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Synthesis, spectral characterization and X-ray crystal structures of mercury(II)-azoimine compounds

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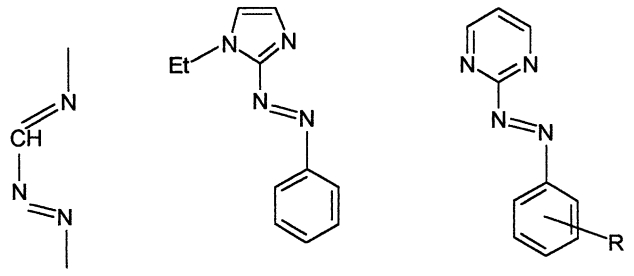
Abstract

1-Ethyl-2-(phenylazo)imidazole (PaiEt, **2**) and 2-(arylazo)pyrimidines (Raapm) (R=H (**3a**), *p*-Me (**3b**), *p*-Cl (**3c**)) are used to synthesize mercury(II) compounds. The complexes are characterized by elemental analysis, IR, UV–Vis, ^{1}H NMR spectral data and single crystal X-ray structures of di[chloro-{1-ethyl-2-(phenylazo)imidazole}(μ-chloro)-mercury(II)] (**4**) and di[chloro-{2-(phenylazo)pyrimidine} (μ-chloro)-mercury(II)] (**5a**). The first complex is a centro-symmetric dimer with two highly asymmetric chloro-bridges which make the rhombohedral plane. The second complex forms an unsymmetric trapezohedral geometrical structure.

Keywords: Arylazoimidazole; Azopyrimidine; Hg(II) complexes; Crystal structures

1. Introduction

Major development in heterocyclic-N donor ligands has been started from transition metal complexes of 2,2′-bipyridine (bpy) and related ligands [1–7]. This has lead to modification of M-bpy systems by choice of substituent(s) and metal. Non-transition metal complexes are a developing field in the area of polypyridine ligands [8–15] and have been used as transition metal supplements. Ligands may be modified substituting pyridine by other heterocycle(s), incorporating steric and electronic factors in the heterocyclic backbone appending an extra donor center [6] etc. One group of conjugated N-heterocycles is constructed by combining with an arylazo (Ar–N$^+$≡N) molecular unit. They are known as arylazoheterocycles [16]. These are π-acidic molecules and the active function is the azoimine group (–N=N–C=N–) (**1**) [16–20]. The π-acidity is dependent on the nature of the heterocycle, number of hetero-atoms, heterocyclic ring size and substituent(s) on the aromatic unit [6]. They have been used successfully to stabilize low valent metal redox states [17] and exhibit versatile reactivity to the organic part of the ligands [21–23].



1 PaiEt (**2**) Raapm (**3**)

The chemistry of non-transition metals of arylazoheterocycles has been started from the synthesis and spectral characterization of mercury(II) complexes of 2-(arylazo)pyridines [24,25]. We have been able to isolate organomercurials of 2-(arylazo)pyridines and the site of mercuration [26] has been established by charge density calculation. In an earlier report [27] of chloromercuri complexes of 1-alkyl-2-(arylazo)imidazole we have established the structure of the complexes by solution ^{1}H NMR spectral data and they have been

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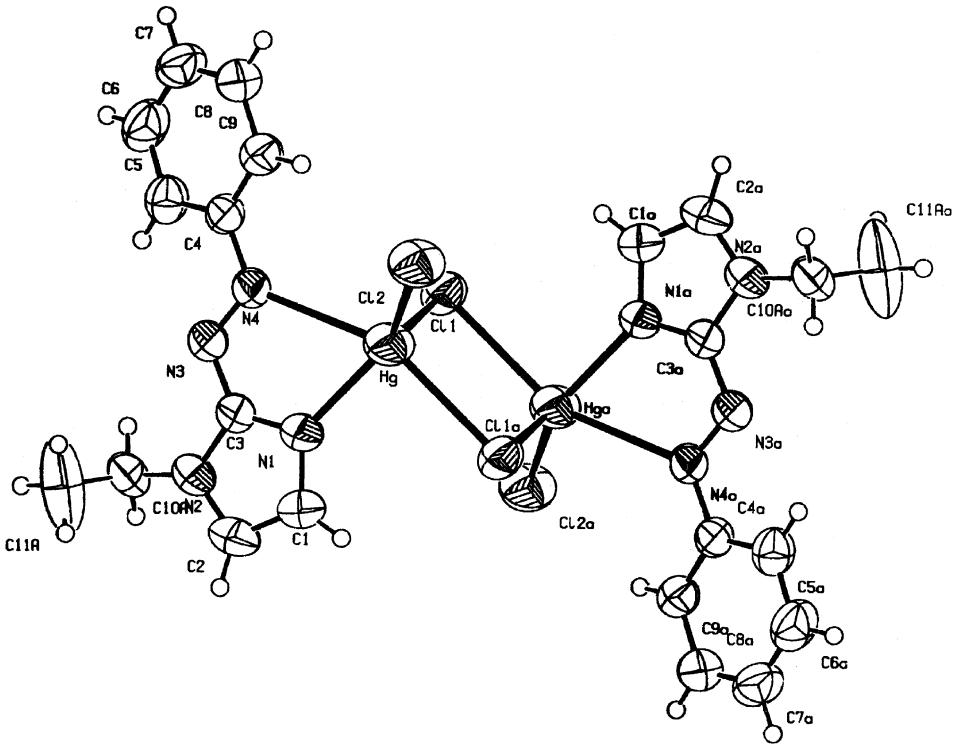

