for π bonding of bridging oxide to the outer 3dπ orbitals of Al(III) is suggested by the unusually short (1.68 Å) Al–O distance.

In summary, the electronic spectral and magnetic properties of the Fe–O–Fe dimers are nicely accommodated by a simple spin–spin coupling model. Extension of this model to include 2pπ(O)–4dπ,4pπ(Fe) interaction allows an interpretation of the Fe–O–Fe bond length and infrared data.

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Molecular Dynamics of Fluxional Molecules in the Solid State. Cyclooctatetraene–Iron Carbonyl Complexes[1]

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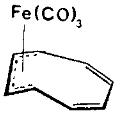
Abstract: "Wide-line" nmr measurements of the "fluxional" molecules $C_8H_8\cdot Fe(CO)_3$ and $C_8H_8\cdot Fe_2(CO)_5$ reveal that the cyclooctatetraene rings possess considerable motional freedom in the solid state, reorienting in their approximate molecular planes, but that the ring in $C_8H_8\cdot(Fe(CO)_3)_2$ is fixed rigidly in the crystal. The results are discussed with respect to the behavior of the complexes in solution and their bonding.



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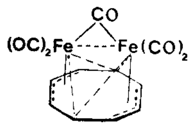

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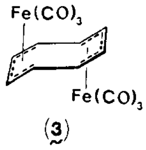

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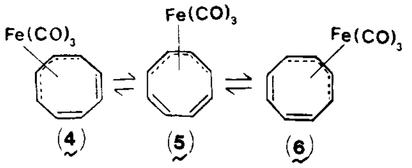

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There has been considerable interest in recent years in the structure and bonding of "fluxional" organometallic molecules.[3] In these molecules the bonding in solution is of a dynamic nature, and the static structure is found only at low temperatures. In this light, the properties of several compounds formed by the reaction of cyclooctatetraene with iron carbonyls[4–14] and with ferric chloride[15,16] have been extensively investigated. Cyclooctatetraene–iron tricarbonyl has been shown to have structure **1** from X-ray measurements,[7] but in solution shows only a single sharp proton resonance at room temperature, due to a rapid equilibrium involving the bonding of the metal atom to the ring. On cooling to −150°, a multiplet structure is found.[10–14] There has been some disagreement as to the nature of the rearrangement, due partly to the low-temperature spectrum observed not being the true limiting spectrum. It is now accepted[3] that a 1,2 shift mechanism of the metal atom round the ring as indicated by **4–6** may well be the rearrangement mechanism for *all* cyclooctatetraene–metal tricarbonyls. Similar mobility in the bonding is also found for $C_8H_8\cdot Fe_2(CO)_5$, known to have structure **2** in the solid state from X-ray diffraction work,[9] but the ring in $(C_8H_8)\cdot(Fe(CO)_3)_2$ (**3**) is found to be quite rigidly bound to the metal atoms.[7]

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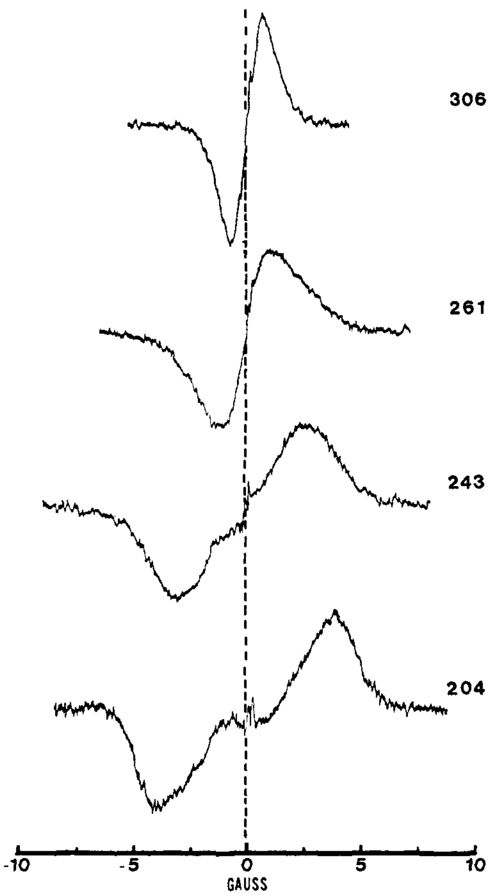

Figure 1. Proton resonance spectra of solid $C_8H_8\cdot Fe(CO)_3$ (**1**) at the various temperatures indicated. The points corresponding to these spectra are indicated by the vertical arrows in Figure 2.

