

Redetermination of tetrakis(*N,N*-diethyl-dithiocarbamato)tin(IV)

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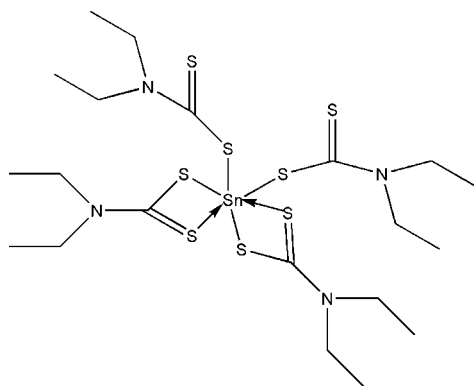
Received 30 April 2009; accepted 15 May 2009

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.037; wR factor = 0.145; data-to-parameter ratio = 54.5.

The crystal structure of the title compound, $[\text{Sn}(\text{C}_5\text{H}_{10}\text{NS}_2)_4]$, was originally determined by Harreld & Schlemper [*Acta Cryst.* (1971), **B27**, 1964–1969] using intensity data estimated from Weissenberg films. In comparison with the previous refinement, the current redetermination reveals anisotropic displacement parameters for all non-H atoms, localization of the H atoms, and higher precision of lattice parameters and interatomic distances. The complex features a distorted S_6 octahedral coordination geometry for tin and a *cis* disposition of the monodentate dithiocarbamate ligands.

Related literature

For the original structure determination, see: Harreld & Schlemper (1971). For related structures, see: Tiekink (2008).



Experimental

Crystal data

$[\text{Sn}(\text{C}_5\text{H}_{10}\text{NS}_2)_4]$
 $M_r = 711.73$
Monoclinic, $C2/c$
 $a = 16.3250$ (2) Å
 $b = 15.7544$ (2) Å
 $c = 13.9478$ (2) Å
 $\beta = 118.995$ (2)°

$V = 3137.64$ (8) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 1.36$ mm⁻¹
 $T = 293$ K
 $0.30 \times 0.25 \times 0.20$ mm

Data collection

Oxford Diffraction GEMINI diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008)

$T_{\min} = 0.794$, $T_{\max} = 1.000$
(expected range = 0.605–0.761)
64449 measured reflections
8173 independent reflections
6349 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.145$
 $S = 1.07$
8173 reflections

150 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 1.24$ e Å⁻³
 $\Delta\rho_{\min} = -0.61$ e Å⁻³

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BX2209).

References

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Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
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supplementary materials

Acta Cryst. (2009). E65, m675 [doi:10.1107/S1600536809018522]

Redetermination of tetrakis(*N,N*-diethyldithiocarbamate)tin(IV)

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Comment

Organotin dithiocarbamate compounds continue to attract interest owing to their use as precursors for Chemical Vapor Deposition (CVD) of SnS, as pharmaceuticals, and their structural diversity (Tiekink, 2008). The title compound (I) has been synthesized and its crystal structure reported here. In the previously reported structure (Harreld & Schlemper, 1971), no hydrogen atoms were included and the crystal was found to be monoclinic with $Z = 4$, $a = 15.64$ (2) Å, $b = 15.75$ (2) Å, $c = 13.91$ (2) Å, $\beta = 112.50$ (2)°. These data are slightly different from the new ones due probably to the significantly improved precision with respect to the geometric parameters provided by this redetermination. The molecular structure and the atom-numbering scheme of the title compound are shown in Fig. 1. The tin atom is octahedrally coordinated by two chelating ligands and two monodentate dithiocarbamate ligands with the latter occupying mutually *cis*-positions. Distortions from the ideal octahedral are clearly related to the restricted bite angle of the chelating ligands and further, the asymmetry in the Sn–S bond distances formed by the chelating ligand is related to the *trans* influence exerted by the monodentate ligands, *i.e.* the longer Sn–S bond distance formed by the chelating ligand is *trans*- to the sulfur atom of the monodentate ligand.

