Anion Binding Properties of *N*-Confused Porphyrins at the Peripheral Nitrogen

HIROMITSU MAEDA[1,2], ATSUHIRO OSUKA[2] and HIROYUKI FURUTA[1*]
[1]*Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 812-8581, Japan;* [2]*Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan.*

Abstract

Ni(II), Pd(II), and Cu(II) complexes of *N*-confused porphyrin (NCP) exhibit anion binding properties through a hydrogen bonding interaction at the peripheral NH of confused pyrrole ring. The binding constants of the tetrakis(pentafluorophenyl)-NCP metal complexes (**1-M**, **M** = Ni, Pd, Cu) for various halide anions in CH_2Cl_2 increase in the order of $F^- > Cl^- > Br^- > I^-$, respectively. Zwitterionic resonance form of the NCP complexes as well as interactions between halide anions and a pentafluorophenyl group are suggested to be important for efficient anion binding.

Introduction

Among various kinds of porphyrin analogs [1], *N*-confused porphyrin (NCP) is unique in that it has a *confused* (i.e., α–β'-linked) pyrrole ring, and thus possesses a reactive inner carbon and a peripheral nitrogen [2–4]. This outward-pointing nitrogen can serve as an important scaffold in supramolecular chemistry. For example, metal-bridged dimers are formed with divalent metals such as Zn(II), Pd(II), and Pt(II) (Figure l) [5–7]. It also binds neutral molecules such as dimethylformamide (DMF) by a hydrogen bonding interaction both in the solid state and in solution (Figure 2(a)) [8]. Like calix [4] pyrrole [9], anions can be associated with NCP at this outer NH in the solid state [10]. Moreover, the free base and the metal complexes of a doubly *N*-confused isomer (*cis*-N₂CP) that contains two neighboring confused pyrroles in the core, have shown the zigzag 1-D chains through the intermolecular hydrogen bonding interactions between N—H···N at the periphery in the solid states (Figure 2(b)) [11]. On the other hand, the Cu(III) complex of *trans*-N₂CP, whose confused pyrrole rings exist at the opposite sites, forms 1-D rod-like supramolecular network in the solid state [12]. Herein, we report the anion binding properties of *N*-confused porphyrin in solution. The zwitterionic resonance forms of the divalent metal NCP complexes and anion–π interactions are emphasized.

Affinity of Ni(II), Pd(II), and Cu(II) complexes of NCP to anions

Square-planar divalent metal complexes of NCP have a peripheral NH, which can serve as an anion binding site through hydrogen bonding interaction (Scheme 1) [10]. In fact, the divalent metal complexes of tetrakis(pentafluorophenyl)-NCP (C_6F_5-NCP, **1**) including Ni(II), Pd(II), and Cu(II) [13] exhibit high affinities to anions such as fluoride and chloride. In contrast, corresponding trivalent metal complexes such as Cu(III) [14] and Ag(III) [13] did not show any anion binding interactions due to the absence of hydrogen on the peripheral nitrogen. To evaluate the association constants (K_a) of metal complex of **1**, the titration experiments were performed using absorption spectral changes upon addition of halide anions as tetrabutylammonium salts (TBAX, X = F^-, Cl^-, Br^-, and I^-) in CH_2Cl_2. The spectroscopic grade solvent was used without further purification. The absorption spectra changed with isosbestic points (Figure 3), thus, the K_a values were estimated by fitting the titration plots to the nonlinear curves for 1:1 binding. The K_a values for each anion with different metal complexes were summarized in Table 1. The magnitudes of the K_a values of divalent metal complexes of **1** (**1-M**) for respective anions in CH_2Cl_2 are nearly equal and increase in the order of $F^- > Cl^- > Br^- > I^-$ in each complex.

