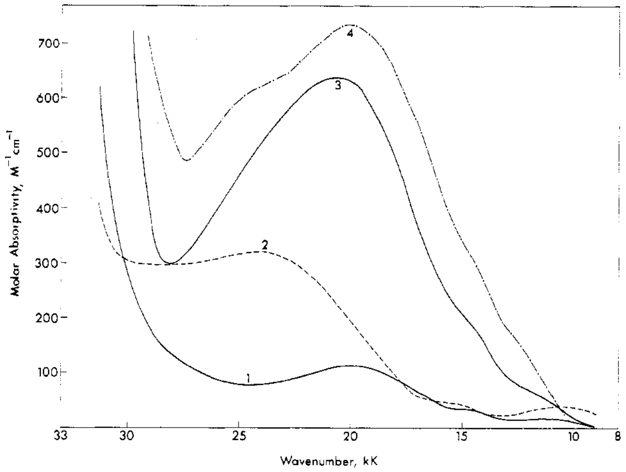

Figure 5. Absorption spectra of tungstovanadate(IV) complexes: 1, $VW_5O_{19}^{4-}$, pH 5; 2, $H_nV_2W_4O_{19}^{-6+n}$, pH 8; 3, $H_2W_{11}VO_{40}^{8-}$, pH 5; 4, $PW_{11}VO_{40}^{5-}$, pH 2.[12]

six metal atoms in the Lindqvist–Aronsson structure occupy sites of C_{4v} symmetry with mutually orthogonal C_4 axes. If it is assumed that the observed charge transfer is from $d_{xy}(V)$ to $d_{xy}(W)$, then the orthogonality of these orbitals might account for the low intensity of this transition compared with the corresponding one in the Keggin anions.

The charge-transfer band in the 2:4 complex occurs at a higher energy than in the 1:5 complex. Again, this behavior parallels that of the heteropolytungstate blues in which addition of a second electron, *e.g.*, $PW_{11}W^VO_{40}^{4-}$ to $PW_{10}W^V{}_2O_{40}^{5-}$, causes a hypsochromic shift of the visible spectral bands.

The tungstovanadate(IV) complexes are therefore electronic analogs of heteropoly blues, differing only in the extent to which the "optical" electron is trapped on a specific metal atom. The present studies indicate that poly anions with the Lindqvist-Aronsson structure should be reducible to heteropoly blue species, and we have noted elsewhere[29] a rationalization for this behavior.

Registry No. $(CH_3NH_3)_2Na_2(VW_5O_{19})$, 37340-33-3; $((CH_3)_2NH_2)Na_2(VW_5O_{19})$, 37340-35-5; $((CH_3)_4N)_2Na_4(SO_4)(VW_5O_{19})$, 37341-43-8; $(C(NH_2)_3)_4(VW_5O_{19})$, 37341-42-7; $(C_2H_4(NH_3)_2)_2(VW_5O_{19})$, 37340-36-6; $(C(NH_2)_3)_5H(V_2W_4O_{19})$, 37340-34-4; $K_8(H_2W_{11}VO_{40})$, 37340-41-3; $(NH_4)_{7.5}H_{0.5}(H_2W_{11}VO_{40})$, 37340-40-2; $((CH_3)_4N)_7H(H_2W_{11}VO_{40})$, 37340-39-9; $((CH_3)_4N)_5H_3(H_2W_{11}VO_{40})$, 37340-38-8.

Acknowledgments. We thank Dr. George Candela, National Bureau of Standards, for the susceptibility measurements, and the Air Force Office of Scientific Research for support of this research through Grant No. AF70-1833. Purchase of the esr spectrometer was made possible through NSF Equipment Grant GP-29184 and the Georgetown University Research Committee.

(29) M. T. Pope, *Inorg. Chem.*, **11**, 1973 (1972).

Contribution from Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87544, and Department of Chemistry, University of Texas at El Paso, El Paso, Texas 79968

Electron Paramagnetic Resonance and Optical Studies of Pentavalent Uranium[1]

W. BURTON LEWIS,*[2a] HARRY G. HECHT,[2a] and MICHAEL P. EASTMAN[2b]

Received September 6, 1972

Epr and optical spectra are reported for uranium-doped $LiNbO_3$, $LiTaO_3$, and $BiNbO_4$. The U^{5+} ion gives rise to an epr signal at $|g| \sim 0.7$ and appears to be a site of almost regular octahedral symmetry in every case. An analysis of the data yields crystal field splittings and orbital reduction factors similar to those involved in the previously studied octahedral fluorides. Attempts to prepare magnetically dilute U^{5+} in oxides with the perovskite structure were unsuccessful. An epr absorption was found at approximately $|g| = 1.2$ in Na_3UF_8 at 7°K which is attributed to U^{5+} in eightfold cubic coordination.

Introduction

The actinide elements have been studied by magnetic resonance techniques to a lesser extent than the other metals, and consequently less is known about the nature of their bonding. Several factors have deterred a thorough study of the bonding in actinides. Experimentally one must frequently deal with highly radioactive materials whose chemistry is greatly complicated by the occurrence of multiple stable oxidation states. Theoretically the problem is encumbered by intermediate coupling, so that the usual perturbation-type calculations are of limited applicability. Also, for more than a single f electron, consideration must be given to electron–electron interactions.

Many of these difficulties can be minimized if one's attention is confined to pentavalent uranium compounds. The f^1 configuration is of comparative theoretical simplicity, and the radiation hazards are minor so that numerous preparative techniques can be readily attempted.

