THE CHEMISTRY OF URANIUM(V)

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I. Introduction

The chemistry of uranium is perhaps as well documented as that of any other metallic element. However, the available literature on the chemistry of uranium(V) is meager when compared to the voluminous data collected for the other oxidation states of uranium, namely the III, IV, and VI oxidation states. This paucity of information is not surprising when one considers the strong tendency of U(V) to disproportionate to U(IV) and U(VI), and the great ease and rapidity of oxidation of U(V) to U(VI). The extreme sensitivity of U(V) compounds to atmospheric oxygen and even trace amounts of water vapor require very rigid experimental controls in their study.

Regardless of its great instability, the U(V) species remains both chemically and spectroscopically interesting and important. The ground-state electronic configuration of uranium(V) is [Rn]$5f^1$, making it isoelectronic with the more common and stable Pa(IV) and Np(VI) species. Absorption spectra in which electron transitions involving the lone f electron are observed should be amenable to relatively simple interpretation. However, it has only been in recent years that the interpretation of $5f^1$ spectra has received any attention. The scarcity and instability of compounds is certainly one reason, but perhaps this is also due in part to the increasing amount of investigation of the near-infrared region, for it is here that most of the "f–f" transitions occur with U(V). The presence of the lone outer electron in uranium(V) species suggests electron spin resonance studies. It is somewhat surprising that there have been only four reports in this area.

Most of the compounds of quinquivalent uranium may be considered to contain the covalently bound U(V) species, the next most prevalent species being the oxo anions, UO_3^-, UO_4^{3-}, and $U_2O_6^{2-}$(and perhaps UO_6^{7-} and $U_2O_7^{4-}$), which are followed in abundance and stability by compounds of the oxo cation species UO_2^+ and UO^{3+}. Our knowledge of these latter two species is extremely limited and a great deal more work needs to be done before these species may even be considered as well characterized. It is one purpose of this short, but comprehensive, review to serve to spur further work in the study of all of these interesting "lone-electron" species of uranium(V).

II. Compounds of Uranium(V)

The syntheses and stabilities of most of the known U(V) compounds will be briefly discussed. For easy reference, the compounds are listed in Tables I through V, along with their colors and melting or boiling points. Abbreviations used are given below.

Ph = phenyl
Me = methyl
Et = ethyl
Pr = propyl
i-Pr = isopropyl
Bu = butyl
i-Bu = isobutyl
s-Bu = *sec*-butyl
t-Bu = *tert*-butyl
Am = amyl (or pentyl)
aca = acetylacetonate ion
bza = benzoylacetonate ion
py = pyridine
Meacac = methyl acetoacetate
Etacac = ethyl acetoacetate

A. HALOGEN COMPOUNDS AND HALO COMPLEXES

Probably the first reported quinquivalent uranium compounds were $UCl_5 \cdot PCl_5$, prepared by Cronander[1] in 1873, and UCl_5, discovered by Roscoe[2] in 1874. Uranium pentachloride has been prepared[3] by bringing together UCl_4 and Cl_2 at elevated temperatures

$$2UCl_4 + Cl_2 \xrightarrow{520\text{–}555°} 2UCl_5 \qquad (1)$$

but the product readily begins to undergo thermal decomposition into UCl_4 and Cl_2 below 100°, and it becomes rapid at 250°.[4] UCl_5 undergoes thermal disproportionation under high vacuum at 120–150°, with the volatile UCl_6 subliming

$$2UCl_5 \xrightarrow[\text{high vacuum}]{120\text{–}150°} UCl_4 + UCl_6\uparrow \qquad (2)$$

away from the solid UCl_4. Uranium pentachloride may also be prepared by the reaction of uranium oxides (UO_3 or

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(2) H. Roscoe, *Ber.*, 7, 1131 (1874).

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Table I

Halides and Halo Complexes of Uranium(V)

Compound	*Color*	*Mp, °C*	*Ref*
UF_5	Gray	348	7, 9, 10
UCl_5	Brown	(327)	5, 6
UBr_5	Red-brown		11
$CsUCl_6$	Yellow	~360	16
$(Me_2H_2N)UCl_6$	Yellow		16
Me_4NUCl_6	Yellow	345 mm[a]	16
Ph_4AsUCl_6	Yellow	224	15, 16
Pr_4NUCl_6	Yellow		17
$RbUCl_6$	Yellow	>280	17
Et_4NUCl_6	Yellow		15
$(Me_4N)_3UCl_8$	Yellow	245 mm[a]	16
MUF_6 (M = Li, Na, K, Rb, Cs, NH_4, Ag, Tl)			18–20, 22, 27, 30
$HUF_6 \cdot 2.5H_2O$	Blue		18
$HUF_6 \cdot 1.25H_2O$	Blue		18
Ph_4AsUF_6			15
$(NH_3OH)UF_6$	Blue		26
$NOUF_6$	Greenish white		23, 27
$N_2H_6(UF_6)_2$	Green-blue		26
$N_2H_6UF_7$	Yellow		26, 28
M_3UF_8 (M = NH_4, Li, Na, K, Rb, Cs, Ag)	White		18, 22, 29, 31
Et_4NUBr_6	Black		14, 15
Ph_4AsUBr_6	Black		14, 15
Ph_4AsUI_6	Black	<25[a]	14, 15

[a] Decomposition point.

U_3O_8) with organic chlorinating agents, although pure UCl_5 may not be isolated in all cases. The liquid-phase chlorination with carbon tetrachloride involves the following reactions.[5]

$$2UO_3 + 6CCl_4 \xrightarrow{250°} 2UCl_5 + 6COCl_2 + Cl_2 \quad (3)$$

$$2U_3O_8 + 16CCl_4 \xrightarrow{250°} 6UCl_5 + 16COCl_2 + Cl_2 \quad (4)$$

The recent report[6] of the crystal structure of UCl_5, which forms monoclinic crystals, showed that the structure is based upon a cubic closest packing (ccp) of chlorine atoms, in which the uranium atoms occupy one-fifth of the octahedral holes. Two such octahedra share an edge to form a dimeric U_2Cl_{10} unit. The U–Cl distances to bridging chlorines are 2.67 and 2.70 Å; those to nonbridging chlorine atoms are 2.43, 2.43, 2.44, and 2.44 Å. The uranium atoms in each dimeric unit are shifted about 0.20 Å away from the centers of the octahedra in directions away from one another. The structure is quite different from that of $PaCl_5$, but similar to that of α-UF_5. The latter is tetragonal[7] with the F atoms in a quasi-ccp lattice and the U atoms again occupying one-fifth of the octahedral holes, but with the difference that the octahedra in this case share *vertices* (rather than *edges*) to form infinite chains.

Uranium pentafluoride was first reported[8] in 1911, when it was formed by the reaction of anhydrous HF with UCl_5. It may also be obtained[5] by reacting UCl_6 with anhydrous HF.

$$2UCl_6 + 10HF \longrightarrow 2UF_5 + 10HCl + Cl_2 \quad (5)$$

Still another preparative method[5] involves the action of F_2 on UF_4.

$$UF_4 + {}^1\!/_2F_2 \xrightarrow{150\text{–}250°} UF_5 \quad (6)$$

The reaction of UF_4 with UF_6 produces[4,9] the four intermediate fluorides α-IF_5, β-UF_5, U_4F_{17} ($UF_{4.25}$), and U_2F_9 ($UF_{4.5}$), the latter two being black and the two UF_5 crystal modifications (both tetragonal, but one I4/m, the other $I\bar{4}2d$)[7] being white. The UF_5 products therefore most likely contain only equivalent uranium atoms (all in the V state), whereas the black color of the other two products undoubtedly reflects their mixed oxidation state compositions.

α-UF_5 has recently[10] been prepared by a new semicontinuous procedure involving a gas-phase reaction of HBr with an excess of UF_6 in an open column operating at 65° and a total pressure of 1 atm.

$$2UF_6 + 2HBr \longrightarrow 2UF_5 + 2HF + Br_2 \quad (7)$$

The product has been characterized[11] by its melting point (348°) and heats of fusion (11.9 ± 4.2 kcal/mole) and vaporization (36.6 ± 3.0 and 24.7 ± 3.8 kcal/mole for solid and liquid, respectively).

Hydrolysis of UF_5 results in violent disproportionation.

$$2UF_5 + 2H_2O \longrightarrow UF_4 + UO_2^{2+} + 2F^- + 4HF \quad (8)$$

Disproportionation is a very common reaction of U(V) compounds and more about this will be said later.

Uranium pentabromide was apparently first prepared in 1954,[12] but it is difficult to obtain it in pure form. It can be stabilized by formation of 1:1 addition compounds with triphenylphosphine oxide (Ph_3PO) or hexamethylphosphoramide (HMPA),[13] or by the formation of the hexabromouranate(V) anion.[14]

Uranium pentaiodide has never been isolated, but the UI_6^- species has been recently prepared.[14,15] The complex is extremently unstable and decomposes above about −30° to U(IV) and I_3^-. The Ph_4As^+ salt decomposes[15] in a few minutes at 25°.

A number of different salts of the hexachlorouranate(V) anion, UCl_6^-, have been prepared (Table I), and these are generally more stable than UCl_5 itself. The most recent and rapid method[14,15] of UCl_6^- preparation is by oxidation of UCl_6^{2-} by Cl_2 in CH_3NO_2 solution at 80–90°. The Et_4N^+ and Ph_4As^+ salts have been made in this way, but presumably others could be produced by this procedure. Other salts of the type $MUCl_6$ (where M = Cs^+, Me_4N^+, $Me_2H_2N^+$, or Ph_4N^+,[16] or M = Rb^+ or Pr_4N^+)[17] have been prepared from

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thionyl chloride solutions of U(V) by addition of the appropriate chloro salt. All of the compounds are unstable to moisture, undergoing rapid hydrolysis and disproportionation. They are, however, relatively stable toward heat, and some even exhibit sharp melting points (Table I). There is some evidence of a UCl_7^{2-} species[16] and the octachloro compound, $(Me_4N)_3UCl_8$, has been isolated.[16]

There are similarly a number[18-30] of hexafluorouranate(V) salts as well as a definite heptafluoro salt,[26,28] several octafluoro salts,[11,18,19,31] and at least three dodecafluorodiuranium, $U_2F_{12}^{2-}$, salts.[32] Crystallographic properties of the hexafluoro salts MUF_6 (M = Li, Na, K, Rb, Cs, and NH_4,[20] and M = Ag, K, NH_4, Rb, and Tl[21,22]) have been measured. The rhombohedral compounds (M = Li, Na, and Cs) are clear blue in color, changing to nearly white as the particle size is reduced. The pseudo-hexagonal compounds (M = K, NH_4, and Rb) came out as pale yellow-green crystals from intense blue HF solutions.[20] The $NaUF_6$ exists in two phases: one rhombohedral, the other cubic.[20] All of the foregoing UF_6^- salts are prepared from UF_5 and the appropriate MF salt, usually employing 48% HF or anhydrous HF as the solvent.

