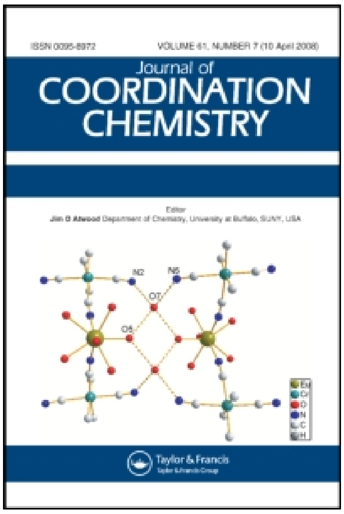

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COORDINATION CHEMISTRY OF URANIUM 1. ETHER COMPLEXES OF URANIUM PENTACHLORIDE

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COORDINATION CHEMISTRY OF URANIUM
1. ETHER COMPLEXES OF URANIUM PENTACHLORIDE

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Carbon disulfide solutions of uranium(V) chloride were found to react with simple cyclic and alkyl ethers to produce solid 1:1 adducts. In addition to tetrahydrofuran (THF) and 1,4–dioxane, the donor molecules involved in our study include dimethyl–, diethyl–, diisopropyl–, dibutyl–, and diisopentyl–ether. These new compounds were characterized by electronic and infrared spectroscopy, conductance, molecular weight and magnetic susceptibility measurements.

INTRODUCTION

Transition metal complexes with the cyclic ethers tetrahydrofuran and 1,4-dioxane have been recently investigated.[1-9] In general, these compounds are thermally stable, but must be prepared and studied under rigidly anhydrous conditions. Less well-known and studied, however, are metal ion complexes with the simple aliphatic ethers. Niobium and tantalum pentachlorides and bromides form 1:1 crystalline adducts with diethyl ether.[10] Thermal decomposition occurs around 100° C to produce the ethyl halide and metal oxytrihalide. Solid diethyl ether complexes of Fe^{3+}[11], In^{3+}[12], Au^{3+}[13], VO^{3+}[14] and UO_2^{2+}[15] have also been isolated.

Although there is an extensive chemistry associated with the element uranium, there are no reports, to our knowledge,[16] of ether complexes with uranium in the oxidation states of III or V. Solubility studies of UCl_5 in varous organic solvents, including ethers, were undertaken during the wartime effort of the early 1940's, by the Atomic Energy Commission. From this source[17] it was reported that UCl_5 would react vigorously with dimethyl and diethyl ether, but not with diisopropyl ether—(no compounds were isolated in these studies). We therefore began our investigations into UCl_5—ether reactions and succeeded in isolating several new coordination compounds of UCl_5, including one with diisopropyl ether.

The donor molecules involved in our study in addition to tetrahydrofuran (THF) and 1, 4-dioxane are dimethyl-, diethyl-, diisopropyl-, dibutyl-, and diisopentyl-ethers. Exposure of any of the isolated compounds to the atmosphere resulted in immediate decomposition. The compounds are insoluble in benzene, carbon tetrachloride and chloroform, and dissolve with apparent decomposition in dimethylsulfoxide and methyl alcohol. No decomposition was detected when the complexes dissolved in dry, degassed nitromethane and acetonitrile.

EXPERIMENTAL

(a) *Preparation of Compounds*

Analytical and other characterizing data for the ether complexes are summarized in Tables I and II.

Uranium tetrachloride was prepared by a slight modification of the method of Suttle.[18]

Uranium pentachloride was prepared by passing Cl_2 gas over UCl_4 at 550° C in a quartz tube.[19] The red-brown solid was collected and stored under dry argon. Analytical data for the UCl_5 so prepared produced a U/Cl ratio of 1 to 5.1.

All ether complexes of U(V) are extremely sensitive to atmospheric oxygen and moisture, decomposition and/or disproportionation occurring immediately upon exposure to air. All experimental work was carried out under an atmosphere of argon. Spectroquality carbon disulfide was used as a solvent for UCl_5, while the respective ethers were refluxed over freshly pressed sodium wire and then distilled to ensure purity.

Analyses for uranium and chlorine were determined potentiometrically using standard solutions of $Ce(SO_4)_2$ and $AgNO_3$ with calomel-platinum and calomel-silver electrode systems, respectively.

