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Synthesis of Polymer-Bound Nitridomolybdenum(VI) Complexes as Model Polymer Complexes of Nitrogenase: Effect of Polymer Environment in the Hydrolytic Formation of Ammonia

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Polymer-bound nitridomolybdenum(VI) complexes, $MoNCl_3$(polystyrene-bound bipyridyl) (I), $MoNCl_2$(bpy)(polystyrene-bound benzylthiolato) (II), and MoNCl (S-t-Bu)(bpy)(polystyrene-bound benzylthiolato) (III), were synthesized by the reaction of $MoNCl_3(CH_3CN)_x$ or $MoNCl_3$(bpy) with polystyrene-bound bipyridyl or benzylthiol. The polymer-bound nitridomolybdenum complexes were characterized by photo-acoustic and resonance Raman spectra. Hydrolysis or hydrolytic reduction of the nitridomolybdenum(VI) complexes resulted in the formation of ammonia in the following order of yield: III > II > I. Coordination of the polymer thiolato ligands is thus important in enhancing reductive cleavage of the nitridomolybdenum bond.

Introduction

The active site of nitrogenase has been speculated to be a Mo ion surrounded by three or four sulfur ligands [1]. Many model reactions of nitrogen fixation have been carried out by using the systems of *e.g.* cysteine/MoO_4^{2-}/$NaBH_4$ [2], or insulin/MoO_4^{2-}/$NaBH_4$ [3], and by electrochemical reduction of $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ [4]. However, the formation of ammonia has not yet been catalytic. Among many dinitrogen complexes, a discrete bis(dinitrogen)molybdenum(0) complex, $Mo(N_2)_2(PMePh_2)_4$, produces only 0.66 equiv. of ammonia when decomposed by addition of sulfuric acid in methanol [5]. Extensive research on protolytic decomposition of dinitrogen complexes of Mo and W have indicated initial protonation at the terminal nitrogen atom followed by cleavage of the N≡N bond to give nitridometal species. Hydrolytic decomposition of the nitridomolybdenum species would release ammonia, and the metal is poised for coordination of dinitrogen when reduced to the low-valent state. Then the hydrolytic reaction of nitridomolybdenum complexes is important as an elementary step of nitrogen fixation.

The protolysis of $MoNCl_2(Ph_3P)_2$ or $MoNCl_3(Ph_3PO)_2$ has been studied by Chatt *et al.* to find almost quantitative yields of ammonia [6, 7]. However, presence of the Ph_3P or Ph_3PO ligands obscures the significance of this as a model of nitrogenase. Since the conversion of nitridomolybdenum species to low-valent molybdenum species is crucial for a catalytic cycle in nitrogen fixation, we proposed an examination of the reactions of nitridomolybdenum complexes. In this report our results on nitridomolybdenum complexes coordinated with N and/or S ligands surrounded by polymer environment will be described. In general nitridomolybdenum complexes are very sensitive to air and moisture [8]. However, no information about the formation of ammonia is given for the nitridomolybdenum complex having ligand atoms such as halide, N, and S. We found that all of nitridomolybdenum complexes gave only a small amount of ammonia by hydrolysis or reductive hydrolysis. The formation of ammonia from a nitridomolybdenum complex is thus thought to be modified by the formation of Mo–Mo or Mo–N=Mo bonds which may stabilize nitridomolybdenum species toward hydolysis.

Super-dilution effect of a polymer support may prevent association of the Mo≡N species to enhance the hydrolytic reactivity. Polymer supports having N or S ligands were thus prepared from cross-linked polystyrene and converted to polymer molybdenum complexes. These were reduced with sodium borohydride or were protonated by acid to cleave the Mo≡N bonding. The difference in reactivities among the nitridomolybdenum complexes with the ligating atoms of N, Cl, and S will be discussed. Implication of the results on the nitrogen fixing catalytic cycle in nitrogenase will also be presented.

Experimental

Chloromethylated, 1% cross-linked co(poly-styrene-divinylbenzene) (Cl content, 0.97 mmol/g)

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was purchased from the Protein Research Foundation. The hexane solution of n-butyllithium was obtained from the Nakarai Chem. Co. Sodium borohydride and bipyridyl (bpy) were of commercial grade. All solvents were purified by distillation under argon atmosphere. All operations for the syntheses of polymer-bound nitridomolybdenum complexes and for the decomposition were carried out under argon atmosphere.

Preparation of $MoNCl_3(bpy)$

The complex was prepared from a reaction mixture of $MoCl_4(CH_3CN)_2$ and sodium azide by addition of bipyridyl, according to the method of Seyferth *et al.* [9]. λ_{max}: 350 nm (ϵ = 8200) in tetrahydrofuran (THF).

