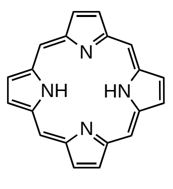
Metal Complexes of an N-Confused Calix[4]phyrin Derivative—The First X-ray Structure of an Organometallic Compound of Divalent Copper

Hiroyuki Furuta,* Tomoya Ishizuka, Atsuhiro Osuka,*
Yoshiya Uwatoko, and Yuichi Ishikawa*

The preparation and properties of new porphyrin analogues have recently received a great deal of attention in the literature.[1] Among them, the so called N-confused porphyrins (NCPs), in which α-α' (normal) and α-β' (confused) linkages of pyrrole rings exist in the porphyrin framework, have shown unique coordination chemistry.[2, 3] In particular, as a consequence of the inward-pointing carbon atom in the core, NCPs can complex with metal ions through formation of a metal–carbon bond to afford organometallic compounds. Thus, it is of interest to prepare a variety of confused analogues to examine the scope and limitation, if any, of coordination in confused systems. The two important questions are: Is the π-conjugated system necessary to stabilize the organometallic compounds? Are the properties of the organometallic compounds maintained with the nonconjugated macrocycles? To answer these questions we have chosen calix[4]phyrin, an intermediate between calix[4]pyrrole and porphyrin, as a confused target, because the conjugation is disconnected only at an sp^3 *meso* carbon atom while the structural rigidity seems relatively preserved.[4, 5] Herein we report the synthesis and X-ray structures of Ni^{II} and Cu^{II} complexes of N-confused calix[4]phyrin. Both Cu^{I} and Cu^{III} complexes are known in organocopper chemistry, but a stable Cu^{II} complex is seldom reported.[6] To the best of our knowledge complex **3** is the first example of an organocopper(II) complex to be characterized by X-ray crystallography.[7]

The title compound was prepared by a modified NCP synthesis,[8] namely, a methanesulfonic acid catalyzed cyclization of a mixture of pyrrole, *p*-tolualdehyde, and acetone (4:3:1), followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). This synthesis afforded N-confused tetratolylporphyrin (NCTTP: 19%) and N-confused calix[4]phyrin **1** containing an sp^3 *meso* carbon atom and an amide group in the confused pyrrole ring in a yield of approximately 3%.[9] Interestingly, the acetone moiety was introduced as a *gem*-dimethyl unit selectively between the α- and β'-position of the pyrrolic rings; the formation of other confused isomers of **1** was not observed. As the reactivity of acetone is lower than *p*-tolualdehyde, it is highly probable that the ring confusion occurs at the final step of the cyclization. The Ni and Cu complexes were synthesized in a refluxing solution of **1** in $CHCl_3$ in the presence of $NiCl_2$ and $Cu(OAc)_2$, respectively (Scheme 1). The optical absorption spectra of free ligand **1** and the metal complexes (Ni: **2** and Cu: **3**) are shown in Figure 1.[10]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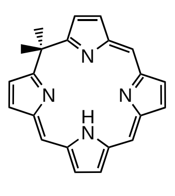
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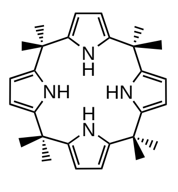
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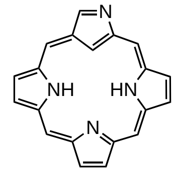
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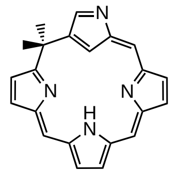
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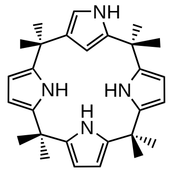
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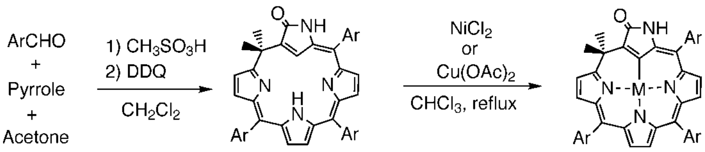

1: (Ar = *p*-tolyl, 3 %)

2: (M = Ni^{II}, 55 %)
3: (M = Cu^{II}, 93 %)

Scheme 1. Synthesis of N-confused calix[4]phyrin **1** and the metal complexes **2** and **3**.

