

## Specific Interaction of Dithiocarbamate Complexes with 1,4-Dioxane

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It was found that the copper(II) dithiocarbamate complexes having amino acid ester moiety as a part of dithiocarbamate ligand, such as proline methyl  $\text{Cu}(\text{S}_2\text{CNC}_4\text{H}_7\text{CO}_2\text{CH}_3)_2$  (**1**) showed a solvatochromism phenomenon against 1,4-dioxane. On the other hand, nickel (II) dithiocarbamate complex, such as  $\text{Ni}[\text{S}_2\text{CNHC}(\text{C}_5\text{H}_{10})\text{CO}_2\text{CH}_3]_2$  (**2**), which also having amino acid ester moiety within the ligand, can include 1,4-dioxane via. hydrogen bonding into its 1 D polymeric chain. On the basis of the structural finding for the nickel complex **2**, mechanistic consideration on the solvatochromism of **1** was discussed.

Key words: specific interaction through hydrogen bonding, solvatochromism, dithiocarbamate, inclusion

### 1. INTRODUCTION

Recently, many attempts have been focused on evolving new supramolecules from metal complexes through their hierarchical assembling [1]. In the introduction of supramolecular complexes, selecting ligands and central metals can control inter- and intramolecular interactions at the specific sites of the complex, which can lead varieties of the complex assemblies. Consequently, such modifications perhaps give specific functionalities that the individual complex molecules cannot assess.

Hydrogen bonding shows relatively strong binding force among several intermolecular interactions and its strength and the direction are readily controllable by the selection of the sites and numbers of donors and acceptors of hydrogen. Using hydrogen bonding as a main binding force of the assemblies leading to supramolecules have a merit of easiness of molecular design suitable for the structures and the size of the guests.

In our continuous studies on the assembling dithiocarbamate complexes having amino acid ester moieties within the ligand to make up self organization, it was found that Cu(II) and Ni(II) dithiocarbamates have two characteristics; (1) they can offer apical coordination sites because of their planner four-coordination geometry, and (2) an introduction of amino acid ester parts enable to associate through hydrogen bonding. Especially, nickel(II) dithiocarbamate of glycine methyl can form the specific 3D assembly which possessing microchannels to include some guest molecules [2].

In this study, we investigated that specific interaction of Cu(II) and Ni(II) dithiocarbamates having amino acid ester moiety with certain small molecules. We found the presence of specific interactions of 1,4-dioxane with  $\text{Cu}(\text{S}_2\text{CNC}_4\text{H}_7\text{CO}_2\text{CH}_3)_2$  (**1**) or  $\text{Ni}[\text{S}_2\text{CNHC}(\text{C}_5\text{H}_{10})\text{CO}_2\text{CH}_3]_2$  (**2**).

### 2. EXPERIMENTAL

#### Synthesis

General synthetic procedure for the complexes **1** and **2** is as following; copper(II) acetate or nickel(II) acetate (5 mmol) and *O*-methylproline or 1-(methoxycarbonyl)-cyclohexylamine (10mmol) were placed in a 100 mL two-necked flask respectively. Then, methanol (40 mL) was added to the mixture and the resulted solution was stirred at room temperature for 1 h. Afterwards, carbon disulfide (10 mmol) was slowly added by syringe work. The mixture was stirred for additional 24 h at room temperature. After the reaction, methanol was removed under reduced pressure, and residual powders were washed with water to remove acetic acid and other remained materials. The powdery product was then dried under reduced pressure at room temperature. Pure complexes were prepared by recrystallization from acetonitrile solution. Identification of them was done with spectral investigation using IR, and  $^1\text{H}$ - and  $^{13}\text{C}$  NMR spectra and TOF-MS. Yields, appearance and melting points of complexes **1** and **2** are displayed in Table I. Selected spectral data of these complexes are also summarized in Table II.

#### Characterization

IR,  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra, TOF-MS and Uv-vis spectra were recorded with a SHIMADZU FT-IR DR8500 spectrophotometer, a Varian UNITY300 (300 MHz) spectrometer and a PE Biosystems Voyager-DE PRO time-of-flight mass spectrometer, SHIMADZU UV-3100PC, respectively. Single crystal automatic X-ray structure analysis was done with a Rigaku AFC-7R four-circle X-ray diffractometer. The structure analyses of the crystals were performed over the reflection range within  $4.0^\circ < 2\theta < 120.1^\circ$  by the  $\omega$ - $2\theta$  scanning using Cu  $K_\alpha$

radiation (1.54178 Å) at 298 K. In addition, the structure was solved by the Crystal Structure program[3,4]. We could get refined structure of Ni[S<sub>2</sub>CNHC(C<sub>5</sub>H<sub>10</sub>)CO<sub>2</sub>CH<sub>3</sub>]<sub>2</sub>·1,4-dioxane (**3**) using Direct Methods(SIR92) [5,6].

