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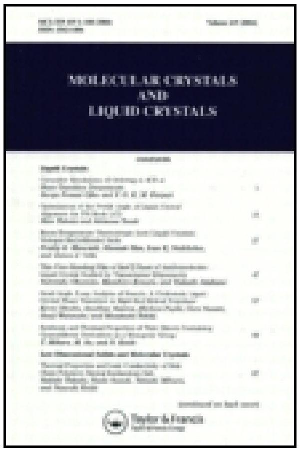

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Coexistence of Ferromagnetic Coupling and Intramolecular Electron Transfer in a Purely Organic Mixed-Valence Molecule with a Triplet Ground State

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COEXISTENCE OF FERROMAGNETIC COUPLING AND INTRA-MOLECULAR ELECTRON TRANSFER IN A PURELY ORGANIC MIXED-VALENCE MOLECULE WITH A TRIPLET GROUND STATE.

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Abstract The magnetic study of a purely organic biradical anion presenting electron transfer and ferromagnetic coupling between two radical centers simultaneously is discussed. The mixed-valence molecule was first generated electrochemically and the electron transfer was detected by optical spectroscopy. ESR measurements not only made the determination of the ground state possible, but also gave further evidence of transient site-localisation of the extra electron.

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INTRODUCTION

Intramolecular electron transfer processes have been a subject of widespread study over the last years, since the understanding of its basic mechanisms could lead to the design of nanometer-sized, molecular-based devices.[1] Although the vast majority of examples in the area belong to the field of organometallic chemistry, some examples of purely organic molecules presenting intramolecular electron transfer have appeared in the literature in recent years.[2] In the present work, our aim was to go one step further by studying purely organic systems which presented both intramolecular electron transfer and a strong ferromagnetic coupling at the same time. Since even the separate properties are known to be at least unusual in organic molecules, the study of such systems in which both were present simultaneously represented a unique chance to investigate the reciprocal influence between them and, particularly, the effect of such a transient phenomenon as an electron transfer on the magnetic coupling between radical centers.

Polychlorotriphenylmethyl radical-based molecules and analogous purely organic systems presenting more than one radical center have been thoroughly studied over the

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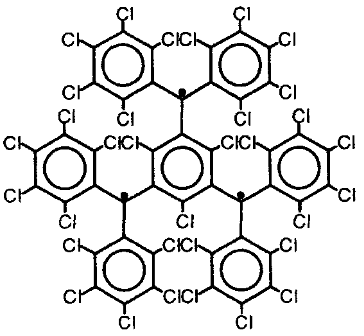
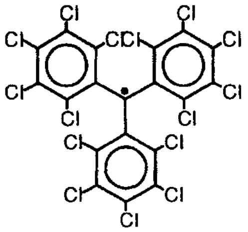
past years and their remarkably high chemical and thermal stability have been firmly established. Moreover, their corresponding anionic derivatives also turned to be very stable compounds.[3] These properties allowed us to characterise them in detail and use them as candidates for model radical compounds.[3a, 4] On the one hand, and as far as their magnetic properties are concerned, molecules such as 2,4,6-trichloro-α,α,α',α',α'',α''-hexaquis (pentachlorophenyl) mesitylenetriyl (**1**), have very robust high-spin ground states, as could be straightforwardly predicted by the McConnell I, spin polarisation mechanism. On the other hand, they show a reversible and well-defined, stepwise electrochemical behaviour, as could be ascertained by cyclic voltammetry.[3b]





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The cyclic voltammetry of **1** showed indeed the formation of three different negatively charged species derived from **1**, namely radical ions $\mathbf{1}^{-\cdot\cdot}$ and $\mathbf{1}^{2-\cdot}$ and trianion $\mathbf{1}^{3-}$. The quartet **1** and the trianion $\mathbf{1}^{3-}$ can be regarded in principle as full-valence species, whereas the radical ions should be regarded as mixed-valence species in view of the simultaneous existence of radical and anionic centers in the molecule. For this reason, an intramolecular electron transfer was to be expected, in the same way it had already been observed in similar organic mixed-valence systems.[2h] Moreover, biradical anion $\mathbf{1}^{-\cdot\cdot}$ presented a very interesting additional feature, consisting of the existence of two radical centers in the molecule, this making it a suitable candidate for our purposes. Accordingly, we considered interesting to generate $\mathbf{1}^{-\cdot\cdot}$ in a controlled fashion, study first the existence of any electron transfer and, once established the nature of this transfer, characterise the molecule magnetically.

