Electronic Structure of Uranium Halides and Oxyhalides in the Solid State. An X-ray Photoelectron Spectral Study of Bonding Ionicity

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Abstract: Core and valence X-ray photoelectron spectra of 18 uranium halides (U^{3+} to U^{5+}) and oxyhalides (U^{3+} to U^{6+}) (fluorides, chlorides, and bromides) are described. The results are discussed, as a function of halogen nature and compounds stoichiometry, in terms of ionicity of the bonds, of U 5f participation in bonding, and effect of oxygen. Evidence is produced that UF_3 has an unexpectedly strong covalent character.

1. Introduction

Besides having interesting nuclear properties, uranium is a fascinating element for the inorganic and, particularly, the solid-state chemist. Not only does it offer one of the most complicated binary compounds phase diagrams with oxygen (in which appear those oxides widely used as nuclear fuel), but it also shows several consistent series of binary and ternary compounds, where the metal appears with a continuous range of oxidation states from 3+ to 6+.

Uranium compounds raise the problem of the 5f valence-shell participation in chemical bonding. While numerous discussions are still focused on the question of 5f electrons (de)localization,[1] much of this debate is based on experimental properties and theoretical studies of metallic systems. However, the behavior of compounds is of obvious relevance when it comes to nuclear technology and materials science. In this respect, understanding the role of U 5f electrons would also be valuable for the chemistry of actinides in general.

The above considerations, and the unique experimental possibilities offered by high-resolution X-ray photoelectron spectroscopy (ESCA), have motivated a systematic investigation of the uranium halides and oxyhalides, which is a logical extension of the work initiated some time ago in the field of oxides[2] and fluorides.[3] It is also a step forward to broadening this method of investigation toward a more general idea, i.e., the assessment of ionicity in solid-state bonding.

2. Experimental Section.

2.1. Compounds. Eighteen compounds have been covered in the present work; they are listed in Table I.

They include the uranium halides (X = F, Cl, Br) for the oxidation states 3+ to 5+. The high vapor pressure of the hexahalides, as well as of all iodides, has prevented so far their study in the solid state by a technique requiring ultrahigh vacuum. Only UF_6 has now been studied by X-ray PES, as a molecular beam condensed onto a metal substrate at low temperature.[25]

The oxyhalides, UO_2X_2, containing uranyl(VI), could be studied along with a number of other compounds with general formulae UOX, UOX_2, and UO_2X, listed in Table I.

The synthesis (except for two commercial compounds) has been described in the literature, and the crystal structures of most compounds are known. References are given as part of Table I. The bulk purity of samples was checked by X-ray powder diffraction techniques.

2.2. X-ray Photoelectron Spectra. Samples were handled in a glovebox, under strictly dry nitrogen atmosphere. Except for UBr_4, where a single crystal could be freshly cleaved, they were ground and presented as powder pellets.

Table I. Uranium Halides and Oxyhalides Included in the Present Work[a]

	uranium formal oxidation state			
	3+	4+	5+	6+
fluorides[b]	(a) ${UF_3}^4$	(b) ${UF_4}^5$	(c) ${UF_5}^6$	
oxyfluorides				${UO_2F_2}_7^8$
chlorides	${UCl_3}_9^{10}$	${UCl_4}_{11}^{12}$	${UCl_5}_{11}^{13}$	
oxychlorides	$UOCl_{14}^{14}$	${UOCl_2}_{15}^{16}$	${UO_2Cl}_{17}$	${UO_2Cl_2}_{11}^{18}$
bromides	${UBr_3}_9^{19}$	${UBr_4}_{11}^{20}$	${UBr_5}_{21}^{22}$	
oxybromides	$UOBr_{14}^{14}$	${UOBr_2}_{23}^{23}$	${UO_2Br}_{24}^{24}$	${UO_2Br_2}_{11}$

[a] References are given for synthesis (subscript) and crystal structure (superscript). Unless specified otherwise, samples were synthesized at Rennes. [b] (a) sample supplied by Dr. B. Kanellakopulos, Kernsforschungszentrum Karlsruhe (GFR), (b) commercial sample (Merck), (c) commercial sample (Cerac).

X-ray photoelectron spectra were obtained at room temperature on a Hewlett-Packard 5950A ESCA system, using monochromatized Al Kα

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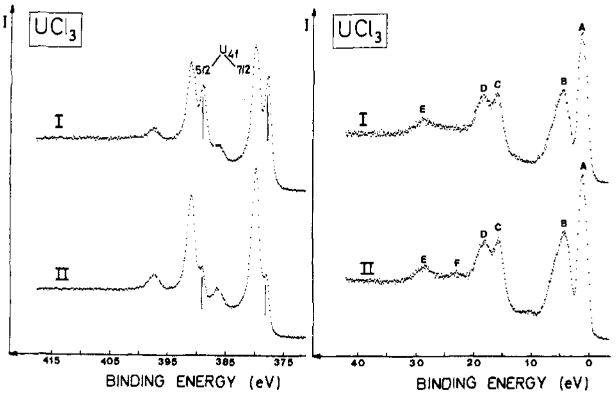

Figure 1. Comparison of U 4f and valence electron spectra for two different samples of UCl_3 obtained by different techniques, from different sources; core levels are very sensitive to surface condition, while valence spectra are not.

radiation ($h\nu = 1486.6$ eV). Line broadening and peak shifts, resulting for nonconducting samples from the inhomogeneous charge buildup at the surface due to the emitted photoelectrons, have been controlled by means of an adjustable low-energy electron "flood gun".

Recordings repeated at different times of exposure to X-rays and vacuum showed negligible changes. During long accumulations, small drifts in binding energy, due to slight changes in conductivity, could easily be corrected in the following way. The binding energy of a strong peak is monitored at regular intervals. The long accumulation is in this way broken into a series of shorter ones, to each of which a binding energy correction, equal to the strong peak shift, is applied before summation.

In spite of the precautions used during sample preparation and handling, and their very good bulk purity as confirmed by X-ray diffraction, most spectra obtained from halides reveal a sometimes strong oxygen peak and sometimes the presence of unwanted uranium core peak components. The reason for this is clearly the high surface sensitivity of the technique, providing evidence for surface chemical reactions, even with traces of water— or just by instability under the experimental conditions. If such observations contain the promise of a bright future for studying these phenomena, they are at this point a disturbance one has to accept. The recording of multiple spectra, when possible on different samples of the same compounds, has been used to locate the peaks corresponding to the bulk solid; these can then be analyzed by computer.

