Electrochemical Synthesis, X-ray Single Crystal, IR Spectroscopic, and Quantum Chemical Investigation of Molybdenum and Tungsten Hexamethoxides

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The anodic oxidation of molybdenum metal in MeOH at both low anodic and cathodic current density (0.025 A/cm^2) and electrolyte temperatures kept below 20 °C provides an efficient approach to Mo(OMe)$_6$ (**I**). W(OMe)$_6$ (**II**) can be obtained from the electrolytes, prepared via anodic dissolution of tungsten, by fractional crystallization. The symmetrically independent units in the structures of **I** and **II**, being isomorphous, follow the C_1 (slightly distorted D_{2d}) symmetry. Theoretical calculations performed for a free molecule of **I** indicate that this low symmetry may be the result of the packing of the molecules in the crystal structure and also an inherent property imposed by the bonding in this compound. Crystal data for **I**: Mo(OMe)$_6$ at 22 °C, $a = 7.0976(13)$, $b = 6.6103(12)$, and $c = 12.286(2)$ Å, $\beta = 90.068(3)°$, $V = 576.41(18)$ Å^3, monoclinic $P2/n$, $Z = 2$. Crystal data for **II**: W(OMe)$_6$ at 22 °C, $a = 7.1164(19)$, $b = 6.6414(18)$, and $c = 12.304(3)$ Å, $\beta = 90.047(5)°$, $V = 581.5(3)$ Å^3, monoclinic $P2/n$, $Z = 2$.

Introduction

At the beginning of 1980s, the hexamethoxide complexes, M(OMe)$_6$, of molybdenum,[1] tungsten,[1−3] and uranium[4] were already attracting considerable attention as comparably simple mononuclear molecular aggregates with octahedral symmetry—useful objects for development of theoretical approaches to modeling of vibration spectra. In the case of uranium, this research was of direct practical interest, since it was proposed to use U(OMe)$_6$ in the processes of isotope separation by means of laser-induced photochemical reduction.[5] However, the real symmetry of these molecules remained an enigma. The molecular structure determination for W(OMe)$_6$ carried out by gas electron diffraction[3] permitted determination of the average W−O bond distance in a molecular symmetry proposed to be D_3, but the data could not provide an unambiguous proof of the symmetry. The single-crystal X-ray structure studies for these compounds have, so far, been hindered by twinning problems. The general synthetic approach to M(OMe)$_6$ described in the literature was based on low-temperature co-condensation of MF$_6$ with Si(OMe)$_4$ and proved to be technically rather complicated and unable to provide large quantities of the complexes under laboratory conditions. An alternative approach developed for U(OMe)$_6$, and based on the oxidation of Li$_2$U(OMe)$_6$ with lead tetraacetate,[4] was obviously inapplicable to tungsten or molybdenum derivatives.

Here, we report a selective electrochemical approach to Mo(OMe)$_6$, X-ray single crystal determination of its structure, and the comparison of experimentally observed and theoretically calculated IR-active vibration modes. The study also includes the isolation and X-ray single-crystal study of the analogous W(OMe)$_6$.

Experimental Section

All the manipulations were carried out in a dry nitrogen atmosphere using the Schlenk technique or a drybox. Methanol was purified by distillation over Mg(OMe)$_2$ and toluene and hexane over LiAlH$_4$ under argon. IR spectra of Nujol mulls were registered with a Perkin-Elmer 1700 spectrometer. The ^{1}H NMR spectra in solution were obtained with a Varian 400 MHz spectrometer using dry deaerated toluene as solvent (employing TMS as internal and 20 vol % of solution of CDCl$_3$ as external standards).

