

## 1,1'-(ETHYLENE-1,2-DIYL)DIPYRIDINIUM [HEXACHLORODIMERCURATE(II)]: SYNTHESIS, CRYSTAL AND MOLECULAR STRUCTURE

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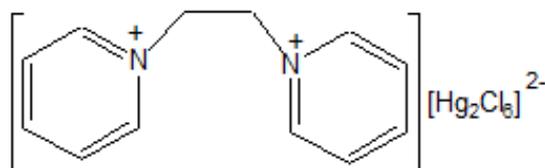
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In order to investigate the possible property of 1,1'-(ethylene-1,2-diyl)dipyridinium dication to form hybrid ionic complexes by treatment with the suitable metal halide, the organic-inorganic hybrid salt 1,1'-(ethylene-1,2-diyl)dipyridinium [hexachlorodimercurate(II)] was prepared by reacting  $[\text{C}_{12}\text{H}_{14}\text{N}_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  with  $\text{HgCl}_2$ . The obtained complex was isolated as a pure powdery salt and fully characterized by multinuclear NMR, FTIR, UV-vis spectroscopy, elemental analyses and its molecular structure was confirmed by

powder X-ray diffraction study. The molecular structure displays the distinctive organic dication  $[\text{C}_{12}\text{H}_{14}\text{N}_2]^{2+}$  and remarkable dimeric anions  $[\text{Hg}_2\text{Cl}_6]^{2-}$ . The Hg center of every particular  $[\text{Hg}_2\text{Cl}_6]^{2-}$  unit is surrounded by four Cl atoms (two terminal  $\text{Cl}_t$  and two bridging  $\text{Cl}_b$  ones) assuming a roughly tetrahedral geometry. The terminal  $\text{Cl}_t$  atoms are covalently bonded to Hg center with a mean bond distance of 2.44 Å and  $\text{Cl}_t\text{—Hg—Cl}_t$  angle of 140.85(5)°, while the two bridging  $\text{Cl}_b$  ligands to Hg centers have comparatively longer average bond length of 2.63(3) Å and smaller mean  $\text{Cl}_b\text{—Hg—Cl}_b$  bond angle of 90.58(5)°. The relatively large  $\text{Cl}_t\text{—Hg—Cl}_t$  angle (140.85°) and small  $\text{Cl}_b\text{—Hg—Cl}_b$  angle (90.58°) refer to a considerable deviation from the ideal geometry of a tetrahedron.



### INTRODUCTION

Organic–inorganic hybrid ionic materials are of current interest, because of their promising applications in various research activities especially in domain of materials science, crystal engineering, supra-molecular chemistry<sup>1-4</sup> and also as optically semiconductor materials.<sup>5,6</sup> Furthermore chloromercurate(II) complexes have a considerable fascination as important materials in different fields particularly in theoretical and structural chemistry, vibration and solid state NMR spectroscopy.<sup>7-10</sup> Some chloromercurate(II) compounds were also reported to show fascinating ferroelectric behavior and the mechanism of the

ferro- to para-electric phase transition of chloromercurate(II) compounds is related to their structural arrangement.<sup>10-12</sup> Because of the relatively large volume of  $\text{Hg}^{2+}$  and its wide spherical charge distribution, chloromercurate(II) anions exhibit a wide range of geometry and stoichiometry depending on the size and nature of combining ligand; such as monomeric unit  $[\text{HgCl}_3]^-$ ,  $[\text{HgCl}_4]^{2-}$ , dimeric unit  $[\text{Hg}_2\text{Cl}_6]^{2-}$  or even more complex polymeric units  $[\text{Hg}_3\text{Cl}_{10}]^{4-}$ .<sup>7,13</sup> Recently, the potential ability of the dication 1,1'-(ethylene-1,2-diyl)dipyridinium  $[\text{C}_{12}\text{H}_{14}\text{N}_2]^{2+}$  to form hybrid organic-inorganic compounds was utilized by us to synthesize the organic-inorganic hybrid salts  $[\text{C}_{12}\text{H}_{14}\text{N}_2][\text{CuCl}_4]$ ,<sup>14</sup>  $[\text{C}_{12}\text{H}_{14}\text{N}_2]$

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[Cu(NO<sub>3</sub>)<sub>4</sub>],<sup>15</sup> [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Fe(CN)<sub>5</sub>NO]<sup>16</sup> and [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][CuCl<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>].<sup>17</sup> Furthermore, the optical nonlinearity of [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Fe(CN)<sub>5</sub>NO]<sup>16</sup> and [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][CuCl<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]<sup>17</sup> were investigated, and they are found to be good candidates in optical field. This was incentive to present the synthesis, spectroscopic characterization, molecular and crystal structure determination of [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>] by powder X-ray diffraction study.