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TABLE I

Some new ether complexes of UCl$_1$

Compound[a]	Color	Decomposition[b] temp. (°C)	Calculated %U	Calculated %Cl	Found %U	Found %Cl	Calculated %C	Calculated %H	Found[c] %C	Found[c] %H
(a) $UCl_5 \cdot (CH_3)_2O$	yellow	80	51.60	38.40	52.1	39.3	5.20	1.30	6.64	1.73
(b) $UCl_5 \cdot (C_2H_5)_2O$	yellow	130	48.65	36.23	49.1	37.3	9.81	2.04	9.87	2.05
(c) $UCl_5 \cdot (C_3H_1)_2O$	yellow	145	46.00	34.22	45.7	35.1	13.92	2.71	13.71	2.97
(d) $UCl_5 \cdot (C_4H_9)_2O$	yellow	125	44.46	33.07	44.9	32.9	17.93	3.36	19.81	3.24
(e) $UCl_5 \cdot (C_5H_{11})_2O$	purple	170	41.64	30.93	41.8	31.6	20.97	3.84	21.8	4.36
(f) $UCl_5 \cdot (C_4H_8O_2)$	yellow	130	47.29	35.17	48.1	35.7	9.54	1.59		
(g) $UCl_5 \cdot (C_4H_8O)$	yellow	150	48.85	36.38	49.4	37.8	9.85	1.64		

[a] The ethers are (a) dimethyl; (b) diethyl; (c) diisopropyl; (d) dibutyl; (e) diisopentyl; (f) 1, 4-dioxane; (g) tetrahydrofuran.

[b] All complexes begin to darken slowly above the temperatures cited.

[c] For some unknown reason the carbon and hydrogen commercial analyses for the p-dioxane and tetrahydrofuran complexes were erratic and therefore are not reported.

TABLE II

Magnetic, molecular weight and conductivity data for some new ether complexes of UCl$_5$

	Compound	Magnetic Properties $\chi m \times 10^6$	Magnetic Properties corr $\mu 295°K$(BM)	Molecular Weights calc.	Molecular Weights found.	Molar conductance in CH_3CN Λ(ohm^{-1}cm^2)
(a)	$UCl_5 \cdot (CH_3)_2O$	1370	1.78	461.3	542	14.0
(b)	$UCl_5 \cdot (C_2H_5)_2O$	1511	1.87	489.3	521	13.0
(c)	$UCl_5 \cdot (C_3H_7)_2O$	1212	1.68	517.3	536	7.3
(d)	$UCl_5 \cdot (C_4H_9)_2O$	1536	1.88	535.3	571	12.0
(e)	$UCl_5(C_5H_{11})_2O$	1814	2.16	572.3	635	2.3
(f)	$UCl_5(C_4H_8O_2)$	1223	1.68	503.3	547	8.8
(g)	$UCl_5 \cdot (C_4H_8O)$	832	1.44	487.3	504	9.4

Sample weighing difficulties were encountered owing to the extreme reactivity of the compounds and are quite likely the main source of experimental error in the analytical determinations. The analytical results reported in Table I are the average of at least five runs. Analyses for carbon and hydrogen were performed by a commercial laboratory (Galbraith Laboratories, Inc., Knoxville, Tennessee).

$UCl_5 \cdot (CH_3)_2O$ [Pentachloro(dimethyl ether)uranium(V)]. Methyl ether was passed through an argon-saturated column containing activated alumina and a suitable molecular sieve to remove peroxides and/or water that may have been present in the gas. The ether, purified in this manner, was passed over a freshly filtered solution of UCl_5 in CS_2 with continuous stirring. A yellow-green coloration developed in the solution almost immediately followed by the formation of a yellow solid. The passage of the gaseous ether was discontinued when the UCl_5–CS_2 solution became colorless. The solution was then filtered under argon and the precipitate was dried under vacuum. The resulting product is a bright yellow solid. An alternate method may be used to obtain the same product. Solid UCl_5 was added to liquified dimethyl ether with continuous stirring. A vigorous reaction ensued and the yellow product separated from the solution. Excess ether was removed by allowing the cold mixture to warm to room temperature under vacuum.

$UCl_5 \cdot (C_2H_5)_2O$ [Pentachloro(diethyl ether)uranium(V)]. A saturated solution of UCl_5 in CS_2 was slowly dripped into a cold 50% solution of diethyl ether in CS_2. The resulting precipitate was isolated as described above.

$UCl_5 \cdot (C_3H_7)_2O$ [Pentachloro(diisopropyl ether)-uranium(V)]. A yellow complex, isolated in a manner similar to that described above, slowly changed to a buff color while stored under argon. The infrared spectrum and analytical data of the different colored products were identical, however.

