

Some Air-stable Unsymmetrical Nickel 1,2-Dithiolenes with Extended Tetrathiafulvalenedithiolato Ligands

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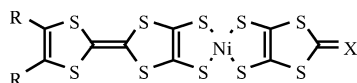
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The air-stable unsymmetrical complexes Ni(dt)(dmit), Ni(dt)(dmio), Ni(tmdt)(dmit), Ni(tmdt)(dmio), Ni(etdt)(dmit), Ni(etdt)(dmio), Ni(ptdt)(dmit), and Ni(ptdt)(dmio) (where dmit is 1,3-dithiol-2-thione-4,5-dithiolate, dmio is 1,3-dithiol-2-one-4,5-dithiolate, dt is tetrathiafulvalenedithiolate, tmdt is trimethylenetetrathiafulvalenedithiolate, etdt is ethylenedithiotetrathiafulvalenedithiolate, and pt dt is propylenedithiotetrathiafulvalenedithiolate) were prepared and characterized analytically, electrochemically and spectroscopically. In the solid state, the compounds exhibit optical absorption edges between 0.70 and 0.82 eV. Their LUMO and HOMO levels occur at ca. 4.5 and 5.3 eV, respectively.

Key words: Metal 1,2-Dithiolenes, Single-component Semiconductors, Thin Films

Introduction

During the last five decades a number of tetrathiafulvalenes (TTFs), metal 1,2-dithiolenes (M 1,2-DTs) and selenium analogs have been prepared and studied (see [1–24]). Their properties depend on the nature and the number of the additional groups and heteroatoms of the TTF or M 1,2-DT core. Compounds with electron-donating groups have low values of redox potentials and are good precursors of conducting and superconducting crystals (see for example [1–4, 11, 13]). Usually, these precursors are oxidized in air. However, TTFs and M 1,2-DTs with electron-withdrawing groups have relatively high redox potentials and are stable in air. Some of them have been used as components of optical and electronic devices (see for example refs. [5, 7–10, 17, 18]). TTFs and M 1,2-DTs can be symmetrical or unsymmetrical. A number of unsymmetrical (mixed-ligand) Ni 1,2-DTs, with an extended-TTF-dithiolate [9, 15] ligand and dmit (*i. e.* 1,3-dithiol-2-thione-4,5-dithiolate) or dmio (*i. e.* 1,3-dithiol-2-one-4,5-dithiolate) [1, 13] as the other ligand, of the general formula



can be formulated. The unsymmetrical complexes

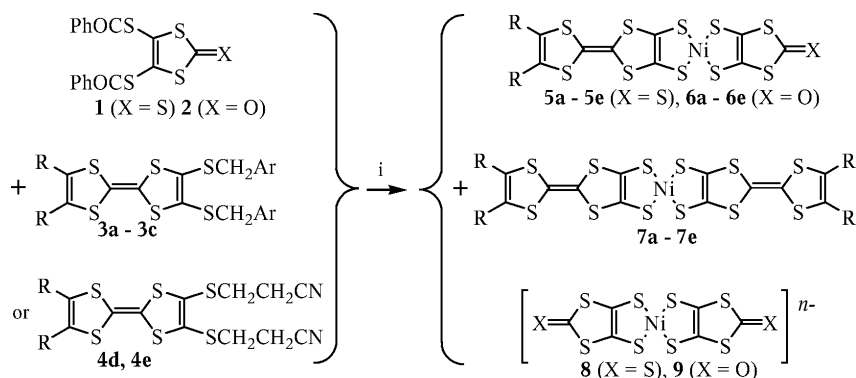
Ni(dmdt)(dmit) ($R = \text{CH}_3$, $X = \text{S}$) and Ni(dmdt)(dmio) ($R = \text{CH}_3$, $X = \text{O}$) have already been reported [9].

