

Table I. Mössbauer Data for Substituted Pyridinehemochromes at 298 K

compound	$\delta^a$	$\Delta^b$	$\Gamma^c$	$N^d$	% effect <sup>e</sup>
[PMXPPFe-(4-DMAPy)]	+0.64	1.20	0.24	0.90	3.6
[PMXPPFe-2(4-AcPy)]	+0.64	1.22	0.24	1.48	2.4
[PMXPPFe-2(3-AcPy)]	+0.66	1.26	0.25	1.44	1.4
[PMXPPFe-2Py]	+0.64	1.27	0.25	1.31	2.8
[PMXPPFe-2(4-CNPy)]	+0.65	1.27	0.24	0.85	3.1
[PMXPPFe-2(4-MePy)]	+0.66	1.29	0.24	1.54	2.9
[PMXPPFe-2(3-CNPy)]	+0.66	1.29	0.23	0.59	3.7
[PMXPPFe-2(3,5-Me <sub>2</sub> Py)]	+0.67	1.31	0.25	0.44	2.5

<sup>a</sup> Isomer shift in mm/s relative to sodium nitroprusside;  $\pm 0.02$  mm/s. <sup>b</sup> Quadrupole splitting;  $\pm 0.02$  mm/s (sign not measured but almost certainly +). <sup>c</sup> Line width in mm/s at half-maximum. <sup>d</sup> Number of  $\gamma$ -ray counts under nonresonant conditions;  $\times 10^6$ . <sup>e</sup> The percent effect is  $[(N - N_p)/N] \times 100$ , where  $N_p$  is the number of counts at the velocity corresponding to a peak of absorption.

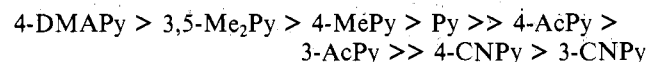
and 4-cyanopyridinehemochromes contained the expected CN frequency at  $2200 \text{ cm}^{-1}$ . The Mössbauer spectra of some of the compounds occasionally showed small contamination with the  $\mu$ -oxo complex, but the data could be easily corrected for this impurity.

Infrared spectra were recorded on a Beckman IR-8 spectrophotometer. Mössbauer spectra were measured on a scanned-velocity spectrometer operating in the time mode and calibrated with both sodium nitroprusside and  $^{57}\text{Fe}$  foil. Spectra were fitted with a least-squares approximation assuming two Lorentzian line shapes of equal width. Estimated error limits on the isomer shift,  $\delta$ , and quadrupole splitting,  $\Delta$ , are  $\pm 0.02$  mm/s. A Calcomp plotter was used to plot data.

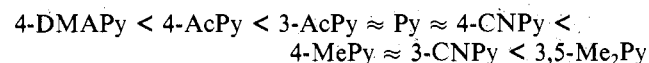
### Results and Discussion

Mössbauer data at 298 K for the eight hemochromes prepared for this study are given in Table I. All spectra consisted of a sharp, well-resolved symmetrical quadrupole doublet.

Because of the very strong crystal field provided by the porphyrin ring in a heme,  $V_{zz}$  (with  $z$  the crystal field  $\sim C_4$  axis) is positive in the bis(pyridine)hemochromes.<sup>3</sup> Thus, the stronger the axial ligand is as a  $\sigma$  donor the smaller should be the quadrupole splitting. The order of decreasing  $pK_a$ 's ( $\sigma$  base strengths) for the substituted pyridines used in this investigation is as follows:<sup>6</sup>



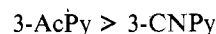
On the assumption that steric effects arising from coordination of the substituted pyridines to the heme are comparable in all cases, this same order should be found for increasing quadrupole splittings if the pyridines are functioning only as  $\sigma$  bases. From Table I it can be seen that the order of increasing splittings (and decreasing  $\sigma + \pi$  bond strengths) is as follows:



It is not possible to account for such splittings on the basis of  $\sigma$  bonding alone; e.g., the 4-DMAPy and 4-AcPy give the smallest, and very similar, splittings, yet their  $pK_a$ 's differ by about 5 units.

