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Mercury Complexes of *meso*-Tetra-(*p*-cyanophenyl)porphyrin and *N*-methylporphyrin: *meso*-Tetra(*p*-cyanophenyl)porphyrinatomercury(II) and Chloro(*N*-methyl-*meso*-tetraphenylporphyrinato)mercury(II)

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Introduction

Several examples of mercury porphyrin complexes have been formulated, but no X-ray structural data were available until 1979.[1−3] In 1974, Hudson et al.[1] reported the reaction of *meso*-tetraphenylporphyrin, H_2tpp, with slightly more than one equivalent of mercury(II) acetate in methylene chloride−THF yielding the "normal" monometallic complex, *meso*-tetraphenylporphyrinatomercury(II) Hgtpp. Because of the difficulties in obtaining a crystal suitable for absolute structural assignment by X-ray method, Hudson and co-workers[1−3] characterized the complex Hgtpp by UV, elemental analysis, and mass spectrum. In 1979, a homodinuculear structure was proposed for the bischloromercury(II) complex of *N*-tosylaminooctaethylporphyrin, $C_{43}H_{51}N_5O_2SCl_2Hg_2$, which represented the first X-ray structural proof for the existence of mercury(II) porphyrin sitting-atop (SAT) complexes.[4] However, still no direct X-ray structural data of mononuclear mercury(II) porphyrin have been published so far. *meso*-Tetra-(*p*-cyanophenyl)porphyrinatomercury(II), Hg(*p*-CN)$_4$tpp (**1**), is a homologue of Hgtpp which is a four-coordinate Hg(II) porphyrin complex. In this paper, we describe the formation and present the crystal structure of this new, mononuclear mercury(II) porphyrin complex **1**.

Several first-row transition metal complexes of *N*-substituted porphyrin M^{II}(*N*-Me-tpp)Cl [M = Zn ($S = 0$),[5] Co ($S = {}^{3}/_{2}$),[6,7] Mn ($S = {}^{5}/_{2}$),[8] Fe ($S = 2$),[9] and tpp = 5,10,15,20-tetraphenylporphyrinate] have been extensively studied by Anderson et al. and [Fe^{III}(*N*-Me-ttp)Cl][$SbCl_6$] ($S = {}^{5}/_{2}$) (*N*-Me-tpp = *N*-methyl tetra-p-tolylporphyrin monoanion) was reported by Latos-Grazynski and co-workers.[10] The common feature in all of these *N*-substituted metalloporphyrins is that the metal atom is no longer coplanar with the four nitrogen atoms of the macrocycle and coordination geometry around the metal ion is a five-coordinate distorted square-based pyramid. M(III) (M = Fe,Tl) complexes of *N*-methylporphyrin with a coordination number (CN) above 5 are known as well. Utilizing the ^{1}H NMR characterization, Latos-Grazynski and co-workers[10] were able to demonstrate the existence of low spin ($S = {}^{1}/_{2}$), six-coordinate iron(III) complexes of *N*-methylporphyrins, i.e., [Fe^{III}(*N*-Me-ttp)$(CN)_2$], [Fe^{III}(*N*-Me-ttp)(5-MeIm)$_2$]$^{2+}$ and [Fe^{III}(*N*-Me-tmp)-Im$_2$]$^{2+}$ (with *N*-Me-ttp = *N*-methyltetra−*p*-tolylporphyrin monoanion, *N*-Me-tmp = *N*-methyltetramesitylporphyrin monoanion, Im = imidazole, and 5-MeIm = 5-methylimidazole). We have recently reported the crystal structures of diacetato(*N*-methyl-*meso*-tetraphenylporphyrinato)thallium(III), Tl(N-Me-tpp)$(OAc)_2$,[11] and bis(trifluoroacetato)−(*N*-methyl-*meso*-tetraphenylporphyrinato)thallium, Tl(N-Me-tpp)$(CF_3COO)_2$.[12] The coordination sphere around the Tl^{3+} ion is described as an eight-coordinate square-based antiprism for the former complex and as a 4:3 tetragonal base piano stool seven-coordinate geometry for the latter complex. Because the coordination numbers and geometries of Hg(II) are known to vary sensitively with the ligand requirements, it will be of interest to investigate how the larger d^{10} Hg(II) ion interacts with the N−CH_3Htpp ligand and the resultant structure out of this interaction. It is observed that the effective ionic radius (γ) for the metal ion with CN = 5 increases from 0.82 Å for Zn^{2+}(or 0.81 Å for Co^{2+}, 0.89 Å for Mn^{2+}, and 0.72 Å for Fe^{3+}) to $\gamma(Hg^{2+})$ [1.10 Å $< \gamma(Hg^{2+}) <$ 1.16 Å].[13] To assess the influence of the large mercury(II) cation on the macrocyclic framework, we report here the first structural determination of chloro(*N*-methyl-*meso*-tetraphenylporphyrinato)mercury(II), Hg(N-Me-tpp)Cl (**2**), by replacing Zn(II), Mn(II), Co(II), Fe(II), Fe(III), and Tl(III) with Hg(II).

