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THE REACTION OF METALLOPORPHYRINS WITH NITROGEN DIOXIDE

J. C. FANNING*, F. S. MANDEL and T. L. GRAY
Department of Chemistry and Geology, Clemson University, Clemson, SC 29631, U.S.A.

and

N. DATTA-GUPTA
Department of Natural Sciences, South Carolina State College, Orangeburg, SC 29115, U.S.A.

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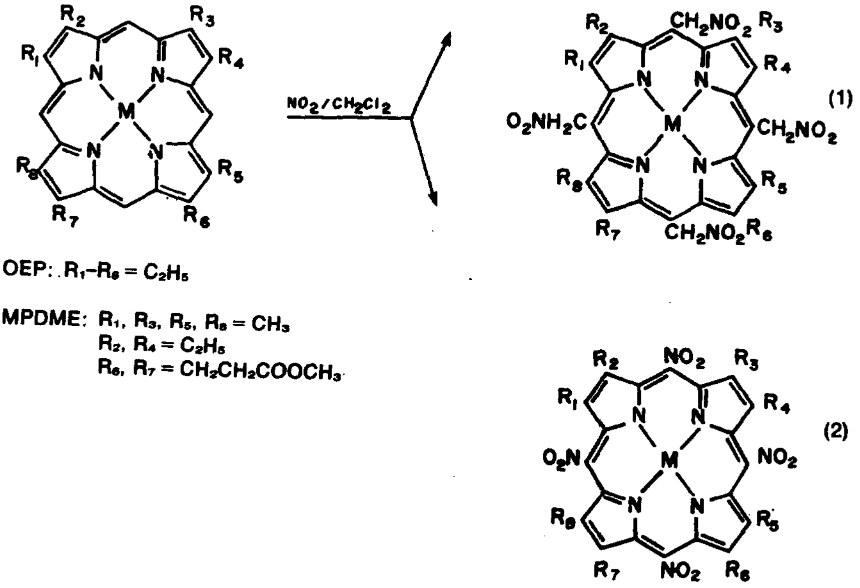
Abstract—The octaethylporphyrin(OEP) complexes of iron(III) chloride, iron(III) acetate, thallium(III) hydroxide, zinc(II), and cobalt(II) and the mesoporphyrin IX dimethyl ester (MPDME) complexes of zinc(II) and iron(III) chloride were reacted with a 20:1 ratio of NO_2 to metalloporphyrin in CH_2Cl_2. The +3 metalloporphyrins gave products which had a nitromethyl group in each of the four *meso* positions of the porphyrin ring and a chloride ion bound to the metal atom. The products of +2 metalloporphyrin reaction had a nitro group bound in each of the *meso* positions. The spectral and electrochemical properties of some of the products were measured. ^{36}Cl labelled OEPFeCl was reacted with NO_2 in CH_2Cl_2. The product, *meso*-tetranitromethyl OEPFeCl, had 17% of the original activity which indicates that the chloride ion bound to the iron is exchanged with chloride ions formed in the reaction. The nitromethylation reaction appears to involve initially the displacement of chloride from iron(III) by NO_2 and solvent attack on the bound NO_2. The *meso*-nitration of the +2 metalloporphyrin by NO_2 has been proposed to proceed by a π-cation radical mechanism (E. C. Johnson and D. Dolphin, *Tetrahedron Letters* 2197 (1976).

The reactivity of the porphyrin ring in metalloporphyrins has received a large amount of attention in recent years.[1] The central metal ion may strongly influence the nature of the reaction by inducing changes in the negative charge on the porphyrin periphery.[2] We reported that the reaction of OEPFeCl with NO_2 in CH_2Cl_2 produced a *meso*-tetranitromethylated product (1).[3] Johnson and Dolphin observed that OEPMg under the same conditions reacts to form the *meso*-tetranitro product (2).[4] They showed that the nitration proceeded in a stepwise manner involving the initial formation of a π-cation radical, $[OEPMg]^+$. Since the two metal complexes gave such different products under the same conditions, we felt it would be of interest to react other metalloporphyrins with NO_2 in CH_2Cl_2 and compare their reactivity with the two reported. Porphyrin complexes of Zn(II), Co(II), TL(III) and other Fe(III) complexes were studied. Shown below are the structures of the porphyrin ligands used and the possible reaction products.

