band in field sweep unlock mode. The spectra were calibrated by the usual audio-side-band method and referenced relative to external $CFCl_3$ by sample interchange. Chemical shifts are estimated to be accurate to ±0.5 ppm.

Raman spectra were obtained with a Spex Industries Model 1400 spectrometer using the 5145-Å radiation from a Spectra Physics Model 164 argon ion laser. Spectra were recorded at −90° by placing the sample tube inside a glass tube surrounded by an evacuated jacket, silvered except at the center. Liquid nitrogen was boiled off from a dewar and passed through the tube. The temperature was monitored with a copper–constantan thermocouple positioned in the stream just ahead of the sample region. The Raman shifts are estimated to be accurate to ±2 cm^{-1}.

Preparation of BrF_6^+ Salts. Solutions of $Kr_2F_3^+SbF_6^-$, $Kr_2F_3^+AsF_6^-$, and $KrF^+AsF_6^-$ were prepared by dissolving approximately 0.2–0.5 mmol of $Kr_2F_3^+$ or KrF^+ salt in approximately 0.25 g of BrF_5 at 0°. The nmr spectra of solutions of the $Kr_2F_3^+$ salts were recorded at −60° and were found to consist of lines readily assignable to $Kr_2F_3^+$, MF_6^-, and BrF_5.[4] Solutions were allowed to warm up rapidly to room temperature at which point vigorous evolution of krypton and fluorine ensued. To avoid excessive pressures within the reaction tube, the reaction was periodically quenched by rapid cooling to −196° and the volatiles were removed under vacuum. After gas evolution had ceased, the solutions were maintained at room temperature for an additional $^1/_2$ hr to ensure that the oxidation was complete. The remaining BrF_5 was removed under vacuum at room temperature. Yields of BrF_6^+ salts were in general low. Owing to inherent experimental difficulties, no effort was made to obtain precise values for the yields, but it is estimated that based on the initial amounts of $Kr_2F_3^+MF_6^-$ and $KrF^+AsF_6^-$ the yields did not exceed 20%. Although the resulting white solids were stable at room temperature for periods up to several days, samples were routinely stored at −78° under a positive pressure of high-purity argon until their Raman or nmr spectra could be recorded.

Attempted Synthesis of $BrF_6^+AsF_6^-$ by Other Means. Mixtures of BrF_5, F_2, and AsF_5 in different mole ratios were heated in a Monel reactor for 3 days at 200–250° under autogenous pressures of 125–200 atm. Only the unreacted starting materials and very small quantities of $O_2^+AsF_6^-$ and metal AsF_6^- salts were recovered.

Displacement Reaction between NOF and $BrF_6^+AsF_6^-$. Nitrosyl fluoride (6.9 mmol) was condensed onto 0.20 g (0.52 mmol) of $BrF_6^+AsF_6^-$ at −196° in a passivated Teflon tube equipped with a Teflon valve. The reaction vessel and contents were warmed to −78° and kept at this temperature for $^1/_2$ hr. The reaction vessel was then cooled to −196° and the F_2 generated at −78° according to eq 9 was removed under vacuum. The vessel was warmed to −63° for an additional $^1/_2$ hr and since upon cooling to −196° no further F_2 gas was pumped off, the reaction was assumed to be complete. The reaction vessel was slowly warmed to 0° while its volatile contents were transferred by static vacuum distillation through all-Teflon and FEP connections to an FEP Raman sample tube equipped with a Teflon valve. At −90°, two phases were present in the FEP sample tube, a colorless volatile liquid phase that was identified from its Raman spectrum as NOF and a white crystalline solid. The Raman spectrum of the white solid was recorded at −90° both in the presence of excess NOF and after the NOF had been removed under vacuum at −78°. Based on a comparison with the known spectra of $Cs^+BrF_6^-$ [37] and $NO^+BrF_6^-$,[38] the white solid was unambiguously identified as $NO^+BrF_6^-$. A less volatile white solid, which remained in the Teflon reaction vessel at 0° and which was rapidly pumped off under dynamic vacuum at room temperature, was identified as $NO^+AsF_6^-$ from its Raman spectrum.[39]

Preparation of $BrF_4^+Sb_2F_{11}^-$ and BrF_4^+ Solutions. The adduct was prepared according to the method of Surles, *et al.*[23] The solid sample was prepared in a 5-mm o.d. glass nmr tube attached to a Teflon valve which also served as the Raman sample tube. After recording the Raman spectrum, 0.108 g (0.177 mmol) of $BrF_4^+Sb_2F_{11}^-$ was transferred in a drybox to an FEP sample tube equipped with a Teflon valve and dissolved in 0.120 g (6.0 mmol) of anhydrous HF. A solution of BrF_4^+ in SbF_5 was prepared in a 5-mm o.d. glass nmr tube by dissolving 0.146 g (0.83 mmol) of BrF_5 in 1.93 g (8.9 mmol) of SbF_5. The nmr spectra of both solutions were recorded at 26°.

