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Synthesis and Properties of a Nitridomolybdenum(VI) Complex Having Benzenedithiolate Ligands. Effect of the Thiolate on the Activation of the Nitrido Ligand

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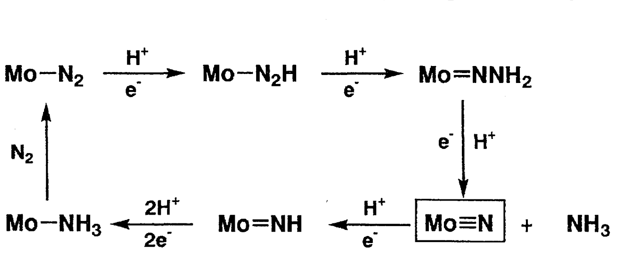
A nitridomolybdenum(VI) complex having 1,2-benzenedithiolate (bdt^{2-}) $(NEt_4)_2[Mo^{VI}N(bdt)_2Cl]$ was synthesized by the reaction of $(NEt_4)[Mo^{VI}NCl_4]$ with 2 equiv of Li_2bdt in DMF/THF solution. This complex was characterized by measurements of the absorption, Raman, IR, and ^{14}N NMR spectra. A lower Mo≡N band (1010 cm^{-1}) in the Raman spectrum and the upfield shifted ^{14}N NMR signal (−374 ppm) of the nitrido ligand compared to those of $(NEt_4)[Mo^{VI}NCl_4]$ (1055 cm^{-1} and −350 ppm) were observed, which strongly suggest the existence of a competitive π-electron donation from S (pπ) to Mo (dπ). The complex readily reacts with O_2 or H_2O to produce an oxomolybdenum(IV) complex $[Mo^{IV}O(bdt)_2]^{2-}$. This extremely air-sensitive complex shows a higher reactivity to O_2 than that of $(NEt_4)[Mo^{VI}NCl_4]$. It is concluded that the observed high reactivity is the result of a weakened Mo≡N bond by thiolate coordination.

A number of dinitrogenmolybdenum(0) complexes have been synthesized to date using phosphorus ligands as model compounds of active sites of nitrogenase.[1,2] However, when those complexes are treated with strong acids, such as HCl, the ammonia is produced in a yield of only less than 50%.[2] During the reduction process, the formation of a nitridomolybdenum complex as an intermediate has been suggested[3—7] (Scheme 1). It has been proposed that the low yield of ammonia is due to a difficulty in the hydrolytic reduction of the strong Mo≡N triple bond. Actually, the known nitridomolybdenum complexes having P, N, or O ligands are reported to give only a small amount of ammonia in reactions with strong acids.[8,9] Therefore, the activation of the nitrido ligand for ready hydrolysis is one of the most important steps for achieving a catalytic reduction of dinitrogen to ammonia.

The Fe–Mo cluster in the active site of nitrogenase is known to have many sulfur ligands based on EXAFS studies[10] and by a recent X-ray analysis of *Azotobacter vinelandii*.[11] These studies suggest that the sulfur ligand causes an activation of the dinitrogen ligand for hydrogenation. In order to clarify the part of the activation effect, we synthesized a nitridomolybdenum(VI) complex having the 1,2-benzenedithiolate (bdt) ligand, and studied the electronic effect of the sulfur on the Mo^{VI}≡N bond. The extremely air-sensitive nitridomolybdenum(VI) complex obtained was characterized by Raman, IR, absorption, and ^{14}N NMR spectroscopic methods.



Scheme 1.

Experimental

Reagents. All of the manipulations were carried out under an Ar atmosphere using standard Schlenk techniques. 1,2-Dimethoxyethane (DME) and tetrahydrofuran (THF) were distilled from sodium/benzophenone ketyl, and dimethylformamide (DMF), acetonitrile (MeCN), MeCN-d_3, dimethylsulfoxide (DMSO), and dichloromethane (CH_2Cl_2) were distilled over calcium hydride before use under Ar.

The starting complexes $(NEt_4)[Mo^{VI}NCl_4]$[8,12] and 1,2-benzenedithiol (H_2bdt)[13,14] were prepared by the literature methods. Dilithium 1,2-benzenedithiolate (Li_2bdt) was obtained by the reaction of H_2bdt with *n*-butyllithium (1.6 M, 1 M = 1 mol dm^{-3}, *n*-hexane soln) in DME at 0 °C. This dilithium salt has a DME molecule as a crystalline solvent.