Synthesis. (1) Mo(OMe)$_6$. The anodic oxidation of molybdenum metal in MeOH was carried out in analogy with the process described for the preparation of MoO(OMe)$_4$,[6] i.e., in a cell without subdivided cathodic and anodic space and using LiCl (0.03 M) as electrolyte. The molybdenum plates (area ca. 6 cm^2) were used as both cathode and anode. The total current through the cell was kept with the aid of a KYORITSU potentiostate at $I = 0.150$ A, with the voltage varying between 28 and 32 V. The duration of the experiments was 24−36 h. The temperature of the electrolyte in the course of the process was kept below 20 °C by water cooling in combination with stirring. The reddish orange electrolytes obtained were reduced in vacuo to half the initial volume (the molybdenum concentration reaching 0.20−0.25 M) and placed in a freezer at −30 °C. The precipitation of Mo(OMe)$_6$ in the form of poorly shaped orange polycrystals occurred with ~40% yield. Found: C 24.67, H 6.22, Mo 35.1. Calcd for C$_6$H$_{18}$O$_6$Mo: C 25.53, H 6.38, Mo 34.0. IR, cm^{-1}: 2932 s, 2916 s, 2803 s, 1458 m, 1418 m, 1377 m, 1148 s, 1060 vs, 1019 sh, 555 s, 525 sh, 448 m. NMR ^{1}H: 5.04 ppm (singlet). The single crystals were obtained by

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Table 1. Crystallographic Data for **I** and **II**

chem formula	$C_6H_{18}MoO_6$ (**I**)	$C_6H_{18}WO_6$ (**II**)
fw	282.14	370.05
space group	P2/n	P2/n
a, Å	7.0976(13)	7.1164(19)
b, Å	6.6103(12)	6.6414(18)
c, Å	12.286(2)	12.304(3)
α, °	90	90
β, °	90.068(3)	90.047(5)
γ, °	90	90
V, Å^3	576.41(18)	581.5(3)
Z	2	2
T, °C	22	22
λ, Å	0.710 73	0.710 73
d_{calc}d, g/cm^3	1.626	2.113
$R(F_o)^a$	0.0270	0.0326
$R_w(F_o2)^b$	0.0654	0.0691

^{a} $R = \Sigma|F_o - F_c|/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^2)^2]^{1/2}$.

cutting the polycrystalline aggregates under a microscope and applying polarized light.

(2) W(OMe)$_6$. Approximately 4.5 g of a mixture of W(OMe)$_6$ and WO(OMe)$_4$ obtained by anodic oxidation of W in MeOH, with subsequent evaporation to dryness and extraction with hexane,[7,8] was dissolved in 10 mL of hexane and left at −30 °C for a week. The precipitation of mainly WO(OMe)$_4$ occurred in the form of white needle-shaped crystals. The mother liquor was separated by syringe, transferred into another vessel, and reduced in volume to 4 mL. The precipitation of colorless transparent prismatic crystals took place in a week at −30 °C. The spectral characteristics of the product were identical to those described in the literature.[9]

Crystallography. Crystal data for Mo(OMe)$_6$ (**I**) are summarized in Table 1. A total of 1302 [R(int) = 0.0261] independent reflections with $I > 2\sigma(I)$ were collected at 22 °C up to $2\theta_{max} = 55.96$ with a Bruker SMART CCD 1K diffractometer. No absorption correction was applied ($\mu = 1.136$ mm^{-1}). The structure was solved by standard direct methods. The molybdenum atom was taken from the initial solution, and the coordinates of all other (non-hydrogen) atoms were determined in subsequent Fourier syntheses. The coordinates of the oxygen atoms for the symmetrically independent unit were chosen in such a way that they provide an octahedron around the molybdenum atom. The determination of the hydrogen atom positions could not be attempted as each carbon atom is bound to two different oxygen atoms (one from the symmetrically independent unit and the other from its image produced by the crystallographic elements of symmetry) and direct geometrical calculation is thus impossible. The final discrepancy factors were R1 = 0.0270, wR2 = 0.0654.

