

A Layered Phyllosilicate Compound Containing 1,12-diaza-3,4:9,10-dibenzo-5,8-dioxacyclopentadecane

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During the past two decades, a variety of macrocyclic ligands have been synthesized.¹⁻² Application of macrocyclic ligands in separation chemistry is based on their superior binding abilities for metal cations in solution. However, one of the major problems for chromatography is the solubility of the macrocyclic ligands adsorbed to a solid support. One way to overcome this problem is not by adsorption but by covalent bonding, thereby greatly enhancing their usefulness. Indeed, silica gel-bound and intercalated macrocyclic ligands have been investigated as stationary phases for chromatography.³⁻⁵ The former is surface-modified material and the latter is two-dimensionally arranged one. In addition, various layered materials containing organic guest molecules have been extensively studied for developing catalysts, conducting polymer, and so on.⁶⁻⁷

Recently, the methacrylate-magnesium (nickel) phyllosilicate materials based on layered phyllosilicate structure have been reported.⁸ It had been generally presumed that a silicon trialkoxide containing a Si-C bond could not generate a phyllosilicate structure due to an inadequacy of bonding sites. In the phyllosilicate materials reported by Fukushima *et al.*,⁸ however, two sheets of C-SiO₃ tetrahedra and a sheet of metal octahedra form a layered phyllosilicate structure.

So, if 3-glycidoxypropyltrimethoxysilane can be used instead of 3-methacryoxypropyltrimethoxysilane, a precursor material containing glycidoxy groups can be prepared. Then, a new phyllosilicate material containing macrocyclic ligand can be also synthesized from the precursor because glycidoxy group readily reacts with amine in macrocyclic ligand. In this study, we prepared a precursor material composed of an inorganic lamellar framework and 3-glycidoxypropyltrimethoxysilane. The precursor was further reacted with macrocyclic ligand to give a novel phyllosilicate compound.

Experimental

Two batches of 3-glycidoxypropyltrimethoxysilane [$\text{[OCH}_2\text{CHCH}_2\text{O(CH}_2\text{)}_3\text{Si(OCH}_3\text{)}_3$, abbreviated as 3G, 0.0100 mole] and nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.0070 mole) were prepared in 100 mL of methanol. These solutions were mixed with 100 mL of 0.10 M sodium hydroxides to form gels, respectively. One of which was aged for 24 h, filtered, washed, and dried in a vacuum at room temperature and the other was further reacted with 1,12-diaza-3,4:9,10-dibenzo-5,8-dioxacyclopentadecane (NtnOenH_4 , 0.0060 mole). The NtnOenH_4 macrocyclic ligand was synthesized according to the reported procedures.⁹ A green 3-glycidoxypropyl-nickel phyllosilicate (3G-NiP)

and a yellow-green 1,12-diaza-3,4:9,10-dibenzo-5,8-dioxacyclopentadecane-(3-glycidoxypropyl)₂-nickel phyllosilicate ($\text{NtnOenH}_4\text{-3G}_2\text{-NiP}$) were obtained, respectively. $\text{NtnOenH}_4\text{-3G}_2\text{-NiP}$ had a very hydrophobic character due to the presence of macrocyclic ligands. The obtained powders were analyzed by thermogravimetric analysis (TGA), elemental analysis (EA), energy-dispersive X-ray spectroscopy (EDS), X-ray powder diffraction (XRPD), and FT-infrared spectroscopy (FT-IR).

Results and Discussion

The organic contents of 3G-NiP and $\text{NtnOenH}_4\text{-3G}_2\text{-NiP}$ by EA and TGA are listed in Table 1. The ratio of 3G to NtnOenH_4 in NtnOenH_4 was in good agreement with 2:1 reaction, which indicates that the reaction between two amine functional groups in NtnOenH_4 and glycidoxy groups occurred stoichiometrically. A rough estimate of Ni to Si ratio by EDS was atomic percentage of 13.2:5.8. This is similar to the composition of 2:1 layer clay.

