acetonitrile (30 mL) was heated under reflux until a clear yellow solution formed. On cooling the reaction mixture to room temperature, partial redeposition of **2** and Me_4NI occurred, indicating the instability of $[ISn(TDT)_2][Me_4N]$ in the solid state.

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An Intermediate-Spin Iron(III) Porphyrin Complex with a Vinylidene Group Inserted into an Fe–N Bond: Paramagnetic Susceptibility, EPR, and Mössbauer Properties

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The $Fe(TPP)[C{=}C(p\text{-}ClC_6H_4)_2](Cl)$ complex **2a** exhibits a magnetic moment of 3.9 μ_B which is constant between 300 and 40 K. The EPR spectrum of a solid sample at 4 K displays a typical rhombic pattern with *g* values of 4.64, 3.55, and 2.01. Mössbauer studies reveal an isomeric shift ($\simeq$0.3 mm/s) typical of an iron(III) complex and a large quadrupole splitting (2.88 mm/s) which is not temperature dependent between 300 and 1.6 K. The visible and EPR spectra and magnetic moment of complex **2a** either in the solid state or in solution are very similar. This complex thus appears as the first example of a Fe(III) porphyrin in a pure intermediate spin state in both conditions. The peculiar coordination state of its iron atom, caused by the insertion of the vinylidene group into a Fe–N(pyrrolic) bond, which yields a highly distorted geometry, should be at the origin of its very stable intermediate spin state in solution and in the solid state.

Introduction

A one-electron oxidation of iron porphyrin–vinylidene carbene complexes, $Fe^{II}(porphyrin)(C{=}CAr_2)$,[1] by $CuCl_2$ leads to very stable compounds of general formula $Fe(porphyrin)(C{=}CAr_2)(Cl)$.[2] These complexes exhibit electronic spectra[2] very similar to those of compounds I of catalase or horseradish peroxidase (HRP), which are formed by reaction of these hemoproteins in their native ferric state with two-electron oxidants such as H_2O_2 or alkyl hydroperoxides.[3]

Very recently, an X-ray structure analysis[4] of one of these complexes, $Fe(TTP)[C{=}C(p\text{-}ClC_6H_4)_2](Cl)$[5] (**2b**) has been made; it shows that the vinylidene group is actually inserted between the iron and one nitrogen atom of a pyrrole ring. This complex involves an unusual, highly distorted five-coordinate geometry, with an iron(III) ion only bound to three pyrrolic nitrogens, to a vinylic carbon, and a chlorine atom in trans position[4] (Figure 1).

Its peculiar electronic spectrum with a broad and weak Soret peak and a single band around 670 nm in the visible region is unexpected for an iron(III) porphyrin and is presumably due to the important distortion of the porphyrin ring. Because of the similarity of this spectrum with that of catalase compound I (CAT I), an analogous structure with an oxygen atom inserted into a Fe–N bond has been proposed for CAT I.[4]

So far, only very few data are available concerning the electronic structure and the spin state of the iron in complexes **2**. They include the magnetic moment of complex **2a** in C_6H_6 at room temperature, determined by the Evans method, and the EPR *g* values of complex **2a** in toluene at 77 K.[2] From these preliminary results, it was not possible to establish the actual spin state of the iron of complexes **2** in solution. Moreover, no data were available concerning the spin state of complexes **2** in the solid state. This paper describes a detailed study of the EPR spectra of complex **2a**, either in solution or in the solid state at 300 and 4 K, and of the Mössbauer spectra and magnetic moment of complex **2a** in the solid state between 300 and 4 K. The data from these studies establish a "pure" intermediate $S = {}^3/_2$ spin state for complex **2a** in the solid state and are in favor of the same spin state for complex **2a** in solution.

Experimental Section

Synthesis of Complexes 2. A 1.1-equiv sample of $CuCl_2$ in 10 mL of dry CH_3CN is added progressively to a solution of complex **1**[1] (100 mg) in CH_2Cl_2 (200 mL) (0.11 equiv/30 min). After the last addition, the solution is stirred for 1 h and then washed with water. The organic layer is dried over $MgSO_4$ and filtered and its volume reduced to about 10 mL. Upon column chromatography on silica gel, unreacted complex **1** is first eluted with C_6H_6 and complex **2** with acetone/C_6H_6 30/70. Complex **2** is then dissolved in the minimum amount of hot acetone, and an equivalent volume of pentane is added. Black shiny crystals of complex **2** (40% yield) are obtained from this solution kept several days at −20 °C.

