diethyl ether and subsequent cooling at −10° yielded off-white crystals of $[Pt(CNC_2H_5)\{C(NHC_2H_5)(OC_2H_5)\}\{P(CH_3)_2C_6H_5\}_2](PF_6)_2$ (0.087 g).

(k) Preparation of $[Pt(CNC_2H_5)\{C(NHC_2H_5)(SCH_2C_6H_5)\}\{P(CH_3)_2C_6H_5\}_2](PF_6)_2$.—The above thioalkoxy(amino)carbene complex was prepared by method (i) using 2 ml of the α-toluenethiol. All operations were performed in a fume hood. Yield of the carbene was 40% after purification.

Acknowledgments.—Financial support of this project by the National Research Council of Canada is gratefully appreciated and the award of an NRC scholarship to L. E. M. is acknowledged. We wish to thank Dr. Gillespie at McMaster University, Hamilton, Ontario, Canada, for the use of the Raman spectrometer and Mrs. B. Spiers for obtaining the spectra. We also wish to thank Dr. M. H. Chisholm for many very helpful discussions.

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New Theoretical and Spectral Studies of Uranium(V) Compounds

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The theory of $5f^1$ systems has been extended from O_h symmetry species, such as UX_6^-, to "tetragonally" distorted, more recently prepared species, UOX_5^{2-} ($X^- = F^-, Cl^-, Br^-$). The semiempirical calculation was carried out specifically for $UOCl_5^{2-}$, by beginning with the $5f^1$ energy levels of U^{5+} (in UCl_6^-) split by the O_h crystal field and by the spin–orbit coupling and perturbed by the effects of the lower symmetry field. The results (using the O_h notation) are that (1) the $\Gamma_7 \rightarrow \Gamma_7'$ transition is left nearly unaltered, (2) the Γ_8 and Γ_8' quadruplet levels are significantly split, (3) the Γ_8 level leads to a very low-lying electronic band, (4) the Γ_6 energy is greatly increased, and (5) the average g value is left relatively unchanged. A careful study of the spectrum of $UOCl_5^{2-}$ in the 300–25,000-cm^{-1} range and of the esr spectrum has demonstrated the accuracy of these predictions. We feel there is now an understanding of the electronic and esr spectra of UOX_5^{2-} and other U(V) compounds whose structures are less certain. New complexes of the UO^{3+} entity are reported.

Introduction

There have been relatively few spectral studies for compounds of uranium(V),[1–4] primarily because of the unavailability of compounds and the great instability of most of those which are known. Nevertheless, the electronic simplicity of this chemical system, [Rn]$5f^1$, presents some unusual opportunities for obtaining a deeper understanding of internal 5f electronic transitions generally and specifically the case of *intermediate* ligand fields not perturbed by interelectron repulsion. With the recently published work of Ryan[3] and with our own recent experimental studies, we now have electronic spectral data on the octahedral species, UF_6^-, UCl_6^-, and UBr_6^-, as well as on the series of lower symmetry new monooxo species, UOF_5^{2-}, $UOCl_5^{2-}$, and $UOBr_5^{2-}$. It therefore seemed appropriate to reexamine the theory of the $5f^1$ system in O_h and to then extend this to lower symmetry species. These new theoretical results are reported in this paper. The new results have also made it possible to rationalize the general features of the spectra of other uranium(V) solid compounds and solution species whose structures are unknown. In addition, we report a new route to $UOCl_5^{2-}$, its esr spectrum, and the first preparations of complexes of monooxouranium(V), UO^{3+}, containing ligands other than just halide ions.

Experimental Section

A. Preparation of Compounds. 1. $UCl_5 \cdot TCAC$ (TCAC = Trichloroacryloyl Chloride, $Cl_2C{=}CClCOCl$).—This was prepared as previously described.[2] Since it, as well as most compounds of uranium(V), is extremely sensitive to both O_2 and H_2O, most preparative and handling work was carried out in a steel drybox with a nitrogen atmosphere rigorously free of oxygen and moisture.

2. $[(C_2H_5)_4N_2]UOCl_5$, Tetraethylammonium Oxopentachlorouranate(V).—Undried tetraethylammonium chloride was dissolved to approximate saturation in nitromethane. The solution was then diluted 10-fold with undried acetone, filtered, and then poured into a flask containing solid (red-orange) $UCl_5 \cdot TCAC$ (about 50 ml of solution per gram of solid). The blue compound which formed immediately was filtered, washed with dried (using anhydrous $CaSO_4$) acetone, and then dried in a stream of dry nitrogen. It proved in every way to be the same compound prepared by Ryan,[3] who used $(C_2H_5)_4NUCl_6$ as starting material. *Anal.* Calcd for $C_{16}H_{40}N_2UOCl_5$: C, 27.78; H, 5.83; N, 4.05. Found: C, 27.61; H, 5.93; N, 4.06.

3. $[(C_2H_5)_4N]_2UOCl_5 \cdot C_8H_6N_2$, Tetraethylammonium Oxopentachlorouranate(V)–Phthalazine Adduct.[5]—Undried tetraethylammonium chloride was dissolved to approximate saturation in spectroquality nitromethane, diluted 10-fold with undried reagent grade acetone, and filtered. The reagent grade phthalazine (recrystallized from ethyl ether and vacuum sublimed) was dissolved in this solution and the resulting solution was added to a flask containing solid $UCl_5 \cdot TCAC$. (A slight excess over 1:1 mole ratio of the phthalazine was used.) The immediate reaction produced a bright green solid, which was filtered, washed with dry acetone, and dried in a stream of dry nitrogen. The electronic spectrum of the product showed that it contained no more than 1–3% U(IV) and U(VI) species. It was characterized by dta, tga, electronic spectra, and ir spectra. *Anal.* Calcd for $C_{16}H_{40}N_2UOCl_5 \cdot C_8H_6N_2$: C, 35.07; H, 5.64; N, 6.82. Found: C, 33.98; H, 5.61; N, 6.68.

