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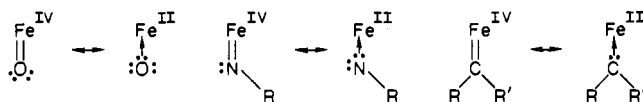
## Iron-Porphyrin-Nitrene Complexes: Preparation, Properties, and Crystal Structure of Porphyrin-Iron(III) Complexes with a Tosylnitrene Inserted into an Fe-N Bond

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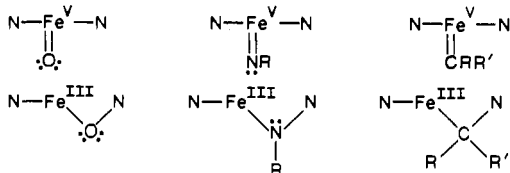
Iron(III)-porphyrins (porphyrin = P = TPP, TTP, and TpClPP) react with [(tosylimino)iodo]benzene,  $\text{PhI}=\text{NTs}$  (1), to give the corresponding tosylimido-bridged iron-porphyrin complexes  $\text{Fe}(\text{P})(\text{NTs})(\text{Cl})$  (P = TPP, **2a**; P = TpClPP, **2b**; P = TTP, **2c**; Ts = tosyl = *p*-tolylsulfonyl). These complexes have been isolated as pure crystalline solids in high yields. The structure of complex **2a** has been fully established by an X-ray structure analysis. It is a pentacoordinate complex where the tosylnitrene moiety is inserted into an iron-pyrrole nitrogen (N(p)) bond. The Fe-N(Ts) (1.951 Å) and N(Ts)-N(p) (1.371 Å) distances are both characteristic of single bonds. The coordination geometry of the iron center is well-described as a distorted trigonal bipyramid with the Cl and N(Ts) atoms and one pyrrole nitrogen lying in the equatorial plane. The porphyrin ring is severely distorted, the pyrrole ring bonded to the NTs ligand making a dihedral angle of 29.9° with the plane containing the three pyrrole nitrogens bonded to the iron. Magnetic susceptibility measurements on the crystalline complex **2a** ( $\mu = 5.6 \pm 0.1 \mu_{\text{B}}$ , from 40 to 300 K) or on its solution in  $\text{CDCl}_3$  ( $\mu = 5.8 \pm 0.1 \mu_{\text{B}}$  at 293 K) as well as EPR ( $g = 4.28$ ) and  $^1\text{H}$  NMR studies on complex **2a** are in favor of a well-defined high-spin ferric ( $S = 5/2$ ) state for this complex together with a rhombic symmetry in the d orbitals of the iron.

High-valent oxo-iron-porphyrin complexes have been proposed as active intermediates in the catalytic cycle of peroxidase<sup>1</sup> and cytochrome P-450.<sup>2</sup> Model oxo-iron(IV)-porphyrin complexes have been prepared and identified by different spectroscopic techniques.<sup>3</sup> Their nitrogen and carbon analogues, respectively the nitrene<sup>4</sup> and carbene-iron-porphyrin<sup>5</sup> complexes, have been isolated and fully characterized.



The one-electron-oxidation products of iron(IV)-oxo complexes are much more reactive and have only been obtained at low temperature; several spectroscopic studies made on one of them indicate a (porphyrin)<sup>•+</sup> $\text{Fe}^{\text{IV}}=\text{O}$  structure.<sup>3h-j,6-8</sup> The one-electron-oxidation products of the carbene complexes  $\text{Fe}^{\text{IV}}=\text{CRR}'$  could have been the corresponding  $\text{Fe}^{\text{III}}=\text{CRR}' \leftrightarrow \text{Fe}^{\text{V}}=\text{CRR}'$  carbene complexes. However, the one-electron-oxidation product of the carbene complex  $\text{Fe}^{\text{II}}(\text{TPP})$  [ $\text{C}=\text{C}(\text{C}_6\text{H}_5\text{Cl})_2$ ] has been isolated and fully characterized as an iron(III) complex where the carbene moiety is inserted between the iron and a pyrrole nitrogen atom.<sup>10</sup> The oxygen analogue of this carbene-bridged complex, which could be derived from an isomerization of (porphyrin) $\text{Fe}^{\text{V}}=\text{O}$  or (porphyrin)<sup>•+</sup> $\text{Fe}^{\text{IV}}=\text{O}$  complexes<sup>10a,11a,b</sup> and could have a  $\text{Fe}^{\text{III}}-\text{O}-\text{N}$  structure, has been proposed as an active species in hydrocarbon oxidations catalyzed by iron-porphyrins<sup>11c</sup> or as an intermediate in the oxidative degradation of these catalysts in such reactions.<sup>10b</sup> In fact, evidence has been recently provided for the formation of such a N-bridged oxo-iron-porphyrin complex upon reaction of an iron(III)-porphyrin with *m*-chloroperoxybenzoic acid at 0 °C.<sup>12</sup>

The nitrogen analogues of iron(V)-oxo or -carbene complexes, the (porphyrin) $\text{Fe}^{\text{V}}=\text{NR}$  complexes, have never been observed but could be the active intermediates in the transfer of the tosylimino moiety of [(tosylimino)iodo]benzene,  $\text{PhI}=\text{NTs}$  (1), to alkanes<sup>13</sup> or alkenes<sup>14</sup> catalyzed by iron(III)-porphyrins.

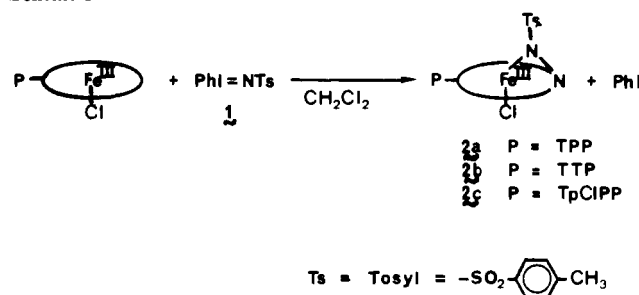


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Scheme I



We have recently reported<sup>15</sup> preliminary results showing that, upon aziridination of alkenes by  $\text{PhI}=\text{NTs}$  (1) catalyzed by

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**Table I.** Compared IR, UV-Visible, and <sup>1</sup>H NMR Spectroscopic Data of Complexes 2

complex	IR (KBr), cm <sup>-1</sup>			UV-vis (CH <sub>2</sub> Cl <sub>2</sub> ), λ nm (ε, mM <sup>-1</sup> )		<sup>1</sup> H NMR, <sup>a</sup> δ					
	ν <sub>as</sub> (SO <sub>2</sub> )	ν <sub>s</sub> (SO <sub>2</sub> )	ν(Fe-Cl)			H(pyr)	H(Ts)	H <sub>m</sub> <sup>b</sup>	H <sub>p</sub> <sup>b</sup>	H <sub>o</sub> <sup>b</sup>	CH <sub>3</sub> <sup>c</sup>
2a	1154	1095	345	420 (111.3), 519 (15.1), 558 (9.7), 693 (4.6)	89.5, 84.5, 81.7-28.4	14.32, 13.71	12.70, 11.22, 10.93, 10.30	6.85, 3.92	6.10, 4.10		
2b	1150	1088	349	422 (118.5), 520 (16.8), 558 (10.1), 691 (5.5)	91.0, 84.4, 82.6, -28.3	14.50, 14.20	12.62, 11.15, 10.91, 10.26		6.10, 4.05		
2c	1150	1087	345	423 (90.7), 521 (12.5), 558 (8.0) 695 (3.2)	89.2, 85.1, 82.1, -28.9	14.15, 13.52	12.84, 11.18, 10.88, 10.24		6.10, 4.10	8.90, 5.40	

<sup>a</sup>In CDCl<sub>3</sub> at 20 °C (relative to Me<sub>4</sub>Si). <sup>b</sup>H<sub>o</sub>, H<sub>m</sub>, and H<sub>p</sub> are the ortho, meta, and para protons of the *meso*-phenyl groups. <sup>c</sup>Of the porphyrin ring.

