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K-edge XANES investigation of octakis(DMSO)lanthanoid(III) complexes in DMSO solution and solid iodides

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Abstract

The potentiality of high energy XANES (X-ray absorption near edge structure) as a structural tool for lanthanoid-containing systems has been explored. The K-edge XANES spectra of La³⁺, Gd³⁺, and Lu³⁺ ions both in DMSO solution and solid octakis(DMSO)lanthanoid(III) iodides have been analysed. Although the K-edges of lanthanoids cover the energy range 38 (La) to 65 (Lu) keV, the large widths of the core hole states do not appreciably reduce the potential structural information of XANES data. We show that, for lanthanoid compounds, accurate structural parameters are obtained from the analysis of K-edge XANES signal if a deconvolution procedure is carried out. We found that in solid octakis(DMSO)lanthanoid(III) iodides the Ln³⁺ ions are coordinated by eight DMSO ligands arranged in a quite symmetric fashion. In DMSO solution the Ln³⁺ ions retain a regular eight-coordination structure and the coordination number does not change along the series. At variance with water the second coordination shell has been found to provide a negligible contribution to the XANES spectra of Ln³⁺ ions in DMSO solution.

1 Introduction

X-ray absorption spectroscopy (XAS) is an excellent tool to investigate the coordination structure of ions in solution and this technique is becoming the method of choice in many fundamental and applicative fields. Environmental chemistry is one important area that can strongly benefit from the use of the XAS technique and one of the most important issues in this field is nuclear waste remediation and disposal processes. Complexation of lanthanoid (Ln) and actinoid ions in solution is a very useful tool for separation of these elements and a

deep characterization of their solvation structure in different systems is mandatory to select the best performing solvents.^{1,2}

XAS spectra have been typically split into a low-energy region, termed XANES (X-ray absorption near-edge structure), and a region which extends from about 50 eV to more than 1000 eV above the edge, which is called EXAFS (extended X-ray absorption fine structure). While the EXAFS technique has been widely employed in the past to gain structural information on ion complexes in solution,³⁻²⁴ the situation is different concerning the XANES region. This part is very sensitive to the structural details of the absorbing site and, in principle, an almost complete recovery of the three dimensional structure can be achieved from the experimental data. However, due to the difficult theoretical treatment of the XANES features the use of this technique on a quantitative basis was rather restricted in the past.²⁵⁻²⁸

The aim of the present work is to explore the potentiality of the XANES spectroscopy above the Ln K-edges in elucidating the coordination structure of lanthanoid ions in non-aqueous solvents. In the past XAS has in general been confined to absorption edges below 30 keV as the structural signal can be strongly damped at very high energy. In fact, the higher the energy of the absorption edge, the shorter the lifetime of the excited atomic state, causing damping and broadening of the edge features. For this reason almost all the XANES investigations dealing with lanthanoid compounds have been carried out above the L₃-edges. Nevertheless, recent investigations on lanthanoid systems both in the solid state and in aqueous solutions have shown that use of Ln K-edge XAS spectra has some advantages compared to the L₃-edges.²⁹⁻³¹ In particular, the quantitative analysis of the XANES spectra at high energy is favoured both by the lower intensity of the white line and by the smaller influence of double-electron excitation processes. From the experimental point of view, an important advantage of using the K-edge spectra is that at very high energy the absorption of most materials is very low, and the samples can be held in cells mounting almost any type of windows. This facilitates, for example, the use of high-pressure cells to perform experiments under extreme conditions of pressure and temperature. Nowadays, high energies are commonly accessible via third-generation synchrotron radiation sources and beamlines that can provide sufficient flux up to 70-80 keV.

