

# Charge transfer salts based on $M(\text{dcbdt})_2$ complexes ( $M=\text{Au}$ and $\text{Ni}$ )

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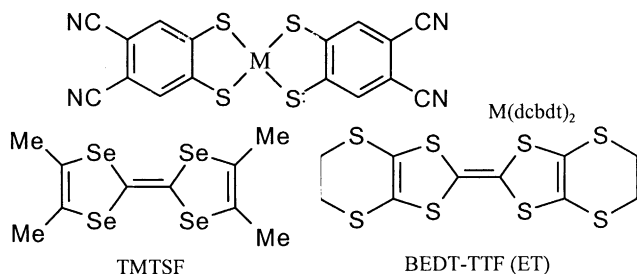
## Abstract

BEDT-TTF [ $\text{Au}(\text{dcbdt})_2$ ] and TMTSF [ $\text{Co}(\text{dcbdt})_2$ ] ( $\text{dcbdt} = 4,5\text{-dicyanobenzene-1,2-dithiolate}$ ) were obtained as small single crystals by electrocrystallisation. BEDT-TTF [ $\text{Au}(\text{dcbdt})_2$ ] is triclinic, space group  $P\bar{1}$ , and its structure consists in alternated donor acceptor stacks, responsible for electrical insulating properties. TMTSF [ $\text{Co}(\text{dcbdt})_2$ ] presents semiconducting properties with a relatively high electrical conductivity ( $\sigma_{\text{RT}} \sim 10\text{-}150 \text{ S/cm}$ ,  $E_a = 78 \text{ meV}$ ) and its thermopower ( $S_{\text{RT}} \sim 9 \mu\text{V/K}$ ) has a temperature dependence suggesting a two band conduction mechanism.

**Keywords:** Organic conductors based on radical anion salts, Electrical transport, Charge transfer salts

## 1. Introduction

The recent synthesis of the new ligand 4,5-dicyanobenzene-1,2-dithiolate, ( $\text{dcbdt}$ ), in our laboratory<sup>1</sup> opened the way to the preparation of a new family of complexes with different transition metals, which are promising building blocks for the preparation of novel molecular materials with interesting electrical and magnetic properties. As first shown for the case with  $M=\text{Ni}$ , these complexes present several stable oxidation states,  $[\text{M}(\text{dcbdt})_2]^{z-}$  corresponding to  $z=2, 1$  and  $2/5$ , all characterised by low oxidation potentials. The partially oxidised complexes present semiconducting properties with a relatively high electrical conductivity.<sup>2,3</sup>



Due to the low oxidation potentials of these complexes, the preparation of charge transfer salts by electrocrystallisation is restricted to good electron donors with lower oxidation potentials, such as BEDT-TTF or TMTSF. In this paper we report the preparation and

characterisation of two new charge transfer salts, BEDT-TTF [ $\text{Au}(\text{dcbdt})_2$ ] and TMTSF [ $\text{Co}(\text{dcbdt})_2$ ].

## 2. Results and Discussion

BEDT-TTF [ $\text{Au}(\text{dcbdt})_2$ ] was obtained by electrocrystallisation from a solution of  $(n\text{-Bu})_4\text{N} [\text{Au}(\text{dcbdt})_2]$  and BEDT-TTF in  $\text{CH}_2\text{Cl}_2$ , and using platinum electrodes under galvanostatic conditions ( $\sim 0.1 \mu\text{A/cm}^2$ ). Small dark brown thin plate shaped crystals ( $\approx 0.52 \times 0.21 \times 0.15 \text{ mm}^3$ ) were collected from the anode surface after a few days. TMTSF [ $\text{Co}(\text{dcbdt})_2$ ] was obtained also as small dark needle shaped crystals ( $\approx 1.5 \times 0.01 \times 0.05 \text{ mm}^3$ ) following a similar procedure. The Au and Co complexes were prepared following procedures similar to those previously reported for the Ni complex.<sup>1,2</sup>

Elemental analyses of these salts are consistent with a 1:1 stoichiometry, BEDT-TTF [ $\text{Au}(\text{dcbdt})_2$ ] and TMTSF [ $\text{Co}(\text{dcbdt})_2$ ], which for the first compound is confirmed by the crystal structure. The crystal structure of the Co salt could not yet be determined.

Table 1- Crystal data of  $\text{ET}[\text{Au}(\text{dcbdt})_2]$

$a = 6.9390(5) \text{ \AA}$	$\alpha = 102.733(5)^\circ$
$b = 8.5890(5) \text{ \AA}$	$\beta = 103.133(5)^\circ$
$c = 13.7540(5) \text{ \AA}$	$\gamma = 97.886(5)^\circ$
$V = 763.4(8) \text{ \AA}^3$	Triclinic, $P\bar{1}$
$Z = 1$	$\rho_{\text{calc}} = 2.093 \text{ g/cm}^3$
$R[I \geq 2\sigma(I)] = 0.0424$	$wR(F^2)$ , all data = 0.0936

