

EFFECT OF ALKYL SPACERS ON SELF-ASSEMBLY OF DITHIOCARBAMATE COMPLEXES

NOMURA Ryôki*^{1,2} and NAKAMOTO Shoichi¹

¹Department of Chemistry and ²Bio Venture Center, Osaka Institute of Technology

Omiya, Asahi, Osaka 535-8585, Japan, Fax; +81-6-6957-2135, e-mail; nomura@chem.oit.ac.jp

Novel nickel complexes with dithiocarbamate ligands having ω -hydroxyl groups, $[\text{Ni}(\text{S}_2\text{NRR}')_2]$, where (R, R') = (Me, CH₂CH₂OH)(**4**), (CH₂CH₂OH, CH₂CH₂OH)(**5**) and (C₃H₉OH)(**6**) were synthesized and their complex assembly was investigated. X-Ray crystal analyses showed that **4** and **5** with acyclic and primary alcoholic moieties are monomeric in the crystals, but that they form characteristic self-assembly to give microchannel structure by hydrogen bonding networks. The sizes of their microchannels were estimated as 0.8x0.8 nm and 0.8x0.3 nm, respectively. Cyclic and secondary alcohol **6**, in contrast, forms no complex assembly.

Key words: Self-Assembly, Hydrogen Bonding, Alkyl Spacer, Dithiocarbamate

1. INTRODUCTION

Recently micropore chemistry of transition metal complexes has been much interested. Combination of rigid and multidentate ligands with bridging by metal ions can afford a polymeric complex assembly with nano-sized micropore or nano-spaces¹⁻⁴. Bipyridine ligands are generally employed to these purposes but they are so rigid as to fix the microstructure of the complex assembly. Consequently we attempted to develop a novel complex assembly by the use of more flexible ligands.

Dithiocarbamate moiety is one of the most popular ligands but only *N, N*-dialkyl-type of dithiocarbamates is generally studied. Previously we found that dithiocarbamate complexes having ω -hydroxyl group can form intermolecular hydrogen bonding which can lead to a self-assembly to some microchannel skeletons^{5,6}. In this paper, preparation of novel nickel dithiocarbamates having hydroxyl group at the end of the ligand and the investigation on their complex assembly will be described.

2. EXPERIMENTAL

2.1 Characterization

IR and ¹H- and ¹³C-NMR spectra were recorded with a

Shimadzu FT-IR DR8500 spectrophotometer and a Varian Unity 300 spectrometer, respectively. X-Ray single-crystal structure analyses were done with a Rigaku AFC7R four-axis X-ray diffractometer. The structure analysis of crystals at 298 K is done over the reflection region of $4.0^\circ < 2\theta < 120.2^\circ$ by the ω - 2θ scanning using Cu K α line ($\lambda=1.54178 \text{ \AA}$).

