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Composition and Structure of the Anion Layer in the Organic Superconductor κ'-(ET)$_2$Cu$_2$(CN)$_3$: Optical Study

Olga Drozdova,*[†,‡,§] Gunzi Saito,[†] Hideki Yamochi,[†] Kenji Ookubo,[†] Kyuya Yakushi,[‡] Mikio Uruichi,[‡] and Lahcène Ouahab[¶]

Contribution from the Division of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan, the Institute for Molecular Science, Okazaki 444-8585, Japan, and Institut de Chimie de Rennes, LCSIM-UMR6511, Université de Rennes 1, 35042 Rennes Cedex, France

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Substitution of a donor or an acceptor component in an organic superconductor is an attractive strategy for modulating its physical properties, including superconducting critical temperature T_c. Intramolecular parameters, degree of the filling of the conduction band, effective volume available for free charge carriers, magnetic moment, etc., can be modified while keeping the crystal structure unchanged. On the other hand, such substitution would inevitably create disorders and defects to which some organic superconductors, in contrast to ordinary metallic ones, exhibit prominent sensitivity.[1] The Mott insulator κ-(ET)$_2$Cu$_2$(CN)$_3$ [ET is bis(ethylenedithio)tetrathiafulvalene] was first reported in 1991 by U. Geiser et al.,[2] and X. Bu et al.[3] Independently, we prepared an ET compound, which showed identical crystal structure but had metallic conducting behavior and superconductivity at 3.8 K and ambient pressure.[4] Because of this difference, our compound was called "κ'" (ref 4) to distinguish it from the Mott-insulator "κ" (refs 2 and 3). EPR spectra at 1.7 K detected in the κ'- samples additional signals coming from 88 to 1200 ppm of Cu^{2+}, which can substitute Cu^{1+} in the anion layer. The extra electron is accepted by the ET molecule, which changes its charge from $+0.5$ to $+0.5(1 - x)$ (where x is the amount of Cu^{2+}), and the insulating state is overcome by deviation of the upper band filling from the exactly 1/2. At large x, superconductivity disappears due to the pair breaking effect of paramagnetic Cu^{2+}.[5]

Our further synthetic efforts have systematically produced new batches of the single crystals, showing crystal structure of the κ-type (ET)$_2$Cu$_2$(CN)$_3$ and exhibiting superconductivity at ambient pressure with T_c ranging from 3 to 10 K. To understand such a drastic difference in the conducting behavior between κ- and κ'-(ET)$_2$Cu$_2$(CN)$_3$, we measured polarized infrared reflectance and Raman spectra on the single crystals of κ'-(ET)$_2$Cu$_2$(CN)$_3$ (17 samples from 10 batches, with $T_c = 3.0-3.2$, 6.4, 7.5−8.8, and 10 K), κ-(ET)$_2$Cu$_2$(CN)$_3$, and on the single crystals of a closely related superconductor, κ-(ET)$_2$Cu(CN)[N(CN)$_2$] ($T_c = 11.2$ K). Besides differences in the electronic spectra between insulating κ-(ET)$_2$Cu$_2$(CN)$_3$ and metallic κ'-(ET)$_2$Cu$_2$(CN)$_3$ and κ-(ET)$_2$Cu(CN)[N(CN)$_2$] in the far-infrared region at low temperatures, spectroscopic data gave another, rather unexpected result. Namely, in the region of the anion C≡N stretching vibrations of the κ'-salt, rather than observing the same spectral pattern as in κ-(ET)$_2$Cu$_2$(CN)$_3$, we found two mixed contributions, one indeed from Cu$_2$(CN)$_3$ while another was characteristic to that of Cu(CN)[N(CN)$_2$]. In this paper, we present results concerning the mixed ligands in the anion layer of κ'-(ET)$_2$Cu$_2$(CN)$_3$ and redefine its chemical formula.