Synthesis of $(NEt_4)_2[Mo^{VI}N(bdt)_2Cl]$ (1). The complex $(NEt_4)[Mo^{VI}NCl_4]$ (0.18 g, 0.47 mmol) was added in portion to the Li_2bdt·dme (0.29 g, 1.2 mmol) in a DMF/THF (5 ml/10 ml) solution with stirring at ca. −70 °C (dry ice–methanol bath). The reaction mixture was stirred at this temperature for 30 min and then at room temperature for 2 h. The green precipitate obtained was collected by filtration, and dissolved in 60 ml of MeCN. After removal of insoluble solids by centrifugation, the solution was reduced in volume to about 5 ml in vacuum. The green microcrystals obtained were collected by filtration, and dried in vacuo. Yield, 0.048 mmol, 23%. Elemental analysis, Calcd for $C_{28}H_{48}ClN_3S_4Mo$: C, 49.00; H, 7.05; N, 6.12%. Found: C, 50.46; H, 7.47; N, 5.43%. A low carbon analysis value is inevitable for this complex, and is due to

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the extreme air-sensitivity.

Reaction of 1 with Oxygen Gas in the Solid State. An O_2-oxidized sample was prepared by mixing green microcrystals of **1** (about 20 mg) with a 5 equimolar amount of oxygen gas for about 5 min at room temperature. The atmosphere was evacuated and Ar gas was admitted three times. The IR spectrum changes of the obtained brownish powder were followed both after and before the operation of the evacuation and admittance of Ar. For the Raman spectrum, only the final brownish powder was measured with 514.5 nm excitation.

Stoichiometric Reaction of 1 with Oxygen Gas at Solution State. To a MeCN solution of **1** (8.7 mM, 0.6 ml, 5.2×10^{-6} mol), 0.1 ml of oxygen gas (5×10^{-6} mol) was bubbled at room temperature. After the red-purple solution changed to blue, absorption spectrum of the solution was measured.

Reaction of $(NEt_4)[Mo^{VI}NCl_4]$ with Oxygen Gas. This reaction was followed by the absorption spectrum. To the complex $(NEt_4)[Mo^{VI}NCl_4]$ in CH_2Cl_2 (4 mM, 0.6 ml, 2×10^{-6} mol), 0.05 ml of oxygen gas (2×10^{-6} mol) was bubbled. After an absorption measurement, excess oxygen gas (0.5 ml, 2×10^{-5} mol) was bubbled to the solution. The time course of the absorption was recorded at 20-min intervals.

Reaction of 1 with H_2O. For preparing an oxidized sample for the IR-spectrum measurement, H_2O (0.02 g, 1×10^{-3} mol) in MeCN (10 ml) was added to the MeCN solution (10 ml) of **1** (0.016 g, 2.3×10^{-5} mol) with stirring at room temperature for 30 min. The obtained brownish solution was evaporated to give a yellow-orange powder. The product was dried in vacuo. The IR spectrum of the product was measured using a KBr pellet.

Physical Measurements. The absorption spectra were recorded on a JASCO Ubest-30 spectrometer in a MeCN solution with 1 mm matched silica cells. Raman spectra were obtained on a JASCO R-800 spectrometer in the solid state with 514.5 nm excitation by using a KBr pellet fixed in a sealed glass tube. ^{1}H NMR spectrum was measured on a JEOL EX 270 spectrometer in MeCN-d_3, and was internally referenced to the residual protio solvent impurity (MeCN-d_2, δ=1.90). The ^{14}N NMR spectrum was taken on a JEOL JNH-GSX spectrometer in a DMSO/MeCN-d_3 (4 : 1) solution; the chemical shifts were reported relative to an external reference of $NaNO_3$.

Results and Discussion

Synthesis. The diamagnetic nitridomolybdenum(VI) complex having bdt ligands, $(NEt_4)_2[Mo^{VI}N(bdt)_2Cl]$ (**1**), was synthesized by the reaction of $(NEt_4)[Mo^{VI}NCl_4]$ with excess Li_2bdt in a DMF/THF solution. This reaction was carried out at low temperature (ca. −70 °C) in order to prevent the reduction of Mo(VI) ion to the Mo(V) state. This complex was obtained as extremely air-sensitive green microcrystals. An elemental analysis showed that this complex has a chloro ligand.

Although a number of nitridomolybdenum(VI) complexes have been synthesized, no complexes ligated by thiolate ligands have been reported. $[Mo^{VI}N(Et_2dtc)_3]$ (Et_2dtc = diethyldithiocarbamate) has been synthesized to date as an example of a nitridomolybdenum complex having an S ligand.[15,16] However, the Et_2dtc is not considered to be pure-thiolate, but has a significant thioketone-like character.

The bdt ligand has been used for the syntheses of oxo- or dioxomolybdenum(IV, V, or VI) complexes,[17,18] because of the stabilization effect on the monomeric molybdenum ion by chelation and electronic delocalization through the phenyl ring. This chelate ligand gave the thermally stable nitridomolybdenum(VI) complex **1**. Our attempts to synthesize a nitridomolybdenum(VI) complex using benzenethiolate, 1,3,5-triisopropylbenzenethiolate, or 1,2-ethanedithiolate ligands were unsuccessful because of the thermal and extreme air sensitivity of the products.

