metal-organic papers

Tris(N,N-dibenzylcarbamato-κ^2S,S')bismuth(III)

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.020 Å
R factor = 0.080
wR factor = 0.222
Data-to-parameter ratio = 15.2

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

The coordination polyhedron in the title compound, [Bi(C$_{15}$H$_{14}$NS$_2$)$_3$] or [Bi{S$_2$CN(C$_7$H$_7$)$_2$}$_3$], is a distorted trigonal antiprism, with three strong (2.664–2.731 Å) and three weak (2.904–2.965 Å) Bi—S bonds.

Comment

The ability of dithiocarbamates to bind to metals has been known for many years. They can form chelates with virtually all transition metals (Xu *et al.*, 2001). The bidentate anion is also well known as a bridging ligand between two transition metal centres (Bardaji *et al.*, 1994). Water-soluble dialkyl-dithiocarbamate complexes have been tested in various medical applications (Xie *et al.*, 1994). Some dialkyl-substituted dithiocarbamate salts have also shown interesting biological effects, which include anti-alkylation (Gringeri *et al.*, 1988) or anti-HIV properties. They are also used as effective antidotes for cadmium intoxication (Kopi-Maier & Klapotke, 1988). In view of the above and as a continuation of our interest in sulfur-containing ligands, we report here the synthesis and crystal structure of the title compound, Bi(S$_2$CNBz$_2$)$_3$, (I).

(I)
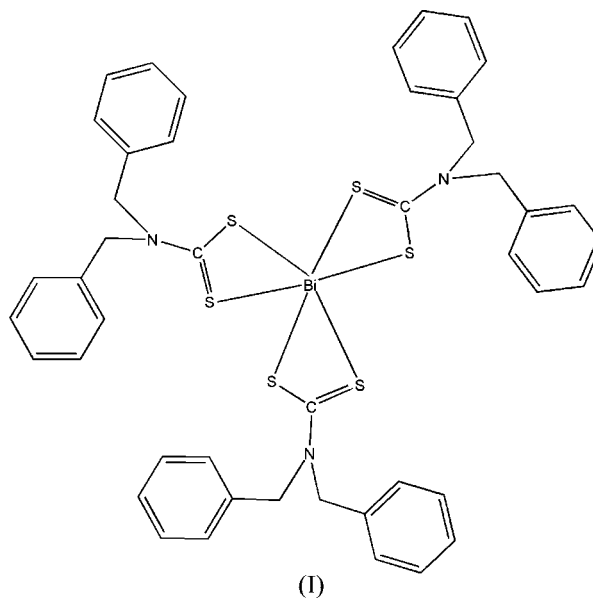
The molecular structure of (I) is shown in Fig. 1. The bidentate ligands are chelated to the Bi atom, forming a polyhedron which can be described as a distorted trigonal antiprism. There are three short and three long Bi—S bonds (Table 1). The three short bonds [mean Bi—S = 2.69 Å] indicate a strong coordination, while the other set corresponds
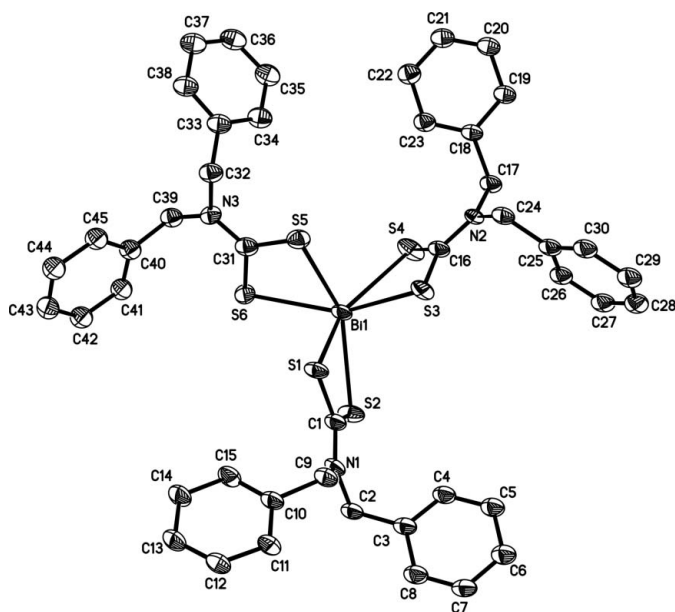
Figure 1
The molecular structure of the title complex, showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

to a weak Bi—S interaction [mean Bi—S = 2.93 Å]. In all ligands of (I), the C—S bond associated with the strong Bi—S bond [mean length 1.76 Å] is longer than that associated with the weak Bi—S bond [mean length 1.72 Å], showing clearly the positions of the double bonds.

