Contribution from the Department of Chemistry,
Oregon State University, Corvallis, Oregon 97331-4003

Preparation and Properties of Dioxomolybdenum Alkoxides, Phenoxide, and Siloxides Prepared by the Cocondensation Reaction of MoO_3 with Alkoxy- or (Aryloxy)silanes

Gyu-Shik Kim, David Huffman, and Carroll W. DeKock*

This paper describes the preparation and properties of a number of dioxomolybdenum compounds prepared by the cocondensation reaction of MoO_3 with appropriate alkoxy- or (aryloxy)alkylsilanes. The compounds reported are $MoO_2(OR)_2$ (R = Me, Et, *n*-Pr, Ph), $MoO_2(OR)_2(py)_2$ (R = Ph, (*t*-Bu)Me$_2$Si; py = pyridine), and $Mo_3O_6(OSiMe_2(t$-Bu$))_4(py)_3$. The ^{1}H NMR, ^{13}C 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 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 co-workers have previously reported the preparation of MoO_2-$(OR)_2$ compounds[3] where R = *t*-Bu, *i*-Pr, and CH$_2$-*t*-Bu, all bulky groups, by the reaction of $Mo_2(OR)_6$ 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 reaction of tri-*tert*-butylsilanol with MoO_3 in a bomb reactor.[4] Klemperer et al. have prepared R$_3$SiOMoO$_3^-$ (R = C$_6$H$_5$, *t*-C$_4$H$_9$) by reaction of the appropriate silanol with (*n*-Bu$_4$N)$_2$(Mo$_2$O$_7$).[5]

About two decades ago Nebelung and Jahr reported the preparation of (MoO$_2$(OEt)$_2$)$_3$(NH$_3$)$_2$ by reacting MoO$_2$Cl$_2$ 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 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 oxomolybdenum compounds by the reaction of MoO_3 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 MoO_3 with appropriate alkoxy- or (aryloxy)alkylsilanes. The compounds reported here are MoO$_2$(OR)$_2$ where R = Me, Et, *n*-Pr, and Ph, MoO$_2$(OR)$_2$(py)$_2$ where R = Ph and (*t*-Bu)Me$_2$Si

and py = pyridine, and Mo$_3$O$_6$(OSiMe$_2$(*t*-Bu))$_4$(py)$_3$. We have also attempted to prepare mixed alkoxide/siloxide oxomolybdenum compounds that may be models for the surface catalytic oxidation of alcohols by molybdenum oxides in silica supports, namely, the reactions of MoO_3 vapor with Me$_3$SiOMe, Me$_2$Si(OMe)$_2$, and Me$_3$SiO-*t*-Bu. The condensation reactions of MoO_3 with (Me$_3$Si)$_2$O and (Me$_3$Si)$_2$ are also reported.

Experimental Section

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$_2$O$_5$ under dinitrogen. Pyridine was dried over KOH and then distilled from BaO. All the silanes except trimethyl-*tert*-butoxy-silane and *tert*-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*-Butyl-dimethylmethoxysilane 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. MoO$_3$ (Matheson Coleman and Bell) was used without further 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.

NMR spectra were taken on either a Varian FT-80A (^{1}H) or a Bruker AM-400 (^{1}H, ^{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 by 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 by 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)$_3$SiOSi(OMe)$_3$. Trace amounts of methanol and poly(methoxysilanes) were also observed. The white solid was washed with 3 × 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 × 10^{-3} Torr) to give 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)$_3$SiOSi(OMe)$_3$ and poly(methoxysilanes). Yield: 18% based on

(1) *Tailored Metal Catalysts*; Iwasawa, Y., Ed.; D. Reidel: Dordrecht, Holland, 1986.
(2) Yermakov, Y. I.; Kuznetsov, B. N.; Zakharov, V. A. *Catalysis by Supported Complexes*; Elsevier: New York, 1981.
(3) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.
(4) Weidenbruch, M.; Pierrard, C.; Pesel, H. *Z. Naturforsch.* **1978**, *33B*, 1468.
(5) Klemperer, W. G.; Mainz, V. V.; Wang, R.-C.; Shum, W. *Inorg. Chem.* **1985**, *24*, 1968.
(6) Nebelung, V. A.; Jahr, K. F. *Z. Naturforsch.* **1964**, *19B*, 654.
(7) Klabunde, K. J. *Chemistry of Free Atoms and Particles*; Academic: New York, 1980.
(8) Blackborow, J. R.; Young, D. *Metal Vapor Synthesis in Organometallic Chemistry*; Springer-Verlag: Berlin, 1979.
(9) DeKock, C. W.; McAfee, L. V. *Inorg. Chem.* **1985**, *24*, 4293.
(10) DeKock, C. W.; Ely, S. R.; Hopkins, T. E.; Brault, M. A. *Inorg. Chem.* **1978**, *17*, 625.

