

Tetrakis(alkoxy) and Tetrakis(trialkylsiloxy) Compounds of Molybdenum(IV)

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Abstract: A series of tetrakis(alkoxy)molybdenum(IV) compounds have been prepared from the reaction $\text{Mo}(\text{NMe}_2)_4 + 4\text{ROH} \rightarrow \text{Mo}(\text{OR})_4 + 4\text{HNMe}_2$, where R = Me, Et, Pr-*t*, CH_2CMe_3 , and Bu-*t*. Related reactions involving trialkylsilanols R_3SiOH (R = Me and Et) yield the amine adducts $\text{Mo}(\text{OSiR}_3)_4(\text{HNMe}_2)_2$. These new compounds have been characterized by a number of physicochemical techniques including cryoscopic molecular weight determinations, mass spectroscopy, infrared spectroscopy, magnetic susceptibility studies and UV-visible spectroscopy. The properties of the alkoxides $\text{Mo}(\text{OR})_4$ are dependent upon the steric requirements of the alkoxy ligand: the methoxide is nonvolatile, insoluble in hydrocarbon solvents, and presumably polymeric; the ethoxide is volatile and trimeric in benzene; the neopentoxide and isopropoxide are volatile and dimeric in benzene; the *tert*-butoxide is volatile and approaches a monomer in benzene. With the exception of the isopropoxide, all compounds are paramagnetic both in toluene solution and in the solid state. The isopropoxide is diamagnetic and shows fluxional properties in toluene-*d*₈; low-temperature limiting NMR spectra (¹H and ¹³C) are consistent with the adoption of the ground-state structure $(\text{Pr-}i\text{-O})_3\text{Mo}(\mu\text{-OPr-}i)_2\text{Mo}(\text{OPr-}i)_3$. A single-crystal x-ray structural determination on $\text{Mo}(\text{O-SiMe}_3)_4(\text{HNMe}_2)_2$ reveals a trans-octahedral geometry for the central MoO_4N_2 moiety. Comparisons are made with the known chemistry of related quadrivalent chromium compounds.

Introduction

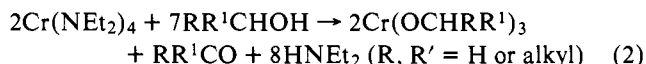
Homoleptic compounds ML_n , where L = R (β -hydrogen elimination stabilized alkyl^{2,3}), NR_2 ,⁴ and OR ,^{5,6} are known for all the early transition elements M for certain values of *n*. For the group 6 metals CrL_3 , CrL_4 , WL_6 , and M_2L_6 (M = Mo and W) compounds are known, the latter containing metal-to-metal triple bonds. For molybdenum and tungsten the ML_4 series is conspicuously absent.⁷ Only the compounds $\text{Mo}(\text{NMe}_2)_4$ and $\text{Mo}(\text{NEt}_2)_4$ are well characterized.⁸ These interesting compounds provide rare examples of monomeric, diamagnetic four-coordinated d^2 ions: spin pairing was attributed⁸ to nitrogen-to-molybdenum π bonding. In this paper we describe a general synthesis of tetrakis(alkoxy) and tetrakis(trialkylsiloxy) compounds of molybdenum(IV) and report our characterization studies of these new compounds. An interesting comparison emerges with respect to the physicochemical properties of other early transition metal quadrivalent alkoxides.

Results and Discussion

Syntheses. Hydrocarbon solutions of $\text{Mo}(\text{NMe}_2)_4$ react rapidly with alcohols (≥ 4 equiv), where R = Me, Et, Pr-*i*, CH_2CMe_3 , and Bu-*t*, to give alkoxides of empirical formula $\text{Mo}(\text{OR})_4$ according to



Alcoholysis reactions analogous to eq 1 are well known for transition metal dialkylamides,⁴ though sometimes a valency change of the metal occurs. $\text{Cr}(\text{NR}_2)_4$ compounds react with alcohols according to⁹



Only tertiary alcohols, which are not susceptible to this type of oxidation, and the sterically demanding 3,3-dimethyl-2-butanol are known to give $\text{Cr}(\text{OR})_4$ compounds.^{9,10} The success of eq 1 in the preparation of $\text{Mo}(\text{OR})_4$ presumably reflects the weaker oxidizing power of Mo^{4+} relative to Cr^{4+} .

Reactions related to 1 but employing trialkylsilanols R_3SiOH (R = Me and Et) gave amine adducts $\text{Mo}(\text{OSiR}_3)_4(\text{HNMe}_2)_2$. This contrasts with the formation of the monomeric compound $\text{Cr}(\text{OSiEt}_3)_4$ in related reactions.⁹ The size of the metal, $\text{Mo} > \text{Cr}$, may, of course, readily account for

this observation but it is interesting to note that alkoxides $\text{Mo}(\text{OR})_4(\text{HNMe}_2)_2$ are not isolated in reaction 1, though such species are presumably intermediates in the synthesis of polymeric compounds $[\text{Mo}(\text{OR})_4]_n$.¹¹

Properties. Some of the physicochemical properties of these new compounds are summarized in Table I. Analytical data are given in the Experimental Section.

