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(2) A preliminary report (by R.E.R. and R.P.) appeared in Abstracts, American Crystallographic Association, Twenty-fifth Anniversary Meeting, Charlottesville, Va., March 9–13, 1975, p 28. Complete results of the survey will be published elsewhere.

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(8) From results of EHMO calculations[9] and other chemical studies,[10] it has been proposed that nucleophiles and electrophiles attack an S—S bond roughly in the same directions as those found in the present study.

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Reactions of Tetrathionaphthalene with Transition Metal Carbonyls. Synthesis and Characterization of Two New Organometallic Semiconductors $(C_{10}H_4S_4Ni)_x$ and $[C_{10}H_4S_4Co_2(CO)_2]_x$ and a Tetrairon Cluster $C_{10}H_4S_4Fe_4(CO)_{12}$

Sir:

In an attempt to synthesize new planar organometallic complexes which will form multiparallel chains[1] bridged by a highly delocalized π system, tetrathionaphthalene (TTN)[2] was reacted with $Ni(CO)_4$, $Co_2(CO)_8$, and $Fe_2(CO)_9$ to give two new organometallic semiconductors $(TTN\ Ni)_x$ (TTN: metal ratio, 1:1) and $[TTN\ Co_2(CO)_2]_x$ (1:2) and a tetrairon cluster TTN $Fe_4(CO)_{12}$ (1:4), respectively. We report here the preparation, characterization, and the intriguing physical properties of these novel compounds.

The compound $(TTN\ Ni)_x$ (**1**) was prepared by reacting TTN with excess $Ni(CO)_4$ in freshly distilled benzene under a nitrogen atmosphere at room temperature. The dark brown-red amorphous precipitate (which shows no x-ray powder pattern but exhibits a copper-metallic luster upon grinding) which formed as the red TTN crystals gradually disappeared was then filtered, washed thoroughly with benzene, and vacuum dried. Insolubility of **1** in most organic solvents precludes further purification by recrystallization. However, elemental analysis[3] indicated the stoichiometry of $C_{10}H_4S_4Ni$. The infrared spectrum of **1** (CsI pellet) exhibits (1) no carbonyl stretching frequencies; (2) four strong bands at 1528 (s), 1338 (s), 1320 (sh), 1185 (m), and 800 (m) cm^{-1} which correspond to the four strongest bands in free TTN;[4] (3) a new band at 965 cm^{-1} which is absent in free TTN; and (4) a weak Ni–S band at 329 cm^{-1}. Based on these observations, and by analogy to the known linear polymers $[M(SR)_2]_x$ (M = Ni, Pd),[5] we propose the linear polymeric structure I for **1**.

