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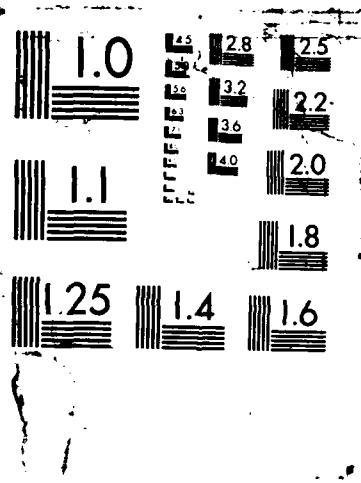
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THE DEVELOPMENT OF ORGANIC FERROMAGNETS

Final Technical Report

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INTRODUCTION

The discovery of conducting organic compounds was the first example of organic materials possessing metallic properties. More recently there has been a growing interest in organic compounds which may possess a different metallic property, ferromagnetism. The development of organic ferromagnets has both scientific interest and a strong technological impetus. Anticipated applications for organic ferromagnets include: sensors-(thermal or optical), magnetic thin films, magnetic affinity chromatography, magnetic shielding, and storage media (such as that used in computers). In addition to such technical applications, the study of organoferromagnetics will lead to the development of synthetic methods for new materials, the discovery of unknown properties and the development of low-dimensional magnets.

This final Technical Report prepared for, and in accordance with the guidelines set forth by the Office of Naval Technology, summarizes the research conducted in the field of Organoferromagnetics sponsored by ONT and the Naval Research Laboratories.

BACKGROUND and RELATED WORK

The origin of the large magnetic moment in ferromagnetic materials results from strong interactions between unpaired electrons causing them to spin align parallel to one another producing a net magnetic moment. Most organic compounds have an even number of electrons and find it energetically favorable to spin pair prohibiting the formation of ferromagnetic domains. This tendency to form diamagnetic electron spin configurations has thwarted most efforts to develop organic ferromagnets.²

In the last year two reports of ferromagnetic organic polymers have been published.^{3,4} Ovchinnikov describes his work as having an "insignificant fraction of the particles [to] possess ferromagnetic properties";³ while Torrance characterizes his work as "very low yield" with an "extreme lack of reproducibility".⁴ No satisfactory organic magnets have been reported to date.

The possibility of constructing a ferromagnetic array of electron spins or radicals in an organic molecule was reported as early as 1963 when McConnell predicted that ferromagnetic coupling would result in solid charge transfer complexes when radicals of positive spin density were adjacent to those of negative spin density.⁵ This theory was further developed by R. Breslow² and J. Torrance,³ and now represents a very promising guideline for the development of organic ferromagnets.¹

The model proposed by McConnell states that a linear regular alternating charge transfer complex in which one the accessible components exists as a triplet will exhibit ferromagnetic coupling as a result of an admixing of the charge-transfer ground state and the excited state. Because the admixing is spin conserving, if one state has a triplet spin configuration, then both the ground and excited states will have to be triplets forcing the adjacent acceptor and donor to spin align (see Fig. 1). In a linear regular alternating stack the donor cannot distinguish between the acceptor to the left and the acceptor to the right; therefore, charge transfer will be occurring to both acceptors. This requires that all three components in the chain be spin aligned. Through this mechanism the entire chain will become spin aligned.

The development of organoferromagnetic materials has been investigated

within the context of McConnell's model.

RESULTS AND DISCUSSION

2,3,7,8-Tetramethoxythianthrene (TMT) will form stable charge transfer complexes with a number of organic electron acceptors.⁶ Because TMT^{+2} exists as a ground state triplet⁷ regular, alternating charge transfer salts in which there is some admixing of the complex ground state with the two electron charge transfer excited state will satisfy the criteria for ferromagnetic electron spin coupling proposed by McConnell. In order to investigate this possibility, TMT charge transfer complexes with some of the strongest organic oxidants available have been prepared and are under investigation. The organic compounds used in this study are illustrated in Fig. 2.

