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2016 J. Phys.: Conf. Ser. 712 012137

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EXAFS characterisation of metal bonding in highly luminescent, UV stable, water-soluble and biocompatible lanthanide complexes

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Abstract. The combination of X-ray diffraction with EXAFS was employed to assess the coordination environment of lanthanide complexes in solutions. This method is based on the assumption that the local structure of lanthanide complexes in solution combines elements of the crystal structure of the complex in the solid state (single- or polycrystalline) and the elements of the local structure of a lanthanide salt, completely dissociated in the solvent (usually chlorides). The success of this approach is demonstrated with the lanthanide (III) 2,3,4,5,6-pentafluorobenzoate complexes, where the local structure in aqueous and methanol solutions were estimated. Moreover, the dissociation degree of the complexes in aqueous and methanol solutions was evaluated.

1. Introduction

Over the past decades EXAFS has been widely used for structural analyses of various compounds and materials, particularly when X-ray diffraction methods are not applicable or their application is relatively limited. For instance, EXAFS has proved to be a useful tool for analyses of metal complexes in solutions. Here we present a comprehensive approach for analysis of coordination environment of lanthanide complexes with pentafluorobenzoates (pfb) in solution with EXAFS by comparison with structural data obtained by conventional X-ray diffraction techniques in single- and polycrystalline samples. Previously it was shown, that combination of X-ray diffraction and EXAFS is a powerful tool in structural elucidation [1, 2].



The main idea underpinning the present study is the finding that pfb ligands possess different coordination modes depending on the metal used, and even complexes with the same metal can give rise to different molecular structures. Such a versatile structural chemistry observed in the complexes with this ligand urged us to investigate their molecular structures in solution. Given the fact that different ligating modes can be easily distinguished due to a large difference in Ln...C contact lengths, the presence of different scattering pathways in EXAFS spectra, corresponding to these contacts in different modes, can be successfully utilized for discrimination between them. Thereby, it is possible to evaluate the composition of coordination spheres of these complexes in solution.

The significance of knowing the coordination environment of these complexes in solution is further augmented by their possible application as bio-imaging probes for cellular studies due to their high photophysical performance, water solubility and low toxicity [3].

2. Experiment

Lanthanide complexes $\text{Ln}(\text{pfb})_3(\text{H}_2\text{O})_n$ were synthesized under the same conditions: concentrated aqueous ammonia was added to aqueous LnCl_3 ($\text{Ln}=\text{Pr-Lu}$ except of Pm) followed by adding a suspension of Hpfb in acetone/methanol (3:1), then the solution was evaporated (Fig. 1). The solid product was dried on air. All the solutions for XAFS measurements were the same concentration of 0.05M and adjusted to $\text{pH}=7.0$. The local structure of $\delta\text{-Ln}$, $\llbracket\epsilon\rrbracket\text{-Ln}$, $\text{H}_2\text{O-Ln}$, $\text{CH}_3\text{OH-Ln}$, $\text{H}_2\text{O-LnCl}_3$, $\text{CH}_3\text{OH-LnCl}_3$, has been elucidated using Ln L_{III} -edge X-ray absorption spectroscopy. The spectra were measured at the Structural Materials Science beamline of the Kurchatov Centre for Synchrotron Radiation (National Research Centre “Kurchatov Institute”, Moscow, Russia) in transmission mode using two ionization chambers filled with appropriate N_2/Ar mixtures. Experimental data reduction and analysis were performed using the IFEFFIT software suite [4] with FEFF [5] ab initio photoelectron phase and amplitude functions.

3. Results and discussion

In the present study crystal structures of polycrystalline samples of $\text{Ln}(\text{pfb})_3(\text{H}_2\text{O})_n$ (Fig. 1) designated as $\delta\text{-Ln}$, $\text{Ln} = \text{Eu, Gd, Tb, Dy, Ho, Er}$, and of $\text{Ln}(\text{pfb})_3$ designated as $\llbracket\epsilon\rrbracket\text{-Ln}$, $\text{Ln} = \text{Tm, Yb, Lu}$) were determined by X-ray diffraction, and their EXAFS spectra were measured at the Ln L_{III} -edge. To estimate the composition of coordination sphere around the lanthanide ion, EXAFS spectra were also obtained for aqueous ($\text{H}_2\text{O-Ln}$) and methanol solutions ($\text{CH}_3\text{OH-Ln}$). The applicability of the proposed method was evaluated using the $\delta\text{-Ln}$ complexes with known crystal structures. The first co-ordination sphere of $\delta\text{-Ln}$ consists of 9 oxygen atoms at the distances of 2.24-2.55 Å, belonging either to water or carboxyl groups of the ligand. These atoms were also revealed in EXAFS as $\text{Ln}\cdots\text{O}$ scattering path in the first coordination sphere. EXAFS spectroscopy allows us to distinguish them by the appearance of the $\text{Ln}\cdots\text{C}$ scattering path in the second shell. Indeed, according to the determined distance $d(\text{Ln}\cdots\text{C})$, the κ^1 ($R = 3.43\text{-}3.61$ Å) or κ^2 ($R = 2.68\text{-}2.73$ Å) ligand these co-ordination modes can be easily discriminated (Fig. 2). It goes without saying that different co-ordination modes of the ligand affect the Ln-O distance as well, but the deviation in the average distance between Ln and all 9 oxygen atoms was beyond the sensitivity of the experiment, and remained the same regardless of the co-ordination mode of the ligands used in the fitting model.