Single crystals of κ-(ET)$_2$Cu$_2$(CN)$_3$, κ'-(ET)$_2$Cu$_2$(CN)$_3$, and κ-(ET)$_2$Cu(CN)[N(CN)$_2$] were grown electrochemically.[6] Superconductivity was detected by the onset of the diamagnetic signals in the magnetic susceptibility, on the whole batch and on a single crystal. Optical experiments were performed at ambient conditions using apparatuses described elsewhere.[8] Crystallographic axes b and c were determined from the angular dependence of the infrared reflectivity on the well-developed *(bc)* plane and were confirmed by X-ray analysis after the experiments.

Figure 1 shows the infrared reflectivity and Raman spectra of κ-(ET)$_2$Cu(CN)[N(CN)$_2$], κ-(ET)$_2$Cu$_2$(CN)$_3$, and κ'-(ET)$_2$Cu$_2$(CN)$_3$ ($T_c = 7.5$ K) in the region of anion C≡N stretching vibrations. A broad electronic background was extracted from the reflectivity data. It is seen that κ'-(ET)$_2$Cu$_2$(CN)$_3$ (curve C) displays more peaks in this spectral region than κ-(ET)$_2$Cu$_2$(CN)$_3$ (curve B), and these additional peaks are present in the spectra of κ-(ET)$_2$Cu(CN)[N(CN)$_2$] (curve A).

Comparing the chemical structures of κ-(ET)$_2$Cu$_2$(CN)$_3$ and κ-(ET)$_2$Cu(CN)[N(CN)$_2$] (Figure 2) with the observed spectra, one can tentatively assign the common mode at ~2114 cm^{-1} to the vibrations of CN groups of −Cu−CN− chains running along the b axis in both compounds. The 2133 cm^{-1} mode in κ-(ET)$_2$Cu$_2$(CN)$_3$ is due to disordered C/N groups connecting the neighboring −Cu−CN− chains. Two higher-frequency modes at 2152 and 2214 cm^{-1} in κ-(ET)$_2$Cu(CN)[N(CN)$_2$] should be

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[†] Kyoto University.

[‡] Institute for Molecular Science.

[¶] Université de Rennes 1.

[§] On leave from A. F. Ioffe Physico-Technical Institute, 194021 St.-Petersburg, Russia. Present address: Department of Physics, University of Florida, Gainesville, FL 32611-8440.

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(6) Single crystals of κ-(ET)$_2$Cu$_2$(CN)$_3$ were prepared by electrocrystallization of ET in the presence of (Bu$_4$N^{1+})$_3$[Fe^{3+}(CN^{1-})$_6$] and Cu^{2+}(CN^{1-})$_2$ in a 2: 1 ratio, under a constant current of 1.0 μA in a 1:1 mixture of CH$_2$Cl$_2$/(CH$_3$)$_2$SO. Despite the deliberate use of Cu^{2+} as a starting material, no such species were detected in the grown single crystals of κ-(ET)$_2$Cu$_2$(CN)$_3$. For the synthesis of κ'-(ET)$_2$Cu$_2$(CN)$_3$ and κ-(ET)$_2$Cu(CN)[N(CN)$_2$], electrolytes containing Cu^{1+}, CN^{1-}, and N(CN)$_2$$^{1-}$ were used, as previously reported.[5,7] Unit cell parameters are as follows: κ- and κ'-(ET)$_2$Cu$_2$(CN)$_3$, monoclinic space group $P2_1/c$, $a = 16.113(5)$, $b = 8.560(3)$, $c = 13.331(6)$ Å, $\beta = 112.94(3)°$, $V = 1693(1)$ Å^3; κ-(ET)$_2$Cu(CN)[N(CN)$_2$], monoclinic space group $P2_1$, $a = 16.00(1)$, $b = 8.631(4)$, $c = 12.90(3)$ Å, $\beta = 110.97(8)°$, $V = 1663(4)$ Å^3. In the crystal structure, the two-dimensional conducting layer composed of the ET dimers is sandwiched by the insulating anion layer along the a axis.

