

Synthesis, X-ray crystal structures and multinuclear NMR characterization of Hg(II) complexes of 2-[(*E*)-2-(aryl)-1-diazenyl]pyridine

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Abstract

Syntheses and structural studies for the two complexes dichloro-{2-[(*E*)-2-(4-methylphenyl)-1-diazenyl]pyridine}Hg(II) (**1**) and dichloro-{2-[(*E*)-2-(3-methylphenyl)-1-diazenyl]pyridine}Hg(II) (**2**) are reported. The solid-state structures of the complexes were determined by X-ray diffraction methods and in addition, the complexes were characterized in solution using ¹H, ¹³C and ¹⁹⁹Hg NMR spectroscopy. The X-ray structures reveal that the complexes adopt surprisingly different structures. Complex **2** has an extended polymeric structure with 2-[(*E*)-2-(3-methylphenyl)-1-diazenyl]pyridine behaving as a monodentate ligand via the pyridyl nitrogen, and all the chlorine atoms serving to bridge mercury atoms, whereas complex **1** has a dimeric structure with 2-[(*E*)-2-(4-methylphenyl)-1-diazenyl]pyridine behaving as a bidentate ligand via the pyridyl nitrogen and one of the azo nitrogens, with a terminal chlorine on each Hg and a μ, μ' -dichloro bridge between the mercury atoms. But the coordination geometry around the mercury atom is similar in both complexes, each showing a distorted trigonal bipyramidal arrangement of the donor atoms. These complexes were characterized in solution by ¹H, ¹³C, ¹⁹⁹Hg NMR spectroscopy.

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Keywords: 2-[(*E*)-2-(aryl)-1-diazenyl]pyridine; Hg(II) complexes; NMR; Crystal structures

1. Introduction

The metal complexes of heterocyclic α -diimine ligands such as 2,2'-bipyridine and 1,10-phenanthroline have proven to be useful for studying such phenomena as luminescence and photo reduction/oxidation. It is

for this reason that extensive studies with the 2-(aryl-azo)pyridine (hereafter named as 2-[(*E*)-2-(aryl)-1-diazenyl]pyridine, Fig. 1) system have been undertaken and a number of studies of metal complexes containing this type of ligand have been reported. These include investigations of complexes of Fe(II) [1,2], Ni(II) [2], Hg(II) [3,4], Os(II) [5,6], Ru(II) [7–19], Cr(0), Mo(0), W(0) [20,21], Cr(II) [22], Cu(I) [23], Rh(III) [24,25], Rh(I) [26], Ag(I) [27], Re(III) [28], Co(II) [29], Mo(IV) [15], Ru(III) [30], Sn(IV) [31] and organometallic complexes of Re(I) [32] and Sn(IV) [33–37]. In spite of such a wide-ranging series of studies on a variety of metal complexes involving these ligands, the structures of the mer-

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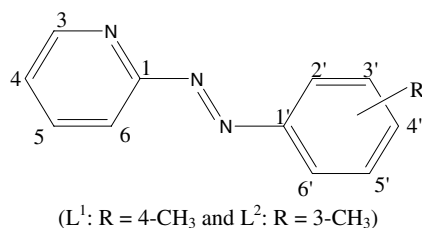


Fig. 1. Generic structure of the ligand.

cury complexes have remained uncertain [3,4]. A mercuration reaction was attempted with 2-[(*E*)-2-(phenyl)-1-diazenyl]pyridine but gave no detectable mercuration products, instead an addition product was isolated [3]. The same product (which was characterized by m.p. and microanalytical data) was again prepared by reacting mercuric chloride and 2-[(*E*)-2-(phenyl)-1-diazenyl]pyridine. Structures for the Hg(II) complexes of analogous ligands have been proposed on the basis of electronic, infrared and ¹H NMR spectra. However these studies cannot provide definitive conclusions concerning the co-ordination geometry of the complexes [4]. In this paper, X-ray diffraction results are reported for two mercury complexes in combination with their detailed ¹H, ¹³C, ¹⁹⁹Hg NMR spectroscopic data. Consequently, we are able to be quite confident of our descriptions of the structures of these complexes at least in the solid state.

