

Mercury(II) Schiff Base Complexes: Synthesis, Spectral Characterization, Thermal Studies and Crystal Structures

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Two new mercury(II) Schiff base complexes [Hg((2,6-Cl-ba)₂-1,2-pn)X₂] (X = Cl (1), I (2) and (2,6-Cl-ba)₂-1,2-pn = N,N'-bis(2,6-dichlorobenzylidene)-1,2-diaminopropane) have been synthesized and characterized by elemental analysis (CHN), FT-IR and ¹H NMR spectroscopy. The crystal structure of complexes 1 and 2 were determined by single-crystal X-ray diffraction. X-ray results shown that the mercury(II) ions in these complexes have a distorted tetrahedral geometry with HgN₂Cl₂ and HgN₂I₂ chromophores, respectively. In these complexes, the Schiff base ligand (2,6-Cl-ba)₂-1,2-pn act as chelating bidentate ligand, coordinating *via* the two iminic nitrogen atoms and it adopts an *E,E* conformation. Finally, the thermal behavior of complexes was study using thermogravimetry in order to evaluate their thermal stability and thermal decomposition pathway.

Keywords: Mercury(II) complexes, Schiff base, Single-crystal, Tetrahedral geometry, Bidentate ligand

INTRODUCTION

Mercury(II) can form molecular complexes and crystal structures with varying coordination numbers (4, 5 and 6) [1-6]. Regardless its toxicity, mercury(II) is still being used various fields [11,12] and exhibits strong coordination to sulfur and nitrogen [10] among other interesting properties [9,13]. By careful selection of Schiff base ligands, we can direct formation of mononuclear [1,2,8,9], dinuclear [4,5,7,9] and polynuclear [2-6,9] mercury(II) complexes. The thermal decomposition studies of mercury(II) Schiff base complexes [14] have shown decomposition in three or four stages. As a part of our ongoing works dealing with the mercury(II) Schiff base complexes [15-21], herein we report the synthesis, characterization, thermal studies and crystal structures of mercury(II) Schiff base complexes with general formula of complexes [Hg((2,6-Cl-ba)₂-1,2-pn)X₂]

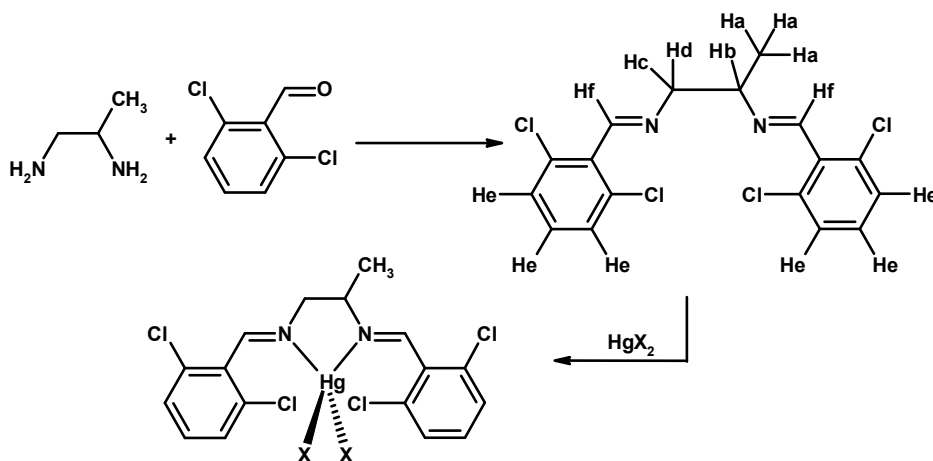
(X = Cl (1), I (2) and (2,6-Cl-ba)₂-1,2-pn = N,N'-bis(2,6-dichlorobenzylidene)-1,2-diaminopropane) (Scheme 1).