Fe<sup>III</sup>(TPP)(Cl), the starting porphyrin was totally converted into a Fe<sup>III</sup> complex, for which a bridged Fe—NTs—N structure was proposed on the basis of its elemental analysis, spectral properties, and ability to form N—NHTs—TPPH upon acidic demetalation.<sup>16</sup>

This paper reports (i) the X-ray structure determination of the Fe<sup>III</sup>(TPP)(NTs)(Cl) complex **2a**, which establishes definitively the Fe<sup>III</sup>—NTs—N structure, (ii) the preparation of several Fe<sup>III</sup>(porphyrin)(NTs)(Cl) bridged complexes, and (iii) an analysis of the electronic and magnetic properties of these complexes by magnetic susceptibility measurements and EPR and <sup>1</sup>H NMR spectroscopy, which shows a rhombically distorted high-spin (*S* = 5/2) iron(III) electronic configuration for them in solution as well as in the crystalline state.

## Results

**Preparation of Tosylimido-Bridged Iron(III) Porphyrin Chloride Complexes (2a-c).** The reaction of chloro(*meso*-tetraphenylporphyrinato)iron(III), Fe(TPP)(Cl), 10<sup>-2</sup> M in anhydrous CH<sub>2</sub>Cl<sub>2</sub>, with solid PhI=NTs<sup>17</sup> (4 equiv relative to Fe(TPP)(Cl)) in the presence of molecular sieves, in order to avoid the easy hydrolysis of PhI=NTs or of a transient Fe=NTs complex,<sup>14</sup> led to the complete formation of the tosylimido-bridged iron-porphyrin complex Fe(TPP)(NTs)(Cl) (**2a**) within 15 min at 20 °C.

Complex **2a** was obtained as purple crystals in 80% yield after precipitation by pentane and recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/

**Table II.** Selected Bond Distances (Å), Angles (deg), and Averages with Their Estimated Standard Deviations

Fe Coordination Sphere				
Fe-N1	2.075 (4)	} 2.070 (2)	Fe-Cl	2.259 (2)
Fe-N17	2.064 (4)		N-N23	1.371 (6)
Fe-N	1.951 (5)	} 1.960 (3)	Fe...N23	2.467 (4)
Fe-N11	1.969 (4)			
Cl-Fe-N	117.6 (1)	N1-Fe-N23	86.3 (2)	
Fe-N-N23	94.3 (3)	N11-Fe-N17	91.3 (2)	
N1-Fe-Cl	93.3 (1)	N11-Fe-N23	158.3 (2)	
N11-Fe-Cl	117.7 (1)	N17-Fe-N23	87.1 (2)	
N17-Fe-Cl	96.5 (1)	N1-Fe-N	84.3 (2)	
N1-Fe-N11	90.9 (1)	N11-Fe-N	124.6 (2)	
N1-Fe-N17	167.6 (2)	N17-Fe-N	84.3 (2)	
Pyrrole Rings <sup>a</sup>				
N <sub>p</sub> -C <sub>α</sub>	1.386 (2)	C <sub>β</sub> -C <sub>β</sub>	1.355 (4)	
C <sub>α</sub> -C <sub>β</sub>	1.427 (3)	C <sub>α</sub> -C(m)	1.398 (3)	
N1, N11, N17 rings		N23 ring		
N <sub>p</sub> -C <sub>α</sub> -C <sub>β</sub>	108.4 (2)		105.1 (3)	
C <sub>α</sub> -N <sub>p</sub> -C <sub>α</sub>	107.4 (2)		111.3 (4)	
C <sub>α</sub> -C <sub>β</sub> -C <sub>β</sub>	107.9 (2)		109.1 (4)	
C <sub>α</sub> -C(m)-C <sub>α</sub>	125.7 (3)		127.9 (3)	
N <sub>p</sub> -C <sub>α</sub> -C(m)	125.8 (2)		126.2 (3)	
C <sub>α</sub> -C(m)-C(phe)	117.4 (2)		113.9 (3)	
Phenyl Rings <sup>a</sup>				
C(m)-C(phe)	1.494 (4)	C(phe)-C(phe)	1.381 (2)	
(C-C-C)		120.0 (1)		
Tosylimido Group				
S-N	1.633 (5)	S-CT1	1.772 (7)	
S-O1	1.414 (4)	(C-C)	1.364 (4)	
S-O2	1.423 (5)	CT4-CT7	1.49 (1)	
Fe-N-S	148.5 (3)	N-S-O2	110.0 (3)	
N23-N-S	117.1 (4)	O1-S-O2	120.1 (3)	
N-S-CT1	105.6 (2)	(C-C-C)	120.0 (2)	
N-S-O1	104.8 (3)			

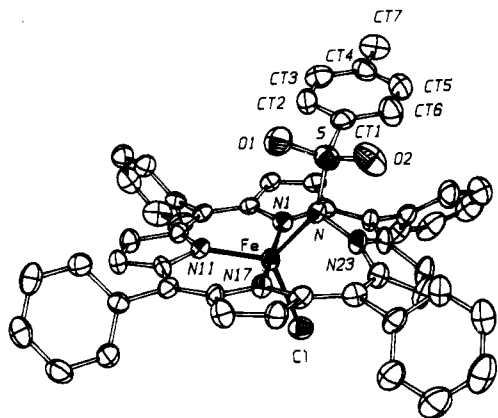
<sup>a</sup>C<sub>α</sub>, C<sub>β</sub>, C(m), and C(phe) stand respectively for the α, β, methine, and phenyl carbon atoms of the macrocycle.

CH<sub>3</sub>OH. The other Fe(porphyrin)(NTs)(Cl) complexes **2b** (porphyrin = TpCIPP<sup>9</sup>) and **2c** (porphyrin = TTP<sup>9</sup>) have been prepared by the same method in 95 and 90% yields, respectively (Scheme I).

**Mass Spectrometry and IR and UV-Visible Spectroscopy Characteristics of Complexes 2.** **Mass Spectrometry.** The spectrum of complex **2a**, obtained at 220 °C by the chemical ionization technique, (NH<sub>3</sub>, negative ions) showed a *M* - 1 peak at *m/e* = 871 and a major fragment at *m/e* = 836 corresponding respectively to Fe(TPP)(NTs)(Cl) and Fe(TPP)(NTs). Thus it appears that complex **2a** loses readily its axial chloride ligand, as do other chloro(porphyrinato)iron(III) complexes.<sup>18</sup> However, it did not release its nitrene NTs ligand, contrary to what was already observed under the same conditions for the Fe<sup>II</sup>(porphyrin)(NNC<sub>3</sub>H<sub>18</sub>) complexes,<sup>4b</sup> which contained a nitrene ligand bound only to the iron by its nitrogen atom.

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**Figure 1.** ORTEP plot of the molecule of complex **2a**. Thermal ellipsoids are scaled to enclose 50% of the electronic density. Hydrogen atoms are omitted for clarity. The numbering scheme used is as follows: N1–C24, porphyrin skeleton atoms, C25–C30, phenyl ring bonded to C<sub>6</sub> between N1 and N11 pyrrole rings; C31–C36, phenyl ring bonded to C18 between N17 and N23 pyrrole rings; C43–C48, phenyl ring bonded to C24 between N23 and N1 pyrrole rings.

