thus accounting for some reduction in the catalysis of decarboxylation. An additional pathway for the inductive effect of the pyridine nitrogen involves the α'-carbon directly. The inductive effect of the pyridine nitrogen is partially distributed around the aromatic ring, so that the azomethine nitrogen is separated from this effect by only a single aliphatic carbon atom. It has been suggested by a reviewer of this paper that deprotonation of the pyridine nitrogen may favor a shift of the azomethine proton to the phenolate oxygen resulting in the formation of a new microspecies, **17a**. This change in bonding would have a considerable influence on the rates, over a wide range of **17** $\rightleftharpoons$ **17a** equilibrium quotient. In other words even a small contribution from **17a** would have a pronounced effect.

As the pH is increased above **11**, the major ketimine initially present is **18**. In this species the azomethine nitrogen is now deprotonated, thus accounting for the observed large decrease in catalytic activity. Species **19** and **20** ketonize rapidly to **21** and **22** and dissociate almost quantitatively into AKBA and pyridoxamine since the Schiff base formation constant is small, as are the concentrations of AKBA and PM. α-Ketobutyric acid was identified as the product by NMR measurement on more concentrated solutions and this product was verified earlier by Sakkab and Martell.[32]

It should be possible to estimate the pK_a's of the OPA:pyridoxamine Schiff bases involved in decarboxylation from the inflection points in the pH-rate constant profile of k_{SB} in Figure 4. Not enough data have been collected below the first inflection and beyond the second inflection, for reasons previously mentioned, to carry out a precise determination of the dissociation constants of the Schiff base. However, an estimate of the K_a's defined by eq 6 and 7 observed inflection regions in Figure 4. Thus, the

$$K_{a_1} = \frac{[\mathbf{17}][H^+]}{[\mathbf{14}]} \tag{6}$$

$$K_{a_2} = \frac{[\mathbf{18}][H^+]}{[\mathbf{17}]} \tag{7}$$

mathematical expression for pyridoxamine catalysis over the entire pH range is

$$k_{SB} = k_{H_2A}\alpha_{H_2A} + k_{HA}\alpha_{HA} + k_A\alpha_A \tag{8}$$

with H_2A, HA, and A representing species **14**, **17**, and **18**, respectively. The fraction of each species and the specific rate constant of decarboxylation for each species are α_i and k_i, respectively. Banks et al.[33] have reported 6.9 and 10.3 for the analogous pK_a's in the pyridoxamine:pyruvate ketimine Schiff base system. The specific rate constants indicated in eq 8 were found to be 41.6 s^{-1}, 19.2 s^{-1}, and 0.3 s^{-1} for species **14**, **17**, and **18**, respectively, with an error of ± 0.6 s^{-1}.

The catalytic effects on OPA decarboxylation by pyridoxamine are dependent on two factors: (1) the extent of Schiff base formation and (2) the protonation of the Schiff base species present. On the basis of the specific rate constants determined above, it is proposed that the fully protonated Schiff base is more active toward decarboxylation than the monoprotonated species while the fully deprotonated species is relatively inactive.

Registry No. 1, 85-87-0; 2, 642-93-3; 3, 84065-57-6; vitamin B_6, 8059-24-3.

Nitrosoalkane Complexes of Iron-Porphyrins: Analogy between the Bonding Properties of Nitrosoalkanes and Dioxygen

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Abstract: Various iron-porphyrin complexes involving an iron-nitrosoalkane bond, Fe^{II}(porphyrin)(RNO)(L), with porphyrin = TPP, TpClPP, TTP, or DPDME, R = *i*-Pr or Me, and L = MeOH, *i*-PrNHOH, *i*-PrNH_2, pyridine, *N*-methylimidazole, or PPhMe_2,[1] have been prepared either by reaction of Fe^{II}(porphyrin) with the RNO dimer or of Fe^{III}(porphyrin)(Cl) with RNHOH, in the presence of the L ligand. These hexacoordinate complexes and the pentacoordinate Fe(porphyrin)(RNO) complexes are in the low-spin state and exhibit IR ν_{NO} frequencies ranging from 1400 to 1445 cm^{-1}. Their trans ligands L are in fast exchange, vs. the ^1H NMR time scale, at 20 °C, and bind to the pentacoordinate complex Fe(porphyrin)(RNO) with rather high affinities (for porphyrin = TPP and R = *i*-Pr, the binding equilibrium constants are respectively 350, 6 × 10^4, and 15 × 10^4 L mol^{-1} for L = MeOH, pyridine, and *N*-methylimidazole at 27 °C). The X-ray structure of Fe(TPP)(*i*-PrNO)(*i*-PrNH_2) shows that *i*-PrNO is bound to the iron by its nitrogen atom, the Fe-N(O)*i*-Pr distance (1.865 (14) Å) being considerably shorter than the Fe-NH_2*i*-Pr distance (2.100 (14) Å). The Fe-N(O)R bond is much stronger than the Fe-N bonds formed with usual amino ligands of iron-porphyrins such as amines, pyridines, or imidazoles. A comparison of some structural, IR, resonance Raman, and Mössbauer data of the Fe(TPP)(*i*-PrNO)(*N*-methylimidazole) and Fe("picket fence"-TPP)(O_2)(*N*-methylimidazole) complexes indicates a great similarity in the bonding properties of the *i*-PrNO and O_2 ligands. These results explain various aspects concerning the formation and properties of hemoglobin- or cytochrome P-450-nitrosoalkane complexes.

There is a considerable current interest in the structural and chemical properties of hemoprotein-iron(II) complexes and in particular in the dioxygen complexes which are the key intermediates in various hemoprotein-dependent enzymatic systems.[2] Recently, evidence has been obtained in favor of the formation of nitrosoalkane complexes of hemoglobin, myoglobin,[3] and cytochrome P-450.[4] In fact, nitrosoalkanes constitute a new class of ligands exhibiting a very high affinity for hemoprotein-iron(II).[5]

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(1) Abbreviations: TPP, *meso*-tetraphenylporphyrinate; TpClPP, *meso*-tetra(4-chlorophenyl)porphyrinate; TTP, *meso*-tetratolylporphyrinate; DPDME, deuteroporphyrinate dimethyl ester; P, porphyrinate; *i*-PrNH_2, 2-aminopropane; *i*-PrNHOH, 2-(hydroxyamino)propane; *i*-PrNO, 2-nitrosopropane; py, pyridine; *N*-MeIm, *N*-methylimidazole; PPhMe_2, dimethylphenylphosphine; Me, methyl; Pyr, pyrrole; Ph, phenyl; MeOH, methanol; s, singulet; d, doublet; t, triplet; h, heptuplet.

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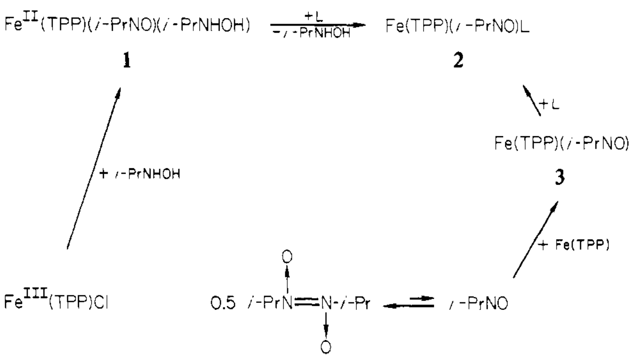
They are interesting ligands for two main reasons. First, they are formed during the oxidative metabolism of several drugs or exogenous compounds containing an amine or hydroxylamine function[4c,6] or during the reduction of the corresponding nitroalkanes,[4b] and they bind tightly to the iron(II) of the hepatic detoxifying cytochromes P-450, causing a severe inhibition of the catalytic functions of these cytochromes.[6a,c] Secondly, they display common features with dioxygen: their nitroso group is isoelectronic with dioxygen and involves a low-lying π^* system readily available for back-bonding,[7] and they present two possible binding modes, either "end on" or "side on".