Most of the compounds, though extremely oxygen and water sensitive, are thermally quite stable and may be sublimed in vacuo. Notable exceptions are $\text{Mo}(\text{OMe})_4$, which is nonvolatile, insoluble in hydrocarbon solvents, and is presumed to adopt a polymeric MoO_6 structure, and $\text{Mo}(\text{OSiEt}_3)_4(\text{HNMe}_2)_2$, which upon heating (60 °C, 10^{-4} cmHg) first gives up its coordinated amine yielding a green liquid, $\text{Mo}(\text{OSiEt}_3)_4$, and then above 70 °C, 10^{-4} cmHg, decomposes by the elimination of $(\text{Et}_3\text{Si})_2\text{O}$. $\text{Mo}(\text{OBu-}t)_4$ is also thermally unstable, decomposing in vacuo above 75 °C by the elimination of isobutylene, *tert*-butyl alcohol, and water. It may, however, be sublimed carefully at 70 °C, 10^{-4} cmHg.

The thermal instability of the $\text{Mo}(\text{OR})_4$ compounds (R = Bu-*t* and Et_3Si) is quite remarkable and contrasts with the thermal stability of related Cr(IV)⁹ and Zr(IV) compounds. For example, $\text{Zr}(\text{OSiEt}_3)_4$, which is a liquid and is monomeric in benzene, may be distilled at 150 °C, 10^{-2} cmHg, without decomposition.¹² $\text{Zr}(\text{OBu-}t)_4$ is monomeric and distills at 50 °C, 10^{-4} cmHg.⁵ The thermal decomposition of tertiary alkoxides of Zr(IV) was studied in detail by Bradley and Faktor¹³ and was shown to proceed according to eq 3 at ca. 200 °C, 1 atm.



Cryoscopic molecular weight determinations showed that, with the exception of trialkylsiloxyamine adducts, all the compounds had a tendency toward oligomerization in solution, $[\text{Mo}(\text{OR})_4]_n$ (see Table I). The degree of oligomerization reflects the steric demand of the R group as is typically found in metal alkoxide chemistry.^{5,6} It is likely, but not proven, that dimerization for R = Me_3C , Me_2CH , and Me_3CCH_2 occurs via the formation of a pair of alkoxy bridges: $(\text{RO})_3\text{Mo}(\mu\text{-OR})_2\text{Mo}(\text{OR})_3$. In this way, molybdenum attains a coordination number of five while for the less sterically demanding alkyl groups, R = Et and Me, molybdenum may attain a coordination number of six. A polymeric MoO_6 structure for

Table I. Characterization Data for Alkoxides and Trialkylsiloxides of Molybdenum(IV)

Compd ^a	Color	Volatility, ^b °C (10 ⁻⁴ Torr)	UV/vis λ_{\max} , nm (ϵ) ^c	μ_{eff} , ^d μ_{B} $T = 313 \text{ K}$	Mol wt ^e (calcd)	Mass spectrum parent peak m/e
Mo(OBu- <i>t</i>) ₄	Green-brown	70–75	600 (40)	1.38	450 ± 20 (388)	388
Mo(OPr- <i>i</i>) ₄	Blue	70–90	640 (700)	Diamagnetic	600 ± 30 (332.28)	664
Mo(OCH ₂ CMe ₃) ₄	Blue-green	150–170	640 (320)	0.70	740 ± 30 (444)	888
Mo(OEt) ₄	Dark green	70–90	700 (340)	0.31	860 ± 30 (276)	828
Mo(OSiMe ₃) ₄ ·2HNMe ₂	Yellow	100–120	955 (2.0) 915 (2.0) 390 (35)	2.63	551 ± 20 (542)	542
Mo(OSiEt ₃) ₄ ·2HNMe ₂	Orange-brown	76 dec	1185 (10) 1150 (10) 885 (20) 730 (30) 480 (40)	2.20	(711.2)	620

^a Mo(OMe)₄ is purple, nonvolatile, and insoluble in hydrocarbon solvents. ^b May be sublimed readily at those temperatures. ^c In cyclohexane. ^d Determined in toluene by the Evans method. ^e Determined cryoscopically in benzene.

the methoxide seems likely, in view of its nonvolatile nature and its insolubility in all common organic solvents. The ethoxide which is trimeric in benzene ($n = 3.1$) could adopt a structure akin to that of Ti(OEt)₄. The latter has enjoyed much attention:⁵ it is tetrameric in the solid state¹⁴ but is trimeric in solution.^{15–17} However, a considerable distortion of the geometry found for M(OR)₄ compounds, M = Ti, Zr, is expected for M = Mo owing to the different electronic configurations of the metals, d⁰ vs. d².

With the exception of the isopropoxide (discussed later) all the compounds are paramagnetic in solution and in the solid state. Magnetic susceptibility measurements were made in toluene using the Evans method¹⁸ and in the solid state by the Faraday method. (See Table I and the Experimental Section for details.) There was general agreement between the values of μ_{eff} determined in solution and the solid state and χ_{M} was not field dependent.

μ_{eff} for Mo(OSiMe₃)₄(HNMe₂)₂ is close to the spin-only value for a d² ion in the temperature range 88–267 K. Since the MoO₄N₂ has D_{4h} symmetry the orbital contribution, which is expected for a d² ion in an O_h field, is quenched.¹⁹ The contribution to μ_{eff} arising from spin-orbit coupling is also expected to be small for a covalent molecule¹⁹ such as Mo(OSiMe₃)₄(HNMe₂)₂. Thus, the observed μ_{eff} for Mo(OSiMe₃)₄(HNMe₂)₂ is readily understood.

