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Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.020\text{ \AA}$
 R factor = 0.058
 wR factor = 0.140
Data-to-parameter ratio = 16.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Bis(*N,N*-diethyldithiocarbamato- $\kappa^2\text{S,S}'$)iodo-
(1,10-phenanthroline)bismuth(III)

The title compound, $[\text{Bi}(\text{C}_5\text{H}_{10}\text{NS}_2)_2\text{I}(\text{C}_{12}\text{H}_8\text{N}_2)]$, is monomeric, with the Bi atom chelated by the S atoms of two *N,N*-diethyldithiocarbamate ligands and the N atoms of 1,10-phenanthroline. An iodo ligand completes the coordination, with the seven-coordinate Bi atom adopting a highly distorted capped octahedral geometry.

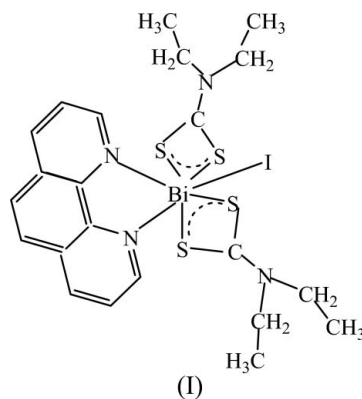
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Comment

The title compound, (I), is monomeric, with the Bi atom chelated by the S atoms of two *N,N*-diethyldithiocarbamate ligands and the N atoms of 1,10-phenanthroline. An iodo ligand completes the coordination environment of the seven-coordinate Bi atom (Fig. 1). The Bi atom is in a distorted octahedral environment, with atoms S3 and N3 in axial positions, and atoms S1, S2, S4 and I1 in the equatorial plane. The remaining N atom (N4) of the 1,10-phenanthroline ligand caps the S1/S4/N3 face of this octahedron, giving a highly distorted capped octahedral coordination geometry. One of the bidentate *N,N*-diethyldithiocarbamate ligands forms a significantly longer Bi–S bond [$\text{Bi1}-\text{S4} = 2.878(4)\text{ \AA}$] 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 chelating phenanthroline ligands are bonded to the Bi atom through two N atoms. The Bi1–N3 and Bi1–N4 distances fall in the same range as in other Bi/N complexes (Baraanyi *et al.*, 1977).



The ability of dithiocarbamate (dtc) binding to metals has been known for many years. It forms chelates with virtually all transition metals (Xu *et al.*, 2001). The bidentate anion is also well known as a bridge between two transition metal centers (Bardaji *et al.*, 1994). Water-soluble dialkyl dithiocarbamate complexes are known to be tested in various medical applications (Xie *et al.*, 1994). Dialkyl dithiocarbamate sodium salts are good extracting agents for many transition metals (Jiri,

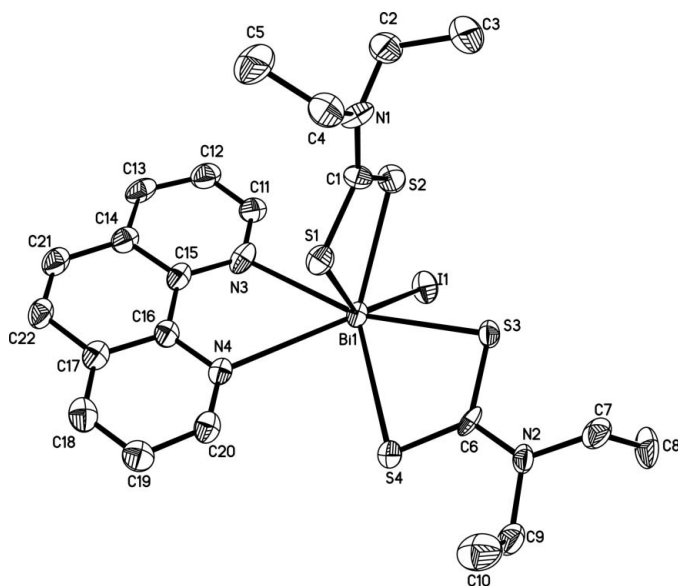


Figure 1
The structure of the title complex, showing 30% probability displacement ellipsoids and the atom-numbering schemes. H atoms have been omitted for clarity.

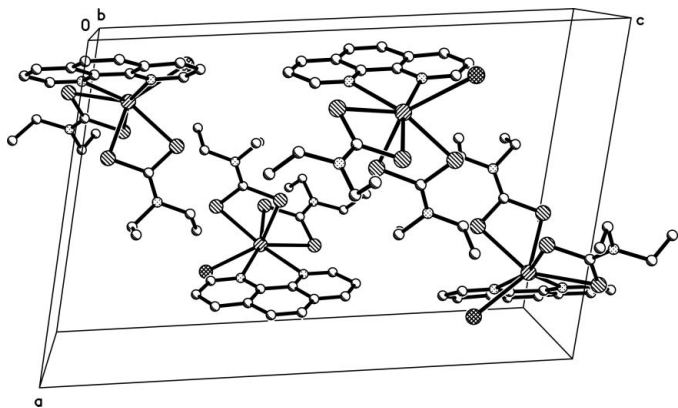


Figure 2
The crystal packing of the title complex. H atoms have been omitted.

