

**Feng Li, Handong Yin\* and Daqi Wang**

College of Chemistry and Chemical Engineering,  
 Liaocheng University, Shandong 252059,  
 People's Republic of China

Correspondence e-mail: handongyin@sohu.com

**Key indicators**

Single-crystal X-ray study  
 T = 298 K  
 Mean  $\sigma(C-C)$  = 0.020 Å  
 Disorder in main residue  
 R factor = 0.049  
 wR factor = 0.128  
 Data-to-parameter ratio = 16.5

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

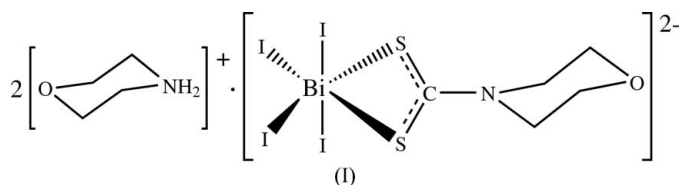
**Bis(morpholinium) tetraiodo(morpholine-4-carbodithioato- $\kappa^2S,S'$ )bismuth(III)**

Received 14 December 2005  
 Accepted 16 February 2006

The crystal structure of the title compound,  $(C_4H_{10}NO)_2[Bi(C_5H_8NOS_2)_4I_4]$ , the  $Bi^{III}$  complex anions and morpholinium cations. The  $Bi^{III}$  ion is coordinated by four  $I^-$  anions and two S atoms from a morpholine-4-carbodithioate (mcd) dianion with a distorted octahedral coordination geometry. In the anion, Bi, the  $CS_2$  atoms, N, O and two I atoms are located on a mirror plane; the morpholine C atoms of the mcd ligand are disordered on both sides of the mirror plane.  $N-H \cdots I$  hydrogen bonding between the morpholinium cation and the  $Bi^{III}$  complex stabilize the crystal structure.

**Comment**

Some dialkyl-substituted dithiocarbamate salts have shown interesting biological effects (Gringeri *et al.*, 1988). They are also used as effective antidotes for cadmium intoxication (Köpf-Maier & Klapötke, 1988). The chemistry of main-group metal complexes with dithiocarbamate has been studied previously (Yin *et al.*, 2003). We report here the structure of the title  $Bi^{III}$  complex, (I), which contains a morpholine-4-carbodithioate (mcd) ligand.



The crystal structure of (I) consists of tetraiodo(morpholine-4-carbodithioato)bismuth(III) dianions and morpholinium cations (Fig. 1). The  $Bi^{III}$  ion is coordinated by four  $I^-$  anions and two S atoms from a mcd dianion with a distorted octahedral coordination geometry. Within the  $Bi^{III}$  complex, while atoms Bi1, C1, S1, S2, O1, N1, I2 and I3 are located on a mirror plane, the morpholine C atoms are disordered on both sides of the mirror plane. The large I2—Bi1—I3 bond angle (Table 1) indicates the distortion of the coordination geometry from a normal octahedron. The morpholine group of the mcd ligand and free morpholinium display chair conformations.  $N-H \cdots I$  hydrogen bonding between the morpholinium cation and the  $Bi^{III}$  complex (Table 2) stabilizes the crystal structure of (I).

**Experimental**

Morpholinium (morpholine-4-carbodithioate) (0.30 mmol) was added to an acetonitrile solution (20 ml) of  $BiI_3$  (0.25 mmol). The solution was stirred for 1 h at 303 K. An orange-red solution was obtained and then filtered. The solvent was gradually removed by

evaporation under vacuum until a solid product was obtained. Single crystals of (I) were obtained by recrystallization from an acetonitrile solution [yield 80%; m.p. 485–488 K (decomposition)]. Analysis calculated (%) for  $C_{13}H_{28}Bi_4N_3O_3S_2$ : C 14.79, H 2.67, N 3.98, S 6.08; found (%): C 14.83, H 2.70, N 3.94, S 6.05.

#### Crystal data

$(C_4H_{10}NO)_2[Bi(C_5H_8NOS_2)_4]$   
 $M_r = 1055.08$   
 Orthorhombic,  $Pnma$   
 $a = 9.3320$  (19) Å  
 $b = 14.561$  (3) Å  
 $c = 19.901$  (4) Å  
 $V = 2704.2$  (10) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 2.592$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 3265 reflections  
 $\theta = 2.4$ – $24.4^\circ$   
 $\mu = 11.26$  mm<sup>-1</sup>  
 $T = 298$  (2) K  
 Block, orange-red  
 $0.25 \times 0.24 \times 0.23$  mm

#### Data collection

Siemens SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.068$ ,  $T_{\max} = 0.075$   
 13326 measured reflections

