^{1}H-NMR and EPR studies of the electronic structure of low-spin ruthenium(III) isocyanide porphyrin complexes: unusual $(d_{xz}, d_{yz})^4$ $(d_{xy})^1$ configuration

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Abstract

The synthesis and characterization of the perchlorato derivatives of bis(isocyanide)tetrakis(phenyl)porphynatoruthenium(III) [Ru(TPP)(RNC)$_2$]ClO$_4$ (**1**, R = ^{t}Bu; **2**, R = 2,6-xylyl) are reported. The ^{1}H-NMR isotropic shifts at 298 K of the pyrrole protons of the two complexes, varied from -5.44 ppm for **1** to $+2.55$ ppm for **2** rather than the expected -31 ppm, based on previously studied aryl complexes of low-spin ruthenium porphyrins. The EPR spectrum of **2** in solution is axial, with $g_\perp = 2.07$ and $g_{II} = 1.99$ at 4 K, $\Sigma g^2 = 12.53$. These spectroscopic observations are indicative of a metal-based electron for complex with a $(d_{xz}, d_{yz})^4 (d_{xy})^1$ ground state at any temperature. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ruthenium porphyrins; Isocyanides complexes; Paramagnetic complexes; Nuclear magnetic resonance

1. Introduction

Many heme proteins which have an accessible sixth coordination position bind molecular oxygen to its heme iron but exhibit a variety of different functions such as hemoglobins and P-450 cytochromes [1]. Thus an attractive attempt regarding the structure-function relationship is to substitute oxygen by various exogen ligands [2]. Several small nonphysiological ligands have been examined by various spectroscopic methods in hope of gaining information about structural and reactivity perturbations of the heme environment. Examples include mainly carbon monoxide [3] and to a less extent isocyanides [4]. These axial-ligand probes have been discussed in terms of both model studies and utility for heme protein studies. Since interest in ruthenium porphyrin chemistry is inspired by the Periodic Table relationship of ruthenium to iron [5], we report here the synthesis and the characterization of isocyanide complexes of ruthenium(III) porphyrins as part of a programme concerned with systematic examination of new probes of heme proteins [6].

Low-spin Fe(III) porphyrins are of major interest because of the relevance of this spin state to a large number of hemoproteins. It has been accepted that most of the low-spin Fe(III) hemes have a $(d_{xy})^2 (d_{xz}, d_{yz})^3$ ground state [7]. However, it was reported that when two molecules of *tert*-butylisocyanide are bound to ferric tetraphenylporphyrin, the ^{1}H-NMR spectrum is indicative of a low spin complex with an unusual pyrrole resonance in the diamagnetic area [8]. The hyperfine shifts have been separated into their dipolar and contact contributions. The separated components reflect the very low magnetic anisotropy of the iron, and the unusual orientation of the unpaired spin density when the nitrogen axial ligands are exchanged for isocyanide ligands leads to complete reverse localization. It should be underlined that a similar situation was very recently reported with low-basicity cyanopyridine complexation to ferriporphyrins [9,10]. The change in ground state of low-spin Fe(III) from $(d_{xy})^2 (d_{xz}, d_{yz})^3$ to $(d_{xz}, d_{yz})^4 (d_{xy})^1$ electron configuration

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occurs softly through the series of pyridine complexes of both TPPFe(III) and TMPFe(III) complexes [9,10], the low-basicity pyridines stabilizing the unusual $(d_{xz}, d_{yz})^4 (d_{xy})^1$ state. Finally, it has been confirmed from X-ray studies that complexation of isocyanides to ferriporphyrins leads to a compound with a pure $(d_{xz}, d_{yz})^4 (d_{xy})^1$ ground state [6,11]. The axial EPR spectra, with $g_\perp > g_{II}$ are also indicative of a $(d_{xz}, d_{yz})^4 (d_{xy})^1$ state. In these systems, 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 by Walker et al. [11].

Here we report the preparation of a new low-spin ruthenium porphyrin bis-isocyanide compound showing also such unusual electronic structure. It is different from the electronic structure of low-spin ruthenium porphyrin alkyl and aryl analogues [12]. Although there are many EPR informations available on low-spin ferric porphyrins, very little has been reported for the low-spin ruthenium(III) porphyrins [13] due to the difficulty to prepare ruthenium porphyrins in this oxidation state [14–18]. It should be underlined however that the ordering of the energy levels is also changed in the carbonyl and chloro complexes of ruthenium(III) Schiff bases [19].

2. Results and discussion

2.1. Synthesis

Two major difficulties may be encountered in preparing ruthenium(III) complexes of porphyrins. First, the rapid disproportionation of the Ru(III) complex to Ru(IV) and Ru(II) complexes may occur, as it was reported previously with amine and porphyrin ligands [20,21]. Second, oxidation of carbonyl ruthenium(II)
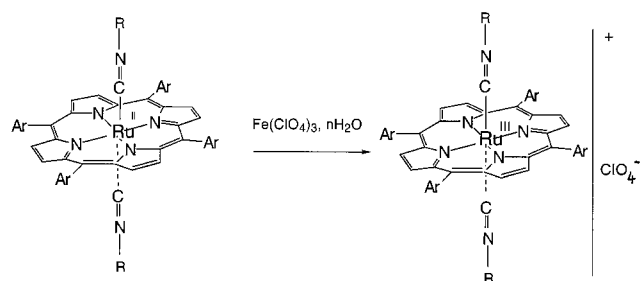
porphyrins occurs at the ring to give a π-cation radical species [22–24]. Both situations were previously reported by Collman [25], James and Dolphin [26] with the synthesis of Ru alkyl and aryl complexes providing a new class of ruthenium(III) porphyrins. The use of ferric perchlorate as oxidant and a π-acceptor axial ligand, such as an isocyanide, allowed us to prepare new low-spin ruthenium(III) porphyrins.