XRPD patterns of 3G-NiP and $\text{NtnOenH}_4\text{-3G}_2\text{-NiP}$ are shown in Figure 1. Although all the peaks for 3G-NiP are rather broad, they are similar to those of the methacrylate-magnesium phyllosilicate and Zn-Al layered double hydroxides (Zn-Al LDH) modified by pillaring of silicate sheets.^{8,10} Indexation of the diffraction lines has been carried out for a hexagonal symmetry with 1H stacking sequence observed in the case of Zn-Al LDH. The peak at $2\theta=5^\circ$ was indexed to (001), indicating a layered structure with basal spacing of 17.5 Å. The large value of the basal spacing indicates the existence of long organic chains within the interlayer spaces. According to the analysis of thermally treated Zn-Al LDH, the thickness of inorganic framework composed of two silicates and one nickel sheet is 6.6 Å.¹⁰ Assuming that the organic alkyl chains are in the all-trans conformation, the maximum molecular lengths are *ca.* 8.00 Å. The interlayer distance ($17.5-6.6=10.9 \text{ Å} > 8.00 \text{ Å}$) suggests that 3G groups within the interlayer are arranged with the tilted bilayer structure. XRPD pattern for $\text{NtnOenH}_4\text{-3G}_2\text{-NiP}$ is also similar to that for 3G-NiP except the peak at

Table 1. The organic contents calculated from EA, TGA, and uptake of Cu^{2+} ion

Compound	EA		TGA		uptake of Cu^{2+} ion
	Carbon (%)	mmol/g	weight loss (%)	mmol/g	
3G-NiP	16.0	2.22	30.2	2.63	
$\text{NtnOenH}_4\text{-3G}_2\text{-NiP}$	44.3	1.19	53.3	1.12	1.18

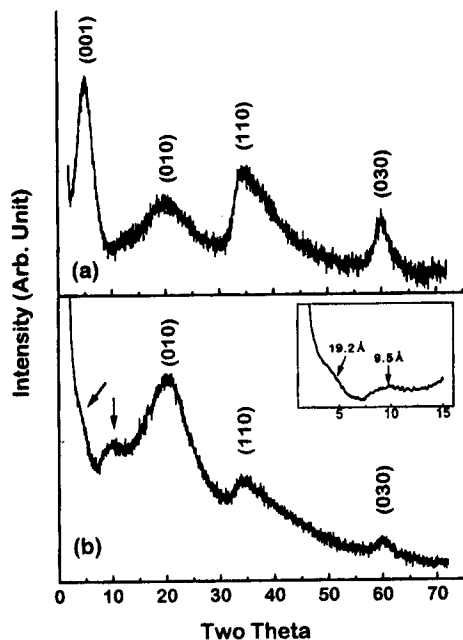


Figure 1. XRPD Patterns of (a) 3G-NiP and (b) NtnOenH₄-3G₂-NiP.

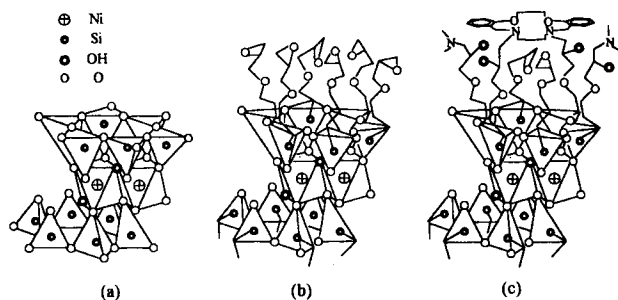


Figure 2. Schematic structures of (a) Ni-phyllsilicate, (b) 3G-NiP, and (c) NtnOenH₄-3G₂-NiP.

$2\theta=9.3^\circ$ and shoulder at $2\theta=4.6^\circ$. These extra peaks could be indexed to (001) and (002), respectively, and may be attributed to the increase of basal spacing by introducing the NtnOenH₄ macrocyclic ligands into the interlayer. It is worthy to note here that the peaks corresponding to (hk0) reflections remain unchanged suggesting that the inorganic framework remain intact during the reaction. The schematic structures of nickel phyllosilicate, 3G-NiP, and NtnOenH₄-3G₂-NiP are shown in Figure 2.

