

Syntheses, structures and properties of two dinuclear mercury(II) iodide compounds containing tetradentate tripodal amine/pentadentate N-donor Schiff base: Control of molecular and crystalline architectures by varying ligand matrices

SUBHASIS ROY^a, SOUMI CHATTOPADHYAY^a, SOMNATH CHOUBEY^a,
KISHALAY BHAR^a, PARTHA MITRA^b and BARINDRA KUMAR GHOSH^{a,*}

^aDepartment of Chemistry, The University of Burdwan, Burdwan 713 104, India

^bDepartment of Inorganic Chemistry, Indian Association for the Cultivation of Science, Kolkata 700 032, India
e-mail: barin_1@yahoo.co.uk

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Abstract. Two dinuclear mercury(II) iodide complexes of the types [(L1)Hg(μ -I)HgI₃] (**1**) and [Hg₂(L2)(I₄)·H₂O] (**2**) [L1 = *tris*(2-aminoethyl)amine and L2 = N,N'-(*bis*-(pyridin-2-yl)benzylidene)diethylenetriamine] have been synthesized and characterized using microanalytical, spectroscopic, thermal and other physico-chemical results. Structures of both the compounds are solved by X-ray diffraction measurements. Structural analyses show that one mercury (II) centre in **1** adopts a distorted tetrahedral geometry with an HgI₄ chromophore surrounded by four iodides, while the other has a distorted trigonal bipyramidal environment with an HgN₄I chromophore bound by four N atoms of L1 and one bridging iodide. Pentadentate Schiff base (L2) in **2** shows unusual binucleating *bis*(bidentate) behaviour to bind two different mercury(II) centres—Hg1 with an HgN₃I₂ chromophore in a distorted square pyramidal geometry and Hg2 with an HgN₂I₂ chromophore in a tetrahedral environment. Weak intermolecular N–H...I hydrogen bonds in **1** and cooperative C–H... π and π ... π interactions in **2** promote dimensionalities. The Schiff base complex, **2**, shows intraligand (π – π *) fluorescence in DMF solution at room temperature, whereas compound **1** containing tripodal amine is fluorescent-inactive.

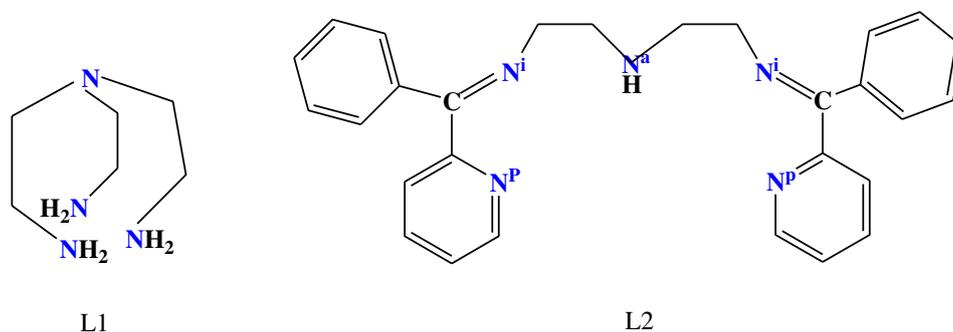
Keywords. Dinuclear mercury(II) iodide; tripodal amine; Schiff base bridge; X-ray structure; luminescence.

1. Introduction

Research on design and synthesis^{1,2} of mono-, di- and polynuclear compounds of mercury(II)^{3–7} continues unabated because of their interesting synthetic, structural, electronic and optoelectronic features^{6,7}. One-pot reactions⁸ using pre-assigned molar ratios of the metal ion, different organic spacers and suitable bridging units give rise to different coordination molecules and supramolecular entities with target properties. Exploiting the veracity in coordination geometries around this 5d¹⁰ ion, diverse molecular and crystalline architectures^{4–6} may be accessed through strong metal ligand covalent bonds⁹ and multiple weak non-covalent forces^{10–13}. Polyamines^{14,15} with bifunctional behaviours are ideal candidates providing coordination sites around the metal and hydrogen bond donors to afford superstructures. Schiff bases^{16,17}

