

# Ion Pairing and Solvation Effects in the Intra-5f<sup>2</sup> Absorption Spectra of Dimeric Uranium(IV) Alkoxide Complexes

John M. Berg,\* Alfred P. Sattelberger, and David E. Morris

Isotope and Nuclear Chemistry Division, Los Alamos National Laboratory,  
Los Alamos, New Mexico 87545

William G. Van Der Sluys and Patrick Fleig

Department of Chemistry, University of Montana, Missoula, Montana 59812

Received May 8, 1992

A spectroscopic study is presented of the [U<sub>2</sub>(OBU<sup>1</sup>)<sub>9</sub>]<sup>-</sup> dimer anion in a series of structurally similar compounds, including a TBA<sup>+</sup> salt reported and characterized here for the first time. Electronic absorption spectra are shown to reveal subtle manifestations of the influence of the coordination sphere on the metal-centered 5f<sup>2</sup> manifold of electronic states. In crystalline KU<sub>2</sub>(OBU<sup>1</sup>)<sub>9</sub> each potassium is known to be closely associated with a single dimer anion. The spectra show this association to be maintained in nonaqueous solution. Weakening the association by increasing the size of the cation is shown to alter the f-f spectra by shifting bands to higher energy. Changing the solvent results in smaller shifts which are observable only at low temperature and are inferred to result from partial solvation of the cation. Quantitative trends in both the solvent-dependent and cation-dependent shifts are interpreted in terms of the influence of the environment on the electron repulsion within the 5f shell and on the crystal-field splitting of the free-ion states.

## Introduction

The f-f electronic absorption spectra of actinide coordination compounds are extremely complex and can be quite sensitive to the ligand environment of the metal center. The implications are that the electronic spectra contain a tremendous amount of information about molecular structure and bonding which has the potential to be useful for studying the solid-state and solution chemistry of these elements but that this information is difficult to extract. Predictive theoretical calculations of 5f<sup>n</sup> electronic structure are simply not available, and empirically-based approaches to systematic quantitative analysis of spectra have generally only been applicable to the limited number of compounds which are available as large single crystals.<sup>1-4</sup> When solution electronic spectra are reported in the chemical literature, discussion is generally limited to qualitative comparisons with spectra of similar compounds to support the conclusion of a certain oxidation state or to argue for a large ligation change or lack thereof.<sup>5,6</sup> Extracting reliable structural information from electronic spectra of otherwise uncharacterized complexes is not possible at present. However, through systematic studies such as that reported here we believe that the current understanding of 5f-5f spectra can be improved and that the spectra can be made into more useful tools in the study of actinide solution chemistry.

The properties common to the absorption spectra of actinide-containing compounds in the ultraviolet, visible, and near-infrared wavelength regions follow directly from the characteristics of the partially-occupied 5f shell. The numerous, sharp absorption bands result from transitions between electronic states which arise from

the 5f<sup>n</sup> electron configuration of the actinide ion. The sharpness is due to the relatively weak coupling of the electronic transitions to nuclear motions, which is a consequence of the degree of shielding of the 5f electrons from the ligands by the electrons of the filled-shell [Rn] core. The shielding is intermediate between that experienced by the 3d electrons in the first-row transition metals and that experienced by the 4f electrons in the lanthanides. The large number of bands typically observed is due to the high multiplicities of 5f<sup>n</sup> configurations, which give rise to up to hundreds of states within the energy range probed by these wavelengths.<sup>7</sup>

The unique characteristics of the 5f shell make absorption spectra due to 5f-5f intraconfigurational transitions difficult to analyze quantitatively. In modeling the 5f<sup>n</sup> energy levels, one must consider electron-electron repulsion and spin-orbit interactions, which are important in an isolated metal ion and continue to be important in the complex, and electron-ligand (ligand-field) interactions which describe the effects of the ligands on the metal-centered orbitals. Sophisticated effective-operator Hamiltonian models exist for calculating energy levels.<sup>8-11</sup> However, their large number of parameters means that their practical application requires either that one possess other information on the electronic structure to supplement the absorption data or that one make initial approximations in which one neglects the terms which are less important for the particular system being modeled. For instance, a useful initial approximation for lanthanide complexes neglects the ligand-field terms because the core electrons shield the 4f electrons from the influence of the ligands.

For most actinide complexes, however, none of the principal types of interactions is small enough to be safely neglected if the goal is to reach a reasonable approximation of the energy level

- (1) Edelstein, N. J. *Less Common Met.* 1987, 133, 39.
- (2) Krupa, J. C. *Inorg. Chim. Acta* 1987, 139, 223.
- (3) Flint, C. D.; Tanner, P. A. *Mol. Phys.* 1987, 61, 389.
- (4) Carnall, W. T. *A Systematic Analysis of the Spectra of Trivalent Actinide Chlorides in D<sub>3h</sub> Site Symmetry*; Argonne National Lab.: Argonne, IL, 1989; Report No. ANL-89/39.
- (5) du Preez, J. G. H.; Zeelie, B.; Casellato, U.; Graziani, R. *Inorg. Chim. Acta* 1987, 129, 289.
- (6) Cotton, F. A.; Marler, D. O.; Schwotzer, W. *Inorg. Chem.* 1984, 23, 4211.

- (7) Carnall, W. T.; Crosswhite, H. M. *Chemistry of the Actinides*, Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: London, 1986; Vol. 1, Chapter 16; pp 1235-1276.
- (8) Wybourne, B. G. *Spectroscopic Properties of Rare Earths*; Interscience: New York, 1965.
- (9) Huffner, S. *Optical Spectra of Transparent Rare Earth Compounds*; Academic: New York, 1978.
- (10) Crosswhite, H. M.; Crosswhite, H. J. *Opt. Soc. Am. B* 1984, 1, 246.
- (11) Judd, B. R.; Crosswhite, H. J. *Opt. Soc. Am. B* 1984, 1, 255.

structure of the  $5f^6$  configuration. Thus, in cases where only absorption data on unoriented molecules is available, the full model cannot be applied effectively. In this paper we employ a simplified approach to the quantitative analysis of intra- $5f$  transition energies which allows small variations in the strengths of the different principal types of interactions to be measured and compared. We show that this method is useful when the experimental data are insufficient to support the assignment of the observed transitions in a manner which would allow the application of the more detailed conventional model.

