1 of 1

TITLE: Low Temperature Absorption Spectra and Ground State Electronic
Structure of Tetrakis(2,6-di-tert-butylphenoxide)uranium(IV)

AUTHOR(S): John M. Berg
Nuclear Materials Technology Division
Los Alamos National Laboratory

SUBMITTED TO: ACTINIDES-93 International Conference Proceedings
(Journal of Alloys and Compounds)

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

RECEIVED
OCT 07 1993
OSTI

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

Los Alamos

MASTER
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

**Low temperature absorption spectra and ground state electronic structure of
tetrakis(2,6-di-*tert*-butylphenoxide)uranium(IV)**

John M. Berg

Nuclear Materials Technology Division

Los Alamos National Laboratory, Los Alamos, NM 87501, USA

The optical spectroscopy of the homoleptic U(IV) aryloxide compound U(*O*-2,6-*t*-Bu₂C₆H₃)₄ could give unique insight into actinide electronic structure because the complex has unusually high symmetry. Its synthesis and characterization were described in a recent paper.[1] The characterization included presentation of several optical spectra in solution accompanied by a brief, qualitative discussion of the molecular properties that give rise to the observed features. In this paper we present optical absorption data on microcrystalline solid samples at low temperature. Our discussion of these data focuses generally on the effect of the ligands on the 5f² electronic configuration of the central U(IV) ion and specifically on the properties of the ground state and the lowest lying electronic state.

Analyses of the complicated 5fⁿ electronic configurations of actinide ions in coordination complexes challenge both spectroscopic assignment methods and the best current ligand field models. In complexes of high symmetry, degeneracies in the 5fⁿ configuration are split less extensively than in complexes of low symmetry, producing a simpler spectrum. The preserved degeneracies also place a number of constraints on the parameters which models produce to describe the energy levels. As a result, the best fit parameters are easier to determine and more reliable than those derived for more complex systems. Because U(*O*-2,6-*t*-Bu₂C₆H₃)₄ has very close to tetrahedral symmetry about the uranium ion, we expect its absorption spectrum to reflect one of the simplest manifolds of 5f² energy levels among known U(IV) compounds.

As discussed in [1], the single-crystal X-ray structure obtained at -145 °C (128 °K) showed that the crystallographic symmetry is S₄. This means that all four ligands are

equivalent through rotations. The symmetry of the UO_4 central group of atoms is only slightly distorted from T_d to D_{2d} . Variable temperature ^1H NMR spectra in benzene- d_6 suggested that the solid state S_4 symmetry is preserved in solution at low temperature, but with warming the protons on opposite sides of the aromatic ring of the ligand become equivalent, indicating the ligands are rotating rapidly on the NMR time scale. The time-averaged symmetry is probably T_d at room temperature and we make the initial simplifying assumption that the optical spectra can be analyzed in this point group. We will discuss the effects of the slight distortions from this idealized symmetry after our initial analysis.

Samples of microcrystalline $\text{U}(\text{O}-2,6\text{-}t\text{-Bu}_2\text{C}_6\text{H}_3)_4$ were ground, mixed with KBr, and pressed into pellets under a dry, O_2 free Ar atmosphere in a glove box. The pellets were mounted on the cold finger of an optical cryostat and cooled with a closed-cycle helium refrigerator. The temperature was measured with a thermocouple located on the sample holder near the edge of the sample. Because of its poor thermal conductivity, the region of the sample probed by the optical beam was probably at a higher temperature than what we measured at the holder. Since we do not have a reliable measurement of this difference, we simply report the measured temperature of the sample holder. Light scattering from the optically cloudy sample pellets increased with increasing photon energy in a nearly linear fashion. We compensated for this by subtracting a linear function of photon energy from the acquired spectra to make the baseline flat over the visible and near infra-red regions.

We collected spectra from samples held at temperatures from 8 °K up to room temperature. Two of these spectra after baseline subtraction are shown in Figure 1. Like the solvent glass spectrum in [1], these spectra show considerable sharpening of the absorption bands due to the $5f\text{-}5f$ transitions with cooling. All of the major sharp features and most of the weaker features match closely those observed in the solvent glass at 75 °K, but there are small differences in some of the peaks.

In a field of T_d symmetry, the $5f^2$ configuration splits into 40 electronic states. Transitions from the ground electronic state to approximately 30 of these should fall within the 4500 cm^{-1} to 20000 cm^{-1} energy window which we were able to scan in the KBr matrix. The number of states that we observe in our spectra will be somewhat less than this because, for a ground state of any possible symmetry representation, symmetry selection rules forbid transitions to a specific subset of the excited states. The number of forbidden transitions depends upon the symmetry transformation properties of the ground state. The four symmetry possibilities for the ground state are A_1 , E , T_1 , and T_2 . There should be one electronic state of each of these symmetries in the lowest energy group of states. The number of forbidden transitions is greatest for an A_1 ground state and decreases progressively with E , T_1 , and T_2 . More than two thirds of the possible transitions are forbidden for an A_1 ground state, while only about one in ten are forbidden for a T_2 ground state.