We have previously discussed the problem of covalency in actinide series compounds and have reported on the ^{17}O nmr studies of ^{17}O-enriched KUO_3, $BiUO_4$, and UO_2.[3] The purpose of this paper is to report the results of epr and optical studies of a number of compounds containing pentavalent uranium.

In the present work particular attention was given to com-

---

(1) Work done at the Los Alamos Scientific Laboratory, supported by the U. S. Atomic Energy Commission.

(2) (a) Los Alamos Scientific Laboratory; (b) University of Texas at El Paso; Los Alamos Scientific Laboratory Postdoctoral Fellow, 1968–1970, and Associated Western Universities Faculty Participant, summer 1971.

(3) M. P. Eastman, H. G. Hecht, and W. B. Lewis, *J. Chem. Phys.*, **54**, 4141 (1971).

Table I. A List of Uranium-Containing Oxides and Oxide Hosts Investigated

Perovskite		Rock salt	Niobite	Pyrochlore	Ilmenite	$LiSbO_3$	Fluorite	Stibiotantalite	Scheelite
$NaTaO_3$	Ba_2ScUO_6	Li_3UO_4	$CaNb_2O_6$	$Ca_2Nb_2O_7$	$LiNbO_3$	$LiSbO_3$	ThO_2	$BiNbO_4$	$LaNbO_4$
$NaNbO_3$	Pb_2YNbO_6	Li_3TaO_4	$MgNb_2O_6$	$Mg_2Nb_2O_7$	$LiTaO_3$		$BiUO_4$	$BiTaO_4$	
$NaUO_3$	Pb_2InNbO_6	Li_3NbO_4	$ZnNb_2O_6$	$Zn_2Nb_2O_7$	$Mg_4Nb_2O_9$			$BiSbO_4$	
$KTaO_3$	Pb_2BiNbO_6	Na_3UO_4							
$KNbO_3$	$LiUO_3$	Na_3NbO_4							
$PbCeO_3$	KUO_3								
Ba_2YTaO_6	$CdThO_3$								
Ba_2LaTaO_6	Ba_2CaWO_6								
Ba_2LaNbO_6									

pounds in which the paramagnetic uranium ion is in a highly symmetric crystal field. A symmetric crystal field leads to energy level splittings large enough so that the length of the longitudinal relaxation time T_1 permits observation of the resonance at experimentally accessible temperatures. The work of Rigny and coworkers[4,5] on highly symmetric uranium fluorides such as $CsUF_6$ has shown that resonances from U^{5+} can be detected in these compounds even at room temperature.

In contrast to these epr spectra of $5f^1$ ions in cubic crystal fields, the epr spectra of the same ion in strongly axial crystal environments is highly anisotropic and observable only in single crystals at 20°K or less. The only extensively investigated example of the latter type is the $NpO_2{}^{2+}$ ion.[6,7] From single crystals of $RbNpO_2(NO_3)_3$ diluted with $RbUO_2(NO_3)_3$ it is observed that $g_{\|} = 3.405$ and $g_{\perp} = 0.205$. It is particularly significant that all of the reported epr spectra can be classified into two groups, those with isotropic or weakly anisotropic g values ($g_{\|} \approx g_{\perp}$) and those with highly anisotropic g values ($g_{\|} >> g_{\perp}$). This feature of the epr spectra of $5f^1$ compounds offers a unique way of distinguishing between actinide ions with strong metal-oxygen multiple bonds and those with only normal single bonds. However, exceptions may occur. These are discussed in some detail in the Discussion section along with other aspects of the theory of g values of $5f^1$ ions in various crystal environments.

Experimental Section

Materials. Table I shows the various cubic oxides studied, arranged according to structural type. A number of pure uranium compounds were made (*e.g.*, Li_3UO_4, Na_3UO_4, $NaUO_3$, $LiUO_3$) to see if an epr resonance was observable in a magnetically concentrated sample, as is the case for the alkali metal hexafluorides. In other cases the sample consisted of the polycrystalline host materials listed in Table I with a 1–5% (mole per cent) uranium doping. In some cases a trivalent metal ion was added (for charge compensation) with pentavalent uranium to a tetravalent host (*e.g.*, $CdThO_3$ and ThO_2), and in one case γ-irradiation of U^{6+} in uranium-doped Ba_2CaWO_6 was attempted. In addition to the oxides listed in Table I the U^{5+}-containing fluoride, Na_3UF_8, was studied.

In general, the samples were prepared either by direct reaction of the solid components, usually *in vacuo*, or by fusing the components in a flux such as B_2O_3, KF, or Li_2SO_4, followed by leaching of the flux with water. Structures were checked by X-ray analysis. Details of the preparation of those compounds which were extensively studied are given below.

$LiNbO_3$. Powder samples of $LiNbO_3$ containing U^{5+} were initially prepared by heating a mixture of Li_2UO_4, $LiNbO_3$, and UO_2 for a day at 750° in a sealed, evacuated quartz tube. The proportions in the mixture were such that the final $LiNbO_3$ had a uranium content of from 1 to 5%.

Later a better method of preparing uranium-doped $LiNbO_3$ in the powder form was found which employed a molten salt medium. Here uranium-doped $LiNbO_3$ was prepared by thoroughly mixing Li_2CO_3, Nb_2O_5, and UO_3 in the proper proportions and adding the mixture slowly to molten Li_2SO_4. After cooling the melt, the Li_2SO_4 was easily leached out, leaving behind insoluble uranium-doped $LiNbO_3$. It was also shown that a LiCl flux can be used in place of Li_2SO_4. $LiNbO_3$ is somewhat soluble in the former but nearly insoluble in the sulfate flux.