4. $[(C_2H_5)_4N]_2UOCl_5 \cdot 2C_{12}H_8N_2$, Tetraethylammonium Oxopentachlorouranate(V)–Bis(1,10-phenanthroline) Adduct.[5]—Undried $(C_2H_5)_4NCl$ was dissolved to approximate saturation in spectroquality nitromethane, then diluted 10-fold with undried reagent grade acetone, and filtered. To 50 ml of this solution was added 0.831 g (4.61 mmol) of *o*-phenanthroline as purchased from Aldrich Chemical Co. The resulting solution was then

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(1) J. Selbin and J. D. Ortego, *Chem. Rev.*, **69**, 657 (1969).

(2) J. Selbin, J. D. Ortego, and G. Gritzner, *Inorg. Chem.*, **7**, 976 (1968).

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

(4) J. L. Ryan, *Int. Rev. Sci.*, in press.

(5) We cannot name our compound more precisely yet since we do not know for sure, but only surmise, that the organic ligands are bonded directly to the uranium in the UO^{3+} replacing chlorides from the first coordination sphere.

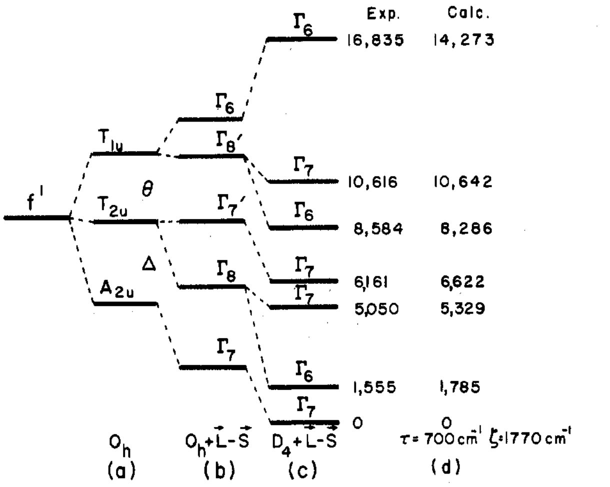

Figure 1.—f^1-orbital energy levels pertubed by (a) the O_h field (where the Δ and θ values are for UCl_6^- assuming $\zeta = 1770$ cm^{-1}), (b) the O_h field plus spin–orbit coupling (where the separations are for UCl_6^-), (c) the D_4 field plus spin–orbit coupling (where the experimental separations are for $UOCl_5^{2-}$), and (d) the calculated energies of the several levels assuming $\tau = 700$ cm^{-1} and $\zeta = 1770$ cm^{-1}.

added to a flask containing 1.251 g (2.06 mmol) of $UCl_5 \cdot TCAC$. The immediate reaction produced a fluffy, irridescent blue precipitate, which was filtered, washed twice with reagent grade acetone (which had been dried over anhydrous $CaSO_4$), and dried *in vacuo*. The compound was characterized by visible–near-ir, ir, and esr spectroscopy, and by dta, tga, and magnetic susceptibility. *Anal.* Calcd for $C_{16}H_{40}N_2UOCl_5 \cdot 2C_{12}H_8N_2$: C, 45.66; H, 5.36; N, 7.99. Found: C, 44.34; H, 5.34; N, 7.81.

B. Physical Measurements.—Infrared spectra were run on both Beckman IR-10 and IR-7 instruments. Samples were mulled in either Nujol or hexachlorobutadiene, and they were also run in KBr pellets. Electronic spectra were obtained, using a Cary 14 instrument, both at ambient temperature and at 77°K with the samples mulled in Nujol and smeared onto filter paper. Differential thermal analysis and thermogravimetric analysis were also used for compound characterization. Esr spectra were obtained for pure solids with a JEOLCO esr spectrometer, Model JES-3BS-X, using 100-kc modulation. The field was measured with an nmr precision gaussmeter. Magnetic susceptibilities were measured using the Gouy technique on a "homemade" balance calibrated with $HgCo(CNS)_4$.

Theory, Results, and Discussion

Although he obtained room-temperature spectra in the 4–25-kK region for solid UOX_5^{2-} ($X^- = F^-, Cl^-, Br^-$) compounds, Ryan[3] was understandably reluctant to attempt to assign the observed bands. For although the observed spectra and the 5f^1 theory for the O_h species UX_6^- ($X^- = F^-, Cl^-, Br^-$)[6,7] are now[1-8] in satisfactory agreement, there was no theoretical model available for the lower symmetry UOX_5^{2-} species. We have therefore introduced the necessary "tetragonal" splittings in a calculation carried out specifically for $UOCl_5^{2-}$, so that we can now understand both the more complete observed spectrum, which we have run at 77°K (Figure 3), and the *trends* in the additional splittings introduced by the symmetry reduction.

Theory.—For a starting point in the treatment of hexacoordinated U^{5+} ions we observe that the spread of the f–f transitions is approximately 11,000 cm^{-1} and that the spin–orbit splitting parameter, ζ, is approximately 2000 cm^{-1} (and hence smaller than the crystal field effects).[1,2] Then for lower than O_h field species it is therefore reasonable to plot an energy diagram which starts from the 5f^1 energy levels split by the octahedral "crystal field" and by "spin–orbit coupling" and perturbed by the effects of the lower symmetry field.

