MÖSSBAUER SPECTROSCOPIC STUDY OF 19 ELECTRON ORGANOMETALLIC PARAMAGNETIC SANDWICHES $n5-C5R5Fe(I)n6-C6R'6$.

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MÖSSBAUER SPECTROSCOPIC STUDY OF 19 ELECTRON ORGANOMETALLIC PARAMAGNETIC SANDWICHES $\eta^5\text{-C}_5\text{R}_5\text{Fe(I)}\eta^6\text{-C}_6\text{R}'_6$ J.P. Mariot, F. Varret, P. Michaud, D. Astruc^{+a}, J.-R. Hamon^{+a}, G. Althoff^{+a} and P. Batail^{+b}

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1. Introduction.-

The most known organometallic sandwich is ferrocene which is a Fe(II) sandwich fullfilling the 18 electrons rule, i.e they are 18 electrons in the iron valence shell. This compound is diamagnetic and its electronic properties have already been calculated with an MO model /1/. Fe(II) d^6 cations have been synthesized through exchange ligand experiments /2/. Mossbauer hyperfine parameters (fig.1) are found to be similar to that of ferrocene (for ferrocene IS = 0.43 mm/s and QS = 2,38 mm/s at room temperature). By reducing the cations /2/ we obtain 19 electron Fe(I) paramagnetic ($\mu = 1,8 \mu_B$) sandwiches which are very sensitive to air action. Thus the Mossbauer samples were very carefully prepared and conditioned under nitrogen inert atmosphere. As a striking example it is worth noting oxygen action on $\text{C}_5\text{H}_5\text{FeC}_6(\text{CH}_3)_6$ (1) leading to $\text{O}_2^{\bullet-}$, a mode active in aging of living cells /3/. We grew crystals for 1 (fig. 6) only.

2. Results and discussion.-

From 4.2 K to room temperature powder quadrupolar spectra are observed. (fig.3). We must notice the IS of Fe(I) compounds higher than that of Fe(II) ones as expected because of their lower oxydation state. The 19th d electron is in an e_{1g}^* /4/ degenerate orbital. The contribution of a e_{1g} electron to the EFG being around 2 mm/s /5/, we can roughly estimate the 19th electron iron character by comparing the QS of the cation and the radical. For most of the compounds the difference in QS is around 1.5 mm/s (fig.2) leading to $\frac{1.5}{2} = 75\%$ iron character.

To illustrate the different oxydation states **successively** observed during the full study of one particular sandwich we show on fig. 3 the spectra of a) the former cation ($18 e^- d^6$ yellow)

b) the radical ($19 e^- d^7$ green)

Fig. 1 : The studied series of Fe(I) radicals [except 2 which is a Fe(II) complex]

Fe(I) sandwiches	DI/Fe mm/s	SQ mm/s	Cations PF_6^-	DI/Fe mm/s	SQ mm/s
$\text{C}_5\text{H}_5\text{FeC}_6(\text{CH}_3)_6$	0.85 0.74	0.56 1.18 0.50	77 K RT	0.56 0.45	2.00 2.00
$\text{C}_5\text{H}_5\text{FeC}_6(\text{CH}_3)_5\text{C}_2\text{H}_5$	0.83 0.73	0.62 1.16 0.50			
$\text{C}_5\text{H}_5\text{FeC}_6\text{H}_6$	0.87 0.74	0.95 0.38		0.52 0.41	1.64 1.64
$\text{C}_5(\text{CH}_3)_5\text{FeC}_6(\text{CH}_3)_6$	0.81 0.74	1.29 0.54		0.52 0.41	1.72 1.72
$\text{C}_5\text{H}_5\text{FeC}_6(\text{C}_2\text{H}_5)_6$	0.84 0.73	1.40 0.7		0.32 0.41	1.96 1.96

Precision: 0.01 mm/s.

Fig. 2 : Mossbauer hyperfine data for d^6 cations and d^7 radicals.

Fig.3 : Yellow, green (1) and red (2) complexes at room temperature.

Fig. 4 : Temperature dependence of the quadrupole splitting QS.

Fig.6 : Aligned crystals of $C_5H_5Fe(CH_3)_6$ at room temperature for the following two configurations :

Upper spectrum : EFG axis is perpendicular to γ ray. The outer peaks are those of the oxydized (2) form.
Lower spectrum : EFG axis is parallel to γ ray. The crystals were positioned with RX results.

Fig.5 : Green complex (1) under a 5T magnetic field. The fit was done with a positive and axial EFG.

c) the oxydized form ($18 e^- d^6$ red).

The d^7 complexes having a single electron on the e_{1g}^* level are Jahn-Teller systems /4/. The low temperature Jahn-Teller distortion is orthorhombic /4/ and is responsible for the thermal variation of QS (Fig. 4). Assuming a Boltzmann law for thermal population of the electronic levels, the energy splitting of the e_{1g} levels was determined in the range 100 cm^{-1} , 140 cm^{-1} for 3, 6, 7.

A particular behaviour is exhibited by $C_5H_5Fe(CH_3)_6$. This compound keeps a symmetrical potential above 185 K (constant quadrupole splitting). Below 185 K the spectrum splits into two quadrupole doublets (fig. 4) indicating a phase transition (probably due to a cooperative Jahn-Teller effect). This phase transition has been confirmed by RX results at 100 K and 300 K. The spectrum under magnetic field /6/ at 4.2 K (fig. 5) shows that the EFG sign is positive. A - 2,3 T hyperfine field for a 5 T applied field is observed in agreement with the paramagnetic character previously found. From aligned single crystal experiments (fig. 6) the EFG sign at room temperature was found to be positive as well.

Our aim is now to investigate this interesting electronic system :

- determination of ligand field parameters and hyperfine field anisotropy
- characterization of high symmetry matrices in order to observe vibronic effects at low temperature.

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