One-, Two- and Three-electron Reduction of C_{60} using the Electron-reservoir Complex $[Fe^{I}(C_5H_5)(C_6Me_6)]$

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The reaction between the 19-electron complex $[Fe^{I}(C_5H_5)(C_6Me_6)]$ **1** and C_{60} in toluene gives the paramagnetic salts $(1^+)C_{60}^-$, $(1^+)_2C_{60}^{2-}$ and $(1^+)_3C_{60}^{3-}$ depending on the stoichiometry of the reactants

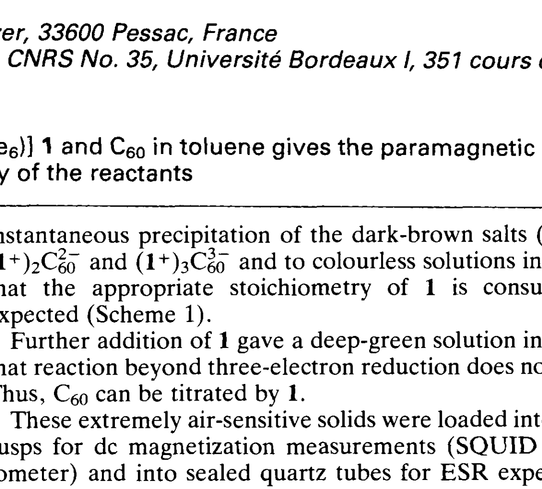
The possibilities of reducing fullerenes have led to the preparation of novel molecular materials.[1] For instance, the electrochemistry of C_{60} has shown six reversible one-electron reductions[2] and the finding of superconducting properties of salts obtained from reactions with alkali metals (M_3C_{60}) has stimulated considerable research in this area.[3] However, the only report on the reduction of fullerenes by molecular compounds concerns the use of a tetramine which gives rise to a low-temperature soft ferromagnet.[4] One way of developing this new series of charge-transfer salts is to use the electron-reservoir complexes[5] which are the most electron-rich molecules so far known, as indicated by their ionisation potentials.[6] We now report the reduction of C_{60} by the 19-electron complex $[Fe^{I}(C_5H_5)(C_6Me_6)]$ **1**.[5,6]

The standard potential of the redox system $1^{0/+}$ is $-$ 1.55 V *vs.* standard calomel electrode (SCE) in dimethylformamide (DMF) at a mercury cathode. Thus, **1** should reduce C_{60} up to the 3− anion since the standard redox potentials of C_{60} determined in PhCN are −0.5, −0.9, −1.3 V *vs.* SCE.[2] Both the coulombic attraction (Weller equation[7]) of the ions formed and precipitation add to the driving force.

After purification of buckminsterfullerene either on an alumina column[8a] or by preparative HPLC,[8b] the reactions between C_{60} and **1** were carried out in an inert atmosphere drybox by adding a purple toluene solution of C_{60} to a deep green toluene solution of **1** or *vice versa*. C_{60} and $1^+PF_6^-$ were most accurately weighed outside the drybox and **1** was quantitatively synthesized from $1^+PF_6^-$ and Na/Hg in tetrahydrofuran (THF) in the drybox followed by toluene extraction. Three stoichiometic ratios of **1** to C_{60} of 1 : 1, 2 : 1 and 3 : 1 were used and mixing toluene solutions of **1** and C_{60} led to instantaneous precipitation of the dark-brown salts $(1^+)C_{60}^-$, $(1^+)_2C_{60}^{2-}$ and $(1^+)_3C_{60}^{3-}$ and to colourless solutions indicating that the appropriate stoichiometry of **1** is consumed as expected (Scheme 1).

Further addition of **1** gave a deep-green solution indicating that reaction beyond three-electron reduction does not occur. Thus, C_{60} can be titrated by **1**.

These extremely air-sensitive solids were loaded into closed cusps for dc magnetization measurements (SQUID magnetometer) and into sealed quartz tubes for ESR experiments (X-band Varian spectrometer). Both types of experiment were carried out on each compound. For each complex, we observed an intrinsic solid-state ESR signal at 300 K.† A rather symmetrical sharp line (ΔH = 2.6 and 4 G at g = 2.0020) was observed for respectively $(1^+)C_{60}^-$ and $(1^+)_2C_{60}^{2-}$. However, for the third compound a quite large single line (ΔH = 43 G at g = 2.0040) was recorded whose linewidth depended



Scheme 1

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† We have checked by ESR spectroscopy that the pristine C_{60} exhibits only a weak signal (ΔH = 1 G) usually found in the presence of air because of the oxygen effect[9] ($1^+PF_6^-$ is a diamagnetic compound without any apparent spin signal).