2. Experimental

2.1. Materials

HgCl₂ (Merck) was used without further purification. All the solvents used in the reactions were of AR grade and dried using standard literature procedures. The ligands, viz., 2-[(*E*)-2-(4-methylphenyl)-1-diazenyl]pyridine and 2-[(*E*)-2-(3-methylphenyl)-1-diazenyl]pyridine (abbreviated as L¹ and L², respectively) were prepared according to the literature methods [38,39]. The complexes, dichloro-{2-[(*E*)-2-(4-methylphenyl)-1-diazenyl]pyridine}Hg(II); L¹HgCl₂ (**1**) and dichloro-{2-[(*E*)-2-(3-methylphenyl)-1-diazenyl]pyridine}Hg(II); L²HgCl₂ (**2**) were prepared by a method similar to that reported earlier with slight modifications [4]. A typical procedure is described below (see Section 2.3).

2.2. Physical measurements

Carbon, hydrogen and nitrogen analyses were performed with a Perkin–Elmer 2400 series II instrument. IR spectra in the range 4000–400 cm^{−1} were obtained on a Perkin Elmer 983 spectrophotometer with samples as KBr discs. For the ¹H (500.13 MHz) and ¹³C (125.76 MHz) NMR spectra and two-dimensional experiments,

the instrument used was a Bruker Avance 500 NMR spectrometer equipped with a triple (¹H/¹³C/broadband) 5 mm inverse probe. The ¹H and ¹³C chemical shifts were referred to internal TMS (δ = 0.00). Samples were dissolved either in acetone-d₆ or DMSO-d₆. Two-dimensional experiments (gradient-selected (gs)-COSY, gs-HSQC and gs-HMBC) were performed using the manufacturer's software (XWINNMR version 3.1). The ¹⁹⁹Hg (64.50 MHz) NMR spectra were recorded on a Bruker AMX 360 NMR spectrometer equipped with a 5 mm tunable broadband probe. The ¹⁹⁹Hg chemical shifts were referred to Hg(CH₃)₂ (δ = 0.0) by a calculation procedure using Ξ(¹⁹⁹Hg) = 17910841 Hz and Ξ(¹H) = 100000000 Hz for proton resonance in tetramethylsilane [40]. Positive values of chemical shifts denote shifts to higher frequencies.

2.3. Preparation of dichloro-{2-[(*E*)-2-(4-methylphenyl)-1-diazenyl]pyridine}Hg(II) (**1**)

HgCl₂ (0.345 g, 1.27 mmol) in 25 ml of acetone was added drop-wise to a stirred acetone solution (15 ml) containing L¹ (0.25 g, 1.26 mmol). The reaction mixture was stirred for 6 h at ambient temperature, and the solvent was removed using a rotary evaporator. The resulting dry mass was washed thoroughly with petroleum ether to remove any unreacted ligand, extracted into acetone (20 ml) and filtered. The red solution was allowed to evaporate slowly at ambient temperature until crystallization occurred. This yielded red crystals of **1** in 90 % yield; m.p.: 192–194 °C (180–181 °C) [4]. *Anal.* Calc. for C₁₂H₁₁N₃HgCl₂: C, 30.73; H, 2.35; N, 8.96. Found: C, 30.71; H, 2.38; N, 8.92%. IR (cm^{−1}): ν(C=N)_{py}: 1599 vs. ¹H NMR (acetone-d₆) δ: 8.83 (dd, 1H, 3-H), 8.20 (ddd, 1H, 5-H), 8.00 (a part of AA'MM' system, 2H, 2' and 6'-H), 7.96 (dd, 1H, 6-H), 7.70 (ddd, 1H, 4-H), 7.47 (a part of AA'MM' system, 2H, 3' and 5'-H), 2.47 (s, 3H, CH₃), ppm. (DMSO-d₆) δ: 8.80 (dd, 1H, 3-H), 7.96 (a part of AA'MM' system, 2H, 2' and 6'-H), 7.90 (dd, 1H, 6-H), 7.70 (ddd, 1H, 4-H), 7.49 (a part of AA'MM' system, 2H, 3' and 5'-H), 7.17 (ddd, 1H, 5-H), 2.46 (s, 3H, CH₃), ppm. ¹³C NMR (acetone-d₆) δ: (C-1; not observed due to very low solubility), 151.09 (C-1'), 150.31 (C-3), 144.87 (C-4'), 140.69 (C-5), 131.12 (C-3' and 5'), 127.24 (C-4), 124.56 (C-2' and 6'), 117.85 (C-6), 21.34 (CH₃), ppm. (DMSO-d₆) δ: 161.40 (C-1), 149.93 (C-1'), 149.65 (C-3), 144.08 (C-4'), 140.37 (C-5), 130.58 (C-3' and 5'), 126.73 (C-4), 123.68 (C-2' and 6'), 116.11 (C-6), 21.51 (CH₃), ppm. ¹⁹⁹Hg NMR (DMSO-d₆) δ: = −1460.2 ppm.

