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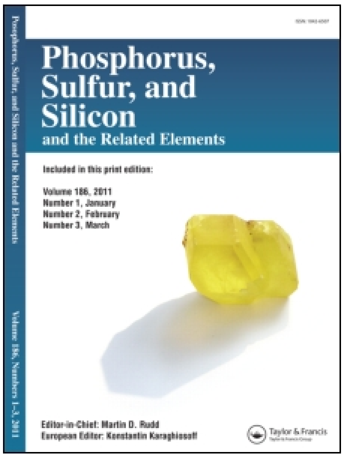

Phosphorus, Sulfur, and Silicon and the Related Elements

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Chemistry of Multi-Sulfur Substituted Arenes and Sulfur Rich Heterocycles - Relations to Advanced Materials

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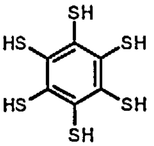
Abstract The synthesis and properties of perthio-substituted benzene derivatives and of electron donor molecules with extended π-conjugation - derived from benzenehexathiol - are described. The corresponding cation radical salts of the donor molecules are characterized as semiconducting solids. From 2,3,6,7-tetrachloro-naphthalene-1,4,5,8-tetrathiol oligomeric nickel and cobalt complexes with ferromagnetic spin ordering between 10 and 20 K are synthesized.

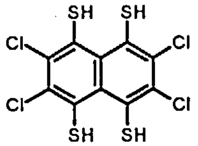
The 4H,8H-thiopyrano[3,2-c]thiopyran-4,8-dione-3,7-dicarboxylic acid is obtained by cycloaddition reactions of 3H,6H-[1,2]-dithiolo[3,4-c]dithiole-3,6-dithione with dimethyl acetylenedicarboxylat. This new ligand for oxophilic metal ions gives polymeric complexes with transition metal ions. The crystal structure of the manganese complex was determined.

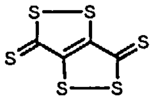
Key Words benzenehexathiol; benzo-1,2,3-trithioles; oligomeric dibenzo-TTF; 2-(fluorene-9-ylidene)-benzo-1,3-dithioles; 2,3,6,7-tetrachloro-naphthalene-1,4,5,8-tetrathiol; oligomeric transition metal complexes; organic ferromagnets; 4H,8H-thiopyrano[3,2-c] thiopyran-4,8-dione-3,7-dicarboxylic acid; cycloaddition reactions

INTRODUCTION

The benzenehexathiol, the tetrachloro-naphthalene-tetrathiol and 1,2-dithiolo-1,2-dithiole-dithione are versatile building blocks for the synthesis of electron donor molecules and ligands for transition metal complexes. The resulting materials are of interest as electrical conductors or semiconductors and as organic solids with unusual magnetic behavior.



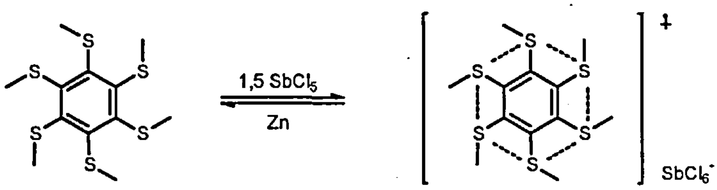




Common to these three species is the high content of sulfur. Considering the high polarizability of the divalent sulfur in organic compounds and its well known capability of stabilizing cationic or radical states, these species could be good candidates for obtaining organic solids with strong electronic interactions between open shell molecules. Such efficient and more dimensional interactions via sulfur-sulfur contacts are one essential prerequisite for instance for a high mobility of charge carriers in organic solids and therefore for electrical conductivity [1,2] as well as for spin-spin-interactions and consequently for unusual magnetic behavior such as ferro- or antiferromagnetic spin coupling [3,4].

BENZENEHEXATHIOL AND HEXAKIS(ALKYLTHIO)-BENZENES

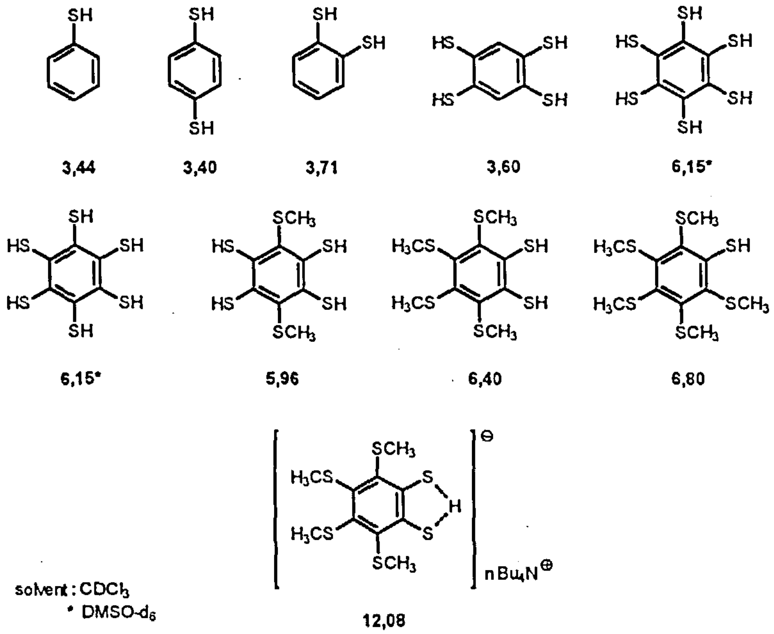
Benzenehexathiol and its precursors, the known hexakis(alkylthio)-benzenes, are interesting species. The perthiosubstitution of the benzene ring leads under different aspects to special properties of these compounds, to be shown by some examples.



λ_{max} : 952 nm
(ClCH$_2$-CH$_2$Cl)
σ_{RT} : $1{,}7 \cdot 10^{-4}$ Scm^{-1}

Hexakis(alkylthio)-benzenes are electron donors and produce stable radical cation salts by the oxidation for instance with antimony pentachloride, shown for the hexakis-(methylthio)-benzene. A stable radical cation salt was isolated as semiconductor. The spin-concentration [5] of the complex is high (~ 0,5 spin/molecule) and by treatment with zinc the starting material is obtained back. That means, the oxidation is reversible, also to be seen by the cyclovoltammetric oxidation [6] ($E^1_{1/2} = 1{,}28$V). But only the first oxidation step is reversible, at higher potentials the molecule loses even more electrons, but in a non reversible way. These findings demonstrate that the six sulfur atoms around the benzene ring stabilize a radical cationic state of the molecule in an excellent way. Hexakis(alkylthio)-benzene radical cations in solution were described and studied ESR spectroscopically for the first time by Testaferri and co-workers [7].

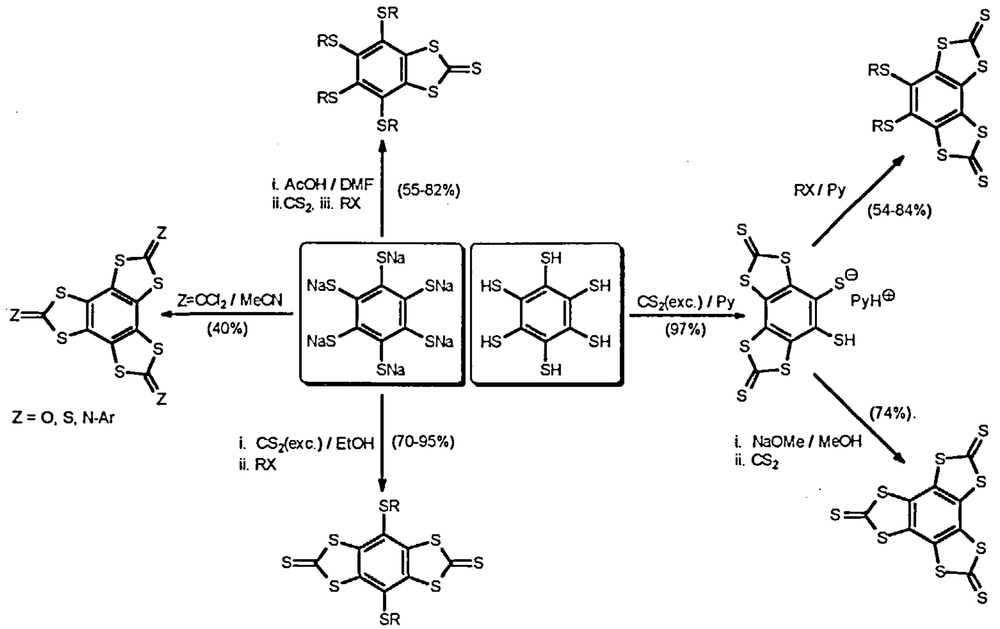
The perthio-substitution of the benzene ring causes also unusual chemical shifts of thiol protons of the corresponding thiophenols.



