Preparation and Characterization of Some Nickel 1,2-Dithiolene Complexes as Single-Component Semiconductors

G. C. Anyfantis\textsuperscript{a}, G. C. Papavassiliou\textsuperscript{a}, A. Terzis\textsuperscript{b}, C. P. Raptopoulou\textsuperscript{b}, Y. F. Weng\textsuperscript{c}, H. Yoshino\textsuperscript{c}, and K. Murata\textsuperscript{c}

\textsuperscript{a} Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48, Vassileos Constantinou Ave., Athens 116-35, Greece
\textsuperscript{b} Institute of Materials Science, NCSR, Demokritos, Athens 153-10, Greece
\textsuperscript{c} Graduate School of Science, Osaka City University, Sumiyoshi-Ku, Osaka 558-8585, Japan

Reprint requests to Prof. G. C. Papavassiliou. Fax (30210)7273794. E-mail: pseria@eie.gr

Z. Naturforsch. 61b, 1007 – 1011 (2006); received March 6, 2006

The unsymmetrical (mixed-ligand) nickel 1,2-dithiolene complexes Ni(pddt)(dmio) and Ni(pddt)(dmit) (where pddt is 6,7-dihydro-5H-1,4-dithiepin-2,3-dithiolate, dmio is 1,3-dithiol-2-one-4,5-dithiolate, and dmit is 1,3-dithiol-2-thione-4,5-dithiolate) were synthesized and characterized. The new complexes were found to be soluble in organic solvents, from which single crystals and/or thin deposits can be obtained. In the solid state, the compounds behave as single-component semiconductors with low room temperature conductivity values.

Key words: Metal 1,2-Dithiolenes, Organic Semiconductors

Introduction

During the last ten years, a number of single-component metal 1,2-dithiolene complexes have been prepared and studied [1 – 9]. Some of these compounds exhibit semiconducting or metallic behaviour in the solid state. The complexes, which are based on ligands containing an alkylenedithio- or an alkylenedioxy-group are soluble in organic solvents, but are easily oxidized in air, because of their low redox potentials [2, 4]. Generally, the solubility is enhanced by introducing long alkyl chain or highly polar substituents. Complexes with extended-tetrathiafulvalene-dithiolate ligands [3] are sparingly soluble or insoluble in common organic solvents and consequently, thin films cannot be obtained. Also, complexes based on the well known 1,3-dithiole-2-thione-4,5-dithiolate ligand are stable in air, but insoluble in common organic solvents [10 – 14]. Very recently, neutral complexes of nickel and gold with bis(trifluoromethyl)tetrathiafulvalene-4,5-dithiolate ligands [3] are sparingly soluble or insoluble in common organic solvents and consequently, thin films cannot be obtained. Also, complexes based on the well known 1,3-dithiole-2-thione-4,5-dithiolate ligand are stable in air, but insoluble in common organic solvents [10 – 14]. Very recently, neutral complexes of nickel and gold with bis(trifluoromethyl)tetrathiafulvalene ligands, M(hfdt)\textsubscript{2} (M = Ni, Au) were prepared and found to be single-component conducting materials, which are soluble in organic solvents [8]. Their room temperature conductivity was found to be of the order of 10\textsuperscript{−3} S/cm and the activation energy 0.12 – 0.14 eV [8]. It is expected that the mixed-ligand (unsymmetrical) complexes will exhibit intermediate features [2, 9].

In this paper, the preparation and characterization of the unsymmetrical complexes Ni(pddt)(dmio) and Ni(pddt)(dmit) (where pddt is 6,7-dihydro-5H-1,4-dithiepin-2,3-dithiolate, dmio is 1,3-dithiol-2-one-4,5-dithiolate, and dmit is 1,3-dithiol-2-thione-4,5-dithiolate) were synthesized and characterized. The new complexes were found to be soluble in organic solvents, from which single crystals and/or thin deposits can be obtained. In the solid state, the compounds behave as single-component semiconductors with low room temperature conductivity values.