The dimeric and trimeric alkoxides show very low values of μ_{eff} , which may be attributed to large antiferromagnetic couplings between neighboring metal centers. Alternatively this may be termed metal-metal bonding.²⁰ The latter is found in the chemistry of oxides of Mo⁴⁺, e.g., MoO₂²¹ and Zn₂Mo₃O₈²², and thus might be expected to occur for Mo⁴⁺ alkoxides. However, in the absence of any detailed structural knowledge, further speculation on the observed paramagnetism of these alkoxides is fruitless.

Mo₂(OPr-*i*)₈. The isopropoxide is diamagnetic and dimeric in solution. In contrast to the other alkoxides it gives sharp NMR spectra. It is a fluxional molecule on the NMR time scale. The low-temperature limiting spectra (¹H and ¹³C) are consistent with the adoption of a structure having a pair of bridging alkoxy ligands: [(RO)₃Mo(μ -OR)]₂. See ref 20. ¹H and ¹³C NMR data are recorded in the Experimental Section.

Mo(OSiMe₃)₄(HNMe₂)₂. The isolation of a thermally stable and sublimable amine adduct Mo(OSiMe₃)₄(HNMe₂)₂ is unusual, if not unprecedented, in the chemistry of transition-metal alkoxides and trialkylsiloxides.^{11,23,24} Consequently, we

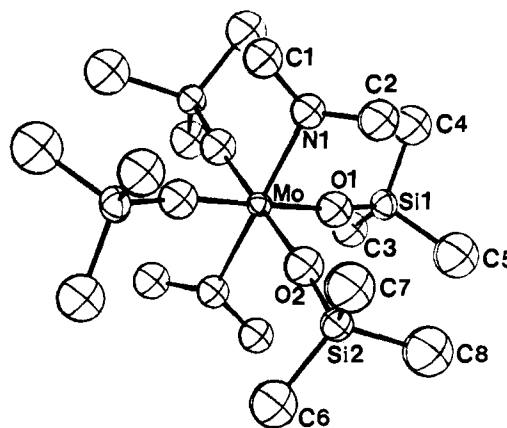


Figure 1. An ORTEP view of Mo(OSiMe₃)₄(HNMe₂)₂ showing 50% probability ellipsoids and atomic numbering scheme.

obtained a full structural characterization of this interesting compound.^{25,26} An ORTEP view of the molecule is shown in Figure 1 and important bond distances and bond angles are given in Table II. The molecule is centrosymmetric with the central MoO₄N₂ moiety closely approaching an idealized trans-octahedral geometry. The geometry about the nitrogen atoms is pyramidal, cf. all structural characterizations of M(NMe₂)_n compounds which reveal planar M-NC₂ units,⁴ and the Mo-O-Si angles approach linearity indicative of strong O-to-Mo π bonding. An interesting comparison of bond distances and bond angles may be made between Mo(OSiMe₃)₄(HNMe₂)₂ and the structurally characterized dinuclear compound Mo₂(OSiMe₃)₆(HNMe₂)₂.²⁴ In both compounds the average Mo-O distance is 1.950 Å, but the Mo-N distances are 2.219 (4) Å in the mononuclear compound and 2.282 (4) Å in the dinuclear compound, which correlates with the experimental observation that amine is readily eliminated upon heating in vacuo for Mo₂(OSiMe₃)₆(HNMe₂)₂, but not for Mo(OSiMe₃)₄(HNMe₂)₂.

The structural characterization of Mo(OSiMe₃)₄(HNMe₂)₂ leads us to believe that Mo(CH₂SiMe₃)₄ would be a coordinatively unsaturated molecule and would be unstable with respect to either oligomerization or the binding of additional ligands. In this respect, it is interesting to note that whereas Cr(CH₂SiMe₃)₄ may be readily synthesized,²⁷ attempts to prepare Mo(CH₂SiMe₃)₄ have so far failed. The dinuclear compound Mo₂(CH₂SiMe₃)₆²⁸ and mononuclear carbene

Table II. Pertinent Bond Distances and Bond Angles for Mo(OSiMe₃)₄(HNMe₂)₂^a

Bond Distances, Å			Bond Distances, Å			Bond Distances, Å		
Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Mo	O1	1.950 (4)	Si1	C4	1.850 (7)	Si2	C8	1.928 (9)
Mo	O2	1.951 (4)	Si1	C5	1.895 (8)	N1	C1	1.472 (6)
Mo	N1	2.219 (4)	Si2	O2	1.539 (4)	N1	C2	1.478 (6)
Si1	O1	1.551 (4)	Si2	C6	1.889 (7)			
Si1	C3	1.875 (7)	Si2	C7	1.852 (8)			

