

at $-78\text{ }^{\circ}\text{C}$ for 1 h, treated with ethyl iodide (0.49 g, 3.0 mmol), stirred for 15 min, warmed to room temperature, and stirred for an additional 5 h. The reaction mixture was poured into a separatory funnel containing 10 mL of cold 3 N HCl. The layers formed were separated and the aqueous phase was extracted with pentane ($3 \times 10\text{ mL}$). The combined organic extracts were successively washed with 3 N HCl ($2 \times 10\text{ mL}$), saturated aqueous NaHCO_3 , and brine. The organic phase was dried (MgSO_4), filtered, and concentrated. Distillation (Kugelrohr) yielded 0.28 g (78%) of **9**: bp $99\text{--}102\text{ }^{\circ}\text{C}$ (1 mmHg); n_{D}^{25} 1.4709; IR (neat) 2950, 2920, 2850, 1455, 1173, 1113, 1060 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 0.88 (t, $J = 7.5\text{ Hz}$, 3 H, CH_3), 0.91 (t, $J = 7.5\text{ Hz}$, 3 H, CH_3), 1.18 (t, $J = 7.5\text{ Hz}$, 3 H, $\text{C}\equiv\text{CCCH}_3$), 1.2-1.4 (m, 12 H, CH_2), 1.77 (s, 3 H, $\text{C}=\text{CCH}_3$), 2.05 (t, $J = 7.5\text{ Hz}$, 2 H, $\text{C}=\text{CCH}_2$), 2.28 (t, $J = 7.5\text{ Hz}$, 2 H, $\text{C}=\text{CCH}_2$), 2.35 (q, $J = 7.5\text{ Hz}$, 2 H, $\text{C}=\text{CCH}_2$); high-resolution MS, m/z 234.2369 (calcd for $\text{C}_{17}\text{H}_{30}$, 234.2349). GLC analysis (DB-1 glass capillary column, 30 m) revealed that the compound was at least 96% isomerically pure.

(**1Z,3E**)-1-(Trimethylsilyl)-3-*n*-butyl-4-methyl-1,3-decadiene (**10**). Into a 25-mL three-necked flask maintained under a static pressure of nitrogen was placed 0.56 g (2.0 mmol) of **7g** in ether (2 mL). To the well-stirred solution was added dropwise at $25\text{ }^{\circ}\text{C}$ diisobutylaluminum hydride (neat, 0.41 mL, 2.2 mmol). The solution was stirred for 15 min and then heated at $40\text{ }^{\circ}\text{C}$ for 4 h. After cooling to room temperature, the reaction mixture was hydrolyzed by slowly pouring it into ice-cold 3 N NaOH. The layers were separated and the aqueous phase was extracted with pentane ($3 \times 15\text{ mL}$). The combined organic extracts were washed successively with 3 N NaOH and brine ($2 \times 10\text{ mL}$) and dried (MgSO_4). The solvents were removed and the residue obtained was distilled (Kugelrohr) to furnish 0.38 g (90%) of **10**: bp $78\text{--}80\text{ }^{\circ}\text{C}$ (0.05 mmHg); n_{D}^{25} 1.4622; IR (neat) 2950, 2935, 2850, 2135, 1455, 1240, 840, 755 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 0.10 (s, 9 H, SiMe_3), 0.8-1.0 (m, 6 H, CH_3), 1.1-1.5 (br m, 12 H, CH_2), 1.75 (s, 3 H, $\text{C}=\text{CCH}_3$), 2.05 (t, $J = 7.5\text{ Hz}$, 2 H, $\text{C}_3\text{CH}_2\text{C}=\text{C}$), 2.35 (t, $J = 7.5\text{ Hz}$, 2 H, $\text{C}_3\text{CH}_2\text{C}=\text{C}$), 5.35 (d, $J = 14.4\text{ Hz}$, 1 H, $\text{C}=\text{CCHC}=\text{CSi}$), 5.35 (t, $J = 7.5\text{ Hz}$, 1 H, $\text{RCH}=\text{C}$), 6.65 (d, $J = 14.4\text{ Hz}$, 1 H, $\text{C}=\text{CHSi}$);

high-resolution MS, m/z 280.2576 (calcd for $\text{C}_{18}\text{H}_{36}\text{Si}$, 280.2588). GLC analysis ($150\text{ }^{\circ}\text{C}$) indicated that the compound was at least 97% isomerically pure.

(**E**)-3-*n*-Butyl-4-methyl-3-decenoic Acid (**11**). To a 1.90 M solution of BH_3SMe_2 (2.2 mmol) in THF maintained under a positive pressure of nitrogen was added at $-15\text{ }^{\circ}\text{C}$ (CaCl_2 -dry ice bath) 2-methyl-2-butene (0.31 g, 4.4 mmol). The diisiamylborane formed was stirred at $0\text{ }^{\circ}\text{C}$ for 2 h, cooled to $-15\text{ }^{\circ}\text{C}$, and added dropwise to the enyne **7g** (0.56 g, 2.0 mmol) in THF (2 mL) maintained at $-15\text{ }^{\circ}\text{C}$. The solution was stirred for an additional 30 min at $-15\text{ }^{\circ}\text{C}$, warmed to room temperature, and stirred for 1 h. The reaction mixture was diluted with methanol (2 mL), treated with 3.8 mL of a 3 N aqueous solution of NaOH, and oxidized by dropwise addition of 1.5 mL of 30% H_2O_2 while the temperature was maintained below $50\text{ }^{\circ}\text{C}$ during the addition. The mixture was treated at $0\text{ }^{\circ}\text{C}$ with 20 mL of 6 N HCl. The layers formed were separated and the aqueous phase was extracted with ether ($3 \times 5\text{ mL}$). The combined organic extracts were washed with brine and dried (MgSO_4). The solvents were removed and the residue obtained was distilled (Kugelrohr) to afford 0.43 g (90%) of **11**: bp $105\text{--}115\text{ }^{\circ}\text{C}$ (10^{-3} mmHg); n_{D}^{24} 1.4620; IR (neat) 3600-2400, 3200, 2950, 2860, 1700, 1460, 1405, 1255, 1150, 950, 800 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 90 MHz) δ 0.75-1.00 (m, 6 H, CH_3), 1.05-1.65 (br m, 12 H, CH_2), 1.65 (s, 3 H, $\text{CH}_3\text{C}=\text{C}$), 1.80-2.25 (m, 4 H, $\text{CH}_2\text{C}=\text{C}$), 3.0 (s, 2 H, $\text{CH}_2\text{C}=\text{O}$), 10.95-11.20 (s, 1 H, COOH). Esterification of the acid with diazomethane furnished the methyl ester **12** in 80% yield: bp $83\text{--}85\text{ }^{\circ}\text{C}$ (10^{-3} mmHg); n_{D}^{25} 1.4551; IR (neat) 2950, 2930, 2855, 1730, 1455, 1155, 1015 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 0.86-0.91 (m, 6 H, CH_3), 1.27-1.32 (m, 12 H, CH_2), 1.65 (s, 3 H, $\text{C}=\text{CCH}_3$), 1.93-2.09 (m, 4 H, $\text{C}=\text{CCH}_2$), 3.04 (s, 2 H, $\text{CH}_2\text{C}=\text{O}$), 3.65 (s, 3 H, OCH_3); high-resolution MS, m/z 254.2262 (calcd for $\text{C}_{16}\text{H}_{30}\text{O}_2$, 254.2243). GLC analysis (DB-1701 glass capillary column, 15 m, $150\text{ }^{\circ}\text{C}$) showed that the compound was at least 95% isomerically pure.

Acknowledgment. We thank the National Science Foundation for financial support of this work.

Charge-Transfer Complexes as Potential Organic Ferromagnets

Teresa J. LePage and Ronald Breslow*

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. Received April 24, 1987

Abstract: One proposal for the synthesis of an organic ferromagnetic material has been investigated. Two new derivatives of hexaazatritetralin have been prepared carrying electron-withdrawing substituents on nitrogen. These form crystalline one-to-one charge-transfer complexes with tris(dicyanomethylene)cyclopropane. The physical and chemical data for these systems indicate that one of them exists as the cation radical/anion radical complex in the solid, but the other has additional partial second charge transfer. Although the dications of the electron donors have triplet spin multiplicity and the charge-transfer solid appears to fulfill the requirements of our model for ferromagnetism, the charge-transfer solids show antiferromagnetic, not ferromagnetic, ordering.

There has been much recent interest in the design of organic materials with special properties, such as electrical conductivity. Ferromagnetism is another very useful physical property that has not yet clearly been detected in any purely organic compound, although two groups have reported organic materials with small, irreproducible ferromagnetic components.^{1,2} Several groups are currently trying to prepare ferromagnetic organic materials, using several very different proposals.¹⁻⁵

Ferromagnetism is the result of a high-spin solid state, with many electrons aligned parallel. Proposals for the construction of ferromagnetic interactions in organic compounds have been around for many years. The first proposal of which we are aware for the production of intermolecular ferromagnetic interactions in organic solids was published by McConnell in 1963.⁶ His idea has been investigated experimentally by several groups.⁷ In 1968, Mataga proposed a method for preparing macroscopic ferromagnets based on intramolecular ferromagnetic interactions in large molecules.⁸ The high-spin polycarbene molecules of

(1) Torrance, J. B.; Oostra, S.; Nazzari, A. *Synth. Met.* **1986**, *19*, 709.

(2) Korshak, Yu.; Medvedeva, T. V.; Ovchinnikov, A. A.; Spectro, V. N. *Nature (London)* **1987**, *326*, 370-372.

(3) (a) Iwamura, H. *Pure Appl. Chem.* **1986**, *58*, 187-196. (b) Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1986**, *108*, 368-371 and references therein.

(4) Dormann, E.; Nowak, M. J.; Williams, K. A.; Angus, R. O., Jr.; Wudl, F. *J. Am. Chem. Soc.* **1987**, *109*, 2594-2599.

(5) Radhakrishnan, T. P.; Soos, Z. G.; Endres, H.; Azevedo, L. *J. Chem. Phys.* **1986**, *85*, 1126-1130.

(6) McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910.

(7) (a) Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, *107*, 1786-1787. (b) Azuma, N.; Yamauchi, J.; Mukai, K.; Ohya-Nishiguchi, H.; Deguchi, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2728-2734. (c) Agawa, K.; Sugano, T.; Kinoshita, M. *J. Chem. Phys.* **1986**, *85*, 2211-2218 and references therein.

(8) Mataga, N. *Theor. Chim. Acta* **1968**, *10*, 372-376.

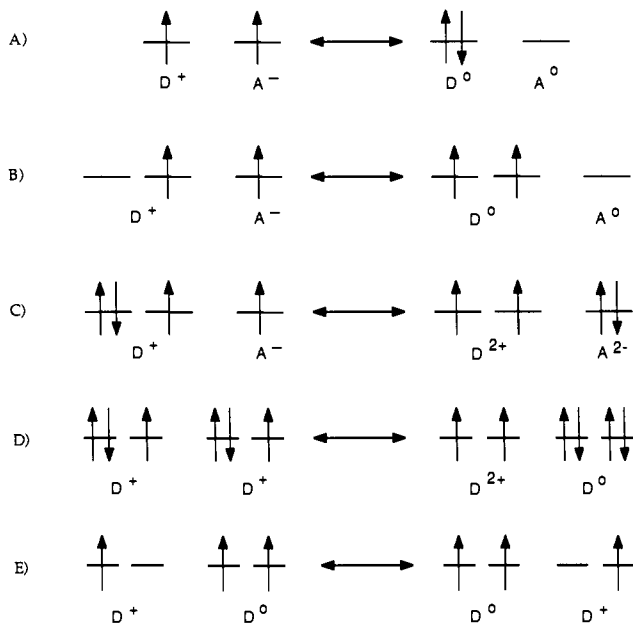


Figure 1. Charge-transfer mixing in (A) normal ionic charge-transfer dimer, (B) McConnell's charge-transfer ferromagnet, (C) Breslow's modification, (D) Torrance's modification, and (E) Wudl's modification.