EXPERIMENTAL

General. Metalloporphyrins were prepared following literature procedures:[5] OEPFeCl, MPDMEFeCl, OEPFeOAc, $(OEPFe)_2O$, OEPZn, MPDMEZn, OEPTlOH and OEPCo. Reagent grade



(1)

(2)

OEP: R_1–R_8 = C_2H_5

MPDME: R_1, R_3, R_5, R_8 = CH_3
R_2, R_4 = C_2H_5
R_6, R_7 = $CH_2CH_2COOCH_3$

organic solvents were distilled prior to use and stored over molecular sieves. Porphyrin ligands were purchased from Sigma Chemical Corp. and made in one (N.D-G.) of our laboratories. Microanalyses were performed by Galbraith Laboratories Inc., Knoxville, Tennesse. IR spectra were obtained on a Perkin-Elmer Model 621 Recording Spectrometer. UV -visible spectra were measured using a Cary 14 Spectrometer. A Bruker FT HX-90 Spectrometer was used to obtain ^1H and ^2H NMR spectra. TMS was used to reference ^1H spectra and deuterated cyclohexane was used to reference the ^2H spectrum.

Electrochemical measurements. Half-wave reduction potentials, $E_{1/2}$, were measured using a hanging Hg drop electrode and a PAR Model 174A Polarographic Analyzer. The solvent used was 0.1 M tetraethylammonium perchlorate (TEAP) in freshly distilled N,N-dimethylformamide (DMF). Sample concentrations were 1.4×10^{-3} M.

NO_2–CH_2Cl_2 *Solution.* NO_2 gas (Matheson C.P.) was slowly bubbled into 50 ml of CH_2Cl_2 at room temp. until the soln became light red. The NO_2 concentration used for the reactions described below was about 0.2–0.3 M as determined by acid-base titration. For this determination an aliquot of the soln was shaken with a known volume of standard aqueous base and the excess base titrated with standard acid. *Care was taken with the* NO_2–CH_2Cl_2 *soln since it is known to be shock-sensitive.*[6] The ^1H NMR spectrum of fresh and old (*ca* 1 month) solns showed no bands other than that due to the CH_2Cl_2.

Metalloporphyrin reactions. A typical reaction was carried out by dissolving 25 mg of the metalloporphyrin in 50 ml of CH_2Cl_2. Enough of the NO_2 soln was added to give a NO_2 to metalloporphyrin ratio of 20:1. The soln was allowed to stand from 15–30 min after which the solvent and NO_2 were removed by a dry N_2 stream. The product was redissolved in a small amount of CH_2Cl_2. The Fe(III) complexes were chromatographed on a Sephadex LH-20 (Pharmacia Fine Chemicals) column and then on a talc column. They were recrystallized from CH_2Cl_2. The products from MPDMEZn and the OEPCo reactions were purified by passing the solns through a Sephadex LH-20 column and recrystallized from CH_2Cl_2. The OEPZn product was purified by passing the soln through a silica gel column, eluting the major product with petroleum ether, and recrystallizing the product from CH_2Cl_2. All solid products were dried *in vacuo* at 100° over P_2O_5 for about 16 hr.