Elemental analyses were obtained after powdering and lyophilization of the samples. Anal. Calcd for $C_{58}H_{36}N_4FeCl_3$ (**2a**): C, 73.22; H, 3.78; N, 5.89; Cl, 11.20. Found: C, 73.10; H, 3.96; N, 5.83; Cl, 12.00. λ (ϵ) in C_6H_6: 424 (54) and 669 (7.8 n^{-1} cm^{-1}) nm. Calcd for

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(1) Mansuy, D.; Lange, M.; Chottard, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 3214.

(2) Mansuy, D.; Lange, M.; Chottard, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6437.

(3) (a) Dunford, H. B.; Stillman, J. S. *Coord. Chem. Rev.* **1976**, *19*, 187. (b) Yonetani, T. *Adv. Enzymol.* **1970**, *33*, 309. Yamasaki, I. In "Molecular Mechanisms of Oxygen Activation"; Hayaishi, O., Ed.; Academic Press: New York, 1974; p 33.

(4) (a) Chevrier, B.; Weiss, R.; Lange, M.; Mansuy, D.; Chottard, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2899. (b) During the submission of this paper a ^1H NMR study of complex **2a**, concluding to the same bridged structure, has appeared: Latos-Grazynski, L.; Cheng, Ru-Jen; La Mar, G. N.; Balch, A. L. *Ibid.* **1981**, *103*, 4270. The authors also mention preliminary data on an independent X-ray structure determination of complex **2b**.

(5) Abbreviations: TPP and TTP are respectively the dianions of *meso*-tetraphenylporphyrin and *meso*-tetra-*p*-tolylporphyrin.

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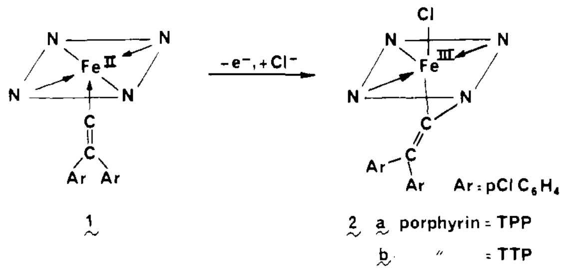

Figure 1.

$C_{62}H_{44}N_4FeCl_3$ (**2b**): C, 73.91; H, 4.37; N, 5.56; Cl, 10.58. Found: C, 73.59; H, 4.09; N, 5.61; Cl, 11.20. λ (ε) in C_6H_6: 424 (54) and 669 (7.8). ^{1}H NMR (10^{-2} M in $CDCl_3$, 24 °C, vs. Me_4Si): δ +26.2 (2 H), +20.5 (2 H), −23.7 (2 H), −40.0 (2 H) (pyrrole H)), +4.4 (6 H), and 2.9 (6 H (CH_3)), 9.9 (1 H), 8.0 (2 H), 7.8 (2 H), 7.7 (2 H), 6.0 (1 H, v br), 4.7 (1 H, v br), 2.3 (1 H), and 1.3 (6 H (aromatic H)).

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 mercury tetrakis(thiocyanato)cobaltate(II) and the manganese(II) Tutton salt were used as susceptibility standards. Agreements depending upon the calibration were estimated at better than 2% in the range of magnetic fields used at $T > 80$ K and less than 4% under 80 K. All magnetic data were corrected for diamagnetism taken as -860×10^{-6} cgsu from free porphyrin base measurements[6] and Pascal's rules.

EPR Spectra. EPR spectra were recorded with a Bruker ER-200 spectrometer, operating at the X-band frequency of 9.46 Hz and fitted with an helium continuous-flow Oxford Instruments cryostat. Variable-temperature studies were performed between 4 and 300 K. Polycrystalline samples and toluene glasses were mounted in standard 4-mm quartz EPR tubes and sealed under vacuum.

