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Antiferromagnetic Interaction Achieved by a 3-D Supramolecular Cu^{II} Complex with Pyrazino-Fused TTF as the Ligand, [CuCl$_2$(BP-TTF)]

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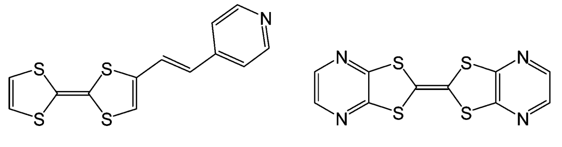
The diffusion reaction of TBA$_2$Cu^{II}Cl$_4$ (TBA = tetrabutylammonium) and a N-containing organic donor, BP-TTF [=bis(pyrazino)-tetrathiafulvalene], yielded a 3-D supramolecular Cu complex, [CuCl$_2$(BP-TTF)] (**1**). The magnetic measurement of **1** exhibits an antiferromagnetic interaction by fitting a Bonner–Fisher model from 2 to 300 K with $S = {}^1/_2$ and $J = -3.5$ K between Cu^{II} mediated by self-assembling donor columns.



TTF-py BP-TTF

Figure 1. Molecular structures of TTF-py and BP-TTF.

The molecular-based multifunctional materials have attracted great interests owing to a large degree of freedom in spin, charge, lattice, and designable molecules. Especially, the materials with conductivity and magnetism have been intensively investigated in the experimental[1−6] and theoretical[7] aspects. Among them, metal complexes coordinated by organic donors have a smaller donor−metal distance than those of ordinary noncoordination charge transfer complexes and possess an ability to construct self-assembling donor columns or layers. Therefore, this system is expected to exhibit π−d interactions. For example, the radical cation salt of the Cu^{II} complex, [Cu^{II}(hfac)$_2$(TTF-py)$_2$](PF$_6$)$_2$·2CH$_2$Cl$_2$ [hfac = hexafluoroacetylacetonate and TTF-py = 4-(2-tetrathiafulvalenylethenyl)pyridine); Figure 1], contains TTF moieties substituted by a pyridinylethene function as cation ligands.[8] Although magnetic and conducting systems are covalently linked through a delocalized bridge, the magnetic interaction is not so large, with $\theta = -3.8$ K owing to the long distance between the spin and charge sources. Other novel Cu^{I} complexes coordinated to ET [=bis(ethylenedithio)tetrathiafulvalene] are (ET)Cu$^{I}_2$Br$_4$, (ET)$_2$Cu$^{I}_6$Br$_9$, (ET)$_2$[Cu$_4$Br$_6$ET], (ET)$_2$Cu$^{I}_2$Br$_4$, (ET)$_2$Cu$^{I}_3$Br$_7$(H$_2$O), and (ET)$_2$Cu$^{I}_6$Br$_{10}$, where ET molecules are coordinated to Cu ions with the S atoms of the ethylenedithio groups in various coordination modes, such as monodentate, *trans*-bidentate, and *cis*-bidentate.[9] These materials are conducting but diamagnetic owing to Cu^{I}. Much more than a S atom, a N atom is a good Lewis base, so that N-containing organic donors could be good candidates as ligands. Therefore, we have first synthesized the supramolecular Cu complex, where Cu^{II} is coordinated by the *pyrazino-fused* TTF as a ligand, [CuCl$_2$(BP-TTF)] (Figure 1). Herein, the preparation, X-ray crystal structure analysis, and measurements of the magnetic and electrical properties of **1** are reported.

BP-TTF was synthesized as described in the literature.[10] The Cu complex [CuCl$_2$(BP-TTF)] was prepared by a diffusion method; BP-TTF (10 mg) in CHCl$_3$ and TBA$_2$CuCl$_4$ (223 mg) in dry CH$_3$OH were added in the diffusion cell under a N$_2$ atmosphere. After about 2 weeks, black needle crystals of [CuCl$_2$(BP-TTF)] were collected by filtration and washed with dry CH$_3$OH. The composition of this complex was determined by scanning electron microscopy−energy-dispersive spectrometry (JEOL JCM-5000 and Oxford WDX 400 spectrometers) and structure analysis.[11]

The X-ray single crystal analysis of **1** shows the 3-D supramolecular network, as shown in Figure 2a,b. The zigzag [Cu^{II}Cl$_2$(BP-TTF)]$_n$ chain extends along the *b* axis, where

