Electronic and atomic structure studies of rare earth metalloporphyrins by XAFS

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Abstract

The rare earth porphyrins represent a promising class of materials, due to their physical-chemical properties. A detailed study of the local structure of the RE series of porphyrins RETPP (RE = Yb, Er) was carried out by X-ray absorption spectroscopy (XAFS) using the synchrotron radiation. XAFS experiments prove the trivalent state of rare earth metals (Er, Yb) in metalloporphyrins. The relationship between the extended fine structure and the atomic structure of the porphyrin macrocycle with a central rare earth element (Yb, Er) is presented and discussed.

Keywords: XAFS; rare earth metals, state; electronic states

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1. Introduction

1.1. Introduction

Family of porphyrines is very attractive due to its interesting physical and chemical properties and the perspectives for the future applications in modern bio- and nanotechnologies Ivanov et al. (2010). The interest in rare earth porphyrins complexes is determined by a possibility of their use as effective markers in luminescent diagnostics of malignant tumors, Ivanov et al. (2010), since porphyrins are capable to accumulate in various types of cancer cells and tumors. Er and Yb(acetylacetone)-tetraphenylporphyrins are a few organic materials which emit infrared radiation in the solid state, which makes compounds potentially very important material for phototherapy. The information about bonding metal ion with ligand molecules is crucial for luminescence properties of such materials. XAFS was used for a structural characterization of the samples because it provides a structural information even for non crystalline materials and also for solutions.

1.2. Structure

Porphyrins are cyclic amines having a multiloop conjugated system, which is based on a 16-membered macrocycle containing usually 4 nitrogen atoms. The most famous member of the family of porphyrins - tetraphenylporphyrin (Fig. 1a). The rare earth element is incorporated into the central cavity of the molecule, Er and Yb metalloporphyrins are presented in Fig.1b,c.

![Fig. 1. Porphyrins: (a) tetraphenylporphyrin (TPP) (b) Yb(acac)TPP (c) Er(acac)TPPBr₄.](image)

1.3. Synthesis

The works about synthesis of porphyrin lanthanide complexes, both hydrophobic tetraarylporphyrins, Wong et al. (1974), and water-soluble, Horrocks and Hove (1978), were started at the end of the XX century. In these studies the incorporation of Yb and Er was made by heating of a porphyrin and ytterbium acetylacetonate in a microwave oven. A mix of solvents 1,2-dichlorobenzene and distillated dimethylformamide were used in the ratio (1:9) with an addition of dry lithium chloride. The reaction time was 15-20 min., the temperature of the oven was 145 °C, and the power was 650 w. After cooling, solvents were removed by pumping out of the reaction chamber. Metallocomplexes were separated one from another by preparative chromatography on aluminum oxide of II activity degree or on 5/40 μm silica gel. As a result of the synthesis metalloporphyrin Yb and Er -complexes were obtained with an yield of 58.4% and yield 58.7% respectively, Gorshkova et al. (2014).
2. Experimental

2.1. Materials

All measurements were performed for three series of samples: Ytterbium-based porphyrin (Yb(acac)TPP, Yb(acac)TPPBr₈), Erbium containing (Er(acac)TPP, Er(acac)TPPBr₈) and free-base porphyrin ligands bromine (TPPBr₈).

2.2. Calculations

The calculations were carried out using a plane-wave density functional theory (DFT) with the local density approximation (LDA) functional. The calculations were done taking periodic boundary conditions, plane wave basis set and ultrasoft pseudopotential. The changes in the position of atoms occur in steps of 0.01 Å.

2.3. General methods

All K-edge X-ray spectra were measured on the "Structural Materials" beamline of Kurchatov synchrotron radiation source, Chernyshov et al. (2009). The energy of the electrons in the storage ring was ~2.5 GeV, the typical current 80-100 mA. The measurements were carried out at room temperature in transmission geometry (channel-cut Si(111) monochromator), i.e. the intensity of X-ray beam was measured before and after of the sample by ionization chambers (with N₂/Ar mixtures for optimal detection efficiency) by the digital picoampermeter KEITHLEY. The monochromator was calibrated in accordance with a maximum jump derivative absorption spectra of the metal foils \( E_0 = 8949, 8363 \) and \( 13473 \) eV) for the K-edges Yb, Er and Br, respectively.

3. Results and discussion

3.1. Calculation

In order to describe obtained spectra we performed the model calculations of the geometric structures of porphyrins in a frame of DFT approximation. The geometrical parameters for the optimized structures of Yb(acac)TPP, Yb(acac)TPPBr₈ and Er(acac)TPP, Er(acac)TPPBr₈ interatomic distances are shown in Table 1.

3.2. EXAFS data

X-ray absorption spectra of RE metalloporphyrins were analyzed using IFEFFIT data analysis package 1.2.8, Colpas et al. (1991). The obtained spectra are shown in Fig. 2 in the energy scale relative to the absorption edge.

