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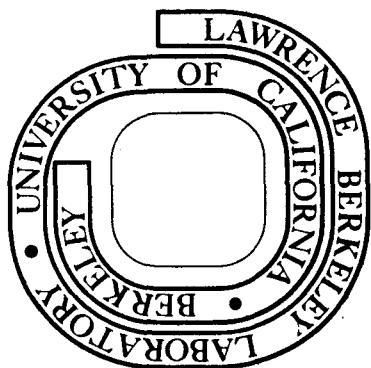
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MAGNETIC SUSCEPTIBILITIES OF URANOCENES WITH
HYDROCARBON SUBSTITUENTS AND THEIR ELECTRONIC GROUND STATES[†]

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ABSTRACT

The low temperature magnetic susceptibilities of $[(\text{CH}_3)_4\text{COT}]_2\text{U}$, $[(\text{C}_6\text{H}_5)_4\text{COT}]_2\text{U}$, and $[(\text{C}_6\text{H}_5)\text{COT}]_2\text{U}$ are reported. These measurements are consistent with the calculation of Hayes and Edelstein but are in contradiction with the results of Amberger, Fischer and Kanellakopulos. Furthermore, it is shown the empirical parameters of the latter authors fail to give a diamagnetic ground state for $\text{Pu}(\text{COT})_2$ as found experimentally.

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Introduction

The successful syntheses of neutral cyclooctatetraene sandwich complexes with the first five tetravalent ions of the actinide series (Th^{4+} - Pu^{4+}) has generated much interest in the electronic structures of these compounds.¹⁻⁵ The original impetus for the synthetic work came from the recognition that the highest filled orbitals of the cyclooctatetraene (COT) dianion (a 10 π electron system) and an f electron metal ion which could be involved in bonding were similar to the bonding orbitals of iron series bis cyclopentadienyl compounds except that the orbitals had one more node in rotating about the symmetry axis. This qualitative picture was later supported by a molecular orbital calculation by Hayes and Edelstein⁶ (HE) which showed considerable mixing of the ligand $\ell_z = \pm 2$ orbitals and the corresponding metal f-orbital. This calculation showed that the main feature of their electronic ground states was determined by the one electron antibonding metal-like orbitals occurring in two groups with the $\ell_z = \pm 1, \pm 3$ orbitals lying below the $\ell_z = \pm 2, 0$ orbitals. This ordering was reproduced with an effective crystalline field potential. By this method the results of the one-electron molecular orbital calculation were included in the diagonalization of the electrostatic, spin-orbit, and crystalline field matrices for the f^n systems of interest. The calculated ground state magnetic properties for $\text{U}(\text{COT})_2$, $\text{Np}(\text{COT})_2$, and $\text{Pu}(\text{COT})_2$ were in good agreement with the experimental results.

This calculation predicts Curie-Weiss behavior for the magnetic susceptibility of uranocene below $\sim 300^\circ\text{K}$. The experimental evidence, however, indicates that the susceptibility becomes temperature independent below 10°K .⁷ It was suggested this deviation from the predicted behavior could be explained by a low symmetry crystalline field lifting the ground

state degeneracy of the $J_z = \pm 3$ states which was imposed by the assumption of a C_8 molecular axis in the molecular orbital model.^{6,7}

An alternative model has been proposed to explain the temperature dependence of the magnetic susceptibility of $U(COT)_2$ by Amberger, Fischer and Kanellakopoulos (AFK). In this model, which also assumes a C_8 symmetry axis, the lowest state for the ground $J=4$ term is a singlet $J_z = 0$ level. The $J_z = \pm 1$ level is then placed 17 cm^{-1} above the ground state in order to reproduce the experimental susceptibility. A number of theoretical approaches were used in an attempt to verify this model. Values were also given for the crystalline field parameters which gave the optimal fit to the measured susceptibility.

This alternative model seriously challenges the concept of the uranocenes as an aromatic f-electron organometallic series homologous to d-electron metallocenes. A distinction between these two models can be made by the study of the magnetic behavior of related organoactinide compounds. In this paper we present magnetic measurements on several substituted uranocenes. We also extend the calculations of AFK to include $Np(COT)_2$ and $Pu(COT)_2$. This work will demonstrate that at this time only the HE model is consistent with all of the data and supports Streitwieser's original concept.

Experimental

The compounds were prepared by the methods previously described.^{9,10,11} The samples were sublimed immediately before use. The empty sample container was weighed, passed into an inert atmosphere box, and the sample was transferred into it. The filled sample container was then removed from the inert atmosphere box, reweighed, and then placed in a Schlenk tube until measured.