Fig. 1. X-ray crystal structure of **4**.

defined as mononuclear complexes, $Hg(RaaiR')Cl_2$. We have now been able to crystallize mercury(II) complexes of 1-ethyl-2-(phenylazo)imidazole and the X-ray structure shows a chloro bridged dinuclear system (Fig. 1). 2-(Arylazo)pyrimidine (Raapm, **3**) is a new class of arylazoheterocycle [28,29] and mercury(II) complexes are also described in this article. The single crystal X-ray structure of one of the complexes 2-(phenylazo)pyrimidine-chloro mercuri shows a chloro-bridged dimeric type (Fig. 2). The structures and spectral properties are described hereunder.

2. Experimental

2.1. Materials

2-Aminopyrimidine and imidazole were purchased from Aldrich. $HgCl_2$ was obtained from Loba Chemicals, Bombay, India. All other chemicals and solvents were reagent grade and used as received. 2-(Arylazo)pyrimidine (Raapm) [28] and 1-ethyl-2-(arylazo)imidazole (PaiEt) [16] were prepared by reported procedure.

2.2. Physical measurements

Microanalytical (C, H, N) data were obtained from a Perkin–Elmer 2400 CHNS/O elemental analyzer. Spectroscopic data were obtained using the following instruments: UV–Vis, JASCO UV/Vis/NIR model V-570; IR (KBr disk, 4000–200 cm^{-1}), JASCO FT-IR model 420 spectrophotometer, and ^1H NMR, Bruker 300 MHz FT-NMR spectrometer.

2.3. Synthesis of $[Hg(PaiEt)Cl_2]_2$ (**4**)

1-Ethyl 2-(phenylazo)imidazole (0.02 g, 0.1 mmol) in MeOH (10 ml) was added dropwise to a stirred methanolic solution (10 ml) of $HgCl_2$ (0.0271 g, 0.1 mmol) at room temperature. The brownish–orange solution was filtered and left undisturbed for 2 weeks. The bright brownish-orange crystals were obtained by the slow evaporation process. The crystals were collected by filtration, washed with cold water–methanol (1:1, v/v) and dried over $CaCl_2$ in vacuo. The yield was 0.033 g (70%). Detailed analyses and spectral characterization are reported elsewhere [27].

2.4. Synthesis of $[Hg(Raapm)Cl_2]_2$ (**5a**)

$[Hg(Raapm)Cl_2]_2$ complexes were synthesized by the same procedure described above with the use of the respective 2-(arylazo)pyrimidine. The yield varied in the range 45–60%.

The microanalytical data of the complexes are: $[Hg(Haapm)Cl_2]_2$ (**5a**): *Anal*. Found: C, 26.31; H, 1.73; N, 12.27. Calc. for $C_{20}H_{16}N_8Cl_4Hg_2$: C, 26.35; H, 1.76; N, 12.29%. $[Hg(p\text{-}Meaapm)Cl_2]_2$ (**5b**): *Anal*. Found: C, 28.09; H, 2.10; N, 11.88. Calc. for: $C_{22}H_{20}N_8Cl_4Hg_2$: C,

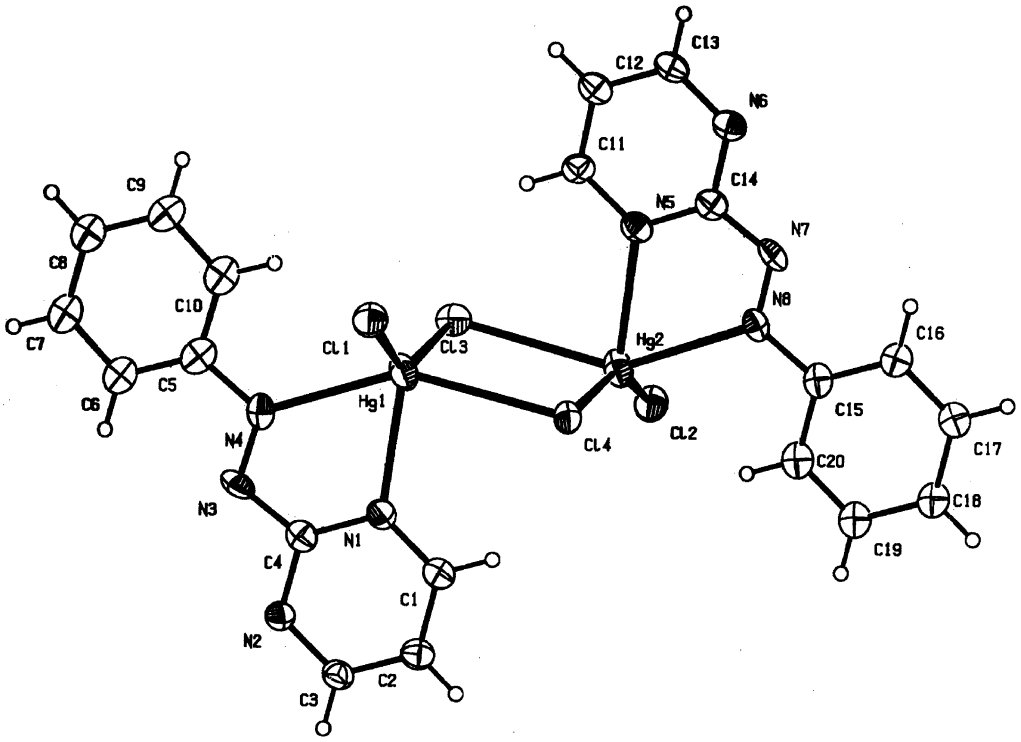

Fig. 2. X-ray crystal structure of **5a**.