A crystal structure determination[33] of $CsUF_6$ finds it to be rhombohedral ($R\bar{3}$) with one formula unit per unit cell. Each U atom has six F neighbors at 2.057 Å which form an octahedron slightly compressed along the three fold axis, in agreement with earlier deductions from epr studies.[27]

Ammonium hexafluorouranate(V) has recently been prepared[30] by the reaction of liquid UF_6 with solid NH_4F at 120° for 49 hr. Moisture decomposes it, but nevertheless its magnetic properties could be measured. It has been found[24] to be stable in concentrated (48%) HF solutions. The products formulated as $HUF_6 \cdot (2.5H_2O)$ and $HUF_6 \cdot (1.25H_2O)$ are prepared[25] by cooling a solution of U(V) saturated with HF, the first compound precipitating at $-10°$ and the second at $-80°$ after additional HF had been added. This apparent resistance to hydrolysis is somewhat surprising, but it does suggest that fluoride ion is quite strongly coordinated. Ryan[15] claims the formation of Ph_4AsUF_6 upon treatment of the corresponding chloro compound with 40% aqueous HF. Also, the addition of excess CsF to a concentrated HF solution of the Et_4NUCl_6 salt precipitates $CsUF_6$, since the Cs^+ salt is less soluble than the Et_4N^+ salt.

Table II

Addition Compounds of Uranium(V) Halides

Compound	*Color*	*Mp, °C*	*Ref*
$UCl_5 \cdot PCl_5$	Red-orange	154^a	1, 34
$UCl_5 \cdot SOCl_2$	Brown		35, 36
$UCl_5 \cdot Ph_3PO$	Red-orange	120^d	37
$UCl_5 \cdot (C_8H_{17})_3PO$	Red-orange oil		37
$UCl_5 \cdot TCAC^b$	Red-orange	147^c	17
$UBr_5 \cdot Ph_3PO$	Dark red		13
$UBr_5 \cdot HMPA^d$	Dark red		13

[a] Melting point in evacuated sealed tube. [b] TCAC = trichloroacrylyl chloride, $Cl_2C{=}CClCOCl$. [c] Melting point in sealed capillary. [d] HMPA = hexamethylphosphoramide.

Addition of a 48-50% solution of UF_5 in HF to a hydrated metal difluoride dissolved in HF of the same concentration at room temperature gave an almost immediate heavy precipitate of $MU_2F_{12} \cdot 4H_2O$ (M = Co, Ni, or Cu).[32] The presence of the H_2O was confirmed by ir spectra, but the exact number of water molecules per formula unit requires confirmation, since only F, U(IV), total U, and the M were analyzed.

It has already been mentioned that UBr_6^- is more stable than UBr_5, and Ryan[14,15] has found a very simple procedure for obtaining the hexabromo anion which involves oxidation of UBr_6^{2-} by Br_2 in CH_3NO_2 solutions at 25°. He has prepared the Et_4N^+ and Ph_4As^+ salts in this way. Salts of the very unstable black UI_6^- may be made[15] by condensing anhydrous liquid HI on the chloro salts and allowing the mixture to evaporate slowly, or by reacting $UO_2Cl_4^{2-}$ salts with liquid HI.

B. ADDITION COMPOUNDS OF HALIDES

Only five chloro compounds and two bromo compounds of the general type $UX_5 \cdot L$, where L = some molecule with may or may not be coordinated to the uranium, have been reported. These are summarized in Table II.[34-37] The first one listed, $UCl_5 \cdot PCl_5$, may be synthesized[34] by the reaction

$$UO_3 + 4PCl_5 \longrightarrow UCl_5 \cdot PCl_5 + 3POCl_3 + {}^1/_2Cl_2 \qquad (9)$$

When an excess of PCl_5 was used, orange crystalline products were obtained whose formulas corresponded to $UCl_5 \cdot PCl_5$ and $UCl_5 \cdot 3PCl_5$. However, extraction with dry toluene yielded the original $UCl_5 \cdot PCl_5$. It is not known whether the latter compound exists as $(PCl_4^+)(UCl_6^-)$ in the solid state, but this is very likely, since PCl_5 can hardly coordinate to the U atom. The similar compound,[35,36] $UCl_5 \cdot SOCl_2$, is believed[38] to exist as $(SOCl^+)(UCl_6^-)$ in the solid. There is very good evidence that the PCl_5 addition compound is ionized in liquid $POCl_3$ yielding the expected ions.[34] $UCl_5 \cdot PCl_5$ reacts readily with H_2O, one-half being reduced to U(IV), the other half oxidized to U(VI) (as UO_2^{2+}). Phosphates are also

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Table III

Uranium(V) Alkoxides, Halide Alkoxides, and Related Compounds[a]

Compound	*Color*	*Bp (mm) or mp, °C*[b]	*Mol complexity*[c] *(degree of polymerization)*	*Ref*
		Alkoxides		
$U(OMe)_5$	Red	Sub 140–150 (0.01)	3.01	43, 45, 46
$U(OEt)_5$	Brown liq	123 (0.001)	1.90	37, 43, 45
		161 (0.05)		46, 49, 52
		180 (0.1)		
$U(OPr)_5$	Brown liq	162 (0.001)	1.95	43
		181 (0.07)		45, 46
$U(OPr^i)_5$	Brown	320 dec	1.93	37
		150 (0.05)		43, 46
$U(OBu)_5$	Brown liq	193 (0.001)	1.94	43
		206 (0.15)		45, 46
$U(OBu^i)_5$	Brown	102	1.97	43
		192 (0.01)		46
$U(OBu^s)_5$	Brown	85	1.85	43
		175 (0.05)		46
$U(OBu^t)_5$	Tan	120 (0.05)	1.35	43, 46
$U(OAm)_5$	Brown liq	246 (0.05)	1.94	45, 46
$U(OCH_2CH_2Pr^i)_5$		225 (0.05)	1.76	46
$U(OCH_2CHEtMe)_5$		220 (0.05)	1.82	46
$U(OCH_2Bu^t)_5$		Sub 160–170 (0.1)	1.61	46
$U(OCHEt_2)_5$		180 (0.1)	1.66	46
$U(OCHPrMe)_5$		175 (0.1)	1.70	46
$U(OCHPr^i)_5$		Sub 160 (0.1)	1.58	46
$U(OCMe_3)_5$		120–130 (0.1)	1.35	47
$U(OCMe_2Et)_5$		Sub 130 (0.05)	1.26	46
$U(OCMeEt_2)_5$		Sub 200 (0.1)	1.09	46
$U(OCEt_3)_5$		Sub 210 (0.1)	1.00	46
$U(OCMe_2Pr)_5$		200 (0.1)	1.28	46
$U(OCMe_2Pr^i)_5$		Dec		46
$U(OCMeEtPr^i)_5$		Dec	1.01	46
$U_2(OEt)_5(OBu^t)_5$		150 (0.1)		46
$U_2(OEt)_4(OBu^t)_6$		150 (0.1)		46
$U(OEt)(OBu^t)_4$				46
$U(OBu^t)_5 \cdot Bu^tOH$		130 (0.1)		46
$U(OBu^t)_5 \cdot py$				46
$U(OCH_2CH{=}CH_2)_5$		Sub 178 (0.015)		43
$U(OCH_2CH_2NEt_2)_5$				43
$U(OCH_2CH_2SCH_2CF_3)_5$				43
$U(OCH_2CF_3)_5$	Brown-green liq	125–130 (0.002)		43, 44
$NaU(OEt)_6$	Green			43
$Ca[U(OEt)_6]_2$	Light green	Sub 200 (0.001)		44
$Al[U(OEt)_6]_3$	Green liq	111–115 (0.0012)		44
		Trialkylsilyloxides		
$U(OSiMe_3)_5$	Yellow-brown	140–150 (0.1)	1.77	47
$U(OSiMe_2Et)_5$	Yellow-brown	155 (0.1)	1.31	47
$U(OSiMeEt_2)_5$	Orange	160 (0.1)	1.13	47
$U(OSiEt_3)_5$	Green-brown	170–180 (0.1)	1.00	47
		Chloride Alkoxides		
$U(OEt)_4Cl$	Brown liq or	160 (0.05)		51
	green liq	145–150 (0.005)		46
		140–147 (0.003)		44
$U(OEt)_3Cl_2$	Brown solid or			51
	green syrup			
$U(OEt)_2Cl_3$	Brown			51
	or green			43
$U(OEt)Cl_4 \cdot CH_3COOEt$				51
$U(OPr)_4Cl$		186–192 (0.095)		44
$U(OPr^i)_4Cl$				51
$U(OPr^i)_3Cl_2$				51
$U(OPr^i)_2Cl_3$				51
$U(OPr^i)Cl_4 \cdot CH_3COOPr^i$				51
$U(OAm)_4Cl$				51

Table III (Continued)

Compound	*Color*	*Bp (mm) or mp, °C*[b]	*Mol complexity*[c] *(degree of polymerization)*	*Ref*
		Bromide Alkoxides		
$U(OEt)_4Br$	Brown liq	Dec		49
$U(OEt)_3Br_2$	Brown liq	Dec		49
$U(OEt)_2Br_3$	Brown liq			49
$U(OEt)Br_4 \cdot CH_3COOEt$	Red-brown liq			49
$U(OAm)_4Br$	Dark brown liq			49
$U(OAm)_2Br_3$	Dark brown liq			49
$U(OAm)Br_4 \cdot CH_3COOAm$	Dark brown liq			49

[a] For the purposes of this table and Table IV, the abbreviations for the alkyl radicals are Pr^i = isopropyl, Bu^i = isobutyl, Bu^s = *sec*-butyl, and Bu^t = *t*-butyl. [b] Abbreviations used are: sub = sublimes; dec = decomposes. Numbers standing alone are melting points. [c] The molecular complexity (degree of polymerization) was determined from M_{found}/M_{calcd}, where the experimental molecular weight was determined ebullioscopically in benzene.

produced and a mixture of the U(IV) and UO_2^{2+} phosphates is actually produced.

$UCl_5 \cdot SOCl_2$ is obtained either by refluxing UO_3 with excess $SOCl_2$ for 2–3 weeks, followed by removal of excess $SOCl_2$ by distillation,[36] or in a much shorter time[43] by allowing UO_3 to react with an excess $SOCl_2$ in a sealed tube at 180°.

