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## WIDELINE NMR STUDIES OF SOLID DICYCLOPENTADIENYL, DIBENZENE, AND DICYCLOOCTATETRAENYL METAL COMPLEXES

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### Summary

The wideline NMR spectra of a number of solid metallocene, dibenzene, and dicyclooctatetraenyl metal complexes were examined in the temperature range 178–381 K and the second moments of the linewidths were calculated. Experimental second moments were then compared with theoretical values based on the Van Vleck model. The calculations are consistent with essentially free rotation about the principle molecular symmetry axes, which is indicative of very low ring rotational barriers in all species studied. No substantial difference in metal–ring bonding is found between metallocene and dibenzene complexes. In the case of  $U(C_8H_8)_2$ , the second moment investigations support the results of recent crystallographic work showing the existence of distinct rotomers.

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### Introduction

The unique structure of “sandwich” molecules involving transition metals (or lanthanides and actinides) with hydrocarbon ligands such as benzene, or hydrocarbon anions such as cyclopentadienyl or cyclooctatetraenyl ions, has prompted recent investigations by us [1–4] and other workers [5–7] of the structure and bonding in these compounds. Except for a few early reports, however, a fairly important spectroscopic tool, namely wideline NMR, has been neglected in the study of these species. Because of the high symmetry ( $D_{5d}$ ,  $D_{6h}$ , and  $D_{8h}$ ) rendering the protons of the unsubstituted molecules magnetically equivalent, the NMR spectra of solids are simple and the linewidths can be interpreted in terms of intra- and intermolecular reorientation which occurs in the solid state [8]. In particular, the second moment,  $(\Delta H)^2$  of the observed lineshape gives direct information about these processes. For example, Holm and Ibers [9] studied the proton wideline NMR spectra of polycrystalline samples of ferrocene, ruthenocene, and titanocene dichloride and were able to determine the barriers of rotation about the five-fold cyclopentadienyl ring

axes. The barrier for ferrocene of  $1.8 \pm 0.2$  kcal agrees with more recent electron diffraction work [10]. Similarly, Mulay, Rochow and Fischer were able to interpret the temperature-dependence of the NMR of ferrocene and  $\text{Cr}(\text{C}_6\text{H}_6)_2$  in terms of ring rotation [11]. Nakajima [12] reported a difference in behavior at 77 K for nickelocene and chromocene; motion in the latter seemed to be severely restricted, judging from the comparative second moments.

Wideline NMR data have been reported by us for various dibenzene complexes in previous work [1], but no detailed explanation of the data was given at that time. Furthermore, the second moments reported in that work were calculated from an assumed Gaussian lineshape and the peak-to-peak separation of the experimental derivative curve [13]. We have redetermined the second moments for these and several additional compounds by the more accurate procedure of numerically integrating the derivative curves and then calculating the second moment exactly without any approximations regarding the NMR lineshape. Finally, recent X-ray structural results for uranocene [14] and bis(1,3,5,7-tetramethylcyclooctatetraenyl)uranium(IV) [15, 16], the latter of which suggest the absence of a unique  $D_{8h}$  geometry due to a low rotational barrier, prompted us to measure the wideline NMR spectrum of uranocene and determine the second moment. Experimental second moments for the series of five, six, and eight-membered ring species were then compared with theoretical values based on the Van Vleck model [17, 18], which allows calculation of both the rigid lattice and rotational second moments. Conclusions regarding intra- and intermolecular reorientation were then related to current theory of bonding in sandwich molecules.

## Results and discussion

The theory of NMR lineshapes and second moment calculations has been adequately described in the literature and the reader is referred there for such discussion [8, 17, 18]. Experimental values of second moments,  $(\Delta H)^2$ , and linewidths,  $(\Delta H)_{1/2}$ , defined at half-height, are given in Table 1 for a number of dibenzene metal complexes. The average deviations reported are for two or three experimental determinations and are usually less than 5%. For comparison, Table 2 contains second moments for some metallocene compounds and analogous unsubstituted ring species.