Experimental Section

Hg(*p*-CN)$_4$tpp (1). A mixture of H_2(*p*-CN)$_4$tpp (200 mg, 2.8×10^{-4} mol) in CH_2Cl_2 and $Hg(OAc)_2$ (133.89 mg, 4.2×10^{-4} mol) in MeOH was refluxed for 1 h. After concentrating, the residue was crystallized from CH_2Cl_2/MeOH [1:1 (v/v)] as a deep blue solid of **1**. Crystals were grown by diffusion of ether vapor into a CH_2Cl_2 solution. ^{1}H NMR (599.95 MHz, CD_2Cl_2, 20 °C): δ 8.83 [s, β-pyrrole H or H_β]; 8.35 [d, ^3J(H−H) = 8.4 Hz], and 8.33 [d, ^3J(H−H) = 8.4 Hz] for ortho protons; 8.09 [d, ^3J(H−H) = 7.8 Hz, meta protons]. MS, *m*/*z* (assignment, rel intensity): 914 ([Hg(*p*-CN)$_4$tpp + H]$^+$, 1.23); 715 ([H_2(*p*-CN)$_4$tpp]$^+$, 19.37); 714 ([H(*p*-CN)$_4$tpp]$^+$, 15.30). UV/visible spectrum, λ (nm) [$\epsilon \times 10^{-2}$ (M^{-1} cm^{-1})] in CH_2Cl_2: 420 (416), 514 (30.4), 546 (18.5), 589 (15.5).

Hg(*N*-Me-tpp)Cl (2). A mixture of *N*-CH_3Htpp (0.40 g, 6.22×10^{-4} mol) in $CHCl_3$ (50 cm^3) and $HgCl_2$ (0.50 g, 1.87×10^{-3} mol) in MeOH (5 cm^3) was refluxed for 5 h. After concentrating, the residue was dissolved in $CHCl_3$ and filtered through Celite. The filtrate was concentrated to yield a green solid of **2** (0.44 g, 5.09×10^{-4} mol, 81.8%). Compound **2** was redissolved in $CHCl_3$ and layered with MeOH to afford green crystals for single-crystal X-ray analysis. ^{1}H NMR (599.95 MHz, $CDCl_3$, 20 °C): δ 8.91 [s, H_β(13,14), ^4J(Hg−H) = 22 Hz], where H_β(a,b) represents the two equivalent β-pyrrole protons attached to carbons a and b, respectively; 8.77 [d, H_β(8,19), ^3J(H−H) = 4.2 Hz]; 8.66 [s, H_β(9,18), ^3J(H−H) = 4.8 Hz]; 8.00 [s, H_β(3,4)]; 8.58 (s) and 8.26 (s) for ortho protons, i.e., H (28,32); 8.32 (s) and 8.12 (s) for ortho protons, i.e., H (34,38); 7.74−7.88 [m, meta

