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I am submitting herein a dissertation written by Michael Francis Hurley entitled "Synthesis and Characterization of Bis-Tetradentate Tetrathiafulvalene Ligands." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

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James Q. Chambers, Major Professor

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SYNTHESIS AND CHARACTERIZATION OF BIS-TETRADENTATE TETRATHIAFULVALENE LIGANDS

A Dissertation

Presented for the

Doctor of Philisophy

Degree

The University of Tennessee, Knoxville

Michael Francis Hurley

June 1980

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And last but perhaps most of all the author wishes to express his most sincere thanks to Jan Williams for typing this dissertation.

ABSTRACT

The electrochemical reduction of carbon disulfide was examined. Investigations were made in order to elucidate the mechanism of this process. The principal product of this reduction, the dianion 4,5-dimercapto-1,3-dithiolen-2-thione ($C_3S_5^{2-}$), which was realized in quantitative yield, was used to prepare some polysulfur organic compounds.

The preparation and characterization of some nickel-dithiolene complexes is presented. These complexes are formed by the reaction of nickelous salts with the product of the electrochemical reduction of carbon disulfide. The electrochemical and some physical properties of these compounds are reported.

The preparation of some new bis-tetradentate ligands was carried out. These compounds consist of two chelating centers joined via a tetrathiafulvalene moiety. These ligands should react with certain transition metal ions to form new and interesting binuclear complexes.

Attempts to prepare the platinum (II) and nickel (II) complexes of these ligands are also discussed.

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CHAPTER I

INTRODUCTION

The chemistry described in this thesis involves the synthesis of multisulfur ligand species which may augment the set of materials known as "organic metals." The research touches several areas of our science including the following: synthetic organosulfur and transition metal chemistry, electrochemistry, and the physics of the organic solid state. This introductory chapter reviews three areas of recent activity pertinent to this thesis. First, the properties of materials belonging to the class of quasi-one-dimensional electronic conductors are described with emphasis on structural variations which result in increased conductivity. Second, synthetic approaches are reviewed for the preparation of key components of many of the "organic metal" materials, the tetrathiafulvalene derivatives. Lastly, some recent chemistry of binuclear metal-ditholene complexes is described.

A. Quasi-One-Dimensional Conductors

In the past several years, a number of materials such as $K_2Pt(CN)_4\ X_{0.3}$, X = Cl, Br (KCP)[1-3]; the tetracyanoquinodimethane (TCNQ) charge transfer salts[4-5]; and the sulfur-nitrogen polymer $[(SN)_x]$[6-8] have been discovered to possess microscopic structure consisting of a collection of weakly coupled highly conducting

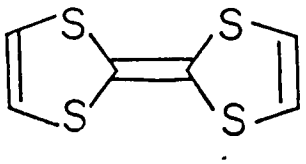
chains. These materials are electronic conductors, possessing conductivities in several cases well into the metallic region. They have been dubbed in the literature as "organic" or "molecular metals." Polymers such as $(SN)_x$ and $(CH)_x$ "doped" with substoichiometric amounts of halogens or other materials show marked increases in conductivity.[9-13]

These materials exhibit a high degree of anisotropy in their electronic, spectroscopic, and electrochemical behavior.[14,15] The electronic conductivity along the chain axis can be quite high, into the metallic region ($> 10^3\ \Omega^{-1}\ cm^{-1}$),[16] while the materials are insulators or semiconductors in the direction perpendicular to the chain axis.[18,19] Because of their high conductivities, these materials have been dubbed "organic metals." Recently, in fact, tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) and $(SN)_x$ have been used as electrodes in electrochemical experiments.[14,15,17] The resultant voltammograms were comparable to those generated with a Pt electrode.

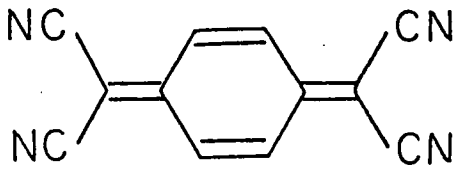
Prior to the synthesis of the above materials and others, quasi-one-dimensional conductors were unknown, but because of their unusually high electrical conductivities, they became of immediate interest to solid-state physicists. Recently the field has developed rapidly in several directions.[20] Detailed studies of the conductivity of single crystals of the TTF-TCNQ charge transfer salt have shown a maximum conductivity of $10^{-4}\ \Omega^{-1}\ cm^{-1}$ at 60° K, whereas at room

temperature, single crystals of this material have conductivites up to ca. 500 Ω^{-1} cm^{-1}.[21]

Much work, both experimental and theoretical, has been done toward the elucidation of the intrinsic properties of this charge-transfer salt.[21] However, owing to the complex structural and electronic characteristics of such compounds, further study will be necessary.



TTF



TCNQ

In general, the high electrical conductivity exhibited by these compounds is due in part to the abundance of electrons in extended π-orbital systems. Crystals of these charge-transfer salts consist of segregated stacks of donor and acceptor molecules.[20] In the TTF-TCNQ salt, for example, the TTF stack is separated from the TCNQ stack by 3.0 A and the planes of the TTF molecules are at an angle of 58.5° with respect to the planes of the TCNQ molecules.[22] Electrical current is thus carried through the primary axis of these stacks.

Within the stacks there exist only weak π to π-orbital interactions. Yet there is considerable π-orbital interaction

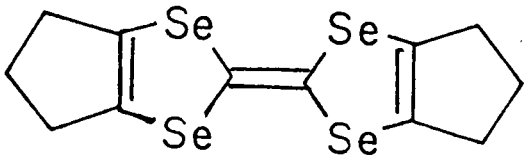
between the stacks of donor and acceptor molecules. This interaction as, well as a fairly strong coulombic attraction, gives rise to an energy band such that current may flow.

The electronic effects giving rise to this band are two-fold. Firstly, increased overlap between the orbitals of donor and acceptor molecules lowers the energy of the system making the band more accessible. This is exemplified by substitution of selenium for sulfur in the fulvalene donor molecule. The room temperature single crystal conductivity of tetraselenafulvalene-tetracyanoquinodimethane (TSeF-TCNQ) is 800 Ω^{-1} cm^{-1}.[21] It has been suggested that the more diffuse 3p orbitals on selenium atoms allow considerably more overlap between donor molecules than the sulfur 2p orbitals. However, the larger selenium atom also causes certain crystal lattice defects which can severly interfere with band energetics. Measurements performed on crystals of dithiadiselenafulvalene-tetracyanoquinodimethane (DTDSeF-TCNQ), and TTF-TCNQ doped with TSeF show significant decreases in conductivity relative to TTF-TCNQ.[21]

The second effect contributing to conductance is the percent charge transfer between adjoining stacks in the crystal. High conductivity is found only in cases of incomplete charge transfer. For the well studied TTF-TCNQ salt the extent of partial charge transfer is 0.6, i.e. average charge on a TTF unit is +0.6. This value has been established by a variety of physical measurements including neutron diffraction, photoelectron, and resonance Raman spectroscopy.[23-26]

The extent of charge transfer depends upon a number of factors, e.g. the ionization potential of each species involved, the internuclear distances, and the coulombic interactions between neighboring molecules in the crystal. Of these, only the ionization potential can be measured on separate samples of the donor species. Toward this end, electrochemical methods have been applied as a tool to examine the usefulness of new donor molecules. For a series of related donor compounds, trends in oxidation potential of each species in solution correlates very well with trends in conductance of the charge transfer salts.[27] Thus, donor molecules with oxidation potentials such that partial electron transfer is indicated with a given acceptor molecule in solution tend to form conducting charge transfer salts.

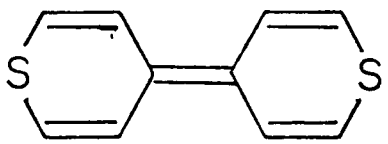
Often the steric effects of substitution on the TTF molecule are profound. Minor changes in structure can lead to large changes in conductivities due to the demands made upon the crystal lattice. These demands can enhance or destroy the aforementioned electronic requirements. For example, hexamethylenetetrathiafulvalene-tetracyanoquinodimethane (HMTTF-TCNQ) is a semiconductor at room temperature.[28] The trimethylene ring apparently prohibits proper alignment in the crystal. However, the selenium analogue, HMTSeF-TCNQ, is one of the most highly conducting salts known. While selenium analogues are generally better conductors, the difference in



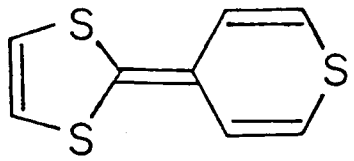
HMTSeF

conductivity for this case cannot be rationalized solely by increased orbital overlap. In fact, it has been argued that the enchancement is steric rather than electronic in origin.[29,30]

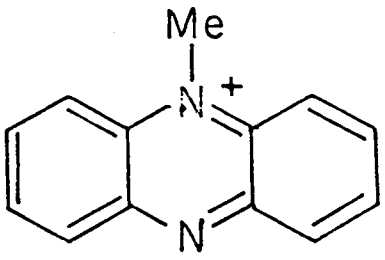
Attempts to investigate and augment the TTF-TCNQ couple have been carried out. Several other TCNQ salts have been prepared. Among these are bithiopyran (BTP),[31] thiopyranyldithiole (TPD),[32] and N-methylphenazinium (NMP).[33] Although TPD-TCNQ is a semiconductor, BTP and NMP salts have conductivities comparable with TTF-TCNQ.



BTP



TPD



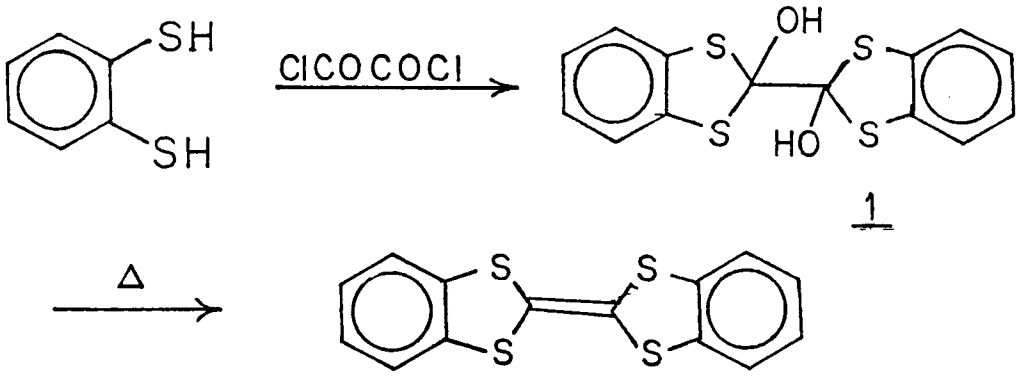
NMP

Replacement of TTF by metal ions such as K^+, Na^+, Cs^+ or Rb^+ yields only insulators.[34] Substitution of substoichiometric amounts of halogens for TCNQ, however, afforded new semiconducting solids.[35-39] In this material, the TTF stacks alone are the conducting medium. Other investigators have substituted selenium for sulfur in TTF to produce more highly conducting salts. More recently others have altered the structure of the TCNQ acceptor molecule or replaced it with other highly conjugated electron acceptors.[40-42]

B. Synthesis of TTF and Derivatives

Substitution of the hydrogens on TTF by various organic functionalities has afforded a variety of new and useful charge-transfer donor molecules. Several methods of preparation have been used, the more general schemes of which are outlined herein.

The first TTF synthesis was reported in 1926 by Hurtley and Smiles.[43,44] When oxalyl chloride is slowly added to orthodithiolbenzene a 2,2′-dihydroxy-derivative of TTF is obtained (1). Upon heating in neutral solvent, dibenzotetrathiafulvalene 2 is formed (Equation 1).



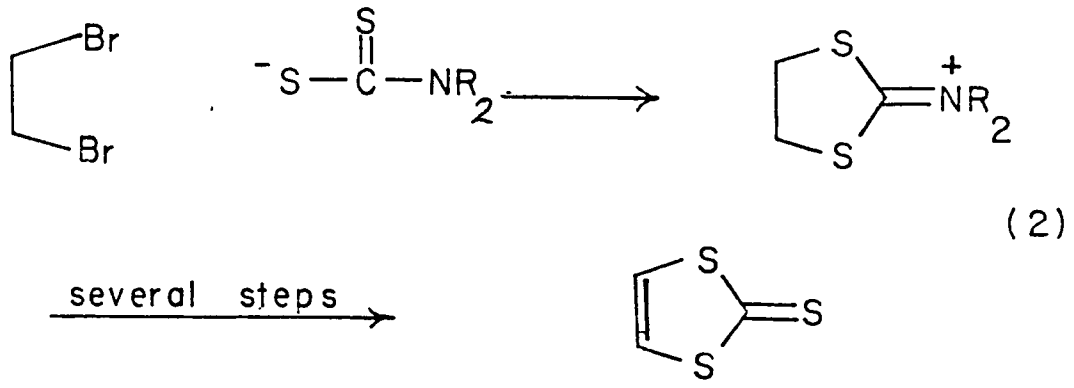
1

(1)

2

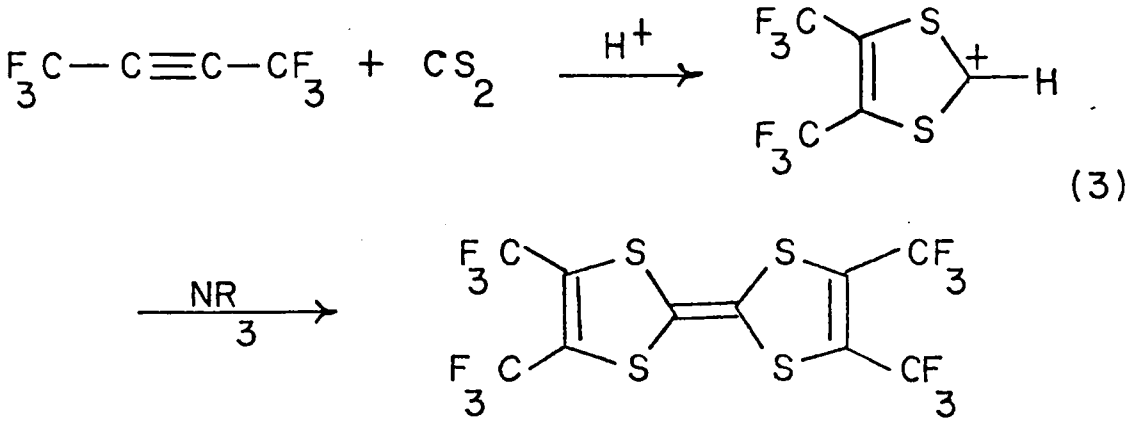
Unfortunately, the yield of this reaction is rather low. Further synthetic investigations were not carried out until 1964. These later attempts usually involve two steps. First, the 1,3-dithole ring system is constructed, then two rings are joined forming the exocyclic double bond.

The direct formation of the 1,3-dithiole ring via alkylation of thiocarbamates or trithiocarbonates affords the desired thione in fair to poor yields (Equation 2).[45-47] Substituted alkynes have been

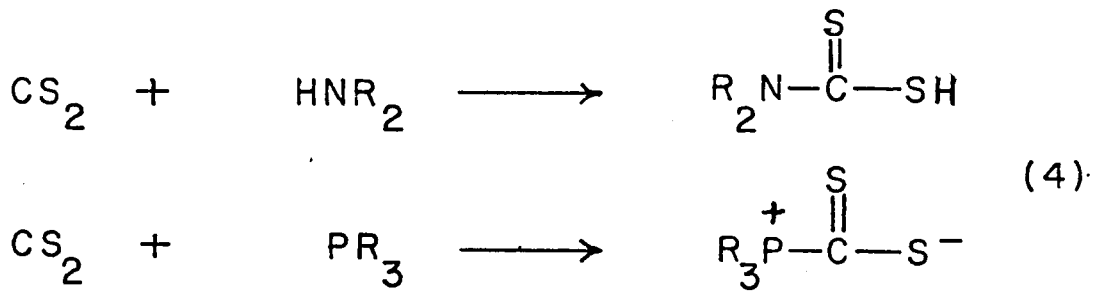


(2)

used with more success in addition and substitution reactions. For instance, alkynes substituted with one or more strong electron withdrawing groups readily react with carbon disulfide in strongly acidic media yielding symmetric TTF compounds directly (Equation 3, p 9).[48,49] Carbon disulfide can be made more reactive by forming amine or phosphine complexes, Equation 4 (p 9), which readily react with a variety of alkynes to form the 1,3-dithiole ring system.[50,51]

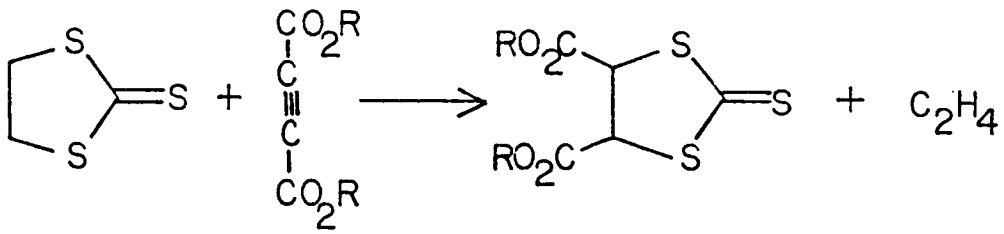


(3)



(4)

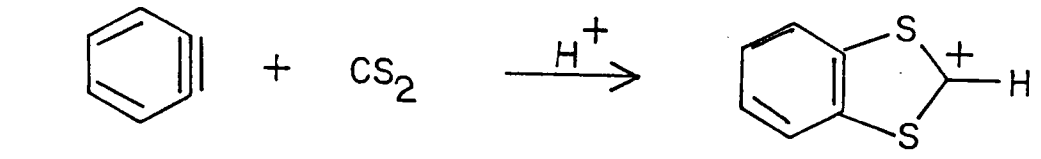
In 1965, a novel substitution reaction was reported by Easton and Leaver.[52] Dialkylacetylenedicarboxylate 3 was shown to react with ethylenetrithiocarbonate 4. Ethylene and disubstituted thione 5 are formed. A dipolar addition mechanism has been proposed (Equation 5).



