AN ABSRACT OF THE THESIS OF

<u>Gyu Shik Kim</u> for the degree of <u>Doctor of Philosophy</u> in <u>Chemistry</u> presented on <u>February 24, 1989.</u> TITLE: <u>Synthesis, Properties, and Structural Characterizaton of</u> <u>Novel Oxo, Nitrido Molybdenum Compounds with Alkoxy and</u> <u>Siloxy Ligands</u> Abstract approved: <u>(Redacted for Privacy</u> Dr. Carroll W. DeKock

Oxomolybdenum(VI, V, IV), nitridomolybdenum(VI), and oxonitridomolybdenum(VI) compounds were synthesized using cocondensation reaction of MoO_3 with appropriate organosilanes. Polymeric dioxomolybdenum(VI) dialkoxides $MoO_2(OR)_2$ (R = Me, Et, Pr) were prepared by reacting MoO₃ with corresponding tetraalkoxysilanes. The reaction of MoO3 with trialkylalkoxy (aryloxy) silanes is believed to proceed via an intermediate, [MoO2(OSiR3)(OR')], evidenced by mass spectrometric results. $MoO_2(OPh)_2(py)_2$, $MoO_2(OSiMe_2(t-Bu))_2(py)_2$, and $Mo_3O_6(OSiMe_2(t-Bu))_4(py)_3$ were isolated from MoO_3/R_3SiOR' system. The cocondensation reaction of MoO_3 with Me_3SiNMe_2 yielded Mo(V)compound, $Mo_4O_4(\mu_3-0)_4(OSiMe_3)_4(HNMe_2)_4$. The compound is believed to be formed through the reduction/protonation of coordinatively unsaturated Mo(VI) intermediate. The solution synthesis using MoO_2Br_2 as an $Mo{0_2}^{+2}$ source confirmed this process. An X-ray diffraction study shows a novel cubane type structure with two localized Mo-Mo single bonds for the compound. The cocondensation reaction of ${\rm MoO}_3$ with HN(SiMe₃)₂ yielded two nitrido compounds, i.e., Mo₂(N)₂(OSiMe₃)₆-

 $(NH_3)_2$ and $Mo_4N_4O_2(OSiMe_3)_8(py)_4$. An X-ray diffraction study of $Mo_2(N)_2(OSiMe_3)_6(NH_3)_2$ reveals the molecule is composed of two fivecoordinate units and is the first example of a siloxo-bridged nitridomolybdenum(VI) dimer. The molecular structure of $Mo_4N_4O_2(OSiMe_3)_8^ (py)_4$ shows an Mo₄ skeletal tetrahedron bonded through symmetric μ_2 -0 and asymmetric μ_2 -N bridges which show bonding nature of the isoelectronic 0^{-2} and N^{-3} bridges in the same molecule. The solution reaction of $MoO_3 \cdot 2H_2O$ with $HN(SiMe_3)_2$ yielded only $Mo_2(N)_2(OSiMe_3)_6(NH_3)_2$ in high yield. The reactions of $Mo_2(N)_2(OSiMe_3)_6(NH_3)_2$ with pyridine and methanol yielded [MoN(OSiMe₃)₃(py)] and Mo₄(N)₄O₆(H₂O)₅(MeOH)₃ respectively. Variable temperature NMR studies show that $Mo_2(N)_2$ - $(OSiMe_3)_6(NH_3)_2$ and $[MoN(OSiMe_3)_3(py)]$ are fluxional, but the tetranuclear cage compound is rigid in solution. $Mo_4N_4O_2(OSiMe_3)_8(py)_4$ slowly disproportionates to give the fluxional [MoN(OSiMe₃)₃(py)] and an Mo(VI)-oxide-nitride-pyridine adduct. Thiol reduction reactions of $MoO_2(OR)_2$ (R = Me, Et) compounds generate oxomolybdenum(IV, V) alkoxide cluster compounds and the reactions were rationalized in terms of Mo=O_t \rightarrow Mo-OH and Mo-OR \rightarrow Mo-(ROH) conversion processes. The structural implications of these compounds are also discussed.

Synthesis, Properties and Structural Characterization

of

Novel Oxo, Nitrido Molybdenum Compounds with Alkoxy and Siloxy Ligands

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Contribution of Authors

The synthetic work on $MoO_2(OR)_2$ compounds, where R is Me, Et, n-Pr, and the cocondensation reaction of MoO_3 with Me_3SiOMe , Me_3SiO -t-Bu, and $(Me_3Si)_2O$ has been performed by Dr. David E. Huffman, a former graduate student of Dr. Carroll W. DeKock. The synthesis of $MoO_2(acac)_2$ from the $MoO_2(OEt)_2$ was also done by DEH. The work done by DEH is described in Chapter 2 together with the author's work.

The X-ray diffraction study of the cubane compound $Mo_4O_8(OSiMe_3)_4(HNMe_2)_4$ described in Chapter 3 has been exclusively performed by Dr. Douglas A. Keszler, the OSU Chemistry professor and X-ray crystallographer. Significant help has been given to the author in doing X-ray structure determinations on the nitridomolybdenum compounds by DAK. The X-ray results are described in Chapter 4.

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Synthesis, Properties and Structural Characterization

of

Novel Oxo, Nitrido Molybdenum Compounds with Alkoxy and Siloxy Ligands

CHAPTER 1.

General Introduction

Molybdenum is the most abundant transition metal in sea water, and the presence of water-soluble $[MoO_4]^{-2}$ and polymolybdates enables the incorporation of this element into living organisms.¹ In general, molybdoenzymes, other than the nitrogenase, are believed to contain an oxomolybdenum moiety which functions in redox processes as evidenced by molybdenum EXAFS (K-edge extended X-ray absorption fine structure) measurements.^{1,2} In addition, molybdenum ,as an oxide form, is one of the heavily used constituents of petrochemical catalysts.³ Usually, molybdenum oxide is dispersed in a metal oxide matrix such as silica, alumina, or titania to function as a catalyst.

In both of the above two areas, i.e., molybdoenzymes and catalysis, the oxidation states +6, +5, and +4 of the molybdenum moiety are involved. Certainly the synthesis and structural characterization of molybdenum compounds in its higher oxidation states with O, S, and N-containing ligands are necessary to understand the role of molybdenum in these systems.

In this laboratory, metal atom chemistry and cocondensation reactions have been explored for many years.⁴⁻⁹ During the study of the interaction of MoO₃ with small organic molecules,^{6,9} it was thought that the interaction of MoO₃ with organosilanes could generate molecular level oxomolybdenum siloxide (alkoxide) compounds.

In this thesis, the synthesis, characterization (including X-ray structural determination), properties, and reactivity studies of the oxo (nitrido) molybdenum compounds are presented. Brief considerations on the synthetic aspects of oxo (nitrido) molybdenum alkoxide (siloxide) compounds, properties of MoO_3 and its dihydrate, and the principles and techniques of the cocondensation reaction are described in this chapter. Subsequent chapters will deal with the synthesis and characterization of dioxomolybdenum dialkoxides (diphenoxide, disiloxide) (chapter 2), an oxo Mo(V) cubane compound (chapter 3), nitrido(oxo)molybdenum compounds (chapter 4). Finally, attempts to prepare tetranuclear oxomolybdenum alkoxide cluster compounds are discussed (chapter 5).

Synthetic Aspects of Oxo, Nitrido Molybdenum Alkoxides and Siloxides

As noted by Bradley in 1967, the metal oxide alkoxides $[MO_x(OR)_{y-2x}]_n$, where M is a metal of oxidation number y and R is an alkyl group, are polymeric compounds which bridge the gap between the oligomeric metal alkoxides $[M(OR)_y]_m$ and the macromolecular metal oxides $[M_2O_y]_{\infty}$.¹⁰ Similarly, the metal oxide trial-kylsiloxides $[MO_x(OSiR_3)_{y-2x}]_n$ may be regarded as intermediates between the oligomeric metal trialkylsiloxides $[M(OSiR_3)_y]_m$ and the mineral silicate macromolecules.¹⁰

The tendency of a metal to achieve the maximum coordination number in its higher oxidation states provides structural complexity for these oligomers. In the metal oxide alkoxide (siloxide) the situation is even more complex due to the bridging nature of the oxide and alkoxide (siloxide) ligands. See Figure 1.1. In addition, two more factors also govern the structural aspects of the oxide alkoxide (siloxide). One is the steric effect of the alkoxide (siloxide) ligand which controls the coordination polymerization. The other factor is the presence of multiply-bonded oxo group(s) which also hinders polymerization.

Oxygen can form three types of bonding toward a metal center as shown in Figure 1.1. In a formal sense, a metal-oxygen bond can be described as a triple, double, or single bond.¹¹ However, the real situation in the known compounds is not so simple. Indeed, M-O bond distances found in oxomolybdenum compounds reveal the complex nature

$$\vec{M} \stackrel{+}{\equiv} \vec{O} : \qquad \vec{M} = \vec{O} : \qquad \vec{M} - \vec{O} :$$
$$\sigma^2 \pi^4 \qquad \sigma^2 \pi^2 \qquad \sigma^2$$

 μ_2 μ_3 μ_6

MEN:	+ - M = N.	2+ 2- M - N:
$\sigma^2 \pi^4$	$\sigma^2 \pi^2$	σ^{2}



Figure 1.1. Metal-oxygen and metal-nitrogen bonding modes

of this bond.¹²⁻¹⁴ In addition, oxomolybdenum compounds show structural diversity depending on the choice of terminal or bridging oxo groups, metal oxidation state, bulkiness of the ligands, and the fulfillment of the coordination number.^{1,10,15-17} Figure 1.2 shows the structural variations for oxomolybdenum centers.¹

For molybdenum in group 6, the possible monomeric unit for metal (oxide) alkoxides (siloxides) are $Mo(OR)_y$, $MoO(OR)_{y-2}$, $MoO_2(OR)_{y-4}$ where y is the oxidation number of molybdenum. There are several synthetic methodologies in the preparation of (oxo) molybdenum alko-xides (siloxides) and some are described below.

(a) halide-alkoxide exchange reaction. For example, $Mo(OMe)_6$, including hexamethoxides of tungsten, uranium, and rhenium, was prepared using a cocondensation reaction of MF_6 with $Si(OMe)_4$ as shown in equation (1).¹⁸

 $MoF_6 + (MeO)_4Si \rightarrow Mo(OMe)_6 + (MeO)_3SiF$ (1)

(b) reaction of metal-metal bonded alkoxides or lower valent metal alkoxides with dioxygen.¹⁹ $MoO_2(OR)_2$ and $MoO(OR)_4$ compounds (R = t-Bu, i-Pr, t-BuCH₂) have been prepared by reacting $Mo_2(OR)_6$ (Mo=Mo) and [Mo(OR)₄]_x compounds respectively with molecular oxygen in hydrocarbon solution as shown below.

 $(RO)_{3}Mo \equiv Mo(OR)_{3} + O_{2} \rightarrow MoO_{2}(OR)_{2}$ (2)

 $[Mo(OR)_4] + O_2 \rightarrow MoO(OR)_4$ (3)

(c) addition of a silyl (siloxy) group over MoO_3 . $MoO_2(OSi(t-Bu)_3)_2^{20}$ and $(MoO_2(OR)_2)_X$,²¹ (R = Me, Et, Pr, Ph, (t-Bu)-Me₂Si) have been prepared using this method.



Figure 1.2. Structurally characterized oxomolybdenum centers.¹

ნ

$$MoO_3 + (t-Bu)_3SiOH \rightarrow MoO_2[OSi(t-Bu)_3]_2$$
(4)

$$MoO_3 + (RO)_4 Si \rightarrow [MoO_2(OR)_2]_{\chi}$$
(5)

(R = Me, Et, Pr)

$$MoO_3 + ROSiMe_3 \rightarrow [MoO_2(OR)_2]_{\times} (R = Ph)$$
(6)

$$MoO_3 + MeOSiMe_2(t-Bu) \rightarrow [MoO_2(OSiMe_2(t-Bu))_2]_{\chi}$$
(7)

(d) reaction of molybdate with bulky silanols.

 $MoO_3(OSiR_3)^-$ (R = t-Bu, Ph)²² were prepared by reacting $Mo_2O_7^{-2}$,²³ with appropriate silanols.

(e) exchange reaction of dialkylamido²⁴ group with an alkoxy group.

$$M-(NR_2) + ROH \rightarrow M-(OR) + HNR_2$$
(8)

 $Mo(OR)_4$ compounds (R = t-Bu, i-Pr, t-BuCH₂, Et) and $Mo(OSiR_3)_4$ -(HNMe₂)₂ (Me₃Si, Et₃Si) were prepared via this route using $Mo(NMe_2)_4$.²⁴ In addition, $Mo_2(OR)_6$ (Mo=Mo) compounds,²⁵ (R = t-Bu, i-Pr, t-BuCH₂, PhMe₂C, OC(CH₃)₂C(CH₃)₂O, Me₃Si, Et₃Si) are accessible through this route.

As described above there are two distinct categories for the syntheses of (oxo) molybdenum alkoxides, i.e., a metathetic ligand exchange or addition reaction, or an oxidation/reduction reaction of metal-metal bonded alkoxide compounds. The structural aspect of the (oxo) molybdenum alkoxides shows the subtle balance among the factors, such as bulkiness of the alkoxy ligand, the bridging nature of oxo, alkoxy groups, and the coordination number of the metal center. Furthermore, the overall geometry of the compounds is influenced

by metal-metal bonding²⁶ which is possible for molybdenum in +5or lower oxidation states. For example, $Mo_4O_8(0-i-Pr)_4(py)_4$ and $W_4(OEt)_{16}$ compounds,²⁷ reported by Chisholm et al. show a fused bioctahedral structure. $Mo_30(0-iPr)_{10}^{28}$ shows a triangulo Mo_30_4 core²⁹ structure. $Mo_6O_{10}(0-i-Pr)_{12}$ compound³⁰ (average oxidation state of Mo = 5.33) prepared via several routes shows a serpentine structure for which semi-bridging has been claimed between Mo and an alkoxy group with 2.88 (1) & interaction. The hexanuclear molybdenum alkoxide, $Mo_6(OMe)_{14}^{2-}$, ³¹ was structurally characterized to show an Mo_6 octahedron supported by 8 μ_3 -OMe and 6 terminal OMe groups with metal-metal bonding. Recently Chisholm et al. reported the preparation of Mo₄ cluster compounds, Mo₄(OMe)₂(O-i-Pr)₁₀, Mo₄(OR)₁₂ (R = CH₂-cyclohexyl, CH₂-i-Pr, CH₂-cyclopentyl, CH₂-cyclobutyl) by reacting Mo₂(O-t-Bu)₆ (Mo≡Mo) with corresponding alcohol.³² The rare examples of monomeric Mo(II) alkoxides are $Mo(0-iPr)_2(bpy)_2$ and Mo(O-t-Bu)₂(CO)₂(py)₂.^{33,34}

For metal-nitrogen bonding³⁵ in N-containing transition metal compounds, triple, double, and single bonds are possible as shown in Figure 1.1. However, a metal-bonded bare nitrogen (nitrido) shows a much stronger multiple bond character compared to that of terminally bonded oxygen. Metal-nitrogen bonds can be classified as terminal, doubly-bridging, and triply-bridging which are similar to M-O bonds.

Only a few nitrido molybdenum or tungsten alkoxides have been prepared as shown below: 36

 $MoNCl_3 + 3 LiO-t-Bu \rightarrow MoN(O-t-Bu)_3 + 3 LiCl$ (9)

 $MoN(O-tBu)_{3} + 3 ROH \rightarrow MoN(OR)_{3} + 3 t-BuOH$ (10) where R = Et, i-Pr, and t-BuCH₂

 $W_2(0-t-Bu)_6 + RCN \neq WN(0-t-Bu)_3 + W(\equiv CR)(0-t-Bu)_3 (11)$ where R = CH₃, Ph.

Recently a tetranuclear nitrido Mo (+4.25 average oxidation state) alkoxide $Mo_4N_2(0-i-Pr)_{12}$ has appeared in the literature. The X-ray structure shows a planar Mo_4N_2 structure with metal-metal bonds and T-shaped NMo₃ cores which are further supported by both terminal and bridging i-PrO groups.³⁷

Properties of Molybdenum Trioxide and its Dihydrate

Molybdenum trioxide is produced by roasting the molybdenum ore, molbdenite. High purity oxide (99.95%) is obtained by subliming the technical grade oxide.³⁹ The oxide is a white solid at room temperature, but turns yellow when hot and melts at 795°C to a deep yellow liquid.³⁹ A summary of molybdenum trioxide properties is given in Table 1.1. Molybdenum trioxide is soluble in excess alkali by forming molybdates, however, it is slightly soluble in water (0.49 g/L at 28°C) and is, in general, insoluble in common organic solvents.^{39,40}

 MoO_3 forms pale greenish yellow orthorhombic needle crystals with the directions of the largest and smallest dimensions, [0 0 1], and [0 1 0], respectively.⁴¹ The molybdenum atoms are surrounded by six oxygen atoms to form MoO_6 octahedron.⁴² The crystal has a layer structure

Formula weight	143.94
Color	White (yellow at elevated tempera- ture)
Density	Solid: 4.692 g/ml (21°C) Liquid: 3.08 g/ml (832°C) 2.98 g/ml (909°C)
Melting point	795°C (1068 K)
Heat of fusion	$\Delta H_{1068} = 12.54 \text{ kcal/mol}$ $\Delta H_{1074} = 11.69 \text{ kcal/mol}$
Heat of formation	$\Delta H_{298.15} = -178.1 \text{ kcal/mol} (crystals)$ $\Delta H_{1074} = -162.8 \text{ kcal/mol} (liquid)$
Boiling point	1155°C (1428 K) sublimes below this temperature
Heat of vaporization	(MoO ₃) ₃ ;∆H ₈₅₀ = 80.5 kcal/mol (MoO ₃) ₄ ;∆H ₈₅₀ = 93.6 kcal/mol (MoO ₃) ₅ ;∆H ₈₅₀ =105.6 kcal/mol
Heat of sublimation	∆H ₉₇₃ = 65 kcal/mol ∆H ₉₈₉ = 68.1 kcal/mol
Photosensitivity	sensitive to radiation < 360 nm

with the layers parallel to the [0 1 0] plane. Each layer is built up of two levels of distorted MoO₆ octahedra which are connected by sharing edges to form zigzag-shaped rows as shown in Figure 1.3.⁴³ The rows are mutually connected by corners to layers, which are placed on top of each other without having atoms in common. Therefore, three oxygen atoms are common to three adjacent octahedra, two 0 atoms are shared between two octahedra, and the sixth 0 atom is unshared. Although the MoO₆ octahedron is commonly thought to be an octahedron, it is highly distorted as shown in Figure 1.4. The Mo atom is off-center with a characteristic (2+2+2) coordination (pairs of bond distances are ca. 1.7, 1.9, 2.3 Å, respectively).⁴⁴

MoO₃ vaporizes without decomposition in contrast to the decomposition of most metal oxides which, in general, give metal or a lower oxide and dioxygen.⁴⁵ WO₃ and OsO₄ also show, in general, no decomposition when vaporized.^{45A} The major species observed in vaporization of MoO₃ consists of dimer, trimer, tetramer, and pentamer, with the trimer being the predominant species.⁴⁶ An electron diffraction study of MoO₃ vapor suggests the cyclic geometry of the trimer.⁴⁴ The structure of the trimer is believed to be a planar ring with D_{3h} symmetry and four coordinate molybdenum. The molybdenum atom is surrounded by two terminally-bonded oxygens at 1.67 Å and two doubly-bridging oxygens at 1.89 Å.⁴⁴ This four coordination renders reactivity toward ligands when cocondensed with a ligand matrix. The vapor pressure of the trimer at 861 K (588°C) is 1.64 x 10⁻⁶ atm. It was reported that the fractions of tetramer and pentamer are



Figure 1.3. Molybdenum trioxide viewed along [0 0 1], molybdenum atoms (small circles), unit cell is indicated by dashed lines.⁴³



Figure 1.4. The coordination of oxygen atoms (large circles) around the molybdenum atoms (small circles) in MoO₃. All atoms are situated on mirror planes perpendicular to the "c" axis. Not shown are the two angles (98° and 104°) which are symmetry-related to the others. increased at higher temperature.

Molybdenum trioxide dihydrate $MoO_3.2H_2O$ can be prepared from ammonium molybdate and nitric acid in a nearly quantitative yield. 47 Usually it takes 8-10 days to form the canary yellow crystalline solid. The X-ray crystallographic study on $MoO_3 \cdot 2H_2O^{48}$ shows two types of water molecule in the solid state. (see Figure 1.5) It consists of infinite layers parallel to [0 1 0]. Mo atoms are surrounded by five oxygen atoms and one coordinated water molecule. Each octahedron shares a corner with each of four adjacent octahedra within the layer. The octahedra forms characteristic zigzag rows within the layers, with alternating short and long average Mo-Ob bond distances of 1.77 and 2.16 Å in the direction of [1 0 1(-)], and 1.80 and 2.05 Å in the direction of [1 0 1]. Mo-O(terminal) and Mo-O(H₂O) bond distances are 1.69 and 2.29 Å respectively. The second water molecule is not bonded to molybdenum, but fills the interlayer voids with hydrogen bonding contacts. The interrelationship of this hydrate with MoO_3 ·H₂O and MoO_3 is given in Figure 1.6.



Figure 1.5. Crystal structure of molybdenum trioxide dihydrate. (a) asymmetric unit of the structure, (b) projection of the structure viewed along [0 0 1] plane.⁴⁸



Figure 1.6. Interrelationship of molybdenum trioxide hydrates and $$\rm MoO_3$$. Black circles denote $\rm H_2O.^6$

Vapor Synthesis and Cocondensation Reaction 49,50

"Vapor synthesis", "metal vapor synthesis(MVS)", and "metal atom synthesis" all refer to "the use in synthesis of high temperature gaseous species such as metal atoms by their reactions with themselves or other materials in a condensed phase" and the usage of the term may be broadly interpreted as "a use of gaseous species of any vaporizable reactants whether it is metal atom or any other diatomics or higher molecules or even polymers". This technique originated from the work of Pimentel and others in the late 1950s and has been used in synthesis of novel compounds which may not be accessible through conventional synthetic methods, and in matrix isolation spectroscopy (MIS).

The reactive vapor species can be generated at high temperature in vacuum and subsequently brought together with the ligands on a cold surface. The vapor species generated by this technique have virtually no kinetic barrier towards ligand addition. Even the reaction between the highly reactive vapor species frozen in an excess of ligand affords thermodynamically more favorable reaction conditions. See Figure 1.7.

As in the case of molybdenum trioxide, the reactivity of the solid state oxide with organic compounds is quite low and, in most of the cases, it is zero at room temperature. Indeed, for solid MoO_3 , the severe reaction condition and prolonged reaction times are essential.





The low reactivity of the solid-liquid heterogeneous reaction may be ascribed to the relatively low surface area and strong cohesive forces of the MoO₃ solid lattice. In contrast to this, the cocondensation reaction of molybdenum trioxide proceeds readily and may yield novel compounds or intermediates. It is not well understood at what stage the isolated products are formed, but, in general, it is believed that the reaction proceeds by forming several non-isolable intermediates either at the cocondensation temperature or upon warming the cocondensate.

The success of the cocondensation experiment depends critically on maintaining moderate vacuum $(10^{-4}-10^{-5} \text{ Torr})$ inside the reaction pot which enables continuous vaporization of the reactants and ligands. The reaction apparatus consists of the reaction pot in which reactant is vaporized, pumping system, pressure measuring instrument, and a cold bath which keeps the desired low temperature for the reaction pot. (see Cocondensation Apparatus section)

The vaporized reactants travel by essentially collision-free paths from the source to the cold wall of the reaction pot (the pot must be designed to allow this criterion; i.e., MFP \geq distance between heating source and pot wall) and finally condensed on the cold wall along with a large excess of ligand molecules (10 to 100fold) which allow dispersion of the reactant species to prevent aggeregation of the reactants. However, the frozen-out reactant in the ligand matrix cage cannot react with the ligand at such a low temperature (for example liquid nitrogen temperature, -196°C, 77 K)

and hence warm-up is needed to allow the reactant to interact with the ligand.

Further detailed accounts of the theoretical and practical considerations of the technique are well described in two excellent monographs, one by Blackborow and Young, and the other by Klabunde. 49 , 50

Cocondensation Reaction Apparatus

The cocondensation reactions are carried out in the pot shown in Figure 1.8.^{4,8} The pot is constructed of a Pyrex 2-L round bottom flask and a three-inch glass pipe flange. The pot is equipped with three ports and a removable top plate. A one-inch port is connected to a Consolidated Vacuum Corporation type PMC model 2C oil diffusion pump equipped with a CVC model VCS-21A high vacuum valve which is used for constant pumping on the system during the cocondensation reaction. A 3/8-inch port connected to a vacuum line is used for pumping of the volatile product and an inlet for dry inert gas, while the other 3/8-inch port, not shown in the drawing, is fitted with a Granville-Phillips model 274002 ionization gauge for pressure measurement during the reaction. Port connections are made using Cajon Ultra-Torr fittings. The top plate is vacuum fitted to the flange using an aluminum collar of which two grooves accomodate two O-rings for the interface sealing. A 1/8-inch copper tube, through which the ligand is introduced, and two water-cooled copper electro-



Figure 1.8. Schematic graving of the cocondensation reaction vessel.⁴,⁸

des are in the top plate which are insulated and vacuum-sealed with Teflon flanges and Buna-N O rings. Adequate dispersion of the ligand is obtained by placing a tee and many small holes in the 1/8-inch copper line.

Molybdenum trioxide is sublimed by resistive heating from a 10 mm diameter, 45 mm long niobium tube in which five 1.5 mm holes are punched. The tube is connected to the electrodes with stainless steel screws and washers. The power source is a Variable autotransformer (The Superior Electric Co, Type 1256D, Input 240 V, Output 0-280 V, 28 KVA) which steps down AC line voltage to a desired value and the line voltage is further controlled by means of a transformer (Electran Mfg. Co. Type H-7823B, Input 220 V, Output 10 V, 2 KVA).

During cocondensation, the walls of the flask are kept at -196° C with liquid nitrogen and the pressure in the pot was kept at less than 3 x 10^{-4} Torr to minimize vapor-vapor interactions. A distinct advantage of this pot is its size. It is large enough to produce millimole quantities of product, yet small enough to be easily transferred into the inert glovebox. This allows the isolation and study of non-volatile, air-sensitive reaction products. MoO₃ is usually cocondensed with the ligands in a mole ratio of 1:5 to 1:20 depending on the ligands involved. After reaction is complete and the cocondensate was warmed to room temperature, the volatile components, including unreacted excess ligand, are pumped off using the vacuum line and cold traps. The reactor is then filled with either dry nitrogen or argon, sealed, and finally taken into the

glove box (Vacuum Atmospheres Model HE-493-2) where the solid materials are physically removed for further work-up.

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CHAPTER 2

Preapration and Properties of Dioxomolybdenum Alkoxides, Phenoxides, and Siloxides Prepared by the Cocondensation Reaction of MoO_3 with Alkoxy or Aryloxysilanes^{1a}

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Abstract

This paper describes the preparation and properties of a number of dioxomolybdenum compounds prepared by the cocondensation reaction of MoO₃ with appropriate alkoxy- or (aryloxy)alkylsilanes. The compounds reported are MoO₂(OR)₂ (R = Me, Et, n-Pr, Ph), MoO₂(OR)₂-(py)₂ (R = Ph, (t-Bu)Me₂Si; py = pyridine), and Mo₃O₆(OSiMe₂(t-Bu))₄-(py)₃. The ¹H NMR, ¹³C NMR, infrared, and mass spectroscopic properties of the above compounds are reported. Attempts to prepare mixed alkoxide/siloxide compounds by the cocondensation reactions are also described.

Introduction

Molybdenum trioxide is one of the heavily used components in heterogeneous catalysis. Recently significant interest has been placed on the inorganic oxide attached metal catalysts.^{1,2} Bearing in mind these new generation catalysts, we explored the reaction chemistry of molybdenum trioxide with various organosilanes in the hope that possible precursor compounds could be obtained and furthermore some insight into molybdenum-oxide-alkoxide (siloxide) chemistry could be gained.

In recent years a number of the Mo(VI)-oxo-alkoxide (siloxide) compounds have been prepared. For example, Chisholm and coworkers have previously reported the preparation of $MoO_2(OR)_2$ compounds³ where R = t-Bu, i-Pr, and t-BuCH₂, all bulky groups, by the reaction of $Mo_2(OR)_6$ (Mo=Mo) with molecular oxygen, but isopropoxy and neopentoxy compounds were unstable in the solid state and hence were stabilized as nitrogen-base adducts. Weidenbruch and co-workers have also prepared $MoO_2(OSi(t-Bu)_3)_2$ by the reaction of tri-tert-butylsilanol with MoO_3 in a bomb reactor.⁴ Klemperer et al. have prepared $R_3SiOMoO_3^-$ (R = C_6H_5 , t- C_4H_9) by reaction of the appropriate silanol with (n-Bu₄N)₂(Mo₂O₇).⁵

About two decades ago Nebelung and Jahr reported the preparation of $(MoO_2(OEt)_2)(NH_3)_2$ by reacting MoO_2CI_2 with a stoichiometric amount of ethanol in ammonia-saturated benzene solution.⁶ However, they gave no physical measurements of the compound.

