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Bis(1,2,3-trimethylindenyl)iron(III) 2,3-Dicyanonaphtho-1,4-quinonide, a Non-Metallocene, Charge-Transfer Salt Metamagnet with Complementary Donor−Acceptor Geometries

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Bis(1,2,3-trimethylindenyl)iron(III) can be paired with 2,3-dicyanonaphtho-1,4-quinone to give an air-stable π-stacked metamagnet with $T_c = 4.1$ K, the first example of a non-metallocene CT salt magnet in this class. A single crystal X-ray structure of the Fe(1,2,3-$Me_3C_9H_4)_2$[DCNQ] salt indicates that it consists of stacks of alternating donors and acceptors, in which the DCNQ ring systems are aligned with indenyl groups above and below, and the long axes of the DCNQ and the indenyl ligand are parallel to each other. This arrangement suggests that the magnetic properties arise from favorable interactions due to geometric similarities between the donor and acceptor, and not from a unique property of the donor itself.

The charge-transfer (CT) salt approach has been one of the most successful strategies for producing magnetically ordered compounds based on molecular building blocks.[1] Typically, an electron-rich organometallic donor (most commonly a decamethylmetallocene, $MCp*_2$; M = Cr, Mn, Fe, or Ni) and an electron-poor acceptor (usually an olefin or quinone substituted with electron-withdrawing groups) are combined in a one-pot, single electron transfer reaction. The choice of a donor and acceptor pair is based principally on their reversible electrochemical characteristics. Although such considerations are important, we describe here the application of an additional design principle derived from crystal engineering,[2] i.e., the matching of the donor with an acceptor of roughly the same size, shape, and symmetry. Using this concept as a guide, we have produced the first non-metallocene CT salt in its class that exhibits long-range magnetic order.

Attempts to vary the donors in magnetic CT salts have been limited almost exclusively to close analogues of the decamethylmetallocenes, such as decaethylferrocene[3] and octamethylferrocene.[4] We have previously investigated the properties of alkyl- and silyl-substituted bis(indenyl)metal complexes that exhibit various spin states including spin crossover behavior.[5] Unlike bis(pentamethylcyclopentadienyl) complexes, the bis(indenyl) architecture should provide a tunable platform for new CT salt synthesis, directed at understanding the magnetic coupling in this class of compounds. In this regard, it was particularly interesting that O'Hare and co-workers had described the reactions of bis(heptamethylindenyl)iron(II) with tetracyanoethylene (TCNE), 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to produce CT salts.[6] None of the three compounds unequivocally order magnetically,[7] but the TCNQ analogue was reported to exhibit ferromagnetic coupling with $\theta = 6$ K.

Compared to the good cation−anion centering that occurs in the π-stacked chains of CT salts such as the ferromagnetic $FeCp*_2$[TCNQ],[8] the TCNQ anion is considerably skewed in $Fe(Me_7C_9)_2$[TCNQ] (Figure 1). With the assumption that improved donor−acceptor alignment could enhance magnetic exchange in bis(indenyl)-based CT salts, it seemed reasonable that an acceptor with two fused rings would provide better

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(1) Yee, G. T.; Miller, J. S. Metallocene-based Magnets. In *Magnetism: Molecules to Materials V*; Miller, J. S., Drillon, M., Eds.; Wiley-VCH: Mannheim, Germany, 2005.

(2) Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, 1989.

(3) Chi, K.-M.; Calabrese, J. C.; Reiff, W. M.; Miller, J. S. *Organometallics* **1991**, *10*, 688−693.

(4) Miller, J. S.; Glatzhofer, D. T.; O'Hare, D. M.; Reiff, W. M.; Chakraborty, A.; Epstein, A. J. *Inorg. Chem*. **1989**, *28*, 2930−2939.

(5) Brady, E. D.; Overby, J. S.; Meredith, M. B.; Mussman, A. B.; Cohn, M. A.; Hanusa, T. P.; Yee, G. T.; Pink, M. *J. Am. Chem. Soc.* **2002**, *124*, 9556−9566.

(6) Murphy, V. J.; O'Hare, D. *Inorg. Chem*. **1994**, *33*, 1833−1841.

(7) No ac susceptibility data, low field dc data, or T_c was reported.

(8) Broderick, W. E.; Eichhorn, D. M.; Liu, X.; Toscano, P. M.; Owens, S. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1995**, *117*, 3641−3642.

