

FORMATION OF 3-D CHANNEL ON SELF-ORGANIZATION OF Ni(II) DITHIOCARBAMATE COMPLEXES CONTAINING AMINO ACID FRAGMENTS

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New class of self-organized Ni(II) dithiocarbamate complexes $[\text{Ni}(\text{S}_2\text{CR})_2]$ consisting of amino acid esters as side-arms from dithiocarbamoyl moieties; R = Gly-OMe(**1**), Gly-OEt(**2**), Ala-OMe(**3**), Ala-OEt(**4**), and Ser-OMe(**5**) were synthesized. Among complexes **1**, **2** and **3** having C_2 symmetry methyl esters **1** and **3** can form microchannel spaces. The dimension of such microchannel spaces are estimated to be 1.0-1.5 nm.

Key words: Self-Organization, Hydrogen Bonding, Dithiocarbamate, Amino Acid

1. INTRODUCTION

Recently, microchannel chemistry of transition metal complexes has been widely studied. Combination of flat and rigid multidentate ligands and cross-linking by metal ions can offer specific 3-D network microchannel skeletons[1-5]. Such a microchannel structure derived from rigid functional building blocks becomes rigid and can be hosting and storing some small molecules such as methane, etc. without tight intermolecular interactions. In this context the shape and size of the microchannels, which can be arranged by the selection of ligands and metal ions, are used for molecular recognition.

In contrast, if flexible microchannel structure built up from self-organization of complexes via intermolecular interaction can be realized, we should get a different type of molecular recognition tool. Thus we attempted to synthesize novel complex assemblies through intermolecular hydrogen bonding. Our recent results showed that some metal dithiocarbamate complexes having ω -hydroxyl group form unique microchannel structure[6], and indicated the potentiality of flexible complex assembly. For example, it has been reported that nickel(II) dithiocarbamate complexes containing hydroxyethyl side arms form microchannel structure of 0.8-1 nm in diameter in solid state. Consequently we tried to prepare different flexible complex assemblies using amino acid moieties.

In this paper, synthesis and structure analysis of nickel(II) dithiocarbamate complexes with amino acid esters as side arms will be reported.

2. EXPERIMENTAL

Synthesis

General synthetic method is as following. Nickel(II) acetate (5 mmol) and the corresponding amino acid methyl esters or amino acid ethyl esters(10 mmol) (HGly-OMe, HGly-OEt, HAla-OMe, HAla-OEt, HSer-OMe) were placed in a 100 ml three-necked flask under N_2 . Then, CH_3CN (40 ml) was added to the mixture and the resulted solution was stirred at room temperature for 1 h. Afterwards, CS_2 (10 mmol) was slowly added by syringe with cooling. The reaction system was stirred for 24 h at room temperature. After the reaction, acetonitrile was removed under reduced pressure, and residual powders were washed with water to remove acetic acid and unreacted materials. The powdery product in deep green was then dried under reduced pressure at room temperature. Pure complexes were recrystallized from CH_3CN . Identification was done with IR, ^1H - and ^{13}C -NMR spectra and TOF-MS. Result of preparation and spectral data of these complexes are shown in Table I and Table II, respectively.

Characterization

IR, ^1H - and ^{13}C -NMR spectra and TOF-MS 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, respectively. Single crystal automatic X-ray structure analysis was done with a Rigaku AFC-7R four-circle X-ray diffractometer. The structure analyses of crystals were done over the

reflection range within $4.0^\circ < 2\theta < 120.1^\circ$ by the ω - 2θ scanning using CuK α radiation (1.54178 Å) at room temperature (298 K). In addition, the structures were solved by teXsan program⁷. We could get refined structure of complexes **1**, **2**, and **3** using Direct Methods (SAPI90) [8,9], Direct Methods (SIR92) [9,10], Patterson Methods (DIRDIF92 PATTY) [9,11], respectively.

