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## Copper(II) and nickel(II) hexafluorophosphate complexes derived from a monoanionic porphyrin analogue: Solvato- and thermochromism of the Ni complexes by spin-interconversion<sup>†</sup>

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Phenanporphodimethene (1) is a porphyrin analogue which has a dipyrromethene unit replaced by a 1,10-phenanthroline moiety. This modification effectively coverts a dianionic porphyrin to a monoanionic porphyrin analogue with a porphyrin-like N4 coordination sphere. The ligand 1 forms copper and nickel hexafluorophosphate complexes, **Cu-1** and **Ni-1**, respectively. X-ray crystallographic analysis of **Cu-1** indicates that the Cu(II) complex is tetracoordinated by two pyrrolic nitrogen atoms and two phenanthrolic nitrogen atoms and includes a non-bonding PF<sub>6</sub> counter-anion. The **Ni-1** complex has similar geometry with a tetracoordinate square-planar structure in non-coordinating solvents such as CHCl<sub>3</sub>. In coordinating solvents such as MeOH, the coordination structure adopts an octahedral geometry. These results indicate that **Ni-1** can be converted from a low-spin to high-spin configuration by the coordination of two solvent molecules to the nickel center. This solvatochromic conversion of **Ni-1** is accompanied by thermochromic behavior resulting from the transformation between square planar and octahedral configurations in THF solution. The redox peak responsible for the nickel-centered redox reaction of **Ni-1** is observed at -0.66 V (*vs.* Fc/Fc<sup>+</sup>) in CH<sub>2</sub>Cl<sub>2</sub> solution, which indicates generation of low valent Ni(1) species. Thus, **Ni-1** may be useful for future investigations as a novel structural model of the active site of cofactor  $F_{430}$  in methyl-coenzyme M reductase.

#### Introduction

Chemical modifications of the porphyrin skeleton involving the replacement of a pyrrole unit with other aromatic rings have revealed unusual and interesting physical properties relating to aromatic characteristics, redox potentials, magnetic features and metal-binding behavior.<sup>1</sup> Several porphyrin-related macrocycles have been synthesized which contain pyridine,<sup>2</sup> benzene,<sup>3</sup> phenol (oxybenzi),<sup>4</sup> and other moieties<sup>5</sup> in place of a pyrrole subunit of the porphyrin macrocycle in order to investigate the diverse electronic features of the natural porphyrin ring. In this work, we investigate the relationships between the ligand charge state of porphyrin analogues and the physico-chemical characteristics of the corresponding metal complexes. It is known that the charge state of the coordination core of porphyrin-like macrocycles can produce greater variances in complexation of transition metal cations and redox properties thereof. Whereas natural porphyrins are dianionic, corrole is a trianionic tetrapyrrole macrocycle which has the ability to stabilize high-oxidation states of transition metal ions, such as Mn and Cu for example, which may be employed as oxidation catalysts.<sup>6</sup> Other heteroporphyrins<sup>7</sup> with partially modified cores designated N3X (where X = O, S, Se, Te) and N-alkylated (arylated) porphyrins<sup>8</sup> represent well known monoanionic porphyrinoids. These N-substituted porphyrins show

a tendency to stabilize lower oxidation states of the coordinated metal ions.<sup>9</sup>

Examples of skeleton-modified N4-donor porphyrinoid ligands with pyrrole moieties replaced by different nitrogen donor units such as pyridine<sup>2</sup> are relatively rare and the properties of their metal ion complexes and redox potentials have not yet been well characterized. Metal complexes with monoanionic tetradentate ligands<sup>10</sup> exhibit fascinating properties which have led us to undertake the synthesis and investigation of new metal complexes with monoanionic porphyrin-like ligands constructed by the pyrrole replacement strategy.

Recently, we have successfully synthesized phenanporphodimethene (1) as a novel monoanionic porphyrin analogue which has a dipyrromethene unit replaced by a 1,10-phenathroline moiety.<sup>11</sup> 1,10-phenanthroline is a remarkable heteroaromatic compound which has the ability to form stable complexes with a variety of metal ions. It has been widely employed as a bidentate ligand unit in applications such as catalysis,12 as a therapeutic agent for Alzheimer's disease,<sup>13</sup> as a component of solar cells,<sup>14</sup> and as a component of enzyme model systems.<sup>15</sup> Furthermore, studies of the coordination chemistry of dipyrrins<sup>16</sup> (dipyrromethenes) have attracted interest with respect to development of luminescent compounds such as the boron difluoride dipyrrin complex (BODIPY).<sup>17</sup> Our porphyrin analogue (1) provides a square planar N4 donor environment by combining both heme (dipyrrin) and non-heme (1,10-phenanthroline) units in the macrocycle. This hybrid coordination platform is expected to provide uncommon coordination properties as a result of its small coordination sphere, and reduced charge (-1) relative to natural porphyrins. In the present study, we report the synthesis and characterization of novel

