

# Syntheses and Characterization of Two New Mixed-Ligand Bismuth(III) Complexes, Crystal Structure of $[\text{Bi}(\text{phen})_2(\text{NO}_3)(\text{NCS})_2(\text{MeOH})]$

Ali Morsali

Department of Chemistry, School of Sciences, Tarbiat Modarres University,  
P. O. Box 14155-4838, Tehran, Iran

Reprint requests to Dr. Ali Morsali. Fax: +98 21 8006544. E-mail: morsali\_a@yahoo.com

Z. Naturforsch. **60b**, 389 – 392 (2005); received September 13, 2004

Complexes  $[\text{Bi}(\text{phen})_2(\text{NO}_3)(\text{NCS})_2(\text{MeOH})]$  and  $[\text{Bi}(\text{phen})_2(\text{NO}_3)_2(\text{NCS})]$  have been synthesized and characterized by their IR spectra and elemental analyses. The structure of the  $[\text{Bi}(\text{phen})_2(\text{NO}_3)(\text{NCS})_2(\text{MeOH})]$  complex has been confirmed by X-ray crystallography. The Bi atoms are unsymmetrically eight-coordinated,  $\text{N}_6\text{O}_2$ . The arrangement of the ligands does not show a gap in the coordination geometry around the Bi(III) ion, indicating that its lone pair of electrons is not active. The thiocyanate ligands are coordinated to the bismuth atom *via* the nitrogen atom. There is  $\pi$ - $\pi$  stacking interactions between the parallel aromatic rings belonging to adjacent chains.

**Key words:** Bismuth(III) Complexes, Crystal Structure, Mixed-Ligand Complexes,  $\pi$ - $\pi$  Stacking

## Introduction

Building new molecular species and address their architectures in order to control their physical and structural properties has been a topic for many research groups. Bismuth(III) complexes are of interest in the treatment of gastric ulcer [1–3]. The coordination chemistry of bismuth(III) is disproportionately sparse when compared with that of other metals [4–9]. Typically, mixed-ligand Bi(III) complexes have rarely been reported until recently. In the present paper, we report the syntheses and characterization of two new mixed-ligand bismuth(III) complexes with the aromatic  $\text{N,N}'$ -bidentate ligand 1,10-phenanthroline (phen),  $[\text{Bi}(\text{phen})_2(\text{NO}_3)_m(\text{NCS})_n]$  ( $m, n = 1$  and  $2$ ).

## Experimental Section

### Physical property measurements

IR spectra were recorded as nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected.

### Preparation of $[\text{Bi}(\text{phen})_2(\text{NO}_3)(\text{NCS})_2(\text{MeOH})]$

1,10-Phenanthroline (0.2 g, 1 mmol) was placed in one arm of a branched tube and mixtures of bismuth(III) nitrate (0.36 g, 1 mmol) and potassium thiocyanate (0.196 g,

2 mmol) in the other. Methanol was carefully added to fill both arms, then the tube was sealed and the ligand-containing arm immersed in a bath at  $60^\circ\text{C}$  while the other was at ambient temperature. After 10 d, yellow-white crystals, (m.p.  $207^\circ\text{C}$ ) had deposited in the cooler arm, which were filtered off, washed with acetone and diethylether and dried in air (0.504 g, yield 60%).  $\text{C}_{27}\text{H}_{20}\text{N}_7\text{O}_4\text{S}_2\text{Bi}$ : calcd. C 38.50, H 2.38, N 11.64; found: C 38.65, H 2.29, N 11.31. IR ( $\text{cm}^{-1}$ ) selected bands:  $\nu = 720(\text{s}), 850(\text{s}), 1380(\text{s}), 1590(\text{s}), 1648(\text{s}), 2025(\text{vs}), 3140(\text{w})$ .

