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The structures of (phenylato)(*N*-2-thiophenecarboxamido-*meso*-tetraphenylporphyrinato)mercury(II) and bisphenylmercury(II) complex of 21-(4-*tert*-butyl-benzenesulfonamido)-5,10,15,20-tetraphenylporphyrin

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Abstract

The reaction of PhHgOAc with *N*-NHCO-2-C_4H_3S-Htpp (**5**) and *N*-*p*-HNSO2C6H4^{t}Bu-Htpp (**4**) gave a mercury (II) complex of (phenylato) (*N*-2-thiophenecarboxamido-*meso*-tetra phenylporphyrinato)mercury(II) 1.5 methylene chloride solvate [HgPh(*N*-NHCO-2-C_4H_3S-tpp) · CH_2Cl_2 · 0.5C_6H_{14}; **6** · CH_2Cl_2 · 0.5C_6H_{14}] and a bismercury complex of bisphenylmercury(II) complex of 21-(4-*tert*-butyl-benzenesulfonamido)-5,10,15,20-tetraphenylporphyrin, [(HgPh)2(*N*-*p*-$NSO_2C_6H_4{}^t$Bu-tpp); **7**], respectively. The crystal structures of **6** · CH_2Cl_2 · 0.5C_6H_{14} and **7** were determined. The coordination sphere around Hg(1) in **6** · CH_2Cl_2 · 0.5C_6H_{14} and Hg(2) in **7** is a sitting-atop derivative with a seesaw geometry, whereas for the Hg(1) in **7**, it is a linear coordination geometry. Both Hg(1) in **6** · CH_2Cl_2 · 0.5C_6H_{14} and Hg(2) in **7** acquire 4-coordination with four strong bonds [Hg(1)–N(1) = 2.586(3) Å, Hg(1)–N(2) = 2.118(3) Å, Hg(1)–N(3) = 2.625(3) Å, and Hg(1)–C(50) = 2.049(4) Å for **6** · CH_2Cl_2 · 0.5C_6H_{14}; Hg(2)–N(1) = 2.566(6) Å, Hg(2)–N(2) = 2.155(6) Å, Hg(2)–N() = 2.583(6) Å, and Hg(2)–C(61) = 2.064(7) Å for **7**]. The plane of the three pyrrole nitrogen atoms [i.e., N(1)–N(3)] strongly bonded to Hg(1) in **6** · CH_2Cl_2 · 0.5C_6H_{14} and to Hg(2) in **7** is adopted as a reference plane 3N. For the Hg^{2+} complex in **6** · CH_2Cl_2 · 0.5C_6H_{14}, the pyrrole nitrogen bonded to the 2-thiophenecarboxamido ligand lies in a plane with a dihedral angle of 33.4° with respect to the 3N plane, but for the bismercury(II) complex in **7**, the corresponding dihedral angle for the pyrrole nitrogen bonded to the $NSO_2C_6H_4{}^t$Bu group is found to be 42.9°. In the former complex, $Hg(1)^{2+}$ and N(5) are located on different sides at 1.47 and −1.29 Å from its 3N plane, and in the latter one, $Hg(2)^{2+}$ and N(5) are also located on different sides at −1.49 and 1.36 Å form its 3N plane. The Hg(1)···Hg(2) distance in **7** is 3.622(6) Å. Hence, no metallophilic Hg(II)···Hg(II) interaction may be anticipated. NOE difference spectroscopy, HMQC and HMBC were employed to unambiguous assignment for the ^{1}H and ^{13}C NMR resonances of **6** · CH_2Cl_2 · 0.5C_6H_{14} in CD_2Cl_2 and **7** in $CDCl_3$ at 20 °C. The ^{199}Hg chemical shift δ for a 0.05 M solution of **7** in $CDCl_3$ solution is observed at −1074 ppm for Hg(2) nucleus with a coordination number of four and at −1191 ppm for Hg(1) nucleus with a coordination number of two. The former resonance is consistent with that chemical shift for a 0.01 M solution of **6** in CD_2Cl_2 having observed at −1108 ppm for Hg(1) nucleus with a coordination number of four.

Keywords: Mercury porphyrin; X-ray diffraction; Mercury NMR; *N*-carboxamido; Bismercury

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1. Introduction

Hg(II) is a diamagnetic ion and maintains d^{10} electron configuration which minimizes intrinsic coordination geometry preferences while favoring coordination by softer ligands. In 1979, a homo-dinuclear structure was proposed for the bischloromercury(II) complex of *N*-tosylaminoctaethylporphyrin, $C_{45}H_{51}N_5OSCl_2Hg_2$ [or $(HgCl)_2$(N-NTs-OEP); **1**] (NTs = tosylimido, OEP = dianion of octaethylporphyrin), which represented the first X-ray structural proof for the existence of mercury(II) porphyrin sitting-atop (SAT) complexes [1]. Later, the mononuclear mercury(II) porphyrin sitting-atop structure of a *N*-monoalkylated porphyrin, i.e., [chloro(*N*-methyl-*meso*-tetraphenylporphyrinato) mercury(II)] [Hg(*N*-Me-tpp)Cl; **2**] (tpp = dianion of *meso*-tetraphenylporphyrin) was reported [2].

