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# Preparation, structural and physical studies of mercury(II) halide complexes with the N,N′-chelating biheteroaromatic ligand 2-(2′-pyridyl)quinoxaline

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## Abstract

The mercury(II) complexes $[Hg_2X_4L_2]$ (X = Cl, Br) and $[HgI_2L]$, where L is 2-(2′-pyridyl)quinoxaline, have been prepared and studied by a combination of conductivity measurements and FT-IR and far-IR, Raman and $^1H$ NMR spectroscopy. The structures of the free ligand L and $[Hg_2Cl_4L_2]$ have been determined from three-dimensional X-ray data collected by counter methods. Compound L crystallizes in space group $P2_1/c$ with $a = 4.163(2)$, $b = 16.953(4)$, $c = 14.509(3)$ Å, $\beta = 94.79(2)°$ and $Z = 4$. The complex $[Hg_2Cl_4L_2]$ crystallizes in space group $P2_1/n$ with $a = 7.627(3)$, $b = 15.617(4)$, $c = 11.099(4)$, $\beta = 92.03(3)°$ and $Z = 2$. In free L, the pyridine nitrogen and the nearest quinoxaline nitrogen are located on the opposite side of the carbon–carbon bond which connects the two rings; the reverse conformation has been observed on complexation. The structure of $[Hg_2Cl_4L_2]$ consists of two Hg(II) centres bridged by two chloro ligands, with a terminal chloride and a chelating molecule of L completing five-coordination at each metal. The geometry at mercury is a distorted trigonal bipyramid with the bridging chlorides occupying apical and equatorial sites of each Hg(II) atom. The bromo compound is isostructural with $[Hg_2Cl_4L_2]$, while a monomeric pseudotetrahedral structure is assigned for the iodo complex in the solid state.

*Keywords:* Crystal structures; Mercury complexes; Bidentate ligand complexes; Chelate complexes; Dinuclear complexes

## 1. Introduction

It is 105 years since Blau first reported [1] the synthesis of 2,2-bipyridine (bpy) and described the first transition metal complexes of this important ligand. Since then bpy has been continuously and extensively used in both analytical and coordination chemistry [2–4]. It is only recently, however, that systematic studies of substituted derivatives of bpy and related α-diimine ligands have been undertaken [4]. Much of this work has been stimulated by the intense interest in the redox and photocatalytic properties of the $[Ru(bpy)_3]^{2+}$ cation [5]. Although substituents on the pyridine rings can significantly modify the properties of complexes containing bpy ligands, much greater changes result from the replacement of one (or both) of the pyridine rings by other nitrogen-containing heterocycles [4] due to the different electronic properties of the various heterocycles. However, only a few such ligands have been extensively employed in coordination chemistry. It is certain [4] that there is rich, untouched chemistry in the syntheses of many possible ligands formed by replacing one of the pyridine rings of bpy with another N-heterocycle and in the systematic study of their coordination chemistry. Recently, we became witnesses for this by unexpectedly synthesizing the novel ligand 2-(2′-pyridyl)quinoxaline (L) from the reaction between 2-acetylpyridine and 1,2-phenylenediamine [6] and studying its interesting coordinating properties toward 3d metals [6–8].

Compound L, which may combine the chelating properties of bpy [2–4] with the bridging properties of quinoxaline [9] and act as a binucleating ligand, has two non-equivalent sites for metal coordination. Such

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ligands offer great potential, particularly for the synthesis of heteronuclear complexes, since different metals can selectively complex at the different coordination sites [10]. Surprisingly, little effort has thus far been directed towards the systematic investigation of the coordination chemistry of such ligands [10].

As an extension of our studies of transition metals/L chemistry [6–8], we have begun to investigate the reactions of $MX_2$ (M = Zn, Cd, Hg; X = Cl, Br, I) with L. The $d^{10}$ metal(II)–halide adducts are rather interesting because they show a variety of coordination numbers and geometries closely dependent on many factors, among which are interactions due to crystal-packing and hydrogen-bonding forces as well as metal ion and halide dimensions [11]. This paper reports the preparation and detailed characterization of the 1:1 $HgX_2$/L complexes; the chloro complex has been structurally characterized by X-ray crystallography. Furthermore, we describe the X-ray structure of free L.

## 2. Experimental

### 2.1. Materials and physical measurements

All manipulations were performed under aerobic conditions using materials as received. Mercury(II) chloride, bromide and iodide were purchased from Aldrich. L was synthesized as described recently [6]. Microanalyses were performed by the Imperial College, Microanalytical Service, London.

