

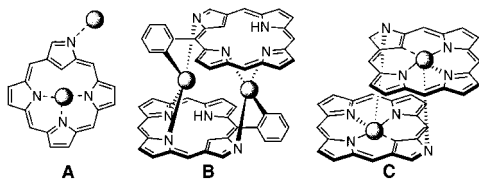
## Flexible Inner and Outer Coordination of Zn(II) N-Confused Porphyrin Complex

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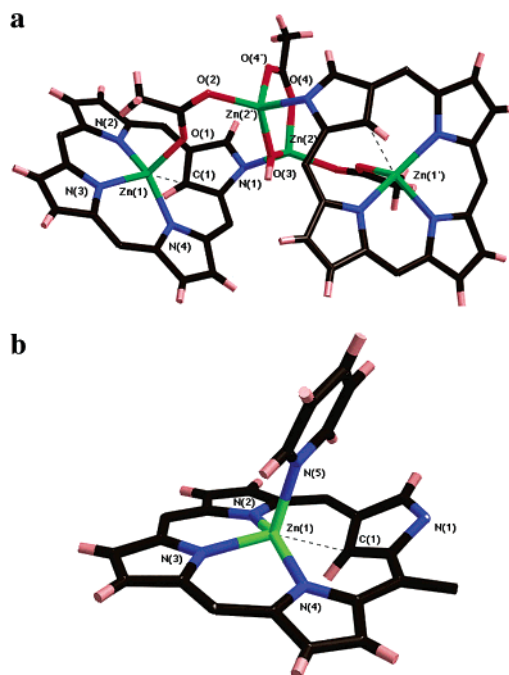
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Construction of the metal-assisted porphyrin assembly is attracting considerable attention for the use in electron- and energy-transfer systems, catalysts, and so on.<sup>1</sup> Among a variety of porphyrins and metalloporphyrins, an inverted porphyrin isomer, N-confused porphyrin (NCP), is unique in that it can bind two metal ions both inside and outside of the porphyrin core.<sup>2–4</sup> For example, NCP affords a monomeric bis-metal complex with Rh(I) (Type A)<sup>3</sup> and a double-decker dimer with Pd(II) (Type B).<sup>4</sup> Such versatile metal binding can be attributed to the different location of the coordinating nitrogens, the well-preorganized inner and the flexible peripheral. In this context, it is of interest to investigate the possibility of dimer formation of Type C because it may be a general coordination mode of NCP and may open the way to the oligomerization of the multiply N-confused porphyrins.<sup>5</sup> Herein, we report the syntheses and characterization of tetranuclear and dinuclear Zn(II) NCP dimers (**1**, **2**) and pyridine-coordinating Zn(II) monomer complex (**3**). To the best of our knowledge, this is the first characterization of Zn(II) NCP complexes by X-ray analyses.



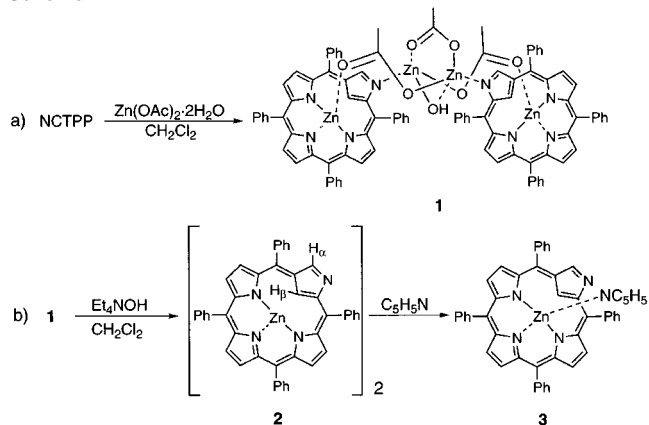
When N-confused tetraphenylporphyrin (NCTPP) was treated with 2 equiv of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  in  $\text{CH}_2\text{Cl}_2$  at room temperature, the red color solution changed into green immediately. After the solvent was removed and after crystallization from toluene, green-colored crystals of tetra-Zn(II)-coordinated NCTPP dimer (**1**) were obtained quantitatively (Scheme 1a). Subsequent treatment with 1%  $\text{Et}_4\text{NOH}$  aqueous solution to remove the acetate ligands of **1** in  $\text{CH}_2\text{Cl}_2$  led to the formation of brownish dimer **2**. The dimeric molecular mass of **2** was confirmed by the FABMS peak ( $m/z = 1352$ ) as well as vapor pressure osmometry (VPO) measurements, 1301 g/mol.<sup>7</sup> The Zn dimer complex **2** was further transformed into monomeric pyridine complex **3** by adding pyridine.<sup>6</sup>

