Notes

Metal Complexes of *N*-*p*-Nitrobenzoylamido-*meso*-tetraphenylporphyrin: *cis*-Acetato-*N*-*p*-nitrobenzoylimido-*meso*-tetraphenylporphyrinatothallium(III) and *N*-*p*-Nitrobenzoylimido-*meso*-tetraphenylporphyrinatonickel(II)

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Introduction

Metalloporphyrins with a bridged structure between the central metal and one of the four pyrrole nitrogens have drawn much attention in recent times. Bridged metalloporphyrins with only metal−NTs−N linkages (metal = Zn,[1] Ni,[2] Fe,[3] Hg,[4] Ga,[5] Tl,[5] Ts = tosyl) have so far been reported. Callot et al.[2] reported the synthesis and ^{1}H NMR investigation of the metalation of *N*-*p*-nitrobenzoylamido-*meso*-tetraphenylporphyrin [*N*-*p*-$HNCOC_6H_4NO_2$-Htpp] (tpp = dianion of *meso*-tetraphenylporphyrin) leading to mononuclear complexes of *N*-*p*-nitrobenzoylimido-*meso*-tetraphenylporphyrinatonickel(II) Ni(*N*-*p*-$NCOC_6H_4NO_2$-tpp) (**1**) and *N*-*p*-nitrobenzoylimido-*meso*-tetraphenylporphyrinatocopper(II) Cu(*N*-*p*-$NCOC_6H_4NO_2$-tpp) (**2**).

There are no X-ray structural data available for the metal ion [M(II) and M(III)] complexes of $HNCOC_6H_4NO_2$-Htpp. In this paper, we report the X-ray structural determination of the title compound Ni(*N*-*p*-$NCOC_6H_4NO_2$-tpp) (**1**), and we also present the results upon replacing Ni(II) with Tl(III) in **1** forming a new compound (**3**). This replacement increases the coodination number (CN) from 4 for **1** to 6 for *cis*-acetato-*N*-*p*-nitrobenzoylimido-*meso*-tetraphenylporphyrinatothallium(III) Tl(*N*-*p*-$NCOC_6H_4NO_2$-tpp)(OAc) (**3**). The presence of acetate ligands in **3** plays a role in somewhat artificially increasing the coordination number. Because of the larger size of the Tl^{3+} (r_{ion} = 1.025 Å),[6] the relative position of OAc^- and *p*-nitrobenzoyl (NB) group coordinated to the Tl atom might lead to a cis configuration in **3**. In addition, the acetato exchange of Tl(*N*-NTs-tpp)(OAc) observed in CD_2Cl_2 prompted us to investigate a similar intermolecular exchange for complex **3** in THF-d_8 by ^{1}H and ^{13}C dynamic NMR method.[5]

Experimental Section

Ni(*N*-*p*-$NCOC_6H_4NO_2$-tpp) *(1).*[2] Compound **1** was dissolved in CH_2Cl_2 and layered with MeOH, and thus the purple crystals of **1** were obtained for single-crystal X-ray analysis. ^{1}H NMR (599.95 MHz, $CDCl_3$, 25 °C): δ 8.99 [d, H_β(18,39), ^3J(H−H) = 4.8 Hz], H_β(a,b) represents the two equivalent β-pyrrole protons attached to carbons a and b, respectively; 8.72[s, H_β(28,29)]; 8.68 [d, H_β(17,40), ^3J(H−H) = 4.8 Hz]; 7.66−8.14 (m, phenyl protons); 7.57 [s, H_β(50,51)]; 6.80 [d, H_{NB}(4,6) or NB-$H_{3,5}$, ^3J(H−H) = 9.0 Hz], H_{NB}(c,d) represents the two equivalent protons attached to carbons c and d of *p*-nitrobenzoyl (NB) group, respectively; 4.93 [d, H_{NB}(3,7) or NB-$H_{2,6}$, ^3J(H−H) = 9.0 Hz].