Conductivity measurements were carried out at 25 °C with a Metrohm-Herisau E-527 bridge and a cell of standard constant. TG, DTG and DTA data (30–600 °C) were obtained on a Seiko 200 instrument in a dinitrogen gas flow (50 $cm^3$ $min^{-1}$). Sample weights of 2–5 mg and a heating rate of 5 °C $min^{-1}$ were used. X-ray powder diffraction patterns were obtained on a Siemens D500 diffractometer using Cu K$\alpha$ radiation ($4 < 2\theta < 70°$). IR and far-IR spectra were recorded on a Bruker IFS 113v Fourier-transform spectrometer with a liquid nitrogen-cooled MCT detector, using KBr (4000–400 $cm^{-1}$) and polyethylene (400–40 $cm^{-1}$) pellets; the resolution was 1 $cm^{-1}$. The spectra were also recorded in the range 4000–200 $cm^{-1}$ as Nujol and hexachlorobutadiene mulls between CsI discs. Solid-state, room-temperature Raman spectra were excited with 200 or 80 mV of $Ar^+$ 514.5 nm radiation using a Spectra-Physics model 2020 argon ion laser, and were recorded at 4.0 $cm^{-1}$ resolution using a SPEX 1403, 0.85 m double monochromator spectrometer. One- and two-dimensional COSY $^1H$ NMR spectra were recorded in DMSO-$d_6$ at 25 ± 1 °C with a Bruker AC200 spectrometer equipped with an Aspect 3000 computer system. Field stabilization was provided by an internal deuterium lock-signal. The 2QF-COSY Bruker microprogram, with presaturation of solvent, was used for the 2D homonuclear study.

### 2.2. Preparations

#### 2.2.1. [$Hg_2Cl_4L_2$]

To a stirred, colourless solution of $HgCl_2$ (0.27 g, 1.0 mmol) in EtOH (8 ml) was added a solution of L (0.21 g, 1.0 mmol) in the same solvent (10 ml). No noticeable colour change occurred, but, after a few minutes, a fine white precipitate was deposited. Stirring was continued for a further 90 min at room temperature. The solid was collected by filtration, washed with cold EtOH (5 ml) and $Et_2O$ (2×5 ml) and dried in vacuo over silica gel. The yield was 0.29 g (61%). *Anal.* Calc. for $C_{26}H_{18}N_6Cl_4Hg_2$: C, 32.6; H, 1.9; N, 8.8. Found: C, 32.5; H, 1.9; N, 8.8%. The molar conductance ($\Lambda_M$) value for a $\sim 1\times10^{-3}$ M DMF solution at 25 °C was 4 S $cm^2$ $mol^{-1}$. Crystals of [$Hg_2Cl_4L_2$] suitable for X-ray structure analysis were obtained by slow cooling of a hot concentrated solution of this complex in MeOH.

#### 2.2.2. [$Hg_2Br_4L_2$]

Using $HgBr_2$ and following the same procedure as described above for the corresponding chloro complex, a pink microcrystalline material was isolated. Yield 70%. Recrystallization can be effected from MeOH–$CH_3COCH_3$ (80:20, vol./vol.). *Anal.* Calc. for $C_{26}H_{18}N_6Br_4Hg_2$: C, 27.5; H, 1.6; N, 7.4. Found: C, 27.3; H, 1.7; N, 7.5%. $\Lambda_M$ (DMF, $10^{-3}$ M, 25 °C): 5 S $cm^2$ $mol^{-1}$.

#### 2.2.3. [$HgI_2L$]

To a solution of L (0.15 g, 0.7 mmol) in EtOH (8 ml) was added a solution of $HgI_2$ (0.33 g, 0.7 mmol) in MeOH (20 ml). To the obtained pale yellow solution was added triethyl orthoformate (3 ml). The solution was stirred under reflux for 30 min and a yellow precipitate was formed. Stirring was continued at room temperature and, when precipitation was judged to be complete, the microcrystalline powder was filtered off, washed with cold EtOH (5 ml) and $Et_2O$ (4×5 ml) and dried in air. The yield was 0.25 g (54%). Recrystallization can be effected from MeOH. *Anal.* Calc. for $C_{13}H_9N_3I_2Hg$: C, 23.6; H, 1.4; N, 6.3. Found: C, 23.8; H, 1.5; N, 6.4%. $\Lambda_M$ (DMF, $10^{-3}$ M, 25 °C): 9 S $cm^2$ $mol^{-1}$.

