

^1H NMR and EPR studies of the electronic structure of low-spin iron(III) isocyanide mesotetraphenylchlorin complexes: a $(d_{xz}, d_{yz})^4(d_{xy})^1$ configuration from 293 to 4 K †

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Reaction of (tetraphenylchlorinato)iron(III) chloride with eight equivalents of *tert*-butyl isocyanide and 2,6-xylyl isocyanide in the presence of zinc amalgam afforded $\text{Fe}(\text{TPC})(\text{t-BuNC})_2$ **1** and $\text{Fe}(\text{TPC})(2,6\text{-xylylNC})_2$ **2**, respectively. The synthesis and characterization of the trifluoromethanesulfonato derivatives of (tetraphenylchlorinato)iron(III) **3**, bis(*tert*-butyl isocyanide)(tetraphenylchlorinato)iron(III) **4**, and bis(2,6-xylyl isocyanide)(tetraphenylchlorinato)iron(III) **5** are reported: $[\text{Fe}(\text{TPC})]\text{CF}_3\text{SO}_3$ **3**, $[\text{Fe}(\text{TPC})(\text{t-BuNC})_2]\text{CF}_3\text{SO}_3$ **4** and $[\text{Fe}(\text{TPC})(2,6\text{-xylylNC})_2]\text{CF}_3\text{SO}_3$ **5**. The ^1H NMR isotropic shifts at 20  C of the pyrrole protons of the two complexes **4** and **5**, varied from 5 ppm for **4** to 8 ppm for **5** rather than the expected -10 to -30 ppm, based on previously studied bis-ligated complexes of low-spin iron(III) chlorins. EPR spectra of $[\text{Fe}(\text{TPC})(\text{t-BuNC})_2]\text{CF}_3\text{SO}_3$ **4** in solution are axial, with $g_\perp = 2.15$ and $g_\parallel = 1.97$ at 4 K, $\Sigma g^2 = 14.7$. All physical properties are consistent with a low-spin iron(III) with an unusual ground-state configuration $(d_{xz}, d_{yz})^4(d_{xy})^1$.

Introduction

The study of the binding of small ligands to heme proteins has played an important role in our ability to understand protein–substrate interactions in general.^{1,2} Probably the most familiar examples of bioinorganic chemistry are the oxygen carriers such as hemoglobins. The simplicity of the ligands (O_2 , CO, NO, CN^- and CNR) and the wealth of structural data available for heme proteins have led to a better understanding of these systems. Thus an attractive objective in connection with structure–function relationships is to substitute oxygen by various exogenous ligands. Surprisingly though there are numerous examples of iron porphyrin complexes bearing isocyanide ligands,³ the use of isocyanides as structural and functional probes of reduced-ring hemes such as iron chlorins and iron isobacteriochlorins is still rare.⁴ In this article, the purpose is to compare the isocyanide complexation on iron chlorin and iron porphyrin, both metallomacrocycles being considered as models of active site of heme proteins.

Investigations of the structural and spectroscopic properties of model compounds such as iron(III) chlorins^{4–20} and isobacteriochlorins^{7,10,12,15,21–23} have been useful in understanding the active site of numerous heme enzymes such as heme d found in a terminal oxidase complex^{24–27} or a catalase, hydroxyperoxidase II,²⁸ all from *Escherichia coli*. In sulfmyoglobin, a nonfunctional form of myoglobin, the porphyrin macrocycle has been reduced to a chlorin by addition of a sulfur atom to a pyrrole ring.²⁹ Various hemoproteins such as myoglobins,^{30,31} horseradish peroxidase and cytochrome b_5 ³¹ have also been reconstituted with iron chlorin prosthetic groups. A chlorin is a hydroporphyrin with one reduced pyrrole double bond. There are currently not enough results available of the physical properties of iron chlorins to explain their biological properties and their electronic ground state is still problematic.³² In contrast, much more information is available with iron porphyrins.³³ Thus it has been accepted that most low-spin iron(III)