There is very good evidence that iron(II) in a hemochrome can be a  $\pi$ -electron donor, and pyridine can be a  $\pi$  acceptor.<sup>2,7</sup> The stronger the substituted pyridine is as a  $\pi$  acid, the smaller the quadrupole splitting of the resulting hemochrome. Cole et al.<sup>2</sup> determined the thermodynamic functions of various hemochromes and obtained good evidence that  $\sigma$  bonding predominated in 4-amino-, 4-methyl-, and 4-vinylpyridines and  $\pi$  bonding predominated in 4-cyano- and 4-carboxy-*n*-butylpyridines. Pyridine itself showed intermediate bonding. Accordingly, for our substituted pyridines,  $\pi$  bonding is ex-

pected to be especially important for 4-cyano- and 4-acetylpyridines and weakest for 4-methyl-, 3,5-dimethyl-, and 4-dimethylaminopyridines.<sup>8</sup> There are no directly applicable literature data on the  $\pi$ -bonding ability of 3-acetyl- and 3-cyanopyridines, but these probably have similar  $\pi$ -acceptor strengths; however 3-acetylpyridine is the stronger base. Although 4-acetylpyridine may be a somewhat weaker  $\pi$  acid than 4-cyanopyridine,<sup>9</sup> it is a much stronger  $\sigma$  base. Also, 4-dimethylaminopyridine is a much stronger base than either 4-methylpyridine or 3,5-dimethylpyridine. From these comparisons, involving both  $\sigma$ - and  $\pi$ -bonding characteristics, the partial orderings of strengths of interactions with heme iron should be as follows:



The Mössbauer splittings follow these partial orderings.

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**Registry No.** [PMXPPFe-(4-DMAPy)], 68757-63-1; [PMXPPFe-2(4-AcPy)], 68715-77-5; [PMXPPFe-2(3-AcPy)], 68715-78-6; [PMXPPFe-2Py], 50914-95-9; [PMXPPFe-2(4-CNPy)], 68715-79-7; [PMXPPFe-2(4-MePy)], 68715-80-0; [PMXPPFe-2(3-CNPy)], 68738-49-8; [PMXPPFe-2(3,5-Me<sub>2</sub>Py)], 68715-81-1.

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### Reactions on an Aromatic Heterocycle Containing Nickel: Electrophilic Substitution

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The oxidation of the aliphatic amine-oxime nickel complex (2,2,3,9,10,10-hexamethyl-5,7-dioxa-6-hydra-1,4,8,11-tetraazacyclotetradeca-3,8-diene)nickel(II) ion,  $[\text{Ni}(\text{PnAO})\text{-H}]^+$  (Figure 1a), has been shown to give the neutral, square-planar complex (2,2,3,9,10,10-hexamethyl-5,7-dioxa-6-hydra-1,4,8,11-tetraazacyclotetradeca-3,8,11,13-tetraene)nickel(II),  $[\text{Ni}(\text{PnAO})\text{-6H}]^{12}$  (Figure 1b), having aromatic-like properties and containing the heteroatom, nickel, in the ring. The aromatic nature of this compound relative to that of the parent unoxidized complex,  $[\text{Ni}(\text{PnAO})\text{-H}]^+$ , was shown by both chemical and spectral data.<sup>3</sup>

Table I.  $^1\text{H}$  NMR Spectra in Chloroform- $d_1$  (Downfield, ppm, Compared with Internal  $\text{Me}_4\text{Si}$ )

[Ni(PnAO)-6H]								
1.34 (12,c) <sup>d</sup>	1.96 (6,d)	5.07 <sup>a</sup> (1,a)	7.04 <sup>b</sup> (2,b)					19.1 <sup>c</sup> (1,e)
[Ni(PnAO)-7H(X)] (X = Cl, Br, I, or NO <sub>2</sub> )								
1.34 (12,c)	1.96 (6,d)		7.22 (Cl) (2,b)	7.26 (Br) (2,b)	7.29 (I) (2,b)	8.52 (NO <sub>2</sub> ) (2,b)	18.9 <sup>c</sup> (NO <sub>2</sub> ) (1,e)	19.1 <sup>c</sup> (Cl, Br, I) (1,e)
[Ni(PnAO)-7H(NO)]								
1.38 (6,g)	1.58 (6,c)	2.02 (3,f)	2.07 (3,d)	7.58 (1,h)	8.80 (1,b)		18.9 <sup>c</sup> (1,e)	

<sup>a</sup> Average triplet. <sup>b</sup> Average doublet. <sup>c</sup> Disappear upon addition of D<sub>2</sub>O. <sup>d</sup> Relative signal intensities and their assignment.

