Preparation, crystal structures, EHT band calculations and physical properties of $\kappa$-(EDS-EDT-TTF)$_2$[Ag$_2$(CN)$_3$]$_1$ and $\alpha$-(BETS)$_2$Ag(CN)$_2$

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Preparation, crystal structures, EHT band calculations and physical properties of a semi-conducting $\kappa$-(EDS-EDT-TTF)$_2$[Ag$_2$(CN)$_3$]$_1$ (1) and a new metal-like species $\kappa$-(BETS)$_2$Ag(CN)$_2$ (2) are reported. $\kappa$-(EDS-EDT-TTF)$_2$[Ag$_2$(CN)$_3$]$_1$ units form an infinite two-dimensional polymeric sheet. This compound shows a semi-conducting behaviour, with $\sigma=3.0 \times 10^{-5}$ S cm$^{-1}$. $\kappa$-(BETS)$_2$Ag(CN)$_2$ is a good candidate for stabilization of the metallic state; a series of organic conductors and superconductors based on state was stabilised down to 2 K.

Introduction
Most of the known organic superconductors are based on the organic electron donor molecule bis(ethyleneedithio)tetrathiafulvalene (BEDT-TTF) or ET) and its derivatives which are known to yield molecular materials with alternate layers of organic radical cations and inorganic anions. The substitution of some inner or outer sulfur atoms in this molecule by oxygen or selenium atoms led to several modifications, namely, BO, BEDSe-TTF, EDS-EDT-TTF, EDS-EDT-TTF and BETS (Scheme 1). Interesting materials were obtained in many cases.

Scheme 1

Experimental
Preparation of compounds
EDS-EDT-TTF$^{24}$ and BETS$^{25}$ were prepared according to the literature procedures.


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deposited at the Cambridge Crystallographic Data centre of DMF were placed in the other compartment. Both compart-
ments (10 ml)–1,1,2-trichloroethane (5 ml) were placed in the anionic

\[ Ag(N_2) \]

Independent reflections \((hkl)\) data collected at room temperature on a Enraf-Nonius CAD4
tained. The stoichiometries were checked by X-ray analysis.

\( D_{\text{m}} = \text{mm}^{-1} \)

\[ \rho = 5.894 \] 9.857

\( F(000) \) 1218

\( \delta \) range \([-21 \leq \delta \leq 21]

\[ 0 \leq \epsilon \leq 15 \]

\[ 0 \leq \epsilon \leq 8 \]

\[ 0 \leq \epsilon \leq 55 \]

Total reflections collected 5462

Independent reflections \((R_{int})\) 5919 (0.0222)

Refinement method Full-matrix least-squares on \(F^2\)

\[ R_{int} = 0.0552, wR_{int} = 0.1069 \]

\[ R_f = 0.070, wR_f = 0.1138 \]

Largest diff. peak and hole \(e\) \(-3 \)

\[ 0.874, -0.792 \]

\[ 1.207, -1.373 \]

Table 1 Crystal data and structure refinement for 1 and 2

\[ \text{[EDS-EDT-TTF]Ag(NCN)\(_2\)} \]

\[ \text{[BETS]Ag(NCN)\(_2\)} \]

