Electronic, local atomic structure of lutetium tetraphenylporphyrin: XPS and XAFS spectroscopy studies

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Abstract. The electronic and local atomic structure of lutetium metalloporphyrins Lu(acac)TPP and precursor tetraphenylporphyrin (TPP) have been studied by X-ray photoelectron spectroscopy (XPS) and absorption spectroscopy (XAFS). The XPS spectroscopy data show changes in the electronic structure of tetraphenylporphyrins under incorporation of the lutetium atom: a redistribution of the electron density between the nitrogen atoms of the pyrrole- and aza-group and appearance of one broadened peak of the N1s state. The integer trivalent state of the rare-earth metal (Lu³⁺) in metalloporphyrins has been confirmed by both XPS and XAFS methods.

1. Introduction
Because of nonlinear optical properties the metalloporphyrins are very promising compounds as an active substance for optical communications, optical and electrical signals processing, information storage [1]. Porphyrins are of interest as low-dimensional conductors [2], promising for nanotechnology and the creation of elements and devices based on sensitivity of individual macromolecules to electrical, magnetic and electromagnetic fields [1].

Molecules of porphyrins form stable complexes with rare-earth (RE) metals, which have intense absorption in the near-IR region of the spectrum [3]. Substitution of various metals into the meso- and/or β-positions of the macrocycle makes it possible to change the physico-chemical properties of metalloporphyrins. This plays an important role in their use in medicine and photochemistry [4].

This paper is devoted to the study of the electron and local atomic structures of lutetium tetraphenylporphyrin.

2. Methods
The porphyrin complexes were synthesized in the laboratory of the Moscow Technological University (MIREA), the synthesis was described in details in [5].
The electronic structure and the chemical bonding in porphyrins were studied experimentally by X-ray photoemission spectroscopy (XPS). High resolution Lu4d, Br3d, N1s, C1s, O1s and valence band (VB) spectra were measured at Kratos AXIS Ultra DLD spectrometer with the photon energy 1486.69 eV, AlKα mono, total resolution Ag3d5/2 was about 0.48 eV. Spectra were calibrated using Ag3d5/2 and In3d5/2 lines. Samples for XPS spectroscopy were pressed in to the indium substrate ex-situ. The surfaces of prepared samples were additionally cleaned by resistive heating up to ~ 400 K in ultra high vacuum (UHV) in-situ. The base pressure during measurements was in the range 5∙10^{-10}-2∙10^{-9} torr.

L3-Lu-L edge X-ray spectra were measured on the “Structural Materials” beamline of Kurchatov synchrotron radiation source [6]. The energy of electrons in the storage ring was 2.5 GeV, the typical current was 80-100 mA. The measurements were carried out at room temperature in transmission geometry (channel-cut Si(111) monochromator), the intensity of X-ray beam was measured before and after the sample by ionization chambers filled with N2/Ar mixtures for optimal detection efficiency. The monochromator was calibrated according with maximum jump derivative absorption spectra of K-Cu absorption spectra (E0= 8979 eV) of the metal foil.

3. Results and discussion

3.1. The XPS study.

The analysis of wide XPS spectra of the investigated porphyrins demonstrated the presence of all the elements making up the compounds (Lu4d, N1s, C1s, O1s). It is worth to note that the relative concentrations of elements, according to XPS, in the first approximation, correspond to the chemical composition.

A characteristic two-peak structure with binding energies of 399.4 and 397.2 eV was observed, in the XPS spectra of the core levels of N1s tetraphenylporphyrin (Fig.1a). This structure, corresponding to nitrogen in the pyrro-group (sp³ bond configuration) and aza-group (sp²), respectively, agrees well with the results for thiolporphyrins and related phthalocyanine compounds. There is a change in the state of N1s spectra of metalloporphyrins (Fig. 1b), indicating redistribution of the electron density between pyrro- and aza-N in porphyrins after addition of lutetium (deprotonation). Such a change is in a good agreement with the data obtained for RE and 3d metalloporphyrins (Me=RE, Fe, Co, Ni) and copper phthalocyanines [7,8,9]. The so-called “metallization” (introducing of a metal into the center of the TPP molecule) leads to the replacement of two hydrogen ions by a metal ion, which in turn equally interacts with all the nitrogen ions in the coordination cavity, thereby causing more uniform redistribution of the electron density between nitrogen and appearance of the single broadened peak N1s. It should be noted that splitting of the nitrogen line observed in the spectrum (Fig. 1b) can be explained by presence of the porphyrin, caused by the peculiarity of the synthesis.

