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Chemistry of Mixed Ligand Complexes. VII.* The Mössbauer Investigation of Cyclopentadienyl Iron Carbonyl Mixed Complexes

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The Mössbauer parameters of $(C_5H_5)Fe(CO)_2X$ mixed complexes were determined, where $X = CS$, CO, CN^-, $P(C_6H_5)_3$, NCO^-, NCS^-, Br^-. The Mössbauer isomer shifts indicated the order of π–acceptor ability of these ligands and the partial isomer shift parameters of the ligands could be calculated. The quadrupole splittings gave information on the formal coordination number of iron in the complexes.

Introduction

The cyclopentadienyl iron carbonyl mixed complexes are among the most covalent compounds of iron. By substitution of one carbonyl in the parent complex $[C_5H_5Fe(CO)_3]^+$ a great variety of mixed complexes of the composition $C_5H_5Fe(CO)_2X$ can be prepared.[1-6] Depending on the charge of X these molecules can be complex cations having one positive charge or neutral complexes. (Henceforth the charge of the complex will be omitted for simplicity).

The Mössbauer effect was used by several authors for the investigation of iron organic complexes.[6] The Mössbauer isomer shift gives information on the electronic density on the iron nucleus, the quadrupole splitting measures the electric field gradient at the iron nucleus. Thus, the Mössbauer parameters give information on the electronic structure and symmetry of the central atom in the complex.

Our former investigations[7] showed—in accordance with the literature[6]—that in the mixed carbonyl complexes containing the same number of carbonyl ligands, $[Fe(CO)_{5-n}L_n]$ ($n = 0$, 1, 3) and $[\pi\text{–allyl}Fe(CO)_2L]^+$ ($L =$ neutral ligand), the nature of the substituting ligands L causes only small changes in the isomer shift values, indicating a similar electronic density on the iron nucleus in the different complexes. Conversely, changes in the CO stretching frequencies indicated that the electronic structure of the coordinated carbonyl groups was influenced by the different substituting ligands L. Thus, the low spin iron atom in these complexes seemed to behave as a good electronic conductor, which made it possible for the carbonyls to compensate for the differences between the substituting ligands.

It seems to be of interest to study how this tendency obtains in other iron complexes. A series of $C_5H_5Fe(CO)_2X$ complexes was studied therefore by Mössbauer spectroscopy, where X denotes CN^-, NCO^-, NCS^-, Br^-, CS or $P(C_6H_5)_3$ (Table I).

Groups of similar complexes were investigated by Herber *et al.*,[8] who set up the table of partial isomer shift (PIS) values for the individual ligands. Thus, our measurements could serve to get the PIS values of those X ligands which were not included in Herber's investigations.

Experimental Section

The complexes were prepared by methods described in former papers published by two of us.[1-5] (U.B. and L.B.).

The Mössbauer spectra were recorded by an apparatus constructed in the Atomic Physics Department of the L. Eötvös University, provided with a driving equipment of constant acceleration, using a ^{57}Co isotope diffused into stainless steel as a Mössbauer source. The source was prepared by the Radiochemical Centre, Amersham, England. The full line width at half height of this source was found to be 0.42 mm/sec against sodium ferrocyanide absorber containing 0.25 mg ^{57}Fe per cm^2. The Mössbauer isomer shift values refer to that of metallic iron at room temperature. Metallic iron of special high purity prepared by Reanal, Hungary especially for this purpose was used for the calibration of the velocity scale.(**) The velocity scale was stricly linear.

The Mössbauer spectrum of each compound was recorded in several independent experiments (2-5

(*) Previous paper of the series: K. Buerger, L. Korecz, S. Papp, B. Mohai: Radiochem. Radioanal. Letters 2, 153 (1969).

(1) L. Busetto and R.J. Angelici, *J. Am. Chem. Soc.*, *90*, 3283 (1968).

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(4) L. Busetto and R.J. Angelici, *Inorg. Chim. Acta*, *2*, 391 (1968).

(5) L. Busetto, M. Graziani, and U. Belluco, *Inorg. Chem.*, *9*, 0000 (1970).

(6) V.I. Goldanskii and R.H. Herber, Chemical Aplications of Mössbauer Spectroscopy, Academic Press, New York, 1968.

(7) L. Korecz, K. Burger, *Acta Chim. Hung.*, *58*, 253 (1968).

(**) To check the velocity scale the spectrum of a standard $Na_2[Fe(CN)_5NO]$ was also recorded.

(8) R.H. Herber, R.B. King, and G.K. Wertheim, *Inorg. Chem.*, 3, 101 (1964).

times). The Mössbauer parameters of each run were evaluated by a curve fitting method made with computer using the usual least square method.

The average of the Mössbauer parameters of the independent runs are shown in Table I. The differences in the Mössbauer parameters given by the parallel experiments were not higher than ±0.02 mm/second.

Two representative spectra are shown in Figures 1-2.

The samples were thermostated with the help of liquid air. The temperature was checked by thermocouples and found to be constant: 85.0±1.0 °K.

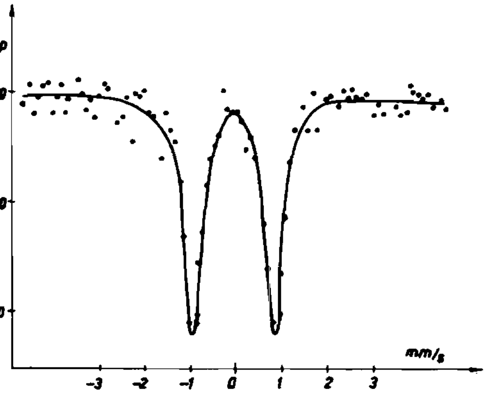

Figure 1. The Mössbauer spectrum of $[C_5H_5Fe(CO)_2CS^+PF_6^-$ measured at 85.0±1.0 °K.

