Unsymmetrical Single-Component Nickel 1,2-Dithiolene Complexes with Extended Tetrachalcogenafulvalenedithiolato Ligands

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The unsymmetrical complexes Ni(dmdt)(dmio) and Ni(dmstfdt)(dmio) (dmdt = dimethyltetrathiafulvalenedithiolate, dmstfdt = dimethyldiselenadithiafulvalenedithiolate, dmio = 1,3-dithiol-2-one-4,5-dithiolate) were prepared and characterized analytically and spectroscopically. The complexes exhibit strong third-order nonlinear optical response in the visible and near-infrared spectral regions.

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

Introduction

In our previous papers, the preparation and characterization of some neutral metal 1,2-dichalcogenolene complexes have been reported [1-5]. Crystal structure determinations of two of them showed strong intermolecular interactions, due to $S \cdots S$ and/or $S \cdots Se$ contacts [3a, 4]. Their r.t. conductivity values were found to be in the range $10^{-9} - 10^{-5}$ S cm⁻¹ [3,4]. Also, the complexes exhibited strong optical absorption (OA) bands in the near infrared (near IR) spectral region. Some unsymmetrical complexes with a "push-pull" (donor-acceptor) character were found to exhibit enhanced nonlinear optical (NLO) properties in solution [5] (see also [6]). In some unsymmetrical complexes, the distribution of electrons in the $(C_2S_2)_2$ Ni core and the terminal groups is estimated and related with the NLO properties (see [6a] and refs. therein). Very recently, the electrical properties of some neutral symmetrical and unsymmetrical complexes such as Ni(dpedt)₂ and Ni(pddt)(dmio) have been reported (where dpedt is diphenyl-ethylenedithiolate, pddt is 6,7-dihydro-5H-1,4-dithiepin-2,3dithiolate, and dmio is 1,3-dithiol-2-one-4,5-dithiolate) [3, 4a, 7]. These compounds exhibit semiconducting behaviour under conditions of field-effect transistors (FETs) [3b, 4, 7–9].

In this paper, the preparation and characterization of the unsymmetrical complexes Ni(dmdt)(dmio) and Ni(dmstfdt)(dmio) (where dmdt is dimethyltetrathiafulvalenedithiolate and dmstfdt is dimethyldiselenadithiafulvalenedithiolate) are described. The complexes were prepared by the cross-coupling type method [2-4], according to the procedure outlined in Scheme 1. The starting materials (1-3) were prepared by methods reported in [10-13]. The required unsymmetrical complexes were separated from the corresponding symmetrical byproducts by column chromatography and characterized analytically and spectroscopically. In this particular kind of unsymmetrical complexes one ligand is a π -donor (extended tetrachalcogenafulvalenedithiolate) [13] and the other one is a π -acceptor (dmio) [6, 11]. From a number of unsymmetrical complexes with an extended tetrachalcogenafulvalenedithiolato ligand, which we have designed and prepared [3-5], these two complexes were found to be most interesting for further investigation.

Results and Discussion

From equimolar amounts of compounds **1** and **2**, the complex Ni(dmdt)(dmio) was obtained in 3 % yield while the complex Ni(dmstfdt)(dmio) was obtained

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i = 1) NaOMe, 2) NiCl₂ in MeOH, 3) aqu. HCl, in air; Ar = p-AcOC₆H₄-



Fig. 1. OA spectra of 0.1 mM solutions of Ni(dmdt)(dmio) (a) and Ni(dmstfdt)(dmio) (b) in CS₂.

from equimolar amounts of 2 and 3 in 7 % yield. Both complexes are soluble in CS₂ and in some other organic solvents. The corresponding symmetrical complexes Ni(dmdt)₂ and Ni(dmstfdt)₂ [11, 13] are not soluble in organic solvents. Moreover, the complex Ni(dmio)₂ cannot be isolated in a pure form, but instead a cation-deficient product can be obtained, which also is not soluble in organic solvents [11]. The unsymmetrical complexes were found to be stable in air, as it is expected from the redox behaviour of the corresponding symmetrical ones [2, 11, 13]. From solutions of Ni(dmdt)(dmio) and Ni(dmstfdt)(dmio) thin needles