are widely used as classical chelators binding a single metal ion and congregators encapsulating more than one metal ions with interesting molecular aggregates and crystalline architectures coupled with different functional behaviours. Iodide^{14,18,19} is a suitable terminal/bridging unit which in combination with organic ligands gives rise to different coordination frameworks around metal ions through its versatile ligational behaviours. Recently, we have reported^{20,21} some bivalent mercury complexes in combination with polyamines and Schiff bases of different densities. In the present endeavour, a tetradentate tripodal amine, *tris*(2-aminoethyl)amine (L1) and an N-donor pentadentate Schiff base, N,N'-(*bis*-(pyridin-2-yl)benzylidene)diethylenetriamine (L2) have been chosen (scheme 1) to isolate mercury(II) compounds with different geometries and molecular properties. Successfully, two neutral mercury(II) iodide compounds, [(L1)Hg(μ -I)HgI₃] (**1**) and [Hg₂(L2)(I₄)·H₂O] (**2**) are isolated. The syntheses, structures, and thermal and luminescence behaviours of these compounds are described below.

*For correspondence



Scheme 1. Frameworks of L1 and L2

2. Experimental

2.1 Materials

High purity *tris*(2-aminoethyl)amine (Fluka, Germany), 2-benzoylpyridine (Lancaster, UK), diethylenetriamine (SRL, India) and mercury(II) iodide (E Merck, India) were purchased from respective companies and used as received. The Schiff base, (N,N'-(bis-(pyridin-2-yl)benzylidene)diethylenetriamine (L2), was prepared following a reported method.²² All other chemicals and solvents used were AR grade. The synthetic reactions and work-up were done in 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 MeCN was used as solvent. Thermal behaviours was examined with a Perkin-Elmer Diamond TG/DT analyzer heated from 30–600°C under nitrogen. Ground state absorptions were made with a Shimadzu model UV-2450 UV-VIS spectrophotometer and steady-state fluorescence measurements (in DMF) was done using Perkin Elmer LS55 Fluorescence Spectrometer.

2.3 Preparation of the complexes

2.3a Synthesis of $[(L1)Hg(\mu-I)HgI_3]$ (1): A colourless methanolic solution (20 mL) of L1 (0.073 g, 0.5 mmol) was added drop-wise to a solution of HgI_2 (0.454 g, 1 mmol) in the same solvent (20 mL). The resulting colourless solution was filtered and the supernatant liquid was kept undisturbed in open air for slow

evaporation. After a week, rectangular crystals of **1** that deposited were isolated by filtration, washed with dehydrated alcohol and dried *in vacuo* over silica gel. Yield: 0.717 g (68%). *Anal.* Calc. for $C_6H_{18}N_4I_4Hg_2$ (**1**): C, 6.8; H, 1.7; N, 5.3. Found: C, 6.6; H, 1.8; N, 5.2%. IR (KBr, cm^{-1}): $\nu(\text{C-H})$ 2954, 2926; $\nu(\text{N-H})$ 3312, 3241, 3157. UV-Vis (DMF, $\lambda_{\text{max}}/\text{nm}$): 262. Λ_M (MeCN, $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$): 6.

2.3b Synthesis of $[Hg_2(L2)(I)_4] \cdot H_2O$ (2): L2 (0.216 g, 0.5 mmol) in methanol (20 mL) was added slowly to HgI_2 (0.454 g, 1 mmol) solution dissolved in same solvent (20 mL), and the reaction mixture was stirred continuously for 15 min. The resulting yellow solution was filtered and left undisturbed in open air for slow evaporation. After a week crystals of **2** that separated, were collected by filtration, washed with dehydrated alcohol and dried *in vacuo* over silica gel. Yield: 1.01 g (75%). *Anal.* Calc. For $C_{56}H_{56}N_{10}OI_8Hg_4$ (**2**) C, 24.86; H, 2.08; N, 5.18. Found: C, 25.1; H, 2.2; N, 5.0%. IR (KBr, cm^{-1}): $\nu(\text{C-H})$ 2972, 2919; $\nu(\text{C=N}) + \nu(\text{C=C})$ 1624, 1587. UV-Vis (DMF, $\lambda_{\text{max}}/\text{nm}$): 280. Λ_M (MeCN, $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$): 7.