An interesting observation should be reported here: valence photoelectron spectra are much less affected by surface conditions than U 4f core level peaks. This is not unexpected; the U 4f photoelectrons, with a kinetic energy of about 400 eV lower, have a shorter mean free path in the solid, and thereby originate from a thinner surface layer. The unusual sharpness of the observation seems to demonstrate that the unwanted chemical species are strictly limited to the surface, rather than present as a gradient in the bulk, which would indicate solid-state diffusion of the contaminant. The effect is illustrated in Figure 1, by comparing the U 4f and the valence spectra of two UCl_3 samples of different origin; their core levels are notably different, while valence spectra are essentially the same. This is encouraging as to the interpretation of valence data.

Considering these difficulties, it seems appropriate to give a brief comment on each specific case. It is uncertain, though, that it would be possible to obtain better results without considerable experimental effort; and this might not be worth it, as the analysis of the present data can nonetheless be presented with a good degree of confidence.

The full widths at half-maximum (fwhm) of U $4f_{7/2}$ levels give an idea of the spectral resolution. This value can vary as a function of sample quality and experimental conditions, but sometimes also reflects more fundamental properties of the system.

Table II. Uranium Halides, UX_n: U 4f Binding Energies (eV)

	$n = 3$		$n = 4$		$n = 5$	
X	U $4f_{5/2}$	U $4f_{7/2}$	U $4f_{5/2}$	U $4f_{7/2}$	U $4f_{5/2}$	U $4f_{7/2}$
F	390.9	379.9	392.8	382.0	393.3	382.4
Cl	388.9	378.1	390.9	380.0	392.6	381.7
Br	388.9	378.2	390.7	379.7	(390.3)[a]	(379.5)[a]

[a] Less certain data.

Table III. Uranium Oxyhalides: U 4f Binding Energies (eV)

	U^{3+} UOX		U^{4+} UOX_2		U^{5+} UO_2X		U^{6+} UO_2X_2	
X	$4f_{5/2}$	$4f_{7/2}$	$4f_{5/2}$	$4f_{7/2}$	$4f_{5/2}$	$4f_{7/2}$	$4f_{5/2}$	$4f_{7/2}$
F	–[a]		–[a]		–[a]		393.7	382.8
Cl	390.5	379.8	390.9	380.1	(391.0)[b] (392.4)	(380.3) (381.8)	392.3	381.4
Br	390.7	379.9	391.0	380.2	391.2	380.3	391.8	380.9

[a] Not measured. [b] Parentheses denote less certain data.

(a) U^{3+} Compounds. UF_3, well-shaped and nonnegligible O 1s and 2s peaks observed, indicating adsorbed oxygen, as U 4f levels are undisturbed ($fwhm_{7/2} = 2.15$ eV); UCl_3, core levels reveal a strong but variable contribution (Figure 1) which we identify as UCl_4 (the sample is prepared by reduction of this compound) [$UOCl_2$ could also be formed by hydrolysis, but the O 1s peak is very small. X-ray powder diffraction patterns correspond to pure UCl_3; contamination is, therefore (and for the reasons given above), located at the surface of powder grains.]; UBr_3, small oxygen contamination, but spurious U 4f peaks coinciding with the UBr_4 ones (same deductions as for UCl_3); UOCl, good sample, fwhm (U4 $f_{7/2}$) = 2.2 eV; UOBr, good sample, fwhm (U $4f_{7/2}$) = 1.9 eV.

(b) U^{4+} Compounds. UF_4, good, O 1s peak negligible [Note in Figure 4 that peaks at the left of E are the 4f's from a little tungsten evaporated from a bad flood-gun filament. Other tungsten peaks are negligible. There is no effect on the UF_4 spectrum.]; UCl_4, good, slight O 2s contribution in valence band; UBr_4, spectra completely free of any contamination, data obtained on a freshly cleaved single crystal: $UOCl_2$, good, shoulder noted in the U 4f peaks which could indicate some contamination or decomposition, fwhm (U $4f_{7/2}$) = 2.0 eV; $UOBr_2$, good.

(c) U^{5+} Compounds: UF_5, small O 1s contamination, broad U 4f peaks, $fwhm_{7/2} = 2.5$ eV; UCl_5, presence of oxygen, fwhm (U $4f_{7/2}$) = 2.0 eV; UBr_5, contaminated by oxygen and a small amount of fluorohydrocarbon (F 2s contribution at left of peak E in valence band, Figure 8), which was identified as a residual gas from another experiment (U 4f shapes are unaffected); UO_2Cl, poorest sample of all, broad O 1s peak, fwhm (U $4f_{7/2}$) = 2.9 eV (can be resolved in two peaks, indicative of dismutation or decomposition); UO_2Br, good, sharp U 4f and O 1s peaks, fwhm (U $4f_{7/2}$) = 1.3 eV.

(d) U^{6+} Compounds: UO_2F_2, UO_2Cl_2, UO_2Br_2, good, with rather broad U 4f peaks; fwhm = 1.7, 2.5, and 2.4 eV.

3. Results

X-ray photoelectron spectra are presented in Figures 3–14. The illustrations correspond to the raw data (with rare exceptions, indicated in the captions).

The zero of the binding energy scale was set by reference to the Au $4f_{7/2}$ level (83.8 eV), using the gold decoration technique.[26] Its reliability was checked by its constant result for various settings of the electron flood gun; in fact, several samples were found to present little charging effect.

Numbers required for interpretation and discussion were obtained by weighted least-squares fitting of model curves to the experimental data, using a PDP 11/03 computer and a χ^2 minimizing simplex algorithm.[27]

The model curves are a combination of 50% Gaussian and Lorentzian shapes; peak widths are initially given as inspired by well-known spectra, then refined together with positions and heights. The number of peaks in a model was adjusted to account for shake-up satellites (where these could be observed) and surface species. Peak intensities, when used, are calculated from the surface of the model curve.

