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XAS study of americium complexes with calixarene bearing carbamoylmethylphosphine oxide moieties

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Sample preparation for the EXAFS-spectroscopy study

The ARG reagents were used in this work. Calix[4]arene bearing four CMPO moieties on the upper rim **1**, 5,11,17,23-tetrakis[(diphenylphosphoryl)acetylamino]-25,26,27,28-tetra(pent-1-yloxy)calix[4]arene, and 2-(1-adamantyl)sulfoacetic acid **2** were produced at the Chemical Department of Lomonosov Moscow State University as reported.[S1,S2] 1,2-Dichloroethane was additionally purified by distillation under reduced pressure.[S3]

Complexes **3a,b** were synthesized as follows:

^{243}Am(NO$_3$)$_3$ aqueous solution in 4 M HNO$_3$ of 6 MBq ml^{-1} specific activity ($T_{1/2}$ = 7364 years) was placed in two dishes of 0.5 ml in each. Then contents of the dishes were calcined until black residue was formed.

Complex **3a**. The black residue in the first dish was solved in 0.3 ml of 3 M HNO$_3$ and dried. The formed pink crystals were solved again in 0.3 ml of 3 M HNO$_3$ aqueous solution, the mixture was placed in a tube. 0.3 ml of $2\cdot10^{-3}$ M of modified calix[4]arene in 1,2-dichloroethane was added to the tube. The tube was shaken for 10 minutes. After the complete delamination, 0.25 ml of the organic phase (with (Am) = $2\cdot10^{-3}$ M) were taken for the EXAFS study.

Complex **3b**. The black residue in the second capsule was solved in 0.3 ml of 0.3 M aqueous solution of 2-(1-adamantyl)sulfoacetic acid and dried. The formed pink crystals were solved again in 0.3 ml of water, the mixture was placed in a tube. 0.3 ml of $2\cdot10^{-3}$ M of modified calix[4]arene in 1,2-dichloroethane was added in the tube. After the complete delamination, 0.3 ml of the organic phase (with (Am) = $2\cdot10^{-3}$ M) were taken for the EXAFS study.

Americium concentrations in the samples prepared for the EXAFS study in both cases were approximately $2\cdot10^{-3}$ M.

EXAFS–spectroscopy

Solutions to be studied were placed in carefully sealed polypropylene cells. X-ray absorption spectra near the Am L$_{\text{III}}$-edge were collected in the X-ray fluorescence yield registration mode at the “Structural materials science” beamline of the Kurchatov Synchrotron Radiation Center of the NRC “Kurchatov Institute”.[S4] A 2.5 GeV electron storage ring operated at an electron current at 80-100 mA was used for synchrotron radiation generation. The beam intensity was monitored using an ionization chamber filled with argon. A silicon avalanche photodiode produced by FMB Oxford (UK) used as a fluorescence detector was located at 90º to the incident beam. The beam spot at the sample was 0.5×2 mm^2. A Si(220) channel-cut monochromator was used. The experimental spectrum of niobium foil was used for the monochromator energy scale calibration. The maximum derivative in the XANES Nb K-edge was accepted to be 18985 eV. The spectra were processed using the Athena program as follows: background subtraction; normalization by the Am L_{III}-edge edge jump; extraction of atomic absorption μ_0; Fourier transform with the weighting factor k^2 in the range k=2÷8 $Å^{-1}$. Ionization threshold energy E_0 was chosen as a maximum of the first derivative in the Am L_{III}-edge absorption spectrum and further refined during non-linear curve fitting. The spectra fitting was performed in the R-space using the Artemis program and atomic coordinates of the reference compound $Eu(CMPO)_2(NO_3)_3$ on the basis of the XRD results.[S5]