Only a few transition-metal complexes having nitrosoalkane ligands have been reported.[8,9] Nitrosoalkanes, particularly those which are not hindered around their nitrogen atom, are especially unstable, leading almost irreversibly to the corresponding dimers or tautomers.[7] On the contrary, nitrosoarenes exist predominantly as monomers in solution, allowing an easy study of their interactions with transition-metal complexes.[9]

Among the few described transition-metal-nitrosoalkane complexes, three types of coordination have been indicated. In the particular case of chelate nitrosoalkyl ligands, nitrogen coordination has been established from X-ray data for a cobalt(I) bidentate dinitrosoalkyl complex[8a,b] and for tris(violurato)iron(III)[8c] and -ruthenium(II)[8d] complexes and is very probable for a tris(3-nitroso-2,4-pentanedionato)cobalt(III) complex.[8e] A side-on η^2 coordination has been proposed for nitrosomethane bridging the two metal atoms of a cobalt(I) dinuclear complex.[8f] Finally, the monodentate N-bonding mode has been established from an X-ray study for the $PtCl_2(t\text{-}BuNO)_2$ complex,[8g] proposed for a ruthenium(II) complex on the basis of IR results,[8h] and seems possible for some ferrocyanide complexes.[8i,j]

In order to prove definitely the involvement of an Fe^{II}-N(O)R bond in the hemoprotein-nitrosoalkane complexes previously described[4] and to get an insight into the mode of binding of the nitrosoalkane ligand in these complexes, we have prepared "model" Fe(porphyrin)(RNO) complexes. The preparation of such complexes from reaction of iron(III)-porphyrins with aliphatic hydroxylamines has been reported in a preliminary communication.[10] One of them, Fe(protoporphyrin IX)(*N*-methylimidazole)(*i*-PrNO), exhibited an electronic spectrum in benzene-DMF almost superimposable to that of myoglobin-Fe^{II}(*i*-PrNO) complex. The present paper describes different preparations of iron-porphyrin-nitrosoalkane complexes and their study by various spectroscopic methods including an X-ray analysis. This study definitely proves the existence of the Fe^{II}-RNO bond, establishes the end-on N-binding mode of nitrosoalkanes in these ferroporphyrin complexes and gives information on the electronic structure of the Fe-RNO bond. Moreover, it points out a striking similarity between the bonding properties of nitrosoalkanes and dioxygen as ligands of iron(II)-porphyrins.

Scheme I



2a, L = py; 2b, L = $i\text{-}PrNH_2$; 2c, L = *N*-MeIm; 2d, L = MeOH; 2e, L = $PPhMe_2$

Results

Preparation of *i*-PrNO-Iron-Porphyrin Complexes. Reaction of chloro(*meso*-tetraphenylporphyrinato)iron(III), Fe(TPP)(Cl), with an excess of 2-(hydroxyamino)propane (*i*-PrNHOH), for a few hours at room temperature, under argon, followed by crystallization upon addition of MeOH, affords a nearly quantitative yield of the hexacoordinate complex Fe(TPP)(*i*-PrNO)(*i*-PrNHOH) (**1**). For preparation of other hexacoordinate complexes Fe(TPP)(*i*-PrNO)(L) (**2**), with L ligands such as 2-aminopropane ($i\text{-}PrNH_2$), pyridine (py), or *N*-methylimidazole (*N*-MeIm), the same procedure can be used with the addition of a few equivalents of L before the crystallization step. In the case where L is a weak ligand such as an alcohol, the preparation of the corresponding complex has to be carried out with only 2 mol of *i*-PrNHOH per mol of Fe(TPP)(Cl) in a 1:1 alcohol-CH_2Cl_2 solvent mixture. The yields obtained for the preparation of complexes **1**, **2a**, **2b**, **2c**, and **2d** (Scheme I) are always higher than 90%. These complexes have been fully characterized in the solid state by elemental analysis, mass spectrometry, and IR spectroscopy. The hexacoordinate complex **2e**, Fe(TPP)(*i*-PrNO)($PPhMe_2$), has been obtained from the Fe(TPP)(*i*-PrNO)(MeOH) complex, by displacement of the weak ligand MeOH, upon addition of about 1 equiv of $PPhMe_2$. It is noteworthy that this strong ligand has been found able to partially displace the nitrosoalkane ligand, leading also to the formation of about 10% of the hemochrome $Fe(TPP)(PPhMe_2)_2$. Complex **2e** has been characterized in solution by IR, visible, and ^1H NMR spectroscopy (Tables I, III, and IV).

For a better understanding of the stoichiometry of the reaction between Fe(TPP)(Cl) and *i*-PrNHOH, experiments were done with a Fe(TPP)(Cl):*i*-PrNHOH 1:2 molar ratio. In the absence of oxygen, a mixture of iron complexes is obtained; after treatment of this mixture by pyridine, one observes by ^1H NMR the quantitative formation of complex **2a**. Moreover, $i\text{-}PrNH_2$ is formed in this reaction with a 24% yield (in mole per mole of starting *i*-PrNHOH) and about 23% of unreacted *i*-PrNHOH) is recovered, indicating the following stoichiometry:

$$Fe^{III}Cl + 2RNHOH \rightarrow Fe^{II}N(O)R + 0.5RNH_2 + 0.5RNHOH + 0.5H_2O + HCl$$

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Table I. IR and UV–Visible Spectroscopy Characteristics of Fe(P)(*i*-PrNO)(L) Complexes

Fe(P)(RNO)L		IR,[a] ν_{NO}, cm^{-1}	UV and visible,[b] λ, nm (ε, mM^{-1} cm^{-1})		*K*,[b,c] L M^{-1}
P = TPP, R = *i*-Pr					
L = *i*-PrNHOH	1	1432	422 (270)	535 (12)	
= py	2a	1432	424 (256)	536 (11)	60000
= *i*-PrNH$_2$	2b	1432	425 (255)	539 (12)	125000
= *N*-MeIm	2c	1432	426 (262)	540 (12)	150000
= MeOH	2d	1445	420 (264)	536 (12)	350
= PPhMe$_2$	2e[d]	1433	417–444	556–600	
Fe(TPP)(*i*-PrNO)	3	1445	413 (219)	525 (11)	
L = Py, R = *i*-Pr					
P = TpClPP	4	1438	424 (233)	535 (11)	
= TTP	5	1432	424 (243)	535 (15)	
= DPDME	6	1430	408 (218)	523 (12), 552 (12)	
Fe(TPP)(MeNO)py		^{14}N 1400; ^{15}N, 1390	423 (285)	536 (12)	
free MeNO[7]		1564			
free C$_5$H$_{11}$NO[7]		1558			

[a] KBr pellets, cm^{-1} (±2). [b] Deaerated benzene solutions at 27 °C. [c] Equilibrium 1 constant (see text). [d] 2e was obtained as a mixture with 6% Fe(TPP)(PPhMe$_2$)$_2$, ε was not determined in this case.

The Fe(TPP)(*i*-PrNO)(L) complexes have been also prepared by direct interaction of Fe(TPP) with the *i*-PrNO dimer. 2-Nitrosopropane exists as a dimer in the solid state and is mostly dimeric in solution.[7] However, the affinity of *i*-PrNO for Fe(TPP) is so high that one can observe the fast and quantitative formation of the Fe(TPP)(*i*-PrNO)(MeOH) complex, after reaction of Fe(TPP) with 5 excess of (*i*-PrNO)$_2$ in benzene at 70 °C followed by MeOH addition (Scheme I).

The above described methods are general and have been used for the preparation of the Fe(porphyrin)(*i*-PrNO)(py) complexes **4**, **5**, and **6**, respectively, with porphyrin = *meso*-tetra(4-chlorophenyl)porphyrin (TpClPP), *meso*-tetratolylporphyrin (TTP), and deuteroporphyrin dimethyl ester (DPDME). These complexes have been identified by mass spectrometry and IR, visible, and ^{1}H NMR spectroscopy (Tables I, III, and IV).

Characteristics of the Crystalline Complexes. Mass Spectrometry. Upon direct introduction of the complexes at 25–100 °C (70 eV), one observes the peaks corresponding to the two axial ligands, *i*-PrNO and L. When the temperature reaches 200 °C, the peaks corresponding to Fe(TPP) appear. Because of the fast decomposition of the complexes under the mass spectrometry conditions, we never observed the molecular peaks corresponding to Fe(TPP)(*i*-PrNO)(L), either with a lower energy source (30 eV) or by using field desorption and ionization techniques.

IR Spectroscopy. The IR spectra of complexes **1** and **2** are very similar to those of Fe(TPP)(py)$_2$ or Fe(TPP)(Cl) but they all exhibit an intense additional band between 1400 and 1450 cm^{-1}. For definite assignment of this band to the N–O stretching vibration, a complex containing a nitrogen-15-labeled R^{15}NO ligand was synthesized. Preparation of a Me^{15}NO complex was preferred to that of an *i*-Pr^{15}NO complex, since MeNHOH is easier to prepare than *i*-PrNHOH from commercially available ^{15}N-labeled precursors. Me^{15}NHOH was prepared by reaction of Na^{15}NO$_2$ with ClCH$_2$COOH[11] followed by reduction of Me^{15}NO$_2$ by zinc and NH$_4$Cl.[12] The Fe(TPP)(Me^{15}NO)(py) complex was then obtained by reaction of Fe(TPP)(Cl) with Me^{15}NHOH in the presence of pyridine. In the IR spectrum of the Fe(TPP)(Me^{14}NO)(py) complex, the band assigned to the N–O vibration is at 1400 cm^{-1}. In agreement with this assignment, this band exhibits a 10-cm^{-1} shift to lower frequencies upon replacement of Me^{14}NO by Me^{15}NO (Figure 1). This is the only significant difference between the IR spectra of Fe(TPP)(Me^{14}NO)(py) and Fe(TPP)(Me^{15}NO)(py) complexes, apart from a shift of a weak band from 930 to 918 cm^{-1}.[13]

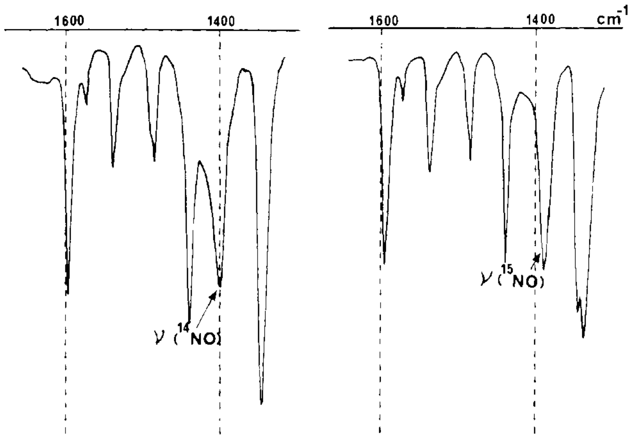

Figure 1. Infrared spectra of (a) Fe^{II}(TPP)(Me^{14}NO)(py) and (b) Fe^{II}(TPP)(Me^{15}NO)(py) (KBr pellet, ±2 cm^{-1}). Bands due to the bound nitrosomethane are indicated by arrows.

