

# Lawrence Berkeley National Laboratory

## LBL Publications

### Title

[Th(III){n5-c5H3(SiMe3)2}], AN ACTINIDE COMPOUND WITH A 6dI GROUND STATE

### Permalink

<https://escholarship.org/uc/item/6z5799ft>

### Author

Kot, W.K.

### Publication Date

1987-10-01



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Chemical  
Sciences Division

RECEIVED  
LAWRENCE  
BERKELEY LABORATORY

NOV 20 1987

LIBRARY AND  
DOCUMENTS SECTION

Submitted to the Journal of the  
American Chemical Society

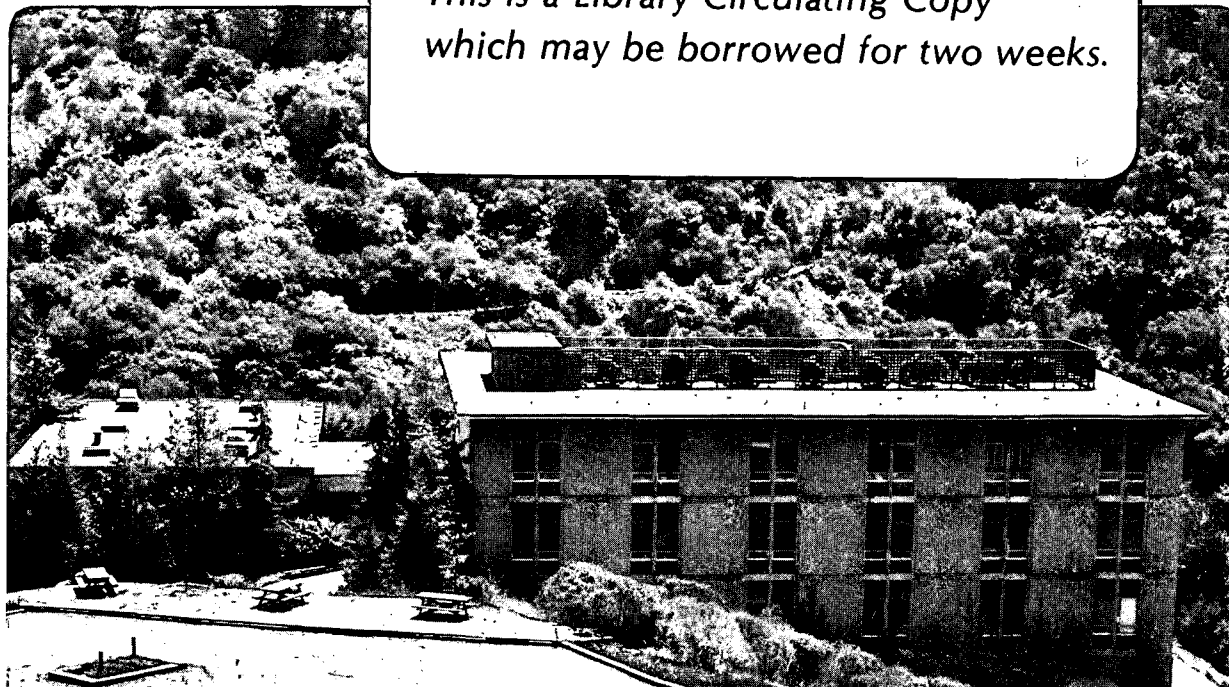
$[\text{Th(III)}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\}_3]$ , An  
Actinide Compound with a  $6d^1$  Ground State

W.K. Kot, G.V. Shalimoff, N.M. Edelstein,  
M.A. Edelman, and M.F. Lappert

October 1987

**TWO-WEEK LOAN COPY**

*This is a Library Circulating Copy  
which may be borrowed for two weeks.*



LBL-24136  
c-2

## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal 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 its 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, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-24136

**[Th(III){ $\eta^5$ -C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>], An Actinide Compound  
With a 6d<sup>1</sup> Ground State**

Wing K. Kot, George V. Shalimoff, and Norman M. Edelstein\*

Materials and Chemical Sciences Division

Lawrence Berkeley Laboratory

and

Department of Chemistry

University of California

Berkeley, California 94720 U.S.A.

and

Michael A. Edelman and Michael F. Lappert\*

School of Chemistry and Molecular Sciences

University of Sussex

Brighton BN1 9QJ, United Kingdom

**Abstract**

EPR (electron paramagnetic resonance) spectra of Th[ $\eta^5$ -C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (ThCp<sub>3</sub><sup>II</sup>) have been measured in methylcyclohexane solution and as a powder at various temperatures. From an analysis of the spin-Hamiltonian parameters it is concluded that ThCp<sub>3</sub><sup>II</sup> has a 6d<sup>1</sup> ground state.