### 2.3. X-ray crystallography and structure solution

Colourless crystals of L were isolated from a concentrated ethanolic solution. Data were collected on a Rigaku AFC6S diffractometer controlled by TEXRAY software. Crystal data and details of data collection and refinement are given in Table 1. Empirical absorption corrections were made. Standard intensities

Table 1
Summary of crystal and intensity collection data for compounds L and $[Hg_2Cl_4L_2]$

| Compound | L | $[Hg_2Cl_4L_2]$ |
|---|---|---|
| Chemical formula | $C_{13}H_9N_3$ | $C_{26}H_{18}N_6Cl_4Hg_2$ |
| Formula weight | 207.23 | 957.46 |
| Crystal colour | colourless | white |
| Crystal size (mm) | 0.50×0.07×0.07 | 0.33×0.30×0.20 |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/c$ | $P2_1/n$ |
| $a$ (Å) | 4.163(2) | 7.627(3) |
| $b$ (Å) | 16.953(4) | 15.617(4) |
| $c$ (Å) | 14.509(3) | 11.099(4) |
| $\beta$ (°) | 94.79(2) | 92.03(3) |
| $V$ (Å$^3$) | 1020.4(5) | 1321.2(8) |
| $Z$ | 4 | 2 |
| $D_{calc}$ (g cm$^{-3}$) | 1.349 | 2.407 |
| $F(000)$ | 432 | 888 |
| Scan method | $\theta/2\theta$ | $\theta/2\theta$ |
| $\lambda$ (Å) | 0.70930 | 0.70930 |
| $2\theta_{max}$ (°) | 45.0 | 45.0 |
| $h$ Range | −4 to 4 | −8 to 8 |
| $k$ Range | 0–18 | 0–16 |
| $l$ Range | 0–15 | 0–11 |
| Reflections collected | 1496 | 1882 |
| Reflections unique | 1282 | 1735 |
| Reflections used ($I > n\sigma(I)$) | 575 ($n = 2.0$) | 1345 ($n = 2.5$) |
| Parameters refined | 182 | 173 |
| $GOF$ [a] | 1.38 | 1.91 |
| $R_b$ (obs., all data) | 0.045, 0.136 | 0.037, 0.060 |
| $R_w$ [c] (obs., all data) | 0.038, 0.044 | 0.040, 0.040 |
| $[\Delta/\sigma]_{max}$ | 0.102 | 0.090 |
| $(\Delta p)_{max}$, $(\Delta p)_{min}$ (e Å$^{-3}$) | 0.31, −0.25 | 0.94, −1.46 |

[a] $GOF = [\Sigma w(|F_o| - |F_c|)^2/(N-P)]^{1/2}$, where $P$ = number of parameters and $N$ = number of observed reflections.

[b] $R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$.

[c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

varied an average of 0.7% for L and only 0.3% for $[Hg_2Cl_4L_2]$ over the course of collection. The structures were solved by direct methods and refined by blocked full-matrix least-squares. For both compounds all non-hydrogen atoms were readily located and refined with anisotropic thermal parameters: all hydrogen atoms were clearly visible in a subsequent difference Fourier map, and were included in the final cycles and refined with isotropic thermal parameters. All computing was done using the NRCVAX system of crystallographic software [12]. Scattering factors were taken from Ref. [13].

## 3. Results and discussion

### 3.1. Preparation and physical properties of the complexes

2-(2′-Pyridyl)quinoxaline (L) was reacted with the mercury(II) halides $HgX_2$ (X = Cl, Br, I) in mole ratios of 0.5:1, 1:1 and 2:1. Complexes of 1:1 stoichiometry were obtained in all cases (Eqs. (1) and (2)). This

$$2HgX_2 + 2L \xrightarrow[\text{r.t.}]{\text{EtOH}} [Hg_2X_4L_2] \tag{1}$$

X = Cl, Br

$$HgI_2 + L \xrightarrow[\text{reflux}]{\text{MeOH–EtOH–TEOF}} [HgI_2L] \tag{2}$$

behaviour contrasts with that of the halides of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II), all of which form a complete set of 1:1 [6] and 2:1 [14] complexes with L. An important point of synthetic interest is the fact that the amount of $H_2O$ in the solvents affects the purity of the iodo complex. Pure $[HgI_2L]$ could be isolated only in water-free (use of triethylorthoformate, reflux) reaction mixtures.

The complexes are stable in the normal laboratory atmosphere and soluble in $CHCl_3$, $CH_2Cl_2$, warm MeOH, hot MeCN, DMF and DMSO, but to varying extents. The $\Lambda_M$ values in DMF are in accord with the three complexes being formulated as non-electrolytes [15]. X-ray powder diffraction patterns indicate that each solid represents a definite compound, which is not contaminated with starting materials or/and by-products. The pattern of the bromo compound shows that this is isostructural with the chloro complex, whose centrosymmetric dinuclear structure has been established by crystallography (vide infra). The different pattern observed for the iodo complex suggests a different structure. We had hoped to structurally characterize the iodo complex by single-crystal X-ray crystallography, but were thwarted on numerous occasions by poor diffraction or twinning problems; thus, the characterization of this compound was based on spectroscopic techniques.

