An Iron−Carbonyl Derivative of C$_{60}$ Examined with Mössbauer Spectroscopy

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Mössbauer measurements performed between 5 and 300 K on polycrystalline powder of an iron−carbonyl derivative of C$_{60}$ reveal two inequivalent iron sites. The first site displays a quadrupole split doublet at all temperatures, assigned to an [{Fe(CO)$_4$}$_x$(η^2-C$_{60}$)] adduct (x unknown). This iron site presents an $S = 0$ spin state and a negative isomer shift indicating that C$_{60}$ acts as an electron pair donor to the metal center. The average effective hyperfine field for the second site is characteristic of an Fe(III) high-spin ($S = {}^5/_2$) state and exhibits relaxation effects. This Fe(III) sextet splits into two subspectra, on the application of a magnetic field, which can be assigned to the octahedral and tetrahedral sites of γ-Fe$_2$O$_3$ microparticles formed on the grain surface.

Introduction

The formation of transition-metal (TM) fullerene complexes, where the TM is bound to one[1−3] or two[4] hexagonal C═C bonds shared by two six-membered rings, is one of the new active fields of research in organometallic chemistry. Single-crystal X-ray structural analysis[1] of [Pt(PPh$_3$)$_2$(η^2-C$_{60}$)] shows that only those carbon atoms which interact with the Pt are pulled away from the C$_{60}$ sphere, whereas other, more distant, carbon bonds are perturbed only slightly. Recently a new C$_{60}$ derivative of iron, [Fe(CO)$_4$(η^2-C$_{60}$)], has been reported[5] where ^{13}C NMR spectra in a CS$_2$ + C$_6$D$_6$ solution were consistent with a C$_{60}$ molecule occupying an equatorial position at the iron center and with the carbonyls undergoing rapid exchange, on the NMR time scale, between axial and equatorial positions.

The determination of the strength and degrees of covalency of the bonds linking the central atom to the ligands in C$_{60}^-$ metal complexes is a question of great importance in studies of the chemistry of these complexes. The existence of a C$_{60}^-$ iron−carbonyl derivative presents a first opportunity to investigate the electronic charge transfer in the bond between the metal and the C$_{60}$ ligand by measuring the hyperfine parameters at the iron nucleus. It is to be expected that in complexes of iron with different ligands the decreasing sequence of isomer shifts (IS) will be approximately the same as the increasing sequence of covalency of the bond between metal and ligand.[6] In the present study, ^{57}Fe Mössbauer spectroscopy is employed to obtain information about the bonding and iron coordination environment of the iron−carbonyl derivatives of C$_{60}$ in the solid state (not in solution).

Preparation and Characterization

Since [TM(PEt$_3$)$_2$]$_x$(η^2-C$_{60}$) (TM = Ni, Pd, Pt) complexes have been observed[1] for x up to 6, we have made attempts to prepare a six-coordinate iron−carbonyl−C$_{60}$ complex using mixtures of C$_{60}$ and Fe$_2$(CO)$_9$ in dry benzene for molar ratios from 1:6 to 1:20. Optimum crystallinity, as judged by powder X-ray diffraction (XRD), was obtained for a 1:10 mixture. All measurements below refer to this product. The precipitated red microcrystals were collected from solution by filtration, washed with dry benzene, and dried in vacuo. The polycrystalline powder is practically insoluble in common organic solvents and is stable to heat up to 360 K. Therefore, preparation of single crystals is impossible in this way. The XRD pattern of the red powder, measured with Cu Kα radiation in a SIEMENS D5000 diffractometer, corresponds to a crystalline phase with a low-symmetry structure (mono- or triclinic). There were no detectable traces from other secondary phases like pure (fcc) C$_{60}$ or iron carbonyls and oxides. Cold neutron capture prompt γ-ray activation analysis[7] has been used in the National Institute of Standards and Technology (NIST, USA) reactor to analyze the fullerene complex for Fe and H. The iron content is 23 (1) and the hydrogen 0.28 (3) wt %.

Fourier-transform infrared transmission spectra (FTIR) were collected with a Perkin-Elmer 1072 spectrometer for microcrystals on a KBr substrate at a resolution of 4 cm^{-1}. The observed IR lines show at least three CO modes: one sharp at 2090 cm^{-1} and two broad and overlapping at 2018 and 1985 cm^{-1} to be compared with those observed in ref 5 [IR (CS$_2$) 2096, 2033, 2005, 1974 cm^{-1}]. In addition there are 10 IR active modes at 1371, 782, 737, 708, 618, 591, 537, 524, 475, and 412 cm^{-1}, which may signify a drastic lowering of the icosahedral symmetry for the C$_{60}$ [in pure C$_{60}$ there are only four IR active modes at 1429, 1183, 577, and 527 cm^{-1} with T_{1u} symmetry].