Using the nomenclature (Δ and θ) of Reisfeld and Crosby[8] (see Figure 1a) and the irreducible representations of the seven f orbitals in O_h symmetry, a_{2u} (nonbonding), t_{2u} (π antibonding), and t_{1u} (σ and π antibonding) (Figure 1a), the appropriate secular determinants after simultaneous diagonalization of both the crystal field and the spin–orbit interactions are (see Figure 1b)

$$\Gamma_8 \begin{vmatrix} \Delta + \frac{1}{4}\zeta - W_8 & \frac{3\sqrt{5}}{4}\zeta \\ \frac{3\sqrt{5}}{4}\zeta & \Delta + \theta - \frac{3}{4}\zeta - W_8 \end{vmatrix} = 0 \quad (1)$$

$$\Gamma_7 \begin{vmatrix} -W_7 & \sqrt{3}\zeta \\ \sqrt{3}\zeta & \Delta - \frac{1}{2}\zeta - W_7 \end{vmatrix} = 0 \quad (2)$$

$$\Gamma_6 \begin{vmatrix} \frac{3}{2}\zeta + \Delta + \theta - W_6 \end{vmatrix} = 0 \quad (3)$$

Now from (2) we see that the $\Gamma_7 \rightarrow \Gamma_7'$ transition energy depends only upon ζ and Δ. Therefore we get from (2)

$$\Delta W(\Gamma_7 \longrightarrow \Gamma_7') = \sqrt{(\Delta - {}^1/_2\zeta)^2 + 12\zeta^2} \quad (4)$$

Setting the left side equal to 6790 cm^{-1} and ζ equal to 1770 cm^{-1}, we calculate Δ as 3810 cm^{-1} and $W(\Gamma_7) = -1940$ cm^{-1}, which as the ground state is the zero of energy of the manifold of spin–orbit split levels in O_h symmetry (Figure 1b). It should be noted, however, that Δ is actually quite poorly determined, since small variations in ζ lead to large variations in the estimated value of Δ (but not of θ; *vide infra*). This may be seen from the following values (given in kK units): ζ, 1.74, 1.77, 1.80, 1.85, 1.90, 1.95; Δ, 4.00, 3.81, 3.59, 3.17, 2.62, 1.66; θ, 3.08, 3.11, 3.18, 3.29, 3.49, 3.88.

Using the ζ value of 1770 cm^{-1} and its corresponding Δ value of 3810 cm^{-1} and solving eq 3, after putting in 11,520 cm^{-1} (from ref 2) for the $W(\Gamma_6)$, we obtain θ as 3110 cm^{-1}. Next we can solve eq 1 for the two Γ_8 levels and the transitions specifically for UCl_6^- are then calculated to be $\Delta W(\Gamma_7 \rightarrow \Gamma_8) = 3820$ cm^{-1} and $\Delta W(\Gamma_7 \rightarrow \Gamma_8') = 9910$ cm^{-1}. These are to be compared with the experimental values[2] of 3800 and 9910 cm^{-1}, respectively. Thus although there is actually quite a large variation of Δ with small variations in ζ, nevertheless the spectrum is adequately described.[9]

The true octahedral ground-state wave function is given as

$$\psi = a\psi(\Gamma_7) - b\psi(\Gamma_7'); \; a^2 + b^2 = 1 \quad (5)$$

and evaluating the g factor leads to

$$g = 2(a^2 + 4\sqrt{{}^1/_3}ab) \quad (6)$$

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(6) The UF_6^- octahedron is known to be slightly distorted in $CsUF_6$,[7] but the situation for UCl_6^- and UBr_6^- is unknown. However, we are tempted to believe that in the latter two cases the octahedron is much more nearly regular due to the much larger chloride and bromide ligands. The distortion in the fluoro complex might be caused by the repulsion of the fluoride ions (which have a filled shell and high charge density) by the lone 5f electron of U(V).

(7) A Rosenzweig and D. T. Cromer, *Acta Crystallogr.*, **23**, 865 (1967).

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

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

Introducing "tetragonal" splittings will introduce three additional terms into the Hamiltonian in addition to the "octahedral" terms

$$\mathcal{V} = \tau V_2{}^\circ + \gamma V_4{}^\circ + \delta V_6{}^\circ \qquad (7)$$

Here, τ, γ, and δ are parameters which depend upon the radial functions, and $V_2{}^\circ$, $V_4{}^\circ$ and $V_6{}^\circ$ transform like the spherical harmonics of order 2, 4, and 6, respectively.

Now with the amount of information we possess and remembering how poorly Δ and θ were determined, we cannot of course hope to evaluate τ, γ, and δ. We shall therefore only keep the term in $V_2{}^\circ$, thereby truncating the full "tetragonal" Hamiltonian. Hence we "lump" all of the tetragonal effects together into one parameter. This means again that our calculation can only be illustrative, and we should not make any claims as to exact numerical fits.

With the foregoing in mind, we take as a representative case the values $\zeta = 1770\ \text{cm}^{-1}$, $\Delta = 3810\ \text{cm}^{-1}$, and $\theta = 3110\ \text{cm}^{-1}$ and substitute into the tetragonal matrices given in eq 8 and 9. The results are plotted in Figure 2 for the values of $\tau = 0\text{–}1400\ \text{cm}^{-1}$. Examination of Figure 2 reveals with regard to the excited states of a "tetragonal" f^1 complex that (1) the $\Gamma_7 \rightarrow \Gamma_7'$ transition is nearly unaltered, (2) the Γ_8 and the Γ_8' levels are significantly split, (3) the Γ_6 energy is moved to much higher wave numbers, and (4) there should be a very low-lying electronic band. A fifth prediction is that the average g value should vary only very slightly as the symmetry is lowered. All of these predictions are fulfilled as described in the following section.