The range of the NMR signals is shifted by about 3 ppm to lower field in comparison with thiophenols with one, two or four thiol groups. We explain this behavior by a strong stabilization of an internal sulfur-hydrogen bonding in the perthio-substituted moieties. Due to the same reason a more dramatical shift down to 12 ppm was observed in the corresponding tetrabutylammonium 1,2-thiol-thiolates. These 1,2-thiolates represent - in the presence of tetrabutylammonium ions - a new type of proton sponges because they pick up a proton even from a very strong alkaline medium [8].

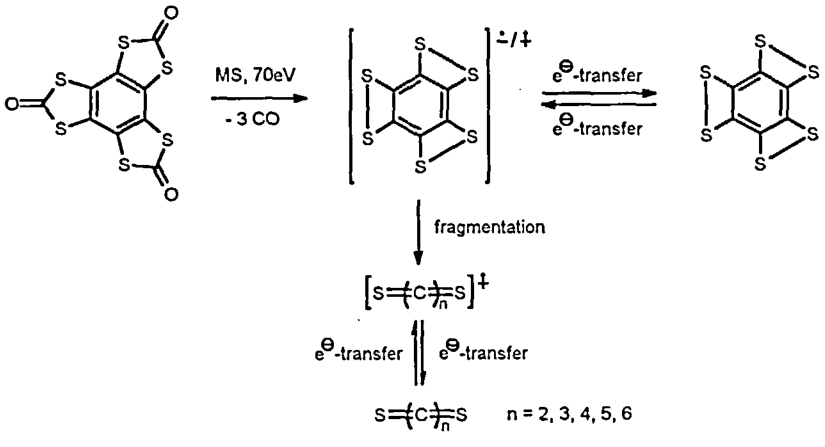
The starting material for synthesizing all the perthio-substituted thiophenols was benzenehexathiolate. For the first time this compound was described as an "in situ reagent" by Testaferri [9]. We made the hexasodium benzenehexathiolate accessible in substance via the sodium induced reductive dealkylation of the benzyl derivative in liquid ammonia. Protonation of the thiolate gave the remarkable stable hexathiol. It is less sensitive to air than the hexathiolate and therefore better to handle and to store [10]

From these two starting compounds and carbon disulfide we could synthesize a large variety of mono-, di- and tri-benzo-1,3-dithiole-2-thiones [11,12] as known precursors of tetrathiafulvalenes, using for instance trialkylphosphites as dimerizing reagents [1,13].



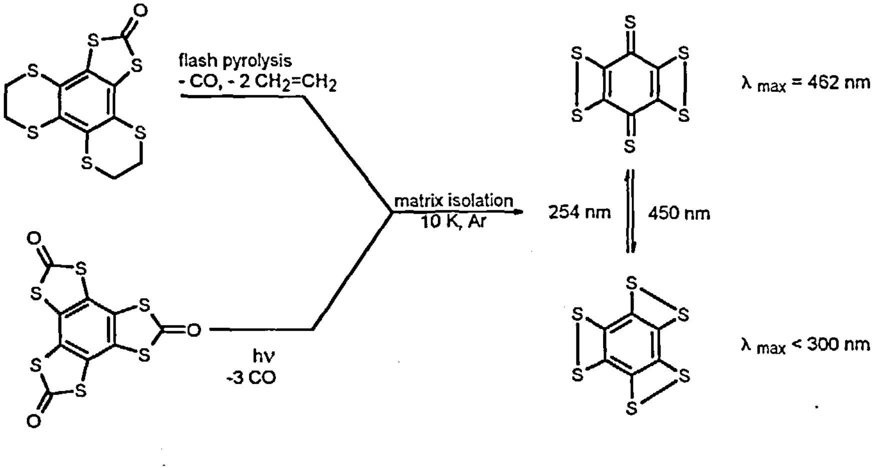
Dependent on the reaction conditions different 1,3-dithiole-2-thiones are regioselectively formed and the yields are among 70 and 90 percent. Whereas the symmetrical tetrathiaindacenedithione was available by cyclization of the hexathiolate with carbon disulfide in ethanol as solvent, the asymmetrical analogue was obtained from the hexathiol in pyridine. Treatment of the hexathiolate with phosgene and phosgene analogues results in the corresponding benzo(tris-dithiole) derivatives [11]. The conversion of the hexathiolate in presence of one equivalent carbon disulfide in a mixture of DMF/acetic acid afforded the "mono"-benzodithiole-thiones after alkylation. These examples demonstrate the value of the benzenehexathiolate for the synthesis of 1,3-dithiole-thiones as TTF-precursors.

A third example, that sulfur atoms as substituents around the benzene ring stabilize unusual structures, is the following one. We observed a stepwise lost of three molecules of carbon monoxide in the mass spectroscopic fragmentation of benzo-tri(1,3-dithiol-2-one) and the benzo-tri(dithiet) cation represented the basis peak of the spectrum [14]. The answer, if the benzo-tri(dithiet) is a real existing molecule, was found in a neutralization-reionization experiment in a tandem mass spectrometer.



After mass selection of the C_6S_6-ions and their neutralization and reionization by electron transfer the existence of the neutral molecule was proved by registration of the recovering signal of the C_6S_6-ion. The life time of the C_6S_6-molecule was determined to be more than 2 μs [15].

With the same technique of neutralization and reionization of mass selected fragment ions of C_6S_6 it was possible to show for the first time that in the series of dithiacumulenes the homologues with n equal five and six are real existing molecules too. In this way the series of homologues could be extended for two members [16]. These sulfur containing cumulenes are of general interest, because some of them are believed to play a crucial role in the genesis of interstellar organic compounds.



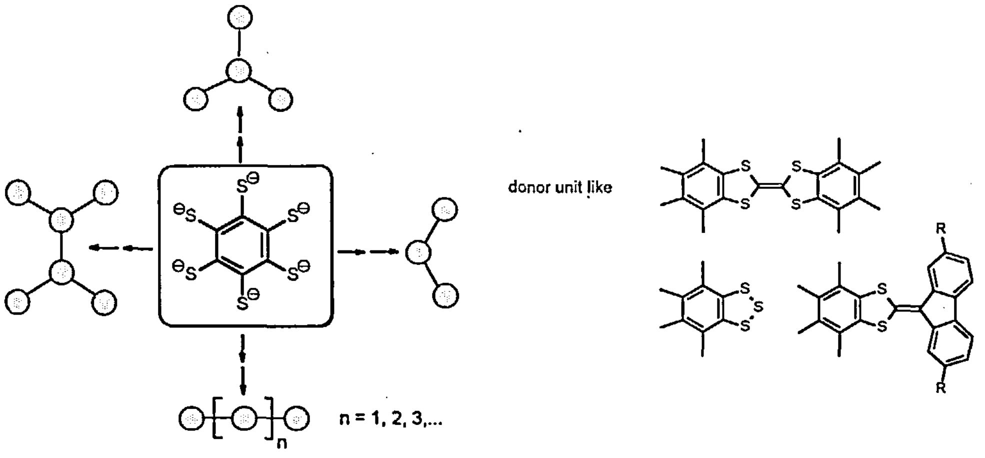
For the benzo-tri(1,2-dithiet) it could be shown by Maier with the help of the matrix isolation technique that there exists at 10 K a photoinduced valence tautomerization between the benzo-tri(1,2-dithiet) and the p-dithio-benzoquinone isomer [17,18].