The measurements were obtained with a PAR Model 155 vibrating sample magnetometer in conjunction with a homogenous magnetic field produced by Varian Associates 12 inch electromagnetic capable of a maximum field strength of 12.5 kilogauss. The magnetometer was calibrated with $\text{Hg Co}(\text{CNS})_4$.¹² A variable temperature liquid helium dewar provide sample temperatures in the range 1.5 - 100°K. The temperature was measured with a calibrated GaAs diode placed approximately one half inch above the sample.

Results and Discussion

The results of the measurements are summarized in Table I. Typical graphs of the inverse susceptibility vs temperature for two compounds are shown in Figs. 1 and 2. The measured susceptibilities of the substituted uranocenes (Table 1 and earlier measurements⁷) fall into two classes, one which shows a Curie-Weiss dependence in the temperature range measured, the second, which follows the Curie-Weiss dependence down to approximately 10 - 20°K where at these temperatures the susceptibility becomes temperature independent.

In this paper we make the assumption that the gross electronic structure of uranocene and its substituted analogs are basically similar. The experimental evidence supports this assumption, for the optical spectra show only minor shifts from one compound to another and the ring proton magnetic resonance spectra of the various uranocenes occur in the same region.¹⁰ Furthermore, the empirical electronic magnetic moments are very similar.⁷ Therefore, we expect the model which explains the uranocene data should also hold as a first approximation for its substituted analogs even though the local symmetry is certainly lower in the latter compounds.

The ring substituents appear to have only minor effects on the electronic properties of these compounds.

The magnetic data presented earlier show Curie-Weiss behavior for two of the compounds over the entire temperature range. This type of magnetism is incompatible with the model given by AFK which requires the $J_z = 0$ level to be the lowest crystalline field level.

We have extended the AFK calculations to include $\text{Np}(\text{COT})_2$ and $\text{Pu}(\text{COT})_2$. We used their empirical crystalline field parameters with the spin orbit and electrostatic parameters described previously⁶ to determine the ground state level structure and magnetic properties for these higher Z actinide complexes. Since AFK did not use the complete f^2 basis set we have slightly different crystalline field parameters. The results of the calculations are shown in Table 2 and the values of the crystalline field parameters are given in Table 3.

These calculations give the effective moment for $\text{Np}(\text{COT})_2$ as 2.35 BM, in fair agreement with the experimental value of 1.8 BM. However the ground state of $\text{Pu}(\text{COT})_2$ is predicted to be the $J_z = \pm 4$ state which would be paramagnetic and follow the Curie-Weiss law. This prediction is in contradiction with the striking diamagnetic behavior of $\text{Pu}(\text{COT})_2$ and shows again the inadequacies of the AFK model.

Conclusion

At this time there have been two models proposed to explain the experimental results on actinide cyclooctatetraene compounds. In this paper we have presented further experimental evidence and calculations which support the HE model. Further experiments are necessary to guide more detailed theoretical calculations.

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TABLE 1. Magnetic properties of some substituted uranocenes.*

Compound	Temperature (°K)	μ_{eff} BM	θ (°K)
$[(\text{CH}_3)_4\text{COT}]_2\text{U}$	1.9 - 73.7	2.2 ± 0.2	11.3 ± 3
$[(\text{C}_6\text{H}_5)_4\text{COT}]_2\text{U}$	4.2 - 100	2.5 ± 0.1	6.7 ± 1
$[\text{C}_6\text{H}_5\text{COT}]_2\text{U}$	14 - 100 < 8	2.65 ± 0.2 TIP ($\chi_M = 0.036 \pm 0.001$ emu)	12.2 ± 3
<p>*$\chi_M = C/T + \theta$</p> <p>$\mu_{\text{eff}} = 2.84\sqrt{C}$ BM</p> <p>TIP = temperature independent paramagnetism</p>			

TABLE 2. Ground state energy levels and magnetic properties of $\text{Ac}(\text{COT})_2$ compounds, $\text{Ac} = \text{U}, \text{Np},$ and Pu , predicted by the AFK models.

$\text{U}(\text{C}_8\text{H}_8)_2^a$			$\text{U}(\text{C}_8\text{H}_8)_2^b$			$\text{Np}(\text{C}_8\text{H}_8)_2^b$			$\text{Pu}(\text{C}_8\text{H}_8)_2^b$		
J_z	E, cm^{-1}	g_{\parallel}	J_z	E, cm^{-1}	g_{\parallel}	J_z	E, cm^{-1}	g_{\parallel}	J_z	E, cm^{-1}	g_{\parallel}
0	0	--	0	0	0	$\pm 7/2$	-2612.6	4.694	± 4	-5901.7	4.552
± 1	17	--	± 1	19.1	.654	$\pm 1/2$	-2404.6	1.302 ^c	± 2	-3849.4	2.230
± 2	200	--	± 2	202.6	3.454	$\pm 5/2$	-2011.3	3.802	± 1	-3314.8	-.427
± 3	1535	--	± 3	1537.5	6.380	$\pm 3/2$	-1691.9	3.307	± 3	-2287.3	5.835
± 4	6600	--	± 4	6779.3	9.098	$\pm 9/2$	-683.0	8.187	0	-1770.6	0

