

A new stable organic metal: κ -(BETS)₂C(CN)₃. The first κ -type radical cation salt with a planar-triangular discrete organic anion

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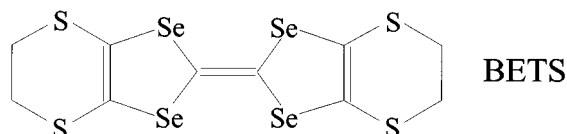
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Abstract. The κ -(BETS)₂C(CN)₃ radical cation salt was prepared by electrocrystallization, and its crystal structure was determined by single crystal X-ray diffraction. The electronic structure of κ -(BETS)₂C(CN)₃ was studied by means of the extended Hückel tight binding method. The electrical conductivity of this salt as a function of temperature shows a metallic behaviour down to 1.3 K. Shubnikov-de Haas oscillations reveal both the classical and magnetic breakdown orbits on the Fermi surface typical of the κ -type organic conductors. In addition, a low frequency oscillation (250 T) which is not predicted by the band structure calculations has been found in the oscillation spectrum.

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1 Introduction

In recent years considerable attention has been devoted to the study of the bis(ethylenedithio)tetraselenafulvalene (BEDT-TSF or BETS) radical cation salts. BETS is a tetraselenium analogue of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) and it has yielded



a large number of organic metals stable down to low temperatures [1-15]. Several of them are known to be superconductors [5, 16-20]. Some of the BETS radical cation salts such as α -(BETS)₂MHg(XCN)₄ (M = K, NH₄, Tl; X = S, Se) [10, 12, 13, 15] and κ -(BETS)₂Cu[N(CN)₂]Br [8] have been found to be isostructural with their BEDT-TTF analogues.

In this paper we report the synthesis, crystal structure and some physical properties of the κ -(BETS)₂C(CN)₃

radical cation salt. This new salt is not isostructural with the corresponding BEDT-TTF salt, (BEDT-TTF)₂C(CN)₃ [21]. Remarkably, this is the first salt to have a κ -type donor arrangement with a planar-triangular discrete anion. All previous examples of κ -type BETS salts have polymeric [8] or discrete MX₄ tetrahedral anions (M = Co, Ga, Fe, In, Tl; X = Cl, Br) [2, 3, 9, 13, 14, 18]. We also report on the band structure and Fermi surface as well as on the resistive properties of this new stable organic metal.

2 Experimental

2.1 Synthesis

The crystals of κ -(BETS)₂C(CN)₃ were obtained by electrochemical oxidation of BETS in 1.1.2-trichloroethane at 50 °C in the galvanostatic regime. The current values were varied from 0.1 to 0.5 μ A. Thicker and less strained crystals grew if a current of 0.1 μ A was applied. The (CH₃)₄NC(CN)₃ salt was used as a supporting electrolyte. The electrolyte (5 \times 10⁻³ mol/l) was put into two chambers of an H-shaped electrochemical cell. BETS (1 \times 10⁻³ mol/l) was loaded into the anode chamber. The romb-like black crystals were grown on a Pt anode for a period of 14-60 days depending on the current.

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Table 1. Atomic coordinates and isotropic equivalent thermal parameters U_{eq} (\AA^2) for non-hydrogen atoms of κ -(BETS) $_2$ C(CN) $_3$.