The two phosphine oxide complexes[37] have been prepared by suspending an excess of $CsUCl_6$ in CH_2Cl_2 to which the appropriate ligand was then added. The precipitated CsCl and unreacted $CsUCl_6$ were filtered off and the red solution was evaporated to dryness. The desired complex could also be obtained by the addition of isopentane to the red CH_2Cl_2 solution. The compounds seem to be indefinitely stable in a dry, inert atmosphere. Efforts to prepare analogous complexes with Ph_3AsO, pyNO, DMA, dimethyl sulfone, diphenyl sulfone, acetylacetone, and ethyl acetoacetate were not successful.[37]

A complex formulated[39] as $5UCl_5 \cdot TCAC$, where TCAC = trichloroacrylyl chloride, $Cl_2C{=}CClCOCl$, appears to have been incorrectly formulated (or obtained impure) since the 1:1 complex, $UCl_5 \cdot TCAC$, has now been firmly established.[17] The latter is an orange-red product in which the oxygen atom of the ligand is coordinated to the U(V) atom. It is prepared by heating together hexachloropropene and a uranium oxide. A strongly exothermic reaction ensues when the boiling point (210°) of the C_3Cl_6 is approached. The reaction mixture must then be cooled if necessary, in order to maintain the temperature at about 100°. After the exothermic reaction has subsided, the now dark red solution is filtered in an inert atmosphere to remove unreacted oxide and UCl_4, which is also formed in this reaction. The deep red solution is allowed to cool whereupon it deposits orange-red $UCl_5 \cdot TCAC$. It should be noted that this is a modification of a procedure that was originally designed[40] to prepare pure UCl_4. The compound appears to be indefinitely stable under dry nitrogen, but it decomposes, turning green, within seconds if exposed to the atmosphere.

It has been possible to prepare[41] 1:1 addition compounds of UCl_5 with several phosphorus and arsenic donor atom ligands, such as $Ph_2PCH_2CH_2PPh_2$, Ph_3P, Ph_3As, $Ph_2AsCH_2CH_2AsPh_2$, simply by adding benzene solutions of these ligands to a benzene solution of the $UCl_5 \cdot TCAC$ compound and isolating the green solid which forms immediately. Both optical and esr spectra support the formulations as U(V) compounds. It is likely that this simple procedure will yield a great many complexes of U(V) with other soft base ligands. Even Ph_3Sb and Ph_3Bi have yielded products in an analogous manner, but these have not yet been purified and analyzed.

C. ALKOXIDES, HALIDE ALKOXIDES, AND RELATED COMPOUNDS

This class of compounds is easily the largest group of uranium(V) compounds known,[42–52] as reference to Tables III and IV will quickly reveal. However, it is probably also the most poorly characterized set of compounds since little more than elemental analysis and one or two physical properties are known for the large majority of the compounds. Indeed, the more recent emphasis with these compounds appears to be on simply making more of them rather than on trying to more fully characterize any of them. Clearly more intensive study of these interesting compounds is called for.

The compound types appear to fall into the following categories (Tables III and IV):

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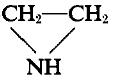
Table IV

Uranium(V) Alkoxide Complexes with Amines, β-Diketones, and β-Ketoesters[a]

Compound	*Color*	*Bp (mm) or mp, °C*	*Ref*
	Amines		
$U(OCH_2CF_3)_5\cdot 2Me_3N$	Green liq	95–100 (0.02)	44
$U(OCH_2CF_3)_5\cdot 2PrNH_2$	Green liq	105 (0.009)	44
$U(OCH_2CF_3)_5\cdot 2Pr^iNH_2$	Green liq	100 (0.01)	44
$U(OCH_2CF_3)_5\cdot 2Pr_2NH$	Green liq	97 (0.006)	44
$U(OCH_2CF_3)_5\cdot 3Me_2NH$	Green liq	95–100 (0.01)	44
$U(OCU_2CF_3)_5\cdot 3$CH_2—CH_2 NH	Green liq	125 (0.002)	44
	β-Diketones		
$U(OEt)_4aca$	Brown viscous liq	118 (0.55)	50
$U(OEt)_3(aca)_2$	Red-brown	Dec	50
$U(OEt)_2(aca)_3$	Orange-brown	Dec	50
$U(OEt)_4bza$	Brown viscous liq	110 (0.4)	50
$U(OEt)_3(bza)_2$	Brown viscous liq	Dec	50
$U(OEt)_2(bza)_3$	Brown pasty solid	Dec	50
$U(OBu^t)_4aca$	Orange		50
$U(OBu^t)_3(aca)_2$	Yellow	Sub 195 (0.1)	50
$U(OBu^t)_2(aca)_3$	Orange-yellow		50
$U(OBu^t)_4bza$	Brown	Sub 210 (0.4)	50
$U(OBu^t)_2(bza)_3$	Brown	Sub 215 (0.9)	50
	β-Ketoesters		
$U(OEt)_4(Meacac)$	Brown liq	140 (0.5)	48
$U(OEt)_3(Meacac)_2$	Brown viscous liq	152 (0.6)	48
$U(OEt)_2(Meacac)_3$	Brown paste		48
$U(OEt)_4(Etacac)$	Brown paste		48
$U(OEt)_3(Etacac)_2$	Orange-brown paste		48
$U(OEt)_2(Etacac)_3$	Orange-brown paste		48

[a] Abbreviations are the same as for Table III.

1. $U(OR)_5$, where R = alkyl, fluoroalkyl, amine alkyl, or sulfide alkyl
2. $U(OR)_x(OR')_{5-x}$, where R and R′ = alkyl
3. $U(OR)_5\cdot L$, where L = ligand and R = alkyl
4. $U(OEt)_6^-$, where compounds with Na^+, Ca^{2+}, and Al^{3+} are known
5. $U(OSiR_xR'_{3-x})_5$, where R and R′ = alkyl
6. $U(OR)_xX_{5-x}$, where X = Cl or Br, and R = alkyl
7. $U(OCH_2CF_3)_5\cdot x$ amine
8. $U(OR)_x$ (β-diketonate ion)$_{5-x}$
9. $U(OR)_x$ (β-ketoester ion)$_{5-x}$

Several methods are reported[36,42,43] for the preparation of uranium pentaalkoxides, including the following:[43]

1. Uranium(IV) alkoxides may be oxidized by dry O_2

$$UCl_4 + 4NaOR \longrightarrow U(OR)_4 \xrightarrow[NaOR]{(O)} U(OR)_5 \qquad (10)$$

or by Br_2, as for example, in yields approaching 95% according to

$$U(OEt)_4 + {}^1/_2Br_2 \longrightarrow U(OEt)_4Br \xrightarrow{NaOEt} U(OEt)_5 + NaBr \qquad (11)$$

$$2.\quad UCl_4 + ROH + NH_3 \longrightarrow U(OR)_4 \xrightarrow{(O)} U(OR)_5 \qquad (12)$$

$$3.\quad UCl_5 + ROH + NH_3 \longrightarrow U(OR)_5 \qquad (13)$$

4. Perhaps the best method for most alkoxides involves an exchange of alkoxide groups

$$U(OEt)_5 + 5ROH \longrightarrow 5EtOH + U(OR)_5 \qquad (14)$$

in which the ethanol is then removed by distillation from the equilibrium mixture.

5. A novel preparation of $U(OR)_5$ compounds has also been accomplished by the following route, discovered by accident[36]

$$(C_5H_5N)_2UOCl_5 + 5NH_3 + 3ROH \longrightarrow UO(OR)_3 + 5NH_4Cl + 2C_5H_5N \qquad (15)$$

$$nUO(OR)_3 \xrightarrow{heat} U(OR)_5 + U_{n-1}O_n(OR)_{3n-5} \qquad (16)$$

The starting material had been obtained as the product of the treatment of $UCl_5\cdot SOCl_2$ with pyridine in an alcoholic solution, instead of the intended product $(C_5H_6N)UCl_6$.

As a group, the alkoxides may be distilled or sublimed under reduced pressure, most are resistant to thermal decomposition, but all undergo very rapid hydrolysis. They are generally soluble in common organic solvents, and, for many, the molecular weights have been determined ebullioscopically in benzene. These molecular weights have suggested that many of the pentaalkoxides are dimers, although $U(OMe)_5$ appears clearly to be a trimer and $U(OEt)_5$ appears just as clearly to be a monomer (Table III). Certain other compounds exhibit molecular weight data which suggests only partial dimerization.

Chloride[44,51] and bromide[49] alkoxides, of general formula $U(OR)_{5-n}X_n$, are prepared by treating the pentaalkoxides with varying quantities of acetyl halide in dry benzene.

$$U(OR)_5 + nMeCOX \longrightarrow U(OR)_{5-5}X_n + nMeCO_2R$$

The reactions are exothermic and yield products which are brown viscous liquids or dark brown solids. However, these materials have been poorly characterized.

β-Diketones[50] and β-keto esters[48] react readily with uranium(V) pentaethoxide, forming derivatives of the general type $U(OEt)_{5-x}L_x$ (where L = aca, bza, Meacac, or Etacac; $x = 1$, 2, or 3). The compounds are prepared by dissolving the $U(OEt)_5$ in benzene, to which are added varying molar ratios of the organic reactant. The reactions are exothermic and yield brown viscous liquids or dark brown solids (Table IV). The β-diketone compounds will exchange their ethoxy groups with *t*-butoxy groups when they are refluxed with *t*-butyl alcohol. The apparent coordination numbers seem to be 5, 6, 7, and 8 (Table IV), and so electronic absorption spectra should prove very interesting. The effect of the various symmetries on the uranium 5f electronic energy levels should yield important information, particularly for testing existing theories of electronic structure of 5f ions.

Amine complexes[44] of $U(OCH_2CH_3)_5$ (Table IV), of general formula $U(OCH_2CF_3)_5 \cdot xL$ (where L = amine ligand, $x = 2$ or 3), likewise appear to display coordination numbers of 7 and 8, and deserve to be studied in much greater detail than they have been.

Unfortunately, for all of the aforementioned compounds, only elemental analysis is offered as proof of the oxidation state of the uranium. So, additional work just substantiating the oxidation state of the metal would appear to be the first order of business in subsequent studies on these compounds.