Table I Characteristics of **1**, **2** and **3**

complexes	color	%-yield	mp / °C
<b>1</b>	dark green	34	232.0-233.0
<b>2</b>	dark green	8	148.0-149.0
<b>3</b>	dark green	-	148.0-149.0

Table II Selected spectral data of **1**, **2** and **3**

complexes	IR wavenumbers / cm <sup>-1</sup>				<sup>13</sup> C-NMR	M <sup>+</sup> a
	ν(N-H)	ν(C=O)	ν(C-N)	ν(CS)	δ(CS)	m/z
<b>1</b>	-	1753	1475	1157	- <sup>b</sup>	470.7(471.0)
<b>2</b>	3282	1739	1510	999	208	521.9(522.0)
<b>3</b>	3282,3183	1740	1510	999	208	521.9(609.9) <sup>c</sup>

a Calculated mass numbers for **1**, **2** and **3** are described in the parentheses. b This copper complex is paramagnetic. c M<sup>+</sup>-C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>.

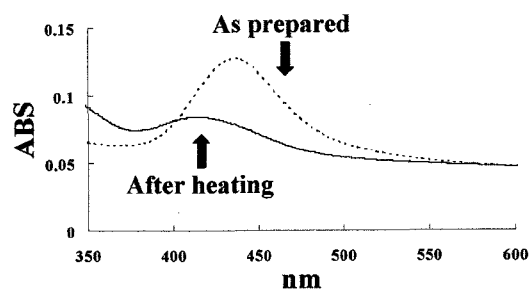
### 3. RESULTS AND DISCUSSION

#### 3.1 Cu(II) Bis(*O*-methylproline dithiocarbamate) complex (**1**)

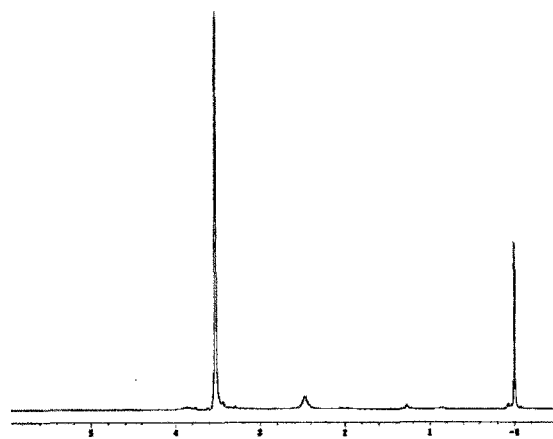
A dark green solution was prepared by dissolving the complex **1** in 1,4-dioxane. The color of the solution of **1** in 1,4-dioxane disappeared during the mild heating. Again, dark green crystals of the complex **1** were recovered after the evaporation of 1,4-dioxane to dryness. Complex **1** were soluble into many other polar organic solvents, such as methanol, ethanol, acetone, THF, dimethylformamide, and their combination with 1,4-dioxane to give similar dark green solutions, but any color change of these solutions could not be observed by heating. Additionally, any color change could not detect for the crystals of the complex **1** by heating nor storage for a long term under air. Thus, it can be said that the complex **1** showed a solvatochromism phenomenon against 1,4-dioxane. In other wards, the complex **1** should interact with 1,4-dioxane in specific manner.

Such a change of Uv-vis spectra of the solution of the complex **1** in 1,4-dioxane before and after the heating is represented in Fig.1. A broken line in Fig. 1 indicates the spectrum recorded for the freshly prepared solution of complex **1** in 1,4-dioxane, and the solid line after heating. Complex **1** shows its C-T or π-π band in medium strength at 430 nm. While, in the spectrum

after heating, small absorption maxim was detected at 410 nm. We tentatively concluded that the C-T band of the complex **1** shifted to lower wave length region because of some change of electronic structure of the complex **1** [7].

Fig. 1 Change of Uv-vis spectra of **1** in 1,4-dioxane

Moreover, NMR spectroscopic investigations indicated that the complex **1** itself is paramagnetic from its d<sup>9</sup> nature, and broad signals were observed in NMR measurement of complex **1**. Sharpening of the signals in NMR can be, however, observed after heating and discoloring in 1,4-dioxane-d<sub>8</sub> as shown in Fig. 2. Therefore, the electronic structure of the central copper nuclei should be changed by an interaction with 1,4-dioxane molecules [8].

