Syntheses, characterization, crystalline architectures and luminescence of two halidomercury(II) compounds containing a bidentate (N,O) chelator: variation in nuclearities and superstructures by varying halides

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Abstract. A neutral coordination polymer of chloridomercury(II) of the type $[\text{Hg}(\text{bzpy})(\mu - \text{Cl})\text{Cl}]_n$ (**1**) and a dinuclear complex of bromidomercury(II) of the type $[\text{Hg}(\text{bzpy})(\mu - \text{Br})\text{Br}]_2$ (**2**) (bzpy = 2-benzoylpyridine) were synthesized using a 1:1 molar ratio of $\text{HgCl}_2/\text{HgBr}_2$ and bzpy in methanolic solvent at room temperature and X-ray crystallographically characterized. Structural analyses show that each mercury(II) center in both the compounds adopts a distorted square pyramidal geometry with an HgNOX_3 [$\text{X} = \text{Cl}$ in **1** and $\text{X} = \text{Br}$ in **2**] chromophore. Each mercury(II) center in the coordination polymer **1** is connected to two other metal(II) centers through two different chlorido bridges affording a zigzag one-dimensional (1D) chain. In the crystalline state, 1D chains in **1** are stabilized through weak non-covalent $\text{C}-\text{H} \cdots \pi$ interactions promoting to a 2D sheet structure, and these 2D sheets, in turn, are further associated through intermolecular $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds resulting in a 3D network structure. In **2**, two bromide ions bridge two metal(II) centers to form a dinuclear entity. The dinuclear units in **2** are packed through $\pi \cdots \pi$ stacking and intermolecular $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds to afford a 2D sheet structure. These 2D sheets self-assemble through intermolecular $\text{C}-\text{H} \cdots \text{Br}$ hydrogen bonds promoting to a 3D network structure. The thermally stable compounds **1** and **2** exhibit intraligand $^1(\pi - \pi^*)$ fluorescence in DMF solutions at room temperature.

Keywords. Halidomercury(II); chlorido/bromido bridge; bidentate (N, O) chelator; X-ray structure; luminescence.

1. Introduction

Extensive in-depth research on the design and synthesis^{1–3} of mono-, di- and polynuclear coordination compounds of mercury(II)^{4–10} has spawned great interest for isolation of different advanced functional materials^{11–14} with interesting electronic and optoelectronic properties.^{14–18} The sheer necessity for such research is the judicious choice¹⁹ of organic ligands and inorganic/organic bridging units that may lead to directed physicochemical properties. Single-pot synthesis²⁰ of the building components is one of the widely used

synthetic approaches towards the preparation of such materials. Exploiting the different varieties of coordination geometries around this $5d^{10}$ ion, diverse molecular aggregates and crystalline architectures^{21,22} of different shapes and sizes²³ may be obtained through strong metal–ligand covalent bonds²⁴ and multiple weak lateral non-covalent forces.^{22,25–27} 2-Benzoylpyridine (bzpy; Scheme 1)^{28,29} has recently been used as an organic spacer to isolate different coordination molecules and supramolecular entities because of its precise steric and electronic features. Halides^{30–32} are suitable terminal/bridging units which in combination with organic

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Scheme 1. (N, O) donor set in bzpy.

ligands result in different molecular aggregates through their versatile ligational modes. Recently, we reported the syntheses and structural characterizations of different pseudohalidomercury(II) compounds in combination with Schiff bases of different denticities.^{33–39} In our present endeavor, we have chosen bzpy, a bidentate (N,O) organic ligand to isolate halidomercury(II) compounds with different nuclearities coupled with varied molecular and crystalline architectures. We have successfully synthesized a neutral coordination polymer of chloridomercury(II) of the type $[\text{Hg}(\text{bzpy})(\mu-\text{Cl})\text{Cl}]_n$ (**1**) and a dinuclear complex of bromidomercury(II) of the type $[\text{Hg}(\text{bzpy})(\mu-\text{Br})\text{Br}]_2$ (**2**) using a 1:1 molar ratio of $\text{HgCl}_2/\text{HgBr}_2$ and bzpy in methanolic solvent at room temperature. The details of syntheses, crystal structures, and thermal and luminescence behaviors of these compounds are described below.

2. Experimental

2.1 Materials and methods

High purity 2-benzoylpyridine (Lancaster, UK), mercury(II) chloride (E. Merck, India) and mercury(II) bromide (E. Merck, India) were purchased from respective concerns and used as received. All other chemicals and solvents used were AR grade. The synthetic reactions and work-up were done in the open air.