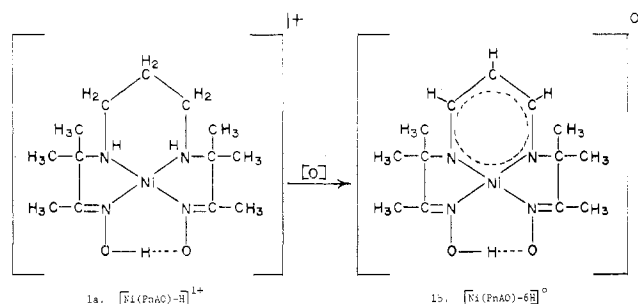


Figure 1. Oxidation of  $[\text{Ni}(\text{PnAO})-\text{H}]^{+}$  to  $[\text{Ni}(\text{PnAO})-6\text{H}]^0$  in basic solution using (1) molecular oxygen and (2) other oxidizing agents.

Previous work, utilizing several different experimental methods, has shown that 15-membered macrocyclic complexes of nickel(II) containing two charge-delocalized six-membered chelate rings have undergone electrophilic displacement of acetyl groups attached to the central ring carbon atoms by nitro groups.<sup>4</sup> Electrophilic substitution of a formyl group on the central ring carbon atom of a 13-membered macrocyclic nickel(II) complex has also been carried out.<sup>5</sup> Systematic electrophilic substitution reactions involving halogenation, nitration, thiocyanation, acylation, formylation, chloromethylation, and aminomethylation have been conducted upon the quasi-aromatic tris(acetylacetonates) of chromium(III), cobalt(III), and rhodium(III).<sup>6</sup>

The present work shows that a macrocyclic tetradentate nickel(II) complex having a quasi-aromatic ring containing the metal ion can undergo electrophilic substitution employing the usual type organic reactions. The substituted compounds are formed by replacing the a proton (Figure 2) with a halogen atom (Cl, Br, I), a nitroso group, or a nitro group. Conductivity and magnetic susceptibility measurements show all compounds to be nonionic and diamagnetic.

The stability (at least kinetic) of these complexes toward cyanide ion is worthy of mention. Each complex was dissolved in a 1:1 solution of ethanol-KCN (1.0 M) and maintained near the boiling point for 1 h. No change was apparent in any of these solutions or in the recovered complexes which contrasted sharply with the behavior of  $[\text{Ni}(\text{PnAO})-\text{H}]\text{ClO}_4$  which decomposed immediately at room temperature. The IR and  $^1\text{H}$  NMR spectra of  $[\text{Ni}(\text{PnAO})-6\text{H}]$  recovered from the ethanol-KCN solution were identical with the original spectra.

The IR spectra of the three halogenated compounds are essentially identical and are quite similar to the one of  $[\text{Ni}(\text{PnAO})-6\text{H}]$ . The presence of the nitro group is indicated by strong bands occurring at  $1520\text{ cm}^{-1}$  (asymmetric stretch) and  $1325\text{ cm}^{-1}$  (symmetric stretch).<sup>7</sup> The nitrosated complex shows a strong band at  $1530\text{ cm}^{-1}$ . These data are consistent with the attachment of the nitro and nitroso groups to an aromatic ring since the corresponding bands for aliphatic nitro and nitroso compounds occur at higher wavenumbers.<sup>7</sup> All five substituted complexes show a weak, broad band at  $1800\text{ cm}^{-1}$  which has previously been shown to be due to intramolecular hydrogen bonding.<sup>3,8</sup>