**IR Spectroscopy.** The IR spectrum (KBr) of complex **2a** was very similar to those of Fe<sup>II</sup>(TPP) and Fe<sup>III</sup>(TPP)(Cl). However, it exhibited additional bands characteristic of the axial ligands of the iron. First, two intense bands characteristic of the tosyl substituent of the nitrene ligand appeared at 1154 cm<sup>-1</sup> ( $\nu_{as}(\text{SO}_2)$ ) and 1095 cm<sup>-1</sup> ( $\nu_s(\text{SO}_2)$ ). These bands were located respectively at 1235 and 1135 cm<sup>-1</sup> in the spectrum of PhI=NTs<sup>17</sup> and at 1305 and 1155 cm<sup>-1</sup> in that of *p*-toluenesulfonamide.<sup>17</sup> Coordination of the nitrene to Fe(TPP)(Cl) thus results in an important lowering of the  $\nu_{as}(\text{SO}_2)$  and  $\nu_s(\text{SO}_2)$  frequencies. Another band at 345 cm<sup>-1</sup> has been assigned to a Fe–Cl stretching vibration. Accordingly, this band is absent in the spectrum of Fe(TPP)(py)<sub>2</sub> and Fe<sup>II</sup>(TPP) and is replaced by a new band at 270 cm<sup>-1</sup> ( $\nu(\text{Fe–Br})$ ) when Cl is replaced by Br in Fe(TPP)(NTs)(Br).<sup>19</sup> The Fe–Cl band of complex **2a** appears 35 cm<sup>-1</sup> lower than the Fe–Cl band of Fe(TPP)(Cl).<sup>20</sup> Table I shows that the positions of the 1154-, 1095-, and 345-cm<sup>-1</sup> bands are very similar in complexes **2b** and **2c**.

**UV-Visible Spectroscopy.** The UV-visible characteristics of complexes **2** are compared in Table I. Their spectra are very similar to those of iron<sup>III</sup>(*N*-alkyl-TPP) complexes such as [Fe<sup>III</sup>(*N*-CH<sub>3</sub>-TPP)(Br)]<sup>+</sup>X<sup>-</sup> ( $\lambda_{\text{max}}$  (CHCl<sub>3</sub>) = 423, 528, 560, 630, 680 nm).<sup>21</sup>

**X-ray Structure of Complex 2a.** Single crystals of complexes **2a–c** were obtained by slow evaporation of CH<sub>3</sub>OH–CH<sub>2</sub>Cl<sub>2</sub> solutions at room temperature. Analysis of suitable single crystals of complex **2a** showed that it cocrystallizes with a (Cl<sup>-</sup>, H<sub>3</sub>O<sup>+</sup>) ion pair and a CH<sub>3</sub>OH molecule.

Figure 1 shows the molecule as it exists in the crystal together with the labeling scheme used. Individual bond lengths and angles are given in Table II.

As shown in Figure 1, the tosylimido moiety is inserted into the Fe–N23 bond of chloroiron(III) *meso*-tetraphenylporphyrin. The iron–nitrogen (N(Ts)) distance (1.951 (5) Å) is in agreement with a single Fe–N bond,<sup>22</sup> and the N–N23 distance (1.371 (6) Å) is equally characteristic of a single nitrogen–nitrogen bond.<sup>22</sup>

The iron atom is five-coordinate and is bonded to the three pyrrole nitrogens of the porphyrin ring N1, N11 and N17, to the nitrene ligand nitrogen N, and to a chlorine atom. The pyrrole nitrogen N23 seems no longer bonded to the iron as shown by the long Fe–N23 distance (2.467 (4) Å; Table II). Consequently, the distance between the iron atom and the pyrrole nitrogen N11

(1.969 (4) Å) is slightly shorter than the two other iron–pyrrole nitrogen distances: Fe–N1 (2.075 (4) Å) and Fe–N17 (2.064 (4) Å). These two distances are similar to those observed for the iron–pyrrole nitrogen bond of high-spin ( $S = 5/2$ ) iron(III)–porphyrin complexes (Fe–N(p) = 2.070 Å<sup>23</sup>), but they are longer than those measured in the intermediate-spin ( $S = 3/2$ ) N-bridged iron(III)–porphyrin–carbene complex Fe<sup>III</sup>(TPP)(C=CAR<sub>2</sub>)(Cl) (Fe–N(p) = 1.990 Å).<sup>10a,d</sup>

The Fe–Cl distance of 2.259 (2) Å is slightly longer than that present in Fe<sup>III</sup>(TPP)(Cl) (2.193 (3) Å)<sup>23</sup> and somewhat shorter than that observed in the N-bridged iron–porphyrin–carbene complex (Fe–Cl = 2.299 Å).<sup>10a,d</sup> These variations of the Fe–Cl distances are most probably related to the distortions of the macrocycle that appear by insertion of a carbene or a nitrene moiety into a M–N(p) bond of a metalloporphyrin.<sup>10a,d,24</sup>

The iron center, the pyrrole nitrogen N11, the nitrene nitrogen N, and the chlorine atom are coplanar, and the bond angles in this mean plane around the iron center are close to 120° (Table II). Moreover, this mean plane is almost normal to the plane defined by the three pyrrole nitrogens N1, N11, and N17 bonded to the metal, the corresponding dihedral angle being 91.1°. Thus, the coordination geometry of the iron center present in **2a** is best described as a distorted trigonal bipyramid with N11, N, and Cl lying in the equatorial plane. The pyrrole nitrogen N23 also lies very close to this equatorial plane.

Because of the insertion of the nitrene moiety in the Fe–N23 bond, the porphyrin macrocycle is severely distorted. The individually planar pyrrole rings bearing respectively the N1, N11, N17, and N23 nitrogen atoms make dihedral angles of 9.6, 5.8, 8.5, and 29.9° with the plane containing the three pyrrole nitrogens N1, N11, and N17 bonded to the metal. This distortion is, however, less important than that present in the N-bridged tosylimido–Ni(II)–TPP complex in which the dihedral angle between the mean plane of one pyrrole ring and the mean plane of the four pyrrole nitrogens is as large as 40.5°.<sup>16</sup> Whereas in the N-bridged carbene–iron(III)–porphyrin complex Fe<sup>III</sup>(TPP)(C=CAR<sub>2</sub>)(Cl) the four pyrrole nitrogens are almost coplanar,<sup>10a,d</sup> in **2a** the pyrrole nitrogen N23, not bonded to the iron, lies 0.44 Å above the plane containing N1, N11, and N17. At the opposite end, the iron atom lies 0.21 Å below this plane toward the chlorine atom.

The distortion of the porphyrin skeleton seems to have very little or no effect at all on the  $\pi$ -electron delocalization in the porphyrinato core. Indeed, the distances between the porphyrin carbons (C <sub>$\alpha$</sub> , C <sub>$\beta$</sub> , and C <sub>$m$</sub>  being the  $\alpha$ - and  $\beta$ -pyrrole and meso carbons, respectively) C <sub>$\alpha$</sub> –C <sub>$\beta$</sub>  (1.427 (3) Å), C <sub>$\alpha$</sub> –C <sub>$m$</sub>  (1.398 (3) Å), and N(p)–C <sub>$\alpha$</sub>  (1.386 (2) Å) are almost identical with those found in nondistorted porphyrin complexes such as Fe(TPP)(pip)<sub>2</sub><sup>25</sup> (pip = piperidine). This has also been observed in the previously described porphyrin derivatives in which a carbene or a nitrene moiety is inserted into a metal–pyrrole nitrogen bond.<sup>10,16,24</sup>

Concerning the nitrene ligand, the sulfur atom is contained in the plane defined by the Cl, N11, Fe, and N atoms but neither the oxygen atoms O1 and O2 nor the CT (Ph) carbons are contained in this plane. Indeed, the value of the N–S–CT1 angle (105.6°) is far from 180° as well as that of the O1–S–O2 angle, which is 120.1°.

