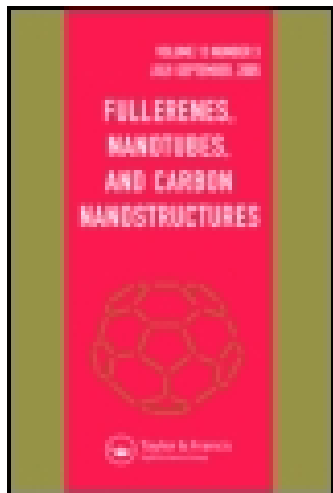


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### ESR Studies on $C_{60}\cdot O_X$ and $C_{60}\cdot HMTTEF$

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## ESR STUDIES ON $C_{60}O_x$ AND $C_{60}HMTTEF$

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### Abstract

The electron spin resonance (esr) of  $C_{60}O_x$  and  $C_{60}HMTTEF$  (hexamethylentetratellurafulvalene) has been investigated at 9.36 GHz as a function of temperature,  $T$  ( $298 \geq T \geq 4$  K).  $C_{60}O_x$  shows an esr absorption of equal 'g' value to that of  $C_{60}$  exposed to  $O_2$  and light but is more intense. The  $C_{60}$  in its pure form is in a singlet state. The impurity sites introduced by  $O_2$  produce the esr absorption. The Curie - Weiss plots of inverse esr absorption intensity versus temperature indicate an

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antiferromagnetic  $\Theta \approx 50$  for air exposed  $C_{60}$  and 90K for  $C_{60}O_x$ . From the esr intensity at room temperature, the calculated number of free spins ( $S = 1/2$ ) is  $\approx 1/3$  per mole of  $C_{60}O_x$ . In case of  $C_{60} \cdot HMTTEF$ , there is a very weak esr absorption at room temperature suggesting that the room temperature form is diamagnetic with very small charge transfer between  $C_{60}$  and HMTTEF. This conclusion is consistent with the structure and magnetic susceptibility of this cocrystal. As the temperature is lowered, the equilibrium:  $AD \rightleftharpoons A^{*-} + D^{*+}$  is displaced towards the formation of free radical species,  $A^{*-}$  and  $D^{*+}$ .

## Introduction

$C_{60}$  is in a singlet ground state and should be esr silent. However  $C_{60}$  exposed to air and light as well as its charge transfer compounds are esr active. ESR spectra have given useful information, on  $C_{60}^{-1,-2,-3}$  anions produced as a result of electron transfer to  $C_{60}^{1-10}$  and on  $C_{60} \cdot R$  adducts<sup>11-13</sup>. We have applied esr to study two new derivatives:  $C_{60} \cdot O_{22}$  and  $C_{60} \cdot HMTTEF$ .

## Experimental

$C_{60} \cdot O_x$  was prepared by the procedure described earlier<sup>14</sup>. Samples weighed immediately after reaction in  $10^3$  bar  $O_2$  pressure at room temperature showed a weight increase of  $\approx 48\%$  giving  $x \approx 22 \pm 2$ . The material is esr active, and the

results presented here throw interesting light on the nature of this compound. The other new compound studied is  $C_{60}$ -HMTTEF, a compound reported recently<sup>15</sup>. This was synthesised using the method reported by Pradeep et al.<sup>15</sup>. X-ray diffraction measurements were made on samples on a Scintag PAD-V diffractometer using  $Cu-K\alpha$  radiation and an intrinsic Ge solid state detector with 200 eV energy resolution. The diffraction pattern ( $2\theta$  values and intensity) matched with our earlier patterns obtained from single phase  $C_{60}$ -HMTTEF samples. This was presumed to be a charge transfer complex between  $C_{60}$  and HMTTEF and esr was expected to throw light on the extent of charge transfer and on the energy states of the system. The results, however, indicate very little charge transfer.

The esr data were obtained using a Bruker esr spectrometer ER200 with a dual cavity, which allows one to obtain absolute intensity measurements. The sample cavity was equipped with an Oxford 900 liquid He Cryostat and the reference cavity contained a known amount of free radical 1,1'-bis(diphenyl)ethylene with  $g = 2.0027$  (ref. 16). The number of spins,  $S$  was determined using the calibration relation:

$$\text{Unknown(s) } N_s = f[(T, MA)_r / S(S+1)] * (A_u / A_r) * (\Delta B_{ms, \text{unknown}})^2 \quad (1)$$

where  $A_u$  and  $A_r$  are the derivative amplitudes of sample and

reference respectively and  $\Delta B_{ms}$  is the line width between the points of maximum slope in mT. The accuracy of scan rates  $dB/dt \leq 2mT/s$  was better than  $\pm 10\%$ .  $f(T, MA) = MA * 5.3E11 * (T/298)$  when Boltzmann statistics are obeyed and the line shapes are Lorentzian. MA is the modulation amplitude and saturation was ruled out using  $B1 \leq 10mT$ .