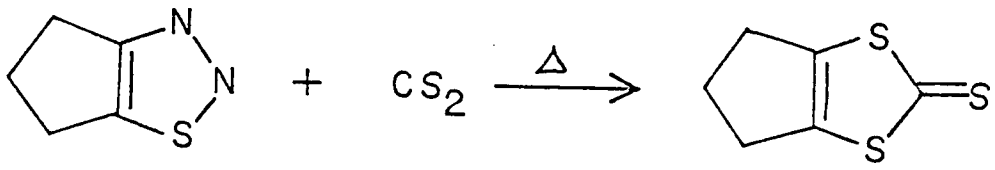
(5)

4 3 5

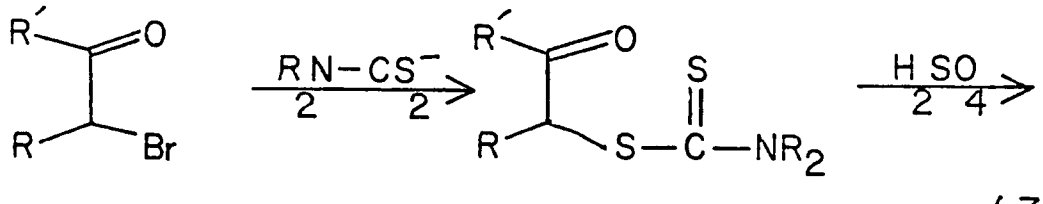
Later Cava, et al.[53,54] used this method to prepare some TTF donor molecules. Other electrocyclic ring formations were investigated also. Highly energetic moieties such as benzyne and carbenes were found to react with carbon disulfide.[53-57] In reactions with benzyne, best results were obtained at low pH (Equation 6).



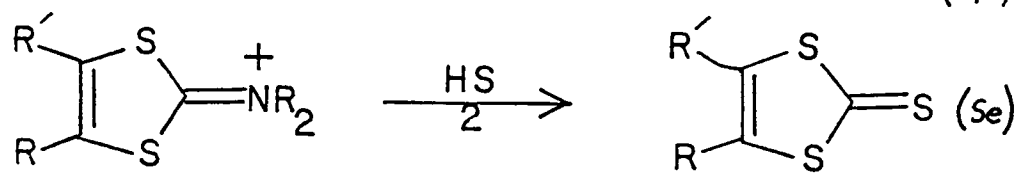
(6)



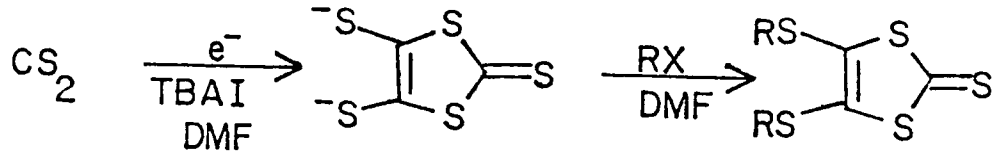
A more versatile synthesis of thiones and selenones has been developed by several researchers.[58-61] In this approach, α-bromocarbonyl compounds are allowed to react with carbon disulfide-amine complexes. The desired thiones are realized in three steps (Equation 7).



(7)



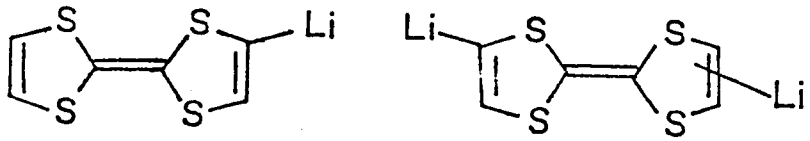
In another scheme,[62-68] carbon disulfide is reduced electrochemically in one step to give thione 6 (Equation 8). Further reaction with various alkylating agents (RX) affords a variety of compounds suitable for coupling.



(8)

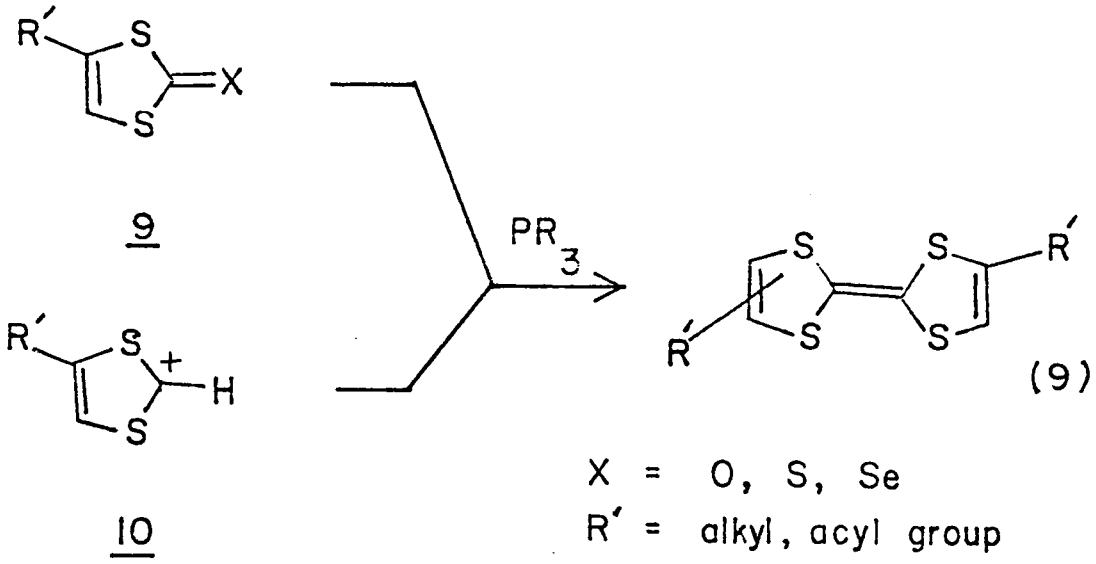
6 R = alkyl group

Substituted TTF compounds are available via reaction with unsubstituted TTF. Treatment of TTF with either butyllithium or lithium diisopropylamide affords vinyl lithium salt 7.[69,70] Under more vigorous conditions a mixture of dilithium salts are realized (8). These salts readily react with various electrophiles.



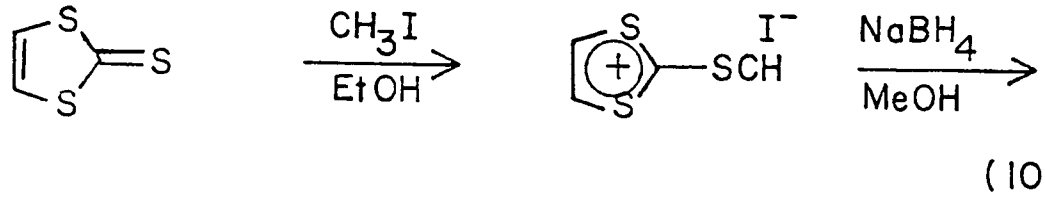
7 8

Several methods have been employed to prepare substituted tetrathiafulvalenes from various 1,3-dithioles. Thiones, selenones, ketones (9), dithiolium salts (10) are coupled by reaction with trivalent phosphorus reagents.[54,59] The mechanistic details of this reaction have not yet been resolved, and yields for thiones are sometimes very low (Equation 9).

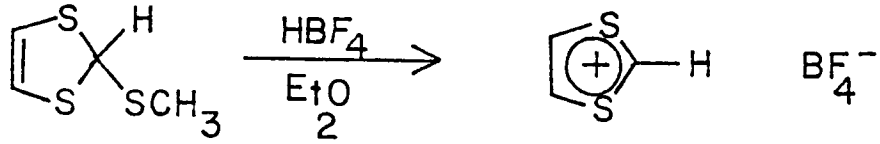


Thiones are converted to 1,3-dithiolium salts easily via a procedure developed by Wudl, et al.[74,75] (Equation 10, p 13). Alkylation of the thione followed by reduction with $NaBH_4$ affords the trithioorthoformate 11 (p 13). Upon treatment with strong acid, the dithiolium salt 12 (p 13) is realized. Alternatively, the thiones can be alkylated and the resulting sulfonium salt 13 (p 13) electrochemically reduced to a radical which quickly dimerizes. Thermolysis of the dimer affords the desired TTF[68] (Equation 11, p 13). Dithiolium

salts are easily converted to tetrathiafulvalenes by treatment with non-nucleophilic bases.[75] Presumably this occurs through a carbene intermediate (Equation 12).



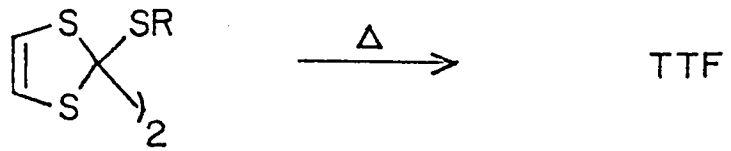
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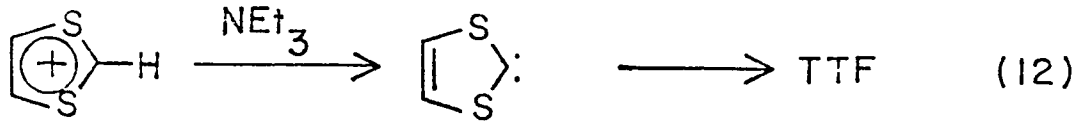


11 12



13 (11)

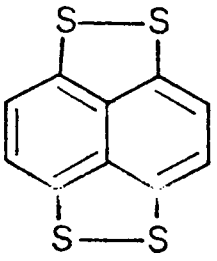




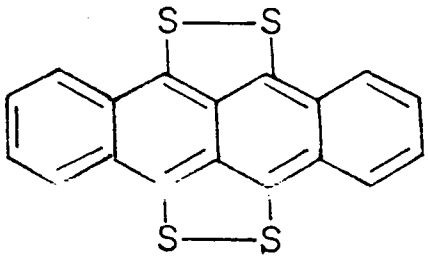
(12)

C. Dithiolene-Transition Metal Complexes

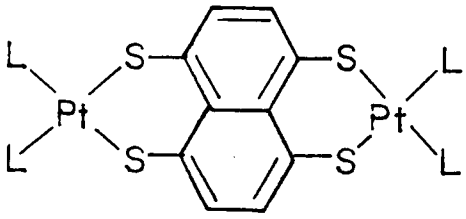
There have been relatively few reports in the literature of binuclear thiolene complexes. Notable exceptions to this are the complexes of tetrathionaphthelene 14.[76] Platinum tetrathiolene 15, a square planar complex, has been prepared (L=triphenylphosphine), and it exhibits a very rich and interesting electrochemistry. Five oxidation states are accessible for this compound in solution over a range of only 0.6 volts.[77]



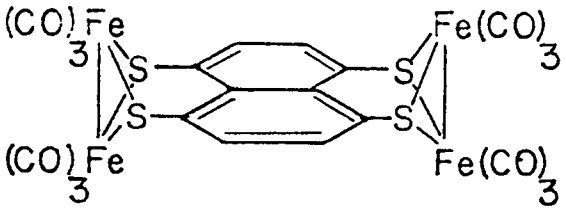
14



17



15



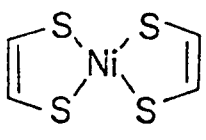
16

Several other complexes of this type have been realized. Treatment of 14 with $Fe(CO)_5$ yields the tetraferro complex 16, which has been shown to contain a pair of iron-iron bonds.[78] Complexes of

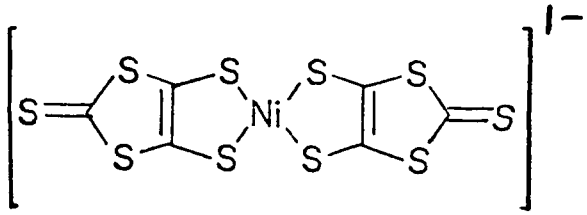
14 with nickel or cobalt have been prepared but only in polymeric form.[78]

Compound 14 and the related tetrathiotetracene 17 are also of interest because of the high electrical conductivities of their charge transfer salts. Measurements made of pressed pellets of 14 and 17 indicate room temperature conductivities of 40 Ω^{-1} cm.$^{-1}$ and 1.0 Ω^{-1} cm.$^{-1}$, respectively.[78] Other polysulfur systems have been examined also. Thiosquarate-metal complexes such as oligomeric $[Pd_{10}(C_4S_4)_9K_2Cl_2 \cdot 7H_2O]$ and $[Ni_{25}(C_4S_4)_{26}K_2 \cdot 8H_2O]$, and the platinum squarate polymer $[Pt(C_4S_4)_x]$ have been prepared and found to be semiconducting solids at room temperature.[79]

Bis-dithiolene nickelate complex 18 and other related compounds have been found to form 1:1 charge-transfer salts with TTF.[80] Unfortunately all these salts are insulators. More highly conducting dithiolene complexes have been developed. This work utilizes as a basic building block the carbon disulfide reduction product 6 (p 11).[81] The bis-1,3-dithiol-2-thione-4,5-dimercaptonickelate complex 19 was first prepared in 1975 by Steimecke, et al.[82,83] More recently the zinc complex has been prepared, and its use in synthetic schemes is under investigation.[83,84] This labile complex can be used as a virtual source of pure thione 6.

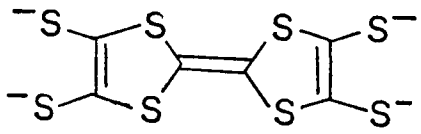


18



19

In other work, this ligand has been manipulated to form a binuclear metal complex containing a tetrathiafulvalene unit which bridges the metal centers. The polymeric nickel complex of tetramercapto ligand 20 has been prepared and it exhibits a room temperature conductivity of 30 Ω^{-1} cm^{-1}.[84,85]



20

D. Statement of Thesis Problem

The purpose of the work describe herein is to prepare and characterize some new tetrasubstituted tetrathiafulvalenes. These compounds will be constructed such that they may act as bis-tetradentate ligands. Addition of transition metal ions to these ligands should produce binuclear complexes.

The binuclear complexes described above consist of two metal centers joined by an π-electron moiety. The ligands described herein are modeled after these systems. The ligand centers will be joined by TTF moieties. The synthetic routes which are investigated draw from the methods described in this chapter.

CHAPTER II

EXPERIMENTAL

A. Solvents

Acetonitrile (MeCN) and N,N-dimethylformamide (DMF) were the principal solvents used for electrochemical preparation and investigations in this work. Originally practical grade MeCN was purified by a procedure outlined by Mann, et al.,[86] and Wallace and Ramely.[87] To 1.5 L of MeCN, 20 g of $KMnO_4$ and 15 g of Li_2CO_3 were added. The solvent was rapidly distilled. Amine impurities were removed by treatment with six drops of concentrated H_2SO_4. After standing overnight the MeCN was filtered. Calcium hydride (3 g) was added and the mixture was allowed to reflux overnight. This was followed by one final distillation. Background voltammograms were performed prior to use as an electrochemical solvent. Purified solvent was stored in glass containers under an N_2 or Ar atmosphere.

In later work, spectra-grade MeCN was used without further purification (Gold Label-Aldrich).

DMF was purified by a procedure of Faulkner and Bard.[88] To 750 mL of DMF, 10 g of anhydrous $CuSO_4$ was added. After stirring at room temperature for 24 hours, the mixture was distilled under vacuum (0.1 mm Hg, 28° C).

Methylene chloride ($MeCl_2$) was used occasionally for electrochemical investigations. Spectra-grade $MeCl_2$ (Fisher Scientific) was used without further purification.

For routine use in the laboratory, drum-grade solvents were distilled once and stored in glass bottles.

Ethanol was purified by a two-step process. To 2.0 L of drum-grade 100% ethanol, 40 g of KOH was added. The resultant mixture was allowed to reflux overnight and was then distilled. Magnesium turnings (30 g) were added to the distillate, and the mixture again was refluxed overnight. After final distillation , the dry ethanol was stored in glass bottles under inert atmosphere.

Tetrahydrofuran was purified by distillation after the addition of 3 to 4 g of $LiAlH_4$ per liter. The purified solvent was used immediately.

All other solvents were used without further purification.

B. Supporting Electrolytes. Tetraethylammonium perchlorate (TEAP) (Eastman) or tetrabutylammonium perchlorate (TBAP) (Eastman) were used exclusively for voltammetric investigations. They were purified prior to use by three successive recrystallizations from water. The final crop was dried under vacuum for two days. Tetrabutylammonium iodide (TBAI) (Eastman) was used exclusively for all bulk electrolyses. It was used without further purification.