2.2 Synthesis of nickel (II) dithiocarbamate complexes

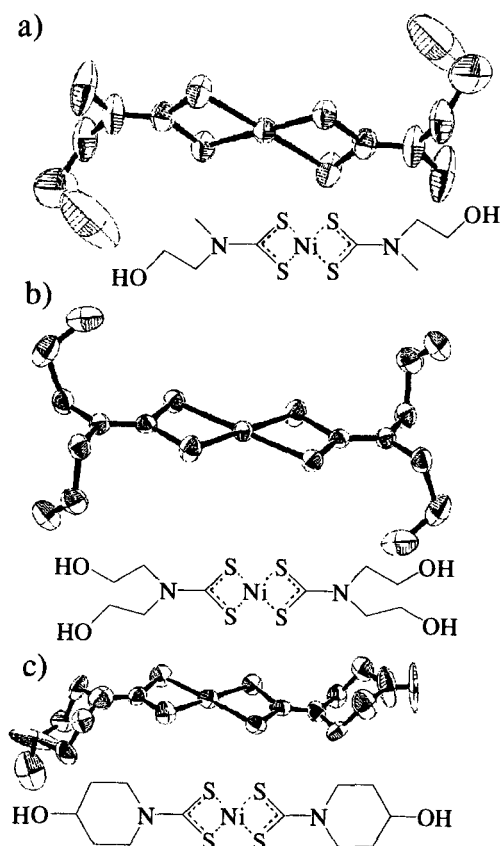
General preparation procedure is as following⁶; nickel oxide (10 mmol) was suspended in methanol (30 mL) under N₂. Methylethanolamine (20 mmol) was added drop-by-drop to the suspension and the mixture was stirred for 2 h at room temperature. Then carbon disulfide (20 mmol) was added dropwise to the ice-cooled suspension. The mixture was stirred for 24 h at room temperature and additionally for 8 h at 80 °C. During the stirring, complex **4** was precipitated and filtered off. Fine single crystals of **4** could be obtained after recrystallization from acetonitrile. Similarly complexes **1**, **2**, **3**, **5** and **6** were prepared and their properties and selected spectral data are summarized in Table 1 and Table 2, respectively.

Table 1 Preparation of Ni(S₂CNRR') complexes

complexes	color	%-yields	mp/ °C
Ni(S ₂ CNEt ₂) ₂	1 deep green	78.2	242.0-242.5
Ni(S ₂ CNC ₄ H ₈) ₂	2 brown	60.0	153.0-154.0
Ni(S ₂ CNC ₃ H ₁₀) ₂	3 brown	67.2	140.0-143.5
Ni(S ₂ CNMeC ₂ H ₄ OH) ₂	4 deep green	40.0	185.0-186.0
Ni[S ₂ CN(C ₂ H ₄ OH) ₂] ₂	5 green	45.3	218.0-218.5
Ni(S ₂ CNC ₃ H ₅ OH) ₂	6 green	57.2	250.0-250.5

Table 2 Selected spectral data of complexes 1-6

complexes	IR ν/cm ⁻¹		¹³ C NMR	
	ν(CN)	ν(CS ₂)	ν(OH)	δ(N ¹³ CS ₂)
1	1529.1	993.5	-	203.0
2	1542.1	997.1	-	207.9
3	1542.6	999.1	-	211.8
4	1514.4	975.9	3230.5	205.1
5	1514.1	975.9	3334.7 3330.2	204.3
6	1491.5	983.6	3379.5	203.2

Figure 1 Ortep drawings of a) complex **4**, b) complex **5** and c) complex **6**.

3. RESULTS AND DISCUSSION

Most of the nickel complexes have planner four coordinated structure. The central nickel and four coordination sites coexist on a same plain. Additionally dithiocarbamate ligands offer π -conjugated planner chelating site; S₂CN (dithiocarbamoyl fragment)⁷⁾⁻⁹⁾. Dialkyl type nickel (II) dithiocarbamate, such as Ni(S₂CNEt₂)₂, **1**, has typical planner structure and is monomeric even in the solid state and whole S₂CN moieties and the central Ni atom placed on a plain to form a rigid sheet.

Table 3 Crystal data and structure refinements of complexes **4**, **5** and **6**.

	4	5	6
Crystal system	tetragonal	monoclinic	monoclinic
Space group	P4 ₂ /n (#86)	P2 ₁ /C (#14)	P2 ₁ /C (#14)
a / Å	16.351(2)	6.375(1)	6.1717(8)
b / Å	-	11.826(1)	17.7769(7)
c / Å	6.274(2)	11.463(1)	15.7086(4)
β / °	-	93.66(1)	94.27(9)
V / Å ³	1677.6(5)	862.5(2)	1718.6(2)
Z	4	4	4
Dcalc / g cm ⁻³	1.422	1.614	1.589
Crystal size / mm	0.20x0.20x0.50	0.10x0.10x0.20	0.10x0.10x0.20
Diffractometer	Rigaku AFC 7R		
Radiation	graphite		
monochromator	Cu Kα (λ = 1.54178 Å)		
F(000)	744.00	436.00	856.00
Data collection range 2θ / °	4.00 - 120.2		
Total reflections	1488	1493	2935
Independent reflections	1381	1360	2660
Rint	0.018	0.053	0.026
Temperature / °C	25		
R	0.079	0.055	0.083
Rw	0.146	0.065	0.068

