Inorganica Chimica Acta, *139* (1987) 319–321

Anisotropy in the Proton NMR Paramagnetic Shift of Cyclooctatetraene and Cyclopentadiene Anions Coordinated to U(IV)*

B. R. McGARVEY† and S. NAGY

Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, N9B 3P4, Canada

NMR spectra for uranocene, $U(C_8H_8)_2$, and chloro-tris(η_5-cyclopentadienyl)uranium(IV), $U(C_5H_5)_3Cl$, powders have been obtained at temperatures from 90 K to 298 K using a Bruker CXP-90 FT spectrometer operating at 90.02 MHz. The samples were in spherical glass containers to minimize shifts due to internal magnetic fields induced by the paramagnetism of the samples. Normal techniques, such as the solid state echo, used to get reliable line shapes in these broad resonances did not work due to the motional processes taking place in the solids. We finally resorted to the baseline correction technique of Henrichs *et al.* [1] in which both first- and second-order phase corrections were carried out instrumentally and the baseline appropriately corrected for pulse breakthrough. 90° pulse times were 2.5 μs, giving more than adequate B_1 values for the line widths found in this work.

Typical spectra are shown in Figs. 1 and 2. Both systems display a distinctly anisotropic shape at all temperatures. For uranocene the anisotropy is to high magnetic field while for $U(C_5H_5)_3Cl$ it is to low field. The marked line-width variation in $U(C_5H_5)_3Cl$ must be due to random reorientations of the molecule that are rapid enough above ~220 K to produce a liquid-like resonance.

Anisotropies of the sort observed here are often seen in paramagnetic powders and are generally due to the dipolar interaction between the unpaired f electrons on the metal atom and the nuclear spin being observed. In this work we attempted to analyse the line shapes to extract the principal shifts and then compare these to the values calculated for these systems. To do this calculation we need X-ray structural data, which is available [2, 3] and magnetic susceptibility data [4–7].

The line shapes appear to be of axial symmetry but are impossible to simulate if we assume a constant line width over all orientations. One major broadening mechanism is the dipolar spin–spin interaction of protons in the ring. This interaction is angularly dependent, with the line width in the parallel direction, being double that in the perpendicular direction. We have successfully simulated the line shape by assuming the line shape of the signal to be Gaussian with the second moment of the form

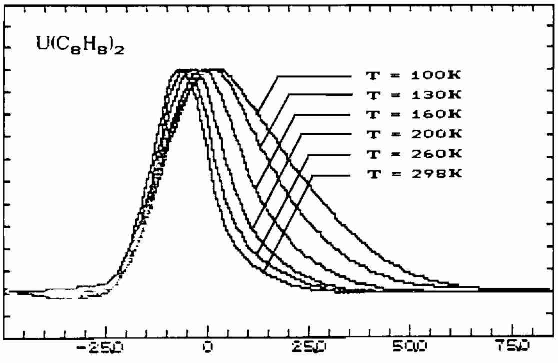

Fig. 1. Absorption proton NMR spectra for $U(C_8H_8)_2$ powder at different temperatures.

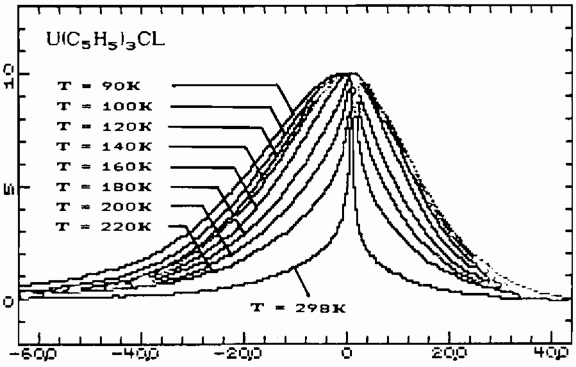

Fig. 2. Absorption proton NMR spectra for $U(C_5H_5)_3Cl$ powder at different temperatures.

$$\langle \Delta\nu^2 \rangle = A(3\cos^2\alpha - 1)^2 + B \qquad (1)$$

in which α is the angle between the magnetic field and the parallel axis. A and B are parameters to be adjusted in the fitting process. An example of the fitted *versus* experimental line shape is given in Fig. 3. In both systems the value of A remained constant with temperature. In the case of uranocene, the value of B increased linearly with T^{-1}. For $U(C_5H_5)_3Cl$ the temperature interval was too small to come to any conclusion. Comparison of A with values calculated for the ring systems from Van Vleck's equation [8] are consistent with a rotating ring in the case of uranocene and a rigid ring in the case of $U(C_5H_5)_3Cl$. Values for $\Delta H = (H_{\parallel} - H_{\perp})$ from these fittings are given in Tables I and II.