In the present study we carried out a thorough investigation of the coordination geometry of dimethylsulfoxide (DMSO) solvated lanthanoid(III) ions in solid iodide salts and in solution, using K-edge XANES spectroscopy. DMSO is a very efficient solvent for electrolytes because of its high dipole moment, and high permittivity. The electron-pair donor ability is higher than that for water,³² and DMSO is sterically more demanding as a ligand. For the fully DMSO-solvated lanthanoid(III) ions all crystal structures reported show discrete octakis(DMSO)lanthanoid(III) complexes, e.g., in the iodide, bromide, and perchlorate salts, often with disordered DMSO ligands.³³⁻⁴¹

All octakis(DMSO)lanthanoid(III) iodides display an eight-fold coordination with a distribution of Ln-O bond distances with alternative positions for at least one of the ligands.⁴¹ The coordination state of Ln³⁺ ions in DMSO solution is still controversial; spectroscopic and crystallographic studies of lanthanoid iodides revealed that lanthanoid(III)

ions have a similar eight-coordinated configuration both in liquid DMSO and in the solid state.⁴¹⁻⁴³ In these works it was found that the coordination number did not change along the series, although the decrease in the mean Ln-O bond distances was greater than expected on the basis of existing ionic radius data for eight-coordination.⁴¹ However, according to other studies, some changes in the average coordination number occur along the lanthanoid series;⁴⁴ a similar irregularity was reported by Buenzli et al. on the basis of FT-IR studies of lanthanoid trinitrates in the presence of DMSO in anhydrous acetonitrile.⁴⁵ This result was confirmed in a very recent investigation dealing with apparent molar volumes and compressibilities of Ln³⁺ trifluoromethanesulfonates in DMSO.⁴⁶

Here, we present a detailed description of the K-edge XANES data analysis for three ions namely La³⁺, Gd³⁺ and Lu³⁺ with the aim of providing definitive insights into the coordination structure of Ln³⁺ ions in DMSO solution. Moreover, we show the feasibility and the power of XANES performed at high energy in providing important information on the coordination structure of lanthanoid containing systems.

2 Experimental Section

2.1 XAS data collection

Crystalline octakis(DMSO) lanthanoid(III) iodides, [Ln(OS(CH₃)₂)₈]I₃ (Ln = La, Gd, and Lu), and hexakis (N,N'-dimethylpropyleneurea) gadolinium(III) iodide were prepared as described elsewhere.^{41,47} 0.2 M solutions were prepared by dissolving the solid compounds in DMSO (Aldrich) and N,N'-dimethylpropyleneurea (dmpu), (reagent grade, BASF AG), freshly distilled over calcium hydride (Fluka) under reduced pressure. K-edge XANES spectra were collected at the bending magnet beamline BM29,⁴⁸ at the European Synchrotron Radiation Facility (ESRF), in transmission geometry. The storage ring was operating in 16-bunch mode with a typical current of 80 mA after refill. The K-edge spectra were collected using a Si(511) double crystal monochromator with the second crystal detuned 20% for harmonic rejection. The L₃-edge measurements were performed at the wiggler beam line 4-1 and the bending magnet beamline 2-3 at the Stanford Synchrotron Radiation Laboratory (SSRL), Stanford, CA, which was operated at 3.0 GeV and a maximum current of 100 mA. The DMSO and dmpu solutions were kept in cells with Kapton film windows and Teflon spacers. Solid samples were diluted with boron nitride to give an absorption change over the edge of about one logarithmic unit.

2.2 XANES data analysis

The XANES data analysis was carried out with the MXAN code in the framework of the full multiple scattering scheme.⁴⁹ The MXAN method is based on the muffin tin (MT) approximation for the shape of the potential and uses a complex optical potential, based on the local density approximation of the self-energy of the excited photoelectron. At the beginning the MT radii are chosen according to the Norman criterion and then empirically adjusted to take into account the charge of the molecular complexes, while the potential is recalculated at each step of the minimization procedure. The self-energy is calculated in the framework of the Hedin-Lundqvist scheme. To avoid the relevant overdamping at low energies, MXAN uses a phenomenological approach to calculate the inelastic losses on the