The K_a values of the divalent complexes (**1-M**) with F^- in CH_2Cl_2 are too high to estimate accurately by this method ($>3 \times 10^5$ M^{-1}). The affinities for Cl^- show almost the same values (ca. 5×10^4 M^{-1}) in each complex and K_a values for Br^- and I^- are ca. 1×10^4
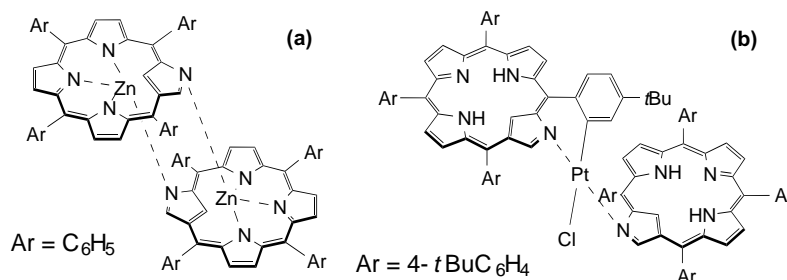
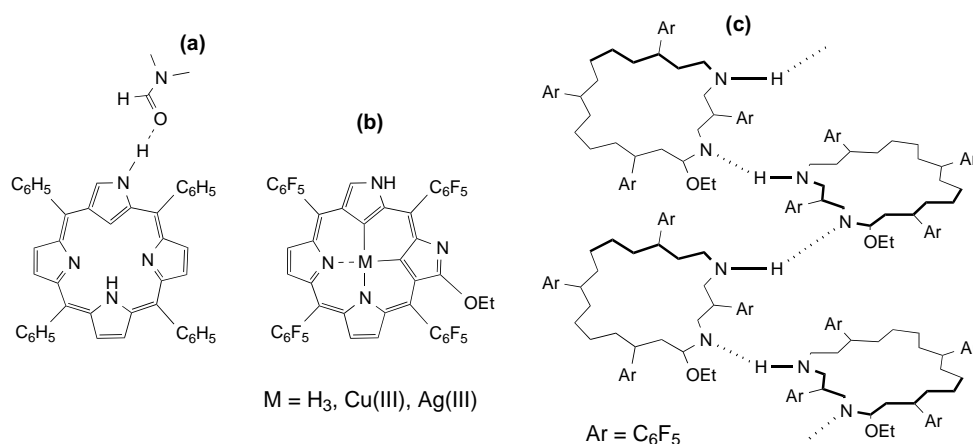*Figure 1.* Examples of metal-bridged NCP dimmers, (a) Zn(II) complex and (b) Pt(II) complex.
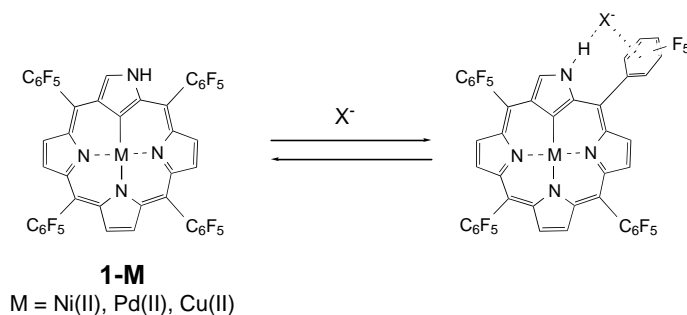

Figure 2. (a) Binding of *N*-confused tetraphenylporphyrin (NCTPP) with DMF and (b) schematic drawings of hydrogen bonding self-assembly of doubly *N*-confused porphyrins (*cis*-N_2CP).

1-M
M = Ni(II), Pd(II), Cu(II)

Scheme 1. Anion binding of divalent metal complexes of C_6F_5-substituted *N*-confused porphyrin (**1-M**).

and 1×10^3 M^{-1}, respectively. The small differences among the metal complexes may be attributed to the total charge included in the core cation which affects the acidity of outer NH through the confused pyrrole. Supporting the hydrogen bonding interaction with anions, the outer NH signal of diamagnetic Ni(II) complex (**1-Ni**, 2.0×10^{-3} M) in CDCl$_3$ shifted from 10.05 to 14.65 ppm and the doublet signal of the peripheral α-CH at 8.45 ppm *(J = 3.3 Hz)* changed into singlet at 8.80 ppm upon addition of 1 equiv of TBACl (Figure 4). The 1:1 stoichiometry was also supported by the continuous variation method where the binding saturation was observed at almost 1 equiv of anion.