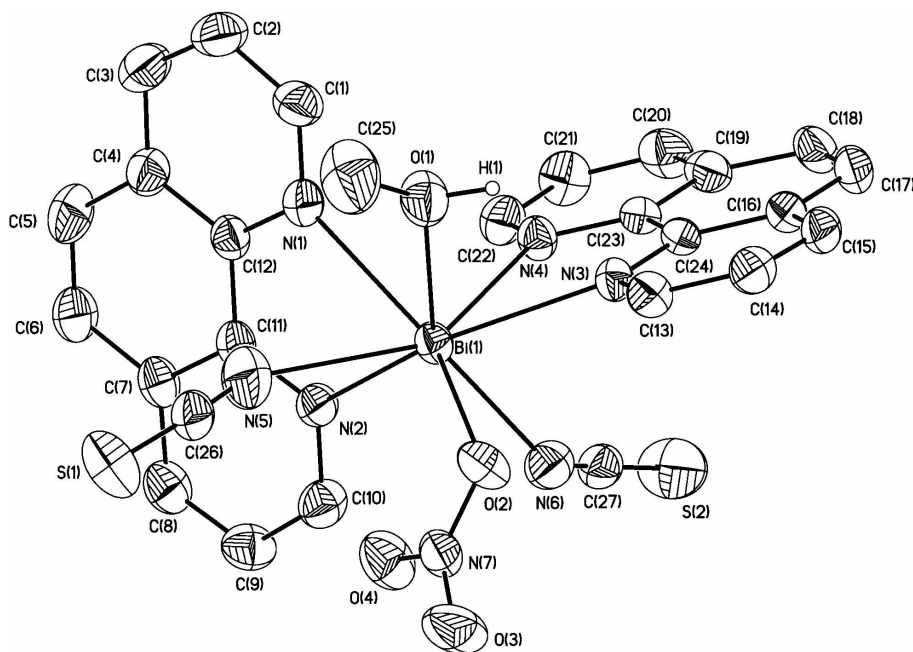
### Preparation of $[\text{Bi}(\text{phen})_2(\text{NO}_3)_2(\text{NCS})]$

1,10-Phenanthroline (0.2 g, 1 mmol) was placed in one arm of a branched tube and a mixture of bismuth(III) nitrate (0.36 g, 1 mmol) and potassium thiocyanate (0.097 g, 1 mmol) in the other. Methanol was carefully added to fill both arms, then the tube was sealed and the ligand-containing arm immersed in a bath at  $60^\circ\text{C}$ , while the other was at ambient temperature. After 10 d, yellow crystals (m.p.  $211^\circ\text{C}$ ) had deposited in the cooler arm, which were filtered off, washed with acetone and diethylether and dried in air (0.325 g, yield 40%).  $\text{C}_{25}\text{H}_{16}\text{N}_7\text{O}_6\text{SBi}$ : calcd. C 36.88, H 1.97, N 12.05; found C 36.65, H 1.90, N 12.31. IR ( $\text{cm}^{-1}$ ) selected bands:  $\nu = 720(\text{s}), 840(\text{s}), 1375(\text{vs}), 1590(\text{s}), 1648(\text{s}), 2020(\text{s}), 3140(\text{w})$ .

### X-ray crystallography

### Crystal data and refinement details

$\text{C}_{27}\text{H}_{20}\text{BiN}_7\text{O}_4\text{S}_2$ ,  $M = 779.60$ , triclinic, space group  $P\bar{1}$ ,

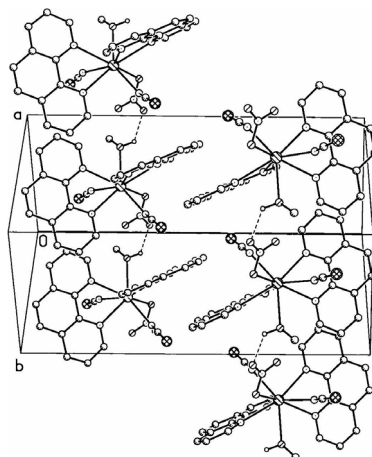
Fig. 1. ORTEP diagram of  $[\text{Bi}(\text{phen})_2(\text{NO}_3)(\text{NCS})_2(\text{MeOH})]$ .Table 1. Selected bond lengths (Å) and angles (°) for the  $[\text{Bi}(\text{phen})_2(\text{NO}_3)(\text{NCS})_2(\text{MeOH})]$ .