In this paper, the preparation and characterization of the following unsymmetrical complexes are described: Ni(dt)(dmit) ($R = \text{H}$, $X = \text{S}$), Ni(dt)(dmio) ($R = \text{H}$, $X = \text{O}$), Ni(tmdt)(dmit) ($2R = \text{CH}_2\text{CH}_2\text{CH}_2$, $X = \text{S}$), Ni(tmdt)(dmio) ($2R = \text{CH}_2\text{CH}_2\text{CH}_2$, $X = \text{O}$), Ni(etdt)(dmit) ($2R = \text{SCH}_2\text{CH}_2\text{S}$, $X = \text{S}$), Ni(etdt)(dmio) ($2R = \text{SCH}_2\text{CH}_2\text{S}$, $X = \text{O}$), Ni(ptdt)(dmit) ($R = \text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$, $X = \text{S}$), and Ni(ptdt)(dmio) ($R = \text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$, $X = \text{O}$).

Using **1–4** as starting materials [19–22] (see also refs. [1–3]), the new unsymmetrical complexes have been prepared by cross-coupling [6] (see also refs. [7, 9, 10]) according to the procedure of Scheme 1. The products have been characterized analytically, electrochemically and spectroscopically. The results are compared with those obtained for related symmetrical and unsymmetrical complexes.

Results and Discussion

From the reactions of Scheme 1, a number of products (**5**, **6**) and byproducts (**7–9**) (dianionic, monoanionic, cation deficient, neutral, and other forms) can be expected [1, 6, 16], but after oxidation in air and chromatographic separation using a silica-gel column and CS_2 as eluent, only the neutral unsymmetrical



i = 1) NaOMe in MeOH, 2) NiCl₂ in MeOH, 3) aq. HCl (35 %), in air;
 Ar = *p*-OAc-C₆H₄; (a) R = H, (b) R = CH₃, (c) 2R = CH₂CH₂CH₂,
 (d) 2R = SCH₂CH₂S, (e) 2R = SCH₂CH₂CH₂S; 0 ≤ *n* < 1.

Scheme 1.

Table 1. Redox potentials (V)^a.

Complex	E _{1/2} (2-/-1-)	E _{1/2} (1-/0)	E _{1/2} (0/+)
Ni(dmdt) ₂	-0.49	-0.18	+0.70
Ni(tmtdt) ₂	-0.50	-0.16	+0.85
Ni(etdt) ₂	-0.45	-0.09	?
Ni(dt) ₂	-0.29	-0.03	?
Ni(ptdt) ₂	-0.30	0.00	+1.35
Ni(dmdt)(dmit)	(-0.34)	(+0.020)	?
Ni(dmdt)(dmio)	(-0.355)	(+0.035)	?
Ni(tmtdt)(dmit)	(-0.345)	(+0.030)	?
Ni(tmtdt)(dmio)	(-0.37)	(+0.045)	?
Ni(etdt)(dmit)	(-0.32)	(+0.065)	?
Ni(etdt)(dmio)	(-0.345)	(+0.08)	?
Ni(dt)(dmit)	(-0.24)	(+0.095)	?
Ni(dt)(dmio)	(-0.265)	(+0.11)	?
Ni(ptdt)(dmit)	(-0.245)	(+0.11)	?
Ni(ptdt)(dmio)	(-0.27)	(+0.125)	?
Ni(dmit) ₂	-0.19	+0.22	≥ 1.2
Ni(dmio) ₂	-0.24	+0.25	≥ 1.2

^a Data converted to values *versus* SCE as reference electrode. Calculated values, using the equation E(AB) = [E(AA)+E(BB)]/2, are given in parentheses (AB is the unsymmetrical, AA and BB are the corresponding symmetrical complexes, respectively).

complexes were obtained. The yields were low (0.5–2 %), perhaps because of the contamination with other species (see [7, 16] and refs. therein). The new complexes were found to be soluble in CS₂ and DMF, but only slightly soluble in CH₂Cl₂ and other organic solvents. From the solutions thin deposits on quartz plates and other substrates can be obtained after evaporation of the solvents. Crystals obtained from solutions were not suitable for crystal structure determination.

