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Synthesis and Magnetic Properties of a Mix-Stacked Charge-Transfer Complex of Triplet Donor 2,3,6,7,10,11-Hexamethoxytriphenylene and Symmetrical Acceptor Tris(dicyanomethylene)cyclopropane

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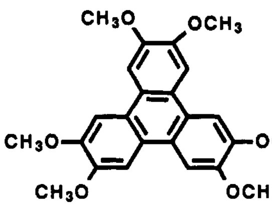
We succeeded in the preparation of single crystals of HMT–HCTMC complex from neutral tris(dicyanomethylene)cyclopropane. The complex was found to consist of a mix-stacked structure with triplet donor HMT and symmetrical acceptor HCTMC molecules alternating along both the stacking *c* axis and the [120] direction in the *ab* plane. This structure along with a one-electron charge transfer between HMT and HCTMC makes it a good complex model for the study of Breslow's approach for organic ferromagnetism. As a result, the analysis of static magnetic susceptibility data of the HMT–HCTMC complex has not let to the realization of positive interspin interactions between D^+ and A^- radicals. The negative Weiss temperature Θ of -14 K indicated that the intermolecular spin interactions in this complex are highly antiferromagnetic in nature.

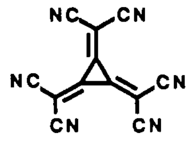
Introduction

The extended π-orbital overlap in organic charge-transfer complexes comprising stacks of planar anionic radical and cationic radical has been demonstrated to promote various electronic phenomena along the molecular stacking direction and exhibit distinctive high conductivities.[1] However, the effective intrastack orbital interactions without activating spin alignment often induce antiferromagnetic couplings between adjacent alike anionic or cationic radicals, making them diamagnetic or weakly paramagnetic in the bulk phase. An inherent ferromagnetic interaction between neighboring spins is essential to produce an enhanced magnetic ordering in solids. It remains as a challenge to design organic neutral or ionic radical molecules or polymers displaying cooperative long-range intermolecular spin ordering throughout the materials. A theoretic model describing a spin-exchange stabilization principle for extended ferromagnetic intermolecular interactions has been proposed by McConnell.[2] This spin-exchange mechanism was further modified by Breslow[3] to propose a practical approach for the stabilization of ferromagnetic coupling between molecular monoionic spins. It composes a concept of arraying an alternate mixing of monocationic donors and monoanionic acceptors into a $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ chain, so that the further charge transfer between $D^{\bullet+}$ and $A^{\bullet-}$ favors the formation of an excited triplet state of one of the partners leading such parallel spin correlations to possible long-range positive spin coupling.

Here we report the synthesis and magnetic properties study of a charge-transfer complex derived from a triplet donor of 2,3,6,7,10,11-hexamethoxytriphenylene (HMT, 1) and a symmetrical acceptor tris(dicyanomethylene)cyclopropane (HCTMC, 2). This complex possesses well-defined stacks of alternate donor and acceptor as confirmed from its crystal structure and one-electron charge transfer between HMT and HCTMC. It represents an ideal molecular configuration for the study of the Breslow's approach which predicts a mechanism of ferromagnetic intermolecular interactions between $D^{\bullet+}$ and $A^{\bullet-}$.[4]



1, HMT



2, HCTMC

Experimental Section

All melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra were measured with either a Bruker 360 spectrometer or a JEOL FX-100 Fourier transform spectrometer. Infrared spectra were recorded with a Perkin-Elmer 783 instrument. UV spectra were recorded with an IBM 9430 UV–visible spectrophotometer. Sodium hydride, malononitrile, tetrachloropropane, trifluoroacetic acid, nitrosonium tetrafluoroborate, and veratrole were purchased from Aldrich Chemical Co. and used as received. Tetrahydrofuran was filtered through dry alumina and then freshly distilled from sodium and benzophenone under N_2 prior to use. Both acetonitrile and methylene chloride were distilled from CaH_2 under N_2. The syntheses of neutral tris(dicyanomethylene)cyclopropane and its complexation with 2,3,6,7,10,11-hexamethoxytriphenylene were performed in a glovebox with argon as an inert gas.

The static magnetic susceptibility data were obtained with a Faraday magnetometer (4–300 K) and a vibrating sample magnetometer (1.3–4.2 K), where the significant contribution of ferromagnetic impurities to the measured magnetizations were corrected for via magnetization vs magnetic field isotherms at several temperatures for each sample. The spin densities (n) were computed from the molar Curie constant C_M using the relation $C_M = N_{A}g^2S(S+1)\mu_B{}^2/3K_B$, where N_A is a Avogadro's number, μ_B is the Bohr magneton, K_B is Boltzmann's constant, and where we have assumed the Lande factor $g = 2$ and spin $S = {}^1/_2$.