The FT-IR spectra on 3G, 3G-NiP, NtnOenH₄, and NtnOenH₄-3G₂-NiP are shown in Figure 3. Absorption bands at 2940, 2870, and 1465 (aliphatic alkyl chain), 1260 (epoxide), and 1196 cm⁻¹ (Si-C) for 3G-NiP indicate that 3G groups linked to Si atoms were retained. Absorption bands of the silicate layer at 1110-1050 and 1014 (asymmetric, $\nu_{\text{Si-O}}$), 860 (symmetric, $\nu_{\text{Si-O}}$), and 1200 cm⁻¹ ($\delta_{\text{Si-O-Si}}$) indicate that 3G-NiP structure is similar to mineral talc. Above all, the absence of NH stretching bands at 3292 and 3189 cm⁻¹ for the NtnOenH₄-3G₂-NiP indicates certainly the formation of C-N bonds by reaction between glycidoxo and amine groups. Generally, no catalyst is needed for the reaction between aliphatic amines and glycidoxo

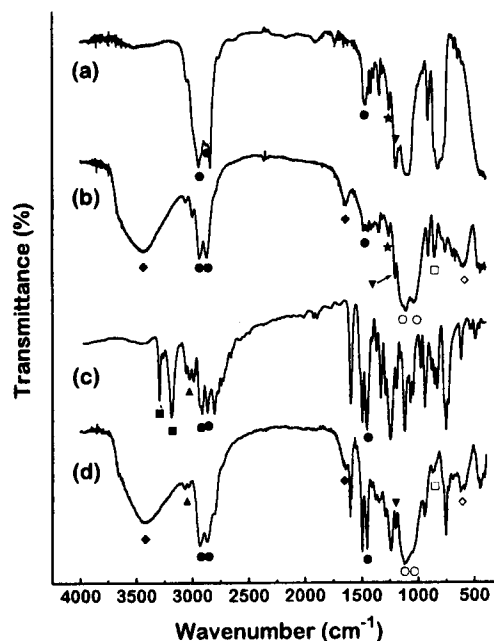


Figure 3. FT-IR spectra of (a) 3G, (b) 3G-NiP, (c) NtnOenH₄, and (d) NtnOenH₄-3G₂-NiP. ♦ (OH), ■ (NH), ▲ (aromatic CH), ● (aliphatic CH₂), ★ (epoxide), ▼ (Si-C), ○ (asymmetric Si-O), □ (asymmetric Si-O), and ◇ (Ni-O).

Table 2. Binding constants and stability constants for the interaction with transition metal cations

	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺
NtnOenH ₄ -3G ₂ -NiP	1.7 ± 0.12	1.2 ± 0.1	3.5 ± 0.2	1.0 ± 0.1
free NtnOenH ₄ *	3.6	4.76	7.29	4.1

*from reference 12.

groups.¹¹

Therefore, it is considered that 3G-NiP and NtnOenH₄-3G₂-NiP had a slightly disordered -C-SiO₃ tetrahedral sheets and a well ordered nickel octahedral sheets. This suggests that the growth of the octahedral sheets dominated in the formation of the layered material. Then, the arrangement of the organic groups caused by hydrophobic interactions might also promote the formation of the phyllosilicate structure.⁸

The binding constants (log *K*) were determined to investigate the binding ability of NtnOenH₄-3G₂-NiP. Detailed procedures for determining the binding constants have been presented elsewhere.⁴ After small amounts of NtnOenH₄-3G₂-NiP powder were equilibrated with transition metal cations studied, the suspensions were centrifuged and filtered. The metal concentrations were determined by UV-Visible spectrophotometer and EDTA titration.