Raman and IR Spectra. **1** shows an intense $\nu(Mo^{VI}\equiv N)$ band at 1010 cm^{-1} in the Raman spectrum in the solid state (see Fig. 1a). This band disappears upon O_2-oxidation in the solid state (Fig. 1b), because of the production of an oxomolybdenum(IV) complex (vide infra). The differential spectrum between **1** and the oxidized sample more clearly shows the $\nu(Mo^{VI}\equiv N)$ band at 1010 cm^{-1} (Fig. 1c). This band is lower by 46 cm^{-1} than that of the starting material $(NEt_4)[Mo^{VI}NCl_4]$ (1056 cm^{-1}).[8] The shift indicates that the $Mo^{VI}\equiv N$ bond of **1** is weaker than that of $(NEt_4)[Mo^{VI}NCl_4]$.

It is known that the $\nu(Mo\equiv N)$ band is delicately affected by the coordinating atoms, molecular structure, crystal packing, and identity of counter ions. Table 1 summarizes the $\nu(Mo\equiv N)$ data of several nitridomolybdenum complexes reported to date. The $[Mo^{VI}NCl_4]^-$ anion has different values of the $\nu(Mo\equiv N)$ band for the several cations: NEt_4^+ (1056 cm^{-1}),[8] NMe_4^+ (1054 cm^{-1}),[12] $AsPh_4^+$ (1060 cm^{-1}),[12,19] PPh_4^+ (1060 cm^{-1}),[20] and $Cl_3PNPCl_3^+$ (995 cm^{-1}).[21] X-Ray crystallographic studies of these complexes have shown that the extremely lower shift of the Mo≡N stretching frequency of the $Cl_3PNPCl_3^+$ complex is due to a trans influence of the neighboring nitrido ligand coordinated at the trans position, which is the result of an infinite –Mo≡N–Mo≡N– structure found in this complex. The Cl ligand at the trans position

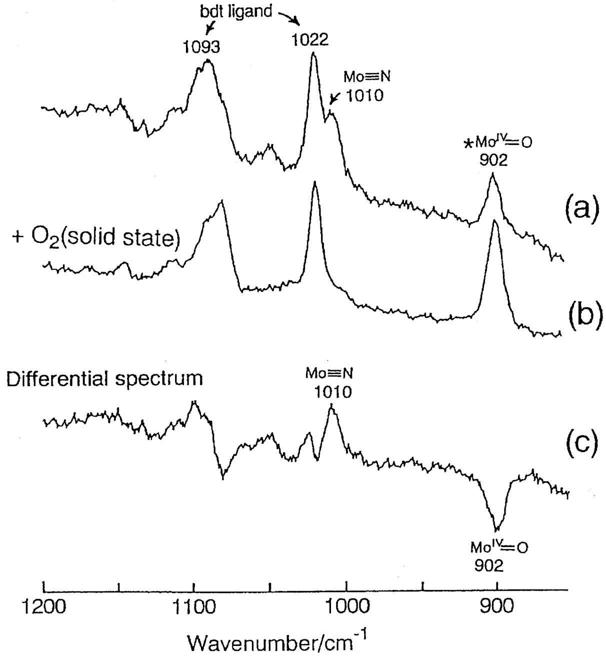


Fig. 1. Raman spectra of **1** (a), the oxidized product (b), and the differential spectrum (c).

Table 1. Frequencies of $\mathrm{Mo^{VI}{\equiv}N}$ Bond of Nitridomolybdenum Complexes

Complex	$\nu(\mathrm{Mo^{VI}{\equiv}N})$ /cm^{-1}	Mo≡N/Mo–N / Å	Ref.
$(\mathrm{NEt_4})[\mathrm{Mo^{VI}NCl_4}]$	1056(1055)$^{a)}$		8
$(\mathrm{NMe_4})[\mathrm{Mo^{VI}NCl_4}]$	1050(1058)$^{a)}$		8
	1054		12
$[(n\text{-Bu})_4\mathrm{N}][\mathrm{Mo^{VI}NCl_4}]$	1065(1063)$^{a)}$		8
	1065		37
$(\mathrm{AsPh_4})[\mathrm{Mo^{VI}NCl_4}]$	1060$^{b)}$	1.66(4)	19
$(\mathrm{PPh_4})[\mathrm{Mo^{VI}NCl_4}]$	1060	1.637(4)	20
$(\mathrm{Cl_3PNPCl_3})[\mathrm{Mo^{VI}NCl_4}]^{c)}$	995	1.75(4)/2.43(4)	21
$(\mathrm{AsPh_4})[\mathrm{Mo^{VI}NF_4}]$	969	1.83(4)	26
$(\mathrm{PPh_4})[\mathrm{Mo^{VI}NBr_4}]$	1060	1.63(2)	28
$(\mathrm{NEt_4})_2[\mathrm{Mo^{VI}NCl_5}]$	1028		22
$[\mathrm{Mo^{VI}NCl_3}]^{\ d)}$	1045	1.64(1)/2.13	28
		1.67(1)	
$[\mathrm{Mo^{VI}NCl_3(bpy)}]^{\ e)}$	1027(1023)$^{a)}$		8
	1009		2
$\{\mathrm{HB(Me_2pz)_3}\}\mathrm{Mo^{VI}N(N_3)_2}^{f)}$	1023	1.646(4)	22
$[\mathrm{Mo^{VI}N(N_3)_2Cl(terpy)}]^{\ g)}$	1005	1.662(7)	23
$[\mathrm{Mo^{VI}N(N_3)_3(bpy)}]$	972	1.642(5)	23
$[\mathrm{Mo^{VI}NCl_3(OPPh_3)_2}]$	1042(1038)$^{a)}$		8
	1038		2
$(\mathrm{PPh_4})[\mathrm{Mo^{VI}N(OPh)_4}]$	1033		24
$[\mathrm{Mo^{VI}N}(t\text{-BuO})_3]^{\ c)}$	1020	1.661(4)/2.883(8)	25
$[\mathrm{Mo^{VI}N(NRAr_3)_3}]^{\ h)}$	1042		38
$[\mathrm{Mo^{VI}N(S_2CNEt_2)_3}]$	1015	1.641(9)	15
$(\mathrm{NEt_4})_2[\mathrm{Mo^{VI}N(bdt)_2Cl}]$ (**1**)	1010		This work
$(\mathrm{NEt_4})_2[\mathrm{Mo^{V}NCl_4}]$	1050		22
$\{\mathrm{HB(Me_2pz)}\}\mathrm{Mo^{V}NCl_2}$	1020		22