The bis(isocyanide) ruthenium(II) porphyrins were first synthetized by stirring Ru(TPP)(CO) [27] in dichloromethane or chloroform in the presence of an excess of *tert*-butyl isocyanide or 2,6-xylyl isocyanide as described previously [28–30]. They were all characterized by ^{1}H-NMR, IR, UV–vis and mass spectrometry. Subsequent addition under argon of an excess of ferric perchlorate (large excess) to Ru(TPP)(^{t}BuNC)$_2$ in dichloromethane affords the hexacoordinated compound [Ru(TPP)(^{t}BuNC)$_2$]ClO$_4$ (**1**) (Scheme 1). Thus, the color of the solution readily changes from purple to dark brown, and after 1 h, precipitation of a purple powder occurred and the product was collected by filtration (80% yield). For the preparation of the other ruthenium derivatives with the 2,6-xylyl isocyanide ligand, [Ru(TPP)(2,6-xylylNC)$_2$]ClO$_4$ (**2**), the same procedure can be used with the corresponding rurhenium(II) analogues in dichloromethane solvent.

2.2. IR and UV-vis spectroscopy

The [Ru(TPP)(^{t}BuNC)$_2$]ClO$_4$ compound exhibited an electronic spectrum with a Soret band at 398 nm ($\varepsilon = 90$ dm^3 mmol^{-1} cm^{-1}). To get further insight into the reaction, the evolution of the UV–vis spectra of Ru(TPP)(^{t}BuNC)$_2$ ($\lambda_{max} = 417$ nm) was studied during oxidation (Fig. 1). The titration curve reveals an isobestic point ($\lambda = 407$ nm) with less intense absorption, similar to those of carbonyl ruthenium(II) porphyrin π-cation radicals, with a blue-shifted Soret band and a broad absorption in the 500–700 region [22–24].

The IR spectra of the new complexes [Ru(TPP)-(CNR)$_2$]ClO$_4$ are different to those of Ru(TPP)(CO) [27] since they all exhibit a major additional band at ~ 2170 cm^{-1}, $\bar{v}$(C≡N) in KBr, and the disparition of the CO band. The $\bar{v}$(C≡N) stretching frequency of CNR is increased upon coordination of the isocyanide to the metal, increasing from 2130 cm^{-1} for the free ligand to 2170 cm^{-1} in [Ru(TPP)(^{t}BuNC)$_2$]ClO$_4$. Isocyanide ligands are both good σ donnor and good π acceptor ligands [31,32]. In the case of a formal positive charge, this increase of the frequency indicates a higher bond order in the complex than in the free ligand which is attributed to the good donor properties of isocyanides and to the concomitant decrease in the σ* population of the CN bond. In contrast, the isocyanide frequency decreases in the reduced complex such as Ru(II)(TPP)(^{t}BuNC)$_2$ ($\bar{v}$(C≡N) = 2116 cm^{-1}).
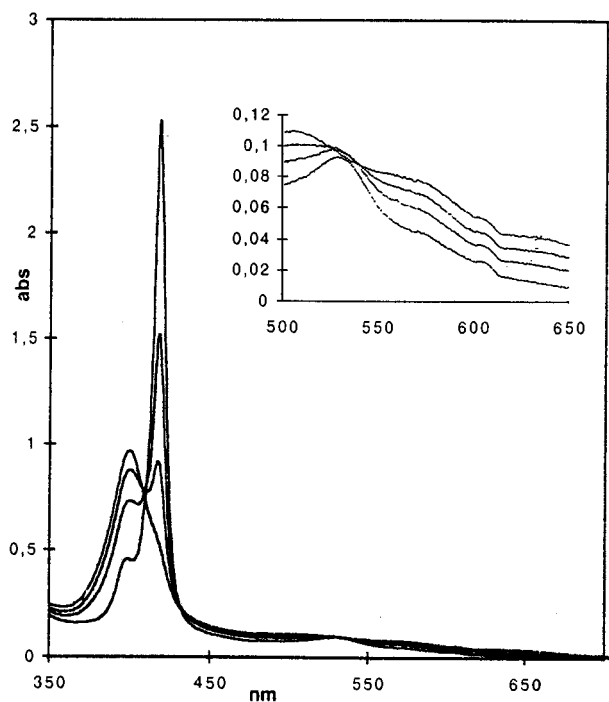

R = 2,6-xylyl, R = t-Bu

Scheme 1.

Fig. 1. Oxidation of Ru(TPP)(^{t}BuNC)$_2$ (0.8 mM) with an excess of Fe(ClO$_4$)$_3$ in dichloromethane.