The instability of dioxo-Mo(VI) compounds bearing primary and secondary alkoxy groups suggests that the light congeners with simple primary alkoxy groups, $MoO_2(OR)_2$ (R = Me, Et, Pr) are all thermally sensitive and difficult to prepare by standard solution techniques. In this regard the cocondensation method^{7,8} is particularly appropriate for the preparation of these unstable compounds because many of the reactions of MoO_3 with precursor silanes occur below room temperature, which may allow the preparation of these compounds.

We have been interested in the preparation of oxo molybdenum compounds by the reaction of MoO₃ with small organic molecules.⁹ In this paper we describe the preparation and properties of a number of simple dioxomolybdenum compounds prepared by the cocondensation reaction of MoO₃ with appropriate alkoxy- or (aryloxy)silanes. The compounds reported here are MoO₂(OR)₂ where R = Me, Et, n-Pr, and Ph, and MoO₂(OR)₂(py)₂ where R = Ph, (t-Bu)Me₂Si and py = pyridine, and Mo₃O₆(OSiMe₂(t-Bu))₄(py)₃. We have also attempted to prepare mixed alkoxide/siloxide oxomolybdenum compounds which may be models for the surface catalytic oxidation reactions of alcohols by molybdenum oxides in silica supports, namely, the reaction of MoO₃ vapor with Me₃SiOMe, Me₂Si(OMe)₂, and Me₃SiO-t-Bu. The cocondensation reactions of MoO₃ with (Me₃Si)₂O and (Me₃Si)₂ are also reported.

Experimental

General Considerations. All manipulations were performed under argon or dinitrogen atmosphere in a Vacuum Atmospheres glovebox or on a high vacuum line. Schlenk techniques under dinitrogen were used when appropriate. Toluene was dried and deoxygenated by distilling from sodium benzophenone under dinitrogen. Methylene chloride was distilled from P_2O_5 under dinitrogen. Pyridine was dried over KOH and then distilled from BaO. All the silanes except trimethyl-<u>tert</u>-butoxysilane and <u>tert</u>-butyldimethylmethoxysilane were commercially available from Petrarch and used without further purification. Trimethyl-tert-butoxysilane was prepared by the reaction of tert-butyl alcohol (Baker) with trimethylchlorosilane (Aldrich) using N,N-dimethylaniline (Matheson Coleman and Bell) as the solvent and HCl acceptor. tert-Butyldimethylmethoxysilane was prepared in a similar manner using tert-butyldimethylchlorosilane (Petrarch) and methanol (Baker). The product was distilled from the reactant mixture and used without further purification. MoO₂ (Matheson Coleman and Bell) was used without futher purification. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

IR spectra were obtained on a Mattson Sirius 100 FT-IR or a Nicolet 5XDB FT-IR with 2 cm⁻¹ resolution. Solid samples were taken in KBr pellets unless otherwise specified. NMR spectra were taken on either a Varian FT-80A (¹H) or a Bruker AM-400 (¹H, 13 C) spectrometer. Gas chromatography/mass spectrometry (GC/MS) and mass spectrometry were performed on a Finnigan 4000-23 spectrometer with a 4500 ion source. Mass spectrometry was performed using pulsed-ion-positive-ion-negative-ion chemical ionization (PIPINICI) with methane as the secondary ion generator and by using a 70-100-eV ionization potential. Mass data based on 98 Mo for mononuclear species and on 96 Mo for dinuclear species are reported. Melting point determinations were done using the sealed-capillary method.

The cocondensation reactions were carried out in equipment that has previously been described.¹⁰ MoO_3 was sublimed from a resistively heated niobium tube with holes punched in from the upper side. Cocondensation occurred over a period from 0.5 to 1.5 h.

Yields based on MoO_3 condensed on the wall of the reactor were determined by taking the mass difference before and after the cocondensation reaction.

 $MoO_2(OMe)_2$. MoO_3 (5.55 g, 38.5 mmol) was cocondensed at 77 K with Si(OMe)_4 (31.5 g, 207 mmol). When the mixture was warmed to 323 K, a white solid formed. The volatiles were distilled from the solid. Analysis of the volatiles by GC/MS showed the major components to be unreacted Si(OMe)_4 and $(MeO)_3SiOSi(OMe)_3$. Trace amounts of methanol and poly(methoxysilanes) were also observed. The white solid was washed with 3 x 10 mL aliquots of dry toluene and vacuum-dried to give pale blue-white product (4.44 g). This was purified by sublimation at 393 K (5 x 10^{-3} Torr) to give a white solid (1.33 g) contaminated with traces of poly(methoxysilanes). Finally, the white

solid was washed several times with toluene and vacuum-dried to remove all traces of $(MeO)_3SiOSi(OMe)_3$ and poly(methoxysilanes). Yield: 18% based on MoO_3. It was shipped for analysis packed in dry ice under dinitrogen. Anal. calc: C, 12.64; H, 3.18; Mo, 50.49. Found: C, 12.94; H, 3.17; Mo, 49.93. 80-MHz ¹H NMR (pyridine-d₅ referenced to TMS): & 4.41(s,br). ¹³C NMR (pyridine-d₅ referenced to TMS): & 4.41(s,br). IR data: 522 (s), 596 (s), 927 (vs), 947 (vs), 997 (vs), 1088 (m), 1147 (m), 1457 (m), 2849 (m), 2975 (m) cm⁻¹. Mass spectral data m/z [% int, assgn]: 177 [100, MoO_3(OMe)⁻], 192 [62, MoO_2(OMe)_2⁻], 365 [11, Mo_2O_5(OMe)_3⁻], 380 [33, Mo_2O_4(OMe)_4⁻].

 $MoO_2(OEt)_2$. MoO_3 (2.78 g, 19.3 mmol) was cocondensed at 77 K with Si(OEt)_4 (19 g, 91 mmol). When the mixture was warmed to ambient temperature, a white solid formed. The volatiles were stripped from the solid to give a waxy white solid. Analysis of the volatiles by GC/MS showed the major components to be unreacted ligand and (EtO)_3SiOSi(OEt)_3. The solid was purified by sublimation at 373 K and 5 x 10⁻³ Torr, washed with 3 x 6 mL of dry toluene, and then vacuum-dried to remove all (EtO)_3SiOSi(OEt)_3 to give pure white solid (2.7 g, 12 mmol, 65% yield). It was shipped for analysis packed in dry ice under dinitrogen atmosphere. Anal. calc: C, 22.03; H, 4.62; Mo, 44.00. Found.: C, 21.74; H, 4.60; Mo, 44.07. 80-MHz ¹H NMR (in benzene-d₆, referenced to the solvent at 7.15 ppm) § 1.3 (br), 4.0 - 5.0 (br). ¹H NMR after addition of two equiv of pyridine/eqiv of $MoO_2(OEt)_2$ to benzene-d₆ solution: S 1.26 (t, 3H, CH₃), 4.65 (q, 2H, CH₂). IR data: 419 (vw), 476 (w), 481 (w), 567 (m), 633 (m), 819 (vs), 872 (m), 920 (m), 947 (s), 1027 (s), 1048 (s), 1087 (m), 1130 (w), 1159 (w), 1277 (vw), 1351 (w), 1357 (w), 1386 (m),1394 (m), 1442 (w), 1466 (w), 2871 (w), 2887 (vw), 2901 (w), 2930 (w), 2969 (m), 2988 (m) cm⁻¹. Mass spectral data m/z [% int, assgn]: 191 [17, MoO₃(OEt)⁻], 220 [100, MoO₂(OEt)₂⁻], 407 [1, Mo₂O₅(OEt)₃⁻], 436 [21, Mo₂O₄(OEt)₄⁻].

 $MoO_2(O-n-Pr)_2$. MoO_3 (4.04 g, 28.0 mmol) was cocondensed at 77 K with $(n-PrO)_4$ Si (24.4 g, 92 mmol). When the mixture was warmed to 323 K and the volatiles were stripped, a blue/white solid formed. A white solid was obtained in very low yield (less than 5%) by vacuum sublimation at 363 K and 5 x 10^{-3} Torr. IR data: 484 (m), 522 (s), 566 (s), 635 (s), 757 (m), 837 (vs), 881 (s), 945 (s), 993 (s), 1066 (s), 1380 (m), 1467 (m), 2876 (m), 2936 (m), 2967 (m) cm⁻¹. Mass spectral data m/z [% int, assgn]: 205 [3, $MoO_3(OPr)^-$], 248 [100, $MoO_2(OPr)_2^-$], 492 [7, $Mo_2O_4(OPr)_4^-$].

 $MoO_2(OPh)_2$ and $MoO_2(OPh)_2(py)_2$. MoO_3 (3.93 g, 27.3 mmol) was cocondensed at 77 K with Me_3SiOPh (32.27 g, 194 mmol). Warming to room temperature and stripping the volatiles at 316 K yielded a dark solid (6.8 g). Analysis of the volatiles by ¹H NMR spectroscopy showed unreacted starting ligand and $Me_3SiOSiMe_3$. A sample (2.9 g) of the crude product was dissolved in toluene (100 mL), and the

solution was filtered in the dry box. Half of the deep purple solution was vacuum-dried to give a dark solid (0.817 g) that was shown to contain $MoO_2(OPh)_2$ with a slight amount of other contaminants by ¹H NMR and IR spectroscopy. 80-MHz ¹H NMR in acetonitrile-d₃ (referenced to the solvent at 1.93 ppm): \$ 6.6-7.4 (m, br, PhO, 10 H), 2.33 (s, unknown impurity, 0.04 H), 0.26 (s, OSiMe₃, 0.4 H). IR data: 468 (m), 506 (m), 577 (m), 609 (s), 622 (s), 650 (s), 688 (s), 735 (s), 754 (vs), 811 (s,br), 844 (s), 875 (s), 962 (s), 1000 (w), 1022 (m), 1069 (m), 1122 (w), 1161 (s), 1212 (s), 1252 (sh), 1264 (sh), 1283 (w), 1451 (m), 1476 (s), 1484 (s), 1497 (m), 1585 (s), 2958 (w), 3062 (m).

To the other half of the deep purple toluene extract was added pyridine (5 mL), and the solution was stirred for 24 h. The solution turned from deep purple to greenish yellow during this time. The mixture was filtered and the solvent removed under vacuum, yielding a golden yellow crystalline solid (0.610 g, 1.29 mmol, 30% yield), $Mo(0)_2(OPh)_2(py)_2$. Anal. calc: C, 55.94; H, 4.27; N, 5.93; Mo, 20.31. Found: C, 55.12; H, 4.23; N, 5.13; Mo, 19.38. 400-MHz ¹H NMR (in CD₂Cl₂ referenced to the solvent at 5.32 ppm): & 6.88 (m, 1 H, <u>p</u>-H of PhO), 6.95 (m, 2 H, <u>o</u>-H of PhO), 7.22 (m, 2 H, <u>m</u>-H of PhO), 7.36 (m, 2 H, <u>m</u>-H of py), 7.80 (m, 2 H, <u>p</u>-H of py), 8.69 (m, 2 H, <u>o</u>-H of py). 100.614-MHz ¹³C NMR (in CD₂Cl₂ referenced to the solvent at 53.80 ppm): & 118.51 (C-2 of PhO), 121.26 (C-4 of PhO), 124.87 (<u>m</u>-C of py), 129.57 (C-3 of PhO), 138.64 (<u>p</u>-C of py), 150.03 (<u>o</u>-C of py), 163.42 (C-1 of PhO). IR data: 429 (w), 486 (w), 514 (w), 551 (vw), 563 (vw), 560 (m), 604 (m), 631 (m), 635 (m), 651 (w), 680 (m), 689 (s), 697 (s), 750 (s), 761 (s), 813 (w), 827 (m), 850 (s), 858 (m), 873 (w), 904 (vs), 932 (s), 997 (w), 1014 (m), 1022 (w), 1041 (m), 1068 (m), 1073 (m), 1152 (w), 1158 (w), 1168 (m), 1218 (s), 1249 (vs), 1279 (m), 1356 (w), 1384 (w), 1443 (s), 1447 (m), 1481 (vs), 1587 (s), 1603 (s), 1605 (s). Mass spectral data: No Mo-containing envelope was observed under CI or EI conditions.

 $MoO_2(OSiMe_2(t-Bu))_2(py)_2$. $Mo_3O_6(OSiMe_2(t-Bu))_4(py)_3$ (see below) was recrystallized from pyridine at 255 K to yield a yellow solution and a colorless, crystalline solid, $MoO_2(OSiMe_2(t-Bu))_2(py)_2$. Anal. Calc: C, 48.16; H, 7.35; N, 5.11; Mo, 17.49. Found: C, 48.27; H, 7.59; N, 5.06; Mo, 16.79. 80-MHz 1 H NMR (CD₃NO₂ referenced to the solvent at 4.33 ppm): & 0.04 (s, 6H, CH₃), 0.90 (s, 9H, <u>t</u>-Bu), 7.45 (m, 2H), 7.88 (m, 1H), 8.55 (m, 2H). 100.614-MHz ¹³C NMR (CD₃NO₂) referenced to the solvent at 62.80 ppm): S -3.41, 20.37, 26.50, 125.84, 139.02, 150.61. IR data: 419 (w),436 (m), 458 (w), 472 (w), 493 (m), 511 (s), 585 (m), 628 (s), 652 (w), 666 (m), 674 (s), 700 (vs), 755 (vs), 775 (vs), 833 (vs), 876 (vs), 898 (vs), 912 (vs), 939 (s), 948 (s), 957 (s), 983 (m), 1005 (m), 1011 (m), 1039 (s), 1076 (s), 1156 (m), 1216 (s), 1220 (m), 1246 (vs), 1313 (vw), 1319 (vw). Mass spectral data m/z [% int, assgn]: 335 [2, (392-t-Bu)⁻], 377 [2, (392-CH₃)⁻], 392 [100, MoO₂(OSiMe₂(t-Bu))₂⁻], 780 [1, $Mo_2O_4(OSiMe_2(t-Bu))_4$].

Mo₃O₆((OSiMe₂(t-Bu))₄(py)₃. MoO₃ (2.05 g, 14.2 mmol) was cocondensed with (t-Bu)Me₂SiOMe (11.70 g, 80.0 mmol) at 77 K. A white-green powdery solid (2.40 g) was recovered after pumping off the volatiles. All of the solid was dissolved in toluene (60 mL) and the mixture was filtered through a fine frit to give a green solution. To this solution was added pyridine (12 mL, 148 mmol). A blue precipitate formed immediately and was filtered off from the mixture to give a light yellow solution. The solvent was removed from the solution by vacuum distillation to give a tan solid (0.86 g) which by elemental analysis and spectroscopic characterization is $Mo_3O_6(OSiMe_2(t-Bu))_4(py)_3$. Anal. Calc: C, 40.87; H, 6.60; N, 3.67; Mo, 25.11. Found: C, 40.79; H, 6.65; N, 3.69; Mo, 25.20. 400-MHz ¹H NMR (in CD₃NO₂ referenced to the solvent at 4.33 ppm): S 0.11 (s, 8H, CH₃), 0.92 (s, 12H, t-Bu), 7.52 (m, 2H), 7.96 (m, 1H), 8.59 (m, 2H). 100.614-MHz $^{13}\mathrm{C}$ NMR (CD_3NO_2 referenced to the solvent at 62.80 ppm): -3.4, 20.3, 26.4, 126.3, 140.4, 149.9. IR data: 507 (w), 546 (w), 567 (m), 584 (w), 609 (w), 634 (m), 678 (s), 697 (s), 759 (s), 778 (vs), 804 (s), 821 (vs), 836 (vs), 893 (vs), 915 (vs), 948 (s), 986 (s), 1012 (m), 1019 (m), 1042 (m), 1070 (m), 1155 (w), 1218 (m), 1251 (s), 1361 (m), 1389 (m), 1405 (m), 1448 (s), 1464 (m), 1471 (s), 1486 (m), 1534 (w), 1606 (m), 1636 (w), 1857 (vw), 1924 (vw), 2710 (vw), 2739 (vw), 2771 (vw), 2803 (w), 2824 (w), 2857 (s), 2884 (m), 2895 (m), 2929 (s), 2953 (s), 3072 (w), 3108 (w), 3135 (w), 3214 (w) cm^{-1} . Mass spectral data m/z [% int, assgn]: 392 [100, MoO₂(OSiMe₂(t-Bu))₂⁻], 466 [6, MoO₂(OSiMe₂(t-Bu))₂(OSiMe₂)⁻],

780 [4, $Mo_2O_4(OSiMe_2(t-Bu))_4^{-}]$.

Reaction of MoO₃ with Me₃SiOMe. MoO₃ (2.41 g, 16.7 mmol) was cocondensed at 77 K with Me₃SiOMe (25.0 g, 240 mmol). The cocondensate was warmed to 298 K over a period of 1 h. A pale greenish yellow solid formed on the wall, and white solid on the bottom of the flask. After the volatiles were stripped, a small fraction of the white solid (50 mg) was separated for a separate analysis. The remainder of the crude material (4.50 g) was recovered. GC analysis of the volatiles showed starting ligand, hexamethyldisiloxane, and a few trace impurities. Sublimation (373 K, 5×10^{-3} Torr) led to recovery of a powdery white solid (30 mg). The decomposition products from the sublimation were a dark blue solid and volatile components shown to be starting ligand (26 mol %), hexamethyldisiloxane (22 mol %), methanol (42 mol %), dimethoxymethane (9 mol %), methylformate (2 mol %), dimethylether (trace), and a trace of formaldehyde shown by GC/MS and 1 H NMR spectroscopy. The white solid from either the reaction pot or sublimation slowly decomposes at ambient temperature and is also sensitive to light. The compound decomposes very rapidly in DMSO and over the course of a few hours in pyridine at ambient temperature but is stable in pyridine at 255 K for more than 1 week. The decomposed product is solely starting ligand confirmed by ¹H NMR spectroscopy. 80-MHz ¹H NMR (pyridine-d₅ referenced to TMS): S 0.26(br), 0.33(br), 4.47 (vbr, fwhh = 12.8 Hz), 5.0(vbr). IR data: 492 (w), 539 (w), 570 (m), 634 (w), 692

(w), 754 (w), 828 (s), 844 (m), 902 (m), 944 (m), 960 (m), 1008 (m), 1250 (m), 1445 (m), 2827 (m), 2899 (w), 2932 (m), 2959 (m) cm⁻¹. Mass spectral data m/z [% int, assgn]: 250 [12, $MoO_2(OMe)(OSiMe_3)^-$], 308 [100, $MoO_2(OSiMe_3)_2^-$], 382 [4, $MoO_2(OSiMe_3)_2(OSiMe_2)^-$], 496 [0.1, $Mo_2O_4(OMe)_2(OSiMe_3)_2^-$].

¹H NMR spectrum of a pyridine-d₅ solution of this crude white solid showed approximately a 1:1 group ratio between methoxy and siloxy groups bound to Mo. The ¹H NMR spectrum of a pyridine-d₅ solution of the white sublimate showed the ratio 1:1.6 for MeO:Me₃SiO. The IR spectrum of the sublimate is exactly the same as that of the white solid from the reaction pot except for minor differences in the CH₃ bending region (1320-1470 cm⁻). The pale greenish yellow crude solid in pyridine-d₅ showed by ¹H NMR spectroscopy a group ratio of 2:1 for MeO:Me₃SiO.

Reaction of MoO_3 with $Me_2Si(OMe)_2$. MoO_3 (3.35 g, 23.3 mmol) was cocondensed at 77 K with $Me_2Si(OMe)_2$ (26.05 g, 217 mmol). The cocondensate was warmed to ambient temperature, and a crude material (4.82 g) was recovered. ¹H NMR spectrum of the solid in benzene-d₆ gave a complex series of resonances: S = 0.2-0.5 ($Me_2SiO-Mo$), 3.3-3.5 (MeO-SiO-Mo), and 4.0-4.7 (MeO-Mo). IR data: 418 (m), 563 (s), 704 (m), 803 (vs), 856 (s), 926 (vs), 936 (vs), 953 (vs), 969 (vs), 995 (vs), 1055 (s), 1092 (s), 1262 (s), 1384 (m), 1401 (m), 1435 (m), 1451 (m), 2834 (m), 2906 (m), 2942 (m), 2962 (m).

The group ratio between methoxy and dimethylsiloxy is 1.3:1 by $^{1}\mathrm{H}$ NMR spectroscopy.

Pyrolysis of the Crude Solid. A sample of the crude solid (280 mg) was pyrolyzed at 407 K for 1 h under an argon blanket to yield blue solid (218 mg) and colorless liquid trapped in a liquid-nitrogen-cooled U-tube. The mass difference 61 mg corresponds to 22 wt % loss. The volatiles were vacuum-transferred into an NMR tube. The volatiles by ¹H NMR spectroscopy were shown to be mostly starting ligand with a trace amount of methanol and other uniden-tified poly(methoxysilanes).

Reaction of MoO_3 with Me_3SiO -t-Bu. MoO_3 (5.37 g, 37 mmol) was cocondensed at 77 K with trimethyl-<u>tert</u>-butoxysilane (29.62 g, 202 mmol). When the mixture was warmed to 313 K, the solid changed from yellow to blue. GC analysis of the volatiles distilled from the cocondensate gave a mixture of isobutene, tert-butyl alcohol, hexamethyldisiloxane and starting ligand with trace amounts of <u>cis</u>-butene, <u>trans</u>-butene, and 1-butene. No sublimable product was obtained from the solid.

Reaction of MoO_3 with $(Me_3Si)_2O$. MoO_3 (4.74 g, 32 mmol) was cocondensed at 77 K with $(Me_3Si)_2O$ (25.00 g, 154 mmol). When the reactor was warmed to 293 K, the solid cocondensate changed from yellowish white to greenish blue. The volatiles were stripped and showed starting ligand only. No sublimate was collected on heating to 453 K (5 \times 10⁻³ Torr) under vacuum.

Reaction of MoO₃ with $(Me_3Si)_2$. MoO₃ (2.609 g, 18.12 mmole) was cocondensed at 77 K with $(Me_3Si)_2$ (25.0 g, 170 mmole). When the reactor was warmed to 293 K, white cocondensate changed to dark blue. Stripping of the volatiles gave dark blue solid (2.608 g). The solid was not soluble in benzene, toluene, and methylenechloride. The volatiles collected were shown to be unreacted starting ligand by ¹H NMR spectroscopy.

Preparation of Molybdenum(VI) dioxide-2,4-pentanedionate. $MoO_2(OEt)_2$ (100 mg, 0.46 mmole) was partially dissolved in toluene (30 ml). A solution of 2.4-pentanedione (100 µl, 0.97mmol) in toluene was added dropwise to the solution of $MoO_2(OEt)_2$ at room temperature. The resulting greenish solution was stirred for 2 h at room temperature. The solvent was stripped, yielding a yellow-green solid which was shown to be $MoO_2(acac)_2$ by IR^{11} and ¹H NMR spectroscopy. The reaction was quantitative and complete within 15 minutes, which was confirmed by ¹H NMR spectroscopy. One mole of ethanol was liberated per mole of Hacac consumed.

Preparation

A standard 2-L metal vapor reactor was used which has been previously described.¹⁰ MoO₃ vapor was deposited with the appropriate alkoxy- or (aryloxy)alkylsilane on the reactor wall, which was cooled with liquid nitrogen. Reaction occurred as the reactor was brought to ambient temperature. In the case of the tetraalkoxysilanes analysis of the products confirms the reaction to be

 $MoO_3(g) + 2 Si(OR)_4 \rightarrow MoO_2(OR)_2 + (RO)_3SiOSi(OR)_3$ for R = Me, Et and Pr.

The reaction is quite efficient with yields of 75 to 80% of crude material based on MoO_3 deposited on the wall of the reactor.

For R = Ph, the silicon precursor of choice was Me_3SiOPh with the reaction

 $MoO_3(g) + 2 Me_3SiOPh \rightarrow MoO_2(OPh)_2 + (Me_3Si)_2O$

The reaction is quantitative with slight contamination of a Mo-oxo-siloxy compound. Work-up in pyridine yielded the pyridine adduct $MoO_2(OPh)_2(py)_2$.

For R = $(t-Bu)Me_2Si$, the ligand used was $(t-Bu)Me_2SiOMe$. In this case the ¹H NMR spectrum of the crude cocondensed material in benzene-d₆ shows a complex series of resonances in the siloxy region, which indicates a number of different types of molybdenum siloxy groups.

A mass spectrum of the crude material shows all three of the basic dioxo products; $MoO_2(OSiMe_2(t-Bu))_2$, $MoO_2(OSiMe_2(t-Bu))(OMe)$,

and $MoO_2(OMe)_2$. See Figure 2.3. Extraction of this mixture in toluene gave a dark green solution and an insoluble dark brown solid. Addition of 10 equiv of pyridine to the toluene extract led to the isolation of $Mo_3O_6(OSiMe_2(t-Bu))_4(py)_4$. Further addition of pyridine to a toluene solution of this compound followed by crystallization gave the dioxo compound $MoO_2(OSiMe_2(t-Bu))_2(py)_2$. Alternatively, $MoO_2(OSiMe_2(t-Bu))_2(py)_2$ may be obtained by recrystallization the multinuclear compound in pure pyridine:

$$Mo_{3}O_{6}(OSiMe_{2}(t-Bu))_{4}(py)_{3} \rightarrow MoO_{2}(OSiMe_{2}(t-Bu))_{2}(py)_{2}$$

+ yellow soln.

Solution and Physicochemical Properties

 $MoO_2(OMe)_2$ is a white solid that may be sublimed at 393 K (5 x 10^{-3} Torr) in approximately 30% yield. It is moderately stable under dry nitrogen at 273 K but slowly decomposes at room temperature to blue molybdenum oxides. Rapid decomposition occurs when the solid is exposed to moisture. It is insoluble in hydrocarbon solvents but modestly soluble in dimethyl sulfoxide and pyridine. The ¹H NMR spectrum (80 MHz) shows a broad single resonance at 4.40 ppm (fwhh = 8 Hz), but ¹³C NMR shows two very broad resonances centered at 64 and 68 ppm.^{12,13} The half-width suggests the compound to be oligomeric even in pyridine, and ¹³C NMR data suggests two types of Mo-bound methoxy groups are present.

 $MoO_2(OEt)_2$ is a white solid that may be sublimed at 368 K (5 x 10^{-3} Torr) in approximately 90% yield. It can be stored at 253 K for long periods under dry nitrogen but slowly decomposes at ambient temperature to yield a blue solid. Rapid decomposition occurs when exposed to moisture. It is modestly soluble in aromatic solvents and moderately soluble in pyridine and dimethyl sulfoxide. The ¹H NMR spectrum of $MoO_2(OEt)_2$ in d₆-benzene is shown in Figure 2.1a. The broad resonance at 1.3 ppm is assigned to the methyl group, while those between 4.0 and 5.0 ppm are assigned to the methylene protons of the ethoxy group. Addition of two equiv or more of dimethylsulfo-xide-d₆ or pyridine-d₅ resulted in the typical ethoxy spectra shown in Fig 2.1b,c, a result of the ability of a coordinating base to break up the polymers in benzene solution to form a monomeric pyridine adduct.

 $MoO_2(OPr)_2$ is a white powder which may be sublimed at 358 K (5 x 10^{-3} Torr) in very low yield. It is very unstable, decomposing in a few hours at ambient temperature to the blue molybdenum oxides. Decomposition occurs in seconds with exposure to atmospheric moisture.

MoO₂(OPh)₂ is a dark solid, very soluble in aromatic hydrocarbons, pyridine, and moderately soluble in acetonitrile. It is stable under dinitrogen at room temperature. It slowly decomposes when exposed to moisture.



Figure 2.1. 80 MHz ¹H NMR Spectra of $MoO_2(OEt)_2$. (a) in benzene-d₆, (b) in DMSO-d₆/benzene-d₆, (c) in pyridine-d₅ (the same spectrum was obtained in pyridine-d₅/benzene-d₆ solution).

MoO₂(OPh)₂(py)₂ is a golden yellow microcrystalline solid which decomposes upon heating to 376 K. It is stable under dry nitrogen at room temperature, but slowly decomposes upon exposure to moisture. It is soluble in aromatic hydrocarbons, and moderately soluble in dichloromethane, nitromethane, and pyridine.

 $MoO_2(OSiMe_2(t-Bu))_2(py)_2$ is a colorless crystalline compound that melts at 347K. It is soluble in aromatic hydrocarbons, dichloromethane, nitromethane, and pyridine. It is stable under dry nitrogen at ambient temperature and decomposes slowly when exposed to moisture.

 $Mo_3O_6(OSiMe_2(t-Bu))_4(py)_3$ is a tan solid that decomposes very slowly at ambient temperature. It is soluble in aromatic hydrocarbons and nitromethane. It decomposes slowly when exposed to moisture.

Mass Spectra. All the compounds were examined by mass spectrometry using direct insertion with chemical ionization. All compounds, except $MoO_2(OPh)_2$ and its pyridine adduct, show a monomeric molecular ion. See Figure 2.2. For $MoO_2(OPh)_2(py)_2$ no Mo-containing envelope was observed under CI or EI conditions. All of the pyridine adducts lose the Lewis base in the vapor state. The compounds, including pyridine adducts, show a molecular dimer ion. Significant concentration of dimeric ions suggests the compounds are polymeric in the



Figure 2.2. PIPINICI mass spectrum of MoO₂(OSiMe₂(Bu^t))₂(py)₂.

solid state. In general, two distinct types of ions were observed for either mononuclear or dinuclear ions, i.e., $MoO_3(OR)^-$ and $MoO_2(OR)_2^-$ (MoO_4 skeleton) for mononuclear ions, and $Mo_2O_5(OR)_3^-$ and $Mo_2O_4(OR)_4^-$ (Mo_2O_8 skeleton) for dinuclear ions. The mononuclear MoO_4^- species is expected to have a tetrahedral structure, and the dinuclear Mo_2O_8 species, the edge-sharing square-pyramidal structure.