meso-*Tetra*(*nitromethyl*)*octaethylporphyrin iron*(III) *chloride*, 48% yield. (Found: C, 55.64; H, 5.51; N, 13.02; Cl, 4.59; Fe, 6.40. $C_{40}H_{48}N_8O_8FeCl$ requires: C, 55.85; H, 5.62; N, 13.03; Cl, 4.12; Fe, 6.49%). λ (CH_2Cl_2) 375(68600), 510(8300), 644(3800). IR ν_{NO_2}(CH_2Cl_2) 1537, 1362 cm^{-1}. ^1H NMR δ($CDCl_3$) 38(24H), 4(16H), −1(8H).

meso-*Tetra*(*nitromethyl*)*mesoporphyrin IX dimethyl ester iron*(III) *chloride*, 48% yield. (Found: C, 52.45; H, 4.67; N, 12.00. $C_{40}H_{44}N_8O_{12}FeCl$ requires: C, 52.21; H, 4.82; N, 12.18%). λ(CH_2Cl_2) 375(36000), 510(3400), 545(2900), 642(1300). IR ν_{NO_2} (CH_2Cl_2) 1532, 1360 cm^{-1}. $E_{1/2}$ vs Ag/AgCl (DMF, 0.1 M TEAP) −0.07, −0.55, −1.18 V. $E_{1/2}$ values for MPDMEFeCl under the same conditions: −0.32, −1.26, −1.88 V.

meso-*Mono*(*nitromethyl*)*mesoporphyrin IX dimethyl ester iron*(III) *chloride*. The ratio of NO_2 to complex was 1:1 for this preparation. The rest of the procedure was the same as that for the other Fe(III) complexes. 59% yield. (Found: C, 60.02; H, 5.44; N, 9.22. $C_{37}H_{41}N_5O_6FeCl$ requires: C, 59.81; H, 5.56; N, 9.43%). λ(CH_2Cl_2) 378(97000), 510(8000), 535(7800), 638(3900). IR ν_{NO_2} (KBr disc) 1530, 1370 cm^{-1}.

meso-*Tetranitrooctaethylporphyrin zinc*(II), 51% yield. This compound was isolated, dissolved in $CDCl_3$ (10% C_5H_5N) and the ^1H NMR spectrum obtained. The excess solvent was removed and a portion of the sample dissolved in CH_2Cl_2 and the visible spectrum measured. The remainder of the sample was analyzed and from the analysis the sample appeared to be the bispyridine adduct. (Found: C, 59.72; H, 5.77; N, 14.42. $C_{46}H_{50}N_{10}O_8Zn$ requires: C, 59.00; H, 5.38; N, 14.96%). λ(CH_2Cl_2) 430(76500), 510(5900), 578(10800), IT ν_{NO_2} (KBr) 1530, 1365 cm^{-1}. ^1H NMR δ($CDCl_3$ and 10% C_5H_5N) 1.33(5, 24H), 3.45(q, 16H).

meso-*Tetranitromesoporphyrin IX dimethylester zinc*(II), 38% yield. (Found: C, 50.99; H, 4.94; N, 13.20; Zn, 7.89. $C_{36}H_{36}N_8O_{12}Zn$ requires: C, 51.59; H, 4.33; N, 13.37; Zn, 7.80%). λ(CH_2Cl_2) 360(23000), 426(56700), 560(8700). λ(C_5H_5N) 365(6100), 433(56700), 567(6900). IR ν_{NO_2} (KBr) 1530, 1370 cm^{-1}.

$E_{1/2}$ vs Ag/AgCl(DMF, 0.1 M TEAP) − 0.05, − 0.24 V. $E_{1/2}$ values for MPDMEZn under the same conditions: − 0.11, − 1.98, − 2.40 V.

meso-*Tetranitrooctaethylporphyrin cobalt*(III) *hydroxide trihydrate*, 40% yield. This product apparently added four moles of water at some stage during its preparation and handling. (Found: C, 51.21; H, 5.73; N, 13.33. $C_{36}H_{48}N_8O_{12}Co$ requires: C, 51.24; H, 5.73; N, 13.28%). λ(CH_2Cl_2) 410(31700), 545(6600), 580(6200), 671(5300). IR ν_{NO_2} (KBr) 1530, 1383 cm^{-1}. ^1H NMR δ($CDCl_3$) 1.21(24H), 3.72(16H). This compound is diamagnetic.