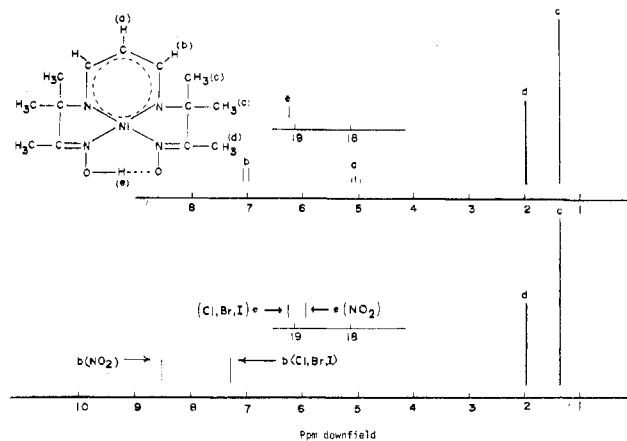


Figure 2.  $^1\text{H}$  NMR spectra (60 MHz) of  $[\text{Ni}(\text{PnAO})-6\text{H}]^0$  (above) and  $[\text{Ni}(\text{PnAO})-7\text{H}(\text{X})]^0$  (X = Cl, Br, I, or NO<sub>2</sub>) in chloroform- $d_1$  relative to internal  $\text{Me}_4\text{Si}$ . The X group replaces the a proton. The b proton signals for the three halogen compounds occur within a range of 0.10 ppm.

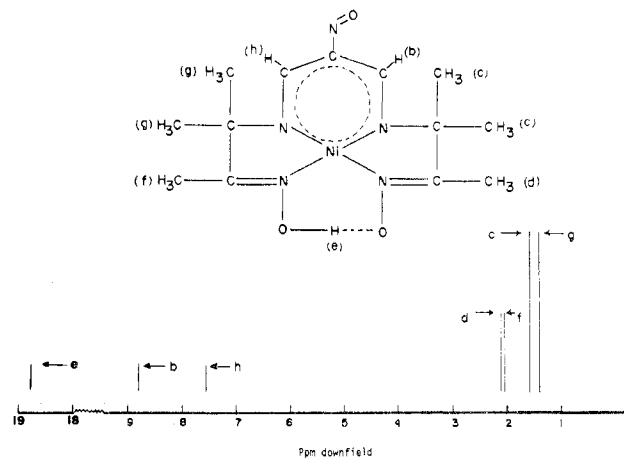


Figure 3.  $^1\text{H}$  NMR spectra (60 MHz) of  $[\text{Ni}(\text{PnAO})-7\text{H}(\text{NO})]^0$  in chloroform- $d_1$  relative to internal  $\text{Me}_4\text{Si}$ .

The  $^1\text{H}$  NMR spectra of  $[\text{Ni}(\text{PnAO})-6\text{H}]$ , the halogen and nitro complexes, are shown in Figure 2 and are consistent with assignment to the  $C_{2v}$  point group. As expected, the signal for the two ring protons on the nitro complex occurs further downfield than the one occurring for each of the halogen compounds (Table I).

The  $^1\text{H}$  NMR spectrum of the nitroso compound shows several distinct differences from those of the other complexes which are consistent with its assignment to the  $C_s$  point group. The c and d protons (Figure 2) on each side of the molecule become nonequivalent causing the singlets that occur at 1.34 and 1.96 ppm for  $[\text{Ni}(\text{PnAO})-6\text{H}]$ , the nitro and halogen complexes, to each split into two signals of equal intensity (Figure 3, Table I). Also, the b protons became nonequivalent giving separate signals in the aromatic region at 7.58 and 8.80

ppm. These data are consistent with trigonal hybridization of the nitrogen atom with the NO group lying in the symmetry plane of the molecule.