The preparation of *N*-substituted-*N*-aminoporphyrins has been described by three groups [3–7]. Upon replacement of CH_3^- of tosyl by a bulkier and heavier $^tBu^-$ group, the free base *N*-*p*-$HNSO_2C_6H_4CH_3$-Htpp (**3**) became 21-(4-*tert*-butyl-benzenesulfonamido)- 5,10,15,20-tetraphenylporphyrin *N*-*p*-$NSO_2C_6H_4{}^tBu$-Htpp (**4**) [8]. In *N*-substituted-*N*-aminoporphyrin, the H atom of NH_2 when replaced by 2-thiophenecarboxyamino group, it forms a new free aminated porphyrin, namely, *N*-2-thiophenecarboxamido-*meso*-tetraphenylporphyrin (*N*-NHCO-2-C_4H_3S-Htpp; **5**) which is a derivative of 2-acyl-thiophenes [9]. The phenylmercury(II) cation which binds to a variety of ligand sites ranging from N, O and C atoms serves as a good probe ion because it is unifunctional, gives complexes with a well defined stereochemistry and participates readily in electrophilic substitution [10]. A thorough review of the literature shows that there is no prior report on phenylmercury(II) with free bases **4** and **5** [8,9]. The coordination chemistry of phenylmercury(II) explored with anions derived from bases **4** and **5** reveals the formation of the phenylmercury(II) complex of (phenylato)(*N*-2-thiophenecarboxamido-*meso*-tetraphenylporphyrinato) mercury(II) [HgPh(*N*-NHCO-2-C_4H_3S-tpp); **6**] and bisphenylmercury(II) complex of 21-(4-*tert*-butyl-benzenesulfonamido)-5,10,15,20-tetraphenylporphyrin, $[(HgPh)_2$(*N*-*p*-$NSO_2C_6H_4{}^tBu$-tpp); **7**], respectively. The lack of previous work on metal complexes of these two ligands prompted us to undertake the synthesis and structural studies of Hg(II) complexes. Apparently, upon replacing Cl^-, OEP^{2-}, and CH_3^- with $C_6H_5^-$, tpp^{2-}, and the *tert*-butyl anion respectively, the complex **1** became **7** [1]. Likewise, upon replacement of Cl^- and N–CH_3 by $C_6H_5^-$ and N–NHCO-2-C_4H_3S, respectively, the complex **2** became **6** [2]. The compounds **6** and **7** are the first two organomercury(II) porphyrin complexes with the $HgPh^+$ moiety. The ring current effect of the porphyrin was employed to unambiguously assignment of the ^1H resonances of the phenyl group coordinated to Hg(1) in **6** or that group coordinated either to Hg(1) or Hg(2) in **7**. The bulky ^tBu group in this system enhances the crystallization of complex **7** [8]. The complexes **6** and **7** were investigated by ^{199}Hg NMR spectroscopy in order to clarify the coordination behavior of **6** in CD_2Cl_2 and **7** in $CDCl_3$ solutions. In this paper, we describe here on the synthesis, ^1H, ^{13}C and ^{199}Hg NMR spectroscopic characterization of complexes **6** and **7**. Our hope is that such structure-spectroscopic correlations will prove useful in the further development of the degradation reactions for environmental poisoning of mercury.

2. Experimental

2.1. HgPh(N-NHCO-2-C_4H_3S-tpp) (6)

A mixture of PhHgOAc (0.05 g, 1.48×10^{-4} mol) in MeOH (10 cm^3) and *N*-NHCO-2-C_4H_3S-Htpp (**5**) (0.07 g, 9.46×10^{-5} mol) in CH_2Cl_2 (20 cm^3) and CH_3CN (20 cm^3) was refluxed overnight [5,9]. After concentrating, the residue was dissolved in a trace amount of toluene, dried with anhydrous Na_2SO_4, and filtered. The filtrate was concentrated and recrystallized from CH_2Cl_2–hexane [1:2 (v/v)] yielding a bluish purple solid of **6** (0.056 g, 5.49×10^{-5} mol, 58%) which was again dissolved in CH_2Cl_2 and layered with hexane to get bluish purple crystals for single crystal X-ray analysis. ^1H NMR (599.94 MHz, CD_2Cl_2, 20 °C): δ 8.86 [s, H_β(7,8)]; 8.73 [d, H_β(2,13), ^3J(H–H) = 4.8 Hz]; 8.71 [d, H_β(3,12), ^3J(H–H) = 4.8 Hz]; 7.70 [s, H_β(17,18)]; 8.21 [s, *o*-H(22,32) and *o*-H(26,28)]; 8.48 [bs, *o*′-H(38,40) and *o*′-H(34,44)]; 7.76–7.83 (m, *m*, *p*-H), 6.15[d, S–H_5 or H(49), ^3J(H–H) = 5.1 Hz], where S = thiophene group; 6.03 [t, Hg–Ph–H_4 or H(53), ^3J(H–H) = 7.5 Hz], where Hg–Ph is the phenyl group (Ph) coordinated to Hg atom; 5.82 [t, Hg–Ph–H_3,5 or H(52, 54), ^3J(H–H) = 7.8 Hz and ^4J(Hg–H) = 50 Hz]; 5.27 [t, S–H_4 or H(48), ^3J(H–H) = 3.6 Hz]; 3.13 [d, Hg–Ph–H_2,6 or H(51,55), ^3J(H–H) = 6.0 Hz and ^3J(Hg–H) = 194 Hz]; 1.78 [d, S–H_3 or H(47), ^3J(H–H) = 3.0 Hz]; −0.10 [s, NH]. ^{199}Hg NMR (107.24 MHz, CD_2Cl_2, 20 °C): δ −1108 [s, Hg(1)]. MS (FAB): M^+ 1017 (calc. for $C_{55}H_{34}Hg_1N_5O_1S_1$:1017). UV/Vis spectrum, λ(nm) [$\varepsilon\times10^{-3}$ (M^{-1} cm^{-1})] in CH_2Cl_2: 430 (585.2), 546 (26.7), 582 (25.3), 637 (16.6).

2.2. (HgPh)2(N-p-$NSO_2C_6H_4{}^tBu$-tpp) (7)

A mixture of PhHgOAc (0.081 g, 2.41×10^{-4} mol) in MeOH (10 cm^3) and *N*-*p*-$HNSO_2C_6H_4{}^tBu$-Htpp (**4**) (0.05 g, 6.03×10^{-5} mol) in CH_2Cl_2 (20 cm^3) and CH_3CN (20 cm^3) was refluxed for 12 h [5,8]. After concentrating, the residue was dissolved in a trace amount of toluene, dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated and recrystallized from $CHCl_3$–hexane [1:1 (v/v)] yielding bluish purple solid of **7** (0.055 g, 3.98×10^{-5} mol, 66%) which was again dissolved in $CHCl_3$ and layered with hexane to get bluish purple crystals for single crystal X-ray analysis. ^1H NMR (299.95 MHz, $CDCl_3$, 20 °C) : δ 8.84 [d, H_β(3,12), ^3J(H–H) = 4.2 Hz]; 8.79 [d, H_β(2,13), ^3J(H–H) = 4.2 Hz]; 8.56 [s, H_β(7,8)];

