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MOLECULAR CONDUCTORS BASED ON THE [Au(dmit)$_2$] COMPLEX ANION

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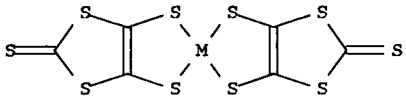
ABSTRACT

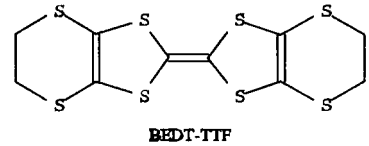
The salts $TTF_3[Au(dmit)_2]_2$, $TMTSF_3[Au(dmit)_2]_2$ and BEDT–TTF[Au(dmit)$_2$] have been prepared. The electrical conductivities of the salts are 0.1 Scm^{-1}, 6.5 x 10^{-2} Scm^{-1} and 1.8 x 10^{-4} Scm^{-1} respectively. The salts exhibited the temperature dependance of semiconductors, with band gaps of 60 meV, 30 meV and 500 meV for the TTF, TMTSF,and BEDT–TTF salts respectively. The salts are compared with their [Ni(dmit)$_2$] analogues.

INTRODUCTION

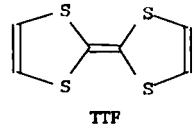
During the past twenty-five years there has been great interest in the synthesis and application of materials which exhibit novel magnetic and electronic properties in the solid state. Many transition metal complexes of sulphur donor ligands have been shown to exhibit high electrical conductivity, with a number of complexes of "dmit" (dimercaptoiso-trithione) with d^8 transition metals exhibiting the phenomenon known as superconductivity[1,2,3]. Interest has concentrated on the salts of dmit complexes because of their similarity to the organic donors BEDT-TTF (bis(ethylenedithio)-tetrathiafulvalene) and TTF (tetrathiafulvalene).



[M (dmit)]
2



BEDT-TTF



TTF

The search for new molecular metals and superconductors involving the dmit ligand has broadened to include other metals containing the d^8 electronic configuration, the most widely studied being the dmit complexes of gold(III) [4,5,6]. Gold(III) complexes have been studied because they are stable and are often isostructural to analogous nickel(II) complexes[7]. In this study organic open shell cation salts of $[Au(dmit)_2]$ were prepared and compared with the analogous nickel, palladium and platinum salts.

RESULTS AND DISCUSSION

Electrocrystallisation of a solution of $TBA[Au(dmit)_2]$ and TTF, TMTSF and BEDT-TTF in acetonitrile using platinum electrodes, produced the salts $TTF_3[Au(dmit)_2]_2$, $TMTSF_3[Au(dmit)_2]_2$ and BEDT-TTF$[Au(dmit)_2]$ respectively.

$TTF_3[Au(dmit)_2]_2$

This salt formed on the anode as a black microcrystalline powder, using a constant current density of $4\mu A cm^{-2}$ over a period of 4 days. Analysis showed the salt to possess the somewhat unusual stoichiometry of $TTF_3[Au(dmit)_2]_2$. The nickel analogue of this salt possesses the stoichiometry of $TTF[Ni(dmit)_2]_2$, which is a common stoichiometry for many of the partially oxidised nickel salts. Attempts to prepare $TTF_3[Au(dmit)_2]_2$ by slow inter-diffusion of solutions of $TTF_3(BF_4)_2$ and $TBA[Au(dmit)_2]$ in acetonitrile were unsuccessful.

The room temperature electrical conductivity of a compressed pellet of $TTF_3[Au(dmit)_2]_2$ was found to be 0.1 Scm^{-1}. The material exhibited decreasing conductivity with decreasing temperature with a band gap of 60meV. Figure 1 shows the temperature dependence of the conductivity.

$TMTSF_3[Au(dmit)_2]_2$

This salt formed on the anode as fibrous fine shiny black needles, over a period of 9 days using a constant current density of $4\mu A cm^{-2}$. The crystals produced were too

fibrous and too fine for the structure to be determined by x-ray diffraction or for single crystal conductivity measurements. This salt possesses the same stoichiometry as the TTF salt described above.

The room temperature electrical conductivity of a compressed pellet of $TMTSF_3[Au(dmit)_2]_2$ was 6.5 x 10^{-2} Scm^{-1}. On lowering the temperature the material exhibited semiconducting behaviour, with a band gap of 30meV (figure 1).

BEDT-TTF[Au(dmit)$_2$]

This salt was obtained as small fibrous needles on the anode, using a constant current density of 6 $\mu A cm^{-2}$ over a period of 21 days. Analysis showed the material to possess a stoichiometry of BEDT-TTF[$Au(dmit)_2$], which is the same as that of the analogous nickel complex, BEDT-TTF[$Ni(dmit)_2$].

The room temperature electrical conductivity of a compressed disc of this material was 1.8 x 10^{-4} Scm^{-1}. On lowering the temperature the material exhibited semiconducting behaviour, with a large band gap of 500meV (figure 1).

