J Chem Crystallogr (2011) 41:763–766
DOI 10.1007/s10870-010-9970-9

ORIGINAL PAPER

Preparation and Crystal Structural Study of a Novel Coordinated Polymer $[HgI_2(4\text{-bped})_2]$ (bped = bis(4-pyridyl)ethylene diamine)

Yu Liang · Fukai Zhao · Qingli Wang · Yunyin Niu

Received: 13 June 2009 / Accepted: 31 December 2010 / Published online: 21 January 2011

Abstract A novel coordinated polymer $[HgI_2(4\text{-bped})_2]$ was synthesized through the reaction of bis(4-pyridyl) ethylene diamine and HgI_2 in mixed MeOH–THF (5:2). The crystal structural analysis indicated that the complex crystallized in a monoclinic space group $P2_1/c$, $a = 10.8392(12)$, $b = 19.841(2)$, $c = 8.8279(10)$, $\beta = 95.452(2)$, $V = 1889.9(4)$ Å^3, $Z = 4$. The complex possessed a novel three-dimensional supramolecular framework formed by hydrogen bonds among repeating $[HgI_2(4\text{-bped})]_2$ dimeric units.

Keywords Coordinated polymer · Crystal structure · HgI_2 adducts · Metallamacrocycle

Introduction

Metallosupramolecular species with fascinating structures and topology had become one of the most active areas of material science and chemical research, because of their potential applications on magnetism, electrical, conductivity, ion exchange, separation and catalysis [1–10]. In the supramolecular compounds, coordination interactions between metal centers and multidentate organic ligands formed the primary structure, which could be further organized to supramolecular frameworks through weak noncovalent interactions, such as hydrogen bonding, halogen bonding, and π–π interactions [11–14]. It was found that metallosupramolecule of mercuric iodide presented the important utility in the fields such as optical detector and superconducting materials, and the self-assemble of metallosupramolecule of mercuric iodide had attracted much attention [15–17]. Recently, some macrocyclic coordination polymers of mercuric iodide were designed and constructed with the introduce of the organic nitrogen-containing heterocyclic bridging ligands [18–23].

In the study, a novel three-dimensional metallosupramolecular complex $[HgI_2(4\text{-bped})_2]$ was obtained through the reaction of bis(4-pyridyl)ethylene diamine and HgI_2 in mixed MeOH–THF (5:2). The crystal structural analysis indicated that the complex crystallized in a monoclinic space group $P2_1/c$, and was a binuclear metal macrocyclic complex with symmetry of center.

Experimental

General Information and Materials

Iso-Nicotinic acid and Ethylene diamine anhydrous were obtained from Aldrich Chemical Company. All other chemicals were of A. R. Grade and used without further purification. The IR spectrum was recorded on a Shimazu IR435 spectrometer as KBr disk (4000–400 cm^{-1}).

Syntheses of the Ligand Bped

A solution of 0.1 mol ethylene diamine anhydrous (6 g) in pyridine anhydrous was added to a solution of 0.2 mol iso-Nicotinic acid (24.6 g) in pyridine anhydrous, and then 2 mL triphenyl phosphate was added to the mixture. The

Y. Liang
College of Chemistry and Chemical Engineering,
Xinxiang University, Xinxiang 453000,
People's Republic of China

F. Zhao · Q. Wang · Y. Niu (✉)
Department of Chemistry, Zhengzhou University,
Zhengzhou 450052, Henan, People's Republic of China
e-mail: niuyy@zzu.edu.cn

mixture was stirred while heating at reflux for 40 min. The resultant precipitate was collected by suction filtration, rinsed with water to remove pyridine and washed with acetone to remove triphenyl phosphate. The product was recrystallized from a methanol–water mixture in about 71% yield.

Syntheses of the Complex [HgI_2(4-bped)$_2$]

A solution of bped (0.1 mmol) in CH_3OH (5 mL) was added to a solution of HgI_2 (45.4 mg, 0.1 mmol) in THF (2 mL). The solution was then filtered and slowly evaporated in a vial at room temperature. Colorless crystals of the complex were obtained after approximate 3 days in about 51% yield. IR (KBr): 2942.0(m), 1608.9(vs), 1426.6(s), 1221.5(s), 1067.3(m), 1010.7(s), 813.7(s), 608.2(m), 514.8(s) cm^{-1}.

