A Novel Two-Dimensional Copper(I) Coordination Polymer with Bridging TTF: Crystal Structure of $[Cu(dmtpn)_2(TTF)_{0.5}](ClO_4)$(dmtpn: 2,5-dimethylterephthalonitrile)

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The X-ray crystal structure analysis of a copper(I) coordination compound, $[Cu(dmtpn)_2(TTF)_{0.5}](ClO_4)$ revealed the novel two-dimensional polymer framework bridged by dmtpn and TTF, which is the first example of bridging TTF coordinated to transition metal ions.

Although TTF is well known as a good electron donor, its sulfur atoms themselves are not so good donor to coordinate to metal ions. As far as we know[1] the only one example of TTF sulfur coordinating to a metal ion is a dirhodium tetra-acetate derivative, $Rh_2(O_2CCH_3)_4(TTF)_2$,[2] where one of four sulfur atoms in TTF coordinates to a rhodium atom in monodentate fashion. During the course of our study to developing new material with functionality, we could obtain a novel polymeric structure of copper(I) coordination compounds bridged by both TTF and 2,5-dimethylterephthalonitrile (dmtpn). This is the first example of TTF bridging two metal ions and shows future possibility of TTF being utilized as a bridging ligand in functional coordination polymer compounds.

Red crystals of $[Cu(dmtpn)_2(TTF)_{0.5}](ClO_4)$ (**1**) suitable for X-ray crystallography were obtained by slow diffusion of *n*-pentane into an ethanol solution containing copper(I) perchlorate, dmtpn, and TTF with a molar ratio of 1:2:1.[3] The single crystal X-ray analysis[4] revealed that a copper(I) ion in **1** is coordinated by three nitrogen atoms of three dmtpn and one sulfur atom of TTF as shown in Figure 1. The copper(I) ion has trigonal pyramidal geometry with the sulfur atom in the apical position. The copper atom is located 0.414 Å above the basal plane defined by three nitrogen atoms. The Cu-S bond length of 2.493(1) Å is fairly longer than those of 2.28-2.44 Å in copper(I) complexes with other thioether[5-7] indicating that TTF sulfur atom is not so strong donor to metal ions. The other example of coordinating TTF in $Rh_2(OC_2CH_3)_4(TTF)_2$ also shows weak coordination bond: the Rh-S bond length of 2.519(4) Å should be compared to those of 2.27-2.43 Å in rhodium(II) complexes with other thioether.[5]

There are three, crystallographically independent dmtpn: two of them named A (containing N(3) atom) and B (containing N(4) atom), have the inversion center at the center of their aromatic rings and act as bridging ligands to copper(I) ions resulting in the formation of one-dimensional zigzag chain, while the other one named C coordinates to a copper(I) ion in monodentate fashion (Figure 2(a)). Three dmtpn are roughly parallel to each other with

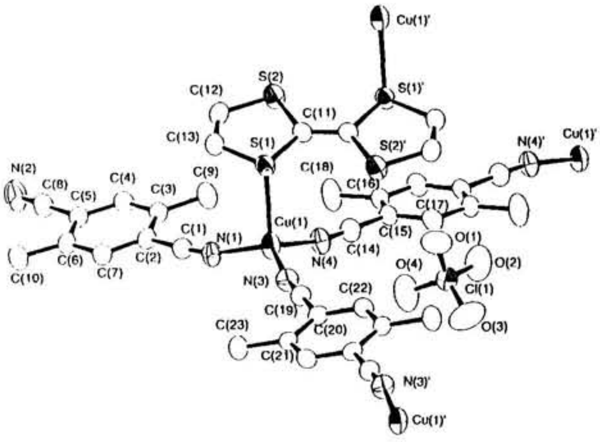

Figure 1. ORTEP drawing of asymmetric unit and a part of symmetry expanded atoms of $[Cu(dmtpn)_2(TTF)_{0.5}](ClO_4)$ (**1**) showing 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

