A bilayer molecular metal with polymeric anion; β'' -(CNB-EDT-TTF) $_6$ Ag $_{-7.95}$ I $_{-9.19}$

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ABSTRACT: (CNB-EDT-TTF) $_6$ Ag $_{-7.95}$ I $_{-9.19}$ (CNB-EDT-TTF = 5-cyanobenzene-ethylenedithio-tetrathiafulvalene) is reported as the first bilayer conducting salt with a polymeric anion. The anion is a silver deficient iodoargentate layered polymer with composition close to Ag $_{7.95}$ I $_{9.19}$, as deduced from single crystal X-Ray diffraction. In spite of disorder in the silver iodide polyanion layer, and the large unit cell with 6 inequivalent donor molecules, this compound presents clear metallic properties down to 1.5 K, comparable to those of the β'' -type 4:1 salts of this donor with small discrete anions, with room temperature electrical conductivity in the range of 3-10 S/cm and thermoelectric power of $\sim 100 \mu\text{V/K}$.

During the last few years a new type of two dimensional metals and superconductors with a bilayer arrangement of electrically conducting layers has emerged among molecular conducting systems. This type of bilayer structures, enabling a pairwise interaction between conducting layers, was achieved in compounds based on the electron CNB-EDT-TTF donor (5-cyanobenzene-ethylenedithio-tetrathiafulvalene),¹ in salts of general formula (CNB-EDT-TTF) $_4$ A, with different anions A. In these salts the partially oxidized donors, are tightly packed and held head to head in bilayers, by a network of effective C-N...H-C interactions.^{2,3,4,5} This unique bilayer arrangement has so far been restricted to salts with small discrete monoanions with linear, tetrahedral or octahedral geometry, such as I $_3$, ClO $_4$ and PF $_6$, and quite different structures are obtained with larger anions such as FeBr $_4$, or complexes with square planar geometry.⁶ The CN group position in the donor benzene ring, also plays a crucial role on the bilayer arrangement, as shown by several similar compounds based on the recently synthesized donor isomer 4-CN-EDT-TTF without the bilayer arrangement.^{7,8,9,10}

Scheme 1. Molecular Structures of CNB-EDT-TTF and 4-CN-EDT-TTF.

Aiming at extending the family of double layer conductors based on CNB-EDT-TTF to other anions, polymeric in nature rather than discrete, we tested silver iodide anions which in addition may bring ionic conductivity. In this paper we describe the compound (CNB-EDT-TTF) $_6$ Ag $_{-7.95}$ I $_{-9.19}$ as the first bilayer conducting salt with a polymeric anion arrangement

in spite of the disordered nature of the polyanion and a larger unit cell, presents clear metallic properties down to 1.5 K.

Crystals of (CNB-EDT-TTF) $_6$ Ag $_{-7.95}$ I $_{-9.19}$ were grown by electrochemical oxidation of CNB-EDT-TTF (2 mM) in the presence of an excess (2-3 fold) of TBA AgI $_2$ in dichloromethane under anaerobic conditions. A constant current density of 0.5-1 μAcm^{-2} was kept for 15 days, at 18-20 °C. The collected crystals are semitransparent orange brown thin foils or elongated plates, typically up to 2×2×0.010 mm³.

Figure 1. Crystal structure of (CNB-EDT-TTF) $_6$ Ag $_{-7.95}$ I $_{-9.19}$: a) view along b axis; b) view of one layer of donors along their long axis with 6 nonequivalent molecules depicted in different colors, packed in a β'' -type pattern; c) view of the polyanion double layer along c .

The structure of these crystals is triclinic space group P-1 (Table S1) the asymmetric unit containing 6 inequivalent donor molecules, 10 partially occupied positions for silver and 10 partially occupied positions for iodine, with composition close to 7.95 and 9.19 respectively.¹¹ Within experimental uncertainty the donors present the same geometrical parameters and they adopt a β'' -packing pattern in bilayers (**Figure 1**), virtually identical to that observed in recently described β'' -(CNB-EDT-TTF)₄A salts with small anions.^{2,3,5} In the donor layers the donors molecules present several S...S short contacts below the sum of Van de Waals radii (S10...S13 at 3.598 Å, S19...S8 at 3.573 Å and S19...S34 at 3.557 Å)(Table S2). The donor bilayers alternate along *c* with anionic layers of Ag_{7.95}I_{9.19}, arranged as bilayers with iodine positions outside the silver positions. There are several S...I and I...H short contacts between the donors and the outer iodine atoms in the Ag_xI_y polyanions. (Table S2 and Figure S1). It should be noted that the structural refinement in different crystals measured by X-ray diffraction lead to identical iodine silver composition.

Silver iodine polyanions [Ag_xI_y]^{(y-x)-} are known to adopt a large diversity of geometries, mostly as isolated clusters or chains, but the polyanion in this compound is among uncommon cases presenting a layered structure.^{12,13,14,15,16,17} In this respect it is worth mentioning that with the closely related donor bis-(ethylenedithio)tetrathiafulvalene (BEDT-TTF), it was obtained a salt with composition (BEDT-TTF)₃Ag_xI₈ (*x*~6.4), although with a slightly different double layered anion.¹⁸

The stoichiometry (CNB-EDT-TTF)₆Ag_{7.95}I_{9.19} implies a donor average oxidation state of +0.21, slightly smaller than +0.25, which was observed in the 4:1 salts of this donor with small discrete monoanions. Therefore, in view of the very similar β'' -packing pattern, 2D conducting properties are expected also in this compound.