EXPERIMENTAL

Materials and Methods

All materials were commercially available and used as received without further purifications. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer, and results agreed with calculated values. Fourier transform infrared (FT-IR) spectra were recorded on a KBr disk on an FT-IR Perkin-Elmer spectrophotometer. ¹H NMR spectra were recorded on a BRUKER DRX-400 AVANCE spectrometer at 400 MHz. All chemical shifts are reported in δ units downfield from tetramethylsilane (TMS). The thermal stability were performed on a Perkin Elmer TG/DTA lab system 1 (Technology by SII) in argon atmosphere with a heating rate of 20 °C min⁻¹ in the temperature span of 50-800 °C.

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Scheme 1. Chemical procedure synthesis of (2,6-Cl-ba)₂-1,2-pn and its mercury(II) complexes

Structure Analysis

Suitable single crystals of mercury(II) complexes of the dimensions 0.23 mm × 0.16 mm × 0.04 mm (1) and of the dimensions 0.43 mm × 0.24 mm × 0.05 mm (2) were chosen for an X-ray diffraction study. The experiments were done at 120 K on a four-circles diffractometer Gemini of Oxford Diffraction using a graphite monochromated Mo-K α ($\lambda = 0.71073 \text{ \AA}$) radiation from a classical sealed X-ray tube, CCD detector Atlas S2. Crystal structures were solved by charge flipping with program SUPERFLIP [22] and refined with the Jana2006 program package [23] by full-matrix least-squares technique on F^2 . The molecular structure plots were prepared by Diamond 4.0 [24]. The hydrogen atoms were discernible in difference Fourier maps and could be refined to a reasonable geometry. According to common practice, the hydrogen atoms attached to carbons were kept in ideal positions during the refinement with a C-H distance of 0.96 Å and their isotropic atomic displacement parameters were set to 1.2 U_{eq} of their parent atoms. Crystal data, data collection, structure solution, and refinement details are summarized in Table 1.

Preparation of (2,6-Cl-ba)₂-1,2-pn. The bidentate Schiff base ligand (2,6-Cl-ba)₂-1,2-pn was prepared in high yield following the literature [25] using 1,2-propanediamine instead of 1,2-ethanediamine. Yield: 89%. M.p. (°C): ≈ 115 . *Anal.* Calcd. for C₁₇H₁₅Cl₄N₂: C, 52.44; H, 3.86; N, 7.20; Found: C, 52.46; H, 3.84; N, 7.22%. FT-IR (cm⁻¹): 1610 (-C=N-). ¹H NMR (DMSO-*d*₆, δ ppm): 1.29 (d, 3H_a), 3.72-3.93 (m, 3H_{b,c,d}), 7.36-7.50 (m, 6H_e), 8.45 (s, 2H_f).

Preparation of Hg((2,6-Cl-ba)₂-1,2-pn)Cl₂ (1). This complex was prepared in high yield following the literature [25] using (2,6-Cl-ba)₂-1,2-pn instead of (2,6-Cl-ba)₂-1,2-en. To a solution of HgCl₂ (0.1 mmol) in CH₃CN (5 mL) was added, with continuous stirring, a solution of (2,6-Cl-ba)₂-1,2-pn (0.1 mmol) in the minimum amount of CH₃OH. The mixture was stirred at room temperature for about 10 min to give a clear colorless solution. Colorless single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent at room temperature for several days. Yield: 88%. M.p. (°C): ≈ 142 . *Anal.* Calcd. for C₁₇H₁₅Cl₆HgN₂: C, 30.92; H, 2.12; N, 4.24%; Found: C, 30.81; H, 2.30; N, 4.27%. FT-IR (cm⁻¹): 1627 (-C=N-). ¹H NMR (DMSO-*d*₆, δ ppm): 1.30 (d, 3H_a), 3.70-4.04 (m, 3H_{b,c,d}), 7.15-7.60 (m, 6H_e), 8.52 (s, 2H_f).

