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Synthesis and crystal structure of a mixed-ligand bismuth(III) complex, [Bi_2(phen)_2Br_5(NO_3)]_n (phen = 1,10-phenanthroline)

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Synthesis and crystal structure of a mixed-ligand bismuth(III) complex, [Bi₂(phen)₂Br₅(NO₃)]ₙ (phen = 1,10-phenanthroline)

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Complex $[Bi_2(phen)_2Br_5(NO_3)]_n$ has been synthesized by reaction of $Bi(NO_3)_3$ with potassium bromide and 1,10-phenanthroline. The complex has been isolated and characterized by IR-, ^1H NMR-, ^{13}C NMR spectrum and elemental analysis. The structure of the $[Bi_2(phen)_2Br_5(NO_3)]_n$ was confirmed by X-ray crystallography which shows the complex to be a one-dimensional polymer as a result of bridging bromides. The two Bi atoms have different environments, six and seven coordinate.

Keywords: Bismuth(III); Crystal structure; Mixed-anion complexes; π–π stacking

1. Introduction

The coordination chemistry of bismuth(III) is disproportionately sparse when compared to other metals [1–6]. Bismuth(III) complexes are of interest in the treatment of gastric ulcers [7–9]. Recent reports of the crystal structure of bismuth(III) [10] and lead(II) [11–14] complexes described the presence of different ligands and their influence on the coordination stereochemistry of the metal ions. In the present article, we report the synthesis and characterization of a new mixed-ligand bismuth(III) complex with 1,10-phenanthroline (phen), $[Bi_2(phen)_2Br_5(NO_3)]_n$.

2. Experimental

2.1. *Physical measurements*

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

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2.2. *Preparation of [Bi$_2$(phen)$_2$Br$_5$(NO$_3$)]*

The complex was prepared by dissolving bismuth(III) nitrate (0.360 g, 1 mmol) and potassium bromide (0.097 g, 2 mmol) in water and adding an alcoholic solution of 1,10-phenanthroline (0.2 g, 1 mmol). The resulting solution was stirred for 5 h at room temperature, and then allowed to stand for 2–3 days in a refrigerator (ca 6°C). Yellow crystals of the product precipitated, were filtered off, washed with acetone and ether and air dried (0.251 g, yield 40%), m.p. 280°C. Found C, 23.1; H, 1.18; N, 5.43: calculated for C$_{24}$Br$_5$H$_{16}$N$_5$O$_3$Bi$_2$; C, 22.88; H, 1.27; N, 5.56%. IR (cm^{-1}) selected bands: 720(s), 810(s), 1370(vs), 1530(s), 1610(s), 3050(w). ^{1}H NMR (DMSO; δ): 8.10–8.30 (m, 4H), 8.50–9.00 (m, 2H), 9.20–9.45 (m, 2H). ^{13}C–{^{1}H} NMR (DMSO; δ): 124.30, 127.55, 129.45, 139.30, 144.50, 149.30.

2.3. *Crystallography*

2.3.1. Crystal data and refinement details. [Bi$_2$(phen)$_2$Br$_5$(NO$_3$)]. C$_{24}$H$_{16}$Bi$_2$Br$_5$N$_5$O$_3$, $M = 1239.93$, monoclinic, Space group $P2_1/c$, $a = 20.228(9)$, $b = 8.956(3)$, $c = 17.828(4)$ Å, 159) $\beta = 113.83(3)°$, $V = 2954(2)$ Å^3, D_c ($Z = 1$ f.u.) $= 2.788$ Mg m^{-3}, $F(000) = 2240$. Specimen: $0.30 \times 0.20 \times 0.05$ mm^3; $T_{max,min} = 0.735$, 0.324, $N = 5264$, $N_0 = 5085$, $R = 0.0980$, $R_w = 0.2372$.

2.3.2. Determination of the structure. Crystallographic measurements were made at 293(2) K using a Siemens $R3$ m/V diffractometer. The intensity data were collected within the range $2.29 \leq \theta \leq 25.06°$ using graphite monochromated Mo-Kα 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 unique reflections were measured, from which 3597 with $I > 2\sigma(I)$ were used. The structure has been solved by direct methods and refined by full-matrix least-squares techniques on F^2.

