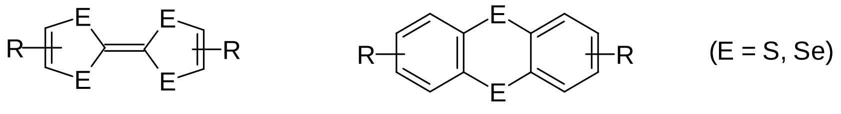
Abstract

A series of organic conductors base upon partial oxidized chalcogene compounds like tetrachalcogenafulvalene.

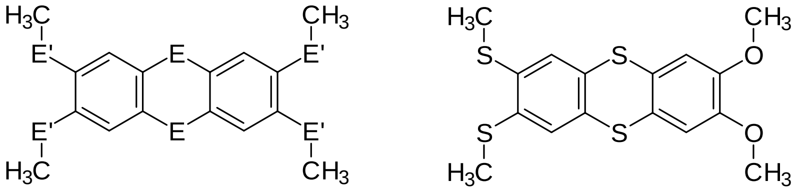


a **b**

Fig.81: a) tetrachalkogenafulvalene b)chalkogenanthrene

Electron-rich chalcogenanthrenes can be partially oxidized, too, as has been reported in several theses[22,59,73,88,89]. CT-complexes are formed with suitable acceptorsas well as radical cations by using suitable oxidants.

While previous investigations dealt with symmetrical substituted chalcogenanthrenes like **8**, **9** and **12**, the first part of this paper is concerned with the study of the unsymmetric 2,3-di-(methoxy)-7,8-di(methylthio)thianthrene (**11**).

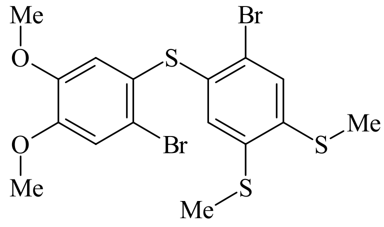


E = S, E' = O (**8**)
E = S, E' = S (**9**)
E = Se, E' = O (**12**)

11

Fig. 82: Symmetrical substituted (left) chalkogenanthrenes and unsymmetric 2,3-di(methoxy)-7,8-di(methylthio)thianthrene (right)

First of all a new synthesis for **11** had to be developed with 2,2'-dibromo-3,4-di(methoxy)-3',4'-di-(methylthio)diphenylsulfide (**25**) as an intermediate.



25

Fig. 83: The intermediate compound 2,2‘-dibromo-3,4-di(methoxy)-3‘,4‘-di(methylthio)diphenylsulfide (**25**)

A X-ray analyses of **25** in comparison with the corresponding symmetric bis[2-bromo-4,5-di(methoxy)phenyl]sulfide (**26**) shows the compounds to minimize the interaction between the nonbonding p-orbital of the sulfur atom and the π-system of the phenyl rings which is typical for diarylsulfides having electron donating substituents.The minimization is achieved by a perpendicular position of one of the aryl rings relative to the C-S-C-plane. This can be found in both compounds **25** and **26.** In **25** only the methoxy-substituted ring is found in the vertical position showing the (+)M-effect of the methoxy substituent is stronger than that of the methylthio group, as was to be expected.

As has been shown in earlier investigations of **8**[66], **9**[22] and **12**[54] the methoxy and methylthio groups have nearly the same steric requirements. In **11** they occupy equivalent positions therefore the formation of disordered crystals is most probable. For this no cystalls suitable for X-ray analysis have been obtained.

In a second part of this thesis new CT-complexes with derivatives of thianthrene were investigated by variiation of the alkoxy substituents in thianthrene units and by variation of the acceptors.

The so far unknown 2,3,7,8-tetrakis(2-propoxy)thianthrene (**10**) was synthezised. The compound shows a better solubility than tetramethoxy derivatives but the steric expansion of *ortho*-standing isopropoxy groups forces them to take non-coplanar positions in the crystal.

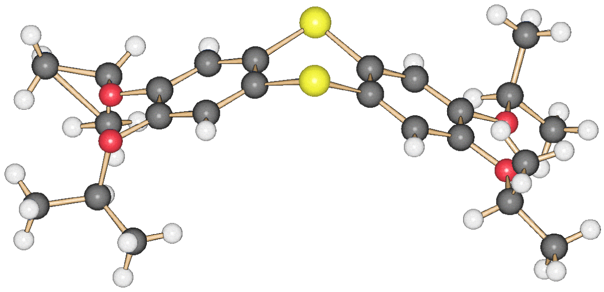


Fig. 84: non-coplanar isopropoxygroups in **10**

In this way the ability of building stacks is lowered but nonetheless a new CT-complex (**28**) could be formed with DDQ. The crystal structure is defined by columnar stacks with alternating donor and acceptor molecules. The remarkable feature of **28** is the disordered molecule of the acceptor.