OPTICAL SPECTROSCOPY

We studied the generation of the anionic species by coulommetric titration of **1** in CH_2Cl_2 solutions at suitable and controlled potentials. The UV-Vis spectra of different samples, each taken at a different average reduction state, showed well-defined trends for the two main bands, centered at 368 nm and 510 nm, corresponding to the radical and anionic cromophores, respectively. Because of its high basicity, the trianionic species $\mathbf{1}^{3-}$ turned to be rather unstable under the experimental conditions, as the two isosbestic points were lost after having reached an average reduction state of about 2.17 e^-/mol, which we took as our last reliable point. Much more interesting were the NIR spectra recorded throughout, in which a moderately intense and extremely broad band showed up immediately after having started passing current through the solution, while it started disappearing after having reached about 2e^-/molec (Fig. 1). This was already a clear indication that some electron transfer was taking place in both generated radical-anionic species.[6] In order to definitely rule out either any *inter*molecular transfer giving rise to a similar band, or any other artefacts, the same experiment was carried out with a monoradical analogue, radical perchlorotriphenylmethyl **2**, which generates a single reduction species. Since $\mathbf{2}^-$ is a full-valence anion, no 'extra' NIR band was observed throughout the coulommetric titration, as expected. We were finally able to simulate the spectroelectrochemical titration curve of **1** with an *ad-hoc* model, based on simple considerations such as the Nernst and Lambert-Beer laws, the mass and charge balances and standard potentials derived straightforwardly from the cyclic voltammetry.[2m] The excellent fit of the experimental data made us confident that the assignment of the NIR band, as being due to intramolecular electron transfer, was correct.

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any interference by recording the dependence of the intensity of this band with temperature between 4K and 100K. Indeed, experimental results showed that the intensity of the half-field band fits excellently to a Curie law for a paramagnet (Fig. 2b), thus discarding an antiferromagnetic coupling which could yield a singlet, low-spin ground state and clearly pointing either to a nearly-degenerate singlet-triplet ground state or, much more likely, to a triplet high-spin ground state in which the radical centers are ferromagnetically coupled. The latter case is further supported by the fact that all the synthesised molecules belonging to the same family as **1** and having *meta*-connected radical centers at about 5Å from each other -indeed quite a short distance- show, without any exception, a strong ferromagnetic coupling between their radical centers.[3, 5] As shown in Figure 2a, a striking feature of the half-field band is its remarkably asymmetrical shape, which becomes more asymmetrical as temperature decreases. Although we have not yet a sound explanation for this fact, we suspect that it could be related to the geometrical distortions arising from the site-localisation of the negative charge, which should accordingly increase at lower temperatures.

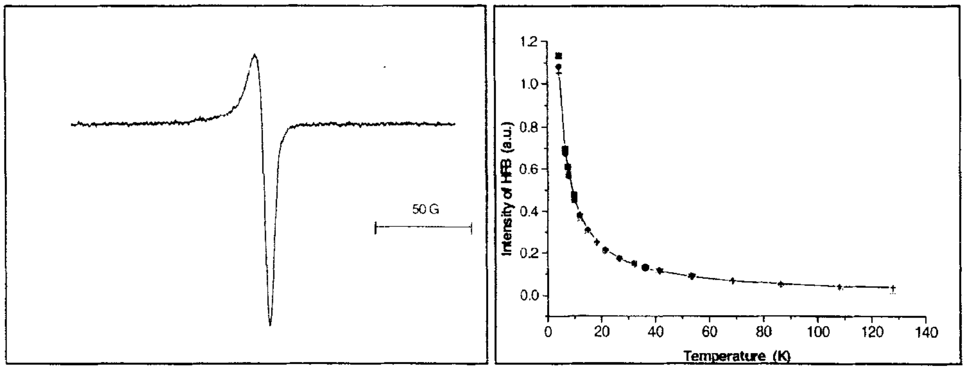

FIGURE 2 *a)* Half-field band of the biradical anion in solution at 4K (left) and *b)* dependence of the intensity of this band with temperature (right). Experimental data fit a Curie law for a paramagnet; the symbols correspond to a different microwave power each.

