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Metal Complexes of *N*-Benzamidoporphyrin: (*N*-Benzimido-*meso*-tetraphenylporphyrinato)(methanol)zinc(II) Methanol Solvate and (Acetato)(*N*-benzamido-*meso*-tetraphenylporphyrinato)cadmium(II) Benzene Solvate

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The crystal structures of *N*-benzamido-*meso*-tetraphenylporphyrin ($NHCOC_6H_5$-Htpp; **1**), (*N*-benzimido-*meso*-tetraphenylporphyrinato)(methanol)zinc(II) [Zn(*N*-$NCOC_6H_5$-tpp)(MeOH); **2**(MeOH)], and (acetato)(*N*-benzamido-*meso*-tetraphenylporphyrinato)cadmium(II) [Cd(*N*-$NHCOC_6H_5$-tpp)(OAc); **3**] were established. The coordination sphere around Zn^{2+} ion in **2**(MeOH) is a distorted trigonal bipyramid with N(2), N(5), and O(2) lying in the equatorial plane, whereas, for Cd^{2+} ion in **3**, it is a sitting-atop derivative with a distorted trigonal bipyramidal geometry in which the apical site is occupied by atoms N(2) and O(2). Cd in **3** acquires five-coordination with five strong bonds [Cd(1)–N(1) = 2.319(5) Å, Cd(1)–N(2) = 2.252(5) Å, Cd(1)–N(3) = 2.332(5) Å, Cd(1)–O(2) = 2.292(5) Å, and Cd(1)–O(3) = 2.317(5) Å] and with one secondary intramolecular interaction [Cd(1)•••N(4)]. The porphyrin ring in these two complexes is distorted to a large extent. The plane of the three pyrrole nitrogen atoms [i.e., N(1)–N(3)] strongly bonded to Zn^{2+} in **2**(MeOH) and to Cd^{2+} in **3** is adopted as a reference plane 3N. For the Zn^{2+} complex, the pyrrole nitrogen bonded to the benzamido (BA) ligand lies in a plane with a dihedral angle of 33.8° with respect to the 3N plane, but for the Cd^{2+} complex, this dihedral angle is found to be 31.4°. In the former complex, Zn^{2+} and N(5) are located on the different side at –0.08 and 1.39 Å from its 3N plane, and in the latter one, Cd^{2+} and N(5) are also located on the different side at 1.08 and –1.51 Å from its 3N plane. VT NMR (^1H and ^{13}C) studies of **3** show that the acetate acts as a bidentate ligand and the OAc^- exchange does not occur in CD_2Cl_2. Moreover, the NH proton [i.e., H(5)] of **3** in CD_2Cl_2 is observed as a sharp singlet at $\delta = -1.13$ ppm with $\Delta\nu_{1/2} = 4$ Hz at 20 °C indicating that the intermolecular proton exchange between water and NH proton is rapid.

Introduction

The preparation of *N*-substituted-*N*-aminoporphyrins has been described by two groups.[1−4] Metalation of these aminated porphyrins led to a series of bridged porphyrins bearing a nitrene moiety inserted between the metal and a pyrrole nitrogen. Many bridged metalloporphyrins with M−NTs−N [M = Zn(II),[5] Ni(II),[3] Fe(III),[6] Ga(III),[7] Tl(III);[7] Ts = tosyl] and with M−NNB−N linkages [M = Zn(II),[8]

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Ni(II),[9] Fe(III),[8] Tl(III);[9] NNB = *N*-*p*-nitrobenzoylimido] have so far been reported. However, in certain cases the metal may be coordinated with only three porphyrinic N atoms as previously reported for bis(chloromercury(II)) complex of (*N*-tosylamino)octaethylporphyrin, $C_{43}H_{51}N_5O_2SCl_2Hg_2$.[10] In related areas, *N*-monoalkylated porphyrins form metal complexes in which the metal is coordinated to the four (or three) porphyrinic N atoms.[11−14] Moreover, we have found no example of the metal complexes in which the metal is coordinated to the four (or three) porphyrinic N atoms in the aminated porphyrin. This result prompted us to synthesize a new *N*-benzamido-*meso*-tetraphenylporphyrin ($NHCOC_6H_5$-Htpp) **(1)** [tpp = dianion of *meso*-tetraphenylporphyrin] and to study its metalation which might lead to mononuclear metal complexes where the metal is four-coordinate either to four porphyrinic N atoms or to three porphyrinic N atoms plus one side-chain N atom. However, in certain cases the metal in this new monometallic complexes might be fixed to the porphyrin with three M−N bonds and form a Tsutsui's "sitting-atop" (SAT) complex.[15]

The d^{10} configuration permits a wide variety of geometries and coordination numbers. In this paper, we described the X-ray structural investigation on the metalation of **1** leading to mononuclear complexes of (*N*-benzimido-*meso*-tetraphenylporphyrinato)(methanol)zinc(II) [Zn(*N*-$NCOC_6H_5$-tpp)(MeOH); **2**(MeOH)] and (acetato)(*N*-benzamido-*meso*-tetraphenylporphyrinato)cadmium(II) [Cd(*N*-$NHCOC_6H_5$-tpp)(OAc); **3]**. The structural analysis of complexes **2**(MeOH) and **3** was undertaken to discover the effects of incorporating the d^{10} metal ions (i.e., Zn^{2+} and Cd^{2+}) into the highly distorted and relatively rigid coordination environment provided by the *N*-substituted-*N*-aminoporphyrin ligand system.