Reaction of octaethylporphyrin thallium(III) *hydroxide.* A 10 mg sample of OEPTlOH was reacted with NO_2 in CH_2Cl_2 by the method described above. The product soln was chromatographed twice on a Sephadex LH-20 column. Recrystallization from CH_2Cl_2 gave 8 mg of product, presumably the *meso*-tetranitromethylated OEPTlCl. The 8 mg sample was used to obtain the visible, NMR, and IR spectra. Only enough sample was available for carbon and hydrogen analysis. (Found: C, 48.44; H, 5.98. $C_{40}H_{48}N_8O_8TlCl$ requires: C, 47.63; H, 4.80%). λ(CH_2Cl_2) 426(99200), 516(7920), 556(5540), 591(3500). IR ν_{NO_2} (KBr) 1537, 1362 cm^{-1}. ^1H NMR δ($CDCl_3$) 1.95(24H), 4.2(16H), 4.9(8H).

Labeling experiment. A ^{36}Cl sample of OEPFeCl was prepared by stirring a benzene soln of $(OEPFe)_2O$ with a 6M aqueous $H^{36}Cl$(50 μc) soln (Tracerlab Inc.). The benzene layer was passed through anhy Na_2SO_4, the solvent removed and the solid dried at 100° under vacuum. The total count rate of the 5 mg sample of $OEPFe^{36}Cl$ prepared was 725 cpm. The sample was reacted with NO_2 in CH_2Cl_2 following the procedure given above. After passing the soln of the product through the Sephadex column, the soln was collected, solvent removed and product dried at 100° under vacuum. The total count rate of the sample was 125 cpm (17.2% of the original rate). There was no evidence of any residue on the Sephadex column.

The activities of the labeled samples were measured on a Nuclear Chicago Model 8775 Scaler. The samples were mounted on Mylar windows and placed in a Technical Associates Model 156 Lead Shield. Background counts were negligible. Each count rate was determined for several different times and average counts per minute reported.

RESULTS AND DISCUSSION

The reaction of metalloporphyrins with NO_2 in CH_2Cl_2 is rapid and appears to be instantaneous at room temperature. However, in order to insure complete reaction, the solution of reactants was allowed to stand for at least 15 min before isolating the product. An attempt was made to slow the reaction of OEPFeCl with NO_2 by lowering the reaction temperature to 0°. The visible spectrometer sample compartment was fitted with a low temperature solution cell and the reaction carried out in the cell. Qualitatively the reaction was just as fast at the low temperature as at room temperature. Most of the reactions were carried out at metalloporphyrin concentrations of about 10^{-3} M. Reducing the concentration and ratio of NO_2 to metalloporphyrin did not appear to reduce the rate. Fresh and month old NO_2 solutions gave the same results.

Using solvents (benzene, dibromomethane, and nitromethane) other than CH_2Cl_2, or using Fe(II and III) porphyrin pyridine adducts instead of the chloroiron(III) porphyrins, gave considerable porphyrin decomposition with no isolable iron porphyrin product. A large amount of porphyrin decomposition occurred when the μ-oxoiron(III) porphyrin dimers were reacted with NO_2 in CH_2Cl_2.

Reaction products

The *meso*-tetranitromethyl product of the OEPFeCl reaction has been characterized by analysis, ^1H NMR spectrum, and magnetic susceptibility measurements.[3] A similar product is formed when MPDMEFeCl reacts with NO_2 in CH_2Cl_2. Using a small ratio of NO_2 to MPDMEFeCl produced a *meso*-mononitromethyl product. Nitromethylation appears to occur in a stepwise manner as does nitration.[4]

The methylene groups added come from the solvent. When the reaction was carried out in CD_2Cl_2 a product resulted which when dissolved in CH_2Cl_2 showed a single ^2H NMR line at -13.7 Hz from C_6D_{12}. (CD_2Cl_2 had a resonance at -46 Hz from C_6D_{12}.)