Fig. 2 <sup>1</sup>H-NMR of **1** in 1,4-dioxane-d<sub>8</sub> after discoloring by heating

#### 3.2 Ni(II) 1-(methoxycarbonyl)cyclohexyl-dithiocarbamate complex

The single crystals of dark green suitable for X-ray structural analysis were prepared by recrystallization with vapor diffusion method from 1,4-dioxane/hexane system. The ORTEP diagram [9] of the complex **2** as shown in Fig.3 was obtained by X-ray structural analysis. It is confirmed that complex **2** was monomer and possessed the planar four coordinated geometry around the central nickel atom similarly to many other nickel(II) dithiocarbamate complexes. Crystallographic data for this nickel(II) dithiocarbamate are shown in Table III.

Table III Crystallographic data for  
 $\text{Ni}[\text{S}_2\text{CNHC}(\text{C}_5\text{H}_{10})\text{CO}_2\text{CH}_3]_2 \cdot 1,4\text{-dioxane}$  (**3**)

description	$\text{Ni}[\text{S}_2\text{CNHC}(\text{C}_5\text{H}_{10})\text{CO}_2\text{CH}_3]_2 \cdot 1,4\text{-dioxane}$
Formula	$\text{NiC}_{22}\text{H}_{36}\text{N}_2\text{O}_6\text{S}_4$
Formula weight	611.48
$T / ^\circ\text{C}$	25.0
Crystal system	triclinic
Space group	P-1(#2)
$A / \text{Å}$	7.892(1)
$B / \text{Å}$	12.390(2)
$C / \text{Å}$	7.797(2)
$A / ^\circ$	101.70(1)
$\beta / ^\circ$	102.05(1)
$\gamma / ^\circ$	79.64(1)
$V / \text{Å}^3$	722.6(2)
Z	1
$D(\text{calc.}) / \text{g}\cdot\text{cm}^{-3}$	1.405
Crystal size / mm	0.20×0.10×0.30
Monochromator	$\text{CuK}\alpha(\lambda=1.54178\text{Å})$
$F(000)$	322.00
No. reflections	
Total	1134
Unique	992
Observed	857
$R[I > 2\sigma(I)]$	
R	0.054
Rw	0.046

It is interesting that the complex **2** should be associated with 1,4-dioxane forming complex **3**. 1,4-Dioxane is one component of the solvent system for preparing single crystals of the complex. A typical ORTEP diagram of the complex **3** is illustrated in Fig. 3. It can be seen from Fig. 3 that the 1,4-dioxane molecule is placed within the space made by a folding of terminal ester moiety of the complex **2**, and one of oxygen atom of 1,4-dioxane is faced on the carbamoyl hydrogen. Molecular packing diagram of the complex **3** is also displayed in Fig. 4, where one molecule of 1,4-dioxane should bridge two molecules of complex **2** through hydrogen bondings between oxygen and carbamoyl hydrogens. Consequently, the complex **2** and 1,4-dioxane forms a 1D-chain toward the  $c$ -axis direction. The length of the intermolecular hydrogen bonding  $[\text{N}(1)\text{-H}(1)\cdots\text{O}(4)]$  was estimated as 2.94(11) Å. Elemental analysis data also supported the formation of 1:1 aggregation (Calc. for  $\text{C}_{22}\text{H}_{36}\text{N}_2\text{NiO}_6\text{S}_4$ : C, 43.21; H, 5.93; N, 4.58%. Found: C, 42.75; H, 5.86; N, 4.54%). Unfortunately, since any single crystals of **2** from other solvents than 1,4-dioxane, could be prepared, molecular structure of complex **2** without 1,4-dioxane is not clear.

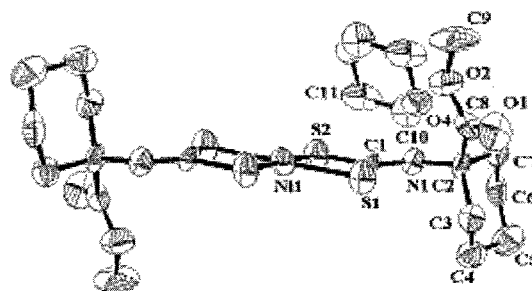


Figure 3 An ORTEP drawing of **3**

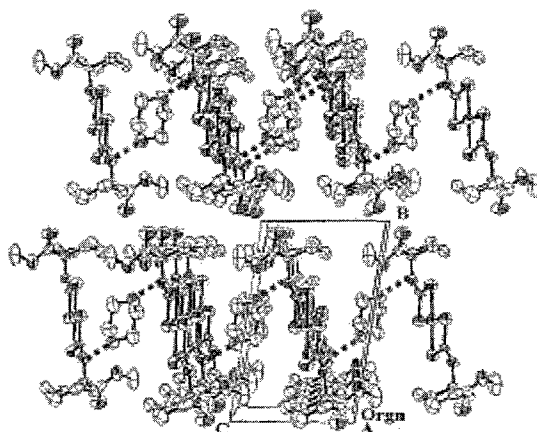


Figure 4 Molecular packing diagrams of **3** viewed along  $a$ -axis to the  $[100]$  direction

The powders of the complex **2** showed strong and sharp stretching absorption band at  $3280\text{ cm}^{-1}$  assignable to  $\nu_{\text{N-H}}$ . This absorption band should indicate that the complex **2** should not form any aggregation through hydrogen bonding. While the complex **3** displayed additional and somewhat broad band at  $3183\text{ cm}^{-1}$ , which should support the presence of hydrogen bonding between carbamoyl protons and 1,4-dioxane molecules (Figure 5) [10].