Experimental Section

Preparation of $NHCOC_6H_5$-Htpp (1).[3] A solution of Zn(tpp) (206 mg, 0.33 mmol) and benzoyl azide (0.5 g, 3.3 mmol) in CH_2Cl_2 (200 cm^3) in a stoppered 250 mL Erlenmeyer flask was left for ca. 8 h in the sunlight. To this solution was added 0.5 N HCl (250 cm^3) with vigorous shaking for 0.5 h. After the organic layer was separated, solid ammonium carbonate was added to it and then dried with anhydrous Na_2SO_4. The excess $(NH_4)_2CO_3$ and Na_2SO_4 were removed by filtration. After concentration, the residue was dissolved in a minimum of $CHCl_3$ and chromatographed either on aluminum oxide 90 (50 g, neutral, activity V) or on silica gel (100 g, 70−230 mesh). The desired compound was eluted with $CHCl_3$ either as dark green band on aluminum oxide or as dark brown band on silica gel. Removal of the solvent and recrystallization from CH_2Cl_2−MeOH [1:5 (v/v)] gave the purple solid of **1** (130 mg, 0.18 mmol, 54%). Compound **1** was dissolved again in $CHCl_3$ and layered with MeOH to give purple crystals for single-crystal X-ray analysis. ^{1}H NMR (499.85 MHz, $CDCl_3$, 20 °C): δ 9.10 [d, H_β(4,13), ^3J(H−H) = 5 Hz], where H_β(a,b) represents the two equivalent β-pyrrole protons attached to carbons a and b, respectively; 8.89 [s, H_β(8,9)]; 8.80 [d, H_β(3,14), ^3J(H−H) = 5 Hz]; 8.10 [s, H_β(18,19)]; 7.75−8.21 (m) for phenyl protons; 6.22 [t, H_{BA}(49) or BA-H_4, ^3J(H−H) = 9 Hz], where BA = benzamido ligand; 5.63 [t, H_{BA}(48,50) or BA-$H_{3,5}$, ^3J(H−H) = 8 Hz]; 3.41 [d, H_{BA}(47,51) or BA-$H_{2,6}$, ^3J(H−H) = 8 Hz]. MS [*m*/*z* (assignment, rel intensity)]: 734 ([$NHCOC_6H_5$-Htpp]$^+$, 100); 733 ([$NHCOC_6H_5$-tpp]$^+$, 61.32); 614 ([Htpp]$^+$, 82.68); 613 ([tpp]$^+$, 27.24) UV/visible spectrum [λ, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})] in CH_2Cl_2: 324 (16.7), 430 (246), 557 (9.6), 639 (6.3).

Preparation of Zn(*N*-$NCOC_6H_5$-tpp)(MeOH)·MeOH [2(MeOH)·MeOH]. Compound **2** in 74% yield was prepared in the same way as described for Zn(*N*-*p*-$NCOC_6H_4NO_2$-tpp) using $NHCOC_6H_5$-Htpp.[8] Compound **2** was dissolved in CH_2Cl_2 and layered with MeOH to obtain purple crystals for single-crystal X-ray analysis. ^{1}H NMR (499.85 MHz, $CDCl_3$, 20 °C): δ 9.09 [d, H_β(4,13), ^3J(H−H) = 5 Hz]; 8.88 [d, H_β(3,14), ^3J(H−H) = 5 Hz]; 8.86 [s, H_β(8,9)]; 7.76 [s, H_β(18,19)]; 7.79−8.41 (m) for phenyl protons; 6.26 [t, H_{BA}(49) or BA-H_4, ^3J(H−H) = 7 Hz]; 5.82 [t, H_{BA}(48,50) or BA-$H_{3,5}$, ^3J(H−H) = 8 Hz]; 3.95 [d, H_{BA}(47,51) or BA-$H_{2,6}$, ^3J(H−H) = 9 Hz]; 3.36 [d, MeOH−CH_3, ^3J(H−H) = 5 Hz]; 1.16 [q, MeOH−OH, ^3J(H−H) = 5 Hz]; 1.71(s, H_2O). MS [*m*/*z* (assignment, rel intensity)]: 797 ([M^+, 9.64]); 796 ([M − 1]$^+$, 11.05); 692 ([M − C_6H_5CO]$^+$, 12.43); 678 ([Zn(tpp)]$^+$, 74.44); 676 ([Zntpp − 2H]$^+$, 100) UV/visible spectrum [λ, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})] in CH_2Cl_2: 325 (18.6), 440 (214.3), 565 (17.8), 612 (18.2), 664 (10.5).

Cd(*N*-$NHCOC_6H_5$-tpp)(OAc)·C_6H_6 (3·C_6H_6). A mixture of **1** (73.3 mg, 0.1 mmol) in CH_2Cl_2 (50 cm^3) and $Cd(OAc)_2 \cdot 2H_2O$ (69 mg, 0.3 mmol) in MeOH (50 cm^3) was refluxed in CH_3CN (100 cm^3) for 8 h. After concentration, the residue was dissolved in CH_2Cl_2 and extracted with distilled water to remove the excess $Cd(OAc)_2 \cdot 2H_2O$. The CH_2Cl_2 layer was concentrated to dryness affording a bluish-green precipitate, which was recrystallized from toluene−hexane [1:3 (v/v)] yielding a blue solid of **3** (47 mg, 0.052 mmol, 52%). Compound **3** was redissolved in CH_2Cl_2, with a few drops of benzene added, and layered with toluene to afford blue crystals for single-crystal X-ray analysis. ^{1}H NMR (599.95 MHz, CD_2Cl_2, 20 °C): δ 8.91 [s, H_β (4,5), |^4J(Cd−H)| = 4.2 Hz]; 8.80 [d, H_β(10,19), ^3J(H−H) = 5 Hz]; 8.76 [d, H_β(9,20), ^3J(H−H) = 5 Hz]; 8.60 [s, H_β(14,15)]; 8.57 (s) for *ortho* protons *O*-H(38,40) and *O*-H(34,44); 8.39 [s, *ortho* protons *O′*-H(22,32)]; 8.16 [bs, *ortho* protons *O′*-H(26,28)]; 7.79−7.89 (m, *meta* and *para* protons); 6.44 [t, H_{BA}(49) or BA-H_4, ^3J(H−H) = 7 Hz]; 5.93 [t, H_{BA}(48,50) or BA-$H_{3,5}$, ^3J(H−H) = 8 Hz]; 3.82 [d, H_{BA}(47,51) or BA-$H_{2,6}$, ^3J(H−H) = 8 Hz]; 0.08 (s, OAc−Me); −1.13 (s, NH). ^{1}H NMR (599.95 MHz, CD_2Cl_2, −90 °C): δ 8.96 [s, H_β(4,5)] 8.77 [s, H_β(10,19)]; 8.72 [bs, H_β(9,20)]; 8.65 [s, H_β(14,15)]; 8.51 [d, *ortho* protons *O*-H(38,40), ^3J(H−H) = 7 Hz]; 8.42 [d, *ortho* protons *O*-H(34,44), ^3J(H−H) = 7 Hz]; 8.35 [d, *ortho* protons *O′*-H(22,32), ^{3}J(H−H) = 6 Hz]; 8.16 [d, *ortho* protons *O′*-H(26,28), ^3J(H−H) = 6 Hz]; 7.89(m) for *meta* H(37,41) and *meta* H(35,43); 7.82 [m, *para* H(36,42)]; 7.79 [m, *meta* H(23,31)]; 7.78 [m, *para* H(24,30)]; 7.74 [m, *meta* H(25,29)]; 6.41 [t, H_{BA}(49) or BA-H_4, ^3J(H−H) = 7 Hz]; 5.92 [t, H_{BA}(48,50) or BA-$H_{3,5}$, ^3J(H−H) = 7 Hz]; 3.72 [d, H_{BA}(47,51) or BA-$H_{2,6}$, ^3J(H−H) = 7 Hz]; 0.01 (s, OAc-Me); −1.42