The explicit structural evidence of the tetra-nuclear Zn(II) complex of NCP dimer (**1**) was derived from a single-crystal X-ray diffraction analysis (Figure 1a).<sup>8</sup> The two Zn(1) atoms in the core were pentacoordinated with three pyrrolic nitrogens, N(2), N(3), and N(4), one carbon of the *confused* pyrrole, C(1), and an axial acetate oxygen, O(1). The two Zn(2) atoms at the periphery were in a tetrahedral fashion, forming a six-membered ring with an acetate and a hydroxyl group, O(3), and the remaining coordination



**Figure 1.** Molecular structures of **1** (a) and **3** (b). *meso*-Phenyl groups are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **1**: Zn(1)–C(1), 2.49(1); Zn(1)–N(2), 2.07(1); Zn(1)–N(3), 2.02(1); Zn(1)–N(4), 2.09(1); Zn(1)–O(1), 2.032(9); Zn(2)–N(1), 2.02(2); Zn(2)–O(2), 1.950(9); Zn(2)–O(3), 2.01(1); Zn(2)–O(4), 1.922(8);  $\angle\text{O}(3)\text{–Zn}(2)\text{–O}(4)$ , 109.3(5);  $\angle\text{Zn}(2)\text{–O}(3)\text{–Zn}(2')$ , 113.3. For **3**: Zn(1)–C(1), 2.42(1); Zn(1)–N(2), 2.094(8); Zn(1)–N(3), 1.995(9); Zn(1)–N(4), 2.087(8); Zn(1)–N(5), 2.113(8).

## Scheme 1

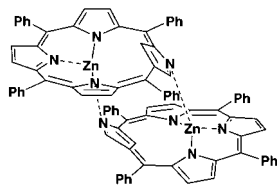


sites were occupied by the outer nitrogen, N(1), and the other oxygen atom of the acetate, O(2). The *confused* ring bent at  $36.10^\circ$  to the mean-plane consisting of core 24 atoms, and the two

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**Figure 2.** A possible structure of Zn dimer complex **2**.

porphyrin planes were tilted  $34.2^\circ$  toward each other. The Zn(1) atom was located  $0.448 \text{ \AA}$  above the plane and coordinated to the inner CH carbon in a side-on  $\eta^1$ -fashion with the distance of  $2.49(1) \text{ \AA}$ .<sup>9</sup> The coordination environment around the two outer Zn(II) atoms of **1** resembles the active center of bis-Zn(II) metal enzyme such as phosphotriesterases.<sup>10</sup>

The similar C–Zn coordination mode was also observed in the crystal structure of the pyridine-bearing monomer **3**, wherein the Zn(II) atom was  $0.472 \text{ \AA}$  above the plane and the C–Zn bond length and the tilting angle of the *confused* pyrrole ring were  $2.42(1) \text{ \AA}$  and  $29.23^\circ$ , respectively (Figure 1b).<sup>11</sup> Thus, such a side-on  $\eta^1$ -coordination of the *confused* pyrrole ring seems to be general in the inner-coordinated Zn(II) NCP complex. The unfavorable interaction between the fully occupied  $d_{x^2-y^2}$  orbital of  $d^{10}$  Zn(II) ion and the  $sp^2$ -orbital of the inner carbon<sup>12</sup> might induce the tilting of the *confused* pyrrole ring, resulting in a side-on  $\eta^1$ -type coordination.<sup>9</sup> The binding mode described above is completely different from the reported square-planar NCP complexes of  $d^8$  metals, such as Ni(II),<sup>2b</sup> Pd(II),<sup>4</sup> Cu(III),<sup>5a</sup> and Ag(III).<sup>5a,13</sup>

The dimeric structure observed in the solid state was also maintained in solution as judged by the  $^1\text{H}$  NMR spectrum of **1** in  $\text{CDCl}_3$ . Namely, the four singlet signals were observed in the shielded region at  $0.72$ ,  $-1.30$ ,  $-3.06$ , and  $-3.90$  ppm, in the ratio of  $3:6:2:1$ , respectively, among which the first two signals were ascribable to the methyl signals of the acetate groups and the latter two signals were that of the inner  $\beta$ -CH ( $H_\beta$ ) of the *confused* pyrrole rings and the coordinating hydroxyl group, respectively.

