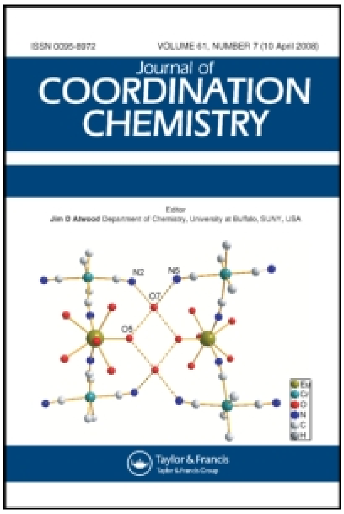


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Nanoparticles of a new mercury(II) coordination polymer: synthesis, characterization, thermal and structural studies

Ghodrat Mahmoudi[a]; Ali Morsali[a]
[a] Faculty of Sciences, Department of Chemistry, Tarbiat Modares University, Tehran, Islamic Republic of Iran

To cite this Article Mahmoudi, Ghodrat and Morsali, Ali(2008) 'Nanoparticles of a new mercury(II) coordination polymer: synthesis, characterization, thermal and structural studies', Journal of Coordination Chemistry, 61: 17, 2787 — 2792
To link to this Article: DOI: 10.1080/00958970801975091
URL: http://dx.doi.org/10.1080/00958970801975091

Journal of Coordination Chemistry
Vol. 61, No. 17, 10 September 2008, 2787–2792

Taylor & Francis
Taylor & Francis Group

Nanoparticles of a new mercury(II) coordination polymer: synthesis, characterization, thermal and structural studies

GHODRAT MAHMOUDI and ALI MORSALI*

Faculty of Sciences, Department of Chemistry, Tarbiat Modares University,
P.O. Box 14155-4838, Tehran, Islamic Republic of Iran

(*Received 2 September 2007; in final form 25 October 2007*)

Nanoparticles of a new Hg(II) one-dimensional coordination polymer, {$[Hg(4\text{-bpdb})I_2]_n$, 4-bpdb = 1,4-*bis*(4-pyridyl)-2,3-diaza-1,3-butadiene} were synthesized by reaction of HgI_2 and 4-bpdb by a sonochemical method. The new nanoparticles were characterized by scanning electron microscopy, X-ray powder diffraction (XRD) and FT-IR spectroscopy; $[Hg(4\text{-bpdb})I_2]_n$ was structurally characterized by single crystal X-ray diffraction. This compound consists of one-dimensional polymeric units of $[Hg(4\text{-bpdb})I_2]$. The thermal stability of $[Hg(4\text{-bpdb})I_2]_n$ was studied by thermal gravimetric (TG) and differential thermal analyses (DTA).

Keywords: Sonochemical; Nanoparticle; Coordination polymer; Mercury(II)

1. Introduction

Inorganic as well as organic polymeric substances have attracted attention because of their potential applications as functional materials [1]. Several organic and inorganic materials [2] have been synthesized and investigated. In contrast, examples [3, 4] of nanoscale particles of metal-organic coordination polymers are limited. Their preparation is challenging owing to their ability to tailor their physical and chemical properties through deliberate selection [5] of metal and multifunctional ligands. In contrast to coordination polymers of transition metal ions, the formation of polymers with heavy metal ions such as mercury(II) is sparse and there have been very few reports on Hg(II) complexes with rigid or flexible organic nitrogen donor-based ligands. This article focuses on the simple synthetic preparation of nanoparticles of a new mercury(II) coordination polymer, $[Hg(4\text{-bpdb})I_2]_n$ {4-bpdb = 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene}.

---

*Corresponding author. Email: morsali_a@yahoo.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970801975091

2. Experimental

With the exception of 4-bpdb which was prepared according to the literature procedure [5], all reagents and solvents were commercially available and used as received. 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 of X'pert company with monochromated Cu-Kα radiation. The crystallite sizes of selected samples were estimated using the Sherrer method. The samples were characterized with a scanning electron microscope with gold coating.

Crystallographic measurements were made using a Bruker APEX area-detector diffractometer. The intensity data were collected using graphite monochromated Mo-Kα radiation. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2. Structure solution and refinement were accomplished using SHELXL-97 program packages [6]. The molecular structure plots were prepared using ORTEP software [7a] and simulated XRD powder pattern based on single crystal data was prepared with Mercury software [7b].

