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Construction of a New One-Dimensional Hg(II) Coordination Polymer $[Hg_4(Chbz)_4(4,4'\text{-}Bipy)_2(NO_3)_4 \cdot H_2O]_n$ Involving in situ Chlorobenzene Synthesis[1]

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Abstract—A new 1D Hg(II) coordination polymer, $[Hg_4(Chbz)_4(4,4'\text{-}Bipy)_2(NO_3)_4 \cdot H_2O]_n$ (**I**) (Chbz = 2-chlorophenyl, 4,4'-Bipy = 4,4'-bipyridine), has been synthesized by the in situ synthesis of 2-chlorophenyl from the reaction of 2-chlorobenzoic acid, 4,4'-Bipy and mercury salt under hydrothermal conditions and characterized by elemental analysis, IR, TGA and single-crystal X-ray diffraction. Complex **I** exhibits an interesting 1D infinite zigzag polymeric chain along the *x* axis. The photoluminescent measurements reveal that complex **I** exhibits fluorescent emission in the solid state at room temperature.

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INTORDUCTION

The design and construction of coordination polymers materials are receiving growing attention due to their potential applications in magnetism, ion exchange, catalysis, gas separation, sensor, and many other areas [1–6]. The rational selection of organic ligands is crucial to design and synthesize the target coordination polymers, which not only determine their structure and dimensionality, but also influence their potential properties and applications [7, 8]. So far, a variety of fascinating coordination polymers have been constructed by carboxylate ligands and N-containing ligands as the auxiliary ligands. As is well known, 4,4'-bipyridine ligands may act in bidentate bridging or monodentate terminal modes, which is an excellent candidate for construction novel structures as the auxiliary ligands, and leading to the formation of a variety of 1D chain, 2D layer, and 3D network motifs [9]. The advantage of hydrothermal route to access many kinetically controlled reactions with comparative ease, which can be made use of in realizing such coordination polymers with unique structural features in many cases. It has been shown that many phenomena of in situ ligands synthesis, such as reductive coupling [10], oxidation-hydrolysis [11], decarboxylation [12], nitration substitution [13] and so on, occurred under such hard conditions as in hydrothermal methods. Herein, the results of an attempt to generate a Hg(II)-based coordination framework utilizing 2-chlorobenzoic acid, having potential O-donor atoms, and 4,4'-bipyridine (4,4'-Bipy) as bridging ligands are described. A new 1D coordination polymer, $[Hg_4(Chbz)_4(4,4'\text{-}Bipy)_2(NO_3)_4 \cdot H_2O]_n$ (**I**) (Chbz = 2-chlorophenyl), was isolated under hydrothermal condition which has been characterized by elemental analysis, IR spectroscopy, X-ray crystallography, and by solid-state photoluminescence measurements. From the analysis it revealed that the 2-chlorobenzoic acid ligand is not present. Rather, it is revealed that $2\text{-}ClC_6H_4$ (Chbz) was formed in situ by the decarboxylation of 2-chlorobenzoic carboxylate under the reaction conditions employed. It has been proved that the decarboxylation reaction was easy observed under hydrothermal conditions in the presence of transition-metal mediators, usually copper, silver, or mercury salts [14].

EXPERIMENTAL

Materials and measurements. All chemicals purchased were of reagent grade and used without further purification. All syntheses were carried out in 23 mL Teflon-lined autoclaves under autogenous pressure. Elemental analyses (C, H, and N) were performed on a PerkinElmer 240 CHN elemental analyzer. The IR spectra were acquired using Nicolet Avatar 360 FT-IR spectrophotometer. Luminescence spectra for crystal solid samples were recorded at room temperature on a Hitachi F-4500 fluorescence spectrophotometer. Thermogravimetry analyses (TGA) were performed on a simultaneous SDT thermal analyzer (STA449C,

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Netzsch) under a flow of N_2 at a heating rate of 10°C/min between ambient temperature and 800°C.

Synthesis of complex I. A mixture of $Hg(NO_3)_2 \cdot 1/2H_2O$ (0.17 g, 0.5 mmol), 2-chlorobenzoic acid (0.08 g, 0.5 mmol), 4,4'-Bipy (0.075 g, 0.5 mmol) and H_2O (15 mL) was stirred for 30 min in air and then sealed in a 23 mL Teflon reactor and kept under autogenous pressure at 150°C for 72 h. The mixture was cooled to room temperature at a rate of 5°C h^{-1} and colorless block crystals were obtained in a yield of 42% based on the 4,4'-Bipy.

For $C_{44}H_{34}N_8O_{13}Cl_4Hg_4$

anal. calcd., %:	C, 28.90;	H, 1.86;	N, 6.68.
Found, %:	C, 28.86;	H, 1.88;	N, 6.70.

