metal-organic papers

1,10-Phenanthrolinium tetraiodo(1,10-phenanthroline-κ^2N,N')bismuthate(III) 1,10-phenanthroline

Feng Li, Han-Dong Yin,* Jun Zhai and Da-Qi Wang

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

Correspondence e-mail: handongyin@sohu.com

Key indicators

The asymmetric unit of the title compound, $(C_{12}H_9N_2)$-$[BiI_4(C_{12}H_8N_2)]\cdot C_{12}H_8N_2$, comprises a 1,10-phenanthrolinium cation and a tetraiodo(1,10-phenanthroline)bismuthate(III) anion, together with a neutral 1,10-phenanthroline molecule. The Bi^{III} ion adopts a distorted octahedral coordination geometry, binding to the two N atoms of a chelating 1,10-phenanthroline ligand and four iodide ions. N—H⋯N and C—H⋯I hydrogen bonding between the 1,10-phenanthroline molecule, the 1,10-phenanthrolinium cation and the Bi^{III} complex cation stabilize the crystal structure.

Comment

The coordination chemistry of bismuth(III) is relatively scarcely studied. Nevertheless, a number of adducts formed by nitrogen-containing ligands with bismuth(III) salts have been reported (Summers *et al.*, 1994). More recently, however, bismuth(III) coordination chemistry has gained more prominence, particularly in light of the role of bismuth compounds in ^{212}Bi isotope therapy in cancer research (Sun *et al.*, 1997) and the use of bismuth complexes in the treatment of peptic ulcers (Sun *et al.*, 1997; Baxter, 1992). In particular, the interaction of bismuth(III) salts with chelating nitrogen ligands has been actively studied (Hancock *et al.*, 1993). The affinity of bismuth(III) salts for chelating nitrogen donors has been reported for a range of ligands including glycine and a number of bidentate nitrogen donors; most of the coordination compounds in the literature are of this type (Hancock *et al.*, 1993). More recently, the interaction of bismuth(III) halides with 1,10-phenanthroline (phen) has revealed some very interesting coordination chemistry for this heavy metal with varying degrees of agglomeration. Furthermore, in the phen complexes of $Ln(NO_3)_3$ (Ln = La and Lu) high coordination numbers dominate (Semenova *et al.*, 1996). Since the ionic radius of Bi^{3+} is very similar to that of La^{3+} for the same coordination number (Shannon, 1976), similar compounds may be expected.

As a continuation of our interest in nitrogen-containing ligands, we report here the synthesis and structure of (I), a new bismuth(III) complex with 1,10-phenanthroline, $[BiI_4(C_{12}H_8N_2)](C_{12}H_7N_2)$, cocrystallized with a molecule of 1,10-phenanthroline (Fig. 1 and Table 1).

The asymmetric unit of (I) comprises a 1,10-phenanthrolinium cation and the tetraiodo(1,10-phenanthroline-κ^2N,N')bismuthate(III) anion together with a neutral 1,10-phenanthroline molecule. The Bi^{III} ion adopts a distorted octahedral coordination geometry, binding to the two N atoms of a chelating 1,10-phenanthroline ligand and four iodide ions. Atoms I1 and I2 adopt axial positions in the coordination of

the Bi^{III} atom, with I3, I4, N1 and N2 in the equatorial plane. The I1—Bi1—I2 bond angle (Table 1) indicates a significant distortion from normal octahedral geometry.
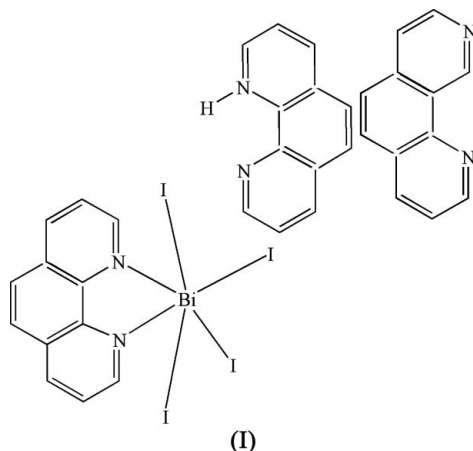
(I)

N—H···N and C—H···I hydrogen bonding between the 1,10-phenanthroline molecule, the 1,10-phenanthrolinium cation and the Bi^{III} complex stabilizes the crystal structure, forming a three-dimensional network (Fig. 2 and Table 2).

Experimental

A stirred solution of BiI$_3$ (0.25 mmol) in acetonitrile (20 ml) and 1,10-phenanthroline (0.25 mmol) was heated at 333 K. An orange-coloured solution was obtained, and after concentration and cooling, small orange–red crystals (0.212 g) were obtained. These were collected and dried in vacuum [yield 80%, m.p. 405–408 K (decomposition)]. Analysis calculated for C$_{36}$H$_{25}$BiI$_4$N$_6$ (Mr = 1258.20): C 34.36, H 2.00, N 6.68%; found: C 34.77, H 2.13, N 6.42%.

