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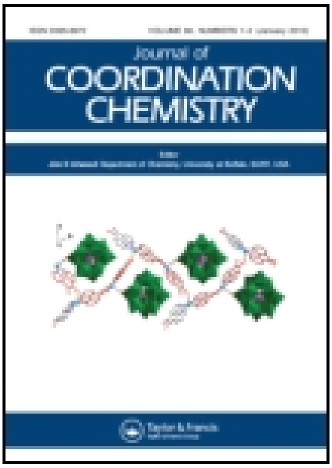

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Mercury(II) complexes containing new ortho-functionalized asymmetric triazene ligands: synthesis, crystal structures, and solution studies

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Mercury(II) complexes containing new *ortho*-functionalized asymmetric triazene ligands: synthesis, crystal structures, and solution studies

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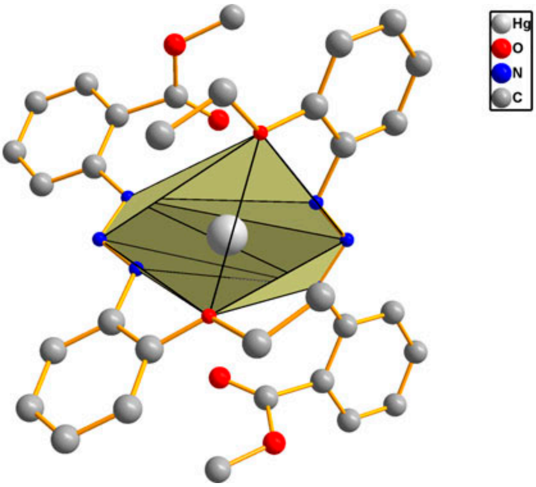

Synthesis of two new asymmetric ligands: 1-(2-ethoxyphenyl)-3-(2-methoxycarbonylphenyl)triazene (H**L**) (**1**) and 1-(2-methoxyphenyl)-3-(2-methoxycarbonylphenyl)triazene (H**L′**) (**2**) are reported. The prepared triazenes are functionalized by ethoxy and methoxy groups in the *ortho* positions, respectively. The related monomeric complexes, [Hg$\mathbf{L}_2$] (**3**) and [Hg$\mathbf{L'}_2$] (**4**), were prepared by the reacting of the corresponding ligands with $Hg(NO_3)_2$ salt in methanol as solvent. All compounds were characterized by CHN analysis, FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. According to the crystal structures of **1** and **2**, the N–N bond distances indicate the presence of alternating single and double bonds, and hence the –N=N–NH– moiety. On coordination, each triazene was deprotonated and as a result, a resonance structure is formed between nitrogens which let them to be a tridentate ligand. In the crystal structure of **3**, [Hg$\mathbf{L}_2$], the central Hg(II) is surrounded by two N atoms from interlocked **L** forming linear geometry, in which the other four Hg–N and Hg–O bonds are longer and can only be regarded as weak secondary bonds. An interesting feature of **3** is also the

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presence of π···π [centroid–centroid distance of 3.744(3) Å] and C–H···π interactions. The results of solution studies for the formation of **3** in methanol support its solid-state stoichiometry.

Keywords: Mercury(II); Asymmetric triazene; X-ray; Crystal structure; C–H···π Interaction

