

# Some New Nickel 1,2-Dichalcogenolene Complexes as Single-component Semiconductors

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The complexes Ni(dmeds)(dmit), Ni(dmedt)(dmit), Ni(dpedit)(dsit), Ni(dpedit)(dmit), and Ni(dcddt)(dmit) (where dmeds is dimethylethylenediselenolate, dmedt is dimethylethylenedithiolate, dpedit is diphenylethylenedithiolate, dcddt is 1,2-bis-decylsulfanyl-ethene-1,2-dithiolate, dmit is 1,3-dithiol-2-thione-4,5-dithiolate, and dsit is 1,3-dithiol-2-thione-4,5-diselenolate) were prepared and characterized. The new complexes exhibit semiconducting behavior, with band gap values around 0.8 eV.

*Key words:* Metal 1,2-Dichalcogenolenes, Single-component Semiconductors

## Introduction

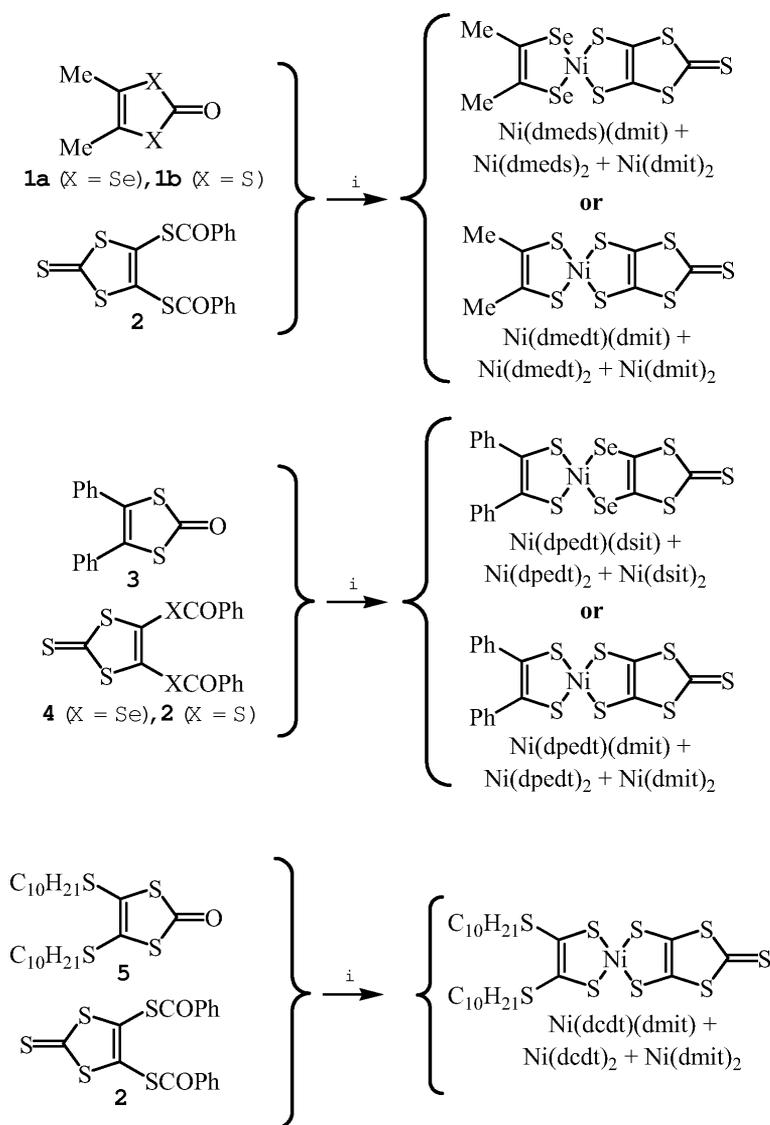
During the last five years a number of single-component (neutral) metal 1,2-dichalcogenolenes have been prepared and studied in our laboratories and/or in a collaboration with others [1–6]. Some unsymmetrical complexes were found to be stable in air and soluble in organic solvents. They exhibit strong nonlinear optical (NLO) properties [5, 6] and/or show semiconducting behavior under the conditions of field-effect transistors (FETs) [3, 4].