28.12; H, 2.14; N, 11.92%. $[Hg(p\text{-Claapm})Cl_2]_2$ (**5c**): *Anal*. Found: C, 24.47; H, 1.41; N, 11.40. Calc. for: $C_{20}H_{14}N_8Cl_6Hg_2$: C, 24.50; H, 1.43; N, 11.43%.

2.5. X-Ray diffraction study

Suitable single crystals of complexes **4** and **5a** were mounted on a Siemens CCD diffractometer equipped with graphite monochromated Mo Kα ($\lambda = 0.711073$ Å) radiation. The crystallographic data, conditions for the intensity data collection and some features of the structure refinements of all the complexes are listed in Table 1. The unit cell parameters and crystal-orientation matrices were determined for two complexes by least squares refinements of all reflections. The intensity data were corrected for Lorentz and polarisation effects and an empirical absorption correction was also employed using the SAINT program [30]. Data were collected applying the condition $I > 2\sigma(I)$. All these structures were solved by direct methods and followed by successive Fourier and difference Fourier syntheses. Full matrix least squares refinements on F^2 were carried out using SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were constrained to ride on the respective carbon or nitrogen atoms with isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement of their parent atom in all cases. During refinements of complex **4**, the ethyl group was found to occupy two orientations (C10a, C11a and C10b, C11b) with 0.55/0.44 occupancy. Complex neutral atom scattering factors were used throughout for all cases. All calculations were carried out using SHELXS-97, [31], SHELXL-97 [32], PLATON-99 [33] and ORTEP-3 [34] programs.

3. Result and discussion

3.1. Synthesis

1-Ethyl-2-(phenylazo)imidazoles (PaiEt, **2**) and 2-(arylazo)pyrimidines (Raapm, **3**) are unsymmetric bidentate N,N′-donor ligands. On stirring a methanolic solution of $HgCl_2$ and the ligand **2/3** in a 1:1 mole proportions the brownish-orange title compounds (**4/5**) have been isolated. The molar conductivity measurements in MeCN exhibit non-conducting ($\Lambda_m \sim 15$–20 $\Omega^{-1}\,cm^{-1}$) behaviour of the complexes. Microanalytical data (C, H, N) support the general composition of the complexes and in both cases the structures have been established by single-crystal X-ray diffraction study.

3.2. Molecular structures

The crystals of dichloro-mercury(II)-1-ethyl-2-(phenylazo)imidazole (**4**) and dichloro-mercury(II)-2-(phenylazo)-pyrimidine (**5a**) were grown by slow evaporation of the reaction mixture in methanol at ambient condition for a week.

Table 1
Summarised crystallographic data for $[Hg(PaiEt)Cl_2]_2$ (**4**) and $[Hg(Haapm)Cl_2]_2$ (**5a**)

	$[Hg(PaiEt)Cl_2]_2$ (**4**)	$[Hg(Haapm)Cl_2]_2$ (**5a**)
Empirical formula	$C_{22}H_{24}Cl_4Hg_2N_8$	$C_{20}H_{16}Cl_4Hg_2N_8$
Formula weight	943.47	911.39
Temperature (K)	293(2)	297(2)
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/n$
Crystal size (mm)	$0.40 \times 0.30 \times 0.20$	$0.22 \times 0.16 \times 0.07$
Unit cell dimensions		
a (Å)	16.2363(12)	7.5548(9)
b (Å)	11.1765(8)	26.801(3)
c (Å)	15.9223(12)	12.8035(15)
β (°)	98.7030(10)	97.235(2)
V (Å)^3	2856.1(4)	2571.8(5)
Z	4	4
λ (Å)	0.71073	0.71073
μ (Mo Kα) (mm^{-1})	11.139	12.366
Θ range	2.2–28.3	1.5–28.3
$h\ k\ l$ range	$-21 \leqslant h \leqslant 20$	$-10 \leqslant h \leqslant 10$
	$-9 \leqslant k \leqslant 14$	$-35 \leqslant k \leqslant 23$
	$-20 \leqslant l \leqslant 18$	$-16 \leqslant l \leqslant 16$
D_{calc} (Mg m^{-3})	2.194	2.354
Refine parameters	181	305
Reflection number total	9011	16140
Unique reflections	3446	6056
R_1[a] $[I > 2\sigma(I)]$	0.0424	0.0476
wR_2[b]	0.1022	0.0719
Goodness of fit	1.050	1.08

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\ \Sigma w(F_o^2)^2]^{\frac{1}{2}}$, where; $w = 1/[\sigma^2(F_0)^2+(0.0346P)^2+11.5057P]$ for $[Hg(PaiEt)Cl_2]_2$ and $w = 1/[\sigma^2(F_0)^2+(0.0178P)^2+5.9766P]$ for $[Hg(Haapm)Cl_2]_2$ where $P = ({F_0}^2+2{F_c}^2)/3$ Goodness of fit is defined as $[\Sigma[w({F_o}^2-{F_c}^2)^2]/(n_o-n_v)]^{\frac{1}{2}}$, where n_0 and n_v denote the numbers of data and variables, respectively.

