Inorg. Chem. **2003**, *42*, 8125–8127

Inorganic Chemistry

Communication

Ni(III) Complex of an N-Confused Porphyrin Inner C-Oxide

Ziwei Xiao, Brian O. Patrick, and David Dolphin*

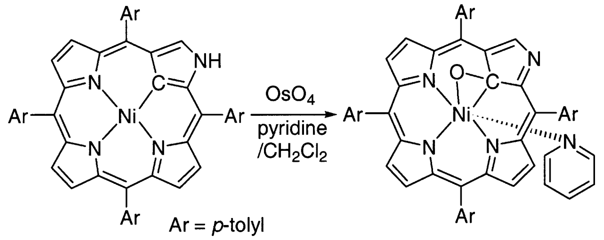
*Department of Chemistry, University of British Columbia, 2036 Main Mall,
Vancouver, British Columbia, V6T 1Z1 Canada*

Received December 3, 2002

A novel, structurally characterized Ni(III) complex of an N-confused porphyrin inner C-oxide has been synthesized from the oxidation of a Ni(II) N-confused porphyrin using OsO_4. Crystal data: $C_{53}H_{40}N_5NiO{\cdot}CH_2Cl_2$, monoclinic, space group $P2/a$ (No. 13), $a = 21.229(1)$ Å, $b = 8.6451(5)$ Å, $c = 25.762(2)$ Å, $\beta = 93.004(3)°$, $V = 4721.6(5)$ Å^3, and $Z = 4$.

Ni(III) tetrapyrrolic macrocycles have been intensively studied.[1] Wolberg reported on the generation of a Ni(III) porphyrin via electrochemical oxidation of Ni(II) tetraphenylporphyrin at 77 K.[2] This reaction was re-examined by Dolphin and his colleagues where it was observed that a Ni(II) porphyrin π-cation radical was formed at room temperature and a low spin Ni(III) porphyrin was generated upon cooling to 77 K, showing intramolecular electron transfer.[3,4] N-confused porphyrins are porphyrin isomers with an inverted pyrrolic ring and were first reported independently by Latos-Grazynski[5] and Furuta.[6] They can stabilize transition metals in high oxidation states, and some Ni(III) complexes have been prepared by Latos-Grazynski.[7] Factor 430 (F430), a nickel tetrapyrrole, is the cofactor of methyl-coenzyme M reductase, which catalyzes the final steps of CO_2 conversion to methane by methanogenic *Archaea*, and a methyl−Ni(III) transient is suggested to be a key intermediate.[8] Ni(III)−alkyl intermediates are also considered to be involved in the reactions of Ni(I) macrocycles with alkyl halides.[9] However, crystallographically characterized Ni(III) tetrapyrrolic macrocycles are rare, and to the best of our knowledge, the only related example is an oxidized nickel porphyrin $[Ni(OETPP)(BTD)]^+$ (OETPP = β-octaethyl-*meso*-tetraphenylporphyrin, BTD = 2,1,3-benzothiadiazole) with an EPR spectrum typical of Ni(III).[10] The Ni−N (2.00 Å) distance in this complex is rather long relative to other Ni(III) complexes, and this complex was better described as a high spin Ni(II) porphyrin π cation ($d^1_{x^2-y^2}$, $d^1_{z^2}$, π^1) in which the electron in the $d_{x^2-y^2}$ orbital is antiferromagnetically coupled to the unpaired electron of the porphyrin π radical, resulting in a pseudo-Ni(III) species.[10]

Scheme 1



1 **2**

Here, we report the synthesis and structural characterization of a Ni(III) complex of an N-confused porphyrin inner C-oxide (**2**) prepared by oxidation of Ni(II) N-confused tetra-(*p*-tolyl)porphyrin (**1**) with OsO_4 (Scheme 1).

