IV-C Magnetic Organic Superconductors and Related Systems

Molecular materials are expected to play an important role in the future development of electronic devices. For the realization of molecular electronic devices, it is essential to develop a “dual-action system” whose conducting properties can be sharply controlled by external forces. One of the prospective dual-action molecular system is a composite system consisting of organic layers responsible for electron conduction and inorganic layers with localized magnetic moments, whose conductivity can be controlled by tuning magnetic state of the inorganic layers. We have recently discovered the first example of dual-functional magnetic organic conductor whose superconducting state can be sharply switched on or off by controlling the metamagnetic transition of the magnetic anion layers. In addition to the dual functionality of molecular conductors, the field-induced superconductivity of the organic conductors reported by us in 2001 has attracted an increasing interest. In organic systems, there are two well-known conductors showing field-induced superconducting transition: Chevrel type compound $Eu_{0.75}Sn_{0.25}Mo_6S_{7.2}Se_{0.8}$ and heavy Fermion system $CePb_3$. Unlike these inorganic conductors, λ-$(BETS)_2FeCl_4$ has an antiferromagnetic insulating ground state. That is, λ-$(BETS)_2FeCl_4$ is the first conductor exhibiting the insulator → metal → superconductor transitions with increasing magnetic field. We have recently discovered that the first antiferromagnetic organic superconductor, κ-$(BETS)_2FeBr_4$ undergoes a field-induced superconductiviting transition. The field-induced superconductivity seems to be a common feature of the organic superconductor with localized magnetic moments in the anion layers.

IV-C-1 An Indication of Magnetic-Field-Induced Superconductivity in a Bi-Functional Layered Organic Conductor, κ-$(BETS)_2FeBr_4$

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[*J. Am. Chem. Soc.* **124**, 6816 (2002)]

We have investigated BETS conductors, λ- and κ-$(BETS)_2FeX_4$ (X = Cl and Br), and reported several interesting properties, such as the novel magnetic-field-induced superconductivity under very high magnetic field (18 T < H < 41 T) in λ-$(BETS)_2FeCl_4$. Here we report the magnetoresistance of the antiferromagnetic organic superconductor, κ-$(BETS)_2FeBr_4$ up to 15 T and the observation of the onsets of the magnetic-field-induced superconductivity as the cooperative phenomena between the superconductivity and magnetism. As shown in the upper inset of Figure 1, with an increase of the applied magnetic field at 0.58 K, the resistivity suddenly increased at about 1.6 T for the magnetic field applied parallel to the *a* axis (// easy-axis), and the system recovered its metallic state. These results suggest that the internal field originated from the AF coupling between the π electrons and the ferromagnetically aligned Fe^{3+} spins, which was sharply induced at 1.6 T, destroyed abruptly the superconducting state. In addition, a conspicuous resistivity decrease was observed just below the abrupt resistivity increase at 1.6 T. This decrease around 1.6 T suggests the compensation of the external field by the internal field created by Fe^{3+} spins and the stabilization of the superconducting state. Further anomalies were observed at 10–15 T below 0.75 K both for $H//a$ and $H//c$ as shown in Figure 1. The resistivity changes between 1.19 K (the normal state) and the lowest measured temperatures strongly suggest the onset of the magnetic-field-induced superconductivity around 12.5 T. Because of the existence of the metamagnetic transition which makes this system a dual functional material and gives rise to the field-induced resistivity decreases suggesting the stabilization of the superconducting state at two characteristic magnetic fields of 1.6 T and 12.5 T.

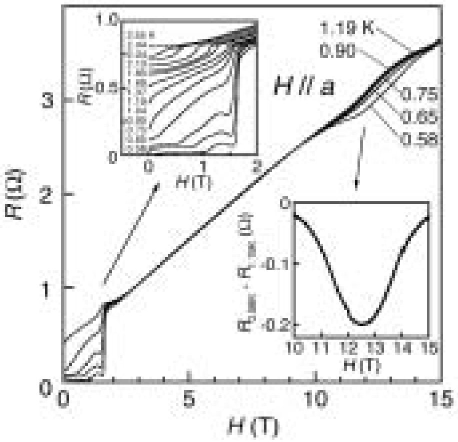

Figure 1. Magnetic field dependence of the magnetoresistance up to 15 T at the indicated temperatures in the figures with an application of the magnetic field in parallel with the *a* axis. The upper inset is the data measured between 0 T and 2 T. The lower insets are the resistivity differences between the data at 1.19 K and one at the lowest measured temperature (0.58 K).