C. Reagents. All reagents were used without further purification.

D. Coulometry. Coulometric experiments were carried out in a three compartment cell. A medium porosity glass frit at the

bottom of the working compartment allowed for degassing and stirring of the solution by the purging gas during the experiment. The compartments were separated by medium porosity glass frits. A diagram of the cell is shown elsewhere.[89] A solution of 0.4 Molar TBAI in either DMF, MeCN, or $MeCl_2$ was used. A platinum foil working electrode, 28 cm^2 in area, a saturated calomel reference electrode, and a carbon rod counter electrode were employed. The experiment was performed with a PAR 173 potentiostat/galvanostat equipped with a PAR 176 current follower. The electrical charge passed was measured by a Koslow Scientific Model 541 Coulometer.

E. Voltammetry. Voltammetry was carried out in a one compartment electrochemical cell. A medium porosity glass frit at the bottom of the cell allowed degassing prior to the measurements. During the course of the experiment, an inert atmosphere was maintained above the solution. A diagram of the cell is shown elsewhere.[89] DMF, MeCN, or $MeCl_2$ were used as solvents as needed. In DMF and MeCN solutions, TEAP was the supporting electrolyte. In $MeCl_2$ solutions, TBAP was used. In all cases, the concentration of electrolyte was 0.1 Molar. Voltammetry was performed using a combination PAR Model 173 potentiostat/galvanostat equipped with a PAR model 176 current follower and a PAR 175 universal programmer, or a three electrode potentiostat designed and built in this laboratory. Experimental curves were recorded on either a Hewlett-Packard Model 136 X-Y-Y recorder or an Esterline-Angus Spartain Model X-Y-575 recorder. Reference electrodes

were either a 0.01 $AgNO_3/Ag$ or a saturated calomel electrode. The counter electrode was a platinum foil between 2 and 28 cm^2 in area. The working electrode was a 0.22 cm^2 Beckman platinum disc electrode.

F. Spectroscopy. Infrared spectroscopy was carried out utilizing a Perkin-Elmer model 727 spectrophotometer. For solid samples a KBr pellet was prepared using a Blackhawk pellet press. Neat liquid samples were obtained with a Barnes Engineering Co. liquid cell between sodium chloride crystals. All spectra were standardized with a polystyrene film.

Ultraviolet and visible spectroscopy were carried out using a Cary Instruments model 17I spectrophotometer. Samples dissolved in either MeCN or $MeCl_2$ were examined in a 2.0 mm quartz cell. No reference cell was used, but a solvent background spectrum was recorded each time.

Nuclear magnetic resonance spectra were recorded on a Varian model T-60A spectrometer. A tetramethylsilane (TMS) internal standard was included in all samples. Chloroform-d was routinely used as a solvent.

Mass spectra were obtained from a Hewlett-Packard Model 5934A gas chromatograph/mass spectrometer.

G. Miscellaneous. Melting points of samples were obtained on a Mel-Temp melting point apparatus and were uncorrected.

Elemental analyses were performed by Gailbraith Laboratories, Inc. of Knoxville, Tennessee.

Elemental analyses were performed by Gailbraith Laboratories, Inc. of Knoxville, Tennessee.

H. Preparation of Compounds Under Investigation

1. Tetra-n-butylammonium 4,5-dimercapto-1,3-dithiolen 2-thione (6, p 11), was prepared by reduction of carbon disulfide by sodium, potassium, or electrochemically. Electrochemical reduction of CS_2 was carried out in either DMF or MeCN. During the electrolysis, the solution was continuously purged with argon and the current was maintained at about 0.2 amps. Higher currents resulted in excessive heating of the frits in the electrolysis cell. The working electrode potential was generally between -1.8 to -2.1 volts versus SCE. Additional amounts of CS_2 were added when the volume in the cell decreased. Typically 20 to 60 milliequivalents of electricity was passed over a period of three to eight hours. If DMF was used, the next step in the preparation was carried out directly after the electrolysis. In cases where MeCN was used, the electrolysis solution was evaporated to dryness prior to further manipulation. The resulting deep red salt, which consists of a mixture of the tetrabutylammonium (TBA^+) salt of 6 and TBAI, is extremely air sensitive and decomposes upon standing after one or two days.

Sodium reductions were carried out according to a procedure outlined by Steimecke, et al.[83] To a degassed mixture of 180 mL of carbon disulfide and 200 mL of DMF, either 24 g (1 mole) of sodium wire or 39 g (1 mole) of potassium wire was added. The mixture was allowed to reflux under inert atmosphere until all metal had reacted.

carbonate in quantitative yield according to the scheme expressed in Equation 8 (p 11).

The polymeric form of the carbon disulfide reduction product was prepared by electrolyzing CS_2 in DMF, 0.4 Molar in TBAI, at -1.7 volts versus SCE. Addition of the solution from the working compartment of the electrolysis cell to 500 mL of a saturated aqueous solution of KI resulted in the precipitation of a near crystalline, red solid. This solid was isolated by filtration and washed with a 0.5 Molar aqueous KI solution until the washings became clear. Based on the empirical formual $(CS_2^-)_x$, the calculated yields varied between 400 to 700%. The red solid decomposes slowly in air. This decomposition is accelerated at higher temperatures.

Carbon disulfide was electrochemically reduced in DMF which was 0.4 Molar TBAI as described above. Carbon dioxide was used to purge the working electrode compartment in place of argon. After passing 30 milliequivalents of electricity the electrolysis was halted and 4.3 g of methyl iodide (Aldrich) was added. The mixture was stirred with gentle warming for one hour, and then treated with 100 mL each of water and methylene chloride. The organic layer was washed with water five times and dried with $MgSO_4$. Elution with benzene on alumina afforded an oil which recrystallized from MeCN to give light brown needles in 90% yield: mp 52-3°; ir (KBr) 3000 w, 2900 w, 1465 m, 1418 m, 1382 , 1310 w, 1052 s, 1025 m, 970 w, 960 m, 890 m, 873 w cm^{-1}. From these data it was deduced that no carbon dioxide was incorporated into thione 6.

2. 1,3-dithiol-4,5-dithiomethyl-2-thione, (27). To a DMF solution of 7.5 mmoles of the carbon disulfide reduction 6 was added 4.3 g of methyl iodide (Aldrich). The mixture was stirred with gentle warming for one hour, and then treated with 100 mL each of water and methylene chloride. The organic layer was washed with water five times and dried with $MgSO_4$. Elution with benzene on alumina afforded an oil which recrystallized from MeCN to give light brown needles in 90% yield: mp 52-3°; ir (KBr) 3000 w, 2900 w, 1465 m, 1418 m, 1382 , 1310 w, 1052 s, 1025 m, 970 w, 960 m, 890 m, 873 w cm^{-1}.

3. Tetra-n-butylammonium bis-(4,5-dimercapto-1,3-dithiolen-2-thione)-nickelate(III), (25, z=1). To a DMF solution of 7.5 mmoles of carbon disulfide reduction product, one equivalent (2.6 g) of $Ni(ClO_4)_2 \cdot 6H_2O$ was added. Addition of water precipitated the crude nickel salt. After washing the black solid with copious amounts of water, it was air-dried. Separation of this crude material via elution with benzene-methylene chloride on a neutral Al_2O_3 column (activity III) gave the green monovalent salt 25 (z=1) in 70 to 80% yield. Recrystallization from MeCN affords small black cubes: mp 187-8°; d 1.33. Recrystallization from methylene chloride-benzene mixtures affords black needles: mp 187-8°; d 1.67. A phase transition was observed by differential scanning calorimetry of the needles at 80°.

Addition of 1.0 mL of methyl iodide (Aldrich) to 25 mL of a warmed DMF solution (60°) of 1.0 g of this nickel salt resulted in a

gradual decoloration of the solution. Elution of this mixture with ether on Al_2O_3 afforded the dimethyl adduct of thione 6 (p 11), thione 27 (p 23) in quantitative yield based on the weight of nickel complex.

Coulometry. To a degassed solution of 0.4 Molar TEAP in DMF in a three compartment electrochemical cell, was added 1.0 g of this TBA^+ nickel salt 25 (z=1). This mixture was electrolyzed at 0.20 volts versus SCE until the current decreased to five milliamperes. The number of coulombs passed was recorded. Calculations indicated one electron passed per molecule of the salt. Anal. Calcd for $C_{22}H_{36}NS_{10}Ni$: C, 38.10; H, 5.19; N, 2.02; S, 46.18; Ni, 8.51. Found: C, 38.28; H, 5.23; N, 1.99; S, 46.43; Ni, 8.36. Ir (KBr) 2930 w, 1470 w, 1445 m, 1380 w, 1360 s, 1175 vw, 1070 vs, 1035 s, 925 w, 875 w, 670 w, 750 w, 790 w cm^{-1}; uv-vis (MeCN) 340, 395, 435, 584, and 620 nm.

4. Di-tetra-n-butylammonium-bis-(4,5-dimercapto-1,3-dithiolen-2-thione) nickelate (II), (25, z=2). The preparation was as above except the crude, black precipitate was dissolved in a 50/50 methylene chloride-benzene mixture and placed on a rotary evaporator. Black-blue microcrystals formed as methylene chloride is preferentially removed. These were isolated by filtration and washed with benzene. The blue divalent salt 25 (z=2) was realized in 90% yield: mp 204° d; ir (KBr) 2930 m, 1460 m, 1445 s, 1360 w, 1375 w, 1115 w, 1160 w, 1180 w, 1040 s, 1060 s, 893 w, 920 w, 925 w, 750 w, 705 m cm^{-1}.

Reactions of 25 (z=2). Addition of 1.0 mL of methyl iodide (Aldrich) to 1.0 g of this nickel salt in 25 mL of DMF resulted in immediate decoloration of the mixture. Elution with ether on Al_2O_3 afforded the dimethyl adduct of 6 (p 11), thione 27 (p 23), in quantitative yield.

5. Bis (4,5-dimercapto-1,3-ditholen-2-thione) nickel (IV), (25, z=0). Into a two compartment electrochemical cell was put 7.0 g (0.01 moles) of the monovalent salt 25 (z=1) dissolved in a 0.4 Molar TBAP methylene chloride solution. After the passage of about 0.01 equivalents of current at +0.50V versus SCE, the electrolysis was halted, and the solution was filtered. The black, insoluble neutral nickel complex 25 (z=0) was recovered in 90% yield: mp 200° d; ir (KBr) 1240 vs, 1050 s, 880 w, 780 w cm^{-1}.

6. Methylated Nickel Complex, (28). This compound was prepared by the addition of a large excess of methyl iodide (Aldrich) to a methylene chloride solution of the monovalent salt 25 (z=1) (p 23). Upon standing for several days, the solution decolored and a black precipitate formed. This insoluble amorphous solid was isolated by filtration and washed with a variety of organic solvents including benzene, chloroform, and ether.

Addition of 0.5 mL of methyl iodide (Aldrich) to 25 mL of a warmed DMF solution (60°) of 0.1 g of this nickel compound gave after elution with ether on Al_2O_3 the dimethyl adduct of 6 (p 11), thione 27 (p 23) in near quantitative yield. Anal. found: C, 23,59; H, 2.28,

N,10.38; S, 63.11, Ni, 10.38; Calculated for $C_7H_3S_{10}Ni$: C, 18.38; H, 0.64; S, 68.67; Ni, 12.66; ir (KBr) 2940 w, 1410 w, 1375 w, 1330 m, 1245 w, 1055 s, 1020 m cm^{-1}.

7. 1,3-dithiol-2-thione-4,5-bis-(1,4-dithiapentane)(29, Y=CH_3S, m=2). To a DMF solution of 7.5 mmoles of the carbon disulfide reduction product 6, was added 0.50 mL of 2-chloroethylmethyl sulfide (Aldrich). After stirring overnight, 100 mL each of water and methylene chloride were added. The organic layer was washed five times with water and then dried with $MgSO_4$. Elution with ether on neutral alumina afforded a yellow oil which was recrystallized from acetonitrile in 70% yield: mp 40-2°; ir (KBr) 2900 w, 1453 m, 1413 m, 1253 w, 1204 s, 1125 m, 1060 vs, 945 w, 890 m, 745 w, 725 w, 700 w, 675 m cm^{-1}; nmr ($CDCl_3$) δ 2.2 (singlet, 3); 2.4 ppm (multiplet, 4).

8. 1,3-dithiol-2-thione-4,5-bis-(1,5-dithia-6-heptanone)(29, Y=CH_3COS, m=3). To a DMF solution of 7.5 mmoles of the carbon disulfide reduction product was added 0.50 mL of 3-chloropropyl-thioacetate. After stirring overnight, 100 mL each of water and methylene chloride were added. The organic layer was washed with water five times and dried with $MgSO_4$. Elution with ether on alumina yielded a yellow oil which was recrystallized by addition of bits of dry ice to a chloroform solution in 70% yield: mp 48-50°; ir (KBr) 2910 w, 1710 s, 1430 w, 1388 m, 1360 w, 1300 w, 1250 w, 1145 m, 1110 w, 1060 s, 1040 w, 915 m, 890 w cm^{-1}; nmr ($CDCl_3$) δ 2.0 (multiplet, 2); 2.1 (singlet, 3); 2.7 ppm (multiplet, 4).

9. 1,3,5,7,8-pentathiaindene-2,6-dithione, (22). Carbon disulfide was reduced electrochemically in a three compartment cell

previously (p 21). After the passage of 30 milliequivalents of electricity, the electrolysis was halted and the contents of all compartments were combined. The yellow precipitate was separated by filtration and washed with 50 mL portions each of ethanol, benzene, and ether successively. The amorphous yellow solid is realized in quantitative yield: mp 60° d; ir (KBr) 1725 w, 1465 s, 1405 w, 1383 w, 1245 m, 1171 m, 1110 m, 1070 s (broad), 929 m, 890 s, 802 w, 743 m cm^{-1}. Mass spectrum (70 eV) m/e (relative intensity): 44 (6.5), 64 (3.9), 76 (100.0), 78 (7.8), 160 (4.3), 192 (7.3), 228 (4.7). Anal. found: C 17.48; S 82.66; calculated for C_4S_7: C 17.65; S 82.35. Several attempted reactions of this material with benzoquinone (Eastman) were unsuccessful. A mixture of 0.1 g of this yellow solid and 0.1 g of benzoquinone was refluxed for one hour in either ether, ethanol, benzene, or methylene chloride. The yellow solid darkened slowly, but did not dissolve. Evaporation of the supernatant liquid yielded benzoquinone in near quantitative yield.

Alternatively, 5.0 g of benzoquinone was added to a MeCN solution containing 0.03 equivalents of the CS_2 reduction product. Upon addition of the contents of the counter electrode compartment (I_3^- solution) to this mixture, the red color disappeared, and a brown solid formed. After evaporation of solvent, this mixture was eluted on Al_2O_3 with a 50/50 chloroform/ether mixture. Benzoquinone was recovered in near quantitative yield.

10. 1,3,5,7-tetrathiapentalene-2,6-dithione, (31). Carbon disulfide was reduced electrochemically as described earlier. The solvent was

then removed under vacuum and the resulting salt cake was dissolved in degassed ethanol. Thiophosgene was then added slowly until the solution was decolorized. The solid yellow thione was isolated by filtration and washed with ethanol and ether successively. The amorphous yellow solid was realized in quantitative yield: mp 208-210° d; ir (KBr) 1068 vs, 959 m, 900 w, 776 m cm^{-1}. Mass spectrum (70 eV) m/e (relative intensity): 44 (20.9), 64 (7.5), 76 (100.0), 88 (85.1), 240 (88.1), 242 (20.9). In an attempt to alkylate this compound, 0.1 g of the yellow solid was added to 25 mL of $MeCl_2$ and 0.1 g triethyloxonium tetrafluoroborate (Aldrich) under argon atmosphere. Cyclic voltammetry of both the residual solids and supernatant liquid indicated electroactive cations present but in very low concentrations.

11. Attempted acylation of thione 6 with dichloroisocyanides. To a MeCN solution of 7.5 mmoles of carbon disulfide reduction product was added 1.5 mL of N-ethyl dichloroisocyanide (Chemical Intermediates). Immediately, the solution lost its red color and copious amounts of a yellow solid formed. This solid was separated via filtration and washed with 100 mL of methylene chloride. Spectral analysis indicated this solid was the carbon disulfide oxidation product 22 (p 26). The solid was isolated in quantitative yield.

12. Attempted acylation of thione 6 with phosgene. Into a degassed solution of 7.5 mmoles of carbon disulfide reduction product in dry ethanol, phosgene gas was bubbled until the red color of thione 6 (p 11) disappeared. The dark brown lump formed in the reaction vessel

was highly insoluble. The supernatant liquid from the reaction mixture afforded the desired oxy-thio-thiapen in 3% yield after elution on Al_2O_3 with $CHCl_3$.

13. 1,3,5,7-tetrathiapentalene-2,6-dione, (34). A mixture of 5.0 g of 27 (p 23), 30 g of $Hg(OAc)_2$, and 250 mL of a 50/50 chloroform-acetic acid solution was heated under reflux with rigorous stirring for three hours. After cooling, 200 mL of water was added and the mixture was filtered. The organic layer was washed with water three times and a saturated $NaHCO_3$ solution once. The solvent was evaporated and the residue purified by sublimation (90°, 0.05 mm Hg). The resultant yellow solid was purified further by recrystallization from acetonitrile. Fine white needles were realized in 22% yield: mp 150°; ir (KBr) 1727 m, 1678 s, 973 w, 914 w cm^{-1}.

