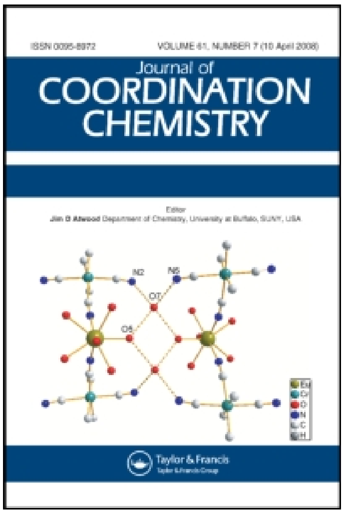

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Syntheses and characterization of a new nano-structured bismuth(III) bromide coordination polymer; new precursor for preparation of bismuth(III) bromide and bismuth(III) oxide nanostructures

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Syntheses and characterization of a new nano-structured bismuth(III) bromide coordination polymer; new precursor for preparation of bismuth(III) bromide and bismuth(III) oxide nanostructures

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Nanoparticles of a Bi(III) coordination polymer, $\{[\mathrm{Bi}(\mu\text{-}4,4'\text{-bipy})\mathrm{Br}_4]\cdot(4,4'\text{-Hbipy})\}_n$ (**1**) (4,4′-bipy = 4,4′-bipyridine), were synthesized by a sonochemical method. The new nanoparticles were characterized by scanning electron microscopy, X-ray powder diffraction (XRD), IR spectroscopy, and elemental analyses. Compound **1** was structurally characterized by single-crystal X-ray diffraction. The thermal stabilities of **1** as bulk and at nanosize were studied by thermal gravimetric (TG) and differential thermal analyses (DTA). The Bi_2O_3 and $BiBr_3$ nanostructures were obtained by calcinations of nanostructure of **1** in air and argon.

Keywords: Nanostructure; Coordination polymer; Bismuth(III); Crystal structure

1. Introduction

Chemical and physical properties of solid materials depend on both size and shape of the microscopic particles they are made from, especially for materials with morphological features smaller than a micron in at least one dimension, commonly called nanoscale materials or simply nanomaterials. In these materials the ratio of surface area to volume is vastly increased compared to compounds with larger grain sizes. These effects are minor when going from macro to micro dimensions, but become increasingly important when reaching the nanometer size [1–4].

Coordination polymers exhibit potential applications as molecular wires [5–8], electrical conductors [9, 10], molecular magnets [11, 12], in host–guest chemistry [13–15], and in catalysis [16]. In contrast to inorganic materials, specific syntheses of nano-structured supramolecular compounds are surprisingly sparse. Similarly, use of organometallic supramolecular compounds as precursors for nanomaterials has not yet been investigated thoroughly.

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In this article we describe a simple sonochemical preparation of a Bi(III) coordination polymer, $\{[\mathrm{Bi}(\mu\text{-}4,4'\text{-bipy})\mathrm{Br}_4]\cdot(4,4'\text{-Hbipy})\}_n$ (**1**), and use this compound for preparation of Bi_2O_3 and $BiBr_3$ nanostructures.

2. Experimental

All reagents and solvents for synthesis and analysis were commercially available and used as received. A multiwave ultrasonic generator (Sonicator_3000; Misonix, Inc., Farmingdale, NY, USA), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 600 W, was used for ultrasonic irradiation. The ultrasonic generator automatically adjusted the power level. The wave amplitude in each experiment was adjusted as needed. IR spectra were recorded 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. The thermal behavior was measured with a PL-STA 1500 apparatus. X-ray powder diffraction (XRD) measurements were performed using a Philips diffractometer manufactured by X'pert with monochromated Cu-Kα radiation and simulated XRD powder patterns based on single crystal data prepared using Mercury [17]. Crystallite sizes of selected samples were estimated using the Scherrer method. The samples were characterized with a scanning electron microscope with gold coating. Single crystal diffraction measurements were made at 100(2) K using a Bruker AXS SMART APEX CCD diffractometer. The intensity data were collected using graphite monochromated Mo-Kα radiation. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. Molecular structure plots were prepared using Mercury [17] and ORTEPIII [18]. Crystal data for $C_{20}H_{17}BiBr_4N_4$, $M = 842.00$, Orthorhombic, Space group Fdd2, $a = 14.909(2)$, $b = 24.873(3)$, $c = 12.1801(17)$ Å, $V = 4516.9(11)$ Å^3, D_c ($Z = 8$ f.u.) $= 2.31\ \mathrm{Mg\,m^{-3}}$, $F(000) = 3104$. Specimen: $0.31 \times 0.20 \times 0.16\ \mathrm{mm}^3$; $R(wR) = 0.0327(0.0763)$ for 2741 reflections with $I > 2\sigma(I)$. The observed anisotropic thermal parameters, calculated structure factors, and full lists of bond distances, bond angles and torsion angles are given in "Supplementary material".