a) Raman (IR) values. b) The $\nu(\mathrm{Mo^{VI}{\equiv}N})$ value was cited from Dehnicke et al.[12) c) Polymeric structure; $-\mathrm{Mo^{VI}{\equiv}N{-}Mo^{VI}{\equiv}N}-$ d) Tetrameric structure; $(\mathrm{Mo^{VI}{\equiv}N})_4$ unit. e) bpy = 2,2′-bipyridine. f) $\{\mathrm{HB(Me_2pz)_3}\}$ = tris(3,5-dimethylpyrazol-1-yl)hydroborate. g) terpy = terpyridine. h) $\mathrm{R=C(CD_3)_2CH_3}$, $\mathrm{Ar=3,5\text{-}C_6H_3Me_2}$.

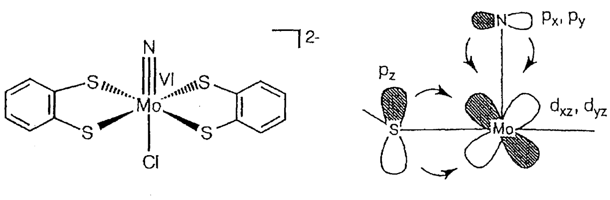
to the nitrido ligand also gives a lower shift of the $\nu(\mathrm{Mo{\equiv}N})$ band. Thus, the $\nu(\mathrm{Mo{\equiv}N})$ band of $(\mathrm{NEt_4})_2[\mathrm{Mo^{VI}NCl_5}]$ (1028 cm^{-1}) is lower by 28 cm^{-1} than that of $(\mathrm{NEt_4})[\mathrm{Mo^{VI}NCl_4}]$.[22)

On the other hand, complexes having soft ligands, such as O, N, S give a lower $\nu(\mathrm{Mo^{VI}{\equiv}N})$ band compared to that of $(\mathrm{NEt_4})[\mathrm{Mo^{VI}NCl_4}]$. For example, $[\mathrm{Mo^{VI}NCl_3(bpy)}]$, $[\mathrm{Mo^{VI}N(N_3)_3(bpy)}]$, $[\mathrm{Mo^{VI}NCl_3(OPPh_3)_2}]$, $(\mathrm{PPh_4})[\mathrm{Mo^{VI}N(OPh)_4}]$, $[\mathrm{Mo^{VI}N}(t\text{-BuO})_3]$, and $[\mathrm{Mo^{VI}N(S_2CNEt)_3}]$ show $\nu(\mathrm{Mo{\equiv}N})$ bands at 1027,[8) 972,[23) 1042,[8) 1033,[24) 1020,[25) and 1015[15) cm^{-1}, respectively, which are lower than that of $(\mathrm{NEt_4})[\mathrm{Mo^{VI}NCl_4}]$ (1056 cm^{-1}). The lower shifts of the $\nu(\mathrm{Mo{\equiv}N})$ band of these complexes are considered to be the result of a competitive π-donation from pπ of the N, S, O ligands to the dπ of Mo. Similar effect has also been observed for F ligand, i.e. $\nu(\mathrm{Mo^{VI}{\equiv}N})$ band of $(\mathrm{AsPh_4})[\mathrm{Mo^{VI}NF_4}]$ is observed at 969 cm^{-1}.[26)

The $\nu(\mathrm{Mo^{VI}{\equiv}N})$ band of **1** is not clear in the observed IR spectrum because of the presence of the strong bands ascribed to phenyl rings. However, a decrease of intensity at 1004 cm^{-1} was observed in the differential IR spectrum between **1** and the slightly $\mathrm{O_2}$-oxidized sample. This band is assignable to the $\nu(\mathrm{Mo^{VI}{\equiv}N})$ band, which is close to that (1010 cm^{-1}) of the Raman spectrum (Fig. 1).