IV-C-2 Dual-Action Molecular Superconductors with Magnetic Anions

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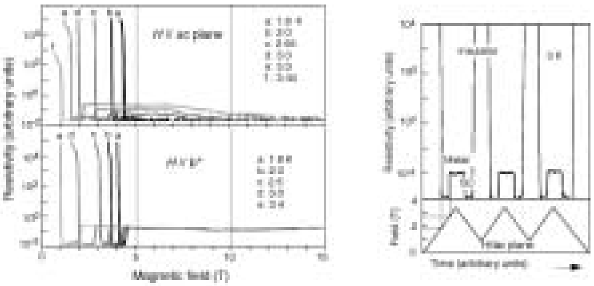
[*J. Am. Chem. Soc.* **124**, 9982 (2002)]

Recently, the reports on the marvelous field-effect switching between insulating and superconducting states, which is the widest possible variation of electrical properties of materials, have attracted an extremely large attention though it has not been reconfirmed yet. We have found that similar switching phenomena can take place in bulk organic superconductors with magnetic anions. It is easily imagined that the superconducting state will be broken if the magnetic moments in the anion layers are forced to orient ferromagnetically. We found that the unprecedented combination of metamagnetism and organic superconductivity is realized in the first antiferromagnetic organic superconductor, κ-$(BETS)_2FeBr_4$ (BETS = bis(ethylenedithio) tetraselenafulvalene) and observed the superconducting state to be sharply switched on or off by controlling the magnetic state of the anion layers by external field (the critical magnetic field of metamagnetic transition is 1.6 T). More novel switching phenomena was also found in the other modification of BETS salts. As reported before, the diluted magnetic anion system, λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ ($0.35 < x < 0.5$) undergoes metal → superconductor → insulator transitions with lowering temperature ($T_c \approx$ 4 K, $T_{SC\rightarrow Ins} \approx$ 3.4 K). We measured the magnetoresistance up to 15 T at $T <$ 3.4 K. When magnetic field was applied to the direction perpendicular to the *ac* conduction plane, the insulator → superconductor → metal transitions were observed with increasing magnetic field. While for the field perpendicular to the *ac* conduction plane, the insulator → superconductor → metal → superconductor transitions and insulator → superconductor transition took place at $2.5 < T < 3.4$ K and $T <$ 2 K, respectively. *T-H* phase diagram indicates that the field induced superconducting phase appear around 14 T. Owing to the unique phase diagram with narrow superconducting region neighboring both insulating and metallic phases, the sharp insulator ⇆ superconductor ⇆ metal switching can be realized by modulating the external magnetic field.



(a) (b)

Figure 1. (a) The magnetoresistance of λ-$(BETS)_2Fe_{0.4}Ga_{0.6}$-Cl_4 up to 15 T at 1.6–3.4 K for the magnetic fields parallel and perpendicular to the conduction plane. (b) An example of the insulator-superconductor-metal triple step switching behavior of λ-$(BETS)_2Fe_{0.4}Ga_{0.6}Cl_4$ coupled with the periodic modulation of magnetic field around 2.5 T (*H*//*ac* plane) at 3 K.

IV-C-3 A Series of Organic Conductors κ-$(BETS)_2FeBr_xCl_{4-x}$ ($0 \le x \le 4$) Exhibiting Successive Antiferromagnetic and Superconducting Transitions

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[*Adv. Mater.* **14**, 1376 (2002)]