2.2 Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. IR spectra (KBr discs, 4000–400 cm^{-1}) were recorded using a Perkin-Elmer FTIR model RX1 spectrometer. Molar conductances were measured using a Systronics conductivity meter where the cell constant was calibrated with 0.01(M) KCl solution, and DMF was used as a solvent. Thermal behavior was examined with a Perkin-Elmer Diamond TG/DT analyzer heated from 30 to 700 °C under nitrogen. Ground state absorption and steady-state fluorescence measurements (in DMF) were made with a Shimadzu model UV-2450 UV-Vis spectrophotometer and a Hitachi model F-7000 fluorescence spectrophotometer, respectively.

2.3 Preparation of the complexes

2.3a $[\text{Hg}(\text{bzpy})(\mu-\text{Cl})\text{Cl}]_n$ (**1**): A colorless methanolic solution (20 mL) of bzpy (0.183 g, 1 mmol) was added dropwise to a solution of HgCl_2 (0.271 g, 1 mmol) in the same solvent (20 mL). The resulting colorless solution was filtered and the supernatant liquid was kept undisturbed in the open air for slow evaporation. After a week, colorless crystalline product of **1** was isolated by filtration, washed with dehydrated alcohol and dried *in vacuo* over silica gel. Yield: 0.318 g (70%). Anal. Calc. for $\text{C}_{12}\text{H}_9\text{NOCl}_2\text{Hg}$ (**1**) C, 31.69; H, 1.99; N, 3.08%. Found: C, 31.61; H, 2.05; N, 3.14%. IR (KBr, cm^{-1}): $\nu(\text{C}-\text{H})$ 3056, 2923; $\nu(\text{C}=\text{O})+\nu(\text{C}=\text{N})+\nu(\text{C}=\text{C})$ 1660, 1614, 1589. UV-Vis (DMF, λ_{max} , nm): 270. Λ_{M} (DMF, $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): 6.

2.3b $[\text{Hg}(\text{bzpy})(\mu-\text{Br})\text{Br}]_2$ (**2**): HgBr_2 (0.360 g, 1 mmol) in methanol (20 mL) and colorless methanolic solution (20 mL) of bzpy (0.183 g, 1 mmol) were mixed together slowly. The resulting colorless solution was filtered and left undisturbed in an open air for slow evaporation. After a week, colorless crystals of **2** were collected in pure form as described in **1**. Yield: 0.407 g (75%). Anal. Calc. for $\text{C}_{24}\text{H}_{18}\text{N}_2\text{O}_2\text{Br}_4\text{Hg}_2$ (**2**) C, 26.51; H, 1.66; N, 2.67%. Found: C, 26.58; H, 1.58; N, 2.63%. IR (KBr, cm^{-1}): $\nu(\text{C}-\text{H})$ 3058, 2928; $\nu(\text{C}=\text{O})+\nu(\text{C}=\text{N})+\nu(\text{C}=\text{C})$ 1659, 1614, 1590. UV-Vis (DMF, λ_{max} , nm): 272. Λ_{M} (DMF, $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): 7.

2.4 X-ray crystallographic analyses

Single crystals of **1** and **2** suitable for X-ray analyses were selected from those obtained by slow evaporation of methanolic solutions at 298 K. Diffraction data were collected on a Bruker SMART APEX-II CCD area-detector diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). For unit cell determination, the single crystal was exposed with X-ray for 10 s in three frames. The detector frames were integrated by use of the program SAINT⁴⁰ and absorption corrections were performed with SADABS.⁴¹ The structures were solved by direct methods, using the SHELXTL⁴² program. All atomic displacement parameters for non-hydrogen atoms have been refined with the anisotropic term. For all structures, the hydrogen atoms were fixed geometrically and refined using a riding model. All calculations were carried out using SHELXTL, PLATON⁴³, MERCURY 3.3⁴⁴ and ORTEP-3⁴⁵ programs. Further details are given in Table 1.

3. Results and Discussion

3.1 Synthesis and formulation

The neutral chlorido bridged coordination polymer $[\text{Hg}(\text{bzpy})(\mu-\text{Cl})\text{Cl}]_n$ (**1**) was isolated as colorless crystals through the one-pot synthesis of a 1:1 molar

Table 1. Crystallographic data and structure refinement parameters for **1** and **2**.