^{57}Fe Mössbauer Results

Mössbauer spectra were recorded in the temperature range 5−300 K by using a conventional constant acceleration spectrometer with a ^{57}Co(Rh) moving source at room temperature. The iron spectra were referenced against iron foil at 298 K. The absorption spectra in zero applied field are plotted in Figure 1 for the three characteristic temperatures and the hyperfine parameters (HP) are listed in Table 1. There are two inequivalent iron sites. The first component (site I) presents a significant negative IS and remains a simple quadrupole split (QS) doublet for all the examined temperature range. The second component

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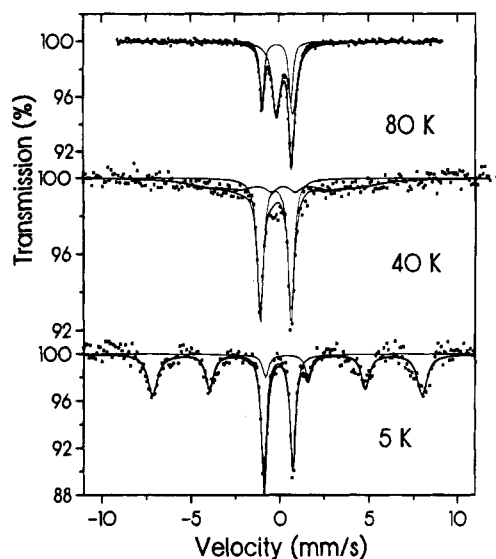**Figure 1.** ^{57}Fe Mössbauer spectra. The solid lines correspond to Lorentzian line-shape components used in the fitting procedure of the spectra in order to derive the HF parameters.

TABLE 1: Observed ^{57}Fe Mossbauer Isomer Shift (IS), Quadrupole Splitting (QS), and Average Effective Field $\langle B_{eff} \rangle$ Parameters

T, K	site	IS (Fe), mm/s	QS mm/s	$\langle B_{eff} \rangle$ T
RT	I	−0.26 (2)	1.58 (3)	
	II	0.17 (2)	0.88 (3)	
80	I	−0.14 (2)	1.63 (3)	
	II	0.32 (2)	0.93 (3)	
40	I	−0.08 (2)	1.66 (3)	
	II	0.34 (6)		25.2 (8)
5	I	−0.07 (2)	1.62 (3)	
	II	0.40 (2)		47.2 (7)

(site II), is subject to strong temperature-dependent relaxation effects. The doublet at higher temperatures splits to a broad subspectrum at 40 K, which relaxes to a six-line pattern at lower temperatures. Lorentzian line shapes have been used for the fitting. The hyperfine field parameters for site II are characteristic of high-spin ($S = \frac{5}{2}$) Fe(III) complexes. A careful comparison of the obtained HP with those observed in the known iron—carbonyl complexes[8] excludes any possibility for formation of isolated admixtures with mono- or di- or triiron— carbonyl species. The application of a 6-T field, perpendicular to the γ-ray propagation direction, causes a modification of the doublets in the Mössbauer spectrum at 5 and 60 K (Figures 2 and 3). The observed splitting of the quadrupole doublet on application of the field at 5 K (Figure 2) is characteristic[9] of a diamagnetic iron component ($S = 0$). In the event of an axially symmetric electric field gradient q (η small), when the quadrupole line pair splits into a doublet and a triplet, the presence of the doublet in the more positive (Figure 2) velocity range means that q is positive. Simulation of an $S = 0$ quadrupole splitting in a 6-T applied field with $\eta = 0.1$ and area 33% of the total spectrum matches satisfactorily with some of the observed absorption lines at 60 K (Figure 3). Furthermore, the broad six-line subspectrum for site II at 5 K splits into two components on the application of a 6-T field (Figure 2), which reveal an antiparallel magnetic coupling of the Fe moments.

Discussion and Conclusions

The HP of component II, the antiferromagnetic coupling, and the temperature variation of the spectra, typical of superparamagnetic phenomena, lead to the conclusion that this component corresponds to some iron oxide phase in the form of small
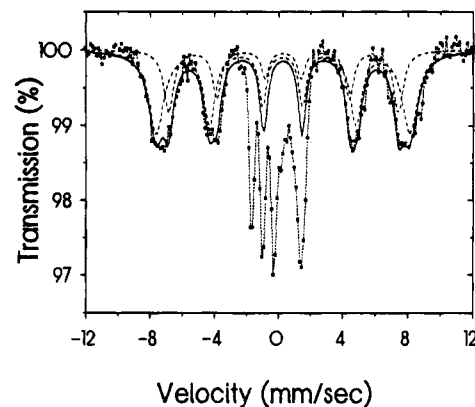

Figure 2. Mössbauer spectrum at 5 K in an applied field of 6 T. The dashed lines correspond to six-line Lorentzian fit of the A and B sites of γ-Fe$_2$O$_3$ and the solid line is the sum of the two. The dotted line in the experimental spectrum is a guide to the eye.
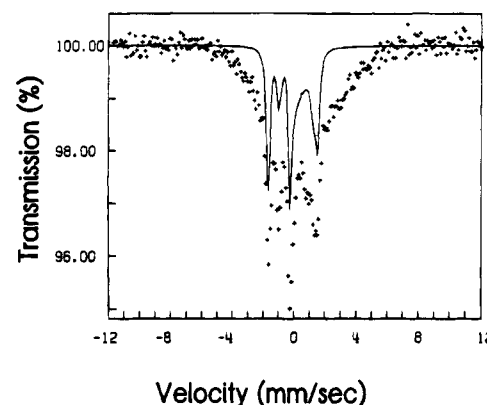