## RESULTS AND DISCUSSION

In a similar manner to the very recently reported organic-inorganic salt [(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>CH<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>],<sup>18</sup> the analogous novel hybrid ionic compound [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>] was obtained by treatment of [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O with HgCl<sub>2</sub>. The product was purely isolated as a pale beige powdery salt. It is insoluble in common polar solvents such ethanol, pyridine or water, but it is rather soluble in DMSO. The obtained complex was characterized by multinuclear NMR, FTIR, UV-vis spectroscopy, and elemental analyses. Since no single-crystal could be obtained due to insolubility of the product, the molecular structure (Figure 1) of the obtained complex was determined by powder X-ray diffraction study.

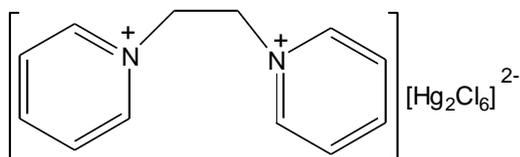


Fig. 1 – Molecular structure of [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>].

The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra for [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>] (Figure 2) are very similar to their corresponding ones of the parent salt [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O<sup>19</sup> and the structurally related hybrid ionic complexes [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][CuX<sub>4</sub>] (X = Cl<sup>-</sup> or NO<sub>3</sub><sup>-</sup>).<sup>14,15</sup> The observed <sup>1</sup>H NMR spectrum exhibits four resonances corresponding to four different proton environments, the obtained peaks are in their expected chemical shifts and relative intensity ratios. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum also shows the expected four resonances consistent with four environmentally different C centers.

As expected, the FTIR spectrum of [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>] (Figure 3) has a similar feature to the analogue [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][CuCl<sub>4</sub>].<sup>14</sup> It is distinguishable the existence of the characteristic

absorption bands at 1195 cm<sup>-1</sup> (C–N), 1632 cm<sup>-1</sup> (C=N), 674 and 1489 cm<sup>-1</sup> (CH<sub>2</sub>).

The UV-Vis spectrum of [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>] in DMSO solution at concentration of 20×10<sup>-6</sup> M is shown in Figure 4. The absorption band at λ<sub>max</sub>= 265.8 nm is due to the combination of π – π\* and/or intraligand charge-transfer (ILCT) transitions.

In a similar manner to the structurally related analogous salt [(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>CH<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>],<sup>18</sup> the molecular structure of the obtained complex displays the distinctive organic dications [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>]<sup>2+</sup> and dimeric anions [Hg<sub>2</sub>Cl<sub>6</sub>]<sup>2-</sup> (Figure 5). Each Hg center of every particular [Hg<sub>2</sub>Cl<sub>6</sub>]<sup>2-</sup> unit is surrounded by four Cl atoms (two terminal Cl<sub>t</sub> and two bridging Cl<sub>b</sub> ones) assuming a roughly tetrahedral geometry, presuming the Cl<sub>b</sub>—Cl<sub>b</sub> side is a shared edge by the two distorted tetrahedra to form [Hg<sub>2</sub>Cl<sub>6</sub>]<sup>2-</sup> unit. The terminal Cl<sub>t</sub> atoms are covalently bonded to Hg center with an average bond distance of 2.44(0) Å and Cl<sub>t</sub>—Hg—Cl<sub>t</sub> angle of 140.85(5)°. In contrast, the two bridging Cl<sub>b</sub> ligands to Hg centers have relatively longer average bond length of 2.63(3) Å and smaller mean Cl<sub>b</sub>—Hg—Cl<sub>b</sub> bond angle of 90.58(5)°. Both the obtained terminal and bridging bond distances and angles are in their normal ranges and consistent with their corresponding ones in the structurally related compounds [(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>CH<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>]<sup>18</sup> and (C<sub>7</sub>H<sub>11</sub>N<sub>2</sub>)<sub>2</sub>[Hg<sub>2</sub>Cl<sub>6</sub>].<sup>20</sup> The relatively large Cl<sub>t</sub>—Hg—Cl<sub>t</sub> angle (140.85°) and small Cl<sub>b</sub>—Hg—Cl<sub>b</sub> angle (90.58°) refer to a pronounceable deviation from the ideal geometry of a tetrahedron (Table 1). In contrast to the corresponding complex [(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>CH<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>],<sup>18</sup> the Hg(II)···Hg(II) distance (3.84 Å) of each [Hg<sub>2</sub>Cl<sub>6</sub>]<sup>2-</sup> unit in [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>] is longer than the sum of the van der Waals radii for Hg(II) (3.5 Å) suggesting there is no significant Hg···Hg interaction.<sup>21,22</sup> Noteworthy, the obtained dimeric anion [Hg<sub>2</sub>Cl<sub>6</sub>]<sup>2-</sup> of the salt [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>] is rather consistent with some predictive generalizations stating that [Hg<sub>2</sub>Cl<sub>6</sub>]<sup>2-</sup> units are commonly formed with large cations particularly those forming layers.<sup>7</sup> The C–C, C–N bond distances as well as C–N–C and C–C–C bond angles for the organic dications [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>]<sup>2+</sup> are in their normal values and in agreement to their corresponding ones of the parent salt [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O<sup>19</sup> and the related complex [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][CuCl<sub>4</sub>].<sup>14</sup>