2.4 X-ray data collection and structure refinement

Single crystals of **1** and **2** suitable for X-ray analyses were selected from those obtained by slow evaporation of methanolic solutions of the reaction mixtures at room temperature. Diffraction data were collected on a Bruker SMART APEX-II CCD area-detector diffractometer (293 K) with the Oxford Cryosystem Cobra low-temperature attachment using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). 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 SAINT²³ and absorption corrections were performed with SADABS.²⁴ The structures were solved by direct methods, using the

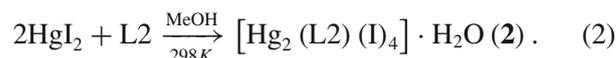
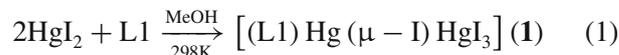
SHELXTL²⁵ program. All atomic displacement parameters for non-hydrogen atoms have been refined with anisotropic term. For both the structures, the hydrogen atoms were placed in calculated positions after checking their positions in the difference map and refined using a riding model. The U_{iso} values were constrained to be $1.2U_{\text{eq}}$ of the carrier atoms for all H atoms. In **2**, the oxygen atom of the water molecule is in disordered state over two positions (O1 and O1A) with half occupancies. All calculations were carried out using SHELXTL, PLATON²⁶ and ORTEP-3²⁷ programs. Further details are given in table 1.

3. Results and discussion

3.1 Synthesis and formulation

The iodide bridged dinuclear compound **1** was prepared using a 2:1 molar ratio of HgI_2 and L1 in methanolic solution at room temperature. Complex **2** was isolated from reaction of HgI_2 and the pentadentate Schiff

base (L2) in methanol with the same molar ratio as used in **1**. All the reactions are reproducible as is evident from repetitive microanalytical results, spectral behaviour and other physicochemical properties. The details of the reactions are summarized in Eqs. (1) and (2):



The new complexes 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 compounds are stable over long periods of time in powdery and crystalline states and are soluble in methanol, ethanol, acetonitrile, dimethylformamide and dimethylsulphoxide. In water, compound **1** is soluble but **2** is insoluble. In MeCN solutions, they behave non-electrolytes as reflected from their low conductivity values ($\sim 5 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$).²⁸

Table 1. Crystallographic data for **1** and **2**.

| Crystal parameters | 1 | 2 |
|---|--|---|
| Empirical formula | $\text{C}_6\text{H}_{18}\text{N}_4\text{I}_4\text{Hg}_2$ | $\text{C}_{56}\text{H}_{56}\text{N}_{10}\text{OI}_8\text{Hg}_4$ |
| Formula weight | 1055.02 | 2702.67 |
| Crystal system | Orthorhombic | Monoclinic |
| Space group | Pbca | C2/c |
| a (Å) | 15.790(2) | 42.323(5) |
| b (Å) | 15.0073(18) | 11.8616(13) |
| c (Å) | 16.132(2) | 15.2535(17) |
| β (°) | 90.00 | 105.351(5) |
| V (Å ³) | 3822.8(8) | 7384.3(14) |
| λ (Å) | 0.71073 | 0.71073 |
| ρ_{calcd} (gm cm ⁻³) | 3.666 | 2.429 |
| Z | 8 | 4 |
| Crystal size (mm ³) | 0.26 × 0.24 × 0.22 | 0.25 × 0.23 × 0.21 |
| Temperature (K) | 293(2) | 293(2) |
| μ (mm ⁻¹) | 22.492 | 11.676 |
| $F(000)$ | 3632 | 4856 |
| θ ranges (°) | 2.26, 25.00 | 1.00, 25.00 |
| $h/k/l$ | -18/18, -17/17, -19/19 | -50/50, -14/14, -17/18 |
| Reflections collected | 34195 | 34256 |
| Independent reflections (R_{int}) | 3365 | 6503 |
| T_{max} and T_{min} | 0.007 and 0.004 | 0.067 and 0.086 |
| Data/restraints/parameters | 3365/0/146 | 6503/14/366 |
| Goodness-of-fit on F^2 | 1.044 | 1.035 |
| Final R indices [$I > 2\sigma(I)$] | R = 0.0297 and wR = 0.0544 | R = 0.0333 and wR = 0.0634 |
| R indices (all data) | R = 0.0476 and wR = 0.0590 | R = 0.0567 and wR = 0.0709 |
| Largest diff. peak and hole (eÅ ⁻³) | 1.080 and -0.795 | 0.897 and -0.908 |