Bond Angles, deg				Bond Angles, deg				Bond Angles, deg			
Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1	Mo	O1	180.0 (3)	O2	Mo	N1	86.4 (1)	O2	Si2	C7	108.0 (3)
O1	Mo	O2	89.2 (1)	O2	Mo	N1	86.4 (1)	O2	Si2	C8	111.0 (3)
O1	Mo	O2	90.8 (1)	O2	Mo	N1	93.6 (1)	C6	Si2	C7	108.6 (4)
O1	Mo	N1	94.6 (1)	N1	Mo	N1	180.0 (3)	C6	Si2	C8	110.4 (4)
O1	Mo	N1	85.4 (1)	O1	Si1	C3	111.8 (2)	C7	Si2	C8	108.5 (4)
O1	Mo	O2	90.8 (1)	O1	Si1	C4	111.8 (3)	Mo	O1	Si1	170.8 (2)
O1	Mo	O2	89.2 (1)	O1	Si1	C5	112.2 (3)	Mo	O2	Si2	174.2 (2)
O1	Mo	N1	85.4 (1)	C3	Si1	C4	106.0 (3)	Mo	N1	C1	117.0 (3)
O1	Mo	N1	94.6 (1)	C3	Si1	C5	107.9 (4)	Mo	N1	C2	115.5 (3)
O2	Mo	O2	180.0 (5)	C4	Si1	C5	106.9 (4)	C1	N1	C2	114.3 (4)
O2	Mo	N1	93.6 (1)	O2	Si2	C6	110.2 (3)				

^a For atomic numbering scheme see Figure 1; numbers in parentheses are estimated standard deviations in the least significant digits.

(Me₃SiCH₂)₃MoCHSiMe₃ and carbyne (Me₃SiCH₂)₃-MoCSiMe₃ compounds have been isolated.²⁹

Experimental Section

Materials. Mo(NMe₂)₄ was prepared as previously described.⁸ The alcohols were commercially available. *tert*-Butyl alcohol (Mallinckrodt) was distilled from benzene as an azeotrope, and the azeotrope was stored under nitrogen over molecular sieves prior to use. Neopentyl alcohol (Aldrich) and pinacol (Matheson Coleman and Bell) were dissolved in benzene and stored over molecular sieves. Methanol (Mallinckrodt), ethanol (Mallinckrodt), and 2-propanol (Mallinckrodt) were distilled over sodium under nitrogen atmosphere and stored over molecular sieves. Trimethylsilanol and triethylsilanol were prepared according to the method of Sommer et al.³⁰

General Procedures. All preparations and other operations were carried out under a dry and oxygen-free nitrogen atmosphere or in vacuo, using standard Schlenk-type techniques. Solvents (pentane, hexane, benzene, and toluene) were dried and freed from dissolved molecular oxygen by distillation from a solution of the solvent, benzophenone, phenyl ether, and sodium. When not needed for immediate use, solvents were stored over calcium hydride under nitrogen. Owing to the highly reactive nature of Mo(NMe₂)₄ and Mo(OR)₄ compounds, traces of oxygen were removed from the solvent (pentane or hexane) immediately prior to preparative work by freeze/thaw procedures under a high vacuum. A standard procedure involved three of these outgassing cycles. Samples were stored and handled in a Vacuum Atmospheres Dri Lab System.

Physical and Analytical Methods. Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elabach, West Germany, using drybox sampling techniques. Molecular weight determinations were made under a purified nitrogen atmosphere in an all-glass cryoscopic apparatus incorporating a thermistor bridge.

Infrared spectra were obtained from Nujol mulls between CsI plates using a Perkin-Elmer IR 283 spectrophotometer.

Electronic absorption spectra were measured with a Cary 14 spectrophotometer using quartz cells of 2-mm path length fitted with ground-glass seals. Hexane was used as solvent.

Mass spectra were obtained using an AEI MS9 mass spectrometer and the method of direct insertion (70–150 °C).

Magnetic susceptibility measurements were done in solution and in solid state. Solution measurements were made according to the Evans method.¹⁸ Toluene was used as solvent with 2% HMDS (hexamethyldisiloxane) as reference. NMR solution magnetic susceptibility measurements were made on a Varian Associates A-60 spectrometer. Magnetic susceptibility measurements of the solid samples were made on Faraday equipment³¹ calibrated with (NH₄)₂Mn(SO₄)₂·6H₂O.³² Measurements were taken at three field strengths over the temperature range 291–88 K.³³

Preparation of Mo(OBu-*t*)₄. *t*-BuOH (29.2 mmol) in benzene was added to a pentane solution (25 mL) of Mo(NMe₂)₄ (7.29 mmol) at ca. 0 °C; the reaction flask was cooled in an ice bath. Upon the addition, the solution turned dark blue. The solution was allowed to warm to room temperature and was stirred for 6 h. The solvent was then removed in vacuo. As the solvent was removed, the solution turned dark green and the removal of the last traces of solvent yielded a dark green, almost black, gummy-residue. Overnight the residue became a black-green powdery solid. The residue was purified by sublimation (70 °C, 10⁻³ Torr) (the sublimer was equipped with a liquid N₂ cold finger) yielding a green-brown solid, Mo(OBu-*t*)₄ (438 mg). Anal. Calcd: C, 49.47; H, 9.36; N, 0.00. Found: C, 49.20; H, 9.36; N, 0.23. Note: Sublimation occurs with decomposition. Above 70 °C, Mo(OBu-*t*)₄ has been observed to decompose, yielding isobutylene, H₂O, and *tert*-butyl alcohol as gaseous products, and a blue, water-soluble, nonvolatile solid.

Infrared data (Nujol mull between CsI plates): 312 (w), 379 (m), 474 (m), 575 (s), 774 (s), 785 (s), 902 (vs), 923 (vs), 994 (sh), 1025 (m), 1171 (vs), 1232 (s), 1262 (m), and 1358 cm⁻¹ (s).

A low-intensity peak of highest *m/e* 461 corresponds to Mo(OBu-*t*)₅⁺. The base peak (peak of highest intensity) occurs at *m/e* 388, corresponding to Mo(OBu-*t*)₄⁺ (based on ⁹⁶Mo).