The NMR spectrum of the product of the reaction of OEPTlOH with NO_2 in CH_2Cl_2 indicated that *meso*-tetranitromethylation took place. The spectrum had broad peaks and no peak at δ 10.3 ppm due to *meso* protons.[7] The area ratios showed that four methylene groups had added to the porphyrin. It is assumed on the basis of the reactivity of the Fe(III) complexes (see below) that the porphyrin thallium(III) chloride is formed; however, this is not known for certain.

The product of the reaction of OEPZn, MPDMEZn, and OEPCo with NO_2 in CH_2Cl_2 is the *meso*-tetranitro compound. The same *meso*-tetranitro OEPZn compound was made when metal-free $OEPH_2$ is nitrated with zinc(II) nitrate hexahydrate.[8] The reactivity of the Zn(II) and Co(II) complexes with NO_2 is identical to that reported for OEPMg;[4] however for Co(II), metal oxidation to the +3 state occurs. The same type of product was obtained with OEPZn and with MPDMEZn. Changing the porphyrin ligand did not change the reactivity behavior of either the Zn(II) or the Fe(III) complexes. More decomposition of the porphyrin ligand, as shown by the amount of materials left on the columns during purification, was observed in the Zn(II) and Co(II) reactions than in the Fe(III) reaction. Little material is left on the columns when purifying the Fe(III) compounds. The product yield of the Fe(III) compounds is reduced in the recrystallization procedure.

The color change of the Zn(II) complex solutions upon NO_2 reaction was much larger than that for the Fe(III) complexes (Fig. 1). The visible spectral bands of the products are shifted to longer wavelengths as compared to the starting compounds. This is expected since electron-withdrawing NO_2 groups are attached to the ring.[9] The direct attachment of the group to the ring produces a larger spectral change with the Zn(II) complexes than when a mediating CH_2 group is between the ring and NO_2 group, as in the case of the Fe(III) complexes.

The difference between *meso*-nitro and *meso*-nitromethyl compounds is also shown by the half-wave reduction potentials. The attachment of the NO_2 group to the ring causes the reduction potentials to be more positive as expected.[10] Like the spectral changes, there is a greater difference between the values for MPDMEZn and those for the *meso*-tetranitro product than between values for the MPDMEFeCl and the *meso*-tetranitromethyl product.

The IR frequencies of the bands due to the NO_2 group[11] were not significantly different whether the NO_2 group was bound directly to the ring or bound to the CH_2 group on the ring. The other bands in the spectrum due to the ring or attached groups were not shifted by nitration or nitromethylation.