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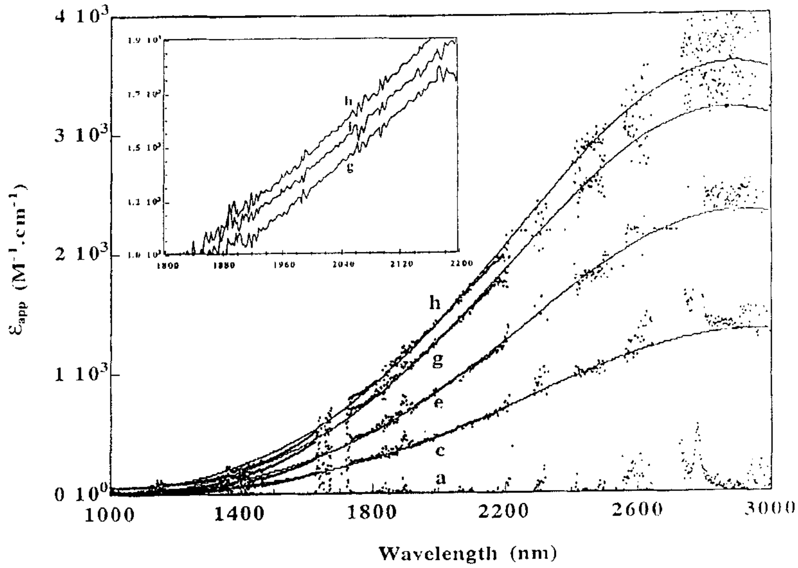

FIGURE 1 Evolution of the electronic NIR spectra throughout the reduction of **1**. The intervalence band increases until 2e⁻/molec. (h) and then starts decreasing (i).

MAGNETIC CHARACTERISATION BY ESR

The magnetic characterisation of $\mathbf{1}^{-\cdot\cdot}$ was carried out by ESR spectroscopy. In principle, the appearance of fine structure due to zero-field splitting in a frozen solution (150K) of $\mathbf{1}^{-\cdot\cdot}$ containing a certain amount ($\simeq$ 20%) of $\mathbf{1}^{2-\cdot}$ indicated that the predicted high-spin triplet state for $\mathbf{1}^{-\cdot\cdot}$ was at least significatively populated.[2m] Due to the high concentration of ionic species (electrolyte), the resolution of the spectrum was somewhat poor, showing nevertheless six broad lines, which were interpreted as belonging to a single asymmetrical triplet species ($\mathbf{1}^{-\cdot\cdot}$). A certain amount of doublet impurities of $\mathbf{1}^{2-\cdot}$ had to be invoked in order to account for the existence of a central line.

In order to study the nature of the magnetic coupling between the two radical centers in $\mathbf{1}^{-\cdot\cdot}$, we thought it would be more convenient to look at the half-field transition (Fig. 2a), since the other species derived from **1** are silent in the half-field range. Thus, it would be possible to investigate the ground state of $\mathbf{1}^{-\cdot\cdot}$ straightforwardly and without

