

The Preparation, Chemistry, and Structure of the Lithium Salt of the Octamethyldimolybdate(II) Ion

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Abstract: The preparation of compounds of general formula $\text{Li}_4[\text{Mo}_2(\text{CH}_3)_8] \cdot 4(\text{ether})$ is accomplished by reactions of LiCH_3 with $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. These compounds are thermally stable at 25° but are extremely pyrophoric. They react rapidly with acetic acid at -78° to regenerate $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. A variety of other reactions occur readily but the products have generally been intractable owing to instability, insolubility, or both. A method of forming single crystals of $\text{Li}_4[\text{Mo}_2(\text{CH}_3)_8] \cdot 4\text{C}_2\text{H}_5\text{O}$ in soft glass capillaries was developed, and one such crystal was used to collect data for an X-ray crystallographic determination of the structure. The compound crystallizes in the monoclinic system: space group $P2_1/n$; $a = 11.473$ (3), $b = 12.766$ (3), $c = 12.373$ (3) Å; $\beta = 116.32$ (1)°. With $Z = 2$, each $\text{Mo}_2(\text{CH}_3)_8^{4-}$ ion is situated at a crystallographic center of inversion. The virtual symmetry of $[\text{Mo}_2(\text{CH}_3)_8]^{4-}$ is D_{4h} ; the eclipsed structure can be attributed to the δ component of the quadruple bond. Structure parameters of greatest interest are $\text{Mo-Mo} = 2.148$ (2) Å, $\text{Mo-C}(\text{mean}) = 2.29 \pm 0.01$ Å, and $\angle \text{Mo-Mo-C}(\text{mean}) = 105.8 \pm 0.8^\circ$.

Reports appeared several years ago of two compounds having the shortest metal-to-metal bonds ever found. Both of these are chromium(II) to chromium(II) quadruple bonds, and they occur in tetraallyldichromium(II) (1.97 Å)² and tetralithium octamethyldichromium(II) tetrahydrofuranate (1.98 Å).³ Since molybdenum(II) appears to have an even greater tendency than chromium(II) to form strong, short quadruple bonds⁴⁻¹² but had not been known to form analogs to these compounds, work directed to the preparation and characterization of such analogs was considered to be important and was undertaken. Several years ago, tetraallyldimolybdenum(II) was prepared¹³ and the molecular structure determined by X-ray crystallography.¹⁴

Attempts were also made several years ago to prepare a compound containing the octamethyldimolybdate(II) ion, employing several salts of the octachlorodimolybdate(II) ion⁷ as starting materials. Reactions occurred promptly with LiCH_3 , but no well-defined product was isolated.

More recently, as a part of an investigation of the preparation and stability of transition metal alkyls,¹⁵⁻¹⁷

the possibility of forming the $\text{Mo}_2(\text{CH}_3)_8^{4-}$ ion was again considered. In this instance $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ was selected as the starting material, and it proved possible to isolate etherates of $\text{Li}_4[\text{Mo}_2(\text{CH}_3)_8]$. This paper reports on the preparation, the chemistry, and the structure of such compounds.

Because of the extreme reactivity of the $\text{Li}_4[\text{Mo}_2(\text{CH}_3)_8]$ etherates it was advantageous to employ a technique in which single crystals were grown in a sealed capillary in order to obtain specimens suitable for crystallography. This technique is also described.

Experimental Section

Preparations. All solvents were dried and deoxygenated prior to use. All operations were carried out under nitrogen, with rigorous exclusion of air.

$\text{Li}_4\text{Mo}_2(\text{CH}_3)_8(\text{ether})_4$. A suspension of molybdenum(II) acetate (1 g, 2.3 mmol) in diethyl ether (30 ml) was cooled to 0° and methyl lithium (18.4 mmol) in diethyl ether (18 ml) was syringed in. An immediate red color appeared. The mixture was stirred at 0° for 6-12 hours, when most of the acetate had been consumed. After warming to room temperature the solution was filtered and the dark residue was washed with successive 10-ml portions of ether until the washings were almost colorless. The combined filtrate and washings were reduced to small volume under vacuum, and the product was crystallized on cooling to -78° . The mother liquor was drawn off, leaving bright red crystals which were stored under nitrogen at -20° : yield 0.6 g (81%); nmr (benzene) τ 6.3 (quartet, CH_2 of ether), 8.8 (triplet, CH_3 of ether), 10.3 (singlet, Mo-CH_3). Analysis for methyl groups was accomplished by decomposition with 1-butanol⁴ and measuring the CH_4 evolved, then determining molybdenum in the residue: found $\text{CH}_4:\text{Mo} = 4.2$; required, 4.0. A separate molybdenum determination gave Mo, 30.5%; $\text{C}_2\text{H}_6\text{Li}_4\text{Mo}_2\text{O}_4$ requires 30.2%.