D. OXIDES AND OXO COMPOUNDS

The first report in the general available literature of the pure pentavalent oxide, U_2O_5, appears to be that[53] from the Institure for Atomic Research at Iowa State College, where a great deal of contract work for the Manhattan Project was being performed. In the paper cited,[53] it is reported that R. Raeuchle prepared the first U_2O_5, but there is no mention of how, and that O. Johnson prepared single crystals of U_2O_5 by thermal decomposition of UO_2Cl_2 at 900°. The crystals were reported to be orthorhombic, $a = 8.27$ Å, $b = 31.65$ Å, $c = 6.72$, with 16 U_2O_5 per unit cell. The X-ray density was given as 8.35 g/cc. Furthermore, it was believed that in the uranium-oxygen system there is a two-phase region[54] between $UO_{2.3}$ and U_2O_5, and a one-phase region from U_2O_5 to UO_3 in which the various structures continuously transform from one to another.[53]

A more thorough study of U_2O_5 has recently been made[55] including the conditions for its synthesis, composition, structure, and thermal resistance. Violet hexagonal crystals have been made[55] by dissolution of U_3O_8 in 10–15% H_2SO_4, but α-UO_3 (at 80°) or amorphous UO_3 (at 0°) may be substituted[56,57] for the U_3O_8. If the temperature goes above 160°, the product[54] is UO_2. Air oxidation[54] of the U_2O_5 at room temperature gives U_5O_{13}, whereas at 250° the U_2O_5 decomposes into U_3O_8 and U_4O_9. Magnetic properties (*vide infra*) have been investigated[57] and suggest the presence of UO_2^+ in U_2O_5 ($UO_2^+O_{0.5}{}^{2-}$). Other stoichiometric oxides which might contain some U(V) are U_3O_8,[54,57,58] U_5O_{13},[57] and U_4O_9.[57] Various higher oxides, with compositions between UO_2 and UO_3, presumably containing some U(V), have been obtained from time to time, but their characterizations have usually been ambiguous (see, for example, ref 59 and 60).

In the Introduction it was indicated that most of the oxo compounds may be classified as derivatives of the following two cationic and three anionic species: UO^{3+}, UO_2^+, UO_3^-, UO_4^{3-}, and $U_2O_6^{2-}$. The few known compounds of the monoxo and dioxo species are listed in Table V,[58–63] as well as the more numerous anionic oxo compounds.[58,64–74]

Uranium(V) oxochloride may be prepared[61] by heating together UCl_4 and UO_2Cl_2. A more recent preparative method which claims[62] to produce a pure product is outlined in the following reactions,

$$\begin{aligned} MoCl_5 + UO_3 &\longrightarrow UO_2Cl_2 + MoOCl_3 \\ UO_2Cl_2 + MoOCl_3 &\longrightarrow UOCl_3 + MoO_2Cl_2 \end{aligned} \qquad (17)$$

The reaction in eq 17 is carried out around 200° for 5–6 hr in a closed evacuated ampoule. The MoO_2Cl_2 evaporates and condenses in the cooler part of the ampoule, leaving behind a residue of pure $UOCl_3$. $UOBr_3$ has been prepared[64] by heating UO_3 with CBr_4 at 110° in a dry nitrogen atmosphere. (If the reaction is carried out at 130° in a sealed tube, UBr_5 is produced instead.[65]) Both $UOBr_3$ and UBr_5 are readily decomposed in oxygen-containing solvents,[65] but they appear to decompose much more slowly in $CHCl_3$ or $CHBr_3$. This has allowed some of the $UOBr_3$ optical spectral bands to be detected.[65]

The green salt, $(pyH)_2UOCl_5$, was formed by treatment of $UCl_5 \cdot SOCl_2$ with pyridine in an alcoholic solution.[36] R_2UOCl_5 salts (R = Et_4N^+ or Ph_4As^+) should soon be reported, as well as the $(Et_4N)_4UOBr_5$ salt,[15] along with some spectral data (ir and visible–uv) for these compounds. The $(Et_4N)_2UOCl_5$ salt seems to be stable toward atmospheric oxidation, but not toward high humidity.

The preparation of a stable (to 500°) brown powder believed to be UO_2Br, perhaps the only compound of UO_2^+ to be isolated as a pure solid thus far, is reported to result from the following reaction.[66]

$$UO_3 + 2HBr \xrightarrow{250°} UO_2Br + {}^1/{}_2Br_2 + H_2O \qquad (18)$$

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Table V

Oxides and Oxo Compounds

Compound (*color*)	*Ref*
U_2O_5 (violet or black)	53–57
UO_3^- oxides	
$LiUO_3$ (brown-violet)	58, 70–71
$NaUO_3$ (red-brown)	68
KUO_3 (brown)	
$RbUO_3$ (bright brown)	
$Ba(UO_3)_2$ (olive green)	67
$U_2O_6^{2-}$ oxides	
With Co^{2+}, Ni^{2+}, Mg^{2+}, Cd^{2+}, Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}	58, 71, 73
And $0.15\ Li_2O \cdot U_2O_5$	
$0.50\ Li_2O \cdot U_2O_5$	
UO_4^{3-} oxides	
With Cr(III), Fe(III), Sc(III)	57–58
Nd(III), Sm(III), Eu(III)	72, 74
Gd(III), Yb(III), Bi(III)	68
Li^+, Ca^{2+}, Ba^{2+}	67
UO_2^+ derivatives	
UO_2Br (brown)	66
UO_2^+ in various solutions	75–105
UO^{3+} derivatives	
$UOCl_3$	5, 61–63
$UOBr_3$ (red-brown)	62–64
$UOCl_3 \cdot EtOH$ (brown)	36
$(pyH)_2UOCl_5$ (green)	36
R_2UOCl_5 ($R = Et_4N^+$, Ph_4As^+)	15
$(Et_4N)_2UOBr_5$ (green)	15
Miscellaneous species	
Li_7UO_6, Sr_2InUO_6	58
$Pb_2U_2O_7$, α-U_3O_8	58
$Ba_2U_2O_7$	69

The ir spectrum is not unlike that of UO_2^{2+} compounds, as would be expected, showing band maxima at 940, 890, and 850 cm^{-1}.

The dioxuroanium(V) species, UO_2^+, has been obtained many times in solution,[75–105] even though this oxidation state is the least stable one under these conditions. Numerous studies of UO_2^+ have dealt with (a) its production, either in polarographic investigations,[75–84,86,87,90–92,95,96,100–105] by controlled-potential electrolysis,[81,83,84,91,92,96,100,101,105] or by chemical means;[85,86,93,94] (b) its disproportionation;[81,83,84,86,87,90,91,95–99,102,104,105] (c) its redox potential relative to the IV and VI oxidation states;[81,83–85,88] (d) its equilibrium with the VI oxidation state;[86,94] and (e) its role as an intermediate[89,97] in certain reactions of U(VI).

From the numerous polarographic studies, all but two[100,105] of which have been carried out in aqueous systems, the conclusion is that the one-electron reduction of UO_2^{2+} results in the formation of UO_2^+. The reversible nature of the reduction is strong evidence for the identical degree of oxygenation in both the U(VI) and U(V) species. Supporting evidence[88] for UO_2^+ as the species in solution comes from the constancy of the $E°$ value (at -0.062 V *vs.* nhe) in the range 0.01–0.05 M $HClO_4$, when the ionic strength is fixed at 0.5 M with $NaClO_4$–$HClO_4$. Additional confirmation of the formula comes from analogy with the Np(V) and Am(V) ions which have been assigned formulas NpO_2^+ and AmO_2^+ from both ir and X-ray crystallographic studies.[4] Detailed studies of the chemistry of aqueous U(V) solutions were first carried out 20 years ago.[84–86] Millimolar solutions of UO_2^+ can be obtained (a) by electrolytic reduction[84] of UO_2^{2+}, (b) by reduction of UO_2^{2+} with zinc analgam or hydrogen,[84] (c) by dissolving[85] UCl_5, or (d) by mixing certain U(IV) and U(VI) solutions;[84] but the most satisfactory method seems to be (a), and it is the one used most commonly. The UO_2^+ species is comparatively stable in only a narrow pH range $(2.0–4.0)^{84-85}$ where the disproportionation into U^{4+} and UO_2^{2+} is quite slow. However, the hydrolytic behavior of UO_2^+ is difficult to study because of this narrow range.

An estimate[84] of the acid hydrolysis of UO_2^+, by comparison with the pK values of *ca.* 8.9 and 9.7 for Np(V) and Pu(V), respectively, places the pK of UO_2^+ at *ca.* 8, indicating that at a pH somewhat above 8 negative species (*e.g.*, $UO_2(OH)_2^-$) would be formed.

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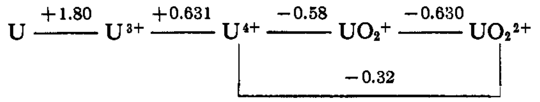
The following formal oxidation-reduction potentials[82,83,88] for uranium in 1 *M* $HClO_4$ at 25° do not apply at infinite dilution in the strict thermodynamic sense, since the requisite experimental data have either not been obtained or cannot be obtained, but the relationships are useful nevertheless.



$$U \overset{+1.80}{\text{———}} U^{3+} \overset{+0.631}{\text{———}} U^{4+} \overset{-0.58}{\text{———}} UO_2^{+} \overset{-0.630}{\text{———}} UO_2^{2+} \qquad (U^{4+} \text{ — } UO_2^{2+}: -0.32)$$

Complexing anions usually strongly affect potential values, but in the case of the $UO_2^+|UO_2^{2+}$ couple only weak complexing by Cl^- has been found.[82] Potentials are also affected by reversibility, and experimentally it is found that the $U^{3+}|U^{4+}$ and the $UO_2^+|UO_2^{2+}$ couples are reversible and attain their final potentials rapidly, whereas the $U^{4+}|UO_2^+$ and $U^{4+}|UO_2^{2+}$ couples are irreversible. Obviously one criterion for the reversibility of a couple is that no strong metal–oxygen bonds be created or broken during redox.

The most thoroughly studied reaction of UO_2^+ is its disproportionation into U(VI) and U(IV). Almost all papers which deal with UO_2^+ are concerned at least partially with this reaction for obvious reasons. The equilibrium constant for the reaction

$$2UO_2^+ + 4H_3O^+ = UO_2^{2+} + U^{4+} + 6H_2O \tag{19}$$

has been determined[86] to be (1.7 ± 0.3) × 10^6. A mechanism of disproportionation which involves proton transfer[81]

$$\begin{gathered} UO_2^+ + H^+ = UOOH^{2+} \\ UO_2^+ + UOOH^{2+} \longrightarrow UO_2^{2+} + UOOH^+ \text{ (rate limiting)} \\ UOOH^+ \longrightarrow \text{stable U(IV) species} \end{gathered} \tag{20}$$

has been questioned by workers[87] who studied the reaction in D_2O in order to ascertain the role of the proton in the mechanism. The deuterated intermediate ($UOOD^{2+}$) would be expected to decrease the reaction rate, but this was not observed, making the foregoing mechanism highly improbable. A more acceptable mechanism involving OH radical transfer has been proposed[91] on the basis of studies of the effect of hydrogen ion concentration[83,91] (increasing rate with increasing concentration), the effect of chloride ion concentration[90–91] (increasing rate with increasing concentration), and the effect of other anions[91] (NO_3^-, ClO_4^-, Br^-, and I^-).

$$\begin{gathered} UO_2^+ + H^+ = UOOH^{2+} \\ UO_2^+ + UOOH^{2+} = HOUO_2^+ + UO^{2+} \end{gathered} \tag{21}$$

The two species on the right side of the rate-determining step would rapidly revert, respectively, to UO_2^{2+} (by loss of OH^- to the acid medium) and whatever stable U(IV) species exists in the given medium (perhaps UOH^{3+}(aq)).