IR (KBr; ν, cm^{-1}): 3470 v.s, 1617 m, 1384 v.s, 808 m, 762 w, 616 s.

X-ray crystal determination. A colorless crystal with dimensions of 0.31 × 0.22 × 0.20 mm was selected for X-ray analyses. All diffraction data were collected on a Bruker APEXII area-detector diffractometer operating at 50 kV and 30 mA using a MoK_α radiation ($\lambda = 0.71073$ Å) at 296(2) K by using a ω scan mode. In the range $1.35° \le \theta \le 27.55°$, a total of 20531 reflections were collected, 5648 of which were unique ($R_{int} = 0.0266$) and were used in the succeeding structure calculations. Data collection and reduction were performed using the APEX II software [15]. Multi-scan absorption corrections were applied for all the data sets using the APEX II program [15]. The programs SHELXS-97 and SHELXL-97 were used for structure determination and refinement. The structures were solved by direct methods. Metal atom centers were located from the E-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinements were performed by full matrix least-squares methods on F^2 [16]. All non-hydrogen atoms were treated anisotropically. The hydrogen atoms attached to C were added according to theoretical models. The final $R = 0.0317$ and $wR = 0.0900$ ($w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 2.8052P]$, where $P = (F_o^2 + 2F_c^2)/3$) for 4568 observed reflections with $I > 2\sigma(I)$. $S = 1.040$, $(\Delta/\sigma)_{max} = 0.000$, $(\Delta\rho)_{max} = 2.104$ and $(\Delta\rho)_{min} = -0.933$ $e/Å^3$. Crystal parameters and details of the data collection and refinement are given in Table 1. Selected bond lengths and angles are given in Table 2.

Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 850833; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 1. Crystallographic data and experimental details for complexes **I**

Parameter	Value
	I
Formula	$C_{44}H_{34}N_8O_{13}Cl_4Hg_4$
Molecular weight	1826.95
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	8.0257(5)
b, Å	10.8731(7)
c, Å	15.1979(10)
α, deg	83.7610(10)
β, deg	82.7140(10)
γ, deg	70.7270(10)
V, $Å^3$	1238.63(14)
Z	1
ρ_{calcd}, g cm^{-3}	2.449
Crystal size, mm	0.31 × 0.22 × 0.20
$F(000)$	846
$\mu(MoK_\alpha)$, mm^{-1}	12.644
θ Range for data collection, deg	1.35~27.55
Limiting indices h, k, l	$-10 \le h \le 10$,
	$-14 \le k \le 13$,
	$-19 \le l \le 19$
Type of scan	φ and ω scan
Reflections collected	20531
Independent reflections, R_{int}	0.0266
Reflections with $I > 2\sigma(I)$	4568
Number of parameters	334
Goodness-of-fit on F^2	1.040
Final R_1, wR_2, $I > 2\sigma(I)$	
R_1, wR_2, all data	$R_1 = 0.0317$
	$wR_2 = 0.0840$
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, e $Å^{-3}$	$R_1 = 0.0433$
	$wR_2 = 0.0900$

Note: $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o)^2]^{1/2}$.

Table 2. Selected bond lengths (Å) and bond angles (deg) for complex **I***

Bond	*d*, Å	Angle	ω, deg
Hg(1)–C(16)	2.060(7)	C(16)Hg(1)N(1)	175.6(2)
Hg(1)–O(4)^i	2.809(5)	C(16)Hg(1)O(1)	101.3(2)
Hg(1)–O(1)	2.756(5)	N(1)Hg(1)O(1)	83.00(19)
Hg(1)–N(1)	2.125(5)	N(1)Hg(1)O(4)^i	73.60(18)
Hg(1)–O(3)	2.908(6)	N(1)Hg(1)O(3)	89.54(19)
Hg(2)–C(17)	2.048(7)	O(1)Hg(1)O(3)	44.54(16)
Hg(2)–N(2)	2.102(5)	O(4)Hg(1)O(3)	120.28(15)
Hg(2)–O(4)	2.683(5)	C(17)Hg(2)N(2)	177.8(2)
		O(4)Hg(2)N(2)	83.40(18)
		C(17)Hg(2)O(4)	98.6(2)

* Symmetry codes: ^{i}*x*, 1 + *y*, *z*.