6.78 [s, H_β(17,18)]; 8.21 (bs) and 8.12 (s) for *o*-H(26,28) and *o*-H (22,32); 7.69–7.78 (m, *m*, *p*-H), 7.04 [d, ^{t}BuBS-$H_{3,5}$ or H(47, 49), ^3J(H–H) = 8.4 Hz], where ^{t}BuBS = 4-*tert*-butylbenzenesulfonyl; 6.72 [t, Hg(1)–Ph–H_4 or H(58), ^3J(H–H) = 7.5 Hz], where Hg(1)–Ph is the phenyl group (Ph) coordinated to Hg(1) atom; 6.63 [t, Hg(1)–Ph–H_3,5 or H(57, 59), ^3J(H–H) = 7.2 Hz]; 6.09 [d, ^{t}BuBS-$H_{2,6}$ or H(46, 50), ^3J(H–H) = 8.4 Hz]; 5.99 [t, Hg(2)–Ph–H_4 or H(64), ^3J(H–H) = 7.5 Hz], where Hg(2)-Ph is the phenyl group (Ph) coordinated to Hg(2) atom; 5.74 [t, Hg(2)–Ph–$H_{3,5}$ or H(63, 65), ^3J(H–H) = 7.5 Hz and ^4J(Hg–H) = 53 Hz]; 4.72 [d, Hg(1)–Ph–$H_{2,6}$ or H(56, 60), ^3J(H–H) = 7.2 Hz and ^3J(Hg–H) = 196 Hz]; 3.08 [d, Hg(2)–Ph–$H_{2,6}$ or H(62, 66), ^3J(H–H) = 7.5 Hz and ^3J(Hg–H) = 198 Hz]; 1.15 [s, t-butyl protons]. ^{199}Hg NMR (107.24 MHz, $CDCl_3$, 20 °C) : δ −1074 [s, Hg(2)]; −1191 [s, Hg(1)]. MS (FAB): M^+ 1379 (calcd for $C_{66}H_{51}Hg_2N_5O_2S$: 1379). UV/Vis spectrum, λ (nm) [$\varepsilon \times 10^{-3}$ (M^{-1} cm^{-1})] in CH_2Cl_2: 433 (516.5), 461 (67.0), 549 (23.1), 585 (24.8), 638 (22.5).

2.3. Spectroscopy

Proton and ^{13}C NMR spectra were recorded at 299.95 (or 599.94) and 75.43 (or 150.87) MHz, respectively, on Varian VXR-300 (or Varian Unity Inova-600) spectrometers locked on deuterated solvent, and referenced to the solvent peak. Proton NMR is relative to CD_2Cl_2 or $CDCl_3$ at $\delta = 5.30$ or 7.24 and ^{13}C NMR to the center line of CD_2Cl_2 or $CDCl_3$ at $\delta = 53.6$ or 77.0. ^{199}Hg NMR was obtained at 107.24 MHz on a Bruker DMX-600 spectrometer locked on deuterated solvent. Chemical shifts of ^{199}Hg were measured relative to an external reference of 0.5 M phenylmercury(II) acetate in DMSO-d6 (−1439.5 ppm) but reported relative to dimethylmercury (0.0 ppm). 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 102 A mass spectrometer. UV/Vis spectra were recorded at 20 °C on a HITACHI U-3210 spectrophotometer.

2.4. Crystallography

Table 1 presents the crystal data as well as other information for $\mathbf{6}\cdot CH_2Cl_2\cdot 0.5C_6H_{14}$ and **7**. Measurements were taken on a Bruker AXS SMART-1000 diffractometer using monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were made for both complexes. The structures were solved by direct methods (SHELXTL97) [11] and refined by the full-matrix least-squares method. The phenyl group coordinated to Hg(1) within $\mathbf{6}\cdot CH_2Cl_2\cdot 0.5C_6H_{14}$ is disordered with an occupancy factor of 0.65 for C(52)–C(55) and 0.35 for C(52′)–C(55′). S(1)

Table 1
Crystal data and structure refinement for HgPh(*N*–NHCO-2-C_4H_3S-tpp)·($CH_2Cl_2\cdot 0.5C_6H_{14}$) ($\mathbf{6}\cdot CH_2Cl_2\cdot 0.5C_6H_{14}$) and (HgPh)2(*N*-*p*-NSO2C6H4^{t}Bu-tpp) (**7**)

Empirical formula	$C_{59}H_{46}C_{12}HgN_5OS$ ($\mathbf{6}\cdot CH_2Cl_2\cdot 0.5C_6H_{14}$)	$C_{66}H_{51}Hg_2N_5O_2S$ (**7**)
Formula weight	1144.56	1379.36
Space group	$P\bar{1}$	$P\bar{1}$
Crystal system	triclinic	triclinic
a (Å)	13.1989(9)	9.7004(12)
b (Å)	14.4506(10)	18.148(2)
c (Å)	14.7071(10)	19.241(2)
α (°)	90.1320(10)	72.233(2)
β (°)	112.0980(10)	82.798(2)
γ (°)	95.8480(10)	88.430(2)
V (Å^3)	2583.0(3)	3200.0(7)
Z	2	2
F(000)	1146	1348
D_{calc} (g cm^{-3})	1.472	1.432
μ (Mo Kα) (mm^{-1})	3.169	4.868
S	0.864	0.981
Crystal size (mm)	0.80 × 0.46 × 0.46	0.35 × 0.10 × 0.04
θ (°)	2.02–26.01	1.36–28.26
T (*K*)	293(2)	293(2)
Number of reflections measured	10163	15835
Number of reflections observed	8988	8424
R_1^a [$I > 2\sigma(I)$]	0.0360	0.0522
wR_2^b	0.0996	0.1289

[a] $R_1 = [\sum||F_o| - F_c||/\sum|F_o|]$.
[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°) for compounds $\mathbf{6}\cdot CH_2Cl_2\cdot 0.5C_6H_{14}$ and **7**

Complex $\mathbf{6}\cdot CH_2Cl_2\cdot 0.5C_6H_{14}$			
Bond lengths (Å)			
Hg(1)–N(1)	2.589(3)	Hg(1)–C(50)	2.047(4)
Hg(1)–N(2)	2.119(3)	Hg(1)···N(4)	3.171(3)
Hg(1)–N(3)	2.627(3)	Hg(1)···N(5)	3.402(3)
Bond angles (°)			
C(50)–Hg(1)–N(1)	107.20(15)	N(1)–Hg(1)–N(2)	76.11(11)
C(50)–Hg(1)–N(2)	173.58(12)	N(1)–Hg(1)–N(3)	105.97(10)
C(50)–Hg(1)–N(3)	107.66(15)	N(2)–Hg(1)–N(3)	76.19(11)
Complex **7**			
Bond lengths (Å)			
Hg(1)–N(5)	2.103(5)	Hg(2)–N(1)	2.566(6)
Hg(1)–C(55)	2.065(8)	Hg(2)–N(2)	2.155(6)
Hg(1)···Hg(2)	3.622(6)	Hg(2)–N(3)	2.583(6)
Hg(1)···N(1)	3.033(6)	Hg(2)–C(61)	2.064(7)
Hg(1)···N(2)	2.860(6)	Hg(2)···N(4)	3.182(6)
Hg(1)···N(3)	2.850(6)	Hg(2)···N(5)	3.669(6)
Hg(1)···N(4)	3.203(6)		
Bond angles (°)			
N(5)–Hg(1)–C(55)	160.7(3)	N(1)–Hg(2)–N(2)	76.0(2)
C(61)–Hg(2)–N(1)	103.4(3)	N(1)–Hg(2)–N(3)	104.42(17)
C(61)–Hg(2)–N(2)	167.4(2)	N(2)–Hg(2)–N(3)	75.1(2)
C(61)–Hg(2)–N(3)	116.8(2)		