A typical example (experimental and reconstructed spectrum) is shown in Figure 2. The numerical results are collected in Tables II–IX; for clarity, markers are used in Figures 3–14 at the values

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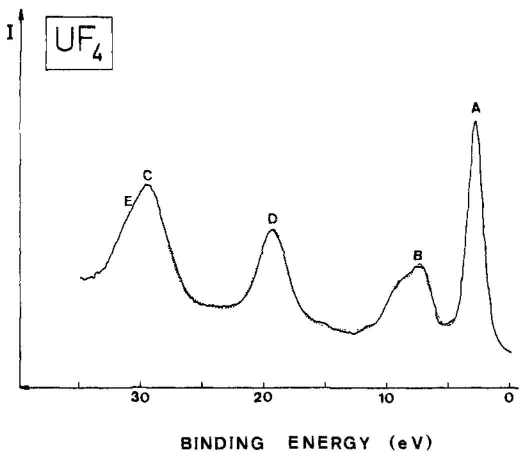

Figure 2. Example of peak analysis procedure: experimental (···) and reconstructed (—) spectra. Fwhm (eV) peaks used in the latter: E, U $6p_{1/2}$ (2.5); C, F 2s (3.4); D, U $6p_{3/2}$ (2.9); B, U–X band (2.4 and 2.1); A, U 6f (1.5).

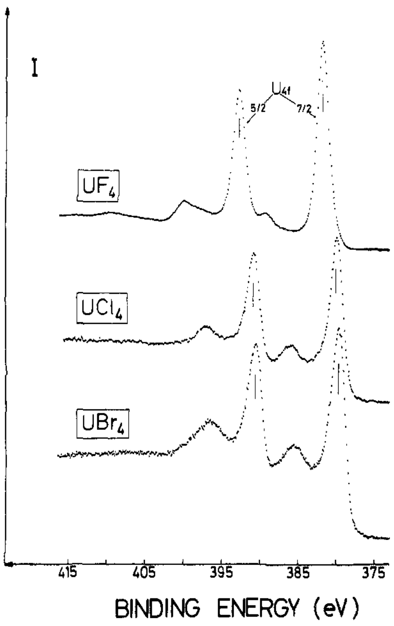

Figure 3. Uranium tetrahalides, UX$_4$: U 4f core level spectra.

Table IV. Uranium Halides, UX$_n$; Halogen Core Level Binding Energies (eV)

X	level	$n = 3$	$n = 4$	$n = 5$
F	1s	685.1	684.5	684.6
Cl	$2p_{3/2}$	197.9	197.5	197.5
	$2p_{1/2}$	199.4	199.0	199.0
Br	$3p_{3/2}$	181.5	181.2	180.8
	$3p_{1/2}$	188.2	187.8	187.5

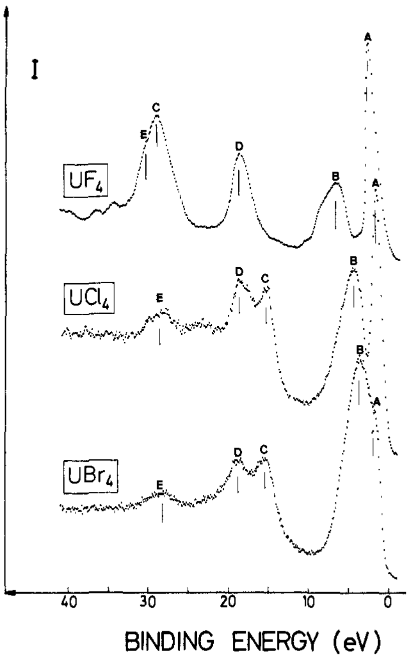

Figure 4. Uranium tetrahalides, UX$_4$: valence level spectra.

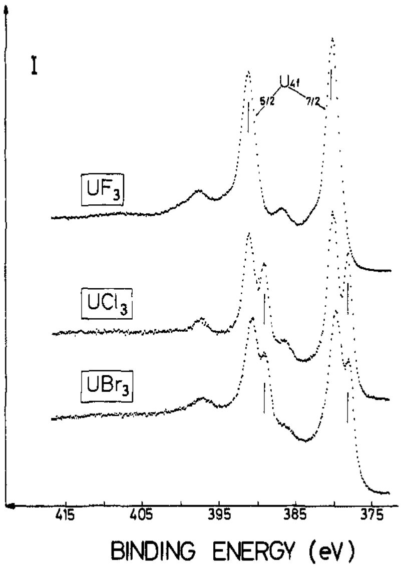

Figure 5. Uranium trihalides, UX$_3$: U 4f core level spectra.

Table V. Uranium Oxyhalides: Halogen Core Level Binding Energies (eV)

X	level	U^{3+} UOX	U^{4+} UOX$_2$	U^{5+} UO$_2$X	U^{6+} UO$_2$X$_2$
F	1s	–[a]	–[a]	–[a]	685.4
Cl	$2p_{3/2}$	198.3	198.1	(197.5)[b]	(196.6)
	$2p_{1/2}$	199.9	199.8	(199.1)	(198.5)
Br	$3p_{3/2}$	182.0	181.1	180.9	180.7
	$3p_{3/2}$	188.5	188.4	187.5	187.4

[a] Not measured. [b] Parentheses denote less certain data.

Table VI. Uranium Oxyhalides: O 1s Core Level Binding Energies (eV)

X	U^{3+} UOX	U^{4+} UOX$_2$	U^{5+} UO$_2$X	U^{6+} UO$_2$X$_2$
F				532.0
Cl	529.8	530.3	530.6[a]	531.0
Br	530.2	530.9	530.0	530.6

[a] Broad.

reported in the tables for valence band components as well as for the relevant core peak components. The estimated standard deviations on binding energies are ±0.1 eV or less, except for values in parentheses, for which they are ±0.2 eV or more.

The model used in valence peak B, with two or three components, does not attempt to identify the underlying components; at this stage, it is only aimed at obtaining the best curve fitting with the lowest number of peaks.

