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Regioselective Oxidative Liberation of Aryl-Substituted Tripyrrinone Metal Complexes from N-Confused Porphyrin

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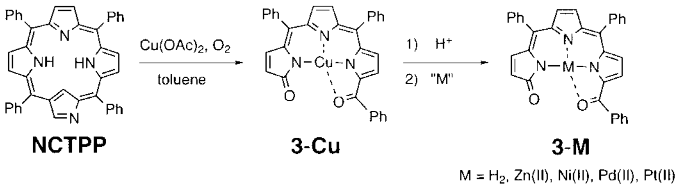
ABSTRACT



A Cu(II) complex of the first aryl-substituted tripyrrinone derivative, 14-benzoyl-5,10-diphenyl-1-oxo-tripyrrinato copper(II) (3-Cu) was obtained in the reaction of N-confused tetraphenylporphyrin (NCTPP) and Cu(OAc)$_2$ in refluxing toluene, and subsequent treatment with acid afforded a free tripyrrolic ligand that could bind a variety of transition metals.

Degradation of porphyrinoids has long been interesting in relation to the bile pigments in the natural system.[1−8] The ring opening of the porphyrin core by photo or metal oxidation is known to afford linear tetrapyrrolic compounds. For example, octaethylporphyrin (OEP) and *meso*-tetraphenylporphyrin (TPP), typical representatives of artificial porphyrins, are shown to convert into *meso*-oxo formyl bilinone (**1**) and benzoyl bilinone (**2**), respectively (Figure 1).[2,3] In the course of our N-confused porphyrin (NCP)[9] studies, we have frequently encountered the instability of NCP compounds, especially during metalation with various transition metals such as Cu, Mn, Fe, and so on.[10−16] From our interest in the fate of NCP ligand, we have carefully investigated the Cu(II) complexation reaction of N-confused tetraphenylporphyrin (NCTPP) under an aerobic atmosphere. Surprisingly, the decomposed product identified was not a tetrapyrrolic oligomer but a tripyrrolic, tripyrrinone derivative (**3**), in which both the confused pyrrole and a *meso*-phenyl group were lost and one of the terminal pyrroles was benzoylated. Herein, we wish to report the Cu(II)-assisted

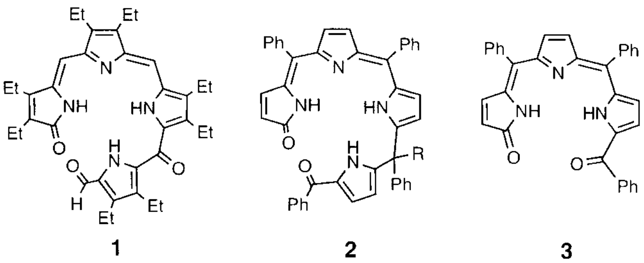


Figure 1. Structures of the ring-opening products from OEP, TPP, and NCTPP.

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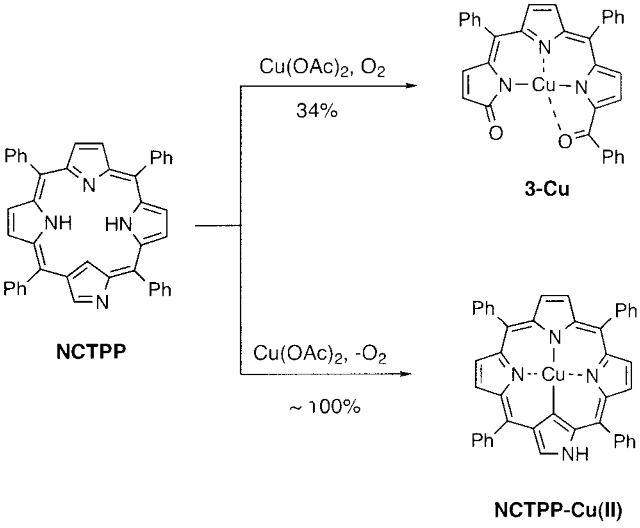
oxygenolysis reaction of NCP and identification of the fragmented product, 14-benzoyl-5,10-diphenyl-1-oxo-tripyrrin Cu(II) complex (**3-Cu**). The chemistry of the conjugated tripyrrole is rare,[17] and to the best of our knowledge, this is the first characterization of aryl-substituted tripyrrinone metal complex by X-ray analysis.

