

The Tetrabutylammonium Salt of 2-Thioxo-1,3-dithiol-4,5-dithiolate as a Starting Material for Preparation of Organometallic Conductors

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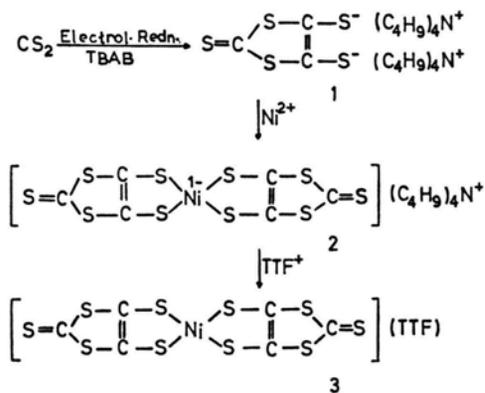
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Tetrabutylammonium Salt,
Organometallic Conductors

The tetrabutylammonium salt of 2-thioxo-1,3-dithiol-4,5-dithiolate (TDD) was isolated and new one-dimensional conducting solids of the donor-acceptor type with TDD as a ligand were prepared.

Metal 1,2-dithiolenes (or dithienenes) have been of great interest to researchers mainly because of their redox and catalytic properties (see [1] and references therein). Some of these compounds are strong π -acceptors. They are coupled with strong π -donors, such as the tetrathiotulvalene (TTF), to give one-dimensional (1-D) conducting solids [2–4]. In this communication the preparation of new 1-D organometallic conductors by using the tetrabutylammonium salt of 2-thioxo-1,3-dithiol-4,5-dithiolate (TDD) as a starting material (compound 1) is reported. The following Scheme shows the method of preparation.



Compound 1. A solution of this compound in dimethylformamide was prepared by electrolytic reduction of carbon disulfide in the presence of tetrabutylammonium bromide (TBAB) [5]. The unreacted carbon disulfide and a part of dimethylformamide were removed by warming the solution and flushing it with N_2 . The concentrated solution was then poured into water. After one hour the

product was filtered, washed with water and dried in vacuum over calcium chloride. The dry product was washed with a small quantity of methanol and carbon disulfide and the purple powder obtained was recrystallized from an acetone-methanol 1:1 mixture. Red needles of m.p. 163 °C were obtained.

Analysis: $\text{C}_{35}\text{H}_{72}\text{N}_2\text{S}_5$

Calcd C 61.73 H 10.58 N 4.11 S 23.56,
Found C 60.80 H 9.75 N 4.00 S 24.73.

Compound 1 is insoluble in water, soluble in methanol and very soluble in acetone. The optical absorption spectrum of 1 in methanol shows a peak at 485 nm, in acetone at 517 nm (solvent effect). Treatment of 1 with methyl iodide or thiophosgene gives 4-methylthio-1,3-dithiole-2-thione [5] or 1,3,4,6-methylene-2,5-dithione [6], respectively.

Compound 2. A solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in methanol was added dropwise to a solution of 1 in an acetone-methanol 1:1 mixture until a greenish colour appeared. The mixture was evaporated to dryness, washed with warm water and a small quantity of methanol and dried. The crude product was then recrystallized from acetone. Shiny black plates or needles of 2 give green solutions in acetone.

Analysis: $\text{C}_{22}\text{H}_{36}\text{NS}_{10}\text{Ni}$

Calcd C 38.11 H 5.19 N 2.02 S 46.19 Ni 8.47,
Found C 38.17 H 5.06 N 2.15 S 46.26 Ni 8.50.

Compound 2 is insoluble in water, soluble in methanol and very soluble in acetone. A compound with Ni^{2+} is obtained if one uses the mother-electrolytic solution of 1 which contains a large amount of tetrabutylammonium bromide. This is a brown powder and gives compound 2 after treatment with iodine.

Compound 3. A solution of a TTF-halide in acetone-methanol 1:1 was added to a solution of 2 in an acetone-methanol 1:1 mixture. The black precipitate obtained was washed with methanol and acetone and air-dried.

Analysis: $\text{C}_{12}\text{H}_4\text{S}_{14}\text{Ni}$

Calcd C 22.00 H 0.61 S 68.43 Ni 8.97,
Found C 21.45 H 0.88 S 67.83 Ni 9.28.

Compound 3 is insoluble in water, methanol and acetone. The dc conductivity of 3 in pellets is of the same order as that of a TTF-TCNQ pellet ($\sigma > 100 \Omega^{-1} \text{cm}^{-1}$) [8]. The reflectance spectrum of a pellet of 3 shows a Drude edge at 900 nm.

The above described conducting compound 3 is one example only. One can obtain conductors similar to 3 from complexes of TDD with other transition metals (Pd, Pt, etc.) and tetrathio-tetracene, perylene etc. as donors. We intend to publish a paper on the single crystal properties of 2, 3 and similar compounds in the near future.

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