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Inclusion Phenomena by Self-Organized Nickel(II) Dithiocarbamate Complexes of Amino Acid Esters

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Novel nickel(II) dithiocarbamate complexes having amino acid ester moieties, such as valine methyl $Ni[S_2CNH\{CH(CH_3)CO_2CH_3\}]_2$ (1), leucine methyl $Ni[S_2CNHCH\{CH_2CH(CH_3)_2\}CO_2CH_3]_2$(2), methionine methyl $Ni[S_2CNHCH(CH_2SCH_3)CO_2CH_3]_2$ (3) and $Ni[S_2CNHC(C_5H_{10})CO_2CH_3]_2$ (4) were synthesized. Complex 1 could form a self-organized assembly of micropore structure through intermolecular hydrogen bonding. While complexes 3 and 4 could not form such assembly but they offer chlathrate type assemblies bridged with benzene-1,4-diamine or pyridine-4-ol, respectively.

Key words: Hydrogen bonding, Dithiocarbamate, Amino acid esters, Self-organized assembly

1. INTRODUCTION

Recently, assemblies derived from transition metal complexes have been widely studied in the context of supramolecular chemistry. Thus, bridging of linear multidentate ligands by transition metal ions can afford 2-D or 3-D networks. These higher order structures offer specific and regulated microchannnels, which can be applicable for gas adsorption, chemical adsorption, and heterogeneous catalysis [1,2]. However, these rigid complex assemblies should recognize only size of the molecules to be adsorbed.

In contrast, more flexible assemblies play important roles in some bio-catalytic systems such as enzymes within the organisms, in which flexible polypeptide chains can serve specific sites for the catalysis through complementary hydrogen bondings. Consequently, we started to attempt constructing a novel complex assembly from flexible ligand systems. In our continuous studies, we already reported that some dithiocarbamate complexes having amino acid ester or amino alcohol moieties can form 2-D or 3-D assemblies of microchannel structures through intermolecular hydrogen bondings [3].

In this research, we investigated that the formation of some chlathrates from transition metal dithiocarbamates of amino acid esters with some proton donors and/or acceptors, such as benzene-1,4-diamine and pyridine-4-ol as guest molecules.

2. EXPERIMMENTAL

2.1 Characterization

^1H- and ^{13}C-NMR spectra and TOF MS were recorded with a Varian UNITY300 (300 MHz) spectrometer and a PE Biosystems Voyager-DE PRO time-of-flight(TOF) mass spectrometer, respectively. IR spectra were measured with a SHIMADZU FT-IR DR8500 spectrophotometer using KBr pellets. 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 ω-2θ scanning using Cu K_α radiation (1.54178 Å) at 298 K. In addition, the structures were solved by the Crystal Structure program [4,5].

2.2 Synthesis

General synthetic method of complexes **1**-**4** is as following; nickel(II) acetate (5 mmol) and of the corresponding amino acid methyl esters (10 mmol), such as HVal-OMe, HLeu-OMe, $H_2NCH(CH_2SCH_3)CO_2Me$, and $H_2NC(C_5H_{10})CO_2Me$, were placed into a 100 ml three-necked round-bottomed flask. Then, methanol (40 mL) was added to the mixture and the resulted solution was stirred for 1 h at room temperature. Afterwards, carbon disulfide (10 mmol) was slowly added to the solution by syringe work with cooling. The reaction mixture was stirred for additional 24 h at room temperature. After the reaction, methanol was removed under reduced pressure, and the residual powders were collected and washed with water to remove acetic acid and other impurities. The powdery product was dried under reduced pressure at room temperature. Purification was performed by recrystallization from methanol. Identification of $Ni(S_2CValOMe)_2$ (**1**), $Ni(S_2CLeuOMe)_2$ (**2**), $Ni(S_2CN(H)CH(CH_2SCH_3)$-$CO_2Me)_2$ (**3**), and $Ni(S_2CN(H)C(C_5H_{10})CO_2Me)_2$ (**4**) was done with EA, IR, ^1H- and ^{13}C-NMR and TOF-MS. Yields, mps and m/z of the parent peaks of **1**-**4** are summarized in Table I and the selected spectral data are also displayed in Table II.

Chlathrate formation was investigated as following; benzene-1,4-diamine or pyridine-4-ol (0.8 mmol) was added to a solution of the complexes (0.4 mmol) in the prescribed solvents (20 mL). Precipitation was urged by vapor diffusion with hexane. Crystal-like precipitates were deposited from the systems of **3** with benzene-1,4-diamine(ethyl acetate), and of **4** with pyridine-4-ol(THF), and were collected.

