

High Conductivity of the New Supramolecular Copper Complex with Oxidized Pyrazinoselenathiafulvalene (=pyra-STF) as the Ligand, $[\text{Cu}^{\text{I}}\text{Cl}_{1.5}(\text{pyra-STF})^{0.5+}]$

Shun Ichikawa* and Hatsumi Mori*

The Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba 277-8581, Japan

Received March 6, 2009

A new supramolecular copper complex with pyrazinoselenathiafulvalene (=pyra-STF) as the ligand, $[\text{CuCl}_{1.5}(\text{pyra-STF})]$, has been synthesized. This complex forms a peculiar crystal structure; Cu^{I} and Cl^- construct 1D supramolecular chains with coordination of the oxidized donor molecules, $\text{pyra-STF}^{0.5+}$, as ligands. The pseudo-1D donor-ligand columns afford high conductivity, 25 S cm^{-1} , at 298 K and are prohibited to be a complete singlet state below 190 K by the linked, rigid 1D $[\text{CuCl}_{1.5}]_n$ chains.

Functional charge-transfer complexes have attracted a great deal of attention, and their magnetism, conductivity, and permittivity have been investigated in view of fundamental science and application to molecular devices. Recently, in addition to the magnetic charge-transfer salts,^{1–4}

some metal complexes containing organic donors or acceptors as “ligands” have been synthesized and studied.^{5–19} Such complexes are expected to show conductivity and magnetism; ligands such as tetrathiafulvalene (TTF) derivatives or 7,7,8,8-tetracyanoquinodimethane^{12,13} and DCNQI^{14–16} derivatives can create conduction paths, and the d spins of the metal centers can generate magnetism. Moreover, these metal complexes would have shorter donor–metal distances than noncoordination charge-transfer complexes and could exhibit peculiar structures and a wide range of magnetic interactions between donor ligands and metal cations.

We have recently synthesized and studied copper complexes coordinated by “pyrazino-fused” TTF derivatives, which have much shorter donor–metal distances because there is no spacer between the donor part and the pyrazine ring (Figure 1). The short donor–metal distance could effectively generate interactions between TTF parts and coordinated metals or halogen’s parts. By taking advantage of the interactions, we have constructed new complexes possessing novel crystal structures, conductivities, and peculiar magnetisms. First, we synthesized $[\text{Cu}^{\text{II}}\text{Cl}_2(\text{BP-TTF})]$ [BP-TTF = bis(pyrazino)tetrathiafulvalene].¹⁷ This metal complex is the first example with a pyrazino-fused TTF derivative as a ligand. The magnetic susceptibility of $[\text{CuCl}_2(\text{BP-TTF})]$ follows the 1D Heisenberg model with $2J = -7 \text{ K}$ due to the antiferromagnetic interactions between Cu^{II} spins through BP-TTF ligands. However, $[\text{CuCl}_2(\text{BP-TTF})]$ is an insulator because of the absence of carriers; because BP-TTF has a high first-oxidation potential ($E_1 = 1.05 \text{ V vs SCE}$), BP-TTF cannot be oxidized by Cu^{II} . Second, we selected pyrazinotetrathiafulvalene (=pyra-TTF), which has a lower oxidation potential than that of

*To whom correspondence should be addressed. E-mail: ichikawa@issp.u-tokyo.ac.jp (S.I.), hmori@issp.u-tokyo.ac.jp (H.M.). Fax: +81-4-7136-3444.

(1) Day, P.; Kurmoo, M.; Mallah, T.; Marsden, I. R.; Friend, R. H.; Pratt, F. L.; Hayes, W.; Chasseau, D.; Gaultier, J. *J. Am. Chem. Soc.* **1992**, *114*, 10722–10729.

(2) Kobayashi, H.; Tomita, H.; Naito, T.; Kobayashi, A.; Sakai, F.; Watanabe, T.; Cassoux, P. *J. Am. Chem. Soc.* **1996**, *118*, 368–377.

(3) Fujiwara, H.; Wada, K.; Hiraoka, T.; Hayashi, T.; Sugimoto, T.; Nakazumi, H.; Yokogawa, K.; Teramura, M.; Yasuzuka, S.; Murata, K.; Mori, T. *J. Am. Chem. Soc.* **2005**, *127*, 14166–14167.

(4) Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C. J.; Laukhin, V. *Nature* **2000**, *408*, 447–449.

(5) Setifi, F.; Ouahab, L.; Golhen, S.; Yoshida, Y.; Saito, G. *Inorg. Chem.* **2003**, *42*, 1791–1793.