**Electronic and Magnetic Properties of Complex 2. Magnetic Susceptibility Measurement.** The temperature dependence of the magnetic moment of the crystalline complex **2a** is shown in Figure 2. In the higher temperature range ( $T > 40$  K), the magnetic moment is constant and equal to 5.6 ± 0.1  $\mu_B$ . As the temperature approaches 4 K, the moment drops to 4.9  $\mu_B$ . Compound **2a** thus behaves in the crystalline state as expected for a sextuplet spin state ( $S = 5/2$ ). A similar value of 5.8 ± 0.1  $\mu_B$  has been found

(19) Fe(TPP)(NTs)(Br) was synthesized by the method used for complexes **2a–c**, from the reaction of PhI=NTs (**1**) with Fe(TPP)(Br).  
 (20) Alben, J. O. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. 3, p 332.  
 (21) Balch, A. L.; La Mar, G. N.; Latos-Grazynski, L.; Renner, M. W. *Inorg. Chem.* **1985**, *24*, 2432–2436.  
 (22) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123–175.

(23) Scheidt, R. W. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. 3, p 463.  
 (24) (a) Chevrier, B.; Weiss, R. *J. Am. Chem. Soc.* **1976**, *98*, 2985. (b) Johnson, A. W.; Ward, D. J. *J. Chem. Soc., Perkin Trans. 1* **1976**, 720. (c) Johnson, A. W.; Ward, D. J.; Batten, P.; Hamilton, A. L.; Skelton, G.; Elson, C. M. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2076.  
 (25) Hoard, J. L. *Ann. N. Y. Acad. Sci.* **1973**, *206*, 18.

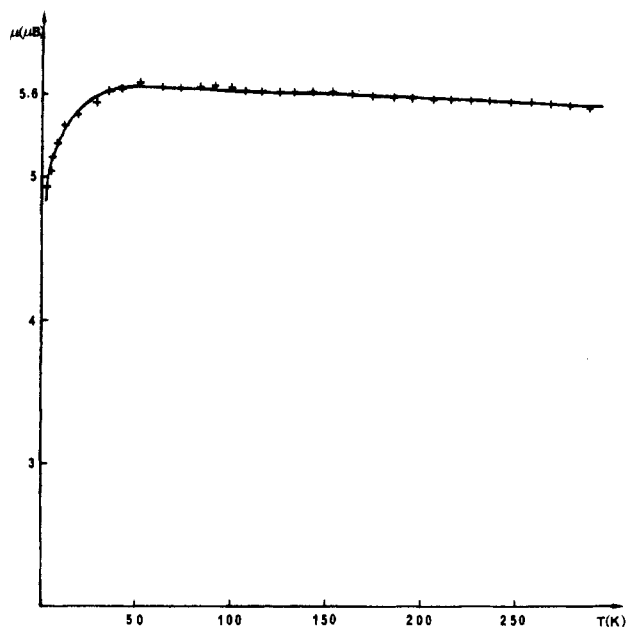


Figure 2. Temperature dependence of the magnetic moment of complex **2a** (crystalline state).

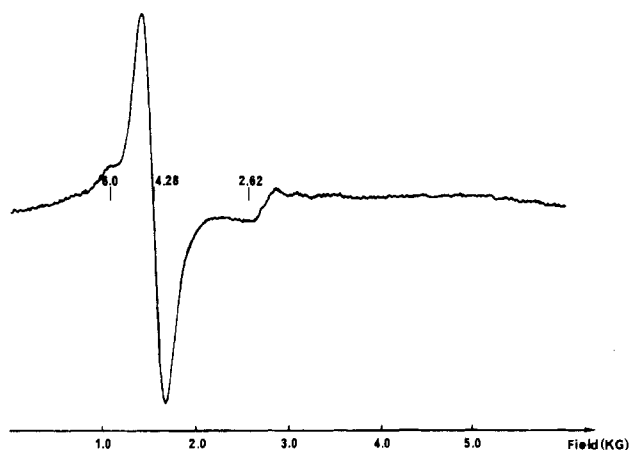


Figure 3. EPR spectrum of complex **2a** (powder) at 4 K.

by the Evans method<sup>26</sup> for the magnetic moment of complex **2a** 0.2 M in  $\text{CDCl}_3$  at 34 °C.

**EPR Spectroscopy.** The EPR spectrum of complex **2a** (powder) at 4 K (Figure 3) exhibits a signal centered at  $g = 4.28$  as a main feature. This result together with those from magnetic susceptibility measurements leads to a  $S = 5/2$  spin-state assignment for the ground state of complex **2a** and indicates a rhombic symmetry around its iron. Two very weak signals, which probably belong to another iron(III) species in very small amounts, appear at  $g = 6$  and  $g = 2.67$ .

**$^1\text{H}$  NMR Spectroscopy.** The  $^1\text{H}$  NMR spectrum of complex **2a** in  $\text{CDCl}_3$  at 20 °C is shown in Figure 4. The assignments of its signals have been done by comparison of the spectra of complexes **2a** and **2b** (Table I) and those of  $\text{Fe}(\text{TPP}-d_{20})(\text{NTs})(\text{Cl})$  and  $\text{Fe}(\text{TPP}-d_8)(\text{NTs})(\text{Cl})$ , the analogues of **2a** prepared respectively from a tetraphenylporphyrin completely deuteriated in the phenyl rings ( $\text{TPP}-d_{20}$ )<sup>27</sup> or in the pyrrole rings ( $\text{TPP}-d_8$ ).<sup>27</sup>

(26) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(27)  $(\text{TPP})\text{H}_2-d_{20}$  and  $(\text{TPP})\text{H}_2-d_8$  were respectively prepared by condensation of pentadeuteriobenzaldehyde and pyrrole and by condensation of benzaldehyde and pentadeuteriopyrrole in  $\text{CH}_3\text{CH}_2\text{COOD}$  by the usual technique: Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476. They were found completely deuteriated on the phenyl rings and on the pyrrole rings, respectively ( $^1\text{H}$  NMR and mass spectroscopy). Their dianions correspond respectively to the formulas *meso*-tetrakis(pentadeuteriophenyl)porphyrinate ( $\text{C}_{44}\text{H}_8\text{D}_{20}\text{N}_4$ ) and *meso*-tetraphenylporphyrinate- $d_8$  ( $\text{C}_{44}\text{H}_{20}\text{D}_8\text{N}_4$ ).

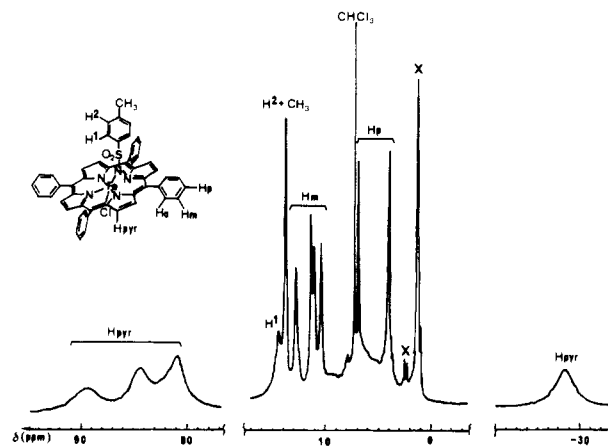


Figure 4.  $^1\text{H}$  NMR spectrum of complex **2a** ( $10^{-2}$  M in  $\text{CDCl}_3$  at 20 °C;  $\delta$  ( $\text{CH}_3$ )<sub>4</sub>Si; X = impurities).