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Table 1. Crystal Data for Hg(p-CN)$_4$tpp (**1**) and Hg(N-Me-tpp)Cl·CH$_2$Cl$_2$ (**2**·CH$_2$Cl$_2$)

empirical formula	$C_{48}H_{24}HgN_8$ (**1**)	$C_{46}H_{33}Cl_3HgN_4$ (**2**·CH_2Cl_2)
fw	913.34	948.70
space group	$P\bar{1}$	$P\bar{1}$
cryst syst	triclinic	triclinic
a, Å	9.968(1)	12.6343(9)
b, Å	12.666(1)	13.3035(9)
c, Å	16.783(2)	13.952(1)
α, deg	71.756(2)	67.650(1)
β, deg	80.519(2)	88.698(1)
γ, deg	84.567(2)	64.591(1)
V, Å^3	1983.0(4)	1931.3(2)
Z	2	2
F_{000}	896	936
D_{calcd}, g cm^{-3}	1.530	1.631
μ(Mo Kα), cm^{-1}	39.26	42.32
S	0.801	0.955
cryst size, mm^3	0.10 × 0.12 × 0.18	0.28 × 0.55 × 0.70
$2\theta_{max}$, deg	50.06	51.94
T, K	293(2)	293(2)
no. of reflns measd	10475	10784
no. of reflns obsd	6924($I>2\sigma(I)$)	7382($I>2\sigma(I)$)
R^a (%)	4.74	3.54
$R_w{}^b$ (%)	11.39	10.43

^{a} $R = [\sum||F_o|-|F_c||/\sum|F_o|]$. ^{b} $R_w = [\sum w(||F_o|-|F_c||)^2/\sum w(|F_o|)^2]^{1/2}$; $w = A/(\sigma^2 F_o + BF_o{}^2)$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds Hg(p-CN)$_4$tpp **1** and Hg(N-Me-tpp)Cl·CH$_2$Cl$_2$ (**2**·CH$_2$Cl$_2$)

	Hg(p-CN)$_4$tpp (**1**)		
	Distances		
Hg−N(1)	2.177(6)	Hg−N(3)	2.169(6)
Hg−N(2)	2.255(6)	Hg−N(4)	2.212(6)
	Angles		
N(1)−Hg−N(2)	84.9(2)	N(2)−Hg−N(3)	86.7(2)
N(1)−Hg−N(3)	152.3(3)	N(2)−Hg−N(4)	148.4(3)
N(1)−Hg−N(4)	86.9(2)	N(3)−Hg−N(4)	86.6(2)
	Hg(N-Me-tpp)Cl·CH$_2$Cl$_2$ (**2**·CH$_2$Cl$_2$)		
	Distances		
Hg−N(2)	2.370(3)	Hg−Cl	2.333(1)
Hg−N(3)	2.190(3)	Hg−N(1)	2.807
Hg−N(4)	2.380(3)		
	Angles		
Cl−Hg−N(2)	113.53(9)	N(3)−Hg−N(4)	80.2(1)
Cl−Hg−N(3)	149.22(9)	Cl−Hg−N(1)	92.9
Cl−Hg−N(4)	111.05(9)	N(1)−Hg−N(2)	71.7
N(2)−Hg−N(3)	80.2(1)	N(1)−Hg−N(3)	117.8
N(2)−Hg−N(4)	121.9(1)	N(1)−Hg−N(4)	70.6

and para protons]; −4.27 [s, N-Me]. UV/visible spectrum, λ (nm) [$\epsilon \times 10^{-3}$(M^{-1}cm^{-1})] in CH$_2$Cl$_2$: 459 (84.8), 570(10.5), 618 (16.0), 666 (11.7).

Spectroscopy. Proton and ^{13}C NMR spectra were recorded at 599.95 and 150.87 MHz, respectively on Varian Unity Inova-600 spectrometers locked on deuterated solvent and referenced to the solvent peak. Proton NMR is relative to CD$_2$Cl$_2$ or CDCl$_3$ at $\delta = 5.30$ or 7.24 and ^{13}C NMR to the center line of CD$_2$Cl$_2$ or CDCl$_3$ at $\delta = 53.6$ or 77.0. HMQC (heteronuclear multiple quantum coherence) was used to correlate protons and carbon through one-bond coupling and HMBC (heteronuclear multiple bond coherence) for two- and three-bond proton−carbon coupling. Nuclear Overhauser effect (NOE) difference spectroscopy was employed to determine the ^{1}H−^{1}H proximity through space over a distance of up to about 4 Å.

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.

Crystallography. Table 1 presents the crystal data as well as other information for Hg(p-CN)4tpp (**1**) and Hg(N-Me-tpp)Cl·CH$_2$Cl$_2$ (or **2**·CH$_2$Cl$_2$). Measurements were taken on a Bruker AXS SMART-1000 diffractometer using monochromatized Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The SADABS absorption corrections were made for **2**. 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 both complexes.

