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Synthesis, characterization and crystal structure of four new asymmetric triazene ligands: An example of linear Hg^{II} complex with Hg...π secondary bonding interactions

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Abstract. In this work, the asymmetric ligands [1-(phenyl)-3-(2-nitro-4-methylphenyl)]triazene (**1**), [1-(4-methylphenyl)-3-(2-nitro-4-methylphenyl)]triazene (**2**), [1-(4-ethylphenyl)-3-(2-nitro-4-methylphenyl)]triazene (**3**) and [1-(4-ethoxyphenyl)-3-(2-nitro-4-methylphenyl)]triazene (**4**), were synthesized. The reaction of the ligand (**3**) with $HgCl_2$ in methanol resulted in the formation of the [Hg$\mathbf{L}_2$] complex, (**5**). All compounds were characterized by means of CHN analysis, FT-IR, ^{1}H NMR, ^{13}C NMR spectroscopy. In addition, the crystal structures of the ligands (**2**) to (**4**) were investigated by single crystal X-ray analysis. In the solid state, all ligands exhibited *trans* conformation about the –N=N– double bond. The Hg^{II} complex (**5**) crystallized in monoclinic system with $C2/c$ space group. The triazene ligand was found to be deprotonated prior to coordination and acts as monodentate ligand. The Hg^{II} which lies on inversion center (site symmetry $\bar{1}$), is surrounded by two N atoms from **L** ligands forming a linear geometry. The other two Hg–N bonds are relatively longer and can only be regarded as weak secondary bonds. Also, Hg-η^3-arene π-interactions are present in this compound. Hydrogen bonds, $\pi\cdots\pi$ and C–H$\cdots\pi$ stacking interactions help in the stabilization of the resulted frameworks. These C–H$\cdots\pi$ edge-to-face interactions are present with H$\cdots\pi$ distance of 3.00 Å.

Keywords. Mercury(II) complex; Hg$\cdots\pi$ interaction; asymmetric triazene; crystal structure.

1. Introduction

Aryl triazenes have been studied over several years for their interesting structural and anticancer reactivity properties.[1–5] The study of transition-metal complexes containing 1,3-diaryltriazene ligands has greatly increased in the past few years due to the potential reactivity of these ligands.[6,7] As ligands, the (–NH–N=N–) moieties can show different types of coordination in metal complexes. The coordination modes can be monodentate, (N1, N3)-chelating towards one metal atom or (N1, N3)-bridging over two metal atoms over a wide variety of transition metal complexes.[8–10] In these compounds secondary bonds or interactions such as hydrogen bonds and metal π-aryl interactions can play important roles in the structural stability.[11–18] Several bis(diaryl) symmetric and asymmetric-substituted triazenide complexes of Hg^{II} which have a remarkable ability to self-assemble in different manners through metal-η-arene π-interactions have been reported.[11] In recent years, our group has been involved in the complexation of transition metal ions with several triazene compounds, starting from different bis(diaryl) symmetric and asymmetric-substituted triazenides. In this regard, the synthesis of 1,3-bis(2-methoxyphenyl)]triaz-1-ene[19] [1,3-bis(2-ethoxyphenyl)]triaz-1-ene[20] [1,3-bis(2-cyanophenyl)]triaz-1-ene[21] 1-(3,5-dichlorophenyl)-3-(2-methoxyphenyl)triaz-1-ene[22] and 3-(2-ethoxyphenyl)-1-(3-nitrophenyl)triaz-1-ene[23] molecules have been reported to act as ligands. Additionally, we have published the Hg^{II} complexes with [1,3-bis(2-methoxyphenyl)]triazene by using $HgCl_2$[24] $HgBr_2$[25] $Hg(CH_3COO)_2$ and $Hg(SCN)_2$ salts as starting materials.[26] Just recently, a Hg^{II} complex with [1,3-bis(2-ethoxyphenyl)]triazene as ligand has been reported, in which $HgCl_2$ has been used as starting salt.[27] From recent structural studies, it was

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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 reported.[28–30]

To investigate the effect of the substituted derivatives on coordination behavior of the triazene ligands, we have introduced *ortho*-, *meta*- and *para*- bis(phenyltriazene) benzenes (and substituted derivatives), as ligands in order to investigate the stoichiometry of the resulting mercury(II) complexes. In continuation with previous work, we herein report the synthesis, characterization, and molecular structure of new asymmetric [[1-(phenyl)-3-(2-nitro-4-methylphenyl)]triazene (**1**), [1-(4-methylphenyl)-3-(2-nitro-4-methylphenyl)]triazene (**2**), [1-(4-ethylphenyl)-3-(2-nitro-4-methylphenyl)]triazene (**3**) and [1-(4-ethoxyphenyl)-3-(2-nitro-4-methylphenyl)]triazene (**4**), and a linear Hg^{II} complex [Hg**L**$_2$], (**5**) in methanol as solvent. Scheme 1 presents the starting materials and the reaction procedure.

