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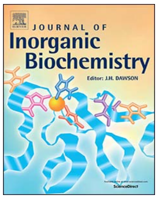

Nickel (II) pyrrocorphin: Enhanced binding ability in a highly reduced porphyrin complex

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ABSTRACT

Pyrrocorphin is an air-sensitive porphyrinoid with a highly reduced hexahydroporphyrin core. In contrast, pyrrolidine-fused pyrrocorphin (Pyr) obtained by successive 1,3-dipolar cycloaddition reactions of azomethine ylide to 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin is less air-sensitive. In order to reveal the effect of highly reduced porphyrin rings on the physicochemical properties of their metal complexes, we have prepared diamagnetic ($S = 0$) Ni(II) complex Ni(II)(Pyr). The addition of excess pyridine (Py) to the toluene solution of Ni(II)(Pyr) yielded five-coordinate Ni(II)(Pyr)(Py), which was then completely converted to six-coordinate paramagnetic ($S = 1$) Ni(II)(Pyr)$(Py)_2$. The latter was characterized by UV–Vis, ^{1}H NMR, CV, SQUID, and X-ray crystallography as well as DFT calculations. As compared with analogous complexes of porphyrin (Por), chlorin (Chl), and isobacteriochlorin (Iso) reported by Herges and co-workers (R. Herges et al., Inorg. Chem. 2015), Ni(II)(Pyr)$(Py)_2$ has longer equatorial Ni—N and shorter axial Ni—N bonds. The CV study has shown a large decrease in HOMO–LUMO gap as the reduction of porphyrin ring proceeds, which has further been confirmed by UV–Vis and DFT calculation. Titration studies using ^{1}H NMR and UV–Vis have shown that the first binding constant of pyridine toward Ni(II)(Pyr) is ca. 4 times as large as that of Ni(II)(Iso) and ca 230 times as large as that of Ni(II)(Por). Thus, we have concluded that the binding constant of pyridine to Ni(II) porphyrinoid increases by the following order: Por < Chl < Iso < Pyr. The high affinity of pyridine binding in Ni(II)(Pyr) was discussed both from the structural and thermodynamic point of view.

1. Introduction

Porphyrinoids are macrocycles with porphyrin-like skeletons [1–4]. In recent years, great effort has been focused on the development and improvement of new methods to convert porphyrins into hydroporphyrins such as dihydroporphyrins (chlorins), tetrahydroporphyrins (isobacteriochlorins and bacteriochlorins), and hexahydroporphyrins (pyrrocorphin). This is mainly due to the potential use of these compounds as photosensitizers in photodynamic therapy (PDT) for various cancers [5–7]. Although there are ample studies on the synthesis and characterization of hydroporphyrins such as chlorin, bacteriochlorin, and isobacteriochlorin as well as their metal complexes, little is known on the spectroscopic properties of further reduced porphyrinoids such as pyrrocorphins and their metal complexes [1,2,8–13].

In nature, highly reduced hydroporphyrins and their metal complexes are playing important roles. For example, coenzyme F430, which is the prothetic group of methyl coenzyme M reductase in methanogenic and anaerobic methanotrophic archaea, is known to have Ni(II) corphin structure with only five peripheral double bonds [14–16]. Recently, Zheng et al. reported that the biosynthesis of coenzyme F430 from sirohydrochlorin proceeds via four steps [17]. The sequence begins with the insertion of nickel mediated by a chelatase, similar to the biosynthesis of vitamin B12; vitamin B12 is a Co(III) complex of another highly reduced porphyrinoid named corrin [18–20]. In the case of metal-free compounds, pyrrocorphin is less stable than the corresponding porphyrinogen. In the presence of a complexing metal ion and a base, however, the equilibrium lies on the side of the pyrrocorphin. Some years ago, Kratky et al. reported the X-ray structural analyses of Ni(II) complexes of diastereomeric 2,3,7,8,12,13,17,18-octaethylpyrrocorphins [21]. More recently, Cavaleiro et al. reported three kinds of