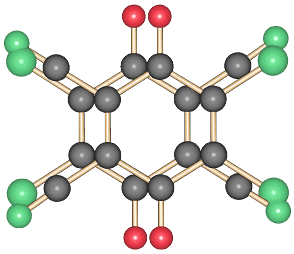


Fig. 85: disordered molecules of DDQ in **28**

The strong interactions between the phenyl rings of donor an acceptor molecules have an effect on the orientation of isopropoxy groups . The short distance of 238 pm between a hydrogen atom of an isopropoxy group and a oxygen atom of DDQ indicates a C-H···O hydrogen bond.

Tetramethoxythienathrene and DCID –which has been used for the first time as an acceptor in CT-complexes of thianthrenes- formed an 1:1 complex (**30**). This compound shows also stacks of alternating donor and acceptor molecules.

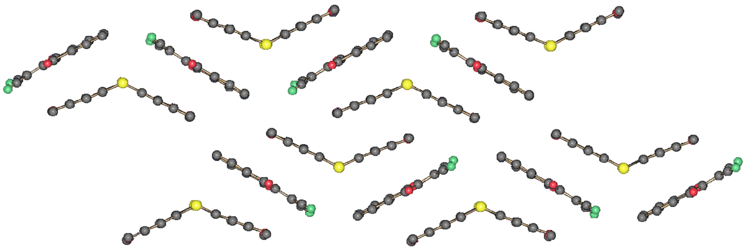
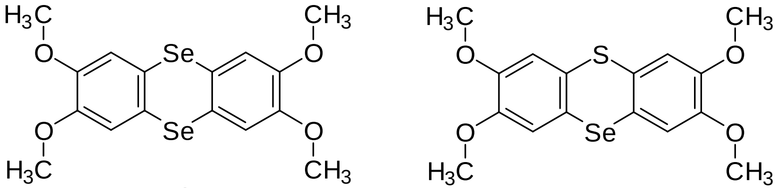


Fig.86: stacks of alternating donor and acceptor molecules in **30**

The dark colour of the complex (black needles) indicates an electron-transfer between donor and acceptor molecules. A charge transfer should affect the bond lengths and angels of both the donor and acceptor molecules. However, the structure data of the donor do not differ very much. But the data of the acceptor show distances between those of the neutral molecule and ist radical anion, in accordance with a small charge transfer.

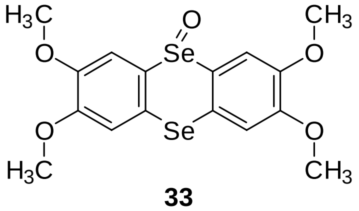
Finally the radical cations of the chalcogenanthrenes **12** and **13** have been investigated. A X-ray analysis of a derivative of **13** has been characterised at first. The structure of this *unsymmetric* derivative turned out to be isotypic with the corresponding *symmetric* 2,3,7,8-tetramethoxythianthrene and –selenanthrene.



12 **13**

Fig. 87: chalcogenanthrenes used for synthesis of radical cations

Until now radical cations of chalcogenanthrenes have been formed by oxidation of chalcogenanthrenes themselves. This thesis showed that it is also possible to synthesize a 2,3,7,8-tetramethoxyselenanthrenium-ion by reduction of 2,3,7,8-tetramethoxyselen-anthrene-5-oxide (**33**).



33

Fig. 88: 2,3,7,8-tetramethoxyselenanthrene-5-oxide (**33**)

By dissolving **33** in formic acid in the presence of tetrafluoroboric acid a compound of composition $[Vn_2Se_2]BF_4\cdot CHCOOH$ (**32**) has been obtained.

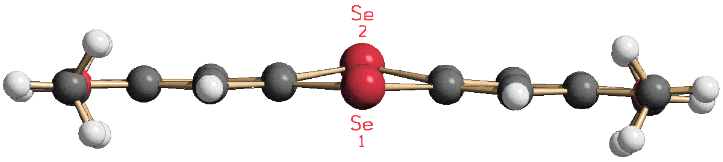


Fig. 89: Sideview of radikalcations in **32**

X-ray analysis shows the radical cation to be nearly totally flattened. Shortened Se-C and Se-O-bond lengths are found, indicating an mesomeric system spread over the whole molecule. In the crystal data seperate stacks of cations and anions are found. One molecule of formic acid is intercalated between the chains and some strong interactions between fluoro and hydrogen atoms can be detected. Interactions between the acid molecule and the hydrogen atoms of the phenyl rings have to be mentioned, too.