Acknowledgments. We thank the National Research Council of Canada for financial support of this work and for a scholarship to G. J. S. We are grateful to Dr. K. O. Christe and Dr. W. Sawodny for making their manuscript pertaining to the ^{19}F nmr and Raman spectroscopy of BrF_4^+ available to us prior to its publication.

Registry No. $Kr_2F_3^+SbF_6^-$, 50921-18-1; $Kr_2F_3^+AsF_6^-$, 50921-17-0; $KrF^+AsF_6^-$, 50859-36-4; BrF_5, 7789-30-2; NOF, 7789-25-5; Xe, 7440-63-3; O_2, 7782-44-7; $BrF_6^+Sb_2F_{11}^-$, 51063-28-6; BrF_4^+-$Sb_2F_{11}^-$, 36445-03-1; $BrF_6^+AsF_6$, 51063-29-7; $NO^+BrF_6^-$, 50859-39-7; ^{79}Br, 14336-94-8; ^{81}Br, 14380-59-7.

(37) J. Shamir and I. Yaroslovsky, *Isr. J. Chem.*, 1, 495 (1969).
(38) R. J. Gillespie and G. J. Schrobilgen, unpublished results.
(39) A. M. Qureshi and F. Aubke, *Can. J. Chem.*, 48, 3117 (1970).

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Spectral Studies of Oxouranium(V) Species

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Received September 14, 1973 AIC306816

Electronic spectral studies and semiempirical theoretical calculations of energy levels of UOF_5^{2-} and $UOBr_5^{2-}$ have been made in order to locate and assign all of the six electronic transitions in these $5f^1$ species. The data are compared with previous results for $UOCl_5^{2-}$ and reveal that each of the six electronic transitions is shifted to higher energy in the expected order: $Br^- < Cl^- < F^-$. The best-fit spin–orbit coupling constants also increase in this same order: 1750, 1770, and 1850 cm^{-1}, respectively. Electron paramagnetic resonance spectra have been obtained for polycrystalline solids at ambient temperature for all species UX_6^- and UOX_5^{2-} ($X^- = F^-, Cl^-, Br^-$) except for UF_6^-. The significance of these epr results is discussed.

In an earlier paper[1] we elaborated a theoretical treatment of a tetragonally distorted hexacoordinated U^{5+} species, making calculations specifically for the $UOCl_5^{2-}$ anion and utilizing the theory to make assignments of the observed electronic spectral bands for this complex. We have now extended both the theory and the experimental data to encompass the other two known oxohalo species, UOF_5^{2-} and $UOBr_5^{2-}$. These new results are presented in this paper along with an analysis of the data for all three oxohalo complexes.

Experimental Section

A. Preparation of Compounds. Since most compounds of uranium(V) are sensitive to both oxygen and moisture, compounds were prepared and handled in an inert atmosphere. Both a steel drybox

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(1) J. Selbin, C. J. Ballhausen, and D. G. Durrett, *Inorg. Chem.*, 11, 510 (1972).

and plastic glove bags were employed. Pressure rather than suction filtration was used. Solvents were dried over anhydrous $CaSO_4$, Linde 3A molecular sieves, or CaH_2.

1. UCl_5·TCAC (TCAC = Trichloroacryloyl Chloride, Cl_2C=CCl-COCl). This valuable starting compound was prepared as previously described.[2]

2. $[(C_2H_5)_4N]_2UOF_5$, Tetraethylammonium Oxopentafluorouranate(V). This compound was prepared by two different procedures, one being a slight modification of that first described by Ryan[3] and the other a new method.

a. A saturated solution of $(C_2H_5)_4NF$ in 90% acetone–10% ethanol was prepared by first mixing 5 ml of a saturated solution of the salt in ethanol with 50 ml of dry acetone and then decanting the solution from the precipitate. To this solution was slowly added 1.09 g (1.9 mmol) of $(C_2H_5)_4NUCl_6$, producing a pink precipitate. The solid was separated by filtration, washed with acetone, and dried and stored *in vacuo*; yield 33%. *Anal.* Calcd for $C_{16}H_{40}N_2UOF_5$: C, 31.52; H, 6.61; N, 4.59. Found: C, 31.35; H, 7.12; N, 4.41. The purity of the compound was further verified by analysis of its electronic spectrum.

b. In the second procedure a saturated solution of $(C_2H_5)_4NF$ in 95% acetone–5% ethanol was prepared by adding 57 ml of dry acetone to 3 ml of saturated solution of the salt in absolute ethanol. With continuous stirring, 1.11 g (1.8 mmol) of solid UCl_5·TCAC was slowly added to the solution. There was immediate reaction to produce a fluffy pink precipitate. The product was separated by filtration, washed with dry acetone, and dried and stored *in vacuo*; yield 65%. *Anal.* Calcd for $C_{16}H_{40}N_2UOF_5$: C, 31.52; H, 6.61; N, 4.59. Found: C, 31.31; H, 7.01; N, 4.84.

