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The Preparation of New Metallic Charge-Transfer Complexes: Anthra [9.1-cd:10.5-c′,d′] bis [1.2] dithiol (TTA), -diselenol (TSA) and their Polyiodides

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THE PREPARATION OF NEW METALLIC CHARGE-TRANSFER COMPLEXES: Anthra [9.1-cd:10.5-c',d'] bis [1.2] dithiol (TTA), -diselenol (TSA) AND THEIR POLYIODIDES+

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The donors TTA and TSA were prepared starting from 1.5-dichloro-9.10-anthracenedione which was converted into 1.5.9.10-tetrachloroanthracene (TCA) by two alternating chlorination and elimination steps. TCA was reacted under a dry argon atmosphere with suspensions of Na_2S_2 and Na_2Se_2 to yield TTA and TSA, respectively. Action of elemental iodine gives highly conductive polyiodides of both donors. Single crystals of $TSA \cdot I_{1.2}$ actually behave metallic between 220 and 300 K. The X-ray structure of TSA and $TSA \cdot I_{1.2}$ allows a comparison of intermolecular distances in the neutral and the partially oxidized, ionic stacks of the donor.

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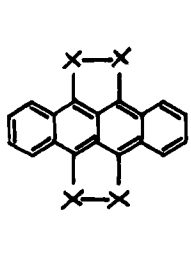
INTRODUCTION

There has been considerable recent interest in the solid state properties of charge-transfer complexes containing sulfur and/or selenium heterocycles as donors[1-6]. The field could be structured by discerning two groups of donors:

(i) those with "exocyclic" heteroatoms bonded directly to each other;

(ii) heterocycles with "isolated" S and Se atoms built into mainly carbocyclic rings.

Typical examples for (i) are tetrathia- or tetraselenatetracene (1) and tetrathia- or tetraselenaperylene (2). Derivatives of tetrathia- or tetraselenafulvalene (3) as well as Δ-4,4'-dithia- or Δ-4,4'-diselenadipyranes (4) are typical representatives of group (ii) donors.



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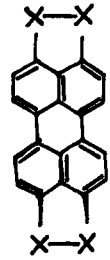

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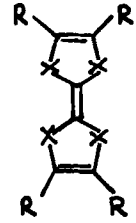

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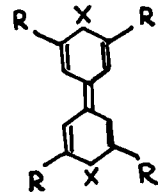
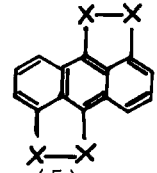


(4)

X = S (a), Se (b), [Te]

At a first glance group (i) materials promise more intermolecular interactions (short intermolecular X·····X contacts) in the solid state. These intermolecular interactions could influence the solid state properties of metals made up of these donors: three-dimensional interactions might wipe out the instabilities which are common for "one-dimensional" conductors and which destroy the metallic state at lower temperatures. (For summarizing reviews on these topics see ref. 1-6).

In the aim to find new highly conducting "three-dimensionally" correlated salts we used the group (i) donors (2a) and (2b) and investigated their charge transfer chemistry[7]. But the very low solubility especially of (2b) in all common organic solvents impedes any reasonable solution chemistry (especially electrochemistry and redox reactions). Additionally in spite of much efforts the charge transfer complexes of (2a) and (2b) have been obtained so far in microcrystalline powders only and their pressed pellet conductivities were not very promising. The rather unsatisfactory electrical properties of one of these materials have been independently investigated at the same time by another group[8]. We turned to the synthesis of other group (i) donors, therefore, and prepared tetrathia- (TTA, 5a) and tetraselenaanthracene (TSA, 5b).



X = S (a), Se (b)

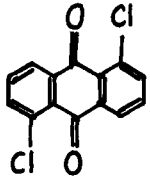
(5)

It turned out that 5b and a partially oxidized iodide of 5b crystallize both in stacks with short interstack contacts. Single crystal conductivity measurements on the latter compound showed a metallic regime between room temperature and 220 K. The preparation of these new conducting solids and of some interesting related materials is reported here.

