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

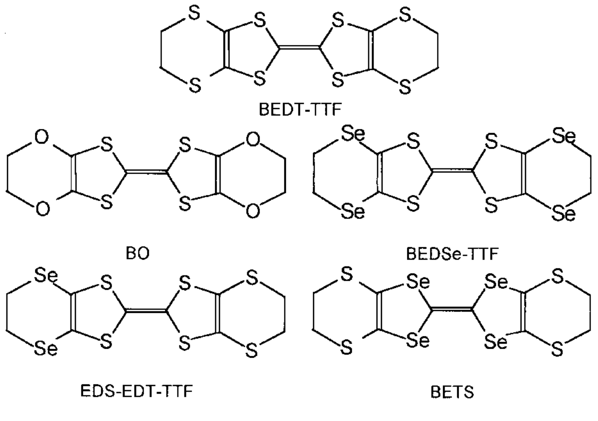
Stéphane Golhen,[a] **Lahcène Ouahab,***[a] **Albert Lebeuze,**[a] **Mounir Bouayed,**[a]† **Pierre Delhaes,**[b] **Yoshiaki Kashimura,**[c] **Reizo Kato,**[c] **Laurent Binet**[d] **and Jean-Marc Fabre**[d]

[a]*Laboratoire de Chimie du Solide et Inorganique Moléculaire, UMR 6511, Groupe Matériaux Moléculaires, Université de Rennes 1, 35042 Rennes cedex, France*
[b]*Centre de Recherche Paul Pascal, CNRS, Av. Albert Schweitzer, 33600 Pessac, France*
[c]*The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan*
[d]*Laboratoire de Chimie Organique Structurale, Université de Montpellier II, Place Eugène Bataillon 34095 Montpellier, France*

Preparation, crystal structures, EHT band calculations and physical properties of a semi-conducting κ-(EDS-EDT-TTF)$_2$[Ag$_2$(CN)$_3$] (**1**) and a new metallic-like species α-(BETS)$_2$Ag(CN)$_2$ (**2**) are reported. κ-(EDS-EDT-TTF)$_2$[Ag$_2$(CN)$_3$] **1**: $M_r = 625.3$, monoclinic space group $P2_1/c$, $a = 15.157(9)$, $b = 8.732(2)$, $c = 13.51(2)$ Å, $\beta = 90.94(3)°$, $V = 1788$ Å^3, $Z = 2$, $D_c = 2.324$ g cm^{-3}, $R = 0.055$ for 2572 reflections with $F^2 \geqslant 2\sigma(F^2)$. In this compound the organic molecules adopt the so-called κ type of packing. In the inorganic sublattice the [Ag$_2$(CN)$_3$]$^-$ units form an infinite two-dimensional polymeric sheet. This compound shows a semi conducting behaviour, with $\sigma_{300\ \mathrm{K}} = 3.0 \times 10^{-4}$ S cm^{-1} and $E_a = 120$ meV. α-(BETS)$_2$Ag(CN)$_2$ **2**: $M_r = 1304.4$, orthorhombic space group $P2_12_12$, $a = 9.5839(8)$, $b = 4.983(3)$, $c = 34.645(6)$, $V = 1654$ Å^3, $Z = 2$, $D_c = 2.618$ g cm^{-3}, $R = 0.057$ for 1136 reflections with $F^2 \geqslant 2\sigma(F^2)$. Its crystal structure consists of two-dimensional organic sheets separated by linear Ag(CN)$_2$$^-$ anions. The organic molecules adopt the so-called α type of packing with a dihedral angle between two molecules belonging to two adjacent chains of *ca.* 78°. This compound shows metallic behaviour in the range 300–2 K, with $\sigma_{300\ \mathrm{K}} = 100$ S cm^{-1}.

