Table II. Solvent Viscosity Effects on Emission Mode Ratios for $Mo_2X_2(bridge)_2(PR_3)_2$ Complexes

complex			I(400 nm)/I(600 nm) by solvents[a]		
X	bridge	PR_3	n-PrOH[b]	n-BuOH[b]	77 K[c]
Cl	mhp	PEt_3	0[d]	0[d]	0.097
Cl	mhp	PMe_2Ph	0.11	0.56	1.0
Cl	mhp	$PMePh_2$	0.44	2.0	7.5
Cl	dmhp	PEt_3	0[d]	0[d]	0.054
Br	mhp	PEt_3	0[d]	0[d]	0[d]
Br	mhp	PMe_2Ph	0.073	0.19	0.24
Br	mhp	$PMePh_2$	0.084	0.27	0.76
Br	dmhp	PEt_3	0[d]	0[d]	0[d]

[a] A 600-nm emission was observed in all experiments. No 400-nm emission was observed in methanol at room temperature. The boxcar delay and window width were adjusted to allow intercomparison of trends as a function of solvent or compound. [b] Measurements at room temperature. [c] 4:1 ethanol:methanol glass. [d] No 400-nm emission was observed.

at room temperature. The effect of solvent viscosity is reduced by replacing the chlorine ligands with bromine. As an example, $Mo_2Br_2(mhp)_2(PMePh_2)_2$ has 10 times less 400-nm radiation in a low-temperature glass than does its chlorine counterpart. It appears that the larger size of the bromine atoms makes the entire compound more cylindrical, thereby reducing the effect of the bulky phosphine ligands.

The model used to explain the bimodal luminescence involves the large structural changes expected between those states having an intact δ bond and the nonbonding $\delta \rightarrow \delta^*$ excited state. The ground state and the ligand-localized excited state should have an eclipsed configuration, while the $\delta \rightarrow \delta^*$ state should have a staggered configuration that is restrained by the bridging ligands. When the molecule is excited into the ligand-localized excited state, it must internally convert to the metal–metal bond manifold before 600-nm emission can occur. For facile internal conversion, the geometry must change from eclipsed to staggered within the lifetime of the ligand-localized excited state. The apparent role of the bulky phosphines and the mhp ligands is the retardation of the twisting about the metal–metal bond, which allows emission to compete effectively with internal conversion. This same effect can be achieved through the use of a highly viscous solvent. An alternative model involves the suggestion that the $\delta \rightarrow \delta^*$ excited singlet state has a large deal of ionic character and distorts to the localized configuration, M^+M^-.[20] This drastic change in electron density would require that the nonbridging ligands undergo a geometric distortion. Such structural changes should have a similar effect on viscosity, as does the eclipsed/staggered postulate made above.

On the basis of either of the proposed models, the viscosity should have an effect on the decay of the two emission bands. One would expect that the lifetime of the ligand-localized transition would get longer as the structural changes necessary for radiationless internal conversion are retarded by viscosity. Indeed, the lifetime does increase with viscosity, going from 2.3 ns in methanol to approximately 6.7 ns in ethylene glycol. For identical reasons, one would expect that the lifetime of the $\delta \rightarrow \delta^*$ transition would get shorter as the structure is held in a configuration similar to that of the ground state. As well, this expectation is realized with a lifetime of 20 ns in methanol and 3 ns in ethylene glycol.

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Supplementary Material Available: Table SI, giving ^1H NMR spectral data for $Mo_2X_n(mhp)_{4-n}(PEt_3)_n$ and $Mo_2X_2(dmhp)_2(PEt_3)_2$ (1 page). Ordering information is given on any current masthead page.

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Preparation and Properties of Iron(II), Cobalt(III), and Zinc(II) *N*-Alkylporphyrin Complexes Involving Five-Membered Metal—O—C═C—N Metallacycles

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The preparation and properties of new *N*-alkylporphyrin complexes involving five-membered metal—O—C═C—N metallacycles are described. Iron(II) complexes exhibiting such a structure were prepared by chemical or electrochemical reduction of previously reported chloro N—C═C—O—Fe^{III} porphyrin complexes obtained by reaction of the iodonium ylide $C_6H_5I{=}X$ (X = CC(O)$CH_2C(CH_3)_2CH_2C$(O)) with Fe^{III}(porphyrin)(ClO_4) (porphyrin = TPP or TpClPP). These pentacoordinated Fe(II) complexes were rapidly oxidized by dioxygen and exhibited a high affinity for ligands such as CO or pyridine. The hexacoordinated CO complexes are the first examples of diamagnetic Fe(II) *N*-alkylporphyrin complexes. Acid demetalation of the pentacoordinated ferrous TPP derivative led to the corresponding free *N*-alkylporphyrin, which was isolated and further transformed into the corresponding Zn(II) complex. Elemental analyses and mass, ^1H NMR, and ^{13}C NMR spectra of the latter showed that it was also a metallacyclic *N*-alkylporphyrin complex involving a N—C═C—O—Zn(II) metallacycle. Finally, the reaction of the iodonium ylide $C_6H_5I{=}X$ with bromo Co^{III}(TPP) led to a similar bromo N—C═C—O—Co^{III}(TPP) complex, which is also the first example of a metallacyclic *N*-alkylporphyrin complex with a Co(III) ion. These results illustrate the generality of the access to this new class of metallacyclic *N*-alkylporphyrin complexes.

N-Alkylporphyrins have been identified as products from the metabolism of drugs by animal liver cytochromes P-450.[1,2] In the particular case of the oxidative metabolism of alk-1-enes, *N*-(2-hydroxyalkyl)protoporphyrin IX compounds have been isolated after acidic extraction from livers of animals treated by alkenes.[3] Taking into account previously known data on the structure and reactivity of the oxygen-active species and on the

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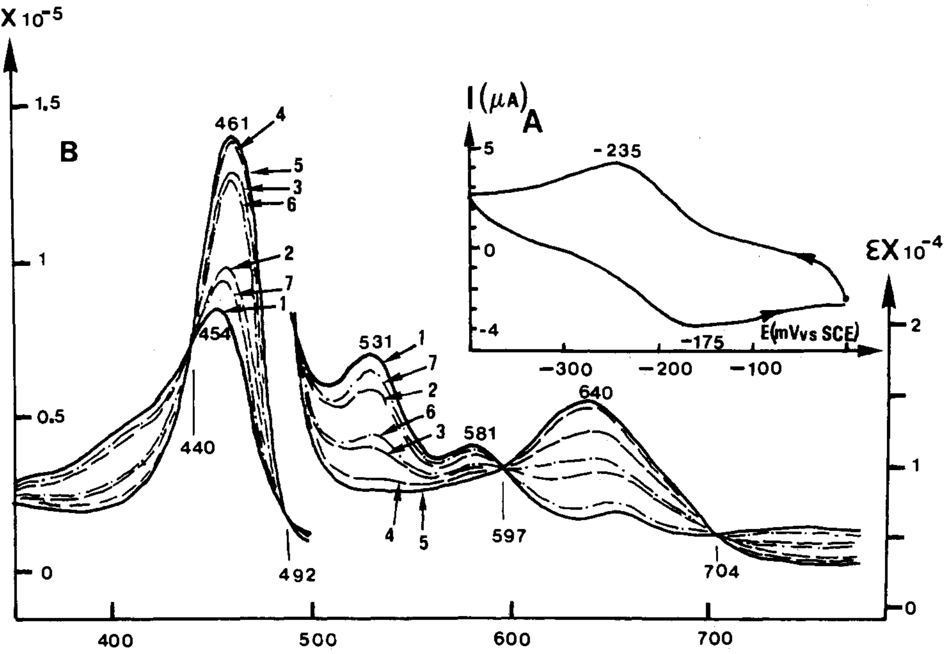
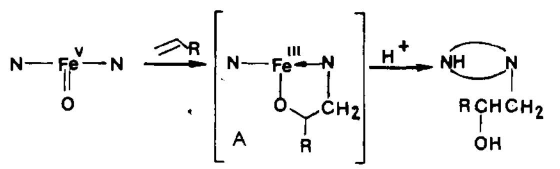


Figure 1. (A) Cyclic voltammogram of complex **4a** (0.9 mM in DMF, 0.2 M LiCl) at a glassy-carbon electrode. Potential sweep rate: 50 mV/s. (B) Spectroelectrochemical reduction of complex **3a** (0.1 mM in deaerated DMF, 0.2 M LiCl), followed by the oxidation of the resulting complex **4a** at a platinum minigrid electrode. At a potential of −0.6 V, spectra 1–5 were obtained after respectively 0, 5, 10, 15, and 20 minutes; then, at a potential of +0.1 V, spectra 6–8 (identical with spectrum 1) were obtained after respectively 5, 10, and 15 min.