The thermal decomposition of the complexes was studied using TG/DTG/DTA techniques. The thermograms show that the chloro and bromo complexes undergo sublimation. The data reveal only a single endothermic step (one DTG maximum, one DTA peak), corresponding to total mass loss, at 132–226 (X = Cl) and 122–237 (X = Br) °C. Sublimation of these complexes was confirmed by the observation of a condensed sublimate at the outlet of the furnace after each run [16] and by the fact that the IR spectrum of this sublimate is identical with that of the corresponding original complex [17]. The thermogram of $[HgI_2L]$ shows a 98.3% mass loss between 145 and 230 °C. The observation of only one DTG peak clearly identifies one process, i.e. the thermal decomposition by loss of L followed by vaporization of $HgI_2$ can be ruled out. However, there are two endothermic DTA peaks, a sharp one at 204 °C and a broader one (this has exactly the same profile as in the case of $[Hg_2X_4L_2]$) at 228 °C. A possible explanation of this peculiar behaviour is that the first DTA peak corresponds to the melting of the complex during sublimation. In accord with this, the visually observed melting point of [$HgI_2L$], at a slow heating rate, is 201–205 °C.

### *3.2. Description of structures*

ORTEP diagrams and atomic labelling schemes for L and [$Hg_2Cl_4L_2$] are given in Figs. 1 and 2. Fractional atomic coordinates and selected bond distances and angles for the two compounds are listed in Tables 2–5.

As the X-ray crystal structure analysis of free L shows, the two nitrogen atoms N(1) and N(3) are located on opposite sides of the C(1)–C(9) bond. The length of the bond between the pyridine and the quinoxaline ring is 1.486(7) Å, almost identical with the distance between the pyridine rings of bpy (1.50 Å) [18]. The forces which hold the molecules of L in the crystal are van der Waals forces. This situation would accord for the rather low melting point (114–116 °C) of L and its propensity to sublime slowly at 35–40 °C.

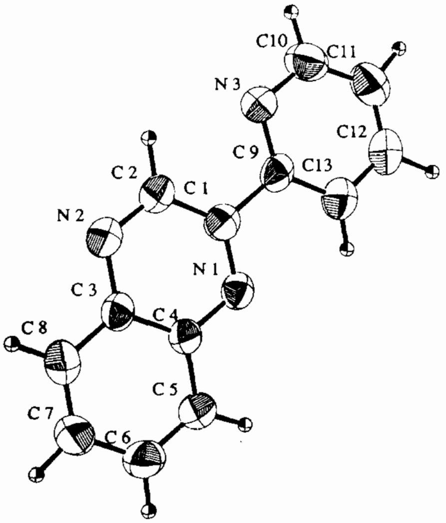

Fig. 1. ORTEP plot of the molecular structure of L showing the atom labelling scheme; thermal ellipsoids scaled to enclose 50% of the electron density.

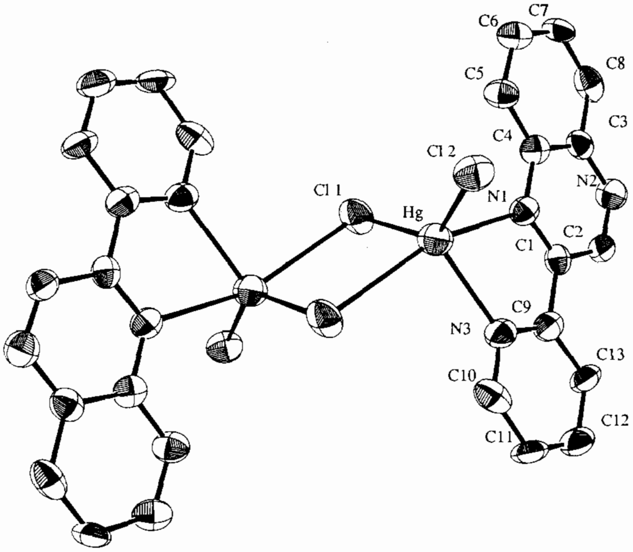

Fig. 2. ORTEP plot of the molecular structure of [$Hg_2Cl_4L_2$] showing the atom labelling scheme used; thermal ellipsoids scaled to enclose 50% of the electron density. Atoms generated by the centre of symmetry are not labelled.

Table 2
Atomic coordinates and equivalent isotropic thermal parameters (Å$^2$) for the non-hydrogen atoms of L (e.s.d.s in parentheses)