## Results and Discussion

Figure 1 shows the esr powder absorption derivative  $dP/dB$  versus  $B_z$  for the  $C_{60}$  (air exposed),  $C_{60}.O_x$  ( $x \approx 22$ ) and  $C_{60}.HMTTEF$  samples at 298 K together with the esr absorption parameters. As is well known, pure  $C_{60}$  has a singlet ground state and esr silent. However, epr signals are observed for  $C_{60}$  that has been exposed to oxygen and light. This is shown in figure 1. The behavior of  $C_{60}O_x$  is also quite similar to that of  $C_{60}$  exposed to  $O_2$  and light. Both have the same line shape, line width, absorption intensity and the same  $g$  value (Table 1). The number of unpaired spins is estimated to 1/3 per  $C_{60}$  molecule. This is much larger than what has hitherto been observed. Furthermore, linear variation of the inverse esr signal intensity with for  $C_{60}.O_x$  as shown in Fig. 2a implies absence of any activated term suggesting that the signal is coming from ground state and not from an excited state. The observed  $g$  value is 1.9975 (below 20 K) is also close to the value observed for  $C_{60}.TDAE^{12}$  and that for electrochemically produced  $C_{60}^{-1}$  (1.9991). Such a similarity in the  $g$  values suggests that spins

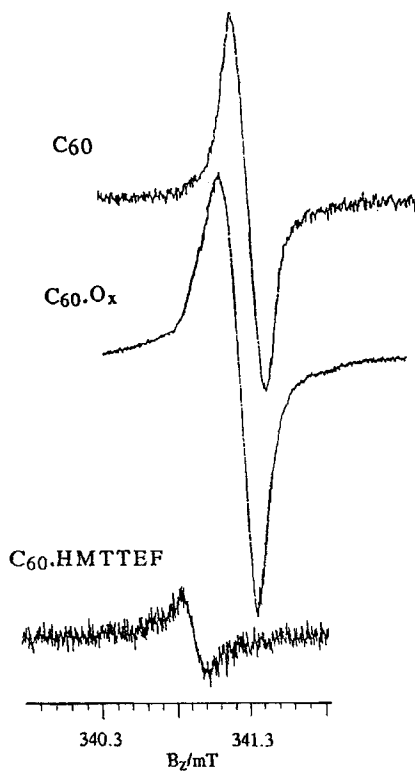


Fig. 1 ESR powder absorption derivatives  $dP/dB$  versus  $B_z$  of  $C_{60}$  (air exposed),  $C_{60}O_x$  and  $C_{60}HMTTEF$  at 298 K.

Table 1

ESR absorption parameters

Comounds	$g$	$\Delta H_{ms}/mT$
$C_{60}$ (exposed to $O_2$ )	1.9983	0.2
$C_{60}O_x$	1.9985	0.2
$C_{60}HMTTEF$	0.9986	0.16

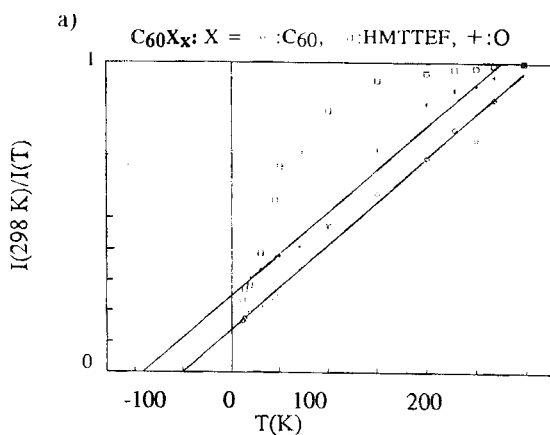


Fig. 2(a) Normalized inverse ESR Intensity vs T of  $C_{60}$  complexes:  $C_{60}(\diamond)$ ,  $C_{60}\cdot O_x(+)$  and  $C_{60}\cdot HMTTEF(\square)$ .