Weighting Scheme: $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$, $wR = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}}{\text{Calc. } w = 1/[\sigma^2(F_o^2) + (0.0166P)^2 + 5.0595P]}$ (**1**), $\text{Calc. } w = 1/[\sigma^2(F_o^2) + (0.0255P)^2 + 7.5118P]$ (**2**) where $P = (F_o^2 + 2F_c^2)/3$

3.2 Spectroscopic features

In IR spectra, $\nu(\text{N-H})$ stretching frequencies of the metal bound tripodal amine are seen in the range of 3320–3150 cm^{-1} for compound **1** (figure S1). The Schiff base L2 in the bound state exhibits $\nu(\text{C=N})$ plus $\nu(\text{C=C})$ stretching vibrations at 1624 and 1587 cm^{-1} in **2**. A strong absorption for $\nu(\text{O-H})$ at 3442 cm^{-1} is seen (figure S2) suggesting the presence of water molecule in **2**, which is absent in free L2 (figure S3). Weak bands in the range of 2980–2910 cm^{-1} are assignable to the aliphatic C–H stretching frequencies. All other characteristic organic ligand vibrations are seen in the range of 1600–600 cm^{-1} .²⁹ In DMF solutions, complexes **1** and **2** show absorptions at 262 and 280 nm, respectively assignable to ligand-based transition.³⁰ The photoluminescence behaviours of the free Schiff base (L2) and its corresponding mercury(II) iodide complex **2** were examined in DMF solutions at room temperature. Upon photoexcitation at the corresponding absorption band (280 nm), L2 exhibits a broad fluorescent emission centred at 339 nm, whereas compound **2** shows less intense photoluminescence with main emission centred at almost same wavelength as displayed by the free Schiff base (figure 1). The luminescence in **2** may be attributed to the intraligand ($\pi-\pi^*$) emission^{31,32} and the decrease in its intensity as compared to that of free L2 may presumably be due to the heavy atom effect on ligand³³ upon coordination and better quenching ability of the iodide.³² On the other hand, compound **1** does not exhibit luminescence behaviour upon photoexcitation at the corresponding absorption maximum (262 nm) as the building units viz. the tripodal amine (L1), mercury(II) and iodide are non-luminescent. The absence of unsaturation in the ligand network of L1 may be one of the

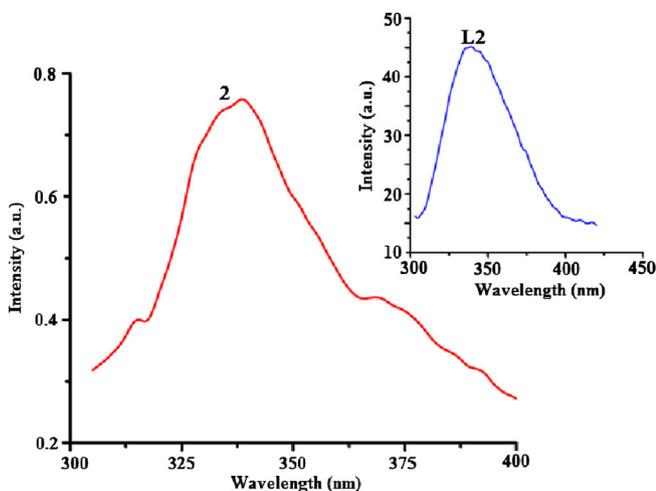


Figure 1. Fluorescence behaviour of L2 and compound **2** in DMF solutions.

major reasons for the instability of the excimeric form of **1**.

