

Preparation and structural characterization of mercury 21-thiaporphyrin complex: $\text{Hg}^{\text{II}}(\text{Stpp})\text{Cl}$ (Stpp = tetraphenyl-21-thiaporphyrin anion)

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Abstract

Treatment of tetraphenyl-21-thiaporphyrin (StppH) with $\text{Hg}(\text{OAc})_2$ in CH_2Cl_2 yields diamagnetic $\text{Hg}^{\text{II}}(\text{Stpp})\text{Cl}$ complex. The coordination sphere around Hg^{2+} in the monomeric molecule is described as a five-coordinate distorted trigonal bipyramid with the bonding to the three pyrrole nitrogens [$\text{Hg}(1)-\text{N} = 2.104(4), 2.626(4), 2.640(4)$ Å], the thiophene sulfur [$\text{Hg}(1)-\text{S} = 2.801(1)$ Å], and one axial chloride ligand [$\text{Hg}(1)-\text{Cl}(1) = 2.318(1)$ Å]. The plane of the three pyrrole nitrogen atoms [i.e., N(1), N(2), N(3)] bonded to Hg^{2+} is adopted as a reference plane 3N. Because of its larger size, the Hg^{2+} is considerably out of the 3N plane; its displacement of 1.41 Å is in the same direction as that of the apical Cl^- ligand. The thiophene ring is slightly folded so that the dihedral angle between the C(13)–C(14)–C(15)–C(16) and C(13)–S(1)–C(16) planes is 7.3°. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Crystal structure; Mercury thiaporphyrin; Diamagnetic; Distorted trigonal bipyramid

1. Introduction

The structures of the metal derivatives of the tetraphenyl-21-thiaporphyrin (StppH) have been solved in the early 1990s by Latos-Grazynski et al. [1] who reported three penta-coordinated, high-spin, and paramagnetic complexes $\text{Fe}^{\text{II}}(\text{Stpp})\text{Cl}$ ($S = 2$), $\text{Ni}^{\text{II}}(\text{Stpp})\text{Cl}$ ($S = 1$) and $\text{Cu}^{\text{II}}(\text{Stpp})\text{Cl}$ ($S = 1/2$) having a number of features in common. All of them have roughly square pyramidal geometry with the metal bonded to three pyrrole nitrogen atoms, the thiophene sulfur and an axial chloride. The thiophene ring is sharply bent out of the plane of the N_3 porphyrin core, while the three pyrrole rings are slightly tipped away from that plane. The thiophene sulfur is coordinated to the metal in a pyramidal fashion. Tetraphenyl-21-thiaporphyrin also

forms six-coordinate, diamagnetic $\text{Rh}^{\text{III}}(\text{Stpp})\text{Cl}_2$, [2] which have two axial chloro ligands, and forms four-coordinate, paramagnetic $\text{Ni}^{\text{I}}(\text{SDPDTP})$ ($S = 1/2$, SDPDTP is the monoanion of diphenyldi-*p*-tolyl-21-thiaporphyrin) [3], and also $\text{Pd}^{\text{I}}(\text{SDPDTP})$ ($S = 1/2$) [4]. In recent times, Arnold and co-workers [5] synthesized and studied the complex of lithium diphenylditolylmonothiaphyrin $\text{Li}(\text{SDPDTP})(\text{THF})$. This five-coordinate and diamagnetic lithium [Li(I)] complex is still in a roughly square pyramidal arrangement.

However, until now there are no X-ray structural data available for the diamagnetic metal ion M(II) complexes of five-coordinate $\text{M}(\text{Stpp})\text{Cl}$. Since the coordination numbers and geometries of $\text{Hg}(\text{II})$ are known to vary sensitively with the ligand requirements, the resultant structure of $\text{Hg}(\text{II})$ with the heteroporphyrin ligand would be a subject of interest. In this paper, we present the study about chloro tetraphenyl-21-thiaporphyrinatomercury(II), $\text{Hg}^{\text{II}}(\text{Stpp})\text{Cl}$, by replacing Fe(II), Ni(II), Cu(II), and Li(I) with Hg(II). It is noted