X-ray Crystallography

Suitable crystals were selected for the structure analysis. The diffraction data were collected on a Bruker APEX-II area-detector diffractometer operating at 50 kV and 40 mA using MoKα radiation (0.71073 Å). Data collection and reduction were performed using the SMART and SAINT softwares [24]. The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F2 using SHELXTXL package [25]. The hydrogen atoms were generated geometrically and included in structure factor calculations. Crystal data and refinement details were summarized in Table 1. Selected bond lengths and bond angles were listed in Table 2.

Table 1 Crystal data and structure refinement for [HgI_2(4-bped)$_2$]

CCDC deposit no.	628787
Compound	[HgI_2(4-bped)$_2$]
Formula	$C_{14}H_{14}HgI_2N_4O_2$
Formula weight	724.68
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.8392(12)
b (Å)	19.841(2)
c (Å)	8.8279(10)
α (°)	90
β (°)	95.452(2)
γ (°)	90
Volume (Å^3)	1889.9(4)
Z	4
Calculated density (Mg m^{-3})	2.547
μ (mm^{-1})	11.423
F(000)	1312
Crystal size (mm)	0.20 × 0.17 × 0.16
Crystal color	White
Temperature (K)	297(2)
Wavelength (Å)	0.71073
$2\theta_{max}$ (°)	28.25
Reflections collected	12932
Independent reflections	4477
R_{int}	0.0355
Data/restraints/parameters	4477/0/208
Goodness-of-fit on F^2	1.036
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0354$, $wR2 = 0.0819$
R indices (all data)	$R1 = 0.0440$, $wR2 = 0.0857$
Largest diff. peak and hole (e A^{-3})	0.999 and −1.244

Results and Discussion

Infrared Spectrum Analysis

The IR spectra of [HgI_2(4-bped)$_2$]exhibits characteristic strong absorption around 1608 cm^{-1} for the carbonyl groups, and 1221.5(s)–1010.7 cm^{-1} belong to the –NH– groups. The strong bands centered at 813.7, 608.2, and 514.8(s) cm^{-1} are attributed to the ring of pyridines, and the moderate bands at 2942.0 and 1426.6 cm^{-1} is attributed to –CH_2– in the title compound.

Crystal Structure of the Complex [HgI_2(4-bped)$_2$]

Single crystal X-ray diffraction analysis revealed that the complex was a novel neutral binuclear metallamacrocycle with a crystallographic center of symmetry. As was shown in the Fig. 1, the binuclear metallamacrocycle was composed of two Hg(II) ions, two bridging 4-bped ligands and

Table 2 Selected geometric parameters (in Å and °) for [HgI_2(4-bped)$_2$]

Complex [HgI_2(4-bped)$_2$]	
Hg(1)–N(4)#1	2.454(4)
Hg(1)–N(1)	2.457(5)
Hg(1)–I(2)	2.6391(5)
Hg(1)–I(1)	2.6425(5)
N(4)#1–Hg(1)–N(1)	98.52(6)
N(4)#1–Hg(1)–I(2)	100.31(1)
N(1)–Hg(1)–I(2)	102.42(1)
N(4)#1–Hg(1)–I(1)	103.52(1)
N(1)–Hg(1)–I(1)	100.95(1)
I(2)–Hg(1)–I(1)	143.52(7)
C(1)–N(1)–Hg(1)	122.5(4)
C(5)–N(1)–Hg(1)	119.9(4)
C(14)–N(4)–Hg(1)#1	119.9(4)
C(10)–N(4)–Hg(1)#1	122.1(4)