3. $[(C_2H_5)_4N]_2UOCl_5$, Tetraethylammonium Oxopentachlorouranate(V). This compound was prepared by the procedure developed by Durrett.[1,4]

4. $[(C_2H_5)_4N]_2UOBr_5$, Tetraethylammonium Oxopentabromouranate(V). This compound was prepared by the procedure of Ryan.[3] It has been our experience, as well as that of others who work with pentavalent uranium, that it is extremely difficult to obtain a compound of uranium(V) free of at least traces of uranium(IV) and/or uranium(VI). If for no other reason, this occurs because of disproportionation of the relatively unstable 5+ species into the relatively stable 4+ and 6+ species. Although our analytical analysis fits well for our desired compound, we estimate from electronic spectral bands that about 6% of our $UOBr_5^{2-}$ compound disproportionated into uranium(IV) and -(VI). *Anal.* Calcd for $C_{16}H_{40}N_2UOBr_5$: C, 21.02; H, 4.41; N, 3.06. Found: C, 20.57; H, 4.62; N, 2.76.

5. Salts of Hexahalouranate(V). It was necessary in the course of this investigation to have salts of UF_6^-, UCl_6^-, and UBr_6^- available for spectral studies, so that we have our own actual spectral data and parameters derived therefrom required for the semiempirical calculations made on the lower symmetry oxohalo species. Salts of UCl_6^- with the cations $(C_2H_5)_4N^+$, NH_4^+, K^+, $(C_6H_5)_4As^+$, and Cs^+ were prepared, in each case using UCl_5·TCAC as the starting material and $SOCl_2$ as the solvent and following the established[2] procedure. *Anal.* Calcd for NH_4UCl_6: Cl, 45.37. Found: Cl, 45.03. Calcd for $KUCl_6$: Cl, 43.42. Found: Cl, 42.88.

The $(C_6H_5)_4As^+$ and $(C_2H_5)_4N^+$ salts of UBr_6^- were prepared by the procedure of Ryan, *et al.*[3,5] and their purity checked by their electronic spectra. $(C_6H_5)_4AsUF_6$ was prepared in 85% yield by the procedure of Ryan, *et al.*,[5] and its purity checked spectrally. $CsUF_6$ was prepared by two procedures, one being that of Ryan, *et al.*,[5] and the other a new method elaborated here.

In a dry nitrogen glove bag a solution of UCl_5·TCAC in dry nitromethane was prepared by dissolving 3.095 g (5.1 mmol) of UCl·TCAC in 4 ml of the solvent and filtering to remove any insoluble impurities. To this solution was added 7 ml of 48% aqueous HF in which 1.3 g (8.6 mmol) of anhydrous CsF had been dissolved. A blue precipitate formed and the supernatant liquid was decanted. The precipitate was washed with 48% aqueous HF and then dried and stored *in vacuo*. *Anal.* Calcd for $CsUF_6$: U, 49.09. Found: U, 49.01.

B. Physical Measurements. Infrared spectra were recorded on both Beckman IR-10 and IR-7 instruments or on a Perkin-Elmer Model 180. Solids were mulled in Nujol, hexachlorobutadiene, or Kel-F polymer oil, or they were pressed into KBr pellets. Electronic spectra were recorded on a Cary Model 14 spectrophotometer. Mulls were placed between two plates of quartz or Suprasil No. 2 and clamped between brass plates which were suspended in an optical quartz dewar. This allowed both ambient temperature and 77°K spectra to be obtained reproducibly. Esr spectra were recorded by means of a JEOLCO esr spectrometer, Model JES-3BS-X, using 100-kc modulation. The magnetic field was measured with an nmr precision gaussmeter. Polycrystalline solids were studied in either 2- or 5-mm od quartz tubes.

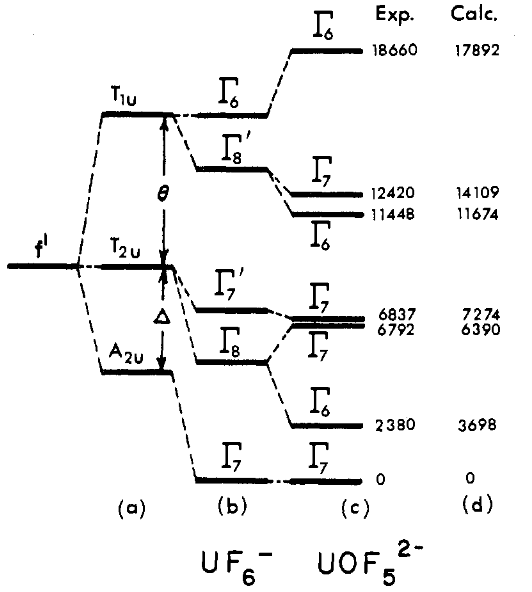

Figure 1. The f^1-orbital energy levels perturbed by (a) the O_h field (where the Δ and θ are those of UF_6^- and $\zeta = 1850$ cm^{-1}), (b) the O_h field plus spin–orbit coupling (where the separations are those of UF_6^-), (c) the D_4 field plus spin–orbit coupling (where the experimental separations are those of UOF_5^{2-}), and (d) the calculated energies of the several levels assuming $\tau = 700$ cm^{-1} and $\zeta = 1850$ cm^{-1}.