1964), and are good floating agents of flotation concentrate for novel metal ores (Jian, 1981). Some dialkyl substituted dithiocarbamate salts have also shown interesting biological effects which include anti-alkylation (Gringeri *et al.*, 1988) or anti-HIV properties (Dupuy *et al.*, 1987). They are also used for the effective antidotes for cadmium intoxication (Gale *et al.*, 1984; Shinobu *et al.*, 1984). However, the chemistry of main-group metal complexes with dithiocarbamate has been scarcely studied, and few reports have appeared on the syntheses and structures of bismuth(III) complexes of dithiocarbamate (Yin *et al.*, 2003). As a continuation of our interest in sulfur-containing ligands, we report here the synthesis and structure of a novel bismuth(III) complex, (I).

Experimental

To a stirred solution of BiI₃ (0.0884 g, 0.15 mmol) in acetonitrile (*ca* 20 ml) were added phenanthroline (0.0297 g, 0.15 mmol) and sodium

N,N-diethyldithiocarbamate (0.0383 g, 0.17 mmol). An orange-coloured solution was obtained and, after concentration and cooling, small orange crystals of the title compound were obtained (0.1212 g). These were collected and dried in a vacuum [yield 80%, m.p. 583 K (decomposition)]. IR (KBr, cm⁻¹): ν 3060 (*w*), 1600 (*m*), 1510 (*s*), 1481 (*m*), 1429 (*m*), 1279 (*m*), 1107 (*s*), 949 (*m*), 849 (*m*), 415 (*w*). Analysis calculated for C₂₂H₂₈BiIN₄S₄: C 32.52, H 3.47, N 6.89, S 15.78%; found: C 32.58, H 3.30, N 6.93, S 15.84%.

Crystal data

[Bi(C₅H₁₀NS₂)₂I(C₁₂H₈N₂)]
M_r = 812.60
 Monoclinic, *P*2₁/*c*
a = 13.174 (6) Å
b = 10.506 (5) Å
c = 20.259 (8) Å
 β = 100.993 (7)°
V = 2753 (2) Å³
Z = 4

D_x = 1.961 Mg m⁻³
 Mo K α radiation
 Cell parameters from 2669 reflections
 θ = 2.5–22.5°
 μ = 7.85 mm⁻¹
T = 298 (2) K
 Block, orange
 0.41 × 0.38 × 0.34 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.056, *T_{max}* = 0.069
 13358 measured reflections

4740 independent reflections
 2671 reflections with *I* > 2 σ (*I*)
R_{int} = 0.110
 θ_{max} = 25.0°
h = -15 → 15
k = -12 → 12
l = -24 → 18

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.058
wR (*F*²) = 0.140
S = 1.00
 4740 reflections
 289 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0498P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 2.28 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -1.44 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Bi1–S3	2.681 (3)	Bi1–I1	3.1856 (13)
Bi1–S1	2.697 (4)	S1–C1	1.743 (14)
Bi1–S2	2.708 (4)	S2–C1	1.717 (13)
Bi1–N3	2.748 (11)	S3–C6	1.727 (15)
Bi1–S4	2.878 (4)	S4–C6	1.663 (15)
Bi1–N4	2.879 (11)		
S3–Bi1–S1	87.52 (11)	S1–Bi1–N4	74.4 (2)
S3–Bi1–S2	81.89 (12)	S2–Bi1–N4	123.6 (2)
S1–Bi1–S2	65.94 (11)	N3–Bi1–N4	58.5 (3)
S3–Bi1–N3	163.4 (3)	S4–Bi1–N4	77.1 (2)
S1–Bi1–N3	89.1 (2)	S3–Bi1–I1	85.74 (8)
S2–Bi1–N3	81.9 (3)	S1–Bi1–I1	146.40 (8)
S3–Bi1–S4	63.51 (11)	S2–Bi1–I1	80.52 (8)
S1–Bi1–S4	93.66 (12)	N3–Bi1–I1	88.1 (2)
S2–Bi1–S4	140.97 (12)	S4–Bi1–I1	112.36 (10)
N3–Bi1–S4	133.0 (3)	N4–Bi1–I1	130.43 (19)
S3–Bi1–N4	135.4 (2)		

All H atoms were positioned geometrically and treated as riding on their parent atoms [*C*–H = 0.93 Å and *U_{iso}* = 1.2*U_{eq}* (C) for aromatic, *C*–H = 0.97 Å and *U_{iso}* = 1.2*U_{eq}* (C) for CH₂, and *C*–H = 0.96 Å and *U_{iso}* = 1.5*U_{eq}* (C) for CH₃ H atoms]. The highest peak and deepest hole in the final difference map were 1.01 and 0.96 Å, respectively, 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*.

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