porphyrins have a $(d_{xy})^2(d_{xz}, d_{yz})^3$ ground state. However it should be underlined that an unusual $(d_{xz}, d_{yz})^4(d_{xy})^1$ situation was first reported with low-basicity 4-cyanopyridine complexation to ferriporphyrins.³⁴ The axial EPR spectra, with $g_\perp > g_\parallel$ are also indicative of a $(d_{xz}, d_{yz})^4(d_{xy})^1$ state. When two molecules of *tert*-butyl isocyanide are bound to iron(III) tetraphenylporphyrin, the ^1H NMR spectrum is indicative of a low spin complex which shows the chemical shifts of the pyrrole protons in the diamagnetic region.³⁵ Subsequently, it was recognized that the unusual ^1H NMR behavior results from the formation of a pure $(d_{xz}, d_{yz})^4(d_{xy})^1$ ground state.³⁶ With the TPP compound, the X-ray structure shows an extensively S_4 -ruffled porphyrin core which is related to electronic factors rather than steric factors. This electronic contribution may be due to the partial delocalization of the $(d_{xy})^1$ unpaired electron into the $3a_{2u}(\pi)$ orbital of the porphyrin ring, which is made possible by the twisting of the nitrogen p_z orbitals of the nitrogen out of the plane of the porphyrin ring, as suggested recently.^{36,37} More recently, several groups reported also low-spin iron(III) porphyrins with an unusual $(d_{xz}, d_{yz})^4(d_{xy})^1$ ground state due in part to *meso*-substitution.^{38–40}

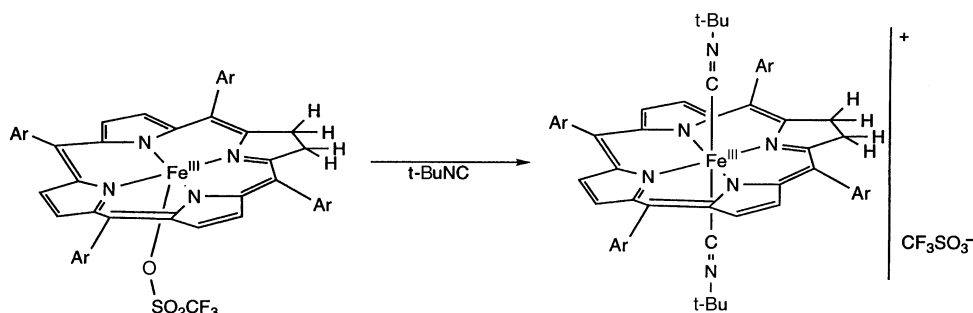
Despite their g -values, which according to the Proper Axis system of Taylor,⁶ have been classified as having $(d_{xz}, d_{yz})^4(d_{xy})^1$ ground states for many years,^{5,6} the chlorins studied thus far by ^1H NMR spectroscopy clearly have a $(d_{xz}, d_{yz})^3(d_{xy})^2$ ground state.³³ We have previously reported unusual low-spin iron(III) porphyrin bis-isocyanide complexes showing the $(d_{xz}, d_{yz})^4(d_{xy})^1$ ground state,³⁵ and now describe the preparation of new low-spin iron(III) chlorin bis-isocyanide complexes also showing the unusual $(d_{xz}, d_{yz})^4(d_{xy})^1$ electronic structure. This result contrasts sharply with the electronic structure of low-spin iron(III) tetramesitylchlorin bis-imidazole analogues¹⁸ which show, according to ^1H NMR spectroscopy, a probable $(d_{xz}, d_{yz})^3(d_{xy})^2$ ground state.

Results and discussion

Syntheses

The synthesis of symmetric bis-isocyanide complexes in the iron(II) state, $\text{Fe}(\text{TPC})(\text{CNR})_2$, was *via* a variation of our

† Abbreviations used: TPC = 7,8-dihydro-5,10,15,20-tetraphenylporphyrin dianion (tetraphenylchlorin), TMC = 7,8-dihydro-5,10,15,20-tetra(2,4,6-trimethylphenyl)porphyrin dianion (tetramesitylchlorin), TPP = 5,10,15,20-tetraphenylporphyrin dianion.