Mössbauer Spectra. The samples used for Mössbauer spectroscopy experiments were composed of a powder layer pressed between two plastic foils. The Mössbauer experiments were carried out with a constant-acceleration electromechanical drive system together with a multichannel analyzer for collecting and storing the data. ^{57}Co in rhodium was used at room temperature as a source. The velocity calibrations have been done with a thin iron metal absorber, and all the isomer shift data given in this paper refer to the symmetry center of the iron metal Mössbauer sextuplet at 300 K. Mössbauer parameters (δ, ΔEq, Γ_1, and Γ_2) were determined by adjustment of experimental data with a least-square refinement program.

Results and Discussion

Synthesis. The most convenient route to Fe(TPP)[C=C(p-$ClC_6H_4)_2$](Cl) (**2a**) is the careful oxidation of the vinylidene carbene complex Fe(TPP)[C=C(p-$ClC_6H_4)_2]^2$ (**1a**) by progressive addition of 1 equiv of $FeCl_3$ or $CuCl_2$ in CH_3CN. In these conditions, the reaction is rather slow with 95% conversion of complex **1a** into complex **2a** within 6 h. Addition of greater excess of the oxidizing agent leads to a faster reaction but also to the formation of a secondary product which is a N-alkylated porphyrin having lost the iron.[7] Separation of complex **2a** from nonreacted complex **1a** is easily made by column chromatography on silica gel. Samples used for the following studies were obtained by crystallization from an acetone–pentane solution of purified complex **2a**.

Magnetic Moment Measurements. The temperature dependence of the paramagnetic susceptibility and magnetic moment of complex **2a**, in the solid state, is shown in Figure 2. Its magnetic moment at room temperature is 3.9 μ_B, consistent with three unpaired electrons, the theoretical spin-only value for a $S = {}^3/_2$ state being 3.87 μ_B. No variation of the moment is observed between 40 and 300 K within experimental errors, the absence of curvature implying no thermal spin-state equilibrium and negligible orbital second-order contributions. The observed moment value and its constancy with temperature indicates a spin quartet nonorbitally degenerated state ($^4A_2$) strongly stabilized by ligand field effect. In fact, between 300 and 40 K, only the Zeeman effect could be considered, leading to an average g value of 2.03 (0.01).

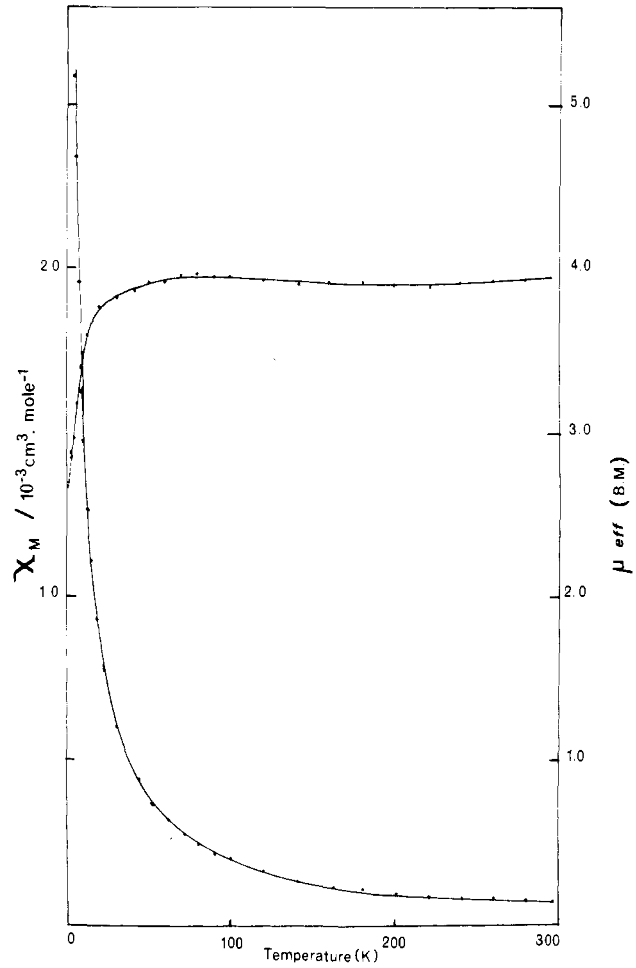

Figure 2. Temperature dependence of the magnetic susceptibility and magnetic moment of complex **2a** (between 300 and 4 K).

