# Cadmium complexes of *meso*-tetra-(*p*-chlorophenyl)porphyrin: [*meso*-tetra-(*p*-chlorophenyl)porphyrinato](pyridine)cadmium(II) pyridine solvate and [*meso*-tetra-(*p*-chlorophenyl)porphyrinato] (dimethylformamide)cadmium(II) toluene solvate

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## Abstract

The crystal structures of [*meso*-tetra-(*p*-chlorophenyl)porphyrinato](pyridine)cadmium(II) pyridine solvate Cd[(*p*-Cl)$_4$tpp](py) · py [or **5** · py], and [*meso*-tetra-(*p*-chlorophenyl)porphyrinato](dimethylformamide)cadmium(II) toluene solvate Cd[(*p*-Cl)$_4$tpp](DMF) · toluene [or **6** · toluene] were determined. The ring current effect provides a complementary method for the investigation of coordinated pyridine and DMF ligand in complexes **5** and **6**, respectively.
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*Keywords:* Crystal structures; Cadmium *meso*-tetra-(*p*-chlorophenyl)porphyrin complexes; Ring current effect; Five-coordinate square-based pyramidal geometries

Previously, Ellis and coworkers reported the multinuclear ([113]Cd, ^{15}N, ^{13}C, ^{1}H) NMR study of the pyridine adduct of cadmium *meso*-tetraphenylporphyrin Cd(tpp)(py) (py = pyridine) (**1**) and ^{15}N multiply labeled cadmium *meso*-tetraphenylporphyrin Cd([[15]N$_4$]tpp)(py) (**2**) [1]. Amma et al. [3] reported the crystal structures and [113]Cd NMR spectra of the piperidine adduct of (5, 10, 15, 20-tetraphenylporphyrinato)cadmium(II) Cd(tpp)(pip) · o-xylene (pip = piperidine) (**3**) [2] and (5, 10, 15, 20-tetraphenylporphyrinato)cadmium(II)-bis(dioxane)

solvate Cd(tpp) · (dioxane)$_2$ (**4**). The solution [113]Cd NMR is relatively insensitive to the nature of the axial nitrogen donor ligand in Cd(tpp)L (L = py, pip, etc.) five-coordinated complexes with a range of 418–438 ppm [2]. Even the very weak oxygen of donor dioxane at +435 ppm falls into this range. As a result the characteristics of [113]Cd NMR spectra of Cd(tpp)L complexes are dictated by the porphyrin ring system. Hence, the [113]Cd chemical shift in solution is unsuitable to probe the subtle differences in the local environment for cadmium in "free, unliganded" Cd(tpp) and in "liganded" Cd(tpp)L [2]. The chemical shifts for the pyridine carbons of **2** were observed at 149.3 (py-C$_{2,6}$), 123.5 (py-C$_{3,5}$) and 135.8 ppm (py-C$_4$) [2]. This observation

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indicates that only free pyridine is found in **2** while axially coordinated pyridine is absent. Furthermore, the ^{1}H and ^{15}N chemical shifts of coordinated pyridine in **2** remain unreported. Apparently more spectroscopic data would be necessary to identify the pyridine being coordinated to cadmium in **1** or **2** in the solution state. The electron density and the donating ability of the pyrrole nitrogen, which is the first bonding atom toward the cadmium ion in the cadmium porphyrin complex, are considered to be lowered in the case of $H_2(p$-Cl$)_4$tpp, as it contains electron-withdrawing chlorine atom. Upon replacing tpp$^{2-}$ with $(p$-Cl$)_4$tpp$^{2-}$, the complex **1** became [*meso*-tetra-(*p*-chlorophenyl)porphyrinato](pyridine)cadmium(II) Cd[$(p$-Cl$)_4$tpp](py) (**5**), and further replacement of the pyridine fragment in **5** by *N,N*-dimethylformamide (DMF) ligand, it became [*meso*-tetra-(*p*-chlorophenyl)porphyrinato](dimethylformamide)cadmium(II) Cd[$(p$-Cl$)_4$tpp](DMF) (**6**). The upfield shifts of the axial ligand due to the porphyrin ring current might provide a strategy to observe the coordinated pyridine and DMF in **5** and **6**, respectively by ^{1}H NMR spectroscopic studies. We report herein, X-ray structures of two new complexes namely **5** and **6** and resolved unambiguously the binding mode of pyridine and DMF to the cadmium atom in **5** and **6** through the ^{1}H and ^{13}C NMR measurements.

