Syntheses, Crystal Structures, and Physical Properties of Copper Complexes
with Dimethylthio-Pyrazino-Selenathiafulvalene (= Dmt-Pyra-STF) as ligand:

Running head: Research into copper complexes with Dmt-Pyra-STF as ligand

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Abstract

New copper complexes with Dmt-Pyra-STF (= dimethylthio-pyrazinoselenathiafulvalene) as the ligand—*trans*-[Cu^{II}Cl₂(Dmt-Pyra-STF)₂] (**1**) and [Cu^I₂Br_{2.5}(Dmt-Pyra-STF)] (**2**)—have been synthesized by a vertical diffusion method. In complex **1**, the donors form uniform stacking columns along the *c* axis to have a θ -type donor arrangement, but **1** is an insulator due to the absence of carriers. The magnetic susceptibility of **1** can be fitted to the Curie-Weiss rule ($\theta = -9.02$ K) and suggests that the oxidation state of Cu ions in **1** is 2+. In contrast, complex **2** has supramolecular chains along the *c* axis, which are formed by Cu^I and Br⁻. In addition, this complex is a semiconductor with $\sigma_{\text{rt}} = 0.16$ Scm⁻¹ and $E_a = 0.10$ eV. The magnetic susceptibility of **2** suggests that the oxidation state of Cu ions in **2** is 1+, namely [Cu^I₂Br_{2.5}(Dmt-Pyra-STF)^{0.5+}]. Both complexes **1** and **2** demonstrate that pyrazino-fused STF derivatives can be coordinated to a copper even though the atomic orbital of Se is so large. Furthermore, we can firstly synthesize complex **2**, in which both charge transfer and coordination occurs simultaneously.

Graphical Abstract

Two figures are used for the graphical abstract (Figure 2a and Figure 3a).

Keywords: Copper complex; Pyrazino-fused organic donor; supramolecular complex; multifunctional material

Introduction

The synergy or interplay between electrical conductivity, magnetism, permittivity, and optical properties in the use of the spin, charge, lattice, and molecular degrees of freedom has attracted great interest from the perspectives of both fundamental science and potential applications. Among these systems, the use of organic donors containing nitrogen atoms as ligands has been tried with a view

toward the creation of new molecular-based multifunctional materials [1-4]. These metal complexes tend to have shorter donor-metal distances than ordinary non-coordination charge transfer complexes, and are expected to exhibit interactions between itinerant π electrons and the magnetic d moment, the so-called π -d interaction. We have synthesized copper complexes with pyrazino-fused TTF derivatives, which have much shorter donor-metal distances due to the absence of a spacer between the donor part and the pyrazine ring. First we synthesized a 3-D supramolecular copper(II) complex with pyrazino-fused TTF (BP-TTF) as the ligand, $[\text{CuCl}_2(\text{BP-TTF})]$ (BP-TTF = bis(pyrazino)tetrathiafulvalene, Figure 1) [5]. In this complex, a zigzag $[\text{Cu}^{\text{II}}\text{Cl}_2(\text{BP-TTF})]_n$ chain extends along the b axis, where the Cu^{II} atom in a planar geometry is coordinated by two Cl^- and two N atoms of BP-TTF. The donors form uniform stacking columns to have the β -type donor arrangement. In addition, the π -d interaction of this complex derives an antiferromagnetic behavior fitted by a Bonner-Fisher model from 2 to 300 K with $S = 1/2$ and $2J = -7$ K between Cu^{II} mediated by self-assembling donor columns. However, ESR measurement reveals that the donors in this complex are completely neutral, that this complex is an insulator due to the absence of carriers; electron transfer from the donors to Cu^{II} does not occur due to the high first oxidation potential of BP-TTF ($E_1 = 1.05\text{V}$). We therefore next selected Pyra-TTF ($E_1 = 0.68\text{V}$, Figure 1), which is more easily oxidized than BP-TTF, and synthesized new copper complexes such as $[\text{CuCl}_2(\text{Pyra-TTF})]$ and $(\text{Pyra-TTF})_2[\text{Cu}_3\text{Cl}_4(\text{Pyra-TTF})]$ [6]. These two complexes are not insulators but semiconductors due to the lower oxidation potential of Pyra-TTF. In $[\text{CuCl}_2(\text{Pyra-TTF})]$, an intrinsic slight carrier doping occurs from a coordinated Pyra-TTF center to a Cu^{II} , and the conductivity at room temperature, σ_{rt} , is $1.0 \times 10^{-4} \text{ Scm}^{-1}$. Furthermore, the doping enhances the dielectric constant ($\epsilon' = 45$ $\epsilon'' = 2240$) and the antiferromagnetic interaction (2D Heisenberg model with $2J = -20$ K) between Cu^{II} ions through d- π interactions. On the other hand, $(\text{Pyra-TTF})_2[\text{Cu}_3\text{Cl}_4(\text{Pyra-TTF})]$ has two kinds of Pyra-TTFs: a coordinated donor and a noncoordinated one. The coordinated donor is completely neutral, but the