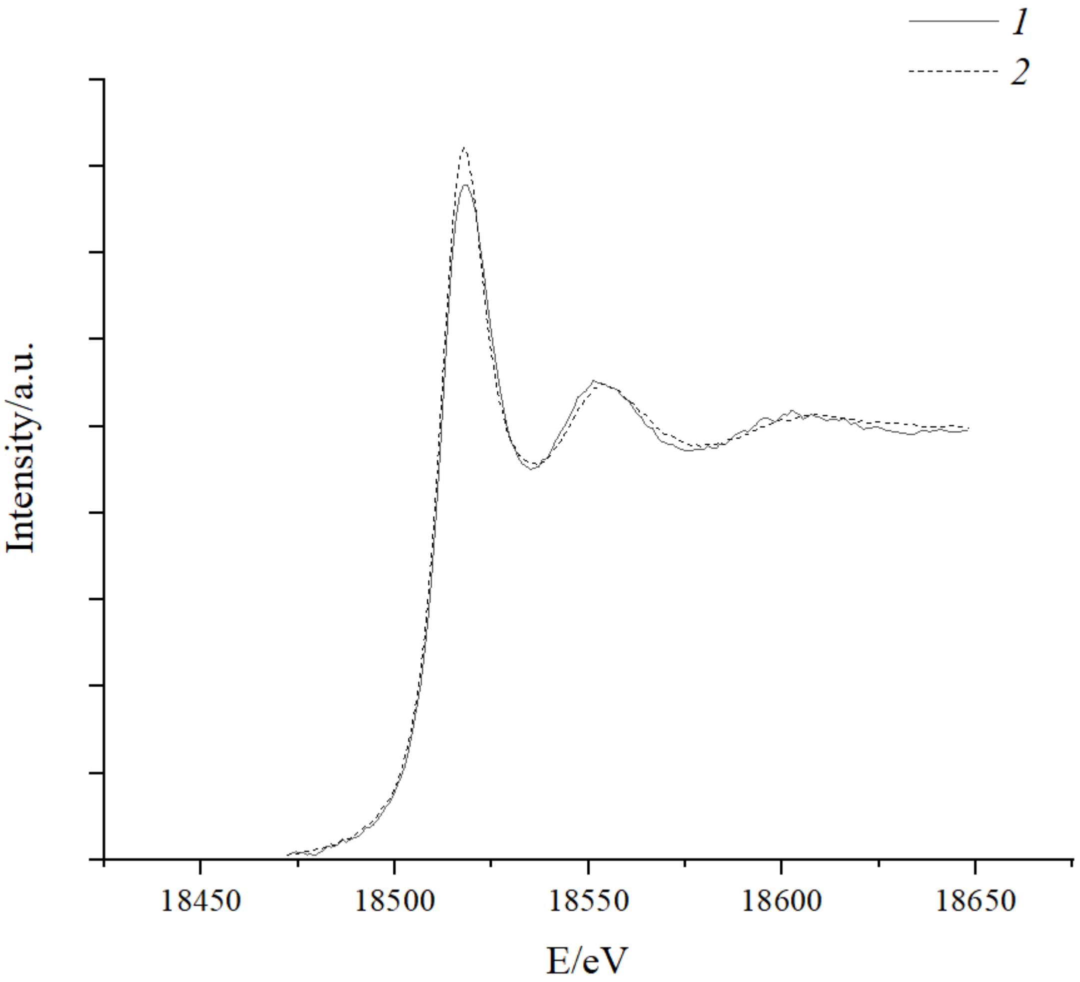

Figure S1 Experimental Am L_{III}-edge XANES spectra for complexes **3a** (*1*) and **3b** (*2*).

Since the fluorescence spectra (Figure S1) coincide by shape with the corresponding absorption spectra μ(E), they were used for interpretation of the EXAFS spectra. One can see from experimental Am L_{III}-edge XANES spectra (Figure S1) that positions of absorption edge are identical in both complexes **3a,b**. In these results, it is expected that the oxidation level of americium is the same in these compounds.

The function χ(k) was extracted from experimental data as (S1):

$$\chi(k) = \frac{\mu(k) - \mu_0\ (k)}{\mu_0\ (k)}, \qquad \text{(S1)},$$

where $\mu(k)$ is the experimentally measured absorption coefficient, $\mu_0\ (k)$ – absorption coefficient of a free atom modelled by a set of cubic splines, k – photoelectron wave number.

The EXAFS spectra were approximated as (S2):[S6]

$$\chi(k) = \sum_j \frac{S(k)N_i}{kr_j^2} \left|f_j(k,\pi)\right| \sin\left(2kr_j + \varphi_j(k)\right) e^{-2\sigma_j^2 k^2} e^{-2r_j/\lambda(k)} \qquad \text{(S2)},$$

where summation was done by all surrounding coordination spheres, N_i – is the number of atoms in the i-th sphere (coordination number), $S(k)$ – is the term taking into account the non-zero probability of the many-body processes, r_j is the distance to the j-th sphere, $f_j(k,\pi)$ is the backscattering amplitude by atoms of the j-th sphere of a photoelectron with the wave vector k, σ_j^2 is the Debye-Waller factor. The secondary wave phase shift is added up from the geometric raid of phase $2kr_j$ on the way to the atom of the j-th sphere and back, φ_j is the phase shift due to the electron motion in the potential of the neighboring atoms, λ is the photoelectron inelastic mean-free path.

The number of independent data points (N_{ind}) was calculated as (S3):

$$N_{ind} = \frac{2\Delta k \Delta r}{\pi} \qquad \text{(S3)},$$

where parameters Δk and Δr correspond to data ranges in the k- and R- spaces used for the fit respectively. In order to reduce the number of the varied parameters for both complexes the value S(k) = 0.9 was fixed.

The fitting was done by the functional minimization (S4):

$$\chi_\nu^2 = \frac{N_{ind}}{\nu N_{pts}} \sum_{i=1}^{N_{pts}} \frac{\left(\chi_{data}(R_i) - \chi_{th}(R_i)\right)^2}{\varepsilon_i^2} \qquad \text{(S4)},$$

where N_{pts} is the number of points in the fitted range, ν is the number of degrees of freedom, $\chi_{data}(r_i)$ and $\chi_{th}(r_i)$ are the calculated and experimental EXAFS-response respectively, ε_i is the measurement uncertainty associated with point *i*.

The fitting quality was determined by the R-factor (R_f) (absolute standard deviation between the model and experimental spectra) calculated as (S5):

$$R_f = \sum_{i=1}^{N_{pts}} \frac{\left(\chi_{data}(R_i) - \chi_{th}(R_i)\right)^2}{\left(\chi_{data}(R_i)\right)^2} \qquad \text{(S5)}$$

The values of the parameters are shown in Table S1.

Table S1 The values of the parameters for complexes **3a,b** obtained as a result of fitting.

Parameter	Value for complex **3a**	Value for complex **3b**
N_{ind}	5.9	9.3
χ^2_ν	4.7	11.4
R_f	0.011	0.006

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