of the complexes were obtained. These needles were not suitable for successful single crystal X-ray diffraction experiments, however. Conductivity measurements on compressed pellets of the complexes showed weak semiconducting behaviour, arising from the intermolecular interactions as in the cases of similar complexes [3, 4]. By application of the cross-coupling method of Scheme 1 (see also [2, 5]), it is possible to obtain complexes stable in air and soluble in organic solvents. Also, it is possible to tune the position of the optical absorption band to the desired wavelength [6]. This is a way to create the optimum trade-off between the near resonance and the low optical absorption coefficient, as required for NLO devices [6b]. In the present cases, the optical absorption (OA) spectra of solutions of Ni(dmdt)(dmio) and Ni(dmstfdt)(dmio) in CS₂ exhibit the low-energy bands at 977 and 988 nm, respectively (see Fig. 1). These bands arise from the low-energy π - π^* transitions (see [6] and references therein). The OA spectrum of Ni(dmdt)(dmio) as a thin deposit on a quartz plate is shown in Fig. 2a. The spectrum exhibits a broad low-energy band at ca. 1270 nm, *i.e.*, at shorter wavelength than that of the symmetrical complex Ni(dmdt)₂, but almost at the same wavelength as that of Pd(dt)₂ (where dt is tetrathiafulvalenedithiolate), which is a semiconducting material insoluble in organic solvents [13]. This band is shifted towards shorter wavelengths (ca. 1130 nm) after grinding the deposit (Fig. 2b). Similar results were ob-

Table 1. Nonlinear optical parameters of complexes at 532 and 106	54 nm.
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	532 nm			1064 nm			
Dithiolene complex	α_0^*	$\operatorname{Re}\chi^{(3)}_{(\times 10^{-13} \text{ esu})}$	γ (×10 ⁻²⁹ esu)	α_0^*	$\operatorname{Re}\chi^{(3)*}$	$\operatorname{Im}\chi^{(3)*}_{(\times 10^{-13} \text{ esu})}$	γ (×10 ⁻²⁹ esu)
Ni(dmdt)(dmio)	0.192	-80	$\frac{(\times 10^{-10} \text{ csu})}{2.3 \pm 0.2}$	3.1	-3100	-760	$\frac{(\times 10^{\circ} \text{ csu})}{92\pm 5}$
Ni(dmstfdt)(dmio)	0.23	-129	3.7 ± 0.8	3.5	-3400	-1356	106 ± 5

* α_0 is the linear absorption, corresponding to a concentration of 0.1 mmol.



Fig. 2. OA spectra of thin deposits of Ni(dmdt)(dmio) before (a) and after (b) grinding on a quartz plate. The arrow indicates the OA band-position of a solution in CS_2 .



Fig. 3. OA spectra of thin deposits of Ni(dmstfdt)(dmio) before (a) and after (b) grinding on a quartz plate. The arrow indicates the OA band-position of a solution in CS_2 .

tained from thin deposits of Ni(dmtsfdt)(dmio), with OA bands at 1312 and 1010 nm before and after grinding, respectively (Fig. 3). The OA bands of the grinded deposits of both complexes occur close to those of solutions in CS_2 , but are broader. The shift

of the OA bands to shorter wavelengths after grinding is attributed to the decrease of the intermolecular interactions. Similar effects have been observed in other synthetic materials with semiconducting behaviour [14]. In the similar complexes Ni(dmdt)(dmit) and Ni(dmtsfdt)(dmit) (where dmit is 1,3-dithiol-2thione-4,5-dithiolate [11c]), obtained by the same method but in very low yields, the OA bands occur at longer wavelengths than those of Ni(dmdt)(dmio) and Ni(dmtsfdt)(dmio). In another unsymmetrical complex, Ni(eodt)(dmit) (where eodt is ethylenedioxytetrathiafulvalenedithiolate [12, 13]), the OA bands occur at shorter wavelengths. The results indicate that the complexes Ni(dmdt)(dmio) and Ni(dmtsfdt)(dmio) are suitable to obtain near resonance and low absorption for the near IR lasers (Figs. 1-3).

Important transient NLO response of solutions of the complexes in CS₂ was observed at 532 and 1064 nm using 8 ns pulses. Table 1 presents the determined values of the third-order susceptibility $\chi^{(3)}$ and the second hyperpolarizability γ . As seen in Table 1, hyperpolarizability values at 1064 nm are significantly larger than those at 532 nm, reflecting the strong resonant enhancement taking place at this wavelength. A similar behaviour has been observed by the authors of ref. [5] for some other unsymmetrical dithiolene complexes.