The benzo-tri(1,2-dithiet) was obtained by photolysis or flash vacuum pyrolysis of two different precursors [18].

These findings about the stabilization of unusual structures in mind, we hoped to find interesting physical properties in sulfur rich donor molecules derived from benzenehexathiol.

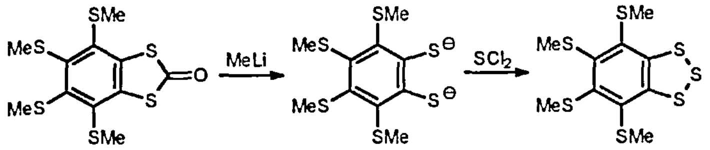
Target Structures of Donor Molecules with Extended π-System Based on Benzenehexathiolate

It was our strategy to synthesize linear, angular and cross-conjugated systems by using 1,3-dithiole-, 1,2,3-trithiole and fluorenylidene-dithiafulvene units.



The comparison of the linear systems on the one hand and the angular or cross-conjugated systems on the other hand should answer the question, whether the latter can exist in their oxidized form in a stable triplet state. From molecules with such states unusual magnetic properties are to be expected.

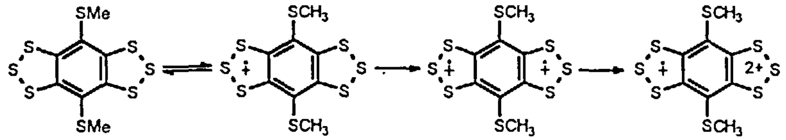
Benzotrithioles. We have found that the perthio-substituted benzo-1,2,3-trithioles are a new type of donor molecules with interesting properties. These compounds are available from the corresponding 1,3-dithiol-2-ones by cleavage of the dithiole ring with bases like alkoxid, sodium hydroxide in DMSO or methyllithium in THF and cyclization of the resulting 1,2-dithiolates with sulfur dichloride [19]. By oxidation of the tetrakis(methylthio)-benzotrithiole with antimony pentachloride a stable mono radical cation is formed, which has semiconducting properties [19].



$E^{1}_{1/2}$ [6]: 1,01V; E^{2}_{ox} : 1,55V
σ_{RT} : $2{,}7\,10^{-6}$ Scm^{-1}
[spin]: 1/molecule

Compared with the octakis(methylthio)-dibenzo-TTF the tetrakis(methylthio)-benzotrithiole is a weaker electron donor. The reversible first oxidation potential is about 300 mV higher than that of the corresponding TTF. But it was surprising that the trithiole can also deliver a second electron at higher potential. The first representative of a 1,2,3-trithiolium radical cation, obtained from bis-trifluoromethyl-acetylene, sulfur and AsF_5, was described by Cameron [20] in 1992.

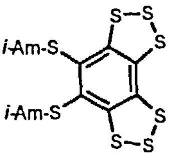
A three-electron donor results from a linear annelation of a second trithiole unit at the benzene ring [21].



$E^{1}_{1/2}$ (V) [6]	0,97
E^{2}_{ox} (V)	1,23
E^{3}_{ox} (V)	2,17

Obviously there exists a strong conjugative interaction between the two positively charged centers of the molecule and therefore a third electron is lost only at high potential. Chemically, the bis-trithiole could be oxidized by antimony pentachloride into a mono- and a bis-cation, both with radical properties. The cations absorb in the near-ir region (1000-1600 nm; $ClCH_2$-CH_2Cl), which is an indication of an intervalence transition (see also [22]). The salts are semiconductors (σ_{RT} ~ 10^{-5} Scm^{-1}).

From the point of view of the cyclovoltammetry the angular annelated bis-trithiole behaves differently [21]. It could be detected as a four electron donor.

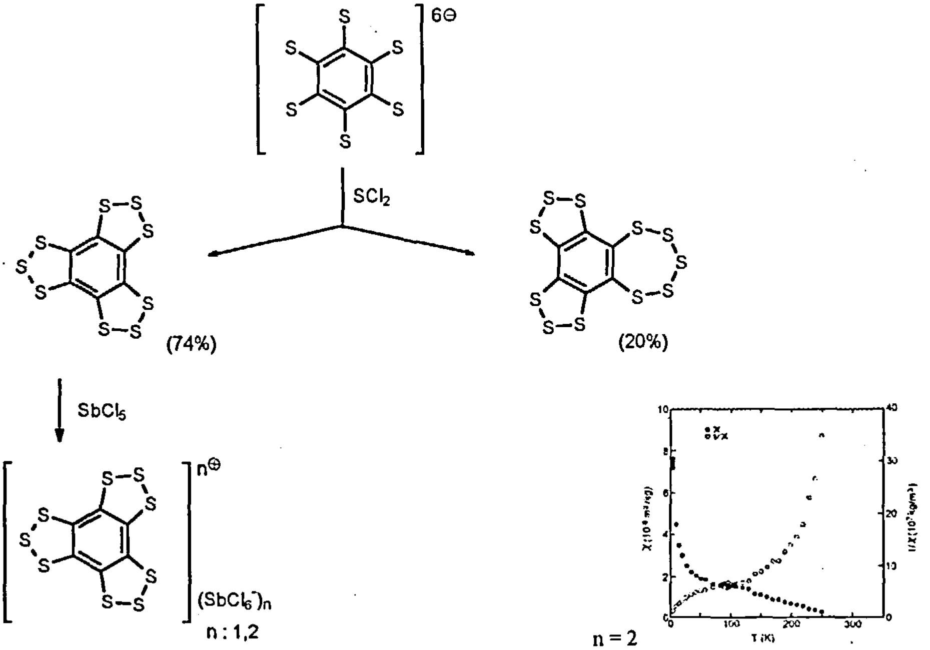


E (V) [6]	$E^{1}_{1/2}$	$E^{2}_{1/2}$	E^{3}_{ox}	E^{4}_{ox}
	1,12*	1,12*	1,44	1,70

* non dissolved two electron step

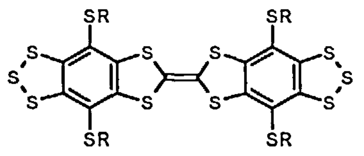
We believe that the two 1,2,3-trithiolerings were oxidized more or less independently from each other and thus a tetracation is formed. At the first oxidation potential two electrons were lost. We infer from these results a surprisingly low conjugative interaction between the charged angular annelated trithiole units via the benzene ring.

The benzenehexathiolate itself reacts with sulfur dichloride to produce a mixture of the benzo-tris-1,2,3-trithiole as main product and the benzo-bis(1,2,3-trithiolo)-pentathiepine as by-product, which was extracted from the mixture by carbon disulfide.



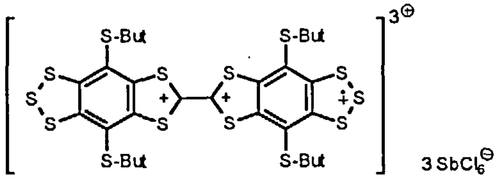
A mono- and a dication radical was obtainable from the very low soluble tris-trithiole by oxidation with antimony pentachloride [19,23]. Both salts are semiconductors ($\sigma_{RT} \sim 10^{-6}$ and 10^{-5} Scm^{-1}). The bis-cation does not represent a triplet state and shows a tendency to an antiferromagnetic spin coupling at low temperature. The unusual susceptibility-temperature-dependency is still under investigation.

The electron donor properties of benzotrithioles could be improved, when two trithiole rings were annelated with the dibenzo-TTF structure.