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Cu(II) (Cu-1) and Ni(II) (Ni-1) hexafluorophosphate complexes of 1, which have porphyrin-like N4 coordination in both Cu-1 and Ni-1. This modulation of the electronic characteristics of Ni-1 provides noteworthy low- and high-spin interconversion as solvatochromism in various solvents and thermochromic properties in THF solution. The structural and electrochemical features of Ni-1 indicate that it may be useful as a model of the nickel-dependent enzyme cofactor  $F_{430}$  of methyl coenzyme M-reductase.<sup>18</sup>

#### **Results and discussion**

#### Syntheses of Cu(II) and Ni(II) complexes

Ligand 1 was synthesized as described previously.<sup>11</sup> In the complexation reaction with metal ions, 1 produced Cu(II) and Ni(II) complexes upon reaction with the corresponding metal acetate salts  $[M^{II}(OAc)_2]$  (M = Cu, Ni) in a chloroform-methanol solution conducted with short refluxing in the presence of 2,6-lutidine as a base. The reddish orange reaction mixture converts to blue (Cu) and green (Ni) as the reaction proceeds. An additional anion is required to balance the charge of the metal dication, because the ligand acts as a monoanionic ligand coordinating through the porphyrin-like four nitrogen atom donors. The products were washed with NaPF<sub>6</sub> to exchange the counter anion of the complexes, and then purified by SiO<sub>2</sub> column chromatography to afford Cu-1 and Ni-1 as M(II) hexafluorophosphate complexes (M = Cu, Ni) in 81 and 63% yields, respectively (Scheme 1). The metal insertion was confirmed by HR-FAB mass spectra of Cu-1 and Ni-1, revealing  $[M]^+ m/z = 798.1780$  for Cu-1 and 793.1837 for Ni-1. The complexes were further characterized by elemental analysis.



Scheme 1 Synthesis of Cu-1 and Ni-1.

#### X-Ray structural and spectroscopic characterization of Cu-1

The molecular structure of **Cu-1** determined by X-ray crystallographic analysis is shown in Fig. 1, and crystal data are given in Table 1. The macrocycle framework of **Cu-1** has a gable-type non-planar structure with a dihedral angle of  $124^{\circ}$ between the 1,10-phenanthroline plane and the dipyrromethene plane. One methanol molecule provided by the recrystallization solvent occupies the axial position of the copper ion, which adopts a distorted square pyramidal geometry. The copper ion lies only 0.268 Å above the N4 mean plane. The relatively small displacement of the copper ion from the N4 plane is caused by tight binding of the copper ion which has a smaller ionic radius (0.73 Å). The Cu–N (phenanthroline) bond separations are 2.009 (2) and 2.031(2) Å and the Cu–N (pyrrole) bond separations are 1.931(2) and 1.942(2) Å. The latter values are in agreement with the corresponding Cu–N bond distances of a



Fig. 1 The molecular structure of Cu-1 with thermal ellipsoids at 50% probability level. (a) top view: Hydrogen atoms and solvents are omitted for clarity and (b) side view: Substituents at the *meso*-positions and the counter anion are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu–N(1) 2.009(2), Cu–N(2) 2.031(2), Cu–N(3) 1.931(2), Cu–N(4) 1.942(2), Cu–O(ax) 2.289(2), N(1)–Cu–N(2) 82.21(10), N(1)–Cu–N(3) 164.19(10), N(2)–Cu–N(3) 91.04(11), N(1)–Cu–N(4) 90.70(10), N(2)–Cu–N(4) 163.16(9), N(3)–M–N(4) 91.82(11), N(1)–Cu–O 94.04(11), N(2)–Cu–O 97.22(10), N(3)–Cu–O 101.01(10), N(4)–Cu–O 98.56(10).

(tetraphenylporphyrin) copper(II) complex (av. Cu–N; 1.981 Å)<sup>19</sup> and a (1,10-phenanthroline-methionine) copper(II) perchlorate MeOH adduct (Cu–N; 1.978–2.034 Å).<sup>20</sup> The average Cu–N<sub>3,4</sub> separation distances are significantly longer than the Cu–N<sub>1,2</sub> separation ones. This indicates that the copper ion lies in an asymmetric Cu–N coordination environment. Each of the N–Cu–N bond angles also reflects these features. In particular, the N<sub>1</sub>–Cu–N<sub>2</sub> bond angle is smaller than the corresponding N<sub>3</sub>–Cu–N<sub>4</sub> bond angle at the opposite position.