14. 2,2-bis-(1,3,5,7-tetrathiapentalene-6-one), (36). A mixture of 4.0 g of 34, 4.0 mL of triethylphosphite (Aldrich), and 200 mL of benzene was heated under reflux for 24 hours. The olive green solid was isolated by filtration and then washed with 25 mL portions of benzene and ether respectively. The amorphous solid was realized in 36% yield: mp 360°; ir (KBr) 1740 m, 1720 s, 1700 s, 1510 w, 970 w, 880 w, 845 w, 765 w, 745 m cm^{-1}.

15. Tetrapotassium 2,2-bis-(1,3-dithiole-4,5-dimercaptide), (37). A mixture of 100 mL of ethanol, 10 g of potassium hydroxide, and 1.0 g of 36 was stirred for 10 hours. The resulting pink salt was isolated by filtration and washed with a 10 mL portion of ethanol under inert

atmosphere. The salt which darkens upon drying was realized in 90% yield.

Coulometry. Exhaustive coulometry was carried out by dissolving 40 mg of this salt 37 in a degassed solution of 0.1 Molar TEAP in DMF. The resulting mixture was oxidized at 0.0 volts versus SCE until the current decreased to 1.0 milliampere. The number of coulombs passed was recorded. Calculations indicated four electrons passed per molecule of the salt: mp 120° d; ir (KBr) 1730 m, 1610 s, 1440 s, 1385 s, 1305 s, 1140 m, 115 m, 1050 w, 990 s, 870 m, 750 w, 740 w, 680 m, 650 m cm^{-1}; epr (DMF, 0.1 Molar TBAP) 1 line (g=2.0386 G).

16. 2,2-bis-[1,3-dithiole-4,5-bis(1,4-dithiapentane)], (38). A mixture of 0.5 g of 37 (p 29), 25 mL of DMF and 7.6 mL of 2-chloro-ethyl-methylsulfide was stirred for ten hours under inert atmosphere. With stirring, 50 mL of water was added slowly. After cooling, the mixture was extracted with chloroform. The chloroform layer was washed with four 50 mL portions of water and then was dried with $MgSO_4$. The resultant brown solution was eluted on neutral Al_2O_3 with chloroform. After evaporation of the solvent, the compound was recrystallized from acetonitrile. Golden brown needles were realized in 60% yield: mp 110°; ir (KBr) 2900 w, 1450 m, 1410 m, 1258 w, 1204 s, 1125 m, 1060 s, 945 w, 890 m, 745 w, 725 w, 700 w, 675 w cm^{-1}.

17. 2,2-bis-[1,3-dithiole-4,5-bis-(1,5-dithia-6-heptanone)], (39). A mixture of 0.5 g of 37 (p 29), 25 mL of DMF, and 3.0 mL of 3-chloropropyl-thioacetate was stirred under inert atmosphere for ten hours. With

stirring 50 mL of water was added slowly. After cooling the mixture was extracted with chloroform. The chloroform layer was washed with four 50 mL portions of water and then was dried with $MgSO_4$. The resultant green-brown solution was eluted on SiO_2 with a 50/50 chloroform-ether mixture. The brown solid was realized in 60% yield and was used without further purification: mp 95°, ir (KBr) 2910 w, 1710 s, 1420 m, 1390 w, 1350 w, 1300 w, 1253 m, 1135 s, 1107 s, 948 m, 874 w, 766 w cm^{-1}.

18. 2,2-bis-[1,3-dithiol-4,5-bis-(1-thia-3-propyl)amine)], (40). To a 0.5 g sample of the tetrapotassium salt $K_4C_6S_8$ (37, p 29) in 15 mL of DMF was added 1.0 g of 2-chloroethylamine hydrochloride. The mixture was stirred under Ar overnight, and then 40 mL of H_2O was added with stirring. A pellet of KOH (ca. 50 mg), 0.5 mL of triethylamine, and 0.5 g of $KHCO_3$ were added to the mixture. A deep blue precipitate was isolated by filtration and washed with water. The solid is slightly soluble in $CHCl_3$ and fairly soluble in DMSO. It was recovered from the reaction in 60% yield as a mixture of hydrochlorides: mp 130°d; ir (KBr) 3500 m(broad), 2910 w, 1680 m (broad), 1510 m (broad), 1390 m, 1350 m (broad), 1310 m, 1200 m, 1005 m, 890 w, 845 w, 805 w cm^{-1}, Anal. found: C, 26.68; H, 2.96; N, 6.27; S, 41.46; Cl, 4.13; epr (DMSO) 9 lines (g=2.0323 G, a_H=1.20 G).

19. Attempted Preparation of Binuclear Platinum Complexes. To a stirred solution of 0.200 g of arm-ligand 38 (p 30) in 500 mL of MeCN was added slowly 0.64 mmoles of platinum as $Pt(CH_3CN)_4(ClO_4)_2$

in 300 mL of MeCN. This platinum compound was prepared from platinic acid, H_2PtCl_4. The acid was first reduced with hydrazine, the chloride ion was precipitated with $AgClO_4$ in MeCN.[90] After stirring overnight the mixture had become turbid. The solvent was removed under reduced pressure affording 400 mg of a highly insoluble black solid: mp 150°d; ir (KBr) 2900 w, 1650 m (broad), 1430 m (broad), 1390 m, 1080 s (broad) cm^{-1}. Anal. found: C, 14.15; H, 1.54; S, 27.61; Pt, 39.75; Cl, 7.54; O, 5.89.

20. Attempted Preparation of Binuclear Nickel Complex. To a stirred solution of 0.200 g of arm-ligand 38 (p 30) in 500 mL of MeCN was added slowly 0.64 mmoles of NiI_2 in 300 mL of MeCN. After stirring overnight the mixture had become turbid. As the solvent was removed, long needle crystals formed. An examination of the spectral properties and melting point indicated this solid was arm-ligand 38. The unreacted ligand was recovered in quantitative yield.

CHAPTER III

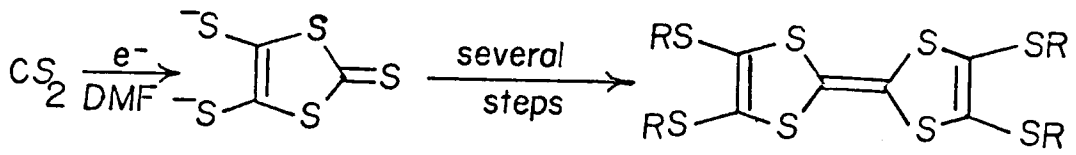
RESULTS AND DISCUSSION

A. Introduction

Reported in this chapter are the syntheses and characterizations of some new ligands which can be used to prepare binuclear transition metal-dithiolene complexes in which the metal centers are bridged by a TTF moiety. Examined also are the chemical and physical properties of the intermediate compounds involved in the syntheses of these ligands. The work is divided into three major sections. The first section examines some aspects of the electrochemical reduction of carbon disulfide (Equation 8, p 11). The resulting dianion 6 (p 11) is the basis of all synthetic work described in this dissertation. Of all the methods discussed in Chapter I for the preparation of the 1,3-dithiole ring system, this method best suited our needs. By this method, the desired dithiole is prepared in one step. Also, the 4,5-dimercapto group can be used for complexation of transition metal ions.

In our synthetic scheme, two of these dithiole moieties are coupled to form the TTF core of the proposed binuclear complexes (Equation 13, p 34).

The second section of this chapter reports the synthesis and characterization of the nickel dithiolene salts formed by the



6 (13)

reaction of Ni^{2+} and thione 6. Also reported are attempts to prepare binuclear complexes from these nickel salts.

Finally, the third section reports the total synthesis of some bis-tetradentate ligands which should react with certain transition metal ions (Pt^{2+}, Ni^{2+}, Pd^{2+}, Co^{3+}) to form binuclear complexes.

B. The Electrochemical Reduction of Carbon Disulfide.

The mechanistic details of the electrochemical reduction of carbon disulfide are not completely understood. As mentioned earlier (p 12) several schemes have been postulated in the literature. Herein are reported some new data which elucidate further the nature of this process.

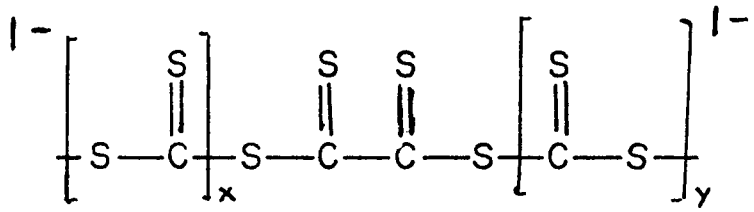
Carbon disulfide exhibits an irreversible one electron reduction at about -1.80 volts versus a saturated calomel electrode (SCE) in DMF.[64-68] When CS_2 is electrolyzed at this potential, or allowed to react with sodium or potassium metal, a deep red colored solution is realized. This solution is a mixture of thione 6 (p 11) and trithiocarbonate (CS_3^{2-}) dianions. The presence of the latter species in these electrolysis solutions has been shown in previous

investigations in our laboratory.[91] The work described herein rests upon the subsequent reaction of the thione. A deeper understanding of the formation and a procedure for the isolation of 6 (p 11) and its use as a synthetic intermediate were desired. Toward these ends, the following investigations were carried out.

Analogous to the reduction of carbon disulfide, CO_2 undergoes a reversible one electron electrochemical reduction at -2.3 volts versus SCE. The product of this reaction is the oxalate ion ($C_2O_4^{2-}$).[92,93] It was hoped that the reduction of carbon disulfide in the presence of carbon dioxide would yield a CS_2-CO_2 co-reduction product. Electrochemical reduction of carbon disulfide in the presence of carbon dioxide followed by alkylation with methyl iodide afforded only thione 27 (p 23).

In an attempt to isolate by precipitation the potassium salt of thione 6, an apparent carbon disulfide oligomer was obtained. After electrolysis at a potential on the foot of the CS_2 reduction wave (-1.7 volts versus SCE in DMF), it was found that the addition of this solution to an aqueous KI solution resulted in the formation of a dark red, near crystalline precipitate. When treated with an alkylating agent such as methyl iodide, this solid reacts as if it were thione 6. However, the weight of the isolated red solid greatly exceeds the amount of thione 6 expected based on the number of coulombs passed during the electrolysis. Unlike thione 6, this solid is fairly stable to air over prolonged periods of time. Also, unlike 6, the solid is insoluble in dilute aqueous KI solutions. For these

reasons it was postulated that the solid is a partially reduced polymer of CS_2, as in 21, which contains the same functionalities as the 1,3-dithiole, 6. The synthetic or commercial utility of this new substance seems limited due to its lability, sensitivity to O_2, and foul odor. Also, the quantity of solid realized varied greatly from one experiment to another. Electrolyses at voltages more negative than -1.9 volts versus SCE, or at slightly elevated temperatures yielded little or no precipitate upon addition to KI-H_2O solutions.



21

No oligomeric material could be isolated from sodium or potassium reductions of CS_2. Presumably under these conditions the oligomer is further reduced and thione 6 becomes the predominant species in solution.

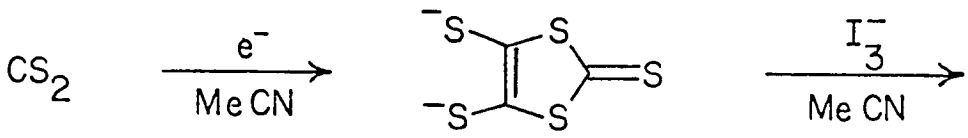
Electrolyses carried out at slightly elevated temperatures (30° to 60°) and high currents give rise to another curious phenomenon. Under these conditions, CS_2 quickly evaporates from the reaction mixture and a marked color change ensues. The typical red color of 6

gives way to a deep green and then blue. Upon addition of small amounts of CS_2 to the mixture, the red color returns. Treatment of these green or blue solutions with alkylating agents affords the same products as are obtained by treatment of 6 with the same alkylating agents but in slightly lesser yields. On the basis of their color these mixtures were initially believed to contain radicals or solvated electrons. However, EPR experiments in a flow cell indicated that the solutions were only weakly paramagnetic.

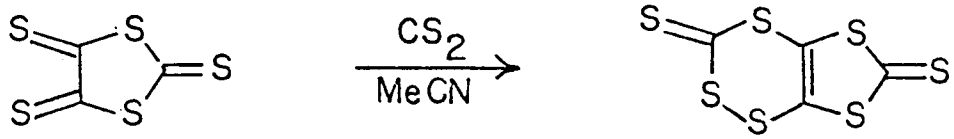
Also of interest is the reaction of thione 6 with strong oxidizing agents. In the course of a routine electrochemical reduction of CS_2, it was noticed that a yellow solid was formed at the junction between the counter electrode compartment and the middle compartment of the H-cell. It was suspected that this solid resulted from the reaction of 6 with triiodide formed in the counter electrode compartment. In order to investigate this solid further, a larger amount was prepared. This was carried out by halting the electrolysis and combining the contents of all compartments of the electrolysis cell. The blood red color of thione 6 immediately disappeared and copious amounts of the yellow solid were realized. This solid, which is highly insoluble, is stable in air at room temperature, but decomposes to a dark brown solid slowly upon heating above 60°. Decomposition also occurs when the solid is wet with solvent in air. The nature of the decomposition product was not investigated. Elemental analysis was in excellent agreement with the chemical formula C_4S_7. Contamin-

ation by elemental sulfur is ruled out by the solubility, electrochemical, and mass spectral properties of this material. The structure of thione 6 and the elemental analysis of the yellow solid suggest the structure 22 shown below for this compound. We also propose the following scheme as a probable route for formation of 22 (Equation 14).

This scheme is supported by the following arguments. Under our reaction conditions CS_2 is present in large excess and is probably the best dienophile present in solution. Trithione 23 should also be



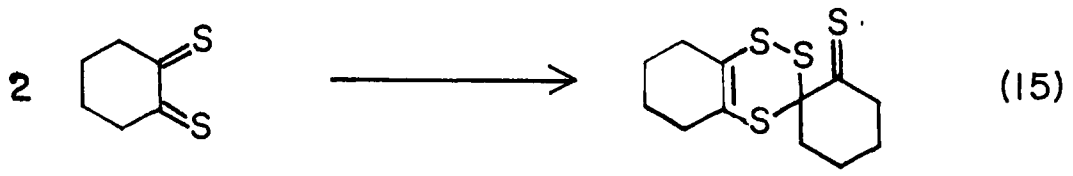
6 (14)



23 22

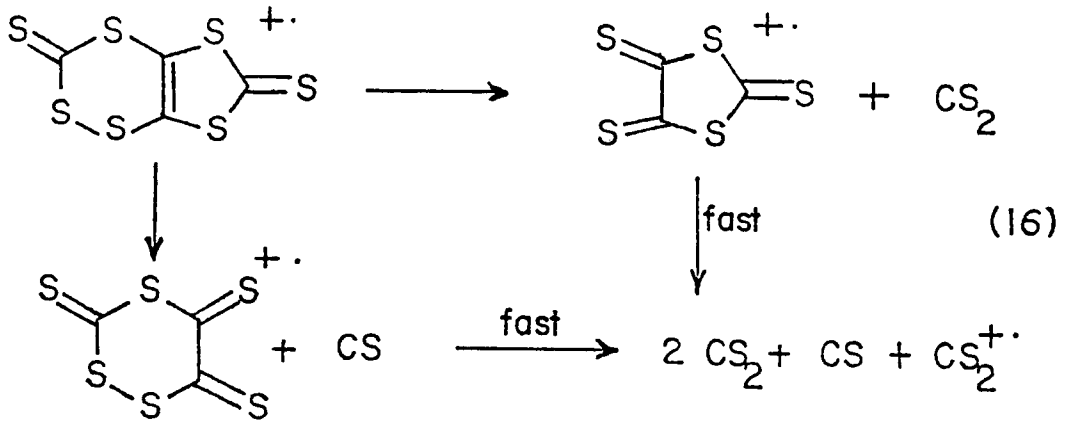
a formidable enophile. Other α-dithiones have been examined and have been shown to react readily with double bonds (Equation 15, p 39).[94-97]

In order to elucidate further the structure of this new compound mass spectra were obtained. Both chemical and electron



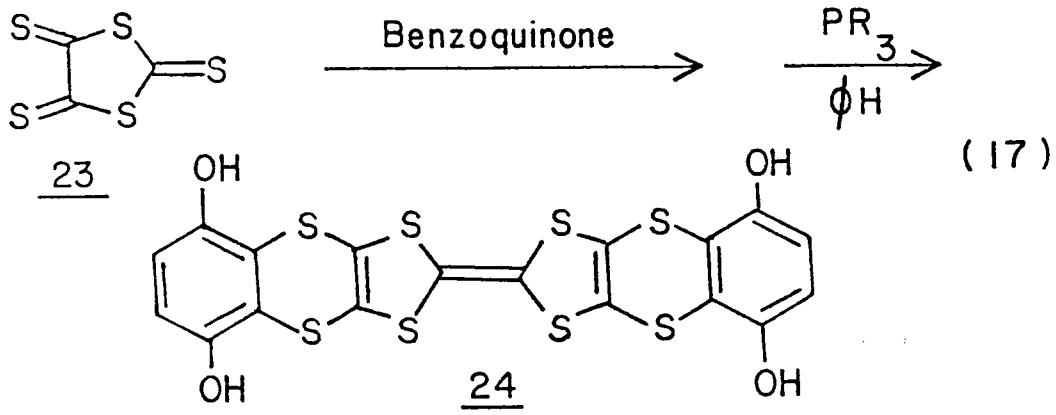
(15)

ionization were used. Structure 22 is consistent with these results as outlined in the fragmentation pattern suggested in Equation 16. The infrared spectrum of this substance is consistent with this structure. A very strong absorbance at 1070 cm^{-1} indicates one or more trithiocarbonate moieties, and a weak absorbance at 1725 cm^{-1} is consistent with a slightly asymmetric carbon-carbon double bond surrounded by four sulfur atoms.