Tl(*N*-*p*-$NCOC_6H_4NO_2$-tpp)(OAc*) (3).* A mixture of *N*-*p*-$HNCOC_6H_4NO_2$-Htpp (50 mg, 0.0068 mmol) in CH_2Cl_2(10 cm^3) and $Tl(OAc)_3$ (40 mg, 0.12 mmol) in MeOH (2.5 cm^3) was refluxed for 1 h. After concentrating, the residue was dissolved in $CHCl_3$, dried with anhydrous Na_2SO_4, and filtered. The filtrate was concentrated and recrystallized from CH_2Cl_2−MeOH [1:5 (v/v)] yielding purple solid of **3** (39 mg, 0.037 mmol, 55%) which was again dissolved in CH_2Cl_2−ether [1:1 (v/v)] and layered with MeOH to get purple crystals for single-crystal X-ray analysis. ^{1}H NMR (599.95 MHz, CD_2Cl_2, 25 °C): δ 9.32 [d d, H_β(8,17), ^4J(Tl−H) = 20 Hz and ^3J(H−H) = 4.5 Hz]; 8.96 [dd, H_β(7,18), ^4J(Tl−H) = 14 Hz and ^3J(H−H) = 4.8 Hz]; 8.63 [d, H_β(12,-13), ^4J(Tl−H) = 75.3 Hz]; 7.20 [d, H_β(2,3), ^5J(Tl−H) = 6 Hz]; 8.50(m), 8.22 (m) and 8.12 (m) for phenyl ortho protons (*o*-H); 7.75−7.89 (m) for phenyl meta and para protons (*m*-, *p*-H); 7.04 [d, H_{NB}(48,50) or NB-$H_{3,5}$, ^3J(H−H) = 8.4 Hz], 5.25 [t, H_{NB}(47,51) or NB-$H_{2,6}$, ^3J(H−H) = 8.4 Hz]; 0.17 (s, OAc). MS, *m*/*z* (assignment, rel intensity): 1040 ([Tl(*N*-*p*-$NCOC_6H_4NO_2$-tpp)(OAc)]$^+$, 1.65), 981([Tl(*N*-*p*-$NCOC_6H_4NO_2$-tpp)]$^+$, 42.89), 817 ([Tl(tpp) + H]$^+$, 23.28), 779([H-*N*-*p*-$NCOC_6H_4NO_2$-Htpp)]$^+$, 20.88), 614 (Htpp$^+$, 16.99), 205 ($^{205}Tl^+$, 64.34), 203 ($^{203}Tl^+$, 26.22). UV/visible spectrum, λ (nm)[$\epsilon \times 10^{-3}$ (M^{-1} cm^{-1})] in CH_2Cl_2: 325 (13.6), 432 (124.0), 547 (6.2), 585 (6.8), 639 (5.2).

Spectroscopy. Proton and ^{13}C NMR spectra were recorded at 299.95 (or 599.95) 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, $CDCl_3$, or THF-d_8 at δ = 5.30, 7.24, or 1.73 (the upfield resonance) and ^{13}C NMR to the center line of CD_2Cl_2, $CDCl_3$, or THF-d_8 at δ = 53.6, 77.0, or 25.3 (the upfield resonance). Next, the temperature of the spectrometer probe was calibrated by the shift difference of methanol resonance in the ^{1}H NMR spectrum. ^{1}H−^{13}C COSY 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.

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 Ni(*N*-*p*-$NCOC_6H_4NO_2$-tpp) (**1**) and Tl(*N*-*p*-$NCOC_6H_4NO_2$-tpp)(OAc) (**3**). Measurements were taken on a Siemens SMART

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Table 1. Crystal Data for (**1**) and (**3**)

empirical formula	$C_{51}H_{32}N_6NiO_3$ (**1**)	$C_{53}H_{35}N_6O_5Tl$ (**3**)
fw	835.54	1040.24
space group	*C*2/*c*	$P2_1/c$
cryst syst	monoclinic	monoclinic
a, Å	22.5402(11)	12.5257(14)
b, Å	15.7500(8)	24.360(3)
c, Å	22.6703(11)	14.5349(17)
α, deg	90	90
β, deg	96.8100(10)	101.124(2)
γ, deg	90	90
V, Å^3	7991.4(7)	4351.7(9)
Z	8	4
F_{000}	3456	2064
D_{calcd}, g cm^{-3}	1.389	1.588
μ(Mo Kα), cm^{-1}	5.40	37.70
S	1.058	0.864
cryst size, mm^3	0.8 × 0.3 × 0.2	0.11 × 0.26 × 0.28
$2\theta_{max}$, deg	56.58	52.06
T, K	295(2)	293(2)
no. of reflns measd	23 412	24 296
no. of reflns obsd	8921 ($I > 2\sigma(I)$)	8546 ($I > 2\sigma(I)$)
R^a (%)	4.21	4.45
$R_w{}^b$ (%)	11.25	11.47