In this paper, the preparation and characterization of Ni(dmeds)(dmit), Ni(dmedt)(dmit), Ni(dpedit)(dsit), Ni(dpedit)(dmit) and Ni(dcddt)(dmit) are described (where dmeds is dimethylethylenediselenolate [7, 8], dmedt is dimethylethylenedithiolate [7], dpedit is diphenylethylenedithiolate [7], dcddt is 1,2-bis-decylsulfanyl-ethene-1,2-dithiolate [9], dmit is 1,3-dithiol-2-thione-4,5-dithiolate [9, 10] and dsit is 1,3-dithiol-2-thione-4,5-diselenolate [9, 10]). These new unsymmetrical (mixed ligand) complexes were prepared by the cross-coupling method [2] according to the procedures of Scheme 1. The starting materials **1–5** were prepared by methods reported in [11–17] (see also [7, 8, 10]). The required unsymmetrical complexes were separated from the corresponding symmetrical byproducts

by liquid column chromatography. For one of them, Ni(dmeds)(dmit), the crystal structure determination is reported. All the complexes exhibit semiconducting behavior similar to that observed in Ni(pdtdt)(dmio) and Ni(pdtdt)(dmit), where pdtdt is 6,7-dihydro-5H-1,4-dithiepin-2,3-dithiolate and dmio is 1,3-dithiol-2-one-4,5-dithiolate [3].

## Results and Discussion

From equimolar amounts of starting materials the unsymmetrical complexes Ni(dmeds)(dmit), Ni(dmedt)(dmit), Ni(dpedit)(dsit), Ni(dpedit)(dmit) and Ni(dcddt)(dmit) were obtained in 0.9, 2.4, 2.5, 21.0, and 0.8% yields, respectively. The unsymmetrical complexes containing the ligands dmit, dsit (or dmio) are expected to have redox-potential values higher than those of the corresponding symmetrical ones, Ni(dmedt)<sub>2</sub>, Ni(dmeds)<sub>2</sub>, Ni(dpedit)<sub>2</sub> and Ni(dcddt)<sub>2</sub>, *i. e.*, they are expected to be stable in air (see [3, 4, 7, 9, 10, 18, 19]). The new complexes were found to be soluble in CS<sub>2</sub> and some other organic solvents. From the solutions single crystals and/or thin deposits of complexes on quartz and Si-SiO<sub>2</sub> substrates were obtained. Solutions and thin deposits were found spectroscopically to be stable in air, as it was expected



Scheme 1.  $i = 1$ : NaOMe in MeOH,  $i = 2$ :  $NiCl_2$  in MeOH,  $i = 3$ : aq. HCl (35 %) in air.

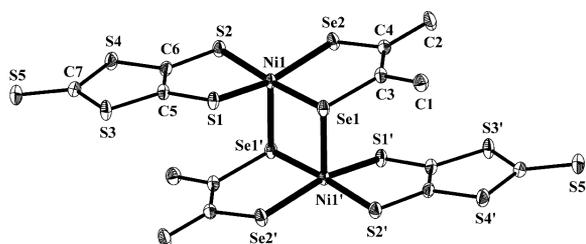
from the electrochemical data, and moreover stable in light for a long time. By treatment with  $NaBH_4$  in acetone and in the presence of  $Bu_4N^+$  the anionic species can be obtained.

Single crystals of  $Ni(dmeds)(dmit)$  had a rectangular shape and were found to be suitable for X-ray crystal structure determination. The complex  $Ni(dmeds)(dmit)$  crystallizes in the triclinic space group  $P\bar{1}$ . Crystal and refinement data are summarized in Table 1. Fig. 1 shows the molecular structure and Fig. 2 shows a partially labelled plot of the complex. The structure consists of centrosymmetric

dimers [20] with the inversion center sitting on the center of the  $Ni_2Se_2$  core. The closest  $Ni \cdots S$  and  $Ni \cdots Se$  bond lengths in the coordination sphere are *ca.* 2.2 and 2.3 Å, respectively, while the longer  $Ni \cdots Se$  bond (2.56 Å) is responsible for the formation of the dimers. The closest intramolecular  $Ni \cdots Ni$  distance is *ca.* 3.06 Å. It was found that the largest surface of the rectangular crystals is almost parallel to the crystallographic  $ab$  plane. There are  $S \cdots S$  and  $S \cdots Se$  intermolecular contacts of 3.594 and 3.610 Å, respectively, slightly smaller than the sums of the van der Waals radii (3.70 and 3.82 Å, respectively), which give rise to

Table 1. Crystal data and structure refinement for Ni(dmcds)(dmit).