Spin concentration for the UOX_5^{2-} species was determined by double integration of the epr signal using a sample of pure $K_3Mo(CN)_8$ as a standard. The number of spins per molecule was found to be 1, within experimental error.

Theory and Results

The theoretical treatment of the $5f^1$ electronic system in an octahedral field appropriate to U^{5+} hexacoordinated complexes has been carried out several times,[2,6] and we recently[1] extended this treatment to tetragonally distorted octahedral fields appropriate to complexes of UO^{3+}. We shall not repeat here the detailed theory given in ref 1 where application to $UOCl_5^{2-}$ was made, but we shall use the terminology and symbolism of that paper to present the results and conclusions of an analogous treatment of the UOF_5^{2-} and $UOBr_5^{2-}$ species.

Figure 1 shows the effects of perturbing the f^1 orbital energy levels successively by an octahedral field, spin–orbit coupling, and finally a D_4 field for the UF_6^- and UOF_5^{2-} ions. The actual experimental and calculated values shown are for the latter ion. The general procedure for setting up and solving the appropriate secular determinants used to arrive at the semiempirical calculated values is given in ref 1. Here we only sketch the results for our new species.

From the UF_6^- spectrum we took $\Delta\omega(\Gamma_7' \leftarrow \Gamma_7)$ as 7400 cm^{-1} and determined the best-fit spin–orbit coupling constant, $\zeta = 1850$ cm^{-1}. Using these values allowed calculation of Δ

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(2) J. Selbin, J. D. Ortego, and G. Gritzner, *Inorg. Chem.*, 7, 976 (1968); H. J. Sherrill, D. G. Durrett, J. Selbin, D. Brown, and T. L. Hall, *Inorg. Syn.*, 15, in press.

(3) J. L. Ryan, *J. Inorg. Nucl. Chem.*, 33, 153 (1971).

(4) D. G. Durrett, Ph.D. Dissertation, Louisiana State University, Baton Rouge, La., 1972.

(5) J. L. Ryan, D. G. Durrett, H. J. Sherrill, and J. Selbin, *Inorg. Syn.*, 15, in press.

(6) See, *e.g.*, C. J. Ballhausen, *Theoret. Chim. Acta*, 24, 234 (1972), and references therein; W. B. Lewis, H. G. Hecht, and M. P. Eastman, *Inorg. Chem.*, 12, 1634 (1973), and references therein.

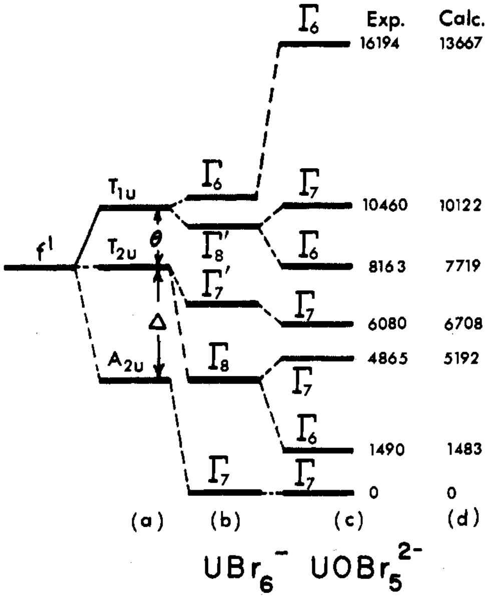

Figure 2. The f^1-orbital energy levels perturbed by (a) the O_h field (where the Δ and θ are those of UBr_6^- and ζ = 1750 cm^{-1}, (b) the O_h field plus spin-orbit coupling (where the separations are those of UBr_6^-), (c) the D_4 field plus spin-orbit coupling (where the experimental separations are those of $UOBr_5^{2-}$), and (d) the calculated energies of the several levels assuming τ = 700 cm^{-1} and ζ = 1750 cm^{-1}.

