

# Design and Synthesis of a Library of Molecule-Based Magnets: The Charge-Transfer Salt Approach

Bharat B. Kaul, Bruce C. Noll, and Gordon T. Yee<sup>1</sup>

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

E-mail: yeeg@colorado.edu

Received March 20, 2001; accepted March 21, 2001

IN DEDICATION TO THE LATE PROFESSOR OLIVIER KAHN FOR HIS PIONEERING CONTRIBUTIONS TO THE FIELD OF MOLECULAR MAGNETISM

The rules governing magnetic coupling in molecule-based materials are still being defined. Until they are clear, synthetic efforts should ideally yield many new candidate magnets for a minimal investment of time and effort. One approach that satisfies this requirement is the synthesis of magnetic charge-transfer salts from metallocenes and easily identifiable organic acceptors. This strategy offers the possibility of synthesizing a library of structurally related compounds utilizing tunable building blocks and has yielded examples exhibiting interesting magnetic phenomena including ferromagnetism, metamagnetism, canted (weak) ferromagnetism, and spin glass behavior. In principle, this work should permit a systematic examination of structure–property relationships, leading to a better understanding of intermolecular magnetic coupling. © 2001 Academic Press

**Key Words:** molecule-based magnetism; metallocene charge-transfer salt.

## INTRODUCTION

In the field of molecule-based magnets, what we now understand reasonably well is how spin-containing species communicate with each other through covalent bonds. Rules, such as those of Goodenough and Kanamori (1), allow us to predict the sign of a magnetic interaction based on orbital symmetry considerations. However, we know much less about how spins couple *intermolecularly*, through van der Waals interactions or through space. To understand these better, it makes sense to prepare families of compounds that allow one to probe, systematically, the effects of structure, including electronic structure, on the observed magnetic coupling and bulk magnetic properties.

As a strategy for doing just this, the charge-transfer (CT) salt approach has been quite successful. By way of example, we show that it allows the variation of *d* electron count

while maintaining crystal structure or allows perturbation of the structure while leaving the electronic structure essentially unchanged. Importantly, it appears to work for a wide variety of building blocks to give interesting magnetic compounds. In conjunction with structural information, spin density calculations should give insight into coupling in the  $\pi$  stacking direction, which seem to be reasonably systematic. However, it is clear that less well understood weak interstack interactions determine bulk behavior and apparently the case that both ferromagnetic and antiferromagnetic interstack coupling can be present.

At the foundation to the CT salt approach is the observation that neutral electron-rich donor molecules (*D*) can react with neutral electron-poor acceptors (*A*) to transfer an electron and give an ionic product. The resulting  $D^+$  and  $A^-$  ions, if stable, tend to assemble in a mixed one-dimensional  $\pi$  stack,  $D^+A^-D^+A^-$ . If  $D^+$  and  $A^-$  both possess unpaired electrons, then the observation, in general, is that these spins will couple ferromagnetically within the stack. The strength of this coupling and its dependence on the electronic structure of the building blocks has not been explored. Additionally, in the right circumstances (that are not yet entirely understood), interstack coupling can lead to a phase transition giving an overall ferromagnetically or antiferromagnetically ordered state.

The first well-characterized example of this idea was the CT salt ferromagnet, decamethylferrocenium tetracyanoethenide,  $[Fe(Cp^*)_2][TCNE]$ , that results from the reaction of decamethylferrocene and tetracyanoethylene, and which orders below 4.8 K (2). This was followed by work that showed that five related compounds are also ferromagnets (Table 1, where TCNQ is 7,7,8,8-tetracyanoquinodimethane,  $Cr(Cp^*)_2$  is decamethylchromocene, and  $Mn(Cp^*)_2$  is decamethylmanganocene) (3).

As of 1994, a complete list of magnetically ordered pure metallocene-based CT salts included these compounds as well as only four other phases (that are all metamagnetic, not ferromagnetic, *vide infra*): a second polymorph of

<sup>1</sup> To whom correspondence should be addressed.

**TABLE 1**  
Curie Temperatures for Known CT Magnets circa 1994

Compound	$T_c$	Compound	$T_c$
[Cr(Cp*) <sub>2</sub> ][TCNE]	3.8	[Cr(Cp*) <sub>2</sub> ][TCNQ]	3.1
[Fe(Cp*) <sub>2</sub> ][TCNE]	4.8	[Fe(Cp*) <sub>2</sub> ][TCNQ]	3.0
[Mn(Cp*) <sub>2</sub> ][TCNE]	8.8	[Mn(Cp*) <sub>2</sub> ][TCNQ]	6.2

[Fe(Cp\*)<sub>2</sub>][TCNQ] and the CT salt derived from Mn(Cp\*)<sub>2</sub> and bis(bis(trifluoromethyl)ethylenedithiolato)) *M*(II), (*M*(tfd)<sub>2</sub>) where *M* = Ni, Pd, Pt (4). Reviews by Miller and Epstein at that time included comprehensive lists of the magnetic properties of approximately 50 other CT salts including nonordering compounds and solid solutions with positive and negative Curie–Weiss  $\theta$ 's (5, 6).