Figure 3. ^{57}Fe Mössbauer spectrum at 60 K in a 6-T applied field perpendicular to the propagation of γ-rays. Experimental spectrum (dots) and simulated diamagnetic spectrum (solid line) with an area 33% of the total spectrum.

particles. Such a phase could possibly form from free iron on the surface of the precipitate grains in the solution, which are converted to small particle oxides after exposure of the crystallites to the atmosphere. Such small grains may not show up in XRD. A possible candidate for the oxide is the inverse spinel γ-Fe$_2$O$_3$ with Fe^{3+} ions in tetrahedral and octahedral sites.[10] It should be mentioned, however, that the hyperfine field and the ratio of the tetrahedral to octahedral site occupancy observed in our sample deviate from bulk values. This discrepancy may arise from the size and the shape of the particles, which in turn affects the amount of defects and the cation distribution, as was observed recently by Morales et al.[11] In any case, we consider this phase to be unrelated to the iron— carbonyl complexes and will not give any further attention to it.

The present data also permit an assignment of the chemical environment for site I. The negative value of IS for site I is comparable to that observed in many organometallic compounds with an [Fe(CO)$_4$]$^-$ adduct[8] and supports formation of a [{Fe-(CO)$_4$}$_x$(η^2-C$_{60}$)] (x undetermined) compound in the solid state. This site gives a diamagnetic splitting on the application of the 6-T field, indicating that the spin state is $S = 0$. The IS of iron—carbonyl complexes lie in a narrow range of 0.3 mm/s, even for carbonyl mixed complexes of most varied compositions,[8] indicating that the electronic structure of the central atom changes to a lesser degree. For example, the IS of tetracarbonyl complexes that contain a different fifth ligand, relative to Fe-(CO)$_5$ [IS(Fe) = −0.09 mm/s at 80 K], differs by barely more than the experimental error. The decrease in IS ($=$−0.14 mm/s

at 80 K) observed here, by replacement, e.g., of a single carbonyl group with a C=C hexagonal pair of C_{60}, can be explained from a direct comparison with a series of substituted derivatives of $Fe(CO)_5$ with chemical formula $LFe(CO)_4$, where L is an electron pair donor[8] such as Ph_3P- or π-allyl. The observed interdependence of the IS and QS with a change of ligands,[12] in $LFe(CO)_4$ compounds at 80 K, suggests that the $-Fe(CO)_4$ group be regarded as a fixed structure. Remarkably enough, the HP observed here at 80 K fall in the range of IS and QS values observed in $LFe(CO)_4$ derivatives. By considering the conventional view of iron organometallic bonds, where the ligands act as donors of electrons, forward coordination and back-donation *both* can lead to an IS with negative values.[12] Since the IS (=−0.14 mm/s) in the C_{60} adduct is more negative than for $Fe(CO)_5$, according to the results obtained in $-Fe(CO)_4$ cations,[8,12] it is clear that forward coordination dominates the net IS. In addition, the observed FTIR CO modes are different from the spectra of other $-Fe(CO)_4$ complexes. Generally, such differences among iron−carbonyl complexes show that the replacement of even a single carbonyl group with some other ligand leads to a significant difference in the frequencies of vibration of the carbonyls,[13] indicating that formation of the mixed complex is associated with a change in the electronic structure of the carbonyl ligand. Consequently the C_{60} ligand can be considered as an electron pair donor with a lesser π-acceptor ability than the CO groups, which, to a certain extent, seems to compensate for the charge due to the ligand exchange. Recently, an ^{193}Ir Mössbauer study[14] of $IrCl(CO)(PPh_3)_2(\eta^2-C_{60})\cdot5C_6H_6$ has shown also a weaker π-acceptor ability of C_{60} relative to other substituted adducts (tetracyanoethylene). The strength and degree of covalency of the bond linking the C_{60} to iron can be judged from the IS, which lies between that of $[Na^+]_2[Fe(CO)_4]^{2+}$ (IS(Fe) = −0.18 mm/s) and $Fe(CO)_5$ at 80 K.

In conclusion, two inequivalent iron sites were observed: one related to the $[\{Fe(CO)_4\}_x(\eta^2-C_{60})]$ adduct and the second one to $\gamma-Fe_2O_3$ particles. Since the site I iron−carbonyl adduct is diamagnetic ($S = 0$), one way to investigate the possible formation of Fe(II), with $S \neq 0$, C_{60}−organoiron species should be directed to substitutional chemistry with mixed carbonyl and other ligands that may alter the electronic states in a way to give a nonzero effective spin in the ground state.

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