(see Figure 1) and $\omega(\Gamma_7)$, which are 4630 cm^{-1} and −1850 cm^{-1}, respectively. Taking $\omega(\Gamma_6)$ from the observed spectrum of UF_6^- to be 15,800 cm^{-1}, it was then possible using ζ, Δ, and $\omega(\Gamma_6)$ and the appropriate secular determinant to calculate the value of θ (see Figure 1), which is 6540 cm^{-1}. With ζ, Δ, and θ all now determined it was then possible to solve the appropriate secular determinant for the two Γ_8 levels. These are calculated to be $\Delta\omega(\Gamma_8 \leftarrow \Gamma_7)$ = 5400 cm^{-1} and $\Delta\omega(\Gamma_8' \leftarrow \Gamma_7)$ = 13,180 cm^{-1}. These values compare well with the experimental values for UF_6^- of 5200 and 13,500 cm^{-1}, respectively.

Exactly the same procedure was used in the case of UBr_6^- and the corresponding values are $\Delta\omega(\Gamma_7' \leftarrow \Gamma_7)$ = 6850 cm^{-1}, ζ = 1750 cm^{-1}, Δ = 4070 cm^{-1}, θ = 2150 cm^{-1}, $\omega(\Gamma_6)$ = 10,680 cm^{-1}, $\Delta\omega(\Gamma_8 \leftarrow \Gamma_7)$ = 3600 cm^{-1}, and $\Delta\omega(\Gamma_8' \leftarrow \Gamma_7)$ = 9480 cm^{-1}. These latter two calculated values correspond well with the experimental values of 4050 and 9640 cm^{-1}, respectively. Figure 2 shows the energy levels appropriate to UBr_6^- and $UOBr_5^{2-}$.

The next steps in the calculation of the energy levels of the UOX_5^{2-} species involve setting up and solving the appropriate tetragonal matrices, which have been simplified by assuming that all tetragonal effects can be lumped together into one (rather than three) parameter, τ (see ref 1). The 4 X 4 and 3 X 3 determinants were solved by means of a standard computer program for matrix diagonalization. The values of ζ, Δ, and θ obtained for the UX_6^- species were used to calculate the energy levels as a function of the tetragonal splitting parameter τ. The results are plotted in Figures 3 and 4 for UOF_5^{2-} and $UOBr_5^{2-}$, respectively.

The observed spectral bands for $[(C_2H_5)_4N]UOF_5$ and $[(C_2H_5)_4N]UOBr_5$ are listed and assigned in Tables I and II, respectively. The 0-0 band assignments are compared with the values calculated for τ = 700 cm^{-1} for UOF_5^{2-} and $UOBr_5^{2-}$ in Figures 1 and 2. Table III summarizes the best-fit parameter data and the experimental bands with assignments for all three of the oxo species.

Electron paramagnetic resonance spectra have been run now on all six species UX_6^- and UOX_5^{2-} (X^- = F^-, Cl^-, Br^-) as well as on UF_8^{3-}. Signals have been obtained at ambient temperature on the polycrystalline solids for all species except UF_6^- and UF_8^{3-}. The signals are reproduced in Figures 5 and 6. We previously published the epr spectra of UCl_6^- [2] and $UOCl_5^{2-}$,[1] but the other spectra are reproduced here for the first time. In view of several comments in a recent paper by Lewis, Hecht, and Eastman,[6] we feel that it is important that these spectra have been obtained and discussion of them will be made in the next section.

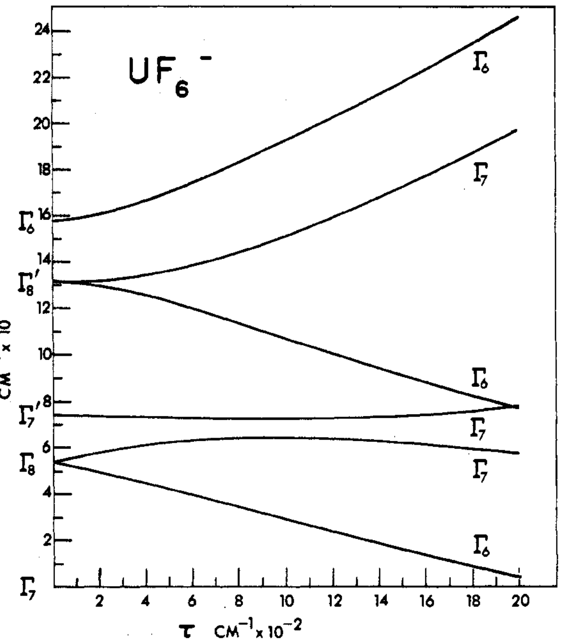

Figure 3. The splitting of the 5f manifold of O_h energy levels for UF_6^- obtained by lowering the symmetry field.

