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The first polymorph, κ''-$(ET)_2Cu[N(CN)_2]Cl$, in the family of κ-$(ET)_2Cu[N(CN)_2]X$ ($X = Cl, Br, I$) radical cation salts

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ABSTRACT

The first polymorph, κ''-$(ET)_2Cu[N(CN)_2]Cl$, of the well known Mott insulator κ-$(ET)_2Cu[N(CN)_2]Cl$ has been prepared and its crystal and electronic structures have been examined. The polymorph has monoclinic symmetry in contrast with the orthorhombic one of the isostructural κ-salts of the family $(ET)_2Cu[N(CN)_2]X$ ($X = Cl$, Br, I). The monoclinic phase exhibits a layered structure in which the conducting layers are packed in a κ-type arrangement and the anion sheets consist of polymeric zigzag chains formed by $Cu[N(CN)_2]Cl$ units. The main structural differences with the orthorhombic κ-salts are that the anion sheets are disordered and the ET molecules are less planar. The new polymorph shows metallic type resistivity down to 4.2 K.

1. Introduction

The family of isostructural orthorhombic κ-salts with general formula $(ET)_2Cu[N(CN)_2]X$, where ET = bis(ethylenedithio)-tetrathiafulvalene and $X = Cl$, Br, I, $Br_{1-x}I_x$, $Br_{1-x}Cl_x$ (in the following, these salts are designated by their X) was discovered in the 1990s [1–6] and has been studied intensively up to now [7–13]. The quasi-two-dimensional organic superconductors with the highest transition temperature T_c at ambient and mild pressure have been found in this family of compounds. According to one-electron band structure calculations, all of these κ-salts should be metallic [14–16]. However, they exhibit a wide diversity of electronic properties depending on X. The κ-Br, κ-$Br_{0.5}Cl_{0.5}$ and κ-$Br_{0.7}Cl_{0.3}$ salts undergo a transition to a superconducting state with $T_c = 11.4$–11.6 K at ambient pressure [15,17,18], whereas κ-Cl, κ-I, and κ-$Br_{0.9}I_{0.1}$ are semiconductors [16,19,20]. At a pressure of 0.3 kbar κ-Cl and κ-$Br_{0.9}I_{0.1}$ become superconductors with $T_c = 12.8$ [16] and 3.5 K [20], respectively, and κ-I enters into a superconducting state at 1.2 kbar with $T_c = 8$ K [7,21]. Recently, we reported on another salt with the $Cu[N(CN)_2]Cl$ anion (referred to as κ'-Cl) [13,22] which is isostructural with the κ-Cl Mott insulator. However, the κ'-Cl crystals show a metallic temperature dependence of the conductivity and undergo a transition to a superconducting state with $T_c = 11.3$–11.9 K (depending on the crystals) at ambient pressure. The difference in the transport properties of these salts has been attributed to the smaller unit cell volume and the greater deficiency of Cu of κ'-Cl [13,22].

In this paper we report on the synthesis, crystal and band structure as well as conducting properties of the κ''-$(ET)_2Cu[N(CN)_2]Cl$ salt (referred to as κ''-Cl) which is the first polymorph within the family of κ-$(ET)_2Cu[N(CN)_2]X$ radical cation salts.

2. Experimental

The crystals of the κ''-salt were prepared as a minor product simultaneously with crystals of the known salt $(ET)_2CuCl_2$ [23] by electro-oxidation of ET ($C = 10^{-3}$ mol/l) in 1.1.2-trichloroethane with 10 vol% of alcohol on a Pt anode under galvanostatic regime at 25 °C. The mixed electrolyte containing $Na[N(CN)_2]$, 18-crown-6 ether, CuCl (in a 1:1:1 molar ratio, 2.5×10^{-3} mol/l) and $Co[N(CN)_2]_2 \cdot H_2O$ (5×10^{-4} mol/l) was used. A constant current of 0.3 μA was applied for the crystals grow. The crystals of $(ET)_2CuCl_2$ appeared on the anode as rectangular strips after one day, whereas irregular hexagon plates of κ''-Cl started to grow after 2–3 weeks.

The electron probe microanalysis (EPMA) was carried out on a JEOL JSM-5800L raster electron microscope with thousand times

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increasing and electron beam energy from 10 to 20 keV. The penetration depth of the beam in a sample was equal to 1–3 μm. The S, Co, Cu and Cl concentrations were detected.

