Synthesis and Properties of Tetrathiafulvalene–Metal Bisdithiolene Macromolecules

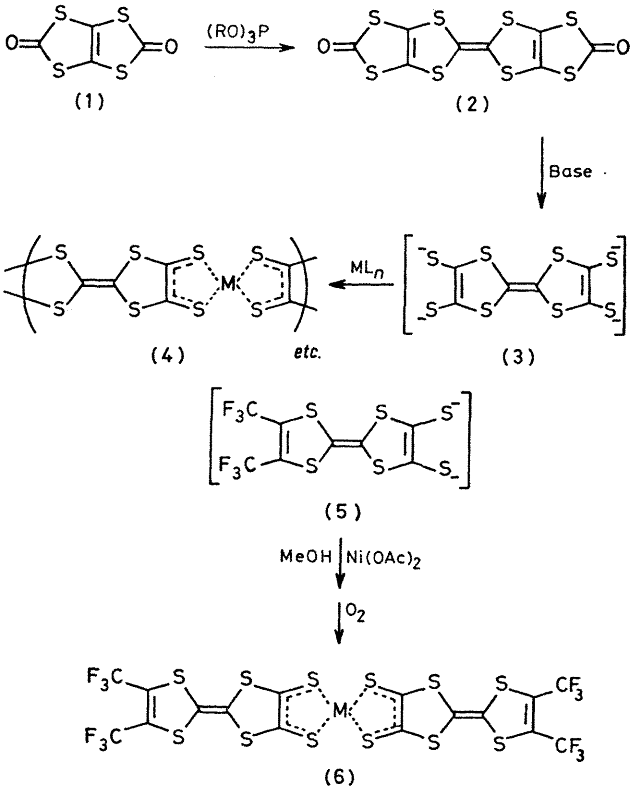
By Nilda Martinez Rivera* and Edward M. Engler
(*IBM Thomas J. Watson Research Center, Yorktown Heights, New York* 10598)
and Robert R. Schumaker
(*IBM Research Laboratory, San Jose, California* 95193)

Summary Reaction of tetrasodium tetrathiafulvalene-tetrathiolate with transition metal salts leads to the formation of tetrathiafulvalene-metal bisdithiolene oligomers which in the case of the nickel derivative possesses unusually high conductivity (*ca.* 30 Ω^{-1} cm^{-1}).

Two well-studied π-systems which display interesting solid state electronic properties are tetrathiafulvalene (TTF),[1] a π-electron donor, and metal bisdithioleneato-complexes,[2] π-electron acceptors. While studying the chemistry of thiapendione[3] (**1**), we discovered a means of coupling these two π-systems into a single conjugated molecular framework.

Treatment of (**1**) with trialkyl phosphites provided the dimer dithiapendione (**2**) which was subsequently treated with base [NaOMe–MeOH or MeLi–tetrahydrofuran (THF)] to give the thermally and air sensitive tetrathiafulvalene-tetrathiolate intermediate (**3**).† Reaction of (**3**) with transition metal salts (ML$_n$) led to the precipitation of insoluble, amorphous powders (non-crystalline *X*-ray powder pattern) with metal:ligand ratio *ca.* 1:1. The insolubility of these materials precluded rigorous characterization of their structure, but based on the chemistry (see later), and by analogy with the known linear polymers [M(SR)$_2$]$_x$ (M = Ni or Pd)[4] and (TTNNi)$_x$[5] (TTN = tetrathianaphthalene) a repeating TTF–metal bisdithiolene composition with the oligomeric structure (**4**) seems reasonable.

In the case of (**4**; M = Ni), elemental analysis for this stoicheiometry gave: C 18·10, Ni 15·15%; calc. for C$_6$NiS$_8$ C 18·10, Ni 15·24%. Spectrophotometric measurements in



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† The presence of this intermediate in solution is confirmed by its near-quantitative conversion on treatment with methyl iodide into the independently synthesized tetrathiomethyl-TTF; see ref. 3 for details.

KBr show strong electronic absorptions at 34,500 and 32,250 cm^{-1}, characteristic of the dithiolene and an intense broad absorption in the i.r. region (*ca.* 2 μm). This latter absorption is characteristic[6] of the highly conducting crystalline charge-transfer salts, and in fact, the oligomer (**4**; M = Ni) was found to have the surprisingly high conductivity of *ca.* 30 Ω^{-1} cm^{-1}.[7] Other transition metal derivatives of (**4**) displayed lower conductivities (*e.g.*, M = Cu, *ca.* 10^{-1} Ω^{-1} cm^{-1}; M = Fe, *ca.* 10^{-5}; M = Pt, *ca.* 10^{-2} and M = Pd, *ca.* 10^{-3}). A more characterizable model system of (**4**) could be prepared by the reaction of disodium di(trifluoromethyl)tetrathiafulvalenedithiolate[8] (**5**) with nickel acetate followed by treatment with O_2 which precipitates (**6**). Compound (**6**) was purified by Soxhlet extraction (PhCl) to give green-black platelets, m.p. >360 °C [ν (KBr) 1600 m, 1494m, 1250s,br, 1162s,br, 945w, 915m, 838w, 715m, and 690w cm^{-1}]; satisfactory C, F, Ni, and S analyses were obtained for this compound. An unusually low-energy electronic absorption at 1·35 μm (ϵ *ca.* 10^4 in Me_2SO) was observed, considerably shifted from the characteristic low-energy absorption (0·8—1·0 μm)[2] found for nickel bis-dithiolene derivatives. The preparation of (**6**) suggests that the structure proposed for oligomer (**4**) is reasonable. Compound (**6**) is insulating; however, this may be due to the presence of strongly electron withdrawing substituents on TTF which greatly decrease its donor properties.

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