Empirical formula	C <sub>14</sub> H <sub>12</sub> Ni <sub>2</sub> S <sub>10</sub> Se <sub>4</sub>
Formula weight [g/mol]	934.10
Temperature [K]	293(2)
Wavelength [Å]	1.54180
Crystal system, space group	monoclinic, <i>P</i> 1̄
Unit cell dimensions	
<i>a</i> [Å]	6.592(4)
<i>b</i> [Å]	8.236(4)
<i>c</i> [Å]	12.476(7)
$\alpha$ [deg]	87.91(2)
$\beta$ [deg]	75.36(2)
$\gamma$ [deg]	74.49(2)
<i>V</i> [Å <sup>3</sup> ]	631.1(6)
<i>Z</i> ; calculated density [mg cm <sup>-3</sup> ]	1; 2.458
Absorption coefficient [mm <sup>-1</sup> ]	16.238
<i>F</i> (000) [e]	448
Crystal size [mm <sup>3</sup> ]	0.525 × 0.150 × 0.075
$\theta$ Range for data collection, deg	5.58 – 59.00
Limiting indices	–6 ≤ <i>h</i> ≤ 0, –9 ≤ <i>k</i> ≤ 8, –13 ≤ <i>l</i> ≤ 13
Reflections collected/unique	1981/1799 ( <i>R</i> <sub>int</sub> = 0.039)
Completeness to $\theta = 59.03$	99.1 %
Absorption correction	analytical
Max./min. transmission	0.877/0.132
Data/restraints/parameters	1799/0/140
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.068
Final <i>R</i> indices [ <i>I</i> ≥ 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0604, <i>wR</i> <sub>2</sub> = 0.1615
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0616, <i>wR</i> <sub>2</sub> = 0.1646
Largest diff. peak and hole [e Å <sup>-3</sup> ]	0.962 and –0.840

Fig. 1. Molecular structure of Ni(dmcds)(dmit) with displacement ellipsoids drawn at the 30 % probability level (H-Atoms have been omitted for clarity). Primed atoms are related to unprimed ones by the symmetry operation  $1 - x, -y, 1 - z$ .

the formation of layers almost parallel to the *ab* plane (Fig. 2). In other directions the contacts are larger. This indicates a *quasi* two-dimensional behavior of the material. Single crystals of the other complexes were not good enough for crystal structure determination. However, similar intermolecular interactions (S···Se and S···S contacts) are expected for these complexes.

Conductivity measurements on single crystals of Ni(dmcds)(dmit) showed an anisotropic behavior, in accordance with the crystallographic results. Fig. 3

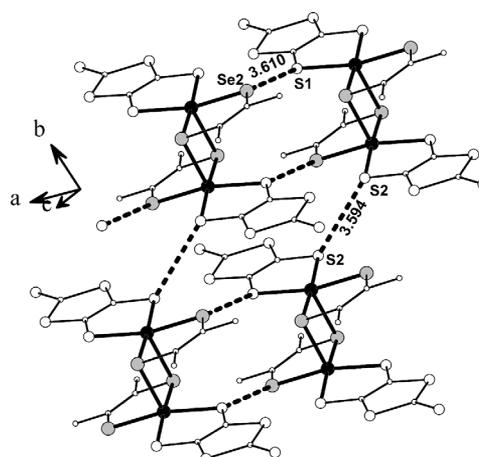
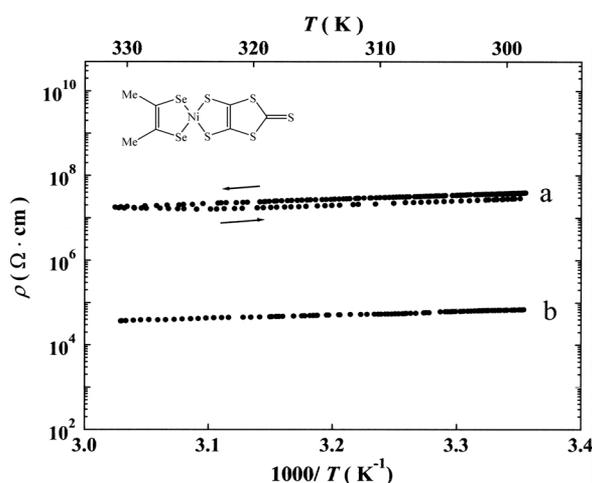


Fig. 2. Partially labeled plot of Ni(dmcds)(dmit) showing the shortest S···S and Se···Se intermolecular interactions.