The absorption spectrum of **Cu-1** in CH<sub>2</sub>Cl<sub>2</sub> exhibits a porphyrin-like Q band at 590 nm (log  $\varepsilon = 4.43$ ) which can be assigned as a ligand  $\pi$ - $\pi^*$  transition (Fig. 2).<sup>21</sup> The band is significantly red-shifted and its intensity is enhanced relative to that of ligand **1**, which has a maximum absorbance at 489 nm (log  $\varepsilon = 4.28$ ). The zinc complex of the quinoidal porphyrin bearing *meso*-exocyclic double bonds has demonstrated the significant red-shift of the longer absorption band compared to the normal porphyrins due to the extension of  $\pi$ -conjugation through the *meso*-substituents and the inductive effect of these electronwithdrawing moieties.<sup>22</sup> Since their structures are different from those of our complexes, direct comparison between them is

#### Table 1 Crystallographic data for Cu-1

Compound	Cu-1·PF <sub>6</sub> ·2CH <sub>3</sub> OH				
Crystal Dimensions/mm	$0.57 \times 0.15 \times 0.11$				
Formula Weight	1009.37				
Formula	$C_{45}H_{43}O_{10}N_4F_6PCu$				
Color	Blue				
Crystal System	Triclinic				
Space Group	P -1				
Lattice Parameters:					
a/Å	12.227(5)				
b/Å	12.954(5)				
c/Å	15.455(7)				
$\alpha$ (°)	109.09(3)				
$\beta$ (°)	106.78(3)				
$\gamma$ (°)	92.90(3)				
$V/Å^3$	2186(1)				
Temperature/°C	-140				
Z	2				
$D_{\rm s}/{\rm g~cm^{-3}}$	1.532				
$\mu$ (Mo-K $\alpha$ )/cm <sup>-1</sup>	6.26				
F(000)	1038				
No. of observed reflections	39888				
No. of unique reflections	9739				
Reflections used	9739				
Reflection/Parameter Ratio	30.82				
No. of Variables	647				
$R_1 \left[ I > 2\sigma(I) \right]^a$	0.088				
$wR_2$ (all data) <sup>b</sup>	0.245				
GOF	0.886				

 ${}^{a} R_{1} = \Sigma ||F_{o}| - |F_{c}|| \Sigma ||F_{o}||^{b} w R_{2} = \{\Sigma w(|F_{o}| - |F||)^{2} / \Sigma w F_{o}^{2}\}^{1/2}; \omega = 1/\sigma^{2}(F_{o}) = \{\sigma^{2}_{c}(F_{o}) + p^{2} / 4 \cdot F_{o}^{2}\}^{-1}.$ 



**Fig. 2** UV-vis absorption spectra of 1 (dotted line) and **Cu-1** (full line) in  $CH_2Cl_2$  at 25 °C. [1] = [**Cu-1**] =  $2 \times 10^{-5}$  M.

difficult. The quinoid structures in our complexes, however, may contribute to their absorption spectra to some extent.

The effective magnetic moment  $(\mu_{eff})$  determined by the Evans method<sup>23</sup> at room-temperature is 1.81. The magnitude of  $\mu_{eff}$  is consistent with the spin-only value for an independent d<sup>9</sup> copper(II) center with  $S = 1/2 (1.7-2.2 \,\mu_B)$ .<sup>24</sup> Moreover, the ESR spectrum of **Cu-1** in CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature includes four lines with a nuclear hyperfine spin 3/2, having  $g_{\parallel}$  and  $g_{\perp}$  values of 2.122 and 2.019, respectively, which are less than 2.3 in agreement with the covalent character of the metal ligand bond (Fig. 3). The relationship  $g_{\parallel} > g_{\perp}$  is typical of d<sup>9</sup> copper(II) complexes in a ground state doublet with the unpaired electron residing in a  $d_{x^2-y^2}$  orbital.<sup>25</sup> The hyperfine  $A_{\parallel}$  splitting of 83.8 indicates that the electron is interacting with only one copper nucleus. The *g* and  $A_{\parallel}$  values of **Cu-1** are significantly different



Fig. 3 EPR spectrum of Cu-1 in  $CH_2Cl_2$  at 25 °C. (microwave frequency 9.2124, microwave power 1 mW, modulation amplitude 4 G, modulation frequency 100 kHz.)

from the typical Cu(II) porphyrin complexes (*e.g.*, CuTPP:  $g_{\parallel} = 2.190$ ,  $g_{\perp} = 2.045 A_{\parallel} = 615$  MHz),<sup>26</sup> because **Cu-1** has distorted square-planar geometry with asymmetric coordination between the copper center and the four nitrogen atoms.