Compounds	1	2
Formula	C ₁₂ H ₉ NOCl ₂ Hg	C ₂₄ H ₁₈ N ₂ O ₂ Br ₄ Hg ₂
Formula weight	454.69	1087.18
Crystal system	Orthorhombic	Monoclinic
Space group	P 212121	P21/c
<i>a</i> /Å	5.9379(2)	8.252(2)
<i>b</i> /Å	13.6605(4)	9.910(3)
<i>c</i> /Å	15.4057(5)	16.315(4)
α^0	90	90.00
β^0	90	96.416(4)
γ^0	90	90.00
<i>V</i> /Å ³	1249.63(7)	1325.9(6)
λ /Å	0.71073	0.71073
ρ_{calcd} /gm cm ⁻³	2.417	2.723
<i>Z</i>	4	2
Crystal size (mm)	0.09 × 0.11 × 0.13	0.10 × 0.11 × 0.12
<i>T</i> /K	293(2)	293(2)
μ (mm ⁻¹)	12.724	17.618
<i>F</i> (000)	840	984
θ ranges (°)	1.992–28.397	2.409–27.796
<i>h</i> / <i>k</i> / <i>l</i>	–7, 7/–18, 18/–20, 19	–10, 10/–12, 12/–20, 21
Reflections collected	18376	21137
Independent reflections (<i>R</i> _{int})	3111	3041
Data/restraints/parameters	3111/0/154	3041/0/154
Goodness-of-fit on <i>F</i> ²	1.074	1.076
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> = 0.0336, <i>wR</i> = 0.1220	<i>R</i> = 0.0532, <i>wR</i> = 0.1395
<i>R</i> indices (all data)	<i>R</i> = 0.0368, <i>wR</i> = 0.1273	<i>R</i> = 0.0864, <i>wR</i> = 0.1748
Largest peak and hole (eÅ ⁻³)	1.198 and –1.770	1.605 and –3.894

Weighting scheme: $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)]^{1/2}$, $\text{calcd } w = 1/[\sigma^2(F_o^2) + (xP)^2]$; $x = 0.1000$ for both **1** and **2**, where $P = (F_o^2 + 2F_c^2)/3$.

ratio of HgCl₂ and bzpy from methanolic solution at room temperature. The bromido bridged dinuclear compound [Hg(bzpy)(μ – Br)Br]₂ (**2**) was prepared using 1:1 molar ratio of HgBr₂ and bzpy in methanol at room temperature. Several attempts to isolate corresponding iodo compounds using HgI₂ and bzpy result in free bzpy and HgI₂ without any complex formation. The reactions for isolation of **1** and **2** were reproducible as was evident from repetitive microanalytical results, spectral behaviors and other physicochemical properties. The details of the reactions are summarized in Eq. (1):

The new compounds (**1** and **2**) were characterized by microanalytical (C, H and N), spectroscopic, thermal and other physicochemical results. The microanalytical data are in good conformity with the formulations **1** and **2**. The moisture-insensitive complexes are stable

over long periods of time in powdery and crystalline states and are soluble in methanol, ethanol, acetonitrile, dimethylformamide (DMF) and dimethylsulphoxide but are insoluble in water. In DMF solutions they behave as non-electrolytes, as reflected from their low conductivity values (~5 Ω⁻¹ cm² mol⁻¹).⁴⁶ In IR spectra for **1** and **2** (Figures S1a and S1b, Supplementary Information), the organic ligand in metal bound states exhibit ν(C = O) + ν(C = N) + ν(C = C) stretching vibrations at ~1660, ~1614 and ~1589 cm⁻¹. Weak bands found in the range 3050–2920 cm⁻¹ are assignable to the aromatic C–H stretching frequency. All other characteristic organic ligand vibrations are seen in the range 1600–600 cm⁻¹.⁴⁷ In DMF solutions the compounds exhibit absorptions at ~270 nm assignable to ligand-based π–π* transition.⁴⁸

3.2 Molecular and crystal structures

In order to define the coordination spheres of **1** and **2** conclusively, single-crystal X-ray diffraction

Figure 1. Molecular structure of the individual unit in **1** (ORTEP, 50% thermal ellipsoid).

measurements were made. Displacement ellipsoid diagrams with atom labelling schemes and perspective views of the crystal structures of **1** and **2** are shown in Figures 1, 2, 3, 4, 5, 6 and 7. Selected bond distances, angles and non-covalent bond parameters are given in Tables 2, 3 and 4, respectively. Single crystal X-ray structure analyses show that compounds **1** and **2** consists of poly-/dinuclear units which are further engaged in different kinds of cooperative hydrogen bonds like C–H...O and C–H...Br and along with C–H... π and π ... π interactions as the case among themselves resulting in different crystalline architectures.