Interestingly, the different coordination mode for the dimer **2** was inferred from the comparison of the  $^1\text{H}$  and  $^{15}\text{N}$  NMR signals of the *confused* pyrrole ring of **1–3**. The *outer*  $\alpha$ -CH ( $H_\alpha$ ) in **2** was observed in the shielded region at  $2.88$  ppm, while the corresponding signals of **1** and **3** were observed in the deshielded region at  $6.59$  and  $7.96$  ppm, respectively, in  $\text{CDCl}_3$ . The inner  $\beta$ -CH ( $H_\beta$ ) signals of **1–3**, on the other hand, appeared in the shielded region at  $-3.06$ ,  $-3.69$ , and  $-3.68$  ppm, respectively.<sup>14,15</sup> Furthermore, the  $^{15}\text{N}$  NMR signal of the *outer* nitrogen in **2** was observed at  $208.09$  ppm in the same region as that of **1** ( $207.08$  ppm) but away from that of **3** ( $296.43$  ppm). It is pertinent to point out here that Zn(II) tetraphenylporphyrin shows the  $^{15}\text{N}$  signals around  $200$  ppm<sup>16</sup> and the *naked* outer nitrogen of NCTPP free base appears at  $303.58$  ppm;<sup>14</sup> thus, the *outer* nitrogen in **2** is most likely interacts with Zn(II) metal in the solution. Here, one could attribute the upfield shift of the  $H_\alpha$  signal of **2** toward the ring current of the counteracted porphyrin, as a result of the slipped dimer formation of Type C. As both the sharp singlet signals of *outer*  $H_\alpha$  and inner  $H_\beta$  did not change even at  $-40^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$ , one of the dimer among the two possible structures seems to be formed preferentially (Figure 2).<sup>17,18</sup>

In conclusion, we have shown here the inner and outer coordination of Zn metal to afford two types of NCP dimer complexes. The flexible tilting of the *confused* pyrrolic ring and such ditopic metal coordination would be important for constructing a multimetal NCP assembly.