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Table 1. Crystal Data for $NHCOC_6H_5$-Htpp (**1**), **2**(MeOH)·MeOH, and **3**·C_6H_6

param	**1**	**2**(MeOH)·MeOH	**3**·C_6H_6
empirical formula	$C_{51}H_{35}N_5O$	$C_{53}H_{41}N_5O_3Zn$	$C_{59}H_{43}CdN_5O_3$
fw	733.84	861.28	982.38
space group	$P\bar{1}$	$P2_1/n$	$C2/c$
cryst syst	triclinic	monoclinic	monoclinic
a, Å	10.881(2)	14.790(1)	26.345(1)
b, Å	13.003(2)	17.160(1)	11.4355(6)
c, Å	14.094(2)	17.425(1)	32.317(2)
α, deg	95.976(4)	90	90
β, deg	95.902(4)	98.369(1)	91.548(1)
γ, deg	90.611(3)	90	90
V, Å^3	1972.3(6)	4375.1(5)	9732.4(8)
Z	2	4	8
F_{000}	768	1792	4032
D_{calcd}, g cm^{-3}	1.236	1.308	1.341
μ(M*o* Kα), mm^{-1}	0.075	0.612	0.50
S	0.893	0.981	1.105
cryst size, mm^3	0.11 × 0.29 × 0.51	0.08 × 0.13 × 0.56	0.21 × 0.16 × 0.10
θ, deg	25.06	26.04	28.28
T, K	293(2)	293(2)	294(2)
no. of reflcns measd	10 427	24 533	30 708
no. of reflcns obsd	6910 ($I > 2\sigma(I)$)	8590 ($I > 2\sigma(I)$)	11 695 ($I > 2\sigma(I)$)
R,[a] %	6.71	5.36	9.79
R_w,[b] %	15.19	14.88	17.51

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

(s, NH). UV/visible spectrum [λ, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})] in CH_2Cl_2: 332 (37.1), 442 (375.3), 563 (14.2), 617 (23.9), 664 (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_2Cl_2 or $CDCl_3$ at δ = 5.30 or 7.24, and ^{13}C NMR, to the center line of CD_2Cl_2 or $CDCl_3$ at δ = 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 **1**, **2**(MeOH)·MeOH, and **3**·C_6H_6. Measurements were taken on a Bruker AXS SMART-1000 diffractometer using monochromatized Mo Kα radiation (λ = 0.710 73 Å). The SADABS absorption corrections were made for **1** and **2**(MeOH)·MeOH. Empirical absorption corrections were made for **3**·C_6H_6. 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 complexes **2**(MeOH)·MeOH and **3**·C_6H_6.

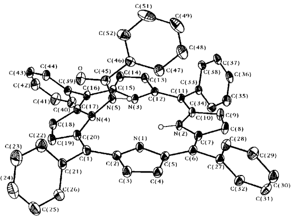
Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds **2**(MeOH)·MeOH and **3**·C_6H_6

2(MeOH)·MeOH			
Distances			
Zn−N(1)	2.057(3)	Zn−N(5)	2.036(3)
Zn−N(2)	1.945(3)	Zn−O(2)	2.142(3)
Zn−N(3)	2.067(3)		
Angles			
N(5)−Zn−N(1)	86.1(1)	N(2)−Zn−N(3)	94.0(1)
N(5)−Zn−N(2)	131.6(1)	O(2)−Zn−N(1)	94.8(1)
N(5)−Zn−N(3)	84.8(1)	O(2)−Zn−N(2)	111.3(1)
N(5)−Zn−O(2)	116.8(1)	O(2)−Zn−N(3)	86.3(1)
N(1)−Zn−N(2)	94.6(1)	N(4)−N(5)−Zn	94.8(2)
N(1)−Zn−N(3)	170.3(1)		
3·C_6H_6			
Distances			
Cd(1)−N(1)	2.319(5)	Cd(1)−N(4)	2.612(5)
Cd(1)−N(2)	2.252(5)	Cd(1)−O(2)	2.292(5)
Cd(1)−N(3)	2.332(5)	Cd(1)−O(3)	2.317(5)
Angles			
O(2)−Cd(1)−O(3)	55.9(2)	O(3)−Cd(1)−N(1)	117.1(2)
O(2)−Cd(1)−N(1)	112.2(2)	O(3)−Cd(1)−N(2)	101.1(2)
O(2)−Cd(1)−N(2)	156.6(2)	O(3)−Cd(1)−N(3)	117.7(2)
O(2)−Cd(1)−N(3)	106.4(2)	O(3)−Cd(1)−N(4)	137.5(2)
O(2)−Cd(1)−N(4)	81.7(2)		