2.4. Preparation of dichloro-{2-[(*E*)-2-(3-methylphenyl)-1-diazenyl]pyridine}Hg(II) (**2**)

An identical method to that used to prepare **1** was employed. This led to the formation of red crystals of

2 which were dried in vacuo. Yield, 82%; m.p.: 178–179 °C (158 °C) [4]. *Anal.* Calc. for $C_{12}H_{11}N_3HgCl_2$: C, 30.73; H, 2.35; N, 8.96. Found: C, 30.70; H, 2.36; N, 8.95%. IR (cm^{-1}): $\nu(C=N)_{py}$: 1593 vs. ^1H NMR (acetone- d_6) δ : 8.88 (dd, 1H, 3-H), 8.26 (ddd, 1H, 5-H), 8.07 (dd, 1H, 6-H), 7.93 (m, 1H, 2'-H), 7.92 (m, 1H, 6'-H), 7.76 (ddd, 1H, 4-H), 7.55 (m, 1H, 5'-H), 7.50 (m, 1H, 4'-H), 2.48 (s, 3H, CH_3), ppm. (DMSO- d_6) δ : 8.83 (dd, 1H, 3-H), 8.22 (ddd, 1H, 5-H), 7.93 (dd, 1H, 6-H), 7.66 (m, 2H, 2' and 6'-H), 7.74 (ddd, 1H, 4-H), 7.56 (m, 2H, 5'-H), 7.51 (m, 1H, 4'-H), 2.46 (s, 3H, CH_3), ppm. ^{13}C NMR (acetone- d_6) δ : 161.68 (C-1), 152.79 (C-1'), 150.33 (C-3), 141.35 (C-5), 140.66 (C-3'), 134.80 (C-4'), 130.41 (C-5'), 127.94 (C-4), 124.60 (C-2'), 122.38 (C-6'), 119.77 (C-6), 21.33 (CH_3), ppm. (DMSO- d_6) δ : 160.89 (C-1), 151.72 (C-1'), 149.61 (C-3), 140.56 (C-5), 139.57 (C-3'), 133.99 (C-4'), 129.76 (C-5'), 126.89 (C-4), 123.42 (C-2'), 121.34 (C-6'), 116.44 (C-6), 20.08 (CH_3) ppm. ^{199}Hg NMR (acetone- d_6) δ : = -1349.8 and (DMSO- d_6) δ : = -1433.2 ppm.

2.5. X-ray crystallography

The intensity data for dark red block-shaped crystals of complexes **1** and **2** were measured on a Bruker P4S using Cu $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) and on a Bruker SMART 1K using Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), respectively. Empirical corrections were made from psi-scan curves [41]. The structures were solved by direct methods. All hydrogen atoms were given calculated positions. Neutral atom scattering factors were taken from the literature [42]. All computations were performed using the SHELXTL programmes [43]. All refinements were performed by full-matrix least-squares on F^2 . The data were corrected for Lorentz and polarization effects.

