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THE ANION STRUCTURE WHICH FACILITATES BEDT-TTF TO CONSTRUCT THE κ-TYPE SUPERCONDUCTING SALT

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Abstract The systematic comparison of the crystal structures of the BEDT-TTF salts with the planar anion layers elucidated that the pattern of the openings in the anion layer governs the packing motif of the donor molecules. On the ambient pressure BEDT-TTF superconductors, an almost linear relationship between the V_{mes2} and Tc was found out, where V_{mes2} is the estimated volume of the space, mainly in which the carrier can distribute.

INTRODUCTION

From the discovery of the first example, $(TMTSF)_2PF_6$ in 1980, a dozen years of the investigations have provided almost fifty kinds of molecular superconductors.[1] Among them, BEDT-TTF recorded the highest Tc's with κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]X$ (Tc = 12.8 K at 0.3 kbar for X = Cl, Tc = 11.8 K at 1 bar for X = Br) as the planar molecule, and has provided the richest variety of the superconductors in view of the crystal structure. The salts which exhibit the metallic conductivity and/or the superconductivity show the layered structure in which the donor and anion layer pile up alternately. This donor has the strong tendency to form the various packing motives in the salts and often provides multiple modifications with the same anion. It is suspected that the production of the polymorphism may originate from the extreme flexibility of the outer six-membered ring of BEDT-TTF.[2] For the geometry of the donor molecules and for the physical properties of the salts, the importance of the weak hydrogen bonds between the anion and the hydrogen atoms of the ethylene group is claimed.[3] However, no proposals have been presented on the factors which determine the packing motif of the donor molecules.

Analyzing the crystal structures of the newly obtained ambient pressure superconductors[4], κ-(BEDT-TTF)$_2$Cu(CN)[N(CN)$_2$] (Tc = 11.2 K) and κ'-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ (Tc = 3.8 K), it became apparent that the pattern of the openings in the anion layer governs the packing motif of the donor molecules in the salts with the planar anion layers. This paper describes the generalized patterns of the openings in the anion layers which give the κ-type BEDT-TTF salts along with the structural parameter, V_{mes2} which is almost proportional to Tc.

CRYSTAL STRUCTURES OF THE NEWLY OBTAINED BEDT-TTF SUPERCONDUCTORS

Both of the superconductors, κ-(BEDT-TTF)$_2$Cu(CN)[N(CN)$_2$] and κ'-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, belong to the κ-type BEDT-TTF salt in which the donor molecules form face-to-face dimers packed orthogonally to each other in the conducting donor layers (Fig.1). In the former salt, the anion layer consists of the infinite ⟨Cu-C-N⟩ chains having the pendants of N(CN)$_2$ which coordinate to Cu atoms at the terminal nitrogen atoms. Including the pendants, no atomic contacts shorter than the sum of the van der Waals radii (vdW) were observed between the infinite chains, and hence the anion layer consists of the one dimensional polymeric anions. On the other hand, the anion layer of the κ'-Cu$_2$ (CN)$_3$ salt consists of the infinite two dimensional polymeric anion in which the infinite chains of ⟨Cu-C-N⟩ are linked by the disordered CN ions at the Cu atoms.[5] Despite the difference in the anion structure, both of

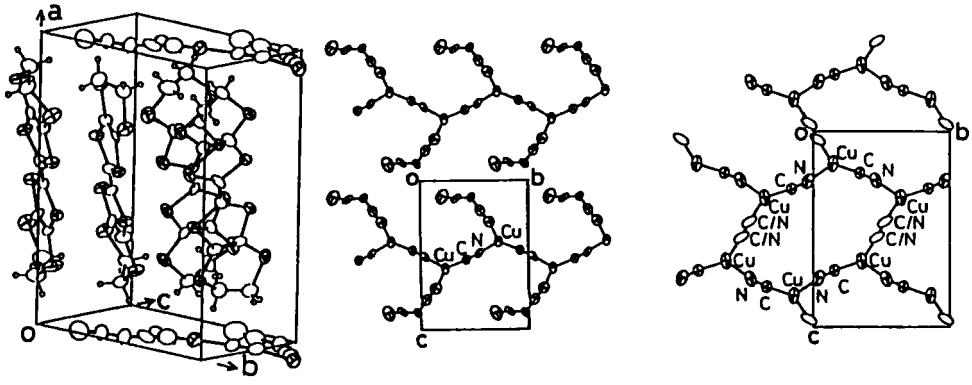

FIGURE 1 The crystal structure of κ-(BEDT-TTF)$_2$Cu(CN)[N(CN)$_2$] (left). The anion layers of this salt and κ'-(BEDT-TTF)$_3$Cu$_2$(CN)$_3$ are projected along the a-axes (middle and right, respectively).