(6) Kanehama, R.; Umemiya, M.; Iwahori, F.; Miyasaka, H.; Sugiura, K.; Yamashita, M.; Yokochi, Y.; Ito, H.; Kuroda, S.; Kishida, H.; Okamoto, H. *Inorg. Chem.* **2003**, *42*, 7173–7181.

(7) Iwahori, F.; Golhen, S.; Ouahab, L.; Carlier, R.; Suter, J. P. *Inorg. Chem.* **2001**, *40*, 6541–6542.

(8) Benbellat, N.; Gavrilenko, K. S.; Gal, Y. L.; Cador, O.; Golhen, S.; Gouasmia, A.; Fabre, J. M.; Ouahab, L. *Inorg. Chem.* **2006**, *45*, 10440–10442.

(9) Jia, C.; Liu, S. X.; Ambrus, C.; Neels, A.; Labat, G.; Decurtins, S. *Inorg. Chem.* **2006**, *45*, 3152–3154.

(10) Han, Y. F.; Zhang, J. S.; Lin, Y. J.; Dai, J.; Jin, G. X. *J. Organomet. Chem.* **2007**, *692*, 4545–4550.

(11) Pointillart, F.; Le Gal, Y.; Golhen, S.; Cador, O.; Ouahab, L. *Inorg. Chem.* **2008**, *47*, 9730–9732.

(12) Miyasaka, H.; Izawa, T.; Takahashi, N.; Yamashita, M.; Dunbar, K. R. *J. Am. Chem. Soc.* **2006**, *128*, 11358–11359.

(13) Motokawa, N.; Oyama, T.; Matsunaga, S.; Miyasaka, H.; Sugimoto, K.; Yamashita, M.; Lopez, N.; Dunbar, K. R. *Dalton Trans.* **2008**, *31*, 4099–4102.

(14) Aumüller, A.; Erk, P.; Klebe, G.; Hunig, S.; Schutz, J. U.; Werner, H. P. *Angew. Chem., Int. Ed.* **1986**, *25*, 740–741.

(15) Kato, R.; Kobayashi, H.; Kobayashi, A.; Mori, T.; Inokuchi, H. *Chem. Lett.* **1987**, 1579–1580.

(16) Bartley, S. L.; Bazile, M. J. Jr.; Clerac, R.; Zhao, H.; Ouyang, X.; Dunbar, K. R. *Dalton Trans.* **2003**, *14*, 2937–2944.

(17) Ichikawa, S.; Kimura, S.; Mori, H.; Yoshida, G.; Tajima, H. *Inorg. Chem.* **2006**, *45*, 7575–7577.

(18) Ichikawa, S.; Kimura, S.; Kazuyuki, T.; Mori, H.; Yoshida, G.; Manabe, Y.; Matsuda, M.; Tajima, H.; Yamaura, J. *Inorg. Chem.* **2008**, *47*, 4140–4145.

(19) Ichikawa, S.; Mori, H.; Takahashi, K.; Yamaura, J. *Solid State Sci.* **2008**, *10*, 1724–1728.

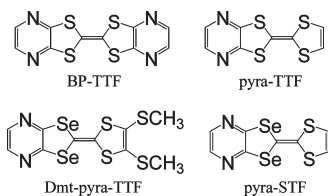


Figure 1. Pyrazino-fused TTF derivatives.

BP-TTF ($E_1 = 0.68$ V vs SCE), to induce electron transfer in a copper complex.¹⁸ The obtained complex, $[\text{Cu}^{\text{II}-\delta}\text{Cl}_2(\text{pyra-TTF})^{\delta+}]$, is also a supramolecule, and the magnetic susceptibility of this complex follows the 2D Heisenberg model with $2J = -20$ K. In contrast with $[\text{CuCl}_2(\text{BP-TTF})]$, this complex is a semiconductor with $\sigma_{\text{RT}} = 10^{-4}$ S cm^{-1} . A slight amount of intrinsic carrier doping occurred in $[\text{CuCl}_2(\text{pyra-TTF})]$ because of the low first-oxidation potential of pyra-TTF. In the following step, we synthesized *trans*- $[\text{Cu}^{\text{II}}\text{Cl}_2(\text{Dmt-pyra-STF})_2]$ (Dmt-pyra-STF = dimethylthio-pyrazinoselenathiafulvalene).¹⁹ Dmt-pyra-STF ($E_1 = 0.75$ V vs SCE) is a pyrazino-fused organic donor containing Se atoms and two methylthio groups. The pyrazino-fused “STF” derivatives can coordinate to a Cu ion, even though the atomic orbital of Se is quite large. Moreover, systematic studies of copper complexes with pyrazino-fused TTF ligands indicate that donor ligands with oxidation potentials in the range of 0.75–0.68 V (vs SCE) have the ability not only to be oxidized by Cu^{II} but also to coordinate to Cu ions.