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| N(1) | 0.8140(10) | 0.40787(21) | 0.11668(23) | 3.92(20) |
| N(2) | 1.0122(11) | 0.26135(22) | 0.19437(24) | 4.66(22) |
| N(3) | 0.4986(11) | 0.41922(22) | 0.3373(3) | 4.71(22) |
| C(1) | 0.7519(12) | 0.3867(3) | 0.2002(3) | 3.99(24) |
| C(2) | 0.8504(12) | 0.3139(3) | 0.2393(3) | 4.4(3) |
| C(3) | 1.0756(12) | 0.2810(3) | 0.1062(3) | 4.0(3) |
| C(4) | 0.9779(112) | 0.3540(3) | 0.0683(3) | 3.7(3) |
| C(5) | 1.0482(14) | 0.3714(3) | −0.0226(3) | 4.9(3) |
| C(6) | 1.2036(14) | 0.3178(3) | −0.0727(3) | 5.3(3) |
| C(7) | 1.3001(13) | 0.2449(3) | −0.0337(3) | 5.3(3) |
| C(8) | 1.2422(13) | 0.2277(3) | 0.0541(3) | 4.8(3) |
| C(9) | 0.5706(12) | 0.4440(3) | 0.2535(3) | 3.9(3) |
| C(10) | 0.3374(14) | 0.4697(3) | 0.3870(3) | 5.6(3) |
| C(11) | 0.2498(14) | 0.5451(3) | 0.3570(4) | 5.6(3) |
| C(12) | 0.3174(14) | 0.5681(3) | 0.2710(4) | 5.5(3) |
| C(13) | 0.4843(14) | 0.5173(3) | 0.2179(3) | 4.7(3) |

Table 3
Atomic coordinates and equivalent isotropic thermal parameters (Å$^2$) for the non-hydrogen atoms of [$Hg_2Cl_4L_2$] (e.s.d.s in parentheses)

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Hg | 0.08788(8) | 0.97911(4) | 0.16611(5) | 3.81(2) |
| Cl(1) | −0.1273(5) | 0.90953(23) | 0.0220(3) | 4.15(18) |
| Cl(2) | 0.3822(5) | 0.94707(23) | 0.2314(3) | 4.03(18) |
| N(1) | −0.0721(14) | 0.9097(6) | 0.3305(9) | 3.0(5) |
| N(2) | −0.2875(14) | 0.8444(7) | 0.5060(10) | 3.7(5) |
| N(3) | −0.0531(14) | 1.0805(7) | 0.2833(9) | 3.3(5) |
| C(1) | −0.1691(16) | 0.9601(8) | 0.3933(10) | 2.7(6) |
| C(2) | −0.2768(18) | 0.9251(8) | 0.4821(11) | 3.4(6) |
| C(3) | −0.1854(17) | 0.7917(8) | 0.4415(11) | 3.2(6) |
| C(4) | −0.0731(17) | 0.8231(8) | 0.3522(11) | 2.9(6) |
| C(5) | 0.0369(17) | 0.7674(8) | 0.2894(12) | 3.4(7) |
| C(6) | 0.0323(18) | 0.6827(9) | 0.3151(12) | 3.8(7) |
| C(7) | −0.0737(19) | 0.6483(8) | 0.4015(12) | 3.7(7) |
| C(8) | −0.1808(18) | 0.7022(9) | 0.4630(11) | 3.7(7) |
| C(9) | −0.1589(17) | 1.0540(8) | 0.3732(11) | 3.2(6) |
| C(10) | −0.0349(19) | 1.1654(9) | 0.2666(13) | 3.9(7) |
| C(11) | −0.1172(20) | 1.2259(8) | 0.3332(13) | 4.2(7) |
| C(12) | −0.2250(19) | 1.1987(9) | 0.4225(12) | 4.3(7) |
| C(13) | −0.2466(18) | 1.1115(8) | 0.4418(12) | 3.5(6) |

The structure of [$Hg_2Cl_4L_2$] consists of centrosymmetric dinuclear molecules with two bridging chloro ligands; a terminal chloro ligand and a bidentate chelating L molecule complete five-coordination at each mercury(II) atom. In contrast to the conformation of free L, in the coordinated L molecule, the pyridine

Table 4
Selected bond distances (Å) and angles (°) for L

| | | | |
|---|---|---|---|
| C(1)–N(1) | 1.311(5) | N(2)–C(2) | 1.322(6) |
| N(1)–C(4) | 1.369(6) | C(2)–C(1) | 1.405(7) |
| C(4)–C(5) | 1.405(6) | C(1)–C(9) | 1.486(7) |
| C(5)–C(6) | 1.362(7) | C(9)–N(3) | 1.344(6) |
| C(6)–C(7) | 1.403(7) | N(3)–C(10) | 1.335(6) |
| C(7)–C(8) | 1.349(6) | C(10)–C(11) | 1.389(8) |
| C(8)–C(3) | 1.398(7) | C(11)–C(12) | 1.360(7) |
| C(3)–C(4) | 1.401(6) | C(12)–C(13) | 1.382(7) |
| C(3)–N(2) | 1.368(5) | C(13)–C(9) | 1.381(7) |
| C(1)–N(1)–C(4) | 115.9(4) | C(1)–C(9)–N(3) | 115.3(4) |
| N(1)–C(4)–C(5) | 119.5(4) | C(9)–N(3)–C(10) | 116.6(4) |
| C(5)–C(6)–C(7) | 120.3(4) | N(3)–C(10)–C(11) | 123.5(4) |
| C(2)–C(1)–N(1) | 122.7(4) | C(12)–C(13)–C(9) | 118.6(4) |