3. Results and discussion

3.1. Syntheses

The complexes dichloro-{2-[(*E*)-2-(4-methylphenyl)-1-diazenyl]pyridine}Hg(II) (**1**) and dichloro-{2-[(*E*)-2-(3-methylphenyl)-1-diazenyl]pyridine}Hg(II) (**2**) were prepared in good yield by stirring stoichiometric amounts of $HgCl_2$ and L^1 or L^2 in acetone. The complexes are stable and can be stored in the solid state at room temperature for months. Selected characterization data for the complexes are presented in the experimental section. The microanalytical data are in agreement with the calculated values and thus confirm the composition. They are highly soluble in acetone and DMSO but poorly soluble in common organic solvents.

3.2. NMR data

The ^1H and ^{13}C NMR spectra of the complexes display distinct signals for the ligand skeletons. The numbering scheme employed for the assignments of individual ^1H and ^{13}C signals are shown in Fig. 1. The efforts to use the NMR data in the elucidation of the coordination mode of the ligand and the geometries of the complexes were not successful since the solvents used for the spectra (DMSO- d_6 and acetone- d_6) could influence the nature of the coordination sphere.

3.3. X-ray diffraction analysis for complexes **1** and **2**

Pertinent crystallographic parameters are summarised in Table 1. The atomic numbering scheme and the coordination around the mercury atom for the complexes **1** and **2** are illustrated in Figs. 2 and 3, respectively. Selected bond lengths and bond angles are listed in Table 2 (for **1**) and 3 (for **2**). Considering the similarity of the ligands, the two complexes adopt surprisingly different structures. Complex **2** has an extended polymeric structure with 2-[(*E*)-2-(3-methylphenyl)-1-diazenyl]pyridine behaving as a monodentate ligand via the pyridyl nitrogen, and all the chlorine atoms serving to bridge mercury atoms, whereas complex **1** has a dimeric structure with 2-[(*E*)-2-(4-methylphenyl)-1-diazenyl]pyridine behaving as a bidentate ligand via the pyridyl nitrogen and one of the azo nitrogens, with a terminal chlorine on each Hg and a μ, μ' -dichloro bridge between the mercury atoms. But the coordination geometry around the mercury atom is similar in both complexes, each showing a distorted trigonal bipyramidal arrangement of the donor atoms.

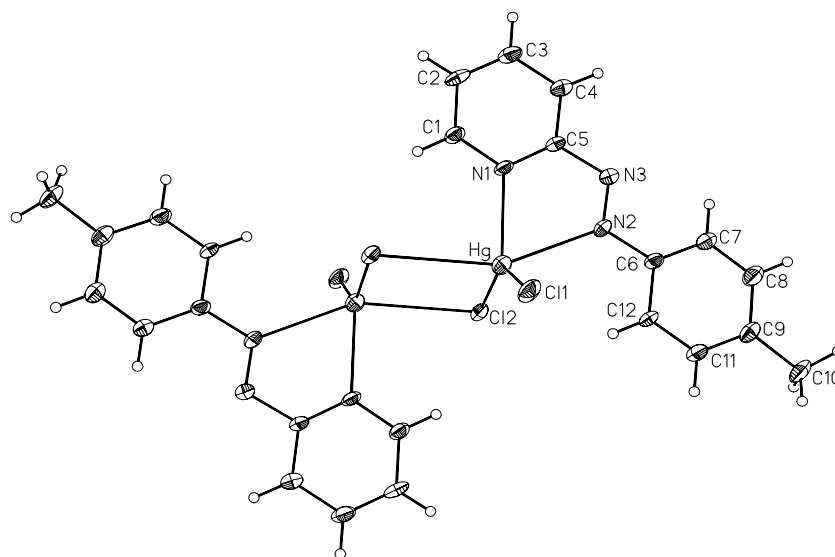
3.3.1. Dichloro-{2-[(*E*)-2-(4-methylphenyl)-1-diazenyl]pyridine}Hg(II) (**1**)

