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PROTON MAGNETIC RESONANCE SHIFTS IN BIS(CYCLOOCTATETRAENYL)URANIUM(IV)[†]

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The measured proton resonance shifts of $U(COT)_2$ are analyzed on the basis of a crystalline field model and magnetic susceptibility data. It is pointed out that in $U(COT)_2$ the orbital and spin angular momenta are coupled antiparallel for the ground state, so that a positive hyperfine coupling constant due to the Fermi contact term will result in an upfield proton resonance shift. The hyperfine coupling constant arising from the Fermi contact term is found to be $A_F = +0.90 \text{ Mhz} \pm 25\%$.

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I. Introduction

The question of the extent of participation of the f orbitals in the metal-ligand covalency of organometallic actinide complexes has received renewed attention recently [1-4], with the emphasis on interpreting the Fermi contact contribution to the observed proton nmr shift of such paramagnetic complexes [1]. In complexes with magnetic anisotropy [2,3], both the contact and dipolar interactions [5,6] contribute to the isotropic shift, and before any interpretation of the contact shift can be put forth, an estimate of the dipolar shift must be made. The lack of reliable structural or magnetic data has prevented detailed and unambiguous analyses for most systems. We wish to present here solution proton nmr data for bis (cyclooctatetraenyl)uranium(IV), $U(COT)_2$ [7], also called "uranocene", for which both the structural [8] and magnetic [9] data are available, and interpret the shifts in terms of a crystalline field model [9]. From our analysis, we determine that part of the isotropic shift arises from the Fermi contact term, and reach some qualitative conclusions as to its electronic origin in relation to the metal-ligand bonding.

II. Experimental

Samples of uranocene prepared according to the method of Streitwieser and Müller-Westerhoff [7] were dissolved in hot THF- d_8 or deuterated toluene and sealed under argon. The proton magnetic resonance shifts were measured on a Varian HR-100 spectrometer modified for variable frequency modulation. The temperature was controlled by a precalibrated Varian V-4343 unit. The shifts measured are plotted in fig. 1 and tabulated in Table I. All shifts are referenced to the proton resonance in COT^{--} which was taken as -5.9 ppm with respect to TMS. The actual data were measured with respect to the trace amounts of protons in the deuterated solvents and were later corrected to the proton resonance of COT^{--} . The shifts in both solvents agreed within experimental error. The lines widths appeared to be temperature independent and of the order of 10 Hz.

III. Discussion

The magnetic susceptibility data on polycrystalline $U(COT)_2$ of Karraker, et al. [9], followed the Curie-Weiss law in the temperature range $4.2^\circ K - 45^\circ K$ with an effective moment of 2.4 BM. Measurements of the magnetic susceptibility of $U(COT)_2$ in the temperature range $10^\circ K - 300^\circ K$ have been performed by Dr. D. K. Fujita of the Lawrence Radiation Laboratory who found Curie-Weiss behaviour with an effective moment of 2.6 BM. The above magnetic data were interpreted on the basis of a crystalline field model with covalency parameterized by use of the orbital reduction factor [9]. We shall use the same model to interpret the proton magnetic resonance shifts.

We make the following assumptions: 1) only the ground crystalline field state is populated in the temperature range of interest; that is, $E_1 \gg kT$ where E_1 is the energy of the first excited crystalline field state, 2) the crystalline field does not mix different J states; 3) the effects of intermediate coupling are negligible.

For U^{4+} (Ac core, $5f^2$) the ground term is a 3H_4 . In a crystalline field of D_{8h} symmetry this ninefold degenerate level will split into four doublets ($J_z = \pm 4, \pm 3, \pm 2, \pm 1$) and 1 singlet ($J_z = 0$). It was shown previously that the magnetic susceptibility data were consistent with the $J_z = \pm 4$ doublet lying lowest if an orbital reduction factor of $k \approx .8$ was introduced [9]. We have calculated the dipolar shift using the equation [10]

$$\left\langle \frac{\Delta H_D}{H_0} \right\rangle = (3R^3)^{-1} [\chi_{\parallel} - \chi_{\perp}] [3 \cos^2 \Omega - 1]$$

which is applicable when $T_1 \ll \tau_c$; where T_1 is the electronic relaxation time, τ_c is correlation time of complex, $\chi_{\parallel}$ is the magnetic susceptibility along the

C_8 axis, and $\chi_{\perp}$ is the magnetic susceptibility in the plane perpendicular to the C_8 axis and is zero according to our model. The angle Ω is the angle between the C_8 symmetry axis and the vector of length R connecting the U nucleus with a proton nucleus. This angle can be calculated from the previously determined crystallographic structure [8]. Because the quantity $(3 \cos^2 \Omega - 1)$ is close to zero, it is very sensitive to the uncertainty in the structure. We have used in our calculations the two extreme values and the average value for the angle and a C-H distance of 1.09 Å, the results for the dipolar shift at 302°K are shown in Table II. The last column in Table II shows the possible range of the Fermi contact shift at 302°K due to the uncertainty of the angle Ω .

The Hamiltonian for the Fermi contact term may be written in the effective operator formalism as

$$\mathcal{H}_F = A_F \vec{I} \cdot \vec{S} ,$$

where A_F is hyperfine coupling constant for this type of interaction.

