The role of spin state on the local atomic and electronic structures of some metalloporphyrin complexes

S A Suchkova¹, A Soldatov¹, K Dziedzic-Kocurek², M J Stillman³
¹ Southern Federal University, Sorge str. 5, 344090 Rostov-on-Don, Russia
² Yagellonian University, Krakow, Poland
³ University of Western Ontario, London, Ontario, Canada

E-mail: suchkova_sv@inbox.ru

Abstract. The Porphyrin molecule is an archetypal metalloorganic complex, which shows up in many biochemical molecules like chlorophyll, haemoglobin and cytochrome. The prospect of switching the spin in the metalloporphyrin ring is a particularly interesting one, as this could be used, for example, for spin-dependent electric transport through biomolecular devices. These molecules can be used in various applications like optical switches, information storage and non-linear optics. Here, we study the molecular spin state of chloro-hemin, hemin cyanide and hemin carbonyl molecules by ADF code. Chloro-hemin has been studied by analyzing the Fe K-edge X-Ray Absorption Near Edge Structure (XANES) spectra. At first stage of investigation we assume an approximate initial geometry, then we perform the geometry optimization with different molecular spin states and search for configuration with minimal total energy with the use of Density Functional Theory (ADF 2008). The results of geometry optimization of chloro-hemin molecule performed with the GGA OPBE functional showed that configuration with total spin \( S=5/2 \) has minimal total energy. This configuration corresponds well with the geometry structure obtained via X-Ray diffraction method (Fe-N-N angle is 13.3°). The similar calculations that were carried out for hemin carbonyl and hemin cyanide molecules showed that for these structures minimal energy is found to be for \( S=1/2 \). The experimental Fe K-XANES spectra of the investigated compound have been collected. The theoretical analysis of the experimental data has been performed on the basis of finite difference method (FDMnes2007 program code).

1. Introduction

The heme group plays a vital role in biological systems. It is encountered as an active site which determines the biological activities of some proteins. The heme group present in oxygen transport proteins, hemoglobin and myoglobin, metabolizing enzymes such as peroxidase, and enzymes catalyzing important redox reactions in cytochrome [1,2] is the main active site which controls a wide variety of chemical reactions. Hence, understanding properties of heme group, by probing chemical environment of the heme active site, is of great importance for studying catalytic and structural role of these proteins [3, 4]. Although the structures of heme group have already been investigated by many research groups [5, 6] only a few studies on the chloro-hemin geometry related to spin states have been carried out [7, 8].
Metalloporphyrins are expected to be used as building blocks in spintronic devices. At present more and more attention is being given to the study of structure and properties of porphyrins. In the present work a chloro-hemin molecule was studied (Fig.1). Chloro-hemin reveals a strong correlation between atomic structure and spin state. Numerous experimental techniques, including X-ray diffraction, Mossbauer [10], EPR and nuclear magnetic resonance spectroscopies have been applied to study the heme group and iron–porphyrin systems in different spin states [9]. Furthermore, quantum mechanical calculations with the DFT approach have been reported for different spin states of iron–porphyrin systems models [11]. At present there is no evident description given to the relation between the local atomic and electronic structure of the molecule and relative spin state energies in its doublet, quartet, and sextet spin states. Therefore we decided to study this association by means of XANES spectroscopy and DFT approach.

One of the most effective methods of the investigation of the local atomic structure of compounds under investigation is the X-ray absorption spectroscopy (XAS). The X-ray Absorption Near Edge Structure (XANES) Spectroscopy is known as an effective tool to provide full information about local geometry including not only bond length, but also the bond angles [12,13] instead of the Extended X-ray Absorption Fine Structure (EXAFS) Spectroscopy that gives information about the coordination numbers and bond length around the absorbing atom. The experimental Fe K-edge XANES spectra of chloro-hemin have been analyzed on the basis of full-potential calculations of XANES (FDMNES 2007).

The geometry optimizations were performed using DFT approach. Actually the DFT calculations were used to study the electronic properties of coordination compounds [14].

2. Experiment and method of calculation

Iron porphyrin was prepared from protoporphyrin IX (Sigma) and FeCl$_3$. Further, the aggregates (porphyrin dimmers) were obtained by precipitation from water-N,N-dimethylformamide (DMF) solution according to the modified Adler’s procedure [15].

The powder of Fe-PPiX-Cl (commercial ferrirprotoporphyrin IX chloride (Fe-PPiX-Cl) (Alfa Aesar)) and lyophilized samples of Fe-porphyrin aggregates (specimen) were studied by X-ray absorption spectroscopy. The EXAFS spectra were taken between 5 K and 295 K at the beamline A1 at DESY, Hamburg, and evaluated numerically using ATHENA program [16].