these two ambient pressure superconductors show the isostructural donor packing motif.

COMMON STRUCTURAL FEATURE OF THE PACKING PATTERNS IN THE κ-TYPE SALTS

To seek out the origin of the common packing motif of the κ-type BEDT-TTF salt, the relative orientations between the anion layers and the donor molecules were reviewed on the salts with the planar anion layers.[7] Viewing along the perpendicular direction to the anion layers, all of the salts exhibit the common feature that the ethylene groups of the donor molecules locate at the openings in the anion layer (Fig. 2(a-f)). Here the "opening" means the space where no anion atoms occupy. J. M. Williams et al. had already recognized such vacant space

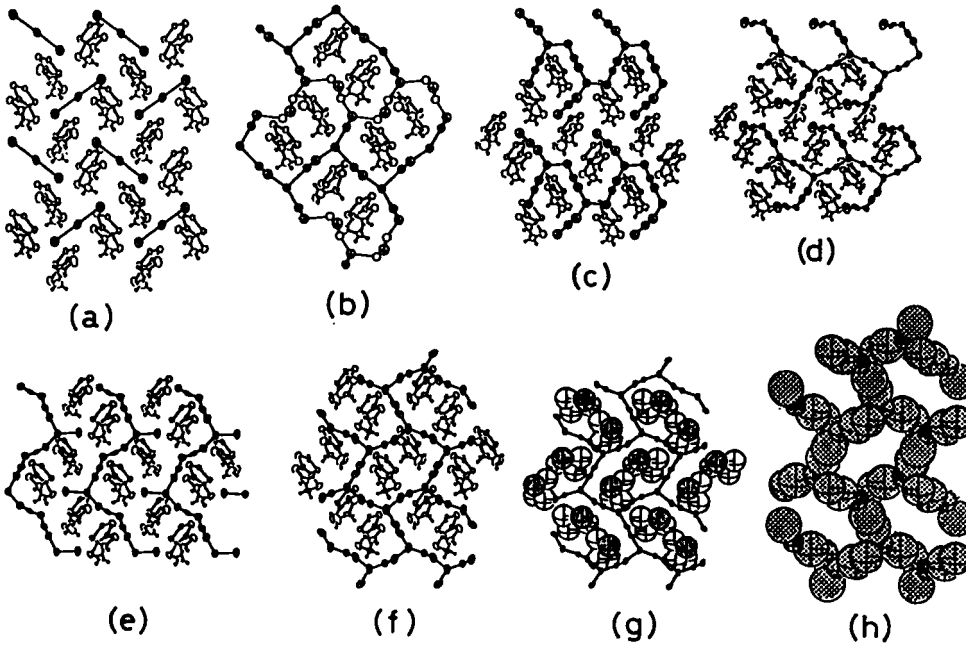

FIGURE 2 The arrangements of the donor molecules and the anion layers in κ-type BEDT-TTF salts projected onto the anion layers. (a) κ-I_3, (b) κ-$Ag(CN)_2 \cdot H_2O$, (c) κ-$Cu(NCS)_2$, (d) κ-$Cu(CN)[N(CN)_2]$, (e) κ-$Cu[N(CN)_2]Br$ and (f,g) κ'-$Cu_2(CN)_3$ salt. In all cases, only half parts of the donor molecules were depicted to simplify the figures. In (g), the hydrogen atoms were illustrated as the spheres with the radius of 1.20 Å and the one closest to the anion layer in each ethylene group is hatched. (h) The anion atoms in κ'-$Cu_2(CN)_3$ are illustrated with the spheres of the radii of vdW.