<table>
<thead>
<tr>
<th>Formula</th>
<th>( \text{C}_9\text{H}_9\text{AgN}_3\text{S}_3\text{S}_4 )</th>
<th>( \text{C}<em>{14}\text{H}</em>{14}\text{AgN}_3\text{S}_3\text{S}_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight</td>
<td>258.6</td>
<td>312.4</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>( a )</td>
<td>15.157(1)</td>
<td>15.157(1)</td>
</tr>
<tr>
<td>( b )</td>
<td>8.732(18)</td>
<td>8.732(18)</td>
</tr>
<tr>
<td>( c )</td>
<td>13.507(15)</td>
<td>13.507(15)</td>
</tr>
<tr>
<td>( \beta )</td>
<td>90.94(1)</td>
<td>90.94(1)</td>
</tr>
<tr>
<td>( V )</td>
<td>178(2)</td>
<td>178(2)</td>
</tr>
<tr>
<td>( Z )</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Space group</td>
<td>( P2_1/c )</td>
<td>( P2_2_12_1 )</td>
</tr>
<tr>
<td>( T_{K} )</td>
<td>292(2)</td>
<td>292(2)</td>
</tr>
<tr>
<td>( d(\text{MoKx}))( \AA )</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>( D_{\text{m}} ) ( \text{g cm}^{-3} )</td>
<td>2.324</td>
<td>2.324</td>
</tr>
<tr>
<td>( \rho )</td>
<td>5.894</td>
<td>9.857</td>
</tr>
<tr>
<td>( F(000) )</td>
<td>1218</td>
<td>1218</td>
</tr>
</tbody>
</table>

\( \delta \) range \([-21 \leq \delta \leq 21]\) 1.34–20.97

\[ 1.18–34.92 \]

Range of \( hkl \)

\[ -21 \leq \delta \leq 21 \]

\[ 0 \leq \epsilon \leq 15 \]

\[ 0 \leq \epsilon \leq 8 \]

\[ 0 \leq \epsilon \leq 55 \]

X-Ray crystal analysis

Single crystals were mounted on a glass fiber and the X-ray
data collected at room temperature on a Enraf-Nonius CAD4
diffactrometer equipped with graphite-monochromated Mo-
Kα (\( \lambda = 0.71073\AA \) radiation. The unit cell parameters were
determined and refined from setting angles of 25 accurately
centred reflections. Data were collected with the 0–2θ scan
method. Intensities were corrected for Lorentz and polarisation
effects and a preliminary space group search performed with
MoELEN.35 Some empirical \( F^2 \)-scan absorption corrections36
were applied. Both structures were solved by direct methods with
SHELXS-9737 and refined using full-matrix least-squares on \(F^2\)
using SHELXL-9738. The crystal data of the two compounds are
defined in Table 1. Selected bond data are given on Tables 2 and
3, respectively for 1 and 2. Full
crystallographic details, excluding structure factors, have been
deposited at the Cambridge Crystallographic Data Centre
(CCDC); see Information for Authors, Issue 1. Any request to
the CCDC for this material should quote the full literature
citation and the reference number 1145:127.

Table 2 Selected bond distances (\(\AA\)) for 1

\[ \text{[EDS-EDT-TTF]Ag(NCN)\(_2\)} \]

\[ \text{[BETS]Ag(NCN)\(_2\)} \]

| \( \text{Se}(1)-\text{C}(2) \) | 1.837(13) | 1.846(6) |
| \( \text{Se}(2)-\text{C}(1) \) | 1.794(10) | 1.805(7) |
| \( \text{Se}(3)-\text{C}(5) \) | 1.757(6) | 1.748(7) |
| \( \text{Se}(4)-\text{C}(3) \) | 1.741(6) | 1.748(6) |
| \( \text{S}(3)-\text{C}(3) \) | 1.750(6) | 1.750(7) |
| \( \text{S}(4)-\text{C}(4) \) | 1.709(6) | 1.709(6) |
| \( \text{Se}(7)-\text{C}(8) \) | 1.836(9) | 1.851(8) |
| \( \text{Se}(8)-\text{C}(7) \) | 1.872(6) | 1.898(7) |
| \( \text{C}(1)-\text{C}(2) \) | 1.460(15) | 1.347(9) |
| \( \text{C}(5)-\text{C}(6) \) | 1.364(8) | 1.348(8) |
| \( \text{N}(12)-\text{N}(13) \) | 1.210(10) | 1.207(10) |
| \( \text{Ag}(1)-\text{N}(1) \) | 2.047(7) | 2.079(11) |
| \( \text{Ag}(1)-\text{N}(1) \) | 2.531(7) | 2.096(11) |
| \( \text{N}(12)-\text{N}(12) \) | 1.146(11) | 1.136(9) |
| \( \text{Ag}(1)-\text{C}(2) \) | 2.047(7) | 2.079(11) |
| \( \text{N}(11)-\text{N}(13) \) | 1.210(10) | 1.207(10) |
| \( \text{C}(1)-\text{C}(2) \) | 1.384(4) | 1.384(4) |