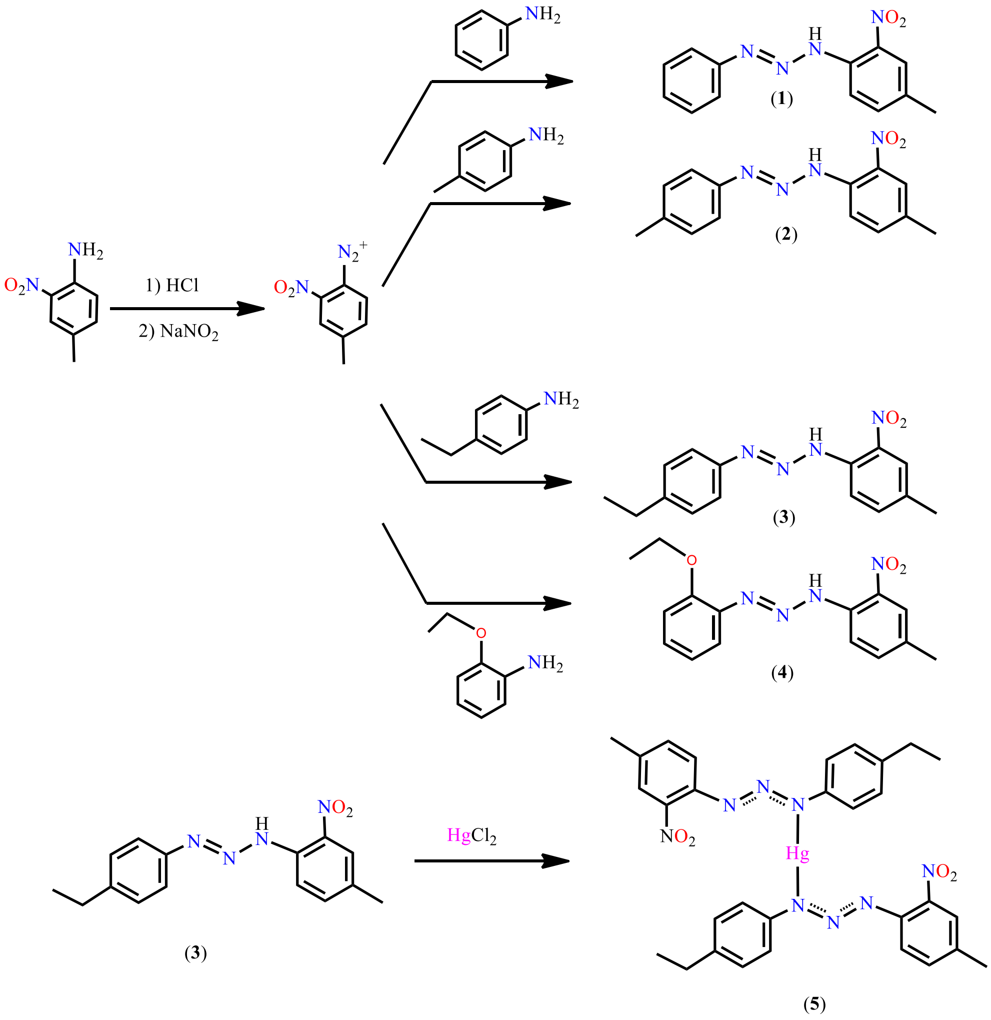
2. Experimental

2.1 *Materials and physical techniques*

All chemicals were of analytical grade and were used without further purification. FT-IR spectra in the frequency range of 4000–400 cm^{-1} were recorded using Perkin–Elmer RXI spectrometer using KBr disks. Elemental analysis was carried out using a Perkin–Elmer 2400(II) CHNS/O analyzer. Melting points were measured on a Barnstead Electrothermal 9200 apparatus. ^1H NMR and ^{13}C NMR spectra were recorded using Bruker Avance 300 instrument.

2.2 *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 ($\lambda = 0.71073$ Å). Cell constants and orientation matrices for data collection were



Scheme 1. General procedure for the preparation of the triazenes (**1**) to (**4**) and a linear Hg^{II} complex, (**5**).

Table 1. Crystallographic and structure refinement data for (**2**) to (**5**).

Compound reference	(2)	(3)	(4).MeOH	(5)
Chemical formula	$C_{14}H_{14}N_4O_2$	$C_{15}H_{16}N_4O_2$	$C_{15}H_{16}N_4O_3.CH_3OH$	$C_{30}H_{30}HgN_8O_4$
Formula Mass	270.29	284.32	332.36	767.21
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$C2/c$
a/Å	12.994(3)	7.7526(16)	6.7762(14)	14.527(3)
b/Å	5.7068(11)	9.3955(19)	18.031(4)	17.691(4)
c/Å	18.004(4)	11.264(2)	13.732(3)	12.011(2)
$\alpha/°$	–	67.73(3)	–	–
$\beta/°$	91.66(3)	75.55(3)	104.22(3)	110.95(3)
$\gamma/°$	–	88.64(3)	–	–
Crystal size (mm)	0.45 × 0.15 × 0.02	0.5 × 0.5 × 0.3	0.5 × 0.3 × 0.2	0.35 × 0.25 × 0.2
Unit cell volume/$Å^3$	1334.5(5)	732.9(2)	1626.4 (6)	2882.7(12)
Density (Mg m^{-3})	1.345	1.288	1.357	1.768
Temperature/K	120(2)	298(2)	120(2)	120(2)
No. of formula units per unit cell, Z	4	2	4	4
Absorption coefficient, mm^{-1}	0.094	0.089	0.10	5.391
Data collected	9605	7923	11054	11319
Unique data, (R_{int})	2348, (0.1782)	3912, (0.0672)	4353, (0.0967)	3865, (0.0491)
parameters / restraints	187 / 0	196 / 0	227 / 0	198 / 0
Final R indices [I>2σ(I)]	$R_1 = 0.0736$ $wR_2 = 0.1691$	$R_1 = 0.0596$ $wR_2 = 0.1513$	$R_1 = 0.0698$ $wR_2 = 0.1511$	$R_1 = 0.0310$ $wR_2 = 0.0633$
R indices (all data)	$R_1 = 0.1032$ $wR_2 = 0.1825$	$R_1 = 0.1223$ $wR_2 = 0.1768$	$R_1 = 0.1114$ $wR_2 = 0.1700$	$R_1 = 0.0594$ $wR_2 = 0.0699$
Goodness-of-fit on $F^2(S)$	1.1091	0.878	1.071	1.010
Largest diff. peak and hole, (e. $Å^{-3}$)	0.255, −0.264	0.224, −0.260	0.275, −0.307	1.719,−1.205

obtained by least-squares refinement of diffraction data from 2348 unique reflections for (**2**), 3912 for (**3**), 4353 for (**4**) and 3865 for compound (**5**). Data were collected to a maximum 2θ value of 50° for (**2**), 58.4° for (**3**), 58.3° for (**4**) and 58.3° for (**5**), in a series of ω scans in 1° oscillations and integrated using Stoe X-AREA[31] software package. A numerical absorption correction was applied using X-RED[32] and X-SHAPE[33] software. The data were corrected for Lorentz and Polarizing effects. The structures were solved by direct methods[34] and subsequent difference Fourier maps and then refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters.[35] The atomic factors were taken from the International Tables for X-ray Crystallography.[36] All refinements were performed using the X-STEP32 crystallographic software package.[37] A summary of crystal data, experimental details and refinement results are given in table 1.

2.3 *Syntheses*

2.3a *Synthesis of $C_{14}H_{14}N_4O_2$, (**1**):* All materials and solvents were obtained from commercial source and used without further purification The asymmetric ligand (**1**), [1-(phenyl)-3-(2-nitro-4-methylphenyl)]triazene, was prepared as follows: 10 g of ice and 150 mL of water were poured into a 250 mL flask. Then 0.304 g (2 mmol) of 4-methyl-2-nitroaniline and 15 mL of hydrochloric acid (37%) were added to this flask. After that, a solution containing $NaNO_2$ (0.13 g) in 5 mL of water was then added slowly to the resultant solution during a 15 min period. The pH of the solution was then adjusted to 6 by adding a solution containing 4 g of sodium acetate in 15 mL of water. After mixing for 15 min, the obtained solution was added to a solution of 0.25 mL (2 mmol) of aniline, 10 mL of methanol and 5 mL of water. After mixing for 24 h, the orange precipitate was filtered off and dried. Properties: IR (KBr): $\upsilon(cm^{-1})$: 3320(s), 3050 (w), 2966(w), 1660(w), 1602(s), 1569(s), 1523(s), 1459(s), 1407(s), 1339(s), 1303(s), 1286(w), 1144(s), 1077(s), 934(w), 847(s), 819(s), 761(s), 614(s). ^1H NMR (300 MHz, d^6-DMSO): δ 1.16 (3H, CH_3), 2.36 (3H, CH_3), 2.58 (2H, CH_2), 7.2–7.85 (7H, aromatic), 12.91 (1H, NH) ppm.^{13}C NMR (d^6-DMSO): δ 15.7, 20.1, 27.7, 117.8-145.5 ppm. Elemental Anal. calc. for $C_{15}H_{16}N_4O_2$: C, 63.37; H, 5.67; N, 19.7%. Found: C, 63.49; H, 5.26; N, 19.56%.