1. Introduction

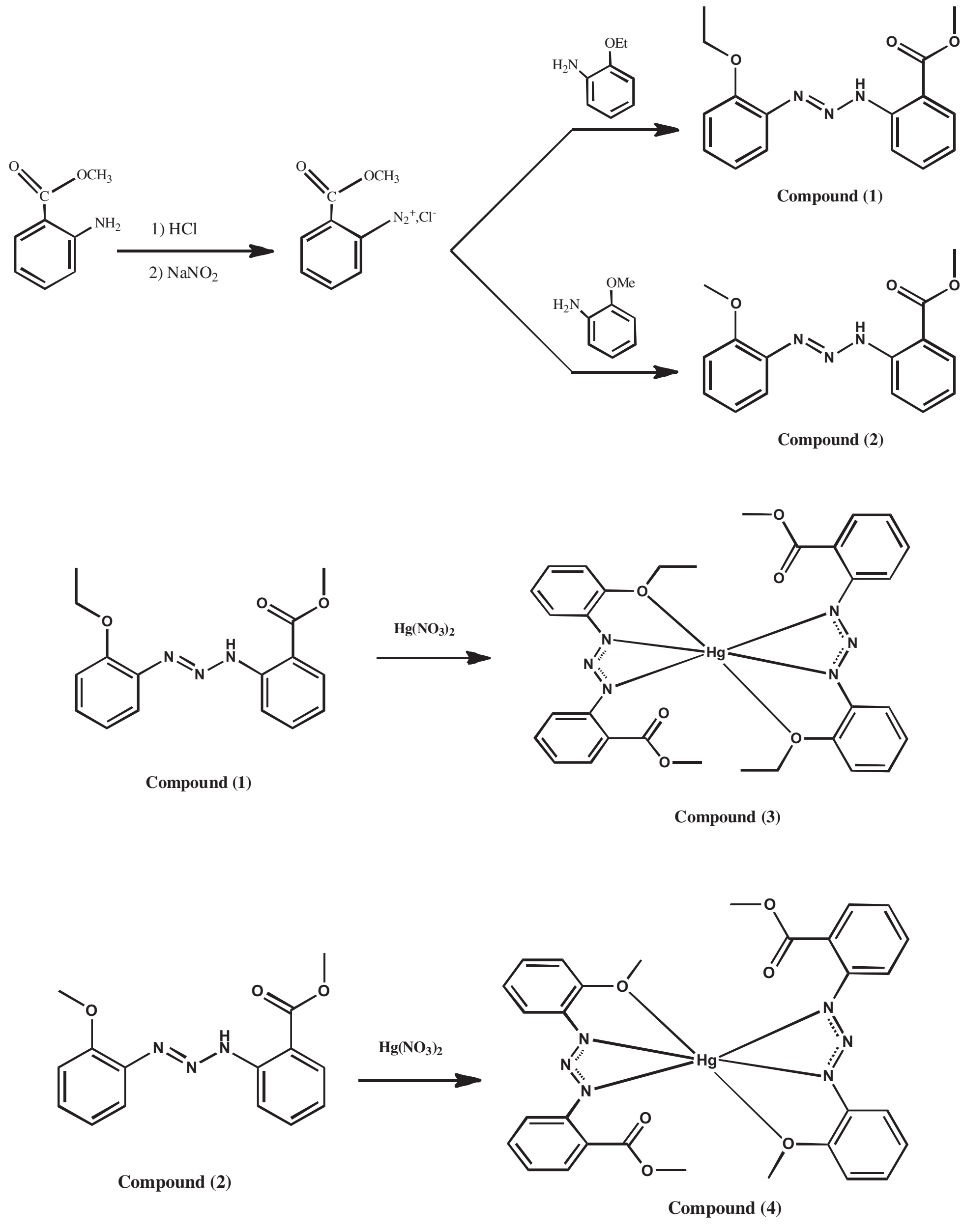
Aryl triazenes have been studied for their interesting structural, anticancer, and reactivity properties [1–5]. Transition metal complexes containing 1,3-diaryltriazene ligands have increased due to the potential reactivity of these ligands [6, 7]. As ligands, the (–NH–N=N–) moieties can show different types of coordination, monodentate, (N1, N3) chelating towards one metal or (N1, N3) bridging over two metals for a variety of transition metal complexes [8–10]. In these compounds, secondary bonds or non-covalent interactions such as hydrogen bonds and metal π-aryl interactions play important roles in the structural stability [11–18]. Several bis(diaryl) triazenides with symmetric and asymmetric substituents and their related metal complexes have been reported which have a remarkable ability to self-assemble through metal-η-arene π-interactions [19]. Our group has been involved in the complexation of transition metal ions with triazene compounds, starting from different bis (diaryl) symmetric and asymmetric-substituted triazenides. Synthesis of 1,3-bis(2-methoxyphenyl)]triaz-1-ene [20], [1,3-bis(2-ethoxyphenyl)]triaz-1-ene [21], [1,3-bis(2-cyanophenyl)] triaz-1-ene [22], 1-(3,5-dichlorophenyl)-3-(2-methoxyphenyl)triaz-1-ene [23], and 3-(2-ethoxyphenyl)-1-(3-nitrophenyl)triaz-1-ene [24] have been reported as ligands. We have published Hg(II) complexes with [1,3-bis(2-methoxyphenyl)]triazene by using $HgCl_2$ [25], $HgBr_2$ [26], $Hg(CH_3COO)_2$, and $Hg(SCN)_2$ as starting materials [27]. Recently, a Hg(II) complex with [1,3-bis(2-ethoxyphenyl)]triazene has been reported in which $HgCl_2$ was used as starting salt [28]. From recent structural studies, it was argued that counter anions play an important role in determining the solid-state lattices of these compounds. More recently, Hg(II) complexes with several asymmetric triazenes have been prepared and their crystal structures have been reported [29–31].

To investigate the effect of the substituents on the coordination behavior of the triazene, we have introduced *ortho*-, *meta*-, and *para*-bis(phenyltriazene) benzenes (and substituted derivatives) with two triazene groups as ligands to investigate the stoichiometry of the resulting Hg(II) complexes. In continuation with previous work, we herein report the synthesis, characterization, and molecular structure of new asymmetric 1-(2-ethoxyphenyl)-3-(2-methoxycarbonylphenyl)triazene, H**L** (**1**), 1-(2-methoxyphenyl)-3-(2-methoxycarbonylphenyl)-triazene, H**L′** (**2**) ligands and their related Hg(II) complexes $[Hg(C_{16}H_{16}N_3O_3)_2]$, $[HgL_2]$, (**3**), and $[Hg(C_{15}H_{14}N_3O_3)_2]$, $[HgL'_2]$, (**4**) in methanol. Scheme 1 presents the starting materials and the reaction procedure.

2. Experimental

2.1. *Materials and physical techniques*

All chemicals were analytical grade and used without purification. FT-IR spectra from 4000 to 400 cm^{-1} were recorded using a Perkin-Elmer RXI spectrometer using KBr disks.



Scheme 1. General procedure for the preparation of **1**–**4**.

Elemental analyses were carried out using a Perkin-Elmer 2400(II) CHNS/O analyzer. Melting points were measured on a Barnstead Electrothermal 9200 apparatus.