The immediate goal of this work is to investigate the sensitivity of  $5f$ - $5f$  spectra to small changes in ligation and conversely to demonstrate the utility of these spectra in characterizing such ligation changes. The work presented in this paper shows that extremely subtle complexation changes produce spectroscopic changes which are systematic and that the spectroscopic changes contain useful information about actinide solution chemistry.

Organoactinide complexes of U(IV) for which synthetic strategies have recently been developed are potentially interesting materials for spectroscopic studies because their ligation can be tailored to some extent. A significant number of complexes of U(IV) with organic ligands are now available.<sup>1,5,12</sup> We concentrate on the dimeric species  $KU_2(OBu^t)_9$ , which was first synthesized and characterized by Cotton's group,<sup>6</sup> and on a closely related compound  $U_2(HOBu^t)(OBu^t)_8$  whose chemistry has been explored by Van Der Sluys and Sattelberger.<sup>13</sup> We also present results on  $(TBA)U_2(OBu^t)_9$  ( $TBA =$  tetrabutyl ammonium), the synthesis and characterization of which is reported here for the first time.

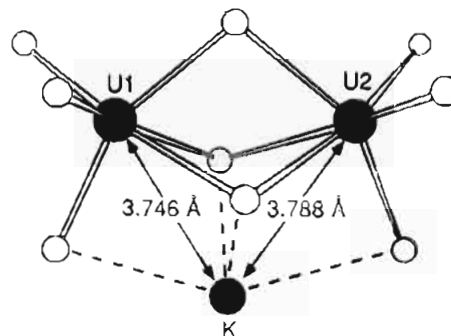
Since these complexes are soluble in many organic solvents without apparent change in the inner coordination sphere of the metal, it is possible to conduct studies on an isostructural series of complexes in solution. It is also possible to study the subtle effects of solvation on the  $5f^2$  manifold by varying the solvent for a single compound. We demonstrate the spectroscopic effects of solvation and discuss this perturbation of the  $5f^2$  energy level structure relative to that of other types of ligation changes, particularly those due to changing the cation and to inner sphere solvation. We use the information about the relative magnitudes of spectroscopic shifts due to different types of coordination changes to discuss the likely structures of the solvated complexes. Finally, we develop a simple, quantitative description of the band shifts which gives some information on how the major types of electronic interactions vary with small coordination changes without requiring use of the full effective-operator model.

### Experimental Section

**Synthesis.** All manipulations were carried out under an oxygen-free ( $<1$  ppm  $O_2$ ) He atmosphere in a Vacuum-Atmospheres glovebox. Solvents were dried over NaK, distilled, degassed with three freeze-pump-thaw cycles, and stored in the glovebox until use. Deuterated solvents were degassed via three freeze-pump-thaw cycles and stored in the glovebox over 3-Å molecular sieves.

$(TBA)U_2(OBu^t)_9$ . In an Erlenmeyer flask, 2.00 g (5.25 mmol) of  $UCl_4$  was dissolved in ca. 20 mL of THF. While this green solution was being stirred, 2.65 g (23.7 mmol) of  $KOBu^t$  was slowly added, producing an initially burgundy solution, which slowly turned dark green after several hours and was accompanied by precipitation of KCl. The solution was stirred for 12 h after which the solvent was removed in vacuo. Hexane (ca. 20 mL) was added to the resulting green solid, and 0.73 g (2.63 mmol) of  $(TBA)Cl$  was added. Stirring was continued for an additional 2 h. The solution was filtered through Celite, and the solvent was removed in vacuo to provide a green oil. The oil was tritiated with hexane and decanted. The green powder was dried in vacuo, providing 1.20 g (33% yield) of product.

$^1H$  NMR (24 °C, THF- $d_8$ ):  $\delta$  3.37 (terminal  $Bu^t$ );  $\delta$  2.37 (bridging  $Bu^t$ ). Shifts of the  $n$ -butyl protons of TBA for  $(TBA)U_2(OBu^t)_9$  in THF solution were indistinguishable from those of the same protons for  $(TBA)Br$  in THF.



**Figure 1.** Structure of the central portion of the  $KU_2(O-Bu)_9$  molecular unit in the crystalline solid. X-ray data were taken from ref 6. Only the U, K, and O atoms are shown and are represented by progressively lighter circles. The two U-K distances are indicated.

**Spectroscopy.**  $^1H$  NMR spectra were recorded at 24 °C on a JEOL SX90Q spectrometer at 90 MHz in dry and oxygen-free THF- $d_8$ .  $^1H$  NMR chemical shifts are reported in  $\delta$  (ppm) relative to the  $\alpha(^1H)$  impurity in THF- $d_8$  set at 1.73 ppm. Because NMR spectra of paramagnetic species are very temperature dependent, the temperature was measured using methanol shifts.

Ultraviolet through near-infrared spectra were recorded on a Perkin-Elmer Lambda 9 dual-beam absorption instrument at 1-nm resolution in the ultraviolet and visible regions ( $\lambda < 860$  nm) and variable slit width normally producing  $<2$  nm resolution in the near-infrared. Solution spectra were taken in 1-cm path length quartz cuvettes with tightly-fitted Teflon stoppers to maintain the  $O_2$  free conditions necessary for the moderate stability of these compounds. Low-temperature solvent glass spectra were taken in capped NMR tubes immersed in liquid  $N_2$  in a small dewar fitted with a clear quartz extension. Base-line distortions introduced by this cylindrical optical cell were corrected by subtracting solvent spectra taken under the same conditions. KBr pellet spectra were taken in a closed-cycle He refrigerator in which the sample was held in an evacuated chamber and cooled by conduction through the holder. Wavelength-dependent scattering produced a base line which sloped upward to shorter wavelength. This was removed for presentation of the spectra by subtracting a linear function of energy. Spectra are presented in energy units rather than wavelength in order to clearly portray relative line widths, energy shifts, and splittings across the broad energy range covered by the  $5f^2$  states.

