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Note

One-pot dodecanitration of Zn(II) and Ni(II) *meso*-tetrakis-(2,6-dichlorophenyl) porphyrin, and extreme redox properties of the obtained complexes

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Abstract

Introduction of 12 nitro substituents on Zn(II) and Ni(II) [*meso*-tetra-(2,6-dichlorophenyl)porphyrin = TDCPP] was performed by adapting a recently described method for polynitration of metalloporphyrins, allowing the one-pot synthesis of metallododecanitroporphyrins from commercially available compounds. The corresponding complexes exhibit the highest reduction potentials ever described for such metalloporphyrins, which are shifted by more than + 1.6 V when compared with those of Zn and Ni(TDCPP). The Ni (dodecanitroporphyrin) complex underwent four successive, reversible one-electron reductions between + 470 and − 555 mV (vs. SCE). The one-electron reduction product of the Ni dodecanitroporphyrin is stable for hours at room temperature even in aerobic conditions; its visible and EPR spectra indicate a Ni (porphyrin radical anion) structure. © 2002 Elsevier Science B.V. All rights reserved.

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Iron, manganese and ruthenium complexes of *meso*-tetraarylporphyrins have been used as oxidation catalysts that mimic some of the properties of cytochromes P450 [1–6]. It has been shown that metalloporphyrins bearing many electron-withdrawing β-substituents such as halogeno or nitro groups, are particularly efficient catalysts for monooxygenation of hydrocarbons including alkanes [4,6–9]. In an effort to obtain metalloporphyrins with significantly altered redox potentials and unusual reactivities, we have recently developed a very powerful nitrating system based on red fuming HNO_3 and the superacid CF_3SO_3H in the presence of $(CF_3SO_2)_2O$. Application of this system to Zn[*meso*-tetra-(2,6-dichlorophenyl)porphyrin = TDCPP) allowed us to prepare the corresponding Zn(β-octanitroporphyrin), as well as all the Zn (porphyrins) bearing between one and seven β-nitro substituents in high yields, from titration of Zn (TDCPP) with increasing amounts of HNO_3 and CF_3SO_3H in the presence of $(CF_3SO_2)_2O$ Eq. (1)) [10].

$$\mathrm{Zn(TDCPP)} \xrightarrow[(CF_3SO_2)_2O]{HNO_3 - CF_3SO_3H} \underset{1 \le x \le 8}{\mathrm{Zn[TDCP(NO_2)_{\mathit{x}}P]}} \qquad (1)$$

We here describe an application of this system for the one-pot dodecanitration of the Zn(II) and Ni(II) complexes of $TDCPPH_2$, by using a modified version of the previously described method. This led to the synthesis of metalloporphyrins that exhibit the highest reduction potentials described so far for Zn(II) and Ni(II) porphyrins.

During our study of the best conditions for polynitration of the β-positions of the tetrapyrrole ring of Ni(II) or Zn(II) (TDCPP), we have observed that the use of too high concentrations of CF_3SO_3H or $(CF_3SO_2)_2O$ led to a partial nitration of the *meso*-phenyl rings besides the expected nitration of the tetrapyrrole β-positions. This led us to use the following conditions that result in a one-pot synthesis of $Ni[TDCm(NO_2)P(NO_2)_8P]$ in which eight β-nitro substituents have been introduced on the tetrapyrrole ring of Ni(TDCPP) and a *meta*-nitro substituent on each *meso*-aryl ring of Ni(TDCPP) (Fig. 1). In a first step, Ni(TDCPP), 5×10^{-3} M in CH_3NO_2, was treated with 380 equivalents of red fuming HNO_3 in the presence of

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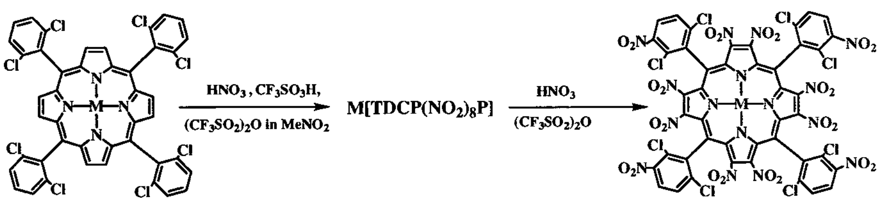

M[TDCPP]
M= Ni, Zn

M[TDCm(NO$_2$)P(NO$_2$)$_8$P]
M= Ni, Zn

Fig. 1. One-pot dodecanitration of Zn(II) and Ni(II).