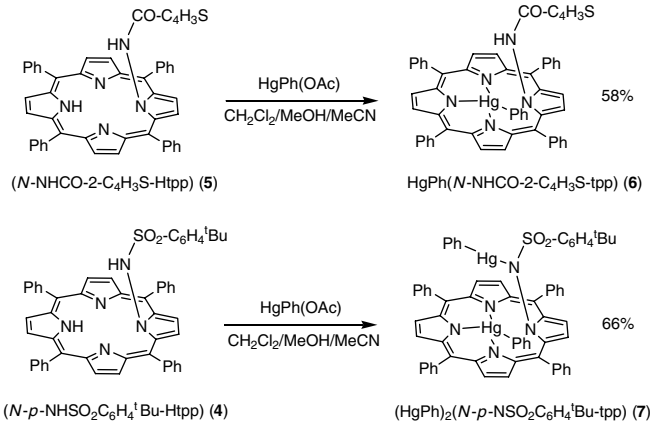
[or O(1)] within $\mathbf{6}\cdot CH_2Cl_2\cdot 0.5C_6H_{14}$ is also disordered with an occupancy factor of 0.55 [or 0.55] for S(1) [or O(1)] and 0.45 [or 0.45] for S(1′) [or O(1′)], respectively. One equivalent of CH_2Cl_2 solvent in $\mathbf{6}\cdot CH_2Cl_2\cdot 0.5C_6H_{14}$ is disordered with an occupancy factor of 0.62 [or 0.51] for Cl(1) [or Cl(2)] and 0.38 [or 0.49] for Cl(1′) [or Cl(2′)], respectively. The *tert*-butyl group within **7** is disordered with an occupancy factor of 0.46 [or 0.53] for C(52) [or C(53)] and 0.54 [or 0.47] for C(52′) [or C(53′)], respectively. All disordered atoms and solvent (CH_2Cl_2) were refined with isotropic displacement parameters. All non-hydrogen atoms, except the disordered atoms and solvent (CH_2Cl_2), were refined with anisotropic thermal parameters, whereas all hydrogen atoms were placed in calculated positions and refined with a riding model. Table 2 lists selected bond lengths and angles for complexes $\mathbf{6}\cdot CH_2Cl_2\cdot 0.5C_6H_{14}$ and **7**.

3. Results and discussion

3.1. Molecular structures of $\mathbf{6}\cdot CH_2Cl_2\cdot 0.5C_6H_{14}$ and 7

Using the d^{10} metal mercury(II), new mononuclear mercury $\mathbf{6}\cdot CH_2Cl_2\cdot 0.5C_6H_{14}$ and new bismercury **7** complexes were synthesized. The synthetic strategy is outlined in Scheme 1.

During the metallation of free base *N*-NHCO-2-C_4H_3S-Htpp (**5**) with PhHg(OAc) (Scheme 1) [9], the soft acid Hg^{2+} prefers to retain one phenyl ligand (soft base) and coordinates to the N [i.e., N(2)] of **5** to form a four-coordinate complex $\mathbf{6}\cdot CH_2Cl_2\cdot 0.5C_6H_{14}$ with a seesaw geometry and the angle of N(2)–Hg(1)–C(50) is 173.58(12)° in $\mathbf{6}\cdot CH_2Cl_2\cdot 0.5C_6H_{14}$ (Table 2). The complex $\mathbf{6}\cdot CH_2Cl_2\cdot 0.5C_6H_{14}$ is first example of an *N*-substituted *N*-aminoporphyrin-mercury complex with retention of the *N*-2-thiophenecarboxamido group. Two strongly electronegative oxygen atoms of the sulfonamide group in the free base *N*-*p*-$HNSO_2C_6H_4{}^tBu$-Htpp (**4**) enhance the acidity of the amido proton of $HNSO_2C_6H_4{}^tBu$ ligand in **4** [8]. During the metallation of *N*-*p*-$HNSO_2C_6H_4{}^tBu$-Htpp (**4**) with PhHg(OAc) one Hg^{2+} prefers to retain the phenyl group and coordinate to nitrogen [i.e., N(5)] of the *N*-*p*-HNSO2C6H4^{t}Bu group to form a two-coordinate, linear coordination around Hg(1) atom and with an angle of N(5)–Hg(1)–C(55) = 160.7(3)° in **7**. The other Hg^{2+} retains the phenyl group and attacks the nitrogen [i.e., N(2)] of the porphyrin ring to form a four-coordinate with a seesaw coordination around Hg(2) atom with an angle of N(2)–Hg(2)–C(61) = 167.4(2)° in **7**. The molecular frameworks are depicted in Fig. 1a for $\mathbf{6}\cdot CH_2Cl_2\cdot 0.5C_6H_{14}$ and Fig. 1b for **7**. The metal–ligand bond distances and the angles are summarized in Table 2. The covalent bond of Hg(1)–C(50) = 2.047 (4) Å in $\mathbf{6}\cdot CH_2Cl_2\cdot 0.5C_6H_{14}$ and of Hg(2)–C(61) = 2.064(7) Å and Hg(1)–C(55) = 2.065(8) Å in **7** are smaller than the sum of the covalent radii of Hg and C (2.26 Å) [12]. The mercury nitrogen bond distances [Hg(1)–N(1) = 2.589(3), Hg(1)–N(2) = 2.119(3), and Hg(1)–N(3) = 2.627(3) Å] in $\mathbf{6}\cdot CH_2Cl_2\cdot 0.5C_6H_{14}$ and [Hg(2)–N(1) = 2.566(6), Hg(2)–N(2) = 2.155(6), and



Scheme 1.