Figure 2. Temperature dependent normalized electrical resistivity *R* (left) and thermoelectric power, *S*, (right) of single crystals of (CNB-EDT-TTF)₆Ag_{7.95}I_{9.19}. The inset shows typical thin foil and elongated plate shaped crystals, with identical temperature dependence of resistivity.

The electrical conductivity, measured along several plate shaped crystals, all with identical behavior, was found in the range 3-10 S/cm at room temperature, slightly smaller than for the 4:1 salts (typically 20-40 S/cm),² but its temperature dependence shows a clear metallic behavior down to 1.5 K. (Figure 2). The resistivity ratio between room temperature and

the minimum at 1.5 K is ~50-60, significantly larger than that observed in the (CNB-EDT-TTF)₄A salts, which in general present a sample dependent broad minima at lower temperatures that has been ascribed to localization effects induced by anion disorder.¹⁹

The metallic properties of this compound were also confirmed by the thermoelectric power measurements, which gave values of ~100 μ V/K at room temperature, decreasing regularly upon cooling in a fashion comparable to the other CNB-EDT-TTF salts, although with slightly larger values, comparable to the BF₄ salt.⁵ The thermopower values of this compound are among the largest in molecular metallic compounds, placing it as a good candidate for an efficient thermoelectric material. The larger thermopower values relative to the observed in the other 4:1 salts are consistent with the slight decrease in the average degree of oxidation (+0.21), deduced from the chemical composition, as compared to that of the simple 4:1 salts (+0.25). In all compounds the Fermi level is placed near the top of a band in a region of high density of states.

The present results indicate that neither the less regular packing of the donors with a large unit cell with 6 nonequivalent molecules, neither the disorder of the anionic layer with iodine atoms in short contacts with donor molecules, prevent the metallic properties of the donor bilayers down to 1.5 K.

It should be mentioned that the polyanion being silver deficient is expected to present ionic conductivity, as often observed in similar silver iodide compounds.^{18,20} Therefore this compound can be regarded as an hybrid ionic-electronic conducting material. However, the possible ionic contribution when compared with the electronic metallic conductivity of the organic donors will be very small, even at higher temperatures.

The electronic properties of this compound can be better understood by a calculation of the band structure (Figure 3 left) which was performed for the donor bilayers, using a tight binding extended Hückel approach.²¹ The six distinct donor molecules in the unit cell present eighteen distinct interactions between molecules in the same layer (Figure S2). These are however of three different types characteristic of β'' -type packing; those along the π -stacks, the lateral contacts, and those along the step-chains. In addition, there are four weaker interactions between donors in different layers of the bilayer. The average value of the $|\beta_{\text{HOMO-HOMO}}|$ interaction energies²² for the interactions along the stacks, step-chains, lateral and inter-layer directions are 70, 195, 53 and 1.5 meV, respectively (Tables S3 and S4). These values are very similar to those for the related bilayer salt β'' -(CNB-EDT-TTF)₄BF₄.⁵

Figure 3. Band structure (left) and Fermi surface (right) for the donor layers of (CNB-EDT-TTF)₆Ag_{7.95}I_{9.19} where $\Gamma=(0,0)$, $X=(a^*/2,0)$, $Y=(0,b^*/2)$ and $M=(a^*/2,b^*/2)$. The dashed line refers to the Fermi level for an average +0.21 charge of the donors.

The six pairs of molecules in the bilayer unit cell lead to six pairs of almost degenerate bands because the interlayer interactions are very weak. The Fermi level cuts two pairs of bands: the upper one leads to a pair of open components whereas the second leads to closed portions around Γ (Figure 3 right). As usual for β'' -type salts such Fermi surface results from the hybridization of pairs of ellipses. However, because of the small average charge (and the slight differences between the six donors) the Fermi level is very near the top of the second pair of bands, responsible for the closed portions. In fact, the closed portions disappear for a small decrease of the average charge to +0.17 (see SI, Figure S3). Thus, the occurrence of the closed pockets at low temperature which can lead to Shubnikov-de Haas oscillations may subtly depend on small structural changes brought by thermal contraction and/or small variations in the actual anion stoichiometry.

Magnetoresistance measurements under magnetic fields up to 16 T, at temperatures down to 1.5 K show positive values up to 12% at the lowest temperatures but without any sign of oscillations (Figure S4), which in view of the closed Fermi surfaces predicted by the theoretical calculations could be expected to occur at very low temperatures in clean samples. In addition to the above-mentioned possibilities, their absence can be also due to the disorder associated with the anion.

In conclusion, (CNB-EDT-TTF)₆Ag_{~7.95}I_{~9.19} is the first bilayer molecular metal with a polymeric anion. The anion is a silver deficient iodoargentate with a rare type of double layered structure. Neither the large unit cell with six inequivalent donor molecules, and the consequent modulation of intermolecular interactions, nor the anion disorder prevent clear metallic properties in this bilayer compound down to liquid helium temperatures. The large resistivity ratio observed ($R_{300K}/R_{1.5K} \sim 60$) places this compound among the bilayer compounds with smaller effective disorder effects, such as the ordered phase of the triiodide salt β'' -(CNB-EDT-TTF)₄I₃.

ASSOCIATED CONTENT

Supporting Information. The supporting information is available free of charge via at <http://pubs.acs.org/>...

X-ray crystal structure file for (CNB-EDT-TTF)₆Ag_{~7.95}I_{~9.19} (CIF).

Experimental Details on crystallographic data, computational work, and electrical transport measurements including Figures S1-S3 and Tables S1-S4 (PDF).

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interests.

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ABBREVIATIONS

CNB-EDT-TTF, 5-cyanobenzene-ethylenedithio-tetrathiafulvalene;
BEDT-TTF, bis-(ethylenedithio)tetrathiafulvalene.

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