Infrared Spectra. All alkoxy compounds show the expected resonances in the C-H stretching region around 2900 $\rm cm^{-1}$ and C-H bending region around 1450 cm^{-1} . The 800-1150 cm^{-1} region is particularly rich. This region contains the C-O stretch in the 1000 -1150 \mbox{cm}^{-1} region but more importantly the Mo=0 $_{\rm t}$ stretching frequencies from 800 to 1000 $\rm cm^{-1}$. Closer examination of the spectra of the polymeric $MoO_2(OMe)_2$, $MoO_2(OEt)_2$, and $MoO_2(O-n-Pr)_2$ compounds reveal the common, strong to medium absorption bands around 947, and 920 ${\rm cm}^{-1},$ which are assignable to $Mo=0_+$ stretchings of <u>cis</u>-dioxomolybdenum(VI) compounds.¹⁴⁻¹⁶ Also, all of the spectra show two bands from 520 to 635 cm^{-1} , which probably arise from the Mo-O stretching vibrations of alkoxy groups 17, 18 in the solid state. The methyl, ethyl and n-propyl groups are not sterically demanding; hence, the compounds are expected to exist as polymers in the solid state. IR spectrum of $MoO_2(OMe)_2$ reveals a broad, strong peak at 997 cm⁻¹, which assignable to bridging (C-O) stretches along with a medium shoulder at 1088 cm^{-1} . In contrast, the spectrum of MoO₂(OEt)₂ shows very strong, broad band at 819 cm⁻¹, which is assignable to $\nu(\text{Mo=O}_+ \rightarrow \text{Mo})^{19}$

together with ν (C-O) at 1027, 1048, 1087 cm⁻¹ assigned to bridging and terminal ν (C-O). IR spectrum of MoO₂(OPr)₂ shows ν (Mo=O_t+Mo) at 837 (vs,br), and ν (C-O) at 993 and 1066 cm⁻¹ respectively. Based on these results, MoO₂(OMe)₂ in solid state appeared to be polymerized exclusively through methoxy bridges, however, for ethoxy and propoxy analog, the compounds are polymerized through both bridging alkoxy and Mo=O_t+Mo interaction.

Discussion

 MoO_3 solid consists of molybdenum coordinated to six oxygens, forming an MoO_6 distorted octahedron. The molybdenum is off center with a characteristic (2+2+2)-coordination with bond lengths of ca. 1.7, 1.9, and 2.3 Å.²⁰ The vapor sublimes without decomposition to yield the cyclic dimer, trimer, tetramer and pentamer with the trimer being the predominant species.²¹ In the trimer each molybdenum is surrounded by two terminal oxygens (Mo-O = 1.67 Å) and two bridging oxygens (Mo-O = 1.89 Å) in a tetrahedral arrangement.²⁰

Cocondensation of an $R_n Si(OR')_{4-n}$ (n = 0, 2, 3) into MoO₃ at 77 K is expected to yield a molybdenum adduct with the organosilane coordinated to the molybdenum center through the ether oxygen. Cleavage of the organosilane occurs upon warming to ambient temperature, through either the C-O or Si-O bond to give the final product. This is in sharp contrast to codeposition of either organic ethers or silicon ethers for which an adduct forms but no further cleavage occurs.⁹ For the tetraalkoxysilanes one driving force for the reaction is the formation of the good leaving group, the hexaalkoxydisiloxane. In general, we have found that organosilanes, which are prone to hydrolysis, react readily in cocondesation reactions with MoO₃, a consequence of the Lewis acid character of the Mo(VI) center. No reaction occurs for the cocondensation of MoO₃ with (Me₃Si)₂, a compound having a comparatively weak Si-Si bond (80.5 kcal mol⁻¹)²² but not prone to hydrolysis. Also, no reaction was observed for the $MoO_3/(Me_3Si)_2O$ system.

The isolated product for the cocondensation reaction of MoO_3 with trialkylalkoxysilanes (R_3SiOR') is very dependent on the particular silane and workup conditions. In this case, the mass spectral data of the initial crude product indicate that all of the species are formed; $MoO_2(OR')(OSiR_3)$, $MoO_2(OSiR_3)_2$, and $MoO_2(OR')_2$. (Figure 2.3) The compound $MoO_2(OSiMe_2(t-Bu))_2$ could only be isolated as the pyridine adduct. Therefore, for $MoO_2(OSiMe_2(t-Bu))_2$, it appears that the more toluene-soluble species is isolated because $MoO_2(OMe)_2$ is insoluble in toluene and, by inference, the compound $MoO_2(OSiMe_2(t-Bu))(OMe)$ is only sparingly soluble in the solvent. ¹H NMR spectrum of the toluene extract indeed shows no methoxy resonance.

The cocondensation reaction of MoO₃ with $(t-Bu)Me_2SiOMe$ gives a more complicated chemical system than is implied by the above discussion. In addition to isolating MoO₂(OSiMe₂(t-Bu))₂(py)₂, we have also isolated Mo₃O₆(OSiMe₂(t-Bu))₄(py)₃ and have spectroscopic evidence for Mo₃O₅(OSiMe₂(t-Bu))₆(py)₂. The latter two compounds are isolated under addition of limited amounts of pyridine to the toluene solution and may be viewed as a combination of coordinatively unsaturated Mo(VI) and Mo(IV) fragments presumably through Mo=0 \rightarrow Mo interaction. This view may be supported by the observation that MoO₂(OSiMe₂(t-Bu))₂(py)₂ was obtained as a colorless crystalline solid from Mo₃O₆(OSiMe₂(t-Bu))₄(py)₃.

The cocondensation reaction of $\rm Me_3SiOPh$ with $\rm MoO_3$ appears to be far simpler with the crude reaction product showing, by $^1\rm H$ NMR spec-



Figure 2.3. PIPINICI mass spectrum for MoO₃/t-BuMe₂SiOMe cocondensate.

troscopy, $MoO_2(OPh)_2$ and $(Me_3Si)_2O$ with only trace amounts of other contaminants. This shows phenoxide to have a stronger affinity for the Mo(VI) center than does the trimethylsiloxy group. Furthermore, the reaction is enhanced by the formation of a good leaving group, i.e., hexamethyldisiloxane.

The cocondensation reaction of Me_3SiOMe with MoO_3 is expected to give $MoO_2(OSiMe_3)(OMe)$ along with the symmetric products $MoO_2(OMe)_2$ and $MoO_2(OSiMe_3)_2$.

Mass spectral data for the crude product indeed show the possible monomeric fragment ions, which indicates both methoxy and siloxy groups are actually incorporated in the cocondensate. The $^{1}\mathrm{H}$ NMR spectrum of the crude product in pyridine- d_5 shows very broad, methoxy peaks at 4.5 (fwhh = 12.8 Hz) and 5.0 ppm along with two broad siloxy peaks at 0.26 and 0.33 ppm. The broadness of the peaks suggests that the compound does not dissociate totally even in pyridine, a powerful coordinating agent. The total ratio of groups between MeO and Me₃SiO in the crude solid is approximately 2, which indicates more methoxy groups are incorporated in the crude product and is consistent with the observation that hexamethyldisiloxane was formed from the cocondensation reaction as indicated by $^{1}\mathrm{H}$ NMR spectroscopy and GC/MS. Attempts to purify the compound by vacuum sublimation were unsuccessful. Most of the product decomposed to give a blue molybdenum oxide residue and volatiles along with a trace amount (approximately 1 % by weight) of a white solid. The $^1\mathrm{H}$ NMR spectrum of this white sublimate in pyridine-d5 shows more siloxy

groups relative to methoxy group (the ratio is 1.6). This suggests that the dioxodisiloxomolybdenum(VI) fragment is more volatile than the methoxy counterpart and that the stoichiometric dioxomethoxysiloxymolybdenum(VI) compound could not be obtained by sublimation.

It is interesting to note that $MoO_2(OSiMe_3)(OMe)$ product is much less thermally stable than $MoO_2(OMe)_2$. Easy formation of hexamethyldisiloxane without reduction is probably one of the reasons. The solution decomposition is particularly facile, giving primarily starting ligand and presumably MoO_3 as a white precipitate. The thermal decomposition in the solid state (363 K, 1 × 10⁻⁴ Torr) gives starting ligand (26 mol %), hexamethyldisiloxane (22 mol %), methanol (42 mol %), dimethoxymethane (9 mol %), methylformate (2 mol %), formaldehyde (trace), and dimethylether (trace). It is interesting to note that the solid state decomposition shows a diverse product distribution compared to that of solution decomposition. Apparently, the presence of excess methoxy groups accompanied by the ease of reduction of Mo=O moiety at elevated temperature may accounts for this discrepancy.

The cocondensation reaction of $Me_2Si(OMe)_2$ with MoO_3 was studied. Reaction readily occurs on warming to room temperature. The ¹H NMR of the crude material in benzene-d₆ gave a complex series of resonances in the methoxy region, from 3.3 to 3.5 ppm (methoxy bonded to Si) and from 4.0 to 4.7 ppm (methoxy bonded to Mo), and in the alkylsiloxy region from 0.2 to 0.5 ppm. This indicates the formation of many products involving Mo-OMe and Mo-O-Si units. Of interest is that

volatiles from thermal decomposition of the crude product were shown to be primarily starting material, $Me_2Si(OMe)_2$ rather than oxidized products of the methoxy ligand as was observed for the thermal decomposition of the product from the reaction of Me_3SiOMe and MoO_3 . This may be ascribed to the inability to form disiloxane by the Me_2Si groups in a localized environment.

¹H NMR data of all of the compounds (except pyridine adducts) studied here show them to be polymeric in noncoordinating solvents. Pyridine serves as an excellent coordinating agent, and solvent, and breaks down the polymers in solution for all except $MoO_2(OMe)_2$, and the nonstoichiometric crude products from the MoO_3/Me_3SiOMe and the $MoO_3/Me_2Si(OMe)_2$ systems, which still display polymeric behavior in pyridine. A dramatic change in the ¹H NMR spectrum is shown in Figure 2.1, for which the addition of two equiv or more of coordinating agent to a benzene solution of $MoO_2(OEt)_2$ gives the characteristic sharp ethoxy resonances.

It is interesting to note that, while Chisholm et al. have isolated $MoO_2(O-t-Bu)_2$, we were unable to prepare this compound by the cocondensation reaction of MoO_3 with $Me_3SiO-t-Bu$. In this case the reaction products of isobutene and <u>tert</u>-butyl alcohol indicate catalytic H abstraction by Mo=O moiety occurs extensively for <u>tert</u>butyl group, presumably due to the proximity of hydrogen atoms of <u>tert</u>-butyl groups toward oxygen of MoO_3 .

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CHAPTER 3

Preparation and Structure of $Mo_4O_4(u_3-0)_4(OSiMe_3)_4(HNMe_2)_4$: A Novel Tetranuclear Molybdenum Oxo Compound with a Distorted Cubane Structure^{1a}

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Abstract

The unusual cubane type compound $Mo_40_4(\mu_3-0)_4(OSiMe_3)_4(HNMe_2)_4$ was synthesized via. two distinctly different synthetic routes, i.e. cocondensation reaction of ${\rm MoO}_3$ with ${\rm Me}_3{\rm SiNMe}_2$ and solution technique employing MoO_2Br_2 . The compound was characterized by a variety of techniques including single crystal X-ray crystallography. The molecule was shown to consist of $Mo_4(\mu_3-0)_4$ core with two localized metal-metal single bonds (d(Mo-Mo) = 2.605 (5) Å avg) and three different Mo- μ_3 -O bonds (1.94, 1.98, 2.38 Å, all avg., respectively) which clearly demonstrate trans influence of coordinated dimethylamine, trimethylsiloxy and terminal oxygen. The molecule is believed to be formed via. self-assembly of coordinatively unsaturated $[MoO_2(OSiMe_3)(NMe_2)]_x$, where x = 1 or 2, units on reduction/protonation to achieve octahedral coordination for the molybdenum center. The structural aspects of the compound are discussed in comparison to the structurally related oxo(alkoxo)bridged tetranuclear molybdenum compounds. Crystal Data: monoclinic, space group $P_{21/c}$; a = 20.248(4) Å, b = 20.151(6) Å, c = 24.576(7) Å, β = 114.14⁰(2); V = 9150(4) Å³; Z = 8; R = 0.065, $R_{w} = 0.072.$

Introduction

Numerous types of transition metal cluster compounds have been synthesized and structurally characterized during last two decades.^{1,2} Among them the cubane type $M_4(\mu_3-X)_4$ core-containing compounds² have been prepared, some fortuitously, for the transition metals ranging from groups³ 5 to 9. For example, some of the metals involved are V, Cr, Mo, W, Re, Fe, Os, Co, and Pt with a varying number of excess cluster electrons and supporting ligands.^{2,4} The cubane cores show several distinct symmetries depending on the number of the excess cluster electrons and also ligand properties.^{2,4} The most important class of these compounds is the sulfido-bridged metal clusters as found in Mo₄S₄ and Fe₄S₄-core containing compounds mainly due to their relevance with respect to nitrogenase and nitrogenase-related enzymes.⁵

Our recent interest has centered on the preparation of new oxomolybdenum compounds prepared by the cocondensation reaction of molybdenum trioxide with silicon reagents. 6

Herein we report on a minor product in the cocondensation reaction of MoO₃ with Me₃SiNMe₂, Mo₄O₄(μ_3 -O)₄(OSiMe₃)₄(HNMe₂)₄, which contains Mo₄(μ_3 -O)₄ cubane-core in the solid state and is a rare example of tetranuclear oxomolybdenum(V) cluster compound.

To our knowledge, this is the first structurally characterized example of $Mo_4O_4(Mo(V))$ cubane type compound which is exclusively supported by monodentate ligands. An improved synthesis employing
solution techniques is also reported.

Experimental

General considerations: All manipulations were performed under argon or dinitrogen atmosphere in a Vacuum Atmospheres glovebox or on a high vacuum line. Schlenk techniques under dinitrogen were used when appropriate. Solvents were dried rigorously using proper procedures. All the chemicals were reagent grade. For details in cocondensation reactions and analytical procedures, See chapters 1 and 2.

Synthesis of $Mo_40_8(OSiMe_3)_4(HNMe_2)_4$

Method 1. (cocondensation reaction) MoO_3 (2.40 g, 16.7 mmol) was cocondensed at 77 K with Me_3SiNMe_2 (25.2 g, 215 mmol). The reactor was warmed to room temperature and the volatiles were stripped at 307 K. A dark brown sticky solid (4.2 g) was recovered from the pot. ¹H NMR spectrum of the volatiles showed mostly unreacted starting ligand. After standing in the dinitrogen-filled glove box for 9 days at room temperature, a sample (4.0 g) of the cocondensate was dissolved in warm toluene (60 mL) and the mixture was vacuumfiltered through a fine frit to give red-brown solution by leaving a brown solid on the frit (2.3 g). The volume of the resulting redbrown solution was reduced to 15 mL and placed in a freezer at ca. 255 K. After 16 days red crystals were observed along with brown precipitate. The solution was warmed to room temperature followed by filtration using a fine frit to remove the brown amorphous solid. The resulting red-brown solution was placed again in a freezer at 255 K. Red crystalline solid formed overnight. The crystals were filtered and vacuum-dried to give red crystalline plates (29 mg). Further solvent removal and recrystallization gave a second crop (40 mg). A total of 69 mg was harvested. Yield is 1.6 % based on MoO_3 . The compound can be easily purified by dissolving the mixture in pentane followed by filtration. The compound may be recrystallized in toluene or nitromethane/dichloromethane mixture. The compound is air stable in solid state and very soluble in methylenechloride, soluble in benzene, toluene, pyridine, pentane, Anal. Calcd for $C_{20}H_{64}N_4O_{12}MO_4$: C, 22.90; H, 6.15; N, and hexane. 5.34; Mo, 36.59. Found: C, 22.93; H, 6.13; N, 5.03; Mo, 36.49. 400-MHz $^{1}\mathrm{H}$ NMR (in toluene-d_8, referenced to the solvent at 2.09 ppm); § 0.38 (s, 9H, OSiMe₃), 2.61 (d, 3H, NMe_A, J_{H-H} = 5.7 Hz), 2.72 (d, 3H, NMe_B , $J_{H-H} = 5.7 Hz$), 7.24 (sept, 1H, NH, $J_{H-H} = 5.7 Hz$). 100.614-MHz 13 C NMR (in toluene-d₈, referenced to the solvent at S 128.00); S 2.41 (OSi(CH₃)₃), 41.23 (NCH_{3(A)}), 44.23 (NCH_{3(B)}). IR data; 464 (m), 482 (m), 522 (m), 623 (w), 665 (vs), 748 (s), 834 (vs), 882 (vs), 900 (vs,br), 956 (vs), 968 (vs), 1026 (m), 1029 (m), 1060 (vw), 1110 (m), 1126 (m), 1220 (vw), 1242 (s), 1257 (m), 1317 (m), 1384 (m), 1405 (m), 1465 (s), 2418 (w), 2617 (w), 2794 (vw), 2839 (w), 2851 (w), 2880 (w), 2909 (w), 2947 (m), 2974 (m), 3001 (w), 3060 (m) cm^{-1}

Electronic spectrum (λ_{max} in toluene solution, 1 cm cell); 352 nm (ϵ = 3420), 472 nm (ϵ = 790). Mass data m/z [% int, assgn]; 308 [100, MoO₂(OSiMe₃)₂⁻], 434 [3, Mo₂O₄(OSiMe₃)₂⁻], 612 [8, Mo₂O₄(OSiMe₃)₄⁻], 779 [2, Mo₄O₈(OSiMe₃)₃⁻], 868 [50, Mo₄O₈(OSiMe₃)₄⁻].

Method 2. (solution synthesis) MoO_2Br_2 (0.985 g, 3.42 mmole) was suspended in 5 mL methylenechloride. To this was added 30:70 mole % mixture of hexamethyldisiloxane (8.8 mmole) and Me₃SiNMe₂ (20 mmole) (5.0 mL) while stirring. A brown solution formed with mild gas evolution. The volatiles were pumped off from the solution under dynamic vacuum to give a brown sticky solid. The solid was dissolved in methylenechloride (30 mL). To this solution was added NaOSiMe_R (0.407 g, 3.63 mmole) and 1.0 mL of the mixture of hexamethyldisiloxane (1.8 mmole) and Me_3SiNMe_2 (4.0 mmole). The brown solid was filtered off and the solution volume was reduced to 10 mL. Toluene (20 mL) was added to this solution and the resulting solution was heated while stirring at 323 K for 18 hours in a sealed flask. To this dark red-brown solution was added H_2O (50 μ L, 2.8 mmole) drop by drop while stirring. During this time a dark brown solid formed. The resulting mixture was stirred another 5 h at 323 K and the brown solid was filtered off to give a brown-red solution. The solution volume was reduced to 10 mL and placed in a freezer at 253 K. Red plate-shaped crystals formed overnight. Filtration and drying gave the red crystalline solid (7.5 mg). The rest of the compound was obtained by vacuum drying and extraction with pentane

followed by recrystallization (106 mg). Yield is 13 % based on molybdenum. The identity of the compound was confirmed by $^{1}\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectroscopy.

Method 3. (solution synthesis) MoO₂Br₂ (0.712 g, 2.47 mmole) was suspended in toluene (10 mL). To this suspension ${\sf HNEt}_2$ (1.5 mL, 15 mmole) and NaOSiMe₃ (0.554 g, 4.94 mmole) were added while stirring. The mixture was stirred overnight. A red solution with a milk brown precipitate formed. Filtration gave a milk brown solid (1.019 g) and a red solution. Stripping the volatiles from the red solution gave a dark red dense oil on which no further characterization was performed. The milk brown solid was dissolved in CH_2Cl_2 (10 mL) and 0.30 mL of 30:70 mole % mixture of hexamethyldisiloxane (0.53 mmole)/ Me_3SiNMe_2 (1.2 mmole) was added. The solution was stirred overnight and filtered through a fine frit to give a red-brown solution. Stripping the volatiles gave a brown-red solid. This solid was dissolved in toluene (8 mL) and placed in the freezer at 253 K. Red crystalline solid was formed after 2 days. Stripping the volatiles gave a red-brown sticky solid. $^{1}\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectroscopy confirmed that this mixture contained the title compound together with byproducts. Extraction with pentane followed by concentration and crystallization yielded the title compound (126 mg). Yield is 20 % based on molybdenum.

X-ray Crystallography

A plate shaped single crystal with a dimension of $0.3 \times 0.3 \times 0.3$ mm was mounted on a glass fiber with epoxy cement and transferred onto an arcless goniometer head. Data collection was performed with $2\theta-\omega$ scan method. The first 20 reflections were used to calculate initial lattice parameters. After refining the orientation matrix and lattice parameters, data collection was initiated with a 2θ - ω scan technique at a scan rate 16°/min and scan width, ω = 0.92° + tan Intensities of the three standard reflections monitored throughω. out data collection period exhibited fluctuations below 2 %. A summary of crystallographic data, final positional parameters, anisotropic temperature factors, bond distances, and bond angles are given in Appendix I. The structure was solved using "TEXAN, Texray Structure Analysis Package" of the Molecular Structure Corporation, College Station, TX, U.S.A., with a PDP micro-VAX II computer. A difference Fourier map phased on the molybdenum atoms revealed the non-hydrogen atom positions. Only molybdenum atoms were refined anisotropically due to the lack of the dimension of the computer program. Several cycles of least squares refinements converged to the R factors of R = 6.5 % and R_{v} = 7.2 %. Hydrogen atoms were calculated at 0.95 Å. Seventeen hydrogen atoms were not calculated due to the limitation of the dimensions of the computer program. However, this account for only 0.43 % of the total scattering electron density.

Results and Discussion

Preparation

The cocondensation reaction of molybdenum trioxide utilizes the high reactivity of the coordinatively unsaturated MoO3 vapor $species^7$. The cocondensation reaction of molybdenum trioxide with Me₃SiNMe₂ is expected to produce initially the addition products, i.e., $[Mo0_x(OSiMe_3)_v(NMe_2)_v]_n$, where x = 0, 1, 2, x + y = 3, and n is an integer. Typically 50 - 60 % of the cocondensate was toluenesoluble and the toluene extract in deuterated pyridine shows several molybdenum-bound siloxy and dimethylamido resonances by 1 H and 13 C NMR spectroscopy. The IR spectrum of the extract shows intense bands from siloxy groups (1249, 843, 753 $\rm cm^{-1}$) and molybdenum-oxygen stretches as not-well-resolved broad bands between 700 and 1000 $\rm cm^{-1}$. The mass spectrum of this extract shows base peaks centered at m/z = 308 (assigned to $MoO_2(OSiMe_3)_2^-$) along with traces of other species. However, crystallization of this extract gave a red crystalline compound in a low yield which was characterized to be a tetranuclear cubane-type compound (see X-ray structure section). The remainder of the product was a hydrocarbon-insoluble brown solid on which no further characterizations were performed. The low yield (1.6 % based on MoO₃) prompted a conventional solution synthesis employing MoO₂Br₂. This was successful with yields of 13 and 20 % for the two syntheses (see experimental section). The possible origins of the protons in HNMe₂ ligands are adventitious water or perhaps from the

metallaton of the dimethylamido ligand bound to the coordinatively unsaturated Mo center. The metallation reactions of dimethylamidotransition metal compounds have been documented 8 and tungsten compounds with MeNCH_2 moieties 9 have been structurally characterized. For example, Bercaw et al. reported the room temperature decomposition of $(\eta^5-C_5Me_5)Ta(NMe_2)Me_3$ to $(\eta^5-C_5Me_5)Ta(CH_2NMe)Me_2$ by liberating methane.¹⁰ Nugent and co-workers showed facile reversible cyclometalation of d^0 dialkylamido transition metal complexes at elevated temperature.⁸ Our synthesis of the title compound employing HNEt₂ as the only possible proton source gave a 20 % yield while cocondensation reactions to which traces of external water were added gave no title compound. This argues that the proton found in the coordinated HNMe₂ is not from externally-added water. However, the title compound was obtained by adding dihydrogen to the toluene extract of the cocondensate followed by crystallization at 253 K in two days. The cocondensate did not yield the title compound prior to the addition of dihydrogen for more than 1 month at 253 K. This interesting observation supports the reduction process of Mo(VI) species to Mo(V) species which leads to the formation of the title compound. We suggest that the reduction of Mo-bound dimethylamido to dimethylamine is probably through a process similar to that found in cyclometallation. However, this issue is clouded because synthesis through cocondensation was erratic, with only three successes out of six attempts and the fact that the dimethylamido groups bound to transition metals have such a high reactivity toward protons.

Characterization and Properties

¹H, ¹³C, IR, Mass, and analytical data are recorded in the experimental section. The compound exists as red plates and is indefinitely air-stable in the solid state. This stability could be attibutable, in part, to the hydrophobic nature of the trialkylsiloxy group. However, in solution the compound slowly hydrolyzes. A decomposition half-life, $t_{\frac{1}{2}}$, of 40 hours was observed with addition of water (47 mmole/L water with 5.2 mmole/L of the compound in a 50:50 volume % mixture of acetonitrile-d₃/toluene-d₈) to yield dimethylamine and hexamethyldisiloxane at ambient temperature followed by ¹H NMR spectroscopy. Much slower decomposition rate were observed with primary alcohols or acetic acid.

The ¹H NMR spectrum of the compound is given in Figure 3.1. The compound shows two doublets (NMe₂) and a clean septet (NH) along with a sharp singlet (OSiMe₃). The inset of Figure 3.1 shows two singlets when the NH proton at 7.25 ppm is spin-decoupled. This observation confirms the diastereotopic nature of the methyl groups of the coordinated dimethylamine in the compound. Variable temperature ¹H NMR spectra in toluene-d₈ show no change in the splitting pattern in the temperature range of 233 to 323 K. Only line-broadening and a temperature-dependent chemical shift change were observed. Amine exchange reactions followed by ¹H NMR tube reactions show no exchange between dimethylamine and either pyridine or diethylamine. The compound is diamagnetic judged by the sharp resonances of the ¹H NMR spectrum which is the consequence of the



well-known tendency of the d^1-d^1 spin pairing in dioxo-bridged dinuclear molybdenum(V) compounds.¹¹

Mass spectrum (Figure 3.2) shows the characteristic Mo-containing isotope patterns with the base peak centered at m/z = 308 assigned to monomeric MoO₂(OSiMe₃)₂⁻ (MoO₄ skeleton). The other peaks demonstrate Mo₂O₆⁻, Mo₂O₈⁻, Mo₄O₁₁⁻, and Mo₄O₁₂⁻ skeletons. Of particular interest is the 50 % intensity of the Mo₄O₈(OSiMe₃)₄⁻ peaks (m/z = 868) compared to the 3 % intensity of the dinuclear ion Mo₂O₄(OSiMe₃)₂⁻ (m/z = 434). This demonstrates the robust nature of the Mo₄O₁₂ skeleton in the vapor phase. The base peak MoO₂(OSiMe₃)₂⁻ indicates easy migration of the siloxy group from one metal center to another under the mass conditions used.

The IR spectrum shows two asymmetric strong peaks at 968 and 956 cm⁻¹ which are assigned to the Mo=O(terminal) stretching vibrations. A strong, broad IR peak at 970 cm⁻¹ was reported for the Mo₄O₈(OSPMe₂)₄ compound¹² which shows the same core structure with that of the title compound, i.e., $Mo_4O_4(u_3-0)_4$. The IR spectra of the compounds with the syn- $(Mo_2O_4)^{2+}$ core usually show one or two strong Mo=O_t stretchings in the range of 980 - 930 cm⁻¹ and strong to medium peaks arising from the $Mo(O_b)_2Mo$ moiety in the two ranges, i.e., 765-710, and 480-430 cm⁻¹.¹³ However, the IR spectrum of the title compound shows no band in the regions, instead, it reveals 665 (vs), 482 (m) peaks which are presumably arising from the bridging moiety.¹⁴ Probably bonding mode change along with the overall symmetry change from dioxo-bridged Mo₂ skeleton to tetranuclear structure alters



Figure 3.2. PIPINICI mass spectrum of $Mo_4O_8(OSiMe_3)_4(HNMe_2)_4$

the Mo- O_b frequences to the lower values. For the comparison of the IR spectra of tetranuclear oxomolybdenum compounds, see chapter 5.

X-ray Structure

The compound crystallizes in the monoclinic space group with 8 molecules per asymmetric unit cell. The crystal data are summarized in Appendix I. The ORTEP drawings of two views are given in Figures 3.3 and 3.4. The average bond distances and bond angles are shown in Tables 3.1 and 3.2 respectively. See also appendix I. There are two kinds of crystallographically independent molecules in the unit cell. As shown in Tables 3.1 and 3.2, the dimensions of the two molecules do not differ from each other by more than three standard deviations for any distance and angle. These differences apparently arise from a slight packing variation for each of the molecules. The molecule has virtual S_{Δ} symmetry and the $Mo_4(\mu_3-0)_4$ core shows approximate D_{2d} symmetry although the symmetry is not crystallographically imposed. The most interesting feature in the molecule is the $Mo_4(\mu_3-0)_4$ cubane core which is highly distorted and elongated. Each Mo is in a distorted octahedral environment similar to Mo in solid MoO₃.¹⁵ There are four triply bridging O atoms on alternating corners of the cube. Average Mo- μ_3 -O bond distances are 1.94 Å (trans to N), 1.98 Å (trans to OSi) and 2.38 Å (trans to 0_t) respectively, which clearly demonstrate the trans







Figure 3.4. Ball-and-spoke drawing of $Mo_4O_8(OSiMe_3)_4(HNMe_2)_4$ looking down through centers of Mo-Mo bonds.