Symmetry for compound: #1 −x + 1, −y, −z + 1

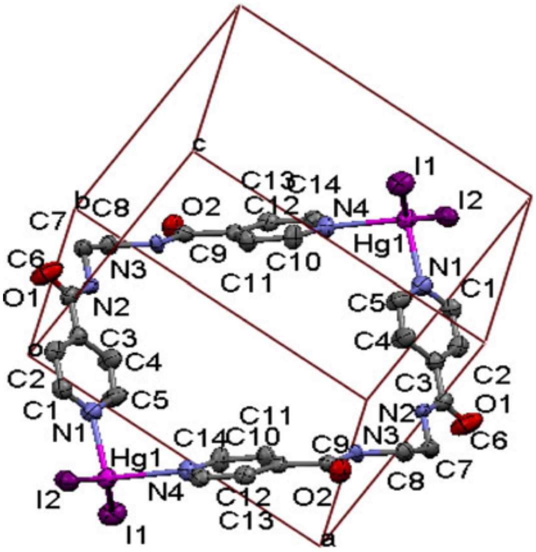

Fig. 1 The ORTEP diagram (50% probability ellipsoids) showing the binuclear metallamacrocycle of the complex [HgI$_2$(4-bped)$_2$] **1**. The hydrogen atoms were omitted for clarity

Table 3 D–H···A interactions and their distance and angle parameters for the complex [HgI$_2$(4-bped)$_2$]

D–H···A interaction	$D_{D\cdots A}$ (Å)	$D_{H\cdots A}$ (Å)	∠DHA (°)
C(11)–H(11A)···O(1)	3.661	2.707	167.90
C(8)–H(8B)···O(2)	3.410	2.577	149.36
C(8)–H(8A)···I(2)	3.968	3.177	139.86

four terminal I anions. The distorted tetrahedral coordination center Hg(II) was bound to two iodide atoms and two N-donors from 4-bped ligands, and the Hg1–I1, Hg1–I2, Hg1–N1 and Hg1–N4 bond lengths were 2.6425(5), 2.6391(5), 2.457(5) and 2.454(4) Å, respectively, which were similar to those of the related polymers [HgI$_2$(L)]$_n$ (Hg–I ranging from 2.6377(0) to 2.7125(8) Å and Hg–N from 2.3626(6) to 2.5917(0) Å) [26–29]. Additionally, the angles around Hg center ranged from 98.52(6) to 143.52(7)°. Two bridging 4-bped ligands and two Hg atoms consisted of an interesting, ring-like structure unit with dimensions of 13.0255 × 12.7413 Å (Hg1–Hg1 × C7–C7).

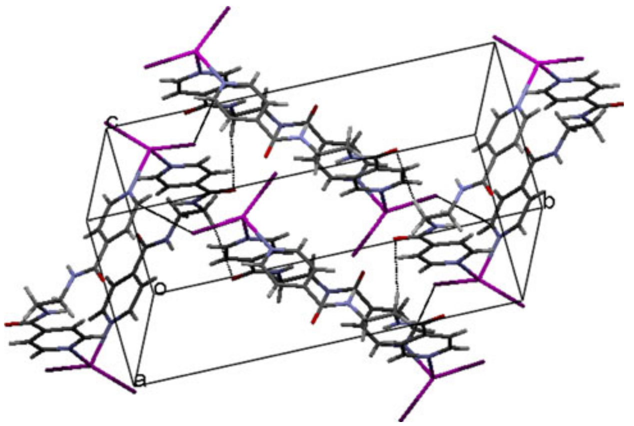

Fig. 2 Three-dimensional supramolecular framework of complex [HgI$_2$(4-bped)$_2$] with CH···O, CH···I interaction indicated by *dotted lines*

In the solid state structure, there existed three types of outer sphere intermolecular interactions: the terminal I2 atom had a C–H···I hydrogen bonding with the aliphatic C(8)H(8A)s group from 4-bped ligand of the neighboring dimeric unit; on the other hand, there were aromatic C(11)–H(11A)···O(1), aliphatic C(8)–H(8B)···O(2) hydrogen bonding between 4-bped ligands of the neighboring dimeric unit along c-direction. Although the C–H···I(O) hydrogen bonds (Table 3) were relatively weak, they were very important in holding crystal framework. As a result of these C–H···I(O) inducing contacts, the repeating [HgI$_2$(4-bped)$_2$]$_2$ dimeric units grow infinitely in the *a*, *b*, *c* directions, and then a final supramolecular structure was built (Fig. 2). Indeed all these intermolecular interactions are weak, which can be proved that this binuclear complex become melting state at 140 °C, and begin continuous decomposition at 162 °C. The melting/decomposition temperatures are comparable to the related mononuclear Hg complex [27].