### Results

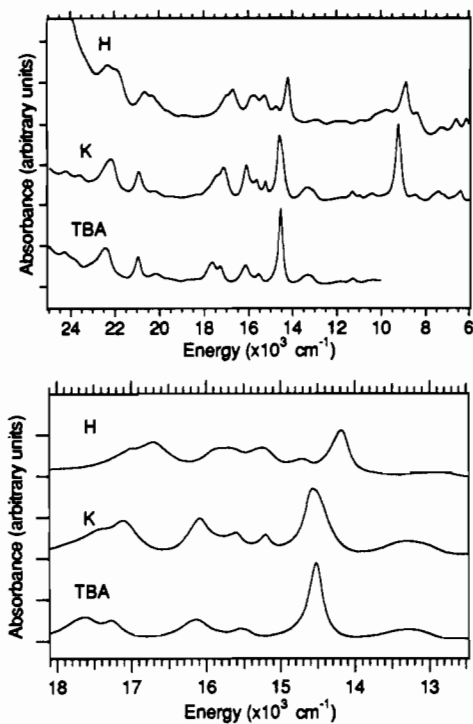
The dimeric species  $KU_2(OBu^t)_9$  and  $U_2(HOBu^t)(OBu^t)_8$  each contain the  $U_2(OBu^t)_9^-$  anion, which adopts a confacial bioctahedral geometry.<sup>6,13</sup> The skeletal structure of the  $K^+$  salt with the alkyl groups omitted for simplicity is shown in Figure 1.  $^1H$  NMR spectra of the  $(TBA)U_2(OBu^t)_9$  salt indicate two types of paramagnetically shifted  $Bu^t$  resonances in a 2:1 ratio. This is the same signature as that found for the terminal and bridging  $Bu^t$  resonances in potassium salt and suggests that the same triply-bridged dimer is present in solutions of the TBA salt.

Figure 2 shows room-temperature electronic spectra of the  $K^+$ ,  $TBA^+$  and protonated forms of the dimer complex in solution. While the spectra have very similar appearances, there is a general shift of bands to higher energy in changing the cation from  $H^+$  to  $K^+$  to  $TBA^+$ . The range of the shift is about 500  $cm^{-1}$  for bands in the visible region of the spectrum.

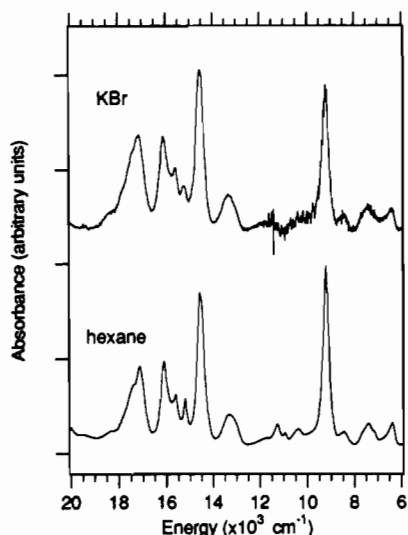
The room-temperature electronic absorption spectrum of  $KU_2(OBu^t)_9$  in hexane solution is identical to that of the powdered solid in a KBr pellet, as shown in Figure 3. We know from above that changing the cation results in substantial band shifts. Therefore, we expect that removing the cation completely would result in a clear spectroscopic effect, presumably producing somewhat larger shifts than the cation change. Since no shifts of this magnitude are observed, the spectra in Figure 3 confirm that there is ion pairing in solution. They suggest that the cation remains associated with the dimer anion in the same manner in solution as in the crystalline solid.

(12) Berg, J. M.; Clark, D. L.; Huffman, J. C.; Morris, D. E.; Sattelberger, A. P.; Strieb, W. E.; Van Der Sluys, W. G.; Watkin, J. G. *J. Am. Chem. Soc.*, in press.

(13) Van Der Sluys, W. G.; Sattelberger, A. P.; McElfresh, M. *Polyhedron* 1990, 9, 1843.

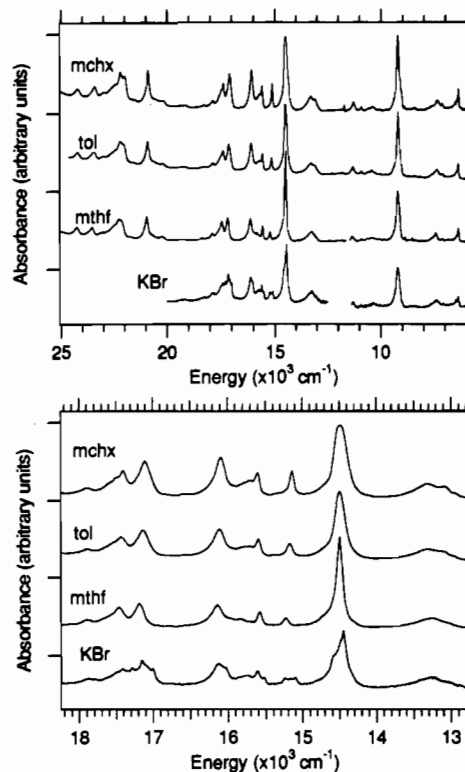


**Figure 2.** Room temperature visible-near-IR absorption spectra of  $MU_2(OBu)_9$  in solution: (a)  $M = H$ , solvent = hexane; (b)  $M = K$ , solvent = hexane; (c)  $M =$  tetrabutylammonium, solvent = toluene. The upper plot shows the full spectral range accessible between the charge transfer bands to higher energy and prohibitively strong solvent vibrational absorptions at lower energy. The bottom plot shows the central energy region in expanded scale to illustrate the peak shifts.



**Figure 3.** Room-temperature absorption spectra of  $KU_2(OBu)_9$ , powdered solid in a KBr pellet and of the same compound in hexane solution.

Cooling solution samples to lower temperatures narrows the absorption bands, revealing more detail than the room-temperature spectra in congested regions and allowing observation of smaller differences between spectra. Figure 4 shows spectra of  $KU_2(OBu)_9$  in three glassing solvents at liquid nitrogen temperature (75 K) in part of the visible region. In the region expanded in the lower plot the band shifts average about  $80\text{ cm}^{-1}$  to higher energy in 2-MeTHF relative to their positions in methylcyclohexane. In toluene they are found at intermediate energies, with the average shift being about  $30\text{ cm}^{-1}$  to higher energy relative to methylcyclohexane. The prominent band at  $14\,500\text{ cm}^{-1}$  narrows in 2-MeTHF solution relative to methylcyclohexane solution, shrinking from 210 to  $100\text{ cm}^{-1}$  full width at half-maximum (FWHM). The toluene solution shows intermediate behavior in the width of this band as well. Its integrated