Owing to the low solubility of the complexes in CH₂Cl₂ or CH₃CN, their redox potentials were not observed experimentally, but their values were calculated

from those obtained for the anionic forms of the corresponding symmetrical complexes [11a, 13, 15]. From the redox potentials of several complexes of nickel observed in CH₃CN *versus* SCE [11, 12] and those observed in CH₃CN *versus* Ag/0.01 M Ag⁺ [11a, 13] as reference electrodes, one finds that the factor for the conversion Ag/Ag⁺ → SCE has values from 0.30 to 0.38 V, while that given in the literature [14] (see also ref. [13b]) is 0.559 V. Using the value 0.30 V, one can find from the data of [11a, 13] that the redox potentials E_{1/2}(2-/-1-) and E_{1/2}(1-/0) of Ni(dmit)₂ have values -0.19 and 0.22 V, respectively, *versus* SCE as a reference electrode. These values are close to those found experimentally *versus* SCE [11, 12a]. Also, using the factor 0.30, the redox potentials of the symmetrical complexes Ni(L)₂ (where L is an extended TTF-dithiolate ligand) and Ni(dmit)₂, given in refs. [11a, 13, 15] *versus* Ag/Ag⁺, were converted to values *versus* SCE. The redox potentials of the unsymmetrical complexes Ni(L)(dmit) or Ni(L)(dmio) were calculated as the mean values of the corresponding symmetrical complexes Ni(L)₂ and Ni(dmit)₂ or Ni(L)₂ and Ni(dmio)₂, respectively. Generally, in M 1,2-DTs the calculated values are in agreement with those observed experimentally, when the redox waves are reversible [1, 11a, 12, 13]. In the present cases, the calculated values of redox potentials E_{1/2}(2-/-1-), E_{1/2}(1-/0) and E_{1/2}(0/+*x*) (0 < *x* ≤ 1) for the unsymmetrical and those of symmetrical complexes are listed in Table 1 for comparison. It appears that by substitution of one ligand L in Ni(L)₂ by an electron-withdrawing ligand like dmit

or dmio, the redox potentials of the corresponding complexes Ni(L)(dmit) and Ni(L)(dmio) increase. The redox potential of Ni complexes with ligands containing alkylthio groups as additional substituents are close to those of the corresponding complexes with L = tmdt [15c]. The values of $E_{1/2}(1 - /0)$ of unsymmetrical complexes are larger than 0 V (*versus* SCE). Using the conversion factor 0.559 V, the calculated values were found to be much larger. This indicates that the neutral unsymmetrical complexes Ni(L)(dmit) and Ni(L)(dmio) described here must be stable in air (see [14] and refs. cited therein). Experimentally (spectroscopically) it was found that solutions or thin deposits of the complexes are stable in air for at least several months. Moreover, the successful preparation of the complexes under strongly oxidizing conditions (see Scheme 1 and Experimental Section) confirms their stability in air (see [10b] and refs. cited therein).

The optical absorption (OA) spectra of thin deposits of the complexes on quartz plates as well as the spectra of solutions were found to exhibit strong bands in the near IR spectral region. Fig. 1 shows the OA spectra of a thin deposit of Ni(dt)(dmit) on a quartz plate before and after rubbing it, and the spectrum of a solution in CS₂ for comparison.