To prepare nanosized particles of $\{[\mathrm{Bi}(\mu\text{-}4,4'\text{-bipy})\mathrm{Br}_4]\cdot(4,4'\text{-Hbipy})\}_n$, 10 mL of 0.3 M solution of bismuth(III) bromide in MeOH was positioned in a high-density ultrasonic probe. To this solution 10 mL of 0.3 M solution of 4,4′-bipy was added dropwise. The obtained precipitates were collected by filtration, washed with methanol and then dried in air, m.p. >300°C. Found: C, 28.10; H, 2.10; N, 6.50%. Calcd for $C_{20}H_{17}BiBr_4N_4$: C, 28.50; H, 2.02; N, 6.65%. IR bands: 479s, 616m, 813s, 1058m, 1213m, 1398m, 1587s, 3015w.

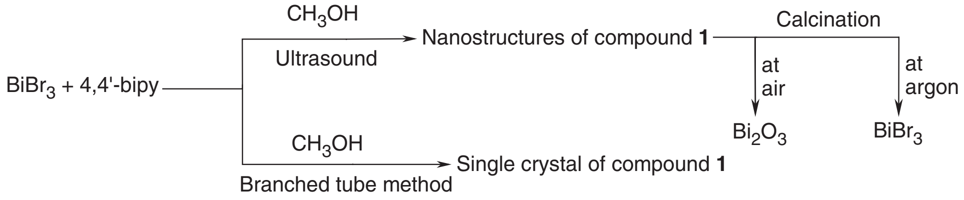
To isolate single crystals of **1**, 4,4′-bipy (0.156 g, 1 mmol) and bismuth(III) bromide (0.448 g, 1 mmol) were placed in the main arm of a branched tube [19]. Methanol was carefully added to fill both arms, the tube was sealed and the ligand-containing arm immersed in an oil bath at 60°C while the other arm was kept at ambient temperature. After 7–10 days, yellow crystals deposited in the cooler arm were isolated, filtered off, washed with acetone and ether and air dried, m.p. >300°C. Found: C, 28.14; H, 2.15; N, 6.40%. Calcd for $C_{20}H_{17}BiBr_4N_4$: C, 28.50; H, 2.02; N, 6.65%. IR bands: 479s, 616m, 814s, 1059m, 1212m, 1398m, 1585s, 3015w.

3. Results and discussion

An elegant approach to nanomaterials is sonochemistry [20–24] where molecules are induced to undergo a chemical reaction and form nanoscale features due to application of powerful ultrasound radiation (20 kHz–10 MHz) [25]. Scheme 1 gives an overview of the synthesis of **1** using two different routes. Nanoparticles of **1** were obtained by ultrasonic irradiation of a mixture of 4,4′-bipy and bismuth(III) bromide in methanolic solution. Single crystalline material was obtained using a heat gradient applied to a solution of the reagents (the "branched tube method").

IR spectra of the nanoparticles and the single crystalline material are indistinguishable and show characteristic absorption bands for 4,4′-bipy with variable intensity from 1400 to 1580 cm^{-1} corresponding to ring vibrations of py.

Single-crystal X-ray data of **1** show anionic and cationic 1D chains, $[4,4'\text{-bipyH}]_n^{n+}[\text{Bi}(4,4'\text{-bipy})\text{Br}_4]_n^{n-}$ (figure 1). Two 1-D systems grow into a 3-D network by an extensive hydrogen-bond network. The anionic complex is polynuclear with nitrogens of 4,4′-bipy linked to two different bismuths; the four bromides are also coordinated. The coordination around Bi is a distorted octahedron. The $[4,4'\text{-bipyH}]^+$ cations formed by proton transfer in solution are systematically disordered in a 1 : 1 ratio and linked by hydrogen bonding (figure 1). The hydrogen of $4,4'\text{-bipyH}^+$ is a hydrogen-bond donor with N atoms from $4,4'\text{-bipyH}^+$. The hydrogen bond distances $d(\text{D–H})$, $d(\text{H}\cdots\text{A})$, $d(\text{D}\cdots\text{A})$, and the angle $\angle(\text{DHA})$ for $\text{N4–H4}\cdots\text{N3}$ are 0.86, 1.79, 2.608, and 158.4°, respectively. As shown in figure 1, hydrogen bonding yields infinite chains of $4,4'\text{-bipyH}^+$ perpendicular to 1-D chains of $[\text{Bi}(4,4'\text{-bipy})\text{Br}_4]_n^-$.