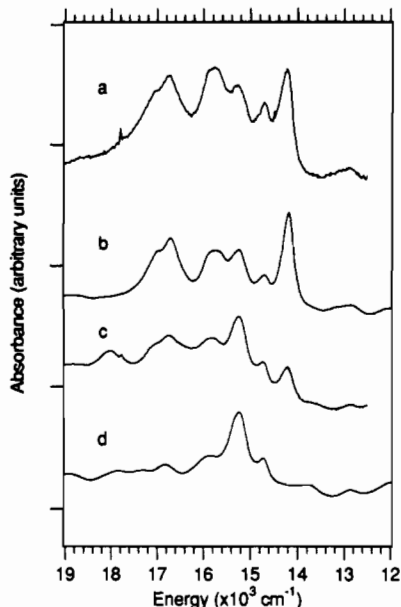
**Figure 4.** Low temperature absorption spectra of  $KU_2(OBu)_9$  at 75 K: mchx = methylcyclohexane glass; tol = toluene glass; mthf = 2-MeTHF glass; and KBr = powdered solid in a KBr pellet. The upper plot shows the full accessible spectral range, and the lower plot shows the central energy region in expanded scale to illustrate the peak shifts.

intensity remains roughly the same in all the solvents. Low-temperature spectra of the solid in a KBr pellet (Figure 4) show slight splittings of many bands into multiplets. The average energies of these multiplets do not differ from those of the corresponding single bands in the low-temperature solution spectra, and the total splittings are about the same as the range of band positions in the different solvents.

Spectra of  $U_2(HOBu^t)(OBu^t)_8$  are effectively the same in room-temperature solution as in the solid, as shown in the top two spectra in Figure 5. This indicates that the proton remains associated with the dimer anion in solution. Study of solvent effects for the protonated form of the dimer presents some complications because this compound is less stable than the potassium salt. Van Der Sluys et al. showed that it reacts with water to form the trimeric species  $U_3O(OBu^t)_{10}$ .<sup>13</sup> Absorption spectra of  $U_2(HOBu^t)(OBu^t)_8$  in hexane and in THF solutions are compared with the KBr pellet spectrum in Figure 5. The spectra show differences which can be explained by partial degradation of the dimer to form a compound whose electronic absorption spectrum matches that of  $U_3O(OBu^t)_{10}$ . A spectrum of  $U_3O(OBu^t)_{10}$  in hexane is shown in Figure 5 for comparison. The degradation is the most extreme in THF solution, with the strong trimer band at  $15\,250\text{ cm}^{-1}$  clearly growing in intensity relative to the hexane solution and pellet spectra. Taking this sample degradation into account by considering only those bands which do not match bands in the  $U_3O(OBu^t)_{10}$  spectra, it appears that the solvent has a smaller effect on the energy levels of  $U_2(HOBu^t)(OBu^t)_8$  than it does on those of  $KU_2(OBu^t)_9$ . Shifts are more difficult to measure at the lower resolution afforded by these room-temperature spectra, but they appear to be in the same direction and no more than half the magnitude of those observed for the potassium salt in the same solvents.

## Discussion

**Molecular Structure Implications of the Spectra.** The published structural data on crystalline  $KU_2(OBu^t)_9$  show each potassium



**Figure 5.** Room-temperature absorption spectra of  $U(HOBU)(OBU)_8$ : (a) powdered solid in a KBr pellet; (b) complex in hexane solution; (c) complex in THF solution. Spectrum d is of  $U_3O(OBU)_{10}$  in hexane at room temperature.

to be associated closely with a single uranium dimer.<sup>6</sup> The nearest neighbors of the potassium are two bridging oxygen atoms and two terminal oxygen atoms (Figure 1). These form a pocket of net negative charge that can stabilize the cation. Distances from the potassium to oxygens on other molecular units in the crystal are more than twice as great.

The fact that spectroscopic shifts are observed in solution upon substituting  $TBA^+$  for  $K^+$  indicates that  $K^+$  remains associated closely enough with the dimer in solution to influence the metal-centered  $f-f$  transitions. Since  $TBA^+$  is much larger than  $K^+$  and therefore is not able to approach as close to the dimer, the spectroscopic shifts in changing the cation to  $TBA^+$  are taken to be indicative of the effect which the weakening of the ion-pairing has on the U  $5f^2$  manifold.

Less is known about structure of the  $U_2(HOBU)(OBU)_8$  molecular unit, so the electronic spectra can offer valuable insight. The location of the proton in the molecular unit was not determined directly because X-ray quality crystals were not obtained.<sup>13</sup> Furthermore, the  $^1H$  NMR spectrum at room temperature showed only a broad resonance due to the proton even after cooling to  $-90^\circ C$ , indicating that it is fluxional in solution, moving from one site to another in the molecule at a rate which is comparable to the NMR time scale.<sup>13</sup> The electronic absorption spectrum in solution at room temperature samples the molecular structure on a much faster time scale. The observed spectrum represents an average of the spectra due to the different ligand arrangements which are present. The sharpness of the observed transitions and the rough equivalence of their number to those of the two salts indicates that the proton fluxionality on the NMR time scale is due to hopping between sites which are equivalent as far as the two metal centers are concerned. Furthermore, the similarity between the solid-state and solution spectra of this complex strongly suggests that the site occupied by the proton in the solid is very close to one of the equivalent sites between which the proton moves in solution.

The electronic spectra contain additional information about the location of the proton. If the proton occupied a site significantly closer to one uranium than the other, the resulting electronic absorption spectrum would be a convolution of the spectra of the two distinguishable uranium centers. The extreme case would be when the proton is associated with one or more of the terminal  $[OBU]^-$  ligands on a single uranium. In such a configuration the other uranium would produce a spectrum similar

to that of the  $TBA^+$  salt, in which the cation is assumed to have minimal influence. The upper limit for electronic splittings which could be present but not resolved in the visible spectral region is about  $150\text{ cm}^{-1}$ . This is less than one-third of the observed shifts caused by substituting the proton for a remote cation ( $TBA^+$ ). Thus, we would expect a significant increase in the number of resolved peaks if the proton were associated with a terminal ligand. Since there is no evidence for such an effect, it is inferred that the proton is associated with the bridging ligands and that it probably moves rapidly between three equivalent sites which are very similar to that known to be occupied by  $K^+$ .

