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# Effect of Robust $\pi$ - $\pi$ Stacking Synthons on the Formation of Mercury Coordination Compounds; an Unusual Pseudo-Square Planar Geometry

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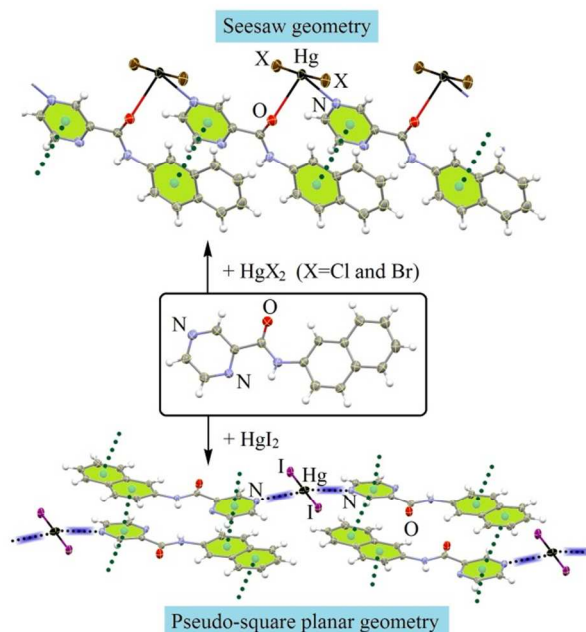
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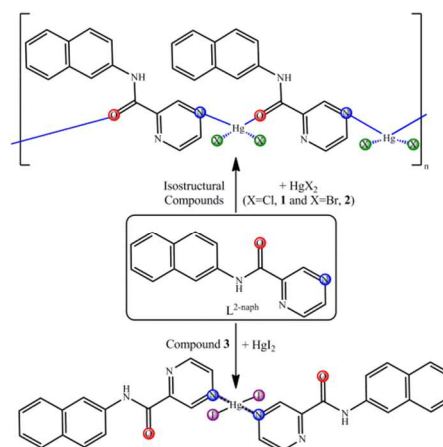
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In this study, three Hg(II) complexes,  $[\text{HgCl}_2(\text{L}^{2\text{-naph}})]_n$ , **1**,  $[\text{HgBr}_2(\text{L}^{2\text{-naph}})]_n$ , **2** and  $[\text{HgI}_2(\text{L}^{2\text{-naph}})_2]$ , **3** where  $\text{L}^{2\text{-naph}}$  is *N*-(naphthalene-2-yl)pyrazine-2-carboxamide ligand have been synthesized and characterized. X-ray single crystal diffraction analysis of these compounds reveals that **1** and **2** are isostructural coordination polymers and **3** is a discrete compound. In comparison to homologues complexes containing *N*-(naphthalene-1-yl)pyrazine-2-carboxamide ligand, interestingly, structural analysis clearly shows that displacing substituent position plays an important role in the formation of the supramolecular organization of molecular complexes. The common feature in the crystal packing of these complexes is that there is a strong tendency to form  $\pi$ - $\pi$  stacking interaction between pyrazine and naphthalene rings. These  $\pi$ - $\pi$  stacking interaction synthons affect the coordination geometry and structural assembly. Also, theoretical methods show the  $\pi$ - $\pi$  stacking interaction energies within a range of -64.13 to -70.51 kJ.mol<sup>-1</sup>. It is notable that in **3**, cooperation of intermolecular  $\pi$ - $\pi$  stacking synthon and intramolecular C-H<sub>pyz</sub>...I-Hg hydrogen bond resulted in the formation of unusual pseudo-square planar geometry around Hg(II) center. This study reveals an undeniable contribution of  $\pi$ - $\pi$  stacking interaction to the organization and stabilization of some of the crystal structures reported here.

## Introduction

Programmed self-assembly of coordination compounds has attracted great attention for not only their usage in different areas such as catalysis, materials and nanotechnology, but also their structural topologies.<sup>1</sup> This assembly is based on the use of supramolecular synthons which assemble molecular building blocks through non-covalent interactions.<sup>2</sup> By controlling the weak interactions in the crystal packing of coordination compounds and understanding the reliable synthons, interesting networks can be constructed.<sup>3</sup> In addition to these interactions, other factors such as coordination geometry of metal center,<sup>4</sup> ligand structure,<sup>5</sup> which can provide suitable interaction sites, counter ions,<sup>6</sup> and experimental conditions<sup>7</sup> can affect the final structures of crystalline coordination compounds. The influence of hydrogen bonding interactions on the formation of crystal packing has been well studied.<sup>8</sup> Because of its directionality, it has been described as “the master key interaction in supramolecular chemistry”.<sup>9</sup> Other than the hydrogen bonds, the  $\pi$ - $\pi$  interaction synthons undoubtedly play important roles in assembling building blocks and directing the crystal packing.<sup>10</sup> Unlike hydrogen bonding, control of  $\pi$ - $\pi$  interaction is too difficult due to the lack of strength and directionality. In the recent years, there are some examples reported in the literature describing the influence of  $\pi$ - $\pi$  interactions in the secondary structure-directing on the formation of special arrangement.<sup>11</sup> Also, study of the  $\pi$ - $\pi$  stacking effect on the primary structure-directing coordination geometry has been reported by us.<sup>12</sup> Recently, we showed that interplay between the coordination

of carbonyl group and  $\pi$ - $\pi$  interaction leads to the formation of two dimensional structures.<sup>12a</sup> Reger and his co-workers have focused on exploiting the  $\pi$ - $\pi$  stacking capabilities of the  $\pi$ -deficient 1,8-naphthalimide supramolecular synthon.<sup>13a-g</sup> Lu and his colleagues illustrated that halide alone is not sufficient to induce linearity and effect of face-to-face  $\pi$ - $\pi$  stacking interactions between bipyrimidine ligand lead to the formation of infinite mercury metal chains.<sup>10c</sup> Also



**Scheme 1.** Schematic representation of synthetic route of **1-3** and presence of secondary bond (blue dashed line).

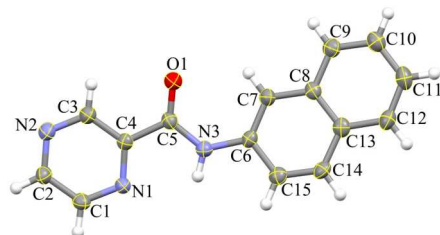
in 2012, Carey and his co-workers have been reported the effects of substituent on the geometry of  $\pi$ - $\pi$  interactions.<sup>14</sup> Their experiment described that substituents stabilize  $\pi$ - $\pi$  interactions regardless of their electronic character.

