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Formation of Extended π Electron System Based on Nickel(II) Complex with Non-Innocent N_2S_2 Ligand

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New bridging ligand, 2,6-diphenylbenzo[1,2-*d*:4,5-*d'*]bisthiazoline, have been synthesized by reaction of 2,5-diamino-1,4-benzenethiol dihydrochloride with benzaldehyde in a 1:2 stoichiometry. Reaction of this ligand with nickel(II) acetate tetrahydrate gave some nickel(II) complexes which show a strong near-infrared absorption due to extended π-conjugation. Structural assignment of two complexes was made on the basis of IR and electronic spectroscopic studies as well as elemental analyses.

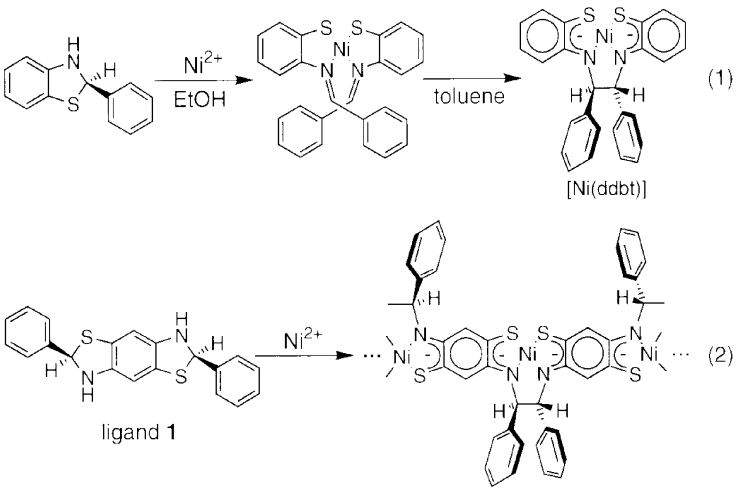
Keywords: nickel(II); near-infrared absorption; non-innocent ligand

INTRODUCTION

The transition metal complexes with non-innocent ligands, which are represented by the metal dithiolene complexes, have attracted considerable attention due to conducting materials as well as molecular models for the active center of enzymes in bioinorganic chemistry[1,2]. In addition, they have been also expected as metal complex dyes due to a strong near-infrared (NIR) absorption with a remarkable high absorption coefficient[3].

Recently, we have reported the facile synthesis of nickel(II) complex with non-innocent N_2S_2 ligand (Scheme 1, (1))[4]. As an application of reaction (1), we report herein the synthesis and characterization of nickel(II) complexes with a strong NIR absorption obtained by reaction (2).

SCHEME 1



EXPERIMENTAL

Preparation

All reactions were carried out under inert gas atmosphere using standard Schlenk techniques.

2,6-Diphenylbenzo[1,2-*d*:4,5-*d'*]bisthiazoline (ligand **1**)
To a solution of NaOH (0.19 g, 4.8 mmol) in 80 cm^3 of hot ethanol was added 2,5-diamino-1,4-benzenethiol dihydrochloride (0.58 g, 2.4 mmol) and benzaldehyde (0.51 g, 4.8 mmol). The mixture was refluxed for 30 min and then allowed to cool to room temperature. Further, it was stood in a freezer overnight. The resulting light yellow powder was collected by filtration. The powder was dissolved in 400 cm^3 of CH_2Cl_2, and NaCl was removed by filtration. The resulting light yellow solution was evaporated to dryness to afford a light yellow powder. Anal. Found: C, 68.58; H, 4.67; N, 8.01%. Calcd for $C_{20}H_{16}N_2S_2$: C, 68.93; H, 4.63; N, 8.04%. ^1H NMR (270 MHz, $CDCl_3$): $\delta = 7.55$ (d, $J = 8$ Hz, 4H), 7.3 - 7.4 (m, 6H), 6.59 (s, 2H), 6.33 (d, $J = 3$ Hz, 2H). IR (Nujol; cm^{-1}): 3242 (ν_{NH}).