Key words: Metal 1,2-Dithiolenes, Organic Semiconductors

Results and Discussion

It has been found that nickel complexes with dmit as ligand can be isolated in dianionic [10], monoanionic [11], cation-deficient [12] and neutral [13] forms (see also [14]). Dianionic and monoanionic forms are soluble in organic solvents, while cation-deficient and neutral complexes are stable in air but insoluble in common organic solvents. Some features have been established for the nickel complexes based on dmio [15]. However, in the case of the complexes based on pdtt [5, 16], dddt (which is the ligand 5,6-dihydro-1,4-dithiin-2,3-dithiolate) [2, 4] and similar ligands [1, 2, 4], the behaviour is different. The neutral complexes are soluble in organic solvents but are oxidized in air. Some of them give cationic complexes by electrocrystalliza-
tion in the presence of several inorganic anions ([2, 4] and refs therein). These features are due to the low
redox potentials [2, 4, 16]. In the case of the mixed ligand complexes Ni(pddt)(dmio) and Ni(pddt)(dmit) the features were found to be intermediate. The complexes were obtained in yields of 7.3 and 14% respectively.

They were found to be soluble in CH\textsubscript{2}Cl\textsubscript{2}, CS\textsubscript{2}, DMF and other organic solvents, from which single crystals or thin film deposits on several substrates can be obtained. Also, from the solutions the complexes can be incorporated into guest-host polymer films. Solutions, deposits or thin films were found to be stable in air for a long time. Similar complexes such as Ni(dddt)(dmio) and Ni(dddt)(dmit) were prepared by the same procedure, but the formation of cation-anion complexes of the type [Ni(dddt)\textsubscript{2}]\textsuperscript{+}[Ni(dmit)\textsubscript{2}]\textsuperscript{3} [17] competes favorably with the formation of the unsymmetrical complexes. Single crystals of Ni(pddt)(dmio) were obtained from solutions by slow evaporation of the solvent CS\textsubscript{2} or by a diffusion method using coaxial tubes and CS\textsubscript{2}/n-hexane as solvents. The crystals obtained by both methods had a rectangular shape, and were suitable for structure determination and conductivity measurements. The crystals obtained from recrystallization of Ni(pddt)(dmit) by this method were small needles not suitable for structure determination and conductivity measurements.

Single crystals of the complex Ni(pddt)(dmio) crystallize in the monoclinic space group \textit{P2\textsubscript{1}}/\textit{c}. Crystal and refinement are summarized in Table 1. It was found that the largest surface of the rectangular crystals is almost parallel to the \textit{ab}-plane. Fig. 1 shows the molecular structure of Ni(pddt)(dmio) and Fig. 2 the packing of the Ni(pddt)(dmio) molecules, approximately along the \textit{c}-axis. In a layer almost parallel to the \textit{ab}-plane, there are S--S intermolecular contacts of 3.495 and 3.666 Å, which are slightly smaller than the sums of the van der Waals radii (3.70 Å). In other directions the contacts are larger. This indicates a quasi-two-dimensional behaviour of the material.

Conductivity measurements on single crystals of Ni(pddt)(dmio) have shown an anisotropic behaviour, in accordance with the crystallographic results. Fig. 3 shows the inverse-temperature dependence of the resis-
Some Nickel 1,2-Dithiolene Complexes

Fig. 2. Perspective view the Ni(pddt)(dmio) structure, approximately along the c-axis. Hydrogen atoms omitted for clarity.

Fig. 3. Plots of resistivity versus the inverse temperature for a single-crystal of Ni(pddt)(dmio) with current approximately parallel (a) and perpendicular (b) to the ab-plane.

The resistivity obtained from single crystals of Ni(pddt)(dmio) with current (almost) parallel to the ab-plane (∥) and perpendicular to this (⊥). The r.t. conductivity is $\sigma_{RT}(∥) = 2.5 \times 10^{-5}$ S/cm and $\sigma_{RT}(⊥) = 1 \times 10^{-9}$ S/cm. This means that the anisotropy is almost $2.5 \times 10^4$. The activation energy values were found from the plots of Fig. 3 to be $E_a(∥) = 0.13$ and $E_a(⊥) = 0.18$ eV. Conductivity measurements on compressed pellets of Ni(pddt)(dmio) gave almost the same value, $\sigma_{RT}(\text{pellet}) = 1.3 \times 10^{-7}$ S/cm. Also, conductivity measurements on compressed pellets of Ni(pddt)(dmit) gave $\sigma_{RT}(\text{pellet}) = 1 \times 10^{-7}$ S/cm.