Atom	x/a	y/b	z/c	U_{eq}
BETS				
Se1	0.0167(1)	0.5296(2)	0.2781(0)	0.0352(5)
Se2	0.2142(1)	0.2813(2)	0.2596(0)	0.0374(5)
Se3	0.1443(1)	0.2984(2)	0.1669(0)	0.0394(5)
Se4	-0.0614(1)	0.5347(2)	0.1835(0)	0.0356(5)
S1	0.0944(3)	0.5582(5)	0.3611(1)	0.050(1)
S2	0.3075(3)	0.2781(5)	0.3406(1)	0.049(1)
S3	0.0909(4)	0.2943(6)	0.0814(1)	0.057(1)
S4	-0.1305(4)	0.5556(7)	0.0996(1)	0.076(2)
C1	0.092(1)	0.413(2)	0.2408(4)	0.033(3)
C2	0.062(1)	0.415(2)	0.2037(4)	0.030(3)
C3	0.120(1)	0.470(2)	0.3170(4)	0.032(3)
C4	0.203(1)	0.364(2)	0.3091(4)	0.034(3)
C5	0.053(1)	0.369(2)	0.1258(4)	0.040(4)
C6	-0.036(1)	0.473(2)	0.1322(4)	0.045(4)
C7	0.180(2)	0.450(3)	0.3940(4)	0.084(7)
C8	0.292(2)	0.395(3)	0.3830(5)	0.083(7)
C9	0.028(2)	0.432(3)	0.0520(6)	0.095(7)
C10	-0.080(2)	0.490(3)	0.0566(6)	0.119(10)
C(CN) $_3^*$				
C11	0.284(2)	-0.038(3)	-0.003(1)	0.059(9)
C12	0.264(4)	0.127(3)	-0.001(2)	0.057(9)
N12	0.260(5)	0.262(3)	0.004(1)	0.061(9)
C13	0.385(3)	-0.096(4)	-0.020(1)	0.084(13)
N13	0.467(3)	-0.134(5)	-0.036(1)	0.123(14)
C14	0.199(3)	-0.146(4)	0.010(1)	0.082(12)
N14	0.117(4)	-0.211(7)	0.019(2)	0.170(21)

* Site-occupation factor for the atoms in C(CN) $_3$ is 0.5.

2.2 X-ray structural analysis

X-ray experimental data (3236 non-zero reflections) from the single crystal ($0.2 \times 0.2 \times 0.09 \text{ mm}^3$) were collected at room temperature on an Enraf Nonius CAD-4F diffractometer [$\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$, graphite monochromator, ω -scan, $2\theta_{max} = 46^\circ$]. The main crystallographic data are as follows: $a = 11.583(3)$, $b = 8.475(1)$, $c = 35.086(5) \text{ \AA}$, $\beta = 91.10(2)^\circ$, $V = 3444(1) \text{ \AA}^3$, $\text{C}_{24}\text{S}_8\text{H}_{16}\text{Se}_8\text{N}_3$, $F(000) = 2324$, $M = 1234.6$, $d_{calc.} = 2.38 \text{ g/cm}^3$, $\mu(\text{MoK}\alpha) = 90.0 \text{ cm}^{-1}$, $Z = 4$, space group $A2/a$.

The structure was solved by a direct method using the AREN programs [22] and was refined in the anisotropic-isotropic (for the anion atoms) approximation by the SHELXL-93 program [23] to $R = 0.062$ for 1493 $F > 4\sigma(F)$. The positions of the hydrogen atoms were

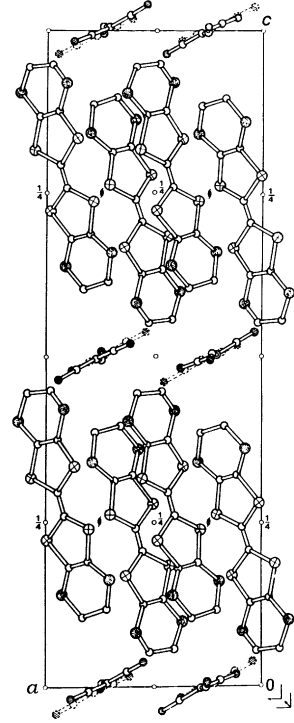


Fig. 1. Crystal structure of κ -(BETS) $_2$ C(CN) $_3$ viewed along the b -axis.

determined geometrically and included in the calculation without refinement. The coordinates of the non-hydrogen atoms and their temperature parameters are listed in Table 1.

2.3 Resistance and magnetoresistance

Resistivity was measured by the standard four-probe ac technique ($f = 320 \text{ Hz}$). Contacts to the single crystal were glued with a graphite paste using $30 \mu\text{m}$ diameter platinum wires. The magnetic field up to 14 T was generated by a superconducting magnet.

2.4 Band structure calculations

The full tight-binding band structure calculations were based upon the effective one-electron Hamiltonian of the extended Hückel method [24]. The off-diagonal matrix elements of the Hamiltonian were calculated according to the modified Wolfsberg-Helmholz formula [25]. All valence electrons were explicitly taken into account in the calculations and the basis set consisted of double- ζ Slater-type orbitals for C, S and Se and single- ζ Slater-type orbitals for H. The exponents, contraction coefficients and atomic parameters for C, S, Se and H were taken from previous works [26-27].

