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Synthesis, spectroscopic and structural characterization of the pentacoordinate high-spin Fe(III) isothiocyanate "picket fence" porphyrin complex

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Habib Nasri^{a,*} and Mongi Debbabi^b

^a Faculté des Sciences de Monastir, 5000 Monastir, Tunisia

^b Ecole Nationale d'Ingénieurs de Monastir (E.N.I.M.), 5000 Monastir, Tunisia

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Abstract—The preparation and the characterization of the (isothiocyanato)(α , α , α , α -tetrakis(*o*-pivalamidophenyl)porphinato)iron(III) complex is described. The synthesis procedure utilizes the crown ether 18-C-6 to solubilize potassium thiocyanate. ¹H NMR and EPR data of the isolated product are in accordance with a high-spin (S = 5/2) ferric porphyrin species. The X-ray molecular structure confirms the above deductions. The iron atom is pentacoordinated by the four nitrogen atoms of the pyrrole rings of the porphyrin and the nitrogen atom of the NCS⁻ group. It lies at 0.504 Å out of the porphinato plane and 0.462 Å out of the four nitrogen plane. The Fe–N(NCS) bond length is 1.956(5) Å and the Fe–N–C(NCS) bond angle is 176.1(5)°. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: porphyrin; iron(III) complex; isothiocyanate complex; high-spin Fe(III); molecular structure.

INTRODUCTION

The interest in iron porphyrins stems not only from the diverse biological roles of the iron porphyrin moiety found in proteins, cytochromes, peroxidases, etc. but also from the array of physical properties observed for the coordinated Fe(II) and Fe(III).

In most cases, when weak crystal field ligands such as halides or pseudohalides are bound to an iron(III) of a metalloporphyrin or a hemoprotein, the resulting porphyrinate is high spin and five coordinate. Nevertheless, many examples of six coordinate high-spin heme-like species exist, i.e. (2-MeHIm)[Fe(F)₂(TPP)] [1]. In some special circumstances the ferric ion may be in the spin "crossover" region and show thermal spin-equilibrium. Thus, in the case of the azide ligand, Scheidt *et al.* [2], confirmed the high spin (S = $5/2) \Leftrightarrow$ low spin (S = 1/2) equilibrium of the bisazide Fe(III) porphyrin species; [Fe(N₃)₂(TpivPP)]⁻. Korszun and Moffat [3] have determined the structure of the isothiocyanato-liganded hemoglobin which shows a spin equilibrium between the high-spin NCS⁻ pentacoordinate heme and the "(NCS)MetHb proximal histidine" low spin six coordinate methemoglobine.

The isothiocyanate ferric porphyrinate was mentioned in the literature for decades [4] as a high-spin (S=5/2) pentacoordinate derivative. However, a complete characterization of such species has not been previously reported.

It is the aim of this work to synthesize and spectroscopically and structurally characterize the isothiocyanate Fe(III) picket fence porphyrin complex.

We also report in this paper the use of crown ethers to solubilize the inorganic potassium thiocyanate salt in organic solvents typically used with iron porphyrinates.

The use of the picket fence porphyrin for the characterization of this ferric porphyrinate was directly related to the fact that ionic not very bulky ligands as it is shown by X-ray molecular structures [5], are in

^{*} Author to whom correspondence should be addressed.



Fig. 1. Visible spectrum of [Fe(NCS)(TpivPP)] in chlorobenzene solution (room temperature).

all cases bound to the iron by the pocket side of the protected porphyrin. Consequently, these complexes are remarkably stable.

RESULTS AND DISCUSSION

The reported synthesis for halide and pseudohalide Fe(III) porphyrin species make use of organic-soluble iron porphyrinates and typically water-soluble inorganic salts [6] (KCl, KBr, NaN₃, etc.) or aqueous acids (CH₃COOH [7], HNO₃ [8], etc.). In our case, the (isothiocyanato)($\alpha, \alpha, \alpha, \alpha$ -tetrakis(*o*-pivalamido-phenyl)porphinato)iron(III) complex has been prepared by using only one organic phase. The 18-C-6 crown ether was used to solubilize the potassium thiocyanate in chlorobenzene solution¹. Our synthetic strategy has the advantage of avoiding the use of a mixture of an organic and an aqueous solution and obtaining the anionic reagent in high concentration.

Figure 1 represents the electronic spectrum of the [Fe(NCS)(TpivPP)] species recorded in chlorobenzene. The spectrum belongs to the hyper class [9]. The Soret and the β bands values (respectively, 417 and 513 nm) are quite identical to those of other pentacoordinate Fe(III) high-spin *meso*-porphyrin species [10].

The EPR spectra carried out at 77 K show similar features in solution and in solid state. Both spectra

are axially symmetric; $g \perp = 5.8$ and $g_{\parallel} = 1.98$ for the frozen chlorobenzene solution and $g \perp = 5.7$ for the powder (crushed single crystals). These results provide unequivocal evidence that either in solid state or in solution the [Fe(NCS)(TpivPP)] complex is high-spin (S = 5/2).