This complex occurs as centro-symmetric dimers in the solid state with the ligand 2-[(*E*)-2-(4-methylphenyl)-1-diazenyl]pyridine behaving as a bidentate via the pyridyl nitrogen and one of the azo nitrogens, with one bridging and one terminal chlorine atom. The geometry around each mercury atom is probably best described as being that of a distorted trigonal bipyramid, with the terminal chlorine, one bridging chlorine and the pyridyl nitrogen forming the trigonal plane and the other bridging chlorine and one of the azo-nitrogen atoms taking the axial positions. The structure is very similar in many regards to that recently reported for dichloro-mercury(II)-2-(phenylazo)-pyrimidine [44]. The bond angles making up the trigonal plane in **1** are N(1)–Hg–Cl(2), 105.3(2)°; Cl(1)–Hg–Cl(2), 137.5(9)° and N(1)–Hg–Cl(1), 117.0(2)°, giving a total of 359.8°. The corresponding bond angles found for dichloro-mercury(II)-2-(phenylazo)-pyrimidine are 105.3(2)°, 137.53(9)° and 117.0(2)°, giving a total of 359.8°. The

Table 1

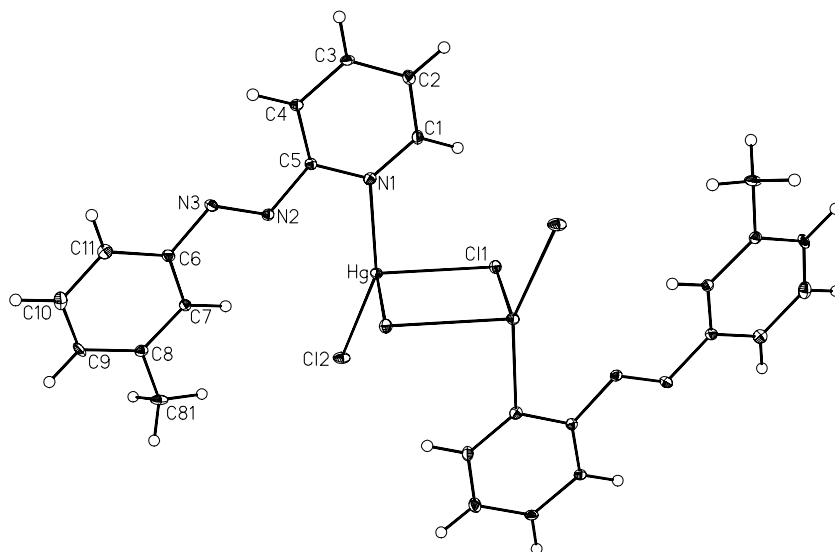
Crystallographic data and structure refinement for L^1HgCl_2 (**1**) and L^2HgCl_2 (**2**)

Parameters	L^1HgCl_2 (1)	L^2HgCl_2 (2)
Empirical formula	$C_{24}H_{22}Cl_4Hg_2N_6$	$C_{24}H_{22}Cl_4Hg_2N_6$
Formula weight	937.46	937.46
Temperature (K)	293 (2)	103 (2)
Crystal size (mm)	$0.06 \times 0.25 \times 0.04$	$0.12 \times 0.40 \times 0.48$
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Radiation (λ , Å)	Cu $K\alpha$ (1.54178)	Mo $K\alpha$ (0.71073)
a (Å)	7.4967 (13)	7.5149 (6)
b (Å)	9.416 (2)	9.2126 (6)
c (Å)	10.224 (3)	10.6784 (8)
α (°)	87.363 (16)	111.1840 (10)
β (°)	78.346 (15)	97.7140 (10)
γ (°)	80.456 (15)	91.3030 (10)
V (Å ³)	696.9 (3)	681.06 (9)
Z	1	1
D_{calc} (Mg/m ³)	2.234	2.286
μ (mm ⁻¹), $F(000)$	23.211, 436	11.676, 436
θ Range (°)	4.42–68.05	2.38–28.28
Reflections collected	2657	5226
Independent reflections (R_{int})	2447 (0.0540)	3194 (0.0399)
Absorption correction	empirical	semi-empirical from equivalents
Maximum and minimum transmission	0.94 and 0.11	0.89 and 0.62
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	2447/0/165	3194/0/165
Goodness-of-fit on F^2	1.040	1.080
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0540$, $wR_2 = 0.1448$	$R_1 = 0.0433$, $wR_2 = 0.1177$
R indices (all data)	$R_1 = 0.0588$, $wR_2 = 0.1514$	$R_1 = 0.0433$, $wR_2 = 0.1186$
Extinction coefficient	0.0008 (3)	0.0018 (11)
Largest differential peak and hole (e/Å ³)	1.566 and –2.092	4.345 and –4.800

