Discussion

An FeB II-type phase has been found to occur in the GdNi–GdCu section. This phase possesses similar lattice parameters as reported by Baenziger and Moriarty[13] for the GdNi(FeB II) phase. In the present investigation alloys of nominal composition $Gd_{50}Ni_{50}$ have shown only the CrB-type structure.[11] Also, the FeB II-type phase obtained in the ternary alloys was found to be in equilibrium with the CrB II-type phase. Since no trace of the FeB II-type phase was detectable in the binary alloy, the author believes that it is a true ternary phase. ErNi possesses only the FeB II-type structure. Hence the CrB II-type phase obtained in the ErNi–ErSi section is a ternary one. Likewise the CrB I-type phase found in the GdAl–GdSi section is also a true ternary one, since the CrB I-type structure does not occur in GdSi. The other newly found phases are inferred to be ternary ones since their structural characteristics are different from those of the binary phases of the respective sections.

Er and Si (in ErSi) do not substitute for Gd and Ni, respectively in GdNi, even though the structures of GdNi and ErSi are similar. In either GdNi or ErSi, the prism characteristics of one are not influenced on alloying with the other. It is highly probable that the other phases with particular prism characteristics from one branch do not modify the prism characteristics of phases from the other branch when they are alloyed.

In the ternary alloys of the LaNi–GdNi section, the prism ratio reduces to minimum values at about the middle of the section, although both LaNi and GdNi have nearly the same prism ratios. However, in the YSi–ErSi section the prism ratio remains fairly constant.

The phases of the group IV transition elements with similar structures generally have smaller prism ratios than the rare earth phases. When Zr substitutes for Nd in NdNi, the prism ratio decreases further, but not continuously, to the value of ZrNi.

The maximum prism ratio (0.915) for a phase in branch II is obtained, for the CrB-type ternary phase, in the ErNi–ErSi section. The Er_2NiCu(CrB I) phase has the minimum prism ratio (1.10) among phases with the CrB-type structure in branch I. In general, the ternary phases with the CrB-type structure have prism ratios that do not differ widely from those of the binary phases within the same branch.

In the present investigation, the prism ratio in the CrB-type phases is not found to be affected appreciably by alloying with elements which reduce the valence electron concentrations. Several other sections (not reported here) indicate that phases with possible new structures are stabilized before the prism ratio is brought to unity. In this respect, ZrSi(CrB I)[4,5] and ZrAlSi(CrB)[4,5] with square prism sides (prism ratio = 1), are apparently unique in branch I. No MoB-type phase has yet been detected in ternary alloys.

Acknowledgments.—The alloys for this project were prepared in the arc furnace at the Department of Chemical Engineering, University of Texas, Austin, Texas. The author is very grateful for the kind permission and cooperation of Dr. H. Steinfink.

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[13] N. C. Baenziger and J. L. Moriarty, Jr., *Acta Cryst.*, **14**, 946 (1961).

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Electronic Spectral Studies of Some Uranium(V) Compounds[1]

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The following solid compounds were prepared and characterized in inert atmospheres: $MUCl_6$ (M = Rb and $(n\text{-}C_3H_7)_4N$), both new compounds in regard to the cation present; $UCl_5 \cdot SOCl_2$; $UCl_5 \cdot PCl_5$; and $UCl_5 \cdot$TCAC (TCAC = trichloroacrylyl chloride, $Cl_2C{=}CClCOCl$), a new compound. In addition, solutions of UCl_5 in CCl_4 and $SiCl_4$ were prepared. Infrared spectra were obtained. Electronic spectra in the near-ir and visible region were obtained for the $MUCl_6$ compounds dissolved in $SOCl_2$; for $UCl_5 \cdot$TCAC dissolved in $SOCl_2$, C_6H_6, CS_2, and CCl_4; for $UCl_5 \cdot SOCl_2$ dissolved in $SOCl_2$ and CCl_4; and for UCl_5 in CCl_4 and $SiCl_4$. Electronic as well as vibronic band assignments have been made for these $5f^1$ electronic systems and several of the vibrational frequencies of the UCl_6^- species have been deduced from the electronic spectra. The first esr spectra for pure U(V) compounds, obtained with powdered samples, are reported, and the average g values are all 1.1.

Introduction

The literature available on the chemistry of uranium(V) is meager when compared to the voluminous data collected for the other three oxidation states (III, IV, and VI) of the element. The lack of information about the quinquevalent state is not surprising in light of the large inherent thermodynamic instability of this oxidation state relative to the quadri- and sexivalent states, leading to rapid and easy disproportionation and the ready oxidation to the latter state. In spite of its instability however, the U(V) entity is chemically and

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[1] Abstracted in part from the Ph.D. thesis of J. D. Ortego, Louisiana State University, 1968.

spectroscopically important and interesting. The ground electronic configuration is [Rn] $5f^1$, making it isoelectronic with the more stable species Pa(IV) and Np(VI).

There are very little electronic spectral data available for U(V) compounds. A careful spectral study of the solid compound $CsUF_6$ has recently appeared,[2] and solution spectra have been obtained for: $MUCl_6$ (M = Cs,[3] $(CH_3)_4N$);[4] $UCl_5 \cdot SOCl_2$ in $SOCl_2$[4] and in CCl_4;[5] $UCl_5 \cdot (C_6H_5)_3PO$ and $UCl_5 \cdot (n\text{-}C_8H_{17})_3PO$;[3] $[U(OC_2H_5)_5]_2$;[5] and $UCl_5 \cdot PCl_5$ in $POCl_3$.[6] Elsewhere we[7] have dealt with the electronic spectrum of the dioxouranium(V) species, UO_2^+. Here we shall report and analyze electronic spectral studies of UCl_6^- and certain addition compounds of UCl_5, all carried out in solution. Also we report here the first esr measurements of pure U(V) compounds.