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that the ionic radius increases from $\gamma(\text{Li}^+)$ for Li^+ [$0.73 \text{ \AA} < \gamma(\text{Li}^+) < 0.90 \text{ \AA}$], $\gamma(\text{Fe}^{2+})$ for Fe^{2+} [$0.77 \text{ \AA} < \gamma(\text{Fe}^{2+}) < 0.92 \text{ \AA}$], 0.77 \AA for Ni^{2+} , 0.79 \AA for Cu^{2+} to $\gamma(\text{Hg}^{2+})$ for Hg^{2+} [$1.10 \text{ \AA} < \gamma(\text{Hg}^{2+}) < 1.16 \text{ \AA}$] [6]. This replacement causes the magnetic property to change from paramagnetism for $\text{M}(\text{Stpp})\text{Cl}$ [$\text{M} = \text{Fe}(\text{II})$, $\text{Ni}(\text{II})$, and $\text{Cu}(\text{II})$] [1] to diamagnetism for $\text{Hg}(\text{Stpp})\text{Cl}$. At the same time, a five-coordinate geometry changes from square pyramid for $\text{M}(\text{Stpp})\text{Cl}$ [$\text{M} = \text{Fe}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$] [1] and $\text{Li}(\text{SDPDTP})$ [5] to distorted trigonal bipyramid for the monomeric molecules of $\text{Hg}(\text{Stpp})\text{Cl}$. In this direction, we prepared the mercury complex of 21-thiaporphyrin.

2. Experimental

2.1. Preparation of $\text{Hg}(\text{Stpp})\text{Cl}(\mathbf{1})$

Compound **1** was synthesized by refluxing a mixture of StppH [7] (100 mg, 0.16 mmol) in CH_2Cl_2 (30 cm^3) and $\text{Hg}(\text{OAc})_2$ (102 mg, 0.32 mmol) in MeOH (5 cm^3) for 30 min. After concentrating, the residue was dissolved in CH_2Cl_2 , dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated and crystallized from CH_2Cl_2 -*n*-hexane yielding a purple solid of **1**. Compound **1** was redissolved in CH_2Cl_2 and layered with *n*-hexane under N_2 to afford purple crystals (104 mg, 0.12 mmol, 75%) for single-crystal X-ray analysis.

^1H NMR (199.98 MHz, CDCl_3 , 20 °C): δ 9.55 (s, $\text{H}_\beta(14, 15)$ or thiophene), 8.83 (d, $^3J(\text{H}-\text{H}) = 5 \text{ Hz}$) and 8.76 (d, $^3J(\text{H}-\text{H}) = 5 \text{ Hz}$) for $\text{H}_\beta(9, 20)$ and $\text{H}_\beta(10, 19)$, 8.69 (s, $\text{H}_\beta(4, 5)$), 7.78–8.38 (m, phenyl protons). ^{13}C NMR (150.87 MHz, CDCl_3 , 20 °C): δ 157.6 (s) and 154.3 (s) for $\text{C}_\alpha(\text{C}10, \text{C}18)$ and $\text{C}_\alpha(\text{C}1, \text{C}8)$; 151.9 [s, $\text{C}_\alpha(\text{C}3, \text{C}6)$]; 145.9 [s, $\text{C}_\alpha(\text{C}13, \text{C}16)$]; 142.6 (s) and 141.1 (s) for phenyl- C_1 ; 136.2 (s) and 133.2 (s) for $\text{C}_\beta(\text{C}10, \text{C}19)$ and $\text{C}_\beta(\text{C}9, \text{C}20)$; 135.0 [s, $\text{C}_\beta(\text{C}14, \text{C}15)$]; 131.4 [s, $\text{C}_\beta(\text{C}4, \text{C}5)$]; 131.2 [s, $\text{C}_m(\text{C}12, \text{C}17)$]; 128.3 [s, $\text{C}_m(\text{C}2, \text{C}7)$]; 135.7 (s), 135.5 (s), 134.5 (s), 134.4 (s), 128.2 (s), 134.2 (s), 127.9 (s), 127.4 (s), 126.6 (s) for phenyl- $\text{C}_{2,6}$, $\text{C}_{3,5}$ and C_4 . MS, m/z (assignment, rel. intensity): 867 ($[\text{Hg}(\text{Stpp})\text{Cl}]^+$, 1.51), 832 ($[\text{Hg}(\text{Stpp})]^+$, 2.59), 632 ($[\text{StppH}]^+$, 30.03), 631 ($[\text{Stpp}]^+$, 58.98), 630 ($[\text{Stpp}-\text{H}]^+$, 100). UV/visible spectrum, λ (nm) [$\epsilon \times 10^{-3} (\text{M}^{-1} \text{cm}^{-1})$] in CH_2Cl_2 : 430 (58.3), 515 (5.1), 548 (1.3), 616 (0.87), 676 (1.0).

