

PREPARATION AND PHYSICAL PROPERTIES OF HIGHLY CONDUCTING METAL
(M = Ni, Co, Cu) COORDINATION POLYMERS

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ABSTRACT

Coordination polymers of nickel, cobalt and copper with the linking polydentate ligands tetrathiafulvalenetetrathiolate, benzene-1,2,4,5-tetrathiolate and phthalocyaninate have been prepared. The environmentally very stable materials have dc conductivities ranging between 10^{-2} S·cm⁻¹ for the polyphthalocyaninato derivatives and 10^2 S·cm⁻¹ for the tetrathiafulvalenetetrathiolates. The temperature dependence of the dc conductivity of the latter compounds is remarkably low.

INTRODUCTION

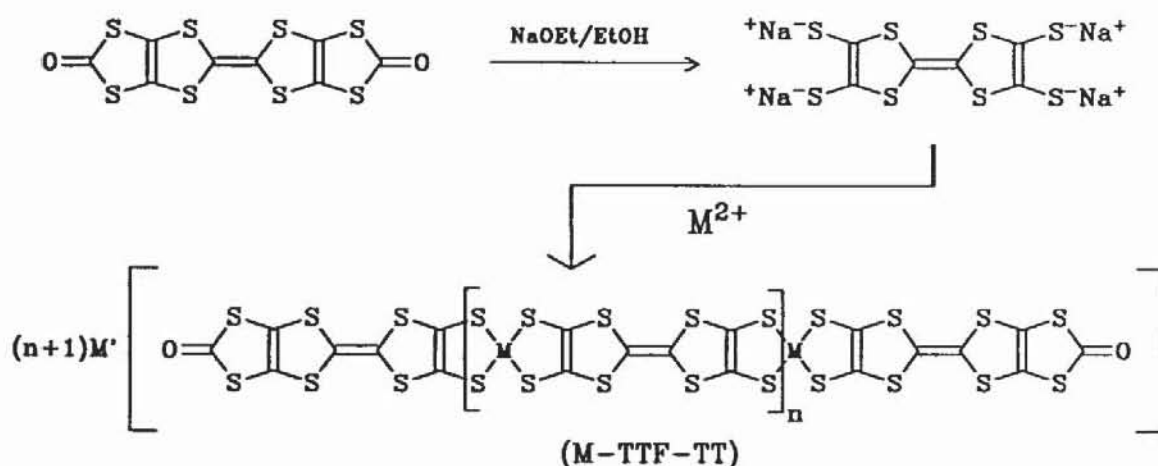
Highly conducting and environmentally stable polymers are desired for a variety of technical applications. The well-known conducting organic polymers like polyacetylene or polypyrrole etc. are more or less restricted to applications in "closed systems" like galvanic cells because of their sensitivity to oxygen and moisture especially at elevated temperatures. We, therefore, reinvestigated different classes of coordination polymers, which were known to be chemically inert compared to the above mentioned organic systems. Principally two different routes were used in the synthesis of these compounds:

- (i) Precipitation of the metal coordination polymers by mixing solutions containing tetrathiolato ligands as anions on one side and particular solvated metal ions like Ni²⁺ or Cu²⁺ on the other hand.

- (ii) By reaction of finely dispersed metals like nickel and copper, obtained by "in situ" decomposition of the corresponding metal oxalates or metal formiates with organic cyano compounds like 1,2,4,5-tetracyanobenzene at elevated temperatures.

POLYMERS FROM TETRATHIAFULVALENETETRATHIOLATES (TTF-TT)

Following the first mentioned route to sulfur containing coordination polymers we prepared tetrasodiumtetrathiafulvalenetetrathiolates using the following synthetic scheme :



Polymers of this type have been obtained earlier [1,2]. We found, that the reaction of tetrasodiumtetrathiafulvalenetetrathiolate with Cu^{2+} and Ni^{2+} salts in ethanol under oxidation and reduction conditions yields black amorphous coordination polymers. Typical electrical conductivities on pressed pellets range between $50\text{-}100 \text{ S}\cdot\text{cm}^{-1}$. The temperature dependence of these conductivities is rather low, which means only a decrease of the conductivity of a factor of 3 between 300K and 4K is observed (figure 1). As shown in figure 1 for Cu-TTF-TT-polymers small amounts of a reducing agent added during the synthesis slightly increases the roomtemperature conductivity of the products and leads to a decrease of the temperature dependence. On the other side addition of an oxidant results in polymers with a lower conductivity and a stronger temperature dependence as well. Similar results have been obtained for the corresponding nickel polymers.