These previous studies have provided us with two strategies to enhance the conductivity of a complex: (1) tuning of the oxidation potential of an organic donor and (2) use of an STF derivative. We therefore selected pyra-STF ($E_1 = 0.71$ V vs SCE) in consideration of the above strategies and synthesized a copper complex, $[\text{CuCl}_{1.5}(\text{pyra-STF})]$. We report herein the synthesis, crystal structure, and physical properties of $[\text{CuCl}_{1.5}(\text{pyra-STF})]$.

The synthesis of pyra-STF was carried out by general methods.^{20–22} Single crystals of $[\text{CuCl}_{1.5}(\text{pyra-STF})]$ were prepared by a diffusion method with an H-shaped cell; 10 mg of pyra-STF and 260 mg of $\text{TBA}_2\text{Cu}^{\text{II}}\text{Cl}_4$ were added to the diffusion cell, and *n*-butanol was then slowly added to the cell under an argon atmosphere. After approximately 2 weeks, black pillar crystals were collected by filtration and washed with CH_3OH . The composition of this complex was determined by scanning electron microscopy–energy-dispersive spectrometry (JEOL JCM-5000–Oxford WDX 400) and structural analysis.²³

The single-crystal X-ray analysis of $[\text{CuCl}_{1.5}(\text{pyra-STF})]$ reveals that Cu^+ and Cl^- construct 1D supramolecular chains along the *c* axis, while Cu^+ is coordinated by $\text{pyra-STF}^{0.5+}$. The donor is oxidized to 0.5+ by electron transfer from two pyra-STF^0 to Cu^{2+} ; the Cu “cation” is directly coordinated by the “cationic” donor ligand (Figure 2a). An ORTEP drawing

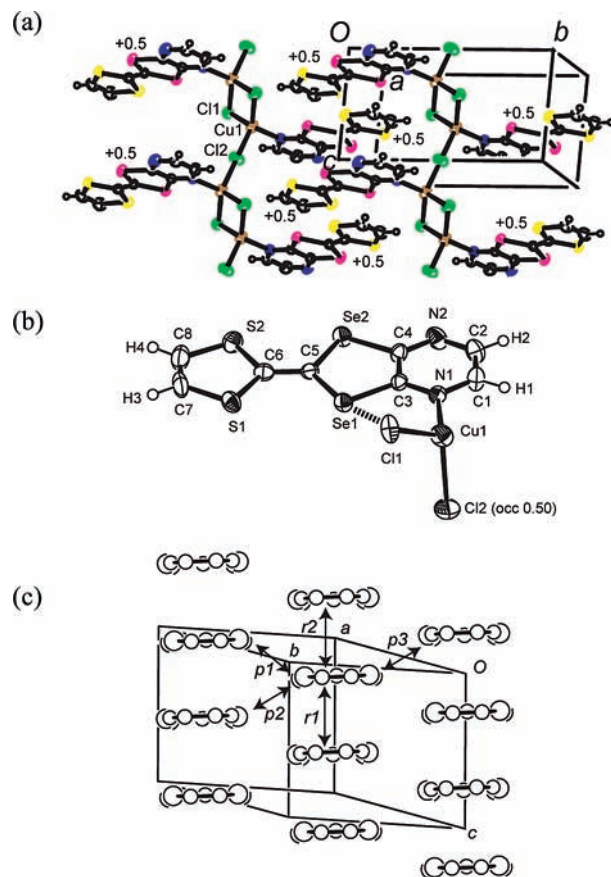


Figure 2. (a) Crystal structure and distribution of positive charge. (b) ORTEP diagram and atomic numbering scheme (dotted line; $\text{Se} \cdots \text{Cl}$ contact). (c) Donor arrangement and overlap integrals of $[\text{CuCl}_{1.5}(\text{pyra-STF})]$.