Γ_7 (tetragonal)

$$\begin{vmatrix} \Delta + \theta + 2\tau - \frac{3}{4}\zeta - W_7 & \frac{3\sqrt{5}\zeta}{4} - \sqrt{5}\tau & -\sqrt{10}\tau & 0 \\ \frac{3\sqrt{5}\zeta}{4} - \sqrt{5}\tau & \Delta + \frac{1}{4}\zeta - W_7 & 0 & 0 \\ \sqrt{10}\tau & 0 & \Delta - \frac{1}{2}\zeta - W_7 & \sqrt{3}\zeta \\ 0 & 0 & \sqrt{3}\zeta & -W_7 \end{vmatrix} = 0 \qquad (8)$$

Γ_6 (tetragonal)

$$\begin{vmatrix} \Delta + \theta - 2\tau - \frac{3}{4}\zeta - W_6 & \frac{3\sqrt{5}\zeta}{4} + \sqrt{5}\tau & 2\sqrt{2}\tau \\ \frac{3\sqrt{5}\zeta}{4} + \sqrt{5}\tau & \Delta + \frac{1}{4}\zeta - W_6 & \sqrt{10}\tau \\ 2\sqrt{2}\tau & \sqrt{10}\tau & \Delta + \theta + \frac{3}{2}\zeta - W_6 \end{vmatrix} = 0 \qquad (9)$$

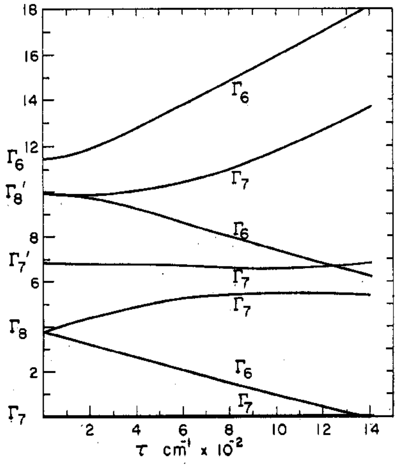

Figure 2.—The splitting of the 5f manifold of O_h energy levels with increasing lower symmetry (D_4) field.

Results and Discussion.—The bands observed in the 77°K spectrum of solid $(Et_4N)_2UOCl_5$ (in Nujol mull) are tabulated in Table I and the visible–near-ir spectrum (4000–17,000 Å) is shown in Figure 3. The strongest peaks are assigned as pure electronic (0–0) transitions, and the vibronic bands, most of which, expectedly, are found on the high-energy side of the 0–0 band, are listed as are their separations from the center peak. *Other* bands in the $UOCl_5{}^{2-}$ spectrum, not directly attributable to the organic cation, to small amounts of H_2O in the optics, or to trace amounts of U(IV), are found at 5060, 5030, 1555, 917, and 818 cm^{-1}. Of these, only the latter two are very strong and narrow and *appear to be* vibrational in origin. These will be considered first.

TABLE I

THE ELECTRONIC AND VIBRONIC BANDS FOUND FOR $(Et_4N)_2UOCl_5$

Assignment in D_4 symmetry[a]	0–0 transition	Vibronic bands Low	Vibronic bands High	Separation from 0–0 Low	Separation from 0–0 High
$\Gamma_7 \rightarrow \Gamma_6(\Gamma_8)$	1,555[b]				
$\Gamma_7 \rightarrow \Gamma_7(\Gamma_8)$	5,030, 5060				
$\Gamma_7 \rightarrow \Gamma_7(\Gamma_7')$	6,161 vs		6254 s		93
		5,981 w		180	
		5,935 w	6406 m	226	245
			(6496)		333
			6623 w		462
			(6711)		550
			6969		808
$\Gamma_7 \rightarrow \Gamma_6(\Gamma_8')$	8,584 vs	(8,475)	8696 s	109	112
			(8826)		242
			8873 m		289
		8,264 w	(8913)	320	329
		7,764 w	9398 m	820	814
$\Gamma_7 \rightarrow \Gamma_7(\Gamma_8')$	10,616 vs	(10,834)			218
		11,442 m			826
$\Gamma_7 \rightarrow \Gamma_6(\Gamma_6)$	16,835 vs				

[a] The symbol in parentheses represents the irreducible representation of the O_h molecular species $UCl_6{}^-$. [b] This band was taken from room-temperature ir spectra obtained on a Beckman IR-7; all others are taken from spectra obtained at 77°K on a Cary 14.

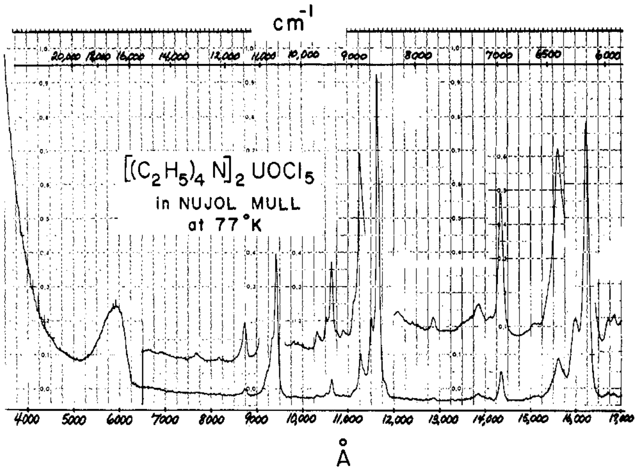

Figure 3.—The 77°K electronic spectrum of solid $[(C_2H_5)_4N]_2$-$UOCl_5$ in Nujol mull.