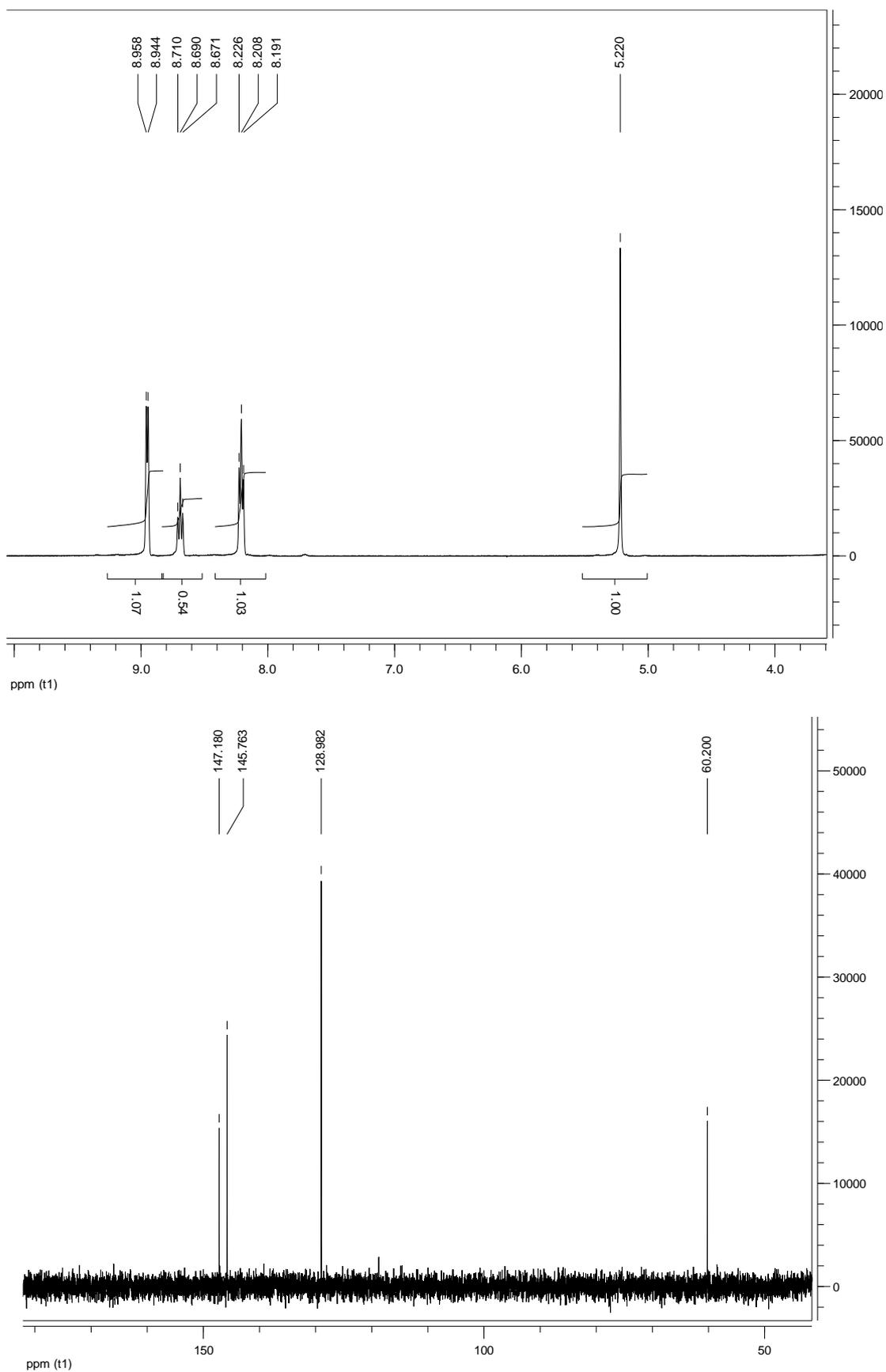


Fig. 2 –  $^1H$  (above) and  $^{13}C\{^1H\}$  NMR (below) spectra of  $[C_{12}H_{14}N_2][Hg_2Cl_6]$  ( $DMSO-d_6$ ,  $25^\circ C$ ).