In contrast to λ-type salt, where the crystals of λ-$(BETS)_2FeBr_xCl_{4-x}$ are obtained only for small *x*-range ($x <$ 1.0), Br and Cl atoms are exchanged freely in κ-type salts κ-$(BETS)_2FeBr_xCl_{4-x}$ ($0 \le x \le 4$). Therefore, the magnetic and superconducting properties of κ-type salt can be changed continuously in the wide range. In this paper, we have examined the *x*-dependence of the electromagnetic properties of a series of the antiferromagnetic organic superconductors, κ-$(BETS)_2FeBr_x$-Cl_{4-x} ($0 \le x \le 4$). By collecting the experimental results of the electrical resistivities and magnetic susceptibilities, the temperature *vs.* *x*-value phase diagram of κ-$(BETS)_2FeBr_xCl_{4-x}$ ($0 \le x \le 4$) was obtained. Both superconducting and antiferromagnetic transition temperatures are lowered with decreasing *x*. It is interesting that the lattice constants *a* and *c* in the conduction plane exhibit small *x*-dependences, in spite of the strong *x*-dependence of resistivity behavior. In addition, despite of the shortening of the lattice constant along the direction perpendicular to the conduction plane (//*b*), the magnetic interaction tends to be decreased with increasing the Cl content, suggesting the importance of the intermolecular magnetic interaction through the Br atom.

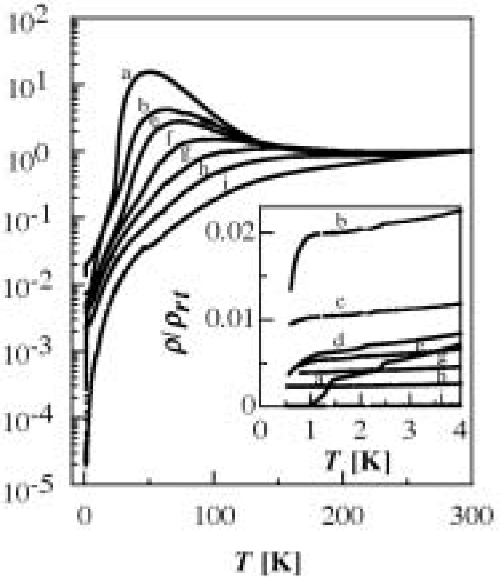

Figure 1. Temperature dependences of electrical resistivities of κ-$(BETS)_2FeBr_xCl_{4-x}$. a: x = 4, b: x = 3.86, c: x = 3.54, d: x = 3.43, e: x = 2.96, f: x = 2.82, g: x = 1.69, h: x = 1.04 and i: x = 0. The inset shows the resistivity behavior at low temperature region.

IV-C-4 Magnetic Molecular Conductors Based on BETS Molecules and Divalent Magnetic Anions [BETS = Bis(ethylenedithio)-tetraselenafulvalene]

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[*Inorg. Chem.* **41**, 3230 (2002)]

Several conducting salts based on BETS molecules and divalent magnetic anions such as the $(CoCl_4)^{2-}$, $(CoBr_4)^{2-}$ and $(MnBr_4)^{2-}$ were prepared. Electrocrystallization by using the $(CoCl_4)^{2-}$ anion gave two kinds of crystals. Block-shaped crystals were cleared to be $(BETS)_2CoCl_4$, which is an insulator with the high-spin state of cobalt 3*d* spin. On the other hand, the X-ray crystal structure analysis of a plate-shaped crystal of the $(CoCl_4)^{2-}$ salt revealed the system to be κ-$(BETS)_4CoCl_4(EtOH)$, which is metallic down to 0.7 K. The electronic band structure calculation gave a typical two-dimensional cylindrical Fermi surface. However, there is only very weak antiferromagnetic interaction between the s = 3/2 cobalt 3*d* spins due to its anion-solvent-intermingled layer structure. On the other hand, the electrocrystallization by using the $(MnBr_4)^{2-}$ anion yielded the plate-shaped black crystals of the $(MnBr_4)^{2-}$ salt. Crystal structure analysis of the $(MnBr_4)^{2-}$ salt showed that the salt is θ-$(BETS)_4MnBr_4(EtOH)_2$ with alternating the donor and anion/solvent mixed layers. The stacking direction in one donor layer is perpendicular to those of the neighboring layers. The electrical and magnetic properties of the θ-$(BETS)_4MnBr_4(EtOH)_2$ salt showed the metallic behavior down to *ca.* 30 K and the paramagnetism of the high-spin manganese 3*d* spins. Band structure calculation of this salt gave an elliptical cylindrical Fermi surface. Since the Fermi surfaces of the adjacent donor layers are rotated to each other by 90°, the θ-$(BETS)_2MnBr_4(EtOH)_2$ salt becomes a two-dimensionally isotropic metal.

