peaks, each of intensity 2, at 3.93 and 3.34 ppm, with the upfield peak showing a poorly defined shoulder of approximate intensity 1 near 3.10 ppm. The sums of the weighted averages of the chemical shifts of the terminal and bridge resonances observed at −100 °C (Figure 2B) are each equal, within experimental error, to the chemical shifts of the single resonances observed for the terminal and bridge protons, respectively, at higher temperatures.

The proton-decoupled boron-11 spectra were also obtained in this temperature range. The single resonance observed at 25 °C broadens upon cooling of the solution and finally at −70 °C resolves into two resonances (Figure 3C) at +15.2 and +4.8 ppm of relative areas 4:1. When the solution is cooled further, these resonances only broaden, and the expected resolution of the lower field resonance into two peaks was not observed. Again the sum of the weighted averages of the chemical shifts at −70 °C is equal to the chemical shift of the single resonance at 25 °C.

It is clear from the above data that at low temperatures spectra can be obtained which are consistent with the structure shown in Figure 1 and that the C_{5v} structure apparent at room temperature arises, as in hexaborane(10), from the rapid migration of the bridging hydrogens about the five-boron ring.

Also obtained in this reaction was a second new cobaltaborane complex, 2-(η-C_5H_5)CoB_9H_{13}, which is the third isomer of this cage system to be isolated. The compound was separated, along with the previously reported complexes 2-(η-C_5H_5)CoB_4H_8[7] and 1,2-(η-C_5H_5)$_2Co_2B_4H_6$,[7] by TLC from the solids remaining in the reactor and was obtained as an air-stable, yellow, crystalline solid. Again, exact mass measurements are in agreement with the proposed formula. The boron-11 NMR spectrum[6] in CD_2Cl_2 solution consists of five doublets at 17.0 (J = 133 Hz), 14.6 (164), 9.0 (173), 1.7 (156), and −38.2 ppm (155) with relative intensities 2:1:1:4:1. The boron-11 spin-decoupled ^1H NMR spectrum[5] consists of eight resonances: a sharp peak of intensity 5 at 4.96 ppm due to the cyclopentadienyl hydrogens, five broad peaks of relative intensity 2:1:1:4:1 at 4.60, 4.01, 3.70, 3.03, and 0.26 ppm due to terminal B–H hydrogens, and two upfield peaks of relative intensity 2:2 at −2.00 and −4.54 ppm which may be assigned to nonequivalent boron bridging hydrogens.

Both of the previously discovered isomers, 5-(η-C_5H_5)CoB_9H_{13}[7,8] and 6-(η-C_5H_5)CoB_9H_{13},[9] are proposed to have structures based on a decaborane(14) framework in which a cobalt occupies one of the positions in the open face. Likewise, the NMR data presented above are also consistent with a decaborane(14)-like structure for the new isomer, but in this case the number and relative intensity of the resonances observed in both the ^{11}B and ^1H spectra clearly indicate that cobalt substitution occurs at the 2 position.

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Registry No. (η-C_5H_5)$Co(CO)_2$, 12078-25-0; 1-(η-C_5H_5)CoB_5H_9, 68457-41-0; 2-(η-C_5H_5)CoB_9H_{13}, 68457-40-9.

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Mössbauer Spectra of Substituted Pyridinehemes

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The interaction of bases with hemes (porphyrinatoiron(II) complexes) has been studied extensively because of the similarity of the resulting hemochromes to several hemoprotein systems. Particularly, the affinity of pyridine and various substituted pyridines for hemes with several differently substituted porphyrins has been measured spectrophotometrically,[1] and, more recently, thermodynamic functions have been reported for the reactions of six substituted pyridines with four different hemes.[2] The strength of the iron–pyridine bonds has been found to depend upon the substituents on both the pyridine and porphyrin rings; differences have been rationalized in terms of σ and π bonding characteristics of the substituted pyridine ligands.

We felt it worthwhile to determine whether Mössbauer spectroscopy would be sensitive enough to reflect the differences in the strengths of $\sigma + \pi$ interactions between tetraarylporphinehemes and substituted pyridines. The few Mössbauer data reported so far include only the bis(pyridine)hemes of a few different porphyrins and the bis(3-picoline)- and bis(4-picoline)hemes of octaethylporphyrin.[3]

Experimental Section

$\alpha,\beta,\gamma,\delta$-Tetra($p$-anisidyl)porphyrin, $PMXPPH_2$, was prepared by the standard procedure from anisaldehyde and pyrrole in refluxing propionic acid.[4] The iron complex [PMXPPFeCl] was prepared in dimethylformamide,[5] isolated, treated with gaseous hydrogen chloride in methylene chloride solution to remove traces of the binuclear μ-oxo complex, [$(PMXPPFe)_2O$], and recrystallized several times by diethyl ether precipitation from methylene chloride solution.