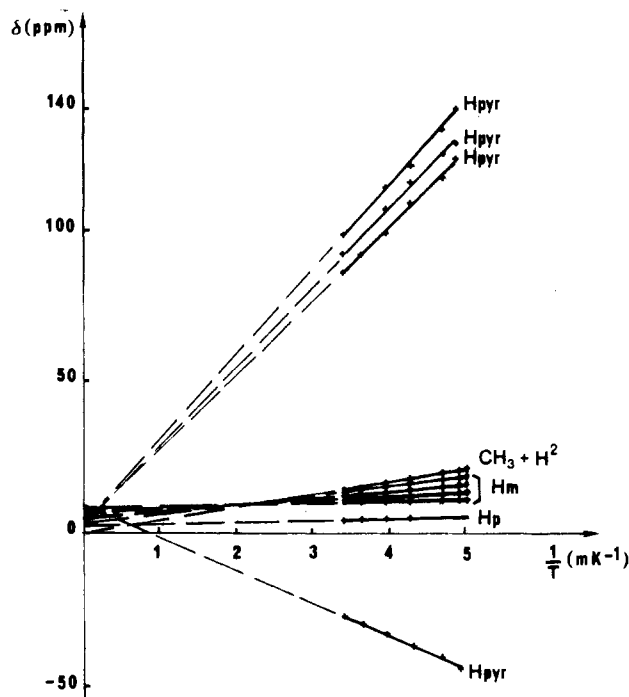


Figure 5. Thermal dependence of the chemical shifts ( $\delta$  referred to  $\text{Me}_4\text{Si}$ ) of the protons of complex **2a** (for the labeling of hydrogens, see Figure 4).

In the spectrum of the  $\text{TPP}-d_8$  complex, the signals at 89.5, 84.5, 81.7, and -28.4 ppm, which are each integrated for 2 H, are lacking. These signals have thus been assigned to the pyrrole protons. The signals at 12.70, 11.22, 10.93, 10.30, 6.85, 6.10, 4.10, and 3.92 ppm, which are lacking in the spectrum of the  $\text{TPP}-d_{20}$  complex, are due to the protons of the phenyl rings of the *meso*-tetraphenylporphyrin. The signals at 6.85 and 3.92 ppm, which are absent in the spectrum of **2b** (Table I), have consequently been assigned to the para protons of the phenyl rings. Concerning the other signals of the phenyl ring protons, those at 6.10 and 4.10 ppm, integrated each for 2 H, are considerably broader than those at 12.70, 11.22, 10.90, and 10.30 ppm, which are also each integrated for 2 H. These properties are expected for the ortho and meta protons of the phenyl rings, respectively, since the ortho protons are closer to the paramagnetic center than the meta protons. Two other very broad signals, corresponding

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(29) (a) Felton, R. H.; Owen, G. S.; Dolphin, D.; Forman, A.; Borg, D. C.; Fager, J. *Ann. N. Y. Acad. Sci.* **1973**, *206*, 504-514. (b) Hoard, J. L.; Cohen, G. H.; Glick, M. D. *J. Am. Chem. Soc.* **1967**, *89*, 1992-1996.

**Table III.** Spectroscopic and Structural Data of Different Iron-Porphyrin Complexes Compared to Those of **2a**

complex	<i>S</i>	$\mu_{\text{eff}}, \mu_{\text{B}}$	$\delta(\text{H}(\text{pyr})) (\text{Me}_4\text{Si})$	EPR		Fe-N(p), Å	ref
				<i>T</i> , K	<i>g</i>		
Fe <sup>II</sup> (TPP)	1	4.4	4.2			1.972	28
Fe <sup>II</sup> (TPP)(NNC <sub>5</sub> H <sub>18</sub> )	2	5.1	66.8			2.096	4b
Fe <sup>III</sup> (TPP)(C=CAr <sub>2</sub> )(Cl) (bridged)	$3/2$	3.94	21.3, -21.0, -28.9, -42.1	4	4.64, 3.55, 2.03	1.990 <sup>a</sup>	10
Fe <sup>III</sup> (TPP)(NTs)(Cl) ( <b>2a</b> , bridged)	$5/2$	5.8	89.5, 84.5, 81.7, -28.4	4	4.28	2.036 <sup>a</sup>	this work
Fe <sup>III</sup> (TPP)(Cl)	$5/2$	5.9	79.4	4	5.66, 2.03	2.060	29
[Fe <sup>III</sup> ( <i>N</i> -CH <sub>3</sub> -TPP)(Cl)] <sup>+</sup> Cl <sup>-</sup>	$5/2$		128, 92, 79, 2.4	77	5.86, 2.16		21
Fe <sup>III</sup> (TMP)(O)(OCOAr) (bridged)	$5/2$	5.4		273	4.3		12
Fe <sup>IV</sup> (TPP)(O)(1-CH <sub>3</sub> -Im)	1	2.9	5				3a,d

<sup>a</sup> Average of the three Fe-N(p) bond lengths in those complexes.

to the other four ortho protons, have not been precisely located. However, it seems that they are superimposed on the signals of the meta protons as indicated by a total integration of 12 H for the signals between 14 and 10 ppm.

The last two signals at 14.32 and 13.7 ppm are the only ones to be present both in the TPP-*d*<sub>8</sub> complex and in the TPP-*d*<sub>20</sub> complex. They have thus been assigned to the protons of the nitrene ligand. The broader signal at 14.32 ppm is integrated for 2 H and has been assigned to the ortho protons of the tosyl group, which are closer to the paramagnetic center than its meta protons. The signal at 13.71 ppm is integrated for 5 H and corresponds to the meta protons and the CH<sub>3</sub> protons of the tosyl group.

The temperature dependence of the chemical shifts of the protons of complex **2a** between -80 and +40 °C corresponds to the Curie law (Figure 5). This is in agreement with a monomeric iron-porphyrin complex in a well-defined paramagnetic noninteracting state. As shown in Table I, the <sup>1</sup>H NMR characteristics of complexes **2a-c** are very similar.

## Discussion

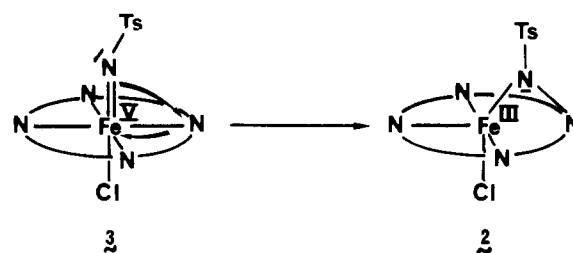
Compounds **2** are the first described iron-porphyrin complexes bearing a nitrene ligand inserted into an iron-pyrrole nitrogen bond.<sup>15</sup> It is however noteworthy that nitrene-bridged complexes of Cu-, Zn-, and Ni-porphyrins have been previously prepared and that the X-ray structure of one of them, the Ni complex, has been described.<sup>16</sup>

Complexes **2** have been prepared by a simple technique that has never been used so far for the synthesis of transition-metal-nitrene complexes.<sup>22</sup> It involves the one-step reaction at room temperature of a nitrene donor, [(tosylimino)iodo]benzene, PhI=NTs (**1**), a nitrogen analogue of iodosylbenzene, PhI=O, with iron(III)-porphyrins. Though the precise mechanism of this reaction remains unknown, it is reasonable to think, by analogy with the mechanism generally admitted now for the reactions between PhI=O and iron(III)-porphyrins,<sup>6</sup> that PhI=NTs transfers its nitrene moiety to the iron-porphyrin to give the iron(V)-nitrene complex Fe<sup>V</sup>(NTs)(TPP)(Cl) (**3**) (Scheme II). This species could be the active intermediate in the tosylimido aziridination of alkenes<sup>14</sup> or tosylimido amidation of alkanes.<sup>13</sup> It is unstable at room temperature and could isomerize with the nucleophilic assistance of a pyrrole nitrogen to yield the nitrene-bridged complex **2** (Scheme II).