The following solid compounds were prepared and characterized in inert atmospheres: $MUCl_6$ (M = Rb and $(n\text{-}C_3H_9)_4N$), both new compounds with regard to the cation present; $UCl_5 \cdot SOCl_2$; $UCl_5 \cdot PCl_5$; and $UCl_5 \cdot$TCAC (TCAC = trichloroacrylyl chloride, $Cl_2C{=}CClCOCl$), a new compound since the compound reported earlier[8] as $5UCl_5 \cdot$TCAC was incorrectly formulated due to impurities. In addition, solutions of UCl_5 in CCl_4 and $SiCl_4$ were prepared. Infrared spectra were obtained. Electronic spectra in the near-ir and visible region were obtained for the $MUCl_6$ compounds dissolved in $SOCl_2$; for $UCl_5 \cdot$TCAC dissolved in $SOCl_2$, C_6H_6, CS_2, and CCl_4; for $UCl_5 \cdot SOCl_2$ dissolved in $SOCl_2$ and CCl_4; and for UCl_5 in CCl_4 and $SiCl_4$. Finally, esr spectra were obtained for the solids $UCl_5 \cdot PCl_5$, $UCl_5 \cdot SOCl_2$, and $UCl_5 \cdot$TCAC.

Experimental Section

A. Preparation of Compounds. 1. Uranium(V) Chloride–Trichloroacrylyl Chloride, $UCl_5 \cdot (Cl_2C{=}CClCOCl)$ or $UCl_5 \cdot$TCAC.—To 175 ml (1.24 mol) of hexachloropropene was added 20 g (~0.02 mol) of U_3O_8. The mixture was heated to about 60° at which point a strongly exothermic reaction began, as evidenced by rapid boiling and intensive fuming of the solution. The heating mantle was then replaced by ice–water in order to maintain the temperature of the reaction mixture below 100°. When the reaction appeared to be complete (30–45 min), the dark red solution was transferred to a dry, oxygen-free apparatus in order to permit dry argon to be bubbled through the hot mixture. The cooling effect thus produced caused a bright red-orange solid to deposit. The solid was removed by filtration under argon, washed several times with dry CCl_4, in which it is slightly soluble, and then vacuum dried. An alternate procedure may be used to isolate the product after the exothermic reaction has subsided. The dark red solution may be cooled several hours in an ice bath in order to effect precipitation. When this method is employed, the crystals are much larger and are dark red. In either case the compound is extremely moisture sensitive, fuming upon exposure to the atmosphere.

$UCl_5 \cdot$TCAC appears to be stable indefinitely in a dry, inert atmosphere. It is slightly soluble in CCl_4 and $CHCl_3$ and is soluble in C_6H_6, CS_2, and $SOCl_2$. Disproportionation occurs rapidly in dimethyl sulfoxide as well as in water, alcohols, and amines. It melts at 147–149° in a sealed tube and it has a magnetic moment, measured at 300°K, of 1.54 BM. *Anal.* Calcd for $UCl_5 \cdot C_3Cl_4O$: U, 39.1; Cl, 29.1 (water-soluble or ionic chloride). Found: U, 40.0; Cl, 29.8. The U/Cl ratio is $^1/_{4.9}$ for the water-soluble chloride.

2. Rubidium Hexachlorouranate(V), $RbUCl_6$.—A weighed amount of $UCl_5 \cdot$TCAC was dissolved in $SOCl_2$ under argon to produce a red solution. Dry RbCl was then added (in a 1:1 molar ratio), which produced a deep yellow coloration of the mixture. Stirring of the reaction mixture was effected by bubbling argon through the solution. After approximately 15 min, dry CS_2 was added, causing the precipitation of a bright yellow solid. This solid was filtered and washed with CS_2 under argon and vacuum dried. The product is extremely sensitive to moisture and oxygen but is quite stable under argon. Its melting point is above 280° in a sealed capillary. *Anal.* Calcd for $RbUCl_6$: U, 44.3; Cl, 39.7. Found: U, 44.4; Cl, 37.9.

3. Tetra-*n*-propylammonium Hexachlorouranate(V), $(n\text{-}C_3H_7)_4NUCl_6$.—This compound was prepared in a manner similar to that described above for $RbUCl_6$. However, before addition of CS_2 to effect precipitation, the $SOCl_2$ solution must be concentrated by vacuum evaporation because of the high solubility of $(n\text{-}C_3H_7)_4NUCl_6$ in $SOCl_2$. The stability of this compound appears to be greater than that of either $RbUCl_6$ or $UCl_5 \cdot$TCAC. However, it decomposes within seconds if exposed to the atmosphere. *Anal.* Calcd for $(C_3H_7)_4NUCl_6$: U, 37.4; Cl, 33.4. Found: U, 37.6; Cl, 33.2.