To prepare nanoparticles of $[\mathrm{Hg(4\text{-}bpdb)I_2}]_n$, a proper amount of the solution of mercury(II) iodide (0.1 M) in EtOH was placed in an ultrasonic bath, then into this solution, a proper volume of 4-bpdb solution (0.1 M) was added in drops. The obtained precipitates were filtered, subsequently washed with EtOH and then dried (Found C: 21.40, H: 1.50, N: 8.30: Calcd for $C_{12}H_{10}HgI_2N_4$; C: 21.67, H: 1.51, N: 8.43%). IR (cm^{-1}) bands: 450(m), 680(s), 808(s), 999(m), 1054(m), 1236(m), 1407(s), 1541(s), 1592(vs), 3025(w).

To isolate single crystals of $[\mathrm{Hg(4\text{-}bpdb)I_2}]_n$, 4-bpdb (0.5 mmol, 0.105 g) and mercury(II) iodide (0.159 g, 0.5 mmol) were placed in main arm of the branched tube (figure 1). Methanol was carefully added to fill the 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 2–3 days, yellow crystals (d.p. 246–248°C), which had

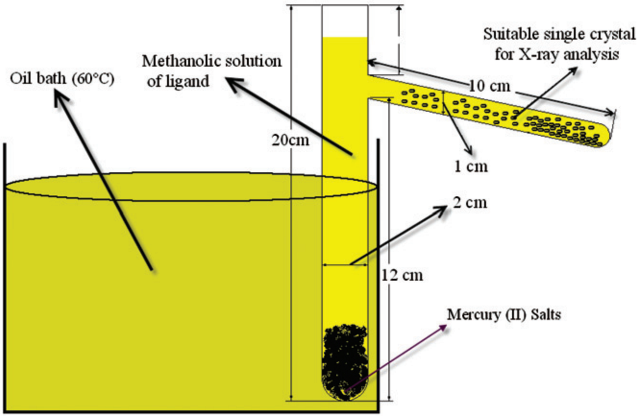


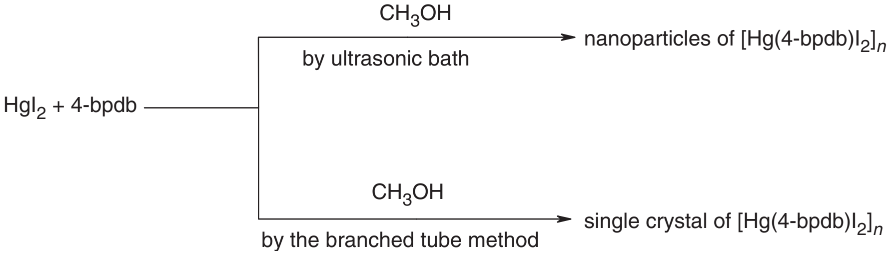
Figure 1. Depiction of the branched tube for syntheses and isolation of single crystals of $[\mathrm{Hg(4\text{-}bpdb)I_2}]_n$.

deposited in the cooler arm, were isolated, filtered off, washed with acetone and ether and air dried (0.128 g, yield 65%) (Found C: 21.50, H: 1.58, N: 8.40: Calcd for $C_{12}H_{10}HgI_2N_4$; C: 21.67, H: 1.51, N: 8.43%). IR (cm^{-1}) bands: 450(m), 680(s), 808(s), 999 (m), 1054(m), 1236(m), 1407(s), 1541(s), 1592(vs), 3025(w).

3. Results and discussion

Scheme 1 shows the reaction between mercury(II) iodide and 4-bpdb to form $[Hg(4\text{-bpdb})I_2]_n$ in two different conditions.

Figure 2(a) shows the simulated XRD pattern from single crystal X-ray data of the above compound and figure 2(b) shows the XRD pattern of a typical sample of



Scheme 1. Materials from reaction of 4-bpdb with mercury(II) iodide in two different conditions.