In general, thiolate ligation at the site trans to the nitrido ligand is unstable compared with that of the Cl ligation because of the stronger σ and π electron donating ability.[27—29) Although the crystal structure of **1** is unknown, the Cl ligand is believed to occupy the trans position to the Mo≡N bond. We assume that the lower $\nu(\mathrm{Mo^{VI}{\equiv}N})$ band observed in **1** (1010 cm^{-1}) is due to a competitive pπ-donation from the S ligand to dπ of the Mo atom, as shown on Scheme 2. Thus, the electron donation from the nitrido N(px py) to Mo(dxz, dyz) decreases due to this pπ-donation.

The Absorption Spectrum. The green microcrystals of **1** give a deep-red color by dissolution in MeCN. Figure 2 shows the absorption spectrum of **1**. The distinct absorption maxima of **1** appeared at 325 (2880), 448 (220), and 566 nm (200 M^{-1} cm^{-1}). Since **1** has no d electron, these two



Scheme 2.

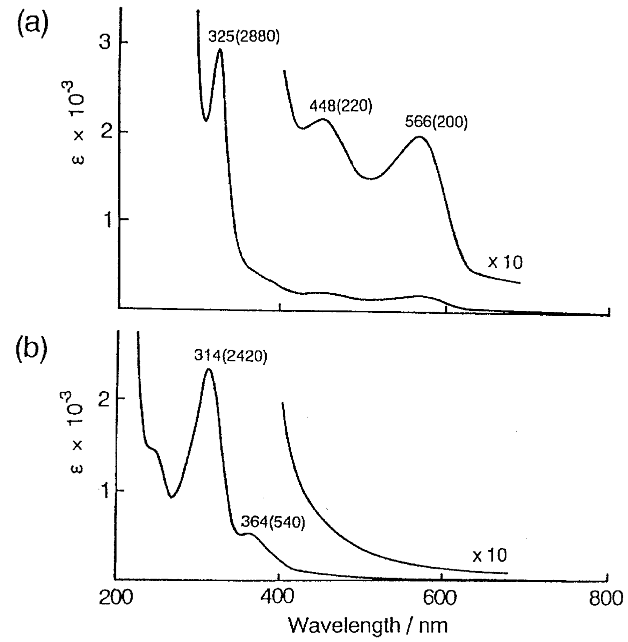


Fig. 2. Absorption spectra of $(NEt_4)_2[Mo^{VI}N(bdt)_2Cl]$ (**1**) (a) and $(NEt_4[Mo^{VI}NCl_4]$ (b) in MeCN solution.

bands at 448 and 566 nm are assigned to the CT transition from S(pπ) to Mo(dπ). The observation of this transition is taken as support for the electronic interaction between S(pπ) and Mo(dπ), which is suggested from the results of the Raman and IR spectra. A similar CT transition between the molybdenum(VI) ion and the bdt ligand was reported in $(NEt_4)_2[Mo^{VI}O_2(bdt)_2]$, which shows two CT bands at 420 and 540 nm in a MeCN solution.[30)]

NMR Studies. The ^{1}H NMR and ^{14}N NMR spectra of diamagnetic **1** were measured in MeCN-d_3 and DMSO/MeCN-d_3 (4 : 1), respectively. The broad proton signals of the bdt ligands are observed at 7.48 and 6.74 ppm in ^{1}H NMR spectrum measurements, because of the rapid spin exchange between **1** and paramagnetic $[Mo^{V}O(bdt)_2]^-$ contaminated by the oxidation reaction with a trace amount of air. Sharp signals were obtained by a reduction of the contaminating Mo(V) complex by the addition of 0.01 equiv (to **1**) of NEt_4BH_4. Similar broadened signals by a rapid spin exchange between the Mo(IV) and Mo(V) states were observed in the ^{1}H NMR spectrum of an oxomolybdenum(IV) complex, $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ or $(NEt_4)_2[Mo^{IV}O(\alpha,2\text{-tdt})_2]$ (α,2-tdt = α,2-toluenedithiolate).[31)]

