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Evolution of the metal coordination sphere in homoleptic amido uranium compounds

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Amido complexes of d and f transition metals have been the subject of tremendous interest lately. In particular, uranium amido complexes allow scanning a wide range of U oxidation states. As a consequence, both structural and electronic evolutions within complex series are to be probed by XAS, especially when single crystal are lacking. We present here a series of homoleptic U(IV) amide species. It involves oligomeric bridging amido complexes (from monomeric to trimeric) in which U-U intra-cluster interaction was probed by uranium L_3 edge measurements.

Keywords : uranium ; amide ; ab initio simulation ; EXAFS

1. Introduction

Initially synthesized as part of the search during the Manhattan Project, the tetrakis(diethylamido)uranium (IV) $[U(NEt_2)_4]_2$ is particularly interesting because of the reactivity of the U-NEt_2 bond toward small insaturated molecules like heteroallenes and weak acids. Besides UCl_4, $[U(NEt_2)_4]_2$ has been used very frequently as a starting material for the synthesis of organometallic species. Other uranium dialkylamide were synthesized to study the influence of the alkyl group on the reactivity of the U-NR_2 bond with R= Phenyl (Ph), Ethyl (Et) and Methyl (Me).

Depending on the R alkyl type, uranium dialkylamides can be found under monomeric, dimeric and trimeric structures with R respectively equal to phenyl, ethyl and methyl groups. In all of these complexes, no bond between the metallic centers does exist. We propose here to probe by EXAFS the weak U-U interactions which exist in the dimeric and trimeric structure. In the case of the trimeric adduct, due to the linearity of the 3 U centers, we propose to estimate the contribution of the multiple scattering through the metallic centers in the EXAFS spectrum.

2. Experimental

2.1. Sample preparation

Due to the extreme sensitivity of uranium(IV) amido compounds to air and water, all reactions and sample manipulations were carried out in a glove box filled with purified argon atmosphere.

The $[U(NPh_2)_4]$ complex was synthesized by mixing UCl_4 with 4 equivalents of $LiNPh_2$ in diethylether. After ether extraction and washing with pentane, a red powder was obtained.

The $[U(NEt_2)_4]_2$ complex was synthesized by mixing UCl_4 with 4 equivalents of $LiNEt_2$ in diethylether. After pentane extraction, a green powder was obtained.

The $[U(NMe_2)_4]_3$ complex was synthesized by mixing UCl_4 with 4 equivalents of $LiNMe_2$ in toluene. After toluene extraction and washing with pentane, an orange powder was obtained.

All samples were prepared in a glove box under argon by mixing an appropriate quantity of complex (to have an absorption jump equal to 1) with cellulosa. The prepared pellets were placed in an air-tight chamber closed by aluminum foil.

2.2. EXAFS data acquisition and treatments

X ray absorption spectra were recorded at the LURE DCI ring on the D44 beam line. Data acquisition parameters (beam line resolution and energy calibration) as well as data extraction parameters (background removal and normalization, FT parameters) are given in the complementary materials. All the EXAFS simulations and adjustments were achieved respectively by ATOM2.46 [Stern *et al*, 1995], FeFF7.02 [Ankudinov, 1996] and FeFFIT [Newville *et al*, 1995] codes.

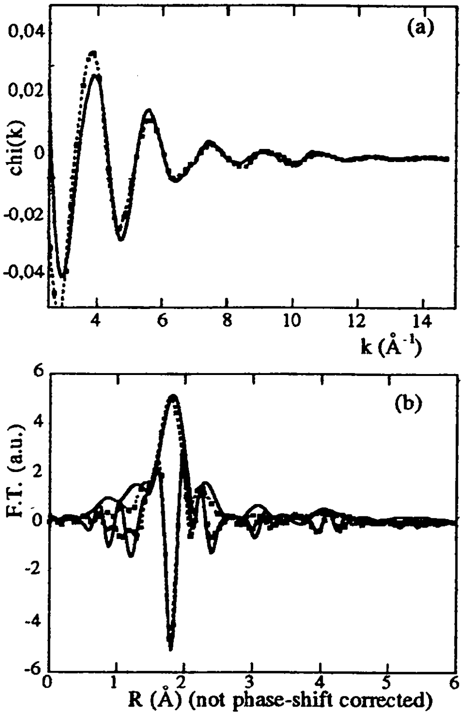

Figure 1
(a) U L_3-edge EXAFS data and (b) corresponding Fourier transforms for $[U(NPh_2)_4]$; experimental data (——) ; theoretical fit (- -•- -)