Recrystallization from diethyl ether containing 10% THF or dioxane gave the corresponding adduct.

$\text{Mo}_2(\text{C}_2\text{H}_5)_4$. Allyllithium was prepared by the reaction of allyltriphenyltin with phenyllithium in diethyl ether;¹⁸ precipitated tetraphenyltin was filtered off before use.

A suspension of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ (1 g, 2.3 mmol) in diethyl ether (10 ml) was cooled to -78° and allyllithium in ether (8.4 ml of 1.1 M solution, 9.2 mmol) was then added by syringe. No reaction

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occurred immediately. The suspension was stirred and allowed to warm slowly toward room temperature. A green color appeared at -20° ; all the yellow $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ disappeared after stirring 30 min at 20° . (Direct addition of the reactants at 20° caused considerable decomposition in the course of reaction.) The white precipitate of lithium acetate was filtered from the dark green ethereal solution, the solution was reduced in volume under vacuum, and $\text{Mo}_2(\text{C}_2\text{H}_5)_4$ was crystallized on cooling to -78° , yield 0.7 g (83%).

Allyllithium could be replaced by allylmagnesium bromide (9.2 mmol) in diethyl ether, in which case magnesium salts were precipitated by addition of dioxane (9.2 mmol) to the reaction mixture prior to filtering.

Reactions of $\text{Li}_4\text{Mo}_2(\text{CH}_3)_8$ Etherates. These were carried out in diethyl ether by freezing the solution to liquid nitrogen temperature, introducing the reagent under an atmosphere of nitrogen, and then evacuating the system, to ensure oxygen free conditions. After reintroduction of the nitrogen atmosphere, the mixture was warmed to -78° in an acetone-Dry Ice bath and reaction occurred as the bath was allowed to come slowly to room temperature.

Acetic acid reacted rapidly at -78° giving a pale yellow precipitate. The crude product showed strong bands in the infrared spectrum at 1500, 1430, and 670 cm^{-1} . Recrystallization from acetic acid gave yellow crystals with an infrared spectrum identical with an authentic sample of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. *Anal.* Calcd for $\text{C}_8\text{H}_{12}\text{Mo}_2\text{O}_8$: C, 22.5; H, 2.8. Found: C, 22.6; H, 2.9.

Preparation of Crystals in a Capillary. A small quantity (0.3 g) of molybdenum(II) acetate was placed in a Schlenk tube under argon and methylolithium in ether (5.0 ml of 6.0 M) was added slowly by syringe with shaking at 23° . The resulting red solution was taken to dryness *in vacuo* and 3.0 ml of dry tetrahydrofuran was added. During the addition of tetrahydrofuran the solution warmed to about 40° . The thick red solution was shaken for 2 min and then syringed into several 0.7-mm thin-walled glass capillaries which were then sealed. Crystals were grown by heating the capillaries in a boiling water bath for a few minutes and allowing them to cool to room temperature over a period of several hours. After centrifuging the capillaries, crystals suitable for an X-ray diffraction study were observed attached to the capillary walls. A crystal measuring approximately $0.5 \times 0.5 \times 0.2\text{ mm}$ was chosen for data collection.

Collection of the Data. Examination of the crystal on the diffractometer indicated that the crystal belonged to the monoclinic system. Systematic absences in the subsequent data set ($0k0$ for $k \neq 2n$, $h0l$ for $h + l = 2n$) indicated the space group to be $P2_1/n$, a nonstandard setting of $P2_1/c$. The half-height width (ω scans) of several strong reflections was measured as $<0.15^\circ$. Accurate cell constants were obtained by carefully centering 15 reflections in a range $25^\circ < 2\theta < 30^\circ$; the cell constants and calculated volume are $a = 11.473(3)$, $b = 12.766(3)$, $c = 12.373(3)\text{ \AA}$, $\beta = 116.32(1)^\circ$, and $V = 1624.3(6)\text{ \AA}^3$. Delaunay reduction of this cell indicated it to be the cell of highest symmetry. For $Z = 2$, the calculated density is 1.28 g/cm^3 ; the extreme reactivity of this compound precluded a direct determination of the density. For $Z = 2$ a center of inversion is imposed on the molecule.

