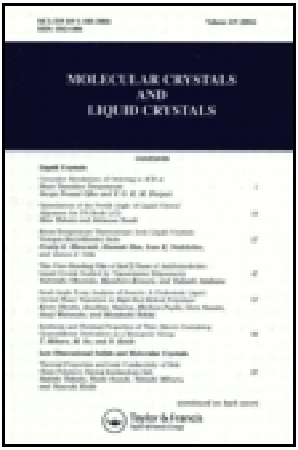

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Exchange Mechanisms in Ferrocinium Complexes

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EXCHANGE MECHANISMS IN FERROCINIUM COMPLEXES

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Abstract We examine kinetic and potential exchange in 1:1 ion-radical complexes of ferrocene (Fc) and π-acceptors like tetracyanoethylene (TCNE). Spin-orbit and asymmetry split the $(e_{2g})^3$ configuration of Fc^+ and lead to anisotropic magnetic moments. The partly-filled Fc^+ and $TCNE^-$ orbitals are almost orthogonal and suggest alternative charge-transfer processes involving the acceptor and ligands.

INTRODUCTION

Magnetic interactions presuppose unpaired spins in degenerate or nearly degenerate orbitals ϕ_A and ϕ_B. Parallel or ferromagnetic (F) spin alignment is favored by Heisenberg exchange,

$$J_H = \langle\phi_A(1)\phi_B(2)|e^2/r_{12}|\phi_A(2)\phi_B(1)\rangle \qquad (1)$$

for electrons in orthogonal orbitals. For atoms or ions, the resulting splittings of ~ $10^4 cm^{-1}$ are familiar as Hund's rules. Orthogonal ϕ_A and ϕ_B on different centers also lead to F coupling with reduced J_H ~ 10 cm^{-1} due to reduced overlap region. Recent magnetostructural studies[1,2] of transition-metal complexes by Hatfield, Willett, and others have elegantly demonstrated such overlap considerations.

When $S = \langle \phi_A | \phi_B \rangle$ does not vanish, however, opposite or antiferromagnetic (AF) alignment is favored even for small overlap. Hay et al.[3] have reviewed in chemical terms the Van Vleck-Anderson[4] argument for kinetic exchange. We suppose electron transfer between ϕ_A and ϕ_B and note that the charge-transfer (CT) state at ΔE is necessarily a singlet when the orbitals are not degenerate. Thus kinetic exchange is inherently AF,

$$J_k \sim t^2/\Delta E \qquad t = \langle\phi_A(1)|H|\phi_B(1)\rangle \qquad (2)$$

and involves the Mulliken CT integral t. Kinetic exchange accounts for the prevalence of AF coupling found among organic radicals and inorganic complexes. The latter often require superexchange via ligands whose orbitals are invoked in the virtual state.

McConnell[5] observed that the CT argument in Eq.(2) could equally well favor F alignment, provided that either the donor (D) or acceptor (A) has a triplet ground state. The generalization to a triplet CT excited state has provided much of the theoretical impetus for organic ferromagnetism.[6] Orbital degeneracy for either ϕ_A or ϕ_B is in turn required, as discussed below, and is central to Miller and Epstein's detailed analysis[7] of DA pairs leading to either F or AF coupling.

A completely different approach to molecular magnets is discussed by Kahn,[8] who exploits AF coupling between S=5/2 Mn(II) complexes and S=1/2 Cu(II) complexes to obtain a ferrimagnet. Still another approach,[9] so far primarily theoretical, is based on Hückel theory for conjugated polymers with bands of partly-filled nonbonding orbitals. The realization of high spin oligomers based on dicarbenes[10] and preliminary indications[6] of ferromagnetic polymers provide some confirmation. Polymers should eventually offer the best hope of substantial three-dimensional F coupling.