The electronic absorption spectrum of  $U_2(HOBU)(OBU)_8$  is very similar in appearance to those of the two salts except that most bands are shifted relative to their energies in the  $K^+$  salt by a significantly greater amount than the shifts seen between spectra of the  $K^+$  and  $TBA^+$  salts. The bands shift predominantly in one direction along the series  $TBA \rightarrow K \rightarrow H$ , which is consistent with a progressively closer association with the dimer anion along the series.

The spectra of  $KU_2(OBU)_9$  in different solvents at 75 K (Figure 4) show band shifts of up to  $80\text{ cm}^{-1}$ . We believe that the influence of the solvent on the  $5f^2$  manifold occurs through interaction with the cation. By partially solvating the cation, more polar solvents increase its effective size and stabilize it at a greater distance from the anionic  $[U(OBU)_9]^-$  than do less polar solvents. On the basis of observed  $K^+/TBA^+$  shifts discussed above, this solvation should shift transitions to higher energy. This is exactly what is observed in the series changing from the less polar methylcyclohexane to the more polar MeTHF. The solvent effect appears to produce a milder form of the same electronic perturbation as changing the cation. The significant narrowing of the band at  $14\,500\text{ cm}^{-1}$  is also consistent with greater ion separation in more polar solvents because the limiting case of complete removal of the cation would make the three bridging ligands equivalent on the optical time scale, with the increased symmetry resulting in more degenerate states and consequently fewer bands in the spectra. Recall that the room-temperature spectrum of the  $TBA^+$  salt showed some narrowing of this same band (Figure 2).

The influence of the solvent on the spectra in Figure 4 is clearly too small to be due to inner-sphere complexation of one or both of the uranium atoms by solvent molecules. This is illustrated by comparison with the spectra of  $UCl_4$  in solution, where the spectra are altered radically by changing the solvent because the solvent complexes the metal directly.<sup>14</sup> At the other extreme is the  $U(O-2,6-Bu^t_2C_6H_3)_4$  complex in which bulky ligands prevent the solvent molecules from approaching the metal center. In that case the solvent does not produce measurable ( $>10\text{ cm}^{-1}$ ) shifts even at 75 K.<sup>12</sup>

An intermediate case with spectral shifts closer to those due to dimer solvation is that of the different environments of  $U^{4+}$  in the incommensurate, low-temperature phase of crystalline  $\beta\text{-ThBr}_4:U^{4+}$ .<sup>15</sup> Below 95 K the 8-fold coordinate Th (or U) exists in a continuous distribution of sites which vary by slight rotations of the bromines around the metal center. Total ligand displacements are believed to be a few percent of the unit cell dimension in the form of rotations about the metal center, and metal-ligand distances do not appear to change.<sup>16</sup> Electronic transitions in the visible region are observed to shift by about  $30\text{ cm}^{-1}$  over the full range of distortion.<sup>15</sup> This is comparable to the full range of the solvent shifts we have observed in the dimer system. In the dimer it is likely that slight changes in ligand arrangement occur with solvation of the cation. It is reasonable that spectroscopic changes will be of the same magnitude as those

(14) Van Der Sluys, W. G.; Berg, J. M.; Barnhart, D.; Sauer, N. N. *Inorg. Chim. Acta* **1993**, *204*, 251.

(15) (a) Delamoye, P.; Krupa, J. C.; Conway, J. G.; Edelstein, N. *Phys. Rev. B* **1983**, *28*, 4913. (b) Delamoye, P.; Rajnak, K.; Genet, M.; Edelstein, N. *Phys. Rev. B* **1983**, *28*, 4923.

(16) Bernard, L.; Currat, R.; Delamoye, P.; Zeyen, C. M. E.; Hubert, S.; de Kouchkovsky, R. *J. Phys. C: Solid State Phys.*, **1983**, *16*, 433.



due to this site distortion in  $\beta$ -ThBr<sub>4</sub> if the relative positions of the oxygens in the dimer change by a comparable amount.

The spectrum of solid KU<sub>2</sub>(OBU)<sub>2</sub> at low temperature, powdered and pressed into a KBr pellet, shows signs of more complicated band structure than that found for the same compound in the low temperature glasses. Single bands in the 75 K solvent glass spectra in Figure 4 appear as multiple bands split by as much as 150 cm<sup>-1</sup> in the powder spectrum. At this point we cannot completely rule out the possibilities that disorder is introduced in the pressing of the pellet or by a phase change during cooling. However, a promising explanation for the powder spectrum may be found in the reported crystal structure,<sup>6</sup> which shows that at room temperature there are slight differences between the environments of the two uranium atoms. The K<sup>+</sup> is 0.04 Å closer to U1 than to U2, and the bridging oxygen on the opposite side of the U-U axis from K<sup>+</sup> is 0.07 Å closer to U1 than U2. While terminal U-O distances do not differ significantly for the two uraniums, there is angular distortion in which the oxygens on U1 are bent toward the U-U axis (away from the waist of the molecule) by an average of 0.7° relative to those on the opposite end. The greatest angular difference is for the terminal oxygens closest to the K<sup>+</sup>, which is consistent with their moving to accommodate the off-center K<sup>+</sup> position. These distortions create slightly different environments for the 5f electrons on the two uranium ions and hence complicate the electronic absorption spectrum. If one presumes that the distortions are due to crystal packing forces, they would all disappear in solution and the spectrum would collapse into that of a single uranium environment. This would explain the simpler solution spectra.

The splitting of bands in the spectrum of the solid K<sup>+</sup> salt is of the same magnitude as the band shifts found for the K<sup>+</sup> salt in the different frozen solvent glasses, suggesting that the differences in uranium environments introduced by changing the solvent are comparable to the range of different ligand environments in the solid. The band splittings in the spectrum of the solid K<sup>+</sup> salt are distinctly less than the shifts induced by substituting TBA<sup>+</sup> or H<sup>+</sup> for K<sup>+</sup>, however, showing that the distortion of the coordination sphere due to crystal packing forces is less significant than that caused by changing the cation.

**Quantitative Analysis of Transition Energies.** The observed transition energies in intra-5f<sup>n</sup> spectra can be modeled by considering only those electronic interactions which affect the relative energies of the levels within the 5f<sup>n</sup> configuration. The largest effects are due to electron-electron repulsion, spin-orbit interactions, and ligand field interactions, in decreasing order of importance. These effects are usually quantified for f<sup>n</sup> configurations of lanthanide and actinide complexes using an effective-operator Hamiltonian model which incorporates the crystal-field formalism.<sup>10,17</sup> Analyses of the free-ion energy levels can be used to estimate the parameters in the electron-repulsion and spin-orbit terms. A least-squares fitting procedure is then applied in which these parameters are varied along with the crystal-field parameters until the best correspondence between the calculated energy levels and the transition energies observed in the spectra is achieved.