The positions of hydrogen atoms were idealized and included in calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotopic thermal parameter. R, R_w, with goodness of fit on F^2 0.916 are 0.0980, 0.2372. The final difference density map showed a maximum peak and hole of 4.701, -3.835 e Å^{-3}. Corrections for the Lorentz and polarization effects as well as the empirical correction for absorption using the Psi-scan programs were applied. All structural calculations were carried out with a PDP $-11/23+$ computer using the SDP-PLUS program package [27, 28].

3. Discussion

3.1. *Synthesis*

Reaction between 1,10-phenanthroline (phen) and a mixture of bismuth(III) nitrate and potassium bromide provided crystalline material analyzing as [Bi$_2$(phen)$_2$Br$_5$(NO$_3$)]. The IR spectrum of the [Bi$_2$(phen)$_2$Br$_5$(NO$_3$)] complex shows ν(NO$_3$) at ca 1370 cm^{-1}.

3.2. *Crystal structure of [Bi$_2$(phen)$_2$Br$_5$(NO$_3$)]$_n$*

Determination of the structure of [Bi$_2$(phen)$_2$Br$_5$(NO$_3$)] by X-ray crystallography (figure 1) showed the complex in the solid state (figure 2) to be a novel one-dimensional polymer with similarities to monomeric structures [Bi(phen)$_2$Br$_3$] and [Bi(phen)$_2$(NO$_3$)$_3$]. The bismuth atoms are linked within a classical 'stair-polymer' array by bromides with a pair making up the unit *c* component of the polymer. In fact, the complex is polymeric, possessing a rarely observed double-chain 1D framework for a new mixed-ligand complex containing three ligands. The structure of the complex, shown in figures 1 and 2, can be thought of as a polymeric chain with the basic repeating dimeric [Bi$_2$(phen)$_2$Br$_5$(NO$_3$)] units, the bridging bromides increase the coordination number of both bismuth(III) ions. For Bi1 the coordination is BiN$_2$O$_2$Br$_2$ (two nitrogen atoms of 1,10-phenanthroline, two bromides and two oxygen atoms of nitrate anion); Bi2 contains BiN$_2$Br$_4$ (two nitrogen atoms of 1,10-phenanthroline, and four bromides).

Further analysis indicates that this interpretation is a simplification, since the zig-zag chains of Bi atoms lying parallel to the *a* axis result from close "intermolecular"
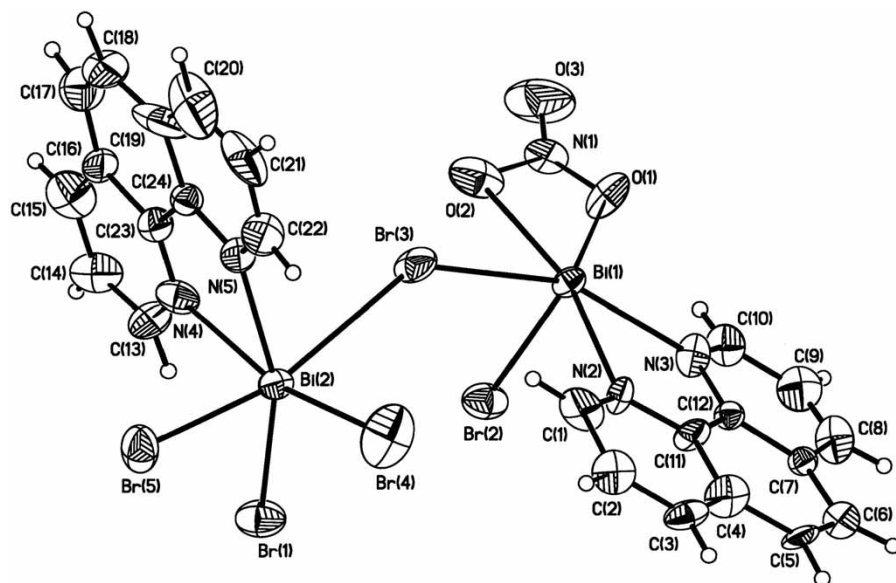