The DFT calculations were performed using ADF 2008 program [17]. The chloro-hemin structure (Cambridge Crystallographic Data Centre code: chemin.cif) was set as initial to start the geometry optimization. At the first stage of investigation we guessed the approximate geometry. Then we performed the geometry optimization with different molecular spin states and looked for a configuration with minimal total energy. We suggested that the doming of Fe atom depends extremely on the correct fraction of high spin. These optimizations with no constraints were performed in the doublet, quartet, and sextet spin states by using Generalized Gradient Approximation (GGA) with OPBE, BP, OLYP exchange-correlation potentials [18]. For the geometry optimization the TZP basis set was used. Then the calculations of Fe K-edge XANES spectra were performed with the full-potential FDMNES 2007 code [19], which runs within the real space cluster approach and uses the finite difference method (FDM) to solve Schrödinger equation.

3. Results and discussion

The structure of chloro-hemin determined from X-Ray diffraction shows quiet strong doming of Fe atom out of nitrogen atoms plane (0.475 Å) [20]. The Fe-N-N angles and total energies of optimized geometries are presented in Table1. The structure with S=5/2 spin state was found to have minimal total energy among other structures. This result is in accordance with a series of studies of five-coordinated Fe(III) porphyrinates [7,8]. The most significant differences between the three spin states lie in the iron–axial ligand distance and N-Fe-N angle (Fig. 1). The four iron–nitrogen distances are nearly equal for doublet (S=1/2), quartet (S=3/2), and sextet (S=5/2) spin states. The obtained values are comparable with experimental data observed in high resolution XRD studies [20]. Since the Cl–
ligand is a weak field ligand of the spectrochemical series, this five-coordinated porphyrin complex might have high spin state. The geometry optimization of the high spin state has led to the increase of distances between the central Fe atom and other atoms. Also structure in this state reveals large value of Fe-N-N angle.

The similar calculations were carried out for hemin carbonyl and hemin cyanide molecules. The structures with low spin state were found to have minimal energies. Since the CO and CN ligands are high field ligands of the spectrochemical series, the mentioned five-coordinated porphyrin complexes might have the low spin state (Table 1).

Comparison of the experimental XANES spectra for chloro-hemin sample with theoretical Fe K-edge spectra is given on the figure 2. From this figure it is obvious that all features of experimental spectra are present in the theoretical ones. As one can see the agreement for the experimental spectra with theoretical one calculated for S=5/2 spin state is better than for S=3/2 spin state because relative intensities of peaks D and E on the curve b are nearly equal instead of curves c and d. Besides it is shown that the pre-edge feature A on the curve b is clearer than that on the curves c and d. Therefore one should conclude that comparison of theoretical curves b, c and d to experimental one reveals better agreement for curve b and c. So one can see from Fig. 2 that XANES spectrum calculated using the FDMNES code for S=5/2 spin state is in a good agreement with the experimental one, while the spectrum for S=3/2 spin state and for XRD datum differs from the experimental one.

![Figure 1](image1.png)  
**Figure 1.** Schematic view of the chloro-hemin molecule. The central angle that determines the doming of Fe atom is highlighted.

![Figure 2](image2.png)  
**Figure 2.** Comparison of the experimental XANES spectra for chloro-hemin sample with theoretical Fe K-edge spectra.

**Table 1.** Energies and other parameters of optimized structures of chloro-hemin, hemin cyanide and hemin carbonyl molecules obtained from DFT calculations. Spin density is a number of
spin-up minus spin down electrons. The abbreviation HCl is chloro-hemin, HCy – hemin cyanide, HC – hemin carbonyl.

| Molecule and spin state | E: LDA+GGA-XC, eV | angle Fe-N-N | Spin density on Fe atom | Charge on Fe atom | Spin density on axial ligand | Charge on axial ligand |
|------------------------|------------------|-------------|------------------------|------------------|-----------------------------|-----------------------|
| HCl 1/2                | -499.176         | 13.3        | 0.76                   | 0.59             | 0.03                        | -0.25                 |
| HCl 3/2                | -499.625         | 8.0         | 2.49                   | 0.67             | 0.33                        | -0.38                 |
| HCl 5/2                | -499.988         | 16.7        | 3.97                   | 0.77             | 0.26                        | -0.38                 |
| HCy 1/2                | -281.96          | 4.0         | 1.03                   | 0.54             | 0.01                        | -0.22                 |
| HCy 3/2                | -281.18          | 8.0         | 2.75                   | 0.6              | 0.25                        | -0.36                 |
| HC 1/2                 | -281.72          | 5.1         | 1.18                   | 0.44             | -0.03                       | 0.06                  |
| HC 3/2                 | -281.28          | 6.4         | 3.09                   | 0.56             | -0.04                       | 0.08                  |

4. Conclusions

It was shown that the significant doming of the local 3D atomic structure of the active site is due to the high spin state of the chloro-hemin molecule. The local atomic structure of this molecule was refined by geometry optimization using ADF2008 program. The results of geometry optimization revealed that chloro-hemin has high spin state (S=5/2) instead of hemin cyanide and hemin carbonyl that have low spin state (S=1/2). Theoretical XANES spectrum for the optimized high spin structure is in a good agreement with experimental one.

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