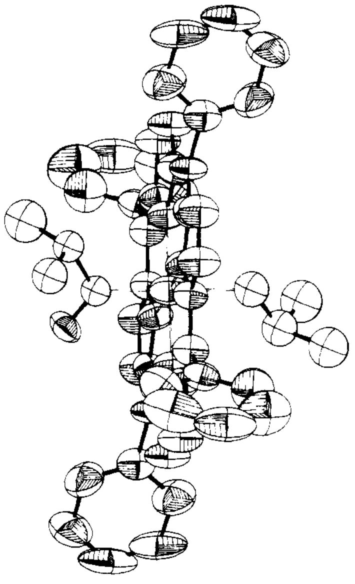

Figure 2. General view of the molecule—50% probability ellipsoids are used for anisotropic atoms. The darker ellipsoids and the centered light spheres represent, respectively, the anisotropically and isotropically refined atoms.

As shown in Table I, the N–O stretching frequency of RNO is greatly lowered upon coordination to iron–porphyrins (from 1558 cm^{-1} for the free ligand[7] to about 1430 cm^{-1}). This shift to lower frequencies depends significantly upon the electron-donor ability of the trans L ligand (1445 cm^{-1} for L = MeOH to 1432 cm^{-1} for L = *N*-MeIm) and upon that of the porphyrin (1438 cm^{-1} for

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(13) A similar band, also present in the IR spectrum of Ru[bpy]$_2$[N-(O)C$_6$H$_4$NMe$_2$]Cl at 875 cm^{-1} (^{14}N) and 866 cm^{-1} (^{15}N) was tentatively assigned to a ν_{N-C} rock.[9b]

Table II. Selected Bond Distances (Å) and Angles (deg) in the Ligands of Complex **2b**[a,b]

bonds	molecule 1	molecule 2	angles	molecule 1	molecule 2
Fe-N(1)	2.005 (7)	1.990 (8)	N(3)-Fe-N*(3)	176.8 (6)	178.4 (6)
Fe-N(2)	1.981 (7)	1.995 (7)	Fe-N(3)-O(1)	124 (1)	124 (1)
Fe-N(3)	1.862 (14)	1.867 (13)	Fe-N(3)-C(23)	119 (1)	121 (1)
Fe-N*(3)	2.105 (15)	2.094 (13)	O(1)-N(3)-C(23)	117 (1)	115 (1)
N(3)-O(1)	1.26 (2)	1.26 (2)	N(3)-C(23)-C(24)	105 (2)	107 (1)
N(3)-C(23)	1.55 (2)	1.54 (2)	N(3)-C(23)-C(25)	110 (2)	104 (1)
C(23)-C(24)	1.58 (3)	1.55 (2)	C(24)-C(23)-C(25)	118 (2)	119 (1)
C(23)-C(25)	1.48 (3)	1.61 (2)	Fe-N*(3)-C*(23)	126 (1)	123 (1)
N*(3)-C*(23)	1.49 (3)	1.47 (2)	N*(3)-C*(23)-C*(24)	113 (2)	109 (1)
C*(23)-C*(24)	1.39 (3)	1.51 (3)	N*(3)-C*(23)-C*(25)	99 (2)	110 (2)
C*(23)-C*(25)	1.48 (3)	1.49 (3)	C*(24)-C*(23)-C*(25)	115 (2)	104 (2)

[a] For the two independent molecules of the asymmetric unit. The estimated standard deviations appear in parentheses. [b] Bond distances and angles in the TPP are available in the supplementary material (Tables 4 and 5).

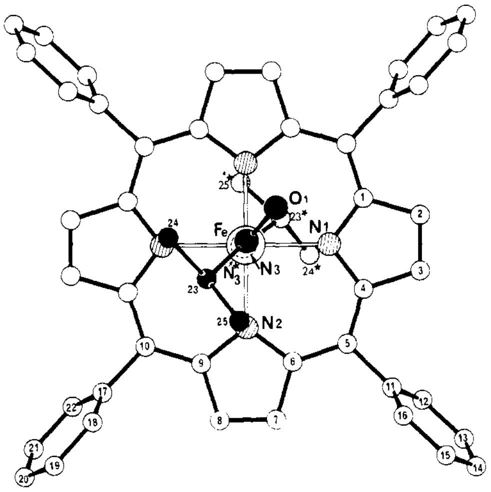

Figure 3. Computer drawn model in perspective of complex **2b** showing the relative orientation of the axial ligands. The phenyl rings make dihedral angles of 90 and 87° (molecule 1), 76 and 75° (molecule 2) with the respective mean plane of the porphinato core.

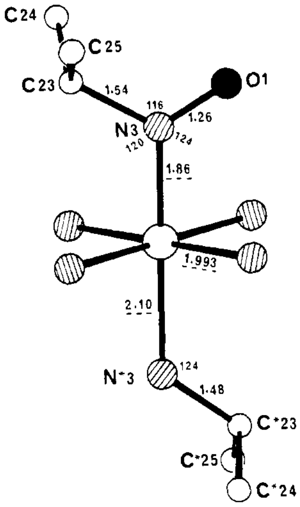

Figure 4. Representation of the ligands position in complex **2b** (only the nitrogen atoms of the porphyrin are represented). The labeling scheme and the mean bond distances and angles are shown.

TpClPP to 1430 cm^{-1} for DPDME).

X-ray Analysis of Complex 2b. Crystals of complex **2b** suitable for an X-ray structure determination were obtained by slow crystallization from a $CHCl_3$–MeOH solvent mixture.

The structure consists of two independent Fe(TPP)(*i*-PrNO)(*i*-$PrNH_2$) molecules with the Fe atoms lying on crystallographic imposed centers of symmetry (Figures 2 and 3). Hence, the *i*-PrNO and *i*-$PrNH_2$ ligands have been considered statistically disordered between the two symmetric related sites. Nevertheless, the precision has not been limited by the disorder involving ligands. The geometries of the two crystallographic independent molecules are in excellent agreement with each other. Bond distances and angles of the ligands are compared in Table II, mean distances and angles being reported in Figure 4. In addition, there are two $CHCl_3$ molecules in the unit cell. The molecular stereochemistry is displayed in Figures 3 and 4.

The Fe–N pyrrolic bond length, 1.993 (7) Å, is consistent with those observed for low-spin hexacoordinate iron(II)–porphyrin complexes.[14] The geometry of the nitrosoalkane ligand is characterized by a N–O bond length of 1.26 (20) Å and an axial Fe–N distance of 1.86 (14) Å. The Fe–N distance of 2.10 (14) Å between the iron and *i*-$PrNH_2$ ligand is considerably longer and comparable to the Fe–N bond length of 2.127 (3) Å found in the low-spin Fe(TPP)(piperidine)$_2$ complex.[15]

Characteristics of the Complexes in Solution. Electronic Spectroscopy. The behavior of complexes **1** or **2** in deaerated noncoordinating solvents such as benzene or chloroform is dominated by the existence of equilibrium 1. The possible irreversible

$$\underset{\mathbf{3}}{\mathrm{Fe(TPP)}(i\text{-PrNO})} + \mathrm{L} \rightleftarrows \underset{\mathbf{2}}{\mathrm{Fe(TPP)}(i\text{-PrNO})(\mathrm{L})} \quad (1)$$

reaction (2) has only been observed upon addition of an excess

$$\mathrm{Fe(TPP)}(i\text{-PrNO})(\mathrm{L}) + \mathrm{L} \rightarrow \mathrm{Fe(TPP)(L)_2} + \mathrm{(CH_3)_2C{=}NOH} \quad (2)$$

of good ligands such as pyridine, imidazoles, amines, or phosphines. The spectral characteristics of the pentacoordinate complex **3** are those of a dilute solution of complex **2d** in benzene (5×10^{-6} M), since, under these conditions, equilibrium 1 is almost completely shifted to the left, taking into account the relatively low affinity of MeOH for complex **3** (Table I). Upon addition of increasing amounts of ligand L to complex **3**, the spectra of the corresponding hexacoordinate complexes progressively appear with isosbestic points, allowing the determination of the equilibrium 1 constants indicated in Table I. Because of the high affinity of L ligands such as py, *i*-$PrNH_2$, or *N*-MeIm for complex **3**, only a moderate excess of these ligands is necessary to shift equilibrium 1 almost completely to the right, thus giving the spectra of complexes **2**. In fact, addition of a larger excess of these L ligands leads to the progressive irreversible formation of the hemochromes Fe(TPP)(L)$_2$. For instance, complex **2a**, 8.5×10^{-5} M in deaerated benzene, is half transformed into Fe(TPP)(py)$_2$ in about 6 h in the presence of 1 M pyridine.

