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Ferromagnetic Interactions in Decamethylferrocenium Salts of Nickel Bis(dichalcogolenes)

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A number of strategies have been proposed for the design of ferromagnetically ordered molecular assemblies,[1-6] and recent efforts have resulted in several examples of bulk molecular ferromagnets.[7,8] In seeking crystals that display three-dimensional ferromagnetic phenomena we have prepared a series of molecular charge-transfer salts of the type, $[Fe(C_5Me_5)_2][Ni(X_2R)_2]$ ($[D^+][A^-]$), where X_2R represents one of a series of dichalcogolene ligands designed to meet the requirements of the McConnell[1a,b,2,4] model for the stabilization of ferromagnetism by virtual charge transfer between donor and acceptor, $(D^+) \leftrightarrow (A^-)$. Nickel bis(dichalcogolene) complexes are excellent candidates as anions for the synthesis of mixed-stack molecular charge-transfer salts that display cooperative magnetic phenomena due to (1) their planar structures, (2) delocalized electronic states, (3) $S = {}^1/_2$ spin state for monoanionic species, and (4) the possibility of extended magnetic interactions mediated by the chalcogen atoms.[9,10] We report here preliminary results of structural and magnetic studies of two such materials, $[Fe(C_5Me_5)_2][Ni(dmit)_2]$,[11] **1**, and $[Fe(C_5Me_5)_2][Ni(bds)_2]\cdot CH_3CN$, **2**, which adopt dramatically different structural motifs and yet display ferromagnetic coupling in each case.

The charge-transfer salts **1** and **2** were prepared by combining equimolar acetonitrile solutions of $[Fe(C_5Me_5)_2][BF_4]$[7] and the appropriate tetrabutylammonium nickel bis(dichalcogolene) salt.[12,13] In each case, dark crystals deposited on standing. Crystals suitable for X-ray analysis were obtained by slow evaporation of saturated solutions of **1** or **2**.

The 1:1 $[D^+][A^-]$ salt, **1**, crystallizes in the triclinic space group $P\bar{1}$, and its unusual structure[14] consists of $..D^+D^+A^-A^-D^+D^+A^-A^-..$ stacks in which side-by-side pairs of cations alternate with face-to-face pairs of anions (Figure 1). The Fe–Fe distance within a (D^+D^+) pair is 8.412 Å; within an (A^-A^-) pair the Ni–Ni distance is 5.56 Å, and the shortest S–S distance is 3.87 Å. Considering the intrastack $(D^+) \leftrightarrow (A^-)$ contacts, the Fe–Ni distances are 6.557 and 7.299 Å. However, in terms of magnetic interactions the Fe–S distances probably are more important because the HOMO of paramagnetic monoanionic metal dithiolene complexes has significant spin density (ca. 50–65%) delocalized onto the chalcogen atoms;[10a,15,16] the shortest intrastack Fe–S distances range from 5.45 to 6.59 Å.

The structure of **2**,[14] which also crystallizes in the triclinic space group $P\bar{1}$ (Figure 1), is significantly different than that of **1**. It consists of two-dimensional layers composed of $..D^+D^+A^-D^+D^+A^-..$ stacks that also have side-by-side pairs of cations but a net (+) charge per $(D^+D^+A^-)$ repeat unit. These charged stacks are separated by sheets in the a–c plane composed of $[Ni(bds)_2]^-$ anions that neutralize the charge. The Fe–Fe distance within the $..D^+D^+A^-D^+D^+A^-..$ stack is 9.096 Å, whereas the Fe–Ni distances within the stack are 5.847 and 8.034 Å. The closest relevant Fe–Se distances within the $..D^+D^+A^-D^+D^+A^-..$ stack are 5.597 and 6.883 Å. Full details of structural information including intra- and interstack interactions for **1** and **2** will be discussed later.[17]

The magnetic susceptibilities of **1** and **2** were measured with a SQUID susceptometer from 300 to 1.5 K and magnetic fields between 10 and 55 000 G. The $\chi_M \cdot T$ versus T plots for **1** and **2** recorded at 500 G are shown in Figure 2. In each case $\chi_M \cdot T$ is constant to ca. 25 K, but as the sample is further cooled $\chi_M \cdot T$ increases rapidly, a definitive signature of ferromagnetic interactions.[1a,7,8,18] In the case of **2**, $\chi_M \cdot T$ is still increasing at the lowest temperature attainable, ca. 1.5 K. Thus, over the entire accessible range of temperatures the net exchange interaction is dominated by ferromagnetic interactions, which we take as arising from quantum mechanical admixture of a forward charge-transfer excited state,[1a] e.g. $[D^{2+}][A^{2-}]$. Studies of the field dependence of the magnetization for **2** do not show spontaneous magnetization or hysteresis at 1.9 K.