Table 1
Electrochemical data (V vs. SCE) for ruthenium porphyrin complexes

Complex	$E^{1/2}$ (1)	$E^{1/2}$ (2)
Ru(TPP)(CO) [a]	0.82	1.21
Ru(TPP)(py)$_2$ [a]	0.21	1.26
Ru(T(o,o'-OMe)PP)(^{t}BuNC)$_2$	0.28	0.92
Ru(TPP)(^{t}BuNC)$_2$	0.58	1.37
Ru(TPP)(2,6-xylylNC)$_2$	0.58	1.31 [b]
Ru(TTP)(2,6-xylylNC)$_2$	0.51	1.20 [b]

[a] Ref. [22].
[b] Non reversible system.

2.3. Electrochemical studies

As indicated by cyclic voltammograms in dichloromethane, the first reversible oxidation potential of the low-spin complexes ($E^{1/2} = 0.51$ V for **1** and 0.58 V for **2** vs. SCE) is between the potentials observed with σ-donor ligands ($E^{1/2} = 0.21$ V for Ru(TPP)(py)$_2$) and strong π-acceptor ligand ($E^{1/2} = 0.82$ V for Ru(TPP)(CO)) [22]. In the latter case, the electron location is on the macrocycle ring (porphyrin π-cation radical), while in the former the unpaired electron is metal-based. It can be seen from Table 1 that the complexes also exhibit a second oxidation potential which is reversible for **1** at 1.37 V versus SCE. These second oxidation couples can be tentatively assigned to a Ru(III)–cation radical complex due to an oxidation of the porphyrin ring as it was previously suggested by

Che and coworkers [30]. The one-electron oxidation of the ruthenium(II) tetraphenylporphyrin complexes containing the axial thiocarbonyl ligand led also to the formation of the porphyrin π-cation radical [15]. Since the nature of the axial ligand in ruthenium porphyrin systems can regulate electron transfer between metal and porphyrin [33] and isocyanide ligands are both good σ donnor and good π-acceptor ligands [4], the complexes were investigated by ^{1}H-NMR and EPR spectroscopies to discriminate between a porphyrin radical and a Ru(III) species.

2.4. NMR spectroscopy

The signals in the paramagnetic ^{1}H-NMR spectra of Ru(P)(CNR)$_2$ClO$_4$ complexes are sharp and shifted considerably from their diamagnetic positions. The ^{1}H-NMR spectrum of [Ru(TPP)(^{t}BuNC)$_2$]ClO$_4$ is shown in Fig. 2 (293 K) and the isotropic shifts are listed in Table 2 (293 K). The isotropic shifts of [Ru(TPP)(2,6-xylylNC)$_2$]ClO$_4$ are listed in Table 3 (293 K). The peaks for the phenyl protons of the porphyrin ring are assigned completely by methyl substitution and in combination with proton decoupled experiments. For isocyanide axial ligands, measurements of the relative intensities completely determine the assignment. The shift of the isocyanide ligand is totally independent of the presence of excess ligand. Hence axial ligand dissociation is not expected to become significant at ambiant temperature. ^{1}H-NMR magnetic measurements [34,35] were made for 0.03M CD$_2$Cl$_2$ solutions of [Ru(TPP)(CNR)$_2$]ClO$_4$ employing Me$_4$Si as the reference (293 K). The solution magnetic moment ($\mu = 1.90\mu_B$) is compatible with a low-spin state $S = 1/2$. However, the spectrum of [Ru(TPP)(CNR)$_2$]ClO$_4$ shows unexpected behavior for a Ru(III) species in that the pyrrole proton signal is found in a downfield position at 2.55 ppm (R = 2,6-Me$_2$Ph) and -5.44 ppm (R = ^{t}Bu) (293 K). It contrasts with the pyrrole proton of that of Ru(III)(TPP)Phe ($\delta = -30.9$ ppm) [12] and provides an essential proof for a different electronic structure in these derivatives. The chemical shifts of [Ru(TPP)(2,6-xylylNC)$_2$]ClO$_4$ are similar to those reported for Br$_2$ oxidation of Ru(TPP)(CO) (pyrrole: $\delta = 3.35$ ppm) [36]. Thus the description of the electronic structure should account for a large spin density at the meso position. Two alternative electronic structures can be considered: a $(d_{xz}, d_{yz})^4 (d_{xy})^1$ Ru(III) species and a porphyrin a_{2u} radical Ru(II). However, the sharpness of the ^{1}H-NMR signals is inconsistent with a porphyrin radical.