4. Discussion

4.1. Uranium Tetrahalides. The results obtained for UF$_4$, UCl$_4$, and UBr$_4$, shown in Figures 3 and 4 and Tables II, IV, VII, VIII, and IX, offer six characteristics, which can be described as follows, for decreasing ligand electronegativity: (a) the U 5f valence peak (A) comes closer to zero binding energy; (b) the splitting between

Table VII. Uranium Fluorides and Oxyfluorides: Valence Band Peak Positions (eV)[a]

U oxidn state	compd	U $6p_{1/2}$ E	F 2s C	O 2s F	U $6p_{3/2}$ D	(UO_2^{2+}) G	U 7s,6d,5f + F 2p B	U 5f A
3+	UF_3	29.2	27.2	(22.1)[c]	17.1	-[b]	3.6	0.6
4+	UF_4	30.9	29.1	-[b]	19.2	-[b]	7.0	2.8
5+	UF_5	30.6	29.2	-[b]	19.2	(14.9)[c]	5.7	2.7
6+	UO_2F_2	30.9	30.1	24.6[d]	20.3	14.9	5.8	-[b]

[a] Peak labels refer to Figures 4, 6, 8, and 10. [b] Missing peak. [c] Less certain value. [d] Uranyl.

Table VIII. Uranium Chlorides and Oxychlorides: Valence Band Peak Positions (eV)[a]

U oxidn state	compd	U $6p_{1/2}$ E	O 2s F	U $6p_{3/2}$ D	Cl 3s C	U 7s,6d,5f + Cl 3p B	U 5f A
3+	UCl_3	27.9	-[b]	17.9	15.5	4.4	1.1
	UOCl	28.1	23.1	18.0	16.9	4.9	1.4
4+	UCl_4	28.9	-[b]	18.8	15.4	4.4	1.6
	$UOCl_2$	(28.2)	23.7	18.8	15.8	4.8	1.8
5+	UCl_5	30.5	(24.6)	19.5	15.5	4.3	2.1
	UO_2Cl	(28.5)	(22.9)	(17.9)	(15.5)	(4.4)	(1.1)
6+	UO_2Cl_2	28.6	23.7	18.6	14.5	4.1	-[b]

[a] Peak labels refer to Figures 4, 6, 8, 10, and 12. Values in parentheses denote less certain values. [b] Missing peak.

Table IX. Uranium Bromides and Oxybromides: Valence Band Peak Positions (eV)[a]

U oxidn state	compd	U $6p_{1/2}$ E	O 2s F	U $6p_{3/2}$ D	Br 4s C	U 7s,6d,5f + Br 4p B	U 5f A
3+	UBr_3	27.9	(22.9)[c]	17.6	15.0	3.6	1.0
	UOBr	27.2	20.2	17.1	15.4	3.1	0.1
4+	UBr_4	27.9	-[b]	18.6	15.2	3.6	1.7
	$UOBr_2$	28.3	23.2	18.1	15.2	3.6	1.6
5+	UBr_5	28.6	23.0	18.0	14.4	3.2	0.6
	UO_2Br	28.1	22.1	17.0	14.7	3.0	0.8
6+	UO_2Br_2	29.4	22.9	18.0	13.9	3.2	-[b]

[a] Peak labels refer to Figures 4, 6, 8, 10, and 14. [b] Missing Peak. [c] Less certain value.

Table X. Uranium Halides: U 5f Relative Intensities (Surfaces Ratio)

	U 5f/ U 4f(total)	U 5f/ U $6p_{3/2}$		U 5f/ U $6p_{3/2}$
UF_4	0.0105	1.28	UF_3	0.82
UCl_4	0.0096	0.89	UCl_3	1.32
UBr_4	0.0066	0.41	UBr_3	0.56

Table XI. Uranium Tetrahalides: U $4f_{7/2}$ Shake-up Satellites

	splitting from main peak (eV)	intensity ratio (satellite/ main peak)
UF_4	7.3	0.12
UCl_4	6.1	0.30
UBr_4	5.8	0.67

peak A and band B decreases; (c) the U 5f intensity (peak A) decreases with respect to the U 4f core peaks and to U $6p_{3/2}$ (peak D), taken as quasi-atomic (Table X); (d) the U 4f core level binding energy decreases; (e) their shake-up satellites become closer to the main peak (Table XI); (f) the shake-up satellites have increasing intensity, relative to the main peak (Table XI).

Such a consistent set of observations can be interpreted by a single statement: from fluoride to bromide, there is an increasingly covalent character, which involves an increasingly strong U 5f participation in the bonding orbitals, represented in the spectrum by peak B.

There are two main reasons supporting this proposal. The first reason is the intensity decrease of the U 5f peak (A), while the formal oxidation state for all three compounds calls for a $5f^2$ structure. Two independent references were selected for checking this (Table X). Both sets of intensity ratios decrease in the same direction, but not in the same proportion. It should be noticed that intensity calculations are far from easy for U 5f and U $6p_{3/2}$ where these peaks are merged with either the U–X band or a halogen valence s peak (Cl 3s, Br 4s). In UCl_4 and UBr_4 the strong difference may indicate some combination between U 6p and these levels, but estimations of such an overlap are completely

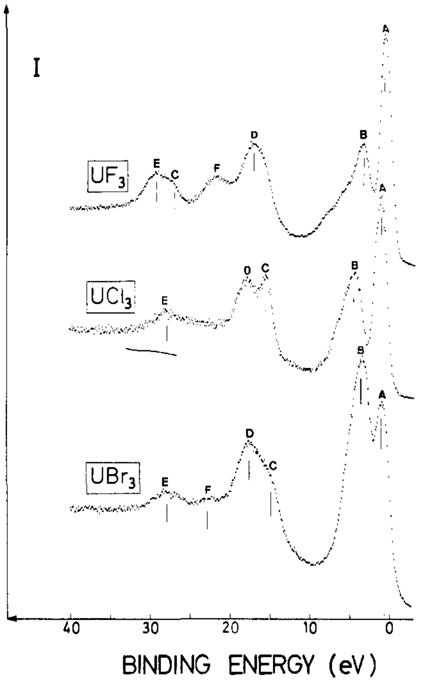

Figure 6. Uranium trihalides, UX_3: valence level spectra.