UV/vis data are reported in Table I.

Preparation of Mo(OPr-*i*)₄. Isopropyl alcohol (17.32 mmol) was added to a hexane solution (25 mL) of Mo(NMe₂)₄ (4.33 mmol) at ca. 0 °C; the reaction flask was cooled in an ice bath. Upon addition of the alcohol, the solution immediately turned blue. The reaction mixture was allowed to warm to room temperature, and was stirred for 30 min. The solvent was then removed in vacuo. The residue, obtained upon complete evaporation to dryness, was a blue powder which sublimed at 70–90 °C (10⁻³ Torr) to yield blue, crystalline Mo(OPr-*i*)₄ (700 mg). Anal. Calcd: C, 43.37; H, 8.49; N, 0.00. Found: C, 43.11; H, 8.28; N, 0.17. (Note: Mo(OPr-*i*)₄ can be further purified by recrystallization from hexane.) A cryoscopic molecular weight determination in benzene gave 600 ± 30; calcd mol wt for Mo(OPr-*i*)₄, 332. ¹H NMR data: at 35 °C, δ 1.28 (d, 6), 5.18 (sept, 1); at -40 °C, δ 1.15 (d, 18), 1.63 (d, 6), 4.98 (sept, 3), 6.07 (sept, 1) (relative to HMDS (hexamethyldisiloxane)). ¹³C NMR (integration in parentheses): at 60 °C, δ 77.1 (1), 26.2 (2); at -60 °C, δ 81.3 (1), 76.0 (2), 26.7 (6), 24.9 (3) (relative to Me₄Si). Molecular weight and NMR data are indicative of a diamagnetic, dimeric species: (Pr-*i*O)₆Mo₂(μ-OPr-*i*)₂.

Infrared data (Nujol mull between CsI plates): 320 (w), 332 (w), 420 (m), 442 (m), 456 (m), 518 (m), 602 (s), 628 (s), 638 (s), 832 (s), 841 (s), 935 (sh), 969 (vs), 1102 (vs), 1112 (vs), 1160 (s), 1260 (w), and 1315 cm⁻¹ (s).

A parent ion at *m/e* 664 in the mass spectrum corresponds to Mo₂(OPr-*i*)₈⁺ (based on ⁹⁶Mo).

Preparation of Mo(OCH₂CMe₃)₄. Neopentyl alcohol (15.24 mmol)

in benzene (10 mL) was added to a pentane solution (20 mL) of $\text{Mo}(\text{NMe}_2)_4$ (3.81 mmol) at ca. 0 °C; the reaction flask was cooled in an ice bath. Upon addition of the alcohol, the solution immediately turned blue-green. The solution was allowed to warm to room temperature and was stirred for 2 h. The solvent was removed in vacuo to yield a blue solid which sublimed (140–180 °C, 10^{-3} Torr) to yield a dark blue solid, $\text{Mo}(\text{OCH}_2\text{CMe}_3)_4$. Anal. Calcd: C, 54.05; H, 9.98; N, 0.00. Found: C, 53.84; H, 9.82; N, 0.19. UV/visible data are reported in Table I. A cryoscopic molecular weight determination in benzene gave mol wt 740 ± 30 ; calcd for $\text{Mo}(\text{OCH}_2\text{CMe}_3)_4$, 444. $\text{Mo}(\text{OCH}_2\text{CMe}_3)_4$ is very sparingly soluble in hydrocarbon solvents.

A parent ion at m/e 888 in the mass spectrum corresponds to $[(\text{Mo}(\text{OCH}_2\text{CMe}_3)_4)_2]^+$ (based on ^{96}Mo).

Preparation of $\text{Mo}(\text{OEt})_4$. Ethanol (8.0 mmol) was added to $\text{Mo}(\text{NMe}_2)_4$ (2.0 mmol) dissolved in hexane (20 mL). The reaction flask was cooled in an ice bath. The solution turned dark blue immediately. After stirring for 30 min, the solvent was removed in vacuo leaving a green, gummy solid which sublimed (70–90 °C, 10^{-3} Torr) giving a dark green solid of empirical formula $\text{Mo}(\text{OEt})_4$. Anal. Calcd: C, 34.79; H, 7.30. Found: C, 34.63; H, 7.23. A cryoscopic molecular weight determination in benzene gave mol wt 860 ± 30 ; calcd for $\text{Mo}(\text{OEt})_4$, 276. UV/vis data are reported in Table I.

Infrared data (Nujol mull between CsI plates): 430 (w, br), 520 (m), 602 (s, br), 802 (w), 980 (s), 1052 (vs), 1092 (vs), 1151 (m), and 1348 cm^{-1} (s).

A parent ion at m/e 828 in the mass spectrum corresponds to $[\text{Mo}(\text{OEt})_4]_3^+$ (based on ^{96}Mo).

Preparation of $\text{Mo}(\text{OMe})_4$. Methanol (19.2 mmol) was added to a hexane solution (25 mL) of $\text{Mo}(\text{NMe}_2)_4$ (4.80 mmol) at 0 °C; the reaction flask was cooled in an ice bath. The solution immediately turned brown and a purple solid precipitated out of solution. The solution was stirred for 1 h. The solution was concentrated and filtered. The purple solid which was collected was washed with cold hexane and dried in vacuo yielding the purple, nonvolatile compound $[\text{Mo}(\text{OMe})_4]_x$ (468 mg). Anal. Calcd: C, 21.83; H, 5.50; N, 0.00. Found: C, 22.06; H, 5.61; N, 0.46. $[\text{Mo}(\text{OMe})_4]_x$ is insoluble in hydrocarbon solvents.

