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MÖSSBAUER STUDIES ON FERROCENE COMPLEXES

II *. IRON—HYDROGEN-BONDED COMPLEXES OF FERROCENE

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Summary

Iron—hydrogen-bonded complexes of ferrocene have been studied by Mössbauer spectroscopy. The high quadrupole splittings are interpreted in terms of ring-tilting and charge distribution and compared with results from ferrocene mercuric chloride adducts. Correlations are found between isomer shift and quadrupole splittings in the compounds studied.

Introduction

Mössbauer spectroscopy has been used extensively to investigate the structure of ferrocene and ferrocinium derivatives. There is general agreement that for a series of ferrocene derivatives the variation in quadrupole splitting (QS) is relatively small. This is a consequence of the fact that the electric field gradient at the nucleus arises largely from the π-bonding ligands. These are not greatly influenced by changes in the σ-bonding of ring substituents.

We have recently reported abnormally large quadrupole splitting data in the ferrocene/mercuric chloride adducts [1], and interpreted this data in terms of strong evidence for Fe—Hg bonding.

In a Mössbauer study of trimethylene-bridged ferrocene derivatives [2], marked decreases in both quadrupole splitting and isomer shift (IS) were observed as the number of bridges increased, This effect was interpreted in terms of ring tilt and non-planarity of the cyclopentadienyl rings causing a weakening of the metal-ring bonds. Thus it is likely that ring tilt causes a lowering of both QS and IS, though in these compounds there is no bonding to the Fe other than that of the two rings.

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* Part I see ref. 1.

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Protonation of ferrocene [3] at the metal site has been known for some time and attempts have been made to quantify the interaction and the evaluate the importance of such protonated metal species in hydrogen exchange reactions [4]. Such interactions have been reviewed in the general area of Lewis basicity of transition metals [5].

The purpose of this paper is to report Mössbauer data on protonated ferrocene and to interpret the results in terms of the site of protonation and its stereochemical consequences.

Experimental

The Mössbauer spectra were from frozen solutions prepared as follows.

The solution was prepared by adding solid ferrocene (resublimed, Aldrich Chemical Co. Lts.) to trifluoromethanesulphonic acid. Part of this yellow solution was quickly transferred to a Teflon cell which was quench cooled in liquid nitrogen and loaded into a precooled RICOR cryostat; the temperature rise was kept to a maximum of 40°C.

The remaining solution was sealed, with air in the container; this turned green during 24 hours, and was then loaded as above.

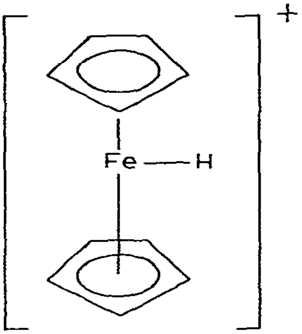
The solution in ethanoic acid was prepared by saturating the solvent with ferrocene, and then diluting this solution twice before loading in the cell. Solutions in methanol and chloroform were prepared without saturation; in the case of chloroform, the absorption of γ-radiation by the solvent was excessive with a full cell; a half-full cell was used and frozen in such a way as to keep the window covered with solution.

Spectra were fitted as described previously: the velocity scale was calibrated using iron foils of 10 mg cm^{-2} thickness to which isomer shifts are referred.

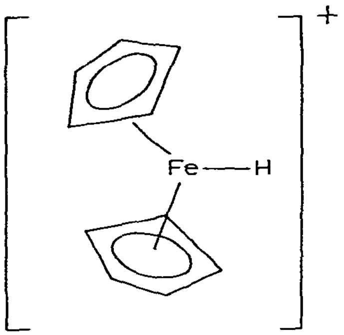
NMR spectra of ferrocene and neopentylferrocene in solvent CF_3SO_3H were run on a Varian EM 360 spectrometer housed in a constant temperature room (probe temperature 28.4°C).

Results and discussion

Protonation at the metal atom in transition metal complexes is well documented [6]. Metal—proton interactions have been studied by NMR spectroscopy and characterised by abnormally high chemical shifts (δ = —30 ppm). Infrared spectroscopy [7,8] has also been used to detect such interactions in ferrocene derivatives through a detailed examination of ν(OH) bands and the appearance of what has been assigned as a ν(metal—H) mode in the region 1700—2100 mn^{-1}. Thus for 2-ferrocenylethanol, ν(OH) bands at 3632, 3605, and 3533 cm^{-1} were assigned to free, π-bonded and Fe-bonded hydroxyl groups [8]. A detailed study of the IR spectrum of ferrocenonium tetrachloroaluminate showed that protonation of the iron atom caused a weakening of the Fe—cyclopentadienyl bond with a concommitant small increase in π-electron density in the rings [9]. However no decision could be reached concerning possible structures I and II.