Symmetry transformations used to generate equivalent atoms: \(-x,-y,z+1; \quad -x,-y+1,z \quad \text{and} \quad x+1,-y,z-1 \quad \text{for} \quad \text{1} \quad \text{and} \quad -x+1,-y,z-1 \quad \text{for} \quad \text{2} \).

Table 3 Selected bond distances (\(\AA\)) for 2

| \( \text{[EDS-EDT-TTF]Ag(NCN)\(_2\)} \)
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Z}(1)-\text{Z}(2) )</td>
<td>1.846(2)</td>
</tr>
<tr>
<td>( \text{Z}(2)-\text{Z}(4) )</td>
<td>1.830(16)</td>
</tr>
<tr>
<td>( \text{N}(1)-\text{N}(2) )</td>
<td>1.146(11)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms: \(-x,-y,-z \quad \text{for} \quad \text{1} \quad \text{and} \quad x,-y,-z \quad \text{for} \quad \text{2} \).

Electrical conductivity and electron paramagnetic resonance measurements

The dc electrical conductivity measurements over the range 4–300 K were performed on single crystals by the standard four-probe method. Using a phase detector, electrical contacts on crystals were made directly by gold wires using silver paint. The EPR experiments on single crystals were performed on an X-band Bruker spectrometer equipped with an Oxford variable temperature accessory (4–300 K). The crystals were mounted with silicone grease on a quartz rod. The field was calibrated using the diphenylpicrylhydrazyl free radical (DPPH, $g = 2.0036$) as a reference. For each phase several crystals were employed to check the reproducibility of the presented results.

Band calculations

The overlap integrals, band structure and Fermi surface of the title compounds have been obtained with the semi-empirical extended Huckel method (EHT), (using the program from ref. 29 on a PC computer). The d orbitals for Se and S atoms were included in the calculations. For compound 1, the peripheral Se and S atoms of the organic molecule (EDS-EDT-TTF) are disordered (see below). To take into account this disorder, we considered a mean situation between two ordered molecules.

Results and discussions

Crystal structures

The crystal structures are built up of alternating layers of the organic donors and the inorganic anions characteristic of these types of materials. However the main difference lies in the packing mode of the organic and inorganic units used to generate the layer.

$k$-(EDS-EDT-TTF)$_2$Ag$_2$(CN)$_3$. Fig 1 shows the crystal structure and Fig 2 and 3 show details of the organic and inorganic sublattices, respectively. The asymmetric unit contains one crystallographically independent organic molecule and one Ag(CN)$_3$ unit.

The organic molecule EDS-EDT-TTF is disymmetrical and consists of the linkage of one half of a BEDT-TTF molecule and one half of a BEDSe-TTF molecule. From the refinement of the occupancy factors for the four peripheral heteroatom sites, we found a statistical occupancy of selenium and sulfur atoms. The molecule is non planar, as shown in Fig. 2(a). The terminal ethylenic groups show two different conformations [Fig. 2(a)] and high thermal motion or disorder are observed. In the dimer the two organic molecules show a ring-to-double bond overlap with an interplanar separation of 3.355(8) Å. The interdimer contacts are indicated in Fig. 2(b).