From 40 to 4 K, the magnetic moment decreases down to a value near 2.9 μ_B. A possible origin of this behavior is the existence of a significant zero-field splitting that leads to an unequal population of the Kramer's doublets originating from the $S = {}^3/_2$ state, this difference of population becoming perceptible from about 40 K. This is further substantiated by EPR data.

EPR Spectroscopy. The EPR spectrum of complex **2a** (powder) at 4 K (Figure 3) is remarkably well shaped, exhibiting a typical rhombic pattern with g values of 2.01, 3.55, and 4.64. The EPR spectrum at 300 K displays a broadening of the signal around $g = 2$ and a lesser resolution of that centered around $g = 4$. This result together with those from magnetic susceptibility measurement leads to a $S = {}^3/_2$ spin-state assignment for the ground state of complex **2a**. In the following, data are interpreted within the formalism of the appropriate spin Hamiltonian for this system

$$\mathcal{H} = \mu_B(S(g))H + D[S_{z^2} - {}^1/_3S(S+1)] + E(S_{x^2} - S_{y^2})$$

with D and E being the zero-field-splitting parameters.

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(6) Eaton, S. S.; Eaton, G. R. *Inorg. Chem.* **1980**, *19*, 1095.

(7) In this compound, two adjacent pyrrolic nitrogens are bridged by the C=C(p-$ClC_6H_4)_2$ group. Its visible spectrum[2] is very similar to that of the N,N-bridged compound *cis*-21,22-(ethoxycarbonylmethylene)-*meso*-tetraphenylporphyrin hydrochloride obtained upon oxidation of the complex chloro(ethoxycarbonylmethylene-*Co,N*)(*meso*-tetraphenylporphyrinato)cobalt(III).[19]

Table I. Magnetic and Structural Data of Intermediate (Pure or Admixed) Spin Ferric Complexes

	Mössbauer parameters					EPR			
complexes (samples in solid state)	T, K	δ, mm s^{-1}	ΔEq, mm s^{-1}	T, K	μ_{eff}, μ_B	T, K	g	Fe–N, Å	ref
Fe(TPP)[C=C(p-ClC$_6$H$_4$)$_2$](Cl) (**2a**)	300	0.225	2.87[b]	300	3.94	4	4.64, 3.55	1.990 (5)[a]	this paper
	77	0.306	2.87				2.03		
	4.2	0.315	2.85	80	3.95				
Fe[Ph$_2$[15]N$_4$SPh]	77	0.13	2.55	295	3.97				13
Fe[Ph$_2$[16]N$_4$SPh]	77	0.26	2.28	295	4.17				13
Fe[S$_2$CN(C$_2$H$_5$)$_2$](Br)	1.2		2.88	1.2	3.96				10a
				288	4.05		4.08, 2.01		10b
	275		2.55						10c
Fe(TPP)(ClO$_4$)	197	0.34	3.17	298	5.19	10	4.75, 2.03	2.001 (5)	
	77	0.34	3.48						
	4.2	0.38	3.50						14
Fe(OEP)(ClO$_4$)	295	0.29	3.16	275	4.78	78	~4, ~2		
	115	0.37	3.52	77	4.16			1.994 (10)	15
	4.2	0.37	3.57						
Fe(TPP)[C(CN)$_3$]	298	0.30	3.18	298	5.4	78	5.26, 2.0	1.995 (3)	16
	78	0.30	3.03	78	5.4				
Fe(OEP)(EtOH)$_2$·ClO$_4$	295	0.28	2.97	295	4.5				
	115	0.36	3.32						15a
	4.2	0.38	3.47						

[a] From X-ray determinations on complex **2b**.[4] [b] For complex **2a**, Γ_1 = 0.48 (4.2 K), 0.58 (77 K), 0.48 (300 K) and Γ_2 = 0.47 (4.2 K), 0.50 (77 K), and 0.42 (300 K). Γ_1 and Γ_2 are line widths at half-height for the lower and higher energy lines, respectively.