3.2.1. $[Hg(PaiEt)Cl_2]_2$ (**4**)

The crystal structure of the complex is shown in Fig. 1 and the bond parameters are listed in Table 2. The structure shows a chloro bridged dinuclear Hg_2Cl_2 unit. PaiEt acts as a N,N′-donor organic capping agent and a non-bridged-Cl atom lies in a semi-axial position. The complex exists as a centro-symmetric dimer with two highly asymmetric chloro bridges [Hg–Cl(1), 2.579(2) and Hg–Cl(1)*, 2.797(18) Å] and two terminal Cl with 2.344(2) Å distance. The atomic arrangements N(1), C(3), N(3), N(4), Hg constitute a chelate plane with a mean atomic deviation < 0.07 Å. The atoms N(1), N(4), Hg, Cl(1), Cl(1)* constitute a highly distorted square plane and Hg lies 0.81(8) Å above the mean plane. The Hg–Cl(2) bond lies in a semi-axial manner above the Hg–N(2)–Cl(2) plane in which the chelate plane is twisted so that Hg–N(4) bond moves towards Cl(2) and Hg–N(1) is away from the Hg–Cl(2) bond. This is reflected from the bond angle data; N(4)–Hg–Cl(2), 102.53(12)°; N(1)–Hg–Cl(2), 135.20(17)°. The dimeric bridging unit Hg_2Cl_2 describes a rhombohedral plane. The rhombohedral angles are Cl(1)–Hg–Cl(1)*, 87.28(6)° and Hg*–Cl(1)–Hg, 92.72(6)°. The chelate plane makes a dihedral angle of 73.2(8)° with the rhombohedral plane. The pendant phenyl ring in chelated PaiEt is no longer planar with the chelate plane and is inclined at an angle of 20.85(5)°. The N=N bond length is 1.252(7) Å which is close to the free ligand value [36,37]. The Hg–N(1) bond distance of 2.204(5) Å is shorter than Hg–N(4), 2.757(5) Å. The Hg–N(azo) [Hg–N(4)] bond length is less than that of the sum of the van der Waals radii [35] of Hg(II) and N(sp^2). This supports some sort of interaction of N(azo) with Hg(II). The bond length data of Hg–N(imidazole), [Hg–N(1)] accounts the preferential bonding of Hg(II) to imidazole-N [38,39]. This selectivity has been employed during purification of polluted water or separation of mercury from mixtures/ores [39,40]. In addition to van der Waals forces, the crystal structure is mainly stabilized by C–H–π interactions (Table 2).

Table 2
Selected bond distances (Å) and angles (°) for $[Hg(PaiEt)Cl_2]_2$ (**4**)

Bond distances		Bond angles	
Hg–Cl(1)	2.579(2)	Cl(1)–Hg–Cl(2)	112.22(7)
Hg–Cl(2)	2.344(2)	Cl(1)–Hg–Cl(1)*	87.28(6)
Hg–Cl(1)*	2.7971(12)	Cl(1)–Hg–N(1)	109.59(16)
Hg–N(1)	2.204(5)	Cl(1)–Hg–N(4)	85.25(11)
Hg–N(4)	2.757(5)	Cl(1)*–Hg–N(1)	88.78(15)
N3–N(4)	1.252(7)	Cl(1)*–Hg–N(4)	148.77(12)
Hg–Hg*	4.822(7)	Cl(1)*–Hg–Cl(2)	108.36(6)
		Cl(2)–Hg–N(1)	135.20(17)
		Cl(2)–Hg–N(4)	102.53(12)
		N(1)–Hg–N(4)	65.53(18)
		Hg–Cl(1)–Hg*	92.72(6)
C–H···π bonds			
C–H···π[a]	d(H···π) (Å)	d(C···π) (Å)	<(CHπ) (°)
C(10a)–H(10a)···Cg(1)	3.079	3.402	101.21
C(10a)–H(10b)···Cg(1)	3.059	3.402	102.50
C(11a)–H(11c)···Cg(1)	2.728	3.443	131.41
C(10b)–H(10c)···Cg(1)	2.714	3.553	145.11
C(11b)–H(11f)···Cg(1)	3.370	3.903	117.18

[a] Cg(1) denotes ring: C4–C5–C6–C7–C8–C9.