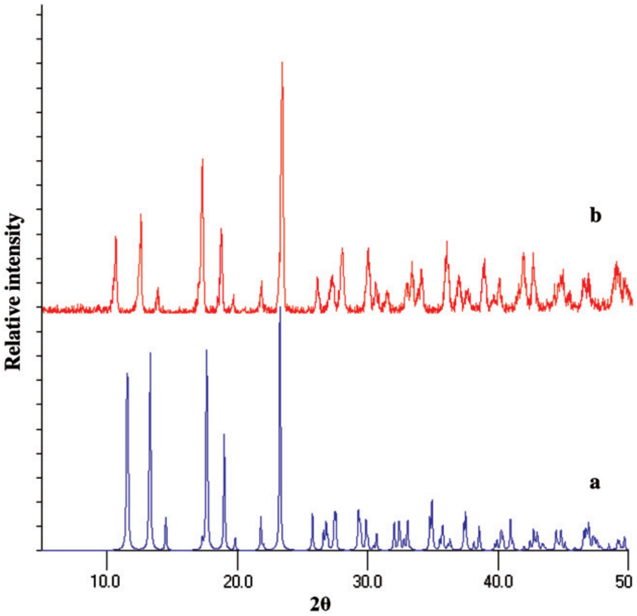


Figure 2. (a) The simulated XRD pattern from single crystal X-ray data of the compound $[Hg(4\text{-bpdb})I_2]_n$, (b) The XRD pattern of $[Hg(4\text{-bpdb})I_2]_n$ nanoparticles.

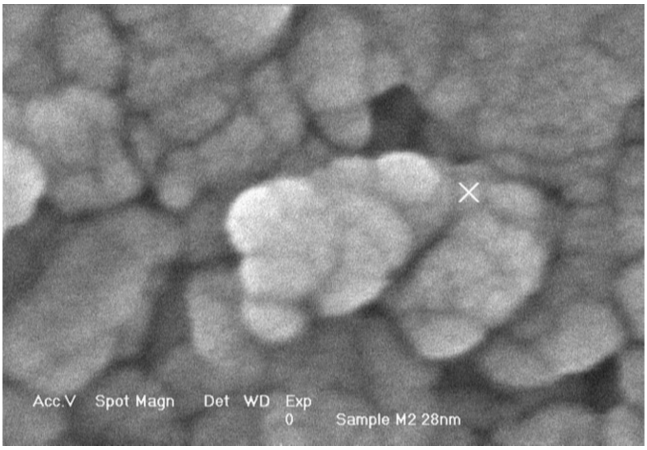


Figure 3. SEM photographs of $[Hg(4\text{-bpdb})I_2]_n$ nanoparticles.

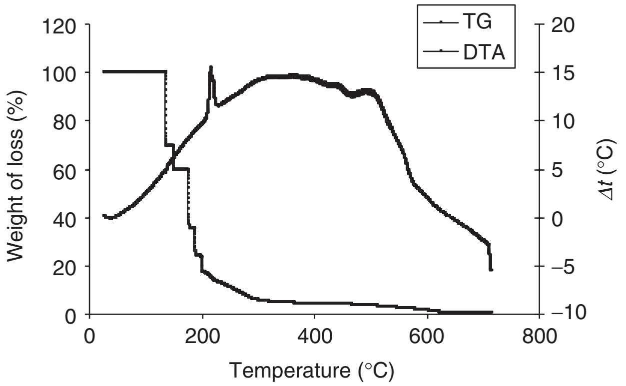


Figure 4. DTA and TGA diagrams of $[Hg(4\text{-bpdb})I_2]_n$.

$[Hg(4\text{-bpdb})I_2]_n$ prepared by the sonochemical process. Acceptable matches, with slight difference in 2θ, were observed between the simulated from single crystal X-ray data patterns (figure 2a) and those from the experimental powder X-ray diffraction patterns for nanoparticles as obtained from the sonochemical method (figure 2b). Results of XRD powder patterns indicate that the experimental data are in good agreement with the simulated XRD powder patterns based on single crystal data, hence this compound is obtained as a mono-phase. Broadening of the peaks indicated that the particles were of nanometer scale. Estimated from the Sherrer formula, $D = 0.891\lambda/\beta\cos\theta$, 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 [8]. The average size of the particles was 55 nm, in agreement with that observed from SEM images. Figure 3 shows the SEM images of $[Hg(4\text{-bpdb})I_2]_n$ particles. The particle size ranged from 20 to 50 nm.

