Synthesis, UV/vis, FT-IR and Mössbauer spectroscopic characterization and molecular structure of the Bis[4-(2-aminoethyl) morpholine](tetrakis(4-metoxyphenyl)porphyrinato) iron(II) complex

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ABSTRACT

The synthesis, the UV−visible, FT-IR and Mössbauer spectroscopy and the crystal structure characterizations of the bis[4-(2-Aminoethyl)morpholine]tetrakis(4-metoxyphenyl)porphy-rinato)iron(II) complex are described. The title compound crystallizes in the triclinic, space group P-1, with a = 11.1253(4) Å, b = 11.2379(4) Å, c = 11.5488(4) Å, α = 72.304(2)°, β = 86.002(2)°, γ = 72.066(2)°, V = 1308.28(8) Å^3, Z = 1. The Mössbauer data are consistent with an iron(II) low-spin (S = 0) porphyin species. The spin-state is confirmed by the value of the average equatorial iron-nitrogen pyrrole distance (Fe−Np = 1.988(2) Å) which is in the normal range of low-spin iron(II) porphyrins. The supramolecular architecture involve hydrogen bonding including C−H … O and weak C−H … Cg π intermolecular interactions involving centroides (Cg) pyrrole and phenyl rings.

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1. Introduction

Since the middle of the last century, hexa-coordinated imidazole and pyridine complexes of iron(II) porphyrins have been amply used to mimic hemoproteins such as hemoglobin, myoglobin and cytochromes c. In 1994, the X-ray molecular structure of the turnip cytochrome *f* was determined [1]. which shows that the α-amino group of the Tyr-l coordinated trans to His-25 in the *c*-type heme protein [1]. Thus, the bis-amines Fe(II) metalloporphyrins appears to be functionally significant as models for cytochrome *f*. By the other hand, it has been shown that the reaction of primary and secondary amines with iron(III) metalloporphyrins results in base-catalyzed one electron reduction and concomitant dissociation of the deprotonated amine radical [2]. It is also known that the addition of an excess of sterically unhindered alkyamines to an Fe(III) porphyrin derivative leads to six-coordinated bis(amines)-iron(II) porphyrins [3]. It is noteworthy that very few investigation

on iron(II) amine metalloporphyrins have been reported [4,5] and in the Cambridge Structural Database (CSD, Version 5.35) [6], there are only six bis(amine)-iron(II) porphyrin structures. In order to gain more insight into the stereochemical and electronic structure of bis(amine)-iron(II) porphyrin species, the synthesis, UV/vis and Mössbauer spectroscopic data and the X-ray molecular structure of the bis[4-(2-Aminoethyl)morpholine]tetrakis(4-metoxyphenyl) porphyrinato) iron(II) complex with the formula [Fe^{II}(TMPP)(amp)$_2$] are reported here.

2. Experimental

2.1. General

All reagents and solvents employed were commercially available and were used as received without further purification. All reactions and manipulations for the preparation of the Fe(II) porphyrin derivative were carried out under argon using a double-manifold vacuum line, Schlenkware, and cannula techniques. The tetrakis(4-metoxyphenyl)porphyrin (H$_2$TMPP) was prepared according to the standard literature method [7]. Electronic spectra

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were recorded with a WinASPECT PLUS (validation for SPECORD PLUS version 4.2) scanning spectrophotometer using dry degassed chlorobenzene solutions in 1.0 cm path length cuvettes under argon. MALDI-TOF MS spectra were recorded on an Ultraflex mass spectrometer (Bruker Daltonics) without a matrix. Accurate mass measurements (high-resolution mass spectrometry) were obtained on an Orbitrap spectrometer. The measurements were made at the Pôle Chimie Moléculaire. IR spectra were registered on a FT-IR Nexus (Nicolet) spectrometer with a micro-ATR accessory (Pike). Mössbauer measurements were performed with a $_{57}$Co source in a Rhodium matrix using a constant acceleration spectrometer from 25 to 300 K with 500G field transverse to the gamma ray beam (Knox College). Samples for Mössbauer spectroscopy were prepared by immobilization of the crystalline material in Apiezon M grease."

2.2. Synthesis of [Fe^{II}(TMPP) (amp)$_2$] (1)

[Fe^{II}(TMPP) (SO$_3$CF$_3$)] (TMPP = tetrakis(4-metoxyphenyl)porphyrinato ligand) [8] (100 mg, 0.106 mmol) and 4-(2-Aminoethyl) morpholine (3 mg, 23.223 mmol) in 25 mL of chlorobenzene were stirred overnight at room temperature and the color of the reaction mixture changed from brown red to blood red. Crystals of the bis(4-(2-aminoethyl)- morpholine)tetrakis(4-metoxyphenyl)porphyrinato)iron(II) complex [Fe^{II}(TMPP) (amp)$_2$] (1) (amp = 4-(2-Aminoethyl)morpholine) were prepared by slow diffusion of hexanes into the chlorobenzene solution. Anal. Calc. for 1, C$_{60}$H$_{64}$N$_8$O$_6$Fe (1049.07 g/mol): C, 68.69; H, 6.15; N, 10.68%. Found: C, 68.14; H, 6.10; N, 10.72%. UV−Vis (C$_6$H$_5$Cl: λ_{max} in nm (logε)): 424 (5.95), 534 (4.99), 574 (4.95), 620 (5.86). IR (cm^{-1}): 2793, 1536, 1500, 1453, 1343, 1171, 1109, 1061. MS (MALDI-TOF) m/z: 788.10 [Fe(TMPP)]$^+$, 805.18 [Fe(TMPP) (NH$_3$)]$^+$, 821.06 [Fe(TMPP) (Et−H$_2$)+2H]$^+$.