Association constants of tetraphenyl-substituted NCP (NCTPP, **2**) [2] with Cl$^-$ are extremely small (<10 M^{-1}) in Ni(II) [3] and Pd(II) [5] complexes (**2-M**), respectively, compared with C_6F_5-derivatives (**1-M**). Binding constants of the **2-M** with F$^-$ in CH$_2$Cl$_2$ are rather high as seen in **1-M** (>3 $\times 10^5$ M^{-1}). Partially, the anion-binding ability of divalent metal complexes (**1**, **2**) is ascribable to the zwitterionic resonance form [15], whose contribution to the aromatic feature is supported by ^{1}H NMR in spite of the disruption of 18π full conjugation at the confused pyrrole ring in the neutral form (Scheme 2) [3, 5, 13]. Moreover, higher K_a values of C_6F_5-substituted NCP (**1**) than phenyl derivative (**2**) are ascribable not only to the enhancement of
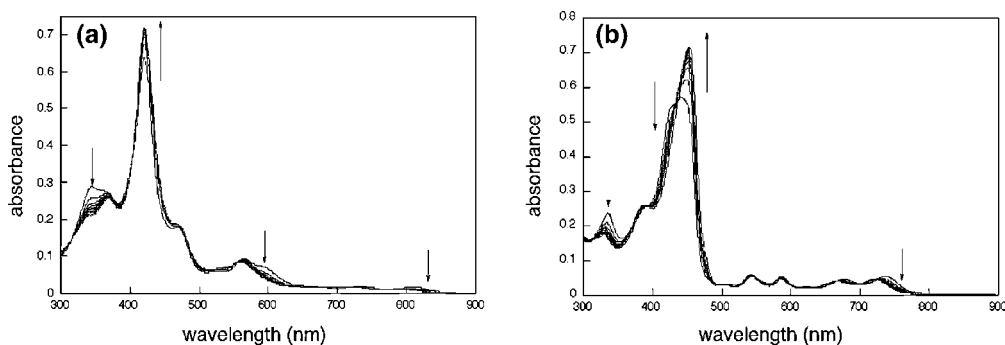
Figure 3. Examples of absorption spectral changes of (a) Ni(II) complex (**1-Ni**) (6.6×10^{-6} M) and (b) Cu(II) complex (**1-Cu**) (6.2×10^{-6} M) and Cl$^-$ used as a tetrabutylammonium salt inCH$_2$Cl$_2$.

Table 1. Association constants K_a (M^{-1}) for anion binding by Ni(II), Pd(II), and Cu(II) complexes of pentafluorophenyl-substituted NCP (**1-M**) as determined by the absorption spectral changes upon addition of tetrabutylammonium salts in CH$_2$Cl$_2$[a]

	1-Ni	**1-Pd**	**1-Cu**
Cl$^-$	$5.7(\pm 0.4) \times 10^4$	$4.6(\pm 0.7) \times 10^4$	$4.9(\pm 0.4) \times 10^4$ [b]
Br$^-$	$8.4(\pm 0.4) \times 10^3$	$1.4(\pm 0.1) \times 10^4$	$6.9(\pm 0.2) \times 10^3$ [b]
I$^-$	$1.2(\pm 0.02) \times 10^3$	$300(\pm 20)$	$1.2(\pm 0.06) \times 10^3$
ClO$_4^-$	–	–	$3.6(\pm 0.06) \times 10^6$ [b]
PF$_6^-$	–	–	50 ± 7 [b]
Ph$_4$B$^-$	–	–	ND[c]

[a] In the case of fluoride binding of all of the complexes (**1-M**), the affinity is too large to determine the accurate binding constants; [b] See also ref[14]; [c] Not determined due to the low affinity.
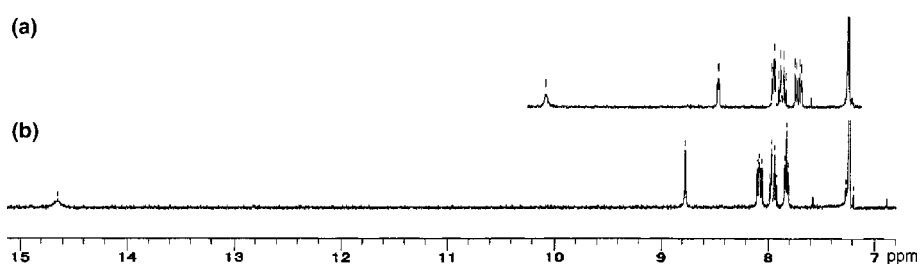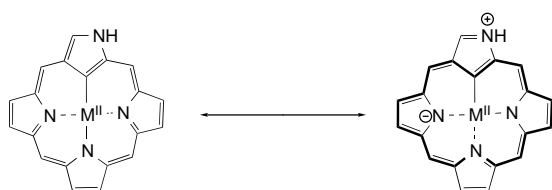

Figure 4. ^{1}H NMR spectra of Ni(II) complex (**1-Ni**, 2.0×10^{-3} M) (a) without anion and (b) with 1 equiv of tetrabutylammonium chloride in CDCl$_3$.