Bi(1)-N(6)	2.386(4)	Bi(1)-N(4)	2.523(3)
Bi(1)-N(2)	2.531(3)	Bi(1)-N(3)	2.550(3)
Bi(1)-O(2)	2.564(3)	Bi(1)-O(1)	3.622(3)
Bi(1)-N(1)	2.624(3)	Bi(1)-N(5)	2.669(5)
N(6)-Bi(1)-N(4)	74.05(12)	N(6)-Bi(1)-N(2)	79.86(12)
N(4)-Bi(1)-N(2)	87.62(11)	N(6)-Bi(1)-N(3)	77.95(12)
N(4)-Bi(1)-N(3)	65.29(11)	N(2)-Bi(1)-N(3)	148.75(11)
N(6)-Bi(1)-O(2)	77.73(12)	N(4)-Bi(1)-O(2)	134.48(10)
N(2)-Bi(1)-O(2)	121.59(11)	N(3)-Bi(1)-O(2)	74.44(10)
N(6)-Bi(1)-O(1)	143.33(12)	N(4)-Bi(1)-O(1)	98.06(11)
N(2)-Bi(1)-O(1)	136.38(10)	N(3)-Bi(1)-O(1)	66.55(10)
O(2)-Bi(1)-O(1)	84.01(11)	N(6)-Bi(1)-N(1)	132.02(12)
N(4)-Bi(1)-N(1)	73.78(11)	N(2)-Bi(1)-N(1)	64.19(11)
N(3)-Bi(1)-N(1)	118.02(11)	O(2)-Bi(1)-N(1)	148.02(11)
O(1)-Bi(1)-N(1)	75.95(11)	N(6)-Bi(1)-N(5)	129.06(15)
N(4)-Bi(1)-N(5)	146.43(13)	N(2)-Bi(1)-N(5)	75.46(14)
N(3)-Bi(1)-N(5)	135.79(14)	O(2)-Bi(1)-N(5)	78.51(14)
O(1)-Bi(1)-N(5)	76.49(14)	N(1)-Bi(1)-N(5)	72.77(14)

$a = 7.6122(15)$ ,  $b = 9.4769(19)$ ,  $c = 19.712(4)$  Å,  $\alpha = 92.19(3)$ ,  $\beta = 93.23(3)$ ,  $\gamma = 109.29(3)^\circ$ ,  $V = 1337.6(5)$  Å<sup>3</sup>,  $D_c(Z = 4)$  1.936 g/cm<sup>3</sup>,  $F(000)$  756. Specimen:  $0.3 \times 0.2 \times 0.05$  mm;  $T_{\text{max,min}}$  0.922, 0.590,  $N$  6270;  $N_0$  5821,  $R$  0.0247;  $R_w$  0.0582.

#### Determination of the structure

X-ray measurements were made at 293(2) K using a Siemens R3m/V diffractometer. The intensity data were col-

Fig. 2. The unit cell of  $[\text{Bi}(\text{phen})_2(\text{NO}_3)(\text{NCS})_2(\text{MeOH})]$ .

lected within the range  $2.29 \leq \theta \leq 25.06^\circ$  using graphite-monochromated Mo- $K_\alpha$  radiation ( $\lambda = 0.71073$  Å). Accurate unit cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. Intensities of 5264 reflections were measured, 3597 of which were unique. The structure was solved by direct methods and refined by full-matrix least-squares techniques on  $F^2$ .

The positions of hydrogen atoms were calculated at idealized geometrical position and included in the structure-factor calculation as fixed-atom contributions. Corrections for Lorentz and polarization effects as well as a semi-

empirical absorption correction were applied. All calculations were carried out with a PDP-11/23+ computer using the SDP-PLUS program package [10–11].

Selected bond lengths and angles are given in Table 1. ORTEP diagrams and a perspective view of the packing in the unit cell are shown in Figures 1 and 2.

## Discussion

### Synthesis

Reactions between the “phen” ligand and mixtures of bismuth(III) nitrate and potassium thiocyanate in ratios 1:2 or 1:1 by diffusion along a thermal gradient in methanol solution (the branched tube method) provided crystalline materials analyzing as  $[\text{Bi}(\text{phen})_2(\text{NO}_3)(\text{NCS})_2(\text{MeOH})]$  and  $[\text{Bi}(\text{phen})_2(\text{NO}_3)_2(\text{NCS})]$ , respectively. The IR spectra of the complexes show  $\nu(\text{NO}_3)$  at *ca.*  $1380\text{ cm}^{-1}$  and  $\nu(\text{SCN})$  at *ca.*  $2020\text{--}2025\text{ cm}^{-1}$ . This is very similar with the lead(II) complexes, for example  $[\text{Pb}(\text{phen})_2(\text{NO}_3)(\text{NCS})]$  ( $2020\text{ cm}^{-1}$ ) [12],  $[\text{Pb}(\text{phen})(\text{O}_2\text{CCH}_3)(\text{NCS})]$  ( $2040\text{ cm}^{-1}$ ) [13] and  $[\text{Pb}(\text{phen})_2(\text{O}_2\text{CCH}_3)(\text{NCS})]$  ( $2040\text{ cm}^{-1}$ ) [14] but a significant change from mercury(II) complexes, for example  $[\text{Hg}(\text{bq})(\text{SCN})_2]$  ( $2070\text{ cm}^{-1}$ ) [15] and  $[\text{Hg}(\text{DABTZ})(\text{SCN})_2]$  ( $2065\text{ cm}^{-1}$ ) [16]. It suggests that the thiocyanate anions are coordinated *via* the nitrogen atoms. Attempts to isolate mixed-ligand complexes with perchlorate and acetate ligands  $\{[(\text{phen})\text{Bi}(\text{NO}_3)_n(\text{ClO}_4)_m](n+m=3)\}$  and  $\{(\text{phen})\text{Bi}(\text{NO}_3)_n(\text{CH}_3\text{COO})_m\}$  were not successful, and each time the  $\text{Bi}(\text{phen})_2(\text{NO}_3)_3$  compound was isolated.