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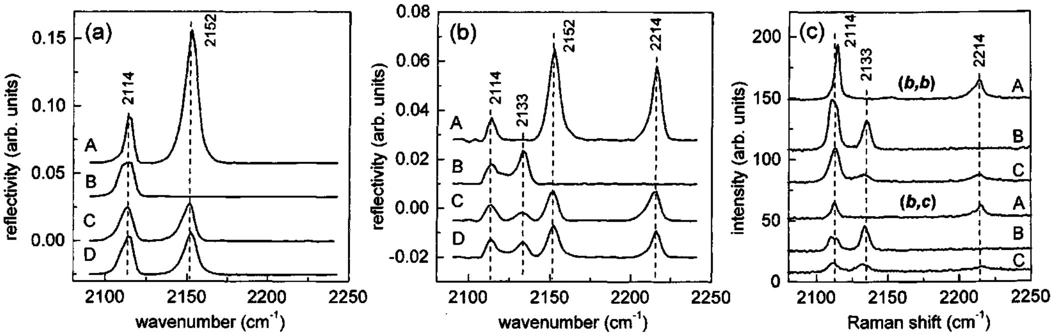

Figure 1. C≡N stretching vibrations (a) in the IR reflectivity for E||*b*, (b) in the IR reflectivity for E||*c*, and (c) in the Raman spectra in (*b*,*b*) and (*b*,*c*) configurations. A, κ-(ET)$_2$Cu(CN)[N(CN)$_2$]; B, κ-(ET)$_2$Cu$_2$(CN)$_3$; C, κ'-(ET)$_2$Cu$_2$(CN)$_3$ (T_c = 7.5 K); D, result of the linear combination of A and B (see text).

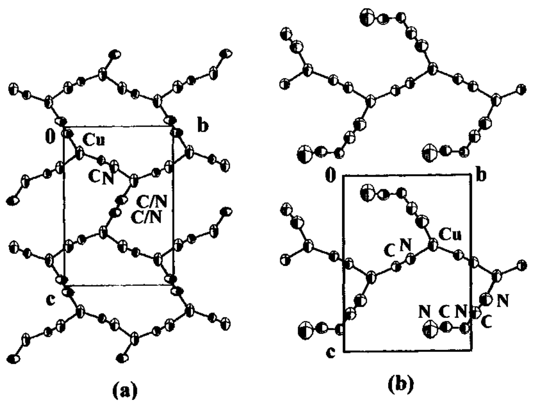

Figure 2. Structure of the anion layer of (a) κ-(ET)$_2$Cu$_2$(CN)$_3$ and (b) κ-(ET)$_2$Cu(CN)[N(CN)$_2$].

identified with the vibrations of N(CN)$_2$ ligand. This assignment was confirmed by the factor group analysis, as described in the Supporting Information.