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

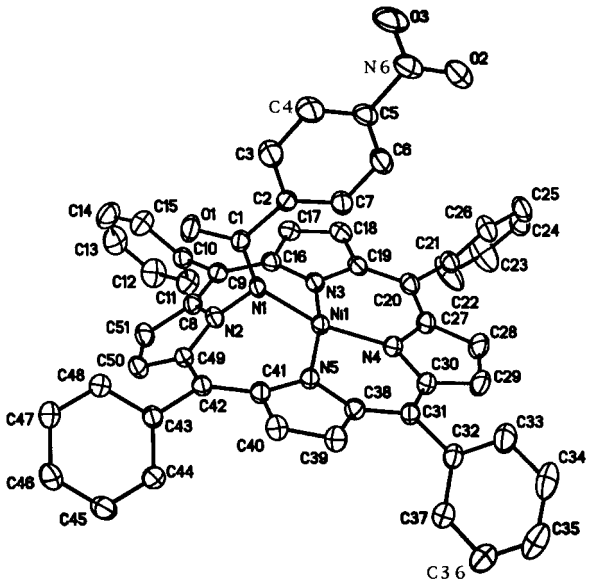
Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds **1** and **3**

Ni(*N*-*p*-NCOC$_6$H$_4$NO$_2$-tpp) (**1**)			
Distances			
Ni(1)−N(1)	1.843(2)	N(1)−C(1)	1.343(2)
Ni(1)−N(3)	1.937(2)	C(1)−O(1)	1.227(2)
Ni(1)−N(4)	1.874(2)	C(1)−C(2)	1.504(3)
Ni(1)−N(5)	1.940(2)	N(1)−N(2)	1.390(2)
Angles			
N(3)−Ni(1)−N(5)	166.39(7)	Ni(1)−N(1)−N(2)	104.8(1)
N(3)−Ni(1)−N(1)	86.92(7)	Ni(1)−N(1)−C(1)	141.2(1)
N(3)−Ni(1)−N(4)	93.87(7)	N(1)−C(1)−O(1)	123.9(2)
N(1)−Ni(1)−N(5)	88.34(7)	N(1)−C(1)−C(2)	116.4(2)
N(1)−Ni(1)−N(4)	164.18(7)	N(4)−Ni(1)−N(5)	94.16(7)
Tl(*N*-*p*-NCOC$_6$H$_4$NO$_2$-tpp)(OAc) (**3**)			
Distances			
Tl−O(4)	2.356(5)	N(5)−N(1)	1.409(6)
Tl−O(5)	2.365(4)	O(4)−C(52)	1.250(8)
Tl−N(2)	2.337(5)	O(5)−C(52)	1.248(8)
Tl−N(3)	2.157(4)	C(52)−C(53)	1.496(9)
Tl−N(4)	2.343(4)	N(5)−C(45)	1.345(7)
Tl−N(5)	2.147(5)	C(45)−O(1)	1.225(7)
Angles			
O(4)−Tl−O(5)	54.9(2)	Tl−O(4)−C(52)	92.0(4)
O(4)−Tl−N(2)	146.9(2)	Tl−O(5)−C(52)	91.6(4)
O(4)−Tl−N(3)	93.2(2)	O(4)−C(52)−O(5)	121.3(6)
O(4)−Tl−N(4)	91.3(2)	Tl−N(5)−C(45)	133.1(4)
O(4)−Tl−N(5)	112.5(2)	Tl−N(5)−N(1)	106.6(3)
O(5)−Tl−N(2)	93.1(2)	O(5)−Tl−N(4)	146.0(2)
O(5)−Tl−N(3)	95.4(2)	O(5)−Tl−N(5)	110.8(2)