2.3. X-ray structural analysis

A suitable crystal (0.25, 0.25, 0.25 mm) of 1 was selected and mounted on a glass fiber oil on a Nonius Kappa, APEX II diffractometer. The crystal was kept at 115 K during data collection. Using Olex2 [9], the structure was solved with the Superflip structure solution program [10], using the charge flipping solution method. The model was refined with the SHELXL [11] refinement package using Least squares minimization. The molecular graphic were drawn using the ORTEP-3 for Windows [12]. H-atoms were positioned geometrically and refined using a riding model with C−H = 0.95, 0.98 and 0.99 Å and N−H = 0.92 Å, with U_{iso}(H$_{phenyl, methylene, amine}$) = 1.2$U_{eq}$(C/N) and U_{iso}(H$_{methyl}$) = 1.5U_{eq}(C). All non-hydrogen atoms were refined anisotropically. In the final difference Fourier map, the highest peak is 0.97 and the deepest hole is 0.59. Crystallographic data and structure refinement of [Fe^{II}(TMPP) (amp)$_2$] are given in Table 1. Selected bond distances and angles for 1 are listed in Table 2.

3. Results and discussion

3.1. UV-visible

Fig. 1 represents the UV/vis spectra of 1 and the starting material [Fe^{III}(TMPP) (SO$_3$CF$_3$)] complex. The position of the Soret band of the iron(II)-bis(aminomorpholine) derivative is red-shifted vis-à-vis of the iron(III)-triflato starting material (Fig. 1). The values of the Soret and the Q bands of our Fe(II) porphyrin species are 424 nm, 534 nm and 574 nm respectively which are very close to the related iron(II)-bis(amine) meso-tetraphenylporphyrins (see Table 3).

Table 1
Crystal data and structural refinement for [Fe^{II}(TMPP) (amp)$_2$] (1).

Compound	[Fe^{II}(TMPP) (amp)$_2$]
Formula	C$_{60}$H$_{64}$FeN$_8$O$_6$
D$_{calc.}$/g cm^{-3}	1.331
μ/mm^{-1}	0.349
Formula Weight	1049.06
Colour	dark purple
Shape	prism
Size/mm^3	0.25 × 0.25 × 0.25
T(K)	115
Crystal System	triclinic
Space Group	P-1
a (Å)	11.1253(4)
b (Å)	11.2379(4)
c (Å)	11.5488(4)
α (°)	72.304(2)
β (°)	86.002(2)
γ (°)	72.066(2)
V(Å^3)	1308.28(8)
Z	1
θ$_{min}$ (°)	1.852
θ$_{max}$ (°)	27.607
Reflections measured	31281
Independent reflections	6029
Reflections used	4280
R$_{int}$	0.0604
Parameters	343
Largest Peak Largest Peak	0.960
Deepest Hole	0.585
GooF (S)	1.134
wR$_2$ (all data)	0.1614
wR$_2$[b]	0.1304
R$_1$ (all data)	0.0876
R$_1$[a]	0.0510

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_o|^2)^2]\}^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°) of [Fe^{II}(TMPP) (amp)$_2$] (1).

Iron coordination polyhedron			
Fe−N1	1.982(2)	N1−Fe−N2	89.70(8)
Fe−N2	1.994(2)	N1[a]−Fe−N2	90.30(8)
Fe−N3	2.037(2)	N1−Fe−N3	90.01(8)
N2−Fe−N3	93.41(7)	N1[a]−Fe−N3	89.99(8)
N2[a]−Fe− N3	86.59(7)		
4-(2-aminoethyl)morpholine Axial ligand			
O3−C29	1.423(3)	N4−C30	1.457(3)
N4−C26	1.458(3)	C29−C30	1.508(4)
C25−C26	1.525(3)	N3−C25	1.470(3)
N3−C25−C26	112.5(2)	N4−C26−C25	111.2(2)
C30−N4−C26	111.4(2)	N4−C30−C29	110.0(2)
O3−C29−C30	111.7(2)	C29−O3−C28	109.8(2)

[a] Symmetry Code: 2-x,1-y,-z.

3.2. Structural properties of [Fe^{II}(TMPP) (amp)$_2$] (1)

In the title compound, the Fe(II) center is coordinated by four pyrrole N atoms of the porphyrin macrocycle and the amino nitrogen atom of two trans amp axial ligands in a octahedral geometry. Fig. 2 is an ORTEP diagram of the [Fe^{II}(TMPP) (amp)$_2$] (1) complex. An extensive number of molecular structures of iron(II) porphyrin complexes are reported in the literature. Nevertheless in the Cambridge Structural Database (CSD, Version 5.35; Allen, 2002) there are only four reported structures of iron(II) porphyrins with aliphatic amines as axial ligands (Table 4).

It has been noticed for iron(II) porphyrins that there is a relationship between the spin-state of the iron(II) and the value of the average equatorial iron-pyrrole N atoms distance (Fe−N$_p$) [13]. Thus, for the high-spin state (S = 2) species, the Fe−N$_p$ distance