Also analysis of the curve in the Curie plot was made for the [Ru(TTP)(2,6-xylylNC)$_2$]ClO$_4$ compound (Fig. 3). The isotropic shifts vary linearly with $1/T$, but the extrapoled lines do not pass through the origin at $1/T = 0$ and the pyrrole protons show an anti-Curie
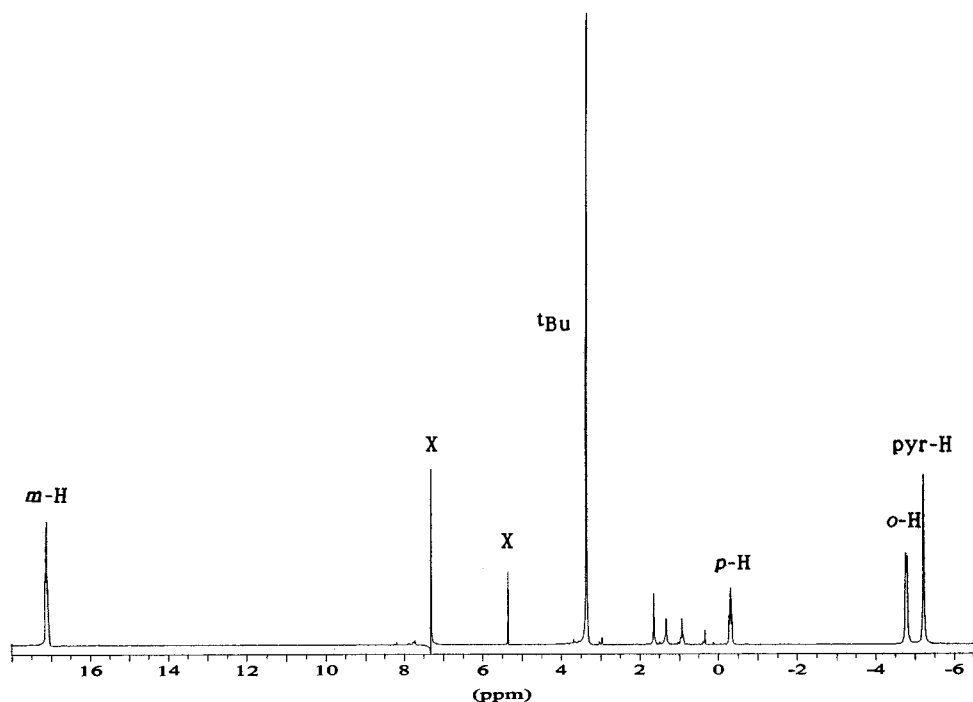
Fig. 2. Proton NMR spectrum of [Ru(TPP)(^{t}BuNC)$_2$]ClO$_4$ in CDCl$_3$ at 293 K. Assignment of the various resonances are indicated; x marks the residual solvent and impurity peaks.

behavior. As reported previously [7], the pattern of isotropic shifts observed and the anti-Curie behavior of the pyrrole protons are indicative of a $(d_{xz}, d_{yz})^4 (d_{xy})^1$ ground state. The chemical shifts observed for the axial ligands (2,6-xylylNC: 8.0 (4H, d, H$_m$); 6.4 (2H, t, H$_p$); 3.5 (s, 12H, CH$_3$) (Table 3) are close to those expected for groups located in the diamagnetic region. Thus there is essentially no spin density on the axial ligands, as expected because the orthogonality of the isocyanide p$_\pi$ orbitals and the metal d$_{xy}$ orbital that contains the unpaired electron.

Analysis of the chemical shifts were made according to the method of La Mar et al. [37]. In this method, the plot $(\Delta H/H)_{iso}$ versus $(3\cos^2\theta - 1)/r^3$ for proton *meso*-aryl positions (and methyl substituents) permits a quantitative separation of the dipolar and contact contribution. The results are summarized in Tables 2 and 3. It is clearly observed that there is a large contact contribution to the *meso*-phenyl-H resonance. This contribution is about 30% higher in [Ru(TPP)(2,6-xylylNC)$_2$]ClO$_4$ than in [Ru(TPP)(^{t}BuNC)$_2$]ClO$_4$. This is in contrast with previous work on low-spin ruthenium(III) derivatives as Ru(TPP)Phe complex for example [12]. As previously reported for ferric porphyrin complexes, this pattern of observed isotropic shifts and the anti-Curie behavior of the pyrrole protons are indicative of a $(d_{xz}, d_{yz})^4 (d_{xy})^1$ ground state. This can be ascribed to the electronic interaction between (d$_\pi$) and isocyanide(p$_{\pi*}$) orbitals. The interaction stabilizes the d$_\pi$ orbitals and induces $(d_{xz}, d_{yz})^4 (d_{xy})^1$ configuration.

Table 2
Observed shifts and separation of the isotropic shift into contact and dipolar contributions in [Ru(TPP)(^{t}BuNC)$_2$]ClO$_4$ (ppm)

Proton type	$\Delta H/H$ [a]	$(\Delta H/H)_{iso}$ [b]	$(\Delta H/H)_{dip}$	$(\Delta H/H)_{con}$
H$_o$	−4.97	−13.1	6.50	−19.6
H$_m$	17.2	9.51	3.17	6.33
m-CH$_3$	0.22	−2.50	2.15	−4.6
H$_p$	−0.46	−8.16	2.91	−11.1
p-CH$_3$	14.4	11.6	2.13	9.51
H$_{pyrr}$	−5.44	−13.8	12.1	−25.9

[a] Chemical shift at 298 K with TMS as internal reference. ^{t}BuNC: 3.36 ppm.
[b] Isotropic shift with diamagnetic Ru(TPP)(^{t}BuNC)$_2$ complex as reference.