$UCl_5 \cdot (C_4H_9)_2O$ [Pentachloro(dibutyl ether)uranium(V)]. A saturated UCl_5–CS_2 solution was slowly dripped into the cold dibutyl ether at about 0° C. Immediately a yellow precipitate formed, but caution had to be exercised to prevent an excess of dibutyl ether from accumulating, since the complex is extremely soluble in the parent ether.

$UCl_5 \cdot (C_5H_{11})_2O$ [Pentachloro(diisopentyl ether)-uranium(V)]. Addition of a UCl_5–CS_2 solution to diisopentyl ether at ice-bath temperature produced a purple solution. This solution was cooled for approximately 10 hours and a dark purple crystalline solid was collected and dried.

$UCl_5 \cdot C_4H_8O_2$ [Pentachloro(1,4-dioxane)uranium(V)]. Cold p-dioxane (5°) was slowly added to a concentrated solution of UCl_5 in CS_2 until the solution became yellow. After several minutes a precipitate formed which was collected in a manner similar to that described earlier. Both a yellow and a pink precipitate were recovered and both compounds yield identical IR spectra. The presence of excess dioxane causes a dark-coloured oil to form. This oil was extremely difficult to handle, and no characterization was possible.

$UCl_5 \cdot C_4H_8O$ [Pentachloro(tetrahydrofuran)uranium(V)]. This new complex was prepared by the method used for the preceding compounds. As with the p-dioxane complex, excess ether resulted in the formation of a thick viscous oil.

(b) *Molecular Weight Determinations.*

Molecular weights of the seven ether complexes were determined using the Rast method.[20] Small weighed amounts of dry naphthalene and the ether complex were sealed in a capillary tube and then repeatedly melted and solidified to insure thorough mixing. The results of the cryoscopic determination of molecular weights are listed in Table II.

(c) *Conductivity Data.*

Conductance measurements were obtained at room temperature using an Industrial Instruments RC 16B2 conductivity bridge in conjunction with a standard glass conductivity cell (1 cm^2 platinum electrodes). The molar conductance values are recorded in Table II.

(d) *Magnetic Susceptibility.*

Magnetic susceptibility data were obtained by the Gouy method. The equipment consisted of a Cahn RH electrobalance, an Alpha Scientific 4 inch adjustable gap electromagnet (Model 4600) and matching power supply. The system was calibrated using tris(ethylenediamine)nickel(II) thiosulphate and mercury tetrathiocyanatocobaltate(II). The molar susceptibilities and the effective magnetic moments at 295° K are tabulated in Table II.

(e) *Electronic Spectra.*

The visible and near-infrared spectra were recorded on a Cary Model 14 spectrophotometer. The compounds were dissolved in acetonitrile and spectra were obtained using matched 5 cm quartz cells.

(f) *Infrared Spectra.*

Infrared spectra were recorded on a Perkin-Elmer 337 spectrophotometer. Nujol and KF-10 polymer oil were used as mulling agents. The resulting mulls were pressed between KBr plates. Decomposition spectra were obtained by separating the plates and exposing the mull to the atmosphere for approximately two minutes. The plates were then placed together again and the spectra recorded. This procedure was repeated several times for each sample until no further change was detected in the spectrum.

RESULTS AND DISCUSSION

Infrared Data

Tentative assignments of the symmetric and asymmetric COC stretching vibrations for seven ethers and their UCl_5 complexes are listed in Table III. The asymmetric COC stretch for the free ethers falls between 1105 and 1135 cm^{-1}, with the exception of tetrahydrofuran, which has a value of 1065 cm^{-1}. Upon oxygen coordination, one expects a lowering of the COC stretching frequency due to

TABLE III

Tentative assignments of selected IR bands (in cm^{-1}) for some ethers and their UCl_5 complexes

