metal-organic papers

## (Morpholine-1-dithiocarboxylato-κ²S,S′)bis(piperidine-1-dithiocarboxylato-κ²S,S′)bismuth(III)

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.012 Å
Disorder in main residue
R factor = 0.036
wR factor = 0.091
Data-to-parameter ratio = 17.0

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

In the title compound, $[Bi(C_5H_8NOS_2)(C_6H_{10}NS_2)_2]$, the Bi^{III} atom adopts a distorted pentagonal–pyramidal coordination, due to its stereochemically active lone pair of electrons. A long Bi···S contact of 3.2727 (19) Å leads to dimeric associations of molecules in the crystal structure.

Comment

Dithiocarbamates have been known as effective ligands for transition metal ions for many years. They can form chelates (Xu *et al.*, 2001) or act as bridging ligands (Bardaji *et al.*, 1994). However, the chemistry of main-group metal complexes with dithiocarbamates has been less extensively studied, and only a few reports describing bismuth(III) dithiocarbamate complexes have appeared (Yin *et al.*, 2003). As a continuation of our interest in sulfur-containing ligands, we report here the synthesis and structure of the title compound, (I).

(I)
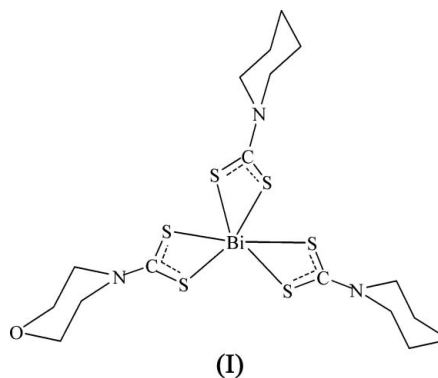
The molecular structure of (I) is shown in Fig. 1 and selected geometrical data are presented in Table 1. In this complex, the Bi atom is six-coordinated by S atoms belonging to two bidenate dithiopiperidylcarbamate ligands and one bidentate dithiomorpholinecarbamate ligand. The resulting BiS_6 coordination polyhedron approximates to a pentagonal pyramid with atoms Bi1 and S2–S6 at the base of the pyramid and S1 in the apical position. Three of the five equatorial Bi—S bonds are long [to S3, S2 and S6; mean = 2.884 (2) Å], two are short [to S4 and S5; mean = 2.787 (2) Å], while the apical donor atom forms the strongest bond [Bi1—S1 = 2.592 (2) Å]. The r.m.s. deviation from the mean plane for atoms S2–S6 is 0.1645 Å, and Bi1 deviates from this mean plane by 0.3549 (3) Å, in the opposite sense to S1. The Bi^{III} lone pair of electrons may project in a direction roughly *trans* to the Bi1—S1 bond.
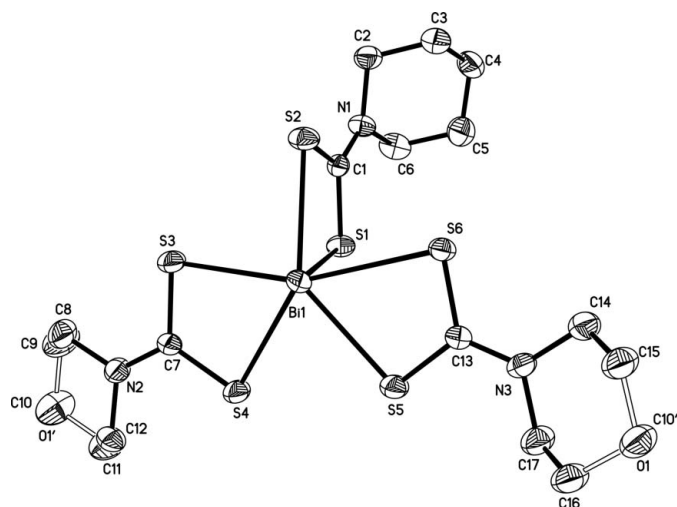
Figure 1
The structure of (I), showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.
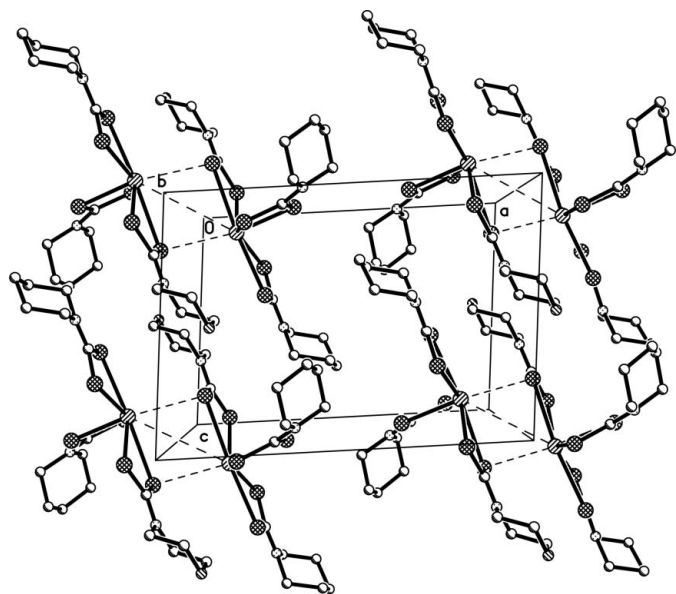

Figure 2
Crystal packing of (I), viewed approximately down [010], with the long Bi···S interactions and Bi···Bi contacts shown as dashed lines. H atoms have been omitted for clarity.