Table 3
Observed shifts and separation of the isotropic shift into contact and dipolar contributions in [Ru(TPP)(2,6-xylylNC)$_2$]ClO$_4$ (ppm)

Proton type	$\Delta H/H$ [a]	$(\Delta H/H)_{iso}$ [b]	$(\Delta H/H)_{dip}$	$(\Delta H/H)_{con}$
H$_o$	−10.7	−18.9	9.12	−28.0
H$_m$	21.5	13.8	4.47	9.30
(*m*-CH$_3$)	−0.82	−3.46	3.00	−6.46
H$_p$	−4.63	−12.3	3.99	−16.3
(*p*-CH$_3$)	19.9	17.2	3.09	14.1
H$_{pyrr}$	2.55	−5.97	17.2	−23.1

[a] Chemical shift at 298 K with TMS as internal reference. 8.0 (4H, d, H$_m$ ligand); 6.4 (2H, t, H$_p$ ligand); 3.5 (s, 12H, CH$_3$, ligand).
[b] Isotropic shift with diamagnetic Ru(TPP)(2,6-xylylNC)$_2$ complex as reference.

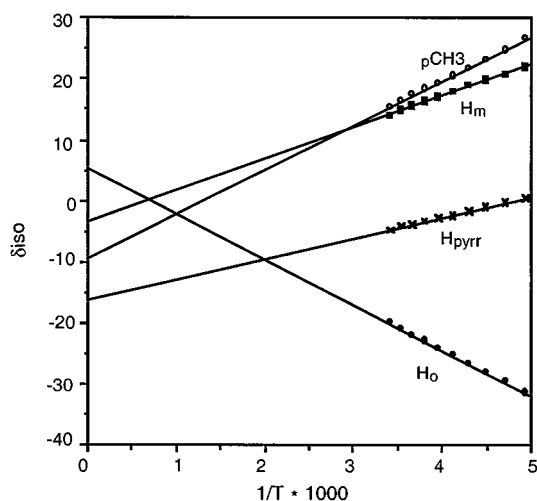Fig. 3. Curie plot for protons resonances of [Ru(TPP)(2,6-xylylNC)$_2$]ClO$_4$ in CD$_2$Cl$_2$.

Such interpretation was recently proposed by Naka-mura et al. for the ground state of bis(cyano) complexes of ferric porphyrins [38]. In order to explain the anti-Curie behavior, the presence of excited states has been recently proposed in several model heme systems having unsymmetrical substitution patterns [39]. The same two level approach [40] could also be applied to our system but the theoretical treatment is beyond this current work.

Different reasons have also been suggested to explain this large spin delocalization on the *meso* position, such as an increasing π delocalization on the *meso* carbon positions [41] or a partial delocalization of the unpaired electron into the (d_{xz}, d_{yz}) orbitals [7]. However, a possible contribution of a partial porphyrin π cation radical character to the electronic configurations of these derivatives has been also suggested [9]. although, to our knowledge, the typical visible spectrum of such radical cation has never been observed with the ferric isocyanide porphyrin complexes.

2.5. EPR spectroscopy

As expected from ¹H-NMR results, no radical-like EPR spectrum is observed at room temperature. In contrast, the complex [Ru(TPP)(2,6-xylylNC)$_2$]ClO$_4$ displays a broad EPR spectra (4 K, frozen dichloromethane) with two *g*-values (2.07 and 1.99) with axial symmetry (Fig. 4). This rules out the possibility of a ruthenium(II) porphyrin π-cation radical, which typically displays a single sharp signal with $g = 2.00$ [24,42]. It should be underlined that an axial spectrum was also observed with [Fe(III)(TPP)-(^{t}BuNC)$_2$]ClO$_4$ ($g = 2.21$ and 1.93) and [Fe(OEP)-(^{t}BuNC)$_2$]ClO$_4$ ($g = 2.28$ and 1.83) [11]. These results

were imputed to the localisation of the unpaired electron in the d_{xy} orbital of the metal, leading to a (d_{xz}, d_{yz})^4 (d_{xy})^1 electronic ground state of the iron(III). 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 [43]. Thus, Δ/λ is negative (-26.3) for [Ru(TPP)(2,6-xylylNC)$_2$]ClO$_4$, indicating that the ground state is largely (d_{xz}, d_{yz})^4 (d_{xy})^1. Consequently, we propose, in accordance with previously reported EPR results, a (d_{xz}, d_{yz})^4 (d_{xy})^1 electron configuration both at low and room temperatures for bis(isocyanide) ruthenium porphyrin complexes.

3. Conclusion

In conclusion, these spectroscopic observations are indicative of a metal-based electron in the d_{xy} orbital for [Ru(TPP)(CNR)$_2$]ClO$_4$ compounds at any temperature. In contrast, it should be underlined the coordination of ^{t}BuNC to iron(III) isobacteriochlorin 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 the tetrahydroporphyrin macrocycle [44] and one electron oxidation of Ru(TPP)CS led also to the formation of the π-cation radical [15].

