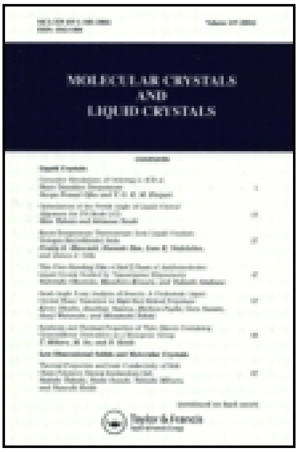

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Multifunctional Nickel-Bisdithiolate Complexes with *trans*-4-[2-(1-Ferrocenyl)Vinyl]-1-Methylpyridinium Cation

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Nickel-bisdithiolate complexes with a ferrocene-containing 2nd order nonlinear optical chromophore as a cation, (FcCH=CHPyMe)[NiL_2] where L = dmit (1a), dddt (1b) and debt (1c) were synthesized by the cation exchange reaction. In the X-ray crystal structure of complex (1a), no intrastack but interstack S…S interactions less than 3.7 Å are observed. This complex was revealed to be an insulator at room temperature. However, $(FcCH{=}CHPyMe)_x[Ni(dmit)_2]$ ($0 < x < 1$) (3) needle grown in an H-type electrochemical cell shows semiconductor behavior (E_a = 106 meV) over the temperature range measured (30 ~ 300 K) with $\sigma_{RT} = 1\ \Omega^{-1}cm^{-1}$. The electronic transition at UV-vis-NIR region was measured for the nickel complexes and discussed.

Keywords 2nd order NLO chromophore, electrical conductivity, nickel-bisdithiolate, UV-vis-NIR absorption

INTRODUCTION

There has been considerable interest in the development of new active multifunctional materials.[1],[2] Metal-bisdithiolate complexes were chosen as the potent entries with the properties such as electrical conductivity, strong near-IR(NIR) absorption, molecular magnetism and non-linear optical property.[1]-[4] *trans*-4-[2-(1-Ferrocenyl)vinyl]-1-

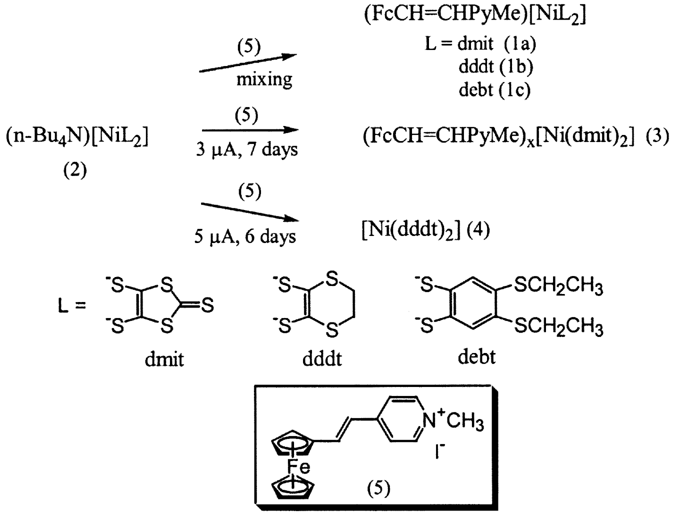
methylpyridinium iodide, (FcCH=CHPyMe)·I (5) is known to have the large second-harmonic generation(SHG) activity which is necessary for an effective second order nonlinearity.[5],[6] The nickel-bisdithiolate complexes with this pyridinium cation are expected to show unusual solid-state properties. Here, we report the syntheses of several new nickel-bisdithiolate complexes (FcCH=CHPyMe)[NiL_2] where L= 1,3-dithiole-2-thione-4,5-dithiolate or dmit (1a), 5,6-dihydro-1,4-dithiin-2,3-dithiolate or dddt (1b) and 1,2-diethylthio benzene-4,5-dithiolate or debt (1c). Electronic absorption data of nickel-bisdithiolates and electrical conductivity of $(FcCH{=}CHPyMe)_x[Ni(dmit)_2]$ $(0 < x < 1)$ (3) were also described.