Compound	ν_{as}(COC)	ν_{sym}(COC)	Compound	ν_{as}(COC)	ν_{sym}(COC)
$(CH_3)_2O$[a]	1120s 1110s (1094) 1090s	940m 920m (920)	$UCl_5 \cdot (CH_3)_2O$	1030s	955s 880s 860s
$(C_2H_5)_2O$	1115s	930w 900w	$UCl_5 \cdot (C_2H_5)_2O$	1010s	940s 890s
$(C_3H_7)_2O$	1125s 1110s	935w 900m	$UCl_5 \cdot (C_3H_7)_2O$	1078s	965sh 935s
$(C_4H_9)_2O$	1120sh 1135s	928w 896w	$UCl_5 \cdot (C_4H_9)_2O$	1097m	935s 950sh
$(C_5H_{11})_2O$	1105s 1125sh	915vw	$UCL_5 \cdot (C_5H_{11})_2O$	960s	
C_4H_8O	1065s	905s	$UCl_5 \cdot (C_4H_8O)$	995s 1035m	915m 995m
$C_4H_8O_2$	1120s	875s	$UCl_5 \cdot (C_4H_8O_2)$[b]	1115s $\left\{\begin{matrix}1045s\\1055s\\1065s\end{matrix}\right.$	938s $\left\{\begin{matrix}889s\\865s\\850s\end{matrix}\right.$

[a] Values in parentheses for this compound are for liquid dimethyl ether, other values apply to the gaseous ether.

[b] Values listed in brackets are from well defined triplets.

weakening of the C–O bonds through electron delocalization. In all cases ν_{as}(COC) is lower in the complex when compared to the free ether. The frequency shifts range from a low of 38 cm^{-1} for the dibutyl ether compound to a high of 145 cm^{-1} in the diisopentyl ether compound. Other shifts are 80 cm^{-1} for $UCl_5 \cdot (CH_3)_2O$; 105 cm^{-1} for $UCl_5 \cdot (C_2H_5)_2O$; 47 cm^{-1} for $UCl_5 \cdot (C_3H_7)_2O$; 70 cm^{-1} for $UCl_5 \cdot C_4H_8O$ and 65 cm^{-1} for $UCl_5 \cdot C_4H_8O_2$. All of these values imply that, indeed, coordination has occurred via the oxygen atom.

$UCl_5 \cdot$ tetrahydrofuran Spectral evidence for coordination between THF and $TiCl_3$, VCl_3, $VOCl_2$ and $CoCl_2$ is based on the shift of the asymmetric COC band at 1065 cm^{-1} with the appearance of sharp, intense peaks at lower frequencies (around 1000 cm^{-1})[6, 7]. The IR spectra of our complex ($UCl_5 \cdot$THF) exhibits a similar pattern.

$UCl_5 \cdot$ 1,4-dioxane Burket and Badger,[12] in a detailed analysis of the infrared spectrum of 1, 4-dioxane, assigned the absorption at 1120 cm^{-1} to the asymmetric COC ring vibration, while the bands at 870 cm^{-1} and 610 cm^{-1} are due to symmetric ring stretching and ring wagging, respectively. Because of its structure, 1,4-dioxane may coordinate either as a uni- or bidentate ligand. When functioning as a bidentate in such compounds as $Cr(CO)_6$ (dioxane)$_3$[22] and the 1:1 and 2:1 adducts with the divalent metal halides of Mn, Fe, Co and Ni[1], the structures most probably contain bridging dioxane molecules in the chair conformation. It is expected that should both oxygen atoms coordinate, the 1125 cm^{-1} asymmetric stretch would be shifted to lower energy and no bands would be observed in this region of the spectrum. Should only one oxygen coordinate, the free ligand band (1120 cm^{-1}) would still appear in the spectrum of the complex, while additional bands due to the coordinated oxygen should manifest themselves. Infrared spectra of 1:1 adducts formed between 1, 4-dioxane and $TaCl_5$ and $NbCl_5$[9] exhibit peaks

around 1025–1075 cm^{-1} (in addition to the 1120 cm^{-1} band) of approximately the same shape and intensity as the free ligand asymmetric COC vibration. This additional band is an indication that the 1, 4-dioxane molecule is acting as a monodentate ligand yielding absorptions of both a free and coordinated COC vibrational mode. This is in contrast to the $TiBr_4$–dioxane complex reported by Ralston and Sisler,[3] which shows no IR bands in the 1120 cm^{-1} region. The absence of this "free ligand" stretching absorption indicates that both oxygens are bonded in some bidentate fashion. In our complex, $UCl_5 \cdot 1$, 4-dioxane, the presence of a strong band at 1115 cm^{-1} and a triplet centered at 1055 cm^{-1} offers strong evidence that the ligand is monodentate, exhibiting both "free" and "coordinated" asymmetric COC vibrations.

$UCl_5 \cdot$dimethyl ether The symmetric and asymmetric COC stretches for dimethyl ether (gas phase) have been assigned[23] as 940–920 cm^{-1} and 1110 cm^{-1}, respectively.

