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n-Butyltris(2-pyrimidinethiolato-*N*,*S*)tin(IV): Change in Space Group

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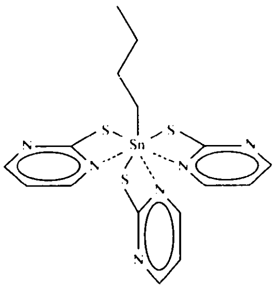
Abstract

The structure of $[Sn(C_4H_3N_2S)_3(C_4H_9)]$, which was originally described in space group $P2_1$ [Schmiedgen, Huber & Schürmann (1994). *Acta Cryst.* **C50**, 391–394], is better described and refined in $P2_1/n$. Revised coordinates and bond lengths are given.

Comment

In their report of the structure of the title compound, (I), Schmiedgen, Huber & Schürmann (1994, hereinafter, SHS) noted that the systematic absences were consistent with space group $P2_1/n$, but that 'the structure could not be solved in this space group'; accordingly, the structure was solved and refined in $P2_1$ [monoclinic; $a = 9.523$ (2), $b = 12.849$ (3), $c = 17.079$ (3) Å, $\beta = 92.67$ (3)°, $Z = 4$], with two independent molecules in the asymmetric unit. In fact, the two molecules are closely related by an *n*-glide plane and further refinement in $P2_1/n$ was straightforward.



(I)

The starting model was derived from the coordinates in Table 1 of SHS by shifting the origin by 0.25 in *x* and *z*, and by about 0.24 in *y*, so as to place a center of symmetry at the conventional origin in $P2_1/n$. Full-matrix refinement, with the heavier atoms anisotropic and the H atoms in calculated positions, was based on the 2664 'observed' *F* values recovered from SUP 71555. At convergence (maximum shift, 0.03σ), *R* was 0.0311 for 259 parameters, compared with an *R* of 0.0293 for 471 parameters reported for the $P2_1$ model (SHS). For the entire set of 3707 reflections in SUP 71555, including those tagged as unobserved [but excluding the space-group absences $h0l$ with $(h + l)$ odd], *R* was 0.0525 and there were no obvious outliers. The only abnormality during the refinement resulted from disorder of the *n*-butyl group, which led to two sets of partially populated sites for the outer atoms C(2), C(3) and C(4); the resulting occupancy factor was 0.67 (3) for one set of sites (and 0.33 for the other). Since the two sites for C(2) are separated by only 0.67 Å, the occupant of the minor site, C(2*a*), would not tolerate refinement of its anisotropic coefficients U_{ij} and was represented as isotropic; this atom also shows unsatisfactory bond lengths, with C(1)—C(2*a*) 1.29 (4) Å and C(2*a*)—C(3*a*) 1.65 (5) Å. The *n*-butyl groups also caused problems in the earlier $P2_1$ refinement, where SHS report 'conspicuous deviations' of the C(1)—C(2)—C(3) angles from 109.5° that are 'probably caused by lattice effects'. (To the extent that 'lattice effects' are responsible for the disorder, this is a correct assessment.)

Bond lengths and angles given in Table 2 are considerably more reasonable, and more precise, than those reported earlier (SHS), and deserve some further comment. The bonds Sn—S(1) and Sn—S(2) to the equatorial 2-pyrimidinethiolato ligands are approximately equal in length but the axial bond Sn—S(3) is nearly 0.1 Å shorter. This difference in Sn—S bond lengths seems too large to blame merely on steric effects and it is tempting to invoke some sort of *trans* influence by the alkyl group on the opposite side. [Note, though, that the axial array C(1)—Sn—S(3) is far from linear, at 147.6 (1)°.] The Sn—N bonds, which are weaker than Sn—S, show

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† Contribution No. 8943.

considerable scatter with no obvious pattern. The bite angles, S—Sn—N, in the three pyrimidinethiolato groups range from 61.1 (1) to 62.2 (1)°, a slightly smaller range than reported by SHS.