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The molecular framework is depicted in Fig. 1a for compound **5** · py and in Fig. 1b for **6** · toluene. [1,2] Their structures are five-coordination Cd(II) metalloporphyrin complexes, having four nitrogen atoms of the porphyrins in common, but they are different with a pyridine for **5** and a DMF for **6** [4]. Bond distance (Å) for Cd(1)–N(5) is 2.315(4) and the mean Cd–N(p) for **5** · py is 2.203(3); for **6** · toluene the values are Cd(1)–O(1) = 2.28(2) and the mean Cd–N(p) = 2.197(8) [5]. The Cd–N (axial) distance of 2.315(4) Å in **5** is comparable to that of Cd–N(3) = 2.387(3) Å in bis[tetrakis(1-pyrazoly)borato]cadmium(II)[B(pz)$_4$]$_2$Cd [6] and is also smaller than the upper limit 2.54(1) Å for the typical covalent bond distance of Cd–N(13) in Cd(C$_{32}$H$_{34}$N$_5$)(C$_7$H$_6$N$_2$)NO$_3 \cdot$ CHCl$_3$ [7]. Hence N(1), N(2), N(3), N(4) and N(5) are bonded strongly as well as covalently to Cd atom in **5** · py. The Cd(1)–O(1)(axial) distance of 2.28(2) Å in **6** is smaller than those of Cd(2)–O(1) = 2.379(4) and Cd(2)–O(2) = 2.391(4) Å in [(bmnpaCd)$_2$($\mu$-CO$_3$)](ClO$_4$)$_2 \cdot$ CH$_3$CN [8]. Hence N(1), N(2), N(1A), N(2A) and O(1) are covalently bonded to Cd in **6** · toluene.

The fivefold coordination geometry adopted may be quantified by using the $\tau$ descriptor for five-coordination as suggested by Addison et al. [9]. This distortion index is defined as $\tau = (\beta - \alpha)/60$, where $\beta$ is the largest and $\alpha$ is the second largest of the L$_{basal}$–M–L$_{basal}$ angles. For an ideal C$_{4v}$ sp, $\tau = 0$; for a C$_{3v}$ tbp, $\tau = 1$. In the present case, we find $\beta = 145.9(1)°$ [N(3)–Cd(1)–N(1)] and $\alpha = 145.3(1)°$ [N(4)–Cd(1)–N(2)] for **5**, and $\beta = 143.1(4)°$ [N(1)–Cd(1)–N(1A)] and $\alpha = 142.3(5)°$ [N(2)–Cd(1)–N(2A)] for **6**. Thus the value $\tau = 0.01$ is obtained for both **5** and **6**. Hence, the geometries around Cd(II) for both complexes are best described as a square-based pyramid with N(1), N(2), N(3) and N(4) [or N(1), N(1A), N(2), and N(2A)] lying in the basal plane for **5** (or **6**). Because of the larger size of Cd$^{2+}$ ($r$ = 1.01Å), Cd lies 0.65(1) Å above the 4N plane toward the pyridine nitrogen [i.e., N(5)] for **5** · py compared to 0.70(2) Å for Cd(1) in **6** [cf. 0.65(2) Å for Cd(II) in **3** [2], 0.03(1) Å for Cd(II) in **4** [2], and 0.578(6) Å for Cd(II) in Cd(tpp) [10]]. The dihedral angles between the mean plane of 4N and the planes of the phenyl groups are 80.3° [C(24)], 61.2° [C(30)], 66.1° [C(36)] and 89.1° [C(42)] for **5** · py and the corresponding angles are 79.4° [C(14)], 75.8° [C(20)], 79.4° [C(14A)] and 75.8° [C(20A)] for **6**. The radii of the central 'hole' [Ct···N, the distance from the geometrical center (Ct) of the mean plane of the 4N-atom core to the porphyrinato-core N atoms] are 2.10 Å for **5** and 2.08 Å for **6** which are larger than 2.01 Å as suggested by Collin and Hoard [11]. The cadmium(II) is bonded in a modestly expanded porphyrinato core (C$_{20}$N$_4$) for both the complexes.

