

NEW CHARGE TRANSFER SALTS CONTAINING BEDT-TTF AND STRUCTURALLY RELATED TRANSITION METAL COMPLEXES

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ABSTRACT

The two-dimensional behaviour of BEDT-TTF salts is normally explained with the typical geometry of this donor and its arrangement in the crystal lattice. In order to extend the range of physical properties produced by BEDT-TTF like compounds, we synthesized sulfur containing transition metal complexes with a molecular structure very similar to BEDT-TTF. The bis(5,6-dihydro-1,4-dithiin-2,3-dithiolate)metallates of the nickel triad can be prepared in different oxidation states as anions and in a fully oxidized neutral form.

INTRODUCTION

Many highly conducting BEDT-TTF [bis(4,5-ethylenedithiolo)tetrathiafulvalene] salts are known. Some of them are superconductors [1-7]. These surprising physical properties are normally explained by the special molecular structure of BEDT-TTF. Its central planar part is characterized by high π -electron densities above and below the molecular plane. The peripheral non-planar part is held together by σ -bonds. Close interstack contacts between "aliphatic" and "aromatic" sulfur atoms of different molecules lead to strong two-dimensional electronic interactions. The central π -electron system is not involved in these intermolecular interactions but remains more or less "isolated".

The reverse is true for the so-called one-dimensional transition metal complexes with organic ligands [8]. The conduction path in these solids is mainly maintained through interactions between the "central" electrons of the metal ions extending far above and below the molecular plane. The organic ligands - e.g. the 1,2-dioximes in the bis(1,2-dioximato)metal compounds of the nickel triad [8] -

are not involved in the intermolecular electronic interactions. Thus strong intrastack and very weak interstrand correlations result leading to the typical one-dimensional properties of these materials.

It is the aim of the project described here to combine the different features of BEDT-TTF like compounds with those of the "linear" metal complexes in one molecule. This in our opinion is best achieved by using transition metal complexes with the ligand 5,6-dihydro-1,4-dithiin-2,3-dithiole. The schematic molecular structure of a metal compound with two such chelating ligands is depicted in figure 1. Formally the central C = C double bond part of BEDT-TTF is substituted by a metal ion in the complexes shown in figure 1. Stereochemically one should expect only minor changes caused by this "substitution".

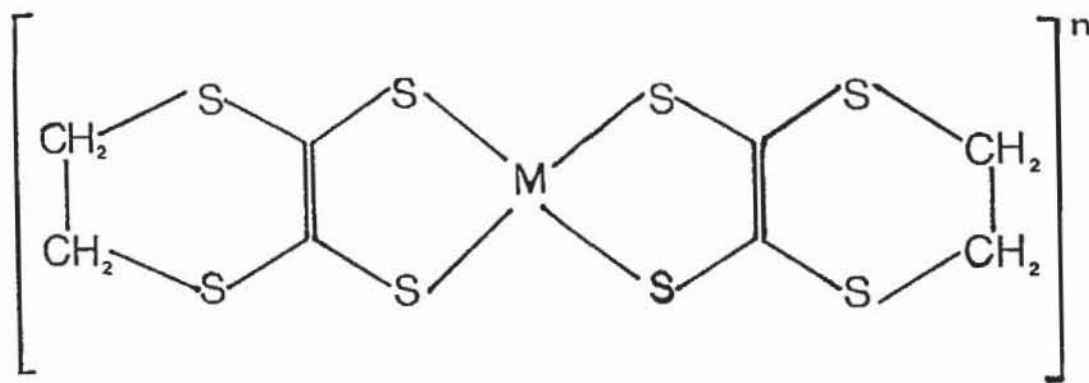


Fig. 1. Schematic molecular structure of bis(5,6-dihydro-1,4-dithiin-2,3-dithiolato)metallates. M represents metal ions of the elements Ni, Pd, Pt, Cu, Au. n may vary between 0 and -2 allowing also for non integer values like -0.3 or -0.5.

So far only a nickel derivative with $n = 0$ was reported but in a different context [9]. Details of its structure or physical properties were not presented at that time.

METHODS AND MATERIALS

The metal complexes can be isolated from the reaction of the corresponding metal(II) salts (NiCl_2 , K_2PtCl_4 e. g.) with disodium-5,6-dihydro-1,4-dithiin-2,3-dithiolate which is obtained by cleavage of 4,5-ethylenedithiolo-1,3-dithiol-2-one with sodiummethylate. This is readily achieved by adding a solution of sodium methylate in methanol to a suspension of 4,5-ethylenedithiolo-1,3-dithiol-2-one in methanol. The green nickel(II) complex can be recrystallized from an acetone-isopropanol (4:1) mixture. The analytical data suggest the composition $[\text{N}(\text{C}_4\text{H}_9)_4][\text{Ni}(\text{C}_4\text{H}_4\text{S}_4)_2]$ for the green solid.

The green needles of $[\text{N}(\text{C}_4\text{H}_9)_4][\text{Ni}(\text{C}_4\text{H}_4\text{S}_4)_2]$ can be dissolved in THF and oxidized electrochemically. Routine electrochemical procedures were used in the isolation of another green solid of composition $[\text{N}(\text{C}_4\text{H}_9)_4]_{0.5}[\text{Ni}(\text{C}_4\text{H}_4\text{S}_4)_2]$.

The latter complex can be further oxidized chemically - using bromine as oxidant e.g. - to the neutral solid $\text{Ni}(\text{C}_4\text{H}_4\text{S}_4)_2$. If this oxidation is carried out in the presence of an excess of neutral BEDT-TTF in CS_2 black, shiny crystals of neutral BEDT-TTF are obtained which contain small amounts of the nickel species isomorphically substituting small amounts of the BEDT-TTF units. The amount of "incorporated" nickel complex depends on the relative concentrations during the crystallization process. It dominates the relevant physical properties of the obtained crystals, e.g. their optical and e.s.r. absorption and their electrical conductivity.

ACKNOWLEDGEMENT

We gratefully acknowledge financial support of this work through Stiftung Volkswagenwerk, Hannover and Fonds der Chemischen Industrie, Frankfurt.

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