Electronic Supplementary Information

Uranyl-Halide Complexation in *N*,*N*-Dimethylformamide: Halide Coordination Trend Manifests Hardness of UO_2^{2+}

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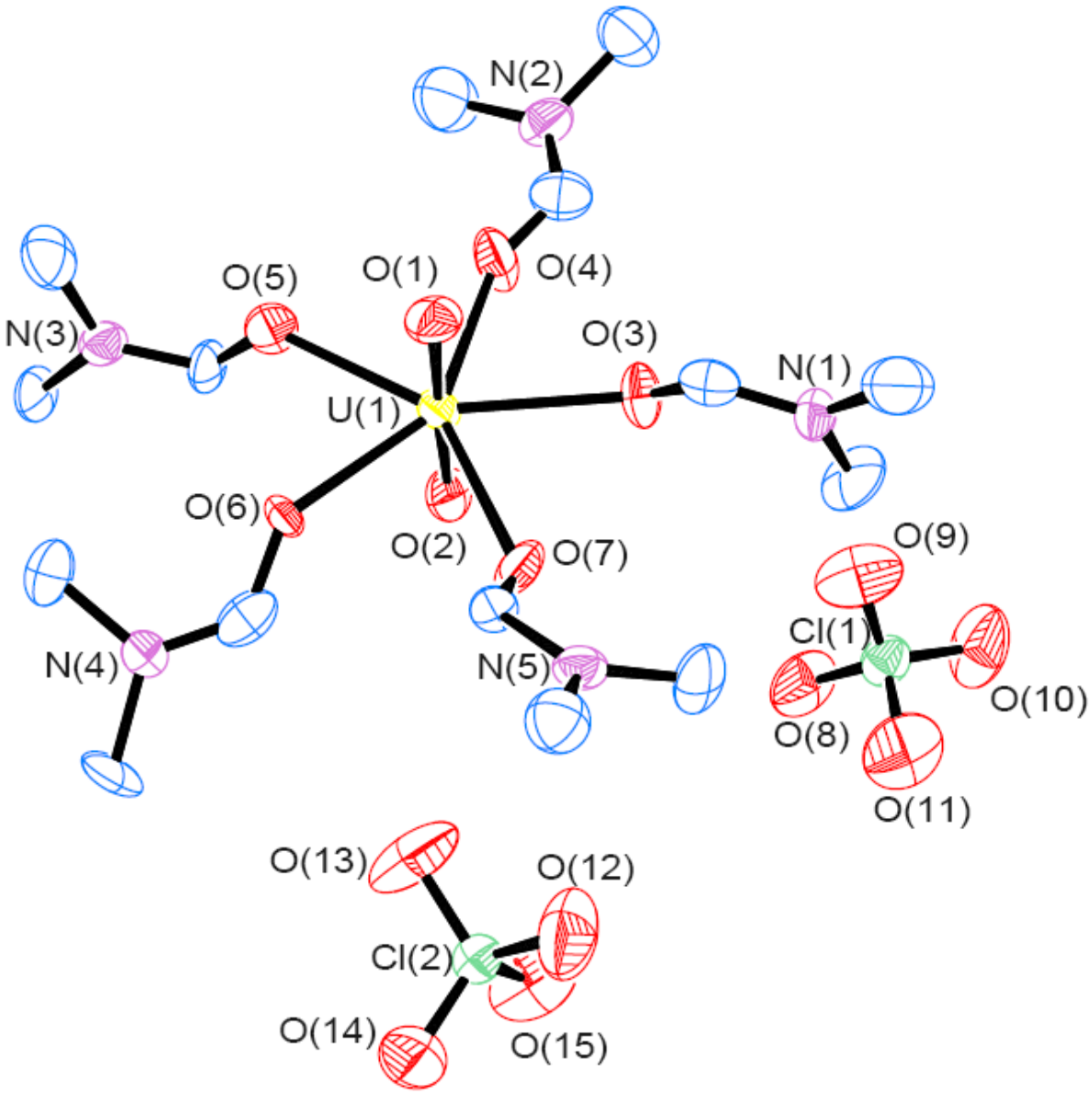