A long 'secondary' Bi1···S6($-x$, $-y$, $1 - z$) interaction of 3.2727 (19) Å results in a packing motif (Fig. 2) involving dimeric associations of (I).

Experimental

To a stirred solution of BiI_3 (0.2 mmol) in acetonitrile (20 ml), $C_5H_{10}NCS_2Na$ (0.4 mmol) and $C_4H_8ONCS_2Na$ (0.2 mmol) were added. The reaction mixture was stirred for 5 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 81%, m.p. 438 K (decompostion).

Analysis calculated for $C_{17}H_{28}BiN_3OS_6$: C 29.51, H 4.08, N 6.07%; found: C 29.73, H 4.18, N 6.26%.

Crystal data

$[Bi(C_5H_8NOS_2)(C_6H_{10}NS_2)_2]$	$Z = 4$
$M_r = 691.76$	$D_x = 1.870$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 13.169$ (4) Å	$\mu = 7.70$ mm^{-1}
$b = 20.089$ (6) Å	$T = 298$ (2) K
$c = 9.319$ (3) Å	Block, orange–red
$\beta = 94.785$ (4)°	$0.37 \times 0.35 \times 0.33$ mm
$V = 2456.9$ (13) Å^3	

Data collection

Siemens SMART CCD diffractometer	12666 measured reflections
φ and ω scans	4325 independent reflections
Absorption correction: multi-scan	3309 reflections with $I > 2\sigma(I)$
(*SADABS*; Sheldrick, 1996)	$R_{int} = 0.065$
$T_{min} = 0.163$, $T_{max} = 0.186$	$\theta_{max} = 25.0°$
(expected range = 0.069–0.079)	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0354P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$+ 0.3861P]$
$wR(F^2) = 0.091$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} = 0.001$
4325 reflections	$\Delta\rho_{max} = 1.13$ e Å^{-3}
254 parameters	$\Delta\rho_{min} = -0.81$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Bi1—S1	2.5920 (18)	Bi1—S3	2.835 (2)
Bi1—S4	2.7793 (19)	Bi1—S2	2.8707 (19)
Bi1—S5	2.7948 (19)	Bi1—S6	2.947 (2)
S1—Bi1—S4	92.66 (6)	S5—Bi1—S2	135.33 (6)
S1—Bi1—S5	89.00 (6)	S3—Bi1—S2	81.05 (6)
S4—Bi1—S5	72.90 (6)	S1—Bi1—S6	83.92 (6)
S1—Bi1—S3	85.99 (7)	S4—Bi1—S6	134.78 (5)
S4—Bi1—S3	63.50 (5)	S5—Bi1—S6	61.99 (5)
S5—Bi1—S3	135.77 (6)	S3—Bi1—S6	159.42 (6)
S1—Bi1—S2	65.77 (5)	S2—Bi1—S6	78.46 (5)
S4—Bi1—S2	140.07 (6)		

One of the dithiopiperidylcarbamate ligands and the dithiomorpholinecarbamate ligand are disordered, such that all atoms overlap and the CH_2 and O atoms are superimposed as atoms C10 and O1. For the N2 molecule, occupancies of 0.63 (3) and 0.37 (3) resulted for C10 and O5, and for the N3 molecule, equivalent values of 0.37 (3) and 0.63 (3) for C10′ and O5′. Models assuming no disorder led to slightly poorer residuals and anomalous displacement factors for these atoms. The chemical analysis is in good accord with the presence of one dithiomorpholinecarbamate ligand. All H atoms were placed geometrically (C—H = 0.97 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}$(carrier). The highest density peak in the final difference map was 1.14 Å from atom Bi1.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

References

Bardaji, M., Connelly, N. G., Gimeno, M. C., Jimenez, J., Jones, P. G., Laguna, A. & Laguna, M. (1994). *J. Chem. Soc. Dalton Trans.* pp. 1163–1168.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*a*). *SHELXL97* and *SHELXS97*. University of Göttingen,Germany.
Sheldrick, G. M. (1997*b*). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Systems Inc., Madison, Wisconsin, USA.
Xu, L. Z., Zhao, P. S. & Zhang, S. S. (2001). *Chin. J. Chem.* **19**, 436–440.
Yin, H. D., Wang, C. H. & Xing, Q. J. (2003). *Chin. J. Inorg. Chem.* **19**, 955–958.