The uranium-doped crystals of $LiNbO_3$ were prepared by slowly cooling a melt prepared from Li_2CO_3 and Nb_2O_5 with 1–5% of the Nb_2O_5 replaced by a mixture of UO_2 and UO_3. The atmosphere over the melt was about 200 mm of CO_2 and 200 mm of Ar to prevent reduction of the Nb^{5+} by U^{5+} or by evolution of oxygen from the melt. CO_2 appears to have the proper oxygen fugacity at 1250° to stabilize both U^{5+} and Nb^{5+} in $LiNbO_3$, since it makes very little difference whether the uranium is added as UO_2 or UO_3 in obtaining U^{5+} in the final crystals (as judged by the epr and optical spectra). The crystals were reddish in color and possessed one cleavage plane.

Some of the larger 1% crystals were ground down to thin plates to obtain optical absorption spectra by transmitted light. The 5% crystals were unfortunately not solid solutions; a black phase, perhaps U_3O_8, appeared to be present as occlusions in the $LiNbO_3$ crystals.

$LiTaO_3$. Powder samples of $LiTaO_3$ containing 1–10% uranium were prepared in a manner similar to that described for $LiNbO_3$. The best results (as determined by the strength of the epr signal) were obtained from samples prepared in LiCl melts.

$BiNbO_4$. The powder samples of uranium-doped $BiNbO_4$ were prepared by heating to 1000° the appropriate amounts of Bi_2O_3, Nb_2O_5, and UO_3 in a sealed quartz tube for about 1 day. Small single crystals of $BiNbO_4$ containing 1% uranium were grown by slowly cooling a melt prepared from $(BiO)_2CO_3 \cdot 0.5H_2O$, UO_2, UO_3, and Nb_2O_5. The atmosphere over the melt was similar to that used in the growth of $LiNbO_3$ crystals. The crystals were similar in color to those of $LiNbO_3$, or brownish red, but differed in possessing two directions of easy cleavage.

Na_3UF_8. Powder samples of Na_3UF_8 were prepared by the direct reaction of UF_5 with NaF. This method has been described in detail by Penneman, Sturgeon, and Asprey.[8]

Equipment. A Cary 14 spectrophotometer was used to determine the optical absorption spectra. Spectra at liquid nitrogen temperatures were taken with the aid of a Jencons Scientific Ltd. liquid nitrogen optical dewar. In general, fluorolube mulls were employed to obtain the optical spectra of powder samples. The absorption spectra of the 1% doped $LiNbO_3$ crystals were obtained from thin plates ground from large crystals formed in the manner described above.

The epr spectrometer used has been described previously.[9] An Air Products & Chemicals Model LT-3-110 liquid He Cryo-tip refrigerator attached to a Varian V-4533 rotating cavity provided sample temperatures which were estimated to be about 7°K.

Experimental Results

An extensive and systematic search was made for oxides of pentavalent and tetravalent cations having cubic or nearly cubic structures. Although there was no difficulty in finding pure cubic oxide compounds containing U, Nb, Ta, Th, Sb, etc., U^{5+} proved to be highly resistant to forming solid solutions with the other pentavalent or tetravalent oxide compounds. Approximately half of the oxides investigated had the perovskite structure (see Table I). We were unable to

---

[4] P. Rigny and P. Plurien, *J. Phys. Chem. Solids*, **28**, 2589 (1967).

[5] M. Dryford, P. Rigny, and P. Plurien, *Phys. Lett. A*, **27**, 620 (1968).

[6] B. Bleaney, P. M. Llewellyn, M. H. L. Pryce, and G. R. Hall, *Phil. Mag.*, **45**, 992 (1954).

[7] J. C. Eisenstein and M. H. L. Pryce, *Proc. Roy. Soc., Ser. A*, **229**, 20 (1955); **238**, 31 (1956); *J. Res. Nat. Bur. Stand., Sect. A*, **69**, 217 (1965).

[8] R. A. Penneman, G. D. Sturgeon, and L. B. Asprey, *Inorg. Chem.*, **3**, 126 (1964).

[9] W. B. Lewis, M. Alei, Jr., and L. O. Morgan, *J. Chem. Phys.*, **44**, 2409 (1966).

verify the presence of U^{5+} in any of these perovskite-type oxide preparations. It was found that in the cases of $KNbO_3$ and $KTaO_3$ a black cubic, semimetallic compound formed. This semimetallic compound was easily crystallized from the melt and was assumed to be related to the tungsten bronzes which are also cubic and which have a typical composition range of $Na_{0.4}WO_3$–$Na_{0.93}WO_3$.

Of all the compounds listed in Table I, only those with the ilmenite structure and $BiNbO_4$ with the stibiotantalite structure yielded epr and optical absorptions definitely attributable to U^{5+}. Resonances were observed in all three of the hosts with the ilmenite structure. However, the resonance from $Mg_4Nb_2O_9$ was not extensively studied and will not be described further. No epr signals were observed for the pure uranium oxides listed in Table I. This contrasts sharply with the case of symmetric octahedral uranium fluorides where resonances are easily observed at room temperature.[4,5] The probable reason for this is the rapid spin–spin relaxation times (of order 10^{+13} sec^{-1}) which have previously been observed in uranium oxides.[3]

Llewellyn[10] has attributed an absorption at $|g| = 1.25$ and $T = 20°K$ in UO_2, ThO_2 solid solution to U^{5+}. Preparations of solid solutions of $LaUO_4$ in ThO_2 were attempted in this work, but the only epr absorption which was observed appeared to be due to traces of Fe^{3+} and defect centers. The absorption due to Fe^{3+}, specifically a sharp peak at $g = 4.28$, was present only when $LaUO_4$ was added to the ThO_2 and the resulting mixture precipitated from Li_2WO_4 flux. When $LaUO_4$ was omitted from the preparations, the broad resonance with many sharp hyperfine lines superimposed on it remained. The latter resonance is believed to be due to a lattice defect center, possibly a trapped electron located at a site surrounded by multiple interstitial Li^+ ions. It is known that $YTaO_4$ forms bronze-type solid solutions in the presence of BaO,[11] particularly in the presence of melts whose overall compositions deviate slightly from the stoichiometric ABO_4 composition. The presence of this broad resonance in the $LaUO_4$, ThO_2 solid solutions made it impossible to search for U^{5+} epr absorption at low temperatures where one would expect to find it (see later discussion of Na_3UF_8).