Fig. 3. Plots of resistivity versus the inverse temperature for a single crystal of Ni(dmcds)(dmit) with currents approximately parallel (a) and perpendicular (b) to the *ab* plane.

shows the inverse temperature dependence of the resistivity obtained from single crystals of Ni(dmcds)(dmit) with currents almost parallel to the *ab* plane (||) and perpendicular to this plane (⊥). The r. t. conductivity values are  $\sigma_{RT}(||) = 1.5 \times 10^{-5} \text{ S cm}^{-1}$  and  $\sigma_{RT}(\perp) = 2.5 \times 10^{-8} \text{ S cm}^{-1}$ . This means that the anisotropy is almost  $10^3$ . The activation energy values were found from the plots of Fig. 3 to be  $E_{\alpha}(||) = 0.19 \text{ eV}$  and  $E_{\alpha}(\perp) = 0.18 \text{ eV}$ . The corresponding band gap ( $E_g = 2E_{\alpha}$ ) values are 0.38 and 0.36 eV. After a series of heating/cooling cycles, the resistance in a number of crystals decreased. Conductivity measurements on compressed pellets of Ni(dmcds)(dmit), Ni(dmcdt)(dmit) and Ni(dpedit)(dsit) gave  $\sigma_{RT}(\text{pellet}) = 1 \times 10^{-6}, 1.2 \times$

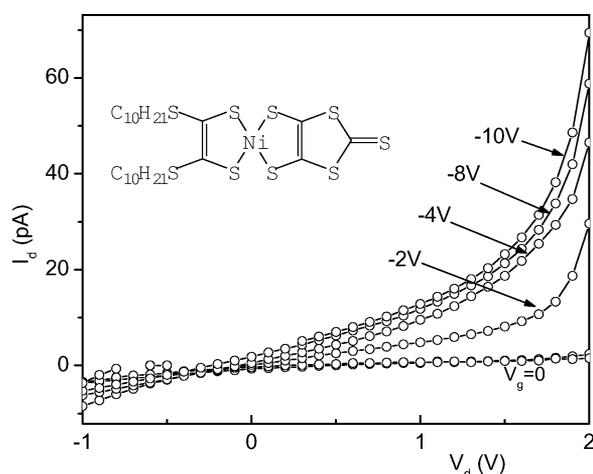


Fig. 4. Plots of  $I_d$  vs.  $V_d$  for several  $V_g$  values of a device based on Ni(dcdt)(dmit).

$10^{-7}$ , and  $1 \times 10^{-7} - 5 \times 10^{-6} \text{ S cm}^{-1}$ , respectively. The  $E_g$ (pellet) values were found to be 0.45, 0.50–0.80 and 0.46 eV, respectively. The  $\sigma_{RT}$  values of Ni(dpdt)(dmit) and Ni(dcdt)(dmit) were found to be very small ( $< 10^{-9} \text{ S cm}^{-1}$ ).

The optical absorption (OA) spectra of thin deposits on quartz plates showed strong bands with maxima around 1.24 eV (1000 nm) and optical band gaps (absorption edges) close to 0.7–0.8 eV. This means that, in some complexes, the  $E_g$  values obtained from resistivity measurements are smaller than those obtained from the OA spectra of thin deposits (or solutions). This is due to the fact that in compressed pellets and/or single crystals the intermolecular interactions are stronger than those in thin films (or solutions) (see also [5, 6]).

All these air-stable complexes have the electrical and optical features required for candidates for FETs and NLO devices. Preliminary results of measurements under the conditions of FETs were obtained for Ni(dcdt)(dmit) thin deposits on Si-SiO<sub>2</sub> substrates. Fig. 4 shows the curves of drain current ( $I_d$ ) versus the drain voltage ( $V_d$ ) for several values of gate voltage ( $V_g$ ) of a device based on Ni(dcdt)(dmit). These curves demonstrate the sensitivity of the channel (semiconductor deposit) to the gate voltage. Several complexes exhibit *p*-type as well as *n*-type conductance. The  $I_d$ - $V_d$  curves obtained from Ni(dpdt)(dmit) were similar to those obtained for Ni(dpdt)<sub>2</sub>, a material which has been found to exhibit *n*-type conductance [21]. It should be noticed that the best results were obtained for the complexes with the lower values of dc conductivity.