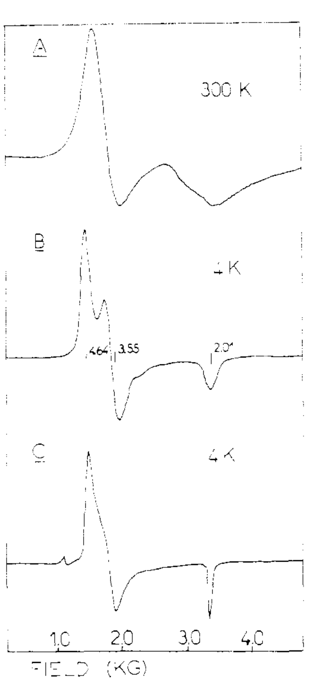

Figure 3. X-Band ESR spectra of complex **2a**: A, **2a** as a powder at 300 K; B, **2a** as a powder at 4 K; C, **2a** in toluene at 4 K.

In the case of a strong zero-field splitting ($D >> h\nu$), only the transitions within the lower energy Kramer's doublet $|\pm{}^1/_2\rangle$ from the $S = {}^3/_2$ state can be observed.[8,9] An effective spin $S' = {}^1/_2$ is then assigned to the ground state. According to perturbations calculations, for an axial symmetry and when $D >> g\beta$, theory predicts g' values for the $S' = {}^1/_2$ state related to g values of the $S = {}^3/_2$ state as $g'_{\parallel} = g_{\parallel} = 2$ and $g'_{\perp} = 2$, $g_{\perp} = 4$. Quite identical experimental g' values, $g'_{\parallel} = 2.01$ and $g'_{\perp} = 4.1$ (mean value, the two components at $g' = 3.55$ and 4.64 being considered as the split $g'_{\perp}$ signal because of rhombic symmetry), are deduced from the EPR spectrum of complex **2a**. The mean g value of 2.04 deduced from EPR data is in perfect agreement with the g value of 2.03 from magnetic susceptibility measurements. Consistency with magnetic data is also provided by the comparison of the value of 3.1 (0.1) μ_B for the magnetic moment deduced from ESR g values and that of 2.7 (0.2) μ_B obtained by extrapolation of the curve $\mu = f(T)$ when $T \rightarrow 0$. The slight discrepancy could be due to weak antiferromagnetic intermolecular interactions.

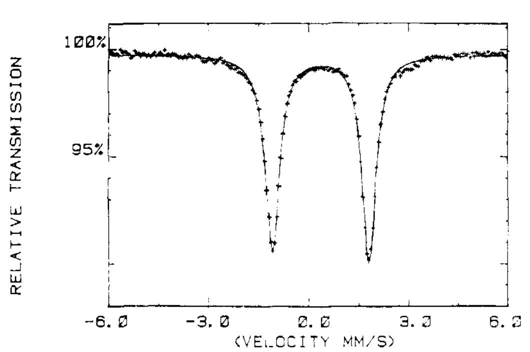

Figure 4. Mössbauer spectrum of complex **2a** at 4 K.

Mössbauer Spectra. The Mössbauer spectra obtained for complex **2a**, as a powder, in the absence of an applied magnetic field, are sharp quadrupole pairs at all temperatures between 300 and 1.8 K (Figure 4), showing that this complex is a magnetically pure single compound in the solid state. The obtained isomeric shifts and quadrupole splitting values are shown in Table I; they are remarkably constant between 300 and 1.8 K. The isomeric shift value ($\simeq$0.3 mm/s) is typical of a Fe(III) complex, and the large, temperature-independent, quadrupole splitting is strongly indicative of a $S = {}^3/_2$ state. Very similar quadrupole splittings have been observed for well-characterized intermediate spin *bis*(N,N-dialkyldithiocarbamato)iron(III) complexes (Table I).[10]

Solution Behavior. The visible spectra of crystals of complex **2a** and of their solution in toluene are compared in Figure 5.[12] These spectra are very similar and both exhibit the peculiar

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(8) Pilbrow, J. R. *J. Magn. Reson.* **1978**, *31*, 479.