#### <sup>1</sup>H-NMR spectroscopic characterization of Ni-1

Although suitable single crystals of Ni-1 for X-ray diffraction measurements could not be obtained, the molecular structure of Ni-1 is expected to have a similar conformational geometry to Cu-1, based on the results of the 1H-NMR spectroscopic experiment. The <sup>1</sup>H-NMR spectrum of Ni-1 in CDCl<sub>3</sub> indicates a typical diamagnetic square planar nickel(II) complex as shown in Fig. 4b. Compared with ligand 1, the spectrum of Ni-1 in CDCl<sub>3</sub> has similarity in the chemical shift and splitting of each of the resonances (Fig. 4a). The simple resonance patterns include sets of peaks of the phenanthroline moiety (at 8.1, 8.2 and 8.8 ppm), the meso-phenyl group (at 7.3–7.5 ppm), and two sets of the  $\beta$ pyrrole units (at 6.8 ppm) in an aromatic proton region. The sets of the methylene and methyl proton peaks of the ester moiety appear in the high field region of the spectrum with equal intensity as expected for the  $C_s$  symmetric binding mode of the ligand. The disappearance of the inner NH resonance peak is also expected due to the symmetric coordination of the nickel ion into the core of Ni-1. Furthermore, the DFT optimized structure of cationic Ni-1 at the singlet ground state (S = 0) is quite similar to the X-ray crystal one of Cu-1. (Fig. 5) Therefore, the coordination geometry of Ni-1 in CDCl<sub>3</sub> could be square planar.

#### Solvato- and thermo-chromisms of Ni-1

When Ni-1 is dissolved in MeOH, the solution color is changed from dark green to bluish purple. The UV-vis absorption spectra of the CH<sub>2</sub>Cl<sub>2</sub> solution of Ni-1 containing different amounts of MeOH indicate blue-shifting of the Q-like band from 620 to 569 nm in a manner dependent upon the amount of MeOH (Fig. 6). This implies that a new species is generated in MeOH solution. The <sup>1</sup>H-NMR spectrum of this MeOH solution of Ni-1 demonstrates formation of a paramagnetic nickel species (Fig. 4c). Latos-Grażyński *et al.* have reported that a core-modified porphyrin with an incorporated phenolate donor affords a four coordinated diamagnetic Ni(II) complex and that, upon treatment with gaseous hydrogen chloride, the complex is converted into a paramagnetic Ni(II) complex.<sup>27</sup> The observed pattern of chemical



Fig. 4 <sup>1</sup>H-NMR spectra of (a) 1 in CD<sub>2</sub>Cl<sub>2</sub> (inlet; inner NH resonance) and Ni-1 (b) in CDCl<sub>3</sub> and (c) in CD<sub>3</sub>OD, at 25 °C.



**Fig. 5** Optimized structure of **Ni-1** obtained by B3LPY DFT Calculation. (a) top view and (b) side view: Hydrogen atoms and substituents at the *meso*-positions are omitted for clarity. Selected bond lengths (Å) and angles (deg); Ni-N<sub>1</sub> 1.947, Ni-N<sub>2</sub> 1.935, Ni-N<sub>3</sub> 1.884, Ni-N<sub>4</sub> 1.885, N<sub>1</sub>-Ni-N<sub>2</sub> 83.83, N<sub>2</sub>-Ni-N<sub>3</sub> 90.74, N<sub>3</sub>-Ni-N<sub>4</sub> 93.16, N<sub>4</sub>-Ni-N<sub>1</sub> 91.30.

shifts is similar to the high spin (HS, where S = 1) Ni(II) complexes of a porphyrin analogue,<sup>28</sup> with β-pyrrole resonances in the downfield region of 10-30 ppm and the 1,10-phenanthroline resonances in the 45-55 ppm range. The effective magnetic moment of the nickel species at room temperature was determined by the Evans method to be  $3.28\,\mu_B.$  This value was concluded to be consistent with that of common HS Ni(II) complexes<sup>29</sup> (2.8–4.0 $\mu_B$ ), indicating that the spin state of the nickel ion in methanol solution is high-spin (HS). The conversion of spin states of Ni(II) from lowspin (LS, where S = 0) to HS must be due to the conversion from square planar to the octahedral geometry as a result of axial ligation (in the HS state, the d<sup>8</sup> ion presents two unpaired electrons in the  $z^2$  and  $x^2-y^2$  orbitals, which are at similar energy levels).<sup>30</sup> The absorption spectra of Ni-1 in the other coordinating solvents (e.g., DMSO and DMF) have similar spectral features such as blueshifting of the Ni-1-solv adducts, which implies formation of the 6-coordinated (6cHS) Ni(II) species (Table 2). Binding constants  $(K_{\rm b})$  for the coordinated complexes with solvents are defined in eqn (1), where  $A_{\rm L}$  and  $A_{\rm H}$  are the absorbance values corresponding to the LS and HS Ni(II) species, respectively. K<sub>b</sub> values were calculated using the following relationship:

$$K_{\rm b} = [\mathbf{Ni-1} \cdot \mathbf{solv}] / [\mathbf{Ni-1}] = (A_{\rm L} - A) / (A - A_{\rm H})$$
(1)