The X-ray analysis was carried out on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo$K\alpha$ radiation using the $\omega/2\theta$ scanning technique. The crystallographic data and structure determination are summarized in Table 1. The crystal structure was solved by direct methods and subsequent Fourier synthesis using SHELXS-97 software package [24]. The structure was refined by full-matrix least-squares procedures by the SHELXL-97 program packet [25]. The hydrogen atoms were placed at geometrically calculated positions and a riding model was used for their refinement. Full crystallographic details were deposited at the Cambridge Crystallographic Data Centre as supplementary Publication no. CCDC 693006.

Table 1
Crystallographic data and structure refinement details for the single crystals of κ-type $(ET)_2Cu[(N(CN)_2)]Cl$ salts.

Compound	κ''-Cl	κ'-Cl [13]	κ-Cl [13]
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	C_2/c	*Pnma*	*Pnma*
Temperature (K)	293	297	293
a (Å)	30.420(7)	12.963(2)	12.963(2)
b (Å)	8.489(1)	29.879(2)	29.897(4)
c (Å)	12.874(2)	8.457(1)	8.467(1)
β (deg)	97.57		
V (Å^3)	3295.5(10)	3267.0(5)	3281.5(13)
Z	4	4	4
D_{calc} (g cm^{-3})	1.883		
μ (mm^{-1})	1.783		
Total no. of reflections	2951		
No. of unique reflections	2895		
No. of observed reflections	2464		
No. of refined parameters	225		
θ_{max} (deg)	25.00		
Range of h, k, l	$0\rightarrow h\rightarrow 36$ $0\rightarrow k\rightarrow 10$ $-15\rightarrow l\rightarrow 15$		
R, wR	0.0709, 0.1866		
GOF	1.089		

The tight-binding band structure calculations were of the extended Hückel type [26]. A modified Wolfsberg–Helmholtz formula was used to calculate the non-diagonal $H_{\mu\nu}$ values [27]. All valence electrons were taken into account in the calculations and the basis set consisted of Slater-type orbitals of double-ζ quality for C2s and C2p, S3s and S3p and of single-ζ quality for H1s. The ionization potentials, contraction coefficients and exponents were taken from previous work [28].

The dc-resistivity measurements were performed on single crystals by the standard four-probe method. The samples were thin plates with ~0.7–0.5 × 0.3 × 0.1 mm^3 characteristic sizes. The largest surface of the plates was parallel to the conducting layers.

3. Results and discussion

The study of ET electro-oxidation in the presence of $M[N(CN)_2]_2$ (M = Cu, Mn, Co) as electrolytes showed that the composition of the anion subsystem in the resulting salts depends on the nature of the transition metal (M) and solvent. Thus, the use of $Cu[N(CN)_2]_2$ in a solution of 1.1.2-trichloroethane leads to the preparation of κ'-Cl and ET_2CuCl_2 radical cation salts [13]. When using a Mn salt instead of the Cu one crystals of $ET_2Mn[N(CN)_2]_3$ were obtained [29,30]. When the $Co[N(CN)_2]_2\cdot H_2O$ salt in 1.1.2-trichloroethane was employed as electrolyte, crystals of ET_3CoCl_4 and $ET_3Cl_2\cdot 2H_2O$ were formed (the compositions of the salts ET_3CoCl_4 and ET_2CuCl_2 were determined by using energy dispersion X-ray spectroscopy and X-ray analysis, respectively). The combination of two salts $Mn[N(CN)_2]_2$ and CuCl as electrolyte yielded the $ET_2CuMn[N(CN)_2]_4$ and ET_2CuCl_2 crystals [30]. We studied the electrochemical oxidation of ET in the presence of a mixed electrolyte including $Co[N(CN)_2]_2$ and CuCl and obtained two types of crystals. Chemical analysis of both crystals by EPMA exibited no Co in their composition whereas the S:Cu:Cl ratio was approximately equal to 16:1:2 and 16:1:1 for the strips- and rhombus-like crystals, respectively. X-ray analysis