Fig. S1. ORTEP drawing of $[UO_2(DMF)_5](ClO_4)_2$ showing 50% probability displacement ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: U(1)-O(1) 1.79(2), U(1)-O(2) 1.76(2), U(1)-O(3) 2.414(11), U(1)-O(4) 2.338(7), U(1)-O(5) 2.377(12), U(1)-O(6) 2.332(11), U(1)-O(7) 2.465(14), O(1)-U(1)-O(2) 177.8(7), O(1)-U(1)-O(3) 89.4(6), O(1)-U(1)-O(4) 90.3(8) O(1)-U(1)-O(5) 90.4(6), O(1)-U(1)-O(6) 90.6(6), O(1)-U(1)-O(7) 89.8(6), O(3)-U(1)-O(4) 69.3(6), O(4)-U(1)-O(5) 75.6(6), O(5)-U(1)-O(6) 71.0(4), O(6)-U(1)-O(7) 73.1(4), O(3)-U(1)-O(7) 70.9(5).

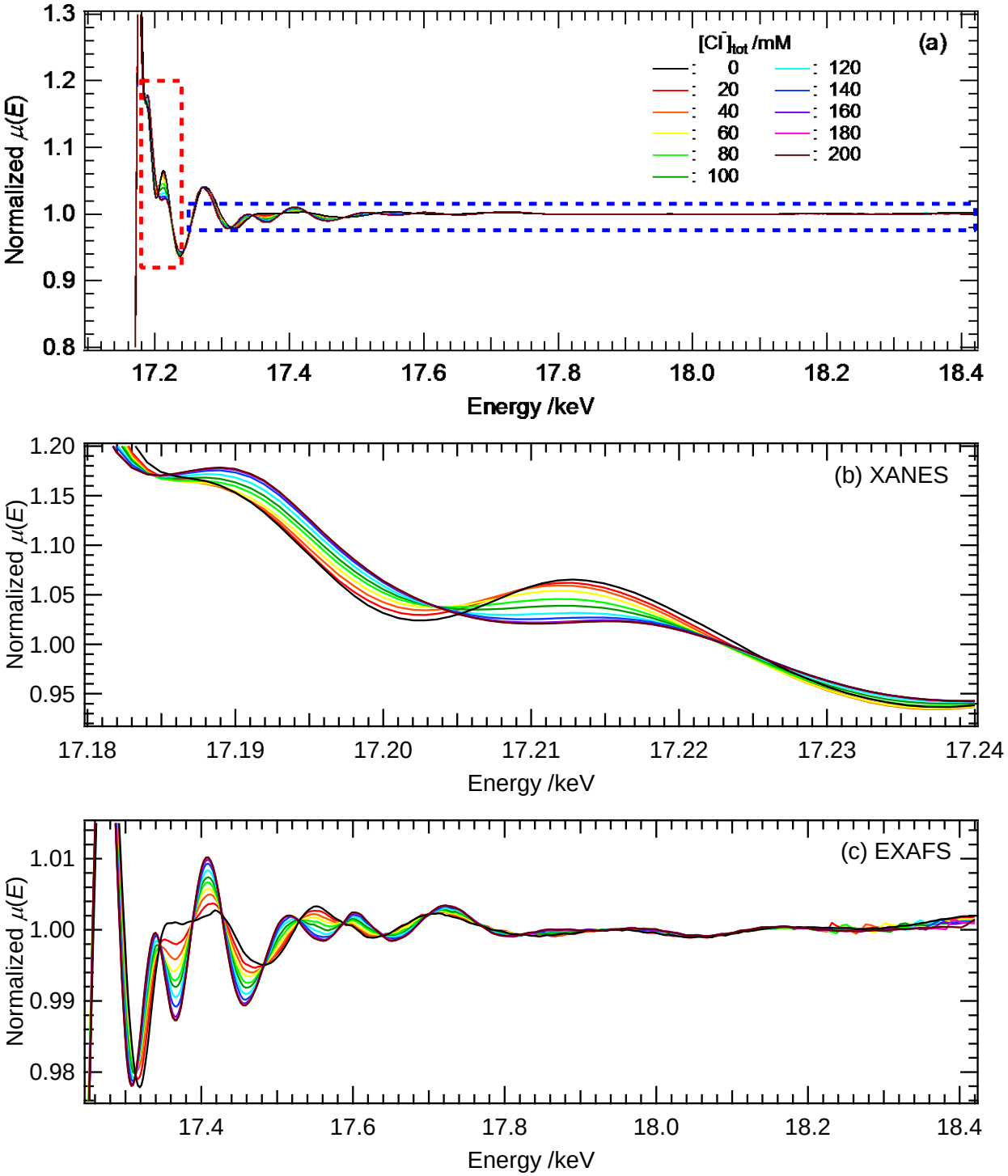

Fig. S2. Normalized X-ray absorption spectra of DMF solution dissolving $[UO_2(DMF)_5](ClO_4)_2$ (4.0×10^{-2} M) and [TBA]Cl (0-2.0×10^{-1} M) at 295 K. Panels b and c are magnified pictures of the regions surrounded by dashed rectangles in red and blue, respectively.