![EXAFS-spectra of porphyrins RETPP](image-url)
Note, that the intensity decrease of the ytterbium white line (Fig. 2a) and erbium (Fig. 2b), after bromination, indicates changes in the structure of the macrocycle ring. Such decrease of “white line” in spectra can be described by spreading of the distances from metal ion to the nearest atoms. The investigation of bromine by XANES (Fig. 2c) additionally demonstrates the presence of free molecular bromine in metalloporphyrins: the presence of the line B (Fig. 2c) Joshua (2009).

3.3. Analysis of EXAFS

EXAFS data ($\chi_{\text{exp}}(k)$) were analyzed using the IFEFFIT data analysis package, Colpas et al. (1991). EXAFS data reduction used standard procedures for the pre-edge subtraction and spline background removal. Fourier transformation (FT) of the $k^2$-weighted EXAFS functions $\chi_{\text{exp}}(k)$ over the ranges of photoelectron wave numbers $k = 2.5–13.0$ Å$^{-1}$. The structural parameters, including interatomic distances ($R_i$), coordination numbers ($N_i$) and Debye–Waller factors ($\sigma^2$), were found out by the non-linear fit of theoretical spectra to experimental ones. Fitting the spectra, in the $R$-space range for $k$ is selected to minimize the distortion of the Fourier transforms of insufficient statistics signal / noise in the measured spectra Fig.3.

Fig. 3 The oscillating part of EXAFS-spectra in the scale of the pulse, the experimental part - black, the fit- red. To: (a) Yb(acac)TPP; (b) Yb(acac)TPPBr; (c) Er(acac)TPP; (d) Er(acac)TPPBr.

Since the atomic structure of the compounds has been of the same type, the fitting was carried out for all compounds using the same scheme. In the primary consideration the maximum contribution to the resulting single path scattering corresponding to the first three coordination spheres of the metal atom M and 4 adjacent nitrogen atom, oxygen atoms, 8 carbon atoms were introduced. Next step consists of adding of the multiple scattering paths to the model because it contributes visible changes to the structure due to the high symmetry of the molecules.

The results of EXAFS-spectra processing and a systematic comparison of the experiments for complexes RE-TPP are presented in Table 1. As a result of the experimental and theoretical structural investigation it was established that bromination of porphyrines decrease the symmetry of porphyrine ring, this fact appears in splitting of the distances from carbon atoms which belong to porphyrin ring to the metal ion. But during the bromination a chemical state of the metal ion isn’t changed. Also by EXAFS shown that the metal ion is connected with two acetylacetone groups. Both experimental EXAFS and theoretical DFT study show consistent results.

| Table 1. The main geometrical parameters (bond lengths and coordination number), defined according to EXAFS spectroscopy. |
|----------------------------------------|
| Bond Type | Compound | Bond Length (Å) | Coordination Number | Debye-Waller Factor (^2) | 
| M-N, n,sig^2, M-N(cal) | Yb(acac)TPP | 2.35, 4, 0.003, 2.37 | 3.37, 4, 0.005, 2.43 | 4.20, 4, 0.003, 2.44 | 2.37, 4, 0.004, 2.43 |
| M-O, n,sig^2, M-O(cal) | Yb(acac)TPPBr | 2.33, 4, 0.002, 2.49 | 2.33, 4, 0.009, 2.60 | 2.2, 4, 0.004, 2.59 | 2.34, 4, 0.003, 2.32 |
| M-Ca, n,sig^2, M-Ca(cal) | Er(acac)TPP | 3.30, 8, 0.003, 3.35 | 3.10, 4, 0.008, 3.16 | 3.35, 8, 0.003, 3.15 | 3.26, 4, 0.012, 3.28 |
| M-Cb, n,sig^2, M-Cb(cal) | Er(acac)TPPBr | 3.34, 4, 0.008, 3.40 | 3.34, 4, 0.008, 3.40 | 3.33, 4, 0.012, 3.42 | |
| M-Cm, n,sig^2, M-Cm(cal) | Er(acac)TPP | 3.68, 4, 0.005, 3.66 | 3.56, 4, 0.003, 3.67 | 3.70, 4, 0.003, 3.69 | 3.57, 4, 0.030, 3.72 |
| M-Cb, n,sig^2, M-Cb(cal) | Er(acac)TPPBr | 4.38, 8, 0.007, 4.58 | 3.95, 4, 0.012, 4.08 | 4.45, 8, 0.003, 4.53 | 3.98, 4, 0.010, 4.33 |
| M-Cm, n,sig^2, M-Cm(cal) | Er(acac)TPPBr | 4.54, 4, 0.004, 4.63 | 4.7, 4, 0.005, 4.66 | 4.7, 4, 0.005, 4.66 |
4. Conclusion

Performed studies of rare-earth metal-based porphyrin compounds by XANES demonstrated:
- trivalent state of the metal in the compound, well agreed with the photoemission studies by Gorshkova et al. (2014).
- the possible presence of free molecular bromine in macrocycle, as well as the presence of water near the center of molecule, probably, directly connected to the RE metal.

Investigation of RE metalloporphyrins by EXAFS reveals:
- the changes in the molecular geometry in connection with the bromination
- good agreement of treated experimental data with calculations for all compounds.

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6. References

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