A diagram of the coordination polyhedron showing the two trigonal faces of the antiprism is depicted in Fig. 2. The plane defined by atoms S1, S3 and S5, which are the strongly coordinated S atoms, is essentially parallel to that defined by atoms S2, S4 and S6 [the acute angle between the two planes is 4.1 (3)°] and Bi is displaced by 1.66 and 0.83 Å, respectively, from the planes.

Experimental

To a stirred solution of BiI$_3$ (0.2 mmol) in acetonitrile (20 ml), $(C_7H_7)_2NCS_2Na$ (0.6 mmol) was added. The reaction mixture was stirred for 4 h at 298 K. A yellow solution was obtained and then filtered. The solvent was gradually removed by evaporation under vacuum and a solid product was obtained. The solid was recrystallized from ethanol and orange–red crystals of (I) were formed [yield 77%; m.p. 421 K (decomposition)]. Analysis, calculated (%) for $C_{45}H_{42}N_3S_6Bi$: C 52.67, H 4.13, N 4.09; found: C 52.44, H 4.32, N 4.00.

Crystal data

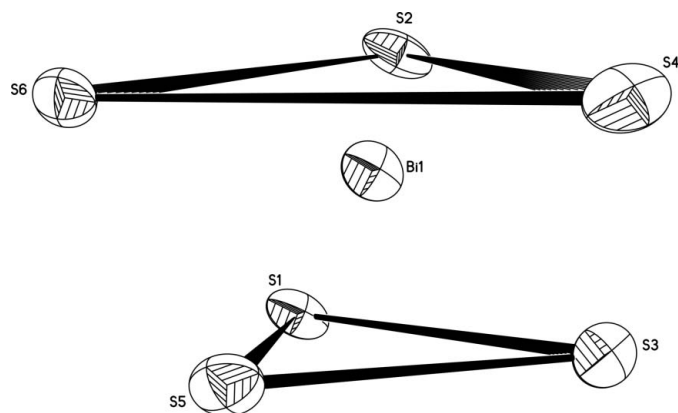|	
[Bi(C$_{15}$H$_{14}$NS$_2$)$_3$]	$V = 2187$ (3) Å^3
$M_r = 1026.16$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.558$ Mg m^{-3}
$a = 10.004$ (9) Å	Mo $K\alpha$ radiation
$b = 13.319$ (12) Å	$\mu = 4.35$ mm^{-1}
$c = 17.439$ (16) Å	$T = 298$ (2) K
$\alpha = 93.785$ (13)°	Block, orange-red
$\beta = 99.392$ (13)°	$0.32 \times 0.31 \times 0.30$ mm
$\gamma = 106.116$ (13)°	

Figure 2
The coordination polyhedron in (I). S—S 'bonds' indicate the two trigonal faces of the antiprism.

Data collection

Siemens SMART CCD area-detector diffractometer	11052 measured reflections
φ and ω scans	7536 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	3897 reflections with $I > 2\sigma(I)$
$T_{min} = 0.337$, $T_{max} = 0.355$	$R_{int} = 0.074$
(expected range = 0.257–0.271)	$\theta_{max} = 25.0°$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.080$	$w = 1/[\sigma^2(F_o^2) + (0.092P)^2]$
$wR(F^2) = 0.223$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} < 0.001$
7536 reflections	$\Delta\rho_{max} = 2.44$ e Å^{-3}
496 parameters	$\Delta\rho_{min} = -2.83$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Bi1—S1	2.664 (4)	S1—C1	1.753 (15)
Bi1—S5	2.682 (4)	S2—C1	1.736 (15)
Bi1—S3	2.731 (4)	S3—C16	1.759 (14)
Bi1—S6	2.904 (5)	S4—C16	1.691 (16)
Bi1—S2	2.931 (4)	S5—C31	1.765 (18)
Bi1—S4	2.965 (5)	S6—C31	1.718 (16)
S1—Bi1—S5	86.34 (14)	S3—Bi1—S2	103.40 (15)
S1—Bi1—S3	84.88 (13)	S6—Bi1—S2	102.90 (14)
S5—Bi1—S3	85.08 (15)	S1—Bi1—S4	148.17 (14)
S1—Bi1—S6	93.02 (14)	S5—Bi1—S4	93.00 (15)
S5—Bi1—S6	64.63 (13)	S3—Bi1—S4	63.39 (12)
S3—Bi1—S6	149.71 (13)	S6—Bi1—S4	115.41 (14)
S1—Bi1—S2	64.67 (13)	S2—Bi1—S4	118.10 (15)
S5—Bi1—S2	148.45 (13)		

All H atoms were positioned geometrically and treated as riding on their parent atoms, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H, and C—H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for CH$_2$ H. The highest peak and deepest hole in the final difference Fourier map are 1.10 and 1.02 Å from Bi1, respectively.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics:

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