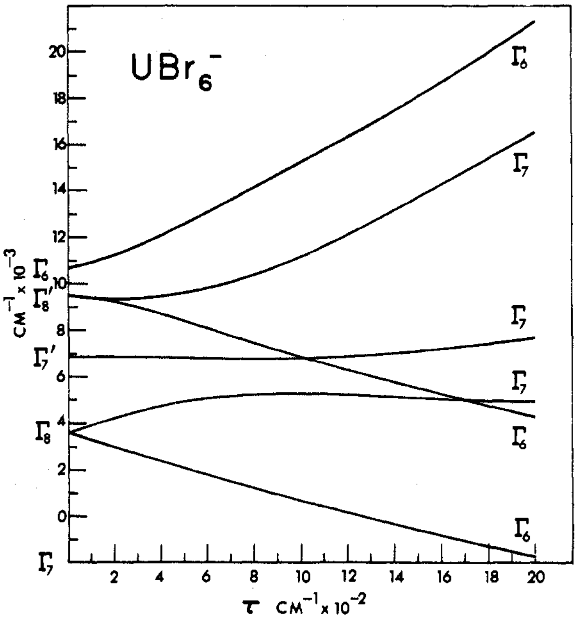

Figure 4. The splitting of the 5f manifold of O_h energy levels for UBr_6^- obtained by lowering the symmetry field.

Discussion

There is nothing unexpected in the new electronic spectral data or in the theoretical treatment reported here for the UOF_5^{2-} and $UOBr_5^{2-}$ species. Reference to Table III shows that the value for the best-fit spin-orbit coupling constant, which has been determined by relativistic Hartree-Fock cal-

Table I. Electronic and Vibronic Bands for $(Et_4N)_2UOF_5$ (cm^{-1})

Assignment in D_4 symmetry[a]	0–0 transition	Vibronic bands		Sepn from 0–0	
		Low	High	Low	High
$\Gamma_7 \rightarrow \Gamma_6(\Gamma_8)$	2,380[b]				
$\Gamma_7 \rightarrow \Gamma_7(\Gamma_8)$	6,792	6,295		497	
			6,887		95
			6,988		196
			7,163		371
			7,540		748
$\Gamma_7 \rightarrow \Gamma_7(\Gamma_7')$	6,837	6,330		507	
			6,953		116
			7,072		235
			7,220		383
			7,599		762
$\Gamma_7 \rightarrow \Gamma_6(\Gamma_8')$	11,448		11,920		472
			12,147		699
$\Gamma_7 \rightarrow \Gamma_7(\Gamma_8')$	12,420		12,910		490
			13,123		703
$\Gamma_7 \rightarrow \Gamma_6(\Gamma_6)$	18,660	17,990		670	
		18,380		280	
			19,080		420
			19,420		760

[a] The symbol in parentheses represents the irreducible representation of the O_h molecular species UF_6^-. [b] This band was taken from room-temperature infrared spectra obtained by means of a Beckman IR-7; all others were taken from spectra obtained at 77°K by means of a Cary 14.

Table II. Electronic and Vibronic Bands for $(Et_4N)_2UOBr_5$ (cm^{-1})

Assignment in D_4 symmetry[a]	0–0 transition	Vibronic bands		Sepn from 0–0	
		Low	High	Low	High
$\Gamma_7 \rightarrow \Gamma_6(\Gamma_8)$	1,490[b]				
$\Gamma_7 \rightarrow \Gamma_7(\Gamma_8)$	4,865, 4,888				
$\Gamma_7 \rightarrow \Gamma_7(\Gamma_7')$	6,080	5941		139	
			6,231		151
			6,275		195
			6,898		818
$\Gamma_7 \rightarrow \Gamma_6(\Gamma_8')$	8,163	1944		219	
			8,333		170
			8,980		817
$\Gamma_7 \rightarrow \Gamma_7(\Gamma_8')$	10,460		11,055		595
			11,267		807
$\Gamma_7 \rightarrow \Gamma_6(\Gamma_6)$	16,194		16,835		641
			17,007		813

[a] The symbol in parentheses represents the irreducible representation of the O_h molecular species UBr_6^-. [b] This band was taken from room temperature infrared spectra obtained by means of a Beckman IR-7; all others were taken from spectra obtained at 77°K by means of a Cary 14.

culations[7] to be 2172 ± 50 cm^{-1} for the free ion, is reduced below the free ion value and in the expected order, $F^- > Cl^- > Br^-$, with the latter two values rather close.[8] All six electronic transitions are shifted to higher energy in the expected order $F^- > Cl^- > Br^-$, emphasizing the class a metal ion or hard acid character of U^{5+} and UO^{3+}.

Electron paramagnetic resonance spectra have been recorded for the polycrystalline solids at ambient temperature for all species except UF_6^- (and UF_8^{3-}, which we have also studied but are not reporting on here). (See Figures 5 and 6.) The signals are all extremely broad; they are symmetric for the UX_6^- ($X^- = Cl^-, Br^-$) species and unsymmetric for the UOX_5^{2-} ($X^- = F^-, Cl^-, Br^-$) species; the spin concentration is approximately one spin per molecule; and the $\langle g \rangle$ values are in the ranges ~0.6–0.8 for the fluoro,[9] ~1.1 for the chloro, and ~1.2 for the bromo compounds. (See Table IV.)