The 1–5% uranium-doped $LiNbO_3$ powder samples produced an isotropic single line resonance at $|g| = 0.727$ which was 250 G wide. At liquid nitrogen temperatures there was little change in the uranium resonance other than an increased intensity which varied no more than linearly with temperature.

The powder samples of uranium-doped $LiTaO_3$ produced a broad asymmetric resonance extending over about 2000 G. A room temperature spectrum is shown in Figure 1. The shape of the resonance indicates an axial g tensor with $|g_{\parallel}| = 0.773$ and $|g_{\perp}| = 0.685$.

Single-crystal epr spectra of $LiNbO_3$ doped with 1% $LiUO_3$ were obtained at 7°K. The resonance is shown in Figure 2. The peak-to-peak line width was less than half that at room temperature, or about 120 G. In addition to the main peak we have observed three weak satellite peaks. Both the main peak and its satellites showed anisotropy, that of the satellites being considerably greater.

Epr studies of polycrystalline Na_3UF_8 yielded no observable resonance at room temperature or at liquid nitrogen temperatures. At 7°K a very broad and asymmetric resonance was obtained. The signal was centered about $|g| = 1.2$.

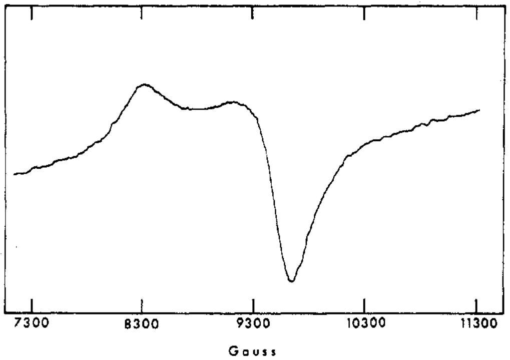

Figure 1. Epr spectrum of $LiTaO_3$ containing 5% U^{5+}. The spectrum was recorded at about 24°.

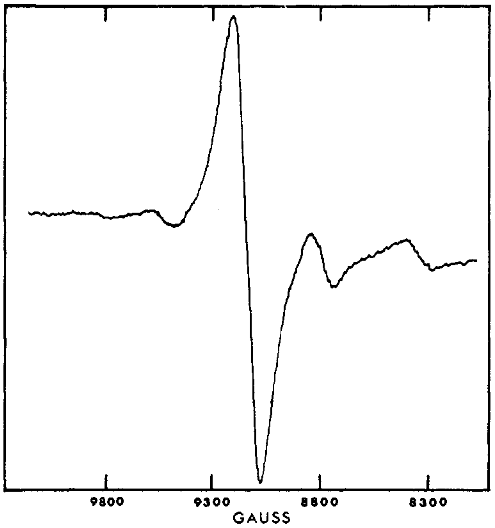

Figure 2. Epr spectrum of a $LiNbO_3$ single crystal containing 1% U^{5+}. The spectrum was recorded at 7°K.

A single crystal of $BiNbO_4$ containing 1% uranium did not yield a resonance at room temperature or at liquid nitrogen temperatures. At 7°K four resonances were observed in the region $|g| \sim 0.7$. These resonances were anisotropic and depended greatly on crystal orientation.

The room temperature near-infrared optical spectra of fluorolube mulls of uranium-doped $LiNbO_3$ and $BiNbO_4$ are shown in Figure 3. Similar spectra were obtained from mulls of uranium-doped $LiTaO_3$. However, in this case only very weak broadened transitions could be obtained in $LiTaO_3$ samples. No absorption could be observed in samples containing less than 10% uranium. The near-infrared spectra obtained from the fluorolube mulls at liquid nitrogen temperatures did not differ greatly from those obtained at room temperature.

Figure 4 shows the room temperature near-infrared crystalline spectrum of $LiNbO_3$ containing 1% uranium. The most striking difference between the crystalline and mull spectra is the appearance of a band at 15,000 Å in the crystalline spectrum. The near-infrared spectrum of Na_3UF_8 shows profound temperature effects which apparently reflect the appearance of a low-temperature distortion.[12,13]

Discussion of Experimental Results

In $LiNbO_3$, which has the ilmenite structure, there exists a slightly distorted hexagonal closest packing oxygen structure with one third of the octahedral sites occupied by Li^+,

---

(10) P. M. Llewellyn, Thesis, Oxford University, 1956.

(11) G. K. Layden and W. L. Darby, *Mater. Res. Bull.*, **1**, 235 (1966).

(12) E. Fukushima and H. G. Hecht, *J. Chem. Phys.*, **54**, 4341 (1971).

(13) H. G. Hecht, unpublished results.

