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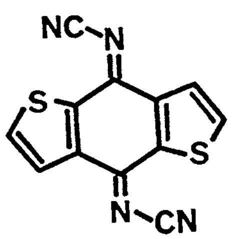
Novel Conducting Copper Complexes Based on Thiophene-fused DCNQI

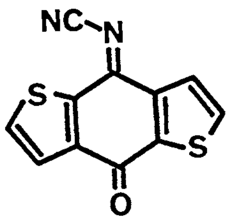
Keiji KOBAYASHI,[*] Yasuhiro MAZAKI, Koichi KIKUCHI,[†]
Kazuya SAITO,[†] Isao IKEMOTO,[†] and Shojun HINO[††]
Department of Chemistry, College of Arts and Sciences,
The University of Tokyo, Komaba, Meguro-ku, Tokyo 153
[†]Department of Chemistry, Faculty of Science,
Tokyo Metropolitan University, Fukazawa, Meguro-ku, Tokyo 158
[††]Graduate School of Science and Technology, Chiba University,
Yayoi-cho, Chiba 260

Novel copper complexes (DTQI)(CuI)$_2$ and (DTQI)$_2$Cu(H$_2$O) were prepared by using a new acceptor DTQI, i.e., thiophene-fused DCNQI. The former was metallic down to 170 K with the room temperature conductivity of 45 S cm^{-1} (compaction).

Since the discovery of a new type of conducting materials based on N,N'-dicyanoquinonediimines (DCNQIs), metal salts of DCNQIs have attracted a great deal of attention.1) In particular, copper(I) salts are of considerable current interest due to their high conductivities and metallic behavior down to liquid helium temperature.2) A variety of substituted DCNQIs have also been prepared and investigated. As a structural modification for extended π-framework of DCNQI we have prepared a new acceptor species DTQI **1**, in which a DCNQI molecule is fused to two thiophene rings. An annelation of thiophene rings to 7,7,8,8-tetracyanoquinodimethane (TCNQ) has been shown to bring about an excellent acceptor species for organic conductors.3) We report here entirely novel classes of highly conducting copper complexes derived



1
DTQI



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from DTQI.

Acceptor DTQI **1** was prepared by the titanium tetrachloride-mediated Knoevenagel reaction of the precursor quinone with bis(trimethylsilyl)carbodiimide. The resulting condensation products were purified by chromatography on silica gel column with dichloromethane as eluant to give **1** in 12% yield as deep orange crystalline solid [mp; decomp. above ca. 280 °C to colorless solid, IR(KBr): 2156 cm^{-1}, MS: m/e 268(M^+)] along with 15% of mono-cyanoimine derivative **2** [mp; 198-200 °C, IR(KBr): 2156, 1642 cm^{-1}, MS: m/e 244(M^+)]. Cyclic voltammetry of DTQI revealed two one-electron reduction waves at +0.10 and -0.22 V in DMF-Bu_4NClO_4 vs. S. C. E.

The reaction of acetonitrile solution of DTQI with copper wire gave black fine crystalline solids of unexpected formula including H_2O, $(DTQI)_2Cu(H_2O)$. On the other hand, the reaction of copper(I) iodide with DTQI in acetonitrile afforded the black fine needle crystals again with unusual stoichiometry including iodine, $(DTQI)Cu_2I_2$. The compositions of these new copper complexes, confirmed by microanalysis$^{4)}$ as well as XPS analysis, are quite novel since the DCNQI-metal complexes contain no additional elements such as H_2O or iodine.$^{5)}$ Furthermore, the reaction of dimethylDCNQI with Cu yields the same compound as that prepared by the reaction with CuI; both form Cu_2(dmDCNQI).$^{2)}$ Thus, DTQI shows completely different complexation properties from those of DCNQIs explored extensively by Hunig.$^{6)}$

The d. c. conductivities of the complexes were measured using the standard four probe method on the compacted powder samples. In spite of powder conductivities those were very high values. The $(DTQI)_2Cu(H_2O)$

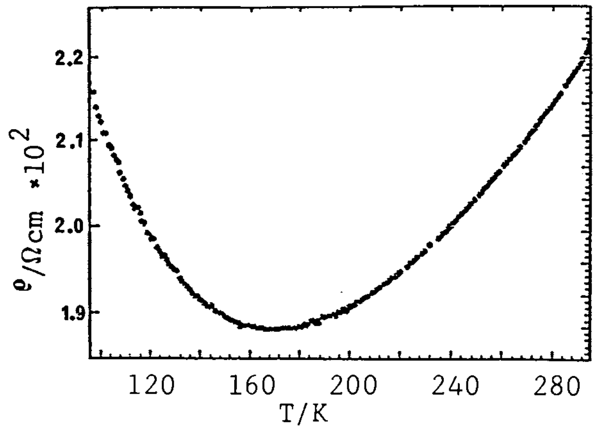

Fig. 1. Temperature dependence of the electrical resistivity of $(DTQI)(CuI)_2$ measured as compaction pellets.