The X-ray structure of complex **2a** clearly shows that the nitrene NTs moiety is inserted in the Fe-N23 bond of Fe<sup>III</sup>(TPP)(Cl). Indeed, Fe and N23 are not bonded, as indicated by the large Fe...N23 distance. For comparison, metal-nitrogen bond lengths for complexes of transition metals generally range between 2.131 and 1.801 Å for bond orders between 1 and 2.<sup>22</sup> Consequently, the iron is pentacoordinate, its coordination geometry being a distorted trigonal bipyramid with an equatorial plane containing the nitrene nitrogen N and two pyrrole nitrogens N1 and N11. A similar geometry has also been observed in the carbene-bridged complex Fe(TPP)(C=CAr<sub>2</sub>)(Cl).<sup>10a,d</sup>

Several spectroscopic data of various iron-porphyrin complexes that are characteristic of different spin and oxidation states are compared to those of complex **2a** in Table III. The characteristics of complex **2a** are very similar to those of previously reported high-spin pentacoordinate iron(III)-porphyrin complexes, but very different from those of high-spin ferrous (*S* = 2), intermediate-spin

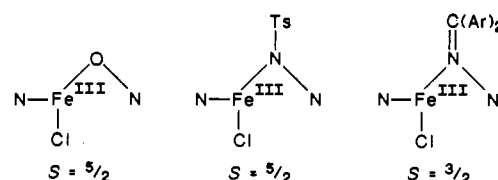
Scheme II



ferrous (*S* = 1), intermediate-spin ferric (*S* =  $3/2$ ), and low-spin Fe(IV) (*S* = 1) complexes. When they are taken together, the magnetic moment  $\mu = 5.8 \pm 0.1 \mu_{\text{B}}$ , the EPR signal at *g* = 4.28, the Fe-N(p) distance 2.036 Å, and the NMR shifts of the pyrrole protons ( $\delta = 89.5, 84.5, 81.7, -28.4$  (vs Me<sub>4</sub>Si)) firmly establish a high-spin ferric (*S* =  $5/2$ ) state for complex **2a**. The appearance of four signals integrated for 2 H each for the pyrrole protons is characteristic of a C<sub>s</sub> symmetry for complex **2a**. Its plane of symmetry contains two opposite pyrrole nitrogens N11 and N23, the nitrene ligand nitrogen, and the sulfur atoms (Figure 4). Similar splitting and chemical shifts of the pyrrole proton signals have been already observed in other iron-porphyrin complexes retaining a C<sub>s</sub> symmetry such as [Fe(*N*-CH<sub>3</sub>-TPP)(Cl)]<sup>+</sup>X<sup>-21</sup> (Table III).

A rhombic symmetry of the iron d orbitals has been found for complex **2a**, as shown by the EPR signal at *g* = 4.28. Such a rhombic symmetry has also been found for the iron d orbitals of other carbene-bridged (Fe(TPP)(Cl)(C=CAr<sub>2</sub>))<sup>10</sup> or oxo-bridged (Fe(TMP)(OCOAr)(O))<sup>12</sup> iron(III)-porphyrin complexes (*g* = 4.64, 3.55, 2.03 and *g* = 4.3, respectively; Table III). It is noteworthy that, in iron(III)-*N*-alkyl-TPP complexes such as [Fe<sup>III</sup>(*N*-CH<sub>3</sub>-TPP)(Cl)]<sup>+</sup>Cl<sup>-</sup>, the iron is coordinated with an octahedral symmetry and exhibits EPR signals at *g* = 5.86 and 2.16<sup>21</sup> (Table III). Since (i) the magnetic moments measured at room temperature for crystalline **2a** ( $\mu = 5.6 \pm 0.1 \mu_{\text{B}}$ ) and for its solution in CDCl<sub>3</sub> ( $\mu = 5.8 \pm 0.1 \mu_{\text{B}}$ ) are identical and (ii) the UV-visible spectrum of powdered **2a** ( $\lambda = 435, 521, 559, 692$  nm) is very similar to that of complex **2a** 10<sup>-5</sup> M in CH<sub>2</sub>Cl<sub>2</sub>,<sup>30</sup> it is likely that complexes **2** have similar structures in solution and in the solid state.

As a conclusion, if we come back to the analogy between oxo-, carbene-, and nitrene-bridged iron-porphyrin complexes (see the introduction of this paper), it is noteworthy that both the oxo-<sup>12</sup> and nitrene-bridged iron complexes exhibit a high-spin Fe(III) (*S* =  $5/2$ ) structure whereas the carbene-bridged iron complex is the only one to involve an intermediate Fe(III) (*S* =  $3/2$ ) spin state:



(30) The powder of complex **2a** shows broader bands generally red-shifted as usually found when passing from complexes in solution to powdered samples.<sup>4b,10c</sup>

Table IV. Positional Parameters of Each Atom of Complex 2a<sup>a</sup>

atom	x	y	z	B, Å <sup>2</sup>	atom	x	y	z	B, Å <sup>2</sup>
Fe	0.34686 (4)	0.3160 (1)	0.11275 (3)	2.36 (2)	C33	0.3727 (3)	0.6761 (8)	-0.0646 (2)	3.5 (2)
N1	0.2846 (2)	0.2040 (5)	0.1277 (2)	2.4 (1)	C34	0.3950 (3)	0.7917 (7)	-0.0543 (2)	3.5 (2)
C2	0.2870 (3)	0.1042 (6)	0.1556 (2)	2.4 (1)	C35	0.4085 (3)	0.8225 (7)	-0.0148 (2)	3.5 (2)
C3	0.2352 (3)	0.0482 (7)	0.1535 (2)	2.8 (2)	C36	0.4006 (3)	0.7347 (7)	0.0152 (2)	2.9 (2)
C4	0.2030 (3)	0.1131 (7)	0.1259 (2)	2.7 (1)	C37	0.5413 (3)	0.2936 (7)	0.1551 (2)	3.0 (2)
C5	0.2339 (2)	0.2110 (6)	0.1100 (2)	2.2 (1)	C38	0.5700 (3)	0.1815 (7)	0.1610 (2)	3.5 (2)
C6	0.2156 (3)	0.2993 (7)	0.0804 (2)	2.3 (1)	C39	0.6206 (3)	0.1848 (8)	0.1802 (2)	4.0 (2)
C7	0.2472 (2)	0.3834 (7)	0.0608 (2)	2.5 (1)	C40	0.6437 (3)	0.2964 (9)	0.1932 (3)	4.8 (2)
C8	0.2289 (3)	0.4748 (7)	0.0314 (2)	2.9 (2)	C41	0.6169 (3)	0.4074 (9)	0.1868 (3)	4.7 (2)
C9	0.2712 (3)	0.5373 (7)	0.0198 (2)	2.9 (2)	C42	0.5648 (3)	0.4074 (8)	0.1675 (2)	4.0 (2)
C10	0.3178 (3)	0.4859 (6)	0.0415 (2)	2.4 (1)	C43	0.3184 (3)	-0.0064 (7)	0.2183 (2)	2.9 (2)
N11	0.3020 (2)	0.3909 (5)	0.0673 (2)	2.4 (1)	C44	0.2772 (3)	0.0304 (8)	0.2406 (2)	3.7 (2)
C12	0.3697 (3)	0.5215 (7)	0.0378 (2)	2.5 (1)	C45	0.2651 (3)	-0.043 (1)	0.2737 (2)	5.2 (2)
C13	0.4147 (2)	0.4745 (6)	0.0609 (2)	2.3 (1)	C46	0.2935 (4)	-0.1468 (9)	0.2851 (3)	5.8 (2)
C14	0.4684 (3)	0.5008 (7)	0.0543 (2)	3.0 (2)	C47	0.3354 (4)	-0.1815 (9)	0.2638 (3)	6.2 (3)
C15	0.4996 (3)	0.4349 (7)	0.0817 (2)	3.0 (2)	C48	0.3479 (3)	-0.1125 (8)	0.2303 (2)	4.4 (2)
C16	0.4658 (3)	0.3651 (7)	0.1059 (2)	2.6 (1)	Cl	0.35338 (7)	0.4216 (2)	0.17185 (5)	3.47 (4)
N17	0.4141 (2)	0.3918 (5)	0.0922 (2)	2.4 (1)	N	0.3842 (2)	0.1541 (5)	0.1109 (2)	2.6 (1)
C18	0.4842 (3)	0.2886 (7)	0.1389 (2)	2.9 (2)	S	0.39950 (7)	0.0300 (2)	0.08475 (6)	3.44 (4)
C19	0.4546 (3)	0.2092 (7)	0.1620 (2)	2.8 (2)	O1	0.3869 (2)	0.0664 (5)	0.0441 (1)	4.9 (1)
C20	0.4652 (3)	0.1806 (8)	0.2033 (2)	3.7 (2)	O2	0.4513 (2)	-0.0124 (5)	0.0983 (2)	5.1 (1)
C21	0.4217 (3)	0.1224 (8)	0.2155 (2)	3.8 (2)	CT1	0.3549 (3)	-0.0910 (7)	0.0957 (2)	3.3 (2)
C22	0.3823 (3)	0.1084 (7)	0.1828 (2)	3.0 (2)	CT2	0.3049 (3)	-0.0921 (8)	0.0762 (2)	3.7 (2)
N23	0.4052 (2)	0.1596 (5)	0.1503 (2)	2.6 (1)	CT3	0.2697 (3)	-0.1811 (8)	0.0857 (2)	4.1 (2)
C24	0.3301 (3)	0.0705 (7)	0.1832 (2)	2.6 (1)	CT4	0.2822 (3)	-0.2687 (7)	0.1152 (2)	3.7 (2)
C25	0.1574 (3)	0.3049 (6)	0.0701 (2)	2.6 (1)	CT5	0.3332 (4)	-0.2671 (8)	0.1346 (3)	4.7 (2)
C26	0.1338 (3)	0.2688 (7)	0.0330 (2)	3.3 (2)	CT6	0.3692 (3)	-0.1798 (8)	0.1247 (3)	4.4 (2)
C27	0.0793 (3)	0.2743 (8)	0.0244 (2)	4.1 (2)	CT7	0.2419 (4)	-0.3596 (9)	0.1272 (3)	5.2 (2)
C28	0.0482 (3)	0.3202 (8)	0.0519 (3)	4.7 (2)	CIS	0.0193 (1)	0.2889 (3)	0.18740 (8)	7.15 (7)
C29	0.0713 (3)	0.3589 (9)	0.0889 (3)	4.9 (2)	OS	-0.037 (1)	0.094 (3)	0.2305 (7)	15.7 (8)*
C30	0.1254 (3)	0.3500 (8)	0.0979 (2)	4.0 (2)	CS	-0.032 (1)	0.145 (3)	0.1907 (8)	8.7 (7)*
C31	0.3784 (3)	0.6166 (6)	0.0055 (2)	2.3 (1)	OW	0.000	0.269 (4)	0.250	17 (1)*
C32	0.3649 (3)	0.5886 (7)	-0.0349 (2)	2.9 (2)					