Before the rubbing, the spectrum shows an OA onset or an OA edge at *ca.* 1700 nm (0.73 eV) and an OA maximum at *ca.* 1245 nm (1 eV). The positions of OA onset and OA maximum are shifted to shorter wavelengths after rubbing the deposit, and are close to those of solutions. Some changes in the shape and intensity of the spectra after rubbing appear to be due to the partial orientation of molecules (see ref. [25]

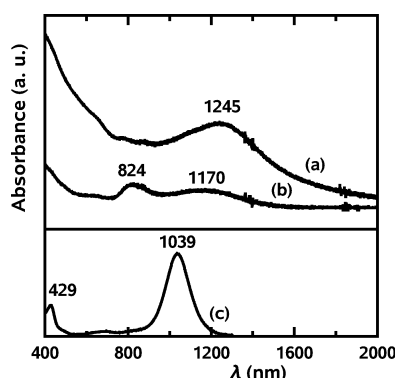


Fig. 1. OA spectra of Ni(dt)(dmit) thin deposits on a quartz plate before (a) and after (b) rubbing, and the OA spectrum of the complex in CS₂ (c).

and refs. therein). Similar results were obtained for other (unsymmetrical) complexes, Ni(L)(dmit) and Ni(L)(dmio). The positions of OA onset (OA maximum) in the spectra of thin deposits of Ni(dt)(dmio), Ni(dmdt)(dmit), Ni(dmdt)(dmio), Ni(tmdt)(dmit), Ni(tmdt)(dmio), Ni(etdt)(dmit), Ni(etdt)(dmio), Ni(ptdt)(dmit), and Ni(ptdt)(dmio) are at 0.72 (1.00), 0.72 (0.99), 0.70 (0.97), 0.70 (0.91), 0.82 (1.00), 0.72 (1.02), 0.82 (1.03), 0.71 (0.98) and 0.73 eV (1.00 eV), respectively. The OA bands of the unsymmetrical complexes occur at shorter wavelengths than those of the corresponding symmetrical Ni(L)₂ complexes [15d].

The LUMO- and HOMO-level values of the unsymmetrical complexes were calculated from electrochemical and spectroscopic data by methods reported in [5, 10b] and were found to be *ca.* −4.5 and −5.3 eV, respectively. These values are comparable to those obtained for some other complexes stable in air [10b, 17]. In the case of Ni(dpdt)(dmit) (where dpdt is diphenylethylenedithiolate), which is a channel material for ambipolar field-effect transistors stable in air [10b], the LUMO- and HOMO-level values were found to be −4.67 and −5.42 eV, respectively [12b].

The chemical, electrochemical and spectroscopic data described above indicate that the new complexes can be candidates for optical and electronic devices [5, 7–10, 17, 18, 26, 27].

Experimental Section

(*Tetrathiafulvalenedithiolato*)(*1,3-dithiol-2-thione-4,5-dithiolato*)nickel, Ni(dt)(dmit) (**5a**)

In a two-necked 100 mL flask, a solution of NaOMe, freshly prepared from Na (110 mg, 4.8 mmol) and deoxygenated MeOH (25 mL), was added to a mixture of compound **1** (324 mg, 0.8 mmol) and **3a** (450 mg, 0.8 mmol), under nitrogen atmosphere, and the mixture was stirred for 35 min. To the obtained red-brown solution, a solution of NiCl₂ · 6H₂O (381 mg, 1.6 mmol) in deoxygenated MeOH (25 mL) was added dropwise within 20 min. The solution turned brown and was stirred under nitrogen atmosphere for 1 h at r. t. Then, aq. HCl (1 mL, 35 %) was added, the mixture was transferred to a beaker and stirred in air for 2 h and then diluted slowly (0.5 h) with water (100 mL). The precipitate was filtered, washed with water and MeOH and dried in air. The green-brown solid was extracted with CS₂ and chromatographed on silica gel, using CS₂ as eluent. The first green fraction contained **5a** (8.5 mg, 2%). M. p. ≥ 250 °C (dec.). – UV/vis/nearIR (CS₂): $\lambda_{\text{max}}(\lg \epsilon_{\text{max}})$ = 1039 nm (4.47). – IR (KBr): ν = 1042, 1067 (C=S), 2854, 2870, 2920,

2954, 2966 (CH) cm^{-1} [23, 24]. – $\text{C}_9\text{H}_2\text{S}_{11}\text{Ni}$ (521.5): calcd. C 20.73, H 0.39; found C 20.81, H 0.45.