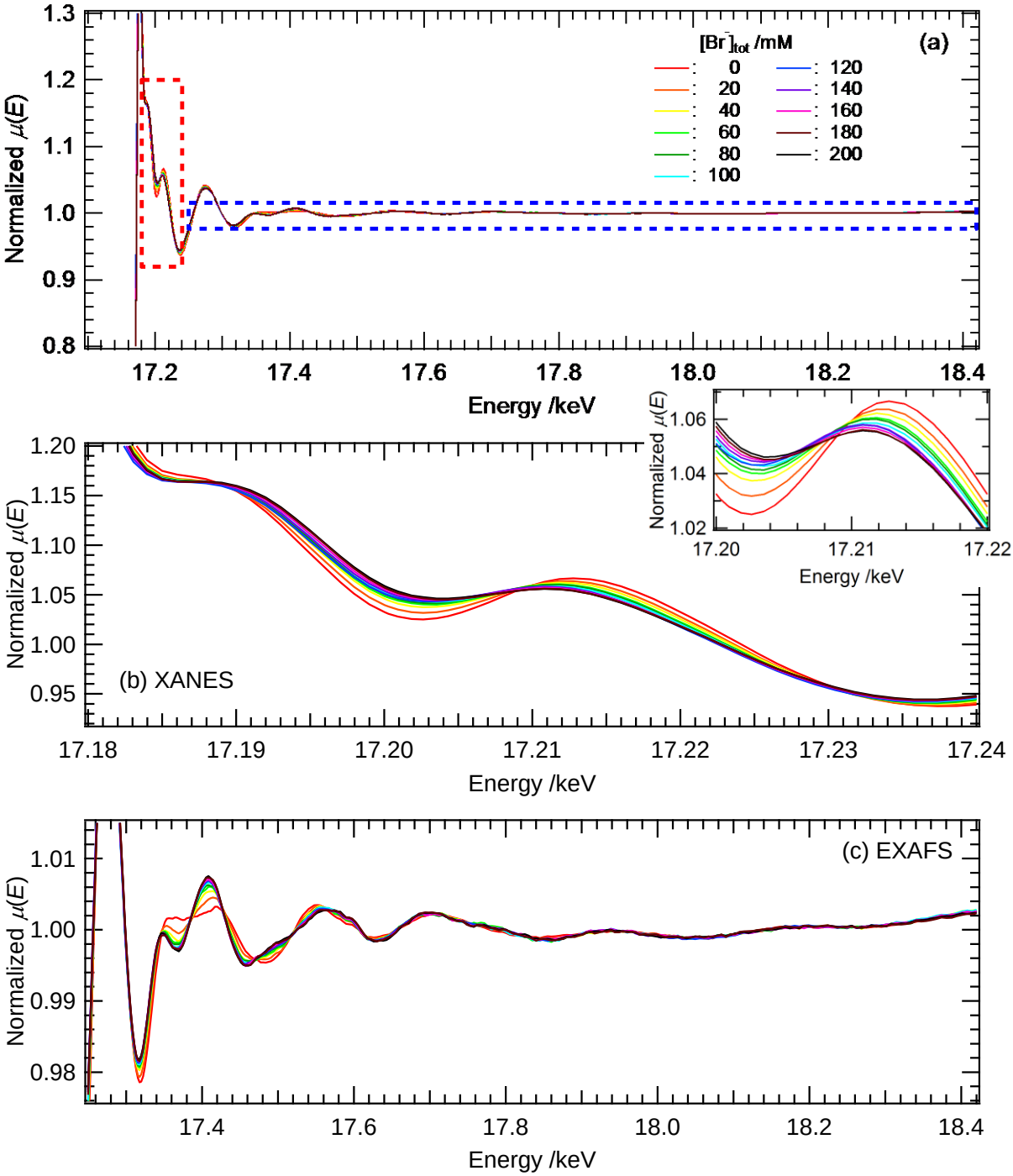

Fig. S3. Normalized X-ray absorption spectra of DMF solution dissolving $[UO_2(DMF)_5](ClO_4)_2$ (4.0×10^{-2} M) and [TBA]Br (0-2.0×10^{-1} M) at 295 K. Panels b and c are magnified pictures of the regions surrounded by dashed rectangles in red and blue, respectively. Inset in panel b is a further magnification of 17.20-17.22 keV region.

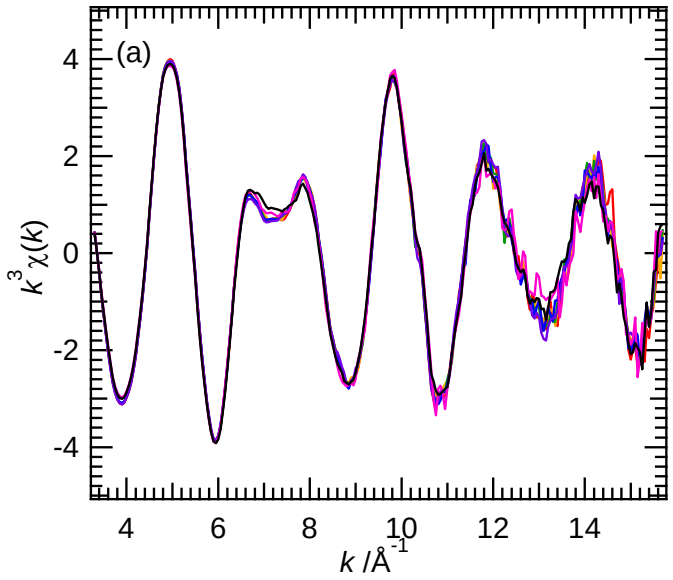

Fig. S4. k^3-weighted U L_{III}-edge EXAFS spectra of DMF solution dissolving $[UO_2(DMF)_5](ClO_4)_2$ (4.0×10^{-2} M) and [TBA]I (0-2.0×10^{-1} M) at 295 K.