2.3b *2.Synthesis of $C_{14}H_{14}N_4O_2$, (**2**):* The [1-(4-methylphenyl)-3-(2-nitro-4-methylphenyl)]triazene (**2**) ligand was prepared according to the method described above with the difference that 4-methylaniline was used instead of aniline. Suitable crystals of this compound were obtained by slow evaporation of the solvent during three days. Properties: M.p.: 98–100°C. IR (KBr): υ(cm^{-1}): 3432(br), 3305(s), 2913(w), 1626(s), 1568(s), 1520(s), 1457(s), 1405(s), 1305(s), 1208(w), 1142(s), 1071(br), 818(s). ^{1}H NMR (300 MHz, d^6-DMSO): δ 2.28 (3H, CH$_3$), 2.36 (3H, CH$_3$), 7.19–7.66 (7H, aromatic), 12.82 (1H, NH).^{13}C NMR, (d^6-DMSO): δ 20.2, 20.7 and 114-145 ppm. Elemental Anal. calc. for $C_{14}H_{14}N_4O_2$: C, 62.21; H, 5.22; N, 20.73%. Found: C, 62.3; H, 5.66; N, 20.8%.

2.3c *Synthesis of* $C_{15}H_{16}N_4O_2$, (***3***): The ligand (**3**) was prepared with the same procedure with this difference that 4-ethylaniline was used instead of aniline as starting material. Suitable crystals of this compound were obtained by slow evaporation of the solvent during three days. Properties: M.p.: 92–94°C. IR (KBr): υ(cm^{-1}): 3435(br), 3320(s), 2966(w), 1625(s), 1569(s), 1523(s), 1459(s), 1407(s), 1339(s), 1303(s), 1286(s), 1202(w), 1144(s), 1077(s), 819(s). ^{1}H NMR (300 MHz, d^6-DMSO): δ 1.17 (3H, CH$_3$), 2.36 (3H, CH$_3$), 2.58 (2H, CH$_2$), 7.22–7.85 (6H, aromatic), 12.82 (1H, NH).^{13}C NMR, (d^6-DMSO): δ 15.7, 20.1, 27.7 and 128-145 ppm. Elemental Anal. calc. for $C_{15}H_{16}N_4O_2$: C, 63.37; H, 5.67; N, 19.71%. Found: C, 63.49; H, 5.26; N, 19.56%.

2.3d *Synthesis of* $C_{15}H_{16}N_4O_3$, (***4***): In the synthesis of the ligand (**4**), 4-ethoxylaniline was used as starting material and the preparation method was the same as above. Properties: M.p.: 100–102°C. IR (KBr): υ(cm^{-1}): 3449(s), 3336(s), 2976(w), 1629(s), 1586(s), 1521(s), 1493(s), 1471(w), 1426(s), 1389(s), 1334(s), 1257(br), 1158(w), 1120(s), 1065(s), 1044(s), 926(s), 918(s), 836(s), 745(s), 715(s). ^{1}H NMR (300 MHz, d^6-DMSO): δ = 1.36 (3H, CH$_3$), 2.35 (3H, CH$_3$), 4.08 (2H, CH$_2$), 6.93–7.76 (6H, aromatic), 11.93 (1H, NH).^{13}C NMR, (d^6-DMSO): δ = 14.6, 20.0, 20.5, 63.9 and 102-145 ppm. Elemental Anal. calc. for $C_{15}H_{16}N_4O_3$: C, 59.99; H, 5.37; N, 18.66%. Found: C, 63.49; H, 5.26; N, 19.56%.

2.3e *Synthesis of* $C_{30}H_{30}HgN_8O_4$, (***5***): The complex was prepared by mixing 0.6 g (2 mmol) of [1-(4-ethylphenyl)-3-(2-nitro-4-methylphenyl)]triazene (**3**), in 25 mL of anhydrous methanol with 0.27 g (1 mmol) of mercury(II) chloride in 15 mL of anhydrous methanol. After mixing for an hour, a precipitate was obtained. The resultant precipitate after filtration and washing was dissolved in THF. Yellow needle-like crystals suitable for X-ray analysis of the complex (**5**) were obtained by slow evaporation of the solvent in two weeks. Properties: air stable, yellow crystalline material. M.p.: 201–203°C. IR (KBr): υ(cm^{-1}): 3650(w), 3435(br), 2966(w), 1601(s), 1568(s), 1520(s), 1504(s), 1392(s), 1320(s), 1273(s), 1197(s), 1148(s), 1080(w), 835(s), 817(s), 791(s), 765(s), 676(w), 534(w). ^{1}H NMR (300 MHz, d^6-DMSO): δ = 1.19 (6H, CH$_3$), 2.30 (6H, CH$_3$), 2.35 (3H, O-CH$_3$), 2.62(4H, -CH$_2$), 7.20–7.65 (14H, aromatic).^{13}C NMR (300 MHz, d^6-DMSO): δ 20.0, 20.5, 118.5-124.3 and 174.6 ppm. Elemental Anal. calc. for $C_{30}H_{30}HgN_8O_4$: C, 46.97; H, 3.94; N, 14.61%. Found: C, 47.09; H, 3.41; N, 14.1%.

3. Results and Discussion

In the FT-IR spectrum of the ligand (**2**), the band at 3305 cm^{-1} is responsible for N–H bond stretching. The N–N and N=N bond stretching modes appear at 1142 and 1457 cm^{-1}, respectively. The peak at 1520 cm^{-1} is assigned to the stretching of N–O bond of NO$_2$ fragment and the stretching frequency of the formal C–N single band appears at 1305 cm^{-1}. In ^{1}H NMR spectrum, the peak at δ = 12.82 ppm can be assigned to the presence of N–H group. Hydrogen atoms of methyl groups exhibit signals at 2.28 and 2.36 ppm, respectively. The seven hydrogen atoms of the two aromatic rings appear from 7.19 to 7.66 ppm. In the ^{13}C NMR spectrum, the carbon atoms of methyl groups on the aromatic ring show signals at 20.2 and 20.7 ppm, respectively. The carbon atoms belong to two aromatic rings show signals ranging from 114 to 145 ppm, indicating the presence of twelve different carbon atoms. The molecular structure of compound (**2**) is shown in figure 1 with thermal ellipsoids drawn at 50% probability level. Compound (**2**) crystallized in monoclinic system with $P2_1/n$ space group and four molecules per unit cell. Crystallographic data and parameters for complex are summarized in table 1. Also, selected bond lengths and angles are listed in table 2. As it can be seen, the molecule adopts *trans* configuration with respect to the (–N=N–) bond. The N1=N2 and N2–N3 bond lengths are 1.261(4) Å and 1.352 (4) Å, respectively, which proves the presence of distinct single and double bonds between nitrogen atoms and hence the (–NH–N=N–) moiety. These values are in good agreement with the reported data for N–N and N=N bond distances.[25] For example, in 1,3-bis(2-cyanophenyl)triazene, the N–N and N=N bond distances are 1.335(5) and 1.289(5) Å.[21] Also, the N1–N2–N3 bond angle is 109.2 (3)°. The angle between two planes of the aromatic rings of triazene molecule is