Scheme 1



When a toluene solution of NCTPP was refluxed with Cu(OAc)$_2$ for 24 h in air, a bluish-green solid was isolated from the reaction mixture in 34% yield (Scheme 1). No other products could be identified. The ^{1}H NMR in CDCl$_3$ showed very broad signals around 9.28, 7.74, 7.37, 7.30, and 6.75 ppm, suggesting the involvement of paramagnetic Cu(II) ion.[18] The FABMS spectrum of the product showed a molecular ion peak at 554 au, indicating the fragmentation of the NCTPP ligand ($m/z = 614$). When the reaction was performed under rigorous anaerobic condition, on the other hand, *normal* inner core complex, NCTPP-Cu(II),[14a] was formed quantitatively.

The structure of Cu(II) complex, **3-Cu**, was elucidated explicitly by a single-crystal X-ray diffraction analysis[19] (Figure 2). The complex revealed a benzoylated tripyrrinone structure where the *confused* pyrrole ring and one of the *meso*-phenyl moieties were absent. **3-Cu** was nearly planar, and the mean plane deviation of the core 24 atoms was 0.21 Å. The Cu(II) ion showed (3N + O) coordination, namely, three pyrrolic nitrogens and a benzoyl oxygen were bound to Cu(II) metal in a distorted square planar fashion. The distances of the Cu(II)−N bonds were in the range of 1.893(5)−1.961(5) Å, which were shorter than that of TPP−Cu(II) complex, 1.981(7) Å,[20] and the Cu(II)−O was 2.045(4) Å. Interestingly, the benzoyl group was almost flat, and the dihedral angle between the tripyrrane unit and the phenyl ring was only 6.72°.[21] In the solid state, the two complexes were stacked in a *face-to-face* fashion at an average distance

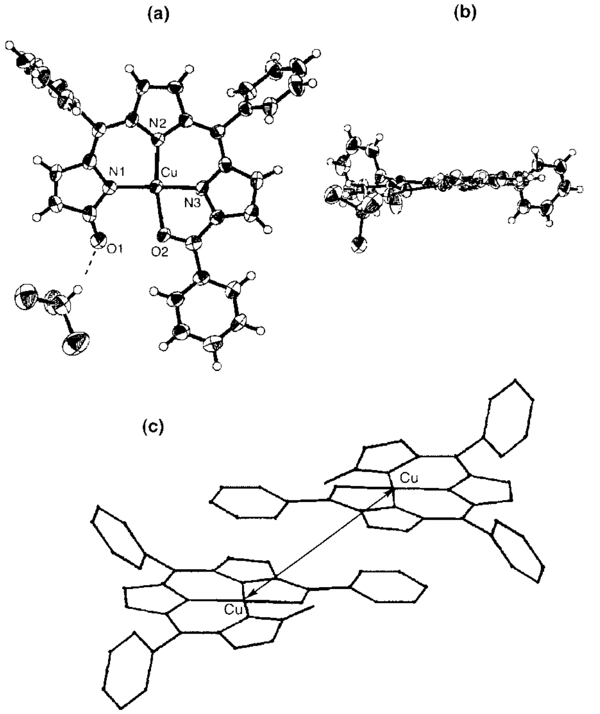


Figure 2. X-ray crystal structures of **3-Cu**: (a) top view and (b) side view. Solvent is omitted for clarity in (c). Selected bond lengths (Å) and angles (deg): Cu−N1, 1.914(5); Cu−N2, 1.961(5); Cu−N3, 1.893(5); Cu−O2, 2.045(4); ∠N1−Cu−O2, 97.8(2); ∠N1−Cu−N2, 93.6(2); ∠N2−Cu−N3, 89.5(2); ∠N3−Cu−O2, 79.4(2). The hydrogen bonding interaction of CHCl$_3$ and O1 is indicated in a broken line.