Introduction

Most of the known organic superconductors are based on the organic electron donor molecule bis(ethylenedithio)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.[1–4] This spatial organization resulted in the stabilization of quasi two-dimensional electronic systems with an improvement of the superconducting transition temperature (T_c) by one order of magnitude by comparison to the quasi one-dimensional Bechgaard's salts.[1–6] 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 and BETS (Scheme 1). Interesting materials were obtained in many cases.[1] In particular, it has been found that BETS is a good candidate for stabilization of the metallic state, and a series of organic conductors and superconductors have been obtained with this molecule.[1,2,7–11] On the other hand it has been found that the inorganic anions play a crucial role in the physical properties of these BEDT-TTF derivative materials.[1,12] Using Ag$_n$(CN)$_{n+1}$$^-$ as an isolated anion ($n = 1$)[13–18] or as a polymeric sheet ($n = 4$),[19,20] a series of materials with rich polymorphism and physical properties ranging from semiconducting to superconducting were reported for BEDT-TTF. We report here, the preparation, X-ray crystal structures, EHT (extended Huckel theory) band calculations, EPR and magnetic investigations of two selenium based donors with this type of anion, namely, κ-(EDS-EDT-TTF)$_2$Ag$_2$(CN)$_3$ **1** and α-(BETS)$_2$Ag(CN)$_2$ **2**. In the former a polymeric Ag$_2$(CN)$_3$$^-$ anionic sheet is observed for the first time. A similar compound has already been obtained with the Cu$_2$(CN)$_3$$^-$ anion, namely κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$.[12,21–23] For the second compound a metallic state was stabilised down to 2 K.



Scheme 1 Compounds discussed in this work: BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene, BO = bis(ethylenedioxo)tetrathiafulvalene, BEDSe-TTF = bis(ethylenediseleno)tetrathiafulvalene, EDS-EDT-TTF = ethylenedithio(ethylenediseleno)tetrathiafulvalene, BETS = bis(ethylenedithio)tetraselenafulvalene.

Experimental

Preparation of compounds

EDS-EDT-TTF[24] and BETS[7] were prepared according to the literature procedures. The title compounds were obtained on a platinum wire electrode by anodic oxidation of the organic donor. The crystal growth apparatus for electrocrystallization consists of a glass U-cell with its two compartments (10 ml

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†Permanent address: Université Ibn Tofail, LCT, BP 133, Kénitra, Morocco.

Table 1 Crystal data and structure refinement for **1** and **2**

	κ-(EDS-EDT-TTF)$_2$[Ag$_2$(CN)$_3$]	α-(BETS)$_2$Ag(CN)$_2$
Empirical formula	$C_{23}H_{16}Ag_2N_3S_{12}Se_4$	$C_{22}H_{16}AgN_2S_8Se_8$
Formula weight	1250.69	1304.40
Crystal system	Monoclinic	Orthorhombic
a/Å	15.157(9)	9.5839(8)
b/Å	8.7321(18)	4.983(3)
c/Å	13.507(15)	34.645(6)
β/°	90.94(3)	90.0
V/Å^3	1788(2)	1654.4(11)
Z	2	2
Space group	$P2_1/c$	$P2_12_12$
Temperature/K	293(2)	293(2)
λ(Mo-Kα)/Å	0.71073	0.71073
D_c/g cm^{-3}	2.324	2.618
μ/mm^{-1}	5.894	9.937
F(000)	1194	1218
θ range/°	1.34–29.97	1.18–34.92
Range of hkl	$-21 \leqslant h \leqslant 21$	$0 \leqslant h \leqslant 15$
	$-12 \leqslant k \leqslant 0$	$0 \leqslant k \leqslant 8$
	$0 \leqslant l \leqslant 18$	$0 \leqslant l \leqslant 55$
Total reflections collected	5402	4179
Independent reflections (R_{int})	5191 (0.0222)	4179 (0.0000)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
No. of variables	205	175
S, goodness-of-fit on F^2	1.035	0.926
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0552$, $wR_2 = 0.1069$	$R_1 = 0.0570$, $wR_2 = 0.1158$
Largest diff. peak and hole/e Å^{-3}	0.874, −0.792	1.207, −1.373

each) separated by a glass frit, and two platinum wire electrodes (diameter = 1 mm). A low constant current intensity was maintained. The stoichiometries were checked by X-ray analysis.

For κ-(EDS-EDT-TTF)$_2$Ag$_2$(CN)$_3$ **1**, 200 mg (0.53 mmol) of Ag$_2$Ni(CN)$_4$ in 10 ml of *N*,*N*-dimethylformamide were placed in the two compartments and 15 mg (0.0315 mmol) of EDS-EDT-TTF added to the anodic compartment. The electrolyte Ag$_2$Ni(CN)$_4$ was prepared by metathesis of K$_2$Ni(CN)$_4$ and Ag(NO$_3$) in water. Dark plate like crystals of κ-(EDS-EDT-TTF)$_2$Ag$_2$(CN)$_3$ were obtained after a few days with a constant current density fixed at 1.6×10^{-2} μA mm^{-2}.