Table 1
Description of the paths calculated by FeFF7 and EXAFS best fit structural parameters for $[U(NPh_2)_4]$

$[U(NPh_2)_4]$			
Paths description		N*	σ(Å)
U—>N—>U	SS N of the amidure	4	0.04
U-->C_1-->U	SS C of the phenyl group linked to N	8	0.09
U-->C_2-->U	SS C of the phenyl group adjacent to C_1	12	0.14
U--->C_1—>N—>U	MS N and C of the phenyl group linked to N	16	0.21
U-->C_2--->N—>U	MS N and C of the phenyl group adjacent to C_1	8	0.06

* Here, the number of paths of the same type are defined as the degenerated paths even if the total path length for each process is nearly identical and not strictly.

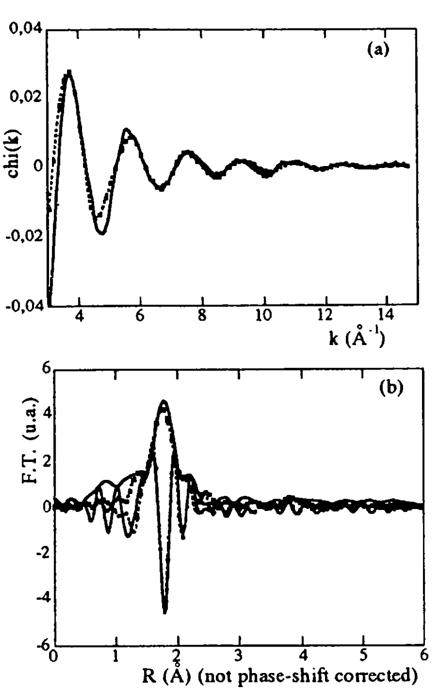

Figure 2
(a) U L_3-edge EXAFS data and (b) corresponding Fourier transforms for $[U(NEt_2)_4]_2$; experimental data (——) ; theoretical fit (- -•- -)

Table 2
Description of the paths calculated by FeFF7 and EXAFS best fit structural parameters for $[U(NEt_2)_4]_2$

	$[U(NEt_2)_4]_2$		
	Paths description	N*	σ(Å)
U—>N—>U	SS Non-bridging N of the amidure	3	0.05
U—>N_b—>U	SS Bridging N of the amidure	2	0.06
U--->C--->U	SS C of the ethyl group linked to a non-bridging N	6	0.14
U--->C_b--->U	SS C of the ethyl group linked to a bridging N	4	0.15
U-->U-->U	SS	2	0.1
U--->C—>N—>U	MS C of the ethyl group linked to a non-bridging N	12	0.13
U--->C_b—>N_b—>U	MS C of the ethyl group linked to a bridging N	8	0.12

* Here, the number of paths of the same type are defined as the degenerated paths even if the total path length for each process is nearly identical and not strictly.

3. Structure description

$[U(NPh_2)_4]$: This complex crystallizes in the P -1 triclinic space group [Reynolds *et al*, 1977]. In this four-coordinated uranium (IV) compound, the uranium atom is enclosed by a severely distorted tetrahedron of nitrogen atoms. The four U-N distances average at 2.27 Å.

$[U(NEt_2)_4]_2$: This complex crystallizes in the P 2_1/n monoclinic space group [Reynolds *et al*, 1976]. In this five-coordinated uranium (IV) compound, the uranium atom is enclosed by a distorded trigonal bipyramid of nitrogen atoms. Two of these bipyramids share an edge to form a dimeric complex located on a center of symetry. The three non-bridging U-N distances average at 2.22 Å whereas the bridging U-N distances are 2.46 and 2.57 Å. The distance between the two uranium centers is 4.00 Å.

$[U(NMe_2)_4]_3$: This complex crystallizes in the I 2/a monoclinic space group [Boisson, 1996]. In this six-coordinated uranium (IV) compound, the central uranium atom U(1) lies on the inversion center and is contained within a distorted octahedron. U(2) is contained within a triangular prism [Berthet *et al*, 1998].

