Disodium 5-Cyanoisothiazoledithiolate as a Starting Material for Preparation of New Conductive Solids

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Z. Naturforsch. **42b**, 1050–1051 (1987);
received March 23, 1987

Heterocycles, Metal 1,2-Dithiolenes,
Tetrathiafulvalenes

Starting from disodium 5-cyanoisothiazoledithiolate some new substituted derivatives of the tetrathiafulvalene and some metal 1,2-dithiolenes with at least an isothiazolo-ring have been prepared. From these compounds a number of conductive cation radical salts have been obtained.

Substituted derivatives of tetrathiafulvalene having at least one pyrazino ring [1] or one pyridino ring [2] and metal 1,2-dithiolenes with pyrazino rings

[1, 3] or pyridino rings [4] have been reported recently.

In this paper we report the preparation of some derivatives of the tetrathiafulvalene having at least one isothiazolo ring, some metal 1,2-dithiolenes having two isothiazolo rings and a few of their cation radical salts. The new compounds were prepared from disodium 5-cyanoisothiazoledithiolate [5], as starting material, according to the following Scheme 1.

Experimental

Disodium 5-cyanoisothiazoledithiolate (**1**) was transformed to the corresponding 1,3-dithiole-2-thione (**2a**) or 1,3-dithiole-2-one (**2b**), after treatment with Cl_2CS or Cl_2CO in benzene, respectively, by well known procedures [6]. **2b** can be also obtained from **2a** after treatment with $\text{Hg}(\text{OAc})_2$ in a mixture of CH_3COOH and CH_2Cl_2 (1:1) [7]. Self-coupling of **2a** or **2b** and cross-coupling of **2b** with **4** [8] via triethyl phosphite at 120 °C for 0.5–1 h, afforded the bis(cyanoisothiazole)tetrathiafulvalene (**3**) and a mixture of **3**, **5** and **5'**, respectively. The unsymmetrical tetrathiafulvalene (**5**) was separated from the mixture using silica gel column chromatog-

Scheme 1.

a: $\text{M} = \text{Zn}$; **b**: $\text{M} = \text{Ni}$; **c**: $\text{M} = \text{Pd}$; **d**: $\text{M} = \text{Pt}$

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Table I. Preparative and UV-spectral data.

Compound	Yield [%]	m.p. [°C]	Colour	Analysis [%]*				UV-spectrum [λ/nm]**
				C	H	N	S	
1	50	300 (lit. 172–178) [5]	yellow	+	+	+	+	396
2a	85	147	yellow	27.94(27.76)	00(000)	12.51(12.95)	59.29(59.29)	371
2b	70	110	white	+	+	+	+	310–318
3	52	>300	yellow	32.17(32.60)	00(000)	15.13(15.21)	52.04(52.17)	400
5a	2.6	≥136	brown	+	+	+	+	430
5b	5.5	234	brown	+	+	+	+	430
5c	10	247	orange-red	31.84(31.91)	1.08(1.06)	7.42(7.44)	59.43(59.57)	434
6a	63	136	yellow	55.33(55.46)	8.34(8.32)	6.43(6.47)	22.03(22.19)	375–389
6b	80	170	brown-golden	54.09(54.09)	8.13(8.17)	9.67(9.46)	22.01(21.66)	466–503
6c	41	171	brown	52.84(52.96)	7.80(7.94)	6.16(6.18)	22.03(21.18)	433–448
6d	45	168	brown-golden	48.11(48.24)	7.07(7.23)	5.60(5.63)	19.18(19.29)	474–502

* Calculated values are given in parentheses; ** position of the low frequency band (solvent: CH₃CN); + this element-analysis was not done.

raphy with CH₂Cl₂ as eluent solvent. Treatment of **1** with salts of transition metals M (= Zn, Ni, Pd, Pt), by well known procedures [9], in a mixture of ethanol and water 1:1 and in presence of tetra-*n*-butylammonium bromide (Bu₄NBr), afforded the corresponding (Bu₄N)₂M(dcit)₂ [where H₂dcit = 3,4-dimercapto-5-cyanoisothiazole] complexes (**6**). The compounds **2a**, **2b** and **6b** can be also prepared from compound **6a** after treatment with Cl₂CS, Cl₂CO, and NiCl₂, respectively. Preparative and UV spectral data are given in Table I.

The compounds **5a**, **5b** and **5c** gave brown precipitates of the type (6)Br₃, after reaction with Br₂ in CH₂Cl₂. Electrooxidation of **6b**, **6c** and **6d** in CH₂Cl₂ gave the corresponding cation deficient compounds of the type (Bu₄N)_xM(dcit)₂ (where 0 < *x* < 1). However, electrooxidation of **6b**, **6c** and **6d**, in CH₂Cl₂ and in the presence of a donor such as tetrathiafulvalene (TTF), bis(ethylenedithio)tetrathiafulvalene (BEDTTTF) (**5'c**), afforded a number of complexes with a composition 1:1.

Results and Discussion

Dc-conductivity (σ) measurements on compressed polycrystalline pellets of the compounds (**6**)Br₃ and (Bu₄N)_xM(dcit)₂ showed that the former are semiconductors (σ ~ 10⁻³ Ω⁻¹cm⁻¹) and the latter are insulators. Similar measurements on compressed pellets of (TTF)M(dcit)₂ and (BEDTTTF)M(dcit)₂ showed that these compounds are conductive with σ of the order 1–30 Ω⁻¹cm⁻¹. The behaviour of these last materials is similar to that observed from materials with the same π-donors and similar metal 1,2-dithiolenes [10–13]. Materials containing Ni(dmit)₂ [where H₂dmit is dimercaptoisotrithiocarbonate] have been found to be conductive solids in two or three dimensions [11, 12] because of the S–S intermolecular contacts. In the present case both S–S and S–N contacts are expected. However, more accurate measurements are required on single crystals of these compounds. Also, it is expected that the compounds **3** and **5** will become better π-donors after substitution of CN-group by hydrogen.

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