

Solid Uranium(VI) Complexes with Different Amino Acids Studied by EXAFS

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As a continuation of our project dealing with the complex formation of uranium with alpha-substituted carboxylic acids in aqueous solution, we investigated the structure of solid complexes of uranyl with selected amino acids /1/. The aim of this EXAFS study was the observation of structural changes of solid uranium(VI) complexes with selected amino acids having the amino group at different positions within the organic molecule.

Experimental

The amino acids (HL) used were α -aminoisobutyric acid (HL¹), β -aminobutanoic acid (HL²), and γ -aminobutanoic acid (HL³). The reactions were performed in aqueous solution at different molar ratios (UO₂:HL = 1:1, 1:2, 1:3). The products were isolated by slow evaporation of the solvent. The elemental composition of the compounds were determined using TOC, TN ICP-MS, and ion chromatography. Furthermore, the solids were analyzed by XRD and thermal analysis. For the EXAFS measurements, the precipitates were mixed with teflon powder and pressed into pellets of 13 mm diameter. The EXAFS data were recorded at the Rossendorf Beamline (ROBL) at the ESRF in Grenoble /2/.

Results

We observed the formation of three types of complexes of uranium(VI) and α -aminoisobutyric acid (1:1, 1:2, 1:3). Only the tris complex was isolated with γ -aminobutanoic acid (HL³). This is in agreement with the findings of Bismondo et al. /3/. Whereas no solid complexes could be obtained with β -aminobutanoic acid (HL²).

Table 1. Summary of the EXAFS structural parameters.

Sample	Shell	N	R (Å)	σ (Å ²)
A UO ₂ [HL ¹](NO ₃) ₂	U-O _{ax}	2f	1.76	0.0017
	U-O _{eq}	5.0	2.39	0.0126
B UO ₂ [HL ¹] ₂ (NO ₃) ₂ ·H ₂ O	U-O _{ax}	2f	1.77	0.0017
	U-O _{eq}	5.2	2.36	0.0152
C UO ₂ [HL ¹] ₃ (NO ₃) ₂ ·H ₂ O	U-O _{ax}	2f	1.77	0.0016
	U-O _{eq}	4.8	2.37	0.0103
D UO ₂ [HL ³] ₃ (NO ₃) ₂ ·H ₂ O	U-O _{ax}	2f	1.77	0.0022
	U-O _{eq}	5.7	2.47	0.0058
	U-C	3.0	2.87	0.0034

The 95% confidence limits for the bond length (R) and coordination numbers (N) are the following: U-O_{ax} ±0.003 Å; U-O_{eq} ±0.01 Å and 16%; U-C ±0.01 Å and 33%, respectively. f: parameter fixed during the fit.

Figure 1 depicts the EXAFS spectra and the corresponding Fourier transforms (FT) measured for the synthesized compounds, whereas Table 1 summarizes the structural parameters determined. The U-O_{eq} distance can be used as an indicator for the coordination mode of carboxylate ligands to the uranyl center (see Table 1). For sample A, we measured a U-O_{eq} distance

of 2.39 Å. This value is shorter than expected for a bidentate coordination of the carboxyl group of the amino acid. Most likely the α -aminoisobutyric acid is coordinated in the 1:1 complex via one oxygen of the carboxyl group to the uranyl center.

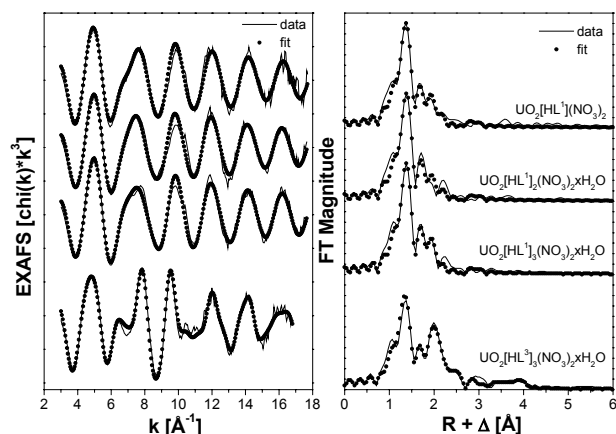


Fig. 1. Uranium L_{III}-edge k³-weighted EXAFS spectra (left) and corresponding Fourier transforms (right) of the synthesized solids. Solid line – experiment; dots – theoretical fit.

If more than one amino acid is coordinated, we observed a slight decrease of the U-O_{eq} distance by 0.03 Å. The results indicate that the amino acid is monodentate coordinated via one oxygen of the carboxyl group independent from the coordination number of the α -aminoisobutyric acid. The presented results are in agreement with findings of these complexes in solution /1/. The EXAFS spectrum of UO₂[HL³]₃(NO₃)₂·H₂O looks different compared to the other data (see Fig. 1). The measured U-O_{eq} and U-C distances of 2.47 and 2.87 Å, respectively, are characteristic for bidentate coordination of the carboxyl group. The structural parameters are in agreement with those reported by Bismondo et al. /3/. If the amino group moves farther away from the carboxyl group, we detected a bidentate coordinated amino acid via the two oxygens of the carboxyl group. The coordination mode changed to monodentate coordination of the ligand via one oxygen of the carboxyl group when the amino group is in α -position. Based on the presented experimental results, we found no evidence for the formation of chelate species involving the amino group.

References

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- /3/ Bismondo, A., et al., Inorg. Chim. Acta **110**, 205 (1985).