Scheme I



basis of the structure of the *N*-alkylporphyrins, the following scheme for the formation of these green pigments, in which the key intermediate is an iron *N*-alkylporphyrin exhibiting a monometallacyclic structure, has been proposed (complex A, Scheme I).

Very recently, the formation of *N*-alkylporphyrins has been shown upon oxidation of alk-1-enes by model systems using iodosylbenzene in the presence of iron tetraarylporphyrins.[4,5] The metallacyclic structure indicated in Scheme I has been proposed for an iron(III) *N*-alkylporphyrin complex formed in such a model reaction.[4] However, although *N*-alkylporphyrin complexes of several metals have been isolated and completely characterized,[6] only very few *N*-alkylporphyrin complexes involving a $\overline{\text{metal—O—C—C—N}}$ metallacyclic structure have been so far described. Iron(II) *N,N′*-Dialkylporphyrin complexes involving two $\overline{\text{Fe—O—C=C—N}}$ metallacycles[7] and chloroiron(III) *N*-alkylporphyrin complexes involving one $\overline{\text{Fe—O—C=C—N}}$ metallacycle[8] have been prepared upon reaction of iron porphyrins with the iodonium ylide $C_6H_5I{=}X$ (X = $\overline{CCOCH_2C(CH_3)_2CH_2CO}$), and completely characterized.

This paper shows that analogous complexes containing a $\overline{\text{Co}^{\text{III}}\text{—O—C=C—N}}$ metallacycle can be prepared upon reaction of BrCo^{III}(porph) (porph = porphyrin) with PhI═X, and describes the preparation and spectral characteristics of zinc(II) and iron(II) porphyrin complexes containing a $\overline{\text{M}^{\text{II}}\text{—O—C=C—N}}$ (M = Fe or Zn) metallacycle. It compares the properties of these complexes to those of previously described metalla-*N*-alkylporphyrins that do not contain such a metallacycle.

Results

I. Preparation of Iron(II) Complexes 4. According to our previous publication,[8] the iodonium ylide[9] PhI═X (**1**) reacts with the Fe^{III}(porph)(ClO$_4$) complexes **2** (**2a** = TPP, **2b** = TpClPP)[10] to give the metallacyclic Fe^{III}(*N*-alkylporph) complexes **3**, which are very stable and have been isolated in good yield and completely characterized. The monoelectronic reduction of these complexes leads to the corresponding Fe^{II}(*N*-alkylporph) complexes **4**, which, contrary to complexes **3**, are very air-sensitive and had been so far only characterized by UV–visible spectroscopy (Scheme II).[8] Hereinafter, we report a more complete characterization of complexes **4** and some of their properties.

Complexes **4** are obtained, in quantitative yield, by reduction of complexes **3**. This reduction has been done either in a biphasic medium (CH_2Cl_2 or C_6H_6–H_2O) with an excess of sodium dithionite used as a reducing agent or in DMF solution with the use of electrochemical techniques. In both cases, the initial brown solution of complexes **3** turned rapidly green, indicating the formation of a new species, **4**.

Complexes **4** are stable under the reductive conditions used for their preparation but are rapidly reoxidized to the starting complexes **3** in the presence of dioxygen and Cl$^-$. Because of their high reactivity toward dioxygen (for example, $t_{1/2}$ of complex **4a**, 10^{-4} M in aerated DMF, is about 3 min), complexes **4** have not been isolated and completely purified in the solid state. They have been characterized in solution by UV–visible and ^{1}H NMR spectroscopy and by their quantitative transformation into the

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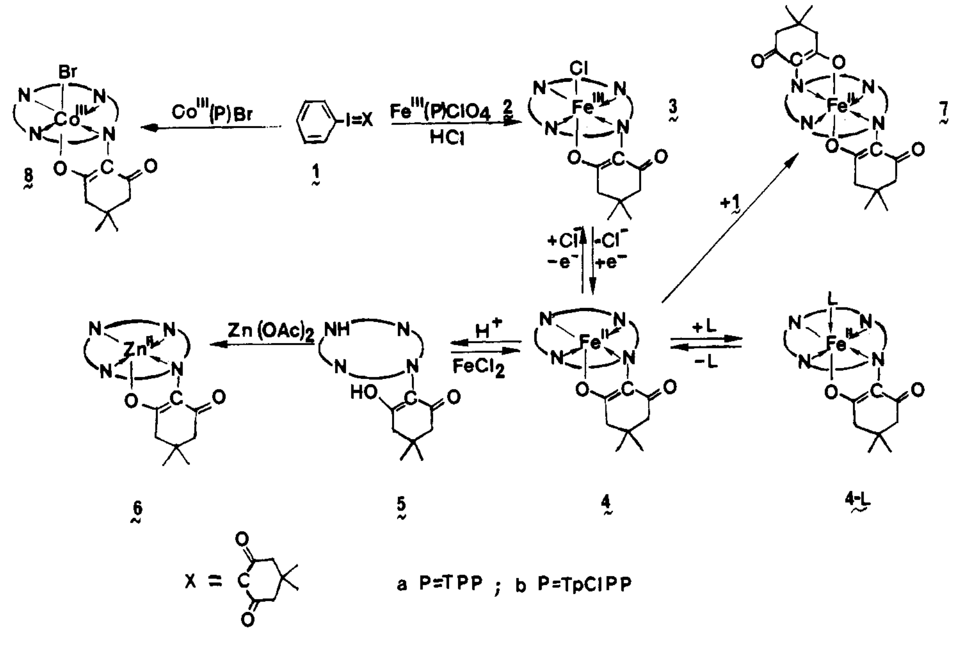
(10) TPP and TpClPP are respectively used for the dianion of *meso*-tetraphenyl- and *meso*-tetrakis(*p*-chlorophenyl)porphyrin.

Scheme II



previously described complexes 3 and 7.

Structure of Complexes 4. The structure of complexes 4 has been deduced from (i) their reversible oxidation into complexes 3 by chemical or electrochemical methods (cyclic voltammetry) and (ii) their total transformation into the corresponding bis(metallacyclic) complexes 7 upon reaction with the iodonium ylide 1.

The *reversible* transformation 4 ⇌ 3 has been confirmed by cyclic voltammetry in DMF solutions. The cyclic voltammogram of complexes 4 (0.9 mM in deaerated DMF, LiCl 0.2 M) exhibits a single reversible wave with $E_{1/2}$ = 205 and 103 mV vs. SCE, respectively, for complexes **4a** and **4b** (Figure 1A). Moreover, spectroelectrochemistry confirms the reversible transformation of complexes 4 into 3. Indeed, upon reduction at -0.6 V of complex **3a** for instance, the characteristic UV-visible spectrum of complex **4a** is obtained with isosbestic points at 440, 492, 597, and 704 nm. The spectrum of complex **3a** is regenerated upon oxidation at 0.1 V of complexes **4a** with the same set of isosbestic points (Figure 1B). Similarly, the reversible transformation of complex **4b** into **3b** occurs with isosbestic points at 449, 499, 501, and 711 nm.

The addition of a CH_2Cl_2 solution of complexes **4a** or **4b** to few equivalents (about 3 equiv) of the iodonium ylide 1 gives *immediately and quantitatively* the corresponding bis(metallacyclic) iron(II) complexes **7a** or **7b** whose structure have been previously established by various spectroscopic methods, including a X-ray analysis of complex **7a**.

These data support a monometallacyclic structure for complexes 4 where a O—C=C moiety derived from the X group is inserted into a Fe–N bond as shown in Scheme II.

UV–Visible Spectra of Complexes 4. The UV–visible characteristics of complexes 4, in DMF at 25 °C, are reported in Table I. As expected for iron(II) *N*-alkylporphyrin complexes,[6,11] they exhibit a red-shifted Soret band around 465 nm with a relatively low molar extinction coefficient. The main difference with the spectra of the previously reported non-metallacyclic chloroiron(II) *N*-alkylporphyrins is the presence, in the visible spectra of complexes 4, of only one broad band around 640–650 nm.

^{1}H NMR Spectra of Complexes 4. Complexes 4 have been prepared directly in CD_2Cl_2 by reduction of the corresponding complexes 3 using a saturated solution of sodium dithionite in D_2O as a reducing agent. The organic solutions were dried over anhydrous SO_4Na_2 before being transferred into a 5-mm NMR tube.

