

New Metalloporphyrins with Extremely Altered Redox Properties: Synthesis, Structure, and Facile Reduction to Air-Stable π -Anion Radicals of Zinc and Nickel β -Heptanitroporphyrins

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Iron and manganese *meso*-tetraarylporphyrins act as efficient catalysts for cytochrome P450-mimetic oxygenations of hydrocarbons.¹ The introduction of *ortho*-halogen substituents on the *meso*-aryl groups in Fe or Mn tetrakis(2,6-dichlorophenyl)porphyrin, [TDCPP], leads to robust catalysts for alkene epoxidation by various oxygen atom donors including H₂O₂.¹ Metalloporphyrins bearing eight halogen substituents on the β -pyrrole positions are even better catalysts for hydrocarbon hydroxylation by iodosobenzene, presumably because the electron-withdrawing substituents increase the reactivity of the high-valent metal-oxo intermediates involved in these reactions.¹ Those Cl and Br β -substituents induce positive shifts of about 0.5 V in the redox potentials of the corresponding metallotetraarylporphyrins,² as well as saddle distortions of the macrocycles because of steric interactions between the β - and *meso*-substituents.³

In an effort to obtain metalloporphyrins with extremely altered redox potentials and unusual reactivities, we have synthesized metalloporphyrins bearing a large number of strongly electron-withdrawing β -nitro substituents. We report here the first syntheses and characterizations of Zn(II) and Ni(II) *meso*-tetrakis(2,6-dichlorophenyl)- β -heptanitroporphyrins, [TDCP(NO₂)₇P]. These exhibit unusually positive redox potentials and are easily reduced at 0 V (vs SCE) to π -anion radicals, at room temperature and even in the presence of O₂. We also describe the X-ray structure of the Ni complex which readily binds two axial tetrahydrofurans (THF) to form the first structurally characterized high-spin Ni(II) porphyrin with oxygenous axial ligands and which adopts a near-planar macrocycle conformation in spite of its multiple peripheral substituents.

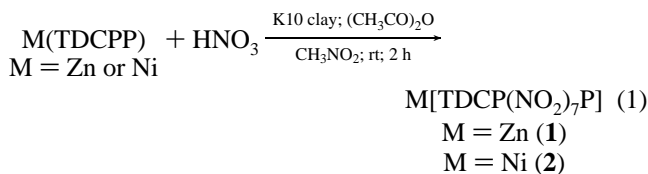
Nitration of Zn(TDCPP) with red fuming HNO₃ normally yields mixtures of stereoisomers of β -pentanitro- and β -hexanitro-Zn(TDCPP).⁴ We recently found a method for selective heptanitration of Zn (or Ni) (TDCPP) by using an excess of acetyl nitrate generated *in situ* from HNO₃ and (CH₃CO)₂O in

Table 1. Comparison of the Spectral and Redox Properties of **1** and **2** with Those of Zn(TDCPP) and Ni(TDCPP)

| | 1 | Zn(TDCPP) | 2 | Ni(TDCPP) |
|--|-----------|-----------|-----------|-----------|
| UV-vis | 459 (262) | 420 (371) | 465 (198) | 412 (332) |
| λ (nm) (ϵ in mM ⁻¹ cm ⁻¹) | 599 (18) | 550 (21) | 582 (22) | 529 (23) |
| in CH ₂ Cl ₂ | 645 (15) | | 624 (14) | 562 (13) |
| $E_{1/2}$ (mV vs SCE) ^a | | | | |
| 1st redn | 0 | -1285 | +170 | -1215 |
| 2nd redn | -225 | n.o. | -210 | n.o. |
| 3rd redn | -850 | n.o. | -700 | n.o. |

^a In CH₂Cl₂ containing 0.1 M NBu₄BF₄ at room temperature; working electrode: glassy carbon; scan rate: 50 mV/s; under these conditions, the Fe(III)/Fe(II) ferrocene couple is at 500 mV; n.o.: not observed.

the presence of K10 montmorillonite (eq 1).⁵ This reaction,



carried out in CH₃NO₂ at 20 °C for 2 h affords Zn[TDCP(NO₂)₇P] (**1**) as the major product in good yields (~50%) after purification by column chromatography on silica. The formulation of **1** is in complete agreement with its elemental analysis (C, H, N) and spectral characteristics. Its mass spectrum (MALDI) shows an isotopic cluster centered at $m/z = 1267$ for the molecular ion with an isotopic distribution identical to that calculated for Zn[TDCP(NO₂)₇P]. Its ¹H NMR spectrum (in CDCl₃) shows only one singlet for the pyrrole proton at 8.71 ppm (1H) and a multiplet at 7.81–7.56 ppm for the *meso*-aryl protons (12H). Its UV-visible spectrum is that of a Zn tetraarylporphyrin but with large red shift of the major bands to 459, 599, and 645 nm (Table 1).