# [Th(III){ $\eta^5$ -C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>], An Actinide Compound

## With a 6d<sup>1</sup> Ground State

The free ion of trivalent thorium [Th(III)] has a 5f<sup>1</sup> ground configuration whose center of gravity is 9897 cm<sup>-1</sup> below the center of gravity of the excited 6d<sup>1</sup> configuration. The 7s<sup>1</sup> level is at 23,120 cm<sup>-1</sup> while the 7p<sub>1/2,3/2</sub> levels are found at energies greater than 60,000 cm<sup>-1</sup> above the ground state.<sup>1</sup> Although the free ion spectrum of the isoelectronic ion Pa(IV) is not known, the difference between the centers of gravity of the ground 5f<sup>1</sup> configuration and the excited 6d<sup>1</sup> configuration for this ion is estimated to be ~ 50,000 cm<sup>-1</sup> from the interpolation of the known free ion data for the isoelectronic series Ra(I), Ac(II), Th(III), and U(V).<sup>2,3</sup> Optical spectra of Pa(IV)/ThBr<sub>4</sub> and PaCl<sub>6</sub><sup>2-</sup> showed the lowest 5f<sup>1</sup> → 6d<sup>1</sup> crystal field transition appeared at ~ 20,000 cm<sup>-1</sup>.<sup>4,5</sup> Two factors contribute to the decrease of the energy of this transition as compared to the free ion. The first is the decrease of the 6d<sup>1</sup> center of gravity relative to the center of gravity of the 5f<sup>1</sup> configuration which is caused by the electrostatic interaction of the metal ion orbitals with the negatively charged ligands. The second is the much greater crystal field splitting of the 6d orbitals relative to the 5f orbitals. The first interaction is formulated as the spherically symmetric term in crystal field theory and is usually ignored when relative crystal field energies within a configuration are determined.<sup>6</sup> Assuming the total crystal field splitting for the 6d<sup>1</sup> orbitals for PaCl<sub>6</sub><sup>2-</sup> is ~ 20,000 cm<sup>-1</sup>, we estimate the splitting between the centers of gravity of the 5f<sup>1</sup> and 6d<sup>1</sup> configuration for PaCl<sub>6</sub><sup>2-</sup> to be ~ 25,000 cm<sup>-1</sup>. Thus in this compound, the Pa(IV) 5f<sup>1</sup> → 6d<sup>1</sup> (centers of gravity) splitting is lowered by 25,000 cm<sup>-1</sup> from the free ion to

the crystal. These arguments suggest that for Th(III) in a crystal field, the ground state could arise from the  $6d^1$  configuration.

The Th(III) compound,  $\text{ThCp}_3''$  [ $\text{Cp}'' = \eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2)_3\text{-1,3}$ ], has recently been synthesized and structurally characterized.<sup>7</sup> EPR (electron paramagnetic resonance) spectra of powdered samples and of solutions in dry, degassed methylcyclohexane were obtained at 10K-300K.<sup>8</sup> The spectra obtained could be fit with the parameters of the spin-Hamiltonian<sup>9</sup>

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y).$$

Representative values of the  $g$  tensor components at various temperatures are given in Table 1.

