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## NOVEL DITHIOLENE COMPLEXES AND TETRATHIAFULVALENES

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**Abstract** Novel dithiolene metal complexes, some of which absorb in the near infrared, and tetrathiafulvalenes, in particular tetraiodotetrathiafulvalene, have been prepared, and their magnetic properties studied.

Dithiolene metal complexes are the basis for the preparation of many compounds displaying interesting properties such as electrical conductivity,<sup>1</sup> superconductivity,<sup>2</sup> ferromagnetic interactions<sup>3</sup> and absorptions in the near infrared.<sup>4</sup> Tetrathiafulvalenes (TTFs) show similar properties (electrical conductivity,<sup>5</sup> superconductivity,<sup>6</sup> antiferromagnetic interactions<sup>7</sup>); the discovery of the high electrical conductivity of the TTF-TCNQ complex was a major breakthrough in the development of materials with unusual properties.

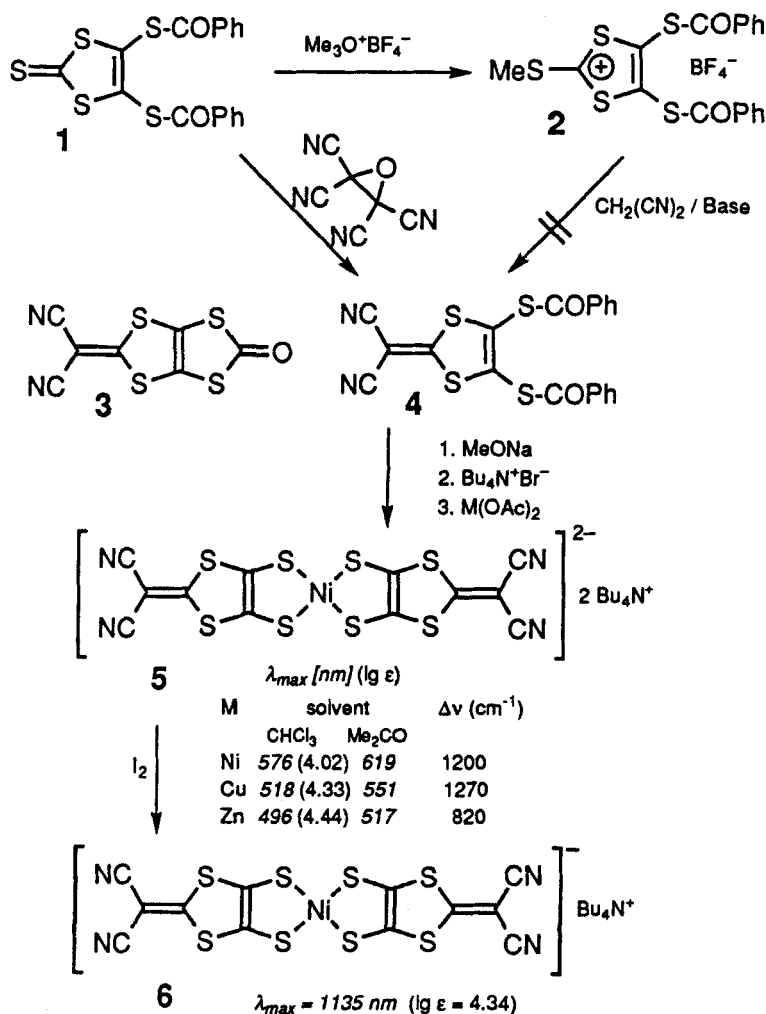
For the syntheses of dithiolenes and tetrathiafulvalenes the same starting materials can be employed in many cases. One the most important dithiolenes is the dmit dianion.<sup>8</sup> It was the objective of our work to synthesize dmit<sup>2-</sup> derivatives in which the sulfur atom of the thiocarbonyl group is replaced with a (substituted) methylene group, and to use the starting materials for those compounds for the synthesis of novel TTF derivatives as well.

The reaction of heterocyclic alkylthio-onium salts with active methylene compounds in the presence of bases is a standard method for the synthesis of methylene derivatives of the corresponding dihydroheterocycles. The condensation of dithiolium salt **2**<sup>9</sup>, prepared from trithione **1**, with malononitrile, however, failed. Eventually, a simple and efficient synthesis of the target molecule **4** was found in the reaction of **1** with tetracyanoethylenoxide (cf. related reactions with other thiones<sup>10</sup>). Compound **3** could be obtained in the same way.