Table I. UV–Visible Spectra of Compounds 4, 5, 6, and 8

compd	solvent	λ, nm (ε, mM^{-1} cm^{-1})			
4a	DMF	461 (141)		640 (14.7)	
4b	DMF	467 (169)		650 (18)	
4a-py	CH_2Cl_2[a]	448 (120)	540 (10.6)	587 (12.8)	632 (7.7)
4a-CO	CH_2Cl_2[b]	435 (150)		655 (10.5)	
5a	C_6H_6	462 (153)	578 (sh)	636 (sh)	692 (25.5)
6a	C_6H_6	463 (205)	578 (4.9)	652 (17.6)	678 (sh)
8a	CH_2Cl_2	458 (62)		612 (6.7)	668 (sh)

[a] In the presence of 20% of pyridine. [b] After bubbling CO.

The ^{1}H NMR spectra of complexes 4 are characteristic of their paramagnetic nature with a large range (+72 to -39 ppm) and broad shapes of the signals (Figure 2). The assignment of these signals has been made by comparison of the spectra of complexes 4 with those of their analogues **4a**-d_{20} and **4b**-d_8 prepared from the tetraarylporphyrin selectively deuteriated on the aryl groups (d_{20}) or on the pyrrole rings (d_8).

In agreement with the C_s symmetry of complexes 4, their pyrrole protons appear as four signals (2 H each). Complexes **4a** and **4b** exhibit three signals at very low field around 70, 40, and 12 ppm and one signal at very high field, around -38 ppm. These signals are absent in the ^{1}H NMR spectrum of complex **4b**-d_8 (Table II). It is noteworthy that a similar resonance pattern of the pyrrole protons has been also recently observed in the ^{1}H NMR spectra of the high-spin (S = 2) chloroiron(II) *N*-methylporphyrin complexes.[12]

The para hydrogens of the phenyl groups of complex **4a** appear as two signals at 8.1 (2 H) and 7.7 (2 H) ppm. These two signals are absent in the spectra of complexes **4b** and **4a**-d_{20}. The signals of the ortho protons of the phenyl groups of complexes **4a** and **4b** appear as a set of three signals: two of them are sharp signals located around 16–17 (2 H) and 10.5 (2 H) ppm; the latter signal is in part masked by the third one, a very broad signal between 11 and 9 (4 H) ppm. These signals are missing in the spectrum of complex **4a**-d_{20}. Finally, the meta protons of the phenyl groups of complexes **4a** and **4b** appear as two signals of unequal intensity around 7.5 (6 H) and 6.2 (2 H) ppm.

As far as the signals of group X are concerned, the same set of three signals are found in the spectra of all complexes 4. The signals of the *gem*-dimethyl proton groups are found around 14

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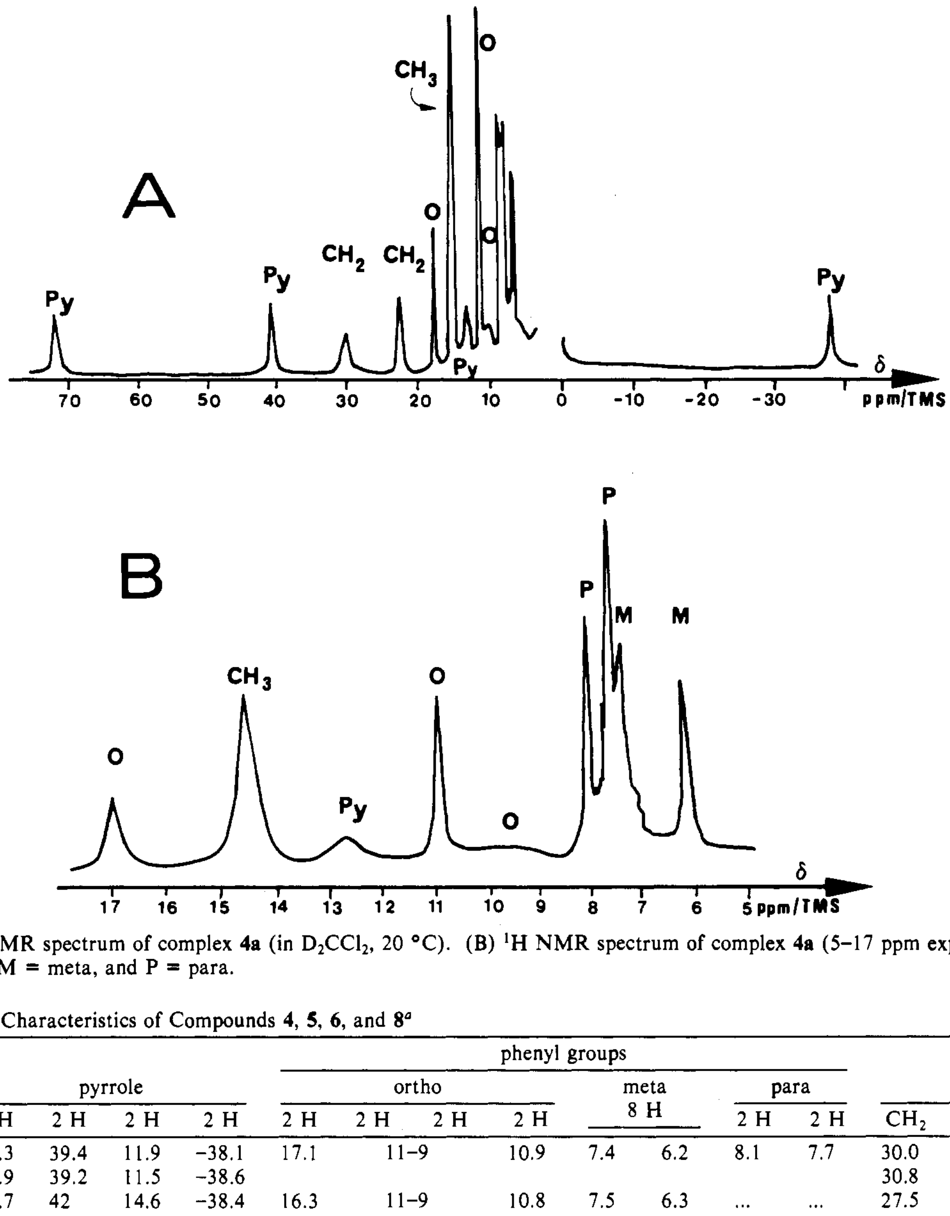

Figure 2. (A) ^1H NMR spectrum of complex **4a** (in D_2CCl_2, 20 °C). (B) ^1H NMR spectrum of complex **4a** (5–17 ppm expanded region). Py = pyrrole, O = ortho, M = meta, and P = para.

Table II. ^1H NMR Characteristics of Compounds **4**, **5**, **6**, and **8**[a]

					phenyl groups										
	pyrrole				ortho				meta		para		X group		
compd	2 H	2 H	2 H	2 H	2 H	2 H	2 H	2 H	8 H		2 H	2 H	CH_2	CH_2	$(CH_3)_2$
4a	71.3	39.4	11.9	−38.1	17.1	11–9		10.9	7.4	6.2	8.1	7.7	30.0	22.1	14.7
4a-d_{20}	71.9	39.2	11.5	−38.6									30.8	22.6	14.9
4b	69.7	42	14.6	−38.4	16.3	11–9		10.8	7.5	6.3	...	...	27.5	20.4	13.6
4b-d_8					16.3	11–9		10.8	7.5	6.4	...	...	27.9	20.5	13.8
4a–py[b]	22.6	18.5	15.6	0.3	9.16	8.70	8.06	6.67	9.48	7.38	8.48	7.55	2.31	−0.65	1.00
4a-d_{20}–py[b]	22.7	18.5	15.7	0.3									2.30	−0.69	1.00
4a-d_8–py[b]					9.14	8.71	8.06	6.66	9.48	7.34	8.46	7.56	2.30	−0.69	0.99
4a-CO	8.62 d 5	8.55 d 5	8.51 d 5	8.05 d 5	8.34 d 7.5		8.11 m		7.75 m		7.84 t 7.5		1.14 s	0.22 s	−0.10 s
5a	8.58 d 5	8.39 s	8.33 d 5	6.88 s	8.65 d 7.5		8.48 m	8.18 m	7.82 m		7.92 t 7.5		1.11 s	−0.63 s	−0.34 s
5a-d_{20}	8.57 d 5	8.38 s	8.27 d 5	6.84 s									1.12 s	−0.64 s	−0.34 s
6a	8.97 d 5	8.76 d 5	8.58 s	7.23 s	8.46 d 7.5		8.42 d 7.5	8.02 d 7.5	7.77 m		7.86 t 7.5		1.43 s	−0.04 s	−0.04 s
8a	8.87 d 5	8.83 d 5	8.77 s	8.51 s	8.49 d 7.5		8.27 m		7.81 m		7.88 t 7.5		1.06 s	−0.47 s	−0.33 s

[a] Conditions: complexes 4, 10 mM in CD_2Cl_2; compound **5** and complexes **6** and **8**, 10 mM in $CDCl_3$, at 20 °C. δ in ppm from Me_4Si; *J* in Hz. Key: s = singlet, d = doublet, m = multiplet. [b] 10 mM in CD_2Cl_2–pyridine-d_5 (4:1 in volume) at 20 °C.

ppm (2 × 3 H) whereas those of the methylene groups appear at low field around 30 and 21 ppm (2 H each), indicating that the two methylene groups are different, as expected for the monometallacyclic structure of Scheme II.