Scheme 1

method, previously reported for the synthesis of $\text{Fe}(\text{TPP})(\text{CNR})_2$.³⁵ Starting from $\text{Fe}(\text{TPC})\text{Cl}$,⁴¹ the reduction of $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$ was carried out with zinc amalgam under argon. The compounds were obtained as crystalline solids in 70–80% yield and characterized by ^1H NMR (see below). The stability of the reduced complexes was satisfactory at ambient temperature so that it was not necessary to add excess ligand in the solution to record NMR spectra. This result was expected since it was previously reported that the stability constants for ligand binding to metal complexes generally increase with increasing saturation of the macrocycle.^{42,43}

Two major difficulties may be encountered in preparing iron(III) isocyanide complexes of chlorins. First oxidation of the chlorin ring to a porphyrin ring may occur, as previously reported with imidazole ligands.¹⁷ Second, isocyanide is probably a weakly coordinating ligand for the iron(III) state due to the lower basicity of the ligand^{44,45} in comparison to imidazole and pyridine, thus making iron(III) complexation difficult. This situation was previously encountered, with iron(III) porphyrins.³⁵ Using perchlorate or triflate, a weak axial ligand, as an intermediate, allowed us to solve this problem. Thus, a similar strategy was employed to prepare low-spin iron(III) tetraphenylchlorins.

Starting from $\text{Fe}(\text{TPC})\text{Cl}$ ⁴¹ in tetrahydrofuran solution, $[\text{Fe}(\text{TPC})]\text{CF}_3\text{SO}_3$ **3** was readily obtained, after addition of AgCF_3SO_3 , in 78% yield. The $[\text{Fe}(\text{TPC})]\text{CF}_3\text{SO}_3$ complex exhibited a UV–VIS spectra with a Soret band at 402 nm ($\epsilon = 66 \text{ dm}^3 \text{ mmol}^{-1} \text{ cm}^{-1}$) and a characteristic chlorin second band at 649 nm ($\epsilon = 9 \text{ dm}^3 \text{ mmol}^{-1} \text{ cm}^{-1}$). Addition under argon of 4 equiv. of *tert*-butyl isocyanide to $[\text{Fe}(\text{TPC})]\text{CF}_3\text{SO}_3$ in dichloromethane afforded the hexacoordinated complex $[\text{Fe}(\text{TPC})(\text{t-BuNC})_2]\text{CF}_3\text{SO}_3$ **4** (Scheme 1). Precipitation of purple crystals occurred and the product was collected by filtration (81% yield). The $[\text{Fe}(\text{TPC})(\text{t-BuNC})_2]\text{CF}_3\text{SO}_3$ complex exhibited a UV–VIS spectrum with a Soret band at 414 nm ($\epsilon = 66 \text{ dm}^3 \text{ mmol}^{-1} \text{ cm}^{-1}$) and a characteristic chlorin band at 648 nm ($\epsilon = 9 \text{ dm}^3 \text{ mmol}^{-1} \text{ cm}^{-1}$). $[\text{Fe}(\text{TPC})(2,6\text{-xylylNC})_2]\text{CF}_3\text{SO}_3$ **5** was prepared by a similar method, using 2,6-xylylNC instead of *t*-BuNC.

IR spectroscopy

The IR spectra of the new complexes $[\text{Fe}(\text{TPC})(\text{CNR})_2]\text{CF}_3\text{SO}_3$ are different from that of $[\text{Fe}(\text{TPC})]\text{CF}_3\text{SO}_3$, exhibiting a major additional band at *ca.* 2180 cm^{-1} due to $\tilde{\nu}(\text{C}\equiv\text{N})$ in Nujol. The $\tilde{\nu}(\text{C}\equiv\text{N})$ stretching frequency of CNR is increased upon coordination of the isocyanide to the metal, increasing from 2130 cm^{-1} for the free ligand⁴⁶ to 2192 cm^{-1} in $[\text{Fe}(\text{TPC})(\text{t-BuNC})_2]\text{CF}_3\text{SO}_3$. This increase of the frequency indicates a higher bond order in the complex than in the free ligand which is attributed to the donor properties of isocyanides and to the concomitant decrease in the σ^* population of the CN bond. These results are consistent with the presence of a positive formal charge on the compound in the former case. By contrast, the isocyanide frequency decreases in the reduced complex $\text{Fe}(\text{II})(\text{TPC})(\text{t-BuNC})_2$ ($\tilde{\nu}(\text{C}\equiv\text{N})$ 2117 cm^{-1}). The data