X-ray Diffraction Studies. The structural measurement of HMT–HCTMC crystal was made on a computer-controlled four-circle Nicolet autodiffractometer with Nickel-filtered Cu Kα ($\lambda = 1.54184$ Å) radiation and a 12-kW rotating anode generator. A dark blue needle crystal in hexagonal prism shape having approximate dimensions of 0.18 × 0.18 × 0.96 mm mounted on a thin glass fiber having a tip diameter of 0.15 mm was used for

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the measurement. The crystal was oriented with its longest edge nearly parallel to the ϕ axis of the diffractometer. A total of 2745 independent reflections were collected at 20 ± 1 °C using the θ–2θ scan technique to a maximum 2θ value of 120° (the equivalent of 0.65 limiting Cu Kα spheres). The data were corrected for Lorentz and polarization effects. The structure was solved using direct methods techniques with the Nicolet SHELXTL-PLUS software package as modified at Crystalytics Co. The resulting structural parameters have been refined to convergence $\{R_u$(unweighted, based on F) = 0.086 for 1731 independent data having 2θ(Cu Kα) $< 120°$ and $I > 3\sigma(I)\}$ using full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for the six non-methyl-hydrogen atoms. The water molecule of crystallization appears to be slightly disordered (or present only part of the time); the occupancy factor of an oxygen atom at the position specified by O_w refined to a final value of 0.89 (2). Hydrogen atoms were included in the structure factor calculations as idealized atoms on their respective carbon atoms by assuming sp^2 hybridization of the carbon atoms and C–H bond lengths of 0.96 Å. The isotropic thermal parameter of each hydrogen atom was fixed at 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which it is covalently bonded. The methyl hydrogen atoms could not be located or refined.

The model of molecular packing and the atom labeling, intramolecular bond lengths, and intramolecular bond angles for HMT–HCTMC–$(H_2O)_{0.89}$ (complex **3**) can be found in Figure S1 and Tables S1 and S2, respectively (supplementary material; see paragraph at end of paper). Tables of atomic coordinates, the anisotropic thermal parameters, torsion or conformation angles, and intermolecular nonbonded distances for **3** are provided in the Tables S3, S4, S5, and S6, respectively. Structural factor amplitude tables for $C_{24}H_{24}O_6$–$C_{12}N_6$–$(H_2O)_{0.89}$ (**3**) are available in Table S7.

2,3,6,7,10,11-Hexamethoxytriphenylene (HMT, 1). The synthetic procedure was modified from the Musgrave's method.[5] The isolated product was purified by chromatography and recrystallized from a chloroform–ethanol/5:1 solution to give white needle crystals of HMT in 42% yield, mp 312–14 °C; ^{1}H NMR ($CDCl_3$) δ 4.1 (s, 18 H) and 7.71 (s, 6 H); ^{13}C NMR ($CDCl_3$ and solid state) 54.0, 56.6, 103.8, 123.6, and 149.4 ppm; IR (KBr) ν_{max} 2996, 2940, 2840, 1640, 1518, 1462, 1436, 1418, 1265, 1210, 1182, 1155, 1050, 1023, 975, 835, and 780 cm^{-1}.

Tris(dicyanomethylene)cyclopropane (HCTMC, 2). The synthetic procedure was modified from the Fukunaga's method,[6] and all the reaction sequences were carried out in a Plexiglass glovebox under an inert atmosphere. Bis(tetra-*n*-butylammonium) tris(dicyanomethylene)cyclopropanediide, $(Bu_4N^+)_2HCTMC^{2-}$ (2.86 g, 4.0 mmol) dissolved in trifluoroacetic acid (100 mL) was treated with nitrosonium tetrafluoroborate, $NO^+BF_4^-$ (1.03 g, 8.8 mmol). The mixture was stirred at ambient temperature until the disappearance of the blue color was observed to give bright yellow precipitates. The precipitates were filtered through a fine frit glass, washed repeatedly with a mixture of trifluoroacetic acid and acetonitrile, and dried under vacuum to afford tris(dicyanomethylene)cyclopropane (**2**) as a yellow powder in 76% yield (695 mg); IR (KBr) ν_{max} 2215 (s), 2202, 1563 (s), 1483 (w), 1220, 1060, and 577 cm^{-1}.