Ability of Complexes 4 To Bind Ligands. Addition of a ligand L, such as pyridine or CO, to complexes **4** gives the corresponding hexacoordinated complexes **4**–py and **4**–CO where the ligand is bound in a position trans to the oxygen atom (Scheme II).

In UV–visible spectroscopy, a hypochromic shift is observed for both types of hexacoordinated complexes, the Soret bands being respectively blue-shifted to 448 and 435 nm (Table II). Addition of increasing amounts of pyridine to complex **4a** (7.3×10^{-5} M in CH_2Cl_2) results in a spectral change with clear isosbestic points (497 and 596 nm). This allows one to determine the equilibrium constant for the formation of the hexacoordinated complex **4a**–py ($K = 15000$ L mol^{-1} at 25 °C). Moreover, the spectrum observed at the highest concentrations of pyridine used during the titration (10^{-3} M) is the same as the spectrum of complex **4a** in neat pyridine.

For the NMR studies, complexes **4**–py have been prepared, either by using pyridine-d_5 as solvent and solid sodium dithionite as reducing agent or by adding pyridine-d_5 (20% in volume) into

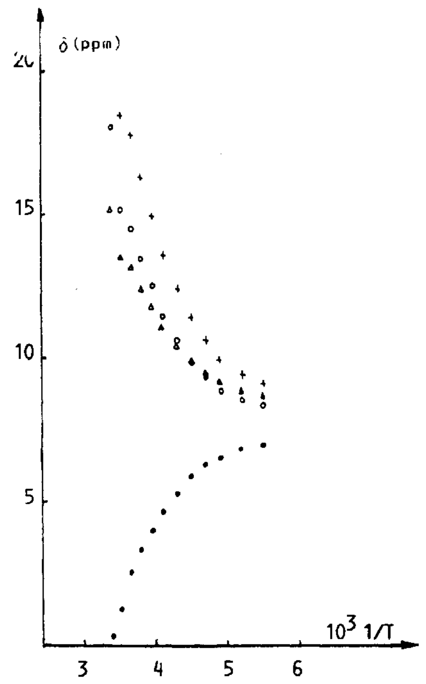

Figure 3. Temperature dependence of the chemical shifts of pyrrole protons of complex **4a**-d_{20} (6×10^{-3} M in 4:1 CD_2Cl_2–pyridine-d_5).

a solution of complexes **4** in CD_2Cl_2 (addition of further amounts of pyridine do not change significantly the NMR spectra).

Because of the higher concentrations of complexes **4** used for ^1H NMR studies (about 10^{-2} M) compared to those used for UV–visible spectroscopy (10^{-5}–10^{-4} M), at 20°C and *even* in pure pyridine-d_5, the equilibrium between **4** and **4**–py is not completely shifted toward **4**–py. Thus, the ^1H NMR spectrum of **4a** in the presence of an excess of pyridine-d_5 reveals a rapid equilibrium between the pentacoordinated paramagnetic complex **4a** and the hexacoordinated diamagnetic complex **4**-py (Scheme II). The signals of the protons of phenyl groups and that of the X moiety appear in the diamagnetic region (between +9 and −0.7 ppm). On the contrary, three of the four signals of the pyrrolic protons appear at low field (for instance, for the pyrrolic protons of complex **4a** in the presence of pyridine: 22.6, 18.5, 15.6, and 0.3 ppm instead of 71.3, 39.4, 11.9, and −38.1 ppm for **4a** in neat CD_2Cl_2) (Table II). As the temperature decreases, the signals of pyrrole protons gradually shift towards the 9–7 ppm region (i.e. for pyrrole protons of complex **4a**–d_{20}, in CD_2Cl_2–pyridine-d_5 4:1 v/v at −90 °C: 9.09, 8.37, 8.71, and 7.02 ppm) (Figure 3).

These data are in agreement with an equilibrium between a pentacoordinated paramagnetic complex **4a** and a hexacoordinated diamagnetic complex **4a**–py,[13] the equilibrium constant of formation of the latter increasing by lowering the temperature.

Complex **4a**–CO, which can be easily prepared by bubbling CO into a CD_2Cl_2 solution of complex **4a**, is diamagnetic (S = 0) even at 20 °C, exhibiting two doublets (8.62 and 8.55 ppm) and two singlets (8.51 and 8.05 ppm) for the pyrrole resonances (Table II), a very characteristic pattern for diamagnetic porphyrin complexes with a C_s symmetry. The signals of *meso*-phenyl groups are found at 8.34, 8.11 (8 H, ortho phenyl hydrogens), 7.75 (8 H, meta phenyl hydrogens) and 7.84 ppm (4 H, para phenyl hydrogens) and those of the X moiety are found at high field: 1.14 (2 H), 0.22 (2 H), and −0.10 (6 H) ppm, respectively, for the two methylene groups and for the *gem*-dimethyl group (Table II). Moreover, the strong ligation of CO in complex **4a**–CO is confirmed by IR spectroscopy. The carbonyl stretching frequency is found at 1975 cm^{-1} (KBr pellets), a value similar to that observed for various Fe^{II}(porph)(CO) complexes.[14]

Complex **4a**–CO is the first example of a diamagnetic iron(II) *N*-alkylporphyrin complex.

The monometallacyclic structure proposed in Scheme II for complexes **4** implies that the metal is almost in the four-nitrogen porphyrin plane and leaves a very accessible position trans to the enolate axial ligand for different ligands. The observed easy binding of pyridine or CO to complexes **4**, with the formation of new low-spin hexacoordinated complexes, is completely consistent with the metallacyclic structure proposed for complexes **4**. On the contrary, Fe(II)(*N*-alkylporph)(Cl) complexes, which do not involve such a metallacycle, are pentacoordinated with the metal displaced out of the four-nitrogen plane toward the chloride axial ligand.[6] The access of the only free axial position is made difficult by the hindered *N*-alkyl group. This explains why the Fe^{II}(*N*-MeTPP)(Cl) complex failed to bind pyridine since its UV–visible spectrum is very similar in pyridine or in CD_2Cl_2 solution. Balch and co-workers have also recently observed by ^1H NMR a similar poor coordination of imidazole on the Fe^{II}(*N*-MeTPP)(Cl) complex.[12]

Thus, the observed easy binding of ligands to complexes **4** is a good evidence for the proposed metallacyclic structure and the existence of a Fe–O bond in these complexes.

II. Preparation of the Free Base 5a and of the Corresponding Zinc(II) Complex 6a. A more detailed study has been done with the tetraphenylporphyrin derivatives. Treatment of complex **4a** by a deaerated solution of dry HCl in methanol, leads to a new compound, **5a**, characterized by a UV–visible spectrum (C_6H_6) exhibiting a Soret band at 462 nm and only one band in the visible region at 692 nm (yield 80%).

Metal ions can be reinserted into the porphyrin ring. Treatment of the free base **5a** by $FeCl_2$ in THF leads back to complex **4a**, which is rapidly oxidized into complex **3a** during the workup. Treatment of **4a** with $Zn(OAc)_2$ in methanol leads to the corresponding complex **6a** with a nearly quantitative yield.

The *N*-alkylporphyrin structure shown in Scheme II for compound **5a** and for complex **6a** has been deduced from their elemental analysis and their mass, ^1H NMR, and ^{13}C NMR spectra. Moreover, the data reported herein show unambiguously that complex **6a**, like complexes **4**, has a monometallacyclic structure with the O–C–C moiety of the X group inserted into a metal–nitrogen bond.