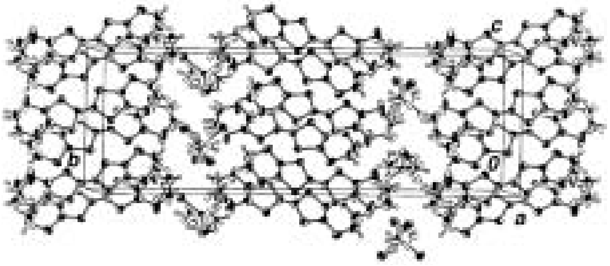

Figure 1. Crystal structure of κ-$(BETS)_4CoCl_4(EtOH)$.

IV-C-5 Crystal Structure of $BETS^{2+}$ Dication Salt $(BETS)TlCl_5$ and Formal Charge Dependence of Bond Lengths of $BETS^{+Q}$ (Q = 0–2)

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([1]Univ. Tokyo; [2]Inst. Chem., China)

It is necessary to find out the BETS salt with higher oxidation state of BETS for getting the relation between bond lengths and formal charge (Q) of BETS ($BETS^{+Q}$). But the molecular structure of BETS with oxidation state greater than +1 has not been reported so far. Thin, black plate $(BETS)TlCl_5$ crystal was got from electrocrystallization method. The composition was determined by EDS (Energy Dispersive X-ray Spectrometer). The crystal has a triclinic unite cell and the cell parameters are: a = 9.052(3) Å, b = 10.542(3) Å, c = 6.210(1) Å, α = 103.56(2), β = 100.76(2), γ = 67.07(2)°, V = 527.6(2) Å^3. Donors are packed with side-by-side mode to form segregated column along b axis. The linear $[TlCl_5]^{2-}$ unit with octahedral $[TlCl_6]$ unit shared an apex along a axis in the crystal. The Tl–Cl bond lengths are in the range 2.416(3)–2.692(3) Å which are consistent with the length of Tl^{3+}–Cl. There are short contacts between S···S and S···Se atoms in the BETS columns and donor-anion contacts between Cl···Se, Cl···S atoms. The C–H···Cl hydrogen bonds also exist as shown in Figure 1. The crystal is an insulator and shows paramagnetic behavior from 300 K to 1.9 K. Combining the data of the bond lengths of various charge-transfer salts of BETS with different oxidation states ($BETS^{+Q}$), we can get a relation of $Q = 10.76 - 9.58\delta$, and $\delta = (b + c) - (a + d)$, where a, b, c, d are the bond lengths of TTF core.

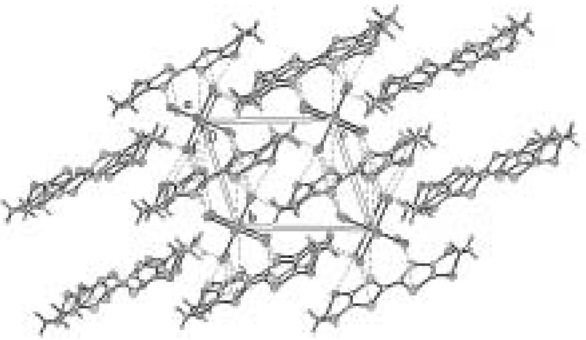

Figure 1. Packing diagram of $(BETS)TlCl_5$ viewed along c axis

IV-C-6 Charge-Transfer Salt of $[C_{12}H_8S_4Se_4Cl_2]FeCl_4\cdot C_6H_5Cl$

ZHANG, Bin; KOBAYASHI, Hayao; WANG, Zheming[1]; ZHU, Daoben[2]
([1]Peking Univ., China; [2]Inst. Chem., China)

Crystals of the title salt were obtained electrochemically. The donor $C_{12}H_8Cl_2S_4Se_4$: 2,2’-(1,2-dichoro-ethanediyli-dene)bis(4,5-dithiolene-1,3-diselena) was formed from BETS under high voltage. The cell parameter is: a = 8.669(4), b = 30.571(1), c = 10.388(4) Å, β = 102.13(4)°, V = 2691.5(6) Å^3, $P2_1/n$, Z = 4. Except ethylene groups, all the atoms of the donor are coplanar with the maximum derivation of 0.09 Å. The donor molecules form dimers. $FeCl_4^-$ anions and C_6H_5Cl molecules are in the intersticial positions between the deimers. C_6H_5Cl plane is perpendicular to that of dimer. The crystal is a semiconductor and shows paramagnetic behavior.