Ato	oms	molecule I	molecule II	Average		
Mo ₄ 0,	4 core					
Mo(a) Mo(a) Mo(a) Mo(a) O(a) O(a)	Mo(b) Mo(c) O(a) O(b) O(c) O(b) O(c)	2.608(1) 3.415(7) 1.948(18) 1.977(15) 2.372(24)	2.602(5) 3.424(8) 1.926(29) 1.990(31) 2.384(40)	2.605(5) 3.420(8) 1.940(30) 1.981(24) 2.378(31)		
Core	-ligand					
Mo(*) Mo(*) Mo(*)	0(t) 0(s) N	1.661(6) 1.989(18) 2.194(13)	1.656(10) 1.995(21) 2.201(14)	1.658(8) 1.992(19) 2.197(13)		
Intraligand						
Si Si N	0 C C	1.652(11) 1.849(45) 1.457(23)	1.636(25) 1.838(52) 1.473(28)	1.645(18) 1.844(48) 1.465(26)		
						

Table 3.1. Selected average bond distances (Å) for $Mo_40_8(OSiMe_3)_4(HNMe_2)_4^{a,b}$

^a The number in parentheses is the standard deviation of an individualvalue from the mean value.
^b See Figure 3.3 for the letter designations in the parentheses.

Atoms	molecule I	Molecule II	average
Mo ₄ O ₄ core			
Mo(b)-Mo(a)-O(c) Mo(a)-Mo(b)-O(a) Mo(a)-O(a)- Mo(b) Mo(a)-O(b)- Mo(c) O(a)- Mo(a)-O(b) O(a)- Mo(a)-O(c)	91.8(6) 48.4(7) 83.3(7) 103.5(10) 89.2(7) 76.4(9)	91.8(8) 48.4(13) 83.2(13) 103.6(15) 89.1(9) 76.3(16)	91.8(7) 48.4(10) 83.3(9) 103.6(15) 89.2(8) 76.4(13)
core-ligand			
$\begin{array}{l} Mo(a) - Mo(b) - O(t) \\ Mo(a) - Mo(b) - O(s) \\ Mo(a) - Mo(b) - N \\ O(a) - Mo(a) - O(t) \\ O(b) - Mo(a) - O(t) \\ O(c) - Mo(a) - O(t) \\ O(a) - Mo(a) - O(s) \\ O(b) - Mo(a) - O(s) \\ O(c) - Mo(a) - O(s) \\ O(c) - Mo(a) - N \\ O(c) - Mo(a) - N \\ O(b) - Mo(a) - N \\ O(t) - Mo(*) - N \\ O(s) - Mo(*) - N \\ O(s) - Mo(*) - N \end{array}$	96.6(8) 135.9(14) 129.5(5) 112.8(16) 105.9(8) 170.2(13) 87.6(17) 157.1(13) 81.0(5) 153.9(14) 81.6(9) 77.5(12) 96.3(11) 93.3(7) 91.5(16)	96.3(6) 136.3(5) 128.5(13) 113.3(11) 105.2(15) 169.6(19) 87.3(12) 157.9(21) 82.2(14) 153.1(18) 81.3(12) 76.5(13) 96.3(8) 93.5(15) 92.3(8)	$\begin{array}{c} 96.5(7)\\ 136.1(10)\\ 129.0(11)\\ 113.0(13)\\ 105.5(12)\\ 169.9(15)\\ 87.4(13)\\ 157.5(16)\\ 81.6(11)\\ 153.5(15)\\ 81.5(10)\\ 77.0(13)\\ 96.3(9)\\ 93.4(11)\\ 91.9(13)\end{array}$
Mo-ligand			
Mo(*)-O(s)-Si Mo(*)-N -C	130.1(19) 114.9(31)	130.4(12) 114.5(20)	130.2(15) 114.7(25)
intraligand			
0- Si- C C- Si- C C- N- C	109.6(22) 109.3(16) 110.4(20)	109.9(24) 109.1(18) 108.7(10)	109.7(23) 109.2(17) 109.5(17)

Table 3.2. Selected average bond angles (°) for $Mo_40_8(OSiMe_3)_4(HNMe_2)_4^{a,b}$

^a The number in parentheses is the standard deviation of an individual value from the mean value.
 ^b See Figure 3.3 for letter designations in the parentheses.

influence of each group. Therefore, the trans influence observed is in the decreasing order of terminal oxygen>>siloxy≥dimethylamine. The four siloxy and four coordinated $HNMe_2$ groups are all equivalent structurally within the error limit and also chemically as evidenced by ¹H NMR spectroscopy. There are two Mo-Mo distances at 2.605 Å and four distances at 3.42 Å spanning diagonally on the six faces of the cube. The Mo-Mo distance, 2.605 Å, is an Mo-Mo single bond distance while the distance 3.42 Å is apparently the nonbonding distance.¹⁶

The faces of the cube containing Mo-Mo single bond show acute Mo-O-Mo bond angle which is an additional evidence for Mo-Mo interactions.¹⁷ The dihedral angle of the two $Mo(O_b)_2$ planes of this face is $137^{\circ}(2)$ and that of the two Mo_2O_b planes is $139^{\circ}(2)$. The $Mo(O_b)_2$ dihedral angle value 137° is smaller that that of the dinuclear ${\rm Mo_2O_4}{\mbox{-}core}$ containing compounds (152°) and that of $Mo_40_6Cl_4(OPr)_4(PrOH)_2$ (157°).^{13,27} The smaller dihedral angle of the title compound may indicate a distortion of $Mo_2(O_b)_2$ moiety arising from the cluster formation of the dimeric fragments. The other dihedral angle subtending two $[(0_b)_2(0(Si))(N)]$ planes is 172(1)°. Molybdenum atoms are 0.42(1) Å above the planes defined by $(0_b)_2^-$ O(Si)-N atoms toward terminal oxygen. The four faces which do not contain an Mo-Mo single bond show an Mo-O_b-Mo angle, $103.6^{\circ}(13)$ and an O_b -Mo- O_b angle of 76.4° These angles are very close to the values observed in several other cubane compounds.^{12,17b,18} The multiply bonded terminal oxygens have the bond distance, 1.66 Å, which is

comparable to that found in solid MoO_3 (1.67 Å)¹⁵ and other oxomolybdenum compounds. 11 The two terminal oxygens are syn to each other on the face with the Mo-Mo bond and are tilted a 6.5° outward from the norm of the plane which contains the Mo-Mo vector. Compare the Mo-Mo distance 2.605 Å with the van der Waals contact of two oxygens 2.80 Å.¹⁶ The Mo-O(Si) bond distances are slightly longer than those of terminally bound siloxy groups observed in nitridomolybdenum compounds by 0.07-0.08 Å. However, these values are comparable to that of the bridging siloxy group (1.98 Å) in the siloxy-bridged dinuclear nitrido Mo(VI) compound. Refer to chapter 4 for the structures of these nitrido compounds. The Mo-O-Si bond angle is 130°(2) which is the most acute angle of terminally bonded siloxy group observed for (oxy)siloxy molybdenum compounds. The Si-O-Si angle in hexamethyldisiloxane is reported to be 143° and the angle in $(Me_2SiO)_3$ is 131° in which some strain is present.¹⁹ Some structurally characterized aluminum siloxides show Al-O-Si angles of the bridging siloxy groups in the range of 130°-134° and that of the terminal one at 169° presumably due to the competing π -bonding between Al-O and O-Si bonds.²⁰ Chisholm et al. noted for $Mo_2(OSiMe_3)_6(HNMe_2)_2$ an average bond angle of 135° for those siloxy groups which were trans to the N of the dimethylamine and for the remainder four siloxy groups much larger values (157°-176°).²¹ The reason for this discrepancy is not clear. The angle observed in the title compound, 130° is believed to be the lower limit for terminally bonded OSiR3 group. However, no correlation between the Mo-O-Si

bond angle, Mo-O, and Si-O bond distances can be found in the known molybdenum siloxide compounds.

Comparisons with other relevant structures

Tetranuclear oxomolybdenum compounds show diverse structural variations depending on the ligand types and their bonding nature. For example, in the fused bioctahedral $Mo_4O_8(OEt)_2(tme)_2^{22}$ (Mo(VI)), two tridentate ligands, tme $(CH_3C(CH_2O)_3)^{-3}$, hold the four Mo atoms together. The Mo-Mo distances observed in this compound are 3.44, 3.49, 3.70 Å, evidently all nonbonding distances.

In $Mo_4 0_4 (u-0)_4 (u-0Me)_2 (HB(pz)_3)_2 (MeOH)_2 (Mo(V))$ two dioxo-bridged Mo₂ fragments are combined through the methoxy bridges because one of the molybdenum moiety is blocked by tris-chelate which prevent the more compact association modes.²³ $Mo_4 0_4 (u_3-0)_2 Cl_2 (CH_3 COO)_4 (Mo(V))$ was structurally characterized to reveal only one Mo-Mo single bond, and consequently showed magnetic moment 2.35 B.M. for the tetrameric unit at 294 K.²⁴ As were observed in these compounds, the structures of tetranuclear oxo-molybdenum compounds assisted by multidentate ligands (usually molybdenums are in +6 or +5 oxidation state) are critically dependent on the bonding nature of the ligands. However, for (oxo)molybdenum alkoxide compounds, only two distinct structural variations have been observed, namely fused bioctahedral and cubane structures. There are two fundamental ways to combine the two dioxo-bridged Mo₂ fragments. See Figure 3.5. One way is exclusively through the bridging oxo groups to form the cubane



SCHEME II.



where X = bridging ligand

Figure 3.5. Two ways to form ${\rm Mo}_4$ cluster compound from dimeric fragments.

structure observed in the title compound. (Scheme I) The other way is through one bridging oxo group and a terminal X-ligand to form a fused bioctahedral structure which has a more open structure. (Scheme II) What factors influence the structural preference of one against the other? Apparently one of the governing factors is the bridgeforming ability of the X-group compared to that of the bridging oxo group. Another factor is the steric constraint imposed by the terminally-bound X-groups.

Numerous examples of the fused bioctahedral structure have been observed in transition metal (oxide) alkoxide compounds. For example, the well-known $\text{Ti}_4(\text{OR})_{16}^{25}$ with no M-M bond, $W_4(\text{OR})_{16}^{26}$ with M-M bonds (R = Me, Et), and $\text{Mo}_40_8(\text{O-i-Pr})_4(\text{py})_4^{26}$ (M-M) show this structure. It is quite likely that the interplay of the oxo and alkoxo (siloxo) groups in forming bridge bonds is important. The structural preference of one compound over the other may be accounted for by the differences in π -donating ability of the alkoxy and trialkylsiloxy groups together with the steric bulkiness of the ligands involved.

The structural data for several Mo_4 cluster compounds are shown in Table 3.4. Beaver and $Drew^{27}$ originally formulated the compound (a) as a mixed valence Mo(V)-Mo(VI) compound but Koch and Lincoln later reformulated²³ the compound as an Mo(V) compound based on the argument that terminally bonded propoxy groups have unreasonably long bond distances and these groups were reassigned to coordinated propanols. During structure comparison survey we found the same anomaly is present in the compound (e),²⁸ and we reformulate the

compd	a	b	с	d	e	 f
<pre>structural type # cluster d e(-) Mo ox. state # Mo-Mo bonds [bond distances]</pre>	f.b. 4 5 2	c.b. 4 5 2	c.b. 4 5 2	f.b. 4 5 2	f.b. 4 5 2	с.ь. 10 3.5 6
Mo-Mo Mo-Mo nonbond	2.669(2) 3.36 3.43	2.635(5)) 2.605(5) 3.42	2.600(1) 3.22 3.47	2.587(3) 3.39 3.44	2.579(6)
Mo-Ot	1.62 1.63	1.64	1.66	1.68 1.70	1.70	-
Mo-ORt	2.13	2.08	1.99	1.94	2.23	2.07
Mo-u ₂ 0	-	-	-	1.94 1.95	1.93 1.95	-
Mo-u ₂ OR	1.98 1.99 2.05 2.18	- - -	- - -	- 2.12 2.24	2.12	-
Mo-u ₃ 0	1.96 - 1.99 2.24	1.98 2.38	1.94 1.98 2.38	1.98 2.04 2.18	1.97 1.98 2.28	2.03
Mo-N	-	-	2.20	2.23	-	
[bond angles] Mo-O(c)-Mo	84.6 84.9	83.6	83.3	2.27 80.6	- 81.8	n.a.
10-0(t)-Mo D(c)-Mo-O(c)	104.9 92.5	102.5 89.8	103.6 89.2	101.2 93.4	83.7 105.8 93.8	n.a.
0(c)-Mo-O(t)	93.6 75.1	77.3	76.3	95.0 78.8	94.4 74.2	n.a.
Mo ₂ 0 ₂ 180.0		179.8	179.9	180.0	180.0	
# The esd's o are vithin a. $Mo_4O_6(OPr)_4$ b. $Mo_4O_8(OSPMe_1)_4$ c. $Mo_4O_8(OSIMe_1)_4$ d. $Mo_4O_8(O-i-Pi)_4$ e. $Mo_4O_8(OEt)_5$ f. $Cs_3Mo_4O_4(PO_1)_6$ n.a. = not sed by	f all the n $= 0.02 \pm 0.02 \pm 0.02$ $Cl_4(PrOH)_2$ $(PrOH)_2$ $(PrOH)_2$ $(PrOH)_2$ $(PrOH)_2$ $(PrOH)_4$ $(PrOH)_4$ $(PrOH)_4$ $(PrOH)_4$ $(PrOH)_4$ $(PrOH)_4$ $(PrOH)_4$ $(PrOH)_2$	distance v ; ref 27. 2. 4; this vo ref 26. ; ref 28. 3. the cited	alues exce rk. literature	pt shown i	n the parer	othes is

• bond angles of the face bearing two Mo's with no Mo-Mo bond and two μ_3 -O's.

compound to be an Mo(V) compound, not the originally claimed mixed valence compound. See Table 3.3 for the suspected bond distances in both compounds. The five compounds (a)-(e) are all Mo(V) compounds in a formal sense, but show some interesting structural variations. As Koch and Lincoln have already noted, 2^{3} the rather long Mo-Mo bond distance of the compound (a), 2.669(2) Å, is the consequence of the mixed $\mu\text{-}0/\mu\text{-}OPr$ bridge in a $\text{Mo}_2\text{O}_4^{+2}$ unit. However, the remaining four compounds are all composed of two $Mo_2O_2(\mu-0)_2$ -core containing fragments and show similar Mo-Mo and Mo-O_b distances. The compounds (a)-(e) possess two localized Mo-Mo single bonds as expected for Mo(V) compounds and these metal-metal bond distances are affected by the bridging groups and chelate ligands. The longest Mo- μ_3 -O bond distances in the cubane compounds which are trans to the terminal oxygens are longer than those of the fused bioctahedral compounds by 0.14-0.20 Å which clearly demonstrates the more compact nature of the cubane core compared to that of the fused bioctahedral counterpart.

The Mo-Mo bond distance of (b) is 0.030 Å longer than that of (c) although both compounds have the same cubane core structure. This bond lengthening could be due to the presence of the bidentate ligands, $OSPMe_2$, which cover four faces of the cube with no M-M bond and consequently exert some strain on the M-M bonds. Bond angles of the Mo₄O₄ core in (b) and (c) are very similar to each other. This indicates the core dimensions in Mo₄O₈L₄L'₄ cubane compounds are not much sensitive to the ligand environment.

It is interesting to note that there exist structural differences and similarities for both types of tetranuclear compounds, such as trans influence, $Mo-\mu_2-0$, $Mo-\mu_3-0$ bond distances, and the characteristic bond angles.

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CHAPTER 4

Synthesis, Reactivity, Dynamical Solution Behavior, and Molecular Structures of (Oxo) Nitrido Molybdenum(VI) Silioxides 1

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ABSTRACT

The nitrido(oxo)molybdenum compounds, $Mo_2(N)_2(OSiMe_3)_6(NH_3)_2$ (1), [MoN(OSiMe₃)₃(py)]_n (2), Mo₄N₄O₂(OSiMe₃)₈(py)₄·2py (3), and $Mo_4N_4O_6(H_2O)_5(MeOH)_3$ (4) have been prepared from the cocondensation reaction of MoO_3 with hexamethyldisilazane. High yield synthesis of compound (1) was achieved by the reaction of molybdenum trioxide dihydrate (MoO_3 ·2H₂O) with the ligand. The compounds have been characterized by a number of physicochemical techniques including single crystal X-ray crystallography for (1) and (3). An X-ray diffraction study shows compound (1) is a siloxo bridged dimer with a rather long $Mo-O_b$ bonds (2.669(4) Å) which are trans to the apical Mo≡N bonds. In contrast, the X-ray structure of compound (3) revealed a tetranuclear cage structure with four equal Mo- μ_2 -O bonds (1.91 Å avg), four short Mo=N (1.68 Å avg), and four long Mo-N bridging bonds (2.16 Å avg). The four molybdenum atoms are situated at the vertices of a regular Mo_A tetrahedron. The two bridging oxygens and four bridging nitrogen atoms lie along the six edges of the tetrahedron. Mo-O-Mo and Mo≡N-Mo angles are all within the range of 144°-147°. Variable temperature NMR spectroscopic studies show that compounds (1) and (2) are fluxional, but compound (3) is rigid in toluene-d₈ solution. However, compound (3), when dissolved in aromatic hydrocarbon solvents, slowly disproportionates to give compound (2) and a probable $Mo_4N_4O_6(py)_X$ species, where x = 8-12, confirmed by low temperature ¹H and ¹³C NMR spectroscopy.

X-ray Data for (1): Space group is $P_{21/a}$ with a = 10.851(4), b = 16.082(3), c = 12.282(4) Å, β = 109.14(2)°, V = 2025(1) Å³, and Z = 2, R = 0.055, R_w = 0.070 with no. of observation of 2528 (I>3 σ (I)) and 163 variables. For (3): Space group is $C_{2/c}$ with a = 26.06(2), b = 14.250(6), c = 24.524(6) Å, β = 116.66(3)°, V = 8141(11) Å³, and Z = 4, R = 0.053, R_w = 0.059 with no. of observation of 3238 (I>3 σ (I)) and 359 variables.

Introduction

Molybdenum nitride chemistry is interesting because of the relevance with the nitrogen fixation process involved in nitrogenase enzymes.² The nitrido ligand, along with the carbyne ligand, forms the strongest π -bond to a transition metal center.³ The lower electronegativity of nitrogen as compared with oxygen allows an effective orbital overlap between nitrogen and the metal in its higher oxidation states.³ Metal-nitrogen multiple bonds⁴ are found in transition metals ranging from group 4 to 9. Numerous transition nitride compounds are reported for Mo, W, Re, Ru, and Os.³

The synthesis for the above metal nitride compounds, for the most part, involve the use of azides, ammonolysis reaction, NCl₃, and, in a few cases, hydrazine.⁶ In particular, many examples of molybdenum nitride compounds, viz., $MoNX_3^5$ and its adducts,⁶ $[MoN(S_2CNEt_2)_3)_2]_4$,⁷ $[MoN(S_2P(OR)_2)_2]$,⁸ AsPh₄ $[MoNX_4]$,⁹ AsPh₄ $[MoN(N_3)_4]$,¹⁰ $MoN(N_3)_3(bpy)^{11}$ have been reported, but only a few molybdenum nitride alkoxides are known. These include $MoN(OR)_3$,¹² (R = Et, i-Pr, t-Bu, t-BuCH₂), $Mo_4(N)_2(0-i-Pr)_{12}$ ¹³ recently prepared by Chisholm and coworkers.

Herein we report the synthesis, reactivity, molecular structure, and solution behavior of (oxo)nitridomolybdenum(VI) siloxides and molybdenum(VI)-nitride-oxide compounds prepared from the cocondensation reaction and conventional solution synthesis.

Experimental

General Considerations: All manipulations were performed under argon atmosphere in a Vacuum Atmospheres glovebox or on a high vacuum line. Schlenk techniques under argon were used when appropriate. Solvents were dried rigorously using proper procedures. All the chemicals were reagent grade. $MoO_3 \cdot 2H_2O$ was prepared by the literature method.¹⁴ For the details of cocondensation reactions and analytical procedures, refer to chapter 2.

Synthesis of $M_{02}(N)_2(OSiMe_3)_6(NH_3)_2$, (1).

Method 1.(cocondensation reaction) MoO_3 (1.574 g, 10.94 mmole) was cocondensed at 77 K with $HN(SiMe_3)_2$ (48.6 g, 301 mmole). When the reactor was warmed to room temperature and the volatiles were stripped at 10^{-3} Torr overnight, a yellowish green solid was formed. Scraping gave yellow/green solid (2.558 g). A portion (1.193 g) of this crude cocondensate was dissolved in hexane (30 mL) and filtered twice through a coarse frit to give a yellow brown solution. The solution was condensed to 10 mL and placed at 253 K. A colorless needle-shaped crystalline solid formed overnight. Decanting the solution followed by washing with cold hexane (5 mL) and vacuum drying gave a colorless crystalline solid (0.180 g). Crystallization of the decanted solution gave another crop (0.112 g). Total yield is 15 % based on MoO₃ cocondensed. Anal. Calcd for $C_{18}H_{60}N_4O_6Si_6Mo_2$: C, 27.40; H, 7.66; N, 7.10; Mo, 24.32. Found: C, 27.47; H, 7.75; N, 7.05; Mo, 23.99. 400-MHz ¹H NMR (in benzene-d₆, referenced to the solvent at 7.15 ppm); & 0.381 (s, 27 H, OSiMe₃), 1.804 (s, br, 3 H, NH₃). 100.614-MHz ¹³C NMR (in benzene-d₆, referenced to the solvent at 128.00 ppm); & 2.17. IR data; 473 (s), 481 (s), 632 (m), 684 (m), 713 (m,sh), 750 (s), 815 (s), 844 (vs), 867 (sh), 942 (s), 1049 (s), 1215 (m), 1249 (s), 1313 (m), 1384 (m), 1402 (m), 1434 (m), 1612 (m), 1876 (vw), 1932 (vw), 2000 (vw), 2098 (vw), 2667 (vw), 2726 (vw), 2899 (m), 2954 (s), 3156 (m), 3234 (m), 3350 (m), 3401 (m) cm⁻¹. Mass spectral data m/z [% int, assgn]; 308 [5, Mo0₂(OSiMe₃)₂⁻], 379 [100, MoN(OSiMe₃)₃⁻].

Method 2. (solution preparation) $MoO_3 \cdot 2H_2O (0.189 \text{ g})^{14}$ was placed in a 25 mL round-bottomed flask along with a Teflon stir bar. To this solid was added HN(SiMe₃)₂ (7 mL) and the solution was stirred at 358 K for 5 h. The yellow solid dissolved in 15 minutes to give a pale yellow solution. Further heating resulted in a color change from yellow to orange to finally red-brown. The volatiles were pumped off from the solution to give a colorless plate-shaped crystalline solid slightly contaminated with red-brown thick oil (0.363 g). ¹H, ¹³C NMR, and IR spectra showed this solid was spectroscopically-pure $Mo_2(N)_2(OSiMe_3)_6(NH_3)_2$ (1). The compound may be recrystallized in hexane.

Synthesis of $Mo_2(N)_2(OSiMe_3)_6(ND_3)_2$

 ND_3 was bubbled through a hexane solution of $Mo_2(N)_2(OSiMe_3)_6$ -(NH_3)₂ in a 100 mL flask for 5 minutes. The flask was quickly sealed and placed at 253 K in a freezer. The colorless crystalline solid formed was separated and used to obtain an IR spectrum.

IR Data: 631 (m), 684 (m), 751 (s), 819 (sh), 846 (vs), 939 (s), 1019 (m), 1052 (s), 1250 (s), 1310 (w), 1313 (m), 1402 (m), 1434 (m), 1612 (w,br), 2318 (w), 2370 (w), 2491 (w), 2538 (w), 2901 (m), 2954 (m), 3136 (m,br) cm⁻¹.

Synthesis of [MoN(OSiMe3)3(py)], (2).

 $M_{02}(N)_2(OSiMe_3)_6(NH_3)_2$ (0.419 g) was dissolved in pyridine (5 mL) to give a dark yellow solution. This solution was placed at 253 K for 9 days but no crystallization occurred. The volatiles and excess pyridine were pumped off under 10^{-3} Torr vacuum at room temperature. Pale yellow solid (0.452 g) was obtained. Anal. calcd for $C_{14}H_{32}N_2O_3Si_3Mo$: C, 36.85; H, 7.07; N, 6.14; Mo, 21.02. Found: C, 35.04; H, 6.83; N, 5.79; Mo, 20.90. 400-MHz ¹H NMR (in toluene-d₈, referenced to the solvent at 2.09 ppm): & 0.264 (s, 27 H, OSiMe_3), 6.538 (m, 2 H, py), 6.875 (m, 1 H, py), 8.379 (m, 2 H, py). 100.614-MHz ¹³C NMR (in toluene-d₈, referenced to the solvent at 2.09 ppm): & 1.389, 124.413, 137.970, 150.611. IR Data (KBr): 458 (m), 486 (m), 630 (sh), 638 (m), 685 (m), 700 (m), 749 (s), 838 (vs), 872 (vs), 882 (vs), 904 (vs), 963 (s), 1015 (m), 1044 (m), 1057 (s), 1069 (m), 1150 (w), 1185 (vw), 1219 (w), 1249 (s), 1320 (w), 1355

(w), 1384 (m), 1399 (m), 1446 (s), 1606 (m), 1870 (vw), 1932 (vw), 1993 (vw), 2788 (w), 2837 (w), 2898 (m), 2959 (s), 3143 (w,br) cm⁻¹.

Synthesis of $Mo_4N_4O_2(OSiMe_3)_8(py)_4 \cdot 2py$, (3).

To the brown hexane solution after crystallization of $Mo_2(N)_2(OSiMe_3)_6(NH_3)_2$ (from the cocondensation reaction, see above) was added pyridine (2 mL) and the brown solid formed was filtered twice through a coarse frit. The resulting solution was placed at 253 K. Many block-shaped yellow crystals formed overnight. Decanting the solution followed by a cold hexane wash and vacuum drying gave yellow crystalline solid (0.162 g). Yield 7.6 % based on MoO_3 cocondensed.

Anal. calcd for $C_{54}H_{102}N_{10}O_{10}Si_8Mo_4$: C, 39.07; H, 6.19; N, 8.44; Mo, 23.12. Found: C, 38.48; H, 6.50; N, 7.95; Mo, 22.58. 400-MHz ¹H NMR (in toluene-d₈, referenced to the solvent at 2.09 ppm); S 0.061 (s, 36 H), 0.247 (s, 36 H), 6.796 (m, 12 H), 7.008 (m, 6 H), 8.821 (m, 12 H). 100.614-MHz ¹³C NMR (in toluene-d₈, referenced to the solvent at 20.40 ppm); S 1.41, 2.36, 123.83, 13.58, 150.69. IR data; 434 (vs), 451 (s), 459 (s), 622 (s), 630 (s), 650 (vs), 659 (vs), 697 (s), 751 (s), 835 (vs), 911 (vs), 1005 (s), 1026 (m), 1036 (s), 1051 (m), 1072 (m), 1150 (m), 1215 (s), 1246 (vs), 1313 (w), 1353 (w), 1384 (m), 1401 (m), 1444 (s), 1482 (m), 1573 (w), 1580 (w), 1598 (s), 1629 (w), 1872 (w), 1926 (vw), 1953 (vw), 1990 (vw), 2087 (vw), 2470 (vw), 2802 (vw), 2827 (vw), 2896 (m), 2954 (m), 2999 (vw), 3020 (vw), 3041 (vw), 3074 (m), 3089 (sh), 3111 (sh), 3146 (vw) cm⁻¹. Mass data m/z [% int, assgn]; 308 [62, MoO₂(OSiMe₃)₂⁻], 379 [100, MoN(OSiMe₃)₃⁻], 453 [5, Mo(OSiMe₃)₃(HNSiMe₃)⁻], 527 [1, Mo(OSiMe₃)₃(HNSiMe₃)₂⁻], 612 [1, Mo₂O₄(OSiMe₃)₄⁻], 684 [2, Mo₂O₃(OSiMe₃)₅⁻], 754 [1, Mo₂(N)₂(OSiMe₃)₆⁻].

Synthesis of $Mo_4N_4O_6(H_2O)_5(MeOH)_3$, (4).