Charge-Transfer Complex of 2,3,6,7,10,11-Hexamethoxytriphenylene and Tris(dicyanomethylene)cyclopropane, HMT–HCTMC (3). The reaction procedure was carried out under an inert atmosphere in the Vacuum Atmospheres Dri-Lab HE-43 glovebox fitted with a HE-493 Dri-Train and AO 316-C oxygen analyzer. 2,3,6,7,10,11-Hexamethoxytriphenylene (408 mg, 1 mmol) was dissolved in a chloroform solution (100 mL) at the refluxing temperature of chloroform. In a separated flask tris(dicyanomethylene)cyclopropane (228 mg, 1 mmol) was suspended in an acetonitrile solution. These two solutions were mixed together and stirred at ambient temperature for 2–4 h to give a deep blue solution with dark precipitates. The mixture was then cooled to 0 °C to cause the precipitation of purple-blue microcrystalline solids. The precipitation was completed by a further evaporation of solvents. The resulting solids were repeatedly washed with a cool mixture of methylene chloride–acetonitrile/1:1 (20 mL) to afford HMT–HCTMC (**3**) as a dark blue complex in 81% yield (515 mg). Elemental analysis indicated that the composition of complex **3** is best fit with a unit formula of HMT–HCTMC–H_2O. Anal. Calcd for $C_{36}H_{26}N_6O_7$: C, 66.05; H, 4.0; N, 12.84; O, 17.11. Found: C, 65.63; H, 3.89; N, 12.58; O, 17.90. IR (KBr) ν_{max} 3453, 2932, 2829, 2209, 2195, 2176, 1618, 1517, 1465, 1419, 1263 (s), 1207, 1195 (w), 1158, 1048, 843, and 779 cm^{-1}; UV (CH_3CN, absorbance) 672 (1.19), 598 (0.81), 542 (sh, 0.44), and 320 nm; ^{13}C NMR (acetone-d_6, weak peaks) 56.2, 81.8, 106.1, and 150.1 ppm; ^{1}H NMR (CD_3CN, weak peaks) δ 4.12 (br s, 18 H) and 7.94 (br s, 6 H).

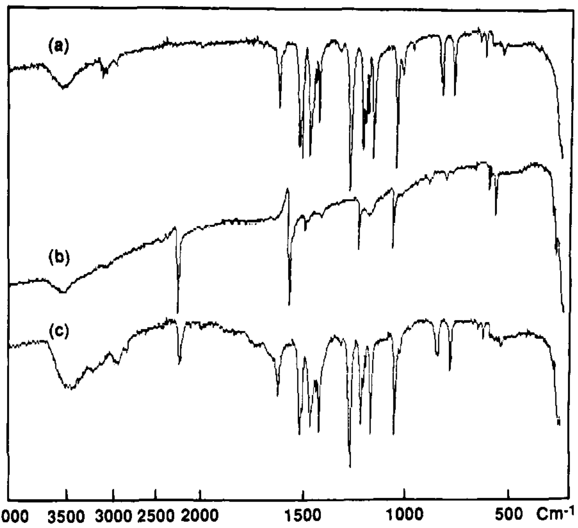

Figure 1. Infrared spectra of (a) neutral HMT, (b) neutral HCTMC, and (c) HMT–HCTMC complex (**3**).

Hexagonal prismlike needle crystals of HMT–HCTMC were prepared as follows: The solid of HMT–HCTMC complex was dissolved in a solvent mixture of chloroform and acetonitrile (1:1) at ambient temperature. The solubility of freshly prepared HMT–HCTMC complex in this solvent mixture is roughly 0.6 mg/mL. The blue solution was filtered through Celite to remove insoluble residual solids. The crystal of complex **3** can be grown by a slow evaporation of solvents under N_2. Elemental analysis indicated that these needle crystals have a nearly identical chemical composition as that of a poor crystalline form of complex **3**, with a small variation of H_2O.