Characteristics of Compound 5a and Complex 6a. In mass spectrometry (desorption chemical ionization technique, I^-, NH_3), compound **5a** exhibits a protonated molecular peak at *m/e* 753 (5%); (M^+ + 1) corresponding to the formal incorporation of the X moiety into the free base $TPPH_2$. The major fragment at *m/e* = 615 (100%) corresponds to $TPPH_3^+$ (loss of the X moiety). The mass spectrum of complex **6a** (I^-, CH_4) exhibits also a molecular peak at *m/e* 814 (for ^{64}Zn) (100%) and a peak corresponding to the loss of the X moiety at *m/e* 676 ((TPP)Zn) (5%).

Accordingly, the elemental analysis (C, H, N) of **5a** corresponds to the formula $(N\text{-}C_8H_{11}O_2)TPPH\cdot H_2O$, indicating the insertion of the X moiety into the porphyrin and a residual solvatation by one molecule of water (detected by ^1H NMR, see Figure 4). The elemental analysis of complex **6a** (C, H, N, Cl) is in good agreement with the formula $Zn((N\text{-}C_8H_{10}O_2)TPP)$, corresponding to the structure given in Scheme II. This analysis shows that complex **6a** has no other axial ligand than the one internally provided by the X group (oxygen enolate). Actually, a zinc(II) *N*-alkylporphyrin) complex that would have exhibited a nonmetallacyclic structure, such as Zn^{II}(*N*-MeTPP)(Cl), should have an axial anionic ligand, such as Cl^-, HO^-, or CH_3COO^-. Thus, the elemental analysis of complex **6a** strongly supports the monometallacyclic structure (Scheme II) where the fifth anionic ligand is the enolate oxygen at the X moiety.

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(13) Preliminary results show that the complex prepared from reduction of Fe^{III}(N-$C_8H_{10}O_2$-*meso*-tetramesitylporph)(Cl)[7] is paramagnetic in CD_2Cl_2 (^1H NMR spectrum similar to those of complexes **4a** and **4b**) but diamagnetic in the presence of pyridine-d_5 (20%) or in neat pyridine-d_5, even at 20 °C. δ (Me_4Si) in pyridine-d_5: pyrrole 8.55 (4 H), 8.26 (2 H), 8.20 (2 H); phenyl meta protons 7.20 (4 H), 7.17 (2 H), 7.09 (2H); phenyl ortho and para protons 2.58 (6 H), 2.45 (12 H), 2.16 (6 H), 11.66 (6 H), 1.31 (6 H); X group 1.24 (2 H), 0.04 (2H), −0.30 (6 H).

(14) Alben, J. O. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York 1978; Vol. III, pp 323–345.

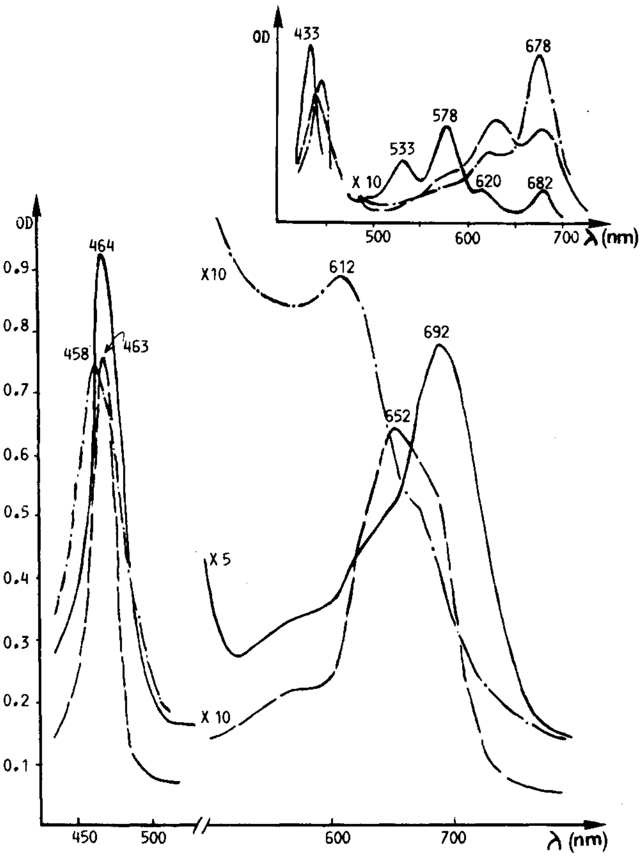

Figure 4. UV-visible spectra of compound **5a** (6.1×10^{-5} M in C_6H_6) (—) and complexes **6a** (3.7×10^{-5} M in C_6H_6) (‒ ‒) and **8a** (1.2×10^{-5} M in CH_2Cl_2) (‒ · · ‒). Inset: Spectra of (N-CH_3)TPPH (—) free base, (‒ ‒) monocation, and (‒ · · ‒) dication from ref 22.

UV-Visible Spectroscopy of Compound 5a and Complex 6a. In benzene, the UV–visible spectrum of compound **5a** exhibits a Soret band at 462 nm and only one band in the visible region at 692 nm with two shoulders at 578 and 636 nm. This spectrum is unusual for a *N*-alkylporphyrin in the neutral free base form but it is not without analogy with that of a protonated free base (Figure 4). Indeed, the addition of trifluoroacetic acid (10^{-2} M in CH_2Cl_2) to a solution of complex **5a** (1.15×10^{-5} M in CH_2Cl_2) gives a UV–visible spectrum similar to that of the neutral free base, the only change being the higher value of the molar extinction coefficients.

As shown in Scheme II, a hydrogen bond between a nitrogen atom of one pyrrole ring and the hydroxyl of the enolic form of the X group would lead to a structure similar to that of a protonated *N*-alkylporphyrin, explaining the unusual UV–visible spectrum of compound **5a**.

The UV–visible spectrum of complex **6a** exhibits a Soret band at 463 nm and only one visible band at 652 nm with two shoulders at 578 and 678 nm (Figure 4).

^{1}H NMR Spectra of Compound 5a and of Complex 6a. Complex **6a** and compound **5a** are diamagnetic and their well-resolved ^{1}H NMR spectra range from +9 to −1 ppm. Moreover, they exhibit very similar spectra with the characteristic pattern of the pyrrole proton resonances of *N*-alkyl porphyrins, with a C_s symmetry. Thus, compound **5a** exhibits two doublets (2 H each) at 8.58 (J = 5 Hz) and 8.33 (J = 5 Hz) ppm and two singlets (2 H each) at 8.39 and 6.88 ppm (Figure 5). The signals of the para protons of the phenyl groups appear as a triplet at 7.92 (J = 7.5 Hz, 4 H) ppm and those of meta protons as a multiplet centered at 7.82 ppm (8 H). The ortho protons of the phenyl group are split into one doublet located at 8.65 (J = 7.5 Hz, 4 H) ppm and two broad signals (2 H each) centered at 8.48 and 8.18 ppm, indicating a hindered rotation of the two phenyl groups nearest to the X moiety ($\omega_{1/2}$ = 30 Hz for the 8.18 ppm signal; $\omega_{1/2}$ for the 8.48 ppm signal cannot be measured because it is in part masked by a pyrrole proton signal). The assignments of pyrrole and phenyl protons are made by comparison with compound **5a**-d_{20}, completely deuteriated on the phenyl rings (Table II).

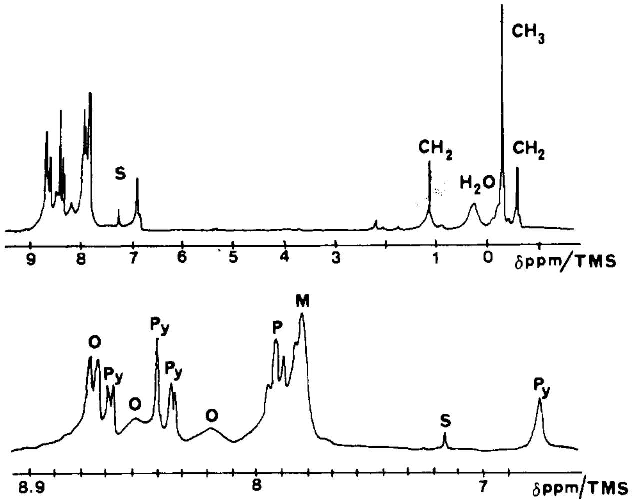

Figure 5. (A) ^{1}H NMR spectrum of compound **5a** (in $DCCl_3$, 20 °C). (B) ^{1}H NMR spectrum of compound **5a** (6.7–9 ppm expanded region). Py = pyrrole, O = ortho, M = meta, P = para, and S = $HCCl_3$; H_2O disappears upon addition of D_2O.