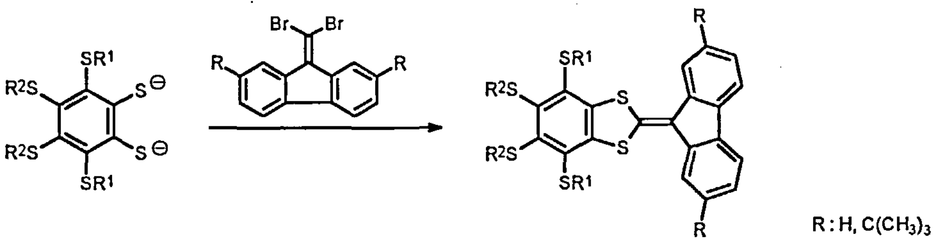
E (V)[6]	$E^1_{1/2}$	$E^2_{1/2}$	$E^3_{1/2}$	$E^4_{1/2}$	E^5_{ox}	E^6_{ox}
R = but	0,55	0,94	1,43	1,66	1,89	2,11
R = *i*-am	0,58	0,96	1,45	1,66	1,88	2,09

The synthesis of this new type of a TTF corresponds to those of the benzo-trithioles. By cyclovoltammetry six one-electron redox steps were detectable [21]. Two for the TTF unit and in each case two for one trithiole unit. By oxidation with antimony pentachloride mono-, bis- and tris-cations were obtained as solids. They are all radicals. The mono cation should be a TTF-radical cation, because the TTF-unit is easier to oxidize than the trithiole unit. In the bis-cation we could determine two spins per molecule [6]. For this reason this species has a stable triplet state at room temperature. We suppose a lost of an electron both from the TTF unit and from one trithiole unit and a low conjugation interaction between both oxidized parts of the molecule.

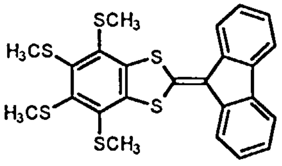


In the higher oxidized form the spin concentration drops down and thus the given formula could reflect the structure of the tris-cation ([spin] ~ 0,8/molecule). The compounds, which have lost more than one electron absorb strongly in the near-ir region (absorption band between 1000 and 1800 nm). This absorption is again an indication that the radical salts are mixed valance species with intervalence transitions (see also [22]).

Dithiafulvenes. Hoping to stabilize the radical state of cation radicals in one part of the molecule and the cation in another part, we synthesized the fluorenylidene-benzodithiafulvenes from the 1,2-dithiolates and the corresponding fluorenylidene-dibromomethane.



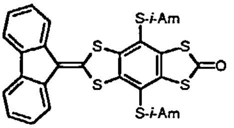
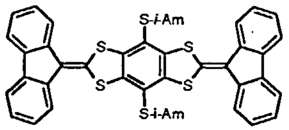
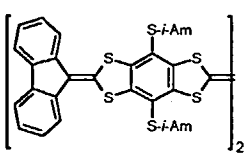
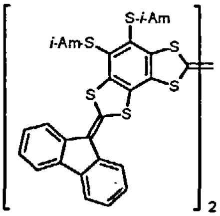
In their oxidized form the radical electron should be more localized in the fluorenylidene part and the cation could be stabilized best in the 1,3-dithiole part of the molecule, particularly when the two parts are twisted around the C-C-bond. With the aim to improve the solubility of the compounds we have introduced the tertiary butyl substituents into the fluorenylidene moiety. All the different types of the target structures with one, two, three and five donor units could be synthesized. They are weak electron donors.

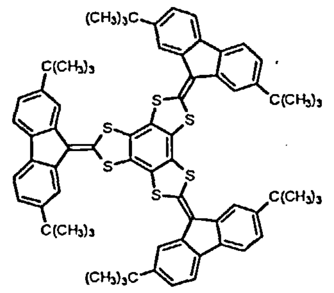


$E^1_{1/2}$ (V)^6 1,14
E^2_{ox} (V) 1,76

The first oxidation potential of the mono donor is reversible and with 1,14 V in the range of that of the benzotrithioles. The molecule can lose even more than one electron, but in that case the redox-steps are no longer reversible. The molecules with one, two or three donor units were oxidized by antimony pentachloride into radical cations, which are semiconductors.

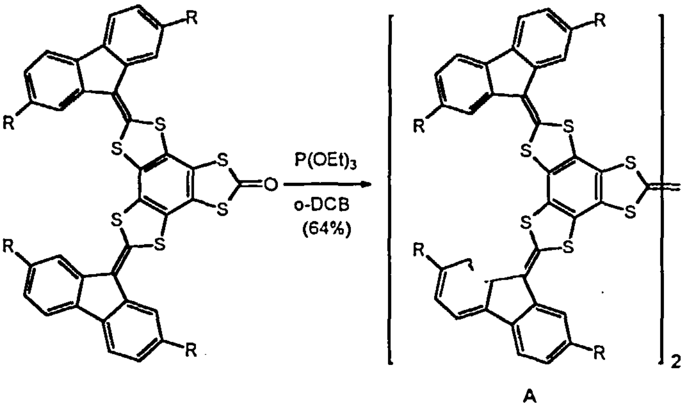
TABLE 1

donor	donor/$SbCl_6^-$	spin/molec.	σ_{RT} [Scm^{-1}]	g-value
	1:1	0,64	$8{,}9\cdot10^{-4}$	2,0065
	1:0,9	0,60	$1{,}4\cdot10^{-3}$	2,0060
	1:1,4	0,055	$3{,}9\cdot10^{-5}$	2,0057
	1:1	1	$3{,}6\cdot10^{-3}$	2,0072
	1:2	0,76	$1{,}4\cdot10^{-3}$	2,0075
	1:2,2	0,74	$2{,}8\cdot10^{-3}$	2,0067
	1:3	0,32	$8{,}8\cdot10^{-5}$	2,0070
	1:1,2	0,45	$3{,}0\cdot10^{-3}$	2,0051
	1:2	0,076	$3{,}9\cdot10^{-6}$	2,0069

	1:0,9 1:1,2	0,28 0,10	$1{,}7 \cdot 10^{-4}$ $6{,}5 \cdot 10^{-4}$	2,0051 2,0048

Contrary to the twofold oxidized linear bis-trithiolo-DBTTF the corresponding bis-(fluorenylidene-dithiolo)-DBTTF (see TABLE 1) does not exist in a triplet state. There was only less than one electron per molecule detectable in the bis-cations. Similar results were obtained for the cross-conjugated "trimer" system.

This situation changes in the cross-conjugated system with one DBTTF- and four fluorenylidene-1,3-dithiole units.



$A / SbCl_6^-$	1:1	1:1,5
Spin/molec	1	1,5
σ_{RT} [Scm^{-1}]	$6{,}5\ 10^{-6}$	$3{,}5 \cdot 10^{-6}$
g-value	2,0065	2,0056

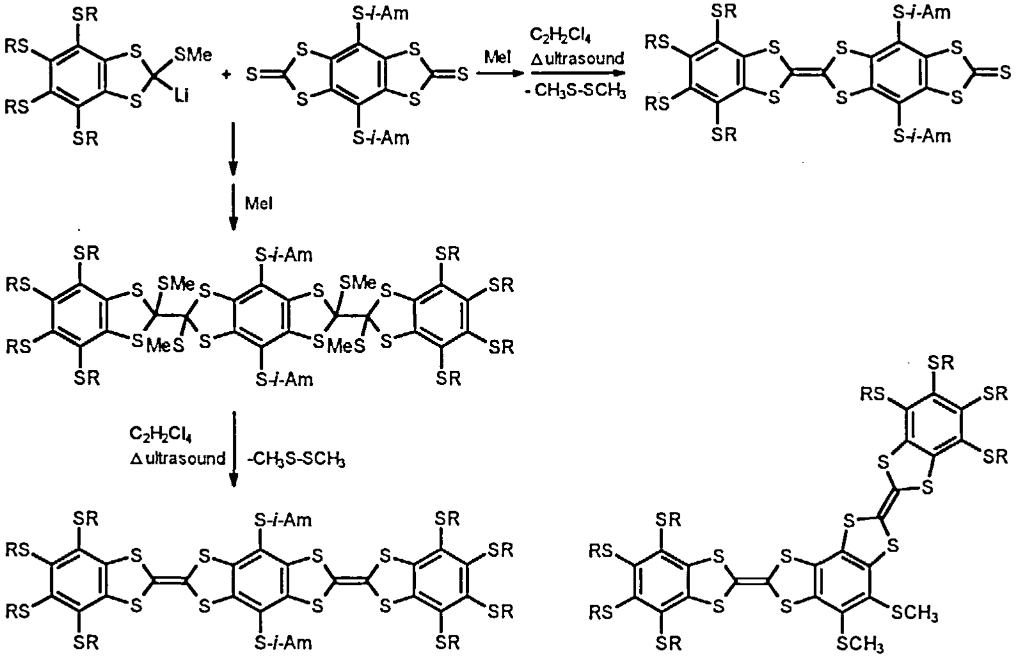
R : $C(CH_3)_3$
M : 1706,67 g/mol

This donor was synthesized from the corresponding angular substituted benzo-1,3-dithiole-one by dimerization with triethyl phosphite. The structure could be proved by the determination of the molecular mass with a time of flight mass spectrometer via matrix assisted laser desorption ionization. By oxidation of this donor molecule with antimony pentachloride a 1,5 radical cation salt could be isolated. The spin concentration was determined to be 1,5 too. That means this molecule exists probably - in the oxidized form - in a triplet state.