Infrared data (Nujol mull between CsI plates): 350 (m), 432 (s), 459 (s), 527 (s), 545 (vs), 562 (sh), 805 (w), 974 (s), 1010 (s), 1041 (vs), 1057 (sh), 1157 (s), and 1263 cm^{-1} (sh).

Preparation of $\text{Mo}(\text{OSiMe}_3)_4 \cdot 2\text{HNMe}_2$. Trimethylsilanol³⁰ (24.2 mmol) was added to $\text{Mo}(\text{NMe}_2)_4$ (6.05 mmol) dissolved in pentane (20 mL). The reaction flask was cooled in an ice bath. After 5 min, a yellow, crystalline solid precipitated out of solution. The solution was stirred for an additional 30 min and then was concentrated. The solution was cooled at -15 °C overnight to promote further crystallization. The solution was filtered and the yellow, crystalline solid was washed with cold pentane. Yellow $\text{Mo}(\text{OSiMe}_3)_4 \cdot 2\text{HNMe}_2$ (1.95 g) was obtained. Anal. Calcd: C, 35.40; H, 9.30; N, 5.16. Found: C, 35.42; H, 8.84; N, 5.52. $\text{Mo}(\text{OSiMe}_3)_4 \cdot 2\text{HNMe}_2$ sublimes (80–100 °C, 10^{-3} Torr) without loss of HNMe_2 . A cryoscopic molecular weight determination in benzene gave mol wt 551 ± 20 (calcd for $\text{Mo}(\text{OSiMe}_3)_4 \cdot 2\text{HNMe}_2$, 542). UV/visible data are given in Table I.

Infrared data (Nujol mull between CsI plates): 300 (m), 320 (s), 391 (m), 435 (s, br), 624 (m), 671 (s), 742 (s), 830 (s, br), 930 (vs, br), 1015 (s, br), 1124 (m), 1208 (m), 1245 (s), 1255 (sh), 1301 (m), and 3291 cm^{-1} (s).

A parent ion at m/e 542 in the mass spectrum corresponds to $[\text{Mo}(\text{OSiMe}_3)_4 \cdot 2\text{HNMe}_2]^+$ (based on ^{96}Mo).

Preparation of $\text{Mo}(\text{OSiEt}_3)_4 \cdot 2\text{HNMe}_2$. Triethylsilanol³⁰ (22.4 mmol, 3.6 mL) was added to $\text{Mo}(\text{NMe}_2)_4$ (5.61 mmol) dissolved in hexane (20 mL). The reaction flask was cooled in an ice bath. Upon addition, the solution turned yellow-brown. The solution was stirred for 2 h and the solvent was removed in vacuo, leaving yellow-brown crystals, $\text{Mo}(\text{OSiEt}_3)_4 \cdot 2\text{HNMe}_2$. Anal. Calcd: C, 47.29; H, 10.49; N, 3.94. Found: C, 47.11; H, 10.35; N, 3.96. Attempts to sublime $\text{Mo}(\text{OSiEt}_3)_4 \cdot 2\text{HNMe}_2$ (60 °C, 10^{-3} Torr) led to the formation of a green liquid, presumably $\text{Mo}(\text{OSiEt}_3)_4$, and the release of HNMe_2 (2 equiv). The green liquid decomposed over a period of time (ca. 15–30 min) to an orange-brown liquid which was not analyzed. $(\text{Et}_3\text{Si})_2\text{O}$ was formed in this decomposition. UV/visible data are given in Table I.

Infrared data (Nujol mull between CsI plates): 331 (m), 454 (m), 579 (m), 674 (w), 734 (vs), 910 (vs, br), 969 (sh), 1017 (s), 1075 (w,