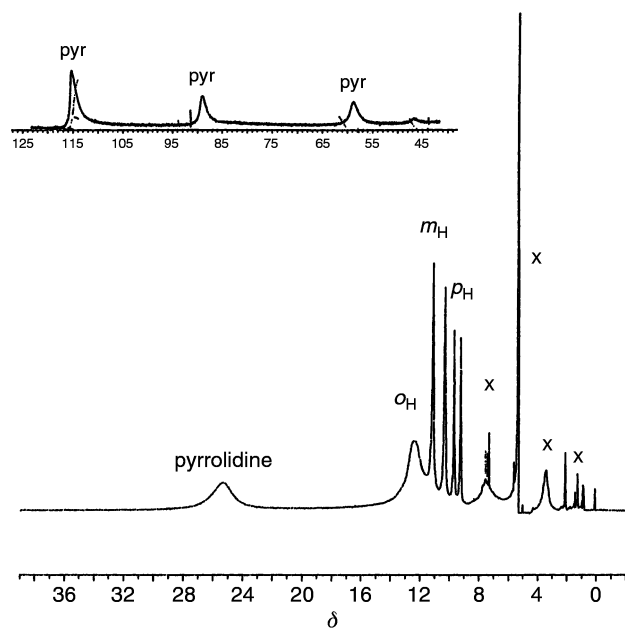


Fig. 1 Proton NMR spectrum of $[\text{Fe}(\text{TPC})]\text{CF}_3\text{SO}_3$ **3** in CD_2Cl_2 at 273 K. Assignment of the various resonances are indicated; X indicates the residual solvent and impurity peaks.

also suggest that the observed isocyanide stretching frequencies are influenced by the reduction of the porphyrin ring (*cis*-macrocycle influence). Thus, isocyanide ligands bonded to iron(II) chlorins ($\tilde{\nu}(\text{C}\equiv\text{N})$ 2117 cm^{-1}) have lower CN stretching frequencies than those in $\text{Fe}(\text{TPP})(\text{t-BuNC})_2$ ($\tilde{\nu}(\text{C}\equiv\text{N})$ 2129 cm^{-1}).⁴⁷ As expected, the more electron donating the macrocycle the lower the (CN) frequency due to an increase in the π^* population of the CN bond of the iron(II) complexes.

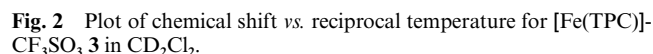
^1H NMR spectroscopy

The ^1H NMR spectrum of $\text{Fe}(\text{TPC})(\text{t-BuNC})_2$ **1** displays two groups of signals corresponding to the chlorin ring protons: (8.19, 8.18 and 7.85 (H_{pyr}); 7.80 (H_o); 7.56–7.6 (H_{m+p}); 4.02 ($\text{H}_{\text{pyrrolidine}}$) and to the ligand (-0.07 ppm). These chemical shifts are very similar to those found for $\text{Fe}(\text{TPC})(\text{PMe}_2\text{Ph})_2$ ²⁰ and are as expected for diamagnetic iron(II) chlorin derivatives. The protons of the ligand are shifted to high field (*vs.* free ligand) due to the ring current shift of the macrocycle. Similar results were obtained with complex **2**.

A representative ^1H NMR spectrum of $[\text{Fe}(\text{TPC})]\text{CF}_3\text{SO}_3$ **3** is shown in Fig. 1. The pyrrole (pyr) proton resonances for **3** at 114, 88 and 58 ppm (273 K) are within the range of 50–120 ppm found for the pyrrole resonances in other high-spin chlorin complexes.¹⁴ These values are much further downfield than the values of 40–10 ppm found for spin-admixed ($S = 3/2, 5/2$) complexes such as $[\text{Fe}(\text{TPP})]\text{CF}_3\text{SO}_3$ and $[\text{Fe}(\text{TPP})]\text{ClO}_4$.⁴⁸ A magnetically simple molecule is expected to follow Curie-law behavior in that a plot of the chemical shifts *vs.* $1/T$ is linear with an intercept equal to the resonance in the diamagnetic

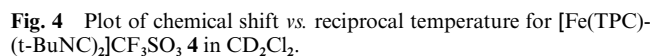
	Chlorin										
	H _o	H _{o'}	H _m	H _{m'}	H _p	H _{p'}	H _{pyrro}	H _{pyr}	H _{pyr}	H _{pyr}	t-Bu
($\Delta H/H$) ^a	1.3	-0.39	12.9	14.7	3.07	3.42	-36.0	5.11	7.15	7.92	-0.81
($\Delta H/H$) ^b	7.79	7.76	7.6	7.6	7.6	7.6	4.02	7.85	8.18	8.19	-0.07
($\Delta H/H$) _{iso} ^c	-6.6	-8.15	5.39	7.1	-4.5	-4.18	-40.0	-2.89	-0.85	-0.73	-0.74

^a Chemical shifts for [Fe(TPC)(t-BuNC)₂]CF₃SO₃ **4** at 298 K with TMS as internal references. ^b Chemical shifts for Fe(TPC)(t-BuNC)₂ **1** at 298 K with TMS as internal reference. ^c Isotropic shift of **4** relative to the diamagnetic complex Fe(TPC)(t-BuNC)₂ **1** as reference. A medium value of 8 ppm for the chemical shifts of the diamagnetic pyrroles was used since the relative assignment was not possible at this stage.