Preparation of Hg((2,6-Cl-ba)₂-1,2-pn)I₂ (2). This complex was prepared in high yield following the procedure of 1 using HgI₂ instead of HgCl₂. Yield: 86%. M.p. (°C): ≈ 150 . *Anal.* Calc. for C₁₇H₁₅Cl₄I₂HgN₂: C, 24.21; H, 1.66; N, 3.32%; Found: C, 24.51; H, 1.77; N, 3.31%. FT-IR (cm⁻¹): 1627 (-C=N-). ¹H NMR (DMSO-*d*₆, δ ppm): 1.30 (d, 3H_a), 3.74-3.93 (m, 3H_{b,c,d}), 7.39-7.52 (m, 6H_e), 8.50 (s, 2H_f).

RESULTS AND DISCUSSION

FT-IR

In the FT-IR spectrum of Schiff base ligand (Fig. 1), a sharp peak at 1610 cm⁻¹ confirmed the presence of C=N

Table 1. Experimental Details of Mercury(II) Complexes 1 and 2

	1	2
Chemical formula	C ₁₇ H ₁₄ Cl ₆ HgN ₂	C ₁₇ H ₁₄ Cl ₄ HgI ₂ N ₂
Mw	659.6	842.5
Crystal system, Space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
a (Å)	8.0386 (3)	8.3233 (3)
b (Å)	8.2250 (3)	8.3980 (3)
c (Å)	18.1164 (5)	18.6346 (7)
α (°)	94.781 (3)	96.692 (3)
β (°)	96.984 (3)	97.956 (3)
γ (°)	115.467 (3)	114.843 (4)
V (Å ³)	1061.03 (7)	1148.30 (9)
Z	2	2
μ (mm ⁻¹)	8.01	9.86
Crystal size (mm)	0.23 × 0.16 × 0.04	0.43 × 0.24 × 0.05
T_{\min} , T_{\max}	0.328, 0.722	0.103, 0.587
R _{int} , S	0.034, 1.35	0.027, 1.02
$R[F^2 > 2\sigma(F^2)]$	0.039	0.031
$wR(F^2)$	0.100	0.083
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	1.86, -1.42	0.82, -0.60
Independent reflections	5193	5287
Reflections with $I > 3\sigma(I)$	4049	4275
Measured reflections, parameters	16704, 235	8434, 235

group [25-29]. This peak shift to the higher frequency (≈ 1627 cm⁻¹) in the mercury(II) complexes (Fig. 1) and confirmed the coordination of the azomethine group (-C=N-) to the mercury(II) ion [25]. The ligands stretching vibrations at 2900-3050 cm⁻¹ and 1450-1580 cm⁻¹, assigned to the C-H and C=C bonds, respectively.

¹H NMR

¹H NMR spectra of Schiff base ligand and its mercury(II)

complexes 1 and 2 were recorded using DMSO-*d*₆ solution and are shown in Fig. 2. All compounds have been showed four peaks groups. Two groups appear between 1.30-4.05 ppm indicating the aliphatic protons and one group appears between 7.15-7.60 ppm corresponding to aromatic protons. Also, the iminic protons (-HC=N-) appears as singlet at about 8.45-8.52 ppm. This peak is shifted to a higher region and shows that the coordination of iminic nitrogen to the mercury ion [21,23].

