

Metallic Coordination Polymers Using CS₂ as Starting Material

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Organic polymers with "metallic" properties have found widespread interest during the last few years /1,2/. Acetylene and aniline as well as different nitrogen and sulfur heterocycles have been used as starting materials. One main problem hampering the technical application of these solids up to now is their environmental and thermal instability. Therefore, we introduced metal ions to stabilize polymeric backbones with high electrical conductivity. Because of the enormous coordination ability of sulfur to many transition metal ions we decided to use a polymeric carbon-sulfur backbone. In view of a future technical application one has to start from less expensive and readily available chemicals like CS₂ e.g., in order to obtain a carbon-sulfur polymer. Since CS₂ cannot be readily polymerized to highly conducting solids a different approach has to be found. As reported earlier /3,4,5/ CS₂ can be reacted to thiapendione which can be converted into ethylenetetrathiolate (TT) by cleavage with strong chemical bases. Additionally thiapendione can be "dimerized" to bis(1.3-dithiole-2-one)tetrathiafulvalene which can be converted into tetrathiolatotetrathiafulvalene (TTF-TT) again by a cleavage reaction with strong bases. Both tetrathiolates react with transition metal ions like nickel(II) or copper(II) to coordination polymers which are remarkably inert chemically as well as thermally /6/. The reactions and their final products are schematically summarized in figure 1.

In the case of nickel (M = Ni) m = 0 and p = 0. The polynuclear compound contains formally nickel(IV) without counterions. Using copper(II) as metal ion a Cu(III)/Cu(I) mixed valence solid with m = 1 and p = 1 is obtained.

The compounds which are obtained as powders can be pressed to compact pellets which show conductivities up to 150 S/cm. The electrical conductivity of some of these materials varies only slightly in the temperature range between 4.2 K and 400 K (figures 2 and 3). Thermopower measurements (figure 4) indicate a metallic character of these solids. Principally the conductivity of the isolated TT derivatives is somewhat lower (2 - 7 S/cm) compared with the TTF-TT compounds (40 - 150 S/cm). A comparison between equivalent nickel and copper compounds shows that the copper species usually conduct better than the nickel derivatives which are much more stable environmentally compared to the copper compounds. The higher stability of the nickel species may be explained by the surprising fact that these materials are obtained in an electrically neutral "undoped" state.

SYNTHESIS

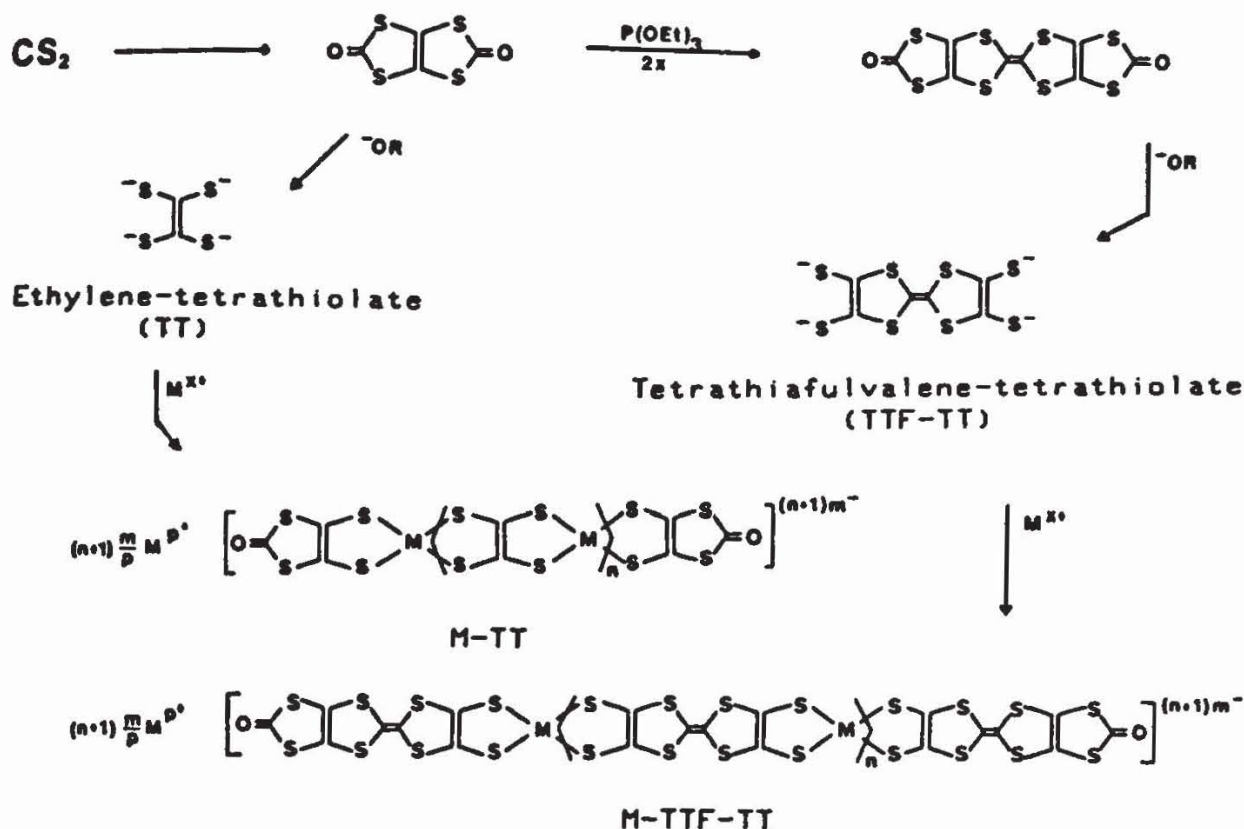


Fig. 1 Schematic description of the syntheses of "polymer" metal tetrathiolates starting from CS_2 ($M = Ni$ or Cu)