The H$_\beta$ of **5** (or **6**) in toluene-d$_8$ at 20 °C was observed at $\delta = 8.90$ (or 8.86 ppm) having $|^4J(Cd-H_\beta)|$ = 4.8 Hz (or 5.4 Hz), respectively (Fig. 2). This coupling satellites
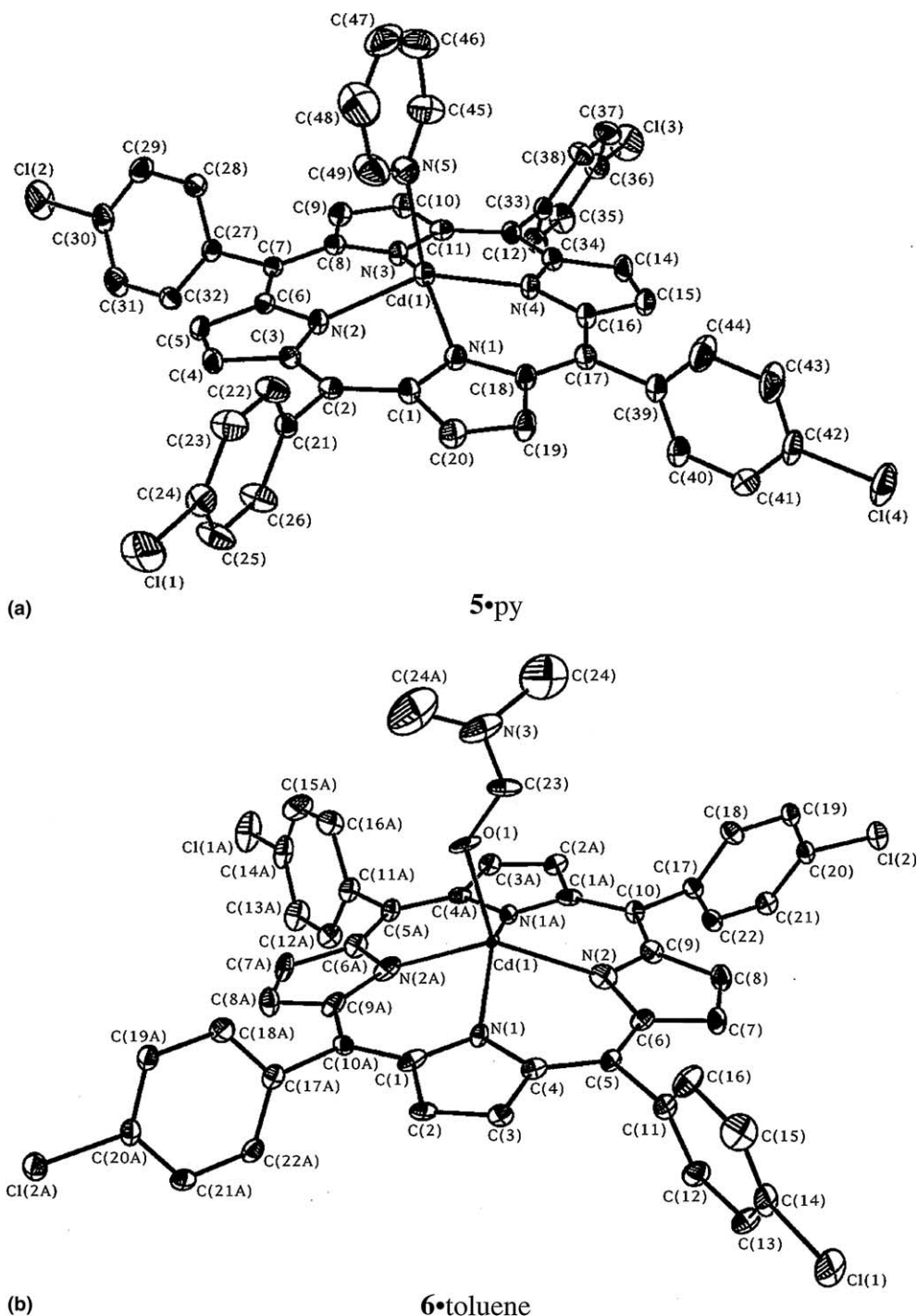
Fig. 1. Molecular configuration and atom-labeling scheme for (a) 5 · py, (b) 6 · toluene, with ellipsoids drawn at 30% probability. Hydrogen atoms for all compounds and solvent pyridine for 5 · py and toluene for 6 · toluene are omitted for clarity.

