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# Synthesis and Properties of Bis(N-phenyl-$\beta$-mercaptothiocinnamamido)Ni(II)

SUSUMU KITAGAWA and HISASHI TANAKA

*Faculty of Pharmaceutical Sciences, Kyoto University*[1]

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Bis(N-phenyl-$\beta$-mercaptothiocinnamamido)Ni(II) was synthesized and its properties were examined. This complex decomposed gradually in pyridine to 3-phenyl-5-phenylimino-1,2-dithiol, while the corresponding palladium complex never decomposed in pyridine and produced its pyridine clathrate. These differences seemed to be caused by the "soft" and "hard" character of the metal ions.

**Keywords**——dithio nickel(II) complex; decomposition of dithio nickel complex in pyridine; electronic spectra; NMR spectra; infrared spectra

In the previous papers, we have reported the synthesis of a new type of dithio ligand, N-phenyl-$\beta$-mercaptothiocinnamamide[2] and the synthesis and properties of its palladium complex.[3] The new ligand interacts with a lot of transition metal ions producing its corresponding metal chelates. These chelates, however, show a very low solubility to usual organic solvents except pyridine in which the complexes are a little more soluble, but most of the complexes decompose in pyridine gradually. Among these complexes, palladium complex is very stable in pyridine and never decomposes, and its feature was therefore studied previously[3] It was revealed that the complex contained two pyridine molecules when it was recrystallized from its pyridine solution. These pyridine molecules were not coordinated with the palladium ion, but were supposed to be included as clathrate and probably interacted with the protons of the thioamido groups of the ligands.

On the contrary, most of the complexes decomposed gradually in pyridine producing a non-metal-containing organic compound instead of pyridine clathrate. Since such decomposition has not been observed for the metal complexes of monothio- and dithio-$\beta$-diketone derivatives, it was therefore investigated employing the nickel chelate.

## Experimental

**Materials**——N-Phenyl-$\beta$-mercaptothiocinnamamide (LH): LH was synthesized by the same procedure as reported previously.[2]

Bis(N-phenyl-$\beta$-mercaptothiocinnamamido)Ni(II) ($NiL_2$): To 2 mmol of LH in 100 ml EtOH was added 1 mmol of nickel chloride in 100 ml $H_2O$ with stirring. The brown precipitate was filtered, washed

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[1] Location: *Yoshida, Shimoadachi-cho, Sakyo-ku, Kyoto, 606, Japan.*

[2] S. Kitagawa and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), 26, 1021 (1978).

[3] S. Kitagawa and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), 26, 1026 (1978).

with MeOH and recrystallized from 50% aqueous dimethylsulfoxide (DMSO) solution, mp 238° (dec.). Yield 80%. *Anal.* Calcd. for $C_{30}H_{24}N_2NiS_4$: C, 60.10; H, 4.01; N, 4.67; Ni, 9.85; S, 21.37. Found: C, 60.51; H, 4.80; N, 4.66; Ni, 8.85, S, 21.12.

3-Phenyl-5-phenylimino-1,2-dithiol (L′): L′ was prepared by the following two methods.

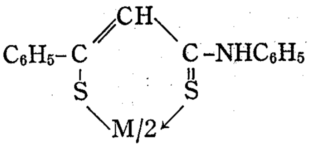
Method 1: $NiL_2$ was boiled in pyridine for 30 min and to the solution was added excess water. The solution was cooled and allowed to stand for an hour. Yellow thin flakes precipitated were collected and recrystallized from 50% aqueous EtOH, mp 128°. Yield 85%. *Anal.* Calcd. for $C_{15}H_{11}NS_2$: C, 66.91; H, 4.09; N, 5.20; S, 23.79. Found: C, 67.09; H, 4.23; N, 5.12; S, 23.90.

Method 2: LH was dissolved in EtOH and boiled for 30 min and to the solution was added excess water. Yellow thin flakes were obtained by the same procedure as the method 1, mp 128°. Yield 90%. *Anal.* Found: C, 67.21; H, 3.90; N, 5.18; S, 23.54.

**Apparatus**——Ultraviolet and visible absorption spectra were recorded on a Shimadzu multiconvertible spectrophotometer Model Double-40. Infrared spectra were measured as potassium bromide disks with a Hitachi Infrared Spectrophotometer model EPI-S2. Nuclear magnetic resonance (NMR) spectra were measured on a Varian A-60 spectrophotometer at 60 MHz with tetramethylsilane as an internal standard.

## Results and Discussion

$PdL_2$ was very stable in pyridine and produced a pyridine clathrate, $PdL_2py_2$. $NiL_2$, however, gave yellow thin flakes when it was heated in pyridine. It was revealed by the elemental analysis that the compound contained no metal and the stoichiometry, $C_{15}N_{11}NS_2$, was given, which means the decomposition of $NiL_2$.