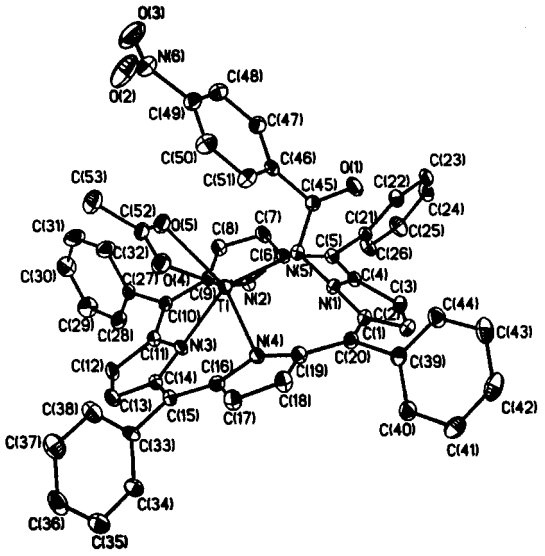
CCD diffractometer using monochromatized Mo Kα radiation (λ = 0.710 73 Å). The empirical absorption corrections were made for **1**. The structures were solved by direct methods (SHELXTL PLUS) and refined by the full-matrix least-squares method. All non-hydrogen atoms were refined with anisotropic thermal 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 both complexes.

Results and Discussion

Molecular Structures of 1 and 3. The X-ray framework is depicted in Figure 1a for the complex Ni(*N*-*p*-NCOC$_6$H$_4$NO$_2$-tpp) (**1**) and in Figure 1b for Tl(*N*-*p*-NCOC$_6$H$_4$NO$_2$-tpp)(OAc) (**3**). Both these structures, four-coordinate nickel of **1** and six-coordinate thallium of **3**, have bonding with three nitrogen atoms of the porphyrins and one extra nitrogen atom of the nitrene fragment in common, but compound **3** has in addition one more chelating bidentate OAc$^-$ ligand in the axial site. In **1** and **3** it appears that the *N*-*p*-nitrobenzoyl (NB) moiety is inserted into the Ni−N bond of *meso*-tetraphenylporphyrinatonickel(II), Ni(tpp),[7] and the Tl−N bond of acetato(*meso*-tetraphenylporphyrinato)thallium(III) Tl(tpp)(OAc).[8] The unusual metal−ligand bond distances, i.e., from Ni(II) and Tl(III) atoms to the ligand, and the angles are summarized in Table 2. The interaction of the acetate with thallium is chelating bidentate. This kind of



(a) Ni(*N*-*p*-NCOC$_6$H$_4$NO$_2$-tpp)



(b) Tl(*N*-*p*-NCOC$_6$H$_4$NO$_2$-tpp)(OAc)

Figure 1. Molecular configuration and atom-labeling scheme for (a) Ni(*N*-*p*-NCOC$_6$H$_4$NO$_2$-tpp) (**1**) and (b) Tl(*N*-*p*-NCOC$_6$H$_4$NO$_2$-tpp)(OAc) (**3**), with ellipsoids drawn at 30% probability. Hydrogen atoms for both compounds are omitted for clarity.

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bidentate interaction was previously observed for Tl(*N*-NTs-tpp)(OAc) with Tl−O(1) = 2.410(8) Å and Tl−O(2) = 2.292(9) Å.[5]