is shown in Figure 2b. Two kinds of Cl^- ions exist at a normal position and on an inversion center in the complex. There is an interaction between Cl1 of the chain and Se1 of the donor, $\text{Se1} \cdots \text{Cl1} = 3.542(2)$ Å, due to the “donor–metal shorter distance” [sum of the van der Waals radii, $r(\text{Se}) + r(\text{Cl}^-) = 3.57$ Å]. This interaction can be an important factor in stabilizing the novel crystal structure. Furthermore, the donors form weakly dimerized stacking columns to give a β -type donor arrangement (Figure 2c). The molecular orbital of pyra-STF including N and Se atoms is calculated by *WinMOPAC* (version 3.9.0, Fujitsu Ltd.). On the basis of the obtained orbital, the overlap integrals are calculated²⁴ to be $r_1 = 17.6$, $r_2 = 22.5$, $p_1 = -1.13$, $p_2 = 0.52$, and $p_3 = 1.43 (\times 10^{-3})$. The interplanar distance of r_1 is 3.500(4) Å and that of r_2 is 3.487(4) Å. These overlap integrals and band calculations (see the Supporting Information) suggest that this complex is a pseudo-1D conductor with weakly dimerized donor molecules.

In order to confirm the oxidation state of the Cu ion and the donor ligand, the electron spin resonance (ESR) measurement was carried out with a Bruker EMS 9.3 GHz X-band ESR spectrometer between 300 and 4 K. The observed Lorentzian signal at 300 K is broad ($\Delta H = 200$ G) because of the Se atoms of the ligands. The temperature-independent *g* value of 2.014 indicates the Cu^{I} and the oxidized pyra-STF states (see the Supporting Information).

(20) Melby, L. R.; Hartzler, H. D.; Sheppard, W. A. *J. Org. Chem.* **1974**, *39*, 2456–2458.

(21) Papavassiliou, G. C.; Yiannopoulos, S. Y.; Zambounis, J. S. *Chem. Scr.* **1987**, *27*, 265–268.

(22) Papavassiliou, G. C.; Gionis, V.; Yiannopoulos, S. Y.; Zambounis, J. S.; Mousdis, G. A.; Kobayashi, K.; Umemoto, K. *Mol. Cryst. Liq. Cryst.* **1988**, *156*, 277–287.

(23) Crystal data for $[\text{CuCl}_{1.5}(\text{pyra-STF})]$ at 298 K: $\text{C}_8\text{H}_4\text{N}_2\text{S}_2\text{CuCl}_{1.5}$, fw 466.90, triclinic, *P*1 (No. 2), $a = 7.5330(12)$ Å, $b = 11.746(2)$ Å, $c = 7.003(3)$ Å, $\alpha = 90.85(2)^\circ$, $\beta = 103.36(2)^\circ$, $\gamma = 83.618(14)^\circ$, $V = 599.1(3)$ Å³, $Z = 2$, $D_{\text{calc}} = 2.588$ g cm^{-3} , $R = 0.0429$, $R_w = 0.1009$, GOF = 1.011.

(24) Mori, T.; Kobayashi, A.; Sasaki, Y.; Kobayashi, H.; Saito, G.; Inokuchi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 627–633.

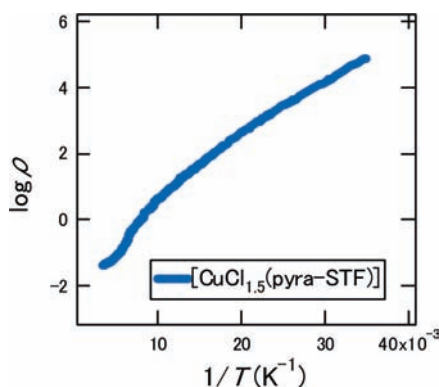


Figure 3. $1/T$ vs $\log \rho$ plot for $[\text{CuCl}_{1.5}(\text{pyra-STF})]$.

The resistivity measurement was performed on single crystals of $[\text{CuCl}_{1.5}(\text{pyra-STF})]$ with carbon paint as four-probe contacts. The conductivity at room temperature is high, with $\sigma_{\text{RT}} = 25 \text{ S cm}^{-1}$ owing to the introduction of carriers and the contribution of large orbitals by Se atoms in pyra-STF ligands. The resistivity shows semiconducting behavior due to the slight dimerization of donors and reveals a small anomaly around 190 K in Figure 3 ($T > 190 \text{ K}$, $E_a = 31 \text{ meV}$; $T < 190 \text{ K}$, $E_a = 51 \text{ meV}$).