Single crystals suitable for X-ray crystallography of complexes **1** and **2**, and chlathrate **5** from **3** with benzene-1,4-diamine were grown by the diffusion in solution method from 2-propanol/hexane or ethyl acetate/hexane system, and the vapor diffusion method from ethyl acetate/hexane, respectively. We could perform refined structure analyses for complexes **1** and **2** and chlathrate **5** using the Direct Methods (SIR92) [6,7] and their crystallographic data are summarized in Table III. On the other hand, no attempt to grow single crystals of the precipitates from **4** and pyridine-4-ol was successful, but several spectral discussions suggested the formation of a chlathrate.

Table I Characteristics of complexes **1-5** a)

	% - yields	mps / °C	M^+ (*m/z*) a)
1	76	162.8-163.5	470.7(470.0)
2	92	130.0-131.0	498.6(498.0)
3	88	127.0-128.5	534.1(534.1)
4	46	203.0-204.0	522.3(522.0)

a) Complexes **1-4** appeared as dark green. b) Calculated values are in the parentheses.

Table II Selected IR spectral data a) of complexes **1-5**

	wavenumber / cm^{-1}			
	ν(N-H)	ν(C=O)	ν(C-N)	ν(C=S)
1	3258	1747	1521	989
2	3265	1732	1514	1003
3	3230br 3130	1740 1704	1533	991
4	3283	1738	1510	986
5	3385 3320 3140 2840br	1740	1540	990
6	3280w	1740	1520	990

a) IR spectrum was measured by KBr pellets.

3. RESULTS AND DISCUSSTION

The ORTEP diagram [9] of complex **1** as shown in Figure 1 was obtained by X-ray structural analysis. It was confirmed that complex **1** is monomeric and possesses a planar four coordinated geometry around the central nickel ion similarly to the other nickel(II) dithiocarbamate complexes reported[3]. Moreover, complex **1** has C_2 symmetry and amino acid ester residues exist in trans position. Further, complex **1** forms a 1D self-organized structure via intermolecular hydrogen bonding between the carbonyl oxygen (proton acceptor) of the terminal ester and the carbamoyl NH (proton donor) as can be seen from Figure 2. The length of the hydrogen bonding [N(1)-H(1)···O(3)] was estimated as 2.91 Å.

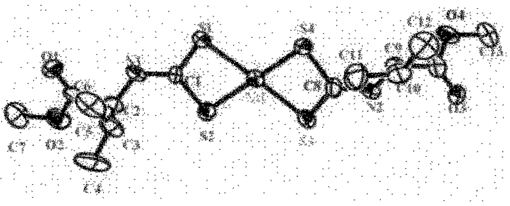

Figure 1 An ORTEP drawing of **1**

Table III Crystallogrphic date for **1, 2** and **5**

description	**1**	**2**	**5**
Formula	$C_{14}H_{24}N_2NiO_4S_4$	$C_{16}H_{28}N_2NiO_4S_4$	$C_{20}H_{32}N_4NiO_4S_6$
FW	471.29	499.35	643.56
T / °C	25.0	25.0	25.0
Crystal system	Orthorhombic	monoclinic	Monoclinic
Space group	$P2_12_12_1$(#19)	C2(#5)	C2(#5)
A / Å	12.082(6)	18.350(2)	17.309(5)
B / Å	15.49(2)	8.5089(16)	10.154(2)
C / Å	11.197(5)	15.521(2)	9.970(3)
α / °	-	-	-
β / °	-	101.004(10)	122.27(2)
γ / °	-	-	-
V / Å^3	2095.4(2)	2378.8(6)	1481.6(7)
Z	4	5	2
D(calc.) / g·cm^{-3}	1.494	1.743	1.442
Crystal size / mm	0.10×0.25×0.60	0.20×0.05×0.05	0.10×0.20×0.40
Monochromator	CuKα (λ=1.54178Å)	CuKα (λ=1.54178Å)	CuKα (λ=1.54178Å)
F(000)	984.00	1310.00	672.00
No. reflections			
Total	1825	1988	1221
Unique	1802	1918	1177
Observed	1697	1666	1054
R[*I*>2 σ (*I*)]			
R	0.052	0.059	0.073
R_w	0.046	0.049	0.049

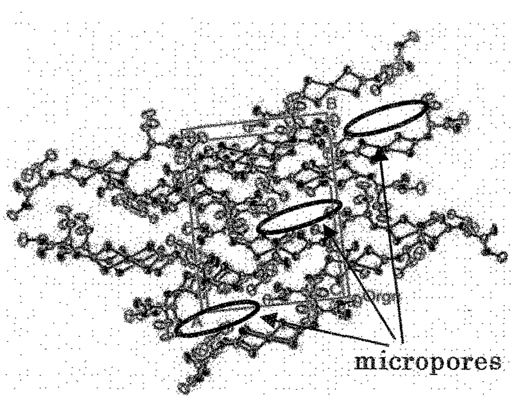

Figure 2 Molecular packing diagram of **1** viewed along *c*-axis to the [001] direction