4. Uranium(V) Chloride–Thionyl Chloride, $UCl_5 \cdot SOCl_2$.—This compound was obtained according to the procedure of Hecht, Jander, and Schlopmann,[9] by allowing UO_3 to react with an excess of $SOCl_2$ in a sealed tube at 180°. The orange modification of UO_3 used here was prepared by first precipitating $UO_4 \cdot 2H_2O$ with H_2O_2 from an aqueous solution of $UO_2(NO_3)_2$. The $UO_4 \cdot 2H_2O$ was then converted to UO_3 by drying it at 350° for 4 hr. This modification of UO_3 was used exclusively as a starting material for all other preparative reactions. *Anal.* Calcd for $UCl_5 \cdot SOCl_2$: U, 44.6; Cl, 46.5. Found: U, 44.2; Cl, 46.8.

5. Uranium(V) Chloride–Phosphorus Pentachloride, $UCl_5 \cdot PCl_5$.—This compound was prepared according to the procedure of Panzer and Suttle.[6] It was crystallized from $POCl_3$ solvent. *Anal.* Calcd for $UCl_5 \cdot PCl_5$: U, 38.2; Cl, 56.8. Found: U, 38.0; Cl, 57.1.

6. The Reaction of UO_3 with $SiCl_4$.—A small amount of UO_3 was heated in a sealed tube with an excess of $SiCl_4$ at 250° for 18 hr. No reaction was evident. The temperature was raised to 400° and a dark red solution was produced. The U(V) compound, later shown to be UCl_5 (probably the dimer, U_2Cl_{10}), is soluble in the $SiCl_4$, and it was therefore possible to separate it by filtration from the small amount of reacted or partly reacted UO_3. Evaporation of the filtered $SiCl_4$ solution yielded an extremely hygroscopic, dark red-brown precipitate, which proved to be UCl_5. *Anal.* Calcd for UCl_5: U, 57.3; Cl, 42.7. Found: U, 56.5; Cl, 42.1. The spectrum of the $SiCl_4$ solution taken prior to isolation of the solid product and the spectrum of a freshly prepared $SiCl_4$ solution of the solid product were essentially identical. Furthermore the spectrum of the solid compound dissolved in CCl_4 was essentially the same as that in the $SiCl_4$ solution.

7. Reaction of UO_3 with $TiCl_4$ and $SbCl_5$.—Heating UO_3 with $TiCl_4$ in a sealed tube at 400° did not form any detectable U(V) compounds but rather produced some U(VI) species, which were not further investigated.

After heating a mixture of UO_3 and $SbCl_5$ at 190° for 24 hr, the only change evident appeared to be the conversion of the orange modification of UO_3 into a yellow modification.

B. Spectral Measurements.—Infrared spectra were recorded in the 600–5000-cm^{-1} region using either a Perkin-Elmer

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

[3] K. W. Bagnall, D. Brown, and J. G. H. du Preez, *J. Chem. Soc.*, 5217 (1965).

[4] K. W. Bagnall, D. Brown, and J. G. H. du Preez, *ibid.*, 2603 (1964).

[5] D. G. Karraker, *Inorg. Chem.*, **3**, 1618 (1964).

[6] R. E. Panzer and J. F. Suttle, *J. Inorg. Nucl. Chem.*, **20**, 229 (1961).

[7] J. Selbin and G. Gritzner, *ibid.*, in press.

[8] R. E. Panzer and J. F. Suttle, *ibid.*, **13**, 244 (1960).

[9] H. Hecht, G. Jander, and H. Schlopmann, *Z. Anorg. Chem.*, **254**, 255 (1947).

Model 21 or a Beckman IR-7 spectrophotometer. For the 200–600-cm^{-1} region a Beckman IR-10 or a Beckman IR-7 fitted with CsI optics was utilized. Nujol mulls pressed between NaCl plates were used in the NaCl region, whereas Nujol mulls pressed between CsI plates were used for the longer wavelength range.

All visible and near-ir spectra were recorded on a Cary Model 14 spectrophotometer. Room-temperature spectra were obtained in solution using 1- or 5-cm matched quartz cells.

Esr spectra were obtained with a JEOLCO esr spectrometer, Model JES-3BS-X, using 100-kc modulation. The field was measured with an nmr precision gaussmeter, Model G-502. No signals were obtained with U(V) solutions, employing CCl_4, CS_2, and $SOCl_2$ as solvents. However very broad (~4000-G) signals were obtained with powdered samples of $UCl_5 \cdot SOCl_2$, $UCl_5 \cdot PCl_5$, and $UCl_5 \cdot$TCAC. The equation $h\nu = g\beta H_0$ was used to calculate g values of 1.097, 1.11, and 1.095, respectively, for these compounds. Measurements were also made for $RbUCl_6$ and $(n\text{-}C_3H_7)_4NUCl_6$ before the field-measuring device was available, but g values were estimated at about 1.1 for these compounds also.

Theory

In the absence of spin–orbit or crystal field effects, the $5f^1$ system with the ground-state term $^2F_{5/2}$ (sixfold degenerate) and the excited-state term $^2F_{7/2}$ (eightfold degenerate) should yield a single electronic band due to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition. However, the inclusion of crystal field and spin–orbit interactions[10] will split these levels further and additional bands should be observed. Optical spectra and paramagnetic resonance of the more stable $5f^1$ systems, Pa(IV) and Np(VI), have been previously measured and interpreted,[11–16] and optical spectra of a few U(V) compounds have likewise been previously measured and interpreted.[2,5,17] Therefore we shall do no more here than repeat that part of the $5f^1$ theory that is sufficient for interpretation of our own new U(V) optical spectra.