As a part of our research line about  $\pi$ - $\pi$  interaction effect in the crystal packing of mercury coordination compounds containing pyrazine carboxamide ligands, that the authors are developing, we recently reported the structural analysis of Hg(II) complexes containing *N*-(naphthalene-1-yl)pyrazine-2-carboxamide ligand.<sup>12b</sup> As a result, it was found that there is a strong tendency to form  $\pi$ ... $\pi$  synthon between naphthyl and pyrazine rings. Our results showed that this  $\pi$ - $\pi$  stacking interaction has been affected the geometry around the mercury ion.<sup>12b</sup> In the present study, the crystal structures of three Hg(II) complexes of *N*-(naphthalene-2-yl)pyrazine-2-carboxamide ligand, **L**<sup>2-naph</sup>, [HgCl<sub>2</sub>(**L**<sup>2-naph</sup>)]<sub>n</sub>, **1**, [HgBr<sub>2</sub>(**L**<sup>2-naph</sup>)]<sub>n</sub>, **2** and [HgI<sub>2</sub>(**L**<sup>2-naph</sup>)<sub>2</sub>], **3**, have been analysed, scheme 1, and compared to the previously reported structures of similar complexes with *N*-(naphthalene-1-yl)pyrazine-2-carboxamide ligand, **L**<sup>1-naph</sup>. X-ray diffraction analysis of these complexes gives details about the effect of aromatic interactions on the coordination geometry of metal center and formation of unusual geometry around central atom in **3**.

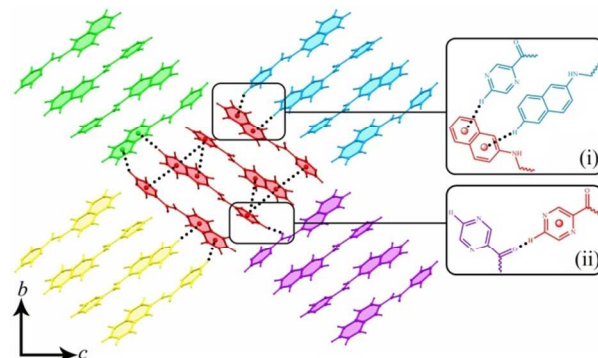
## Results and Discussion

**Synthesis.** The ligand **L**<sup>2-naph</sup> was prepared by simply mixing of the same equivalents of 2-naphthylamine and pyrazinecarboxylic acid in pyridine in the presence of triphenyl phosphite. Reaction of equimolar amounts of this ligand and HgX<sub>2</sub> (X = Cl, Br and I) in methanol:chloroform (1:1) gave the corresponding complexes. Slow evaporation of the solvent resulted in the air-stable yellow block crystals of **1**, yellow needle crystals of **2** and colorless block crystals of **3**, after a few days.

**Structural analysis of **L**<sup>2-naph</sup>, [HgCl<sub>2</sub>(**L**<sup>2-naph</sup>)]<sub>n</sub>, **1**, [HgBr<sub>2</sub>(**L**<sup>2-naph</sup>)]<sub>n</sub>, **2** and [HgI<sub>2</sub>(**L**<sup>2-naph</sup>)<sub>2</sub>], **3**; formation of an unusual pseudo-square planar geometry in [HgI<sub>2</sub>(**L**<sup>2-naph</sup>)<sub>2</sub>].** To have a better insight into the structural changes of **L**<sup>2-naph</sup> from free ligand to coordination compounds **1**, **2** and **3**, we determined its structure by X-ray diffraction study. X-ray single crystal diffraction analysis demonstrates that **L**<sup>2-naph</sup> crystallizes in the monoclinic crystal system with *P*<sub>2</sub><sub>1</sub>/*n* space group, Table 1. Asymmetric unit of this compound consists of two molecules. An ORTEP view of **L**<sup>2-naph</sup> is shown in Figure 1. In the solid state, **L**<sup>2-naph</sup> has a sandwich-herringbone structure.<sup>15</sup> As depicted from Figure 2, in the crystal packing of **L**<sup>2-naph</sup>, adjacent molecules are assembled through the  $\pi$ - $\pi$  stacking interaction to generate a four-membered unit. The centroid-to-centroid ring distances are ranged from 3.818(2) Å to 3.856(3) Å, Table 2. These units connect to adjacent units through non-classical C<sub>naph</sub>/pyz-H... $\pi$ <sub>naph</sub> and C<sub>naph</sub>/pyz-H...O=C hydrogen bonds. The dihedral angle between pyrazine and naphthalene rings in each unit is ranged between 8.76° and 11.15°.



**Figure 1.** ORTEP diagram of *N*-(naphthalene-2-yl)pyrazine-2-carboxamide ligand, **L**<sup>2-naph</sup>. Ellipsoids are drawn at 30% probability level.



**Figure 2.** Representation of the sandwich-herringbone structure of **L**<sup>2-naph</sup> along *a*-axis.  $\pi$ - $\pi$  stacking interaction is shown by dashed lines. Different colors show different layers. For clarity aromatic interaction in other layers is not displayed and they are as same as this interaction which is shown in red layer. C-H... $\pi$  and C-H...O=C non-classical hydrogen bonds are shown in (i) and (ii) boxes.

The coordination ability of **L**<sup>2-naph</sup> was also tested with Mercury(II) halides. A simple reaction between HgX<sub>2</sub> (X = Cl, Br) and **L**<sup>2-naph</sup> in a 1:1 solution of methanol and chloroform at 313 K afforded well-formed crystals of [HgCl<sub>2</sub>(**L**<sup>2-naph</sup>)]<sub>n</sub>, **1** and [HgBr<sub>2</sub>(**L**<sup>2-naph</sup>)]<sub>n</sub>, **2**. X-ray diffraction analysis on a single crystal of these complexes revealed that both of them crystallize in the monoclinic crystal system with *P*<sub>2</sub><sub>1</sub>/*n* space group and they are isostructural, Table 1. The asymmetric unit of them consists of one crystallographically independent Hg<sup>2+</sup> ion, one carboxamide ligand **L**<sup>2-naph</sup> and two halide anions. As depicted in Figure 3, in these compounds, the highly distorted tetrahedral geometry of the Hg(II) center can be better described as a seesaw structure. The X1-Hg-X2 angle is 175.95(8)° and 175.09(5)° for **1** and **2** respectively, where the two Hg-X bonds form the plank (Hg-Cl: 2.298(2) and 2.301(2) Å, and Hg-Br: 2.426(1) and 2.428(1) Å, Table 3). The angle between the other two bonds, (Hg-N: 2.657(7) Å and Hg-O: 2.773(5) Å for **1** and Hg-N: 2.672(8) Å and Hg-O: 2.908(7) Å for **2**, Table 3), which form the pivot, is 88.3(2) and 93.0(2)°, respectively. The X-Hg-X and N-Hg-O planes are nearly perpendicular, with a dihedral angle of 87.0°. Houser and co-workers<sup>16</sup> have proposed a new geometry index,  $\tau_4$ , for a four coordinate complexes which is defined by the equation  $\tau_4 = [360 - (\alpha + \beta)] / 141$  ( $\alpha$  and  $\beta$  are the two largest angles around the metal) and ranges from 0 for a square planar geometry to 1 for tetrahedral geometry. For both complexes, the four-coordinate geometry index,  $\tau_4$ , of 0.64 fits with a seesaw description. In the crystal packing of these complexes, neighboring mercury atoms are linked by bridging ligand **L**<sup>2-naph</sup> through oxygen of carbonyl group and nitrogen of pyrazine ring to form 1D polymeric chain expanded along *a*-axis, Figure 4. The interchain distances of adjacent mercury atoms (Hg1 and Hg1', symmetry codes, (i): 1+x, y, z for **1** and (i): -1+x, y, z for **2**) are 7.215(9) Å and 7.446(3) Å for **1** and **2** respectively. The dihedral angle between pyrazine and naphthalene rings is 8.03° for **1** and 7.66° for **2** which is shorter than the related value for free ligand.