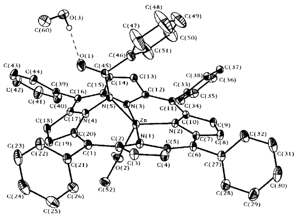
Results and Discussion

Structure of 1. The X-ray structure of **1** with the numbering is displayed in Figure 1a. The atoms of the porphyrin core are nonplanar, while the pyrrole rings [N(1)], [N(2)], [N(3)], and [N(4)] are individually planar. The three pyrrolic nitrogens N(1), N(2), and N(3) are coplanar, which define the 3N reference plane. The BA-substituted pyrrole N(4) is most highly canted from the 3N plane (30.4°). The *N*-protonated pyrrole N(2) is tilted by 11.7°, while the other two pyrroles are tilted by 2.4 [N(3)] and 8.5° [N(1)]. The N−H protons are attached to N(2) and N(5) atoms in **1**. The deviations from the 3N plane of the BA atoms N(5) and H(5A) are 1.20 and 1.10 Å, respectively. Moreover, H(2A) is located on different side at −0.17 Å from the 3N plane (Figure 2a).

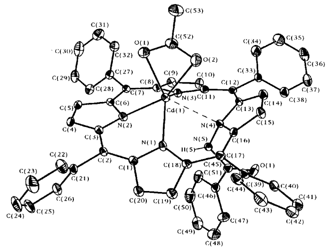
Molecular Structures of 2(MeOH)·MeOH and 3·C_6H_6. Using the d^{10} metals zinc(II) and cadmium(II), new zinc [**2**(MeOH)·MeOH] and new cadmium (**3**·C_6H_6) complexes were synthesized. The synthetic strategy is outlined in Scheme 1.



(a) $NHCOC_6H_5$-Htpp (**1**)



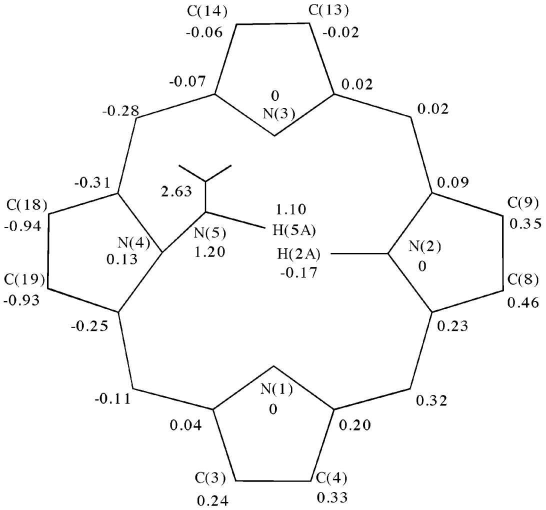
(b) Zn(N-$NCOC_6H_5$-tpp)(MeOH)·MeOH [**2**(MeOH)·MeOH]



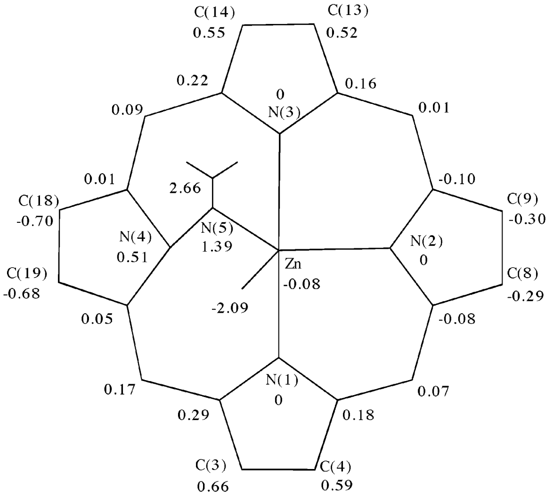
(c) Cd(N-$NHCOC_6H_5$-tpp)(OAc) (**3**)

Figure 1. Molecular configuration and atom-labeling scheme for (a) $NHCOC_6H_5$-Htpp (**1**), (b) **2**(MeOH)·MeOH, and (c) **3**·C_6H_6, with ellipsoids drawn at 30% probability. Hydrogen atoms for all compounds and solvent C_6H_6 for **3**·C_6H_6 are omitted for clarity.

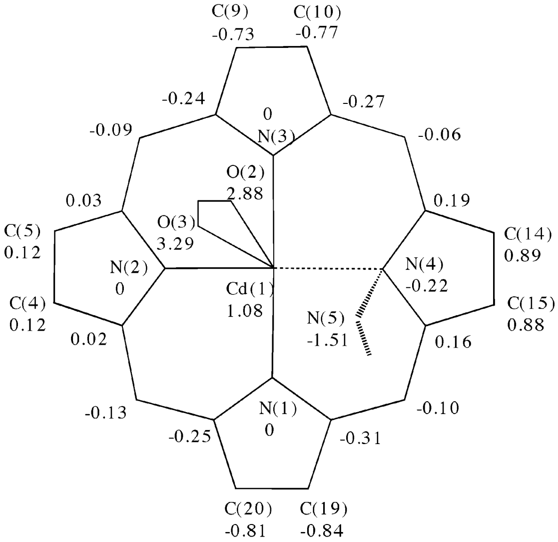
The absolute values of hardness η for Zn^{2+} and Cd^{2+} are 10.88 and 10.29 eV, respectively.[16] The softness of acidity increases from Zn^{2+} to Cd^{2+}. During the metalation of Cd-$(OAc)_2$ with free base **1** (Scheme 1), the soft acid Cd^{2+} prefers to retain one OAc^- ligand and coordinates to the N−H proton [i.e., H(2A)] of **1** to form a five-coordinate complex **3**. Complex **3** is the first example of an *N*-substituted-*N*-aminoporphyrin−metal (cadmium) complex with retention of the *N*-benzamido substituent. Moreover, the borderline (or intermediate)[17] acid Zn^{2+} prefers to attack the two N−H protons [i.e., H(2A) and H(5A)] of **1** and leads to a five-coordinate distorted trigonal bipyramidal zinc(II) derivative **2**(MeOH) possessing a nitrene moiety inserted between the zinc and one nitrogen atom [N(4)] (Scheme 1). The molecular frameworks are depicted in Figure 1b for **2**(MeOH)·MeOH and in Figure 1c for **3**·C_6H_6. The geometry around Cd in **3** is a distorted square-based pyramid in which the apical site is occupied by atoms N(2) and O(2), whereas, for Zn^{2+} in **2**, it is also described as a distorted trigonal bipyramid with N(2), N(5), and O(2) lying in the equatorial plane. Compound **3** is a five-coordinate *N*-benzamidoporphyrin complex of the porphyrin N_3 [i.e., N(1), N(2), and N(3)] with two oxygen atoms of the chelating bidentate OAc^- ligand. The zinc is also pentacoordinated with three nitrogen atoms of the porphyrins, one methanol oxygen, and one extra nitrogen atom of the nitrene fragment in **2**. The metal−ligand bond



