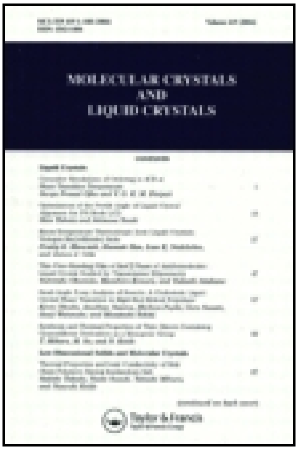

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ONE-DIMENSIONAL SOLIDS CONTAINING BIS(η-ARENE)CHROMIUM CATIONS.

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Abstract Charge transfer salts based on bis(η-arene)chromium cations and TCNE (TCNE = tetracyanoethylene) exhibit both para and ferromagnetic behaviour depending on their structural motif. In contrast, magnetic susceptibility measurements on the thermodynamic phase of $[Cr(\eta\text{-}C_6H_3Me_3)_2]^{\cdot+}[TCNQ]^{\cdot-}$ (TCNQ = 7,7',8,8'-tetracyano-*p*-quinodimethane) indicate that the material does not obey the Curie-Weiss law. However, the magnetic susceptibility can be fitted over all temperatures by considering a paramagnetic component from $[Cr(\eta\text{-}C_6H_3Me_3)_2]^{\cdot+}$ and $[TCNQ]_2^{2-}$ S = 0 dimers with a thermally accessible S = 1 excited state.

INTRODUCTION.

One-dimensional, (1-D), charge transfer complexes have been shown to exhibit unusual optical and electrical properties.[1-4] Recently we have reported on the occurrence of unusual cooperative magnetic properties for several alternating donor/acceptor charge transfer complexes. Metamagnetic behaviour was observed for the 1-D phase $[Fe(C_5Me_5)_2]^{+\cdot}[TCNQ]^{-\cdot}$ [TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane][5] however, the tetracyanoethylenide[6,7] and hexacyanobutadienide[8] salts of $[Fe(C_5Me_5)_2]^{+\cdot}$ salts have been characterized to exhibit bulk (3-D) ferromagnetic behaviour. The former charge transfer complex possesses a spontaneous magnetic moment at zero applied field.[9]

With our observation of meta- and ferromagnetic behaviour in 1-D molecular charge transfer complexes and the theoretical encouragement initially supplied by McConnell[10] and that charge transfer complexes of this structural type possessing either cations or anions with an accessible triplet (e^2) state may stabilize ferromagnetic coupling, we are continuing to prepare new materials exhibiting ferromagnetic coupling.

As part of these studies we purposely sought to prepare the isoelectronic d^5 bis-(arene) $\{[M(\eta^6\text{-}C_6Me_xH_{6-x})_2]^{\cdot+}$ (x =0,3, 6; M = Cr)$\}$ charge transfer salts for direct comparison with the highly magnetic $[Fe(\eta^5\text{-}C_5Me_5)_2]^{\cdot+}$ based charge transfer complexes.

The best conceptual framework within which to view the stabilization of ferromagnetic coupling in molecular-based donor/acceptor complexes is the extended mechanism of McConnell. Within this model, the stabilization of ferromagnetic coupling arises from the configurational mixing of a charge transfer excited state with the ground state.[10b] The model predicts that for excitation from the HOMO of a donor to an acceptor with a half-filled nondegenerate HOMO, as is the case for $[TCNE]^{\cdot-}$, only antiferromagnetic coupling is stabilized. Thus, since $[Cr(\eta\text{-Arene})_2]^{\cdot+}$has a $^2A_{1g}$ ground state, its radical anion charge transfer salts provide a means to test some of these concepts. Here we report complexes based on $[Cr(\eta\text{-}C_6H_xMe_{6-x})_2]^{\cdot+}$ and $[TCNE]^{\cdot-}$ and $[TCNQ]^{\cdot-}$.

SYNTHESIS AND CHARACTERIZATION OF $[Cr(\eta\text{-Arene})_2]$ [TCNE] SALTS.

The reaction of TCNE with metallocenes can result in a variety of 1:1 products products with a variety of structural motifs. The bis-η-arene transition metal complexes, although of different symmetry are also electron rich and can be readily oxidized by organic cyano acceptors such as TCNE. Reaction of bis(η-arene)chromium complexes with a stoichiometric amount of TCNE in acetonitrile results in spontaneous electron transfer giving solutions containing $[Cr(\eta^6\text{-arene})_2]^{\cdot+}$ $[TCNE]^{\cdot-}$. The structures of $[Cr(\eta\text{-}C_6H_6)_2]^{\cdot+}[TCNE]^{\cdot-}$ (**1**) and $[Cr(\eta\text{-}C_6Me_3H_3)_2]^{\cdot+}[TCNE]^{\cdot-}$.MeCN (**2β**) have been determined. Attempts to reproduce the β-phase were unsuccessful and an insufficient amount of the β-phase was available for physical measurements.