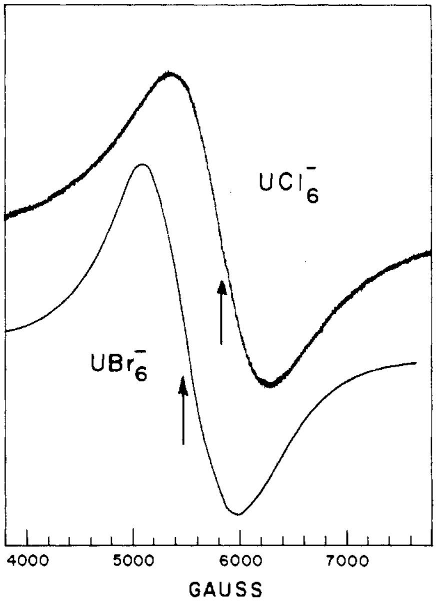

Figure 5. The epr spectra of the UX_6^- ($X^- = Cl^-, Br^-$) ions.

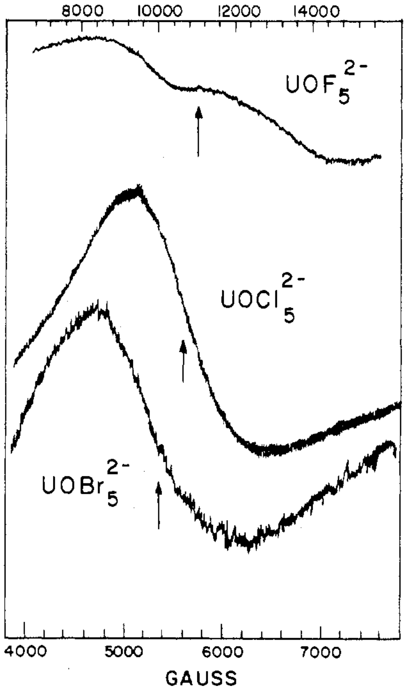

Figure 6. The epr spectra of the UOX_5^{2-} ($X^- = F^-, Cl^-, Br^-$) ions. Note that the magnetic field scale for UOF_5^{2-} which is given at the top of the figure is different from that for the chloro and bromo compounds, which is given at the bottom of the figure.

We do not have an explanation for why we observe room-temperature epr signals for the chloro and bromo compounds (and for the oxofluoro species), but not for UF_6^- and UF_8^{3-}. We are, however, quite confident of our spectral data and *their* interpretation, which show that the lowest lying excited electronic levels are above 1500 cm^{-1} for the chloro and bromo compounds and above 2000 cm^{-1} for the fluoro com-

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(7) W. B. Lewis, J. B. Mann, D. A. Liberman, and D. T. Cromer, *J. Chem. Phys.*, 53, 809 (1970).

(8) It should be noted that in fact the spin-orbit coupling constants were obtained as best-fit values for the UX_6^- species and used without further "fitting" for calculations on the UOX_5^{2-} species. This was certainly justified by the crudeness of the calculation which involved only one tetragonalization parameter in place of three. Surely the values for ζ would be even lower, but in the same order, in the more covalent oxo species.

(9) P. Rigny and P. Plurien, *J. Phys. Chem. Solids*, 28, 2589 (1967); M. Dryford, P. Rigny, and P. Plurien, *Phys. Lett. A*, 27, 620 (1968).

Table III. Summary of Spectral Data for the Three Oxopentahalouranate(V) Species

	Best-fit parameters, cm^{-1}			Electronic transitions obsd, cm^{-1}					
	ζ	Δ	θ	$\Gamma_6(\Gamma_8)$	$\Gamma_7(\Gamma_8)$	$\Gamma_7(\Gamma_7')$	$\Gamma_6(\Gamma_8')$	$\Gamma_7(\Gamma_8')$	$\Gamma_6(\Gamma_6)$
UOF_5^{2-}	1850	4630	6540	2380	6792	6837	11,448	12,420	18,660
$UOCl_5^{2-}$	1770	3810	3110	1555	5050	6161	8,584	10,616	16,835
$UOBr_5^{2-}$	1750	4070	2150	1490	4880	6080	8,163	10,460	16,194

Table IV. Epr Data for Uranium(V) Complexes

Complex	$\langle g \rangle$	peak-to-peak signal width, G
UF_6^-	*a*	*a*
UOF_5^{2-}	0.58	~8000
UCl_6^-	1.12	~1200
$UOCl_5^{2-}$	1.09	~1400
UBr_6^-	1.21	850
$UOBr_5^{2-}$	1.24	~1600

[a] Values of the average *g* tensor for polycrystalline MUF_6 (M = Li, Na, Cs) at 77°K have been reported[9] as −0.768, −0.748, and −0.709, respectively.