Ni[TDCP(NO₂)₇P] (**2**) was prepared from Ni(TDCPP) under identical conditions (55% yield) and exhibits similar spectral characteristics (Table 1). Its molecular structure was confirmed by X-ray crystallography (Figure 1).⁶ Interestingly, the Ni is axially coordinated by two THFs (from the crystallization solvent mixture) with Ni–O distances of 2.138(8) Å. The two ligands are parallel to each other and are offset 6° from the Ni–N₂ vector. The average Ni–N distances of 2.061(9) Å are diagnostic of high-spin Ni(II) porphyrins with d^{1_x2-y²}, d^{1_z2} configurations.⁷ In further accord with the crystallographic evidence for high-spin Ni(II), Ni[TDCP(NO₂)₇P][THF]₂ exhibits a magnetic susceptibility of 3.0 μ_B (in THF, Evans method¹³) and a large chemical shift⁸ of the β -pyrrole hydrogen to 60.77 ppm in deuterated THF, the *meso*-aryl hydrogens at 8.42 ppm

(5) This procedure was an adaptation of that described by Thomas and Pews (Thomas, P. J.; Pews, R.G. *Synth. Commun.* **1993**, *23*, 505–508) for organic aromatic compounds.

(6) NiN₁₁C₄₄H₁₃O₁₄Cl₈·2(C₄H₈O)·4(C₄H₈O) (two THFs are bound to the Ni, and four THFs are located in the lattice) crystallized from CH₂Cl₂/THF in space group P1 with $a = 12.003(4)$ Å, $b = 14.081(4)$ Å, $c = 11.754(2)$ Å, $\alpha = 102.47(2)^\circ$, $\beta = 103.02(2)^\circ$, $\gamma = 76.76(3)^\circ$, $V = 1856(1)$ Å³, and $Z = 1$. Data were collected at 298 K on an Enraf-Nonius CAD4 diffractometer with Mo K α radiation in the range $2^\circ \leq \theta \leq 22.5^\circ$. A total of 5122 reflections ($h \pm k \pm l$) were measured with 4844 unique and 2854 with $F_o > 3\sigma(F_o)$. Refinement yielded $R_F = 0.096$ and $R_{wF} = 0.099$. Additional details are available in the Supporting Information. How the disorder was located and resolved is described in the Supporting Information (the experimental section contains a CIF file on this point).

(7) In several high-spin Ni(II) porphyrins with nitrogenous ligands, the Ni–N distances to the pyrroles range between 2.0 and 2.1 Å: (a) Kirner, J. F.; Garofalo, J.; Scheidt, W. R. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 107. (b) Balch, A. L.; Noll, B. C.; Phillips, S. L.; Reid, S. M.; Zovinka, E. P. *Inorg. Chem.* **1993**, *32*, 4730–4736. (c) Renner, M. W.; Barkigia, K. M.; Melamed, D.; Smith, K. M.; Fajer, J. *Inorg. Chem.* **1996**, *35*, 5120–5121. (d) Duval, H.; Bulach, V.; Fischer, J.; Weiss, R. *Acta Crystallogr., Sect. C*, in press.

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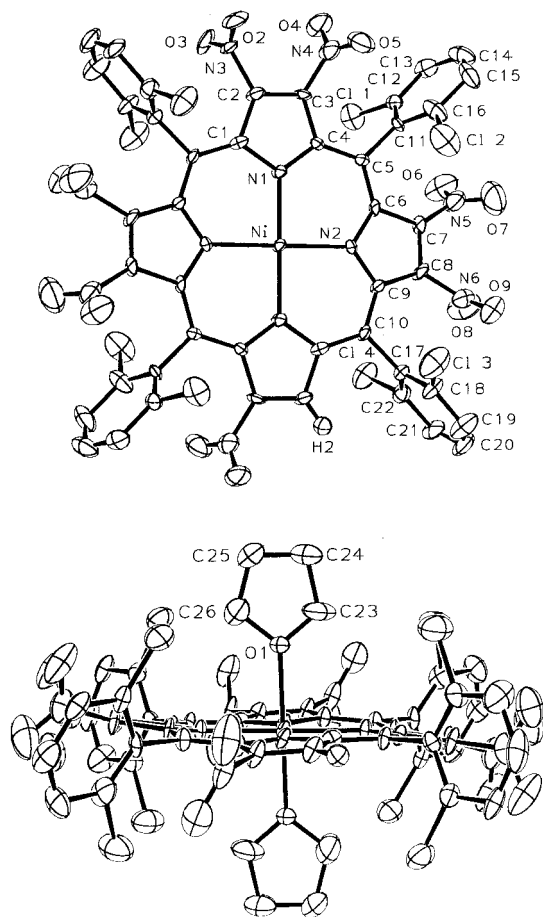