The ORTEP drawing and the packing diagram of complex **2** are illustrated in Figure 3 and 4, respectively. A monomeric geometry and C_2 symmetry similar to complex **1** were confirmed for complex **2**. Complex **2**, however, does not show any intermolecular interaction because of the bulkiness of the alkyl side chains. So only intramolecular hydrogen bonding between the carbonyl oxygen of the terminal ester and the carbamoyl hydrogen can be observed. The length of the intramolecular hydrogen bonding [N(1)-H(1)...O(1)] was estimated as 2.80 Å. The presence of such shorter hydrogen bonding may lead the lower wavenumber shift of ν(C=O) of **2**, comparing with **1**.

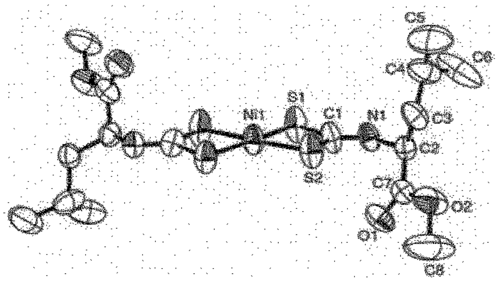

Figure 3 An ORTEP drawing of **2**

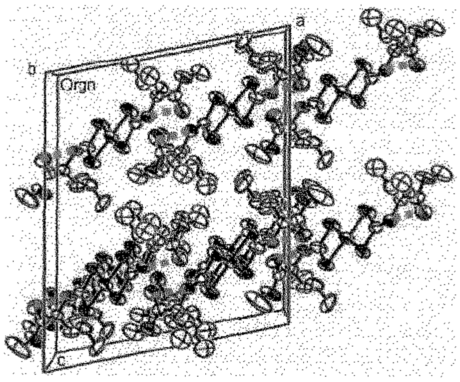

Figure 4 Molecular packing diagram of **2** viewed along *b*-axis to the [010] direction

Unfortunately no single crystal of complex **3** was grown, however, we could prepare single crystals of chlathrate **5** from **3** and benzene-1,4-diamine from 2-propanol/hexane. The refined structural analysis of **5** was successfully done and the ORTEP drawing and the molecular packing diagram of chlathrate **5** are illustrated in Figures 5 and 6, respectively. The ORTEP drawing indicates that the chlathrate **5** contains one benzene-1,4-diamine molecule per a molecule of complex **3**.

The formation of such a chlathrate should lead to cis conformation of the side chains of the amino acid ester within the dithiocarbamate ligands. Additionally, it was found that a three-centered hydrogen bonding among the ester carbonyl and the neighboring carbamoyl within the complex molecules and one amino group of benzene-1,4-diamine exists. The molecular packing diagram indicates that benzene-1,4-diamine should bridge two complex molecules and that the bridging leads to the formation of a 1D assembly. The lengths of the hydrogen bondings of N···H···N and N···H···O were estimated as 3.00 and 2.96 Å, respectively. Further, it is notable that the methylthio terminal functionality in complex **3** is free from any intra- and intermolecular donor-acceptor interaction.

The formation of such a three-centered hydrogen bonding reflects in IR spectral observations, especially in the region of higher than 2800 cm^{-1} as shown in Figure 7 (b). Some selected absorption bands are also summarized in Table II. A broad band of chlathrate **5** could be detected at ca.2850 cm^{-1}, and this absorption band suggests that the amino group of phenylenediamine should perform as both proton acceptor and donor. No change was observed for ν(C=O) between complex **3** and chlathrate **5**, which should suggest the presence of intramolecular hydrogen bonding in complex 3 similar to complex **2**.