Experimental

Compound (I) was obtained by reacting tin (IV) tetrachloride (883 mg, 3.39 mmol) with sodium *N,N*-diethyldithiocarbamate (1160 mg, 6.78 mmol) in ethanol. Orange crystals suitable for X-ray analysis were grown by recrystallization from dichloromethane/hexane.

Refinement

H atoms were positioned geometrically, with C–H distances in the range 0.96 - 0.97 Å, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$.

Figures

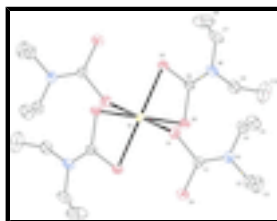


Fig. 1. The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted. Unlabeled atoms are related to labeled by the symmetry code $(-x+2, y, 1/2-z)$.

tetrakis(*N,N*-diethyldithiocarbamate)tin(IV)

Crystal data

| | |
|---|---|
| [Sn(C ₅ H ₁₀ N ₁ S ₂) ₄] | $F_{000} = 1464$ |
| $M_r = 711.73$ | $D_x = 1.507 \text{ Mg m}^{-3}$ |
| Monoclinic, <i>C2/c</i> | Mo <i>K</i> α radiation |
| Hall symbol: -C 2yc | $\lambda = 0.7107 \text{ \AA}$ |
| $a = 16.3250 (2) \text{ \AA}$ | Cell parameters from 33587 reflections |
| $b = 15.7544 (2) \text{ \AA}$ | $\theta = 3.0\text{--}37.7^\circ$ |
| $c = 13.9478 (2) \text{ \AA}$ | $\mu = 1.36 \text{ mm}^{-1}$ |
| $\beta = 118.995 (2)^\circ$ | $T = 293 \text{ K}$ |
| $V = 3137.64 (8) \text{ \AA}^3$ | Prism, orange |
| $Z = 4$ | $0.3 \times 0.25 \times 0.2 \text{ mm}$ |

Data collection

| | |
|--|--|
| Oxford Diffraction GEMINI diffractometer | 8173 independent reflections |
| Radiation source: Enhance (Mo) X-ray Source | 6349 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{\text{int}} = 0.024$ |
| Detector resolution: 10.4186 pixels mm^{-1} | $\theta_{\text{max}} = 37.9^\circ$ |
| $T = 293 \text{ K}$ | $\theta_{\text{min}} = 3.0^\circ$ |
| π scans | $h = -27 \rightarrow 27$ |
| Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2008) | $k = -27 \rightarrow 27$ |
| $T_{\text{min}} = 0.794$, $T_{\text{max}} = 1.000$ | $l = -23 \rightarrow 23$ |
| 64449 measured reflections | |

Refinement

| | |
|--|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.037$ | H-atom parameters constrained |
| $wR(F^2) = 0.145$ | $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ |
| $S = 1.07$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 8173 reflections | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| 150 parameters | $\Delta\rho_{\text{max}} = 1.24 \text{ e \AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{\text{min}} = -0.61 \text{ e \AA}^{-3}$ |
| | Extinction correction: none |