Data were collected on a Syntex P1 autodiffractometer¹⁹ operated at $22 \pm 1^\circ$ using Mo $K\alpha$ radiation. The θ - 2θ scan technique was employed, using a variable scan rate from 4.0 to $24.0^\circ/\text{min}$, with a scan range from 0.6° below $K\alpha_1$ to $+0.8^\circ$ above $K\alpha_2$; the minimum scan rate of $4.0^\circ/\text{min}$ instead of our more customary $2.0^\circ/\text{min}$ was employed to reduce the time needed to collect a data set in case the crystal was unstable to X-irradiation. However, no such problems were encountered; the intensities of three standard reflections measured each 100 reflections did not change with time. Data were collected in the range $0^\circ < 2\theta < 40^\circ$; a partial shell of 40.0 - 45.0° was also taken, but only a few reflections were obtained from this shell, and its collection was terminated before completion. A total of 2108 independent reflections were collected of which 1160 had intensity $>3\sigma$. Lorentz and polarization corrections were applied to the data; the p factor¹⁹ was set at 0.05. The linear absorption coefficient for Mo $K\alpha$ radiation is 11.4 cm^{-1} ; the difficulty of defining some of the faces, especially the cylindrical face against the capillary wall, precluded an absorption correction. No extinction corrections were made.

Solution of the Structure.²⁰ The position of the Mo atom was

determined from the three-dimensional Patterson function; two cycles of refinement gave $R_1 = 0.258$ and $R_2 = 0.309$.²¹ The carbon and oxygen atoms were located in a difference Fourier and refined ($R_1 = 0.112$, $R_2 = 0.132$). The lithium ions were then found in a difference Fourier ($R_1 = 0.103$). This map did not indicate the presence of any additional atoms, but the large numbers of ghost peaks around the THF rings indicated that there was either severe anisotropic motion or a partial disorder consisting of randomized puckering of the rings, which at this stage appeared to be almost planar.

Scattering factors for neutral Mo, O, C, and Li were obtained from Cromer,²² while values for H were taken from Stewart, Davidson, and Simpson.²³ Anomalous dispersion effects for Mo were included in F_o ;²⁴ the values of $\Delta f'$ and $\Delta f''$ were those of Cromer and Liberman.²⁵

Two cycles of anisotropic full-matrix refinement were carried out; R_1 fell to 0.050 and R_2 to 0.062. An analysis of the structure factors indicated that $p = 0.07$ was a better value than 0.05 as originally employed; a third cycle was run using the new value, with no effect on the R factor. A difference Fourier revealed 8 of the 12 methyl hydrogen atoms; the others were placed in calculated positions. Refinement of all positional and thermal parameters except hydrogen temperature factors (B of 7.0 \AA^2) was carried out. At convergence, no parameter shifted by more than half a standard deviation. The final values of R_1 and R_2 were 0.043 and 0.053, respectively, and the error in an observation of unit weight was 1.10. Because of the large thermal motion/disorder in the THF rings, no effort was made to locate their hydrogen atoms. The calculated and observed values of the structure amplitudes are listed in Table I. See paragraph at end of paper regarding supplementary material.

Results

Structural. The atomic positional parameters are listed in Table II. The anisotropic thermal parameters and rms components of thermal ellipsoids for non-hydrogen atoms are listed in Tables III and IV, respectively. Tables V and VI list bond distances, bond angles, and average values (assuming D_{3h} symmetry). The structure is shown in Figure 1, which defines the atom numbering scheme.

Chemical. Reaction of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ with eight equivalents of methylolithium in diethyl ether under nitrogen produces an immediate red coloration. Stirring the mixture for several hours at 0° and crystallization of the product from ether give a bright red solid of stoichiometry $\text{Li}_2\text{Mo}(\text{CH}_3)_4(\text{C}_4\text{H}_{10}\text{O})_2$ (**1**). Recrystallization from ether-tetrahydrofuran and ether-dioxane mixtures gives the corresponding tetrahydrofuran and dioxane adducts.

The complexes are thermally stable at room temperature but extremely pyrophoric in air. They are readily soluble in ethers, slightly soluble in benzene, and in-

by Lawton; DATARED, a data reduction program by Frenz; FOURIER, a Fourier summation program (based on Zalkin's FORDAP) by Dellaca and Robinson and modified by Hodgson; NUCLS, a full-matrix least-squares program by Ibers and Doedens, similar to Busing and Levy's ORFLS; SADIAM, a distance and angles program by Baur, rewritten by Frenz and Brice; PERFECT, a program for analysis of structure factors by Frenz; HYDROGEN, a program for calculating atomic positions for known geometries by Stanislawski and Frenz, based in part on FINDH by Ibers and Raymond; ORFFE, a function and error program of Busing, Martin, and Levy as modified by Brown, Johnson, and Thiessen; ORTEP, a plotting program by Johnson; and LIST, a program for listing the data by Snyder.