Crystal data for W(OMe)$_6$ (**II**) are summarized in Table 1. A total of 1116 [R(int) = 0.0493] independent reflections with $I > 2\sigma(I)$ were collected at 22 °C up to $2\theta_{max} = 50.00°$ with a Bruker SMART CCD 1K diffractometer. An empirical absorption correction was applied using the Bruker SADABS program ($\mu = 9.931$ mm^{-1}). Structure solution and refinement were carried out using the same procedure as for **I**. A specific general feature of the crystals of **II** was the formation of merohedral twins with a 3-fold axis as an external symmetry element that could even be traced in the habitus of larger crystals obtained on very slow cooling of concentrated solutions (shaped as hexagonal prisms). Twin refinement of the experiment on the crystal, the structure of which is reported here, indicated that it contained additional domains of minor volume but improved noticeably the observed values of standard deviations on bond lengths (from 0.020 to 0.010−0.12 Å). The final discrepancy factors were R1 = 0.0326, wR2 = 0.0691.

All calculations were carried out on an IBM PC using the SHELXTL-NT program package.[10] The supplementary data are available from Cambridge Crystallographic Data Center, reference numbers 157605 (**I**) and 157606 (**II**).

Calculations. All calculations were made at Hartree−Fock (HF) and hybrid density functional levels (B3LYP) employing the program package Gaussian98.[11] A *quasi*-relativistic effective-core potential (ECP) was used for Mo, replacing 28 core electrons, amended by a contracted (8s7p6d)/[6s5p3d] valence space.[12] The basis sets for H, C, and O were of 6-31G quality supplemented by one diffuse s and p function; that of H was only supplemented by a diffuse s function. The calculations were performed for the neutral, diamagnetic Mo(OCH$_3$)$_6$ of various symmetries. The higher symmetries of S_6 and C_i turned out to be improper minima on the potential energy surface (PES), where the negative eigenvalues of the Hessians indicated a preferred deformation to C_3 and C_1 symmetries. These were subsequently verified to be true minima.

Results and Discussion

In our earlier work on anodic oxidation of rhenium metal in alcohols,[7] we observed that the decreased current density decreases the possibility of cathodic reduction, which has been proposed to be at least partially responsible—in combination with subsequent reoxidation by oxygen dissolved in the solvents—for the formation of oxospecies upon electrolysis.[8] The other factor leading to the formation of oxospecies, mainly MoO(OMe)$_4$, in the previously reported experiments on anodic oxidation of molybdenum metal was apparently the elevated temperature,[6] since all molybdenum alkoxides have a pronounced trend to ether elimination on heating that yields the deeper oxo-substituted derivatives.[13] The decomposition of solid samples of Mo(OMe)$_6$ was reported[1] to occur at temperatures as low as 60 °C. The elimination of these two factors has in the present work permitted us to access Mo(OMe)$_6$ as the only product isolable on direct crystallization from the electrolyte at low temperature. It is worth noting that this separation technique permits us to avoid the precipitation of MoO(OMe)$_4$, where solubility is stongly increased by the presence of both LiCl and especially LiOR.[8]

The crystal structure of compound **I** has been solved in the centrosymmetric monoclinic space group *P*2/*n*, which provided the best model in relation to such factors as *R*, R_w, goodness-of-fit, and observed standard deviations for the Mo−O distances, see Table 2. The crystal structure of **I** is thus centrosymmetric, but the symmetrically independent unit (Figure 1), while having a composition corresponding to that of a Mo(OMe)$_6$ molecule, is in contrast not centrosymmetric. The arrangement of the oxygen atoms around the central metal atom is nearly undistorted octahedral: the O−Mo−O angles for the neighboring (*cis*-) alkoxide groups vary between 87.6(2) and 91.3(2)° and those in *trans*-orientation to each other by 177.8(2)−178.4(2)°. All Mo−O bond lengths fall into the range usually observed

