Inorganic Chemistry, Vol. 17, No. 11, 1978 **3237**

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A Well-Characterized Compound Containing a Heteronuclear (Molybdenum–Tungsten) Quadruple Bond

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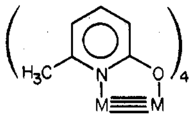
Received June 5, 1978

The compound MoW(mhp)$_4$ (Hmhp = 2-hydroxy-6-methylpyridine), which contains a heteronuclear quadruple bond, has been isolated in pure form and structurally characterized. MoW(mhp)$_4$ is formed in good yield from a reaction of Mo(CO)$_6$, W(CO)$_6$, and Hmhp in a molar ratio of 1.5:1:5. Purification was accomplished by oxidation with iodine followed by reduction with zinc amalgam to eliminate Mo$_2$(mhp)$_2$ which is the major contaminant. The dichloromethane solvate of MoW(mhp)$_4$ is isomorphous with M$_2$(mhp)$_4$·CH$_2$Cl$_2$, where M = Cr, Mo, W. The space group is $P2_1/n$ with cell parameters a = 12.909 (2) Å, b = 16.910 (3) Å, c = 13.014 (2) Å, β = 104.85 (1)°, and Z = 4. The compound contains a very short Mo–W bond length, 2.091 (1) Å, and has a Mo–W stretching frequency of 384 (3) cm^{-1}.

Introduction

Compounds with heteronuclear multiple metal-to-metal bonds have, so far, proven to be very elusive. Only two have been well characterized, viz., the two quadruply bonded ones, CrMo(O$_2$CCH$_3$)$_4$[1] and MoW(O$_2$CCMe$_3$)$_4$I,[2] while certain reactions which, it was hoped, might have led to products with Mo–W triple bonds were found not to do so.[3] Such heteronuclear compounds are of potential interest in a number of ways. There is, first of all, the problem of which ones can be synthesized, how they can be synthesized, and how stable they are. Given the existence, availability, and stability of any such compound, a variety of properties merit investigation, inter alia, reactivity, redox behavior, vibrational spectra, electronic absorption spectra, photoionization spectra, and the strength of the heteronuclear M–M′ bond compared to the strengths of the homonuclear M–M and M′–M′ bonds.

The recent report[4] from this laboratory of a complete series of very stable homonuclear, quadruply bonded compounds of the group 6 elements, Cr, Mo, and W, of type I clearly suggested that an investigation of heteronuclear compounds with the same ligand might offer a fruitful field of study. In this paper we report on the mixed molybdenum–tungsten compound, beginning with an efficient method of preparation and progressing through an extensive series of studies of its chemical, structure, physical, and spectroscopic properties.



I

Experimental Section

General Procedures. All operations were performed under dry nitrogen or argon unless otherwise indicated. Diglyme was distilled from calcium hydride, toluene was distilled from Na–K/benzophenone, and acetonitrile and methylene chloride were distilled from P$_2$O$_5$. The hexacarbonyls of molybdenum and tungsten (Pressure Chemical) and 2-hydroxy-6-methylpyridine, Hmhp (Aldrich), were used without further purification. Mass spectra and elemental analyses were obtained at the Center for Trace Characterization, Texas A&M University.

Preparation of MoW(mhp)$_4$. In a 500-mL round-bottom flask, 5.6 g of Mo(CO)$_6$ (21.2 mmol), 5.1 g of W(CO)$_6$ (14.4 mmol), and 7.8 g of Hmhp (71.5 mmol) were added to 300 mL of diglyme and 40 mL of heptane. The reactants were refluxed for 7 h. After the reaction mixture was slowly cooled to room temperature, the red crystalline product was filtered quickly in air and washed with heptane. Recrystallization was effected by Soxhlet extraction of the product into methylene chloride. Although the ratio of Mo$_2$(mhp)$_4$ to MoW(mhp)$_4$ obtained from this procedure was somewhat variable, W$_2$(mhp)$_4$ was virtually eliminated.