This noncomprehensive update will focus on advances in this area in the past couple of years and specifically on compounds that exhibit order. Essentially all of the progress has involved the utilization of new organic one-electron acceptors (Table 2). Candidates have been drawn from the Diels–Alder reaction literature and the conductive charge-transfer salt literature for reasons that will be discussed. To illustrate these ideas, we also report the synthesis and crystal structure of a new CT salt magnet, decamethylchromocenium diethyl dicyanofumarate, and compare it to both its decamethylmanganocenium analogue and its dimethyl dicyanofumarate analogue, which we have previously described.

## BACKGROUND

For the purposes of clarity, we define a charge-transfer salt here to be a compound that results from the reaction of an electron donor with an electron acceptor in which the product is bound by intermolecular Coulomb and van der Waals interactions, but no covalent bonding. Thus, we are

**TABLE 2**  
Curie or Neel Temperatures of Some New CT Magnets

Compound	$\theta$	$T_c$ (K)	Comments
[Mn(Cp*) <sub>2</sub> ][DMeDCF]	16 K	10.6	Hard glassy ferromagnet
[Cr(Cp*) <sub>2</sub> ][DMeDCF]	23 K	5.7	Soft ferromagnet
[Mn(Cp*) <sub>2</sub> ][DEtDCF]	16 K	12 K, $T_N$	Metamagnet, reentrant spin glass, hysteretic
[Cr(Cp*) <sub>2</sub> ][DEtDCF]	22 K	5.4 K, $T_N$	Metamagnet, frustrated?
[Cr(Cp*) <sub>2</sub> ][DCNQ]	6 K	< 4 K, $T_N$	Metamagnet with $H_c \sim 0$ ?
[Mn(Cp*) <sub>2</sub> ][DCNQ]	11 K	8 K, $T_N$	Canted metamagnet, hysteretic
[Fe(Cp*) <sub>2</sub> ][DCNQ]	4 K	4 K, $T_N$	Canted metamagnet, hysteretic

specifically excluding coordination polymers such as those involving bridging TCNE.

To synthesize an ionic charge transfer salt, the donor must be sufficiently reducing to transfer an electron completely to the acceptor. Further, both the resulting donor cation and acceptor anion must be stable, which can be determined by electrochemical reversibility; thus, solution cyclic voltammetry may be used as a guide. A distinct advantage of the charge-transfer salt strategy over other methods of preparing molecule-based magnets (7) is that, in principle, with only these electrochemical constraints, the donor and acceptor may be varied independently. This translates to the ability to investigate an array of new materials from each new acceptor by pairing it with all available donors with which it is predicted to react. If a newly synthesized acceptor is rather weak (i.e.,  $E_{(0/-1)}^\circ \ll 0$ ), one can pair it with a strong donor to enable the pair to satisfy the charge-transfer criterion. As a rough guide, every acceptor on the scale in Fig. 1 will react by outersphere electron transfer with every donor located to the right of it.

The future of CT salt magnet research relies on the identification of new donor and acceptor building blocks. Focusing on acceptors and using the properties of TCNE and TCNQ as guides, we asked the question: in what other kinds of reactions do these molecules participate? The answer is that TCNE is recognized as a good dienophile in the context of the Diels–Alder reactions and an electron-poor co-monomer for olefin polymerization. TCNQ was the “original” acceptor in conductive organic salt synthesis (*vide infra*). As demonstrated below, other compounds that perform well in these three types of reactions are apparently excellent starting points for the synthesis of new molecule-based magnets.

## DIELS–ALDER REACTIONS

The conjugate addition of an olefin to a diene to give a cyclohexene is known as the Diels–Alder reaction. The most simple of these, ethylene plus 1,3-butadiene to give cyclohexene, actually requires forcing conditions of high temperature and pressure and results in poor yield. This is because the lowest unoccupied molecular orbital (LUMO) of the olefin, also known as the dienophile, must be relatively low in energy to accept electron density from the highest occupied molecular orbital (HOMO) of the diene. Placing electron-withdrawing functional groups such as C=O or C≡N in conjugation with the double bond achieves this. Thus, it makes sense that other known good dienophiles should also make good one-electron acceptors since lowering the LUMO is correlated with making the molecule easier to reduce.

However, there is one other condition that must be met: chemical stability of the radical anion. This is demonstrated by an examination of the good dienophiles *trans*-1,

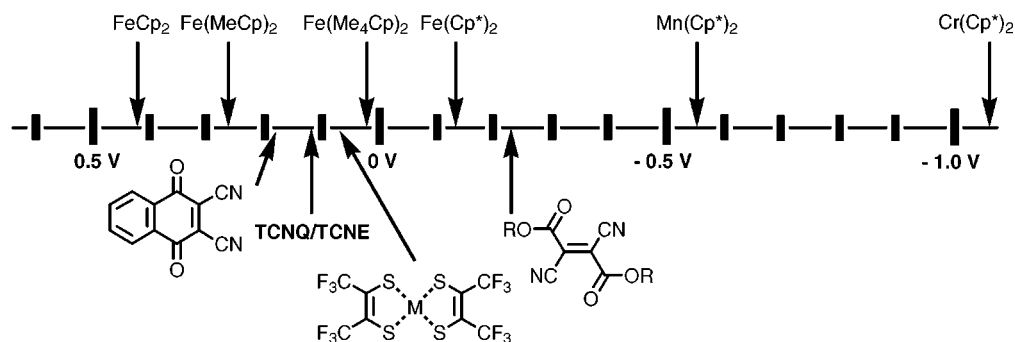


FIG. 1. Electrochemical properties of some donors and acceptors (vs SCE).