Table 2. Bond lengths d (Å) and angles ω (°) in BETS.

Bond	d	Angle	ω
Se1-C1	1.87(1)	C1Se1C3	93.8(5)
Se1-C3	1.87(1)	C1Se2C4	92.1(6)
Se2-C1	1.91(1)	C2Se3C5	94.3(6)
Se2-C4	1.88(1)	C2Se4C6	94.4(6)
Se3-C2	1.90(1)	C3S1C7	104.7(8)
Se3-C5	1.87(1)	C4S2C8	102.1(8)
Se4-C2	1.88(1)	C5S3C9	100.3(9)
Se4-C6	1.91(1)	C6S4C10	103.1(9)
S1-C3	1.75(1)	Se1C1Se2	114.9(7)
S1-C7	1.77(2)	Se1C1C2	124(1)
S2-C4	1.78(1)	Se2C1C2	121(1)
S2-C8	1.80(2)	Se3C2Se4	114.4(7)
S3-C5	1.75(1)	Se3C2C1	122(1)
S3-C9	1.71(2)	Se4C2C1	124(1)
S4-C6	1.72(1)	Se1C3S1	114.6(7)
S4-C10	1.72(2)	Se1C3C4	118(1)
C1-C2	1.34(2)	S1C3C4	127(1)
C3-C4	1.35(2)	Se2C4S2	111.2(8)
C5-C6	1.38(2)	Se2C4C3	120(1)
C7-C8	1.43(3)	S2C4C3	129(1)
C9-C10	1.35(3)	Se3C5S3	115.1(8)
		Se3C5C6	120(1)
		S3C5C6	125(1)
		Se4C6S4	114.2(8)
		Se4C6C5	117(1)
		S4C6C5	129(1)
		S1C7C8	119(1)
		S2C8C7	120(1)
		S3C9C10	124(2)
		S4C10C9	123(2)

3 Results and discussion

3.1 Crystal structure

Figure 1 shows the crystal structure of κ -(BETS)₂C(CN)₃ viewed along the b -axis. The structure is characterized by BETS radical cation layers alternating with anion layers along the c -direction. The unit cell contains two BETS slabs and two anion layers. The bond lengths and angles for the BETS radical cation are listed in Table 2 (see Fig. 2a for the atom labeling).

Insufficient accuracy in the determination of the bond lengths prevents us from analyzing them in detail. However, we can suggest that their values correspond to BETS^{0.5+}. It should be noted that the ethylenedithio groups of BETS are disordered at room temperature,

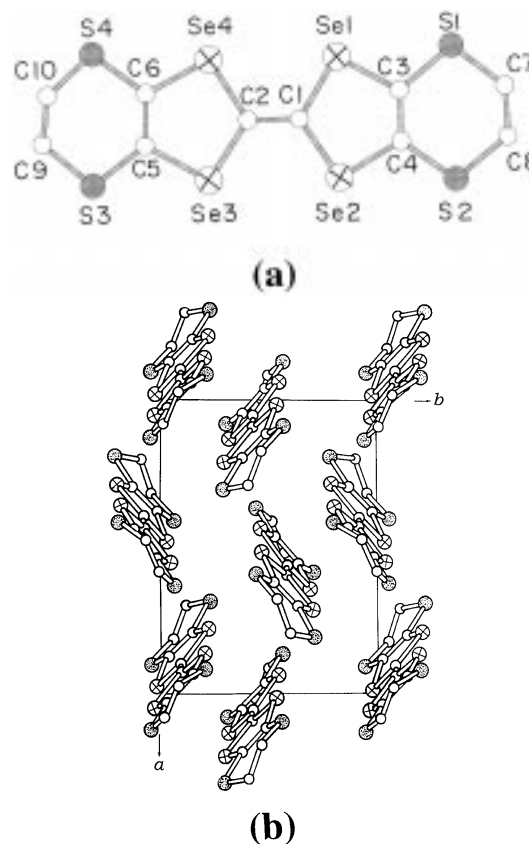


Fig. 2. (a) Labeling scheme for the BETS donor; (b) Structure of the radical cation layer of κ -(BETS)₂C(CN)₃ viewed along the c -axis.

which is indicated by the lengths of the C7–C8 and C9–C10 bonds as well as the higher temperature parameters of the corresponding atoms (Tab. 1).