3.2.2. $[Hg(Haapm)Cl_2]_2$ (**5a**)

The molecular structure of the complex is shown in Fig. 2 and the bond parameters are listed in Table 3. Each discrete molecular unit consists of a dinuclear chloro bridged Hg_2Cl_2 fragment. Haapm acts as N,N′-donor end capping agent and a non-bridged-Cl atom lies in a semi-axial position. The bridged Hg_2Cl_2 constitutes a good plane with maximum deviation (< 0.01 Å) and is unsymmetric unlike the preceding example. This is

Table 3
Selected bond distances (Å) and angles (°) for $[Hg(Haapm)Cl_2]_2$ (**5a**) and some non-covalent bond parameters

Bond distances		Bond angles	
Hg(1)–Cl(1)	2.373(2)	Cl(1)–Hg(1)–N(1)	116.97(13)
Hg(1)–Cl(3)	2.419(2)	Cl(1)–Hg(1)–N(4)	93.33(12)
Hg(1)–Cl(4)	2.924(2)	Cl(1)–Hg(1)–Cl(3)	137.35(6)
Hg(2)–Cl(2)	2.349(2)	Cl(1)–Hg(1)–Cl(4)	97.86(5)
Hg(2)–Cl(3)	2.964(2)	N(1)–Hg(1)–N(4)	64.85(17)
Hg(2)–Cl(4)	2.386(2)	N(1)–Hg(1)–Cl(3)	105.67(13)
Hg(1)–N(1)	2.411(5)	N(1)–Hg(1)–Cl(4)	85.70(12)
Hg(1)–N(4)	2.548(5)	N(4)–Hg(1)–Cl(4)	150.41(12)
Hg(2)–N(5)	2.409(5)	N(4)–Hg(1)–Cl(3)	103.88(12)
Hg(2)–N(8)	2.615(5)	Cl(3)–Hg(1)–Cl(4)	86.09(5)
N(7)–N(8)	1.210(7)	Cl(3)–Hg(2)–Cl(4)	85.78(5)
N(3)–N(4)	1.265(7)	Cl(3)–Hg(2)–Cl(2)	95.2(6)
Hg(1)–Hg(2)	3.929(1)	Cl(3)–Hg(2)–N(5)	84.45(13)
		Cl(3)–Hg(2)–N(8)	147.83(12)
		Cl(4)–Hg(2)–Cl(2)	144.79(6)
		Cl(4)–Hg(2)–N(8)	99.88(12)
		Cl(4)–Hg(2)–N(5)	100.99(13)
		N(5)–Hg(2)–N(8)	63.38(17)
		N(5)–Hg(2)–Cl(2)	114.18(13)
		N(8)–Hg(2)–Cl(2)	97.08(12)
		Hg(1)–Cl(3)–Hg(2)	93.20(6)
		Hg(1)–Cl(4)–Hg(2)	94.92(5)

Hydrogen-bonds

D–H···A	d(D–H)(Å)	d(H···A) (Å)	d(D···A) (Å)	∠ (DHA) (°)
C(1)–H(1)···Cl(4)	0.93	2.805	3.502(6)	132.58
C(9)–H(9)···Cl(3)^{I}	0.93	2.783	3.567(8)	142.50
C(11)–H(11)···Cl(3)	0.93	2.720	3.447(6)	135.65

π···π Interactions

π···π Interactions Ring(*i*)→Ring(*j*)	Cg–Cg distance (Å)	Dihedral angle (°)	Perpendicular distance to *J* ring (Å)	Perpendicular distance to *J* ring (Å)
Cg(1)→Cg(3)^{ii}	3.596(4)	1.54	3.492	3.507
Cg(1)→Cg(3)^{iii}	3.834(4)	7.55	3.360	3.554
Cg(2)→Cg(2)^{iv}	4.112(3)	0.03	3.456	3.456
Cg(2)→Cg(4)^{i}	3.578(4)	3.53	3.537	3.502
Cg(4)→Cg(4)^{v}	3.718(4)	0.00	3.444	3.444

Cg(I) denotes rings: Cg(1)=N1–C1–C2–C3–N2–C4; Cg(2)=N5–C11–C12–C13–N6–C14; Cg(3)=C5–C6–C7–C8–C9–C10; Cg(4)=C15–C16–C17–C18–C19–C20. Symmetry code: (i)$1+x,y,z$; (ii) $-1+x,y,z$; (iii) $-1/2+x$, $3/2-y,1/2+z$; (iv) $1-x,1-y,-z$; (v) $-x,1-y,1-z$.

trapezohedral in geometry [41]. The atomic arrangements Hg(1), N(1), C(4), N(3), N(4) and Hg(2), N(5), C(14), N(7), N(8) constitute the chelate plane(s) with a maximum deviation <0.09 Å. The atoms Hg(1), N(1), N(4), Cl(3), Cl(4) and Hg(2), N(5), N(8), Cl(3), Cl(4) constitute two square planes (maximum deviation $<$ 0.06 Å) and their dihedral angle is 4.60(0)°. Hg(1) and Hg(2) lie 0.13 Å and—0.09 Å above their respective square planes. The bond angle values Cl(3)–Hg(1)–Cl(4), 86.09(5)° and Hg(1)–Cl(4)–Hg(2), 94.92(5)° provide support for the distorted geometry. The acute chelate bite angles extended by 2-(phenylazo)pyrimidine on coordination to Hg(II), N(1)–Hg(1)–N(4), 64.85(17)° and N(5)–Hg(2)–N(8), 63.38(17)° may be the reasons for geometrical distortion. The chelate plane(s) makes dihedral of av. 105° with the respective square plane. The ligand (Haapm) is almost planar (maximum deviation <0.08 Å). The pendent phenyl ring lies in a plane of the chelate ring (av. deviation, 1.9°).