Figure 4 shows the DTA and TGA curves of $[Hg(4\text{-bpdb})I_2]_n$ recorded in static air from ambient temperature to 700°C. The DTA and TGA curves, both crystalline and nanoparticles of $[Hg(4\text{-bpdb})I_2]_n$ are the same, indicate the release of the 4-bpdb

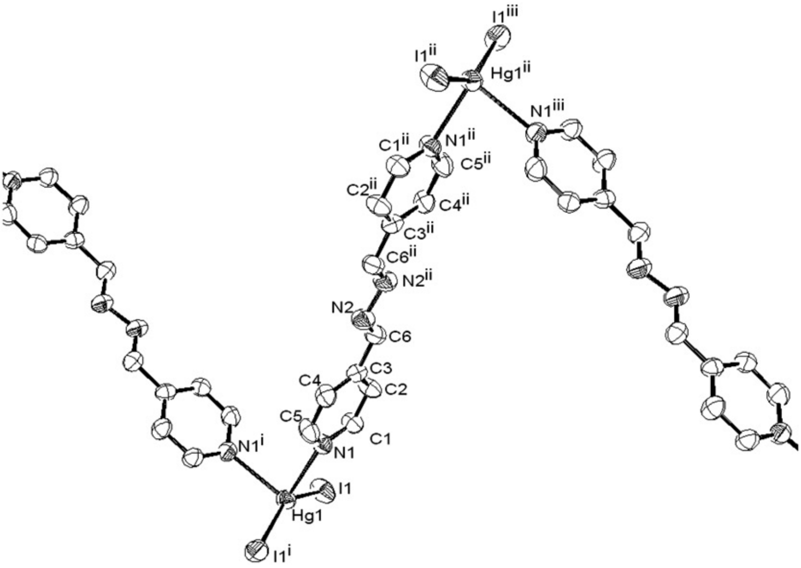


Figure 5. X-ray crystal structure showing the one-dimensional zig-zag polymer of [Hg(4-bpdb)I$_2$]$_n$ (i): $-x$, y, $-z+1/2$; (ii): $-x$, $-y$, $-z$; (iii): x, $-y$, $z+1/2$) (50% thermal displacement ellipsoids).

takes place at 175°C (observed 31.40%, Calcd. 31.59%). The solid residue formed at 180°C is suggested to be HgI$_2$. At even higher temperatures it is further decomposed, ultimately giving solid that appears to be HgO that under higher temperature is evaporated (figure 4).

Single X-ray crystal analysis reveals that [Hg(4-bpdb)I$_2$]$_n$ crystallizes in the monoclinic space group *P*2/*c*. The crystal structure consists of one-dimensional polymeric units of [Hg(4-bpdb)I$_2$] (figure 5) with the terminal nitrogens of 4-bpd linked to two different mercury atoms, resulting in one-dimensional polymeric units in the solid state. The coordination environment of Hg is distorted tetrahedral with 4-bpd generating angular nodes at the metal resulting in 1D zig-zag chains. The Hg $\cdots$ Hg distance is 16.24(2) Å. The N–Hg1–N and I–Hg1–I angles are 84.2(2) and 148.17(2)°, respectively.

4. Conclusions

New nanoparticles of mercury(II) coordination polymer, [Hg(4-bpdb)I$_2$]$_n$, were produced by sonochemical method using HgI$_2$ and 4-bpdb in an efficient and quick way. The new nanoparticles were characterized by scanning electron microscopy, X-ray powder diffraction (XRD), TGA, DTA and FT-IR spectroscopy. Compound [Hg(4-bpdb)I$_2$]$_n$ was structurally characterized by single crystal X-ray diffraction. The sonochemical method is rarely used for syntheses of coordination polymer nanoparticles, but can be easily controlled and is expected to be applicable to fabrication of other nano-sized particles of other metal ion coordination polymers.

Supplementary material

Complete bond lengths and angles, coordinates and displacement parameters have been deposited with the Cambridge Crystallography Data Center. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 643431 for compounds $[Hg(4\text{-bpdb})I_2]_n$.