Results and Dicussion

Crystal Structure of Hg(p-CN)$_4$tpp (1). The molecule is a four-coodinate mercury with four nitrogen atoms of the porphyrin (Figure 1a). The most interesting bond distances and angles of the mercury(II) atom with respect to the ligand are summarized in Table 2. The covalent mercury−nitrogen bond distances are [Hg−N(1) = 2.177 (6), Hg−N(2) = 2.255 (6), Hg−N(3) = 2.169 (6), and Hg−N(4) = 2.212 (6) Å], which are close to the sum of the Hg and N covalent radii (2.23 Å). The geometrical configuration around the Hg(II) is markedly distorted from square planar to tetrahedron.

The displacements of the metal center from the planes of the macrocycle atoms (C$_{20}$N$_4$) and the four porphyrin nitrogens [i.e., N(1)−N(4)] are labeled as Δ24 and Δ4N, respectively. The Hg atom is 0.64/0.56 Å (i.e., Δ24/Δ4N) out of the porphyrin or 4N plane. The dihedral angles between the mean plane (C$_{20}$N$_4$) and the plane of the phenyl groups are 80.5° [C(24)], 48.5° [C(30)], 50.5° [C(36)], and 49.4° [C(42)]. The radius of the central “hole” [Ct′···N, the distance from the geometrical center (C$_t$′) of the mean plane of the 24-atom core to the porphyrinato-core N atoms] is 2.132 Å, which is larger than 2.01 Å as suggested by Collin and Hoard.[14] The mercury(II) is bonded in a highly expanded porphyrinato core (C$_{20}$N$_4$). Figure S1a (in the Supporting Information) illustrates the displacement (in Å) of each atom of the porphyrin (C$_{20}$N$_4$ and Hg) from the porphyrin mean plane (C$_{20}$N$_4$) and the mean 4N plane. The large metal ions, such as mercury(II), cannot fit well into the porphyrin core and just sit out-of-plane in the metalloporphyrin. It will be interesting to compare the structure of **1** with its analogous Zn(II) porphyrin complex. Zn(II)($\gamma = 0.74$ Å) in Zn(tpp)·2C$_6$H$_5$CH$_3$ [15] and Hg(II) ($\gamma = 1.12$ Å) in **1** with CN = 4 are situated apart from the 4N plane by 0 and 0.56 Å, respectively. This large displacement was expected because of the large size of the Hg. Compound **1** appears to show C$_4$ axial symmetry in solution. Hence, only one kind of H$_\beta$, meta protons, C$_\beta$, C$_\alpha$, C$_m$, and phenyl-C$_1$ were observed for **1** in CDCl$_3$ at 20 °C.

Molecular Structure of 2. Figure 1b illustrates the skeletal framework of complex **2**·CH$_2$Cl$_2$. The geometrical configuration around the Hg^{2+} is described as a distorted square-based pyramid in which the N(1) atom occupies the apical site, whereas the three nitrogen atoms [N(2), N(3), and N(4)] and one chlorine atom Cl define the basal plane. The unusual bond distances and angles are summaried in Table 2.

According to Grdenic,[16,17] the mercury coordination sphere can be categorized in terms of their primary, or characteristic, (m; m = number of covalently bonded atoms) and effective coordination ($m + n$, the total number of primary and secondary bonds; n = number of atoms at distances greater than the sum of the covalent radii but less than or equal to the sum of the