(21) We define $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2}$. The function minimized in least-squares refinement is $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2 / \sigma^2(F_o^2)$.

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(20) The following computer programs written for the IBM 360 were used: TRACER, a lattice transformation and cell reduction program

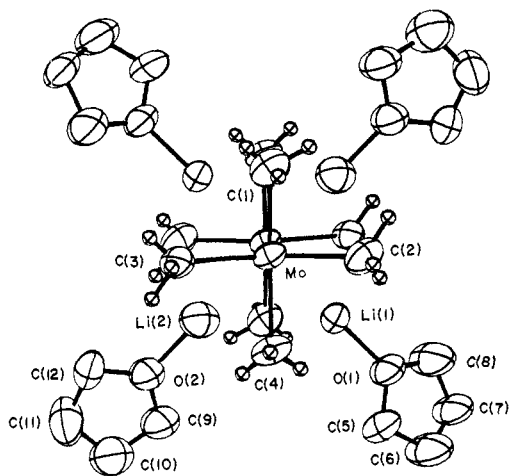


Figure 1. The structure of the $\text{MoO}_2(\text{CH}_3)_6^{4-}$ anion and its Li^+ and THF neighbors. The atom numbering scheme is defined. Hydrogen atoms have been reduced for clarity.

Table II. Positional Parameters for All Atoms^a

	x	y	z
Mo	0.0428 (1)	0.0758 (1)	0.0050 (1)
O(1)	0.2869 (8)	0.4700 (6)	0.1039 (6)
O(2)	0.1604 (7)	0.3536 (7)	-0.4856 (7)
C(1)	0.2579 (12)	0.0602 (12)	0.1393 (11)
C(2)	0.1171 (15)	0.0755 (14)	-0.1382 (11)
C(3)	0.0154 (12)	0.1609 (10)	0.1532 (10)
C(4)	-0.1219 (12)	0.1837 (10)	-0.1229 (11)
C(5)	0.1898 (16)	0.3908 (13)	0.0420 (11)
C(6)	0.1398 (17)	0.4158 (14)	-0.0887 (11)
C(7)	0.1867 (22)	0.5176 (14)	-0.0979 (11)
C(8)	0.2932 (23)	0.5441 (14)	0.0223 (14)
C(9)	0.0327 (11)	0.3463 (11)	0.4110 (11)
C(10)	-0.0438 (12)	0.2746 (13)	0.4507 (13)
C(11)	0.0290 (14)	0.2691 (16)	-0.4145 (12)
C(12)	0.1510 (15)	0.3215 (14)	-0.3784 (11)
Li(1)	0.3793 (19)	0.4809 (16)	0.2778 (15)
Li(2)	0.3094 (18)	0.4140 (17)	-0.4923 (19)
H(11)	0.283 (11)	0.118 (10)	0.126 (10)
H(12)	0.314 (10)	0.021 (8)	0.105 (9)
H(13)	0.273 (12)	0.035 (9)	0.200 (10)
H(21)	0.144 (12)	0.128 (9)	-0.147 (11)
H(22)	0.191 (10)	0.012 (9)	-0.130 (9)
H(23)	0.072 (11)	0.073 (11)	-0.198 (10)
H(31)	-0.084 (10)	0.185 (8)	0.139 (9)
H(32)	0.056 (10)	0.230 (9)	0.168 (9)
H(33)	0.045 (10)	0.145 (9)	0.229 (9)
H(41)	-0.214 (10)	0.182 (8)	-0.121 (9)
H(42)	-0.072 (10)	0.244 (9)	-0.103 (9)
H(43)	-0.155 (10)	0.176 (8)	-0.201 (10)

^a The numbers in parentheses in this and other tables are the estimated standard deviations in the least significant digits.

soluble in petroleum ether. Decomposition occurs in the presence of other solvents (acetone, dichloromethane and other chlorinated solvents, alcohols, water, carbon disulfide). The proton nuclear magnetic resonance (nmr) spectrum (benzene solution) shows a methyl singlet at τ 10.3 as well as peaks due to the solvating ether. Attempts to obtain Raman spectra in the solid state have proved unsuccessful.

Compound 1 reacts rapidly with acetic acid (containing a little acetic anhydride) at -78° giving methane and regenerating $\text{MoO}_2(\text{O}_2\text{CCH}_3)_4$ thus indicating retention of the dimeric molybdenum-molybdenum bonded structure in 1.