A measurement of ^{14}N NMR spectrum of **1** was carried out in the presence of 0.01 equiv (to **1**) of NEt_4BH_4 to remove the paramagnetic Mo(V) species. A ^{14}N NMR signal of the nitrido ligand of **1** and $(NEt_4)[Mo^{VI}NCl_4]$ appears at −374 and −350 ppm (relative to $NaNO_3$), respectively (Fig. 3). Only a few ^{15}N NMR spectra of nitrido complexes of molybdenum, tungsten, or rhenium have been reported to date.[29)] Table 2 summarizes the ^{14}N and ^{15}N NMR spectral data. The ^{15}N NMR data of nitridomolybdenum complexes, $[Mo^{VI}(^{15}N)(S_2CNEt_2)_3]$,[5)] *trans*-$[Mo^{IV}Cl(^{15}N)(dppe)_2]$ {dppe=bis(diphenylphospino)ethane},[32)] and *trans*-$[Mo^{IV}Br(^{15}N)(dppe)_2]$[32)] show the ^{15}N signal at 40.0, 166.8, and 190.6 ppm (relative to nitromethane, which is regarded to have the same chemical shift as $NaNO_3$), respectively. These investigations have shown that the chemical shifts of the nitrido ligand depend on the coordination number at the metal center, on the type of the ligand, and also on the π-electron accepting characters of the metal ion, i.e. a decrease in π-donation of the nitrido to the metal ion leads an upfield chemical shift.[29)]

The observation of the ^{14}N signal of **1** and $(NEt_4)[Mo^{VI}NCl_4]$ in the upfield region compared to other known complexes is likely to be due to their anion character. The nitrido ligand of **1** shows the strongest shielding in these complexes, suggesting a rich electron density. These results

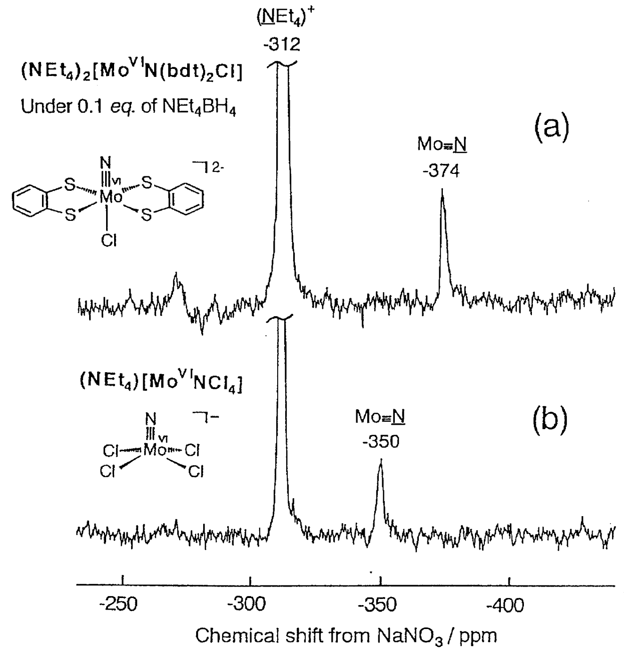


Fig. 3. ^{14}N NMR spectra of $(NEt_4)_2[Mo^{VI}N(bdt)_2Cl]$ (**1**) (a) and $(NEt_4)[Mo^{VI}NCl_4]$ (b) in DMSO/MeCN-d_3 (4/1).

Table 2. ^{14}N and ^{15}N NMR Data of Nitrido Complexes

Complex	Solvent	δ[a)]	Ref.
trans-$[Mo^{VI}Cl(^{15}N)(dppe)_2]$	THF	166.8	32
trans-$[Mo^{VI}Br(^{15}N)(dppe)_2]$	THF	190.6	32
$(NEt_4)_2[Mo^{VI}N(bdt)_2Cl]$ [b)]	c)	−374 [d)]	This work
$(NEt_4)[Mo^{VI}NCl_4]$		−350 [d)]	This work
$[Re^{V}Cl_2(^{15}N)(PnPrPh_2)_2]$	CH_2Cl_2	85.8	5
$[Re^{V}Cl_2(^{15}N)(PMe_2Ph)_3]$	CH_2Cl_2	68.2	5
$[Re^{V}Cl_2(^{15}N)(dppe)_2]Cl$ [e)]	CH_2Cl_2	67.1	5
$[Mo^{VI}(^{15}N)(S_2CNEt_2)_3]$	CH_2Cl_2	40.0	5
$[W^{VI}_2(^{15}N)Cl_9\cdot CH_3CN]$	CD_2Cl_2	211.2	39
$[\{W^{VI}(^{15}N)Cl_3\cdot CH_3CN\}_4]$	CD_2Cl_2	222.7	39
$(PPh_4)[W^{VI}(^{15}N)Cl_4]$	CH_2Cl_2	258.8	39
$(PPh_4)[W^{VI}_2(^{15}N)Cl_{10}]$	CH_2Cl_2	251.0	39

a) Chemical shifts relative to nitromethane. b) bdt = 1,2-benzenedithiolate. c) Solvent = DMSO-d_6/MeCN-d_3 (4/1). d) Chemical shifts relative to $NaNO_3$. e) dppe = Ph_2CH_2-CH_2PPh_2.

show that the nitrido ligand of **1** has a higher electron density than does that of $(NEt_4)[Mo^{VI}NCl_4]$, which is consistent with the Raman, IR, and absorption spectral results.