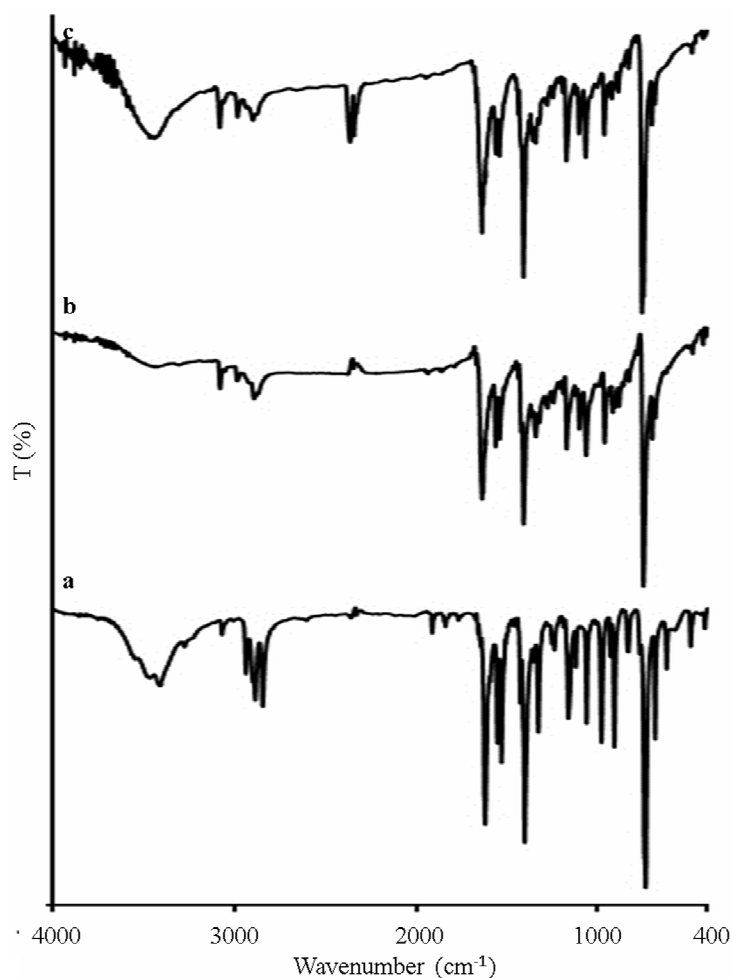


Fig. 1. FT-IR spectra of a) Schiff base ligand (2,6-Cl-ba)₂-1,2-pn; b) Hg((2,6-Cl-ba)₂-1,2-pn)Cl₂ (1) and c) Hg((2,6-Cl-ba)₂-1,2-pn)I₂ (2).

Thermal Study

TGA of the Schiff base ligand (2,6-Cl-ba)₂-1,2-pn and its mercury(II) complexes 1 and 2 are shown in Fig. 3. Schiff base ligand is stable until 140 °C showing the absence of water molecules adsorbed in the surface. After that, the ligand decomposed in two stages. The first stage is between 150-400 °C with weight losses of 45% and the second stage is between 400-780 °C with weight losses of 50%. Mercury(II) complexes 1 and 2 are stable until 240 °C. After this temperature, the complexes lose about 80% of their weight during three stages between 240-410 °C, 410-570 °C and 570-780 °C. Figure 3 show that the thermal

decomposition of the complexes is similar [28-30].

Crystal Structures of Mercury Complexes 1 and 2

The molecular structures of mercury(II) complexes 1 and 2 with the atom-numbering schemes are presented in Fig. 4. Selected bond distances and angles are given in Table 2. In these complexes, Schiff base acts as bidentate chelating ligand and coordinates to mercury(II) *via* two iminic nitrogen atoms. Two other coordination sites are occupied by two halogen atoms, Cl in 1 and I in 2 resulting in distorted tetrahedral coordination. The complexes are iso-structural and only difference is the type of halogen