The projection of the radical cation layer along the c -axis is shown in Figure 2b. It is a κ -type layer, first discovered in the organic superconductor (BEDT-TTF)₄Hg₃Cl₈ [28–29] and then in a number of organic metals and superconductors. Like in all k -phase salts, the radical cation layer is formed by dimers of BETS oriented in a roughly orthogonal manner. The intradimer distance between BETS molecules is 3.52 Å and the dihedral angle between the dimers interrelated by the twofold screw axis is 80°. The mode of intermolecular overlap in the dimer is of the so-called ring-over-bond type, which is a common feature observed in the superconducting κ -type salts. There is a lot of shortened Se...Se, Se...S and S...S contacts in the radical cation layer. Every BETS molecule has 22 such contacts with its six neighboring molecules, four of them being intradimer contacts.

The projection of the anion layer on the ab -plane is shown in Figure 3. The [C(CN)₃] anions are situated in general positions close to a twofold axis and so there are two equiprobable (50%) positions for them. Thus, some kind of disorder exists in the anion layer. In fact one may suppose that the [C(CN)₃] anions are located in the crystal in a regular manner and then some of the parameters

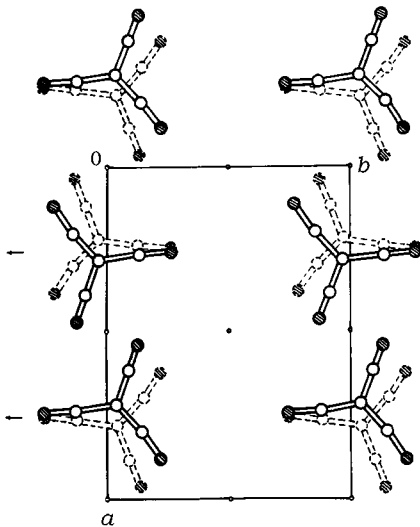


Fig. 3. Anion arrangement of κ -(BETS) $_2$ C(CN) $_3$ viewed along the c -axis.

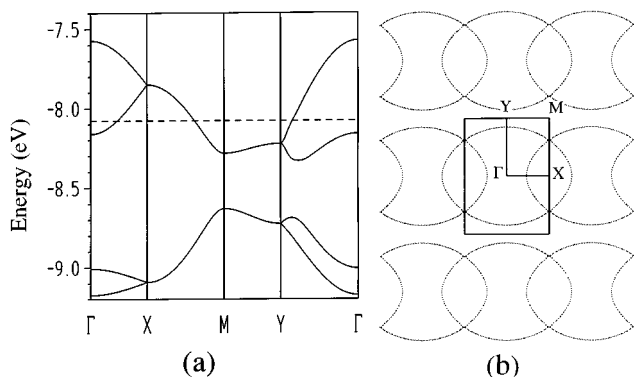


Fig. 4. (a) Dispersion relations for the four highest occupied bands of κ -(BETS) $_2$ C(CN) $_3$, and (b) Fermi surface associated with the partially filled bands. The dashed line in (a) indicates the Fermi level. Γ , X, Y and M refer to the $(0, 0)$, $(a^*/2, 0)$, $(0, b^*/2)$ and $(a^*/2, b^*/2)$ wave vectors, respectively.

would be n -fold increased, or maybe the twofold axis is absent in the crystal and the space group would be Aa . However, in order to verify whether any of these suppositions is true, special investigations are necessary because the scattering power of the $[C(CN)_3]$ anion makes a very small contribution to the total scattering power of the crystal. It is possible that anion ordering will take place at low temperature or at high pressure.

It should be emphasized that the κ -(BETS) $_2$ C(CN) $_3$ radical cation salt is not isostructural with the corresponding BEDT-TTF salt, (BEDT-TTF) $_2$ C(CN) $_3$ [21]. In the latter the $[C(CN)_3]$ anion is located on a twofold axis.