3.3 Thermal analyses

To examine thermal stabilities of the compounds, thermogravimetric analyses (TG) were made between 30 and 600°C in the static atmosphere of nitrogen. The TG curve (figure S4) indicates that the complex **1** is stable up to 192°C and decomposes completely with no residual part remaining after total decomposition (calc.: $\text{L1} + 4\text{I} + 2\text{HgO} = 103.40\%$, obs.: 99.01%). This may be due to the evaporation of the final residue (probably HgO) at higher temperature. Compound **2** starts to decompose (figure S5) from 136°C temperature. The first small step is associated with the removal of a non-coordinated water molecule between 106 and 136°C temperature (calc.: 1.33%, obs.: 1.28%). Similar to that in **1**, no residual part is left at the end of the total pyrolysis process (calc.: $\text{L2} + 4\text{I} + 2\text{HgO} + \text{H}_2\text{O} = 103.11\%$, obs.: 97.30%).

3.4 Description of the crystal structures

In order to define the coordination spheres conclusively, single-crystal X-ray diffraction measurements of **1** and **2** were made. Displacement ellipsoid diagrams with atom labelling schemes and perspective views of the crystal structures are shown in figures 1, 2 and figures S6–S8. Selected bond distances, angles, hydrogen bonds, C–H \cdots π and $\pi\cdots\pi$ interactions are given in tables 2, 3, tables S1 and S2 (supplementary information).

3.4a $[(\text{L1})\text{Hg}(\mu\text{-I})\text{HgI}_3] (\text{I})$: The asymmetric unit of **1** consists of the neutral $[(\text{L1})\text{Hg}(\mu\text{-I})\text{HgI}_3]$ molecule (figure 2). The dinuclear unit contains two mercury(II) centres viz. Hg1 and Hg2 with different geometries. Hg1 has a distorted tpb geometry ($\tau = 0.85$)³⁴ with

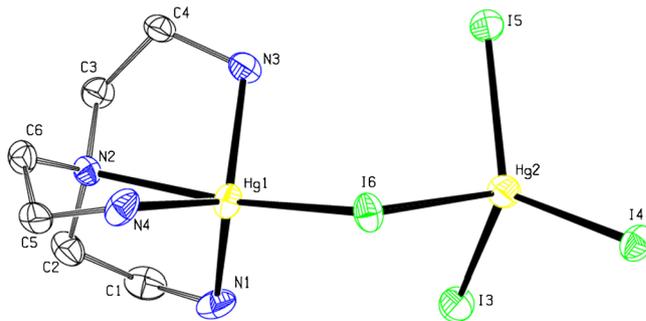


Figure 2. Molecular view of **1** with 30% thermal ellipsoid probability.

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

| Bond distances for 1 | | Bond distances for 2 | |
|-----------------------------|-----------|-----------------------------|-----------|
| Hg1-N1 | 2.300(7) | Hg1-N1 | 2.413(6) |
| Hg1-N2 | 2.484(7) | Hg1-N2 | 2.523(6) |
| Hg1-N3 | 2.339(7) | Hg1-N3 | 2.526(5) |
| Hg1-N4 | 2.378(7) | Hg1-I2 | 2.6974(6) |
| Hg1-I6 | 2.7305(8) | Hg1-I5 | 2.6884(7) |
| Hg2-I3 | 2.7926(8) | Hg2-N4 | 2.448(6) |
| Hg2-I4 | 2.7206(8) | Hg2-N5 | 2.335(6) |
| Hg2-I5 | 2.7293(8) | Hg2-I3 | 2.6795(7) |
| Hg2-I6 | 3.0139(8) | Hg2-I6 | 2.6360(8) |

HgN₄I chromophore while Hg₂ centre adopts a distorted tetrahedral geometry with HgI₄ chromophore. The two different mercury(II) centres are connected through an iodide ion with a bridging angle Hg1/I6/Hg2 of 97.65(2)°. The ethylenic arm of L1 is to some extent puckered. Hg1 centre deviates 0.63 Å from the corresponding basal plane towards apical bridging iodide. In the dinuclear unit Hg1··Hg2 separation through iodide bridge is 4.328 Å.