Examination of the complex spectrum reveals the absence of the two intense peaks in the region of 1185 cm^{-1} (CH_3 rocking motion) and 1110 cm^{-1}. Again, as in the previous discussions, one expects bonding via the ethereal oxygen to lower the COC stretching frequencies. The sharp band at 1030 cm^{-1} is assigned to the coordinated asymmetric COC vibration. The two sharp peaks located at 880 and 860 cm^{-1} are strikingly similar to the symmetric COC bands of free dimethyl ether (at 940 and 920 cm^{-1}) and are tentatively assigned to this vibrational mode.

The remaining akyl ethers and their complexes exhibit similar patterns in their infrared spectra and will not be discussed here.

DECOMPOSITION STUDIES

Infrared studies of the decomposition products of $UCl_5\cdot$ether complexes lead us to postulate that the following series of reactions occur when the compounds are exposed to the atmosphere. It is known that UCl_5 undergoes immediate disproportionation when contacted by water according to eq. (1). The IR spectrum of a Nujol$\cdot UCl_5$

$$2\,UCl_5 + 2\,H_2O \rightarrow UO_2Cl_2 + UCl_4 + HCl \quad (1)$$

slurry, after exposure to the moist atmosphere, shows a broad intense band at 900 cm^{-1}. This band is due to the OUO antisymmetric stretch of the decomposition product UO_2Cl_2. The hydrates, $UO_2(NO_3)_2\cdot 6H_2O$ and $UO_2(CH_3COO)_2\cdot 2H_2O$, both yield this broad band at about 940 cm^{-1}. A controlled decomposition spectrum of any of the $UCl_5\cdot$ether complexes exhibits this UO_2Cl_2 absorption peak along with vibrations indicative of the free ether released during decomposition. When $UCl_5\cdot O(CH_3)_2$ is exposed to moist air, some gaseous ether is liberated. This was confirmed by allowing the complex to decompose inside an infrared gas cell and recording the spectrum of the gaseous decomposition products. The spectrum so obtained was identical to that of pure $(CH_3)_2O$. Equation (2) summarizes the above general reaction.

$$2\,UCl_5\cdot OR_2 + 2\,H_2O \rightarrow UO_2Cl_2 + UCl_4 + 4\,HCl + 2\,ROR \quad (2)$$

Figure (1) shows the change in spectral characteristics as the $UCl_5\cdot 1$, 4-dioxane complex is exposed to air for increasing lengths of time. The multiplicity of the COC absorption at 1055 cm^{-1} changes progressively as the exposure time is increased. Upon total decomposition the only prominent vibrational modes present are those of uncoordinated 1,4-dioxane and the 900 cm^{-1} UO_2^{2+} absorption.

Decomposition of the $UCl_5\cdot$THF complex (Figure 2) shows the increasing concentration of the UO_2Cl_2 species upon increased exposure to the atmosphere. Similar results were observed with all of the $UCl_5\cdot$ether complexes.

Two sharp intense peaks in the 3500–3600 cm^{-1} region appear in the decomposition spectra of all the complexes, in addition to a broad H_2O absorption band. These peaks, of course, fall within the O–H stretching range. Attempts to explain the presence of these two sharp bands were centered upon the possibility of the presence of either a coordinated H_2O species or an alcoholic OH group. Consideration of equation (1) produces two possibilities for a coordinated aquo species, that is, $UCl_4\cdot nH_2O$ and $UO_2Cl_2\cdot nH_2O$. Mull spectra of these two compounds do not produce the two sharp peaks witnessed in the decomposition spectra of the ether complexes.

The presence of these two absorption bands could conceivably be explained by postulating some acid type cleavage mechanism for the ethers, although the experimental evidence for such a process is limited. Traditionally, cleavage of ethers is produced by the action of a strong acid, HI or HBr, on the desired ether. The weaker HCl is seldom