A representative ^1H NMR spectrum of $[\text{Fe}(\text{TPC})(\text{t-BuNC})_2]\cdot\text{CF}_3\text{SO}_3$ **4** is shown in Fig. 3 and ^1H NMR isotropic shifts are listed in Table 1. The peaks for the phenyl protons of the porphyrin ring are fully assigned by proton COSY experiments. For isocyanide axial ligands, measurements of the relative intensities and relative line-widths fully determine the assignment. The shift of the isocyanide ligand is unchanged in the presence of excess ligand. Hence axial ligand dissociation is not expected to be significant at ambient temperature.

Fig. 3 Proton NMR spectrum of [Fe(TPC)(t-BuNC)₂]CF₃SO₃ **4** in CD₂Cl₂ at 298 K. Assignment of the various resonances are indicated; X indicates the residual solvent and impurity peaks.



are found in a downfield position at 5.11, 7.15 and 7.92 ppm (293 K). This is in contrast with the pyrrole protons of [Fe(TMC)(MeIm)₂]ClO₄ (MeIm = *N*-methylimidazole) (−47.4, −12.3 and −2.4 ppm)¹⁷ and provides strong proof for a different electronic structure in these derivatives. Magnetic measurements *via* the Evans' method were made for CD₂Cl₂ solutions of [Fe(TPC)(*t*-BuNC)₂]CF₃SO₃ **4** employing TMS as the reference (293 K).⁵⁰ The solution magnetic moment ($\mu = 1.92 \mu_B$) is compatible with the low-spin state $S = 1/2$.

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Table 2 Observed proton shifts for [Fe(TPC)(2,6-xylylNC)₂]CF₃SO₃ **5** and Fe(TPC)(2,6-XylylNC)₂ **2** (δ , CD₂Cl₂, ppm) and relative differences

	Chlorin										2,6-Xylyl		
	H _o	H _{o'}	H _m	H _{m'}	H _p	H _{p'}	H _{pyrro}	H _{pyr}	H _{pyr}	H _{pyr}	Me	H _p	H _m
($\Delta H/H$) ^a	-0.42	-2.51	13.95	16.12	1.63	2.02	—	-3.29	-2.0	3.3	1.20	7.11	6.50
($\Delta H/H$) ^b	7.99	7.81	7.66	7.66	7.66	7.66	4.12	7.85	8.27	8.29	0.79	6.67	6.49
($\Delta H/H$) _{iso} ^c	-8.41	-10.32	6.29	8.46	-6.03	-5.64	—	-11.3	-10.0	-4.7	0.41	0.44	0.01

^a Chemical shifts for [Fe(TPC)(2,6-xylylNC)₂]CF₃SO₃ **5** at 298 K with TMS as internal references. H_{pyrrolidine} not detected. ^b Chemical shifts for Fe(TPC)(2,6-xylylNC)₂ **2** at 298 K with TMS as internal reference. ^c Isotropic shift of **2** relative to the diamagnetic complex Fe(TPC)(2,6-xylylNC)₂ as reference. We used a medium value of 8 ppm for the chemical shifts of the diamagnetic pyrroles since the relative assignment was not possible at this stage.

the pyrrole resonances based upon the Curie plot shown in Fig. 4 leads to isotropic shift sign reversal. This sign reversal of the pyrrole shift was previously observed as recently reported for low-spin iron(III) quinoxalinoporphyrin complexes.¹⁹