(a) $NHCOC_6H_5$-Htpp (**1**)



(b) Zn(N-$NCOC_6H_5$-tpp)(MeOH) [**2**(MeOH)]



(c) Cd(N-$NHCOC_6H_5$-tpp)(OAc) (**3**)

Figure 2. Diagram of the porphyrinato core ($C_{20}N_4$, M, BA, and OAc^-) of (a) **1**, (b) **2**(MeOH)·MeOH, and (c) **3**·C_6H_6 . The values represent the displacements (in Å) of the atoms from the mean 3N plane [i.e., N(1)−N(3)].

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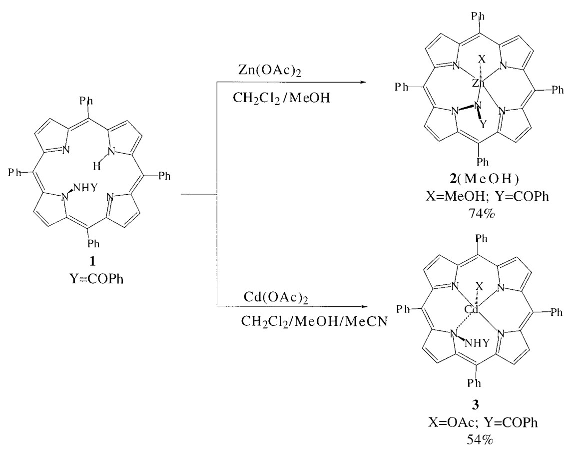
Scheme 1



distances and the angles are summarized in Table 2. In **2**, it appears that the benzamido (BA) moiety is inserted into the Zn−N bond of (*meso*-tetraphenylporphyrinato)zinc(II) [Zn(tpp)] resulting in the elongation of the N(2)⋯N(4) distance from 4.245 Å in **3** to 4.475 Å in **2**. But the N(1)⋯N(3) distance of 4.108 Å remains the same for **2** and **3**.

The bond distance (Å) of Zn−O(2) is 2.142(3), and the mean Zn−N(p) = 2.026(3) for **2**(MeOH)·MeOH; for **3**·C_6H_6 the values are Cd(1)−O(2) = 2.292(5) and Cd(1)−O(3) = 2.317(5) and the mean Cd(1)−N(p) = 2.301(5). The Zn−O(2)(MeOH) distance of 2.142(3) Å is slightly longer than the sum of the covalent radii of Zn and O (1.93 Å) but is significantly shorter than the sum of the van der Waals radii of Zn and O (2.90 Å).[18] This Zn−O(2) contact may be described as a weak covalent bond. This type of Zn⋯O(MeOH) contact was also previously observed for Zn(*N*-$PNCOC_6H_5NO_2$-tpp) with Zn(1)−O(4) = 2.106(3) Å.[8] The pyrrole nitrogen N(4) and BA nitrogen N(5) are no longer bonded to zinc and cadmium as indicated by their longer internuclear distances, 2.570(3) Å for Zn⋯N(4) and 3.094(5) Å for Cd(1)⋯N(5). The cadmium−nitrogen bond distances [Cd(1)−N(1) = 2.319(5), Cd(1)−N(2) = 2.252(5), and Cd(1)−N(3) = 2.332(5)] are comparable to those of Cd−N(3) = 2.387(3) Å in bis[tetrakis(1-pyrazolyl)borato]cadmium(II), $[B(pz)_4]_2Cd$,[19] and are also smaller than the upper limit 2.54(1) Å for the typical covalent bond distance of Cd−N13 in $Cd(C_{32}H_{34}N_5)(C_7H_6N_2)NO_3\cdot CHCl_3$.[20] Hence N(1), N(2), and N(3) are bonded strongly as well as covalently to Cd atom in **3**. Cadmium(II) is bonded to fewer than four nitrogen atoms, and so **3** may be considered as a Tsutsui's sitting-atop (SAT) complex.[15] The similar kind of SAT complex was previously reported for bis(chloromercury(II)) complex of (*N*-tosylamino)octaethylporphyrin.[10] The Cd(1)⋯N(4) distance of 2.612(5) Å is longer than 2.54(1) Å but is signficantly shorter than the sum of the van der Waals radii of Cd and N (3.15 Å).[18] This longer Cd(1)⋯N(4) contact is too long to be considered as a true coordinated bond and may be viewed as a secondary intramolecular interaction. This kind of secondary interaction was previously observed for $[Cd(H_3daps)Cl]\cdot CH_3CN\cdot 0.25H_2O$ [H_4daps = 2,6-bis(1-salicyloylhydrazonoethyl)pyridine] with Cd⋯N(6) = 2.74(1) Å.[21]

