

Investigations of iron adducts of C_{60} : Novel FeC_{60} in the solid state with Fe inside the C_{60} cage

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By carrying out contact-arc vaporization of graphite in a partial atmosphere of $Fe(CO)_5$, an iron-adduct with C_{60} has been obtained. The adduct has been characterized by various techniques including mass spectrometry, ^{57}Fe Mössbauer spectroscopy and Fe K-EXAFS. Properties of this adduct are compared with those of an adduct prepared by solution method where Fe is clearly outside the cage. Results suggest that FeC_{60} obtained from the gas phase reaction has the Fe atom in the cage.

The 7 Å diameter cavity in buckminsterfullerene has long been considered as a possible host for various atoms and molecules¹. There have been several attempts to incorporate metal atoms such as La in this cavity. In all these studies²⁻⁶ the species identified were generally in the gas phase and were characterized by mass spectrometry. The question whether the metal atom is inside or outside the spheroidal hollow cage in these species has not been resolved fully. Freiser and coworkers⁴ have generated a FeC_{60} complex in the gas phase by means of a ligand-exchange reaction and have also characterized NiC_{60} and $Ni(C_{60})_2$ in the gas phase.

One example where an atom has been entrapped in C_{60} is that where a high-energy beam of C_{60} was made to interact with helium to give HeC_{60} in the gas phase⁵. Chai *et al.*⁶ have more recently prepared fullerenes with La trapped in the cages by laser vaporization. Metal complexes of C_{60} where the metal is present outside the cavity have been prepared by solution methods and characterized^{7,8}. We have investigated an iron adduct of C_{60} , $FeC_{60}(I)$, where iron atoms were introduced during the contact-arc vaporization of graphite, expecting that this would result in the entrapment of Fe in the cavity. In order to understand some of the unique features of this adduct prepared by the gas phase reaction, we have compared its properties with those of a solid $FeC_{60}(II)$ adduct prepared by solution method, wherein Fe was clearly bound externally to the fullerene. We have primarily employed mass spectrometry, ^{57}Fe Mössbauer spectroscopy and extended X-ray absorption fine structure (Fe K-EXAFS) in these investigations.

Materials and Methods

In our effort to obtain the Fe adduct of C_{60} with the metal inside the cage, we carried out the contact-arc vaporization of graphite in an atmosphere of $Fe(CO)_5$. The arc chamber was pumped to a base vacuum of $\sim 10^{-6}$ torr and He gas admitted to about 50 torr through a needle valve. $Fe(CO)_5$ was admitted to the system from a reservoir at the same rate as He. ^{57}Fe Mössbauer spectrum of the soot so obtained was recorded with a constant acceleration spectrometer with a ^{57}Fe source. The spectrum showed a 6-finger pattern due to Fe_3C and α -Fe along with a singlet due to a new species. The soot was Soxhlet-extracted with toluene for about 3 hours and the extract vacuum-dried at 380 K to remove any volatile iron compounds. The mass spectrum of the product of solvent extraction was then recorded. It showed the presence of mass peaks other than those due to C_{60} and C_{70} which could be ascribed to FeC_{60} . The mass spectrum of the residue left over after solvent extraction did not show any volatile species upto 400°C. The product of solvent extraction showed an additional spot in the TLC other than those due to C_{60} and C_{70} with an R_f value close to that of C_{70} . After separating out C_{60} by column chromatography, the new product was eluted out along with a small proportion of C_{70} . The product was then examined by mass spectrometry and ^{57}Fe Mössbauer spectroscopy. Magnetic susceptibility (with a Lewis Coil magnetometer) and X-ray diffraction (STOE diffractometer) measurements as well as UV-visible and infrared spectroscopic measurements were also carried out.

In order to compare $FeC_{60}(I)$ obtained from the

gas-phase reaction with that of an adduct where Fe is definitely outside the cage we prepared $\text{FeC}_{60}(\text{II})$ by the reaction of the solid Na compound with C_{60} (prepared by the reaction of Na with C_{60} in toluene solution) with FeCl_2 in THF solution. $\text{FeC}_{60}(\text{II})$ was also investigated by the various techniques mentioned earlier.