2.2. Spectroscopy

Proton and ^{13}C NMR spectra in CDCl_3 (99.8% from Aldrich) were recorded at 199.98 (or 599.95) and 50.29 (or 150.87) MHz, respectively, on Varian Gemini-200 (or Varian Unity Inova-600) spectrometers locked on deuterated solvent, and referenced to the solvent peak. Proton NMR is relative to CDCl_3 at $\delta = 7.24$ and ^{13}C

Table 1
Crystal data for $\text{Hg}(\text{Stpp})\text{Cl} \cdot 2\text{CH}_2\text{Cl}_2$

Chem. formula ^a	$\text{C}_{46}\text{H}_{32}\text{Cl}_5\text{HgN}_3\text{S}$
fw	1036.65
Space group	P1
<i>a</i> (Å)	12.4049(15)
<i>b</i> (Å)	14.1670(17)
<i>c</i> (Å)	14.8438(18)
α (deg)	97.232(2)
β (deg)	114.504(2)
γ (deg)	112.167(2)
<i>V</i> (Å ³)	2071.2(4)
<i>d</i> (calcd) (g cm ⁻³)	1.662
Radiation, λ (Å)	Mo; 0.71073
Temperature (K)	295(2)
Abs. coeff. (cm ⁻¹)	41.26
<i>R</i> (%) ^b	3.95
<i>R</i> _w (%) ^c	10.58
GOF on <i>F</i> ²	1.054

^a Including solvated molecules.

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

^c $R_w = \left\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \right\}^{1/2}$; $w = A / (\sigma^2 F_o + B F_o^2)$.

NMR to the centre line of CDCl_3 at $\delta = 77.0$. ^1H - ^{13}C COSY was utilized to correlate protons and carbon through one-bond coupling and heteronuclear multiple-bond coherence (HMBC) for two- and three-bond proton-carbon coupling.

The positive-ion fast atom bombardment mass spectrum (FAB MS) was obtained in a nitrobenzyl alcohol (NBA) matrix using a JEOL JMS-SX/SX 102A mass spectrometer. UV/visible spectra were recorded at 25 °C on a HITACHI U-3210 spectrophotometer.

2.3. Crystallography

Table 1 presents the crystal data as well as other information for $\text{Hg}(\text{Stpp})\text{Cl} \cdot 2\text{CH}_2\text{Cl}_2$ (**1** · $2\text{CH}_2\text{Cl}_2$). Measurements were taken on a Siemens SMART CCD diffractometer using monochromatized Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The empirical absorption corrections were made for **1**. The structures were solved by direct methods (SHELXTL PLUS) and refined by the full-matrix least-squares method. All non-hydrogen atoms were refined with anisotropic thermal parameters, whereas all hydrogen atom positions were calculated using a riding model and were included in the structure factor calculation. Table 2 lists selected bond distances and angles for **1**.

3. Results and discussion

3.1. Molecular structure of **1** · $2\text{CH}_2\text{Cl}_2$

Fig. 1 illustrates the skeletal framework of complex **1** · $2\text{CH}_2\text{Cl}_2$. The geometrical configuration around Hg^{2+} in the monomeric molecules is described as a

Table 2
Selected bond distances (Å) and angles (deg) for Hg(Stpp)Cl(1)