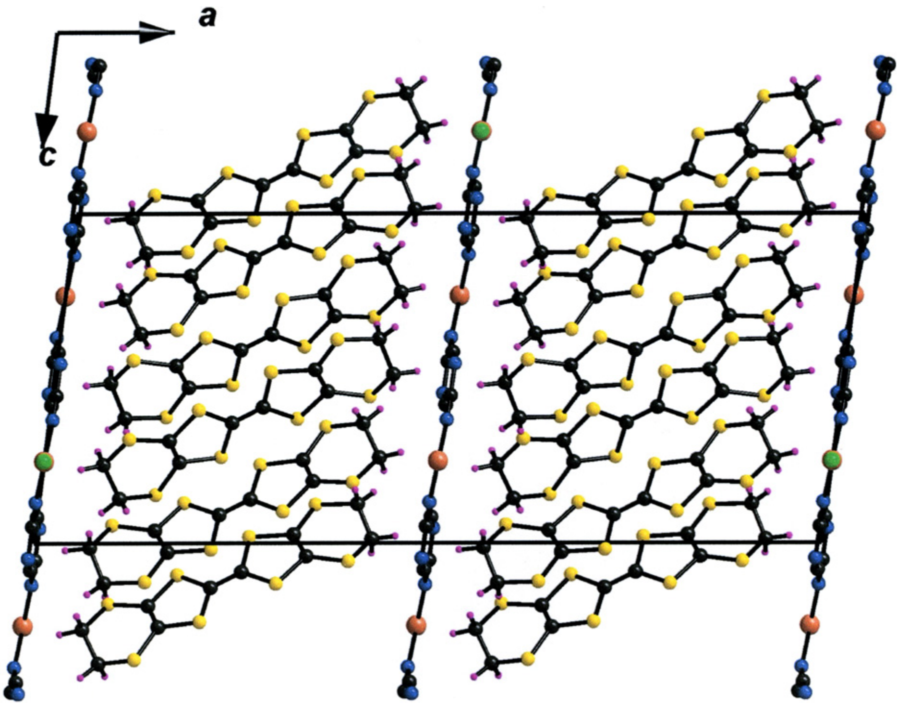

Fig. 1. Projection of the structure of the radical cation salt κ''-$(ET)_2Cu[N(CN)_2]Cl$ along the b axis.

showed that one type of crystals (strips-like crystals) are those of the already known radical cation salt ET_2CuCl_2 [23], while the other (rhombus-like crystals) have the same composition, $(ET)_2Cu[N(CN)_2]Cl$, of the κ-Cl and κ'-Cl salts. As it is the case for these two salts, it is characterized by a κ-type arrangement of the ET conducting layers but now the structure is monoclinic, in contrast with the orthorhombic structure of the κ- and κ'-Cl salts (see Table 1). The comparison of the crystal data for the three types of crystals shows that the κ''-salt has the unit cell with the largest volume. This is a result of the notable increase (more than 0.5 Å) of the parameter in the direction of alternation of the conducting and insulating layers (*a* or *b* axis for the monoclinic and orthorhombic crystals, respectively). The two cell parameters in the plane of the conducting layers only slightly differ.

As for the orthorhombic salts, the crystal structure of the κ''-type polymorph consists of conducting radical cation layers which alternate along the *a* direction with the dielectric ones built up from $Cu[N(CN)_2]Cl$ units (see Fig. 1). The radical cation layer in the κ''-salt is composed of ET pairs, which are packed perpendicular to each other (κ-type packing). A two-dimensional network of short S…S contacts is formed in the plane of the conducting ET layers. The values of the short S…S contacts for the κ''-salt are listed in Table 2. The terminal ethylene groups of the ET molecule can adopt either an eclipsed (E) or staggered (S) conformation. One of the ET terminal ethylene group in the κ''-salt is disordered (Fig. 2) and the ratio of E to S conformations is 0.81:0.19. Practically, the same ratio was found in both the κ- and κ'-crystals (E:S = 0.8:0.2) [13]. There is some difference in the structure of the ET molecules in the monoclinic and orthorhombic phases. The ET radical cation in the κ''-Cl crystals is less flat than in the κ- and κ'-salts. Whereas in the κ''-salt there is a folding around the line joining the inner S(3)…S(4) sulfur atoms (i.e. perpendicular to the long molecular axis) leading to a dihedral angle of 171.1°, in the κ-salt this angle is 180° [31]. The comparison of the central C=C bond length in the κ- and κ''-Cl crystals shows that it is noticeably shorter in the latter (1.362 [31] and 1.341 Å, respectively) probably as a consequence of the less planar structure of the ET radical cation.