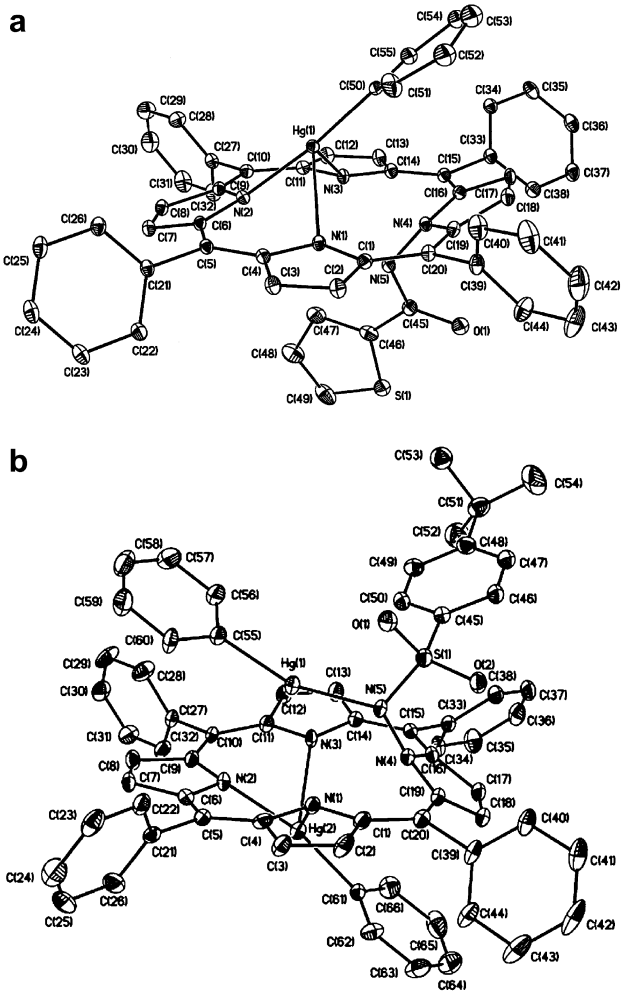


Fig. 1. Molecular configuration and atom-labeling scheme for (a) $\mathbf{6}\cdot CH_2Cl_2\cdot 0.5C_6H_{14}$, and (b) **7**, with ellipsoids drawn at 30% probability. Hydrogen atoms for both compounds and solvent CH_2Cl_2 for $\mathbf{6}\cdot CH_2Cl_2\cdot 0.5C_6H_{14}$ are omitted for clarity.

Hg(2)–N(3) = 2.583(6) Å] in **7**, are well below the upper limit of a typical Hg–N covalent bond [2.75(2) Å] [2,13]. The pyrrole nitrogen N(4) is no longer bonded to the Hg(1) in **6** · CH_2Cl_2 · $0.5C_6H_{14}$ and Hg(2) in **7** as indicated by their longer internuclear distances, 3.171(3) Å for Hg(1)···N(4) in **6** · CH_2Cl_2 · $0.5C_6H_{14}$ and 3.182(6) Å for Hg(2)···N(4) in **7**. Hence, C(50), N(1), N(2), and N(3) are bonded covalently to the Hg(1) atom in **6** · CH_2Cl_2 · $0.5C_6H_{14}$. Hg(1) is bonded to fewer than four nitrogen atoms, and so compound **6** · CH_2Cl_2 · $0.5C_6H_{14}$ may be considered as a Tsutsui's sitting-atop (SAT) complex [14]. In a similar way, the Hg(2) is tetracoordinated with three nitrogen atoms [i.e., N(1), N(2), and N(3)] of porphyrins and one carbon atom [i.e., C(61)] of phenyl group in **7**. The coordination around Hg(2) in **7** is also a mercury(II) porphyrin SAT complex. The similar kind of SAT complex was previously reported for complexes **1** and **2** [1,2].

We adopt the plane of three strongly bound pyrrole nitrogen atoms [i.e., N(1), N(2), N(3)] as a reference plane 3N for **6** · CH_2Cl_2 · $0.5C_6H_{14}$ and **7**. Because of the larger size of Hg^{2+} [$\gamma(Hg^{2+}) = 1.10$ Å with coordination number (CN) = 4 and $\gamma(Hg^{2+}) = 0.83$ Å with CN = 2] [12], Hg(1) and N(5) lie 1.47 and −1.29 Å respectively, above the 3N plane in **6** · CH_2Cl_2 · $0.5C_6H_{14}$, compared to −1.49 Å for Hg(2) and 1.36 Å for N(5) in**7**. The Hg(1) of **7** is 2.12 Å out of its 3N plane in the opposite direction of the Hg(2) atom. The separation between atoms Hg(1) and Hg(2) in **7** is 3.622(6) Å, which is larger than the sum of van der Waals radii of two Hg(II), 3.50(7) Å [13]. Hence, no metallophilic Hg(II)···Hg(II) interaction in **7** may be anticipated. The porphyrin macrocycle is indeed distorted because of the presence of the 2-thiophenecarboxamido (NCO-2-C_4H_3S) and the NSO2C6H4^{t}Bu group in **6** · CH_2Cl_2 · $0.5C_6H_{14}$ and **7**, respectively (Figure S1 in Supplementary material). Thus, N(4) pyrrole rings bearing the 2-thiophenecarboxamido (NCO-2-C_4H_3S) and the $NSO_2C_6H_4{}^tBu$ group in **6** · CH_2Cl_2 · $0.5C_6H_{14}$ and **7** deviate most from the 3N plane and as oriented separately with a dihedral angle of 33.3° and of 42.9°, whereas small angles of 4.9°, 21.0° and 8.7° occur with N(1), N(2), and N(3) pyrroles for **6** · CH_2Cl_2 · $0.5C_6H_{14}$ and 7.7°, 15.2°, and 11.1° with N(1), N(2), and N(3) pyrroles for **7**. In **6**, such a large deviation from planarity for the N(4) pyrrole is also reflected by observing a 10–12 ppm upfield shift in the ^{13}C NMR spectrum of $C_\beta(17,18)$ at 121.0 ppm compared to 133.4 ppm for $C_\beta(3,12)$, 133.2 ppm for $C_\beta(2,13)$, and 131.2 ppm for $C_\beta(7,8)$ (Table S1 in Supplementary material). In **7**, a similar deviation is also found for the N(4) pyrrole by observing a 14–15 ppm upfield shift of the $C_\beta(17,18)$ at 118.8 ppm compared to 134.2 ppm for $C_\beta(2,13)$, 133.4 ppm for $C_\beta(7,8)$, and 132.7 ppm for $C_\beta(3,12)$ (Table S2 in Supplementary material). The dihedral angles between the mean plane of the skeleton (3N) and the plane of the phenyl group are 56.7° [C(24)], 64.4° [C(30)], 49.7° [C(36)], and 59.7° [C(42)] for **6** · CH_2Cl_2 · $0.5C_6H_{14}$ and the corresponding angles are 60.1°, 81.4°, 45.3°, and 50.3° for **7**. Likewise, the dihedral angles between the mean plane of the 3N and the plane of the phenyl group coordinated to the Hg atom are 45.1° [C(53)] for **6** · CH_2Cl_2 · $0.5C_6H_{14}$ and 43.7° [C(58)], and 43.1° [C(64)] for **7**.