To obtain MoW(mhp)$_4$ free from Mo$_2$(mhp)$_4$, the following procedure was used. One gram of a mixture of MoW(mhp)$_4$ and Mo$_2$(mhp)$_4$ (ca. 1.0 mmol of MoW(mhp)$_4$ as determined by mass spectral analysis) was dissolved in 200 mL of toluene. Iodine, 0.12 g (0.40 mmol), was dissolved in 40 mL of toluene and added by syringe to the solution of MoW(mhp)$_4$. An amorphous brown precipitate formed immediately. Stirring was continued for 16 h. The product was separated by filtration, washed with toluene, and dried under vacuum. Consistent elemental analysis of this material was difficult to obtain although it analyzed most closely for C$_{24}$H$_{24}$N$_4$O$_4$MoWI$_3$. Anal. Calcd: C, 27.4; H, 2.20; N, 5.12. Found C, 26.2; H, 2.64; N, 4.72.

Freshly prepared dry zinc amalgam was added to the brown solid. This mixture was stirred in 25 mL of acetonitrile overnight. After removal of the solvent, the residue was extracted with a minimum of CH$_2$Cl$_2$ and filtered. The solution was concentrated and slowly cooled to give crystals of pure MoW(mhp)$_4$; yield 0.15 g (20%). No molecular ions for Mo$_2$(mhp)$_4$ or W$_2$(mhp)$_4$ were observed in the mass spectrum (see Figure 1).

X-ray Structure Determination.[5] A crystal of MoW(mhp)$_4$·CH$_2$Cl$_2$ measuring 0.15 × 0.25 × 0.40 mm was sealed in epoxy cement in a glass capillary tube. Preliminary examination and X-ray data collection were performed using a Syntex $P\bar{1}$ computer-controlled diffractometer equipped with a graphite-crystal monochromator in the incident beam. The crystal is isomorphous with those of the homologous compounds Cr$_2$(mhp)$_4$, Mo$_2$(mhp)$_4$, and W$_2$(mhp)$_4$. The space group is $P2_1/n$. The widths at half-heights of several strong reflections were less than 0.20°. The cell constants, evaluated by centering on 15 reflections in the range $15° \le 2\theta \le 24°$, are a = 12.909 (2) Å, b = 16.910 (3) Å, c = 13.014 (2) Å, and β = 104.85 (1)°. The linear absorption coefficient is 54 cm^{-1} for Mo Kα radiation.

Using Mo Kα radiation, 3960 reflections, of which 2507 had I greater than $3\sigma(I)$, were collected in the range $0° < 2\theta \le 45°$ using the θ–2θ method. Scan rates varied from 4 to 24°/min depending on the intensity of the reflection.

An absorption correction was applied using an empirical procedure based on ψ scans at χ = 90°. Four sets of ψ-scan data were collected, each consisting of a measurement every 10° from 0 to 350°. The range of normalized transmission factors was from 1.0000 to 0.6324. Refinement was initiated using the atomic positions found for Mo$_2$(mph)$_4$·CH$_2$Cl$_2$. Because of disordering of the Mo and W atoms, the metal positions were considered to be occupied by a hypothetical atom, M, of scattering power equal to the average of the scattering power of a molybdenum and a tungsten atom. Hydrogen atoms were omitted and carbon atoms were treated isotropically. Refinement in which all other atoms were treated anisotropically converged and gave final discrepancy indices of R_1 = 0.053 and R_2 = 0.070. The CH$_2$Cl$_2$ carbon atom is designated C(100) in Table I.

Spectra. Raman spectra were measured on a Cary Model 82 Raman spectrometer equipped with a Coherent Radiation Laboratory Model 53 argon ion laser. Samples were mixed with KBr and placed in a rotating sample holder. Spectra were recorded using the 5145-Å line for excitation.

Mass spectra were obtained on an HP5980-A mass spectrometer with an HP7333 data system. The probe temperature was in the range of 250 to 280 °C. Ionization was accomplished either by a 70-eV electron beam or a CH$_5^+$ plasma. Chemical ionization using CH$_5^+$ gives only M$^+$ and (M + 1)$^+$ ions as well as some H$_2$mhp$^+$ ions.