Scheme 1. Materials produced and synthetic methods.

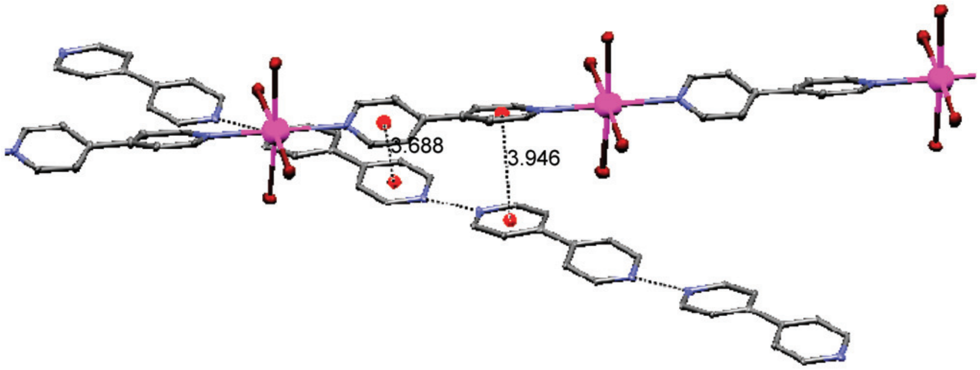


Figure 1. Showing two perpendicular 1D chains in the $[4,4'\text{-bipyH}]_n^{n+}[\text{Bi}(4,4'\text{-bipy})\text{Br}_4]_n^{n-}$ (**1**).

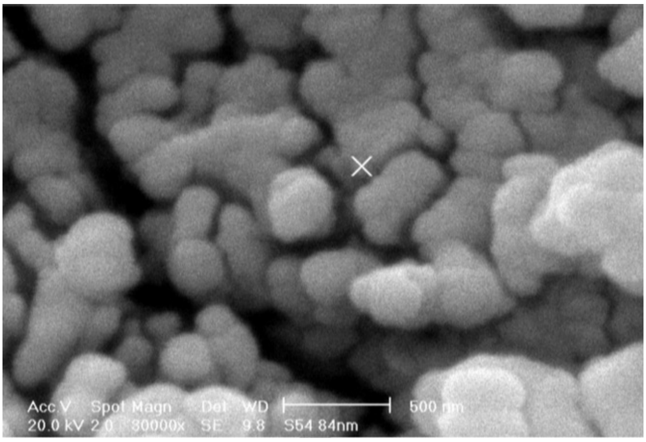


Figure 2. SEM photographs of $\{[\mathrm{Bi}(\mu\text{-}4,4'\text{-bipy})\mathrm{Br}_4]\cdot(4,4'\text{-Hbipy})\}_n$ (**2**) nanoparticles (the scale bar is 500 nm).

π–π stacking of pyridyl rings occurs between the two, one-dimensional systems (3.688(1) and 3.946(1) Å centroid to centroid distances) (figure 1).

Nanosized particles of **1** were prepared *via* immersion of a high-density ultrasonic probe into solution of 4,4′-bipy in methanol; bismuth(III) bromide was added dropwise into this solution. The nanoparticles were characterized by scanning electron microscopy (SEM) (figure 2) which shows well-separated particles with sizes ranging from 80 to 120 nm.

Matches of **1** prepared by the branched tube and the sonochemical process with XRD patterns simulated from the single crystal X-ray data indicate the presence of only one crystalline phase in all the samples regardless of the method of preparation (Supplementary material). Using the Scherrer formula for the calculation of particle sizes from the broadening of the XRD peaks ($D = 0.891\lambda/\beta\cos\theta$, where D is the average grain size, λ is the X-ray wavelength (0.15405 nm), and θ and β are the diffraction angle and full-width at half maximum of an observed peak, respectively [26–29]), the average size of the particles prepared *via* the sonochemical method was 85 nm, in agreement with the value obtained from the SEM images (figure 2). We also investigated the use of other solvents such as water, acetonitrile, dichloromethane, benzene, and chloroform in the sonochemical procedure, but the particle sizes obtained were not in the nanoscale.