Preparation of $MoNCl_2(S\text{-}t\text{-}Bu)(bpy)$

t-Butylthiotrimethylsilane was prepared by the modified method reported by Abel [10]. To a suspension of $MoNCl_3(bpy)$ (0.84 g, 2.26 mmol) in 40 ml of THF, 1.3 ml (6.8 mmol) of t-butylthiotrimethylsilane was added at room temperature. After refluxing for 4 h, the mixture gave a light brown precipitate which was collected by filtration and dried *in vacuo*. *Anal.* Calcd for $C_{14}H_{17}N_3Cl_2SMo$: Mo, 22.51; Found: Mo, 18.10. IR spectra; 1025 cm^{-1} ($Mo\equiv N$). Raman spectra; 1025 cm^{-1} ($Mo\equiv N$). λ_{max}; 400 nm (ϵ = 2000), 460 nm (ϵ = 1650).

Preparation of Polymer-bound Benzylthiol (PSt-SH) (I)

The polymer-bound benzylthiol was prepared by the procedure of Imoto [11]. The content (0.55 mmol/g) of the thiol group in the polymer was determined by elemental analysis.

Synthesis of $MoNCl_2(bpy)(PSt\text{-}S)$ (II)

To a mixture of PSt-SH (3 g) in 20 ml of THF was added a THF solution of n-butyllithium (2.56 mmol). The reaction mixture was shaken for 1 h. The polymer gel was collected by filtration and washed with THF and n-hexane. To the polymer gel dispersed in THF, $MoNCl_3(bpy)$ was added at room temperature. The red-purple polymer-bound nitridomolybdenum complex obtained was washed with THF and n-hexane and dried *in vacuo*. Mo content: 0.38 mmol/g.

Synthesis of $MoNCl(S\text{-}t\text{-}Bu)(PSt\text{-}S)$ (III)

To a dispersion of II (0.96 mmol) in THF, t-butylthiotrimethylsilane (1.91 mmol) was added at room temperature. The purple polymer was washed with THF and n-hexane and dried *in vacuo*. Mo content: Mo/St unit = 1/39.

Preparation of Polymer-bound Bipyridyl (IV)

The bromination of the cross-linked polySt with HBr/CH_3COOH was carried out by the literature method [12]. To the brominated polySt dispersed in THF, a solution containing n-butyllithium (8.0 mmol) and bipyridyl (4.8 mmol) were added at room temperature. The content (0.22 mmol/g) of the bipyridyl group was estimated by the elemental analysis for nitrogen.

Synthesis of $MoNCl_3(PSt\text{-}bpy)$ (V)

To 2.8 g of PSt-bpy dispersed in THF (30 ml), 3.4 mmol of $MoNCl_3(CH_3CN)_x$ was added at room temperature. The red-brownish polymer-bound nitridomolybdenum complex was washed with THF and n-hexane and dried *in vacuo*. Mo content: 0.17 mmol/g.

The syntheses of the polymer-bound ligands and nitridomolybdenum complexes are shown in Fig. 2.

Analysis of Molybdenum Content

To a dispersion of the polymer-bound nitridomolybdenum complexes in THF (5 ml), 10^{-2} mmol of lithium thiophenolate in THF was added at room temperature and the mixture was stirred for 20 h. Fifty ml of 2 *N* NaOH aq was added to the mixture for decomposition of Mo complexes in solution. After 3 h, the mixture was heated at 90 °C until it became colorless. The molybdenum content in the mixture was determined by a literature method [13].

Determination of Ammonia Formed from the Nitridomolybdenum(VI) Complexes

To a dispersion of the nitridomolybdenum complexes, $MoNCl_3(bpy)$, $MoNCl_2(S\text{-}t\text{-}Bu)(bpy)$, **II**, **III** and **V** in 4 ml of ethanol/THF (1:3 v/v), 20 equiv. of H_2SO_4 was added at room temperature. The yield of ammonia was determined by the colorimetric method [14]. The reduction of the nitridomolybdenum complexes was carried out with 20 equiv. of sodium borohydride in 4 ml of ethanol/THF (1:3 v/v). The yield of ammonia was determined by the same method as mentioned above.

Physical Measurements

Absorption spectra were recorded on a Jasco Model UVIDEC-5A spectrophotometer. Photoacoustic spectra were obtained on the instruments reported by Ikeda *et al.* [15]. Raman spectra were taken on a JASCO R-800 spectrometer.