In the inorganic layer (Fig. 3) one disordered, CN (C12/N12) group is observed in which the carbon and nitrogen
atoms are not distinguishable along with one ordered CN group \((\text{C11-N1})\). The Ag atom is bonded to these two CN groups with a mean bond length of 2.047(8) Å and an angle \(\text{C11-Ag-C12} = 160.9(3)°\). Two adjacent \(\text{AgCN}_2\) units are connected through a longer \(\text{Ag1-N1}\) bond of length 2.531(7) Å. The angles \(\text{C11-Ag1-N1}\) and \(\text{C12-N1-Ag1}\) are equal to 103.8(3) and 94.0(3)°, respectively.

The crystal structure of this compound is isomorphous to that of \(\kappa-(\text{BEDT-TTF})_2\text{CuCN}_3\)\(^\text{23-25}\) with however some differences. For the unit cell parameters, we observed a shorter \(c\) parameter \([15.157(9)\text{ cf. 16.084(1) Å}]\) and a lower value of \(b\) \([90.94(3)\text{ cf. 113.39(3)°}]\). In the Cu containing polymer the bond lengths around the copper atom are similar \([1.879(4)\text{ with C11}, 1.903\text{ with N12 and 2.020(4) Å with N1}]\).

**Fig. 4** Crystal structure of \(\kappa-(\text{BETS})_2\text{Ag(CN)}_2\) with alternating layers \(A\) and \(B\).

**Fig. 5** ORTEP drawing of layers \(A\) and \(B\) projected onto the \(ab\) plane with overlap integrals \(\times 10^3\) and minimum chalcogen-chalcogen distances for \(Z\): \(d_1\): S3-S4 \(= 3.61(2)\text{ Å}\), Se3-Se4 \(= 3.76(8)\text{ Å}\), \(d_2\): Se3-Se3 \(= 3.837(9)\text{ Å}\), \(d_3\): S2-Se2 \(= 3.68(1)\text{ Å}\), \(d_4\): Se1-Se1 \(= 3.875(8)\text{ Å}\).

**Fig. 6** Resistivity vs. temperature for (a) \(\kappa-(\text{EDS-EDT-TTF})_2\text{Ag(CN)}_2\), (b) \(\kappa-(\text{BETS})_2\text{Ag(CN)}_2\).

**Fig. 7** Resistivity vs. temperature at different pressures for \(\kappa-(\text{BETS})_2\text{Ag(CN)}_2\).

while the corresponding bond lengths differ significantly in the silver salt.

\(\kappa-(\text{BETS})_2\text{Ag(CN)}_2\). The crystal structure of this salt is isomorphous to that of \(\kappa-(\text{ET})_2\text{Ag(CN)}_2\) reported by Kurmoo et al.\(^\text{13}\). The asymmetric unit contains two half BETS molecules.
Physical properties

Electrical properties. Electrical conductivity measurements are shown in Fig. 6. For compound 1, the temperature dependence of the resistivity shows a semiconducting behaviour with $\sigma_{300 \, K} = 3 \times 10^{-8} \, \text{S cm}^{-1}$ and $E_a = 120 \, \text{meV}$ [Fig. 6(a)]. For compound 2, the temperature dependence of the resistivity shows a metallic behaviour down to 4.2 K with $\sigma_{300 \, K} = 100 \, \text{S cm}^{-1}$ [Fig. 6(b)]. For compound 2, the electrical conductivity was measured under hydrostatic pressure in the range 1.9–6.9 kbar and revealed a pressure independent behaviour (Fig. 7) characteristic of an extrinsic behaviour due to the lattice disorder.

EPR properties. The room temperature $g$ values and linewidths (Fig. 8) were measured at room temperature as well as their temperature dependence have been examined for both salts 1 and 2 (Fig. 8 and 9). For the $\kappa$-phase salt 1, we observed a weak anisotropy of the EPR signal at room temperature; the linewidth is large, ca. 100 G, characteristic for quasi-2-D electronic systems.

Fig. 8 Temperature dependence of the EPR $g$ factor (●) and linewidth ($\Delta H$) for an arbitrary crystal orientation ($H_0$ the resonant magnetic field perpendicular to the platelet large face for 1).