2.1.1. Synthesis of $C_{16}H_{17}N_3O_3$, HL, (1).

The asymmetric ligand, 1-(2-ethoxyphenyl)-3-(2-methoxycarbonylphenyl)triazene, was prepared as below: 10 g of ice and 150 mL of water were poured in a 100 mL flask and then the flask was cooled to 273 K in an ice bath. Then, 3.2 mL (0.023 M) methyl 2-aminobenzoate and 10 mL (0.12 M) of hydrochloric acid (37%) were added to this flask. After that, a solution containing $NaNO_2$ (1.72 g, 0.025 M) in 10 mL of water was added slowly to the resultant solution for 15 min. The pH of the solution was then adjusted at 6 by adding a solution containing 1 g of sodium acetate in 10 ml of water. After mixing for 15 min, the obtained solution was added to a solution of 3 mL (0.023 M) of 2-ethoxyaniline, 5 mL of methanol, and 4 mL of water. After mixing for 24 h, the yellow precipitate was filtered off and dried. After recrystallization from hexane, suitable crystals of the compound were obtained by slow evaporation of the solvent. *Properties*: m.p.: 91–93 °C. IR (KBr): $\nu(cm^{-1})$: 3242(s), 2983(s), 1686(s), 1586(s), 1508(s), 1433(s), 1328(s), 1311(w), 1280(s), 1246(s), 1150(s), 1041(s), 961(w), 918(w), 752(s), 745(s), 699 (s). ^1H NMR (300 MHz, d^6-DMSO): $\delta = 1.36$ (3H, Ar-OCH_2CH_3), 3.87 (3H, Ar-$COOCH_3$), 4.10 (2H, Ar-OCH_2CH_3), 6.94–7.94 (8H, aromatic rings), 12.28 (1H, NH). ^{13}C NMR (d^6-DMSO): $\delta = 14.7$, 52.5, 64.0, 112–153.1 and 167.4 ppm. Elemental Anal. Calcd for $C_{16}H_{17}N_3O_3$: C, 64.21; H, 5.68; N, 14.04. Found: C, 64.10; H, 5.66; N, 14.08%.

2.1.2. Synthesis of $C_{15}H_{15}N_3O_3$, HL′, (2). The asymmetric ligand, 1-(2-methoxyphenyl)-3-(2-methoxycarbonylphenyl)triazene, was prepared as the method described above with 2-methoxyaniline used instead of 2-ethoxyaniline. After recrystallization from hexane, suitable crystals for X-ray were obtained by slow evaporation of the solvent within two weeks. *Properties*: m.p.: 83–85 °C. IR (KBr): $\nu(cm^{-1})$: 3429(br), 3379(s), 2951(w), 1687(s), 1604(s), 1585 (s), 1507(s), 1431(s), 1330(w), 1317(w), 1280(s), 1261(s), 1113(s), 1084(s), 1030(s), 962(w), 753(s), 743(s), 696(s). ^1H NMR (300 MHz, d^6-DMSO): $\delta = 1.35$ (3H, Ar-OCH_3), 3.85 (3H, Ar-$COOCH_3$), 6.95–7.95 (8H, aromatic rings), 12.3 (1H, NH). ^{13}C NMR (d^6-DMSO): $\delta = 14.5$, 55.6, 112–153.9 and 167.4 ppm. Elemental Anal. Calcd for $C_{15}H_{15}N_3O_3$: C, 63.15; H, 5.30; N, 14.73. Found: C, 63.09; H, 5.18; N, 14.7%.

2.1.3. Synthesis of $C_{32}H_{32}HgN_6O_6$, [HgL_2], (3). This complex was prepared by mixing 0.5 g (2 mM) of 1-(2-ethoxyphenyl)-3-(2-methoxycarbonylphenyl)triazene (**1**) in 25 mL of anhydrous methanol with 0.32 g (1 mM) of mercury(II) nitrate in 15 mL of anhydrous methanol. After mixing for an hour, a precipitate was obtained. The resultant precipitate was dissolved in THF and crystals suitable for X-ray analysis of **3** were obtained by the slow evaporation of the solvent in two weeks. *Properties*: air stable, yellow crystalline material. $C_{32}H_{32}HgN_6O_6$; m.p.: 143–145 °C. IR (KBr): $\nu(cm^{-1})$: 3433(br), 3055 (w), 2887(w), 1731(s), 1587(s), 1492(s), 1480(s), 1377(br), 1289(s), 1077 (s), 1034 (s), 920 (s), 762 (s), 741(s). ^1H NMR (300 MHz, d_6-DMSO): $\delta = 1.14$ (6H, Ar-OCH_2CH_3), 3.33 (6H, Ar-$COOCH_3$), 4.07 (4H, Ar-OCH_2CH_3), 7.01–7.93 (16H, aromatic rings). ^{13}C NMR (d_6-DMSO): $\delta = 14.0$, 51.5, 64.5, 112.7–146.9, 168.1 ppm. Elemental Anal. Calcd for $C_{32}H_{32}HgN_6O_6$: C, 48.2; H, 4.02; N, 10.54. Found: C, 48.0; H, 3.94; N, 10.3%.

2.1.4. Synthesis of $C_{30}H_{28}HgN_6O_6$, [HgL'_2], (4). The reaction of 0.533 g (2 mM) 1-(2-methoxyphenyl)-3-(2-methoxycarbonylphenyl)triazene (**2**) with 0.32 g (1 mM) of mercury (II) nitrate in 20 mL of anhydrous methanol resulted in the formation of a yellow precipitate. After filtration, the resultant precipitate was washed with methanol and dried. Our attempt to get suitable crystals was not successful. *Properties*: m.p.: 188–190 °C. IR (KBr): $\nu(cm^{-1})$: 3462(br), 3073(w), 2954(w), 1665(s), 1599(s), 1496(s), 1436(s), 1383(br), 1275 (s), 1087(s), 1032(w), 766(w), 702(w). ^{13}C NMR (d$_6$-DMSO): $\delta = 51.4$, 114.8–134.0 ppm. Elemental Anal. Calcd for $C_{30}H_{28}HgN_6O_6$: C, 46.85; H, 3.67; N, 10.93. Found: C, 46.07; H, 3.75; N, 10.5%.