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|---------------|--------------|----------------------------------|
| Sn | 1.0000 | 0.202248 (11) | 0.2500 | 0.03412 (6) |
| S4 | 0.80944 (4) | 0.24306 (5) | 0.33596 (5) | 0.05278 (14) |
| S3 | 1.17240 (3) | 0.16968 (3) | 0.37176 (4) | 0.03869 (10) |
| S2 | 1.01793 (3) | 0.09568 (4) | 0.39719 (5) | 0.04590 (12) |
| S1 | 0.98344 (4) | 0.32210 (4) | 0.35808 (4) | 0.04406 (12) |
| C1 | 0.91736 (14) | 0.27902 (13) | 0.41621 (15) | 0.0378 (3) |
| N1 | 0.95774 (13) | 0.28033 (13) | 0.52591 (14) | 0.0433 (3) |
| C2 | 0.9021 (2) | 0.25988 (19) | 0.5803 (2) | 0.0554 (6) |
| H2A | 0.8384 | 0.2794 | 0.5345 | 0.066* |
| H2B | 0.9278 | 0.2905 | 0.6492 | 0.066* |
| C3 | 0.9003 (3) | 0.1671 (3) | 0.6025 (3) | 0.0771 (9) |
| H3A | 0.8628 | 0.1579 | 0.6374 | 0.116* |
| H3B | 0.9630 | 0.1476 | 0.6497 | 0.116* |
| H3C | 0.8740 | 0.1364 | 0.5346 | 0.116* |
| C4 | 1.05786 (18) | 0.29665 (16) | 0.5989 (2) | 0.0528 (6) |
| H4A | 1.0920 | 0.2834 | 0.5601 | 0.063* |
| H4B | 1.0802 | 0.2589 | 0.6615 | 0.063* |
| C5 | 1.0788 (2) | 0.3865 (2) | 0.6392 (2) | 0.0725 (8) |
| H5A | 1.1450 | 0.3930 | 0.6861 | 0.109* |
| H5B | 1.0466 | 0.3998 | 0.6794 | 0.109* |
| H5C | 1.0583 | 0.4243 | 0.5778 | 0.109* |
| C6 | 1.13681 (12) | 0.10712 (12) | 0.44702 (14) | 0.0351 (3) |
| N2 | 1.19789 (12) | 0.06819 (10) | 0.53695 (14) | 0.0405 (3) |
| C7 | 1.29923 (14) | 0.07507 (16) | 0.5782 (2) | 0.0543 (6) |
| H7A | 1.3309 | 0.0810 | 0.6574 | 0.065* |
| H7B | 1.3121 | 0.1256 | 0.5480 | 0.065* |
| C8 | 1.3367 (3) | -0.0006 (3) | 0.5485 (4) | 0.0923 (13) |
| H8A | 1.4028 | 0.0062 | 0.5761 | 0.139* |
| H8B | 1.3059 | -0.0063 | 0.4702 | 0.139* |
| H8C | 1.3256 | -0.0505 | 0.5800 | 0.139* |
| C9 | 1.16890 (17) | 0.01398 (14) | 0.60174 (17) | 0.0477 (5) |
| H9A | 1.1044 | -0.0033 | 0.5556 | 0.057* |
| H9B | 1.2072 | -0.0369 | 0.6238 | 0.057* |