(Tetrathiafulvalenedithiolato)(1,3-dithiol-2-one-4,5-dithiolato)nickel, $\text{Ni}(\text{dt})(\text{dmio})$ (**6a**)

As in the case of $\text{Ni}(\text{dt})(\text{dmit})$, using **2** (312 mg, 0.8 mmol) instead of **1**, and **3a** (450 mg, 0.8 mmol), complex **6a** (4.1 mg, 1 %) was obtained. M.p. ≥ 240 °C (dec.). – UV/vis/nearIR (CS_2): $\lambda_{\text{max}}(\lg \epsilon_{\text{max}}) = 978$ nm (4.45). – IR (KBr): $\nu = 1619, 1671$ (C=O), 2852, 2870, 2922, 2954, 2965 (CH) cm^{-1} [23, 24]. – $\text{C}_9\text{H}_2\text{OS}_{10}\text{Ni}$ (505.5): calcd. C 21.39, H 0.40; found C 21.20, H 0.48.

(Trimethylenetetrathiafulvalenedithiolato)(1,3-dithiol-2-thione-4,5-dithiolato)nickel, $\text{Ni}(\text{tmdt})(\text{dmit})$ (**5c**)

As in the case of $\text{Ni}(\text{dt})(\text{dmit})$, using **1** (324 mg, 0.8 mmol) and **3c** (485 mg, 0.8 mmol) instead of **3a**, complex **5c** (1.8 mg, 0.4 %) was obtained. M.p. ≥ 245 °C (dec.). – UV/vis/nearIR (CS_2): $\lambda_{\text{max}}(\lg \epsilon_{\text{max}}) = 1046$ nm (4.50). – IR (KBr): $\nu = 1025, 1064$ (C=S), 2854, 2870, 2919, 2968 (CH) cm^{-1} . – $\text{C}_{12}\text{H}_6\text{S}_{11}\text{Ni}$ (561.5): calcd. C 25.66, H 1.08; found C 26.60, H 1.14.

(Trimethylenetetrathiafulvalenedithiolato)(1,3-dithiol-2-one-4,5-dithiolato)nickel, $\text{Ni}(\text{tmdt})(\text{dmio})$ (**6c**)

As in the case of $\text{Ni}(\text{dt})(\text{dmit})$, using **2** (312 mg, 0.8 mmol) instead of **1**, and **3c** (485 mg, 0.8 mmol) instead of **3a**, complex **6c** (3.5 mg, 0.8 %) was obtained. M.p. ≥ 240 °C (dec.). – UV/vis/nearIR (CS_2): $\lambda_{\text{max}}(\lg \epsilon_{\text{max}}) = 978$ nm (4.48). – IR (KBr): $\nu = 1621, 1670$ (C=O), 2852, 2871, 2921, 2953 (CH) cm^{-1} . – $\text{C}_{12}\text{H}_6\text{OS}_{10}\text{Ni}$ (545.5): calcd. C 26.42, H 1.11; found C 26.28, H 1.01.

(Ethylenedithiotetrathiafulvalenedithiolato)(1,3-dithiol-2-thione-4,5-dithiolato)nickel, $\text{Ni}(\text{etdt})(\text{dmit})$ (**5d**)

In a two-necked 100 mL flask, a solution of NaOMe, freshly prepared from Na (97 mg, 4.2 mmol) and deoxygenated MeOH (30 mL), was added to a suspension of compound **4d** (325 mg, 0.7 mmol) in deoxygenated MeOH (5 mL), under nitrogen atmosphere, and the mixture was stirred for 4 h. Compound **1** (284 mg, 0.7 mmol) was added and stirring continued for 15 min. To the red-brown solution, a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (333 mg, 1.4 mmol) in deoxygenated MeOH (25 mL) was added dropwise within 20 min. The solution turned brown and was stirred under nitrogen atmosphere for 1 h at r.t. Then, aq. HCl (1 mL, 35 %) was added, the mixture was transferred to a beaker, stirred in