Results and Discussion

The synthesis of 2,3,6,7,10,11-hexamethoxytriphenylene was carried out by a trimerization of veratrole in the presence of sulfuric acid.[5] A pure sample of HMT can be obtained by a repeated chromatographic fractionation, followed by recrystallization from a solvent mixture of chloroform and ethanol. The synthesis of neutral tris(dicyanomethylene)cyclopropane ($HCTMC^0$) was performed by the oxidation reaction of bis(tetra-*n*-butylammonium) tris(dicyanomethylene)cyclopropanediide, $(Bu_4N^+)_2HCTMC^{2-}$, prepared by the reported procedure,[6] with nitrosonium tetrafluoroborate, $NO^+BF_4^-$ (2.2 equiv) in trifluoroacetic acid at ambient temperature. The resulting insoluble bright yellow $HCTMC^0$ was found to be reasonably stable under N_2 in the presence of a trace amount of trifluoroacetic acid. It can be stored in glovebox over a period of several weeks. A sharp decrease of stability was observed on the acid-free HCTMC molecule with a visible darking of the sample within several hours. The neutral HCTMC exhibited a simple infrared spectrum with five absorption bands at 2215, 1563, 1220, 1060, and 577 cm^{-1}, as shown in Figure 1b, consistent with those reported

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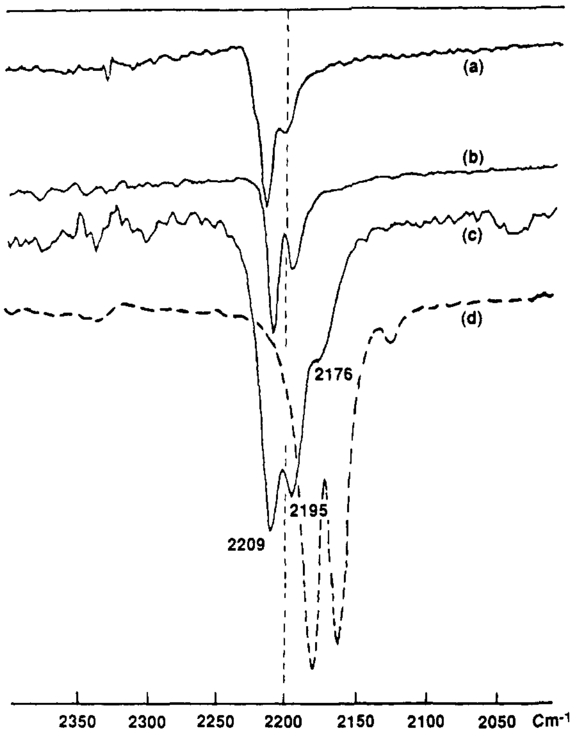

Figure 2. Infrared spectra showing the expanded CN stretch of (a) neutral HCTMC, (b) monoanionic HCTMC–TBA, (c) HMT–HCTMC complex (**3**), and (d) dianionic HCTMC–$(TBA)_2$.

previously.[6] The cyano frequency of $HCTMC^0$ shows two peaks at 2215 and 2202 cm^{-1}.

The charge-transfer complex of HMT and HCTMC was prepared by the treatment of 2,3,6,7,10,11-hexamethoxytriphenylene in chloroform solution with neutral HCTMC suspended in acetonitrile solution under an inert atmosphere. The hexagonal prismlike needle crystals were grown from a solution mixture of chloroform and acetonitrile by a slow evaporation of solvent. During the complexation process, the HMT–HCTMC complex was found to absorb a fraction of a water molecule from the solution medium. The water content was detected by both the elemental analysis of bulk microcrystalline solids and the single-crystal structure determination. Presumably, the source of the water molecule can be traced back to that in trifluoroacetic acid, which was used as a solvent as well as a stabilizer in the preparation of neutral HCTMC. The elemental analysis of the complex is in good agreement with a chemical composition of HMT–HCTMC–H_2O (**3**). The infrared spectrum of complex **3** (Figure 1c) showed all the characteristic peaks of HMT, in close resemblance to Figure 1a, and a band at 2205 cm^{-1} corresponding to the cyano frequency of HCTMC moiety in the complex. The extended spectrum of this cyano band, as shown in Figure 2c, displays three peaks at 2209, 2195, and 2176 (sh) cm^{-1}, which are nearly identical to the two major peaks at 2209 and 2195 cm^{-1}, and a small shoulder at 2182 cm^{-1} of tetra-*n*-butylammonium salt of monoanionic HCTMC (Figure 2b). These peaks can be differentiated clearly from those of the tetra-*n*-butylammonium salt of dianionic HCTMC complex at 2182 and 2163 cm^{-1} (Figure 2d). In addition, the UV–visible spectrum of HMT–HCTMC in acetonitrile showed three absorption bands at 672, 598, and 320 nm and a shoulder centered at roughly 542 nm. This spectrum can be superimposed with that of monoanionic TBA–HCTMC as shown in Figure 3. These spectroscopic data along with the cyano frequency analysis allowed us to conclude that the complex **3** involves one-electron transfer from HMT to HCTMC.