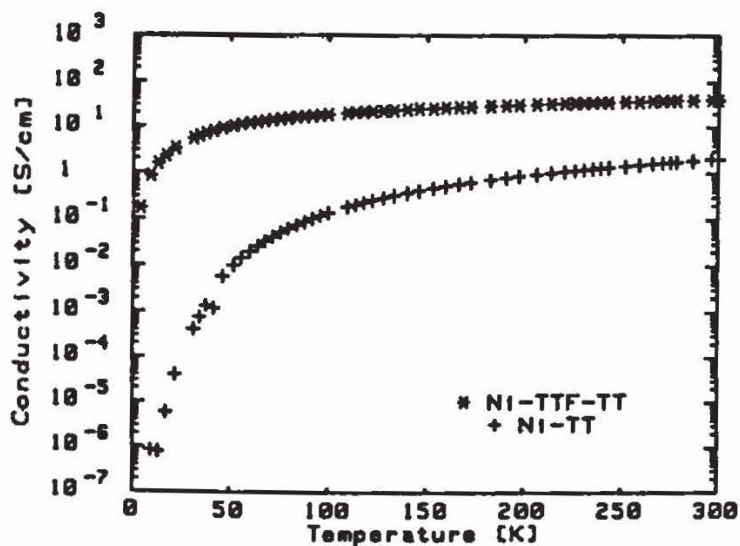


Fig. 2 Electrical conductivity of Ni-TT (crosses) and Ni-TTF-TT (stars) as pressed pellets in the temperature range between 4.2 K and 300 K

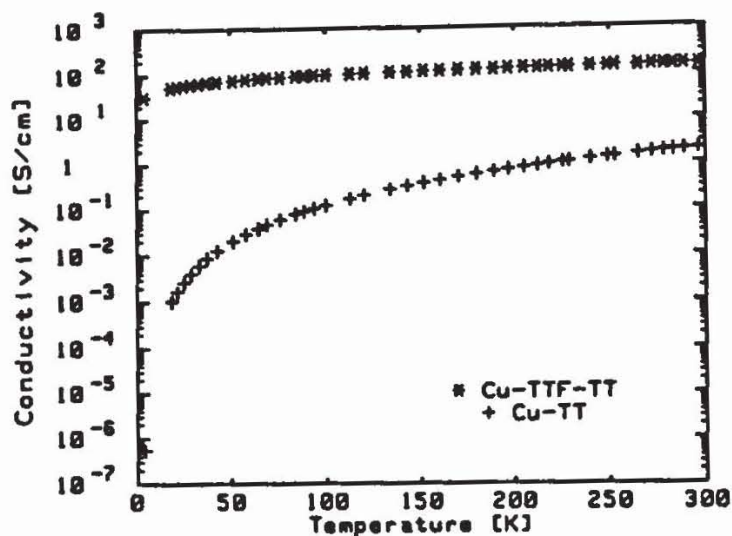


Fig. 3 Electrical conductivity of Cu-TT (crosses) and Cu-TTF-TT (stars) as pressed pellets in the temperature range between 4.2 K and 300 K

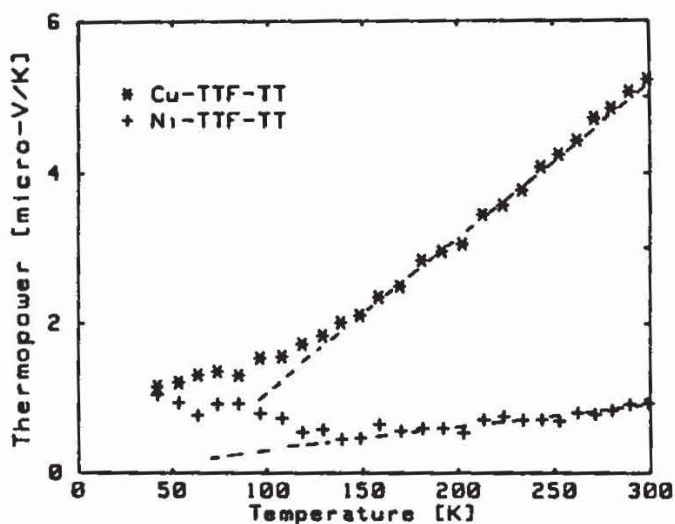


Fig. 4 Thermopower of pressed pellets of Ni-TTF-TT (crosses) and Cu-TTF-TT (stars) in the temperature range between 40 K and 300 K

Literature

1. Proceedings Int. Conf. Science and Technol. of Synthetic Metals, Synth. Met., Vol. 19 (1987)
2. Proceedings Yamada Conf. Phys. Chem. Quasi One-dimensional Conductors, Physica B, (1987)
3. H. Poleschner, W. John, G. Kempe, E. Hoyer, E. Fanghänel: Z. Chem. 15, 345 (1978)
4. G. E. Holdcroft, A. E. Underhill: Synth. Met. 10, 427 (1985)
5. R. Vicente, J. Ribas, P. Cassoux, L. Valade: Synth. Met. 13, 265 (1986)
6. G. Renner: Dissertation, University of Heidelberg, (Heidelberg 1987)