

MOLECULAR SOLIDS CONTAINING BEDT-TTF AND STRUCTURALLY RELATED TRANSITION METAL COMPLEXES

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The special physical properties of BEDT-TTF salts, e.g. their two-dimensional behaviour, are caused by the typical geometry of this donor and the arrangement of the cations in the crystal lattice of its salts. 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 neutral form. The anionic complexes can be reacted with BEDT-TTF cations.

1. INTRODUCTION

BEDT-TTF [bis(4,5-ethylenedithiolo)tetra-thiafulvalene] is at this time the most promising donor in the search for new, highly conducting organic materials, especially in the search for organic superconductors¹⁻⁷. The surprising physical properties of radical cation salts containing this donor are caused by the special molecular structure of BEDT-TTF. It consists of a central planar part characterized by high π -electron densities above and below the molecular plane and additional peripheral non-planar moieties held together by σ -bonds. This geometry leads to the typical packing of the units in the crystal lattice allowing the well-known close interstack contacts between "aliphatic" and "aromatic" sulfur atoms of different molecules. Strong two-dimensional electronic interactions result. In contrast to other electrically conducting "stacked" radical cation salts (e.g. the perylenium compounds⁸) in the BEDT-TTF solids the central π -electron system is not involved in the intermolecular interactions. The central "aromatic" part of the molecule remains more or less "isolated".

The reverse is true for the so-called one-dimensional transition metal complexes with organic ligands. The conduction path in these so-

lids 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 triad⁹ - are not involved in the intermolecular electronic interactions. Thus strong intrastack and very weak inter-strand 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 type of 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 fig. 1.

Stereochemically one should expect only minor changes caused by this "substitution". We, therefore, decided to prepare these compounds and to investigate their solid state properties in different oxidation states of the complex

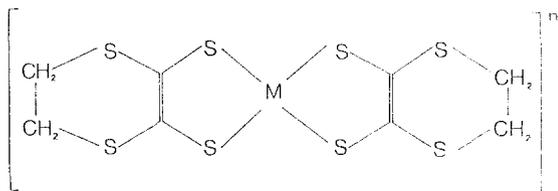


FIGURE 1

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

units. A nickel derivative with $n = 0$ was reported earlier in a different context¹⁰, but no details of its structure or physical properties were reported at that time. Additionally we planned metathetical reactions between BEDT-TTF cations and the metallate anions in the aim to obtain "mixed" solids. A 1:1 compound, structurally closely related to the neutral BEDT-TTF, would be of special interest.

2. METHODS AND MATERIALS

The metal complexes can be isolated from the reaction of the corresponding metal(II) salts (NiCl₂, K₂PtCl₄ 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. A typical synthesis using nickel(II) as central metal ion is as follows.

To a suspension of 2.2 g (10.5 mmole) 4,5-ethylenedithiolo-1,3-dithiol-2-one in 40 ml methanol a solution of 1.139 g (21.1 mmole) sodium methylate in 60 ml methanol was added dropwise under stirring. All materials were dried before handling and the whole procedure was carried out under a dry argon atmosphere. After stirring for another 4 hours at room temperature the solvent

was removed by evaporation under vacuum. 25-30 ml methanol and 12-15 ml water were added to the yellow residue and the mixture was filtered. To the filtrate 21 ml aqueous ammonia (2N), 21 ml methanol and finally 0.68 g (5.3 mmole) nickel(II)chloride were added. A solution of 3.38 g (10.5 mmole) tetra-n-butylammoniumbromide in 14.5 ml water was dropped into this mixture under stirring which was continued over night. The green precipitate was collected next day and recrystallized from an acetone-isopropanol (4:1) mixture. The analytical data suggest the composition [N(C₄H₉)₄][Ni(C₄H₄S₄)₂] for the isolated green needles. $M_r = 661.22$.

Cal. for C₂₄H₄₄N NiS₈:

43.55%C; 6.65%H; 2.11%N; 38.79%S

Found: 43.23%C; 7.67%H; 2.10%N; 37.71%S.

The green needles of [N(C₄H₉)₄][Ni(C₄H₄S₄)₂] can be dissolved in THF and oxidized electrochemically. Routine electrochemical procedures were used in the isolation of another green solid of composition [N(C₄H₉)₄]_{0.5}[Ni(C₄H₄S₄)₂].

$M_r = 540.39$.

Cal. for C₃₂H₅₂N Ni₂S₈

35.56%C; 4.81%H; 1.38%N; 47.46%S

Found: 35.74%C; 4.79%H; 0.89%N; 45.73%S.

The above mentioned complex anions can be further oxidized chemically - using bromine as oxidant e.g. - to the neutral solids, e.g. Ni(C₄H₄S₄)₂. If this oxidation is carried out in the presence of an excess of neutral BEDT-TTF in CS₂ 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. These incorporated nickel complexes, the amount of which depends on the relative concentrations during the crystallization process, dominate the relevant physical properties of these crystals, e.g. their optical absorption and their electrical conductivity.

ACKNOWLEDGEMENTS

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

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