2.1.5. Crystal structure determination and refinement. The X-ray diffraction measurements were made on a STOE IPDS-II diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation. Yellow plates of **1**, yellow needle-like crystals of **2**, and yellow block-shape crystals of **3** were chosen using a polarizing microscope and mounted on a glass fiber which was used for data collection. Cell constants and orientation matrices for data collection were obtained by least-squares refinement of diffraction data from 2206 for **1**, 2501 for **2** and 4157 unique reflections for **3**. Data were collected to a maximum 2θ value of 58.38° for **1**, 50° for **2** and to a maximum 2θ value of 58.34° for **3** in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA [32] software package. A numerical absorption correction was applied using X-RED [33] and X-SHAPE [34] software. The data were corrected for Lorentz and polarizing effects. The structures were solved by direct methods [35] and subsequent difference Fourier maps, and then refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [36]. The atomic factors were taken from the International Tables for X-ray Crystallography [37]. All refinements were performed using the X-STEP32 crystallographic software package [38]. Crystal data, experimental details, and refinement results are given in table 1.

Table 1. Crystallographic and structure refinement data for **1**–**3**.[a]

Compound	**1**	**2**	**3**
Formula	$C_{16}H_{17}N_3O_3$	$C_{15}H_{15}N_3O_3$	$C_{32}H_{32}HgN_6O_6$
Formula weight	299.33	285.30	797.23
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	$Pca2_1$	*Pbca*	*C2/c*
a (Å)	13.743(3)	15.626(3)	22.032(4)
b (Å)	14.625(3)	8.1866(16)	8.7283(17)
c (Å)	7.5821(15)	22.247(4)	18.226(4)
β (°)			117.72(3)
Volume (Å^3)	1523.9(5)	2845.9(9)	3102.6(14)
D (g cm^{-3})	1.305	1.332	1.707
F (0 0 0)	632	1200	1576
Temperature (K)	120(2)	298(2)	120(2)
Crystal size (mm)	0.5 × 0.45 × 0.2	0.5 × 0.1 × 0.08	0.22 × 0.20 × 0.15
θ Range for data collection (°)	2.79–29.19	1.83–25.00	2.41–29.17
Index ranges	$-18 \le h \le 15$	$-16 \le h \le 18$	$-30 \le h \le 29$
	$-19 \le k \le 20$	$-9 \le k \le 9$	$-10 \le k \le 11$
	$-10 \le l \le 8$	$-26 \le l \le 26$	$-24 \le l \le 24$
Z	4	8	4
Wavelength (Å)	0.71073	0.71073	0.71073
Absorption coefficient (mm^{-1})	0.092	0.095	5.015
Data collected	10862	21449	11668
Unique data (R_{int})	2206, (0.0927)	2501, (0.1510)	4157, (0.0625)
Parameters/restraints	204/1	196/0	206/0
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0800$	$R_1 = 0.0677$	$R_1 = 0.0345$
	$wR_2 = 0.1650$	$wR_2 = 0.1325$	$wR_2 = 0.0733$
R indices (all data)	$R_1 = 0.1123$	$R_1 = 0.1125$	$R_1 = 0.0453$
	$wR_2 = 0.1791$	$wR_2 = 0.1291$	$wR_2 = 0.0761$
Goodness-of-fit on F^2 (*S*)	1.132	1.075	1.010
Largest diff. peak and hole (e Å^{-3})	0.311 and −0.186	0.119 and −0.195	2.305 and −2.032

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$.

3. Results and discussion

In the FT-IR spectra of **1**, the band at 3242 cm^{-1} is from N–H bond stretch. The N–N and N=N bond-stretching modes are at 1150 and 1433 cm^{-1}, respectively. The peak at 1686 cm^{-1} is assigned to C=O stretch. In ^1H NMR spectra, the peak at 12.28 ppm can be assigned to the N–H group. Hydrogens of $–CH_3$ and $–CH_2–$ groups from ethoxy appear at 1.36 and 3.87 ppm, respectively. Also, hydrogens of the $–CH_3$ group attached to $–COOCH_3$ are at 4.10 ppm. In the ^{13}C NMR spectrum, the carbons of $–CH_3$ and $–CH_2$ show signals at 14.7 and 55.6 ppm, respectively. Also, carbons of $–CH_3$ attached to $–COOCH_3$ appear at 64.0 ppm. The carbon of the carboxylic group has a distinct peak at 167.4 ppm. The carbons of aromatic rings show signals ranging from 112 to 153.1 ppm, indicating the presence of 12 different carbons.

The crystal structure of **1** was investigated by single crystal X-ray analysis. The molecular structure is represented in figure 1, with thermal ellipsoids drawn at 30% probability level. The above compound crystallizes in space group $Pca2_1$ with four molecules per unit cell. The unit-cell parameters are: $a = 13.743(3)$ Å, $b = 14.625(3)$ Å, and $c = 7.5821(15)$ Å. The final R value was 0.080 based on 2206 reflections (see table 1).

The molecule adopts *trans* configuration with respect to the (–N=N–) bond. Selected bond lengths and angles are listed in table 2. The dihedral angle between two aromatic rings is 9.8(3)°. The C8–N1–N2–N3 and C9–N3–N2–N1 torsion angles are 176.3(4)° and 177.5(4)°, respectively, and indicate that N1N2N3 is coplanar with the aromatic rings. The N1–N2 and N2=N3 bond lengths are 1.334(5) and 1.264(5) Å, respectively, which proves the presence of distinct single and double bonds between nitrogens and hence the (–NH–N=N–) moiety. These values are in agreement with the reported data for N–N and N=N bond distances [26]. For example, in 1,3-bis(2-cyanophenyl)triazene, the N–N and N=N