4. Experimental

4.1. General procedures

UV–vis spectra were recorded on an Uvikon 941 spectrophotometer in dichloromethane. Infrared spectra were obtained on a Bruker IFS 28 FT-IR spectrophotometer. ¹H-NMR spectra were recorded in CDCl$_3$ on a Bruker 200 DPX (200 MHz) and chemical shifts are referenced to internal TMS. EPR spectra were recorded in CH$_2$Cl$_2$ 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$_2$Cl$_2$, the temperature of which was controlled by an Oxford Instruments ESR 900 cryostat. Cyclic voltammetric measurements were performed using an EG&G Princeton Applied Research Model 273 potentiostat. A three-electrode cell was utilized and consisted of a platinum working electrode, a platinum counter electrode, and a saturated calomel reference electrode (SCE). All electrochemical experiments were carried out in dichloromethane, with 0,1 M {^{n}Bu$_4$N}{PF$_6$} acting as the supporting electrolyte (scan rate 0.1 V s^{-1}).

Abbreviations used: TTP = 5,10,15,20-tetra-*para*-tolylporphyrin dianion, TPP = 5,10,15,20-tetraphenyl-porphyrin dianion, OEP = octaethylporphyrin dianion.

4.2. Ru(TPP)('BuNC)$_2$

The complex was prepared by a modified procedure [28,30]. To a solution of 50 mg (67 μmol) of of Ru(TPP)CO in 3 cm^3 of dichloromethane was added four equivalents of *tert*-butyl isocyanide ('BuNC) under stirring at room temperature (r.t.). After filtration, 10 cm^3 of pentane was added and the solution was set aside 1 day for crystallization at 0°C. Purple crystals of Ru(TPP)('BuNC)$_2$ were collected by filtration and washed with hexane. The yield was 52 mg (88%). UV–vis (CH$_2$Cl$_2$): λ_{max}/nm 399 (ε 40 dm^3 mmol^{-1} cm^{-1}), 417 (ε 260), 527 (ε 13). ^{1}H-NMR (δ, CDCl$_3$, ppm) 8.42 (s, 8H, H$_{pyrr}$); 8.17 (8H, d, H$_o$); 7.70 (12H, m, H$_m$ + H$_p$); − 0.42 (18H, s, H ligand). FAB MS (m/z): 880, [M]$^+$; 797 [M − 'BuNC]$^+$. IR $\bar{v}$(CN) = 2116 cm^{-1} in KBr.

4.3. Ru(TTP)('BuNC)$_2$

To a solution of 50 mg (63 μmol) of Ru(TTP)CO in 3 cm^3 of dichloromethane was added four equivalents of *tert*-butyl isocyanide ('BuNC) under stirring at r.t. After filtration, 10 cm^3 of pentane was added and the solution was set aside 1 day for crystallization at 0°C.

Purple crystals of Ru(TTP)('BuNC)$_2$ were collected by filtration and washed with hexane. The yield was 49 mg (83%). UV–vis (CH$_2$Cl$_2$): λ_{max}/nm 398 (ε 40 dm^3 mmol^{-1} cm^{-1}), 417 (ε 264), 527 (ε 12). ^{1}H-NMR (δ, CDCl$_3$, ppm) 8.46 (s, 8H, H$_{pyrr}$); 8.06 (8H, d, H$_o$); 7.52 (8H, d, H$_m$); 2.72 (s, 12H, CH$_3$, porphyrin); − 0.42 (18H, s, H ligand). FAB MS (m/z): 936, [M]$^+$; 853 [M − 'BuNC]$^+$. IR $\bar{v}$(CN) = 2116 cm^{-1} in KBr.