RESULTS AND DISCUSSION

Single-crystal X-ray diffraction analysis reveals that compound **I** displays a 1D zigzag chain structure. A thermal ellipsoid plot view of **I** is shown in Fig. 1. In the asymmetric unit of **I**, there are one 4,4'-Bipy ligand, two Chbz ligands, two nitrate ligands, one free water molecular and two Hg^{2+} ions. Atom Hg(1) is five-coordinated by three oxygen atoms from two different nitrate ligands, one nitrogen atom from 4,4'-Bipy and one carbon atom of Chbz ligand and displays a hemidirected coordination. Atom Hg(2) is four coordinated by two nitrate O atoms, one 4,4'-Bipy N atom and one C atom of 2-ClC_6H_4 ligand in a considerably distorted tetrahedral environment. The Hg–O, Hg–N, Hg–C bond lengths and OHgO, OHgN, CHgN, CHgO bond angles are within the ranges of those for other analogical Hg complexes [17, 18]. In the complicated structure, nitrate ligands adopt two different coordination modes: one acts a μ_2 bridging mode to link two Hg^{2+} ions, and the other uses a chelating mode to link one Hg^{2+} ion. Whilst the 4,4'-Bipy ligand takes in *trans* coordination motif and bidentate bridging to link two Hg^{2+} ions. On the basis of above connections, Hg(II) centers were connected together to form an infinite zigzag chain in the *x* axis direction (Figs. 2a, 2b), and the adjacent separations of Hg^{2+} ions are 4.495(2) and 11.226(3) Å, respectively. These chains are further self-assembled into a dimer through intermolecular O–H···O, O–H···Cl hydrogen bonds involving the free water molecules, nitrate oxygen atoms and chlorine atoms of 2-ClC_6H_4 ligands, C–H···π and π–π stacking interactions between phenyl of neighboring Chbz ligands, with the centroid-to-centroid distance of 3.640(5) Å (Fig. 2c). The H-to-centroid distance of H(4A)···Cg(1)^i 2.90(2) Å (Cg(1) is the centroid of the C(17)–C(22) ring).

The IR spectra of compound **I** shows broad bands in the 3470 cm^{-1}, which may be assigned to the ν(O–H) stretching vibrations of the free water molecules. The feature at 1384 cm^{-1} is attributed to ν(NO_3) stretching vibrations of nitrate ligands.

Thermal gravimetric analyses (TGA) was carried out to examine the thermal stability of **I**. The samples were heated up in flowing N_2 with a heating rate of 10°C/min. The TGA curve is depicted in Fig. 3, which

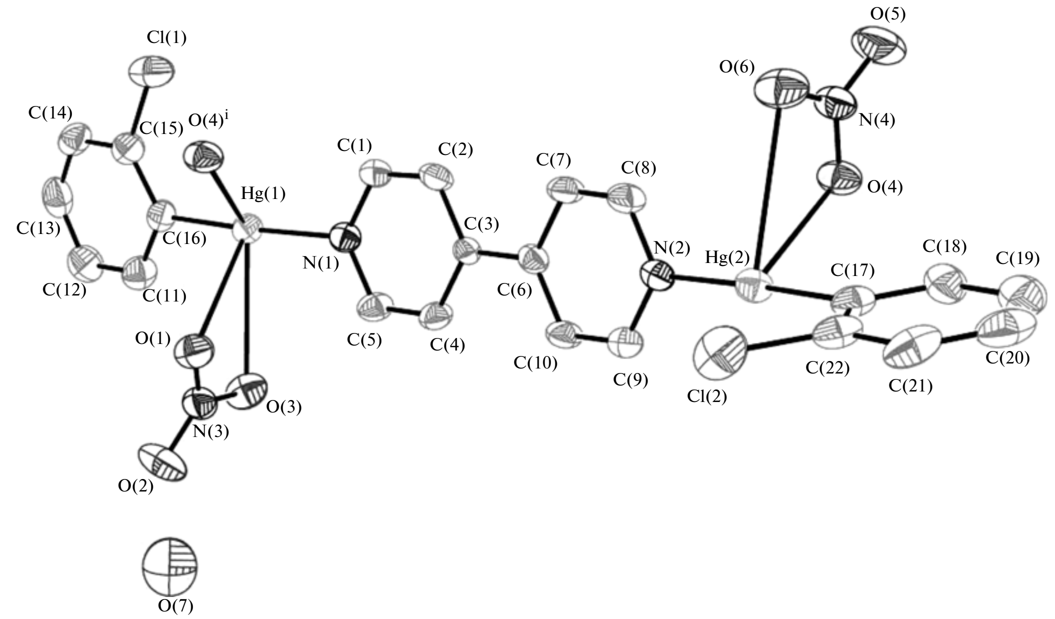

Fig. 1. A thermal ellipsoid plot view of **I** (30% probability ellipsoids; all H atoms were omitted for clarity; symmetry codes: ^{i}*x*, 1 + *y*, *z*).