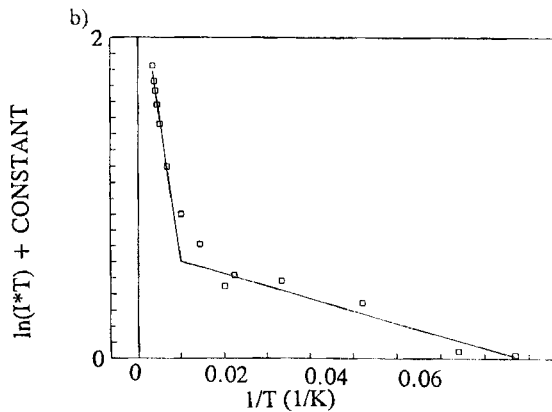


Fig. 2(b)  $\ln [I \cdot T]$  vs  $1/T$  plot of  $C_{60}\cdot HMTTEF$ . This indicates that there are definitely two temperature regimes. From 298 K to 150 K,  $\Delta H^\circ_1 = -3.1$  KJ/mole and from 100 K to 11 K,  $\Delta H^\circ_2 = -128$  J/mole.



are primarily located on  $C_{60}$  having  $S = 1/2$  and singlet orbital state as deduced for  $C_{60}^-$  anions.

It looks highly probable that the spin resides on the  $C_{60}$  moiety rather than on oxygen in  $C_{60}O_{22}$  for the following reasons:

- (i) Whereas  $C_{60}$  and  $C_{70}$  are highly electronegative molecules, with  $C_{60}$  able to undergo up to six reversible reduction steps, no reversible oxidation steps have been observed in the cyclic voltametry of either molecule.  $C_{60}^+$  appears very difficult to form.
- (ii) The unpaired electron resides on the oxygen site is also ruled out because the  $g$  value observed (1.9975) is smaller than that observed for oxygen centered radicals (they have a typical  $g$  value of  $\sim 2.01$ ). The observed  $g$  value indeed matches with that for  $C_{60}^{-1}$ .
- (iii) Lorentzian line shape implies delocalization of the observed electron over a large molecule e.g.  $C_{60}$
- (iv) The temperature dependence of the linewidth similar to those of singly ionized fullerene molecule in various diamagnetic organic solvents<sup>10</sup>.
- (v) This still leaves the question of identifying the donor unit (D) open. The donor mechanism has to involve the trapped oxygen and has to leave a epr silent  $D^+$  after the transfer of electron to  $C_{60}$ .

We are also not sure about any additional changes that have taken place to the solid  $C_{60}$  in addition to the loss of

crystallinity. As is known the residue is no longer soluble in toluene.

The close proximity of the observed  $g \approx 1.9975$  to the pure spin value indicates that the electron is in an orbitally singlet and not in orbitally triplet state. This is the same situation as in  $C_{60}^{-1}$ . The  $g$  value observed in case of  $C_{60}^{-1}$  (1.9991-1.9998) is close to the free electron  $g$  value of 2.0023. Although it is known that the lowest unoccupied orbital state in neutral  $C_{60}$  is triply degenerate, the esr results strongly suggest a lifting of orbital degeneracy and quenching of orbital angular momentum possibly as a result of crystal field effects due to surrounding counter ions or solvent molecules and Jahn Teller effects. The temperature dependence of the spectral line width also points towards the existence of close lying states near the ground state, presumably as a result of the splitting of the triply degenerate ground state of the free molecules.

The esr of both  $C_{60}$  (air exposed) and  $C_{60}.O_x$  ( $x \sim 22$ ) materials seem to follow a Curie - Weiss susceptibility temperature dependence in a wide temperature range of 5 K to 300 K. The inverse intensity shows a Curie - Weiss dependence in the observed temperature range (fig. 2a). Extrapolation of the inverse intensity to zero gives an antiferromagnetic Curie - Weiss temperature,  $\Theta = -50$  K for air exposed  $C_{60}$  and  $-90$  K for  $C_{60}.O_x$  ( $x \sim 22$ ) sample.