^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of complex **2a**, 2.4×10^{-2} M in $CDCl_3$ at 20 °C, is shown in Figure 4. The signals corresponding to the porphyrin ring protons (between 7.5 and 8.6 ppm) are as expected for diamagnetic Fe^{II}(TPP) complexes such as Fe(TPP)(py)$_2$,[16] Fe(TPP)(CS),[17] or Fe(TPP)(carbene)[18]

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Table III. ^1H NMR Data of Fe(P)(*i*-PrNO)L Complexes[a]

	porphyrin				*i*-PrNO		
		H_{Ph}			CH	CH_3	
	H_{Pyr}	*o*	*o'*	*m,p*	(h, 6.5)	(d, 6.5)	L
1	8.73	8.09		7.71	−1.09	−2.15	*c*
2a	8.65	8.10	8.01	7.69	−0.82	−2.02	1.53 (d, 6.5), 5.23 (t, 6.5), 6.11 (t, 6.5)
2b	8.65	8.09	8.06	7.72	−0.94	−2.03	−3.16 (h, 6.5), −1.84 (d, 6.5), −4.64
2c	8.61	8.08	8.02	7.67	−0.84	−2.01	0.70 (s), 1.23 (s), 2.18 (s), 4.8 (s)
2d	8.72	8.12	8.06	7.70	−1.19	−2.10	*c*
2e	8.54	8.07	7.95	7.71	−0.54	−2.01	4.09 (t, 7.5), 6.53 (t, 7.5), 6.85 (t, 7.5), −2.57 (d, 8.5)
3	8.72	8.10		7.72	−0.46	−2.26	
4	8.61	7.98	7.92	7.64	−0.86	−2.07	1.52 (d, 6.5), 5.21 (t, 6.5), 6.13 (t, 6.5)
5[d]	8.64	7.96	7.86	7.46	−0.86	−2.04	1.58 (d, 6.5), 5.19 (t, 6.5), 6.10 (t, 6.5)
6	8.86	*b*	*b*	*b*	−1.71	−2.45	0.89 (d, 6.5), 4.96 (t, 6.5), 5.88 (t, 6.5)

[a] 0.1 M in deaerated $CDCl_3$, at −63 °C, 250 MHz, δ (ppm/Me_4Si) (multiplicity,[1] *J* in Hz). [b] H meso δ 9.79, 9.68, 9.66, 9.57; CH_2: 4.26, 3.17; CH_3 3.61, 3.58, 3.52, 3.47. [c] An excess of L is required in order to get the spectra of the hexacoordinate species. [d] CH_3 of TTP δ 2.66.

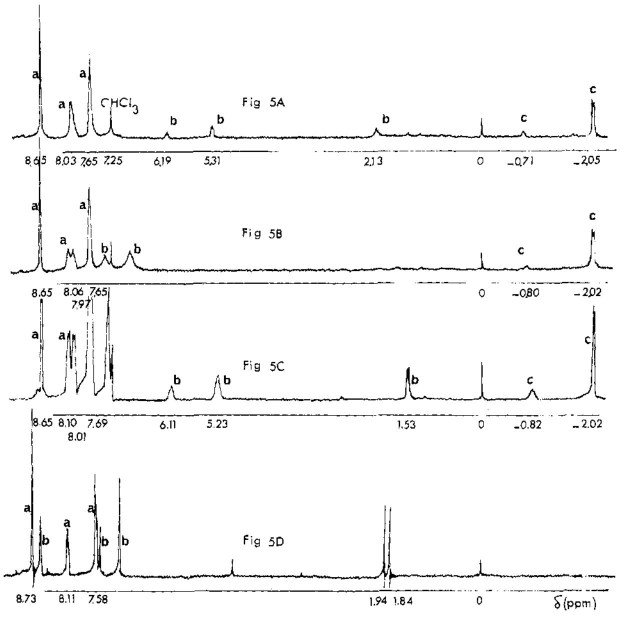

Figure 5. ^1H NMR study of complex **2a**: Fe^{II}(TPP)(*i*-PrNO)(py). Signals: a (porphyrin), b (pyridine), c (*i*-PrNO). (A) **2a**, 2.4×10^{-2} M in $CDCl_3$ at 20 °C; (B) addition of 2 μL of pyridine-d_5 at 20 °C; (C) conditions as in (B) but at −63 °C; (D) decomposition of **2a** in neat C_5D_5N giving Fe(TPP)$(C_5D_5N)_2$.

complexes. The other signals, corresponding to the protons of the axial ligands py and *i*-PrNO are well separated because of the large ring current-induced shifts which depend on the distance of these protons to the porphyrin plane.

Upon addition of 2 equiv of pyridine to the solution (Figure 5B), one observes average signals for pyridine which are indicative of a rapid exchange of this ligand (vs. NMR time scale) under these conditions. This exchange becomes slow upon cooling to −63 °C as shown by the appearance of both signals of free and bound pyridine (Figure 5C), allowing the determination of the NMR characteristics of complex **2a** itself. Therefore, from the chemical shifts of the pyridine protons of complex **2a** at 20 °C (Figure 5A), one can estimate that about 93% of starting complex involved in equilibrium 1 is in the hexacoordinate form **2a**, under the ^1H NMR spectrum recording conditions at 20 °C. When the solution of complex **2a** without any excess of pyridine is cooled to −63 °C, two sets of signals appear corresponding respectively to complexes **2a** (δ −2.02 and −0.82 for *i*-PrNO) and **3** (−2.26 and −0.41) which are in slow equilibrium. Under these conditions, the solution contains no more than 5% of complex **3**.

Similar results have been obtained with the other nitrosoalkane complexes, the ^1H NMR data of which are compared in Table III. It is noteworthy that in the case of complexes **1** and **2d**, the exchange rate between free and bound L (L = *i*-PrNHOH or MeOH) is fast even at −63 °C.

From its ^1H NMR characteristics, one can conclude that the pentacoordinate complex **3** is diamagnetic and, at least formally, a Fe(II) low-spin complex, like other previously described pentacoordinate complexes involving a strong axial ligand such as Fe(TPP)(CO),[16] Fe(TPP)(CS),[17] Fe(TPP)(CCl_2),[18] Fe(TPP)-$(C{=}CAr_2)$,[19] or Fe("capped porphyrin")$(PnBu_3)$.[20] It is different from Fe(II) pentacoordinate complexes involving axial ligands such as alcohols, ethers, or the sterically hindered 2-methylimidazole ligand, which are in the high-spin ($S = 2$) state.[21]

^1H NMR spectroscopy allows an easy determination of the nature of the axial ligands present in the iron–porphyrin–nitrosoalkane complexes obtained as crystalline solids by the aforementioned techniques. Accordingly, upon dissolution of a Fe(porphyrin)(R_2CHNO)(L) complex in neat pyridine-d_5, the L ligand is immediately replaced by pyridine-d_5 and the signals of free L appear. Then, reaction 2 slowly occurs (within a few hours for a 8×10^{-2} M complex), with appearance of the signals corresponding to the oxime $R_2C{=}NOH$ and Fe(TPP)(pyridine-d_5)$_2$ (Figure 5D). The only exception to this general behavior is the reaction of complex **1** in neat pyridine-d_5, since in this case, the liberated L ligand, *i*-PrNHOH, is able to further react with Fe(TPP)(py-d_5)$_2$ transiently generating complex **2b**, presumably via dismutation of *i*-PrNHOH in the medium.[8i]

^{13}C NMR Spectroscopy. The ^{13}C NMR spectrum of complex **2a** (0.2 M in $CDCl_3$ at 20 °C) displays seven signals, corresponding to the porphyrin carbons, whose shape and chemical shifts are very similar to those of $TPPH_2$,[22] Zn(TPP),[23] Cd(TPP),[24] or Fe(TPP)(CCl_2).[18] This is a further argument in favor of the diamagnetism of complex **2a**. The signals corresponding to bound *i*-PrNO are at 82.1 and 16.4 ppm. These porphyrin and *i*-PrNO resonances are not modified upon addition of 1 equiv of pyridine, whereas the pyridine resonances are shifted in a position intermediate between those of free and bound pyridine. This indicates