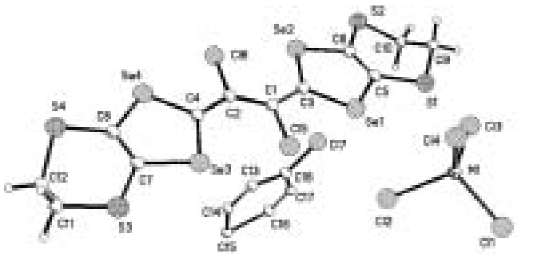

Figure 1. Molecular configuration.

IV-C-7 A New Charge-Transfer Salt of $(BETS)_4Fe_2(C_2O_4)_5$

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The preparation, crystal structure and physical properties of charge-transfer salt based on BETS molecules and metal oxalate counter ions $(BETS)_4Fe_2(C_2O_4)_5$ were examined. There are two phases. One is monoclinic $P2_1/n$ and the cell parameters are a = 17.078(4), b = 11.180(2), c = 19.975(5) Å, β = 102.026(5)°, V = 3730.3(15) Å^3. The other takes $C2/m$ space group and the lattice constants are a = 23.3982(7), b = 11.1365(4), c = 16.9771(7), β = 123.798(1)°, V = 3676.2(2) Å^3. In these two phases, $Fe_2(C_2O_4)_5$ groups and BETS molecules are arranged in " checker board " mode. In the $P2_1/n$ phase, BETS molecules are packed with the longest directions parallel to [101] direction. The formal charge of BETS is +1. The crystal showed a semiconductor-to-insulator transition around 80 K. There are antiferromagnetic interaction between Fe(III) ions. The χ *vs.* T curve gave g = 2.0 and J = –6.1 cm^{-1}.

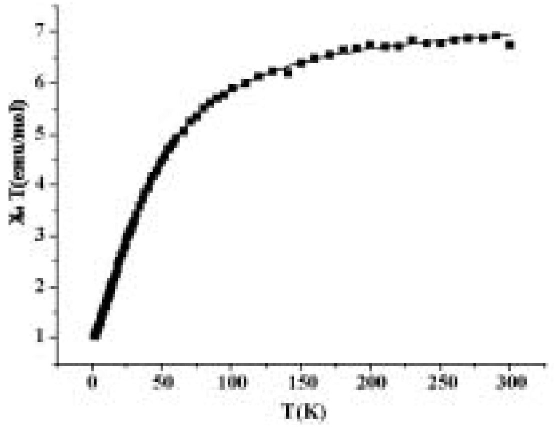

Figure 1. The $\chi_M T$ *vs* T curve of $BETS_4Fe_2(C_2O_4)_5$ (magnetic field = 1000 Oe). The solid line represents the best fit using the Heisenberg isotropic exchange model for a linear dimer Fe^{III}–Fe^{III}.

IV-D Development of New Conducting Molecular Materials

Molecule can be regarded as the smallest nano-system where various functions can be assembled. Although physics and chemistry of the bulk systems with typical electronic functions such as molecular superconductors and molecule-based magnets have been developed greatly in the last two decades, the development of the basic science of the "nano-molecular systems" seems to be insufficient. It seems that many fascinating ideas on the electronically functional molecular systems such as molecular circuit remain to be realized for a long time. Although present our starting point seems to be rather trivial, we hope to contribute in future to make a bridge between the well-established field of bulk molecular functionls and that of molecular nano-systems for the steady progress in the studies of electronic molecular functions. Presently we are trying to develop new types of molecular systems with novel electrobic functions. The "dual-functional" magnetic conductors exhibiting superconducting switching mentioned before is one example. Other main targets are: (1) magnetic conductors and superconductors composed of single-component molecules and (2) pure organic magnetic metals.