basis of a convolution of the theoretical spectrum. This calculation uses only the real part of the HL potential, with a suitable Lorentzian function having an energy-dependent width of the form $\Gamma_{tot}(E)=\Gamma_c+\Gamma_{mfp}(E)$. The constant part, Γ_c , includes the core hole lifetime, while the energy-dependent term, $\Gamma_{mfp}(E)$, represents all the intrinsic and extrinsic inelastic processes. The $\Gamma_{mfp}(E)$ function is zero below an onset energy, E_s (which in extended systems corresponds to the plasmon excitation energy), and begins to increase from a value, A_s , following the universal functional form of the mean free path in solids. Both the onset energy E_s and the jump A_s are introduced in the $\Gamma_{tot}(E)$ function via an arctangent functional to avoid discontinuities and to simulate the electron-hole pair excitations. Their numerical values are derived at each computational step (i.e., for each geometric configuration) on the basis of a Monte Carlo fit. The experimental resolution is taken into account by a Gaussian convolution. The minimization procedures have been carried out starting from the X-ray structure of octakis(DMSO) lanthanid(III) iodides,⁴¹ and testing different coordination models. The Ln-O and S-O distances, and the O-Ln-O and Ln-O-S angles were optimized while the geometry of the DMSO molecules and the relative orientation of the ligands were kept fixed. The hydrogen atoms have been included in the MXAN analysis.

Least-square fits of the experimental data in the space of the structural parameters were achieved by minimizing the residual function defined as:

$$R_{sq} = \frac{\sum_{i=1}^m w_i (y_i^{th} - y_i^{exp})^2}{\varepsilon_i^2 \sum_{i=1}^m w_i} \quad (1)$$

where m is the number of data points, y_i^{th} and y_i^{exp} are the theoretical and experimental values of absorption, respectively, ε_i is the individual error in the experimental data set, and w_i is a statistical weight. For $w_i=\text{constant}=1$, the square residual function, R_{sq} , becomes the statistical χ^2 function. Here, we assumed a constant experimental error, $\varepsilon=1.2\%$, for the whole experimental data set. Six non-structural parameters have been optimized, namely the Fermi energy level E_F , the core hole lifetime Γ_c , the experimental resolution Γ_{exp} , the threshold energy E_0 , and energy E_s and amplitude A_s of the plasmon.

3 Results

3.1 High energy K-edge X-ray absorption near edge spectra

Since multiple-scattering effects make large contributions to the low-energy region of the absorption spectra, XANES is very sensitive to the geometric environment of the absorbing site. Therefore, its quantitative analysis might provide additional insights into the coordination structure of the photoabsorber atom that are not achievable from the analysis of the EXAFS region. However, when dealing with heavy elements the K-edge transitions occur at high energy and due to the large core-hole widths of the absorbing atoms the XANES signal is strongly broadened and the structural oscillations are smeared out from the spectra. To overcome this problem it has been suggested to apply core-hole width deconvolution methods to XANES data that largely facilitate the detection of spectral features and the comparison with theoretical calculations.⁵⁰