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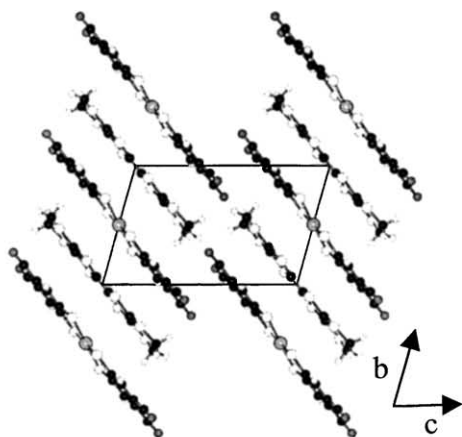


Fig. 1- BEDT-TTF Au(dcbdt)<sub>2</sub> structure viewed along (1,0,0)

Single crystal diffraction data for BEDT-TTF [Au(dcbdt)<sub>2</sub>] were collected at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator selected MoK $\alpha$  radiation ( $\mu = 5.31 \text{ mm}^{-1}$ ). The crystal data is summarised on table 1.

The unit cell comprises one independent donor and one independent acceptor units, which form alternated stacks along  $a+b$ , as shown in Fig. 1. These alternated stacks are connected by a network of S...S interactions between donor-donor, donor-acceptor and acceptor-acceptor, with distances of 3.651Å, 3.573Å and 3.664Å respectively, as shown in Fig. 2. This alternating stacking structure is consistent with the electrically isolating behaviour observed in small single crystals with  $\sigma_{RT} < 10^{-5} \text{ S/cm}$ .

The electrical conductivity and thermoelectric power of TMTSF [Co(dcbdt)<sub>2</sub>] were measured as a function of temperature, using the same measurement cell attached to the cold stage of a closed cycle helium refrigerator. The current imposed for electrical conductivity measurements was 1  $\mu\text{A}$  (77 Hz) and the voltage was measured by a lock-in amplifier, using a four probe configuration.

Electrical conductivity at room temperature was found in the range 10–150 S/cm, an unexpected large variation ascribed to variable crystal quality. In spite of this variation the temperature dependence was found always similar, following a semiconducting behaviour with a rather low activation energy of 0.075 eV as show in Fig. 3.

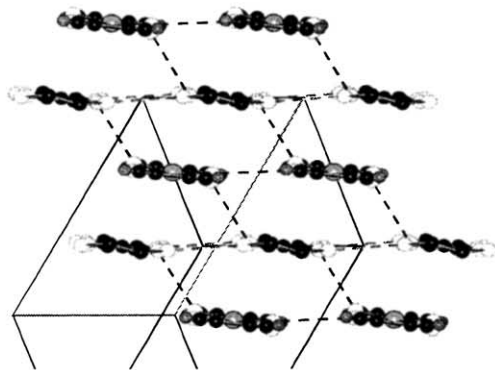


Fig. 2- S...S interactions on BEDT-TTF[Au(dcbdt)<sub>2</sub>]

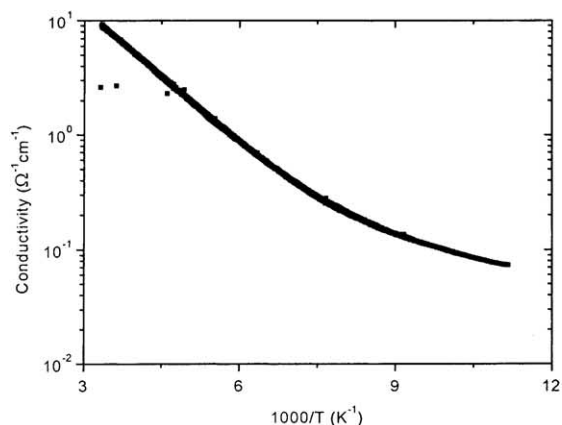


Fig. 3- Electrical conductivity of TMTSF[Co(dcbdt)<sub>2</sub>]

The thermopower was measured using a gradient  $\leq 1 \text{ K}$  in an apparatus previously described.<sup>4</sup> The absolute thermopower,  $S$ , obtained after correction for the gold wires  $S$ , (Fig. 4), presents rather low values with  $S_{RT} = 9 \mu\text{V/K}$ . Upon cooling, thermopower decreases, becomes negative below  $\sim 210 \text{ K}$ , reaching a minimum of  $\sim -30 \mu\text{V/K}$  around 110 K before it starts approaching zero upon further cooling. This behaviour can be attributed to a two band system, but further discussion waits for the crystal structure determination.

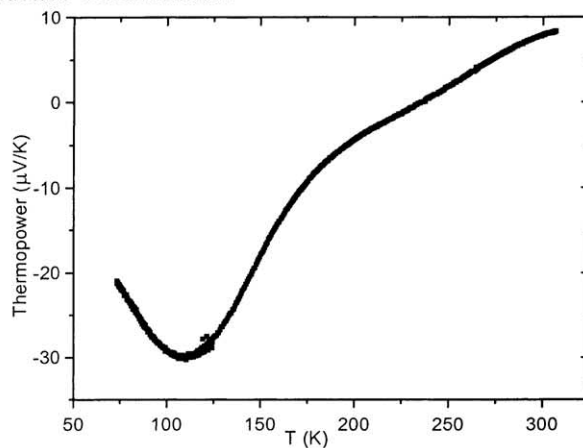


Fig. 4- Absolute termopower of TMTSF[Co(dcbdt)<sub>2</sub>]

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