Iwamura and co-workers can be considered models for the former polymers.³ In 1977, Ovchinnikov suggested a large number of possible polyradical polymeric structures that could have spin-parallel ground states.⁹ Buchachenko has proposed the preparation of organic ferrimagnets from doublet and triplet molecules.¹⁰ Soos has recently proposed extending the concept of inorganic superexchange ferromagnetism to organic charge-transfer solids.⁵

McConnell proposed a second model for ferromagnetic spin alignment in 1967 using ionic charge-transfer salts.¹¹ We have discussed this model elsewhere and in 1982 proposed a modification of it that involves the use of experimentally accessible benzenoid electron donors that have triplet dications.^{12,13}

In normal ion radical charge-transfer solids, intermolecular spin pairing (antiferromagnetic alignment) is the result of the mixing of the ground state and a (singlet) back-charge-transfer state of a charge-transfer pair, as shown in Figure 1A. This interaction causes spins on adjacent radical ions to cancel, resulting in solids that are paramagnetic at high temperatures, but essentially diamagnetic at low temperatures. McConnell proposed that if an ionic charge-transfer pair (D^+A^-) could be built that had a back-charge-transfer excitation to a neutral triplet state instead of a singlet state (i.e., D^0 is a triplet), then the D^+A^- pair could also be a triplet, due to mixing of the charge-transfer state with the ground state. This arrangement is illustrated in Figure 1B. If this mixing of a high-spin arrangement is present between adjacent donors and acceptors in a multidimensional array in a solid, macroscopic parallel alignment and thus ferromagnetic behavior of the solid are possible.

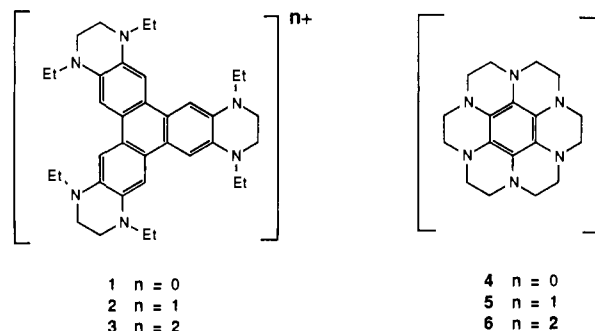
Our adaptation of this proposal¹² involves use of dipositively charged antiaromatic triplets derived from benzenoid systems, for reasons of stability and accessibility. When the dipositively charged oxidation state of the donor has triplet spin multiplicity, a forward charge transfer from D^+A^- to $D^{2+}A^{2-}$ is required, as illustrated in Figure 1C. This leads to greater charge on the molecules than McConnell's original proposal and favors the alternating donor-acceptor stacking (rather than segregated stacking) necessary for the proposed donor-acceptor mixing. We

propose a solid containing a substituted benzene cation radical together with an appropriate anion radical. If charge transfer goes in the forward direction, the cation is the electron donor, and the anion the electron acceptor: thus charge transfer would mix the diionic states of the molecules. If the benzene dication is a ground-state triplet, as threefold symmetric derivatives of it can be, then this charge-transfer interaction should promote a ferromagnetic alignment of the two unpaired spins on the donor and acceptor. If interactions of this sort exist throughout the solid, macroscopic ferromagnetic ordering is possible. Such a system had not been proposed before the work described in this paper.

McConnell's charge-transfer proposal for the preparation of an organic ferromagnet and its modifications call for the use of stable triplet molecules, with two parallel unpaired spins, to help achieve spin correlation in a solid. During the course of our work on antiaromatic compounds, we have investigated their tendency to form high-spin states.¹⁴ In certain symmetric antiaromatic compounds the ground state can have two unpaired electrons and triplet spin multiplicity, rather than the normal singlet state characteristic of most even-electron organic molecules. We consider antiaromatic triplets to be the most promising class of triplets for the preparation of charge-transfer organic ferromagnets; we took up attempts to use them toward this end a little over 10 years ago.^{15,16}

Unsubstituted cyclopentadienyl cation¹⁷ and pentachlorocyclopentadienyl cation,¹⁸ both ground-state triplets, are stable only at low temperatures.¹⁹ Even the pentaphenylcyclopentadienyl cation, a ground-state singlet with a very low-lying triplet state,^{19,20} rearranges at room temperature.²¹ The addition of stabilizing substituents, however, has succeeded in producing more stable triplet molecules.

We have reported that the nitrogen-substituted dication **3** has a triplet ground state.^{12,22} The properties of **3** and related substances will be described further in this paper. We also have reported the preparation of a benzene derivative carrying six nitrogen atoms, **4**, whose dication **6** is also a ground-state triplet.²³ Dication **6** is stable in solution at room temperature for several hours²⁴ although it has two unpaired electrons. Thus it is clear that with appropriate substitution, stable antiaromatic triplet species are accessible.



Recently, other variations of McConnell's model have been reported. Torrance pointed out¹ that a homomolecular π complex

(9) Ovchinnikov, A. A. *Dokl. Akad. Nauk SSSR* **1977**, *236*, 928-931. Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297-304.

(10) Buchachenko, A. L. *Dokl. Akad. Nauk SSSR* **1979**, *224*, 1146-1148.

(11) McConnell, H. *Proc. Robert A. Welch Found. Conf. Chem. Res.* **1967**, *11*, 144 (reproduced in full in ref 12).

(12) Breslow, R.; Jaun, B.; Klutz, R.; Xia, C.-Z. *Tetrahedron* **1982**, *38*, 863-867.

(13) Breslow, R. *Pure Appl. Chem.* **1982**, *54*, 927-938.

(14) Breslow, R. *Acc. Chem. Res.* **1973**, *6*, 393-398.

(15) (a) Johnson, R. W. Ph.D. Thesis, Columbia University, 1976. (b) Klutz, R. Q. Ph.D. Thesis, Columbia University, 1980.

(16) Deuring, L. A. Ph.D. Thesis, Columbia University, 1984.

(17) Saunders, M.; Berger, R.; Jaffe, A.; McBride, J. M.; O'Neill, J.; Breslow, R.; Hoffman, J. M.; Perchonock, C.; Wasserman, E.; Hutton, R. S.; Kuck, V. J. *J. Am. Chem. Soc.* **1973**, *95*, 3017-3018.

(18) Breslow, R.; Hill, R.; Wasserman, E. *J. Am. Chem. Soc.* **1964**, *86*, 5349-5350.

(19) Breslow, R. *Topics in Nonbenzenoid Aromatic Chemistry*; Nozoe, T., Breslow, R., Hafner, K., Ito, S., Murata, I., Eds.; Hirokawa Publishing Co.: Tokyo, 1973; Vol. 1, pp 81-94.

(20) Breslow, R.; Chang, H. W.; Yager, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 2033-2034.

(21) Breslow, R.; Chang, H. W.; Hill, R.; Wasserman, E. *J. Am. Chem. Soc.* **1967**, *89*, 1112-1119.

(22) Breslow, R. *Mol. Cryst. Liq. Cryst.* **1985**, *125*, 261-267.

(23) Breslow, R.; Maslak, P.; Thomaides, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 6453.

(24) Thomaides, J. S.; Maslak, P., unpublished work in our laboratories.

of two benzenoid cation radicals should have the same correlation to a triplet charge-transfer pair as our case. This time the charge-transfer state is a (degenerate) D^{2+}/D^0 pair, as shown in Figure 1D.

Torrance observed true ferromagnetic behavior (hysteresis in the magnetization curves and a large value for the magnetization) over a wide temperature range for a sample of triaminobenzene that had been reacted with iodine, forming a polymer. The saturation magnetization of the best sample, however, represented only 2 mol % (based on monomer) of possible spins in the polymer. Apparently the preparation of this material is capricious and irreproducible.

The solids required by Torrance's model are probably the most synthetically accessible of any of the potentially ferromagnetic solid structures discussed here. In fact some of the precursor compounds described in this paper are candidates for Torrance's model. We found all of these to be antiferromagnetic, as were other threefold symmetric benzenoid radical cation salts prepared in our laboratories.²⁴

Wudl and co-workers have recently reported⁴ another variation of McConnell's idea which uses a neutral donor as the triplet diradical and D^+ as the doublet monoradical, as illustrated in Figure 1E. This model could produce a conducting organic ferromagnet, since the electron that is transferred is isoenergetic in all of its possible sites. Within this material the D^+-D^+ interactions of Torrance's model would combine with the effect of delocalized triplet sites.

Miller and co-workers have recently prepared a ferromagnetic *organometallic* molecular charge-transfer solid, decamethylferrocenium tetracyanoethylene, which they suggest may follow the McConnell/Breslow model.²⁵

Model

There are a number of theoretical and practical questions surrounding this model for ferromagnetism.²⁶ From a practical point of view, it is necessary to find cation radicals that are sufficiently electron rich that they can act as electron donors, and in which the corresponding radical cations will indeed have triplet ground states.

The model relies on π -electron donor-acceptor complexes. Therefore largely one-dimensional magnetic interactions, along the π -stacking axis, are expected between the spins in these complexes. Purely one-dimensional ferromagnetism is presumably impossible, however. The ferromagnetic interactions proposed by the models might operate between stacks as well as within them, solving the problem. Alternatively, interstack interactions could instead be weakly antiferromagnetic, and then interesting magnetic properties such as spin-flop magnetism or metamagnetism might be seen.²⁷

The interactions of donor and acceptor in the solid must favor substantial forward charge transfer (mixing of the monoionic solid with diionic configurations, as shown in Figure 1c), and disfavor back charge transfer (to singlet uncharged configurations, Figure 1A), so that the neutral singlet charge-transfer configuration is high in energy. The forward charge transfer necessary for our model is not well precedented, but should occur if the donor and acceptor potentials are appropriate. Ionic contributions to the structure of some neutral charge-transfer complexes are known to substantially perturb their ground-state electronic structure so that it looks partially ionic, based on bond lengths and vibrational

Table I. Half-Wave Potentials for Donors and Acceptors^a

	E_1	E_2	E_3	E_4
9·(Bu ₄ N ⁺) ₂	387	1178		
10·(Bu ₄ N ⁺) ₂	130 ^b	757		
1	48	296	504	831
11 ^c	459	703	931	1297
12	336	553	770 ^d	1130 ^d

^aIn mV vs Ag/0.01 M AgNO₃, CH₃CN, Bu₄NClO₄, corrected by 310 mV, so that Cp₂Fe = 419 mV. ^bNot reversible. ^cValues were determined by cyclic voltammetry (others were determined by second-harmonic ac voltammetry). ^dValues were determined by using a dilute solution of the electroactive compound, so associated error is large.

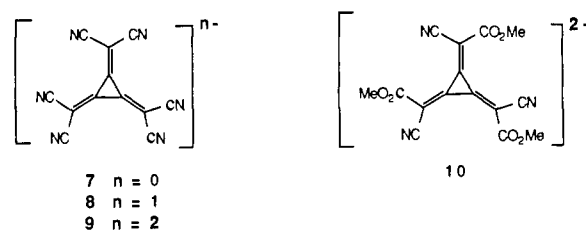
frequencies. Similar mixing of the monoionic and diionic states should be possible.