More recent disproportionation studies have been made by twin-electrode thin layer electrochemistry,[99] and by automatic amperometric titration of U(VI) with Cr(II).[98] Other studies have found the rate of disproportionation to be (a) increased with increasing hydrogen ion concentration[83,91,96,101] (providing no organic acid is present[96]); (b) increased with increasing pH of organic acids (*e.g.*, acetic, ascorbic, lactic, or tartaric) present;[95–96,101] (c) increased with increasing organic acid concentration[95–96,101] (the rate being second order in U(V) and first order in organic anion); (d) increased with decreasing p*K* of the organic acid;[96] and (e) slightly decreased in the presence of hydrazine[103] ($E_{1/2}$ for the U(VI) to U(V) reduction shifting from −0.175 to −0.160 V with increasing N_2H_4 indicating weak but definite complexing by the base). The foregoing results (b–d) suggest that anions and not undissociated organic acid molecules participate in the disproportionation reaction by UO_2^+ complexing of these anions.

In chloride melts (*e.g.*, LiCl-KCl eutectic at 650°) UO_2^+ is believed[93–94] produced by the reaction

$$Cl^- + UO_2^{2+} = {}^1/_2Cl_2 + UO_2^+ \tag{22}$$

for which the equilibrium constant has been determined[94] as

$$K_{eq} = \frac{[UO_2^+]^2}{[UO_2^{2+}]^2}P_{Cl_2} = 1.2 \pm 0.6 \times 10^{-6}\text{ atm} \tag{23}$$

The optical spectrum for UO_2^+ has been obtained (*vide infra*) in such melts. Upon raising the temperature of the melt to 750° the further reaction sets in.

$$Cl^- + UO_2^+ = UO_2 + {}^1/_2Cl_2 \tag{24}$$

Finally the UO_2^+ species has been studied in dimethyl sulfoxide,[105] in which it is formed reversibly at the dme at a half-wave potential of −0.54 V (*vs.* sce) with $LiClO_4$ supporting electrolyte (and −0.53 V with *n*-Bu_4NClO_4). Controlled-potential electrolysis in this solvent (carried out at −0.7 V) produced millimolar amounts of UO_2^+ which could be studied spectrally (*vide infra*) since the half-life of the species was estimated to be about 1 hr under these conditions.

The uranium(V) anionic oxo compounds or oxides, known only in the solid state, appear to fall into one of the following stoichiometric categories (see Table V): UO_3^-, $U_2O_6^{2-}$, UO_4^{3-}, UO_6^{7-}, and $U_2O_7^{4-}$. Characterization of the solids usually has been by magnetic susceptibility measurements (*vide infra*), but at least for $FeUO_4$ and $CrUO_4$ we have reflectance spectra[72] as well.

Uranium(V) oxides of the general formula MUO_3 (M = Li^+, Na^+, K^+, Rb^+) are prepared[62–63] by heating M_2UO_4 with UO_2 at 650–750°. $Ba(UO_3)_2$ has been prepared by reaction of $BaUO_3$ with UO_3 at 550° in a N_2 atmosphere.[67] At 1000° the compound disproportionates into $BaUO_4$ and UO_2. The UO_3^- compounds are relatively stable, aqueous suspensions showing no alkaline reaction. It should be noted that the U(VI) analog, Na_2UO_4, reacts with water to form $Na_2U_2O_7$ and Na^+, OH^-. Furthermore, the compounds do not react with hydrochloric or sulfuric acids, although nitric acid readily destroys them.

The oxides produced when trivalent cations are employed in the following reaction are of the general type MUO_4 (M = Se, Y, Nd, Sm, Eu, Gd, Yb).[72]

$$M_2O_3 + UO_2 + UO_3 \longrightarrow 2MUO_4 \tag{25}$$

The reaction is carried out at 1000° and the products are blue-black to black and are oxidized when dissolved in acids. When M = Bi(III), Cr(III), or Fe(III), the UO_3 in eq 25 is replaced[68,74] by U_3O_8.

The hexaoxodiuranate(V) compounds (MU_2O_6) were first produced in 1952[106] by thermal decomposition of the so-called "diuranates," or $U_2O_7^{2-}$ compounds. Only the M = Mg and Ca compounds had formulas close to the correct stoichiometry required for a pure U(V) compound. A number of these compounds were then made in 1967[58,71,73] (Table V), generally by thermal decomposition under vacuum or by reduction under NH_3 at 600° of the diuranates(VI).

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(106) H. R. Hoekstra and J. J. Katz, *J. Am. Chem. Soc.*, 74, 1683 (1952).

Table VI

Magnetic Data for Some Uranium(V) Compounds[a]

Compound	*Temp*, °*K*	$\chi_M^{corr} \times 10^6$	μ_{eff}, *BM*	*Ref*
UCl_5[b]	398	634	1.42	107
	293	672	1.26	
	193	837	1.14	
$UCl_5 \cdot SOCl_2$	293	704	1.29	107
	193	889	1.17	
	77	1714	1.03	
$CsUCl_6$[c]	308	775.5	1.71[d]	16[c]
	203	977.8		
	100	1521		
$UCl_5 \cdot Ph_3PO$	305	982.6	2.13[e]	3.7
	230	1130		
	153	1142		
$UCl_5 \cdot$TCAC	300	743	1.54	17
NH_4UF_6	93–200		1.74[f]	30
	200–300		2.25[f]	
$N_2H_6UF_7$			1.67[g]	28
Na_3UF_8	293		1.86	31
	195		1.74	
U_2O_5			1.47	57
α-U_3O_8	295	731	1.32	54, 57–58
	168	1021	1.18	
	83	1585	1.03	
$LiUO_3$[h]	480	535	1.44	58, 68
	373	623	1.37	108
	293	701	1.28	
MgU_2O_6[i]	373	851	1.60	58
	195	1239	1.39	
	78	2180	1.17	
CaU_2O_6[j]	292	1120	1.79	57, 73
	190	1426	1.82	
	88	2078	1.68	
$LaUO_4$[k]	473	669	1.60	58
	373	751	1.50	
	195	1050	1.28	

[a] For many of the listed compounds there are more temperature-dependent data than are given in this table. No more than three temperatures are quoted here. [b] In CCl_4 solutions UCl_5 is diamagnetic[107] and presumably dimeric, U_2Cl_{10}. [c] Data are given[16] also for the UCl_6^- salts with the following cations: $Me_2H_2N^+$, Me_4N^+, and Ph_4As^+. [d] The large value of the Weiss constant, −161°, indicates that this moment has little significance. The same is true of the other salts referred to in footnote *c*. [e] The large Weiss constant, −270°, probably renders this value meaningless. [f] The Weiss constant is −129° for the lower temperatures and −353° for the higher temperatures, making the 2.25 value meaningless. [g] Weiss constant is 111°. [h] There are also data for the Na^+, K^+, Rb^+ salts.[58, 107] [i] The data for the Cd^{2+} compound have also been obtained.[58] [j] The data for the Sr^{2+} and Ba^{2+} compounds have also been obtained.[73] [k] Data are also available for the Y^{3+}, Sc^{3+}, and Bi^{3+} compounds,[58, 68] as well as for the Li_3UO_4 compound.[58] There are also data[58] for the following unusual oxides: Li_7UO_6, $Pb_2U_2O_7$, and Sr_2InUO_6, and for[57] $Ca_2U_2O_7$.

In spite of the relatively large number of oxides known, there is really very little information about them available beyond their magnetic susceptibilities. These are discussed next.

III. Magnetic Susceptibilities and Epr Studies

The lone outer electron of U(V) should render its compounds interesting for all magnetic measurements. Some of the available[107] magnetic susceptibility data are given in Table VI, and references to all such data are contained in the table and its footnotes. Most of our knowledge of the magnetic behavior of uranium(V) compounds is consistent with what is expected for an ion with a $5f^1$ ground-state configuration which is perturbed by spin–orbit coupling and octahedral (or cubic) fields. Although temperature-dependent studies have revealed Curie–Weiss behavior in most cases (exceptions occur, for example, in the oxides[71–72] and in the MU_2O_6, M = Ca, Sr, Ba, compounds[73]), the Weiss constants are generally quite large. Magnetic data have been used to deduce the presence of UO_2^+ in U_2O_5 (written as $UO_2^+O_{0.5}^{2-}$ in ref 57) and in[57,73] MU_2O_6 (for example, written as $Ca^{2+}(UO_2^+)_2O_2^{2-}$ in ref 57). The magnetic properties of α-U_3O_8 are in accord with its formulation[70] as $U_2O_5 \cdot UO_3$, in which the uranium is in the V and VI oxidation states rather than the IV and VI states. This substantiates earlier findings[54, 108] that U_3O_8 is composed of U(V) and U(VI) in the molar ratio of 2:1.

There have been very few reports of electron spin resonance data of pure uranium(V) compounds.[17, 109, 110] Crude measurements[17] on powdered samples of $UCl_5 \cdot$TCAC, $UCl_5 \cdot SOCl_2$, $UCl_5 \cdot PCl_5$, $RbUCl_6$, and Pr_4NUCl_6 have yielded average *g* values of ~1.1 with the sign undetermined. This value may be compared with the value of ~1.25 reported[111] for U(V) ions in a matrix of ThO_2. The *g* value is expected to be negative, since $g = -1.14$ for Pa(IV)[112] and $g = -0.60$ for Np(IV),[113] and since Karraker[114] has *calculated* a *g* value for $UCl_5 \cdot SOCl_2$ of −1.18.

Paramagnetic resonance spectra of powdered MUF_6 samples[27] (M = Li, Na, Cs) were recorded at a 3-cm wavelength at 77°K. The three compounds gave an asymmetric line in a field of about 9000 G, the line shape being in agreement with an axial symmetry of the *g* tensor. Axially distorted UF_6^- octahedra are deduced, in agreement with the actual X-ray structure.[33] The g_0 values are given[27] as −0.768, −0.748, and −0.709 for the Li^+, Na^+, and Cs^+ salts, respectively. Curiously, no signals were obtained with the corresponding K^+, NH_4^+, Rb^+, Ag^+, or Tl^+ salts. U(V) esr signals have also been obtained for UF_5 powder,[110] for single crystals of the general formula MUF_6,[109–110] and for single crystals of $NaSbF_6$ doped with U(V).[110] The *g* values fall in the vicinity of −0.7, and some of the spectra are reported[110] to exhibit splitting.

IV. Spectral Studies

A. VIBRATIONAL SPECTRA

Uranium(V)–chlorine stretching frequencies have been assigned for several compounds, and these are given in Table VII. They are seen to fall around 300 cm^{-1} or approximately

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(107) W. Rüdorff and W. Menzer, *Z. Anorg. Allgem. Chem.*, **292**, 197 (1957).

