 ROBL-CRG	<b>Experiment title:</b> Interaction of uranium with bioligands produced by soil bacteria and with related model compounds using X-ray absorption spectroscopy	<b>Experiment number:</b> 20-01-661
<b>Beamline:</b> BM 20	<b>Date of experiment:</b> from: 20.04. to: 24.04.2007 05.10. to: 09.10.2007	<b>Date of report:</b> 11.04.2008
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**Report:** Synchrotron-based EXAFS spectroscopy is a powerful technique to obtain structural information on radionuclide bioligand species in solution. As an example pyoverdins-type siderophores are a unique class of bioligands, with a high potential to dissolve, bind, and thus transport uranium in the environment. Pyoverdins are secreted from fluorescent *Pseudomonas* species which are ubiquitous soil bacteria. The aim of this study is to explore structural parameter of soluble U(VI) species with pyoverdins and related model compounds. This includes also relevant model systems for the cell envelope of bacteria. The present report is focussed on the first topic: soluble U(VI) bioligand species and their structural characteristics.

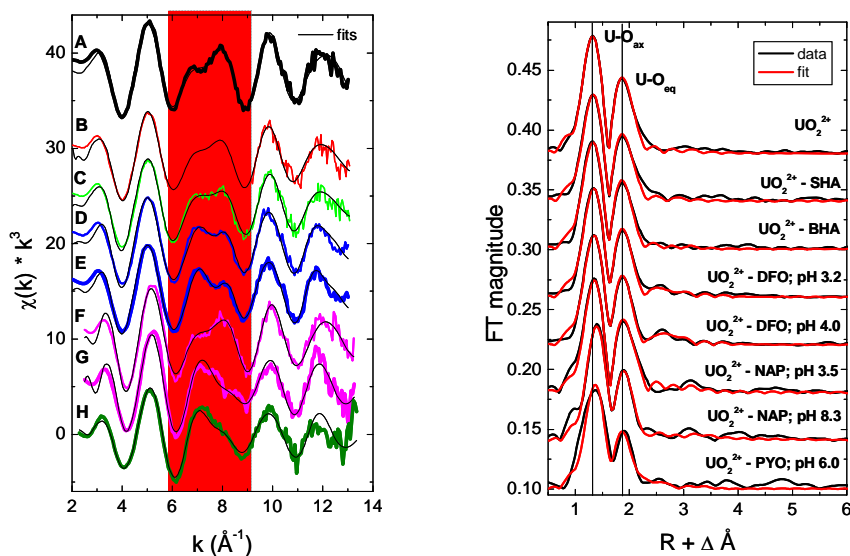


Fig. 1: U  $L_{III}$ -edge  $k^3$ -weighted EXAFS spectra (left) and the corresponding Fourier transforms (right) and the theoretical fits (red line).

**Experimental.** U L<sub>III</sub>-edge EXAFS measurements were carried out with test solutions containing  $5 \times 10^{-4}$  or 0.001 M  $\text{UO}_2^{2+}$  and pyoverdins (PYO) or related model compounds at an ionic strength of 0.1 M  $\text{NaClO}_4$ . The pH was varied between 2 and 8 depending on the bioligand. The samples were measured at room temperature either in fluorescence or in transmission mode. The model compounds simulate the hydroxamate function [salicylhydroxamic acid (SHA), benzohydroxamic acid (BHA) and desferrioxamine B (DFO)] and the chromophore [2,3-dihydroxynaphthalene (NAP)] of the pyoverdinin molecule.

**Results.** A selection of the measured EXAFS oscillations and corresponding Fourier transforms are presented in Fig. 1. The extracted structural parameters are summarized in Table 1.

*Table 1: Summary of the determined structural parameters.*

Sample	Shell	N	R (Å)	$\sigma^2$ (Å <sup>2</sup> )	$\Delta E_0$ (eV)
A	U-O <sub>axial</sub>	2f	1.76 <sub>6</sub>	0.0016	10.5
	U-O <sub>equatorial</sub>	5.0	2.41 <sub>8</sub>	0.0068	
B (SHA)	U-O <sub>axial</sub>	2f	1.77 <sub>5</sub>	0.0026	13.4
	U-O <sub>equatorial</sub>	4.7	2.41 <sub>5</sub>	0.0063	
C (BHA)	U-O <sub>axial</sub>	2f	1.77 <sub>3</sub>	0.0027	12.3
	U-O <sub>equatorial</sub>	4.8	2.40 <sub>2</sub>	0.0064	
D (DFO) pH 3.2	U-O <sub>axial</sub>	2f	1.78 <sub>1</sub>	0.0023	10.3
	U-O <sub>equatorial</sub>	4.9	2.40 <sub>0</sub>	0.0070	
	U-C/N	2f	3.22	0.0040	
E (DFO) pH 4.0	U-O <sub>axial</sub>	2f	1.78 <sub>5</sub>	0.0024	9.7
	U-O <sub>equatorial</sub>	4.8	2.38 <sub>7</sub>	0.0069	
	U-C/N	2f	3.22	0.0015	
F (NAP) pH 3.5	U-O <sub>axial</sub>	2f	1.76 <sub>8</sub>	0.0017	18.6
	U-O <sub>equatorial</sub>	5.6	2.40 <sub>5</sub>	0.0078	
G (NAP) pH 8.3	U-O <sub>axial</sub>	2f	1.79 <sub>7</sub>	0.0018	18.3
	U-O <sub>equatorial</sub>	6.3	2.36 <sub>9</sub>	0.0095	
H (PYO) pH 6.0	U-O <sub>axial</sub>	2f	1.78 <sub>8</sub>	0.0023	12.8
	U-O <sub>equatorial</sub>	6f	2.35 <sub>3</sub>	0.0107	
	U-C/N	2f	2.89	0.0047	
U(VI)-PCA <sup>[1]</sup> pH 10.0	U-O <sub>axial</sub>	2f	1.81	0.0013	-14
	U-O <sub>equatorial</sub>	5.8	2.37 <sub>4</sub>	0.0071	

f: fixed during the fit.

The differences in the EXAFS oscillations of the bioligand containing samples B to H compared to the free uranyl ion (sample A) within a k-range between 6 and 9 Å<sup>-1</sup> clearly indicates the complexation of U(VI). These U(VI)-species are characterized by both a lengthening of the U-O<sub>ax</sub> and a shortening of the U-O<sub>eq</sub> distance with increasing pH. The structural parameters of the U(VI)-pyoverdinin sample shows strong similarities with those of 1:1 complexes of U(VI) with protocatechuic acid and catechol [1]. Hence there is a strong affinity of U(VI) to the catechol functionality of the pyoverdinin molecule. However, the coordination of U(VI) to hydroxamate groups (samples B to E) results also in a shortening of the U-O<sub>eq</sub> distance.

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## Reference

/1/ Roßberg, A. et al. (2000) Radiochim. Acta 88, 593-597.