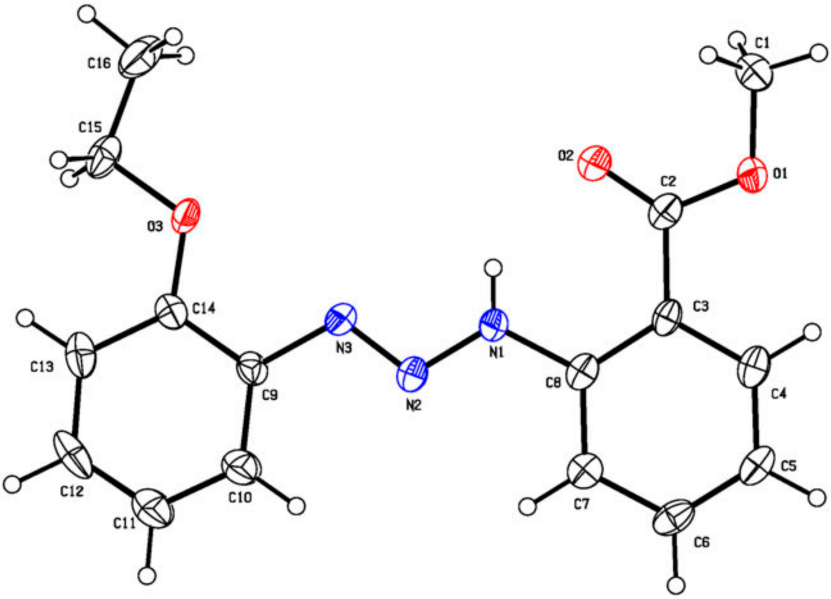


Figure 1. The labeled diagram of the asymmetric unit of **1**. Thermal ellipsoids are at 30% probability level.

Table 2. Selected bond distances (Å) and angles (°) for **1**–**3**.[a]

1			
O3–C14	1.361(5)	N1–N2	1.334(5)
O3–C15	1.435(5)	N2–N3	1.264(5)
N1–N2–N3	111.6(3)	O1–C2–O2	123.4(4)
C8–N1–N2–N3	176.3(4)	C9–N3–N2–N1	177.5(4)
2			
O2–C14	1.202(3)	N1–N2	1.259(3)
O3–C14	1.332(3)	N2–N3	1.427(3)
N1–N2–N3	111.8(2)	O2–C14–O3	122.1(3)
C7–N1–N2–N3	179.8(2)	C8–N3–N2–N1	179.9(2)
3			
Hg1–N1	2.088(3)	Hg1–N3	2.670 (3)
Hg1–O1	2.720(3)		
N1–Hg1–N1$^{\#1}$	178.8(2)	N1–Hg1–N3	51.58 (11)
N3–Hg1–N1$^{\#1}$	127.70 (12)	N3–Hg1–N3$^{\#1}$	124.03 (16)
N1–Hg1–O1	65.39(12)	N3–Hg1–O1	103.25(11)
O1–Hg1–O1$^{\#1}$	90.78(10)		

[a] Symmetry code: #1: $-x+1$, y, $-z+3/2$.

bond distances are 1.335(5) and 1.289(5) Å, respectively [22]. The N1–N2–N3 bond angle is 111.6(3)°, which is common in these compounds. The O1–C2–C3–C4 and O2–C2–C3–C8 torsion angles are 4.2(6)° and 5.0(7)°, respectively, and show that –$COOCH_3$ and phenyl ring lie on one plane.

In the lattice crystal of **1**, intramolecular N1–H1⋯O2 hydrogen bond with N1⋯O2=2.666 (5) Å is present. Also, non-classic C1–H1A⋯O2 #1 (#1: $-x$, $-y+2$, $z+1/2$) hydrogen bonds with C1⋯O2 = 3.464(7) Å connect the individual monomeric [*R*–NH–N=N–*R′*] moieties into chains along the *c* direction.

The FT-IR spectrum of **2**, which is a *methoxy*-substituted compound, shows a band at 3379 cm^{-1} due to N–H stretch. The N=N stretch of 1-(2-methoxyphenyl)-3-(2-methoxycarbonylphenyl)triazene is 1431 cm^{-1}, which is almost the same as compared with the corresponding frequencies in the *ethoxy*-substituted derivative, i.e. **1**, and the N–N stretch is at 1113(s) cm^{-1}. In the ^1H NMR spectrum of **2**, the peak at 12.3 ppm is assigned to the N–H group; hydrogens of methoxy substituted on the aromatic ring are at 1.35 ppm. The methyl group of –$COOCH_3$ is at 3.85 ppm. The hydrogens of aromatic rings have peaks at 6.95–7.95 ppm. In ^{13}C NMR spectra, the carbons of the two methoxy groups are at 14.5 and 55.6 ppm. The peak at 167.4 ppm can be assigned to the carbon of the carboxylic group. The carbons of aromatic rings show signals at 112–153.9 ppm.

The molecular structure of **2** is shown in figure 2, with thermal ellipsoids drawn at 50% probability level. Compound **2** crystallizes in the space group *Pbca* with eight molecules per unit cell. The unit-cell parameters are: $a = 15.626(3)$ Å, $b = 8.1866(16)$ Å, $c = 22.247(4)$ Å. The final *R* value was 0.0677 based on 2501 reflections.