 $Mo_2(N)_2(OSiMe_3)_6(NH_3)_2$ (0.185 g) was dissolved in toluene (2 mL). To this solution was added methanol (0.5 mL) and a white solid began to form after a few minutes. The sample was set aside for a day at room temperature and vacuum-dried for two days at 10^{-3} Torr to give a white powder (0.085 g). This solid may be crystallized in a nitromethane/methanol mixture by slow evaporation. Anal. calcd for $C_3H_{22}N_4O_{14}Mo_4$: C, 4.99; H, 3.07; N, 7.76; Mo, 53.15. Found: C, 4.24; H, 3.06; N, 7.35; Mo, 54.03. 400-MHz ¹H NMR (in DMSO-d_6, referenced to the solvent at 2.49 ppm): \$ 2.290 (s, MeOH), 3.160 (s, CH₃OH), 5.698 (s, br, H₂O). IR Data (Nujol mull): 454 (m), 467 (m), 534 (m), 673 (s), 720 (vs), 857 (s), 886 (vs), 1018 (s), 1158 (v), 1304 (m), 1400 (s), 1616 (v), 1676 (v), 2684 (sh), 2733 (sh), 3157 (vs,br) cm⁻¹.

Preparation of deuterated analog of compound (4).

Using the same procedure as described above, $Mo_2(N)_2(OSiMe_3)_6$ -
$(NH_3)_2$ (62.4 mg) was reacted with CD₃OD to give a white solid (31.9 mg). IR Data (Nujol mull): 452 (s), 465 (s), 484 (m), 493 (m), 522 (m), 593 (m), 669 (s), 721 (vs), 856 (s), 886 (s), 906 (s), 918 (s), 929 (s), 981 (m), 1020 (s), 1053 (m), 1059 (m), 1084 (m), 1109 (m), 1153 (w), 1169 (w), 1187 (w), 1302 (w), 1400 (m), 2067 (m), 2121 (m), 2177 (m), 2223 (m), 2335 (m), 2354 (m), 2368 (m), 2460 (m), 2678 (m), 2727 (m), 3137 (vs,br) cm⁻¹.

X-ray Structure Determinations

 $Mo_2(N)_2(OSiMe_3)_6(NH_3)_2$. A plate-shaped single crystal grown from hexane solution (0.2 x 0.2 x 0.05 mm) was mounted in a glass capillary in a Vacuum Atmospheres glovebox under argon in which a partial pressure of ammonia was present. The end side of the predried capillary was broken and a small amount of quick-setting epoxy (with a 5 minute lifetime) was introduced to the broken end. After 2 - 3 minutes a single crystal was introduced and was slightly embedded in the epoxy. After curing the epoxy resin, the other end (funnel side) was broken and sealed with epoxy. The mounted crystal was transferred to the goniometer head and data collection was initiated with 20- ω scan method. The first 10 reflections were used to calculate initial lattice parameters. The next 10 reflections chosen from the 144 data were used to refine the precise orientation matrix and lattice parameters. Data collection was performed with a 20- ω scan method at a scan rate = 16.0°/min. An average of 25 % intensity loss was observed for the three standard reflections at the end of the data collection, however, the decay was linear and a correction was applied. A set of relevant crystallographic data are presented in Appendix II. The structure was solved using the "TEXAN, Texray Structure Analysis Package of the Molecular Structure Corporation, College Station, TX, U.S.A. with a PDP micro-VAX II computer. A difference Fourier map phased on molybdenum atoms readily revealed the non-hydrogen atom positions. Least-squares refinements with isotropic thermal parameters led to R = 15 %. An emprical absorption correction employing π -scan method was applied at this stage. Three hydrogen atoms of the coordinated ammonia were clearly seen from a difference Fourier map with 0.71 - 0.77 Å distances from the nitrogen atom. However, one of the H-N-H bond angles was too large to be acceptable hence all three positions were discarded. Therefore all the hydrogen atoms were calculated with a 0.95 Å distance. Least-squares refinements with anisotropic thermal parameters for non-hydrogen atoms rapidly converged to give R = 5.5%, R_{ij} = 7.0 %. Final values of the positional parameters are given in Appendix II. Final difference Fourier map was featureless with no peak of structural significance.

 $Mo_4N_4O_2(OSiMe_3)_8(py)_4\cdot 2py$. A block-shaped yellow single crystal with approximate dimension of 0.3 X 0.3 X 0.2 mm was glued on a glass fiber with epoxy in the argon-filled glovebox. A thin epoxy coating was applied on the mounted crystal. The crystal was transferred to a

goniometer head and data collection was initiated. The first 12 search reflections were collected with an ω scan method and used to calculate lattice parameters. Twenty reflections from the next 247 measurements were used to refine the lattice parameters and orientation matrix. Data collection was performed with the ω scan method with a scan rate = 16.0° /min. An average of 37 % intensity loss was observed for the three standard reflections at the end of the data collection, however, the decay was linear and was corrected. A summary of data collection parameters is given in appendix 3. The structure was solved using the "TEXAN, Texray Structure Analysis Package" of the Molecular Structure Corporation, College Station, TX, U.S.A. with a PDP micro-VAX II computer. A difference Fourier map phased on molybdenum atoms readily revealed most non-hydrogen atoms. Solvent molecule of the crystallization was found during subsequent least-squares refinements. All the non-hydrogen atoms except solvent molecule were refined anisotropically. There was no indication of disorder of the solvent molecule, however, the refinement was carried out with occupancy factor of 0.7 for the solvent molecule. Final values of the positional parameters and anisotropic temperature factors given in appendix III. The final cycle gave R = 5.2 %, $R_{\rm u}$ = 5.9 %. The final difference Fourier map was featureless with no peak of structural significance.

Results and Discussion

Synthesis, Properties, and Reactivity

The known nitrido molybdenum(VI) alkoxide¹² has been prepared using MoNCl₃ as shown below;

 $MoNCl_3 + 3 LiO-t-Bu \rightarrow MoN(O-t-Bu)_3 + 3 LiCl$ (1) The ethoxy, isopropoxy, and neopentoxy analogs were prepared via an alkoxide exchange reaction with the t-butoxy compound.¹² The tungsten analog WN(O-t-Bu)_3 has been synthesized via a different route, i.e., the reaction of $(t-BuO)_3W=W(t-BuO)_3$ with nitriles;¹⁶

 $(t-BuO)_{3}W \equiv W(O-t-Bu)_{3} + RCN \rightarrow WN(O-t-Bu)_{3} + W(\equiv CR)(O-t-Bu)_{3}$ (2) where R = Me, Ph.

In this work, we used the cocondensation reaction of MoO_3 with $HN(SiMe_3)_2$ to prepare compounds (1) and, on addition of pyridine, (3). Compound (1), a nitrido Mo(VI) siloxide, was crystallized in a hexane or toluene solution at 253 K in a 15 % yield. The mixed nitrido-oxo-Mo(VI) compound (3) was isolated as a yellow crystalline solid after crystallization in a hexane solution at 253 K in a 7.6 % yield. The presence of NH₃ in (1) was confirmed by comparing the $\nu(N-H)$ with $\nu(N-D)$ in IR spectra. See Figure 4.1 and the experimental section. The IR spectrum of compound (1) shows 1049 cm⁻¹ band which is assignable to $\nu(Mo=N)$. The IR spectrum of compound (3) shows two $\nu(Mo=N)$ at 1026 and 1051 cm⁻¹. Interestingly, the solution synthesis using $MoO_3 \cdot 2H_2O$ with hexamethyldisilazane gave solely $Mo_2(N)_2(OSiMe_3)_6(NH_3)_2$, (1), in 60-80 % yield.



Figure 4.1. Infrared spectra of (a) $Mo_2N_2(OSiMe_3)_6(NH_3)_2$ and (b) its deuterated analog.

The reaction of MoO₃ with HN(SiMe₃)₂ is believed to proceed through the coordination of the ligand via nitrogen to a vacant molybdenum site followed by an N \Rightarrow O silyl group migration. The same behavior has been observed in the reaction of MO₂Cl₂ (M = V, Cr, Mo, Re) with HN(R)SiMe₃ to produce d⁰ organoimido M(NR)₂(OSiMe₃)₂ compounds.¹⁷ In addition, V(O)(OSiMe₃)₂Cl reacts with the same ligand to give V(NR)(OSiMe₃)₃ instead of VO(N(R)SiMe₃)(OSiMe₃)₂.¹⁷ Nugent rationalized this facile rearrangement from oxo imido intermediate to imido siloxy compounds in terms of the greater strength of the Si-O vs. that of the Si-N bond and the relief of steric repulsion in the congested amide intermediate.¹⁷

Pyridine-adduct (2) was prepared in a quantitative yield by reacting (1) with pyridine. The IR spectrum shows $\nu(\text{Mo=N})$ at 1057 cm⁻¹. It is interesting to note that the dimethylamine of $Mo_4O_8(OSiMe_3)_4(HNMe_2)_4$ (chapter 3) was not replaced by pyridine but, in (1), NH₃ is fully replaced by pyridine.

 $MoN(O-t-Bu)_3$ shows alkoxy group exchange reaction with less bulky alcohols as shown earlier, however, compound (1) shows different behavior. ¹H NMR tube reactions of (1) with ROH (R = H, Me, Et, i-Pr, t-Bu, n-Bu) in a hydrocarbon solvent show quantitative generation of Me₃SiOR and a white microcrystalline solid. The reaction rate seems to parallel the bulkiness of the R group, i.e., the bulkier the R group, the slower the reaction. For example, it took 38 h for the completion of the reaction with EtOH, but 1 week with t-BuOH at room temperature. The reaction products Me₃SiOR' were identified using $^{1}\mathrm{H}$ NMR spectroscopy by adding authentic sample to the solution.

The white solid prepared by reaction with MeOH, after thorough vacuum drying at room temperature, was characterized to be a mixed oxo-nitrido-Mo(VI) compound coordinated by water and methanol, (4), confirmed by 1 H NMR, IR spectroscopy, and elemental analysis. The compound is soluble in dimethylsulfoxide and slightly soluble in methanol. There is a possibility of forming a mixture of MoO_3 and a molybdenum nitride, but the solubility behavior, along with the IR and ¹H NMR results, exclude this possibility. MoO_3 is not soluble in DMSO and methanol at room temperature and the IR spectrum of compound (4) is totally different from that of MoO_3 . The IR spectra of normal and deuterated compounds show $u({
m Mo-O}_{
m b}-{
m Mo})$ at 467 and 720 cm⁻¹, ν (Mo=O_t) at 857 and 886 cm⁻¹, and ν (Mo=N) at 1020 ${\rm cm}^{-1}.$ This reaction is in contrast to the alkoxy exchange reaction of the above mentioned $[MoN(0-t-Bu)_3]_n^{12}$ compound and demonstrates the reactivity difference between the nitrido molybdenum alkoxy and siloxy compounds.

 $4 \text{ MoN}(\text{OSiMe}_3)_3(\text{NH}_3) + \times \text{s ROH} \rightarrow \text{Mo}_4\text{N}_4\text{O}_6(\text{H}_2\text{O})_{\times}(\text{ROH})_{8-\times} + 12 \text{ Me}_3\text{SiOR} + 4 \text{ NH}_3 \quad (5)$

It is quite likely that the initial product formed is $[MoN(OH)_3(ROH)_n]_X$ which condenses to give (4) in which the vacant Mo sites are coordinated by H₂O and CH₃OH. The ratio between the coordinated water and methanol may be dependent on the relative concentration of both water and methanol present in the system , but the sum

is believed to be 8 excluding lattice water or methanol. Compound (4) may be structurally related to compound (3) and to one of the species produced by the solution disproportionation of (3). One of the possible structure is that of compound (3) by replacing siloxy and pyridine ligands with four terminal oxygens, H_2O , and MeOH.

A single crystal X-ray structure determination will clarify this possibility. See Dynamical Solution Behavior section for the transformation of (3) to (2) and the mixed oxide-nitride-Mo(VI) pyridine adduct.

Dynamical Solution Behavior

Variable temperature ¹H and ¹³C NMR spectra of $Mo_2(N)_2(OSiMe_3)_6^{-}$ (NH₃)₂ in toluene-d₈ solution are shown in Figure 4.2. At 297 K only a single sharp resonance is observed in both ¹H and ¹³C spectra. At this temperature, monomer or fast monomer=dimer equilibrium is expected. The third possibility is fast bridge=terminal siloxy group exchange without dissociating into monomers. This mechanism was proposed for $Cr_2(NO)_2(O-i-Pr)_6$ compound.¹⁹ When the sample solution was cooled, the singlet of the ¹H NMR spectrum broadens (at 273 K, fwhh = 19 Hz) and becomes a doublet at 260 K with an integral ratio of 1:2, however, the singlet of ¹³C NMR already becomes a doublet at 273 K (1:2 ratio), some 13° higher than that of the ¹H NMR spectrum. On further cooling, the upfield singlet remains as a sharp singlet, but the lower field singlet broadens and begins to separate to two singlets at 210 K and sharpens at 190 K with an integral ratio of



Figure 4.2. Variable temperature ${}^{1}H$ and ${}^{13}C$ NMR spectra of $Mo_2N_2(OSiMe_3)_6(NH_3)_2$ in toluene-d₈.

1:1. The integral ratio of the three singlets is 1:1:1 at 190 K. These observations are totally consistent with the solid state structure described below in the "Molecular Structures" section. The first frozen-out singlet resonance is attributable to the bridging $OSiMe_3$ group and the latter two resonances are due to the terminal $OSiMe_3$ groups. The two terminal siloxy groups are rapidly exchanging down to 220 K, but at around 215 K the exchange slows down, and finally the solid state structure is frozen out below 210 K. However, in CD_2Cl_2 solution, the terminal siloxy groups are not differentiated down to 190 K presumably due to an accidental degeneracy.

The variable temperature NMR experiment (¹H and ¹³C) of MoN(OSiMe₃)₃(py) in toluene-d₈ solution was undertaken to elucidate the difference in solution behavior between the ammonia adduct and the pyridine adduct and to understand the solution NMR behavior of the tetranuclear compound (3).

In the variable ¹H and ¹³C NMR spectra of compound (2), only a singlet is observed down to 273 K and a very broad singlet (fwhh = 75 Hz) in the ¹H NMR spectrum is seen at 253 K, however a sharp singlet is seen in the ¹³C NMR spectrum at this temperature. The ¹H NMR spectrum at 233 K shows two sharp singlets in an integral ratio of 2:1 and this ratio remains the same down to 193 K. The coalescence temperature is somewhere between 253 and 233 K, probably close to 253 K, as deduced from the spectral pattern. The coalescence temperature of the ammonia adduct is around 278 K. It is not possible to deduce the structural assignments for compound (2) in

the solution due to the lack of a solid state structure. However, the frozen-out solution structure is either a siloxy bridged dimer as seen in the solid state structure of compound (1) or a nitrido bridged cyclic tetramer. Both of the structures fit the NMR behavior with the assumption that the terminal siloxy resonances are either not frozen out or accidentally degenerate. The reversal of the integral ratio between the ammonia adduct (1) and the pyridine adduct (2) is probably caused by the different magnetic environment, i.e., the different magnetic anisotropy exerted by pyridine and ammonia respectively. The variable temperature spectra for both (1) and (2) are totally reversible in the temperature range studied.

Tetranuclear compound (3) shows interesting solution behavior in both the variable 1 H and 13 C NMR experiments. The 1 H NMR spectra of compound (3) are given in Figure 4.3. The spectra at 297 K shows three singlets with unequal intensities. On cooling the solution, the singlet at 0.273 ppm (b) broadens and begins to separate into two very broad humps at 250 K and the two resonances (b) become sharp at 210 K. In contrast to this, the two resonances at 0.061 and 0.247 ppm (a) in Figure 4.3 remain the same throughout the temperature range studied. These two resonances have been assigned to compound (3) and are consistent with the solid state structure in which two types of siloxy groups are present, i.e., one trans to oxygen, the other trans to the nitrido group. See the structure section. Even more interesting is the frozen-out 1 H and 13 C NMR spectra of the



Figure 4.3. 400 MHz ¹H NMR spectra of $Mo_4N_4O_2(OSiMe_3)_8(py)_4$ ²Py.

coordinated pyridine molecules at 210 K. Down to 270 K only one kind of pyridine is observed, however, below this temperature the pyridine resonances become broad and below 230 K three types of pyridine resonances are observed. The far downfield pyridine resonances (a) in Figure 4.3 are assigned to compound (3) and the other two pyridine resonances are from a disproportionation reaction which gives (2) and another species which contains coordinated pyridine (c) but no siloxy group. This disproportionation reaction is not caused by hydrolysis since no hexamethyldisiloxane or trimethylsilanol was observed in the ¹H NMR spectra. The pyridine concentration had no effect on the rate of the disproportionation. The rate of the reaction was slowed by lowering the temperature and stopped below 253 K. Based on these experiments, and the variable temperature NMR behavior of both compounds (2) and (3), the following irreversible disproportionation reaction in toluene is proposed.

3 $Mo_4N_4O_2(OSiMe_3)_8(py)_4 \cdot 2py \rightarrow 8 MoN(OSiMe3)_3(py)$

+ 2 $Mo_2(N)_2O_3(py)_5$ (7)

Further visual evidence for this reaction is the color change from bright yellow of the freshly prepared solution to brown after disproportionation. No siloxy resonance was observed for the aged solution other than those from (2) and (3). This rationalization is further supported by the same coalescence temperature and the same NMR patterns observed in compounds (2) and (3).

Molecular Structures

Group 6 transition metal nitrosyl alkoxides show structures I, II, and III of Figure 4.4. However, for group 6 transition metal nitride alkoxides,^{12,16} the only structure observed is the columnar, linear-chain polymer, type I, with L, a nitrido group from another molecule. When the basic four coordinate unit, [MoN(OR)₃], is further supported by a coordinating ligand, structures III and IV are anticipated. Until now, no type III structure for Mo(VI) nitride compound has appeared. Structure IV is exclusively observed in nitrido halide molybdenum compounds with the general formula, [MoNX₃(L)]₄⁶ where X is a halide and L, an O-containing neutral ligand.

Herein two new structural studies of Mo(VI) nitride(oxide) are presented.

 $Mo_2(N)_2(OSiMe_3)_8(NH_3)_2$, (1).

An Ortep drawing of compound (1) is given in Figure 4.5 and important intramolecular distances and angles are given in Tables 4.1 and 4.2 respectively. For details see appendix II. Compound (1), type III, is the first structurally characterized compound of this type for nitrido molybdenum compounds. This basic $Mo_2N_4(\mu_2-0)_2O_4$ skeleton was observed in the nitrosyl compound, $Mo_2(NO)_2(0-i-Pr)_6 (HNMe_2)_2.^{20}$ A similar structure composed of alkoxo bridges, but with TBP coordination, was observed in the alkylidyne tungsten compound,



where Y = N, = CR, and NO, X = 1 igand, L = Lewis base

Figure 4.4. Structural types of group 6 metal compounds containing N, CR, and NO ligands.





-	atom	atom	distance	atom	atom	distance
-	M01	N1	1.626(6)	SI2	02	1.635(5)
	M01	03	1.920(5)	SI2	C21	1.83(1)
	M01	02	1.922(4)	SI2	C22	1.84(1)
	M01	01	1.981(4)	SI2	C23	1.83(1)
	M01	N2	2.272(6)	SI3	03	1.640(5)
	M01	01′	2.669(4)	SI3	C31	1.86(1)
	01	01′	2.857(8)	SI3	C32	1.86(1)
	SI1	01	1.648(5)	SI3	C33	1.858(9)
	SI1	C11	1.867(9)			
	SI1	C12	1.86(1)			
_	SI1	C13	1.862(9)			

Table 4.1. Intramolecular distances for $Mo_2(N)_2(OSiMe_3)_6(NH_3)_2$

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

atom	atom	atom	angle	atom	atom	atom	angle
N1 N1 N1 N1 O3 O3 O3 O2 O2 O2 O2 O2 O2 O2 O2 O1 O1 O1 O1 C12 C12 C12 C13 O2 O2 O2 C23 C23 C23	M01 M01 M01 M01 M01 M01 M01 M01 M01 M01	03 02 01 N2 01' 02 01' 01 N2 01' 01' 01' 01' 01' 01' 01' 01' 01' 01'	100.0(2) 103.0(2) 102.3(2) 95.0(3) 171.6(2) 99.2(2) 151.4(2) 81.3(2) 93.2(2) 161.4(2) 84.9(2) 78.5(2) 74.2(2) 76.9(2) 108.1(4) 112.7(3) 109.5(3) 107.5(4) 112.1(5) 107.0(4) 108.4(4) 112.2(4) 108.0(4) 109.7(6) 111.1(7)	C21 03 03 C33 C33 C32 SI1 SI1 M01	SI2 SI3 SI3 SI3 SI3 SI3 O1 O1 O1 O1	C22 C33 C32 C31 C32 C31 C31 M01 M01' M01'	107.5(6) 109.9(4) 110.2(3) 107.2(4) 110.1(5) 108.9(5) 110.6(5) 133.4(3) 120.8(2)
Angles	aro i	n doaroos	Estimated	standar	civob b	tions ir	the least

Table 4.2. Bond Angles for $Mo_2(N)_2(OSiMe_3)_6(NH_3)_2$

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

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 $[W(\equiv CMe)(0-t-Bu)_3]_2$, and nitrosyl chromium alkoxide, $Cr_2(NO)_2$ - $(0-i-Pr)_6$.^{16,19} It is interesting to note that the compounds with two known strong π -donor ligands, nitrido and alkylidyne, show similar bridging behavior through alkoxy (siloxy) bridges.

The molecule (1) possesses crystallographically imposed C_i molecular symmetry and molybdenum atoms are in a distorted octahedral environment with the nitrido group in an apical position. The dimer molecule is composed of two five coordinate monomeric fragments bridging through two siloxy groups which are trans to Mo≡N of another fragment. The Mo-O bond distances for the two terminally bonded siloxy groups are identical (Mo-O = 1.921(5) Å avg), however, the bridging siloxy group is slightly longer, (Mo(1)-O(1), 1.981(4) Å) than that of a terminal siloxy group presumably due to the bridge formation. These are to be compared with the all terminally bonded Mo-O(Si) distances, 1.99 Å, in $Mo_4O_8(OSiMe_3)_4(HNMe_2)_4$ compound described in chapter 3. The Mo(1)-O(1') bond distance of 2.669(4) Å is too long to be a normal single bond, rather the bond may be described as a weak $0 \rightarrow Mo$ dative bond, a consequence of trans influence.²² This kind of weak bond has been observed in tungsten alkylidyne alkoxide¹⁶ where W-O_b was 2.484(4) Å and in $[MN(OR)_3]_n^{12}$ compounds where M = W, R = t-BuO, M = Mo, R = t-Bu, and i-Pr. These nitrido compounds revealed a polymeric linear-chain columnar structure with M=N \rightarrow M where N \rightarrow M bond distances range from 2.52 to 2.88 A. The Mo-O-Si bond angle of the two siloxy groups which are trans

to each other are $133.4(3)^{\circ}$ and $134.8(3)^{\circ}$, however, that of Me₃SiO trans to NH₃ is $141.7(3)^{\circ}$ and the reason for this difference is not clear. There is no definite correlation between bond distances and bond angles of the Mo-O-Si moiety.

The atoms, Mo(1), O(1), Si(1), Mo(1'), O(1'), and Si(1') are essentially in the same plane and each pair of atoms are related by a crystallographically imposed inversion center.

$Mo_4N_4O_2(OSiMe_3)_8(py)_4.2py$, (3).

Compound (2) shows some interesting structural aspects and is the first example, to our knowledge, of a transition metal cage compound supported both by μ_2 -0 and μ_2 -N bridges. This aspect, for the formally isoelectronic 0^{2^-} and N^{3^-} bridging groups, makes this structure informative. An Ortep view of the molecule is shown in Figure 4.6. Final atomic coordinates and isotropic thermal parameters are given in appendix III. Important intramolecular distances and angles are given in Table 4.3 and 4.4 respectively.

The molecule possesses crystallographically imposed C₂ symmetry with the C₂ axis passing through the atoms O(5) and O(6) and consequently the two oxygens are situated in special positions. Each molybdenum atoms is in a distorted octahedral environment with a MoO_3N_3 skeleton. Interestingly, four Mo atoms are placed at the vertices of a perfect tetrahedron with the average Mo-Mo nonbond distance of 3.656(4) Å and the average Mo-Mo angle of 60.00(9)°. The bridging N and O atoms are placed above the edges of the



Figure 4.6 Ortep drawing of $Mo_4N_4O_2(OSiMe_3)_8(py)_4$ looking down through O(5) and O(6). CH₃ and hydrogens are omitted for clarity.



Figure 4.7. Ball-and-spoke drawing of $Mo_4N_4O_2$ skeleton of the $Mo_4N_4O_2(OSiMe_3)_8(py)_4$ molecule showing Mo_4 tetrahedron.

	atom	atom	distance	atom	atom	distance			
	M01 M01 M01 M02 M02 M02 M02 M02 M02 SI1 SI1 SI1 SI1 SI2 SI2 SI2 SI2 SI2 SI3 SI3 SI3 SI3 SI3 SI4 SI4 SI4 SI4 SI4	N3 05 02 01 N4 N4 06 03 04 N3 01 C13 C12 C11 02 C14 C16 C15 03 C17 C19 C18 04 C21 C20 C22	1.680(7) $1.904(3)$ $1.915(6)$ $1.922(6)$ $2.155(7)$ $1.685(7)$ $1.911(3)$ $1.914(6)$ $1.902(7)$ $2.157(7)$ $1.616(7)$ $1.81(1)$ $1.82(2)$ $1.86(1)$ $1.619(7)$ $1.82(1)$ $1.85(2)$ $1.83(2)$ $1.611(7)$ $1.73(2)$ $1.79(2)$ $1.82(2)$ $1.628(7)$ $1.81(2)$ $1.81(2)$ $1.82(2)$	N1 N1 N2 N2 N5 C1 C2 C3 C4 C6 C7 C8 C9 C23 C24 C25 C26 M01 M02 M01 M01 M01 M02 05	C5 C1 C6 C10 C27 C23 C2 C3 C4 C5 C7 C8 C9 C10 C24 C25 C26 C27 N1 N2 M01' M02' M02' 06	1.28(1) 1.33(1) 1.30(1) 1.32(2) 1.19(3) 1.39(2) 1.35(2) 1.35(2) 1.34(2) 1.36(2) 3.657(2) 3.68(1)			
	Distances are in the least		in angstroms. Estimated standard deviations significant figure are given in parentheses.						

Table 4.3. Intramolecular distances for $Mo_4N_4O_2(OSiMe_3)_8(py)_4$ ·2py

Table 4.4. Bond angles for $Mo_4N_4O_2(OSiMe_3)_8(py)_4.2py$.

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Table 4.4. (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C21 C20 SI1 SI2 SI3 SI4 M01 M02 C5 C5 C5 C1 C6 C6 C10 M01 M02 C27 N1 C3 C2 C3 N1 N2 C3 C2 C3 N1 N2 C8 C7 C8	SI4 SI4 O1 O2 O3 O4 O5 O6 N1 N1 N1 N2 N2 N2 N2 N2 N2 N3 N4 N5 C1 C2 C3 C4 C5 C6 C7 C8 C9	C22 C22 M01 M02 M02 M01 M02 M02 M01 C10 M02 M02 M02 M02 M02 M02 M02 M02 M02 C1 C4 C5 C4 C7 C6 C9 C10	106(1) 110(1) 141.3(4) 152.8(4) 149.2(5) 152.0(5) 147.2(5) 146.1(5) 114(1) 123.3(7) 121.9(8) 115(1) 123.8(9) 122(1) 144.5(4) 144.5(4) 144.4(4) 129(3) 124(1) 118(1) 120(1) 117(1) 127(1) 126(1) 119(2) 118(2)	N2 N5 C25 C26 C25 N5 M01 M02 M02 M02 M01	C10 C23 C24 C25 C26 C27 M01' M01' M02' M02' M02	C9 C24 C23 C24 C27 C26 M02 M02 M01 M01 M01	124(1) 109(3) 115(4) 131(4) 111(3) 122(3) 60.06(3) 60.03(3) 59.98(5) 60.02(3) 60.00(4) 59.91(4)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

tetrahedron. See Figure 4.7. The asymmetric bond distances of Mo-N (1.68(1) and 2.16(1) Å) are similar to the values observed for the cyclic tetramers of $[MoNX_3(L)]_4^6$ (structure IV in Figure 4.4). In contrast to this, the molecule possesses symmetric Mo-O [1.91(1) Å] bridges.

The difference between these two bridges, i.e., asymmetric Mo-N and symmetric Mo-O bonds, may be rationalized, albeit in part, by the geometry of the molecule. The bridging N is trans to two different groups, siloxy and pyridine, however, the bridging O is trans to two siloxy groups.