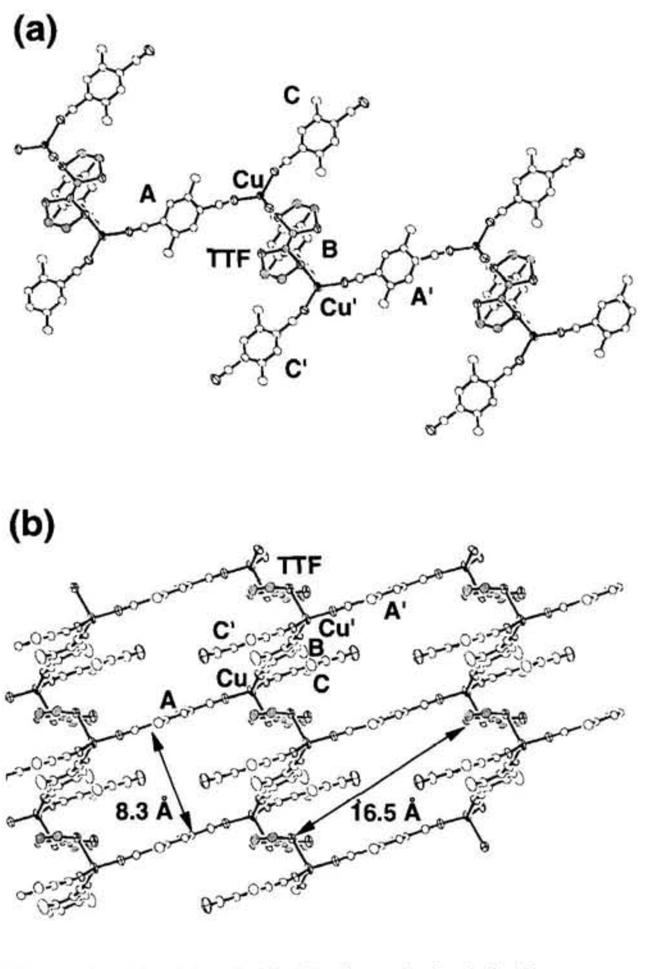

Figure 2. Top (a) and side (b) views of a bookshelf-type two-dimensional framework in **1** composed of one-dimensional $[Cu(dmtpn)_2]^+$ chains and bridging TTF.

dihedral angles of 13.5°, 11.7° and 3.4° for A-B, B-C and A-C planes, respectively. The last value close to zero is corresponding to the existence of π–π interaction between A and C (*vide infra*). The bridged Cu(1)•••Cu(1)' distance in the zigzag chain is 11.76 Å in average and a Cu(1)•••Cu(1)'•••Cu(1)" angle is 111.6°. All copper(I) ions in the chain are lying on the same plane. Dihedral angles between this plane and planes defined by A, B and C are 17.6°, 9.1° and 20.5°, respectively. Adjacent zigzag chains run parallel in [$\bar{1}$11] direction and are interconnected through bridging TTF, resulting in the formation of a bookshelf-type two-dimensional framework as shown in Figure 2. The TTF molecule, having the inversion center, is almost flat and is inclined at 19.8° from the plane defined by the zigzag chain. The two-dimensional framework displays a six-membered ring of copper(I) ions bridged by two TTF and four dmtpn. The approximate size of the six-membered ring is 16.5 × 8.3 Å^2. Figure 3 shows a schematic packing model of 1 viewed from one-dimensional chain axis. Six-membered rings in a two-dimensional framework are filled by monodentate dmtpn (C) residing on the neighboring frameworks so that they are packed closely. Two dmtpn C are located above and beneath of a bridging dmtpn A with the nearest C•••C distance of 3.456(5) Å, indicating π–π interaction between them. The π–π stacking interaction is restricted to these three dmtpn due to the disturbance of perchlorate ions. The structure does not show interwoven nor intercatenated structure as can be seen in some other polymeric two- or three-dimensional coordination polymer compounds.[8]

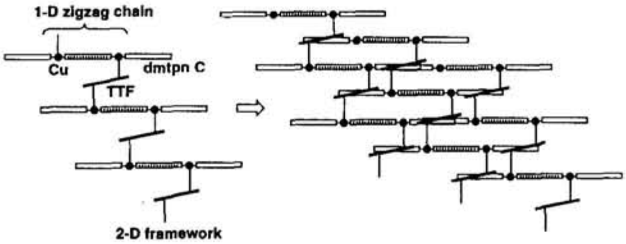

Figure 3. Schematic illustrations of a two-dimensional framework (left) and crystal packing (right) of **1** viewed from the one-dimensional chain axis.

The UV-vis. spectrum of **1** measured with KBr pellet shows a weak absorption band at λ_{max} = 575 nm as a shoulder of a strong absorption band in the UV region. Since TTF itself shows a similar weak band at around 500 nm, the clear red-shift is caused by coordination of sulfur atom to copper(I) ion.

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References and Notes

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3 Synthesis of [Cu(dmtpn)$_2$(TTF)$_{0.5}$](ClO$_4$): A colorless solution of copper(I) perchlorate in ethanol (4 mL) obtained by a reaction of a copper(II) perchlorate hexahydrate (4.6 mg, 0.012 mmol) and copper metal under ethylene was mixed with a solution of TTF (4.1 mg, 0.2 mmol) and dmtpn (6.2 mg, 0.4 mmol) mixture dissolved in 2 mL of ethanol. The resultant yellow solution was transferred to a glass tube under argon and 3 mL of ethanol and 6 mL of *n*-pentane were added slowly in sequence. The glass tube was sealed up and kept at room temperature. After standing for three days, red plate crystals were obtained. Anal: Calc. for $C_{23}H_{18}CuClN_4O_4S_2$, C, 47.8; H, 3.14; N, 9.70. Found: C, 47.6; H, 3.07; N, 9.67%.

4 Crystal data for **1**: $C_{23}H_{18}CuClN_4O_4S_2$, M = 577.54, triclinic, $P1$, a = 10.384(2), b = 12.773(3), c = 9.984(2) Å, α = 98.24(2)°, β = 110.72(1)°, γ = 83.75(2)°, U = 1223.4(4) Å^3, Z = 2, D_{cal} = 1.567gcm^{-3}, Mo-Kα radiation (λ = 0.71069 Å). The data collection was performed on a Rigaku AFC5R diffractometer using the $\omega/2\theta$ scan technique (θ_{max} = 27.5°). The structure was solved by direct methods.[9] The non-hydrogen atoms were refined anisotropically. Full matrix least-squares refinement on $F_o{}^2$ gave a final agreement index R of 0.038 for 3629 significant [$F_o > 3\sigma(F_o)$] absorption corrected data, out of the 5929 unique collected reflections.

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