Counting the peaks in the lowest temperature spectrum in Fig. 1 gives a lower limit for the number of allowed transitions. We observe 19 distinct peaks between 4500 cm^{-1} and 20000 cm^{-1} . Several of the peaks in this list are broad enough that they may consist of two or more unresolved transitions, so the actual number of allowed transitions may be slightly higher. This peak count is more than twice the number of peaks expected using T_d electric dipole selection rules if the ground state transforms as A_1 , so it argues against that ground state symmetry assignment. The peak count also exceeds the number expected for an E ground state, but only by about 20%. For a T_1 or T_2 ground state the number of observed peaks is less than the expected number of symmetry allowed transitions by about 20%. Thus the peak count supports assignment of the ground state as either T_1 or T_2 , and it argues moderately against assignment as E symmetry.

As the temperature is increased, several new absorption bands grow into the spectrum. Each thermally activated transition, or hot band, appears on the low energy side of one of the original absorption bands. However, a hot band does not grow in adjacent to

all of the low temperature absorption bands. This behavior indicates the existence of an electronic excited state 90 cm^{-1} in energy above the ground electronic state. When this state is thermally populated, new transitions appear in the spectrum originating from it and terminating on some, but not all, of the same excited states which are accessible from the ground state.

We do not believe that the observed hot bands can be assigned to transitions originating from a vibronic level of the ground electronic state, primarily because no excited state vibronic levels appear in our spectra. Since the excited states and the ground state all originate from the $5f^2$ configuration, a large effect of vibronic interactions on the transition probabilities should not be unique to the ground state. Also, unlike the case of complexes of O_h symmetry, T_d complexes have no inversion center and hence do not require vibronic interactions to make electric dipole transitions parity allowed.

Because only some of the states accessible from the ground state via the absorption of a single optical photon appear to be accessible from the thermally populated state and no additional excited states are accessible, the thermally populated state must be one from which transitions are allowed only to a subset of the states which are accessible from the ground state. Since there are hot bands associated with six of the eight transitions out of the ground state which are strong and narrow enough that they could be observed, we have a very rough measure of the ratio of the allowed transitions out of the ground and 90 cm^{-1} states. This ratio is consistent with the ground state/excited state combinations T_2/E , T_1/E , and E/A_1 , each of which should result in more than half of the transitions out of the ground state being allowed out of the excited state. It argues moderately against T_2/A_1 and T_1/A_1 combinations because less than half as many states should be accessible out of the A_1 state. And it argues strongly against E/T_1 , E/T_2 or an A_1 ground state in combination with any excited state symmetry because those possibilities all would produce more allowed transitions out of the excited state than the ground state.

One other piece of information may be found in the magnetic susceptibility of this compound, which has been measured [2,3] and is currently being modeled [3]. It shows clear evidence for temperature independent paramagnetic behavior below about 30 K. This is not consistent with a T_1 or T_2 ground state, but it is consistent with either an E or A_1 ground state.

The assignment that our data supports the most strongly is that of an E ground state and an A_1 excited state because this predicts more transitions out of the ground state than out of the excited state and it predicts temperature independent paramagnetic behavior at low temperature. However, we count a slightly greater number of peaks in our absorption spectra than should be allowed by symmetry out of an E ground state. It is possible that additional transitions become slightly allowed through the slight distortion of the complex from the ideal T_d symmetry we have used in our analysis to the actual S_4 symmetry shown in the X-ray structure. In fact, we find that no symmetry assignments for the ground and 90 cm^{-1} states are completely consistent with all of our observations. We anticipate that the full analysis of the magnetic susceptibility results [3] and further low temperature spectroscopic experiments will resolve the remaining uncertainties.

Acknowledgments. We thank Dr. William G. Van Der Sluys for providing the samples of $U(O-2,6-t\text{-Bu}_2\text{C}_6\text{H}_3)_4$ used in the spectroscopic work. This work was initiated while the author was supported by a postdoctoral fellowship generously provided by the Director's office of Los Alamos National Laboratory. All work was performed under the auspices of the U. S. Department of Energy.

References.

- [1] J. M. Berg, D. L. Clark, J. C. Huffman, D. E. Morris, A. P. Sattelberger, W. E. Streib, W. G. Van Der Sluys and J. G. Watkin, *J. Am. Chem. Soc.*, **114** (1992) 10811.
- [2] W. G. Van Der Sluys, A. P. Sattelberger and J. D. Thompson, unpublished results, 1989.
- [3] J. M. Berg, S. D. McKee, C. J. Burns and J. D. Thompson, in preparation, 1993.

Figure 1: Absorption spectra of microcrystalline $\text{U}(\text{O}-2,6\text{-}t\text{-Bu}_2\text{C}_6\text{H}_3)_4$ in a KBr pellet at low temperature. A baseline linear in energy has been subtracted from each spectrum prior to plotting them in order to correct for increasing light scattering by the KBr pellet at shorter wavelengths. Temperatures are reported as measured at the sample holder and are believed to be lower than the actual sample temperatures.

**DATE
FILMED**

12 / 8 / 93

END