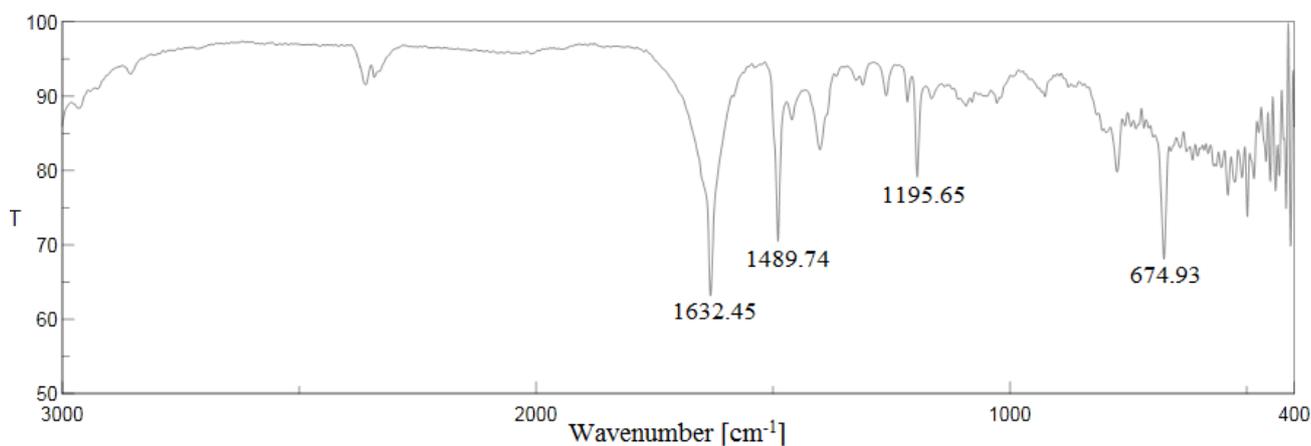


Fig. 3 – FTIR spectrum of  $[\text{C}_{12}\text{H}_{14}\text{N}_2][\text{Hg}_2\text{Cl}_6]$  in the range of 400-3000  $\text{cm}^{-1}$ .

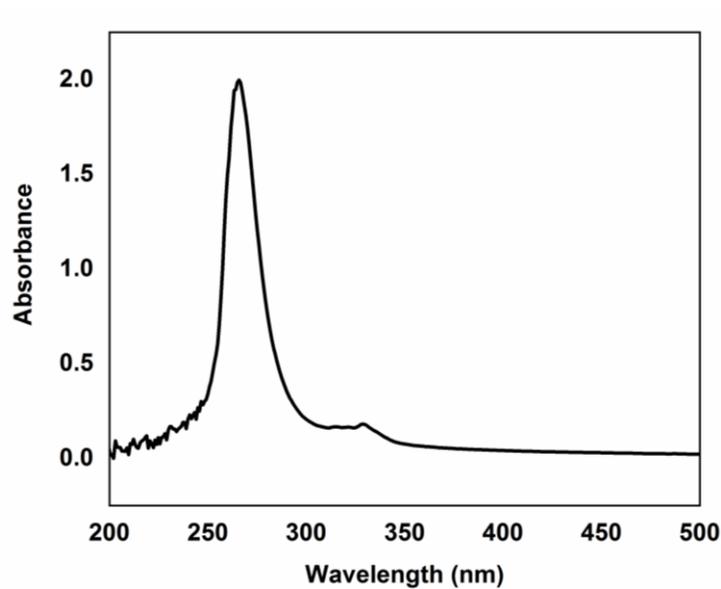


Fig. 4 – UV-Vis absorption spectrum of  $[\text{C}_{12}\text{H}_{14}\text{N}_2][\text{Hg}_2\text{Cl}_6]$  in DMSO at concentration of  $20 \times 10^{-6}$  M.

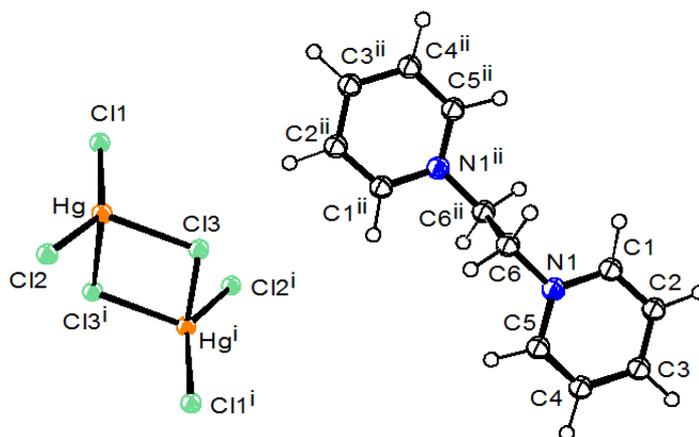


Fig. 5 – The molecular structure of  $[\text{C}_{12}\text{H}_{14}\text{N}_2][\text{Hg}_2\text{Cl}_6]$ , showing the atomic labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as small spheres of arbitrary radii.