(I)



(II)

The latter involves a degree of ring tilt which, it has been suggested from simple molecular orbital treatment [10], does not materially alter the strength of the iron—cyclopentadienide bonds, and yet facilitates proton attack. The strong broad band at 1645 nm^{-1} (Nujol) was tentatively assigned as the ν(Fe—H) mode.

Protonation can occur on ring sites in ferrocene as was demonstrated by Illuminati et al. [4]. In weakly acidic media ($CHCl_3$ etc.) weak π-bonded species were indicated from ^1H NMR studies, whilst in strong acids ($BF_3 \cdot H_2O$/CF_3CO_2H) metal protonation occurred (Fe—H, $\delta = -1.89$ ppm). Bitterwolf and Campbell-Ling [11] have studied a series of alkylated ferrocenes in $BF_3 \cdot H_2O$ and have invoked ring tilting (Structure II) to account for the observed increased shielding (0.22 to 0.32 ppm) of the β with respect to the α protons.

Molecular models show that considerable steric strain occurs for bulky substituents such as mercury on the central iron atom. This must result in considerable ring tilting. Evidence for this distortion comes from the crystal structure of $[Rucp_2I]^+I_3^-$, the derivative being the oxidation product of ruthenocene and iodine [12]. The rings are inclined at an angle of 32.2° and are eclipsed with respect to each other as they are in the parent ruthenocene. Iodine complexation has no effect on the interannular distance which remains at 3.68 Å. Interestingly, the iodine—C(2) hydrogen distance is 2.65 Å, which is well within the sum of the Van der Waal's radii of the two atoms (3.40 Å) i.e. a 25% shortening of interatomic distance with respect to Van der Waal's interaction. Adopting a similar shortening of the Hg—H distance for the corresponding mercury complex results in a calculated ring tilt of 42°. Such a calculation for $[FeCp_2 \cdot HAlCl_4]$ has the additional difficulty that the structure of the $HAlCl_4$ group within the complex is not known. The complex itself is soluble in relatively weakly polar media such as dichloromethane which suggests considerable covalent character, which in turn means that the proton is still closely associated with the $AlCl_4$ moiety. If this is the case, a ring tilt of ~25° is indicated which reduces to zero if a 50% extension in all bonds occurs. Thus the effect of the counterion could be highly significant in determining the degree of ring tilt. To attempt to evaluate these factors we have undertaken a Mössbauer spectroscopic investigation of some of these complexes.

Mössbauer spectroscopy

The relevant Mössbauer data appear in Table 1. The lack of any significant changes in either the isomer shift or quadrupole splitting for frozen solutions of $FeCp_2$ in glacial acetic acid, methanol, and chloroform compared with those for ferrocene itself demonstrates that any weak solvent interaction (π complexes) [4] leaves the electronic environment of the iron nucleus unaltered.

The Mössbauer data for both the $FeCp_2/CF_3SO_3H$ frozen solution and the $FeCp_2/HAlCl_4$ complex compared with those of $FeCp_2$ shows larger QS and smaller IS values, so that in both these materials substantial changes in the electronic environment at the iron nucleus must have occurred.

The lower IS's can be interpreted as an increase in *s* electron density at the Fe nucleus. This change in *s* electron density could result either directly from a change in the proportion of *s* electron density in the bonding orbitals or indirectly from a decrease in the amount of *p* and *d* electron shielding.

The Fe—H interaction found in IR and NMR studies for $FeCp_2/CF_3SO_3H$ and $FeCp_2/HAlCl_4$ would indeed be expected to modify *p* and *d* orbitals in the *xy* plane of $FeCp_2$, affecting possibly the a_{1g}, e_{2g} and e_{1u} orbitals, of these the a_{1g} and e_{1u} are mainly concentrated on the Cp rings but the e_{2g} orbitals are mainly associated with the Fe, and so could be expected to be modified by a Fe—H bond.