Table 5
Selected bond distances (Å) and angles (°) for $[Hg_2ClL_2]^a$

| | | | |
|---|---|---|---|
| Hg–Cl(1) | 2.500(4) | Hg–N(1) | 2.480(4) |
| Hg–Cl(1′) | 2.742(3) | C(10)–N(3) | 1.347(17) |
| Hg–Cl(2) | 2.387(4) | N(3)–C(9) | 1.369(17) |
| Hg–N(3) | 2.336(10) | N(1)–C(4) | 1.373(16) |
| | | Hg…Hg | 3.9329(18) |
| Cl(1)–Hg–Cl(1′) | 82.9(1) | N(3)–Hg–N(1) | 68.8(1) |
| Cl(1)–Hg–N(3) | 110.3(3) | N(3)–Hg–Cl(2) | 114.8(3) |
| Cl(1)–Hg–N(1) | 87.2(1) | N(1)–Hg–Cl(2) | 99.6(1) |
| Cl(1)–Hg–Cl(2) | 133.8(1) | Hg–Cl(1)–Hg | 97.1(1) |
| Cl(1′)–Hg–N(3) | 93.4(3) | Hg–N(3)–C(10) | 122.6(9) |
| Cl(1′)–Hg–N(1) | 155.2(3) | Hg–N(3)–C(9) | 119.7(8) |
| Cl(1′)–Hg–Cl(2) | 103.7(1) | Hg–N(1)–C(1) | 115.7(1) |

[a] Primes are used for the symmetry-related atoms.

nitrogen and the nearest quinoxaline nitrogen are located on the same side of the carbon–carbon bond which connects the two rings; this is a consequence of the chelate effect (formation of a stable five-membered chelate ring). The bridging $Hg_2Cl_2$ unit is constrained to be planar by the presence of the crystallographic inversion centre in the middle of the dimer. The mercury–bridging chloro distances (2.500(4), 2.742(3) Å) are longer than the mercury–terminal chloro distance (2.387(4) Å) as expected, the latter indicating a strong Hg–Cl bond [19, 20]. The bridging bonds in the present complex are nevertheless shorter than the long bridging contacts found in the structures of other chloro Hg(II) complexes with effective coordination number five [19–23]. However, it should be noted that one of the two Hg–Cl (bridging) bonds is ~0.25 Å shorter than the other. Most of the $HgCl_2Hg$ bridges reported in the literature [19,20,24,25] are either symmetrical with two equivalent Hg–Cl distances of ~2.8 Å, or highly unsymmetrical with one short bond of 2.3 Å and one weak contact >3.0 Å; complex $[Hg_2Cl_4L_2]$ has an intermediate asymmetry in this respect. The Hg–N bond lengths are normal for this kind of compound and indicate bonds of intermediate strength [19,20,25–27]. An interesting feature of this structure is the difference in bond lengths of the two Hg–N bonds (~0.11 Å) {the corresponding difference in the structure of $[Hg_2Br_4(bpy)_2]$ is 0.026 Å [26]}. The different Hg–N bond lengths may reflect the changes in donor strength of the respective nitrogen atoms. The small N(1)–Hg–N(3) angle (68.8(1)°) reflects the small bite of chelating L.

The five donor atoms within bonding distances do not define a regular polyhedron around mercury. Analysis of the shape-determining angles using the approach of Reedijk and co-workers [28] yields a value for trigonality index, $\tau$, of 0.36 ($\tau = 0$ and 1 for perfect square pyramidal and trigonal bipyramidal geometries, respectively). Thus, the geometry about Hg(II) is significantly distorted and can be described as either a distorted sp or a distorted tbp arrangement. With use of the tbp description, the apical sites are occupied by Cl(1′) and N(1) with atoms Cl(1), Cl(2) and N(3) making up the equatorial plane; Hg lies 0.146 Å out of the equatorial plane towards Cl (1′). On the basis of bond strength [22, 25], the distorted tbp geometry can be described in terms of a (3+2) coordination with three atoms strongly bonded in the equatorial plane and two weaker bonds to axial positions. For the sp description the basal plane would consist of the atoms Cl(1), Cl(2), N(1) and Cl(1′) with N(3) occupying the apical site. The four basal atoms are not co-planar; N(1) and Cl(1′) lie 0.696 and 0.627 Å, respectively, above the best least-squares plane through the four atoms while Cl(1) and Cl(2) lie 0.784 and 0.539 Å, respectively, below it. The mercury atom is 0.298 Å above the plane toward the apical atom N(3). These distortions from the ideal sp geometry appear greater than in the tbp model; thus, the sp description is less preferred. By virtue of the geometric constraints imposed by the chelating coordination, the two individually planar portions of L (the pyridine and the quinoxaline ring) are slightly twisted out of coplanarity, the dihedral angle between the two planes being 6.9°. In the free ligand, the two planar moieties are more coplanar, the planes making an angle of 3.4°.