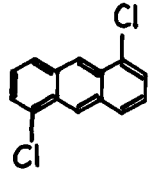
EXPERIMENTAL

Preparation of 1.5.9.10-tetrachloroanthracene

1.5-Dichloro-9.10-anthracenedione (6) (purchased from EGA) was reduced using metallic zinc in a concentrated ammonia solution to 1.5-dichloroanthracene (7) corresponding to reference[9]. Chlorination of the above reaction product yielded 1.5-9.10-tetrachloro-9.10-dihydroanthracene (8). (8) was converted to 1.5.9-trichloroanthracene (9) by



(6)



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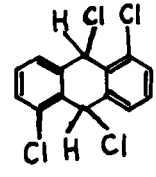

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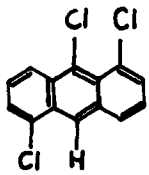

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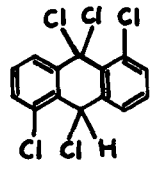

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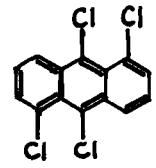

(11)

action of potassiumhydroxide[10] and the reaction product again chlorinated[10] to yield (10). An additional elimination of Cl^- by KOH yields 1.5.9.10-tetrachloroanthracene (11) with a melting point of 196-197°C (mp of ref. 10 = 195°C).

Synthesis of TSA

All used materials have to be free of moisture. All operations have been carried out under a dry argon atmosphere. 882 mg metallic sodium (38.4 mmole) were reacted with 3.033 mg selenium (38.4 mmole) in a 250 ml round bottom flask with two necks by slightly heating them under stirring in about 20-30 ml dimethylformamide (DMF). A suspension of red-brown Na_2Se_2 in DMF is obtained by this procedure. To this mixture a hot solution of 3000 mg (9.6 mmole) of (11) in 150 ml DMF was added at once. The color of the mixture immediately turns green and red-brown afterwards. The mixture was refluxed for three hours, and cooled to -15°C thereafter. Then the precipitate was filtered and washed with ethanol until the filtrate was only slightly yellow. The adherent ethanol was removed by washing with ether and the compound dried in air finally. This product contains TSA, sodium chloride and a number of additional organoselenium compounds which are responsible for the typical odor of the material. This mass was boiled several times with 500 ml toluene and the precipitate filtered off afterwards. This kind of extraction with

toluene (Soxhlet extractions need much more time during which the compound might be decomposed) is completed after about 3 to 4 liters of toluene or earlier if the solution is only of a slight red color. Cooling the combined filtrates yields TSA in black needles. (Decomposition temp.: 310-315 ^{o}C). There are only a few impurities in this product which can be eliminated by vaccum sublimation and additional recrystallization in toluene.

Elemental analysis:	formula	$C_{14}H_6Se_4$	
yield: 47 %	molar mass:	490.04	
Calc.:	%C 34.29	%H 1.22	%Se 64.49
Found:	%C 34.46	%H 1.32	%Se 63.9

Preparation of TTA

The synthesis starting from (11) and Na_2S_2 follows very similar lines.

Elemental analysis:	formula	$C_{14}H_6S_4$	
yield: 41 %	molar mass:	302.44	
Calc.:	%C 55.62	%H 1.99	%S 42.38
Found:	%C 55.88	%H 1.83	%S 42.63

Synthesis of donor-acceptor (DA) compounds of TSA

Mixing anhydrous solutions of TSA in nitrobenzene or 1.2.4-trichlorobenzene with equimolar amounts of the acceptors bromine (elemental or Bu_4NI_3) chlorine (in form of $FeCl_3$), $TCNQF_4$ and tetracyanoethylene (TCNE) results in an immediate color change from light red to an intense dark red (green in the reaction with $FeCl_3$). After a few

minutes of refluxing and cooling to room temperature the violet to black products were filtered, washed with CH_2Cl_2, acetone or methanol and dried in the air. The following compounds could be characterized analytically: $TSA \cdot I_x$, (elemental analysis: %C 24.19; %H 0.94; %Se 44.3; %I 30.4; x=1.7), $TSA \cdot Br_{2.3}$, $TSA \cdot Cl \cdot H_2O$, $TSA\text{-}TCNQF_4$ and TSA-TCNE. Their pressed pellet conductivities range between $6 \cdot 10^{-1}$ ($\Omega^{-1} \cdot cm^{-1}$) ($TSA \cdot I_x$) and $2.9 \cdot 10^{-2}$ ($\Omega^{-1} \cdot cm^{-1}$) ($TSA \cdot Br_{2.3}$).