Oxygen is known to interact with  $C_{60}$  particularly in presence of UV radiation<sup>17-24</sup>. Solid  $O_2$  in contact with

multilayer films of  $C_{60}$  on solid substrates showed conversion to CO,  $CO_2$ , carbonyl like structures and a carbon residue upon exposure to photon sources of appropriate energy. No reaction of  $O_2$  with  $C_{60}$  was observed without photo excitation<sup>17</sup>. A  $C_{60}O$  adduct has been identified by Wood et al. <sup>18</sup>. The  $C_{60}O$  adduct was enhanced relative to  $C_{60}$  and  $C_{60} + OH$  adduct by one order of magnitude upon UV irradiation of  $C_{60}$  solutions in air. Higher oxides  $C_{60}O_n$  ( $n = 2, 3, 4, 5$ ) were also obtained. Of particular interest are surface reaction of  $C_{60}$  with oxygen to form an epoxide at ambient temperature and pressure<sup>23</sup>. Reaction of  $C_{60}$  with oxygen is supported by Raman spectroscopy, which shows an intense peak at  $1458\text{ cm}^{-1}$  upon exposure of  $C_{60}$  films to  $O_2$  (ref.19). Pace et al.<sup>24</sup> have observed an esr signal in chromatographed  $C_{60}$  powder sample that was oxygen dependent. The identity of the radical was not determined by the available data. For  $C_{60}$  in vacuum, the esr signal was constant and the signal intensity did not change upon admitting  $N_2$  gas into the evacuated  $C_{60}$  sample. Admitting  $O_2$  caused an immediate increase in signal by 40%. Heating  $C_{60}$  in air for 24 hr at  $250\text{ }^\circ\text{C}$  resulted in an increase in spin concentration by two orders of magnitude.

Our sample is different, firstly there is no photon irradiation (except daylight) and secondly there is no possibility that a pressure of  $10^3$  bar can cause any excitation or ionization of oxygen. Furthermore loss of CO and  $CO_2$  would entail a weight loss. In our case, the residue obtained after the

oxygen has been taken out by heating the sample to 200 °C, weighs between 100-105 % (ref. 14) of the original C<sub>60</sub> weight. There is no weight loss. The ease with which oxygen can be taken out also rules out any possibility of stable epoxide or ether formation. Also, Raman spectroscopy shows no evidence of any C=O ketone, C-O ether and epoxide bonds<sup>14</sup>.

The ease with which oxygen gets inserted in the structure (under O<sub>2</sub> pressure), the ease with which it can be taken out and the lack of evidence for any possible compound suggests that the material is a weak C<sub>60</sub>.O<sub>x</sub> adduct. There are adequate number of interstitial positions to accommodate oxygen atoms in the structure. And with the breakdown of the structure, the space availability also becomes more abundant.

### **C<sub>60</sub>.HMTTEF**

C<sub>60</sub>.HMTTEF exhibits a very different behavior. It shows a very weak esr absorption intensity near room temperature. The estimated number of spins per C<sub>60</sub> molecule is <0.01. Furthermore, the intensity is essentially independent of temperature as was found for the magnetic susceptibility of this compound in the temperature range of 50 - 300K (ref. 25). There is a sharp increase in the signal intensity below 20 K. However no hyperfine splitting is observed down to 5 K indicating absence of any ordering. Table 1 gives their line widths and 'g' values. The absence of charge transfer in C<sub>60</sub>.HMTTEF is in sharp contrast to several other C<sub>60</sub> adducts,

e.g.  $C_{60}$ .TDAE. Substantial charge transfer and strong ESR spectrum of  $C_{60}$ .TDAE [TDAE = Tetrakis(dimethylamino)ethylene] has a simple Lorentzian form without hyperfine structure at room temperature<sup>12</sup>.

