CHEMISTRY LETTERS, pp. 55-58, 1988.

A New Ambient Pressure Organic Superconductor Based on BEDT-TTF with T_c Higher than 10 K (T_c=10.4 K)

Hatsumi URAYAMA, Hideki YAMOCHI, Gunzi SAITO,* Kiyokazu NOZAWA, Tadashi SUGANO, Minoru KINOSHITA,* Shoichi SATO, Kokichi OSHIMA,+ Atsushi KAWAMOTO,++ and Jiro TANAKA++

Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106

+ Cryogenic Center, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113

++ Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464

An ambient pressure superconductivity of $(BEDT\text{-}TTF)_2Cu(SCN)_2$ was observed by d.c. magnetic susceptibility and electrical conductivity measurements. The superconducting critical temperature is the highest (T_c=10.4 K) among the organic superconductors so far obtained, even though the anion has a positional disorder in the crystal.

More than ten kinds of superconductors have been enrolled in the family of BEDT-TTF (bis(ethylenedithiolo)tetrathiafulvalene) superconductor since the first observation of two-dimensional electrical conductivity in a BEDT-TTF cation radical salt.[1] The manifested feature of the BEDT-TTF superconductors is the strong two-dimensionality in their electronic structures compared to the quasi-one-dimensionality of TMTSF,[2] DMET,[3] and $Ni(dmit)_2$[4] superconductors. Besides that, the relatively high T_c at ambient pressure has attracted a variety of studies on the BEDT-TTF superconductors.

Majority of the BEDT-TTF superconductors include linear counter anions such as I_3^-,[5] IBr_2^-,[6] and AuI_2^-,[7] and BEDT-TTF has uniqueness that several superconductors have been explored with the same anion, I_3^-, namely iodine doped α-,[5a] β-,[5b] γ-,[5c] θ-,[5d] and κ-phases.[5e] Among them T_c of β-$(BEDT\text{-}TTF)_2I_3$ salt was observed to increase from 1.4 K to 7.5 K by an application of a moderate pressure.[8] The release of pressure provides a mixture of two different kinds of superconductors, low T_c β- (T_c=1.4 K) and high T_c β-$(BEDT\text{-}TTF)_2I_3$ (T_c=8.1 K), and T_c of the latter phase is the highest one among those of organic superconductors up to now.[9] But the high T_c β-$(BEDT\text{-}TTF)_2I_3$ phase is metastable and cannot be isolated without some treatment such as the release of the pressure at low temperature.[10]

For the β-phase salts with linear anions, it has been noticed that asymmetry of counter anion (X) tends to destroy the superconductivity and that T_c increases

with increasing the length of X or with decreasing the 'lattice pressure'.[11] Therefore it is worth to use a linear anion longer than I_3^- (10.2 Å) for experimentally searching for high T_c in BEDT-TTF salts.

We have obtained an ambient pressure organic superconductor having T_c higher than 10 K by employing $Cu(SCN)_2^-$ as a counter anion which is expected to be longer than I_3^- if it is linear. In this letter we report the synthesis, structural, and physical properties of this salt briefly.

Distorted-hexagon-shaped crystals of the $Cu(SCN)_2$ salt (2.1 x 0.85 x 0.04 mm^3) were prepared by the electrochemical oxidation of BEDT-TTF in 1,1,2-trichloroethane in the presence of CuSCN, KSCN, and 18-crown-6 ether under a constant current of 1.5 μA. The crystals were obtained after one week and only one phase with 2:1 stoichiometry has been yielded up to date (elemental analysis, Found C, 27.78; H, 1.79; N, 2.94; S, 60.40%. Calcd for $C_{22}H_{16}N_2S_{18}Cu_1$: C, 27.84; H, 1.70; N, 2.95; S, 60.81%).