### Experimental Section

**PnAO and [Ni(PnAO)-6H].** The preparative methods used for these compounds have been described elsewhere.<sup>3</sup>

**[Ni(PnAO)-7H(Cl)].** Five grams (0.0154 mol) of [Ni(PnAO)-6H] was dissolved in 200 mL of methanol followed by addition of a small crystal of anhydrous iron(III) chloride. After cooling of this solution to 0 °C, along with rapid magnetic stirring, 285 mL of a 0.0540 M solution of chlorine gas (0.0154 mol) dissolved in methanol was added dropwise while simultaneously adding the same volume of a 0.200 M methanol solution of sodium hydroxide to keep the reaction mixture neutral. The orange, crystalline product that came out of solution was washed with cold water (0 °C) and dried in a vacuum oven at 60 °C; yield 72% of theory. The product was recrystallized twice as follows: it was dissolved in hot chloroform (5 g in 200 mL), activated charcoal was added, and the mixture was filtered followed by addition of 200 mL of carbon tetrachloride to the filtrate with subsequent removal of the chloroform using a water aspirator. Anal. Calcd for C<sub>13</sub>H<sub>21</sub>O<sub>2</sub>N<sub>4</sub>ClNi: C, 43.43; H, 5.89; N, 15.59; Cl, 9.86; Ni, 16.33. Found: C, 42.45; H, 5.81; N, 15.25; Cl, 9.83; Ni, 16.23. Molecular weight: calcd 359, found 328.

**[Ni(PnAO)-7H(Br)].** Ten grams (0.0308 mol) of [Ni(PnAO)-6H] was dissolved in 400 mL of methanol followed by addition of a small crystal of anhydrous iron(III) chloride. With rapid magnetic stirring at room temperature, 304 mL of 0.100 M bromine (0.0304 mol) dissolved in methanol was added dropwise to this solution while the same volume of a 0.100 M methanol solution of sodium hydroxide was simultaneously added to keep the reaction mixture neutral. The orange crystalline product that came out of solution was washed with cold methanol and dried under vacuum at 60 °C; yield 95% of theory. This complex was recrystallized twice as described for [Ni(PnAO)-7H(Cl)]. Anal. Calcd for C<sub>13</sub>H<sub>21</sub>O<sub>2</sub>N<sub>4</sub>BrNi: C, 38.65; H, 5.24; N, 13.87; Br, 19.78; Ni, 14.53. Found: C, 38.16; H, 5.17; N, 13.57; Br, 19.69; Ni, 14.53. Molecular weight: calcd 404, found 380.

**[Ni(PnAO)-7H(I)].** Ten grams (0.0308 mol) of [Ni(PnAO)-6H] was dissolved in 400 mL of methanol followed by the addition of a small crystal of anhydrous iron(III) chloride. With rapid magnetic stirring at room temperature, 304 mL of 0.100 M (0.0304 mol) iodine dissolved in methanol was added dropwise to this solution while the same volume of a 0.100 M methanol solution of sodium hydroxide was simultaneously added to keep the reaction mixture neutral. The orange, crystalline product that came out of solution was washed with cold methanol and dried in a vacuum oven at 60 °C; yield 94% of theory. This complex was recrystallized twice as described for [Ni(PnAO)-7H(Cl)]. Anal. Calcd for C<sub>13</sub>H<sub>21</sub>O<sub>2</sub>N<sub>4</sub>I<sub>2</sub>Ni: C, 34.62; H, 4.69; N, 12.42; I, 28.14; Ni, 13.02. Found: C, 34.88; H, 4.57; N, 12.40; I, 28.06; Ni, 13.01. Molecular weight: calcd 451, found 390.

**[Ni(PnAO)-7H(NO<sub>2</sub>)].** One gram (0.00308 mol) of [Ni(PnAO)-6H] was dissolved in 60 mL of carbon tetrachloride. After cooling of this solution to 0 °C, concentrated nitric acid was added in a dropwise stream which caused the solution color to change from orange to a pale red. After the addition of 7 mL of acid, the solution color changed to a dark red at which point 3 mL of concentrated nitric acid was added with no further color change. After 3 or 4 s, the reaction mixture was quenched with 200 mL of 0.500 M sodium hydroxide (0.100 mol) solution which resulted in the immediate formation of a green crystalline product. Prolonging the neutralization time results in lower yields of this complex. The pH was adjusted to 7 with additional 0.500 M sodium hydroxide solution after which the green compound was washed with water and dried in a vacuum oven at 60 °C; yield 78% of theory. This compound was recrystallized twice as described for [Ni(PnAO)-7H(Cl)] and chromatographed several times (basic alumina, BA-1) to remove a small quantity of purple impurity. Anal. Calcd for C<sub>13</sub>H<sub>21</sub>O<sub>4</sub>N<sub>5</sub>Ni: C, 42.19; H, 5.72; N, 18.93; Ni, 15.86. Found: C, 42.05; H, 5.53; N, 18.81; Ni, 15.90. Molecular weight: calcd 370, found 384.

