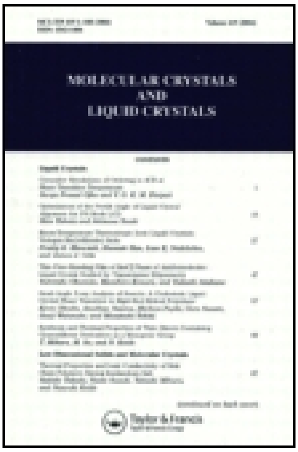

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Ferromagnetic Charge Transfer Complexes

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Ferromagnetic Charge Transfer Complexes

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Some ionic molecular solids comprised of linear chains of alternating S = 1/2 metallocenium donors, D, and S = 1/2 planar polycyanohydrocarbon acceptors, A, *i.e.*, $\cdots D^{\cdot +}A^{\cdot -}D^{\cdot +}A^{\cdot -}\cdots$, exhibit cooperative magnetic phenomena, *i.e.*, ferro-, antiferro-, ferri-, and metamagnetism. The high temperature ($T \geq 50$ K) magnetic susceptibility can usually be fit by the Curie-Weiss expression, $\chi \propto (T - \theta)^{-1}$, with $\theta > 0$ for those salts with dominant ferromagnetic interactions and $\theta < 0$ for those salts with dominant antiferromagnetic interactions.[1]

Quantitative bulk ferromagnetic behavior (spontaneous magnetization) has been established for the organic-like molecular solid $[\mathrm{Fe^{III}(C_5Me_5)_2}]^{\cdot +}[\mathrm{TCNE}]^{\cdot -}$.[1,2] Single crystals exhibits magnetic behavior characterized by a Curie-Weiss constant, θ, of +30 K, a Curie temperature, T_c, of 4.8 K, saturation magnetization of 16,700 emuG/mol and coercive field of 1 kG at 2 K.[3] Above 16 K the dominant magnetic interactions are along a chain (1-D) and near T_c 3-D bulk effects as evidenced by the value of the β, γ, and δ critical exponents dominate the susceptibility.[3] The ^{57}Fe Mossbauer spectra show that this class of charge transfer complexes exhibits zero applied field Zeeman split spectra with large internal fields of 400–450 kG.[1,4]

The structural requirements necessary to prepare molecular ferromagnetic are evolving. The only structure type reported to date possesses parallel $\cdots D^{\cdot +}A^{\cdot -}D^{\cdot +}A^{\cdot -}\cdots$ linear chains where both the donor D and acceptor A are radicals. The best studied systems possess decamethylmetallocenium donors; however, replacement of the C_5Me_5 ligand with C_5H_5 does not lead to materials exhibiting ferromagnetic behavior. Preliminary data suggests that C_6 ligands scan be utilized to prepare charge transfer complexes exhibiting ferromagnetic behavior. Substitution of $[TCNE]^{\cdot -}$ with $[DDQ]^{\cdot -}$, $[C_4(CN)_6]^{\cdot -}$, or $[TCNQI_2]^{\cdot -}$ leads to similarly structured complexes exhibiting dominant ferromagnetic behavior.[1] In contrast the $[TCNQ]^{\cdot -}$ salt exhibits metamagnetic behavior with an Neel temperature of 2.55 K and critical field of ~1.6 kG.[5] The planar $[TCNQF_4]^{\cdot -}$, $[M(S_2C_2(CN)_2]^-$ (M = Ni, Pt) and three polymorphs of the 1:1 $[C_6(CN)_6]^{\cdot -}$ salts as well as the tetrahedral $[FeX_4]^-$ (X = Cl, Br) salts possess different structural motifs and do not exhibit ferromagnetic behavior. Alternate first row (3d) metallocenes as the $[TCNE]^{\cdot -}$ salt lead to differing magnetic behaviors, *i.e.*, $S = 0$ Co^{III} is paramagnetic, $S = 1/2$ Ni^{III} is antiferromagnetic, and $S = 3/2$ Cr^{III} is ferrimagnetic. Analogous complexes based on second (4d) and third (5d) row Ru^{III} and Os^{III} donors have yet to be prepared.[6]

The extended McConnell model[1,7] was developed and provides the synthetic chemist with guidance for making new molecular materials (organic, organometallic, main group, polymer, and/or inorganic coordination complex) to study cooperative magnetic coupling in systems. Assuming the electron transfer excitation arises from the POMO, to achieve ferromagnetic coupling in a molecular solid via the McConnell mechanism a stable radical (neutral, cations/anions, or ions with small diamagnetic counterions) must possess a degenerate POMO that is not half-filled and the lowest excited state formed via virtual charge transfer (retro or forward) possesses the same spin multiplicity and mixes with the ground state. This requirement limits the structure of a radical to D_{2d}, C_3 or higher symmetry where symmetry breaking distortions do not occur. Intrinsic doubly and triply degenerate orbitals are not necessary and accidental degeneracies suffice. The model is expanded to other electron configurations that contain singly, doubly or triply degenerate partially occupied molecular orbitals, POMO, and offers a convenient guide to explore ferro-, antiferro- and ferrimagnetic phenomena in molecular systems.

To achieve bulk ferromagnetism, ferromagnetic coupling must be established throughout the solid and a microscopic model based on the intra- and interchain configurational mixing of excited states was discussed.[1] These requirements are met by $[Fe^{III}(C_5Me_5)_2]^{\cdot +}[TCNE]^{\cdot -}$[2] and $[Fe^{III}(C_5Me_5)_2]^{\cdot +}[C_4(CN)_6]^{\cdot -}$ [8] etc. Additionally this model suggests that the Ni^{III} and Cr^{III} analogues should be respectively antiferromagnetic and ferrimagnetic, as preliminary data suggests. The bulk nature of the magnetic behavior emphasizes the importance of not only the primary and secondary, but the tertiary structure in this class of materials. We are probing these effects via acceptor substitution and studying the structure/property relationship. We are looking toward the development of computational methods to aid in the understanding structure/magnetic behavior. Extensive chemical syntheses of cleverly designed radicals, as well as physical, experimental and theoretical insight are necessary to test these concepts and establish a deeper understanding of cooperative phenomena in molecular solids.

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