We consider exchange in the increasingly well-characterized series of molecular magnets based on the donor D = decamethylferrocene(DMFc). Both structural and spectroscopic studies have been reviewed by Miller, Epstein, and Reiff[11] for complexes of DMFc and Fc with π-acceptors A such as tetracyanoethylene (TCNE), tetracyanoquinodimethane (TCNQ), and hexacyanobutadiene.[12] The 1:1 complexes form mixed ion-radical stacks $\ldots D^+A^-D^+A^- \ldots$, as sketched in Fig. 1(a), with an unpaired electron in the nondegenerate π^* orbital ϕ_A and an unpaired hole in the degenerate e_{2g} (d_{xy}, $d_{x^2-y^2}$) manifold of Fe(III). Instead of emphasizing the potential generality of the McConnell mechanism, we examine the suitability of various CT processes and consider alternatives to a virtual triplet state D^{+2} A^{-2} that rarely contributes in organic complexes.[13] We also note that complex formation and other mechanisms remove the postulated orbital degeneracy.

GROUND-STATE MANIFOLD OF $DMFc^+$

The $DMFc^+$ $TCNE^-$ complex is a molecular ferromagnet with Curie temperature $T_c = 4.8K$ and F exchange $J/k \sim 30K$ along the $D^+A^-D^+A^-$ stacks sketched in Fig. 1(a). It is a prime candidate for closer examination. The $TCNE^-$ and cyclopentadienyl (cp) planes are parallel within experimental uncertainty and tilted by ~ 2.8° from the z axis.[14] We ignore the tilt in the idealized geometry and center the C = C bond on the five-fold axis. Since TCNE then sits in at least a 10-fold potential well, with correspondingly small barriers to rotation, disorder can almost be expected. The precise TCNE location is marred by disorder, at least in the solvent-free ferromagnetic structure. The $(e_{2g})^3$ configuration of $DMFc^+$ involves the d_{xy} and $d_{x^2-y^2}$ orbitals shown in Fig. 1(b), while the π^* TCNE orbital is also shown in the xy plane. The proposed[7] CT state $D^{+2}A^{-2}$ is a triplet according to Hund's rules for $(e_{2g})^2$.

At least in the idealized geometry of Fig. 1, however, the CT matrix element in Eq.(2) vanishes for the π^* orbital and either d_{xy}

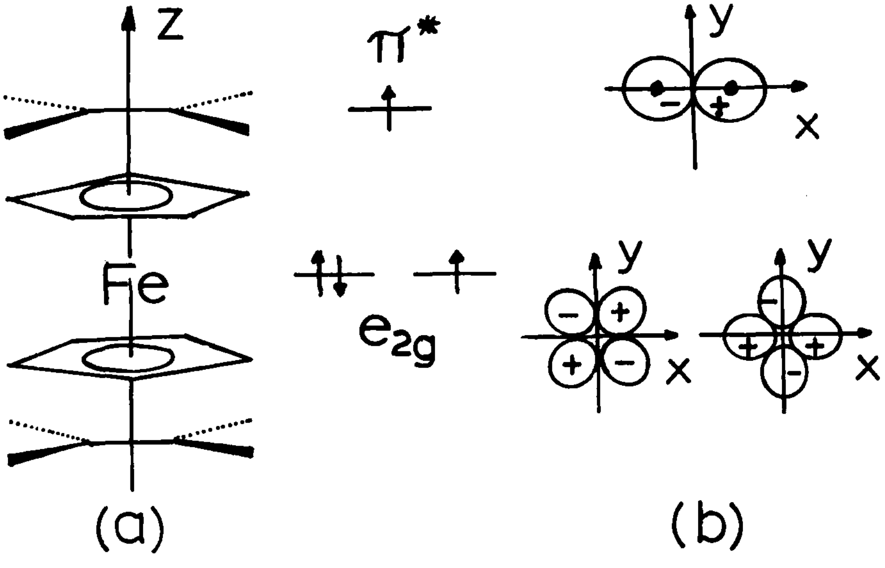

FIGURE 1. (a) Schematic representation of mixed stacking in Fc-TCNE complexes along the z axis. (b) Nodal structure of partly-filled $DMFc^+$ and $TCNE^-$ orbitals in the xy plane.

or $d_{x^2-y^2}$. We have instead a good case for Heisenberg exchange in Eq.(1). But the observed J/k ~ 30K is over an order of magnitude larger then estimated for J_H using standard orbitals. Quite aside from direct calculations, which are hardly reliable for such minute splittings, the Fe-TCNE separation of 5.2A° suggests that J_H is negligible unless admixed with cp orbitals, which is again difficult to quantify. The actual geometry does allow finite J_k in Eq.(2), but requires an additional factor that vanishes on changing the cp and TCNE planes by 2.8° and centering the $TCNE^-$ on the 5-fold axis of $DMFc^+$. Overlap considerations thus reduce an already small t.