The crystal data of $(BEDT\text{-}TTF)_2Cu(SCN)_2$ are: monoclinic, space group $P2_1$, a=16.248(5), b=8.440(2), c=13.124(5) Å, β=110.30(3)°, V=1688.0(9) $Å^3$, and Z=2. Reflection data were collected by the ω-2θ scan technique on a Rigaku automated four-circle diffractometer with graphite monochromated Mo K_α radiation (2θ <60°). The crystal structure is shown in Fig. 1. There are two independent BEDT-TTF molecules in an asymmetric unit. The packing pattern of BEDT-TTF molecules nearly resembles that of κ-$(BEDT\text{-}TTF)_2I_3$ salt in which almost two-dimensional Fermi surface was estimated on the basis of the extended-Hückel MO.[5e] Like the κ-$(BEDT\text{-}TTF)_2I_3$ salt, two BEDT-TTF molecules form a dimer which is connected to one another by short S····S contacts to form a BEDT-TTF sheet in the bc plane. Since several strong reflections ((h0l), l=2n+1) were observed, the space group is lowered from $P2_1/c$ in the κ-$(BEDT\text{-}TTF)_2I_3$ to $P2_1$ in this crystal.

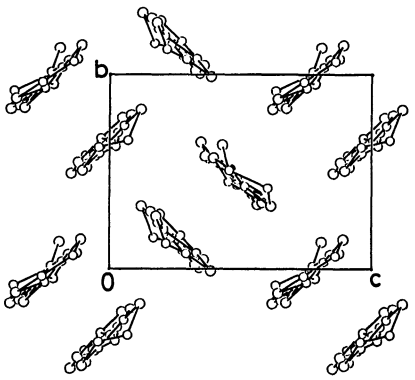

Fig. 1. Crystal structure viewed along the molecular long axis. Only BEDT-TTF molecules are depicted.

The anion is allocated in the plane between BEDT-TTF sheets. The shape of the anion is not linear but bent and there appears the positional disorder in the anion. Owing to this positional disorder of $Cu(SCN)_2$, the R value is considerably large at present (13.8%). A refinement of the crystal structure is underway. The copper atoms in the crystal were identified as Cu(I) by ESCA at room temperature which is consistent with the ESR data.[12]

The d.c. magnetic susceptibility (defined as χ=M/H) was measured with the polycrystalline sample of $(BEDT\text{-}TTF)_2Cu(SCN)_2$ using a Faraday susceptometer. As shown in Fig. 2(a), the paramagnetic susceptibility at 30 kOe is almost constant down to 90 K and then decreases very gradually down to about 10 K followed by an abrupt decrease below 10 K. The behavior above 10 K is characteristic of the Pauli paramagnetism and suggests the metallic nature of this salt all the way down to 10 K.

In the low temperature region (2-20 K), the susceptibility was again measured

with subsequent cooling of the sample under the constant field of 100 Oe. As is shown in Fig. 2(b), the susceptibility starts to decrease at 9.4 ± 0.3 K very drastically and shows quite large diamagnetism below 9 K. At 2.1 K, the magnitude of diamagnetic susceptibility exceeds 5% of the perfect diamagnetism ($-1/4\pi$ emu cm^{-3}). This clearly shows the occurrence of the transition to a superconducting state. The transition temperature is then expected to be somewhat higher than 9.4 K at zero field.

The electrical conductivity of the single crystal was measured by four-probe method using gold paste as a contact. The contact resistance was 40 Ω and slowly increased to 150 Ω after one day suggesting some decomposition of the crystal surface but the contact was ohmic. Figure 3 shows the temperature dependence of the electrical resistivity of the crystal along the b-axis. The room temperature conductivity was about 14 S cm^{-1}. The crystal was metallic down to around 250-270 K with weak temperature dependence. Then an upturn of resistivity was observed down to around 90 K where the conductivity was about 1/6 of the room temperature value. After passing through the maximum at 90 K, the resistivity decreased very rapidly. This kind of resistivity behavior was always observed in the specimens tested though the temperatures giving the resistance minimum and maximum changed slightly from sample to sample. This temperature dependence is reminiscent of those of $(TMTSF)_2ReO_4$ at high pressure,[13] iodine doped α-$(BEDT\text{-}TTF)_2I_3$,[5a] and γ-$(BEDT\text{-}TTF)_3(I_3)_{2.5}$,[5c] all of which have some disorder in the crystals. This together with the temperature independent paramagnetism strongly