Tetrathiafulvalenes. In order to increase the electron donor capability of the benzene hexathiolate derivatives we also synthesized donor molecules with one, two and three

TTF units in a linear and angular conjugated motif. This investigation was done in a fruitful collaboration with K. Müllen, Mainz.

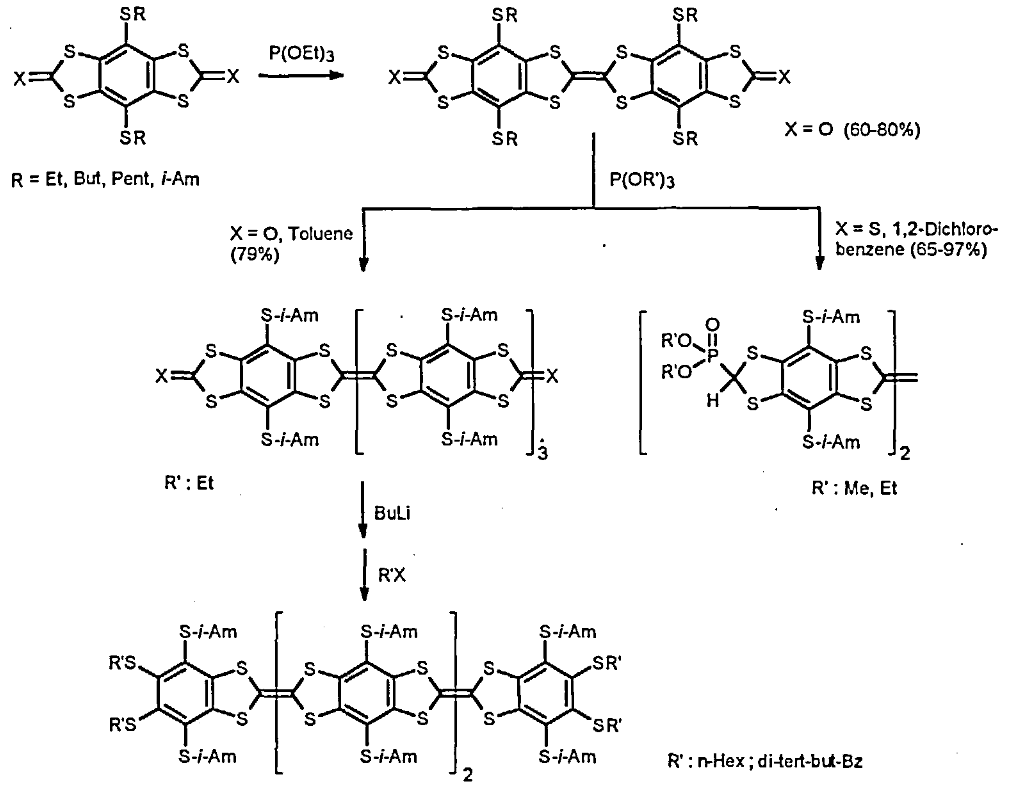
For the synthesis of the bis-DBTTF the known technique of coupling a 1,3-dithiole-2-thione with 2-lithium-1,3-dithiole was used [24].



After quenching the intermediate of the condensation reaction with methyliodide the isolated hexathioorthooxalate was pyrolized in tetrachloroethane, supported by ultrasound, whereby dimethyldisulfide was splitted off and the bis-TTF's moiety results. By a 1:1 stoichiometry, using the linear benzo-bis-dithiole-dithione, the DBTTF with an annelated 1,3-dithiole ring was obtained and dimerized by trialkyl phosphite into a linear tris-TTF donor [25].

An easier way for synthesizing a linear tris-TTF would be a controlled stepwise dimerization of a tetrathia-indacene-dione by trialkylphosphite into the DBTTF-bis-dithiole-dione and its further dimerization to a tris-TTF. The second dimerization step is the only problematic one. The results strongly depend on the reaction temperature and the solubility of the DBTTF-di(1,3-thiole-diones or -dithiones) used [13,26].

In the shown example of dimerizing the DBTTF-bis(1,3-dithiole) derivative the following results were obtained.

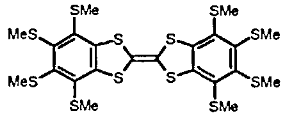
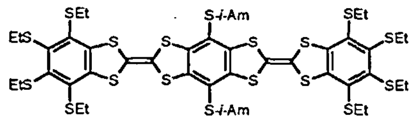
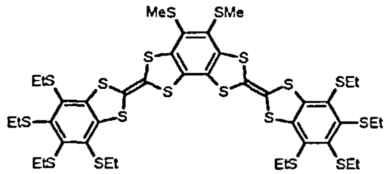
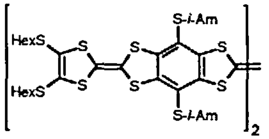
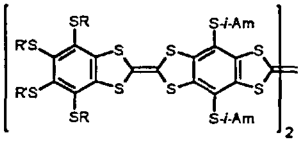


Starting from the dione in boiling toluene the tris-TTF precipitates as a very low soluble product and is thus protected for a further coupling to oligomers. Using the lower soluble DBTTF-dithione derivative and a higher reaction temperature, another reaction occurs. Only the diester of the DBTTF-bis(1,3-dithiole-2-phosphonic acid) results in high yields. Similar transformations were found by Kilburn [27].

The TTF moiety with the phosphonic diester groups can be used for the synthesis of TTF's with extended π-system or for synthesizing dithiafulvalenes in Wittig-like reactions. From the tris-TTF-bis(dithiol-one) alkylthio-substituted tris-TTF were synthesized by the cleavage of the 1,3-dithiol-2-one ring with the help of methyllithium and alkylation of the tris-TTF-tetrathiolate (see TABLE 2).

Charge-transfer complexes with $TCNQF_4$ result from the synthesized mono-, bis- and tris-TTF's. As pellets they are all semiconductors with a conductivity in the range between 10^{-3} up to 10^{-1} Scm^{-1}. A slight increase in the conductivity is to observe with the increasing number of TTF-units in the molecule. The first oxidation potential slightly drops down in the same direction (see TABLE 2).

