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Publisher: Taylor & Francis

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Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl16>

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Version of record first published: 17 Oct 2011.

To cite this article: G. E. Holdcroft & A. E. Underhill (1985): Synthesis and Physical Properties of Transition Metal Tetrathiolate Macromolecules, *Molecular Crystals and Liquid Crystals*, 118:1, 365-369

To link to this article: <http://dx.doi.org/10.1080/00268948508076242>

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SYNTHESIS AND PHYSICAL PROPERTIES OF TRANSITION METAL TETRATHIOLATE MACROMOLECULES

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Abstract The preparation and electrical conduction properties of transition metal tetrathiolate macromolecules are described. The introduction of partial oxidation into the copper compounds is shown to increase the electrical conductivity.

INTRODUCTION

There is much current interest in the preparation of polymers which exhibit high electrical conductivity. In this paper we describe the preparation and properties of a class of these compounds made by the combination of divalent transition metal ions and the sulphur containing tetrathiolate ligand $C_2S_4^{4-}$, (TT), see Figure. Engler and his co-workers¹⁻³ have investigated polymers of the tetrathiolate ligand with nickel and of the related ligand tetrathiafulvalene-tetrathiolate, TTF-TT, with a variety of metal cations. Every effort was made by these workers to prevent the ligand, prepared *in situ*, from being oxidised. However, in the preparation of one-dimensional metallic complexes, it has been shown that controlled oxidation of the stacked anions resulting in non-integral oxidation states for the anion can produce a very large enhancement of the electrical conduction properties of the compounds. Therefore, in this work it was hoped to prepare polymeric complexes with increased electrical conductivities by producing a 'partially oxidised' polymer.

EXPERIMENTAL

1,3,4,6-Tetrathiapentalene-2,5-dione (TED) was synthesised by the method of Engler and Schumaker² and was recrystallised from acetonitrile to yield pale yellow needles.

The polymeric complexes of TT with transition metal ions were all prepared by the same general procedure. However, many variations in the details of the method were undertaken to determine the reaction conditions necessary to give products with the highest electrical conductivity.

The method for the preparation of an unoxidised polymer is as follows. An excess of base in a solvent, typically NaOEt in 100% EtOH, was refluxed and degassed with N₂. TED was then added and a yellow solution was formed as the TT anion was generated. After a few minutes a stoichiometric (based on two metal ions to one ligand) quantity of an appropriate metal salt, preferably the acetate, was added. A fine black precipitate was immediately formed but the mixture was digested for a couple of hours to coagulate the precipitate and aid filtration. The precipitate was filtered off, washed with hot water, acetone and again with hot water. The black powder was then washed with dilute (10%) hydrochloric acid to dissolve any metal oxide or hydroxide formed by reaction with the excess base and after a final wash with water the metal tetrathiolates were dried overnight *in vacuo* at 50°C.

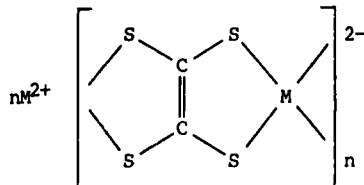
In the preparation of the oxidised polymers the oxidant was added to the reaction mixture immediately the tetra-anion was formed. The yellow solution changed colour on the addition of the oxidant. The final colour varied from light green to green-brown with the formation of a precipitate, depending on the amount and strength of the oxidising agent. The subsequent addition of the metal salt was assumed to quench further oxidation. The oxidants used were air, hydrogen peroxide, chlorine and iodine.

The polymers were characterised by C, H & N analysis. The metal content of some of the polymers was determined by gravimetric analysis and from these results the degree of partial oxidation of the polymers could be calculated.

Four probe d.c. electrical conductivities of the tetrathiolate complexes were made on compressed pellets using Agdag as a contact material, as described previously.⁴ The temperature dependencies of the conductivities were measured between 20 and 310 K.

RESULTS AND DISCUSSION

The elemental analyses of the un-oxidised complexes clearly show that the metal to ligand ratio is 2:1 as might be expected from the reaction of a tetra-anion with a divalent cation. It is postulated that the general structure of the polymers is as shown below in the Figure.



Either one or two water molecules of crystallisation, depending on the cation involved, are associated with the metal cation sited outside the polymer chain.

The room temperature conductivities of the unoxidised complexes appear unaffected by the nature of the metal; σ_{rt} for the Ni, Cu and Pt containing polymers are 5.4, 5.2 and 3.1 S cm⁻¹ respectively. Oxidation of the polymers however does result in a significant increase in conductivity. The change in electrical conductivity with the stoichiometry of the Cu_xTT polymer resulting from oxidation of the ligand, is shown in the Table.

It can be seen that a small amount of oxidation can increase the conductivity by a factor of 10. However, further oxidation reduces the conductivity back to that observed in the unoxidised polymer.

TABLE Dependence of σ_{rt} on x in Cu_xTT complexes.

x	$\sigma_{rt} \text{ S cm}^{-1}$
2.000	5.2
1.945	14.0
1.903	42.0
1.855	27.7
1.794	15.6
1.674	5.0
1.611	4.5
1.514	4.5
1.487	3.9

The presence of the net negative charge on the polymer chain may assist electron hopping along the polymer backbone. In addition to electrical conduction along the polymer chain it is possible to envisage stacking of the chains to facilitate intra stack conduction as in $Li-Pt(mnt)$.⁴ Under these circumstances the polymers could behave as a 2-D conductor. A plot of $\ln(\sigma/\sigma_{rt})$ versus $1/T^3$ is linear as expected for a 2-D conductor.⁵

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