Comp.	Absorption, " $\lambda_{max}/nm$			Potentials, <sup>b</sup> E/V					
	$\overline{\mathrm{CH}_2\mathrm{Cl}_2}$	MeOH	DMF	DMSO	$\overline{Ox(1)}$	Ox(2)	Red(1)	Red(2)	Red(3)
1	489				0.81	1.09	-1.27	-1.58	
Cu-1	590				0.84		-0.77	-1.14	-1.59
Ni-1	620	569	570	576	0.92		-0.66	-1.03	-1.29

Table 2 Summary of spectral and electrochemical data for 1, Cu-1 and Ni-1 in various solvents at 25 °C



**Fig. 6** UV-vis absorption spectral change of Ni-1 in CH<sub>2</sub>Cl<sub>2</sub> upon titration of MeOH, [Ni-1] =  $2 \times 10^{-5}$  M, at 25 °C. Inlet shows the photographs of the solution of Ni-1 in MeOH (left) and CH<sub>2</sub>Cl<sub>2</sub> (right).

The  $K_{\rm b}$  values (M<sup>-1</sup>) calculated from the slopes of the plots are 0.038 for MeOH, 0.132 for DMF, and 0.230 for DMSO, respectively. The similarity of these values indicates that the Ni-1-solv adducts have essentially the same coordination geometry. In non-coordinating solvents such as CH<sub>2</sub>Cl<sub>2</sub>, the formation of a 4-coordinate square-planar (4cLS) Ni(II) complex is preferred, whereas in coordinating solvents such as MeOH, the corresponding 6-coordinate octahedral 6cHS Ni(II) complex with an axial solvent molecule is probably formed. Although we attempted to further characterize the structure of the 6cHS Ni(II) complex of Ni-1 by cold-spray-ionization mass spectroscopy (CSI-MS), the mass peak of the complex (which includes an axially-coordinated solvent molecule) could not be observed due to the small binding constants of the corresponding solvent molecules. However, the structure of Cu-1 exhibits coordination of methanol to the copper center as evidenced by X-ray crystallographic analysis. A supramolecular complex containing a methanol-coordinated HS Ni(II) species with a monoanionic tripyrrin ligand has been reported.<sup>31</sup> Therefore, Ni-1 might be a 6cHS Ni(II) complex in coordinating solvents, as a result of the transformation from a 4cLS square planar complex to a 6cHS octahedral complex.

The difference between the  $K_b$  values of various solvents reflects thermal behavior. **Ni-1** exhibits thermochromism in THF, which is a weaker coordinating solvent than MeOH. Two absorption maxima emerge at 613 and 575 nm in the spectrum of **Ni-1** in THF at 20 °C. This result may indicate the existence of both 4cLS and 6cHS Ni(II) species. Upon cooling of the THF solution of **Ni-1** to -80 °C, the solution color gradually changes from blue to purple. This color change is accompanied by an increase in intensity of the higher energy peak at 573 nm (Fig. 7). This observed spectrum of Ni-1 in THF at -80 °C is similar to that of the 6cHS Ni-1 species observed in coordinating solvents such as MeOH, DMF and DMSO (Table 2). The formation of 6cHS Ni-1·THF adduct was further evidenced by determination of the effective magnetic moment at -40 °C to be 2.47  $\mu_B$ .<sup>32</sup> The thermochromism would be associated with the reversible temperature-dependent transformation between the 4cLS and 6cHS structures. Therefore, this temperature-dependent spectral change can be rationalized by the formation of the 6cHS Ni(II) species when the temperature is decreased.



**Fig. 7** UV-vis absorption spectral change of **Ni-1** observed upon lowering the temperature form 20 to -80 °C in THF. [**Ni-1**] =  $2 \times 10^{-5}$  M. Inlet shows the photographs of the solution of **Ni-1** in THF at low temperature (left) and room temperature (right).

#### **Redox properties of Ni-1**

To gain insight into the electronic character of the porphyrin-like macrocycle, the redox potentials of Ni-1 were measured by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M *n*Bu<sub>4</sub>NClO<sub>4</sub> (TBAP). All potentials were referenced to the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple as a standard. The data are summarized in Table 2. The cyclic voltammogram of the Ni(II) complex (Ni-1) exhibits one oxidation wave at  $E_{ox} = 0.92$  V and three reduction waves at  $E_{red} = -0.66$ , -1.03 and -1.29 V (*vs.* Fc/Fc<sup>+</sup>), as shown in Fig. 8. The metal free



**Fig. 8** Cyclic voltammograms of **Ni-1** in  $CH_2Cl_2$  containing 0.1 M  $nBu_4NClO_4$  at room temperature. Conditions: [**Ni-1**] = 1 mM; working electrode GC; counter electrode, Pt wire; reference electrode, Ag/Ag<sup>+</sup>; scan rate 50 mV s<sup>-1</sup>.