Figure 1 shows the raw K-edge XANES spectra of La^{3+} , Gd^{3+} and Lu^{3+} ions in DMSO solution where the effect of the core-hole life time on high-energy spectra is clearly visible. As expected the edge resonances are strongly damped and the intensity of the main transition peaks becomes much smaller going from lanthanum(III) to lutetium(III). Note that the core-hole widths at the K-edge are $\Gamma_c = 14.1, 22.3$ and 33.7 eV for lanthanum, gadolinium and lutetium, respectively.⁵¹ In Figure 1 overimposed on the raw data we report the XANES spectra where a deconvolution of the tabulated core-hole widths has been performed, applying Gaussian filters with full width at half maximum values of 3.8, 5.7 and 6.0 eV for La, Gd and Lu, respectively. After deconvolution, the threshold regions are considerably sharpened with respect to the original spectra, and the intensity of the structural oscillations is also clearly enhanced. It is important to outline that the white line intensities observed in the deconvolved spectra of Figure 1 are mainly related to the gaussian filter used in the deconvolution procedure, and no direct physical information can be derived from them. An ideal deconvolution with no filter would provide the real shape of the XANES region, but due to the finite noise level of the experimental data, this approach is actually impossible. However, after the deconvolution procedure the K-edge XANES spectra will have a similar shape and intensity as the L_1 -edge ones. In fact, the broadening associated with the core-hole width of the L_1 -edges ($\Gamma_c = 4.06, 5.05$ and 5.54 eV for La, Gd and Lu, respectively) is comparable with the one present in the deconvolved K-edge spectrum due to the adopted Gaussian filters. As a consequence when high quality and low noise K-edge spectra are subject to a deconvolution procedure, most of the structural and electronic information there contained is highlighted. This allows one to use the XANES spectra at the K-edge to obtain structural and electronic information on systems absorbing at very high energies, 30 keV or more. This is an advantage as the theoretical framework for the quantitative analysis of the XANES at K-edges is less problematic and better established. In particular, several XAS investigations on the lanthanoid(III) ions have shown the presence of multielectron excitations at the L-edges of these elements.⁵²⁻⁵⁸ The presence of anomalous peaks, appearing in the region between 60 and 200 eV above the edge and superimposed onto the structural oscillatory signal, has been explained as due to double-electron transitions $2p4d \rightarrow 5d^2$ in the case of the L_3 and L_2 -edges, and $2s4d \rightarrow 6p5d$ for the L_1 spectra.⁵³ When the features associated with the opening of multielectron thresholds are sharp and structured, as in the case of the lanthanoid L-edges, they alter the structural signal hampering an accurate extraction of the structural parameters from the XANES spectra. The presence of multi-electron excitation channels is detected also in the K-edge spectra of lanthanoid containing systems but in this case they do not give rise to the sharp features which are visible in the L-edge spectra due to the broadening effect caused by the short life time of the excited atomic state.

To assess the sensitivity of high energy K-edge XANES spectra towards the geometrical arrangement in the proximity of heavy atoms it is useful to compare the experimental data of systems where the coordination structure around the lanthanoid ions is known to be different. Because of the space-demanding properties of dmpu upon coordination, dmpu solvated metal ions often show coordination numbers lower than those found in corresponding hydrates and solvates of oxygen donor solvents without steric requirements beyond the size of the donor atom. All lanthanoid(III) ions are seven-coordinate in dmpu

solution, except lutetium(III) which is six-coordinated in regular octahedral fashion, whereas in the solid iodide salts the dmpu solvated lanthanoid(III) ions are all six-coordinate in regular octahedral fashion.⁴⁷ The upper panel of Figure 2 shows the raw K-edge XANES spectra of gadolinium in solid hexakis (dmpu) iodide, in solid octakis (DMSO) iodide and in dmpu solution, while the corresponding deconvolved spectra are shown in the lower panel of the same figure. As previously mentioned the number of coordinating oxygen donor ligands is six, seven and eight in the solid dmpu iodide, dmpu solution and solid DMSO iodide, respectively. The raw XANES spectra of Figure 2 show sizable differences in the whole energy region. In particular, there is a leading oscillation whose frequency increases on going from the six- to the eight-coordinated model, as a result of the increasing Gd-O distance. This difference is more evident in the deconvolved spectra that show the presence of additional features over-imposed on the main oscillation. This finding demonstrates the sensitivity of the XANES spectroscopy in determining the number of coordinating ligands and this technique is a valuable tool to establish the coordination geometry of complexes both in solid and liquid systems.

3.2 Coordination structure of La^{3+} , Gd^{3+} and Lu^{3+} ion in solid octakis(DMSO) iodides and in DMSO solution

To shed light on the structure of the solvation complexes of the Ln^{3+} ions in DMSO solution, a useful strategy is to use solid salts of known structure as starting coordination models. To this end we have collected the XANES spectra at the K- and L_3 -edges of solid octakis(DMSO) lanthanoid(III) iodides. In the crystallographic structures the Ln^{3+} ions are coordinated by eight DMSO molecules arranged in a distorted square antiprism with a distribution of Ln-O bond distances with alternative positions for at least one of the ligands.⁴¹ The difficulty to unambiguously determine the mean Ln-O bond distances due to the disorder in the crystal structures prompted an EX-AFS study, which is lattice-independent, that provided mean Ln-O bond distances in good agreement with the crystallographic determinations.⁴²