Reaction of 1 with Oxygen Gas. The reaction of **1** with oxygen gas in the solid state was monitored by the IR and Raman spectra. Figure 4 shows the IR spectrum changes of the reaction of **1** with oxygen gas. Although the $\nu(Mo^{VI}{\equiv}N)$ band is not clear because of the presence of strong bands due to the phenyl ring around 1000 cm^{-1}, the assignment of $Mo^{VI}{\equiv}N$ stretching at 1004 cm^{-1} is shown by the differential spectrum between **1** and the slightly O_2-oxidized sample. The green microcrystals of **1** rapidly change to a brownish powder when the sample is exposed to excess oxygen gas. The IR spectrum of the oxidized product shows an intense band at 830 cm^{-1} (Fig. 4b). This band disappears when the sample is exposed under reduced pressure (ca. 5 mmHg, 1 mmHg = 133.322 Pa). The spectrum of the final brownish powder is consistent with that of $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ having an intense $\nu(Mo^{IV}{=}O)$ band at 902 cm^{-1}.

Regarding the cause of the labile intense band at 830 cm^{-1}, the reversible formation of a peroxo-oxomolybdenum(VI) complex was suggested (Scheme 3). It is known that the η^2-dioxygen complex shows an O–O stretching band around 850 cm^{-1}. For example, $[VO(O_2)(H_2O)(bipicoline)]^-$ shows the $\nu(O_2)$ band at 839 cm^{-1}.[33] Recently, the catalytic oxidation of benzoin by dioxygen in the presence of oxomolybdenum(IV) thiolate complexes has been studied by Ueyama et al.[34,35] They proposed the production of an oxomolybdenum(VI) complex having η^2-dioxygen or μ-dioxygen ligands as the active intermediate.

The production of $[Mo^{IV}O(bdt)_2]^{2-}$ by the oxidation reaction of **1** with O_2 gas was also confirmed by the Raman spectrum measurement. The intense band at 902 ($Mo^{IV}{=}O$) and 358 cm^{-1} ($Mo^{IV}{-}S$) is consistent with those of $(NEt_4)_2[Mo^{IV}O(bdt)_2]$.[36] These results indicate that **1** reacts with O_2 to produce the oxomolybdenum(IV) complex $[Mo^{IV}O(bdt)_2]^{2-}$ in the solid state.

When the reaction of **1** with oxygen gas is carried out in solution, the production of small amounts of $[Mo^{V}O(bdt)_2]^-$ is demonstrated by the absorption spectral measurement. Figure 5 shows the absorption spectral change of the stoichiometric reaction of **1** with O_2 gas in MeCN solution. The absorption spectrum of the reaction exhibits the appearance of λ_{max} at 727 nm with a simultaneous disappearance of the two bands at 448 and 566 nm. The absorption at 727 nm arises from the production of $[Mo^{V}O(bdt)_2]^-$,[17] in about 1% yield. The oxidation reactivity of $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ has been studied in detail by Ueyama et al.[35] In these studies, they showed that the stoichiometric reaction of $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ with air gives $[Mo^{V}O(bdt)_2]^-$ in 5% yield. Thus, the production of $[Mo^{V}O(bdt)_2]^-$ in ca. 1% yield is considered to be obtained by one-electron oxidation of the first main product $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ with O_2.

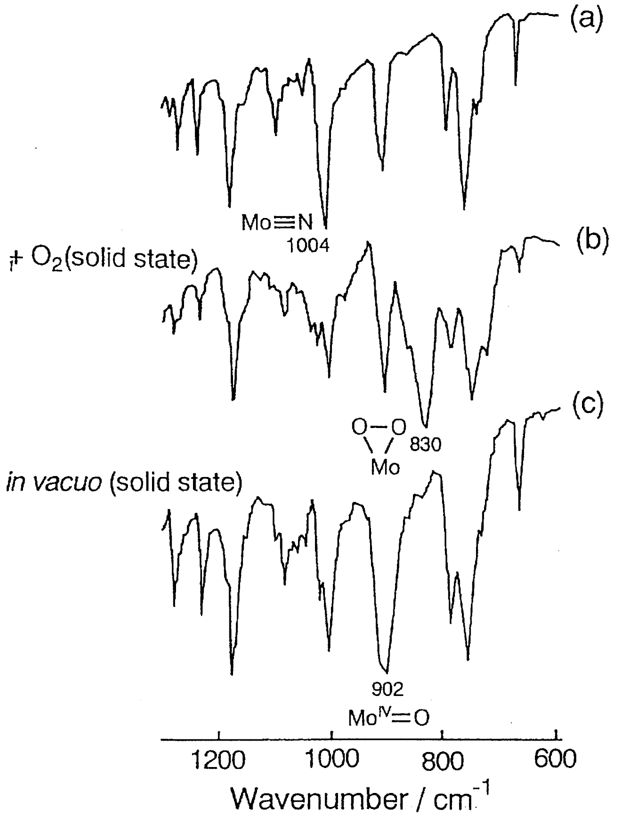


Fig. 4. IR spectra of $(NEt_4)_2[Mo^{VI}N(bdt)_2Cl]$ (**1**) (a), and the O_2-oxidized product before (b) and after (c) in vacuo.