The complexes Ni(dmdt)(dmio) and Ni(dmtsfdt) (dmio) with donor (dmdt or dmstfdt) and acceptor (dmio) moieties could be candidates for second-order NLO properties as it has been shown for some other unsymmetrical complexes with donor-acceptor moieties [6a, 6c]. Also, it is expected that these unsymmetrical complexes and similar ones with extended tetrachalcogenafulvalenedithiolato ligands will exhibit NLO properties in the solid state (thin deposits on several substrates, or dispersions in polymer matrices) with lasers operating at 1064 or longer wavelengths (*e.g.*, 1300 and 1550 nm), considering that the typical wavelength for optical communication is 1550 nm (0.8 eV) (see [15] and references therein). However, some structural and spectroscopic data as well as theoretical calculations are required for the electronic distribution (metal-ligand) and the correlation with the NLOP [6a]. Finally, this kind of unsymmetrical complexes as well as the previously reported ones [2-4, 17], which are weak semiconductors, could be candidate materials of FETs [3,4,7-9] and/or photoconductors [17,18] for various applications [3-8, 15-18].

Experimental Section

(Dimethyltetrathiafulvalenedithiolato)(1,3-dithiol-2-one-4,5-dithiolato)nickel, Ni(dmdt)(dmio)

In a two-necked 250 mL flask, a solution of NaOMe, freshly prepared from Na (80.5 mg, 3.5 mmol) and deoxygenated MeOH (30 mL), was added to a suspension of compound 1 (296 mg, 0.5 mmol) in deoxygenated MeOH (5 mL), under nitrogen atmosphere, and the mixture was stirred for 1 h. Compound 2 (195 mg, 0.5 mmol) was added and the stirring was continued for 15 min. To the obtained red-brown solution, a solution of NiCl₂ · 6 H₂O (120 mg, 0.5 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 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 greenbrown solid was extracted with CS₂ and chromatographed on silica gel, using CS₂ as eluent. The first green fraction contained Ni(dmdt)(dmio) (8 mg, 3 %). M. p. 246 °C (dec.). - UV/vis/near IR (CS₂): λ_{max} (lg ε_{max}) = 977 nm (4.58). - IR (KBr): v = 1621, 1665 (C=O), 2923 (CH₃) cm⁻¹. - C11H6OS10Ni (533.5): calcd. C 24.76, H 1.12; found C 24.80, H 1.17.

(Dimethyldiselenadithiafulvalenedithiolato)(1,3-dithiol-2one-4,5-dithiolato)nickel, Ni(dmstfdt)(dmio)

In a two-necked 250 mL flask, a solution of NaOMe, freshly prepared from Na (72.5 mg, 3.15 mmol) and deoxygenated MeOH (30 mL), was added to a suspension of

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compound 3 (225 mg, 0.45 mmol) in deoxygenated MeOH (5 mL), under nitrogen atmosphere, and the mixture was stirred for 2 h. Compound 2 (175.5 mg, 0.45 mmol) was added and the stirring was continued for 15 min. To the obtained red-brown solution, a solution of NiCl₂ · 6H₂O (107.6 mg, 0.45 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 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. The first green fraction contained Ni(dmstfdt)(dmio) (20 mg, 7%). M. p. 255 °C (dec.). – UV/vis/near IR (CS₂): λ_{max} (lg ε_{max}) = 988 nm (4.56). - IR (KBr): v = 1625, 1657 (C=O), 2922 (CH₃) cm⁻¹. - C₁₁H₆OS₈Se₂Ni (627.28): calcd. C 21.06, H 0.96; found C 21.13, H 1.08.

Instrumentation

All measurements were performed at r. t. Resistivity measurements were performed on compressed polycrystalline pellets by the well known voltage-drive method. Thin deposits of the complexes on quartz plates were obtained by spraying or spinning CS_2 solutions of the complexes. Very dilute deposits were obtained by grinding the original deposits between two quartz plates. The optical absorption spectra of solutions or several deposits in the UV/vis/near IR spectral region were recorded on a Perkin Elmer, model Lambda 19 spectrophotometer. The NLO measurements were performed by the standard Z-scan technique, using a Q-switched 8 ns Nd:YAG laser of 10 Hz operating at 532 and 1064 nm [5, 16].

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