The coordination environment about the Th(III) ion in the  $\text{Cp}''$  compound can be approximated as trigonal planar (considering only  $\text{Th}(\text{Cen})_3$ , where Cen denotes the centroid of the  $\text{Cp}''$  ligand),<sup>7</sup> and in the following discussion we assume  $D_{3h}$  symmetry about the Th(III) ion. In this symmetry the  $d$  orbitals split into a singlet  $A'_1$  and two doublets  $E'$ ,  $E''$ . From simple crystal field arguments the  $A'_1$  state should be lowest in energy. This assignment is consistent with the observed EPR spectrum. Spectra are observed at room temperature, and there is essentially no difference between the powder spectrum and that of the frozen glass. If an  $E'$  or  $E''$  state were lowest, the rapid spin-lattice relaxation time would result in a broadened or unobservable room temperature spectrum. If the  $5f^1$  configuration were lowest, no room temperature spectrum would be observed and the  $g$  values would be markedly different from  $g = 2$ . If the  $7s^1$  configuration were lowest, only an isotropic EPR spectrum would be observed with  $g = 2.00$ .

If we assume the above simplified crystal field model and allow spin-orbit coupling to mix the higher lying  $E''$  state with the ground  $A'_1$  state, we can calculate

values for the  $g$  tensor. The Th(III) free ion value for  $\zeta_{6d}$  is equal to  $2117 \text{ cm}^{-1}$ . Assuming the orbital reduction factor ( $k\bar{l}_i$ ) both for the spin-orbit coupling constant and the orbital angular momentum operator is  $\sim .4$ , and the  $E''$  state is approximately  $20,000 \text{ cm}^{-1}$  above the ground  $A'$  state, we calculate  $g_{\parallel} = 1.994$ ,  $g_{\perp} = 1.896$  which is in satisfactory agreement with the experimental result. The parameters in the above calculation are certainly not unique but show that plausible values of the various parameters give a reasonable fit.

We conclude the EPR spectrum is only consistent with a  $6d^1$  ground state for this Th(III) compound.<sup>10</sup>

#### Acknowledgements

This work was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

## References

- [ 1 ] Klinkenberg, P.F.A.; Lang, R.J.; 1949 *Physica* 15, 774.
- [ 2 ] Moore, C.E.; "Atomic Energy Levels" Vol. III, Nat. Bur. Stand., Washington, D.C., 1958.
- [ 3 ] Kaufman, V.; Radziemski, Jr., L.J.; 1976 *J. Opt. Soc. Am.* 66, 599.
- [ 4 ] Axe, J.D.; 1960, "The Electronic Structure of Octahedrally Coordinated Protactinium(IV)," Ph.D. Thesis, University of California, Berkeley; UCRL-9293.
- [ 5 ] Krupa, J.C. private communication.
- [ 6 ] Griffith, J.S.; "The Theory of Transition-Metal Ions," Cambridge Univ. Press, Cambridge, 1971.
- [ 7 ] Blake, P.C.; Lappert, M.F.; Atwood, J.L.; Zhang, H.; 1986 *J. Chem. Soc. Chem. Commun.* 1148.
- [ 8 ] EPR spectra were measured with an X-band ( $\sim 9.2$  GHz) Varian E-12 spectrometer and an Oxford Instruments Model ESR10 continuous flow cryostat. The magnetic field was monitored with a Varian Model E500 proton gaussmeter and the microwave frequency was measured with an EIP Model 548 frequency counter.
- [ 9 ] Abragam, A.; Bleaney, B.; "Electron Paramagnetic Resonance of Transition Ions," Oxford University Press, Oxford, 1970.
- [ 10 ] Gaseous  $\text{ThCp}_3''$  also has an unusually low value of 4.87 eV for the first ionization potential (Brennan, J.; Edelman, M.A.; Green, J.C.; Lappert, M.F. unpublished work).



Table 1. Spin Hamiltonian parameters for  $\text{Th}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\}_3$   
as a function of temperature.

	$g_{\parallel}$	$g_{\perp}$	$g_{\text{Ave}}$	Temp. ( $^{\circ}\text{K}$ )
Methylcyclohexane solution	-	-	$1.910 \pm .001$	300
Methylcyclohexane solution	$1.9725 \pm .001$	$1.879 \pm .001$	$1.910^a$	10-110
Powdered solid	$1.972 \pm .001$	$1.878 \pm .001$	$1.909^a$	10-300

<sup>a</sup>Calculated from  $\frac{1}{3}(g_{\parallel} + 2g_{\perp})$ .

*LAWRENCE BERKELEY LABORATORY  
TECHNICAL INFORMATION DEPARTMENT  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720*