It is crucial that the donor component of the charge-transfer complex have a stable triplet as one of its redox forms. In fact it is desirable that the triplet-singlet gap of the donor dication be as large as possible, in order to stabilize the spin-parallel arrangement within donor-acceptor pairs. Most challenging, it is necessary that the threefold symmetry of the donor be preserved in the complex, since the donor dication is a triplet only due to its symmetry. Any local distortions of symmetry could cause the dication to have a singlet ground state. There is also a possibility that higher energy singlet configurations of the donor-acceptor pair could mix with the ground-state configuration, to lead to a lower energy spin-paired state. If this happens, one would see *antiferromagnetic* ordering, the usual situation for organic radical ion solids.

Experimental System

To examine this model experimentally, we have used the hexaazatriptetralin system (1) that we have reported previously.¹² The synthesis of 1 allows easy modification of the six substituents on nitrogen in order to adjust the electronic properties of the system. We showed that 1 forms a cation radical 2 under very mild oxidizing conditions and is reversibly oxidized as well to a dication 3. The dication 3 shows a typical triplet ESR spectrum, and the intensity of the $\Delta m = 2$ line follows the Curie law.²⁸ This evidence suggests that 3 has a triplet ground state, but some reservations must be expressed. If the ground state of the system were a singlet and the triplet state were very low in energy, perhaps only 10 or 20 cal above the singlet state, a Curie law study would not detect the singlet at experimentally accessible temperatures.

The choice of an electron acceptor with an appropriate oxidizing strength and of high symmetry for the potentially ferromagnetic charge-transfer solid is limiting; we selected the hexacyano compound 7 reported by Fukunaga,²⁹ as the most suitable partner for



our electron donors. This strong acceptor is prepared as the dianion 9 and can be oxidized to the stable anion radical 8. As expected, the dianion 9 has singlet spin multiplicity. Fukunaga also reported some related compounds, e.g. 10 with ester groups replacing some of the cyano groups.²⁹ We have found that 10 is not as well behaved as 7 so we decided to restrict our studies to the hexacyano compound 7.

The oxidation potential of the donor and reduction potential of the acceptor must be matched so that there is the correct amount of charge transfer in the solid. We decided to accomplish

(25) Miller, J. S.; Calabrese, J. C.; Rommelmann, H.; Chittipeddi, S. R.; Zhang, J. H.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 769-781. Since the donor and acceptor are each monoradical ions, a contribution from $^3[(\text{Me}_2\text{C})_2\text{Fe}]^{2+}[\text{TCNE}]^{2-}$ could in principle be responsible for the observed ferromagnetism. This forward charge transfer is very endothermic for this charge-transfer pair. McConnell's model is not necessary for this example of ferromagnetism: this system may use Soos's molecular superexchange mechanism⁵ or may take advantage of the greater number of degenerate orbitals on iron.

(26) A more detailed discussion of models for organic ferromagnetism is under preparation by T.J.L.

(27) Willett, R. D.; Gaura, R. M.; Landee, C. P. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York, 1983; Vol. 3, p 181.

(28) Selwood, P. W. *Magnetochemistry*, 2nd ed.; Interscience, New York, 1956.

(29) (a) Fukunaga, T. *J. Am. Chem. Soc.* **1976**, *98*, 610-611. (b) Fukunaga, T.; Gordon, M. D.; Krusic, P. J. *J. Am. Chem. Soc.* **1976**, *98*, 611-613.

this by using appropriate substituents on the donor molecule while keeping the hexacyano derivative **7** as the acceptor. The extent of charge transfer is critical, since only when the doublet/doublet monoionic configuration and the triplet/singlet diionic configuration mix does the model predict ferromagnetism.

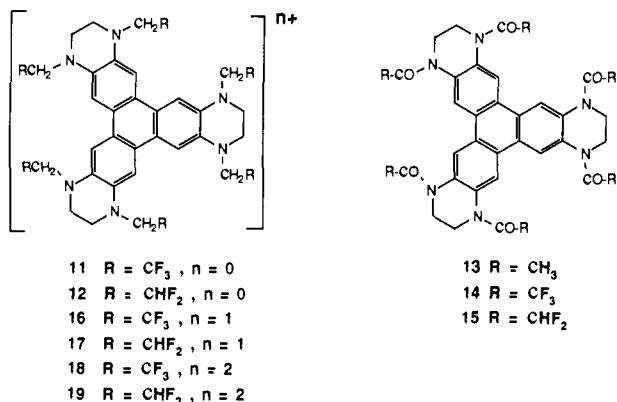
Thus we set out to prepare appropriate solids combining the electron acceptor **7** with derivatives of hexaazatritetralin **1**. We were indeed able to prepare a 1:1 donor-acceptor solid in which the desired monoionic/diionic mixing appears to be occurring. This system proved to adopt antiferromagnetic ordering.

Results and Discussion

Electrochemical Studies. We prepared the dianion (**9**) of tris(dicyanomethylene)cyclopropane (**7**) and the dianionic tricyano triester **10** using Fukunaga's procedures.²⁹ By cyclic voltammetry and second-harmonic ac voltammetry³⁰ we found reversible oxidations with half-wave potentials E_1 and E_2 for **3** but irreversible oxidation of the dianion **10**, suggesting dimerization of the corresponding anion radical. We have also determined the oxidation potentials of donor **1** to form the radical **2** and dication **3**. These data are listed in Table I.

Comparison of these potentials indicates the expected charge-transfer state of a 1:1 mixture of **1** and **7** in solution. Transfer of a single electron to afford a mixture of ion radicals **2** and **8** is exothermic by 1.13 V, a large energy. Transfer of a second electron to afford a mixture of the dication **3** and the dianion **9** is also exothermic, by 91 mV. In a solid with cations and anions alternating in a stack, the strong electrostatic interaction between the counterions results in a shift of potentials favoring more highly charged species. The magnitude of the shift depends of course on the structural details of the system but is around 170 mV for mixed-stack (...DADA...) solids.³¹ Thus a solid composed of equal parts of **1** and **7** would be expected to exist as the doubly charged ions **3** and **9**, with essentially none of the mixing of the single-electron-transferred states required in our model.

We solved the problem of overionization by synthesizing two new donor compounds related to **1** but with more electron-withdrawing groups replacing the ethyl groups. Replacement of all the ethyl groups by 2,2,2-trifluoroethyl groups led to compound **11**, while their replacement by 2,2-difluoroethyl groups afforded



compound **12**. As the data in Table I show, now a single electron transfer from **11** to **7** is exothermic by only 719 mV, and a second electron transfer is endothermic by 316 mV in solution. If in the solid it became 170 mV more favorable, the transfer of a second electron would still be contrathermodynamic by 146 mV, so this charge-transfer pair should exist in the solid state as the monoionic **11/7**.

For **12** one-electron transfer to **7** is favorable by 842 mV, while two-electron transfer is unfavorable by 166 mV. In the solid state in a mixed stack of **12** and **7** the second electron transfer could

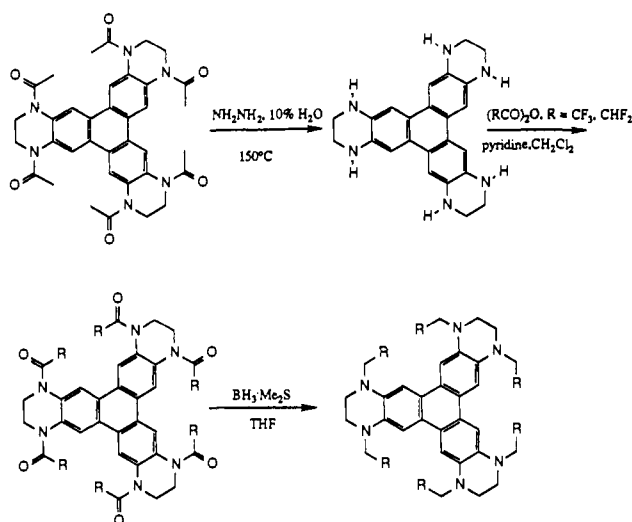


Figure 2. Preparation of fluorinated derivatives of **1**.

be almost perfectly balanced, with a 1:1 contribution of each electronic state. Because of this potential matching, **12** appeared to be the best donor for use with **7** in order to fulfill the electronic criteria for our model.

Syntheses and Properties of Cations. The syntheses of **11** and **12** proceeded from the hexaacyl derivative **13** that we used in the synthesis of **1**.¹² Deacetylation of **13** with hydrazine and acylation with the appropriate anhydride afforded the hexakis-(trifluoroacetyl) derivative **14** and the hexakis(difluoroacetyl) derivative **15**. These were then reduced with borane-dimethyl sulfide complex to the amines **11** and **12**.

Simple salts of the radical cations corresponding to the three donors **1**, **11**, and **12** were prepared. Deuring had synthesized the tetraphenylborate salt of cation **2** by oxidation of **1** with I₂ in the presence of excess NaBPh₄.¹⁶ This mixture was not strong enough to oxidize **11**, but the salt **16** was easily prepared by treatment of **11** with nitrosonium hexafluorophosphate. The more easily oxidized **12** was converted to its PF₆⁻ salt **17** with I₂ in the presence of excess sodium hexafluorophosphate. We have reported the ESR spectrum of **2** elsewhere;¹² the radical cations **16** and **17** gave unresolved lines with 20-G line width at half-height under various conditions.

The three radical cation derivatives **2**, **16**, and **17** had similar visible spectra (cf. Experimental Section). These spectra were unchanged in the solid state, indicating that the cation radicals do not dimerize. In the near-infrared region the cations all showed transitions near 1120 nm, both in solution and in the solid. These bands persisted on dilution down to 3×10^{-5} M, showing that they are probably due to the cation radical monomers and not dimers.

The dications **18** and **19** were prepared by oxidation of the corresponding radical cations with nitrosonium hexafluorostibate in CH₃CN. Both dications showed triplet spectra that followed Curie law behavior in the temperature range experimentally available (-155 to -100 °C), showing that at least in that range the triplet state is not a thermal excited state. Our model requires that the triplet be the ground state. Above -100 °C the triplet signal decayed irreversibly.

Preparation of the Cation/Anion Complexes. Although the cleanest preparation of the complexes might have involved reaction of neutral donors with the neutral acceptor **7** we confirmed the indication by Fukunaga that neutral **7** is unstable and difficult to prepare in a pure state. For this reason we prepared complexes by metathesis of salts of the radical cations **16** and **17** with salts of the radical anion **8**. The analytically pure tetrabutylammonium salt of **8** was prepared by metathesis of its potassium salt with Bu₄N⁺Br⁻.³² Metathesis of this Bu₄N⁺ salt of **8** with the PF₆⁻ salts of **16** or of **17** in CH₃CN solution afforded analytically pure

(30) Smith, D. E. in *Electroanalytical Chemistry*; Bard, A., Ed.; Marcel Dekker: New York, 1966; Vol. 1.

(31) Torrance, J. B.; Vazques, J. E.; Mayerle, J. J.; Lee, V. Y. *Phys. Rev. Lett.* **1981**, *468* 253-257. Kampar, E.; Neilands, O. *Russ. Chem. Rev. (Engl. Transl.)* **1986**, *55*, 334-342.