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Table IV. ^{13}C NMR Data of Fe(P)(*i*-PrNO)L Complexes[a,b]

	δ ^{13}C(porphyrin)			δ ^{13}C(phenyl ring)				δ ^{13}C(*i*-PrNO)	
	α	β	meso	Cq	*o*	*m*	*p*	CH	CH_3
1[c]	145.4	132.8	119.7	142.2	133.7	126.3	127.2	82.0	16.4
2a	145.0	132.3	119.1	142.2	133.5	126.1	127.0	82.0	16.3
2b	145.6	132.9	120.0	142.1	133.7	126.3	127.2	82.7	16.4
2c	145.0	132.2	119.2	142.8	133.8	126.0	126.9	80.9	16.4
2d[c]	145.0	132.0	119.3	142.0	133.3	125.8	126.7	82.2	15.8
2e	145.3	132.6	119.2	142.5	133.7	126.1	126.9	80.4	16.3
4	144.9	132.6	118.2	140.6	134.7	126.5	133.5	82.3	16.4
5[e]	145.0	131.9	119.3	139.5	132.3	126.7	136.3	81.9	16.3
6	*d*							80.9	15.7

[a] 0.2 M in deaerated $CDCl_3$ at 33 °C, δ (ppm/Me_4Si); the assignments given for the porphyrin ^{13}C signals were done according to ref 22–25. [b] ^{13}C NMR signals for the ligand L are given in the Experimental Section. [c] Spectrum obtained with an excess of L. [d] δ 173.3, 143.8, 143.5, 143.2, 141.2, 139.6, 139.4, 137.8, 130.6, 99.9, 99.3, 97.0, 95.5, 51.5, 37.4, 22.1, 13.9, 11.9. [e] CH_3 of TTP δ 21.6.

that equilibrium 1 is completely shifted toward the hexacoordinate species in both conditions, as expected if one takes into account the high concentration of complex **2a** used, the results of ^1H NMR studies, and the high affinity constant of pyridine for complex **3** determined previously (Table I). The ^{13}C NMR characteristics of various nitrosoalkane–iron–porphyrin complexes have been similarly determined except for complexes **1** and **2d** for which addition of an excess of L was needed in order to get the spectra of the hexacoordinate species (Table IV).

Stability of the Fe–RNO Bond. In deoxygenated solvents like $CHCl_3$, C_6H_6, or alcohols, complexes **1** and **2** are stable indefinitely. No dissociation of the Fe–RNO bond could be detected even after an important dilution ([complex] $\approx 10^{-7}$ M). This indicates a very high affinity of the nitrosoalkanes for iron(II)–porphyrins. This high affinity is confirmed by (i) the lack of displacement of the RNO ligand by carbon monoxide (1 atm, even at −63 °C), as already observed for the nitrosoalkane–hemoprotein complexes,[3,4] and (ii) the easy formation of complex **2d** upon interaction of Fe(TPP) with the dimer $(i\text{-PrNO})_2$ which is dissociated to *i*-PrNO to only a minor extent at 70 °C.

In aerated solution, the Fe(porphyrin)(*i*-PrNO)(L) complexes are irreversibly oxidized to the μ-oxo dimer $[Fe^{III}(porphyrin)]_2O$. The half-lives of the Fe(TPP)(*i*-PrNO)(L) complexes, 10^{-4} M in aerated benzene, depend on the nature of the L ligand. They decrease from 48 to 5.3 and 1.6 h when going from L = *N*-MeIm to L = py and MeOH, respectively. The stability of the complexes increases with the binding constant of L (Table I), suggesting that the oxidation proceeds through interaction of dioxygen with the pentacoordinate species **3**. The nature of the solvent also influences the oxidation rate of complexes **2**; for instance, the half-lives of **2a** (10^{-4} M at 27 °C) are respectively 14, 5.3, and 0.3 h in MeOH, benzene, and DMF. In comparison, the Fe^{II}(TPP)(L)(L′) complexes known to give reversible dissociation of both iron–axial ligand bonds in solution, such as $Fe(TPP)(py)_2$ and Fe(TPP)(py)(CO) are considerably more sensitive to dioxygen in identical conditions ($t_{1/2}$) for the oxidation of these complexes 10^{-4} M in benzene at 27 °C: 0.01 and 0.5 h, respectively). On the contrary, Fe^{II}(TPP)(L)(L′) complexes containing one iron–axial ligand bond which is not reversibly dissociated in solution such as the Fe–RNO bond, are more stable to oxygen; for instance, the $Fe(TPP)(CCl_2)$ complex is half-oxidized under identical conditions after 4 h,[18] and the Fe(TPP)(CS)[17] and $Fe(TPP)(C{=}CAr_2)$[19] complexes appear indefinitely stable to oxygen in solution.

Discussion

The aforementioned results show that the formation of very stable iron–porphyrin–nitrosoalkane complexes is a general phenomenon, which allows to understand the previously reported formation and great stability of hemoglobin–, myoglobin–, and (cytochrome P-450)–nitrosoalkane complexes.[3-5] For instance, these results explain the mechanism of formation of the Fe^{II}–RNO bond upon reaction of iron(III)–porphyrin and RNHOH. This reaction implies a two-electron oxidation of RNHOH to RNO. The results of the reaction performed with the Fe(TPP)(Cl):*i*-PrNHOH 1:2 molar ratio indicate that the starting iron(III)–porphyrin acts as a one-electron oxidant and that, under anaerobic conditions, the second one-electron oxidant is *i*-PrNHOH itself. The stoichiometry of the reaction, which involves a dismutation of RNHOH, is as follows:

$$2Fe^{III}(TPP)(Cl) + 3(i\text{-PrNHOH}) \xrightarrow{py} 2Fe^{II}(TPP)(i\text{-PrNO})(py) + i\text{-PrNH}_2 + H_2O + 2HCl$$

Concerning the binding mode of the nitrosoalkanes in the iron–porphyrin complexes, the end-on binding by nitrogen is demonstrated by X-ray crystallography in the case of complex **2b**. It should be involved in the other described Fe(porphyrin)(RNO)(L) complexes because of the close similarity of their spectral data with those of complex **2b**. This binding mode is also very likely in the hemoprotein–nitrosoalkane complexes since the electronic spectra of Fe(protoporphyrin IX)(*i*-PrNO)(*N*-MeIm) and myoglobin–Fe–*i*-PrNO are almost identical.[10]

When compared to other nitrogenous ligands such as amines, pyridines, or imidazoles, nitrosoalkanes appear as particularly strong ligands of iron(II) porphyrins. The great strength of the Fe–RNO bond is underlined by the following results: (i) it does not dissociate at room temperature even upon great dilution of the complexes, (ii) the RNO ligand is not displaced by CO, while one L ligand of the hemochromes $Fe(TPP)(L)_2$ with L = amine or pyridine is readily displaced by CO under these conditions, (iii) the Fe–N(O)R distance of complex **2b** (1.865 (14) Å) is considerably shorter than the $Fe\text{–}NH_2i\text{-Pr}$ distance (2.100 (14) Å) or than the Fe–N distances found in various hemochromes $Fe(TPP)(amine)_2$ (≈2.1 Å).[15] In agreement with a strong Fe–RNO bond, the pentacoordinate Fe(TPP)(*i*-PrNO) complex **3** is low spin as Fe^{II}(TPP)(NO), while pentacoordinate Fe^{II}(TPP)(L) complexes containing weak nitrogen-bound axial ligands (L = amine) are high spin ($S = 2$).[21] In this respect, nitrosoalkanes are closer to strong π-acid ligands such as NO,[26] CO,[16] CS,[17] CCl_2,[18] or $C{=}CAr_2$,[19] the formation of low-spin complexes upon coordination of a π-acid ligand to a iron(II)porphyrin having been related to a destabilization of the iron d_{z^2} orbital.[16]

The extent of back-bonding from iron to RNO in complexes **2** and of the contribution of resonance form B to the description of the Fe–RNO bond is emphasized by (i) the ≈100-cm^{-1} decrease of the ν_{NO} frequency upon coordination of *i*-PrNO (Table V) to iron(II)–porphyrins, (ii) the N–O distance of complex **2b** (1.260 (20) Å) which is longer than the N–O distance assumed for free CH_3NO (1.18 Å)[7] but close to that of the cis and trans nitrosodimers $CH_3N(O){=}N(O)CH_3$ (respectively 1.31 and 1.25 Å).[7]


A, nitroso form B, nitroxide form

Back-donation from the metal to the nitrosoalkane ligand in complex **2b** seems larger than in the $PtCl_2(t\text{-BuNO})_2$ complex, for which ν_{NO} (1555 cm^{-1}) and $d_{N\text{–}O}$ (1.21 Å)[7c] are very close to ν_{NO} (1546 cm^{-1}) and $d_{N\text{–}O}$ (≈1.2 Å) of free *t*-BuNO, but smaller