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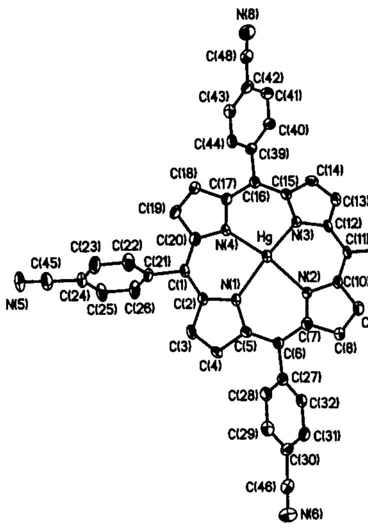
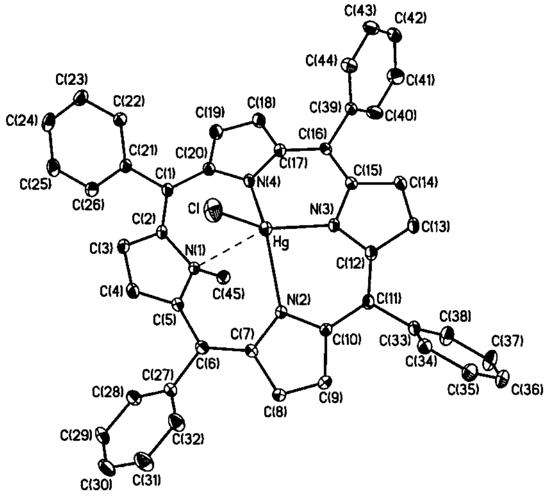


(a) **Hg(*p*-CN)$_4$tpp**



(b) **Hg(N-Me-tpp)Cl**

Figure 1. Molecular configuration and atom-labeling scheme for (a) Hg (*p*-CN)$_4$tpp(**1**) and (b) Hg(*N*-Me-tpp)Cl·CH$_2$Cl$_2$ (or **2**·CH$_2$Cl$_2$), with ellipsoids drawn at 30% probability. Hydrogen atoms for both compounds and solvent C(60)H(60A)H(60B)Cl(1)Cl(2) for **2**·CH$_2$Cl$_2$ are omitted for clarity.

appropriate van der Waals radii). The effective coordination is then denoted as [$m + n$].[18] The Hg−Cl bond distance of 2.333 (1) Å is smaller than the sum of the covalent radii of Hg and Cl (2.47 Å). The covalent bond of Hg−Cl = 2.333 (1) Å in **2** is comparable to those of Hg(1)−Cl(1) = 2.318 (2) Å and Hg(2)−Cl(2) = 2.285 (2) Å in bischloromercury(II) complex of N-tosylaminooctaethylporphyrin[4] and that of Hg(1)−Cl(1) = 2.318 (1) Å in Hg(Stpp)Cl (Stpp = tetraphenyl-21-thiaporphyrin anion).[19] The mercury−nitrogen bond distances [Hg−N(2) = 2.370 (3), Hg−N(3) = 2.190 (3), and Hg−N(4) = 2.380 (3) Å] which are close to the sum of the Hg and N covalent radii (2.23 Å) are also smaller than the upper limit 2.75 (2) Å for the typical covalent bond distance of Hg−N.[20,21] Hence, N(2), N(3), and N(4) are bonded strongly as well as covalently to the Hg atom in **2**. Mecury(II) is bonded to fewer than four nitrogen atoms, and so compound **2** may be considered as a sitting-atop (SAT) complex. The similar kind of SAT complex was previously reported for bischloromercury(II) complex of N-tosylaminooctaethylporphyrin.[4] Although the primary (or characteristic) coordination environment around the mercury atom in **2** is tentatively assigned as a SAT complex, the Hg···N(1) distance of 2.807 Å is longer than 2.75(2) Å but is signficantly shorter than the sum of the van der Waals radii of Hg and N (3.28 Å). This longer Hg···N(1) contact is described as weak (secondary) bond. This kind of secondary bonds have been found between Hg(2) and N(1) [Hg(2)−N(1) 2.99 (1) Å] in [{Hg(C$_6$H$_4$C$_5$H$_4$N)}$_2$(tuc)] (tuc^{2-} = 2-thiouracilate dianion),[22] and with a Hg···N distance of 2.89 (1) Å in bis[2-((dimethylamino)methyl)phenyl]mercury(II).[23] The effective coordination around mercury in **2** may be construed as an expansion of the secondary valency of mercury from four to five {4 + 1[N(1)]}. The distortion in five-coordinate complexes can be quantified by the “degree of trigonality” which is defined as $\tau = (\beta - \alpha)/60$, where β is the largest and α the second largest of the L$_{\text{basal}}$−M−L$_{\text{basal}}$ angles.[24,25] In the present case, we find β = 149.22(9)° [N(3)−Hg−Cl] and α = 121.9(1)° [N(2)−Hg−N(4)], and thus, $\tau = 0.46$; the limiting values are $\tau = 0$ for an ideal tetragonal geometry and $\tau = 1$ for an ideal trigonal−bipyramidal geometry. Hence, the geometry around Hg(II) is best described as a distorted square-based pyramid (or trigonal bipyramidal distorted square-based pyramid, TBPDSBP)[26] with N(1) as the apical atom (Figure S2 in the Supporting Information). The τ values calculated for Zn(*N*-Me-tpp)Cl,[5] Co(*N*-Me-tpp)Cl,[6,7] Mn(*N*-Me-tpp)Cl,[8] Fe(*N*-Me-tpp)Cl,[9] and [Fe$^{\text{III}}$(*N*-Me-ttp)Cl][SbCl$_6$][10] by the same method are 0.05, 0.02, 0.09, 0.06, and 0.09, respectively, and the coordination geometry for these five compounds is closer to regular square-based pyramid (RSBP)[27] with a chloride ion axially coordinated to the metal.