SYNTHESIS

(FcCH=CHPyMe)[NiL_2] (1)

Complexes (1) were synthesized by mixing of 20 mL acetonitrile solution of (2) (2.5 mM) and 40 mL of (5) (12.5 mM) with stirring for 30 min. The crystalline precipitates were collected and washed with ethanol. (Scheme 1)

(1a) Yield 55 %. Anal. Calcd for $C_{24}H_{18}FeNNiS_{10}$ C 38.15, H 2.40, N 1.85, S 42.44. Found C 38.43, H 3.21, N 1.44, S 41.66. FT-IR (KBr,



SCHEME 1. Preparation of nickel-bisdithiolate complexes

cm^{-1}) 3050 (Cp C-H), 1595 (Py C-C), 1514, 1472 (Cp C-C), 1348 (C=C), 1192, 1182 (Py C-H), 1060 (C=S), 864, 821 (Cp C-H), 507, 492 (Cp ring def).

(1b) Yield 86 %. Anal. Calcd for $C_{26}H_{26}FeNNiS_8$ C 43.16, H 3.62, N 1.94, S 35.45. Found C 42.50, H 3.78, N 1.65, S 34.53. FT-IR (KBr, cm^{-1}) 3050 (Cp C-H), 2913 (CH_2), 1599 (Py C-C), 1514,1470 (Cp C-C), 1360, 1283 (C=C), 1192, 1177 (Py C-H), 830 (Cp C-H), 486 (Cp ring def).

(1c) Yield 35 %. Anal. Calcd for $C_{38}H_{42}FeNNiS_8$ C 51.64, H 4.79, N 1.58, S 29.03. Found C 50.98, H 4.88, N 1.74, S 24.70. FT-IR (KBr, cm^{-1}) 2965, 2924, 2855 (Et C-H), 1601 (Py C-C), 1476, 1454 (Cp C-C), 1265 (CH_2), 1101 (C-S-C), 864, 820 (Cp C-H), 492 (Cp ring def).

$(FcCH{=}CHPyMe)_x[Ni(dmit)_2]$ $(0 < x < 1)$ (3)

This complex was grown by the conventional electrochemical crystallization method with (2a) (2×10^{-5} mol, 14 mg) and (5) (5×10^{-5} mol, 22 mg) in dried acetonitrile (15 mL) using an H-type cell. Black needle-like crystals were collected from the anode after applying 3 μA for *ca.* 7 days. Plate-like crystals were also harvested from the glass-frit and identified as x = 1 composition. FT-IR (KBr, cm^{-1}) 1601 (Py C-C), 1516, 1472 (Cp C-C), 1341, 1242 (C=C), 1194 (Py C-H), 1053 (C=S), 494 (Cp ring def).

RESULTS AND DISCUSSION

Complexes (1) were prepared by the cation exchange reaction. (Scheme 1) These complexes were isolated as dark purple crystalline solids after concentration of solvent and were fully analyzed by elemental analysis, FT-IR and UV-vis spectroscopy.

The crystal structure of (1a) is determined by X-ray crystallography[7] and demonstrated in Figure 1. In the crystal structure,

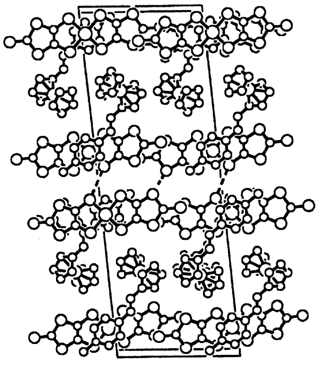


FIGURE 1. Crystal structure of (1a) viewed normal to the (010) plane

the Ni(dmit)$_2$ unit and the methylpyridinium moiety of the cation are stacking alternatively with the nickel ion being just above the center of pyridinium ring. Therefore, the shortest intermolecular S...S interactions in a stack are equal to the *b*-axis distance (7.6997(10) Å) and no intrastack S...S interactions less than 3.7 Å are observed. The short interstack S...S interactions are denoted by a broken line in Figure 1. The structural features are suggesting that (1a) could be an insulator. Actually, it shows very high resistivity at room temperature indicating an insulator.

The electronic absorption spectra of complexes (1), (2) and (5) were recorded and the data are presented in Table 1. Compound (5) in acetonitrile solution shows two strong low-lying bands: The band at 360 nm is ascribed to the *d-d* transition of metal ion and the band at 548 nm is to a ligand-to-metal charge transfer (LMCT) excitation.[8] The band at 548 nm exhibits bathochromic shift as the iodide ion is replaced by an electron-withdrawing nickel-bisdithiolate. The largest bathochromic shift is observed when dissolved in dichloromethane. Thus the absorption maximum (λ_{max}) shifts by up to 50 nm for the low-energy band of complex (1c) and 36 nm for the high-energy band of complex (1a). It means that the ground state of FcCH=CHPyMe cation