The cp rings are staggered in $DMFc^+$. The usual assignment[15] is D_{5d} for analyzing electronic and vibrational spectra of ferrocenes. The TCNEs inevitably reduce the symmetry, even in the idealized geometry, and split d_{xy}, $d_{x^2-y^2}$ degeneracy. Strictly degenerate orbitals are probably restricted to theoretical models and the CT argument for F coupling must tolerate small splittings. Reduced symmetry also alters the CT matrix elements t. Suppose, for example, that the actual geometry gives finite t between π^* and the $d_{x^2-y^2}$ orbital, thereby slightly raising the former and lowering the latter in Fig. 1; there is still rigorously no CT between π^* and d_{xy} for the proposed $D^{+2}A^{-2}$ triplet excited state. Any CT mixing in Eq.(2) of π^* and some linear combination of d_{xy} and $d_{x^2-y^2}$ leads to the same conclusion by elementary quantum theory: the orthogonal combination of d_{xy} and $d_{x^2-y^2}$ will have vanishing CT matrix element with π^*.

In Fe(III) complexes the orbital degeneracy of d_{xy} and $d_{x^2-y^2}$ is quite illusory. The spin-orbit interaction $\xi\, \vec{l}\cdot\vec{s}$, with ξ ~ 400 cm^{-1} for Fe, leads to splittings of ~ 1000 cm^{-1} as discussed by Maki and Berry.[16] In addition, the a_{1g} (d_{z^2}) orbital is comparably close to the e_{2g} levels.[15] Their relative spacing has been extensively explored but remains to be settled quantitatively. The relevant Fe levels are sketched in Fig. 2, where spin-orbit coupling is first used to split the $l_z = \pm 2$ levels in e_{2g}. Since typical crystal field splittings exceed 10^4 cm^{-1}, small distortions from D_{5d} symmetry could further split the levels. The asymmetry parameter δ ~ 300 cm^{-1} mixes the $j_z = \pm 5/2$ and $\pm 3/2$ levels in the simplest approximation[16] and leads to the states in Fig. 2. A single hole in Fc^+ or $DMFc^+$ has lowest energy in the E" configuration, where E" refers to the double group. The energy of a holes in A' is higher by $2(\xi^2 + \delta^2)^{1/2}$, while a hole in E', or primarily in d_{z^2}, has still higher energy.

The reason for including an asymmetry parameter $\delta > 0$ even in unsubstituted Fc^+ or $DMFc^+$ is dictated by epr. There is no epr intensity at $\delta = 0$, where the $j_z = \pm 5/2$ levels of Fig. 2 have $g_\parallel = 6$, $g_\perp = 0$. Finite δ leads to allowed epr transitions with

$$g_\parallel = 2 + 4 \cos 2\chi \qquad (3)$$
$$g_\perp = 2 \sin 2\chi$$

for the E" level, with $\tan 2\chi = \delta/\xi$. Orbital reduction factors (k'~ 75-80%) and lower symmetry lead to more elaborate expressions.[17] Typical epr spectra with $g_\parallel \sim 4$, $g_\perp \sim \sqrt{3}$ indicate $2\chi \sim 30°$. The asymmetry is potentially sensitive to crystal packing, and thus to temperature, with some evidence of sharply decreased δ at He temperature.[18]