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In order to definitely ascertain the ground state of $\mathbf{1}^{-\cdot\cdot}$ by magnetic susceptibility measurements, attempts are in progress in order to synthesise solid ionic salts of the anion. Up to now, microcrystalline powders of mixtures of $\mathbf{1}^{-\cdot\cdot}$ K^+/18-crown-6 with containing small amounts of $\mathbf{1}^{2-\cdot}$ have been obtained, showing a fair stability in an ambient atmosphere. Electrolyte-free, frozen solutions of this salt in THF/toluene (1:1) show a much more resolved ESR spectrum in which the existence of not one, but two triplet species must be invoked in order to interpret this much more complicated pattern (Fig. 3). This result is not at all surprising, since it is well-known that **1** exists in solution in two different conformations, one having a D_3 (axial) symmetry, the other a C_2 (non-axial) symmetry.[3b] If we think about the geometrical distortion that might occur upon placing an 'extra' electron in **1**, and supposing that the negative charge is localized to some extent on a single site at each time, it is straightforward to assume that this distortion will mainly affect the latter site, thus giving rise to an important loss of overall symmetry. In terms of zero field splitting parameters, E values in $\mathbf{1}^{-\cdot\cdot}$ would increase with respect to those of the neutral species **1**, which is in fact our case (see Table 1). If, on the other hand, the extra charge was completely delocalized between the three centers, geometrical distortions should not affect the symmetry and no significant changes in E values would have taken place.

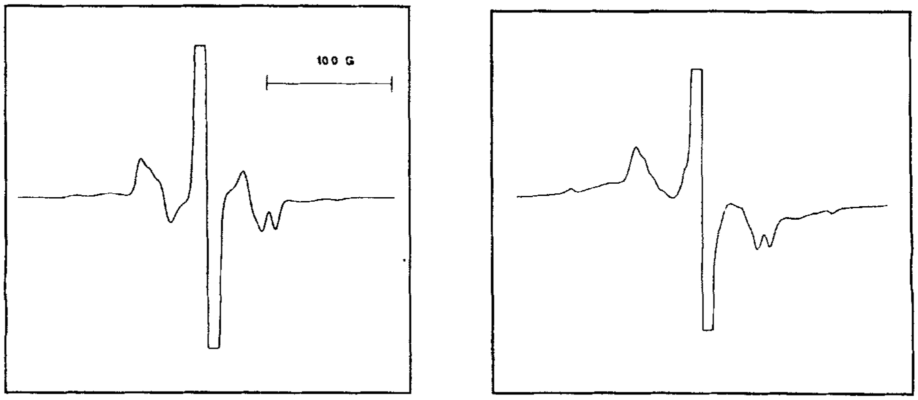

FIGURE 3 *a)* Experimental (right) and *b)* simulated (left) ESR spectra of the salt $\mathbf{1}^{-\cdot\cdot}$ K^+/18-crown-6 in a frozen solution of THF/toluene.

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TABLE 1: ESR spectrum parameters* of **1**, and $\mathbf{1}^{-\bullet\bullet}$.

Isomer[‡]	$\mathbf{1}^{3b}$	$\mathbf{1}^{-\bullet\bullet}$/ electrolyte^{2m}	$\mathbf{1}^{-\bullet\bullet}$ K^+/18-crown-6
C_2	g_{xx}= 2.0029 D'= 39 g_{yy}= 2.0029 E'= 1 g_{zz}= 2.0012	g_{xx}= 2.0020 D'= 73 g_{yy}= 2.0020 E'= 6.5 g_{zz}= 2.0010	g_{xx}= 2.0027 D'= 78 g_{yy}= 2.0030 E'= 4.2 g_{zz}= 2.0026
D_3	g_{xx}= 2.0024 D'= 54 g_{yy}= 2.0024 E'= 0 g_{zz}= 2.0024		g_{xx}= 2.0019 D'= 104 g_{yy}= 2.0023 E'= 0.5 g_{zz}= 2.0027

* D' and E' given as absolute values in Gauss (G).

[‡] Strictly speaking, the assignments of symmetry apply only to the isomers of **1**. Because of the loss of symmetry in $\mathbf{1}^{-\bullet\bullet}$ with respect to **1**, assignments for the isomers of $\mathbf{1}^{-\bullet\bullet}$ are made only for comparison purposes with **1**.

In overall, this result strongly supports that the electronic coupling between radical and anionic centers is high enough to give rise to moderately intense intervalence transitions in the NIR range, but not as high as to completely delocalized the 'extra' electron between them. In other words, anion biradical $\mathbf{1}^{-\bullet\bullet}$ can be considered a Class II compound as far as intramolecular electron transfer is concerned.

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