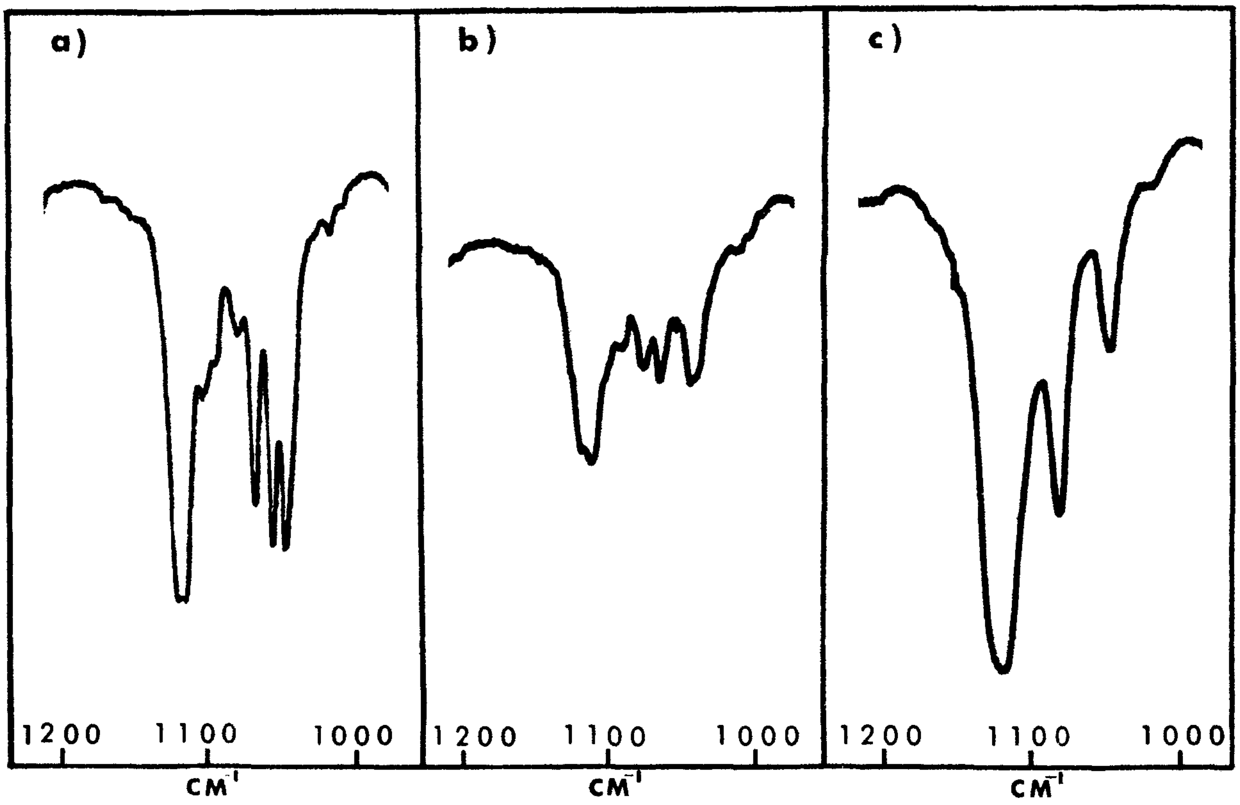


FIGURE 1 Infrared spectra of $UCl_5 \cdot 1,4$-dioxane. (a) Spectrum showing "coordinated" asymmetric COC stretch (triplet), centered at 1055 cm^{-1}. (b) Spectrum of the complex after exposure to the atmosphere for approximately 3 minutes. Note decrease in intensity of "coordinated" asymmetric COC vibration. (c) Spectrum of the complex after complete decomposition. showing bands characteristic of the "free" ether asymmetric COC stretch.