Table I. Characteristics of complexes **1-5**.

complexes	color	%-yields	mp / °C
Ni[S ₂ CNHCH ₂ CO ₂ CH ₃] ₂	1 dark green	41.0	205.0-205.5
Ni[S ₂ CNHCH ₂ CO ₂ CH ₂ CH ₃] ₂	2 dark green	34.7	164.5-165.5
Ni[S ₂ CNHCH(CH ₃)CO ₂ CH ₃] ₂	3 dark green	41.2	185.0-185.5
Ni[S ₂ CNHCH(CH ₃)CO ₂ CH ₂ CH ₃] ₂	4 dark green	49.3	138.0-138.5
Ni[S ₂ CNHCH(CH ₂ OH)CO ₂ CH ₃] ₂	5 dark green	47.4	177.5-178.5

Table II. Selected spectral data of complexes **1-5**.

complexes	IR ν / cm ⁻¹				¹³ C-NMR δ (S ₂ CN)	M ⁺ m/z	
	ν (C=S)	ν (C-N)	ν (O-H)	ν (N-H)			ν (C=O)
1	983.6	1512.1	-	3269.1	1735.8	208.5	385.4(385.9)
2	997.1	1521.7	-	3273.0	1728.1	208.5	413.9(413.9)
3	983.6	1521.7	-	3263.3	1733.9	207.2	413.7(413.9)
4	989.4	1521.7	-	3251.8	1726.2	207.2	441.9(441.9)
5	989.4	1516.9	3334.7	3265.3	1737.7	207.9	445.9(445.9)

3. RESULTS AND DISCUSSION

We have proposed that the reaction of metal oxide or metal salts with dithiocarbamic acids; *i.e.* the mixture of carbon disulfide and alkylamines is the most simple and clear route to prepare metal dithiocarbamate complexes[12]. This methodology is revealed to be applicable to the system of carbon disulfide with amino acid esters and we can synthesize Ni(II) dithiocarbamate complexes containing glycine, alanine and serine esters as side arms under mild conditions and in moderate yields as shown in Table I.

Among five complexes synthesized, fine single crystals of complexes **1**, **2** and **3** were obtained. Molecular structures in ORTEP drawing[13] for **1-3** are illustrated in Figures 1-3, respectively. As can be seen from Figures 1-3, these three complexes are monomeric and have planar four-coordinated geometry. As expected, they have a C₂-axis along the molecular plain perpendicular to Ni-Ni line as illustrated in Figure 4. Complex **1** and **3** has absorption peaks at 1735.8 and 1733.9 cm⁻¹ (ν _{C=O}), 3268.1 and 3263.3 cm⁻¹ (ν _{N-H}), respectively. These absorption maxima are found to be lower wavenumber in comparison to free amino acid esters; *i.e.* ν _{C=O} of the amino acid esters are at 1740-1753 cm⁻¹ and ν _{N-H} at 3109 and 3420 cm⁻¹. Such shifts may be

reflected by the presence of intermolecular hydrogen bondings[14-16]. Although complexes **2** showed similar shifts of absorption maxima, any microchannel structure was not detected. Complexes **4** and **5** are also similar spectral data, and it can be expected that they have similar structure to complexes **1** and **3**.

Crystallographic data by single crystal automatic X-ray structure analysis of nickel(II) dithiocarbamate complexes **1**, **2**, and **3** containing amino acid fragments are shown in Table III.

Table III. Crystallographic data for complexes **1-3**.

	1	2	3
Formula	NiC ₈ H ₁₂ N ₂ O ₄ S ₄	NiC ₁₀ H ₁₆ N ₂ O ₄ S ₄	NiC ₁₀ H ₁₆ N ₂ O ₄ S ₄
Formula weight	387.13	415.19	415.19
T / °C	25	25	25
Crystal system	monoclinic	monoclinic	trigonal
Space group	P2 ₁ /c(#14)	P2 ₁ /a(#14)	P3 ₂ 1(#152)
a / Å	14.844(2)	16.999(2)	18.366(1)
b / Å	10.594(1)	14.886(2)	-
c / Å	18.786(1)	21.368(1)	6.169(2)
β / °	100.970(8)	-	-
V / Å ³	2900.3(4)	5169.8(7)	1802.1(6)
Z	8	12	4
D(calc.) / g·cm ⁻³	1.773	1.600	1.574
Crystal size / mm	0.20 × 0.05 × 0.30	0.20 × 0.20 × 0.30	0.10 × 0.10 × 0.30
Monochromator	CuK α (1.54178 Å)	CuK α (1.54178 Å)	CuK α (1.54178 Å)
F(000)	1584.00	2568.00	880.00
No. reflections			
Total	4788	8361	2088
Unique	4590	8051	999
Observed	3653	4936	926
R[$I > 2\sigma(I)$]			
R	0.072	0.088	0.077
R _w	0.081	0.108	0.141

Molecular packing diagrams of complexes **1-3** are also shown in Figures 5, 7, and 8, respectively. Intramolecular and intermolecular hydrogen bonding sites and arrangement of complexes **1** and **3** are shown in Figure 6 and 9, respectively. It was found that all the N and O atoms in amino acid moieties behave as donors.