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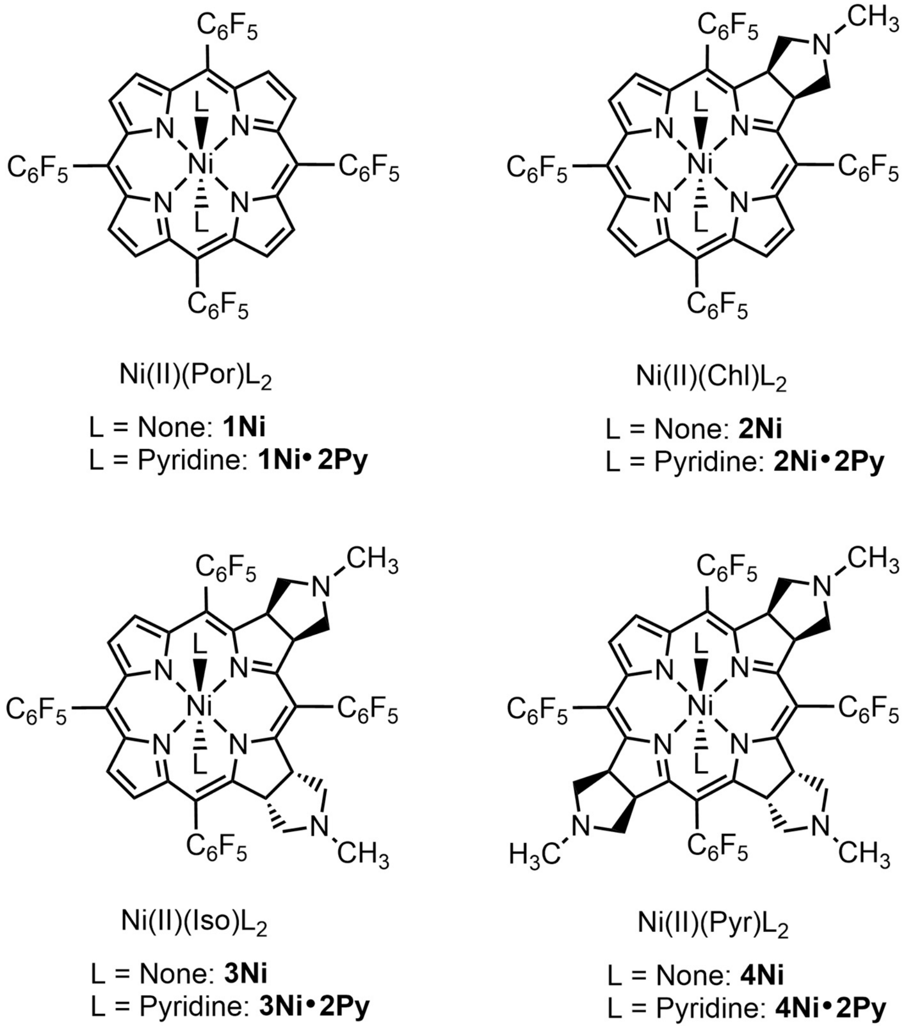

Scheme 1. Ni(II) complexes examined in this study. Abbreviations: porphyrin (Por), chlorin (Chl), isobacteriochlorin (Iso), and pyrrocorphin (Pyr).

diastereomeric pyrrolidine-fused pyrrocorphins by 1,3-dipolar cycloadditions of azomethine ylides to 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin [22]. These compounds are quite stable in spite of the presence of the highly reduced porphyrin ring. Quite recently, Herges et al. used porphyrin **1**, chlorin **2**, and isobacteriochlorin **3** reported by Cavaleiro et al. and converted them to the corresponding Ni(II) complexes, **1Ni**, **2Ni**, and **3Ni** as shown in Scheme 1 [23]. Although square planar Ni(II) complexes were diamagnetic, the corresponding six-coordinate pyridine ligated complexes, **1Ni·2Py**, **2Ni·2Py**, and **3Ni·2Py**, showed paramagnetic S = 1 spin state. Consequently, the spectroscopic properties changed drastically by the addition of pyridine. These authors called the phenomena as *coordination-induced spin-state switching* (CISSS). Interestingly, the binding constants of pyridine toward four-coordinate Ni(II) complexes showed a large increase on going from porphyrin **1Ni** to chlorin **2Ni**, and then to isobacteriochlorin **3Ni**. These results have attracted our attention since we have been studying the effect of the reduced porphyrin ring on the physicochemical properties of the metal complexes [8,24].

In this paper, we would like to show the structural, spectroscopic, redox, and magnetic properties of Ni(II) complexes of pyrrocorphin together with those of the five- and six-coordinate pyridine ligated complexes, **4Ni·Py** and **4Ni·2Py**, by means of UV–Vis, ^{1}H NMR, CV, SQUID, and X-ray crystallography as well as DFT calculations. We will also compare these properties with those of the corresponding porphyrin, chlorin, and isobacteriochlorin complexes reported by Herges et al.

2. Experimental

2.1. Instrumentation

Elemental analyses for carbon, hydrogen, and nitrogen were conducted using a Yanaco CHN CORDER MT-6. UV–Vis absorption spectra were recorded in CH_2Cl_2 and pyridine solution on a Shimadzu UV-3100 spectrometer. Reflectance spectra were recorded on a Shimadzu ISR-3100 spectrometer. ^{1}H and ^{19}F NMR spectra ware recorded on a JEOL Delta ECX-500 spectrometer operating at 500.1 and 470.6 MHz for ^{1}H and ^{19}F, respectively. Chemical shifts for ^{1}H signals were referenced to the residual solvent protons of $CDCl_3$, CD_2Cl_2, and pyridine-d_5 (δ = 7.24, 5.32, and 7.19 ppm, respectively). Chemical shifts of ^{19}F NMR spectra were referenced to hexafluorobenzene (δ = − 164.9 ppm). Mass spectra were recorded on a Bruker microTOF using positive mode ESI-TOF method for acetonitrile solutions by using sodium formate as reference. Cyclic voltammograms were measured on a BAS ALS-DY2325 electrochemical analyzer. Samples were dissolved in CH_2Cl_2 solution containing tetrabutylammonium hexafluorophosphate ($TBAPF_6$). A glassy carbon disk (3.0 mm radius), platinum wire, and saturated calomel electrode (SCE) were used as working, counter, and reference electrodes, respectively. The solid-state magnetic susceptibilities were measured between 2 and 300 K under a magnetic field of 0.5 T on a Quantum Design MPMS-7 and a MPMS-7XL SQUID magnetometer. The fitting curves were obtained by using EasySpin software package [25].