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(18) The ESR spectrum of **3-Cu** in toluene at 77 K showed the broad signal with $A_{\parallel} = 170$ G, $g_{\parallel} = 2.21$. We thank Prof. Y. Ishikawa at Oita University for the help of the ESR measurements.

(19) Crystal data for **3-Cu**: $C_{33}H_{21}N_3O_2{\cdot}CHCl_3$, $M_w = 674.47$, monoclinic $P21/n$ (No. 14), $a = 8.1991(3)$ Å, $b = 23.4409(8)$ Å, $c = 15.6336(6)$ Å, $\beta = 100.742(2)°$, $V = 2952.0(2)$ Å^3, $D_c = 1.517$ g/cm^3, $Z = 4$, $R = 0.041$, $wR = 0.047$, $GOF = 0.05$ for 2602 reflections with $I > 3.0\sigma(I)$.

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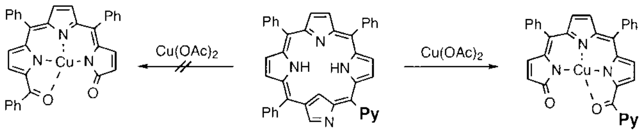
(21) Similar coplanarity of the benzoyl group was also observed in Ni(II) and Cu(II) complex of **2** (R = *n*-butyl). See ref 8.

of 2.901 Å, and the distance of two Cu(II) centers was 7.015 Å. The solvent $CHCl_3$ molecule was placed in the void space of the deleted phenyl group and was interacting with the terminal O1 atom by hydrogen bonding at the distance of 3.085(9) Å.

To obtain clues for the mechanism of the fragmentation reaction of NCTPP, the cleavage site of the *meso*-position, either 5- or 20- or both, was determined by using 5,10,15-triphenyl-20-(2′-pyridyl)-2-aza-21-carbaporphyrin (**4**) (Scheme 2).[22] The isolated tripyrrinone derivative (**5-Cu**) showed the pyridine unit both in ^{1}H NMR[23] and FABMS, and no other tripyrrine derivative was observed in this reaction. Thus, the removal of the *meso*-phenyl moiety in the Cu(II) ion mediated oxygenolysis of NCTPP was regioselective, i.e., next to the β-position of the *confused* pyrrole ring. To examine the possible degradation from the NCTPP−Cu(II) complex, the reaction was performed for 2 h in an anaerobic atmosphere in toluene at first. After confirming the formation of NCTPP−Cu(II), the solution was then exposed to air at reflux temperature. After 17 h, the **3-Cu** was detected in the reaction mixture as a major product (30%). Furthermore, when NCP derivatives bearing a sterically hindered group at *o*-positions of a *meso*-aryl group, such as 2,6-dimethylphenyl, 2,6-dimethoxyphenyl, pentafluorophenyl, and 2-chlorophenyl, were subjected to the reaction in place of NCTPP under the same conditions, the corresponding tripyrrine complexes could not be detected at all. Although it is early to discuss the mechanism at present, one may consider the interaction of NCTPP−Cu(II) and the molecular oxygen as shown in Scheme 3.[24] The (3N + C) coordination of the NCTPP−Cu(II) complex might be changed into the stable (3N + O) coordination, which was subsequently formed from the second oxygenolysis of metalated tetrapyrrolic bilinone intermediate, to yield tripyrrinone Cu(II) complex. As the reaction proceeded in the absence of light, electron transfer from Cu(II) to molecular oxygen can be considered as one of the activation mechanisms of the molecular oxygen.[25] For the development of oxidative catalysts in the future, the role of the *ortho*-substituted phenyl groups in protecting against attack of molecular oxygen at the *meso*-position in NCP would be worth considering.