Complexes **1** and **2**
To a light yellow suspension of ligand **1** (0.11 g, 0.32 mmol) in 100 cm^3 of ethanol was added nickel(II) acetate tetrahydrate (0.076 g, 0.31 mmol). The mixture was stirred at room temperature for 7 d, resulting in a color change to green. Then the resulting green powder was

collected by filtration and redissolved in 10 cm^3 of CH_2Cl_2. After filtration, the resulting green powder (complex **1**) was dried in vacuo, while the green filtrate was loaded on a silica gel column and eluted with CH_2Cl_2 to give two green bands. The first fraction was collected and evaporated to dryness, yielding the desired complex **2** as a green powder. The second adsorbed band of unknown composition was extracted with methanol and evaporated to dryness to give a green powder[5]. Anal. Found for complex **1**: C, 62.53; H, 3.78; N, 7.40%. Calcd for $C_{60}H_{40}N_6Ni_2S_6$: C, 62.41; H, 3.49; N, 7.28%. UV-VIS (DMSO) [λ_{max}/nm (ε / M^{-1} cm^{-1})]: 1990 (19900), 980 (44700), 398 (55500). ^{1}H NMR (270 MHz, DMSO-d_6): δ = 7.95 (br, s), 7.65 (br, s), 7.52 (br, s), 7.27 (br, s), 6.72 (br, s). Anal. Found for complex **2**: C, 62.94; H, 3.92; N, 7.10%. Calcd for $C_{40}H_{26}N_4NiS_4 \cdot H_2O$: C, 62.59; H, 3.68; N, 7.30%. UV-VIS ($CHCl_3$) [λ_{max}/nm (ε / M^{-1} cm^{-1})]: 1306 (9840), 1102 (5770), 923 (53900), 373 (32800). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.28 (s, 2H), 8.02 (d, J = 7 Hz, 4H), 7.66 (s, 2H), 7.2 - 7.6 (m, 16H), 6.42 (s, 2H).

Measurements

The absorption spectra were recorded with a JASCO V-570 spectrophotometer at room temperature. The ^{1}H NMR spectra were recorded with a JOEL EX 270 instrument using tetramethylsilane as internal standard (δ = 0). IR spectra in the 4000 - 400 cm^{-1} were measured on a JASCO FT/IR-5000 instrument by using Nujol mulls and NaCl windows. Elemental analyses were performed at Osaka University.

X-ray Structure Determination of an Oxidized Form (2,6-Diphenylbenzo[1,2-*d*:4,5-*d'*]bisthiazole) of Ligand **1**

The X-ray analysis of this compound has been studied by A. V. Fratini et al.[6] and S. A. Jenekhe et al.[7] The present result is chemically nearly identical to their structures. The cell parameter corresponds well with that of A. V. Fratini et al. However, crystals suitable for X-ray diffraction were obtained by slow evaporation of $CHCl_3$ solution of ligand **1** which is distinct from their methods. X-ray diffraction measurements were made on a Mac Science MXC3 diffractometer with Mo Kα radiation (λ = 0.71073 Å) at room temperature. Crystal data: $C_{20}H_{16}N_2S_2$, monoclinic, space group $P2_1/a$, F.W. = 348.49, a = 11.698(4) Å, b = 6.633(2) Å, c = 11.073(3) Å, β = 112.32(2) °; V = 794.8(4) $Å^3$, Z = 2, D_{calc} = 1.46 g cm^{-3}, μ(Mo-Kα) = 0.323 mm^{-1}, 1654 independent reflections, 1315 observed reflections ($I > 2\sigma(I)$), R = 0.045, R_w = 0.047.

RESULTS AND DISCUSSION

The ligand **1** was synthesized by combining 2,5-diamino-1,4-benzenethiol dihydrochloride with benzaldehyde and was characterized by ^{1}H NMR and IR spectroscopies and elemental analysis. However, X-ray diffraction studies on a crystal obtained by slow evaporation of $CHCl_3$ solution of ligand **1** revealed the structure of 2,6-diphenylbenzo[1,2-*d*:4,5-*d'*]bisthiazole which is an oxidized form of ligand **1**. Furthermore, the ^{1}H NMR spectra of ligand **1** at room temperature show a time-dependent dynamic behavior (Figure 1). This behavior is explained with the oxidative reactions in two steps, resulting in formation of thiazole; each of three spectra for 0 h, 36 h, and 60 h corresponds to three structures in Scheme 2. We can interpret these observations to indicate the instability of the ligand **1** in solution at room temperature.