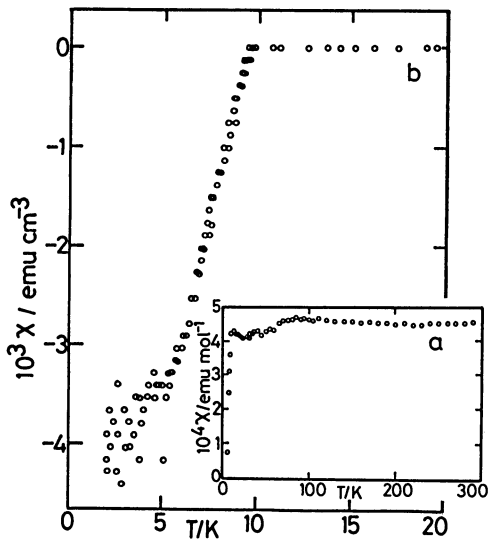

Fig. 2. (a)Temperature dependence of the molar paramagnetic susceptibility, corrected for the diamagnetic contribution (χ_d=-474 x 10^{-6} emu mol^{-1}; 1 emu mol^{-1}=4π cm^3 mol^{-1}). (b)Temperature dependence of the volume susceptibility of $(BEDT\text{-}TTF)_2Cu(SCN)_2$.

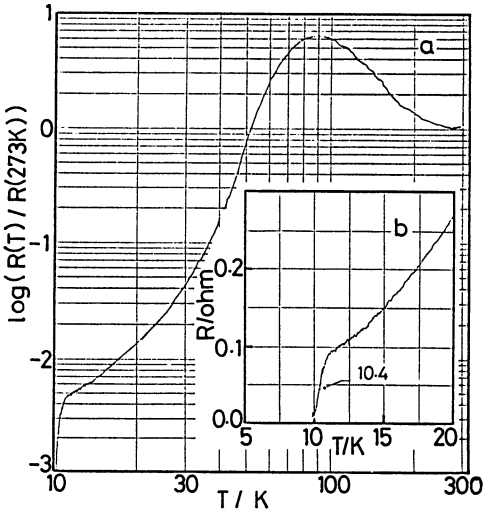

Fig. 3. Temperature dependence of the resistivity (a) and superconducting trasition (b) at ambient pressure in $(BEDT\text{-}TTF)_2Cu(SCN)_2$.

suggests that the increase of resistivity below 250-270 K in $(BEDT\text{-}TTF)_2Cu(SCN)_2$ may not be due to the gap formation but to the increased scattering rate in the transport caused by the disorder.

The superconductivity was observed with an onset at 11 K. T_c was found to be 10.4 ± 0.1 K at zero magnetic field when T_c is defined as the midpoint of the resistive transition. Details of conductivity, magnetic susceptibility and other physical properties will be described very soon.

In summary, we have prepared for the first time a stable organic superconductor, $(BEDT\text{-}TTF)_2Cu(SCN)_2$, exhibiting complete superconductivity above 10 K at ambient pressure, though the crystal has positional disorder concerning with the anion.

This work was partly supported by the Grant-in-Aid for the Scientific Research on Priority Areas, New Functionality Materials-Design, Preparation and Control from the Ministry of Education, Science and Culture (No. 62604014, 62604521).