IV-D-1 Development of Conducting Crystals Based on Single-Component Transition Metal Complex Molecules with Extended-TTF Ligands

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([1]Univ. Tokyo)

Until quite recently, it was believed that molecular conductors consist of more than two chemical species. Charge transfer between molecules comprising conduction bands and another chemical species has been considered indispensable to generate charge carriers. However, we have prepared the crystal of a neutral complex, $[Ni(tmdt)_2]^{0+}$ (tmdt = trimethylenetetrathiafulvalenedithiolate), and found that it is highly conducting (400 Scm^{-1} at room temperature) and metallic behavior down to 0.6 K. Besides $Ni(tmdt)_2$, various molecular conductors composed of neutral transition metal complex molecules with extended TTF-like ligands such as ptdt, dmdt and tmdt were developed (*M* = Ni, Pd, Pt, Cu, Co, Au; ptdt = propylenedithiotetrathiafulvalenedithiolate, dmdt = dimethyltetrathiafulvalenedithiolate, tmdt = trimethylenetetrathiafulvalenedithiolate). The synthetic works were made under strictly inert atmosphere because these metal complexes were very sensitive to oxygen. By electrochemical oxidation, black microcrystals of the neutral complexes were obtained. Since only very small single or powder crystals were obtained, the resistivity measurements were made on the compressed powder samples. However, as shown in Table1, many crystals with very high conductivities were discovered: for example, [Ni(tmdt)$_2$], 250 Scm^{-1}; [Ni(dmdt)$_2$], 200 Scm^{-1}; [Pd(dmdt)$_2$], 150 Scm^{-1}.

Table 1. Single-component molecular conductors based on metal complexes with extended-TTF ligands

complex	starting material	σ(300 K) (compaction pellet sample)	
[Ni(dmdt)$_2$]	$(Me_4N)_2$[Ni(dmdt)$_2$]	200 Scm^{-1}	Metallic down to 230 K
[Pd(dmdt)$_2$]	$(Me_4N)_2$[Pd(dmdt)$_2$]	150 Scm^{-1}	Semiconductor
[Ni(tmdt)$_2$]	$(Me_4N)_2$[Ni(tmdt)$_2$]	250 Scm^{-1}	Metallic down to 70 K
[Co(dmdt)$_2$]	$(Me_4N)_2$[Co(dmdt)$_2$]	0.05 Scm^{-1}	Semiconductor Ea=85 meV
[Co(tmdt)$_2$]	$(Me_4N)_2$[Co(tmdt)$_2$]	1.5 Scm^{-1}	Semiconductor Ea=24 meV
[Cu(dmdt)$_2$]	$(Me_4N)_2$[Cu(dmdt)$_2$]	1.2 Scm^{-1}	Semiconductor Ea=60 meV
[Cu(tmdt)$_2$]	$(Me_4N)_2$[Cu(tmdt)$_2$]	5.1 Scm^{-1}	Semiconductor Ea=63 meV
[Au(tmdt)$_2$]	$(Me_4N)_2$[Au(tmdt)$_2$]	4 Scm^{-1}	Semiconductor Ea=21 meV
[Au(dmdt)$_2$]	$(Me_4N)_2$[Au(dmdt)$_2$]	14 Scm^{-1}	(Metallic)
[Ni(dt)$_2$]	$(Me_4N)_2$[Ni(dt)$_2$]	16 Scm^{-1}	Semiconductor Ea=35 meV
[Pd(dt)$_2$]	$(Me_4N)_2$[Pd(dt)$_2$]	0.3 Scm^{-1}	Semiconductor Ea=94 meV
[Ni(eodt)$_2$]	$(Bu_4N)_2$[Ni(eodt)$_2$]	8 Scm^{-1}	Metallic down to 120 K
[Co(dt)$_2$]	$(Me_4N)_2$[Co(dt)$_2$]	19Scm^{-1}	(Metallic)

IV-D-2 A Conducting Crystal Based on a Single-Component Paramagnetic Molecule [Cu(dmdt)$_2$] (dmdt = dimethyltetrathiafulvalene dithiolate)