3.2 Electronic structure

The dispersion relations calculated for the four highest occupied bands of the donor layers in κ -(BETS) $_2$ C(CN) $_3$ are

shown in Figure 4a. These bands are mainly build from the HOMO (highest occupied molecular orbital) of the BETS donor. The double degeneracy of the bands along some directions of the Brillouin zone is due to the existence of nonsymmorphic symmetry elements. Since the unit cell of the layer contains four BETS donors with an average charge of $+1/2$, there are four HOMO bands and six electrons to fill them. Thus, the upper two bands are partially filled leading to metallic behavior. The lower partially filled band leads to a closed hole Fermi surface whereas the upper partially filled band leads to an open electron Fermi surface. However, because of the double degeneracy along $X \rightarrow M$ it is more convenient to show the Fermi surface on an extended zone scheme (see Fig. 4b). This Fermi surface can be described as a series of superposing ellipses. The calculated area of the closed portion around X is 21.9% of the first Brillouin zone.

It is interesting to note that the band structure and Fermi surface of Figures 4a and 4b are very similar to those calculated with the same method [30] for κ -(MDT-TTF) $_2$ AuI $_2$ [31] (when comparing the two band structures the different labeling of the crystallographic axes must be taken into account). This is not fortuitous. There are four different types of donor...donor intermolecular interactions in the donor layers of both salts. Two of them implicate donor molecules which are almost parallel to each other (either within a dimer (intra) or between two donors of different dimers (inter)) and two implicate donor molecules which are almost orthogonally oriented (\perp). The calculated $\beta_{\text{HOMO-HOMO}}$ intermolecular interaction energies [32], which are a measure of the strength of the interaction between two HOMOs in adjacent sites of the layer, are 0.637 eV (β_{intra}), 0.329 eV (β_{inter}) and 0.120/0.105 eV (β_{\perp}) for κ -(BETS) $_2$ C(CN) $_3$ and 0.451 eV (β_{intra}), 0.258 eV (β_{inter}) and 0.096/0.074 eV (β_{\perp}) for κ -(MDT-TTF) $_2$ AuI $_2$. The ratio between the different interaction energies in the two salts is thus again very similar. The only difference is the larger value of the interaction energies for κ -(BETS) $_2$ C(CN) $_3$. This is easily understandable because of the presence of Se instead of S atoms in the four inner chalcogen positions of the donor. Consequently, from the viewpoint of the HOMO...HOMO interactions, the donor layers of κ -(BETS) $_2$ C(CN) $_3$ and κ -(MDT-TTF) $_2$ AuI $_2$ can be considered to be the same, except for the fact that in κ -(BETS) $_2$ C(CN) $_3$ all interactions are scaled to larger values because of the Se atoms in the TTF core of the donor.

In view of this result it is quite surprising that whereas κ -(MDT-TTF) $_2$ AuI $_2$ is a superconductor ($T_c = 4.5$ K) [31], no traces of superconductivity have been found for κ -(BETS) $_2$ C(CN) $_3$ down to 1.3 K. Assuming that BCS theory applies for these salts, it could be thought that the reason lies in the lower values of the density of states at the Fermi level, $n(e_f)$. The stronger intermolecular interactions in κ -(BETS) $_2$ C(CN) $_3$ should lead to a larger band dispersion and consequently, to a lower $n(e_f)$ value. This is indeed the case. The calculated values of $n(e_f)$ (in units of electrons *per* eV and *per* donor molecule) are 1.38 for κ -(BETS) $_2$ C(CN) $_3$ and 1.99 for

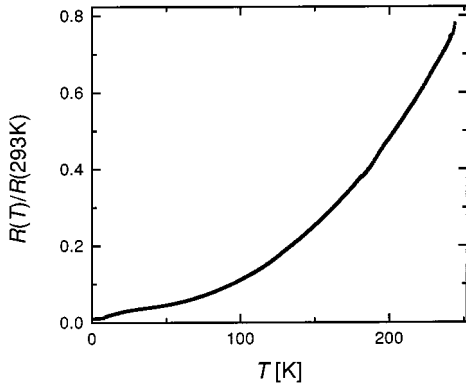


Fig. 5. Temperature dependence of the interplane resistance of κ -(BETS) $_2$ C(CN) $_3$.