Electrochemical measurements were made with a Beckman Electroscan 30 using acetonitrile solutions which were 0.001 M in

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
M(1)	0.76214 (6)	0.94389 (5)	0.17095 (6)	2.21 (3)	2.03 (3)	2.06 (3)	0.16 (3)	0.47 (2)	0.02 (3)
M(2)	0.82312 (6)	0.83244 (5)	0.22426 (6)	2.94 (3)	2.60 (3)	2.45 (3)	0.22 (3)	0.72 (2)	0.25 (3)
Cl(1)	1.1188 (7)	0.5455 (5)	0.1098 (7)	10.5 (2)[b]					
Cl(2)	1.0948 (7)	0.7110 (6)	0.0591 (7)	11.1 (2)[b]					
O(1)	0.6806 (7)	0.7923 (6)	0.2500 (8)	3.4 (4)	2.8 (5)	4.3 (5)	−0.3 (4)	1.1 (4)	1.2 (4)
O(2)	0.7975 (7)	0.9938 (6)	0.3203 (7)	3.1 (4)	2.6 (4)	3.2 (4)	0.1 (4)	0.9 (3)	−0.1 (4)
O(3)	0.7160 (7)	0.9122 (5)	0.0122 (7)	3.0 (4)	2.1 (4)	2.0 (4)	−0.1 (3)	0.2 (3)	0.5 (3)
O(4)	0.9743 (7)	0.8554 (6)	0.2069 (7)	2.7 (4)	3.0 (4)	2.9 (4)	1.0 (4)	1.0 (3)	0.8 (4)
N(1)	0.6068 (9)	0.9107 (7)	0.1913 (9)	2.1 (5)	3.5 (6)	2.5 (5)	0.2 (4)	0.5 (4)	0.4 (5)
N(2)	0.8696 (9)	0.8767 (7)	0.3850 (8)	2.8 (5)	2.6 (5)	2.2 (4)	−0.1 (4)	0.1 (4)	1.2 (4)
N(3)	0.7757 (8)	0.7889 (7)	0.0627 (8)	2.6 (4)	2.4 (5)	2.7 (4)	−0.0 (4)	1.4 (4)	0.3 (4)
N(4)	0.9158 (9)	0.9790 (7)	0.1531 (9)	2.4 (5)	2.7 (5)	3.3 (5)	−0.5 (4)	0.1 (4)	2.0 (4)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(1)	0.597 (1)	0.8373 (9)	0.231 (1)	3.2 (3)	C(32)	0.697 (1)	0.8153 (9)	−0.124 (1)	3.2 (3)
C(2)	0.498 (1)	0.8097 (10)	0.247 (1)	3.8 (3)	C(33)	0.710 (1)	0.7401 (11)	−0.146 (1)	4.4 (4)
C(3)	0.413 (2)	0.8621 (12)	0.219 (2)	5.4 (4)	C(34)	0.762 (1)	0.6862 (11)	−0.068 (1)	4.3 (4)
C(4)	0.423 (1)	0.9364 (11)	0.177 (1)	4.6 (4)	C(35)	0.790 (1)	0.7102 (9)	0.035 (1)	3.1 (3)
C(5)	0.521 (1)	0.9594 (9)	0.166 (1)	2.9 (3)	C(36)	0.839 (1)	0.6574 (11)	0.128 (1)	4.3 (4)
C(6)	0.540 (1)	1.0409 (10)	0.128 (1)	3.8 (3)	C(41)	0.997 (1)	0.9244 (8)	0.176 (1)	2.3 (3)
C(21)	0.846 (1)	0.9528 (9)	0.401 (1)	3.3 (3)	C(42)	1.099 (1)	0.9433 (10)	0.166 (1)	3.4 (3)
C(22)	0.869 (1)	0.9863 (10)	0.504 (1)	3.9 (3)	C(43)	1.120 (1)	1.0200 (10)	0.132 (1)	4.0 (4)
C(23)	0.926 (2)	0.9400 (12)	0.588 (2)	5.6 (4)	C(44)	1.035 (1)	1.0753 (10)	0.111 (1)	3.5 (3)
C(24)	0.954 (1)	0.8618 (12)	0.572 (1)	5.2 (4)	C(45)	0.937 (1)	1.0556 (9)	0.122 (1)	2.9 (3)
C(25)	0.923 (1)	0.8314 (10)	0.470 (1)	3.8 (3)	C(46)	0.844 (1)	1.1110 (11)	0.101 (1)	4.5 (4)
C(26)	0.946 (1)	0.7466 (12)	0.446 (2)	5.4 (4)	C(100)	1.125 (2)	0.6145 (17)	0.011 (2)	9.1 (7)
C(31)	0.732 (1)	0.8417 (9)	−0.015 (1)	2.7 (3)					

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}hlb^*\cdot c^*)]$. [b] Isotropically refined, in units of Å^2.