Formula and formula weight of complexes **4**, **5** and **6** are as following; **4**

C₈H₁₆N₂NiO₂S₄ 359, **5** C₁₀H₂₀N₂NiO₂S₄ 419 and **6** C₁₂H₂₀N₂NiO₂S₄ 411.

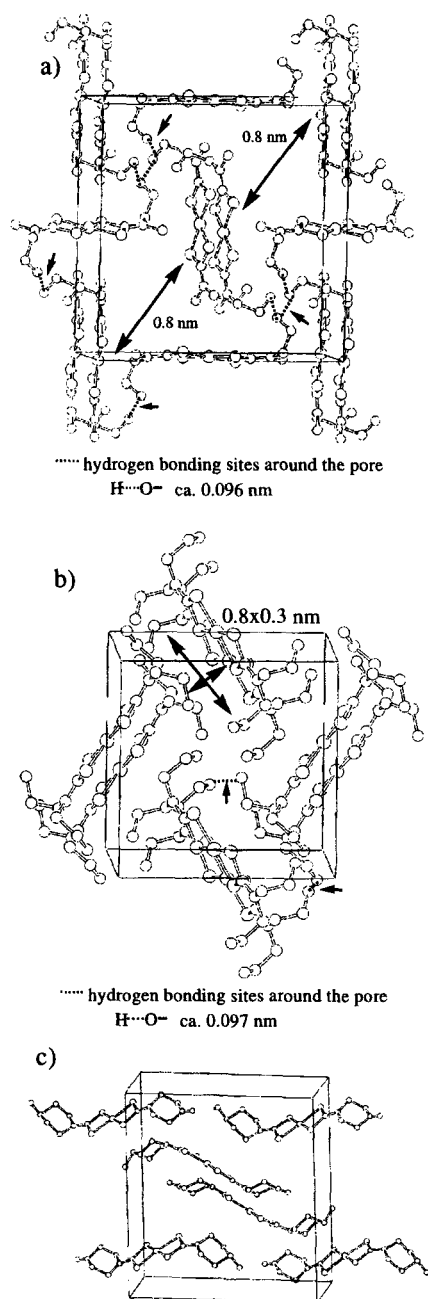


Figure 2 Molecular packing diagrams of the complexes **4**, **5** and **6**.

Introducing OH groups on such a rigid sheet perhaps triggers to afford polymeric hydrogen bonding network leading to the complex assembly. Consequently we synthesize novel three nickel dithiocarbamate complexes having ω -hydroxyl groups **4-6** with the different distances and directions from the Ni center.

Although slight lower wavenumber shifts could be detected for the absorption bands of $\nu(\text{CN})$ and $\nu(\text{CS}_2)$ of **4-6** as shown in Table 2, these values of absorption maxima indicated that complexes **4-6** essentially possessed general planar four coordination geometry like **1** as reported by Van Gaal et al⁹⁾. Further, the presence of some molecular association with hydrogen bonding was expected by their low wavenumbers of absorption bands $\nu(\text{OH})$. It can be said that the introduction of ω -hydroxyl groups did not affect the geometry around the central nickel atoms.

X-Ray crystal structure analyses of the dithiocarbamate complexes having ω -hydroxyl groups such as **4**, **5** and **6** were successfully done and their Ortep drawings are represented in Figure 1. Further their crystal data and structure refinements are summarized in Table 3. It can be seen from Figure 1 that these three complexes synthesized in this study have similar molecular structures to **1**. Especially the geometries around the central Ni atoms are same-manner as that of **1** supporting the above discussion based on IR spectra.