A simple reaction between of **L**<sup>2-naph</sup> with HgI<sub>2</sub> in 1:1 molar ratio leads to the formation of [HgI<sub>2</sub>(**L**<sup>2-naph</sup>)<sub>2</sub>] complex, **3**. Upon slow evaporation of the methanol/chloroform solution of this complex, colorless block crystals were obtained after ca. two weeks. X-ray single crystal diffraction analysis demonstrates that **3** crystallize in the monoclinic crystal system with *C*<sub>2</sub>/*c* space group, Table 1. The asymmetric unit of this complex consists of one Hg<sup>2+</sup> ion, an iodide anion and one crystallographically independent amide ligand **L**<sup>2-naph</sup>. The coordination geometry around the Hg(II) atom is occupied two iodine ions in *trans* positions and two pyrazine nitrogen atom of

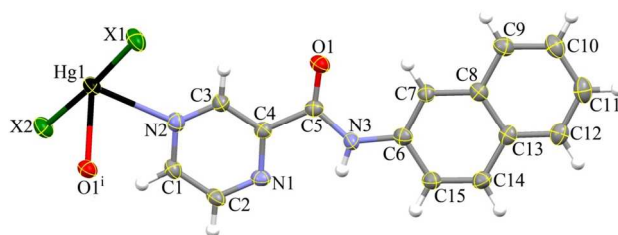
**Table 1.** Crystal data and structural refinement for compounds  $L^{2-naph}$ , **1**, **2** and **3**.

	$L^{2-naph}$	$[HgCl_2(L^{2-naph})]_n$ , <b>1</b>	$[HgBr_2(L^{2-naph})]_n$ , <b>2</b>	$[HgI_2(L^{2-naph})_2]$ , <b>3</b>
Formula	$C_{15}H_{11}N_3O$	$C_{15}H_{11}Cl_2HgN_3O$	$C_{15}H_{11}Br_2HgN_3O$	$C_{30}H_{22}I_2HgN_6O_2$
Fw	249.27	520.76	609.66	952.93
$\lambda/\text{\AA}$	0.71073	0.71073	0.71073	0.71073
$T/^\circ\text{C}$	25	25	25	25
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$C2/c$
$a/\text{\AA}$	5.8657(5)	7.2155(8)	7.446(3)	29.313(3)
$b/\text{\AA}$	17.8891(17)	11.6633(12)	11.885(5)	6.8788(4)
$c/\text{\AA}$	22.837(2)	18.314(2)	18.079(8)	15.5479(12)
$\beta/^\circ$	90.930	97.853(10)	97.47(3)	111.401(7)
$V/\text{\AA}^3$	2396.1(4)	1526.8(3)	1586.3(11)	2918.9(4)
$D_{calc}/\text{Mg.m}^{-3}$	1.382	2.266	2.553	2.168
Z	8	4	4	4
$\mu/\text{mm}^{-1}$	0.090	10.434	14.744	7.428
$F(000)$	1040	976	1120	1784
$\theta_{max}/^\circ$	29.25	26	26	26
Reflection collected, $R_{int}$	26370, 0.0911	12235, 0.1180	13128, 0.0987	11496, 0.0875
GOOF	0.920	1.136	1.134	1.070
$R_1^a(I > 2\sigma(I))$	0.0957	0.0506	0.0521	0.0905
$wR_2^b(I > 2\sigma(I))$	0.1126	0.1244	0.1251	0.1615
CCDC No.	956584	956581	956582	956583

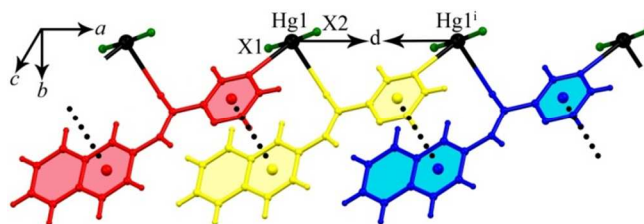
$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b wR_2 = \left[ \frac{\sum (w(F_o^2 - F_c^2)^2)}{\sum w(F_o^2)^2} \right]^{1/2}$$

$L^{2-naph}$  (Hg-N: 2.94(1) Å), Figure 5. In this complex, the Hg-N distance of 2.94 Å is slightly longer than other distances reported previously. To get an idea about the nature of this distance, a Cambridge Structural Database (CSD) search was carried.<sup>17</sup> A search on Hg-N distances (where N is involved in six member ring) that resulted in 709 hits shows four hits<sup>18</sup> have a distance longer than 2.90 Å. Among these hits complexes with refcodes MAVTAF<sup>18b</sup> and LIDMIU,<sup>18c</sup> Hg-N distances are 2.90, 2.93 and 2.98 Å. So, occupation of coordination sphere by pyrazine nitrogen atoms of  $L^{2-naph}$  ligand, suggest Hg...N secondary interaction. This type of interaction is common in compounds of heavy elements (metals and nonmetals in the bottom rows of the periodic table) and can be regarded as a particular case of donor-acceptor bonds.<sup>19i</sup> Recently, contribution of Hg...N<sub>pyz</sub> secondary bonding interaction to the organization and stabilization of some of the crystal structures of mercury(II) coordination compounds containing *N*-(2-halophenyl)-2-pyrazinecarboxamide ligands has been reported by some of us.<sup>20</sup> In previous report,<sup>20</sup> we showed that the stronger secondary bond is the stronger trend for linearity will be. This notion is endorsed by The Cambridge Structural Database (CSD) analysis. The distribution of the data points clearly indicated that at shorter Hg...N distances, there is a strong tendency toward linearity and hence the metal center tends to keep the secondary bond axis collinear with its primary bond.<sup>22</sup> So, besides Hg...N distance, another contributing factor to secondary bond strength might be the angle between Hg...N vector and main plane containing pyrazine ring of coordinated  $L^{2-naph}$  ligand. Here, the mentioned angle is less than 1°. So, the coordination geometry around the Hg(II) atom can be described as a pseudo-square planar with two iodine ions and two pyrazine nitrogen atom of  $L^{2-naph}$  (Hg-N: 2.94(1) Å), Figure 5. This is an unusual coordination geometry around Hg(II) complexes. The four-coordinate geometry index,  $\tau_4$ , as defined by Houser,<sup>16</sup> is 0.10

for **3** which implies that the coordination geometry is best described as square planar. The slightly deviation of perfect square planar geometry is not only due to the spatial orientation of the two ligands



**Figure 3.** Portion of the structure of coordination polymers formed between  $L^{2-naph}$  and  $HgX_2$  (X = Cl, **1** and X = Br, **2**), showing coordination geometry around central metal. Symmetry codes: (i)  $1+x, y, z$ .