Treatment of **4** with sodium methoxide and addition of metal salts and tetrabutylammonium bromide to the so formed dianion gives rise to the novel dithiolene complexes **5**. Surprisingly, they exhibit solvatochromism although they have a symmetrical structure and therefore no dipole moment.

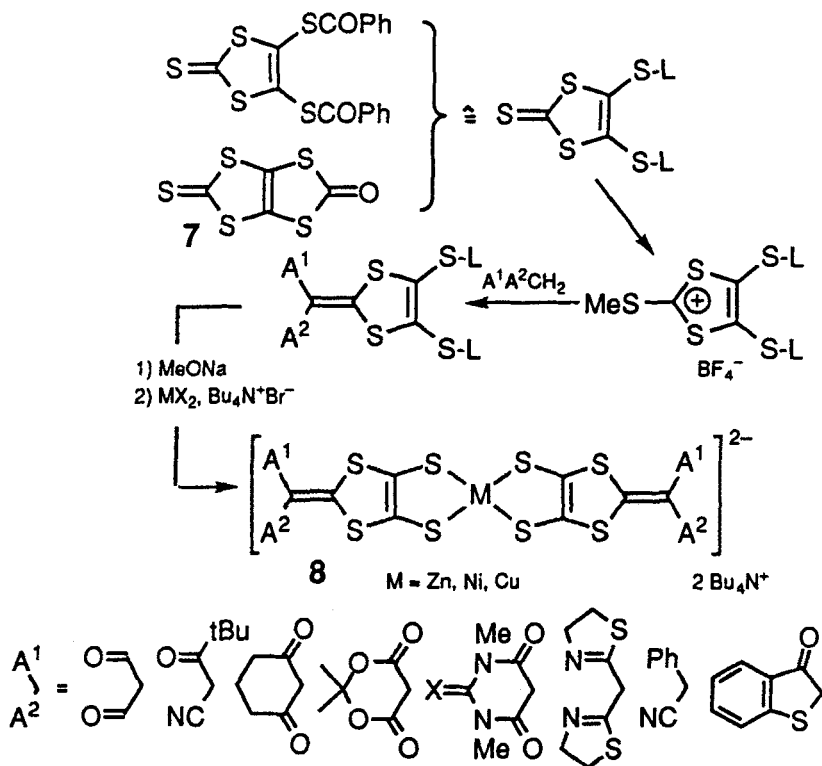
When **5**, M = Ni, is treated with iodine the complex **6** is formed. The strong absorption of **6** in the near infrared is remarkable. The X-ray crystallographic analysis shows the anion of **6** to be planar. An important feature of the crystal structure is the packing mode of the anions (cf., FIGURE 1a). There is a face-to-face stacking of the planar anions along the a-axis. Non-bonded interactions in these segregated stacks lead to short intermolecular S-S, Ni-Ni and Ni-S distances. The stacks can be regarded as columns of dimer of anions. As compared with complexes containing dmit<sup>2-</sup> the dicyanomethylene group in **6**

increases the tendency to form aggregated structures. The short intermolecular distances in **6** suggest a magnetic ordering. Susceptibility measurements indicate antiferromagnetic coupling within the dimers. In order to increase the magnetic interactions in nickel complexes of type **6** we replaced the bulky tetrabutylammonium cation with the decamethylferrocenium cation. The magnetic properties of this material are typical for an alternating chain of antiferromagnetic coupled spins (cf.<sup>11</sup>).



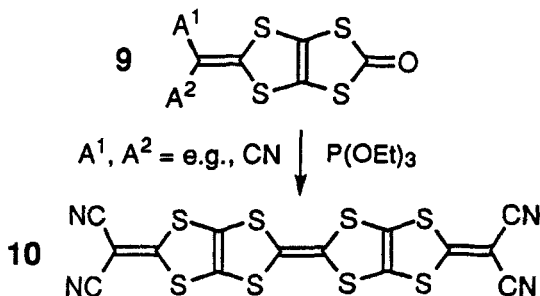
The dicyanomethylene complexes **5** and **6** are the first members in a series of novel dithiolenes and dithiolenes metal complexes **8**. Their preparation is displayed in SCHEME 1. There is virtually no limitation in selection of active methylene compounds.