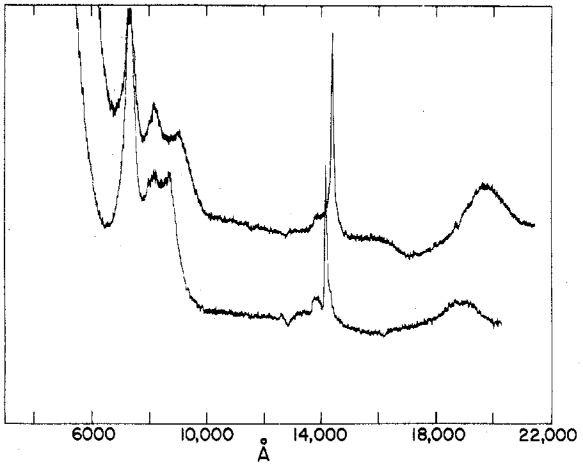

Figure 3. Near-infrared optical spectra of $BiNbO_4$ (upper curve) and $LiNbO_3$ (lower curve) mulls containing 5% uranium. Both spectra were recorded at about 24°.

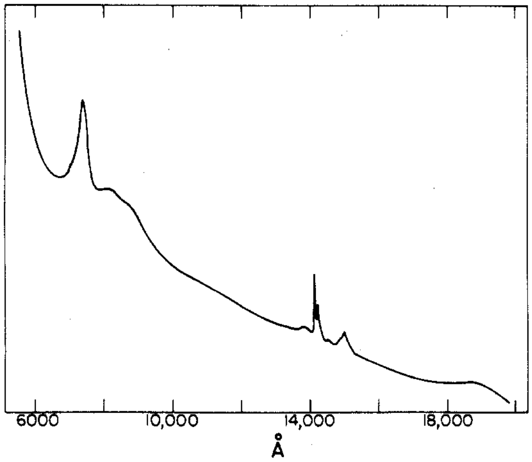

Figure 4. Near-infrared optical spectrum of a $LiNbO_3$ crystal containing 1% U^{5+}. The spectrum was recorded at about 24°.

one third by Nb^{5+}, and one third unoccupied.[14] It seems reasonable that the U^{5+} is substituted for Nb^{5+} and that the coordination is nearly octahedral, with perhaps a small trigonal distortion. However, the single-crystal epr spectra of U^{5+} in $LiNbO_3$ indicate that in this case the distortions from cubic symmetry are small. The anisotropic satellites in Figure 2 apparently arise from a site in the $LiNbO_3$ structure with relatively low abundance. It seems reasonable that these satellites are in some way associated with the ferroelectric domains which exist in $LiNbO_3$ crystals.

For a single f electron in an octahedral field the orbital energy levels, in order of increasing energy, have been shown to be[15,16]

$$\begin{aligned}\Gamma_2&:\omega_{\Gamma_2} = -12b_4 - 48b_6\\ \Gamma_5&:\omega_{\Gamma_5} = -2b_4 + 36b_6\\ \Gamma_4&:\omega_{\Gamma_4} = 6b_4 - 20b_6\end{aligned} \tag{1}$$

Here b_4 and b_6 describe the strength of the crystal field in terms of the crystal field parameters $A_4{}^0\langle r^4\rangle$ and $A_6{}^0\langle r^6\rangle$.

$$\begin{aligned}b_4 &= (8/33)A_4{}^0\langle r^4\rangle\\ b_6 &= -(80/429)A_6{}^0\langle r^6\rangle\end{aligned} \tag{2}$$

The direct products of the orbital states with spin Γ_6 lead to the following decomposition.

$$\begin{aligned}&\Gamma_2 \times \Gamma_6 \rightarrow \Gamma_7\\ &\Gamma_5 \times \Gamma_6 \rightarrow \Gamma_7 + \Gamma_8\\ &\Gamma_4 \times \Gamma_6 \rightarrow \Gamma_8 + \Gamma_6\end{aligned} \tag{3}$$

The ground-state Kramers doublet is a Γ_7 state and is coupled to the excited Γ_7 state, arising from the Γ_5 orbital state, by spin-orbit coupling. The resulting ground state is an admixture of the two Γ_7 levels. The relative admixture can be determined from the solution of the secular equation

$$\begin{vmatrix}\omega_{\Gamma_2} & \sqrt{3k\zeta}\\ \sqrt{3k\zeta} & \omega_{\Gamma_5} - {}^1/_2 k\zeta\end{vmatrix} = 0 \tag{4}$$

Here ζ is the free ion spin-orbit coupling constant and k is the orbital reduction factor for an electron in a Γ_5 orbital state.[16,17]

The secular determinants for the Γ_8 and Γ_6 states are respectively

$$\begin{vmatrix}\omega_{\Gamma_5} + {}^1/_4 k\zeta & {}^3/_4\sqrt{5kk'\zeta}\\ {}^3/_4\sqrt{5kk'\zeta} & \omega_{\Gamma_4} + {}^3/_4 k'\zeta\end{vmatrix} \tag{5}$$

$$\left|\, \omega_{\Gamma_4} + {}^3/_2 k'\zeta \,\right| \tag{6}$$

Here k' represents the orbital reduction factor for the Γ_4 orbital state.[14,15]

From the above the g value for the ground state is determined to be[5,14]

$$g = 2\cos^2\theta - 4\sqrt{k/3}\,\sin 2\theta - {}^2/_3(1-k)\sin^2\theta \tag{7}$$

where θ is the parameter describing the admixture of the Γ_7 levels in the ground state. From the work of Hutchison and Weinstock[18] on neptunium hexafluoride the g values for U^{5+} are presumed to be negative.