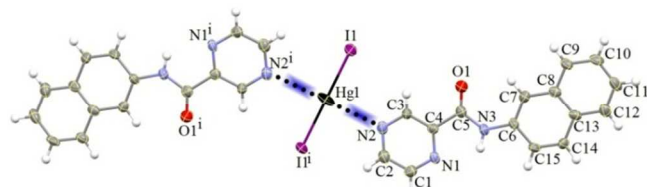
**Figure 4.** Representation of linear polymeric chain in **1** and **2**. Intramolecular  $\pi$ - $\pi$  stacking between naphthalene and pyrazine rings are shown by dashed lines.  $d$  is the distance of neighboring mercury which is 7.215 Å and 7.446 Å for  $[HgCl_2(L^{2-naph})]$  and  $[HgBr_2(L^{2-naph})]$  respectively. Symmetry codes: (i)  $1+x, y, z$ .

**Table 2.** Coordination geometry, dimensionality, C=O-Hg angle and aromatic interaction parameters (Å and °) for description of  $\pi$ - $\pi$  interaction in  $L^{2-naph}$ ,  $[HgCl_2(L^{2-naph})]_n$ , **1**,  $[HgBr_2(L^{2-naph})]_n$ , **2**,  $[HgI_2(L^{2-naph})_2]$ , **3**,  $[HgCl_2(L^{1-naph})_2]_n$ , **1'**,  $[Hg_2Br_4(L^{1-naph})_2]$ , **2'** and  $[Hg_2I_4(L^{1-naph})_2]$ , **3'**.

Complex	Coordination geometry/ dimension	Cg(I)-Cg(J)	$d_{Cg-Cg}^a$	$\alpha^b$	$\beta, \gamma^c$	$d_{plane-plane}^d$	$d_{offset}^e$	C=O-Hg angle	$\pi \dots \pi$ stacking energy (kJ/mol) <sup>f</sup>
$[HgCl_2(L^{2-naph})]_n$ , <b>1</b>	Seesaw/linear chain	Cg(1)-Cg(2) <sup>i</sup>	3.767(4)	8.3(4)	23.63, 29.10	3.291(3), 3.451(3)	1.83, 1.26	130.48	-66.92
		Cg(1)-Cg(1) <sup>ii</sup>	3.702(4)	0	28.59	3.251(3)	1.77		
$[HgBr_2(L^{2-naph})]_n$ , <b>2</b>	Seesaw/linear chain	Cg(1)-Cg(2) <sup>i</sup>	3.743(6)	7.8(4)	23.24, 27.39	3.323(4), 3.439(4)	1.88, 1.47	128.67	-64.53
		Cg(1)-Cg(1) <sup>iii</sup>	3.786(6)	0	29.61	3.291(4)	1.87		
		Cg(3)-Cg(1) <sup>iii</sup>	3.984(6)	7.6(6)	27.37, 33.63	3.317(4), 3.538(4)	2.20, 1.83		
$[HgI_2(L^{2-naph})_2]$ , <b>3</b>	SP/discrete	Cg(1)-Cg(3) <sup>iv</sup>	3.520(8)	3.2(6)	17.07, 19.23	3.324(6), 3.365(5)	1.15, 1.03	-	-92.01
		Cg(1)-Cg(2) <sup>iv</sup>	3.695(7)	2.0(6)	24.07, 22.35	3.374(5), 3.418(5)	1.50, 1.40		
		Cg(2)-Cg(1) <sup>iv</sup>	3.820(8)	32.0(6)	24.18, 26.14	3.429(5), 3.485(5)	1.68, 1.56		
		Cg(3)-Cg(1) <sup>iv</sup>	3.847(8)	3.2(6)	23.68, 25.09	3.523(6), 3.484(5)	1.54, 1.63		
$[HgCl_2(L^{1-naph})_2]_n$ , <b>1'</b>	O <sub>h</sub> / linear chain	Cg(4)-Cg(5) <sup>v</sup>	3.559(3)	0.4(2)	16.40, 16.43	3.414(2), 3.415(2)	1.00, 1.00	104.73	-64.13
		Cg(4)-Cg(6) <sup>v</sup>	3.813(3)	0.7(2)	26.97, 26.31	3.418(2), 3.398(2)	1.68, 1.72		
$[Hg_2Br_4(L^{1-naph})_2]$ , <b>2'</b>	Seesaw/binuclear	Cg(4)-Cg(6) <sup>vi</sup>	3.880(5)	1.9(4)	27.33, 25.71	3.495(3), 3.447(4)	1.68, 1.78	116.24	-69.55
		Cg(4)-Cg(6) <sup>vii</sup>	3.868(5)	1.9(4)	28.57, 26.95	3.449(3), 3.398(4)	1.75, 1.84		
$[Hg_2I_4(L^{1-naph})_2]$ , <b>3'</b>	Seesaw/ dimer	Cg(4)-Cg(6) <sup>viii</sup>	3.780(6)	1.2(5)	25.28, 26.44	3.384(4), 3.418(4)	1.68, 1.61	120.10	-70.51
		Cg(4)-Cg(6) <sup>ix</sup>	4.071(6)	1.2(5)	31.58, 30.47	3.509(4), 3.469(4)	2.06, 2.13		
$L^{2-naph}$	-	Cg(4)-Cg(1) <sup>x</sup>	3.739(3)	5.7(2)	20.69, 25.60	3.372(2), 3.498(2)	1.61, 1.32	-	-
		Cg(7)-Cg(8) <sup>xi</sup>	3.818(2)	10.8(2)	21.55, 26.04	3.431(2), 3.551(2)	1.67, 1.40		
		Cg(9)-Cg(8) <sup>xi</sup>	3.856(3)	11.5(2)	19.56, 27.62	3.417(2), 3.634(2)	1.78, 1.29		

<sup>a</sup>Centroid-centroid distance. <sup>b</sup>Dihedral angle between the ring plane. <sup>c</sup>Offset angles: angle between Cg(I)-Cg(J) vector and normal to plane I, angle between Cg(I)-Cg(J) vector and normal to plane J ( $\beta = \gamma$  when  $\alpha = 0$ ). <sup>d</sup>Perpendicular distance of Cg(I) on ring J and perpendicular distance of Cg(J) on ring I. <sup>e</sup>Horizontal displacement between Cg(I) and Cg(J), two values if the two rings are not exactly parallel ( $\alpha \neq 0$ ). <sup>f</sup>The values are related to the energy of the stacking interaction between two adjacent ligands. For **1**, **2** and **3**, Cg(1): centroid of N(1)-C(1)-C(2)-N(2)-C(3)-C(4), Cg(2): centroid of C(6)-C(7)-C(8)-C(13)-C(14)-C(15), Cg(3): centroid of C(8)-C(9)-C(10)-C(11)-C(12)-C(13), For **1'**, **2'** and **3'**, Cg(4): centroid of N(1)-C(1)-C(2)-N(2)-C(3)-C(4), Cg(5): centroid of C(6)-C(7)-C(8)-C(9)-C(10)-C(15), Cg(6): centroid of C(10)-C(11)-C(12)-C(13)-C(14)-C(15) and for  $L^{2-naph}$ , Cg(7): centroid of C(23)-C(28), Cg(8): centroid of N(4)-C(16)-C(17)-N(5)-C(18)-C(19) and Cg(9): centroid of C(21)-C(22)-C(23)-C(28)-C(29)-C(30). Symmetry codes: (i) 1+x, y, z, (ii) 3-x, 1-y, 1-z, (iii) -x, -y, 1-z, (iv) 1/2-x, 1/2+y, 1/2-z, (v): x, 1+y, z, (vi) -x, 1-y, -z, (vii) 1-x, 1-y, -z, (viii) 1-x, -1-y, 1-z, (ix) -x, -1-y, 1-z, (x) -1+x, y, z and (xi) 2-x, -y, -z.