TABLE 2

Compound	oxidation potentials[6] (V)	TCNQF$_4$-compl.	
		σ_{RT} [Scm^{-1}]	stoich.
	0,74 1,09 - - - -	1,4·10^{-3}	1:1
	0,41 0,63 1,06 1,22 - -	6,6·10^{-2}	1:2
	0,54 0,69 1,06 1,22 - -	1,8·10^{-2}	1:2
	0,34 0,44 0,69 0,78 1,10 1,33	6,0·10^{-2}	1:3
			
R : Et R': Et	0,44 0,61 0,81 1,01 1,28 -	9,0·10^{-2}	1:3
R : *i*-Am R': n-Hex	0,50 0,63 0,83 1,07 1,30 -	6,8·10^{-3}	1:3
R : *i*-Am R': di-tert-but-Bz	0,42 0,54 0,76 1,00 1,23 1,47		

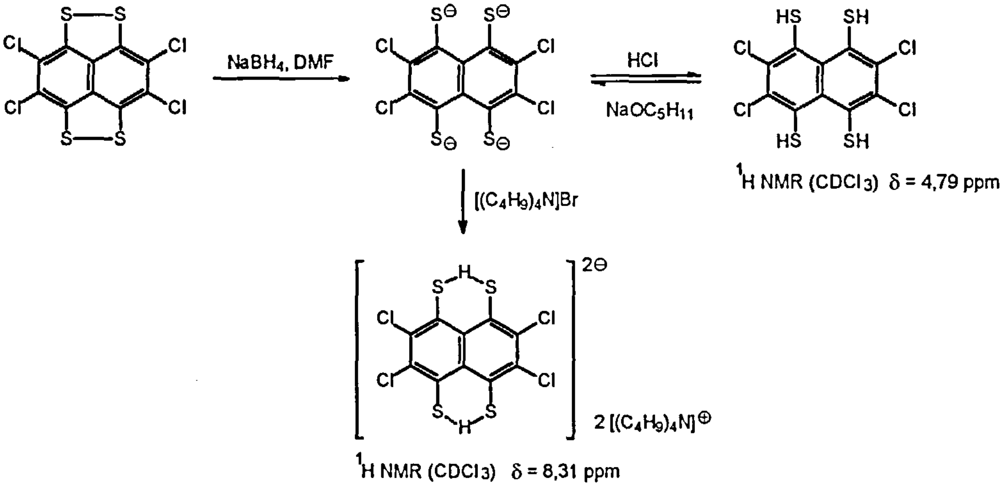
Each TTF-unit acts as a two-electron donor and therefore four one electron oxidation steps could be determined in the case of the bis-TTF's, respectively five or six steps for the tris-TTF's by cyclovoltammetry. In the angular bis-TTF the stabilization of the cation radical state by conjugation is less efficient than in the linear molecule and that is why the angular TTF is the weaker donor with the higher first oxidation potential.

METAL COMPLEXES OF 2,3,6,7-TETRACHLORO-NAPHTHALENE-1,4,5,8-TETRATHIOLATE

The presented efforts for synthesizing radical cations in a triple state on the basis of TTF-oligomers or their analogues have shown that there exist a lot of obstacles which are difficult to overcome. We changed therefore from the organic radical cations to spin bearing transition metal complexes of sulfur containing ligands. We hoped to get more easily "organic solids" with unusual spin-spin interactions by metal complexes.

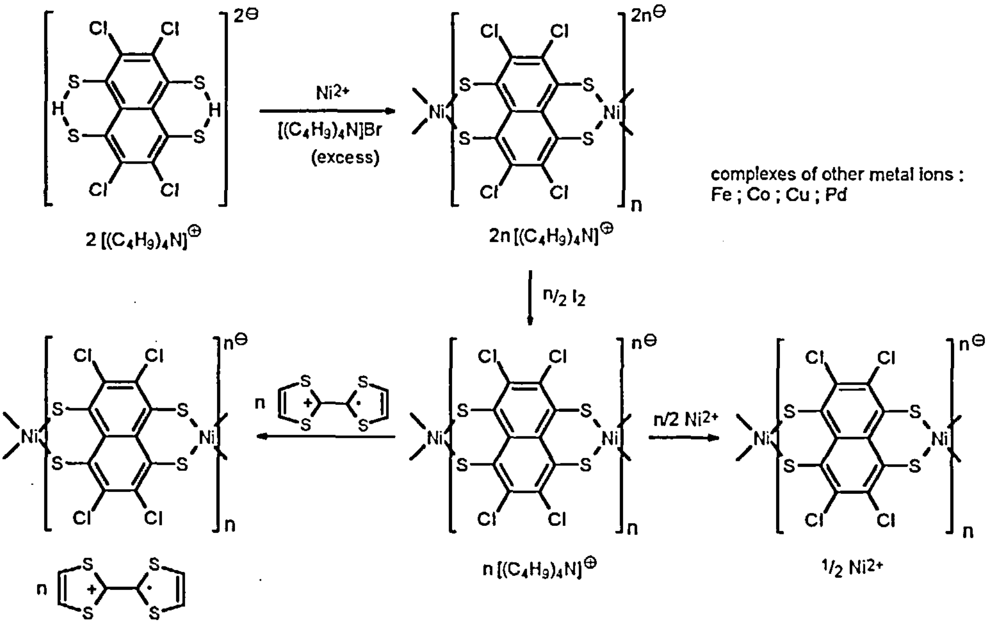
We considered the 2,3,6,7-tetrachloro-naphthalene-1,4,5,8-tetrathiolate as a promising ligand. Besides a 1,3-thiolate structure for complexing metal ions into oligomeric coordination complexes this ligand possesses the chloro substituents and the extended π-system of the naphthalene ring for intermolecular electronic interactions in a solid.

The naphtho-bis-dithiole, described by Klingsberg [28] via sulfurization of perchloronaphthalene, was the starting compound for this ligand.

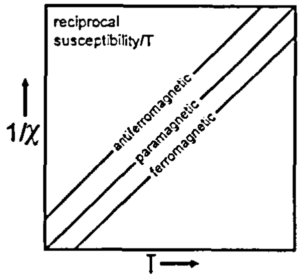


The 1,2-dithiole rings could be splitted off by reduction with sodium borohydride in DMF. Protonation gave the tetrathiol and a lipophilic bis(thiol-thiolate) was obtained with the help of a tetrabutylammonium salt [2,29]. From this twofold negatively charged ligand a large variety of transition metal complexes was synthesized. Only the nickel and cobalt complexes will be described more in detail.

By adding a nickel salt to the solution of the ligand in ethanol the nickel complex was obtained as twofold charged per ligand unit. It did not show an ESR signal.



However, by oxidation with iodine it became ESR active. In this still partly soluble complex we could exchange the bulky and lipophilic tetrabutylammonium ion by the spin bearing TTF radical cation or by nickel ions. In order to study the magnetic behavior of these complexes the magnetic susceptibility was determined in the temperature range down to 4 K.

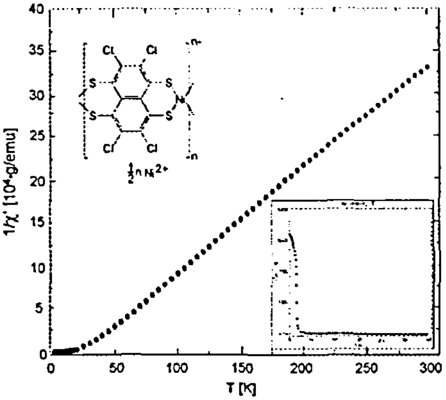


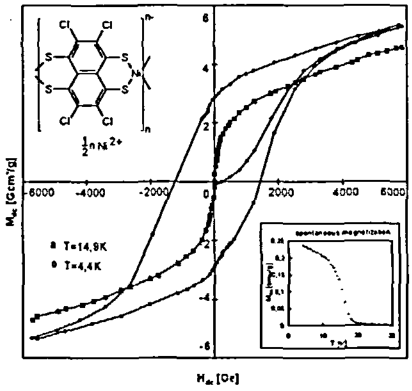
Curie-Weiss law: $1/\chi = (T-\theta)/C$

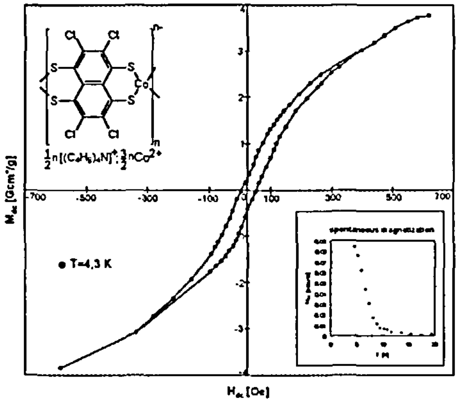
According to the Curie-Weiss-Law a linear correlation exist between the reciprocal susceptibility and temperature. In the case of a paramagnet this straight line goes through zero, the θ-value being zero. Antiferromagnetic behavior can be recognized by a negative intercept of the abscissa, the θ-value being negative and a positive value is to be expected for a ferromagnet.