The distortion in five-coordinate complexes can be quantified by the "degree of trigonality" which is defined as $\tau = (\beta - \alpha)/60$, where "$\beta$" is the largest and "$\alpha$" the second largest of the $L_{basal}-M-L_{basal}$ angles.[22] The limiting values are $\tau = 0$ for an ideal tetragonal geometry and $\tau = 1$ for an ideal trigonal bipyramid. In the present case, we find β = 170.3(1)° [N(1)−Zn−N(3)] and α = 131.6(1)° [N(2)−Zn−N(5)] for **2**(MeOH)·MeOH, and β = 156.2(2)° [N(2)−Cd(1)−O(2)] and α = 124.1(2)° [N(1)−Cd(1)−N(3)] for **3**. Thus, the values $\tau = 0.65$ and 0.54 are obtained for **2**(MeOH)·MeOH and **3**, respectively. Hence, the geometries around Zn(II) in **2**(MeOH)·MeOH and Cd(II) in **3** are best described as a distorted trigonal bipyramid (or a square-based pyramidal distorted trigonal bipyramid, SBPDTBP)[23] with N(2), N(5), and O(2) [or N(1), N(3), and O(3)] lying in the equatorial plane for **2**(MeOH)·MeOH (or **3**). In **2**(MeOH) (Figure 1b), the observed H(3B)⋯O(1) and O(3)⋯O(1) distances were 1.90 and 2.62 Å, respectively, which fall below those values expected for van der Waals distances (2.60 and 2.80 Å, respectively). The O(3)−H(3B)−O(1) angle was 163.4°, and its deviation from linearity was not too severe. Therefore, a hydrogen bond exists between H(3B) and O(1). The intramolecular hydrogen bonds cause the downfield shifts of +6.2 and +8.4 ppm for salicyaldehyde and *O*-hydroxyacetophenone relative to the parent compounds. In a similar fashion this intermolecular hydrogen bonding causes an increased polarization of the carbonyl bond in **2**(MeOH). Consequently, the carbonyl carbon C(45) in **2**(MeOH) becomes more positive, thereby accounting for why the downfield shift of +3.5 ppm is observed at 20 °C, i.e., from 160.7 ppm for C(45) in **3** to 164.2 ppm for the same carbonyl carbon in **2**(MeOH).

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 for **2**(MeOH)·MeOH and **3**. The benzamide nitrogen N(5) in **2** is located considerably far from the 3N plane. In **2**, Zn^{2+} and N(5) are located on different sides at −0.08 and 1.39 Å from its 3N plane (Figure 2). Apparently, chelating bidentate acetate in **3** is trans to the BA group with O(2) and O(3) being located separately at 2.88 and 3.29 Å out of the 3N plane (Figure 2). The N(4) pyrrole rings bearing the BA group in **2** and **3** would deviate mostly from the 3N plane, thus orienting separately in a dihedral angle of 33.8 and of 31.4°, whereas small angles of 16.9, 8.2, and 14.5° occur with N(1), N(2), and N(3) pyrrole for **2** and the corresponding angles are 22.4, 3.3, and 20.4° for **3**. In **2**, such a large deviation from planarity for the N(4) pyrrole is also reflected by observing a 14−16 ppm upfield shift in

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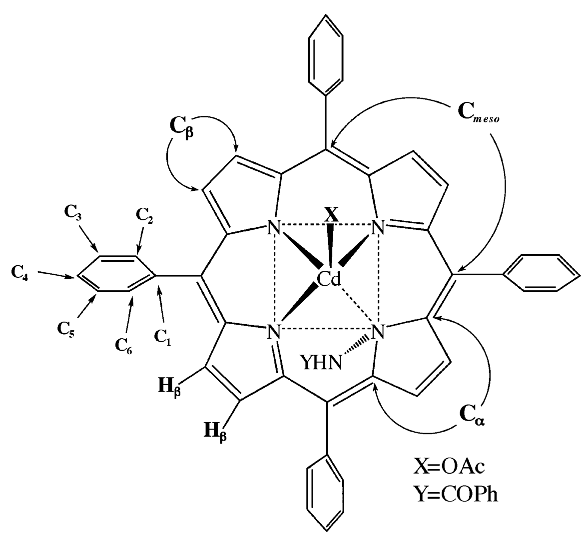
the ^{13}C NMR spectrum of the C_β(18,19) at 118.5 ppm compared to 134.1 ppm for C_β(4,13), 132.5 ppm for C_β(3,14), and 132.2 ppm for C_β(8,9). In **3**, a similar deviation is also found for the N(4) pyrrole by observing a 7−10 ppm upfield shift of the C_β(14,15) at 123.9 ppm compared to 134.2 ppm for C_β(4,5), 131.8 ppm for C_β(9,20), and 131.2 ppm for C_β(10,19).

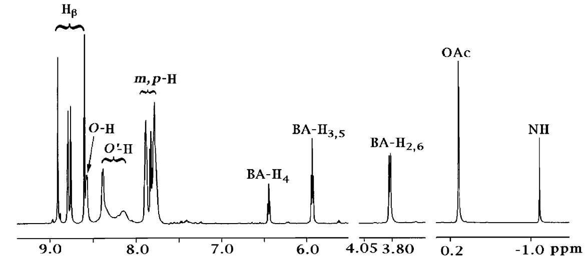
The ionic radius is found to increase from 0.82 Å for Zn^{2+} (with CN = 5) to 1.01 Å for Cd^{2+} (with CN = 5).[18] Because of the large size of Cd^{2+}, Cd(1) lies 1.08 Å above the 3N plane toward the acetate oxygen in **3**, compared to ~0.08 Å for Zn in **2**. The Cd ion in **3** is displaced from 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 Cd ion from the plane of each pyrrole ring are 0.20 Å for pyrrole N(1) ring, 1.20 Å for pyrrole N(2) ring, 0.28 Å for pyrrole N(3), and 2.32 Å for pyrrole N(4) ring. The angles between the Cd−N vector and the corresponding pyrrole rings are 7.5° for pyrrole N(1) ring, 31.6° for pyrrole N(2), 8.8° for pyrrole N(3), and 60.2° for pyrrole N(4) ring.