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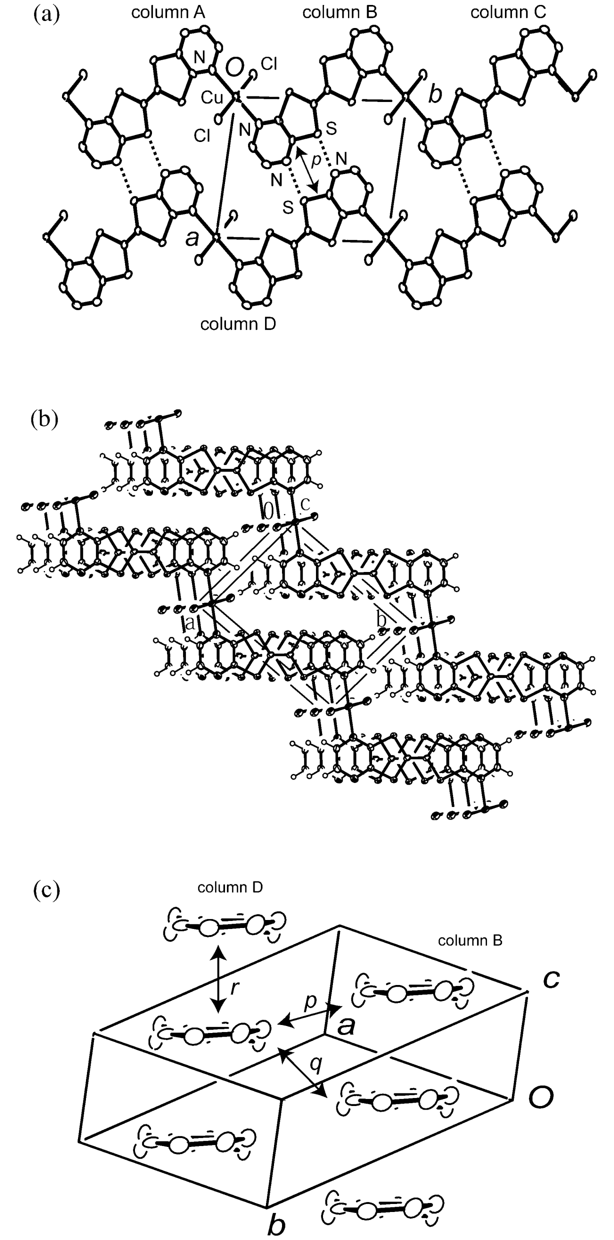

Figure 2. (a) Supramolecular $[CuCl_2(BP\text{-}TTF)]_n$ chains and side-by-side N···S contacts as dashed lines, viewed along the *c* axis, (b) packing of the $[CuCl_2(BP\text{-}TTF)]_n$ chains and the regular stacking donor columns viewed perpendicularly to the donor plane, and (c) donor arrangement of columns B and D of $[CuCl_2(BP\text{-}TTF)]$.

the Cu^{II} atom in a planar geometry is coordinated by two Cl^- and two N atoms of BP-TTF as ligands [Cu−Cl = 2.24 Å; Cu−N = 2.15 Å]. The Cu−Cl bond length is close to Cu^{II} distances; e.g., among Cu^{II} chlorides, one finds for $ET_3Cu^{II}Cl_4\cdot H_2O$ 2.25 Å,[12] for $[(C_2H_5)_2NH_2]Cu^{II}Cl_4$ 2.254 Å,[13] and for $[(R_nH_{4-n})N]_2Cu^{II}Cl_4$ 2.252 Å,[14] while for Cu^I chlorides, one finds for α'-$ET_2Cu^ICl_2$ 2.086 Å,[15] for β'-$ET_2Cu^ICl_2$ 2.098 Å,[16] and for $[(CH_3)_4N]Cu^ICl_2$ 2.107 Å.[17] The nonparallel alignment of the Cl−Cu−Cl fragment with respect to the ligand donor plane by 45° is to satisfy a sizable C−H···Cl hydrogen bond (2.80 Å). On the other hand, the donors form uniform stacking columns to have the β-type donor arrangement with the ring over bond configuration. The donor's interplanar distance is 3.87 Å, which is almost the same as that of $TMTSF_2PF_6$ (TMTSF = tetramethyltetraselenafulvalene) of 3.8−4.0 Å.[18] The molecular orbital of BP-TTF including N atoms is calculated by WinMOPAC (version 3.9.0, Fujitsu Ltd.). Based upon the obtained orbitals, the overlap integrals are calculated[19] to be $r = -5.3$, $p = -0.2$, and $q = 0.6$ ($\times 10^{-3}$). The largest interactions, *r*, are observed in the donor stacking direction, whereas the smaller ones are obtained in the intercolumnar direction, *p* with the close N···S contacts (3.10 Å) and *q* as shown in Figure 2a,c. Therefore, the d−σ coordination along the *b* axis and the π−π interactions in the *ac* plane construct the 3-D supramolecular framework.