Fig. 2. Molecular structure and crystallographic numbering scheme for **1**.

angle between the two “axial” bonds in **1**, [N(2)–Hg–Cl(2)] is 153.5(2)° whereas the corresponding angle for dichloro-mercury(II)-2-(phenylazo)-pyrimidine is 161.3°, indicating considerable distortions from linearity in both complexes. Both of these complexes exhibit both bridging and terminal Hg–Cl bonds, with bridging Hg–

Cl bond lengths of 2.428(2) and 2.909(2) Å for **1** compared to 2.42 and 2.92 Å, for dichloro-mercury(II)-2-(phenylazo)-pyrimidine. The equivalent terminal Hg–Cl distances are found to be 2.368(3) and 2.369(2) Å, respectively, in **1** and **2**, which is similar to terminal Hg–Cl distances reported elsewhere [45]. A fea-

Fig. 3. Molecular structure and crystallographic numbering scheme for **2**.Table 2
Selected bond lengths (Å) and angles (°) for L¹HgCl₂ (**1**)

Bond length		Bond angle	
Hg–N(1)	2.368 (7)	N(1)–Hg–Cl(2)	105.26 (19)
Hg–Cl(1)	2.368 (3)	N(1)–Hg–Cl(1)	117.03 (19)
Hg–Cl(2)	2.428 (2)	N(1)–Hg–N(2)	65.1 (3)
Hg–N(2)	2.541 (8)	Cl(1)–Hg–Cl(2)	137.53 (9)
Hg–Cl(2)#1	2.909 (2)	Cl(2)–Hg–N(2)	95.71 (17)
Cl(2)–Hg#1	2.909 (2)	Cl(1)–Hg–N(2)	98.38 (17)
N(2)–N(3)	1.265 (11)	Cl(1)–Hg–Cl(2)#1	96.67 (9)
N(2)–C(6)	1.413 (12)	N(1)–Hg–Cl(2)#1	88.6 (2)
N(3)–C(5)	1.444 (13)	N(2)–Hg–Cl(2)#1	153.47 (17)
		Cl(2)–Hg–Cl(2)#1	87.68 (8)
		C(1)–N(1)–Hg	123.1 (6)
		Hg–Cl(2)–Hg#1	92.32 (8)
		N(3)–N(2)–Hg	119.8 (6)
		C(5)–N(1)–Hg	119.2 (6)
		N(2)–N(3)–C(5)	113.5 (8)
		N(3)–N(2)–C(6)	114.4 (8)
		N(1)–C(5)–N(3)	121.6 (7)
		C(6)–N(2)–Hg	125.8 (5)
		C(12)–C(6)–N(2)	114.7 (8)
		C(4)–C(5)–N(3)	114.8 (9)
		C(7)–C(6)–N(2)	125.4 (8)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y + 1$, $-z$.

ture of the structures of these two complexes is the occurrence of a dinuclear $\mu_2\mu_2$ -chloro bridged Hg₂Cl₂ fragment, of almost identical dimensions in both. The Hg–N distances in the two complexes are also comparable, being 2.541(8) Å (Hg–N(azo)) and 2.368(7) Å (Hg–N(pyridyl)) in **1** and 2.55 Å (Hg–N(azo)) and 2.41 Å (Hg–N(pyrimidyl)) in dichloro-mercury(II)-2-(phenylazo)-pyrimidine. The N–N distance for the azo groups of the respective coordinated ligand molecules are 1.26 Å in both instances. Despite the great difference in the