Attempts to prepare the TMT:BPTCNQF₈ complex were unsuccessful due to the instability of the neutral acceptor towards polymerization with itself. The more stable BPTCNQF₈⁻² was prepared according to literature methods, and the reaction between $\text{TMT}^{+2}:\text{SO}_4^{-2}$ resulted in the decomposition of TMT^{+2} as evidenced by a rapid color change in solution from dark blue to colorless. No product was isolated. The +2 oxidized state of TMT is susceptible to nucleophilic attack, and the electron rich methylene carbon may be acting as a nucleophile rather than a pi charge transfer donor. Any further effort to produce the desired TMT:BPTCNQF₈ complex will require the use of less traditional synthetic techniques such as electrochemistry. This approach was not pursued at this time.

The acceptor HCTMCP is a very strong organic oxidant which is not readily available in its neutral oxidation state;⁸ however, the tetrabutyl ammonium (TBA) salt is stable and easily handled. The metathesis reaction

ADADADADAD
regular alternating
stack

AAAAAAAAAA
DDDDDDDDDD
segregated stack

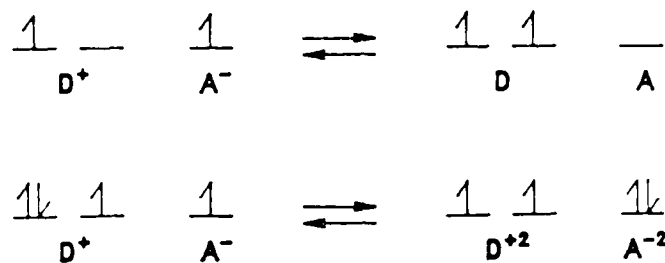
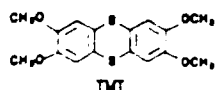


Fig. 1: If one state has a triplet spin configuration then both the ground and excited states will have to be triplets forcing the adjacent acceptor and donor to spin align.

DONOR (Ground State Triplet in the 2⁺ Oxidation State)



ACCEPTORS (Strong Organic Oxidants)

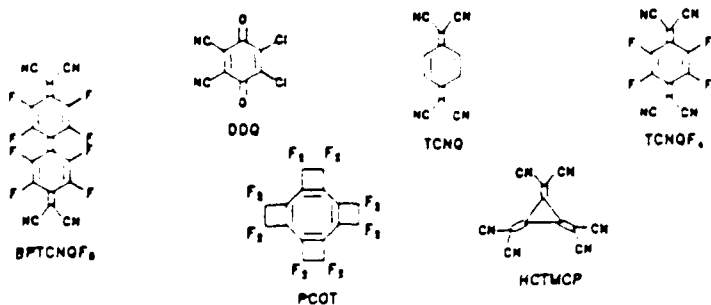
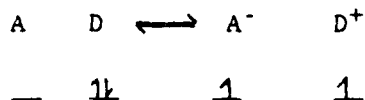


Fig. 2: Donor and Acceptors used in this study.

between TMT:SO₄ and HCTMCP:TBA in acetonitrile produced an immediate color change in the solution from blue to purple. There was no evidence of an isolable charge transfer complex product, and no precipitate formed upon cooling the solution. The reaction was again attributed to a degradative nucleophilic attack rather than the desired metathesis.

Reaction between PCOT and TMT produced a purple crystalline charge transfer complex. Elemental analysis did not indicate a one to one stoichiometry. Accurate analysis of the charge transfer product may have been hindered by the sample decomposition. The available sample of PCOT was very small and in insufficient amounts to repeat the preparation. X-ray diffraction structural analysis was not possible due to disordering within the crystal. The tendency for very large planar molecules to randomly orient within one plane when in a linear stack is very common. Disordering within the chain suggests the stack is not regular; and therefore, the complex is not a good candidate for testing McConnell's model.

The charge transfer salts TMT:DDQ and TMT:TCNQF₄ exhibit a single temperature dependent ESR signal in the $g = 2$ region, which increases exponentially with temperature (See Fig 3.). The room temperature ESR signal indicates some contribution from the forward donation of the equation:



although, the powder pattern spectrum of the complex cannot resolve the

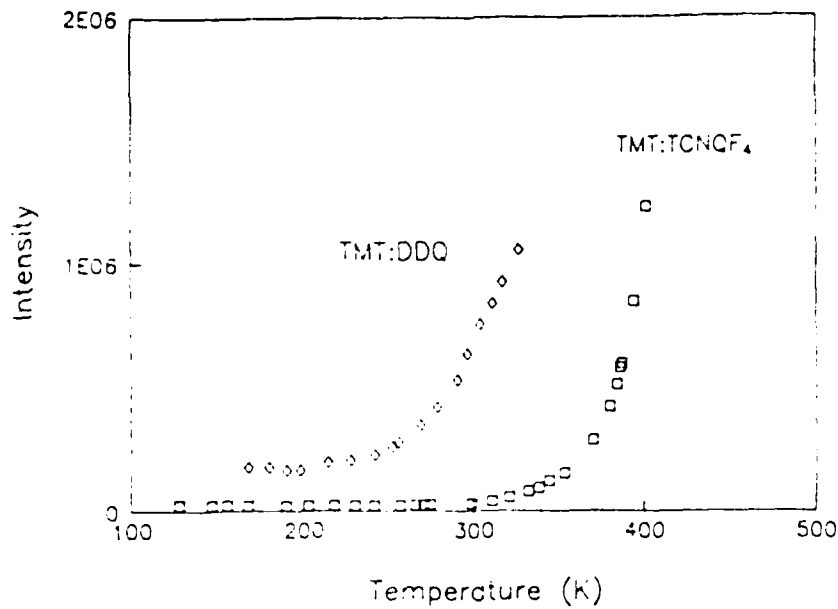


Fig. 3. ESR signal Intensity vs. Temperature for TMT:DDQ and TMT:TCNQF₄.

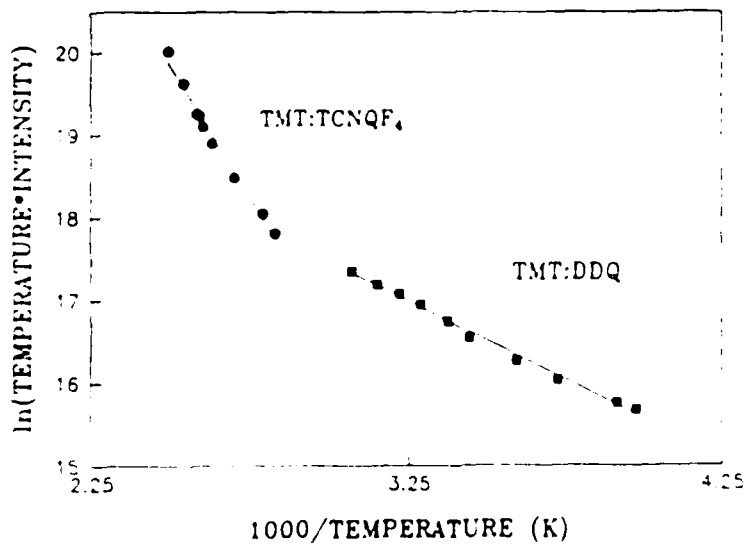


Fig. 4: Activation energies for paramagnetism are calculated from the slope of the line obtained by plotting $\ln(IT)$ vs. $1/T$.

two lines expected for a triplet. The exponential temperature dependence is characteristic of a thermally induced susceptibility. The activation energy of paramagnetism is described by the expression:

$$IT \propto \exp(\Delta E_p/kT)$$

and ΔE_p can be calculated from the slope of the line obtained from the plot of $\ln(IT)$ vs. $1/T$ as illustrated in Fig. 4. The activation energy of paramagnetism has traditionally been a measure of ground state ionic character with a smaller activation energy indicating a large degree of ground state ionic character in the donor acceptor pair. The calculated ΔE_p of TMT:DDQ is .16 eV and that of TMT:TCNQF₄ is .52 eV suggesting a more ionic ground state for the TMT:DDQ complex. Previous studies have found TCNQF₄ to be the better electron acceptor when compared to DDQ in a homologous series.⁹ The observed reversal in this trend may be attributed to structural dissimilarities which can only be determined through X-ray structural analysis.

Attempts to grow crystals of TMT:TCNQF₄ under a variety of conditions invariably resulted in twinning. Crystals grown in a 16 Kgauss field were considerably larger than those produced in the absence of a magnetic field, but the problem with twinning was not resolved. The structure of TCNQ:TMT has been reported to be an alternating stacked charge transfer complex, and the structural similarities between TCNQ and TCNQF₄ make it probable that the TCNQF₄ complex is also an alternating stack.