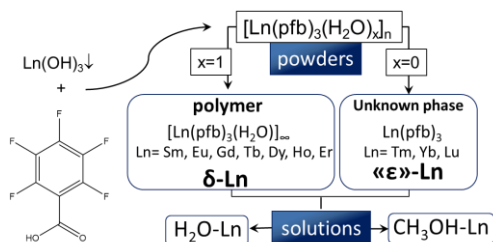


Figure 1. Schematic representation of samples studied in the present work.

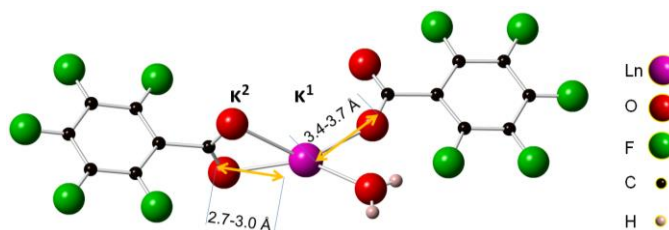


Figure 2. Two types κ^1 and κ^2 of Ln ion co-ordination by perfluorinated aromatic carboxylates.

The second co-ordination sphere of δ -Ln (Fig. 3) contained 2 carbon atoms of κ^2 -carboxylic group ($R=2.68$ - 2.73 Å) and 4 carbon atoms of κ^1 carboxylic group ($R=3.43$ - 3.61 Å). The contribution of the Ln \cdots Ln contacts is apparent for all the Ln complexes in powder state, corresponding to the polymeric structure of δ -Ln. The decrease of the Ln \cdots Ln distances from δ -Eu to δ -Er is in good agreement with the lanthanide contraction (Fig. 4). The obtained EXAFS spectroscopy data are consistent with the XRD results and confirm the same composition for all the complexes in the δ -Ln group, similar composition in the case of $\llbracket\epsilon\rrbracket$ -Tm and $\llbracket\epsilon\rrbracket$ -Yb, and different co-ordination modes of the ligands in $\llbracket\epsilon\rrbracket$ -Lu. Moreover, high accuracy in the determination of the Ln \cdots Ln distance in the EXAFS experiment was employed to optimise this interatomic distance during the Rietveld-refinement in X-ray analysis. At the same time, though the goodness of fit was satisfactory for all the complexes, a considerable deviation was observed in some cases.

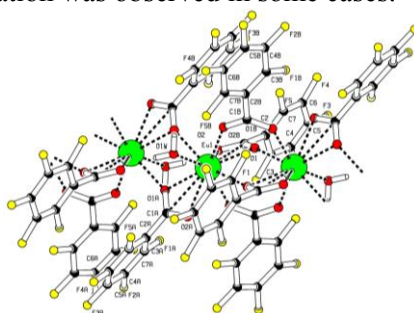


Figure 3. The structure of δ -Eu

To evaluate the dissociation degree of the complexes in aqueous and methanol solutions, their EXAFS spectra were compared with the spectra of corresponding powder samples and spectra of LnCl₃ aqueous solutions (H_2O -LnCl₃). The comparison between solutes and powder samples can provide an estimate for the number of co-ordinated ligands, along with their co-ordination modes. Using crystal structures of powder samples as a starting model, EXAFS spectra of complexes in water were analysed. The presence and the quantity of the Ln \cdots C scattering paths should characterise the number and type of carboxylic-groups, and therefore the number of co-ordinated ligands, as was previously demonstrated for solid-state samples. The FTs of the experimental EXAFS spectra and fitting curves for δ -Ln, $\llbracket\epsilon\rrbracket$ -Lu, H_2O -Ln and H_2O -LnCl₃ are shown in Fig. 4 for Ln = Eu, Er (Table 1). The EXAFS spectra of H_2O -LnCl₃ revealed two co-ordination spheres with the radii of 2.45 Å (oxygen atoms of the water molecules) and 3.28 Å (chloride atoms). It is in a good agreement with the previously reported results of MD simulation [6], which also claim that the second shell of water molecules appears at a distance of more than 4.5 Å.