ligand (1) gives rise to two oxidation waves at  $E_{ox} = 0.81$  and 1.09 V and two reduction waves at  $E_{\rm red} = -1.27$  and -1.58 V. The redox process in Ni-1 observed at -0.66 V represents the redox couple of the metal center, Ni<sup>II</sup>/Ni<sup>I</sup>. This assignment is rationalized as follows: if the reduction potential of Ni-1 was assigned to be a ligand-centered process, the potential gap (1.58 V) between the first reduction and the first oxidation of the ligand would be too small relative to that of the free base ligand, 1 (2.08 V). Thus, the monoanionic coordination core of the porphyrin analogue would be consequently expected to stabilize the lower oxidation state of the transition metals. The Ni(II) porphyrin complex (e.g., NiTPP,<sup>33</sup> tetraphenylporphyrin) has a reduction peak at -1.75 V (vs. Fc/Fc<sup>+</sup>, in CH<sub>2</sub>Cl<sub>2</sub>, 0.1 M TBAP). The one electron-reduced species of the Ni(II) porphyrin complex is assigned as an equilibrated form between the Ni(I) porphyrin anion and the Ni(II) porphyrin  $\pi$ anion radical.<sup>34</sup> The positive shift of the nickel-centered redox peak of Ni-1 relative to that of NiTPP indicates that reduction of the nickel center in Ni-1 occurs more easily than reduction of NiTPP. Moreover, the metal-centered reduction potential of Cu-1 determined by DPV is -0.77 V. A similar positive shift of the Cu<sup>I</sup>/Cu<sup>II</sup> redox couple is observed due to the nature of the macrocycle (Table 2). On the other hand, metal-centered oxidation potentials were not observed for both Ni-1 and Cu-1 when compared with metal-centered oxidation potentials of ligand 1. The replacement of half of the skeleton of the porphyrin core with the 1,10-phenanthroline moiety reduces the ligand charges of the macrocycle from -2 to -1. This clearly affects the redox behavior of the macrocycle to stabilize the low-valent Ni(I) species. The stability of this species may also be increased as a result of the flexibility of the modified macrocycle. The ion-binding cavity of natural porphyrins has a radius greater than 2.0 Å. In contrast, the square-planar 4cLS Ni(II)-N(pyrrole) bond distance of our complex is approximately 1.8–1.9 Å, and the coordination of Ni(II) by a porphyrin introduces strain (ruffling) into the macrocycles.<sup>35</sup> We expect that this effect may be amplified in our modified ligand 1. The rigid coordination environment of the natural porphyrin is unfavorable with regard to accommodation of a Ni(I) center, which has a larger ionic radius, and, as a result, the ligandcentered reduction event becomes energetically more favorable. Thus the redox properties of nickel complexes can be controlled by the rigidity of the macrocycle.<sup>36</sup> Our ligand 1 is flexible at the meso-exocyclic double bonds and more readily allows Ni-centered

reductions to occur without requiring large energy expenditure for geometric rearrangements.

#### Relevance of Ni-1 to nickel dependent cofactor F<sub>430</sub>

The nickel dependent cofactor  $F_{430}$  of methyl-coenzyme M reductase<sup>18</sup> catalyzes the reduction of methyl-coenzyme M (CH<sub>3</sub>-S-CoM) with coenzyme B (HS-CoB) to methane and the heterodisulfide CoM-S-S-CoB in the following equation:

$$CoB-S-H + CH_3-S-CoM \rightarrow CoB-S-S-CoM + CH_4$$
 (2)

This reaction represents the key final step of the process of methanogenesis in Archaea. The highly reduced nickel hydrocorphin, a nonplanar monoanionic porphyrin-related macrocycle of cofactor F<sub>430</sub>, exhibits intriguing spin interconversions<sup>37</sup> and redox properties.38 Nickel complexes of oxaporphyrin39 and nonporphyrinoid tetraazamacrocyles<sup>40</sup> have been developed as synthetic models of Ni(I) F430. Ghosh et al. have recently investigated symmetrized monoanionic porphyrin analogues such as oxaporphyrin (N<sub>3</sub>O coordination) and pyriporphyrin (N<sub>4</sub> coordination with a pyrrole unit replaced by pyridine). These compounds were found to provide excellent models for theoretical investigation.<sup>41</sup> Moreover, on the basis of spectroscopic evidence, the proposed catalytic mechanism of cofactor F<sub>430</sub> includes reduction of the nickel center to the Ni(I) state as an active species.<sup>42</sup> The redox potential of the Ni(II)/Ni(I) couple in aqueous  $F_{430}$  is known to be between -0.6 and -0.7 V (vs. NHE)<sup>43</sup> The potential of the Ni(II)/Ni(I) couple of Ni-1 was estimated to be approximately -0.3 V (vs. NHE),<sup>44</sup> which are close to the native potentials. Thus, our nickel complex, Ni-1 is expected to provide a useful candidate for development of a synthetic model of the Ni-dependent cofactor F<sub>430</sub>.