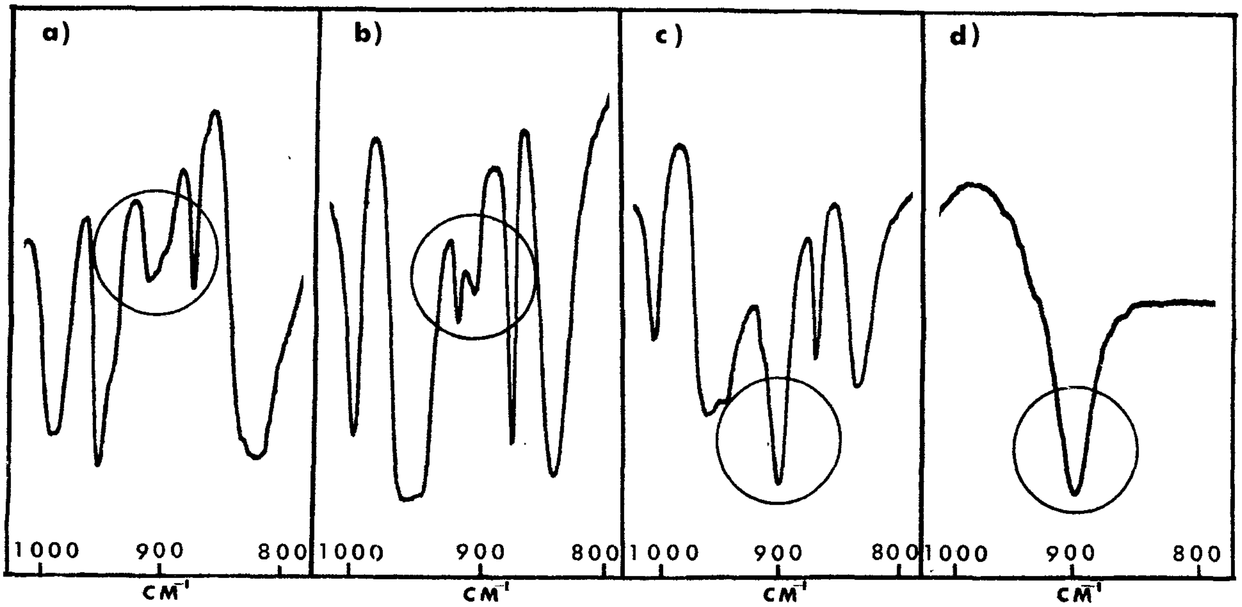
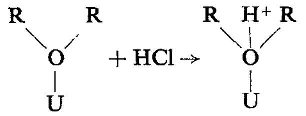


FIGURE 2 (a) Infrared spectra of $UCl_5 \cdot THF$ in the 800–1000 cm^{-1} region. (b), (c) and (d) Spectral changes as the complex is exposed to moist air for increasing lengths of time. (Approximately 2, 4, and 6 minutes.)

effective alone. although a cleavage of THF has been reported with this acid.[24] The cationic complex resulting from attack by the proton on the ether-Lewis acid species cleaves through an S_N1 or S_N2 mechanism yielding the corresponding alcohol and chloride. In the $UCl_5 \cdot$ether compounds, the decomposition of the UCl_5 molecule produces the necessary acid environment, while within the complex a U(IV), U(V) or U(VI) species could serve as the required Lewis acid. These reactions are shown in equation (3).



$$+ Cl^- \xrightarrow{S_N1 \text{ or } S_N2} ROH + RCl \quad (3)$$

ELECTRONIC SPECTRA

The electronic spectra of octahedral U(V), Rn[$5f^1$], has been previously discussed[16, 25], and we will not go into details of the theory or assignments of bands here. (A future communication will deal more explicitly with NMR, electronic and EPR spectral data).

Briefly, for octahedral or pseudo-octahedral symmetry about a U(V) ion one predicts four bands or "groups" of bands. The "groups" of bands arise primarily from vibronic transitions (vibrational-electronic).

The ground state term of an f^1 system is a $^2F_{5/2}$ and is split into a Kramers doublet (Γ_7 ground term) and a quartet (Γ_8). (Kramer's theorum states that in the absence of an external magnetic field, the spin degeneracy of a system having an *odd* number of electrons must always remain *even* though the low symmetry of the surroundings lifts all other degeneracies). The excited state term $^2F_{7/2}$ is split, under the octahedral perturbation, into two doublets (Γ_6 and Γ_7') and a quartet(Γ_8'). The assignments of the four-predicted transitions are labelled (in increasing energy) in the following manner, $\Gamma_8 \leftarrow \Gamma_7$, $\Gamma_7' \leftarrow \Gamma_7$, $\Gamma_8' \leftarrow \Gamma_7$, and $\Gamma_6 \leftarrow \Gamma_7$ (See Figure 3).

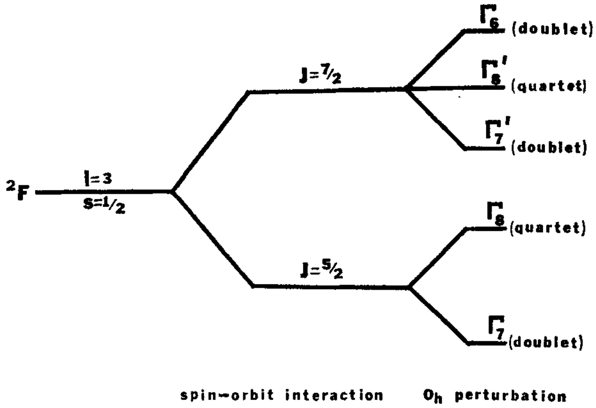
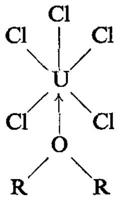


FIGURE 3 Schematic electronic energy level splittings for a $5f^1$ system.