For α-(BETS)$_2$Ag(CN)$_2$ **2**, 200 mg (1 mmol) of KAg(CN)$_2$ and 0.012 g (0.021 mmol) of BETS in a mixture of DMF (10 ml)–1,1,2-trichloroethane (5 ml) were placed in the anionic cell compartment and KAg(CN)$_2$ (200 mg, 1 mmol) in 10 ml of DMF were placed in the other compartment. Both compartments were degassed with nitrogen prior to the experiment for 30 minutes. Dark plate like crystals were obtained after one month with a constant current density fixed at 1.6×10^{-2} μA mm^{-2}.

Table 2 Selected bond distances (Å) for **1**

Se(1)–C(2)	1.831(13)	Se(1)–C(3)	1.843(6)
Se(2)–C(1)	1.794(10)	Se(2)–C(4)	1.805(7)
S(3)–C(5)	1.737(6)	S(3)–C(3)	1.743(7)
S(4)–C(5)	1.741(6)	S(4)–C(4)	1.743(6)
S(5)–C(6)	1.736(6)	S(5)–C(8)	1.750(6)
S(6)–C(6)	1.730(6)	S(6)–C(7)	1.748(6)
Se(7)–C(8)	1.821(6)	Se(7)–C(9)	1.851(8)
Se(8)–C(7)	1.872(6)	Se(8)–C(10)	1.898(7)
C(1)–C(2)	1.401(15)	C(3)–C(4)	1.347(9)
C(5)–C(6)	1.364(8)	C(7)–C(8)	1.343(8)
C(9)–C(10)	1.464(10)		
Ag(1)–C(11)	2.047(7)	Ag(1)–N(12)	2.079(6)
Ag(1)–N(1)	2.531(7)	N(12)–C(12)^{i}	1.145(11)
N(12)–N(12)^{i}	1.145(11)	C(11)–N(1)^{ii}	1.136(9)
N(1)–C(11)^{iii}	1.136(9)		

Symmetry transformations used to generate equivalent atoms: $^{i}-x+1, -y, -z+1$; $^{ii}-x+1, y+1/2, -z+1/2$; $^{iii}-x+1, y-1/2, -z+1/2$.

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 diffractometer equipped with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. The unit cell parameters were determined and refined from setting angles of 25 accurately centred reflections. Data were collected with the θ–2θ scan method. Intensities were corrected for Lorentz and polarisation effects and a preliminary space group search performed with MolEN.[25] Semi empirical Ψ-scan absorption corrections[26] were applied. Both structures were solved by direct methods with SHELXS-97[27] and refined using full-matrix least-squares on F^2 using SHELXL-97.[28] The crystal data of the two compounds are presented 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 3 Selected bond distances (Å) for **2**

Se(1)–C(2)	1.86(2)	Se(1)–C(3)	1.89(2)
Se(2)–C(4)	1.830(16)	Se(2)–C(5)	1.88(3)
S(1)–C(1)	1.69(3)	S(1)–C(2)	1.75(2)
S(2)–C(5)	1.70(3)	S(2)–C(6)	1.82(2)
C(1)–C(1)^{i}	1.28(4)	C(2)–C(2)^{i}	1.42(4)
C(6)–C(6)^{i}	1.53(6)	C(5)–C(5)^{i}	1.48(5)
C(3)–C(4)	1.45(5)		
Se(3)–C(9)	1.86(2)	Se(3)–C(8)	1.97(3)
Se(4)–C(10)	1.94(2)	Se(4)–C(11)	1.94(2)
S(3)–C(8)	1.75(3)	S(3)–C(7)	1.85(4)
S(4)–C(11)	1.77(2)	S(4)–C(12)	1.80(2)
C(7)–C(7)^{ii}	1.32(8)	C(8)–C(8)^{ii}	1.20(7)
C(11)–C(11)^{ii}	1.21(5)	C(12)–C(12)^{ii}	1.41(5)
C(9)–C(10)	1.32(5)		
Ag(1)–C	2.07(2)	Ag(1)–C^{iii}	2.07(2)
N–C	1.38(4)		

Symmetry transformations used to generate equivalent atoms: $^{i}\ -x, 1-y, -z$; $^{ii}1-x, 2-y, -z$; $^{iii}-x, -y, -z$.

See http://www.rsc.org/suppdata/jm/1998/387, for crystallographic files in .cif format.