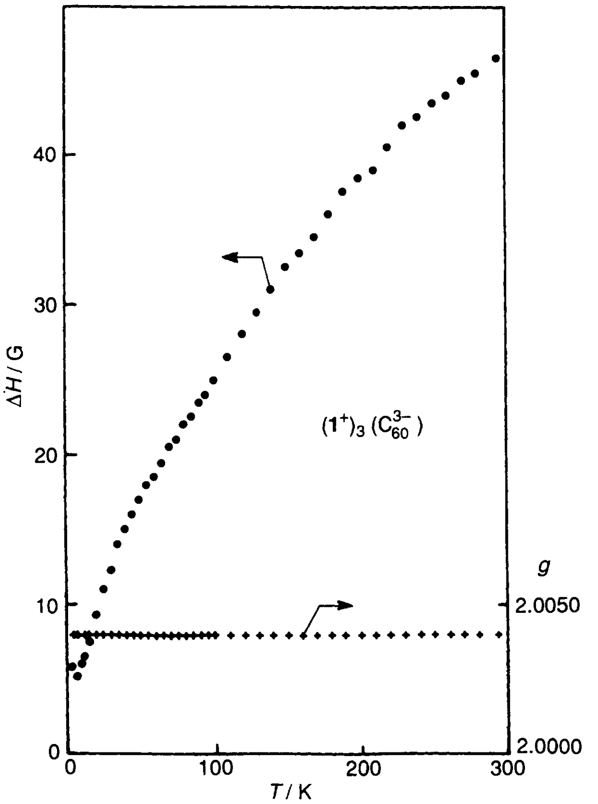

Fig. 1 ESR linewidth (ΔH) and g-factor temperature dependences for a powdered sample of $(1^+)_3C_{60}^{3-}$ in an inert atmosphere of He (1 G = 10^{-4} T)

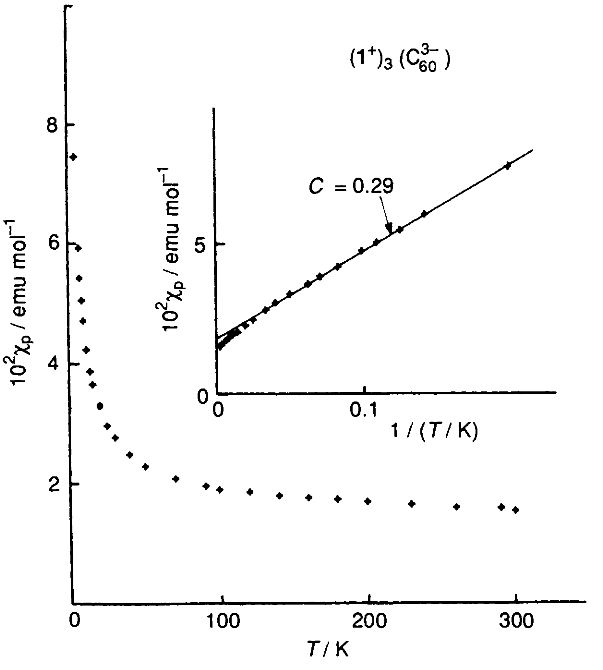

Fig. 2 Temperature dependence of the paramagnetic term (χ_p) of $(1^+)_3C_{60}^{3-}$ determined from dc magnetic measurements at H = 10 kG (the Pascal diamagnetic constant which has been used is $\chi_d = -878 \times 10^{-6}$ emu cgs g^{-1}). The inlet shows a plot of χ_p *vs.* T^{-1}

dramatically on temperature, without any change in the line position (Fig. 1). These results are in qualitative agreement with the ESR characterizations of singly, doubly and triply reduced C_{60} in frozen solutions;[10] in particular, we observed, for the dianion, an intrinsic magnetic state the origin of which is not currently understood (possibility of the existence of a triplet state†).

This point is confirmed by the static magnetic susceptibility measurements between 4 and 300 K which also exhibited for this dianion salt a paramagnetic state over all the temperature range. For the two other compounds, $1^+C_{60}^-$ and $(1^+)_3C_{60}^{3-}$, similar features were observed. In other words, a strong paramagnetic state which follows the Curie–Weiss law has been found. A quantitative experiment was carried out on $(1^+)_3C_{60}^{3-}$ using a field strength of 10 kG (Fig. 2). A Curie constant of about 0.29 is observed but this value is lower than expected for one unpaired spin (C = 0.375). This temperature dependent behaviour is also accompanied by a large constant term of unknown origin (see insert of Fig. 2).

In conclusion, we have shown that salts containing C_{60} anions and organoiron cations with different reduction states of C_{60} can be prepared. Preliminary physical investigations indicate the presence of different magnetic states which have to be investigated in greater detail.

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