Distances			
Hg(1)–N(1)	2.626(4)	S(1)–C(13)	1.733(5)
Hg(1)–N(2)	2.104(4)	S(1)–C(16)	1.739(5)
Hg(1)–N(3)	2.640(4)	Hg(1)–Cl(1)	2.318(1)
Hg(1)–S(1)	2.801(1)		
Angles			
N(1)–Hg(1)–N(2)	77.8(1)	Cl(1)–Hg(1)–N(1)	114.0(1)
N(1)–Hg(1)–N(3)	110.9(1)	Cl(1)–Hg(1)–N(2)	163.3(1)
N(2)–Hg(1)–N(3)	77.2(1)	Cl(1)–Hg(1)–N(3)	107.5(1)
S(1)–Hg(1)–N(1)	61.28(9)	Cl(1)–Hg(1)–S(1)	97.00(5)
S(1)–Hg(1)–N(2)	99.2(1)	Cl(1A)–Hg(1)–N(1)	109.1
S(1)–Hg(1)–N(3)	60.01(9)	Cl(1A)–Hg(1)–N(2)	78.6
C(13)–S(1)–C(16)	92.7(2)	Cl(1A)–Hg(1)–N(3)	126.8
Hg(1)–S(1)–C(13)	108.7(2)	Cl(1A)–Hg(1)–S(1)	170.3
Hg(1)–S(1)–C(16)	109.3(2)		

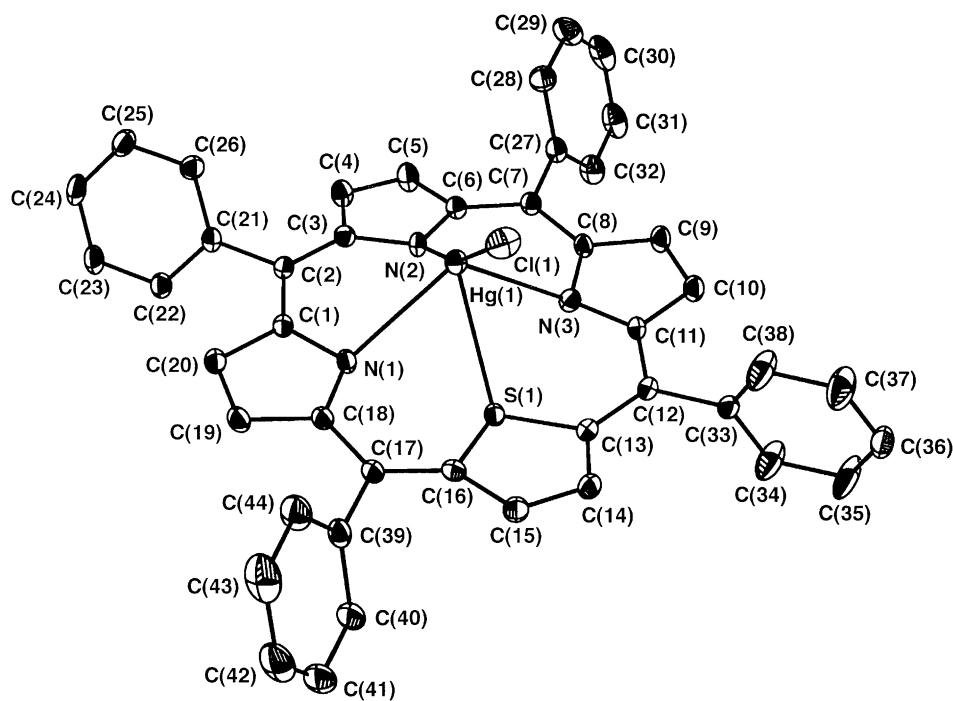


Fig. 1. Molecular configuration and atom-labeling scheme for Hg(Stpp)Cl · 2CH₂Cl₂ (or **1** · 2CH₂Cl₂) monomer, with ellipsoids drawn at 30% probability. Hydrogen atoms and solvents C(45)H₂Cl(2)Cl(3), C(46)H₂Cl(4)Cl(5) are omitted for clarity.

distorted trigonal bipyramid in which the Cl[−], and N(2) occupy two apical sites. The five-coordinate mercury of **1**, like M(Stpp)Cl [M = Fe(II), Ni(II), and Cu(II)], has bonding with three nitrogen atoms of the porphyrin, the thiophene sulfur, and an axial chloride. The unusual bond distances and angles are summarized in Table 2. The bond distances (Å) are Hg(1)–N(1) = 2.626(4), Hg(1)–N(2) = 2.104(4), Hg(1)–N(3) = 2.640(4), Hg(1)–S(1) = 2.801(1), and Hg(1)–Cl(1) = 2.318(1).