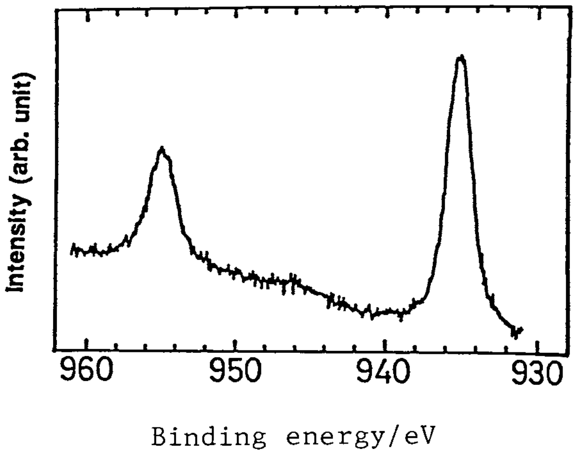

Fig. 2. The XPS of Cu2p of $(DTQI)(CuI)_2$.

complex is a semiconductor with room temperature conductivity as high as 72.5 S cm^{-1} and an activation energy as low as 0.019 eV. On the other hand, the compaction sample of (DTQI)Cu_2I_2 exhibits a metallic conductivity from room temperature down to 170 K (Fig. 1). The room temperature conductivity is 45 S cm^{-1}.

We have measured X-ray photoelecron spectra (XPS) of (DTQI)Cu_2I_2.7) The Cu $2p_{3/2}$ peak is observed at binding energy of 931.5 eV (Fig. 2). The Cu $2p_{3/2}$ peak is wider than the metal Cu 2p peaks, but much narrower to be composed of two peak components of Cu^+ and Cu^{2+}. Furthermore, the binding energy and peak profiles of of I 3d, being observed at 619.5 eV, were almost the same as those of I 3d in CuI. These results indicate that the valency of copper is close to +1 and the charge-transfer from copper to DTQI occurs only slightly.

Another interestng result was seen in the thermoelectric power measurements of (DTQI)Cu_2I_2. A positive value +50 μV/K was obtained on the compressed pellets samples, indicating the charge carriers are holes. For $(DCNQI)_2M$ family, the thermoelectric power is negative as they are acceptor conductors.8)

Unfortunately, the novel copper complexes $(DTQI)_2Cu(H_2O)$ and (DTQI)Cu_2I_2 could be obtained only as microcrystalline needles so that no single-crystal measurement or structure analysis could be performed and therefore the conduction behaviour of these materials are not fully understandable at this stage. However, as a clue to the structure of (DTQI)Cu_2I_2, it is instructve to consider the CuI complex of methyl isocyanide.9) The crystal of CuI(MeNC) is composed of a chain of copper and iodine atoms. At the center of the chain a copper atom (Cul) is bonded tetrahedrally to four iodine atoms. On alternate of the chain a copper atom (Cu2) is bonded tetrahedrally to two iodine atoms, which are shared with Cul, and to two MeCN molecules which are located at the sides of the chain. As DTQI could be a bidentate ligand, we could postulate the structure of (DTQI)Cu_2I_2 as follows: when two molecules of MeNC in CuI(MeNC) are replaced by a DTQI molecule, the CuI chains would be connected by bridging of DTQI ligands to lead the polynuclear complex represented by a formula $(DTQI)(CuI)_2$. A small amount of charge transfer from the CuI chains to the DTQI ligands may bring about the net positive charge in the chain of CuI and hence it assists hole conduction along the CuI polymer backbone. The occupation of the nitrogen and iodine atoms close to the copper atoms was also supported by the EXAFS studies.10)

In conclusion we have demonstrtated the new copper complexes based on thiophene-fused DCNQI, which show high conductivities and are the most unusual compounds in the composition, hence in the structure and properties.

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References

1) A. Aumuller and S. Hunig, Angew. Chem., Int. Ed. Engl., **23**, 447 (1984); A. Aumuller and S. Hunig, Liebigs Ann. Chem., **142**, 165 (1986); S. Hunig, Pure Appl. Chem., **62**, 395 (1990).
2) A. Aumuller, P. Erk, G. Klebe, S. Hunig, J. -U. von Schutz, and H. -P. Werner, Angew. Chem, Int. Ed. Engl., **25**, 740 (1986).
3) K. Kobayashi and C. L. Gajurel, J. Chem. Soc., Chem. Commun., **1986**, 1779; K. Kobayashi, Y. Mazaki, and F. Iwasaki, Syn. Met., **27**, B309 (1988).
4) Elemental analysis for $(DTQI)_2Cu(H_2O)$. Found: C 46.32, H 1.62, N 17.73%. Calcd: C 46.62, H 1.63, N 18.13%. For $(DTQI)(CuI)_2$. Found: C 22.46, H 0.97, N 8.41, I 40.31%. Calcd: C 22.19, H 0.61, N 8.63, I 39.14%.
5) Because of of solubility problems, a large amount of hot acetonitrile is required to dissolve DTQI and CuI, so that contamination of water would not be avoided even if dry acetonitrile is used.
6) The DCNQI complexes that have a composition other than (DCNQI):metal=2:1 have been reported. P. Erk, S. Hunig, H. Meixner, J. -U. von Schutz, and H. -P. Werner, Liebigs Ann. Chem., **1988**, 157; T. Mori and H. Inokuchi, Chem. Lett., **1990**, 2077.
7) K. Kobayashi, K. Kikuchi, K. Saito, and S. Hino, Syn. Met., in press.
8) S. Tomic, D. Jerome, A. Aumuller, P. Erk, S. Hunig, and J. U. von Schutz, Syn. Met., **27**, B281 (1988).
9) P. J. Fisher, N. E. Taylor, and M. M. Harding, J. Chem. Soc., **1960**, 2303.
10) Y. Kosugi, K. Kobayashi, Y. Mazaki, K. Kikuchi, and I. Ikemoto, to be published.

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