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Key indicators

Single-crystal X-ray study
T = 183 K
Mean $\sigma(\text{C}-\text{C}) = 0.014 \text{ \AA}$
R factor = 0.059
wR factor = 0.162
Data-to-parameter ratio = 25.7

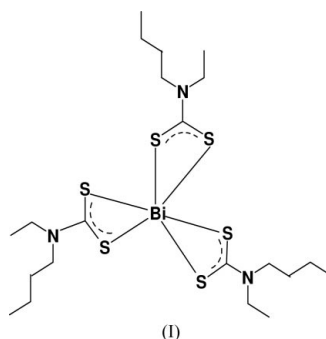
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Tris(*N*-butyl-*N*-ethylthiocarbamato)-bismuth(III)

The Bi atom in the title compound, $[\text{Bi}(\text{C}_7\text{H}_{14}\text{NS}_2)_3]$, is coordinated by six S atoms from three bidentate *N*-butyl-*N*-ethylthiocarbamate ligands; it is also engaged in an additional $\text{Bi} \cdots \text{S}$ interaction which links two tris(*N*-butyl-*N*-ethylthiocarbamato)bismuth fragments into centrosymmetric binuclear dimers. Thus, each of the Bi atoms in the dimer has a distorted pentagonal-bipyramidal environment, with one short axial Bi–S distance of 2.608 (2) Å, one long axial $\text{Bi} \cdots \text{S}$ interaction of 3.334 (2) Å, and five ‘regular’ equatorial bonds in the range 2.819 (2)–2.867 (2) Å.

Comment

The tris(dithiocarbamato)bismuth(III) and tris(dithiocarbamato)antimony(III) complexes generally have the chelated metal atom with a capped octahedral geometry, since the lone pair of electrons is stereochemically active (Raston & White, 1976; Venkatachalam *et al.*, 1997). Our recent study of the tris(2-hydroxyethylisopropyl)bismuth complex has confirmed this geometry for the metal atom (Low *et al.*, 2001).



The nature of the substituents in the dithiocarbamate group appears to affect the stereochemical activity; the Bi atom in the title compound, (I) (Fig. 1), is seven-coordinated and has a distorted pentagonal-bipyramidal environment, with one short axial distance [Bi1–S4 2.608 (2) Å], one long axial interaction [Bi1 \cdots S5ⁱ 3.334 (2) Å; symmetry code: (i) 1 – x, 1 – y, 1 – z], and five ‘regular’ equatorial bonds [2.819 (2)–2.867 (2) Å]; the angle formed by two axial bonds, S4–Bi1 \cdots S5ⁱ, is 141.0 (1) Å. The long axial Bi1 \cdots S5ⁱ interaction links two adjacent tris(*N*-butyl-*N*-ethylthiocarbamato)-bismuth fragments into a centrosymmetric dinuclear entity (Fig. 2).

Experimental

Bismuth trichloride (3.15 g, 10 mmol) was dissolved in a small volume of ethanol. The solution was cooled in an ice bath, then ethylbutylamine (3.03 g, 30 mmol) and an excess of carbon disulfide (2 ml) were added; the mixture was stirred for several hours. The solid which separated had a melting point of 396–397 K. Elemental analysis,

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found: C 33.94, H 4.93, N 5.69, S 26.94%; calculated for $C_{21}H_{42}BiN_3S_6$: C 31.48, H 5.74, N 5.70, S 26.07%.

Crystal data

$[Bi(C_7H_{14}NS_2)_3]$

$M_r = 737.92$

Triclinic, $P\bar{1}$

$a = 10.5120(1) \text{ \AA}$

$b = 10.5128(1) \text{ \AA}$

$c = 14.5755(1) \text{ \AA}$

$\alpha = 99.713(1)^\circ$

$\beta = 99.927(1)^\circ$

$\gamma = 103.383(1)^\circ$

$V = 1506.52(2) \text{ \AA}^3$

$Z = 2$

$D_x = 1.627 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

Cell parameters from 8192

reflections

$\theta = 1.5\text{--}28.3^\circ$

$\mu = 6.28 \text{ mm}^{-1}$

$T = 183(2) \text{ K}$

Block, yellow

$0.30 \times 0.26 \times 0.16 \text{ mm}$

Data collection

Siemens SMART CCD area-detector diffractometer

ω scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.254$, $T_{\max} = 0.433$

11016 measured reflections

7197 independent reflections

6368 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.076$

$\theta_{\max} = 28.3^\circ$

$h = -13 \rightarrow 13$

$k = -13 \rightarrow 12$

$l = -17 \rightarrow 19$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.059$