Tripodal amine (tren) in compound **1** has six hydrogen donor sites which can form hydrogen bonds (table S1) with the hydrogen acceptor iodides. Each dinuclear unit in **1** with five proton donors (H1A, H1B, H3C, H4C and H4D) and two proton acceptors (I3 and I5) is engaged through one intramolecular and five intermolecular hydrogen bonds forming a 2D sheet structures (figure S6) with three different cyclic motifs like R₂¹ (6), R₂² (8) and R₄² (8) in Etter's graph notation.³⁵ The 2D sheet is further propagated through N3-H3D··I4 hydrogen bonds affording a 3D network structure (figure S7). An interesting variation in crystalline architecture is seen in **1** compared to that in

a reported cadmium(II) iodide compound,¹⁴ where dinuclear units are packed in a discrete manner without any appreciable non-covalent interaction forming a 1D zigzag chain.

3.4b [Hg₂(L2)(I)₄]·H₂O (**2**): The asymmetric unit of compound **2** comprises of a neutral dinuclear [Hg₂(L2)(I)₄] molecule and a disordered H₂O molecule (figure 3). The dinuclear entity in **2** is formed through mixed bi-tridentate bridging behaviour of L2 via (N^p, Nⁱ) and (N^a, Nⁱ, N^p) donor sets, respectively [N^p = N(pyridine), Nⁱ = N(imine) and N^a = N(amine)] connecting two different mercury(II) centres (Hg₂ and Hg₁). Hg₁ adopts a distorted square pyramidal (sp) geometry as revealed³⁴ from its tau parameter ($\tau = 0.135$ for Hg₁) whereas Hg₂ has a tetrahedral environment. Hg₁ centre is bound by three N atoms of L2 through donation of one N^p atom (N2), one Nⁱ atom (N1), and one N^a atom (N3). The fourth and fifth coordination sites around Hg₁ are occupied by two terminal iodides (I2 and I5). On the other hand, the coordination around Hg₂ centre is fulfilled by other two N atoms, N^p (N5) and Nⁱ (N4), of L2 and two terminal iodides (I3 and I6). The basal plane around Hg₁ consists of three N atoms (N1, N2 and N3) of L2 along with one terminal iodide (I2). The apical position is occupied by the remaining terminal iodide (I5). The distortion from ideal sp geometry is due to the asymmetric nature of the Schiff base and deviations of the refine angles (90°/180°) formed at the metal centre. Two ethylenic arms (N1-C3-C4-N3 and N4-C8-C9-N5) in L2 that form two five-membered chelate loops respectively around Hg₁ and Hg₂ are to some extent puckered. The C4 atom of this alkylenic arm lies 0.698 Å above the N3, C3, N1, Hg₁ plane in the direction of

Table 3. Selected bond angles (°) for **1** and **2**.

| Bond angles for 1 | | | | Bond angles for 2 | |
|--------------------------|------------|-----------|-----------|--------------------------|------------|
| N1-Hg1-N2 | 75.3(2) | N4-Hg1-I6 | 97.0(2) | N1-Hg1-N2 | 66.41(19) |
| N1-Hg1-N3 | 106.3(3) | I3-Hg2-I4 | 116.46(2) | N1-Hg1-N3 | 68.88(18) |
| N1-Hg1-N4 | 115.9(3) | I3-Hg2-I5 | 108.03(3) | N2-Hg1-N3 | 133.40(18) |
| N3-Hg1-N2 | 74.4(2) | I3-Hg2-I6 | 105.57(2) | N1-Hg1-I5 | 107.72(14) |
| N4-Hg1-N2 | 73.4(2) | I4-Hg2-I5 | 123.11(3) | N2-Hg1-I5 | 105.67(13) |
| N3-Hg1-N4 | 116.6(3) | I4-Hg2-I6 | 94.95(2) | N3-Hg1-I5 | 99.63(13) |
| N1-Hg1-I6 | 116.6(2) | I5-Hg2-I6 | 105.67(2) | N1-Hg1-I2 | 125.28(14) |
| N2-Hg1-I6 | 167.58(15) | | | N2-Hg1-I2 | 95.11(13) |
| N3-Hg1-I6 | 103.98(18) | | | N3-Hg1-I2 | 100.02(12) |
| | | | | I5-Hg1-I2 | 126.99(2) |
| | | | | N5-Hg2-N4 | 69.6(2) |
| | | | | N5-Hg2-I6 | 113.64(16) |
| | | | | N4-Hg2-I6 | 110.73(12) |
| | | | | N5-Hg2-I3 | 107.06(15) |
| | | | | N4-Hg2-I3 | 111.57(12) |
| | | | | I6-Hg2-I3 | 128.89(3) |