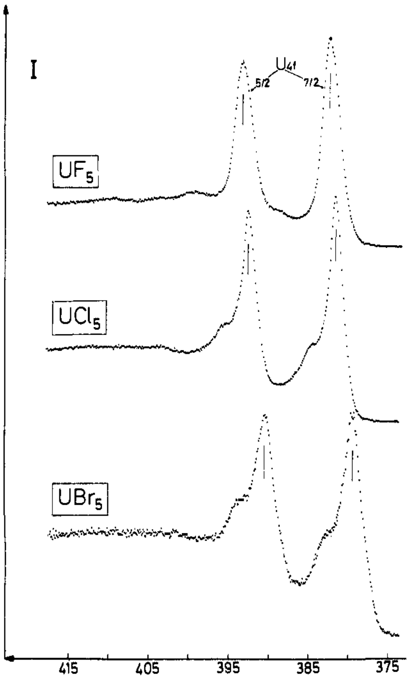

Figure 7. Uranium pentahalides, UX_5: U 4f core level spectra.

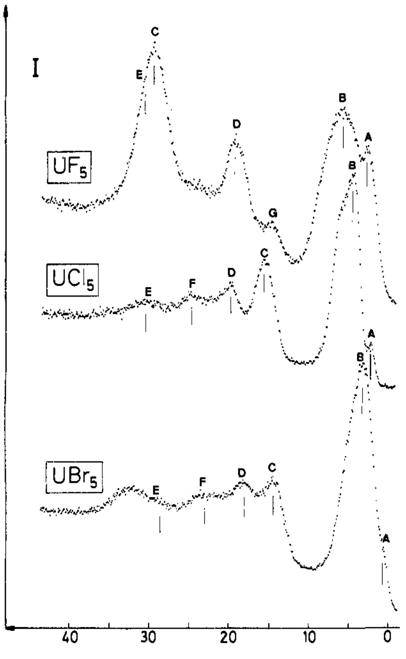

Figure 8. Uranium pentahalides, UX_5: valence level spectra.

missing, to our knowledge, for these compounds in the solid state. In fact, the present experimental data might be useful to such calculations, for which preliminary results exist in the case of the free molecules.[28]

The U $6p_{3/2}$/U 4f intensity ratio, which is a simple atomic model is expected to be constant, might also be modified by differences in the photoelectronic cross-section asymmetry parameter[29] and by differences in paramagnetic coupling effects. However, the theoretical grounds required for a quantitative approach to these phenomena are not available, at present, for these cases.

The second reason, confirming the first, is the increase of U 4f shake-up satellite intensity for the more covalent compounds. This satellite, similar to that observed in UO_2,[2b] corresponds to valence electron excitation simultaneously with photoemission, and therefore obeys the monopole selection rule. The valence transition observed here should concern electrons with 5f character; considering the satellite-to-mean peak splitting, the electrons should be excited from band B (peak A being too close to the "Fermi level" used as zero binding energy, and comparable satellites being observed with ThX_4 ($5f^0$) compounds[30]) into the lowest available 5f levels. Stronger satellites indicate an increased 5f admixture in band B.

The other observations fit with the classical picture of a more ionic (UF_4) or more covalent (UBr_4) solid: lower core-level binding energies for the latter, and smaller energy gap in the valence region.

It would be interesting, at this point, to find a correlation between crystal and electronic structure of the uranium tetrahalides. We could, for instance, attempt to look at ionic radii of U^{4+}. This immediately gives rise to the question of how to define them,[31] as there is a variety of metal-halogen distances observed within every metal coordination polyhedron. Next comes the evaluation of models relating bond lengths with their strengths.[32] This type of discussion, presenting its own difficulties and requiring detailed preliminaries, will therefore be kept for another paper.

4.2. Uranium Trihalides. Results obtained for UF_3, UCl_3, and UBr_3 do not include, at present, reliable data on the U 4f shake-up satellites; the complexity of spectra (Figures 5 and 6) due to the presence of surface species precludes any valid analysis of low-intensity structures. The core and valence spectra being, as indicated in section 2.2., differently affected by the surface contribution, it would also be meaningless to use the U 4f for comparison with valence intensities. Let us then focus on the other significant observations.

(a) All U 4f binding energies (Table II) are lower than in the corresponding tetrahalides. They follow the usual sequence of halogen electronegativities.

(b) The U 5f peak is generally stronger than in the UX_4 compounds, as expected for $5f^3$ vs. $5f^2$ compounds.

(c) Three characteristics of the valence band (Tables VII–IX) are observed simultaneously, as in the UX_4 series (see a-c, in section 4.1): decreasing U 5f binding energy; decreasing U 5f – (U–X) band splitting; decreasing U 5f intensity (Table X). But they lead to the conclusion that UF_3 is much less ionic than UCl_3, and almost as covalent as UBr_3.

This finding is supported, in turn, by an other observation: a look at the F 1s core level binding energies (Table IV) shows that the value in UF_3 (685.1 eV) is significantly higher than in the other fluorides (684.5, 684.6 eV); this is in agreement with a less negatively charged fluoride ion, a rather unusual occurrence according to Ebner.[33] We should note here the coincidence of the UF_4 and UF_5's F 1s values with these literature data, a point which illustrates the validity of our calibration procedure. Using the same references, the F 1s binding energies in organic solids, where the C–F bond is polarized but covalent, can be used for comparison. They range from 687.9 eV in poly(vinyl fluoride) to 689.9 eV in polytetrafluoroethylene (Teflon),[34] and 687.7 eV in a series of neuroleptic drugs.[35]

4.3. Uranium Pentahalides. The spectra of UF_5, UCl_5, and UBr_5 are shown in Figures 7 and 8. As explained in section 2.2, it has not been possible to obtain samples totally free of contamination; however, contamination seems here to have little effect

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[28] Ellis, D. E., private communication.

[29] Gelius, U. In "Electron Spectroscopy"; Shirley, D. A., Ed.; North Holland: Amsterdam, 1972; p 326.

[30] Dyke, J. M.; Josland, G. D.; Morris, A.; Tucker, P. M.; Tyler, J. W. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1273.

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[35] Riga, J.; Verbist, J.; Degelaen, J.; Tollenaere, J. P.; Koch, M. H. J. *Mol. Pharmacol.* **1977**, *13*, 892.

on either core or valence level data.