(9) Maltempo, M. M. *Chem. Phys. Lett.* **1979**, *60*, 441.

(10) (a) Wickman, H. H.; Trozzolo, A. M. *Inorg. Chem.* **1968**, *7*, 63. (b) Martin, R. L.; White, A. H. *Ibid.* **1967**, *4*, 712. (c) Epstein, L. M.; Straub, D. K. *Ibid.* **1969**, *8*, 560.

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

(12) Complexes **2a** and **2b** should have very similar electronic and molecular structure since they only differ by the nature of the para substituent of the phenyl groups in the meso position of the porphyrin ring. Actually, they exhibit identical visible (in toluene and on the crystals) and EPR (toluene glass at 77 K) spectra and magnetic moments (μ = 3.7 ± 0.2 μ_B at 25 °C in C$_6$H$_6$) in solution.

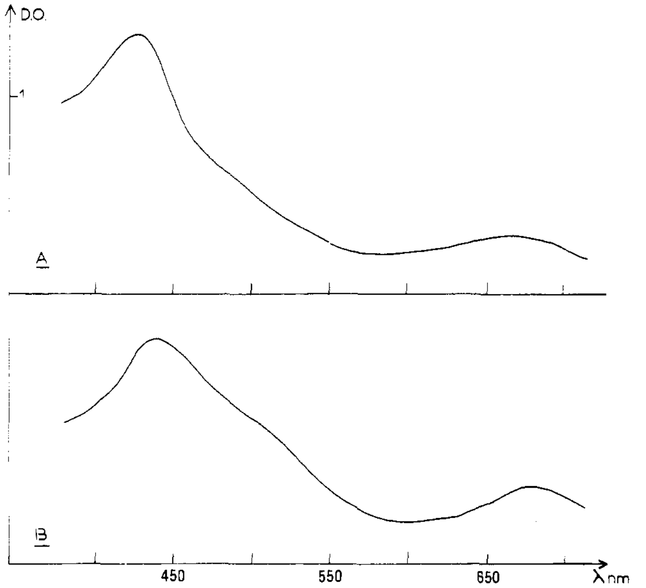

Figure 5. Electronic spectra of complex **2a** at 27 °C: A, 2.3×10^{-5} M **2a** in toluene; B, spectrum of the crystals crushed on a glass plate, recorded on an AMINCO DW 2 spectrophotometer.

characteristics (a weak Soret peak and a single band around 670 nm in the visible region) already mentioned[2] and attributed to an important distortion of the porphyrin ring. They only differ by a general redshift ($\simeq 10$ nm) of the peaks when going from the spectrum of the solution to that of the crystals. A similar phenomenon is observed when the visible spectra of the various following complexes in the crystalline state are compared with those in solution, Fe(TPP)(*i*-PrNO)(py),[20] Fe(TPP)$(py)_2$, Fe(TPP)(Cl), and $[Fe(TPP)]_2C$,[21] and is due to different environments of the porphyrin ring in both conditions. The very similar shape of the visible spectra of crystals of complex **2a** and of their solution indicates that the structure shown in Figure 1 is also involved in solution.

Moreover, the magnetic moment of a C_6H_6 solution of complex **2a**, $3.7 \pm 0.2\ \mu_B$ measured by the Evans' method[11] at room temperature, is very close to that of powdered samples ($\mu_{eff} = 3.9\ \mu_B$, Figure 2), if one takes into account the rather large error made on μ_{eff} measurement in solution. The EPR characteristics of complex **2a** in toluene glass at 4 K are also almost identical with those of the powder despite a lesser resolution (Figure 3). Taken altogether, these results point to a very similar electronic state of the iron of complexes **2**[12] in solution and in the solid state in a wide range of temperature.