EXAFS measurements were carried out at room temperature, using a Rigaku spectrometer attached to a rotating anode X-ray generator (Ru-200B, Rigaku, Japan). A Ge(220) monochromator was used with a 0.1 mm slit for X-rays from a Mo-target. The spectral resolution was about 5 eV at 9 keV incident energy. The samples were pressed into self-supporting wafers after mixing with polyethylene powder (Merck). The thickness of the wafer was adjusted so that the edge jump (μd) was ≈ 1.5 . The pre-edge data were collected in steps of 5 eV for 100 eV and data upto 700 eV after the edge were collected in steps of 1 eV. EXAFS of the reference compound, ferrocene (Fe-C: N = 10, R = 2.05 Å), was also recorded under similar conditions. The EXAFS data were treated using the multishell model involving the additive relationship of EXAFS function. Fourier transforms (FT) were obtained with $k_{\text{min}} \approx 3.5$ and $k_{\text{max}} \approx 12.0 \text{ \AA}^{-1}$ after weighing the data by k^3 .

Results and Discussion

The mass spectrum of $\text{FeC}_{60}(\text{I})$, in mixture with C_{70} , obtained after column chromatography (Fig. 1) showed peaks at 776, 752 and 728 ascribable to FeC_{60} , FeC_{58} and FeC_{56} , besides peaks at 720 and 840; we must note the m/z 720 is also found in the mass spectrum of C_{70} . A mass peak at 388 is seen due to the half-mass of FeC_{60} . The presence of C_2 -loss peaks in the decreasing order of intensity suggests that Fe may be internally bound to the C_{60} frame. Similar C_2 losses found in He-C_{60} and La-C_{60} have been attributed to the entrapment of He and La in the hollow cage^{5,6}. The ^{56}Fe Mössbauer spectrum⁹ of the adduct (anal. Fe 7.2%) shows a singlet with an isomer shift of -0.083 mm/sec with respect to $\alpha\text{-Fe}$, (Fig. 2), characteristic of iron in a near-zero oxidation state. The sharpness of the spectrum suggests a strongly bound Fe species. The compound was weakly paramagnetic over the 10-300 K range. Its electronic absorption spectrum (Fig. 3) showed a slight red shift relative to that of C_{60} . The infrared spectrum was not very different from that of C_{60} . The powder X-ray diffraction pattern of $\text{FeC}_{60}(\text{I})$ could best be fitted into a primitive tetragonal structure ($a = 15.43 \text{ \AA}$, $c = 9.08 \text{ \AA}$) rather than an FCC structure. The most intense line due to the

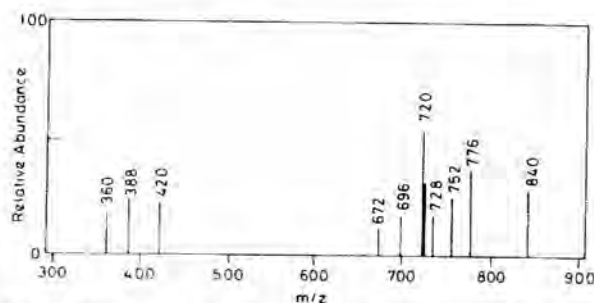


Fig. 1—Mass spectrum of $\text{FeC}_{60}(\text{I})$ (in mixture with C_{70}) from the gas-phase reaction. Peaks at 840, 720, 696 and 672 arise from the parent fullerenes.