Crystals of DDQ:TMT suitable for structural determination were grown by the slow diffusion of acetonitrile solutions of each component using an H

tube under N₂ atmosphere.

TMT:DDQ crystals are monoclinic, space group P2/c, with cell dimensions $a = 7.500(1)$, $b = 13.124(2)$, $c = 23.684(3)\text{\AA}$, $\beta = 93.85(1)^\circ$, and $V = 2325.8(5)\text{\AA}^3$. There are four complexed pairs of molecules (FW = 563.44) in the cell and the calculated density is 1.608 mg mm^{-3} .

When examined with X-rays, apparently single crystals were found to be twinned by a rotation of 180° about the a axis, displaying two distinct diffraction patterns which could be independently measured. Calculation of cell dimensions from the two lattices agree to within the experimental precision, and all diffraction spots seen on photographs could be explained by this twinning hypothesis. The twin lattices overlap exactly on the $h=0$ layer, and approximately on the $h=7$ layer. Other layers are distinct. The structure is characterized by segregated stacks of donors and acceptors, as illustrated in fig. 5, unlike the probable alternating structure of TMT:TCNQF₄. The orbital overlap in alternating stacks is significantly different from that of segregated stacks. Because of this, it is not reasonable to predict ground state ionic character on the basis of relative acceptor strengths.

The donor (TMT) is approximately planar overall, though previously reported thianthrenes display two planar halves, folded with a dihedral angle of $125\text{-}135^\circ$.¹⁰ The donor stack displays two distinct (alternating) interplanar distances, 3.30 and 3.92 \AA , between the planes of the central rings of neighboring molecules, and thus appears to be a stack of TMT dimers. The sulfur sulfur interatomic distances of 3.30\AA is less than the Van der Waals Contact distance of 3.7\AA implying some type of molecular orbital interaction between the sulfurs within one dimer. The implication