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.[1,2] However the main difference lies in the packing mode of the organic and inorganic units used to generate the layer.

κ-(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)$_2^-$ unit.

The organic molecule EDS-EDT-TTF is dissymmetrical 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 for the carbon atoms (C1 and C2) belonging to the twist conformation. The organic molecules form centrosymetric dimers [Fig. 2(b)]. The adjacent dimers are packed orthogonally giving rise to a typical κ-type two-dimensional sheet. In the dimer the two organic molecules show a ring-to-double bond overlap with an interplanar separation of 3.358(8) Å. The interdimer contacts are indicated in Fig. 2(b).

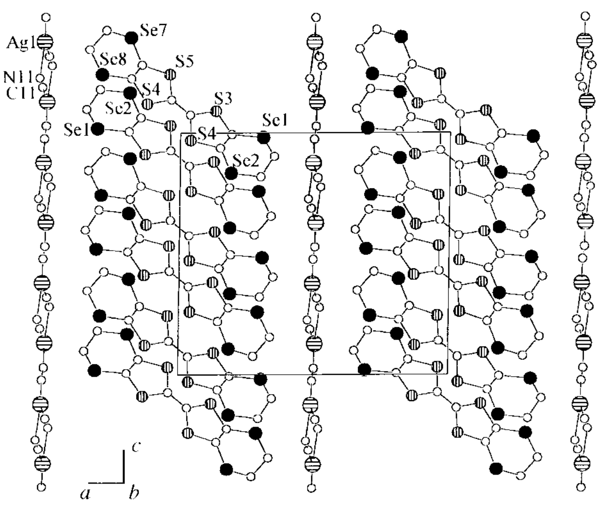

Fig. 1 Crystal structure of κ-(EDS-EDT-TTF)$_2$Ag$_2$(CN)$_3$.

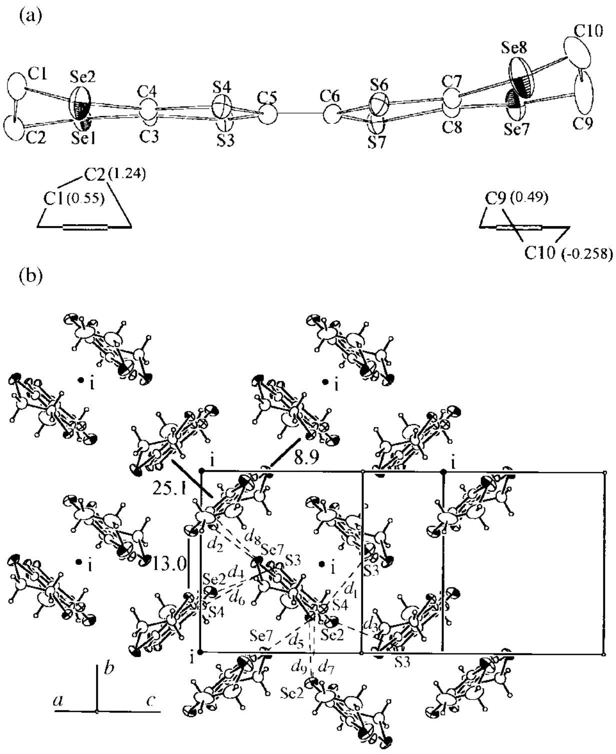

Fig. 2 (a) ORTEP drawing of the organic molecule for kappa phase **1**. (b) Overlap integrals (× 10^3) and minimum intradimer distances: d_1 = S4–S3^i 3.713(3) Å and interdimer distances for **1**: d_2 = Se1–Se8^{ii} 4.377(4) Å, d_3 = Se2–S3^{iii} 3.617(4) Å, d_4 = S3–Se2^{iv} 3.617(4) Å, d_5 = S4–Se7^v 3.615(3) Å, d_6 = S5–S4^{iv} 3.818(4) Å, d_7 = S6–Se2^{vi} 3.762(3) Å, d_8 = Se7–S4^{ii} 3.615(3) Å, d_9 = Se8–Se2^{vi} 3.720(2) Å. *i*: $2-x$, $1-y$, $1-z$; *ii*: $2-x$, $1/2+y$, $1/2-z$; *iii*: x, $1/2-y$, $1/2+z$; *iv*: x, $1/2-y$, $z-1/2$; *v*: $2-x$, $y-1/2$, $1/2-z$; *vi*: $2-x$, $-y$, $1-z$.