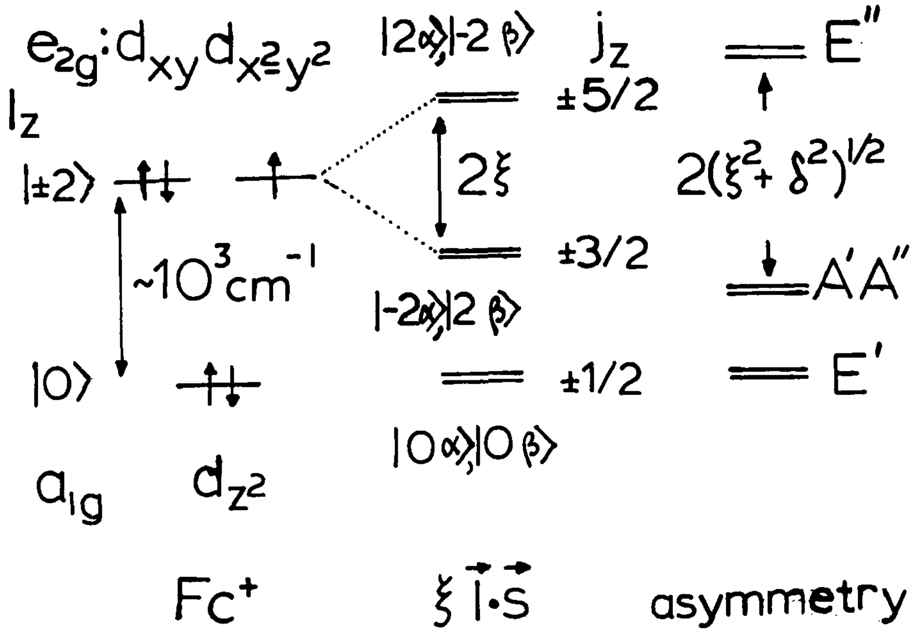

FIGURE 2. Evolution of e_{2g} and a_{1g} orbitals in D_{5d} symmetry on including the Fe spin-orbit coupling ξ and asymmetry δ in the xy plane.

The ground-state manifold in Fig. 2 is certainly preferable to the degenerate e_{2g} levels of Fig. 1. The important question, however, is whether this matters for F coupling between $DMFe^+$ and $TCNE^-$. We suggest three important qualitative differences.

The first is that orbital contributions lead to a highly anisotropic magnetic moment, as indicate in Eq.(3). The $S = 1/2$ ground state of $DMFe^+$ is closer to an Ising than a Heisenberg spin. Ising models order more easily, for many reasons. Moreover, the anisotropy parameter δ may vary from complex to complex and also reflects crystal packing. The wide variety of magnetic behavior found in Fc^+ and $DMFc^+$ complexes with $TCNE^-$, $TCNQ^-$, and other A^- is strong qualitative evidence for variations in δ.

The second point is that the d_{z^2} orbital provides additional CT possibilities at essentially the same excitation energies. The ΔE factor in Eq.(2) discriminates weakly against higher excited states and overlap contributions to t can be far more important. Poor HOMO-LUMO overlap in neutral DA complexes leads[19] to CT bands based on higher energy, but better overlapping orbitals. Fc^+ and $DMFc^+$ complexes offer many CT pathways, as discussed in the next section. The possibilities for F coupling via the McConnell idea increase just as the identification of the most important state becomes difficult.

The third point is that CT integrals are now unambiguous among the nondegenerate orbitals of Fig. 2. We still have $t = 0$ in the idealized geometry for an electron in π^* and a hole in E", in A', or in E'. The actual geometry leads to comparable, but still unfavorable t for E" and A' when $\delta < \xi$ and the j_z states are weakly mixed.

III. CT EXCITATION AND STABILIZATION

Kinetic exchange involves configuration interaction and is fundamentally beyond a single-particle description, no matter how self-consistent. The relevant excitation energies are in turn more sensitive to correlations than most ground state properties. While even the identification of CT states is a major challenge, we are primarily interested in those that favor F over AF coupling or vice versa. Very small admixtures of relatively high-energy configurations are consequently sought. High molecular symmetry and single crystal spectra facilitate the assignment of CT spectra.