The geometry around Ni^{2+} is a distorted square planar, whereas for Tl^{3+} it is described as a distorted square-based pyramid in which the apical site is occupied by a chelating bidentate OAc^- group. The pyrrole nitrogens N(2) and N(1) are no longer bonded to the nickel and thallium as indicated by their longer internuclear distances, 2.576 Å for Ni(1)···N(2) and 2.886 Å for Tl···N(1). The Ni(1)−N(4) bond trans to the N(1) position in compound **1** is slightly shorter than the other two Ni(1)−N bond distances [i.e., 1.874(2) Å for Ni(1)−N(4), compared to 1.937(2) Å for Ni(1)−N(3) and 1.940(2) Å for Ni(1)−N(5)]. Similarly, the Tl−N(3) bond in compound **3** is also shorter than the other two Tl−N distances [2.157(4) Å for Tl−N(3) vs 2.343(4) Å for Tl−N(4) and 2.337(5) Å for Tl−N(2)]. Figure 2 shows the actual porphyrin skeleton of **1** and **3**. We adopt the plane of three strongly bound pyrrole nitrogen atoms [i.e., N(3), N(4), and N(5) for **1** and N(2), N(3), and N(4) for **3**] as a reference plane 3N. Because of the larger size of the Tl^{3+}, Tl and N(5) lie 1.15 and 1.25 Å, respectively, above the 3N plane in **3**, compared to 0.17 Å for Ni and 0.83 Å for N(1) in **1** (Figure 2). For the same reason, i.e., due to the larger size of the Tl^{3+}, the chelating bidentate acetate in **3** is cis to the NB group with O(4) and O(5) being located separately at 2.97 and 3.05 Å out of the 3N plane. The porphyrin macrocycle is indeed distorted because of the presence of the NB group (Figure 2). Thus, the N(2) and N(1) pyrrole rings bearing the NB group would be deviated mostly from the 3N plane and oriented separately in a dihedral angle of 43.8° and of 49.4°, whereas small angles of 11.4°, 4.5°, and 6.8° occur with N(3), N(4), and N(5) pyrroles for compound **1** and 9.9°, 6.5°, and 8.3° with N(2), N(3), and N(4) pyrroles for compound **3**, In compound **1**, such a large deviation from planarity for the N(2) pyrrole is also reflected by observing a 12−19 ppm upfield shift of the C_β (C50, C51) at 118.4 ppm compared to 137.8 ppm for C_β (C18, C39), 133.8 ppm for C_β (C28, C29), and 130.3 ppm for C_β (C17, C40) (Figure S1a in Supporting Information). In compound **3**, a similar deviation is also found for the N(1) pyrrole by observing a 17−21 ppm upfield shift of the C_β (C2, C3) at 115.2 ppm compared to 132.3 for C_β (C12, C13), 133.9 ppm for C_β (C7, C18), and 136.0 ppm for C_β (C8, C17). Similar kinds of upfield shifts of C_β resonances due to the nonplanarity of porphyrin were also observed with a magnitude of 15−17 ppm for Zn(*N*-NTs-tpp),[1] 16−21 ppm for Tl(*N*-NTs-tpp)(OAc),[5] and 5.6−7.0 ppm for Tl(*N*-Me-tpp)$(OAc)_2$.[9]

The pyrrole ring nitrogens N(2) and N(1) are in fact inclined toward the Ni and Tl atoms, in **1** and **3**, respectively. These distortions make the distances between opposite pyrrole nitrogen atoms unusual. The normal diameter of the "hole" in an undistorted metalloporphyrin complex has been estimated to be 4.02 Å.[10] The N(2)···N(4) distance of 4.409 Å in **1** and the N(1)···N(3) distance of 4.439 Å in **3** are unusually long, which is caused by the large deviations of the N(2) pyrrole in **1** and N(1) pyrrole in **3** from the 3N plane, respectively. Also affected by the distortion are the N(3)···N(5) distance of 3.849 Å in **1** and the N(2)···N(4) distance of 4.039 Å in **3**. Hence, in **3**, the thallium(III) atom is bound in an expanded porphyrinato (4N) core [i.e., the plane N(1)−N(4)]. The plane (P) defined by Ni(1), N(1), N(2), and C(1) in **1**, and by Tl, N(5), N(1), and C(45) in **3** is almost perpendicular to the 3N plane with a angle of 87.3° for **1** and 81.4° for **3**. The *p*-nitrobenzoyl group (NB) [i.e., the plane for NB in **1** is C(2)−C(7) and for **3** it is C(46)−C(51)] is bonded to N(1) in **1** and N(5) in **3** so that it lies above the macrocycle, orienting in a dihedral angle of 85.6° and 68.2° with the 3N plane in **1** and **3**, respectively. The dihedral angles between the mean plane of the skeleton (3N) and the planes of the phenyl groups are 59.8° [C(13)], 69.7° [C(24)], 64.0° [C(35)], and 36.9° [C(46)] for **1** and 44.0° [C(24)], 78.7° [C(30)], 87.4° [C(36)], and 42.2° [C(42)] for **3**.