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 ^{1}H NMR (pyridine-d_5, referenced to TMS): δ 4.41 (s, br). 100.614-MHz ^{13}C NMR (pyridine-d_5, referenced to TMS): δ 64 (vbr), 68 (vbr). 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$_2$O$_5$(OMe)$_3^-$], 380 [33, Mo$_2$O$_4$(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)$_3$SiOSi(OEt)$_3$. The solid was purified by sublimation at 373 K and 5 × 10^{-3} Torr, washed with 3 × 6 mL of dry toluene, and then vacuum-dried to remove all (EtO)$_3$SiOSi(OEt)$_3$ to give 2.7 g (12 mmol, 65% yield) of pure white solid. 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 ^{1}H NMR (benzene-d_6, referenced to C$_6$D$_5$H at 7.15 ppm): δ 1.3 (br), 4.0–5.0 (br). ^{1}H NMR after addition of 2 equiv of pyridine/equiv of MoO$_2$(OEt)$_2$ to benzene-d_6 solution: δ 1.26 (t, 3 H, CH$_3$), 4.65 (q, 2 H, CH$_2$). 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, MoO$_3$(OEt)$^-$], 220 [100, MoO$_2$(OEt)$_2^-$], 407 [1, Mo$_2$O$_5$(OEt)$_3^-$], 436 [21, Mo$_2$O$_4$(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 × 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$_2$O$_4$(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$_3$SiOPh (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 ^{1}H NMR spectroscopy showed unreacted starting ligand and Me$_3$SiOSiMe$_3$. A sample (2.9 g) of the crude product was dissolved in 100 mL of dry toluene, and the solution was filtered in the drybox. Half of the deep purple solution was vacuum-dried to give 0.817 g of dark solid that was shown to contain MoO$_2$(OPh)$_2$ with a slight amount of other contaminants by ^{1}H NMR and IR spectroscopy. 80-MHz ^{1}H NMR in acetonitrile-d_3 (referenced to CD$_2$HCN at 1.93 ppm): δ 6.6–7.4 (m, br, PhO, 10 H), 2.33 (s, unknown impurity, 0.04 H), 0.26 (s, OSiMe$_3$, 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) cm^{-1}.

To the other half of the deep purple toluene extract was added 5 mL of dry pyridine, 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 0.610 g (1.29 mmol, 30% yield) of a golden yellow crystalline solid, MoO$_2$(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 ^{1}H NMR (CD$_2$Cl$_2$, referenced to CDHCl$_2$ at δ 5.32): δ 6.88 (m, 1 H, p-H of PhO), 6.95 (m, 2 H, o-H of PhO), 7.22 (m, 2 H, m-H of PhO), 7.36 (m, 2 H, m-H of py), 7.80 (m, 2 H, p-H of py), 8.69 (m, 2 H, o-H of py). 100.614-MHz ^{13}C NMR (CD$_2$Cl$_2$, referenced to δ 53.80 of ^{13}CD$_2$Cl$_2$): δ 118.51 (C-2 of PhO), 121.26 (C-4 of PhO), 124.87 (m-C of py), 129.57 (C-3 of PhO), 138.64 (p-C of py), 150.03 (o-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) cm^{-1}. Mass spectral data: No Mo-containing ion was observed under CI or EI conditions.

Addition of ethanol to a solution of MoO$_2$(OPh)$_2$ in acetonitrile-d_3 yielded a greenish yellow solution that showed fast exchange between OEt and OPh by ^{1}H NMR spectroscopy.