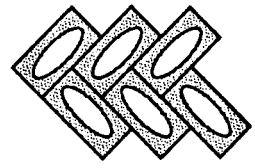

FIGURE 3 The distribution of the openings in the planar anion layers of the κ-type BEDT-TTF salts. Open ellipses indicate the essential areas of the openings. The anion atoms can locate in the hatched region.

representing it as "hole" in κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]X$ (X = Cl, Br, I), however, they have not realized such openings in other salts.[6] In fact, the openings exist in all of the κ-type BEDT-TTF salts with planar anion layers (see Fig.2(h) for example). Drawing the hydrogen atoms as the spheres of vdW, the relationship between the donor molecules and the anion layer is understood obviously, especially in κ'-$Cu_2(CN)_3$ salt. Namely, a face-to-face donor dimer stuffs up one side of an opening with two hydrogen atoms which belong to the different molecules and locate closest to the anion layer in each ethylene group (Fig. 2(g)). The relationship between the hydrogen atoms and the anion layer in this salt may be one of the packing motives which well satisfy the close-packing considerations. The essential pattern of the openings in the two dimensional anion layer can be abstracted as Fig. 3 in which the openings are related by the two-fold screw operation to each other. In this figure, the rectangles illustrated with the thick lines correspond to the repeating unit of the anion area. Referring the structural parameters of the κ-type BEDT-TTF salts, the unit area has the size of ca. 55 $Å^2$. In the κ'-$Cu_2(CN)_3$ and κ-$Ag(CN)_2 \cdot H_2O$ salt, the openings are isolated by the two dimensional network of the anion atoms completely. In contrast to these salts, the essential areas corresponding to the ellipses in Fig. 3 are connected to each other by the additional openings in the other κ-type salts. However, the very interesting feature is that all of the patterns of the openings contain the essential open areas corresponding to those indicated in Fig. 3.

THE PATTERNS OF THE OPENINGS IN THE OTHER MODIFICATIONS

To compare the patterns of the openings between the κ-type salts and

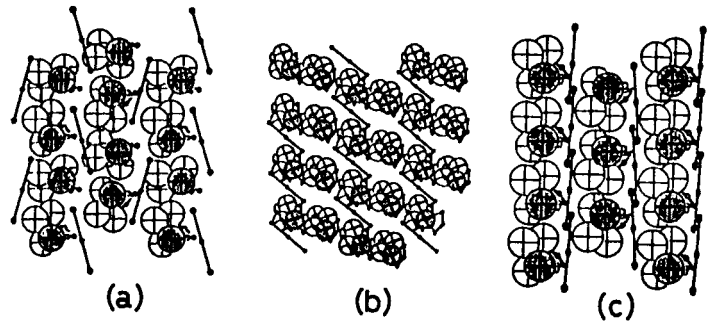

FIGURE 4 The arrangements of the hydrogen atoms of the donor molecules and the anion layers in (a) α-, (b) β-, and (c) θ-(BEDT-TTF)$_2$I$_3$ projected onto the anion layers. The hydrogen atoms were illustrated as the spheres with the radius of 1.20 Å and the one closest to the anion layer in each ethylene group is hatched.

the other modifications of the BEDT-TTF salts with planar anion layers, the I_3 salts are adequate since this anion gives the richest variety of the salts. Viewing along the perpendicular direction to the anion layers, α-, β-, θ-salt show the unique pattern of the openings, respectively (Fig. 4). Since the anion is a discrete one, the essential pattern of the openings in each modification is not discrete. However, it is obvious that the anion layer of the θ-type salt contains openings of the straight streak. The β-I_3 salt seems to contain the wedge shaped openings parallel to each other in the anion layer. The essential pattern of the openings in the anion layer of the κ-type salts (Fig. 3) differs from those of the other modifications. Concerning the before-mentioned fact that this donor gives numerous modifications of the salt even with the same anion species, BEDT-TTF is regarded to have the ability to construct the packing motif which fits to the structure of the counter components. Basing on these discussion, the essential structure of the planar anion layer which gives the κ-type BEDT-TTF salts reveals the one which contains the openings as illustrated in Fig. 3.