For uranocene we have calculated the dipolar shift for the individual molecule and the crystal case

---

*Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

†Author to whom correspondence should be addressed.

0020-1693/87/$3.50

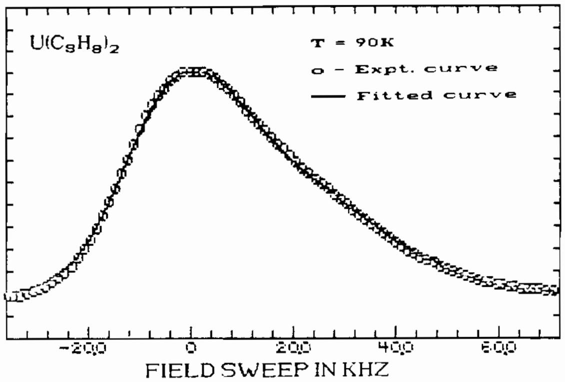

Fig. 3. Fitted and experimental shape for 90 K NMR spectrum of $U(C_8H_8)_2$ (method of simulation explained in text).

for both rotating and non-rotating rings. In the crystal we summed up the contribution of all uranium atoms up to a distance of 15 Å from each H atom. The non-rotating case gave very non-axial principal shifts that were too large. For example, at 100 K we find the principal shifts for one H atom to be –52.75, 2.82 and 55.99 kHz. For rotating rings the equations for a single molecule are:

$$(\Delta H/H_0)_{\parallel} = (1 - 3\cos^2\alpha)\chi_{\parallel}/R^3 \qquad (2)$$

$$(\Delta H/H_0)_{\perp} = (3\cos^2\alpha - 1)\chi_{\perp}/2R_3 \qquad (3)$$

$\chi_{\parallel}$ and $\chi_{\perp}$ are the atomic susceptibilities when the magnetic field is parallel and perpendicular to the C_8 axis of the molecule, R is the distance of the nucleus from the U atom, and α is the angle between the parallel axis and the R vector. Values calculated from these equations and for the crystal case are given in Table I. The crystal case gives three principal shifts but two of them are close to each other at lower field. Table I gives the separation between the highest and lowest calculated shifts. The R and α distances are taken from the X-ray data [2] with the assumption that the C–H bond is 1.08 Å and in the same plane as the carbon atoms while $\chi_{\parallel}$ and $\chi_{\perp}$ are calculated from equations given by Dallinger *et al.* [9]. The rather small values calculated for ΔH are due to α being close to the 'magic angle' which makes $(3\cos^2\alpha - 1) = 0$. The calculated dipolar values can

TABLE I. Summary of Calculations and Experiment on $U(C_8H_8)_2$

T (K)	$\chi_{\parallel}$[a]	$\chi_{\perp}$[a]	Cryst. calc. ΔH[b] (kHz)	One molecule ΔH[c] (kHz)	Expt. ΔH[c] (kHz)	δ (kHz)[d]
298	11.385	1.069	3.46	2.22	18.6	15.1
260	13.197	1.134	3.98	2.45	21.3	17.3
240	14.379	1.168	4.32	2.66	22.7	18.4
220	15.774	1.201	4.71	2.91	22.8	18.1
200	17.440	1.232	5.18	3.21	26.0	20.8
180	19.467	1.259	5.75	3.57	27.0	21.3
160	21.984	1.282	6.46	4.02	29.5	23.0
140	25.198	1.299	7.36	4.59	33.0	25.6
130	27.167	1.306	7.91	4.94	39.5	31.6
120	29.456	1.311	8.56	5.35	42.3	33.7
110	31.837	1.315	9.22	5.77	44.7	35.5
100	35.386	1.318	10.22	6.40	47.3	37.1
90	39.329	1.320	11.32	7.11	51.7	40.4

[a] In emu × 10^{27}. Calculated from equations in ref. 9. [b] $\Delta H = (H_3 - H_1)$ calculated from summation over neighboring uranocene molecules using crystal data from ref. 2. The principal shift H_2 is always close to H_1. [c] $\Delta H = (H_{\parallel} - H_{\perp})$. [d] δ is the difference between ΔH (experimental) and ΔH (crystal calculation).

