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Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.014\text{ \AA}$
Disorder in main residue
 R factor = 0.037
 wR factor = 0.108
Data-to-parameter ratio = 14.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Iodo(1,10-phenanthroline)bis(pyrrolidine-
1-dithiocarboxylato- $\kappa^2\text{S,S}'$)bismuth(III)

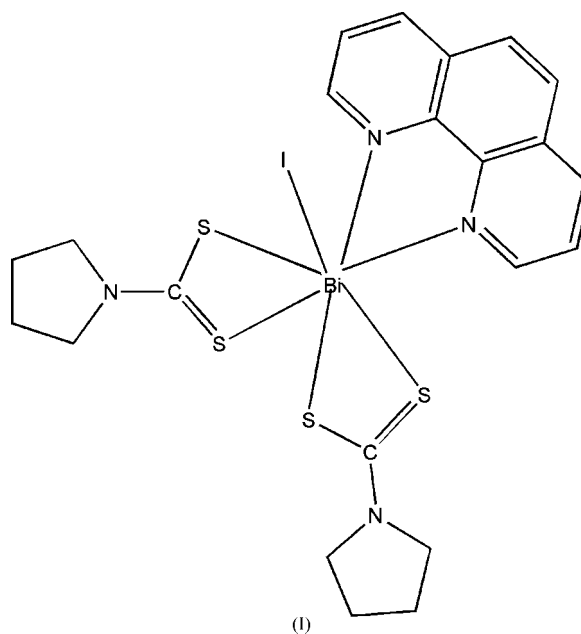
The title compound, $[\text{Bi}(\text{C}_4\text{H}_8\text{NS}_2)_2\text{I}(\text{C}_{12}\text{H}_8\text{N}_2)]$, is monomeric, with the Bi atom chelated by the S atoms of two pyrrolidine-1-dithiocarboxylate ligands and both N atoms of one 1,10-phenanthroline ligand. An iodide ligand completes the coordination, with the seven-coordinate Bi atom adopting a highly distorted capped octahedral geometry.

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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 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).



The title compound, (I), is monomeric, with the Bi atom chelated by the S atoms of two pyrrolidine-1-dithiocarboxylate ligands and both N atoms of one 1,10-phenanthroline. An iodide ligand completes the coordination, yielding seven-coordinate Bi (Fig. 1). The Bi atom is in a distorted capped octahedral environment, with atoms S3 and N4 in axial positions, and atoms S1, S2, S4 and I1 in the equatorial plane. The remaining N atom (N3) of the 1,10-phenanthroline ligand caps the S2/S4/N4 face of this octahedron, giving a highly distorted

capped octahedral coordination geometry. One of the bidentate pyrrolidine-1-dithiocarboxylate ligands forms a significantly longer Bi—S bond [Bi1—S4 = 2.939 (4) Å] than the others in the complex (Table 1). This variation in coordination strength is also signalled by the fact that the C6—S4 bond is significantly shorter than the other C—S bonds, suggesting some delocalization in the system. In addition, the N atoms of the chelating phenanthroline ligands coordinate the Bi atom. The Bi1—N3 and Bi1—N4 distances fall in the same range as in other Bi/N complexes (Baraanyi *et al.*, 1977).

Experimental

To a stirred solution of BiI₃ (0.15 mmol) in acetonitrile (*ca* 20 ml), phenanthroline (0.15 mmol) and sodium pyrrolidine-1-dithiocarboxylate (0.30 mmol) were added. A yellow solution was obtained and, after concentration and cooling, small yellow crystals of the title compound formed. These were collected and dried in vacuum (yield 80%, m.p. 452 K). Analysis calculated for C₂₂H₂₄BiN₄S₄: C 32.68, H 2.99, N 6.93%; found: C 32.58, H 3.30, N 6.77%.

Crystal data

[Bi(C ₄ H ₈ NS ₂) ₂ I(C ₁₂ H ₈ N ₂)]	$V = 1315 (3) \text{ \AA}^3$
$M_r = 808.57$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 2.043 \text{ Mg m}^{-3}$
$a = 10.284 (12) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.560 (13) \text{ \AA}$	$\mu = 8.22 \text{ mm}^{-1}$
$c = 13.545 (16) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\alpha = 79.155 (17)^\circ$	Block, yellow
$\beta = 84.521 (17)^\circ$	$0.21 \times 0.18 \times 0.17 \text{ mm}$
$\gamma = 65.523 (14)^\circ$	

Data collection

Siemens SMART CCD diffractometer	6845 measured reflections
φ and ω scans	4560 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	3642 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.277$, $T_{\max} = 0.336$	$R_{\text{int}} = 0.027$
(expected range = 0.204–0.247)	$\theta_{\text{max}} = 25.0^\circ$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.037$	$w = 1/[\sigma^2(F_o^2) + (0.0604P)^2]$
$wR(F^2) = 0.109$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\text{max}} < 0.001$
4560 reflections	$\Delta\rho_{\text{max}} = 1.17 \text{ e \AA}^{-3}$
308 parameters	$\Delta\rho_{\text{min}} = -1.11 \text{ e \AA}^{-3}$

Table 1

Selected bond lengths (Å).

Bi1—S3	2.702 (3)	Bi1—I1	3.161 (2)
Bi1—S1	2.719 (3)	S1—C1	1.742 (8)
Bi1—S2	2.725 (3)	S2—C1	1.703 (9)
Bi1—N4	2.745 (7)	S3—C6	1.713 (9)
Bi1—N3	2.806 (7)	S4—C6	1.693 (9)
Bi1—S4	2.930 (4)		

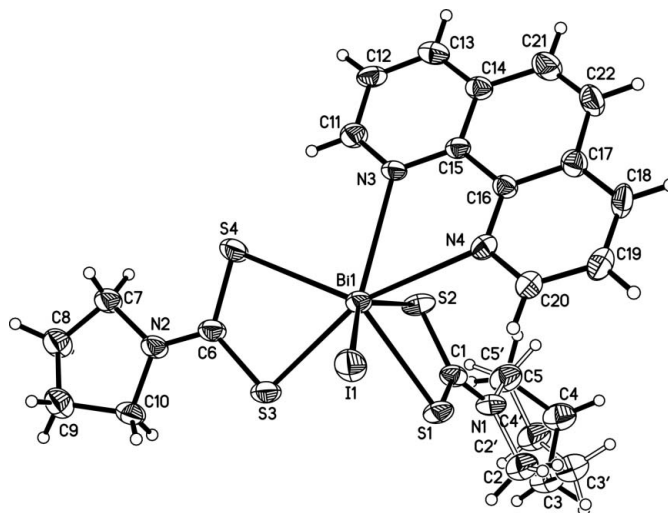


Figure 1

The molecular structure of the title complex, showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity. Both disorder components are shown.

All H atoms were positioned geometrically and treated as riding on their parent atoms [C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic, and C—H = 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for CH₂ H atoms]. Atoms C2, C3, C4 and C5 of one pyrrolidine ring, together with attached H atoms, are disordered over two positions each. The site occupancies refined to 0.48 (4) and 0.52 (4). The highest peak and deepest hole in the final difference Fourier map are 1.40 and 1.09 Å, respectively, from 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.

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References

- Baraanyi, A. D., Cook, J. & Onyszczuk, M. (1977). *Inorg. Nucl. Chem. Lett.* **13**, 385–394.
- 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. (1997a). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997b). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Siemens (1996). *SMART* and *SAINTE*. Siemens Analytical X-ray Instruments 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.