(108) H. Haraldsen and R. Bakken, *Naturwissenschaften*, **28**, 127 (1940).

(109) M. Drifford, P. Rigny, and P. Plurien, *Phys. Letters*, **A27**, 620 (1968).

(110) J. A. Arshem and G. D. Sturgeon, paper presented at the 1968 Midwest Regional American Chemical Society Meeting, Manhattan, Kan.

(111) P. M. Llewellyn, unpublished work, quoted in W. Low, "Paramagnetic Resonance in Solid State Physics," Academic Press, New York, N. Y., 1960, Supplement 2.

(112) J. D. Axe, H. J. Stapleton, and C. D. Jeffries, *Phys. Rev.*, **121**, 1630 (1961).

(113) C. H. Hutchinson, Jr., and B. Weinstock, *J. Chem. Phys.*, **32**, 56 (1960).

(114) D. G. Karraker, *Inorg. Chem.*, **3**, 1618 (1964).

50 cm^{-1} higher than those reported[115,116] for the U(IV) compound $(Et_4N)_2UCl_6$.

The P=O frequencies of $UCl_5 \cdot Ph_3PO$ and $UCl_5 \cdot (C_8H_{17})_3PO$ are lowered 217 and 161 cm^{-1}, respectively, from the free ligand values.[37] These large shifts, reflecting a decrease in the P=O bond strength, indicate a large decrease in the $p\pi$–$d\pi$ bonding in the phosphine oxide molecule and suggest strong U(V)–oxygen bonding. The shifts are large compared to those found in other transition metal–phosphine oxide complexes, but they are comparable to that found[117,118] in $UCl_4 \cdot 2Ph_3PO$.

Infrared data were used[17] to determine the mode of coordination of the ligand to the metal in the $UCl_5 \cdot TCAC$ complex. The C=O stretching frequency for the complexed acid chloride was found to be 200 cm^{-1} lower than that of the free ligand (1760 *vs.* 1560 cm^{-1}), strongly suggesting coordination *via* the oxygen atom.

A report[114] of no ir bands for solid $UCl_5 \cdot SOCl_2$ in the NaCl region seems very strange since the S=O frequency should appear in this range. The ir spectrum[114] of $U(OEt)_5$ showed bands at 2990, 2880, 2720, 1455, 1375, 1350, 1130, 1100, 1052, 908, and 875 cm^{-1}. All of these bands can be assigned to vibrational modes of the ethoxy ion except the last two. Since these are near, but lower than the UO_2^{2+} adsorption frequencies, they might arise from U–O stretching modes. It seems clear, however, that much more work is necessary to allow unambiguous band assignments to be made.

Assignment has been made[26] of the 628-cm^{-1} band in the Raman spectra of $CsUF_6$, $(NH_3OH)UF_6$, and $N_2H_6UF_7$, as the principal symmetric vibration (A_{1g}) of the UF_6^- ion. This value is considerably higher than the 506 cm^{-1} assigned for this same mode from vibronic spectral studies[119] of UF_6^-. However, this latter assignment is almost surely incorrect. Using their[119] data a better assignment for ν_1 (A_{1g}) would be either 609 (5196–4587) cm^{-1} or 612 (7540–6928) cm^{-1}. Either of these values is in far better agreement with both the Raman data and the ν_1 value for UF_6 (*vide infra*). The infrared-active mode ν_3 (T_{1u}) (of the octahedral UF_6^-) has been assigned at 503 cm^{-1} (for $CsUF_6$)[119] or at 526 cm^{-1} (for $N_2H_6(UF_6)_2$ and $(NH_3OH)UF_6$)[26] or at 551 cm^{-1} (for $NOUF_6$).[23] The latter compound also exhibits bands at 2333 cm^{-1} (due to NO^+) and 509 cm^{-1} (a U–F mode).

The ir bands found[66] for UO_2Br are at 940, 890, and 850 cm^{-1}. These are undoubtedly due to U–O vibrations (the U–Br vibration would be expected below 300 cm^{-1}), but their exact assignment has not been made.

Ryan[15] has measured the far-infrared spectra of $CsUF_6$, Et_4NUCl_6, and Et_4NUBr_6 and in addition has measured the electronic spectra from which he is able to deduce the corresponding vibronic levels. The data are collected in Table VIII. Similar, but less complete information is available for several other UCl_6^- salts,[17] and this will be detailed later.

Table VII

Uranium(V)–Chlorine Vibrational Frequencies (cm^{-1})

Compound	ν_3 (T_{1u})	*Ref*
$CsUCl_6$	303	16
Ph_4AsUCl_6	306	16
$(Me_4N)_3UCl_8$	310	16
Me_4NUCl_6	310	16
$UCl_5 \cdot Ph_3PO$	285	37
$UCl_5 \cdot (C_8H_{17})_3PO$	304	37
$UCl_5 \cdot TCAC$	320	17
Pr_4NUCl_6	315	17

Table VIII

Vibrational Data[15] (in cm^{-1}) for Some UX_6^- Salts[a]

$CsUF_6$		*Et_4NUCl_6*		*Et_4NUBr_6*	
Obsd in far-ir	*Obsd in vibronic*	*Obsd in far-ir*	*Obsd in vibronic*	*Obsd in far-ir*	*Obsd in vibronic*
490	490	310 (262, 218)	309	214 (186)	217
~165	(170)	122	122	(92)	(92)
~140	145		96	87	85
62		65	(65)	68	
		56		62	61
			26	47	(48)
					24

[a] Shoulders are in parentheses.

B. ELECTRONIC AND VIBRONIC SPECTRA

Absorption spectra of the lanthanides and actinides in the visible and near-infrared regions of the spectrum are characterized by the presence of several very sharp bands of relatively low intensity. The observed spectra for these metal ions have been ascribed to transitions arising within the manifold of 4f or 5f electronic levels, respectively. The intensities of the 5f electronic bands have been found to be approximately an order magnitude greater than those of the 4f electrons. Perhaps the most intriguing area of uranium(V) chemistry involves the study of f–f transitions in the near-ir region. It might be noted that Laporte-allowed 5f → 6d transitions have generally not been investigated (only Riesfeld and Crosby[119] having examined spectra out to 50,000 cm^{-1}), but these surely would occur in the ultraviolet region and be of much greater intensity than the Laporte-forbidden f–f transitions.

The near-ir electronic spectra of U(V) compounds should lend themselves most easily to theoretical interpretation (*vide infra*) because of the presence of but a single 5f electron. Of course, the dioxo species, UO_2^+, is perhaps best considered a molecule ion which has heavy intermixing of oxygen and uranium orbitals, and the picture then is not quite so simple. In this connection it is pertinent to mention that there have been only three papers which report spectral information on UO_2^+, two of them[93–94] dealing with spectra obtained in molten salt solvents and one[105] dealing with a room-temperature spectrum in which the solvent is dimethyl sulfoxide (DMSO). (Brief mention[120] of a supposed portion of the UO_2^+ spectrum in 0.1 *M* $HClO_4$ appears to be incorrect in light of more certain[93,94,105] spectral data on UO_2^+.) The spectra of molten salt solutions containing the UO_2^+ species are remarkably similar to that of UO_2^+ in DMSO (see Figure 1). The most prominent band of UO_2^+ in DMSO[105] is located at 6620 cm^{-1} (ϵ ~90) with two other less intense maxima at 12,940 and 15,680 cm^{-1}. In the molten chloride solvents[93–94] (LiCl–KCl eutectic at 650 or 750° or 70 mole % LiCl–30

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(115) D. M. Adams, H. A. Gebbie, and R. D. Peacock, *Nature*, 199, 278 (1963).

(116) L. A. Woodward and M. J. Ware, *Spectrochim. Acta*, A24, 921 (1968).

(117) K. W. Bagnall, D. Brown, and J. G. H. DuPreez, unpublished observations.

(118) P. Gans, Doctoral Thesis, University of London, 1963.

(119) M. J. Reisfeld and G. A. Crosby, *Inorg. Chem.*, 4, 65 (1965).

(120) T. W. Newton and F. B. Baker, *ibid.*, 4, 1166 (1965).

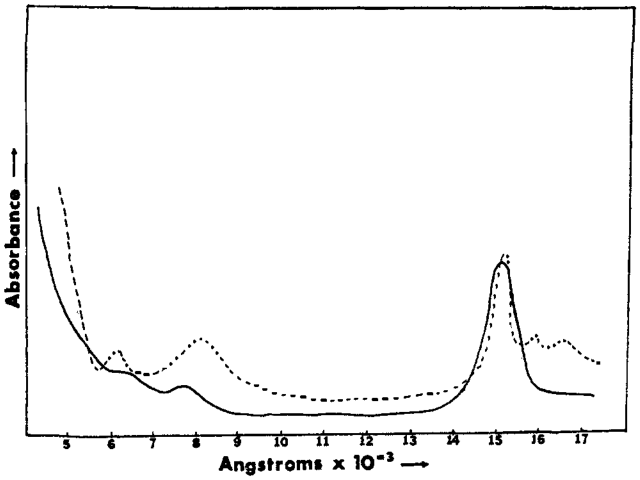

Figure 1. Near-infrared and visible electronic absorption spectrum of UO_2^+ in dimethyl sulfoxide[105] at 25° (—), and LiCl-KCl eutectic[94] at 650° (- - -).

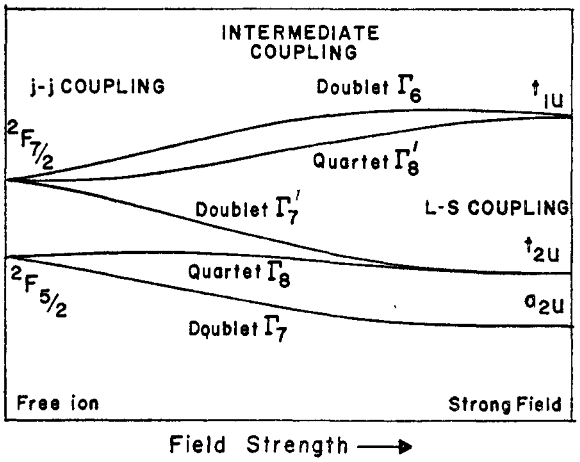

Figure 3. Crystal field effects on the energy levels of a lone 5f electron. The free ion levels are at the extreme left and the levels in a strong O_h field are on the extreme right.