CF_3SO_3H and $(CF_3SO_2)_2O$ [HNO_3:CF_3SO_3H:$(CF_3SO_2)_2O$ molar ratio = 1:0.12:0.06] for 5 days at 30 °C, according to the previously described procedure for β-octanitration of Zn and Ni(TDCPP) [10]. Intermediate formation of Ni[TPCP(NO_2)$_8$P] was observed by visible spectroscopy, as shown by a shift of the Soret peak of the starting metalloporphyrin from 412 to 470 nm. Then, CH_3NO_2 was removed by distillation under vacuum and the resulting solid redissolved in $(CF_3SO_2)_2O$ containing a small amount of CH_3NO_2 (5:1 v/v). The reaction mixture was then treated with 190 equivalents of red fuming HNO_3 for 24 h at 20 °C. In this medium, *meta*-nitration of the *meso*-(2,6-dichloro)phenyl substituents of the metalloporphyrin readily occurred leading to the dodecanitrated complex, Ni[TDCm(NO_2)P(NO_2)$_8$P] as a major product in a 36% yield based on starting Ni(TDCPP) (Fig. 1).

This complex was characterized by a red shifted Soret peak at 466 nm ($\varepsilon = 143$ cm^{-1} mM^{-1}) and α and β bands at 652 (7.8) and 605 (9.8) nm, as expected for a β-octanitro Ni(II)porphyrin [10]. Its mass spectrum (MALDI-TOF) was in agreement with the proposed structure, with a molecular cluster at $m/z = 1485.7$, whose isotopic distribution well corresponds to that calculated for $NiC_{44}H_8N_{16}O_{24}Cl_8$. Its elemental analysis, after lyophilization in a CH_2Cl_2–benzene mixture, was in agreement with a $NiC_{44}H_8N_{16}O_{24}Cl_8$, C_6H_6, 0.5 CH_2Cl_2 formula. Finally, its ^{1}H-NMR spectrum clearly showed the loss of all the β-hydrogens of Ni(TDCPP) and the appearance of two sets of signals at 8.31 (4H, doublet, $J = 8.8$ Hz) and 7.77–7.85 (4H) ppm corresponding to the two hydrogens remaining on the *meso*-aryl rings after nitration of the most reactive position (*ortho* to a Cl substituent). As expected, the signal of the *para*-hydrogens of the *meso*-aryl rings is a doublet ($J = 8.8$ Hz), while that of the *meta*-hydrogens is more complex (mass if between 7.77 and 7.85 ppm, 4H) because the Ni porphyrin complex exists as a mixture of atropoisomers, due to a restricted rotation of the *meso*-aryl substituents of the tetrapyrrole ring. Ni[TDCm(NO_2)P(NO_2)$_8$P] was also prepared by nitration of the β-pyrrole positions of Ni[*meso*-tetra-(3-nitro-2,6-dichlorophenyl)porphyrin = TDCm(NO_2)PP] [11] by the HNO_3–CF_3SO_3H–$(CF_3SO_2)_2O$ system described recently [10]. This confirms the structure proposed for the product obtained by one-pot nitration of Ni(TDCPP).

Polynitration of Zn (TDCPP) by the same method led to the corresponding Zn[TDCm(NO_2)P(NO_2)$_8$P] complex in a similar yield. The spectral characteristics of this complex were very similar to those of Ni[TDCm(NO_2)P(NO_2)$_8$P] (Table 1).