It is found universally that the electron-repulsion and spin-orbit parameters which give the best fits for complexes are smaller than those derived from the free ion energy levels. The decrease typically amounts to 10% of the free-ion parameter values for tetravalent actinide complexes.<sup>1</sup> There has been considerable debate in the literature about the physical mechanism for this apparent reduction in electron-electron repulsion and spin-orbit interaction within the 5f manifold, with various authors ascribing the shifts to covalency<sup>18</sup> and to ligand polarizability.<sup>19</sup> The physical reason for the universal reduction of the parameters in

complexes from those in the free ion, long known as the nephelauxetic effect,<sup>20</sup> must be regarded as unresolved.<sup>21</sup> The spectroscopic consequence is that the energy range spanned by the states of the 5f<sup>n</sup> configuration is decreased, so to a first approximation the transition energies are decreased by an amount proportional to the excited state energy.

The relatively large magnitude of the crystal-field interactions is another characteristic feature of 5f<sup>n</sup> configurations. The overall splittings due to the ligands can be comparable to the spin-orbit splittings. As a result, the energy ordering of electronic states and their free-ion state parentage can vary a great deal for different complexes of the same metal in the same oxidation state, resulting in spectra with dramatically different appearances when examined on the scale of the crystal-field splittings (~2000 cm<sup>-1</sup>). Thus, assignment of crystal-field quantum numbers (symmetry labels) to the initial and final states of the observed transitions is a difficult yet crucial step in explicitly applying the effective-Hamiltonian model to spectroscopic data.

In the present case, there is no basis in our data or in the literature for the confident assignment of quantum numbers to the ligand-field states observed in our spectra. Without transition assignments we cannot apply the standard effective-Hamiltonian model, and so we cannot base our discussion of the spectroscopic effects of changes in ligation on comparisons of electron-repulsion, spin-orbit and ligand-field parameter values. Instead we take a simplified, somewhat unconventional approach to the analysis by using the concepts, but not the details, of the crystal-field model. We take advantage of the fact that the spectroscopic changes we have observed are quite small so that there are clear, one-to-one correspondences between bands in the spectra of the systems being compared. We can follow energy level shifts directly in our spectra and can infer from their direction and scale how the classes of model parameters are varying with subtle changes in ligation.

**Simplified Quantitative Analysis of Spectroscopic Shifts.** Consider the spectra of KU<sub>2</sub>[OBU]<sub>2</sub> in different solvent glasses at 75 K shown in Figure 4. For each transition which is observed in toluene we assign an index *n* and define  $\Delta E_{\text{mchx/tol}}(n)$  as the energy shift of this band upon changing the solvent to methylcyclohexane and  $\Delta E_{\text{mthf/tol}}(n)$  as the energy shift of the same band upon changing the solvent to MeTHF. These energy shifts are plotted in Figure 6 as functions of the transition energy in toluene.

As a first approximation, a change in the electron repulsion within the 5f<sup>2</sup> configuration should be manifested by a trend in the energy shifts which is linearly proportional to the transition energy. As has already been discussed, electron repulsion is the dominant factor in determining the overall spread of the 5f<sup>2</sup> energy levels, and thus the energies of inter-configurational transitions should scale with the strength of this interaction. We extract whatever linear trends are present for each solvent change by determining the linear least-squares fits to the band shifts. The results are superimposed on the data in Figure 6. The standard deviations of the linear fit parameters indicate that the differences in the underlying linear trends between the two sets of data are significant. Changing the solvent from toluene to 2-MeTHF produces a proportional increase in transition energy. The slope of 0.0030 ± 0.0011 indicates an increase in the electron repulsion leading to an expansion of the 5f<sup>2</sup> energy scale by 0.30%. Changing the solvent from toluene to methylcyclohexane produces a proportional decrease in transition energy whose slope of 0.0011 ± 0.0006 indicates a decrease in electron repulsion by 0.11%.

The large residual shifts (i.e. scatter in Figure 6) indicate that the linear trends, on average, account for no more than half of the magnitudes of the observed shifts. We interpret the residual deviations as manifestations of significant changes in classes of

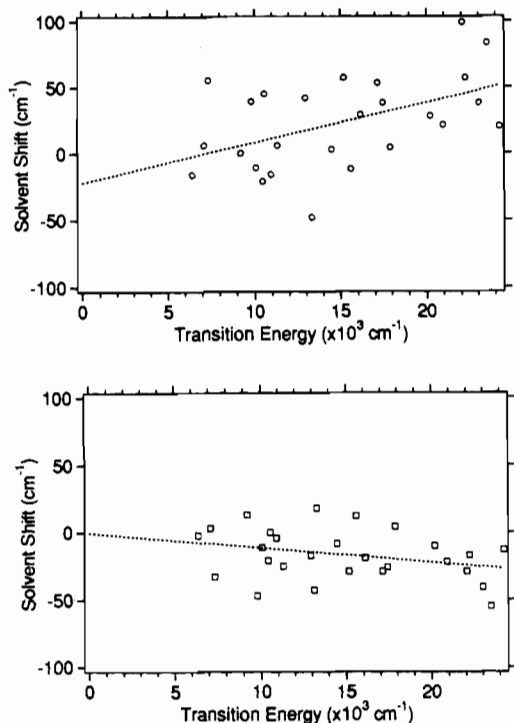
(17) Carnall, W. T.; Liu, G. K.; Williams, C. W.; Reid, M. F.; *J. Chem. Phys.* **1991**, *95*, 7194.

(18) Jorgensen, C. K. *Chem. Phys. Lett.* **1982**, *87*, 320.

(19) Newman, D. J. *Aust. J. Phys.* **1977**, *30*, 315.

(20) Schaffer, C. E.; Jorgensen, C. K. *J. Inorg. Nucl. Chem.* **1958**, *8*, 143.