The metallocene data in Table 2 are entirely consistent with previous work [9] on ferrocene; second moments are in the range  $1.6\text{--}2.9 \text{ G}^2$  \* at room temperature. Theoretical calculations are only in agreement with this data if intra- and intermolecular reorientation processes reduce the rigid lattice second moments in the range  $7.8\text{--}8.8 \text{ G}^2$  to values of  $1.7\text{--}1.9 \text{ G}^2$ , which are obviously in excellent agreement with experiment. It appears that only at 77 K and below in the cases of  $\text{Fe}(\text{C}_5\text{H}_5)_2$  and  $\text{Cr}(\text{C}_5\text{H}_5)_2$ , do the values approach the respective rigid lattice values.

Several conclusions regarding the dibenzene derivatives are evident from the data in Table 1. First, excluding the vanadium and nickel hexamethylbenzene (HMBZ) complexes, the experimental second moments at 299 K for the re-

\*  $1 \text{ gauss (G)} = 10^{-4} \text{ tesla (T)}$ .

TABLE I  
EXPERIMENTAL WIDELINE NMR RESULTS FOR VARIOUS DIBENZENE COMPLEXES

Compound	$n^a$	T (K)	$\Delta H_{1/2}$ (G)	$(\Delta H)^2$ (G <sup>2</sup> )
V(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>	5	299	3.60 ± 0.17	2.61 ± 0.07
V[C <sub>6</sub> (CH <sub>3</sub> ) <sub>6</sub> ] <sub>2</sub>	5	299	2.81 ± 0.02	1.96 ± 0.06
		178	3.00	3.04
Cr[C <sub>6</sub> (CH <sub>3</sub> ) <sub>6</sub> ] <sub>2</sub> I	5	299	2.64	1.76
		179	2.93	1.96 ± 0.05
Fe <sup>I</sup> [C <sub>6</sub> (CH <sub>3</sub> ) <sub>6</sub> ] <sub>2</sub> PF <sub>6</sub>	7	354	2.62	1.96
		299	2.54 ± 0.04	1.73 ± 0.11
		178	2.74	2.11
Fe <sup>II</sup> [C <sub>6</sub> (CH <sub>3</sub> ) <sub>6</sub> ] <sub>2</sub> (PF <sub>6</sub> ) <sub>2</sub>	6	381	1.46	1.10
		299	2.35	1.74
		178	2.82	2.27
Fe <sup>II</sup> [C <sub>6</sub> (CH <sub>3</sub> ) <sub>6</sub> ] <sub>2</sub> PtCl <sub>6</sub>	6	381	2.63	1.81
		354	2.45	1.69
Co <sup>I</sup> [C <sub>6</sub> (CH <sub>3</sub> ) <sub>6</sub> ] <sub>2</sub> PF <sub>6</sub>	8	354	2.50	1.67
		299	2.66 ± 0.01	1.67 ± 0.03
		178	3.06 ± 0.06	2.82 ± 0.07
Co <sup>II</sup> [C <sub>6</sub> (CH <sub>3</sub> ) <sub>6</sub> ] <sub>2</sub> PtCl <sub>6</sub>	7	381	2.32	1.51
		354	2.29	1.69
		299	2.41	1.62
		178	3.26	3.80
Ni[C <sub>6</sub> (CH <sub>3</sub> ) <sub>6</sub> ] <sub>2</sub> PtCl <sub>6</sub>	8	299	2.39 ± 0.13	1.95 ± 0.06
Ni[C <sub>6</sub> (CH <sub>3</sub> ) <sub>6</sub> ] <sub>2</sub> (AlCl <sub>4</sub> ) <sub>2</sub>	8	299	2.21	1.90

<sup>a</sup> Number of *d* electrons (see refs. 1 and 2).