2-dichloro-1,2-dicyanoethylene,<sup>2</sup> 1,2-dicyano-1,2-bis(trifluoromethyl)ethylene,<sup>2</sup> and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene<sup>3</sup> (Fig. 2). All show irreversible electrochemistry and the attempted synthesis of charge-transfer salts with these acceptors and decamethylferrocene results in intractable, nonordering solids.

#### Dicyanofumarates

Dicyanofumarate diesters, well-known dienophiles and polyolefin co-monomers, were first synthesized by Ireland and co-workers (9) and Villemin and Ben Alloum (10) by oxidative dimerization of commercially available  $\alpha$ -cyanoesters ( $R = \text{Me}$  or  $\text{Et}$ ). Mulvaney and co-workers have shown that these diesters exhibit reversible one-electron reductions at approximately  $-200$  mV vs SCE (11). As expected from this result, reaction with  $\text{Fe}(\text{Cp}^*)_2$  does not lead to an ionic product. However, stronger donors do give new CT salts and an interesting advantage of these acceptors in the context of magnetism is their tunability: as shown below, changing the identity of the  $R$  group impacts the properties of the resulting CT salt.

**Dimethyl dicyanofumarate.** Reaction of the dimethyl dicyanofumarate, DMeDCF, with  $\text{Mn}(\text{Cp}^*)_2$  in dichloromethane at  $-50^\circ\text{C}$  followed by slow addition of ether causes microcrystals of  $[\text{Mn}(\text{Cp}^*)_2][\text{DMeDCF}]$  to be deposited. Like the TCNE analog, these are quite air and solvent sensitive and must be isolated and dried thoroughly at low temperature (12).

The plot of  $\chi T$  vs  $T$  shows a sharp peak at 8 K. The corresponding plot of inverse  $\chi$  vs  $T$  shows excellent linear behavior that extrapolates to a Curie–Weiss  $\theta$  of 16.0 K. An extrapolation of the steepest part of the field-cooled data obtained at 2 G suggests a Curie temperature of 10.5 K (Table 2). This surpasses that observed for  $[\text{Mn}(\text{Cp}^*)_2]$

$[\text{TCNE}]$  (8.8 K) (13). The plots of  $M$  vs  $H$  show the evolution of a hard ferromagnet to a soft ferromagnet as the temperature is raised, quite reminiscent of the data for  $[\text{Mn}(\text{Cp}^*)_2][\text{TCNE}]$ . The coercive field, which is sample dependent, is very large at almost 7000 G at 1.8 K (Fig. 3). The ac susceptibility of  $[\text{Mn}(\text{Cp}^*)_2][\text{DMeDCF}]$ , like many other decamethylmanganocenium salts we have investigated, exhibits frequency-dependence indicative of glassiness (Fig. 4). These properties suggest a highly cooperative magnetic state without the usual long-range order associated with true ferromagnetism, something that is being investigated further.

The corresponding chromium analogue, prepared at room temperature, exhibits Curie–Weiss behavior with  $\theta = 23$  K. The crystal structure, which we have previously reported, shows that it adopts the expected donor–acceptor mixed stack arrangement with one in-phase and two-out of phase interstack interactions (14). It is also a ferromagnet below 5.7 K, which is higher than its TCNE and TCNQ analogues (Table 2). Presumably because of its  $^4A$  ground

<sup>4</sup> $[\text{Cr}(\text{Cp}^*)_2][\text{DEtDCF}]$  was synthesized by the method previously reported for  $[\text{Cr}(\text{Cp}^*)_2][\text{DMeDCF}]$ . See Ref. (14). Anal. Calcd. for  $\text{C}_{30}\text{H}_{40}\text{N}_2\text{O}_4\text{Cr} \cdot 0.1\text{CH}_2\text{Cl}_2$  (%) C, 65.36; H, 7.33; N, 5.07; Cl, 1.28. Found: (%) C, 64.30; H, 7.20; N, 4.96; Cl, 1.20. Crystals were examined under light hydrocarbon oil. The selected crystal was affixed with a small amount of silicone grease to a thin glass fiber atop a tapered copper mounting pin. This assembly was transferred to the goniometer of a Siemens SMART diffractometer equipped with a locally modified LT-2a low-temperature apparatus operating at 133 K. To determine cell parameters a series of three orthogonal sets of 20  $0.3^\circ$   $\omega$  scans was collected. Data collection encompassed an arbitrary hemisphere of space to 0.68 Å. Data were truncated to 0.71 Å during refinement, and 99% of the unique data were collected. All data were corrected for Lorentz and polarization effects, as well as for absorption. Structure solution in centrosymmetric space group  $P\bar{1}$  revealed a nonhydrogen structure. All nonhydrogen atoms were refined with anisotropic parameters for thermal motion. Hydrogen atoms were placed at calculated geometries and allowed to ride on the position of the parent atom. Thermal parameters for hydrogen atoms were calculated as 1.2 times the equivalent isotropic  $U$  of the parent atom. There are two molecules of dichloromethane present. The final difference map is essentially flat and featureless.