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Table 2. Comparison of Different Refinement Models for the Structure of I

symmetry and space group	unit cell parameters	R	R_w	GOF	standard deviations for Mo−O bond lengths, Å
hexagonal, $P3$	$a = b = 7.0941(9)$ $c = 6.6103(12)$ Å $\alpha = \beta = 90°$ $\gamma = 120°$	0.0224	0.0493	0.850	0.0092−0.0226
orthorhombic, $Pmmn$	$a = 7.0976(13)$ $b = 12.2857(22)$ $c = 6.6103(12)$ Å $\alpha = \beta = \gamma = 90°$	0.0726	0.1819	1.076	0.0092−0.0154
monoclinic, Pn	$a = 7.0976(13)$ $b = 6.6103(12)$ $c = 12.286(2)$ $\alpha = \gamma = 90°$ $\beta = 90.068(3)$	0.0282	0.0654	0.812	0.0155−0.0226
monoclinic, $P2/n$	$a = 7.0976(13)$ $b = 6.6103(12)$ $c = 12.286(2)$ $\alpha = \gamma = 90°$ $\beta = 90.068(3)$	0.0270	0.0662	0.854	0.0040−0.0045

Table 3. Selected Bond Distances and Angles in the Structure of **I**[a]

Mo(1)−O(1)	1.862(4)	Mo(1)−O(2)	1.897(4)
Mo(1)−O(6)	1.894(4)	Mo(1)−O(5)	1.884(4)
Mo(1)−O(3)	1.880(5)	Mo(1)−O(4)	1.909(4)
O(1)−Mo(1)−O(3)	90.7(2)	O(5)−Mo(1)−O(6)	90.8(2)
O(1)−Mo(1)−O(5)	91.0(2)	O(1)−Mo(1)−O(2)	91.2(2)
O(3)−Mo(1)−O(5)	89.2(2)	O(5)−Mo(1)−O(2)	177.8(2)
O(1)−Mo(1)−O(6)	91.3(2)	O(6)−Mo(1)−O(2)	89.00(19)
O(3)−Mo(1)−O(6)	178.0(2)	O(1)−Mo(1)−O(4)	178.38(18)
O(3)−Mo(1)−O(4)	90.4(2)	O(5)−Mo(1)−O(4)	90.2(2)
O(6)−Mo(1)−O(4)	87.6(2)	O(3)#1−Mo(1)−O(6)	71.4(2)
O(1)#1−Mo(1)−O(1)	109.2(3)	O(5)#1−Mo(1)−O(6)	131.6(2)
O(1)#1−Mo(1)−O(3)	47.5(2)	O(1)#1−Mo(1)−O(6)#1	91.3(2)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + {}^{1}/_{2}, y, -z + {}^{3}/_{2}$.

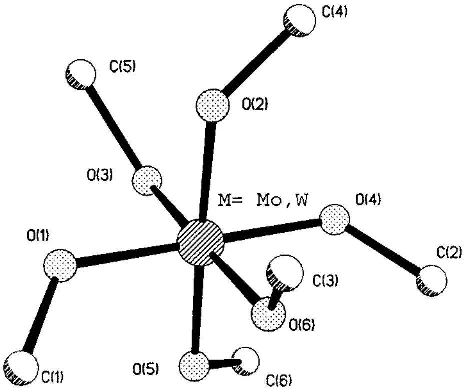

Figure 1. The symmetrically independent unit in the structures of **I** and **II**.