maining chromium, iron, and cobalt species are in the range  $1.7 \pm 0.1 \text{ G}^2$ . Oxidation state and paramagnetism of certain complexes therefore do not seem to affect the second moments. This is consistent with the Van Vleck model assumption that the linewidth (and second moment) is due to the dipolar interaction of magnetic nuclei, which varies inversely with the cube of the internuclear separation. The slightly increased second moment for the neutral vanadium species may possibly be explained by the closer approach of the methyl protons in the absence of an anion\*. Second, in the range 299–178 K, the second moments increase only slightly, in some cases to 3–4 G<sup>2</sup>. This may be interpreted as a decrease in the rates of reorientation; considerably lower temperatures are required to attain "freezing" of such motion. Finally, at room temperature the second moments of the HMBZ species are always less than those for the tabulated benzene compounds of vanadium and chromium. This is to be expected for the following reasons: (1) Methyl group rotation is known to produce additional narrowing of the resonance line and consequently a smaller second moment compared to the unsubstituted dibenzene species [21]; and (2) the second moment is roughly inversely proportional to the number of protons in the ion or molecule, the HMBZ having three times as many as the benzene complexes.

Calculations of the theoretical second moments for Cr(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> and V(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> using a variety of possible bond distances again show excellent agree-

\* This obviously cannot be the explanation for the nickel complexes. It must be noted, however, that the second moments here have more experimental error because of the distortion of the line-shape (overlap with internal reference).

TABLE 2  
RESULTS OF THEORETICAL SECOND MOMENT CALCULATIONS FOR VARIOUS SANDWICH MOLECULES

Compound	$(\Delta H)_{RL}^2$ <sup>a</sup>	$(\Delta H)_{rot}^2$ <sup>b</sup>	$(\Delta H)_{expt.}^2$ <sup>c</sup>	(K)	Ref.
V(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	8.1	1.7	~ 1.9	(298)	20
Cr(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	7.8	1.7	6.85 ± 0.30 ~ 1.6	(77) (298)	12 20
Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	8.5	1.8	1.6 5.0	(80-300) (68)	9 9
Co(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	8.8	1.9	~ 2.7	(298)	20
Ni(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	8.1	1.7	~ 2.9 1.60 ± 0.25 2.4 2.2	(298) (77) (178) (299)	19 12 this work this work
Cr(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>	10.6 <sup>d</sup> (10.7) <sup>e</sup>	2.4 (2.3)	~ 2.3 ~ 2.6	(250-298) (194)	11 11
V(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>	10.9 <sup>f</sup> 13.8 <sup>g</sup>	2.4 2.9	2.61 ± 0.07	(299)	this work
U(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	14.1 <sup>h</sup> (13.6) <sup>i</sup>	3.3 (3.0)	3.45	(298)	this work

<sup>a</sup> Rigid-lattice second moment calculated using Van Vleck model.

<sup>b</sup> Second moment assuming intra- and intermolecular reorientation processes. The value is the sum of one-fourth of the intramolecular contribution to  $(\Delta H)_{RL}^2$  plus one-fifth of the intermolecular contribution to  $(\Delta H)_{RL}^2$  (ref. 9).

<sup>c</sup> Calculated by integration of derivative spectra, or in cases marked (~) by estimation from linewidth reported in ref. cited.

<sup>d</sup> Calculated using H-coordinates in ref. 24 and  $a = 9.553$  Å. Contributions to  $(\Delta H)_{RL}^2$ : intramolecular (5.23 G<sup>2</sup>); intermolecular (5.35 G<sup>2</sup>).

<sup>e</sup> Calculated using Haaland bond distances (ref. 29), C-H distance of 1.095 Å, and  $a = 9.67$  Å (ref. 22). Contributions to  $(\Delta H)_{RL}^2$ : intramolecular (3.45 G<sup>2</sup>); intermolecular (7.20 G<sup>2</sup>).

<sup>f</sup> Calculated for cubic modification (ref. 22).

<sup>g</sup> Calculated for monoclinic modification (ref. 22).

<sup>h</sup> Calculated using H-coordinates in ref. 14. Contributions to  $(\Delta H)_{RL}^2$ : intramolecular (9.51 G<sup>2</sup>); intermolecular (4.61 G<sup>2</sup>).