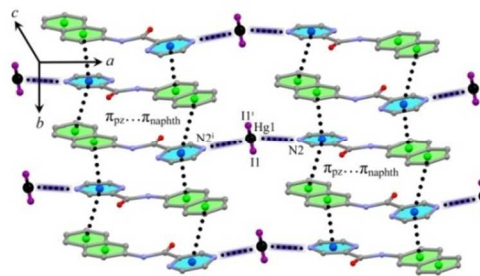
and longer distance of Hg-N secondary bonding but also it is due to the steric effects of iodine atoms. The principle of steric control over secondary bonding interactions and thereby molecular association has been studied by Tiekink,<sup>21</sup> Vargas-Baca,<sup>22</sup> Johnson<sup>23</sup> and others.<sup>24</sup> Most of the  $HgX_2$  complexes tend to coordinate in the tetrahedral geometry rather than square planar, because of the less intra-atomic repulsive interaction in  $T_d$  fashion.<sup>25</sup> Especially in the case of  $HgI_2$  it is more critical due to the greater van der Waals radius of iodide toward chloride and bromide. In addition, the Hg-N bonds are shorter (2.3-2.6 Å) in the tetrahedral case.<sup>26</sup> A CSD search about the geometry around the Hg(II) ions has been performed.<sup>17</sup> We



**Figure 5.** Portion of the structure of complex **3** formed between  $L^{2-naph}$  and  $HgI_2$ , showing pseudo-square planar geometry around mercury atom.

Secondary bonds are presented with dashed blue lines. Symmetry codes: (i) -x, y, 1/2-z.

define geometrical restriction on the database search. The 7A-Hg-7A and X-Hg-X angles were allowed to have values from 160° to 180° (where 7A and X is defined any halogen atom and any atom respectively). Our results show that square planar geometry around Hg(II) halides are rare and among them most of the structures consist of  $HgCl_2$  moiety.<sup>5a, 27</sup> In the case of  $HgI_2$ , there are two



**Figure 6.** A side view representation of **3** showing *Intermolecular*  $\pi$ - $\pi$  stacking interaction between naphthalene and pyrazine rings by dashed lines. Secondary bonding is shown with dashed blue lines. Symmetry codes: (i) -x, y, 1/2-z.

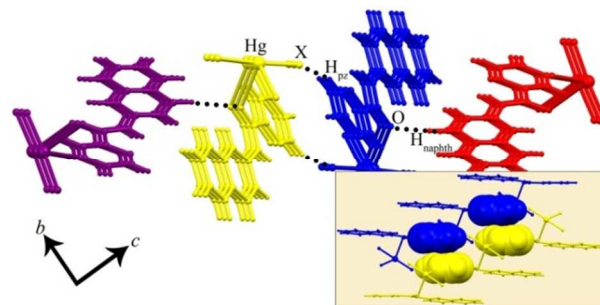
**Table 3.** Selected bond length (Å) and angles (°) around mercury (II) for complexes **1-3**.

		Complex		
		1 (X = Cl)	2 (X = Br)	3 (X = I)
<b>Bond distance</b>	Hg1-X1	2.301(2)	2.428(1)	2.576(1)
	Hg1-X2	2.298(2)	2.426(1)	-
	Hg1-O1	2.773(5) <sup>i</sup>	2.809(7) <sup>a</sup>	-
	Hg1-N2	2.657(7)	2.672(8)	2.94(1)
<b>Bond Angle</b>	X1-Hg1-X2	176.0(1)	175.1(1)	-
	N2-Hg1-O1	88.3(2) <sup>i</sup>	93.0(2) <sup>i</sup>	-
	X1-Hg1-N2	91.3(2)	91.8(2)	87.7(2)
	X1-Hg1-O1	93.0(1) <sup>i</sup>	93.3(1) <sup>i</sup>	-
	X2-Hg1-N2	92.3(2)	92.8(2)	-
	X2-Hg1-O1	88.8(1) <sup>i</sup>	88.2(1) <sup>i</sup>	-
	N2-Hg1-N2	-	-	164.8(3) <sup>ii</sup>
	X1-Hg1-N2	-	-	92.3(2) <sup>ii</sup>
	X1-Hg1-X1	-	-	179.95(6) <sup>ii</sup>

Symmetry codes: (i) 1+x, y, z and (ii) -x, y, 1/2-z.

reports (with refcodes CETJIV<sup>28a</sup> and UZEZUV<sup>28b</sup>) that coordination geometry around Hg(II) may be considered as square planar. In these compounds central Hg is coordinated by two L ligands (L=bis(4-pyridylethenyl)ferrocene<sup>28a</sup> or 1-propyl-3-(pyridin-2-ylmethyl)-benzimidazole<sup>28b</sup>) and two I atoms in *trans* position. In compound reported by Song et. al.,<sup>28a</sup> each bis(4-pyridylethenyl)ferrocene and iodine ligands act as bridge to link the central metal to two terminal Hg ions, meanwhile, the terminal Hg atoms, in a seesaw geometry, are also bonded to two I atoms to form a three-nuclear complex. From the packing diagram of this compound, it is evident that two iodide ligands from the adjacent Hg centers are positioned towards the central Hg atom. The same trend is found in compound reported by Liu and co-workers.<sup>28b</sup> In this compound, pyridine groups of the 1-propyl-3-(pyridin-2-ylmethyl)-benzimidazole are positioned towards the central Hg atom. Therefore it seems there is a tendency to form six coordinated structure and it can be concluded that coordination geometry around the central Hg atom is pseudo-octahedral in both compounds. Also, it is notable that four-coordinated [HgCu<sub>2</sub>I<sub>2</sub>(SePh)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] complex reported by Lang and co-workers,<sup>28c</sup> may be considered as a pseudo-square planar coordination compound, but coordination angles around the central metal of 75.67(1) and 104.33(1)°, show that the geometry around mercury atom is highly distorted square-planar. In complex **3**, coordination angles around the mercury are 88.7(2) and 92.3(2)°, Table 3. As it is clear from Figure 6, below and above the coordination plane in compound **3** are occupied by naphthalene aromatic rings. So, the geometry around Hg center can be considered undoubtedly as pseudo-square planar. To the best of our knowledge, this complex is the first compound which has got pseudo-square planar geometry.