TABLE 1. UV-vis-NIR absorption data of the complexes^{+}

Comp	MeCN	Me$_2$CO	CH$_2$Cl$_2$	CH$_2$Cl$_2$	solid
(1a)	354(5.10) 558(4.43)	352(5.16) 570(4.45)	390(4.81) 606(4.32)	1154 (4.02)	985
(1b)	358(4.92) 550(4.28)	356(5.22) 552(4.54)	374(4.62) 582(4.17)	1189 (3.75)	1162
(1c)	358(5.62) 548(4.87)	352(5.44) 546(4.65)	378(5.36) 598(4.69)	989 (4.20)	843
(2a)	-	-	-	1137*(4.65)	945
(2b)	-	-	-	1175$^{\#}$(4.19)	1125
(2c)	-	-	-	980 (4.21)	827
(5)	360(4.55) 548(3.92)	362(3.93) 548(3.31)	376(3.95) 586(3.39)	-	-

$^{+}$ $\lambda_{max}(\log\varepsilon)$, λ_{max} in nm, * in MeCN, # in C_6H_6[8]

is well-stabilized in a polar solvent. Complexes (1) show strong absorption at 1189 ~ 989 nm corresponding to the π→π* transition of the delocalized dithiolate ligands. The electron delocalization in the coordinated nickel-dithiolate moiety is possible by the strong overlap of sulfur *d*-orbitals and thus will lead to bathochromic shifts of the multi-sulfur complexes. Complex (1c) shows higher energy absorption in NIR region than (1a) and (1b). This is due to the strong electrophilicity of the alkylthiobenzo derivative which stabilizes the HOMO level ($2b_{1u}$) and thereby the transition energy (ΔE_{NIR}) between HOMO and LUMO ($3b_{2g}$) levels will be increased. Solid-state NIR spectra of nickel complexes are also measured to remove the solvent effect. The absorption maxima (λ_{max}) of (2) shift to the lower energy region when the tetrabutylammonium cation is replaced by FcCH=CHPyMe. It can be concluded that the introduction of FcCH=CHPyMe can be a facile

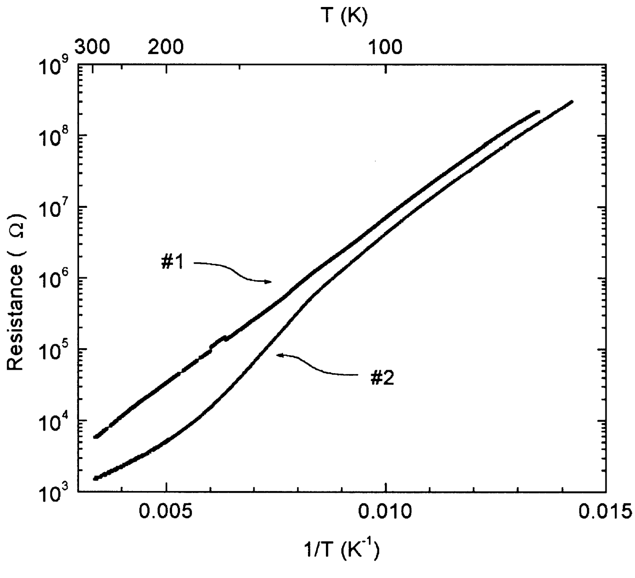


FIGURE 2 Temperature dependence of electrical conductivity of a single crystal (3). Curves #1 and #2 are obtained from the same crystal but from different temperature cycle. Both data are collected during warming.

way to prepare the infrared dye absorbing lower energy.

Partial oxidation of (1b) was tried by using the electrochemical method but a polycrystalline neutral complex (4) was obtained. Partial oxidized $(FcCH{=}CHPyMe)_x[Ni(dmit)_2]$ ($0 < x < 1$) (3) was harvested as a needle-like crystal when the same electrochemical method using (2a) and (5) was applied in an H-type cell. (Scheme 1) Using the conventional 4-probe ac method with a lock-in amplifier, the electrical conductivity of (3) was explored as a function of temperature (Figure 2). Room temperature conductivity was around 1 $\Omega^{-1}cm^{-1}$. Overall temperature dependence indicates that (3) is a single gap semiconductor with E_a = 106 meV all over the temperature range. In some of temperature cycles, an additional anomaly was observed at around 150 K where the resistance increases more rapidly (curve #2 in Figure 2). However, the energy gap at low temperature was independent of the presence of such an anomaly. Although it is not yet clear, the order-disorder transition of asymmetric cations may be related to the anomaly.

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