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Nitrosyl(protoporphyrin IX dimethyl ester)iron(II) Complexes with Nitrogenous Bases. The Basicity Dependence of the NO Stretching Frequency

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Synopsis. The IR spectra of nitrosyl(protoporphyrin IX dimethyl ester)iron(II) [Fe(ppdme)(NO)] complexes with various nitrogenous bases (B), such as imidazoles, pyridines, cyclic secondary amines, and aliphatic amines, were measured in benzene and 1,2-dichloroethane. The NO stretching frequencies (ν_{NO}) of these complexes and the equilibrium constants in equilibrium, [Fe(ppdme)(NO)]+B$\rightleftharpoons$[Fe(ppdme)-(NO)B], decreased and increased respectively with an increase in the basicity, pK_a(BH$^+$), of the bases. These results are discussed in relation to the σ- and π-bonding abilities of the bases.

The investigation of (nitrosyl)(porphyrinato)iron(II) complexes as model systems for nitrosylhemoproteins have played an important role in the identification of an axial ligand *trans* to the nitrosyl group of various nitrosylhemoproteins and the elucidation of the stereochemistry of the heme environment.[1—7]

During the course of this investigation of the model complexes,[1] it has been found that the EPR and IR parameters of the (nitrosyl)(porphyrinato)iron(II) complexes are very sensitive to changes in the *trans* axial base and the solvent. The present work will report on an IR study of the system with [Fe(ppdme)-(NO)] and nitrogenous bases, such as imidazoles, pyridines, cyclic secondary amines, and aliphatic amines, in benzene and 1,2-dichloroethane.

A five-coordinate [Fe(ppdme)(NO)] reacts with a base in a solution to form a six-coordinate [Fe(ppdme)-(NO)B] according to Eq. 1:

$$[\mathrm{Fe(ppdme)(NO)}] + \mathrm{B} \overset{K}{\rightleftharpoons} [\mathrm{Fe(ppdme)(NO)B}],$$

Therefore, in the IR spectra of the solution, two NO bands of five- and six-coordinate species are revealed at different frequencies. It has been demonstrated that the ν_{NO} values and the equilibrium constant of Eq. 1 are markedly sensitive to the polarity and the hydrogen-bonding ability of the solvent.[1f] Accordingly, the essential differences in the *trans* effect of an axial base can be detected only in IR spectral results in the same solvent.

Table 1 lists the ν_{NO} and $\Delta\nu_{1/2}$ values (the full width in wavenumbers at a half-height in absorbance) and the equilibrium constants in benzene and 1,2-dichloroethane. The ν_{NO} values in 1,2-dichloroethane with a greater polarity are smaller than in benzene by about 10 cm^{-1}, and the equilibrium constants in 1,2-dichloro ethane with a hydrogen-bonding ability are also smaller. These trends are consistent with those reported previously.[1f]

Figures 1 and 2 show, respectively, the plots of the ν_{NO} value and the equilibrium constant in 1,2-dichloroethane against the pK_a(BH$^+$) value. Figures similar

TABLE 1. ν_{NO} VALUE AND EQUILIBRIUM CONSTANT OF [Fe(ppdme)(NO)] COMPLEXES WITH NITROGENOUS BASES IN BENZENE AND 1,2-DICHLOROETHANE AT ROOM TEMPERATURE[a)]

No.	Base	pK_a (BH$^+$)[b)]	$\nu_{NO}(\Delta\nu_{1/2})$ / cm^{-1}		K / M^{-1}	
			C_6H_6	$C_2H_4Cl_2$	C_6H_6	$C_2H_4Cl_2$
1	1-Acetylimidazole	3.6	1636(21)	1628	2.0	1.0
2	5-Chloro-1-methylimidazole	4.75	1632(22)	1626(25)	4.8	1.6
3	Imidazole[c),d)]	6.95		1620		2·7
4	1-Methylimidazole[d)]	7.33	1630(21)	1621(24)	11	7.1
5	4-Methylimidazole	7.52	1629(19)	1618(22)	10	6.5
6	3-Chloropyridine	2.84	1641(22)	1635(28)	0.3	0.1
7	4-Acetylpyridine	3.51	1640(15)	1632(27)	1.1	0.2
8	Pyridine[d)]	5.23	1639(15)	1631(27)	1.6	1.1
9	4-Methylpyridine	6.02	1636(21)	1628(25)	1.9	0.8
10	3,4-Dimethylpyridine	6.46	1635(18)	1627(23)	1.9	0.9
11	4-Dimethylaminopyridine	9.70	1631(21)	1618(26)	11	7.6
12	Morpholine	8.7	1639(17)	1629(30)	4.5	4.2
13	Piperazine	9.82	1638(15)	1627(28)	7.0	6.2
14	Piperidine[d)]	11.22	1636(17)	1626(28)	6.9	6.8
15	Benzylamine	9.6	1637(17)	1626(24)	4.6	3.2
16	Isobutylamine	10.42	1636(17)	1625(22)	5.6	2.4
17	Butylamine[d)]	10.64	1636(17)	1625(22)	7.8	3.8

a) Room temperature≈20 °C. [Fe(ppdme)(NO)]=6—8 M. [Base]/[Fe(ppdme)(NO)]=20—200. b) Imidazoles, pyridines, and cyclic secondary amines, Ref. 10; aliphatic amines, Ref. 11. c) Not sufficiently dissolved in benzene. d) Ref. 1f.