Finally, the ^{1}H NMR signals of the X group protons are shifted upfield because of the ring current effect of the porphyrin. The signal of the *gem*-dimethyl group appears at −0.34 (6 H) ppm and those of the methylene groups as two singlets (2 H each), one at 1.11 ppm and the other near 1.75 ppm. These data, indicating two different magnetic environments for the methylene groups, are in agreement with an enolic structure for a X group bound to a nitrogen atom of a pyrrole ring. Moreover, a hydrogen bond with the trans nitrogen retains the C_s symmetry observed for all the *N*-alkylporphyrins. The ^{1}H NMR spectrum of complex **6a**, for which a monometallacyclic structure is clearly deduced from its elemental analysis, is very similar to that of compound **5a** (Table II).

^{13}C NMR Spectra of Compound 5a and of Complex 6a. Figure 6 shows the ^{13}C NMR spectra of compound **5a** obtained by using broad-band decoupling resonance (A), off-resonance (B), and gated-decoupling resonance (D) techniques. Figure 6C shows the ^{13}C NMR spectrum of the corresponding compound **5a**-d_{20} in broad-band decoupling resonance. From all these spectra, which have been analyzed in the context of C_s symmetry, as expected for an *N*-alkyl porphyrin, the individual resonances of all the carbons of compound **5a** can be clearly assigned.

Four signals between 164 and 146 ppm are found for the α-pyrrole carbons of compound **5a**, which remain singlets in spectra A–C and become triplets (^2J = 8 Hz) in the gated-decoupling resonance spectrum (not shown in spectrum D). The β-pyrrole carbons appear as a set of three signals between 130 and 115 ppm. They have been unambiguously assigned since they remain singlets in the spectrum of compound **5a**-d_{20} (C), whereas they become doublets in spectra B and D with a ^2J coupling constant of 175 Hz, a reasonable value for a pyrrole ring.[15] In spectrum D, a small coupling constant (^2J = 4 Hz) is also observed for the first two signals, the third one becoming only wider. The meso carbons appear as two singlets: one around 120.5 ppm; the other one around 129 ppm, which is more easily observed in the spectrum of compound **5a**-d_{20} because all the other carbon atoms with similar resonance frequencies are coupled with a ^{2}H atom and so appear as small triplets (Table III).

Concerning the carbons of the phenyl rings, the quaternary carbon resonances lead to two singlets in spectra A–C and two triplets (^3J = 8 Hz) in spectrum D around 141 ppm. The ortho

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(15) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergmanon: New York, 1969.

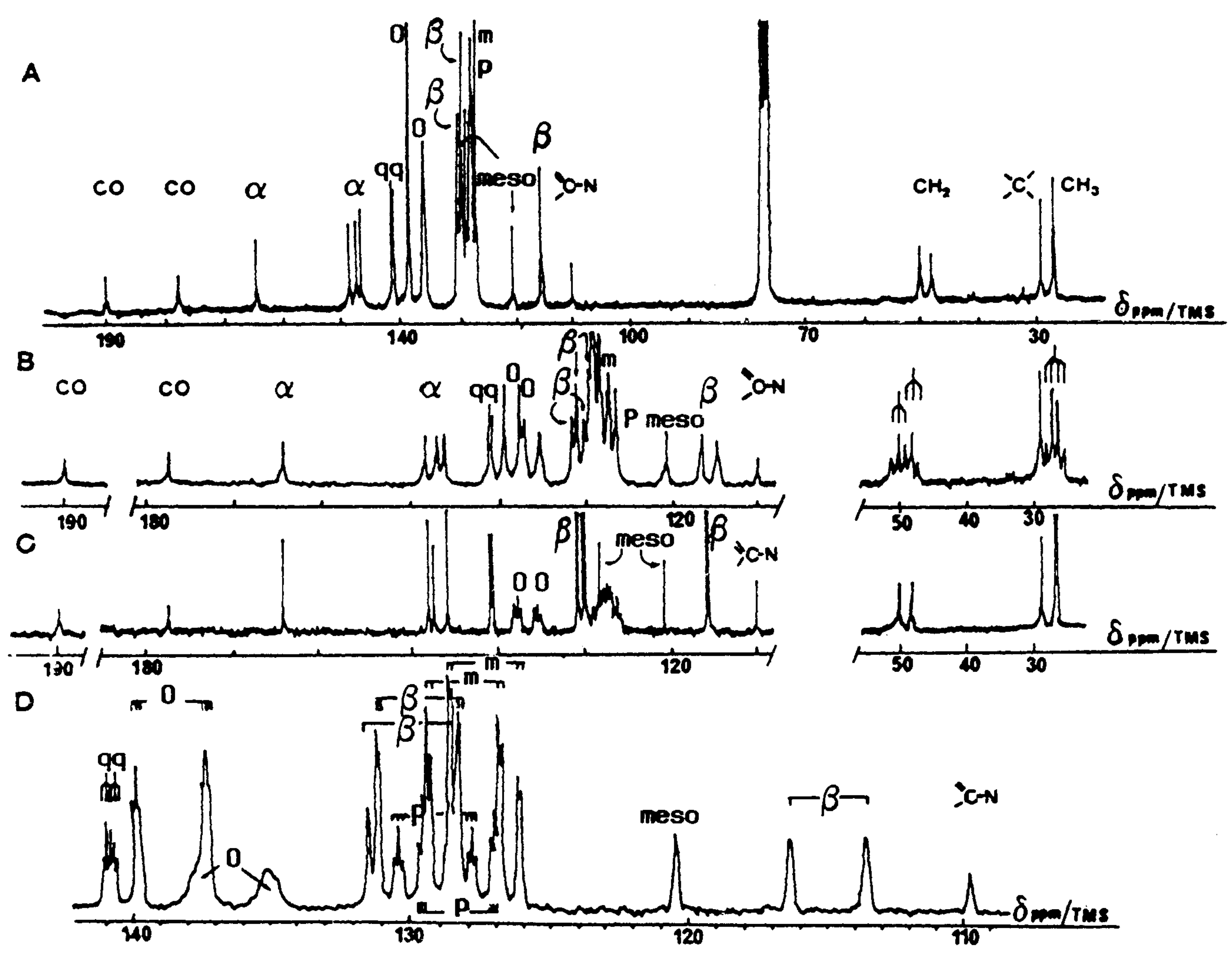


Figure 6. ^{13}C NMR spectra of compound **5a** (in $DCCl_3$, 20 °C): (A) broad-band resonance spectrum; (B) off-resonance spectrum; (D) gated-decoupling resonance spectrum (109–142 ppm region). (C) Spectrum of compound **5a**-d_{20} (broad-band resonance spectrum). o, m, p, and q are used respectively for ortho, meta, para, and quaternary carbons of phenyl groups, α and β for α- and β-pyrrole carbon rings, and meso for the methine carbons.

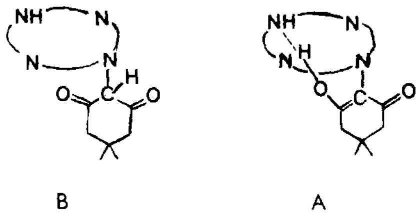
carbons appear around 138 and 136 ppm as two singlets in spectrum A and as two doublets in spectrum B (^1J = 162 Hz). In spectrum C, they appear, as expected, as two triplets ($^1J_{C-D}$ = 22 Hz) whereas in spectrum D they appear as two doublets of triplets (^3J = 6 Hz) for the carbon resonance at 138 ppm and only as broad peaks for the other one. Para and meta carbon resonances can be easily attributed only in spectrum D. The para carbon gives two sets of two doublets of triplets (^1J = 160 Hz, ^3J = 7 Hz) at 129.1 and 128.3 ppm whereas meta carbons give two sets of two doublets of doublets (^1J = 161 Hz, ^3J = 7 Hz) (Table III).

The resonance of CH_3 and CH_2 of the X moiety are assigned by comparison of the spectra A and B. The *gem*-dimethyl carbons appear as a quadruplet at 26.9 ppm (^1J = 126 Hz) and the methylene carbons as two triplets around 49.9 and 47.8 ppm (^1J = 120 Hz), indicating that the two CH_2 moieties are not magnetically equivalent. The singlet at 28.9 ppm is attributed to the saturated quaternary carbon. At very low field, one can observe two singlets corresponding to the carbonyl resonances (around 190 and 177 ppm). These two signals become triplets in the gated resonance spectrum with a small coupling constant (^3J = 2Hz). Finally, the peak at 109.9 ppm, which remains singlet in all the spectra, corresponds to the carbon directly bound to the pyrrolic nitrogen atom.