Explicit evidence for the existence of metal–carbon bonds in the complexes was obtained from single-crystal X-ray analyses (Figure 2).[11] The Ni atom of **2** was located in the middle of the core and the molecule showed a ruffled structure: the pyrrole rings were tilted 20.55, 11.37, 14.63, and 0.00°, and the mean deviation was 0.2981 Å to the mean plane consisting of 25 atoms (including the Ni atom). The Ni(1)–C(2) bond length is 1.905(4) Å, which is slightly shorter than that in Ni^{II}-NCTTP (1.963(3) Å).[2a] The Cu complex **3**, however, showed a more planar structure: the tilting angles of the pyrrole rings were 6.69, 4.25, 2.91, and 4.70° and the mean deviation from the plane was 0.1028 Å. The Cu(1)–C(2) bond length (2.007(4) Å) was intermediate between that of the Cu^{I}–C bond (2.014 Å) of $[Cu(CN)_4]^{3-}$[12] and that of the Cu^{III}–C bond (1.93–4 Å) in the doubly N-confused porphyrin.[3c] Both the Ni and Cu complexes formed dimeric structures through hydrogen bonding between the peripheral amide groups.[13]

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[*] Prof. H. Furuta[+], T. Ishizuka, Prof. A. Osuka
Department of Chemistry
Graduate School of Science
Kyoto University, Kyoto 606-8502 (Japan)
Fax: (+81) 75-753-3970
E-mail: hfuruta@kuchem.kyoto-u.ac.jp
osuka@kuchem.kyoto-u.ac.jp

Dr. Y. Uwatoko
Faculty of Science
Saitama University, Saitama 338-8570 (Japan)

Prof. Y. Ishikawa
Department of Applied Chemistry
Faculty of Engineering, Oita University
Oita 870-1192 (Japan)
Fax: (+81) 97-554-7907
E-mail: ishichem@cc.oita-u.ac.jp

[+] PRESTO, Japan Science and Technology Corporation (JST) (Japan)

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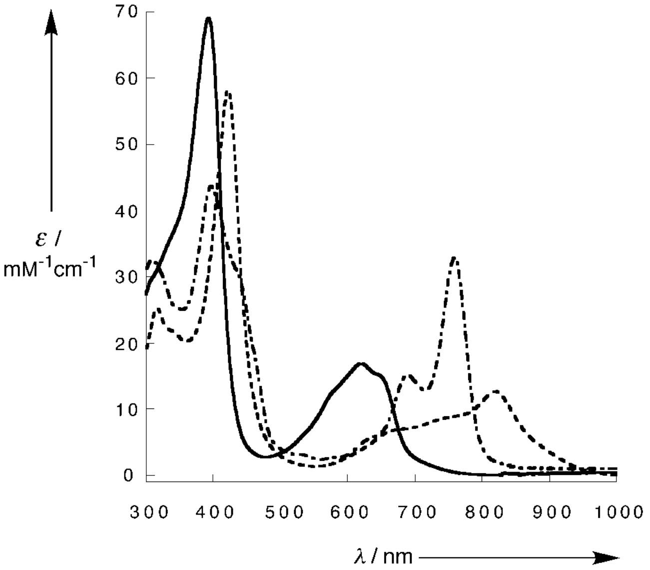

Figure 1. Absorption spectra of N-confused calix[4]phyrin **1** (——), the Ni^{II} complex **2** (– – –), and the Cu^{II} complex **3** (– • –) in CH_2Cl_2.