#### Conclusion

We have described the preparation of copper(II) and nickel(II) complexes of a heme/non-heme hybrid porphyrin analogue, phenanporphodimethene (1) in good yield. The combination of 1,10phenanthroline and a dipyrrin moiety as structural components of a porphyrin-like macrocycle afforded a N4-monoanionic coordination sphere capable of accommodating copper(II) and nickel(II) ions. The molecular structure of Cu-1 was characterized by X-ray crystallographic analysis, which demonstrated a distorted squareplanar coordination structure with a hexafluorophosphate counter anion. The nickel complex, Ni-1, has similar geometry to Cu-1, which are characterized by DFT calculation and demonstrate an intriguing conversion between 4cLS and 6cHS configurations of the nickel center promoted by the solvent axial coordination. This is accompanied by a distinct solution color change representing solvatochromism. Moreover, the thermochromic behavior of Ni-1 was also observed in THF solution. The electrochemical analysis of Ni-1 indicates a positive shift of the nickel(I/II) redox potential relative to that of the NiTPP. This implies stabilization of the low valent oxidation state of the nickel center due to the intrinsic coordination environment of the macrocycle (e.g., flexibility and electronic charge of macrocycle). These remarkable redox features indicate that Ni-1 may give a structural model of the nickel dependent cofactor  $F_{430}$  in methyl coenzyme M reductase. These chemical modifications of the porphyrin framework will provide an attractive strategy for furnishing new metal coordination environments and fine-tuning metal complexes as catalysts and biomimetic enzyme models.

#### Experimental

#### Instruments

<sup>1</sup>H-NMR spectra were recorded on a JEOL JMX-GX400 (400 MHz) spectrometer. <sup>13</sup>C-NMR spectra were recorded on a JEOL ECA500 (500 MHz) spectrometer. Chemical shifts ( $\delta$ -scale) are provided with reference to the peak of residual non-deuterated chloroform (7.26 ppm, for <sup>1</sup>H-NMR spectra, 65.00 ppm, for <sup>13</sup>C-NMR). High resolution mass (HR-MS) spectra were obtained using a JEOL LMS-HX-110 spectrometer. FAB-MS spectra were measured using 3-nitrobenzyl alcohol (NBA) as a matrix. UVvis absorption spectra were recorded on a Shimadzu UV-3100PC spectrometer and an Agilent 8453 diode array spectrometer equipped with a Unisoku thermostatic cell holder for variable temperature measurement. Cold-spray ionization time-of-flight (CSI-TOF) mass spectra were recorded using a JEOL JMS-T100CS spectrometer. ESR spectra were recorded on a JEOL JES-TE 300 spectrometer at room temperature. The magnetic field was calibrated from the hyperfine coupling constants of Mn(II) ion doped in MgO powder (86.9 Gauss). Cyclic voltammetric measurements were carried out on a BAS 100B/W electrochemical analyzer using a conventional three-electrode cell for samples (1 mM) dissolved in dry  $CH_2Cl_2$  containing 0.1 M  $nBu_4NClO_4$ (TBAP) under an Ar atmosphere. A glassy-carbon working electrode and a platinum wire as a counter electrode with an  $Ag/Ag^{+}$  reference electrode were used in all experiments. The potentials were calibrated with ferrocenium/ferrocene.

#### Materials

General chemicals were used without further purification. Solvents were used after appropriate distillation or purification. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 pre-coated aluminium sheets. Column chromatography was carried out using silica gel 60 N (60 mesh, Wako chemical) or neutral alumina (Wako chemical). The ligand used in this study was prepared according to the following procedure.<sup>11</sup>

#### Synthetic procedure

Ni-1. Compound 1 (0.1 g, 0.14 mmol) was dissolved in CHCl<sub>3</sub> (30 ml) and a methanol solution (5 ml) of nickel(II) acetate (excess) and a few drops of 2,6-lutidine were added to the solution. The mixture was refluxed for 15 min under a nitrogen atmosphere. After cooling, the reaction mixture was combined with water and then extracted with CHCl<sub>3</sub>. The organic layer was washed with a saturated NaPF<sub>6</sub> aqueous solution several times to exchange the counter ion of the nickel complex. This was followed by washing with deionized water. The solution obtained from this process was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The residue was purified by SiO<sub>2</sub> column chromatography (CHCl<sub>3</sub> + 4% MeOH) and produced Ni-1 as a green powder. Yield: 80 mg (63%); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.78 (d, J = 8.6 Hz, 2H, Phen-H), 8.19 (s, 2H, Phen-H), 8.13 (d, J = 8.6 Hz, 2H, Phen-H), 7.50 (dd, J = 1.5, 7.1 Hz, 1H, Ph-H), 7.45 (d, J = 7.3 Hz, 2H, Ph-H), 7.37