CRYSTAL STRUCTURE OF TMT:DDQ

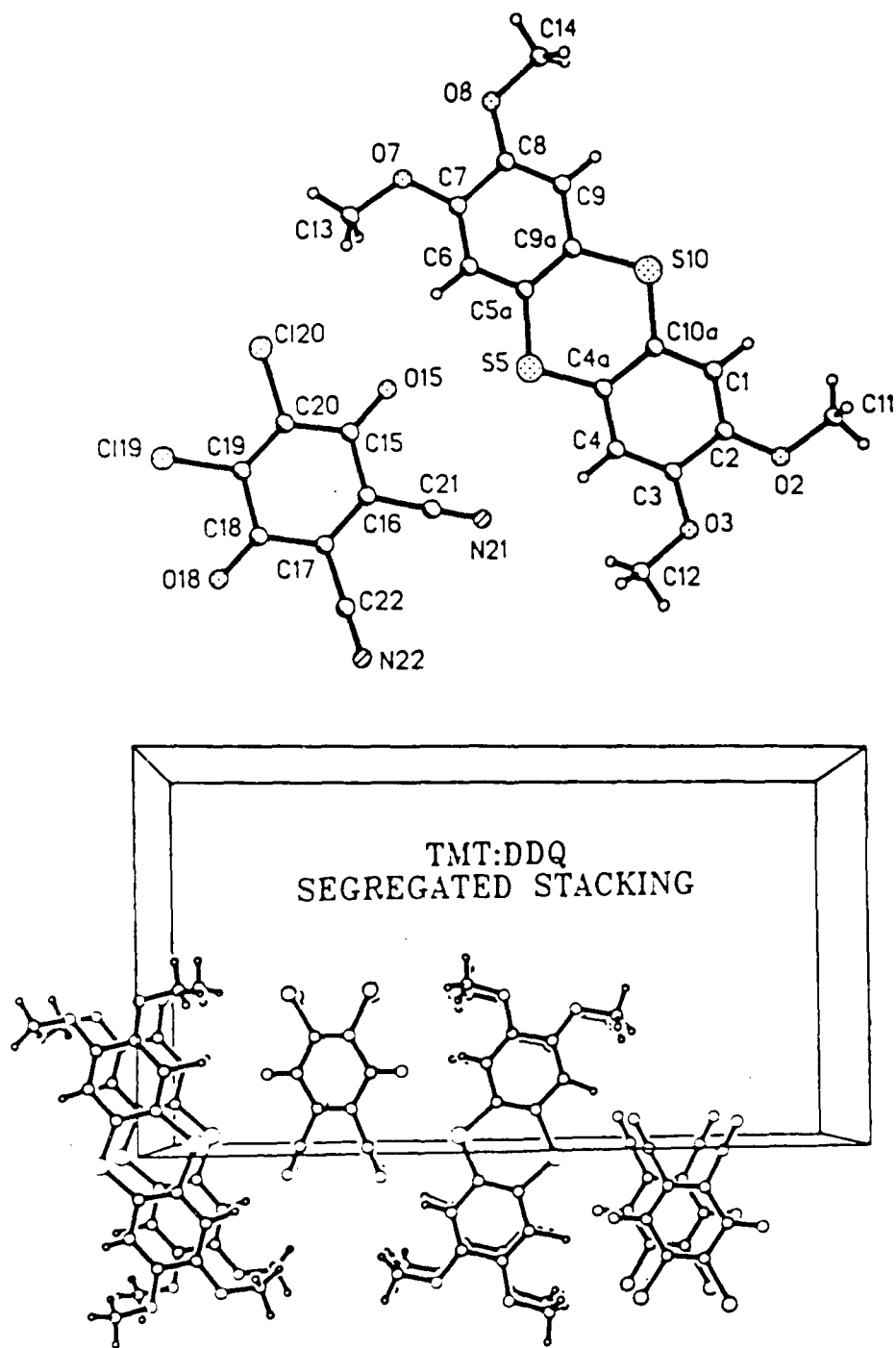


Fig. 5 Structure and packing diagram of TMT:DDQ.

of such an interaction on the electronic and magnetic properties of the complex are not known at this time. A better understanding of the complex orbital makeup and energies will require extensive molecular orbital calculations on the dimers in various configurations. One problem inherent to the investigation of charge-transfer complexes is overcoming the limitations of analyzing solid state properties. Many of the standard techniques of study involve characterizing solutions of the sample. The solvated properties of these complexes of these materials may not be a reliable measure of the solid state magnetic and structural properties. Part of the this year has been devoted to exploring which solid state properties techniques may be useful in characterizing these materials.

A very powerful and often neglected technique is solid state NMR. Utilizing cross polarization and magic angle spinning to overcome problems of linebroadening and poor sensitivity, a solid state NMR study of the TMT complexes of TCNQF₄, TCNQ and DDQ was conducted. The solid state spectra of the following complexes at various cross polarization contact times and spin rates have been recorded: TMT, DDQ, TCNQ, TMT:TCNQF₄, TMT:DDQ, TMT:TCNQ. One feature that distinguishes solid state NMR from that of solution state is the pronounced contributions to the NMR spectral features from dipolar, and quadrupolar interactions among the molecules throughout the sample. This enhances signal to noise and narrows line widths when the complexes contain several methyl groups as does TMT. The presence of the chlorines, nitrogens, and fluorines of the various acceptors reduced the signal to noise through quadrupolar coupling limiting the utility of this technique as a probe of structural and magnetic properties. For this reason, NMR is not the method of choice for

the study this series of complexes.

The Br_2 , SO_4^{-2} , and Cl_2 inorganic salts of TMT were prepared, but satisfactory elemental analysis could not be obtained to verify the compound identity. This could result from the overall instability of the higher oxidation states of TMT. The sulfate salt crystallized as sapphire blue needles, but a diffraction pattern could not be observed.

EXPERIMENTAL

Materials

Solvents were dried and purified using standard methods. DDQ and TCNQ were purchased from Aldrich Chemical Company, and recrystallized from acetonitrile/chloroform three times prior to use. TCNQF_4 was prepared according to the literature,¹¹ and recrystallized from methylene chloride. TMT was prepared by reported methods,¹² and recrystallized from methanol. PCOT was a sample donated by Dr. Bob Soulen.¹³ HCTMCP:TBA and BPTCNQF₈ were prepared and purified according to literature methods.^{8,11}

The TMT:DDQ and TMT:TCNQ complexes were prepared according to the literature.⁶ TMT:TCNQF₄ was prepared by mixing warm equimolar acetonitrile solutions of TMT and TCNQF₄. On standing the complex precipitated as air stable crystals which are dark blue by transmitted light (opaque unless thinner than 10 Microns), and are red by reflected light, with a bright metallic luster. The 1:1 stoichiometry of the new complex, TMT:TCNQF₄, was indicated in UV-VIS studies and by elemental analysis performed by Scharwtzkoff Microanalytical Laboratory (TMT:TCNQF₄, Analysis Calculated for $\text{C}_{28}\text{H}_{16}\text{F}_4\text{N}_4\text{O}_4\text{S}_2$: C, 54.90; H, 2.61; N, 8.84; S, 10.46.