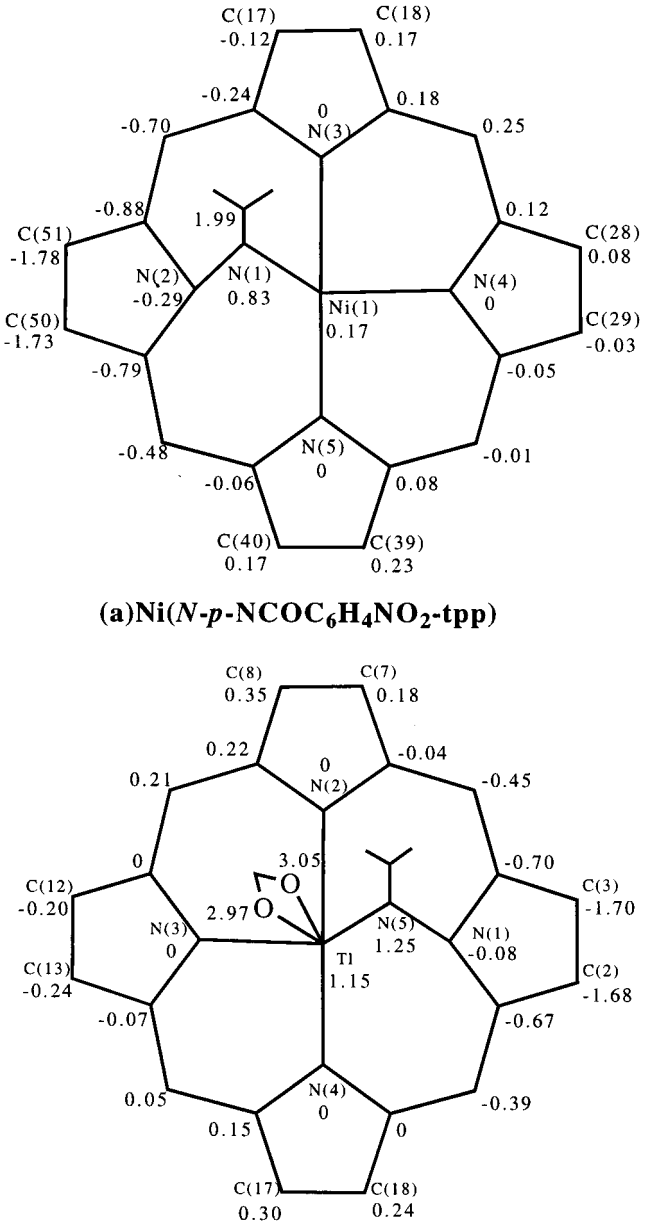

Figure 2. Diagram of the porphyrinato core ($C_{20}N_4$, M, NB, and OAc^-) of (a) compound **1** and (b) compound **3**. The values represent the displacements (in angstroms) of the atoms from the mean 3N plane [i.e., N(3)−N(5) for **1** and N(2)−N(4) for **3**].

The comparison made for Ni(II) derivatives of carbene, nitrene, and oxygen inserted complexes displays severe nonplanarity. Ni(1) and N(1) lie 0.23 and 1.01 Å above the mean plane of the four pyrrole nitrogens N(2)−N(5) (i.e., 4N plane) in **1** compared to 0.19 Å for Ni and 1.04 Å for the extra carbon atom C1 of the ethoxycarbonylcarbene fragment inserted into

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a Ni−N bond of nickel(II) *meso*-tetraphenylporphine.[11] Additionally, Ni(1) and N(1) lie 0.17 and 0.83 Å above the 3N plane in **1** compared to 0.05 Å for Ni and 0.65 Å for O(1) in nickel(II) octaethylporphyrin *N*-oxide.[12] The nonplanarity is further reflected in the angle between the 4N plane and the N(2) pyrrole ring in **1**. This angle is 39.9° for **1** compared to 46.4° for the N(4) pyrrole ring in the complex with an ethoxycarbonylcarbene moiety inserted into a Ni−N bond of nickel(II) *meso*-tetraphenylporphine.[11] Furthermore, the angle between the plane of the N(2) pyrrole ring and the 3N plane is 43.8° in **1,** while that between the plane of *N*-oxide pyrrole and the plane of the other three pyrrole and the two connecting meso carbons is 38.3° in nickel(II) octaethylporphyrin *N*-oxide.[12]