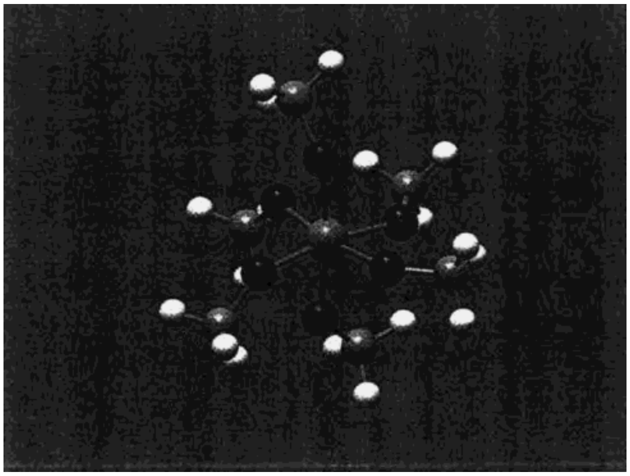

Figure 2. The optimized structure of $Mo(OCH_3)_6$ in C_3 symmetry at the B3LYP level.

for terminal Mo-O(R) groups (see Table 3). It is interesting to note that for Mo(VI) the $[MoO_6]$-octahedron in this case follows the usual strong trend of trans-influence: the sums of bond lengths in the trans-position practically coincide within experimental error (O(1)−Mo(1)−O(4) 3.771(4), O(2)−Mo(1)−O(5) 3.777(4), and O(3)−Mo(1)−O(6) 3.774(4) Å). This is a strong argument in favor of a symmetrically independent metal−oxygen core as that characterizing the real molecule. We thus did not consider the possibility of disorder for molecular structure, having in fact the same geometry in all possible solutions (see Table 2)—12 oxygen atom positions with almost the same population)—but refined the best solution by proposing that each of the two symmetrically bound configurations has 50% probability and 50% population. The symmetrically independent positions of carbon atoms correspond to the gauche-conformation of alkoxide groups. The existence of this, from first glance, unfavorable conformation was surprisingly enough supported by the theoretical calculations for **I**.

In all calculations, the lowest possible symmetry of $Mo(OCH_3)_6$ was the most stable, the formally C_1 symmetry being favored by 1.3 kJ mol^{-1} (HF)/7.5 kJ mol^{-1} (B3LYP). Thus, on going from C_3 symmetry to C_1 only small changes in atom−atom distances can be observed and the major changes are observed in the orientation of the methyl groups of the methoxides. The optimized structure of $Mo(OCH_3)_6$ in C_3 symmetry at the B3LYP level is shown in Figure 2. It should also be noted here that there most likely are several very shallow minima of C_1 symmetry on the PES; however, the results given here are most likely highly representative. As a consequence, the vibrational spectra of $Mo(OCH_3)_6$ of different symmetry are also very similar. In these low symmetries, of course, all modes are essentially both Raman and IR active. The most intensive IR bands are shown in Figure 3. The bands can essentially be divided into three groups: Mo−O stretch vibrations around 400−600 cm^{-1}, C−O stretch vibrations (and some methyl wagging ones) at 1000−1100 cm^{-1}, and, of course, C−H stretch vibrations above 3000 cm^{-1}.

Kaupp et al. attributed the deviations from octahedral symmetry in the heavier transition metal hexamethyls, $M(CH_3)_6$, to relativistic effects.[14] Of course, inherent electronic effects of

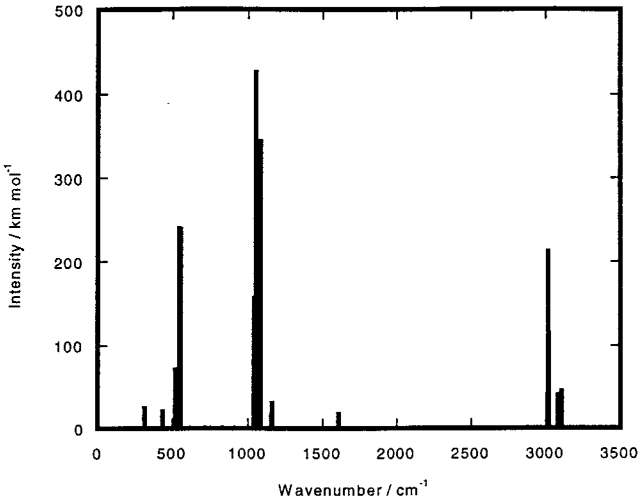

Figure 3. The simulated IR spectrum of $Mo(OCH_3)_6$ in C_3 symmetry at the B3LYP level. Only bands with intensities over 15 km·mol^{-1} are shown.