The N1–N2 and N2=N3 bond lengths are 1.259(3) Å and 1.334(3) Å, respectively, which are comparable with those reported for **1** and indicate the presence of –NH–N=N– fragment. The N1–N2–N3 bond angle is 111.8(2)°, the same as for **1**. The angle between two planes passing from aromatic rings is 9.8(3)° and the C7–N1–N2–N3 and C8–N3–N2–N1 torsion angles are 179.8(2)° and 179.9(2)°, respectively, indicating that this molecule, excluding the substituents on the phenyl rings, is almost planar. The angle between the two

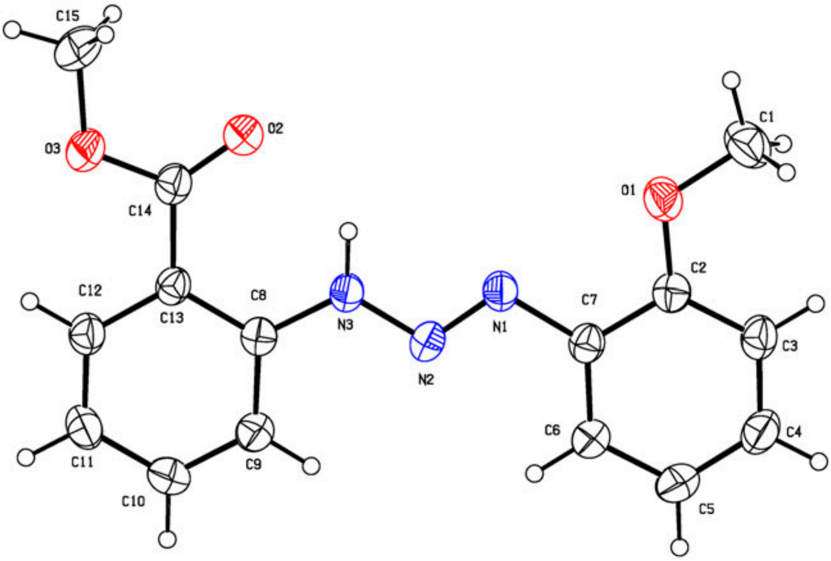


Figure 2. The labeled diagram of the asymmetric unit of **2**. Thermal ellipsoids are at 50% probability level.

planes of the aromatic phenyl rings is 4.13°. The C14=O2 bond distance is 1.202(3) Å, which is relatively shorter than C14–O3 [1.332(3) Å] and C15–O3 [1.450(4) Å]. The C8–C13–C14–O2 and C13–C14–O3–C15 torsion angles are 4.2(5)° and 173.8(3)°, respectively. Similar to **1**, intramolecular N3–H3A···O2 hydrogen bond with N3···O2=2.681(4) Å is present. In addition, C15–H15B···O1 interactions connect the molecules into wave-like chains (see figure 3).

Compound **3**, $[Hg(C_{16}H_{16}N_3O_3)_2]$ or [Hg**L**$_2$], was prepared by reacting **1** with $Hg(NO_3)_2$. By comparison of ^{1}H NMR spectra of **3** with that of the free ligand, the signal

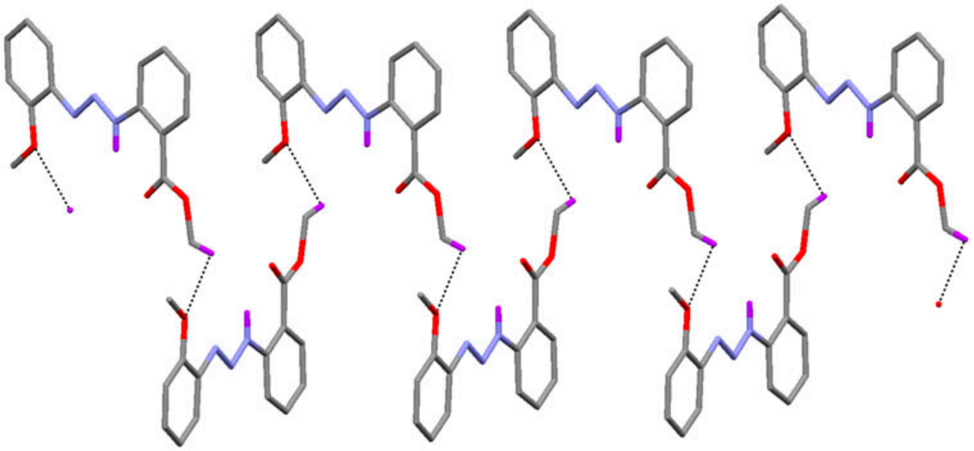


Figure 3. The C–H···O interactions in **2**, resulting in formation of a wave-like structure in **2**.

for N–H (at 12.3 ppm) disappears, indicating deprotonation of N–H due to complexation. The N1–N2 and N2–N3 bond distances are 1.315(5) and 1.280(4) Å, respectively, indicating the formation of a resonance structure. The molecular structure of **3** is shown in figure 4, with thermal ellipsoids drawn at 50% probability. The molecule crystallized in *C*2/*c* space group with four molecules per unit cell. The unit-cell parameters are: $a = 22.032(4)$ Å, $b = 8.7283(17)$ Å, $c = 18.226(4)$ Å, and $\beta = 117.72(3)°$. The final *R* value was 0.0345 based on 4157 reflections.

The Hg(II), lying on a two-fold rotation axis, is coordinated in an octahedral fashion by two interlocked triazenide ions. The asymmetric unit of **3** contains half of the molecules so, the occupancy of mercury in the asymmetric unit is 0.5. Each triazenide is coordinated through two nitrogens [Hg1–N1 = 2.088(3) Å and Hg1–N3 = 2.670 (3) Å] and one oxygen [Hg1–O1 = 2.720(3) Å] which is relatively weaker interaction. The Hg1–N1 is significantly shorter than the Hg1–N3 bond. So, Hg is coordinated in a liner form with the other four Hg–N and Hg–O bonds much longer and can only be regarded as weak secondary bonds. The linear geometry is well known for cations with d^{10} electronic configuration. The N1–Hg1–N1A (symmetry code (A): $-x+1$, y, $-z+3/2$) bond angle is 178.8(2)°, which slightly deviates from linearity. The C9–C14–C15–O2 and C13–C14–C15–O3 torsion angles are 66.7(6)° and 66.3(5)°, respectively, indicating that –$COOCH_3$ is rotated during complexation and is almost perpendicular to the phenyl ring. The N1–N2–N3 bond angle in this complex is 110.8(3)°.