Direct identification of CT states for the McConnell mechanism in $DMFc^+$ complexes is complicated by many competing excitations. Some Fe(III) and M_5cp^- levels are estimated in Fig. 3. Extensive previous work establishes the principal features, although many open questions remain. The ligand-to-metal CT band around $13{,}000cm^{-1}$ is discussed by Duggan and Hendrickson[15] for both Fc^+ and $DMFc^+$. The $e_{2g} \rightarrow e_{1g}$ ligand-field splitting is generally taken to be around $20{,}000cm^{-1}$ and the excited state is also split by spin-

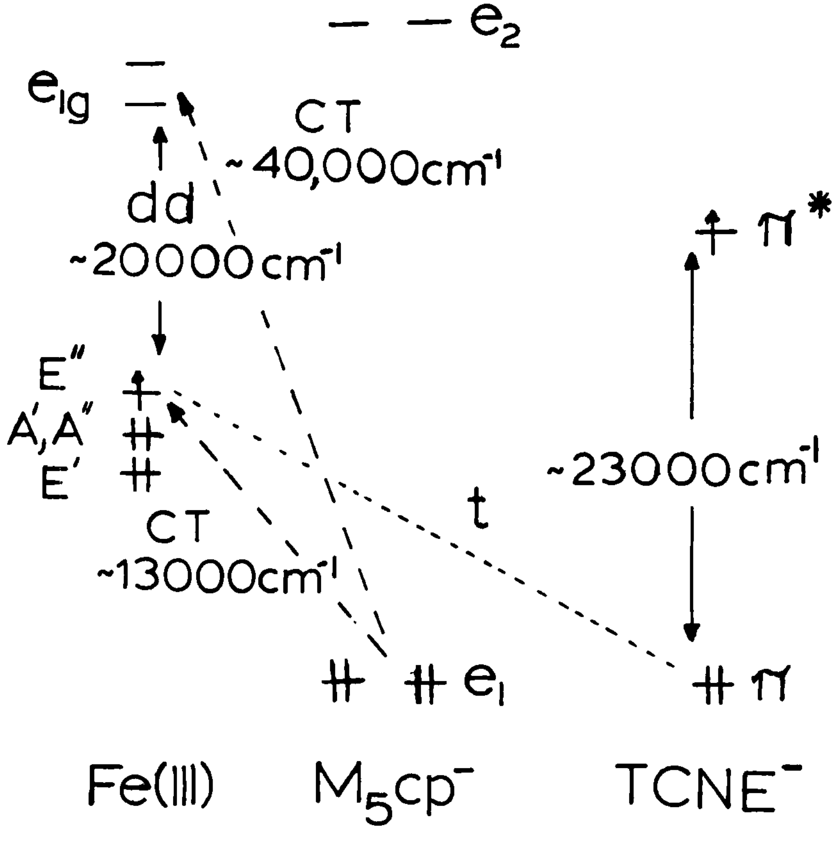

FIGURE 3. Approximate energy levels of $DMFc^+$-$TCNE^-$, including CT bands from the M_5cp^- ligands to Fe(III). The CT integral t involving the π-ground state leads to a virtual triplet $TCNE^*$.

orbit and reduced symmetry. Sohn et al.[20] assign three CT excitations of Fc^+ at 35, 40, and 50,000 cm^{-1} to be from the ligand e_1 orbital to metal e_{1g} manifold. They calculate the ligand π^* (e_2) orbital to be somewhat higher.

The $\pi \rightarrow \pi^*$ excitation of TCNE or of other π-acceptors is known, but the relative positions of the D^+ and A^- levels in Fig. 3 is not. Any CT processes are likely to be weak, in view of the small t in Eq.(2) for radical ions at Van der Waals separations. Nevertheless, low-energy excitations below the 13,000cm^{-1} transition of the complex, might in principle be seen. The lowest CT excitation of a $\cdots D^+A^-D^+A^- \cdots$ stack occurs at the neutral-ionic interface,[21,22] when the Madelung energy M of the ion-radical salt just matches the energy $I_D - A_A$ for ionizing D and transferring the electron to A. Ionic complexes are rare and relatively close to the interface. The higher I_D of Fc, for example, leads to a neutral diamagnetic Fc-TCNE complex.[23] In mixed-stack complexes, we have $M = \alpha V$, with Madelung constant $\alpha \sim 1.5$ and nearest neighbor $D^+ A^-$ Coulomb interaction of $V \sim 3$ ev. The minimum CT excitation for small t is $V(\alpha - 1) \sim 12{,}000cm^{-1}$. The lower CT band around 5000cm^{-1} of tetrathiafulvalene and chloranil reflects[22] direct π-overlap with $t \sim 2000cm^{-1}$. In the small t limit, then, any weak CT transition between $DMFc^+$ and $TCNE^-$ is probably above the ligand to metal band.