A honeycomb molecular packing with microchannel structure was given for the self-organization of complex **1**. As shown in Figure 5 molecules of complex **1** form a head-to-tail and zig-zag polymer binding through two hydrogen bondings between N-H and C=O sites. Two polymer chains make bridges by hydrogen bondings per each two molecular units. Thus, a micro space is surrounded by four molecules of two polymers. Pore size of this microchannel can be estimated as 1.0 × 1.4 nm.

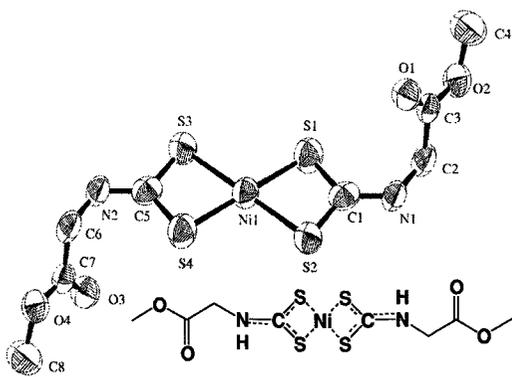


Figure 1. An ORTEP drawing of complex 1.

strictly prevented by sterical bulkiness of ethyl groups. Otherwise complex 2 exist as layered association.

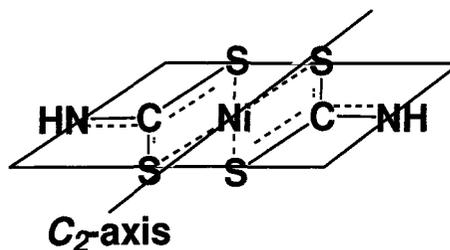


Figure 4. A C_2 -axis of complex 1, 2 and 3.

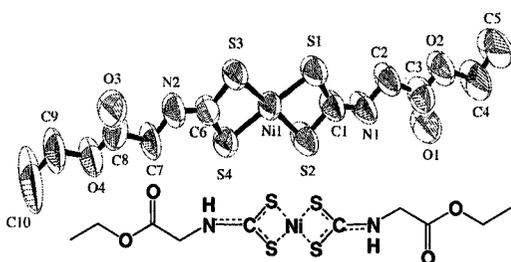


Figure 2. An ORTEP drawing of complex 2.

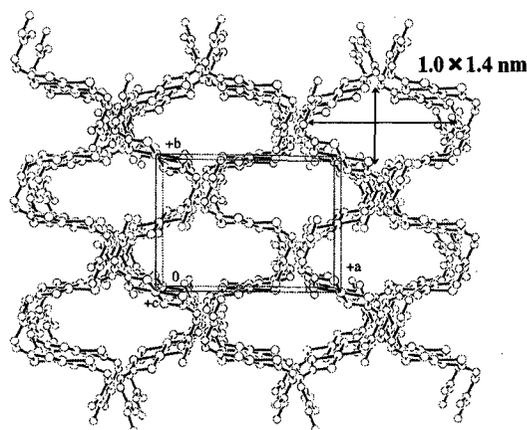


Figure 5. Molecular packing diagrams of complexes 1 viewed along c-axis to the [001] direction.

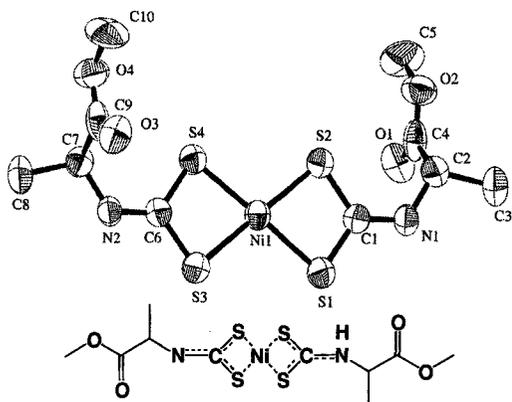


Figure 3. An ORTEP drawing of complex 3.

In contrast, complexes 3 did not form a 1-D polymeric association but form a 2-D network polymer with micro-spaces. Steric hindrance from methyl group perhaps restricts the formation of multi-site and narrow space hydrogen bonding. Each micro-space appeared as triangular and the length of their edge can be estimated to be 1.5 nm. This micro-space is surrounded by six molecules, three in inner surface of the micro-space and the others support them from the back.