There were a number of signals [other than the absence of reflections *h*0*l* with $(h+l)$ odd] that should have led the earlier authors to a presumption that their choice of a non-centrosymmetric space group was incorrect; for example, the S—C bond lengths resulting from the refinement in $P2_1$ varied from 1.641 (7) to 1.855 (7) Å, the pyrimidine rings were severely distorted [the C—N bond lengths ranged from 1.22 (1) to 1.437 (9) Å] and the U_{eq} values for chemically equivalent atoms varied widely, for example, from 0.0330 (4) $Å^2$ for atom C(11) in one molecule to 0.0891 (4) $Å^2$ for the corresponding atom in the second molecule. There were also strong indications in the supplementary listing of F_o and F_c values: for many of the $(h0l)$ reflections with $(h+l)$ odd, the calculated values were far larger than the observational thresholds. But these reflections had been removed from the refinement process and hence the discrepancies might not have been readily apparent. Here is one more reason for retaining all intensity measurements throughout a structure analysis.

Experimental

Crystal data

[$Sn(C_4H_3N_2S)_3(C_4H_9)$]
$M_r = 509.23$
Monoclinic
$P2_1/n$
$a = 9.523$ (2) Å
$b = 12.849$ (3) Å
$c = 17.079$ (3) Å
$\beta = 92.67$ (3)°
$V = 2087.5$ (8) $Å^3$
$Z = 4$
$D_x = 1.620$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 7.8–15.1$°
$\mu = 1.528$ mm^{-1}
$T = 291$ (1) K
Block
0.34 × 0.28 × 0.20 mm
Colorless

Data collection

Nicolet *R*3*m*/*V* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.925$, $T_{max} = 0.961$
6035 measured reflections
3889 independent reflections
2664 observed reflections [$F > 1.5\sigma(F)$]

$R_{int} = 0.018$
$\theta_{max} = 25$°
$h = -11 \rightarrow 4$
$k = 0 \rightarrow 13$
$l = -20 \rightarrow 20$
6 standard reflections
frequency: 150 min
intensity variation: none

Refinement

Refinement on F^2
$R = 0.0311$
2664 reflections
259 parameters
H stoms not refined

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Table 1. *Fractional atomic coordinates and displacement parameters* ($Å^2$), *space group* $P2_1/n$

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq} or B
Sn	0.45783 (3)	0.25783 (2)	0.21856 (2)	0.0512 (1)
S(1)	0.25755 (13)	0.38698 (10)	0.19764 (8)	0.0661 (3)
S(2)	0.58685 (15)	0.35922 (10)	0.11700 (9)	0.0768 (4)
S(3)	0.56789 (14)	0.34273 (9)	0.33364 (8)	0.0643 (3)
C(11)	0.1678 (5)	0.3214 (3)	0.2694 (3)	0.0558 (11)
N(11)	0.2419 (4)	0.2432 (3)	0.3044 (2)	0.0612 (9)
C(13)	0.1812 (6)	0.1923 (4)	0.3614 (3)	0.0816 (16)
C(14)	0.0483 (7)	0.2175 (5)	0.3833 (3)	0.0886 (17)
C(15)	−0.0183 (6)	0.2973 (5)	0.3440 (4)	0.0819 (16)
N(12)	0.0383 (4)	0.3506 (3)	0.2861 (3)	0.0704 (11)
C(21)	0.7257 (5)	0.2726 (3)	0.1343 (3)	0.0663 (13)
N(21)	0.7031 (4)	0.2001 (3)	0.1895 (2)	0.0626 (10)
C(23)	0.8057 (5)	0.1315 (4)	0.2049 (3)	0.0720 (14)
C(24)	0.9295 (6)	0.1345 (4)	0.1673 (4)	0.0842 (17)
C(25)	0.9423 (6)	0.2111 (4)	0.1119 (4)	0.0901 (18)
N(22)	0.8428 (5)	0.2808 (3)	0.0940 (3)	0.0806 (12)
C(31)	0.5941 (4)	0.2210 (3)	0.3785 (3)	0.0517 (10)
N(31)	0.5449 (4)	0.1405 (3)	0.3359 (2)	0.0531 (9)
C(33)	0.5679 (5)	0.0457 (3)	0.3673 (3)	0.0620 (13)
C(34)	0.6342 (6)	0.0332 (4)	0.4379 (3)	0.0699 (14)
C(35)	0.6793 (6)	0.1212 (5)	0.4763 (3)	0.0855 (18)
N(32)	0.6615 (5)	0.2168 (3)	0.4474 (2)	0.0761 (12)
C(1)	0.3853 (6)	0.1169 (4)	0.1650 (3)	0.0773 (15)
C(2*a*)†	0.322 (4)	0.113 (3)	0.097 (2)	8.2 (8)§
C(2*b*)‡	0.3777 (16)	0.1205 (8)	0.0747 (8)	0.075 (3)
C(3*a*)†	0.283 (3)	−0.006 (2)	0.068 (2)	0.128 (10)
C(3*b*)‡	0.3303 (17)	0.0263 (11)	0.0327 (9)	0.104 (4)
C(4*a*)†	0.255 (4)	−0.0108 (18)	−0.0152 (19)	0.129 (10)
C(4*b*)‡	0.1986 (18)	−0.0105 (12)	0.0462 (12)	0.130 (6)

† Site population 0.33 (3).
‡ Site population 0.67.
§ Isotropic displacement parameter, B ($Å^2$).