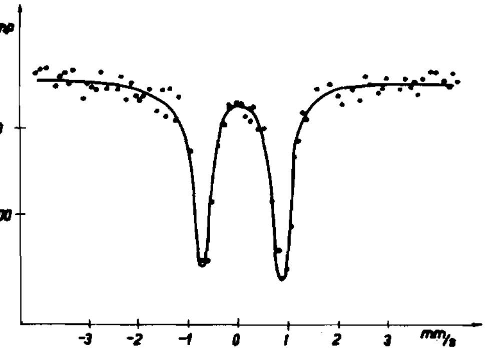

Figure 2. The Mössbauer spectrum of $C_5H_5Fe(CO)_2NCO$ measured at 85.0±1.0 °K.

Results and Discussion

Mössbauer parameters of the complexes are summarized in Table I.

The isomer shift values show definite differences depending on the nature of ligand X in the $C_5H_5Fe(CO)_2X$ complexes. The electron density on the iron nucleus decreases in the following order:

$$CS > CO > CN^- > P(C_6H_5)_3 > NCO^- > NCS^- > Br^-.$$

Thus, the compensation effect of carbonyl ligands[7] mentioned in the introduction seems to be much smaller in these systems than in the tetracarbonyl complexes of the type $[Fe(CO)_4L]$, *i.e.* the influence of X ligands on the nucleus of the central atom seems to increase with decreasing carbonyl content of the compounds.

Table I. The Mössbauer parameters of $C_5H_5Fe(CO)_2X$ complexes.

Complex	Isomer shift, mm/sec	Quadrupole splitting mm/sec
$[C_5H_5Fe(CO)_2CS]^+PF_6^-$	−0.05	1.89
$[C_5H_5Fe(CO)_3]^+PF_6^-$	+0.01	1.78
$[C_5H_5Fe(CO)_2CN]$	+0.04	1.96
$[C_5H_5Fe(CO)_2P(C_6H_5)_3]^+Cl^-$	+0.05	1.92
$[C_5H_5Fe(CO)_2NCO]$	+0.10	1.61
$[C_5H_5Fe(CO)_2NCS]$	+0.25	2.00
$[C_5H_5Fe(CO)_2Br]$	+0.26	2.00

Table II. Partial isomer shift parameters for various ligands, mm/sec

CS	−0.06
CO	+0.002
CN^-	+0.03
$P(C_6H_5)_3$	+0.04
NCO^-	+0.09
NCS^-	+0.24
Br^-	+0.25
π-C_5H_5	+0.006

The differences in electronic density on the iron nucleus might be due to several effects: the different donor strength, the different π–acceptor ability and in a smaller extent the different spacial requirement of X ligands.

The increase of the donor strength of the ligand, and the increase of its π–acceptor ability (this latter causes the increased back-coordination) both increases the electrondensity at the place of the iron nucleus, the former by increasing the s–electrondensity, the latter by decreasing the d–electrondensity and through this the shielding effect of the *d*–electrons of iron. The higher electrondensities at the iron nucleus in the complexes containing the ligands with higher π–acceptor ability indicate that in these systems the difference in π–acceptor ability of the ligand, (*i.e.* the different degree of back-coordination) seems to be the dominant factor which causes the changes in isomer shift values.

The thiocarbonyl group in this contest appears to be the most effective π–bonder. This conclusion is in agreement with i.r. data on the CO stretching frequencies of complexes of the type $[C_5H_5Fe(CO)_2L]^{1-3}$ (L = pyridine, CH_3CH, $P(C_2H_5)_3$, C_2H_4). Furthermore, a molecular orbital treatment of the CS molecule has shown that back donation from the metal to CS should be easier than to CO.[9]

The definite differences in the isomer shift values made possible the calculation of the partial isomer shift (PIS) parameters of the various X ligands (Table II).

For the basis of these calculations the PIS value of the CO ligand was taken from the isomer shift of iron pentacarbonyl determined with the same source in our previous investigations (0.01:5 = 0.002 mm/sec).

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(9) W.G. Richards, *Trans. Faraday Soc.*, *63*, 257 (1967).

On the basis of the PIS values of these ligands we could also calculate the partial isomer shift parameter of the cyclopentadienyl ligand. In contrast to the findings of Herber *et al.*, in our systems the isomert shift values of all of the complexes could be calculated by using this PIS value.

One has to emphasize, however, that this PIS value is different from that calculated on the basis of the isomer shift value of ferrocene. This seems to show that the isomer shift can be considered as an additive molecular parameter only in systems having analogous composition and electronic structure.

The quadrupole splitting values of all of the complexes were between 1.61 and 2.00 mm/sec, *i.e.* much lower than that of iron–pentacarbonyl (2.52 mm/sec). This seems to indicate, in accordance with our previous investigations,[7,10] that iron has a formal coordination number of 6 in the complexes investigated, *i.e.* the cyclopentadienyl group can be surmized to occupy formally 3 coordination sites of iron. The smaller differences in the quadrupole splittings could not be discussed here, because the correlation of the magnitude of this splitting with features of the molecular architecture in these systems is still poorly understood.

(10) . Burger, L. Korecz, and G. Bor, *J. Inorg. Nucl. Chem.*, *31*, 1927 (1969).