(32) The oxidation of Bu₄N⁺/9 with S₂O₈ as reported led to a mixture of **8** and **9** as judged by IR.

samples of the desired complexes **16/8** and **17/8** as amorphous solids. However, a similar metathesis of **8** with **2** afforded only decomposed materials showing the electronic spectrum of the dianion **9**. Apparently the hexacyano acceptor system **7** is too strong an oxidant for the unfluorinated donor series related to **1** as the solution electrochemical potentials had indicated.

The amorphous charge-transfer solids **16/8** and **17/8** could not be recrystallized, and attempts to prepare crystals of the **16/8** or **17/8** complexes by electrocrystallization were unsuccessful as well. However, slow diffusion (over 2 weeks) of a solution of $\text{Bu}_4\text{N}^+\text{-8}$ in CH_2Cl_2 layered over a solution of 17-PF_6^- in nitromethane in a vibrationless inert atmosphere afforded small dark needles of the **17/8** complex in good yield. Crystals of **16/8** were similarly prepared, again as small needles. These crystalline samples gave IR spectra identical with those of the amorphous materials.

Structural Characterization of the Complexes. Unfortunately the crystals so far available are too small to permit a detailed structure determination by X-ray crystallography. However, data taken with a 12-kW rotating-anode generator on a Rigaku AFC6 diffractometer were used to characterize the unit cell. For the **17/8** complex, the cell constants are as follows: orthorhombic, primitive, $a = 12.99$ (1) Å, $b = 15.376$ (7) Å, $c = 23.70$ (1) Å, $V = 4733.15$ Å³, Z (proposed) = 4.

The $hkl \neq 200$ reflection is more than 4 times as intense as any other reflection in the data set, showing that most of the electron density lies in a plane perpendicular to the a axis. Thus most of the flat molecules lie in planes perpendicular to the a axis. The repeat distance of the strong (200) reflection corresponds to an interplane distance of 6.50 Å. Since 6.50 Å is about twice the interplane distance expected for π -stacked aromatic rings, every other molecule in the stack is identical. This is expected for a mixed stack of donors and acceptors (...DADADA...), and no strong diffractions were observed for the 3.2–3.9-Å repeat distance expected from a segregated-stacking arrangement. Since the 6.50-Å spacing is somewhat smaller than that typically seen in neutral donor-acceptor complexes,³³ our system apparently has significant intermolecular attraction (by electrostatic attraction of the excess charge or by bonding).

In the case of the system with trifluoroethyl groups **16/8**, the primitive cell was triclinic while the conventional unit cell was orthorhombic. The most intense spot corresponds to a spacing of 6.59 Å, so again the components are in mixed stacks. The dimensions of the primitive unit cell are as follows: $a = 13.185$ (2) Å, $b = 17.974$ (3) Å, $c = 24.238$ (4) Å, $V = 5141$ Å³, Z (proposed) = 4. This is similar to the dimensions of **17/8**, except that the stacks are probably not vertical since the cell axes are not perpendicular. The conclusion that we have mixed alternating stacks in these two solids is supported by the vibrational spectra, discussed below. The alternating donor-acceptor arrangement is a prerequisite for the interactions necessary for ferromagnetism in our model; this prerequisite is apparently met for the complexes **16/8** and **17/8**.

The electronic spectrum of the **16/8** complex in the solid state showed the bands characteristic of the radical monoions **16** and **8** in isolation. Thus the expectation from solution electrochemical potentials that this complex would exist exclusively as the monocation/monoanion complex is supported. In the case of the **17/8** complex, with a better electron donor, the spectrum is somewhat perturbed from that of the simple monoions. However, there is certainly not a full additional electron transfer to form predominantly a dication and dianion. The spectrum of the dication related to **17** is distinctive, with a sharp maximum at 630 nm that is not seen in our complex. Thus the electronic spectra suggest

Table II. CN Stretching Frequencies (cm^{-1}) of Salts of Acceptors (**8** and **9**)

	cation	nitrile bands in IR		Raman
		ν_1	ν_2	
neutral ^a		2225		2225
monoionic (8)	Na^+	2220.9 (2)	2202	
	Li^+	2215.5 (5)	2203	
	K^+	2215.0 (5)	2201, 2224 (sh)	
	$\text{C}_5(\text{NMe}_2)_3^+$	2211.3 (3)	2189, 2172	
	HMT^+	2211.5 (5)	2195 (sh)	
	$(n\text{-Bu}_4)\text{N}^+$			2209
	solid	2209.1 (3)	2195	
	in CH_2Cl_2 solution	2211.5 (2)	2197	
	$(\text{Ph}_3\text{P})_2\text{N}^+$	2209.2 (2)	2195	2210
diionic (9)	$(n\text{-Bu}_4\text{N}^+)_2$	2182.5 (5)	2165	<i>b</i>
	$((\text{Ph}_3\text{P})_2\text{N}^+)_2$	2184.2 (4)	2168	<i>b</i>
complexes	16	2207.2 (2)	2192	<i>b</i>
	17	2190 (br)		<i>b</i>

^aReference 29. ^bNot observed. ^csh = shoulder, br = broad.

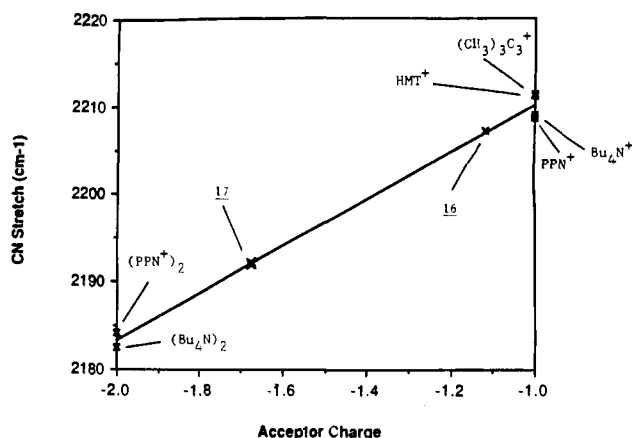


Figure 3. Correlation of CN stretching frequency with charge (ρ) on the electron acceptor **7-p**.

that **17/8** could be monocation/monoanion with some additional charge transfer.

Our conclusions about the charge states of the solid complexes are strongly supported by the vibrational spectra of the complexes and related compounds. Chappell et al. have shown³⁴ that the CN stretching band near 200 cm^{-1} in the IR spectra of TCNQ derivatives varies in an approximately linear fashion with the degree of charge transferred to the TCNQ. Thus we examined the infrared spectra of our complexes to determine the degree of charge transfer in these solids.

All salts of the hexacyano anions showed two IR bands within 15 cm^{-1} of each other in the CN stretch region, and some had Raman bands in the same region that identify this as an E' stretch.

The observed CN stretching frequencies are listed in Table II. For the monoanion **8** the values for the high-frequency band are remarkably constant in salts with a variety of noncoordinating cations. The cations are trimethylcyclopropenium, the hexamethoxytriphenylene cation (whose oxidation potentials are such that it should exist as a simple salt with this anion), tetrabutylammonium (both in solution and in the solid), and bis(triphenylphosphine)iminium. With cations that can coordinate to the CN groups, such as alkali metal cations, some shifts to higher frequency were seen. For the dianion **9** the CN stretching frequencies are lower, as expected because of the lower CN bond order, and quite similar for the two salts measured.

We also list the observed frequencies for **17/8** and for **16/8**. It is clear that in the salt derived from **16** we are dealing with

(33) For dibenzotetrathiafulvalene-tetracyanoquinodimethane (DBTTF-TCNQ), the donor-acceptor spacing is 3.4–3.44 Å. For DBTTF-TCNQ-F₂, the spacing is 3.4–3.46 Å (Emge, T. J.; Wiygul, F. W.; Chappell, J. S.; Bloch, A. N.; Ferraris, J. P.; Cowan, D. O.; Kistenmacher, T. J. *Mol. Cryst. Liq. Cryst.* **1982**, *87*, 137–161. For tetramethyltetraselenofulvalene-TCNQ, the spacing is ~ 3.5 Å (Kistenmacher, T. J.; Emge, T. J.; Bloch, A. N.; Cowan, D. O. *Acta Crystallogr., Sect. B: Structure Crystallogr. Cryst. Chem.* **1982**, *B38*, 1193–1199). For tetramethyl-*p*-phenylenediamine-TCNQ, the spacing is 3.27 Å (Kaufman, F. B. *J. Am. Chem. Soc.* **1976**, *98*, 5339–5344).

(34) Chappell, J. S.; Bloch, A. N.; Bryden, W. A.; Maxfield, M.; Poehler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442–2443.

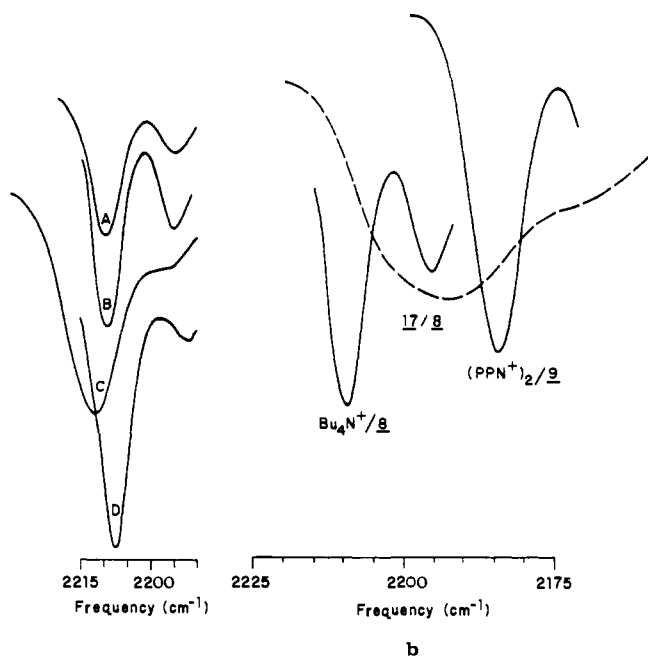


Figure 4. (a) CN stretch in **16/8**, with bands for other monoionic salts of HCTMC: (A) PPN⁺; (B) Bu₄N⁺; (C) HMT⁺; (D) **16**. (b) Broad CN stretch in **17/8**, compared to stretches in typical **8** and **9** salts.

a species that is essentially the monocation/monoanion, a conclusion consistent with our other evidence. In the salt of **17**, we find a CN frequency intermediate between those expected for the monoanion **8** and for the dianion **9**. This is made clearer in Figure 3, in which these data are plotted. Judging from this plot, the anion derived from **7** has a charge of -1.7 , so the donor derived from **12** in this complex has a charge of $+1.7$. However, this plot is deceptive.

In Figure 4a we show the relevant infrared band of the **16/8** complex: it is normal in shape, similar to the CN stretching bands of other derivatives of the monoanion **8**. However, as Figure 4b shows, the CN stretching band in the **17/8** complex is abnormally broad. Girlando and co-workers have discussed the broad bands that may result from vibronic coupling in solids³⁵ and have concluded that fractional charge is a necessary condition for the observation of vibronic bands, which are found at lower frequencies than are "pure" vibrations. Furthermore, vibronic bands may be caused by π dimerization. Thus the infrared spectrum of **17/8** surely indicates a fractional charge, more than 1.0 and less than 1.7, but it is not possible to specify the exact value.

Magnetic Measurements. The magnetic susceptibility (χ) of the complexes was measured on a Faraday balance at Bell Laboratories at temperatures from 4 to 300 K. Several corrections were applied to the raw data to simplify the data analysis and to determine the amount and nature of impurities in the samples. A correction factor accounting for ferromagnetic impurities was applied. Diamagnetic contributions were estimated from Pascal's constants and subtracted. Finally, the low-temperature susceptibility was fit to the Curie-Weiss law to correct for residual paramagnetism at low temperatures.