Acknowledgement

Support of this investigation by Tarbiat Modares University is gratefully acknowledged.

References

[1] (a) H.K. Chae, D.Y. Siberio-Perez, J. Kim, Y. Go, M. Eddaoudi, A.J. Matzger, M. O'Keeffe, O.M. Yaghi. *Nature*, **427**, 523 (2004); (b) Y. Kim, M. Suh, D.Y. Jung. *Inorg. Chem.*, **43**, 245 (2004); (c) Z. Huang, H.-B. Song, M. Du, S.-T. Chen, X.-H. Bu, J. Ribas. *Inorg. Chem.*, **43**, 931 (2004); (d) A.P. Carvalho, C. Castanheira, B. Cardoso, J. Pires, A.R. Silva, C. Freire, B. de Castro, M.B. de Carvalho. *J. Mater. Chem.*, **14**, 374 (2004); (e) J.Y. Lu, A.M. Babb. *Chem. Commun.*, 1346 (2003); (f) Y.-G. Li, N. Hao, Y. Lu, E.-B. Wang, Z.-H. Kang, C.-W. Hu. *Inorg. Chem.*, **42**, 3119 (2003); (g) R. Kitaura, S. Kitagawa, Y. Kubota, T.C. Kobayashi, K. Kindo, Y. Mita, A. Matsuo, M. Kobayashi, H.-C. Chang, T.C. Ozawa, M. Suzuki, M. Sakata, M. Takata. *Science*, **298**, 2358 (2002); (h) B. Moulton, M.J. Zaworotko. *Chem. Rev.*, **101**, 1629 (2001); (i) C. Janiak. *J. Chem. Soc., Dalton Trans.*, 2781 (2003); (j) S.L. James. *Chem. Soc. Rev.*, **32**, 276 (2003); (k) S.–L. Zheng, X.-M. Chen. *Aust. J. Chem.*, **57**, 703 (2004); (l) D. Maspoch, D. Ruiz-Molina, J. Veciana. *J. Mater. Chem.*, **14**, 2713 (2004); (m) S.R. Batten, K.S. Murray. *Coord. Chem. Rev.*, **246**, 103 (2003); (n) Y. Zhou, M. Hong, X. Wu. *Chem. Commun.*, 135 (2006); (o) S. Kitagawa, R. Kitaura, S. Noro. *Angew. Chem. Int. Ed.*, **116**, 2388 (2004); (p) P.J. Hagrman, D. Hagrman, J. Zubieta. *Angew. Chem. Int. Ed.*, **38**, 2638 (1999); (q) M. Eddaoudi, J. Kim, D. Vodak, A. Sudik, J. Wachter, M. O'Keeffe, O.M. Yaghi. *PNAS*, **99**, 4900 (2002); (r) L. Carlucci, G. Ciani, D. Proserpio. *Coord. Chem. Rev.*, **246**, 247 (2003); (s) M.J. Plater, M.R. St. J. Foreman, T. Gelbrich, S.J. Coles, M.B. Hursthouse. *J. Chem. Soc., Dalton Trans.*, 3065 (2000).
[2] X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich, A.P. Alivisatos. *Nature*, **404**, 59 (2000).
[3] T. Uemura, S. Kitagawa. *J. Am. Chem. Soc.*, **125**, 7814 (2003).
[4] S.R. Batten, R. Robson. *Angew. Chem. Int. Ed.*, **37**, 1460 (1998).
[5] D.M. Ciurtin, Y.-B. Dong, M.D. Smith, T. Barclay, H.-C. zur Loye. *Inorg. Chem.*, **40**, 2825 (2001).
[6] G.M. Sheldrick. *SHELXS*-97 *and SHELXL*-97, Göttingen University, Germany (1997).
[7] (a) L.J. Farrugia. *Ortep*-3 *for Windows*, *J. Appl. Cryst.*, **30**, 565 (1997); (b) *Mercury* 1.4.1, Copyright Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (2001–2005).
[8] J. Yang, C. Lin, Z. Wang, J. Lin. *Inorg. Chem.*, **45**, 8973 (2006).