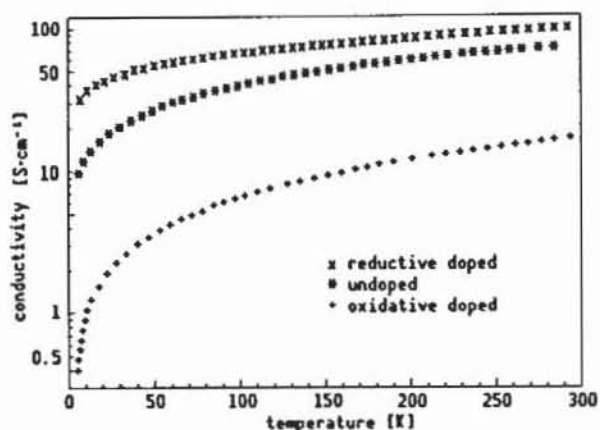


figure 1 : Temperature dependence of the electrical dc conductivity of Cu-TTF-TT polymers

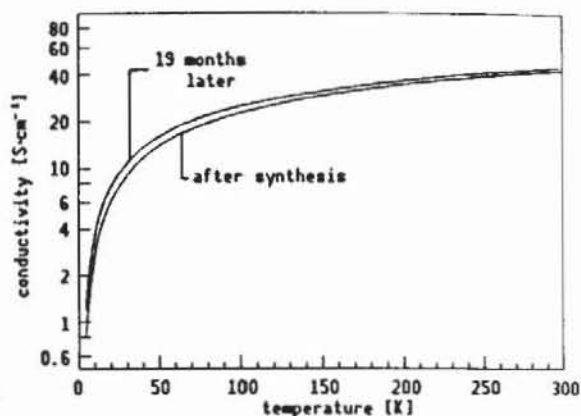
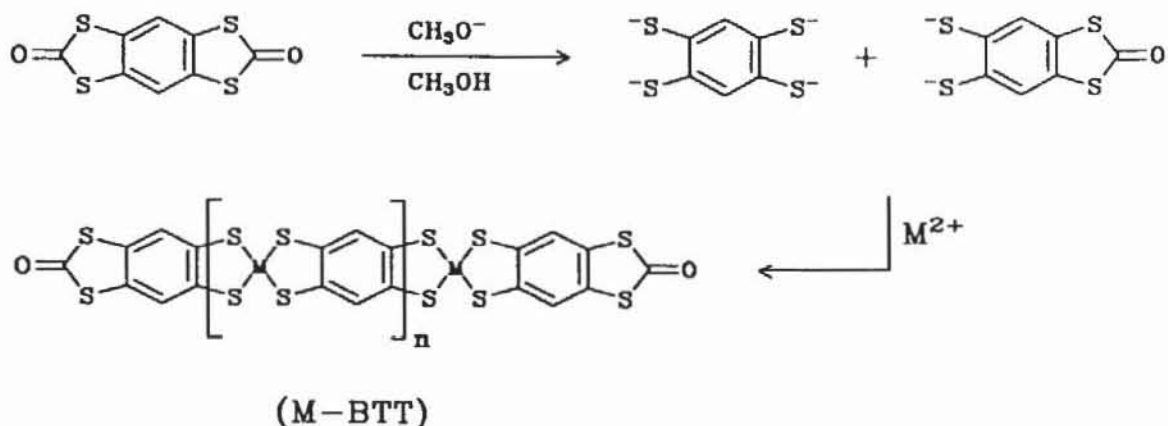


figure 2 : Temperature dependence of the electrical dc conductivity of undoped Ni-TTF-TT

Both polymers are very stable against oxygen and moisture even at higher temperatures. This is especially true for the nickel analogue, which contains nickel in a formal oxidation state of +IV leading to a neutral nonionic coordination polymer. Pellets of the latter material showed no change in conductivity after standing in air at room temperature for approximately two years (figure 2). The temperature dependence of the thermopower indicates a metallic character of these solids.

POLYMERS FROM BENZENE-1,2,4,5-TETRATHIOLATE (BTT)

Besides the metal-tetrathiafulvalenetetrathiolates mentioned above we investigated additionally coordination polymers with benzene-1,2,4,5-tetrathiolate (BTT) as ligand, which was obtained from 1,3,5,7-tetrathia-s-indacene-2,6-dione following the route depicted in the following scheme :



Polymers of this type have been obtained earlier using benzene-1,2,4,5-tetrathiole as starting material [3]. In contrast to the published results we found that the nickel species possesses the highest conductivity ($\sigma_{RT} = 2.7 \text{ S}\cdot\text{cm}^{-1}$ - see figure 3). Similar resistivities were obtained using Co^{2+} as central ion ($\sigma_{RT} = 0.7 \text{ S}\cdot\text{cm}^{-1}$).

The temperature dependence of the thermopower (depicted in figure 4) indicates a metallic character of these compounds between 300 K and 100 K.