Such an Fe—H bond would remove electronic charge from the e_{2g} orbitals, thus deshielding the *s* electron density at the nucleus, and manifesting itself as a decrease in isomer shift in the Mössbauer data, as is in fact observed. It is of interest to note that in the case of the ferrocene/mercuric chloride red adduct, no change in isomer shift was observed, suggesting no removal of electron charge from the Fe environment. (The charge density in an Fe—Hg bond is likely to reside closer to the iron nucleus relative to that in the Fe—H bond.)

The quadrupole splittings observed for $FeCp_2/CF_3SO_3H$ and $FeCp_2/HACl_4$ are both larger than $FeCp_2$ but smaller than that of the red $FeCp_2$/mercuric chloride adduct. As already indicated, in the case of $FeCp_2/HAlCl_4$ it may be

TABLE 1

MÖSSBAUER PARAMETERS FOR FERROCENE

		Isomer shift (mm sec^{-1})	Quadrupole splitting (mm sec^{-1})	Line width (half-width at half max.) (mm sec^{-1})
(A)	$Fe(C_5H_5)_2/CF_3SO_3H$ [a]	0.44(1)	2.59(2)	0.18(1)
	$Fe(C_5H_5)_2/CH_3COOH$ [a]	0.53(1)	2.40(1)	0.12(1)
	$Fe(C_5H_5)_2/CH_3OH$ [a]	0.54(1)	2.40(1)	0.12(1)
	$Fe(C_5H_5)_2/CHCl_3$ [a]	0.52(1)	2.42(2)	0.11(1)
	$Fe(C_5H_5)_2/CF_3SO_3H$ [b]	0.51(2)	0.0	0.26(3)
(B)	$Fe(C_5H_5)_2/HAlCl_4$ [c]	0.46(1)	2.72(1)	0.18(1)
(C)	$Fe(C_5H_5)(C_5H_4 \cdot CH_2CMe_3) \cdot HAlCl_4$ [c]	0.49(1)	2.52(1)	0.20(1)
(D)	$Fe(C_5H_5)_2 \cdot HgCl_2$ [d]	0.53(1)	3.09(1)	0.14(1)

[a] Frozen solution 80°K. [b] Aged in air frozen solution. [c] Solid 80°K. [d] See ref. 1.

expected that some tilt of the rings would be caused due to the close proximity of the $AlCl_4^-$ group. Such a distortion would be less than that in the red $FeCp_2/HgCl_2$ adduct where the large Hg atom would be closer to the rings. The smaller QS of this compound compared to the $FeCp_2/HgCl_2$ adduct would be in keeping with this result.

The smaller QS for the $FeCp_2/CF_3SO_3H$ complex would also be explained in a similar manner; here the ring hydrogens would indeed encounter some steric hindrance from the oxygen atoms of the SO_3H group. However, this group has the ability to bend away from such compressions just as a methoxy group, thus experiencing less repulsion and resulting in a less distorted electronic environment and hence only a relatively small increase in QS. It is also true that changes in the electron distribution of the e_{2g} orbital may also change the electronic environment of the Fe atom, giving rise to changes in QS but it is unlikely that such changes in Fe—H bond strength would cause such a large change in QS on their own.

It is therefore apparent that the changes in QS (electronic environment of the Fe atom) are caused by modifications due to direct bonding and redistributions in electron density due to steric effects causing ring tilt, or by direct field effects of the associated anion.

The greatest change in IS found in $FeCp_2/CF_3SO_3H$ and the concommitant smallest change in QS is in keeping with the fact that here the steric effect will be smallest and here the modification due to direct bonding may be dominant.

The results of protonation of ferrocene in the condensed phase suggest a rather low basicity of the iron atom. However, in the gas phase there is evidence that ferrocene is surprisingly basic, having a proton affinity only slightly less than that of methylamine [13]. Interestingly, the homolytic bond dissociation energy for the reaction,

$$[Cp_2Fe{-}H]^+ \rightarrow (Cp)_2\dot{F}\overset{+}{e} + H^{\cdot}$$

is very low (56 ± 6 kcal mol^{-1}) compared with those of other analogous organic and inorganic compounds (80—130 kcal mol) and reflects the ease with which charge is transferred to the central iron atom.