Table 2
Short contacts S…S ($r \leqslant 3.68$ Å) between the radical cations in the salt κ''-$(ET)_2Cu[(N(CN)_2)]Cl$.

Contact	Distance (Å)
S(3)…S(6)[a]	3.582
S(5)…S(7)[b]	3.495
S(7)…S(4)[c]	3.605
S(1)…S(7)[b]	3.607
S(7)…S(6)[a]	3.664

Symmetry codes for the salt.
[a] (0.5−*x*;−0.5+*y*;0.5−*z*).
[b] (0.5−*x*;0.5−*y*;−z).
[c] (*x*,−*y*,−0.5+*z*).

The anion sheet in the κ''-Cl crystals is built from polymeric zig-zag chains along the *c* direction (Fig. 3). Cu atoms complete the approximately trigonal coordination environment with two bridged dicyanamide groups and a terminal Cl atom. Unlike the κ-Cl and κ'-Cl salts, the central nitrogen atom and both carbon atoms of the dicyanamide group are disordered with respect to the symmetry center, the two positions having an occupancy of 0.5. The N (central atom)…Cl distance between the neighboring anion chains in κ'-Cl is longer than in the κ-Cl Mott insulator (3.669 vs. 3.888 Å). There is also one short contact S(8)…N(3) between the radical cation layer and anion sheet.

The room-temperature conductivity of the κ''-Cl crystals measured in the plane of the conducting radical cation layers is of 25–35 $\Omega^{-1}cm^{-1}$. When cooling down to 4.2 K the resistivity decreases by approximately a factor of 10 (see Fig. 4), demonstrating a metallic behavior. In contrast with κ'-Cl, the crystals of the κ''-Cl polymorph do not undergo a transition to the superconducting state, probably, because of the disorder in the anion layers structure. It is known that disorder in the low-dimensional molecular conductors suppresses the superconductivity.

Tight-binding band structure calculations for the κ-Cl, κ'-Cl and κ''-Cl salts show that the differences in the band structures and Fermi surfaces are indeed very small. The Fermi surface consists of overlapping distorted circles and therefore is two-dimensional in nature, as usual for κ-phase salts [14]. Because of the similarity of these results with those for the other κ-phases of this family [14] they are not reported here. A more sensitive measure of the differences in the electronic structure is provided by a comparison of the different HOMO…HOMO interactions occurring in the donor layers. The strength of such interactions in the three salts may be evaluated from the so called $\beta_{HOMO-HOMO}$ interaction energies [32] (see Fig. 5 for the labeling).

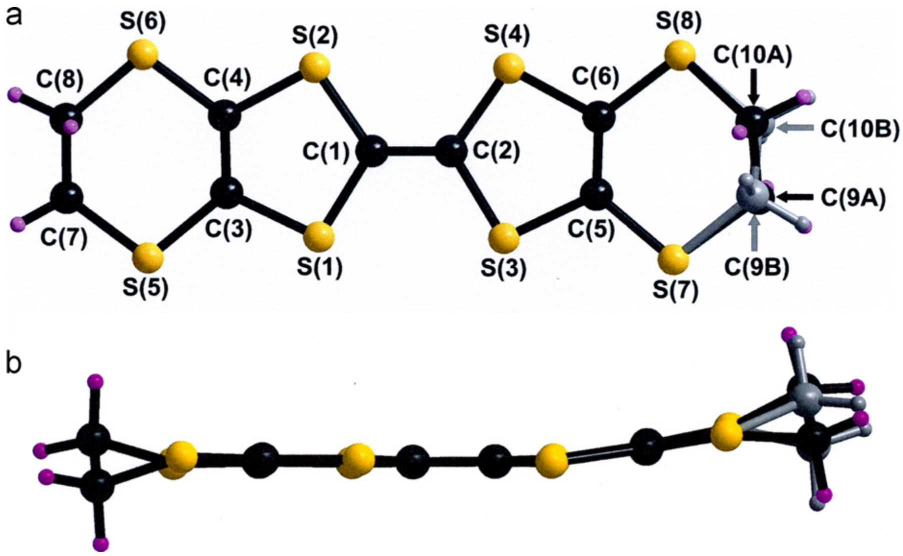

Fig. 2. Atomic notation (a) and side view of the ET molecules (b).