However, more improved techniques are required in order to establish these new materials as semiconductor components of FETs. Also, NLO properties were observed in some of these complexes, which are described separately [5].

## Experimental Section

### (Dimethylethylenediselenolato)(1,3-dithiol-2-thione-4,5-dithiolato)nickel, Ni(dmets)(dmit)

In a two-necked 250 mL flask, a suspension of compounds **1a** (240 mg, 1 mmol) [11, 15] and **2** (406 mg, 1 mmol) [14, 17] in deoxygenated MeOH (10 mL) was prepared. Then, a solution of NaOMe, freshly prepared from Na (115 mg, 5 mmol) and MeOH (10 mL), was added under nitrogen atmosphere and the mixture stirred for 30 min. To the obtained red solution, a solution of NiCl<sub>2</sub> · 6H<sub>2</sub>O (238 mg, 1 mmol) in deoxygenated MeOH (30 mL) was added dropwise within 15 min. The solution was stirred under nitrogen atmosphere for 1 h at r. t., whereupon the color turned brown. Then, aq. HCl (2 mL, 35 %) was added and the mixture was transferred to a beaker and stirred in air overnight. The precipitate was washed with water and MeOH and dried in air. The green-brown solid was extracted with CS<sub>2</sub> and chromatographed on silica gel, using CS<sub>2</sub> as eluent. The second green fraction contained Ni(dmets)(dmit) (4 mg, 0.9 %). M. p. > 285 °C (dec.). – UV/vis/near IR (CS<sub>2</sub>):  $\lambda_{\text{max}}$  ( $\lg \epsilon_{\text{max}}$ ) = 950 nm (4.48). – IR (KBr):  $\nu = 1056, 1073$  (C=S), 2923 (CH<sub>3</sub>) cm<sup>-1</sup>. – C<sub>7</sub>H<sub>6</sub>S<sub>5</sub>Se<sub>2</sub>Ni (467.03): calcd. C 18.00, H 1.28; found C 18.11, H 1.36.

### (Dimethylethylenedithiolato)(1,3-dithiol-2-thione-4,5-dithiolato)nickel, Ni(dmtdt)(dmit)

Using **1b** (162 mg, 1 mmol) [12, 13, 15], instead of **1a**, and **2** (406 mg, 1 mmol), the complex Ni(dmtdt)(dmit) was obtained by the same procedure (9 mg, 2.4 %). M. p. 235 °C (dec.). – UV/vis/near IR (CS<sub>2</sub>):  $\lambda_{\text{max}}$  ( $\lg \epsilon_{\text{max}}$ ) = 933 nm (4.46). – IR (KBr):  $\nu = 1048, 1064$  (C=S), 2920 (CH<sub>3</sub>) cm<sup>-1</sup>. – C<sub>7</sub>H<sub>6</sub>S<sub>5</sub>Ni (373.25): calcd. C 22.52, H 1.61; found C 22.48, H 1.56.

### (Diphenylethylenedithiolato)(1,3-dithiol-2-thione-4,5-diselenolato)nickel, Ni(dpdt)(dsit)

Using **3** (270 mg, 1 mmol) [13], instead of **1a**, and **4** (500 mg, 1 mmol) [14, 16], instead of **2**, the complex Ni(dpdt)(dsit) was obtained by the same procedure (15 mg, 2.5 %). M. p. 280 °C (dec.). – UV/vis/near IR (CS<sub>2</sub>):  $\lambda_{\text{max}}$  ( $\lg \epsilon_{\text{max}}$ ) = 1005 nm (4.52). – IR (KBr):  $\nu = 1039, 1048$  (C=S) cm<sup>-1</sup>. – C<sub>17</sub>H<sub>10</sub>S<sub>5</sub>Se<sub>2</sub>Ni (591.13): calcd. C 34.54, H 1.69; found C 34.37, H 1.78.

*(Diphenylethylenedithiolato)(1,3-dithiol-2-thione-4,5-dithiolato)nickel, Ni(dpdt)(dmit)*

Using **3** (270 mg, 1 mmol) [13], instead of **1a**, and **2** (406 mg, 1 mmol), the complex Ni(dpdt)(dmit) was obtained by the same procedure (104 mg, 21%). M. p. 240 °C (dec.). – UV/vis/near IR (CS<sub>2</sub>):  $\lambda_{\max}$  ( $\lg \epsilon_{\max}$ ) = 974 nm (4.65). – IR (KBr):  $\nu$  = 1066, 1077 (C=S) cm<sup>-1</sup>. – C<sub>17</sub>H<sub>10</sub>S<sub>7</sub>Ni (497.35): calcd. C 41.05, H 2.01; found C 40.92, H 1.93.