$ML_2$ (M: $Pd^{2+}$, $Ni^{2+}$)

The yellow compound was checked by infrared spectrophotometry and it gave prominent changes, compared with those of the original $NiL_2$. As shown Fig. 1. NH stretching vibration at 3250 $cm^{-1}$ seen in $NiL_2$ vanished in case of the yellow compound, whereas a new absorption band appeared at 1670 $cm^{-1}$ in the latter compound. This new band seems to be that of >C=N- group which usually appears in 1690—1635 $cm^{-1}$.[4)]

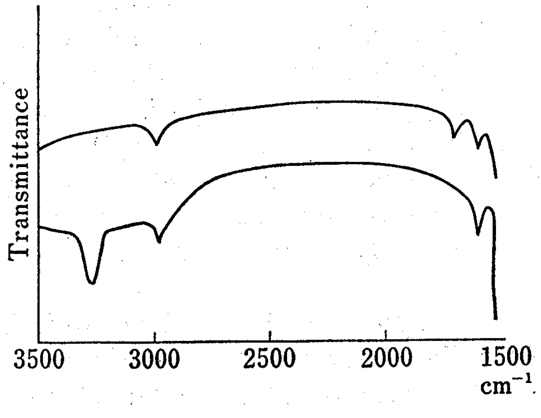


Fig. 1. The Infrared Spectra of the Yellow Compound (above) and $NiL_2$ (below)

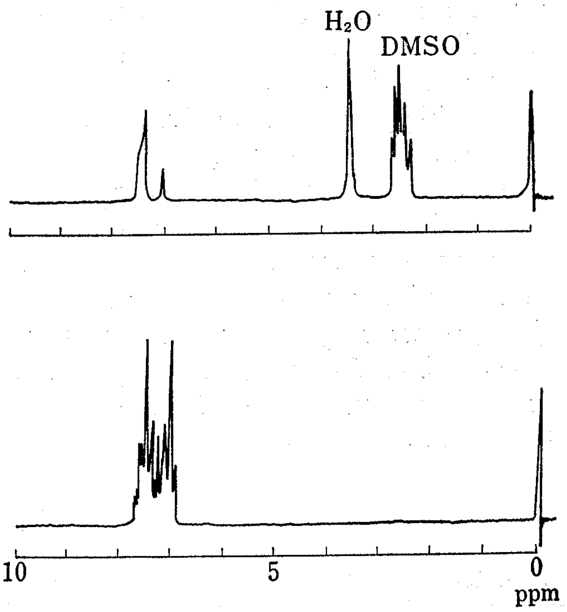


Fig. 2. The NMR Spectra of $NiL_2$ in DMSO-$d_6$ (above) and the Yellow Compoundin $CDCl_3$ (below)

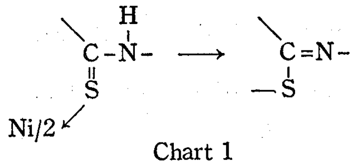


Chart 1

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4) A.D. Cross, "Practical Infrared Spectroscopy," (translated by N. Natori and G. Chihara), Tokyo Kagaku Dojin, Tokyo, 1966, p. 92.

These spectral changes apparently show the dissociation of the thioamido protons of $NiL_2$ and the formation of the imino group as shown in Chart 1.

The NMR spectra also show conspicuous changes between these two compounds as seen in Fig. 2. In $NiL_2$ the phenyl and methine protons were detected at $\delta$ 7.40 and 6.99 ppm, respectively, but the thioamido protons were not observed, probably because of the protons exchange caused by the water in DMSO-$d_6$ as well as the cases of LH and $PdL_2$ shown in Table I. Actually, $NiL_2$ showed $\nu$(NH) in its infrared spectrum. On the other hand, the spectrum of the yellow compound showed a very complicated multiplet feature between $\delta$7.70 and 6.97 ppm which seems to consist of the signals of the two phenyl groups and the methine group. Actually, these spectra are divided into a couple of groups, from $\delta$7.70 to7.35 and from 7.30 to 6.97 ppm, with the integral ratio 5: 6, which tells us that the former consists of one phenyl group and the latter consists of one phenyl group and methine group. The signal of the thioamido proton was not observed in the yellow compound.

TABLE I. The Nuclear Magnetic Resonance Data of the LH and Its Metal Chelates ($\delta$ ppm)

| Compound | Solvent | Proton | | |
|---|---|---|---|---|
| | | -NH- | $C_6H_5$- | =CH- |
| LH | $CDCl_3$ | 8.89 | 7.37 | 6.70 |
| | DMSO-$d_6$ | n.o. | 7.52 | 7.10 |
| $NiL_2$ | DMSO-$d_6$ | n.o. | 7.40 | 6.99 |
| $PdL_2$ | DMSO-$d_6$ | n.o. | 7.52 | 7.08 |

n.o.: not observed.