10.1021/ic048398d CCC: $30.25

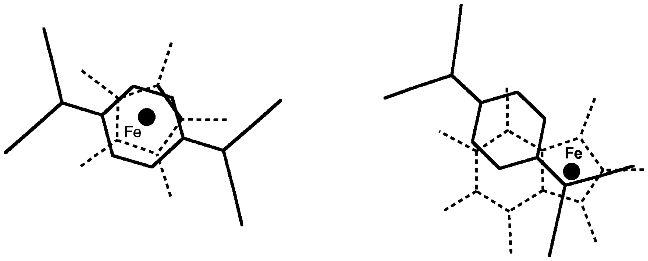

Figure 1. Projections perpendicular to the donor−acceptor planes in $FeCp^*_2[TCNQ]$ (left) and in $Fe(Me_7C_9)_2[TCNQ]$ (right). The TCNQ (—) is on top, with the adjacent ligand of the iron complex (- - -) next. The iron centers (●) are in back.

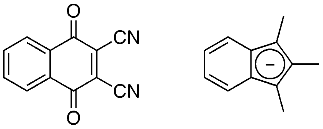

Figure 2. 2,3-Dicyanonaphtho-1,4-quinone (left) and the 1,2,3-trimethylindenyl anion.

π-stacking with bis(indenyl)complexes than could single ring species such as TCNQ or DDQ. The versatile one-electron 2,3-dicyanonaphtho-1,4-quinone (DCNQ, Figure 2) was chosen for this purpose, as it has a reduction potential only slightly less positive than that of TCNE or TCNQ. DCNQ reacts readily with decamethylferrocene, and we have previously reported the structure and properties of the CT salt $FeCp^*_2[DCNQ]$,[9] an unusual metamagnet that exhibits slight hysteresis centered on zero applied field due to canting of the moments in the nominally antiferromagnetic state.

The reaction of purple bis(1,2,3-trimethylindenyl)iron(II) and yellow DCNQ in THF rapidly precipitates the maroon CT salt $Fe(1,2,3\text{-}Me_3C_9H_4)_2[DCNQ]$ as an air-stable powder (see Supporting Information for details). Needlelike crystals grown by slow combination of the donor and acceptor solutions are black. A single crystal X-ray structure (Figure 3) indicates that the CT salt consists of stacks of alternating donors and acceptors.[10] The indenyl planes are essentially parallel, with Fe−C (av) = 2.11(2) Å, and are twisted by 102.4° from an eclipsed configuration. The DCNQ ring systems are aligned with indenyl groups above and below, and the long axes of the DCNQ and the indenyl ligand are almost exactly parallel to each other. Accompanying this alignment is an intrastack Fe···Fe′ separation of 10.19 Å, 13% shorter than the 11.80 Å distance in $Fe(Me_7C_9)_2[TCNQ]$.[6]

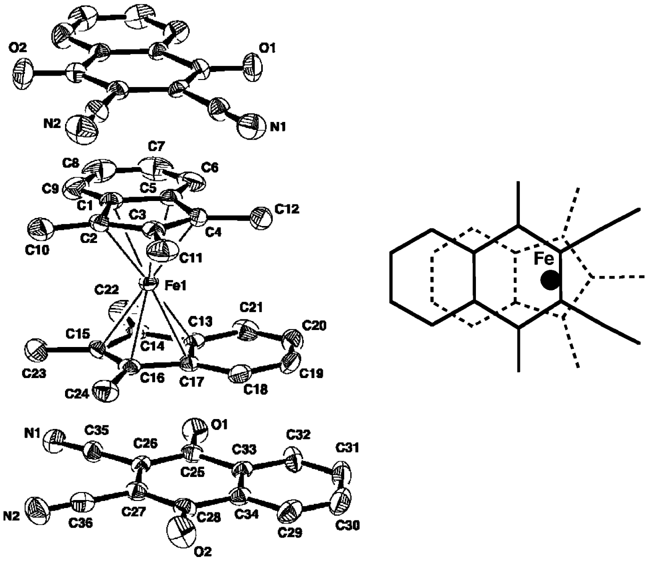

Figure 3. ORTEP of the non-hydrogen atoms of $Fe(1,2,3\text{-}Me_3C_9H_4)_2[DCNQ]$, illustrating the stacking of the donors and acceptors (left). The indenyl plane to DCNQ plane distances alternate between 3.42 and 3.64 Å. A projection perpendicular to the donor−acceptor planes is at right.

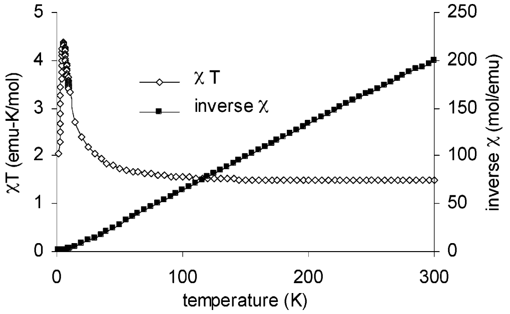

Figure 4. χT versus T and inverse χ versus T for the title compound measured in 5000 G applied field.

