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THE MOLECULAR DYNAMICS OF FLUXIONAL ORGANOMETALLIC MOLECULES IN THE SOLID STATE: TETRACARBONYLBIS(CYCLOOCTATETRAENE)TRIRUTHENIUM(0)

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SUMMARY

The "wide line" NMR spectrum of tetracarbonylbis(cyclooctatetraene)triruthenium(0) is markedly temperature dependent, indicating that the cyclooctatetraene rings are reorienting in the solid state. An energy of activation of 5.15 kcal/mol for ring rearrangement is found from T_1 measurements. A comparison of the experimental second moment, 0.72 G^2 at 304 K, with theoretical second moments calculated for several different modes of reorientation supports a rearrangement process through a series of 1,2 shifts. The results are discussed in relation to the known crystal structure data for the complex.

INTRODUCTION

There has been considerable interest in recent years in the structure and bonding in the class of organometallic molecules which are classed as "fluxional"[1] molecules, *i.e.*, there is localized or semi-localized bonding from the metal atom to a coordinated organic ligand, but where there exists an equilibrium in solution such that the position of attachment of the metal to the organic moiety is continually changing. Examples of this type of interaction are cyclooctatetraeneiron tricarbonyl, (I), in which the bonding is partly delocalized and cyclopentadienylmercuric chloride, (II), in which the bonding from the metal to the organic ligand involves a localized σ-bond.

In both cases, a single proton resonance is observed in solution at room temperature, indicating that the point of attachment is continually changing.

It has recently been shown that several organometallic complexes of cyclooctatetraene with iron carbonyls, which have been characterized as "fluxional" molecules in solution, exhibited a similar reorientation of the cyclooctatetraene rings in the solid state, as evidenced by changes in the "wide line" NMR spectrum of the solid[2]. It is not known, however, how general this phenomenon might be, especially whether or not it might be observed in more complicated molecules containing more than one possible "fluxional site".

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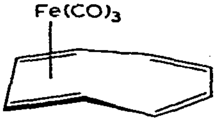
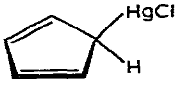


(I)



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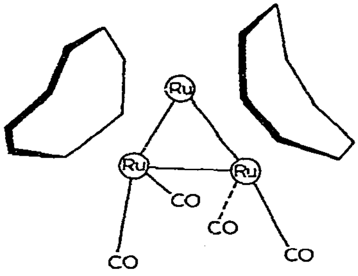

(III)

The most complex molecule of this type to be characterized is bis(cyclooctatetraene)triruthenium tetracarbonyl[3,4] which has been shown by X-ray diffraction to have structure (III) containing two cyclooctatetraene rings and a metal cluster, in the solid[5].

The purpose of the present work was to use "wide line" NMR to investigate the possible reorientation processes in this compound in the solid in order to establish how general the occurrence of such processes might be, and to see if their nature could be deduced.

RESULTS AND DISCUSSION

The proton NMR spectrum of (III) in the solid state is markedly temperature dependent (Fig. 1, inset). The linewidth and second moment* parameters of the

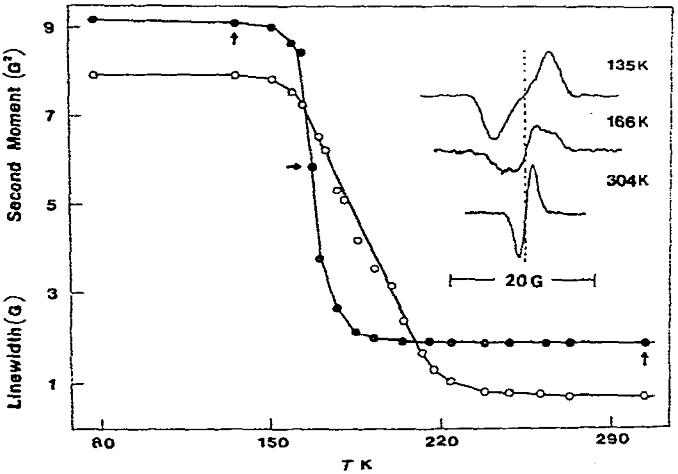

Fig. 1. The temperature dependence of the linewidth (filled circles) and second moment (open circles) parameters of the proton resonance spectrum of bis(cyclooctatetraene)triruthenium tetracarbonyl in the solid state with (inset) representative spectra recorded at the temperatures indicated by the arrows on the linewidth curve.