Preparation of single crystals

Single crystals were prepared by a diffusion method in a H-shaped cell[11], which works especially well using TSA and Bu_4NI_3. Equimolar amounts of TSA and Bu_4NI_3 were placed in either side of the diffusion cell. The donor was dissolved in hot nitrobenzene, Bu_4NI_3 in acetonitrile. Both compartments were filled with acetonitrile up to the connecting tube. After 2-3 days golden lustreous needles up to 10 mm length were obtained. Daylight seems not to influence the crystallization and was not excluded. These crystals of $TSA \cdot I_{1.2}$ were used for electrical conductivity and X-ray investigations. The latter method indicates the stoichiometry $TSA \cdot I_{1.2}$ for these crystals.

Conductivity measurements

Because the cross sections of the $TSA \cdot I_{1.2}$ crystals were very small (between 10^{-6} and $2 \cdot 10^{-6}$ cm^2),

the dc-conductivity could be measured only of a few crystals. The measurements were carried out by the standard four probe method. The samples were mounted on gold wires in a teflon block and measured with the same apparatus as described recently[12]. In addition the usual low frequency method (1-10 Hz) was applied (Lock-In Amplifier: Ithaco Dynatrac 393) which gave the same results.

The room temperature conductivity along the needle axis $\sigma(300)$ varied between 200 and 400 $(\Omega cm)^{-1}$, while the conductivity perpendicular to the needle axis could not be measured, due to the very small cross sections of the crystals.

The temperature dependence of the normalized dc-conductivity of a typical $TSA \cdot I_{1.2}$ crystal $[\sigma(300) = 210\ (\Omega cm)^{-1}]$ is shown in figure 1. Below 100 K the crystals broke during the measurement, whereby it was not clear if that did happen due to stress of the gold wires on the very thin crystals or due to a phase transition. Between 300 and 230K the dc-conductivity increases slightly by lowering the temperature, while below 230 K the conductivity decreases.

RESULTS AND DISCUSSION

The two new potent donors TTA and TSA can be prepared by routine methods. A number of partly ionic DA complexes of these organic sulfur and selenium heterocyclic compounds with acceptors like halogens, TCNE and $TCNQF_4$ which have been isolated

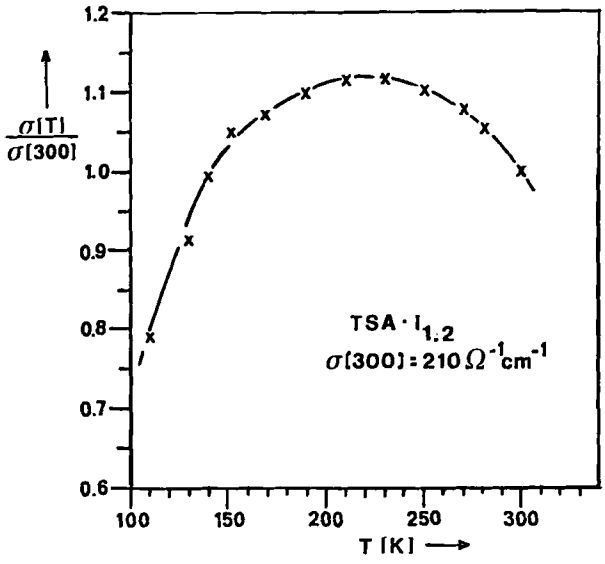

Figure 1: Temperature dependence of the dc-conductivity of $TSA \cdot I_{1.2}$.

as solids and characterized analytically and spectroscopically prove that TTA and TSA have remarkable donor capabilities. Most interesting are the structural relationships between the neutral TSA and its partially oxidized iodide, $TSA \cdot I_{1.2}$, together with the single crystal conductivity of the latter compound. Fig. 2 shows a projection of the TSA stacks onto the ac-plane[+]. The closest interstack (3-dimensional!) Se···Se approaches are be-

[+] Details of the structure determination and the relevant diffractometer data will be published elsewhere.

