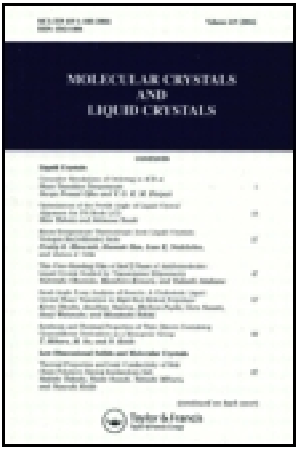

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New Conductors Based on Metal Complexes of Sulphur Chelate Ligands

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NEW CONDUCTORS BASED ON METAL COMPLEXES OF SULPHUR CHELATE LIGANDS

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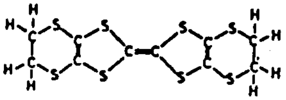
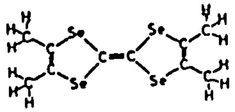
Abstract The results of electrocrystallising solutions of $[M(S_2C_2(CN)_2)_2]$ anions (where M = Ni, Pd or Pt) and BEDT-TTF or TMTSF are presented. The products of BEDT-TTF and the $[M(S_2C_2(CN)_2)_2]$ anion are shown to be semiconductors.

INTRODUCTION

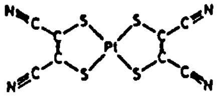
During the past few years there have been remarkable developments in the field of conducting materials. In particular compounds involving planar organic cations and containing selenium (e.g. TMTSF)[1] or sulphur (e.g. BEDT-TTF)[2] have been shown to exhibit metallic properties down to very low temperatures and even become superconducting at temperatures down to 1 K. A second type of metallic conductor has been prepared recently in which the conducting stack is composed of planar transition metal complex anions which contain the sulphur donor ligands maleonitriledithiolato (mnt)3 or dimercapto-1,3-dithiole-2-thione (dmit).[4]



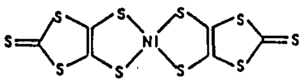
BEDT-TTF



TMTSF



[Pt(mnt)$_2$]



[Ni(dmit)$_2$]

Both series of compounds may be prepared by electrocrystallisation techniques,[5] and it therefore seemed opportune to attempt to grow crystals of compounds which contained both the organic donor cation and the metal complex anion by this technique. The presence of a planar sulphur containing anion might be expected to increase inter-stack interactions which are known to favour the stabilisation of the metallic or superconducting phase. Previous studies of (perylene)$_2$ [M(mnt)$_2$] (where M = Pt or Au) showed that highly conducting salts could be produced by the combination of organic donors with these metal complex anions.[6,7]

Whilst this present study was in progress crystals of TTF[Ni(dmit)$_2$]$_2$, grown by a slow diffusion technique have been shown to exhibit metallic behaviour and high conductivity ($\approx 10^5$ S cm^{-1}) down to 4 K.[8]

EXPERIMENTAL

Preparation of Materials

The solvents to be used were cleaned and dried in a still and passed down an Al_2O_3 drying column under argon immediately prior to use. The anions were prepared as the TBA salts.[9] They were recrystallised twice, dried and stored under argon. Prior to their use the TBA salts were dried in vacuo at 60°C for at least 25 hrs. BEDT-TTF and TMTSF were used as obtained from Strem Chemicals, but some BEDT-TTF was also prepared by the published method.[10,11] All the organic donors were stored in the dark, under argon, in a cold box.

Solutions, typically 1 to 3 mM in organic donor, and 2 to 50 mM in metal salt were placed in an H cell fitted with platinum wire electrodes. The anode and cathode compartments were separated by a fine frit. The cells were rigorously cleaned and dried, the solutions added to the cell were degassed with argon and the cell sealed with parafilm. Electrocrystallisation was carried out at constant current using current densities in the range 0.1 to 10 $\mu A/cm^2$ for 1 to 40 days.

Electrical Conductivity Studies

Single crystal measurements were made using either 4-probe or 2-probe dc techniques with colloidal silver or graphite paint as the contact material. Compressed pellet measurements were used for microcrystalline and powdered products.

RESULTS AND DISCUSSION

Most previous studies on the electrocrystallisation of BEDT-TTF or TMTSF have concentrated on tetrahedral or octahedral anions of fixed oxidation state. The properties of these compounds have been shown to be very dependent on the size of the counter ion, the ordering of the counter ion in the lattice and on the interaction of the anion with hydrogen atoms on the organic cation.[11,12] It has been observed that with BEDT-TTF especially, even simple anions may give several stoicheiometries and crystal shapes on the same electrode.