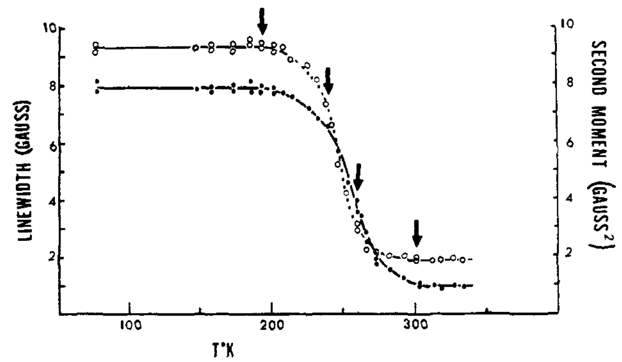

Figure 2. The temperature dependence of the line width (○) and second moment (●) parameters of the proton resonance of solid $C_8H_8\cdot Fe(CO)_3$ (**1**). The vertical arrows indicate points corresponding to the spectra shown in Figure 1.

Many compounds are known to possess motional freedom in the solid state,[17-20] and nuclear magnetic resonance spectroscopy in the solid state ("wide-line" nmr) has been a very useful method for investigating these motions.[21-24]

In the case of complexes of various types, the presence of motion may yield information about the nature of the bonding between the components.[20] The purpose of the present work was thus to investigate possible molecular motions in these compounds in the solid state by nmr.

Experimental Section

The compounds were prepared by literature methods[4,8] and had analyses consistent with their proposed structures. The compound $(C_8H_8)\cdot Fe_2(CO)_7$ described by Manuel and Stone[4] was shown by ir, melting point, and powder X-ray photographs to be identical with $(C_8H_8)\cdot Fe_2(CO)_5$ as suggested by Keller, *et al.*[8] The polycrystalline samples were sealed in 12-mm o.d. thin-walled nmr tubes. Spectra were recorded on a Varian HA-100 spectrometer using a standard variable-temperature accessory. Temperatures were measured directly with a thermocouple fused into the top of the sample. The slow sweep unit was used and field modulation and signal detection was achieved with a PAR HR-8 lock-in amplifier operating at a frequency of 100 cps and an HP 465A amplifier connected to the standard ac sweep coils in the probe. Care was taken to avoid saturation and to use small enough modulation to minimize signal distortion. Several spectra were recorded at each temperature and were corrected for the effects of modulation. All calculations were carried out using Fortran IV programs on an IBM 360/50 computer.

Results

$C_8H_8\cdot Fe(CO)_3$. The proton resonance of $(C_8H_8)\cdot Fe(CO)_3$ is very temperature dependent (Figure 1), indicating motion in the solid state. The complete temperature dependence of the line width and second moments is shown in Figure 2. The dotted line shown in the line-width curve in the region of the transition represents a least-squares fit to the experimental data using the Bloembergen–Purcell–Pound equation[25] modified by Smith.[26] The activation energy thus obtained is 8.3 ± 0.4 kcal/mol.

$C_8H_8\cdot Fe(CO)_3)_2$. The line-width and second-moment parameters of this complex do not change with temperature in the range 77–430°K. The values found experimentally are 8.0 G and 5.6 G^2, respectively.

$C_8H_8\cdot Fe_2(CO)_5$. The room-temperature ^1H resonance of this compound is a very narrow curve with a line width of 1.4 G and second moment of 0.9 G^2, similar to that of $(C_8H_8)\cdot Fe(CO)_3$. In this case, however, there is no marked dependence on temperature down to 77°K.

Discussion

The nature of the changes in the line width and second moment parameters shown in Figure 2 for the $C_8H_8\cdot Fe(CO)_3$ complex can be understood from a consideration of the limiting second-moment values above and below the transition. A theoretical value of the second moment for a completely rigid structure can be calculated by the procedure due to Van Vleck.[27] Such a calculation, based on the crystal structure data[7] and assuming C–H bond lengths of 1.08 Å, yields a

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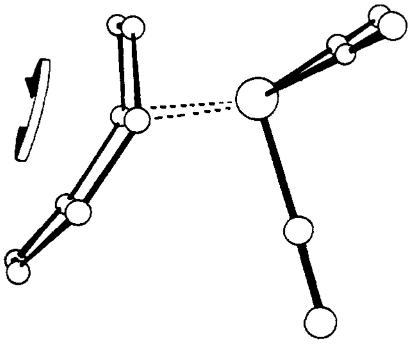

Figure 3. The approximate rotation axis for the cyclooctatetraene ring in $C_8H_8 \cdot Fe(CO)_3$ (**1**).

value of 7.70 G^2, in good agreement with the low-temperature value of 7.9 G^2 found experimentally. At low temperatures then, the whole molecule is (on an nmr time scale) completely rigid in the lattice. Movement of the cyclooctatetraene ring in its approximate molecular plane as shown in Figure 3 must be invoked to explain the extreme narrowing of the spectrum. Since the crystal structure shows no disorder, any motion of the ring must involve its simultaneous rotation and distortion. The theoretical second moment for this motion was calculated after the formulation of Michel, Drifford, and Rigny.[28] Good agreement is found between this value and that found experimentally (Table I).