Table 1

Selected bond lengths (Å) and angles (°) for [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>]

Bond	Bond length (Å)	Angle	Bond angle (°)
Hg—Cl1	2.43(2)	Cl1—Hg—Cl2	140.85(2)
Hg—Cl2	2.44(8)	Cl1—Hg—Cl3	113.96(0)
Hg—Cl3	2.63(4)	Cl1—Hg—Cl3 <sup>i</sup>	101.32(6)
Hg—Cl3 <sup>i</sup>	2.522(2)	Cl2—Hg—Cl3	101.96(6)
N1—C6	1.473(3)	Cl2—Hg1—Cl3 <sup>i</sup>	96.72(9)
C6—C6 <sup>ii</sup>	1.526(4)	Cl3—Hg1—Cl3 <sup>i</sup>	86.42(6)
Hg...Hg	3.839(4)		

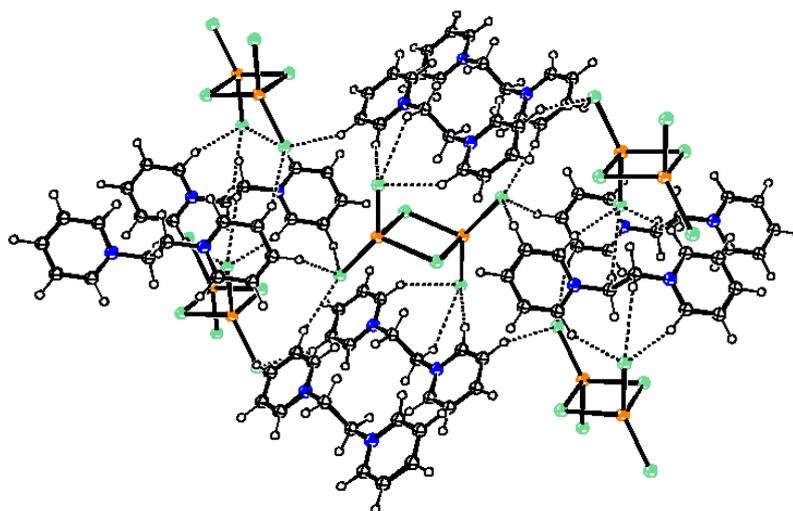
Symmetry codes: (i)  $-x, -y, -z-1$ .Fig. 6 – Portion of the packing diagram of [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>]. Dashed lines indicate hydrogen bonds between molecules [Symmetry codes: (i)  $-x, -y, -z$ ; (ii)  $-x, -y+1, -z+1$ ].

Table 2

Hydrogen bond distances (Å) and bond angles (°) for [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>]

D—H...A	d(D—H)	d(H...A)	d(D...A)	Angle(D—H...A)
C1 <sup>ix</sup> —H2 <sup>ix</sup> ...Cl2 <sup>xv</sup>	1.108	2.511	3.573	164.39
C5 <sup>xvi</sup> —H5 <sup>xvi</sup> ...Cl2 <sup>xv</sup>	1.087	2.545	3.487	144.34
C6 <sup>ix</sup> —H7 <sup>ix</sup> ...Cl2 <sup>xv</sup>	1.086	2.982	3.715	124.57
C3 <sup>vi</sup> —H1 <sup>vi</sup> ...Cl1 <sup>xi</sup>	1.080	2.392	3.343	144.87
C2 <sup>xxi</sup> —H3 <sup>xxi</sup> ...Cl1 <sup>xi</sup>	1.080	2.701	3.524	131.99
C4 <sup>ii</sup> —H4 <sup>ii</sup> ...Cl1 <sup>xi</sup>	1.088	2.778	3.815	159.18

Symmetry code: (ii)  $-x, -y, -z$ ; (vi)  $-x+1/2, y-1/2, -z$ ; (ix)  $x+1/2, -y+3/2, z$ ; (xi)  $-x+1, -y, -z$ ; (xv)  $-x, -y+1, -z$ ; (xvi)  $x, y+1, z+1$ ; (xxi)  $x, y+1, z$ .

The asymmetric unit of [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>] contains one half of the 1,1'-(ethylene-1,2-diyl)dipyridinium dication and one half of a [hexachlorodimercurate(II)] anion. Each ionic [Hg<sub>2</sub>Cl<sub>6</sub>] unit has a twofold axial symmetry at the centroid of the [Hg<sub>2</sub>Cl<sub>6</sub>]<sup>2-</sup> ring and the dications [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>]<sup>2+</sup>, each has also a twofold axial symmetry located at the midpoint of the bond CH<sub>2</sub>—CH<sub>2</sub>.

For simplification, in the crystal packing of [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>], only those hydrogen bonds

C—H...Cl (Table 2) lying within the sum of the van der Waals radii for C and Cl atoms (3.45 Å) were considered as non-standard hydrogen bonds.<sup>23</sup> The crystal packing (Fig. 6) is achieved by C—H...Cl<sub>t</sub> short contacts, where each individual [Hg<sub>2</sub>Cl<sub>6</sub>]<sup>2-</sup> anion is involved symmetrically by its four terminal Cl atoms with eight different surrounding [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>]<sup>2+</sup> dications to form infinite three dimensional network. A particular [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>]<sup>2+</sup> dication is linked to one terminal Cl centre of individual [Hg<sub>2</sub>Cl<sub>6</sub>] unit by

three C—H···Cl<sub>t</sub> short contacts, one with H of ethylene, the second with aromatic H atom (para) of a pyridine ring and the third with aromatic H (para) of the other pyridine ring. In the same manner, the other terminal Cl<sub>t</sub> of the same Hg center has also three short contacts, but with three different aromatic H atoms (two with meta and one with para H atoms) of three different surrounding [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>] dications. Symmetrically, the other two terminal Cl atoms of the second Hg center have identical short contacts. No short contacts were observed for the bridging Cl atoms. The mentioned non-standard hydrogen bondings are more likely effective in the stabilization of the crystal packing of the studied hybrid salt.