Supplemental Material

CCDC-628787 contains the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail:deposit@ccdc.cam.ac.uk].

Acknowledgment We gratefully acknowledge the financial support of The National Science Foundation of China (20671083).

References

1. Fujita M, Ogura K (1996) Coord Chem Rev 148:249
2. Batten SR, Robson R (1998) Angew Chem Int Ed 37:1460
3. Blake AJ, Champness NR, Hubberstey P, Li WS, Withersby MA, Schroder M (1999) Coord Chem Rev 183:117
4. Hagrman PJ, Hagrman D, Zubieta J (1999) Angew Chem Int Ed 38:2638
5. Oshio H, Saito Y, Ito T (1997) Angew Chem Int Ed 36:2673
6. Kobel W, Hanack M (1986) Inorg Chem 25:103
7. Min KS, Suh MP (2000) J Am Chem Soc 122:6834
8. Choi HJ, Lee TS, Suh MP (1999) Angew Chem Int Ed 38:1405
9. Sawaki T, Aoyama Y (1999) J Am Chem Soc 121:4793
10. Zhang JP, Chen XM (2009) J Am Chem Soc 131(15):5516

11. Laborda S, Clerac R, Anson CE, Powell AK (2004) Inorg Chem 43:5931
12. Burchell TJ, Eisler DJ, Puddephatt RJ (2004) Inorg Chem 43:5550
13. Fei BL, Clerac R, Anson CE, Powell AK (2004) Dalton Trans 1381
14. Pennington WT et al (2008) Halogen bonding with dihalogens and interhalogens. In: Metrangolo P, Resnat G (eds) Halogen bonding: fundamentals and applications, structure and bonding, vol 126. Springer, Berlin, pp 65–104
15. Schlesinger TE, James RB (eds) (1995) Semiconductors for room temperature nuclear detector applications; semiconductors and semimetals, vol 43. Academic Press, p 497
16. Yoon JB, Jang ES, Kwon SJ, Ayral A, Cot L, Choy JH (2001) Bull Korean Chem Soc 22:1111
17. Niu YY, Song YL, Hou HW, Zhu Y (2003) Inorg Chim Acta 355:151
18. Nam HJ, Lee HJ, Noh DY (2004) Polyhedron 23:115
19. Su CY, Goforth AM, Smith MD, Loye HC (2003) Inorg Chem 42(18):5685
20. Niu YY, Zhang N, Song YL, Hou HW, Fan YT, Zhu Y (2005) Inorg Chem Commun 8:495
21. Burchell TJ, Puddephatt RJ (2005) Inorg Chem 44(10):3518
22. Li L, Yang JX, Zhou HP, Tian YP, Tao XT, Jiang MH (2007) Inorg Chem Commun 10:163
23. Deiters E, Bulach V, Hosseini MW (2006) New J Chem 30:1289
24. Sheldrick GM (1996) SADABS "Siemens area detector absorption correction". University of Göttingen, Göttingen
25. SHELXTL-PC, version 5.03. Siemens Analytical Instruments, Madison
26. Blachnik R, Lytze K, Reuter H (1996) J Solid State Chem 126:95
27. Lobana TS, Sanchez A, Casas JS, Castineras A, Sordo J, Garcia-Tasende MS (1998) Polyhedron 17:3701
28. Popovic Z, Matkovic-Calogovic D, Hasic J, Vikic-Topic D (1999) Inorg Chim Acta 285:208
29. Almagro X, Clegg W, Sanchez LC, Duarte PG, Traveria M (2001) J Organomet Chem 623:137