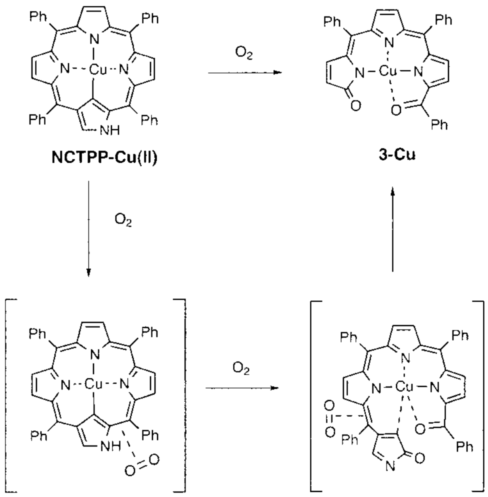
Scheme 2



5'-Cu **4** **5-Cu**

Py: 2-pyridyl

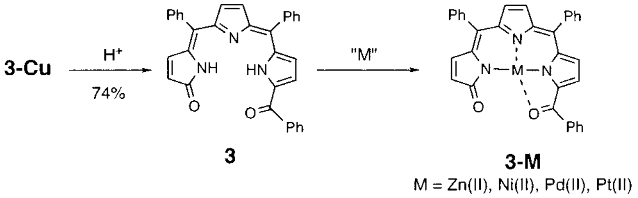
Scheme 3



NCTPP-Cu(II) **3-Cu**

The free-base ligand **3** was obtained in 74% yield by treatment of **3-Cu** with concentrated H_2SO_4 in TFA solution (Scheme 4). The ^{1}H NMR signals at 12.05 and 10.09 ppm, which were ascribable to the two inner NH, showed intramolecular hydrogen bonding in the core.[26] The absorption bands of **3** observed at 355.0 and 537.5 nm were broad and blue-shifted compared to those of **3-Cu**, where the absorption bands were seen at 320.0, 352.0, 410.0, 621.0, and 673.0 nm (Figure 3).

Scheme 4



3 **3-M**

M = Zn(II), Ni(II), Pd(II), Pt(II)

The capability of the metal coordination of **3** was investigated using other metals such as Zn(II), Ni(II), Pd(II), Pt(II), and Co(II). The corresponding metal complexes (**3-Zn**, **3-Ni**, **3-Pd**, **3-Pt**, **3-Co**) were obtained as the major products from the reaction of **3** and $Zn(OAc)_2{\cdot}2H_2O$, $Ni(acac)_2$, $Pd(OAc)_2$, $PtCl_2$, and $Co(OAc)_2{\cdot}4H_2O$, respectively. In the absorption spectra, the Q-like bands of all of the metal complexes were red-shifted compared to that of **3**. Among the metal complexes, on the other hand, Q-like bands of Zn

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[22] Pyridine derivative **4** was synthesized by a mixed aldehyde method using 2-pyridinecarboxaldehyde and benzaldehyde (1:3) and methanesulfonic acid in CH_2Cl_2. The position of the *meso*-pyridine was determined by the ROESY spectrum. Furuta, H.; Ishizuka, T.; Osuka A.; Uwatoko, Y.; Ishikawa, Y. *Angew. Chem., Int. Ed.* **2001**, *40*, 2323.

[23] ^{1}H NMR spectrum was obtained after changing to the Ni(II) complex.

[24] [2 + 2] cycloaddition mechanism was suggested in the ring opening by photo-oxidation of bacteriochlorophyll derivatives. Brown, S. B.; Smith, K. M.; Bisset, G. M. F.; Troxler, R. F. *J. Biolog. Chem.* **1980**, *255*, 8063.

[25] The low oxidation potential value of 390 mV for the Cu(III)/Cu(II) couple of NCTPP−Cu(II) was reported. See ref 14a.