According to Grdenic [8] (see also [9]), the mercury coordination sphere can be categorized in terms of their primary, or characteristic, (*m*; *m* = number of

covalently bonded atoms) and effective coordination (*m* + *n*; *n* = number of atoms at distances shorter than the sum of the van der Waals radii). The effective coordination is then denoted as [*m* + *n*]. The Hg(1)–S(1) bond length of 2.801(1) Å for **1** is smaller than that of Hg1–S11 = 2.922(2) Å in [Hg₅(Et₂dte)₈](ClO₄)₂ (dte = dithiocarbamate) [10], Hg–S(2) = 2.965(4) Å in the β form of Hg₂(S₂CNEt₂)₄ [11], and of Hg(1)–S(3) = 2.888(5) Å in Hg[(*i*-C₃H₇O)₂PS₂]₂ [12]. Hence Hg(1)–S(1) is a covalent bond at intermediate distance. The Hg(1)–Cl(1) bond distance of 2.318(1) Å is smaller than the sum of the covalent radii of Hg and Cl (2.47 Å). The

covalent bond of $\text{Hg}(1)\text{--Cl}(1) = 2.318(1) \text{ \AA}$ in **1** is comparable to those of $\text{Hg}(1)\text{--Cl}(1) = 2.318(2) \text{ \AA}$ and $\text{Hg}(2)\text{--Cl}(2) = 2.285(2) \text{ \AA}$ in bischloromercury(II) complex of *N*-tosylamino-octaethylporphyrin [13]. The $\text{Hg}(1)\text{--N}(2) = 2.104(4) \text{ \AA}$ in **1** which is smaller than the sum of the Hg and N covalent radii (2.23 Å). Hence, N(2) is bonded strongly as well as covalently to the Hg(1) atom in **1**. Mercury(II) is bonded to three atoms of Cl(1), S(1) and N(2) and so compound **1** may be considered as a sitting-atop (SAT) complex. The similar kind of SAT complex was previously reported for bischloromercury(II) complex of *N*-tosylamino-octaethylporphyrin [13]. Although the primary (or characteristic) coordination environment around the mercury atom in **1** is tentatively assigned as a SAT complex, the $\text{Hg} \cdots \text{N}$ distances of 2.626(4) for $\text{Hg}(1)\text{--N}(1)$ and 2.640(4) Å for $\text{Hg}(1)\text{--N}(3)$ are longer than 2.23 Å but are significantly shorter than the sum of the van der Waals radii of Hg and N (3.28 Å) [14]. These two longer $\text{Hg}(1) \cdots \text{N}(1)$ and $\text{Hg}(1) \cdots \text{N}(3)$ contacts are described as weak (secondary) bonds. The coordination around mercury in **1** forms an effective [3 + 2] coordination sphere. The similar $\text{Hg} \cdots \text{N}$ distances of 2.62(3), 2.65(2) and 2.70(2) Å in $\text{Hg}(\text{CF}_3)_2(\text{terpy})$ (terpy = 2,2':6',2''-terpyridine) were observed as three effective coordination in the [2 + 3] coordination sphere [15].

In order to know whether the observed angles allow a description of the geometry around the mercury as either a distorted square pyramid or a distorted trigonal bipyramid, an analysis of the shape-determining bond angles has been carried out following the approach of Reedijk and co-workers [16,17]. Accordingly, the index of trigonality, τ , equals zero or one depending upon whether the geometry is perfect square pyramidal or trigonal bipyramidal, respectively. The bond angles of the $\text{Cl}(1)\text{--Hg}(1)\text{--N}(2)$ [163.3(1)°] and the $\text{Cl}(1)\text{--Hg}(1)\text{--N}(1)$ [114.0(1)°] are the largest and the second largest *trans* angles in the basal plane around the Hg atom in **1**. The τ value 0.82 calculated from these angles for **1** indicates that the geometry around the Hg^{2+} in the monomeric molecules should be a distorted trigonal bipyramid with the atoms Cl(1) and N(2) at the axial sites and the S(1), N(3), and N(1) lying in the equatorial plane. The τ values calculated for $\text{Fe}(\text{Stpp})\text{Cl}$ [1], $\text{Ni}(\text{Stpp})\text{Cl}$ [1], $\text{Cu}(\text{Stpp})\text{Cl}$ [1], and $\text{Li}(\text{SDPDTP})(\text{THF})$ [5] by the same method are 0.30, 0.28, 0.32, and 0.25, respectively, and the coordination geometry for these four compounds is closer to distorted square pyramid.