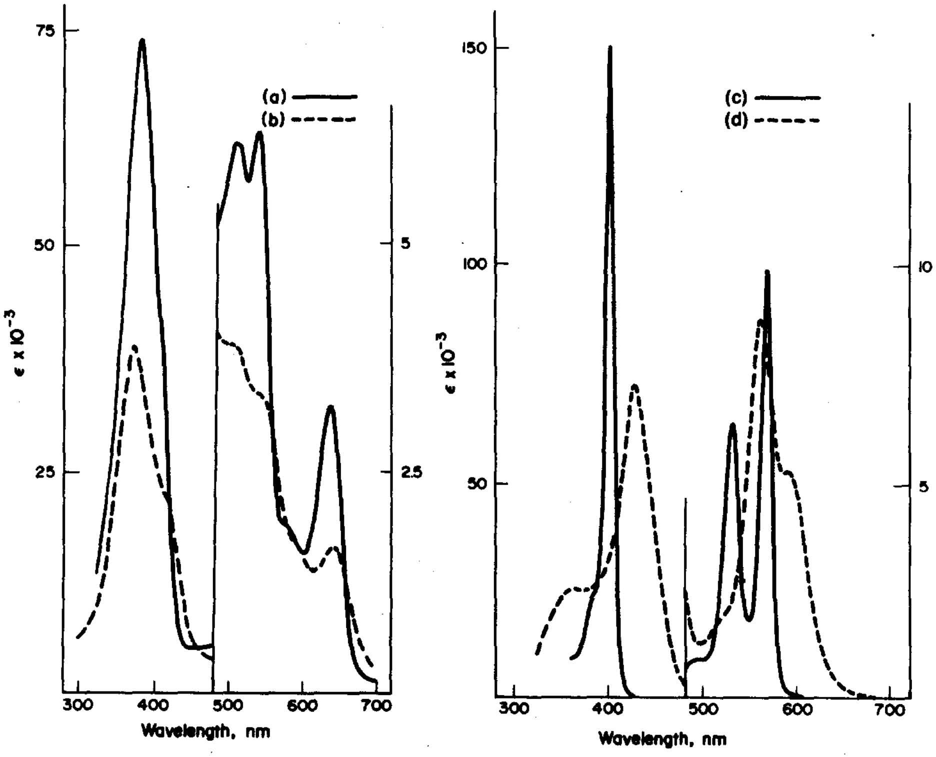


Fig. 1. Electronic spectra of the mesoporphyrin IX dimethyl ester (MPDME) complexes in dichloromethane of: (left spectra) (a) iron(III) chloride; (b) its *meso*-tetra nitromethyl product; (right spectra) (c) zinc(II); (d) its *meso*-tetra nitro product. (Note scale change of ϵ at 475 nm on each spectrum).

Reaction pathways

The *meso*-nitromethylation of the Fe(III) porphyrins is unique. We have been unable to find a similar reaction described in the organic chemistry literature. The addition of nitromethane to aliphatic aldehydes, catalyzed by base,

$$\mathrm{RCHO + CH_3NO_2 \rightarrow RCHOHCH_2NO_2}$$

is one way to introduce CH_2NO_2 groups into certain molecules.[12] NO_2 at high temperatures in the gas phase abstracts hydrogen atoms from CH_2Cl_2,[13] rather than displacing Cl atoms.

The Zn(II), Co(II) and Mg(II) porphyrins are oxidized to the π-cation radical which is then attacked by the NO_2 radical with an accompanying proton loss and, in the Co case, metal oxidation:[4]

$$\mathrm{Por(H)M \xrightarrow[-NO_2^-]{NO_2} Por(H)M^+ \xrightarrow[-H^+]{NO_2} Por(NO_2)M} \quad (3)$$

where H and NO_2 shown in parentheses occupy the *meso*-position. NO_2 is shown as the reactant; however, N_2O_4, which is in equilibrium with NO_2,[14] may be a reactant. The above mechanism is similar to that proposed for metalloporphyrin ring oxidation by hydrogen peroxide in pyridine.[15] Fe(III) porphyrins were found to be unreactive under such conditions.[16]

Meso-nitromethylation may occur in at least two ways:

$$\mathrm{Por(H)FeCl \xrightarrow[-Cl^-]{NO_2} Por(H)FeONO^+}$$
$$\mathrm{\xrightarrow[-H^+, Cl^\bullet]{CH_2Cl_2} Por(CH_2NO_2)FeCl} \quad (4)$$

or

$$\mathrm{Por(H)FeCl \xrightarrow[-Cl^\bullet]{NO_2} Por(H)FeONO}$$
$$\mathrm{\xrightarrow[-H^+, Cl^-]{CH_2Cl_2} Por(CH_2NO_2)FeCl} \quad (5)$$

The initial step for both pathways is the formation of a nitrite iron complex, FeONO, which occurs by displacing either a chloride ion (4) or a Cl atom (5). In 4 the resulting complex is a π-cation radical or an Fe(IV) complex, while in 5 it is an Fe(III) nitrite complex. In either case the NO_2 group has been activated for attack by the solvent within the coordination sphere of the Fe. The exact details of the chloride displacement from CH_2Cl_2 and the resulting attack of the CH_2NO_2 group on the *meso* position are unknown. Nitrite ion displacements of chloride ion from alkyl chlorides are known.[17] In order to have charge balance in 4 when CH_2Cl_2 attacks the cationic complex a Cl atom must form. In 5 solvent attack on the neutral complex must produce a chloride ion to balance the charge of the H^+ ion produced.