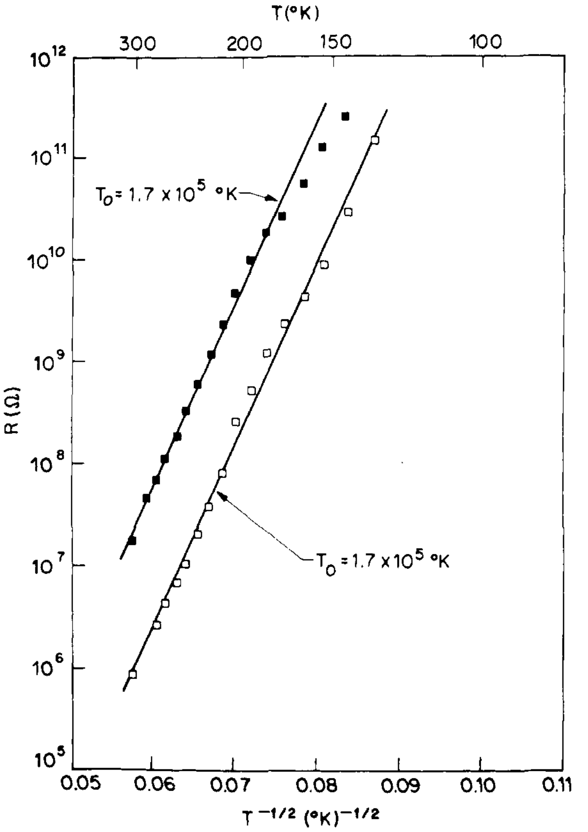


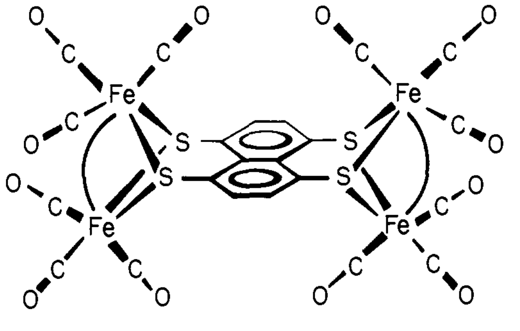
Figure 1. Temperature dependence of the resistance of compressed powder $(C_{10}H_4S_4Ni)_x$ (□) and $[C_{10}H_4S_4Co_2(CO)_2]_x$ (■). The resistance in ohms is approximately equal to three times the resistivity in ohm-centimeters. The bending of the latter curve at low temperature is due to the sample holder.

... Ni TTN Ni TTN ...
I

Reaction of TTN with a stoichiometric amount of $Co_2(CO)_8$ in benzene under similar conditions initially gave rise to a dark green solution which, upon dissolution of the TTN crystals, yielded a dark red precipitate (quantitative reaction). The product, which shows no x-ray powder pattern, is insoluble in most organic solvents and analyzes as $C_{10}H_4S_4Co_2(CO)_2$ (**2**).[3] The infrared spectrum of **2** indicates the presence of (1) only terminal carbonyls (broad band at 2010 (s) with a tailing shoulder at ~1990 cm^{-1}); (2) the coordinated TTN ligand (1525 (m), 1339 (m), 1320 (sh), 1190 (m), and 810 (br, w) cm^{-1}); (3) a weak Co-S stretching frequency at 325 (w) cm^{-1}; and (4) a new band at 970 cm^{-1}. These observations for **2** are consistent with the linear polymeric structure II (where each of the dimeric $Co_2(CO)_2$ units are bridged by four sulfur atoms, two from each of the adjacent TTN ligands) though we cannot rule out other more complicated structures with similar stoichiometry.

... $Co_2(CO)_2$ TTN $Co_2(CO)_2$ TTN ...
II

Reaction of 1 mol of TTN with 2 mol (slight excess) of $Fe_2(CO)_9$ in benzene at room temperature afforded a deep red solution from which a dark red crystalline product was isolated. Elemental analysis[3] suggested the stoichiometry $C_{10}H_4S_4Fe_4(CO)_{12}$ (**3**). The measured molecular weight was 850 (by vapor pressure osmometry with chloroform as solvent and triphenylphosphine as standard) compared with the calculated value of 810. Infrared spectroscopy of **3** indicates the presence of terminal carbonyls (2080 (s), 2041 (vs), and 2000 (vs) cm^{-1}), coordinated TTN ligand (1532 (m), 1341 (m), 1330 (sh), 1192 (m), and 818 (w) cm^{-1}) as well as FeCO (580 (m) and 562 (m) cm^{-1}) bands. The intensity pattern in the carbonyl region closely resembles that observed in $Fe_2(CO)_6S_2$.[6a] The electronic spectrum of **3** in dichloromethane solution is consistent with the presence of both the coordinated TTN (λ_{max} 262 nm (ϵ 2.15 × 10^4), 370 (sh, 1.29 × 10^4), 400 (sh, 1.35 × 10^4), 422 (1.43 × 10^4))[2] and the $Fe_2(CO)_6(SR)_2$ moieties (λ_{max} 338 nm (ϵ 1.44 × 10^4), 472 (sh, 1.23 × 10^4)).[6b] Structure III with two $Fe_2(CO)_6$ groups bridged by the TTN ligand can readily be assigned to **3**.