Fig. 2 shows the actual porphyrin skeleton of **1**. We adopt the plane of three strongly bound pyrrole nitrogen atoms [i.e., N(1), N(2), and N(3)] as a reference plane 3N (or N_3 [1], or the tripyrrolic plane [5]). Because of the larger size of the Hg^{2+} , Hg lie 1.41 Å above the 3N plane, compared to 0.64 Å for Li in $\text{Li}(\text{SDPDTP})(\text{THF})$ [5], 0.538 Å for Fe in $\text{Fe}(\text{Stpp})\text{Cl}$ [1], 0.295 Å for Ni in $\text{Ni}(\text{Stpp})\text{Cl}$ [1], and 0.274 Å for Cu in $\text{Cu}(\text{Stpp})\text{Cl}$ [1].

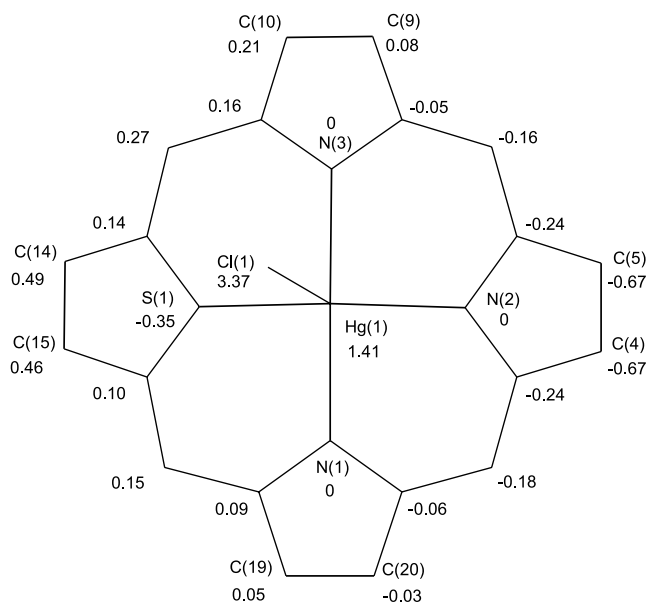


Fig. 2. Diagram of the porphyrin core ($\text{C}_{20}\text{N}_3\text{S}$, Hg, and Cl^-) of compound **1** showing the displacement (in Å) of the atoms from the mean plane of 3N.