The Ni(II) N-confused porphyrin **1** was prepared using the method described by Latos-Grazynski.[5] A solution of complex **1** (0.20 mmol) and OsO_4 (0.25 mmol) in 15% pyridine/CH_2Cl_2 (50 mL) was stirred at room temperature for 24 h and then filtered through a silica gel plug using 10% CH_3OH/CH_2Cl_2. The solvent was removed in vacuo, and the residue was chromatographed using silica gel (230−400 mesh, 16 g). Compound **2**[11] was eluted with 1.5% CH_3OH/CH_2Cl_2 to give a yield of 42% (32% starting material was recovered). When a large excess of OsO_4 (10 equiv) was used, many polar unidentified compounds were produced.

---

* To whom correspondence should be addressed. E-mail: ddolphin@qltinc.com. Fax: 604-822-9678. Phone: 604-822-4571.

(1) Renner, M. W.; Fajer, J. *JBIC, J. Biol. Inorg. Chem.* **2001**, *6*, 823−830.
(2) Wolberg, A.; Manassen, J. *J. Am. Chem. Soc.* **1970**, *92*, 2982−2991.
(3) Dolphin, D.; Niem, T.; Felton, R. H.; Fujita, E. *J. Am. Chem. Soc.* **1975**, *97*, 5288−5290.
(4) Johnson, E. C.; Niem, T.; Dolphin, D. *Can. J. Chem.* **1978**, *56*, 1381−1388.
(5) Chmielewski, P. J.; Latos-Grazynski, L.; Rachlewicz, K.; Glowiak, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 779−781.
(6) Furuta, H.; Asano, T.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 767−768.
(7) Chmielewski, P. J.; Latos-Grazynski, L. *Inorg. Chem.* **1997**, *36*, 840−845.
(8) Ermler, U.; Grabarse, W.; Shima, S.; Goubeaud, M.; Thauer, R. K. *Science* **1997**, *278*, 1457−1462.
(9) Lahiri, G. K.; Stolzenberg, A. M. *Inorg. Chem.* **1993**, *32*, 4409−4413.
(10) Renner, M. W.; Barkigia, K. M.; Melamed, D.; Smith, K. M.; Fajer, J. *Inorg. Chem.* **1996**, *35*, 5120−5121.
(11) R_f (silica−CH_2Cl_2/5%CH_3OH/2%Et_3N) 0.70; UV−vis (CH_2Cl_2) λ_{max}/nm (log ϵ) 382 (4.65), 426 (4.59), 470 (4.56), 646 (sh), 862 (br, 3.26); MS (-LSIMS) 741 (M, 100%); HRMS (-LSIMS) *m*/*e* calcd for $C_{48}H_{35}N_4NiO$ 741.21639, found 741.21609 (M). Anal. Calcd for $C_{48}H_{35}N_4NiO{\cdot}C_5H_5N$: C, 77.47; H, 4.91; N, 8.52. Found: C, 77.36; H, 4.97; N, 8.61.

10.1021/ic020701s CCC: $25.00

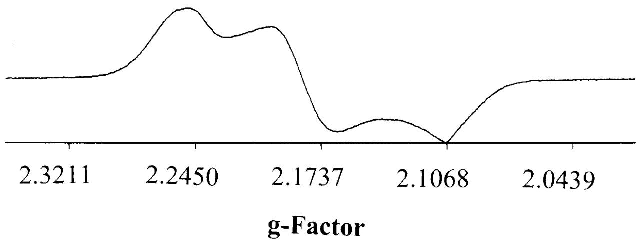


Figure 1. EPR spectrum (X-band, 130 K, toluene) of complex **2**.

The EPR spectrum of **2** was measured in frozen toluene at 130 K (Figure 1), and this spectrum is similar to that of a Ni(III) complex of N-confused tetraphenylporphyrin containing an axial hydroxyl group.[7] The *g*-factor ($g > 2.1$) indicates the unpaired electron is located on the metal center rather than in the porphyrin π system.[3] The EPR signals are broad, and hyperfine splitting is not explicitly observed. N^{14} hyperfine splitting was not observed in the previously reported EPR spectra of Ni(III) N-confused porhyrins.[7]

The room temperature effective magnetic moment of complex **2** in CD_2Cl_2 obtained by Evans' method[12] is 1.87 μ_B, close to the spin-only value for a low spin d^7 Ni(III) center with one unpaired electron ($\mu_{eff} = 1.74\ \mu_B$).