MoO$_2$(OSiMe$_2$(t-Bu))$_2$(py)$_2$. Mo$_3$O$_6$(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 (CD$_3$NO$_2$, referenced to CD$_2$-HNO$_2$ at 4.33 ppm): δ 0.04 (s, 6 H, CH$_3$), 0.90 (s, 9 H, t-Bu), 7.45 (m, 2 H), 7.88 (m, 1 H), 8.55 (m, 2 H). 100.614-MHz ^{13}C NMR (CD$_3$NO$_2$, referenced to ^{13}CD$_3$NO$_2$ at 62.80 ppm): δ −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) cm^{-1}. Mass spectral data m/z [% int, assgn]: 335 [2, 392 − t-Bu$^-$], 377 [2, 392 − CH$_3^-$], 392 [100, MoO$_2$(OSiMe$_2$(t-Bu))$_2^-$], 780 [1, Mo$_2$O$_4$(OSiMe$_2$(t-Bu))$_4^-$].

Mo$_3$O$_6$(OSiMe$_2$(t-Bu))$_4$(py)$_3$. MoO$_3$ (2.05 g, 14.2 mmol) was co-condensed with (t-Bu)Me$_2$SiOMe (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 60 mL of dry toluene, and the mixture was filtered to give a green solution. To this solution was added 12 mL (148 mmol) of pyridine. A blue precipitate formed immediately and was filtered 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$_3$O$_6$(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 ^{1}H NMR (CD$_3$NO$_2$, referenced to CD$_2$HNO$_2$ at δ 4.33): δ 0.11 (s, 8 H, CH$_3$), 0.92 (s, 12 H, t-Bu), 7.52 (m, 2 H), 7.96 (m, 1 H), 8.59 (m, 2 H). 100.614-MHz ^{13}C NMR (CD$_3$NO$_2$, referenced to ^{13}C-D$_3$NO$_2$ at δ 62.80): δ −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 (m), 2857 (s), 2884 (m), 2895 (m), 2929 (m), 2953 (s), 3072 (w), 3108 (w), 3135 (w), 3214 (w) cm^{-1}. Mass spectral data m/z [% int, assgn]: 392 [100, MoO$_2$(OSiMe(t-Bu))$_2^-$], 466 [6, MoO$_2$(OSiMe$_2$(t-Bu))$_2$(OSiMe$_2$)$^-$], 780 [4, Mo$_2$O$_4$(OSiMe$_2$(t-Bu))$_4^-$].

Reaction of MoO$_3$ with Me$_3$SiOMe. MoO$_3$ (2.41 g, 16.7 mmol) was cocondensed at 77 K with Me$_3$SiOMe (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 a white solid, on the bottom of the flask. After the volatiles were stripped, a small fraction of the white solid (50 mg) was saved for a separate analysis. The remainder of the 4.50 g of crude material 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 30 mg of a powdery white solid. 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 %), methyl formate (2 mol %), dimethyl ether (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 ^{1}H NMR spectroscopy. 80-MHz ^{1}H NMR (pyridine-d_5, referenced to TMS): δ 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), 2825 (m), 2899 (w), 2932 (m), 2959 (m) cm^{-1}. Mass 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$_2$O$_4$(OMe)$_2$(OSiMe$_3$)$_2^-$].

The ^{1}H NMR spectrum of a pyridine-d_5 solution of this crude white solid showed approximately a 1:1 group ratio between methoxy and siloxy groups bound to Mo. The ^{1}H NMR spectrum of a pyridine-d_5 solution of the white sublimate showed the ratio 1:1.6 for MeO:Me$_3$SiO. 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 CH$_3$ bending region (1320–1470 cm^{-1}). The pale greenish yellow crude solid in pyridine-d_5 showed by ^{1}H NMR spectroscopy a group ratio of 2:1 for MeO:Me$_3$SiO.

Reaction of MoO$_3$ with Me$_2$Si(OMe)$_2$. MoO$_3$ (3.35 g, 23.3 mmol) was cocondensed at 77 K with Me$_2$Si(OMe)$_2$ (26.05 g, 217 mmol). The cocondensate was warmed to ambient temperature, and 4.82 g of crude material was recovered. The ^{1}H NMR spectrum of the solid in benzene-d_6 gave a complex series of resonances: δ 0.2–0.5 (Me$_2$SiO–Mo), 3.3–3.5 (MeO–SiO–Mo), 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) cm^{-1}.