Although 21-thiaporphyrin free bases are planar, the thiaporphyrin in **1** is non-planar (Fig. 2). The thiophene ring in **1** is characteristically bent out of the 3N plane with the dihedral angle between the $\text{C}(13)\text{--S}(1)\text{--C}(16)$ plane and 3N plane being 23° which is smaller than that of 40.0° in $\text{Fe}(\text{Stpp})\text{Cl}$ [1], 38.1° in $\text{Ni}(\text{Stpp})\text{Cl}$ [1], and 38.4° in $\text{Cu}(\text{Stpp})\text{Cl}$ [1]. The three pyrrole rings are only slightly tipped away from the 3N plane and oriented separately in small dihedral angles of 3.7°, 18.1°, and 6.7° for N(1), N(2), and N(3) pyrroles in **1**. The angle between the $\text{C}(13)\text{--S}(1)\text{--C}(16)$ plane and the $\text{Hg}\text{--S}$ bond is 61.8°. This structural parameter is larger than those found for $\text{Ni}^{\text{I}}(\text{SDPDTP})$ (45.9°) [3], $\text{Pd}^{\text{I}}(\text{SDPDTP})$ (53.4°) [4], and $\text{Rh}^{\text{III}}(\text{Stpp})\text{Cl}_2$ (61.2°) [2] but smaller than found for five-coordinate complexes: $\text{Fe}(\text{Stpp})\text{Cl}$ (69.5°) [1]; $\text{Ni}(\text{Stpp})\text{Cl}$ (63.3°) [1]; $\text{Cu}(\text{Stpp})\text{Cl}$ (65.6°) [1]. The thiophene ring in **1** is somewhat altered from planarity relative to free thiophene and is no longer planar. The thiophene ring is slightly folded so that the dihedral angle between the $\text{C}(13)\text{--C}(14)\text{--C}(15)\text{--C}(16)$ plane and the $\text{C}(13)\text{--S}(1)\text{--C}(16)$ plane is 7.3°. This folding is smaller than that found in four-coordinate complexes $\text{Ni}^{\text{I}}(\text{SDPDTP})$ (14.6°) [3], and $\text{Pd}^{\text{I}}(\text{SDPDTP})$ (15.6°) [4]; five-coordinate complexes $\text{Li}^{\text{I}}(\text{SDPDTP})(\text{THF})$ (12.5°) [5], $\text{Fe}^{\text{II}}(\text{Stpp})\text{Cl}$ (11.8°) [1], $\text{Ni}^{\text{II}}(\text{Stpp})\text{Cl}$ (13.4°) [1], and $\text{Cu}^{\text{II}}(\text{Stpp})\text{Cl}$ (14.7°) [1]; six-coordinate complex $\text{Rh}^{\text{III}}(\text{Stpp})\text{Cl}_2$ (26.4°) [2]. The bending and slight folding of the thiophene ring allows the sulfur to coordinate to the mercury in the usual $\eta^1(\text{S})$ fashion. The dihedral angles between the mean plane of the skeleton (3N) and the planes of the phenyl groups are 55.1° [C(24)], 56.7° [C(30)], 88.4° [C(36)], and 60.9° [C(42)].

3.2. ^1H and ^{13}C NMR for $\text{Hg}^{\text{II}}(\text{Stpp})\text{Cl}(\mathbf{1})$ in CDCl_3

Complex **1** was thoroughly characterized by ^1H and ^{13}C NMR spectra (Fig. 3). In solution, the molecule has effective C_s symmetry with mirror plane running through the $\text{Cl}(1)\text{--S}(1)\text{--Hg}(1)\text{--N}(2)$. There are four β -pyrrole protons H_β , four β -pyrrole carbons C_β , four α -pyrrole carbons C_α , and two different *meso* carbons C_{meso} . The thiophene sulfur bonded to Hg is confirmed by the result that the $\text{H}_\beta(14,15)$ in **1** was observed at

$\delta = 9.55$ ppm with $^4J(^{199}\text{Hg}\text{--H})$ of 16 Hz. This coupling satellites is comparable to $^4J(^{199}\text{Hg}\text{--H})$ values of 20 and 24 Hz for the Hd protons in $([\text{Hg}(\text{TMPA})]\text{ClO}_4)_2$ [18] and in $[\text{Hg}(\text{BMPA})\text{NCCH}_3](\text{ClO}_4)_2$ [19], respectively, {with $\text{TMPA} = \text{tris}[(2\text{-pyridyl})\text{methyl}]\text{amine}$, $\text{BMPA} = \text{bis}[(2\text{-pyridyl})\text{methyl}]\text{amine}$. Because the phenyl groups' rotation around the macrocyclic ring in **1** is slow, this explains that the phenyl proton and phenyl carbon resonances are so broad (Fig. 3).