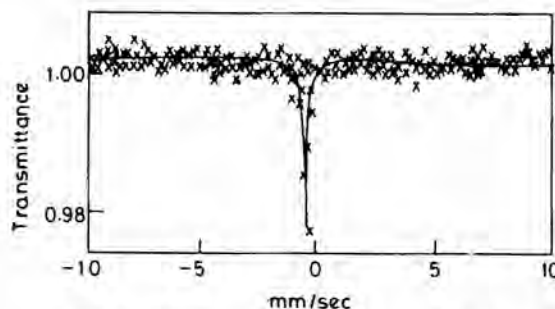


Fig. 2— ^{56}Fe Mössbauer spectrum of $\text{FeC}_{60}(\text{I})$

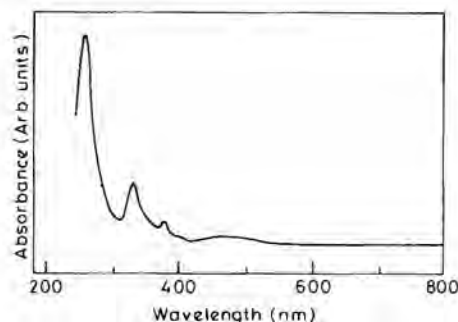
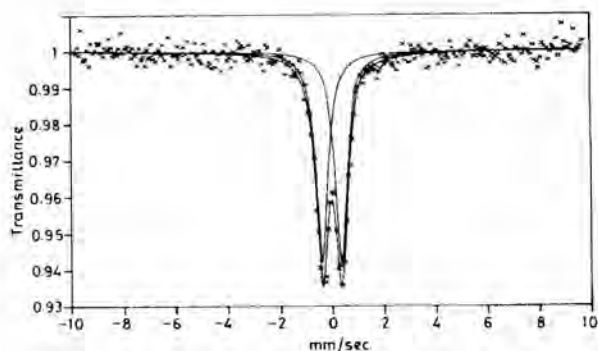
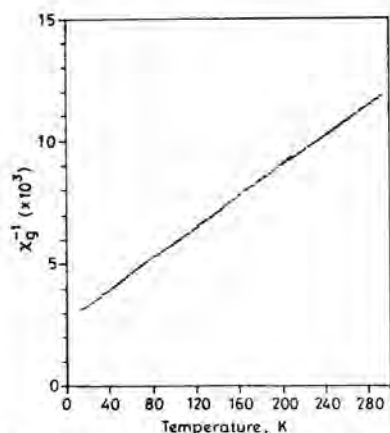
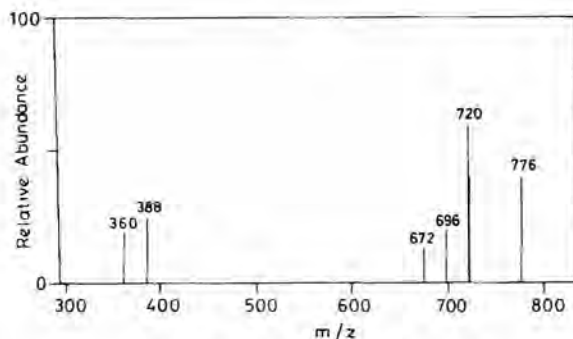


Fig. 3—Electronic absorption spectrum of $\text{FeC}_{60}(\text{I})$ in hexane solution.

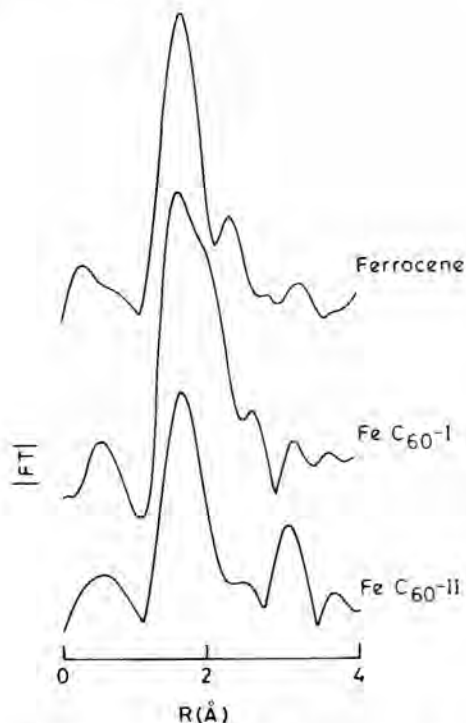
(221) reflection was not consistent with the FCC structure. The tetragonal structure can be understood as resulting from a cell determined primarily from the Fe atoms and the intense line in the diffraction pattern could be simulated with Fe cage atoms 8 Å apart.