4.4. Ru(II)(TPP)(2,6-xylylNC)$_2$

To a solution of 50 mg (67 μmol) of Ru(TPP)CO in 3 cm^3 of dichloromethane was added four equivalents of 2,6-xylyl isocyanide under stirring at r.t. After filtration, 10 cm^3 of pentane was added and the solution was set aside 1 day for crystallization at 0°C. Purple crystals of Ru(TPP)(2,6-xylylNC)$_2$ were collected by filtration and washed with hexane. The yield was 54 mg (82%). UV–vis (CH$_2$Cl$_2$): λ_{max}/nm 399 (ε 42 dm^3 mmol^{-1} cm^{-1}), 417 (ε 250), 528 (ε 12). ^{1}H-NMR (δ, CDCl$_3$, ppm) 8.52 (s, 8H, H$_{pyrr}$); 8.19 (8H, d, H$_o$); 7.72 (12H, m, H$_m$ + H$_p$); 6.47 (2H, t, H$_p$ ligand); 6.26 (4H, d, H$_m$ ligand); 0.29 (s, 12H, CH$_3$). FAB MS (m/z): 976, [M]$^+$; 845 [M − 2,6-xylyl NC]$^+$. IR $\bar{v}$(CN) = 2087 cm^{-1} in KBr.
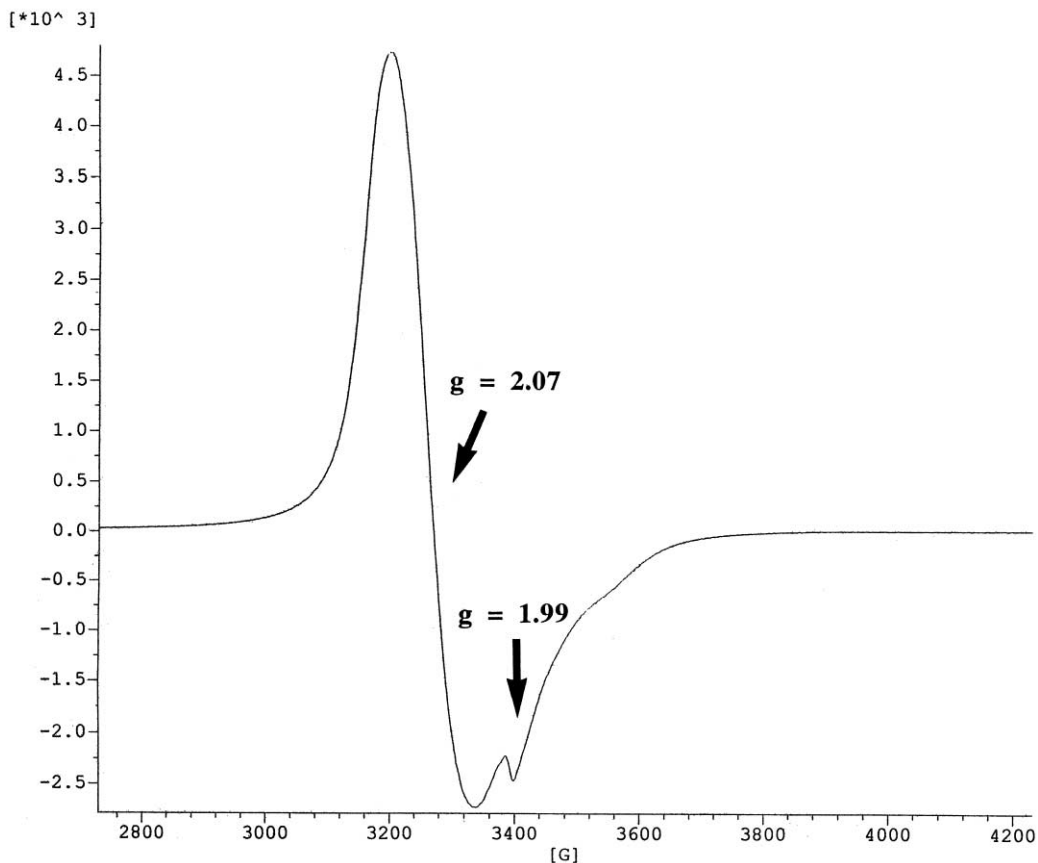
Fig. 4. EPR spectrum of [Ru(TPP)(2,6-xylylNC)$_2$]ClO$_4$ in a CH$_2$Cl$_2$ glass, recorded at 4 K.

4.5. Ru(II)(TTP)(2,6-xylylNC)$_2$

To a solution of 50 mg (62 μmol) of Ru(TTP)CO in 3 cm^3 of dichloromethane was added a four equivalents of 2,6-xylyl isocyanide under stirring at r.t. After filtration, 10 cm^3 of pentane was added and the solution was set aside 1 day for crystallization at 0°C. Purple crystals of Ru(TTP)(2,6-xylylNC)$_2$ were collected by filtration and washed with hexane. The yield was 50 mg (78%). UV–vis (CH$_2$Cl$_2$): λ_{max}/nm 400 (ε 40 dm^3 mmol^{-1} cm^{-1}), 418 (ε 240), 528 (ε 11). ^{1}H-NMR (δ, CDCl$_3$, ppm) 8.54 (s, 8H, H$_{pyrr}$); 8.06 (8H, d, H$_o$); 7.52 (8H, d, H$_m$); 6.44 (2H, t, H$_p$ ligand); 6.24 (4H, d, H$_m$ ligand); 2.72 (s, 12H, CH$_3$, porphyrin); 0.27 (s, 12H, CH$_3$, ligand). FAB MS (m/z): 1032, $[M]^+$. IR $\bar{v}$(CN) = 2086 cm^{-1} in KBr.

4.6. Ru(T(o,o′-OMe)PP)(^{t}BuNC)$_2$

To a solution of 50 mg (51 μmol) of Ru(T(o,o′-OMe)PP)CO in 3 cm^3 of dichloromethane was added a four equivalents of *tert*-butyl isocyanide (^{t}BuNC) under stirring at r.t. After filtration, 10 cm^3 of pentane was added and the solution was set aside 1 day for crystallization at 0°C. Purple solid of Ru(T(o,o′-OMe)PP)(^{t}BuNC)$_2$ was collected by filtration and washed with hexane. The yield was 48 mg (84%). UV–vis (CH$_2$Cl$_2$): λ_{max}/nm 417 (ε 250 dm^3 mmol^{-1} cm^{-1}), 529 (ε 13). ^{1}H-NMR (δ, CDCl$_3$, ppm) 8.28 (s, 8H, H$_{pyrr}$); 7.65 (4H, t, H$_p$); 7.03 (8H, d, H$_m$); 3.55 (24H, s, OMe); − 0.34 (18H, s, H ligand). IR $\bar{v}$(CN) = 2105 cm^{-1} in KBr.