(16)

In an effort to substantiate structure 22 and extend the synthetic utility of this chemistry, several additional syntheses were attempted. As stated above, α-dithiones are highly reactive toward double bonds. The reaction of 23 with activated olefins should yield some new and interesting tetrathiafulvalene species (Equation 17). For example, reaction of 23 with benzoquinone should yield, after coupling, 24.



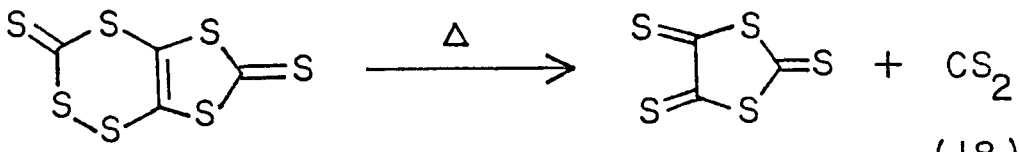
(17)

If Equation 14 (p 38) is a valid explanation of the formation of 22, then by introduction of a more powerful dienophile than CS_2, intermediate 23 should be diverted from its normal course. Thus benzoquinone was added to a MeCN solution of 6 prior to addition of the I_3^- solution. The reaction afforded only the brown decomposition product and benzoquinone.

In another attempt to prepare thione 24, CS_2 was reduced in MeCN. The solvent was removed and the residue was dissolved in ethanol.

Addition of benzoquinone and I_3^- under Ar again yielded only brown decomposition product and benzoquinone.

As this method seemed unsuccessful, attempts were made to produce 24 by heating 22 until CS_2 is expelled (Equation 18). Intermediate 23 should be trapped by benzoquinone.



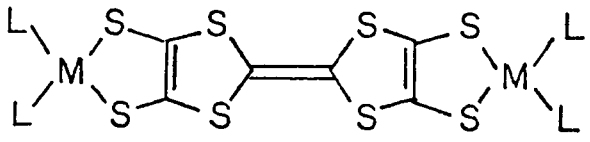
(18)

22 23

Thermolysis of 22 in the presence of benzoquinone was carried out in a variety of solvents including benzene, ether, ethanol, acetonitrile, and methylene chloride under inert atmosphere at each respective boiling point. In all cases, the yellow insoluble powder darkened slowly but did not react with benzoquinone. No further investigation of compound 22 was attempted.

C. Preparation and Characterization of Some Bis-(1,3-Dithiole-4,5-Dimercapto-2-Thione) Nickelates.

A principal goal of this research is to prepare binuclear transition metal complexes which incorporate a tetrathiafulvalene bridging moiety. The general structural formula for these complexes is shown below (M = Ni, Pt, Pd, Co)(L = PR_3, RS-).



Toward this end, we conceived the following scheme (Equation 19, p 41). The nickel dithiolene complex 25 (p 44) is prepared by addition of Ni^{2+} to thione 6 as described previously (p 11). From this reaction mixture, a dark green tetrabutylammonium salt is isolated in quantitative yield. This material had previously been prepared by Steimecke, et al.[82] and was reported to be the dianion salt 25 (z=2) (p 44). Coulommetry and elemental analysis experiments indicate it instead to be the monoanionic salt, 25 (z=1) (p 44). Recently Steimecke, et al. have corroborated these results.[83]

The dianionic salt 25 (z=2), which is realized in quantitative yield upon workup when O_2 is excluded rigorously, is the initial product of the reaction of Ni^{2+} and thione 6. This deep blue solid is isolated as irridescent black needles. The monoanionic salt 25 (z=1) apparently forms upon air oxidation of 25 (z=2) in solution. Both compounds are stable in air as the solids. The monoanionic complex salt, also a black solid, has been realized in two distinct crystalline forms, needles and cubes.

The cyclic voltammetry of 25 (z=1) was investigated (Figure 1, p 43), and it was found to exhibit a reversible one electron reduction

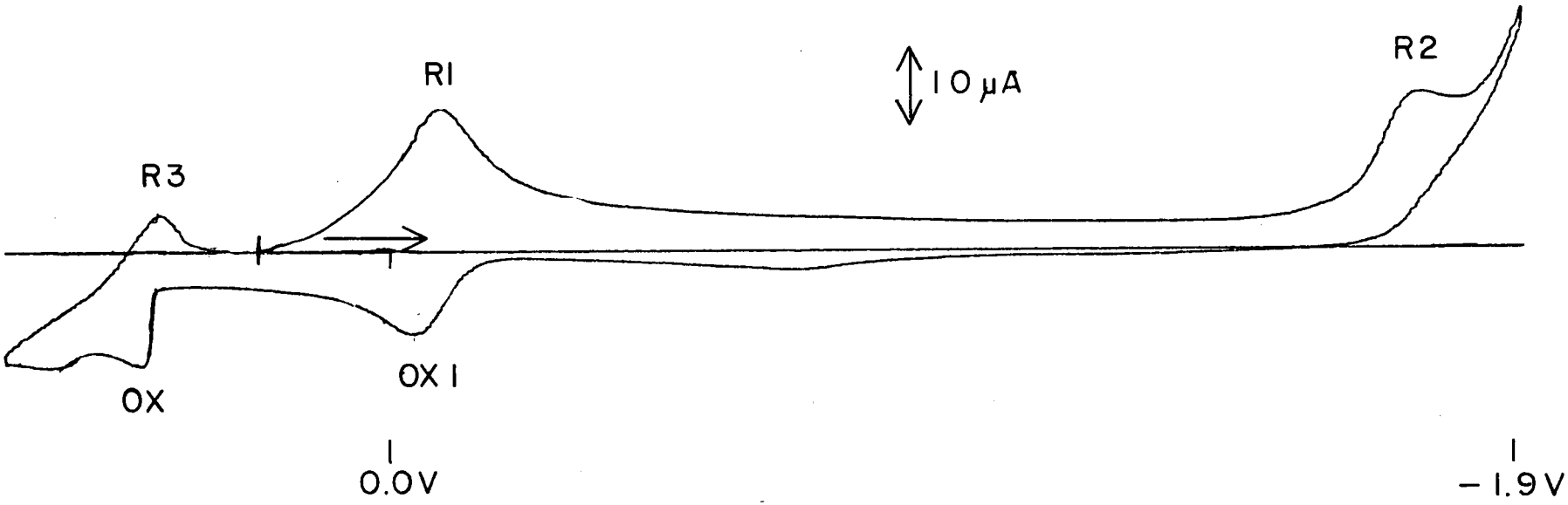
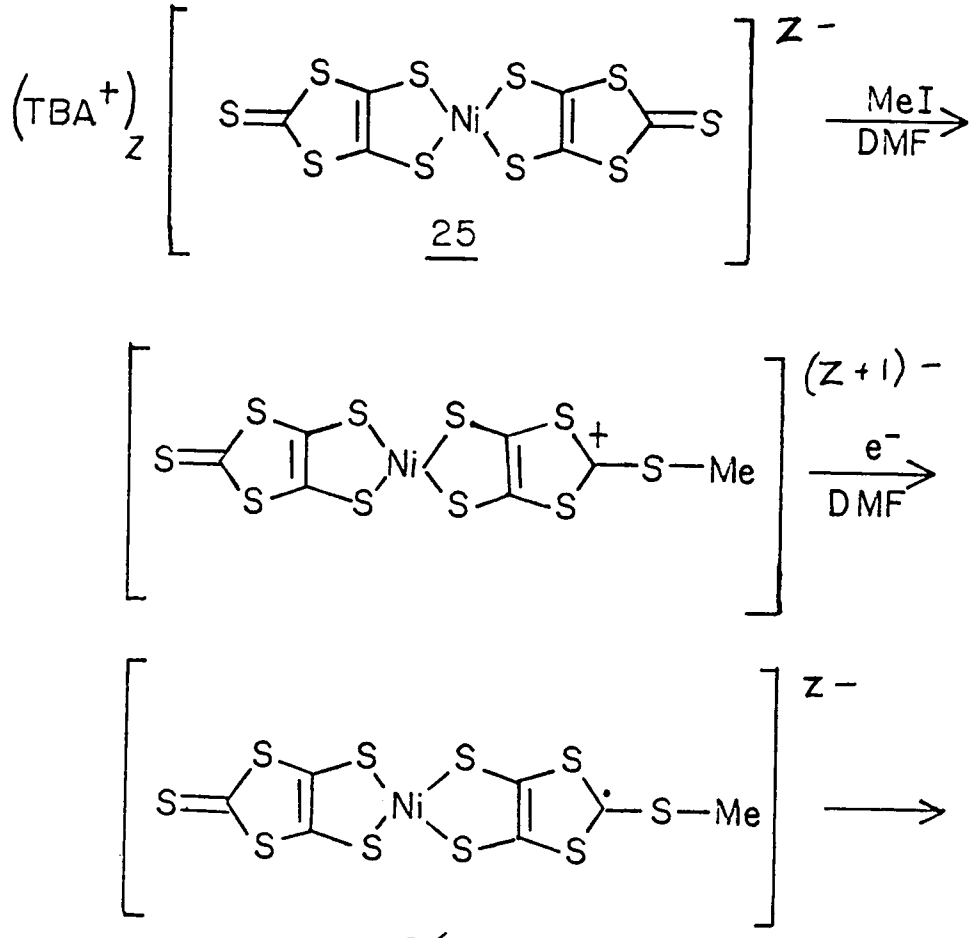
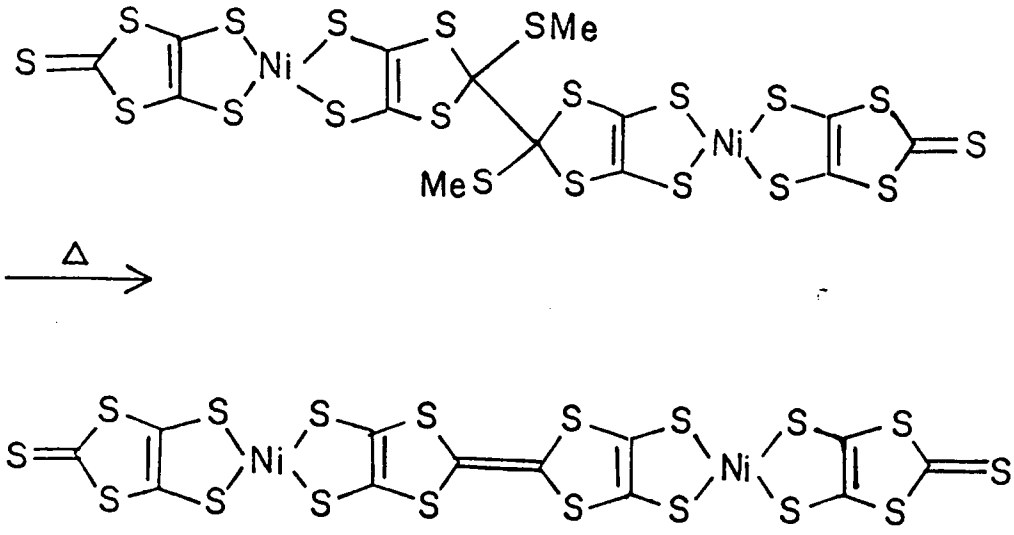


Figure 1. Cyclic voltammogram of $Ni(C_3S_5)_2^{1-}$ at 121 mV $sec.^{-1}$
Platinum; Concentration 1.2g/L; 0.1 Molar TEAP; DMF; versus SCE.



(19)



(R1) at -0.189 volts coupled to a one electron oxidation (OX1) at -0.130 volts, a multielectron irreversible reduction (R2) at -1.79 volts, and a reversible one electron oxidation (OX3) at +0.240 coupled to a one electron reduction (R3) at +0.088 volts versus SCE (Table 1, p 46).

These results are consistent with the chemical properties discussed above. The OX1/R1 couple indicates the facile and reversible interconversion of 25 (z=1) and 25 (z=2)(Equation 20). The multi-electron wave R2 eluded analysis via exhaustive coulometry. Presumably, it involves the reductive disproportionation of the complex via some unknown pathway.

$$\left[Ni(C_3S_5)_2\right]^{1-} + e^- \rightleftharpoons \left[Ni(C_3S_5)_2\right]^{2-} \quad (20)$$

25 (z=1) 25 (z=2)

The process responsible for OX3 represents the oxidation of monoanion 25 (z=1) to the neutral complex 25 (z=0). This hypothesis is reinforced by the observation that wave R3 appears to be a stripping wave which indicates the deposition of the insoluble neutral complex on the electrode surface. In order to verify this, exhaustive coulometry was carried out on 25 (z=1). Electrolysis in DMF or MeCN resulted in

Table I. Peak Potentials and Current Function for $Ni(C_3S_5)_2^{-1}$.[a]

R1	R2	OX1	OX2	R3	Current Function[b]
-0.189V	-1.79V	-0.130V	+0.240V	+0.088V	0.53

(a) 0.1M TEAP, MeCN, SCE, 121 mV sec^{-1}.

(b) Amps liters $sec^{-\frac{1}{2}}$ $volts^{-\frac{1}{2}}$ $moles^{-1}$ cm^{-2}.

the decomposition of the complex and an excessively large number of coulombs. The ligands of the neutral complex are apparently very labile and are displaced by solvent molecules. The ligand molecules are then electrochemically oxidized further to give some unknown product. This type of reaction is common among nickel dithiolene complexes especially in such solvents as DMF and MeCN which are effective ligands.[98]

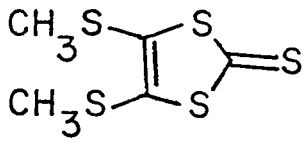
Coulommetry of 25 (z=1) in a weaker nucleophilic solvent ($MeCl_2$) gave the neutral complex 21 (z=1) in quantitative yield, after passage of one equivalent of electrons.

At this point, the chemistry of these nickel complexes was investigated in order to determine their usefulness in the preparation of binuclear metal dithiolene complexes. The green monovalent salt 25 (z=1) was allowed to react with MeI in DMF solution. It was hoped that alkylation would occur on the thione sulfur exclusively as per the above scheme (Equation 19, p 43). Upon standing overnight, a black solid was realized. Owing to its insolubility in all portions of solvents used, it was hoped to be the neutral monomethyl adduct 26 (p 43).

The infrared spectrum of 26 yielded little information other than evidence of a C=S stretch (1055 cm^{-1}). The elemental analysis was somewhat complex indicating a 5.0% by weight loss of nickel with a gain in the number of carbons.

The critical point which arises is where on the complex did alkylation take place. In order to investigate this question further, methyl iodide was added to the dianion salt 25 (z=2) and the monoanion salt 25 (z=1). Heating these mixtures to 80° or above gave no precipitate. Instead, a golden yellow oil was isolated. The spectral properties and melting point of the resulting solid indicated this compound to be the 1,3-dithiole-4,5-dithiomethyl-2-thione, 27 (p 23). Reaction of the black, methylated nickel complex 26 with additional MeI also gave 27.

From these results it seems reasonable to assign the dimercapto sulfurs as the point of alkylation. Based on this and the elemental analysis, it is suggested that the black methyl adduct is a cluster compound. At lower temperatures only partial alkylation ensues, and compound 28 results.