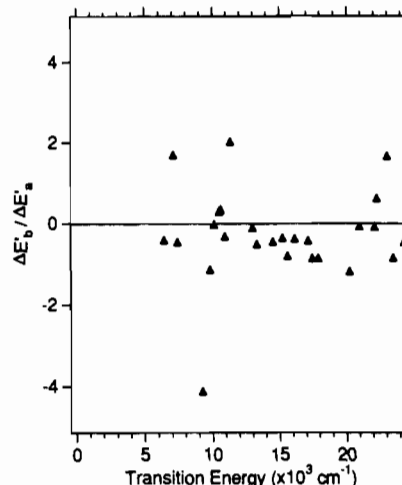
(21) Antic-Fidancev, E.; Lemaitre-Blaise, M.; Caro, P. *New J. Chem.* **1987**, *11*, 467.



**Figure 6.** Peak shifts in  $KU_2(O-Bu)_9$  spectra shown in Figure 4 with change of solvent. Upper plot shows  $\Delta E_{mthf/tol}(n)$ , the shifts of peaks in 2-MeTHF relative to corresponding peaks in toluene, as a function of transition energy. Lower plot shows  $\Delta E_{mchx/tol}(n)$ , the shifts in methylcyclohexane relative to corresponding peaks in toluene, as a function of transition energy. Linear least-squares fits to the shifts are also shown.

terms in the  $5f^2$  Hamiltonian which have a more energy-localized effect on the transition energies. The effects of changes in the crystal-field terms in particular fit this description, since their primary influence is on the relative energies of crystal-field states originating from the same free-ion state. Since neighboring crystal-field states may originate from quite different free-ion states, changes in the strength of the crystal field should produce energy shifts which vary considerably in magnitude from one state to the next and which tend to change sign quite frequently as one progresses through the spectrum. In other words, changes in crystal-field strength should be manifested as "noise" in Figure 6. The deviations of the measured shifts from the linear trend for MeTHF have a root-mean-square (RMS) value of  $29 \text{ cm}^{-1}$ , and for methylcyclohexane they have an RMS value of  $17 \text{ cm}^{-1}$ . We interpret these RMS values as estimates of the portions of the shifts which are due to changes in the crystal field.

A change in the crystal-field energy of the ground state is a special case because it contributes a constant shift to all transition energies. This would be observed in Figure 6 as a nonzero  $y$ -intercept of the underlying linear trend. For instance, a negative  $y$ -intercept would indicate an increase in the ground-state energy relative to what would be expected with a strict linear scaling with transition energy of all the states of the configuration. The source of such a localized energy change can be interpreted as a decrease in crystal field splitting of the free-ion ground state. The value of  $-20 \pm 18 \text{ cm}^{-1}$  for the  $y$ -intercept of the linear fit to the mthf/tol shifts suggests a decrease in the crystal-field splitting of the lowest multiplet by  $\sim 20 \text{ cm}^{-1}$ . This is consistent with the  $29\text{-cm}^{-1}$  average crystal-field shift inferred from the RMS value for all the deviations from the linear fit. For the case of the mchx/tol shifts, the  $y$ -intercept has a value of  $0 \pm 10 \text{ cm}^{-1}$ , while the RMS value of all the deviations from the linear trend is  $17 \text{ cm}^{-1}$ . The apparent lack of a crystal-field component to the ground-state energy shift as indicated by the near-zero  $y$ -intercept may be due to a cancellation of the change in ground state crystal field energy by a decrease in the spin-orbit interaction. Such a decrease is an expected result of  $5f$  orbital expansion manifested by the observed decrease in electron repulsion.



**Figure 7.** Ratios of the residual shifts not accounted for by the linear trends in the solvent pair comparisons in Figure 8. The ratioed quantities,  $\Delta E'_{mchx/tol}(n)/\Delta E'_{mthf/tol}(n)$ , are defined by eqs 1 and 2 in the text and are abbreviated to  $\Delta E'_b$  and  $\Delta E'_a$ , respectively, in the plot.

If only the strength and not the form of the crystal field changes with solvent, then the crystal field components of the solvent shifts should be systematic across the series of solvents. The deviations of band shifts from the best linear fits are defined as

$$\Delta E'_{mthf/tol}(n) = \Delta E_{mthf/tol}(n) - [aE_{tol}(n) + b] \quad (1)$$

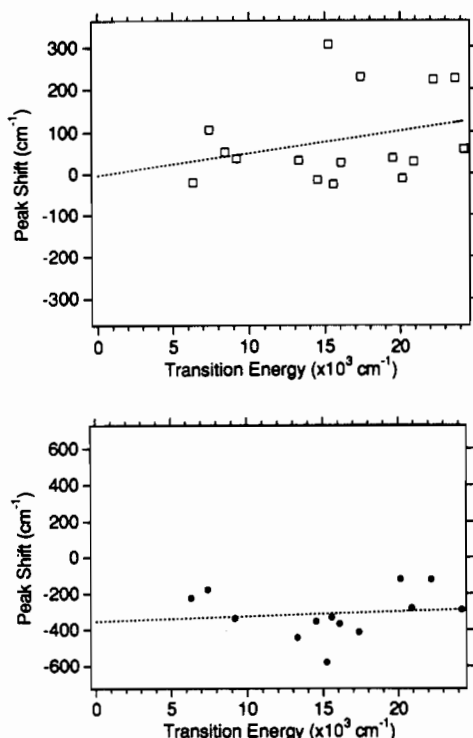
and

$$\Delta E'_{mchx/tol}(n) = \Delta E_{mchx/tol}(n) - [a'E_{tol}(n) + b'] \quad (2)$$

where  $a$  and  $a'$  are the slopes and  $b$  and  $b'$  are the  $y$ -intercepts of the linear fits shown in Figure 6. The ratio of the deviations,  $\Delta E'_{mchx/tol}(n)/\Delta E'_{mthf/tol}(n)$ , for each transition  $n$  are shown in Figure 7 plotted as a function of transition energy. The dominant feature is a clustering of deviation ratios between 0 and  $-1$ , with an average ratio of  $-0.3$ . In other words, bands in the toluene spectrum tend to shift in the opposite directions when changing to the two other solvents, and the shifts tend to have a larger absolute magnitude when changing to MeTHF. Given our assumption that the deviations from the linear trends are due primarily to changes in crystal field interactions, this pattern indicates that the change in crystal field strength upon changing the solvent from toluene to MeTHF is of the opposite sign and about three times the magnitude of that produced by changing the solvent from toluene to methylcyclohexane.