**Influence of  $\pi$ - $\pi$  stacking synthon on the coordination geometry and supramolecular assembly.** To make progress in controlling structural assemblies of coordination compounds, it is desirable to synthesize a series of complexes of predetermined chemical structure, allowing for a comparison between assemblies with specific and controllable changes to their molecular structure. In this regard, a slight difference in the chemical structure of organic ligand, even displacing substituent position, can play an important role in controlling the supramolecular organization of molecular

**Figure 7.** Portion of 1D linear chains of **1** and **2** along *a*-axis which are assembled through *intermolecular*  $\pi$ - $\pi$  stacking interactions between pyrazine rings of adjacent chain and C-H<sub>py</sub>...X-Hg and C-H<sub>naphth</sub>...O=C non-classical hydrogen bonds. Different colors show different adjacent chains.

complexes.<sup>5a, 29</sup> There are some examples reported in the literature describing the influence of  $\pi$ - $\pi$  interactions in the *secondary* structure-directing in the formation of special arrangements,<sup>11</sup> In 2010, the effect  $\pi$ - $\pi$  stacking on the *primary* structure-directing coordination geometry has been discussed by some of us in the structure of Hg(II) complexes containing *N*-(naphthalene-1-yl)pyrazine-2-carboxamide ligand, **L<sup>1-naph</sup>**.<sup>12b</sup> As a result, it was found that there is a strong tendency to form  $\pi$ ... $\pi$  synthon between naphthyl and pyrazine rings. Here, we describe systematic studies of  $\pi$ - $\pi$  stacking synthon on the structural assemblies of Hg(II) complexes of *N*-(naphthalene-2-yl)pyrazine-2-carboxamide ligand, **L<sup>2-naph</sup>**, which have led to an understanding of how position of substituent affects the  $\pi$ ... $\pi$  interactions and coordination geometry.

When compared to the **L<sup>1-naph</sup>** ligand, the displacing substituent position significantly alter the molecular architecture and/or coordination sphere of complexes containing *N*-(naphthalene-2-yl)pyrazine-2-carboxamide ligand, **L<sup>2-naph</sup>**. For HgCl<sub>2</sub> adduct, both complexes have been shown linear chains, but from [HgCl<sub>2</sub>(**L<sup>1-naph</sup>**)<sub>2</sub>]<sub>n</sub>, **1'**, to [HgCl<sub>2</sub>(**L<sup>2-naph</sup>**)<sub>2</sub>]<sub>n</sub>, **1**, the coordination sphere changes from O<sub>h</sub> to seesaw, Table 2. For both HgBr<sub>2</sub> adducts, the coordination sphere is seesaw, but complex [Hg<sub>2</sub>Br<sub>4</sub>(**L<sup>1-naph</sup>**)<sub>2</sub>], **2'**, has discrete dinuclear cyclic units while complex [HgBr<sub>2</sub>(**L<sup>2-naph</sup>**)<sub>2</sub>]<sub>n</sub>, **2**, has 1D polymeric structure. As listed in Table 2, the coordination geometries and structural motifs in HgI<sub>2</sub> adducts, complexes [Hg<sub>2</sub>I<sub>4</sub>(**L<sup>1-naph</sup>**)<sub>2</sub>], **3'** and [HgI<sub>2</sub>(**L<sup>2-naph</sup>**)<sub>2</sub>], **3**, are quite different and 1D chain in **3'** (with seesaw geometry) is changed to discrete monomer structure in **3** (with pseudo-square planar geometry). It is notable that the common feature in crystal structures of all six complexes obtaining of the reaction between HgX<sub>2</sub> and **L<sup>1-naph</sup>** and **L<sup>2-naph</sup>** ligands, is the existence of  $\pi$ - $\pi$  stacking. Thus a systematic study evaluation of supramolecular synthons consisting of  $\pi$ - $\pi$  stacking in a series of mercury complexes containing naphthylpyrazinamides is interesting. In Table 2, coordination geometry, dimensionality and geometrical parameters of  $\pi$ - $\pi$  stacking, scheme 2, are listed for these complexes. In **1** and **2**, the adjacent mercury atoms are linked by C=O-Hg bonds to form a 1D linear polymeric chain spanning along *a*-axis, Figure 7. In these compounds, the phenyl ring involved in the *intramolecular*  $\pi$ - $\pi$  stacking interaction between adjacent naphthalene and pyrazine rings (the centroid-to-centroid distance is 3.767(4) Å for compounds **1** and 3.743(6) Å and 3.984(6) Å for compounds **2**).

As it is clear from Figure 1, the naphthalene and pyrazine rings are in-plane with C=O group (maximum deviation from the mean plane through the naphthalene and pyrazine rings is less than 0.18 Å). In all complexes except **3**, the formation of this nearly parallel head-to-tail *intramolecular*  $\pi$ - $\pi$  stacking between adjacent rings affect the C=O-Hg angle value, Table 2. This interaction arranges the pyrazine

**Table 4.** Hydrogen bonding parameters (Å and °) for  $L^{2-naph}$ ,  $[HgCl_2(L^{2-naph})]_n$ , **1**,  $[HgBr_2(L^{2-naph})]_n$ , **2** and  $[HgI_2(L^{2-naph})_2]$ , **3**.

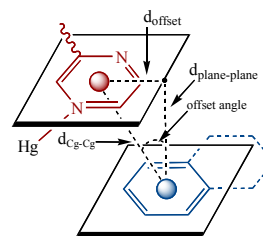
Compound	D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
$L^{2-naph}$	C14-H14...O2	0.93	2.591	3.262(6)	129
	C17-H 17...O1 <sup>i</sup>	0.93	2.544	3.312(6)	139
	C2-H2...π <sup>ii</sup>	0.93	-	3.638	-
	C26-H26...π <sup>iii</sup>	0.93	-	3.814	-
<b>1</b>	C14-H14...O1 <sup>iv</sup>	0.93	2.451	3.367(9)	169
	C1-H1...Cl2 <sup>v</sup>	0.93	2.798	3.558(8)	140
<b>2</b>	C14-H14...O1 <sup>vi</sup>	0.93	2.548	3.461(1)	166
	C1-H1...Br2 <sup>vii</sup>	0.93	2.933	3.658(9)	136
<b>3</b>	C10-H10...O1 <sup>viii</sup>	0.93	2.714	3.31(2)	122
	C2-H2...I1	0.93	3.244	3.93(2)	133
	C3-H3...I1	0.93	3.249	3.89(1)	127

Symmetry codes: (i) 3/2+x, 1/2-y, -1/2+z, (ii) 1/2-x, -1/2+y, 1/2-z, (iii) 3/2-x, -1/2+y, 1/2-z, (iv) 3-x, 1-y, 1-z, (v) 2-x, 1/2+y, 3/2-z, (vi) -1-x, -1/2+y, 3/2-z, (vii) 1-x, -y, 1-z and (viii) 1/2-x, 1/2-y, z.