<sup>2</sup> Synthesized by Professor Jeffrey Fitzgerald, USNA by the method of Proskow (8).

<sup>3</sup> A gift from Dr. Caleb Holyoke, The Dupont Company.

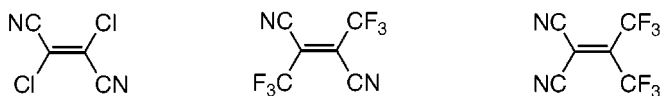


FIG. 2. Trans-1,2-dichloro-1,2-dicyanoethylene, trans-1,2-dicyano-1,2-bis(trifluoromethyl) ethylene, and 1,1-dicyano-2,2-bis(trifluoromethyl) ethylene.

state, it is a soft ferromagnet and shows no hysteresis. In contrast to the Mn analogue, it does not exhibit frequency-dependent ac susceptibility (14).

*Diethyl dicyanofumarate.* As expected, we have found that reaction of diethyl dicyanofumarate, DEtDCF, and decamethylmanganocene at  $-50^{\circ}\text{C}$  in dichloromethane gives rise to another charge-transfer salt magnet (12). Because the only difference between DMeDCF and DEtDCF is two methylene units, while the core  $\pi$  system is essentially unchanged, we would predict that, if the stacking is maintained, the intrastack coupling (as reflected by  $\theta$ ) should be unaffected. This idea is borne out; the compound exhibits excellent Curie–Weiss behavior with  $\theta$  equal to approximately 16 K (Table 2). However, the bulk properties of  $[\text{Mn}(\text{Cp}^*)_2][\text{DEtDCF}]$  are quite different.

Around 12 K, it appears to undergo an antiferromagnetic phase transition as suggested by the ac susceptibility, which shows a peak in the in-phase component and no out-of-phase component (Fig. 5). Below 10 K, a second transition takes place to a reentrant spin glass state. This identification is based on its frequency-dependent ac susceptibility behavior in this temperature regime.

At 9 K the magnetization vs applied field curve is, in fact, indicative of a metamagnetic compound, i.e., an antiferromagnetic ground state that switches to a ferromagnetic-like state upon application of a sufficiently large applied field ( $H_c$ ), in this case, about 500 G at this temperature

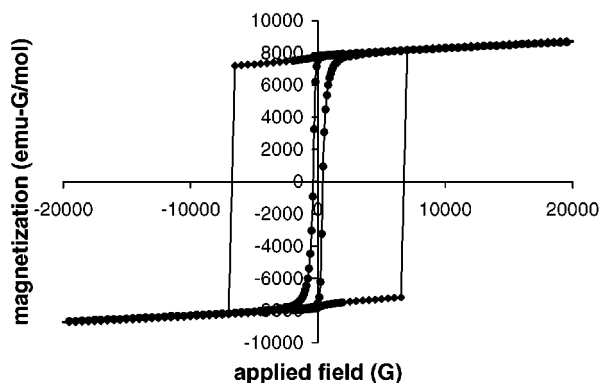


FIG. 3. Magnetization vs applied field at 1.8 ( $\blacklozenge$ ) and 5 K ( $\bullet$ ) for  $[\text{Mn}(\text{Cp}^*)_2][\text{DMeDCF}]$ .

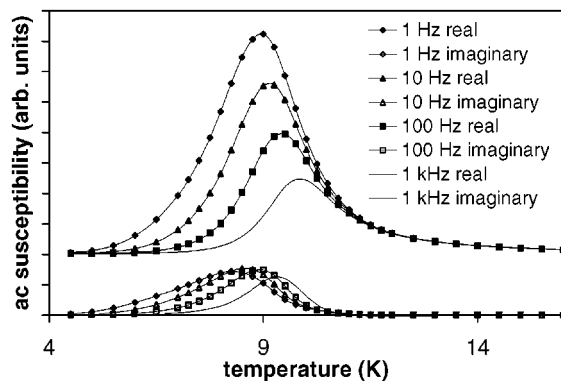


FIG. 4. Ac susceptibility vs temperature for  $[\text{Mn}(\text{Cp}^*)_2][\text{DMeDCF}]$ .

(Fig. 6). Once the temperature is lowered to well into the apparent spin glass regime, hysteresis is observed. Coercive fields around 10 kG are larger than those observed for  $[\text{Mn}(\text{Cp}^*)_2][\text{TCNE}]$  and  $[\text{Mn}(\text{Cp}^*)_2][\text{DMeDCF}]$ . These results suggest the simultaneous presence of both ferromagnetic and antiferromagnetic interstack interactions, which are affected differently by increasing the separation between the stacks.