Trowbridge and Richards,[25] operating on thermally or chemically reduced thin films of UF_6 deposited on Cu or Ni foil, discuss the degradation of UF_5 by disproportionation to volatile UF_6 and to lower fluorides. They report a U $4f_{7/2}$ binding energy of 383.4 eV, shifting down within 20 min to 382.4 eV, which happens to be exactly our measurement. Our respective values for UF_4, however, disagree by 0.3 eV (382.3 and 382.0 eV). As a result, the first authors logically identify the stabilized U 4f peaks with UF_4, while we would not do so. Comparison of Figures 3 and 7 shows the differences between UF_4 and UF_5, both in peak width and in shake-up satellites; they cannot be made to coincide. Only a small "UF_4" contribution could be subtracted from the UF_5 data, repeatedly taken on fresh samples, stored and handled under strictly dry nitrogen (older samples indeed can show severe modifications).

The full widths at half-maximum of the U $4f_{7/2}$ peaks in the other UF_5 and UF_4 study are 3.3 and 2.1 eV. We find 2.5 and 1.9 eV, respectively, indicative of a slightly better resolution. But even then, our UF_5 peak is not resolved into two components, as was the case in U_2O_5[2c] (for a total fwhm of only 2.3 eV, compared to 1.4 eV in UO_2 and 1.6 eV in UO_3). Even the second derivative of the spectra, which often allows the detection of twin peaks,[36] does not indicate such a situation here. We therefore suggest that our data are representative of UF_5, in spite of the nonlinearity of the chemical-shift dependence on U oxidation state (in contradiction with ref 25), and the unusually broad core peaks.

Trowbridge and Richards[25] obtained their UF_5 spectra with many experimental precautions; they kept the samples, obtained from UF_6, under UF_6 pressure until just before measurements, to slow down disproportionation. Their spectra and the reported change with time are not incompatible with an UF_6 contribution, fading after a few minutes. But this way of analyzing the question might not be the final one, and new experiments may be required to solve this important problem. We only hope to contribute in a constructive way.

Following these considerations, let us now check the observations relevant to the uranium pentahalides.

(a) The U 4f binding energies consistently shift to higher values, both as a direct function of halogen electronegativity and stoichiometry for a given halide (Table II).

(b) With the exception of fluorides (discussed in section 4.1), halogen core levels (Table IV) shift in the opposite direction, confirming the increased ionicity of the solid. Comparison can be made, in the case of Cl 2p, with binding energies obtained in a consistent series of molecular solids[35], for a chloride ion and an organo-chlorine atom: Cl $2p_{3/2}$ ranges respectively from 196.7 to 197.0 eV for Cl^-, and from 198.8 to 200.2 eV for Cl (values corrected to the Au $4f_{7/2}$ reference at 83.8 eV).

(c) In all valence-band spectra (Figure 8), peak A is strongly reduced in intensity, as expected for $5f^1$ compounds. The observations, already familiar with UX_4 and UX_3, that peak A has a lower binding energy (Tables VII–IX) and lower intensity, and merges with peak B as we go to less electronegative ligands, are verified again here. The more ionic compound is the fluoride, the less ionic is the bromide.

(d) The U 4f peaks (Figure 7) present significant satellites in UCl_5 and UBr_5, smaller in UF_5. These peaks cannot be confused with unwanted uranium species; looking through all U 4f spectra, the closest aspect is found with the UO_2X_2 compounds. However, the strength of contaminant O 1s peaks in the present case is not sufficient for such interpretation. Also the position on the binding energy scale of these satellites precludes any identity with other uranium species, within a given halide series.

Fitting again into the already given description, the stronger satellites are observed for the least ionic compound, and they are also the closest to the major peak.

4.4. The Oxyhalides. 4.4.1. Uranyl Halides, UO_2X_2 (Figures 9 and 10; Tables III and V–IX). These compounds are the only U^{6+} representatives in this work. All three contain it as the uranyl species, for which it has been shown that the inner-valence shells, U $6p_{3/2}$ and O 2s, reorganize as a result of the short U–O bonding. Two new levels normally appear in the spectra following U $6p_{3/2}$ splitting.[37]

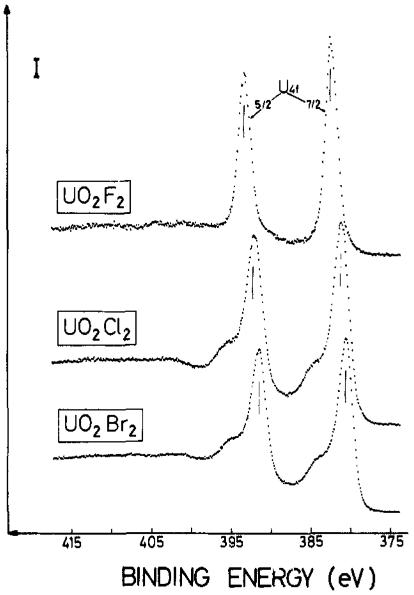

Figure 9. Uranyl halides, UO_2X_2: U 4f core level spectra.

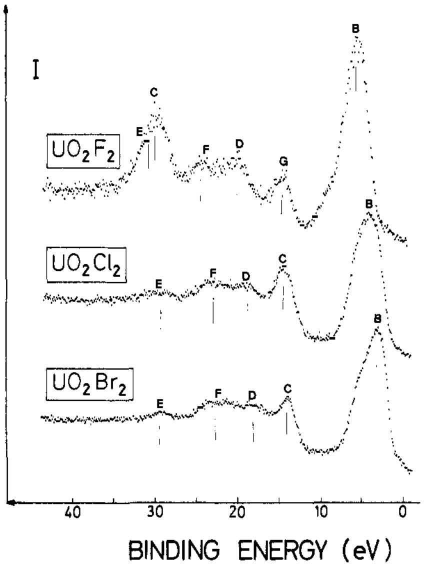

Figure 10. Uranyl halides, UO_2X_2: valence level spectra.

Only in UO_2F_2 (Figure 10, Table VII) can one of these peaks (G) be observed; the other can be distinguished as a shift of peak F. With the other uranyl halides (Tables VIII and IX), there is a valence ns level (peaks C) unfortunately masking the uranyl G peak.

The second observation is that the U 5f peak (A) has completely disappeared as expected.