Molecular packing diagrams of the complexes **4**, **5** and **6** are also illustrated in Figure 2. Packing of complex **6** is similar to that of **1** and we cannot detect the presence of any intra- and intermolecular hydrogen bonding nor complex assembly. Higher steric hindrance around the OH groups in **6** should prevent the formation of an intermolecular association through hydrogen bonding.

The packing mode of **4** and **5** was quite different from **6**. We can observe the presence of complex hydrogen bonding networks for **4** and **5**. Molecules of **4** basically form helical polymers through intermolecular hydrogen bonding with a microchannel of 0.8 nm in diameter. One micropore should consist of four molecules in the unit cell. Complex **5** also forms helical polymers and microchannel structure and its pore size is 0.8 x 0.3 nm.

Meanwhile, NMR studies of the complexes **4-6** showed that they did not form any intermolecular association in

solution. It is known that the chemical shifts of the center carbon within dithiocarbamoyl (S_2CN) are good indexes of the total π -character of S_2CN fragment⁹. Slight lower field shifts of δ (S_2CN) were observed for **4-5**. Such lower field shifts could be explained by an increase of π -bond order in the whole S_2CN fragment¹⁰. Namely, an interaction between ω -hydroxyl group and nitrogen in the dithiocarbamoyl fragment promoted the delocalization of the π -electrons in the CS_2Ni center as shown in Figure 3.

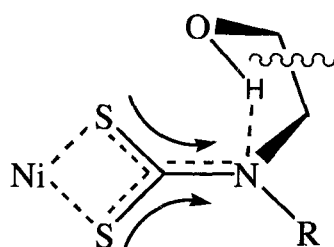


Figure 3 Intramolecular hydrogen bonding of ω -hydroxyl substituted nickel dithiocarbamate complexes and the delocalization of π -electrons.

4. CONCLUSION

New type complex assembly was introduced by using flexible ligands such as ω -hydroxyalkyl dithiocarbamate. Consequently, $Ni(S_2CN(CH_3)CH_2CH_2OH)_2$ **4** and $Ni[S_2CN(CH_2CH_2OH)_2]_2$ **5** form polymeric complex assemblies through hydrogen bonding in solid state developing microchannel skeletons (0.8 x 0.8 nm and 0.8 x 0.3 nm, respectively).

ACKNOWLEDGMENT

Part of this work was financially supported with Grant-in-Aid for Scientific Research (C) 12650678. One of the authors (NR) also acknowledges Bio Venture Center of Osaka Institute of Technology for financial support.

REFERENCES

- 1) S. Kitagawa, *Organometallic News* 15 (2000).
- 2) M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* 116, 1151 (1994).
- 3) O. M. Yaghi, C. E. Davis, G. Li, H. Li, *J. Am. Chem. Soc.* 119, 2861(1997).
- 4) S. Kitagawa, M. kondo, *Bull. Chem. Soc. Jpn.*, 71, 1738 (1998).
- 5) R. Nomura, and H. Matsuda, *Trends Inorg. Chem.* 2, 79 (1991).
- 6) R. Nomura, S. Fujii, A. Takabe and H. Matsuda, *Polyhedron* 8, 1891 (1989).
- 7) G. D. Thorn and R. A. Ludwig, "The Dithiocarbamate and Related Compounds", pp. 7-56, Elsevier, Amsterdam (1962).
- 8) P. Coucouvanis, *Prog. Inorg. Chem.* 22, 301 (1979).
- 9) H. L.M. Van Gaal, J. W. Diesveld, F. W. Pijpers, J. G. M. Van der Linden, *Inorg. Chem.* 18, 3251(1979).
- 10) R. Nomura, A. Takabe and H. Matsuda, *Polyhedron*, 6, 411 (1987).

(Received December 7, 2000; Accepted March 23, 2001)