The electronic spectra of $NiL_2$ in DMSO and the yellow compound in EtOH are presented in Fig. 3 and the tentative assignments are listed in Table II. These two compounds showed quite different spectra. $NiL_2$ has three absorptions in the lower energy region at 15300, 17700 and 23300 cm$^{-1}$ which the yellow compound is lacking in. The absorption at 15300 cm$^{-1}$ seems to be d-d transition from its molar absorbance ($\varepsilon$ 187). Martin *et al.*[5] reported similar absorptions with bis(dithioacetylacetonato)Ni(II) (14890 cm$^{-1}$, $\varepsilon$ 330) and bis(O-ethylthio-

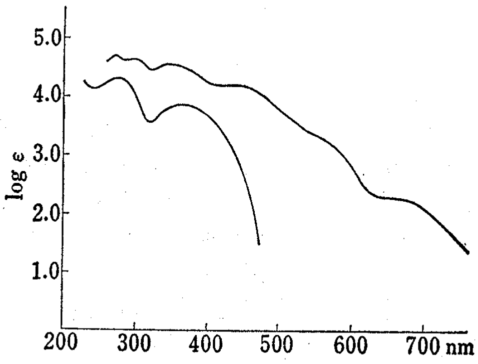

Fig. 3. The Electronic Spectra of $NiL_2$ in DMSO (above) and the Yellow Compound in Ethanol (below)

TABLE II. The Electronic Spectra of $NiL_2$ and the Yellow Compound ($\nu$ in cm$^{-1}$ and $\varepsilon$ in Parenthesis)

| Yellow compound (ethanol) | $NiL_2$ (DMSO) | Tentative assignment |
|---|---|---|
| | 15300sh (187) | $x^2$-$y^2 \longrightarrow xy$ |
| | 17700sh (1700) | |
| | 23300sh (15100) | Charge transfer |
| 27500 (7000) | 29000 (33300) | |
| | 33700 (46100) | L$\longrightarrow$L* |
| 36400 (18900) | 36900 (46700) | |

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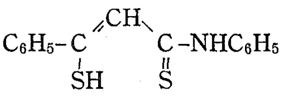
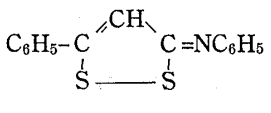
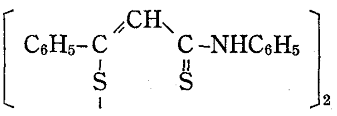
[5] A.R. Hendrickson and R.L. Martin, *Inorganic. Chem.*, 12, 2582 (1973).

acetothioacetato)Ni(II) (14700 cm$^{-1}$, $\varepsilon$ 101) and they assigned these bands to $d_{x^2-y^2} \rightarrow d_{xy}$. Therefore, the band at 15300 cm$^{-1}$ of $NiL_2$ should also be assigned to the same transition. Consequently, the energy (10 Dq) of the $NiL_2$ is located such a position in the following spectrochemical order for the corresponding absorption in other square planar dithio chelates of divalent nickel: $[S_2CC(CN)COOC_2H_5]^{2-}$ (16700 cm$^{-1}$)[6]$>[CS_3]^{2-}$ (16400)[6]$>[S_2CC(CN)C(O)NH_2]^{2-}$ (16000)[6]$\approx[S_2CNCN]^{2-}$ (15870)[6]$\approx$diethyldithiocarbamate (15800)[71]$\approx[S_2CC(CN)_2]^{2-}$ (15700)[6]$\approx$ethylxanthate (15500)[7]$\approx L^-$ (15300)$>$dithioacetylacetone (14890)[8]$\approx$O-ethylthioacetothioacetate (14700)[7]$\approx$diethyldithiophosphate (14500)[7]$\approx$dithiophosphinate (13700)[9] $\approx$dithiocacodylate (13700)[10]$>$maleonitriledithiolate dianion (11690)[11] On the other hand, those bands at 17700 and 23300 cm$^{-1}$ of $NiL_2$ seem to be charge transfer bands from ligand to metal or from metal to ligand, while the yellow compound showed only two absorptions in $\pi$-$\pi$ region.

It was observed that LH is unstable in its solution and gradually decomposed into a yellow compound whose chemical properties all accorded with those of the yellow compound mentioned above. As is known well, a sulfhydryl group is easily oxidized to disulfide, so the decomposition of LH seems to be an intramolecular disulfide(L′) formation, an intermolecular disulfide($L_2$) formation being negligible because the product is lacking in $\nu$(NH) in its infrared spectrum. Therefore, the complete accordance of all the chemical properties between these two yellow compounds makes it sure that $NiL_2$ decomposes in pyridine into L′, similar compounds being often seen in the literatures as dithiols,[12] dithiolium cations[13,14] and their metal complexes.[15,16]


LH


L′


$L_2$

It is said that $Pd^{2+}$ belongs to soft acid and produces very stable complexes with sulfur donors forming $\pi$-bondings with their vacant d orbitals, while $Ni^{2+}$ shows an intermediate character between soft and hard acid. Therefore, the difference of the behaviour in pyridine between $PdL_2$ and $NiL_2$ seems to be caused by the soft and hard character of the metal ions. Actually, $PtL_2$ where $Pt^{2+}$ belongs to soft acid forms a pyridine clathrate, $PtL_2py_2$ as well as $PdL_2$, while $ZnL_2$ and $CoL_2$ where $Zn^{2+}$ and $Co^{2+}$ lie in the borderline between soft and hard acid decompose in pyridine into L′ similarly to $NiL_2$.

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