Two Hg centers are inequivalent unlike $[Hg(PaiEt)Cl_2]_2$. The Hg(1)–Haapm chelate ring suffers higher distortion than the Hg(2)–Haapm unit. In Hg(1)–Haapm the N(3)–N(4), N(3)–C(4) and C(4)–N(1) bond distances are elongated by 0.055, 0.030 and 0.008 Å, respectively than that of the respective bond distances of the Hg(2)–Haapm unit. Although Hg(1)–N(1) and Hg(2)–N(5) have similar bond distances, Hg(1)–N(4) is shortened by 0.067 Å compared to that of Hg(2)–N(8). The free ligand N=N bond distance is not available with this particular molecules, but data from 2-(phenylazo)pyridine [37] and 1-methyl-2-(phenylazo)imidazole [36] show the N=N bond lengths 1.258(1) and 1.250(1) Å, respectively. The N=N bond distances

in this complex are shorter N(3)–N(4), 1.265(7) and N(7)–N(8), 1.210(7) Å compared to the reported values. The average N=N distance is also less than that of the preceding example, [Hg(HaaiEt)Cl_2]. The N=N distances are unusually different; the N(7)–N(8) bond length is shortened by $\sim$0.6 Å. It is unclear at present why this is so and it may be due to distortion in the Hg_2Cl_2 bridging geometry. This perturbation is also propagated to the Hg–N(azo) bond distance value; Hg(2)–N(8), 2.615(5) Å is greater than Hg(1)–N(4), 2.548(5) Å. In the bridged trapezium Hg_2Cl_2 unit the Hg(1)–Cl(3) distance (2.419(2) Å) is longer than that of Hg(2)–Cl(4) (2.386(2)Å); Hg(1)–Cl(4) is 2.924(2) Å and Hg(2)–Cl(3) is 2.964(2) Å.

Hg(1)–Cl(1) and Hg(2)–Cl(2) are in semi-axial positions on their respective square planes. The chelate ring around Hg(1) is twisted in a manner so that Hg(2)–N(4) approaches closer to Cl(1) (N(4)–Hg(1)–Cl(1), 93.33(12)°) and Hg–N(1) is away from Cl(1) (N(1)–Hg(1)–Cl(1), 116.97(13)°). A similar situation is also observed around Hg(2) where Cl(2)–Hg2–N(8) is 97.08(12)° and Cl(2)–Hg2–N(5) is 114.18(13)°. The bond length data show that the Hg(2)–Cl(4) distance (2.386(2) Å) is less than that of Hg(1)–Cl(4) (2.924(2) Å). Thus the bridging Cl binds one Hg center more covalently than the second one. The axial Hg–Cl (Hg(1)–Cl(1), 2.373(2) Å; Hg(2)–Cl(2), 2.349(2) Å) is shorter than bridged Hg–Cl bonds.

The bond length data (Hg–N(pyrimidine), Hg–N(azo), N–N, C–N) reveal that the interaction of Hg(1) with Haapm is stronger than Hg(2). The Hg–N(azo) (Hg(1)–N(4), 2.548(5), Hg(2)–N(8), 2.615(5) Å) bond lengths are less than the sum of the van der Waals radii [35]. This supports the bonding interaction between Hg(II) and N(azo).

The comparison of the Hg–N(heterocycle) bond length between [Hg(PaiEt)Cl_2]$_2$ (**4**), Hg–N(imidazole), 2.204(13) Å and [Hg(Haapm)Cl_2]$_2$ (**5a**) Hg–N(pyrimidine), 2.452(6) Å exhibit overwhelming affinity of Hg(II) to N(imidazole). It is known that imidazole is less π-acidic than pyrimidine [6] and hence N(imidazole) is softer than N-(pyrimidine). Mercury(II) is a soft borderline acid. That is why Hg(II) binds strongly with imidazole-N [38].

Intermolecular hydrogen bonding generates a molecular stair in which the chelated Hg–[N=N–C=N–]fragment functions as a footboard and the perpendicular bridging unit Hg_2Cl_2 acts as a wall connector to the stairs (Fig. 3). Each dimer alternately generate polymer stairs. One of the two non-bridged Cl atoms in the bridging Hg_2Cl_4 unit makes a H-bonding contact with the *o*-H of a pendant phenyl ring of papm of a neighboring dimer. While opposite bridged Cl atoms in this dimer unit hydrogen bond with the *m*-H of a papm of a second neighboring dimer. The process continues to make the molecular stair. In addition to hydrogen bonds, the structure is stabilized by aromatic π–π stacking interactions (Table 3). The rings in adjacent dimers are almost parallel to each other, the dihedral angles between these planes being in the range of 0.0–3.5°. The perpendicular distance between these planes is in range 3.360(2)–3.537(2) Å. Hence, there is a series of essentially parallel units whose relative disposition is ideal for aromatic π–π stacking interactions, forming a 3D supramolecular continuum.