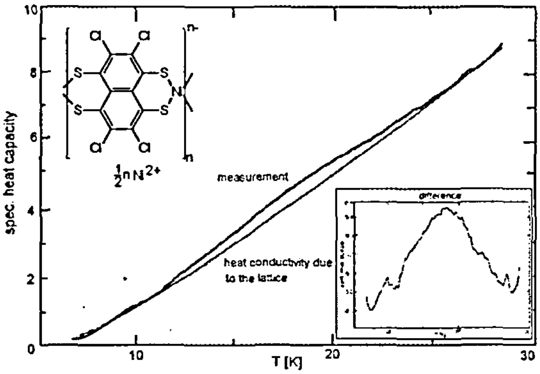
In the nickel complex, in which a part of the tetrabutylammonium ions was substituted by nickel ions, a clear indication of a ferromagnetic coupling of the spins was observed by a positive θ-value of about 10 K.

By a complete substitution of the bulky ammonium ions through the smaller nickel ions or the plane TTF radical cation similar curves result, which allows to infer a ferromagnetic spin ordering near 20 K (complex with Ni^{2+} as counterion). And according to their ferromagnetic behavior these complexes show the typical hysteresis curve for the magnetization dependent on the magnetic field strength and also a spontaneous magnetization. The cobalt complexes are also ferromagnets.





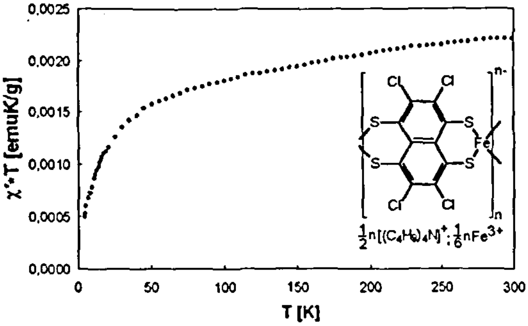




Also the heat capacity of a sample of the ferromagnetic nickel complex showed a characteristic deviation within the temperature range (12 K - 25 K) where the spin-ordering occurs. This is another argument that we observe intrinsic magnetic phenomena of the complexes.

As far as we know, these nickel and cobalt complexes are the first examples of ferromagnets on the basis of sulfur containing coordination polymers.

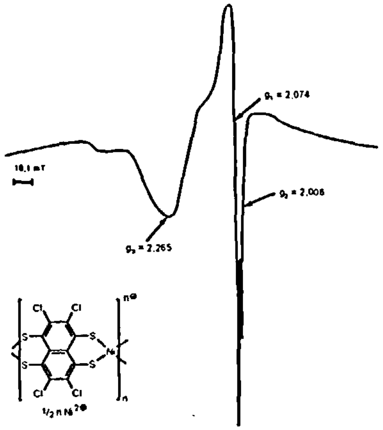
Contrary to the nickel and cobalt complexes the corresponding iron complex shows an antiferromagnetic behavior (θ ~ - 10 K)

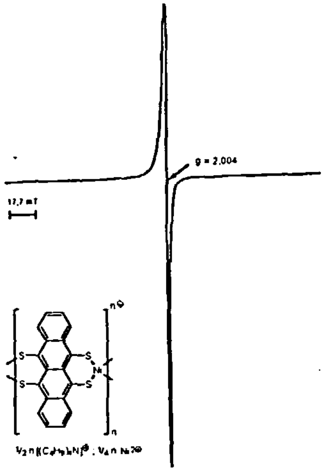


Summarizing these results one can expect that the used ligand should open the possibility for the synthesis of magnetic complexes with tailor made properties by the variation of the metal- and/or the counterion.

We tried to transfer our efforts to synthesize molecular ferromagnets also to the naphthacene-5,6,11,12-tetrathiolate. This ligand was obtained in a similar way as the tetrachloro-naphthalene-tetrathiolate from the corresponding bis-1,2-dithiole [30]. It looked promising because of the extended π-system for electronic interactions.

But only a paramagnetic nickel complex could be isolated. A comparison of the ESR spectra of the two types of complexes reveals the clear difference between the complexes.



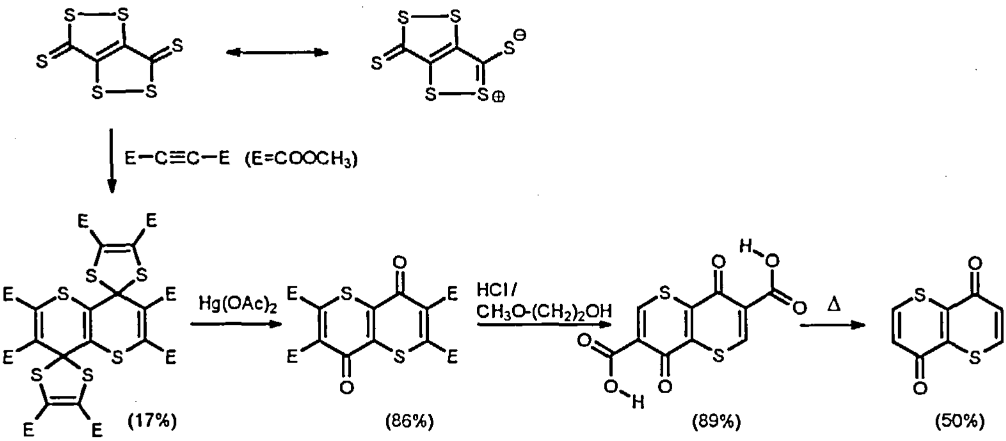


The naphthalene-tetrathiolato nickel complex shows a very broad and the corresponding naphthacene complex a narrow signal. This observation indicates the importance of the chloro substituents in the naphthalene ligand for the ferromagnetic spin-interactions.

4H,8H-THIOPYRANO[3,2-b]THIOPYRAN-4,8-DIONE-3,7-DICARBOXYLIC ACID

A new ligand not for thiophilic but for oxophilic metal ions was obtained from the dithiolo-dithiole-dithione, easily to synthesize by sulfurization of perchlorobutadiene [31].

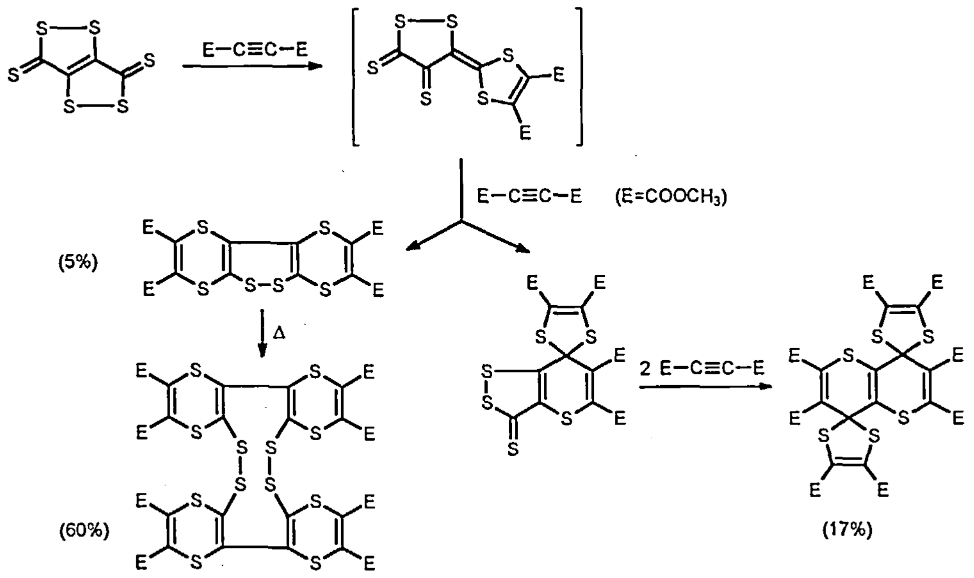
This molecule reacts twice like a trithione as 1,3-dipole with dimethyl acetylenedicarboxylate to produce a bispiro-compound with the novel heterocyclic system of thiopyrano-thiopyran [32,33].