However, crystals of $[Cr(\eta\text{-}C_6Me_3H_3)_2]^{\cdot+}[TCNE]^{\cdot-}$ (**2α**) and $[Cr(\eta\text{-}C_6Me_6)_2]^{\cdot+}[TCNE]^{\cdot-}$ (**3**) grown from thf or CH_2Cl_2/diethylether are not suitable for X-ray diffraction experiments but exhibit cooperative magnetic interactions at low temperatures (*vide infra*). Crystalline samples of (**1**) obtained from thf are not single phase materials.

Solid State Structure.

Unlike the structures found for the $[Fe(\eta\text{-}C_5Me_5)_2]^{\cdot+}$ salts of $[TCNE]^{\cdot-}$,[5,9] $[DDQ]^{\cdot-}$,[11] $[TCNQ]^{\cdot-}$,[6] $[C_4(CN)_6]^{\cdot-}$,[8] and $[C_6(CN)_6]^{\cdot-}$,[12] compounds (**1**) and (**2β**) crystallize as a one-dimensional charge transfer salt with dimer dianions sandwiched between two adjacent $[Cr(\eta\text{-arene})_2]^{\cdot+}$ cations in a $...D^+D^+A_2{}^{2-}D^+D^+..$ one-dimensional arrangement. For $[Cr(\eta\text{-}C_6H_6)_2]^{\cdot+}[TCNE]^-$ (**1**) the unit cell is comprised with three unique interchain interactions, namely **A-B, A-D, B-D,** Figure 1. Chains A-C are essentially in registry, whereas chains A-B and A-D are out-of-registry. The solid consists of parallel chains separated by 6.161, 6.534, and 7.470 Å. The interchain Cr···Cr distances are 6.305, 7.483, 8.307, 9.911, and 10.434 Å. These distances are too great for spin-spin interactions not mediated by a radical.

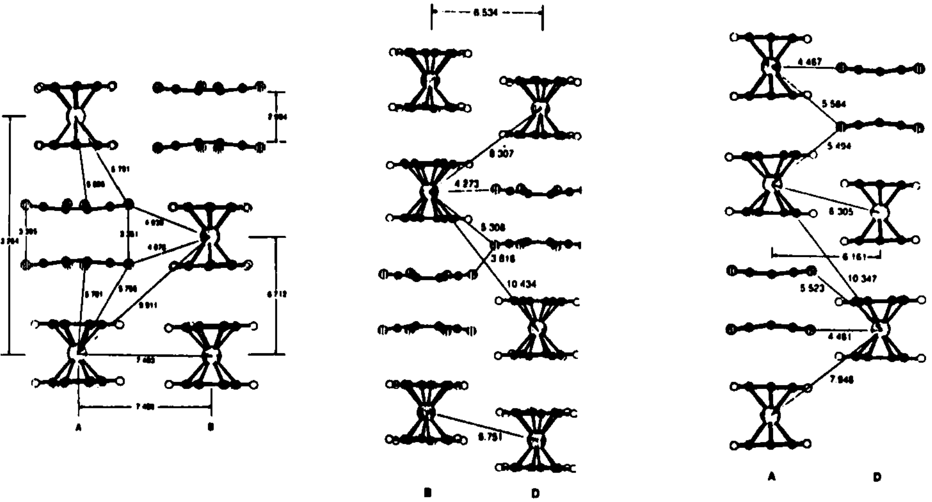

FIGURE 1. View normal to chains showing the four unique chains A,B,C,D for (**1**).

Vibrational spectroscopy.

The C=N stretching bands in the infrared spectrum occur at 2144 and 2183 cm^{-1} for the $[Fe(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ and $[Co(C_5Me_5)_2]^+[TCNE]^{\cdot-}$ salts.[13] For (**1**) and (**2**) crystallized from acetonitrile we observe three strong C=N stretching vibrations in the infrared at 2159, 2170, and 2189 cm^{-1}. The position of the bands indicate that the anion is mono-reduced, but the lowering of the symmetry by deformation out of planarity as revealed by the X-ray diffraction experiment is consistent with the observation of three infrared active bands rather than two for $[TCNE]^{\cdot -}$ isolated anions.[14] A similar infrared spectrum has been reported for the $[TCNE]_2^{2-}$ dimer in the complex $[Fe(\eta\text{-}C_5H_4)_2(CH_2)_3]$ [TCNE].[15]

However, the infrared spectra of either (**2α**) or (**3**) crystallized from thf show strong ν(CN) stretches at 2144, 2183 cm^{-1} which indicate that crystallization from this solvent gives $[TCNE]^{\cdot -}$ and not $[TCNE]_2^{2-}$.