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

Pyrolysis of the Crude Solid. A 279.-6-mg sample of the crude solid was pyrolyzed at 407 K for 1 h under an argon blanket to yield 218.2 mg of blue solid and colorless liquid trapped in a liquid-nitrogen-cooled U-tube. The mass difference of 61.4 mg corresponds to a 22.0 wt % loss. The volatiles were vacuum-transferred into an NMR tube. The volatiles by ^{1}H NMR spectroscopy were shown to be mostly starting ligand with a trace amount of methanol and other unidentified poly(methoxysilanes).

Reaction of MoO$_3$ with Me$_3$SiO-t-Bu. MoO$_3$ (5.37 g, 37 mmol) was cocondensed at 77 K with trimethyl-*tert*-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 *cis*-butene, *trans*-butene, and 1-butene. No sublimable product was obtained from the solid.

Reaction of MoO$_3$ with (Me$_3$Si)$_2$O. MoO$_3$ (4.74 g, 32 mmol) was cocondensed at 77 K with (Me$_3$Si)$_2$O (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 × 10^{-3} Torr) under vacuum.

Reaction of MoO$_3$ with (Me$_3$Si)$_2$. MoO$_3$ (2.609 g, 18.12 mmol) was cocondensed at 77 K with (Me$_3$Si)$_2$ (25.0 g, 170 mmol). When the reactor was warmed to 293 K, the white cocondensate changed to dark blue. Stripping of the volatiles gave a dark blue solid (2.608 g). The solid was not soluble in benzene, toluene, and methylene chloride. The volatiles collected were shown to be unreacted starting ligand by ^{1}H NMR spectroscopy.

Preparation of Molybdenum(VI) Dioxide 2,4-Pentanedionate. 100 mg (0.46 mmol) of MoO$_2$(OEt)$_2$ was partially dissolved in 30 mL of toluene. A solution of 100 μL (97.6 mg, 0.97 mmol) of 2,4-pentanedione 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 ^{1}H NMR spectroscopy. The reaction was quantitative and complete within 15 min, which was confirmed by ^{1}H 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] MoO$_3$ 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 reactions to be

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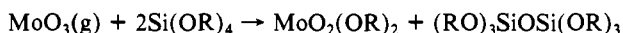
for R = Me, Et, and Pr.

The reaction is quite efficient with yields of 75–80% of crude material based on MoO$_3$ deposited on the wall of the reactor.

For R = Ph, the silicon precursor of choice was Me$_3$SiOPh with the reaction

$$MoO_3(g) + 2Me_3SiOPh \rightarrow MoO_2(OPh)_2 + (Me_3Si)_2O$$
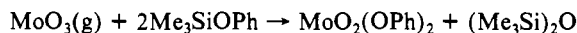
The reaction is quantitative with slight contamination of a Mo–oxo–siloxy compound. Workup in pyridine yielded the pyridine adduct MoO$_2$(OPh)$_2$(py)$_2$.

For R = (t-Bu)Me$_2$Si, the silicon precursor used was (t-Bu)Me$_2$SiOMe. In this case the ^{1}H NMR spectrum of the crude cocondensed material in benzene-d_6 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)$_2$. 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$_3$O$_6$(OSiMe$_2$(t-Bu))$_4$(py)$_3$. Further addition

of pyridine to a solution of this multinuclear 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 of the multinuclear compound in pure pyridine:

$$Mo_3O_6(OSiMe_2(t\text{-Bu}))_4(py)_3 \xrightarrow{\text{py}}$$
$$MoO_2(OSiMe_2(t\text{-Bu}))_2(py)_2 + \text{yellow soln}$$
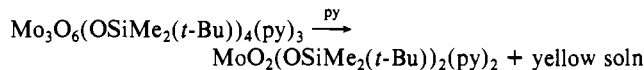
Solution and Physicochemical Properties

MoO$_2$(OMe)$_2$ is a white solid that may be sublimed at 393 K (5 × 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 ^{1}H NMR spectrum (80 MHz) shows a broad single resonance at 4.40 ppm (fwhh = 8 Hz), but the ^{13}C NMR spectrum 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 ^{13}C NMR data suggest 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 × 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 the solid is exposed to moisture. It is modestly soluble in aromatic solvents and moderately soluble in pyridine and dimethyl sulfoxide. The ^{1}H NMR spectrum of MoO$_2$(OEt)$_2$ in benzene-d_6 is shown in Figure 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 2 equiv or more of dimethyl-d_6 sulfoxide or pyridine-d_5 resulted in the typical ethoxy spectra shown in Figure 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 that may be sublimed at 358 K (5 × 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.

