 ROBL-CRG	Experiment title: XANES Evidences of U(V) Stabilization with Novel 12-fold Coordinational Geometry in Oxomolybdate Network	Experiment number: 20-01-758
Beamline: BM 20	Date of experiment: from: 17.06.2015 to: 19.06.2015	Date of report: 20.02.2017
Shifts: 4	Local contact(s): Marisol janeth Lozano rodriguez (email: janeth.lozano-rodriguez@esrf.fr)	<i>Received at ROBL:</i>
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Report:

Here we have two polymorphs of uranium molybdates (U-Mo 1 and U-Mo 2), which were isolated from slow evaporation and hydrothermal methods, respectively. Main difference between U-Mo 1 and U-Mo 2 is that the first is assigned to the hexagonal and second belongs to a cubic symmetry crystal. Single-crystal structure analysis shows that both compounds are based on the same clusters with formula $[UMo_{12}O_{48}]$. This cluster consists of one U which is in a very rare twelve-fold coordination environment surrounded by 12 MoO_6 octahedra. Because of such high coordination number, U cannot be in oxidation state of +6, but in +5 or +4.

The XANES experiments were made to confirm the oxidation state of U. The measurements were performed in transmission mode at the Mo K-edge (20000 eV) and the U L_3 -edge (17166 eV). The Mo-K XANES spectra of $Na_4H_4(UMo_{12}O_{42})(H_2O)_6$ are shown in Fig. 1a., The $MoO_3(+6)$ and $MoCl_5(+5)$ compounds were adopted as oxidation state references. MoO_3 has a distorted octahedral coordination; the presence of a pre-edge peak A' , at 20003 eV, is due to the $1s(Mo) \rightarrow 4d(Mo) + 2p(O)$ transition, as reported in the literature.¹ Such transition is forbidden in the dipole approximation in a perfect octahedral symmetry. However, when the amplitude on the pre-edge peak A' arises in an octahedral coordination, it is associated to the MoO_6 octahedron distortion.² This behaviour has been reported early for 3d transition metal compounds, where the most distorted is the octahedral coordination; the intensity in the pre-edge peak is higher.⁴ Both samples U-Mo 1 and U-Mo 2 show a pre-edge peak similar to that of MoO_3 . Furthermore, the energy of the inflection points of U-Mo 1

(20013.2 eV) and U-Mo 2 (20013.2 eV), is in line with that of MoO₃ (20013.7 eV). In contrast, the XANES spectrum of MoCl₅, which has also a distorted octahedral coordination, shows only a broad and weak pre-edge peak, which is in agreement with a +5 oxidation state of Mo, leading to a partial filling of the initially empty 4d(Mo)-2p(O) band and a somewhat lower octahedral distortion.⁵

U L₃ XANES spectra of samples U-Mo 1 and U-Mo 2 are shown along with those of UO₂ and NaUO₃ references previously published (Fig. 1b).⁶ Their corresponding edge and white line positions are given in Table 1. The white line positions of U-Mo 1 and U-Mo 2 (~17175 eV (peak **A**)) are similar to that of the UO₂ reference compound. The position of the peak **B** at ~17214 eV shifts, however, towards lower energy with the contraction of the U-Mo (~2.48 Å) distances in U-Mo 1 and U-Mo 2, according to their atomic arrangement in the cluster,⁷ comparing with those of U-U (~3.87 Å) in UO₂. The oxidation state +5 can be excluded, since it would give rise to a main peak **D** with a low energy shoulder **C** as shown by the XANES spectra of KUO₃ and NaUO₃.^{8,9} Finally, hexavalent U can also be excluded, since it would give rise to a shoulder ~15 eV after the white line peak.¹⁰

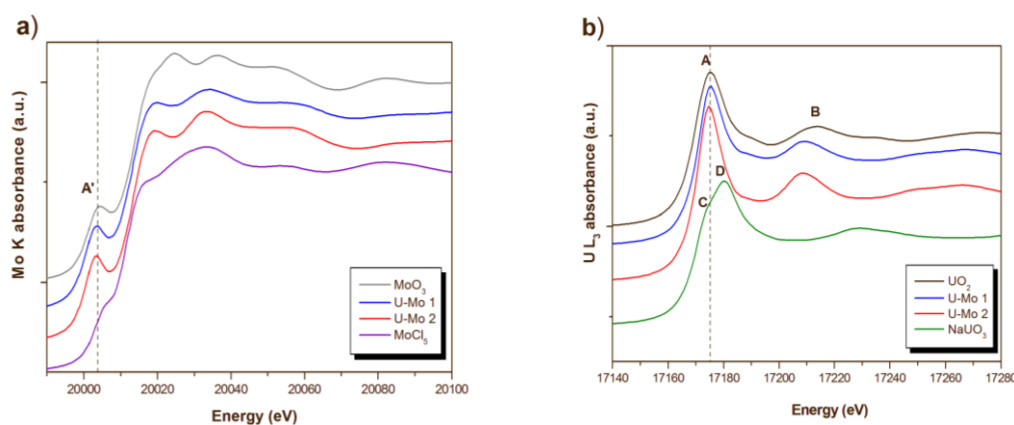


Fig. 1 Mo K XANES and U L₃ spectra

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