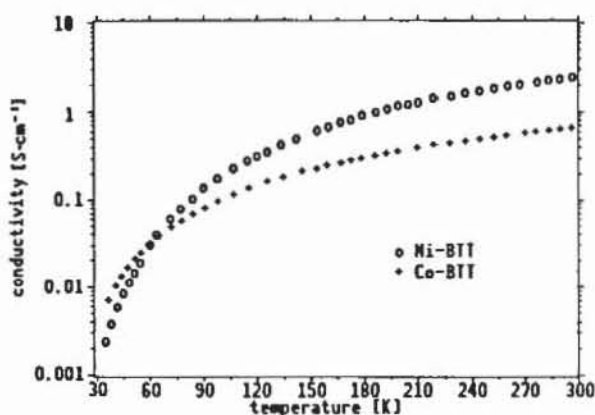


figure 3 : Temperature dependence of the electrical dc conductivity of Ni-BTT (o) and Co-BTT (+)

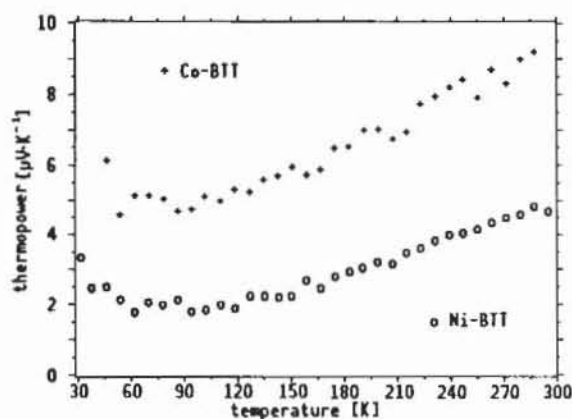
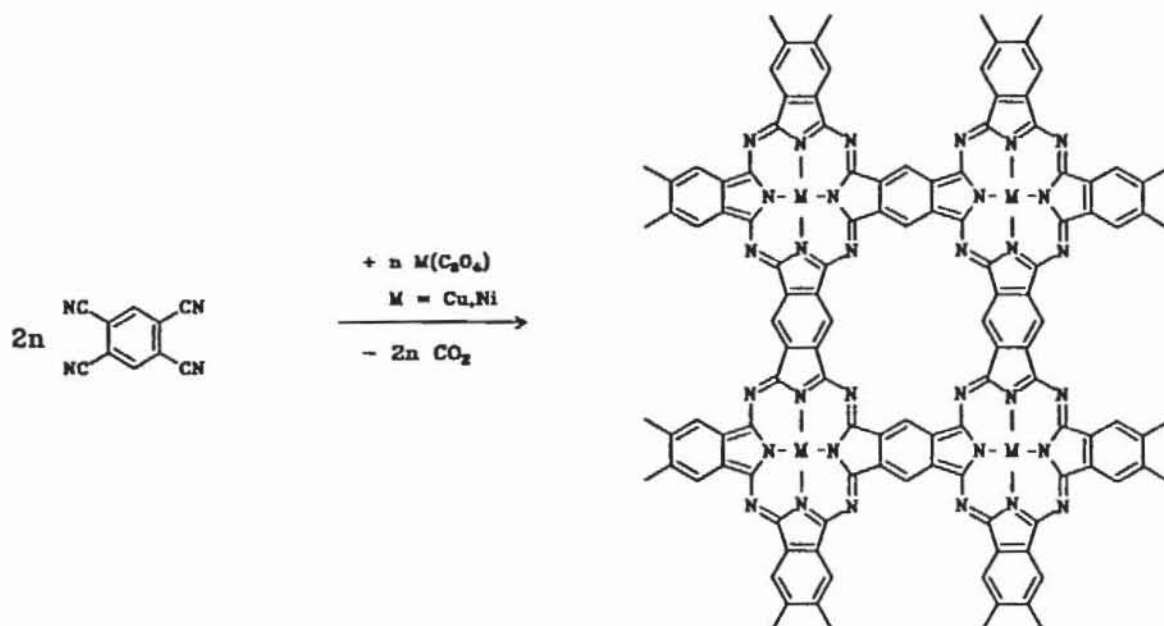


figure 4 : Temperature dependence of the thermopower of Ni-BTT (o) and Co-BTT (+)

POLYMERS FROM 1,2,4,5-TETRACYANO BENZENE (TCNB)

A second kind of coordination polymers - polymeric metal-phthalocyanines (M-TCNB) - have been investigated intensively since thirty years by different groups [4,5]. One of the reasons for this activity is the extraordinary stability of these compounds. The difficulty in the synthesis of these polymers is to get uniform, homogeneous products. This is especially true for a so far unknown Ni-TCNB. We now found that the reaction between finely dispersed metals - "in situ" generated from the corresponding oxalates - and 1,2,4,5-tetracyanobenzene leads to well characterized polyphthalocyaninato metal polymers (see scheme on next page).