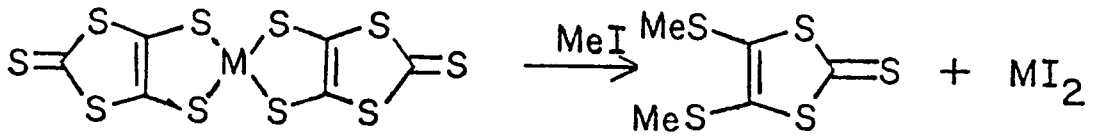


27

$(TBA)_1 Ni_4(C_3S_5)_7(C_3S_5CH_3)_2$

28

This seems reasonable as it has been shown that square-planar dithiolene complexes tend to alkylate at the chelating sulfurs (Equation 21).[99]



(21)

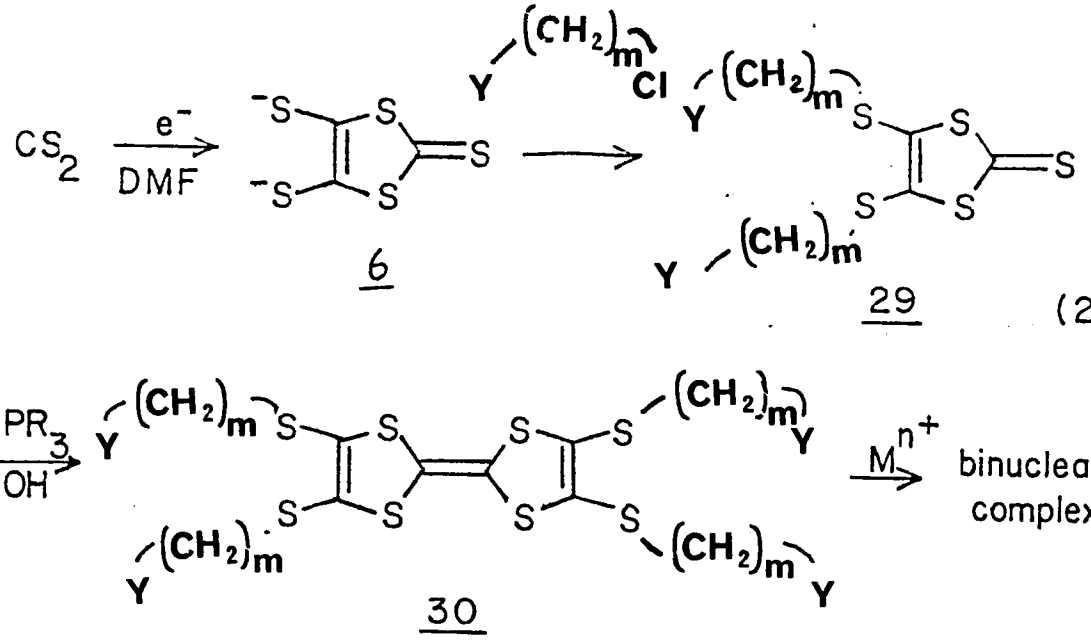
M = transition metal

27

Also, molecular orbital calculations carried out by Gray, et al.[100] indicate the highest electron density is found about the metal bonded sulfur atoms. This is so even through various oxidation states of the complex.

D. Syntheses and Characterization of Arm-TTF.

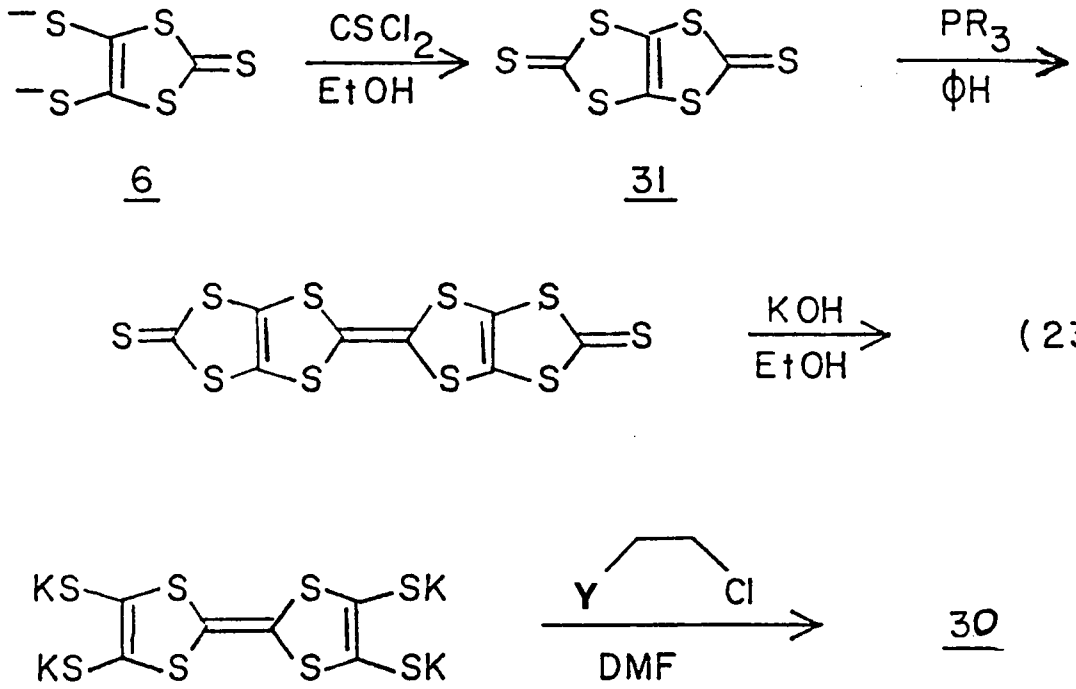
A different approach to the preparation of binuclear complex ligands is now outlined. Again, thione 6 (p 11) was chosen as a convenient starting point. Under this plan, thione 6 is alkylated with either 2-chloroethyl methyl sulfide or 3-chloropropyl thioacetate. These compounds are dimerized at the thione giving tetrasubstituted tetrathiafulvalenes. As a final step, the transition metal will be introduced (Equation 22, p 50).



Thione 6 readily alkylated and yielded "arm-thiones" such as 29. These compounds and others are called "armed" because of the alkyl chains about the chelating site. The coupling reaction to the tetrathiafulvalenes was attempted with various phosphites PR_3 (R = -OMe, -OEt, $-OC_6H_5$) and $P(C_6H_5)_3$ in benzene, toluene, and xylenes without success.

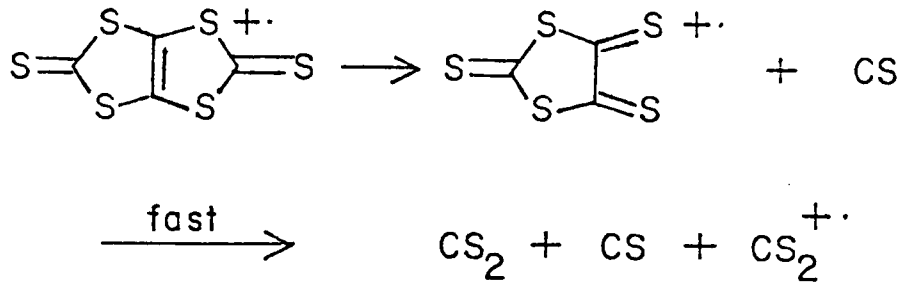
Another approach was devised. The mercapto sulfurs of thione 6 are protected against reaction prior to the coupling step by a chemical protecting group. Once the TTF is formed, the protecting group is removed and alkylation with the "arm" agents is performed. Equation 23 (p 51) outlines this scheme.

Trithiocarbonate was used as the protecting group in this scheme. The advantages of this group are manifold. Treatment of



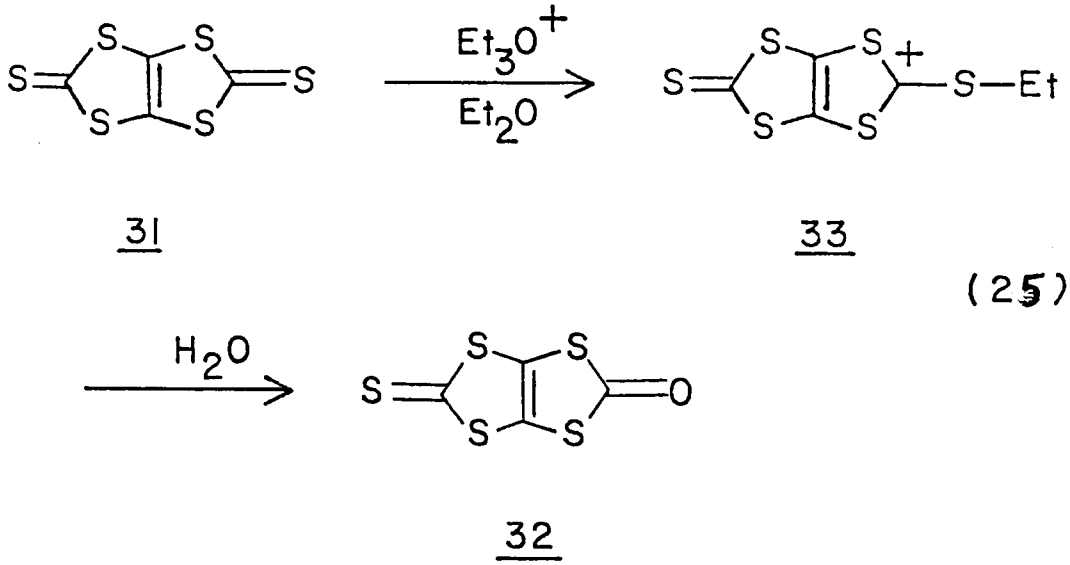
thione 6 in ethanol with thiophosgene gives 31 (p 50) in quantitative yield.[100] This compound is relatively inert, but the 1,3-dithiole ring is easily opened in basic solution.

The chemistry of dithione 31 was investigated. The mass spectrum indicated a parent molecular ion of $^{m}/e$ equal to 240 ($C_4S_6^+$) and a base peak at $^{m}/e$ equal to 76 (CS_2^+). The fragmentation reaction of 31 is shown in Equation 24 (p 52). Attempts to couple dithione 31 to the corresponding TTF met with failure. Again, a variety of phosphorus (III) reagents were used [$P(OEt)_3$, $P(OMe)_3$, $P(OC_6H_5)_3$, $P(C_6H_5)_3$]. In all cases, 31 was completely decomposed in the reaction.



(24)

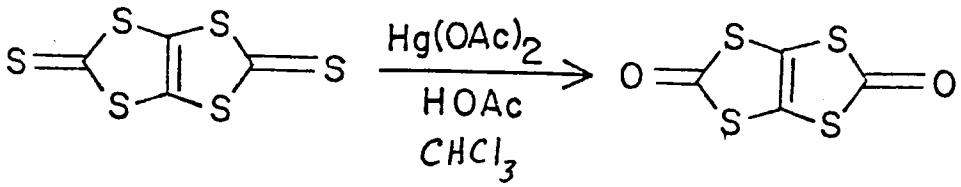
Recently, it was reported that coupling reactions with phosphines are possible with carbonyls or selenones substituted for the thione groups in compound 31.[102] The possibility of replacing thione sulfurs with oxygen was investigated using two strategies. The thione 31 can be replaced with oxygen, or a different, more reactive protecting group can be added to thione 6 directly. Along the former pathway, two methods were postulated (Equations 25, and 26, p 53).



31 33

(25)

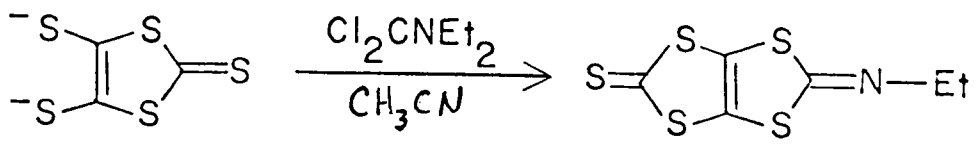
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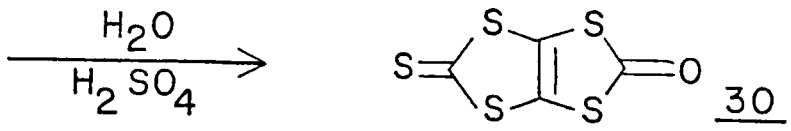
31 34 (26)

In the first method (Equation 25, p 52), 31 is alkylated with triethyloxonium tetrafluoroborate. The resulting salt, 33, could be hydrolyzed to give 32. Alternatively, 33 could be electrochemically reduced to a radical which should couple to the hexathioorthooxylate as in Equation 11 (p 13). Unfortunately, the alkylation reaction does not proceed cleanly, so this method was discontinued. The second method (Equation 26) involves the reaction of 31 with mercuric acetate.[84] Upon treatment of 31 with $Hg(OAc)_2$ in a 50/50 $HOAc/CHCl_3$ mixture, dione 34 is realized but in poor yield.

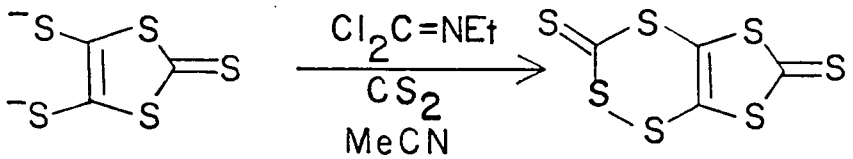
The use of other protecting groups was investigated. Reaction of 6 with isocyanide dichloride was examined (Equation 27, p 54). Isocyanide dichlorides were reported to react with mercaptans in ethanol. When ethyl isocyanide dichloride was added to a solution of 6 in MeCN, the red color of 6 was discharged and a yellow powder was isolated upon work-up. Spectral analysis indicated this solid was not 35 as expected. Instead, the yellow solid was found to be 22 (p 26), the oxidation product of thione 6 (Equation 28, p 54).



6 35 (27)

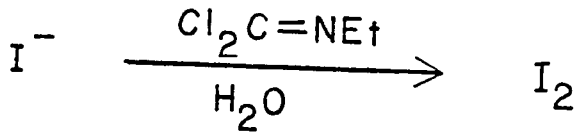


30



6 22 (28)

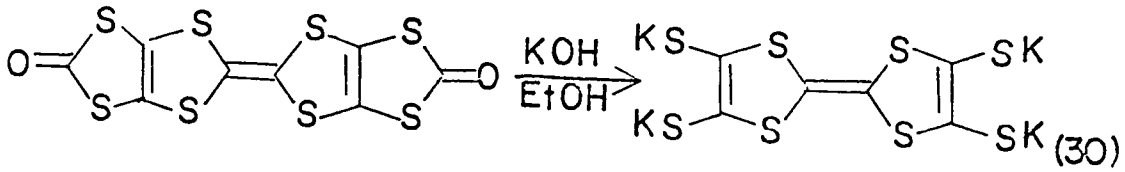
From this experiment it seems that isocyanide dichlorides are better electron transfer agents than electrophiles. This is supported by another experiment. Addition of water to mixtures of isocyanide dichloride, acetonitrile, and TBAI yields copious amounts of iodine via oxidation of I^- by the isocyanide (Equation 29). If isocyanides are capable of oxidizing iodide ion, it is not surprising that they will oxidize thione 6.



(29)

The final possibility for preparation of an oxygen thiapen involves using phosgene (CCl_2O) as a protecting group.[83] Addition of phosgene to solutions of thione 6 or the zinc complex of thione 6 in either acetone or ethanol resulted in the isolation of thione 30 in less than 5% yield. The remaining starting material polymerizes.

As a result of these investigations, the mercuric acetate hydrolysis reaction was chosen as he best source of the oxygen thiapen. Treatment of 34 with $P(OEt)_3$ in benzene yields the tetrathiafulvalene 36 in 22% yield. Treatment of compound 36 in ethanol with KOH yielded compound 37 (Equation 30).



(30)

36 37

The resulting tetrapotassium salt 37 separated as a pink solid in alcoholic KOH but dried to black. Compound 37 is stable in air for several hours. In water, it appears blue, and in DMF it is dark green. Exhaustive coulommetry of 37 indicates it oxidizes to a neutral compound after removal of approximately four electron. Treatment of compound 37 with 2-chloroethyl methy sulfide ($ClCH_2CH_2SCH_3$), 3-chloropropyl thioacetate ($ClCH_2CH_2CH_2SCOCH_3$), and 2-chloroethyl amine

hydrochloride ($ClCH_2CH_2NH_3^+Cl^-$) gave the three desired "arm"-TTF compounds, 38, 39, and 40, respectively (p 58).

Arm-TTF ligands 38 and 39 were isolated as brown solids and were soluble in a variety of organic solvents. The nmr spectra were consistent with the indicated structures. Ligand 40 was more remarkable. It was isolated as a highly insoluble blue solid. The nmr spectrum of a $CDCl_3$ extract of this solid was consistent with the structure shown. The extent of protonation of the amine groups could not be determined due to the complexity of this spectrum. The salt could not be neutralized with NEt_3 or aqueous $KHCO_3$. EPR examination of this solid by epr in a saturated dimethylsulfoxide solution indicated a paramagnetic compound.

The epr spectrum, which is shown in Figure 2, (p 57) exhibited nine lines in an intensity pattern indicative of eight equivalent hydrogen atoms in the radical cation (a_H=1.20 Gauss, g=2.0323). In situ electrolysis in the cavity of the epr spectrometer revealed that the species producing the epr signal was electroactive and coupled to two successive electron transfer reactions. These data are consistent with assignment of structure 40 to the paramagnetic species. However, the elemental analysis indicates that the blue solid isolated was not a simple mixture of the hydrochlorides of 40.