MoO$_2$(OPh)$_2$ is a dark solid, very soluble in aromatic hydrocarbons and pyridine and moderately soluble in acetonitrile. It is stable under dry nitrogen at room temperature. It slowly decomposes when exposed to moisture.

MoO$_2$(OPh)$_2$(py)$_2$ is a golden yellow microcrystalline solid that 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 347 K. 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$_3$O$_6$(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 of the compounds were examined by mass spectrometry using direct insertion with chemical ionization. All compounds, except MoO$_2$(OPh)$_2$(py)$_2$, show a monomeric molecular ion. For MoO$_2$(OPh)$_2$(py)$_2$ no Mo-containing envelope

---

(11) Soptrajanov, B.; Nikolovski, A.; Petrov, I. *Spectrochim. Acta* **1968**, *24A*, 1617.

(12) For Mo(OMe)$_6$: ^{1}H NMR 4.64 ppm; ^{13}C NMR 63.82 ppm in CDCl$_3$ with TMS reference. See: Jacob, E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 142.

(13) ^{13}C data (CP-MAS, 75 MHz): Mo$_2$O$_5$(OMe)$_2$ 71.6 ppm; Na$_4$-[Mo$_8$O$_{24}$(OMe)$_4$]·8MeOH 72.6 (MeO), 69.4 (MeO), 50.6 ppm (MeOH). See: McCarron, E. M., III; Sleight, A. W. *Polyhedron* **1986**, *5*, 1129.
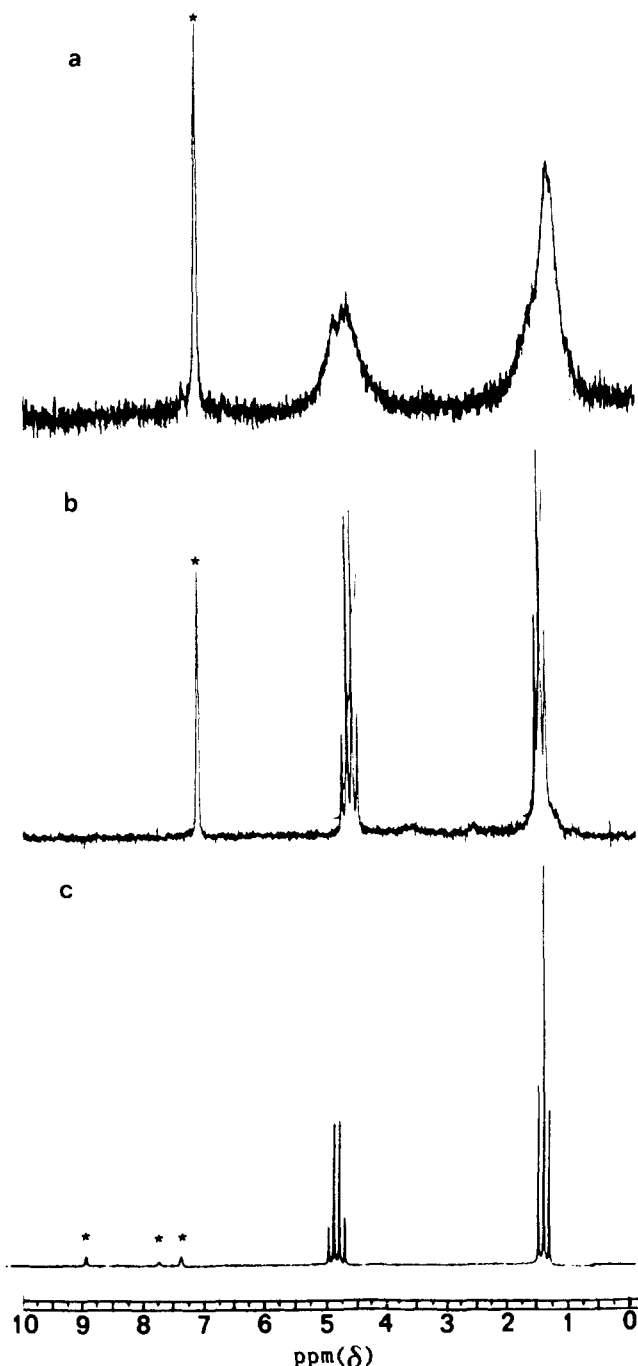
Figure 1. ^{1}H NMR spectra (80 MHz): (a) $MoO_2(OEt)_2$ in benzene-d_6; (b) same solution with 2 equiv of dimethyl-d_6 sulfoxide added; (c) $MoO_2(OEt)_2$ in neat pyridine-d_5 (identical with the spectrum of $MoO_2(OEt)_2$ in benzene-d_6 to which 2 equiv of pyridine-d_5 have been added). Asterisks denote protio impurities of the solvents.