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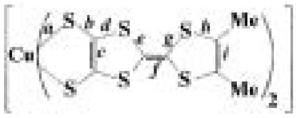
[*J. Am. Chem. Soc.* **124**, 10002 (2002)]

By the realization of single-component molecular metals, the possibility of the development of the new types of molecular conductors has been extended. For example, it will be possible to develop metallic molecular magnets based on single-component molecules containing magnetic ions such as Cu^{2+} and Co^{2+}, where the intermolecular magnetic interactions are mediated by π conduction electrons. We have examined the crystal structure, electrical resistivity and magnetic properties of crystal of [Cu(dmdt)$_2$]$^{0+}$ (dmdt = dimethyltetrathiafulvalenedithiolate), to contribute to clarify the possibility of single-component magnetic molecular conductors. The resistivity measurements on the compaction pellet sample showed fairly high conductivity though the quality of the crystals was poor (about 3 Scm^{-1} at room temperature) and the activation energy was very small (≈ 40 meV). The temperature dependence of the susceptibility was completely fitted by a Curie-Weiss plot ($\chi_{rt} = 1.09 \times 10^{-3}$ emu·mol^{-1}, $C = 0.33$ emu·K·mol^{-1}, $\theta = -4.2$ K). The Curie constant suggests the existence of 84% of $S = 1/2$ spin moments (estimated on the basis of a g-value (2.035) obtained by EPR experiments). These results suggest the possibility of the development of the single-component magnetic conductor. The comparison of the bond lengths of [Cu(dmdt)$_2$]$^{0+}$ and [Cu(dmdt)$_2$]$^{2-}$ showed that by the oxidation from (2–) to (0+), all the C=C bonds become longer, indicating that the LUMO has bonding character on each C=C bond (see Table 1). On the other hand, except the bond h showing very small positive change, S–C bonds tend to be shortened, suggesting antibonding character of LUMO on C–S bonds. Large changes in the bonds b and c indicate the large amplitude of LUMO on the S and C atoms in the central five-membered ring. These features are in good agreement with the general features of the calculated molecular orbitals reported previously.

Table 1. The average bind lengths (Å) of [Cu(dmdt)$_2$]^n (n = 2–, 0+)



	n=2-	n=0+	Δ
a	2.287(1)	2.282(1)	-5
b	1.738(3)	1.683(1)	-55
c	1.341(4)	1.414(9)	73
d	1.766(3)	1.743(4)	-23
e	1.756(3)	1.738(4)	-18
f	1.342(5)	1.361(1)	19
g	1.758(3)	1.737(4)	-21
h	1.748(3)	1.762(4)	14
i	1.330(5)	1.353(9)	23

IV-D-3 Novel π-Electron Donors for Magnetic Conductors Containing a PROXYL Radical

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([1]Univ. Tokyo)

[*Chem. Lett.* 1048 (2002)]

Development of magnetic conductors bearing both conductivity and magnetism has recently played a quite important role in the research of the multifunctionality of organic molecular materials. Recently, we synthesized several new donors containing a TEMPO radical and reported the structures and physical properties of their cation radical salts. Among them, we synthesized the donors **1** and **2** consisting of a TTF moiety and a PROXYL (2,2,5,5-tetramethylpyrrolidin-1-yloxyl) radical part because the PROXYL radical is quite stable to air and heat and the corresponding donor molecules will have a relatively small steric hindrance due to the symmetrical structure and smaller size of the PROXYL radical than that of the TEMPO radical. An X-ray crystal structure analysis revealed the structure of **1**. We also clarified the magnetic and electrochemical properties of novel TTF donors **1** and **2** containing a PROXYL radical. Furthermore we prepared the iodine complex of the ethylenedithio derivative **1** and cleared that the salt has 1:1 ratio (donor:I_3^-) and showed insulating conducting behavior and disappearance of the cation radical moments probably due to the strong singlet formation although the PROXYL radical part showed independent behavior with a weak antiferromagnetic interaction.

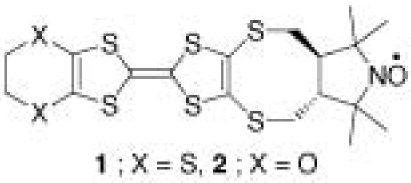

Figure 1. Structure of **1**, **2**.