Compounds **9**, derived from **7**, can also be used as starting material for the preparation of novel TTF derivatives, e.g., **10** (the main problem with these

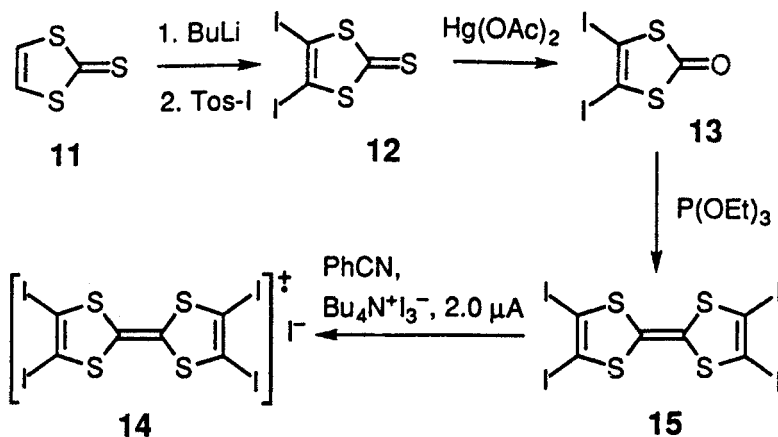


SCHEME 1 Preparation of dithiolene metal complexes

new TTFs is their rather low solubility). In contrast to BEDT-TTF the TTFs **10** have 5-membered rings attached to the TTF moiety instead of 6-membered rings. The donor properties of the sulfur atoms of the dithiane rings which are

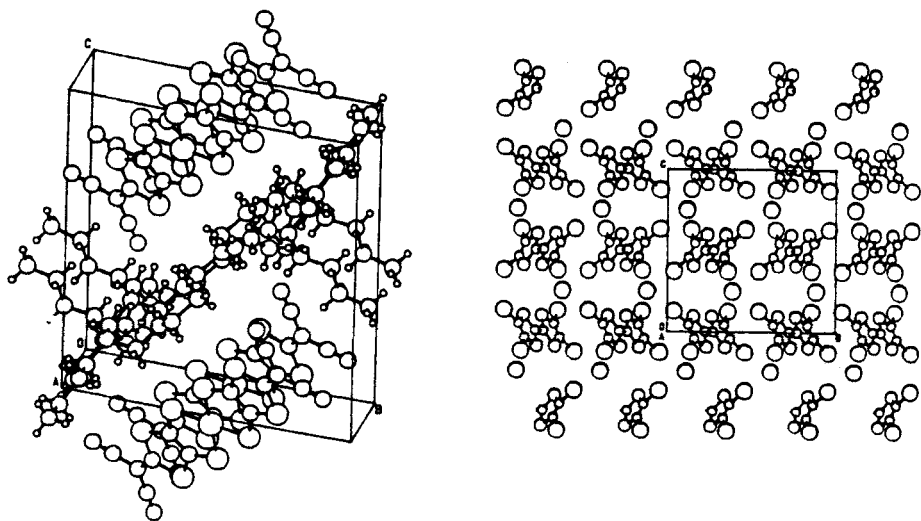


essential for the special properties of BEDT-TTF (e.g., superconductivity) are reduced to some extent in **10**. In order to get new TTFs with properties similar to those of BEDT-TTF, we decided to replace the peripheral sulfur atoms of **10**, or BEDT-TTF for that matter, by even more polarizable iodine atoms. Thus, we set out to synthesize tetraiodotetrathiafulvalene **15** (tetrachloro/bromo-TTF have been prepared before<sup>12</sup>). The synthesis of **15** is outlined in SCHEME 2. Single crystals of the radical cation salt **14** can be grown electrochemically in

SCHEME 2 Synthesis of tetraiodotetrathiafulvalene **15**

the presence of tetrabutylammonium triiodide as supporting electrolyte.

The X-ray crystallographic analysis shows the radical cations of **14** to be planar. The central CC bond is longer than the related CC bond in neutral TTF.<sup>13</sup> The radical cations are arranged in two segregated stacks which are separated by chains of iodide anions (cf., FIGURE 1b). Remarkably, the iodine-iodide distances are shorter than the sum of the van der Waals-radii.

FIGURE 1 a) Packing mode of **6**; b) Packing mode of **14** along the a-axis

The magnetic properties of **14** are typical for a one-dimensional Heisenberg antiferromagnet. In the high temperature range, the data can be described by the superposition of temperature independent diamagnetism and a Curie-Weiss law. The influence of the one-dimensional antiferromagnetic correlations leads to a susceptibility maximum at 3 K.

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