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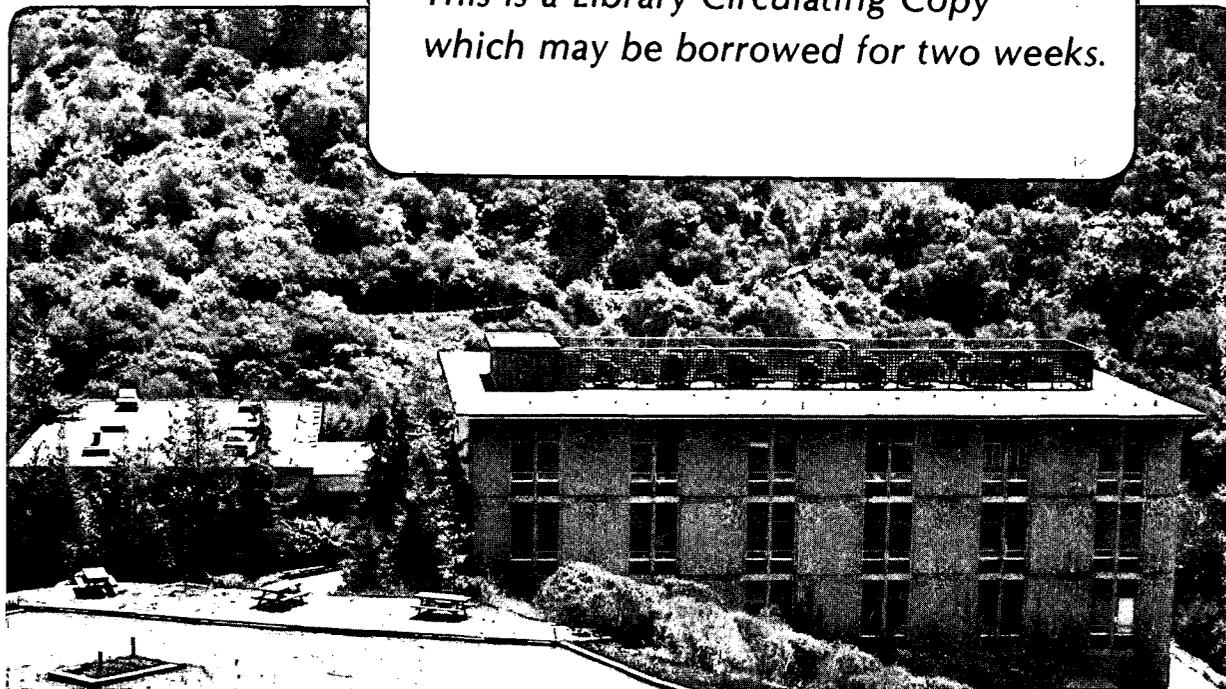
**[Th(III) $\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\}_3$], An
Actinide Compound with a $6d^1$ Ground State**

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[Th(III){ η^5 -C₅H₃(SiMe₃)₂]₃], An Actinide Compound
With a 6d¹ Ground State

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Abstract

EPR (electron paramagnetic resonance) spectra of Th[η^5 -C₅H₃(SiMe₃)₂]₃ (ThCp₃'') 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 ThCp₃''' has a 6d¹ ground state.

[Th(III){ η^5 -C₅H₃(SiMe₃)₂]₃], An Actinide Compound

With a 6d¹ Ground State

The free ion of trivalent thorium [Th(III)] has a 5f¹ ground configuration whose center of gravity is 9897 cm⁻¹ below the center of gravity of the excited 6d¹ configuration. The 7s¹ level is at 23,120 cm⁻¹ while the 7p_{1/2,3/2} levels are found at energies greater than 60,000 cm⁻¹ above the ground state.¹ Although the free ion spectrum of the isoelectronic ion Pa(IV) is not known, the difference between the centers of gravity of the ground 5f¹ configuration and the excited 6d¹ configuration for this ion is estimated to be ~ 50,000 cm⁻¹ from the interpolation of the known free ion data for the isoelectronic series Ra(I), Ac(II), Th(III), and U(V).^{2,3} Optical spectra of Pa(IV)/ThBr₄ and PaCl₆²⁻ showed the lowest 5f¹ → 6d¹ crystal field transition appeared at ~ 20,000 cm⁻¹.^{4,5} 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 6d¹ center of gravity relative to the center of gravity of the 5f¹ 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.⁶ Assuming the total crystal field splitting for the 6d¹ orbitals for PaCl₆²⁻ is ~ 20,000 cm⁻¹, we estimate the splitting between the centers of gravity of the 5f¹ and 6d¹ configuration for PaCl₆²⁻ to be ~ 25,000 cm⁻¹. Thus in this compound, the Pa(IV) 5f¹ → 6d¹ (centers of gravity) splitting is lowered by 25,000 cm⁻¹ 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, 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.⁷ EPR (electron paramagnetic resonance) spectra of powdered samples and of solutions in dry, degassed methylcyclohexane were obtained at 10K-300K.⁸ The spectra obtained could be fit with the parameters of the spin-Hamiltonian⁹

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

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 Cp'' compound can be approximated as trigonal planar (considering only $\text{Th}(\text{Cen})_3$, where Cen denotes the centroid of the Cp'' ligand),⁷ 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 ζ_{6d} is equal to 2117 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.¹⁰

Acknowledgements

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- [10] Gaseous $\text{ThCp}_3^{\prime\prime}$ 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_{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

^aCalculated from $\frac{1}{3}(g_{\parallel} + 2g_{\perp})$.

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