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 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 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 cm^{-1} region but more importantly the Mo=O stretching frequencies from 800 to 1000 cm^{-1}. Closer examination of the spectra of the polymeric $MoO_2(OMe)_2$, $MoO_2(OEt)_2$, and $MoO_2(O\text{-}n\text{-}Pr)_2$ compounds reveals the common, strong to medium absorption bands around 947 and 920 cm^{-1}, which are assignable to Mo=O$_x$ stretching of cis-dioxomolybdenum(VI) compounds.[14,15] 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[16,17] 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.

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.[18] The vapor sublimes without decomposition to yield the cyclic dimer, trimer, tetramer, and pentamer, with the trimer being the predominant species.[19] 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.[18]

Cocondensation of an $R_nSi(OR')_{4-n}$ (n = 0, 2, 3) ligand into MoO_3 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 cocondensation reactions with MoO_3, a consequence of the Lewis acid character of the Mo(VI) center. No reaction occurs for the cocondensation of MoO_3 with $(Me_3Si)_2$, a compound having a comparatively weak Si–Si bond (80.5 kcal mol^{-1})[20] 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 trialkylalkoxy (R_3SiOR') silanes is very dependent on the particular silane and workup conditions. In this case 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 $MoO_2(OR')_2$. The compound $MoO_2(OSiMe_2(t\text{-}Bu))_2$ could only be isolated as the pyridine adduct. Therefore, for $MoO_2(OSiMe_2(t\text{-}Bu))_2$ it appears that the more toluene-soluble species is isolated because $MoO_2(OMe)_2$ is insoluble in toluene and by inference the compound $MoO_2(OSiMe_2(t\text{-}Bu))(OMe)$ is only sparingly soluble in the solvent. The ^{1}H NMR spectrum of the toluene extract indeed shows no methoxy resonance.

The cocondensation reaction of MoO_3 with $(t\text{-}Bu)Me_2SiOMe$ gives a more complicated chemical system than is implied by the above discussion. In addition to isolating $MoO_2(OSiMe_2(t\text{-}Bu))_2(py)_2$, we have also isolated $Mo_3O_6(OSiMe_2(t\text{-}Bu))_4(py)_3$ and have spectroscopic evidence for $Mo_3O_5(OSiMe_2(t\text{-}Bu))_6(py)_2$. The latter two compounds are isolated under addition of limited amounts of pyridine to the toluene solution and may be viewed

(14) Cotton, F. A. *Proceedings of the Climax First International Conference on the Chemistry and Uses of Molybdenum*; Mitchell, P. C. H., Ed.; Climax Molybdenum Co.: London, 1973; pp 6–10.

(15) A series of $MoO_2R_2(bpy)$ compounds with cis-dioxo moieties show two Mo=O stretching frequencies in the region 935–880 cm^{-1} with a separation of approximately 30 cm^{-1}. See: (a) Schrauzer, G. N., et al. *Organometallics* **1983**, *2*, 481. (b) *Ibid.* **1986**, *5*, 2452. (c) *Ibid.* **1988**, *7*, 279.

(16) Knobler, C.; Penfold, B. R.; Robinson, W. T.; Wilkins, C. J.; Yong, S. H. *J. Chem. Soc., Dalton Trans.* **1980**, 248.

(17) Reagan, W. J.; Brubaker, C. H., Jr. *Inorg. Chem.* **1970**, *9*, 827.

(18) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon: Oxford, England, 1984.