of $H_\beta$ in 5 and 6 is comparable to the $|^4J(Cd\text{-}H_\beta)|$ value of 4.8 Hz for $H_\beta$ protons in Cd(N–Me-tpp)Cl [chloro(N-methyl-meso-tetraphenylporphyrinato)cadmium(II)] [12] and that of 5 Hz for $H_\beta$ protons in Cd(tpp)(py) (py = pyridine) (1) [1]. The $^1H$ NMR spectrum (Fig. 2) reveals that the protons of the coordinated pyridine appear as two triplets at 6.03 ppm (py-$H_4$) and 5.49 ppm (py-$H_{3,5}$) and as one broad singlet at 5.31 ppm

(py-$H_{2,6}$) for 5. Due to the porphyrin ring current effect, upfield shifts for the $^1H$ resonances of coordinated py-$H_{2,6}$, py-$H_{3,5}$ and py-$H_4$ for 5 in toluene-$d_8$ are $\Delta\delta = -3.28$ [from 8.59 (obtained for free pyridine) to 5.31 ppm], $-1.74$ (from 7.23 to 5.49 ppm) and $-1.59$ ppm (from 7.62 to 6.03 ppm), respectively (Fig. 2) [13]. The similar ring current effect for the $^1H$ resonances of coordinated DMF–CHO, DMF–NCH$_3$, and
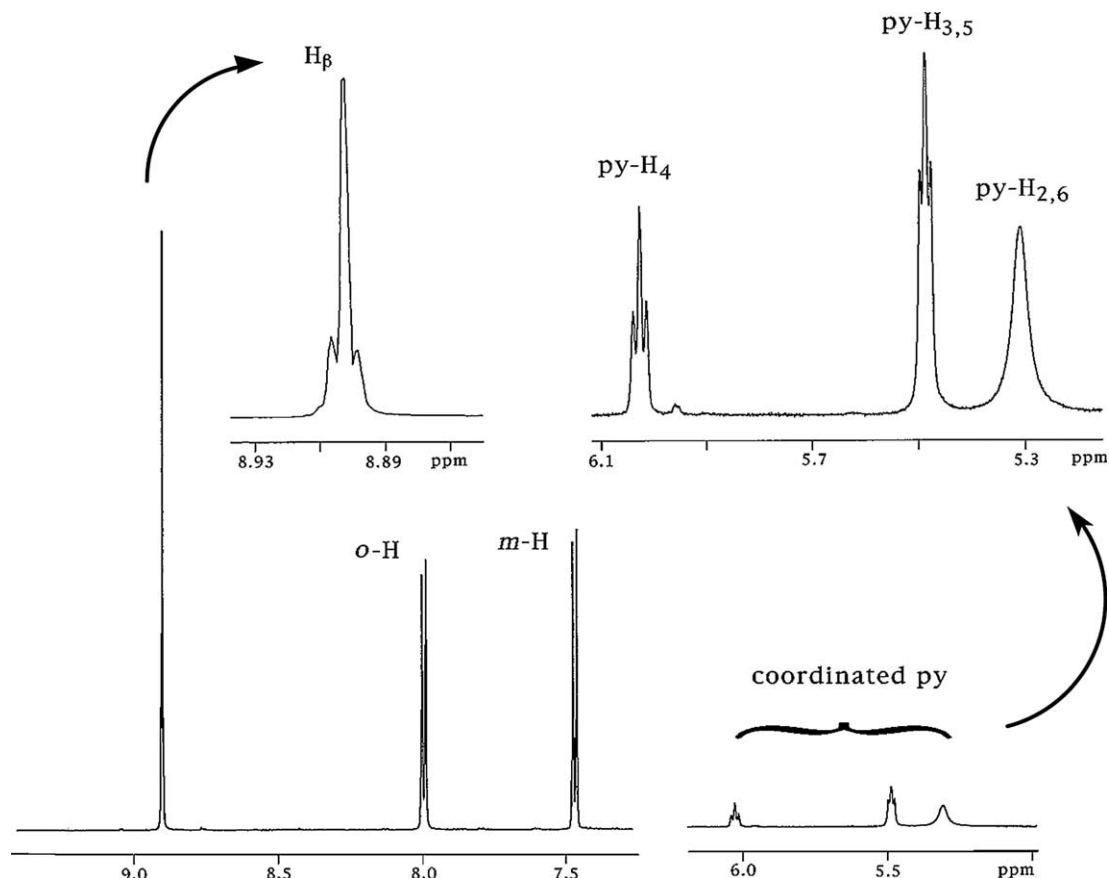
Fig. 2. $^1$H NMR spectra for **5** at 599.95 MHz in toluene-d$_8$ at 20 °C.