**[Ni(PnAO)-7H(NO)].** Two grams of [Ni(PnAO)-6H] (0.00615 mol) was dissolved in 100 mL of carbon tetrachloride followed by addition of 20 mL of aqueous 1.0 M sodium nitrite (0.020 mol) solution. At room temperature, with rapid magnetic stirring, 2.0 mL of concentrated hydrochloric acid (0.024 mol) was added dropwise within a 3-min period during which time green crystals precipitated

from the reaction mixture. The green product was washed with water and dried in a vacuum oven at 60 °C; yield 96% of theory. This compound was recrystallized twice as described for [Ni(PnAO)-7H(Cl)] and chromatographed several times (basic alumina, BA-1), to remove a small quantity of purple impurity. Anal. Calcd for C<sub>13</sub>H<sub>21</sub>O<sub>3</sub>N<sub>5</sub>Ni: C, 44.10; H, 5.98; N, 19.78; Ni, 16.58. Found: C, 43.96; H, 5.88; N, 19.66; Ni, 16.59. Molecular weight: calcd 354, found 330.

All chemicals were of reagent grade. The water was deionized by a double-bed column. Infrared spectra were taken as KBr pellets on a Perkin-Elmer Model 237B instrument. Proton NMR measurements were made on solutions in deuterated solvents at room temperature with a Varian T-60 <sup>1</sup>H NMR spectrometer. Magnetic susceptibility measurements were made with a conventional Gouy apparatus at two field strengths at room temperature (27 °C). The field strength was calibrated using solid Hg[Co(NCS)<sub>4</sub>]. The diamagnetic corrections were approximated from Pascal's constants. Conductance measurements were made with a Beckman conductivity bridge, Model RC16B2, and an immersion type conductivity cell. Analyses for C, H, and N and molecular weight determinations were made by Galbraith Laboratories, Knoxville, Tenn., and the nickel and the halogen analyses were carried out gravimetrically using DMG and Ag<sup>+</sup>, respectively.

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**Registry No.** [Ni(PnAO)-6H], 18195-22-7; [Ni(PnAO)-7H(Cl)], 68707-94-8; [Ni(PnAO)-7H(Br)], 68707-95-9; [Ni(PnAO)-7H(I)], 68738-43-2; [Ni(PnAO)-7H(NO<sub>2</sub>)], 68707-96-0; [Ni(PnAO)-7H(NO)], 68707-97-1.

### References and Notes

- (1) The designation *-nH* implies the removal of *n* hydrogens from the complexed ligand.
- (2) PnAO is an abbreviation for 2,2'-(1,3-diaminopropane)bis(2-methyl-3-butanone) dioxime.
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### Kinetics of the Diperoxovanadate(V)-Monoperoxovanadate(V) Conversion in Perchloric Acid Media

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It has long been recognized that yellow diperoxovanadate(V) complexes are not stable in acidic solution but are converted to red monoperoxo species.<sup>1</sup> VO<sub>2</sub><sup>+</sup>(aq) forms in aqueous acidic solution red 1:1 monoperoxo- and in neutral solution 2:1 diperoxovanadates(V); the precise structures in solution are not known.<sup>1</sup> Orhanović and Wilkins have investigated briefly the kinetics of the very rapid formation of the monoperoxo species from diperoxo species.<sup>2</sup> Their scant data indicated an acid-catalyzed transformation which was found to be likely *independent* of hydrogen peroxide concentration.<sup>2</sup> In the reaction of *cis*-dioxodipicolinatovanadate(V)<sup>3</sup> with H<sub>2</sub>O<sub>2</sub> at low H<sup>+</sup> concentrations transient diperoxo species have been