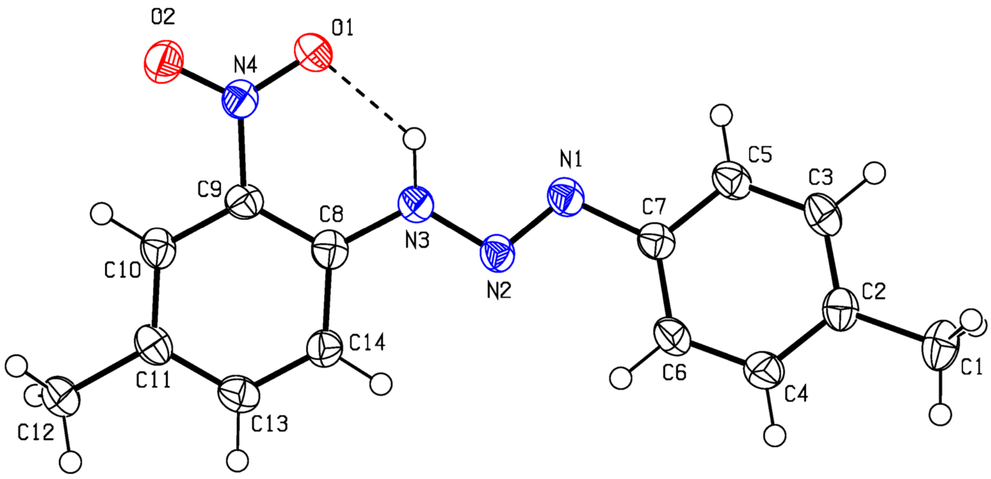


Figure 1. Molecular structure of compound (**2**) with thermal ellipsoids drawn at 50% probability level. The intramolecular N3–H3A· · · O1 hydrogen bond is shown as dashed line.

Table 2. Selected bond distances (Å) and angles (°) for compounds (**2**) to (**5**).

Compound (2)			
N1—N2	1.264(4)	N4—O1	1.235(3)
N2—N3	1.353(4)	N4—O2	1.226(3)
N1—N2—N3	109.3(3)	O1—N4—O2	121.7(3)
Compound (3)			
N1—N2	1.254(2)	N4—O1	1.2256(19)
N2—N3	1.350(2)	N4—O2	1.211(2)
N1—N2—N3	111.01(15)	O1—N4—O2	121.40(17)
Compound (4)			
N1—N2	1.266(3)	N4—O2	1.237(2)
N2—N3	1.353(3)	N4—O3	1.228(2)
O1—C2	1.445(3)	O4—C16	1.411(3)
O1—C3	1.365(3)		
N1—N2—N3	111.33(18)	O2—N4—O3	122.2(2)
Compound (5)			
Hg1—N1	2.067(3)	N2—N3	1.276(5)
N1—N2	1.316(5)	O1—N4—O2	123.5(4)
N1—Hg1—N1	180.000(1)	N1—N2—N3	113.8(3)

15.49(3)° which indicates that this molecule is deviated from planar geometry.

In the lattice structure of the ligand (**2**), intramolecular N3–H3A· · · O1 hydrogen bond with N3· · · O1 = 2.610 (3) Å, as well as non-classic hydrogen bonds, C3–H3· · · O1 #1 (#1: −x+1/2, y+3/2, −z+1/2) and C10–H10· · · O2 #2 (#2: −x, −y−1, −z) with C3· · · O1 = 3.508(4) Å and C10· · · O2 = 3.352(4) Å are present (table 3).

Compound (**3**) was also characterized by using FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy. In the FT-IR spectrum of the ligand (**3**) was very similar to that of ligand (**2**). The band at 3320 cm^{-1} is responsible for N–H bond stretching. The N–N and N=N bond stretching modes appear at 1144 and 1459 cm^{-1}, respectively. The peak at 1523 cm^{-1} is assigned to the stretching of N–O bond of NO_2 fragment and the stretching frequency of the formal C–N single band appears at 1303 cm^{-1}. In ^{1}H NMR spectrum, the peak at $\delta = 12.82$ ppm can be assigned to the presence of N–H group. Hydrogen atoms of methyl groups of (CH_3-CH_2-) exhibit signals at 1.17 ppm. Two hydrogen atoms of -CH_2- group appear at 2.58 ppm and methyl group attached to the aromatic ring shows signal at 2.36 ppm. The seven hydrogen atoms of the two aromatic rings appear from 7.22 to 7.85 ppm. In the ^{13}C NMR spectrum, the carbon atoms of methyl groups show signals at 15.7 and 20.1 ppm, respectively. The carbon atom

Table 3. Hydrogen bonding parameters (Å , °) for compounds (**2**) to (**5**).

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(D–H···A)
Compound (2)				
N3—H3A···O1	0.90(4)	1.91(4)	2.610(3)	133(3)
C3—H3···O1$^{\#1}$	0.95	2.58	3.509 (4)	165.8
C10—H10···O2	0.95	2.34	2.671(4)	100.1
C10—H10···O2$^{\#2}$	0.95	2.47	3.353(4)	155.4
Compound (3)				
N3—H3···O1	0.89	1.99	2.612(3)	127
C4—H4···O1$^{\#3}$	0.93	2.54	3.446 (3)	165
C11—H11···O2$^{\#4}$	0.93	2.59	3.392 (2)	145
Compound (4)				
N3—H3A···O2	0.84	2.09	2.638 (3)	123
N3—H3A···O4$^{\#5}$	0.84	2.24	2.979 (3)	147
O4—H4A···N1$^{\#6}$	0.84	2.17	2.810 (3)	133
C2—H2A···O4$^{\#7}$	0.99	2.53	3.366 (3)	142
C13—H13C···O3$^{\#8}$	0.98	2.57	3.412 (3)	144
Compound (5)				
C6—H6···O1$^{\#9}$	0.95	2.55	3.351 (6)	142
C15—H15···O2$^{\#10}$	0.95	2.43	3.245 (6)	144

Symmetry codes: (#1) −x+1/2, y+3/2, −z+1/2; (#2) −x, −y−1, −z; (#3) −x+1, −y, −z+1; (#4) −x+1, −y−1, −z; (#5) x−1, y, z; (#6) x+1, y, z; (#7) x−2, y, z; (#8) −x+2, −y+1, −z+1; (#9) −x+2, y, −z+3/2; (#10) x−1/2, −y+1/2, z−1/2.