supplementary materials

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|------|------------|------------|------------|-------------|
| C10 | 1.1771 (4) | 0.0561 (3) | 0.7004 (3) | 0.0904 (12) |
| H10A | 1.1575 | 0.0176 | 0.7388 | 0.136* |
| H10B | 1.1380 | 0.1056 | 0.6793 | 0.136* |
| H10C | 1.2410 | 0.0723 | 0.7473 | 0.136* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|-------------|---------------|--------------|---------------|
| Sn | 0.02512 (8) | 0.04321 (10) | 0.03155 (9) | 0.000 | 0.01177 (6) | 0.000 |
| S4 | 0.0354 (2) | 0.0764 (4) | 0.0425 (2) | -0.0047 (2) | 0.01571 (19) | -0.0066 (2) |
| S3 | 0.02504 (17) | 0.0478 (2) | 0.0397 (2) | -0.00161 (15) | 0.01292 (15) | 0.00968 (17) |
| S2 | 0.0283 (2) | 0.0557 (3) | 0.0517 (3) | -0.00264 (17) | 0.01786 (18) | 0.0135 (2) |
| S1 | 0.0497 (3) | 0.0484 (2) | 0.0412 (2) | -0.0090 (2) | 0.0277 (2) | -0.00716 (19) |
| C1 | 0.0360 (8) | 0.0449 (8) | 0.0333 (7) | 0.0028 (7) | 0.0175 (6) | -0.0020 (6) |
| N1 | 0.0409 (8) | 0.0569 (9) | 0.0330 (7) | -0.0002 (7) | 0.0186 (6) | -0.0033 (6) |
| C2 | 0.0600 (14) | 0.0738 (16) | 0.0439 (10) | -0.0090 (12) | 0.0344 (10) | -0.0115 (10) |
| C3 | 0.093 (3) | 0.086 (2) | 0.0622 (17) | -0.0131 (19) | 0.0463 (18) | 0.0043 (15) |
| C4 | 0.0406 (11) | 0.0719 (16) | 0.0365 (9) | 0.0047 (9) | 0.0112 (8) | -0.0020 (8) |
| C5 | 0.0586 (16) | 0.086 (2) | 0.0582 (15) | -0.0105 (15) | 0.0166 (12) | -0.0127 (14) |
| C6 | 0.0277 (6) | 0.0383 (7) | 0.0355 (7) | -0.0030 (5) | 0.0124 (6) | 0.0015 (6) |
| N2 | 0.0316 (7) | 0.0412 (7) | 0.0404 (7) | -0.0035 (5) | 0.0110 (6) | 0.0094 (6) |
| C7 | 0.0301 (8) | 0.0561 (12) | 0.0561 (12) | -0.0041 (8) | 0.0047 (8) | 0.0155 (10) |
| C8 | 0.0567 (18) | 0.079 (2) | 0.143 (4) | 0.0141 (15) | 0.049 (2) | 0.021 (2) |
| C9 | 0.0507 (11) | 0.0436 (9) | 0.0432 (9) | -0.0068 (8) | 0.0183 (8) | 0.0093 (7) |
| C10 | 0.144 (4) | 0.077 (2) | 0.0719 (19) | -0.028 (2) | 0.069 (2) | -0.0128 (16) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|--------------------|-------------|----------|-----------|
| Sn—S1 | 2.5111 (5) | C4—H4A | 0.9700 |
| Sn—S1 ⁱ | 2.5111 (5) | C4—H4B | 0.9700 |
| Sn—S3 ⁱ | 2.5366 (4) | C5—H5A | 0.9600 |
| Sn—S3 | 2.5366 (4) | C5—H5B | 0.9600 |
| Sn—S2 | 2.5567 (5) | C5—H5C | 0.9600 |
| Sn—S2 ⁱ | 2.5567 (5) | C6—N2 | 1.316 (2) |
| S4—C1 | 1.663 (2) | N2—C7 | 1.468 (3) |
| S3—C6 | 1.7327 (19) | N2—C9 | 1.478 (3) |
| S2—C6 | 1.7247 (18) | C7—C8 | 1.488 (5) |
| S1—C1 | 1.769 (2) | C7—H7A | 0.9700 |
| C1—N1 | 1.341 (2) | C7—H7B | 0.9700 |
| N1—C4 | 1.470 (3) | C8—H8A | 0.9600 |
| N1—C2 | 1.474 (3) | C8—H8B | 0.9600 |
| C2—C3 | 1.497 (5) | C8—H8C | 0.9600 |
| C2—H2A | 0.9700 | C9—C10 | 1.474 (4) |
| C2—H2B | 0.9700 | C9—H9A | 0.9700 |
| C3—H3A | 0.9600 | C9—H9B | 0.9700 |
| C3—H3B | 0.9600 | C10—H10A | 0.9600 |
| C3—H3C | 0.9600 | C10—H10B | 0.9600 |
| C4—C5 | 1.501 (4) | C10—H10C | 0.9600 |