*(1,2-Bis-decylsulfanyl-ethene-1,2-dithiolato)(1,3-dithiol-2-thione-4,5-dithiolato)nickel, Ni(dcddt)(dmit)*

Using **5** (462 mg, 1 mmol) [14], instead of **1a**, and **2** (406 mg, 1 mmol), the complex Ni(dcddt)(dmit) was obtained by the same procedure (5.5 mg, 0.8%). M. p. 105 °C (dec.). – UV/vis/near IR (CS<sub>2</sub>):  $\lambda_{\max}$  ( $\lg \epsilon_{\max}$ ) = 1040 nm (4.54). – IR (KBr):  $\nu$  = 1064, 1072 (C=S), 2915 (CH<sub>3</sub>) cm<sup>-1</sup>. – C<sub>25</sub>H<sub>42</sub>S<sub>9</sub>Ni (689.57): calcd. C 43.54, H 6.09; found C 43.50, H 6.14.

*X-Ray crystal structure determination*

A suitable single crystal was mounted in air and diffraction measurements were made on a P<sub>21</sub> Nicolet diffractometer upgraded by Crystal Logic using graphite-monochromated CuK $\alpha$  radiation. Crystal data and other numbers pertinent to the structure determination are collected in Table 1. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range 22 < 2 $\theta$  < 54°. Intensity data were recorded using  $\theta$ -2 $\theta$  scans to 2  $\theta_{\max}$  = 118°, with a scan speed of 4.5 deg min<sup>-1</sup> and a scan width of 2.45° plus  $\alpha_1\alpha_2$  separation. Three standard reflections monitored

every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization and analytical absorption corrections were applied using Crystal Logic software. Symmetry equivalent data were averaged with  $R_{\text{int}} = 0.0389$  to give 1799 independent reflections from a total of 1981 collected. The structure was solved by Direct Methods using SHELXS-86 [22] and refined by full-matrix least-squares techniques on  $F^2$  with SHELXL-97 [23] using 1799 reflections and refining 140 parameters. All hydrogen atoms were introduced at calculated positions as riding on bonded atoms. All non-hydrogen atoms were refined anisotropically. The largest shift/esd in the final refinement cycle was 0.002. Table 1 contains further numbers of the structure refinement. CCDC 628860 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

*Physical measurements*

Thin deposits on quartz plates and/or Si-SiO<sub>2</sub> substrates, with predefined interdigitated gold electrodes spaced 2–25  $\mu\text{m}$  apart, were obtained by spinning, spraying or drop casting solutions of the complexes in CS<sub>2</sub>. The OA spectra of the complexes in CS<sub>2</sub> or of thin deposits were recorded on a Perkin-Elmer, model Lambda 19 spectrophotometer. The dc conductivity was measured by the well known voltage-drive method. The  $I_d$ - $V_d$  characteristics were measured by using a 4140B HP picoammeter.

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- [1] G. C. Papavassiliou, G. A. Mousdis, G. C. Anyfantis, *Z. Naturforsch.* **2002**, *57b*, 707–708.
- [2] G. C. Papavassiliou, G. C. Anyfantis, *Z. Naturforsch.* **2005**, *60b*, 811–813.
- [3] G. C. Anyfantis, G. C. Papavassiliou, A. Terzis, C. P. Raptopoulou, Y. F. Weng, H. Yoshino, K. Murata, *Z. Naturforsch.* **2006**, *61b*, 1007–1011.
- [4] G. C. Papavassiliou, G. C. Anyfantis, B. R. Steele, A. Terzis, C. P. Raptopoulou, G. Tatakis, G. Chaidogiannos, N. Glezos, Y. F. Weng, H. Yoshino, K. Murata, *Abstracts in Proc. of Int. Conf. Synth. Metals* (Dublin, **2006**), No 023 TU.  $I_d$ - $V_d$  characteristics of some unsymmetrical complexes, such as Ni(pddt)(dmit), Ni(pddt)(dmio) and Ni(dpdt)(dmio), have been presented.
- [5] P. Aloukos, S. Couris, J. B. Koutselas, G. C. Anyfantis, G. C. Papavassiliou, *Chem. Phys. Lett.* **2006**, *428*, 109–113; second hyperpolarizability instead of second-order hyperpolarizability should be corrected therein.
- [6] G. C. Anyfantis, G. C. Papavassiliou, P. Aloukos, S. Couris, Y. F. Weng, H. Yoshino, K. Murata, *Z. Naturforsch.* **2007**, *62b*, 200–204.
- [7] a) J. A. McCleverty, *Prog. Inorg. Chem.* **1968**, *10*, 49–221; b) K. Wang in *Dithiolen Chemistry* (Ed.: E. I. Stiefel), John Wiley, Chichester, **2004**, chapter 5, p. 267, and refs. therein.
- [8] F. Wudl, E. T. Zellers, S. D. Cox, *Inorg. Chem.* **1985**, *24*, 2864–2866.
- [9] G. C. Papavassiliou, A. Terzis, P. Delhaes in *Handbook of Organic Conductive Molecules and Polymers*, Vol. 1 (Ed.: H. S. Nalwa), John Wiley, Chichester, **1997**, chapter 3, p. 151.