The magnetization (M) of ferromagnetic impurities should be almost independent of field (H). Therefore a plot of susceptibility vs $1/H$ should give a nearly straight line. The slope of the line is the magnetization of the ferromagnetic material. The magnetic susceptibility in the limit as $1/H \rightarrow 0$ is nearly independent of ferromagnetic contributions.²⁸ Least-squares fitting of the room-temperature magnetic susceptibility vs $1/H$ at fields from 4 to 13 kOe (=kG) showed that there was a significant ferromagnetic contribution to the observed susceptibility, but this corresponded to only 0.02–0.1% of the magnetization that would be observed if all the sample spins were aligning ferromagnetically.

(35) Girlando, A.; Marzola, F.; Pecile, C.; Torrance, J. B. *J. Chem. Phys.* **1983**, *79*, 1075–1085.

Table III. Diamagnetic and Curie-Law Corrections to χ for Crystalline Complexes

complex	$\chi_{\text{dia}}(\text{estd})$, 10^{-6} erg Oe ⁻² g ⁻¹	C_{g} , 10^{-6} erg Oe ⁻² K ⁻¹ g ⁻¹	% spins
16/8	-0.488	13.8	14
17/8	-0.521	27.4	19

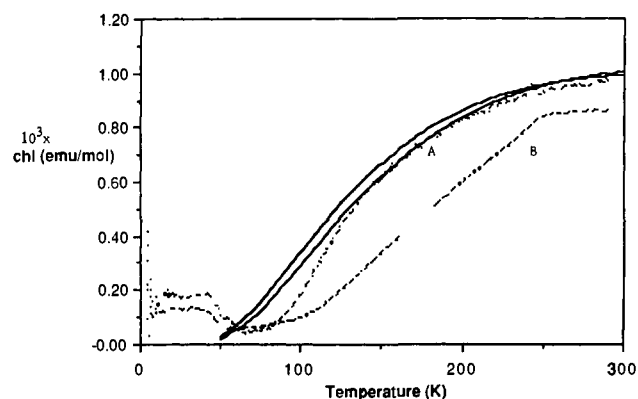


Figure 5. Corrected susceptibility curves for crystalline (A) **16/8**, with calculated values (solid lines); (B) **17/8**.

The difference between the measured susceptibility and the susceptibility at $1/H = 0$ was subtracted from the raw data. Plots of susceptibility vs $1/H$ show curvature, so the error associated with this correction is high. For crystalline **17/8**, the magnetization due to ferromagnetic impurities at 4.5 K was 30% greater than at room temperature.

The diamagnetic susceptibility calculated by Pascal's atomic constants,²⁸ with no group correction factors, was subtracted from the susceptibility data for the crystalline complexes (Table III). The molar susceptibility of a sample of **11** was determined at room temperature from a plot of susceptibility vs $1/H$ to be 4.34×10^{-4} erg Oe⁻² mol⁻¹. This value agrees well with the estimate from Pascal's constants (4.45×10^{-4} erg Oe⁻² mol⁻¹). In this sample ferromagnetic impurities were only 0.007 mol %, and a plot of χ vs $1/H$ did not show curvature.

All of the samples showed "Curie tails"—high susceptibilities at very low temperatures. The low-temperature data followed the Curie-Weiss law.²⁸ From 14 to 20% of the expected two spins per formula is present in the samples at low temperature. Therefore most of the molecules are antiferromagnetically coupled or spin-paired at low temperature, but 1 in every 5–7 is not paired, probably due to crystal defects or impurities. The Weiss constant was 0–1 K for all the fits, indicating that the residual spins do not interact measurably with each other.

The corrected susceptibilities for the crystalline complexes are shown in Figure 5. At 290 K the susceptibility is 60–70% of that expected from the Curie law for the monomeric spin- $1/2$ species. This agreement is within the large experimental error for the absolute magnitude of χ . At low temperatures the susceptibilities of the crystalline samples appear to go to zero, indicating that the complexes are essentially diamagnetic at low temperatures.

The magnetic susceptibilities of **1/BPh₄⁺**, **16/PF₆⁻**, and **17/PF₆⁻** were also examined as a function of temperature at IBM Almaden Laboratories. These salts could be ferromagnetic by the model of Torrance if they have the necessary self-stacked structure. All three salts were antiferromagnetic, with maxima in susceptibility of 200, 50, and <6 K, respectively.

For some of the samples, a small "bump" in the susceptibility is seen at about 45 K. The "bump" corresponds to a tiny fraction of the spins in the samples. It is seen in samples of both of the complexes, so it may be due to an extrinsic effect such as a small amount of oxygen in the atmosphere of the balance or adsorbed to the samples.³⁶

(36) Crystalline O₂ is antiferromagnetic below 43.8 K (ref 28, pp 247–248).

The corrected susceptibility data of the crystalline sample of **16/8** is reasonably well fit in the region above 120 K by a Boltzmann distribution of free spins: $\chi = C/T \exp(-E/kT)$. This relation has been used to explain the susceptibility data of other ionic charge-transfer complexes³⁷ and corresponds to a physical picture of a diamagnetic ground state with activated paramagnetism. The calculated and experimental curves are shown in Figure 5. The value of the Curie constant C obtained from this fit is about 25% higher than the expected value, while E corresponds to about 325 K (650 cal).

The corrected susceptibility curve of crystalline **17/8** shows a sharp transition in slope at about 246 K. This feature may be due to a structural phase transition to a low-temperature spin-paired phase. Below 246 K, the susceptibility decreases linearly with temperature until it reaches a minimum at about 100 K. The susceptibility behavior of **17/8** does not fit any simple model for antiferromagnetic behavior.

The heat capacity of the crystalline complexes was examined at General Electric Laboratories, Schenectady, NY, by differential scanning calorimetry from 300 to 110 K. The two compounds have similar profiles. Both have reproducible exothermic peaks at about 130 K, features characteristic of crystal phase transitions. They also have second-order transitions at about 210 K which are irreproducible. A reproducible second-order transition with a similar profile in $\text{Me}_4\text{N}^+\text{HCTMC}^-$ was shown to correspond to a structural phase transition in which the high-temperature unit cell was doubled.³⁸

The anomalies found in the calorimetry of the complexes would be expected to complicate the magnetic behavior. Curiously, the temperatures of the anomalies do not correspond to the temperatures of the magnetic transitions.

Electron spin resonance of the powder complexes did not shed much light on their magnetic structure. For both complexes, a single narrow line was seen at room temperature, and a broader line was seen at 77 K. This spectrum would be expected for $S = 1/2$ molecules but would also be seen if intermolecular triplets or higher multiplets were in a high enough concentration for rapid spin exchange. Triplet exciton ESR spectra³⁹ are seen in some solids with dilute spins, e.g. $(\text{Ph}_3\text{AsCH}_3^+)(\text{TCNQ}_2)^-$.⁴⁰ Since we see only a single line at $g \sim 2.005$, we were unable to determine from ESR measurements the multiplicity of spins in the solid. Fits of the high-temperature data to the Curie law are not reasonable since they would be over only a small range and near an antiferromagnetic transition. If the complexes were existing as triplet dimers, $\{[(\text{R})_6\text{-HAT}]\text{-HCTMC}\}$, the Curie susceptibility at 300 K would be 150% of the expected susceptibility for doublet monomers. We observe 60–70% (with a high error), so the complexes are probably due to doublet monomers.

In summary, the complexes are both antiferromagnetic. They do not, however, show the sharp maxima in susceptibility and heat capacity vs temperature that is characteristic of the classic antiferromagnetic state. They behave magnetically much like other nonconducting ionic radical solids that have been studied.⁴¹ The maxima in susceptibility around room temperature indicate strong antiferromagnetic coupling of the radical spins and therefore large interactions between neighboring molecules.

Conclusions

1. A solid 1:1 complex of a donor and an acceptor has been prepared that apparently meets the requirements of our adaptation of the McConnell model for organic ferromagnetism: alternating donor-acceptor stacking, partial second charge transfer, and a

triplet donor dication. These factors should allow spin-parallel character in the solid.

2. However, this material proves to have antiferromagnetic ordering.

3. A number of variables in this particular system could be nonideal with respect to the production of ferromagnetic interaction. The triplet state of the donor dication may not be stable enough, the symmetry might be perturbed in the solid so as to favor the singlet state, and the intermolecular interactions may not be general enough or multidimensional enough.

4. Other examples of such systems must be explored in the future to establish whether in appropriate cases the proposed interactions can indeed lead to the production of a ferromagnetic organic compound.

Experimental Section

Solvents. Solvents were from Fisher Chemical Co. or Amend Chemical Co. Acetonitrile was Kodak "Spectro". Dry acetonitrile was refluxed over CaH_2 overnight and then distilled under argon. For use in the drybox, a preliminary step of distilling from KMnO_4 or H_2SO_4 was added. Tetrahydrofuran (THF) was freshly distilled from K^0 and benzophenone under N_2 . Dry CH_2Cl_2 and dry benzene were distilled from CaH_2 under N_2 . Dry nitromethane was distilled from CaCl_2 under argon.

Equipment and Procedures. All experimental work performed in the glovebox was carried out in a Vacuum Atmospheres Dri-Lab HE-43 fitted with a HE-493 Dri-Train (containing 13X sieves and a copper oxygen getter) and HE-63-P Pedatrol, with argon as the inert gas. The glovebag used for crystallizations was from Aldrich. It was filled with N_2 , and no special precautions were taken to exclude air aside from the initial purging and filling (five cycles).

Magnetic susceptibilities were determined at Bell Laboratories with an electronic Faraday balance by Frank Di Salvo and Joe Wacaszak or at IBM Almaden Research Center on a Squid magnetometer by Jerry Torrance. The samples, from 20 to 100 mg each, were transferred from sealed ampules (and briefly exposed to air) to a quartz tube of known susceptibility. The tube was placed between the poles of the magnet, and the area was evacuated and refilled with helium. The magnetic susceptibility was determined at 12.4 kOe (Bell Laboratories) or 50 kOe (IBM), between ca. 300 and 4.5 K.

Voltammetry measurements were made under argon on a 1–5 mM sample of the substrate in 4–10 mL of freshly distilled dry CH_3CN containing 0.10 M tetra-*n*-butylammonium perchlorate (TBAP, Alfa), unless otherwise specified. The cell was assembled in the glovebox for air-sensitive samples or otherwise using syringe/Schlenk techniques. A platinum button was the working electrode and a platinum coil was the counter electrode. The reference electrode was a silver wire immersed in a solution of CH_3CN , 10 mM in AgNO_3 and 90 mM in TBAP, separated from the bulk solution by a Vycor plug (EG&G PAR, part no. G0100). The cell was a 50-mL point-bottom flask with three 14/20 joints, one for each electrode, and a Teflon stopcock side arm.

The Ag/AgCl quasi-reference electrode was used initially. It is less stable in CH_3CN than in other organic solvents because AgCl is significantly soluble in CH_3CN . In addition, we sometimes observed large unexplained irreproducibilities when using this reference system, which may have been caused by reaction of Ag^+ with the substrates. Thus we turned to a simple, well-behaved, truly reversible reference, Ag/AgNO_3 separated by a Vycor plug from the bulk electrolyte. The Vycor plug gave no leakage problems, and acetonitrile as the solvent in the reference compartment obviated the problem of rigorously isolating the reference compartment from the bulk electrolyte solution that would be necessary if aqueous calomel were used.