### Crystal structure of $[\text{Bi}(\text{phen})_2(\text{NO}_3)(\text{NCS})_2(\text{MeOH})]$

Determination of the structure of the  $[\text{Bi}(\text{phen})_2(\text{NO}_3)(\text{NCS})_2(\text{MeOH})]$  by X-ray crystallography showed the complex in the solid state (Fig. 3) to be a monomeric species with various similarities to the monomeric structure of  $[\text{Bi}(\text{phen})_2(\text{NO}_3)_3]$  [6]. The coordination number is eight, the Bi atom being coordinated by eight donor atoms from four different ligands (two 1,10-phenanthroline, two thiocyanate, one nitrate and one methanol ligands). The resulting geometry around the Bi atom is distorted tricapped trigonal prismatic. The arrangement of the ligands suggests no gap in the geometry around the bismuth(III) ion, suggesting that the lone pair of electrons on the bismuth(III) is stereo-inactive. The coordinated

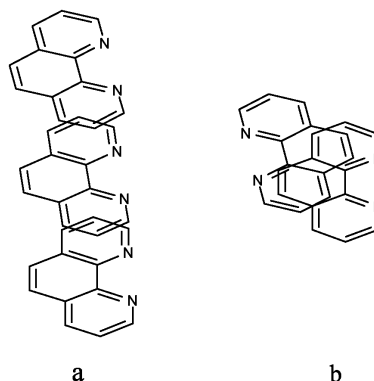


Fig. 3. Projection of nearest neighbor pairs in the  $\pi$ - $\pi$  stacks of heteroaromatic bases in the Bi(III) complex containing the “phen” ligand. (a): Intra-chain edge-to-face interactions between the phen ligands and (b): Inter-chain face-to-face  $\pi$ -stacking.

methanol molecule is involved in hydrogen bonding acting as hydrogen-bond donor with one oxygen atom of the nitrate anion as the hydrogen-bond acceptor (Fig. 2). This intermolecular hydrogen bonding interaction links the molecules into chains along the *a* axis.

There are  $\pi$ - $\pi$  stacking [4–5] interactions between the aromatic rings belonging to adjacent chains of bismuth(III) complex, as shown in Figures 2 and 3. With the mean molecular planes close to parallel and separated by a distance of  $\sim 3.5\text{ \AA}$ , this resembles the planes in graphite.

Parallel arrays of the planes of the aromatic moieties indicate that interactions in this complex are of the inter-chain “ $\pi$ -stacking” and intra-chain “edge-to-face” type of “phen” ligands [17–19]. Projection of the structure perpendicular to the ring plane shows the overall form of a “slipped” stacking [17–19], which is at least qualitatively understandable in terms of optimizing approaches between groups of opposite charges [20]. It has been shown that [20–21] electron-deficient aromatic groups interact most strongly with electron-rich aromatic groups. Hence, it can be expected that in the present crystal the electron-poor pyridyl rings will interact with the less electron-poor phenyl rings (Fig. 3b).

Thus two factors, hydrogen bonding and  $\pi$ - $\pi$  stacking, control the coordination mode of this complex.

In mercury(II) complexes the thiocyanate ions are coordinated *via* the S atom, as in the recently reported  $[\text{Hg}(\text{DPBTZ})(\text{SCN})_2]$  (DPBTZ = 2,2'-diphenyl-4,4'-bithiazole) [23],  $[\text{Hg}(\text{DABTZ})(\text{SCN})_2]$

(DABTZ = 2,2'-diamino-4,4'-bithiazole) [16], [Hg(L)(SCN)<sub>2</sub>] (L = N-(2-pyridyl)carbonylaniline) [24] and [Hg(bq)(SCN)<sub>2</sub>] (bq = 2,2'-biquinoline) [15] complexes. In the present bismuth complex like in the reported lead(II) complexes [Pb(phen)<sub>2</sub>(NO<sub>3</sub>)(NCS)] [12] and [Pb(phen)(O<sub>2</sub>CCH<sub>3</sub>)(NCS)] [13], the thiocyanate ions are coordinated *via* the N atom. This shows that the Bi<sup>+3</sup> ion is harder than the Hg<sup>+2</sup> ion. Indeed, bismuth(III) like lead(II) is a borderline metal ion which has a higher affinity for nitrogen donors as compared to sulfur donors.

