Molecular Motion in Plastic Phases of Organometallic Compounds: Iron-57 Mössbauer and Carbon-13 N.M.R. Spectra of Tricarbonyl(1—5-*hapto*-cyclohexadienyl)iron Tetrafluoroborate and Related Compounds

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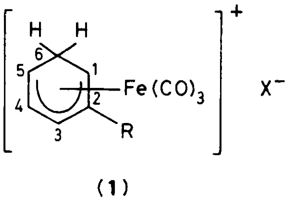
In the solid state, reorientational motion of tricarbonyl (1—5-*hapto*-cyclohexadienyl)iron cations results in a reversible temperature dependence of both the iron-57 Mössbauer and carbon-13 n.m.r. spectra.

The plastically crystalline state is characterised by isotropic molecular reorientation. Chemical interest in these compounds stems from the expectation of correlation between the details of such motion and the reactivity of the solid.[1]



(1)

a; R = H, X = BF_4
b; R = H, X = PF_6
c; R = Me, X = PF_6
d; R = H, X = $SnCl_5$
e; R = OMe, X = BF_4

With the intention of studying certain solid state reactions, we have investigated molecular motion in several organometallic compounds. Here, we report on the title compound and some of its derivatives.

We have previously reported[2] anisotropic reorientational effects in the iron-57 Mössbauer spectrum of the compound $[(C_6H_6)(C_5H_5)Fe]^+[PF_6]^-$. In this case, the symmetry properties of the cation allow good agreement between observed lineshapes and current theoretical models.[3]

Iron-57 Mössbauer spectroscopy has proved less effective in the case of the tricarbonyl(cyclohexadienyl)iron salts. Here, the low symmetry of the electric field gradient (Table 1) means that strict correspondence with these models cannot be expected and it has proved helpful to employ alternative techniques.

A calorimetric investigation of compound (**1a**) showed a first-order phase transition at T_c *ca.* 250 K. Single-crystal

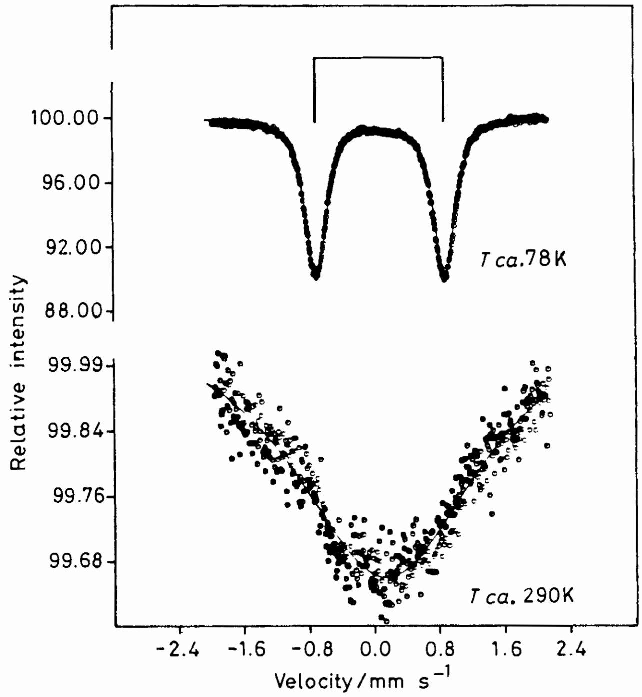


Figure 1. Mössbauer spectra of a powdered sample of compound (**1a**).

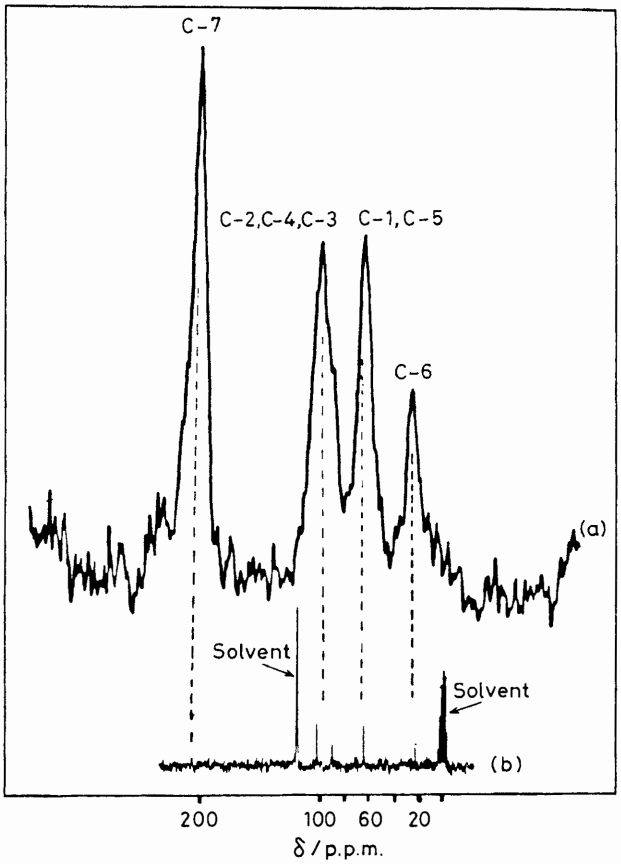


Figure 2. Carbon-13 n.m.r. spectra of compound (**1a**); (a) as a powdered solid, (b) as a methyl cyanide solution. Chemical shifts relative to $SiMe_4$ are; δ C-1, C-5 *ca.* 67, C-2, C-4 *ca.* 104, C-3 *ca.* 92, C-6 *ca.* 26, C-7 (carbonyl) *ca.* 208 p.p.m. In the solution spectrum (b), the low intensity of the carbonyl peak arises from the choice of pulse delay (2 s). In the plastic phase, relaxation times are relatively short and the same pulse conditions allow the carbonyl signal to gain full intensity.