and naphthalene rings in such a way that the angle between the plane normal (involving C-CO-N fragment) and O-Hg vector,  $\theta$  angle, reaches about 40.8° and 38.0° for **1** and **2** respectively. These low angles are undoubtedly due to the  $\pi$ - $\pi$  stacking in the crystal packing of these complexes. The related value for homologous complexes **1'** and **2'** reported previously by us is 14.7° and 26.2° respectively. A CSD search<sup>17</sup> of  $\theta$  angle for the geometry of  $X_2C=O-Hg$  (X is any atom) shows that the most frequent value for the  $\theta$  angle is found in the range of 70-90°. For compounds **1** and **2**, the centroid-to-centroid distances are 3.767(4) Å and 3.743(6) Å and 3.984(6) Å, Table 2. Here, these results confirmed the influence of such  $\pi$ - $\pi$  stacking synthon on the *primary* structure directing coordination geometry around Hg(II) metal center, that has been reported previously in details by some of us.<sup>12b</sup> As shown in Figure 7, these 1D linear chains are closely packed through parallel *intermolecular*  $\pi$ - $\pi$  stacking interactions between pyrazine rings of adjacent chain to form 2D sheets in **1** and **2**. The centroid-to-centroid distances are 3.702(4) Å and 3.786(6) Å for **1** and **2** respectively, Table 2. In addition to this aromatic interaction, these chains are further linked through C-H<sub>naph</sub>...O=C and C-H<sub>pyz</sub>...X-Hg non-classical hydrogen bonds. Hydrogen bonding parameters are given in Table 4.

In **3**, as depicted in Figure 6, discrete  $[HgI_2(L^{2-naph})_2]$  monomers are assembled through head-to-tail *intermolecular*  $\pi$ - $\pi$  stacking synthon between pyrazine and naphthalene rings of neighboring monomers to give 2D sheets. The centroid-to-centroid distances are 3.520(8) Å, 3.695(7) Å, 3.820(7) Å and 3.847(8) Å, Table 2. This interaction is one of the factors controlling orientation of pyrazine rings toward  $HgI_2$  moiety. In addition to this  $\pi$ - $\pi$  stacking interaction, intramolecular C-H<sub>pyz</sub>...I-Hg non-classical hydrogen bonds, Figure 8 and Table 4, is another factor in this special orientation of pyrazine ring and  $HgI_2$  moiety. It seems cooperation of *intermolecular*  $\pi$ - $\pi$  stacking synthon and *intramolecular* C-H<sub>pyz</sub>...I-Hg hydrogen bond influence the nearly linear orientation of pyrazine rings to each other (N2-Hg1-N2<sup>i</sup> = 164.8(3)°), Table 3. So, in fact, interplay between *intermolecular*  $\pi$ - $\pi$  stacking synthon and C-H<sub>pyz</sub>...I-Hg hydrogen bond induces pseudo-square planar geometry around the central metal.

It was thought of interest to further investigate the aromatic interaction energy in these compounds by using theoretical calculations. The binding energies obtained from the DFT calculations were performed with the experimental structures as

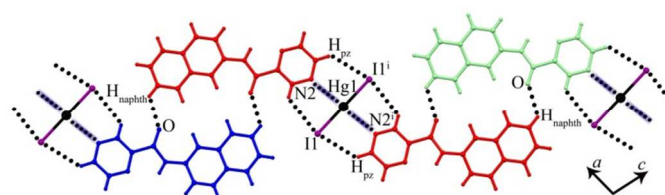


**Scheme 2.** Schematic representation of geometrical parameters for definition of  $\pi$ - $\pi$  stacking between adjacent pyrazine and naphthalene rings.

the starting point at the LDA-ZORA-TZP level. The outcomes are listed in Table 2. From these data, it is obvious that in complexes of  $HgX_2$  (X= Cl and Br) with  $L^{1-naph}$  and  $L^{2-naph}$  ligands, calculated energies are not highly different. It is explicit that in these compounds aromatic interaction parameters are nearly similar. But in the case of  $HgI_2$  compounds,  $[HgI_2(L^{2-naph})_2]$  is -21.5 kJ.mol<sup>-1</sup> more stable than  $[HgI_2(L^{1-naph})]$ . It seems that this stability is not only due to the shorter distance of centroid-to-centroid, but also it is because of shorter offset angles. As depicted above, In  $[HgI_2(L^{2-naph})_2]$  naphthalene and pyrazine rings are not very slipped. So, centroid-to-centroid distances of this aromatic synthon would be shorter followed by binding energy is getting more negative. Finally from the view of energy, this robust aromatic interaction synthon leads the formation of an unusual geometry around Hg(II) and supramolecular assembly.

## Conclusion

The goal of crystal engineering is the assembly of molecular building blocks into the favorable architecture with desired physical and chemical properties. An essential in reaching this goal is understanding and control of inter or intramolecular interactions which assemble the MBBs according to supramolecular synthon. Finding reliable synthons which can be used to design of solids cause to advances in this field. The  $\pi$ - $\pi$  stacking interaction synthon can be one of the most powerful non-covalent interactions for directing the self-assembly process. In this regard, coordination geometry and supramolecular architecture of three coordination compound of mercury(II) complexes based on  $L^{2-naph}$  ligands have been studied and compared with homologues complexes containing  $L^{1-naph}$ , previously reported by some of us. The presence of a strong tendency to form  $\pi$ - $\pi$  stacking between adjacent naphthyl and prazine rings is common feature in the crystal packing of complexes studied here. Our results show that  $\pi$ - $\pi$  stacking synthon has the *primary* effect on the coordination geometry of metal center. In one



**Figure 8.** Representation of discrete monomers of complex  $[HgI_2(L^{2-naph})_2]$  showing C-H<sub>pyz</sub>...I-Hg and C-H<sub>naph</sub>...O=C non-classical hydrogen bonding which lead to assembling the monomers. Secondary bonding is shown with dashed blue lines. Different colors show different monomers. Symmetry codes: (i) -x, y, 1/2-z.



of the complexes Hg(II) has an unusual pseudo-square planar geometry which is due to this intermolecular interaction. Furthermore, theoretical methods also show the interaction energies within a range of -64.13 to -70.51 kJ.mol<sup>-1</sup> are comparable to classical hydrogen bonding. It is notable, coordination geometry around central metal in HgI<sub>2</sub> and L<sup>2-naph</sup> adduct can be described as rarely pseudo-square planar geometry.

## Experimental Section

**Chemicals and instrumentation.** All chemicals were purchased from Aldrich or Merck and used without further purification. The synthesis and recrystallization of *N*-(naphthalene-2-yl)pyrazine-2-carboxamide ligand, L<sup>2-naph</sup>, and compounds **1-3** were carried out in air. Infrared spectra (4000–250 cm<sup>-1</sup>) of solid samples were taken as 1% dispersions in KBr pellets using a BOMEM-MB102 spectrometer. Elemental analysis was performed using a Heraeus CHN-O Rapid analyzer. <sup>1</sup>H NMR spectrum was recorded on a Bruker AC-300 MHz spectrometer at ambient temperature in CDCl<sub>3</sub>. All chemical shifts are quoted in part per million (ppm) relative to tetramethylsilane. Melting point was obtained by a Bamstead Electrothermal type 9200 melting point apparatus and corrected.