A proton NMR spectrum of [Fe(NCS)(TpivPP)] in CDCl₃, recorded at room temperature, supports the latter conclusion. Thus, the pyrrole proton resonance at 75.7 ppm (line with ≈ 365 Hz) is in the range 100– 70 ppm, a downfield region characteristic of high-spin iron(III) tetraarylporphyrin complexes [11]. The *ortho*-phenyl protons of the macrocycle are not observed. Strong dipolar interactions should be the cause of the important broadening. *Meta*-phenyl protons are highly anisotropic giving rise to two singlets at 11.5 and 14.4 ppm.

The IR spectrum of [Fe(NCS)(TpivPP)] shows that the value of the stretching frequency v(CN) which is 2015 cm⁻¹, is a clear evidence that NCS⁻ is N-bonded to the iron (an isothiocyanate) [12].

The molecular structure of the [Fe(NCS)(TpivPP)] complex is illustrated in Fig. 2. The NCS⁻ ligand lies, as expected, in the axial position inside the cavity formed by the pivalamide arms of the picket fence porphyrin. The iron atom is five coordinated and the resulting polyhedron is a slightly deformed square pyramid with the nitrogen atom of the NCS⁻ group in the axial position. Selected bond distances and angles for this complex are given in Table 1. Other distances and angles, fractional coordinates and thermal parameters have been deposited as supplementary data with the editor.

The bond parameters for the coordination environment of the Fe(III) in this compound and for a selec-

¹The Kryptofix 222 can also be used.

² The process is based on an adoption of the DIFABS [19] logic to area detector geometry [18].

 $^{{}^3}$ R-factors based on F² (wR₂) are statistically about twice as large as those based on *F*.

High spin Fe(III) isothiocyanate porphyrin complex



Fig. 2. ORTEP diagram of the [Fe(NCS)(TpivPP)] molecule displaying the atom-labeling scheme used throughout the paper. Ellipsoids are drawn at the 30% probability level.

Iron coordination po	lyhedron		
Fe-N(9)	1.956(5)	N(1)–Fe–N(9)	104.2(2)
Fe-N(1)	2.057(4)	N(2)-Fe-N(9)	100.6(2)
Fe-N(2)	2.054(4)	N(3)-Fe-N(9)	104.5(2)
Fe-N(3)	2.056(4)	N(4)-Fe-N(9)	102.8(2)
Fe–N(4)	2.054(4)		
		Thiocyanate ligand	
N(1)–Fe–N(2)	86.7(2)	N(9)–N(45)	1.149(8)
N(1)-Fe- $N(3)$	151.3(2)	C(45)–S	1.602(7)
N(1)–Fe– $N(4)$	87.5(2)		
N(2)-Fe- $N(3)$	87.3(2)	Fe-N(9)-C(45)	176.1(5)
N(2)-Fe-N(4)	156.6(2)	S-C(45)-N(9)	178.6(6)

Table 1. Selected bond distances (Å) and angles (°) for [Fe(NCS)(TpivPP)]^a

^aThe numbers in parentheses are the estimated standard deviations.

tion of some other Fe(III) metalloporphyrins are given in Table 2. A brief description of the molecular structure of the otherwise analogous [Fe(NCS)(TPP)] complex was mentioned by Bloom and Hoard [13]. The values of the Fe–Np distances of the TpivPP and TPP derivatives are, respectively, 2.055(2) and 2.065 Å. These values are a clear indication that these species are high-spin [14]. In order to accommodate the high-spin iron(III) atom, the porphinato cores undergo a significant radial expansion. This is very well illustrated by the long $Fe-P_C$ and $Fe-P_N$ distances shown by [Fe(NCS)(TpivPP)] and [Fe(NCS)(TPP)].

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Complex	Fe–Np	Fe-X _L	Fe–P _C	Fe–P _N	$\delta^{ m a}$	Spin (S)	Refs.
[Fe(NCS)(PivPP)] [Fe(NCS)(TPP)] [Fe(NCS)(Py)(OEP)] [Fe(NCS)(Py)(TPP)]	2.055 (2) 2.065 2.048 (4) 1.988 (9)	$\begin{array}{l} {\rm Fe-N_{L}}^{\rm b}\!$	0.504 0.550 0.240 ^c 0.050 ^c	0.462 0.485 0.180 ^c 0.050 ^c	0.042 0.065 _	5/2 5/2 5/2 1/2	this work [13] [15] [15]

Table 2. Porphinato core parameters (Å) for selected Fe(III) porphyrin complexes

 $^{a}\delta =$ the doming.

 ${}^{b}Fe-N_{L} = Fe-N(NCS)$ distance.

^cDisplacement toward the isothiocyanate ligand.