Surprisingly, the bond angles, Mo-N-Mo $(144.5(5)^{\circ} \text{ avg})$ and Mo-O-Mo $(146.7(11)^{\circ} \text{ avg})$, are close to each other and the Mo=N-Mo angles are far from the almost linear geometry observed for the cyclic tetramers. For example, two distances for Mo=N-Mo moiety of the cyclic tetramers are 1.65 and 2.17 Å for $[MoNCl_3]_4^{5a}$, 1.66 and 2.16 Å for $[MoNCl_3 \cdot (POCl_3)]_4^{6b}$, and 1.65 and 2.16 Å for $[MoNCl_3 \cdot (OBu_2)]_4^{6c}$. The Mo=N bond distance of compound (3) is 0.02 -0.03 Å longer than those of tetramers, but the Mo-N bond distance is comparable. However, these values are partially overlapped within 3σ esd's. Finally, the Mo=N multiple bond distance (1.68 Å) may be compared with that of the siloxo bridged dimer (1) (d(Mo=N) = 1.63 Å). The difference of 0.05 Å is significant and may account for the differences in bonding nature between these two closely related compounds. If the 1.63 Å Mo=N distance in compound (1) is taken as

an Mo=N triple bond for a nitridosiloxy Mo(VI) compound, then that in (3) should be counted as less than a triple bond. How does one account for the long Mo-N bond and Mo-N-Mo bond angle ? If the long and short Mo-N bonds are composed of a triple bond and a single bond, then the Mo-N-Mo bond angle should be 180°. However, in this molecule, the average bond angle is 144.5° which is some 35° less than the linear geometry. The situation is probably that the short Mo-N multiple bond is somewhere between a double and triple bond and the long Mo-N bond is less than a single bond. This kind of bonding description may leave some electron density on the bridging nitrogen atom and accounts for the bent Mo-N-Mo angle. However, it is quite likely that some distortional strain is present in Mo-O-Mo and Mo=N-Mo moieties as deduced from the solution instability of (3) followed by the NMR study. Although similar Mo-N bond distances are observed in $[MoNX_3(L)]_4$ tetramers⁶ which show almost linear Mo-N-Mo angles, the π -bonding ability of the siloxy oxygen is expected to be stronger than that of the more electronegative halide and this may account for the structural differences. The average Mo-O(Si) bond distance is 1.91(1) Å and is comparable to the terminally bound Mo-O(Si) distances of compound (1), however, again this distance is about 0.08 Å shorter than the average Mo-O(Si)distance, 1.99 Å, found in Mo_{Δ} oxo cubane compound (see chapter 3). It is interesting to note the Mo-O(Si) π -bonding difference between the nitrido siloxy compounds, (1), (3), and the oxo cubane compound (see chapter 3).

The Mo atom is 0.20(4) Å out-of-plane toward the siloxy oxygen from the plane defined by O(1)-O(5)-N(1)-N(3) or O(3)-O(6)-N(2)-N(4)and 0.26(6) Å toward a multiply-bonded N atom.

The Mo-N(py) bond distance (2.47 Å avg) is quite long compared to those of other molybdenum compounds²¹ which is again a consequence of the trans influence²² of the nitrido group. This molecule may be viewed as a pairing of the two five coordinate monooxo-bridged dinuclear fragments in a cross-wise manner exclusively through the Mo=N→Mo bonding.

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CHAPTER 5

Attempted Synthesis of Tetranuclear Molybdenum Oxide Alkoxides

Introduction

Numerous examples of transition metal-centered oxygen atom transfer reactions are well documented.¹ In particular, oxomolybdenum compounds in the oxidation states, 4, 5, and 6, show prominent oxo atom transfer chemistry. Reactions have been carried out on these systems, in most cases, to elucidate the active sites of the oxo-transfer molybdoenzymes.^{1,2} The chemistry is well developed for the oxomolybdenum compounds which bear chelate ligands. The generalized reaction is $MoO_2L + X = MoOL + XO$ where L is a chelate ligand, and X is a substrate (oxygen atom accepter or donor).¹ For example, Holm et al. showed the clean reduction of $MoO_2(L-NS_2)$ to $MoO(L-NS_2)$, where $L-NS_2$ is a tris chelate ligand with N and S binding sites, by arenethiol with the production of disulfide and water.³ In addition, $MoO_2(S_2CNEt_2)_2$ was shown to be reduced to $MoO(S_2CNEt_2)_2$ by benzenethiol with a good yield.⁴ It is known that the oxo(sulfido)molybdenum moiety of molybdoenzymes is functioning as an electron reservoir and hence easily reduced or oxidized in a physiological system.⁵

Thiol redox chemistry of molybdenum compounds for molybdenum in its higher oxidation states is closely related to the function of these enzymes. 6

In the present work, reactions of dioxomolybdenum(VI) dialkoxides⁷ $MoO_2(OR)_2$ (R = Et, Me) with alkyl(aryl)thiols in presence of pyridine was carried out. These reactions liberate alcohol and disulfide and form a reduced molybdenum compound or cluster compounds depending upon the choice of the thiol and the reaction conditions. This study may have relevance to the reduction-oxidation ability of the Mo moiety with sulfur ligands in certain molybdoenzymes.

Experimental

General considerations: All manipulations were performed under inert atmosphere or using Schlenk and vacuum techniques where appropriate. Reagents were dried following the appropriate procedures. For other details, see experimental section of chapter 2.

Reaction of $MoO_2(OEt)_2$ with PhSH. $MoO_2(OEt)_2$ (6.3 mg) was dissolved in pyridine (4.0 µL, 2 equiv/MoO_2(OEt)_2)/CD_2Cl_2 (0.5 mL) solution in an NMR tube. Into this was syringed PhSH (10 µL, 3.2 equiv) and a dark red/brown solution formed immediately. The solution was monitored periodically by ¹H NMR spectroscopy. EtOH was formed with the formation of PhSSPh. The ¹H NMR spectrum of the colorless volatiles which were vacuum transferred into another NMR

tube showed EtOH, pyridine, and excess PhSH. The dark brown solid was extracted with toluene and vacuum-dried to give a light brown solid which was identified as spectroscopically pure PhSSPh by m.p. determination (59°C), ¹H NMR, and IR spectroscopy. The ¹H NMR spectrum of the residual brown/red solid in DMSO-d₆ showed pyridine, PhS, trace EtOH, and two unassignable singlets at 2.25 and 3.25 ppm. The reaction employing DMSO-d6 instead of pyridine showed the same result.

Reaction of $MoO_2(OEt)_2$ with t-BuSH. $MoO_2(OEt)_2$ (0.678 g, 3.11 mmole) was dissolved in toluene (30 mL) by adding pyridine (3.3 mL, 41 mmole) in a 50 mL flask and sealed with a rubber septum. To this was added t-BuSH (0.36 mL, 3.2 mmole) and the solution color changed to yellow immediately and red within 10 minutes. Standing at room temperature orange-red microcrystalline solid was precipitated. To enhance the crystallization, the solution was placed in a freezer at 255 K for 2 days. Subsequent filtration, toluene wash (2 x 5 mL) and vacuum drying yielded orange-red microcrystalline solid (172 mg). (compound A) This solid is only sparingly soluble in pyridine and methylenechloride.

80-MHz ¹H NMR (in pyridine-d₅, referenced to the solvent at 7.19 ppm): \$ 1.00 (t, 3 H, CH₃); 2.01 (t, 3 H, CH₃); 4.02 (m, 1 H, CH₂); 4.57 (m, 1 H, CH₂); 5.62 (m, 1 H, CH₂); 5.91 (m, 1 H, CH₂) along with the peaks due to pyridine. 400-MHz ¹H NMR (in CD₂Cl₂, referenced to the solvent at 5.32 ppm): \$ 0.559 (t, 3 H, CH₃, J = 6.98 Hz,); 1.859

(t, 3 H, CH₃, J = 6.92 Hz); 3.420 (m, 1 H, CH₂, J = 6.84); 3.980 (m, 1 H, CH₂, J = 6.89); 5.298 (m, 1 H, CH₂, J = 6.81); 5.570 (m, 1 H, CH₂, J = 6.83), 7.806 (s,br, 2 H, py); 8.146 (s,br, 1 H, py); 9.838 (s,br, 2 H, py). 100.614-MHz ¹³C NMR (in CD₂Cl₂, referenced to the solvent at 53.80 ppm); \$ 16.43 (CH₃); 18.43 (CH₃); 68.66 (CH₂); 74.56 (CH₂); 125.74 (py); 140.50 (py); 150.80 (py). IR Data: 436 (m), 470 (m), 499 (s), 583 (s), 640 (m), 652 (sh), 661 (m), 694 (s), 735 (s), 756 (s), 803 (vw), 880 (s), 926 (m), 946 (vs), 970 (vs), 1026 (s), 1044 (vs), 1072 (s), 1095 (s), 1155 (m), 1219 (m), 1239 (w), 1288 (vw), 1358 (sh), 1383 (m), 1448 (s), 1486 (m), 1607 (m), 2863 (m), 2891 (m), 2925 (m), 2965 (m), 3079 (w), 3112 (w). cm⁻¹. Mass Data m/z [int, assgn]: 191 [35, Mo0₃(OEt)⁻], 220 [100, Mo0₂(OEt)₂⁻], 436 [3, Mo₂O₄(OEt)₄⁻].

NMR tube reaction in CD_2Cl_2 solution. $MoO_2(OEt)_2$ (30.1 mg) was dissolved in a mixture of pyridine- d_5 (52 µL, 4.4 equiv), triphenylphosphine (0.23 equiv), and CD_2Cl_2 (0.6 mL). To this was added t-BuSH (32 uL, 2 equiv), and the reaction was periodically checked by ¹H NMR spectroscopy. The spectra showed growth of two types of EtO peaks from compound A (40 % yield in 3 days) without forming any solid. A singlet at 2.74 ppm (OH) and a multiplet at 7.5 ppm (Ph3PO, trace) were observed to grow as the reaction was proceeded. Preparation of pyridine-d₅ adduct of compound A. The compound (21 mg) prepared above was partially dissolved in pyridine-d₅ (0.5 mL) and placed at 278 K in a freezer for 1 day and vacuum-dried to give totally pyridine-d₅ exchanged compound. IR Data: 499 (s), 534 (m), 583 (s), 614 (m), 623 (w), 639 (vw), 703 (w), 713 (w), 736 (m), 754 (m), 836 (m), 879 (s), 893 (m), 946 (s), 969 (vs), 1023 (s), 1089 (m), 1155 (w), 1220 (w), 1235 (w), 1319 (m),

1361 (w), 1384 (m), 1349 (w), 1447 (w), 1539 (w), 1567 (m), 2869 (w), 2893 (w), 2927 (w), 2969 (w), 3122 (w,br) cm⁻¹.

Reaction of MoO₂(OEt)₂ with t-BuSH in pure pyridine solution. MoO₂(OEt)₂ (0.133 g, 0.611 mmole) was dissolved in pyridine (5 mL). To this was added t-BuSH (140 μ L, 2 equiv) and the solution color immediately changed to red. After 10 minutes significant amount of red microcrystalline solid began to precipitate. The flask was stored in a freezer at 255 K for 1 day. Filtration and washing with pyridine (3 x 3 mL) and subsequent vacuum drying resulted in redbrown microcrystalline solid (0.107 g), Mo₄O₈(OEt)₄(py)₄·½py; (compound B). Yield 70 %. Anal. calc for Mo₄O₈(OEt)₄(py)₄·½py.: C, 34.95; H, 4.09; N, 6.01; Mo, 36.62. Found: C, 34.37; H, 4.06; N, 6.09; Mo, 35.26. IR Data; 439 (w), 464 (w), 504 (m), 590 (m), 630 (w), 643 (m), 652 (m), 660 (m), 696 (s), 705 (m), 736 (m), 761 (m), 800 (w), 880 (m), 902 (m), 926 (s),947 (vs), 1018 (m), 1045 (s), 1058 (s), 1071 (m), 1098 (s), 1156 (w), 1219 (m), 1242 (vw), 1349 (w),

1356 (w), 1370 (m),1380 (m), 1349 (sh), 1449 (s), 1485 (m), 2836 (m), 2865 (m), 2925 (m), 2966 (m), 3028 (w), 3051 (w), 3081 (w), 3110 (w) cm⁻¹.

Preparation of pyridine-d₅ adduct of compound B. The same procedure was used except the use of pyridine-d₅ instead of normal pyridine. IR Data: 472 (m), 502 (m), 533 (m), 591 (w), 617 (w), 636 (w), 660 (m), 668 (sh), 737 (m), 836 (w), 842 (sh), 880 (m), 889 (m), 902 (w), 926 (m), 949 (vs), 981 (m), 1045 (m), 1059 (m), 1098 (m), 1155 (vw), 1301 (w), 1317 (m), 1325 (w), 1349 (w), 1356 (w), 1369 (w), 1384 (m), 1399 (m), 2863 (w), 2927 (w), 2970 (w) cm⁻¹.

Reaction of $MoO_2(OMe)_2$ with t-BuSH. $MoO_2(OMe)_2$ (0.253 g, 1.16 mmole) was dissolved in pyridine (15 mL) to give a colorless solution. Into this solution was syringed t-BuSH (0.300 mL, 2.66 mmole) and the solution color immediately changed to red-brown. The red microcrystalline solid began to precipitate within 1/2 h. The flask was stored at 255 K for a day. Stripping of the volatiles at room temperature gave yellow-orange solid contaminated with a small amount of yellow thick oil. Contamination by t-BuSSBu-t was confirmed by ¹H NMR and IR spectroscopy. This solid was a mixture of two compounds, one pyridine soluble and the other pyridine insoluble as discussed below.
Pyridine soluble species, compound C: 80-MHz ¹H NMR (in pyridine-d₅, referenced to the solvent at 8.71 ppm): & 2.87 (s, 3 H); 4.16 (s, 3 H); 5.18 (s, 3 H); 5.48 (s, 3 H). IR Data of the impure solid: ν (Mo=Ot); 925, 958, ν (C-O); 1017, 1044, 1071 cm⁻¹. The yield of this component was approximately 30% followed by 1H NMR spectroscopy.

Pyridine insoluble component, compound D: The same procedure was used to prepare the mixture of compounds using deuterated pyridine. The red-brown mixture was washed with pyridine- d_5 to eliminate the pyridine soluble species then vacuum-dried to give a red-brown crystalline solid. IR data (400-1600 cm⁻¹ region): 473 (w), 503 (m), 533 (m), 618 (w), 636 (w), 661 (m), 740 (m), 838 (m), 892 (m), 924 (m), 950 (vs), 982 (m), 1042 (m), 1073 (s), 1156 (w), 1304 (w), 1322 (m), 1386 (m), 1400 (m), 1458 (w), 1541 (w), 1568 (m) cm⁻¹.

Results and Discussion

Reaction of MoO₂(OEt)₂ with PhSH and t-BuSH

 $MoO_2(OEt)_2$ is polymeric in the solid state mainly via Mo=0 \rightarrow Mo and ethoxy bridging interactions. (For synthesis and properties, see chapter 2.) However, when the compound is dissolved in pyridine-d₅ or DMSO-d₆, it is monomeric as judged by the presence of only one type of sharp ethoxy resonance in the ¹H NMR spectrum. This species can be generated in aromatic hydrocarbons by adding two or more equivalents of coordinating base.

Reaction of $MoO_2(OEt)_2$ with PhSH in CD_2CI_2 /pyridine solution followed by a ¹H NMR tube reaction showed the following;

 $MoO_2(OEt)_2(py)_2 + 2 PhSH \rightarrow Mo \ complex + 2 EtOH + PhSSPh$ (1) The formation of the disulfide was quantitative as confirmed by ¹H NMR, IR spectroscopy, and a melting point determination. All the ethoxy groups converted to ethanol. The reaction in DMSO-d₆/ CD₂Cl₂ also gave the same result.

In contrast to this, the reaction of $MoO_2(OEt)_2(py)_2$ with t-BuSH in benzene or toluene at room temperature generated orange-red microcrystalline compound A. Compound A is only slightly soluble in methylenechloride and pyridine. ¹H NMR spectrum in CD_2Cl_2 showed two types of methyl resonances at 0.56 and 1.86 ppm with a difference of 1.30 ppm. The methylene resonances are four envelopes of multiplets centered at 3.42, 3.98, 5.30, and 5.57 ppm. See Figure 5.1.



The coupling constants, J^3 , are 6.8-7.0 Hz and geminal coupling constants, J^2 , are 11.7 and 11.0 Hz respectively.

The spin-decoupling 1 H NMR experiment revealed the correlation of methyl-to-methylene groups, i.e., low-low, and high-high field correlation. See Figure 5.1. Furthermore, when one methyl group is decoupled, the corresponding methylene group simplifies to a doublet of doublets. The 13 C NMR spectrum showed only two types of ethoxy groups in the compound. These experiments clearly demonstrate the diastereotopic nature of the methylene groups in the compound. Similar NMR pattern was observed for the ¹H NMR spectrum of $W_2Cl_2(NEt_2)_4$ compound in toluene-d₈, however, the spectrum was interpreted in terms of proximal and distal arrangements of NEt groups which are influenced by the diamagnetic anisotropy exerted by short $W \equiv W$ bond.⁸ The large chemical shift difference for two methyl groups in compound A is probably arises from the magnetic anisotropy of both Mo-Mo bonds and the pyridine rings. Compare with the ¹H NMR spectra of $Mo_4O_8(OSiMe_3)_4(HNMe_2)_4$ (chapter 3) and $Mo_4N_4O_2$ - $(OSiMe_3)_8(py)_4$ (chapter 4) for the effect. The mass spectrum (Figure 5.3) of this compound showed $MoO_3(OEt)^-$, $MoO_2(OEt)_2^-$, and $Mo_2O_4^ (OEt)_4$. The IR spectrum is shown in Figure 5.4 in which Mo=0_t stretchings are assigned to 969 and 946 $\rm cm^{-1}$.

The reaction of $MoO_2(OEt)_2$ with t-BuSH in pure pyridine solution resulted in a red-brown crystalline solid which is insoluble in toluene, benzene, methylenechloride, and pyridine, and is reminiscent of the $Mo_4O_8(O-i-Pr)_4(py)_4$ compound⁹ which is also insoluble in the



Figure 5.2. PIPINICI mass spectrum of compound (A).

same solvents. Due to the insolubility of compound B it was not possible to study its solution behavior. However, the elemental analysis confirmed the formulation $Mo_4O_8(OEt)_4(py)_4$. Comparison of the IR spectra of both normal and deuterated pyridine adducts (see experimental section and Figure 5.5) confirmed $Mo=O_t$ stretches at 949, 926 cm⁻¹.

Reaction of $MoO_2(OMe)_2$ with t-BuSH in pure pyridine.

The thiol reduction of $MoO_2(OMe)_2$ in pure pyridine solution produces two compounds. One is a pyridine soluble species (compound C) which shows four MeO peaks at 2.87, 4.16, 5.18, and 5.48 ppm with an equal intensity ratio along with coordinated pyridine. (Figure 5.3) The identity of the Mo-bound methoxy was confirmed by hydrolyzing the compound. The hydrolysis of compound C is facile and the 1 H NMR spectrum shows only methanol. All the methoxy groups were converted to MeOH within 10 minutes at room temperature. (see Figure 5.3) The IR spectrum of compound C revealed Mo= 0_+ stretchings at 958 and 925 cm^{-1} . Again, the pyridine insoluble species resulted in (compound D) and the compound showed no solubility in most of the solvents. The IR spectrum of the deuterated pyridine adduct of compound D, surprisingly, resembles that of the ethoxy analog (py-d₅ analog of compound B) in the 400-1200 cm^{-1} region except for a few minor differences in 880-905 and 1040-1100 cm⁻¹ regions. ν (Mo=Ot) of compound D were assigned to 950 and 924 $\rm cm^{-1}$ bands.



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Figure 5.3. 80 MHz ¹H NMR spectra of (a) $MoO_2(OMe)_2$ in pyridine-d₅, (b) compound (c) in pyridine-d₅, (c) a spectrum after adding trace H₂O to (b).

Comparison of the IR spectra and structural consideration.

The IR spectra of polymeric $MoO_2(OEt)_2$ and the four structurally related compounds are given in Figure 5.4 and band assignments are given in Table 5.1. The wavenumbers shown in the Figure 5.4.(c) and 5.4.(d) were selected by comparing the spectra of normal pyridine with those of deuterated pyridine adducts using the elimination method. The spectrum (b) of $MoO_{2}(OEt)_{2}$ in Figure 5.4 shows Mo=Ot stretches at 948 and 919 cm^{-1} and the strongest, broad band at 819 cm^{-1} which may be assigned to Mo=0+Mo stretch.¹⁰ This interaction as well as the bridge formation of OR groups are possible because of the coordinative unsaturation of $[MoO_2(OR)_2]_n$ compounds. This assignment is strongly supported by the disappearance of the 819 $\rm cm^{-1}$ peak after forming discrete molecular compounds. Cf. spectra (c) and (d). Spectra (a) and (c) in Figure 5.4 show the very similar Mo=Ot stretching frequencies in 945 - 970 cm^{-1} range. The monooxomolybdenum compounds show, in general, one or two $Mo=0_+$ stretches in 950 -980 cm^{-1} region,^{2,5} and indeed the structurally characterized cubane compound shows two band at 956 and 968 cm^{-1} . The spectra (d) and (e) in Figure 5.4 also show two similar bands in 920- 950 $\rm cm^{-1}$ assignable to $\nu(Mo=0_+)$. Further comparison reveals common frequencies in $660 - 665 \text{ cm}^{-1}$ for (a), (d), and (e) which may be assigned to the $Mo_2(0_h)_2$ stretches of Mo_4 cluster structures. The two medium to weak bands in the two ranges, i.e., 735-750, and 460-475 $\rm cm^{-1}$ may be assigned to the local $\rm Mo_2(O_b)_2$ stretches. It is well known that, in general, $\nu(M=0_t)>\nu(Mo-0_b)$, and $\nu(M-OR_t)>\nu(M-OR_b)$.¹¹



Figure 5.4. IR spectra of $[MoO_2(OEt)_2]_n$ and tetranuclear cluster oxomolybdenum alkoxides (siloxide).

compound						
1	2	A	В	С	D	assgn.
478 - 566 633 -	464 482 - 665 -	470 499 583 - 736 754	472 502 - 660 737 -	473 503 - 661 740	- - - - -	Mo ₂ (O _b) ₂ Mo-N Mo-u ₃ -OR Mo ₂ (O _b) ₂
819 872 - 919 948 1027 1048	- 882 900 956 968 - -	- 879 - 946 969 1023 -	- 880 902 926 949 - 1045	- - 924 950 - 1042	- - 925 956 1017 1044	Mo=O > Mo Mo=O _t Mo=O _t Mo-u ₃ -OR Mo-u ₃ -OR
- 1087	-	- 1089	1059 1098	- 1073	1071	Mo-OR _t

Table 5.1. Characteristic IR frequencies of oxomolybdenum compounds.

1. [MoO₂(OEt)₂]_x

- A. $Mo_4(u_3-OEt)_4(OEt)_4(py)_4$
- B. Mo₄0₄(u₂-0)₂(u₃-0)₂(u₂-0Et)₂(0Et)₂(py)₄
- C. $Mo_40_4(u_2-0)_2(u_3-0)_2(u_2-0Me)_2(0Me)_2(py)_4$
- D. $Mo_40_4(u_2-OMe)_4(u_3-OMe)_2(OMe)_2(py)_4$

It is also reasonable to assume that $\nu(M-O_b)>\nu(M-OR)$ solely based on mass consideration.

However, spectrum 5.4.(c) shows unique bands at 583 and 754 cm^{-1} which are not present in the spectra of the other three compounds. These bands are presumably arising from the unique structural geometry not possesed by the other three compounds. The C-O stretching region is also informative. Infrared studies of a large number of metal alkoxides show a distinction between bridging and terminal alkoxy ligands in which terminal ν (C-O)= 1056-1079 and bridging ν (C-O)=1024-1053.¹¹ The IR of the polymeric MoO₂(OEt)₂ (Figure 5.4.(b)) shows three bands at 1027, 1048, and 1087 cm^{-1} . Figure 5.4.(c) shows the bands at 1023 and 1089 cm^{-1} . Figure 5.4.(d) shows them at 1045, 1059, and 1098 cm^{-1} . These stretches are found in Figure 5.4.(e) at 1042 and 1073 cm^{-1} . Since Figure 5.4.(e) shows only two bands in this region and considering the resemlance of spectra 5.4.(d) and 5.4.(e), it may be assumed that the 1045 and 1059 cm^{-1} bands of spectrum 5.4.(d) are the split components of the bridging OEt. Based on these observations, the C-O stretches for these structurally-related compounds are classified as 1020-1040, 1040-1060, and 1070-1100 cm^{-1} regions. The 1020-1060 ${\rm cm}^{-1}$ region is related to the $u({
m C-0}){
m M}$ of the bridging alkoxy groups and 1070-1100 cm^{-1} to that of terminally bonded alkoxy groups. Furthermore, the IR spectrum of compound (C) (not shown) reveals the C-O stretching bands at 1017, 1044, and 1071 cm^{-1} which support this assignment at least for these structurally-related compounds. It is

apparent that compounds A and C have a common structural unit and so do the compounds B and D since compounds A and C show the lowest ν (C-O) below 1025 cm⁻¹ which are not present for compounds B and D.

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Considering the NMR spectra and coordination number, the compounds must possess a very symmetric structure and no more than four metal units. Based on these, a cubane-type structure with a $Mo_4(\mu_3-OR)_4$ core can be proposed for compound A which is consistent with all the data, i.e., 1 H, 13 C NMR, IR spectroscopy, and solubility behavior. For compounds B and D, based on analytical data, IR data, and solubility behavior, the fused bioctahedral structure can be proposed. The tetranuclear oxo Mo(V) isopropoxy compound, $Mo_A O_B (O-i-Pr)_A (py)_A$ was structurally characterized and shows a fused bioctahedral structure.⁹ The compound is insoluble in hydrocarbons, methylenechloride, and pyridine which is the same behavior for compounds Band D. The ν (Mo=Ot) of this i-PrO compound have been assigned to 949 and 914 cm^{-1} by an 0¹⁸ labelling experiment.⁹ The probable structure of compound C, considering four distinct MeO resonances in the $^{1}\mathrm{H}$ NMR, IR spectroscopy, and the solubility behavior, is a fused bioctahedral structure, but, exclusively with bridging methoxy groups. It is assumed that with more RO groups present in a given structure, it will be more soluble in a given solvent.

However, further work including X-ray structure determinations of both compounds (proposed cubane and fused bioctahedral structures) is needed to clarify this proposal. Although X-ray structures are not

available and characterization is not firm, it would be interesting to speculate upon the mechanistic aspects of the thiol reduction process of the dioxo molybdenum alkoxides. The solution species of the pyridine adduct is presumed to be the monomeric $MoO_2(OEt)_2(py)_2$. The coordinated pyridine is dynamically exchanged with the excess pyridine at room temperature as evidenced by the presence of only one type of pyridine resonance in the NMR spectrum. When thiol is added to this solution immediate reaction is observed as judged by a dramatic color change.

A catalytic cycle for enzymatic thiol-disulfide formation reactions is proposed.³ The first step is expected to be the replacement of the coordinated pyridine by thiol to form an adduct as shown below.

 $MoO_2(OR)_2 + RSH \Rightarrow MoO_2(OR)_2(RSH)$ (1) Next, a proton transfer is expected either to terminally-bonded oxygen to form a thiolate-hydroxide intermediate or to an alkoxy group to form a thiolate-coordinated alcohol intermediate. See below.

 $M_0O_2(OR)_2(RSH) \rightarrow M_0O(OR)_2(RS)(OH)$ (2) $M_0O_2(OR)_2(RSH) \rightarrow M_0O_2(OR)(ROH)(RS)$ (3)

Following reaction (2) would be the interaction of the dialkoxythiolate with RSH to produce $[MoO(OR)_2]$ intermediate, disulfide RSSR, and H₂O. See the equation (4). This type of RS^{...}SR interaction has been proposed for Mo-bis(thiolate) systems.¹² For reaction (3) dimerization of two intermidiates to form $Mo_2O_4(OR)_2$ and RSSR as shown in (5) is expected.

$$MoO(OR)_{2}(SR)(OH) + RSH \rightarrow MoO(OR)_{2} + RSSR + H_{2}O \quad (4)$$

2 MoO₂(OR)(SR) $\rightarrow Mo_{2}O_{4}(OR)_{2} + RSSR \quad (5)$

The other possibilities are the following reactions;

$$2 \text{ MoO(OR)}_{2}(\text{SR})(\text{OH}) \neq \text{Mo}_{2}\text{O}_{4}(\text{OR})_{2} + 2 \text{ ROH} + \text{RSSR}$$
(6)

$$2 \text{ MoO(OR)}_{2}(\text{SR})(\text{OH}) \neq \text{Mo}_{2}\text{O}_{3}(\text{OR})_{4} + \text{H}_{2}\text{O} + \text{RSSR}$$
(7)

$$\text{Mo}_{2}\text{O}_{3}(\text{OR})_{4} = \text{MoO}_{2}(\text{OR})_{2} + \text{MoO(OR)}_{2}$$
(8)

However, these reactions generate the same intermediates as shown above. The final step would be the cluster formation reactions with the structural choice of either a cubane or a fused bioctahedral type as shown below.

$$4 \operatorname{MoO(OR)}_{2}(\operatorname{py}) \rightarrow \operatorname{Mo}_{4}\operatorname{O}_{4}(\operatorname{OR})_{8}(\operatorname{py})_{4}$$
(9)

$$2 Mo_2 O_4 (OR)_2 (py)_2 \neq Mo_4 O_8 (OR)_4 (py)_4$$
(10)

In all the above equations the coordination by the neutral ligands, i.e., pyridine, RSH, and ROH, are assumed due to the coordinative unsaturation of the Mo center, however these are omitted for clarity.

The adoption of the particular structural preference seems to be dependent on the solvent nature and the pyridine concentration. However, a small variation of the pyridine and thiol concentration seems not to greatly affect the structural preference as observed in a series of control experiments for the ethoxy compound. An example of this kind of behavior was reported in the syntheses of Cu(I)-benzimidazole adducts in which different polynuclear complexes were synthesized starting from the same monomeric precursor simply by altering the solvent system.¹³ It may be true that "the final structure is dependent on the nature of the solvated monomeric precursor existing in the different solutions and acting as building block of the final polynuclear structure". 13

The yield of the proposed compound, $Mo_4O_4(OEt)_8(py)_4$, is only 20 % in aromatic hydrocarbon solvents and at best 40% confirmed by ¹H NMR spectroscopy in CH_2Cl_2 . This may be ascribed to a kinetic effect or the formation of water which may consume the precursor compound. For this reaction, addition of a dehydrating agent along with an oxygen scavenger would increase the yield. However, the yield of $Mo_4O_8(OEt)_4(py)_4$ compound prepared in pure pyridine is approximately 70 %. It was also observed, by ¹H NMR tube reaction, that the yield of the proposed $Mo_4O_4(OMe)_8(py)_4$ compound was 30 %. Note that two compounds C and D were isolated from the reaction in pure pyridine. This implies that at least two types of intermediates are formed which lead to the two structurally different compounds.