**Supporting Information Available:** Synthetic procedures, spectroscopic data, and absorption spectra of **1–3**; VT  $^1\text{H}$  NMR spectra of **2**; Optimized structures for **2** (PDF). Crystallographic data of **1** and **3** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Wojaczynski, J.; Latos-Grażyński, L. *Coord. Chem. Rev.* **2000**, *204*, 113–171. (b) Burrell, A. K.; Officer, D. L.; Plieger, P. G.; Reid, D. C. *W. Chem. Rev.* **2001**, *101*, 2751–2796.
- (2) (a) Furuta, H.; Asano, T.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 767–768. (b) Chmielewski, P. J.; Latos-Grażyński, L.; Rachlewicz, K.; Głowiak, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 779–781.
- (3) Srinivasan, A.; Furuta, H.; Osuka, A. *Chem. Commun.* **2001**, 1666–1667.
- (4) Furuta, H.; Kubo, N.; Maeda, H.; Ishizuka, T.; Osuka, A.; Nanami, H.; Ogawa, T. *Inorg. Chem.* **2000**, *39*, 5424–5425.
- (5) (a) Furuta, H.; Maeda, H.; Osuka, A. *J. Am. Chem. Soc.* **2000**, *122*, 803–807. (b) Furuta, H.; Maeda, H.; Osuka, A.; Yasutake, M.; Shimmyozu, T.; Ishikawa, Y. *Chem. Commun.* **2000**, 1143–1144. (c) Furuta, H.; Maeda, H.; Osuka, A. *J. Org. Chem.* **2001**, *66*, 8563–8572.
- (6) The monomeric Zn(II) NCTPP complex bearing a chloride ligand (Zn(NCTPP)Cl) has been reported previously. (Chmielewski, P. J.; Latos-Grażyński, L.; Schmidt, I. *Inorg. Chem.* **2000**, *39*, 5475–5482). It is noteworthy that NCP behaves as a dianionic ligand in **1–3** and a monoanionic ligand in Zn(NCTPP)Cl, in which the outer nitrogen bears a hydrogen. Such multivalency accompanied by the protonation and deprotonation of the outer nitrogen is one of the fundamental properties of NCP ligand. See ref 13.
- (7) VPO data for **1**:  $1547 \text{ g/mol}$  (calcd 1681); **3**:  $667 \text{ g/mol}$  (calcd 757.2).
- (8) Zn(II) dimer(**1**): green platelet,  $\text{C}_{94}\text{H}_{66}\text{N}_8\text{O}_7\text{Zn}_2\cdot 2\text{C}_7\text{H}_8\cdot 2\text{C}_6\text{H}_6$ ,  $M_w$ : 2008.53, monoclinic, space group  $C2/c$  (no. 15),  $a = 26.327(1) \text{ \AA}$ ,  $b = 17.0084(8) \text{ \AA}$ ,  $c = 26.990(1) \text{ \AA}$ ,  $\alpha = 121.266(2)^\circ$ ,  $V = 10330.2(8) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.300 \text{ g/cm}^3$ ,  $T = 23^\circ\text{C}$ . Final  $R = 0.072$  (GOF = 0.243) for 4028 observed reflections with  $I > 3.00\sigma(I)$ ,  $R_w = 0.105$  for 11742 all unique data.
- (9) The side-on  $\eta^1$ -coordination of NCP metal complex was demonstrated by the X-ray structures of (a) C-methylated Ni(II)NCTPP (Chmielewski, P. J.; Latos-Grażyński, L.; Głowiak, T. *J. Am. Chem. Soc.* **1996**, *118*, 5690–5701) and (b) Fe(II) NCTPP (Chen, W.-C.; Hung, C.-H. *Inorg. Chem.* **2001**, *40*, 5070–5071).
- (10) Vanhooke, J. L.; Benning, M. M.; Raushel, F. M.; Holden, H. M. *Biochemistry* **1996**, *35*, 6020–6025.
- (11) Zn(II) monomer (**3**): green prism,  $\text{C}_{49}\text{H}_{28}\text{N}_5\text{Zn}\cdot\text{C}_5\text{H}_5\text{N}\cdot 2\text{H}_2\text{O}$ ,  $M_w$ : 867.31, triclinic, space group  $P1$  (no. 2),  $a = 13.067(2) \text{ \AA}$ ,  $b = 13.443(2) \text{ \AA}$ ,  $c = 14.917(2) \text{ \AA}$ ,  $\alpha = 75.040(8)^\circ$ ,  $\beta = 70.377(3)^\circ$ ,  $\gamma = 66.321(5)^\circ$ ,  $V = 2237.2(5) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.287 \text{ g/cm}^3$ ,  $T = 23^\circ\text{C}$ . Final  $R = 0.086$  (GOF = 0.245) for 4792 observed reflections with  $I > 3.00\sigma(I)$ ,  $R_w = 0.114$  for 9826 all unique data.
- (12) The  $^{13}\text{C}$  NMR signals of the inner carbons for **1–3** in  $\text{CDCl}_3$  were observed in an  $sp^2$  region, at  $81.22$ ,  $78.33$ , and  $87.25$  ppm, respectively, which were slightly upfield-shifted from the corresponding signal of free base NCTPP ( $99.2$  ppm).
- (13) Furuta, H.; Ogawa, T.; Uwatoko, Y.; Araki, K. *Inorg. Chem.* **1999**, *38*, 2676–2682.
- (14) The assignment of the signals was performed by using the  $^{15}\text{N}$ -labeled NCTPP. The  $^1\text{H}$ – $^{15}\text{N}$  magnetic coupling ( $^2J_{\text{H-N}} = 7.0$  Hz) between the  $H_\alpha$  and the adjacent nitrogen was observed. Furuta, H.; Ishizuka, T.; Osuka, A.; Dejjima, H.; Nakagawa, H.; Ishikawa, Y. *J. Am. Chem. Soc.* **2001**, *123*, 6207–6208.
- (15) In the NCTPP free base, the corresponding signals appear at  $8.77$  ( $H_\alpha$ ) and  $-4.99$  ( $H_\beta$ ) ppm in  $\text{CDCl}_3$ , respectively. See ref 2.
- (16) Gust, D.; Robert, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 3637–3640.
- (17) The optimized two possible structures of **2** at semiempirical PM3 calculation level are shown in the Supporting Information.
- (18) The structural difference of the dimer **2** was also reflected in the intensity of Q-band absorption. Among the four peaks in the Q-bands, both the first and second transition at  $765$  and  $701$  nm in  $\text{CH}_2\text{Cl}_2$ , respectively, were intense in **2**, while the corresponding peaks were weak in **1** and **3**. See Supporting Information.

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