The determination of $A_4{}^0\langle r^4\rangle, A_6{}^0\langle r^6\rangle$, k, k', and ζ for the case of U^{5+} in $LiNbO_3$ requires the assignment of the optical transitions shown in Figures 3 and 4. From the analysis of the $CsUF_6$ absorption spectrum[19] it seems reasonable to assume that some of the spectral lines are due to vibronic transitions. However, the absence of well-defined fine structure precludes the possibility of making an analysis of the fundamental vibrational frequencies. In our approximate analysis of the experimental data for U^{5+} in $LiNbO_3$, all transitions were considered to be purely electronic. With this assumption the following assignments are made.

$$\begin{aligned}&\Gamma_7 \rightarrow \Gamma_8 \sim 5{,}300\ \text{cm}^{-1}\\ &\Gamma_7 \rightarrow \Gamma_{7'} \sim 7{,}050\ \text{cm}^{-1}\\ &\Gamma_7 \rightarrow \Gamma_6 \sim 13{,}500\ \text{cm}^{-1}\end{aligned}$$

The $\Gamma_7 \rightarrow \Gamma_{8'}$ transition is apparently split and is not assigned a value at this point. This splitting may arise from vibronic transitions to the Γ_8 level or from an axially distorted site. Selbin, *et al.*,[20] and Ballhausen[21] have pointed out that the $\Gamma_{8'}$ level is particularly strongly split by a distortion toward D_4 symmetry and that the effect of a small distortion will appear in the $\Gamma_7 \rightarrow \Gamma_{8'}$ transition before it does in the Γ_7 ground state g value. The line at 15,000 Å in the single-

---

(14) S. C. Abrahams, J. M. Reddy, and J. L. Bernstein, *J. Phys. Chem. Solids*, **27**, 997 (1966).

(15) B. R. Judd, "Operator Techniques in Atomic Spectroscopy," McGraw-Hill, New York, N. Y., 1963.

(16) H. G. Hecht, W. B. Lewis, and M. P. Eastman, *Advan. Chem. Phys.*, **21**, 351 (1971).

(17) J. C. Eisenstein and M. H. L. Pryce, *Proc. Roy. Soc., Ser. A*, **255**, 181 (1960).

(18) C. A. Hutchison, Jr., and B. Weinstock, *J. Chem. Phys.*, **32**, 56 (1960).

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

(20) J. Selbin, J. D. Ortego, and G. Gritzner, *Inorg. Chem.*, **7**, 976 (1968); J. Selbin, C. J. Ballhausen, and D. G. Durrett, *ibid.*, **11**, 510 (1972).

(21) C. J. Ballhausen, *Theor. Chim. Acta*, **24**, 234 (1972).

crystal $LiNbO_3$ spectrum in Figure 3 has not been assigned. This line does not occur in the powder spectrum in Figure 2 and its origin is uncertain.

The value of ζ has not been determined experimentally; however, relativistic Hartree–Fock calculations for the free ion have shown that $\zeta = 2172 \pm 50\ \text{cm}^{-1}$.[22] Using this value of ζ and the above optical assignments the following values are obtained.

$$A_4{}^0\langle r^4\rangle \sim 2500\ \text{cm}^{-1} \quad k \sim 0.80$$
$$A_6{}^0\langle r^6\rangle \sim 200\ \text{cm}^{-1} \quad k' \sim 0.34$$

Similar crystal field parameters and orbital reduction factors have been obtained for $CsUF_6$.[16] These are

$$A_4{}^0\langle r^4\rangle = 2602\ \text{cm}^{-1} \quad k = 0.77$$
$$A_6{}^0\langle r^6\rangle = 224.9\ \text{cm}^{-1} \quad k' = 0.53$$

In both the oxide and the fluoride the values of k and k' indicate a considerable degree of covalency. Using the above values the $\Gamma_7 \rightarrow \Gamma_8{}'$ separation is calculated to be 12,300 cm^{-1}. This value is in reasonable agreement with the experimental spectra.

The compound $LiTaO_3$ has the same structure as $LiNbO_3$, and both compounds are ferroelectric. As with $LiNbO_3$ it seems reasonable to assume that U^{5+} substitutes for Ta^{5+} in the uranium-enriched samples. The epr spectrum in Figure 1 indicates that the uranium sites in $LiTaO_3$ are axially distorted and not as symmetric as the sites in $LiNbO_3$. A comparison of the epr and optical spectra for uranium-doped $LiNbO_3$ and $LiTaO_3$ reveals that the crystal field parameters for the tantalate probably do not differ substantially from those of the niobate. In view of the quality of the optical spectrum obtained from uranium-doped $LiTaO_3$, a more detailed analysis is not warranted at this time.

In $BiNbO_4$, which has the stibiotantalite structure, each Nb^{5+} site is octahedrally coordinated to oxygen while each Bi^{3+} site has eightfold coordination. It is likely that the U^{5+} again substitutes for the Nb^{5+} in the octahedral sites. The four peaks in the single-crystal epr spectrum of $BiNbO_4$ are attributed to the presence of four inequivalent lattice sites of Nb^{5+} in the triclinic unit cell. The octahedral coordination of oxygen ions about niobium is highly distorted and accounts for the large observed anisotropy of the g factor. The average g value is close to that in $LiNbO_3$, however. The optical spectrum of uranium-doped $BiNbO_4$ (Figure 3) is not greatly different from that of uranium-doped $LiNbO_3$ and it yields little information concerning the inequivalent lattice sites.