Table III. Magnetic Susceptibility Data

A. Solution Samples					
1. $\text{Mo}(\text{OBU-}t)_4$ ($\chi(\text{diamag}) = 238 \times 10^{-6}$ cgs)					
T, K	213	254	281	313	
$10^6 \chi_M, \text{cgs}$	1092	956	825	745	
μ_{eff}, μ_B	1.37	1.40	1.37	1.37	
2. $\text{Mo}(\text{OCH}_2\text{CMe}_3)_4$ ($\chi(\text{diamag}) = 285 \times 10^{-6}$ cgs)					
T, K	233	273	293		
$10^6 \chi_M, \text{cgs}$	335	264	221		
μ_{eff}, μ_B	0.79	0.76	0.72		
3. $\text{Mo}(\text{OEt})_4$ ($\chi(\text{diamag}) = 143 \times 10^{-6}$ cgs)					
T, K	253	313	328		
$10^6 \chi_M, \text{cgs}$	38	39	37		
μ_{eff}, μ_B	0.31	0.31	0.31		
4. $\text{Mo}(\text{OSiMe}_3)_4 \cdot 2\text{HNMe}_2$ ($\chi(\text{diamag}) = 368 \times 10^{-6}$ cgs)					
T, K	287	313	333	354	
$10^6 \chi_M, \text{cgs}$	3093	2800	2605	2409	
μ_{eff}, μ_B	2.68	2.66	2.65	2.63	
5. $\text{Mo}(\text{OSiEt}_3)_4 \cdot 2\text{HNMe}_2$ ($\chi(\text{diamag}) = 477 \times 10^{-6}$ cgs)					
T, K	212	233	254	274	293
$10^6 \chi_M, \text{cgs}$	3349	2951	2646	2425	2205
μ_{eff}, μ_B	2.40	2.35	2.33	2.31	2.28
B. Solid Samples					
1. $\text{Mo}(\text{OSiMe}_3)_4 \cdot (\text{HNMe}_2)_2$					
T, K	88	100	126	171	219
$10^3 \chi_M, \text{cgs}$	9.125	8.472	6.808	5.144	4.158
μ, μ_B	2.54	2.60	2.62	2.66	2.70
2. $\text{Mo}(\text{OBU-}t)_4$					
T, K	88	100	126	171	219
$10^3 \chi_M, \text{cgs}$	1.975	1.830	1.452	1.100	0.849
μ, μ_B	1.17	1.21	1.21	1.23	1.22
3. $\text{Mo}(\text{OCH}_2\text{CMe}_3)_4$					
T, K	88	100	126	171	219
$10^6 \chi_M, \text{cgs}$	1039	975	813	658	620
μ, μ_B	0.86	0.88	0.91	0.95	1.04
4. $\text{Mo}(\text{OMe})_4 \chi_M = 10^{-4}$ cgs units independent of temperature (88–267 K) corresponding to $\mu_{\text{eff}} \sim 0.5 \mu_B$ at 273 K.					

br), 1123 (m), 1209 (sh), 1235 (s), 1415 (m), and 3282 cm^{-1} (m).

A parent ion at m/e 620 corresponds to $\text{Mo}(\text{OSiEt}_3)_4^+$ (based on ^{96}Mo).

Magnetic Susceptibility Measurements. Magnetic susceptibility measurements of solutions (Table III) were measured by the NMR technique devised by Evans.¹⁸ The solvent and external reference was toluene plus 2% (v/v) hexamethyldisiloxane. The paramagnetic solute concentration in solution was 0.07–0.1 M ($\chi_M = \chi_g \times \text{mol wt (solute)}$) and was corrected for diamagnetic susceptibilities using Pascal's constants.

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Supplementary Material Available: Full crystallographic data (20 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) (a) Princeton University; (b) Queen Mary College.
- (2) (a) G. Wilkinson, *Science*, **185**, 109 (1974); (b) R. R. Schrock and G. W. Parshall, *Chem. Rev.*, **76**, 243 (1976).
- (3) P. J. Davidson, M. F. Lappert, and R. Pearce, *Acc. Chem. Res.*, **7**, 209 (1974); *Chem. Rev.*, **76**, 219 (1976).
- (4) D. C. Bradley and M. H. Chisholm, *Acc. Chem. Res.*, **9**, 273 (1976).
- (5) D. C. Bradley, *Adv. Inorg. Chem. Radiochem.*, **15**, 259 (1972).