Figure 1. Decomposition of XPS spectrum of the N1s level for TPP (a) and Lu(acac)TPP (b).

Lutetium is a rare-earth element with a fully filled f-electron shell and the Lu4d spectrum is represented by a doublet splitting, with an area ratio of 3:2. A doublet of chlorine Cl2p is superimposed on
the Lu4d line (Fig. 2), which is also related to the synthesis features. Parameters of the Lu4d line in oxide and metal were used in the decomposition of the lutetium spectrum in the porphyrin complex.

For all investigated lutetium complexes a wide peak in the XPS spectra of the core level C1s is observed. It corresponds to different carbon states in non-equivalent positions in the molecule whose peaks exhibit small chemical shifts (Fig. 3). Decomposition of O1s level in Lu(acac)TPP gives narrower lines responsible for oxygen in both the compound itself and in small amount of impurities. Decomposition of O1s and C1s level in Lu(acac)TPP is similar to ytterbium complex [8].

The spectra of the VB for studied porphyrins (hv = 1486.69 eV) are compared in Figure 4 with that for metal-free porphyrins.

The analysis of the experimental and published data [4,10] allows us to assume that the valence bands of porphyrins metalloporphyrins of RE, 3d metals and tetraphenylporphyrins are similar. They are formed by π- (in a range 1-6 eV), π+σ- (5-10 eV), and σ-states (6-16 eV) of porphyrin macrocycles and semi-core levels of rare-earth elements (4f, 5p) and according to the published data, in the first
approximation, can be described by a superposition of the spectra of the structural components, benzene and pyrrole.

3.2. XAFS research
The $L_3$-Er XANES (X-ray absorption near edge structure) spectrum in the macrocycle is shown in Fig.5a. The "white line" is observed as a single maximum at an energy of 9245 eV without any splitting for Lu(acac)TPP indicating an integer trivalent state of Lu in both compounds.

Fit of the calculated EXAFS spectrum to the experimental ones was carried out in the application of geometric optimization data (Fig.5b), by using the Artemis program [11].

![Figure 5.](image)

The results of processing EXAFS-spectra for Lu(acac) TPP (Table 1) and a systematic comparison of the results for complexes Yb(acac)TPP and Er(acac)TPP [12] indicate a small difference in the structure of the porphyrin core for various the rare earth element.

| Table 1. | Local structure parameters (bond length, coordination numbers and the Debye-Waller factors) for Lu(acac)TPP. |
|----------|--------------------------------------------------|
| atomic bonds | $R$, $N$, $\sigma^2$ |
| M-N | 2.38, 4, 0.003 |
| M-O | 2.26, 4, 0.005 |
| M-C$_a$ | 3.27, 4, 0.008 |
| M-C$_m$ | 3.63, 4, 0.003 |
| M-C$_b$ | 4.53, 8, 0.004 |

A further investigation of metalloporphyrins and their derivatives should give a better understanding of formation and distortion processes of the porphyrin macrocycle.

4. Conclusions
The change in the electronic state in porphyrins after introduction of rare earth into the central cavity of the molecule was demonstrated. In the XPS spectra of the investigated metalloporphyrins, single broadened peak of N1s states was observed after metallation. It indicates a small difference in the binding energy of pyrrole- and aza-N, while in the N1s spectrum of the tetraphenylporphyrin state a distinctive two-peak structure corresponding to nitrogen in the pyrrole ($sp^3$) and aza-group ($sp^2$), respectively, is observed. Thus, introduction of the RE atom into the central porphyrin area leads to a
more uniform redistribution of the electron density between the pyrrole and aza-group nitrogen and the appearance of broadened N1s peak with a binding energy in a range 398.1-398.3 eV in the XPS spectra.

The integer trivalent state of lutetium in metalloporphyrins was established, which is indicated in Lu(acac)TPP by both the doublet of the 4d lutetium line in XPS spectra and the unsplitted “white line” in \( L_\beta \)-Lu XANES spectra.

The analysis of the valence band of porphyrins formed by \( \pi \)- and \( \sigma \)-states of porphyrin macrocycles and semi-core levels of rare-earth elements (4f, 5p) revealed its similarity with RE metalloporphyrins, which agrees with quantum mechanical calculations.

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