In Na_3UF_8 each uranium is surrounded by eight fluorines having approximately eightfold cubic symmetry. The isolated $UF_8{}^{3-}$ units in this compound undergo temperature-dependent rotations with the low temperature structure definitely containing inequivalent fluorines.[12] The g value of the polycrystalline Na_3UF_8 resonance ($|g| = 1.2$) is very similar to that obtained by Llewellyn for U^{5+} in ThO_2 ($|g| = 1.25$) and indicates that in eightfold cubic as well as in octahedral coordination the ground state is the Γ_7 level. That the Na_3UF_8 resonance is observable only near liquid helium temperatures indicates that the first excited level in this compound lies near the ground state. This conclusion is supported by a preliminary analysis of the Na_3UF_8 optical spectrum.[13]

In the Introduction the highly anisotropic g values associated with the $NpO_2{}^{2+}$ ion were noted. Since the $UO_2{}^+$ ion is isoelectronic with $NpO_2{}^{2+}$ and possesses a similar strong axial field, one can expect only minor differences in their g values, depending on small differences in the environment caused by the other ligands. Thus, the g values of $UO_2{}^+$ are expected to be close to $g_\parallel = 3.405$ and $g_\perp = 0.205$. These g values are close to those of an f electron in a field of strong axial symmetry where $A_2{}^0\langle r^2\rangle + A_4{}^0\langle r^4\rangle + \cdots$ is much greater than ζ_{5f}, *i.e.*, $g_\parallel = 4.00$ and $g_\perp = 0$. Even the reduction of $A_2{}^0\langle r^2\rangle + A_4{}^0\langle r^4\rangle + \cdots$ by a factor of 2 with the removal of one oxygen atom to give UO^{3+} is very unlikely to make the axial field approach ζ_{5f}, so the g values of UO^{3+} are probably very similar to those of $UO_2{}^+$ or $NpO_2{}^{2+}$. For this reason it is highly improbable that the epr spectrum reported by Selbin, *et al.*,[20] can be attributed to UO^{3+}. The spectra of U^{5+} in both $UCl_6{}^-$ and $UOCl_5{}^{2-}$ salts are very similar and nearly isotropic with g close to 1.1. Furthermore, the g values observed by Plurien and Rigny[4] in salts of the type MUF_6 show a greater range of anistropy than that in $UOCl_5{}^{2-}$.

Accompanying this g value anisotropy is a dramatic increase in relaxation rate due to the splitting of the Γ_8 level and a downward shift of one of its components. According to the theory of Orbach[23] the spin-lattice relaxation rate is inversely proportional to the fourth power of this energy level separation from the ground state. In strong octahedral fields such as those in $UF_6{}^-$, NpF_6, U^{5+} in $LiNbO_3$, etc., the Γ_8 is a few thousand reciprocal centimeters above the Γ_7 ground state, whereas in $RbNpO_2(NO_3)_3$ there is an excited level probably less than 1000 cm^{-1} above the ground state.[7] The combination of large g anisotropy and very short relaxation time makes it impossible to detect an epr spectrum unless single crystals are used and the temperature is 20°K or less. It is therefore very unlikely that epr absorption due to UO^{3+} could be observed under the conditions employed by Selbin, *et al.*,[20] namely, powdered samples and room temperature. Their conditions favor only the observation of U^{5+} in nearly octahedral sites. Even in $BiNbO_4$, the distortion is great enough to make the resonance detectable only below 20°K and in single crystals although $g_\parallel - g_\perp$ is only about 20–30% of $g_\parallel$ or much less than in $NpO_2{}^+$.

For these reasons the oxygen ligands about the U^{5+} site in $LiNbO_3$ are believed to form only normal single bonds with uranium and are essentially equivalent, forming a nearly perfect octahedron.

It was also mentioned in the Introduction that exceptions to the identification of oxy cations by their large g anisotropy may occur. One that may be noteworthy is the case of the $4f^1$ ion Ce^{3+} in $Ce(Et_2SO_4)_3 \cdot 9H_2O$.[24] The ninefold coordination of water molecules about the Ce^{3+} ion has D_{3h} symmetry and results in $g_\parallel = 3.72$ and $g_\perp = 0.20$. Hence, while large g anisotropy is associated with oxy cations, it is also associated with other site symmetries lower than cubic.

Conclusions

The principal conclusions of this work are as follows.

1. Compounds of U^{5+} appear to form stable solid solutions with a relatively small number of cubic oxides.

2. The longitudinal relaxation time for pentavalent uranium having octahedral oxide coordination is quite variable with only the most symmetric oxides having relaxation times

---

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

(23) R. Orbach, *Proc. Roy. Soc., Ser. A*, **264**, 458 (1961).

(24) G. S. Bogle, A. H. Cooke, and S. Whitley, *Proc. Phys. Soc., London, Sect. A*, **64**, 931 (1951); R. J. Elliott and K. W. H. Stevens, *Proc. Roy. Soc., Ser. A*, **215**, 437 (1952).

long enough to allow the observation of an epr signal at room temperature. The longitudinal relaxation time for U^{5+} having eightfold cubic coordination is short due to the proximity of the lower Γ_7 and Γ_8 levels.

3. The crystal field parameters for U^{5+} in cubic oxides and fluorides are very similar.

4. Considerable covalency exists in the Γ_4 and Γ_5 orbitals of U^{5+} in uranium doped $LiNbO_3$.

Registry No. Uranium, 7440-61-1; $LiNbO_3$, 12031-63-9; $LiTaO_3$, 12031-66-2; $BiNbO_4$, 12272-28-5; Na_3UF_8, 22991-91-9.