Very recently, Hillman et al. [14] have reported a Mössbauer study on bridged ferrocenes in which they find a correlation between both IS and QS and the interannular ring distance (*d*). Crystallographic data show that small but significant shortening of *d* occurs on bridging ferrocene with trimethylene links. Thus as *d* decreases both IS and QS decrease. It is clear however that such an effect of Fe—ring distance cannot account for the very large values of IS and QS for the proton and mercury complexes discussed here, since the rings would have to be placed in some instances in non-bonding positions with respect to the iron atom. The effect of ring tilt on Mössbauer parameters is not entirely clear. From the data presented by Good and coworkers [15], there is a trend for ring tilted non-bridged species to have lower IS and QS values. Since ring tilt, particularly in the $FeCp_2/HgCl_2$ and $FeCp_2/HAlCl_4$ complexes, is likely to be very large the observed very large QS values cannot be interpreted in terms of this type of distortion. We prefer the explanation given above, that it is the asymmetry in the charge density of the Fe—M bond which

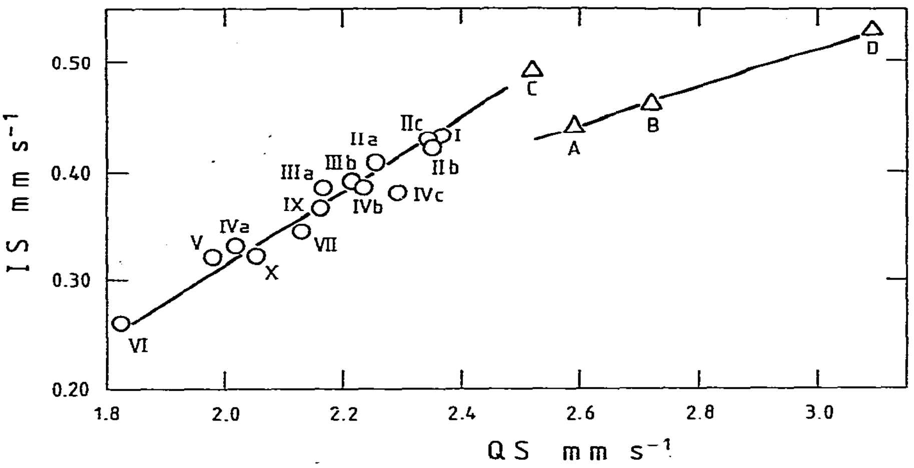


Fig. 1. Correlation between IS and QS for the bridged ferrocenes. (a) The points having Roman numerals refer to Hillman's data (ref. 14) and appear exactly as in the original reference. (b) The points A—D refer to the data in Table 1.

gives rise to these anomalous effects. One interesting feature of Hillman's data is the reasonably good correlation (correlation coefficient 0.970, 14 points, see Fig. 1), between IS and QS for the bridged ferrocene series. This contrasts markedly with the data compiled by Good [15] where such a plot shows almost completely random scatter. Our own results, albeit very limited, also show good correlations. Indeed, excluding the neopentyl-substituted ferrocene where steric factors dictate that the proton attacks in an *anti* sense relative to the bulky substituent, an excellent correlation of IS and QS is found. Interestingly, the neopentyl derivative itself lies on the same line as that of the bridged ferrocenes and may be a reflection of steric hindrance to rotation in the complex. Similar relationships are apparent in other systems [16].

The correlation of QS is interesting. The presence of an electric field gradient (eq) at a Mössbauer nucleus causes a quadrupole splitting (Δ) of the resonance line. The field gradient comprises contributions from the valence electrons, eq_{val} and from the electrostatic charges of the crystal lattice, $eq_{\text{lat.}}$.

It has been shown that the lattice contribution to the e.f.g. is negligibly small compared to the valence contribution for low spin iron(II) compounds [17]. R.L. Collins demonstrated that the sign of e^2qQ in ferrocene was positive in agreement with the prediction of a molecular orbital bonding treatment.

A general correlation between Δ and δ is not expected, but R.W. Grant [19] suggests that if such a correlation does exist, it will be in a series of compounds where the basic structural symmetry of the compound remains unchanged, and only the nature of the bounding of the Mössbauer isotope is varied.

Such a series of compounds would be the ferrocenes studied by Hillman [14], showing that *s* electron density at the nucleus is being affected in a linear fashion by subtle changes in ring tilt and ring distance.

The Mössbauer data for the more distorted ferrocene environments (Fig. 1) also show a direct correlation between IS and QS again showing that *s* electron density is affected by changes in chemical bonding.

The fact that the two correlations exist but are not on the same line indicates that we are dealing with two somewhat different structural environments.

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