Reduction of Ni[TDCm(NO_2)P(NO_2)$_8$P] was studied by cyclic voltammetry in CH_2Cl_2 containing 0.1 M Bu_4NPF_6. Four successive, reversible one-electron reductions of this complex were observed at + 470, + 110, − 420 and − 555 mV (vs. saturated calomel electrode: SCE). By comparison, Ni(TDCPP) was only able to undergo a one-electron reduction at a much more negative potential (− 1215 mV) [12] (Table 2). Under identical conditions, the corresponding Zn complex, Zn[TDCm(NO_2)P(NO_2)$_8$P], underwent four successive, reversible one-electron reductions at + 370, 0, − 635 and − 820 mV, whereas Zn(TDCPP) was only

Table 1
Spectral characteristics of Ni and Zn[TDCm(NO_2)P(NO_2)$_8$P]

Complex	Visible spectrum [a] λ m in nm (ε in cm^{-1} mM^{-1})			^{1}H-NMR [b] δ (ppm)	Mass spectrum [c] molecular ion m/z
Ni[TDCm(NO_2)-P(NO_2)$_8$P]	466, (143)	605, (10)	652, (7.8)	8.31 (*d*, $J = 8.8$ Hz,4H *para*) 7.77–7.85 (m, 4H, *meta*)	1485.7
Zn[TDCm(NO_2)-P(NO_2)$_8$P]	463, (163)	600, (13)	642, (9)	8.3 (*d*, $J = 8.7$ Hz,4H *para*) 7.71–7.88 (m, 4H, *meta*)	1493.6

[a] In CH_2Cl_2.

[b] In $CDCl_3$.

[c] MS (MALDI-TOF): position of the most intense peak of the isotopic cluster corresponding to the molecular ion.

Table 2
Redox potentials for the successive, reversible one-electron reductions of Ni and Zn[TDCm(NO_2)P(NO_2)$_8$P]

Complex	Redox potentials [a] (mV vs. SCE)			
	First	Second	Third	Fourth
	One-electron reductions			
Ni(TDCPP)	−1215	n.o.	n.o.	n.o.
Ni[TDCm(NO_2)P(NO_2)$_8$P]	+470	+110	−420	−555
Zn(TDCPP)	−1285	n.o.	n.o.	n.o.
Zn[TDCm(NO_2)P(NO_2)$_8$P]	+370	0	−635	−820

[a] Conditions: 1 mM complex in CH_2Cl_2 containing 0.1 M Bu_4NPF_6; sweep rate: 50 mV s^{-1}; n.o., reduction not observed in the electroactivity domain of CH_2Cl_2.

able to undergo a one-electron reduction at −1285 mV [12] (Table 2). These results illustrate the remarkable properties of the dodecanitro complexes as electron reservoirs. They exhibit an unusually high redox potential for the first reversible reduction of the metalloporphyrin, the values observed for the Ni and Zn [TDCm(NO_2)P(NO_2)$_8$P] complexes (+470 and +370 mV, respectively) being the highest reduction potentials described so far for Ni and Zn porphyrins. Introduction of the twelve nitro substituents thus led to a positive shift of the reduction potentials of Zn(DCPP) and Ni(TDCPP) of +1615 and +1685 mV, respectively. Therefore, it was particularly easy to obtain the radical anions derived from the one-electron reduction of the Zn(II) and Ni(II) polynitroporphyrin complexes, either by preparative electrochemistry in CH_2Cl_2 at room temperature (r.t.), or by chemical reduction using very mild reducing agents such as $O_2^{\bullet -}$, piperidine or hydroquinone.

The reduced species derived from Ni[TDCm(NO_2)-P(NO_2)$_8$P] was characterized by visible and EPR spectroscopy. Its visible spectrum with two less intense peaks at 475 and 510 nm (relative to the starting complex) and a broad band in the near IR, around 780 nm, and its EPR spectrum (4K) that exhibits a signal at $g = 2$, are characteristic of a Ni(porphyrin radical anion) species [13]. Reoxidation of this species at more positive potentials led to starting Ni[TDCm(NO_2)-P(NO_2)$_8$P] in a quantitative yield. The radical anion of the Ni polynitroporphyrin is remarkably stable at r.t. for hours even in the presence of dioxygen, in contrast to what was observed for the radical anion of Ni(TDCPP) which was only produced at very low redox potentials under highly controlled anaerobic conditions [13]. As far as the extreme redox properties of Zn and Ni polynitroporphyrins are concerned, it is noteworthy that the four-electron reduced species of Ni[TDCm-(NO_2)P(NO_2)$_8$P] was obtained at a much higher redox potential, −555 mV, than the one-electron reduced species of Ni(TDCPP) (−1215 mV, see Table 2). The structure and chemical properties of the two-, three- and four-electrons reduced species derived from Zn and Ni[TDCm(NO_2)P(NO_2)$_8$P] are currently under study.

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