Attempts to remove 1,4-dioxane from the crystals of polymeric complex **3** to obtain 1,4-dioxane-free single crystals of the complex **2** were unsuccessful. Thus, the absorption of  $\nu_{\text{N-H}}$  ( $3183\text{ cm}^{-1}$ ) did not disappear from the crystals by washing them with some organic solvents in which the complex **2** is insoluble. Removing 1,4-dioxane by vaporization under reduced pressure ( $6.7 \times 10^{-2}\text{ Pa}$ ) for weeks is also failed.

On the other hand, the absorption of  $\nu_{\text{N-H}}$  could disappear by heating the crystals above  $100^\circ\text{C}$  for 10 min, however, the crystals became collapsed. Conclusively, the bridging of 1,4-dioxane is found to be an important key factor for the formation of such crystals.

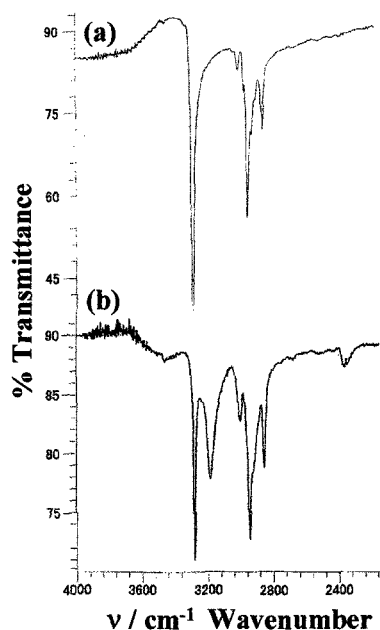


Figure 5 Comparative infrared spectra of (a) complex **2** and (b) complex **3**.

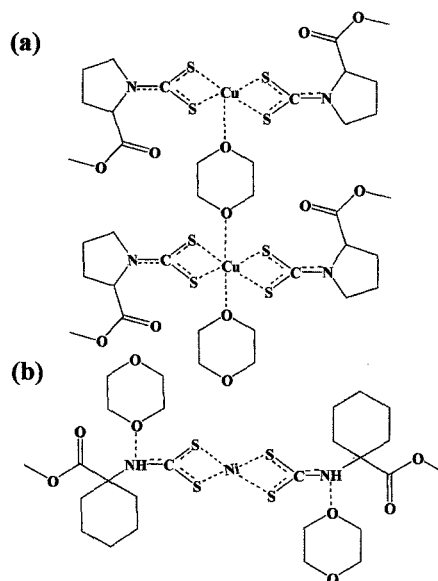
Both copper(II) and nickel(II) dithiocarbamates are generally planar four coordinated complexes. In comparing the interaction of **1** and **2** with 1,4-dioxane, nickel complex **2** possesses carbamoyl protons and can form hydrogen bonding between carbamoyl proton and oxygen atom of 1,4-dioxane leading to 1D polymer as shown in Scheme 1 (b).

In spite, copper complex **1** is not a hydrogen donor, hence the interaction of the complex **1** with 1,4-dioxane is limiting to the coordination to the central copper nuclei. Since it is difficult to image that the solvatochromism occurred by a simple coordination. In the nickel analogues, 1,4-dioxane molecules have strong power to construct polymeric structure as described above. Thus, in the case of the copper complex, 1,4-dioxane should behave as a bridging ligand to connect some copper dithiocarbamates. This perhaps stimulates the formation of polymeric structure in solution. Such polymeric structure should derive some strain on the central metal atom, which may influence the electronic absorption as shown in Scheme 1 (a).

#### 4 CONCLUSION

We found that complexes **1** and **2** can recognize 1,4-dioxane molecule in different mechanism. Complex **1** formed the coordination bond with 1,4-dioxane bridging the complexes in solution changing the electronic structure of central metal, which resulted in the solvatochromism phenomenon. On the other hand, complex **2** offered an inclusion of 1,4-dioxane by intermolecular hydrogen bonding.

Presence of the dithiocarbamoyl hydrogen in the molecular structure influenced such a different mutual action.



Scheme 1 Mechanistic consideration for inclusion of 1,4-dioxane within (a) complex **1** and (b) complex **2**

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