Figure 1. ORTEP drawing of compound [Bi2(phen)2Br5(NO3)]. Selected bond-length (Å) Bi(1)–N(3) 2.45(2), Bi(1)–N(2) 2.46(2), Bi(1)–Br(1)#1 2.925(4), Bi(1)–Br(2) 2.641(3), Bi(1)–Br(3) 2.973(3), Bi(1)–O(1) 2.46(2), Bi(1)–O(2) 2.67(2), Bi(2)–N(4) 2.5(3), Bi(2)–N(5) 2.42(3), Bi(2)–Br(3) 3.050(3), Bi(2)–Br(4) 2.792(5), Bi(2)–Br(5) 2.669(4), Bi(2)–Br(1) 2.925(3). Selected bond angles (°) N(3)–Bi(1)–O(1) 77.1(8), N(3)–Bi(1)–N(2) 68.4(8), O(1)–Bi(1)–N(2) 144.4(8), N(3)–Bi(1)–Br(2) 82.3(6), O(1)–Bi(1)–Br(2) 97.1(6), N(2)–Bi(1)–Br(2) 87.4(6), N(3)–Bi(1)–O(2) 121.7(9), O(1)–Bi(1)–O(2) 48.7(8), N(3)–Bi(1)–Br(3) 154.8(6), N(2)–Bi(1)–O(2) 165.7(7), Br(2)–Bi(1)–O(2) 84.3(5), O(1)–Bi(1)–Br(3) 127.2(5), N(2)–Bi(1)–Br(3) 88.2(5), Br(2)–Bi(1)–Br(3) 87.70(11), O(2)–Bi(1)–Br(3) 85.77(13), N(3)–Bi(1)–Br(1)#1 74.2(6), O(1)–Bi(1)–Br(1)#1 79.0(5), Br(2)–Bi(1)–Br(1)#1 155.88(11), O(2)–Bi(1)–Br(1)#1 112.6(5), Br(3)–Bi(1)–Br(1)#1 111.44(11), N(5)–Bi(2)–N(4) 68.2(9), N(5)–Bi(2)–Br(5) 88.5(6), N(5)–Bi(2)–Br(4) 94.3(6), N(4)–Bi(2)–Br(4) 162.2(7), N(5)–Bi(2)–Br(1) 156.1(6), N(4)–Bi(2)–Br(1) 88.7(7), Br(5)–Bi(2)–Br(1) 88.78(12), Br(4)–Bi(2)–Br(1) 109.03(15), N(5)–Bi(2)–Br(3) 79.0(6), N(4)–Bi(2)–Br(3) 85.1(6), Br(5)–Bi(2)–Br(3) 163.55(12), Br(4)–Bi(2)–Br(3) 88.66(14), Br(1)–Bi(2)–Br(3) 106.20(10), Bi(1)–Br(3)–Bi(2) 135.27(12). #1: *x*, −*y* + 1/2, *z* + 1/2.
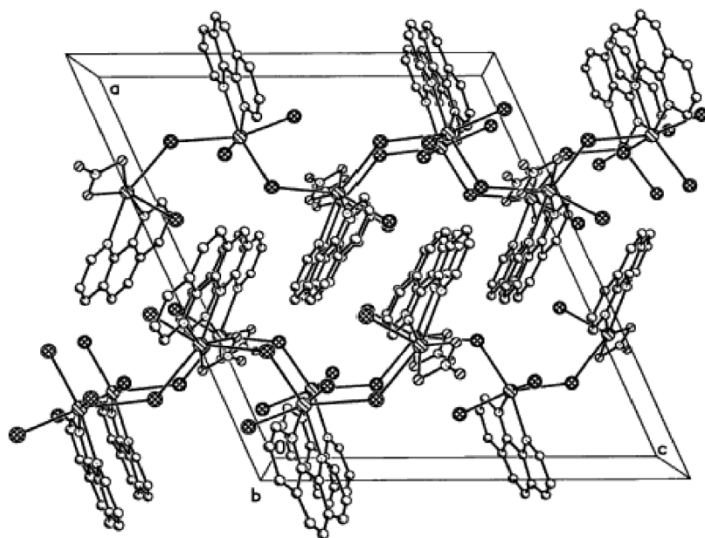
Figure 2.   The unit cell showing the π–π stacking interaction (charge-transfer arrays) between the parallel aromatic rings belonging to adjacent chains in [Bi$_2$(phen)$_2$Br$_5$(NO$_3$)].