For **1**, $\chi \cdot T$ reaches a maximum at ca. 2.1 K and decreases sharply as the temperature is lowered to 1.5 K (see inset, Figure 2). We take this turnover to represent a crossover to antiferromagnetic behavior resulting from antiferromagnetic $(A^-) \leftrightarrow (A^-)$ interactions favored by the short S–S distances between $Ni(dmit)_2^-$ units.[19]

These results show that the simple 1:1, $[D^+][A^-]$ salts prepared from the decamethylferrocenium and metal dichalcogolene ions can display ferromagnetic interactions within a richly variable structural framework. The use of different metal dichalcogolenes

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(11) Abbreviations: $dmit^{2-}$ = 2-thioxo-1,3-dithiole-4,5-dithiolate; bds^{2-} = 1,2-benzenediselenolate.

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(14) Crystallographic data. **1**: $C_{26}H_{30}FeNiS_4$, $M_r = 777.67$; triclinic, space group $P\bar{1}$ (no. 2); $a = 11.347$ (1) Å, $b = 14.958$ (2) Å; $c = 10.020$ (1) Å, $\alpha = 97.68$ (1)°, $\beta = 94.36$ (1)°, $\gamma = 109.52$ (1)°, $V = 1575.2$ (7) Å^3; $Z = 2$, $\rho_{calcd} = 1.64$ g·cm^{-3}; $\mu = 17.17$ cm^{-1}. The structure was solved by direct methods in TEXSAN 4.0. Full-matrix least-squares refinement gave $R(F) = 0.032$ and $R_w(F) = 0.043$ for 3814 reflections with $F^2 \geq 3\sigma(F^2)$ measured up to $2\theta = 48°$ at −120 °C (Mo Kα radiation, $\lambda = 0.71069$ Å). **2**: $C_{34}H_{41}NFeNiSe_4$; $M_r = 874.09$; triclinic, space group $P\bar{1}$ (no. 2); $a = 11.720$ (2) Å, $b = 16.282$ (3) Å, $c = 9.606(2)$ Å, $\alpha = 100.66$ (2)°, $\beta = 106.03$ (2)°, $\gamma = 81.75$ (2)°, $V = 1723$ (1) Å^3; $Z = 2$, $\rho_{calcd} = 1.72$ g·cm^{-3}; $\mu = 51.77$ cm^{-1}. The structure was solved by Patterson and Fourier techniques in TEXSAN 4.0. Full-matrix least-squares refinement gave $R(F) = 0.042$ and $R_w(F) = 0.048$ for 3590 reflections measured up to $2\theta = 50°$ at −120 °C (Mo Kα radiation).

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(19) (a) This interpretation suggests that the susceptibility might be modelled in terms of an antiferromagnetic dimer coupled to a ferromagnetic molecular field.[19b] However, in the absence of greater insight into the interactions within a $[Fe(C_5Me_5)_2]^+$ pair this has not been done. (b) Smart, J. S. *Effective Field Theories of Magnetism*; Saunders: Philadelphia, PA, 1966.