The M_5cp^- levels in Fig. 3 also offer superexchange pathways through either the doubly degenerate e_1 and e_2 orbitals. The e_1 orbitals overlap well with the π^* TCNE orbital in Fig. 1 while the e_2 overlap is good with the metal e_{2g} orbitals. The other CT matrix elements vanish in the idealized geometry and are small for the actual structure.

Overlap considerations, especially in the idealized geometry where π^* $TCNE^-$ level in Fig. 1 cannot be admixed with the hole orbitals of Fe(III), suggest CT mixing between the π ground state and the hole states. These even functions overlap effectively, although t is still small for such distant sites. The excitation energy is at least 25,000cm^{-1} higher, however, since the resulting neutral pair DA^* has an excited acceptor. The coupling is still F, since $^3A^*$ is lower than $^1A^*$ according to Lewis and Kasha's extension of Hund's first rule to molecular excitations. In terms of Eq.(2), we have compensated a larger ΔE with a larger t that does not vanish in the idealized geometry. A 10-fold reduction of t for π^* rather than π in the actual geometry requires a 100-fold decrease in ΔE for comparable J_k.

The hexacyanobatudiene HOMO and LUMO have reversed nodal patterns compared to TCNE. The DMFc complex is again ionic and ferromagnetic,[12] with $T_c \sim 7.5$ K. There is favorable CT mixing between the hole orbitals and the LUMO. The resulting $D^{+2}A^{-2}$ state now agrees with the Miller-Epstein[7] choice and is a triplet due to Hund's rule for the two holes in the e_{2g} manifold. The energy denominator in Eq.(2) may be somewhat larger, but is less important than overlap considerations for maximizing t.

Even the simplified states in Fig. 3 thus allow several CT schemes that favor F coupling between $DMFc^+$ and $TCNE^-$. Such ambiguity is frequently encountered for small admixtures of excited states and such models primarily rationalize observations. The variety of magnetic phenomena already reported[11] in Fc^+ and $DMFc^+$ complexes with strong π-acceptors must clearly involve more than nearly degenerate e_{2g} orbitals. For example, a neutral Fc-TCNE complexes rationalizes the difference with $DMFc^+$-$TCNE^-$. The analogy does not extend to hexacyanobatudiene, however, whose Fc complex[12] has an ion-radical, paramagnetic ground state with weak AF coupling. The metamagnetism of $DMFc^+$ $TCNQ^-$ provides yet another motif $DMFc^+$. Complexes with diamagnetic A^- acceptors are paramagnetic as expected.

In summary, the partly-filled $DMFc^+$-$TCNE^-$ orbitals are almost orthogonal, thus favoring some J_H contribution in Eq.(1), and also offer F coupling via J_k in Eq.(2) based on virtual triplet states of TCNE and M_5cp^- ligands as well as the previously proposed $(e_{2g})^2$ configuration. Strict orbital degeneracy is neither required nor achieved. In Fc^+ complexes the e_{2g} manifold is split by spin-orbit coupling and by asymmetry. Static or dynamic[17] Jahn-Teller distortions may generally be expected in partly-filled degenerate manifolds and the high molecular symmetry is usually lowered by complex formation and crystal packing. The nature of F coupling in DMFc$^+$-TCNE$^-$ and related complexes remains open. Curie temperatures $T_C \sim 5k$ suggest that interchain contributions of $J'/k \sim 1K$ must accompany the intrachain $J/k \sim 30K$ that has primarily been modeled. The anisotropic g-values in Eq.(3) for Fc$^+$ complexes are particularly important, in our opinion, for quantitative analysis of the field and temperature dependence of the magnetism. Studies of actual molecular ferromagnets are needed to test theoretical ideas about F coupling in organic or polymeric systems.

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