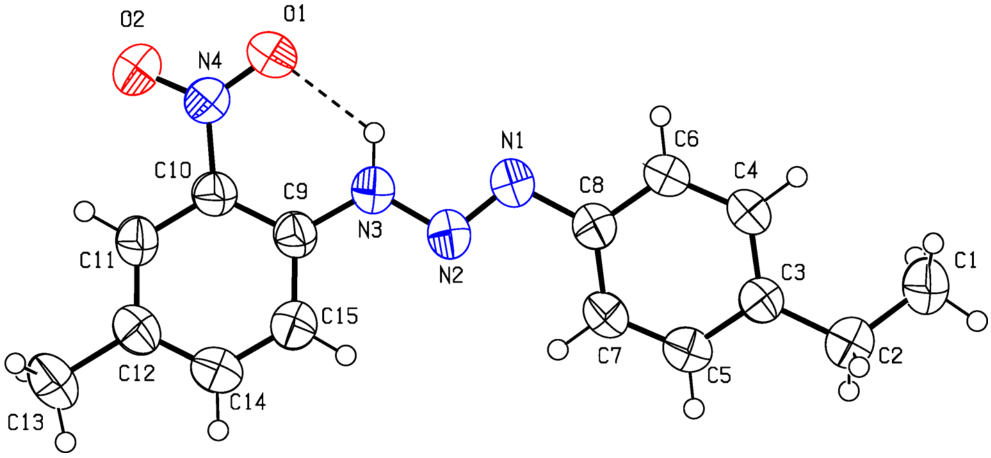


Figure 2. Molecular structure of compound (**3**) with thermal ellipsoids drawn at 50% probability level. The intramolecular N3–H3···O1 hydrogen bond is shown as dashed line.

of methylene group appears at 27.7 ppm. The carbon atoms belong to two aromatic rings show signals ranging from 128 to 145 ppm, indicating the presence of twelve different carbon atoms. The molecular structure of compound (**3**) is shown in figure 2 with thermal ellipsoids drawn at 50% probability level. Compound (**3**) crystallized in monoclinic system with $P2_1/n$ space group and four molecules per unit cell. Selected bond lengths and angles for (**3**) are listed in table 2. The molecule again adopts *trans* conformation with respect to the (–N=N–) bond. The N1=N2 and N2–N3 bond lengths are 1.254(2) Å and 1.350 (2) Å, respectively Also, the N1–N2–N3 bond angle is 111.01 (15)°. The angle between two planes passing from aromatic rings of triazene molecule is 16.20(3)° and indicates that this molecule is deviated from planar geometry.

In the lattice structure of the ligand (**3**), intramolecular N3–H3···O1 hydrogen bond with N3···O1 = 2.612(3) Å is present. Also, oxygen atoms of NO_2 group are involved in the hydrogen bonding. The non-classic C4–H4···O1 #3 (#3: −x+1, −y, −z+1) and C11–H11···O2 #4 (#4: −x+1, −y−1, −z) hydrogen bonds with C4···O1 = 3.446(3) Å and C11···O2 = 3.392(2) Å connect the triazene molecules into chains in [110] direction (figure 3).

The ligand (**4**) is also an asymmetric substituted triazene bearing ethoxy group on the aromatic ring. In the FT-IR spectrum of compound (**4**), the band at 3336 cm^{-1} is responsible for N–H bond stretching. The N–N and N=N bond stretching modes appear at 1120 and 1426 cm^{-1}, respectively. The peak at 1521 cm^{-1} is assigned to the stretching of N–O bond of NO_2 fragment. and the stretching frequency of the formal C–N single band appears at 1334 cm^{-1}. In ^{1}H NMR

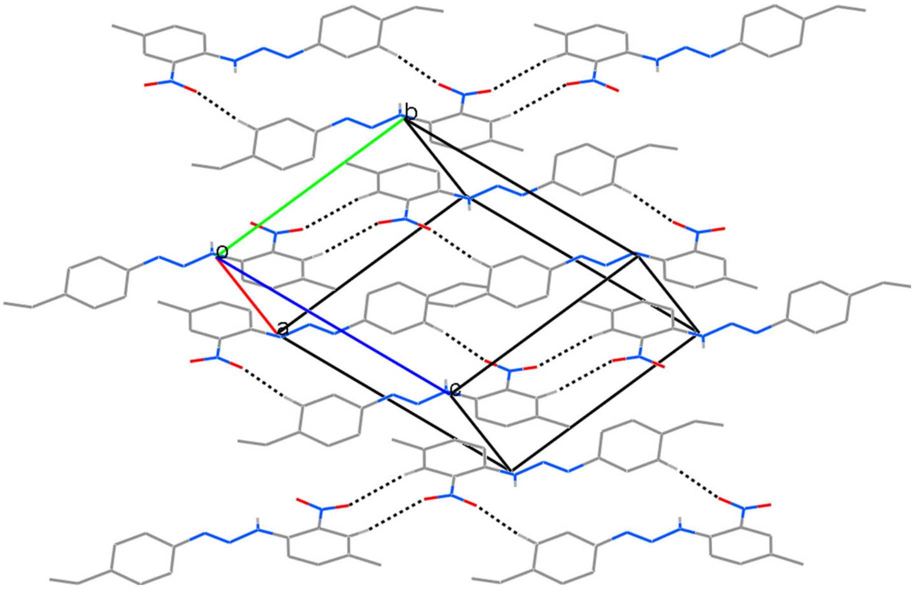


Figure 3. Non-classic C4–H4···O1 and C11–H11···O2 hydrogen bonds connect the triazene molecules (**3**) into chains along [110] direction.