E. Attempted Preparations of Binuclear Complexes.

The preparation of the Pt^{2+} and Ni^{2+} binuclear complexes of arm-TTF 38 was attempted. Addition of 2.0 equivalents of

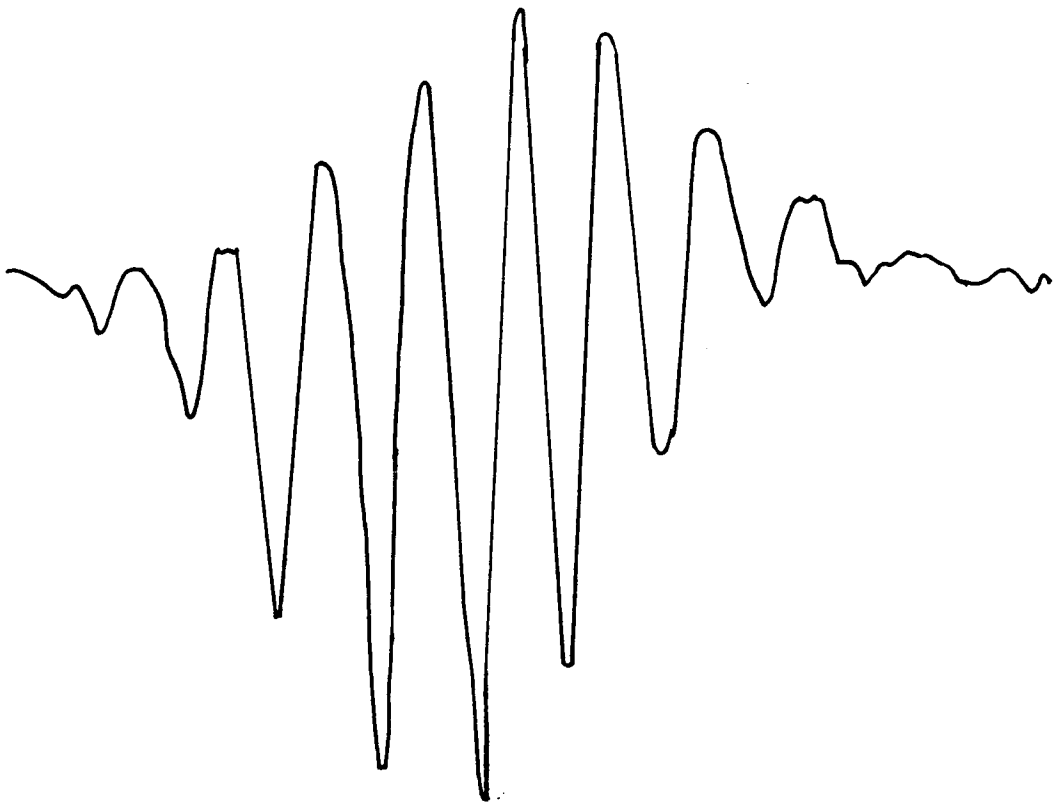
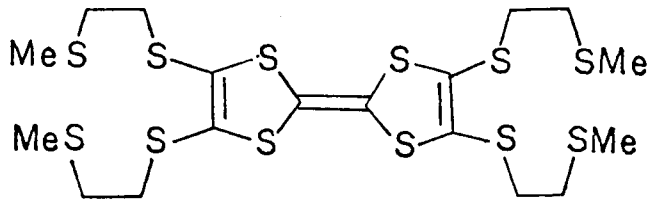
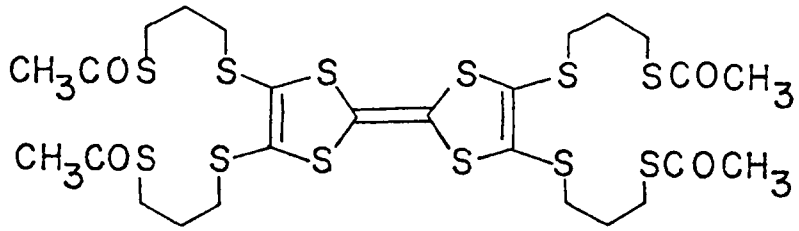


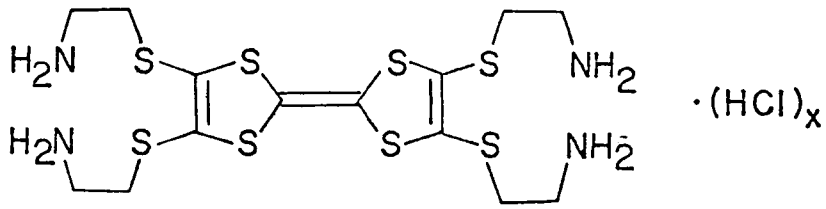
Figure 2. Electron Paramagnetic Resonance Spectrum of the blue solid 40.



38



39



40

$Pt(MeCN)_4(ClO_4)_2$ to the ligand in acetonitrile yielded a black, highly insoluble solid. Cyclic voltammetry of this solid gave no evidence of either starting material. The elemental analysis of this solid suggested the presence of a platinum metal impurity.

Addition of NiI_2, $NiBr_2$, $Ni(ClO_4)_2$, or $NiCl_2$ to ligand 38 in MeCN solution gave only starting materials. Possibly the resulting complexes are too labile to survive work up.

F. The Cyclic Voltammetry of Compounds Under Investigation.

Cyclic voltammetry was used in this work as an analytical tool. This section is a survey of the electrochemical properties of the synthetic intermediates already discussed in the text.

The electrochemical behavior of the thiones prepared via the alkylation of 6 (p 11) are in general all the same. Thus, the discussion of their electrochemical behavior is limited to one illustrative case. The cyclic voltammogram of the dimethyl adduct of 6, thione 27 (p 23), exhibited an irreversible apparent two electron reduction wave (R1) at -1.9 volts versus SCE (Figure 3, p 60). On the reverse sweep an irreversible apparent two electron oxidation wave (OX1) at +0.42 volts is evident.

This behavior is typical of 1,3-dithiol-2-thione moieties.[103] The chemistry concurrent with these data is shown in Equation 31. The apparent two electron reduction (R1) results in the loss of CS from the molecule. On the reverse scan, the resultant dianion is oxidized (OX1) to the dithione. The reduction of this dithione was not observed.

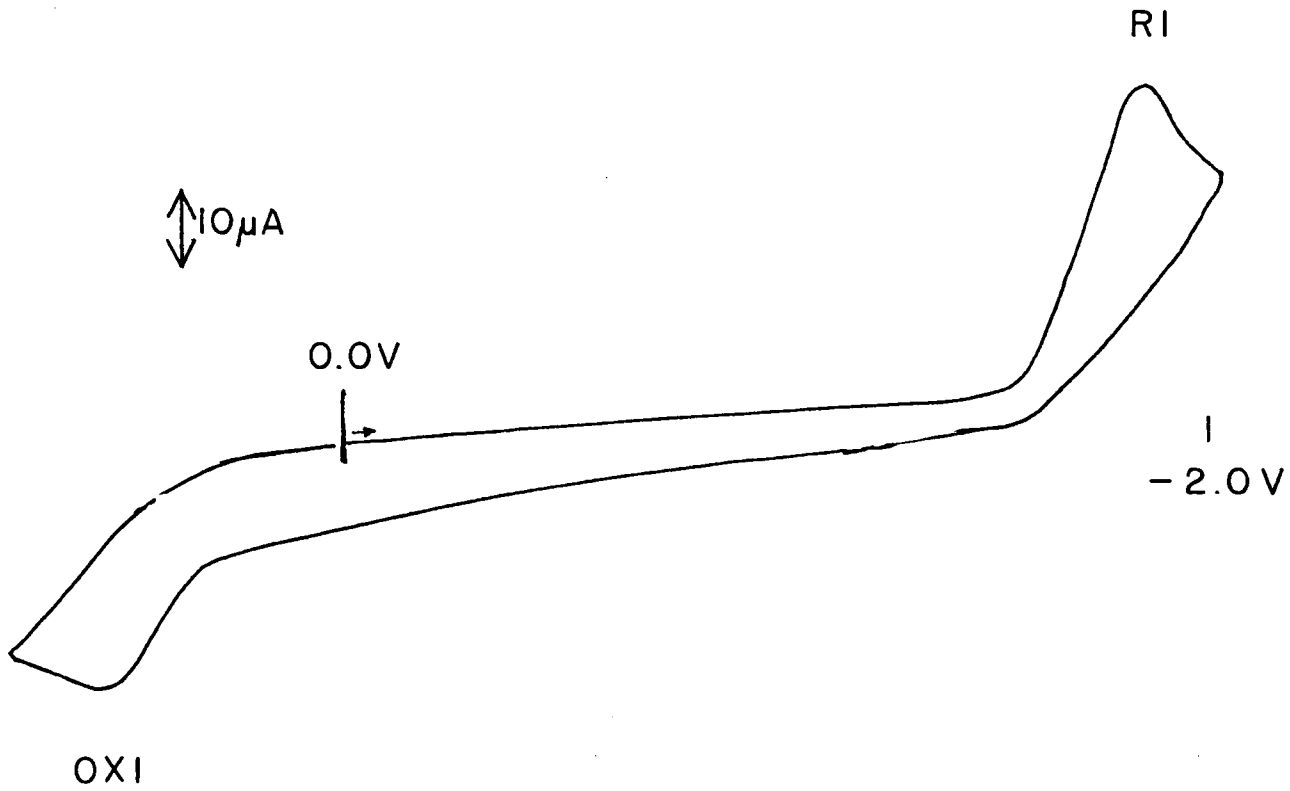
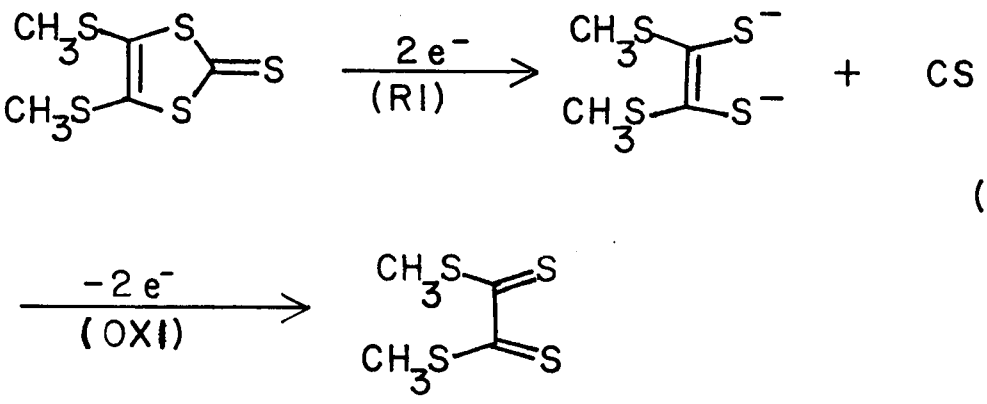


Figure 3. Cyclic Voltammogram of thione 27 at 121 mV sec^{-1}.
Platinum; Concentrate 1.0 g/L; DMF; versus SCE.

The cyclic voltammogram of the dioxy-thiapen 34 (Figure 4, p 62) exhibited an irreversible apparent two electron reduction wave (R1) at -1.93 volts versus SCE. On the reverse sweep a new redox



(31)

couple (OX2/R2) is evident, the shape of which does not correspond to the theoretical behavior for a reversible electron transfer. The reduction wave (R2) of this couple features a spike shaped peak followed by a marked decrease in current. Voltammetric data are given in Table II (p 63). The chemistry concurrent with these data is illustrated in Equation 32 (p 64). The apparent two electron reduction (R1) is typical of cyclic thiocarbonates. The electron transfer is supposedly followed by a very fast loss of CO. On the reverse sweep the resultant dianion is oxidized by an apparent two electron process (OX2) to the neutral dithione 41. The spiked reduction wave R2 is consistent with the reduction of this species adsorbed on the electrode surface.

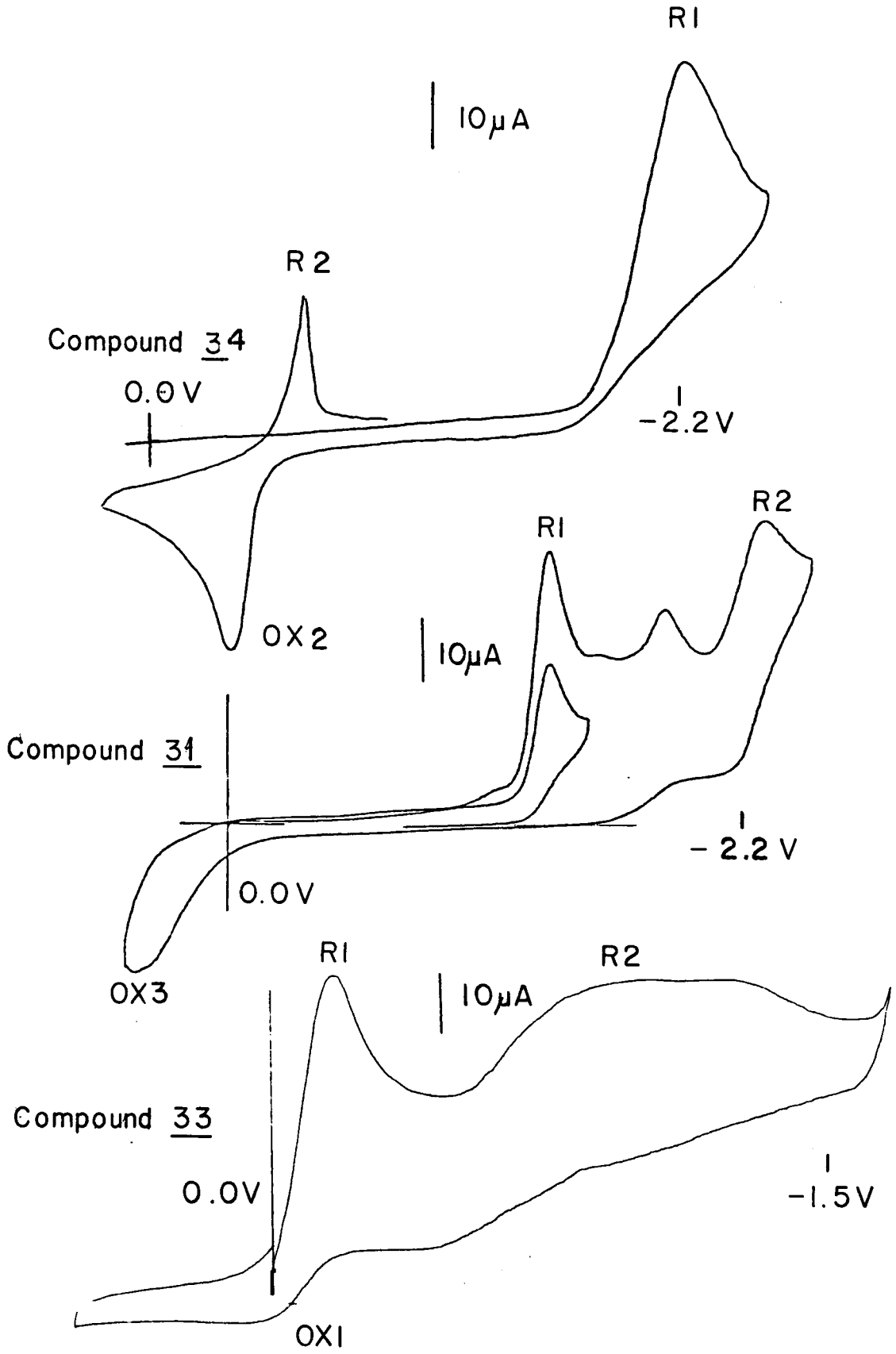


Figure 4. Cyclic Voltammogram of Thiapens 31, 33, and 34 at 10.

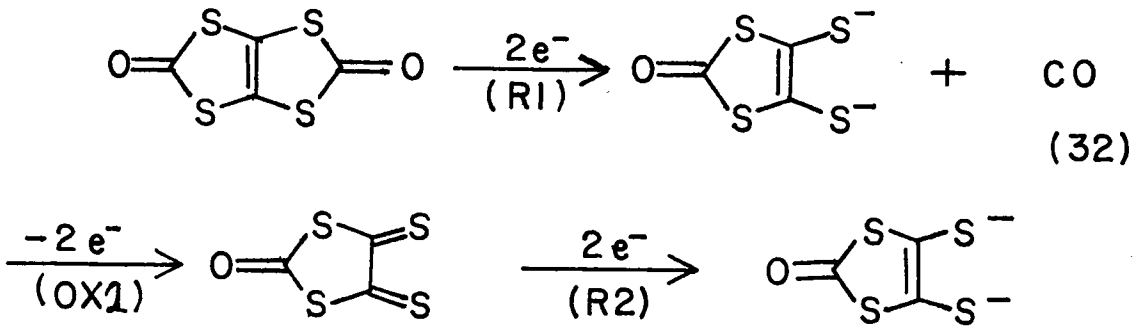
Table II. Peak Potentials and Current Functions of Thiapens

Compound	R1	OX2	R2	Current Function[c]
31[a]	-1.32V	+0.366V	-2.16V	0.33
34[a]	-2.15	-0.300	-0.619	0.40
33[b]	-0.183	-0.522	-0.9±.20	0.40

(a) 0.1M TBABr, DMF, versus SCE, 121 mV sec^{-1}.

(b) 0.1M TEAP, MeCN, versus Ag, 0.01M $AgNO_3$.

(c) R1; amps liters $sec^{-\frac{1}{2}}$ $volts^{-\frac{1}{2}}$ $moles^{-1}$ cm^{-2}.



The cyclic voltammogram of the dithiothiapen 31 (Figure 4, p 62) exhibits an irreversible apparent two electron reduction wave (R1) at -1.32 volts versus SCE. As in the voltammetry of 34 above, an irreversible apparent two electron oxidation wave is evident on the reverse scan (wave OX3). The reduction of the resulting dithione species was not observed. The voltammetric data given in Table II are consistent with a cyclic thiocarbonate structure. The initial two electron reduction (R1) indicates the loss of CS and the formation of dianion 6 (p 11).