In the inorganic layer (Fig. 3) one disordered, CN (C12/N12) group is observed in which the carbon and nitrogen

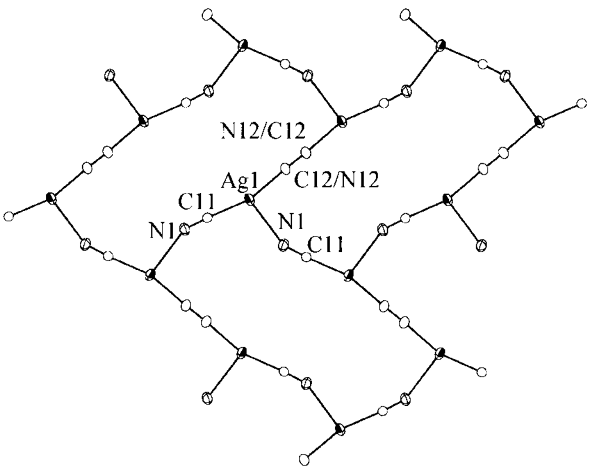

Fig. 3 ORTEP drawing of the inorganic Ag$_2$(CN)$_3$ sublattice.

atoms are not distinguishable along with one ordered CN group (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 C11–Ag–C12/N12 of 160.9(3)°. Two adjacent Ag(CN)$_2$ units are connected through a longer Ag1–N1 bond of length 2.531(7) Å. The angles C11–Ag1–N1 and C12/N12–Ag1–N1 are equal to 103.8(3) and 94.0(3)°, respectively.

The crystal structure of this compound is isomorphous to that of κ- or κ′-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$[21–23,30] with however some differences. For the unit cell parameters, we observed a shorter *c* parameter [15.157(9) *cf.* 16.084(1) Å] and a lower value of *β* [90.94(3) *cf.* 113.39(3)°]. In the Cu containing polymer the bond lengths around the copper atom are similar [1.879(4) with C11, 1.903 with N12 and 2.020(4) Å with N1] while the corresponding bond lengths differ significantly in the silver salt.

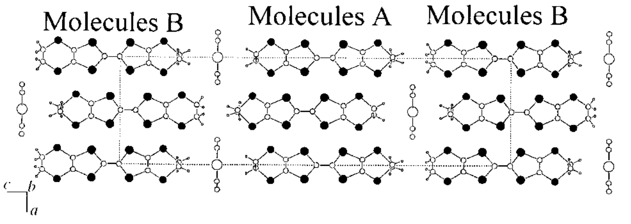

Fig. 4 Crystal structure of α-(BETS)$_2$Ag(CN)$_2$ with alternating layers A and B.