κ -(MDT-TTF) $_2$ AuI $_2$. These values are quite similar to those reported by Whangbo, Montgomery *et al.* [8] for the two isostructural salts κ -(BETS) $_2$ Cu[N(CN) $_2$]Br and κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Br. However, as pointed out by these authors [8], within the context of the BCS theory, the calculated difference in $n(e_f)$ for these isostructural salts should lead to a decrease of only $\approx 10\%$ in T_c , which is in conflict with the results of the resistivity measurements and thus leads to serious doubts on the control of T_c by $n(e_f)$ in these salts. In addition, as Whangbo *et al.* have shown [33], there is no clear relationship between T_c and $n(e_f)$ in other organic metals like the series of superconducting β -type BEDT-TTF salts. Thus, we believe that the relatively low value of $n(e_f)$ brought about by the four Se atoms in the TTF core of the BETS donor does not provide a satisfactory explanation for the non observation of superconductivity in κ -(BETS) $_2$ C(CN) $_3$.

A more likely explanation relies on the observation of disorder in the positions of the ethylenedithio groups of BETS and/or in the anion layer. We note that disorder of the ethylenedithio groups was also reported for the nonsuperconducting κ -(BETS) $_2$ Cu[N(CN) $_2$]Br salt [8]. A recent discussion of the crystal structure of the κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]X (X = Cl, Br, I, Br $_{0.5}$ Cl $_{0.5}$, Br $_{0.7}$ Cl $_{0.3}$ and Br $_{0.9}$ I $_{0.1}$) salts [34] has provided good evidence for the strong control exerted by disorder of the ethylenedithio groups on the existence or absence of superconductivity in the κ -type salts. A low temperature X-ray study of κ -(BETS) $_2$ C(CN) $_3$ would be extremely helpful in order to shed some light into this problem.

3.3 Resistance and magnetoresistance

Figure 5 shows the temperature dependence of the interplane resistance of the κ -(BETS) $_2$ C(CN) $_3$ single crystal below 240 K. The room temperature resistivity is $\rho \approx 50 \Omega\text{cm}$ and monotonically falls down to a value of $\approx 0.5 \Omega\text{cm}$ at the liquid helium temperature. The in-plane resistivity is $0.03 - 0.1 \Omega\text{cm}$ at room temperature. Its temperature dependence is almost the same as that of the interplane resistivity so that there is no significant change

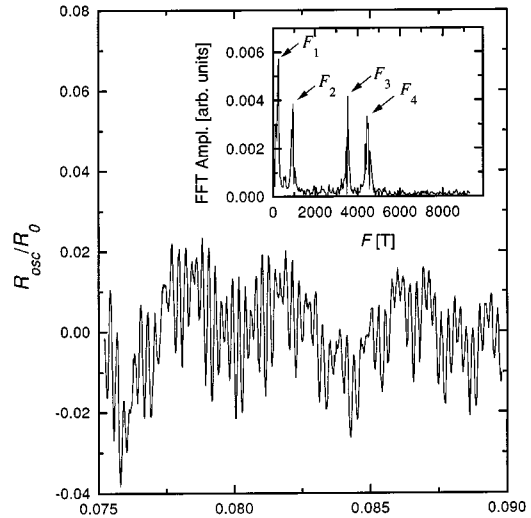


Fig. 6. Field dependence of the oscillatory part of the magnetoresistance for the field direction $H \perp ab$ at $T = 1.3$ K. R_0 is the monotonic resistance background. The inset represents the fast Fourier transform of the data.

in the anisotropy as a function of temperature. As already mentioned, no traces of superconductivity have been detected down to 1.3 K despite the metallic character of the compound.

At temperatures below 4 K the magnetoresistance shows prominent Shubnikov-de Haas oscillations. An example is displayed in Figure 6 for the field normal to the ab -plane at 1.3 K. The fast Fourier spectrum (see inset in Fig. 6) exhibits four main peaks at $F_1 = 250$ T, $F_2 = 950$ T, $F_3 = 3530$ T and $F_4 = 4480$ T. The temperature dependencies of the oscillation amplitudes yield the cyclotron masses $m_2 \approx 1.70 m_0$, $m_3 \approx 1.5 m_0$ and $m_4 \approx 3.3 m_0$, where m_0 denotes the free electron mass. The amplitude of the F_1 oscillations changes only very slightly with temperature preventing the reliable determination of the corresponding m_1 mass.