The Ag/AgNO_3 reference gives an oxidation potential for ferrocene at +98 mV and is therefore offset by about 310 mV from the SCE scale. The data in Table I have been corrected by this 310 mV. Cyclic voltammograms were recorded with an EG&G Princeton Applied Research (PAR) 173/176 potentiostat driven by a PAR 175 universal potential programmer and recorded on an Omnigraphics X-Y recorder. Second-harmonic ac voltammograms³⁰ were measured with a PAR 174A polarographic analyzer with a PAR 174/50 ac interface, a Hewlett-Packard 3300A function generator, and a PAR 122 lock-in amplifier. The applied modulation was 30 mV peak-to-peak, the fundamental frequency was about 50 Hz, and the dc sweep rate was 10 mV/s. The phase angle was adjusted in each case to give the maximum amplitude signal. In-phase and quadrature voltammograms were measured in both the forward and reverse directions for each determination.

Second-harmonic ac voltammetry and cyclic voltammetry gave slightly different results, but they usually differed by less than 10 mV. These differences are due to the slow response of the chart recorder at faster

(37) (a) Soos, Z. G. *Annu. Rev. Phys. Chem.* **1974**, *25*, 121–153. (b) Soos, Z. G. *Chem. Phys. Lett.* **1979**, *63*, 179–183.

(38) Abrahams, S. C.; Bair, H. E.; DiSalvo, F. J.; Marsh, P.; Deuring, L. A. *Phys. Rev. B*, **1984**, *29*, 1259–1262. Deuring, L. A. Ph.D. Thesis, Columbia University, 1984.

(39) Nordio, P. L.; Soos, Z. G.; McConnell, H. M. *Annu. Rev. Phys. Chem.* **1966**, *17*, 237–259.

(40) Chesnut, D. B.; Meinholtz, D. C. *J. Chem. Phys.* **1985**, *83*, 5495–5500 and references therein.

(41) Torrance, J. B. in *Low Dimensional Conductors and Superconductors*, NATO ASI Series, in press.

scan rates and also to the imprecision with which cyclic voltammetry peak positions can be determined. Occasionally greater differences were seen. In these cases the waves may not have been completely reversible. The second-harmonic ac values are reported when possible because we believe them to be more reliable. In all cases reversibility was checked by verifying the equal heights of the oxidation and reduction waves in cyclic voltammetry and by examining the forward and reverse scans in normal and quadrature phase detection for second-harmonic ac voltammetry (looking for approximately equal height of both lobes and of normal and quadrature scans).

Synthesized Materials. Potassium Tris(dicyanomethylene)cyclopropanide, K⁺HCTMC⁻ (8). This procedure is based on a brief report by Fukunaga.²⁹ Na⁺HCTMC²⁻ (500 mg, 1.82 mmol) was dissolved in 35 mL of H₂O, and K₂S₂O₈ (490 mg, 1.81 mmol) was dissolved in 45 mL of H₂O. The two solutions were filtered separately through medium-porosity fritted funnels and then stirred together. The mixture was allowed to stir for ~3 h and then filtered on a medium-porosity fritted funnel. The shiny maroon solid was washed with H₂O and dried in vacuo overnight to give 438 mg (90%).

Anal. Found (Calcd for C₁₂N₆K): C, 53.91 (53.92); H, <0.06 (0.00); N, 30.75 (31.45). IR (KBr) 2215 (n), 2201 (n), 1482 (n), 1467. UV⁴² (CH₃CN, 60 μM, nm (ε × 10⁻³)) 673 (20), 598 (13), 320 (38), 215 (29).

Tetra-*n*-butylammonium Tris(dicyanomethylene)cyclopropanide, Bu₄N⁺HCTMC⁻ (8). To a solution of K⁺HCTMC⁻ (153 mg, 0.571 mmol) in 18 mL of acetone was added a solution of tetra-*n*-butylammonium bromide (184 mg, 0.571 mmol) in 9 mL of acetone, and 2 mL of acetone was used to rinse the flask. The mixture was stirred in air at room temperature for 5 min and then filtered through a coarse-porosity fritted glass funnel. To the filtered solution H₂O was added dropwise with stirring until precipitation was observed (45 mL). The mixture was allowed to stir 25 min, and the resulting solid was filtered and dried under vacuum to give 212 mg (79%) of lustrous dark needles.

Anal. Found (Calcd for C₂₈H₃₆N₇): C, 71.47 (71.45); H, 7.71 (7.91); N, 20.83 (20.83). IR (KBr) 2962, 2938 (sh), 2879, 2211 (n), 2195 (n), 1801, 1479, 1465, 1380. UV⁴² (CH₃CN, 66 μM, nm (ε × 10⁻³)) 673 (17), 598 (11), 320 (29), 215 (23).

Bis(triphenylphosphine)iminium Tris(dicyanomethylene)cyclopropanide, PPN⁺HCTMC⁻ (8). A solution of K⁺HCTMC⁻ (100 mg, 0.374 mmol) in 7 mL of acetone was mixed with a solution of bis(triphenylphosphine)iminium chloride (PPN⁺Cl⁻, Alfa, 215 mg, 0.375 mmol) in 4.5 mL of acetone. The mixture was allowed to stir for 3 min, filtered through a medium-porosity fritted funnel, and washed through with 1 mL of acetone. Then 9 mL of H₂O was added gradually to the stirring solution. The resulting precipitate was collected on a coarse-porosity fritted funnel and dried in vacuo 12 h, yielding 254 mg (89%) of a glossy purple crystalline solid.

Anal. Found (Calcd for C₄₈H₃₀N₇P₂·2H₂O):⁴³ C, 71.66 (71.81); H, 4.31 (4.27); N, 12.26 (12.21). IR (KBr) 3430 (br), 3060, 2925, 2209 (n, s), 2195 (m), 1230 (vbr), 1118 (n, s), 1000 (n), 749, 725 (n, s), 694 (n, s).

Bis(triphenylphosphine)iminium Tris(dicyanomethylene)cyclopropanediide, (PPN⁺)₂HCTMC²⁻ (9). Na⁺HCTMC²⁻ (114 mg, 0.145 mmol) was dissolved in 7.5 mL of H₂O and added to a solution of bis(triphenylphosphine)iminium chloride (PPN⁺Cl⁻, Alfa, 434 mg, 0.756 mmol) in 7.5 mL of CH₃CN with stirring. The solution was diluted with 6 mL of CH₃CN and 10 mL of H₂O at which point it was homogeneous. Then the solution was reduced in vacuo until a precipitate formed. The solid was collected on a medium-porosity fritted funnel, washed copiously with H₂O, and dried in vacuo to yield 344 mg (64%) of a white crystalline solid.

Anal. Found (Calcd for C₈₄H₆₀N₈P₄·H₂O):⁴³ C, 76.32 (76.24); H, 4.92 (4.72); N, 8.13 (8.47). IR (KBr) 3060, 2184, 2168, 1479, 1420 (s), 1360 (br), 1127, 723, 695.

Hexamethoxytriphenylenium Hexafluorostibate, HMT⁺SbF₆⁻. All operations were carried out in the glovebox. Hexamethoxytriphenylene⁴⁴ (24 mg, 0.059 mmol) was dissolved in 6 mL of dry CH₂Cl₂. NO⁺SbF₆⁻ (Alfa, 16 mg, 0.060 mmol) was dissolved in 0.3 mL of dry CH₃CN and added to the first solution with stirring. A blue-green precipitate formed immediately. The solid was collected on a medium-porosity fritted funnel and dried in vacuo to give 24 mg (63%) of a dark greenish blue powder.

(42) Extinction coefficients are omitted or have high associated error due to low solubility, instability, or small quantities available of the compound preventing an accurate determination.

(43) Previous workers have claimed that PPN⁺ salts do not crystallize as hydrates (Martinsen, A.; Songstad, J. *Acta Chem. Scand., Ser. A* 1977, A31, 645-650), but we found otherwise for PPN⁺-HCTMC and PPN₂HCTMC by analysis.

(44) Musgrave, O. C.; Webster, C. J. *J. Chem. Soc. C* 1971, 1397-1401. Matheson, I. M.; Musgrave, O. C.; Webster, C. J. *J. Chem. Soc., Chem. Commun.* 1965, 278-279.

Anal. Found (Calcd for C₂₄H₂₄O₆SbF₆): C, 44.99 (44.82); H, 3.85 (3.76). IR (KBr) 1697, 1595, 1508, 1470, 1437, 1418, 1348, 1260, 1212, 1158, 1044, 960, 833, 776, 705, 657, 622. UV⁴² (CH₃CN, nm) 808, 420.

Hexaacylhexaazatritetralin, (CH₃CO)₆-HAT (13). A large (4.5 × 15 cm) thick-walled tube with a 10-mm-diameter long stem was filled with hexabromotriphenylene (5 g, 1.1 mmol) and cuprous bromide (100 mg, 0.70 mmol), covered with a septum, purged with argon, and filled via syringe with 120 mL of argon-purged ethylenediamine (Fisher, used as received). The tube was chilled in liquid nitrogen and sealed in vacuo. After the mixture thawed, the tube was put in an autoclave (Autoclave Engineers, 1-L bolt-closure packless type) along with about 300 mL of water. The autoclave was sealed, pressurized to 600 psi, and heated to 195 °C for about 48 h. The tube was frozen in dry ice-acetone and opened, and then the mixture was allowed to thaw under vacuum and solvent was removed under vacuum, finally at 0.2 Torr for 10 h. To the resulting viscous dark red oil was added 40 mL of pyridine (stored over molecular sieves). The resulting solution was chilled in an ice bath, and a mixture of 30 mL of pyridine and 30 mL of acetic anhydride was slowly added. The acylation mixture was allowed to stir at room temperature for 1 h and then heated to reflux for 6 h. Then the solvents were removed in vacuo and 100 mL of CH₂Cl₂ was added to the residue. The solution was extracted with 50 mL of 1 M HCl, and the aqueous layer was washed with 50 mL of CH₂Cl₂. The combined organic layers were washed with brine and dried with magnesium sulfate, the solvent was evaporated, and the gummy residue was triturated with 15 mL of methanol overnight.

In some preparations a precipitate formed during the extractions. In this case a larger volume of solvent was used or the solid was filtered off and pooled with the triturate. The bright yellow product was recrystallized several times from DMF until pure by TLC (10% MeOH/CH₂Cl₂) and then dried at 120 °C and 0.2 Torr for 12 h. The yield was 585 mg (13%). The NMR and IR agreed with the reported values.¹²

Hexaethylhexaazatritetralin, Et₆-HAT (1). (CH₃CO)₆-HAT (13) (565 mg, 0.871 mmol) was put in a 250-mL flask with a stopcock side arm and a condenser. The apparatus was flushed copiously with argon and sealed with septa. A 2 M solution of borane in THF (50 mL) was added via syringe to the flask, and the resulting pale yellow solution was heated to reflux for 1 h. Then the solution was cooled in ice, and the solvent was removed in vacuo. To the chilled mixture was added 100 mL of 6 M HCl and 20 mL of methanol, both degassed. The mixture was heated to reflux for 4 h and then chilled in ice, and 6 M NaOH (argon purged) was added until the solution was strongly basic. The resulting precipitate was filtered through a medium-porosity fritted funnel and washed with 4 × 20 mL of H₂O. The solid was dried in vacuo to give 424 mg (86%) of a material that had the reported NMR spectrum.