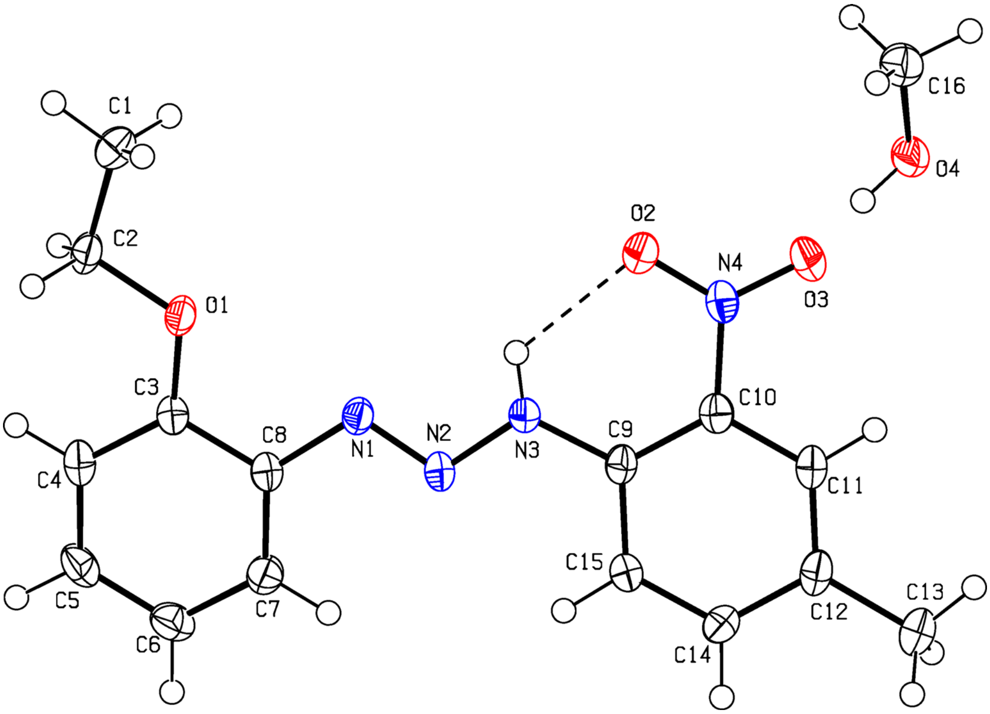


Figure 4. Molecular structure of compound (**4**) with thermal ellipsoids drawn at 50% probability level. The intramolecular N3–H3A···O2 hydrogen bond is shown as dashed line.

spectrum, the peak at $\delta = 11.93$ ppm can be assigned to the presence of N–H group. Hydrogen atoms of methyl groups of (CH_3-CH_2-O) exhibit signal at 1.36 ppm. Two hydrogen atoms of -CH_2- group appear at 4.08 ppm and methyl group attached to the aromatic ring shows signal at 2.35 ppm. The seven hydrogen atoms of the

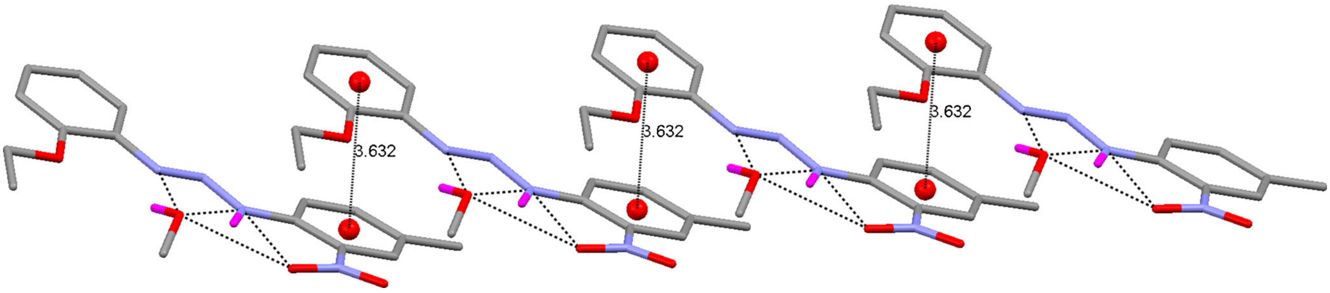


Figure 5. $\pi \cdots \pi$ stacking interactions between $Cg1 \cdots Cg2$ with centroid-centroid distances of 3.632 (15) Å in compound (**4**). All hydrogen bonds are also shown as dashed lines. Methanol molecule makes two distinct hydrogen bonds with triazene (**4**).

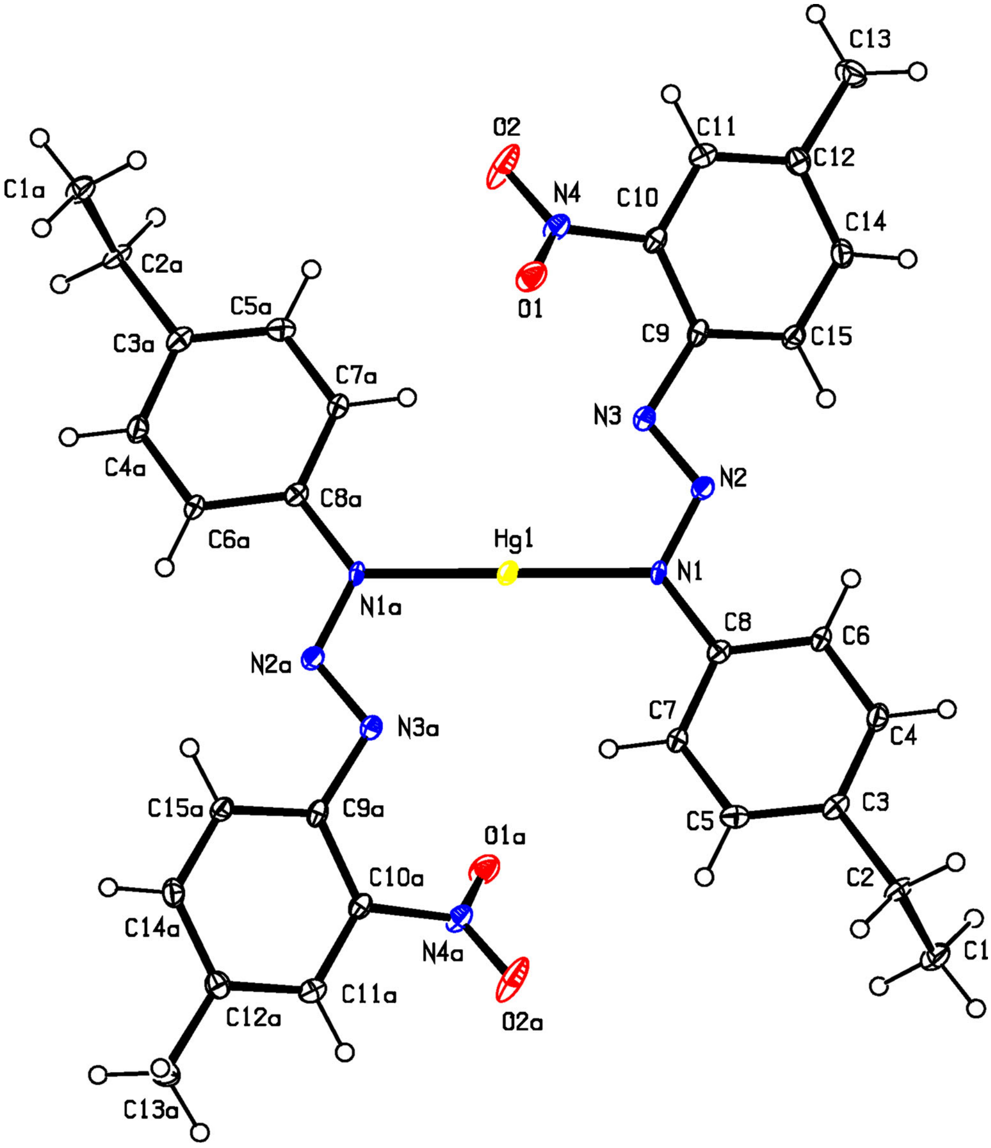


Figure 6. Molecular structure of compound (**5**) with thermal ellipsoids drawn at 30% probability level.

two aromatic rings appear from 6.93 to 7.76 ppm. In the ^{13}C NMR spectrum, the carbon atoms of methyl groups show signals at 14.6 and 20.5 ppm, respectively. The carbon atom of methylene group (-CH$_2$-O) appears at 63.9 ppm. The carbon atoms belong to two aromatic rings show signals ranging from 102 to 145 ppm, indicating the presence of twelve different carbon atoms. The molecular structure of compound (**4**) is shown at figure 4 with thermal ellipsoids drawn at 50% probability level.