THE STRUCTURAL PARAMETER WHICH IS CORRELATED TO Tc

Previously, we had proposed the concept of V_{eff} which is calculated as the difference between the unit cell volume and the anion volume.[1] The definition came from the idea that the less density of BEDT-TTF

results in the narrower band width, the higher density of states at the Fermi level, and hence the higher Tc. V_{eff} is the estimated volume of the space in which the carrier can move around three-dimensionaly. Although a linear relationship between V_{eff} and Tc had been observed for some ambient pressure BEDT-TTF superconductors, the estimated anion volume contains the big ambiguity. For example, the Tc for the β-I_3 salt is estimated as 4.5 to 15 K depending on the choice of the atomic radius of iodine. To avoid such ambiguity, we intended to calculate the volume corresponding to V_{eff} basing only on the atomic parameters.

Concerning the anisotropic conducting nature of the BEDT-TTF salts[1], the carrier density in the conducting layer should affect on the superconductivity mainly. Therefore, firstly, we defined three kinds of the spaces dividing the crystallographical unit cell according to the expected contribution to the carrier distribution. The "most effective space" contains the C_6S_8 skeleton of BEDT-TTF and the intra-donor-layer overlap space between the atomic orbitals belonging to this π-system. The shape of this space will be a sheet-like one parallel to the donor layer having the finite thickness. The "anion space" which is defined as the space occupied by anion atoms. This space contributes nothing to the carrier distribution because of the closed-shell electronic structure. The "secondary effective space" is defined as the rest part in the unit cell in which the donor ethylene groups and the openings in the anion layer are included. This part is sandwiched by the two "most effective spaces" and contributes to the carrier distribution less than the "most effective space".

To simplify the calculation, the "most conductive space" is approximated by the parallelepiped having the same base area to the anion layer. Here we defined the height of this parallelepiped as the base contains the donor sulfur atom which give the shortest interlayer S..S distance through an opening in the anion layer. The volume of the parallelepiped was calculated per two carriers and denoted as V_{mes2}. Despite of the crude approximation, an almost linear relationship between V_{mes2} and Tc was observed for the ambient pressure BEDT-TTF superconductors (Fig. 5). α-$NH_4Hg(SCN)_4$, κ'-$Cu_2(CN)_3$, and β-I_3 salts deviate from the relationship and were omitted in the figure. The crystal structures of the former two salts contain the thick anion

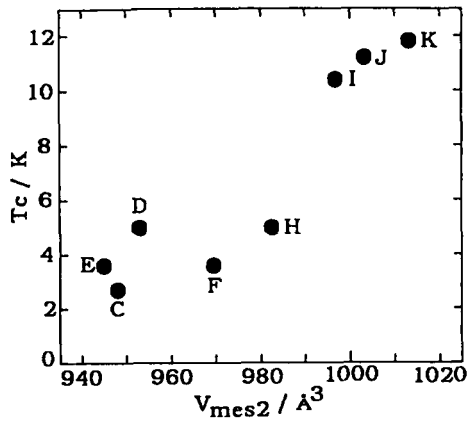

FIGURE 5 The plot of V_{mes2} versus Tc. A: α-$NH_4Hg(SCN)_4$ (V_{mes2} = 959 Å^3), B: β-I_3 (952) C: β-IBr_2 (949), D: β-AuI_2 (952), E: θ-I_3 (945), F: κ-I_3 (969), G: κ'-$Cu_2(CN)_3$ (1019), H: κ-$Ag(CN)_2 \cdot H_2O$ (983), I: κ-$Cu(NCS)_2$ (997), J: κ-Cu(CN)[$N(CN)_2$] (1003), K: κ-Cu[$N(CN)_2$]Br (1013)

layer and the disordered polar groups, respectively, both of which empirically lower the Tc and the effects are not concerned in the calculation of V_{mes2}. For the β-I_3 salt, the origin of the deviation can not be explained yet. However, the existences of the low-Tc and high-Tc phases at low temperature may affect on the deviations. Under the crude approximation assumed here, every κ-type salt gives the bigger V_{mes2} and hence the higher Tc than those of the β-type salt having the similar area of the anion layer.