Results and Discussion

Characterization of Polymer-bound Nitridomolybdenum(VI) Complexes

Nitridomolybdenum complexes such as $MoNCl_3(bpy)$ or $[MoNCl_4]^-$ have been known to be very

TABLE I. Characterization of Polymer-bound Ligands and Polymer-bound Nitridomolybdenum(VI) Complexes.

Polymer	Contents of functional groups
PSt-Cl	Cl 0.97 mmol/g
PSt-SH (I)	SH 0.55
$MoNCl_2$(bpy)(PSt-S) (II)	Mo 0.38
MoNCl(S-t-Bu)(bpy)(PSt-S) (III)	Mo 0.25
PSt-bpy (IV)	bpy 0.22
$MoNCl_3$(PSt-bpy) (V)	Mo 0.17

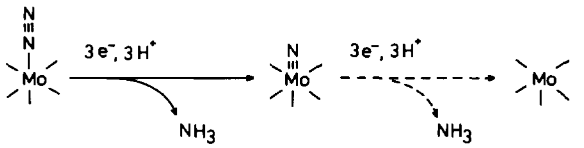

Fig. 1. Reduction of dinitrogen on molybdenum.

sensitive to hydrolysis or air-oxidation [8]. All of the polymer-bound nitridomolybdenum complexes are also susceptible to moisture and dioxygen. Therefore these complexes must be handled under inert atmosphere. Table I lists the contents of the ligand groups and Mo ions in each polymer.

The structures of the polymer-bound nitridomolybdenum complexes were examined by photoacoustic spectroscopy. Figure 3 shows the photoacoustic spectra of $MoNCl_2$(bpy)(PSt-S) (II), MoNCl-(S-t-Bu)(bpy)(PSt-S) (III), and $MoNCl_3$(PSt-bpy) (V) in the solid state. No clear absorption maximum was observed for $MoNCl_3$(PSt-bpy) in the region (400 ~ 700 nm) where the normalized photo-acoustic intensity is relatively small. Actually, $MoNCl_3$(bpy) does not have any absorption maximum over 400 nm

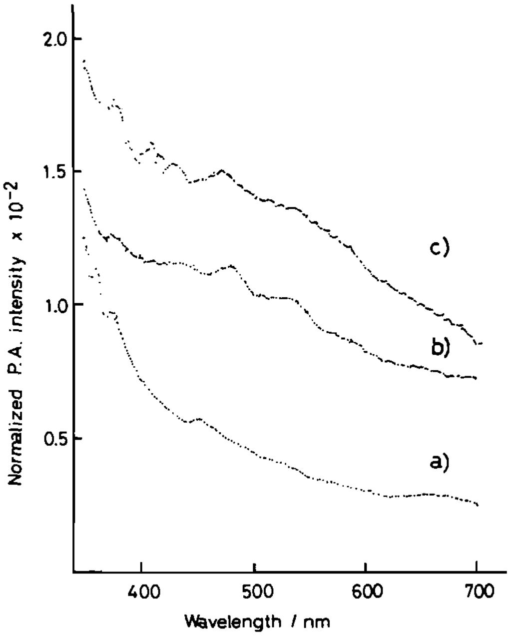

Fig. 3. Photo-acoustic spectra of a) $MoNCl_3$(PSt-bpy), b) $MoNCl_2$(bpy)(PSt-S) and c) MoNCl(S-t-Bu)(bpy)(PSt-S) in the solid state.

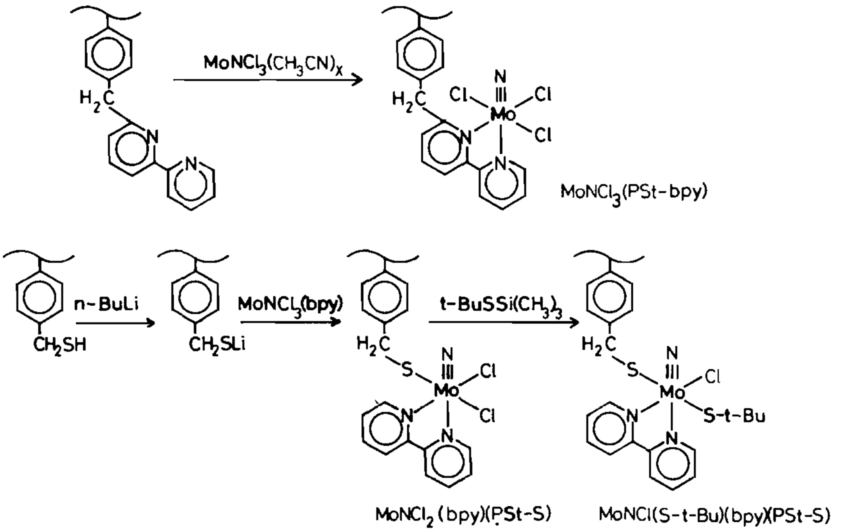

Fig. 2. Syntheses of polymer-bound nitridomolybdenum(VI) complexes.