The ligand (**4**) crystallized in monoclinic system with $P2_1/c$ space group and four molecules per unit cell. The N1=N2 and N2–N3 bond lengths are 1.266(3) Å and 1.353 (3) Å, respectively Also, the N1–N2–N3 bond angle is 111.33 (18)°. The angle between the two planes of the aromatic rings of triazene molecule is 9.53(3)°. In addition, a methanol molecule is present in the crystal structure of this compound. In the lattice structure of the ligand (**4**), intramolecular N3–H3A$\cdots$O2 hydrogen bond with N3$\cdots$O2 = 2.638(3) Å is present. Also, oxygen atom of CH$_3$OH group plays as donor and acceptor atom in the hydrogen bonding and makes N3–H3A$\cdots$O4 #5 (#5: x−1, y, z) hydrogen bond with N3$\cdots$O4 = 2.979(3) Å and O4–H4A$\cdots$N1 #6 (#6: x+1, y, z) hydrogen bond with O4$\cdots$N1 = 2.810(3) Å. Also, non-classic C2–H2A$\cdots$O4 #7 (#7: x−2, y, z) and C13–H13C$\cdots$O3 #8 (#8: −x+2, −y+1, −z+1) hydrogen bonds with C2$\cdots$O4 = 3.366(3) Å and C13$\cdots$O3 = 3.412(3) Å are present. In addition, $\pi\cdots\pi$ stacking interactions help in the stabilization of the resulted framework. These $\pi\cdots\pi$ stacking interactions are present between $Cg1\cdots Cg2$ (−1+x, y, z) with centroid-centroid distance of 3.632 (15) Å. $Cg1$ and $Cg2$ are centroids for C3-C8 and C9-C12, C14,C15 rings, respectively (figure 5).

Compound (**5**), [Hg(C$_{16}$H$_{16}$N$_3$O$_3$)$_2$] or [HgL$_2$], was prepared by reacting the corresponding ligand L (**3**) with HgCl$_2$ salt in methanol as solvent. By comparison of ^{1}H NMR spectrum of the complex (**5**) with that of the free ligand, it is found that the signal for N–H (at 12.82 ppm) has disappeared which indicates deprotonation of the N–H group prior to complexation. The molecular structure of the compound (**5**) is shown in figure 6.

The molecule crystallized in $C2/c$ space group with four molecules per unit cell. The N1–N2 and N2–N3 bond distances are 1.316(5) Å and 1.276(5) Å, respectively which indicates the formation of resonance structure. The N1–N2–N3 bond angle is 113.8 (3)°. The Hg^{II} which lies on inversion center (site symmetry $\bar{1}$), is coordinated by two triazenide ions. Each triazenide ion is coordinated to central atom through two nitrogen atoms [Hg1–N1 = 2.067(3) Å and Hg1–N3 = 2.670 (3) Å] of which the latter one is relatively weaker interaction. Hence, Hg^{II} is coordinated in a linear form, the other two Hg–N bonds are much longer and can only be regarded as weak secondary bonds. The linear geometry

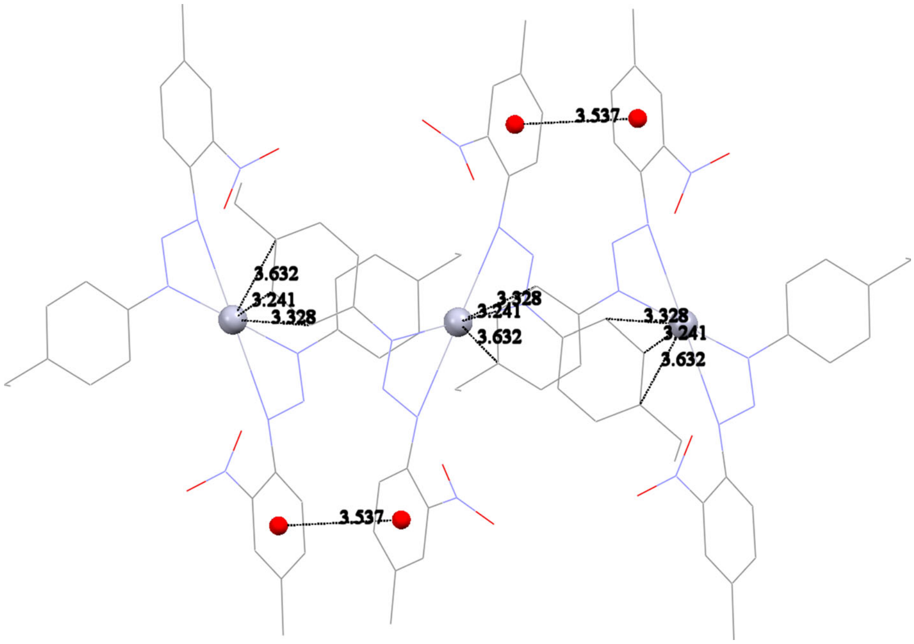


Figure 7. Secondary weak metal-η^3 interactions in compound (**5**) involve the Hg1 atom and C3 [3.632(2) Å], C4 [3.241(1) Å] and C6 [3.328(2) Å] atoms with related symmetry code (2−x, y, 3/2−z).

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 180° .

In addition, the presence of non-classic C6–H6$\cdots$O1 #9 (#9: $-x+2$, y, $-z+3/2$) and C15–H15$\cdots$O2 #10 (#10: $x-1/2$, $-y+1/2$, $z-1/2$) hydrogen bonds with D$\cdots$A distance of 3.351(6) Å and 3.245(6) Å connect the monomeric fragments into infinite chains in a wave-like shape along the crystallographic [010] and [101] directions. Within the chains, each Hg^{II} is additionally coordinated by two peripheral phenyl rings of two neighboring complexes by secondary weak metal-η^3 interactions. These metal-π interactions involve the Hg1 atom and C3 [3.632(2) Å], C4 [3.241(1) Å] and C6 [3.328(2) Å] atoms with related symmetry code ($2-x$, y, $3/2-z$) (see figure 7). As mentioned weaker $\pi\cdots\pi$ and C–H$\cdots\pi$ stacking interactions help to stabilize the resulted structure (details are provided in table 3). These $\pi\cdots\pi$ interactions exist and the mean centroid–centroid distance is 3.537(2) Å for *Cg*2$\cdots$*Cg*2, in which *Cg*2 is center of C9/C15 ring ($2-x$, y, $3/2-z$). Also, there are interesting weak C—H$\cdots\pi$ edge-to-face interactions between the C−H groups and the aromatic phenyl rings with H$\cdots\pi$ distance of 2.71 Å for C1–H1A$\cdots$*Cg*2 ($3/2-x$, -1/2+y, $3/2-z$). The sum of these weak non-covalent interactions seems to play an important role in the crystal packing and the formation of a desired framework.