Contribution from the Chemistry Division, Argonne
National Laboratory, Argonne, Illinois 60439

Kinetic Study of the Oxidation of *p*-Hydroquinone and *p*-Toluhydroquinone by Neptunium(VI) in Aqueous Perchlorate Media[1]

KAREN REINSCHMIEDT,[2] J. C. SULLIVAN,* and MARY WOODS[3]

Received December 18, 1972

The oxidation of *p*-hydroquinone and *p*-toluhydroquinone by Np(VI) in aqueous perchlorate media can be described by the empirical rate law $-d[Np(VI)]/dt = k[Np(VI)][H_2Q]$ where H_2Q is the appropriate hydroquinone. At 25° and $I = 1.00$ values determined for the rate parameters were $(4.52 \pm 0.24) \times 10^4\ M^{-1}\ sec^{-1}$ and $(6.26 \pm 0.33) \times 10^4\ M^{-1}\ sec^{-1}$, respectively. No apparent effect of hydrogen ion was noted over the range $0.05 \leq [H^+] \leq 1.00\ M$. Values calculated for ΔH^* (kcal/mol), ΔS^* (eu) were $8.17 \pm 0.34, -9.8 \pm 1.1$ and $9.17 \pm 0.29, -5.81 \pm 0.97$ for the *p*-hydroquinone- and *p*-toluhydroquinone-Np(VI) reactions, respectively. The results are discussed in terms of Marcus' cross-reaction equation for electron-transfer reactions.

The oxidation of *p*-hydroquinone to the quinone is a reversible two-electron process.[4] Previous kinetic studies for the oxidation of this reactant with 1-,[5] 2-,[6] and 3-equiv[7] acceptors have been reported. The pertinent results of these investigations appear to be as follows: (a) the empirical form of the rate law is first order in each of the reactants; (b) there is no apparent relation between the kinetic parameters and the redox potentials of the oxidants as has been noted for the oxidation of formic acid.[8] However, Marcus[9a] has successfully demonstrated that an electron-transfer theory (based on first principles) is applicable for the oxidation of a series of hydroquinones by ferric ions. In the present investigation the more readily calculated Marcus cross relation is utilized to interpret the results of the oxidation of hydroquinone and toluhydroquinone by the 1-equiv oxidant Np(VI).

Experimental Section

The preparation and standardization of perchloric acid, lithium perchlorate, and neptunium(VI) perchlorate solutions have been previously described.[10] The hydroquinones and quinones (Eastman) were purified by double- and single-vacuum sublimations, respectively. The melting points determined for the products were as follows: *p*-hydroquinone, 171-172°; *p*-benzoquinone, 115-116°; *p*-toluhydroquinone, 125-126°; *p*-toluquinone, 66-67°. All solutions were prepared in triply distilled water that had been deoxygenated with argon and those containing the organic reagents were protected from exposure to light.

A Cary Model 14 recording spectrophotometer was used to determine molar extinction coefficients and reaction stoichiometries. A Durrum stopped-flow spectrophotometer, Model D-110, with a storage oscilloscope was used for the kinetic studies. From photographs of the oscilloscope screen 15-20 values of A,t were read for each experiment with triplicate replications. Initial estimates of the rate parameters were obtained from graphical treatment of the absorptivity *vs.* time data in the usual integrated form of the second-order rate law. Values reported for the rate parameters were obtained from a least-squares adjustment of the data for the functional form previously described.[11] The two-parameter expression reproduced the observed absorptivities to ±0.003 unit. The standard deviation computed for the rate parameters (based on external consistency) ranged from 1 to 4%.

Results and Discussion

For the reactions

$$2Np(VI) + H_2Q = 2Np(V) + Q + 2H^+ \tag{1}$$

$$2Np(VI) + CH_3QH_2 = 2Np(V) + CH_3Q + 2H^+ \tag{2}$$

the values of the potentials for the couples Np(V)-Np(VI) (−1.14 V),[12] H_2Q-Q (−0.699 V),[4] and CH_3QH_2-CH_3Q (−0.645 V)[4] provide necessary evidence that the reactions will go to completion. The products Np(V) and the quinones were identified spectrophotometrically.

At 25° and 1.0 M $HClO_4$, for the initial concentrations $[Np(VI)] = 1.16 \times 10^{-3}$ and $3.50 \times 10^{-3}\ M$ and $[hydroquinone] = 4.96 \times 10^{-4}$ and $9.92 \times 10^{-4}\ M$ the average value determined for the moles of Np(V) produced per mole of hydroquinone consumed was 1.998 ± 0.018 (95% confidence level, six independent determinations). At the same tem-

---

[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] Participant in the Argonne National Laboratory 1972 Summer Student Training Program.

[3] Guest Scientist from the Chemistry Department, Rosary College, River Forest, Ill.

[4] D. J. G. Ives and G. J. Janz, "Reference Electrodes," Academic Press, New York, N. Y., 1961.

[5] (a) J. H. Baxendale and H. R. Hardy, *Trans. Faraday. Soc.*, 50, 808 (1954); (b) G. Davies and K. Kustin, *ibid.*, 65, 1630 (1969); (c) G. Davies and K. O. Watkins, *J. Phys. Chem.*, 74, 3388 (1970).

[6] E. T. Kaiser and S. W. Weidman, *J. Amer. Chem. Soc.*, 86, 4354 (1964).

[7] J. C. Sullivan and J. E. French, *J. Amer. Chem. Soc.*, 87, 5380 (1965).

[8] M. Thompson and J. C. Sullivan, *Inorg. Chem.*, 11, 1707 (1972), and references cited therein.

[9] (a) R. A. Marcus, *J. Chem. Phys.*, 26, 872 (1957); (b) R. A. Marcus, *Annu. Rev. Phys. Chem.*, 15, 155 (1964).

[10] J. C. Sullivan, A. J. Zielen, and J. C. Hindman, *J. Amer. Chem. Soc.*, 82, 5288 (1960).

[11] R. C. Thompson and J. C. Sullivan, *J. Amer. Chem. Soc.*, 89, 1096 (1967).

[12] A. J. Zielen and J. C. Sullivan, *J. Phys. Chem.*, 66, 1065 (1962).