Table 3
Selected bond lengths (Å) and angles (°) for L²HgCl₂ (**2**)

Bond length		Bond angle	
Hg–N(1)	2.223 (6)	N(1)–Hg–Cl(1)	92.51 (16)
Hg–Cl(1)	2.6071(16)	N(1)–Hg–Cl(2)	156.27 (16)
Hg–Cl(2)	2.3691 (17)	N(1)–Hg–Cl(1)#1	88.08 (15)
Hg–Cl(1)#1	2.7857 (15)	Cl(2)–Hg–Cl(1)	109.49 (6)
Cl(1)–Hg#1	2.7857(15)	Cl(1)–Hg–Cl(1)#1	91.30 (4)
N(2)–N(3)	1.249 (8)	Cl(2)–Hg–Cl(1)#1	99.82 (5)
N(2)–C(5)	1.423 (9)	C(5)–N(1)–Hg	113.4 (4)
N(3)–C(6)	1.417 (9)	Hg–Cl(1)–Hg#1	88.70 (4)
		N(2)–N(3)–C(6)	114.4 (6)
		C(1)–N(1)–Hg	126.7 (5)
		N(3)–N(2)–C(5)	113.7 (6)
		C(11)–C(6)–N(3)	114.5 (6)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y + 4$, $-z + 1$.

overall structures of **1** and **2**, the two complexes still share several common structural features. The geometry around the Hg atoms in both is essentially that of a distorted trigonal bipyramid, but in **2**, the axial atoms are the pyridyl nitrogen and one of the bridging chlorines whilst the trigonal plane comprises the remaining three bridging chlorine atoms. Another similar compound, dichloro-mercury(II)-1-ethyl-2-(phenylazo)-imidazole [44] has the same dimeric structure reported here for **1** and dichloro-mercury(II)-2-(phenylazo)-pyrimidine. However, the presence of the five-membered imidazole ring in the ligand of this complex rather than the six-membered pyridine or pyrimidine rings in the other ligands results in some differences in individual bond distances. But the overall structural features are the same in all three complexes.

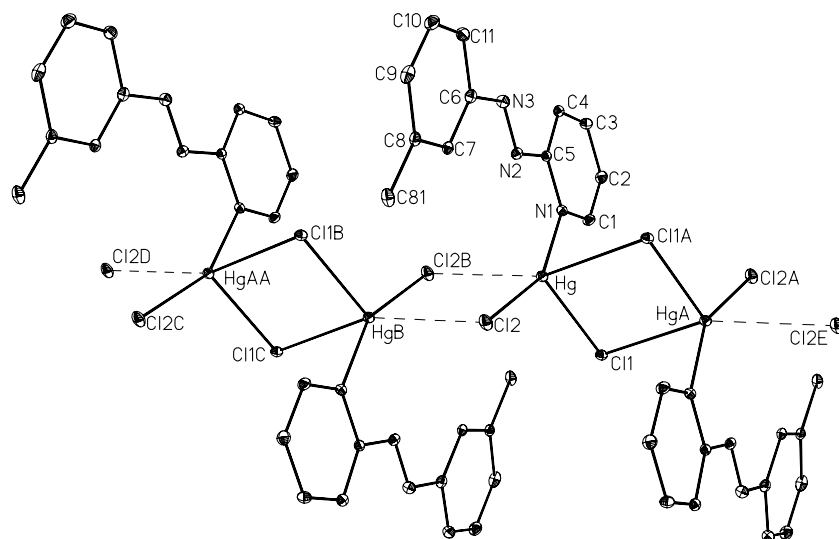


Fig. 4. Illustration of chlorine-bridging and polymeric structure of **2**.