Unfortunately, complexes 2 do not form microchannel structure because it does exist as almost planar molecules as comparing to 1 and 3. Hydrogen bonding between carbamoyl proton at N atom and ester part should be

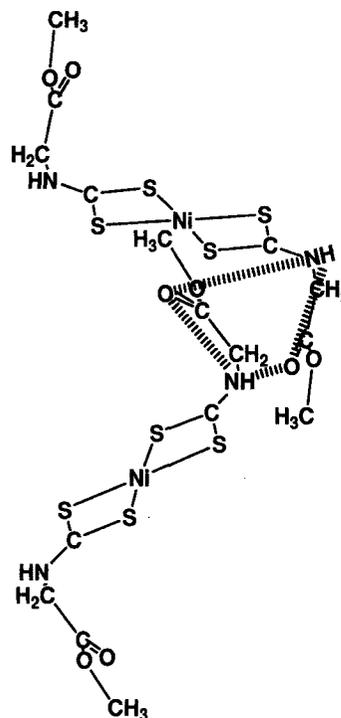


Figure 6. Intermolecular (0.30 nm) and intramolecular (0.28 nm) hydrogen bonding distance in complexes 1.

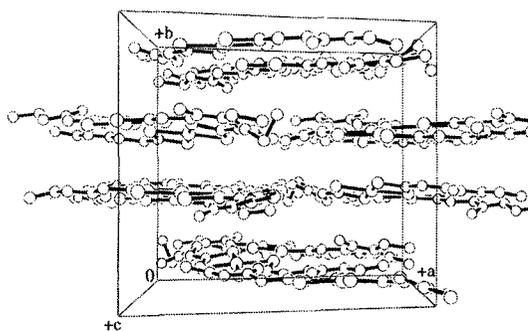


Figure 7. Molecular packing diagrams of complexes **2** viewed along c-axis to the [001] direction.

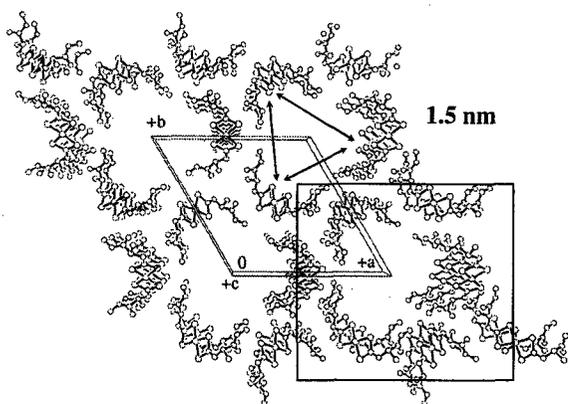


Figure 8. Molecular packing diagrams of complexes **3** viewed along c-axis to the [001] direction.

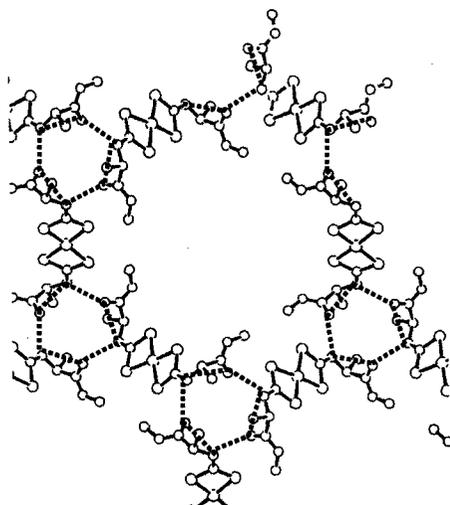


Figure 9. Intermolecular and intramolecular hydrogen bonding distance in complexes **3** (all 0.29 nm).

4. CONCLUSION

Ni(II) dithiocarbamate complexes of the new type containing amino acid fragments are self-organized through the intermolecular hydrogen bonding. Then,

$[\text{Ni}(\text{S}_2\text{CNHCH}_2\text{CO}_2\text{CH}_3)_2]$ (complex **1**) and $[\text{Ni}(\text{S}_2\text{CNHCH}(\text{CH}_3)\text{CO}_2\text{CH}_3)_2]$ (complex **3**) have formed the 3-D microchannel (1.0×1.4 nm and three edges are 1.5 nm, respectively).

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