The difference between  $C_{60}$ .HMTTEF and  $C_{60}$ .TDAE in regard to the extent of charge transfer arises from the difference in structure. The analysis of the high resolution synchrotron X-ray powder diffraction data for  $C_{60}$ .HMTTEF at room temperature gives a triclinic unit cell with  $a = 9.9297\text{\AA}$ ,  $b = 9.9359\text{\AA}$ ,  $c = 13.1472\text{\AA}$ ,  $\alpha = 106.966^\circ$ ,  $\beta = 95.887^\circ$  and  $\gamma = 118.252^\circ$  in the space group P1 (ref. 25). Steric considerations suggest that there is a nearly close packed layer of  $C_{60}$  molecules in the ab plane and the HMTTEF molecules are sandwiched between adjacent layers of closed packed  $C_{60}$  molecules. The inter  $C_{60}$  distance with the ab plane is very close that found in  $K_3C_{60}$ ,  $C_{60}$ .TDAE,  $C_{60}$ .(BEDT-TTF)<sub>2</sub> and several other  $C_{60}$  compounds. However, the interplanar spacing of ca  $12.5\text{\AA}$  is much larger than those found in superconducting  $K_3C_{60}$  and ferromagnetic  $C_{60}$ .TDAE, but close that observed in  $C_{60}$ .(BEDT-TTF)<sub>2</sub>,  $CH_2I_2.C_6H_6.C_{60}$  and  $C_{60}I_4$  (ref. 25 and reference cited therein). The last three have a similar alternating guest - host layer structure. Thus we have two classes in the  $C_{60}$  adducts; (i) charge transfer complexes, e. g.  $C_{60}$ .TDAE or  $K_3C_{60}$  and (ii) cocrystals where the  $C_{60}$  and the organic molecules co-exist without any charge transfer, for example  $C_{60}$ .HMTTEF,  $C_{60}$ .(BEDT.TTF)<sub>2</sub> and  $C_{60}$ .( $CH_2I_2.C_6H_6$ ). This

class of compounds is characterized by larger C<sub>60</sub>-guest distance as compared to that in (i).

The weak ESR signal indicates that there is very little charge transfer between the C<sub>60</sub> molecule and the nearby HMTTEF molecule. Each C<sub>60</sub> molecule is in near contact with other C<sub>60</sub> molecules in the same a-b plane. The charge transfer amongst the adjacent molecules is also decreased as compared to the solid C<sub>60</sub>. It is also likely that below 150 K the free rotation of the C<sub>60</sub> molecule is frozen as a result of the presence of the sandwiched HMTTEF molecule.

It is not clear as to what changes take place to bring about the enhancement of the ESR signal intensity below 150 K. An increase in intensity of the spectrum with increasing temperature, has been observed in ESR of C<sub>60</sub>.R adducts [R = CCl<sub>3</sub>, CBr<sub>3</sub>, C(CH<sub>3</sub>), (CH<sub>3</sub>)<sub>2</sub>CH] (ref. 13). Temperature dependence of this type has been interpreted as due the formation of its dimer and shift in the dimer (S = 0)/monomer (S=1/2) equilibrium. However, the present case is just the opposite.

In a general way, one can assume a dissociation (or charge transfer) reaction for an initial concentration [A:D] = N<sub>0</sub> >> N<sub>s</sub>,

A:D ⇌ A\*<sup>-</sup> + D\*<sup>+</sup> obtains,

$$K_{eq} = \frac{[A^{*-}][D^{*+}]}{[A:D]} \\ \equiv \frac{(N_s/2)^2}{[N_0 - N_s]} = \exp -\Delta G/RT \quad (2)$$

where the number of spins are obtained for a Boltzmann distribution  $\chi \propto N_s/T$ , the data of fig. 2b then gives

$$\partial \ln(I^*T) / \partial 1/T \equiv -\Delta H^\circ / 2R \quad (3)$$

The calibration relation (1) together with (3) give  $\Delta H^\circ = + 0.13$  kJ/mole and  $\Delta S = 90 \pm 8$  J/k. The dissociation reaction (2) is controlled by the energy gap  $\Delta H^\circ > 0$  and  $\Delta S^\circ$  measures the increase in entropy in going from the diamagnetic complex to free spins which is less than the value for the entropy of formation of free electrons in condensed phases:  $\Delta S^\circ(e^-(am)) = 154 \pm 20$  J/K/mole,  $\Delta S^\circ(e^-(YBa_2Cu_3O_7)) = 261 \pm 15$  J/K/mole (ref. 26), but twice as large as the entropy of formation of ions in condensed phases, e.g.,  $\Delta S^\circ(Cu^{2+}(aq)) = 37$  J/K/mole (ref. 27).

### Conclusions:

The behavior of electron donor - acceptor complexes of  $C_{60}$  depends on whether the fullerene acts as a donor or an acceptor. Since  $C_{60}$  and  $C_{60}O_x$  behave similarly it appears that the pure fullerene magnetic properties are due to  $C_{60}^{*+}$  spin - spin interactions. In  $C_{60}HMTTEF$  the nature of the interaction between  $A^{*-}$  and  $D^{*+}$  changes below 150 K. The additional exchange interaction,  $J = -3$  kJ/mole may arise when rotational motion is frozen.

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