Similarly,  $[\text{Cr}(\text{Cp}^*)_2][\text{DEtDCF}]^4$  looks magnetically much like its dimethyl analogue up to a point. It exhibits Curie–Weiss behavior with  $\theta = 22$  K, again showing intrastack interaction strengths are similar. However, its low-temperature behavior is more reminiscent of its manganese analogue, but without hysteresis (Table 2). There appears to be an antiferromagnetic phase transition at about 5.4 K (Fig. 7), which is also identified by a peak in  $\chi'$  and a lack of a  $\chi''$  ac signal (not shown). However, instead of going to 0 as the temperature is lowered, as expected for an antiferromagnet,  $M$  then begins to rise again, suggesting the onset of some sort of frustration (Fig. 7). At 5000 G, the magnetiz-

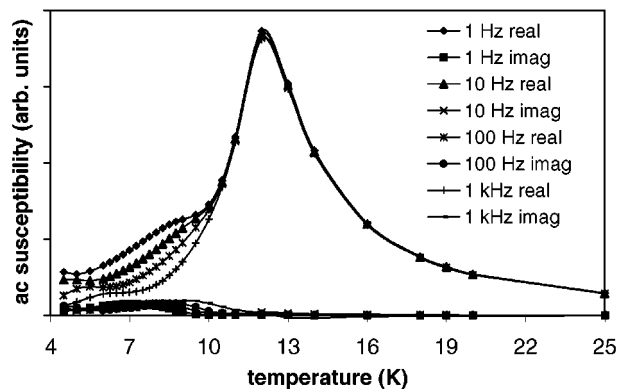


FIG. 5. Plot of real and imaginary ac  $\chi$  vs  $T$  at several frequencies for  $[\text{Mn}(\text{Cp}^*)_2][\text{DEtDCF}]$ .

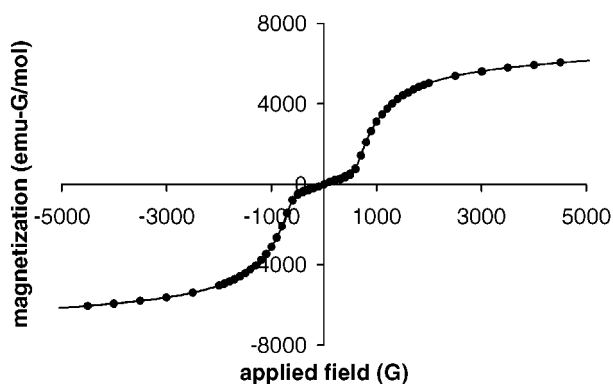


FIG. 6. Plot of magnetization vs applied field at 9 K (●) for  $[\text{Mn}(\text{Cp}^*)_2][\text{DEtDCF}]$ .

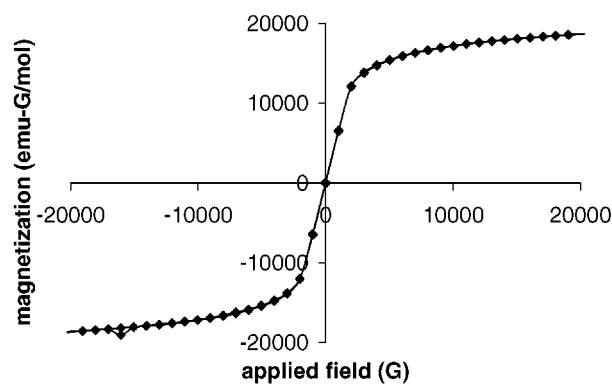


FIG. 8. Plot of magnetization vs applied field at 1.8 K for  $[\text{Cr}(\text{Cp}^*)_2][\text{DEtDCF}]$ .

ation is approximately 70% of its saturation value at 1.8 K, growing rather gradually with field (Fig. 8).

We recently obtained a crystal structure of this latter CT salt as its dichloromethane solvate,  $[\text{Cr}(\text{Cp}^*)_2][\text{DEtDCF}] \cdot 2\text{CH}_2\text{Cl}_2$ . The compound crystallizes in a triclinic unit cell with details of the structure solution given in Table 3. It is clear from the packing diagram and the Table of Contents figure that the stacked donor-acceptor motif is retained as expected. However, the added methylenes in the acceptor create just enough space between the stacks for two dichloromethane molecules to flank each donor (Fig. 9, for clarity, not all solvent molecules shown). These additional solvent molecules act as spacers, changing the interstack interactions in ways that are not understood.

It is important to note that the crystals lose solvent when removed from the mother liquor, so the magnetic data reported above were obtained from the desolvated crystals (see footnote 4). Also, elemental analyses of dried samples of both the chromium and manganese analogues of this CT

salt show that essentially no solvent is present (12). The desolvated crystals are not sufficiently crystalline for single-crystal structural analysis, although powder diffraction indicates a degree of periodicity. This same difficulty plagued earlier efforts involving  $[\text{Fe}(\text{Cp}^*)_2][\text{TCNE}] \cdot \text{CH}_3\text{CN}$  (2).

However, like this latter compound, assuming the desolvated structure does not depart significantly from the solvated one, it still offers some insight into the properties of the desolvated crystal that we have measured. Within the stack, the relative orientation of the donor and acceptor is identical in the two structures and this is reflected in the essentially identical  $\theta$  values. Also, between the stacks, the relative orientation is retained, while the apparent sign of the dominant interaction (from ferromagnetic to antiferromagnetic) has changed. Thus, it seems clear that the general idea of tuning the steric interactions, while holding the electronic structure constant, is valid. Unfortunately, we will need to be more clever in choosing a slightly larger donor that will accommodate both acceptors without incorporating the solvent.