Electron Paramagnetic Resonance.

The EPR spectra of $[Cr(\eta\text{-arene})_2]^{\cdot +}[PF_6]^-$ salts are isotropic with characteristic g-tensors *ca.* 1.987.[16] The room temperature EPR spectrum of (**1**) in 2:1 THF:CH_3CN solution exhibits two equal intensity isotropic signals with g = 2.001 (ΔH_{pp} = 7.3 G) and 1.986 (ΔH_{pp} = 14.4 G) which are assigned to $[TCNE]^{\cdot -}$ anion and $[Cr(\eta\text{-arene})_2]^{\cdot +}$ cations respectively. In the solid state (**3**) exhibits only a broad peak at g = 1.984 (ΔH_{pp} = *ca. 600* G).

Magnetic susceptibility.

The Faraday balance susceptibility measured between 2 and 320 K shows that (**1**) obeys the Curie-Weiss law, $\chi_M^{-1} = C/(T-\Theta)$. The value of $\mu_{eff} = 1.70\ \mu_B$ for (**1**) indicates that only one S = 1/2 radical per formula unit contributes to the susceptibility. This is consistent with the structures possessing S = 0 $[TCNE]_2^{2-}$. The linearity of the χ^{-1} *vs* T plot indicates that the singlet-triplet energy gap must be sufficiently large that there is no detectable triplet concentration at temperatures up to 320 K.

In contrast (**2α**)and (**3**) exhibit different magnetic behaviour. A least squares fit of χ_M^{-1} *vs* T for (**2α**) and (**3**) can be fitted to the Curie-Weiss law, $\chi_M^{-1} = (T-\theta)/C$, between 50 - 300 K with a ferromagnetic Θ of +11.0 K (μ_{eff} = 2.44 μ_B) and 11.8 K (μ_{eff} = 2.37 μ_B), respectively. The magnetic moment is in good agreement for the value expected for two independent doublets i.e. $\{\mu_{eff}(calc) = (2 \times 3)^{1/2} = 2.44\ \mu_B\}$.

Below ~5K, the reciprocal susceptibility deviates from the Curie-Weiss law and the molar susceptibility exhibits a marked field dependence. Enhancement of the low temperature field dependence of the magnetization, M(H), and low field susceptibility is demonstrated by comparison with the Brillouin function. The magnetization (M) for two S = 1/2 systems is given by;

$$M = \Sigma N_i g_i J \tanh(x_i) \qquad (1)$$

where

$$x_i = \mu_i H/k_B T = g_i J_b H/k_B T$$

and N_i, g_i, and μ_i refer to the number, Lande g factor { g = 2 for [TCNE].- and $[Cr(\eta\text{-arene})_2]^{\cdot +}$} and magnetic moment of each of spin site i.

Although the magnetization saturates to 11,000 emuG/mol as expected by Eq. (2) for two g =2.0, S =1/2 radicals at low field there is no evidence for 3-D ordering of spins. Enhancement of M(H) and χ(T) beyond the independent spin model can be parametrized using the exact solution to the classical S = 1/2 1-D Ising model. Through an excellent parametrization χ(T) and M(H), Eq. (3) is obtained for J = +2.4 K. (Figure 2)

$$M_S = NS\mu_B \Sigma g_i \tag{2}$$

$$M(J,H,T) = \frac{\exp\left(\frac{J}{K_BT}\right)\sinh\left(\frac{H}{K_BT}\right)}{\left[\exp\left(\frac{2J}{K_BT}\right)\sinh^2\left(\frac{H}{K_BT}\right) + \exp\left(\frac{-2J}{K_BT}\right)\right]^{1/2}} \tag{3}$$

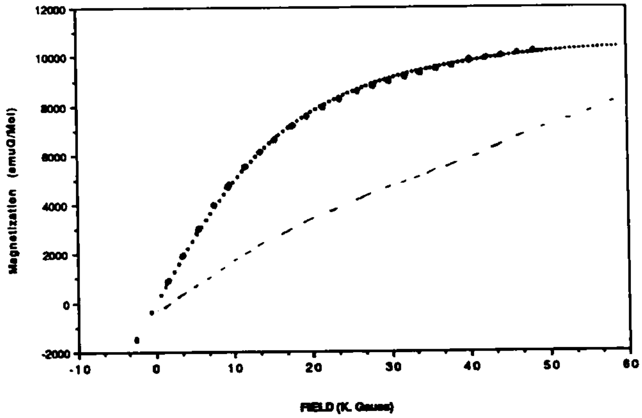

FIGURE 2. Observed (.) and calculated magnetization [Brillouin function (---) and Ising Model (o) as a function of field at 4.2 K for (**3**).