DMF–NCH$_3'$ for **6** in toluene-d$_8$ are $\Delta\delta = -1.24$ (from 8.02 (obtained for free DMF) to 6.78 ppm), $-1.01$ (from 2.97 to 1.96 ppm) and $-1.17$ ppm (from 2.88 to 1.71 ppm), respectively. The observation of these upfield shifts indicate that as the protons of the coordinated pyridine for **5** or the coordinated DMF for **6** in toluene-d$_8$ become closer to the C$_t$, the shielding increases. The ring current effect indicates that the pyridine and DMF are axially bonded to Cd in **5** and **6**, respectively. This bonding argument is further supported by the result that the upfield shift of $\sim 3.0$ ppm [from 149.9 (obtained for free pyridine) to 146.9 ppm] was observed for the coordinated py-C$_{2,6}$ of **5** in toluene-d$_8$.[1] The ring current effects seldom exceed 2 ppm for $^{13}$C NMR [14,15]. Hence, the ring current contribution is relatively less important in determining the $^{13}$C chemical shifts than proton shifts. Herein, this upfield shift of $\sim 3.0$ ppm is due to the shift of $^{13}$C being controlled by the paramagnetic term and not by the ring current effect [14,16]. Such paramagnetic contribution has arisen from the covalent bonding between pyridine and Cd atom and causes a decrease in the bond order between N(5) and C(45) [or C(49)] for compound **5** [14,17]. Notably, we unambiguously analyze the coordinated pyridine of **5** and the coordinated DMF of **6** in solvent toluene-d$_8$

by $^1$H and $^{13}$C NMR method which are hitherto unreported for the cadmiun(II) porphyrin complexes.

In conclusion, we have investigated two pentacoordinate, diamagnetic, mononuclear cadmium complexes of *meso*-tetra-(*p*-chlorophenyl)porphyrin, i.e., **5** and **6** and established their X-ray structures. The value $\tau = 0.01$ is obtained for these compounds indicating that the geometry around Cd(II) in **5** and **6** is described as a square-based pyramid. The coordinated pyridine and DMF in **5** and **6** are clearly identified in toluene-d$_8$ by the porphyrin ring current effect.

### Acknowledgements

### Appendix A. Supplementary material

Crystallographic data in CIF format for **5** and **6** have been deposited with Cambridge Data Centre as CCDC 225194 and 225195.

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[4] Crystal data. For complex **5** · py: $C_{54}H_{34}Cl_4N_6Cd$, $M_r$ = 1021.07, monoclinic, P2(1)/c, $a$ = 11. 5926(8) Å, $b$ = 33.703(2) Å, $c$ = 13.0888(9) Å, $\alpha$ = 90°, $\beta$ = 114.041(1)°, $\gamma$ = 90°, $V$ = 4670.2(6) Å$^3$, $Z$ = 4, $D_c$ = 1.452 g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 0.741 mm$^{-1}$, 1.21 < $\theta$ < 28.28°, GOF on $F^2$ = 0.669, $R_1[I>2\sigma(I)]$ = 0.0392, $wR_2[I>2\sigma(I)]$ = 0.0669. For complex **6** · toluene: $C_{54}H_{39}CdCl_4N_5O$, $M_r$ = 1028.10, monoclinic, C2, $a$ = 20.096(2) Å, $b$ = 9.2653(7) Å, $c$ = 15.633(1) Å, $\alpha$ = 90°, $\beta$ = 128.864(1)°, $\gamma$ = 90°, $V$ = 2266.4(3) Å$^3$, $Z$ = 2, $D_c$ = 1.507 g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 0.765 mm$^{-1}$, 1.67 < $\theta$ < 28.30°, GOF on $F^2$ = 1.169, $R_1[I>2\sigma(I)]$ = 0.0861, $wR_2[I> 2\sigma(I)]$ = 0.2088.

[5] The metal–ligand bond distances. For complex **5** · py: Cd(1)–N(1) = 2.202(3) Å, Cd(1)–N(2) = 2.212(3) Å, Cd(1)–N(3) = 2.190(3) Å, Cd(1)–N(4) = 2.206(3) Å, Cd(1)–N(5) = 2.315(4) Å.

For complex **6** · toluene: Cd(1)–N(1) = 2.214(8) Å, Cd(1)–N(2) = 2.18(1) Å, Cd(1)–O(1) = 2.28(2) Å, C(23)–O(1) = 1.26(3) Å.

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