**Synthesis of *N*-(naphthalene-2-yl)pyrazine-2-carboxamide, L<sup>2-naph</sup>.** A solution of 5 mmol of 2-naphthylamine (0.62 g) in 10 mL pyridine was added to a solution of 5 mmol of pyrazine-2-carboxylic acid (0.72 g) in 10 mL pyridine. The resulting solution was stirred at 313 K for 30 min, then 5 mmol of triphenylphosphite (1.3 mL) was added dropwise, and the reaction mixture was stirred at 373 K for 5 h and at ambient temperature for 24 h. The resulting yellow solution was added to distilled water, filtered and then washed with 50 mL cold methanol. A light yellow solid resulted with a yield of 70%, Mp 172–175°C. Yellow block crystals were obtained upon slow evaporation of chloroform solution of this ligand at room temperature, after *ca.* a week. Anal. Calcd for L (C<sub>15</sub>H<sub>11</sub>N<sub>3</sub>O): C, 72.28; H, 4.45; N, 16.86. Found: C, 72.32; H, 4.50; N, 16.90. FT-IR (KBr pellet, cm<sup>-1</sup>): 3339m, 1679s, 1545s, 1356m, 1003m, 812s. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ from TMS): 9.8371(s, 1H), 9.5573(s, 1H), 8.8184(s, 1H), 8.6010(s, 1H), 8.4877(s, 1H), 7.8794–7.8039(m, 3H), 7.7051, 7.6765(d, 1H), 7.5245–7.4178(m, 2H).

**Synthesis of Mercury(II) complexes; [HgCl<sub>2</sub>(L<sup>2-naph</sup>)]<sub>n</sub>, **1**, [HgBr<sub>2</sub>(L<sup>2-naph</sup>)]<sub>n</sub>, **2** and [HgI<sub>2</sub>(L<sup>2-naph</sup>)<sub>2</sub>], **3**.** To a solution of 0.5 mmol of mercury(II) halide (HgX<sub>2</sub>, X=Cl, Br and I) in 5 mL of methanol, a solution of 0.5 mmol of *N*-(naphthalene-2-yl)pyrazine-2-carboxamide ligand, L, in 5 mL chloroform was added with stirring. The mixture was heated at 313 K for about 15 min and then filtered. Upon slow evaporation of the filtrate at room temperature, yellow block crystals for [HgCl<sub>2</sub>(L<sup>2-naph</sup>)]<sub>n</sub>, **1**, yellow needled crystals for [HgBr<sub>2</sub>(L<sup>2-naph</sup>)]<sub>n</sub>, **2**, and colorless block crystals for [HgI<sub>2</sub>(L<sup>2-naph</sup>)<sub>2</sub>], **3**, suitable for X-ray analysis were obtained after *ca.* two weeks (yield *ca.* 72%, 56% and 52% for **1**, **2** and **3**, respectively). It is notable that using 1:2 molar ratio of HgI<sub>2</sub> to L ligand resulted in the same product as when using 1:1 molar ratio. **1**. Mp (decomposed): 232–235°C. Anal. Calcd for C<sub>15</sub>H<sub>11</sub>Cl<sub>2</sub>HgN<sub>3</sub>O: C, 34.60; H, 2.13; N, 8.07. Found: C, 34.56; H, 2.10; N, 8.05. FT-IR (KBr pellet, cm<sup>-1</sup>): 3310m, 1660s, 1539s, 1354s, 1008m, 813m. **2**. Mp: 158–160°C. Anal. Calc. for C<sub>15</sub>H<sub>11</sub>Br<sub>2</sub>HgN<sub>3</sub>O: C, 29.55; H, 1.82; N, 6.89. Found: C, 29.53; H, 1.79; N, 6.85. FT-IR (KBr pellet, cm<sup>-1</sup>): 3317m, 1665s, 1546s, 1359m, 1017m, 814. **3**. Mp: 162–164°C. Anal. Calc. for C<sub>30</sub>H<sub>22</sub>I<sub>2</sub>HgN<sub>6</sub>O<sub>2</sub>: C, 37.81; H, 2.33; N, 8.82. Found: C, 37.78; H, 2.30; N, 8.79. FT-IR (KBr pellet, cm<sup>-1</sup>): 3534m, 1691s, 1546s, 1341m, 1017m, 804m.

**Single crystal diffraction studies.** X-ray data for compounds L<sup>2-naph</sup> and **1-3** were collected on a STOE IPDS-II diffractometer with graphite monochromated Mo-Kα radiation. For L<sup>2-naph</sup> and [HgCl<sub>2</sub>(L<sup>2-naph</sup>)]<sub>n</sub>, **1**, a yellow block crystal, for [HgBr<sub>2</sub>(L<sup>2-naph</sup>)]<sub>n</sub>, **2**, a yellow needle crystal and for [HgI<sub>2</sub>(L<sup>2-naph</sup>)<sub>2</sub>], **3**, a colorless block crystal was chosen using a polarizing microscope and they were mounted on a glass fiber which was used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 6450 for L<sup>2-naph</sup>, 2999 for **1**, 3134 for **2** and 2874 for **3** unique reflections. Data were collected at a temperature of 298(2) K to a maximum θ value of 29.25° for L<sup>2-naph</sup> and 26.00° for **1**, **2** and **3** and in a series of ω scans in 1° oscillations and integrated using the Stöe X-Area<sup>30</sup> software package. A numerical absorption correction was applied using the X-RED<sup>31</sup> and X-SHAPE<sup>31</sup> software's. The data were corrected for Lorentz and Polarizing effects. The structures were solved by direct methods<sup>32</sup> and subsequent different Fourier maps and then refined on F<sup>2</sup> by a full-matrix least-square procedure using anisotropic displacement parameters. All hydrogen atoms were added at ideal positions and constrained to ride on their parent atoms, with U<sub>iso</sub>(H) = 1.2U<sub>eq</sub>. All refinements were performed using the X-STEP32 crystallographic software package.<sup>33</sup> Structural illustrations have been drawn with MERCURY software.<sup>34</sup> Crystallographic data for L<sup>2-naph</sup> and complexes **1-3** are listed in Table 1. Selected bond distances and angles are summarized in Table 3.

**Computational Details.** DFT calculations were performed using the ORCA quantum chemistry suite.<sup>35</sup> The local density approximation (LDA) exchange correlation potential was used with the local density approximation of the correlation energy.<sup>36</sup> Gradient-corrected geometry optimizations<sup>37</sup> were performed by using the generalized gradient approximation.<sup>38</sup> Large atom basis sets TZP are used to ascribe all the atoms here. Scalar relativistic effects were taken into account by using the zeroth-order regular approximation (ZORA).<sup>39</sup>

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## Notes and references

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† Electronic Supplementary Information (ESI) available: X-ray crystallographic files in CIF format for structural determination of L (CCDC No. 956584), **1**, (CCDC No. 956581), **2**, (CCDC No. 956582) and **3**, (CCDC No. 956583). This material is free of charge via Internet. See DOI: 10.1039/b000000x/

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