pounds and that the spin-orbit coupling constants for the compounds decrease in the order $F^- > Cl^- > Br^-$. We suggest that the symmetry of UOX_5^{2-} should not be characterized as strongly axially distorted (note that the tetragonal distortion parameter $\tau = 700$ cm^{-1} is adequate to account for the electronic spectral bands) in the same way that NpO_2^{2+} and other *trans*-dioxoactinyl species are. For example, the first excited level in $5f^1$ $RbNpO_2(NO_3)_3$ is probably below 1000 cm^{-1}. This low-lying level apparently shortens the longitudinal relaxation time T_1 sufficiently to require very low temperatures for epr signal observation of the NpO_2^{2+} species. Although one might expect relatively shorter relaxation times (due to the Γ_8 splitting into higher and lower levels) and larger *g* anisotropies in the oxo species relative to the hexahalo species, these factors do not appear to be sufficient to eliminate (but only greatly broaden) room-temperature epr signals, as has been suggested by Lewis, Hecht, and Eastman.[6] Their theoretical predictions in this regard simply are not borne out by the experimental facts illustrated in Figures 5 and 6.

Acknowledgment. The authors are grateful for a grant from the National Science Foundation (GP-30661x1) (to J. S.) which supported this research.

Registry No. $(Et_4N)_2UOF_5$, 30917-64-7; $(Et_4N)_2UOBr_5$, 30917-62-5; UCl_6^-, 44491-58-9; $UOCl_5^{2-}$, 41677-65-0; UBr_6^-, 44491-06-7; $(C_2H_5)_4NF$, 665-46-3; $(C_2H_5)_4NUCl_6$, 17141-96-7; $UCl_5 \cdot TCAC$, 20574-41-8.

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Stoichiometry and Kinetics of the Reduction of $Cr(OH_2)_5CH_2I^{2+}$ by Chromium(II)[1]

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Received August 24, 1973 AIC306311

The stoichiometry of the reaction between Cr(II) and $Cr(OH_2)_5CH_2I^{2+}$ was found to be $2Cr^{2+} + 2H^+ + CrCH_2I^{2+} = CrI^{2+} + 2Cr^{3+} + CH_4$. The rate law for the disappearance of Cr(II) was $(-{}^1/_2 d[Cr^{2+}]/dt = k_1[Cr^{2+}][CrCH_2I^{2+}]$; at 25° $k_1 = 2.9 \pm 0.2 \times 10^{-2}$ l. mol^{-1} sec^{-1} with $\Delta H^{\ddagger} = 7.7$ kcal/mol, and $\Delta S^{\ddagger} = -39$ eu. The rate law for the appearance of CH_4 was found to be $d[CH_4]/dt = k_4[I][H^+]$, where I is a long-lived organochromium intermediate; k_4 at 25° was $5.2 \pm 0.3 \times 10^{-3}$ l. mol^{-1} sec^{-1}. Evidence is presented that I was $CrCH_3^{2+}$, and a possible mechanism is proposed.

Introduction

Chromium(II) has been widely used as a reducing agent for a variety of organic compounds,[2] and organochromium species have been proposed as intermediates in some of these reactions.[3,4] Castro and Kray[5] report that some polyhalomethanes are reduced to methane by excess chromium(II), and they suggest "chromium-complexed carbenes" as intermediates. We find that methane is also produced when iodomethylpentaaquochromium(III) ion, $CrCH_2I^{2+}$, is allowed to react with chromium(II). This paper presents the results of our study of this reaction, and a mechanism is proposed.

Experimental Section

Reagents. Reagent grade diiodomethane (MCB) was used without further purification, as was reagent grade perchloric acid. $NaClO_4$ was prepared by the neutralization of Na_2CO_3 (Baker Analyzed Reagent) with $HClO_4$. Stock solutions of $NaClO_4$ were analyzed by passing an aliquot through a cation-exchange column in the H^+ form and titrating the liberated H^+ with standard base. Cr(II) solutions were prepared by dissolving electrolytic grade Cr metal (~99.999% pure, Apache Chemicals) in deoxygenated perchloric acid solutions. All solutions were prepared using H_2O which had been deionized and then distilled using an all-glass still (Corning Model 1-a).

Analysis. Chromium(III) or total chromium content was determined using H_2O_2 in base as an oxidant and measuring chromium as chromate ion (CrO_4^{2-}, ϵ_{372} 4815).[6] Cr(II) was measured by determining the decrease in absorbance of acidic chromium(VI) solutions (λ 348 nm) after reaction with Cr(II).[7] Carbon present in gaseous compounds was measured by absorption of CO_2 on an Ascarite tube after catalytic (CuO) combustion at 930°. (Control experiments were run to ensure that complete combustion occurred under these conditions.) Gravimetric AgI analyses were made for I^-.

$Cr(OH_2)_5CH_2I^{2+}$. Iodomethylpentaaquochromium(III) ion, ($CrCH_2I^{2+}$), was prepared, after the method of Anet,[8] by adding Cr(II) solutions to CH_2I_2. The reactants were stirred for a 2-hr period

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(1) Presented in part at the 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973.

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