The dihedral angles between the mean plane of the skeleton (3N) and the plane of the phenyl group are 37.9° [C(24)], 50.9° [C(30)], 54.6° [C(36)], and 40.6° [C(42)] for **2**(MeOH) and the corresponding angles are 58.1, 49.3, 34.9, and 36.5° for **3**.

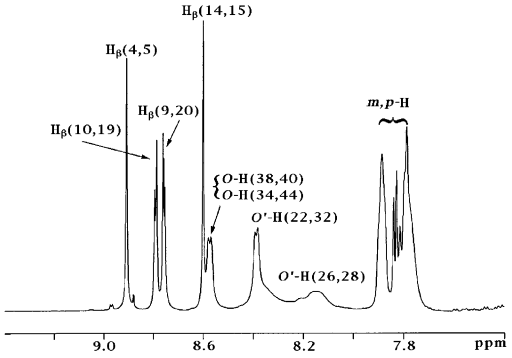
^{1}H and ^{13}C of 2(MeOH) and 3 in CD_2Cl_2. The signal arising from the NH protons of **1** was not observed at 20 °C. At −90 °C, traces of water were frozen from solution of **1** in CD_2Cl_2. Thus, the frozen water inhibits intermolecular proton exchange between water and NH proton of **1** and allows the observation of a broad singlet for NH proton at −0.74 ppm.[24] The cadmium(II) complex of **3** is diamagnetic and hence readily becomes susceptible for studies by ^{1}H (Figure 3) and ^{13}C NMR techniques. Figure 3 reveals that broadening due to intermolecular proton exchange for NH proton is eliminated upon metalation. The ^{1}H NMR spectrum of **3** in CD_2Cl_2 (Figure 3) showed a sharp singlet at $\delta = -1.13$ ppm ($\Delta\nu_{1/2} = 4$ Hz) for the NH proton at 20 °C. These NMR data for **3** suggest that the NH proton [i.e., H(5)] bound to N(5) undergoes rapid intermolecular proton exchange with water at 20 °C.

In solution, the molecule has effective C_s symmetry with a mirror plane running through the N(5)−N(4)−Cd(1)−N(2)−O(2)−O(3) unit for **3**, the N(2)−Zn−N(5)−N(4) unit for **2**(MeOH), or the N(4)−N(5)−C(45)−N(2) unit for **1**. 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 for these three complexes. On the basis of NOE difference spectrum (1-D) studies, the H_β(4,5) of **3** in CD_2Cl_2 at 20 °C was observed at $\delta = 8.91$ ppm with $|^4J(\text{Cd}-H_\beta)| = 4.2$ Hz and the singlet at 8.60 ppm is assigned to H_β(14,15) (Figure 3b). This coupling satellites of H_β(4,5) in **3** is comparable to the $|^4J(^{113}\text{Cd}-H_\beta)|$ value of 4.8 Hz for the H_β protons in Cd(N-Me-tpp)Cl[chloro(*N*-methyl-*meso*-tetraphenylporphyrinato)cadmium(II)].[25] In a

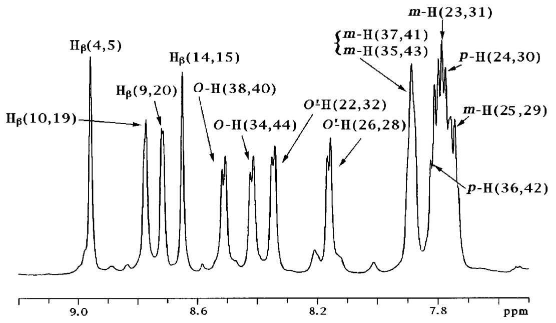




(a) 20°C



(b) expansion of (a)



(c) -90°C

Figure 3. ^{1}H NMR spectra for **3** at 599.95 MHz in CD_2Cl_2: (a) 20 °C, entire spectrum; (b) expansion of the region of 7.6−9.2 ppm of (a) showing four different β-pyrrole protons H_β and phenyl protons (*O*-H, *m*, *p*-H); (c) −90 °C.

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similar case, the sign and magnitude of the coupling constant with $^4J(^{113}\text{Cd}-\text{H}_\beta) = -5$ Hz was obtained for Cd(tpp)(py) (py = pyridine) by using the ^{13}C{H} off-resonance/selective decoupling technique.[26] In **3**, the doublet at 8.80 ppm is assigned to H_β(10,19) with $^3J(\text{H}-\text{H}) = 5$ Hz, and the other doublet at 8.76 ppm is due to H_β(9,20) with $^3J(\text{H}-\text{H}) = 5$ Hz. The ^{1}H NMR spectrum (Figure 3a) reveals that the aromatic protons of the BA group appear as two triplets, one at 6.44 ppm (BA-H_4) and the other at 5.93 ppm (BA-$\text{H}_{3,5}$) and as one doublet at 3.82 ppm (BA-$\text{H}_{2,6}$) for **3** and at 6.26 (t), 5.82 (t), and 3.95 (d) ppm for **2**(MeOH). The ^{1}H NMR spectrum (Figure 3a) for OAc^- of **3** in CD_2Cl_2 displays a sharp singlet for CH_3 at $\delta = 0.08$ ppm with $\Delta\nu_{1/2} = 6$ Hz at 20 °C and remains a sharp singlet for the same methyl protons at $\delta = 0.01$ ppm with $\Delta\nu_{1/2} = 7$ Hz at -90 °C. This minimum deviation in the value of line width ($\Delta\nu_{1/2}$) upon cooling indicates that OAc^- exchange does not occur in compound **3**. All BA and acetato protons are shifted upfield compared to their counterparts in free BA and OAc^-. Such a shift is presumably attributed to the porphyrin ring current effect. The ring current effect indicates that the acetate ligand is bonded to Cd in **3**. This bonding argument is further supported by the result that in ^{13}C NMR the OAc-CO [i.e., C(52)] and the OAc-Me [i.e., C(53)] in **3** were observed at 176.3 ppm with $^2J(\text{Cd}-\text{C}) = 32$ Hz and at 18.5 ppm with $|^3J(\text{Cd}-\text{C})| = 48$ Hz, respectively, at -90 °C. In a series of tetraarylporphyrins with Ga, In, Tl, Ge, or Sn as the central metal atom, ^{13}C NMR chemical shifts were shown to be useful tools for diagnosing whether acetato ligands were monodentate or bidentate.[27] Monodentate acetato ligands were located at 20.5 ± 0.2 and 168.2 ± 1.7 ppm, and the bidentate acetato ligands at 18.0 ± 0.7 and 175.2 ± 1.6 ppm.[27,28] The methyl and carboyl chemical shifts of the acetate group in **3** at 20 °C are separately located at 18.6 and 176.5 ppm confirming that the acetate is chelating bidentately and coordinated to the cadmium atom.[27]

