New Organic Conductor Containing Magnetic Ion of Cu(II): α''-(BEDT-TTF)$_2$KCu(SCN)$_4$

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(Received March 6, 1998; CL-980166)

New organic conductor containing pπ-d electrons, α"-(BEDT-TTF)$_2$KCu(SCN)$_4$, is eventually prepared. The calculated band structure is one-dimensional along the donor stacking direction. The electrical conductivity at room temperature is 0.5 Scm^{-1} with the activation energy of 0.09eV. The magnetic susceptibility is an addition of a Curie contribution of Cu(II) and an organic pπ part. The susceptibility of the pπ part does not follow the simple one-dimensional Heisenberg model.

After the discovery of the first ambient pressure organic superconductor with *Tc* over 10K, κ-(BEDT-TTF)$_2$Cu(NCS)$_2$,[1] two minor phases of Cu(SCN)$_2$ salts have been prepared: α-(BEDT-TTF)$_2$Cu(NCS)$_2$,[2] which undergoes a metal-insulator transition at 200K, and (BEDT-TTF)Cu$_2$(SCN)$_3$[3] with 2 x 10^{-5} S cm^{-1} and Ea= 0.17 eV. Recently we have eventually found the fourth Cu(SCN)$_2$ salt containing 3d localized electrons on Cu(II), α"-(BEDT-TTF)$_2$KCu(SCN)$_4$. Organic conductors possessing pπ-d electrons have attracted interests due to a rich variety of magnetic properties by interactions between pπ and d electrons: for examples, Cu(DMeDCNQI)$_2$ (DMeDCNQI: dimethyl-*N,N'*- dicyanoquionediimine)[4] and λ-(BETS)$_2$FeCl$_4$ (BETS:bis- (ethylenedithio)tetraselenafulvalene).[5] In this paper, the preparation, crystal and band structures, electrical resistivity, and magnetic susceptibility of new pπ-d conductor, α"-(BEDT-TTF)$_2$KCu(SCN)$_4$, are described.

Single crystals were grown by the electrocrystallization method in the presence of CuSCN, KSCN, and 18-Crown-6 in the mixed solvent of 1,1,2-trichloroethane and 10 % vol. ethanol. The only one exceptional batch has afforded α"-(BEDT-TTF)$_2$KCu(SCN)$_4$. The electrical resistivity measurement was carried out by the conventional d.c. four-probe method. The conductivity at room temperature is 0.5 Scm^{-1} and the activation energy is 0.09 eV.

The crystal structure analysis of α"-(BEDT-TTF)$_2$KCu(SCN)$_4$ has been carried out.[6] A donor layer and an anion sheet stack alternately along the a-axis (Figure 1(a)). The donor is located on a general position, K^+ is on a two-fold axis, Cu^{2+} is on an inversion center, two SCN^- ions are on general positions. Therefore, one donor, 1/2 of K^+ and Cu^{2+}, two SCN^- are crystallographically independent. The distances of the central C=C and C-S in a BEDT-TTF molecule are 1.350(6) and 1.74 Å, respectively, indicating that the charge on a donor is +0.5.[7] As a consequence, Cu is divalent.

The anion arrangement indicates that Cu^{2+} is coordinated by two N62 atoms and two S50 atoms of SCN^- ions to form a plane(Figure 1(b); ∠(S50-Cu-N62)=85.2(2), 94.8(2)°). The K^+ atom has ionic contacts with four S60 atoms and two N52 atoms octahedrally.[∠(S60-K-S60)=81.80(4), 98.2(1), 179.98(9)°, ∠(S60-K-N52)=82.4(1), 89.3(1), 90.7(1), 97.6(1)°] Therefore, two-dimensional anion network spreads in the bc plane.

