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Some New Conducting Solids

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SOME NEW CONDUCTING SOLIDS

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Charge transfer salts of 3,4,5,-this (methylthio)-1,2-dithiolium ion and similar ions with TCNQ were prepared and studied. Absorption and reflectance spectra of polycrystalline pellets, or deposits on quartz or CaF₂ plates were measured over a wide spectral range. Electrical conductivity of polycrystalline pellets was also measured at room temperature.

The alkaline metal or electrochemical reduction of carbon disulfide in dimethylformamide (DMF) yields 1,3--dithiole-2-thione-4,5-dithiolates (1') and trithiocar-Compounds (1') in DMF sobonates in equimolar amounts. lutions isomerize to 1,2-dithiole-3-thione-4,5-dithiolates(1) (see[1]). Compounds (1) or the Bu, N and Ph.P analogous (2) react with alkyl halides to give 4,5-bis(alkylthio)-1,2-dithiole-3-thiones (3). Subsequent addition of alkyl (:methyl) iodide yields 3,4-tris (alkylthio) 1,2-dithiolium iodides (4) (see [1] - [3]). Desulfurization of (3) with (EtO), P yields cis-and trans-tetrakis- (alkythio)-1,1',2,2'-tetrathiafulvalenes (5) (see [2]). Compounds (4) and (5) were found to be π -donors [2] and give (donor-acceptor) complexes with tetracyanoquinodimethane (TCNQ) {for (5)-TCNQ see In this paper the preparation and preliminary results on the optical and electrical properties of the complexes of (4) with TCNQ are reported.

Charge transfer complexes of 3,4,5-tris (methylthi-

o)-1,2-dithiolium iodide (4a), (mp=156 $^{\circ}$ C), 4,5-(mehylenedithio)-3-methylthio-1,2-dithiolium iodide (4b) (mp=191 $^{\circ}$ C) 4,5-(ethylenedithio)-3-methylthio-1,2-dithiolium iodide (4c), (mp=160 $^{\circ}$ C) and 4,5-(propylenedithio)-3-methylthio-1,2-dithiolium iodide (4d) (mp=184 $^{\circ}$ C)

$$\begin{array}{c|c} CH_3^{S} & S & I^{-} \\ CH_{3S} & & CH_{2S} & & S \\ (4a) CH_3S & & (4c) CH_3S \\ \hline CH_2 & & & CH_2 & & S \\ (4c) CH_3S & & CH_2 & & S \\ \hline CH_2 & & & & CH_2 & & S \\ \hline CH_2 & & & & & CH_2 & & S \\ \hline (4b) CH_3S & & & & & & & & & \\ \hline (4d) CH_3S & & & & & & & & \\ \hline \end{array}$$

with TCNQ were prepared by the known procedure (Melby et al, 1962) using boiling $CH_{*}CN[(4a),(4c),(4d)]$ or DMF for (4b). The two solutions were mixed, heated for an additional 10min and allowed to cool (at ${\sim}0\,^{\circ}\text{C}$) over several hours to yield crystalline precipitate of (4i')--(TCNQ)₂{where (4i⁻) is the cation}. By diluting these precipitates in boiling CH,CN (or DMF) followed by slow cooling or evaporation, one can obtain small crystals of the complexes. Table 1 gives the colour and the analytical data of (4i')-(TCNQ), . The optical absorption spectra of the complexes after rubbing on quartz or CaF, plates and the reflectance spectra of polycrystalline pellets were measured over a wide spectral range. Fig. 1 shows the absorption spectrum (A) of (4a')-(TCNQ), after rubbing on CaF, and the reflectance spectrum (R) of a polycrystalline pellet of (4a')-(TCNQ),. see a similarity of the spectra of $(4a^-)-(TCNQ)_2$

with those of TEA- $(TCNQ)_2$ (see [5], [6]). Similar spectra were observed for the complexes of $(4b^-)$ - $(4d^-)$ with TCNQ.

Table 1 colour and analytical data.

| Complexes Colour $[(4i^*)-(TCNQ)]$ | | Analysis*(%) | | | |
|---|-------------------------|------------------|----------------|------------------|------------------|
| | | С | H | N | S |
| $(4a^-)$ -TCNQ) ₂ | greenish- black cr. | 55.74 (55.46) | 2.68 (2.62) | 16.45 (17.25) | 24.43 (24.65) |
| (4b ⁻)-(TCNQ) ₂ | bl ack powder | 55.06 (54.97) | 1.86 (2.05) | 17.73 (17.69) | 25.22 (25.27) |
| (4c ⁻) - (TCNQ) ₂ | dark-vio- let cr. | | | | 24.80 (24.73) |
| $(4c^-) - (TCNQ)_2$ | dark vio- let cr. | | | | 24.18 (24.20) |
| *calculated values are given in parentheses | | | | | |

*calculated values are given in parentheses.

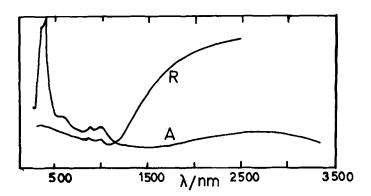


Fig.1. Absorption spectrum (A) of $(4a^{-})$ - $(TCNQ)_{2}$ after rubbing on CaF_{2} and reflectance spectrum (R) of a polycrystalline pellet of $(4a^{-})$ - $(TCNQ)_{2}$.

The dc-conductivity of polycrystalline pellets of the complexes was found to be of the order $0.1-1\Omega^{-1} \, \mathrm{cm}^{-1}$ at room temperature. This means that is one or two orders of magnitude higher than that of TEA-(TCNQ).

(see [7]). Amzil et al [8] found a dc-conductivity of $0.5~\Omega^{-1}~{\rm cm}^{-1}$ for a pellet of $(4a)-({\rm TCN}\Omega)_2$. Results on single crystals measurements will be published in a future paper. Also the preparation and properties of the compounds $(4i^{\circ}){\rm Ni}({\rm dmit})_2$ and $(4i^{\circ})_{\rm X}{\rm Ni}({\rm dmit})_2$ (where x<1 and dmit=4,5-dimercapto-1,3-dithiole-2-thione) will be described elsewhere [9].

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