- [10] R. Kato, *Chem. Rev.* **2004**, *104*, 5319–5346, and refs. therein.
- [11] K. Bechgaard, D. O. Cowan, A. N. Bloch, L. Hernisken, *J. Org. Chem.* **1975**, *40*, 746–749.
- [12] J. P. Ferraris, T. O. Poehler, A. N. Bloch, *Tetrahedron Lett.* **1973**, 2553–2556.
- [13] A. K. Bhattacharya, A. G. Hortmann, *J. Org. Chem.* **1974**, *39*, 95–97.
- [14] a) G. C. Papavassiliou, V. C. Kakoussis, D. J. Lagouvardos, G. A. Mousdis, *Mol. Cryst. Liq. Cryst.* **1990**, *181*, 171–184; b) G. C. Papavassiliou, V. C. Kakoussis, D. J. Lagouvardos, *Z. Naturforsch.* **1991**, *46b*, 1269–1271.
- [15] J.-I. Yamada, *Resent. Res. Devel. In Org. Chem.* **1998**, *2*, 525–545.
- [16] G. C. Papavassiliou, V. C. Kakoussis, J. S. Zambounis, G. A. Mousdis, *Chemica Scripta* **1989**, *29*, 123–125.
- [17] G. Steimecke, H.-J. Sieler, R. Kirmse, E. Hoyer, *Phosphorus, Sulfur Relat. Elem.* **1979**, *7*, 49–55.
- [18] a) G. C. Papavassiliou, *Z. Naturforsch.* **1982**, *37b*, 825–827; b) G. C. Papavassiliou, K. Mayer, unpublished work: cyclic voltametric measurements of  $[\text{Ni}(\text{dmit})_2]^-$  in  $\text{CH}_3\text{CN}$  (0.05 M  $\text{Bu}_4\text{NPF}_6$ ) and Pt electrode vs. SCE gave  $E^1_{1/2}(2-/1-) = -0.180$  V,  $E^2_{1/2}(1-/x-) = 0.125$  V and  $E^3_{1/2}(x-/0) = 0.185 - 0.235$  V ( $0 < x < 1$ ); c) L. Valade, J.-P. Legros, D. de-Montauzon, P. Cassoux, L. V. Interrante, *Isr. J. Chem.* **1986**, *27*, 353–362.
- [19] a) R.-M. Olk, W. Dietzsch, J. Mattush, J. Stach, L. Nieke, E. Hoyer, W. Meiler, R. Robien, *Z. Anorg. Allg. Chem.* **1987**, *544*, 199–208; b) R. M. Olk, E. Hoyer, W. Meiler, P. Cassoux, *Synth. Met.* **1993**, *56*, 2453–2458; c) P. Cassoux, L. Valade in *Inorganic Materials* (Eds.: D. W. Bruce, D. O'Hare), John Wiley, Chichester, **1996**, chapter 1, p. 3.
- [20] S. Alvarez, B. Vicente, R. Hoffmann, *J. Am. Chem. Soc.* **1985**, *107*, 6253–6277.
- [21] T. Tagushi, H. Wada, T. Kobayashi, B. Noda, M. Goto, T. Mori, K. Ishikawa, H. Takezoe, *Chem. Phys. Lett.* **2006**, *421*, 395–398.
- [22] G. M. Sheldrick, SHELXS-86, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) **1986**.
- [23] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.