3.2a $[Hg(bzpy)(\mu - Cl)Cl]_n$ (**1**): A molecular unit with the atom-labelling scheme for **1** is shown in Figure 1. Structural analyses show that each mercury(II) center in **1** adopts a distorted square pyramidal⁴⁹ coordination environment which is confirmed by the value of the τ parameter ($\tau = 0.005$) with a $HgNOCl_3$ chromophore. In the asymmetric unit of **1**, the five-coordinate Hg01 ion is surrounded by N and O atoms of bidentate (bzpy) ligand, one terminal Cl atom and two bridging Cl atoms (Figure 1). The basal plane consists of N atom (N1) and O atom (O1) of the chelated bzpy along with the bridging Cl atom (Cl1) and the terminal Cl atom (Cl2), while the apical position is occupied with the remaining bridging Cl atom (Cl1a). A considerable deviation from ideal square pyramidal geometry is seen which is presumably due to the smaller bite angles produced by bzpy [O1–Hg01–N1 66.9(3)°]. All the Hg–Cl bond distances lie in the range 2.343(4)–2.794(3) Å, where Hg–Cl(terminal) bond length is shorter as compared to Hg–Cl(bridging) bond length. The Hg–N bond length [2.218(9) Å] is shorter than Hg–O bond length [2.719(9) Å] indicating (Table 2) stronger bonding of Hg–N(pyridine N) over Hg–O (keto O). In the molecular unit of **1**, each metal(II) center (Hg01) is connected to two other metal(II) centers (Hg01a and Hg01b)

Figure 2. A view of the 1D chain structure in **1** through chloride bridge along crystallographic *a*-axis.

Figure 3. Supramolecular 2D sheet structure in **1** formed through C–H... π interactions along crystallographic *ac*-plane.

Figure 4. Supramolecular 3D network structure in **1** formed via intermolecular C–H...O hydrogen bonds and C–H... π interactions.

through two different chlorido bridges propagating through $[-Cl-Hg(Cl)(L)-Cl-Hg(Cl)(L)-]$ unit along crystallographic *a*-axis affording a zigzag one-dimensional (1D) chain (Figure 2).

1D chains in **1** self-assemble through weak intermolecular C–H... π lead to a 2D sheet structure along crystallographic *ac*-plane (Figure 3) in the crystalline state. The *para*-hydrogen atom (H4) of benzene ring of one bzpy unit in one 1D chain and benzene ring [Cg(1)] of another bzpy unit in other parallel 1D chain are engaged in weak C–H... π [H4...Cg(1), 2.8700 Å;

Figure 5. An ORTEP view of the dimeric unit in **2** with atom numbering scheme with 50% probability displacement ellipsoids.

Figure 6. Supramolecular 2D sheet structure in **2** formed through weak $\pi \cdots \pi$ interactions and intermolecular C-H $\cdots$ O hydrogen bonds along crystallographic *bc*-plane.

Figure 7. Supramolecular 3D network structure in **2** formed *via* weak intermolecular C-H $\cdots$ Br hydrogen bonds.

C4 $\cdots$ Cg(1), 3.511(18) Å; C4-H4 $\cdots$ Cg(1), 127.00°] interactions (Table 3) resulting in a 2D sheet structure. These 2D sheets, in turn, are further engaged in weak cooperative intermolecular C-H $\cdots$ O [H10 $\cdots$ O1, 2.5700 Å; C10 $\cdots$ O1, 3.370(19) Å; C10-H10 $\cdots$ O1, 144.00°] hydrogen bonds between *para*-hydrogen atom (H10) of pyridine ring of one bzpy unit and O atom (O1) of bzpy unit (Table 3) of different molecular units resulting in a 3D network structure (Figure 4).