Since J is half-integral for the $5f^1$ system ($J = {}^5/_2$ and ${}^7/_2$), 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 octahedral symmetry. The results are

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

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

An energy level diagram may then be drawn to illustrate these levels, but the actual ordering of the levels must be determined by solving the appropriate wave equations. Calculations by Goodman[14] show that the relative ordering of levels is that pictured in Figure 1. In Figure 2 a diagram determined by Goodman[14] and others[13,18] is reproduced, which shows the effects on the free-ion energy levels with increasing field strength.

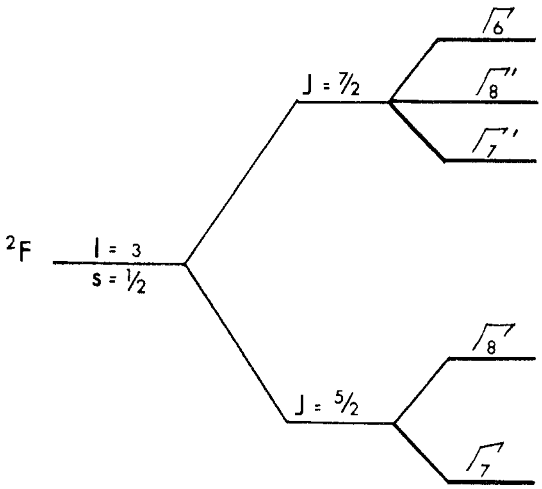

Figure 1.—Energy level splittings for a $5f^1$ system in an octahedral field. The first splitting represents the result of spin–orbit interaction and the second splitting the result of the field of O_h symmetry.

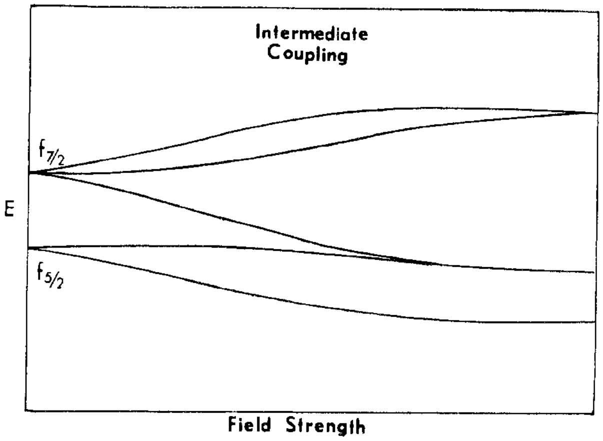

Figure 2.—Crystal field effects on the energy levels of a lone 5f electron. The free ion is to the extreme left and the strong O_h field is on the extreme right.

Since $5f^n$ ions generally fall into the intermediate-field case, we would predict four transitions to be possible in U(V) species in which the lone electron resides in the lowest doublet Γ_7 level in the ground state, namely: $\Gamma_7 \rightarrow \Gamma_8$, $\Gamma_7 \rightarrow \Gamma_7'$, $\Gamma_7 \rightarrow \Gamma_8'$, and $\Gamma_7 \rightarrow \Gamma_6$. Experimentally, however, we find not just four bands, but four *groups* of bands. These additional bands are believed to be due to different vibronic transitions, as discussed later.

For an octahedral U(V) molecule the following normal modes, with their activities and usual designations, 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).

For the purpose of assigning bands later on, it would

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(10) Interelectron repulsion effects are not present since there is but one electron outside the closed core.

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

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

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

(14) G. L. Goodman, Ph.D. Thesis, Harvard University, 1959.

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

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

(17) M. J. Reisfeld and G. A. Crosby, *J. Mol. Spectry.*, **10**, 232 (1963).

(18) J. D. Axe, Ph.D. Thesis, University of California at Berkeley, 1960.

TABLE I

VISIBLE AND NEAR-IR BANDS FOR UCl_6^- IN DIFFERENT SALTS, IN CM^{-1}

$RbUCl_6$ in $SOCl_2$	$(n\text{-}C_3H_7)_4NUCl_6$ in $SOCl_2$	$(CH_3)_4NUCl_6$ in $SOCl_2$[a]	$CsUCl_6$[b]				
			In $POCl_3$	In CH_3CN	In CH_3NO_2	In 5 *M* $(C_6H_5)_2CO\text{–}CH_2Cl_2$	Assignment
3,800 b	3,800 b	3,275					$\Gamma_7 \rightarrow \Gamma_8$
6,485 sh	6,487 w						
6,680 sh	6,674 sh		6,650	6,685	6,660	6,680	
6,702 s	6,702 s	6,710	6,750	6,775	6,750	6,750	$\Gamma_7 \rightarrow \Gamma_7'$
6,794 vs	*6,793 vs*	6,805	6,815	6,860	6,840	6,835	
6,890 s	6,887 s						
6,920 m	6,922 m	*6,905*		7,015	7,080	7,015	
7,110 w	7,112 w		7,100				
9,905 b	9,910 b	9,900	9,930	10,125	9,940	9,955	$\Gamma_7 \rightarrow \Gamma_8'$
10,440 b	10,450 b	10,420	10,460	10,685	10,460	10,480	
11,520 s	11,521 s	11,480	11,510	11,830	11,585	11,590	$\Gamma_7 \rightarrow \Gamma_6$
11,805 sh	11,820 sh						

[a] Data from ref 4. [b] Data from ref 3.

be well to review briefly some of the theoretical predictions which have already been made by several other authors.[5,16,19]

(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[16] 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 $e^{h\nu/kT}:1$.