Table 4. Selected Bond Distances and Angles in the Structure of **II**[a]

W(1)−O(2)	1.846(12)	W(1)−O(3)	1.877(12)
W(1)−O(6)	1.864(11)	W(1)−O(5)	1.884(12)
W(1)−O(1)	1.852(12)	W(1)−O(4)	1.901(11)
O(1)−W(1)−O(3)	93.7(6)	O(5)−W(1)−O(6)	91.0(7)
O(1)−W(1)−O(5)	91.7(5)	O(1)−W(1)−O(2)	91.5(6)
O(3)−W(1)−O(5)	89.0(3)	O(5)−W(1)−O(2)	176.9(5)
O(1)−W(1)−O(6)	89.8(6)	O(6)−W(1)−O(2)	89.1(5)
O(3)−W(1)−O(6)	176.4(6)	O(1)−W(1)−O(4)	178.5(5)
O(3)−W(1)−O(4)	87.3(6)	O(5)−W(1)−O(4)	89.4(6)
O(6)−W(1)−O(4)	89.1(5)	O(3)#1-W(1)−O(6)	68.7(6)
O(1)#1-W(1)−O(1)	110.9(8)	O(5)#1-W(1)−O(6)	130.6(7)
O(3)−W(1)−O(1)#1	46.9(6)	O(1)#1-W(1)−O(6)#1	89.8(6)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + {}^{1}/_{2}, y, -z + {}^{3}/_{2}$.

whatever origin have less importance for highly ionic metal−ligand interactions. The deviations from pure octahedral symmetry in the present study cannot unambiguously be attributed to the same reasons. First, the metal−alkoxide bond is highly polar; an NBO analysis shows that the metal d orbitals participate to about 10% or less in the M−O bonding. Also, the calculations made for the molybdenum model compounds from higher to lower symmetry all display a gradual release of the methoxide orientation. The M−O distances are in accordance with the symmetry release also affected, although the changes are characterized by tetragonal distortions of the M−O distances rather than a twist around the octahedral C_3 axes. The essential symmetry lowering is thus associated with the methoxide reorientation, where the bent M−O−C linkage represents a major difference from the corresponding methyl compounds.

The crystal structure of compound **II** is isomorphous to that of **I**, the major difference between them being the presence of a definitely much better defined hexagonal subcell for **II** with the parameters $a = 7.136(14)$, $c = 6.734(14)$ Å, imposed apparently by the positions of WO_6 octahedra (the nonideal character of which is supposedly giving rise to rather high deviations for the parameters). The solution of the structure was impossible using these parameters and all other symmetries except $P2/n$ (in the course of refinement using all other symmetry groups the positions of the light atoms moved too much, destroying the connectivity in the structure, which is quite usual for the 5d and heavier metal compounds when the wrong symmetry is chosen). We can suppose here that the difficulties experinced by the researchers that tried to solve the structure of **II** before were due to twinning as described in ref 9, with the intergrowth of three domains giving rise to the appearance of a pseudo-3-fold axis being the major motive. The latter was definitely making the choice of the symmetry and finding the proper orientation of the crystal quite unevident. We succeeded in overcoming these difficulties due to good luck in the choice of the single crystal and by exploiting the quite common possibility of isomorphism of 4d and 5d alkoxide complexes. The bond lengths in the molecule of **II** (see Table 4) are in agreement with those found for **II** in the gas phase by Haaland et al.[3] and are slightly shorter than those observed in the structure of $W(OPh)_6$ by Struchkov (1.91 Å).[15]

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Supporting Information Available: Crystallographic data (listings of atomic coordinates, temperature factors, bond distances). This material is available free of charge via the Internet at http://pubs.acs.org.

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