SYNTHESIS AND CHARACTERIZATION OF $[Cr(\eta\text{-Arene})_2]$ [TCNQ] SALTS

Bis(η-Arene)chromium complexes also undergo charge transfer reactions with TCNQ (7,7',8,8'-tetracyano-*p*-quinodimethane).[17,18] The X-ray structure of the 1:1 salt with bis(η-toluene)chromium has been determined[19] and consists of segregated stacks of cations and anions. No spectroscopic properties of these materials have been reported.

Reaction of Cr(η-$C_6Me_3H_3$)$_2$ with TCNQ in thf yields a dark green precipitate. Rapid recrystallization from CH_2Cl_2 gives blue crystals of (**4**α). Slow cooling in CH_2Cl_2 gives the thermodynamic phase (**4**β). Insufficient amounts of the β-phase was available for physical measurements.

Solid State Structures.

For (**4**α) the solid state motif comprises of dimer dianions sandwiched between the two adjacent $[Cr(\eta\text{-}C_6Me_3H_3)_2]^{\cdot+}$ cations in a $...D^+D^+A_2^{2-}D^+D^+..$ one-dimensional arrangement (Figure 3). The anion and arene planes within a given stack are slightly tilted by 6° with respect to each other. The anion-cation separation is 4.03 Å close to the usual van der Waals separation of 3.60 Å. The cations adjacent to each other within a stack are separated by 3.43 Å with a Cr-Cr separations of 6.68 Å.

The β-phase is comprised of a 1-D chain of alternating S =1/2 $[TCNQ]^{\cdot-}$ anions and S = 1/2 $[Cr(\eta\text{-}C_6Me_3H_3)_2]^{\cdot+}$ cations (Figure 3). In this respect it is isostructrual with the $[Fe(C_5Me_5)_2][TCNQ]$ 1:1 kinetic phase, which has been characterized as a metamagnet. The ring centroids of the cations and anions are not perfectly aligned with the chain axis but are displace by *ca.* 2.0 Å. The anion cation separation is 3.50 Å. The nearest neighbour Cr-Cr separations along the chain is 10.77 Å (Figure 3).

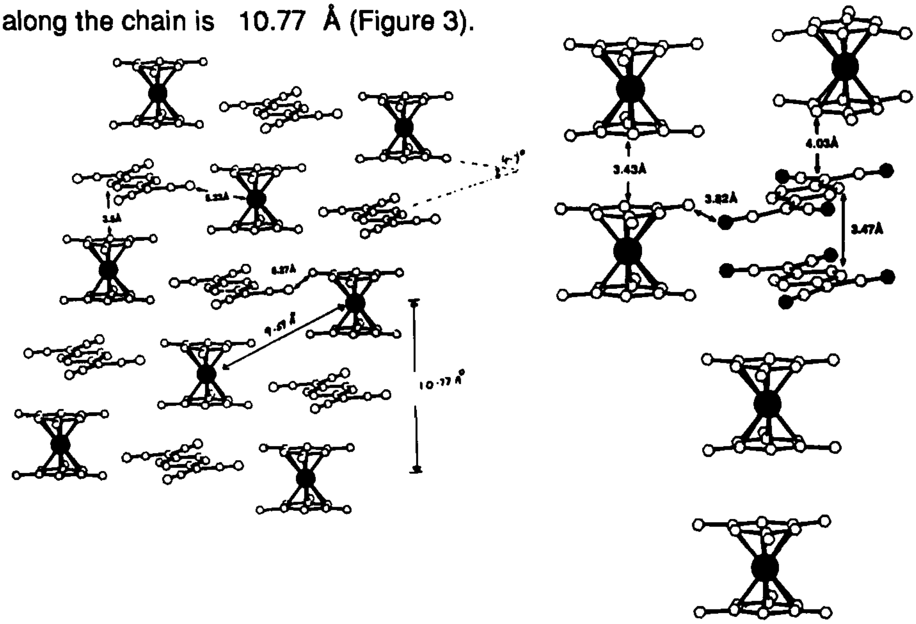

FIGURE 3. X-Ray structure of $[Cr(\eta\text{-}C_6Me_3H_3)_2]^{\cdot+}[TCNQ]^{\cdot-}$ (**4**)α and β phases.