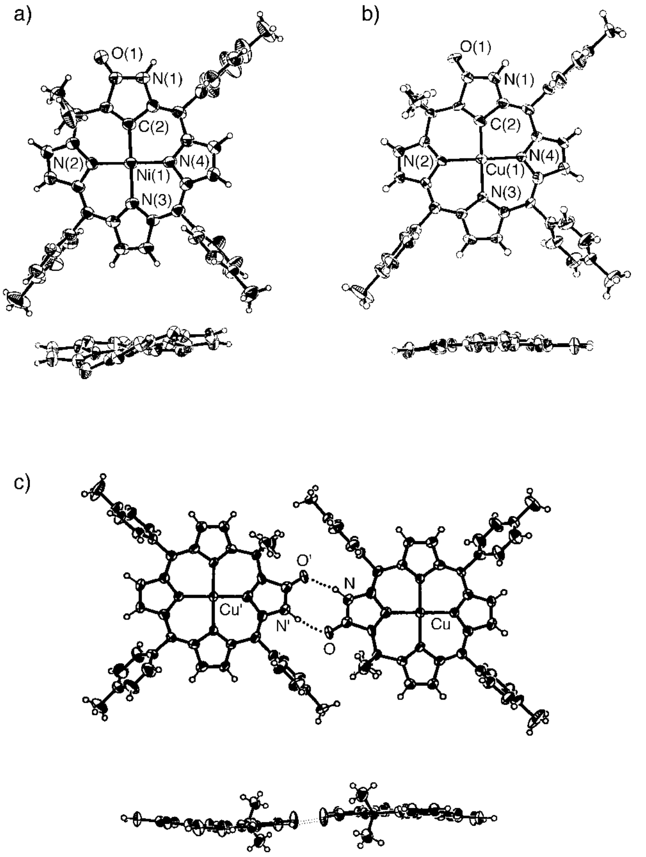

Figure 2. ORTEP structures of a) Ni complex **2**, b) Cu complex **3**, and c) the dimeric structure of **3**. The *meso*-tolyl groups are omitted for clarity in the side views. Selective bond lengths [Å]: a) Ni(1)-C(2) 1.905(4), Ni(1)-N(2) 1.956(3), Ni(1)-N(3) 1.967(3), Ni(1)-N(4) 1.935(3); b) Cu(1)-C(2) 2.007(4), Cu(1)-N(2) 2.076(4), Cu(1)-N(3) 2.010(3), Cu(1)-N(4) 2.056(4); c) N-O′ 2.949.

The ^1H NMR spectrum of the Ni complex **2** displayed distinct signals in the normal diamagnetic region, which indicates a square-planar $Ni^{II}(d^8)$ coordination geometry. On the other hand, a $CDCl_3$ solution of Cu complex **3** showed broad ^1H NMR signals, which suggests the presence of the paramagnetic Cu^{II} ion. We have carried out magnetic susceptibility measurements for the powder sample of **3** by using a SQUID to estimate the percentage of Cu ions present in the paramagnetic d^9 form. The effective magnetic moments (μ_{eff}) at 300 K and 77 K were calculated to be 1.75 and 1.67 μ_B, respectively, which indicates that all the Cu ions exist in the $S = 1/2$ state, namely, in the divalent d^9 form. In addition, the nearest organometallic Cu^{II} ions, separated by 9.005 Å in the single crystal of **3**, were only slightly magnetically coupled, as evidenced by the susceptibility obeying the Curie law.[14]