In order to better characterize the bis-isocyanide iron chlorin structure, a comparison of the present ¹H NMR results to data for the corresponding porphyrin complexes³⁵ has been made. The averaged chemical shifts of [Fe(TPC)(t-BuNC)₂]CF₃SO₃ are similar to those reported for [Fe(TPP)(t-BuNC)₂]ClO₄ (9.73 ppm).³⁵ Thus the small isotropic shift for the pyrrole protons ($\Delta\delta = -2$ ppm for **4**, $\Delta\delta = 1.3$ ppm for [Fe(TPP)(t-BuNC)₂]ClO₄³⁵) favors the interpretation that negligible spin density resides on the pyrrole carbons and so accounts for the observed chemical shifts in the diamagnetic region. As previously reported by Walker,³³ this pattern of isotropic shifts observed and the weak temperature dependence of the pyrrole protons are indicative of a (d_{xz},d_{yz})⁴(d_{xy})¹ ground state. It is interesting that the mechanism of spin transfer appears here to give rise to a result largely different from that observed for low-spin iron(III) bisimidazole complexes of synthetic chlorins.^{18,33} In this latter case for example, one of the pyrrole proton signals of [Fe(TMC)(Im)₂]ClO₄ (Im = imidazole) are found in a high field position (see above) due probably to a large contact contribution in this position. The chemical shift observed for the *tert*-butyl isocyanide axial ligands ($\delta_{\text{CH}_3} = -0.81$ ppm) is close to those expected for groups located in the shielding area of the porphyrin ring ($\delta_{\text{CH}_3} = -0.07$ ppm). A similar situation is observed with xylyl isocyanide ligands. In this case, the isotropic shifts of the ligated isocyanide are very close to zero (see Table 2). Thus, there appears to be essentially no spin density on the axial ligands, as expected because of the orthogonality of the isocyanide p _{π} orbitals and the metal d_{xy} orbital. In contrast, the description of the electronic structure should account for a large spin density at the pyrrolidine position and a large spin density at the *meso* position. As previously suggested, this situation may indicate that there is a significant spin delocalization to the a_{2u}(π) orbital, which is possible only if the porphyrin ring is ruffled causing twisting of the nitrogen p_z orbitals from the normal of the porphyrin ring.³⁷

EPR spectroscopy

It has been recognized that the EPR *g* values of low-spin ferriporphyrins provide valuable information about the orbital of the unpaired electron.⁵¹ EPR properties of [Fe(TPC)(Im)₂]⁺ and other low-spin complexes formed from iron(III) tetraphenylchlorin derivatives have been reported.^{5,6,52} Although the apparent extent of rhombicity is smaller for hydroporphyrin than for porphyrin complexes with the same set of axial ligands, all of the hydroporphyrin complexes evidence rhombic spectra. In contrast, the EPR spectrum of [Fe(TPC)(t-BuNC)₂]CF₃SO₃ **4** is axial in frozen solution with *g*_⊥ = 2.15 and *g*_∥ = 1.97 at 4 K (Fig. 5). The relative energies of the three t_{2g} d orbitals can be calculated from the *g* values in solution, using a general theory elaborated by Taylor.⁶ Thus Δ/λ is negative (−12.4) also indicating that the ground state is largely (d_{xy})¹. On the basis of the

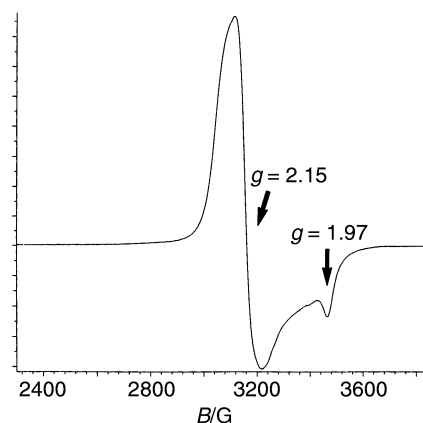


Fig. 5 EPR spectrum of [Fe(TPC)(t-BuNC)₂]CF₃SO₃ **4** as a CH₂Cl₂ glass, recorded at 4 K.

NMR data discussed above, we have found that the ground states of the two complexes [Fe(TPC)(t-BuNC)₂]CF₃SO₃ **4** (*g*_⊥ = 2.15 and *g*_∥ = 1.97) and [Fe(TPP)(t-BuNC)₂]ClO₄ (*g*_⊥ = 2.21 and *g*_∥ = 1.93)³⁶ are of the (d_{xy})¹ type. This is supported by the fact that the EPR spectra of their CH₂Cl₂ solutions are quite similar.