## EXPERIMENTAL

### Materials

All reactions and manipulations were implemented in air with reagent grade solvents. [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O was obtained according to the reported literature method.<sup>19</sup> HgCl<sub>2</sub> (BDH, Germany) was a commercial sample and used as received. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Bruker Bio spin 400 spectrometer (Switzerland). Fourier transform infrared (FTIR) spectrum was recorded on Thermo Nicolet 6700 FTIR Spectrometer, taken as KBr disc with a resolution of 4 cm<sup>-1</sup>. Microanalysis was also performed using EURO EA (Italy). The Ultra-Violet-Visible (UV-Vis) absorption spectrum was acquired in the wavelength range 190-1100 nm using UV-1601 PC Shimadzu Spectrophotometer. Powder X-ray diffraction was taken by Stoe Transmission diffractometer (Stadi P) (Stoe & CIE GmbH, Germany).

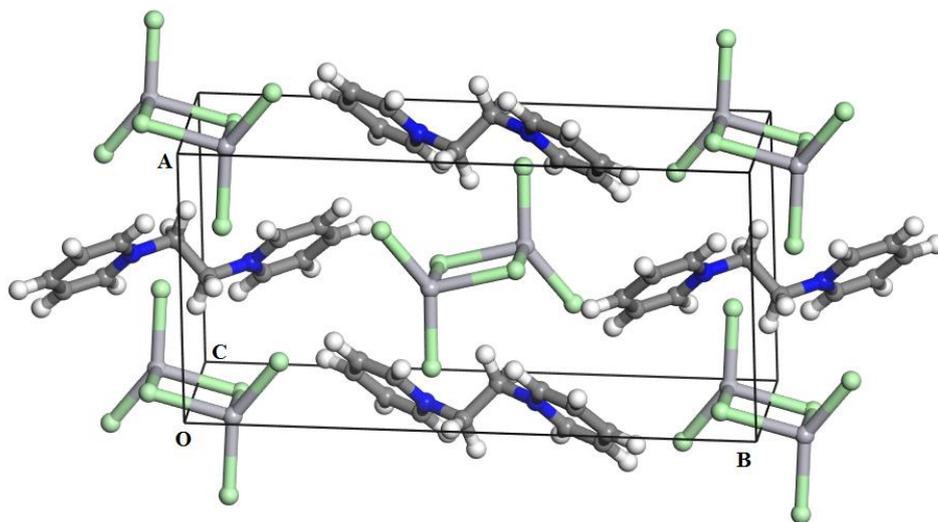


Fig. 7 – A unit cell of [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>] and Miller plane (100) passes through one hydrogen atom.

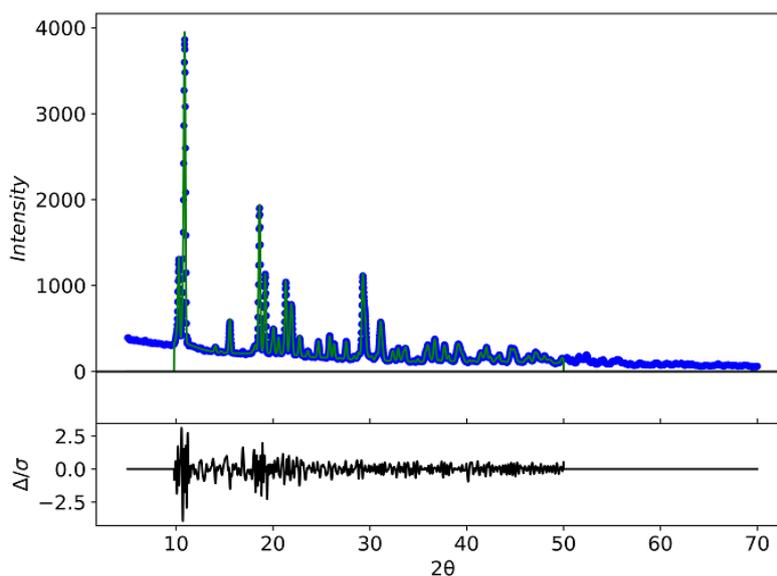


Fig. 8 – The final Rietveld pattern for [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>]. The (blue ●) is the measured values and (green -) are the fitted ones. (Black -) is the difference between the measured and the fitted values.

