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CONDUCTIVE SOLIDS BASED ON SOME NEW MOLECULES WITH ISOTHIAZOLO-RINGS

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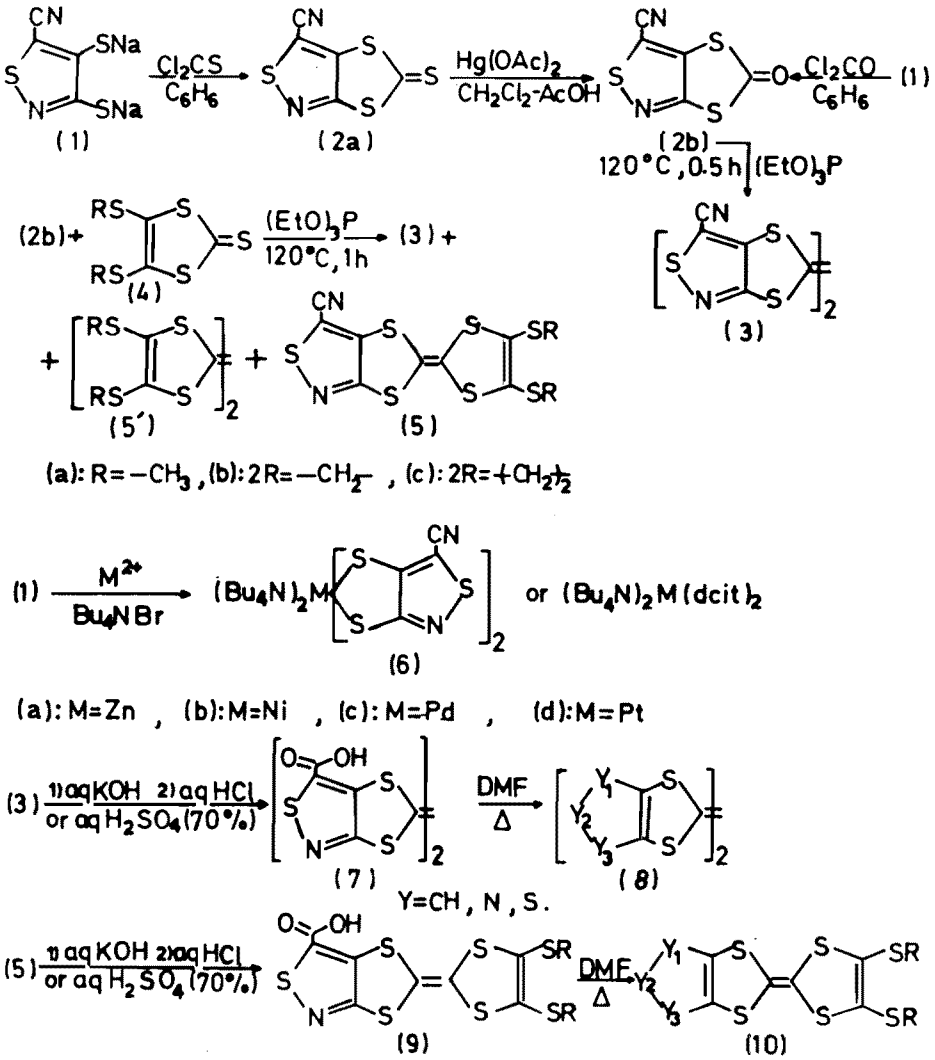
INTRODUCTION

During the last three years, a number of conductive solids based on substituted derivatives of the tetrathiafulvalene with at least one pyrazino-ring [1]or pyridino-ring [2] have been reported. The corresponding metal 1,2-dithiolenes with pyrazino-ring [1], [3] or pyridino-ring [4] do not give conductive solids.

In this paper we report preliminary results on the preparation and investigation of a number of conductive solids based on some derivatives of tetrathiafulvalene with at least one isothiazolo-ring (π-donors) and on some metal 1,2-dithiolenes with two isothiazolo-rings (π-acceptors). The new π-donors and π-acceptors were prepared from disodium 5-cyanoisothiazoledithiolate [5], as starting material, according to the Scheme 1. The conductive solids were prepared from the compounds (3), (5), (8) and (10) by electrocrystallization in presence of Bu_4NX(where X=BF_4, Br_3 etc) and from the compounds (6) by electrocrystallization in presence of a π-donor.