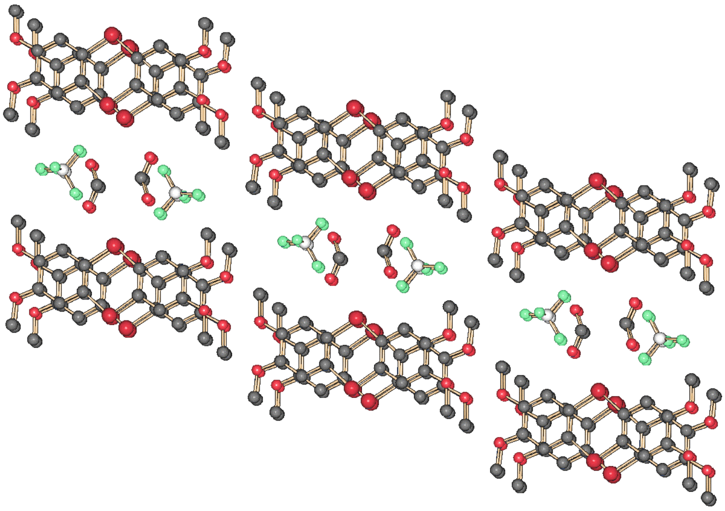


Fig. 90: Tetrafluoroborat-ions and molecules of formic acid between the stacks of 2,3,7,8-tetramethoxyselenanthrenium-ions in **32**

In the last part of this thesis MO-calculations for donor and acceptor molecules are presented. The donor-acceptor interactions can be explained by overlapping orbitals of suitable symmetry which are responsible for the positions of molecules in crystal as is shown below in the complex of 2,3,7,8-tetramethoxythianthrene-DCID (**30)**.

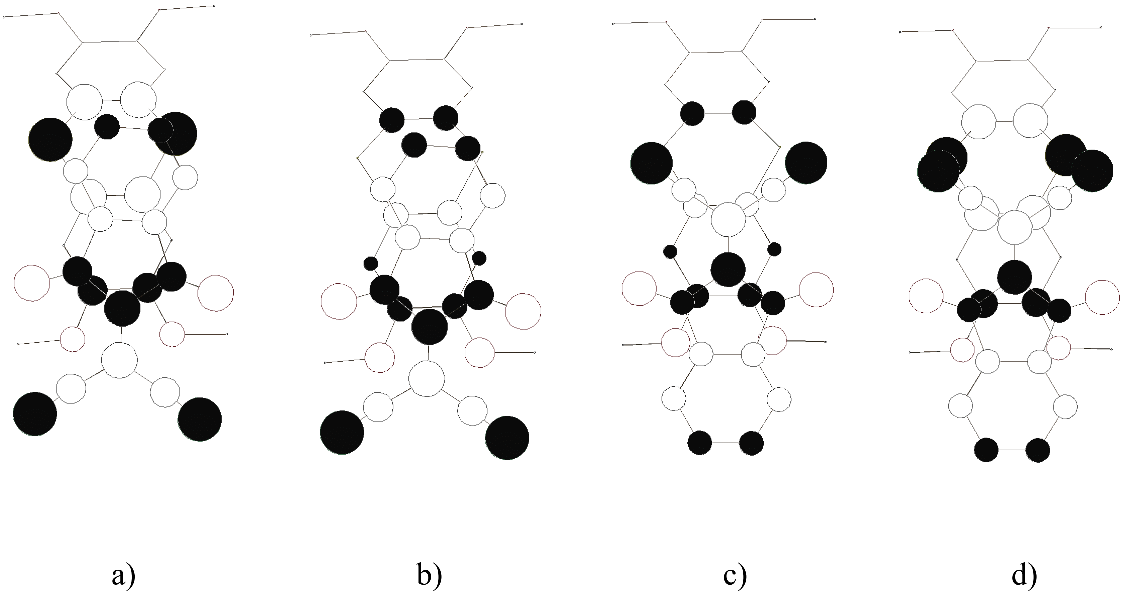

a) b) c) d)

Fig. 91: Interacting orbitals of 2,3,7,8-tetramethoxythianthrene and DCID in solide state. a) and c): HOMO-LUMO-interaction; b) and d): „HOMO -1“-LUMO- interactions