The third observation within the uranyl halides series is made on the relative shifts of U 4f (Table III), halogen core (Table V), and O 1s peaks (Table VI); the core peaks of the uranyl group atoms shift together to lower binding energies for decreasing halogen electronegativity, suggesting that the UO_2^{2+} ion behaves as a real single species. For comparison, the U $4f_{7/2}$ binding energy in γ–UO_3 ("uranyl oxide") is 380.7 eV. We note that the U 4f shifts are larger than the O 1s ones, while the latter are usually considered as more sensitive to a given change in electron popu-

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[36] Pireaux, J. J. *Appl. Spectrosc.* **1976**, *30*, 219.

[37] Veal, B. W.; Lam, D. J.; Carnall, W. T.; Hoekstra, H. R. *Phys. Rev. B* **1975**, *12*, 5651.

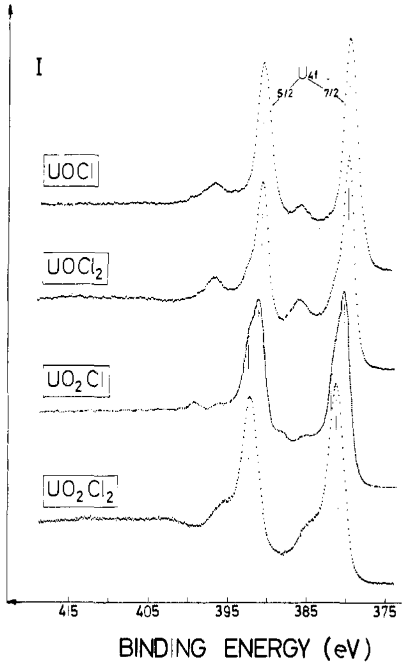

Figure 11. Uranium oxychlorides: U 4f core level spectra.

lation; this then indicates, within the uranyl ion, an unequal response to the effect of the halogen, the metal being more affected than the oxygens.

Taking a look at the halogen core levels binding energies, as compared to the other halides and oxyhalides, we find several surprises: the rather high F 1s value; the singularly low Cl 2p values; and within the two oxyhalide series, the UO_2X_2 halides core levels presenting the lowest binding energies.

The first of these facts is rather difficult to explain. When all core levels of a spectrum have unusually high binding energies (here by ~1 eV) one may suspect in invalid calibration. However, not all valence peaks exhibit the same phenomenon, particularly peaks B and G, compared in UO_2F_2 and UF_5 (where G is present as contaminant) (Table VII). One other work[38] reports core binding energies for UO_2F_2, also calibrated to gold; these are of little help, as the U 4f binding energies are identical (within 0.1 eV), but F 1s is 1.0 eV lower than here (no value is given for O 1s). Chadwick's values[38] for UF_4 are also slightly different from ours (+0.5 eV for U 4f, +0.1 for F 1s, correcting to Au $4f_{7/2}$ at 83.8 eV), illustrating the difficulty of comparing values obtained under different conditions. Unless new experiments lead to revised values, we should understand the present observations as an indication of a particularly high dielectric character of UO_2F_2, in comparison with all other studied compounds. This would result, either in lower relaxation energies for core electron emission (general shift to higher binding energies), or inadequacy of the gold decoration technique for calibration, or both.

However, even by arbitrary "calibration" and setting the F 1s peak at the most common value[25] of 684.5 eV, our present conclusions still hold; only quantitative aspects should then be revised.

The statements on the Cl 2p and Br 3p core levels are very clear. They indicate a strong negative polarization of the halide, which is interesting to note, as the other electronegative atoms in the compounds are involved in the formation of partly (or mainly) covalent uranyl groups. Further discussion of this point will be found in the following paragraphs.

4.4.2. The Oxychloride and Oxybromide Series (Figures 11–14; Tables III and V–IX). These series of compounds offer two interesting characteristics: for a given uranium oxidation state, we can focus on the effect of replacing two halides by one oxygen atom; there are two continuous series of oxyhalides, from U^{3+} to U^{6+}.

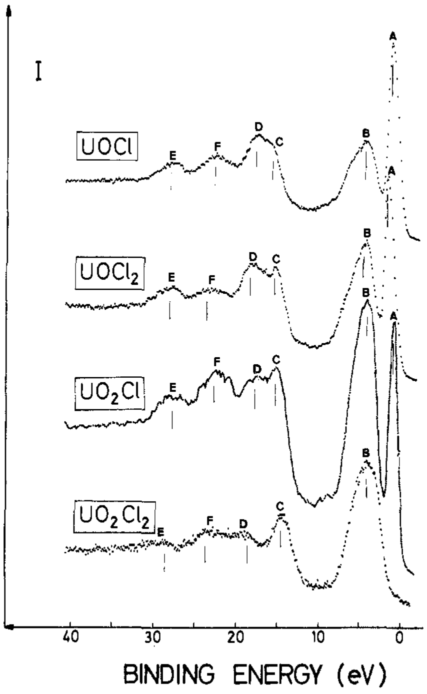

Figure 12. Uranium oxychlorides: valence level spectra.

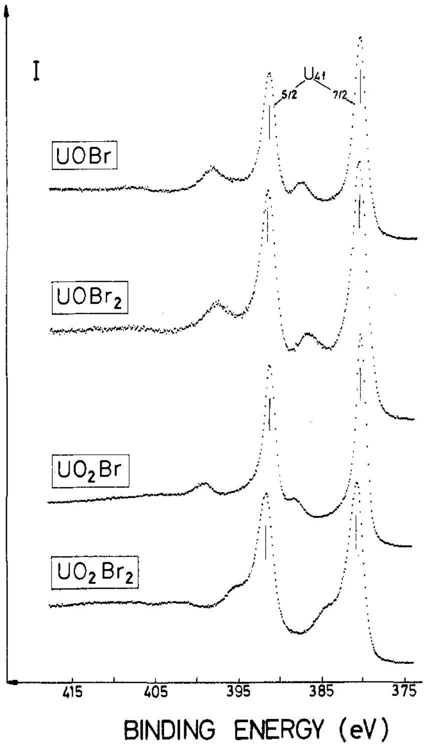

Figure 13. Uranium oxybromides: U 4f core level spectra.