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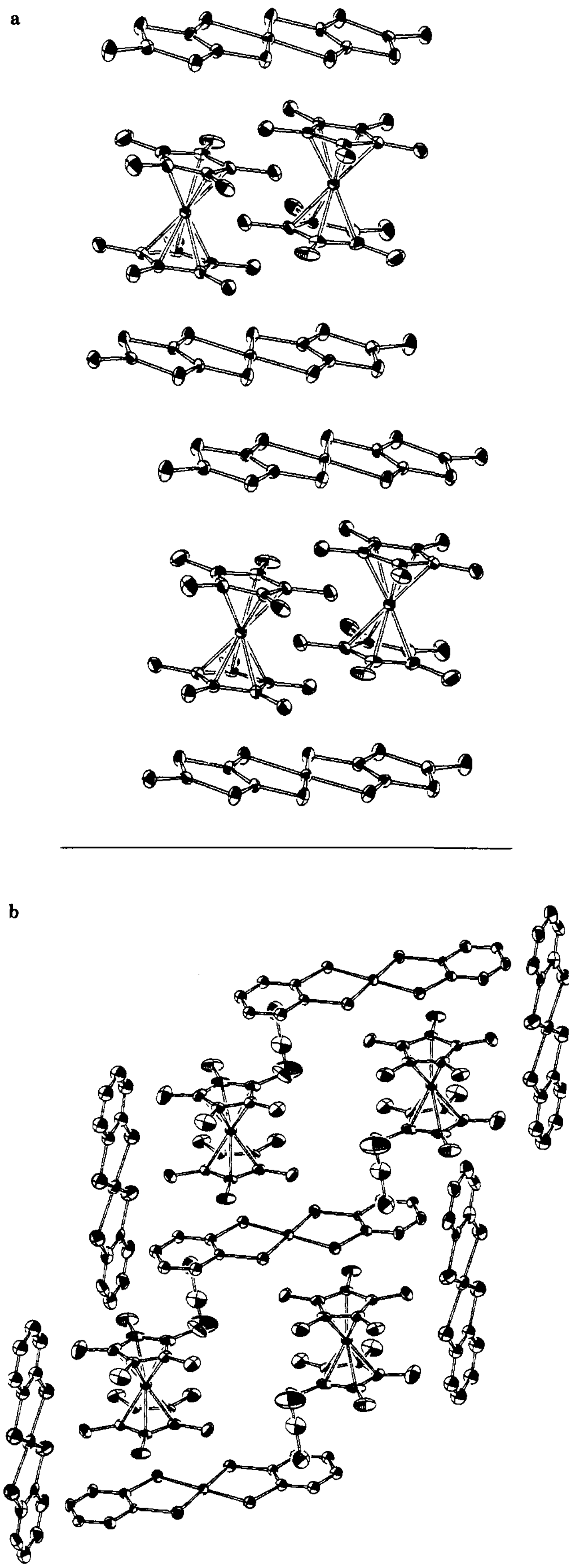

Figure 1. (a) Packing diagram of **1** showing a perspective view of a ..A$^-$D$^+$D$^+$A$^-$A$^-$D$^+$D$^+$A$^-$.. stack. (b) Packing diagram of **2** showing a perspective view of a ..A$^-$D$^+$D$^+$A$^-$D$^+$D$^+$A$^-$.. stack, portions of the flanking A$^-$ sheets, and the CH$_3$CN of crystallization. (The plane of the paper corresponds roughly to the *ab* plane.)

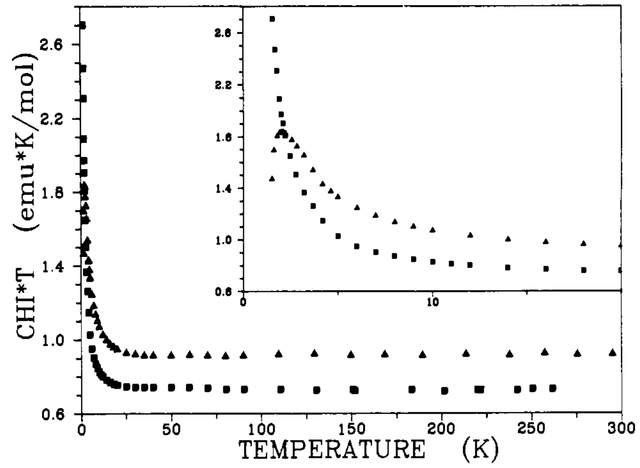

Figure 2. Temperature dependence of $\chi_M \cdot T$ for **1** (triangles) and **2** (squares). Inset: expansion of the 1.5–20 K region.

is sure to expand the range of structural types and magnetic properties exhibited by this class of compounds.[20]

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Supplementary Material Available: Tables of atomic positional parameters, anisotropic thermal parameters, and bond distances and angles (6 pages); table of observed and calculated structure factors for **1** and **2** (26 pages). Ordering information is given on any current masthead page.

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(20) For example, we have observed ferromagnetic interactions in 1:1 decamethylferrocenium salts of [Ni{Se$_2$C$_2$(CF$_3$)$_2$}$_2$]$^-$ and [Ni{S$_2$C$_2$(CF$_3$)$_2$}$_2$]$^-$, and more extensive, independent investigations by the Dupont group show that the latter compound, at least, exhibits a different structural motif from either of those reported here (Miller, J. S., private communication).

Transient Binding of Photodissociated CO to Cu_B^+ of Eukaryotic Cytochrome Oxidase at Ambient Temperature. Direct Evidence from Time-Resolved Infrared Spectroscopy

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The reactions of CO with the metal centers of cytochrome oxidase exemplify the mechanisms open to O$_2$ and other small-molecule ligands. In particular, the fast reactions following photodissociation of CO from cytochrome a_3 yield important information about the pathways available to ligands to and from the active site. FTIR studies have demonstrated that, below 180 K, photodissociated CO binds to Cu_B^+ both in mitochondrial preparations[1,2] and in the detergent-solubilized enzyme.[3,4] We

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