Ryan reported[3] these two bands at 913 and 813 cm^{-1} for his $(Et_4N)_2UOCl_5$, and he stated that they are *both* "apparently due to uranium–oxygen vibrations." (He also reported[3] analogous bands at 853 and 760 cm^{-1} for UOF_5^{2-} and at 919 and 817 cm^{-1} for $UOBr_5^{2-}$.) We cannot understand how *two* such intense and narrow bands can arise in this spectral region from the U=O entity. Indeed there is calculational and experimental evidence, most recently for $ReOX_5^{2-}$ (X = Cl, Br),[10] that only *one* frequency for MOX_5^{2-} species can be high enough to appear in the NaCl region, *viz.*, that arising from the ν_1 (A_1) vibration. We can now eliminate the possibility (admittedly of low probability) that one of these somehow arises from the organic cation, since we have succeeded in preparing the cesium salt, Cs_2UOCl_5 (*vide infra*), and it also exhibits both of the very strong and narrow bands. That one of these two bands might be due to the lowest energy electronic transition, $\Gamma_7 \rightarrow \Gamma_6(\Gamma_8)$ (see Figures 1 and 2), was first considered but the idea was rejected for several reasons, the main two being (a) the similarity in intensity and width (indeed overall appearance) of the two bands and (b) the nature of the *shift* of the bands with change of halogen (using Ryan's[3] data for the bromo and fluoro complexes). Thus we have no explanation at present for the appearance of *two* strong bands in this spectral region.[11] However we do feel that we can tentatively assign the higher of the two bands to the U=O stretching frequency. We cite the following support for this assignment. (1) The ir spectrum of U_2O_5[12] contains a band at 916 cm^{-1} which is assignable to the same entity. (2) There are vibronic bands in the electronic spectrum (Table I) (which clearly arise from the UO^{3+} species) which are separated from the 0–0 (pure electronic) band by ±820 cm^{-1}. It is therefore more likely that the 917-cm^{-1} ir band is due to the metal–oxygen stretch in the ground state than the 818-cm^{-1} band. (3) The metal–oxygen multiple-bond stretching frequencies for several analogous complexes are all much closer to the higher (917 cm^{-1}) value: $NbOCl_5^{2-}$, 930;[10a] $CrOCl_5^{2-}$, 925;[10b] $MoOCl_5^{2-}$, 950;[10a,b] $WOCl_5^{2-}$, 960;[10a] $ReOCl_5^{2-}$, 956;[10] perhaps most significantly we have the value for $NpOCl_5^{2-}$, which is 921 for the Cs^+ salt and 907 for Ph_4As^+ salt.[10d]

We turn next to consideration of the 1555-cm^{-1} band. This broad, relatively weak band (for an ir spectrum run in the NaCl region with a thin mull, much thinner than required for the measurement of electronic peaks in the visible–near-ir) was discovered in the spectrum of the cesium salt, Cs_2UOCl_5. We succeeded in preparing this salt by the following procedure. $CsUCl_6$ and undried Et_4NCl were mixed in undried CH_3NO_2. As in Ryan's[3] preparation of the $UOCl_5^{2-}$ species, the traces of H_2O were sufficient to carry out the hydrolysis of UCl_6^- to $UOCl_5^{2-}$ and the much lower solubility of the Cs^+ salt of this anion in nitromethane permitted separation of the Cs^+ salt from the soluble Et_4N^+ salt. Hower our product is not pure (hence not reported in the Experimental Section) but is contaminated with traces of the latter salt (<1%) as well as some U(IV) and possibly U(VI) products. Nevertheless the blue Cs_2UOCl_5 was pure enough to afford us the spectral information we could not get from the salts having organic cations, which interfere by virtue of their own spectral bands in certain key spectral regions. (Concentrated mulls of the $(Et_4N)_2UOCl_5$ also exhibit the 1555-cm^{-1} band.) We now tentatively assign the 1555-cm^{-1} band as the lowest energy, $\Gamma_7 \rightarrow \Gamma_6$ (from Γ_8 in O_h), transition. This is seen (Figure 1) to fit fairly well with the theoretical prediction for τ = 700 cm^{-1} and ζ = 1770 cm^{-1}, but it should be emphasized that the numerical fit is not as significant as the adherence to the general prediction (number 4 of the previous section) of the model presented above that there should be a very low-lying electronic band.

Next we consider the region of 5000 cm^{-1}. In the near-ir spectrum of $(Et_4N)_2UOCl_5$ there are, at 77°K, two prominent sharp peaks at 5060 and 5030 cm^{-1}. In the 77°K spectrum of Cs_2UOCl_5 there appears only one, somewhat broader band at 5070 cm^{-1}. In both cases these bands are *in addition to* two other bands clearly assignable to U(IV) impurity (the strongest U(IV) band below the ultraviolet is at ~5000 cm^{-1}), and they are found at 5120 and 4960 cm^{-1} in both oxo species. Our 77°K spectrum of the uranium(IV) complex $(Et_4N)_2UCl_6$ has only *two* (presumably vibronic) peaks and these are precisely at 5120 and 4960 cm^{-1}. We recognize the possibility that the new peaks in our $UOCl_5^{2-}$ species *might* be simply new U(IV) bands showing up for the first time. However we feel that our best evidence that the new peaks actually belong to the $UOCl_5^{2-}$ is that in our Et_4N^+ salt which is known to contain less U(IV) impurity than the Cs^+ salt, the 5120- and 4960-cm^{-1} peaks are much weaker but the new (5060- and 5030-cm^{-1}) peaks are just as intense. Thus we tentatively assign the band at ~5050 cm^{-1} to the second transition, $\Gamma_7 \rightarrow \Gamma_7(\Gamma_8)$ (Figure 1).