^{1}H and ^{13}C NMR for Ni(*N*-*p*-NCOC$_6$H$_4$NO$_2$-tpp) (1) and Tl(*N*-*p*-NCOC$_6$H$_4$NO$_2$-tpp)(OAc) (3) in CDCl$_3$ and CD$_2$Cl$_2$ (Figure S1 in Supporting Information). In solution, the molecule has effective C_s symmetry with a mirror plane running through the N(4)−Ni(1)−N(1)−N(2) unit for **1** or the N(3)−Tl−N(5)−N(1) unit for **3**. There are four distinct β-pyrrole protons H$_\beta$, four β-pyrrole carbons C$_\beta$, four α-pyrrole carbons C$_\alpha$, two different meso carbons C$_{meso}$, and two phenyl-C$_1$ carbons for both complexes. The NMR study of **3** showed four different types of Tl−H coupling constants for H$_\beta$ (Figure S1b in Supporting Information). The doublet at 8.63 ppm is assigned as H$_\beta$(12,13) with ^4J(Tl−H) = 75.3 Hz, and the doublet at 7.20 ppm is due to H$_\beta$(2,3) with ^5J(Tl−H) = 6 Hz. The doublet of a doublet at 9.32 ppm is due to H$_\beta$(8,17) with ^4J(Tl−H) = 20 Hz and ^3J(H−H) = 4.5 Hz, and the doublet of a doublet at 8.96 ppm is due to H$_\beta$(7,18) with ^4J(Tl−H) = 14 Hz and ^3J(H−H) = 4.8 Hz. Likewise, there were also four different types of Tl−^{13}C coupling constants for C$_\beta$. The doublet at 132.3 ppm is due to C$_\beta$ (C12, C13) with ^3J(Tl−^{13}C) = 167 Hz, and the doublet at 136.0 ppm is due to C$_\beta$ (C8, C17) with ^3J(Tl−^{13}C) = 39 Hz. The singlet at 133.9 ppm is due to C$_\beta$ (C7, C18) with ^3J(Tl−^{13}C) being unobserved and the doublet at 115.2 ppm is due to C$_\beta$ (C2, C3) with ^4J(Tl−^{13}C) = 82 Hz. The ^{1}H NMR spectra reveal that the aromatic protons of the NB group appear as a doublet at 7.04 (NB-H$_{3,5}$) and triplet at 5.25 ppm (NB-H$_{2,6}$) for **3** (Figure S1b in Supporting Information) and at 6.80 (d) and 4.93 (t) ppm for **1**. All *p*-nitrobenzoylimido and acetato protons are shifted upfield compared to their counterparts in free *N*-*p*-HNC$_6$H$_4$NO$_2$-Htpp and OAc$^-$; such a shift is presumably attributed to the porphyrin ring current effect. The ring current effect indicates that the NB groups are bonded to Ni(1) in **1** and to Tl in **3**. This bonding argument is further supported by the result that in ^{13}C NMR the NB-C$_1$ [i.e., C(46)] and the C(45) in **3** were observed at 138.9 ppm with ^3J(Tl−C) = 22 Hz and at 168.2 ppm with ^2J(Tl−C) = 599 Hz, respectively. Because C(45) in **3** is bonded to an electronegative atom O(1), the 2p-electron density around carbon C(45) is reduced. This removal of electron density increases both the effective nuclear charge and the s-electron density for the C(45) nucleus, and therefore ^2J(Tl−C) coupling constants increase from 65 ± 24 Hz for C$_\alpha$ to 599 Hz for C(45) in **3**.[13]

Dynamic NMR of 3 in THF-*d*$_8$. Upon cooling of a 3.6 × 10^{-3} M THF-*d*$_8$ solution of **3** (Figure S2 in Supporting Information), the methyl proton signals of OAc$^-$ are a single peak at 25 °C (δ = 0.16 ppm), first broadened (coalescence temperature T_c = −98 °C) and then split into two peaks with a separation of 18 Hz at δ = 0.034 ppm at −110 °C. As the exchange of OAc$^-$ within **3** is reversible, the results at 599.95 MHz confirm the separation as a coupling of ^4J (Tl−H) rather than a chemical shift difference. The most likely cause of loss of coupling is due to reversible dissociation of acetate

$$\text{T1}(N\text{-}p\text{-NCOC}_6\text{H}_4\text{NO}_2\text{-tpp})(\text{OAc}) \rightleftharpoons \text{T1}(N\text{-}p\text{-NCOC}_6\text{H}_4\text{NO}_2\text{-tpp})^+ + \text{OAc}^- \quad (1)$$