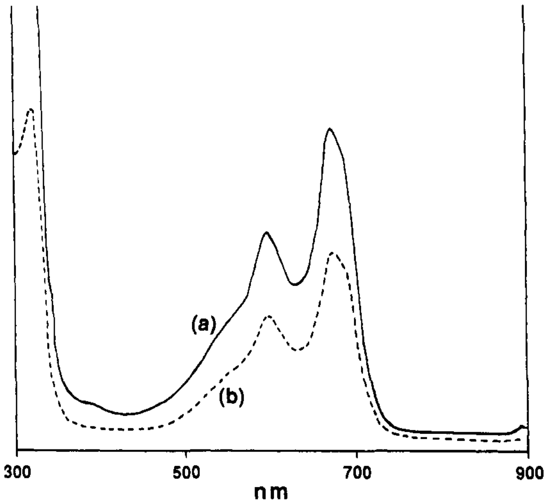

Figure 3. UV–vis spectra of (a) HMT–HCTMC complex (**3**) and (b) monoanionic HCTMC–TBA in CH_3CN.

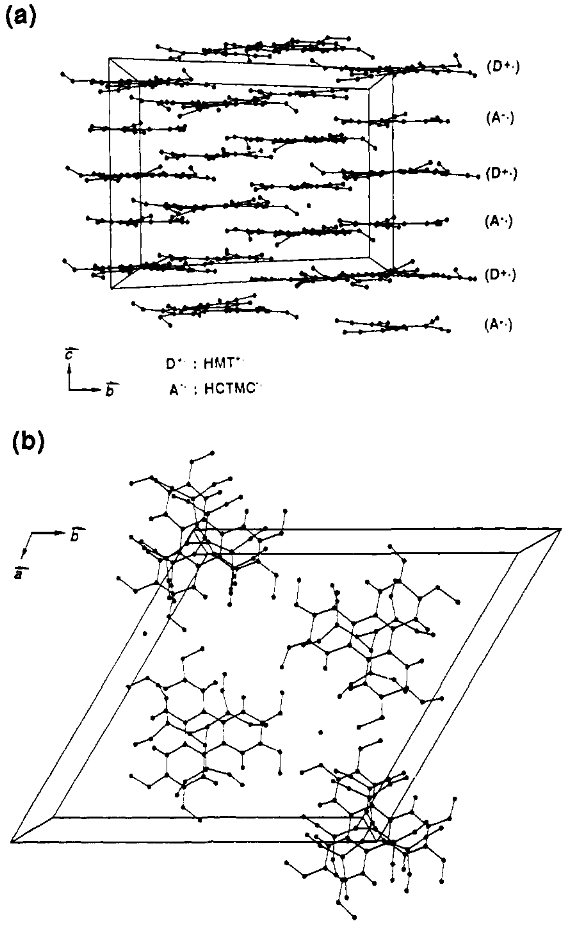

Figure 4. Molecular packing diagram of HMT–HCTMC (a) showing a perspective view of the $\cdots D^+A^-D^+A^-\cdots$ stacking arrangement along the *c* axis and (b) viewing down the $\cdots D^+A^-D^+A^-\cdots$ stacking *c* axis.

The X-ray single-crystal structure data are summarized as follows: Cell constants and an orientation matrix for the data collection, obtained from the least-squares refinement, corresponded to a trigonal cell with dimensions a = 21.094 (5) Å, b = 21.094 (5) Å, c = 13.584 (1) Å, and γ = 120.00°. The crystal is bounded by the planes {001}, {010}, {100}, and {110}. Crystallographic details are presented in Table I. Systematic absences and the subsequent least-squares refinement determined the space group to be $P3c1$–C^3_{3v} (No. 158) with a cell consisting of six formula