Electron Paramagnetic Resonance Spectroscopy

Solutions of (**4**) in CH_2Cl_2 at room temperature exhibit isotropic signals with g = 1.995 (ΔH_{pp} = 11.2 G) presumably due to the overlap of S = 1/2 $[TCNQ]^{\cdot -}$ and $[Cr(\eta\text{-}C_6Me_3H_3)_2]^{\cdot +}$ signals respectively. Neither ^{15}N nor ^{53}Cr hyperfine coupling are resolvable.

At room temperature powdered samples of (**4**α) exhibit two overlapping isotropic resonances resonances centered at g = 1.988 with ΔH_{pp} = 29 G. As the temperature is lowered to 110 K one of the signals splits into a doublet with a splitting of 9.2 G. No $\Delta M_S = \pm 2$ transition is observed between 110 K and room temperature. The two signals observed at room temperature can be explained by an isotropic signal for the $^2A_{1g}$ $[Cr(\eta\text{-}C_6Me_3H_3)_2]^{\cdot +}$ cations and an exchange broadened triplet resonance due to thermal population of the triplet S =1 excited state for the $[TCNQ]_2^{2-}$ dianion. As the temperature is lowered the number of populated triplet states is reduced and dipolar-induced zero-field splitting become resolvable. However, it would be expected that such this exchange broadening effect which removes the dipolar splitting would also remove the dipolar-induced mixing of states resulting in the vanishing of the $\Delta M_S = \pm 2$ transition.

Magnetic susceptibility measurements.

The Faraday balance susceptibility of (**4**α) between 2-320 K does not obey the Curie-Weiss law, $\chi_M^{-1} = C/(T-\Theta)$. The value of μ_{eff} rises steadily from a value of 1.73 μ_B at 2.3 K to 2.34 μ_B at 320 K. At low temperatures the value of the molar susceptibility is consistent with only $[Cr(\eta^6\text{-}C_6Me_3H_3)_2]^{\cdot +}$ (S =1/2) radical cations contributing to the susceptibility. Since the X-ray structure of (**4**α) shows that the $[TCNQ]^{\cdot -}$ form dimers with short interplanar contacts, we presume that the unpaired electron on both radical anions couple antiferromagnetically giving an S = 0 ground state for the $[TCNQ]_2^{2-}$ thus leaving only the $[Cr(\eta\text{-}C_6Me_3H_3)_2]^{\cdot +}$ radical cations to contribute to the magnetic susceptibility at low temperature. As the temperature increases the population of the S = 1 triplet excited state occurs. We can fit the observed χ^{-1} *vs* T plots (Figure 4) using two contributions: (a) simple Curie-Weiss term for $[Cr(\eta^6\text{-arene})_2]^{\cdot +}$ cations and (b) a Bleany-Blowers term for the $[TCNQ]_2^{2-}$ dimers (Eqn 4):

$$\chi = \left(\frac{2Ng^2\mu_B^2}{3kT}\right)\left[1 + \left(\frac{1}{3}\right)\exp\left(\frac{-2J}{kT}\right)\right]^{-1} + \left(\frac{Ng^2\mu_B^2}{3k\left(T - \theta\right)}\right) \quad (4)$$

Singlet-triplet term Curie -Weiss term

$[TCNQ]_2^{2-}$ $[Cr(\eta\text{-Arene})_2]^+$

Where 2J is the singlet-triplet energy gap. The best fit to the data are 2J = -315 K, 0.027 eV , $\Theta = 0\,^{o}$ for (4α).

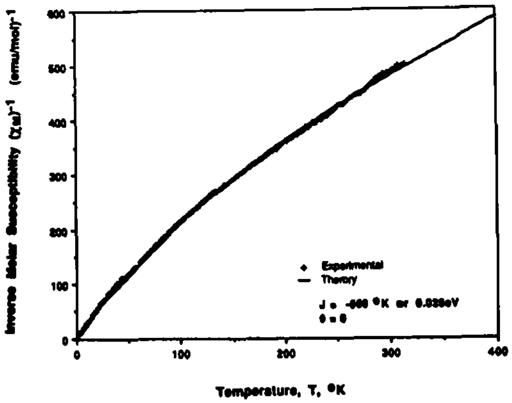

FIGURE 4. Plot of χ^{-1} *vs* T for (4α) [Found (.); calc using Eqn (4) (+).]

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