<sup>a</sup> Estimated standard deviations are given in parentheses. Starred values are for atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters defined as  $\frac{1}{3}[a^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23}]$ .

The difference is presumably related to the greater strength of the Fe–C bond compared to that of the Fe–O and Fe–N bonds. A similar difference has been previously reported for the relative strengths of the Fe–N and Fe–C bonds in porphyrinato–Fe(II)–nitrene<sup>4</sup> and –Fe(II)–carbene<sup>5</sup> complexes exhibiting an axial symmetry. The spin state of the Fe(II)–nitrene complexes ( $S = 2$ ) is higher than that of the Fe(II)–carbene complexes ( $S = 0$ ).

### Experimental Section

**Physical Measurements.** UV–visible spectra were obtained on an Aminco DW2 spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 783 infrared spectrophotometer. Mass spectra were recorded on a Ribermag apparatus. EPR spectra were recorded with a Bruker ER-200D spectrometer operating at the X-band frequency of 9.46 GHz and fitted with an helium continuous-flow Oxford Instruments cryostat. Polycrystalline samples of complex 2a were mounted in standard 4-mm quartz EPR tubes. <sup>1</sup>H NMR spectra were obtained on a Bruker EM 250 spectrometer operating at 250 MHz and fitted with a temperature regulation system. Elemental analyses were performed by the service central de microanalyse at Gif-sur-Yvette, France.

**Magnetic Susceptibility Measurements.** Variable-temperature (4–300 K) magnetic susceptibilities were measured with a Faraday magnetic balance, equipped with an helium continuous-flow Oxford Instruments cryostat. Measurements were run on powdered samples of about 10 mg. The applied magnetic field was in the range 0.1–0.7 T. The independence of the susceptibility from the magnetic field was checked at room temperature. Mercury tetrakis(thiocyanato)cobaltate(III) was used as a susceptibility standard. The magnetic data were corrected for the molecular diamagnetism estimated to  $-860 \times 10^{-6}$  cgsu from free porphyrin base measurements<sup>31</sup> and Pascal's rules.

**X-ray Analysis.** Suitable single crystals of complex 2a were obtained by slow evaporation of methanol–methylene chloride solutions at room temperature. A systematic search in reciprocal space using a Philips PW1100/16 automatic diffractometer showed that crystals of 2a belonged to the monoclinic system.

The unit-cell dimensions and their standard deviations were obtained and refined at  $-100$  °C with Cu K $\alpha$  radiation ( $\lambda = 1.5405$  Å) by using 25 carefully selected reflections, the standard Philips software, and a

locally built low-temperature device. Final results: C<sub>52</sub>H<sub>42</sub>N<sub>5</sub>O<sub>4</sub>SCl<sub>1</sub>Fe,  $M_r$  959.76,  $a = 25.456$  (8) Å,  $b = 10.488$  (3) Å,  $c = 33.452$  (10) Å,  $\beta = 91.84$  (2)°,  $V = 8884.7$  Å<sup>3</sup>,  $Z = 8$ ,  $d_{\text{calc}} = 1.43$  g cm<sup>-3</sup>,  $\mu = 47.20$  cm<sup>-1</sup>,  $F(000) = 3976$ , space group  $C2/c$  or  $Cc$ .

A nearly parallelepipedic crystal of dimensions 0.16 × 0.17 × 0.24 mm was cut out from a cluster of crystals, glued at the end of a glass wire, and mounted on a rotation-free goniometer head. All quantitative data were obtained from a Philips PW1100/16 four-circle automatic diffractometer, controlled by a P 852 computer, using graphite-monochromated radiation and standard software at  $-100$  °C. The vertical and horizontal apertures in front of the scintillation counter were adjusted so as to minimize the background counts without loss of net peak intensity at the  $2\sigma$  level. The total scan width in the  $\theta/2\theta$  flying step scan was  $\Delta\theta = 1.1 + 0.143 \tan \theta^\circ$  with a step width of 0.05° and a scan speed of 0.024° s<sup>-1</sup>. A total of 6430  $h, k, \pm l$  reflections were recorded ( $4^\circ < \theta < 57^\circ$ ). The resulting data set was transferred to a PDP11/60 computer, and for all subsequent computations, the Enraf-Nonius SPD/PDP package was used,<sup>32</sup> with the exception of a local data-reduction program.

The standard reflections measured every 1 h during the entire data-collection period showed no significant trend.

The raw step-scan data were converted to intensities by using the Lehmann–Larson method<sup>33</sup> and then corrected for Lorentz, polarization, and absorption factors; the last was computed by using the empirical method of Walker and Stuart<sup>34</sup> since indexation was not possible (absorption factors between 0.65 and 1.52). A unique data set of 3756 reflections having  $I > 3\sigma(I)$  was used for determining and refining the structure.