Results

Table I records the visible and near-ir data for UCl_6^- obtained by us and by others.[3,4] Table II records our visible and near-ir data for $UCl_5 \cdot TCAC$ in four different solvents, for $UCl_5 \cdot SOCl_2$ in $SOCl_2$ and CCl_4, and for UCl_5 in $SiCl_4$ and CCl_4. Figures 3 and 4 illustrate sample spectra. Table III presents some of the infrared data obtained in this investigation which are pertinent to the question of band assignments. In Figure 6 is shown a sample esr spectrum of powdered $UCl_5 \cdot SOCl_2$.

Assignment of Bands

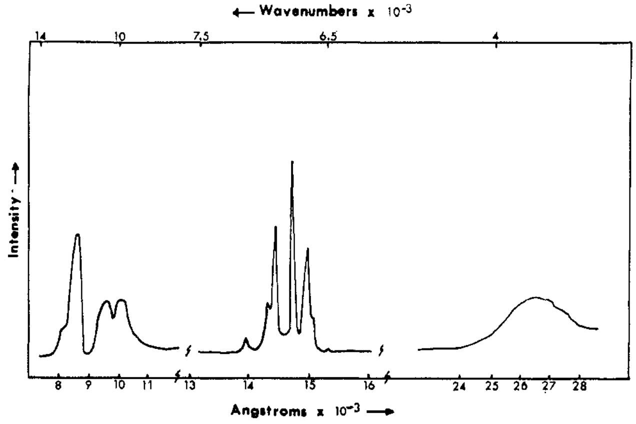

Figure 3.—Near-infrared electronic absorption spectrum of $(n\text{-}C_3H_7)_4NUCl_6$ in $SOCl_2$. The 8000–16,000-Å region was obtained with a Cary 14 and the 24,000–28,000-Å region was obtained on a Beckman IR-7.

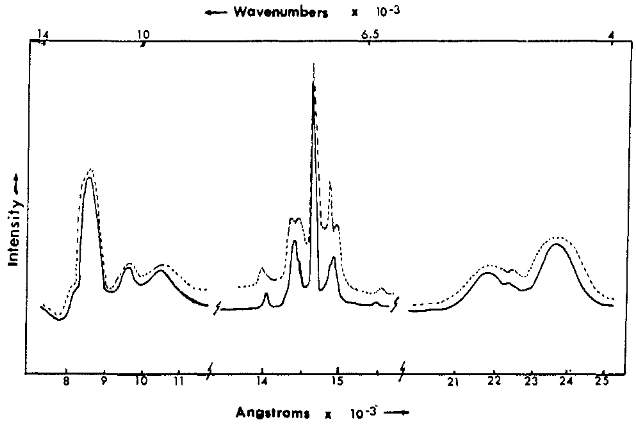

Figure 4.—Near-infrared electronic absorption spectrum of $UCl_5 \cdot TCAC$ in $SOCl_2$ (———) and in CS_2 (- - - -).

The absorption band found at 315 cm^{-1} in the infrared spectrum of UCl_6^- will be assigned to the highest infrared-active mode ν_3. This value compares well with values of 258 cm^{-1} in UCl_6^{2-} [20] and 503 cm^{-1} (for $CsUF_6^2$) or 526 cm^{-1} (for $N_2H_6(UF_6)_2$ and $(NH_3OH)UF_6$[21] or 550 cm^{-1} (for $NOUF_6$).[22] We may then expect to find coupling between electronic states and one quantum of ν_3, as well as with other odd vibrational modes.

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(19) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 200.

(20) R. A. Satten, D. Young, and D. M. Gruen, *J. Chem. Phys.*, **33**, 1140 (1960).

(21) B. Frlec and H. H. Hyman, *Inorg. Chem.*, **6**, 2233 (1967).

(22) J. R. Geichman, E. A. Smith, S. S. Trond, and P. R. Ogle, *ibid.*, **1**, 661 (1962).

TABLE II

VISIBLE AND NEAR-IR BANDS FOR SEVERAL U(V) COMPOUNDS, IN CM^{-1}

$UCl_5 \cdot TCAC$				$UCl_5 \cdot SOCl_2$		UCl_5		
In C_6H_6	In CS_2	In CCl_4	In $SOCl_2$	In $SOCl_2$[a]	In CCl_4[b]	In $SiCl_4$	In CCl_4	Assignment
	4,184 s		4,184 s					$\Gamma_7 \rightarrow \Gamma_8$
	...		4,237 sh	4,300 s (4,195)	4,350 s (4,350)	4,360 s	4,405 s	
	...		4,407 m			4,510 m		
	4,464 m		4,479 m					
	...		4,545 sh					
	4,635 w		6,451 w	6,420 w	6,560 w (6,580)	6,560 w	6,550 w	$\Gamma_7 \rightarrow \Gamma_7'$
6,667 m	6,663 m	6,662 m	6,680 m	6,640 m, 6,660 m	*6,650 s* (6,640)	*6,650 s*	6,600 w, *6,650 s*	
...	6,700 m	...	...	(6,676)	6,710 m (6,730)	6,710 m	6,700 m	
6,575 s	*6,757 s*	*6,752 s*	*6,784 s*	*6,750 s*	6,750 sh	6,750 w	6,750 w	
6,833 m	6,831 m	6,826 m	6,863 sh	6,820 m	6,800 sh			
6,859 m	6,850 m	6,849 m	6,877 m	6,840 m (6,850)		6,870 w	6,880 w	
...	...	...	...					
7,097 w	7,097 w	7,082 w	7,102 w	7,080 w (7,220)				
					8,940 s (8,930)	8,930 s	8,940 s	
	9,381 b	9,478 b		9,320 m (9,325)				$\Gamma_7 \rightarrow \Gamma_8'$
9,578 b			9,592 b		9,700 m (9,710)	9,690 m	9,660 m	
10,357 b	10,277 b	10,395 b	10,417 b	10,370 m (10,360)				
11,675 s	11,710 s	11,682 s	11,751 s	11,750 s (11,710)	11,780 s (11,800)	11,920 s	11,930 s	$\Gamma_7 \rightarrow \Gamma_6$
11,926 sh	11,961 sh	11,969 sh	11,990 sh	12,020 sh		12,220 sh	12,220 sh	

[a] Values in parentheses are taken from ref 4. [b] Values in parentheses are taken from ref 5.