Comparing these results with the calculated Fermi surface (Fig. 4b), we identify the classical lens-like orbit around the X point and the magnetic breakdown orbit with areas of $\approx 22\%$ and 100% of the Brillouin zone cross-section area, respectively, which correspond to the frequencies F_2 and F_4 . The frequency F_3 is equal to $F_4 - F_2$ and can be attributed to the quantum interference effect. The topology of the Fermi surface for this compound, as well as for the other κ -type salts, is very favorable for various magnetic breakdown phenomena, including the quantum interference. The latter effect was observed in κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$ (see for instance Refs. [35, 36]) but due to the higher breakdown field and heavier cyclotron masses, the corresponding oscillation amplitudes were much lower. In the present compound, the oscillatory contribution at F_3 is relatively big and exceeds the single orbit contributions, F_2 and F_4 , already at $B = 10 - 12$ T and $T = 1.3$ K. Note that the combination frequency $F_4 + F_2$ is absent in the Fourier spectrum. This is probably due to its higher effective mass.

Now, turning to the low frequency oscillations, $F_1 = 250$ T, their origin is not clear so far. This frequency cannot be attributed to any single orbit predicted by the band structure calculations nor to their combinations. One could assume that the electron-electron correlations, which are often significant for organic metals, modify the shape of the Fermi surface predicted within the one-electron approximation. In principle, that could induce an intersection of the Fermi surface with the Y-M boundary of the Brillouin zone, giving rise to a small closed pocket. On the other hand, taking into account the Luttinger theorem, the area of the closed orbit around the X point should simultaneously become considerably smaller. However, the F_2 frequency agrees very well with the one-electron calculations and this fact does not seem to support our assumption. Another possible explanation could rely on the existence of a closed pocket at the center of the Brillouin zone which could be associated with an independent group of carriers or arise as a result of strong interlayer interactions. The first assumption apparently contradicts the electron counting based on the stoichiometry of the compound. As to the interlayer interactions, the significant splitting of the peaks in the Fourier spectrum (see inset in Fig. 6) suggests a relatively strong warping of the Fermi surface. Nevertheless, bearing in mind the nature of the interlayer interactions, the energy dispersion along the c^* direction should be too large in order to create a new pocket with the extremal area of 2.4×10^{14} cm $^{-2}$ (6% of the Brillouin zone cross-section area) corresponding to the frequency F_1 .

We note that low frequency oscillations which are not described within the conventional band structure models have also been observed in other organic metals [37-39]. Based on the angular dependence of the oscillation frequency in κ -(BEDT-TTF) $_2$ Cu $_2$ (CN) $_3$, Ohmichi *et al.* [39] suggested the existence of a small 3D part of the Fermi surface originated from a substantial interlayer interaction *via* the anion layers. It is possible that the slow oscillations in κ -(BEDT-TTF) $_2$ Cu $_2$ (CN) $_3$ and κ -(BETS) $_2$ C(CN) $_3$ have a common origin. However, further studies of the Fermi surface, both theoretical and experimental, are required in order to elucidate the problem.

4 Conclusion

A new radical cation salt, κ -(BETS) $_2$ C(CN) $_3$, has been synthesized and its crystal and electronic structures as well as the resistive properties have been studied. It is the first radical cation salt with a κ -type donor arrangement and a planar-triangular discrete anion. κ -(BETS) $_2$ C(CN) $_3$ is a metal stable down to very low temperatures although it is not superconducting above 1.3 K. The lack of superconductivity may be related to the disorder in the positions of the ethylenedithio groups of BETS and in the anion layers. Low temperature X-ray studies which could shed light on this problem are in progress. The observed Shubnikov-de Haas oscillations suggest a multiply connected Fermi surface which, in its main aspects, is that typical of the κ -type salts. However, additional features,

like the slow oscillations of 250 T frequency suggest the existence of a small extremal orbit which is not understood within the context of the present band structure model.

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