In Figure 3a the raw K-edge XANES spectra of solid octakis(DMSO) lanthanum(III), gadolinium(III) and lutetium(III) iodides are compared with the spectra of the DMSO solutions. For all three elements the two spectra are identical in the whole energy range suggesting that the coordination of the ions in the two systems is the same. Any-how, due to the short lifetime of the excited atomic state, both the edge resonance and the structural oscillations are strongly damped and therefore, it is useful to apply a core-hole width deconvolution procedure to the XANES spectra.⁵⁰ As previously mentioned the raw K-edge experimental data have been deconvolved of the whole tabulated core hole widths and a Gaussian filter has been applied. The deconvolved spectra of the Ln^{3+} ions in DMSO solution and in the iodide crystals are shown in Figure 3b. Also in this case the solution and solid XANES spectra are identical, reinforcing the similarity of the first-neighbor coordination geometry.

It is interesting to verify if the content of structural information that has been retrieved from the XANES spectra using the deconvolution procedure is similar to that contained in the L_3 -edge data. To this end in Figure 4 we report the comparison between the L_3 -edge XANES

spectra of solid octakis(DMSO) lanthanum(III), gadolinium(III) and lutetium(III) iodides and those in DMSO solution. The L₃-edge XANES are characterized by the presence of a very intense white line that makes the quantitative analysis of these spectra quite challenging. Nevertheless, the L₃-edge XANES of the solid samples are identical to the DMSO solution ones, thus suggesting that the local structure of the Ln³⁺ ions in the two systems is the same, as previously shown by the K-edge spectra.

In the first step, we carried out a quantitative analysis of the deconvolved K-edge XANES spectra of the solid octakis(DMSO) lanthanum(III), gadolinium(III) and lutetium(III) iodides with the aim of assessing the potentiality of XANES at high energy in elucidating the coordination geometry of lanthanoid-containing systems. We have thus applied the MXAN procedure starting from the crystallographic structures⁴¹ and refining the structural and non-structural parameters. In the fits, eight DMSO molecules were included, and two different minimization strategies were used; in the former, the eight Ln-O first shell distances were refined independently, while in the latter a single Ln-O distance was optimized for all of the ligands. In both cases the best fit geometry resulted in a symmetric distribution of distances around the Ln³⁺ ions. The results of the fitting procedures are shown in the left panels of Figure 5. The agreement between the experimental data and the best-fit calculation is very good for the three ions (R_{sq} =1.5, 1.3 and 1.1 for lanthanum, gadolinium and lutetium, respectively), and the structural parameters obtained from the minimization procedures are listed in Table 1, where they are compared with the average values derived from the crystal structure determinations and from the EXAFS data analysis.⁴² Note that the structural values of the Ln-O distances obtained from the XANES analysis are in perfect agreement with the previous determinations within the reported errors. As far as the non structural parameters are concerned, the Γ_c values obtained from the minimization are 4.4, 6.4 and 7.1 eV for lanthanum, gadolinium and lutetium, respectively. The best fit geometry obtained for the octakis(DMSO) lutetium(III) iodide is depicted in Figure 6, as an example. It is important to stress that, as far as the relative orientation of the methyl groups is concerned, the XANES analysis has been carried out keeping the symmetry of the starting X-ray structure. This strategy has been adopted as with MXAN it is not possible to optimize the Ln-methyl distance and the dihedral angles around the Ln-O and O-S bonds imposing a constrain on the internal DMSO geometry, or taking into account the methyl steric hindrance. As a consequence the increase of the number of structural parameters used in the minimization could lead to an unphysical structure. Therefore, from the XANES analysis it is possible to determine only the symmetry of the first shell and the Ln-O-S angle, and the structure shown in Figure 6 is a very reasonable guess of the actual coordination polyhedron.