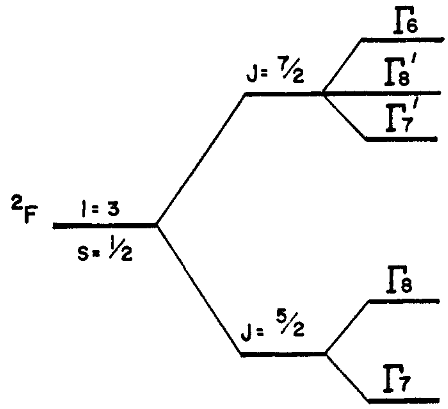

Figure 2. Schematic energy level splittings for a $5f^1$ system. The first splitting represents the result of spin-orbit interaction and the second splitting the result of an O_h crystal field.

mole % KCl at 650°), the corresponding values are 6530, 12,500, and 16,000 cm^{-1}. In addition, however, two weak absorption bands are present in the molten salt spectra at 6210 and 6000 cm^{-1}. The much higher temperature at which these latter spectra are obtained could account for the additional bands. Reflectance spectral data[70] for the U(V) oxides $FeUO_4$ and $CrUO_4$ also show a prominent band near 7000 cm^{-1}. McGlynn and Smith[121] have calculated the $^2F_{7/2} \leftarrow {}^2F_{5/2}$ transition in UO_2^+ to be at 6752 cm^{-1}, in excellent agreement with the experimentally prominent peaks determined after their calculation had been reported.

The remaining (quite limited) number of papers which contain electronic spectral information on U(V) deal with this species in an octahedral (or nearly so) environment. The electronic configuration $[Rn]5f^1$ allows only the $^2F_{5/2,7/2}$ term level which is split by spin-orbit coupling into two levels and in which according to Hund's rule, the $^2F_{5/2}$ component will possess the lower energy. The low-energy absorption spectrum of the *free ion* should therefore be a single line corresponding to the $^2F_{7/2} \leftarrow {}^2F_{5/2}$ transition. However, the crystal field of a complexed U(V) will further split the foregoing degenerate levels. It is therefore of interest to determine how the free ion $^2F_{7/2}$ and $^2F_{5/2}$ levels, which are six- and eightfold degenerate, respectively, are split by an octahedral crystal field. This may be accomplished by using relatively simple group theoretical methods, as outlined, for example, by Cotton.[122]

Since J is half-integral for the $5f^1$ system, it is necessary to use the "double group" representation O_h' for octahedral symmetry. First, the characters for the new operations of the double group must be obtained for the reducible representations $\Gamma_{5/2}$ and $\Gamma_{7/2}$. Next, the irreducible states which belong to these reducible representations are found. These irreducible states will be the levels which arise from the splitting of the $^2F_{5/2}$ and $^2F_{7/2}$ terms in O_h symmetry. The results are as follows.

$$\Gamma_{5/2} \longrightarrow \Gamma_7 + \Gamma_8$$

$$\Gamma_{7/2} \longrightarrow \Gamma_6 + \Gamma_7' + \Gamma_8'$$

The Γ_7, Γ_7', and Γ_6 levels are doubly degenerate (Kramer's doublets), whereas the Γ_8 and Γ_8' levels are quadruply degenerate. An energy level diagram may then be drawn to illustrate these levels, but the actual ordering of the various levels must be determined by solving the appropriate wave equations. Calculations by Goodman[123,124] and others,[27,113,125,126] usually for the case of the isoelectronic Np(VI), have produced the relative ordering which is pictured in Figure 2. In Figure 3, a schematic diagram by Goodman[123] is shown that illustrates the changes in the energy levels on going from the field free ion (where j-j coupling holds) to the strong crystal field limit (where L-S coupling is approximated). The energy levels for the actinides $5f^n$ ions normally lie in the region of intermediate coupling where both spin-orbit coupling and crystal field effects are important and observed. (Note that interelectron repulsion is not involved in the $5f^1$ systems.)

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[121] S. P. McGlynn and J. K. Smith, *J. Mol. Spectry.*, 6, 188 (1961).

[122] F. A. Cotton, "Chemical Applications of Group Theory," John Wiley and Sons, Inc., New York, N. Y., 1963.

[123] G. L. Goodman, Ph.D. Thesis, Harvard University, 1959.

[124] G. L. Goodman and M. Fred, *J. Chem. Phys.*, 30, 849 (1959).

[125] J. C. Eisenstein and M. H. L. Pryce, *Proc. Roy. Soc.* (London), A255, 181 (1960).

[126] J. D. Axe, Ph.D. Thesis, University of California (Berkeley), 1960, UCRL-9293.

Hence, we should predict at least four low-energy transitions to be possible in the U(V) species, namely, $\Gamma_8 \leftarrow \Gamma_7$, $\Gamma_7' \leftarrow \Gamma_7$, $\Gamma_8' \leftarrow \Gamma_7$, and $\Gamma_6 \leftarrow \Gamma_7$, in which the lone 5f electron resides in the lowest doublet Γ_7 level in the ground state. Experimentally, however, not just four bands, but rather at least four *groups* of bands are generally observed (see Figures 4 and 5). These additional bands are mainly the result of different vibronic transitions, but also, of course, they might arise from further removal of the non-Kramer degeneracies which reside in both Γ_8 and Γ_8' levels. This latter situation (degeneracy removal) can arise with the lowering of the symmetry of the complex below O_h, for example, to the important (for known U(V) complexes) C_{4v} symmetry.

For an octahedral U(V) molecule the following normal vibrational modes arise.

infrared-active:	$2T_{1u}$ (ν_3 and ν_4)
Raman-active:	A_{1g} (ν_1); E_g (ν_2); T_{2g} (ν_5)
inactive:	T_{2u} (ν_6)

Before we proceed to a consideration of the actual electronic spectral data and the assignment of bands, it would be helpful to summarize some of the pertinent theoretical predictions which have been put forth by several authors.[114,127]

(1) The doublet levels (Γ_7, Γ_7', Γ_6) arising from Kramer's degeneracy are predicted to be stabilized by spin–orbit coupling and would be unaffected by Jahn–Teller distortions.

(2) Jahn–Teller effects are important in the behavior of the quadruply degenerate Γ_8 levels. These levels are predicted to split into two doublets when the octahedron distorts. Rough calculations by Eisenstein and Pryce[125] indicate that the splitting would be of considerable magnitude. The Γ_8 levels may also interact with the vibration modes to produce weak, broad absorption bands.

(3) Vibrational selection rules indicate that the totally symmetric vibrational mode, A_{1g}, can couple with the electronic transitions to produce bands of greatly diminished intensity.

(4) The *odd* vibrational modes of the molecule are predicted to couple most strongly with the electronic transitions.

(5) For a $0 \rightarrow 0$ transition of frequency ν_0 and vibrational frequency ν, bands of frequency $(\nu_0 + \nu)$ and $(\nu_0 - \nu)$ should be obtained whose intensities are approximately in the ratio of $\exp(h\nu/kT):1$.

Optical and paramagnetic resonance spectra of the more stable $5f^1$ systems, Pa(IV) and Np(VI), have been more frequently measured and interpreted[112,118,123,126,128–130] than for U(V). In Tables IX and X are collected the available electronic spectral data for the non-oxo uranium(V) compounds.

C. ASSIGNMENT OF BANDS

The assignments of the electronic transitions, made in Tables IX and X, merit some discussion.

1. *The $\Gamma_7 \rightarrow \Gamma_8$ Transition*

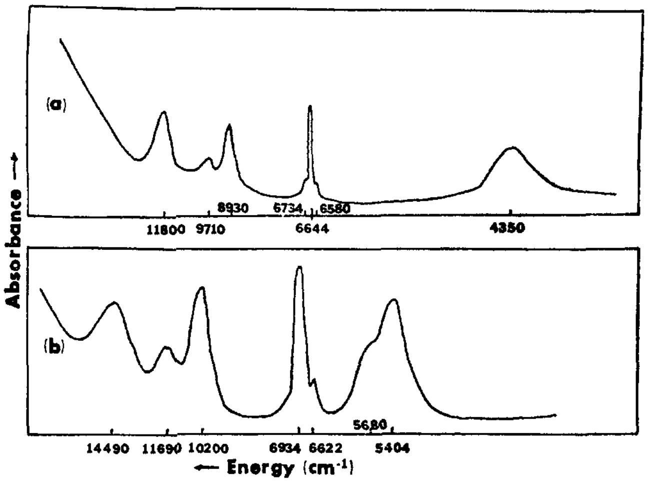

Figure 4. Near-infrared and visible electronic absorption spectra of (a) $UCl_5 \cdot SOCl_2$ in CCl_4,[17] and (b) $[U(OEt)_5]_2$ in CCl_4.[114]

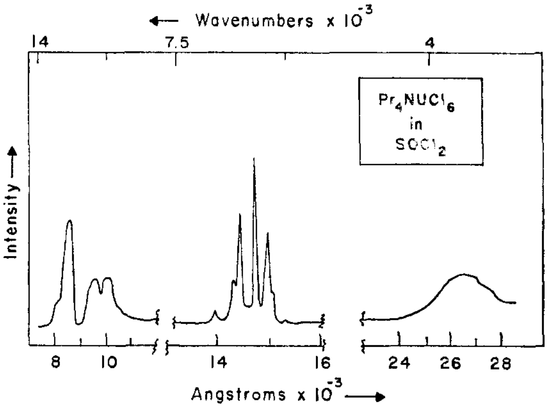

Figure 5. The near-infrared electronic absorption spectrum of Pr_4NUCl_6 in $SOCl_2$.[17]

This lowest energy transition is predicted to produce weak broad absorption bands. As can be seen from the data collected in Tables IX and X, there is often a doublet observed in this region. The energy separation between the two bands is very close to the value of the highest infrared-active stretching mode, ν_3. For example, this separation is $\sim$510 cm^{-1} in $CsUF_6$;[116] $\sim$500 cm^{-1} in Ph_4AsUF_6;[15] $\sim$300 cm^{-1} in $UCl_5 \cdot$TCAC;[17] and $\sim$275 cm^{-1} in $U(OEt)_5$.[114] Whether the pure electronic transition ($0 \rightarrow 0$) is the more intense of the two bands (always the lower of the two in energy) with the less intense band (separated by ν_3) being vibronic is not certain, but this does seem to be a reasonable and more defensible assignment.

2. *The $\Gamma_7 \rightarrow \Gamma_7'$ Transition*

In the optical spectra of all U(V) compounds there is a very characteristic band which appears somewhere in the 6000–7000-cm^{-1} region (including such species as (UO_2^+),[91,92,103] (UO_4^{3-}),[70] ($UOCl_5^{2-}$ and $UOBr_5^{2-}$)[15]). In many cases a cluster of sharp, narrow spikes are observed in this region. The most intense, usually central peak in this cluster is most likely the pure electronic transition, although one report[118] does not make this interpretation. (We believe they should have, however.) Because of the very sharp discrete bands one may obtain

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(127) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 8.

(128) J. D. Axe, R. Kyl, and H. J. Stableton, *J. Chem. Phys.*, 32, 1261 (1960).

(129) L. B. Asprey, F. H. Kruse, and R. A. Penneman, *Inorg. Chem.*, 6, 544 (1967), and references therein.