As pointed out above, the C≡N stretching vibrations characteristic of both κ-(ET)$_2$Cu$_2$(CN)$_3$ and κ-(ET)$_2$Cu(CN)[N(CN)$_2$] were observed in the spectra of κ'-(ET)$_2$Cu$_2$(CN)$_3$. Therefore, the anion layer of the κ'-compound contains a mixture of Cu$_2$(CN)$_3$ and Cu(CN)N(CN)$_2$. By using micro-Raman spectroscopy (λ = 623.6 nm), the spectra in the 2000−2400 cm^{-1} range were measured by moving a 2 μm laser probe continuously on the surface of the κ'-sample. Identical spectra obtained allowed us to suggest that the mixing exists on a much smaller scale, undetectable by such a measurement, and the mixture can be regarded as homogeneous. Angular dependence of the infrared spectra of κ'-(ET)$_2$Cu$_2$(CN)$_3$ crystals was measured on *(bc)* plane with rotation by 10°. It was found that two mixed contributions in κ'-(ET)$_2$Cu$_2$(CN)$_3$ have the same angular dependence as they do, respectively, in the pure compounds κ-(ET)$_2$Cu$_2$(CN)$_3$ and κ-(ET)$_2$Cu(CN)[N(CN)$_2$]. It should be emphasized that in the κ'-samples, no new or symmetry-forbidden modes were found. Therefore, it can be supposed that the orientation and symmetry of the original anion ligands were not much changed in the anion structure of κ'-(ET)$_2$Cu$_2$(CN)$_3$. Indeed, Cu$_2$(CN)$_3$ and Cu(CN)-[N(CN)$_2$] anions have close size and shape which allows them to be easily exchanged. In principle, to mix Cu$_2$(CN)$_3$ and Cu(CN)-[N(CN)$_2$], it would be enough to substitute the (NC−Cu−CN)$^{1-}$ ligand by the (NC−N−CN)$^{1-}$ one, having very similar geometrical features. Another type of structure which would not contradict the spectroscopic data is a layer by layer growth of Cu$_2$(CN)$_3$ and Cu(CN)[N(CN)$_2$]. Since an ordered multilayered structure giving rise to the superstructure along the *a* axis was not found by the X-ray analysis, a rather random alternation of the layers in a fixed ratio can be suggested. Accordingly, the chemical formula of κ'-(ET)$_2$Cu$_2$(CN)$_3$ should be changed to:

$$\kappa\text{-(ET)}_2\,\mathrm{Cu}^{+}{}_{(2-x-y)}\,\mathrm{Cu}^{2+}{}_{x}\,\mathrm{(CN)}_{(3-2y)}\,[\mathrm{N(CN)}_2]_y$$

where x is the amount of Cu^{2+}, and y is the contents of N(CN)$_2$. This formula also represents κ-(ET)$_2$Cu$_2$(CN)$_3$ (x = 0, y = 0) and κ-(ET)$_2$Cu(CN)[N(CN)$_2$] (x = 0, y = 1).

The value of the parameter y can be estimated by a deconvolution of the optical spectra in the region of the CN stretching vibrations. Taking the absolute reflectivity *R(ω)* values of κ-(ET)$_2$Cu(CN)[N(CN)$_2$] without electronic background (curve A in Figure 1a), and the same for κ-(ET)$_2$Cu$_2$(CN)$_3$ (curve B), their linear combination was composed so that the intensity ratio of the peaks in the resulting spectrum (curve D) would correspond to that of κ'-(ET)$_2$Cu$_2$(CN)$_3$ (curve C). The best result for the sample in Figure 1 was 65% (B) + 35% (A) (i.e., y = 0.35), the same for both E||*c* and E||*b* polarizations.

This procedure was applied to all samples studied. Different samples from the same batch tended to display the same value of y. Three typical values of y were 0.05, 0.35, and 0.80. Remarkably, incorporation of a small amount of N(CN)$_2$ (~5%) in the anion layer of a Mott insulator, κ-(ET)$_2$Cu$_2$(CN)$_3$, induced a superconducting phase. The T_c of samples with y = 0.05 (~3 K) was very close to the T_c of κ-(ET)$_2$Cu$_2$(CN)$_3$, under 1.5 kbar.[7] The tendency of the higher T_c with a larger content of N(CN)$_2$ was observed. Most batches have y = 0.35, with T_c ranging from 3.2 to 10 K. The variety of T_c was attributed to the differences in the content of Cu^{2+} (x) in the anion layer. Therefore, two parameters, x [Cu^{2+}] and y [N(CN)$_2$], are influencing superconducting properties in this system. It provides a way to tune T_c by varying the composition of the anion part. The relationship between x, y, and the superconducting properties is an important issue for the future study.

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Supporting Information Available: Factor group analysis, additional information on the calculation of y, and the plot of T_c vs y (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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