Table 1. The data obtained from EXAFS spectra for Eu-series .

Sample		δ -Eu		H_2O -Eu		H_2O -EuCl ₃	
Shell number	Path	N	R, Å	N	R, Å	N	R, Å
1	Eu \cdots O	9	2.38	10	2.46	10	2.45
2	Eu \cdots C (κ^2)	2	2.68	2	2.76		
2	Eu \cdots C (κ^1)	4	3.43				
2	Eu \cdots Cl					1.5	3.28
3	Eu \cdots Eu	2	4.10				

In contrast to H_2O -EuCl₃, the EXAFS spectra of H_2O -Eu reveal the presence of the co-ordination sphere with the radius of 2.8 Å, which corresponds to the two κ^2 -carboxylic carbon atoms.

Therefore the EXAFS spectrum of **H₂O-Eu** shows the partial dissociation of the complex, since only two ligands are co-ordinated, and Eu³⁺ co-ordination sphere is further supplemented by water molecules (Fig. 3). In contrast, in **H₂O-Er** three κ¹-carboxylic carbon atoms are present according to the EXAFS spectrum (Fig. 4), which suggests that erbium pentafluorobenzoate does not dissociate in water. The same behaviour was found for **H₂O-Ho**, **H₂O-Tm** and **H₂O-Yb**, while the second co-ordination shell of **H₂O-Lu** contains two κ² and one κ¹-carbon atom as in the «ε»-Lu powder.

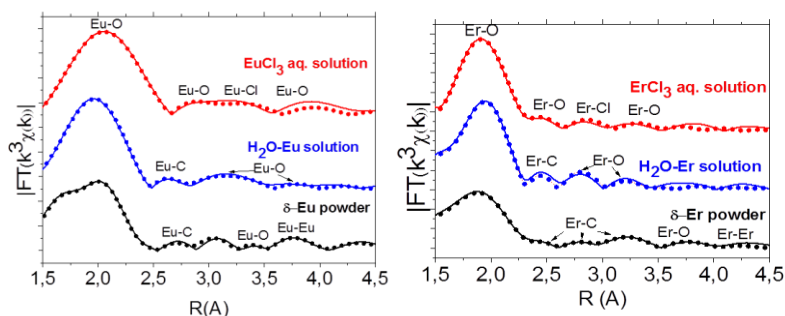


Figure 4. The comparison of the EXAFS spectra of δ -Ln, **H₂O-Ln (0.05M)** and **H₂O-LnCl₃ (0.05M)**: Ln = Eu (left) and Ln = Er (right), lines – experiment, dots - theory

Thus, water solutions of Ln(pfb)₃(H₂O)_x (Ln=Eu, Gd, Tb, Dy, Ho) partially dissociate, while the lanthanides from the end of the row (Ln = Er, Tm, Yb, Lu) do not undergo dissociation, which is consistent with the solubility data [3]. The similar findings were obtained for the methanol solutions of the complexes. The major difference was that all the complexes had the same molecular structure with only one scattering path for Ln···C in the second shell, which is in line with ¹⁹F NMR spectroscopy data and mirrors lower co-ordination ability of methanol compared to water [3].

4. Conclusions

In the present study we have demonstrated, how convenient can be the synergy of X-ray diffraction and EXAFS for elucidation of coordination environment of lanthanide complexes in crystals and solutions. The X-ray diffraction of polycrystalline samples Ln(pfb)₃(H₂O)_x revealed the presence of several phases, depending on the size of the Ln atom. Following the increase of charge density on Ln³⁺, rearrangements in the co-ordination sphere were observed, as water molecules competed with pfb⁻ ligands. This structural change was also observed in EXAFS spectroscopy by the presence of two scattering paths in the second shell. These crystal structures were used as starting models for analysis of molecular structures solutes. In the latter case, we observed the alteration of co-ordination mode in **H₂O-Ho**, which appeared in the change of corresponding scattering path Ln···C, while in the case of **H₂O-Lu** both scattering paths were revealed, similarly to the powder sample, following the lanthanide contraction.

Acknowledgments

A. Kalyakina and V. Utochnikova gratefully acknowledge the financial support of the state Baden-Württemberg (exchange ZOIV program) and RFBR (Grant Nos. 13-03-12453 and 14-03-32052).

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