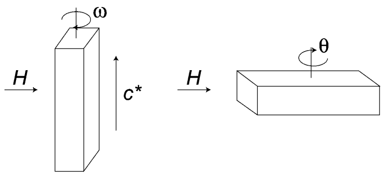

Figure 3. Crystal orientation of $[CuCl_2(BP\text{-}TTF)]$ in the ESR rotation experiment.

The resistivity measurement was performed on single crystals with carbon paint as four-probe contacts. The measurement at room temperature shows that $[CuCl_2(BP\text{-}TTF)]$ is an insulator.

To estimate the oxidation state of Cu, the electron spin resonance (ESR) measurement was carried out from 290 to 4 K with a Bruker EMS 9.3-GHz X-band ESR spectrometer equipped with an Oxford ITC305 cryostat. Figure 4 shows the angular dependences of the *g* value and the line width for one Lorentzian signal of the single crystal, $[CuCl_2(BP\text{-}TTF)_2]$, with the crystal orientation in Figure 3. The *g* value varies from 2.05 to 2.27 when the crystal is rotated about the pseudo-4-fold axis of $Cu^{II}Cl_2N_2$ coordination in **1** with the static field perpendicular to this axis (θ rotation), while the *g* value in the ω rotation is much smaller and the line width is nearly 4-fold rotation. This result is similar to that

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(11) Crystal data for **1**: $C_{10}H_4N_4S_4CuCl_2$, fw 442.86, triclinic, $P\bar{1}$, $a = 7.955(8)$ Å, $b = 11.40$ Å, $c = 3.872$ Å, $\alpha = 98.72(9)°$, $\beta = 91.54(9)°$, $\gamma = 98.28(9)°$, $V = 343.4(6)$ Å^3, $Z = 1$, $D_{calc} = 2.141$ g cm^{-3}, $R = 0.080$, $Rw = 0.098$, reflections used 2153 with $I > 3\sigma(I)$. Data collection was performed on a Rigaku 7R diffractometer (Mo Kα, $\lambda = 0.710\ 69$ Å) at 293 K. The structure was solved with direct methods and refined with a full-matrix least-squares technique using Crystal Structure (version 3.6.0; Rigaku Co. and Rigaku/MSC). Anisotropic thermal parameters were applied to all non-H atoms. The H atoms were generated geometrically (C−H = 0.950 Å).

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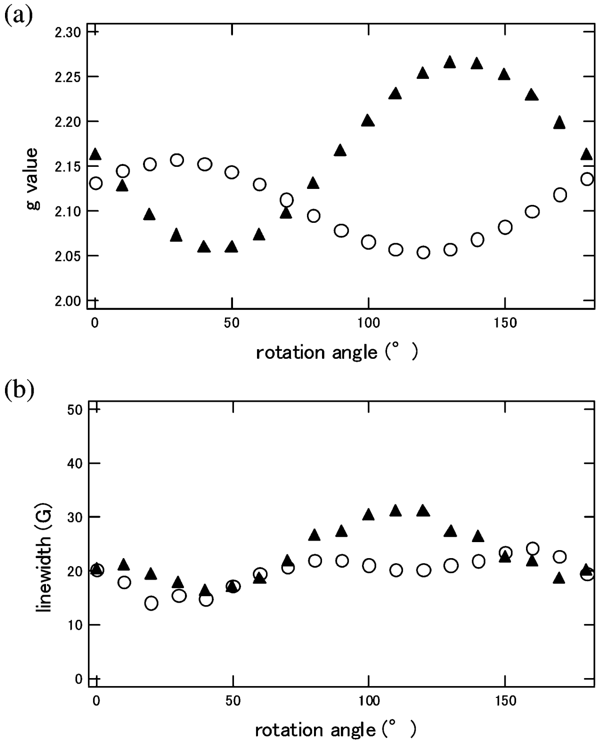

Figure 4. Angular dependence of (a) the g value and (b) the line width for [$CuCl_2$(BP-TTF)] at 290 K (open circle, ω rotation; filled triangle, θ rotation).