Conclusion

In conclusion, these spectroscopic observations are indicative of a metal-based electron in the d_{xy} orbital for the [Fe(TPC)(t-BuNC)₂]CF₃SO₃ **4** at all temperatures. Thus the change in ground state of low-spin Fe(III) from the usual (d_{xy})²(d_{xz},d_{yz})³ to the unusual (d_{xz},d_{yz})⁴(d_{xy})¹ electron configuration occurs both with porphyrin and chlorin macrocycles and seems largely related to the π -acceptor properties of the isocyanide ligand. The bis-cyano iron(III) quinoxalinoporphyrin complex which formally has a chlorin-like structure also show this unusual ground state.¹⁹ In contrast, it should be underlined that the coordination of t-BuNC to iron(III) isobacteriochlorin chloride induces a reversible electronic rearrangement resulting in the reduction of iron(III) to iron(II) with the formation of a π -radical due to the presence of both the tetrahydroporphyrin macrocycle and the chloride ligand.⁴

Experimental

General information

As a precaution against the formation of the μ -oxo dimer [Fe(TPC)]₂O,^{13,53} all reactions were carried out in dried solvents in Schlenk tubes under an Ar atmosphere. Solvents were distilled from appropriate drying agents and stored under argon. ¹H NMR spectra were recorded on a Bruker AC 300P spectrometer in CD₂Cl₂ or CDCl₃ at 300 MHz. Tetramethylsilane was used as internal reference. The temperatures are given within 1 K. EPR spectra were recorded in CH₂Cl₂ on a Bruker EMX 8/2,7 spectrometer operating at X-band

frequencies. Samples were cooled to 4.2 K in a stream of helium gas in frozen CH_2Cl_2 , the temperature of which was controlled by an Oxford Instruments ESR 900 cryostat. Visible spectra were measured on a Uvikon 941 spectrometer in CH_2Cl_2 .

Reagents

The free-base hydroporphyrins were prepared as previously reported.^{54,55} The iron chlorin $\text{Fe}(\text{TPC})\text{Cl}$ was prepared by a literature method.⁴¹ *tert*-Butyl isocyanide and 2,6-xylyl isocyanide are commercially available from Aldrich.

Syntheses

$\text{Fe}(\text{TPC})(t\text{-BuNC})_2$ 1. A solution of $\text{Fe}(\text{TPC})\text{Cl}$ (0.1 g, 0.14 mmol) in 15 ml of dichloromethane was reduced under argon by Zn–Hg amalgam at room temperature. After a reaction time of 60 min, the solution was then filtered and 8 equiv. of *tert*-butyl isocyanide added by a syringe to the $\text{Fe}(\text{TPC})$ species. The solution was then stirred for 12 hours. Hexane (30 cm^3) was then added gradually and the solution set aside for crystallization. Fine crystals were collected by filtration after 3 days. Yield 0.1 g (85%). UV–VIS (CHCl_3): $\lambda_{\text{max}}/\text{nm}$ 427 (ϵ 110 $\text{dm}^3 \text{mmol}^{-1} \text{cm}^{-1}$), 608 (ϵ 17).

^1H NMR (δ , CD_2Cl_2 , ppm) 8.19 (2H, s, H_{pyr}); 8.18 (2H, d, H_{pyr}); 7.85 (2H, d, H_{pyr}); 7.79, 7.76 (8H, m, H_o); 7.6 (12H, d, H_{m+p}); 4.02 (4H, s, $\text{H}_{\text{pyrrolidine}}$); -0.07 (18H, s, H ligand). FAB MS (m/z): $[\text{M} - 2 t\text{-BuNC}]^+ 670$. IR $\tilde{\nu}(\text{CN})$ 2117 cm^{-1} (Nujol).

$\text{Fe}(\text{TPC})(2,6\text{-xylylNC})_2$ 2. A solution of $\text{Fe}(\text{TPC})\text{Cl}$ (0.1 g, 0.14 mmol) in 15 cm^3 of dichloromethane was reduced under argon by Zn–Hg amalgam at room temperature. After a reaction time of 60 min, the solution was then filtered and 8 equiv. of xylyl isocyanide added by syringe to the $\text{Fe}(\text{TPC})$ species. The solution was then stirred for 12 hours. Hexane (30 cm^3) was then added gradually and the solution set aside for crystallization. Fine crystals were collected by filtration after 3 days. Yield 0.09 g (69%). UV–VIS (CHCl_3): $\lambda_{\text{max}}/\text{nm}$ 427 (ϵ 80 $\text{dm}^3 \text{mmol}^{-1} \text{cm}^{-1}$), 610 (ϵ 11).