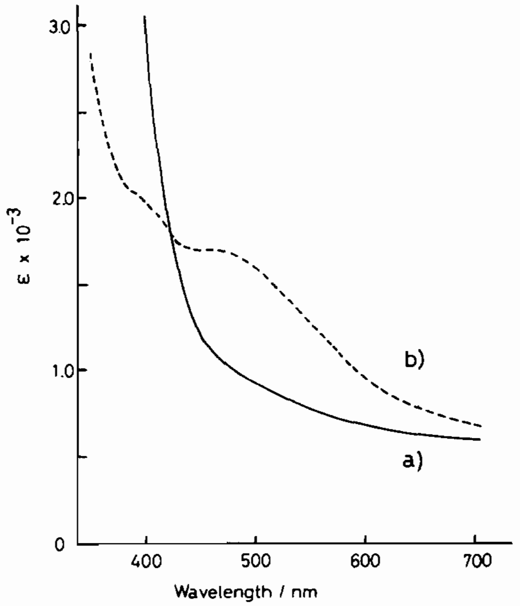

Fig. 4. Visible spectra of a) MoNCl$_3$(bpy) and b) MoNCl$_2$(S-t-Bu)(bpy) in THF.

in THF as shown in Fig. 4, although it gives a maximum at 350 nm. Other nitridomolybdenum complexes **III** or **V** with thiolate ligands provide some broad absorptions having relatively high normalized photo-acoustic intensities in the region 400–700 nm. Characteristic absorption of **II** or **V** at 480 nm was observed as shown in Fig. 3. The solution of MoNCl$_2$(S-t-Bu)(bpy) has maxima at 460 nm (ϵ = 1650) and 400 nm (ϵ = 2000). The results indicate that the polymer-bound nitridomolybdenum complexes have the same coordination structures as that of the unsupported complex.

Detection of a Mo≡N group in the polymer-bound nitridomolybdenum complexes was carried out by Raman spectroscopy. Figure 5 shows the Raman spectra of the polymer-bound ligands and the polymer-bound nitridomolybdenum complexes in the solid state. Unfortunately, strong bands at 1002 and 1032 cm^{-1} due to the phenyl group of polystyrene were observed with 514.5 or 457.9 nm excitations (Fig. 5-a, b, c, and d). Therefore, any bands due to (Mo≡N) may be obscured. MoNCl$_3$(bpy) was found to give a Raman band at 1027 cm^{-1} due to a Mo≡N bond [16]. Each of the polymer-bound complexes, MoNCl$_3$(PSt-bpy) and MoNCl(S-t-Bu)(bpy)(PSt-S), exhibited an intense peak at 1030 cm^{-1} (Fig. 5-g, h, i, and j). The accurate analysis of the peak intensities of the two bands at 1000 and 1027–1032 cm^{-1} lead to the fact that the band at 1027 cm^{-1} was remarkably enhanced with both 514.5 and 457.9 nm excitations. The polymer-bound nitridomolybdenum having thiolate ligands gave visible absorption maxima at 480 and 520 nm (Fig. 4) and MoNCl$_2$(S-t-Bu)(bpy) exhibits a maximum at 460 nm and a Raman band at 1025 cm^{-1} due to the Mo≡N group [16]. Therefore the enhanced intensity of the Raman band at 1027 cm^{-1} is due to a resonance Raman effect by excitation around 480–520 nm. The visible maximum is thus assignable to the absorption associated with the ligand-to-metal charge transfer (LMCT) of the Mo–S bonding.