3.2b $[Hg(bzpy)(\mu-Br)Br]_2$ (**2**): The two bromide ions in **2** bridge two metal(II) centers to form a dinuclear unit, where each mercury(II) center adopts a distorted square pyramidal geometry ($\tau = 0.33$) with a $HgNOBr_3$ chromophore (Figure 5). In asymmetric unit of **2**, Hg01 is surrounded by one N atom (N1) and one O atom (O1) of the ligand (bzpy), and one terminal Br atom (Br1) and two bridging Br atoms (Br2 and Br2a). The neighbouring Hg01a is centrosymmetric with Hg01. The Hg01 and Hg01a metal centers are connected *via* two bridging μ -Br units to form a dinuclear molecular unit of **2**. There is no M $\cdots$ M interaction in the $Hg(bzpy)Br-Br-Hg(bzpy)Br$ moiety of **2** since the intramolecular Hg $\cdots$ Hg distance (4.011 Å) is much longer than the sum of the van der Waals radii of Hg(II) (3.41 Å).⁵⁰ The terminal Hg-Br bond length [2.4545(17) Å] is shorter compared to Hg-Br(bridging) bond length [Hg-Br2, 2.4970(15) and Hg-Br2a, 3.0343(16) Å]. The Hg-N bond length [2.336(9) Å] is shorter than Hg-O bond length [2.704(8) Å] indicating (Table 2) stronger bonding of Hg-N(pyridine N) over Hg-O (keto O).

In crystalline state, the dinuclear units in **2** pack through $\pi \cdots \pi$ stacking (Table 4) between pyridine rings [Cg(1)-Cg(1), 4.448(7) Å, dihedral angles 0.00°; perpendicular distances between the baricenters 4.284(5) Å, Cg(1) = N(1) $\rightarrow$ C(4) $\rightarrow$ C(3) $\rightarrow$ C(2) $\rightarrow$ C(1) $\rightarrow$ C(5)] and intermolecular C-H $\cdots$ O hydrogen bonds [H1 $\cdots$ O1, 2.4900 Å; C1 $\cdots$ O1, 3.262(13) Å; C1-H1 $\cdots$ O1, 141.00°] between *ortho*-hydrogen atom (H1) of pyridine ring of one bzpy unit and O atom (O1) of bzpy unit (Tables 3 and 4) of different molecular units along crystallographic *bc*-plane resulting in a 2D sheet structure (Figure 6). These 2D sheet structure are stabilized through another weak intermolecular C-H $\cdots$ Br hydrogen bonds [H3 $\cdots$ Br1, 3.1700 Å; C3 $\cdots$ Br1, 3.790 Å; C3-H3 $\cdots$ Br1,

Table 2. Selected bond distances (Å) and bond angles (°) for **1** and **2**.

Bond distances for 1		Bond distances for 2	
Hg01–N1	2.218(10)	Hg01–Br1	2.4546(15)
Hg01–Cl1	2.647(3)	Hg01–Br2	2.4971(14)
Hg01–Cl2	2.343(3)	Hg01–N1	2.336(9)
Hg01–O1	2.719(9)	Hg01–O1	2.704(8)
Hg01–Cl1a	2.795(3)	Hg1–Br2a	3.0342(13)
Bond angles for 1		Bond angles for 2	
Cl1–Hg01–Cl2	107.78(15)	Br1–Hg01–Br2	133.65(5)
Cl1–Hg01–O1	153.3(2)	Br1–Hg01–O1	88.58(18)
Cl1–Hg01–N1	96.0(3)	Br1–Hg01–N1	110.6(2)
Cl1–Hg01–Cl1a	88.52(8)	Br1–Hg01–Br2a	106.01(4)
Cl2–Hg01–O1	86.8(2)	Br2–Hg01–O1	98.18(17)
Cl2–Hg01–N1	153.6(3)	Br2–Hg01–N1	113.8(2)
Cl1a–Hg01–Cl2	102.14(14)	Br2–Hg01–Br2a	87.56(4)
O1–Hg01–N1	66.9(3)	O1–Hg01–N1	65.0(3)
Cl1a–Hg01–O1	110.7(2)	Br2a–Hg01–O1	153.69(18)
Cl1a–Hg01–N1	89.5(3)	Br2a–Hg01–N1	89.2(2)
Hg01–Cl1–Hg01b	99.99(10)	Hg01–Br2–Hg01a	92.44(4)

Symmetry code: a = $-1/2+x$, $1/2-y$, $1-z$; b = $1/2+x$, $1/2-y$, $1-z$ for **1** and a = $1-x$, $2-y$, $1-z$ for **2**

Table 3. Hydrogen bond and C–H... π interaction parameters (Å, °) for **1** and **2**.