The corresponding values are, respectively, 0.504 and 0.462 Å for the former complex and 0.55 and 0.485 Å for the latter. For both [Fe(NCS)(Porph)] derivatives, the Fe–N(NCS) distances have the same values; 1.956(5) Å for the picket fence porphyrin product and 1.957 Å for the tetraphenylporphyrin moiety.

As expected for an N-bonded thiocyanate to an iron atom, the Fe–NCS group, is found to be essentially linear for all NCS⁻ derivatives shown in Table 2 (except the ambiguous [Fe(NCS)(Py)(TPP)] [15]

case). Both isothiocyanate TpivPP and OEP derivatives exhibit rather identical values for the Fe–N– C(NCS) angle [respectively, 176.1 (5)° and 176.0 (2)°]. These two derivatives present very close N–C–S angle values with 178.6° (6) for the picket fence complex and 179.6° (2) for the OEP six coordinate species.

The porphyrinato core in [Fe(NCS)(TpivPP) is decidedly non-planar as can be seen from an inspection of Fig. 3. The pattern of the atom displacements in the porphinato core correspond closely to those



Fig. 3. Formal diagram of the porphinato core in the [Fe(NCS)(TpivPP)] molecule displaying the displacement, in units of 0.01 Å, from mean plane of the porphinato core. Also displayed on the diagram is the average value of each type of bond distance and angle in the porphinato core.

required by exact D_{2d} symmetry, often simply called S_4 -ruffling. Least squares planes calculations indicate a small doming of the porphyrin (0.042 Å).

EXPERIMENTAL

The complex [Fe(SO₃CF₃)(H₂O)(TpivPP)] was prepared as described previously [16]. The 18-C-6 crown ether was recrystallized in toluene, dried under vacuum overnight and stored under argon. Toluene and hexanes were distilled from their sodium–benzophenone solution under a nitrogen atmosphere. Chlorobenzene was purified by washing with sulfuric acid and then distilled over P_2O_5 .

UV-VIS spectra were recorded on a Perkin-Elmer Lambda 19 spectrometer, Fourier-transform IR data on a Bio-Rad FT S4000 spectrometer and EPR spectra were obtained at 77 K on a Varian E-line spectrometer operating at X-band frequency.

¹H NMR data were obtained on a Nicolet NT300 spectrometer operating at 300.063 MHz.

Preparation of the [Fe(NCS)(TpivPP)] compound

The (isothiocyanato)($\alpha,\alpha,\alpha,\alpha$ -tetrakis(*o*-pivalamidophenyl)porphinato)iron(III) complex was prepared by reacting [Fe(SO₃CF₃)(H₂O)(TpivPP)] (0.016 mmol) with KSCN (0.32 mmol) and 18-crown-6 (0.16 mmol) in 20 ml of C₆H₅Cl. The resulting red brownish solution was then filtered and an X-ray quality crystals were prepared by slow diffusion of hexanes into C₆H₅Cl. The crystalline material was washed with several portions of water and then with hexanes.

UV-VIS [C_6H_5Cl , λ_{max} in nm, (log ε)]: 417 (4.99); 513 (4.21); 586 sh (3.63); 655 (3.54) IR (KBr, cm⁻¹): ν (CN): 2015. EPR (C_6H_5Cl , 77 K): $g \perp = 5.8$; $g_{\parallel} = 1.98$. ¹H NMR (300 MHz, CDCl₃): H(pyrr): 75.7 ppm; H(*meta*-Ph): 11.5, 14.4; H(*para*-Ph): 8.0 ppm.

Determination of crystal and molecular structure

Crystal data. $C_{65}H_{64}N_9O_4SFe$, M = 1123.2, monoclinic, space group $P2_1/n$, a = 13.237(3) Å, b = 18.272(4) Å, c = 23.678 Å, $\beta = 94.910(10)^{\circ}$, V = 5706.0 Å³, $D_c = 1.31$ g·cm⁻³, Z = 4, F(000) = 2724, $\lambda = 0.71073$ Å, μ (Mo–K α) = 35.3 cm⁻¹.

Data collection and processing. A dark single crystal of approximate size $0.6 \times 0.3 \times 0.3$ mm³ was examined on an Enraf-Nonius FAST area detector diffractometer at 127 K. All measurements were performed with graphite-monochromated Mo–K α radiation. Data collection and reduction were defined as before [17]. Intensity data were corrected for absorption effects using a modified version of the absorption correction program DIFABS². A total of 10020 unique reflections was collected and 6791 having $I > 2\sigma(I)$ [merging R(int) = 0.132].

Structure analysis and refinement. The structure was solved in the centrosymmetric space group P_{2_1}/n using the direct methods program SHELXS-86 [20]. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were idealized with the standard SHELXL-93 [21] idealization method. The final cycles of refinement based on F^2 of 733 variables converged to the final R_1 =0.079 and wR_2 =0.167³ for reflections with $I > 2\sigma(I)$. The final difference Fourier map had the largest peak at 0.76 eÅ⁻³.

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