Table I. Observed and Calculated Second-Moment Parameters (G^2) for the Proton Resonance of Cyclooctatetraene–Iron Carbonyl Compounds in the Solid State[a]

Molecule	State	Calcd	Obsd	Temp, °K
$C_8H_8 \cdot Fe(CO)_3$ (**1**)	Rigid	7.7	7.9	<204
	Rot.	0.7	1.0	>298
$C_8H_8 \cdot Fe_2(CO)_5$ (**2**)	Rigid	6.8 ± 1[b]		
	Rot.	0.5 ± 0.2[b]	0.9	>77
$C_8H_8 \cdot (Fe(CO)_3)_2$ (**3**)	Rigid	5.9	5.6	<430
	Rot.	0.4		

[a] The calculations for motion are based on the permutation of the hydrogen nuclei over all possible positions, *i.e.*, 1,2 shifts (1,4 shifts give the same distribution). Calculations for motion by a 1,3 shift mechanism for **1** and **2** gave similar results to those in the table, and although the 1,2 shift mechanism is much more probable in the solid state, the results cannot be considered to *prove* that this is so. [b] A complete, exact calculation was not possible in this case owing to the incomplete structural data available. The intramolecular contribution in the rigid case was calculated exactly as 4.59 G^2, and the intermolecular contribution was approximated by a value intermediate between the values for **1** and **3**. For motion, the intramolecular contribution is 0.33 G^2, and the intermolecular contribution was again assumed to be intermediate between the values for **1** and **3**.

In the case of $(C_8H_8) \cdot Fe_2(CO)_5$ (**2**), the calculated "rigid-lattice" second moment based on the crystal structure[8] is 6.8 ± 1 G^2. The large difference between this value and the observed value of 0.9 G^2 is considered to be outside the experimental error and is thought to again indicate motion of the organic ring. The second moment calculated for motion is 0.5 ± 0.2 G^2, in reasonable agreement with the experimental value.

$(C_8H_8) \cdot (Fe(CO)_3)_2$ (3). The calculated rigid-lattice second moment from the X-ray data is 5.9 G^2, in reasonable agreement with experimental value, and the whole molecule is considered to be rigid at temperatures studied.

The data for the three complexes are summarized in Table I. There is a general correspondence in all the systems with the results from high-resolution nmr in solution. Thus compound **3** showed quite fixed bonding in solution and is immobile in the solid state, but both **1** and **2** are found to be quite mobile, both in solution and in the solid state. In the case of **2**, the ring is quite mobile at 77°K, and it would seem quite unlikely that high-resolution nmr would ever yield a limiting low-temperature spectrum in solution. In the cases of **1** and **2**, where nmr spectroscopy suggests that the rings reorient in the solid state, there is no indication of any disorder in the structures from the X-ray studies.[7,9] However, it is not true, as suggested by the authors of these papers, that this rules out reorientation. It means that the motion must involve simultaneous rotation *and* distortion of the rings, so that after rotation has occurred, each carbon atom occupies a position previously occupied by a carbon atom and no disorder is found. Because no disorder is introduced, the motion will not be detectable by any method other than nmr or esr spectroscopy, as other methods detect disorder, rather than motion as such. The occurrence of distortion concurrent with motion is unusual, but it is possible that it may occur in some benzene complexes.[20] The present work is the only case found to date, however, where reorientation of a group in the solid state is accompanied by simultaneous bond breaking and formation.

The situation found for the complexes in the solid is thus very similar to that proposed for the equilibria in solution (**4**–**6**), except that, in this case, it is only the ring which is moving. In the crystal, there is no disorder in the metal atoms, and their motion is absolutely ruled out. Movement of the ring as well as "jumping" of the metal atom must occur in solution and one must thus remember that representations of the motion in solution such as **2**–**4** are used as a convenient representation only, and that the actual physical process will involve movement of both parts of the complex, depending on their relative masses.

It is hoped in the future to provide a closer comparison of the results obtained in the solid state obtained in solution by measurements of relaxation times and hence determination of activation energies for these and other complexes.

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