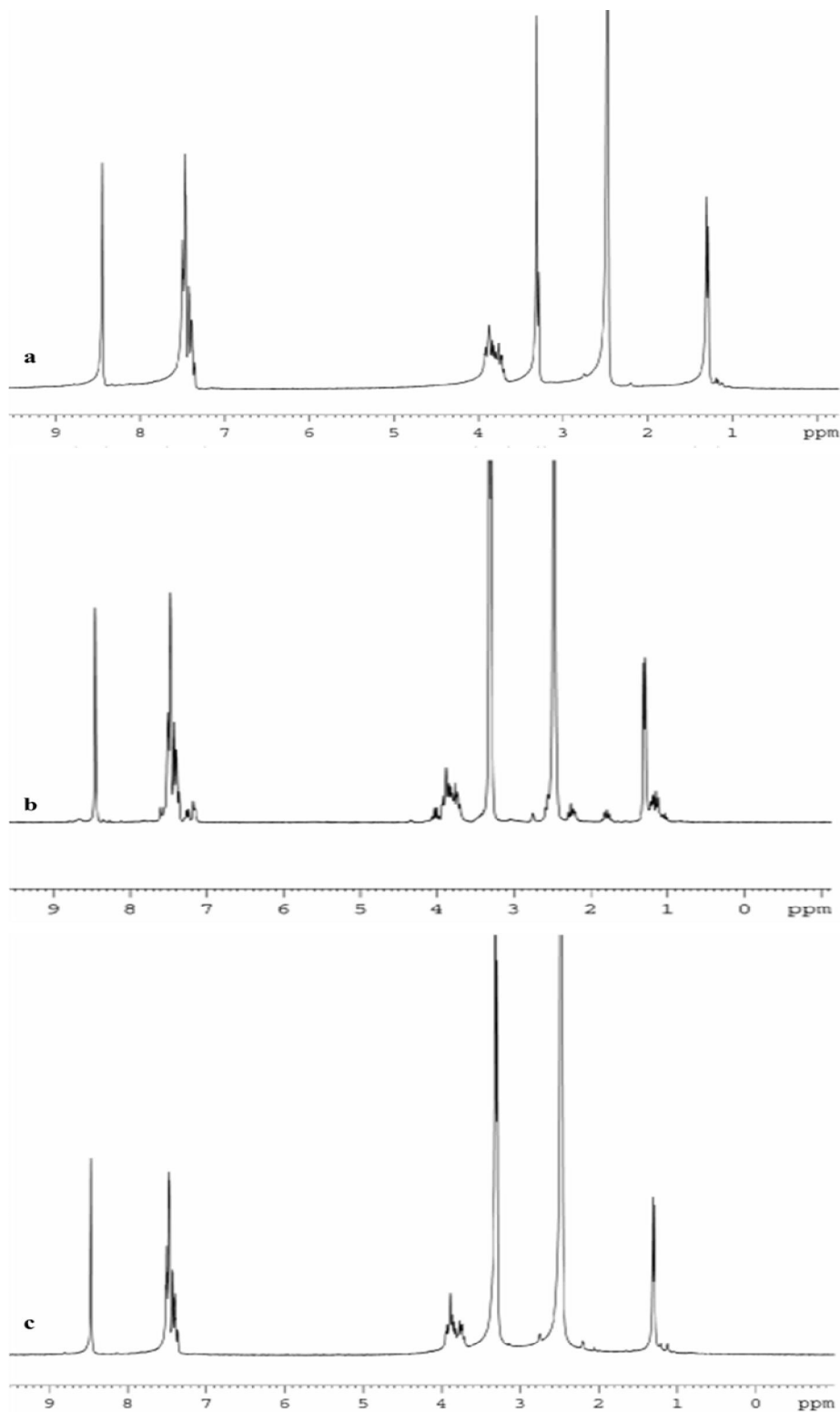


Fig. 2. ¹H NMR spectra of a) Schiff base ligand (2,6-Cl-ba)₂-1,2-pn; b) Hg((2,6-Cl-ba)₂-1,2-pn)Cl₂ (1) and c) Hg((2,6-Cl-ba)₂-1,2-pn)I₂ (2).