Crystal data

(C$_{12}$H$_9$N$_2$)[BiI$_4$(C$_{12}$H$_8$N$_2$)]·C$_{12}$H$_8$N$_2$	Z = 4
M$_r$ = 1258.20	D$_x$ = 2.257 Mg m^{-3}
Monoclinic, P2$_1$/c	Mo Kα radiation
a = 14.732 (3) Å	μ = 8.13 mm^{-1}
b = 17.414 (4) Å	T = 298 (2) K
c = 15.424 (3) Å	Block, orange–red
β = 110.629 (3)°	0.30 × 0.28 × 0.26 mm
V = 3703.1 (13) Å^3	

Data collection

Siemens SMART CCD area-detector diffractometer	19288 measured reflections
φ and ω scans	6517 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	4042 reflections with I > 2σ(I)
T$_{min}$ = 0.194, T$_{max}$ = 0.226	R$_{int}$ = 0.073
(expected range = 0.104–0.121)	θ$_{max}$ = 25.0°

Refinement

Refinement on F^2	w = 1/[σ^2(F$_o^2$) + (0.0264P)^2 + 15.5137P]
R[F^2 > 2σ(F^2)] = 0.042	where P = (F$_o^2$ + 2F$_c^2$)/3
wR(F^2) = 0.104	(Δ/σ)$_{max}$ < 0.001
S = 1.02	Δρ$_{max}$ = 1.84 e Å^{-3}
6517 reflections	Δρ$_{min}$ = −2.01 e Å^{-3}
424 parameters	
H-atom parameters constrained	
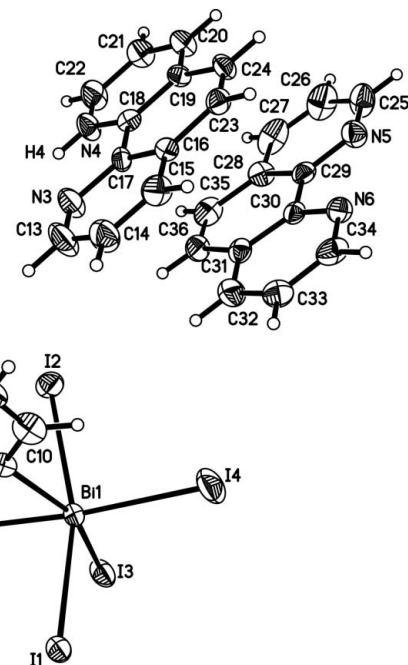
Figure 1
The asymmetric unit of the title complex, showing 30% probability displacement ellipsoids and the atom-numbering scheme.
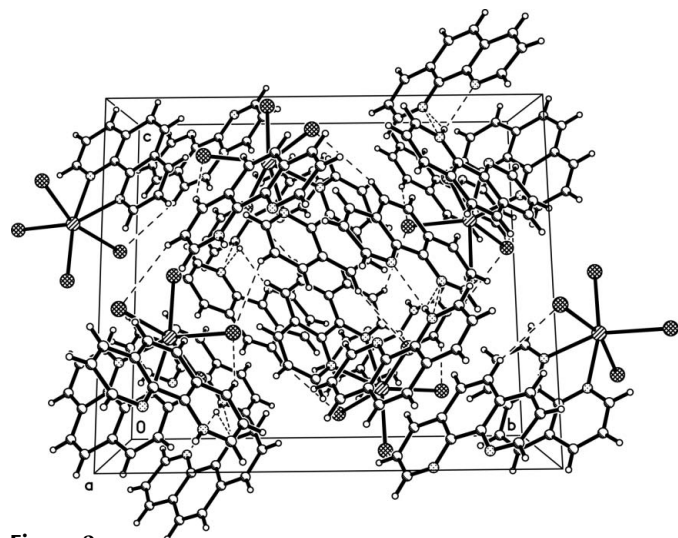
Figure 2
Crystal packing for (I), with hydrogen bonds drawn as dashed lines.

Table 1
Selected geometric parameters (Å, °).

Bi1—N1	2.530 (8)	Bi1—I4	2.9953 (11)
Bi1—N2	2.534 (8)	Bi1—I3	3.0554 (10)
Bi1—I2	2.9886 (10)	Bi1—I1	3.1039 (9)
N1—Bi1—N2	65.3 (3)	I2—Bi1—I3	95.63 (3)
N1—Bi1—I2	84.19 (19)	I4—Bi1—I3	101.29 (3)
N2—Bi1—I2	79.17 (18)	N1—Bi1—I1	82.07 (19)
N1—Bi1—I4	165.5 (2)	N2—Bi1—I1	83.92 (18)
N2—Bi1—I4	100.44 (19)	I2—Bi1—I1	161.55 (3)
I2—Bi1—I4	95.85 (3)	I4—Bi1—I1	94.43 (3)
N1—Bi1—I3	93.1 (2)	I3—Bi1—I1	97.34 (3)
N2—Bi1—I3	158.06 (19)		

Table 2
Hydrogen-bond geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N4—H4$\cdots$N6^{i}	0.86	2.23	2.970 (13)	144
N4—H4$\cdots$N5^{i}	0.86	2.27	2.861 (13)	126
C2—H2$\cdots$I3^{i}	0.93	3.16	3.873 (12)	135
C11—H11$\cdots$I2^{ii}	0.93	3.19	3.960 (12)	141
C35—H35$\cdots$I1^{iii}	0.93	3.25	4.137 (13)	161

Symmetry codes: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x + 1, -y, -z$; (iii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$.

All H atoms were positioned geometrically (C—H = 0.93 Å and N—H = 0.86 Å) and refined as riding, with $U_{iso}(H) = 1.2U_{eq}$(carrier). The highest residual density peak and depest hole are 1.01 and 1.02 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*.

References

Baxter, G. F. (1992). *Chem. Br.* **28**, 445–458.
Hancock, R. D., Cukrowski, I., Baloyi, J. & Summers, S. P. (1993). *J. Chem. Soc. Dalton Trans.* pp. 2895–2901.
Semenova, L. I., Skelton, B. W. & White, A. H. (1996). *Aust. J. Chem.* **49**, 997–1004.
Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.
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.
Summers, S. P., Abboud, K. A., Farrah, S. R. & Palenik, G. J. (1994). *Inorg. Chem.* **33**, 88–92.
Sun, H., Li, H. & Sadler, P. J. (1997). *Chem. Ber.* **130**, 669–702.