In 3, 4 and 5 NO_2 is shown as an oxidizing agent. In water solution NO_2 has an oxidizing ability about equal to that of Br_2.[18] Other pathways involving the reduction of Fe(III) to Fe(II) by NO_2 might be devised but would not be as probable.

A reaction between NO_2 and $OEPFe^{36}Cl$ in dichloromethane resulted in a product which had slightly less than one-fifth the initial ^{36}Cl activity. The partial retention of activity in the product would be explained by assuming that 4 was followed and that the overall reaction was

$$\mathrm{Por(H)_4FeCl + 4NO_2 + 4CH_2Cl_2 \rightarrow Por(CH_2NO_2)_4FeCl + 4HCl + 4[Cl]}$$

where the Cl atoms, [Cl], might be lost as Cl_2 gas or react with excess NO_2 to form NO_2Cl.[19] By 4 all of the chloride bound to the Fe initially is kept in solution and not lost as a free radical (5). The proposed overall reaction shows five chloride ions in the product species (one with the complex and four with HCl). Since porphyrin iron(III) chlorides undergo halide exchange, (OEPFeCl rate of exchange $\geq 60\ \mathrm{sec}^{-1}$ at 45°)[20] the $^{36}Cl^-$ ion will equilibrate between the solution and complex producing one-fifth of the activity in the product. The actual activity would be expected to be slightly less than this because of side reactions.

The ligand bound to Fe(III) in the axial position does influence the nature of the reaction. When OEPFeOAc was reacted with NO_2 in CH_2Cl_2 the product yield was poor (*ca* 10%) and much decomposition was observed. The product was the same as that obtained by reacting OEPFeCl with NO_2.

N_2O_4 is a possible reactant in the nitromethylation reaction as well as in the nitration reaction. Both metalloporphyrins[21] and N_2O_4[22] are known to form donor-acceptor complexes. The first step of the reaction may involve the formation of a donor-acceptor complex between the two reactants. Decreasing the temperature of the N_2O_4–NO_2 equilibrium mixture increases the amount of N_2O_4 in the mixture.[14] The inability to slow the reaction by lowering the temperature might be due to the increase of the N_2O_4 concentration.

In order to rule out other possible reactions which might be producing the *meso*-tetranitromethyl product, OEPFeCl was treated with NO_2BF_4, $NOBF_4$ and NO_2Cl in CH_2Cl_2. No reaction was observed with any of the compounds. $ClCH_2NO_2$ was prepared[23] and added to a CH_2Cl_2 solution of OEPFeCl; again no reaction was observed. NO[24] and NO_2^- ions[25] form axial complexes with Fe(III) porphyrins. The *meso*-mononitro product forms when OEPFeCl reacts with nitrous acid in $CHCl_3$–HOAc–H_2O solution.[26]

Summary. The reaction of NO_2 with metalloporphyrins in CH_2Cl_2 is a striking example of the influence of the central metal atom in a complex on the reactivity of the ligand. There are several ways in which metal ions may influence ligand reactivity.[27] Strong polarization of the porphyrin by the positive charge on the iron and coordination activation of NO_2 by the iron may account for the unusual reactivity of the chloroiron(III) porphyrins. Other metalloporphyrins with the proper axial ligand(s) and porphyrin ring electron distribution may also react to produce a *meso*-nitromethylated product.

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