TABLE III

INFRARED BANDS (CM^{-1}) OF SOME URANIUM(V) COMPOUNDS

TCAC[a]	C_3Cl_6[b]	$UCl_5 \cdot TCAC$	$(n\text{-}C_3H_7)_4\text{-}NUCl_6$	Band assignments
			2890 s	ν(C—H)
			2915 s	
	1750 w	1760 w		
		1560 s		ν(C═O)
1760		1560 s		
		1520 s		
1526	1555 s	1435 s		ν(C═C)
			1470 s	δ_{as}(C—H)
		1260 sh		
			1393 s	δ_{sym}(C—H)
1115	1117 m	1165 s		ν(C—C)
		1112 m	1340 m	
	1086 s	1086 m	1286 w	
997	1012 w	1002 m	1190 m	
960	982 m	1122 w		
	949 s	947 s	1056 m	
	934 s	910 sh	1005 s	
878	908 w	903 s	940 w	
795	867 s	862 s		
744	758–782 s	756 s		ν(C—Cl)
702	750 sh	729 s		
655	657 s	680 w		
588	584 s	567 m	757 s	
536	567 s	528 m	725 sh	
494			520 w	
457				
		455 m		ν(U—O)?
425		420 w		
380		390 w		
338		335 s		
		320 s	315 s	ν(U—Cl)

[a] Raman spectral data for trichloroacrylyl chloride: H. Gerding and coworkers, *Rec. Trav. Chim.*, **69,** 391, 941 (1950); **74,** 957 (1955). [b] Hexachloropropene.

In this connection we shall consider first the near-ir spectrum of $(n\text{-}C_3H_7)_4NUCl_6$ in $SOCl_2$, shown in Figure 3. The broad, ill-defined band at 3800 cm^{-1} will be assigned as the $\Gamma_7 \rightarrow \Gamma_8$ transition. The band is weak and broad as anticipated for the quartet levels (*vide supra*). The next group of bands centered around 6790 cm^{-1} may then be interpreted in the following manner. We note a pair of weak bands ± 312 cm^{-1} from the center spike at 6793 cm^{-1}, a second pair of slightly stronger peaks ± 121 cm^{-1} from the center peak, and a third pair of even more intense bands located 92 cm^{-1} to either side of the main peak. Therefore we assign the $\Gamma_7 \rightarrow \Gamma_7'$ $(0 \rightarrow 0)$ transition to the main peak in the cluster at 6793 cm^{-1}. A calculation of the intensity ratios of the respective vibronic side bands compared to the intensity ratios expected from the relationship $e^{h\nu/kT}:1$ for $(\nu_0 + \nu)$ and $(\nu_0 - \nu)$ (Table IV) supports the assignments shown in Figure 5. The three odd vibrational modes assigned in this way may be compared to those determined in an analogous manner for the UCl_6^{2-} entity,[19] which are: $\nu_3(T_{1u}) = 258$ cm^{-1}, $\nu_4(T_{1u}) = 114$ cm^{-1}, and $\nu_6(T_{2u}) = 94$ cm^{-1}. Since the T_{2u} mode involves only angle deformations, it would not be expected to differ greatly in the corresponding U(IV) and U(V) species. Thus the ν_6 value for the latter of 92 cm^{-1} is quite reasonable. However, with the increased nuclear charge in the U(V) hexachloro species, a vibration in which the U–Cl bonds are stretched would be expected to occur at a higher frequency than the U(IV)–Cl stretching modes. The two T_{1u} modes both involve bond stretching and are of higher frequency in each case, as expected.

Further confirmation of the foregoing assignments was obtained by examining low-temperature spectra. A solution of $RbUCl_6$ in $SOCl_2$ was cooled by using a toluene–liquid nitrogen slush as the cooling agent, and the spectrum was obtained. The three vibronic bands on the *low* energy side of the $0 \rightarrow 0$ band showed a decrease in intensity, whereas the three vibronic bands on the *high* energy side showed a slight increase in intensity. In addition, the sharp $0 \rightarrow 0$ band increased

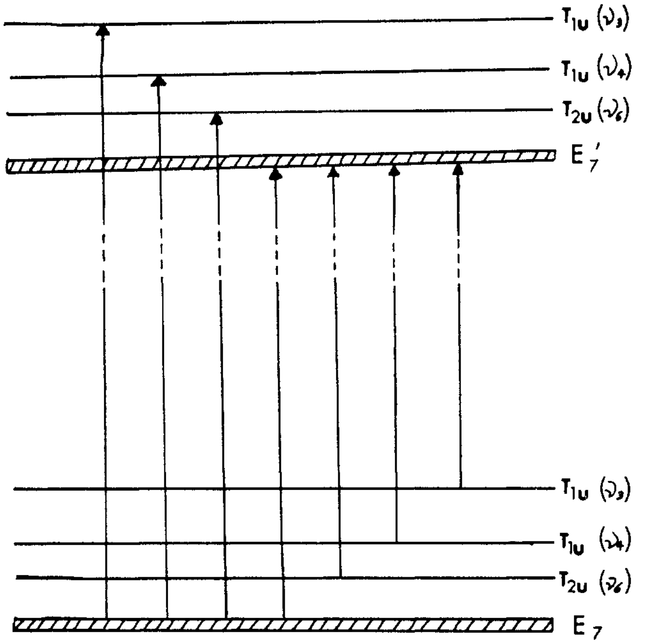


Figure 5.—Vibronic energy levels for the $L_7 \rightarrow L_7'$ transition in UCl_6^-.