During the course of this work, the product from re-

Table III. Anisotropic Thermal Parameters for Nonhydrogen Atoms^a

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	103 (1)	61 (1)	70 (1)	-5 (1)	15 (1)	0.1 (8)
O(1)	211 (12)	125 (8)	76 (7)	-28 (8)	18 (8)	5 (6)
O(2)	143 (10)	146 (9)	109 (8)	-29 (8)	40 (8)	6 (7)
C(1)	126 (14)	105 (13)	120 (13)	-29 (11)	38 (12)	-1 (11)
C(2)	174 (19)	107 (12)	113 (11)	-10 (14)	56 (12)	30 (14)
C(3)	148 (15)	77 (9)	82 (10)	2 (10)	18 (11)	-15 (8)
C(4)	148 (17)	78 (9)	97 (11)	5 (10)	23 (12)	20 (9)
C(5)	311 (26)	187 (19)	93 (13)	-104 (18)	30 (15)	-29 (12)
C(6)	313 (28)	173 (20)	110 (14)	-87 (20)	-12 (15)	11 (14)
C(7)	526 (44)	157 (19)	71 (12)	-57 (23)	8 (19)	5 (11)
C(8)	556 (49)	188 (21)	114 (16)	-155 (25)	33 (22)	17 (14)
C(9)	132 (15)	141 (14)	136 (14)	-17 (13)	22 (12)	11 (11)
C(10)	137 (16)	178 (16)	192 (18)	-31 (15)	54 (15)	25 (14)
C(11)	168 (19)	295 (26)	147 (17)	-30 (20)	73 (16)	48 (16)
C(12)	207 (20)	245 (21)	99 (13)	-53 (18)	67 (14)	13 (13)
Li(1)	147 (25)	115 (17)	84 (16)	0 (16)	50 (19)	13 (13)
Li(2)	132 (21)	103 (17)	175 (23)	-14 (18)	83 (19)	-6 (18)

^a The form of the anisotropic thermal ellipsoids is $\exp[-10^4 \cdot (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table IV. Rms Components of Thermal Displacement (\AA)

	x	y	z
Mo	0.198 (1)	0.224 (1)	0.274 (1)
O(1)	0.214 (10)	0.304 (10)	0.391 (10)
O(2)	0.254 (10)	0.277 (10)	0.365 (10)
C(1)	0.235 (16)	0.280 (16)	0.325 (16)
C(2)	0.229 (19)	0.296 (18)	0.340 (17)
C(3)	0.209 (16)	0.256 (16)	0.324 (16)
C(4)	0.215 (16)	0.268 (15)	0.325 (16)
C(5)	0.222 (18)	0.341 (18)	0.500 (20)
C(6)	0.240 (17)	0.331 (19)	0.526 (21)
C(7)	0.208 (18)	0.348 (21)	0.605 (23)
C(8)	0.264 (19)	0.318 (19)	0.650 (26)
C(9)	0.247 (15)	0.315 (17)	0.368 (17)
C(10)	0.260 (17)	0.334 (16)	0.417 (18)
C(11)	0.268 (18)	0.303 (17)	0.510 (22)
C(12)	0.235 (17)	0.315 (18)	0.469 (20)
Li(1)	0.226 (22)	0.283 (24)	0.308 (23)
Li(2)	0.243 (24)	0.295 (25)	0.331 (22)

Table V. Bond Distances (\AA)

Mo-Mo	2.148 (2)		
Mo-C(1)	2.29 (1)	C(1)-H(11)	0.8 (1)
Mo-C(2)	2.28 (1)	C(1)-H(12)	1.0 (1)
Mo-C(3)	2.27 (1)	C(1)-H(13)	0.8 (1)
Mo-C(4)	2.31 (1)	C(2)-H(21)	0.8 (1)
Av	2.29 (1)	C(2)-H(22)	1.1 (1)
O(1)-Li(1)	1.94 (2)	C(2)-H(23)	0.7 (1)
O(2)-Li(2)	1.91 (2)	C(3)-H(31)	1.1 (1)
Av	1.92 (2)	C(3)-H(32)	1.0 (1)
		C(3)-H(33)	0.9 (1)
O(1)-C(5)	1.45 (1)	C(4)-H(41)	1.1 (1)
O(1)-C(8)	1.41 (2)	C(4)-H(42)	0.9 (1)
O(2)-C(9)	1.46 (1)	C(4)-H(43)	0.9 (1)
O(2)-C(12)	1.44 (1)	Av	0.9 (1)
Av	1.44 (2)		
C(5)-C(6)	1.49 (2)		
C(6)-C(7)	1.43 (2)		
C(7)-C(8)	1.49 (2)		
C(9)-C(10)	1.49 (2)		
C(10)-C(11)	1.50 (2)		
C(11)-C(12)	1.43 (2)		
Av	1.47 (3)		

action of $\text{MoCl}_3(\text{THF})_3$ with methyl lithium was reported to have the composition $\text{Li}_2\text{Mo}(\text{CH}_3)_4(\text{THF})_2$ and properties similar to those described above for 1.²⁶ We have