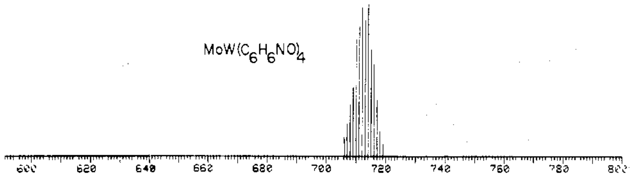

Figure 1. Mass spectrum of $MoW(mhp)_4$ obtained at a probe temperature of 250 °C and using an ionizing plasma of CH_5^+. Not only ions of molecular mass but also those of molecular mass plus 1 are observed. The isotope distribution pattern is therefore skewed to higher m/e values as compared with that of a pure parent ion multiplet. The absence of clusters at m/e values of 624 and 800 indicates that the sample is free of $Mo_2(mhp)_4$ and $W_2(mhp)_4$, respectively.

$M_2(mhp)_4$ and 0.1 M in $(n\text{-}Bu)_4NCl$. Potentials are reported relative to the saturated calomel electrode (SCE).

Results and Discussion

The triad of quadruply bonded compounds represented by I (M = Cr, Mo, W) is the first example of a homologous series in which each member may be readily prepared via the same experimental procedure.[4] Each compound is obtained in high yield simply by refluxing 2-hydroxy-6-methylpyridine with the appropriate metal carbonyl, $M(CO)_6$, in diglyme. Given the extraordinary stability of each compound in this series,[4] it seemed reasonable to suppose that an attempt to prepare heteronuclear quadruple bonds, 4° M–M′, from a mixture of $M(CO)_6$ and $M'(CO)_6$ and Hmhp might lead to a mixture of the three possible products $M_2(mhp)_4$, $MM'(mhO)_4$, and $M_2'(mhp)_4$. The possible combinations of the group 6 metals may, in principle, lead to three heteronuclear quadruple bonds.

The reaction of $Cr(CO)_6$, $Mo(CO)_6$, and Hmhp in a 1:1:4 ratio leads to the formation of less than 1% of $CrMo(mhp)_4$ and approximately equal quantities of $Cr_2(mhp)_4$ and $Mo_2(mhp)_4$. The reaction of $Cr(CO)_6$, $W(CO)_6$, and Hmhp gives a product that shows no evidence in the mass spectrum for the presence of the compound with a Cr–W bond. Much more encouraging results were obtained in the reaction of $Mo(CO)_6$, $W(CO)_6$, and Hmhp. Refluxing a 1:1:4 ratio, respectively, of these reactants for 7 h leads to the formation of $Mo_2(mhp)_4$, $MoW(mhp)_4$, and $W_2(mhp)_4$ in a nonstatistical distribution of approximately 22:74:4 (mole ratios), respectively. Longer reaction times lead to an increased quantity of $W_2(mhp)_4$, but the yield of $MoW(mhp)_4$ was always greater than 50%. $W_2(mhp)_4$ can be virtually eliminated from the reaction mixture by raising the ratio of $Mo(CO)_6$:$W(CO)_6$ to 1.5:1. Apparently the formation of $MoW(mhp)_4$ is favored over formation of the homonuclear species. The reason for this (kinetic vs. thermodynamic) is not known.