$C_{10}H_4S_4Fe_4(CO)_{12}$

The present "tetrathiolene" systems differ from the normal dithiolenes in the following ways. First, the bridging TTN ligand is capable of accommodating up to a total of four valance electrons. Thus, upon coordination to transition metal complexes via oxidative addition of both S-S bonds, the ligand may exist as formally a neutral entity, mono-, di-, tri-, or tetraanion.[7] This charge-buffering ability is qualitatively similar to two dithiolenes combined.[8a] Second, though each of the two chelating rings C_3S_2 contains an "odd" number of π orbitals, yet the ligand as a whole exhibits unusual charge delocalization ability[7] similar to "even" dithiolenes such as $S_2C_2R_2$[8a] but in sharp contrast to "odd" dithiolenes such as SacSac[8b] which behaves "normally". Third, the reaction of $Co_2(CO)_8$ with TTN does not lead to complete elimination of carbonyls as in the case of the reaction of $Co_2(CO)_8$ with the dithiolene ligand $S_2C_2(CF_3)_2$ to give the dimeric $Co_2(S_2C_2(CF_3)_2)_4$.[8c] Fourth, the presumed polymerization of $(TTN\ Ni)_x$ (**1**) rather than the formation of TTN $NI_2(CO)_4$ or $(TTN)_2$ Ni (cf. $Ni(CO)_4 + 2S_2C_2(CF_3)_2 \rightarrow Ni[S_2C_2(CF_3)_2]_2 + 4CO$)[8d] is quite surprising. On the other hand, **1** is probably analogous to the polymeric $[Ni(SR)_2]_x$ (R = Et, Ph) compounds formed by the reaction of $Ni(CO)_4$ with disulfides.[5c]

The most intriguing physical property of **1** and **2** is their electrical conductivity. Figure 1 shows the temperature (T) dependence of the powder resistance (R) of **1** and **2** which can be characterized by the relation

$$\ln \frac{R}{R_0} = \left(\frac{T}{T_0}\right)^{-1/2} \tag{1}$$

where T_0 is the square of the slope of ln R vs. $T^{-1/2}$ and is inversely proportional to the density of localized states.[9,10] Plots of this type have been observed for a number of known one-dimensional systems[9] and taken as evidence for one-dimensional hopping conductivity between localized states. This theory has been questioned recently by Mott.[10] Nevertheless, this type of plot may be used to characterize the conductivity of these materials. The T_0 values of 1.7 × 10^5 K observed for both **1** and **2** are, however, significantly higher than that generally observed for one-dimensional conductors or semiconductors (range: 0.5~5 × 10^4 K).[9]

In conclusion, TTN is a highly versatile tetradentate ligand which can be used in synthesizing new coordination compounds with unusual physical or structural properties. Its reaction chemistry, however, is quite different from the well-known dithiolene systems. We believe that both **1** and **2** are first examples of a new class of organometallic compounds which possess interesting electrical conductivity behavior. We are actively pursuing the reactions of other transition metal complexes with tetrathionaphthalene, tetrathiotetracene, and their analogues.

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Synthesis and Structure of a Novel Perchlorinated Organonickel Complex Containing a Bridging Trichloropropenyl Ligand

Sir:

Previous studies of the interaction of cyclopropenium cations, $C_3R_3^+$, with organometallic substrates have demonstrated a wide variety of different modes of coordination and reactivity for these species. Examples include trihapto coordination,[1-4] carbon monoxide insertion leading to formation of a *trihapto*oxocyclobutenyl ligand,[5,6] oxidative addition with ring cleavage,[7] electrophilic attack on ligands such as the cyclopentadienyl ring,[6] ring opening and oxygen insertion,[8,9] and asymmetric π coordination.[10] Here we wish to report a completely different mode of coordination exhibited by these aromatic but highly strained 2π 3C ring systems.

Tetrachlorocyclopropene, as prepared and characterized by West and coworkers,[11] is easily converted to the aromatic 2π 3C trichlorocyclopropenium ion in the presence of Lewis acids such as $AlCl_3$, $SbCl_5$, or $FeCl_3$. This fact together with the known reactivity of $Ni(CO)_4$ toward allyl chloride[12] and