Analysis of the X-ray absorption spectra near the cobalt K-edge of the Co(2,2'-Bipy)(i-Bu$_2$PS$_2$)$_2$ complex

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Abstract. The chelate Co(2,2'-Bipy)(i-Bu$_2$PS$_2$)$_2$ has been studied by X-ray absorption near-edge structure (XANES) spectroscopy. The experimental Co K-edge XANES of the Co(2,2'-Bipy)(i-Bu$_2$PS$_2$)$_2$ has been recorded. Theoretical analysis of Co K-XANES has been performed on the basis of the full-potential finite difference method using FDMNES code and real-space self-consistent full multiple-scattering approach within the muffin-tin approximation for potential shape (FEFF8.4 program). The comparison of the theoretical spectra with the experimental data has been done and a agreement between the theoretical and experimental XANES has been obtained.

1. Introduction

The chelates are cyclic compounds which are formed by means of a combination of metal ion and at least two reagent atoms. The reagents can have atoms of N, O or S as in the case of Co(2,2'-Bipy)(i-Bu$_2$PS$_2$)$_2$. The majority of chelates are well extracted by organic solvents. That is why the extraction of such compounds is finding a wide range of applications in analytical and radio chemistry as the element separation method [1].

The study of the chelates of 3d transition metals is of great scientific interest as they are applied in the modern material science. The physical and chemical properties of chelates depend on such factors as nature of metal, it’s charge, stoichiometry of the chelate, etc. Thus, studying the electron structure of a number of chelate compounds of 3d transition metals helps to understand their physical and chemical properties. X-ray absorption near-edge structure (XANES) spectroscopy [2,3] is a powerful tool that can give a unique information about geometrical structure (bond length and bond angles) and distribution of unoccupied electron state near the bottom of the conduction band of the compounds under study including complexes of 3d transition metals containing organic ligands. Recently, the XANES spectroscopy has been successfully applied for investigation of some nickel complexes (e.g., Ni(EtOCS)$_2$, Ni((C$_2$H$_5$O)$_2$PS)$_2$) [4-6]. In this study we present the experimental Co K-XANES spectra of complex Co(2,2'-Bipy)(i-Bu$_2$PS$_2$)$_2$ as well as the theoretical spectra simulated on the basis of several approaches.
2. Experiment
The method of synthesis of Co(2,2'-Bipy)(i-Bu₂PS₂)₂ complex is reported in [7].

The experimental Co-K-edge XANES of Co(2,2'-Bipy)(i-Bu₂PS₂)₂ complex was measured in transition using synchrotron radiation (SR) of the Kurchatov Center for Synchrotron Radiation and Nanotechnology (Moscow, Russia). The storage ring of the Kurchatov Synchrotron Radiation centre operates at 2.5GeV electron energy in storage ring and the 300 mA beam current. Monochromator is designed according to the conventional double-crystal scheme. Schematic view of the beamline is presented in Fig. 1.

![Figure 1. Block of monochromator [8]:](image)

- Beam position sensor is placed inside the vacuum channel, allows to control the vertical position of the SR-beam;
- Slits for defining the size of the beam with the step motor control;
- Monochromator with silicon (111) channel-cut crystal;
- Monitor for measuring the intensity of monochromatic beam.

The registration of Co K x-ray absorption spectrum of Co(2,2'-Bipy)(i-Bu₂PS₂)₂ has been carried out in transmission mode using ionization chambers. Energy resolution on the Co K-edge was better than 0.7 eV.

3. Results and discussion
The calculation of the Co K-XANES spectra were made by means of two approaches: the full multiple scattering (FMS) method within the muffin-tin approximation for the potential shape and the full-potential finite difference method (FDM) using software packages FEFF8.4 and FDMNES, correspondently. The algorithms for both methods used in calculations were described earlier in much details [9–11].

The atomic structure of the Co(2,2'-Bipy)(i-Bu₂PS₂)₂ complex and its electronic density intersection in the main plain of molecule are presented in the Figure 2 and 3, respectively. This complex consists of 79 atoms. The atomic coordinates used in the calculation were taken from the Cambridge Crystallographic Database Centre.

They are used as the zero approximation for the structure and were then verified by the fine analysis of XANES spectra. For such a system the muffin-tin model results in too-crude approximation and a full potential XANES calculation is required. Figure 4 proves this idea. Namely, an 'extra' shoulder A1 (not presented in experimental data) appears in the spectrum calculated within MT FMS approach.
Figure 2. Structure of the Co(2,2'-Bipy)(i-Bu₂PS₂)_2 complex.

Figure 3. Electron density distribution in Co(2,2'-Bipy)(i-Bu₂PS₂)_2 complex.

The modeling of electronic density has been made using Density functional theory (DFT), as implemented in ADF2008 code [12]. As one can see from Fig. 4, the comparison of MT FMS and non-MT FDM calculations clearly demonstrates the importance of non-MT effects in the XANES of Co(2,2'-Bipy)(i-Bu₂PS₂)_2 complex. Non muffin-tin effects lead to considerable changes in relative intensities of the Co K-edge XANES features in Co(2,2'-Bipy)(i-Bu₂PS₂)_2 complex. This could be due to existence of interatomic regions with non constant value of potential near the absorbing atom.

Figure 4. Shows the experimental XANES spectrum above the Co K-edge of the Co(2,2'-Bipy)(i-Bu₂PS₂)_2 and simulated ones.
4. Conclusions
Synchrotron based x-ray absorption spectroscopy was used for analysis of the Co(2,2'-Bipy)(i-Bu₂PS₂)₂ complex. Electronic structure of the complex was studied by means of density functional theory. The electronic charge density around the Co atom on the pyridine plane was visualized. A theoretical analysis of the XANES spectrum above the Co K-edge was carried out. It was shown that the non-muffin-tin effects are important to reproduce the features of the Co K-edge XANES spectra.

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