Found: C, 54.58; H, 2.39; N, 8.84; S 10.58.)

Electron Spin Resonance

Variable temperature ESR spectroscopy of powdered samples was measured using a Bruker ER 200D Spectrometer and a Varian variable temperature device. Internal temperatures were measured via an alumel/chromel thermocouple placed three to five millimeters above the sample. Typical power settings ranged from 15 to 30 Decibels, with no power saturation observed in the range of 1 to 30 Db.

X-ray¹⁴

Intensity data were collected from only one of the two twin lattices of a crystal with external size 0.03 x 0.15 x 0.40 mm. An automated Nicolet R3m diffractometer equipped with $\text{CuK}\alpha$ ($\lambda = 1.54183\text{\AA}$) X-rays and an incident-beam graphite monochromator was used. 25 centered reflections within $20 < 2\theta < 72^\circ$ were used for determining cell parameters. Data collection conditions: $2\theta_{\text{max}} = 112^\circ$; range of hkl: $0 < h < 9$. $0 < k < 15$. $-26 < l < 26$. three standards, monitored every 100 reflections with random variation of 2.0% over data collection, $\theta/2\theta$ mode, scan width $[2\theta(k\alpha_1) - 1.0]$ to $[2\theta(k\alpha_2) + 1.0]^\circ$, scan rate a function of count rate (6°min^{-1} minimum, 30°min^{-1} maximum); 3231 reflections measured, 2880 unique, $R_{\text{int}} = 0.014$. Data corrected for Lorentz and polarization effects, and numerical absorption corrections ($\mu = 46.1\text{ cm}^{-1}$) applied based on identification of the faces of the crystal; the shortest and longest dimensions are along b and a respectively.

Structure solved by direct methods, ignoring the twin lattice overlap.

The least-squares refinement used a full-matrix program, the MicroVax version of the SHELXTL system (Sheldrick, 1980). $\text{Sum } w(|F_o| - |F_c|)^2$ minimized where $w = 1/[\sigma^2(|F_o| + g(F_o)^2)]$, $g = 0.000225$, secondary isotropic extinction from $F_c^* = F_c/[1.0 + 0.002(p)F_o^2/\sin 2\theta]^{0.25}$ where $p = 0.004(1)$.

NMR

NMR solid state spectra of DDQ, TMT, TCNQ, TMT:TCNQF₄, TMT:DDQ, and TMT:TCNQ were recorded using a Bruker MSL 300 instrument with a spinning rate of 4000Hz and at 3000Hz and cross polarization times of 50 to 5 microseconds. Pulse delays ranged from 2 seconds with TMT to a longer delay of 60 seconds for DDQ to compensate for lack of protons.

CONCLUSIONS

Organic charge transfer salts of TMT with DDQ, TCNQ, TCNQF₄, were studied in the investigation of organic ferromagnets. No evidence of ferromagnetism was observed in the systems studied. Attempts were made to prepare TMT charge complexes with PCOT, HCTMCP, BPTCNQF₈, but the inherent instability of TMT in its higher oxidation states thwarted these efforts. The recommended course of action to continue this study is to utilize synthetic techniques such as synthetic electrochemistry, to circumvent the reaction of TMT⁺ⁿ with various acceptor salts. Even should the desired new complexes be prepared, the strict requirement of regularity within the complex stacking to produce identical neighbors is very difficult to impose on these systems. Perhaps a more fruitful route would involve the study of radical polymers similar to those thought to contain ferromagnetic domains.^{3,4}

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14. X-ray structural determination performed by Dr. Richard Gelardy and Dr. Judy Flippin-Anderson, at the Naval Research Labs.

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