^1H NMR (δ , CD_2Cl_2 , ppm) 8.29 (2H, s, H_{pyr}); 8.27 (2H, d, H_{pyr}); 7.85 (2H, d, H_{pyr}); 7.99; 7.81 (8H, m, H_o); 7.66 (12H, d, H_{m+p}); 6.67 (2H, t, H_p ligand); 6.49 (4H, d, H_m ligand); 4.12 (4H, s, $\text{H}_{\text{pyrrolidine}}$); 0.79 (12H, s, CH_3 ligand). FAB MS (m/z): $[\text{M} - 2(2,6\text{-xylylNC})]^+ 670$. IR $\tilde{\nu}(\text{CN})$ 2111 cm^{-1} (Nujol).

$[\text{Fe}(\text{TPC})]\text{CF}_3\text{SO}_3$ 3. A solution of $\text{Fe}(\text{TPC})\text{Cl}$ (0.3 g, 0.42 mmol) and AgCF_3SO_3 in 20 ml of tetrahydrofuran was stirred under argon at 60 °C. After a reaction time of 15 min, the solution was then filtered. Hexane (40 cm^3) was added gradually and the solution set aside for crystallization. Fine crystals were collected by filtration after one night. Yield 0.27 g (78%). UV–VIS (toluene): $\lambda_{\text{max}}/\text{nm}$ 402 (ϵ 66 $\text{dm}^3 \text{mmol}^{-1} \text{cm}^{-1}$), 606 (ϵ 13), 649 (ϵ 9); (δ , CDCl_3 , ppm, 273 K): 114 (2H, br, H_{pyr}), 88 (2H, br, H_{pyr}), 58 (2H, br, H_{pyr}), 25.5 (4H, br, $\text{H}_{\text{pyrrolidine}}$), 12.35 (8H, br, H_o); 11 (4H, br, H_m) and 10.3 (4H, br, H_m); 9.6 (2H, br, H_p); 9.2 (2H, br, H_p). EPR: $g = 5.87$ and 1.99.

$[\text{Fe}(\text{TPC})(t\text{-BuNC})_2]\text{CF}_3\text{SO}_3$ 4. To a solution of 100 mg (122 μmol) of $[\text{Fe}(\text{TPC})]\text{CF}_3\text{SO}_3$ 3 in 4 ml of dichloromethane was added 2.5 equiv. of *tert*-butyl isocyanide by syringe under stirring at room temperature. After 15 min, the solution became dark green. Then 8 ml of hexane was added and the solution was set aside for two days at 0 °C for crystallization. Purple crystals of 4 were collected by filtration and washed with hexane. The yield was 98 mg (81%). UV–VIS (toluene): $\lambda_{\text{max}}/\text{nm}$ 414 (ϵ 66 $\text{dm}^3 \text{mmol}^{-1} \text{cm}^{-1}$), 599 (ϵ 10.7), 648 (ϵ 9). FAB MS (m/z): 819 $[\text{M} - 2 t\text{-BuNC}]^+$, 670 $[\text{M} - 2 t\text{-BuNC} - \text{CF}_3\text{SO}_3]^+$. IR $\tilde{\nu}(\text{C}\equiv\text{N})$ 2192 cm^{-1} (Nujol).

$[\text{Fe}(\text{TPC})(2,6\text{-xylylNC})_2]\text{CF}_3\text{SO}_3$ 5. To a solution of 100 mg (122 μmol) of $[\text{Fe}(\text{TPC})]\text{CF}_3\text{SO}_3$ 3 in 4 ml of dichloromethane

was added 2.5 equiv. of 2,6-xylyl isocyanide under stirring at room temperature. After 15 min, the solution became dark green. Then 8 ml of hexane was added and the solution was set aside two days for crystallization at 0 °C. Purple crystals of 5 were collected by filtration and washed with hexane. The yield was 89 mg (67%). UV–VIS (toluene): $\lambda_{\text{max}}/\text{nm}$ 414 (ϵ 76 $\text{dm}^3 \text{mmol}^{-1} \text{cm}^{-1}$), 606 (ϵ 11.2), 654 (ϵ 11.6). FAB MS (m/z): 670, $[\text{M} - 2 (2,6\text{-xylylNC}) - \text{CF}_3\text{SO}_3]^+$. IR $\tilde{\nu}(\text{C}\equiv\text{N})$ 2162 cm^{-1} (Nujol).

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