Figure 1. Molecular structure and atom names of **2**(THF)₂.⁶ (top) View from above with the axial ligands removed. (bottom) Edge-on-view with the two THF axial ligands. Thermal ellipsoids enclose 30% probability (except for H2). The N3 nitro group and H2 hydrogen interchangeably occupy their respective positions half the time.

being less shifted. In contrast, **2** is low spin and diamagnetic in CDCl₃ with the pyrrole hydrogen at 8.51 ppm and the *meso*-aryl protons (12H) at 7.59–7.70 ppm. Unlike low- and high-spin Ni(II) porphyrins with multiple substituents at the *meso* and β positions which are usually severely distorted because of steric interactions,^{3a,7c,9} the macrocycle of **2** is nearly planar and displays only a small ruffling with deviations from the average 24 atom plane of -0.01 , 0.13 , 0.04 , -0.16 , -0.06 , and -0.13 Å at C₂, C₃, C₅, C₇, C₈, and C₁₀, respectively. The modest ruffling results from a minimum of steric crowding between the phenyl and nitro groups. The latter are oriented at steep

angles of 79°, 65°, 67°, and 86° to the porphyrin plane at N3, N4, N5, and N6, respectively, and the phenyl groups also tend towards orthogonal dihedral angles of 73° and 87° at C5 and C10, respectively.

Cyclic voltammograms of **1** and **2** in CH₂Cl₂ first show reversible one-electron reductions at unusually positive potentials for such metalloporphyrins (Table 1).¹⁰ The reductions occur at 0 and +170 mV vs SCE for the Zn and Ni complexes, respectively, 1.20 and 1.4 V higher than the reductions of Zn(TDCPP) and Ni(TDCPP). By comparison, the cathodic shifts observed upon β -octabromination or β -octachlorination of Zn tetrakis(pentafluorophenyl)porphyrin were only 0.47 and 0.48 V, respectively.^{2b} The one-electron reductions of **1** and **2** were monitored by spectroelectrochemistry and EPR spectroscopy. Upon electrolysis of CH₂Cl₂ solutions of **1** and **2** at -150 and -100 mV, respectively, their visible spectra were progressively replaced, with isosbestic points, by those of the corresponding π -anion radicals with characteristic new absorption bands centered at around 900 nm (for **1**) and 770 nm (for **2**).¹¹ Oxidation of the π -anion radicals either electrochemically or chemically with tBuOOH as an oxidant led to complete recovery of the parent complexes. The EPR spectra of the one-electron reduction products of **1** and **2** showed only single signals at $g = 2$ (4 K or room temperature, CH₂Cl₂), characteristic of free radicals delocalized on the porphyrin macrocycles.^{11c} It is noteworthy that the porphyrin π -anion radicals were generated in the presence of dioxygen and were stable at room temperature for several hours.

Cyclic voltammograms of **1** and **2** further show two additional, reversible one-electron reductions, at -225 and -850 mV for **1** and -210 and -700 mV for **2**. Remarkably, it is easier to perform two- and even three-electron reductions of **1** and **2** than a single-electron reduction of Zn(TDCPP) and Ni(TDCPP) (Table 1). This capacity of **1** and **2** to accept three electrons in reversible electrochemical steps at potentials less than -1 V (vs SCE) is striking for metalloporphyrins.¹² The reducing properties of the dianions and trianions of metallo TDCP(NO₂)₂P complexes toward organic substrates are under investigation.

In conclusion, the aforementioned selective access to TDCP-(NO₂)₂P opens the way to a series of metalloporphyrins with drastically altered redox properties and, thus, with potential applications in electrochemistry, organic chemistry, and catalysis.

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Supporting Information Available: Experimental crystallographic details, positional and anisotropic thermal parameters for **2**, and additional structural diagrams and deviations from planarity (9 pages). See any current masthead page for ordering and Internet access instructions. CIF data also available via Internet only.

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(12) By comparison, the Ni and Zn complexes of β -tetracyanotetraphenylporphyrin have been reported to also exhibit potentials shifted by about +1 V relative to Ni and Zn(TPP) for their first and second one-electron reductions. However, they did not exhibit a third reversible reduction wave. Giraudeau, A.; Callot, H. J.; Jordan, J.; Ezahr, I.; Gross, M. *J. Am. Chem. Soc.* **1979**, *101*, 3857–3862.

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