Table I. Crystallographic Parameters for HMT–HCTMC Complex, $\{C_6H_2(OCH_3)_2\}_3\{C_2(CN)_2\}_3$–$(H_2O)_{0.89}$

formula	$\{C_6H_2(OCH_3)_2\}_3\{C_2(CN)_2\}_3$–$(H_2O)_{0.89}$
formula wt, amu	652.7
cryst syst	trigonal
space group	$P3c1$–C^3_{3v} (No. 158)
a, Å	21.094 (5)
b, Å	21.094 (5)
c, Å	13.584 (1)
γ, deg	120.00
V, Å^3	5237 (1)
Z	6 formula units
D_{calc}, g/cm^3	1.242
linear abs coeff, mm^{-1}	0.69
2θ(max), deg	120
function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
least-square wts	$w^{-1} = \sigma^2(F) + 0.0009F^2$
total no. of reflns measd	2745
unique no. reflns measd	2745
no. of observations	1731 ($I > 3\sigma(I)$)
no. of variables	442
residuals R_u; R_w	0.086; 0.115
max peak in final difference Fourier, e$^-$/Å^3	0.42
largest difference hole, e$^-$/Å^3	−0.33

units in a general position of the unit cell. The molecular packing diagram of HMT–HCTMC showing a perspective view of the $\cdots D^+A^-D^+A^-\cdots$ stacking arrangement along the c axis is depicted in Figure 4a. A similar D–A alternating arrangement is also observed along the [120] direction in the ab plane as shown in Figure 4b.

The magnetic properties of complex 3 were studied with a Faraday magnetometer. The ferromagnetic impurities of these samples were determined, via magnetization vs magnetic field isotherms at several temperatures, to be less than 4 ppm of ferromagnetic iron metal atom equivalent. The temperature dependence of reciprocal magnetic susceptibilities of HMT–HCTMC complex, after the correction of ferromagnetism due to impurities and diagmagnetic susceptibilities, were found to follow approximately a linear Curie–Weiss relationship below 250 K as shown in Figure 5b. The molar Curie constant C_M and Weiss temperature Θ, obtained from the Curie–Weiss fitting between 4 and 220 K, were found to be 0.121 and −14 K, respectively. This molar Curie constant can be correlated to an observed residual spin density of about 0.3 spins $^1/_2$ per complex. However, the large negative Θ indicated that the intermolecular spin interactions in this complex are highly antiferromagnetic in nature. The presence of this antiferromagnetic intermolecular spin coupling can also be indicated clearly in the temperature dependence plot (Figure 5a) of the product of molar susceptibility (χ_M) and temperature (T), where χ_MT of 3 display a sharp decrease below 50 K.

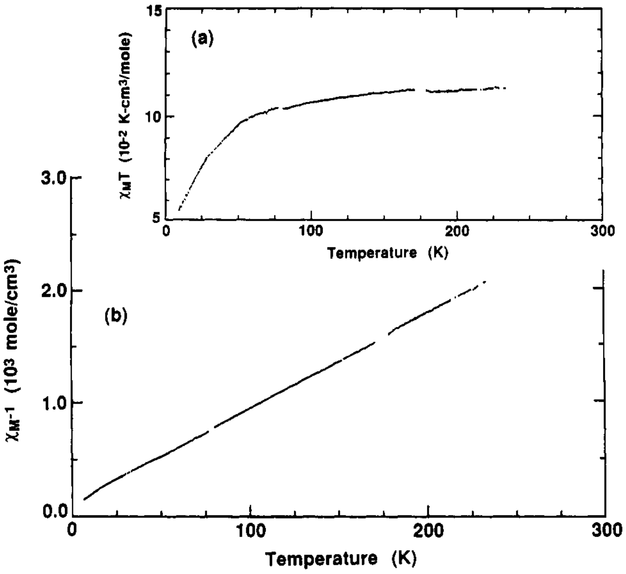

Figure 5. Temperature dependence of (a) the product of molar susceptibility and temperature and (b) reciprocal magnetic susceptibilities of HMT–HCTMC complex (3) from 2 to 250 K.

Conclusion

We succeeded in the preparation of single crystals of HMT–HCTMC complex from neutral tris(dicyanomethylene)cyclopropane. The complex was found to consist of a mix-stacked structure with triplet donor HMT and symmetrical acceptor HCTMC molecules alternating along both the stacking c axis and the [120] direction in the ab plane. This structure along with the one-electron charge transfer between HMT and HCTMC makes it a good complex model for the study of Breslow's approach for organic ferromagnetism. As a result, the analysis of static magnetic susceptibility data of the HMT–HCTMC complex has not let to the realization of positive interspin interactions between D^+ and A^- radicals. In this particular complex composition, partial disordered water in crystal might play a role in determining the spin coupling mechanism.[7]

Acknowledgment. We thank Crystalytics Co. for the X-ray data collection and the structure refinement. We also thank H. E. King of Exxon Research and Engineering Co. for the discussions on the crystal X-ray diffraction data. We are also grateful to the National Science Foundation for the partial financial support (Grant DMR 88-22532) of this work.

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