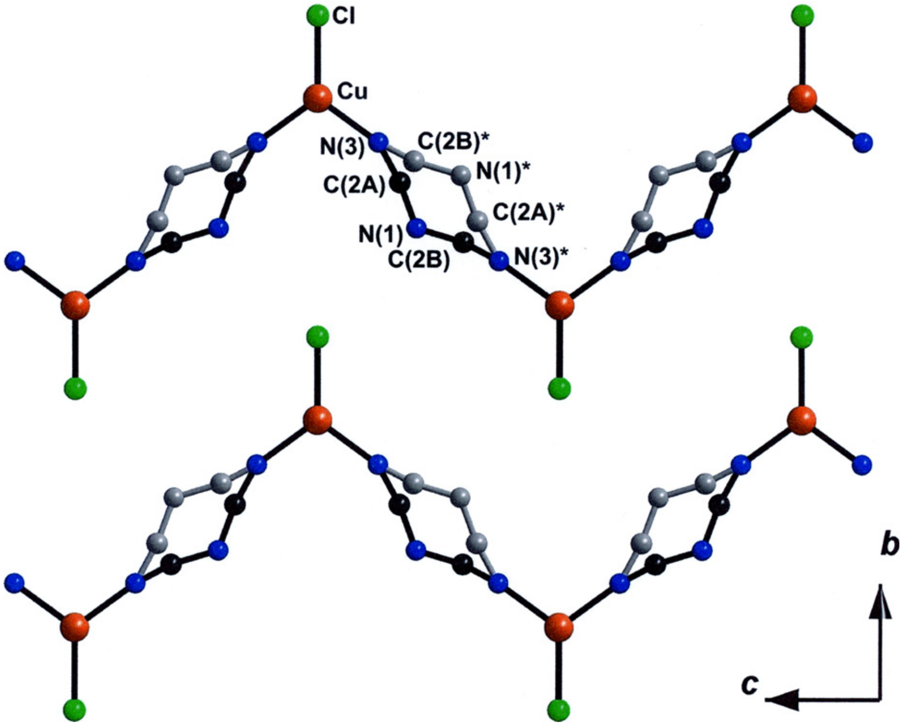

Fig. 3. Anion layers in the crystals of the radical cation salt κ''-(ET)$_2$Cu[N(CN)$_2$]Cl.

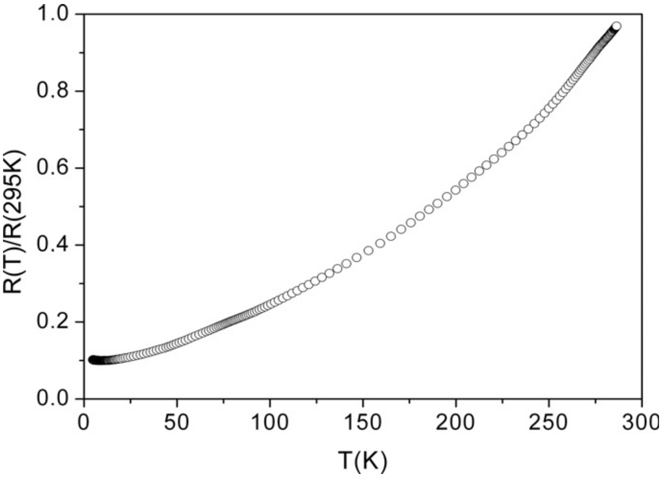

Fig. 4. Temperature dependence of resistivity in the conducting *bc* plane for the crystal κ''-(ET)$_2$Cu[N(CN)$_2$]Cl.

The calculated values for κ-Cl, κ'-Cl and κ''-Cl are reported in Table 3. There are four different intermolecular interactions. The intradimer interaction (I) is larger in κ''-Cl as is the interdimer interaction II. However, the increase in this interaction is practically compensated by the decrease of interaction IV which is also an interdimer interaction between orthogonal donors. The interdimer interaction between non-orthogonal donors (III) is slightly weaker in κ''-Cl. Again, these results suggest that the electronic structure of κ''-Cl is very similar to those of the metallic (and superconducting) κ'-Cl and the Mott insulator κ-Cl. A key to understand the metallic behavior of κ''-Cl is most likely provided by the calculated density of states at the Fermi level (see Table 3): the value for κ''-Cl is in between those for κ'-Cl and κ-Cl. As we previously showed [13], pressure slightly decreases the density of states at the Fermi level in κ-Cl. Thus, in the case of the present salt it seems as if the donor layers were subjected to a small applied pressure which suppresses the Mott localization as it occurs in κ-Cl [19]. This seems at odds with the crystallographic information since the unit cell volume of κ''-Cl is larger than those of κ'-Cl and κ-Cl. However, the relationship between pressure and density of states is regulated by the strength of the HOMO-…HOMO interactions in the donor layer. Thus, it seems more adequate to look at the area of the repeat unit of the donor layer when trying to correlate the effect of pressure on the electronic structure of the three salts. Of course, this area is slightly smaller