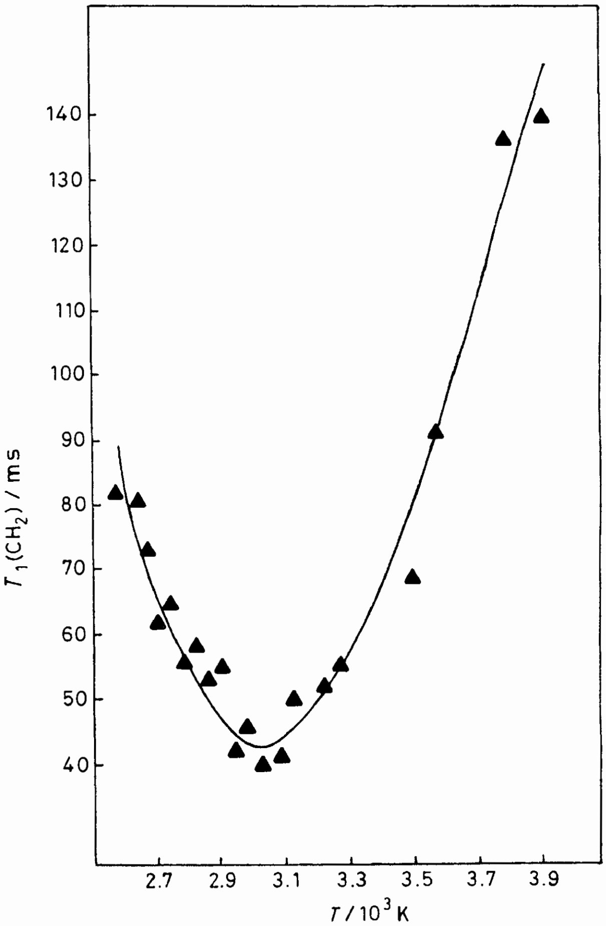


Figure 3. Temperature dependence of the carbon-13 spin–lattice relaxation time T_1 in a powdered sample of compound (**1a**). The relationship between the T_1 values for C-7(CO), C-1–5(CH), and C-6(CH_2) is similar to that found for solutions with T_1 (CO) >> T_1 (CH) = *ca.* 2T_1 (CH_2).

Table 1. Calorimetric and Mössbauer spectral data for tricarbonyl(1—5-*hapto*-cyclohexadienyl)iron(II) salts.

Compound	ΔEq[a]	δ[a]	η[a]	T_c/K[b]	T_H/K[b]	ΔH_T[c]	ΔS_T[c]
(**1a**)	−1.58	0.11	0.7	250	10	4.0	16.5
(**1b**)	−1.66	0.13	0.7	240	8	8.5	36.0
(**1c**)	1.50	0.10	—	242	24	14.5	60.0
(**1d**)	−1.59	0.12	0.7	505	12	8.5	17.0
(**1e**)	−1.36	0.11	0.7	—	—	—	—

[a] ΔEq, δ, and η are the quadrupole splitting, chemical shift, and the asymmetry parameter as determined from zero-field or magnetically perturbed Mössbauer spectra as appropriate. ΔEq and δ are in mm s^{-1}, the latter with respect to natural iron. Both are ± 0.005 mm s^{-1}. [b] T_c and T_H are transition temperatures and thermal hysteresis, both ± 5K. [c] ΔH_T and ΔS_T are the enthalpies and entropies of transition, kJ mol^{-1} ± 0.5 and J(mol $K^{-1})^{-1}$ ± 5 × 10^{-4} respectively.

X-ray diffraction studies[4] of the high temperature phase revealed a face-centred cubic structure with $a = 10.6$ Å. Extensive cation disorder was indicated by characteristic diffuse scattering and this has delayed a more detailed structural analysis. Attempts to investigate the low temperature form resulted in shattering of the crystal on cooling across the phase boundary.

The Mössbauer spectra of compound (**1a**) are shown as Figure 1. At temperatures below T_c *ca.* 250 K, the expected quadrupole doublet is observed. Above T_c, the spectrum exhibits a broad resonance indicative of a reorientational process which is relatively rapid on the Mössbauer time scale ($\leqslant$ *ca.* 10^{-7} s).

Using conventional n.m.r. spectrometers (Bruker WH 400 or Jeol FX 200), without recourse to magic angle spinning or specialized pulse sequences, a powdered sample of compound (**1a**) gave well resolved carbon-13 spectra within 500 scans, *i.e.* about 30 seconds, Figure 2(a).

We used the inversion–recovery method to measure the temperature dependence of the carbon-13 relaxation time T_1, Figure 3. Assuming[5] isotropic reorientation, preliminary data indicates a cation reorientation rate of τ_c *ca.* 2×10^{-9} s at T *ca.* 330 K with E_{act} *ca.* 19 kJ mol^{-1}.

The reorientational motion of the cation is sensitive to the nature of the anion and to substituents in the ring, but no simple correlations are apparent. In the pentachlorostannate compound (**1d**), the spectra of the ambient temperature phase are consistent with a non-plastic structure and the phase transition does not occur until 505 K. At ambient temperatures, the methoxy derivative (**1e**) gives an unperturbed quadrupole doublet and its ordered nature is confirmed by the successful solution of its crystal and molecular structure.[6]

Thus, we have established the existence of plastic phases for a number of organometallic salts through the effect of reorientational motion on spectral and crystallographic properties. We believe that the disorder operates through a mechanism involving co-operative repulsion between neighbouring cations with the anions playing a mainly passive role.

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