- (6) D. C. Bradley and K. J. Fisher, *MTP Int. Rev. Sci., Ser. One*, **5**, 65 (1972).
- (7) Allyl and benzyl compounds of the type ML_4 are known; see ref 2 and 3.
- (8) D. C. Bradley and M. H. Chisholm, *J. Chem. Soc. A*, 1511 (1971).
- (9) E. C. Alyea, J. S. Basl, D. C. Bradley, and M. H. Chisholm, *J. Chem. Soc. A*, 772 (1971).
- (10) G. Kyrkaez and R. J. Rocek, *J. Am. Chem. Soc.*, **95**, 4756 (1973).
- (11) Alkoxides are known to undergo adduct formation with Lewis basis such as amines, e.g., $[Nb(OMe)_5]_2 + 2L \rightleftharpoons 2Nb(OMe)_5L$, and $Mo_2(OR)_6 + 2L \rightleftharpoons Mo_2(OR)_6L_2$: M. H. Chisholm, F. A. Cotton, C. A. Murillo, and W. W. Reichert, *J. Am. Chem. Soc.*, **99**, 1652 (1977); *Inorg. Chem.*, **18**, 1801 (1977).
- (12) D. C. Bradley and I. M. Thomas, *J. Chem. Soc.*, 3404 (1959).
- (13) D. C. Bradley and M. M. Faktor, *Trans. Faraday Soc.*, 2117 (1959).
- (14) J. A. Ibers, *Nature (London)*, **197**, 686 (1963).
- (15) D. C. Bradley and C. E. Hollaway, *Inorg. Chem.*, **3**, 1163 (1964).
- (16) D. C. Bradley and C. E. Hollaway, *J. Chem. Soc. A*, 1316 (1968).
- (17) W. R. Russo and W. H. Nelson, *J. Am. Chem. Soc.*, **92**, 1521 (1970).
- (18) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
- (19) B. N. Figgis in "Introduction to Ligand Fields," Interscience, New York, N.Y., 1966.
- (20) F. A. Cotton, *Acc. Chem. Res.*, **2**, 240 (1968); *Chem. Soc. Rev.*, **4**, 27 (1975). The molecular structure of $Mo_2(OPr-i)_6$ has been deduced from x-ray studies. The molecule has rigorous inversion symmetry and virtual C_{2h} symmetry and there is essentially trigonal bipyramidal coordination about each molybdenum atom. The central planar $Mo_2(\mu-O)_2$ moiety is made from bridging isopropoxy ligands which form alternately long (axial) and short (equatorial) Mo-O bonds. The Mo-Mo distance is 2.525 (1) Å indicative of a Mo-to-Mo double bond which may be considered to arise from overlap of a metal $d_{xz} - d_{yz}$ and $d_{yz} - d_{xz}$ orbitals. Thus in a formal sense the double bond is comprised of a σ and a δ bond. F. A. Cotton and M. W. Extine, private communication.
- (21) MoO_2 has a rutile-like structure but is distorted by the presence of Mo-Mo bonds (2.51 Å): B. G. Brandt and A. C. Skapski, *Acta Chem. Scand.*, **21**, 661 (1967).
- (22) W. H. McCarroll, L. Katz, and R. Ward, *J. Am. Chem. Soc.*, **79**, 5410 (1957).
- (23) M. H. Chisholm, F. A. Cotton, C. A. Murillo, and W. W. Reichert, *Inorg. Chem.*, **16**, 1801 (1977).
- (24) M. H. Chisholm, F. A. Cotton, M. W. Extine, and W. W. Reichert, *J. Am. Chem. Soc.*, **100**, 153 (1978).
- (25) Molecular Structure Corp., P.O. Box DF, College Station, Texas.
- (26) Crystal data: triclinic; space group $P1$; $a = 9.661$ (2), $b = 9.863$ (3), $c = 9.419$ (5) Å, $V = 766.8$ (5) Å³, $\lambda = 0.710$ 73, $\alpha = 115.29$ (2)^o, $\beta = 108.92$ (2), $\gamma = 84.33$ (2)^o, $d_{\text{calcd}} = 1.175$ g/cm³; $M = 542.87$; $Z = 1$. For full crystallographic details see paragraph at end of paper regarding supplementary material.
- (27) W. Mowat, A. J. Shortland, N. J. Hill, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.* 770 (1973).
- (28) F. Huq, W. Mowat, A. C. Skapski, and G. Wilkinson, *Chem. Commun.*, 1477 (1971).
- (29) M. H. Chisholm, W. W. Reichert, R. G. Anderson, G. Wilkinson, and J. F. Gibson, results to be published.
- (30) L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *J. Am. Chem. Soc.*, **66**, 2282 (1946).
- (31) For details of the equipment see M. A. Laffey, Ph.D. Thesis, London, 1977.
- (32) A. H. Cooke, *Prog. Temp. Phys.*, **1**, 224 (1955).
- (33) We thank Mr. K. H. Bhatt for his technical assistance.

A Systematic X-Ray Absorption Study of Molybdenum Complexes. The Accuracy of Structural Information from Extended X-Ray Absorption Fine Structure

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Abstract: X-ray absorption spectra have been collected using synchrotron radiation for a number of mononuclear and dinuclear molybdenum complexes containing carbon, nitrogen, oxygen, and sulfur donor atoms. The extended fine structure (EXAFS) of the Mo absorption edge has been analyzed by a method which combines Fourier transform and curve-fitting techniques. Parameterized phase shift and amplitude functions for describing Mo-C, Mo-N, Mo-O, Mo-S, and Mo-Mo interactions were obtained from spectra of $Mo(CO)_6$, $Mo(NCS)_6^{3-}$, MoO_4^{2-} , $Mo(S_2C_6H_4)_3$, and $Mo_2O_4cys_2^{2-}$. Application of these phase shifts and amplitudes to the EXAFS of other compounds yielded distance determinations to an accuracy consistently better than 0.03 Å for atoms bound to Mo. The number and type of coordinating atoms were also determined with a reasonable degree of certainty. This work demonstrates the applicability (and limitations) of EXAFS for providing structural information about a specific absorbing center under noncrystalline conditions, and it lays a foundation for the analysis of the x-ray absorption spectra of nitrogenase and other Mo proteins.

Introduction

Recent experimental and theoretical advances have made x-ray absorption spectroscopy a promising new method for the study of local structure around a specific absorbing atom in metalloproteins,² catalysts,³ amorphous materials,^{4a} and many other cases where conventional diffraction methods are not feasible.^{4b} To this date, much of the work has centered on the determination of accurate absorber-scatterer distances. This in turn has caused a need for the evaluation of transferable phase shifts, whether by Fourier transform,⁵ curve fitting,⁶ or ab initio⁷ methods. At present, with highly symmetric structures involving only a single absorber-scatterer distance in the first coordination sphere, one can use any one of the above methods to obtain such distances to an accuracy of about 0.01 Å.

Besides radial distance information, EXAFS also contains information about the type and number of scattering atoms and their motion relative to the absorber. The atom type reveals itself through the absolute phase of the fine structure oscillations and through the EXAFS amplitude envelope. This amplitude is also affected by the static and thermal disorder of absorber-scatterer distances. Moreover, simple theory predicts that the magnitude of the fine structure will be linearly proportional to the number of scattering atoms and inversely proportional to the square of the absorber-scatterer distance. Until recently, much of the amplitude information has been discarded,⁸ but in this paper it is demonstrated that a set of transferable total amplitude functions can be used to determine the number of scatterers at a particular distance. Finally, the amplitude envelope and absolute phase shift together will be used to identify the elemental type(s) of scatterers involved.