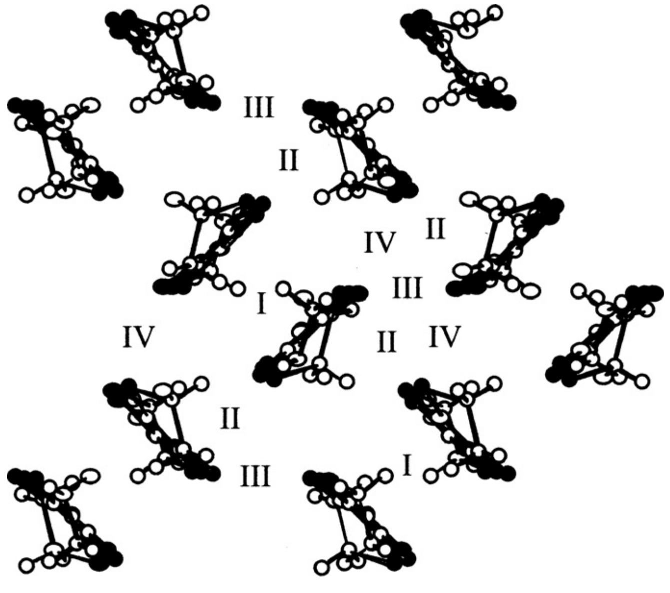

Fig. 5. Donor layer in the crystals of the radical cation salt κ''-(ET)$_2$Cu[N(CN)$_2$]Cl where the different donor…donor interactions are shown.

Table 3
Values of the $|\beta_{\text{HOMO-HOMO}}|$ for the different interactions and density of states at the Fermi level, $n(e_f)$ [electrons/(eV unit cell)], in the three structures.

Compound	κ''-Cl	κ'-Cl [13]	κ-Cl [13]
Interaction I	0.4565	0.4503	0.4521
Interaction II	0.2043	0.1909	0.1904
Interaction III	0.0528	0.0591	0.0581
Interaction IV	0.1199	0.1308	0.1294
$n(e_f)$	7.27	7.21	7.32

for the metallic κ'-Cl than it is for the Mott insulating κ-Cl at room temperature and ambient pressure [13]. Indeed, the area of the repeat unit of the donor layer in κ''-Cl is in between those for κ'-Cl and κ-Cl as it is the density of states at the Fermi level. Thus, both geometrical and electronic arguments suggest that the donor layers in the new κ''-Cl polymorph are slightly compressed with respect to those of κ-Cl at ambient pressure. In view of the well known subtle pressure dependence of the conductivity behavior of κ-Cl [19] this may well be at the origin of the room temperature metallic conductivity of the new polymorph. In addition, the disorder in the acceptor layers most likely renders the transition to the superconducting state impossible. Despite intense effort the relationship between the crystal structure and transport properties of κ-type salts still remains a challenging question.

4. Conclusion

The first polymorphous (monoclinic) modification, κ''-$(ET)_2Cu[N(CN)_2]_2Cl$, in the family of orthorhombic κ-radical cation salts $(ET)_2Cu[N(CN)_2]X$ ($X = $ Cl, Br, I) has been found. It was prepared by electrochemical oxidation of ET in the presence of the $NaN(CN)_2$ –$Co[N(CN)_2]_2$–CuCl mixture as the electrolyte. In contrast with the structure of the well known Mott insulator κ-$(ET)_2Cu[N(CN)_2]_2Cl$, it is characterized by the presence of disorder in the anion layers and relatively non-planar ET radical cations. The differences in the band structures and Fermi surfaces for the κ-Cl, κ'-Cl and κ''-Cl salts are very small. However, the calculated density of states at the Fermi level for κ''-Cl is in between those for κ'-Cl and κ-Cl, suggesting that the donor layers of the new polymorph are slightly compressed with respect to those of the Mott insulator. The polymorph exhibits metallic resistivity behavior from 300 down to 4.2 K.

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