To examine thermal stability of the nanosized sample and single crystals of **1**, thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 30 and 610°C in a static atmosphere of nitrogen (Supplementary material). The bulk material of **1** began decomposition at 215°C. Between this temperature and 322°C exothermic removal of 4,4′-bipy occurs with a mass loss of 54.50% (Calcd 53.20%). Mass loss calculations show that the final decomposition product is $\mathrm{BiBr_3}$. Nanosized particles of **1** are more stable, starting decomposition at 272°C with a distinct decomposition stage between 272 and 325°C with a mass loss of 53.60% (Calcd 53.20%). Detectable decomposition of the nanoparticles of **1** thus starts about 57° later than that of its single crystal. The DTA curves display two distinct endothermic effects at 218 and 330°C for the single crystals of **1**.

Thermal decomposition of the nanosized particles of **1** in either air or argon produced $\mathrm{Bi_2O_3}$ (figure 3a and JCPDS Card No. 41-1449) particles and $\mathrm{BiBr_3}$ (figure 3b and

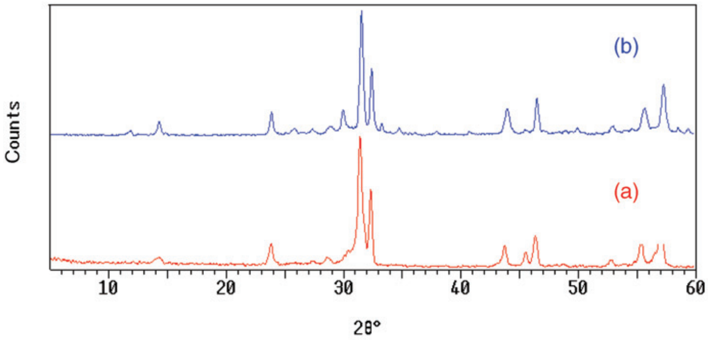


Figure 3. (a) XRD patterns of Bi_2O_3 nanostructures prepared by calcinations of **1** under air and (b) XRD patterns of $BiBr_3$ nanostructures prepared by calcinations of **1** under argon.

JCPDS Card No. 43-0494) nanopowders, respectively, as established by their powder XRD patterns.

From SEM images of nanostructured Bi_2O_3 and $BiBr_3$ obtained from calcination of **1** under air and argon atmosphere (Supplementary material), morphology and size of the structures are different. Calcinations of **1** nanostructure obtained by sonochemical method produce nanoparticles Bi_2O_3 under air and nanopowders $BiBr_3$ under argon.

4. Conclusion

A new Bi(III) coordination polymer, $\{[Bi(\mu\text{-}4,4'\text{-bipy})Br_4]\cdot(4,4'\text{-Hbipy})\}_n$, has been synthesized using a thermal gradient approach and by a sonochemical method. Calcination of **1** under air and argon produces Bi_2O_3 and $BiBr_3$ with different nanostructures. There are three reports discussing the preparation of Bi_2S_3 nanostructures from the solvent thermolysis of bismuth trisxanthate [30], (benzylthiolato)-bismuth [31], and bismuth tris(methyl-*n*-hexyl-dithiocarbamate) [32] precursors which demonstrate supramolecular compounds and may be suitable precursors for preparation of nanoscale materials. This is the first report on the synthesis of nanostructured Bi_2O_3 and $BiBr_3$ from a coordination polymer precursor. Further systematic studies of supramolecular compounds with bismuth(III) and other metal ions are ongoing in our laboratory to offer insight into metal-organic supramolecular assembly and nanochemistry.

Supplementary material

Crystallographic data (excluding structure factors) for **1** has been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number CCDC-685222. Copies of the data can be obtained, free of charge, by application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: data_request@ccdc.cam.ac.uk), or *via* the internet (http://www.ccdc.cam.ac.uk/products/csd/request).