The six bridging U(1)-N distances average 2.39 Å whereas the three bridging U(2)-N distances are longer (2.67 Å). The other three non-bridging distances U(2)-N are at 2.25 Å. The distance between the two uranium centers is 3.64 Å.

4. EXAFS results

For such low symmetry structures (triclinic and monoclinic), the most important preliminary work lies in the determination of the number of paths to be taken into account for EXAFS oscillations refinement. First, for each coumpound, the EXAFS spectra have been simulated by FeFF using cristallographic data in order to extract the different paths with an amplitude ratio greater than 10%. Second, general E_0 and the S_0^2 for all selected paths and specific Debye-Waller factor (σ) for each degenerated paths have been refined by FeFFIT. Figure 1, Figure 2 and Figure 3 show the EXAFS data and the corresponding Fourier transform (FT) respectively for the monomeric, dimeric and trimeric compounds. The calculated curve fits are also shown, and the best fit parameters obtained for all the paths (single scattering paths (SS) and multiple scattering paths (MS)) are summarized in Table 1, Table 2 and Table 3 respectively for the three compounds. In these three complexes, most of the scattering processes which are not associated with a chemical bond have a very large Debye-Waller factor and can be neglected. Only the scattering paths including a chemical bond have a significant contribution to the EXAFS spectra, except the uranium-uranium single scattering process in the dimeric and the trimeric structure. In the case of the trimeric adduct, the triple scattering due to the linearity of the 3 U centers doesn't seem to have a contribution in the EXAFS spectrum.

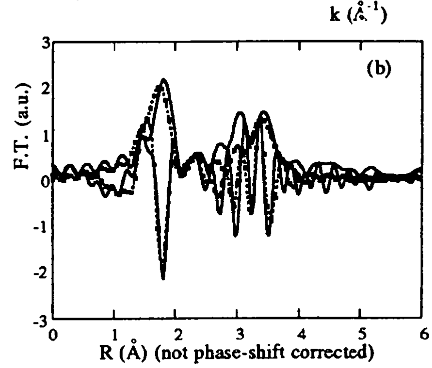

Figure 3
(a) U L_3-edge EXAFS data and (b) corresponding Fourier transforms for $[U(NMe_2)_4]_3$; experimental data (——) ; theoretical fit (- -•- -)

Table 3
Description of the paths calculated by FeFF7 and EXAFS best fit structural parameters for $[U(NMe_2)_4]_3$

$[U(NMe_2)_4]_3$: Central uranium atom U_c			
Paths description		N*	σ(Å)
U_c—>N_b—>U_c	SS Bridging N of the amidure	6	0.08
U_c--->C_b--->U_c	SS C of the methyl group linked to a bridging N	12	0.41
U_c --->U_t--->U_c	SS	2	0.09
U_c--->C_b—>N_b—>U_c	MS C of the methyl group linked to a bridging N	24	0.11
U_c—>N_b—>U_c—> N_b—>U_c	MS	12	0.41
$[U(NMe_2)_4]_3$: Terminal uranium atom U_t			
Paths description		N*	σ(Å)
U_t—>N—>U_t	SS Non-bridging N of the amidure	3	0.08
U_t—>N_b—>U_t	SS Bridging N of the amidure	3	0.08
U_t--->C--->U_t	SS C of the methyl group linked to a non-bridging N	6	0.47
U_t-->C_b--->U_t	SS C of the methyl group linked to a bridging N	6	0.41
U_t--->U_c--->U_t	SS	1	0.09
U_t--->C—>N—>U_t	MS C of the methyl group linked to a non-bridging N	12	0.06
U_t--->C_b—>N_b—>U_t	MS C of the methyl group linked to a bridging N	12	0.11
U_t--->U_t--->U_c--->U_t	MS	2	0.41
U_t--->U_c--->U_t--->U_c—>U_t	MS	1	0.41

* Here, the number of paths of the same type are defined as the degenerated paths even if the total path length for each process is nearly identical and not strictly.

5. Conclusion

In this work, we have demonstrated that in U(IV) amido species, among all, only the scattering paths including a chemical bond and the non-bonding the U---U single scattering path, make a significant contribution to the total EXAFS spectrum.

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