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Table VI. Bond Angles (°)

Mo-Mo-C(1)	106.3 (4)	H(12)-C(1)-H(13)	107 (12)
Mo-Mo-C(2)	105.8 (4)	H(21)-C(2)-H(22)	108 (11)
Mo-Mo-C(3)	104.8 (3)	H(21)-C(2)-H(23)	93 (13)
Mo-Mo-C(4)	106.5 (3)	H(22)-C(2)-H(23)	103 (13)
Av Mo-Mo-C	105.8 (8)	H(31)-C(3)-H(32)	99 (8)
C(1)-Mo-C(2)	84.8 (5)	H(31)-C(3)-H(33)	96 (9)
C(1)-Mo-C(3)	86.9 (5)	H(32)-C(3)-H(33)	95 (9)
C(2)-Mo-C(4)	86.7 (5)	H(41)-C(4)-H(42)	121 (9)
C(3)-Mo-C(4)	84.5 (5)	H(42)-C(4)-H(43)	95 (9)
Av C-Mo-C	85.7 (13)	H(42)-C(4)-H(43)	107 (10)
(cis)		Av H-C-H	104 (11)
C(1)-Mo-C(4)	147.2 (5)	Li(1)-O(1)-C(5)	124 (1)
C(2)-Mo-C(3)	149.5 (6)	Li(1)-O(1)-C(8)	125 (1)
Av C-Mo-C	148.3 (16)	Li(2)-O(2)-C(9)	126 (1)
(trans)		Li(2)-O(2)-C(12)	124 (1)
Mo-C(1)-H(11)	98 (8)	Av Li-O-C	125 (1)
Mo-C(1)-H(12)	114 (6)	C(5)-O(1)-C(8)	111 (1)
Mo-C(1)-H(13)	117 (9)	C(9)-O(2)-C(12)	110 (1)
Mo-C(2)-H(21)	115 (10)	Av C-O-C	110 (1)
Mo-C(2)-H(22)	117 (5)	O(1)-C(5)-C(6)	105 (1)
Mo-C(2)-H(23)	118 (10)	O(1)-C(8)-C(7)	106 (1)
Mo-C(3)-H(31)	120 (5)	O(2)-C(9)-C(10)	105 (1)
Mo-C(3)-H(32)	111 (6)	C(2)-C(12)-C(11)	108 (1)
Mo-C(3)-H(33)	129 (8)	Av O-C-C	106 (1)
Mo-C(4)-H(41)	119 (5)	C(5)-C(6)-C(7)	108 (1)
Mo-C(4)-H(42)	95 (7)	C(6)-C(7)-C(8)	107 (1)
Mo-C(4)-H(43)	121 (7)	C(9)-C(10)-C(11)	106 (1)
Av Mo-C-H	115 (9)	C(10)-C(11)-C(12)	108 (1)
H(11)-C(1)-H(12)	90 (10)	Av C-C-C	107 (1)
H(11)-C(1)-H(13)	128 (13)		

repeated this reaction and shown that the product is in fact $\text{Li}_4\text{Mo}_2(\text{CH}_3)_8(\text{THF})_4$ by a comparison of nmr data and by reaction with acetic acid at -78° .

Reactions of compound **1** in ethereal solution with ammonia, pyridine, acetonitrile, acetamide, and hexamethylphosphoramide give red precipitates, insoluble in ethers, aromatic solvents, and petroleum ether, and decomposing in other solvents (including the added solvent: pyridine, acetonitrile, etc.). All are pyrophoric in air. Their appearance and air sensitivity suggest replacement of the ether in **1** by the N donors, with retention of the general structure of **1**. Loss of ammonia from the ammonia adduct and recovery of the diethyl ether adduct on evaporation of the solvent ether under reduced pressure at 0° support this conclusion. Reaction of **1** with 2,2'-bipyridyl gives a purple product with similar properties and, surprisingly, so does the addition of a stoichiometric amount of methanol at -120° ; removal of solvent at 0° under vacuum leaves a thermally stable purple powder. Reaction of **1** with excess methanol at higher temperature (0°) leads to rapid evolution of methane. The instability and insolubility of these derivatives have not allowed characterization by physical methods.