EXPERIMENTAL

Details on the preparation of the compounds (3), (5) and (6) from disodium 5-cyanoisothiazoledithiolate (1) [5] are described in [6]. The compound (8) was prepared as follows. To a solution of 14g of KOH in 600ml of water, 1.4g of (3) was added and the mixture was heated at reflux temperature for 4 hours. After cooling the mixture was filtered . To the filtrate 30ml of aq.HCl (37%) was added dropwise. The precipitate, which contains (7) was filtered, washed with water and dried. Same product (7) was obtained by heating (3) in aq. H_2SO_4(70%v) at reflux temperature. The crude product (1.6g) was diluted in DMF (60ml) and heated at reflux temperature for 1 hour. After cooling the blue precipitate was filtered off and then the DMF was removed by evaporation. After extraction with CH_2Cl_2 and separation on silica gel column chromatography 250mg of (8) were obtained. Compound (8) is a pale-



Scheme 1

-yellow solid; mp=276°C; mw=318 (:mass spectrum);UV(CH_3CN) (λ/nm, absorbance/a.u.)342(0.65), 310(0.485sh), 279(0.57),260 (0.49sh);IR(KBr) (cm^{-1}) 3071(m), 1380(m), 1293(s), 826(m), 783(m), 655(m). UV-spectrum, in comparison to those of (3) and (7), is an evidence that the structure of (8) is that with Y_1=CH, Y_2=N and Y_3=S. Compound (10c) (mp=197°C)was prepared by similar method. The preparation of (8) and metal 1,2-dithiolene analogous from 8-cyanoisothiazolopentathiepin [7] is in progress.

Compound (5'c)$_x$Ni(dcit)$_2$ (x$\sim$2) was prepared by electrocrystallization at 0.4mm platinum electrode in a stardard H-cell containing a solution of 20mg of (5'c) and 23mg of (6b) [8] in 65ml of CH_2Cl_2 and using a current density of 6μA/cm^2. After 4 days of growth black flakes, green in the reflected light, were obtained at the anode. Analysis:

Cald(for x=2)	C28.71, H2.88, N4.78, S60.13
Found	C30.54, H1.36, N5.32, S60.05

Compound $(8)_xBF_4$ was prepaped by similar method using a solution-suspension of 20mg of (8) and 120mg of Bu_4NBF_4 in 60 ml of CH_2Cl_2 and a current density of $1.5\mu A/cm^2$. After 10 days of growth black needles, green or violet in the reflected light were obtained at the anode.

RESULTS AND DISCUSSION

Fig.1 shows the reflectance spectra of polycrystalline compactions* of $(5'c)_xNi(dcit)_2$ and $(8)_xBF_4$ and the absorption spectra of these compounds rubbed on CaF_2-plates. The spectra indicate that the compounds are semiconductors with activation energy ca 185 and 300meV, respectively. The dc-conductivity on polycrystalline pellets* at room temperature was

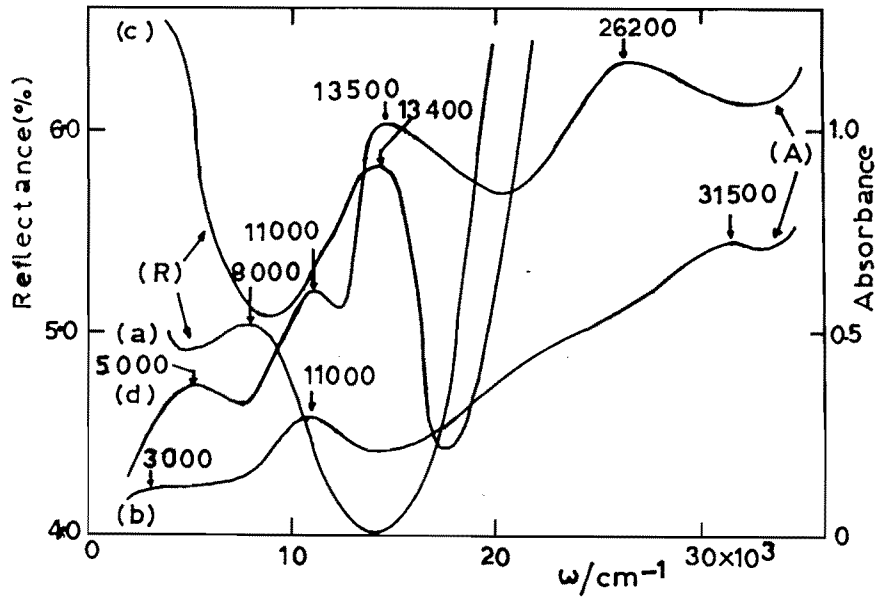


Fig.1. Reflectance (R) and absorption(A) spectra of $(5'c)_xNi(dcit)_2$ (a), (b) and $(8)_xBF_4$ (c), (d).

found to be of the order of 10 and $0.1\Omega^{-1}cm^{-1}$, respectively. These results are similar to those obtained from $Z_xM(dmit)_2$ [9] and $(BPTTF)_2BF_4$ [10] respectively. The preparation and investigation of new materials having at least one isothiazolo-ring are in progress.

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* For instrumentation see ref.2

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