Scheme 2. Resonance forms of divalent metal complex of NCR [18]. Annulenic pathway is indicated in bold.

acidity of the outer NH due to the electron-withdrawing effects but also to the additional anion-π interaction [16].

The interaction of neighboring C$_6$F$_5$ group with anions was suggested by the change of ^{19}F NMR signals of Ni(II) complex (**1-Ni**) upon addition of anions TBAF and TBACl in CDCl$_3$. The ^{19}F NMR signals at -136.80, -150.92, and -160.75 ppm that were assigned to the *ortho*-, *para*-, and *meta*-F of C$_6$F$_5$ substituents

neighboring to the peripheral NH, respectively, shifted to a higher field upon addition of anions. For examples, the corresponding signals were observed at -138.55 (-139.53), -153.8 (-156.60), and -162.6 (-164.56) ppm, respectively, in the presence of Cl$^-$ (and F$^-$). In both cases, the remaining C$_6$F$_5$ signals do not show significant changes. These results indicate that the anions associated at the peripheral NH influences the resonance of *one* of C$_6$F$_5$ substituents nearby due to the shielding effect by the negative charge. At this moment, distinct ^{19}F–^{19}F couplings between F$^-$ anion and C$_6$F$_5$ group, which could be considered as a direct evidence of anion–π interaction [16], is not obtained due to the precipitation of the complex during the measurements. In contrast with the halide anions, the stoichiometry of complexation with oxoanions such as dihydrogenphosphate (H$_2$PO$_4^-$) was complicated and we could not explicitly determine the value neither from the Job plots and continuous variation methods.
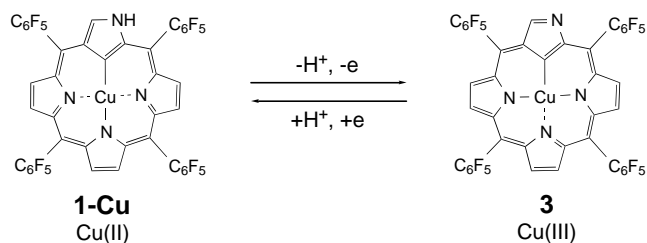
Scheme 3. Interconversion between Cu(II) complex (**1-Cu**) and Cu(III) complex (**3**) by detachment and attachment of the peripheral NH.

Cu(II) and Cu(III) states of *N*-confused porphyrin modulated by anion binding at the peripheral nitrogen

Recently, we have reported the interconversion between Cu(II) complex (**1-Cu**) and Cu(III) complex (**3**) of C_6F_5-substituted NCP (**1**) by the oxidative removal and reductive attachment of hydrogen on the outer nitrogen (Scheme 3) [14]. As shown in Table 1, the Cu(II) complex (**1-Cu**) shows affinity toward various kinds of anions as well as ClO_4^-, even PF_6^-. The Cu(II) complex of outer *N*-methyl-substituted derivative [17], wherein there is no anion binding site at the periphery, does not show spectral changes upon addition of the excess amount of Cl^- (> 5000 equiv). Also, there is no significant change of the ESR spectrum after the addition of chloride salt, which excludes the possibility of axial coordination of halide anions to the center metal under the conditions described in this reports. When measuring the electrochemical redox potentials of Cu(II) species (1 mM) in CH_2Cl_2 by using TBAX (0.1 M) as electrolytes including chloride, ClO_4^-, and PF_6^-, the redox couple for Cu(III)/Cu(II) in differential pulse voltammetry (DPV) shifted according to the anions used. Cl^- affords negative-shifted potential (0.03 V versus Fc^+/Fc) compared to ClO_4^- (0.14 V) and PF_6^- (0.15 V), which suggests anions with higher affinity to the peripheral NH increases the electron density at the core metal *via* the confused pyrrole from the periphery, to facilitate the removal of an electron from Cu(II) center [18]. As the control of metal oxidation states by outer stimuli seems attractive for a variety of applications including molecular switches [19] and anion sensors [18, 20], we think the present NCP complex system is promising for such use.

Acknowledgement

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