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CHAPTER 6

Conclusions and Summary

The cocondensation reactions of molybdenum trioxide with various organosilanes were investigated. The reactions with tetraalkoxysilanes produce polymeric dioxomolybdenum dialkoxides, $[MoO_2(OR)_2]_X$ (R = Me, Et, n-Pr), which may not be accessible through conventional solution synthesis. The cocondensation of trialkylalkoxy (aryloxy) silanes seems to proceed via an addition intermediate, $[MoO_2(OSiR_3)(OR')]_n$ (R₃ = Me₃, R' = Me; R₃= Me₃, R' = Ph; R₃ = t-BuMe₂, R' = Me).

From the reactions, $MoO_2(OSiMe_2(t-Bu))_2(py)_2$, $MoO_2(OPh)_2(py)_2$, and $Mo_3O_6(OSiMe_2(t-Bu))_4(py)_3$ were isolated as stable compounds. The final products depend on the affinity of the ligand fragment toward Mo center and also on the easy formation of disiloxane as a byproduct. The Mo₄ cluster compound, $Mo_4O_8(OSiMe_3)_4(HNMe_2)_4$, was prepared through the interaction of MoO_3 with Me_3SiNMe_2 followed by suitable work-up. A single crystal X-ray structural analysis shows the compound to possess an $Mo_4(\mu_3-O)_4$ cubane core with two localized Mo-Mo single bonds (2.605 Å avg) and four nonbonds (3.42 Å avg), and is the first structurally characterized Mo(V) oxo cubane compound which is exclusively supported by monodentate ligands. The compound is believed to be formed from dioxo-bridged Mo2 fragments through a reduction/protonation process. The solution synthesis using MoO_2Br_2 as an $Mo_2O_4^{-2}$ source was successful with a moderate yield, and supports the idea that the $Mo_4O_8^{-4}$ cluster is formed via. self-assembly of two dimeric units upon reduction. Nitrido(oxo)molybdenum(VI) siloxide compounds, $Mo_2N_2(OSiMe_3)_6(NH_3)_2$ and $Mo_4N_4O_2$ - $(OSiMe_3)_8(py)_4$, were prepared by the cocondensation reaction of MoO₃ with $HN(SiMe_3)_2$ followed by suitable work-up. The pyridine adduct of nitridomolybdenum(VI) siloxide MoN(OSiMe₃)₃(py) was accessible by treating the ammonia adduct with pyridine. The nitrido Mo(VI) siloxides $[MoN(OSiMe_3)_3(L)]_n$ (L = NH₃, pyridine) show fluxional solution behavior, however, the tetranuclear nitrido-oxomolybdenum(VI) siloxide compound is rigid in solution and slowly disproportionates to give $[MoN(OSiMe_3)_3(py)]_n$ and an Mo(VI) oxide-nitride-pyridine adduct. The high yield synthesis of $[MoN(OSiMe_3)_3NH_3]_2$ was achieved by the reaction of MoO_3 ·2H₂O with hexamethyldisilazane. A single crystal X-ray diffraction study for the ammonia adduct shows a dimeric nature of the compound in solid state with siloxy bridges and is the first example of siloxo-bridged structure for nitridomolybdenum(VI) compo-Molecular structure of $Mo_4N_4O_2(OSiMe_3)_8(py)_4$ revealed $Mo_4N_4O_2^{-8}$ unds. cage core in which 4 Mo are assembled by two symmetric bent $\mu_2\text{-}0$ and four unsymmetric bent μ_2 -N bridges and is the first structurally characterized example of molybdenum compounds which contain both $\rm N^{-3}$ and 0^{-2} bridges in the same structure. The four molybdenum atoms in the molecule form a perfect tetrahedron with the average Mo-Mo nonbonding distance of 3.656(3) Å.

Finally, attempted syntheses to prepare tetranuclear Mo(V)- and Mo(IV)-oxide-alkoxide cluster compounds via a thiol reduction process was rationalized in terms of a reduction process occurring either on molybdenum bound terminal oxygen or alkoxy group. This process may have a close relationship with oxomolybdenum moiety of molybdoen-zymes, and demonstrates the synthetic possibility of a series of molybdenum oxide alkoxides compounds which are placed in between the two extremes, i.e., molybdenum alkoxides and molybdenum oxides.

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.

Appendix I

Supplemental X-Ray Data for $Mo_4O_8(OSiMe_3)_4(HNMe_2)_4$

Figure A.I.1. Packing diagram
Table A.I.1. Crystallographic data
Table A.I.2. Intramolecular distances
Table A.I.3. Bond angles
Table A.I.4. Least-squares plane
Table A.I.5. Positional parameters
Table A.I.6. Anisotropic temperature factors



Figure A.I.1. Packing diagram of $Mo_4O_8(OSiMe_3)_4(HNMe_2)_4$. Hydrogen and carbon atoms are omitted for clarity.

```
Mo4Si4012N4C20H64
emprical formula
formula weight
                                              1048.85
crystal color, form, dimensions
                                             red plate, 0.3x0.3x0.15 mm
crystal system
                                             monoclinic
lattice parameters
                                              a = 20.248 (4) Å
                                              b = 20.151 (6) Å
                                              c = 24.576(7) Å
                                              B = 114.14^{\circ}(2)
                                              V = 9150 (4) Å^3
space group
                                              P_{21/c} (# 14)
Z value
                                              8
                                              1.523 \text{ a} \cdot \text{cm}^{-3}
D<sub>calc</sub>
                                              4168
F<sub>000</sub>
\mu (Mo K-\alpha)
                                              11.99 \text{ cm}^{-1}
                                             Rigaku AFC<sub>6</sub>
Diffractometer
Radiation
                                              Mo K-\alpha (\lambda = 0.71069)
                                              graphite-monochromated
                                              23°C
temperature
2 - \theta_{max}
                                              50.1°
scan method
                                              2θ-ω
data collection speed
                                              16.0°/min
h k l limits
                                              ± 24, +24, +29
total no. of measd data
                                              13486
no. observations (I>3.00(\sigma(I)))
                                              3312
no. variables
                                              393
residuals: R; R<sub>w</sub>
                                              0.065; 0.072
goodness of fit indicator
                                              1.35
maximum shift in final cycle
                                             7.16
                                             0.74 e/Å^3
largest peak in final diff. map
                                                           _____
```

atom	atom	distance	atom	atom	distance
M01 M01 M02 M02 M02 M03 M01 M01 M01 M01 M01 M01 M02 M02 M02 M02 M02 M02 M02 M03 M03 M03 M03 M03 M03 M04 M04 M04 M04 M04 M04 M04 M04 M04 M04	M03 M04 M03 M04 M02 M04 01 05 06 011 N1 08 02 06 012 05 N2 07 03 07 03 07 08 013 N3 05 04 07 08 014 N4 06	3.415(4) 3.419(4) 3.406(4) 3.421(4) 2.607(4) 2.608(4) 1.65(2) 1.95(2) 1.97(2) 1.99(2) 2.16(2) 2.39(2) 1.68(2) 1.95(2) 1.98(2) 1.99(2) 2.20(3) 2.34(2) 1.64(2) 1.93(2) 1.97(2) 2.01(2) 2.21(3) 2.37(2) 1.65(2) 1.98(2) 2.02(2) 2.19(3) 2.39(2)	M011 M011 M012 M012 M012 M013 M011 M011 M011 M011 M011 M011 M012 M012	M014 M013 M013 M014 M012 M014 021 026 025 031 N11 027 022 025 025 026 032 N12 028 033 N13 025 028 033 N13 025 024 028 034 027 N14 026	3.414(4) 3.422(4) 3.430(4) 3.431(4) 2.604(4) 2.595(4) 1.66(2) 1.94(2) 2.02(2) 2.02(2) 2.20(2) 2.43(2) 1.67(2) 1.95(2) 2.05(2) 2.05(2) 2.05(2) 2.17(3) 2.38(2) 1.63(2) 1.96(2) 2.01(2) 2.20(3) 2.34(2) 1.96(2) 2.01(2) 2.20(3) 2.34(2) 1.98(2) 1.98(2) 1.98(2) 2.18(3) 2.37(2)

Table A.I.2. Intramolecular distances for $Mo_4O_8(OSiMe_3)_4(HNMe_2)_4$

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table A.I.2. (cont)

atom	atom	distance	atom	atom	distance		
SI1 SI1 SI1 SI2 SI2 SI2 SI2 SI3 SI3 SI3 SI3 SI3 SI3 SI3 SI3 SI3 SI4 SI4 SI4 SI11 SI11 SI11 SI11 SI11 SI	011 C1 C2 C3 012 C4 C5 C6 013 C7 C8 C9 014 C10 C11 C12 031 C31 C31 C31 C32 C33 032 C34 C35 C36 033 C37	$\begin{array}{c} 1.63(2)\\ 1.84(4)\\ 1.90(4)\\ 1.83(4)\\ 1.63(2)\\ 1.81(4)\\ 1.83(3)\\ 1.86(4)\\ 1.63(2)\\ 1.85(4)\\ 1.63(2)\\ 1.85(4)\\ 1.95(4)\\ 1.95(4)\\ 1.83(4)\\ 1.64(2)\\ 1.84(5)\\ 1.91(4)\\ 1.80(4)\\ 1.60(2)\\ 1.82(4)\\ 1.82(4)\\ 1.82(4)\\ 1.82(4)\\ 1.82(4)\\ 1.82(4)\\ 1.93(5)\\ 1.95(5)\\ 1.63(2)\\ 1.86(4)\\ \end{array}$	SI13 SI13 SI14 SI14 SI14 SI14 SI14 N1 N2 N2 N3 N3 N4 N4 N1 N11 N12 N12 N13 N13 N13 N14 N14	C38 C39 O34 C40 C41 C42 C21 C22 C23 C24 C25 C26 C27 C28 C51 C52 C53 C54 C55 C56 C57 C58	1.87(4) $1.86(5)$ $1.63(2)$ $1.87(5)$ $1.80(5)$ $1.42(4)$ $1.50(4)$ $1.43(4)$ $1.48(4)$ $1.51(4)$ $1.42(4)$ $1.42(4)$ $1.42(4)$ $1.53(4)$ $1.51(5)$ $1.42(4)$ $1.53(4)$ $1.51(5)$ $1.42(4)$ $1.46(4)$ $1.48(4)$ $1.43(4)$		
Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.							

							
atom	atom	atom	angle	atom	atom	atom	angle
M02 M03 M01 M03 M04 M04 M03 M04 M03 M01 01 01 01 01 01 01 01 01 01 01 01 01 0	M01 M01 M02 M02 M03 M03 M03 M04 M04 M04 M04 M01 M01 M01 M01 M01 M01 M01 M01 M01 M01	M03 M04 M04 M04 M04 M02 M01 M02 M02 05 06 011 N1 08 M02 06 011 N1 08 M02 011 N1 08 M02 011 N1 08 M02 011 N1 08 M02 011 N1 08 M02 011 N1 08 M02 011 N1 08 M02 011 N1 08 M02 011 N1 07 07	67.3(1) 67.6(1) 44.87(8) 67.7(1) 67.6(1) 44.92(8) 67.8(1) 67.7(1) 44.95(8) 67.5(1) 67.2(1) 44.81(7) 113.5(8) 105.0(8) 95.8(9) 93(1) 169.5(8) 96.8(7) 89.6(7) 85.6(7) 153.4(8) 76.5(7) 49.2(5) 158.8(8) 81.6(8) 77.3(7) 47.8(5) 94(1) 81.5(7) 134.2(6) 77.0(9) 129.4(7) 92.3(5) 111.3(9) 95.0(9) 106.7(8) 94(1) 171.7(8)	M012 M012 M014 M011 M013 M014 M014 M014 M011 M013 M011 02 06 06 06 06 06 06 06 06 06 06 06 06 06	M011 M011 M012 M012 M012 M013 M013 M013 M013 M014 M014 M014 M02 M02 M02 M02 M02 M02 M02 M02 M02 M02	M014 M013 M013 M014 M014 M012 M012 M012 M012 M012 M01 05 N2 07 M01 0 05 N3 N3 05 N3 N3 05 N3 N3 N3 05 N3 N3 05 N3 N3 N3 N3 N3 N3 N3 N3 N3 N3 N3 N3 N3	68.0(1) 67.8(1) 44.62(8) 67.5(1) 67.3(1) 44.46(8) 67.5(1) 67.8(1) 44.68(8) 67.8(1) 44.72(8) 96.4(7) 87.6(7) 89.3(7) 154.4(9) 76.4(7) 48.7(5) 157.7(7) 91.1(9) 81.9(7) 135.9(5) 82.2(9) 75.8(6) 48.0(5) 78.1(8) 130.0(7) 91.1(4) 115.0(8) 105.9(9) 94.8(9) 93(1) 168.4(8) 97.7(7) 89.5(7) 87.9(8) 151.6(9) 76.0(6)

Table A.I.3. Bond Angles for $Mo_4O_8(OSiMe_3)_4(HNMe_2)_4$

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Table A.I.3. (contd)

atom	atom	atom	angle	atom	atom	atom	angle
07 08 08 08 013 013 013 013 013 013 013 013	M03 M03 M03 M03 M03 M03 M03 M03 M03 M04 M04 M04 M04 M04 M04 M04 M04 M04 M04	M04 013 N3 05 M04 N3 05 M04 05 M04 07 08 014 N4 06 M03 012 025 026 032 N12 028 M011 025 026 032 N12 028 M011 025 026 032 N12 028 M011 025 026 032 N12 028 M011 025 026 032 N12 028 M011 025 026 032 N12 028 M011 025 026 032 N12 028 M011 025 028 M011 025 028 M011 025 028 M011 025 028 M011 025 028 M011 025 028 M011 025 028 M011 025 028 M011 025 028 M011 025 028 M011 025 028 M011 025 028 M011 025 028 M011 025 028 M011 025 028 M011 025 028 M011 025 028 M011 025 028 M011 0028 M0110 0028 M01100 0028 M0110000000000000000000000000000000000	$\begin{array}{c} 48.6(5)\\ 158.1(8)\\ 81(1)\\ 76.5(7)\\ 48.9(6)\\ 91(1)\\ 81.8(7)\\ 136.0(6)\\ 75.7(8)\\ 129.6(7)\\ 92.3(4)\\ 106.2(9)\\ 111.6(9)\\ 97.0(9)\\ 94(1)\\ 171.3(8)\\ 95.5(7)\\ 88.1(7)\\ 156.0(8)\\ 82(1)\\ 74.8(6)\\ 47.3(5)\\ 89.0(8)\\ 155(1)\\ 77.0(7)\\ 48.6(6)\\ 91.9(4)\\ 112.9(8)\\ 106.1(8)\\ 95.5(9)\\ 94(1)\\ 172.1(8)\\ 95.6(7)\\ 89.3(8)\\ 86.5(8)\\ 153(1)\\ 74.8(7)\\ 50.0(6)\\ 157.8(8)\\ 81(1)\\ 75.1(7)\\ 47.7(5)\\ 93(1)\\ 82.8(8)\\ \end{array}$	014 014 014 N4 N4 06 021 021 021 021 021 021 021 021	M04 M04 M04 M04 M04 M04 M011 M011 M011 M	N4 06 M03 06 M03 025 031 N11 027 M012 025 031 N11 027 M012 031 N11 027 M012 031 N11 027 M012 025 031 N11 027 M012 025 M014 028 033 N13 025 M014 028 M014 028 M014 028 M014 028 M014 028 M014 028 M014 028 M014 028 M014 028 M014 028 M014 M014 028 M014 M014 028 M014	91(1) 81.4(7) 137.4(5) 77.9(9) 129.0(8) 91.4(4) 114.7(8) 105.7(9) 96(1) 94(1) 168.5(8) 96.6(7) 89.6(8) 86.0(8) 151.4(8) 76.8(6) 50.1(6) 158.1(8) 82.0(9) 74.4(7) 47.9(5) 92(1) 83.6(7) 135.4(6) 74.6(7) 129.8(7) 168.9(9) 97.3(7) 89.7(8) 87.2(8) 155(1) 78.5(7) 49.3(5) 156.2(8) 80(1) 75.5(7) 47.7(6) 93(1) 80.8(7) 136.3(6) 76.8(9) 127.6(8) 92.2(5) 114(1)
Table A.I.3. (contd)

atom	atom	atom	angle	atom	atom	atom	angle
032 N12 N12 028 023 023 023 023 028 028 034 034 034 034 034 034 034 034 034 034	M012 M012 M012 M013 M013 M013 M013 M014 M014 M014 M014 M014 M014 M014 M014	M011 028 M011 M011 027 028 033 N13 026 M013 027 N14 026 M013 026 M013 026 M013 026 M013 026 M013 026 M013 026 M013 026 M013 026 C1 C2 C2 C2 C4 C5 C6 C5 C6 C5 C6 C5 C6 C7 C7 degrees	136.0(6) 78.1(9) 128.3(9) 90.9(5) 112.2(9) 107(1) 96(1) 93(1) 76.9(7) 48.7(6) 160.4(8) 92(1) 82.8(8) 136.3(6) 81.8(9) 77.7(7) 46.8(5) 75.4(8) 128.6(7) 92.5(5) 113(2) 109(2) 108(1) 111(2) 108(2) 108(2) 108(2) 108(2) 108(2) 108(2) 108(2) 108(2) 108(2) 108(2) 108(2) 108(2) 108(2) 108(2) 108(2) 108(2) 108(2) 108(2) 108(2) 109(2) 107(2) 111(2) . Estimated s	024 024 024 024 028 028 028 013 C9 C7 014 014 C12 C12 C12 C10 031 031 031 031 031 031 031 032 032 C32 C32 C34 C34 C35 033 033 C39 	M014 M014 M014 M014 M014 M014 M014 M014	034 027 N14 026 M013 034 027 N14 C8 C7 C8 C8 C12 C10 C11 C10 C11 C10 C11 C10 C11 C32 C31 C33 C31 C33 C31 C33 C31 C33 C33 C34 C35 C36 C35 C36 C35 C36 C35 C36 C37 C38 C37 C38 C37 C38 C37 C38 C37 C38 C37 C36 C35 C36 C35 C36 C35 C36 C37 C38 C37 C37 C38 C37 C37 C38 C37 C37 C38 C37 C37 C37 C37 C37 C37 C37 C37 C37 C37	96(1) 102.9(9) 94(1) 168.9(9) 95.9(8) 88.2(8) 88.4(7) 152.0(9) 109(2) 110(2) 110(2) 110(2) 110(2) 110(2) 110(2) 110(2) 110(2) 112(2) 110(2) 113(2) 106(2) 108(2) 110(2) 112(2) 110(2) 110(2) 113(2) 108(2) 108(2) 113(2) 108(2) 113(2) 108(2) 113(2) 108(2) 113(2) 108(2) 113(2) 108(2) 113(2) 109(2)
significant figure are given in parentneses.							

Table A.I.3. (contd)

					·		
atom	atom	atom	angle	atom	atom	atom 	angle
C39 C37 O34 O34 O34 O34 C42 C42 C42 C41 M03 M01 M01 M01 M02 M02 M02 M02 M02 M03 M03 O7 M02 M02 M03 M03 O7 M02 M02 M01 M01 M01 M01 M01 M01 M01 M01 M01 M01	SI13 SI14 SI14 SI14 SI14 SI14 SI14 SI14 SI14	C38 C38 C42 C41 C40 C41 C40 C40 O13 MO2 MO3 O7 O11 MO3 O7 O11 MO3 O7 O11 O7 O11 O7 O11 O7 O11 O7 O11 O7 MO4 O7 MO4 O7 MO4 O7 MO4 O7 MO4 MO12 MO14 O28 MO14 O25 MO13 MO12 O25 N13 O26 MO12 MO12 MO12 MO13 MO12 O25 N13 O26 MO12 MO12 MO12 MO13 MO12 O25 N13 O26 MO12 MO12 MO12 MO13 MO12 MO14 O27 MO14 O28 MO14 O25 MO13 MO12 MO12 MO12 MO12 MO14 O25 MO13 MO12 MO12 MO12 MO12 MO12 MO12 MO12 MO12	109(2) 105(2) 108(2) 110(2) 111(2) 109(2) 108(2) 108(2) 100(2) 47.8(7) 82.9(6) 103.9(7) 98.5(7) 47.9(6) 102.4(7) 58.0(6) 130.3(9) 44.4(5) 96.7(7) 125.7(8) 83.5(7) 103.8(7) 58.4(6) 102.9(7) 98.2(8) 45.4(5) 84.1(7) 82.2(7) 104.4(7) 98.8(8) 102.8(7) 58.6(6) 44.3(5) 83.8(7) 103.7(8) 48.1(6) 101.0(7) 132(1) 95.0(7) 83.6(8) 105.1(8) 100.9(9) 137(1) 58.8(6) 104.0(8)	M03 M03 M04 M04 M04 M04 M02 M02 06 M03 M03 M04 SI1 SI1 M01 SI2 SI3 SI3 M03 SI4 M012 M012 M012 M012 M012 M012 M012 M012	07 07 07 07 07 07 07 07 07 07 07 07 07 0	M02 06 05 M02 06 05 06 05 05 M04 M01 M01 M01 M01 M01 M03 03 M04 M011 M013 028 M03 028 M04 M011 M013 028 M04 M011 M013 028 M04 M011 M013 028 M04 M011 M012 M03 028 M04 M011 M012 M03 028 M04 M011 M012 M03 028 M04 M011 M012 M03 028 M04 M011 M012 M013 028 M014 M012 M013 027 M014 C22 M01 M012 M012 M013 027 M014 M012 M013 027 M014 M012 M013 027 M014 M012 M013 027 M014 M012 M013 027 M014 M012 M014 M012 M013 027 M014 M012 M013 027 M014 M014 M012 M014 M012 M014 M012 M014 M012 M014 M012 M014 M014 M014 M012 M014 M014 M014 M014 M014 M014 M012 M014	105.7(7) 101.2(8) 59.5(6) 104.9(8) 59.8(6) 100.5(8) 45.2(5) 46.2(5) 62.4(6) 82.5(7) 102.8(8) 102.6(8) 130(1) 124(1) 46.5(5) 129(1) 133(1) 96(1) 37.4(5) 131(1) 82.0(7) 105.6(8) 59.9(6) 103.2(8) 98.3(8) 45.7(5) 127(1) 132(1) 132(1) 132(1) 132(1) 132(1) 132(1) 132(1) 132(1) 132(1) 114(2) 117(2) 111(3) 117(2) 110(3) 119(2) 110(3) 118(3)

Table A.I.3. (contd)

atom at	tom ato	angle	atom	atom	atom	angle
M013 02 M013 02 M013 02 M012 02 M012 02 025 02 025 02	28 025 28 N13 28 026 28 025 28 N13 28 026 28 N13 28 026	58.8(6) 53.8(8) 99.6(8) 45.3(5) 91.7(9) 46.3(5) 63.9(9) 62.9(7)	C27 C51 C52 C54 C54 C53 C55 C55 C55 C56 C56 M013 C58 C56 C56 M013 C58 C57 N1 N1 N2 N2 N2 N3 N3 N4 N4 N11 N11 N12 N12 N13 N14 N14	N4 N11 N11 N12 N12 N12 N13 N13 N13 N13 N13 N13 N13 N13 N13 N13	M04 C52 M011 M011 C53 M012 C56 M013 028 028 C57 M014 C22 C21 C24 C23 C26 C25 C28 C27 C52 C51 C54 C55 C58 C55 C58 C57	$\begin{array}{c} 115(2)\\ 108(3)\\ 112(2)\\ 115(2)\\ 110(3)\\ 118(3)\\ 114(2)\\ 109(3)\\ 117(2)\\ 159(3)\\ 117(2)\\ 159(3)\\ 117(2)\\ 91(2)\\ 46.0(1)\\ 106(3)\\ 113(2)\\ 31(2)\\ 35(2)\\ 35(2)\\ 35(2)\\ 35(2)\\ 35(2)\\ 35(2)\\ 34(1)\\ 34(2)\\ 36(2)\\ 37(2)\\ 34(2)\\ 36(2)\\ 37(2)\\ 36(2)\\ 35(2)\\ 37(2)\\ 36(2)\\ 35(2)\\ 37(2)\\ 36(2)\\ 35(2)\\ 37(2)\\ 36(2)\\ 35(2)\\ 37(2)\\ 38(2)\\ 37(2)\\ 38(2)\\$

 	[]	Dihedral	angle	s for	two planes]	
 p	lane 1		plane	2		. (8)
 atom	atom	atom	atom	atom	atom	angle()
 M01 M03 M011 M013	M02 M04 M012 M014	05 07 025 027	M01 M03 M011 M013	M02 M04 M012 M014	06 08 026 028	140.53 138.83 137.89 140.71
 M01 M03 M011 M013	05 07 025 027	06 08 026 028	MO2 MO4 MO12 MO14	05 07 025 027	06 08 026 028	138.34 136.84 135.19 138.88

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Table A.I.4. Least-Squares Planes for $Mo_40_8(OSiMe_3)_4(HNMe_2)_4$

Table A.I.4. (contd) ----- Plane number 1 -----Atoms defining planeDistanceesdN10.08810.0239011-0.04290.0165050.03560.014406-0.04130.0152 Additional atom -0.4064 M01 Mean deviation from plane is 0.0520 angstroms Chi-squared: 31.3 ----- Plane number 2 -----Atoms defining plane Distance esd N2 0.0589 0.0232 012 -0.0294 0.0163 05 -0.0254 0.0144 06 0.0276 N2 012 05 06 0.0276 0.0152 Additional atom -0.4104 M02 Mean deviation from plane is 0.0353 angstroms Chi-squared: 14.7 _____ ----- Plane 3 ------Atoms defining planeDistanceesdN3-0.09620.02400130.05480.018007-0.04460.0154080.05460.0171 Additional atom M03 0.4299 Mean deviation from plane is 0.0625 angstroms Chi-squared: 40.4 ----- Plane 4 ------Atoms defining plane Distance esd N4 -0.0319 0.0264 014 0.0125 0.0165 07 0.0127 0.0151 07 08 0.0127 -0.0149 0.0154 -0.0149 0.0171 Additional atom M04 0.4246 Mean deviation from plane is 0.0180 angstroms Chi-squared: 3.2

Table A.I.4. (contd) ----- Plane 5 -----
 Atoms defining plane
 Distance
 esd

 N11
 -0.0848
 0.0222

 031
 0.0653
 0.0190

 025
 0.0514
 0.0169

 026
 -0.0491
 0.0158
Additional atom M011 0.4414 Mean deviation from plane is 0.0627 angstroms Chi-squared: 43.2 ----- Plane 6 -----Atoms defining planeDistanceesdN12-0.07910.02710320.03780.0190025-0.03280.01690260.02860.0158 Additional atom MO12 0.4230 Mean deviation from plane is 0.0446 angstroms Chi-squared: 19.4 ----- Plane 7 -----Atoms defining planeDistanceesdN130.02200.0263033-0.00910.01710270.00900.0157028-0.01090.0169 Additional atom -0.4178 M013 Mean deviation from plane is 0.0128 angstroms Chi-squared: 1.6 ----- Plane 8 ------
 Atoms defining plane
 Distance
 esd

 N14
 0.1076
 0.0229

 034
 -0.0700
 0.0181

 027
 -0.0607
 0.0157

 028
 0.0669
 0.0169
Additional atom -0.4006 M014 Mean deviation from plane is 0.0763 angstroms Chi-squared: 62.8