The structure of complex **2** was determined by single crystal X-ray diffraction analysis[13] (Figure 2, Table 1); no counterion was detected. The parent ion peak of **2** at 741 *m*/*z*, detected using LSIMS in the negative ion mode, together with the absence of the counterion, confirms that **2** is a Ni(III) complex, since the corresponding Ni(II) complex would have either N(2) or O(1) protonated to balance the charge and would have a parent ion peak at 742 *m*/*z*. A Ni(I) complex was ruled out in the same way. Cyclic voltammetry (Supporting Information) did not assist in assigning oxidation states to either the metal or the ligand. The UV−vis spectrum of **2** is similar to that of C(21)-methylated Ni(II) N-confused tetraphenylporphyrin,[14] suggesting that the porphyrin ring of **2** is not oxidized and complex **2** is not a pseudo-Ni(III) species as suggested in the case of $[Ni(OETPP)(BTD)]^+$.[10]

Complex **2** is structurally similar to an *N*-oxide of an iron(III) porphyrin, which was proposed as an alternative candidate of compound **I**, as the active intermediate of cytochrome P-450.[15] The X-ray crystal structure of a Ni(II) porphyrin *N*-oxide has been obtained by Balch.[16]

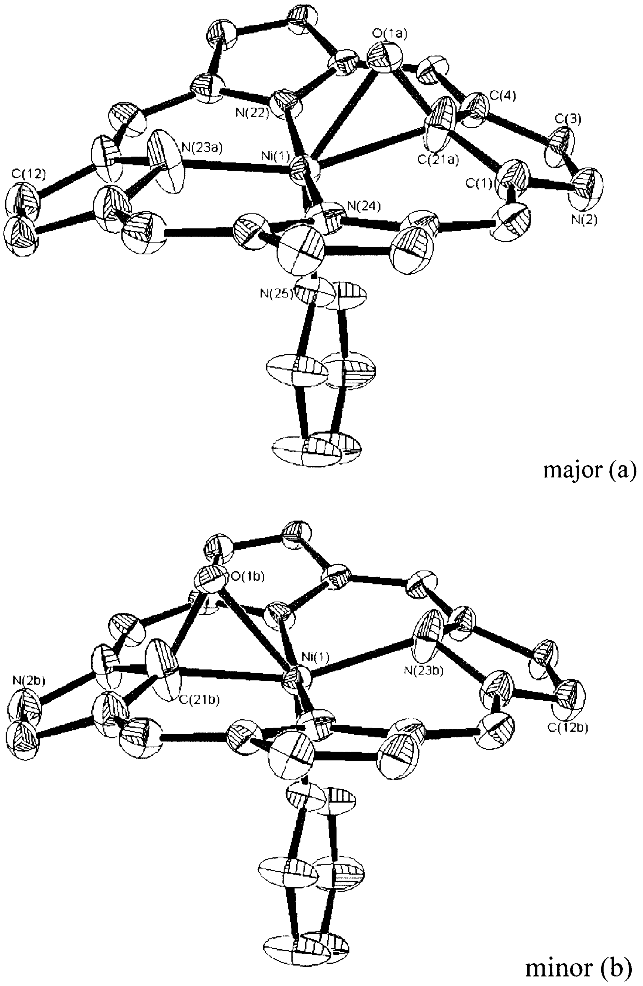


Figure 2. ORTEP drawings of compound **2** showing atomic labeling and thermal ellipsoids at 50% probability. Solvent, *p*-tolyl groups, and H atoms have been removed for clarity. The major (a) and minor (b) contributions to the disorder are shown.