The structure of $[Hg_2Cl_4L_2]$ shows some similarity to that of $[Cu_2Cl_4L_2]$ [8]; obviously, the replacement of Hg(II) by Cu(II) has little structural effect. However, the copper to pyridine-nitrogen distance (2.106(5) Å) is longer than the copper to quinoxaline-nitrogen distance (2.021(5) Å), whereas the opposite trend is observed for the mercury(II) complex (2.336(10) versus 2.480(4) Å) emphasizing the importance of the metal ion in determining the relative donor strength of the two nitrogen atoms.

The complex $[Hg_2Cl_4L_2]$ joins a handful [19,20,25,26] of structurally characterized, five-coordinate complexes of the type $[Hg_2(\mu\text{-}X)_2X_2(\text{bidentate ligand})_2]$ (X = Cl, Br). The closest precedent of $[Hg_2Cl_4L_2]$ is centrosymmetric $[Hg_2Br_4(bpy)_2]$, but the authors [26] prefer to describe its geometry as sp with the terminal bromine at the apex; however, in the extensive collection of structural information on mercury(II) halide complexes by Dean [19], the geometry of this compound has been described as very distorted tpb.

### 3.3. Spectroscopic studies

The IR spectra of the mercury(II) complexes are similar to those of other metal complexes with L [6,8]. The characteristic in-plane and out-of-plane pyridine-ring bands at 620 and 401 cm$^{-1}$, respectively, are shifted upwards in the complexes, showing the involvement of the pyridine nitrogen in bonding to mercury [29]. The ~950 cm$^{-1}$ region is viewed as the key to differentiate between monodentate and bidentate bridging coordination of the quinoxaline ring [30, 31]. In the free ligand, there is a strong band at 960 cm$^{-1}$. The appearance of a sharp single band at 965–970 cm$^{-1}$ in the spectra of the three complexes, i.e. the fact that this band does not split on complexation, is strong evidence for monodentate quinoxaline coordination [31]; this band also appears in the Raman spectra of the complexes at practically the same frequency.

The low-frequency vibrational data of the prepared complexes give an insight into the structure and bonding in the solid state. In the 350–100 cm$^{-1}$ region, the occurrence of $\nu$(Hg–X) and $\nu$(Hg–N) vibrational modes is expected. Assignments of these modes (Table 6) in the IR and Raman spectra have been given by considering the frequencies of internal modes of L in the low-frequency region, the variation in band frequency with changing the anionic ligand (Cl, Br, I) and extensive literature [11,22–24,27,32–39]. As has been noticed previously [38], the Raman scattering ability of the stretching metal–halogen modes increases markedly in the sequence Cl < Br < I. Consequently, the (Hg–Cl)$_t$ and (HgCl)$_b$ modes in [$Hg_2Cl_4L_2$] are rather broad and of lower Raman intensity than the modes of [$Hg_2Br_4L_2$] and [$HgI_2L$]. The IR and Raman spectra of [$Hg_2X_4L_2$] (X = Cl, Br) show one clear terminal Hg–X stretching feature and in the bridging stretch region two bands appear. This spectroscopic behaviour is consistent with the X-ray structure of [$Hg_2Cl_4L_2$] and suggests a similar structure for the bromo complex. The presence of two (Hg–I)$_t$ and (Hg–N) bands in both the IR and Raman spectra of [$HgI_2L$], and the non-appearance of bands attributable to $\nu$(HgI)$_b$ modes, imply a monomeric pseudotetrahedral structure with an idealized $C_2$ symmetry [11,39]. For such a structure, both the antisymmetric and symmetric $HgI_2$ and $HgN_2$ stretching vibrations are IR and Raman active. The observed wavenumbers of the (Hg–I)$_t$ modes compare very well with the values previously reported for other monomeric tetrahedral di-iodo mercury(II) complexes [11,36]. The (Hg–N) wavenumbers are higher in the iodo complex than in [$Hg_2X_4L_2$], probably due to the lower coordination number in [$HgI_2L$] [39].

Table 7 gives the $^1$H NMR chemical shifts of [$Hg_2X_4L_2$] (X = Cl, Br) in DMSO-d$_6$. Conductivity measurements in DMSO indicated these complexes to be non-electrolytes in solution, supporting the conclusion that the solid-state structure remains intact. Although it is soluble in DMSO, complex [$HgI_2L$] gives a complicated spectrum in this solvent, suggesting that several species are interconverting in solution. The $^1$H NMR assignments were based on comparisons with those for L [6] and a number of diamagnetic complexes with related ligands [40–42]. The two-dimensional COSY NMR spectrum of the chloro complex was also obtained, to further confirm the assignments of the observed resonances. For example, on the basis of assignment of 9.10 ppm to H(10) [6], the cross-peak to this resonance leads to the assignment of H(11) at 7.79 ppm. The cross-peak at the chemical shift coordinates 7.79, and 8.21 ppm identifies the H(12) proton at 8.21 ppm, and so on.