air for 2 h, and diluted slowly (0.5 h) with water (100 mL). The precipitate was filtered, washed with water and MeOH and dried in air. The green-brown solid was extracted with CS_2 and chromatographed on silica gel, using CS_2 as eluent. The first green fraction contained **5d** (2.1 mg, 0.5 %). M.p. ≥ 250 °C (dec.). – UV/vis/nearIR (CS_2): $\lambda_{\text{max}}(\lg \epsilon_{\text{max}}) = 1035$ nm (4.32). – IR (KBr): $\nu = 1032, 1057$ (C=S), 2852, 2924, 2969, 2972 (CH) cm^{-1} . – $\text{C}_{11}\text{H}_4\text{S}_{13}\text{Ni}$ (611.7): calcd. C 21.60, H 0.66; found C 21.52, H 0.56.

(Ethylenedithiotetrathiafulvalenedithiolato)(1,3-dithiol-2-one-4,5-dithiolato)nickel, $\text{Ni}(\text{etdt})(\text{dmio})$ (**6d**)

As in the case of $\text{Ni}(\text{etdt})(\text{dmit})$, using **2** (273 mg, 0.7 mmol) instead of **1**, and **4d** (325 mg, 0.7 mmol), complex **6d** (4.5 mg, 1.1 %) was obtained. M.p. ≥ 245 °C (dec.). – UV/vis/nearIR (CS_2): $\lambda_{\text{max}}(\lg \epsilon_{\text{max}}) = 982$ nm (4.20). – IR (KBr): $\nu = 1617, 1662$ (C=O), 2853, 2924, 2959, 2972 (CH) cm^{-1} . – $\text{C}_{11}\text{H}_4\text{OS}_{12}\text{Ni}$ (595.6): calcd. C 22.18, H 0.68; found C 22.29, H 0.77.

(Propylenedithiotetrathiafulvalenedithiolato)(1,3-dithiol-2-thione-4,5-dithiolato)nickel, $\text{Ni}(\text{ptdt})(\text{dmit})$ (**5e**)

As in the case of $\text{Ni}(\text{etdt})(\text{dmit})$, using **1** (284 mg, 0.7 mmol) and **4e** (325 mg, 0.7 mmol) instead of **4d**, complex **5e** (5.5 mg, 1.3 %) was obtained. M.p. ≥ 250 °C (dec.). – UV/vis/nearIR (CS_2): $\lambda_{\text{max}}(\lg \epsilon_{\text{max}}) = 1041$ nm (4.25). – IR (KBr): $\nu = 1020, 1065$ (C=S), 2865, 2929, 2971 (CH) cm^{-1} . – $\text{C}_{11}\text{H}_4\text{OS}_{12}\text{Ni}$ (625.7): calcd. C 23.03, H 0.97; found C 23.17, H 0.82.

(Propylenedithiotetrathiafulvalenedithiolato)(1,3-dithiol-2-one-4,5-dithiolato)nickel, $\text{Ni}(\text{ptdt})(\text{dmio})$ (**6e**)

As in the case of $\text{Ni}(\text{dt})(\text{dmit})$, using **2** (273 mg, 0.7 mmol) instead of **1**, and **4e** (325 mg, 0.7 mmol) instead of **4d**, complex **6e** (6.4 mg, 1.5 %) was obtained. M.p. ≥ 240 °C (dec.). – UV/vis/nearIR (CS_2): $\lambda_{\text{max}}(\lg \epsilon_{\text{max}}) = 978$ nm (4.24). – IR (KBr): $\nu = 1617, 1665$ (C=O), 2853, 2921, 2954, 2972 (CH) cm^{-1} . – $\text{C}_{12}\text{H}_6\text{OS}_{12}\text{Ni}$ (609.7): calcd. C 23.64, H 0.99; found C 23.51, H 0.88.

Instrumentation

Instruments as reported in [9] were used. All measurements were performed at r.t.

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