Table XII. Core Levels Shifts (eV) Following Replacement of Two Halide Ions by One Oxide Ion

X	U^{3+}	U^{4+}	U^{5+a}
	U $4f_{7/2}$		
Cl	+1.7	+0.1	(+0.1)
Br	+1.7	+0.5	(+0.8)
	Halogen Core Levels		
Cl $2p_{3/2}$	+0.4	+0.6	(0.0)
Br $3p_{3/2}$	+0.5	+0.6	+0.1

[a] Parentheses denote differences involving less certain values.

First comparing Table II with III (U4f levels) and IV with V (halide core levels), we note an increase in binding energy for both

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(38) Chadwick, D. *Chem. Phys. Lett.* **1973**, *21*, 291.

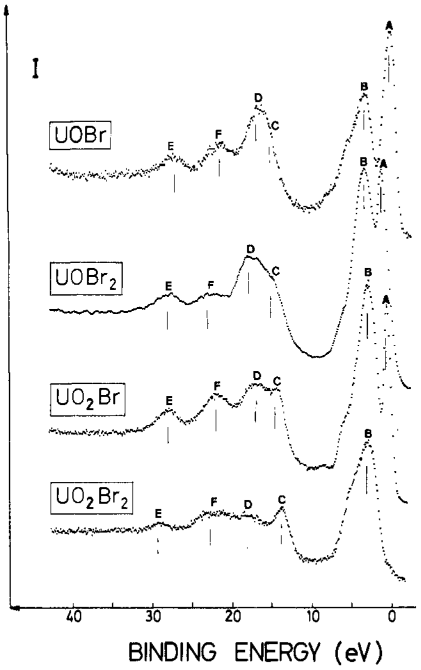

Figure 14. Uranium oxybromides: valence level spectra. (UOBr$_2$ is smoothed).

sets of peaks upon oxygenation (Table XII).

Within each series, U 4f binding energies increase with the metal oxidation state, but halogen levels shift in the opposite way. This behavior is identical with that in simple halides.

The UO$_2$Cl spectrum reveals two U 4f doublets, the low binding energy components being the strongest. None of them can be clearly identified with the use of other U 4f core levels peaks, and it is therefore difficult to decide whether there is dismutation or decomposition of the sample. The experimental difficulties for handling the sample were considerable (also the crystal structure could not yet be determined); therefore, the present data are given for completeness, but in parentheses as a reminder of their lower reliability.

The valence bands (compare Figures 12 and 14 with the appropriate spectra of Figures 6, 4, and 8; see Tables VIII and IX) show in most cases an increase of the ionic characteristics for the oxyhalides, with respect to the corresponding halide. The U 5f peak (A) is a good monitor for this. Peak B is modified in shape by O 2p admixture.

Finally, the trend in O 1s binding energies (Table VI) completes the picture; the negative formal charge on the oxygen seems less important as uranium oxidation state increases, this being compensated by the negative charge of the halogen. The U–O bond gradually acquires a more covalent character, which results in formation of the uranyl group. The available structural data on U–O distances support this proposal, which has already been put forward in the case of oxides.[2c,d] The 2.05-Å U–O distances in UO$_2$Br illustrate the intermediate situation between uranyl (very short) and other U–O bonds.

4.4.3. Uranium 4f Shake-up Satellites. These are observed with nearly all compounds but their interpretation is less obvious than with the halides, as there is no continuous sequence in the evolution of their characteristics along the series. The most intriguing example is the UO$_2$X$_2$ case, where the satellites are absent or weak and quite distant from the main peaks.

It is interesting then to recall what was found in the analysis of UO$_2$ and UO$_3$ satellites;[2b] the nature of shake-up transitions in the latter involves different orbitals and is sufficiently different to be used as a uranyl – U^{6+} "fingerprint".[2c,d]

According to this, we discover that, along the UO$_2$X$_2$ series, the satellites observed with the chloride and bromide resemble the UO$_3$ one, except for their higher intensity. With F$^-$, on the contrary, as in the very ionic halides, there is a low satellite.

We suggest that the explanation for the UO$_2$X "irregularity" is to be found in the special role of uranium–oxygen bonding, for which the details of the structure have to be taken into account. This requires a considerable amount of further work and thought; it will form the substance of another paper, including work on the oxide family.

5. Conclusions

The experimental study of uranium halides (F, Cl, Br) and oxyhalides has brought to light some important information about the nature of chemical bonding in these compounds: (a) The combined examination of valence photoelectron peaks (particularly U 5f), core levels, and U 4f shake-up satellites is a powerful tool in the determination of the ionicity of the solid. Only core level chemical shifts are not sufficient by themselves.

(b) There is evidence for U 5f participation in chemical bonding; this contribution increases when the compound becomes more covalent.

(c) Ionicity is largest for the higher halides (higher uranium oxidation state) and with the more electronegative halogens; an exception to this rule is UF$_3$, which is more covalent than UCl$_3$.

(d) The oxygen in oxyhalides shows a growing tendency to form uranyl groups, as the uranium oxidation state goes up. These uranyl groups have covalent bonding and behave as a single species vs. the halogen.

We hope that the experimental data, as well as the above statements, will be useful to, and stimulate the interest of, scientists involved in research on theoretical models for uranium compounds, on application of other spectroscopies, and—last but not least—in the study of more complicated systems, including surface and solid-state reactions.

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Last, but not least, all authors want to thank their colleagues and co-workers at Namur, especially those who designed the glovebox system, developed the data-handling computer programs, and participated in many other ways in the present work.

Registry No. UF$_3$, 13775-06-9; UCl$_3$, 10025-93-1; UBr$_3$, 13470-19-4; UOCl, 60762-63-2; UOBr, 76371-49-8; UF$_4$, 10049-14-6; UCl$_4$, 10026-10-5; UBr$_4$, 13470-20-7; UOCl$_2$, 13842-38-1; UOBr$_2$, 19173-90-1; UF$_5$, 13775-07-0; UCl$_5$, 13470-21-8; UBr$_5$, 13775-16-1; UO$_2$Cl, 19435-22-4; UO$_2$Br, 26512-08-3; UO$_2$F$_2$, 13536-84-0; UO$_2$Cl$_2$, 7791-26-6; UO$_2$Br$_2$, 13520-80-4.