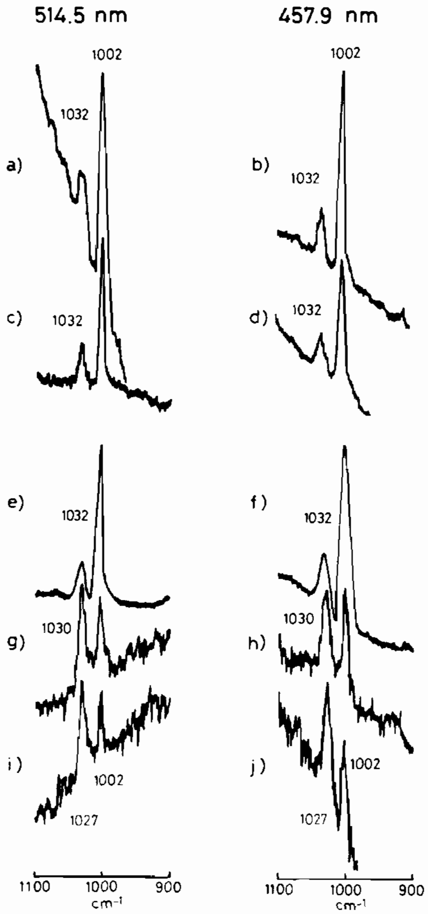

Fig. 5. Raman spectra of polymer-bound ligands and polymer-bound nitridomolybdenum complexes in the solid state: a) and b), PSt-bpy; c) and d), MoNCl$_3$(PSt-bpy); e) and f), PSt-SH; g) and h) MoNCl$_2$(bpy(PSt-S); i) and j) MoNCl(S-t-Bu)(PSt-S). The spectra of a), c), e), g), and i) were obtained with a 514.5 nm excitation line and those of b), d), f), h), and j) were taken with a 457.9 nm excitation line.

Formation of Ammonia from the Polymer-bound Nitridomolybdenum Complexes

Monomeric nitridomolybdenum complexes having Cl or N ligands such as MoNCl$_3$(bpy) are known, whereas nitridotungsten complexes having an alkoxide ligand in addition to the Cl or N ligand are associated to give a polynuclear complex in a lower oxidation state [17]. Such polynucleation may have

TABLE II. Formation of Ammonia by Protolytic Decomposition with Sulfuric Acid and Reductive Hydrolysis with $NaBH_4$.

Nitridomolybdenum(VI) Complexes	Yield of ammonia (%)[a]	
	protolytic decomposition	reductive hydrolysis
$MoNCl_3$(PSt-bpy)	6.8	4.0
$MoNCl_3$(bpy)	6.9	0.6
$MoNCl_2$(bpy)(PSt-S)	19.0	3.5
$MoNCl_2$(S-t-Bu)(bpy)	17.9	2.8
MoNCl(S-t-Bu)(bpy)(PSt-S)	11.6	14.4

[a]The yield is based on Mo. [b]Conditions: $NaBH_4$ or sulfuric acid/Mo = 20 (mol/mol) in ethanol/THF (1/3 v/v) at room temperature for 2 h.

caused the reactivity of the Mo≡N group to decrease. Table II lists the results of the formation of ammonia from polymer-bound nitridomolybdenum complexes and the corresponding unsupported complexes. No appreciable dilution effect due to the polymer support was observed for the protonation by sulfuric acid. The results indicate that deactivation of nitridomolybdenum species by polynucleation is not involved since the metal species is in a high-oxidation state.

The results of the ammonia formation from these complexes on reduction by sodium borohydride in THF/ethanol (3:1 v/v) are listed in Table II. In the reductive decomposition of $MoNCl_3$(PSt-bpy), the yield of ammonia (4.0%) increased compared with that (0.6%) of $MoNCl_3$(bpy). The reduction of MoNCl(S-t-Bu)(bpy)(PSt-S) results in the formation of a larger amount (14.4%) of ammonia than that (2.8%) of the corresponding unsupported system, $MoNCl_3$(bpy)/t-bu-$SSiMe_3$. Therefore, a dilution effect on the reduction of polymer-bound nitridomolybdenum complexes is definitely found. It is likely that the reduced species formed from the polymer-bound nitridomolybdenum complexes is prevented from the extensive polynucleation which is a feature of low-valent molybdenum species.

Introduction of thiolate ligands into the nitridomolybdenum complexes results in a remarkable increase of the yield of ammonia in either cases of acidic hydrolysis or reductive hydrolysis. The reactivity of the Mo≡N group was clearly enhanced by coordination of thiolate ligands, especially at mutually *trans* positions. It has not yet been determined if one of the thiolate ligands coordinates at the *trans* position of the Mo≡N group. Electronic–vibrational coupling between the Mo≡N group and the thiolate ligands was found by the resonance Raman spectra by excitation at the charge-transfer absorption mainly due to Mo–S groups. The present work indicated the importance of thiolate coordination in reductive cleavage of Mo≡N species especially in non-associated state. The polymer environment utilized in the present study is not effective enough to completely regenerate low-valent, coordinatively unsaturated molybdenum species which may add dinitrogen for further reductive cleavage of both N≡N and Mo≡N bonds.

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