Additional fitting procedures have been also applied to the raw XANES spectra and the agreement between the experiment and the calculated model has been found poorer as compared to the deconvolved spectra (for the raw data R_{sq} =1.7, 1.5 and 1.3 for lanthanum, gadolinium and lutetium, respectively). It is known that systematic errors in the MXAN analysis can arise mostly because of the poor approximation used for the phenomenological broadening function $\Gamma_{tot}(E)$ that mimics the electronic damping.⁵⁹⁻⁶¹ This can explain the better agreement between the experimental and calculated spectrum obtained for the

deconvolved data. Note that the structural parameters obtained from the two analyses are equal within the statistical errors. However, as expected, the statistical errors obtained from the minimization are slightly larger in the case of the raw data, as compared to the deconvolved ones.

In the second step, we analysed the deconvolved K-edge XANES spectra of the La^{3+} , Gd^{3+} and Lu^{3+} ions in DMSO solution with the aim of providing a definitive answer on the coordination structure of the solution complexes. To examine the compatibility of the DMSO solution K-edge XANES spectra with the existence of a eight-coordinated complex for all the solvated lanthanoid(III) ions, we performed a minimization of the experimental data including only the first hydration shell and using the distorted eight-fold geometry of the crystals. The XANES data analysis has been carried out using the same strategy previously described, and also in this case the best-fit structure resulted in a symmetric eight-coordinated cluster for all the three Ln^{3+} ions. The results of the fitting procedures are shown in Figure 5 b while the bond metrics are detailed in Table 1. The agreement between the theoretical and experimental spectra is very good for all the three ions (R_{sq} =1.4, 1.2 and 1.1 for lanthanum, gadolinium and lutetium, respectively) and the Γ_c values obtained from the minimization procedures are the same previously determined for the solids. Also the Ln-O first shell distances determined from the XANES analysis of the solutions are the same as those found for the crystals and determined from EXAFS (see Table 1).^{41,42} All together these findings demonstrate that the Ln^{3+} ions in DMSO solution form a coordination complex having a eight-fold geometry and the coordination number does not change along the series.

3.3 Discussion and Conclusions

We have measured XANES spectra at the K-edge of lanthanoid(III) ions in DMSO solution and in solid octakis(DMSO) lanthanoid(III) iodides in the energy region 38-65 keV, demonstrating the feasibility and the power of XANES performed at high energy. The effect of the core-hole lifetime broadening, though apparent, can be removed using deconvolution procedures, if high quality data are collected. It is shown that the analysis of the K-edge XANES data provides accurate structural results and it is easier to carry out as compared to the L_{3-} -edge, in the presence of a well-defined structure. This is due both to the absence of intense white lines and to the smaller influence of the double-electron excitations.

From the analysis of the XANES data we concluded that the Ln^{3+} ions retain a regular eight-coordination structure in DMSO solution along the series. These results confirm previous EXAFS investigations while are in contrast with FT-IR studies that found coordination number changes along the lanthanoid series.⁴⁵ Note that in a more recent FT-IR study it was concluded that such a change in the coordination number value does not occur in pure DMSO.⁴⁴

It is interesting to compare the behaviour of the lanthanoid series in water and in DMSO solution. Recently, it has been shown that the lighter lanthanoid ions are nine-coordinated in trigonal tricapped fashion in water, while the last elements of the series endure a decrease of the hydration number.⁶²⁻⁶⁴ Such a decrease is not found in DMSO solution and this can be explained by the high dipole moment and sterical hindrance of DMSO that dominate the

ion-ligand interaction. Note that the distance contraction across the series is 0.09 Å from lanthanum to gadolinium and 0.2 Å from lanthanum to lutetium, that is smaller than what observed in water.⁶⁵ This is probably due to the fact that the coordination number in DMSO is constant, while in water we have a nine-fold structure (even with ten-fold structures dynamically accessible) for light lanthanoids, while eight-fold structures for heavy ions.