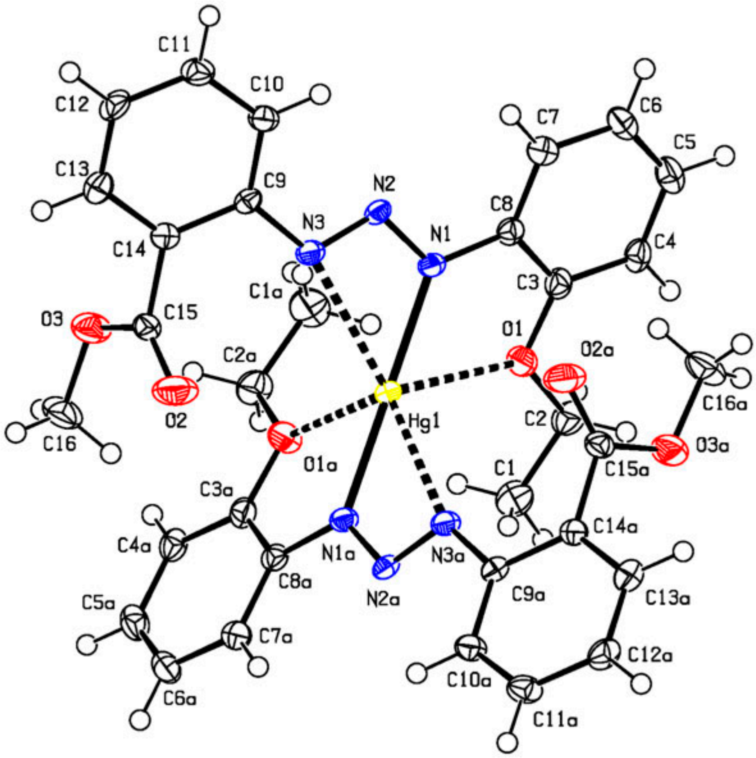


Figure 4. The labeled diagram of molecular structure of **3**. Thermal ellipsoids are at 50% probability level. Weak interactions are drawn as dashed lines.

Table 3. Hydrogen bonding geometries (Å, °) for **1**–**3**.[a]

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(D–H···A)
1				
N1–H1···O2	0.80(6)	2.04(6)	2.666 (5)	135(6)
C1–H1A···O2 #1	0.98	2.58	3.464 (7)	149
2				
N3–H3A···O2	0.90(3)	2.00(3)	2.681(4)	131(3)
C9–H9···N2	0.93	2.45	2.760(4)	100
C12–H12···O3	0.93	2.36	2.699(4)	101
3				
C12–H12···N2 #2	0.95	2.61	3.393 (5)	140
C2–H2A···O3 #3	0.99	2.59	3.559 (6)	167

[a]Symmetry codes: #1: $-x$, $-y+2$, $z+1/2$; #2: $-x+1/2$, $y-1/2$, $-z+3/2$; #3: $x+1/2$, $-y+3/2$, $z+1/2$.

The presence of non-classic C12–H1···N2 (symmetry code: $-x+1/2$, $y-1/2$, $-z+3/2$) and C2–H2A···O3 (symmetry code: $x+1/2$, $y-3/2$, $z+1/2$) hydrogen bonds with D···A distances of 3.394(6) Å and 3.559(6) Å connects the monomeric fragments into infinite chains in a wave-like shape along the crystallographic [010] and [101] directions, in which weaker π···π and C–H···π stacking interactions help to stabilize the structure (details provided in table 3). These hydrogen bonds lead to the formation of chains, resulting in a 2D architecture. As mentioned, π···π interactions exist between parallel phenyl rings that stack the molecules in the *b* direction and the mean centroid–centroid distance of 3.744(3) Å for *Cg*1···*Cg*1, in which *Cg*1 is center of C3/C8 ring ($1-x$, $2-y$, $2-z$). There are weak C–H···π edge-to-face interactions between the C–H groups and the aromatic phenyl rings with H···π distances of 2.81 Å for C1–H1B···*Cg*2 ($1-x$, $1+y$, $3/2-z$) and 2.89 Å for C16–H16A···*Cg*1 ($1-x$, y, $3/2-z$) [*Cg*2 = C9/C14 ring] (figure 5). The sum of these weak non-covalent interactions plays an important role in the crystal packing and the formation of a framework.

4. Solution studies

UV–vis spectra were recorded with a Perkin-Elmer Lambda 25 spectrophotometer using matched 10 mm quartz cells. In a typical procedure, a solution of the ligand (2.0 mL, 5.010^{-5} M) in MeOH was placed in the spectrophotometer cell and the absorbance was measured. Afterward, a known amount of a solution of Hg(II) nitrate in MeOH (2.5×10^{-3} M) was added stepwise using a 10 μL Hamilton syringe. The absorbance spectrum of the mixture was recorded after each addition. The mercury(II) nitrate solution was continually added until the desired metal-to-ligand mole ratio was achieved. Electronic absorption spectra of **1** and **2** in the presence of increasing Hg(II) nitrate concentration at room temperature are shown in figures 6 and 7, respectively. The resulting absorbance (at 373 nm) against $[Hg^{2+}]/[H\mathbf{L}]$ mole ratio plot, which is shown in the inset of figure 6, reveals a distinct injection point at a metal-to-ligand molar ratio of about 0.5 emphasizing the formation of a 1 : 2 complex [**3**, $Hg\mathbf{L}_2$] in MeOH. For evaluation of the conditional formation constants, the mole ratio data obtained by the physicochemical method employed were fitted to the