TABLE II. Summary of Calculations and Experiment on $U(C_5H_5)_3Cl$

T (K)	χ[a]	One molecule ΔH[b] (kHz)	Expt. ΔH[b] (kHz)	δ (kHz)[c]
130	8.777	–63.0	–41.5	21.5
120	9.102	–65.4	–41.0	24.4
110	9.452	–67.9	–42.0	25.9
100	9.830	–70.6	–45.5	25.1
90	10.240	–73.5	–51.0	22.5

[a] In emu × 10^{27}. From ref. 5. [b] $\Delta H = (H_{\parallel} - H_{\perp})$. [c] δ is the difference between ΔH (experimental) and ΔH (one molecule calculation).

be brought closer to the observed values by bending the C–H bond towards the U atom, thus increasing α. The bond would have to be bent at least 20°, however, to get agreement with experiment. We consider such bending to be unacceptable, and must conclude that much of the difference between experiment and calculation (expressed as δ in Table I) must be due to the spin-transfer contribution to the paramagnetic shift.

The line width for $U(C_5H_5)_3Cl$ indicates that below 140 K the C_5H_5 rings are not rotating. In this case the principal shifts for one molecule would be

$$(\Delta H/H_0)_{\parallel} = -2\chi/R^3 \qquad (4)$$

$$(\Delta H/H_0)_{\perp} = \chi/R^3 \qquad (5)$$

if the magnetic susceptibility were isotropic. Values calculated from these equations are given in Table II. R was from the X-ray data [3] and χ was taken from Karraker and Stone [5]. Attempts were made to estimate $\chi_{\parallel}$ and $\chi_{\perp}$ from the ground state and excited parameters used by Amberger [10] to fit the optical and susceptibility data on $U(C_5H_5)_3Cl$, but we could not get reasonable values for χ(ave) from these parameters in the ~100 K region of temperature. We did try various reasonable values for $\chi_{\parallel}$ and $\chi_{\perp}$ but did not get much change in ΔH from what was obtained from the above equations. In this case the dipolar values for ΔH are of the correct sign but larger in magnitude than the observed values. The values of the difference δ are of the same sign as those found for uranocene and only slightly smaller in magnitude.

The spin-transfer contribution to the paramagnetic shift in protons is generally considered to be through the Fermi contact interaction and this is probably true here also, although it has been pointed out [11] that there could be a dipolar contribution from spins in the π-system of the ring. Since the Fermi contact interaction is only with the s orbitals, it has been considered by many workers that this interaction must be isotropic. For this reason these results should come as a major surprise to many. It has, however, been pointed out by a few authors [12–14] that the Fermi contact interaction can be anisotropic when the orbital angular momentum is not quenched. The results of this work are the first direct experimental evidence that such an anisotropy exists in the paramagnetic shift.

Acknowledgements

The uranocene sample was kindly furnished to us by Professor A. Streitweiser of the University of California at Berkeley. The work was supported through an operating grant from the National Science and Engineering Research Council of Canada.

References

1 P. M. Henrichs, J. M. Hewitt and R. H. Henry, *J. Magnetic Reson., 69*, 460 (1986).
2 A. Avdeef, K. N. Raymond, K. O. Hodgson and A. Zalkin, *Inorg. Chem., 11*, 1083 (1972).
3 C. Wong, T. Yen and T. Lee, *Acta Crystallogr., 18*, 340 (1966).
4 L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem., 2*, 246 (1956).
5 D. C. Karraker and J. A. Stone, *Inorg. Chem., 11*, 1742 (1972).
6 C. Aderhold, F. Baumgärtner, E. Dornberger and B. Kanellakopulos, *Z. Naturforsch., Teil A, 33*, 1268 (1978).
7 H. D. Amberger, R. D. Fischer and B. Kanellakapulos, *Theoret. Chim. Acta, 37*, 105 (1975).
8 J. H. Van Vleck, *Phys. Rev., 74*, 1168 (1948).
9 R. F. Dallinger, P. Stein and T. G. Spiro, *J. Am. Chem. Soc., 100*, 7865 (1978).
10 H. D. Amberger, *J. Organomet. Chem., 116*, 219 (1976).
11 B. R. McGarvey, *Can. J. Chem., 62*, 1349 (1984).
12 J. H. H. Thornley, C. G. Windsor and J. Owen, *Proc. R. Soc. London, Ser. A, 284*, 252 (1965).
13 B. R. McGarvey, *J. Chem. Phys., 65*, 962 (1976); *J. Chem. Phys., 70*, 4971 (1979).
14 B. R. McGarvey, in J. A. Weil (ed.), 'Electronic Magnetic Resonance of the Solid State', Chemical Institute of Canada, 1987, in press.