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Some New Conducting Solids

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SOME NEW CONDUCTING SOLIDS

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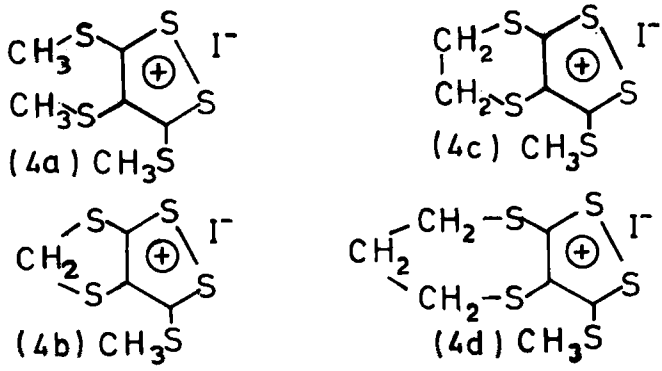
Charge transfer salts of 3,4,5,-this (methylthio)-1,2--dithiolium ion and similar ions with TCNQ were prepared and studied. Absorption and reflectance spectra of polycrystalline pellets, or deposits on quartz or CaF_2 plates were measured over a wide spectral range. Electrical conductivity of polycrystalline 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 trithiocarbonates in equimolar amounts. Compounds (1′) in DMF solutions isomerize to 1,2-dithiole-3-thione-4,5-dithiolates(1) (see[1]). Compounds (1) or the Bu_4N and Ph_4P 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 $(EtO)_3P$ 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 also [4] }. 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°C), 4,5-(mehylene-dithio)-3-methylthio-1,2-dithiolium iodide (4b)(mp=191° C) 4,5-(ethylenedithio)-3-methylthio-1,2-dithiolium iodide (4c), (mp=160°C) and 4,5-(propylenedithio)-3-me--thylthio-1,2-dithiolium iodide (4d)(mp=184°C)



with TCNQ were prepared by the known procedure (Melby et al, 1962) using boiling CH_3CN [(4a),(4c),(4d)] or DMF [for (4b)]. The two solutions were mixed, heated for an additional 10min and allowed to cool (at ~0°C) over several hours to yield crystalline precipitate of (4i$^+$)--(TCNQ)$_2$ {where (4i$^+$) is the cation}. By diluting these precipitates in boiling CH_3CN (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)$_2$. The optical absorption spectra of the complexes after rubbing on quartz or CaF_2 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)$_2$ after rubbing on CaF_2 and the reflectance spectrum (R) of a polycrystalline pellet of (4a$^+$)-(TCNQ)$_2$. One can 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 [(4i´)-$(TCNQ)_2$]	Colour	Analysis*(%) C	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´)-$(TCNQ)_2$	black powder	55.06 (54.97)	1.86 (2.05)	17.73 (17.69)	25.22 (25.27)
(4c´)-$(TCNQ)_2$	dark-violet cr.	56.03 (55.64)	2.43 (2.32)	16.56 (17.31)	24.80 (24.73)
(4c´)-$(TCNQ)_2$	dark violet cr.	56.37 (56.27)	2.51 (2.57)	16.88 (16.94)	24.18 (24.20)

*calculated values are given in parentheses.

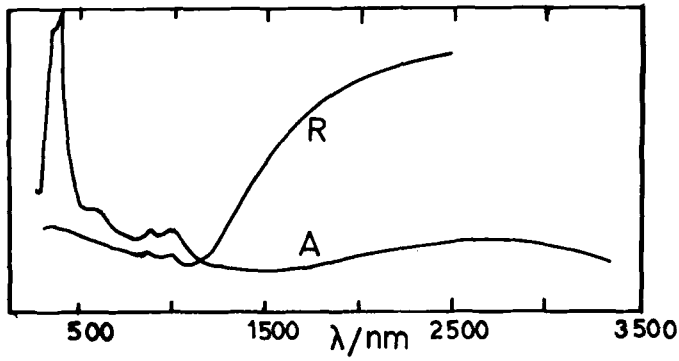


Fig.1. Absorption spectrum (A) of (4a´)-$(TCNQ)_2$ after rubbing on CaF_2 and reflectance spectrum (R) of a polycrystalline pellet of (4a´)-$(TCNQ)_2$.

The dc-conductivity of polycrystalline pellets of the complexes was found to be of the order $0.1\text{-}1\Omega^{-1}cm^{-1}$ at room temperature. This means that is one or two orders of magnitude higher than that of TEA-$(TCNQ)_2$.

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

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