TABLE IV

INTENSITY RATIOS AND VIBRONIC BANDS IN THE $\Gamma_7 \rightarrow \Gamma_7'$ TRANSITION IN $(n\text{-}C_3H_7)_4NUCl_6$

Vibrational freq, cm^{-1}	Calcd intensity ratio, $e^{h\nu/kT}$:1	Exptl ratio	Assignment
312	4.5:1	5:1	$T_{1u}(\nu_3)$
121	1.78:1	1.6:1	$T_{1u}(\nu_4)$
92	1.55:1	1.3:1	$T_{2u}(\nu_6)$

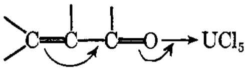
greatly in intensity at the lower temperature. The intensity *ratios* found at the lower (but unknown) temperature were ~10:1 for the 312-cm^{-1} bands, 1.8:1 for the 121-cm^{-1} bands, and 1.6:1 for the 92-cm^{-1} bands. Since the exact temperature was not determined, it is not possible to compare these values with calculated values; however, it is significant that all band intensity changes observed at the lower temperature are in the predicted order.

The next electronic level of interest is the quartet Γ_8'. It has been predicted, as was noted earlier, that the quartet should split into two doublets (*i.e.*, Kramer's doublets) upon any distortion of the octahedral symmetry. With this in mind, it is reasonable to assign the two broad bands at 9910 and 10,450 cm^{-1} as arising from the $\Gamma_7 \rightarrow \Gamma_8$ transitions, in which the Γ_8' level is split into two levels separated by 540 cm^{-1}. Support for this assignment, although by no means conclusive, is that the two bands are of nearly equal intensity and shape. If the transitions were vibronic, equal intensities would not be expected.

The last low-intensity band is located at 11,520 cm^{-1} and it has a weak shoulder at 11,820 cm^{-1}. We are tempted to assign this peak to the $\Gamma_7 \rightarrow \Gamma_6$ transition. The shoulder may be due to a coupling with the totally symmetric A_{1g} vibrational mode, ν_1. The only evidence in support of this assignment is its weak intensity and its recurrence in the other U(V) compounds. No Raman data which would reveal the symmetric vibrations could be found in the literature for comparison purposes.

In summary, therefore, we have assigned the four electronic transitions predicted for an $5f^1$ system in an octahedral symmetry along with three ungerade vibrational modes and (tentatively) the A_{1g} symmetric stretching mode (300 cm^{-1}) of the UCl_6^- ion. Finally, it is of interest to list here the corresponding vibrational frequencies (in cm^{-1}) reported by Reisfeld and Crosby[2] for $CsUF_6$ and obtained in a slightly different manner from electronic and vibronic spectral data at 77°K: $\nu_1(A_{1g}) = 506$, $\nu_3(T_{1u}) = 503$, $\nu_4(T_{1u}) = 150$, $\nu_5(T_{2g}) = 145$, and $\nu_6(T_{2u}) = 100$. These assignments are consistent with ours when the expected differences between U(V)–F and U(V)–Cl bonds are taken into account.

We now wish to consider the spectrum of $UCl_5 \cdot$TCAC. However, first it would be appropriate to consider the evidence that the ligand TCAC ($Cl_2C{=}C$-ClCOCl) is actually coordinated to the uranium through the oxygen atom, producing a lower symmetry environment for the $5f^1$ system, that is, C_{4v} rather than O_h. The bulk of the evidence may be found in the infrared data presented in Table III. In the $UCl_5 \cdot$TCAC complex the carbonyl stretching frequency is found at 1560 and/or 1520 cm^{-1}, or about 200 cm^{-1} lower than that of the free acid chloride value of 1760 cm^{-1}.[23] Coordination of the oxygen to the U(V) ion by a dative bond would produce this effect. The magnitude of this frequency shift (200 cm^{-1}) may be compared to the only other two complexes of UCl_5 which involve coordination to the uranium through an oxygen atom, namely, $UCl_5 \cdot (R_3PO)$ (where R = C_6H_5 or C_8H_{17}).[13] The P=O frequency in $UCl_5 \cdot (C_6H_5)_3PO$ is lowered 217 cm^{-1} (from 1192 to 973 cm^{-1}) and 161 cm^{-1} in $UCl_5 \cdot (C_8H_{17})_3PO$ (from 1144 to 983 cm^{-1}). Furthermore the upward shift in $\nu_{(C-C)}$ (from 1115 to 1165 cm^{-1}) and the downward shift in $\nu_{(C=C)}$ (from 1526 to 1435 cm^{-1}) in our compound also favor the structure



Another possibility, considered quite possible at the beginning of this research, is that the compound is actually ionic, involving a carbonium ion: $[Cl_2C{=}CClC{=}O]^+UCl_6^-$. However, the order of the frequency shifts presented above would be quite different in this case, and in addition the electronic spectrum would have to be that of UCl_6^-, which it is not (compare data in Tables I and II).