We adopt the plane of three strongly bound pyrrole nitrogen atoms [i.e., N(2), N(3), and N(4)] as a reference plane 3N. Figure S1b (in the Supporting Information) illustrates the displacement (in Å) of each atom of the porphyrin (C$_{20}$N$_4$, Hg, N-Me, and Cl$^-$) from the 3N plane. Because of the larger size of the mercury(II) ion, Hg is considerably pushed away from the 3N plane; its displacement of 1.13 Å is in the same direction as that of the apical Cl$^-$ ligand [cf. 0.65 Å for Zn(II) in Zn(N-Me-tpp)Cl,[5] 0.56 Å for Co(II) in Co(N-Me-tpp)Cl,[6,7] 0.69 Å for Mn(II) in Mn(N-Me-tpp)Cl,[8] 0.62 Å for Fe(II) in Fe(N-Me-tpp)Cl,[9] and 0.57 Å for Fe(III) in [Fe$^{\text{III}}$(N-Me-ttp)Cl][SbCl$_6$].[10] The porphyrin macrocycle is indeed distorted [Figure S1b in the Supporting Information] as a result of the *N*-Me group. The pyrrole N(1) [i.e., plane of N(1), C(2)−C(5)] bearing the methyl group is the most deviated one from the 3N plane, making a dihedral angle of 39.1°, whereas smaller angles of 16.2°, 15.3°, and 0.3° occur with pyrroles N(2), N(4), and N(3), respectively.

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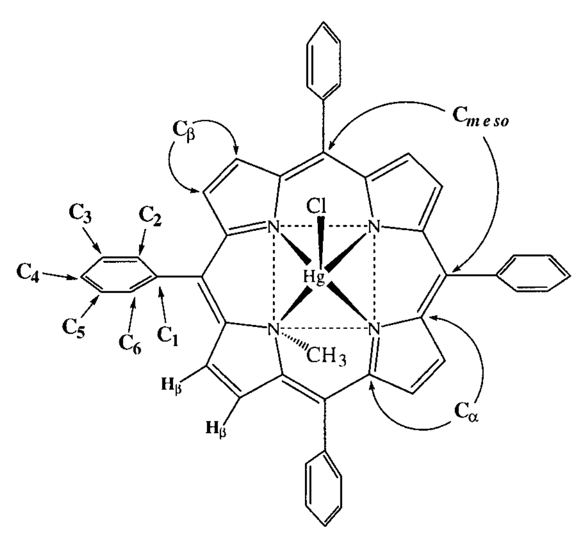
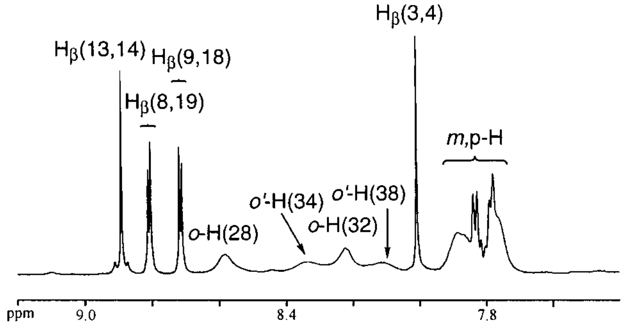
Such a large deviation from planarity is also reflected for pyrrole N(1) by observing a 9.5−10.6 ppm upfield shift of $C_\beta(3,4)$ at 122.5 ppm, compared to 132.0 ppm for $C_\beta(8,19)$, 133.08 ppm for $C_\beta(9,18)$, and 133.11 ppm for $C_\beta(13,14)$ at 20 °C. Similarly the nonplanarity of porphyrin causing upfield shifts of C_β resonances were also observed with a magnitude of 5.6−7.0 ppm for Tl(*N*-Me-tpp)$(OAc)_2$.[11] The dihedral angles between the mean plane of the skeleton 3N and the planes of the phenyl groups are 34.5° [C(24)], 36.2° [C(30)], 63.8° [C(36)], and 72.7° [C(42)].