Values of binding constants of NtnOenH₄-3G₂-NiP for transition metal cations are listed in Table 2. The observed binding order was Zn²⁺ < Ni²⁺ < Co²⁺ < Cu²⁺. This sequence agreed with the respective log *K* values for the complexes of the free NtnOenH₄ except Co²⁺ cation. This exception might be due to the steric hindrances or the conformational changes by the two-dimensional arrangement of NtnOenH₄ within the interlayer. The uptake amount of Cu²⁺ cations by NtnOenH₄-3G₂-NiP is also in agreement with the amount of

NtnOenH₄ calculated from EA and TGA.

In summary, we can prepare the new layered material containing NtnOenH₄. This material is not only interesting as the new layered structure containing macrocyclic ligands, but also of use in the study of the separation chemistry for chromatography. We expect that phyllosilicate compounds similar with these materials will be easily synthesized in other macrocyclic ligand systems. And also, the vast data of free macrocyclic ligand-cation interaction can be applied to new phyllosilicate ones.

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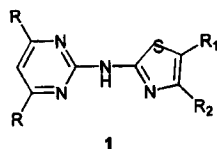
A Facile Method for the Preparation of 2-(N-Pyrimidino)aminothiazoles

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In the course of our studies on the synthesis of novel macrocyclic compounds containing heterocycles such as thiazoles and pyrimidines, we needed a convenient method to prepare α -pyrimidinylthioureas as the synthetic intermediates for obtaining 2-(N-pyrimidino)aminothiazoles **1**.



Substituted thiazoles¹ have been frequently made by the reaction of α -substituted thiourea intermediates with α -haloketones known as the Hantzsch thiazole synthesis.² Simple α -substituted thioureas have been made in various ways³: by treatment of mono-substituted amine with ammonium thiocyanate, thiocyanic acid, thiuram disulfide or silicon thiocyanate, or by the action of ammonia on isothiocyanate. Preparation of α -phenylthiourea described in Organic Syntheses is the classical example where α -phenylthiourea was obtained by the alkaline hydrolysis of α -benzoyl- β -phenylthiourea prepared from the reaction of α -benzoyl- β -phenylisothiocyanate with aniline.³ However, this method is not generally effective for preparing the α -pyrimidinylthioureas because of poor yield or side products of the reaction are obtained. After various unsuccessful attempts on the convenient transformation of 2-aminopyrimidine derivatives into α -pyrimidinylthioureas, we found a facile pro-

cedure of utilizing the isothiocyanate generated by the reaction of thiophosgene⁴ with aminopyrimidine for the efficient preparation of α -pyrimidinylthiourea which was readily used for the Hantzsch reaction to follow.

The preparation of 2-(N-pyrimidino)aminothiazoles has been scarcely documented. The only example of the synthesis of 2-(N-pyrimidino)aminothiazoles known to us was the process giving a poor yield. In the process 2'-pyrimidyl-2-thiazoylamine was prepared from the reaction of the sodium salt of 2-aminopyrimidine and 2-chlorothiazole in 9.5% yield.⁵ This paper reports a new simple method for the synthesis of 2-(N-pyrimidino)aminothiazoles **1** (Scheme). 2-(N-4,6-disubstituted pyrimidino)aminothioureas **3** were obtained in ca. 80% yield by slow addition of thiophosgene to 2-aminopyrimidine **2** during 30 minutes in dichloroethane containing one equivalent of triethylamine at 30 °C and the treatment of the resulting reaction mixture with aqueous ammonia. The reaction of **3** with α -bromoketones **4** in boiling ethanol containing a catalytic amount of sodium bicarbonate gave **1** in a high yield (ca. 95%).

Experimental Section

Preparation of α -pyrimidinylthioureas (**3**)

Typical procedure (3b). To a stirred solution of 2-amino-4,6-dimethoxypyrimidine (310 mg, 2 mmol) in dichloroethane (5 mL) at 30 °C was added slowly thiophosgene (252 mg, 2.2 mmol) in the same solvent (3 mL) during 30 minutes. (Usually 2-aminopyrimidine was dissolved