The electron density on the pyridine ring of L diminishes upon coordination to Hg(II), inducing a downfield shift of H(10) (9.10 ppm in [$Hg_2Cl_4L_2$] versus 8.94 ppm in free L) [42,43]. The downfield shift observed for H(2) is insignificant (0.05 ppm), indicating that the N(2) atom of the quinoxaline ring remains uncoordi-

Table 6
IR [a] and Raman metal–ligand vibrational frequencies (cm$^{-1}$) for [$Hg_2X_4L_2$] (X = Cl, Br) and [$HgI_2L$]

| Complex | Method | $\nu$(Hg–X)$_t$ | $\nu$(HgX)$_b$ | $\nu$(Hg–N) |
|---|---|---|---|---|
| [$Hg_2Cl_4L_2$] | IR | 274s | 230mb, 199m | 182w, 162m |
| | R | 273m | 236w, 185m | 180w, 165m |
| [$Hg_2Br_4L_2$] | IR | 196s | 158mb [b], 134w | 178w, 158mb [b] |
| | R | 197m | 158s, 120m | 180m, 162sh |
| [$HgI_2L$] | IR | 169s, 159m | | 195m, 177sh |
| | R | 171w, 156s | | 190w, 176m |

[a] Fourier-transform spectra.

[b] Coincident bands.

Abbreviations: b = broad; m = medium; s = strong; sh = shoulder; X = Cl, Br, I; $\nu$(Hg–X)$_t$ = the stretching vibration of the terminal Hg–X bond; $\nu$(HgX)$_b$ = the stretching vibrations of the Hg–X bonds in the bridging $HgX_2Hg$ groups.

Table 7
200 MHz $^1$H NMR shifts (ppm) [a,b] and $J$(H–H) coupling constants (Hz) [c] of [$Hg_2X_4L_2$] (X = Cl, Br) in DMSO-$d_6$

| Proton | [$Hg_2Cl_4L_2$] | | [$Hg_2Br_4L_2$] | |
|---|---|---|---|---|
| | Chem. shift | $J$(H–H) | Chem. shift | $J$(H–H) |
| H(2) | 10.06s | 10, 11 = 4.88 | 10.05s | 10, 11 = 4.69 |
| H(5) | 8.37mt | 10, 12 = 1.80 | 8.39mt | 10, 12 = 1.76 |
| H(6) | 8.07mt | 10, 13 = 0.86 | 8.08mt | 10, 13 = 0.85 |
| H(7) | 8.01mt | 11, 12 = 7.60 | 8.00mt | 11, 12 = 7.47 |
| H(8) | 8.28mt | 11, 13 = 1.10 | 8.28mt | 11, 13 = 1.08 |
| H(10) | 9.10mt | 12, 13 = 7.96 | 9.09mt | 12, 13 = 7.65 |
| H(11) | 7.79mt | | 7.80mt | |
| H(12) | 8.21mt | | 8.22mt | |
| H(13) | 8.76mt | | 8.80mt | |

[a] Spectra recorded at ambient temperature.

[b] The spectra were run ~10 min after dissolutions.

[c] Due to the complex nature of the four-spin system of protons H(9)–H(12), direct calculation of coupling constants is not possible.

Abbreviations: mt = multiplet; s = singlet.

nated; a larger downfield shift would be expected if coordination had occurred. The slight downfield shift of H(2) and H(13) resonances may be explained [40,42] by the fact that these protons lie close to each other in the mercury(II) complexes (steric effect), as opposed to the structure of free L; on chelation L has changed its configuration.

## 4. Conclusions and perspectives

The $HgX_2$/L reaction system fulfilled its promise as a source of interesting Hg(II) complexes. According to IR, Raman and X-ray analysis, the 1:1 chloro and bromo complexes are dinuclear, five-coordinate species, while the iodo compound has a monomeric, pseudotetrahedral structure. It seems that the halogen radius decides the coordination geometry. In the iodo compound, the tetrahedral coordination is preferred because of the difficulty of accommodating three (rather than two) iodine atoms and one molecule of L around Hg(II). L behaves as a bidentate, chelating ligand in the present mercury(II) complexes and in the structurally characterized copper(II) compound [$Cu_2Cl_4L_2$] [7,8]. We believe that L is also capable of acting as a tridentate bridging ligand with mixed bidentate–monodentate coordination and that much work still remains to be done exploring the coordination chemistry of L and related ligands. Such studies with transition and lanthanide metals are, in fact, already well advanced, and results will be reported in due course.

## 5. Supplementary material

Tables of hydrogen atoms coordinates, thermal parameters, bond distances and angles, least-squares plane equations, and observed and calculated structure factors are available from the authors on request.

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