#### Supplementary material

Complete bond lengths and angles, co-ordinates and displacement parameters have been deposited at Cambridge Crystallography Data Centre. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 183935 for [Bi(phen)<sub>2</sub>(NO<sub>3</sub>)(NCS)<sub>2</sub>(MeOH)].

#### Acknowledgements

Support of this investigation by Tarbiat Modarres University (TMU) is gratefully acknowledged.

- [1] G. A. Bowmaker, F. M. M. Hannaway, P. C. Junk, A. M. Lee, B. W. Skelton, A. H. White, *Aust. J. Chem.* **51**, 325 (1998).
- [2] R. D. Hancock, I. Cukrowski, J. Baloyi, J. Mashishi, *J. Chem. Soc. Dalton Trans.* 2895 (1993).
- [3] P. J. Sadler, H. Li, H. Sun, *Coord. Chem. Rev.* **689**, 185 (1999).
- [4] N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, pp. 235–236, Pergamon Press, Oxford (1986).
- [5] G. Wilkinson, R. D. Gillard, J. McCleverty (eds): *Comprehensive Coordination Chemistry*, Vol. 1–7, Pergamon Press, Oxford (1987).
- [6] L. J. Barbour, S. J. Belfield, P. C. Junk, and M. K. Smith, *Aust. J. Chem.* **51**, 337 (1998).
- [7] A. Bondi, *J. Chem. Phys.* **68**, 441 (1964).
- [8] R. D. Rogers, A. H. Bond, S. Aguinaga, *J. Am. Chem. Soc.* **114**, 2960 (1992).
- [9] R. D. Rogers, A. H. Bond, S. Aguinaga, A. Reyes, *J. Am. Chem. Soc.* **114**, 2967 (1992).
- [10] G. Ferguson, C. Glidewell, E. S. Lavender, *Acta Crystallogr.* **55B**, 591 (1999).
- [11] G. M. Sheldrick, *SHLXTL-97 V5.10*, 1997, Bruker AXS Inc., Madison, WI-53719, USA (1997).
- [12] A. R. Mahjoub, A. Morsali, *Z. Kristallogr. NCS* **216**, 601 (2001).
- [13] A. R. Mahjoub, A. Morsali, *Polyhedron* **21**, 197 (2002).
- [14] A. Morsali, A. R. Mahjoub, S. Janitabar Darzi, M. J. Soltanian, *Z. Anorg. Allg. Chem.* **629**, 2599 (2003).
- [15] A. Morsali, A. R. Mahjoub, A. Ramazani, *J. Coord. Chem.* **57**, 347 (2004).
- [16] A. Morsali, M. Payheghader, M. R. Poorheravi, F. Jamali, *Z. Anorg. Allg. Chem.* **629**, 1627 (2003).
- [17] I. G. Dance, M. L. Scudder, *J. Chem. Soc., Dalton Trans.* 3755 (1996).
- [18] Z.-H. Liu, C.-Y. Duan, J.-H. Li, Y.-J. Liu, Y.-H. Mei, X.-Z. You, *New J. Chem.* **24**, 1057 (2000).
- [19] T. M. Barclay, A. W. Cordes, J. R. Mingie, R. T. Oakley, K. E. Preuss, *Cryst. Eng. Comm.* **80** (2000).
- [20] C. A. Hunter, J. K. M. Sanders, *J. Am. Chem. Soc.* **112**, 5525 (1990).
- [21] J. M. Steed, T. A. Dixon, W. Klemperer, *J. Chem. Phys.* **70**, 4940 (1979).
- [22] J. C. Collings, K. P. Roscoe, E. G. Robins, A. S. Batsanov, L. M. Stimson, J. A. K. Howard, S. J. Clark, T. B. Marder, *New J. Chem.* **26**, 1740 (2002).
- [23] A. Morsali, A. R. Mahjoub, *J. Coord. Chem.* **56**, 779 (2003).
- [24] A. Morsali, A. Ramazani, A. R. Mahjoub, A. A. Soudi, *Z. Anorg. Allg. Chem.* **629**, 2058 (2003).