^aValues given in Ref. 8
^bThis work $g_{\perp} = 0$ unless noted
^c $g_{\perp} = 2.972$

TABLE 3. Values of the empirical crystalline field parameter.^a

B_0^2	$-11220.^b \text{ cm}^{-1}$	$-10356.4^c \text{ cm}^{-1}$
B_0^4	$-11408.^b \text{ cm}^{-1}$	$-9936.0^c \text{ cm}^{-1}$
B_0^6	$-11680.^b \text{ cm}^{-1}$	$-14324.4^c \text{ cm}^{-1}$

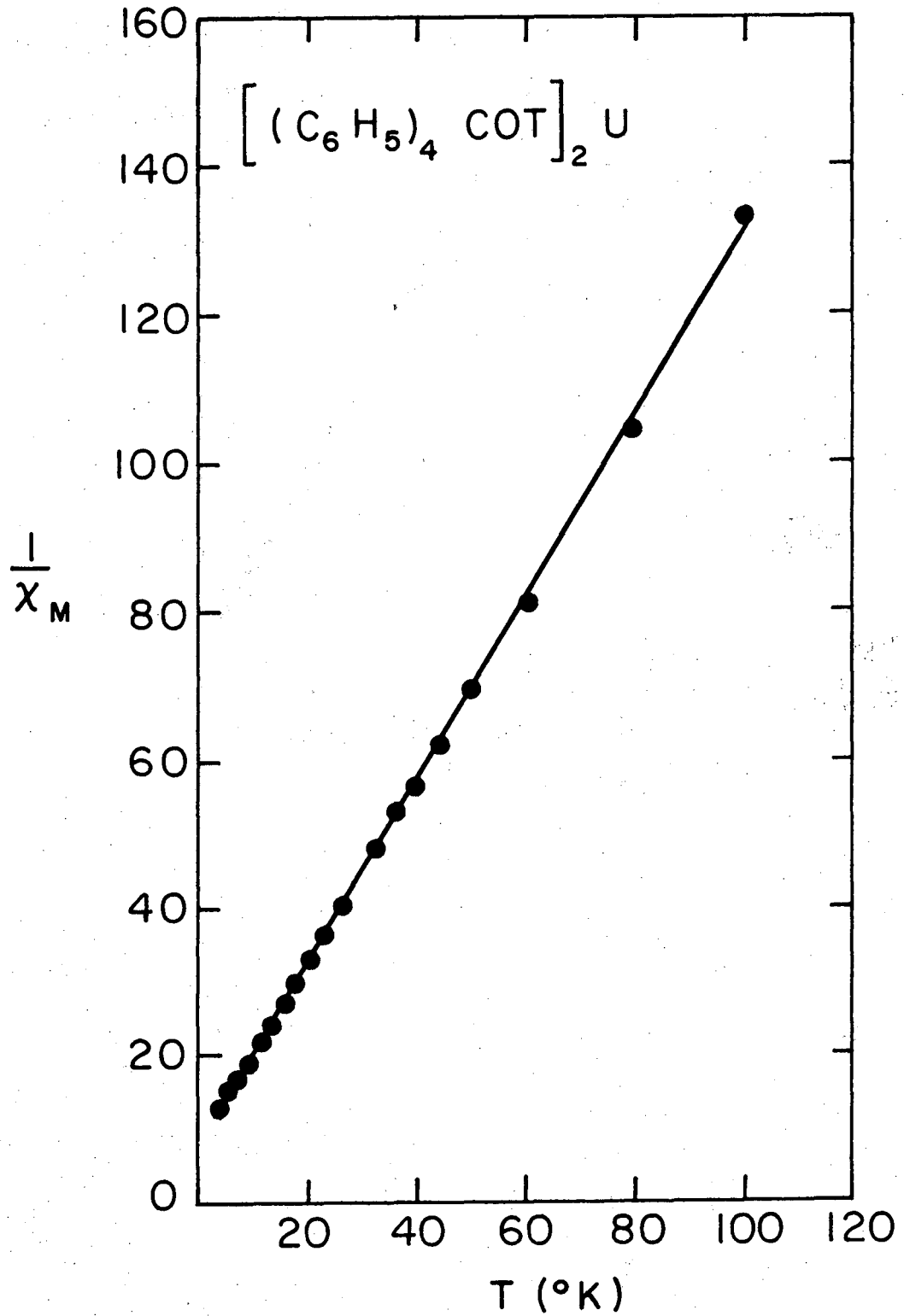
^aNomenclature as given in ref. 6

^bAFK parameters obtained with an incomplete f^2 basis set.