[Et₆-HAT]⁺BPh₄⁻ (2). All operations were carried out in the glovebox. Compound 1 (340 mg, 0.60 mmol) was dissolved in 5 mL of CH₂Cl₂ in the drybox to make a dark green solution. The mixture was diluted with 100 mL of degassed absolute ethanol. Na⁺BPh₄⁻ (206 mg, 0.6 mmol) was added and the mixture was filtered through a medium-porosity fritted funnel. The light green filtrate was titrated with 15 mL of 30 mM I₂ in ethanol and filtered, giving 409 mg (77%). The product was recrystallized from degassed CH₂Cl₂/pentane to give 255 mg (48%) of the salt.

Anal. Found (Calcd for C₆₀H₅₈N₆B): C, 81.54, 81.34 (81.52); H, 7.66, 7.81 (7.75); N, 10.22, 9.96 (9.51); B, 1.25 (1.22). UV⁴² (CH₃CN, nm (absorbance)) 684 (0.117), 640 (0.12), 488 (0.25), 466 (0.23), 370 (1.0), 330 (1.15), 290 (0.861).

Hexakis(trifluoroacetyl)hexaazatritetralin, (CF₃CO)₆-HAT (14). Hexaacyl compound 13 (700 mg, 1.08 mmol) was put in a sealed tube (with a Teflon screw valve, but with the rubber O-ring at the tip removed since it degraded under the reaction conditions) containing 44 mL of anhydrous hydrazine and 5 mL of H₂O. This was degassed by two freeze-pump-thaw cycles and then heated at 150 °C for 140 min. The solvents were evaporated without exposure to air. Then a solution of 12 mL of dry CH₂Cl₂, 24 mL of dry pyridine, and 4 mL of trifluoroacetic anhydride under argon at 0 °C was added to the residue in a chilled flask. After about 12 h of stirring, the acylation mixture was heated at reflux for 3 h.

Then 3 mL of H₂O was added, and the solvents were removed under vacuum. The residue was dissolved in 10 mL of methanol and precipitated with 10 mL of water. The solid was recrystallized from ethyl acetate/acetonitrile to give 541 mg (51%) of a crystalline solid. The product was insoluble in methanol and very soluble in warm pyridine.

MS (Cl-NH₃) *m/e* 972 (M⁺, 8%), 990 (M + 18, 100%), 875 (M - COCF₃, in the later scans). Anal. Found (Calcd for C₃₆H₁₈N₆F₁₈O₆): C, 44.80 (44.46); H, 2.27 (1.87); N, 8.94 (8.64). IR (KBr) 1705 (s), 1511, 1430 (br), 1313, 1276, 1227 (br), 1152, 1140, 1111, 887. UV⁴² (THF, 14 μM, nm (ε × 10⁻³)) 325 (27), 296 (98), 269 (40), 261 (82), 255 (111), 249 (95), 243 (17). NMR (DMF-*d*₇, δ 8.01) 9.04 (br s, 6

H), 4.41 (s, 12 H). Mp 330–340 °C (dec).

Hexakis(trifluoroethyl)hexaazatritetralin, (CF₃CH₂)₆-HAT (11). (CF₃CO)₆-HAT (14) (404 mg, 0.415 mmol) was put in a 250-mL side arm flask with a reflux condenser under argon; then 56 mL of BH₃-Me₂S (2 M in THF, Aldrich) was added, and the mixture was refluxed for 10 h. It was chilled in ice, and 35 mL of methanol was slowly added to avoid excess foaming; the mixture was stirred at room temperature 5 h and then saturated with HCl gas (bubbled for 10 min, until the gas no longer dissolved and the solution was clear yellow). The mixture was heated at reflux for 2.5 h and then chilled in ice, and the crude product (272 mg) was filtered off and dried in vacuo. It was recrystallized from hot pyridine to obtain 244 mg of air-stable pale yellow needles (66%). These were dried at 110 °C and ~0.05 Torr for 12 h.

MS (Cl-NH₃) *m/e* 889 (M + 1, 100%) Anal. Found (Calcd for C₃₆H₃₀N₆F₁₈): C, 49.29 (48.65); H, 3.52 (3.40); N, 9.49 (9.46). IR (KBr) 1618, 1522 (s), 1476, 1364, 1333, 1264 (s), 1225, 1095 (s), 1086, 1070, 997, 840, 662, 650. UV⁴² (THF, 23 μM, nm (ε × 10⁻³)) 375 (10), 348 (20), 311 (59), 286 (27), 261 (63), 255 (73), 249 (62), 244 (51). NMR (pyridine-*d*₅ = δ 8.57) 8.00 (s, 6 H), 4.08 (q, 12 H), 3.32 (s, 12 H). Mp 340 °C (dec).

[(CF₃CH₂)₆-HAT]⁺PF₆⁻ (16). All operations were carried out in the glovebox. To a stirred suspension of (CF₃CH₂)₆-HAT (11) (dried at 110 °C and 0.05 Torr for ~12 h to remove pyridine, 118 mg, 0.13 mmol) in 9 mL of CH₃CN was added dropwise a solution of NO⁺PF₆⁻ (Alfa, stored in a freezer, 28 mg, 0.16 mmol) as a solution in 1.7 mL of CH₃CN. The mixture was filtered through a medium-porosity fritted funnel, and 5 mL of dry ether was added to the stirred filtrate. After 5 min of stirring, the solid was collected in a 15-mL medium-porosity fritted funnel. The glossy dark green solid was dried in vacuo to give 118 mg (86%).

Anal. Found (Calcd for C₃₆H₃₀N₆F₂₄P): C, 42.46 (41.83); H, 3.40 (2.93); N, 8.89 (8.13). IR (KBr) 1600 (w), 1524 (s), 1448, 1345 (br), 1255 (s), 1214, 1142 (s, br), 1083 (n), 1061 (n), 998 (n), 846 (s, br), 934 (w, n), 722 (w), 698, 660, 647. UV⁴² (CH₃CN, 0.34 mM, nm (ε × 10⁻³)) 686 (5.3), 652 (5.0), 467 (14), 404 (11, sh), 354 (39), 312 (32), 286 (31).

[(CF₃CH₂)₆-HAT]⁺HCTMC⁻ (16/8). All operations were carried out in the glovebox. [(CF₃CH₂)₆-HAT]⁺PF₆⁻ (118 mg, 0.114 mmol) was dissolved in 14 mL of dry CH₃CN and filtered through a medium-porosity fritted funnel. Bu₄N⁺HCTMC⁻ (54 mg, 0.114 mmol) was dissolved in 7 mL of CH₃CN and filtered through a medium-porosity fritted funnel, and 7 mL of dry CH₂Cl₂ was filtered and added to the radical anion solution. The radical anion solution was added to the radical cation solution with brisk stirring. The combined solutions were stirred for 10 min, and the resulting solid was collected on a medium-porosity fritted funnel. The solid was washed with 5 mL of CH₃CN and dried in vacuo to give 114 mg (90%) of a dark blue-green solid.

The complex was extremely insoluble and could not be recrystallized. An alternative preparation was necessary to form crystals during the metathesis. All operations were carried out in a glovebag because vibrations are severe in the glovebox. Bu₄N⁺HCTMC⁻ (19 mg, 0.0404 mmol) was dissolved in 4 mL of CH₂Cl₂, filtered through a medium-porosity fritted funnel, and put in an 18 × 150 mm test tube. [(CF₃CH₂)₆-HAT]⁺PF₆⁻ (39 mg, 0.037 mmol) was dissolved in 4 mL of CH₃CN and filtered through a coarse-porosity fritted funnel. CH₂Cl₂/CH₃CN (1:1, 4 mL) was layered onto the radical anion solution. A sharp boundary formed. Then the radical cation solution was layered onto the top. Another sharp boundary formed so that the two salts were kept separate. The tube was covered with a septum and left undisturbed for 12 days, at which time the top and bottom layers appeared completely mixed. The tiny glossy dark needles were filtered and dried in vacuo, yielding 29 mg of product (69%).

Anal. Found (Calcd for C₄₈H₃₀N₁₂F₁₈): C, 51.74 (51.62); H, 2.65 (2.71); N, 15.11 (15.05). IR (KBr) 2970, 2930, 2875, 2207, 2192, 1829, 1526, 1448, 1339, 1259, 1212, 1142, 1098, 1065, 999, 844, 830, 659. UV⁴² (CH₃CN, nm (absorbance)) 673 (0.32), 600 (0.23), 468 (0.16), 309 (1.7), 288 (0.8), 268 (0.6).

Hexakis(difluoroacetyl)hexaazatritetralin, (CF₂HCO)₆-HAT (15). (CH₃CO)₆-HAT (13) (678 mg, 1.05 mmol) was put in an 80-mL tube with a Teflon screw valve (without a rubber O-ring at the tip) with 40 mL of hydrazine and 4 mL of H₂O. The solution was degassed by two freeze-pump-thaw cycles and then heated at 150–155 °C for 11.5 h. The mixture was transferred to a side arm flask under an inert atmosphere, the solvents were removed in vacuo, and the residue was heated at ~110 °C and ~0.05 Torr for 12 h to sublime off most of the acetylhydrazine. The flask was cooled and, under argon, 20 mL of dry pyridine was added, the mixture was chilled in ice, and 3.5 mL of difluoroacetic anhydride was added dropwise. The mixture was allowed to warm to room temperature, stirred for 21 h, and heated at 60 °C for 90 min. The solvents were removed in vacuo, and the residue was dissolved with brisk stirring in 30 mL of ethyl acetate and 30 mL of H₂O.

The aqueous layer was separated and washed with 30 mL of ethyl acetate. The combined organic layers were washed with 2 × (10 mL of saturated NaCO₃ + 10 mL of H₂O), and the aqueous layers were washed with 20 mL of ethyl acetate. Some precipitate, present during the extraction, finally dissolved in the least aliquot of ethyl acetate. The organics were dried with sodium sulfate and flash chromatographed (SiO₂, 3:1, ethyl acetate/petroleum ether) to yield 704 mg (78%) of a pale yellow solid.

Mp 295–300 °C. MS (Cl-NH₃) *m/e* 882 (M + NH₃, 100%), 865 (M + 1, 15%), 706 (M + 1 - 2 (CF₂HCO), 40%). IR (KBr) 1690, 1510, 1433, 1360, 1326, 1139, 1059. UV⁴² (CH₃CN, 10 μM (ε × 10⁻³)) 297 (132), 225 (21), 328 (sh, 40). NMR (CD₃CN = δ 1.95) 8.48 (v br), 5.95 (br t, 6 H, *J* ≈ 52 Hz), 4.15 (s, 12 H).

Hexakis(difluoroethyl)hexaazatritetralin, (CF₂HCH₂)₆-HAT (12). To (CF₂HCO)₆-HAT (15) (417 mg, 0.483 mmol) in a dry flask under argon were added 40 mL of a solution of 2 M borane-dimethyl sulfide in THF and an additional 15 mL of THF. The mixture was heated to reflux to 11 h. Then it was allowed to cool and 24 mL of methanol was slowly added to avoid foaming. The mixture was stirred for 24 h, then chilled in ice, and saturated with HCl gas by bubbling for 20 min. The acidic mixture was heated to reflux for 2 h and allowed to stand at room temperature for 4 days.