In the $SLJJ_z$ representation it is straightforward to evaluate matrix elements of the type [11]

$$\langle SLJJ_z | \vec{O} | SLJJ_z \rangle$$

for a 3H_4 state with $J_z = \pm 4$ and $\vec{O}$ being $\vec{S}$ or $k\vec{L} + 2\vec{S}$. The matrix elements needed are tabulated in Table III. The off-diagonal components (S_x , etc.) are zero since we assumed only the $J_z = \pm 4$ states were populated.

It is important to note that in a magnetic field the $J_z = -4$ state is lowest in energy and for this state $S_z = +4/5$. Thus the ground crystalline field state of $U(COT)_2$ has S_z parallel to the magnetic field. This is opposite to the direction found, for example, in 3d transition metal complexes where the orbital angular momentum is quenched so the spin angular momentum will be anti-parallel to the magnetic field. Thus for the same type of spin delocalization mechanism in iso-structural 3d and 5f complexes, assuming Hund's rules are valid for the ground state, the contact shifts in the two complexes will be of opposite sign if the f shell is less than half filled, and of the same sign if the f shell is more than half filled [12].

The thermal average of $\langle S_z \rangle$ is

$$\langle S_z \rangle = \frac{4/5 \exp \left(+ \frac{4g_J' \beta H_o}{kT} \right) - 4/5 \exp \left(- \frac{4g_J' \beta H_o}{kT} \right)}{\exp \left(+ \frac{4g_J' \beta H_o}{kT} \right) + \exp \left(- \frac{4g_J' \beta H_o}{kT} \right)}$$

If we assume for the temperatures and magnetic fields of interest

$$4g_J' \beta H_o \ll kT$$

so

$$\langle S_z \rangle = \frac{16}{5} \frac{g_J' \beta H_o}{kT}$$

and therefore in the limit $T_1 \ll \tau_c$

$$\langle S_z \rangle_{\text{Ave.}} = \frac{1}{3} \left(\frac{16}{5} \frac{g_J' \beta H_o}{kT} \right)$$

Then if we use frequency units

$$\delta = \frac{1}{3} A_F \left(\frac{16}{5} \frac{g_J' \beta H_0}{kT} \right)$$

where δ is the Fermi contact shift, A_F is the hyperfine coupling constant of the protons and the units are Mhz. From our data assuming $k = .85$ and therefore $g_J = .6$, we obtain

$$A_F = +0.90 \text{ Mhz} \pm 25\%.$$

It should be emphasized that because of the assumptions in our calculations and the uncertainty in the dipolar contribution we place this large error on the value of A_F .

Extrapolation of the experimental shifts of fig. 1 to $1/T = 0$ yields ~ -6 ppm for the intercept. The proton magnetic resonance spectrum of a similar diamagnetic compound has not been obtained so our reference could be off by -2 to -3 ppm. If we consider the $J_z = \pm 3$ level to be at $\sim 400-600 \text{ cm}^{-1}$, an extrapolated shift of ~ -3 ppm can be explained. A crystalline field level around this energy would be consistent with the accuracy of the magnetic susceptibility experiments.

If only pi bonding were present in this complex we would expect much smaller Fermi contact shifts and the opposite sign. Therefore, sigma bonding is certainly important if not dominant, although as yet we do not have enough information to be more quantitative. Furthermore, even the sigma spin delocalization need not be directly related to 5f covalency, since exchange polarization between the 5f and 6s or 6p electrons or other mechanisms cannot be ruled out [12-14]. Further investigations, some of which are currently in progress in our laboratories are required to elucidate the bonding in this complex.

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Table I. Proton resonance shifts of $U(COT)_2$ as a function temperature (referenced with respect to $COT=$).

Temperature $^{\circ}K$	Measured Shift (ppm)
353 ± 2	+ 34.9
328 ± 2	+ 37.6
302 ± 1	+ 41.9
273 ± 2	+ 47.0
248 ± 2	+ 52.0
223 ± 3	+ 58.4
198 ± 3	+ 67.7

Table II. Contributions to the measured proton shifts at 302°K from the dipolar and Fermi contact terms for various values of the angle Ω .

R (Å)	$(3\cos^2\Omega-1)$	$\left\langle \frac{\Delta H_D}{H} \right\rangle$ at 302°K (ppm)	$\left\langle \frac{\Delta H_F}{H} \right\rangle$ at 302°K (ppm)
3.481	-0.092	+ 8.6	+33.3
3.498	-0.152	+14.0	+27.9
3.515	-0.210	+19.2	+22.7

Table III. Values of the matrix elements for various operators for the ground state of $U(COT)_2$.

Operator	J_z	Value of Matrix Element
$kL_z + 2S_z$	-4	$-4g_j^1$
$kL_z + 2S_z$	4	$4g_j^1$
S_z	-4	$+4/5$
S_z	4	$-4/5$

Figure Caption

Fig. 1. Proton resonance shifts as a function of $1/T$ for $U(COT)_2$ (referenced with respect to $COT^{\equiv}$).

Fig. 1

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