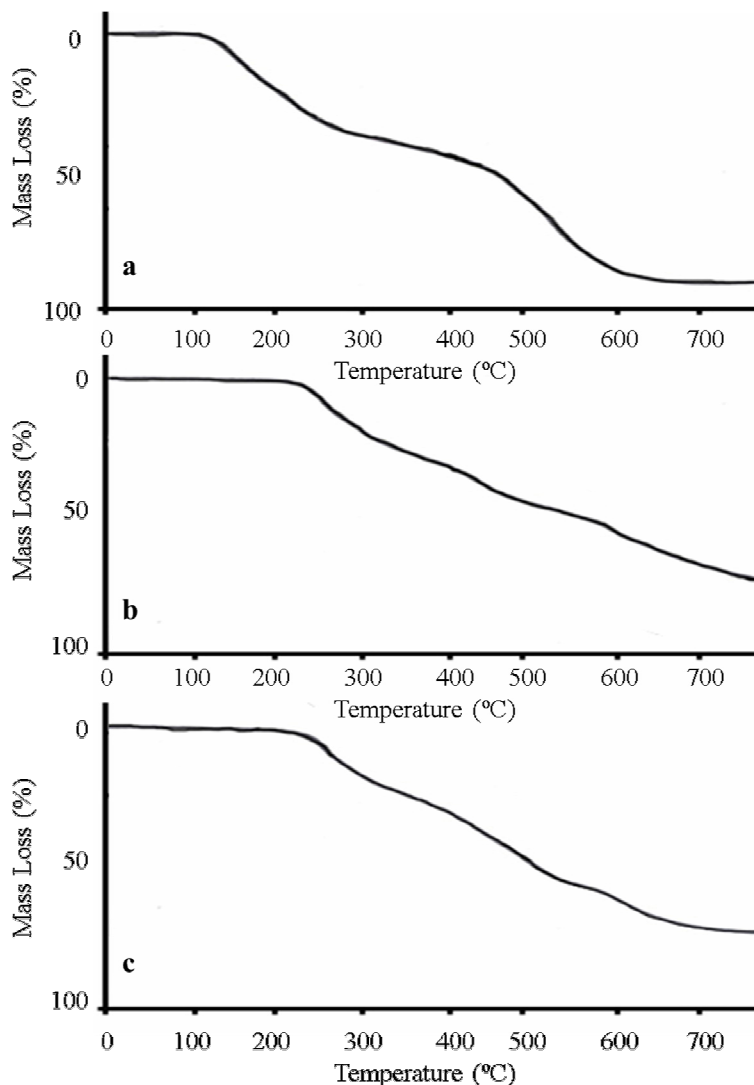


Fig. 3. TGA curves of a) Schiff base ligand (2,6-Cl-ba)₂-1,2-pn; b) Hg((2,6-Cl-ba)₂-1,2-pn)Cl₂ (1) and c) Hg((2,6-Cl-ba)₂-1,2-pn)I₂ (2).

atom that coordinates to mercury(II) ion. The average bond distance Hg-I is larger than the average of bond distance Hg-Cl, because of the bulky iodine atoms. Also, Hg1-N1 bond distance is larger than Hg1-N2 bond distance. The average of N1-C5 and N2-C11 bond distances is 1.26 Å, confirming the double bond character, while the average of N1-C8 and N2-C10 bond distances is 1.48 Å, confirming single bond character [21,25]. The average angle around the iminic nitrogen atoms N1 and N2 is about 118 and 120°,

corresponding to the sp² characteristic for these atoms [21,25].

For Schiff base ligands coordinated to mercury(II) in these complexes, we can define two planes. These planes formed *via* C1-C2-C3-C4-C5-C6 (plane A) and C12-C13-C14-C15-C16-C17 (plane B) (Fig. 5) show that the Schiff base ligand is not planar in the complexes 1 and 2. The dihedral angles between the plan A and B is 69.4 (5)° and 68.6 (4)° in complexes 1 and 2 respectively.