3.3. Spectral studies

The spectral characterization (IR, UV–Vis, ^{1}H NMR) of [Hg(RaaiR′)Cl_2]$_2$ (**4**) are reported elsewhere [27]. [Hg(Raapm)Cl_2]$_2$ (**5**) exhibits ν(C=N) and ν(N=N) at 1600–1625 and 1385–1390 cm^{-1}, respectively. The Hg–Cl stretchings appear at 325–330 and 300–305 cm^{-1}. These support two types of Hg–Cl bonds. This is also supported from the X-ray crystal structure study (vide infra).

The solution electronic spectra of these complexes were recorded in DMSO between 200 and 900 nm (Table 4). There are four bands in the UV–Vis region and three of them are high intensity ($\epsilon \sim 10^4$) bands at 255–260, 315–320 and 340–345 nm. On comparing with the free ligands spectra [27,29], we may conclude that they come from intramolecular charge transfer transitions. The fourth band appears at 435–445 nm and is

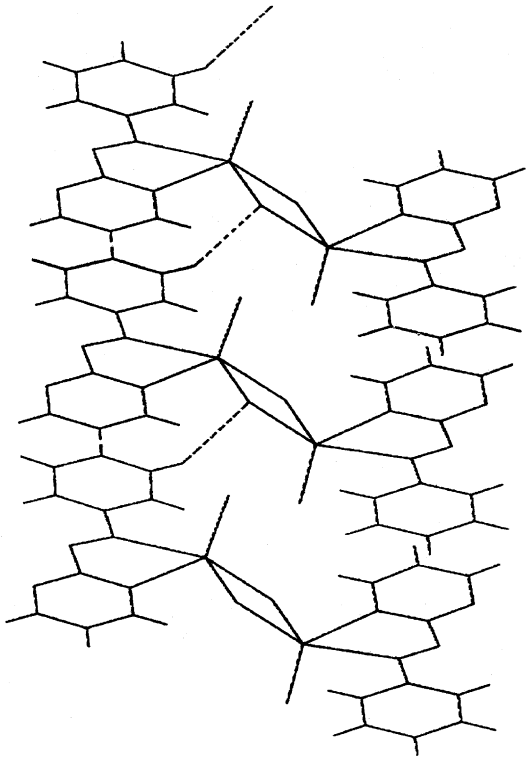

Fig. 3. H-bonding structure of **5a**.

Table 4
UV–Vis [a] and ^{1}H NMR[b] spectral data for $[Hg(Raapm)Cl_2]_2$ (**5**)

Compound	UV–Vis λ_{max}/nm (10^{-3} e/M^{-1} cm^{-1})	^{1}H NMR δ, ppm–(J, Hz)					
		4,6-H [c]	5-H	8,12-H	9,11-H	10-H	Me
(**5a**)	422 (975), 344 (12637)	9.03 (5.4)	7.68 [d]	7.9 9		7.68 [d]	7.68[d]
	316 (9680), 258 (11886)			(8.8)			
(**5b**)	440 (1545), 342 (41072)	9.01	7.65 [c]	7.90 [c]	7.47 [c]		2.44
	318 (44259), 230 (35181)	(6.3)	(7.2)	(8.2)	(8.2)		
(**5c**)	435 (569), 345 (9462)	9.07	7.73 [c]	8.07 [c]	7.85 [c]	–	–
	320 (7609), 240 (9778)	(6.5)	(7.5)	(8.5)	(8.5)	–	

[a] Solvent DMSO.
[b] Solvent DMSO-d_6.
[c] Doublet.
[d] Multiplet.

weak in intensity ($\epsilon \sim 10^3$). This may refer to Hg(II) → π*(azoimine) charge transfer transitions.

The ^{1}H NMR spectra of **5** are recorded in DMSO-d_6 and the signals are assigned (Table 4) unambiguously by spin–spin interaction and the effect of substitution therein. The charge density calculation by the MNDO method supports this observation [26]. It shows that C(5) assumes the highest electronic charge density (~ -0.18e) and it is much higher than the aryl-C centers (C(8) to C(12): 0.115 to −0.086e). The protons of the pyrimidine ring show some unusual perturbation on coordination to Hg(II): the 4-H and 6-H suffer downfield shifting by >0.8 ppm compared to free ligand data while 5-H is upfield shifted by ~ 0.4 ppm. The aryl protons (8-H–12-H) suffer downfield shifting by >0.2 ppm and is supposed to be due to coordination of (Ar–)N=N to Hg(II). Aryl protons (8-H–12-H) are perturbed by the substituents in general and 9, 11-H are affected significantly in particular because of closer proximity to R. The proton movement is in accordance with the electronic nature of the substituent [42].

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic data center, CCDC No. 194 688 for $[Hg(PaiEt)Cl_2]_2$ and CCDC No. 194 789 for $[Hg(Haapm)Cl_2]_2$. Copies of this information may be obtained free of charge from the Director, CCDC,12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.com.ac.uk or http://www.ccdc.cam.ac.uk).