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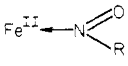
Table V. Comparison of Some Characteristics of RNO- and O_2-Fe^{II}(Porphyrin) Complexes

	IR ν_{XO}, cm^{-1} (X = O or N)	resonance Raman, cm^{-1}		Mössbauer				
				T, K	δ, mm/s	ΔE_q, mm/s	η	ref
Fe(TPP)(i-PrNO)(i-$PrNH_2$)	1432	1365^a	1565	300	0.22	1.19		32
				4.2	0.29	−1.23	0.6	
Fe(TPP)(i-PrNO)(N-MeIm)	1432			300	0.20	1.15		32
				4.2	0.29	−1.15	0.5	
$C_6H_{11}NO$	1558^b							
(t-Bu)$_2$NO·	1345^c							
Fe(TpivPP)(N-MeIm)(O_2)	1159^d	1366^e	1563	295	0.19	1.28		31
				4.2	0.28	−2.10	0.1–0.3	
O_2	1580^f							
O_2	1097^f							

[a] Reference 30. [b] Reference 7. [c] Reference 27. [d] Reference 28. [e] Reference 29. [f] Reference 39.

than in the $(Ru(NH_3)_5[HOC(CH_3)_2CH_2NO)])^{2+}$ complex[9h] for which ν_{NO} = 1370 cm^{-1} is close to the ν_{NO} = 1345 cm^{-1} of the nitroxide (t-Bu)$_2$N-O .[27]

Since the NO group of nitrosoalkanes is isoelectronic with dioxygen and since both O_2[28] and i-PrNO are bound in a bent end-on fashion to the iron of *meso*-tetraphenylporphyrins, it is interesting to compare the characteristics of the Fe–N(O)R and Fe–O_2 bonds. For this purpose, some characteristic spectroscopic data of the Fe(TPP)(i-PrNO)(N-MeIm) and Fe("picket fence"-TPP)(O_2)(N-MeIm)[28] complexes are indicated in Table V. For the data concerning the RNO or O_2 ligands, one notes that for both complexes, the ν_{X-O} (X = N or O) frequency is closer to those of related species involving an X–O simple bond, (t-Bu)$_2$N–O· and O_2·$^-$, respectively, than to those involving an X=O double bond, CH_3NO and O_2. The effects of the RNO or O_2 ligands on the porphyrin ring are similar, as shown by the close resemblance of the electronic and resonance Raman spectral data of the two complexes. Of particular interest are the two strong resonance Raman bands, called A and D, around 1360 and 1560 cm^{-1} which are present in all Fe(TPP) complexes and correspond to porphyrin vibrational modes.[29,30] These bands are sensitive to changes in spin and oxidation state of the iron.[29] For the low-spin Fe(II) complexes, they were shown to be particularly sensitive to dπ(Fe)–π*(TPP) interactions. Band A frequency is more specifically dependent on π acidity of the axial ligands, and band D frequency more specifically reflects the stereochemistry around the iron atom.[30] The nearly identical position of the 1365- and 1565-cm^{-1} bands in the i-PrNO and O_2 complexes (Table V), which are both low spin with the iron in the mean plane of the porphyrin ring, indicate very similar π-accepting ability of these two ligands. The positions of these bands are quite different in low-spin Fe^{II}(TPP)(L)$_2$ complexes with L = py or Im (ca. 1359 and 1560 cm^{-1}) but closer in low-spin Fe(III) complexes like Fe^{III}(TPP)(Im)$_2$(Cl) (1370 and 1568 cm^{-1}), suggesting, in agreement with IR data, an important contribution of resonance forms B or B′ to the description of the Fe–N(O)R and Fe–O_2 bonds.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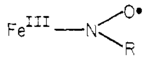
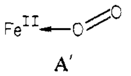

B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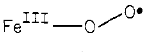
B′

The similarity of the π-accepting abilities of i-PrNO and O_2 is confirmed by the striking similarity of Mössbauer data of their complexes[31,32] (Table V): (i) nearly identical isomer shift δ and quadrupole interaction ΔE_q values at 300 K, (ii) identical isomer shift value at 4.2 K, (iii) a negative sign of the quadrupole interaction and the existence of a significant asymmetry parameter η for both complexes. The only difference is the variation of the ΔE_q value with temperature in the case of the O_2 complex. When comparing these Mössbauer parameters to those of various hexacoordinate Fe^{II}- or Fe^{III}(TPP)(L)(L′) complexes, with L = imidazole, CO, or amine, such a complete similarity is never observed.[32] These data led us to propose[32] that the Fe(TPP)(i-PrNO)(N-MeIm) complex has 3d orbital populations close to those calculated by Kirchner and Loew,[33] for model oxyferroporphyrin complexes.

Taken altogether, the data collected in Table V point to a great similarity between the coordinating properties of the O_2 and RNO ligands, at least in Fe(TPP) complexes.[40] It is noteworthy that an analogous similarity of the binding properties of nitroso-compounds and dioxygen has been reported in the case of molybdenum complexes.[9b,c]

As far as the hemoprotein complexes of O_2 or RNO are concerned, it is noteworthy that the resonance Raman spectra of hemoglobin (Hb)O_2 and $-CH_3NO$ complexes exhibit nearly identical positions of the porphyrin bands considered as markers of the spin and formal oxidation state of the iron (respectively 1377, 1584[3] and 1376, 1585 cm^{-1} [3]). This is a first indication in

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(40) NO is not isoelectronic with O_2 or RNO, and the Fe^{II}–NO complexes are paramagnetic (S = $^1/_2$), contrary to Fe^{II}–O_2 or –RNO complexes which are diamagnetic. However, there is a good parallel between the structural parameters of the Fe–N(O) bond in Fe(TPP)(i-PrNO)(i-$PrNH_2$) and Fe(TPP)(NO)(4-methylpiperidine).[41] In particular, both complexes involve a bent Fe–NO bond with short Fe–N(O) distances and relatively long Fe–N (trans amine) distances. Moreover, some Mössbauer parameters (ΔE_q) of Fe^{II}-i-PrNO[32] and Fe^{II}–NO[42] complexes are similar. One must, however, note that the Fe–N(O) distance in Fe(TPP)(NO)(4-methylpiperidine) is shorter (1.73 Å) than in Fe(TPP)(i-PrNO)(i-$PrNH_2$) (1.86 Å) and that the Fe–N (trans amine) distance is long (2.33 or 2.46 Å) in the former, whereas it is nearly normal (2.1 Å) in the latter.

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favor of similar bonding properties of O_2 and RNO to the iron(II) of hemoproteins.

Nitrosoalkanes thus appear as attractive dioxygen analogues which mimic quite well the bonding properties of dioxygen but which lead to considerably more stable Fe(II) complexes. This could be of interest for "model" studies of the properties of very unstable hemoprotein- or iron–porphyrin–dioxygen complexes. Nitrosoalkanes, which can be formed in vivo by various routes, i.e., oxidation of an amine or an hydroxylamine or reduction of a nitroalkane, and which bind strongly to the iron of hemoproteins,[3-6] leading to the inhibition of their functions,[6] should also play an important role in pharmacology and toxicology.[5]

Experimental Section

Physical Measurements. All experimental operations with Fe(II) complexes were performed on a vacuum line. UV and visible spectra were obtained, at 27 °C, on a Varian Super Scan 418 spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 221 spectrometer. Varian EM 390, Bruker 90, and Cameca 250 instruments were used for the ^{1}H NMR spectra and Bruker 90 for ^{13}C NMR spectra. Mass spectra were performed on a Varian CH7, Rieber spectrometer (70 eV) at temperatures ca. 220 °C. Elemental analyses were performed by the Service de Microanalyse du CNRS at Gif-sur-Yvette.

Reagents and Solvents. All solvents were deaerated before use by argon bubbling for 0.25 h. MeOH was distilled from $(MeO)_2Mg$ in an argon atmosphere. CH_2Cl_2, $CHCl_3$, and all other reagents were used as supplied (puriss, grade). Fe(TPP)(Cl), Fe(TTP)(Cl), Fe(TpClPP)(Cl), and Fe(DPDME)(Cl) were prepared according to literature procedures.[34,35] 2-(Hydroxyamino)propane, mp 87 °C (lit.[36] mp 87 °C) was obtained by reduction of 2-nitropropane by Zn–NH_4Cl. *trans*-2-Nitrosopropane dimer, mp 52 °C (lit.[37] mp 50–52 °C) was prepared by oxidation of the corresponding hydroxylamine with silver carbonate.[37]

Crystallographic Study. Prismatic dark crystals of $C_{50}H_{44}N_6OFe \cdot CHCl_3$ (M_r = 920.185) were grown by slow evaporation from a $CHCl_3$–CH_3OH solution under argon atmosphere. A well-formed crystal of about 0.3 × 0.4 × 0.4 mm was used for data collection and determination of the unit cell on a Philips PW 1100 diffractometer, using graphite monochromated Mo Kα radiation (λ 0.7107 Å).