A number of other substances react with **1** in ether at temperatures ranging from -78 to 20° . These include carbon monoxide, sulfur dioxide, hydrogen, nitric oxide, nitrosonium hexafluorophosphate, hydrogen chloride, acetyl chloride, methyl iodide, allyl chloride, acetylacetone, 1-butyne, tin tetrachloride, dicyclopentadienyltitanium dichloride, dimethylglyoxime, 1,3-diphenyltriazine, and nitromethane. The majority give dark brown or black products commonly intractable, and no isolable molybdenum complexes could be characterized. There is no reaction with ethylene, 1,5-cyclooctadiene, dimethyl sulfate, triphenylphosphine, or ethyldiphenylphosphine.

Reactions of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ with methylmagnesium chloride or iodide in ether under nitrogen give insoluble purple powders which are thermally stable but decompose explosively in air. Their nature has not been investigated but polymeric structures may account for their insolubility.

Molybdenum(II) acetate proves to be a convenient starting material for preparation of the previously characterized¹⁴ tetraallyldimolybdenum $\text{Mo}_2(\text{C}_3\text{H}_5)_4$. Reaction with four equivalents of allyllithium or allylmagnesium bromide gives high yields of the dark green allyl complex.

Discussion

The compounds $\text{Li}_4\text{Mo}_2(\text{CH}_3)_8 \cdot 4(\text{ether})$ can probably be prepared from a number of starting materials. In this work it has been shown that $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ is a very suitable one but that $\text{MoCl}_3(\text{THF})_3$ also leads to the same type of product. Most likely the reaction of $\text{Mo}_2\text{Cl}_3^{4-}$ with LiCH_3 also affords $\text{Mo}_2(\text{CH}_3)_8^{4-}$ although a convenient and successful isolation procedure was not developed.

The fact that the $\text{Mo}_2(\text{CH}_3)_8^{4-}$ ion can be isolated is in accord with the view¹⁵⁻¹⁷ that metal-alkyl bonds to alkyl groups incapable of undergoing a β -hydrogen to metal shift tend to be stable enough to form isolable compounds.

The structure of the $\text{Mo}_2(\text{CH}_3)_8^{4-}$ ion has, as expected, virtual D_{4h} symmetry. The Mo-Mo bond is very short, comparable to those (Table VII) in many other com-

Table VII. Lengths of Some Molybdenum to Molybdenum Multiple Bonds

Compound	Mo_2^{4+} containing entity	Mo-Mo dist, Å	Ref
$\text{K}_4\text{Mo}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$	$\text{Mo}_2\text{Cl}_6^{4-}$	2.139 (4)	8
$(\text{enH}_2)_2\text{Mo}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$	$\text{Mo}_2\text{Cl}_6^{4-}$	2.134 (1)	9
$(\text{NH}_4)_3\text{Mo}_2\text{Cl}_6 \cdot \text{H}_2\text{O}$	$\text{Mo}_2\text{Cl}_6^{4-}$	2.150 (5)	10
$\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$	$\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$	2.11 (1)	11
$\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$	$\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$	2.090 (4)	12
$\text{Mo}_2(\text{O}_2\text{CCF}_3)_4 \cdot 2\text{py}$		2.129 (2)	4
$\text{Mo}_2(\text{C}_3\text{H}_5)_4$	$\text{Mo}_2(\text{C}_3\text{H}_5)_4$	2.183 (2)	13
$\text{K}_4\text{Mo}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$	$\text{Mo}_2(\text{SO}_4)_4^{4-}$	2.110 (3)	5
$\text{Li}_4\text{Mo}_2(\text{CH}_3)_8 \cdot 4\text{THF}$	$\text{Mo}_2(\text{CH}_3)_8^{4-}$	2.147 (3)	This work
$\text{Mo}_2(\text{S}_2\text{COC}_2\text{H}_5)_4 \cdot 2\text{THF}$	$\text{Mo}_2(\text{S}_2\text{COC}_2\text{H}_5)_4$	2.125 (1)	6
$\text{Mo}_2(\text{CH}_2\text{SiMe}_3)_6$		2.167	17

pounds where Mo-Mo quadruple bonds exist, and the eclipsed rotational configuration again supports the existence of the δ component of the bond. Inspection of Table VII shows that the lengths of known Mo-Mo quadruple bonds lie in a relatively narrow range, *viz.*, 2.09–2.15 Å, with the sole exception of the allyl compound, $\text{Mo}_2(\text{C}_3\text{H}_5)_4$,¹⁴ for which Mo-Mo is 2.18 Å. The latter may be exceptional because of the bridging allyl groups. It may be that the demands of the Mo to bridging allyl bonding enforce a slight stretching of what would otherwise be a shorter Mo-Mo distance.