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(10) K. I. Petrov and V. V. Kravchenko, *Russ. J. Inorg. Chem.*, **15**, 1142 (1970). But see also: (a) A. Sabatini and I. Bertini, *Inorg. Chem.*, **5**, 204 (1966), who reported *one* M=O frequency for oxometal(V) complexes, $R_2[MOX_5]$, where R = Rb or Cs, M = Nb, Mo or W, and X = Cl or Br; (b) D. Brown, *J. Chem. Soc.*, 4944 (1964), who also reported only *one* M=O frequency for Cs_2MOCl_5, where M = Nb, Cr, Mo, or W; (c) D. F. Smith and G. M. Begun, *J. Chem. Phys.*, **43**, 2001 (1965), who reported an experimental (Raman and ir) and theoretical study of IOF_5, which has only *one* strong band (at 927 cm^{-1}) in the NaCl region; (d) K. W. Bagnall and J. B. Laidler, *J. Chem. Soc.*, 516 (1966), who reported *one* metal–oxygen frequency for $NpOCl_5^{2-}$.

(11) A suggestion by a referee that the single U=O stretch frequency might be split by site symmetry cannot be unequivocally rejected by us, but it is then strange that this same kind of mechanism does not operate in *any* of the analogous complexes of Nb(V), Cr(V), Mo(V), W(V), Re(V), and Np(V).[10]

(12) T. A. Il'inskaya, V. I. Kuzin, and Yu. M. Tolmachev, *Radiokhimiya*, **11** (4), 433 (1969); *Chem. Abstr.*, **71**, 130380 (1969).

The $\Gamma_7 \rightarrow \Gamma_7$ (from Γ_7' in O_h) 0–0 line is at 6161 cm^{-1}, only 633 cm^{-1} lower than the $\Gamma_7 \rightarrow \Gamma_7'$ transition in O_h, thus bearing out our prediction (number 1 in the previous section) that this transition is left relatively unaltered by the lower symmetry (Figure 2). It has associated with it vibronic components, one of which, namely, that 808 cm^{-1} from the 0–0 line, is undoubtedly due to the U=O stretch frequency. Ryan[3] has recorded the far-ir spectrum of $(Et_4N)_2UOCl_5$ and found bands at 120 and 253 cm^{-1}, with the latter more intense band having weak, narrow side bands at 296 and 197 cm^{-1}. These four bands are probably to be correlated with the low-energy vibronic bands found (Table I) at 93, 226 (245), and 180 cm^{-1}. The 15 normal vibrations of the MOX_5^{2-} group can be reduced to the following 11 symmetry types: 4 A_1 + 2 B_1 + B_2 + 4 E, and therefore no assignments except for the U=O stretch, $\nu_1(A_1)$, can be unambiguously made with the information presently at hand.

It is pertinent to point out just how relatively constant the transition assigned as $\Gamma_7 \rightarrow \Gamma_7'$ in O_h is in other U(V) compounds, since this is one of the important conclusions of the theoretical model presented here. In Table II we have collected all of the compound types whose spectra have been reported and the wave number of their respective $\Gamma_7 \rightarrow \Gamma_7'$ bands.[13–26] Although the ligand atoms encompass only halogen and oxygen, the crystal field spread among the listed compounds is certainly substantial. Nevertheless, the energy of the transition in question can be described by 6920 ± 400 cm^{-1} or, excluding only the UF_6^- values, 6850 ± 200 cm^{-1}. It is clearer now why the Δ and θ values are so poorly determined and the spin–orbit coupling parameter so critical in their determination.[27]

Turning next to the split components of $\Gamma_8'(O_h)$, we find these at 8584 and 10,616 cm^{-1}, a splitting of some 2030 cm^{-1}. We have already pointed out[1] that the splitting in the Γ_8' transition is 540 ± 20 cm^{-1} for UCl_6^- in various media (indicating the $5f^1$ system is not at a pure O_h site) and that for lower symmetry species, such as $UCl_5 \cdot TCAC$ and $[U(OC_2H_5)_5]_2$, it ranges from 720 to 1490 cm^{-1}. Indeed the splitting in UF_6^- of ~1050 cm^{-1} compared to the UCl_6^- and UBr_6^- splittings[3] of 480 and 370 cm^{-1}, respectively, reinforces our knowledge[7] of the lower-than-octahedral symmetry of UF_6^- and our suggestion[6] that the larger Cl^- and Br^- ions confer a more regular geometry upon the hexacoordinated U^{5+}. Thus the even greater splitting of the Γ_8' in $UOCl_5^{2-}$ demonstrates what we had formerly[1] suggested, that the magnitude of the splitting is roughly a measure of the magnitude of the geometrical distortion. It is interesting to note that the splitting of Γ_8' for UF_6^- (1050 cm^{-1}) is slightly larger than it is for UOF_5^{2-} (980 cm^{-1}). We hope to discuss this and analogous symmetry-related effects in a future paper.