3.2. ^1H and ^{13}C NMR for 6 in CD_2Cl_2 and 7 in $CDCl_3$

Complexes **6** and **7** were characterized by ^1H and ^{13}C NMR spectra. In solution, the molecules have effective Cs symmetry with a mirror plane running through the N(2)–Hg(1)–C(50)–N(4) unit for **6** or N(2)–Hg(2)–Hg(1)–N(4) unit for **7**. There are four distinct 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-C1 carbons for these two complexes (Tables S1 and S2 in Supplementary material).

Due to the solubility problem, we observed the NMR spectra of **6** in CD_2Cl_2 and **7** in $CDCl_3$. The NMR spectra for a 0.01 M solution of **6** in CD_2Cl_2 (Fig. 2a) and for a

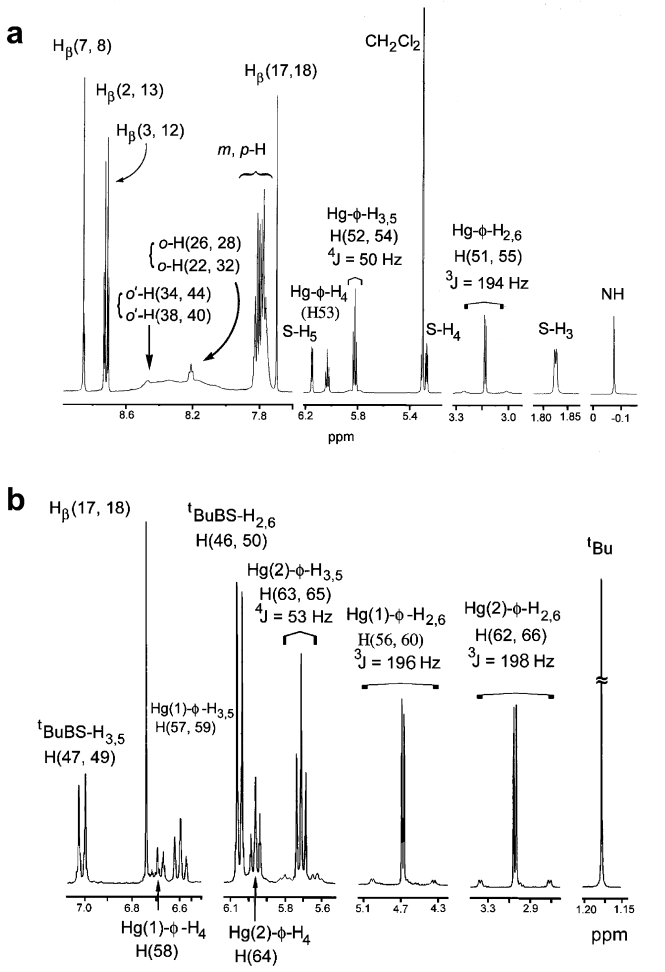


Fig. 2. ^1H NMR spectra at 20 °C (a) for a 0.01 M solution of **6** in CD_2Cl_2 at 599.94 MHz, entire spectrum; (b) for a 0.05 M solution of **7** in $CDCl_3$ at 299.95 MHz, showing Hg(1)-ϕ, Hg(2)-ϕ protons and ^{t}BuBS protons, where S = thiophene group, in **6** and ^{t}BuBS = 4-*tert*-butylbenzenesulfonyl group in **7**, ϕ = phenyl group.

0.05 M solution of **7** in $CDCl_3$ (Fig. 2b and Figure S2 in Supplementary material) showed four different types of H_β at 20 °C. In **6**, the singlet at 8.86 ppm is assigned to $H_\beta(7,8)$ and the doublet at 8.73 ppm to $H_\beta(2,13)$ with $^3J(H–H) = 4.8$ Hz. The doublet at 8.71 ppm is assigned to $H_\beta(3,12)$ with $^3J(H–H) = 4.8$ Hz and the singlet at 7.70 ppm to $H_\beta(7,8)$ (Fig. 2a). Likewise, in **7** the doublet at 8.84 ppm is due to $H_\beta(3,12)$ with $^3J(H–H) = 4.2$ Hz and the other doublet 8.79 ppm is due to $H_\beta(2,13)$ with $^3J(H–H) = 4.2$ Hz. The singlet at 8.56 ppm is due to $H_\beta(7,8)$ and the other singlet at 6.78 ppm is due to $H_\beta(17,18)$ (Fig. 2b and Figure S2 in Supplementary material).

All ^{t}BuBs, Hg–Ph protons in **6** and 2-thiophenecarboxamido (where Hg–Ph = the phenyl group (Ph) coordinated to Hg atom), Hg(2)–Ph, Hg(1)–Ph protons in **7** are shifted upfield compared to their counterparts on free ^{t}BuBs, Hg–Ph, 2-thiophenecarboxamido, Hg(2)–Ph,and Hg(1)–Ph. Such a shift is presumably attributed to the ring current effect. On the basis of the ring model [15], as the distance between the geometrical center (Ct) of the 4N [i.e., N(1), N(2), N(3), and N(4) for **6** and **7**] plane and axial protons gets smaller, the shielding effect becomes larger. In **7**, the average distance between Ct···Hg(2)–Ph–$H_{2,6}$, Ct···Hg(2)–Ph–$H_{3,5}$ and Ct···Hg(2)–Ph–H_4 increases from 3.937, 5.886 to 6.616 Å. Likewise, the average distance between Ct···Hg(1)–Ph–$H_{2,6}$, Ct···Hg(1)–Ph–$H_{3,5}$ and Ct···Hg(1)–Ph–H_4 increases from 4.558, 6.657 to 7.433 Å. The fact that all three distances between Ct···Hg(2)–Ph are shorter than those of Ct···Hg(1)–Ph in **7** indicates that the ring current effect in Hg(2)–Ph protons would be larger and in turn the ^{1}H upfield shifts for Hg(2)–Ph protons would be still higher. This observation is corroborated by the doublet at 3.08 ppm with satellites of $^3J(Hg–H) = 198$ Hz for Hg(2)–Ph–$H_{2,6}$ and the doublet at 4.72 ppm with $^3J(Hg–H) = 196$ Hz for the Hg(1)–Ph–$H_{2,6}$, the triplet at 5.74 ppm with well-resolved $^4J(Hg–H)$ of 53 Hz for the Hg(2)–Ph–$H_{3,5}$ and the triplet at 6.63 ppm with $^4J(Hg–H) = 50$ Hz for Hg(1)–Ph–$H_{3,5}$, the triplet at 5.99 ppm for Hg(2)–Ph–H_4 and the triplet at 6.72 ppm for Hg(1)–Ph–H_4. The ^{1}H NMR also revealed that the aromatic protons of the ^{t}BuBS group in **7** appear as two doublets at 7.04 ppm (^{t}BuBS-$H_{3,5}$) with $^3J(H–H) = 8.4$ Hz and at 6.09 ppm (^{t}BuBS-$H_{3,5}$) with $^3J(H–H) = 8.4$ Hz. This observation is consistent with the fact that the average distance between Ct···^{t}BuBS-$H_{2,6}$ and Ct···^{t}BuBS-$H_{3,5}$ in **7** increases from 5.139 to 6.933 Å. X-ray diffraction analysis unambiguously confirms that **7** is a dimercury complex. In addition, FAB MS indicates that molecular ion (M^+) of **7** is 1379. This further supports that **7** is a dimercury species in the solid phase. The strong diamagnetic shielding observed for all six resonances of the Hg(2)-Ph and the Hg(1)–Ph protons in the ^{1}H NMR spectrum of **7** suggests that **7** remains in a dinuclear mercury(II) complex in the solution phase (Fig. 2b).