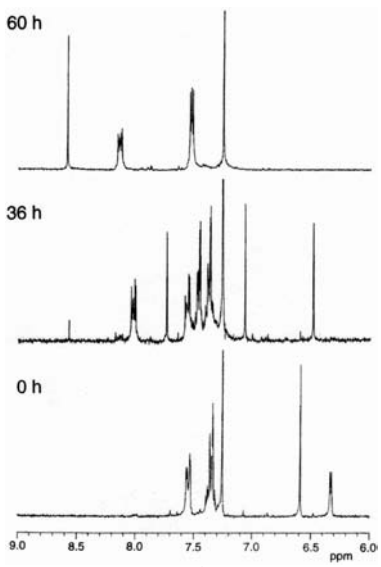
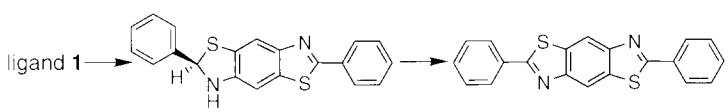


FIGURE 1 Time-dependent ^{1}H NMR spectra for ligand **1** in $CDCl_3$ at room temperature.

SCHEME 2



The nickel(II) complexes **1** and **2** were obtained by reaction of nickel(II) acetate tetrahydrate with ligand **1** in ethanol. The absence of ν(N-H) bands in the IR spectra of these complexes confirms N-H bond cleavage upon coordination to the nickel atom or oxidation to the thiazoles. Comparing the electronic spectrum of [Ni(ddbt)] (Scheme 1) with that of complex **2**, it is seen that the strongest absorption band (835 nm) in [Ni(ddbt)] is shifted to longer wavelength (923 nm) in complex **2**, which is indicative of extensive π delocalization in complex **2**. In addition, the band that occurs at 373 nm in complex **2** is assigned as a π-π* transition for thiazole by comparison with the electronic spectrum of 2,6-diphenylbenzo[1,2-*d*:4,5-*d'*]bisthiazole[6]. Although we could not get high resolution NMR spectrum for complex **2** even at -50 °C, three distinct singlets due to C_2-symmetrical structure were observed in the ^{1}H NMR spectrum. These facts allow us to suggest that complex **2** contains a tetradentate ligand where extensive π delocalization takes place as shown in (II).

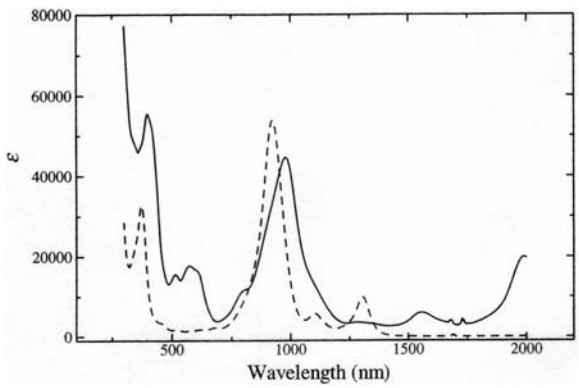
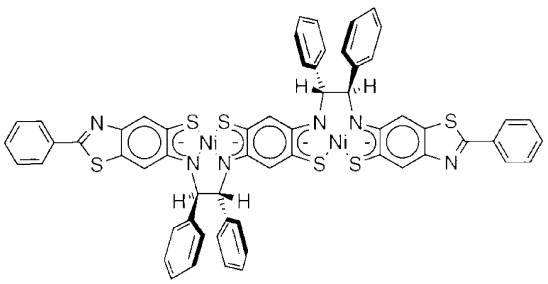


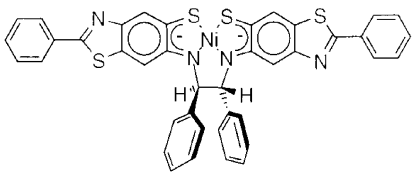
FIGURE 2 Electronic absorption spectra of complex **1** (solid line) in DMSO and complex **2** (dashed line) in $CHCl_3$.

On the other hand, the low solubility in $CHCl_3$ of complex **1**, which is believed to be more polymeric compared with complex **2**, made it necessary to record the absorption and ^{1}H NMR spectra in DMSO. The broadened signals for complex **1** in DMSO-d_6 prevent the confirmation of structural arrangement by ^{1}H NMR spectroscopy. However, the found value of complex **1** by elemental analysis is in agreement with the calculated value, which is for dimer with thiazoles as a terminal group, within the usual limit of variation. Furthermore, complex **1** exhibits three well-resolved absorption bands at 1990, 980,

and 398 nm. A more extended conjugated system in complex **1** is evidenced by the shift of the NIR absorption to longer wavelength (980 nm for complex **1**, 923 nm for complex **2**, and 835 nm for [Ni(ddbt)]). From these results, it is reasonable to assume that complex **1** has a dimeric structure depicted in (I).



(I)



(II)

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