.118 (2)
Sn1—C1	2.117 (2)	Sn1—C13	2.125 (2)
C1—Sn1—C7	115.2 (1)	C7—Sn1—C13	113.2 (1)
C1—Sn1—C13	111.0 (1)	C7—Sn1—O1	107.4 (1)
C1—Sn1—O1	113.7 (1)	C13—Sn1—O1	94.6 (1)

Phenyl rings were refined as rigid hexagons in (I) and (II). In (I), the group was restrained with $\text{C}=\text{C} = 1.54 \pm 0.01$, $\text{N}=\text{C} = 1.45 \pm 0.01$, $\text{N} \cdots \text{C} = 2.44 \pm 0.02$ and $\text{C} \cdots \text{C} = 2.51 \pm 0.02 \text{ \AA}$; a *FLAT* instruction was imposed on the S_2CNC_2 unit. The final difference map had a peak of $1 \text{ e } \text{\AA}^{-3}$ around the dithiocarbamoyl group of molecule a.

For all compounds, data collection: *CAD-4/PC* (Kretschmar, 1994); cell refinement: *CELDIM* in *CAD-4 VAX/PC* (Enraf–Nonius, 1988); data reduction: *XCAD4* (Harms, 1997); pro-

gram(s) used to solve structures: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997b); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

The authors thank the National Science Council for R&D (IRPA 09-02-03-0004 and IRPA 09-02-03-0371) for supporting this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1233). Services for accessing these data are described at the back of the journal.

References

- Enraf–Nonius (1988). *CAD-4 VAX/PC Fortran System. Operator's Guide to the Enraf–Nonius CAD-4 Diffractometer Hardware, its Software and the Operating System*. Enraf–Nonius, Scientific Instruments Division, PO Box 483, 2600 AL Delft, The Netherlands.
- Harms, K. (1997). *XCAD4. Program for the Lp Correction of Nonius Four-Circle Diffractometer Data*. University of Marburg, Germany.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Kretschmar, M. (1994). *CAD-4/PC*. Version 1.5c. University of Tübingen, Germany.
- Nachmias, G. (1952). *Ann. Chim. (Paris)*, **12**, 584–631.
- Ng, S. W., Chen, W. & Kumar Das, V. G. (1988). *J. Organomet. Chem.* **345**, 59–64.
- Ng, S. W. & Kumar Das, V. G. (1991). *J. Organomet. Chem.* **409**, 143–156.
- Ng, S. W. & Kumar Das, V. G. (1995). *Acta Cryst.* **C51**, 2492–2494.
- Ng, S. W. & Kumar Das, V. G. (1996). *Acta Cryst.* **C52**, 1371–1373.
- Ng, S. W. & Kumar Das, V. G. (1997). *Acta Cryst.* **C53**, 548–549.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1997a). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997b). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.