(19) Berkowitz, J.; Inghram, M. G.; Chupka, W. A. *J. Chem. Phys.* **1957**, *26*, 842.

(20) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

as a combination of coordinatively unsaturated Mo(VI) and Mo(IV) fragments presumably through Mo=O→Mo interaction. This view may be supported by the observation that MoO$_2$-(OSiMe$_2$(*t*-Bu))$_2$(py)$_2$ was obtained as a colorless crystalline solid from Mo$_3$O$_6$(OSiMe$_2$(*t*-Bu))$_4$(py)$_3$.

The cocondensation reaction of Me$_3$SiOPh with MoO$_3$ appears to be far simpler with the crude reaction product showing, by ^{1}H NMR spectroscopy, MoO$_2$(OPh)$_2$ and (Me$_3$Si)$_2$O 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$_3$SiOMe 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}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 Me$_3$SiO 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}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}H NMR spectrum of this white sublimate in pyridine-d_5 shows more siloxy groups relative to methoxy groups (the ratio is 1.6). This suggests that the dioxodisiloxymolybdenum(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 the 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 %), methyl formate (2 mol %), formaldehyde (trace), and dimethyl ether (trace). It is interesting to note that the solid-state decomposition shows a diverse product distribution compared to that of the solution decomposition. Apparently, the presence of excess methoxy groups accompanied by the ease of reduction of the Mo=O moiety at elevated temperature accounts for this discrepancy.

The cocondensation reaction of Me$_2$Si(OMe)$_2$ with MoO$_3$ was studied. Reaction readily occurs on warming to room temperature. The ^{1}H NMR spectrum of the crude material in benzene-d_6 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$_2$Si(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$_3$SiOMe and MoO$_3$. This may be ascribed to the inability to form disiloxane by the Me$_2$Si group in a localized environment.

^{1}H 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$_3$SiOMe and the MoO$_3$/Me$_2$Si(OMe)$_2$ systems, which still display polymeric behavior in pyridine. A dramatic change in the ^{1}H NMR spectrum is shown in Figure 1, for which the addition of 2 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$_3$SiO-*t*-Bu. In this case the reaction products of isobutene and *tert*-butyl alcohol indicate catalytic H abstraction by the Mo=O moiety occurs extensively for the *tert*-butyl group, presumably due to the proximity of hydrogen atoms of *tert*-butyl groups to the oxygen of MoO$_3$.

Cocondensation reactions of MoO$_3$ with nitrogen-containing organosilanes and cluster syntheses employing MoO$_2$(OR)$_2$ compounds via reduction processes are in progress.

Contribution from the Department of Chemistry,
National Taiwan University, Taipei, Taiwan, Republic of China

Pillaring of Layered Titanates by Polyoxo Cations of Aluminum

Soofin Cheng* and Tzun-Chin Wang

Layered tetratitanate complexes pillared with [Al$_{13}$O$_4$(OH)$_{24}$(H$_2$O)$_{12}$]$^{7+}$ Keggin ions have been prepared through a stepwise exchange process. The exchange of the large polyoxo cations of aluminum was facilitated by the opened layers of alkylamine-intercalated complexes. The stability of the interlayer alkylammonium ions played an important role in holding the interlayer spacing during the exchange process. Alkylamines were used instead of inorganic bases to hydrolyze aluminum chloride solutions. This effectively excluded any other cations from competing for the ion-exchange sites on the tetratitanate complexes. The best sample was obtained by exchanging a hexylammonium tetratitanate complex in a hexylamine-hydrolyzed AlCl$_3$ solution at 50 °C for 8 h. The physical properties of the resultant pillared complexes were characterized with respect to their thermal stability and porosity.

Introduction

The intercalation of layered metal oxides with polar organic molecules is long established and well documented. Barrer and MacLeod[1] demonstrated in 1955 that porosity can be introduced

in smectite clays by ion-exchanging tetraalkylammonium ions between the silicate layers. The sorptive properties of these intercalated materials were reviewed by Barrer[2] in 1978. Organic molecules have also been reported to be weakly bound in the

(1) Barrer, R. M.; MacLeod, D. M. *Trans. Faraday Soc.* **1955**, *51*, 1290.

(2) Barrer, R. M. In *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*; Academic Press: London, 1978; Chapter 8, p 407.