with a small dissociation constant.[14] Such a scenario would lead to a change in the chemical shift with temperature and no detectable free OAc$^-$ and Tl(*N*-*p*-NCOC$_6$H$_4$NO$_2$-tpp)$^+$ at low temperature, but would lead to the loss of coupling between acetate and thallium at higher temperature. The chemical shift in the high-temperature limit is the average of the two species [i.e., Tl(*N*-*p*-NCOC$_6$H$_4$NO$_2$-tpp)(OAc) and OAc$^-$] in eq 1 weighted by their concentration. A comparison of observed and computed spectra yields $\Delta G^{\ddagger}_{175}$ = 36.7 kJ/mol. At 25 °C, intermolecular exchange of the OAc$^-$ group is rapid as indicated by the appearance of singlet signals due to carbonyl carbons at 175.1 ppm and methyl carbons at 18.5 ppm. At −110 °C, the rate of intermolecular exchange of OAc$^-$ for **3** in THF-*d*$_8$ is slow. Hence, at this temperature, the methyl and carbonyl carbons of OAc$^-$ are observed at 18.9 ppm [with ^3J(Tl−C) = 227 Hz] and 175.9 ppm [with ^2J(Tl−C) = 211 Hz] as doublets, respectively. These ^{13}C resonances are quite close to that of Tl(*N*-NTs-tpp)(OAc) in which the two corresponding carbons were also observed, in CD$_2$Cl$_2$ at −110 °C, at 18.5 ppm [with ^3J(Tl−C) = 220 Hz] and 176.3 ppm [with ^2J(Tl−C) = 205 Hz] as doublets.[5]

At low temperature, some differences in OAc$^-$ resonances were observed. However, the differences for the ^{1}H resonances of pyrrole protons H$_\beta$, meta and para protons in porphyrin, and the resonances of NB-H$_{2,6}$ and NB-H$_{3,5}$ in *N*-*p*-nitrobenzoylamido were small for **3** in THF-*d*$_8$ at 25 and −110 °C. However, for ortho protons, at −110 °C, the rotation of phenyl group along the C$_{1-}$C$_{meso}$ bond in **3** is slow, which is evident from the appearance of the four broad singlets at 8.94, 8.31, 8.17, and 8.06 ppm due to four different ortho protons of the aromatic ring. At 25 °C, this rotation becomes more rapid, and hence the ^{1}H resonances for ortho protons of **3** were observed in THF-*d*$_8$ with two sets of doublet and one broad singlet: one doublet at 8.22 ppm with ^3J(H−H) = 6 Hz and the other doublet at 8.13 ppm with ^3J(H−H) = 7.2 Hz, and one broad singlet at 8.54 ppm.

Though we did not undertake the experiment to observe the OAc$^-$ exchange with O^{13}Ac$^-$, PrO$^-$, or PhCOO$^-$, a similar kind of intermolecular OAc$^-$ (or benzoato) exchange was also observed for Tl(*N*-Me-tpp)(OAc)$_2$[9] in THF-*d*$_8$ [or for Tl(tmp-p)(PhCOO) in CD$_2$Cl$_2$ solvent].[15] From the above analysis, the exchange of OAc$^-$ in **3** should be an intermolecular process. To date, other anions such as Cl$^-$, N$_3^-$, and MeO$^-$ cannot behave as ligands of the cationic thallium complex Tl(*N*-*p*-NCOC$_6$H$_4$NO$_2$-tpp)$^+$.

The properties of complex **1** in the solid state are similar to those properties in solution. However, for **3**, the properties in the solid state are different from those in solution, because complex **3** dissociates into Tl(*N*-*p*-NCOC$_6$H$_4$NO$_2$-tpp)$^+$ and OAc$^-$ in THF solution.

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Conclusions

We have investigated for the first time the two diamagnetic, mononuclear, and bridged metal complexes of *N*-*p*-nitrobenzoylamido-*meso*-tetraphenylporphyrin having M−*N*-(*p*-$COC_6H_4NO_2$)−N [or M−*N*-NB−N, M = Ni(II), Tl(III)] linkage, and their X-ray structures are analyzed. Excepting the phenyl protons and carbons, the unambiguous assignments of ^1H and ^{13}C NMR data for **1** in $CDCl_3$ and **3** in CD_2Cl_2 are reported in this work. Dynamic ^1H and ^{13}C NMR spectra of the acetato group in **3** reveal that this group undergoes an intermolecular exchange with a free energy of activation, $\Delta G^{\ddagger}_{175} = 36.7$ kJ/mol.

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Supporting Information Available: ^{13}C NMR spectrum (Figure S1) and its assignment for **1**, ^1H NMR spectrum of **3** (Figure S1) and its ^{13}C NMR data and ^1H NMR spectra for the acetato protons of **3** (Figure S2) at various temperatures; X-ray crystallographic files in CIF format for compounds **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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