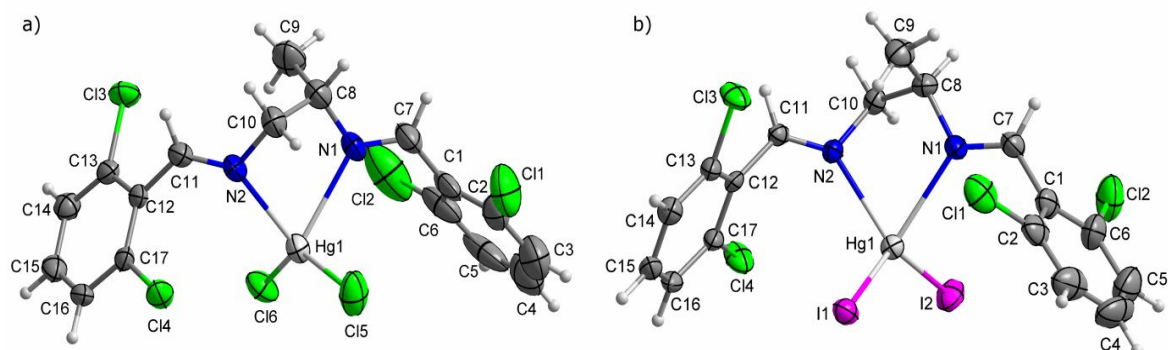


Fig. 4. The molecular structure of a) 1 and b) 2, showing 50% probability displacement ellipsoids and the atomic numbers.

Table 2. Selected Bond Distances and Angles of Mercury(II) Complexes 1 and 2

	1	2
Hg1-X1	2.3790(19)	2.6372(5)
Hg1-X2	2.3431(16)	2.6779(6)
Hg1-N1	2.461(7)	2.458(6)
Hg1-N2	2.386(6)	2.406(5)
N1-C7	1.255(9)	1.260(8)
N1-C8	1.475(11)	1.483(9)
N2-C10	1.476(9)	1.471(8)
N2-C11	1.259(8)	1.259(7)
X1-Hg1-X2	135.15(9)	128.76(2)
X1-Hg1-N1	92.85(14)	121.42(9)
X1-Hg1-N2	105.7(12)	112.59(9)
X2-Hg1-N1	120.00(12)	97.64(11)
X2-Hg1-N2	113.28(12)	110.95(9)
N1-Hg1N2	71.2(2)	70.44(18)
Hg1-N1-C7	127.7(6)	127.0(5)
Hg1-N1-C8	112.3(4)	114.4(4)
C7-N1-C8	118.4(7)	118.0(6)
Hg1-N2-C10	107.6(4)	108.6(3)
Hg1-N2-C11	131.0(4)	130.4(4)
C10-N2-C11	120.0(7)	119.4(6)

X1 represents Cl5 in structure 1 and I1 in structure 2. X2 represents Cl6 in structure 1 and I2 in structure 2.

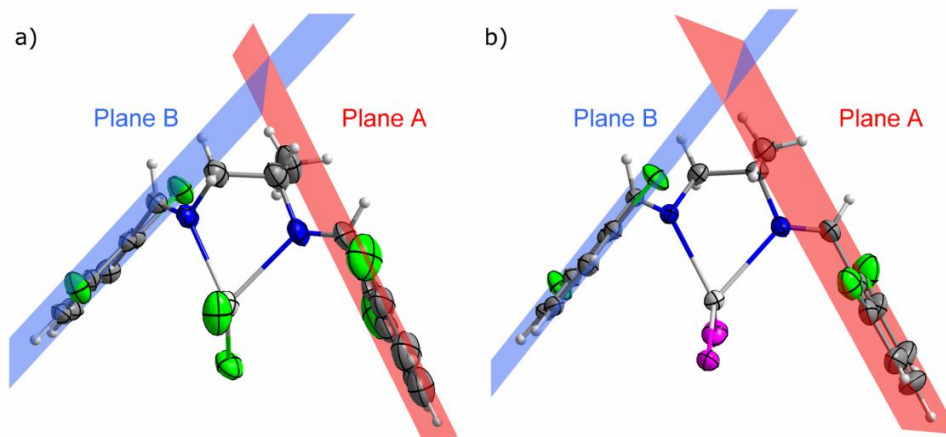


Fig. 5. The planes in mercury(II) complex 1.

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SUPPLEMENTARY DATA

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC Nos. 1989299 (1) and 1989298 (2). Copy of the data can be obtained free of charge on deposit@ccdc.cam.ac.uk.

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