<sup>i</sup> Calculated using C-H bond distance of 1.095 Å and ring-U distance of 1.924 Å (ref. 14). Contributions to  $(\Delta H)_{RL}^2$ : intramolecular (6.31 G<sup>2</sup>), intermolecular (7.24 G<sup>2</sup>).

ment of the reorientation model with what is experimentally observed (Table 2). Rigid lattice second moments are about four times the experimental values. Since the latter for the HMBZ complexes are less than for the benzene complexes, as has been noted, both intra- and intermolecular reorientation should also be important for these substituted species. Calculations for both species also show that 60-70% of the second moment is due to the intermolecular contribution, a conclusion which seems reasonable for the HMBZ complexes. If one compares the second moments of the cationic HMBZ species in Table 1 (with the exception of the nickel) with V[C<sub>6</sub>(CH<sub>3</sub>)<sub>6</sub>]<sub>2</sub>, the difference of ~ 0.3 G<sup>2</sup> is most likely due to the decrease in the intermolecular contribution to  $(\Delta H)^2$ . The introduction of anions into any crystal lattice expands it relative to the neutral species, thus increasing the intermolecular separation between methyl protons. From the experimental data as well as the theoretical calculations, one may therefore conclude that reorientation occurs in the solid state, presumably such that the HMBZ rings rotate about their six-fold axes.

The constant 2.5 G<sup>2</sup> second moment for pure solid HMBZ itself above 200 K has been studied by Allen and Cowking [21] who report an activation energy of 6.7 ± 0.1 kcal/mole for hexad rotation. Given the somewhat smaller

values of  $(\Delta H)^2$  found for the metal complexes of HMBZ, one may postulate this rotational barrier as an upper limit for these species. Such a barrier is consistent with that found for the metallocenes [9].

A further observation regarding  $V(C_6H_6)_2$  is that the second moment is apparently not sensitive enough to distinguish between different crystalline modifications when no distortion of the molecule occurs.  $V(C_6H_6)_2$  exists in both a cubic and monoclinic form depending upon the temperature and medium of crystallization [22]. The sample used in this work was purified by sublimation, which is known to give the monoclinic form. Note that the experimental second moment lies between the theoretical values predicted for the two structures (see Table 2) and is actually closer to the value for the cubic. It must be mentioned however that the 000 coordinates for the theoretical calculations were chosen to maximize the interatomic distances in the case of the monoclinic form, and to have the same orientation as  $Cr(C_6H_6)_2$  in the case of the cubic [24]. No detailed crystallographic structures are reported for the two vanadium modifications on which to base "exact" theoretical second moments.

Perhaps not surprisingly, these calculations also support a relatively low rotational barrier for  $U(C_8H_8)_2$ . The experimental second moment of  $3.45 G^2$  is within experimental error of the theoretical value of  $3.3 G^2$  (assuming free rotation). A rigid lattice value has not been observed but is predicted to be  $\sim 14 G^2$ . Intramolecular contribution to  $(\Delta H)_{rot}^2$  is  $2.4 G^2$  while the intermolecular contribution is  $0.9 G^2$ . This is exactly the reverse of the metallocene and dibenzene calculations;  $\sim 75\%$  of the observed second moment is presumably due to the intramolecular contribution, reflecting the closer approach of the protons in the planar cyclooctatetraenyl moiety compared to benzene or cyclopentadienyl ligands. These values are based on the hydrogen coordinates recently published for  $U(C_8H_8)_2$  [14], which give an unusually short C—H bond length of  $\sim 0.90 \text{ \AA}$ . However, if one uses a more average bond length of  $1.095 \text{ \AA}$ , the intramolecular contribution drops to  $55\%$  of a total  $3.0 G^2$   $(\Delta H)_{rot}^2$  (see Table 2). While the intra- and intermolecular contributions to the second moment are sensitive to bond distances as shown, the total  $(\Delta H)_{RL}^2$  is not particularly sensitive. This is also the case for  $Cr(C_6H_6)_2$ .

A low rotational barrier in uranocene has been confirmed by a recent crystallographic study of bis(1,3,5,7-tetramethylcyclooctatetraenyl)uranium(IV) by Hodgson and Raymond [15, 16]. Two distinct rotomers were found, involving staggered and eclipsed methyl groups, which suggest that there is little steric inhibition to ring rotation.