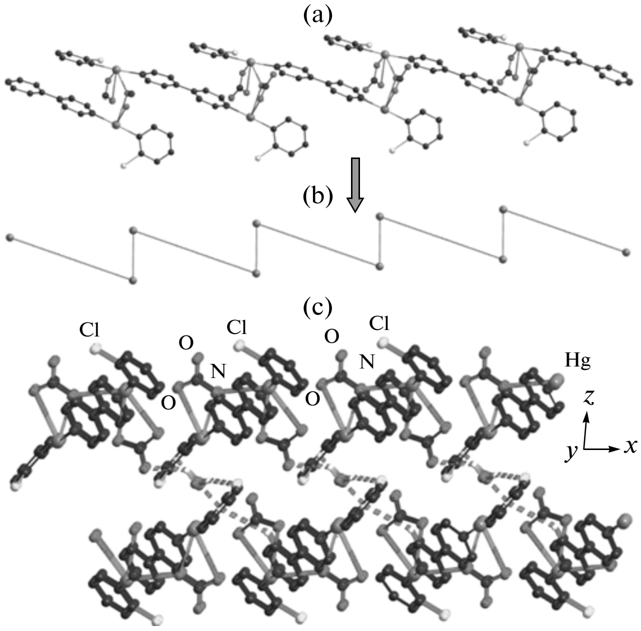

Fig. 2. View of the 1D zigzag chain of **I** in the *x* axis (a); view of the simplified chain of **I** (b); view of a dimer formed by hydrogen bonds (c). C–H···π and π–π stacking interactions are shown as dashed line.

shows that a gradual weight-loss step of 1.2% (50–150°C), corresponding to the escape of one free water molecule (calcd. 1.0%). The weight-loss step that occurs above 180°C corresponds to the decomposition of the framework.

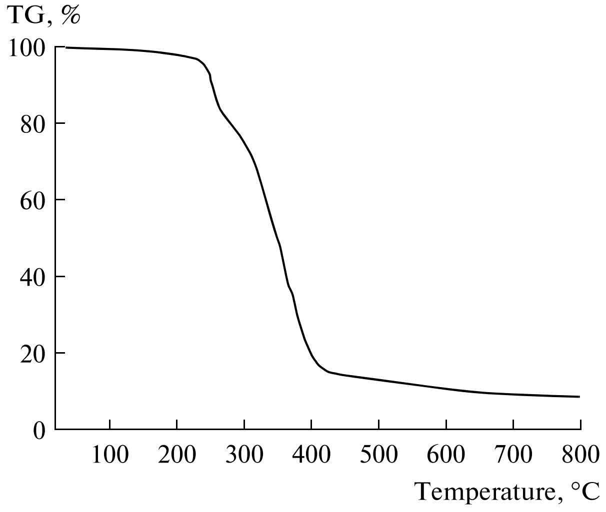

Fig. 3. TGA trace of compound **I**.

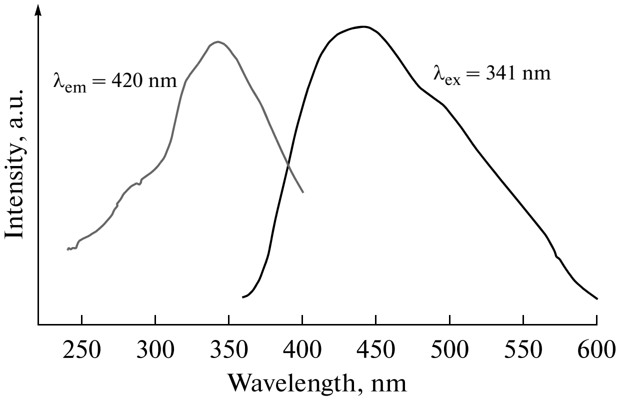

Fig. 4. Photoluminescent spectrum of **I** in the solid state at room temperature.

Among all fluorescent materials with potential applications in light-emitting devices, the d^{10} metal (Cu(I), Ag(I), Au(I), Zn(II) or Cd(II)) complexes have been studied the most extensively. However, only few mercury cations coordination polymers have been investigated for their fluorescence properties [18]. The 4,4'-Bipy ligand with pyridyl groups, which is regarded to be a good candidate for enhanced emissive properties. Photofluorescent measurement of **I** was carried out in the solid state at room temperature. As illustrated in Fig. 4, complex **I** shows broad fluorescent emission bands with maximum intensities at 420 nm upon excitation at 341 nm. Compound **I** represents an obvious qualitative change of luminescence property resulted from the interaction between metal ion and ligand. The emission of compound **I** probably origins from ligand-to-metal charge transfer (LMCT) [19] excited state, because the 4,4'-Bipy ligand has relatively large π-conjugated system of phenyl ring and uses nitrogen donors to coordinate to Hg^{2+} ions, which benefits the charge transfer between Hg^{2+} ion and organic ligands. Thus, compound **I** may has potential application as a luminescent material in blue light-emitting devices.

In summary, a new one-dimensional coordination polymer was successfully constructed from a hydrothermal reaction involving in situ chlorobenzene ligand synthesis. Complex **I** shows an interesting 1D infinite zigzag polymeric chain structure. The intense blue luminescence properties of **I** at room temperature suggest that the complex and related systems have potential for applications as luminescent materials.

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