Table 3

Crystallographic data and refinement parameters for [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>]

CCDC number	
Empirical formula	C <sub>12</sub> H <sub>14</sub> Cl <sub>6</sub> Hg <sub>2</sub> N <sub>2</sub>
<i>Formula Weight</i>	M <sub>r</sub> = 800.16
Temperature (K)	298
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /a
Crystal colour	Pale beige
Unit cell parameters	a = 9.5491 (12) Å b = 17.2961 (6) Å c = 6.2380 (6) Å β = 103.825 (3)°
Volume	V = 1000.45 (7) Å <sup>3</sup>
Z	4
Density (calculated)	D <sub>x</sub> = 2.656 Mg m <sup>-3</sup>
Crystal size	Fine powder
Radiation type	Cu Kα <sub>1</sub> 1.54059 Å
<b>Data collection</b>	
Diffractometer	STOE transmission STADI-P
Specimen mounting	powder loaded between two Mylar foils
Data collection mode	transmission
Scan method	step
2θ min	5.00°
2θ max	70.0°
2θ step =	0.02°
<b>Refinement</b>	
R factors and goodness of fit R <sub>p</sub>	0.022
R <sub>wp</sub>	0.031
R <sub>exp</sub>	0.062
R(F <sup>2</sup> )	0.00000
χ <sup>2</sup>	0.249
Number of data points	3276
Number of parameters	14
Background function:	"chebyshev-1" function with 12 terms: 167.315, -106.084, 44.440, -10.820, 9.887, -7.012, 7.408, 4.805, -2.310, 7.570, -2.240, 2.649,

### Synthesis of 1,1'-(ethylene-1,2-diyl)dipyridinium [hexachlorodimercurate(II)]

A solution of [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O (0.30 g, 1.02 mmol) in H<sub>2</sub>O (3 ml), and a solution of HgCl<sub>2</sub> (0.28 g, 1.02 mmol) in EtOH (3 ml) was stirred overnight at room temperature. Powdery pale beige precipitate was obtained, which was filtered off, washed with ether (4 ml) and dried in vacuo to afford a pale beige powder of [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>].

### Characterization and NMR, FTIR and UV–vis spectroscopic data of [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>]

Pale beige powder, m.p. 184°C (decomposed), Yield: 70%; Anal. Calcd for C<sub>12</sub>H<sub>14</sub>Cl<sub>6</sub>N<sub>2</sub>Hg<sub>2</sub> (800.15): C, 18.01; H, 1.76; N, 3.50 Found: C, 18.00; H, 1.05; N, 3.17; <sup>1</sup>H NMR (400.1 MHz, DMSO-*d*<sub>6</sub>): δ<sub>H</sub> 5.22 (4H, s, CH<sub>2</sub>), 8.21 (4H, t, py), 8.69 (2H, t, py), 9.95 (4H, d, py); <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, DMSO-*d*<sub>6</sub>): δ<sub>C</sub> 60.22 (s, CH<sub>2</sub>), 129.96 (s, py), 145.76 (s, py), 147.18 (s, py). IR (KBr) ν cm<sup>-1</sup>: 1195 (C–N), 1632 (C=N), 674 and 1489 (CH<sub>2</sub>). UV (DMSO): λ<sub>max</sub> (ε) = 265.86 nm (1.99), λ<sub>max</sub> (ε) = 328.41 nm (0.18).

### Crystal structure determination for [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>] from powder X-ray diffraction

After obtaining the pale beige powder [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>], we targeted to get the X-ray diffraction pattern. Therefore, the transmission diffractometer (STADI-P STOE, Darmstadt, Germany), with copper K<sub>α</sub> radiation (λ = 1.54060 Å) and Ge monochromator was used to collect the data of the compound. The angle was scanned from 5° up to 70° with scanning rate of 0.25° per minute.

The *ab initio* and direct methods that are implemented in the EXPO2014 package<sup>24</sup> were first used to determine the crystal structure of [C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>][Hg<sub>2</sub>Cl<sub>6</sub>]. A monoclinic of a = 9.532874 Å, b = 17.267538 Å, c = 6.227915 Å, β = 103.830750° with space group P2<sub>1</sub>/a crystal was found. The goodness factors of the fit R<sub>p</sub> and R<sub>wp</sub> were 4.987 and 6.523 respectively. This crystal structure was further refined using Rietveld method that is implemented in GSAS II.<sup>25</sup> The improved crystal structure is found with a figure of merit [M(20) = 22.64] to be a = 9.5491(12) Å, b = 17.2961(6) Å, c = 6.2380(6) Å, β = 103.8251(28)° and it is shown in Figure 7. The goodness factors are improved to become 3.1 and 6.2 respectively. The values of the crystallographic data

and the refinement goodness factors are shown in Table 3. The Rietveld plots of the X-ray diffraction patterns are shown in Figure 8. The atomic fractional coordinates in the unit cell are presented in appendix (A).

## CONCLUSION

The novel organic-inorganic ionic complex  $[C_{12}H_{14}N_2][Hg_2Cl_6]$  was prepared and isolated as a pure powdery salt. It was fully characterized by spectroscopic methods and its molecular structure was confirmed by powder X-ray diffraction study.