(130) T. Mitsuji, *Bull. Chem. Soc. Jap.*, 40, 2091 (1967), and references therein.

Table IX

Visible and Near-Infrared Bands (in cm^{-1}) for UCl$_6^-$ in Different Salts and in Different Media

		CsUCl$_6$^{c} in				
RbUCl$_6$ in SOCl$_2$^{a}	*[Me$_4$N]UCl$_6$ in SOCl$_2$^{b}*	*POCl$_3$*	*MeCN*	*MeNO$_2$*	*5 M Ph$_2$CO–CH$_2$Cl$_2$*	*Assignment*
3,800 br	3,275					$\Gamma_7 \rightarrow \Gamma_8$
6,485 sh						
6,680 sh		6,650	6,685	6,660	6,680	
6,702 s	6,710	6,750	6,775	6,750	6,750	
6,794 vs	6,805	6,815	6,860	6,840	6,835	
6,890 s						$\Gamma_7 \rightarrow \Gamma_7'$
6,920 m	*6,905* vs		7,015	7,080	7,015	
7,110		7,100				
9,905 br	9,900	9,930	10,125	9,940	9,955	$\Gamma_7 \rightarrow \Gamma_8'$
10,440 br	10,420	10,460	10,685	10,470	10,480	
11,520 s	11,480	11,510	11,830	11,585	11,590	
11,805 sh						$\Gamma_7 \rightarrow \Gamma_6$

[a] Data from ref 17, in which there is also a similar set of data for Pr$_4$NUCl$_6$. [b] Data from ref 16. [c] Data from ref 37.

Table X

Visible and Near-Infrared Bands (in cm^{-1}) for Several U(V) Compounds in Various Media

UCl$_5$^{a} in		UCl$_5$·TCAC^a in		UCl$_5$·SOCl$_2$ in		
SiCl$_4$	*CCl$_4$*	*CS$_2$*	*SOCl$_2$*	*SOCl$_2$^{b}*	*CCl$_4$^{c}*	*Assignment*
4,360 s	4,405 s	4,184 s	4,184 s			
4,510 m			4,237 sh	4,300 s (4195)	4,350 s (4350)	$\Gamma_7 \rightarrow \Gamma_8$
			4,407 m			
		4,464 m	4,479 m			
			4,545 sh			
6,560 w	6,550 w	4,635 w	6,451 w	6,420 w	6,560 w (6580)	
6,650 s	6,600 w, 6,650 s	6,663 m	6,680 m	6,640 m, 6660 m	6,650 s (6640)	
6,710 m	6,700 m	6,700 m		(6676)		$\Gamma_7 \rightarrow \Gamma'$
6,750 w	6,750 w	6,757 s	6,784 s	6,750 s	6,710 m (6730)	
		6,831 m	6,863 sh	6,820 m	6,750 sh	
6,870 w	6,880 w	6,850 m	6,877 m	6,840 m (6850)	6,800	
		7,097 w	7,102 w	7,080 w (7220)		
8,930 s	8,940 s	9,381 br	9,592 br	9,320 m (9325)	8,940 s (8930)	$\Gamma_7 \rightarrow \Gamma_8'$
9,690 m	9,660 m	10,277 br	10,417 br	10,370 m (10,360)	9,700 m (9710)	
11,920 s	11,930 s	11,710 s	11,751 s	11,750 s (11,710)	11,780 s (11800)	$\Gamma_7 \rightarrow \Gamma_6$
12,220 sh	12,220 sh	11,961 sh	11,990 sh	12,020 sh		

			UCl$_5$·Ph$_3$PO^g in			
(Me$_4$N)$_3$UCl$_8$^{d} in SOCl$_2$	*CsUF$_6$^{e} in Nujol*	*[U(OEt)$_5$]$_2$^{f} in CCl$_4$*	*CH$_2$Cl$_2$*	*MeCN*	*UCl$_5$·(C$_8$H$_{17}$)$_3$-PO^g in CH$_2$Cl$_2$*	*Assignment*
	5,102					
	5,624	5,405				$\Gamma_7 \rightarrow \Gamma_8$
	6,126	5,680				
6,715	6,930		6,710	6,665	6,670	
6,810	7,249	6,620	6,800	6,765	6,775	
6,910	7,399 vs	6,935	6,880	6,860	6,860	$\Gamma_7 \rightarrow \Gamma_7'$
9,935	7,540		7,110	7,090	7,110	
10,450	7,912					
11,480						
	13,055	10,200	10,130	10,090	10,100	$\Gamma_7 \rightarrow \Gamma_8'$
	13,200	11,690	10,695	10,610	10,670	
	14,400	14,490	11,850	11,780	11,850	$\Gamma_7 \rightarrow \Gamma_6$

[a] Reference 17. UCl$_5$ is probably a dimer, U$_2$Cl$_{10}$, in these solvents. UCl$_5$·TCAC was also run[17] in C$_6$H$_6$ and CCl$_4$. [b] Reference 17. Values in parentheses from ref 16. [c] Reference 17. Values in parentheses from ref 114. [d] Reference 16. The assignments for this apparently eight-coordinated U(V) have not been suggested by anyone yet. [e] Reference 118. A few other bands are in the 298 °K spectrum and many other bands in the 75 °K spectrum. The 503-cm^{-1} band is the ν_8 ir mode and the intense bands at 36,000, 40,000, and 44,000 cm^{-1} must be due to 5f → 6d transitions. The K$^+$, Rb$^+$, and NH$_4^+$ salts are reported[19, 20] to exhibit a narrow and strong peak at 7040 cm^{-1}, and the Li$^+$, Na$^+$, and Cs$^+$ salts a group of bands with the most prominent at 7350 cm^{-1}. Reference 122 reports the peaks for the former three salts at 7048, 7055, and 7048 cm^{-1}, respectively, and indicates that there are other weaker and broader bands at higher energies. [f] Reference 114. [g] Reference 37.

Table XI

Vibrational Frequencies (cm^{-1}) of Octahedral Uranium Species[a]

Designation	UF_6[b]	UF_6^-		UCl_6^-		UCl_6^{2-}	UBr_6^-
A_{1g} (ν_1)	668	609 (or 612)		300		299	
T_{1u} (ν_3)	626	503 (490)	490	312 (315)	309	262	217 (214)
T_{1u} (ν_4)	189	150 (165, 140)	170, 145	121 (122)	122	144	85 (87)
T_{2g} (ν_5)	202	145					
T_{2u} (ν_6)	144	100		92	96	86	61, 68
Ref	131, 132	119	15	17	15	116	15

[a] Values in parentheses are from far-ir spectra; others are from vibronic spectra. [b] These data are from ir[131] and Raman[132] data.

here, it is possible to make assignments of vibrational modes, of octahedral UX_6^- species in particular, from the vibronic spectra. Table XI lists the vibrational modes of various octahedral uranium hexahalo species which have been assigned from vibronic spectra, including comparison data for UF_6[131,132] and some unpublished[15] far-ir data.

As already pointed out above, the odd vibrational modes (ν_3, ν_4, and ν_6) are expected to couple most strongly with the electronic transitions. The T_{2u} (ν_6) mode involves only angle deformations whereas ν_3 and ν_4 both involve uranium-halogen bond stretching. The values for the highest ir-active stretching mode (ν_3) in the series UF_6^-, UCl_6^-, UBr_6^-, are 503, 312, 217 cm^{-1}, respectively, consistent with the expected decrease in U-X bond strength in the order $F^- > Cl^- > Br^-$. The same effect is deduced from the ν_4 values. A comparison of the ν_3 values for UCl_6^- and UCl_6^{2-}, which are 312 and 262 cm^{-1}, respectively, illustrate the weakening in the U-Cl covalent bond strength expected upon introduction of another nonbonding or slightly antibonding electron into the uranium orbitals. Raman spectral data, not yet available for any solid U(V) species, would greatly assist in the complete elucidation of vibrational band assignments.

3. The $\Gamma_7 \rightarrow \Gamma_8'$ Transition

The next electronic level of interest is the quartet Γ_8'. It has been predicted that the quartet should split into two Kramer's doublets upon any distortion of the octahedral symmetry. Indeed the spectra of UCl_6^- salts exhibit two bands of roughly equal intensity and shape around 10,000 cm^{-1} (see Table IX and Figure 4). The spectra of UF_6^- and UBr_6^- also exhibit the same type bands, but at slightly different energies.[15,118] The doublet is also found in other U(V) spectra as well (Table X). It is surely more than mere coincidence that the splitting for all salts of UCl_6^- in various media is about 540 ± 20 cm^{-1}, whereas it is much higher in all of the lower symmetry species. In the latter (see Table X) the splittings apparent in the Γ_8' level range from 720 to 1050 cm^{-1}, values which almost surely reflect the higher distortions from regular octahedral symmetry. It is indeed tempting to suggest that the magnitude of this splitting measures the magnitude of the geometrical distortion.

Table XII

Spin-Orbit Coupling Constants for $5f^1$ Systems

Compound	*ξ, cm^{-1}*	*Ref*
$CsUF_6$	1955	119
	1770	27
NH_4UF_6 and KUF_6	2013	122
$RbUF_6$	2015	122
$LiUF_6$	1810	27
$NaUF_6$	1825	27
$UCl_5 \cdot SOCl_2$	1900	114
$[U(OEt)_5]_2$	1905	114
Cs_2PaCl_6	1490	126
NpF_6	2405	125
Np(VI)	2450	113

4. The $\Gamma_7 \rightarrow \Gamma_6$ Transition

The electronic f level predicted to lie highest in energy is Γ_6. Solid-state visible-ir spectra of salts of the three UX_6^- anions are very similar in that the highest energy peak is split into a doublet and shows in addition a weak shoulder on the blue side.[15] Solution spectra[17,37] of UCl_6^- exhibit the blue shoulder but the peak is not split, although it does show dissymmetry. These transitions in the UX_6^- salts occur in the 11-15,000-cm^{-1} region. The cause of the splitting and origin of the shoulder is not known, but coupling of the symmetric vibrational mode, A_{1g}, with the electronic transition is a strong possibility for explaining the presence of the weak blue shoulder.

Obviously a great deal of work is needed in the area of spectral studies, and publication of Ryan's[15] excellent work in this area will hopefully serve to stimulate some of the necessary interest.

Finally, it might be of interest to mention that there have been several calculations of spin-orbit coupling constants (ξ) and the values are recorded in Table XII, along with values for Pa(IV) and Np(VI) compounds. If a linear interpolation of the ξ values between the latter two species is made, it yields about 1950 cm^{-1}, which is quite close to the known U(V) values.

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(131) J. Gaunt, *Trans. Faraday Soc.*, 49, 1122 (1953).

(132) H. H. Claassen, B. Weinstock, and J. G. Malm, *J. Chem. Phys.*, 25, 426 (1956).