By dethioketalization with mercury acetate the tetraester of the thiopyrano-thiopyrandione was obtained. The new oxophilic ligand, a thiopyrano-thiopyran-dione dicarboxylic acid, was formed by hydrolysis and decarboxylation of two carboxylic acid groups in a one-pot reaction.

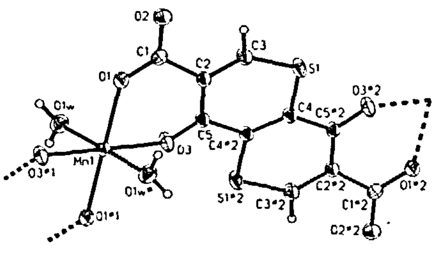
From the chemical point of view we were eager to know, why the yield of the spiro compound was so low. We can give an answer as follows. In the first step of the cyclo-additon reaction an intermediate with two types of heterodiene structures is produced: one with a 1-thia-butadiene and another with a 1,4-dithia-butadiene structure. The main product of the reaction, a dimer of a 1,2-dithiine, should be formed via a cycloaddition of the 1,4-dithia-butadiene structure. The 1,2-dithiine - as intermediate -

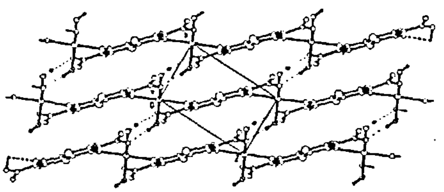
was isolated only in traces, because it dimerizes thermically rather fast, observed by NMR spectroscopy.



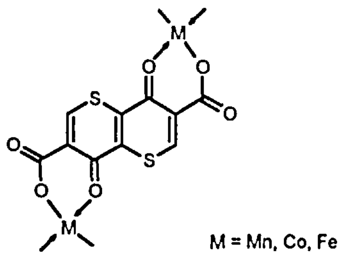
The yield of the desired spiro-compound, formed in a cycloaddition reaction via the 1-thia-butadiene structure, could not be increased in spite of a broad variation of the reaction conditions.

The 4H,8H-thiopyrano[3,2-b]thiopyran-4,8-dione-3,7-dicarboxylic acid forms weak soluble complexes with many transition metal ions. We could breed single crystals from the manganese complex which crystallizes with two molecule of water per metal ion. The x-ray structure shows that the manganese is coordinated by the oxygen of the thiopyranone and of the carboxylat.

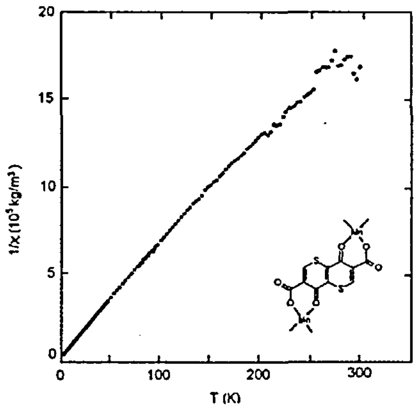




In the sheet structure of the complex the chains of the coordination polymer are connected via hydrogen bonding of the coordinated water into the x- and y-direction. Unfortunately this well defined complex does not show the desired ferromagnetic behavior.



	μ_{theo} [μ_B]	μ_{eff} [μ_B]	θ [K]
Mn^{2+}	5,92	6,02	-0,9
Co^{2+}	4,90	5,33	-3,2
Fe^{2+}	3,87	4,62	-11,3



It is like the cobalt and the iron complex as well a weak antiferromagnet, to be seen by the negative values of θ.

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REFERENCES AND NOTES

1. G. Schukat, E. Fanghänel, *Sulfur Reports* **18**, 1-294 (1996)
2. M. Adam, K. Müllen, *Adv. Mater.* **6**, 439 (1994)
3. J. S. Miller, A. J. Epstein, *Angew. Chem.* **106**, 399 (1994)
4. K. Mukai, K. Konishi, K. Nedachi, K. Takeda, *J. Magn. Magn. Mater.* **140-144**, 1449 (1995)
5. The spin-concentrations were determined by ESR spectroscopy.
6. Oxidation potentials were established by cyclovoltammetry under following condi-

tions: dichloromethane, Bu_4NPF_6, SCE, 20°C (For the hexakis(methylthio)-benzene and the fluorenylidene-dithiafulvene dichloroethane was used as solvent). E_{ox} -values were determined by square wave voltammetry.

7. A. Alberti, G. F. Pedulli, M. Tiecco, L. Testaferri, M. Tingoli, *J. Chem. Soc. Perkin Trans. II* **6**, 975 (1984)
8. E. Fanghänel, J. Bierwisch, K. Strunk, A. Ullrich, *Sulfur Letters* **18**, 129 (1995)
9. F. Maiolo, L. Testaferri, M. Tiecco, *J. Org. Chem.* **46**, 3070 (1981)
10. A. M. Richter, V. Engels, E. Fanghänel, *Z. Chem.* **29**, 444 (1989)
11. A. M. Richter, N. Beye, E. Fanghänel, *Z. Chem.* **28**, 284 (1988)
12. A. M. Richter, N. Beye, E. Fanghänel, *Synthesis* **1990**, 1149
13. E. Fanghänel, R. Wegner, N. Beye, K. Peters, K. Müllen, *J. Prakt. Chem.* **337**, 299 (1995)
14. A. M. Richter, N. Beye, E. Fanghänel, *Z. Chem.* **29**, 141 (1989)
15. D. Sülzle, N. Beye, E. Fanghänel, H. Schwarz, *Chem. Ber.* **122**, 2411 (1989)
16. D. Sülzle, N. Beye, E. Fanghänel, H. Schwarz, *Chem. Ber.* **123**, 2069 (1990)
17. G. Maier, J. Schroth, H. P. Reisenauer, G. Franking, V. Janas, *Chem. Ber.* **125**, 265 (1992)
18. E. Fanghänel, R. Herrmann, J. Bierwisch, H. Hartung, U. Baumeister, G. Maier, H. P. Reisenauer, *J. Prakt. Chem.* **336**, 444 (1994)
19. E. Fanghänel, R. Herrmann, H. Naarmann, *Tetrahedron* **51**, 2533 (1995)
20. T. S. Cameron, R. C. Haddon, S. B. Mattar, S. Parsons, A. P. Ramirez, J. Passmore, *J. Chem. Soc. Dalton Trans.* **1992**, 1563
21. E. Fanghänel, R. Herrmann, R. Reuter, K. Müllen, *unpublished results*
22. K. Lahlie, A. Moradpour, C. Bowlas, F. Menou, P. Cassoux, J. Bouvoisin, J.-P. Launay, G. Dives, D. Dehareng, *J. Am. Chem. Soc.* **117**, 9995 (1995)
23. V. Krinichnyi, E. Fanghänel, R. Herrmann, in print in *Appl. Magn. Reson.*
24. R. Wegner, N. Beye, E. Fanghänel, U. Scherer, R. Wirschem, K. Müllen, *Synth. Met.* **53**, 353 (1993)
25. M. Adam, E. Fanghänel, K. Müllen, Y. J. Shen, R. Wegner, *Synth. Met.* **66**, 275 (1994)
26. E. Fanghänel, K. Strunk, U. Gärtner, *J. Prakt. Chem.* **338**, 146 (1996)

27. R. P. Parg, J. D. Kilburn, T. G. Ryan, *Synthesis* **1994**, 195

28. E. Klingsberg, *Tetrahedron* **28**, 963 (1972)

29. E. Fanghänel, J. Bierwisch, A. Ullrich, A. Herrmann, *Chem. Ber.* **128**, 1047 (1995)

30. C. Marschalk, C. Stumm, *Bull. Soc. Chim. Fr.* **418**, 427 (1948)

31. E. Fanghänel, B. Kordts, A. M. Richter, *Monatshefte Chem.* **122**, 71 (1991)

32. E. Fanghänel, T. Palmer, J. Kersten, R. Ludwigs, K. Peters, H. G. von Schnering, *Synthesis* **1994**, 1067

33. E. Fanghänel, T. Palmer, *J. Prakt. Chem.* **337**, 680 (1995)