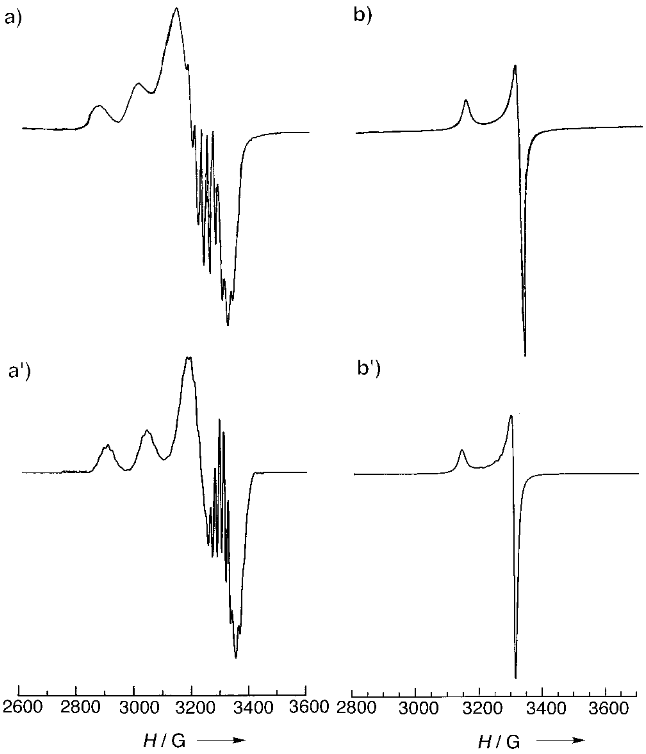

Figure 3. Observed (top) and simulated (bottom) ESR spectra of the Cu complex **3** as a powder at 298 K (a, a′) and in DMF at 77 K (b, b′). a),a′) $g_x = g_y = 2.031$, $g_z = 2.139$, $LW_x = LW_y = 9.5$, $LW_z = 15\times10^{-4}\,cm^{-1}$ (LW = line width), line shape: Lorenzian, frequency, 9405 MHz, mod. $6.3\times10^{-4}\,cm^{-1}$, 5 mW; b),b′) $g_x = 2.01$, $g_y = 2.06$, $g_z = 2.13$, $A_x^{Cu} = 14$, $A_y^{Cu} = 17$, $A_z^{Cu} = 135$, $A_x^N = A_y^N = A_z^N = 10$, $LW_x = 7.5$, $LW_y = 13$, $LW_z = 12.5\times10^{-4}\,cm^{-1}$, 9190 MHz, mod. $12.5\times10^{-4}\,cm^{-1}$, 3 mW.

Although the crystal of **3** shows a planar structure, the sp^3 *meso* carbon atom present in the skeleton seems to us to be a potential trigger for the loss of planarity, especially in solution. Figure 3 compares the ESR spectra of a powder sample and a DMF solution of **3**. The ESR spectrum of the powder consists only of $g_x = g_y = 2.031$ and $g_z = 2.139$ peaks, which are indicative of the square-planar geometry in accordance with the X-ray structure. The rhombic structure ($g_x \neq g_y \neq g_z$) must be taken into account, however, to simulate the observed solution spectrum. The ESR parameters determined are $g_x = 2.01$, $g_y = 2.06$, $g_z = 2.13$ and $A_z^{Cu} = 135(\times10^{-4}\,cm^{-1})$, which suggests a distortion from the square-planar form (Figure 3).[15] A hydrogen-bonding interaction with the DMF molecule through the peripheral amide moiety may also induce the conformational change; the ESR spectra of **3** in toluene showed the superposition of both planar and distorted signals. This conformationally greater flexibility than present in the ordinary porphyrin could provide additional advantages for the molecular design of metal complexes.

The oxidative potential values ($E_{1/2}$) for the Ni^{II}/Ni^{III} and Cu^{II}/Cu^{III} couples of **2** and **3** in CH_2Cl_2 were determined by cyclic voltammetry as +398 and +160 mV (versus the ferrocene/ferrocenium couple (Fc/Fc^+)), respectively. The reductive potentials, however, could not be clearly measured as a consequence of the irreversible reduction of the ligand itself. The observed $E_{1/2}$ values were more anodic-shifted than those of N-confused tetraphenylporphyrin complexes,[2b,c] thus reflecting the poorer electron-donating nature of **1**. This feature might be the cause of the remarkable stability of the Cu^{II} complex **3**.[16]

In conclusion, we have shown here that the N-confused calix[4]phyrin **1** could serve as a carbon ligand to stabilize rare organometallic complexes, such as a Cu^{II} complex. Complete π conjugation was not a prerequisite for the formation of the metal–carbon bond. The facile synthesis of the ligands and the large structural flexibility of the metal complexes would make this type of ligand attractive for the wide study of organometallic reagents.