The ^{13}C NMR spectrum of complex **6a** is very similar to that of compound **5a**. Only small differences are observed for the values of the chemical shifts (Table III), and a better separation of signals allows one to observe the splitting of the β-pyrrole carbons in four signals instead of three as in compound **5a**.

The fact that one observes, in both compounds **5a** and **6a**, two signals for the CO carbons and a singlet for the C–N carbon is in good agreement with a keto–enolic structure for the X moiety (structure A). A structure of type B would have given two identical CO signals and a doublet in spectrum B for the carbon bound to the nitrogen (Chart I).

Chart I



B A

III. Preparation of the Bromocobalt(III) Complex 8a. Addition, at room temperature, of 10 equiv of the iodonium ylide **1** to a benzenic solution of $Co^{III}(TPP)(Br)$ leads, after 48 h of stirring, to the formation of a new complex (85% yield) characterized in UV–visible spectroscopy by bands at 458 and 612 nm (Figure 4).

Characteristics of Complex 8a. The structure of complex **8a** has been deduced from its elemental analysis, and its mass spectrum, and its ^1H and ^{13}C NMR spectra.

Its mass spectrum (DCI, CH_4, I^-) exhibits a molecular peak at *m/e* 890 (M^+, 18% for ^{81}Br) and peaks at *m/e* 809 (100%) corresponding to the loss of the bromine atom and *m/e* 672 (M + 1 for (TPP)Co) corresponding to the loss of the X moiety.

Its elemental analysis (C, H, N, Br) is in good agreement with the formula $Co(TPP)(C_8H_{10}O_2)(Br)\cdot H_2O$ indicating also the insertion of the X moiety into the porphyrin and residual solvatation by one molecule of water.

Table III. ^{13}C NMR Characteristics of Compounds **5**, **6**, and **8**[a,b]

	5a			**5a**-d_{20}		**6a**			**8a**
carbons	i	ii	iii	iv	ii	iv	ii	iii	iv
α-pyrrole	164.1	s	t 8	164.3	s	166.5	s	t 8	162.6
	148.6	s	t 8	148.2	s	154.0	s	t 8	152.4
	147.4	s	t 8	147.6	s	152.0	s	t 8	149.3
	146.6	s	t 8	146.1	s	151.2	s	t 8	148.8
β-pyrrole	130.0	d 175	d 4	130.7	s	133.8	d 175	d 4	134.7
						133.3	d 175	d 4	134.4
	129.7	d 175	d 4	130.0		132.7	d 175	d 4	
	115.0	d 175	*c*	115.6	s	117.7	d 176	d 3	128.3
meso	129.4	s	s	128.6	s	129.2	s	*c*	125.5
	120.5	s	s	120.7	s	121.7	s	t 3	124.8
quarternary phenyl	141.0	s	t 8	141.1	s	142.2	s	t 7	141.0
	140.8	s	t 8	140.8	s	141.9	s	t 7	140.4
ortho phenyl	138.6	d 162	t 6	137.9	t 22	138.8	d 161	t 6	136.8
	136.6	d 162	*c*	135.5	t 22	135.5	d 161	*c*	136.0
						134.9	d 161	t 6	135.5
meta phenyl	128.0	d 161	d 7	*d*		127.9	d 161	d 7	128.3
	127.4	d 160	d 7	*d*		126.7	d 160	d 7	127.9
para phenyl	129.1	d 160	t 7	*d*		128.6	d 160	t 7	127.9
	128.3	d 160	t 7	*d*		127.7	d 160	t 7	127.6
C–O	190.2	s	t 2	188.4	s	190.2	s	t 2	188.7
	177.9	s	t 2	177.4	s	179.2	s	t 2	183.8
N–C	109.7	s	s	109.9	s	111.1	s	s	118.4
CH_2	49.9	t 120		50.1	s	50.9	t 128		50.5
	47.8	t 120		48.1	s	46.2	t 128		44.2
quaternary C	28.9	s	s	29.1	s	29.8	s	s	30.2
CH_3	26.8	q 126		26.9	s	26.8	q 127		26.3

[a] Conditions: 10 mM in $DCCl_3$ at 20 °C. δ in ppm from Me_4Si. [b] Key to column heads: (i) δ value from gated decoupling resonance spectrum; (ii) ^1J in Hz; (iii) ^2J and ^3J in Hz, s = singlet, d = doublet, t = triplet, and q = quadruplet; (iv) value from broad decoupling resonance spectrum. [c] Not measurable because of an overlapping of the signal with another one. [d] Multiplets from 129 to 125.7 ppm.

Its ^{1}H NMR (Table II) and ^{13}C NMR spectra (Table III) are characteristic of a diamagnetic compound as expected for a Co(III) complex and almost identical with those of compound **5a** and complex **6a**. Only small differences are observed in the chemical shifts of one β-pyrrole carbon signal found at 128.3 ppm and of the signal of the carbon of the X moiety directly bound to the nitrogen atom (found at 118.4 ppm).

Furthermore, as for complexes **5a** and **6a**, the two methylene groups of the X moiety of complex **8a** are diamagnetically inequivalent and their signals appear as two singlets located at 1.06 and −0.47 ppm in the ^{1}H NMR (Table II) and as two singlets at 50.5 and 44.2 ppm in the ^{13}C NMR (Table III).

All these results indicate that complex **8a** is a bromo–Co^{III}-((*N*-alkyl)TPP) complex with a monometallacyclic structure similar to that of complexes **4a** and **6a** and corresponding to the insertion of the X moiety into a cobalt–nitrogen bond (Scheme II).

Conclusion

Reaction of the iodonium ylide $C_6H_5I{=}X$, a carbon analogue of $C_6H_5I{=}O$, with $Fe^{III}(porph)(ClO_4)$ complexes allows an easy preparation of ferric *N*-alkylporphyrin complexes **3** that exhibit one five-membered Fe—O—C=C—N metallacycle (Scheme II).[8] The aforementioned results show that similar metallacyclic complexes can be also obtained with iron(II), zinc(II), or cobalt(III) ions, showing the generality of the access to this new type of *N*-alkylporphyrin complexes.

The metal—O—C=C—N structures of these complexes, which formally derived from the insertion of the $^-$O—C=C$^+$ moiety of the X group of $C_6H_5I{=}X$ into one metal–nitrogen bond, are deduced from several evidences: (i) all the complexes **4**, **6**, and **8** are N-alkylated metalloporphyrin complexes as shown by their ^{1}H NMR spectra, which are in good agreement with the C_s symmetry expected for this type of structure; (ii) in all cases and also in the case of the free base **5** the X group directly bound to the pyrrolic nitrogen is in its enolic form as indicated by the magnetic inequivalence of the two CH_2 groups of the X moiety (^{1}H NMR) and by the fact that the atom directly bound to the pyrrolic nitrogen is a quaternary carbon (^{13}C NMR for **5**, **6**, and **8**); (iii) the existence of a metal–oxygen bond is supported by the elemental analysis of the zinc complex **6a** and by the easy binding of ligands such as pyridine or CO in the case of iron(II) complexes **4** as well as for the latter complexes by their reversible transformation into complexes **3** and their total tranformation into complexes **7** after reaction with an excess of iodonium ylide. For the cobalt(III) complex **8a**, the structure is assumed to be identical with those of other complexes **4** and **6** on the basis of its elemental analysis, its mass spectrum, and the great similarity of its ^{1}H and ^{13}C NMR spectra to those of the zinc complex.

The chemical properties of the N—C=C—O—Fe^{II}(porph) complexes **4** (high reactivity toward oxygen, ability to bind a sixth ligand such as pyridine or carbon monoxide) contrast with those observed for the ferrous *N*-alkylporphyrin complexes that do not exhibit such a metallacycle such as, for instance, $Fe^{II}((N\text{-}CH_3)TPP)(Cl)$.[6d] The greater reactivity of the former can be understood if one considers that their metallacyclic structure allows an easy access to the iron atom whereas, in the latter, the two axial positions are hindered by the chloride ligand on one side and by the N–R group on the other side (Chart I).

The spectroscopic data reported here should be important for the isolation and study of analogous metallacyclic complexes that have been postulated as intermediates in the formation of green porphyrin pigments in the liver of animals treated by alkenes and that have been recently described upon reaction of iodosoarenes with alk-1-enes in the presence of iron porphyrins.[4,5]

Experimental Section

Physical Measurements. UV–visible spectra were obtained by using a Kontron Uvikon 810 or an Aminco DW 2 spectrophotometer.