noncoordinated donor is 0.5+ to create a conducting layer. Since electron transfer occurs from the noncoordinated donor to the Cu^{II} center, σ_{H} of this complex is 0.1 Scm⁻¹ and the Cu^{II} is reduced to Cu^I. These previous results suggest that the tuning oxidation potential of a donor molecule should be effective for synthesizing conductive metal complexes. Then, we tried to create new copper complexes by Dmt-Pyra-STF (= dimethylthio-pyrazinoselenathiafulvalene, $E_1 = 0.75\text{V}$ vs SCE, Figure 1), whose oxidation potential is between that of BP-TTF and that of Pyra-TTF, and then investigated the influence of the Se atom, steric hindrance such as that of the methylthio group, and the oxidation potential of donors for its crystal structures and physical properties. Herein, we report the preparation, the crystal structures, and the magnetic and electrical properties of these complexes.

Experimental Section

Synthesis. Dmt-Pyra-STF was synthesized from pyrazino-1,3-diselenole-2-one [7] and 4,5-bis(methylthio)-1,3-dithiol-2-thione. Pyrazino-1,3-diselenole-2-one (0.25 g, 0.95 mmol) and 4,5-bis(methylthio)-1,3-dithiol-2-thione (0.214 g, 0.95 mmol) were heated in triethylphosphite (5 ml) at 120°C under nitrogen atmosphere for 2 h. After the triethylphosphite was evaporated in vacuo, the residue was added to dichloromethane. Orange solid (Dmt-Pyra-TTF) was filtered, washed with methanol, and dried in vacuo. The filtrate was evaporated and chromatographed on silica gel with CH₂Cl₂ as the eluent. The orange band was collected and evaporated to afford an orange solid (Dmt-Pyra-TTF). Copper complexes **1** and **2** were prepared by a vertical diffusion method with a test tube; Dmt-Pyra-STF (5 mg) and 1,1,2-trichloroethane (2 ml) were added to the test tube. Then, *n*-butanol (2 ml) was added slowly to the same test tube as a buffer layer in order to slow the diffusion. Ethanol solution of CuCl₂ (15 mg, for synthesis of complex **1**) or TBA₂CuBr₄ (50 mg, for synthesis of complex **2**) was added slowly to the same test tube. The test tube containing the 3 layered solutions, which were Dmt-Pyra-STF/1,1,2-trichloroethane, *n*-butanol, and CuCl₂ or TBA₂CuBr₄/ethanol, was left until crystals were deposited. After about 2 weeks, black needle crystals of *trans*-[Cu^{II}Cl₂(Dmt-Pyra-STF)₂] (**1**) and black plate crystals of [Cu^I₂Br_{2.5}(Dmt-Pyra-STF)] (**2**) were

collected by filtration and washed with ethanol. The compositions of these complexes were determined by SEM-EDS (JEOL JCM-5000, Oxford WDX 400).

X-ray analysis of these complexes. Both single crystals of **1** and **2** were mounted on a CCD area detector, a Bruker SMART APEX (Mo $K\alpha$, $\lambda = 0.7055$ Å), at room temperature. The structure was solved with direct methods and refined with the full-matrix least-squares technique using Crystal Structure (ver. 3.6.0, Rigaku Co. and Rigaku/MS). Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were generated geometrically (C-H = 0.950 Å).

Resistivity measurement. The temperature dependence of the resistivity of a pellet sample of **2** was measured by the ac four-terminal method at 27 Hz with 15 μm Au wires attached by carbon paint as contacts.

Magnetization measurement. The temperature dependences of magnetic susceptibilities for **1** and **2** were investigated by a Quantum Design MPMS-XL SQUID magnetometer under 10,000 Oe at 2.00-300 K. The diamagnetic core contribution was corrected by Pascal's law.