Now it is interesting to observe in the electronic spectrum of $UCl_5 \cdot$TCAC that the magnitude of the splitting in the Γ_8' level, 825 cm^{-1} for the $SOCl_2$ solution, is larger than that found for UCl_6^- (540 and 535 cm^{-1}, respectively, for the Rb$^+$ and the $(n\text{-}C_3H_7)_4N^+$ salts). This is most probably due to the lower symmetry field present in the TCAC addition compound. The Γ_8'

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[23] H. Gerding and coworkers, *Rec. Trav. Chim.*, **69**, 391, 941 (1950); **74**, 957 (1955).

splitting for $UCl_5 \cdot TCAC$ in the other solvents studied is 896, 879, and 917 cm^{-1}, for CS_2, benzene, and CCl_4, respectively. The reason for this variation is not at all clear at present. However, because the Γ_8' levels tend to split increasingly with decreasing symmetry, it may be that these energy level differences reflect the symmetry lowering or magnitude of distortion from octahedral symmetry.

Esr Spectra

Finally, we report the first esr measurements made on pure U(V) compounds, namely, powdered samples of $UCl_5 \cdot TCAC$, $UCl_5 \cdot SOCl_2$, $UCl_5 \cdot PCl_5$, $RbUCl_6$, and $(n\text{-}C_3H_7)_4NUCl_6$. All of these compounds produced an extremely broad signal similar to that for the compound $UCl_5 \cdot SOCl_2$, shown in Figure 6. The average *g* values were all approximately 1.1, with the sign undetermined. This may be compared with the value of $\backsim$1.25 determined for U(V) ions in a matrix of ThO_2.[24] The value of *g* is expected to be negative, since $g = -1.14$ for Pa(IV)[12] and $g = -0.60$ for Np(IV)[13] and since Karraker[5] has *calculated* a *g* value for $UCl_5 \cdot SOCl_2$ of -1.18. Agreement of this latter value with our experimental values is quite reasonable.

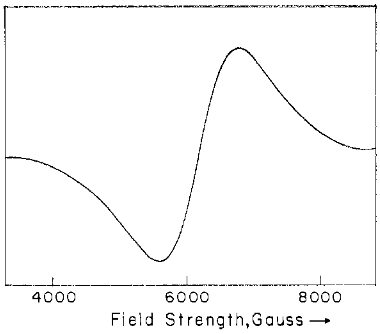

Figure 6.—Esr spectrum of powdered $UCl_5 \cdot SOCl_2$; ν = 9.442 Mc.

[24] P. M. Llewellyn, unpublished work, quoted in W. Low, "Paramagnetic Resonance in Solid State Physics," Academic Press Inc., New York, N. Y., 1960, Supplement 2.

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Diethyldithiocarbamates of Quadrivalent Actinides[1]

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Diethyldithiocarbamates of Th(IV), U(IV), Np(IV), and Pu(IV) were synthesized by the reaction between MCl_4 or $[(C_2H_5)_4N]_2MCl_6$ (M = Th, U, Np, or Pu) and LiL [$L = S_2CN(C_2H_5)_2^-$] in anhydrous ethanol. Elemental analyses show that the products have the formula ML_4, and comparison of the infrared spectra of ML_4 compounds and the sulfur-bonded ZnL_2 indicates that all are similarly bonded. X-Ray diffraction data indicate that all four compounds are isomorphous. Proton magnetic resonance spectra established the spectroscopic equivalence of all C_2H_5 radicals in $CDCl_3$ and C_6D_6 solutions of ThL_4 and UL_4. The proposed structure for the ML_4 compounds is an eight-coordinate metal ion, bonded by four four-atom chelate rings to the ligands.

Introduction

The objective of this investigation was the synthesis and study of sulfur-bonded coordination compounds of the actinides. Qualitative information on actinide(IV) coordination can be obtained from the existence of such compounds. A comparison of the stability of compounds in which actinides are bonded to sulfur with the stability of analogous oxygen-bonded compounds might provide valuable information on the nature of the bonding.

Previous investigators have attempted to synthesize uranium(IV) dialkyldithiocarbamates but obtained uranyl derivatives instead.[3] Uranyl dialkyldithiocarbamates have been investigated thoroughly,[4–6] and an early investigation[7] mentioned a thorium precipitate that was not characterized. The preparation and preliminary results on the crystal structure of uranium(IV) diethyldithiocarbamate were reported[8] during the preparation and review of this paper.

Experimental Section

Reagents. $[(C_2H_5)_4N]_2MCl_6$.—These compounds were prepared by a modification of the method of Bradley, *et al.*[9] The M(IV) hydroxides were precipitated from aqueous solution by addition of base, washed free of excess base, and dehydrated by washing with absolute ethanol. A suspension of the M(IV) hydroxide in absolute ethanol was dissolved by bubbling gaseous HCl into the chilled suspension; $[(C_2H_5)_4N]_2MCl_6$ was precipitated by addition of an ethanol solution of $(C_2H_5)_4NBr$. The solid product was collected by filtration, washed with absolute ethanol, and vacuum dried.

UCl_4, $NpCl_4$.—Anhydrous UCl_4 and $NpCl_4$ were prepared by passing a stream of dry nitrogen, saturated with CCl_4, over UO_2

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[2] ORAU Summer Research Participant at the Savannah River Laboratory.

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