TABLE II

THE $\Gamma_7 \rightarrow \Gamma_7'$ TRANSITION IN VARIOUS U(V) COMPOUNDS

Compound	Band wave number, cm^{-1}	Ref
$CsUF_6$[a]	7400[a]	3, 8
MUF_6 (M = H, Cs, Li, Na)	~7350	13
MUF_6 (M = K, Rb, NH_4)	7050	14
UF_6^- (in CH_3CN)	7386	3
$(NH_3OH)UF_6$	7050	15
$N_2H_6UF_7$	6990	15
Rb_2UF_7	~6770	16
Rb_3UF_8	~6770	16
K_3UF_8	6849	17
UCl_6^- (for several cations)	6800 ± 10	1, 2, 18
$UCl_5 \cdot TCAC$	6760	2
$UCl_5 \cdot Ph_3PO$	6880	19
$UCl_5 \cdot SOCl_2$	6760	2, 19
$UCl_5 \cdot AlCl_3(g)$	6605[a]	20
$U_2Cl_{10}(g)$	6658[a]	20
UBr_5	6710	21
UBr_6^-	6825 (6831)	3 (22)
$UBr_5 \cdot Ph_3PO$	6845	22
UO_2^+	6620	23, 24
$[U(OC_2H_5)_5]_2$	6934	9
$MM'U_2O_6F$ (M = Na, K, Rb; M' = Sr, Ba)		
(M = K, Tl; M' = Pb)	~7000	25
MU_2O_6 (M = Cd, Mg)	~7000	26
MUO_3 (M = K, Rb, Li, Na)	~7000	26
Li_7UO_6	~7000	26

[a] The authors[8] did not assign these bands to the 0–0 transition, but we as well as Ryan[3] feel certain now that they are indeed that transition.

Both electronic components of the split Γ_8' in the $UOCl_5^{2-}$ complex exhibit vibrational components (Table I), with the most prominent ones (820, 814, 826 cm^{-1}) surely arising from the U=O stretch.

Finally, we observe that the last $\Gamma_7 \rightarrow \Gamma_6$ transition has moved to a much higher energy, 16,835 cm^{-1}, in $UOCl_5^{2-}$, compared to its position of 11,540 cm^{-1} in UCl_6^-. This is in agreement with the theoretical prediction (number 3 of the previous section and Figure 2). We note also that this band has no associated vibronic bands and this is perhaps to have been expected due to the much greater broadness of this band which may serve to cover any vibronic components.

Notice (from eq 8) that the octahedral Γ_7 states in the lower symmetry are only coupled weakly to the other lower symmetry Γ_7 states *via* V_2°. Therefore the g factors for the distorted and the regular O_h complexes cannot differ very much. To a good approximation we can use the formula for g(octahedral), and with a splitting of Γ_8' equal to ~2000 cm^{-1} (τ = 600 cm^{-1}), we calculate $g = -1.04$. The sign of g is of course not revealed by the experiment, but we have measured the g values for both UCl_6^- and $UOCl_5^{2-}$ and they are in magnitude, respectively, 1.12 and 1.09, in quite excellent agreement with the calculated value. The esr spectrum of $(Et_4N)_2UOCl_5$ is shown in Figure 4.

In conclusion we mention that the two new compounds containing the UO^{3+} entity complexed by organic N donor ligands exhibit spectra entirely analogous

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(13) L. B. Asprey and R. A. Penneman, *Inorg. Chem.*, **3**, 727 (1964).

(14) G. D. Sturgeon, R. A. Penneman, F. H. Kruse, and L. B. Asprey, *ibid.*, **4**, 748 (1965).

(15) B. Frlec and H. H. Hyman, *ibid.*, **6**, 2233 (1967).

(16) R. A. Penneman, G. D. Sturgeon, and L. B. Asprey, *ibid.*, **3**, 126 (1964).

(17) J. Sherrill and J. Selbin, unpublished results.

(18) E. Stumpp, *Naturwissenschaften*, **56**, 370 (1969).

(19) K. W. Bagnall, D. Brown, and J. G. H. duPreez, *J. Chem. Soc.*, 2603 (1964).

(20) D. M. Gruen and R. L. McBeth, *Inorg. Chem.*, **8**, 2625 (1969).

(21) F. Lux, G. Wirth, and K. W. Bagnall, *Chem. Ber.*, **103**, 2807 (1970).

(22) D. Brown, J. Hill, and C. E. F. Rickard, *J. Chem. Soc. A*, 476 (1970).

(23) G. Gritzner and J. Selbin, *J. Inorg. Nucl. Chem.*, **30**, 1799 (1968).

(24) D. Cohen, *ibid.*, **32**, 3525 (1970).

(25) S. Kemmler-Sack, *Z. Anorg. Allg. Chem.*, **363**, 282 (1968).

(26) S. Kemmler-Sack, *ibid.*, **363**, 295 (1968).

(27) C. J. Ballhausen, *Theoret. Chim. Acta*, in press.

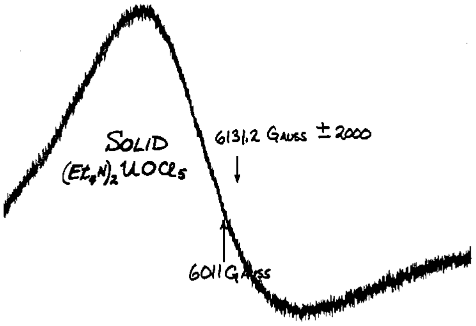

Figure 4.—The esr spectrum of pure solid $[(C_2H_5)_4N]_2UOCl_5$ at ambient temperature.

to electronic spectra of the $UOCl_5^{2-}$ species, with all evidence that the organic molecules are indeed coordinated. The spectra, to be more fully explored in a future paper which will deal with other U(V) complexes now in preparation and study, support all of the deductions made in this paper regarding the $UOCl_5^{2-}$ spectrum. The esr spectra of the new compounds are more complicated and correspondingly more interesting and these also will be discussed at a later time.