Results and Discussion

Crystal structures. The X-ray single crystal analysis of **1** reveals that the Cu^{II} center is in a square planar geometry and is coordinated by two Cl^- and two N atoms of Dmt-Pyra-STF with a *trans* configuration as shown in Figure 2(a) ($\text{Cu-Cl} = 2.228(1)$ Å, $\text{Cu-N} = 2.086(3)$ Å). There is a contact between the Se atom and Cl^- in the complex ($3.516(1)$ Å), which is a key to stabilizing the structure. The complex is not a supramolecule, in contrast to $[\text{CuCl}_2(\text{BP-TTF})]$ [5] and $[\text{CuCl}_2(\text{Pyra-TTF})]$ [6]. Figure 2(b) shows the structure projected along the *c* axis; $[\text{Cu}^{\text{II}}\text{Cl}_2(\text{Dmt-Pyra-STF})_2]$ units have no positional disorder, although the donors have two methylthio groups as the steric hindrance. Figure 2(c) reveals that the donors form uniform stacking columns along the *c* axis in a ring-over-bond configuration to have a θ -type donor arrangement. This complex is an insulator due to the absence of carriers as well as $[\text{CuCl}_2(\text{BP-TTF})]$ [5]; Dmt-Pyra-STF donors are neutral and the copper ions are 2+. The intermolecular overlap integrals [8] of Dmt-Pyra-STF including N atoms are calculated to be $r1 =$

1.08, $p_2 = -0.343$, and $p_3 = -0.377 (\times 10^{-3})$ based on the molecular orbitals obtained by WinMOPAC (ver 3.9.0, Fujitsu Limited). The largest interaction, r , is observed in the donor stacking direction, whereas the side-by-side interactions (p_1, p_2) are one-third of r_1 . This complex is the first example of a copper complex having a pyrazino-fused STF derivative as ligand. This example indicates that pyrazino-fused STF derivatives can be coordinated to a metal even though the atomic orbital of the Se atom is so large. This complex also shows that a donor having steric hindrance such as that of a methylthio group can be coordinated to a metal cation center.

The X-ray single crystal analysis of **2** reveals that the complex has a very complicated supramolecular structure. One-dimensional chains consisting of Cu atoms and Br atoms extend to the c axis, and the donors coordinate to the Cu center. The donors form a uniform stacking column along the a axis, while the chains extend to the c axis. There are two crystallographically independent Cu atoms (Cu1, Cu2) and three Br atoms (Br1, Br2, Br3). The Br3 atom, which is 0.5 occupancy, has contact with the Se2 atom of the donor molecule as shown in Figure 3(a) (3.375(1) Å). Furthermore, there are Cu-Cu bonds in the chain whose bond length is 2.795(2) Å (Figure 3(c)). The structure analysis also reveals that two chains (i) are connected by direct coordination to the donor molecules, but that the other two chains (ii) are interacted by the coordinated molecular π stacking (interplane distance: 3.572(5) Å) as shown in Figure 3(d). The overlap integrals are calculated to be $r_1 = -10.4$, $r_2 = -0.544$, $p_1 = 2.43 \times 10^{-3}$, and $q_1 = -6.98 \times 10^{-2} (\times 10^{-3})$, suggesting a strong localized one-dimensional interaction along the a axis (Figure 3(d)). Complex **2** is the first example of a complex that takes over coordination and charge transfer at the same time, and demonstrates that a cationic donor can coordinate to a metal cation.

Resistivity measurements. The temperature dependences of the resistivities of the pellet of **2** were measured by the ac four-terminal method at 27 Hz with carbon paint contacts as shown in Figure 4. Due to the charge transfer from Cu^{II} to the coordinated Dmt-Pyra-STF, this complex is a semiconductor with $\sigma_{\text{RT}} = 0.16 \text{ Scm}^{-1}$ and $E_a = 0.10 \text{ eV}$. We succeeded in creating a complex with higher

conductivity than that of $[\text{CuCl}_2(\text{Pyra-TTF})]$ ($1.0 \times 10^{-4} \text{ Scm}^{-1}$) [6].

Magnetization measurements. The temperature dependences of magnetic susceptibilities for **1** and **2** were investigated by a Quantum Design MPMS-XL SQUID magnetometer under 10,000 Oe, as shown in Figure 5. The magnetic susceptibility χ_1 at 300 K of compound **1** after the subtraction of the Pascal diamagnetic contribution is $1.30 \times 10^{-3} \text{ emu mol}^{-1}$ and follows the Curie-Weiss rule from 300 to 2 K with $\theta = -9.02 \text{ K}$ and $C = 0.376 \text{ emu mol}^{-1}$. There is a weak antiferromagnetic interaction between Cu^{II} ions, and the value of the magnetic susceptibility of **1** suggests that the oxidation state of Cu ions in complex **1** should be 2+, since no charge transfer occurs. In contrast, the magnetic susceptibility χ_2 at 300 K of compound **2** is $2.65 \times 10^{-4} \text{ emu mol}^{-1}$, which is much lower than the value of complex **1**. This low value suggests that the oxidation state of Cu ions in complex **2** should be 1+, since charge transfer occurs from the donor to the Cu atom.