A last remark we would like to make concerns the different contribution of the second coordination shell to the XANES spectra in water and DMSO solution. In recent works it has been shown that the second hydration shell provides a detectable contribution to the L₃-edge XANES spectra of lanthanoid ions in aqueous solution and to the NEXAFS spectra of blocked alanine in water solution.^{31,66} In particular, even if the first coordination shell is identical in water and in solid trifluoromethanesulfonate, the two XANES spectra show sizable differences both in the edge and higher energy region (see Figure 3 of Ref.³¹). A different behaviour has been found in DMSO as the solution and the solid octakis(DMSO) lanthanoid(III) iodide XANES spectra are identical for all ions both at the L₃- and K-edge. This is a clear indication that the second coordination shell does not provide any detectable contribution to the XANES spectra. Altogether our results show that the sensitivity of XANES to the Ln³⁺ second coordination sphere depends on the nature of the solvent. A detectable contribution of the second This finding has been also Moreover, given the very close similarity of the solid and solution DMSO XANES spectra, the first shell structure is expected to be the same for all the Ln³⁺ ions, as it occurs for the crystallographic structures.⁴¹ The coexistence of different coordination complexes in DMSO solution for the last elements of the series that was suggested in previous works seems to be unlikely as it would give rise to differences in the XANES spectra of the solid and solution samples, as it occurs for water.

In conclusion, the results of this investigation pave the route for the use of the K-edge XANES spectroscopy for structural investigations of systems containing heavy elements.

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Fig. 1. Comparison between the raw K-edge (black dotted line) and deconvoluted (red solid line) XANES spectra of La^{3+} , Gd^{3+} , and Lu^{3+} in DMSO solution.

Fig. 2.

Upper panel: raw K-edge XANES spectra of solid hexakis (dmpu) gadolinium (III) iodide (black line), gadolinium (III) ion in dmpu solution (red line) and solid octakis (DMSO) gadolinium (III) iodide (blue line). Lower panel: deconvoluted K-edge XANES spectra of solid hexakis (dmpu) gadolinium (III) iodide (black line), gadolinium (III) ion in dmpu solution (red line) and solid octakis (DMSO) gadolinium (III) iodide (blue line).

Fig. 3.

a) Comparison of the raw K-edge XANES spectra of La^{3+} , Gd^{3+} and Lu^{3+} in DMSO solution (black dotted line) and solid octakis (DMSO) lanthanoid(III) iodides (red solid line). b) Comparison of the deconvoluted K-edge XANES spectra of La^{3+} , Gd^{3+} and Lu^{3+} in DMSO solution (black dotted line) and solid octakis (DMSO) lanthanoid(III) iodides (red solid line)

Fig. 4. Comparison of the L₃-edge raw XANES spectra of La³⁺, Gd³⁺ and Lu³⁺ in DMSO solution (black dotted line) and solid octakis(DMSO) lanthanoid(III) iodides (red solid line).

Fig. 5.

a) Comparison of the deconvolved K-edge XANES experimental spectra of solid octakis(DMSO) lanthanum(III), gadolinium(III) and lutetium(III) iodides (black dotted line) and the theoretical spectra (red solid line). b) Comparison of the deconvolved K-edge XANES experimental spectra of La^{3+} , Gd^{3+} and Lu^{3+} ions in DMSO solution (black dotted line) and the theoretical spectra (red solid line).

Fig. 6.
Best-fit structure of the octakis(DMSO) lutetium(III) iodide first shell cluster as determined from the XANES analysis.

Table 1

First shell Ln-O distance of solid octakis (DMSO) lanthanum(III), gadolinium(III), and lutetium(III) iodides and of La^{3+} , Gd^{3+} and Lu^{3+} ions in DMSO solution. The crystallographic and EXAFS determinations are reported for comparison.

	La-O $R(\text{\AA})$	Gd-O $R(\text{\AA})$	Lu-O $R(\text{\AA})$
$\text{Ln}(\text{DMSO})_8\text{I}^a$ cry X-ray	2.49	2.38	2.30
$\text{Ln}(\text{DMSO})_8\text{I}^b$ cry EXAFS	2.507	2.391	2.300
$\text{Ln}(\text{DMSO})_8\text{I}^c$ cry XANES	2.49(2)	2.39(2)	2.30(2)
Ln^{3+} in DMSO ^b sol EXAFS	2.503	2.380	2.297
Ln^{3+} in DMSO ^c sol XANES	2.49(2)	2.40(2)	2.29(2)

^aRef. 41,

^bRef. 42,

^cthis work.