Crystals were triclinic, space group $P1$ or $P\bar{1}$ with two molecules in the unit cell of the following dimensions: a = 10.885 (11) Å, b = 15.247 (19) Å, c = 15.516 (24) Å, α = 114.67 (10)°, β = 94.73 (13)°, γ = 89.25 (19°, V = 2331.4 Å^3, d_c = 1.314.

Parameter values were determined by the least-squares refinement of the θ values of 32 well-centered reflections.

The data were collected using the (θ–2θ) scan technique with a speed of 0.1° s^{-1}, a constant width of 2.0° up to five scans depending on the intensity of each reflection. The measurement of the background was performed during 10 s on both sides of each reflection. From 5690 independent intensities (2° < θ < 22°), 2614 were considered as observed, their value being greater than twice $\sigma(I)$ calculated from counting statistics. During the course of the intensity data collection, the crystal showed no loss in intensity due to exposure.

Solution and Refinement of the Structure. The structure was solved by Patterson and Fourier methods in space group $P\bar{1}$. Initially, it was assumed that the Fe atom was in general position. All the atoms of the porphyrin ring could be located but not refined (R = 0.040).

Two independent molecules with iron atoms on centers of symmetry were then considered. The position of the atoms of the porphyrin ring and those of axial 2-nitrosopropane ligand with "N-end-on" geometry were developed by Fourier and difference Fourier syntheses. In addition, a molecule of $CHCl_3$ solvent was found in the asymmetric unit. The structure was refined by least-squares techniques. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where w was taken as $\sigma^{-2}(F_o)$. Atomic scattering factors were taken from ref 38, and the effects of anomalous dispersion for iron were included in F_c. A least-squares refinement involving anisotropic thermal parameters for the Fe atoms and isotropic thermal parameters for the TPP, the solvent molecule, and the centrosymmetric axial 2-nitrosopropane ligands led to the values of R and R_w of 0.109 and 0.110.

At this stage, the B value for the oxygen atom of the 2-nitrosopropane group was 14.7 Å (14 for the second molecule of the asymmetric unit) while B values for the N and C atoms were respectively 4.9 (4.8) and 7.0 (4.2), the Fe–N distance being 1.997 Å (2.002). These results were consistent with the presence of 2-nitrosopropane and 2-aminopropane as axial ligands. It was assumed that the correct space group was the centrosymmetric one, $P\bar{1}$ rather than the noncentrosymmetric one $P1$. With this assumption, the two ligands *i*-PrNO and *i*-$PrNH_2$ are superimposed (because of $\bar{1}$ symmetry). In the next cycles of refinement the disordered groups were included with occupancy factors of 0.5 and Fe–N distances of 1.74 (nitroso) and 2.14 (amine) Å.

Hydrogen positions were calculated for the porphyrin ring, $CHCl_3$, and the phenyl rings [d_{C-H} = 1.00 Å, B(H) = B(C)] and added as fixed contributions. Temperature factors were anisotropic for TPP, $CHCl_3$, and the oxygen atom of *i*-PrNO group, and isotropic for the atoms of the ligands which were superimposed. Parameters were refined in three large blocks including alternatively the porphyrin core, the *i*-PrNO and *i*-$PrNH_2$ groups. Refinement converged to the final R and R_w values of 0.059 and 0.060. The maximum deviations in the last cycles were 0.1σ for the atoms of TPP and 0.5σ for atoms of the disordered ligands.

The disordered space group $P\bar{1}$ has been assumed in our calculations although the *i*-PrNO and *i*-$PrNH_2$ ligands do not need to be disordered in space group $P1$. Several factors suggested that the space group $P\bar{1}$ is correct. The last difference syntheses showed no peak greater than 0.4 e/Å^3 and 28 of the 29 H atoms were located on difference maps. The vibrational ellipsoids of Fe(TPP) portions seemed quite normal. The strongest evidence that the space group is correct is the fact that the two molecules in the asymmetric unit are quite identical.

[2-(Hydroxyamino)propane](2-nitrosopropane)(*meso*-tetraphenylporphyrinato)iron(II), Fe(TPP)(*i*-PrNO)(*i*-PrNHOH) (1). Fe^{III}(TPP)(Cl) (1 g) in $CHCl_3$ (30 mL) was added, under argon, to *i*-PrNHOH (0.5 g) in $CHCl_3$ (10 mL). After the mixture was stirred 6 h, the solvent was removed under vacuum. Recrystallization from $CHCl_3$–MeOH at −15 °C afforded **1**: 1.1 g (95%); mass spectrum, M$^+$ *m/e* 668 [Fe(TPP)], 75 (*i*-PrNHOH), 73 (*i*-PrNO). Anal. Calcd for $C_{50}H_{44}N_6O_2Fe$ (816.8 g/mol): C, 73.52; H, 5.43; N, 10.28. Found: C, 73.92; H, 5.45; N, 10.54.

General Procedure for Preparation of Complexes 2a, 2b, 2c, 2d, 4, 5, 6. Fe^{III}(TPP)(Cl) was treated by *i*-PrNHOH in $CHCl_3$ (40 mL) at 20 °C, under an argon atmosphere in the presence of the L ligand. The volume of the solution was reduced by argon bubbling. Two recrystallizations from $CHCl_3$, MeOH, and L give the expected complexes. Most of their spectral data are indicated in the tables.

(2-Nitrosopropane)(pyridine)(*meso*-tetraphenylporphyrinato)iron(II), Fe(TPP)(*i*-PrNO)(py) (2a). Fe^{III}(TPP)(Cl) (0.6 g), *i*-PrNHOH (0.3 g), pyridine (0.1 mL), reaction time 15 h, recrystallization from $CHCl_3$ (5 mL), MeOH (8 mL), pyridine (0.1 mL): yield 0.7 g (100%); ^{13}C NMR of 6th ligand (py) δ 146, 133, 120.6; mass spectrum, M$^+$ *m/e* 668 [Fe(TPP)], 79 (py), 73 (*i*-PrNO). Anal. Calcd for $C_{52}H_{40}N_6OFe$ (820.2 g/mol): C, 76.07; H, 4.92; N, 10.25. Found: C, 75.92; H, 5.00; N, 9.91.

Complex **2a** has been also prepared by reaction of Fe^{II}(TPP) with (*i*-PrNO)$_2$. Fe^{II}(TPP) in benzenic solution (100 mL) was obtained by reduction of Fe^{III}(TPP)(Cl) (0.07 g) by an aqueous solution of $Na_2S_2O_4$. The organic layer was decanted, dried, and added to a deaerated benzenic solution of (*i*-PrNO)$_2$ (0.062 g) at 70 °C. The mixture was kept at 70 °C for 0.5 h. Then 0.01 mL of pyridine was introduced at room temperature. The solvent was removed by argon bubbling. Recrystallization from CH_2Cl_2–MeOH afforded **2a**, 0.067 g (85%).

(2-Aminopropane)(2-nitrosopropane)(*meso*-tetraphenylporphyrinato)iron(II), Fe(TPP)(*i*-PrNO)(*i*-PrNH$_2$) (2b). Fe^{III}(TPP)(Cl) (0.2 g), *i*-PrNHOH (0.1 g), *i*-$PrNH_2$ (0.04 mL), reaction time 15 h, recrystallization from $CHCl_3$ (2 mL), MeOH (3 mL), *i*-$PrNH_2$ (0.1 mL) at −15 °C: yield 0.2 g (89%); ^{13}C NMR of 6th ligand (*i*-$PrNH_2$) δ 48.7, 16.0; mass spectrum, M$^+$ *m/e* 688 [Fe(TPP)], 73 (*i*-PrNO), 59, 58 (*i*-$PrNH_2$). Anal. Calcd for $C_{50}H_{44}N_6OFe$ (800.8 g/mol): C, 74.99; H, 5.53; N, 10.49. Found: C, 74.99; H, 5.40; N, 10.24.

(*N*-Methylimidazole)(2-nitrosopropane)(*meso*-tetraphenylporphyrinato)iron(II), Fe(TPP)(*i*-PrNO)(*N*-MeIm) (2c). Fe^{III}(TPP)(Cl) (0.22 g), *i*-PrNHOH (0.1 g), *N*-MeIm (0.04 mL), reaction time 15 h, recrystallization from $CHCl_3$, MeOH (3 mL): yield 0.19 g (73%); ^{13}C NMR of 6th ligand (*N*-MeIm) δ 132.5, 124.4, 117.4, 33.2; mass spectrum, M$^+$ *m/e* 668 [Fe(TPP)], 82 (*N*-MeIm), 73 (*i*-PrNO). Anal. Calcd for $C_{51}H_{41}N_4OFe$ (823.8 g/mol): C, 74.35; H, 5.01; N, 11.90. Found: C, 74.46; H, 5.00; N, 11.81.