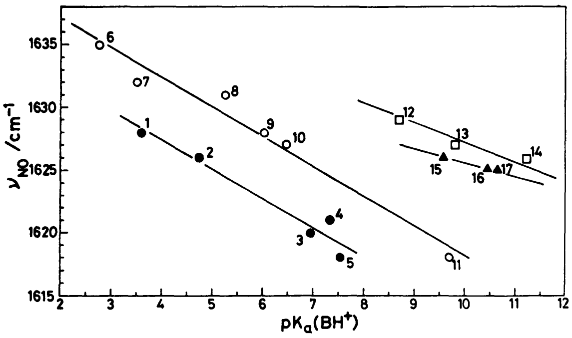

Fig. 1. A plot of ν_{NO} value against pK_a (BH$^+$) value for [Fe(ppdme)(NO)] complexes with nitrogenous bases in 1,2-dichloroethane. ●: Imidazoles, ○: pyridines, ▲: aliphatic amines, ☐: cyclic amines. Numbers refer to bases in Table 1. The Straight line was obtained by the use of least-squares method.

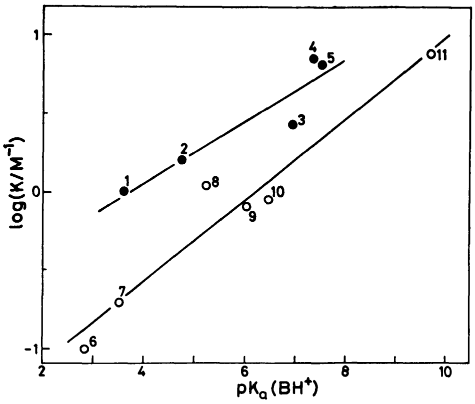

Fig. 2. A plot of log K against pK_a (BH$^+$) value for [Fe(ppdme)(NO)] complexes with imidazoles (●) and pyridines (○) in 1,2-dichloroethane. Numbers refer to bases in Table 1. The straight line was obtained by the use of least-squares method.

to Figs. 1 and 2 were also made by the plots in benzene against pK_a(BH$^+$). The ν_{NO} value and the equilibrium constants, respectively, decrease and increase linearly with the basicity. The plots for imidazoles, pyridines, cyclic amines, and aliphatic amines are on separate lines.

Accordingly, the σ-electron donated from the base to the iron can increase with the basicity of the base to intensify the iron-to-base bond, resulting in an increase in the equilibrium constant. Then, since a molecular orbital consisting primarily of the d_{z^2} and the π^*(NO) orbitals is formed in the complexes with a bent Fe–N–O unit,[3,8,9] the contribution of the π^*(NO) orbital to the molecular orbital will be increased when the d_{z^2} orbital can be destabilized accompanying the σ-electron donation. Consequently, the increased antibonding character of the NO bond may induce the observed decrease in the ν_{NO} value. The concomitant increase in the energy of the d_{z^2} orbital also induces an observed decrease in EPR g values toward the free-electron value, as has been reported previously.[1c,e,7]

As is shown in Fig. 1, the ν_{NO} values decrease in the following order for bases: cyclic amines$\geq$aliphatic amines$>$pyridines$>$imidazoles. As is shown in Fig. 2, the equilibrium constants for imidazoles are larger than those for pyridines. These tendencies have also been observed in the relation of the EPR g values for [Fe(ppdme)(NO)] complexes with various nitrogenous bases to the pK_a(BH$^+$) values of the bases.[1c,e] These results indicate that the extra stabilization of an iron-to-base bond arises from d_π-p_π bonding formation, involving the destabilization of the π^*(NO) orbital, and that the imidazoles have a greater ability for π bonding than do the pyridines.

Experimental

The nitrosyl(protoporphyrin IX dimethyl ester)iron(II) was prepared as has been described previously.[1a] The nitrogenous bases were obtained commercially and purified by distillation, recrystallization, and sublimation as has been described previously.[1] The benzene and 1,2-dichloroethane were of a spectral grade and were used without further purification. The oxygen was removed from the solvents and the liquid bases by bubbling with pure N_2 prior to use. The samples were prepared under N_2 atmosphere.

The IR absorption spectra were recorded in the absorbance mode on a JASCO A-302 apparatus with a DP-A300 data processor. The details of the IR measurements were essentially the same as those reported in a previous paper.[1f]

The equilibrium constants were evaluated from the intensity change in the NO stretching band as has been described previously.[1f]

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