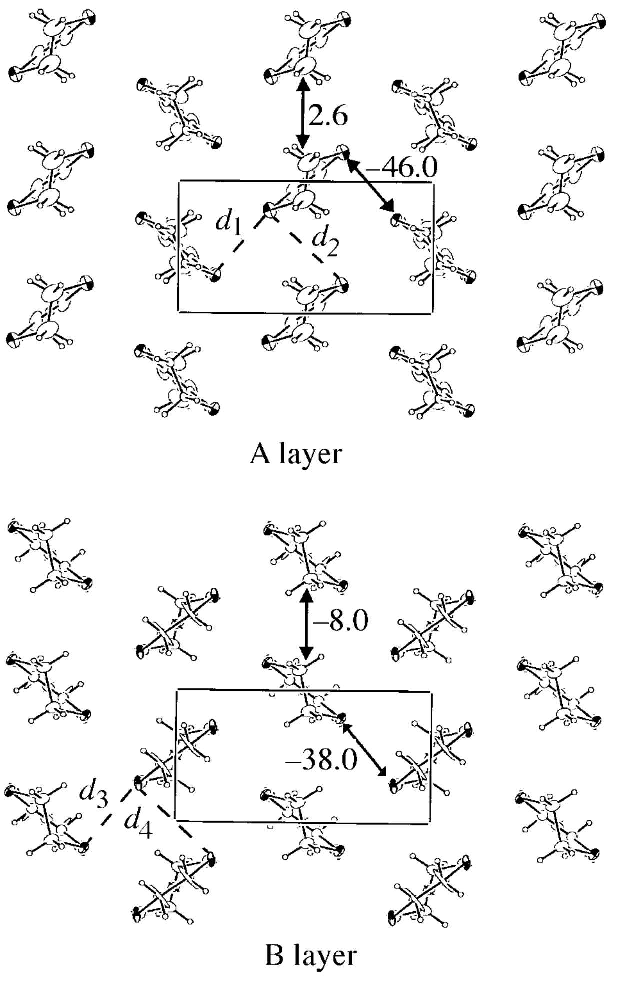

Fig. 5 ORTEP drawing of layers A and B projected onto the *ab* plane with overlap integrals (×10^3) and minimum chalcogen–chalcogen distances for **2**: d_1: S3–S4^i=3.61(2) Å, Se3–S4^i=3.761(6) Å; d_2: Se3–Se3^{ii}=3.837(9) Å; d_3: S2–S1^{iii}=3.60(1) Å, Se1–Se2^{iii}=3.754(6) Å; d_4: Se1–Se1^{iv}=3.875(8) Å. *i*: 1/2−*x*, *y*−1/2, 1−*z*; *ii*: 1−*x*, 1−*y*, *z*; *iii*: 3/2−*x*, *y*−1/2, −*z*; *iv*: 2−*x*, −*y*, *z*.

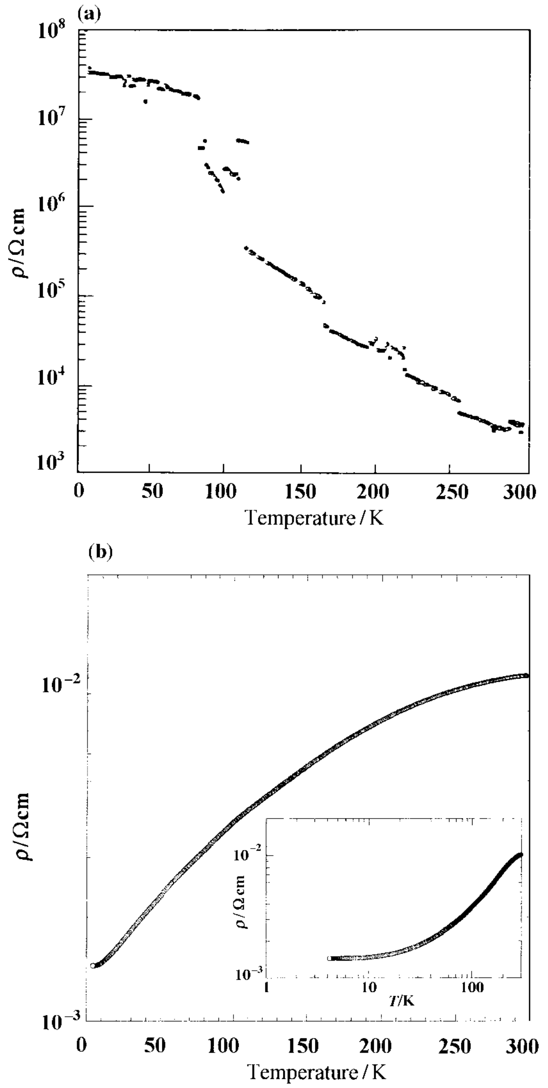

Fig. 6 Resistivity *vs.* temperature for (a) κ-(EDS-EDT-TTF)$_2$-Ag$_2$(CN)$_3$ (b) α-(BETS)$_2$Ag(CN)$_2$.

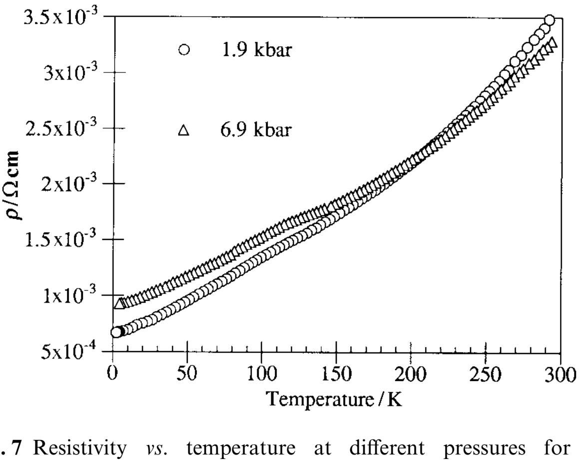

Fig. 7 Resistivity *vs.* temperature at different pressures for α-(BETS)$_2$Ag(CN)$_2$.