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References

[1] Y. Xiong, L.N. Ji, Coord. Chem. Rev. 711 (1999) 185.
[2] K.E. Erkkila, D.T. Odom, J.K. Barton, Chem. Rev. 99 (1999) 2777.
[3] K. Kalyansundram, Coord. Chem. Rev. 46 (1982) 159.
[4] J.M. Lehn, Supramolecular Chemistry, VCH, Weinheim, 1995.
[5] C. Kaes, A. Katz, M.W. Hosseini, Chem. Rev. 100 (2000) 3553.
[6] E.C. Constable, Coord. Chem. Rev. 93 (1989) 205.
[7] H. Chem, J.A. Parkinson, S. Parsons, R.A. Coxall, R.O. Gould, P.J. Sadler, J. Am. Chem. Soc. 124 (2002) 3064.
[8] R.C. Finn, J. Zubieta, J. Chem. Soc., Dalton Trans. (2002) 856.
[9] C. Whitchurch, A.R.J. Andrews, Anal. Chim. Acta 45 (2002) 454.
[10] A. Manohar, K. Ramalingam, Main Group Met. Chem. 24 (2001) 789.
[11] A. Wojciechowska, Z. Staszaka, W. Bronowska, A. Pietraszko, M. Cieslak-Golonka, Polyhedron 20 (2001) 2063.
[12] A. Deak, L. Radics, A. Kalman, L. Parokanyi, I. Haidue, Eur. J. Inorg. Chem. (2001) 2849.
[13] Y.J. Shi, Y. Xu, Y. Zhang, B. Hueng, D.R. Zhu, C.M. Jin, H.G. Zhu, Z. Yu, X.T. Chen, X.Z. You, Chem. Lett. (2001) 678.
[14] M.A. Harvey, S. Baggio, M.T. Garland, R. Baggio, Aust. J. Chem. 54 (2001) 711.
[15] J.H. Luo, M.C. Hong, R. Cao, Y.C. Liang, Y.J. Zhao, R.H. Wang, T.B. Weng, Polyhedron 21 (2002) 893.
[16] G.K. Routh, S. Pal, D. Das, C. Sinha, A.M.Z. Slawin, J.D. Woollins, Polyhedron 20 (2001) 363.
[17] P. Byabartta, J. Dinda, P.K. Santra, C. Sinha, K. Panneerselvam, F.-L. Liao, T.H. Lu, J. Chem. Soc., Dalton Trans. (2001) 2825.
[18] P. Byabartta, P.K. Santra, T.K. Misra, C. Sinha, C.H.L. Kennard, Polyhedron 20 (2001) 905.
[19] P.K. Santra, T.K. Misra, D. Das, C. Sinha, A.M.Z. Slawin, J.D. Woollins, Polyhedron 18 (1999) 2869.
[20] P.K. Santra, U.S. Ray, S. Pal, C. Sinha, Inorg. Chem. Commun. 4 (2001) 269.
[21] J. Dinda, P.K. Santra, C. Sinha, L.R. Falvello, J. Organomet. Chem. 629 (2001) 28.
[22] P.K. Santra, P. Byabartta, S. Chattopadhyay, L.R. Falvello, C. Sinha, Eur. J. Inorg. Chem. (2002) 1124.
[23] A.K. Ghosh, P. Majumdar, L.R. Falvello, G. Mostafa, S. Goswami, Organometallics 18 (1999) 5086.
[24] P.V. Rolling, D.D. Kirt, J.L. Dill, S. Hall, C. Houston, J. Organomet. Chem. 116 (1976) 39.
[25] T.S. Basubaul, D. Dey, Synth. React. Inorg. Met. Org. Chem. 20 (1990) 541.
[26] K. Bag, N.K. De, B.R. De, C. Sinha, Proc. Indian Acad. Sci. (Chem. Sci.) 109 (1997) 159.

[27] K. Bag, T.K. Misra, C. Sinha, J. Indian Chem. Soc. 75 (1998) 421.
[28] J.K. Nag, P.K. Santra, C. Sinha, F.-L. Liao, T.H. Lu, Polyhedron 20 (2001) 2253.
[29] P.K. Santra, Ph.D. Thesis, Burdwan University (2001).
[30] Bruker, SMART and SAINT, Bruker AXS Inc, Madison, WI, 1998, p. 1.
[31] G.M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structure, University of Gottingen, Germany, 1997.
[32] G.M. Sheldrick, SHELXL-97, Program for the Solution of Crystal Structure, University of Gottingen, Germany, 1997.
[33] A.L. Spek, PLATON, Molecular Geometry Program, University of Utrecht, The Netherlands, 1999.
[34] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
[35] A.G. Orpen, L. Brammar, F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, J. Chem. Soc., Dalton Trans. 1 (1989) SI.
[36] D. Das, Ph.D. Thesis, Burdwan University (1998).
[37] A. Saha, C. Das, S. Goswami, S.-M. Peng, Indian J. Chem. 40A (2001) 198.
[38] C.J. Matthews, W. Clegg, S.L. Heath, N.C. Martin, M.N.S. Hill, J.C. Lockhart, Inorg. Chem. 37 (1998) 199.
[39] D. Das, A.K. Das, C. Sinha, Talanta 48 (1999) 1013.
[40] P. Chattopadhyay, C. Sinha, D.K. Pal, Fresenius J. Anal. Chem. 357 (1997) 368.
[41] A. Alvarez-Larena, W. Clegg, L. Curcurull-Sanchez, F. Gonzalez-Duarte, R. March, J.F. Piniella, J. Pons, X. Solans, Inorg. Chim. Acta 266 (1997) 81.
[42] P. Chattopadhyay, C. Sinha, Polyhedron 13 (1994) 2689.