Unlike the $\text{FeC}_{60}(\text{I})$ prepared by the gas-phase reaction, solid $\text{FeC}_{60}(\text{II})$ where Fe was bound externally to the fullerene showed a doublet in the Mössbauer spectrum (Fig. 4) with an isomer shift of 0.45 mm/sec due to Fe(III). Magnetic susceptibility measurements showed evidence for antiferromagnetic interaction (Fig. 5). Both the electronic and infrared spectra were different from those


 Fig. 4—⁵⁷Fe Mössbauer spectrum of FeC₆₀(II)

 Fig. 5—Magnetic susceptibility of FeC₆₀(II)

 Fig. 6—Mass spectrum of FeC₆₀(II)

of C₆₀. Furthermore, the mass spectrum did not show C₂ losses (Fig. 6).

We have examined the structures of the two FeC₆₀ adducts (I) and (II) by means of Fe K-EXAFS measurements. In Fig. 7 we show the Fourier transforms of the EXAFS data of the FeC₆₀ adducts along with the FT of the reference compound, ferrocene. We see significant differences in the FTs though the main peak occurs around the same position (1.62 Å) in all the cases. The FT of


 Fig. 7—Fourier transforms of the Fe K-EXAFS of FeC₆₀(I), FeC₆₀(II) and of ferrocene

the adduct-I has a shoulder on the main peak around 2.0 Å whereas that of the adduct-II shows a distinct peak at 3.0 Å. We have carried out the curve-fitting analysis on the inverse transformed data using phase and amplitude parameters of Fe-C from ferrocene. The best fits obtained are depicted in Fig. 8 and the *r*-windows employed are also given. The inverse transformed data of the main peak of FeC₆₀(I) required two Fe-C distances, 2.06 and 2.34 Å, unlike the case of FeC₆₀(II) which gave a good fit just with one short Fe-C distance. The data of FeC₆₀(II) comprising the second peak were fitted with a Fe-C distance of 3.46 Å. Interestingly, the FeC₆₀(I) adduct showed slightly negative $\Delta\sigma^2$ while FeC₆₀(II) adduct gave a high positive value of $\Delta\sigma^2$. The results of the curve-fitting analysis are listed in Table 1. The negative $\Delta\sigma^2$ indicates strong Fe-C bonding.

In order to interpret the EXAFS results we have simulated the local coordinations of the Fe atom by placing it inside and outside the C₆₀ unit and imposing a constraint that the first Fe-C distance should be 2.05 Å. This was done by generating the (*x,y,z*) coordinates of the 60 carbon atoms and calculating the Fe-C distances for different positions of the Fe atom. A high coordination number was ensured by placing the Fe atom in