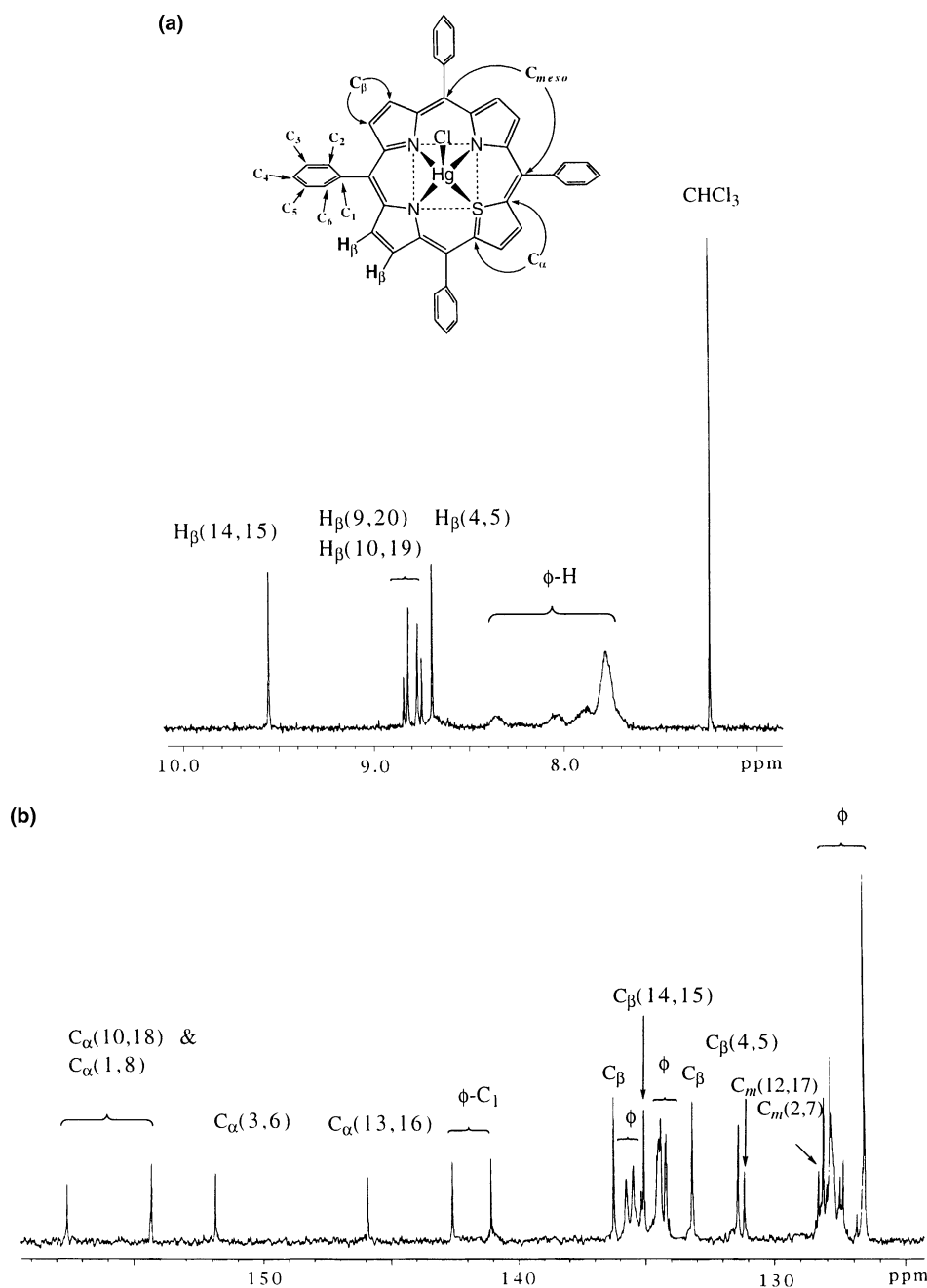


Fig. 3. (a) ^1H NMR (199.98 MHz) and (b) ^{13}C NMR (150.87 MHz) spectra for **1** in CDCl_3 at 20 °C. $\phi\text{-H}$ represents the phenyl protons; $\phi\text{-C}_1$ represents the phenyl C_1 carbons whereas ϕ represents the phenyl $\text{C}_{2,6}$, $\text{C}_{3,5}$, and C_4 carbons.

4. Conclusion

We have acquired for the first time the X-ray structure of a diamagnetic and effective five-coordinate 21-thiaporphyrin complex, Hg(Stpp)Cl (**1**), in the monomeric molecule which is hitherto unreported. This distorted trigonal bipyramidal geometry in monomeric molecule is compared to those of the related high-spin, five-coordinate $M^{II}(\text{Stpp})\text{Cl}$ [$M = \text{Fe}, \text{Co}, \text{Ni}$] and diamagnetic Li(SDPDTP)(THF). Except the phenyl protons and carbons, the unambiguous assignments of ^1H and ^{13}C NMR data for **1** in CDCl_3 are reported in this work.

Supplementary material

Crystallographic data in CIF format for **1** has been deposited with the Cambridge Data Centre as CCDC 154950.

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