In Table I, some magnetic and structural characteristics of complexes **2**[12] are compared to those of ferric porphyrin or chelate complexes previously reported in the literature to be in a pure or mixed $S = {}^3/_2, {}^5/_2$, intermediate-spin state. The magnetic moment (3.9 μ_B between 40 and 300 K), EPR *g* values ($g_\perp \simeq 4$ and $g_\parallel \simeq 2$), and large temperature-independent quadrupole splitting observed for complex **2a** are strong arguments in favor of an intermediate spin only ground state. These characteristics are very similar to those described for the bis(*N*,*N*-dialkyldithiocarbamato)iron(III) bromide complex that involves an orbitally nondegenerate spin quartet ground state[10a,b] and for the $Fe(Ph_2[15]N_4)(SPh)$ intermediate-spin complex.[13]

The iron porphyrin complexes mentioned in Table I exhibit different properties, namely, higher values of the magnetic moment (between 4.16 and 5.4) and a significant temperature dependence of the quadrupole splitting. For instance, the solid-state $g_\perp$ value of Fe(TPP)(ClO_4) and its magnetic moment, which are greatly in excess of the $S = {}^3/_2$ spin-only values, have been interpreted in terms of a quantum mechanically mixed $S = {}^3/_2, {}^5/_2$ state. Moreover, this complex is mainly in the high-spin state in solution.[14] Complex **2a** thus appears as the first iron(III) porphyrin complex in a pure intermediate-spin-only state both in the solid state and in solution.

The short Fe–N(pyrrolic) bond distance in complex **2b** (average value for the three Fe–N bond distances 1.990 Å) is similar to those observed for iron(III) porphyrins in an intermediate-spin state (admixed or pure) (see Table I). This seems consistent[14] with an unoccupied $3d_{x^2-y^2}$ orbital as in the case of low-spin ferric porphyrins exhibiting Fe–N distances around 1.990 (1) Å.[17] On the other hand, larger Fe–N bond distances (2.068 (8) Å) have been observed for high-spin ferric porphyrins.[17] It has also been noticed[14] that intermediate spin haloiron(III) chelates or porphyrins exhibit longer Fe–X bond distances than corresponding high-spin complexes. Accordingly, the Fe–Cl bond distance (2.290 (2) Å) of complex **2b** is significantly longer than that found in the high-spin Fe(TPP)(Cl) complex (2.192 (12) Å).[18]

The highly distorted geometry of complexes **2** with a reduced ligand field due to pyrrole alkylation and a large tetragonal distortion could be at the origin of their pure intermediate-spin state, presumably because of stabilization of the d_{xy} orbital.

The possible existence of such a peculiar coordination state of an iron porphyrin, due to the insertion of a group into a Fe–N bond and resulting in the occurrence of a pure intermediate-spin state in hemoproteins, is under study.

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Registry No. 2a, 79311-02-7.

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(13) Koch, S.; Holm, R. H.; Frankel, R. B. *J. Am. Chem. Soc.* **1975**, *97*, 6714.

(14) (a) Kastner, M. E.; Scheidt, W. R.; Mashiko, T.; Reed, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 666. (b) Reed, C. A.; Mashiko, T.; Bentley, S. P.; Kastner, M. E.; Scheidt, W. R.; Spartalian, K.; Lang, G. *Ibid.* **1979**, *101*, 2948.

(15) (a) Dolphin, D. H.; Sams, J. R.; Tsin, T. B. *Inorg. Chem.* **1977**, *16*, 711. (b) Masuda, H.; Taga, T.; Osaki, K.; Sugimoto, H.; Yoshida, Z. I.; Ogoshi, H. *Ibid.* **1980**, *19*, 950.

(16) Summerville, D. A.; Cohen, I. A.; Hatano, K.; Scheidt, W. R. *Inorg. Chem.* **1978**, *17*, 2906.

(17) Scheidt, W. R. *Acc. Chem. Res.* **1977**, *10*, 339.

(18) Hoard, J. L.; Cohen, G. H.; Glick, M. D. *J. Am. Chem. Soc.* **1967**, *89*, 1992.

(19) Johnson, A. W.; Ward, D. *J. Chem. Soc., Perkin Trans. 1* **1976**, 720.

(20) Mansuy, D.; Battioni, P.; Chottard, J. C.; Lange, M. *J. Am. Chem. Soc.* **1977**, *99*, 6441.

(21) Mansuy, D.; Lecomte, J. P.; Chottard, J. C.; Bartoli, J. F. *Inorg. Chem.* **1981**, *20*, 3119.