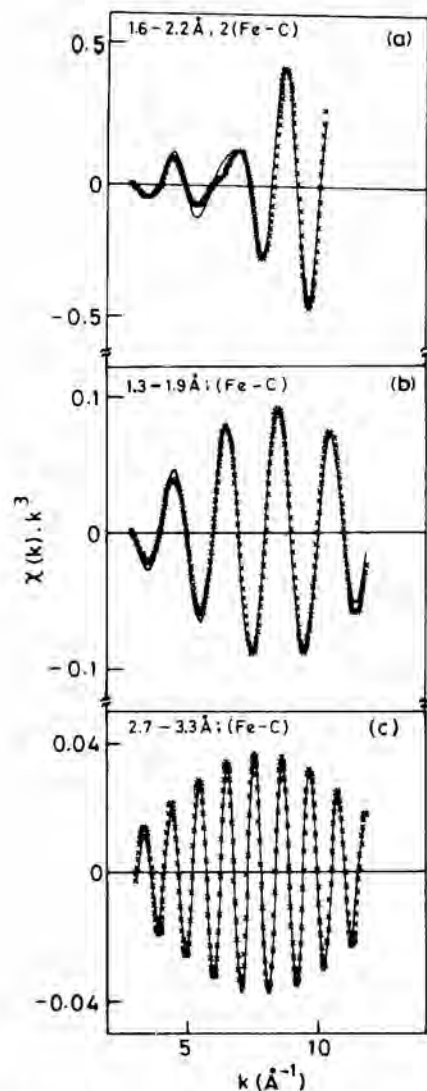


Fig. 8—Curve fitting of the inverse transformed data. The phase and amplitude parameters as well as the r -windows are indicated: (a), $\text{FeC}_{60}(\text{I})$; (b) & (c) $\text{FeC}_{60}(\text{II})$

Table 1—EXAFS results on FeC_{60} adducts

System	N	R (Å)	$\Delta\sigma^2$ (Å ²)
Ferrocene (reference)	10	2.05	—
$\text{FeC}_{60}(\text{I})$	11	2.06	-0.0002
	8	2.34	-0.0003
$\text{FeC}_{60}(\text{II})$	8	2.03	0.0003
	10	3.46	0.001

front of a pentagon or a hexagon of carbon atoms. We find marked differences in the local coordination of the Fe atom when it is placed inside and outside. In the situation wherein Fe atom is

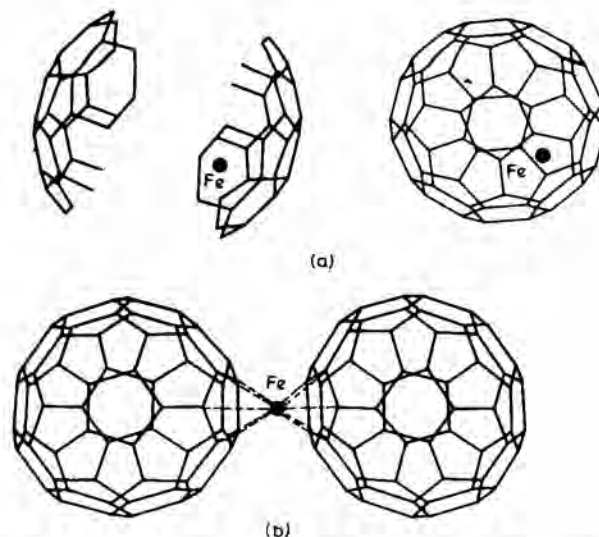


Fig. 9—(a) Formation of endohedral FeC_{60} with Fe in the C_{60} cage (schematic); (b) Ferrocene analogue of C_{60} ($\text{C}_{60} \text{FeC}_{60}$)

bonded externally to the C_{60} unit, we find the second Fe-C distance to be around 3.4 Å which exactly corresponds to the results obtained with adduct-II. We could not obtain two short Fe-C distances (< 3.0 Å) with Fe being outside the cage. The possibility wherein the Fe atom is coordinated to three or more C_{60} units involving short Fe-C distances is negligible because it would bring the C_{60} units at a distance shorter than the van der Waals' sphere. The presence of short Fe-C distances (< 3.0 Å) as found in the case of adduct-I can only be reconciled if the Fe atom is inside the cage (Fig. 9).

We have sought to prepare $(\text{C}_{60})_2\text{Fe}$ by reacting the mono-Na salt of C_{60} with FeCl_2 in solution. A brown solid thus obtained has a different electronic spectrum. Electron-impact mass spectroscopy unfortunately seems to fragment the species. Fe-C distances in this ferrocene analog (Fig. 9) cannot be distinguished from those in $\text{FeC}_{60}(\text{II})$.

The near-zero oxidation state of Fe, C_2 losses in the mass spectrum, occurrence of two short Fe-C distances as well as some of the other features indicate that $\text{FeC}_{60}(\text{I})$ obtained by the gas phase reaction during arc-vaporization of graphite is likely⁹ to be an endohedral species with the Fe atom inside the cage of C_{60} . A possible mode of formation is indicated in Fig. 9.

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