Fig. 4 shows the optical absorption spectra of Ni(pddt)(dmio) and Ni(pddt)(dmit) thin film deposits on quartz substrates in the UV/vis/near IR spectral region. It was found that the low frequency bands are broader than those observed from solutions of the materials in several solvents. This is due to the fact that in the solid state there are weak intermolecular interactions. The absorption bands occur at higher frequencies than those observed for some complexes with extended-tetrathiafulvalene-dithiolate ligands, e.g. Pd(dt)$_2$ (where dt is tetrathiafulvalene-dithiolate) [3, 7]. This indicates that the semiconducting behaviour of Ni(pddt)(dmio) and Ni(pddt)(dmit) is weaker than that of Pd(dt)$_2$ and similar complexes, in accordance with the results obtained from the conductivity measurements. The conductivity values of Ni(pddt)(dmio) and Ni(pddt)(dmit) are smaller than those of M(hfdt)$_2$ compounds, which also are soluble in organic solvents [8]. The compounds reported herein could be candidates for semiconducting components of field-effect transistors (FETs), because these devices require semiconductors with high mobility and low conductivity values ([18] and refs. therein). Measurements of mobility and other properties under the conditions of FETs, using Ni(pddt)(dmio), Ni(pddt)(dmit) and similar complexes, will be performed in the future and the results will be published elsewhere.

**Experimental Section**

The starting materials 1, 2, 3 were prepared by methods reported in [10, 15, 19, 20].

(6,7-Dihydro-5H-1,4-dithiepin-2,3-dithiolato)(1,3-dithiol-2-one-4,5-dithiolato)nickel, Ni(pddt)(dmio)

In a two-necked 250 ml flask, compounds 1 (0.35 g, 1.58 mmol) and 2 (0.59 g, 1.50 mmol) were mixed under ni-
trogen atmosphere. Then, a solution of NaOMe, freshly prepared from Na (165 mg, 7.17 mmol) and MeOH (30 ml), was added and the mixture stirred at room temperature for 30 min. The solution was diluted with deoxygenated MeOH (80 ml) and a solution of NiCl₂·6H₂O (0.4 g, 1.68 mmol) in deoxygenated MeOH (30 ml) was added dropwise within 20 min. The brown solution was stirred under nitrogen atmosphere for 1 h at r.t. Then,aq. HCl (4 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 CS₂ and chromatographed on silica gel, using CS₂ as eluent and dried in air. The green-brown fraction contained Ni(pddt)(dmio) (6,7-Dihydro-5H-1,4-dithiepin-2,3-dithiolato)(1,3-dithiol-2-thione-4,5-dithiolato)nickel, Ni(pddt)(dmio) (49 mg, 7.3%), the second green fraction contained Ni(pddt)(dmit) (64 mg, 9%). The compound Ni(pddt)(dmio) crystallizes in the form of rectangular platelets: m. p. 245 °C (dec.). – UV/vis/nearIR (CS₂): λmax (lg εmax) 978 nm (4.29). – IR(KBr): ν = 1624, 1675 (C=O) cm⁻¹. – C₆H₆O₈S₈Ni (449.32): calcd. C 21.37, H 1.34; found C 21.49, H 1.46.

X-ray crystal structure determination

A single crystal was mounted in air and diffraction measurements were made on a P2₁ Nicolet diffractometer upgraded by Crystal Logic using graphite monochromated Cu radiation. Unit cell dimensions were determined and refined by using the angular settings of 29 automatically centered reflections in the range 22 < 2θ < 54° (Table 1). Intensity data were recorded using θ-2θ scans to 2θmax = 118°, with a scan speed of 4.5°/min and scan a range 2.45 plus ø/2ø 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 Rint = 0.0157 to give 2022 independent reflections from a total of 2069 collected. The structure was solved by direct methods using SHELXS-86 [21] and refined by full-matrix least-squares techniques on F² with SHEXL-97 [22] using 2022 reflections and refining 188 parameters. All hydrogen atoms were located by difference maps and were refined isotropically. All non-hydrogen atoms were refined anisotropically. The final values for R₁, wR₂ and GOF for observed data are shown in Table 1, for all data they are 0.0508, 0.1445, and 1.056, respectively. The maximum and minimum residual peaks in the final difference map were 0.84 and −0.90 e/Å. The largest shift/esd in the final cycle was 0.001.

Crystallographic information files have been deposited in Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ UK (e-mail: deposit@ccdc.cam.ac.uk), Deposition number: CCDC 600090.

Acknowledgement

The work was carried out as a part of the Excellence in the Research Institutes project grant 0684, supported by GSRT/Ministry of Development in Greece.

[17] C. Faulmann, A. Errami, B. Donnadieu, I. Malfant,