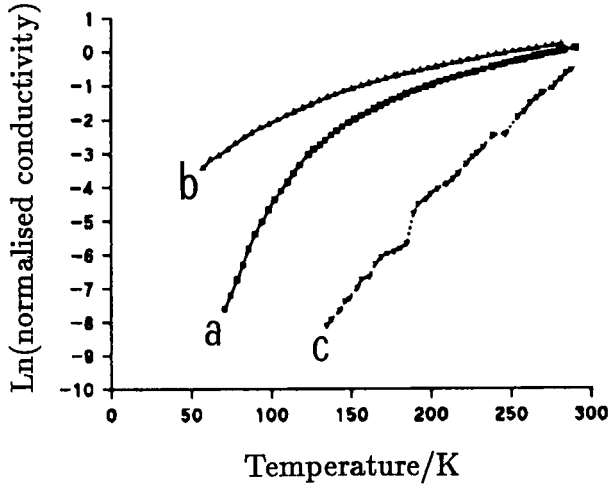


Figure 1: Electrical conductivity of (a) $TTF_3[Au(dmit)_2]_2$, (b) $TMTSF_3[Au(dmit)_2]_2$ and (c) BEDT–TTF[$Au(dmit)_2$].

COMPARISON TO NICKEL COMPLEX SALTS

The electrical properties of the open shell cation salts of $[Au(dmit)_2]$ and the corresponding salts of $[Ni(dmit)_2]$ are shown in table 1.

$[Au(dmit)_2]$ salts	Conductivity Scm^{-1}	$[Ni(dmit)_2]$ salts	Conductivity Scm^{-1}
$TTF_{0.6}$	0.1	$TTF_{0.5}$	300
$TMTSF_{0.6}$	6.5×10^{-2}	$TMTSF_{0.5}$	2-50
BEDT-TTF	1.8×10^{-4}	BEDT-TTF	2×10^{-3}

Table 1: Electrical conductivity results of $[Au(dmit)_2]$ and $[Ni(dmit)_2]$ salts.

Although it is not possible to compare the properties of materials with different, or unknown, crystal structures a tentative analysis of the properties of the salts is given below.

Both the TTF and the TMTSF salts of $[Au(dmit)_2]$ possess a different stoichiometry to those of the corresponding salts of $[Ni(dmit)_2]$, whereas the corresponding BEDT-TTF salts possess the same stoichiometry. There does not appear to be any reason for these differences. All the $[Au(dmit)_2]$ complexes, however, possess lower conductivities than the corresponding $[Ni(dmit)_2]$ complexes. In the absence of detailed crystal structures it is difficult to explain this difference. In previous studies of nickel, palladium and platinum complexes of dmit it has been observed that the nickel complex often possesses the highest conductivity[1]. The results described here agree with the trend of decreasing conductivity with increasing atomic number. This could be due to steric effects resulting from the larger gold atom in the complex which will increase inter-molecular distances and thus reduce S...S overlap. Alternatively it could be that the influence of the gold(III) atom on the energy levels of the metal complex is the most important effect.

EXPERIMENTAL:

Preparation of TBA[Au(dmit)$_2$]

4,5-bis(benzoylthio)-1,3-dithiole-2-thione was prepared as described by Steimecke *et al.*[9]. To a stirred suspension of 1.00g 4,5-bis(benzoylthio)-1,3-dithiole-2-thione in 10cm^3 dry degassed methanol under argon was added a solution of sodium (0.11g) in 10cm^3 dry methanol. Once hydrolysis of the ester was complete (15 min) 3cm^3 of 0.880 gcm^{-3} ammonia solution in water was added, followed by a solution of 0.50g $K_2[AuCl_4]$ in 10cm^3 dry methanol. A solution of 0.4g tetrabutylammonium bromide in 5cm^3 methanol was added, and the resulting precipitate of TBA[Au(dmit)$_2$] was isolated and washed with 5cm^3 methanol and 20cm^3 anhydrous diethyl ether. Recrystallisation from acetonitrile gave brown needles. (Found: C=30.99%, H=4.29%, N=1.25%; calculated for $AuC_{22}H_{36}NS_{10}$: C=31.77%, H=4.33%, N=1.68%.)

Electrocrystallisation

To a solution of 0.1g TBA[Au(dmit)$_2$] in 100cm^3 dry degassed aceotnitrile was added 120mg of the open shell cation (TTF, TMTSF or BEDT-TTF). The mixture was left stirring under argon in the dark for 30min. The mixture was then placed into a two neck round bottomed flask, flushed with argon, and two passified platinum electrodes were fitted. The flask was covered in aluminium foil in order to avoid light, since the organic donors are light sensitive. The apparatus was then connected to a constant current source, previously set to deliver a current relative to the size of the anode, such that a constant current density may be achieved. The experiment was run for two weeks and any product formed on the anode was removed by careful washing using ice cold acetonitrile.

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