In a similar fashion, in compound **6**, the average distance between Ct···Hg–Ph–$H_{2,6}$, Ct···Hg–Ph–$H_{3,5}$ and Ct···Hg–Ph–H_4 increases from 3.932, 5.808 to 6.638 Å. The ^{1}H NMR indicates that the aromatic protons of Hg–Ph in **6** appears as a doublet at 3.13 ppm with a coupled satellites $^3J(Hg–H)$ of 194 Hz for Hg–Ph–$H_{2,6}$, a triplet at 5.82 ppm with $^4J(Hg–H) = 50$ Hz for Hg–Ph–$H_{3,5}$, and a triplet at 6.03 ppm for Hg–Ph–H_4. Broadly, the ^{1}H NMR for phenyl protons of Hg–Ph in **6** is similar to those of Hg(2)–Ph in **7**. Due to the ring current effect, upfield shifts for the ^{1}H resonances of S–H_5, S–H_4 and S–H_3 in **6** with O, S-*cis* conformer in CD_2Cl_2 at 20 °C are $\Delta\delta = -1.48$ [from 7.63 (obtained from 2-acetylthiophene) to 6.15 ppm], −2.42 (from 7.69 to 5.27 ppm) and −5.35 ppm (from 7.13 to 1.78 ppm), respectively.

Heteronuclear coupling constants for ^{199}Hg in alkyl mecurials have been determined to decrease in the order $^1J \gg {}^3J > {}^2J > {}^4J$ [16]. Recently, a Karplus-type relationship was suggested for the magnitude of $^3J(Hg–H)$ which would predict weak coupling for torsion angle (Ψ) close to 90° and the largest coupling for torsion angles that approach 0 or 180° [17]. In **6**, the average torsion angle (Ψ) between Hg(1) and H (51A) [or H(55A)] was 10.5°. In **7**, the average torsion angle (Ψ) between Hg(1) and H(56A) [or H(60A)] was 5.0° while that angle between Hg(2) and H(62A) [or H(66A)] was 11.2°. In **6** and **7**, all the average torsion angles (Ψ) were within 12° of either 0 or 180°. Hence, $^3J(Hg–H)$ of 194 Hz for the Hg–Ph–$H_{2,6}$ protons in **6** was observed and was approximate to that of 197 ± 1 Hz for the Hg(2)–Ph–$H_{2,6}$ and Hg(1)–Ph–$H_{2,6}$ protons in **7**. The proton spectra clearly show $^3J(Hg–H)$ coupling. The presence of the mercury–proton coupling is an important indicator of slow ligand exchange in **6** and **7** [18,19]. The $^4J(Hg–H)$ of 50 Hz was observed for the Hg–Ph–$H_{3,5}$ protons in **6** and for the Hg(2)–Ph–$H_{3,5}$ and Hg(1)–Ph–$H_{3,5}$ protons in **7**. In **6** and **7**, the coupling constant of $^3J(Hg–H) = 197 \pm 1$ Hz is larger than that of $^4J(Hg–H) = 50$ Hz. These two coupling constants are consistent with those of $^3J(Hg–H) = 204$ Hz and $^4J(Hg–H) = 54$ Hz, respectively, for PhHgOAc in DMSO-d6 at ambient temperature [20].

3.3. ^{199}Hg NMR for 6 in CD_2Cl_2 and 7 in $CDCl_3$

The ^{199}Hg spectrum at 20 °C shows a sharp signal at −1074 ppm for a 0.05 M solution of **7** in $CDCl_3$, which is near the position of the Hg(1) signal observed in the spectrum for a 0.01 M solution of **6** in CD_2Cl_2, −1108 ppm (Fig. 3). Hence the signal at δ −1074 ppm of **7** is assigned to the Hg(2) nucleus with a coordination number of four. Therefore, the other signal at δ −1191 ppm of **7** is assigned to the Hg(1) nucleus with a smaller coordination number of two. It is known in the case of Hg NMR spectroscopy that on increasing coordination number generally lowers the chemical shift [16]. This fact explained that the ^{199}Hg signal of the Hg(2) nucleus in **7** lies at a downfield shift of 117 ppm from that of the Hg(1) nucleus. The ^{199}Hg chemical shift δ of Hg(1) in **7** is quite close to that of −1147 ppm for HgPh (DABRd) [where HDABRd = 5-(4′-dimethyl-

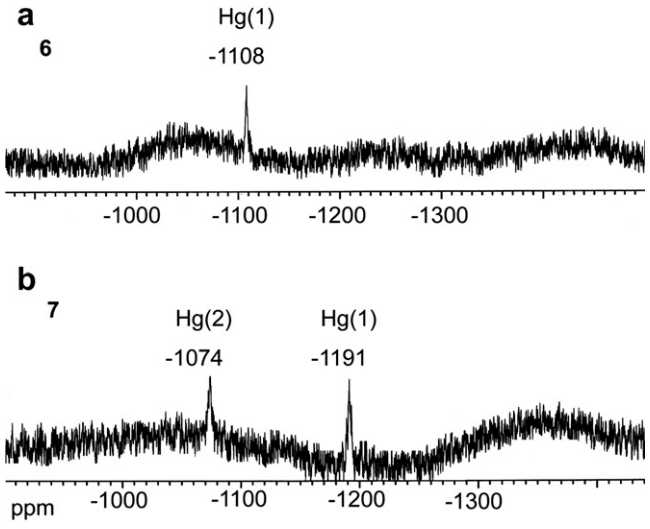


Fig. 3. The ^{199}Hg NMR spectra at 107.24 MHz (a) for a 0.01 M solution of **6** in CD_2Cl_2 at 20 °C and (b) for a 0.05 M solution of **7** in $CDCl_3$ at 20 °C.