The temperature dependence of magnetic susceptibility for $[\text{CuCl}_{1.5}(\text{pyra-STF})]$ was investigated by a Quantum Design MPMS-XL SQUID magnetometer under 10 000 Oe (Figure 4). The magnetic susceptibility χ after subtraction of the Pascal diamagnetic contribution at 300 K is comparably small, $1.25 \times 10^{-4} \text{ emu mol}^{-1}$, and temperature-independent down to 190 K. The χ values decrease slightly from 190 to 100 K to $1.05 \times 10^{-4} \text{ emu mol}^{-1}$ because of slight distortion to the singlet state. Below 100 K, χ values increase because of the Curie impurity.

The X-ray structural analysis of $[\text{CuCl}_{1.5}(\text{pyra-STF})]$ at 120 K was carried out to investigate changes of the crystal structure, the overlap integrals, and the dimensionality of this complex below the anomaly. The structure at 120 K is isostructural to that at room temperature.²⁵ There are neither drastic changes of the cell parameters nor the appearance of a superlattice. The overlap integrals at 120 K are $r1 = 18.3$, $r2 = 23.7$, $p1 = -0.97$, $p2 = 0.62$, and $p3 = 1.62 (\times 10^{-3})$.

The degree of dimerization of the donors was a little strengthened at 120 K ($r2/r1$ is 1.28 at 293 K and 1.30 at 120 K). According to these results, a charge ordering and a distinct charge density wave (CDW) are ruled out as origins

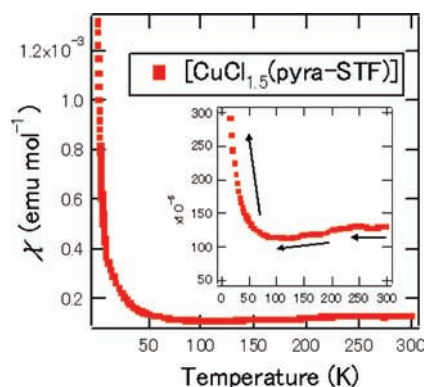


Figure 4. Temperature dependence of the magnetic susceptibility of $[\text{CuCl}_{1.5}(\text{pyra-STF})]$.

of the anomaly. Moreover, the anomaly might not originate from an antiferromagnetic order because of the constant g value and no rapid increase of the line width by the ESR measurement. No sudden phase transition to singlet states has been observed by the linked, rigid 1D $[\text{CuCl}_{1.5}]_n$ chains and the larger molecular orbital of pyra-STF. The slight distortion to an incomplete singlet state such as the quasi-CDW state might induce the anomaly.

In conclusion, we have synthesized the supramolecular copper(I) complex with oxidized pyrazino-fused TTF as the ligand, $[\text{Cu}^{\text{I}}\text{Cl}_{1.5}(\text{pyra-STF})^{0.5+}]$. The supramolecular 1D $[\text{CuCl}_{1.5}]_n$ chain with coordination of pyra-STF^{0.5+} ligands as a pendant was revealed by X-ray analysis. It is remarkable that the cation ligands directly coordinate to the Cu^+ cation. The assembled pyra-STF^{0.5+} ligands construct highly conducting paths with $\sigma_{\text{RT}} = 25 \text{ S cm}^{-1}$. The incomplete single state below 190 K is observed by the competition between pseudo-1D instability of conduction columns and the suppression of a sudden transition by the linked, rigid 1D supramolecular $[\text{CuCl}_{1.5}]_n$ chains and the larger molecular orbital of pyra-STF^{0.5+}. The search for a more conductive supramolecular metal complex is in progress by utilizing extended strategies for tuning of the oxidation potential and the introduction of STF derivatives.

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research from MEXT (Grants 20340087 and 20110007). The authors thank H. Tajima and M. Matsuda for use of facilities, ESR, and SQUID.

Supporting Information Available: Synthesis of the donor, X-ray crystallographic data with CIF files, EDX analysis, band structures, and data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(25) Crystal data for $[\text{CuCl}_{1.5}(\text{pyra-STF})]$ at 120 K: $\text{C}_8\text{H}_4\text{N}_2\text{S}_2\text{CuCl}_{1.5}$, fw 466.90, triclinic, $P\bar{1}$ (No. 2), $a = 7.523(4) \text{ \AA}$, $b = 11.723(6) \text{ \AA}$, $c = 6.955(4) \text{ \AA}$, $\alpha = 90.71(5)^\circ$, $\beta = 103.86(5)^\circ$, $\gamma = 83.88(4)^\circ$, $V = 592.1(6) \text{ \AA}^3$, $Z = 2$, $D_{\text{calc}} = 2.619 \text{ g cm}^{-3}$, $R = 0.0442$, $R_w = 0.1058$, GOF = 1.004.