Experimental Section

1: *p*-Tolualdehyde (691.0 mg, 5.75 mmol), pyrrole (525.1 mg, 7.83 mmol), and acetone (110.3 mg, 1.90 mmol) were dissolved in CH_2Cl_2 (750 mL). Methanesulfonic acid (0.35 mL, 5.4 mmol) was then added and the reaction mixture stirred for 30 min at room temperature. After the addition of DDQ (1.48 g, 6.52 mmol), the solvent was removed and the residues were separated by column chromatography on alumina and, subsequently, on silica gel using CH_2Cl_2/MeOH as the eluent. The blue-colored fraction was evaporated and the residue was recrystallized from CH_2Cl_2/MeOH to give **1** as a violet powder; 41.2 mg (3.4 %).

2: A solution (1 mL) of $NiCl_2 \cdot 6H_2O$ (15.4 mg, 0.0648 mmol) in MeOH was added to a solution of **1** (17.8 mg, 0.0285 mmol) in $CHCl_3$ (25 mL). After refluxing the mixture for 1 h, the solvent was removed and the residue was separated by column chromatography on silica gel with CH_2Cl_2 as the eluent. The first eluted, green-colored fraction was evaporated and the residue was recrystallized from CH_2Cl_2/MeOH to afford **2** as greenish crystals; 10.7 mg (55 %).

3: The Cu complex was obtained by a similar procedure as above but using **1** (20.4 mg, 0.0327 mmol) and $Cu(OAc)_2$ (6.87 mg, 0.0378 mmol). Complex **3** was isolated as greenish crystals; 20.9 mg (93 %).

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[7] The spectroscopic and electrochemical studies of Cu^{II} complexes of N-confused porphyrin derivatives have been reported recently, see ref. [2c].

[8] G. R. Geier III, D. M. Haynes, J. S. Lindsey, *Org. Lett.* **1999**, *1*, 1455–1458.

[9] The formal nomenclature of **1** is 5,5-dimethyl-3-oxo-10,15,20-tris-*p*-tolyl-2-aza-21-carbaporphyrin.

[10] The spectral data of **1**–**3** and the NMR spectra of **1** and **2** are given in the Supporting Information.

[11] Crystal data for **2**: $C_{43}H_{34}N_4ONi \cdot 0.5\,C_7H_8 \cdot CH_2Cl_2$, $M_r = 814.49$, monoclinic, space group *C2/c* (no. 15), $a = 24.617(3)$, $b = 19.584(2)$, $c = 18.278(2)$ Å, $\beta = 113.475(2)°$, $V = 8083(1)$ Å^3, $\rho_{calcd} = 1.339$ g cm^{-3}, $Z = 8$, $R = 0.101$, $wR = 0.106$, GOF = 10.04. Crystal data for **3**: $C_{43}H_{34}N_4OCu \cdot H_2O$, $M_r = 704.33$, monoclinic, space group $P2_1/a$ (no. 14), $a = 14.763(2)$, $b = 10.368(1)$, $c = 24.206(2)$ Å, $\beta = 102.790(3)°$, V = 3613.0(6) Å^3, $\rho_{calcd} = 1.295$ g cm^{-3}, $Z = 4$, $R = 0.061$, $wR = 0.040$, GOF = 2.470. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-155130 (**2**) and -155131 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[13] The dimerization constant K_d for **1** was determined from ^1H NMR measurements in $CDCl_3$ at 25 °C as 14 M^{-1}.

[14] The temperature dependence of the magnetic moment and the crystal packing diagram of **3** are shown in the Supporting Information.

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[16] The introduction of an electron-withdrawing group at the outer α-position of the confused pyrrole ring in the Cu^{II}-NCTTP complex raised the $E_{1/2}$ value to 120 mV (versus Fc/Fc^+) and, consequently, made the complex stable enough for column chromatography on silica gel. (Y. Ishikawa, H. Dejima, H. Furuta, unpublished results.)