The cyclic voltammogram of the methylated dithiothiapen 33 (Figure 4, p 62) exhibited an irreversible reduction wave (R1) at -0.138 volts versus SCE and a broad, irreversible reduction wave (R2) at -0.9 volts. On the reverse sweep a small irreversible wave, (OX1)

at 0.0 volts, are evident. The shapes of these waves do not correspond to the theoretical behavior for a reversible electron transfer. In the event of repeated scans, all these waves diminish in intensity. This is probably due to passivation of the electrode surface by the species produced. The chemical reactions involved were not investigated further.

The cyclic voltammogram of the TTF tetra-potassium salt 37 (Figure 5, p 66) exhibited a reversible apparent one electron oxidation (OX1) at -1.51 volts versus a silver reference electrode. Upon further scanning a second reversible apparent one electron oxidation (OX2) and two quasi-reversible apparent one electron oxidations, (OX3) and (OX4), are evident. On the reverse sweep a spike shaped reduction wave (R3) at -0.823 volts is observed. This is followed by two reversible apparent one electron reductions, (R2) and (R1). If only OX1, OX2, and OX3 are traversed on the return sweep, the OX3/R3 couple is revealed to be reversible. The voltammetric data are presented in Table III (p 67).

The redox couple (OX1/R1) indicates a facile and reversible interconversion of the tetra-anion 37 and the radical trianion. The redox couple (OX2/R2) arises from the interconversion of this radical trianion and the dianion. The other oxidation waves, (OX3) and (OX4), represent the formation of the radical monoanion and neutral tetrathione species, respectively. The spike shaped reduction wave (R3) indicates the reductive removal of a surface adsorbed moiety,

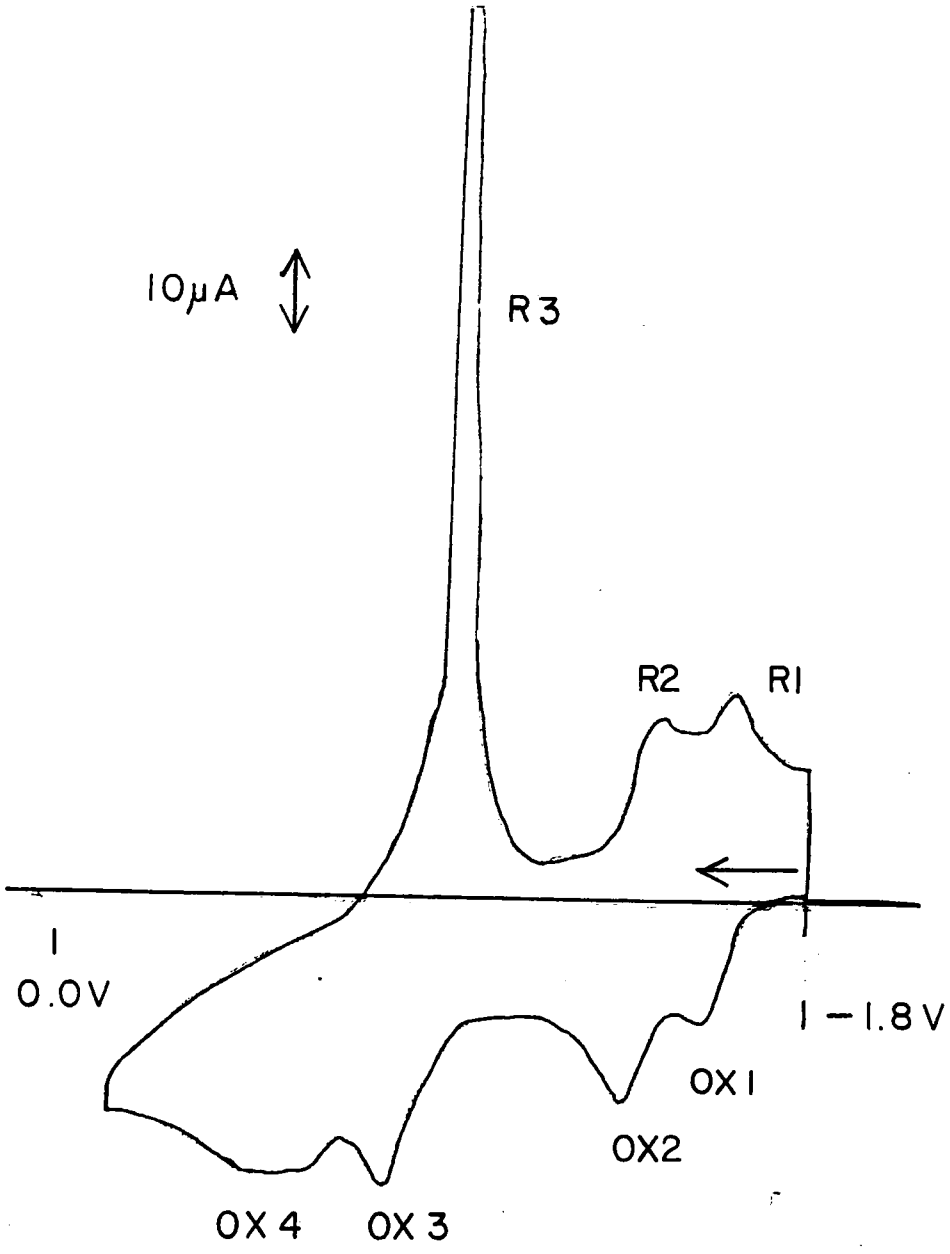


Figure 5. Cyclic Voltammogram of $K_4C_6S_8$ at 50 mV sec^{-1}.
Platinum; Concentration 0.2 g/L; 0.10 Molar TEAP; DMF; versus SCE.

Table III. Peak Potentials and Current Functions of $K_4C_6S_8$.[a]

OX1	OX2	OX3		Current Function[b]
-1.50V	-1.31V	-0.660V	-0.367V	0.52

R3	R2	R1
-0.823V	-1.39V	-1.59V

(a) 0.1M TEAP, DMF, versus SCE.

(b) OX1; amp liters $sec^{-\frac{1}{2}}$ $volts^{-\frac{1}{2}}$ $moles^{-1}$ cm^{-2}.

which is probably the neutral tetrathione. When the working electrode is maintained at a potential on the (OX4) wave, there forms on the electrode surface a bright red-yellow film.

The cyclic voltammetry of the arm-TTF compounds was investigated. The voltammetric data are expressed in Table IV, (p 69). The electrochemical behavior of compounds 38 and 39 are nearly identical and will be discussed together. The voltammetric behavior exhibited by compound 40, however, was unique in appearance and is discussed separately.

The cyclic voltammograms of 38 and 39 (Figure 6, p 70) exhibited two reversible apparent one electron oxidiations, (OX1) and (OX2) at about +0.25 volts and +0.50 volts, respectively, versus a silver reference electrode. On the reverse sweep two reversible apparent one electron reductions, (R2) and (R1), are observed. The voltammetric data are given in Table IV. The shapes of these waves correspond to theoretical behavior for reversible electron transfers. These data are typical of those exhibited by other TTF moieties. The (OX1/R1) couple indicates a facile and reversible electron transfer corresponding to the interconversion of the neutral TTF and the radical cation. The (OX2/R2) couple indicates the facile and reversible interconversion of the TTF radical cation and its dication.

The cyclic voltammogram of the blue ammonium salt 40 exhibited a reversible apparent one electron reduction (R2) at -0.273 volts versus SCE (Figure 6, p. 70). Further scanning revealed a

Table IV. Peak Potentials and Current Functions of Tetrathiafulvalenes.

Compound	OX1	OX2	R1	R2	Current[c] Function
38[a]	+0.260V	+0.506V	+0.189V	+0.428V	0.44
39[a]	+0.225	+0.463	+0.159	+0.385	0.46
40[b]	-0.607	-0.273	-0.398	-0.658	0.36

(a) 0.1M TEAP, MeCN, versus Ag, 0.01M $AgNO_3$, 121 mV sec^{-1}.

(b) 0.1M TBAP, DMSO, versus SCE, 121 mV sec^{-1}.

(c) OX1; amps liter $sec^{-\frac{1}{2}}$ $volts^{-\frac{1}{2}}$ $moles^{-1}$ cm^{-2}.

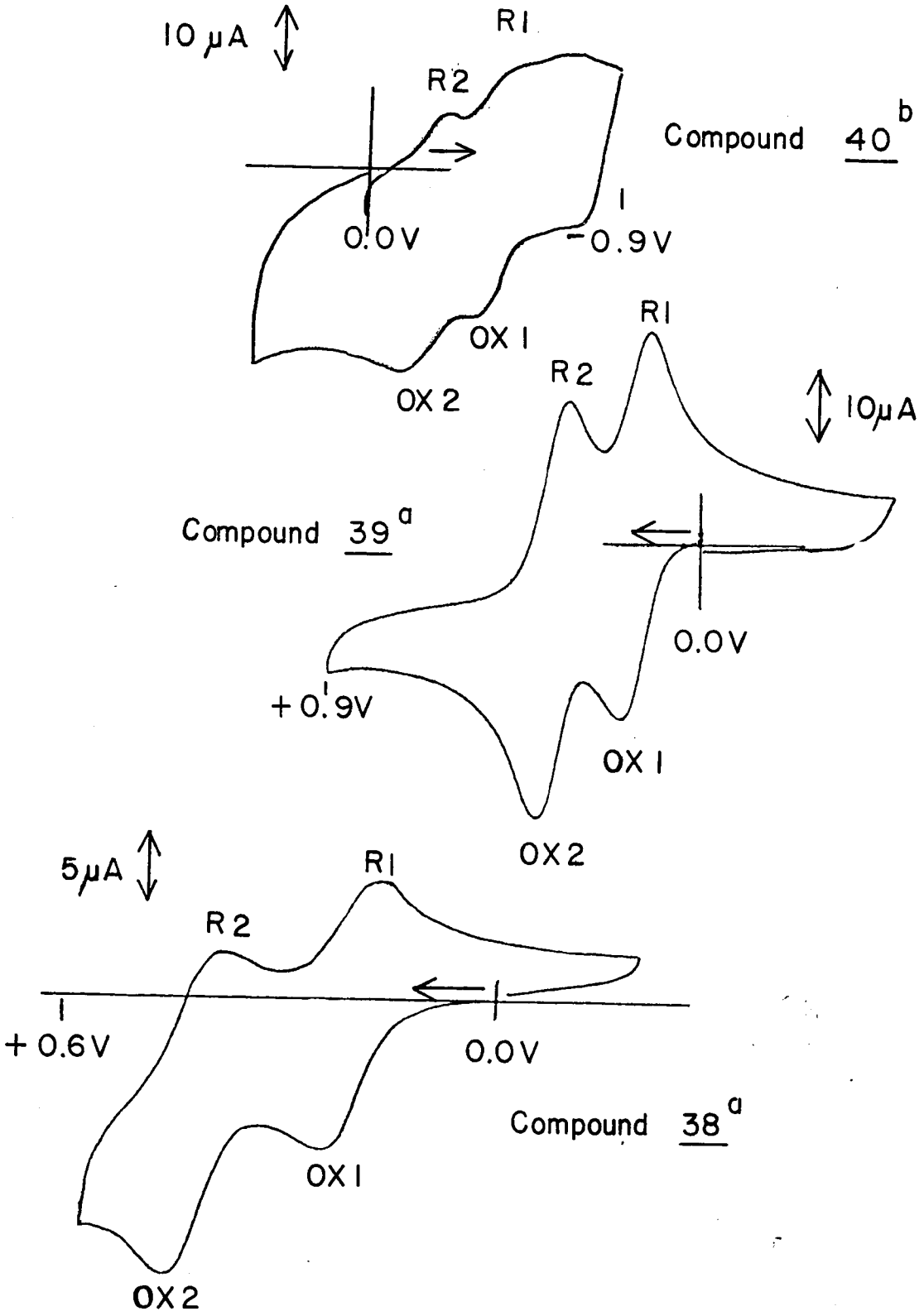


Figure 6. Cyclic Voltammograms of "arm" ligands 38, 39, and 40 at 121 mV sec^{-1}. Platinum; Concentration 0.5 g/L (a) 0.1 Molar TEAP; MeCN; versus Ag_1 0.01 Molar $AgNO_3$; (b) 0.1 Molar TBAP; DMSO; versus SEC.

second reversible apparent one electron reduction (R1) at -0.607 volts. On the reverse sweep two reversible apparent one electron oxidations, (OX1) and (OX2), are observed. The voltammetric data are given in Table IV (p 70). Maximum intenstiy in the nine-line epr signal was obtained by *in situ* electrolysis at potentials between waves OX1 and OX2, see discussion on page 56. The voltammogram of 40 is nearly identical to those observed for 38 and 39 except that the waves for 40 appear at potentials nearly one volt more negative. This phenomenon is probably due to the use of dimethylsulfoxide (DMSO) as a solvent.

The electrochemistry of the solid realized from the reaction of platinum (II) with TTF ligand 38 was examined. The cyclic voltammogram of this substance exhibited a quasi-reversible oxidation (OX1) at +0.677 volts versus SCE. On the reverse sweep an irreversible reduction wave (R1) was observed (Figure 7). The voltammetric data for this substance are given in Table V, (p 73). No attempts were made to discern the concurrent chemical reactions involved.

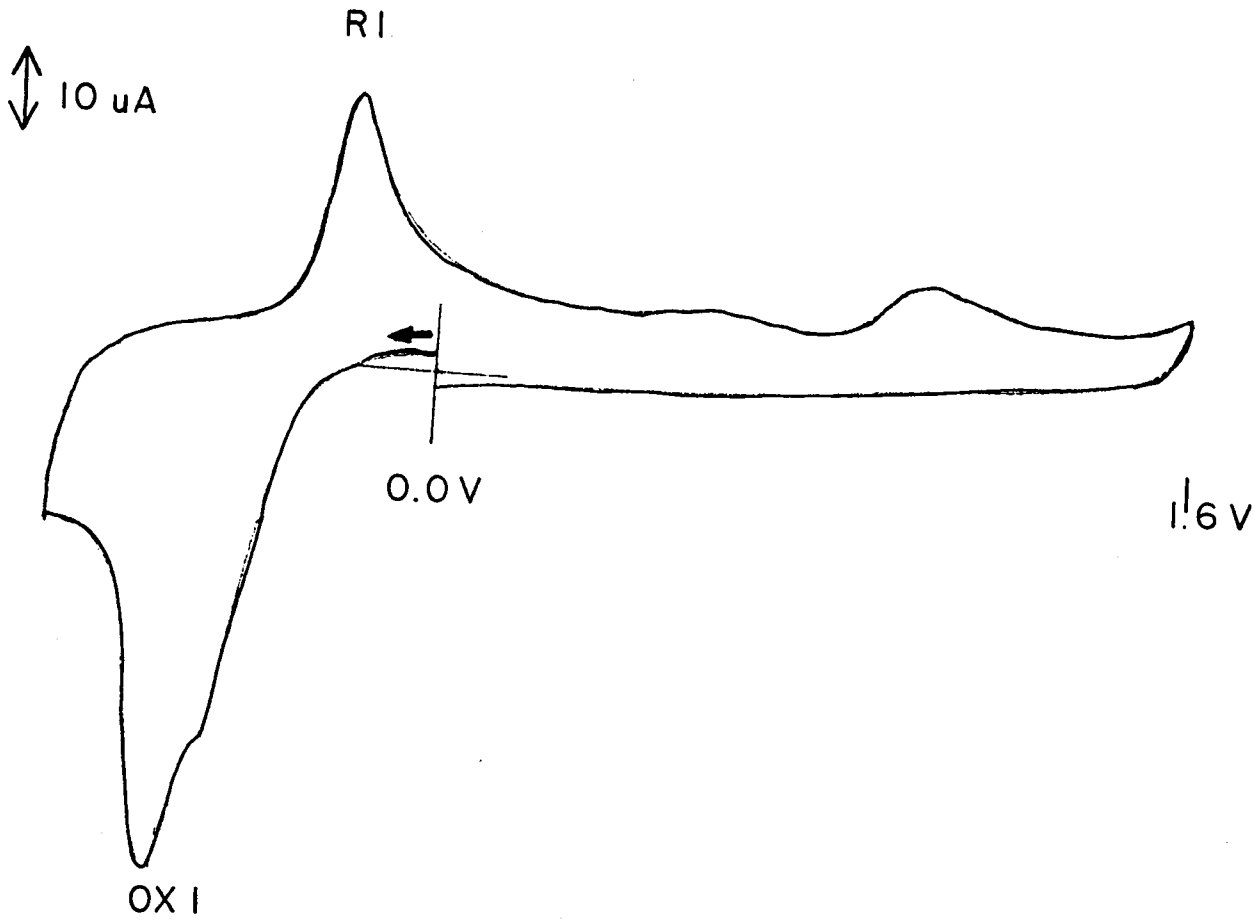


Figure 7. Cyclic Voltammogram of the oxidate of the Binuclear Platinum Complex at 121 mV sec^{-1}. Platinum; Concentration 0.8 g/L; 0.10 Molar TEAP; DMF; versus SCE.

Table V. Peak Potentials and Current Function for Binuclear Platinum Complex.[a]

OX1	R1	Current Function[b]
+0.211V	+0.677V	0.27

(a) 0.1M TEAP, DMF, SCE, 121 mV sec^{-1}.

(b) Amps $liters^{\frac{1}{2}} sec^{-\frac{1}{2}}$ $volts^{-\frac{1}{2}}$ $moles^{-1}$ cm^{-2}.

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