3.3.2. Dichloro- $\{2-[(E)-2-(3\text{-methylphenyl})-1\text{-diazenyl}]pyridine\}Hg(II)$ (**2**)

Modifying the structure of the ligand by shifting the methyl group on the phenyl ring from the *para*- (in **1**) to the *meta*- (in **2**) position has a profound effect on the structure of the resulting complex. In contradistinction to **1** (as described above), compound **2** has an extended polymeric structure with 2-[(*E*)-2-(3-methylphenyl)-1-diazenyl]pyridine behaving as a monodentate ligand via the pyridyl nitrogen, and all the chlorine atoms serving to bridge mercury atoms. In this case, neither of the azo nitrogens is coordinated to mercury. A skewed repeating chain of Hg_2Cl_2 rhombohedra links the molecular units together, as shown in Fig. 4. Adjacent Hg_2Cl_2 units are staggered, whereas alternate ones lie in planes aligned parallel to one another. The coordinated ligand molecules are all aligned along planes parallel to each other, but in a third direction, roughly at right angles to the planes of each of the Hg_2Cl_2 rhombohedra. In addition to the chlorine bridges, which hold the units together in the polymeric structure, there are hydrogen-bonding interactions which provide some end-to-end cohesion between the monomeric units. These hydrogen bonds link the hydrogen atom on the carbon *para*- to the nitrogen in the pyridyl ring of each ligand with one of the bridging chlorines on an adjacent unit. The relevant bond distances are $C(3)-H(3A) = 0.95$ Å, $H(3A) \cdots Cl(1) = 2.80$ Å and $C(3)-Cl(1) = 3.49$ Å and the angle $C(3)-H(3A) \cdots Cl(1)$ is 130.3° . These hydrogen-bonding interactions as well as the packing arrangements in the crystal and the chlorine bridges are shown in Fig. 5. The bond angles making up the trigonal plane in **2** are $N(1)-Hg-Cl(1)$, $92.5(2)^\circ$; $N(1)-Hg-Cl(2)$, $156.3(2)^\circ$; and $Cl(1)-Hg-Cl(1A)$, $109.5(6)^\circ$ giving a total of 358.3° . The angle between the two axial bonds in **2**,

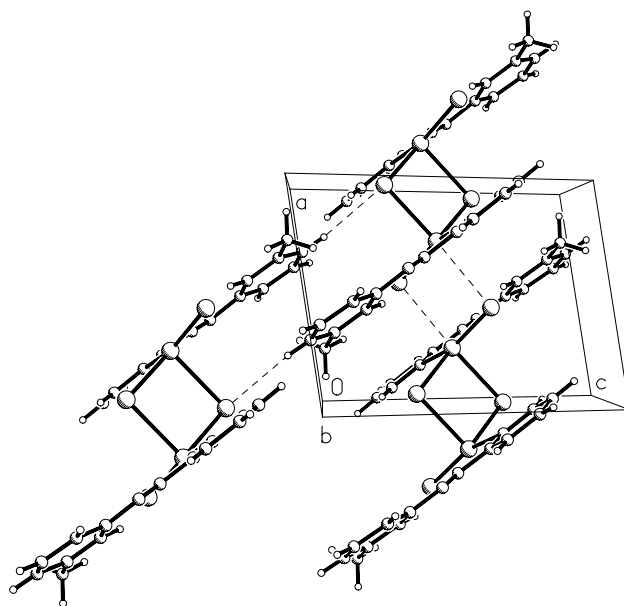


Fig. 5. Unit cell, chlorine bridging, and hydrogen bonding for **2**.

$[Cl(1A)-Hg-Cl(2B)]$ is 161.3° . These values are comparable to those in **1**.

4. Supplementary material

Full tables of bond lengths and angles, tables of non-hydrogen and hydrogen atomic coordinates, anisotropic thermal parameters for non-hydrogen atoms have been deposited with Cambridge Crystallographic data center, CCDC No. 230005 and 230006 for L^1HgCl_2 (**1**) and L^2HgCl_2 (**2**), respectively. 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.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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