As shown in Figure 1(c), the donor arrangement is α"-type. The donors stack regularly in the b-direction and the donor dihedral angle between columns of I and II or III and IX (θ; Figure 1(c)) is 128°. This donor stacking behavior is similar to θ-phase, but the donor interactions among columns II and III resemble those of β"-type salts[11]; the donor stacks in the 0°(p2), 30°(b), and 60°(p3) directions and the p3 interaction is the largest. Namely, the donor stacking behavior of α"-type is the combination of θ-type and β"-type.

In order to investigate the electronic state of α"-(BEDT-TTF)$_2$-KCu(SCN)$_4$ and other α"-type salts, the transverse integrals were calculated[12] and summarized in Table 1. By increasing a dihedral angle (θ), the transverse integral (|p1|) decreases; this behavior is similar to θ−type salts.[13] In θ-type BEDT-TTF salts, a metal-insulator transition temperature (T_{MI}) increases with an increase of a dihedral angle (θ) or a decrease of a overlap integral (|p1|). At the same time the bandwidth decreases in proportion to |p1|. T_{MI} of α"-type salt seems to follow this rule except for α"-ET$_2$Cu$_5$I$_6$ due to a two-dimensional rigid network. The calculated Fermi surface is one-dimensional along the donor stacking direction, which is characteristic of α"-type BEDT-TTF salts (Figure 1(d)).

Magnetic susceptibility is measured by SQUID (Quantum Design MPMSXL7). The magnetization curves in the magnetic field at 5K and 10K follow the Brillouin function with g=2.0 and S=1/2 originated from Cu^{2+}. The temperature dependence of magnetic susceptibility is shown in Figure 2. The spin susceptibility of BEDT-TTF, χ_{ET}, is calculated by subtracting a Curie contribution of Cu^{2+} (S=1/2, g=2.0) from the total susceptibility, χ_{total}. χ_{ET} at room temperature is 7.4x10^{-4} emu mol^{-1}, which is a little higher than that of θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$, 6.3x10^{-4} emu mol^{-1},[13] indicating a highly correlated system and the temperature dependence of χ_{ET} does not follow the simple one-dimensional Heisenberg model.

In summary, an organic conductor containing pπ-d electrons, α"-(BEDT-TTF)$_2$KCu(SCN)$_4$, was newly prepared. The con-

Table 1. The calculated overlap integrals (b,p1,p2,p3), dihedral angle (θ), metal-insulator transition temperature (T_{MI}) of α"-type BEDT-TTF (ET) salts

	overlap integral (x10^{-3})				θ/°	T_{MI}/K	reference
	b	p1	p2	p3			
ET$_2$K$_{1.4}$Co(SCN)$_4$	-1.5	-10.5	-9.3	-0.1	99	130	8
ET$_2$CsHg(SCN)$_4$	5.1	-8.9	-6.5	17.7	119	210	9
ET$_2$Cu$_5$I$_6$	5.3	-7.5	-7.7	16.4	125	<4	10
ET$_2$KCu(SCN)$_4$	4.1	-7.6	-6.7	19.8	128	semicon.	this work