α-(BETS)$_2$Ag(CN)$_2$. The crystal structure of this salt is isomorphous to that of α-(ET)$_2$Ag(CN)$_2$ reported by Kurmoo *et al.*[13] The asymmetric unit contains two half BETS molecules

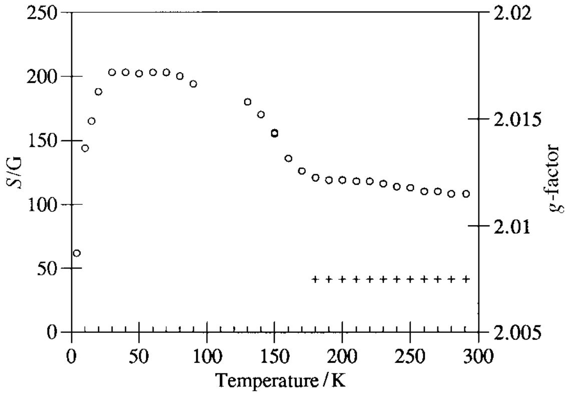

Fig. 8 Temperature dependence of the EPR *g* factor (+) and linewidth (*S*) (○) for an arbitrary crystal orientation (H_o the resonant magnetic field perpendicular to the platelet large face for **1**).

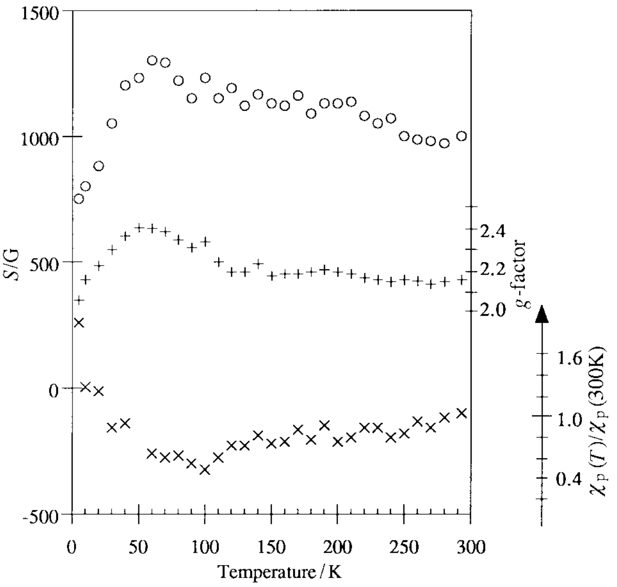

Fig. 9 Temperature dependence of the EPR *g* factor (+) and linewidth (*S*) (○) for **2**, and $\chi_p(T)/\chi_p(300\ K)$ (×).

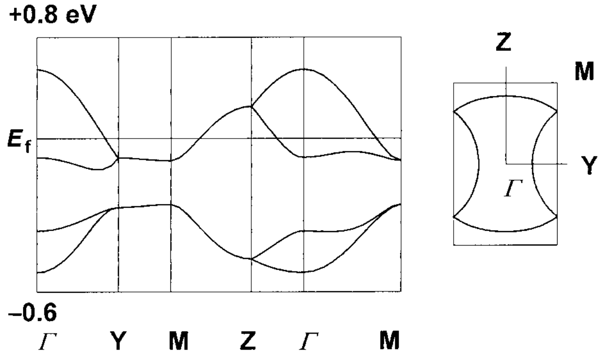

Fig. 10 Dispersion energy bands and Fermi surface for compound **1**.

denoted A and B and half of a $Ag(CN)_2^-$ anion located on a 222 symmetry element. The $Ag(CN)_2^-$ anion is linear. The entire organic molecules (A and B) are generated by a two fold rotation axis along the central C9–C10 and C3–C4 bonds. The crystal structure shown in Fig. 4 consists of alternate organic and inorganic layers along the *c* direction. Both A and B molecules generate structurally independent layers. The projections of the two organic layers in the *ab* plane are shown in Fig. 5. The ethylenic groups on the A molecules are eclipsed while those of the B molecule are staggered. The A molecules are inclined with respect to the *ac* and *bc* plane with angles of 39.16(8) and 50.82(9)°, while molecules from the B layer form angles of 38.60(8) and 51.40(9)°. The organic molecules are inclined in the same sense in the *b* direction and are inclined in the opposite sense in the *a* direction with an angle between two adjacent molecules of 78.34(9)° for the A layer and 77.19(9)° for B layer, similar to what is found for α-(ET)-$KHg(SCN)_2$. Significant intermolecular heteroatom contacts (Fig. 5) occur between adjacent stacks. However, the presence of short intrastack Se1–Se2 contacts of 3.754(6)Å should also be noted.