The preliminary results given in Tables 1 and 2 show that new compounds can be produced by electrocrystallisation of BEDT-TTF and TMTSF with the large planar metal dithiolate anions. The 'redox' nature of the anions results in the simultaneous production of several compounds or phases clearly distinguishable under the microscope. This is well illustrated by reference to the combination of BEDT-TTF and [Pd(mnt)$_2$] anions where two types of crystals have been obtained exhibiting different c-axis unit cell dimensions. The products are only obtained in low yield partly because of the low solubility of the starting materials. The small amount of product makes analysis unreliable and crystals of sufficient quality for detailed X-ray and spectroscopic studies are as yet unavailable.

TABLE 1 Experiments involving BEDT–TTF

Anion	Solvent	Product
$[Ni(mnt)_2]^-$	THF	Black needles[a]
		Black plates
$[Ni(mnt)_2]^{2-}$	DMF	No Product
$[Pd(mnt)_2]^-$	THF	Small black plates
	TCE	Small black plates
$[Pd(mnt)_2]^{2-}$	TCE	Black needles[b]
		Black plates
	DMF	Small black plates
	TCE	Very dark green needles[d]
		Light green pleochroic needles
$[Pt(mnt)_2]^-$	THF	Very small black plates[c]

TABLE 2 Experiments involving TMTSF

Anion	Solvent	Product
$[Ni(mnt)_2]^{2-}$	THF	No product
$[Ni(mnt)_2]^-$	DCM	Black needles
$[Pd(mnt)_2]^-$	THF	Very small dark needles
$[Pd(mnt)_2]^{2-}$	DCM	Small needles
$[Pt(mnt)_2]^-$	THF	Small black needles

Because the redox potentials of $[Ni(mnt)_2]^{2-}$ and $[Pt(mnt)_2]^{2-}$ are lower than that of BEDT–TTF it is not possible to prepare compounds containing the di-anion since oxidation of the di-anion to the mono-anion occurs preferentially to the oxidation of BEDT–TTF.

The redox potentials of $[Pd(mnt)_2]^{2-}$ and $[Cu(mnt)_2]^{2-}$ are however much higher and comparable with BEDT-TTF. It may therefore be possible for these complex anions to produce two series of compounds containing either the mono-anion or the di-anion.

Electrical conduction studies have been performed on some of the products (see Table 3). All the compounds examined are semiconductors with room temperature conductivities in the range 10^{-3} to 10^{-6} S cm^{-1} and activation energies of about 300 meV. The apparent absence of metallic phases suggests that the compounds possess a 1:1 stoicheiometry and this is supported by analytical results obtained for the (BEDT-TTF) $[Ni(mnt)_2]$ salt.

TABLE 3 Electrical Conductivity

Compound	Single crystal (SC) or Disc (D)	σ_{RT} S cm^{-1}	ΔE meV
BEDT-TTF$(Ni(mnt)_2)$ Black needle[a]	SC (4-probe)	1×10^{-6}	360
BEDT-TTF$(Pd(mnt_2)_x$ Black needle[b]	SC (4-probe)	1.1×10^{-3}	227
BEDT-TTF$(Pt(mnt)_2)_x$[c] Black plates	D	1.5×10^{-6}	327
BEDT-TTF$(Pd(mnt)_2)_x$ Very dark green needles[d]	SC (2 probe)	0.2×10^{-5}	197

D - Disc measurement on microcrystallation product

The conductivities are in the range previously reported for either the simple salts of the $[M(mnt)_2]$ mono-anions or the organic cations. It is therefore not possible to tell whether the conduction process involves the anions, the cations or both species. Until a full crystal structure determination is made on one of the compounds it is uncertain whether they possess segregated or mixed stack structures. However, Kobayashi et al. have recently prepared crystals of the charge transfer complex $[BEDT\text{-}TTF][Ni(dmit)_2]$ and showed it to possess BEDT-TTF and $Ni(dmit)_2$ molecules loosely stacked to form mixed-stacking columns.[13] The room temperature conductivity in the inter-stack direction was 2×10^{-3} S cm^{-1} with an activation energy of 280 meV. This is not unlike the values quoted above for BEDT-TTF $(Pd(mnt)_2)_x$.

The results show that the electrocrystallisation technique for the synthesis of new conductors can be applied to a range of planar metal complex anions in conjunction with organic donors. However, the structural and electronic requirements necessary for metallic and superconductivity are very specific and no evidence of these conducting states has been observed so far.

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