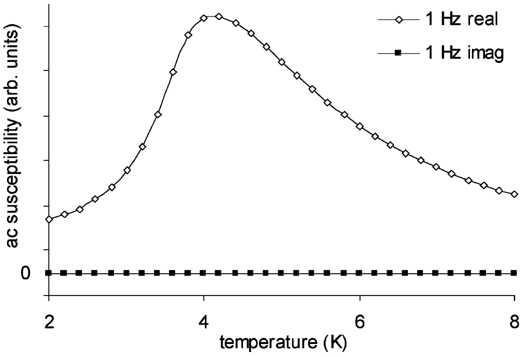

Figure 5. The frequency-independent ac susceptibility at 1 kHz for the title compound.

The magnetic properties of $Fe(1,2,3\text{-}Me_3C_9H_4)_2[DCNQ]$ are those of a ferromagnetically coupled metamagnet[11] with $T_c = 4.1$ K. Evidence for this description is first given in the plot of χT versus T and inverse χ versus T,[12] which shows Curie−Weiss behavior with $\theta = 6.8$ K, indicating ferromagnetic coupling (Figure 4). We assume that this represents the in-stack interaction due to π overlap between the donor and acceptor, as occurs for decamethylmetallocene analogues.

The ac susceptibility data (Figure 5) are characterized by a peak in χ' at 4.1 K and zero χ'' at all temperatures, which

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(9) (a) Yee, G. T.; Whitton, M. J.; Sommer, R. D.; Frommen, C. M.; Reiff, W. M. *Inorg. Chem.* **2000**, *39*, 1874−1877. (b) Hamlin, J. J.; Beckett, B. R.; Tomita, T.; Schilling, J. S.; Tyree, W. S.; Yee, G. T. *Polyhedron* **2003**, *22*, 2249−2252.

(10) Crystals of $Fe(1,2,3\text{-}Me_3C_9H_4)_2[DCNQ]$ are orthorhombic, space group *Pbca*, with $a = 17.020(1)$ Å, $b = 15.989(1)$ Å, $c = 20.364(2)$ Å, $V = 5541.8(7)$ Å^3, $Z = 8$, and $\rho_{calc} = 1.387$ g cm^{-3} for fw = 578.47. Refinement of 4896 independent reflections (2606 with $I > 2.0\sigma(I)$) collected at the University of Minnesota at 173 ± 2 K led to residuals of $R(F^2) = 0.0580$ and $R_w(F^2) = 0.117$ (for $I > 2.0\sigma(I)$).

(11) Metamagnetism is characterized by antiferromagnetic order in zero applied field that gives way to a ferromagnet-like state upon the application of a sufficiently high magnetic field.

(12) The data have been corrected for temperature independent paramagnetism equal to 6.38×10^{-4} emu/mol as determined by a fit to the Curie−Weiss law.

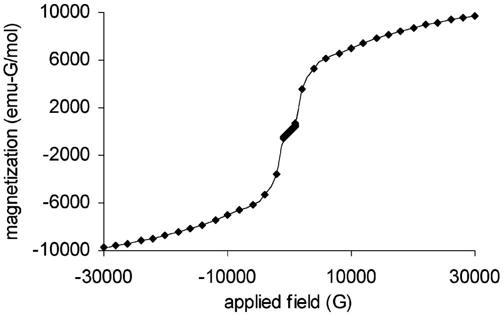

Figure 6. Magnetization versus applied field at 1.8 K for Fe(1,2,3-$Me_3C_9H_4$)$_2$[DCNQ].

means that the observed phase transition is to an antiferromagnetic state. These data are frequency independent from 1 Hz up to 1 kHz, indicating the magnetic order is free of glassiness. The plot of magnetization versus applied field has the classic shape of a metamagnet with a critical field of about ±2 kG at 1.8 K, as given by the steepest part of the *M*(*H*) curve. At this point, the compound switches from antiferromagnetic ordering to a ferromagnet-like state (Figure 6).

In preliminary work, we have found that the corresponding TCNE and TCNQ CT salts of Fe(1,2,3-$Me_3C_9H_4$)$_2$ exhibit no evidence for magnetic order down to 1.8 K, consonant with previous data with Fe(Me_7C_9)$_2$[TCNQ].[6] Hence, the present results are consistent with the enhanced coupling in Fe(1,2,3-$Me_3C_9H_4$)$_2$[DCNQ] being attributable to the geometric similarity of the DCNQ molecule and trimethylindenyl anion. Efficacious non-metallocene donors clearly exist as potential building blocks for CT salt magnets, and large multiring donor−acceptor combinations appear to be promising for this purpose.

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Supporting Information Available: Synthetic and crystallographic details and an X-ray crystallographic file in CIF format for the title compound. This material is available free of charge via the Internet at http://pubs.acs.org.

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