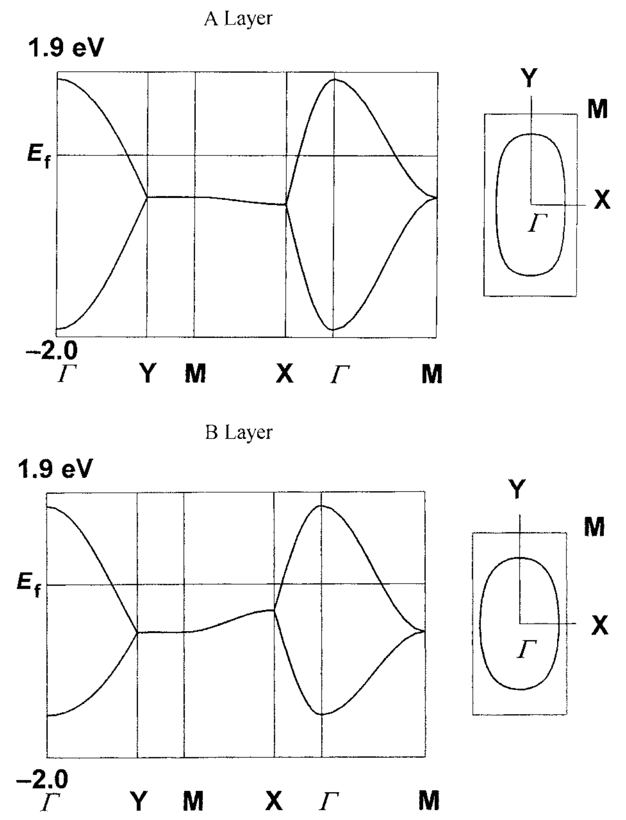

Fig. 11 Dispersion energy bands and Fermi surface for compound **2**, layers A and B.

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 $\sigma_{300\ K}=3\times10^{-4}\ S\ cm^{-1}$ and $E_a=120\ meV$ [Fig. 6(a)]. For compound **2**, the temperature dependence of the resistivity shows a metallic behaviour down to 4.2 K with $\sigma_{300\ K}=100\ S\ cm^{-1}$ [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 linewidth (*S*) anisotropies at room temperature as well as their temperature dependence have been examined for both salts **1** and **2** (Fig. 8 and 9).

For the κ-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. The 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[31] as already observed for other unsymmetrical TTF type molecules.[32] 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 the effects being associated with the presence of a strong Curie tail. At room temperature the EPR signal shows a very large linewidth, *ca.* 1000 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 κ-$(DMET)_2AuBr_2$.[33]

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 similar to results obtained for other κ-salts.[1,12] From these results this compound has a closed 2-D Fermi surface. The half filled upper band is cut by the Fermi level indicating a metallic behaviour which is not in line with the electrical conductivity measurements which show a semiconducting behaviour (see above). This is probably due to the fact that these calculations neglect the effects of the on-site Coulomb repulsion (U) and the presence of disorder.

For compound **2**, calculations were performed considering two independent organic layers. The overlap integrals are shown in Fig. 5 and dispersion bands and Fermi surfaces for each layer are given in Fig. 11. The results are almost the same for both layers. As mentioned above from the electrical conductivity measurements, this compound is metallic. Accordingly, we found a 2-D Fermi surface and the 3/4 filled band is cut by the Fermi level.

Conclusion

Two new radical ion salts containing silver cyanide anions have been prepared and characterised. α-$(BETS)_2Ag(CN)_2$ is metallic down to 2 K and its conductivity is pressure independent.

For the semiconducting κ-$(EDS\text{-}EDT\text{-}TTF)_2Ag_2(CN)_3$ we have shown that a polymeric $Ag_2(CN)_3^-$ anion sheet associated with the κ-phase can be obtained with the dissymmetrical donor EDS-EDT-TTF, as in other κ phase salts[34,35] an insulating ground state has been evidenced which is not reflected in the electronic band calculation. This results from the strong influence of disorder[36] at low temperature which prevents the appearance of an ordered superconducting or magnetic ground state

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