2449 independent reflections  
 1731 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.111$   
 $\theta_{\text{max}} = 25.0^\circ$   
 $h = -10 \rightarrow 11$   
 $k = -13 \rightarrow 17$   
 $l = -23 \rightarrow 23$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.049$   
 $wR(F^2) = 0.128$   
 $S = 1.04$   
 2449 reflections  
 148 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0326P)^2 + 20.8113P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 2.09$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -2.09$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Bi1–I1	3.0631 (11)	Bi1–S2	2.701 (5)
Bi1–I2	3.2539 (13)	S1–C1	1.694 (17)
Bi1–I3	3.2099 (15)	S2–C1	1.700 (15)
Bi1–S1	2.648 (4)		
I1 <sup>i</sup> –Bi1–I1	173.33 (4)	I1–Bi1–I3	86.69 (2)
S1–Bi1–S2	66.61 (13)	S1–Bi1–I2	142.19 (10)
S1–Bi1–I1	88.96 (2)	S2–Bi1–I2	75.57 (9)
S2–Bi1–I1	92.49 (2)	I1–Bi1–I2	92.76 (2)
S1–Bi1–I3	78.10 (10)	I2–Bi1–I3	139.71 (4)
S2–Bi1–I3	144.72 (9)		

Symmetry code: (i)  $x, -y + \frac{1}{2}, z$ .

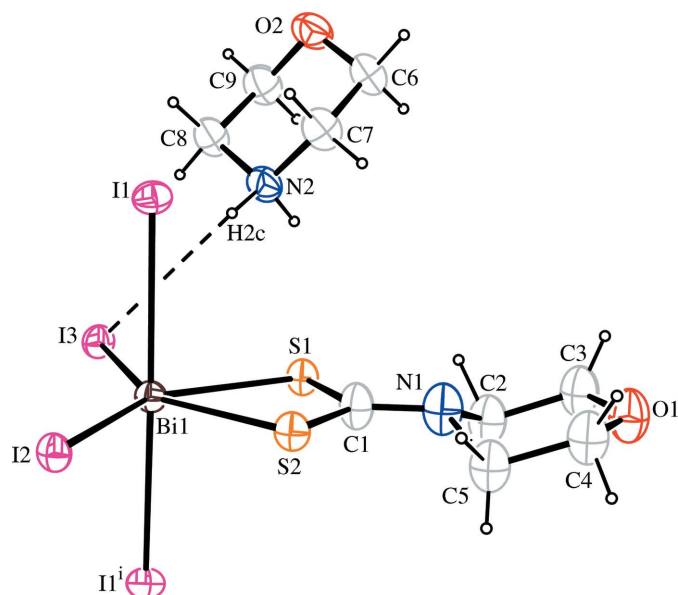
**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2–H2A $\cdots$ I3	0.90	3.03	3.665 (10)	129
N2–H2B $\cdots$ I2 <sup>ii</sup>	0.90	2.75	3.636 (12)	169

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

H atoms were positioned geometrically and treated as riding on their parent atoms, with C–H = 0.97 Å, N–H = 0.90 Å and  $U_{\text{iso}}(\text{H}) =$



**Figure 1**

The structure of (I), shown with 30% probability displacement ellipsoids (arbitrary spheres for H atoms) [symmetry code: (i)  $x, \frac{1}{2} - y, z$ ]. The dashed line indicates a hydrogen bond

$1.2U_{\text{eq}}(\text{carrier})$ . The highest peak and deepest hole in the final difference Fourier map are 0.91 and 0.92 Å, respectively, from Bi1. Atoms O1, C2, C3, C4 and C5 of morpholine ring are disordered over two positions each, with different orientations; all atoms therefore appeared in both positions with different site-occupancy factors. The occupancies were fixed at 0.52 and 0.48 for all five atoms in the final stage of the refinement.

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.

We acknowledge the financial support of the Shandong Province Science Foundation and the State Key Laboratory of Crystalline Materials, Shandong University, China.

#### References

- Gringeri, A., Keng, P. C. & Borch, R. F. (1988). *Cancer Res.* **48**, 5708–5715.  
 Köpf-Maier, P. & Klapötke, T. (1988). *Inorg. Chim. Acta*, **152**, 49–53.  
 Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.  
 Sheldrick, G. M. (1997a). SHELXS97 and SHELXL97. University of Göttingen, Germany.  
 Sheldrick, G. M. (1997b). SHELXTL. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Siemens (1996). SMART and SAINT. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Yin, H.-D., Wang, C.-H. & Xing, Q.-J. (2003). *Chin. J. Inorg. Chem.* **19**, 955–958.