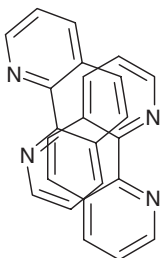
Figure 3.   Projection of nearest neighbor pairs in the π–π stacks of heteroaromatic bases in [Bi$_2$(phen)$_2$Br$_5$(NO$_3$)].

contacts (figure 2). Parallel arrays of the planes of the aromatic moieties indicate that these interactions are of the "pi-stacking", rather than "edge-to-face" or "vertex-to-face" types [15–18]. Projection of the structure perpendicular to the ring plane shows the overall form of the "slipped" stacking [18, 19], which is at least qualitatively understandable in terms of optimizing approaches between atoms of opposite charges [20]. There are π–π stacking interactions (charge-transfer arrays) [1, 2] between parallel aromatic rings belonging to both intra- and interdouble-chains of adjacent chains. The mean molecular planes are almost parallel and separated by a distance of ~ 3.5 Å, close to that of the planes in graphite. A simple model to describe the nature of π–π interactions has been developed by Hunter *et al.* [20]. This model predicts that face-to-face π-stacked interactions will be disfavored due to the dominance of π–π repulsion [21, 22]. Hence, it can be expected that within the molecule discussed here the electron-poor pyridyl rings will interact with less electron-poor rings such as phenyl groups (figure 3).

The arrangement of the 1,10-phenanthroline ligand, bromide and NO_3^- anions suggests coordination geometry around the bismuth(III) ions is regular and there is no gap in the geometry around the bismuth(III) ions, possibly the lone pair of electrons on the bismuth(III) is stereo-inactive [23].

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 183933 for $[Bi_2(phen)_2Br_5(NO_3)]$.

Acknowledgements

References

[1] N.N. Greenwood, A. Earnshaw. *Chemistry of the Elements*, pp. 235–236, Pergamon Press, Oxford (1986).
[2] G. Wilkinson, R.D. Gillard, J. McCleverty (Eds). *Comprehensive Coordination Chemistry*, Vols 1–7, Pergamon Press, Oxford (1987).
[3] L.J. Barbour, S.J. Belfield, P.C. Junk, M.K. Smith. *Aust. J. Chem.*, **51**, 337 (1998).
[4] A. Bondi. *J. Chem. Phys.*, **68**, 441 (1964).
[5] R.D. Rogers, A.H. Bond, S. Aguinaga. *J. Am. Chem. Soc.*, **114**, 2960 (1992).
[6] R.D. Rogers, A.H. Bond, S. Aguinaga, A. Reyes. *J. Am. Chem. Soc.*, **114**, 2967 (1992).
[7] 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).
[8] R.D. Hancok, I. Cukrowski, J. Baloyi, J. Mashishi. *J. Chem. Soc., Dalton Trans.*, 2895 (1993).
[9] P.J. Sadler, H. Li, H. Sun. *Coord. Chem. Rev.*, **689**, 185 (1999).
[10] A. Morsali, A.R. Mahjoub. *J. Coord. Chem.*, **56**, 571 (2003).
[11] A.K. Hall, J.M. Harrowfield, A. Morsali, A.A. Soudi, A. Yanovsky. *Cryst. Eng. Commun.*, (13), 82 (2000).
[12] A. Morsali, M. Payheghader, M.S. Salehi. *Z. Anorg. Allg. Chem.*, **628**, 12 (2002).
[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] V. Russell, M. Scudder, I. Dance. *J. Chem. Soc., Dalton Trans.*, 789, and references therein (2001).
[16] I.G. Dance, M.L. Scudder. *J. Chem. Soc., Dalton Trans.*, 3755 (1996).
[17] C. Janiak. *J. Chem. Soc., Dalton Trans.*, 3885 (2000).
[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.*, (15), 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] L. Shimoni-Livny, J.P. Glusker, C.W. Bock. *Inorg. Chem.*, **37**, 1853 (1998).