Compound	D–H...A	D–H	H...A	D...A	D–H...A
1	C10–H10...O1 ^c	0.9300	2.5700	3.370(19)	144.00
	C4–H4...Cg(1) ^d	0.9300	2.8700	3.511(18)	127.00
2	C1–H1...O1 ^e	0.9300	2.4900	3.262(13)	141.00
	C3–H3...Br1 ^f	0.9300	3.1700	3.790	126.00

Symmetry code: c = $-x$, $-1/2+y$, $1/2-z$; d = $1/2+x$, $1/2-y$, $-z$; e = $1-x$, $-1/2+y$, $1/2-z$; f = $1+x$, y , z ; Cg(1) = C(1) $\rightarrow$ C(2) $\rightarrow$ C(3) $\rightarrow$ C(4) $\rightarrow$ C(5) $\rightarrow$ C(6).

Table 4. π ... π interactions parameters (Å, °) in **2**.

Ring-ring	π ... π interactions (Å, °) in 2			
	Cg–Cg distance	Dihedral angle (i, j)	Perpendicular distances between baricenters (i, j)	Slippage
Cg(1)–Cg(1) ^c	4.448(7)	0.00	4.284(5)	1.203

Symmetry code: c = $1-x$, $1-y$, $1-z$; Cg(1) = N(1) $\rightarrow$ C(4) $\rightarrow$ C(3) $\rightarrow$ C(2) $\rightarrow$ C(1) $\rightarrow$ C(5).

126.00°] between *para*-hydrogen atom (H3) of pyridine ring of one bzpy unit and terminal Br atom (Br1) different molecular units affording a 3D network structure (Figure 7).

3.3 Luminescence properties

The photoluminescence spectra of free ligand (bzpy) and its corresponding halidomercury(II) compounds

(**1** and **2**) in DMF solutions at room temperatures (298 K) are shown in Figure 8. Upon photoexcitation at the corresponding absorption bands (269 nm)⁵¹ free ligand exhibits broad fluorescent emission centered at 346 nm, whereas the corresponding halidomercury(II) compounds **1** and **2** show more intense photoluminescence with the main emissions at 345 and 344 nm, respectively, due to the intraligand¹(π – π^*) transition. This is rationalized taking into account

Figure 8. Emission spectra of bzpy, **1** and **2** in DMF solutions at 298 K (Excitation wavelength: 280 nm and Concentration: 10^{-4} M).

the conformational rigidity and thereby reducing the non-radiative decay of the intraligand ($\pi - \pi^*$) excited state upon coordination of bzpy ligand to mercury(II); similar results are reported in $[\text{Cd}(\text{bzpy})\text{Cl}_2]$ complex.⁵¹ The luminescence^{52–54} of **1** is more intense than that of **2** which may presumably be due to the greater conformational rigidity of bzpy upon coordination in **1**.

3.4 Thermal analyses

To examine the thermal stabilities of compounds **1** and **2**, thermogravimetric analyses (TG) were made between 30–700 °C in the static atmosphere of nitrogen. The TG curve (Figure S1a, Supplementary Information) indicates that the compound **1** is stable up to 214 °C and then releases one bzpy unit and two chloride units (weight loss: observed 62.55%; calc. 55.91%) in the temperature range 214–435 °C. The compound **2** is stable up to 197 °C; the TG curve (Figure S2b, Supplementary Information) indicates that its decomposition takes place in one step corresponding to loss of ligand bzpy and two bromide groups per mercury(II) unit (observed, 68.9%; calc. 63.13%) at 197–495 °C.

4. Conclusions

One neutral coordination polymer and one dinuclear compound of mercury(II) have been successfully isolated through one-pot reactions of the molecular building components in preassigned molar ratios. X-ray crystallographic study demonstrates that the soft mercury(II) ion is able to form dinuclear or polynuclear compounds through judicious choice of halide ions. In crystalline states, the compounds afford different

crystalline architectures. Such variation in long-range structures shows how composition may tailor topology with different networks through malleable strong coordination bonds and lateral multiple weak non-covalent forces. The preparation of such compounds illustrates a potentially versatile approach towards the construction of uncharged metal-organic frameworks.

Supplementary Information (SI)

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center Nos. 1834943 (**1**) and 1834944 (**2**). Copies of this information can be had free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>). IR spectra and thermal behavior of compounds **1** and **2** (Figures S1a, S1b, S2a and S2b, respectively) are shown in Supplementary Information, available at www.ias.ac.in/chemsci.

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