4.7. [Ru(TPP)(^{t}BuNC)$_2$]ClO$_4$

To a solution of 30 mg (34 μmol) of Ru(TPP)(^{t}BuNC)$_2$ in 3 cm^3 of dichloromethane was added a large excess of ferric perchlorate (Fe(ClO$_4$)$_3$·nH$_2$O) under stirring at r.t. After filtration, 10 cm^3 of pentane was added and the solution was set aside 2 days for crystallization at 0°C. Purple solid of [Ru(TPP)(^{t}BuNC)$_2$]ClO$_4$ was collected by filtration and washed with hexane. The yield was 28 mg (84%). UV–vis (CH$_2$Cl$_2$): λ_{max}/nm 398 (ε 90 dm^3 mmol^{-1} cm^{-1}), 515 (ε 5.7). FAB MS (m/z): 880, $[M]^+$; 797 $[M − {^t}BuNC]^+$. IR $\bar{v}$(C∫N) = 2170 cm^{-1} in KBr.

4.8. [Ru(TPP)(2,6-xylyl NC)$_2$]ClO$_4$

To a solution of 30 mg (31 μmol) of Ru(TPP)(2,6-xylylNC)$_2$)$_2$ in 3 cm^3 of dichloromethane was added a large excess of ferric perchlorate (Fe(ClO$_4$)$_3$·nH$_2$O) under stirring at r.t. After filtration, 10 cm^3 of pentane was added and the solution was set aside 2 days for crystallization at 0°C. Purple crystals of [Ru(TTP)(2,6-xylyl NC)$_2$]ClO$_4$ were collected by filtration and washed with hexane. The yield was 26 mg (78%). UV–vis (CH$_2$Cl$_2$): λ_{max}/nm 397 (ε 90 dm^3 mmol^{-1} cm^{-1}), 515 (ε 5.8). FAB MS (m/z): 976, $[M]^+$; 845 $[M − 2,6$-xylyl NC]$^+$. IR $\bar{v}$(C∫N) = 2160 cm^{-1} in KBr.

4.9. [Ru(TTP)(^{t}BuNC)$_2$]ClO$_4$

To a solution of 30 mg (32 μmol) of Ru(TTP)-(^{t}BuNC)$_2$ in 3 cm^3 of dichloromethane was added a large excess of ferric perchlorate (Fe(ClO$_4$)$_3$·nH$_2$O) under stirring at r.t. After filtration, 10 cm^3 of pentane was added and the solution was set aside 2 days for crystallization at 0°C. Purple crystals of [Ru(TTP)-(^{t}BuNC)$_2$]ClO$_4$ were collected by filtration and washed with hexane. The yield was 22 mg (66%). UV–vis (CH$_2$Cl$_2$): λ_{max}/nm 398 (ε 90 dm^3 mmol^{-1} cm^{-1}), 515 (ε 5.7). ^{1}H-NMR (δ, CDCl$_3$, ppm) 18.7 (8H, s, H$_m$); 14.36 (s, 12H, CH$_3$, porphyrin); − 3.2 (s, 8H, H$_{pyrr}$); 3.7 (s, 18H, ligand); − 6.0 (8H, s, H$_o$). FAB MS (m/z): 936, $[M]^+$; 853 $[M − {^t}BuNC]^+$. IR $\bar{v}$(CN) = 2163 cm^{-1} in KBr.

4.10. [Ru(TTP)(2,6-xylyl NC)$_2$]ClO$_4$

To a solution of 30 mg (29 μmol) of Ru(TTP)(2,6-xylylNC)$_2$)$_2$ in 3 cm^3 of dichloromethane was added a large excess of ferric perchlorate (Fe(ClO$_4$)$_3$·nH$_2$O) under stirring at r.t. After filtration, 10 cm^3 of pentane was added and the solution was set aside two days for crystallization at 0°C. Purple crystals of [Ru(TTP)(2,6-xylyl NC)$_2$]ClO$_4$ were collected by filtration and washed with hexane. The yield was 26 mg (79%). UV–vis (CH$_2$Cl$_2$): λ_{max}/nm 398 (ε 92 dm^3 mmol^{-1} cm^{-1}), 515 (ε 5.9). ^{1}H-NMR (δ, CDCl$_3$, ppm) 22.7 (8H, s, H$_m$); 19.9 (s, 12H, CH$_3$, porphyrin); 7.8 (4H, d, H$_m$ ligand); 6.7 (2H, t, H$_p$ ligand); 4.2 (s, 8H, H$_{pyrr}$); 3.3 (s, 12H, CH$_3$, ligand); − 13.2 (8H, s, H$_o$). FAB MS (m/z): 1032, $[M]^+$. IR $\bar{v}$(CN) = 2158 cm^{-1} in KBr.

For the preparation of the *meta*-methylated derivatives of tetraphenylporphyrin, the same procedure can be used with the corresponding ruthenium perchlorate analogues in dichloromethane solvent and the suitable ligand. However for *meta*-methyl derivatives, a partial decomposition was observed; the solutions were reduced in volume to ensure precipitation, due to the high solubility of *meta*-methyl derivatives in dichloromethane. These complexes were not isolated but used directly for NMR experiments.

Caution: perchlorate ions are susceptible to spontaneous detonation and should be handled in quantities of less than 50 mg.

Acknowledgements

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