(d, J = 7.1 Hz, 2H, Ph-H), 6.80 (d, J = 4.6 Hz, 2H, Pyrr-H), 6.76 (d, J = 4.6 Hz, 2H, Pyrr-H), 4.18–4.36 (m, 8H, CH<sub>2</sub>), 1.31 (t, J = 7.3 Hz, 6H, CH<sub>3</sub>), 1.23 (t, J = 7.3 Hz, 6H, CH<sub>3</sub>) ppm. <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  163.48, 162.40, 154.04, 151.05, 147.83, 145.41, 139.81, 138.21, 137.56, 135.55, 135.02, 133.30, 130.39, 130.26, 130.03, 129.58, 128.30, 128.04, 127.29, 122.24, 63.28, 62.95, 13.96, 13.79 ppm. HR-MS (FAB) m/z = 793.1837 (found), 793.1808 (calcd. For C<sub>43</sub>H<sub>35</sub>N<sub>4</sub>O<sub>8</sub>NiPF<sub>6</sub>). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ [mm] (log  $\varepsilon$  [M<sup>-1</sup> cm<sup>-1</sup>]) = 444 (3.92), 622 (4.25); (MeOH):  $\lambda_{max}$  [nm] (log  $\varepsilon$  [M<sup>-1</sup> cm<sup>-1</sup>]) = 310 (4.41), 573 (4.39). Elemental analysis (Found: C 51.71; H 3.81; N 5.38. C<sub>43</sub>H<sub>35</sub>N<sub>4</sub>O<sub>8</sub>NiPF<sub>6</sub>+CH<sub>2</sub>Cl<sub>2</sub> requires C 51.59; H 3.69; N 5.47%).

**Cu-1.** The copper complex, **Cu-1** was prepared by a procedure similar to the procedure for preparing **Ni-1**. Compound **1** (0.1 g, 0.14 mmol), a slight excess of copper(II) acetate dihydrate and a few drops of 2,6-lutidine were treated in CHCl<sub>3</sub>–MeOH solution. The reaction mixture was combined with water and extracted by CHCl<sub>3</sub>. The organic layer was washed several times with saturated NaPF<sub>6</sub> aqueous solution. The resulting solution was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The residue purified by SiO<sub>2</sub> column chromatography (CHCl<sub>3</sub> + 5% MeOH) gave **Cu-1** as a blue powder. Yield: 102 mg (81%); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  [nm] (log  $\varepsilon$  [M<sup>-1</sup> cm<sup>-1</sup>]) = 590 (4.43). HR-MS (FAB) *m/z* = 798.1780 (found), 798.1751 (calcd. for C<sub>43</sub>H<sub>35</sub>N<sub>4</sub>O<sub>8</sub>CuPF<sub>6</sub>). Elemental analysis (Found: C 53.68; H 3.73; N 5.79. C<sub>43</sub>H<sub>35</sub>N<sub>4</sub>O<sub>8</sub>CuPF<sub>6</sub> requires C 54.69; H 3.74; N 5.93%).

#### Theoretical calucations

The calculations were performed with the Gaussian03 program.<sup>45</sup> The geometry optimization of cationic Ni-1 at the singlet ground state (S = 0) was performed by using the B3LYP DFT method with the 6-31G(d) basis set for C, N, O and H atoms and the LANL2DZ basis set for Ni and Cu atom without any symmetry restriction.<sup>46</sup> All calculations of the complexes were performed without the counter anion of hexafluorophosphate (PF<sub>6</sub><sup>-</sup>).

#### X-Ray crystallographic determination

The X-ray experiments for Cu-1 were carried out using a Rigaku RAXIS Rapid imaging plate area detector with graphitemonochromated MoK $\alpha$  radiation ( $\lambda = 0.71075$  Å). The crystals were mounted on a glass fiber. The data were collected for Cu-1  $(2\theta = 54.8^{\circ})$  at  $-140 \,^{\circ}$ C. Refraction data were corrected for both Lorentz and polarization effects. The structures were solved by the direct method and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. All hydrogen atoms were located at the calculated positions, assigned a fixed displacement and constrained to ideal geometry with C-H = 0.95 A. The thermal parameters of calculated hydrogen atoms were related to those of their parent atoms by  $U(H) = 1.2U_{eq}(C,N)$ . The crystallographic calculations were performed using the crystal structure software package of the Rigaku Corporation [CrystalStructure Ver. 3.8.2: Crystal structure analysis package, Rigaku (3-9-12 Akishima, Tokyo, Japan) and Rigaku/MSC (9009 New Trails Dr, The Woodlands, TX 77381 USA)].

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