Their conductivities are quite low compared to the metal-tetrathiolates showing semiconductive behaviour over the measured temperature range.



Results of elemental analysis (table 1) and IR-spectra (figure 4) indicate a complete reaction of both NiC_2O_4 and CuC_2O_4 with 1,2,4,5-tetracyanobenzene. It should be noted that the IR-spectra are in good agreement with those polymers which were obtained by double source evaporation of copper and tetracyanobenzene [5].

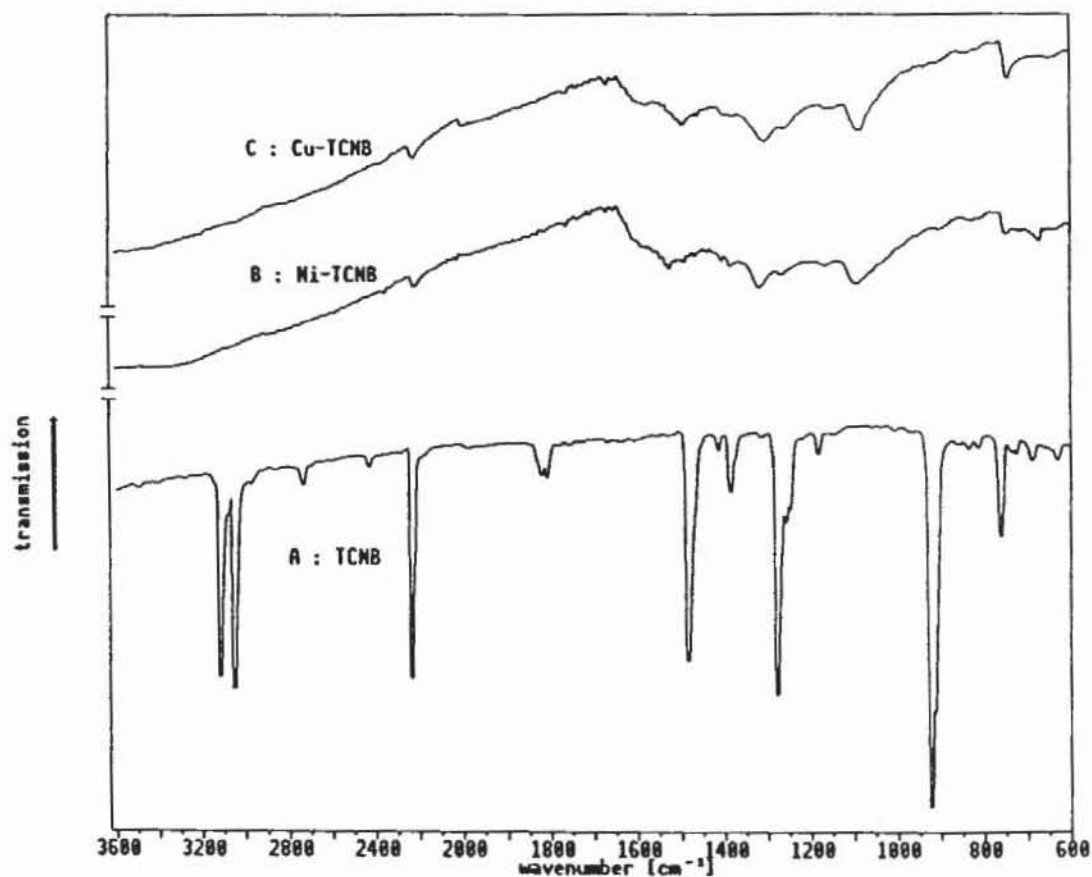


figure 5 : comparison of the IR-spectra of Cu-TCNB (C), Ni-TCNB (B) and the starting compound 1,2,4,5-tetracyanobenzene (A)

table 1 : Reaction time and temperature together with the results of elemental analysis for the polymers from 1,2,4,5-tetracyanobenzene and metal oxalates (molar ratio 2 : 1) :

Cu-TCNB :	40 h, 420 °C;	C%	Cu%	H%	N%	Σ%
calculated for $C_{20}CuH_4N_8$:		57.22	15.14	0.96	26.69	
found :		57.30	13.58	1.39	26.52	98.79
Ni-TCNB :	48 h, 420 °C;	C%	H%	N%	Ni%	Σ%
calculated for $C_{20}H_4N_8Ni$:		57.88	0.97	27.00	14.14	
found :		58.73	1.49	24.43	12.08	96.73

Details of the experimental procedure to obtain the mentioned materials and the complete results of their chemical and physical characterization are summarized in reference [6].

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