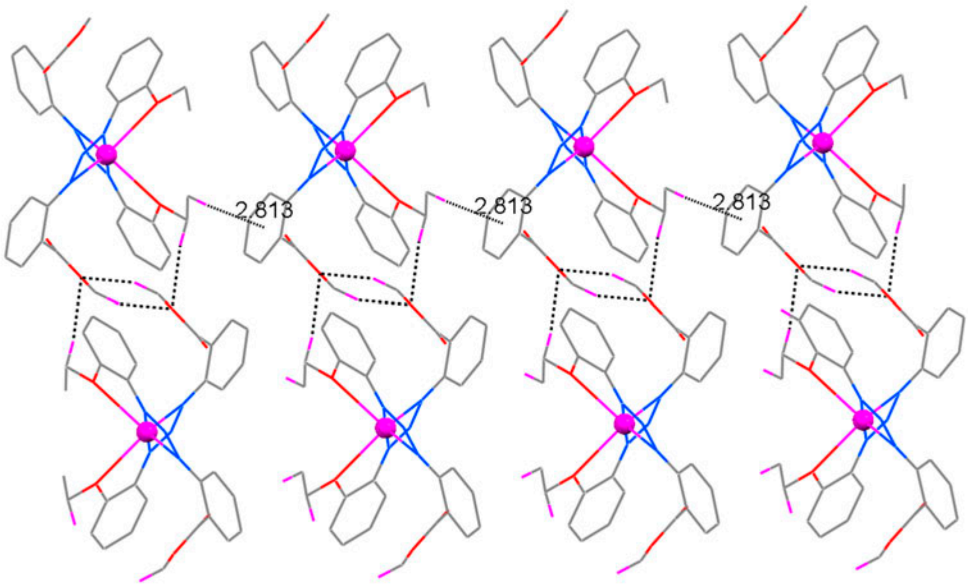


Figure 5. Representation of C–H···O and C–H···π interactions of **3**.

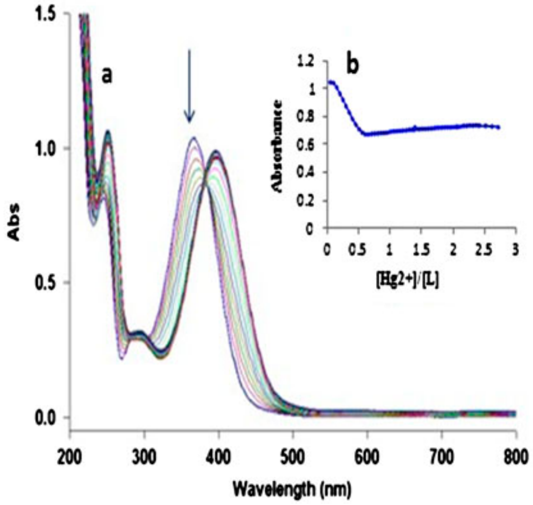


Figure 6. (a) Electronic absorption spectra of **1**, [H**L**], in MeOH (5.0×10^{-5} M) in the presence of increasing concentration of mercury(II) nitrate (2.5×10^{-3} M) at room temperature. (b) Corresponding mole ratio plot at 373 nm.

previously reported equations [39, 40] using a non-linear least squares curve fitting program KINFIT [41]. The conditional formation constant was evaluated as log $K = 4.78$ for the formation of 1 : 2 complex. The results of solution studies for the formation of **3** in methanol

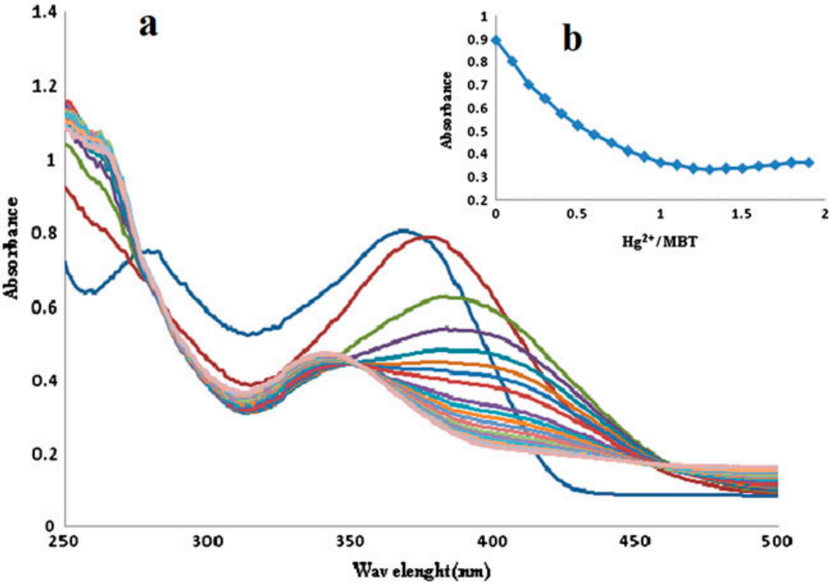


Figure 7. (a) Electronic absorption spectra of **2**, [H**L′**], in MeOH (5.0×10^{-5} M) in the presence of increasing concentration of mercury(II) nitrate (2.5×10^{-3} M) at room temperature. (b) Corresponding mole ratio plot at 360 nm.

solution support its solid-state stoichiometry. Also, the resulting absorbance (at 360 nm) against [Hg^{2+}]/[H**L′**] mole ratio plot, which is shown in the inset of figure 7, reveals a distinct injection point at a metal-to-ligand molar ratio of about one, emphasizing the formation of a 1 : 1 complex [**4**, Hg**L′**]. Compound **4** has different behavior in the solid state and in solution.

Supplementary material

CCDC 859577, 982032 and 871223 contains the supplementary crystallographic data for **1**, **2** and **3**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223 336 033; or Email: deposit@ccdc.cam.ac.uk.

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