Figure 3 depicts the representative ^{1}H spectra for **3** in CD_2Cl_2 at 20 and -90 °C. At 20 °C, the rotation of phenyl group along the $\text{C}_{1-}\text{C}_{meso}$ [C(12)−C(33) or C(17)−C(39)] bond is near fast.[29] This near-fast rotation is supported by assigning the singlet at 8.57 ppm to *ortho* protons *O*-H(38,40) and *O*-H(34,44) (Figure 3b). Moreover, the rotation of phenyl group along the C(2)−C(21) [or C(7)−C(27)] bond is intermediately slow. This intermediately slow rotation is also supported by assigning the two broad singlets at 8.39 and 8.16 ppm to ortho protons *O′*-H(22,32) and *O′*-H(26,28), respectively (Figure 3b). At -90 °C, this rotation is extremely slow. Hence, the rate of intramolecular exchange of the *ortho* protons for **3** in CD_2Cl_2 is also extremely slow. The doublet at 8.51 ppm is assigned to *ortho* protons *O*-H(38,40) with $^3J(\text{H}-\text{H}) = 7$ Hz (Figure 3c). The other doublet at 8.42 ppm is due to *ortho* protons *O*-H(34,44) with $^3J(\text{H}-\text{H}) = 7$ Hz.[29] Likewise, the doublet at 8.35 ppm is due to the *ortho* protons *O′*-H(22,32) with $^3J(\text{H}-\text{H}) = 6$ Hz. The corresponding doublet at 8.16 ppm is due to the *ortho* protons *O′*-H(26,28) with $^3J(\text{H}-\text{H}) = 6$ Hz (Figure 3c). In a similar way, the *meta* and *para* protons appearing as multiplet (7.79−7.89 ppm) at 20 °C (Figure 3b) changed to 7.89 [m, *m*-H(37,41) and *m*-H(35,43)], 7.79 [m, *m*-H(23,31)], 7.74 [m, *m*-H(25,29)], 7.82 [m, *p*-H(36,42)], and 7.78 ppm [m, *p*-H(24,30)] at -90 °C (Figure 3c). The analysis of these data was confirmed by the NOE difference spectroscopy for **3** in CD_2Cl_2 at -90 °C.

In previous work,[8] we reported the electronic and magnetic properties of paramagnetic complex Fe(*N*-*p*-$\text{NCOC}_6\text{H}_4\text{NO}_2$-tpp)Cl (**4**) and diamagnetic species Zn(*N*-*p*-$\text{NCOC}_6\text{H}_4\text{NO}_2$-tpp)(MeOH) [**5**(MeOH)] by magnetic susceptibility measurements and EPR spectroscopic studies. In this work we investigated the metal-binding ability of porphyrin *N*-substituted pyrroles, leading to formation of a diamagnetic metal complex **3**, with substituted groups on the nitrogen. Meanwhile, we also reported the insertion of Zn^{2+} into the rigid environment to form a diamagnetic complex **2**. The three bridged metalloporphyrins **2**(MeOH), **4,** and **5**(MeOH) are five-coordinate, and the value $\tau = 0.65$ is obtained for these compounds. Hence the geometry around Zn(II) in **2**(MeOH) and **5**(MeOH) and Fe(III) in **4** is described as a distorted trigonal bipyramid (or SBPDTBP). The sitting-atop structure of **3** is definitely different from those structures of compounds **2**(MeOH), **4**, and **5**(MeOH) but is quite similar to that of *N*-monoalkylated porphyrins, i.e., Hg(N-Me-tpp)-Cl [chloro(*N*-methyl-*meso*-tetraphenylporphyrinato)mercury(II)].[14]

Conclusion

We have investigated the new free base **1** and two diamagnetic and mononuclear zinc(II) and cadmium(II) porphyrin complexes **2**(MeOH) and **3** and their X-ray structures are established. NOE difference spectroscopies, HMQC (Figures S4 and S5 in the Supporting Information) and HMBC (Figures S1−S3 in the Supporting Information), were employed to unambiguous assignment of the ^{1}H and ^{13}C NMR resonances of **3** in CD_2Cl_2 at -90 °C and in CDCl_3 at 20 °C.

Acknowledgment. The financial support from the National Science Council of the ROC under Grant NSC 91-2113-M-005-015 is gratefully acknowledged.

Supporting Information Available: Tables and figures presenting crystal structure information for Cd(*N*-Me-tpp)Cl and ^{13}C NMR data for complexes **1**, **2**(MeOH), and **3**, Figure S1−S3, showing the HMBC spectra of **3** in CDCl_3 at 20 °C, Figure S4 and S5, showing the HMQC spectra of **3** in CDCl_3 at 20 °C, and X-ray crystallographic files in CIF format for compounds **1**, **2**(MeOH), and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) The crystal structure of Cd(*N*-Me-tpp)Cl is shown in the Supporting Information.

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