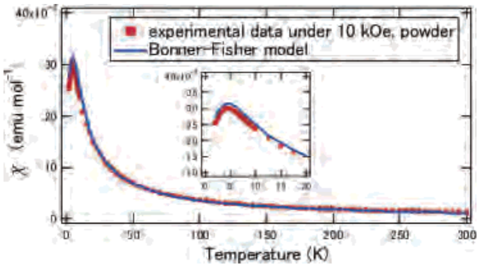

Figure 5. Temperature dependence of magnetic susceptibility for [$CuCl_2$-(BP-TTF)]. The solid line denotes the theoretical fitting for the 1-D Bonner−Fisher model ($H = -2J\sum S_iS_{i+1}$)[21] in the temperature range 2−300 K, where Cu^{II} $S = {}^1/_2$ and the antiferromagnetic interaction $J = -3.5$ K are estimated.

of (BEDT-TTF)$_3$$Cu^{II}Cl_4{\cdot}H_2O$,[12] within the range for Jahn−Teller distorted $Cu^{II}X_4$ ions.[20] Therefore, the Cu complex is expected to be [$Cu^{II}Cl_2$(BP-TTF)^0] in correspondence with the insulating behavior without carriers. The temperature dependence of ESR measurements was carried out from 290 to 4 K in the magnetic field parallel and perpendicular to the c^* axis. With lowering temperatures, the line widths decrease from 29 G (290 K) to 16 G (4 K) for $H \perp c^*$ and from 23 G (290 K) to 18 G (4 K) for $H \parallel c^*$, while the g values are almost constant over the temperature range.

The temperature dependence of magnetic susceptibility after subtraction of the Pascal diamagnetic contribution for [$CuCl_2$(BP-TTF)] was investigated by a Quantum Design MPMS-XL SQUID magnetometer under 10 000 Oe, as shown in Figure 5. The magnetic susceptibility χ at 300 K is 1.334×10^{-3} emu mol^{-1} and fits to a Bonner−Fisher model[21] from 2 to 300 K with $S = {}^1/_2$ and $J = -3.5$ K. The preliminary torque measurements indicate that **1** has no long-range magnetic order down to 1.7 K. Above the hump at 4.4−300 K, χ also follows the Curie−Weiss law, $\chi = C/(T - \theta)$, with $\theta = -7.4$ K and $C = 0.4076$ emu mol^{-1} K^{-1}. Utilizing the g value 2.12 observed from ESR measurements, the spin density is estimated at $N \sim 1$ spin ($S = {}^1/_2$)/formula unit. These results reveal that the oxidation states are Cu^{II} and BP-TTF^0, which are in agreement with the crystal structure and transport and ESR measurements. Moreover, it should be kept in mind that $Cu^{II}-Cu^{II}$ and $Cu^{II}Cl{\cdots}Cu^{II}$ distances are at least 3.87 and 5.56 Å, respectively, so the direct and superexchange interaction between the Cu^{II} ions through Cl^- can be ruled out. Therefore, it is concluded that the antiferromagnetic interaction between Cu^{II} $S = {}^1/_2$ spins appears through coordinated BP-TTF donors as ligands, namely, the d−π interaction.

In conclusion, we have synthesized the Cu^{II} complex with pyrazino-fused TTF as the ligand, [$CuCl_2$(BP-TTF)]. The crystal structure reveals the 3-D supramolecular framework, where the 1-D zigzag chain [$CuCl_2$(BP-TTF)]$_n$ extends along the b axis, the BP-TTF donors stack to form columns along the c axis, and the donor side-by-side interactions appear in the a axis. Owing to this supramolecular structure, the magnetic susceptibility measurement demonstrates the antiferromagnetic interactions between Cu^{II} $S = {}^1/_2$ spins mediated by BP-TTF donors, namely, d−π interactions. A further study aimed at the synergetic action of magnetism and conductivity in the novel Cu^{II} complex with other pyrazino-fused donors is promising to open to the novel d−π system.

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Supporting Information Available: X-ray crystallographic data for **1** in CIF format and X-ray analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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