Fig. 9 Temperature dependence of the EPR $g$ factor (●) and linewidth ($\Delta H$) for 2, and $H_0$ the resonant magnetic field perpendicular to the platelet large face for 1.)

Fig. 10 Dispersion energy bands and Fermi surface for compound 1.

Fig. 11 Dispersion energy bands and Fermi surface for compound 2, layers A and B.
temperature dependences of the g-factor and linewidth are shown in Fig. 8 for a given orientation of the single crystal. As expected the g-factor is constant with a gradual increase of the linewidth from room temperature to around 15 K, below this temperature a slope change is observed which could be a precursor effect of some phase transition\(^2\) as already observed for other unsymmetrical TTF type molecules.\(^2\) At low temperature (below 20 K), a narrowing effect is observed due to the appearance of a strong Curie tail which indicates the presence of disorder or impurities. Indeed it turns out that the dimer disorder detected by X-ray diffraction appears to be the dominant effect in this compound: it precludes any appearance of ordered ground states (superconducting or magnetic).

The temperature dependences of the g-factor and linewidth for compound 2 are shown in Fig. 9 for a given orientation of the single crystal. The g-factor is equal to 2.1500 at room temperature and remains almost constant down to 100 K and then increases to reach a maximum of 2.4200 at 60 K. Below 60 K the g-factor decreases sharply to reach a value of 2.0500 at 4 K. A similar behaviour is observed for the linewidth for the effects being associated with the presence of a strong Curie tail. At room temperature the EPR signal shows a very large linewidth, \(1000 \text{ G}\) which increases to reach a maximum value of 1250 G at 10 K and then decreases to a value of about 750 G at 4 K. A similar behaviour was reported for \((DME)\)_2AgBr\(_4\).\(^2\)

Electronic band calculations

Overlap integrals for compound 1 are given in Fig. 2(b). Dispersion bands and the Fermi surface, shown in Fig. 10, are given in independent. For the semiconducting \((EDS-EDT-2TF)\)Ag(CN)_2, we have shown that a polymeric Ag(CN)_2\(^-\) anion sheet associated with the \(x\)-phase can be obtained with the dimerisation donor EDS-EDT-TTF, as in other \(x\)-phase salts\(^2\) an insulating ground state has been evidenced which is not reflected in the electronic band calculation. This results from the strong influence of disorder\(^2\) at low temperature which prevents the appearance of an ordered superconducting or magnetic ground state.

Conclusion

Two novel radical salts containing silver cyanide anions have been prepared and characterized. \((\text{BET})_2\text{Ag(CN)}_2\) is metallic down to 2 K and its conductivity is pressure independent.

For the semiconducting \((x\text{-EDS-EDT-2TF})\)Ag(CN)_2, we have shown that a polymeric Ag(CN)_2\(^-\) anion sheet associated with the \(x\)-phase can be obtained with the dimerisation donor EDS-EDT-TTF, as in other \(x\)-phase salts\(^2\) an insulating ground state has been evidenced which is not reflected in the electronic band calculation. This results from the strong influence of disorder\(^2\) at low temperature which prevents the appearance of an ordered superconducting or magnetic ground state.

Acknowledgements

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Notes and references

28. G. M. Sheldrick, SHELXL-97 Program for the refinement of Crystal Structures, University of Göttingen, Germany.
30. There are four reports (references 12, 21–23) concerning the crys- tallographic structure of \((ET)_2Cu(CN)_3\). Owing to the poor quality of crystals, the \(X\)-ray results for this salt are reported with low accuracy and rather high errors. We obtained very recently an accurate crystal structure \((R=0.038)\) with good quality single-crystal results that will be published elsewhere.
31. Accordiely, the compared structural data refer to these structural results.
32. A second line is also observed at \(y = 2.12\), the origin of which is unknown.