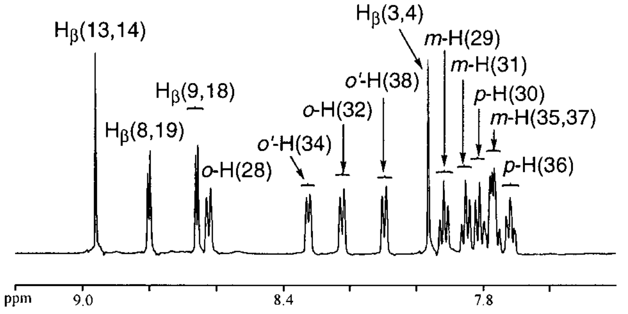
The Hg ion is displaced from the plane of the four individual pyrrole groups, suggesting that the pyrrole nitrogen lone pairs are not optimally situated for covalent bonding to the metal. The displacements of Hg ions from the plane of each pyrrole ring are 0.50 Å for pyrrole N(2) ring, 1.13 Å for pyrrole N(3), 0.55 Å for pyrrole N(4), and 2.64 Å for pyrrole N(1) ring. The angles between Hg−N vector and the corresponding pyrrole ring are 13.9° for pyrrole N(2) ring, 30.6° for pyrrole N(3), 14.7° for pyrrole N(4), and 70.2° for pyrrole N(1) ring.

^{1}H and ^{13}C of 2 in $CDCl_3$ and CD_2Cl_2. Complex **2** was thoroughly characterized by ^{1}H (Figure 2) and ^{13}C NMR spectra. In solution, compound **2** has effective C_s symmetry, with the mirror plane running through the C(45)−N(1)−Hg−Cl−N(3). There are four β-pyrrole protons H_β, four β-pyrrole carbons C_β, four α-pyrrole carbons C_α, two different meso carbons C_{meso}, and two phenyl-C_1 carbons. The $H_\beta(13,14)$ of **2** in $CDCl_3$ at 20 °C was observed at $\delta = 8.91$ ppm with a $^4J(^{199}Hg-H)$ value of 22 Hz (Figures S3−S6 in the Supporting Information). This coupling satellites is comparable to $^4J(^{199}Hg-H)$ values of 20 and 24 Hz for the H_d protons in $[Hg(TMPA)](ClO_4)_2$ [28] and in $[Hg(BMPA)NCCH_3](ClO_4)_2$,[29] respectively, {with TMPA = tris[(2-pyridyl)methyl]amine and BMPA = bis[(2-pyridyl)methyl]amine} and that of 16 Hz in Hg(Stpp)Cl.[19] The singlet at 8.00 ppm assigned to $H_\beta(3,4)$ is confirmed by NOE difference spectrum (1-D). We irradiated *N*-Me at $\delta = -4.27$ and observed the enhancement for $H_\beta(3,4)$ (Figure S3 in the Supporting Information). The average distance between $H_\beta(3,4)$ and phenyl-*ortho* protons of *o*-H(28,32) [or *o*-H(22,26)] is 3.43 Å, and the same between those ortho protons and $H_\beta(8,19)$ is 3.46 Å. Irradiation of $H_\beta(3,4)$ strongly enhanced ortho protons of *o*-H(28,32) at 8.58 and 8.26 ppm (Figure S4 in the Supporting Information). Likewise, irradiation of *o*-H(28,32) at 8.58 ppm resulted in enhancement of both $H_\beta(8,19)$ at 8.77 ppm and $H_\beta(3,4)$ at 8.0 ppm (Figure S4 in the Supporting Information). The average distance between $H_\beta(13,14)$ and phenyl-ortho protons of *o*-H(34,38) [or *o*′-H(40,44)] is 3.42 Å. Irradiation of $H_\beta(13,14)$ enhanced ortho protons of *o*′-H(34,38) at $\delta = 8.32$ and 8.12 ppm (Figure S6 in the Supporting Information).