(Methanol)(2-nitrosopropane)(*meso*-tetraphenylporphyrinato)iron(II), Fe(TPP)(*i*-PrNO)(MeOH) (2d). Fe^{III}(TPP)(Cl) (0.45 g), *i*-PrNHOH (0.1 g), MeOH (20 mL), reaction time 6 h, recrystallization from CH_2Cl_2–MeOH: yield 0.45 g (90%); mass spectrum, M$^+$ *m/e* 668 [Fe(TPP)], 73 (*i*-PrNO). Anal. Calcd for $C_{48}H_{39}N_5O_2Fe$ (773.2 g/mol): C, 74.56; H, 5.08; N, 9.05. Found: C, 74.61; H, 4.64; N, 8.87.

(Dimethylphenylphosphine)(2-nitrosopropane)(*meso*-tetraphenylporphyrinato)iron(II), Fe(TPP)(*i*-PrNO)(PPhMe$_2$) (2e). Fe(TPP)(*i*-PrNO)(MeOH) (0.15 g) was treated by $PPhMe_2$ (0.023 g, 0.8 equiv) in deaerated CH_2Cl_2 during 2 min. MeOH (10 mL) was added, and purple crystals were filtered and washed with MeOH, yield 0.152 g (88%). As shown by ^{1}H NMR spectroscopy, these crystals contain a mixture of Fe(TPP)(*i*-PrNO)($PPhMe_2$) (94%) and Fe(TPP)($PPhMe_2$)$_2$ (6%): ^{31}P NMR ($CDCl_3$) δ 5.35 (from H_3PO_4); mass spectrum, M$^+$ *m/e* 668 [Fe(TPP)], 138 ($PPhMe_2$), 73 (*i*-PrNO).

(2-Nitrosopropane)(*meso*-tetraphenylporphyrinato)iron(II), Fe(TPP)(*i*-PrNO) (3). Fe(TPP)(*i*-PrNO)(*i*-PrNHOH) (0.08 g) in C_6H_6 (5 mL) was treated by HCl (0.1 N, 5 mL), under an argon atmosphere, during 5 min. The organic layer was washed twice with water (5 mL) and dried (deaerated Na_2SO_4), and the solvent removed by argon bubbling. The resulting crystalline complex has been heated (60–70 °C) under vacuum (0.1 mmHg) for 4 h: yield 0.07 g (94%); mass spectrum, M^+ m/e 668 Fe(TPP), 73 (*i*-PrNO).

(2-Nitrosopropane)(pyridine)(*meso*-tetra(4-chlorophenyl)-porphyrinato)iron(II), Fe(TpClPP)(*i*-PrNO)(py) (4). Fe^{III}(TpClPP)(Cl) (0.33 g), *i*-PrNHOH (0.12 g), pyridine (0.01 mL), reaction time 4 h, recrystallization from $CHCl_3$ (2 mL), MeOH (6 mL), pyridine (0.01 mL): yield 0.34 g (90%); ^{13}C NMR of 6th ligand (py) δ 146, 133.5, 120.8; mass spectrum, M^+ m/e 806 [Fe(TpClPP)], 79 (py), 73 (*i*-PrNO).

(2-Nitrosopropane)(pyridine)(*meso*-tetratolylporphyrinato)iron(II), Fe(TTP)(*i*-PrNO)(py) (5). Fe^{III}(TTP)(Cl) (0.3 g), *i*-PrNHOH (0.12 g), pyridine (0.01 mL), reaction time 4 h, recrystallization from $CHCl_3$ (2 mL), MeOH (6 mL), pyridine (0.01 mL): yield 0.32 g (93%); ^{13}C NMR of 6th ligand (py) δ 146.2, 132, 120.7; mass spectrum, M^+ m/e 724 [Fe(TTP)], 79 (py), 73 (*i*-PrNO).

(2-Nitrosopropane)(pyridine)(deuteroporphyrinato dimethyl ester)-iron(II), Fe(DPDME)(*i*-PrNO)(py) (6). Fe^{III}(DPDME)(Cl) (0.077 g), *i*-PrNHOH (0.5 g), pyridine (0.05 mL), reaction time 6 h, recrystallization from $CHCl_3$ (1 mL), MeOH (7 mL), pyridine (0.01 mL) at 5 °C: yield 0.07 g (67%); ^{13}C NMR of the 6th ligand (py) δ 145.8, 133, 120; mass spectrum, M^+ m/e 586 [Fe(DPDME)], 79 (py), 73 (*i*-PrNO).

Labeled [^{15}N]Nitromethane, Me^{15}NO$_2$. To a stirred mixture of 2.63 g of $ClCH_2COOH$ and 50 g of cracked ice was added cold 1 M NaOH just enough to make the solution alkaline to phenolphthalein. The solution was mixed with 1.4 g of $^{15}NO_2Na$ in 10 mL of water and with 1.3 g of boric acid. The solution was heated slowly until bubbles of carbon dioxide appeared. Nitromethane and water were then distilled and nitromethane extracted with ether and dried (Na_2SO_4). Careful distillation of ether gave a 0.62-g residue which was found by ^{1}H NMR to contain a 70:30 mixture of Me^{15}NO$_2$ and Et_2O: IR (neat) $\nu_{^{15}NO}$ 1515 cm^{-1}; ^{1}H NMR δ 4.29 (d, $J_{^{15}N-CH_3} = 2.5$ Hz).

(Hydroxy[^{15}N]amino)methane Chlorohydrate, Me^{15}NHOH·HCl. Me^{15}NO$_2$ (0.35 g) in 20 mL of MeOH was added to a solution of NH_4Cl (1 g) in 25 mL of cold water. To the vigorously stirred mixture was added 1 g of Zn powder slowly. After the mixture was stirred for 0.3 h, the solid was filtrated and washed with MeOH. The solution was made acidic with concentrated HCl. Water was distilled off and MeOH added in order to precipitate NH_4Cl. Upon removal of MeOH, the resulting colorless oil crystallized upon cooling to −15 °C and was used without any further purification.

([^{15}N]Nitrosomethane)(pyridine)(*meso*-tetraphenylporphyrinato)iron(II), Fe(TPP)(Me^{15}NO)(py). Fe^{III}(TPP)(Cl) (0.14 g) was treated by Me^{15}NHOH, HCl (0.4 g) in MeOH–CH_2Cl_2 (1:1) (25 mL), under an argon atmosphere, in the presence of 0.15 mL of pyridine during 4 h. The volume of the solution was reduced by argon bubbling. The purple crystals were recrystallized from CH_2Cl_2, MeOH, and pyridine: yield 0.11 g (70%); visible spectrum (CH_2Cl_2) 424, 536 nm; IR 1390, 918 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 8.66 (s, 8 H, pyrrole), 8.08 (m, 8 H, *o*-Ph), 7.70 (m, 12 H, *m*-, *p*-Ph), 6.17 (t, $J = 6.5$ Hz, 1 H, *p*-py), 5.30 (t, $J = 6.5$ Hz, 2 H, *m*-py), 2.05 (d, $J = 6.5$ Hz, 2 H, *o*-py), −1.29 (d, $J_{^{15}N-CH_3} = 3$ Hz, MeNO); mass spectrum, M^+ m/e 688 [Fe(TPP)], 79 (py), 46 (Me^{15}NO).

Stoichiometry of the Reaction between Fe^{III}(TPP)(Cl) and *i*-PrNHOH. To a deaerated solution of Fe^{III}(TPP)(Cl) in CH_2Cl_2 (0.35 g, 0.5 mmol) under argon was added a solution of *i*-PrNHOH (0.075 g, 1 mmol) in CH_2Cl_2. The argon bubbling was kept for 6 h. The solvents were removed by argon bubbling, giving 0.42 g of a crude mixture. This crude mixture (0.020 g) was dissolved in deaerated $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy. After addition of 5 μL of C_5D_5N, the chemical shifts (8.60, 8.00, 7.65, −0.74, −2.00 ppm) were those of the Fe(TPP)(*i*-PrNO)(py) complex **2a**. Additional signals at 1.42 and 1.34 ppm were attributed to *i*-PrNH$_2$, HCl, and *i*-PrNHOH·HCl by comparison with those of authentic samples added to the NMR tube.

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Registry No. 1, 84040-45-9; **2a**, 84027-23-6; **2b**, 73233-48-4; **2c**, 73233-49-5; **2d**, 84027-24-7; **2e**, 84027-25-8; **3**, 84027-26-9; **4**, 84027-27-0; **5**, 84027-28-1; **6**, 84027-29-2; Fe(TPP)Cl, 16456-81-8; Fe(TPP), 16591-56-3.

Supplementary Material Available: Tables of the final atomic coordinates for the non-hydrogen and hydrogen atoms, atomic thermal parameters, comparative bond distances and angles, and a list of the observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.