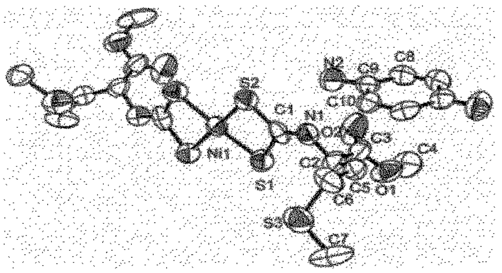

Figure 5 An ORTEP drawing of **5**

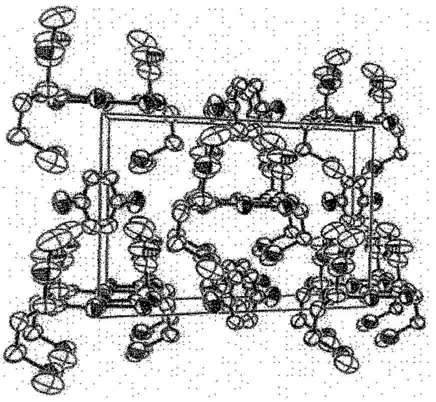

Figure 6 Molecular packing diagram of **5** viewed along *c*-axis to the [001] direction

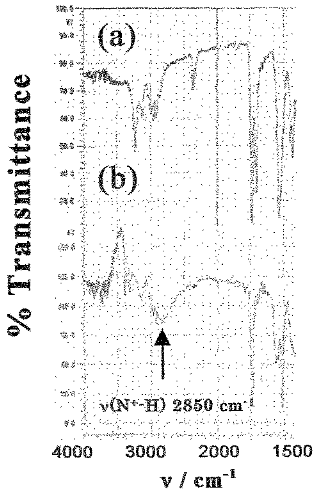

Figure 7 Comparative infrared spectra of (a) complex **3** and (b) complex **5**

Complex **4** formed no precipitate with benzene-1,4-diamine. While, we could obtain precipitates from complex **4** with pyridine-4-ol. No color change was observed during this precipitation, which perhaps suggested that pyridine-4-ol should not coordinate to the central nickel ions directly. We tried to recrystallize them to give single crystals for X-ray crystallography, but we could obtain no single crystal of the chlathrate. An analysis of the precipitates using ^{1}H NMR indicated that the precipitates contain both complex **4** and pyridine-4-ol in 1:1 molar ratio. Thus, we tentatively called this precipitates as chlathrate **6**.

Complex **4** showed ν(N-H) and ν(C=O) absorption bands at 3283 and 1738 cm^{-1}, respectively, suggesting the presence of intramolecular hydrogen bonding [3]. In IR spectrum of chlathrate **6** as shown in Figure 8, characteristic broad band of ν(O-H) of pyridine-4-ol disappeared but its ν(C=C) band remained at 1630 cm^{-1}. Additionally, no shift of ν(N-H) and ν(C=O) of complex **4** and an appearance of relatively sharp ν(O-H) at 3200 cm^{-1} were observed. These findings hint the formation of intermolecular hydrogen bonding between pyridine-4-ol and complex **4**. We tentatively supposed that pyridine-4-ol bridges two molecules of **4** *via* two types of hydrogen bondings such as the carbamoyl-pyridyl nitrogen and the phenolic OH-terminal ester carbonyl.

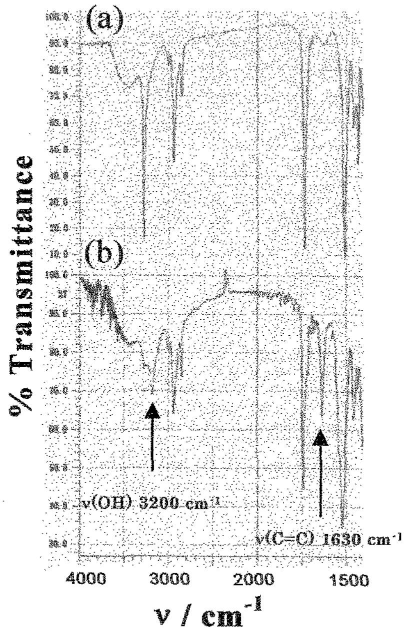

Figure 8 Comparative infrared spectra of (a) complex **4** and (b) chlathrate **6**

4. CONCLUSION

Novel nickel(II) dithiocarbamate complexes having amino acid ester moieties, such as valine methyl $Ni[S_2CNH\{CH(CH_3)CO_2CH_3\}]_2$ (**1**), leucine methyl $Ni[S_2CNHCH\{CH_2CH(CH_3)_2\}CO_2CH_3]_2$(**2**), methionine methyl $Ni[S_2CNHCH(CH_2SCH_3)CO_2CH_3]_2$ (**3**) and $Ni[S_2CNHC(C_5H_{10})CO_2CH_3]_2$ (**4**) were synthesized. X-Ray crystallography displayed that **1** formed a self-organized assembly through an intermoleculare hydrogen bonding between the carbamoyls and the terminal ester carbonyls. While, **2** possessed an intramoleculer hydrogen bonding but would not form any specific assembly. Additionally, complex **3** and **4** could form chlathrates **5** and **6** with benzene-1,4-diamine and pyridine-4-ol, respectively.

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