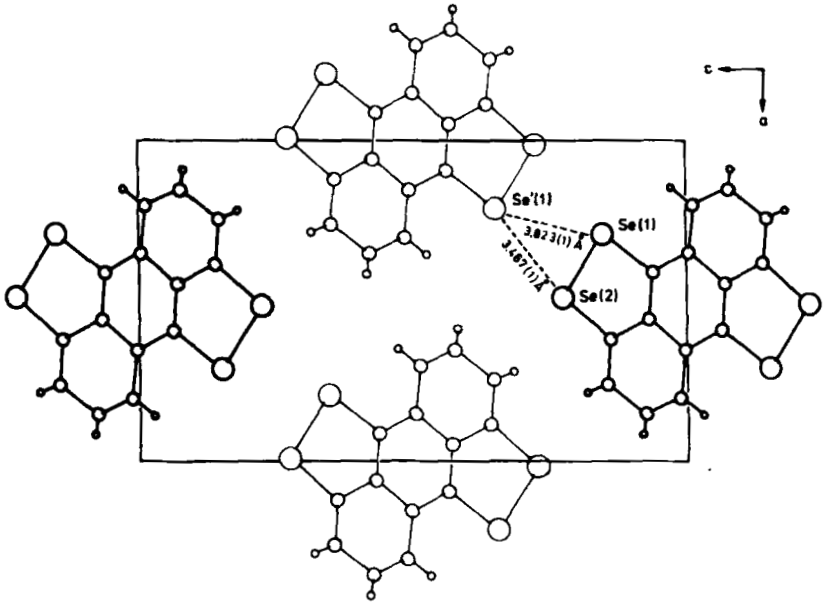

Figure 2: Projection of the TSA structure onto the ac-plane. Possible short interstack Se···Se contacts are shown in one part of the projection and given in Å. Thikker lines indicate molecules with their centers 1/2b above those drawn with thinner lines.

low 3.5 Å. The arrangement of the donors in the polyiodide (fig. 3) is quite similar. The closest interstack contacts are nevertheless somewhat larger. (In the order of 3.7 Å). The oxidation does not enhance the intermolecular contacts.

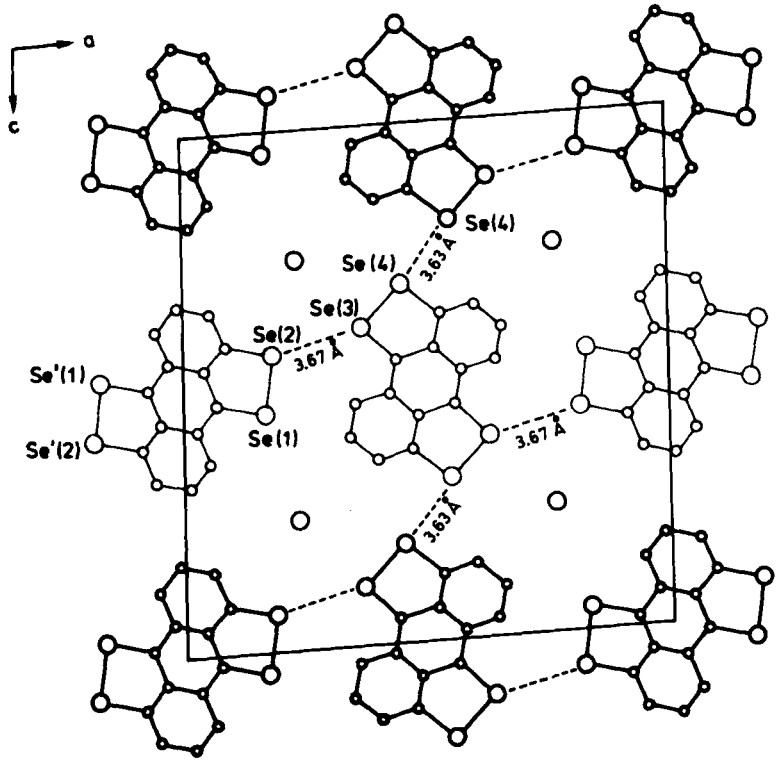

Figure 3: Projection of the $TSA \cdot I_{1.2}$ structure onto the ac-plane. Short interstack Se···Se contacts are indicated in Å. Thicker lines indicate molecules with their centers 1/2b above those molecules drawn with thinner lines.

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