Table 1. Selected Bond Lengths (Å) for Complex **2**

Ni−C(21)	2.068(4)	N(2)−C(1)	1.394(5)
Ni−N(22)	2.087(3)	N(2)−C(3)	1.346(5)
Ni−N(23)	2.007(4)	C(3)−C(4)	1.409(5)
Ni−N(24)	2.100(3)	C(21)−C(1)	1.444(5)
Ni−N(25)	2.004(3)	C(21)−C(4)	1.427(5)
Ni−O(1)	2.037(4)	C(21)−O(1)	1.376(5)

In the Ni(II) complex of the porphyrin *N*-oxide,[16] the nitrogen atom which is bonded to oxygen is not bonded to the metal ion whereas the nickel ion, in complex **2**, is bonded to both the oxygen atom and C(21). The planarity of the porphyrin skeleton of **2** is distorted, but not as severe as that of the C(21)-methylated Ni(II) N-confused porphyrin, in which the inverted pyrrole plane deviates from the N(22)N(23)N(24) plane by 42.2°.[14] For complex **2**, the dihedral angles between the pyrrole planes and the plane defined by N(22)N(23)N(24) are as follows: C(21) 20.5(2)°, N(22) −17.61(7)°, N(23) 22.5(2)°, N(24) −15.3(2)°. The Ni−N(C) bond distances (2.007−2.100 Å) in **2** are longer than those of the high spin Ni(II) complex of N(2),C(21)-dimethylated N-confused porphyrin,[14] contrary to what might be expected for the Ni(III) complex.[1] The strain associated with coordination of Ni to both C(21) and O(1) might

---

(12) Evans, D. A. *J. Am. Chem. Soc.* **1959**, *81*, 2003−2005.

(13) Crystal data for **2**: $C_{53}H_{40}N_5NiO \cdot CH_2Cl_2$, $M = 906.54$, monoclinic, space group *P*2/*a* (No. 13), $D_c = 1.275$ g cm^{-3}, $a = 21.229(1)$ Å, $b = 8.6451(5)$ Å, $c = 25.762(2)$ Å, $\beta = 93.004(3)°$, $V = 4721.6(5)$ Å^3, $T = 173$ K, $Z = 4$, $\lambda = 0.71069$ Å, μ(Mo Kα) = 5.68 cm^{-1}, $R(F) = 0.071$ and $R_w(F) = 0.185$. The structure displays disorder in the locations of C(21) pyrrole ring, and the O(1) atom. The structure has been refined to give 64% of the major and 36% of the minor occupancy as shown in Figure 2. The unit cell also contains one molecule of disordered CH_2Cl_2.

(14) Chmielewski, P. J.; Latos-Grazynski, L.; Glowiak, T. *J. Am. Chem. Soc.* **1996**, *118*, 5690−5701.

(15) Watanabe, Y. *JBIC, J. Biol. Inorg. Chem.* **2001**, *6*, 846−856.

(16) Balch, A. L.; Chan, Y. W.; Olmstead, M.; Renner, M. W. *J. Am. Chem. Soc.* **1985**, *107*, 2393−2398. Balch, A. L.; Chan, Y. W.; Olmstead, M. *J. Am. Chem. Soc.* **1985**, *107*, 6510−6514.

well prevent the porphyrin from adopting a structure with shorter Ni−N(C) bond lengths. Elongation of Ni(III)−C bond lengths has also been observed in the case of $[\mathrm{Ni^{III}(C_6Cl_5)_4}]^-$.[17] The bond distances of N(2)−C(1), N(2)−C(3), and C(3)−C(4) are shorter than those of C(21)−C(1) and C(21)−C(4) (Table 1), suggesting that the C(21) atom approaches sp^3 hybridization. The Ni−O(1)−C(21) ring distorts the octahedral coordination geometry of the center metal. While the pyridine ring is almost perpendicular to the N(22)N(23)N(24) plane with a dihedral angle of 83.3(2)°, the O−Ni−C(21) angle is only 39.15(16)°.

In summary, a Ni(III) complex of an N-confused porphyrin inner C-oxide has been synthesized and characterized. The ability of N-confused porphyrin inner C-oxide to stabilize other high oxidation state metals is currently under investigation.

Acknowledgment. This work was supported by NSERC of Canada. We thank Dr. Barry Liboiron for his help with the EPR spectroscopy.

Supporting Information Available: X-ray crystallographic file (CIF) and cyclic voltammogram for compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC020701S

---

(17) Alonso, P. J.; Falvello, L. R.; Fornies, J.; Martin, A.; Menjon, B.; Rodriguez, G. *Chem. Commun.* **1997**, 503−504.