IV-D-4 Novel TTP Donors Containing a PROXYL Radical for Magnetic Molecular Conductors

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The development of new electron donors involving a magnetic centre are of quite interest to investigate the interplay between the π conducting electrons generated by an oxidation and the localized radical spins, and several donors containing a stable radical have been synthesized to try for novel bifunctional materials. We synthesized novel electron donors **1** and **2** consisting of the TTP framework and a stable PROXYL (2,2,5,5-tetramethyl-pyrrolidin-1-yloxyl) radical part as racemic mixtures, where TTP framework was developed by Y. Misaki *et al.* and regarded as a series of promising donors for the realization of stable metallic states. We cleared the structures of the TTP derivatives containing a PROXYL radical **1** and **2** and investigated the magnetic and electrochemical properties of these donors. Furthermore, we prepared the cation radical salts of these donors and studied their electrical and magnetic properties. Among them, the $FeCl_4^-$ salts of **1** showed the highest conductivity (1 Scm^{-1}) in the cation radical salts based on the donors containing a localized radical spin. The χT values of this salt around room temperature correspond to the sum of the contributions from one PROXYL radical, high spin Fe^{3+} and small amount of conducting electrons from the cation radical moments, suggesting the coexistence of these three different magnetic moments.

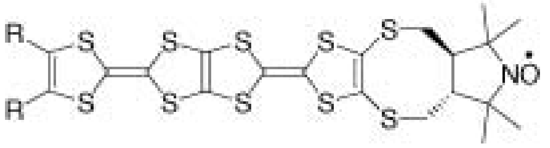

Figure 1. Structure of **1** and **2**.

IV-D-5 Synthesis and Physical Properties of New Molecular Conductors Based on Lanthanoid Nitrate Complex Anions

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Molecular conducting salts based on BDT-TTP [2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6- tetrathiapentalene] donor molecules and lanthanide nitrato complex anions $[Ln(NO_3)_5]^{-2}$. (Ln = Tb, Dy, Ho, Er, Tm, Yb and Lu) were synthesized as plate-shaped crystals whose compositions are $(BDT\text{-}TTP)_5[Ln(NO_3)_5]$ and they are all isostructural. All these crystals were metallic down to 2K. The electronic band structure calculation gave a two-dimensional Fermi surface that explained their stable metallic states. Magnetic susceptibility measurements of the seven salts $[Ln(NO_3)_5]^{-2}$ (Ln = Tb, Dy, Ho, Er, Tm, Yb and Lu) showed paramagnetic moments on rare-earth ions which were superimposed on the Pauli paramagnetism of metallic π electrons. Especially, the magnetic susceptibilities of the $(BDT\text{-}TTP)_5[Ho(NO_3)_5]$ and $(BDT\text{-}TTP)_5[Tm(NO_3)_5]$ salts showed that there seem to be some antiferromagnetic interactions. On the other hand, the Weiss temperatures for $(BDT\text{-}TTP)_5[Ln(NO_3)_5]$ (Ln = Tb, Dy, Er and Yb) salts are rather small.

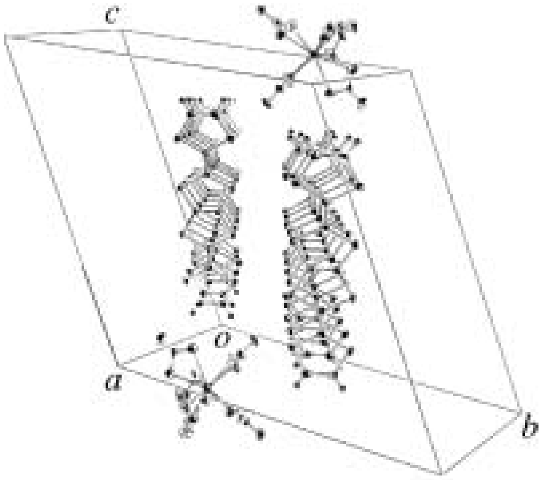

Figure 1. Crystal structure of $(BDT\text{-}TTP)_5[M(NO_3)_5]$.