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* The second moment $(\Delta H)^2$ is the mean square width of a curve, $(\Delta H)^2 = \int_0^\infty (H - H_{AV})^2 \cdot f(H) \cdot dH$. Its usefulness in the present context is that it can be calculated theoretically as well as measured from the experimental spectra.

spectra show a large change, centred at about 180 K, and are quite continuous in nature. The second moment for a completely rigid lattice can be calculated by the procedure of Van Vleck[6] using the atomic coordinates provided by the X-ray study[5] and assuming the C–H distance is 1.08 Å, giving a value of 7.99 G^2 in good agreement with the value observed experimentally below 135 K (Table 1). These results suggest that the molecule is quite rigid in the lattice at these low temperatures.

TABLE 1

THE OBSERVED SECOND MOMENT PARAMETERS (G^2) OF THE PROTON RESONANCE OF SOLID (III) AND VALUES CALCULATED[a] FOR VARIOUS MOTIONS OF THE TWO RINGS

Reorientation mechanism	*Second moments*				
	Calcd.			*Obsd.*	*Temp. (K)*
	Intra	*Inter*	*Total*		
Both rings rigid	5.63	2.36	7.99	7.89	135
One ring rigid, one rotating	2.40	0.61	3.01		
Both rings rotating; concerted motion 1,2 Shift	0.90	0.26	1.16		
Both rings rotating independently					
1,2 Shift	0.33	0.26	0.59	0.72±0.2	304
1,3 Shift	0.66	0.30	0.96		

[a] For details, see text.

The large drop in the linewidth and in the second moment is indicative of some reorientation process of the ring. A BPP plot[7] of the linewidth changes gives an energy of activation of 8.7±0.5 kcal/mol for reorientation; however this must be regarded as a very approximate value only, since the line-shape changes during the transition and the equation is in any case an empirical one. Measurements of the spin lattice relaxation time (T_1) yield a value of 5.15±0.1 kcal/mol and this is considered to be the true value.

Theoretical second moments for several models for the reorientation process have been calculated according to the formalism of Rigney *et al.*[8] and are shown in Table 1 together with the experimentally observed high temperature value of 0.72± 0.2 G^2. As can be seen (Table 1), there is no agreement with the values calculated for the case where only one of the two rings is reorienting, or where both rings reorient in a concerted manner, and it is thought that in fact both rings reorient independently of each other. A 1,5 shift can be eliminated as a possible mechanism for the rearrangement, since the intramolecular second moment for such a process would be the same as that for the rigid molecule. The experimental second moment falls between the values calculated for 1,2 and 1,3 shifts, and it is not possible to state unambiguously which of these mechanisms is the correct one; however it seems more likely that reorientation proceeds through a series of 1,2 shifts as indicated by the high-resolution NMR spectra of similar molecules[1]. Motions through larger angles would be considerably hindered by steric effects in the solid.

Taking into account the results of the X-ray study, several comments may be made concerning the mechanism of the reorientation process. Thus, since the crystal structure shows discrete atomic positions, the reorientation must be by a "jumping" process involving a potential barrier, rather than "free rotation" of the ring. Furthermore, since the ring is not planar, there must be a simultaneous rotation and distortion of the ring, concomitant with a breaking of the covalent bonding to the metal atoms during the jumping motion.

This is exactly the relative motion of the two moieties postulated in solution. In the solid, the metal atoms are fixed however, emphasizing that in solution the motion is a composite of the motion of the two parts. This study suggests that solid-state NMR will be a useful complement to solution NMR and X-ray crystallography for the study of these molecules, and also that the occurrence of reorientation processes in these compounds may be quite a general phenomenon, at least when the rings are unsubstituted.

EXPERIMENTAL

Apparatus

"Wide line" proton resonance spectra were recorded at 100 MHz using a standard Varian H.A. 100D spectrometer modified with a Princeton Applied Research H.R. 8 lock-in amplifier and a Hewlett Packard 465A amplifier to give field modulation and signal detection.

Temperature variation was achieved by a standard temperature controller and temperatures were recorded directly with a thermocouple inserted into the sample. Spectra were measured using 12 mm (outside diameter) thin-walled glass tubes and the samples were stored at low temperatures when not in use. All calculations were performed on an IBM 360/50 computer using Fortran IV programs written by the authors.

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This complex was prepared as described by Cotton *et al.*[3], and recrystallised twice from chloroform and dried *in vacuo* at 25°. The solution NMR spectrum in $CDCl_3$ agreed with that reported previously. (Found: C, 38.88; H, 2.60. $C_{20}H_{16}O_4Ru_3$ calcd.: C, 38.52; H, 2.57%.)

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