| | | | |
|-------------------------------------|--------------|---------------|-------------|
| S1—Sn—S1 ⁱ | 82.48 (3) | N1—C4—H4B | 108.9 |
| S1—Sn—S3 ⁱ | 98.433 (17) | C5—C4—H4B | 108.9 |
| S1 ⁱ —Sn—S3 ⁱ | 99.063 (19) | H4A—C4—H4B | 107.7 |
| S1—Sn—S3 | 99.064 (19) | C4—C5—H5A | 109.5 |
| S1 ⁱ —Sn—S3 | 98.434 (17) | C4—C5—H5B | 109.5 |
| S3 ⁱ —Sn—S3 | 156.66 (2) | H5A—C5—H5B | 109.5 |
| S1—Sn—S2 | 90.89 (2) | C4—C5—H5C | 109.5 |
| S1 ⁱ —Sn—S2 | 166.429 (19) | H5A—C5—H5C | 109.5 |
| S3 ⁱ —Sn—S2 | 93.599 (17) | H5B—C5—H5C | 109.5 |
| S3—Sn—S2 | 70.827 (15) | N2—C6—S2 | 121.35 (14) |
| S1—Sn—S2 ⁱ | 166.427 (19) | N2—C6—S3 | 121.40 (14) |
| S1 ⁱ —Sn—S2 ⁱ | 90.89 (2) | S2—C6—S3 | 117.23 (10) |
| S3 ⁱ —Sn—S2 ⁱ | 70.826 (15) | C6—N2—C7 | 121.91 (17) |
| S3—Sn—S2 ⁱ | 93.599 (17) | C6—N2—C9 | 122.20 (17) |
| S2—Sn—S2 ⁱ | 97.91 (3) | C7—N2—C9 | 115.89 (17) |
| C6—S3—Sn | 86.08 (6) | N2—C7—C8 | 111.7 (2) |
| C6—S2—Sn | 85.61 (6) | N2—C7—H7A | 109.3 |
| C1—S1—Sn | 104.69 (7) | C8—C7—H7A | 109.3 |
| N1—C1—S4 | 123.21 (16) | N2—C7—H7B | 109.3 |
| N1—C1—S1 | 116.44 (15) | C8—C7—H7B | 109.3 |
| S4—C1—S1 | 120.30 (11) | H7A—C7—H7B | 108.0 |
| C1—N1—C4 | 124.02 (19) | C7—C8—H8A | 109.5 |
| C1—N1—C2 | 119.95 (19) | C7—C8—H8B | 109.5 |
| C4—N1—C2 | 115.94 (19) | H8A—C8—H8B | 109.5 |
| N1—C2—C3 | 113.5 (2) | C7—C8—H8C | 109.5 |
| N1—C2—H2A | 108.9 | H8A—C8—H8C | 109.5 |
| C3—C2—H2A | 108.9 | H8B—C8—H8C | 109.5 |
| N1—C2—H2B | 108.9 | C10—C9—N2 | 113.6 (2) |
| C3—C2—H2B | 108.9 | C10—C9—H9A | 108.8 |
| H2A—C2—H2B | 107.7 | N2—C9—H9A | 108.8 |
| C2—C3—H3A | 109.5 | C10—C9—H9B | 108.8 |
| C2—C3—H3B | 109.5 | N2—C9—H9B | 108.8 |
| H3A—C3—H3B | 109.5 | H9A—C9—H9B | 107.7 |
| C2—C3—H3C | 109.5 | C9—C10—H10A | 109.5 |
| H3A—C3—H3C | 109.5 | C9—C10—H10B | 109.5 |
| H3B—C3—H3C | 109.5 | H10A—C10—H10B | 109.5 |
| N1—C4—C5 | 113.6 (2) | C9—C10—H10C | 109.5 |
| N1—C4—H4A | 108.9 | H10A—C10—H10C | 109.5 |
| C5—C4—H4A | 108.9 | H10B—C10—H10C | 109.5 |

Symmetry codes: (i) $-x+2, y, -z+1/2$.

Fig. 1