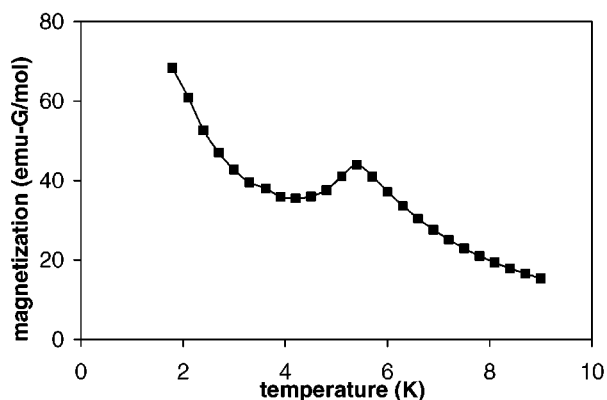


FIG. 7. Plot of field-cooled (2 G) magnetization ( $M$ ) vs temperature for  $[\text{Cr}(\text{Cp}^*)_2][\text{DEtDCF}]$ .

TABLE 3

Crystallographic Data for  $[\text{Cr}(\text{Cp}^*)_2][\text{DEtDCF}] \cdot 2\text{CH}_2\text{Cl}_2$

Chemical formula = $\text{C}_{32}\text{H}_{44}\text{Cl}_4\text{CrN}_2\text{O}_4$	Formula weight = 714.51
$a = 9.6239(17) \text{ \AA}$	Space group = $P\bar{1}$ (no. 2)
$b = 9.688(2) \text{ \AA}$	$T = 133(2) \text{ K}$
$c = 11.1488(16) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$ (MoK $\alpha$ )
$\alpha = 81.365(5)^\circ$	$\rho_{\text{calc}} = 1.337 \text{ g} \cdot \text{cm}^{-3}$
$\beta = 69.092(6)^\circ$	$\mu = 0.660 \text{ cm}^{-1}$
$\gamma = 66.018(6)^\circ$	$R_1(F) = 0.0544$ [ $I > 2\sigma(I)$ ]
$V = 887.2(3) \text{ \AA}^3$	$wR_2(F^2) = 0.1489$ (all data)
$Z = 1$	

Note. (1)  $R_1 = \sum \|F_o\| - |F_c| / \sum |F_o|$ ;  $wR_2 = \sqrt{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]}$ .  
(2)  $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ , where  $P = (F_o^2 + 2F_c^2)/3$ .

(3)  $\text{GooF} = S = \sqrt{\sum [w(F_o^2 - F_c^2)^2] / (M - N)}$ , where  $M$  is the number of reflections and  $N$  is the number of parameters refined.

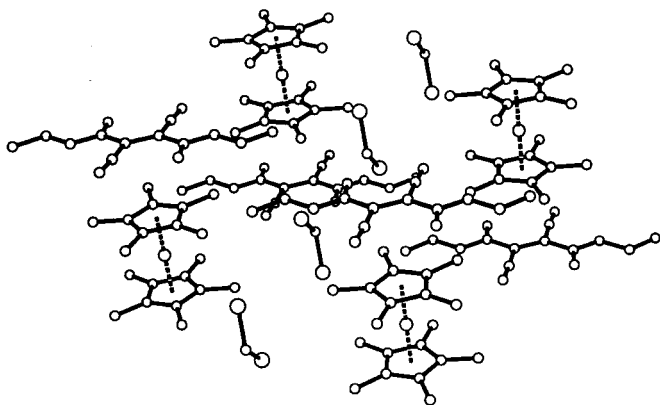


FIG. 9. Packing diagram for  $[\text{Cr}(\text{Cp}^*)_2][\text{DEtDCF}] \cdot 2\text{CH}_2\text{Cl}_2$ .

### CONDUCTIVE CHARGE-TRANSFER SALTS

Organic charge-transfer salts have been widely investigated for their unusual ability to conduct electrons. The most well known of these is the compound that results from the reaction of tetrathiafulvalene (TTF) and TCNQ. The former is a relatively electron-rich heterocycle and the latter a relatively electron-poor benzoquinone derivative.

Upon mixing, a partial electron transfer occurs (roughly  $0.6 e^-$ ), made possible by the formation of a segregated stack structure in the solid state (Fig. 10). Electronically, a partially filled band arises from the overlap of  $\pi$ -type orbitals on both stacks. The magnetic properties of this compound reflect the Pauli paramagnetism associated with delocalized electrons. In contrast, if the driving force for charge-transfer is greater (as can occur for an electron-rich metallocene as donor) then the degree of charge-transfer is integral, rather than fractional as above, and the product is ionic and adopts a mixed stack geometry for electrostatic reasons. This geometry within a stack is common to all CT salt magnets crystallized so far.

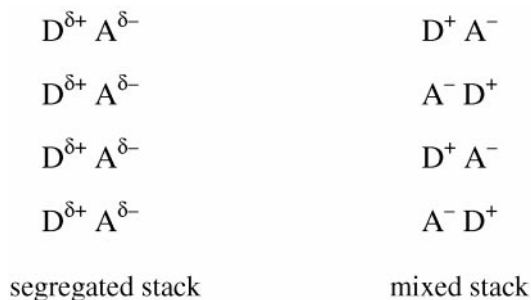


FIG. 10. Schematic illustrating the differences between segregated stacks and mixed stacks.