4. Conclusions

In this article, the synthesis of four new asymmetric triazene ligands are described and characterized by FT-IR, NMR, elemental analysis and single crystal X-ray technique. In the solid state, all ligands exhibited *trans* conformation about the –N=N– double bond. Hydrogen bonding (O–H$\cdots$N, N–H$\cdots$O and C–H$\cdots$O) and slipped $\pi\cdots\pi$ stacking interactions played an essential role in the creation and stabilization of their 3D networks. A linear Hg^{II} complex was also synthesized in which central atom is coordinated by two triazenide ions by their nitrogen atoms (HgL_2). Each Hg^{II} is additionally coordinated by two peripheral phenyl rings of two neighboring complexes by secondary weak metal-η^3 interactions.

Supplementary Information

CCDC 1008066, 1008067, 1008068 and 1008069 contain the supplementary crystallographic data for compounds (**2**) to (**5**), 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 Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

1. De Oliveira G M, Horner M, Machado A, Back D F, Monteiro J H S K and Davolos M R 2011 *Inorg. Chim. Acta* **366** 203
2. Zhao Y, Cao Q E, Hu Z and Xu Q 1999 *Anal. Chim. Acta* **388** 45
3. Jean-Claude B J, Mustafa A, Damian Z, De Marte J, Vasilescu D E, Yen R, Chan T H and Layland-Jones B 1999 *Biochem. Pharmacol.* **57** 753
4. Rudolf M F, Ciunik Z, Gatner K and Wolny J A 1992 *Polyhedron* **11** 2591
5. Aneetha H, Padmaja J and Zacharias P S 1996 *Polyhedron* **15** 2445
6. Leman J T, Wilking J B, Cooling A J and Barron A R 1993 *Inorg. Chem.* **32** 4324
7. Vrieze K and Van Koten G 1987 In *Comprehensive Coordination Chemistry* (Oxford: Pergamon Press) p. 189
8. Moore D S and Robinson S D 1986 *Adv. Inorg. Chem. Radiochem.* **28** 1
9. Horner M, Carratu V S, Bordinhao J, Silva A and Niquet E 2004 *Acta Crystallogr. Sect. C* **60** m140
10. Horner M, Bortoluzzi A J, Beck J and Serafin M 2002 *Z Anorg. Allg. Chem.* **628** 1104
11. Horner M, Manzoni de Oliveira G, Bonini J S and Fenner H 2006 *J. Organomet. Chem.* **691** 655
12. Desiraju G R 2011 *Angew. Chem. Int. Ed. Engl.* **50** 5590
13. Roesky H W and Andruh M 2003 *Coord. Chem. Rev.* **236** 91
14. Biradha K 2003 *CrystEngComm* **5** 374
15. Chen X M and Liu G F 2002 *Chem. Eur. J.* **8** 4811
16. Batten S R, Hoskins B F and Robson R 1995 *J. Am. Chem. Soc.* **117** 5385
17. Gardner G B, Venkataraman D, Moore J S and Lee S 1995 *Science* **374** 792
18. Hoskins B F and Robson R 1990 *J. Am. Chem. Soc.* **112** 1546
19. Rofouei M K, Shamsipur M and Payehghadr M 2006 *Anal. Sci.* **22** x79
20. Rofouei M K, Melardi M R, Salemi Y and Kazemi S R 2009 *Acta Crystallogr. Sect. E* **65** o719
21. Melardi M R, Khalili Ghaydari H R, Barkhi M and Rofouei M K 2008 *Anal. Sci.* **24** x281
22. Melardi M R, Aghamohamadi M, Attar Gharamaleki J, Rofouei M K and Notash B 2012 *Acta Crystallogr. Sect. E* **68** o724
23. Melardi M R, Ghannadan A, Peyman M, Bruno G and Amiri Rudbari H 2011 *Acta Crystallogr. Sect. E* **67** o3485
24. Melardi M R, Rofouei M K and Massomi J 2007 *Anal. Sci.* **23** x67
25. Hematyar M and Rofouei M K 2008 *Anal. Sci.* **24** x117
26. Rofouei M K, Hematyar M, Ghoulipour V and Attar Gharamaleki J 2009 *Inorg. Chim. Acta* **362** 3777
27. Melardi M R, Salemi Y, Razi Kazemi S and Rofouei M K 2009 *Acta Crystallogr. Sect. E* **65** m302

28. Rofouei M K, Ghalami Z, Attar Gharamaleki J, Ghoulipour V, Bruno G and Amiri Rudbari H 2012 *Z. Anorg. Allg. Chem.* **638** 798
29. Rofouei M K, Attar Gharamaleki J, Fereyduni E, Aghaei A, Bruno G and Amiri Rudbari H 2012 *Z. Anorg. Allg. Chem.* **638** 220
30. Rofouei M K, Attar Gharamaleki J, Melardi M R, Hosseini S M, Hosseinzadeh F, Peyman M, Ghannadan A, Notash B, Bruno G and Amiri Rudbari H 2012 *Polyhedron* **44** 138
31. Stoe and Cie 2005 *X–AREA: Program for the Acquisition and Analysis of Data*, Version 1.30 (Darmstadt, Germany: Stoe & Cie GmbH)
32. Stoe and Cie 2005 *X–RED: Program for Data Reduction and Absorption Correction*, Version 1.28b (Darmstadt, Germany: Stoe & Cie GmbH)
33. Stoe and Cie 2004 *X–SHAPE: Program for Crystal Optimization for Numerical Absorption Correction*, Version 2.05 (Darmstadt, Germany: Stoe & Cie GmbH)
34. Sheldrick G M 1997, *SHELX97 Program for Crystal Structure Solution* (Göttingen Germany: University of Göttingen)
35. Sheldrick G M 1997 *SHELX97 Program for Crystal Structure Refinement* (Göttingen Germany: University of Göttingen)
36. International Tables for X-ray Crystallography, Vol C 1995 (Dordrecht, The Netherlands: Kluwer Academic Publisher)
37. Stoe and Cie 2000 *X-STEP32: Crystallographic Package* Version 1.07b (Darmstadt, Germany: Stoe & Cie GmbH)