While the difference in relative signs of the crystal field change is clear, caution must be exercised in discussing the absolute signs of the changes in crystal field strength with solvent. The only basis for determining the absolute signs is the apparently negative  $y$ -intercept of the linear fit to the mthf/tol shifts, which had a large standard deviation. If it is accepted that the negative sign of this  $y$ -intercept is reliable, then it indicates a decrease in the crystal-field splitting of the ground state multiplet for the mthf/tol solvent change, and the mchx/tol solvent change can then be inferred to cause an increase in the crystal-field strength.

Earlier in our discussion the spectroscopic energy shifts with increasing solvent polarity were taken to indicate that the cation is partially solvated in more polar solvents, leading to greater charge separation between the  $K^+$  and the dimer anion and spectroscopic shifts in the same direction as those given by substituting a larger cation for  $K^+$ . Combining this interpretation and the assumption above that the linear trends in band energies are due to changes in electron repulsion, it follows that cation-dimer separation leads to greater electron repulsion within the  $5f$  shell. This in turn suggests that the  $5f$  shell becomes more spatially contracted and less well-shielded from the uranium nucleus as the cation is removed.



**Figure 8.** Energy shifts  $f-f$  of spectroscopic transitions with changing cation (spectra in Figure 2). The upper plot shows  $\Delta E_{TBA/K}(n)$ , the shifts of absorption peaks of the  $TBA^+$  salt relative to corresponding peaks in  $K^+$  salt, as a function of transition energy. The lower plot shows  $\Delta E_{H/K}(n)$ , the shifts in protonated form relative to  $K^+$  salt, as a function of transition energy. Linear least-squares fits to the shifts are also shown.

The larger changes in transition energies with change of the cation can be treated in the same manner as the solvent shifts. The results are shown in Figure 8, with cation-dependent band shifts  $\Delta E_{TBA/K}(n)$  and  $\Delta E_{H/K}(n)$  defined in the same way as the solvent-dependent shifts. Substitution of  $TBA^+$  for  $K^+$  gives positive band shifts which increase linearly with energy, the slope indicating a 0.5% increase in the electron repulsion energies. The  $y$ -intercept is nearly zero, but the uncertainty is large ( $\pm 40 \text{ cm}^{-1}$ ). The deviations from the linear fit have an RMS value of  $98 \text{ cm}^{-1}$ , providing an estimate of the crystal-field shifts which can be compared with the solvent effect. The directions of these deviations correlate remarkably well with those of the corresponding bands for the solvent change from toluene to 2-MeTHF, and their magnitudes are about 3 times larger. This is evidence that the crystal-field changes are caused by the same basic form of ligation change as in the solvent series and differ only in that scale is greater. It argues strongly that the change in the ligation with solvent involves changing the separation of the cation from the dimer by solvating the cation.

Replacement of  $K^+$  by a proton results in negative band shifts which are of even larger magnitude, but which are less well-behaved. The slope of the best linear fit to the shifts as a function as transition energy is poorly defined (Figure 8). A reasonable estimate of the uncertainty in the slope is about twice its absolute value. The  $y$ -intercept of  $-350 \text{ cm}^{-1}$  is better-defined and points to a large upward shift of the energy of the ground crystal-field state relative to the rest of the configuration. This in turn suggests a large decrease in the ground-state crystal-field splitting. It appears that the alteration of the crystal-field is more significant than the isotropic change in electron repulsion for this change in ligation. The qualitative difference of this case from the others we have considered is consistent with the tighter binding of the proton and the expected greater distortion of the ligand positions.

As in the solvent series, the two cation substitutions produced band shifts which are correlated with each other. The largest negative shifts for the  $H^+$  substitution occur for the same bands which show the largest positive shifts for the  $TBA^+$  substitution, and there is a general trend for the deviations from the linear fits to balance each other. However, the balancing is much less pervasive than was the case in the solvent series. This observation also supports the suggestion that an alteration of the form of the crystal field occurs due to a more significant perturbation of the ligand positions when the proton is substituted.

The results of analysis of both the solvent and cation series suggest that electron repulsion within the  $5f^2$  configuration increases as the dimer anion is isolated from the cation. This can be interpreted as indicating a decrease in the nephelauxetic effect as the ions are separated. Extrapolation from the current understanding of the nephelauxetic effect in transition metals suggests that it should increase (less intra- $5f$  electron repulsion) when the ligand system becomes more capable of providing electron density to shield the metal valence electrons from the nucleus,<sup>18,19,21</sup> either through increased covalency or increased ligand polarizability. Since removal of the cation would seem to make the  $[OBU']^-$  ligands more capable of donating electron density to the uranium ions and thus would be expected to decrease the electron repulsion, it would seem that our results run counter to this understanding.

The apparent anomalous nature of this system is not particularly disturbing at this point because the effects of covalency in actinide complexes, particularly with regard to the  $5f$  electrons, remain poorly understood. Indeed the fact that our approach has yielded results which do not fit expectations suggests that this avenue of study will provide useful insight into the interaction between ligands and actinide valence electrons.

## Conclusions

By comparing the electronic absorption spectra of  $KU_2(OBU')_9$  in nonaqueous solution to that of the powdered solid and to a  $TBA^+$  salt of the same dimer, we have confirmed that  $K^+$  remains associated with the dimer anion in solution and that the structure of the molecular unit is likely the same in solution as in the crystalline solid. We have also shown that the electronic absorption spectra of  $U_2(HOBU')(OBU')_8$  support the hypothesis that the extra proton is associated with the bridging rather than the terminal ligands.

By comparing the spectra of different salts of  $[U_2(OBU')_9]^-$  and of a single salt in different solvents, we have established the magnitude of the perturbations of the  $5f^2$  configuration caused by two types of changes in outer-sphere ligation of  $U(IV)$  complexes. We have shown that an increase in the size of the cation and an increase in solvent polarity produce the same type of perturbations, which points to a common physical mechanism related to increasingly isolating the dimer anion from the influence of the cation.

Finally, we have shown that a quantitative analysis of the spectroscopic differences between similar actinide complexes can be pursued usefully even in the absence of band assignments. Indeed, this highly empirical approach is preferable in cases where assignments cannot be confirmed independently because it minimizes the likelihood of serious misinterpretation of physical effects due to incorrect assumptions about the identities of spectroscopic bands.

**Acknowledgment.** This work was supported in part by the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy. J.M.B. thanks the Director's Office, Los Alamos National Laboratory, for a postdoctoral fellowship.