The structure was solved by direct methods using Multan<sup>35</sup> in space group  $C2/c$  on the basis of  $|Ehk|$  statistics. After refinement of the

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heavy atoms, a difference-Fourier map revealed maxima of residual electronic density close to the positions expected for hydrogen atoms of the porphyrin and the tosyl group; they were introduced in structure factor calculations by their computed coordinates ( $C-H = 0.95 \text{ \AA}$ ) and isotropic temperature factors of  $B(H) = 1 + B_{eq}(C) \text{ \AA}^2$  but not refined.  $CH_3OH$  and water hydrogens were omitted. Full least-squares refinement minimizing  $\sum w(|F_o| - |F_c|)^2$  converged to  $R(F) = 0.058$  and  $R_w(F) = 0.087$  with  $\sum w(F^2) = (\sigma^2(\text{counts}) + (pI)^2)^{-1}$ . The unit-weight observation was 1.73 for  $p = 0.08$ . A final difference map revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients come respectively from ref 36 and 37.

Table IV gives the X-ray coordinates of each atom of complex **2a**.

**Reagents and Solvents.** Methylene chloride was purified by distillation from  $P_2O_5$  and kept over molecular sieves. Pentane and methanol for crystallization were used as supplied by Prolabo (purissimum grade) [(tosylimino)iodo]benzene,  $PhI=NTs$  (**1**), was synthesized according to an already described procedure<sup>17</sup> and stored at  $0^\circ C$ , in the dark, under argon to avoid decomposition.  $Fe(TPP)(Cl)$ ,  $Fe(TTP)(Cl)$ , and  $Fe(TpClPP)(Cl)$  were prepared according to literature procedures.<sup>38,39</sup>

**Synthesis of Complexes 2a–c: Tosylimido-Bridged Iron(III) meso-Tetraphenylporphyrin Chloride,  $Fe^{III}(TPP)(NTs)(Cl)$  (**2a**).** A solution of  $0.07 \text{ g}$  of  $Fe^{III}(TPP)(Cl)$  in  $10 \text{ mL}$  of  $CH_2Cl_2$  at  $20^\circ C$  was added

under argon to  $0.15 \text{ g}$  of solid  $PhI=NTs$ , in the presence of molecular sieves. After  $15 \text{ min}$  of stirring, the formation of complex **2a** was complete. The solution was then filtered, and complex **2a** precipitated as a red-brown powder with ca.  $20 \text{ mL}$  of pentane. Purple shining crystals of **2a** were obtained with a  $80\%$  yield ( $0.07 \text{ g}$ ) after recrystallization from  $CH_2Cl_2-CH_3OH$  (2:1). Anal. Calcd for  $C_{51}H_{33}N_5O_2SFeCl$ : C, 70.15; H, 4.04; N, 8.02; S, 3.67; Cl, 4.06. Found: C, 69.94; H, 4.24; N, 8.20; S, 3.62; Cl, 3.87.

**Tosylimido-Bridged Iron(III) meso-Tetrakis(p-chlorophenyl)porphyrin Chloride,  $Fe^{III}(TpClPP)(NTs)(Cl)$  (**2b**).** **2b** was prepared as described above, by starting from  $0.084 \text{ g}$  of  $Fe^{III}(TpClPP)(Cl)$  and  $0.15 \text{ g}$  of  $PhI=NTs$  ( $0.096 \text{ g}$ , yield  $95\%$ ). Anal. Calcd for  $C_{51}H_{31}N_5SO_2Cl_3Fe$ : C, 60.59; H, 3.09; N, 6.92; S, 3.17. Found: C, 60.45; H, 3.36; N, 6.30; S, 3.45.

**Tosylimido-Bridged Iron(III) meso-Tetra-p-tolylporphyrin Chloride  $Fe^{III}(TTP)(NTs)(Cl)$  (**2c**).** **2c** was prepared by starting from  $0.076 \text{ g}$  of  $Fe^{III}(TTP)(Cl)$  and  $0.15 \text{ g}$  of  $PhI=NTs$  ( $0.083 \text{ g}$ , yield  $90\%$ ). Anal. Calcd for  $C_{55}H_{43}N_5SO_2ClFe$ : C, 71.09; H, 4.66; N, 7.54; S, 3.45. Found: C, 70.92; H, 4.89; N, 7.80; S, 3.61.

The other characteristics of complexes **2a–c** (mass, UV-vis,  $^1H$  NMR, and IR spectral data) are included in the tables.

**Registry No.** **1**, 55962-05-5; **2a**, 111468-47-4; **2b**, 111468-48-5; **2c**, 111468-49-6;  $Fe(TPP)(Cl)$ , 16456-81-8;  $Fe(TpClPP)(Cl)$ , 36965-70-5;  $Fe(TTP)(Cl)$ , 19496-18-5;  $Fe(TPP)(NTs)(Br)$ , 111468-50-9;  $Fe(TP-P)(Br)$ , 25482-27-3.

**Supplementary Material Available:** Thermal parameters ( $U_{ij}$ ) for all anisotropic atoms (Table V), positional parameters for hydrogen atoms (Table VI), a full set of bond lengths (Table VII), and a full set of bond angles (Table VIII) (8 pages); observed and calculated structure factor amplitudes ( $\times 10$ ) for all observed reflections (Table IX) (16 pages). Ordering information is given on any current masthead page.

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## Correlation of Redox and Spectroscopic Properties in Seven-Coordinate Oxomolybdenum(VI) Hydroxylamido Catecholato Complexes

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Seven-coordinate  $MoO(cat)(ONR_2)_2$  complexes ( $R = Me, Et, Bz$ ) are prepared by reaction of *cis*- $MoO_2(ONR_2)_2$  with catechol and its 4-nitro, 4-methyl, and 3,5-di-*tert*-butyl derivatives. Correlations among the electrochemical and IR, UV-visible, and  $^{95}Mo$  NMR spectroscopic properties of these compounds are reported and contrasted with the behavior of compositionally similar  $MoO(cat)(S_2CNEt_2)_2$  species. Both series of complexes undergo Mo-centered reductions and catechol-centered oxidations and exhibit an intense, visible wavelength absorption band that is assigned to  $cat \rightarrow Mo$  charge transfer. Linear correlations exist between the difference in Mo- and catechol-centered redox potentials ( $\Delta E_{redox}$ ) and the energy ( $h\nu_{ct}$ ) of the LMCT; however, values of  $\Delta E_{redox}$  and  $h\nu_{ct}$  are consistently larger for  $MoO(cat)(ONR_2)_2$ . This result implies that  $R_2NO^-$  interacts more strongly than  $Et_2NCS_2^-$  with the  $[MoO(cat)]^{2+}$  center, thus producing a greater separation between the filled catecholato and vacant Mo orbitals involved in the electrochemical and spectroscopic transitions. The  $MoO(cat)(ONR_2)_2$  ( $R = Me, Et$ ) complexes exhibit a  $^{95}Mo$  NMR chemical shift that correlates linearly with the wavelength of the LMCT in accord with shielding theory for heavy nuclei. A secondary correlation exists between  $\delta(^{95}Mo)$  and the Mo-centered reduction potentials, apparently as a result of the relationship between electrochemical and optical properties. Solid-state FT/IR spectra of the 4-nitro and 3,5-di-*tert*-butyl derivatives of  $MoO(cat)(ONR_2)_2$  show two  $Mo=O$  stretching frequencies between  $915$  and  $930 \text{ cm}^{-1}$ . These are attributed to the two geometric isomers that become possible when an unsymmetrically substituted catechol ligand is bound to  $[MoO(ONR_2)_2]^{2+}$ .

### Introduction

Interest in oxomolybdenum compounds derives, in part, from the presence of this functionality at the active site of molybdenum hydroxylase enzymes.<sup>2</sup> Discovery of a pterin ring in the cofactor

of these enzymes<sup>3</sup> raises the possibility that this organic unit may participate in electron transfer with the metal center, possibly during catalysis. Thus, we have become interested in oxomolybdenum complexes with redox-active ligands. Recently, we described<sup>4</sup> the preparation and electrochemical characterization of a series of oxomolybdenum(VI)-catecholato complexes with

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