CONCLUSION

Reviewing the crystal structures of the ambient pressure BEDT-TTF superconductors with the planar anion layers, the factors which determine the donor packing motif and the Tc became apparent.

Tc is almost proportional to V_{mes2} which is the estimated volume of the "most effective space" for the carrier distribution. Although the approximation is crude, the κ-type salt gives the higher Tc than that of the β-type salt having the same area of the anion layer. Therefore, we propose that the development of the κ-type salt will facilitate to raise the Tc of BEDT-TTF superconductors.

To obtain the κ-type salt, the concept of the pattern of the openings is useful. The pattern of the openings in the anion layer governs the

packing motif of BEDT-TTF and the κ-type salts are provided by the anion layers which posses the pattern as illustrated in Fig. 3.

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REFERENCES

1. G. Saito, Phosphorus, Sulfur, and Sillicon, 67, 345 (1992), J.M. Williams, A.J. Schultz, U. Geiser, K.D. Carlson, A.M. Kini, H.H. Wang, W.-K. Kwok, M.-H. Whangbo, and J.E. Shirber, Science, 252, 1501 (1991) and the references cited in.
2. S.S.P. Parkin, E.M. Engler, V.Y. Lee, and R.R. Schumaker, Mol. Cryst. Liq. Cryst., 119, 375 (1985)
3. P.C.W. Leung, T.J. Emge, A.J. Schultz, M.A. Beno, K.D. Karlson, H.H. Wang, M.A. Firestone, and J.M. Williams, Solid State Commun, 57, 93 (1986).
4. H. Yamochi, T. Nakamura, T. Komatsu, N. Matsukawa, T. Inoue, G. Saito, T. Mori, M. Kusunoki, and K. Sakaguchi, Solid State Commun., 82, 101 (1992)
5. Although the crystal structure of this salt is identical to those of the $Cu_2(CN)_3$ salts reported by U. Geiser et al (κ-salt: a semiconductor which becomes superconductor only under the pressure above 1.5 kbar (Tc = 2.8 K as onset)), by G.C. Papavassiliou et al (metal), and by X. Bu et al (semiconductor), we denote our salt as κ'-salt because of the difference in the conducting property. See, U. Geiser, H.H. Wang, K.D. Carlson, J.M. Williams, H.A. Charlier Jr., J.E. Heindl, G.A.Yaconi, B.J. Love, M.W. Lathrop, J.E.Schirber, D.L. Overmyer, J. Ren, and M.-H. Whangbo, Inorg. Chem., 30, 2586 (1991), G.C. Papavassiliou, D.J. Lagouvardos, V.C. Kakoussis, A. Terzis, A. Hountas, B. Hilti, C. Mayer, J.S. Zambounis, J. Pfeiffer, M.-H. Whangbo, J. Ren, and D.B. Kang, Mat. Res. Symp. Proc., 247 , 535 (1992), X. Bu, A. Frost-Jensen, R. Allendoerfer, B. Lederle, and M.J. Naughton, Solid State Commun., 79, 1053 (1991)
6. J.M. Williams, H.H. Wang, K.D. Carlson, A.M. Kini, U. Geiser, A.J. Schultz, W.K. Kwok, U. Welp, G.W. Crabtree, S. Fleshler, M.-H. Whangbo, and J.E. Schirber, Physica C, 185-189, 355 (1991).
7. The atomic parameters were taken from: H. Mori, Personal communication for κ-$Ag(CN)_2 \cdot H_2O$ and κ-$Cu(NCS)_2$ salt, A.M. Kini, U. Geiser, H.H. Wang, K.D. Karlson, J.M. Williams, W.K. Kwock, K.G. Vandervoort, J.E. Thompson, D.L. Stupka, D. Jung, and M.- H. Whangbo, Inorg. Chem., 29, (1990) 2555 for κ-$Cu[N(CN)_2]Br$, K. Bender, I. Hennig, D. Schweitzer, K. Dietz, H. Endres, and H.J. Keller, Mol. Cryst. Liq. Cryst., 108, (1984) 359 for α-I_3 salt, T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, and H. Inokuchi, Chem. Lett., (1984) 957 for β-I_3 salt, H. Kobayashi, Personal communications for θ- and κ-I_3 salt.