The solvent was reduced in vacuo, and an excess of degassed 0.5 N NaOH was added till the mixture had pH >13. The residue was extracted with 2 × 75 mL of degassed CH₂Cl₂, and the organic layers were dried with sodium sulfate and evaporated in vacuo to a gummy gray solid. Flash chromatography (silica, 8% ethyl acetate/benzene eluent) gave the desired product pure by TLC (165 mg, 44%) (and 94 mg of a more polar impurity which was (CF₂HCH₂)₆-HAT minus a difluoroethyl group).

Mp 310–325 °C. MS (EI) *m/e* 780 (M⁺, 100%), 390 (M²⁺, 4%). IR (KBr) 1612, 1520, 1479, 1443, 1365, 1337, 1269, 1248, 1166, 1120, 1048, 982, 932, 858, 841, 754, 732. UV⁴² (CH₃CN, ~13 μM (ε × 10⁻³)) 381 (30), 355 (52), 318 (152), 288 (61), 270 (61), 243 (sh, 34). NMR (CD₃COCD₃) 7.53 (s, 6 H), 6.38 (tt, 6 H, *J* = 4.0, 56.0 Hz), 3.92 (dt, 12 H, *J* = 3.9, 14.9 Hz), 3.61 (s, 12 H).

Impurity: IR (KBr) 3420 (n), 1615, 1521, 1474, 1367, 1323, 1262, 1118, 1048, 981, 838 (br). MS (EI) *m/e* 716 (M⁺), 358 (M²⁺). NMR (CD₃CN, CD₂H₂CN = δ 1.95) 7.45 (s, 2 H), 7.42 (s, 1 H), 7.38 (s, 1 H), 6.26 (tt, 5 H), 3.85 (br t, 10 H), 3.81 (br s, ~10 H).

[(CF₂HCH₂)₆-HAT]⁺PF₆⁻ (17). All operations were carried out in the glovebox. (CF₂HCH₂)₆-HAT (12) (145 mg, 0.186 mmol) was partially dissolved in 28 mL of CH₃CN and 50 mL of degassed absolute ethanol. Na⁺PF₆⁻ (Alfa, 50 mg, 0.30 mmol) was added, and then a solution of I₂ (Fisher, 32 mg, 0.126 mmol) in ~3 mL of ethanol was added gradually with stirring. The solution turned green and after a few minutes a precipitate formed. This was filtered through a medium-porosity fritted funnel and then dried in vacuo, yielding 127 mg of a dark green solid (74%).

Anal. Found (Calcd for C₃₆H₃₆N₆F₁₂P): C, 46.63 (46.71); H, 4.09 (3.92); N, 9.13 (9.08). IR (KBr) 1524, 1370, 1332, 1309, 1263, 1120, 1076, 1043, 983, 842 (PF₆⁻). UV (CH₃CN, nm) 686, 652, 467, 404, 354, 311, 285.

[(CF₂HCH₂)₆-HAT]⁺HCTMC⁻ (17/8). All operations were carried out in the glovebox. Bu₄N⁺HCTMC⁻ (63 mg, 0.134 mmol) was dissolved in 8 mL of CH₃CN and filtered through a medium-porosity fritted funnel. The funnel was rinsed with 2 mL of CH₃CN and the rinsings were added. [(CF₂HCH₂)₆-HAT]⁺PF₆⁻ (104 mg, 0.112 mmol) was dissolved in 10 mL of CH₃NO₂ and filtered into the stirred solution of the anion. An additional 10 mL of CH₃NO₂ and then 4 mL of CH₃CN were used to dissolve the residue, which was filtered into the reaction mixture. The mixture was stirred for 5 min and then filtered through a medium-porosity fritted funnel. The dark blue-green solid collected was dried in vacuo for 8 h, yielding 108 mg (96%).

The complex was extremely insoluble and could not be recrystallized. An alternative preparation was necessary to form crystals during the metathesis. All operations were carried out in a glovebox because vibrations are severe in the glovebox. Bu₄N⁺HCTMC⁻ (20 mg, 0.042 mmol) was dissolved in 4 mL of CH₂Cl₂, filtered through a coarse-porosity fritted funnel, and put in an 18 × 150 mm test tube. [(CF₂HCH₂)₆-HAT]⁺PF₆⁻ (40 mg, 0.43 mmol) was dissolved in 8 mL of CH₃NO₂ and filtered through a coarse-porosity fritted funnel. Then 4 mL of CH₃NO₂ was layered onto the radical anion solution. A sharp boundary formed. Then the [(CF₂HCH₂)₆-HAT]⁺PF₆⁻ solution was layered onto the top. The top two layers mixed slightly, but the two salts were kept separate. The tube was covered with a septum and left undisturbed for 4 days, at which time the top and bottom layers were still not completely mixed. The glossy dark needles were filtered and dried in vacuo, yielding 25 mg of product (58%).

Anal. Found (Calcd for C₄₈H₃₆N₁₂F₁₂): C, 57.22 (57.14); H, 3.82 (3.60); N, 16.83 (16.66). IR (KBr) 2192, 1813, 1520, 1414, 1334, 1307,

1260, 1220, 1119, 1079, 983. UV⁴² (CH₃CN, nm (absorbance)) 673 (0.15), 602 (0.10), 471 (0.12), 452 (1.08), 358 (0.51), 318 (1.07), 291 (0.71), 218 (0.90).

Hexamethoxytriphenylene-Tris(dicyanomethylene)cyclopropane 1:1 Complex, HMT-8. All operations were carried out in the glovebox. Hexamethoxytriphenylene⁴⁴ (10 mg, 0.024 mmol) was dissolved in 4 mL of dry CH₂Cl₂. Dissolution required stirring for several minutes. Freshly prepared HCTMC (5 mg, 0.022 mmol) was added as a solid. The reaction mixture immediately turned violet. It was allowed to stir for 45 min, and the solid was collected on a medium-porosity fritted funnel. After drying under vacuum the violet solid weighed 10 mg.

Anal. Found (Calcd for C₃₆H₂₄N₆O₆): C, 59.48 (67.92); H, 3.75 (3.80); N, 11.35 (13.20). Ratio (calcd/found) for C = 87.6, N = 86.0%. IR (KBr) 2211 (n), 2195 (sh), 1616, 1502, 1467, 1439, 1417, 1352, 1262, 1211, 1157, 1042, 967, 846, 779, 708, 669, 646, 626.

Preparation and ESR Spectroscopy of Dications 18 and 19. A suspension of 17·PF₆⁻ (15 mmol, 0.016 mg) in 0.40 mL of CH₃CN under argon was cooled in a -35 °C bath. To this suspension was added with stirring 0.15 mL of a 0.175 M solution of NOSbF₆ in CH₃CN (1.6 equiv)

via a Teflon needle. The resulting blue-green solution of 19 was evacuated briefly and then transferred rapidly via cannula to a -35 °C ESR tube under argon. A $\Delta m = 2$ line was observed as well as *z* and *xy* lines and a broad, intense singlet at *g* ~ 2. A *D* value of 0.0219 was found (*E* = 0), which agrees well with the value found for 3, *D* = 0.022. An identical procedure was followed for the preparation of 18 for which *D* = 0.022.

Acknowledgment. We are indebted to Dr. Frank DiSalvo, Joe Waszczak, and Dr. Lynn Schneemeyer at AT&T Bell Laboratories for the magnetic susceptibility determinations on the complexes and to Dr. Jerry Torrance for magnetic susceptibility measurements on the radical cations. We also thank Dr. Bruce Johnson at General Electric for the differential scanning calorimetry measurements. We thank J. Miller, J. Torrance, and F. Wudl for advising us of their results in advance of publication. We acknowledge the National Science Foundation for support and for a predoctoral fellowship to T.J.L.

Chemical and Spectroscopic Studies of the Coupled Binuclear Copper Site in Type 2 Depleted *Rhus* Laccase: Comparison to the Hemocyanins and Tyrosinase

Darlene J. Spira-Solomon and Edward I. Solomon*

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. Received June 27, 1986

Abstract: The active site of native laccase contains four copper ions, one of which can be removed generating the type 2 depleted (T2D) form which contains a blue (type 1, T1) and a coupled binuclear (type 3, T3) copper center. Deoxy (T3: [Cu(I)Cu(I)]), half met (T3: [Cu(II)Cu(I)]), met and uncoupled met-N₃⁻ (T3: [Cu(II)Cu(II)]) T2D laccase active site derivatives have been prepared, and their chemical and spectroscopic study provides insight toward a spectroscopically effective model for the coupled binuclear copper site in T2D laccase. CO, Cl⁻, Br⁻, I⁻, N₃⁻, and SCN⁻ are found to bind to the type 3 site in deoxy T2D, and from competition studies, all appear to coordinate to one exchangeable position at the deoxy active site; thus, while dioxygen is found not to react with the type 3 site in T2D, this site is still accessible to small molecule binding. Peroxide oxidizes deoxy to met T2D, and spectral studies of this derivative indicate that like met hemocyanin and tyrosinase, met T2D contains two tetragonal, EPR nondetectable Cu(II) ions which are thus antiferromagnetically coupled. Addition of N₃⁻ to met T2D at pH < 6 produces a triplet EPR signal characteristic of two uncoupled dipole-interacting Cu(II)'s indicating that a protonatable endogenous bridge is present at the type 3 site in laccase. One-electron reduction of met T2D by ferrocyanide generates half met T2D. For all anions investigated, one exogenous ligand binds to the cupric ion in half met and is readily removed by dialysis (*K* ~ 10² M⁻¹). This behavior is in marked contrast to anion binding in half met hemocyanins and tyrosinase (*K* > 10⁴ M⁻¹, where exogenous ligands bridge the binuclear copper site) and indicates a nonbridged binding mode for exogenous ligands to the type 3 site in laccase. The N₃⁻ → Cu(II) charge-transfer spectrum of the met-N₃⁻ derivative, where the absorption and CD transitions are maximum at the same energy, also supports this nonbridging coordination geometry of exogenous ligands, which is reasonably attributed to there being only one exchangeable coordination position at the type 3 site. Thus, this comparison of the coupled binuclear copper site in T2D laccase to that in the hemocyanins and tyrosinase indicates a strong geometric and electronic structural similarity in the endogenous bridge but an important difference in the exogenous ligand coordination mode; this difference in active site structure provides insight into the differences in dioxygen reactivity of these coupled binuclear copper active sites.

A number of important biological systems contain a coupled binuclear copper active site¹ that interacts with dioxygen. The simplest of these metalloproteins are the hemocyanins and tyrosinase which reversibly bind oxygen. Tyrosinase² in addition functions to hydroxylate phenols to *o*-diphenols (monooxygenase activity) and to oxidize the resulting diphenol to the *o*-quinone (diphenolase activity). The multicopper oxidases³ *Rhus* and

Polyporus laccase, ceruloplasmin and ascorbic acid oxidase, contain a number of copper centers that include one or two coupled binuclear copper sites (designated as "type 3" copper) and are the more complicated of the binuclear copper containing proteins. These enzymes couple one-electron oxidations of substrate to the four-electron reduction of dioxygen to water.

In the hemocyanins and tyrosinase, a series of systematically varied coupled binuclear copper active site derivatives¹ have been

(1) Solomon, E. I. In *Copper Proteins*; Spiro, T. G., Ed.; Wiley Interscience: New York, 1981; Chapter 2.

(2) Makino, N.; Mason, H. S. *J. Biol. Chem.* 1973, 248, 5731-5735.

(3) (a) Malkin, R.; Malmstrom, B. G. *Adv. Enzymol.* 1970, 33, 177. (b) Fee, J. A. *Structure and Bonding*; Springer-Verlag: Berlin, 1975; Vol. 23, pp 1-60.