Effects of donor molecules on structural and physical properties of copper complexes. We have synthesized copper complexes with some pyrazino-fused organic donors to investigate their crystal structures. The obtained complexes and their properties are summarized in Table I. The table suggests that a charge transfer coordinated complex can appear within the range of about $E_1 = 0.75$ to 0.68V. The only coordination occurs in $[\text{CuCl}_2(\text{BP-TTF})]$ [5], which is an insulator since the E_1 of BP-TTF is too high. On the other hand, DM-Pyra-TTF forms only common charge transfer complexes, and does not form any coordination bond [9]. In the DM-Pyra-TTF system, the rate of charge transfer is very fast due to the low E_1 , and DM-Pyra-TTF cannot form a coordination bond. In Pyra-TTF and Dmt-Pyra-TTF, which have the intermediate E_1 , both charge transfer and coordination to a copper center occur simultaneously. Until now, the structures and physical properties of copper complexes have been expected to depend on the oxidation potentials of organic donors. The tuning of oxidation potential for the development of magnetic conductors is in progress.

Conclusion

We have synthesized copper complexes with Dmt-Pyra-STF as the ligand:

trans-[CuCl₂(Dmt-Pyra-STF)] (**1**) and [Cu^I₂Br_{2.5}(Dmt-Pyra-STF)] (**2**). The X-ray single crystal analysis of **1** reveals that the Cu^{II} center is in a square planar geometry and is coordinated by two Cl⁻ and two N atoms of Dmt-Pyra-STF with a *trans* configuration. The donors form uniform stacking columns along the *c* axis to have a θ -type donor arrangement. The complex is an insulator due to the absence of carriers. The magnetic susceptibility χ_1 at 300 K of complex **1** is 1.30×10^{-3} emu mol⁻¹ and follows the Curie-Weiss rule from 300 to 2 K with $\theta = -9.02$ K and $C = 0.376$ emu mol⁻¹. Complex **2** has a very complicated supramolecular structure. The complex forms 1D chains consisting of Cu atoms and Br atoms along the *c* axis, and the coordinated donor molecules of **2** form uniform stacking columns along the *a* axis. This complex is a semiconductor with $\sigma_{RT} = 0.16$ Scm⁻¹ and $E_a = 0.10$ eV due to the charge transfer from the Cu^{II} center to the coordinated Dmt-Pyra-STF. The magnetic susceptibility of **2** at room temperature is 2.65×10^{-4} emu mol⁻¹, which suggests that the oxidation state of Cu ions in complex **2** should be 1+, since the charge transfer occurs from the donor to the Cu center. These complexes proved two important things: first, pyrazino-fused STF derivatives can coordinate to a copper cation even though the atomic orbital of the neighboring Se is large. Second, it is possible that donors having steric hindrance, such as methylthio groups, can coordinate to metal cations. The structures and physical properties of copper complexes having organic donors as ligands are expected to depend on the oxidation potentials of organic donors and the stabilization of molecular packing by Se atom, steric hindrance groups, and so on.

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Figure captions

Figure 1. The molecular structures of organic donors.

Figure 2. (a) ORTEP drawing and atomic numbering scheme and the Se...Cl contacts (dotted lines), (b) structure projected along the *c* axis, and (c) donor arrangement for **1**.

Figure 3. (a) ORTEP drawing and atomic numbering scheme and the Se...Br contact (dotted line), (b) projected along the *b* axis with only donors and the interactions between two chains (ii) (arrows), (c) anion chain structure, and (d) donor arrangement for **2**.

Figure 4. Temperature dependence of the resistivity of a pellet sample for **2**.

Figure 5. Temperature dependence of the magnetic susceptibility of **1**.

Table

Table I. The relation between donor oxidation potential and the crystal structure of the complex.

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Figures

Figure 1

Figure 2(a)

Figure 2(c)

Figure 3(a)

Figure 3(d)

Figure 4

Figure 5

Figure 2(b)

Figure 3(b)

Figure 3(c)

Table 1

<div>Donor (D)</div> <div> </div>				
	BP-TTF	Dmt-Pyra-TTF	Pyra-TTF	Dm-Pyra-TTF
$E_1(\text{V})$	1.05	0.75	0.68	0.64
Cl	coordination [Cu ^{II} Cl ₂ D ⁰] [5]	coordination [Cu ^{II} Cl ₂ D ₂ ⁰] [this work]	coordination charge transfer [Cu ^{II} Cl ₂ D ⁰] D ₂ ^{0.5+} [Cu ₃ Cl ₄ D ⁰] [6]	non-coordination charge transfer D(CuCl ₂) [9]
Br		coordination charge transfer [Cu ₂ Br _{2.5} D ^{0.5+}] [this work]	coordination charge transfer [Cu ^I Br ₂ D ¹⁺] [9]	non-coordination charge transfer D(CuBr ₃) [9]