^cParameters obtained in this work with the complete f^2 basis set.

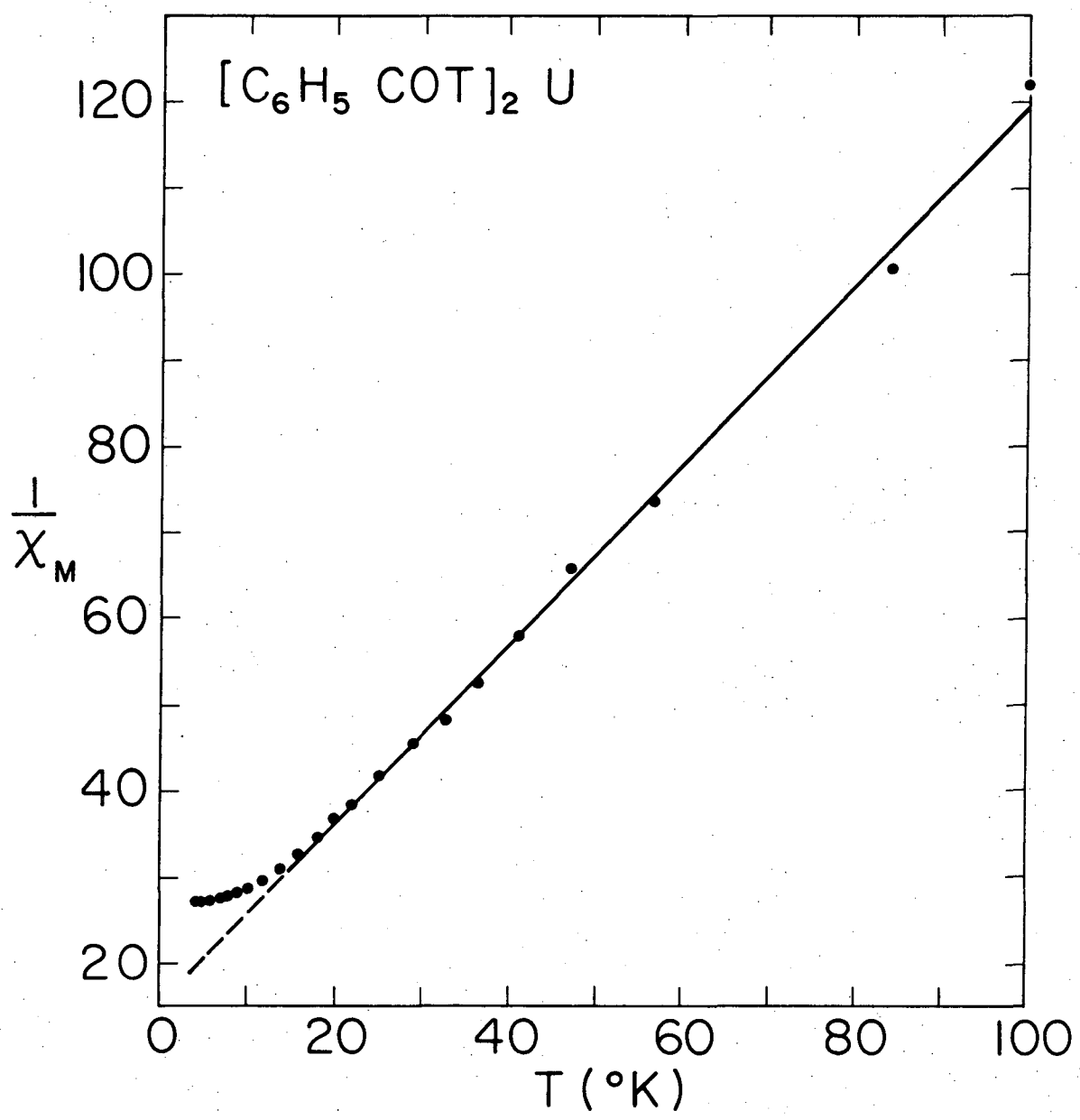
Fig. 1. $1/\chi_M$ vs T for a sample of $[(C_6H_5)_4COT]_2U$. The smooth line represents a least-square fit to the experimental data.

Fig. 2. $1/\chi_M$ vs T for a sample of $[C_6H_5COT]_2U$. The smooth line represents a least-square fit to the experimental data.



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Fig. 1



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Fig. 2

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