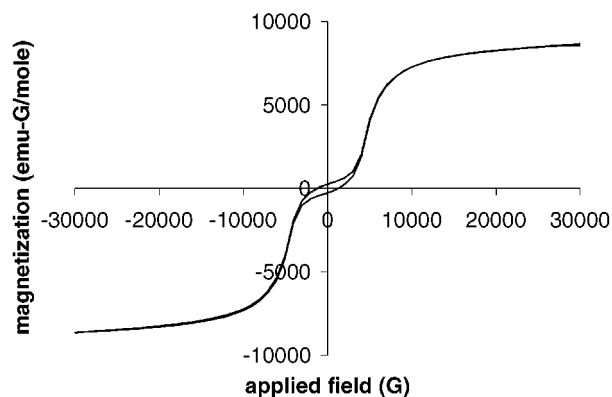


FIG. 11. Plot of magnetization vs applied field at 1.8 K for  $[\text{Fe}(\text{Cp}^*)_2][\text{DCNQ}]$ .

We have recently identified new acceptors for magnetism research by examining the extensive electrically conducting organic CT salt literature (15). For both disciplines, candidates must possess stable radical anionic states and extended  $\pi$  orbitals for facilitating stacking, as well as exhibit reversible electrochemistry at appropriate potentials. One such compound that has been investigated in the context of conductivity (16), but that has not been previously reacted with a dexamethylmetallocene is 2,3-dicyano-1,4-naphthoquinone, DCNQ (Fig. 1). This compound can be synthesized from 2,3-dichloro-1,4-naphthoquinone by published procedures (17).

Reaction of  $\text{Fe}(\text{Cp}^*)_2$  with DCNQ in dichloromethane gives a red-brown solid that we have structurally characterized (18).  $[\text{Fe}(\text{Cp}^*)_2][\text{DCNQ}]$  exhibits Curie-Weiss behavior with a positive  $\theta$ , indicating ferromagnetic intrastack interactions. At 4 K, it undergoes a phase transition to give long-range antiferromagnetic order between the stacks (Table 2). However, two things about this state are unusual.

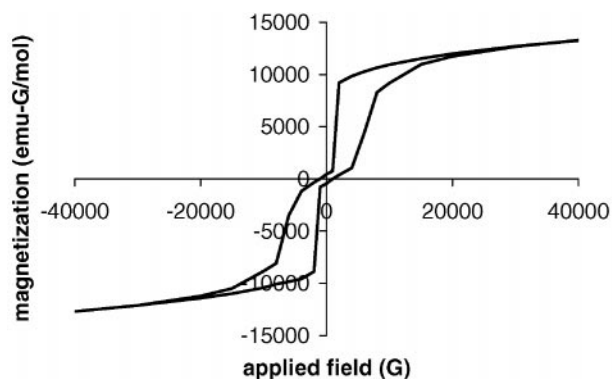


FIG. 12. Plot of magnetization vs applied field at 1.8 K for  $[\text{Mn}(\text{Cp}^*)_2][\text{DCNQ}]$ .

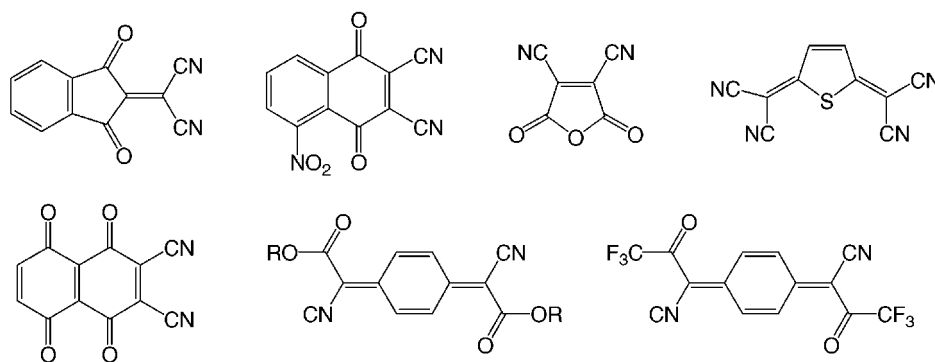


FIG. 13. Other potential acceptors for charge-transfer salt magnets.

First, the compound is metamagnetic with a critical field,  $H_c$ , of 3 kG at 1.8 K (Fig. 11), and second, unlike the metamagnet,  $[\text{Mn}(\text{Cp}^*)_2][\text{DEtDCF}]$ , the moments in the nominally antiferromagnetic state of  $[\text{Fe}(\text{Cp}^*)_2][\text{DCNQ}]$  are apparently canted, giving rise to weak ferromagnetism and hysteresis centered about 0 G. The inorganic/organic compound, cyclohexylammonium copper(II) trichloride, exhibits the same phenomenon (19).

The isostructural manganese analogue,  $[\text{Mn}(\text{Cp}^*)_2][\text{DCNQ}]$ , exhibits a higher  $\theta$  and related behavior at the higher temperature of 8 K (Table 2). It shows the same hysteresis centered at 0 G, but also hysteresis in the antiferromagnetic-to-ferromagnet-like transition (Fig. 12). This latter phenomenon probably occurs because the single-ion anisotropy for Mn(III) is greater than that for Fe(III) in this coordination environment, so there is a larger barrier to reorientation of the spins for the former.