## SUPPLEMENTARY INFORMATION

CCDC 2158270 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://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).

### Appendix (A)

The atomic fractional coordinates in the unit cell

Atom	X	Y	Z
Hg	0.02969	-0.07419	-0.26455
Cl1	-0.17626	-0.15767	-0.27088
Cl2	0.29166	-0.06984	-0.12093
Cl3	-0.03598	0.07367	-0.31569
C1	-0.07067	0.65112	0.44427
C2	-0.09628	0.71883	0.32506
C3	-0.02098	0.73378	0.16442
C4	0.07859	0.68012	0.12662
C5	0.10457	0.61397	0.25308
N1	0.02998	0.60047	0.40891
H1	-0.04164	0.78658	0.06663
H2	-0.12737	0.63532	0.57027
H3	-0.17398	0.75966	0.36270
H4	0.13802	0.68876	-0.00018
H5	0.18165	0.56980	0.23368
C6	0.05796	0.53008	0.54531
H6	0.16546	0.50842	0.54423
H7	0.05739	0.54540	0.71554

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## REFERENCES

1. N. Kimizuka and T. Kunitake, *Adv. Mater.*, **1996**, *8*, 89–91.
2. D. B. Mitzi, M.T. Prikas and K. Chondroudis, *Chem. Mater.*, **1999**, *11*, 542–544.
3. F. Bonhomme and M. G. Kanatzidis, *Chem. Mater.*, **1998**, *10*, 1153–1159.
4. M. Wachhold and M. G. Kanatzidis, *Chem. Mater.*, **2000**, *12*, 2914–2923.
5. C. R. Kagan, D. B. Mitzi and C. D. Dimitrakopoulos, *Science*, **1999**, *286*, 945–947.
6. H. Li, Z. Chen, L. Cheng, J. Liu, X. Chen and J. Li, *Cryst. Growth Des.*, **2008**, *8*, 4355–4358.
7. D. A. House and W.T. Robinson, *Coord. Chem. Rev.*, **1994**, *155*, 533–586.
8. G. A. Bowmaker, R. K. Harris and S. Oh, *Coord. Chem. Rev.*, **1997**, *167*, 49–94.
9. G. A. Bowmaker, A. V. Churakov, R. K. Harris and S. Oh, *J. Organometallic Chem.*, **1998**, *550*, 89–99.
10. F. Milia and E. Giannacopoulos, *Jap. J. Appl. Phys.*, **1985**, *24*, 637–639.
11. J. Liesegang, B. D. James and Z. T. Jiang, *Integrated Ferroelectrics*, **1995**, *9*, 189–198.
12. Z. T. Jiang, B. D. James, J. Liesegang, K. L. Tan, R. Gopalakrishnan and I. Novak, *J. Phys. Chem. Solids*, **1995**, *56*, 277–283.
13. A. Linden, B. D. James, J. Liesegang and N. Gonis, *Acta Cryst.*, **1999**, *B55*: 396–409.
14. M. K. Sabra, M. M. Al-Ktaifani, A. A. Alsharif and F. Maksoud, *Rev. Roum. Chim.*, **2021**, *66*, 625–632.
15. M. D. Zidan, M. M. Al-Ktaifani and A. Allahham, *JOAM*, **2019**, *21*, 93–100.
16. M. D. Zidan, M. M. Al-Ktaifani, M. S. EL-Daher, A. Allahham and A. Ghanem, *Iran. J. Sci. Techn., Transaction A: Science*, **2020**, *44*, 1577–1583.
17. M. D. Zidan, M. M. Al-Ktaifani, M. S. EL-Daher, A. Allahama, A. Ghanem and A. Alsharif, *JOAM*, **2021**, *23*, 22 – 28.
18. M. M. Al-Ktaifani, M. K. Sabra, A. A. Alsharif and F. Maksoud, *J. Chem. Crystallography*, **2022**, <https://doi.org/10.1007/s10870-021-00915-z>.
19. M. K. Rukiah, M. M. Al-Ktaifani and M. K. Sabra, *Acta Cryst.*, **2016**, *C72*, 112–118.
20. F. Garci, H. Ferjani, H. Chebbi, M. Ben Jomaa and M. F. Zida, *Acta Cryst.*, **2019**, *E75*, 1600–1606.
21. P. Pyykkö and M. Straka, *Phys. Chem. Chem. Phys.*, **2000**, *2*, 2489–2493.
22. A. K. Pandey, M. Usman and S. P. Rath, *Inorg Chem.*, **2020**, *59*, 12988–12993.
23. A. Bondi, *J. Phys. Chem.*, **1964**, *68*, 441–451.
24. A. Altomare, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi, N. Corriero and A. Falcicchio, *J. Appl. Cryst.*, **2013**, *46*, 1231–1235.
25. B. H. Toby and R. B. Von Dreele, *J. Appl. Cryst.*, **2013**, *46*, 544–549.