References

1) G. Saito, T. Enoki, K. Toriumi, and H. Inokuchi, Solid State Commun., 42, 557 (1982).
2) D. Jerome and H. J. Schulz, Adv. Phys., 31, 299(1982).
3) K. Kikuchi, M. Kikuchi, T. Namiki, K. Saito, I. Ikemoto, K. Murata, T. Ishiguro, and K. Kobayashi, Chem. Lett., 1987, 931.
4) L. Brossard, M. Ribault, M. Bousseau, L. Valade, and P. Cassoux, C. R. Acad. Sci. Paris, Ser. 2, 302, 205(1986); A. Kobayashi, H. Kim, Y. Sasaki, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita, and W. Sasaki, Chem. Lett., 1987, 1819.
5) a) E. B. Yagubskii, I. F. Shchegolev, V. N. Laukhin, R. P. Shibaeva, E. E. Kostyuchenko, A. G. Khomenko, Yu. V. Sushko, and A. V. Zvarykina, Pis'ma Zh. Eksp. Teor. Fiz., 40, 387(1984); b) E. B. Yagubskii, I. F. Shchegolev, V. N. Laukhin, P. A. Kononovich, M. V. Karatsovnik, A. V. Zvarykina, and L. I. Buravov, ibid., 39, 12(1984); c) R. P. Shibaeva, V. F. Kaminskii, and E. B. Yagubskii, Mol. Cryst. Liq. Cryst., 119, 361(1985); d) H. Kobayashi, R. Kato, A. Kobayashi, Y. Nishio, K. Kajita, and W. Sasaki, Chem. Lett., 1986, 789, 833; e) A. Kobayashi, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita, and W. Sasaki, ibid., 1987, 459.
6) J. M. Williams, H. H. Wang, M. A. Beno, T. J. Emge, L. M. Sowa, P. T. Copps, F. Behroozi, L. N. Hall, K. D. Carlson, and G. W. Crabtree, Inorg. Chem., 23, 3839 (1984).
7) H. H. Wang, M. A. Beno, V. Geiser, M. A. Firestone, K. S. Webb, L. Nunez, G. W. Crabtree, K. D. Carlson, J. M. Williams, L. J. Azevedo, J. F. Kwash, and J. E. Schirber, Inorg. Chem., 24, 2466(1985).
8) K. Murata, M. Tokumoto, H. Anzai, H. Bando, G. Saito, K. Kajimura, and T. Ishiguro, J. Phys. Soc. Jpn., 54, 1236(1985); V. N. Laukhin, E. E. Kostyuchenko, Yu. V. Sushko, I. F. Shchegolev, and E. B. Yagubskii, Pis'ma Zh. Eksp. Teor. Fiz., 41, 68(1985).
9) M. Tokumoto, K. Murata, H. Bando, H. Anzai, G. Saito, K. Kajimura, and T. Ishiguro, Solid State Commun., 54, 1031(1985).
10) F. Creuzet, G. Creuzet, D. Jerome, D. Schweitzer, and H. J. Keller, J. Phys. (Paris) Lett., 46, L1079(1985); V. B. Ginodman, A. V. Gudenko, I. I. Zasavitskii, and E. B. Yagubskii, Pis'ma Zh. Eksp. Teor. Fiz, 42, 384(1985).
11) J. M. Williams, A. J. Schultz, H. H. Wang, K. D. Carlson, M. A. Beno, T. J. Emge, U. Geiser, M. E. Hawley, and K. E. Gray, Physica, 143B, 345(1986); M. Tokumoto, H. Bando, K. Murata, H. Anzai, N. Kinoshita, K. Kajimura, T. Ishiguro, and G. Saito, Synth. Metals, 13, 9(1986).
12) H. Urayama, T. Sugano, G. Saito, M. Kinoshita, T. Mori, and Y. Maruyama, to be published.
13) S. S. P. Parkin, D. Jerome, and K. Bechgaard, Mol. Cryst. Liq. Cryst., 79, 213 (1982).

(Received October 6, 1987)