The bis(pyrrolidine)hemochrome [PMXPPFe·2Pyr][3d] was prepared by gently refluxing a solution of about 1 g of [PMXPPFeCl] in about 60 mL of pyrrolidine for 15 min, filtering to remove insoluble [$(PMXPPFe)_2O$], and reducing to small volume by vacuum distillation of excess amine. The crystals which resulted upon cooling of the solution to room temperature were collected and recrystallized from hot pyrrolidine. Finally the product was washed with ether and dried under vacuum at room temperature for 24 h.

Bis(4-methylpyridine)tetra(p-anisidyl)porphyrinatoiron(II), [PMXPPFe·2(4-MePy)]. A 0.65-g sample of the bis(pyrrolidine)-hemochrome was placed in a test tube with approximately 3 mL of 4-methylpyridine and heated with stirring to 105 °C. The heterogeneous solution was kept at 105–110 °C for 10 min, placed under vacuum, and held at the same temperature for an additional 30 min to remove free pyrrolidine. After the solution was cooled to room temperature, the crystalline product was collected on a glass frit and washed with ether.

This general method was used to prepare the pyridine (Py), 3- and 4-acetylpyridine (3/4-AcPy), and 3,5-dimethylpyridine (3,5-Me_2Py) hemochromes. For the 3- and 4-cyanopyridine (3/4-CNPy) and 4-dimethylaminopyridine (4-DMAPy) hemochromes, about 3 g of the solid pyridines was used in the reactions.

Purity of the pyridinehemochromes was established by Mössbauer spectroscopy and from the complete disappearance of the infrared NH deformation mode which occurs at 895 cm^{-1} in the pyrrolidinehemochrome. The 3- and 4-acetylpyridinehemochromes contained the expected carbonyl stretching frequency at 1700 cm^{-1}, and the 3-

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Table I. Mössbauer Data for Substituted Pyridinehemochromes at 298 K

compound	δ^a	Δ^b	Γ^c	N^d	% effect^e
[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_2Py)]	+0.67	1.31	0.25	0.44	2.5

[a] Isomer shift in mm/s relative to sodium nitroprusside; ±0.02 mm/s. [b] Quadrupole splitting; ±0.02 mm/s (sign not measured but almost certainly +). [c] Line width in mm/s at half-maximum. [d] Number of γ-ray counts under nonresonant conditions; $\times 10^6$. [e] 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 cm^{-1}. The Mössbauer spectra of some of the compounds occasionally showed small contamination with the μ-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}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, δ, and quadrupole splitting, Δ, are ±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, Vzz (with z the crystal field $\sim C_4$ axis) is positive in the bis(pyridine)hemochromes.[3] Thus, the stronger the axial ligand is as a σ donor the smaller should be the quadrupole splitting. The order of decreasing pK_a's (σ base strengths) for the substituted pyridines used in this investigation is as follows:[6]

4-DMAPy > 3,5-Me_2Py > 4-MePy > Py >> 4-AcPy > 3-AcPy >> 4-CNPy > 3-CNPy

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 σ bases. From Table I it can be seen that the order of increasing splittings (and decreasing $\sigma + \pi$ bond strengths) is as follows:

4-DMAPy < 4-AcPy < 3-AcPy ≈ Py ≈ 4-CNPy < 4-MePy ≈ 3-CNPy < 3,5-Me_2Py

It is not possible to account for such splittings on the basis of σ 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 π-electron donor, and pyridine can be a π acceptor.[2,7] The stronger the substituted pyridine is as a π acid, the smaller the quadrupole splitting of the resulting hemochrome. Cole et al.[2] determined the thermodynamic functions of various hemochromes and obtained good evidence that σ bonding predominated in 4-amino-, 4-methyl-, and 4-vinylpyridines and π bonding predominated in 4-cyano- and 4-carboxy-*n*-butylpyridines. Pyridine itself showed intermediate bonding. Accordingly, for our substituted pyridines, π bonding is expected to be especially important for 4-cyano- and 4-acetylpyridines and weakest for 4-methyl-, 3,5-dimethyl-, and 4-dimethylaminopyridines.[8] There are no directly applicable literature data on the π-bonding ability of 3-acetyl- and 3-cyanopyridines, but these probably have similar π-acceptor strengths; however 3-acetylpyridine is the stronger base. Although 4-acetylpyridine may be a somewhat weaker π acid than 4-cyanopyridine,[9] it is a much stronger σ base. Also, 4-dimethylaminopyridine is a much stronger base than either 4-methylpyridine or 3,5-dimethylpyridine. From these comparisons, involving both σ- and π-bonding characteristics, the partial orderings of strengths of interactions with heme iron should be as follows:

4-AcPy > 4-CNPy

4-DMAPy > 4-MePy ≈ 3,5-Me_2Py

3-AcPy > 3-CNPy

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_2Py)], 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, $[Ni(PnAO)-H]^+$ (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), [Ni(PnAO)-6H][1,2] (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, $[Ni(PnAO)-H]^+$, was shown by both chemical and spectral data.[3]

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