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Sn—S(1)	2.541 (1)	C(21)—N(22)	1.342 (6)
Sn—S(2)	2.533 (1)	N(21)—C(23)	1.333 (6)
Sn—S(3)	2.441 (1)	C(23)—C(24)	1.369 (8)
Sn—N(11)	2.588 (4)	C(24)—C(25)	1.376 (8)
Sn—N(21)	2.522 (4)	C(25)—N(22)	1.328 (7)
Sn—N(31)	2.612 (4)	C(31)—N(31)	1.337 (5)
Sn—C(1)	2.130 (5)	C(31)—N(32)	1.316 (6)
S(1)—C(11)	1.744 (5)	N(31)—C(33)	1.345 (6)
S(2)—C(21)	1.743 (5)	C(33)—C(34)	1.345 (7)
S(3)—C(31)	1.754 (4)	C(34)—C(35)	1.366 (8)
C(11)—N(11)	1.351 (6)	C(35)—N(32)	1.332 (7)
C(11)—N(12)	1.332 (6)	C(1)—C(2a)	1.289 (35)
N(11)—C(13)	1.326 (7)	C(1)—C(2*b*)	1.540 (14)
C(13)—C(14)	1.375 (8)	C(2a)—C(3a)	1.653 (47)
C(14)—C(15)	1.366 (8)	C(2*b*)—C(3*b*)	1.467 (20)
C(15)—N(12)	1.336 (7)	C(3a)—C(4a)	1.432 (45)
C(21)—N(21)	1.350 (6)	C(3*b*)—C(4*b*)	1.370 (23)
S(1)—Sn—S(2)	87.29 (4)	C(23)—N(21)—C(21)	117.1 (4)
S(1)—Sn—S(3)	96.47 (4)	C(24)—C(23)—N(21)	121.9 (5)
S(2)—Sn—S(3)	96.76 (4)	C(25)—C(24)—C(23)	116.7 (5)
S(1)—Sn—C(1)	105.6 (1)	N(22)—C(25)—C(24)	123.8 (5)
S(2)—Sn—C(1)	107.5 (1)	C(25)—N(22)—C(21)	115.4 (4)
S(3)—Sn—C(1)	147.6 (1)	N(31)—C(31)—S(3)	114.4 (3)
N(11)—C(11)—S(1)	114.0 (3)	N(32)—C(31)—S(3)	118.7 (3)
N(12)—C(11)—S(1)	120.2 (3)	N(32)—C(31)—N(31)	126.8 (4)
N(12)—C(11)—N(11)	125.8 (4)	C(33)—N(31)—C(31)	115.9 (4)
C(13)—N(11)—C(11)	117.0 (4)	C(34)—C(33)—N(31)	121.8 (4)
C(14)—C(13)—N(11)	121.4 (5)	C(35)—C(34)—C(33)	117.1 (5)
C(15)—C(14)—C(13)	117.0 (5)	N(32)—C(35)—C(34)	123.7 (5)
N(12)—C(15)—C(14)	123.7 (5)	C(35)—N(32)—C(31)	114.6 (4)
C(15)—N(12)—C(11)	115.0 (4)	C(3a)—C(2a)—C(1)	113.0 (25)
N(21)—C(21)—S(2)	114.5 (3)	C(3*b*)—C(2*b*)—C(1)	117.6 (11)
N(22)—C(21)—S(2)	120.3 (4)	C(4a)—C(3a)—C(2a)	111.1 (26)
N(22)—C(21)—N(21)	125.2 (4)	C(4*b*)—C(3*b*)—C(2*b*)	117.8 (14)

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: CR1153). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Reference

Schmiedgen, R., Huber, F. & Schürmann, M. (1994). *Acta Cryst.* **C50**, 391–394.