$wR(F^2) = 0.162$

$S = 1.07$

7197 reflections

280 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0686P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 4.01 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -5.77 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Bi1—S1	2.834 (2)	Bi1—S5	2.867 (2)
Bi1—S2	2.858 (2)	Bi1—S6	2.819 (2)
Bi1—S3	2.830 (2)	Bi1—S5 ⁱ	3.334 (2)
Bi1—S4	2.608 (2)		
S1—Bi1—S2	62.8 (1)	S3—Bi1—S6	138.0 (1)
S1—Bi1—S3	137.5 (1)	S4—Bi1—S5	86.2 (1)
S1—Bi1—S4	88.1 (1)	S4—Bi1—S6	93.9 (1)
S1—Bi1—S5	135.6 (1)	S5—Bi1—S6	63.1 (1)
S1—Bi1—S6	73.4 (1)	S4—Bi1—S5 ⁱ	141.0 (1)
S2—Bi1—S3	81.1 (1)	S6—Bi1—S5 ⁱ	114.2 (1)
S2—Bi1—S4	85.4 (1)	S3—Bi1—S5 ⁱ	74.9 (1)
S2—Bi1—S5	159.5 (1)	S1—Bi1—S5 ⁱ	124.5 (1)
S2—Bi1—S6	136.1 (1)	S2—Bi1—S5 ⁱ	91.4 (1)
S3—Bi1—S4	66.2 (1)	S5—Bi1—S5 ⁱ	83.5 (1)
S3—Bi1—S5	78.4 (1)		

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Although the cell dimensions define almost exactly a C-centered monoclinic lattice ($\beta = 89.87^\circ$), the structure does not have true monoclinic symmetry ($R_{\text{int}} = 0.468$) and was solved and refined as triclinic. The C—C distances in the ethyl and butyl groups were restrained to $1.54 \pm 0.01 \text{ \AA}$; in the butyl chain, an additional restriction of $C \cdots C = 2.51 \pm 0.01 \text{ \AA}$ was used. The N—C_{alkyl} distances in each dithiocarbamate unit were restrained to be equal to each other by a SADI 0.01 instruction in *SHELXL97*. The H atoms were positioned geometrically and allowed to ride on their parent C atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for the methylene H atoms and $1.5U_{\text{eq}}(\text{C})$ for the methyl H atoms. The final difference Fourier map had a large peak and hole near the Bi atom.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

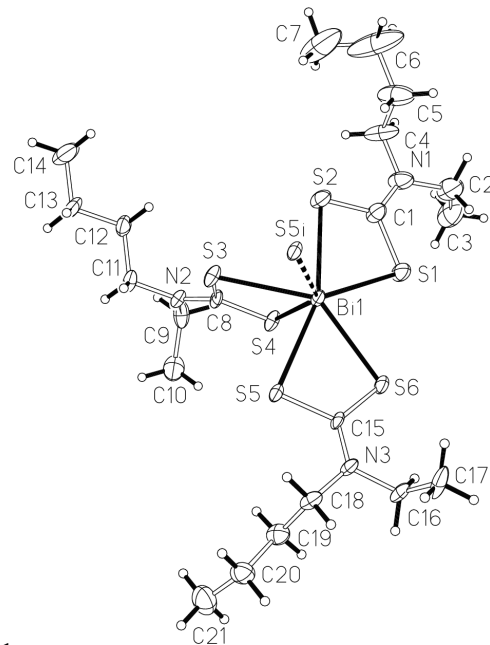


Figure 1

ORTEPII (Johnson, 1976) plot of the molecule of the title compound; displacement ellipsoids are drawn at the 50% probability level. The long Bi···S interaction is shown as a dashed line. H atoms are drawn as spheres of arbitrary radii.

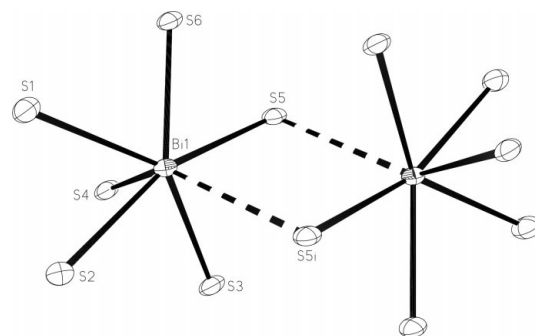


Figure 2

The centrosymmetric binuclear aggregates in the structure of the title compound. Only Bi and S atoms are shown; displacement ellipsoids are drawn at the 50% probability level.

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