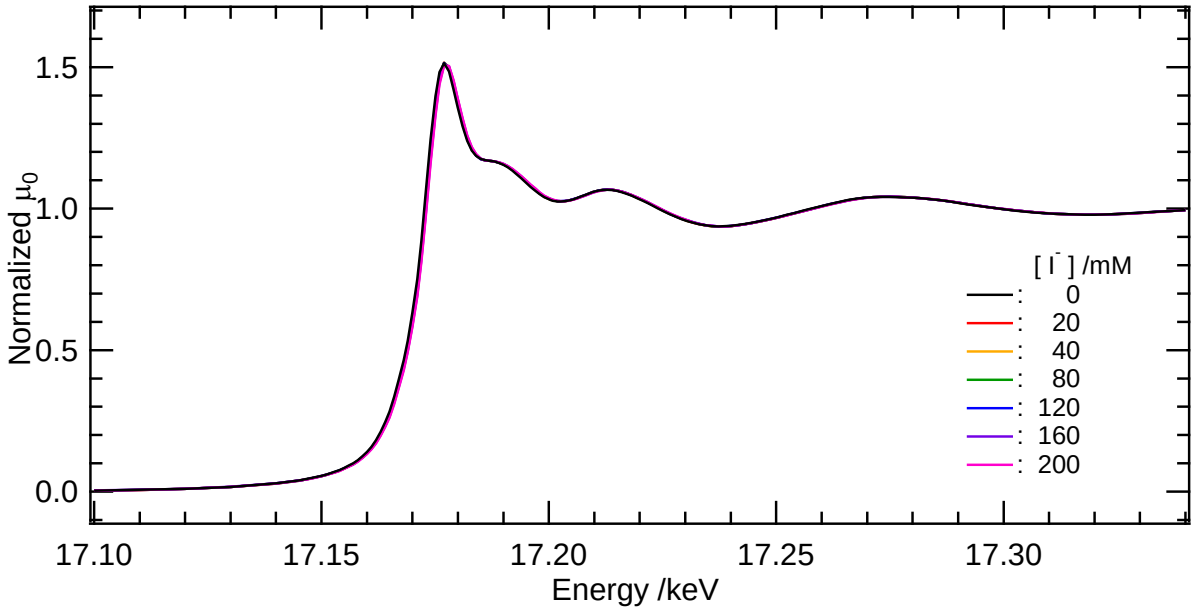

Fig. S5. U L_{III}-edge XANES spectra of DMF solution dissolving $[UO_2(DMF)_5](ClO_4)_2$ (4.0×10^{-2} M) and [TBA]I (0-2.0×10^{-1} M) at 295 K.

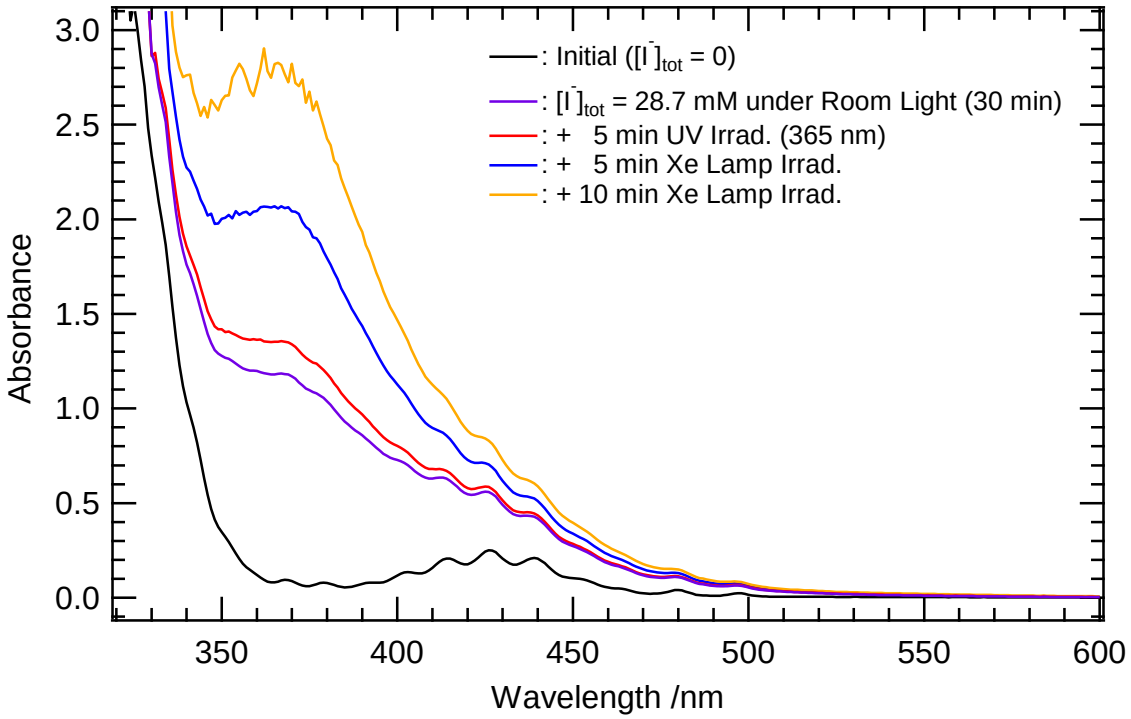

Fig. S6. UV-vis absorption spectra of the photo-irradiated DMF solution dissolving $[UO_2(DMF)_5](ClO_4)_2$ (6.64×10^{-3} M) at different total I^- concentrations ($[I^-]_{tot}$) and 295 K.

Table S1. Cone Angles (θ) of Coordinating Cl^- and Br^-

ion	r_{vdw} /Å[a]	R(U–X) /Å[b]	θ /°
Cl^-	2.252	2.68-2.71	112-114
Br^-	2.298	2.88-2.89	105-106

[a]Van der Waals radius brought from *J. Am. Chem. Soc.* 1964, **86**, 979-982. [b]Interatomic distance from U to X (= Cl^-, Br^-) determined from EXAFS (Tables 3, 4).