aminobenzylidene)rhodanine] [21],−1152 ppm for HgPh (TRd) [where HTRd = 5-(2′-thiophenomethylene)rhodanine] [21] and −1156 ∼ −1346 ppm for the *N*-phenylmecury derivatives of *N*-aryl- and *N*-alkyl-substituted benzenesulfonamides (Ph–Hg–N(R)SO2Ph; R = Me, Et, Pr^i, Bu^t, Ph, 2-NO_2-C_6H_4, 4-NO_2–C_6H_4) [22]. The ^{199}Hg NMR data in $CDCl_3$ solution clearly reveal that there are two different Hg nuclei, i.e. Hg(1) and Hg(2), in **7**. These ^{199}Hg NMR data provide a second evidence that **7** remains as a dimercury(II) species in $CDCl_3$ solution. The chemical shift of ^{13}C for HgPh carbons was controlled by the paramagnetic term and not by the ring current effect [23–25]. Hence, the ^{13}C NMR data revealed that HgPh carbons in Hg(2)–Ph of **7** and Hg(1)–Ph of **6** · CH_2Cl_2 · $0.5C_6H_{14}$ are marginally affected (Tables S1 and S2 in Supplementary material). Moreover, the ^{13}C chemical shift of Hg(2)–Ph–C_1(C61) at an upfield of 3.3 ppm from that of Hg(1)–Ph–C_1(C55) (Table S2 in Supplementary material). This upfield shift is correlated with the ^{199}Hg signal of Hg(2) nucleus that shows a downfield shift from that of the Hg(1) nucleus in **7**.

4. Conclusions

We have investigated two new diamagnetic porphyrin complexes, namely, a mononuclear mercury(II) complex **6** · CH_2Cl_2 · $0.5C_6H_{14}$ and a dinuclear mercury(II) complex **7**, and their X-ray structures are established. These two porphyrin complexes are of a SAT type. NOE difference spectroscopy, HMQC and HMBC were employed to unambiguously assign the ^{1}H and ^{13}C NMR resonances of **6** in CD_2Cl_2 and **7** in $CDCl_3$ at 20 °C. Our results demonstrate the tetracoordination for Hg(1) in **6** · CH_2Cl_2 · $0.5C_6H_{14}$and Hg(2) in **7**. On the other hand, a linear coordination is described for Hg(1) in **7**. The transmetallation and degradation reactions for **6** and **7** are under investigation.

Acknowledgment

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Appendix A. Supplementary material

CCDC 637230 and 637231 contain the supplementary crystallographic data for **6** · CH_2Cl_2 · $0.5C_6H_{14}$ and **7**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.06.019. Figure S1 showing the diagram of the porphyrinato (C20N4, Hg, ^{t}BuBS, and thiophene) of **6** · CH_2Cl_2 · $0.5C_6H_{14}$ and **7**. Figure S2 showing the ^{1}H NMR spectra for **7** at 299.95 MHz in $CDCl_3$ at 20 °C. Tables S1 and S2 showing the ^{13}C NMR (150.87 MHz) data of **6** CH_2Cl_2 · $0.5C_6H_{14}$ in CD_2Cl_2 and **7** in $CDCl_3$ at 20 °C, respectively.

References

[1] H.J. Callot, B. Chevrier, R. Weiss, J. Am. Chem. Soc. 101 (1979) 7729.
[2] M.C. Wang, L.S. Sue, B.C. Liau, B.T. Ko, S. Elango, J.H. Chen, Inorg. Chem. 40 (2001) 6064.
[3] H.J. Callot, Tetrahedron 35 (1979) 1455.
[4] H.J. Callot, J. Fischer, R. Weiss, J. Am. Chem. Soc. 104 (1982) 1272.
[5] H.J. Callot, B. Chevrier, R. Weiss, J. Am. Chem. Soc. 100 (1978) 4733.
[6] K. Ichimura, Bull Chem. Soc. Jpn. 51 (1978) 1444.
[7] F.A. Yang, J.H. Chen, H.Y. Hsieh, S. Elango, L.P. Hwang, Inorg. Chem. 42 (2003) 4603.
[8] W.Z. Shil, K.Y. Cho, C.W. Cheng, J.H. Chen, S.S. Wang, F.L. Liao, J.Y. Tung, H.Y. Hsieh, S. Elango, Polyhedron 25 (2006) 1864.
[9] J.Y. Tung, J.H. Chen, Polyhedron 26 (2007) 589.
[10] G.C. Stocco, A. Tamburello, M.A. Girasoli, Inorg. Chem. Acta 78 (1983) 57.
[11] G.M. Sheldrick, SHELXL97, A Program for Crystal Structures Refinement, University of Göttingen, Germany, 1997.
[12] J.E. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry, fourth ed., Harper Collins College Publishers, New York, 1993, pp. 114, 292.
[13] S. Das, C.H. Hung, S. Goswami, Inorg. Chem. 42 (2003) 8592.
[14] J.P. Macquet, M.M. Millard, T. Theophanides, J. Am. Chem. Soc. 100 (1978) 4741.
[15] C.E. Johnson Jr., F.A. Bovey, J. Chem. Phys. 29 (1958) 1012.
[16] B. Wrackmeyer, R. Contreres, Annu. Rep. NMR Spectrosc. 24 (1992) 267.
[17] R.P. Blake, B. Lee, M.F. Summers, J.B. Park, Z.H. Zhou, M.W.W. Adams, New. J. Chem. 18 (1994) 387.
[18] M.L. Helm, G.P. Helton, D.G. VanDerveer, G.P. Grant, Inorg. Chem. 44 (2005) 5696.
[19] T.S. Lobana, A. Sanchez, J.S. Casas, A. Castineiras, J. Sordo, M.S. Garcia-Tasende, E.M. Vazquez-Lopez, J. Chem. Soc., Dalton Trans. (1997) 4289.

[20] W. McFarlane, J. Chem. Soc. A (1968) 2280.
[21] J.S. Casas, E.E. Castellano, A. Macias, N. Playa, A. Sanchez, J. Sordo, J.M. Varela, E.M. Vazquez-Lopez, Polyhedron 20 (2001) 1845.
[22] Y.K. Grishin, Y.A. Ustynyuk, T.I. Voevodskaya, A.S. Peregudov, D.N. Kravtsov, Bull. Acad. Sci. USSR Div. Chem. Sci. 34 (1985) 1399.
[23] S.J. Lin, T.N. Hong, J.Y. Tung, J.H. Chen, Inorg. Chem. 36 (1997) 3886.
[24] A. Carrington, A.D. McLachlan, Introduction to Magnetic Resonance, Harper and Row, New York, 1967, p. 57.
[25] J.A. Pople, W.G. Schneider, H.J. Bernstein, High-Resolution Nuclear Magnetic Resonance, McGraw-Hill, New York, 1959, p. 172.