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CONTRIBUTION FROM THE LABORATORIO DI CHIMICA E TECNOLOGIA DEI RADIOELEMENTI DEL CONSIGLIO NAZIONALE DELLE RICERCHE, PADUA, ITALY, AND ISTITUTO DI CHIMICA GENERALE, UNIVERSITÀ DI CATANIA, CATANIA, ITALY

Soluble Intermediates in the Hydrolysis of Neptunium(VI) and Comparison with Other Actinides(VI)

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The soluble hydroxo complexes of the neptunyl(VI) ion have been studied in aqueous solution with 1 *M* (Na)ClO$_4$ at 25° by emf measurements of $[H^+]$. Trial values of the equilibrium constants were estimated by graphical procedures and refined by a least-squares program. The main species produced and their refined hydrolysis constants are as follows: NpO_2OH^+, $\log {}^*\beta_{11} = -5.17 \pm 0.03$; $(NpO_2)_2(OH)_2^{2+}$, $\log {}^*\beta_{22} = -6.68 \pm 0.02$; $(NpO_2)_3(OH)_5^+$, $\log {}^*\beta_{53} = -18.25 \pm 0.02$. Comparison of these results with some available data on the hydrolysis of uranyl(VI) and plutonyl(VI) indicates a close analogy in hydrolysis schemes for the three ions. The trend in acidity with increasing atomic number is briefly discussed.

Introduction

The four actinide elements uranium, neptunium, plutonium, and americium in their 6+ oxidation states exist in acid solution as hydrated species of the type MO_2^{2+} [1] and these species constitute a series of ions which are interesting for comparative studies.

As far as the hydrolytic behavior in aqueous solutions of these oxy cations is concerned the most detailed studies available relate to the uranyl(VI) ion.[2,3] From these studies it is now well known that by increasing the pH of an acidic U^{VI} solution soluble hydroxo species are formed, which are predominantly polynuclear in nature, and finally, on addition of sufficient base, highly insoluble products are obtained. In particular, by means of accurate experimental methods and adequate treatments of the data, it has been possible more recently to determine the stoichiometry and the formation constants of the soluble hydroxo complexes present in important amounts in U^{VI} solutions with various ionic media.[4-11]

Data regarding the hydrolytic reactions of Pu^{VI} are rather scant in the literature. Until 1955 there were some studies of Kraus and his collaborators carried out by acid-base titrations and high-speed centrifugations (see references in ref 3). From those works it was possible to acquire some fundamental information on the hydrolytic behavior of plutonyl(VI), but the polynuclear species were not identified and their equilibrium constants were not obtained. Some data on this subject were subsequently published by Russian workers,[12,13] but they differ considerably from those reported by Kraus. More recently, in our laboratory the hydrolytic reactions of Pu^{VI} were reexamined experimentally in 1 *M* perchlorate medium at 25° and the soluble hydroxo complexes present in important amounts in the range $0 \leqslant \bar{n} \leqslant 1$ ($\bar{n}$ is the average number of OH^- bound per PuO_2^{2+}) were determined together with their equilibrium constants.[14]

There is essentially no published information regarding the hydrolytic reactions of Am^{VI}.

As for the hydrolysis of Np^{VI}, the only data available at the present time are those reported by Kraus and Nelson.[3,15] They refer to acid-base titrations which

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(1) J. J. Katz and G. T. Seaborg, "The Chemistry of Actinide Elements," Methuen, London, 1957.

(2) L. G. Sillén and A. E. Martell, *Chem. Soc., Spec. Publ.*, **No. 7** (1964).

(3) K. A. Kraus, *Proc. Int. Conf. Peaceful Uses At. Energy*, **7**, 245 (1956).

(4) S. Ahrland, S. Hietanen, and L. G. Sillén, *Acta Chem. Scand.*, **8**, 1907 (1954).

(5) R. M. Rush, J. S. Johnson, and K. A. Kraus, *Inorg. Chem.*, **1**, 378 (1962).

(6) R. M. Rush, J. S. Johnson, and K. A. Kraus, U. S. Atomic Energy Commission, Report ORNL-3278, 1963.

(7) C. F. Baes, Jr., and N. J. Meyer, *Inorg. Chem.*, **1**, 780 (1962).

(8) R. M. Rush and J. S. Johnson, *J. Phys. Chem.*, **67**, 821 (1963).

(9) H. S. Dunsmore, S. Hietanen, and L. G. Sillén, *Acta Chem. Scand.*, **17**, 2644 (1963).

(10) H. S. Dunsmore and L. G. Sillén, *ibid.*, **17**, 2657 (1963).

(11) S. Hietanen, B. R. L. Row, and L. G. Sillén, *ibid.*, **17**, 2735 (1963).

(12) Y. Ye. Krevinskaia, V. D. Nikolski, B. G. Pozharskii, and Ye. Ye. Zastenker, *Radiokhimiya*, **1**, 238 (1960).

(13) A. I. Moskvin and V. P. Zaitseva, *ibid.*, **4**, 73 (1962).

(14) A. Cassol, L. Magon, R. Portanova, and E. Tondello, *Radiochim. Acta*, in press.

(15) K. A. Kraus and F. Nelson, U. S. Atomic Energy Commission Document AECD-1864, 1948.