Table A.I.5. Positional parameters and B(eq) for $Mo_40_8(OSiMe_3)_4(HNMe_2)_4$

Table A.I.5. (contd)

atom	x	У	Z	B(eq)
N(1) N(2) N(3) N(1) N(12) N(13) N(14) C(1) C(2) C(3) C(4) C(5) C(6) C(7) C(2) C(2) C(2) C(2) C(21) C(22) C(21) C(22) C(23) C(24) C(22) C(23) C(24) C(25) C(26) C(27) C(28) C(27) C(28) C(27) C(28) C(27) C(28) C(27) C(23) C(31) C(32) C(33) C(34) C(35) C(36) C(37) C(36) C(37) C(36) C(37) C(38) C(37) C(36) C(37) C(38) C(37) C(36) C(37) C(37) C(38) C(37) C(36) C(37) C(37) C(38) C(37) C(37) C(38) C(37) C(52) C(53) C(54)	0.176(1) 0.216(1) 0.343(1) 0.258(2) 0.886(1) 0.631(2) 0.632(2) 0.359(1) 0.233(2) 0.134(2) 0.092(2) 0.031(2) 0.036(2) 0.116(2) 0.497(2) 0.361(2) 0.379(2) 0.361(2) 0.245(2) 0.374(3) 0.203(2) 0.225(2) 0.179(2) 0.399(2) 0.349(2) 0.349(2) 0.349(2) 0.349(2) 0.349(2) 0.349(2) 0.349(2) 0.349(2) 0.349(2) 0.349(2) 0.349(2) 0.349(2) 0.521(2) 0.614(3) 0.470(2) 0.894(2) 0.701(3) 0.574(3) 0.609(2) 0.645(2)	0.132(1) 0.422(1) 0.217(1) 0.333(1) 0.320(1) 0.335(1) 0.244(1) 0.214(1) 0.077(2) 0.074(2) 0.362(2) 0.480(2) 0.479(2) 0.377(2) 0.465(2) 0.475(2) 0.171(2) 0.070(2) 0.086(2) 0.121(2) 0.066(2) 0.485(2) 0.431(2) 0.244(2) 0.368(2) 0.307(2) 0.317(2) 0.454(2) 0.415(2) 0.473(2) 0.454(2) 0.368(2) 0.117(2) 0.218(2) 0.121(2) 0.368(2) 0.317(2) 0.375(2) 0.290(2) 0.377(2)	0.177(1) 0.280(1) 0.369(1) 0.111(1) 0.209(1) 0.293(1) 0.110(1) 0.374(1) 0.409(2) 0.376(2) 0.300(2) 0.052(2) 0.125(2) 0.425(2) 0.425(2) 0.424(2) 0.069(2) 0.054(2) 0.256(2) 0.256(2) 0.320(2) 0.320(2) 0.380(1) 0.425(2) 0.320(2) 0.380(1) 0.425(2) 0.380(1) 0.425(2) 0.371(2) 0.450(2) 0.371(2) 0.450(2) 0.371(2) 0.429(2) 0.371(2) 0.429(2) 0.371(2) 0.054(2) 0.371(2) 0.429(2) 0.371(2) 0.429(2) 0.371(2) 0.054(2) 0.371(2) 0.429(2) 0.429(2) 0.450(2) 0.371(2) 0.054(2) 0.371(2) 0.054(2) 0.371(2) 0.054(2) 0.371(2) 0.343(2) 0.343(2)	$\begin{array}{c} 4(1)\\ 5(1)\\ 5(1)\\ 5(1)\\ 5(1)\\ 5(1)\\ 4(1)\\ 5(2)\\ 7(2)\\ 5(1)\\ 9(3)\\ 9(2)\\ 9(3)\\ 9(2)\\ 9(3)\\ 9(2)\\ 9(2)\\ 8(2)\\ 6(2)\\ 8(3)\\ 10(3)\\ 11(3)\\ 10(3)\\ 12(3)\\ 7(2)\\ 8(2)\\ 7(2)\\ 8(2)\\ 7(2)\\ 8(2)\\ 7(2)\\ 8(2)\\ 7(2)\\ 8(2)\\ 11(3)\\ 10(2)\\ 11(3)\\ 10(2)\\ 11(3)\\ 10(2)\\ 11(3)\\ 10(2)\\ 11(3)\\ 10(2)\\ 11(3)\\ 11(3)\\ 10(2)\\ 11(3)\\ 11(3)\\ 11(3)\\ 11(3)\\ 14(3)\\ 11(3)\\ 14(3)\\ 11(3)\\ 14(3)\\ 11(3$

Table A.I.4. (contd)

$\begin{array}{cccccccccccccccccccccccccccccccccccc$
$\Pi(39) 0.2400 0.0699 0.2348 9.4$

Table A.I.5. (contd)

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atom	×	У	Z	B(eq)
atom H(40) H(41) H(42) H(42) H(43) H(44) H(45) H(46) H(46) H(47) H(50) H(51) H(52) H(52) H(55) H(55) H(55) H(55) H(56) H(57) H(56) H(57) H(56) H(61) H(62) H(62) H(66) H(66) H(66) H(66) H(66) H(66) H(66) H(66) H(66) H(66) H(66) H(66) H(67) H(71) H(72) H(75) H(77) H(77) H(78) H(79)	\times 0.8655 0.9144 0.9285 0.9237 0.9146 0.8604 0.6710 0.7238 0.7380 0.5460 0.5942 0.5456 0.6463 0.5942 0.5456 0.6463 0.5813 0.5778 0.2113 0.2571 0.2718 0.1776 0.1061 0.1113 0.5621 0.4958 0.4911 -0.0104 0.0572 0.0183 0.0643 -0.0060 0.0219 0.1481 0.1419 0.0754 0.7362 0.7403 0.7934 0.4174 0.3386 0.3700 1.0109	y 0.0948 0.0866 0.1441 0.2432 0.1876 0.2464 0.0614 0.0694 0.1074 0.1693 0.1112 0.2245 0.2446 0.1021 0.2245 0.2446 0.1091 0.2215 0.2239 0.1801 0.4937 0.5068 0.4539 0.3817 0.3378 0.3354 0.3354 0.5171 0.4960 0.4550 0.5133 0.4506 0.4965 0.0985 0.1491 0.0896 0.5066 0.4968 0.4505 0.2863	2 0.1888 0.1543 0.1997 0.1152 0.0690 0.0524 0.4123 0.3814 0.4400 0.2719 0.2681 0.3026 0.4395 0.3812 0.4143 0.4329 0.3971 0.4347 0.4025 0.3454 0.3990 0.1843 0.1248 0.1688 0.0221 0.0345 0.0773 0.1453 0.0918 0.1503 0.0666 0.0282 0.0137 0.0649 0.0188 0.0386 0.4449 0.3981 0.4532 0.4633	$\begin{array}{c} \text{B(eq)}\\ 10.0\\ 10.0\\ 10.0\\ 14.7\\ 14.7\\ 14.7\\ 15.3\\ 15.3\\ 15.3\\ 15.3\\ 15.3\\ 14.9\\ 14.9\\ 14.9\\ 14.9\\ 14.9\\ 14.4\\ 14.4\\ 14.4\\ 14.4\\ 14.4\\ 14.4\\ 11.5\\ 11.5\\ 9.8\\ 9.8\\ 9.8\\ 13.1\\ 13.1\\ 10.5\\ 10.5\\ 10.5\\ 7.9\\ 7.9\\ 7.9\\ 8.6\\ 8.6\\ 8.6\\ 12.7\\ 12.7\\ 11.6\\ 11.6\\ 11.6\\ 11.6\\ 10.7\\ \end{array}$
H(81) H(82)	1.0640	0.2976 0.3459 0.4551	0.4315 0.4813 0.3999	10.7 10.7 12.1

Table	A.I.5.	(contd)

atom	×	у	Z	B(eq)
H(83) H(84) H(85) H(86) H(87) H(88) H(90) H(90) H(91) H(92) H(92) H(93) H(93) H(94) H(95) H(95) H(95) H(96) H(97) H(99) H(99) H(101) H(102) H(103) H(104) H(105) H(107)	1.0399 0.9769 0.9481 0.8820 0.3882 0.3268 0.3931 0.2185 0.2155 0.2723 0.6516 0.6262 0.5831 0.5303 0.5420 0.5267 0.9594 0.9813 0.9929 0.0609 0.1106 0.0712 0.6962 0.6262	0.4056 0.4553 0.4415 0.4442 0.3856 0.1414 0.1938 0.2057 0.0500 0.0945 0.0380 0.4718 0.4209 0.4861 0.3698 0.2986 0.3095 0.2542 0.2770 0.3240 0.1013 0.0393 0.0578 0.3785	0.3507 0.3384 0.4611 0.4000 0.4433 0.0579 0.0343 0.0942 0.0727 0.0202 0.0433 0.1148 0.0629 0.0571 0.2413 0.2229 0.2792 0.2665 0.2159 0.2691 0.2691 0.2691 0.2690 0.2837 0.3240 0.3650 0.2391	$12.1 \\ 12.1 \\ 10.9 \\ 10.9 \\ 10.9 \\ 13.3 \\ 13.3 \\ 13.3 \\ 12.6 \\ 12.6 \\ 12.6 \\ 12.6 \\ 16.5 \\ 16.5 \\ 16.5 \\ 16.5 \\ 16.5 \\ 10.7 \\ $
H(107) H(108)	0.6266	0.4188 0.3586	0.3291 0.3674	9.7 9.7
H(109) H(110) H(111)	0.3521 0.4028 0.4107	0.0666 0.0557	0.1949 0.1625 0.2006	14.2 14.2
	0.4107	U.113U	0.2000	14.2

ATOM	U11	U22	U33	U12	U13	U23
Mo(1)	0.053(2)	0.046(2)	0.057(2)	0.002(2)	0.026(2)	0.006(2)
Mo(2)	0.046(2)	0.045(2)	0.047(2)	0.003(2)	0.016(2)	0.006(2)
Mo(3)	0.042(2)	0.054(2)	0.044(2)	0.003(2)	0.011(2)	0.001(2)
Mo(4)	0.049(2)	0.053(2)	0.046(2)	-0.001(2)	0.023(2)	0.001(2)
Mo(11)	0.045(2)	0.050(2)	0.065(2)	0.002(2)	0.025(2)	-0.001(2)
Mo(12)	0.041(2)	0.053(2)	0.052(2)	0.001(2)	0.017(2)	-0.004(2)
Mo(13)	0.063(2)	0.046(2)	0.047(2)	-0.001(2)	0.025(2)	-0.008(2)
Mo(14)	0.064(2)	0.047(2)	0.050(2)	-0.001(2)	0.032(2)	-0.000(2)
		·				

Table A.I.6. U values for $Mo_40_8(OSiMe_3)_4(HNMe_2)_4$

Appendix II

Supplemental X-ray Data for $Mo_2(N)_2(OSiMe_3)_6(NH_3)_2$

Figure	A.II.1.	Packing diagram
Table	A.II.1.	Crystallographic data
Table	A.II.2.	Least-squares planes
Table	A.II.3.	Positional parameters
Table	A.II.4.	Anisotropic temperature factors



Figure A.I.1. Packing diagram of $Mo_2N_2(OSiMe_3)_6(NH_3)_2$. Hydrogen atoms are omitted for clarity.

Table A.II.1. Crystallographic data for $Mo_2N_2(OSiMe_3)_6(NH_3)_2$ Empirical Formula Mo2Si606N4C18H60 789.09 Formula Weight Crystal color, form, dimensions colorless plate, 0.2x0.2x0.05 mm Crystal System Monoclinic Lattice Parameters: 10.851 (4) Å a = 16.082 (3) Å 12.282 (4) Å b = с = $109.14^{\circ}(2)$ β = $V = 2025 (1) Å^3$ P_{21/a} (#14) Space Group Z value 2 $\overline{1.29}$ g/cm³ D_{calc} F₀₀₀ μ(Mo K-α) 824 8.09 cm^{-1} Rigaku AFC₆ Mo K-α (λ= 0.71069) Diffractometer Radiation Graphite-monochromated Temperature 23°C 50.0° 2θ_{max} scan method 2θ-ω 16.0°/min Data collection speed +13, +20, ±14 (7 4 1), (0 10 4), (0 10 -4); h k l limits standards, (h k l); freq. of meas. every 199 Total no. of measd data 3910 No. Observations [I>3.00(sig(I))] 2528 No. Variables 163 Residuals: R; R, Goodness of Fit Indicator 0.055; 0.070 1.83 Maximum Shift in Final Cycle 0.28 $1.02 e/Å^3$ Largest Peak in Final Diff. Map

		2
Plane numbe	er 1	
Atoms Defining Plane 01 02 03 N2	Distance 0.0259 -0.0273 0.0292 -0.0513	esd 0.0037 0.0039 0.0039 0.0052
Additional Atoms MO1	Distance -0.3629	
Mean deviation from plane Chi-squared: 244.3	is 0.0334	angstroms

Table A.II.2. Least Squares Planes for $Mo_2(N)_2(OSiMe_3)_6(NH_3)_2$

atom	X	У	Z	B(eq)
M01 SI1 SI2 SI3 01 02 03 N1 N2 C11 C12 C13 C21 C22 C23 C31 C32 C33	0.38204(5) 0.2987(2) 0.1750(2) 0.4255(2) 0.3947(4) 0.3091(4) 0.2560(5) 0.5229(6) 0.3967(9) 0.2185(8) 0.1674(8) 0.0370(9) 0.135(1) 0.203(1) 0.545(1) 0.437(1) 0.2586(9)	0.55948(4) 0.5371(1) 0.4137(2) 0.6616(1) 0.5249(3) 0.4548(3) 0.5928(3) 0.6208(4) 0.6557(4) 0.6557(4) 0.6150(7) 0.4357(6) 0.6150(7) 0.3224(7) 0.3224(7) 0.384(1) 0.6474(7) 0.7687(6) 0.6425(7)	0.38023(5) 0.6170(2) 0.2274(2) 0.1638(2) 0.5384(4) 0.3141(4) 0.2680(4) 0.3451(5) 0.4883(5) 0.7635(7) 0.622(1) 0.5550(8) 0.195(1) 0.300(1) 0.094(1) 0.02242(8) 0.0619(7)	3.73(2) 5.1(1) 5.8(1) 5.2(1) 3.9(2) 4.4(2) 4.6(2) 4.7(2) 5.2(3) 7.1(4) 7.7(5) 9.3(6) 11.9(7) 13.2(9) 9.0(6) 7.6(5) 7.9(5)

Table A.II.3. Positional parameters and B(eq) for $Mo_2(N)_2(OSiMe_3)_6(NH_3)_2$ (Nonhydrogen atoms)

Table A.II.3. (contd)

Positional	parameters (H	and B(eq) for ydrogen atoms)	Mo ₂ N ₂ (OSiMe ₃) ₆ (NH ₃) ₂
atom	x	у	Z	B(eq)
H1 H2 H3 H4 H5 H6 H7 H8 H9 H10 H11 H12 H13 H14 H15 H16 H17 H18 H19 H20 H21 H22 H23 H24 H25 H26 H27 H28 H29 H30	0.4624 0.4360 0.3411 0.1615 0.2830 0.2055 0.1155 0.1144 0.0224 0.0554 -0.0389 0.1222 0.0579 0.2051 0.1264 0.2242 0.2732 0.52732 0.5378 0.5280 0.6311 0.5233 0.4155 0.3778 0.3778 0.1974 0.2384 0.2547 0.5979 0.5481 0.5481 0.5481	0.5354 0.6266 0.5821 0.4415 0.4187 0.3952 0.6676 0.5979 0.6192 0.5003 0.5337 0.4589 0.3390 0.2969 0.2835 0.3595 0.4325 0.3459 0.5927 0.6866 0.6556 0.7786 0.8081 0.7743 0.6462 0.6829 0.5885 0.6284 0.6926 0.6926	0.7993 0.7568 0.8086 0.6664 0.5464 0.5507 0.4800 0.6028 0.2650 0.1593 0.1452 0.3692 0.2504 0.3166 0.0428 0.0586 0.1103 0.0551 0.0247 0.1376 0.2741 0.1631 0.2662 0.1020 0.0295 0.5381 0.4391 0.5202	$\begin{array}{c} 8.5\\ 8.5\\ 8.5\\ 9.3\\ 9.3\\ 9.3\\ 9.3\\ 9.3\\ 9.3\\ 9.3\\ 9.3$

Positio and R(an) fam Ma N (OCiMa)

				gon acoms,		
ATOM	U11	U22	U33	U12	U13	U23
M01 SI1 SI2 SI3 01 02 03 N1 N2 C11 C12 C13 C21 C22 C23 C31 C32 C33	0.0334(3) 0.046(1) 0.054(1) 0.051(1) 0.043(2) 0.043(2) 0.049(3) 0.051(3) 0.059(3) 0.065(5) 0.062(5) 0.060(6) 0.12(1) 0.13(1) 0.123(8) 0.084(6)	0.0537(4) 0.087(2) 0.075(1) 0.076(1) 0.059(3) 0.069(3) 0.068(4) 0.060(4) 0.116(8) 0.117(8) 0.142(9) 0.142(9) 0.142(9) 0.142(9) 0.116(9) 0.091(8) 0.26(2) 0.15(1) 0.081(6) 0.117(8)	0.0491(3) 0.063(1) 0.075(2) 0.057(1) 0.051(2) 0.064(3) 0.054(3) 0.057(3) 0.069(4) 0.058(5) 0.121(8) 0.097(7) 0.15(1) 0.20(1) 0.11(1) 0.092(7) 0.078(6)	-0.0004(3) 0.009(1) -0.015(1) -0.008(1) 0.002(2) -0.004(2) 0.003(2) 0.003(3) -0.008(3) 0.031(6) -0.018(5) 0.042(6) -0.013(6) -0.053(7) -0.03(1) -0.007(8) -0.021(6)	0.0061(2) 0.021(1) 0.000(1) 0.013(1) 0.011(2) 0.006(2) 0.014(2) 0.012(3) 0.022(4) 0.022(4) 0.036(5) -0.009(6) -0.005(9) 0.028(8) 0.028(8) 0.015(5) -0.001(5)	0.0006(3) -0.000(1) -0.014(1) 0.010(1) 0.001(2) -0.002(2) 0.007(2) 0.012(3) -0.007(3) -0.002(5) 0.003(6) 0.001(6) -0.006(7) 0.020(8) -0.10(1) 0.027(7) 0.014(5) 0.015(5)

Table A.II.4. U values for Mo₂N₂(OSiMe₃)₆(NH₃)₂ (Nonhydrogen atoms)

.

Appendix III

Supplemental X-ray Data for $Mo_4N_4O_2(OSiMe_3)_8(py)_4\cdot 2py$

Figure	A.III.1.	Packing diagram
Table	A.III.1.	Crystallographic data
Table	A.III.2.	Least-squares planes
Table	A.III.3.	Positional parameters
Table	A.III.4.	Anisotropic temperature factors



Figure A.III.1. Packing diagram of $Mo_4N_4O_2(OSiMe_3)_8(py)_4$ ·2py. Hydrogen atoms are omitted for clarity.

_____ Mo4Si8010N10C54H102 Empirical Formula Formula Weight 1659.90 Crystal color, form, dimensions yellow block, 0.3x0.3x0.2 mm Crystal System Monoclinic Lattice Parameters: 26.06 (2) Å a = 14.250 (6) Å 24.524 (6) Å b = с = 116.66° (3) B = $V = 8141 (13) Å^3$ Space Group C_{2/c} (#15) Z value 4 1.35 g·cm⁻³ Dcalc F₀₀₀ μ(Mo K-α) 3424 7.52 cm^{-1} Rigaku AFC₆ Mo K- α (λ = 0.71069) Diffractometer Radiation Graphite-monochromated Temperature 23°C $2-\theta(\max)$ 50.1° Scan method ω Data collection speed 16.0°/min h k l limits ±31, +16, +29 (4 -2 -9), (0 -6 -1), (1 -3 -7); Standards, (h k 1); freq. of meas. every 199 Total no. of measd data 7721 No. Observations [I>3.00(sig(I))] 3238 No. Variables 359 Residuals: R; R, Goodness of Fit Indicator 0.053; 0.059 1.30 Maximum Shift in Final Cycle 8.88 Largest Peak in Final Diff. Map $0.63 \text{ e/}\text{\AA}^3$

Table A.III.1. Crystallographic data for Mo₄N₄O₂(OSiMe₃)₈(py)₄·2py

----- Plane number 1 ------Atoms Defining Plane Distance esd 01 0.0222 0.0059 05 0.0226 0.0055 N1 -0.0408 0.0080 N3 -0.0291 0.0064 Additional Atoms Distance MO1 -0.1924 Mean deviation from plane is 0.0286 angstroms Chi-squared: 80.6 ----------- Plane number 2 ------Atoms Defining Plane Distance esd 03 -0.0604 0.0061 04 0.0669 0.0064 06 -0.0523 0.0056 Additional Atoms Distance MO2 0.2625 NЗ 0.0718 0.0064 Mean deviation from plane is 0.0629 angstroms Chi-squared: 406.8 ----- Plane number 3 ------Atoms Defining Plane Distance esd 03 0.0072 0.0061 06 0.0068 0.0056 -0.0150 N2 0.0088 N4 -0.0084 0.0063 Additional Atoms Distance M02 -0.2046 Mean deviation from plane is 0.0094 angstroms Chi-squared: 7.3

Table A.III.2. Least Squares Planes for Mo₄N₄O₂(OSiMe₃)₈(py)₄·2py

Table A.III.2.	(contd)		
	Plane numbe	er 4	
Atoms Defining O4 N2 N3 N4	Plane	Distance -0.0398 0.0645 -0.0412 0.0418	esd 0.0064 0.0088 0.0064 0.0063
Additional Aton MO2 Mean deviation Chi-squared:	ns from plane 178.1	Distance -0.0747 is 0.0468	angstroms
	Plane numbe	er 5	
Atoms Defining N1 C1 C2 C3 C4 C5	Plane	Distance 0.0023 -0.0122 0.0155 0.0053 -0.0218 0.0105	esd 0.0080 0.0115 0.0145 0.0160 0.0165 0.0133
Additional Aton SI1 SI2 SI3 SI4 Mean deviation Chi-squared:	from plane 4.3	Distance 0.0193 -3.4409 -2.5546 1.8604 is 0.0113	angstroms
Atoms Defining N2 C6 C7 C8 C9 C10 Additional Atom SI1 SI2 SI3 SI4	Plane Plane	Distance -0.0061 0.0143 -0.0143 0.0137 -0.0148 0.0141 Distance 4.6156 5.7310 0.3865 -3.3759	esd 0.0088 0.0135 0.0161 0.0188 0.0174 0.0142
Mean deviation Chi-squared:	from plane 4.6	is 0.0129	angstroms

Table A.III.2.	(contd)		
	Plane number	r 7	
Atoms Defining N5 C23 C24 C25 C26 C27 Mean deviation	Plane	Distance -0.0459 0.0272 0.1002 -0.0764 0.0038 0.0545 is 0.0513	esd 0.0202 0.0316 0.0362 0.0286 0.0327 0.0224 angstroms
Chi-squared:	24.6		

Table A.III.3. Positional parameters and B(eq) for $Mo_4N_4O_2(OSiMe_3)_8(py)_4$ 2py

Table A.III.3. (contd)

.

atom	x	У	Z	B(eq)
H1 H2 H3 H4 H5 H6 H7 H8 H9 H10 H112 H12 H13 H14 H15 H16 H17 H18 H10 H112 H13 H14 H15 H16 H17 H18 H10 H112 H12 H12 H12 H12 H12 H12 H13 H14 H15 H16 H17 H12 H12 H12 H12 H12 H12 H12 H12 H12 H12	0.5647 0.6325 0.6612 0.6244 0.5640 0.4824 0.4659 0.3785 0.3044 0.3253 0.4695 0.4794 0.5306 0.5573 0.5060 0.5104 0.3924 0.3900 0.3795 0.4661 0.4112 0.4084 0.3123 0.3179 0.3224 0.4084 0.3123 0.3179 0.3224 0.4661 0.4112 0.4084 0.3123 0.3179 0.3224 0.4330 0.4299 0.4834 0.2768 0.3422 0.3097 0.2237 0.2194 0.1942 0.2618 0.2792 0.3261 0.2759 0.2910 0.2821	0.0913 -0.0239 -0.1217 -0.0990 0.0256 0.5336 0.6486 0.6572 0.5609 0.4496 0.1767 0.2750 0.2202 0.3849 0.4264 0.3393 0.4264 0.3393 0.3575 0.2573 0.2573 0.0118 -0.0447 0.0637 0.0400 -0.0669 -0.0287 -0.1204 -0.1639 -0.1065 0.1440 0.1630 0.1131 0.3567 0.3690 0.2801 0.1693 0.2664 0.1936 0.6036 0.5376 0.4965	0.1125 0.1263 0.2104 0.2790 0.2643 0.1079 0.0251 0.0217 0.0965 -0.0299 -0.0508 -0.0013 0.0839 0.0348 0.0996 0.0434 -0.0201 -0.0025 0.0358 -0.0050 -0.0050 -0.0012 0.0362 0.0362 0.0280 0.0362 0.0280 0.0362 0.0280 0.0362 0.0280 0.0362 0.0280 0.0280 0.0362 0.0280 0.02244 0.1616 0.0255 0.0898 0.2214 0.1803 0.2341	$\begin{array}{c} 7.3\\ 10.6\\ 12.4\\ 14.1\\ 9.5\\ 9.8\\ 13.3\\ 14.1\\ 14.0\\ 10.7\\ 12.5\\ 12$

Table A.III.3. (contd)

.

atom	x	У	Z	B(eq)
H41 H42 H43 H44 H45 H46 H47 H48 H49 H50 H51	0.3717 0.4243 0.3639 0.4400 0.3956 0.3802 0.1322 0.2078 0.2553 0.2763 0.2118	0.5366 0.5980 0.6430 0.6723 0.6561 0.7201 0.2410 0.1169 0.0988 0.2107 0.3384	0.3638 0.3736 0.3491 0.2749 0.2076 0.2493 0.6453 0.6453 0.6837 0.6248 0.5842 0.5586	17.4 17.4 19.7 19.7 19.7 16.3 20.5 14.7 16.7 10.9

Table A.III.4. U values for $Mo_4N_4O_2(OSiMe_3)_8(py)_4\cdot 2py$

ATOM	U11	U22	U33	U12	U13	U23
M01	0.0420(5)	0.0385(5)	0.0384(5)	-0.0023(5)	0.0252(4)	-0.0008(5)
M02	0.0343(5)	0.0388(6)	0.0569(6)	0.0048(5)	0.0175(4)	-0.0055(5)
SI1	0.082(2)	0.091(3)	0.053(2)	0.007(2)	0.041(2)	0.023(2)
SI2	0.094(3)	0.071(3)	0.093(3)	-0.029(2)	0.055(2)	-0.042(2)
SI3	0.042(2)	0.105(3)	0.081(3)	-0.014(2)	0.021(2)	-0.001(2)
SI4	0.083(3)	0.068(3)	0.131(4)	0.030(2)	0.036(3)	-0.027(3)
01	0.065(5)	0.063(5)	0.049(4)	0.012(4)	0.039(4)	0.016(4)
02	0.067(5)	0.048(4)	0.057(4)	-0.009(4)	0.034(4)	-0.016(4)
03	0.035(4)	0.067(5)	0.068(5)	0.002(4)	0.018(3)	-0.009(4)
04	0.055(5)	0.059(5)	0.090(6)	0.020(4)	0.021(4)	-0.024(4)
05	0.037(5)	0.039(6)	0.041(5)	0	0.024(4)	0
06	0.035(5)	0.033(5)	0.064(6)	0	0.015(5)	0
N1 NO	0.067(6)	0.066(7)	0.053(6)	0.017(5)	0.047(5)	0.007(5)
NZ NO	0.060(7)	0.044(6)	0.097(8)	0.018(5)	0.027(6)	0.019(5)
N3	0.032(4)	0.041(5)	0.041(5)	-0.010(4)	0.015(4)	-0.001(4)
N4	0.034(4)	0.041(5)	0.045(5)	-0.001(4)	0.027(4)	-0.010(4)
N5	0.141(7)	0.00(1)				
	0.084(9)	0.09(1)	0.078(9)	0.025(8)	0.057(8)	0.017(8)
C2	0.14(1)	0.12(1)	0.12(1)	0.07(1)	0.10(1)	0.02(1)
03	0.16(2)	0.13(1)	0.14(2)	0.10(1)	0.10(1)	0.04(1)
	0.24(2)	0.13(2)	0.16(1)	0.11(2)	0.16(2)	0.07(1)
C5 CC	0.16(1)	0.09(1)	0.11(1)	0.07(1)	0.10(1)	0.03(1)
	0.08(1)	0.08(1)	0.15(1)	0.00(1)	0.05(1)	0.06(1)
	0.10(1)	0.11(1)	0.16(2)	-0.01(1)	0.01(1)	0.09(1)
	0.15(2)	0.14(2)	0.14(2)	0.03(2)	0.06(1)	0.09(1)
C10	0.11(1)	0.14(2)	0.15(2)	0.00(1)	0.01(1)	0.09(1)
	0.00(1)	0.10(1)	0.13(1)	-0.00(1)	0.02(1)	0.05(1)

Table A.III.4. (contd)

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ATOM	U11	U22	U33	U12	U13	U23
C11	0.20(2)	0.17(2)	0.09(1)	0.04(1)	0.11(1)	0.04(1)
C12	0.17(2)	0.10(1)	0.12(1)	-0.01(1)	0.08(1)	0.04(1)
C13	0.08(1)	0.24(2)	0.08(1)	0.06(1)	0.020(8)	0.05(1)
C14	0.22(2)	0.15(2)	0.09(1)	-0.06(1)	0.09(1)	-0.07(1)
C15	0.13(2)	0.23(2)	0.36(3)	-0.11(2)	0.13(2)	-0.22(2)
C16	0.35(3)	0.06(1)	0.15(2)	-0.04(1)	0.15(2)	-0.04(1)
C17	0.084(8)	0.41(4)	0.50(3)	-0.14(1)	-0.06(1)	0.26(3)
C18	0.034(9)	0.24(2)	0.34(3)	-0.02(1)	0.05(1)	-0.17(2)
C19	0.15(2)	0.36(4)	0.31(3)	-0.10(2)	0.10(2)	-0.25(3)
C20	0.09(1)	0.17(2)	0.19(2)	0.07(1)	0.02(1)	-0.03(1)
C21	0.16(2)	0.17(2)	0.17(2)	0.09(1)	0.03(1)	-0.10(1)
C22	0.21(2)	0.07(1)	0.39(3)	0.02(1)	0.16(2)	-0.04(2)
C23 C24	0.17(1) 0.21(2)	0.01(1)	0.03(0)	0.02(1)	0.10(2)	0.04(2)
C25 C26 C27	0.16(1) 0.18(1) 0.119(8)					