[26] The relative energy of inner core tautomers of **3** was estimated by DFT calculation (B3LYP/6-31G** level). The tautomeric form of **3** in Scheme 4 is the most stable by 7.78−22.15 kcal/mol compared to the other tautomers. See Supporting Information.

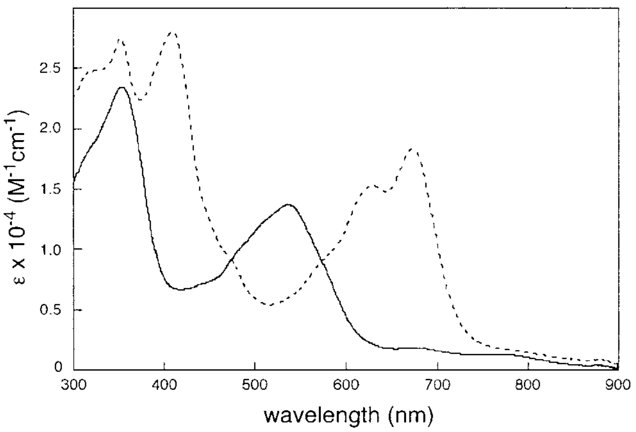

Figure 3. UV−vis absorption spectra of **3** (solid line) and **3-Cu** (broken line) in $CHCl_3$.

and Co complexes were broad and appeared at 20−30 nm shorter wavelengths than those of group 10 metals, Ni(II), Pd(II), and Pt(II). Interestingly, the absorption bands of **3-Pd** at 626.5 and 685.0 nm were sharp and blue-shifted compared to the corresponding bands of **3-Ni** (642.5 and 698.0 nm) and **3-Pt** (636.5 and 691 nm). The absorption profiles did not change in the wide range of the concentration for each metal complex, which may preclude the possibility of the dimer formation. As the trend is matched with the ionic size of metals, the largest Pd(II) cation may fit into the ligand core, but the smaller Ni(II) and Pt(II) cations may make the ligand distort slightly to yield the broad and red-shifted absorption bands of the complexes (Figure 4).[27]

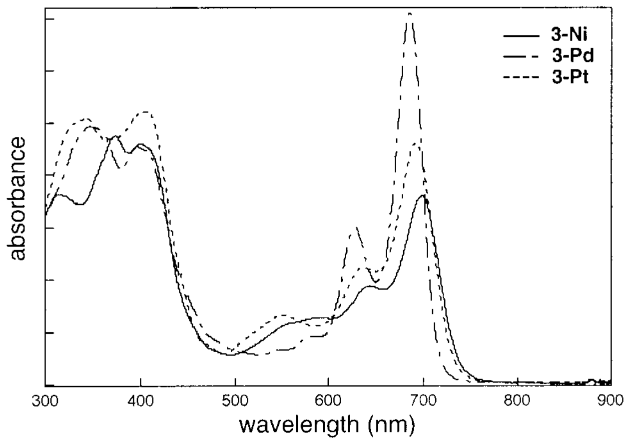

Figure 4. UV−vis absorption spectra of **3-Ni** (—), **3-Pd** (− • −), and **3-Pt** (- - -) in $CHCl_3$.

In conclusion, the first conjugated aryl-substituted tripyrrinone derivative **3** was synthesized by Cu(II)-mediated oxygenolysis of NCTPP. The conjugated tripyrrinone **3** could serve as a coordination ligand for various metals. Owing to the flexible and less crowded metal binding site, such metal complexes would be interesting for the use as catalysts and metal carriers.[28] Detailed study including the mechanism is currently under way.

Supporting Information Available: Synthetic procedures and spectral data of free base **3** and the metal complexes, DFT calculations on the tautomers of **3**, and data for the X-ray structure analysis of **3-Cu**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[27] The ionic radii of group 10 metals were reported as follows: Ni(II) 0.63 Å, Pd(II) 0.78 Å, and Pt(II) 0.74 Å. Cotton, F. A.; Wilkinson, G.; Nurillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999; p 1304.

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