The near-infrared spectral bands, with their assignments, for the dimethyl ether, diethyl ether and dioxane complexes are listed in Table IV. For comparison, data for the octahedral hexachlorouranate(V) ion (from $RbUCl_6$) is included. For the ether compounds, the absorbing species in solution is almost surely a six-coordinate one, with the sixth position of UCl_5 occupied by an ether oxygen, as shown below. (Solid state IR data also indicate coordination via oxygen.)



The most obvious absorption band in the near-ir spectra U(V) ions is the cluster of very sharp, narrow bands centered around 6800 cm^{-1} and assigned to the $\Gamma_7' \leftarrow \Gamma_7$ transition. The central spike, underlined in Table IV is assigned to the pure electronic transition. The side bands result from vibronic interactions. (As indicated earlier, a more detailed interpretation will be forthcoming in a later paper, including vibrational assignments from the vibronic spectra). Because of the very characteristic shape and appearance of the $\Gamma_7' \leftarrow \Gamma_7$ cluster, it alone may be used as an indication of the presence or absence of U(V) ions, including U(V) species such as UO_2^+.

Theoretical considerations indicate that the quartet level, Γ_8', should split into two Kramer's doublets upon distortion of pure octahedral symmetry. Two bands in the spectra of the ether complexes of approximately the same intensity and shape occur around 10,000 cm^{-1}. The difference in energy between these two bands is found to be 535 cm^{-1} for $RbUCl_6$ in thionyl chloride which compares

TABLE IV

Visible and Near-IR Bands for Some Ether Complexes of UCl_5, in cm^{-1}

$UCl_5 \cdot (CH_3)_2O$ in CH_3CN	$UCl_5 \cdot (C_2H_5)_2O$ in CH_3CN	$UCl_5 \cdot (C_4H_8O_2)$ in CH_3CN	$RbUCl_6$ in $SOCl_2$	Assignment
4255	4219	4278	3800	$\Gamma_8 \leftarrow \Gamma_7$
			6485	
6686	6728	6718	6680	
6712	6752	6752	6702	
6799	6807	6805	6794	$\Gamma_7' \leftarrow \Gamma_7$
6889	6896	6889	6890	
6917	6924	6923	6920	
			7110	
9756	9756	9756	9905	$\Gamma_8' \leftarrow \Gamma_7$
10675	10667	10587	10440	
11486	11594	11461	11520	$\Gamma_6 \leftarrow \Gamma_7$
11624		11621	11805	

with 919 and 911 cm^{-1} for the dimethyl and diethyl ether complexes in CN_3CN, respectively. Now, if the magnitude of the splitting does indeed reflect the degree of octahedral distortion, as it appears, the following sequence for various U(V) compounds may be recognized: UCl_6^- in various solvents, 540 ± 20 cm^{-1} [16]; UCl_5 in CCl_4, 720 cm^{-1} [16,26,27]; $UCl_5 \cdot$dioxane in CH_3CN, 831 cm^{-1}; $UCl_5 \cdot SOCl_2$ in CCl_4, 880 cm^{-1} [26], $UCl_5 \cdot (C_2H_5)_2O$ in CH_3CN, 911 cm^{-1}; $UCl_5 \cdot (CH_3)_2O$ in CH_3CN, 919 cm^{-1}; and $UCl_5 \cdot SOCl_2$ in $SOCl_2$[28], 1035 cm^{-1}. The larger splitting for all the above compounds compared to the UCl_6^- ion must almost certainly be a result of greater distortion and hence lower symmetry around the central metal ion.

Conductance and molecular weight values (Table II) indicate that the complexes are non-ionic and monomeric in acetonitrile and naphthalene. Initial molar conductance measurements yield values between 7 and 15A. Upon exposure to atmospheric moisture, the conductance values increase dramatically (up to 300Λ). As expected then, decomposition results in the formation of ionic products. (The near-infrared electronic spectra of such solutions is heavily contaminated with U(IV) species).

Finally the magnetic moments of the new ether compounds fall in the range of 1.4 to 2.2 Bohr Magnetons, indicative of the single unpaired 5f electron in U(V). Room temperature measurements only were made.

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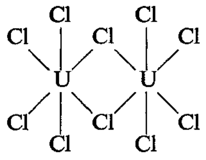
    In the dimer, two chlorine bridges allow the uranium to form a stable octahedral arrangement as pictured below.



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