The second moment data in Tables 1 and 2 cannot be correlated with models (Fig. 1) suggesting that metal—ring bonding in metallocene and dibenzene complexes differs appreciably [23, 24]. If dibenzene species (other than  $d^5$ ) actually exhibit pseudo-octahedral coordination rather than axial, pseudo-linear coordination proposed for the metallocene and  $d^5$  dibenzene species, one would expect at least reduced intramolecular reorientation about the six-fold axes for most dibenzene complexes (see Fig. 1), giving much larger second moments relative to the metallocenes. There simply is not enough difference in the observed second moments, either within or between the two series, to support this theory, as further corroborated by the excellent agreement of experimental and free rotation second moments. The experimental second moments of

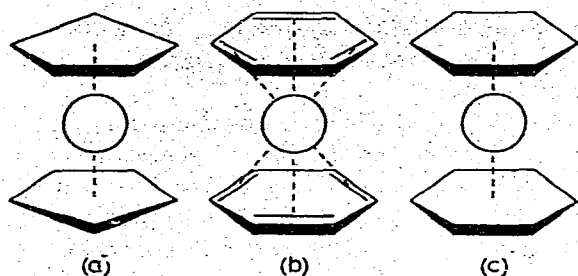


Fig. 1. Proposed bonding models for metallocene and dibenzene complexes: (a) pseudo-linear; (b) pseudo-octahedral; (c) pseudo-linear for  $d^5$  dibenzene species.

$V(C_6H_6)_2$  which is  $d^5$  and  $Cr(C_6H_6)_2$  which is  $d^6$  contradict this theory; one would expect the second moment for the vanadium species to be smaller than for the chromium, but the reverse is actually observed. Our conclusions are supported by recent vibrational spectral studies on  $Cr(C_6H_6)_2$  which have resolved the controversy regarding alleged alternation of bond lengths invoked to support pseudo-octahedral coordination [25–28]. In the gas phase, at least, all C–C bond lengths are equal; electron diffraction also supports these vibrational analyses [29].

While gas phase  $Cr(C_6H_6)_2$  apparently has  $D_{6h}$  symmetry [26], some distortion within the crystal does occur due to packing effects [30] which lower the symmetry to  $D_{3d}$ . Such a lowering, however, does not seem to affect the second moment appreciably at room temperature, but does cause reorientation to freeze out completely around 77 K, similar to chromocene where Jahn–Teller effects are likely to cause distortion (Table 2). It is therefore possible that second moment techniques are not sensitive enough at ambient temperatures to test for minor distortions, particularly in cases where intramolecular reorientation contributes only a minor amount to the observed second moment ( $\sim 30\%$ ). The second moment of  $Cr(C_6H_6)_2$ , at any rate, has not been thoroughly investigated in this work as a function of temperature, but judging from the data in Table 1, the noticeable temperature variation of all second moments appears to establish a criterion of suitable sensitivity.

## Experimental

Metallocene and dibenzene compounds and spectra were obtained as reported previously [1]. Uranocene was prepared according to Streitwieser [31]. The second moment calculations using the Van Vleck model were carried out on an IBM 1130 computer at Pahlavi University. Experimental derivative spectra were digitized and integrated using a separate computer program which automatically corrected the baseline. The experimental second moment was corrected for modulation broadening of the resonance lineshape, although this effect was negligible in most cases because the modulation amplitude was minimized during the recording of the spectra\*.

\* Computer program listings can be obtained on request from the author.

A variety of data was used for the theoretical calculations: metallocene lattice constants [32], V—C bond distance for  $V(C_6H_6)_2$  [33], uranocene X-ray structure [14],  $Cr(C_6H_6)_2$  X-ray structure [22, 25], electron diffraction analysis of gaseous  $Cr(C_6H_6)_2$  [29], and the orientation of the molecule at 000 for metallocenes from the ferrocene X-ray structure [34]. Ring coordinates for all metallocene calculations were taken from electron diffraction results for ferrocene [10, 35].

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