Mass spectra were recorded on a VG 70-250 double-focusing instrument (from VG Analytica, Manchester, U.K.) equipped with a fast atom bombardment gun (from Ion Tech Ldt, Teddindton, U.K.). The scanning acquisition parameters were as follows: accelerating voltage, 4 kV; scan time, 15 s/decade; interscan time, 2 s. The FAB gun was operated with xenon (N45, Air Liquide, France) at 7.5 kV and 1.2 mA. The apparatus was calibrated with cesium iodide, and different matrices were used: glycerol, thioglycerol, and dimethyl sulfoxide.

^{1}H NMR spectra for complexes 10^{-2} M in $CDCl_3$ or CD_2Cl_2 were run at 20 °C, on a Bruker WM 250 spectrometer operating at 250 MHz; chemical shifts are reported in ppm downfield from Me_4Si (sweep width, 50 000 Hz; 256–1024 scans; 60° pulses; 3.0 Hz/pt resolution; 32K point memory blocks; acquisition time, 0.32 s; repetition delay, 1 s). ^{13}C NMR spectra were run at 62.9 MHz (sweep width, 5680 Hz; 30 000–40 000 scans; 60° pulses; 0.71 Hz/pt resolution; 16K point memory blocks; acquisition time, 1.4 s with broad band of ^1H decoupling; repetition delay, 1 s). $DCCl_3$ was used as internal reference.

Elemental analyses were done by the Servive de Microanalyse du CNRS at Gif sur Yvette, France.

Materials. Compound **1**, PhI=X (X = $C_8H_{10}O_2$), was prepared according to ref 9. $TPPH_2$ and $TpClPPH_2$ were synthesized according to ref 16; TPP-d_{20} and TpClPP-d_8 were synthesized according to ref 17. All the porphyrins were made chlorine free[18] and were metalated by $FeCl_2 \cdot 4H_2O$ in DMF.[19] $BrCo^{III}(TPP)$ was prepared according to ref 20. The preparation of complexes **3** has been previously described.[8]

Cyclic Voltammetry and Spectroelectrochemistry of Complexes 4. Experiments were carried out with a Princeton Applied Research Model 173 potentiostat, monitored with an Apple IIe microcomputer and a PAR Model 276 GPIB interface. A three-electrode system was used with a platinum-disk or a glassy-carbon-disk working electrode, a platinum-wire counter electrode and a saturated calomel electrode. The reference electrode was separated from the bulk of the solution by a fritted glass bridge and was filled with the solvent and supporting electrolyte at appropriate concentration. The spectroelectrochemical device (analogue to a previously described one[21]) consisted of a three-electrode cell, with a quartz cell as a compartment of electrolysis (optical length, 0.5 mm; inner volume, 0.08 mL). The working electrode was a platinum minigrid.

All the solutions of complexes **3** were deaerated by an argon stream before experiments and then protected by a blanket of argon. Dimethylformamide was distilled under reduced pressure; reagent grade quality $LiClO_4$ and LiCl, purchased from Fluka Co., were used without further purification.

Preparation of Complexes 4. To a deaerated solution of 84 mg (0.1 mmol) of complex **3a** in 40 mL of C_6H_6 was added 20 mL of a saturated aqueous solution of $S_2O_4Na_2 \cdot H_2O$, previously deaerated. The brown solution turned rapidly green, indicating the formation of complex **4a**. The end of the reaction was checked by recording the electronic spectra of a sample. Similarly, complex **4b** was obtained from 100 mg (0.1 mmol) of complex **3b**. Complexes **4** were very air-sensitive and were used only in solution under these reductive conditions.

Preparation of Compound 5a, (N-$C_8H_{11}O_2$)TPPH. Complex **4a** (160 mg) was prepared as above, and the organic solution was transferred, under anaerobic conditions, directly into 100 mL of a methanolic solution of HCl. After 0.25 h of stirring, the solvents were removed, the crude product was dissolved into CH_2Cl_2, and 50 mL of a NH_4OH solution (6 N) was added. The organic layer was washed two times with distilled water and the solvent removed. Crystallization of complex **5a** was achieved by dissolving the crude product in a minimum amount of CH_2Cl_2 and adding an excess of pentane (80% yield). Anal. Calcd for (N-$C_8H_{11}O_2$)TPPH·H_2O, $C_{52}H_{42}N_4O_3$: C, 81.04; H, 5.45; N, 7.27. Found: C, 81.01; H, 5.33; N, 7.40.

Insertion of Iron into Compound 5a. To 33 mg (0.044 mmol) of compound **5a** dissolved in 50 mL of deaerated THF containing 2 drops of collidine were added 50 mg of $FeCl_2 \cdot 4H_2O$ (0.25 mmol) and 20 mg of iron powder. The solution was refluxed under argon for 3 h. The end of the reaction was checked by UV–visible spectroscopy. The solvent was evaporated, the crude product dissolved in CH_2Cl_2, washed with a HCl solution, and purified by column chromatography (SiO_2, CH_2Cl_2:acetone, 98:2), and complex **3a** (corresponding to the oxidation of complex **4a**) crystallized from CH_2Cl_2–pentane solution (70% yield). The UV–visible and ^1H NMR spectra are identical with those of an authentic sample.[8]

Preparation of Complex 6a, Zn((N-$C_8H_{10}O_2$)TPP). To 150 mg (0.2 mmol) of compound **5a** dissolved in 80 mL of CH_2Cl_2 was added 110 mg (0.5 mmol) of $Zn(OAc)_2 \cdot 2H_2O$ in 20 mL of CH_3OH, and the mixture was stirred at 40 °C for 1 h. After solvent evaporation, the crude product was dissolved in CH_2Cl_2, washed with a NaCl solution, and recrystallized from a CH_2Cl_2–pentane solution (95% yield). Anal. Calcd for Zn(TPP)($C_8H_{10}O_2$), $C_{52}H_{38}N_4O_2Zn$: C, 76.51; H, 4.69; N, 6.86. Found: C, 76.19; H, 5.12; N, 6.26. Chlorine has been also analyzed and found to be less than 0.2% (probably due to traces of CH_2Cl_2 used for the recrystallization).

Preparation of Complex 8a, Co((N-$C_8H_{10}O_2$)TPP)(Br). To a solution of 150 mg (0.2 mmol) of Co^{III}(TPP)(Br) in 50 mL of C_6H_6 was added 340 mg (1 mmol) of iodonium ylide **1**. The reaction mixture was stirred for 48 h at room temperature. After evaporation of the solvent, the crude product was purified by column chromatography (SiO_2, cyclohexane, and CH_2Cl_2–CH_3COCH_3 as eluents) and recrystallized from CH_2Cl_2–pentane (85% yield). Anal. Calcd for Co(TPP)($C_8H_{10}O_2$)·H_2O, $C_{52}H_{40}N_4O_3BrCo$: C, 68.80; H, 4.44; N, 6.17; Br, 8.80. Found: C, 68.85; H, 4.41; N, 6.19; Br, 8.62.

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Solvation of Triphenylamine, -phosphine, -arsine, -stibine, and -bismuthine in Polar and Nonpolar Solvents

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The enthalpies of solvation for the triphenyl compounds $(C_6H_5)_3X$ (X = N, P, As, Sb, Bi) have been studied in seven nonaqueous solvents of different properties, at 25 °C. The values were determined from the known heats of crystallization and the heats of solution, which were measured calorimetrically. In both polar and nonpolar solvents low values of much the same magnitude are found. This indicates that the solvation is essentially due to London forces. Even lower heats of solvation are found for the tetraphenylarsonium, $(C_6H_5)_4As^+$, and the tetraphenylborate, $B(C_6H_5)_4^-$, ions, which implies that these also interact with the solvent essentially through London forces. This affords further support to the TATB assumption, viz. that the enthalpies of solvation (as well as the free energies, and entropies, of solvation) are indeed equal for these two ions.

Introduction

The simple triphenyl derivatives $(C_6H_5)_3X$ (X = N, P, As, Sb, Bi), abbreviated Ph_3X, are suitable ligands for the investigation of the affinities of various metal acceptors for donor atoms of the nitrogen group.[1] Such investigations must be performed in polar nonaqueous solvents where the ligands, and also the complexes formed, are readily soluble, which is not the case in aqueous solutions. Thus, in dimethyl sulfoxide, successful studies of the thermodynamics of the copper(I) and silver(I) systems of all of these ligands have been carried out.[2,3] For mercury(II), only the

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