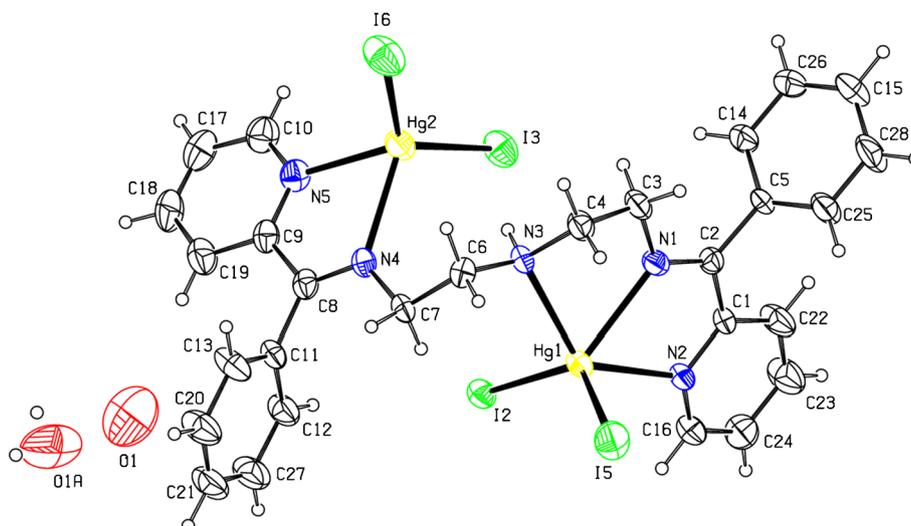


Figure 3. Molecular structure of **2** with 30% thermal ellipsoid probability.

apical iodide (I5), whereas C8 and C9 atoms of that arm lie on the N4, C8, C9, N5, Hg2 plane. Hg1 centre exhibits considerable deviation from ideal sp geometry presumably due to different bite angles [N1/Hg1/N2 (66.41(19)°, N1/Hg1/N3 (68.88(18)° and N2/Hg1/N3 (133.40(18)°] in L2. Hg1 centre deviates (0.945 Å) from the mean basal plane (N1, N2, N3 and I2) towards the apical halide (I5). The basal plane containing N2 and N3 atoms deviate towards the apical I5 by 0.222 and 0.208 Å, respectively whereas N1 and I2 atoms depart 0.298 and 0.131 Å, respectively opposite to the apical I5. Hg–I bond distances (table 2) are much longer than the Hg–N bonds as expected due to the larger radius of iodine over nitrogen. The intramolecular Hg...Hg separation through ethylenic arm is 5.403 Å.

Unlike **1**, individual dinuclear units in **2** with only N–H...I intramolecular hydrogen bonds do not propagate further; however, intermolecular cooperative C–H... π and π ... π interactions (tables S1 and S2) afford a 3D network structure (figure S8).

4. Conclusion

Two interesting neutral iodide/Schiff base bridged coordination molecules have been synthesized through single-pot reactions of the appropriate building components in pre-assigned molar ratios. Iodide bridged dinuclear compound **1** has two different mercury(II) centres with tetrahedral and tbp geometry. Photoluminescent complex **2** shows unusual congregation behaviour of pentadentate Schiff base to bind two mercury(II) centres with mixed bi-tridentate behaviour via (N^P, N^I) set and (N^A, N^I, N^P) set, respectively. This study

demonstrates that the soft mercury(II) ion is able to form compounds with varied geometries (sp, tbp and tetrahedral) and coordination numbers through judicious choice of the polyamine/Schiff base and thereby afford different crystalline architectures in long-range forms. Such variation of superstructures shows how composition may tailor topology with different networks through malleable strong coordination bonds and lateral multiple weak non-covalent forces.

Supplementary information

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre Nos. 914667 (**1**) and 953639 (**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>). Supramolecular architectures of **1** and **2**, thermal behaviours of compounds **1** and **2** and IR spectra of free ligand (L2), **1** and **2** can be seen in supplementary information (figures S1–S8 and tables S1–S2). For details, see www.ias.ac.in/chemsci.

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