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References

[1] H.T. Shi, L.M. Qi, J.M. Ma, H.M. Cheng. *J. Am. Chem. Soc.*, **125**, 3450 (2003).
[2] H. Zhang, D.R. Yang, D.S. Li, X.Y. Ma, S.Z. Li, D.L. Que. *Cryst. Growth Des.*, **5**, 547 (2005).
[3] D.B. Kuang, A.W. Xu, Y.P. Fang, H.Q. Liu, C. Frommen, D. Fenske. *Adv. Mater.*, **15**, 1747 (2003).
[4] F. Kim, S. Connor, H. Song, T. Kuykendall, P.D. Yang. *Angew. Chem. Int. Ed.*, **43**, 3673 (2004).
[5] K.-T. Wong, J.-M. Lehn, S.-M. Peng, G.-H. Lee. *Chem. Commun.*, 2259 (2000).
[6] J.A. Ramsden, W. Weng, A.M. Arif, J.A. Gladysz. *J. Am. Chem. Soc.*, **114**, 5890 (1992).
[7] W. Weng, J.A. Ramsden, A.M. Arif. *J. Am. Chem. Soc.*, **115**, 3824 (1993).
[8] N. Le Narvor, L. Toupet, C. Lapinte. *J. Am. Chem. Soc.*, **117**, 7129 (1995).
[9] A. Aumuller, P. Erk, G. Klebe, S. Hunig, J.U. von Schutz, H.-P. Werner. *Angew. Chem.*, **98**, 759 (1986).
[10] A.G. Bunn, P.J. Carroll, B.B. Wayland. *Inorg. Chem.*, **31**, 1297 (1992).
[11] M.A.M. Abu-Youssef, A. Escuer, D. Gatteschi, M.A.S. Goher, F.A. Mautner, R. Vicente. *Inorg. Chem.*, **38**, 5716 (1999), and references therein.
[12] A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M.G. Pini, M.A. Novak. *Angew. Chem. Int. Ed.*, **40**, 1760 (2001).
[13] M. Aoyagi, K. Biradha, M. Fujita. *J. Am. Chem. Soc.*, **121**, 7457 (1999).
[14] A. Tanatani, M.J. Moi, J.S. Moore. *J. Am. Chem. Soc.*, **123**, 1792 (2001).
[15] (a) K. Biradha, C. Seward, M.J. Zaworotko. *Angew. Chem.*, **111**, 584 (1999); (b) K. Biradha, C. Seward, M.J. Zaworotko. *Angew. Chem. Int. Ed.*, **38**, 492 (1999).
[16] M. Fujita, Y.J. Kwon, S. Washizu, K.J. Ogura. *J. Am. Chem. Soc.*, **116**, 1151 (1994).
[17] Mercury 1.4.1, Copyright Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (2001–2005).
[18] L.J. Farrugia. *J. Appl. Cryst.*, **30**, 565 (1997).
[19] G. Mahmoudi, A. Morsali, A.D. Hunter, M. Zeller. *CrystEngComm.*, **9**, 704 (2007).
[20] M. Sugimoto. *J. Magn. Chem. Mater.*, **133**, 460 (1994).
[21] M.V. Landau, L. Vradman, M. Herskowitz, Y. Koltypin. *J. Catal.*, **201**, 22 (2001).
[22] H. Wang, Y.N. Lu, J.J. Zhu, H.Y. Chen. *Inorg. Chem.*, **42**, 6404 (2003).
[23] J.H. Zhang, Z. Chen, Z.L. Wang, N.B. Ming. *J. Mater. Res.*, **18**, 1804 (2003).
[24] T. Ding, J.J. Zhu, J.M. Hong. *Mater. Lett.*, **57**, 4445 (2003).
[25] K.S. Suslick, S.B. Choe, A.A. Cichowlas, M.W. Grinstaff. *Nature*, **353**, 414 (1991).
[26] K.-T. Wong, J.-M. Lehn, S.-M. Peng, G.-H. Lee. *Chem. Commun.*, 2259 (2000).
[27] J.A. Ramsden, W. Weng, A.M. Arif, J.A. Gladysz. *J. Am. Chem. Soc.*, **114**, 5890 (1992).
[28] W. Weng, J.A. Ramsden, A.M. Arif. *J. Am. Chem. Soc.*, **115**, 3824 (1993).
[29] N. Le Narvor, L. Toupet, C. Lapinte. *J. Am. Chem. Soc.*, **117**, 7129 (1995).
[30] Y.W. Koh, C.S. Lai, A.Y. Du, E.R.T. Tiekink, K.P. Loh. *Chem. Mater.*, **15**, 4544 (2003).
[31] P. Boudjouk, M.P. Remington, D.G. Grier, B.R. Jarabek, G.J. McCarthy. *Inorg. Chem.*, **37**, 3538 (1998).
[32] O.C. Monteiro, H.I.S. Nogueira, T. Trindade. *Chem. Mater.*, **13**, 2103 (2001).