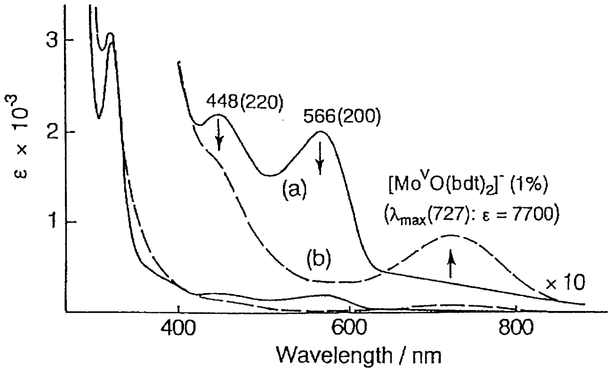
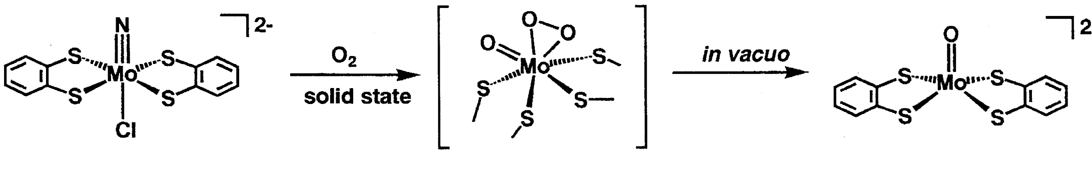


Fig. 5. Absorption spectrum change for the stoichiometric reaction of $(NEt_4)_2[Mo^{VI}N(bdt)_2Cl]$ (**1**) with O_2 gas in MeCN solution.



Scheme 3.

The reaction of **1** with excess oxygen gas in solution gives a diamagnetic yellow product. The yellow solution does not show any characteristic absorption band in the visible region. The finely separated multiplet ^{1}H NMR signals of the product at 7.1 and 6.9 ppm are quite close to those of the reaction solution of $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ with excess oxygen gas. These results show that the reaction between **1** and O_2 produces the $[Mo^{IV}O(bdt)_2]^{2-}$.

Reaction of $[Mo^{VI}NCl_4]$ with Oxygen Gas in Solution. For a comparison of the reactivity of **1**, the reaction of $(NEt_4)[Mo^{VI}NCl_4]$ with oxygen gas was carried out. This nitrido complex is fairly stable to O_2 gas compared to **1**. Although Dehnicke et al. reported that $[Mo^{VI}NCl_4]^-$ reacts with dry O_2 in boiling CH_2Cl_2 to produce $[Mo^VOCl_4]^-$,[28] the absorption-spectrum change of the CH_2Cl_2 reaction solution of the complex $(NEt_4)[Mo^{VI}NCl_4]$ with O_2 is almost negligible at room temperature for 1 h. The results show that the bdt ligand highly activates the reaction of the nitrido ligand with oxygen gas.

The Reaction of 1 with H_2O. Generally, a Mo-nitrido moiety is moisture sensitive. The addition of excess H_2O to the red-purple MeCN solution of **1** rapidly gave a yellow solution. IR spectrum of the orange powder obtained from the reaction solution is the same with that of $[Mo^{IV}O(bdt)_2]^{2-}$. The identification of the reaction product $(NEt_4)_2[Mo^{IV}O(bdt)_2]$ was also carried out by determining the cell parameter.[17] The results clearly indicate that the reaction of **1** with H_2O gives an oxomolybdenum(IV) complex $[Mo^{IV}O(bdt)_2]^{2-}$ similar to that in the reaction with O_2 gas.

Although the formation of N_2, NH_3, or other N compounds is expected as the fate of the nitrido ligand for reaction products of **1** with O_2 or H_2O, attempts to identify the produced small molecules using the mass spectrum were unsuccessful because of the intense background of nitrogen, water, and oxygen in the atmosphere. Dehnicke et al. have proposed that the nitrido ligand of $[Mo^{VI}NCl_4]^-$ changes to the N_2 molecule in a reaction with O_2.[28]

Conclusion

The nitridomolybdenum(VI) complex having two bdt ligands was synthesized, and characterized by Raman, IR, absorption, and NMR spectroscopic methods. This complex readily reacts with oxygen gas or H_2O to produce the oxomolybdenum(IV) complex $[Mo^{IV}O(bdt)_2]^{2-}$. The reactivity is higher than that of $(AsPh_4)[Mo^{VI}NCl_4]$. The observed higher reactivity is due to the competitive pπ-donation from S to dπ of Mo, which polarizes the $Mo^{VI}\equiv N$ bond.

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