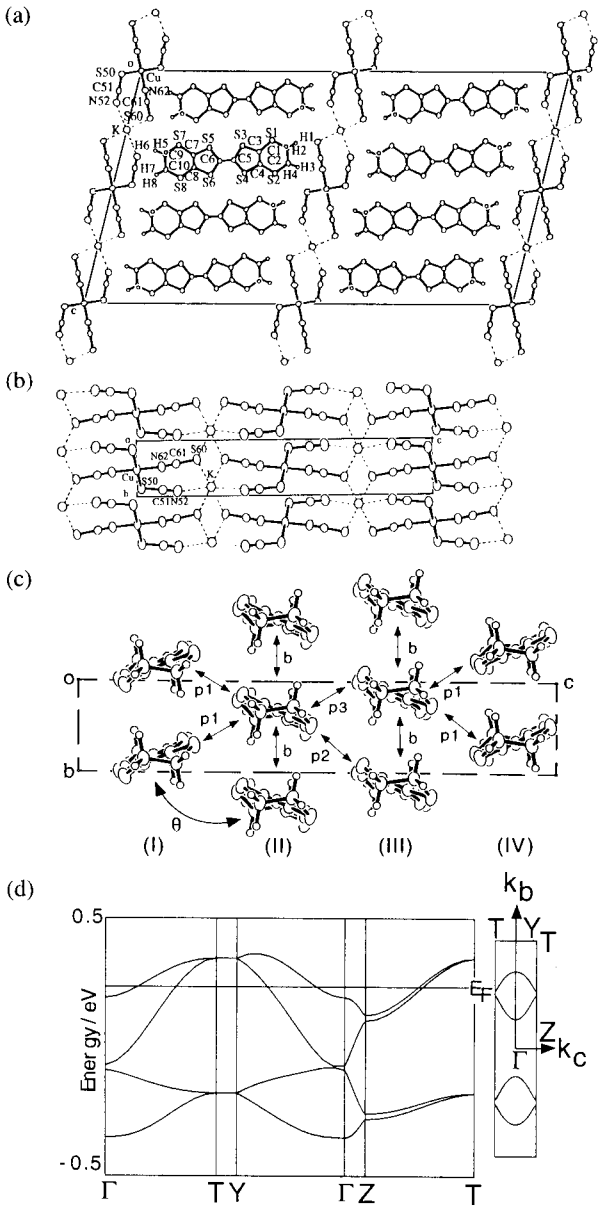

Figure 1. (a)Crystal structure, (b)anion arrangement, (c)donor arrangement, and (d)band structure and Fermi surface of α"-(BEDT-TTF)$_2$KCu(SCN)$_4$.

ductivity at room temperature is 0.5 Scm^{-1} and the activation energy is 0.09eV. The crystal structure analysis shows a two-dimensional layered structure, where the donor arrangement is α"-type and in an anion layer the charge of Cu is (2+). A magnetization curves in a magnetic field at 5 and 10K follow the Brillouin function with g=2.0 and S=1/2 originated from Cu^{2+}. The temperature dependence of magnetic susceptibility is analyzed by an addition of a Curie contribution of Cu^{2+} and highly correlated organic pπ spins, which does not follow a simple one-dimensional Heisenberg model.

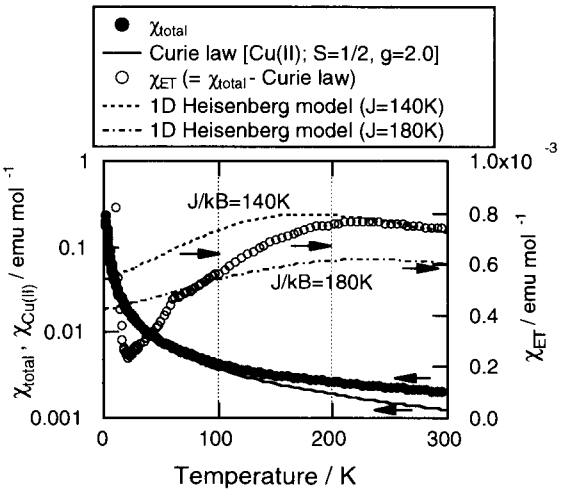

Figure 2. Temperature dependence of magnetic susceptibility of α"-(BEDT-TTF)$_2$KCu(SCN)$_4$.

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6 Crystal data: $C_{24}H_{16}S_{20}CuN_4K$, Fw=1104.38, monoclinic, space group C2/c (#15), a=41.112(2), b=4.257(3), c= 23.086(2) Å , β=103.463(5) °, V=3929(2)Å^3, Z=4, $D_{calc.}$=1.867 g cm^{-3}. Intensity data were collected using Rigaku-AFC5R automated four-circle diffractometer with graphite monochro- mated Mo-Kα radiation (λ=0.71073 Å). 2396 independent reflections (I>3σ(I)) were used for the structure analysis. The crystal structure was solved by the direct method (SHELX86) and refined by a full-matrix least squares method . Final R and Rw values were 0.046 and 0.028, respectively.

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