(a) 20°C



(b) -90°C

Figure 2. ^{1}H NMR spectra for **2** at 599.95 MHz in CD_2Cl_2 showing four different β-pyrrole protons H_β and phenyl protons (*o*-H, *m*, *p*-H): (a) 20 °C and (b) −90 °C.

Figure 2 depicts the representative ^{1}H spectra for **2** in CD_2Cl_2 solvent at +20 and −90 °C. At 20 °C, the rotation of phenyl group along the C_1-C_{meso} bond is intermediately slow. This intermediately slow rotation is supported by assigning the two broad singlets at 8.23 (or 8.12) and 8.59 (or 8.31) ppm to ortho protons *o*′-H(28,32) [or *o*′-H(34,38); Figure 2a]. At −90 °C, this rotation is extremely slow. Hence, the rate of intramolecular exchange of the ortho protons for **2** in CD_2Cl_2 is also extremely slow. The doublet at 8.62 ppm is assigned to ortho protons *o*-H(28) [or *o*-H(26)] with $^3J(H-H) = 7.3$ Hz (Figure 2b). The other doublet at 8.22 ppm is due to ortho protons *o*-H(32) [or *o*-H(22)] with $^3J(H-H) = 7.3$ Hz. Likewise, the doublet at 8.32 ppm is due to the ortho protons *o*′-H(34) [or *o*′−H(44)] with $^3J(H-H) = 6.8$ Hz. The corresponding doublet at 8.09 ppm is due to the ortho protons *o*′-H(38) [or *o*′-H(40)] with $^3J(H-H) = 6.8$ Hz (Figure 2b). In a similar way, the meta and para protons appearing as multiplet (7.79−7.89 ppm) at 20 °C (Figure 2a) changed to 7.92 [t, $^3J(H-H) = 7.4$ Hz, *m*-H(29)], 7.85 [t, $^3J(H-H) = 7.4$ Hz, *m*-H(31)], 7.81 [t, $^3J(H-H) = 7.6$ Hz, *p*-H(30)], 7.77 [m, *m*-H(35,37)], and 7.72 ppm [m, *p*-H(36)] at −90 °C (Figure 2b). The analysis of this data was confirmed by the NOE difference spectroscopy for **2** in CD_2Cl_2 at −90 °C (Figures S7−S15 in the Supporting Information). In addition, the unambiguous assignment of ^{13}C NMR in CD_2Cl_2 at −90 °C were shown in the Supporting Information (page S16).

The change in orientation of the pyrrole N(1) ring in **2** is the result of altered hybridizaton at the pyrrole nitrogen atom N(1)

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from sp^2 for **1** to sp^3 for **2**. The rehybridization of the substituted porphyrin nitrogen atom and steric bulk of the substituted methyl group lead to a large displacement of the Hg ion above the 4N plane toward the chloro ligand in **2**. Furthermore, the ionic radius of Hg^{2+} is larger in **2** than in **1**. Hg is found to be 1.19 Å above this 4N plane in **2**, and the corresponding displacement was 0.56 Å for Hg in **1** (Figure S1 in the Supporting Information).

Conclusions

We have investigated the first two diamagnetic and mononuclear mercury(II) porphyrin complexes **1** and **2** and their X-ray structures are established. The NOE difference spectroscopy, HMQC, and HMBC were employed to unambiguous assignment of the ^1H and ^{13}C NMR resonances of **2** in CD_2Cl_2 at −90 °C.

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Supporting Information Available: Figure S1 shows the diagram of porphyrinato core for both complexes. Figure S2 illustrates the oriented X-ray geometry of **2** to show a trigonal bipyramidal distorted square-based pyramidal structure. Figures S3−S15 consist of the NOE difference spectroscopy for compound **2** in $CDCl_3$ at 20 °C and in CD_2Cl_2 at −90 °C. The X-ray crystallographic files in CIF format for compounds **1** and **2** are also depicted. This material is available free of charge via the Internet at http://pubs.acs.org.

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