Finally, the chromium analogue is probably a metamagnet with a negligible critical field (Table 2). The chromium result suggests that canting of the moments is related to the single-ion anisotropy, since canting is not apparent for this compound and it should be isotropic ( $^4A$  ground state).

#### OTHER COMPOUNDS

Da Gama and coworkers have reported that bis(bis(trifluoromethyl)ethylenediselenato)Ni(II) complexes (i.e., the selenium analogue of TFD discussed above) also support metamagnetism in CT salts with decamethylmanganocene. The Curie-Weiss  $\theta$  for this compound is 24.6 K and  $T_N = 2.1$  K. The critical field is  $H_c = 60$  G at 2 K (20).

#### CONCLUSIONS

We have found several other candidate organic one-electron acceptors that give rise to magnetic phases when paired with decamethylmetallocenes. A new crystal structure shows that interstack distance can be tuned, but that structure-property relationships are more subtle than pre-

viously thought. What bodes well for this research is that we have only scratched the surface and there are many examples of other molecules utilized in both Diels-Alder and olefin polymerization chemistry and the conductive charge-transfer salt field that await investigation. In Fig. 13, we show a sample of the compounds we are currently investigating. Recall also that each new acceptor can be paired with many donors. The development of that facet of the field is relatively less mature, yet promises to be equally fruitful.

#### ACKNOWLEDGMENTS

We thank the National Science Foundation and the Donors of the Petroleum Research Fund administered by the American Chemical Society for funding of this work. We also thank Dr. Ron Goldfarb for many helpful discussions and the National Institute of Standards and Technology, Boulder, CO for use of the SQUID magnetometers.

#### REFERENCES

1. A. P. Ginsberg, *Inorg. Chem. Acta Rev.* **5**, 45 (1971).
2. J. S. Miller, J. C. Calabrese, H. Rommelmann, S. R. Chittipeddi, J. H. Zhang, W. M. Reiff, and A. J. Epstein, *J. Am. Chem. Soc.* **109**, 769-781 (1987).
3. W. E. Broderick, X. Liu, S. Owens, P. M. Toscano, D. M. Eichhorn, and B. M. Hoffman, *Mol. Cryst. Liq. Cryst.* **273**, 17-20 (1995) and references therein.
4. W. E. Broderick, J. E. Thompson, and B. M. Hoffman, *Inorg. Chem.* **30**, 2958-2960 (1991).
5. J. S. Miller and A. J. Epstein, in "Research Frontiers in Magnetochemistry" (C. J. O'Conner, Ed.), pp. 283-302. World Scientific, Singapore, 1993.
6. J. S. Miller and A. J. Epstein, *Angew. Chem. Int. Ed. Engl.* **33**, 385-415 (1994).
7. O. Kahn, "Molecular Magnetism." VCH, New York, 1993.
8. S. Proskow, H. E. Simmons, and T. L. Cairns, *J. Am. Chem. Soc.* **88**, 5254 (1966).
9. C. J. Ireland, K. Jones, J. S. Pizey, and S. Johnson, *Synth. Commun.* **3**, 185-191 (1976).
10. D. Villemain and A. Ben Alloum, *Synth. Commun.* **22**, 3169-3179 (1992).
11. J. E. Mulvaney, R. J. Cramer, and H. K. Hall, Jr., *J. Polym. Sci. Polym. Chem. Ed.* **21**, 309-314 (1983).

12. B. B. Kaul, W. S. Durfee, and G. T. Yee, *J. Am. Chem. Soc.* **121**, 6862–6866 (1999).
13. G. T. Yee, J. M. Manriquez, D. A. Dixon, R. S. McLean, D. M. Groski, R. B. Flippen, K. S. Narayan, A. J. Epstein, and J. S. Miller, *Adv. Mater.* **3**, 309–311 (1991).
14. B. B. Kaul, R. D. Sommer, B. C. Noll, and G. T. Yee, *Inorg. Chem.* **39**, 865–868 (2000).
15. (a) N. Martin, J. L. Segura, and C. Seoane, *J. Mater. Chem.* **7**, 1661–1676 (1997). (b) F. Ogura and T. Otsubo, in “Handbook of Organic Conductive Molecules and Polymers, Vol. 1, Charge-Transfer Salts, Fullerenes and Photoconductors” (H. S. Nalwa, Ed.), pp. 229–248. Wiley, New York, 1997.
16. M. R. Bryce, S. R. Davies, M. Hasan, G. J. Ashwell, M. Szablewski, M. G. B. Drew, R. Short, and M. B. Hursthouse, *J. Chem. Soc. Perkin Trans. II* 1285–1292 (1989).
17. G. A. Reynolds and J. A. Van Allan, *J. Org. Chem.* **29**, 3591–3593 (1964).
18. G. T. Yee, M. J. Whitton, R. D. Sommer, C. M. Frommen, and W. M. Reiff, *Inorg. Chem.* **39**, 1874–1877 (2000).
19. R. D. Willett, C. P. Landee, R. M. Gaura, D. D. Swank, H. A. Groenendijk, and A. J. van Duynevelt, *J. Magn. Magn. Mater.* **15–8**, 1055–1056 (1980).
20. V. Da Gama, S. Rabaca, C. Ramos, D. Belo, C. Santos, and M. T. Duarte, *Mol. Cryst. Liq. Cryst.* **335**, 81–90 (1999).