It is interesting to compare the Mo-Mo distance for the quadruple bond in $\text{Mo}_2(\text{CH}_3)_8^{4-}$ with that for the triple Mo-Mo bond in $\text{Mo}_2(\text{CH}_2\text{SiMe}_3)_6$.¹⁷ While the latter is longer, as would be expected, it is so by only 0.02 Å (with an unspecified uncertainty, since no esd was reported for the latter), which is perhaps less than

might have been expected. This small difference is not unreasonable, however. Bond lengths become relatively insensitive to bond order at high bond orders, so that, on general principle, no large change is expected. In fact, we have recently found that loss of one δ bonding electron in passing from $\text{Mo}_2(\text{SO}_4)_4^{4-}$ to $\text{Mo}_2(\text{SO}_4)_4^{3-}$ causes an increase of only 0.054 (3) Å.²⁷ When the bond order reduction is accompanied by an increase in oxidation state, we have the additional factor that the metal atoms become intrinsically smaller. This will work to offset the increased distance expected from loss of the δ bond component. In $\text{Mo}_2(\text{CH}_3)_8^{4-}$ the Mo–C bonds have a mean length of 2.29 Å, whereas in $\text{Mo}_2(\text{CH}_2\text{-SiMe}_3)_6$ the Mo–C bonds are 2.13 Å in length. Moreover, in the latter compound, with only three R groups on each metal atom and a staggered rotational configuration, nonbonded repulsions, tending to stretch the Mo–Mo bond, will be less severe. It seems clear that when the many, often countervailing, factors which influence the length of the Mo–Mo bond are considered, it is not possible to make any unequivocal, quantitative predictions. The best that can be said is that no great change is necessarily to be expected, although such change as there may be is more likely to be in the direction of a lengthening as the bond order decreases. On that basis, the observed result is a reasonable one.

It is also of interest to note that the apparent Mo covalent radius differs a little between $\text{Mo}_2\text{Cl}_8^{4-}$ and $\text{Mo}_2(\text{CH}_3)_8^{4-}$. In the former, the Mo–Cl distance¹⁰ (2.45 Å) less the single bond radius of Cl (0.99) yields 1.46 Å, while in the present case the corresponding arithmetic is $2.29 - 0.77 = 1.52$ Å. This may indicate that there is a small amount of π character in the Mo–Cl bonds.

There are several features of the crystal and molecular structures which are worthy of comment. One of these is the fact that the $\text{Mo}_2(\text{CH}_3)_8^{4-}$ ion, despite the fact that it is prepared in and isolated from ether solvent, *i.e.*, from a medium rich in donor molecules, does not bind any coaxial ligands. The small methyl groups exert little if any steric hindrance to the approach of such ligands. It is notable that in the analogous chromium compound³ coaxial ligands were also absent. A possible explanation for this is the large overall negative charge of the $\text{M}_2(\text{CH}_3)_8^{4-}$ ions. This would

(27) F. A. Cotton, B. A. Frenz, and T. R. Webb, *J. Amer. Chem. Soc.*, **95**, 4431 (1973).

perhaps reduce their electrophilicity to the point that additional electron donors cannot be bound.

A second point concerns the environment of the lithium ions, each of which is coordinated to one THF molecule. There is a set of four lithium ions surrounding each $\text{Mo}_2(\text{CH}_3)_8^{4-}$ ion; the arrangement can be described by saying that each Li^+ ion lies over the center of one vertical face of the Mo_2C_8 parallelepiped on a perpendicular bisector of the Mo–Mo bond. The lithium ions lie at distances of 2.43–2.56 Å from the methyl carbon atoms and at *ca.* 2.5 Å from the inversion center at the midpoint of the Mo–Mo bond; thus there is the possibility of C–H···Li three-center bonding and also interaction with the π and δ electrons in the Mo–Mo bond. It is interesting that in the analogous chromium compound,³ the same arrangement occurs, even though the two compounds do not crystallize in the same space group.

Finally, the tetrahydrofuran molecules refined poorly and appear to be disordered. The situation appears to be similar to one reported earlier by Brauer and Stucky²⁸ for $[\text{Na}(\text{THF})_2]_2[\text{Al}(\text{CH}_3)_2\text{C}_{10}\text{H}_8]_2$. These authors proposed that the poorly defined electron density in the neighborhood of the THF carbon atoms suggested a disordered puckering of the rings so that a different carbon atom deviated from the mean plane of the ring in each unit cell. It appears that a similar phenomenon is consistent with our results.

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Supplementary Material Available. Table I, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-3824.

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