Electrochemical study of each of the three products revealed that each one undergoes a reversible one-electron oxidation. The potentials (vs. SCE) for $Mo_2(mph)_4$, $MoW(mhp)_4$, and $W_2(mhp)_4$ are 0.20, −0.16, and −0.35 V, respectively. This indicates that selective oxidation of $MoW(mhp)_4$ in a mixture of $Mo_2(mhp)_4$ and $MoW(mhp)_4$ may be used to purify the heteronuclear compound. A similar method has recently been used to prepare pure $MoW(O_2CCMe_3)_4$.[2] In the absence of $W_2(mhp)_4$, the addition of a calculated quantity of I_2 to a toluene solution of $Mo_2(mhp)_4$ and $MoW(mhp)_4$ causes the precipitation of an amorphous brown solid whose elemental analysis is approximately fitted by the formula $MoW(mhp)_4I_3$. $MoW(mhp)_4I_3$ is then readily reduced by zinc amalgam to give pure $MoW(mhp)_4$.

Figure 1 shows the experimental mass spectrum of pure $MoW(mhp)_4$ which was obtained by the procedure just described. Chemical ionization using a CH_5^+ plasma was used to generate the spectrum. There are no detectable molecular ion clusters for $Mo_2(mhp)_4$ and $W_2(mhp)_4$ indicating that the sample is virtually 100% pure. An 11-line spectrum centered at m/e ~800 is expected for $W_2(mhp)_4$ and a 17-line spectrum at m/e 624 is expected for $Mo_2(mhp)_4$. The pattern in the parent ion peak for $MoW(mhp)_4$ is slightly skewed toward higher m/e values compared with the pattern calculated from isotope abundances. This is due to the presence of both M^+ and $(M + 1)^+$ ions generated by the chemical-ionization technique.

Crystal Structure of $MoW(mhp)_4$. The crystal structure determination was performed on the same sample whose mass

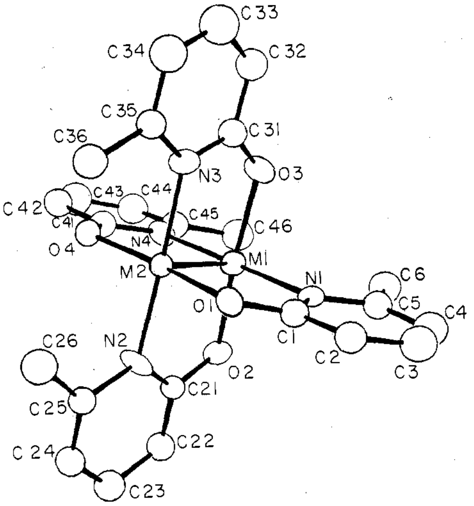

Figure 2. Molecular structure of MoW(mhp)$_4$. Atoms are represented by projections of spheres or ellipsoids with radii proportional to their thermal vibration parameters. The atom numbering scheme used in the tables is defined.

Table II. Comparison of Key Bond Lengths in M$_2$(mhp)$_4$ Molecules

compd	M-M, Å	mean length M-O, Å	mean length M-N, Å
1 Mo$_2$(mhp)$_4$·CH$_2$Cl$_2$	2.065 (1)	2.086 (4)	2.167 (5)
2 MoW(mhp)$_4$·CH$_2$Cl$_2$	2.091 (1)	2.063 (9)	2.156 (19)
3 W$_2$(mhp)$_4$·CH$_2$Cl$_2$	2.161 (1)	2.037 (8)	2.115 (12)

spectrum is shown in Figure 1. Recrystallization of MoW(mhp)$_4$ from dichloromethane gives the CH$_2$Cl$_2$ solvate. Crystals of this compound are isomorphous with those obtained for the series of homonuclear compounds represented by I. Figure 2 shows the molecular structure of MoW(mhp)$_4$ in the crystal and defines the atom numbering scheme. The metal atoms are identified only as M$_1$ and M$_2$ because of the disorder of the Mo and W atoms.

A comparison of the M–M, M–N, and M–O bond distances in Mo$_2$(mhp)$_4$, **1**, MoW(mhp)$_4$, **2**, and W$_2$(mhp)$_4$, **3**, is given in Table II. The Mo–W bond length in **2**, viz., 2.091 (1) Å, is 0.022 (2) Å shorter than the average of the M–M bond lengths in **1** and **3**. This is a small but significant difference. Thus the heteronuclear M–M bond in **2** is "formally shorter"[6] than the homonuclear M–M bonds in **1** and **3**, presumably indicating an enhanced overlap of orbitals leading to stronger bonding in MoW(mhp)$_4$.

The mean M–O and M–N distances in **2** might be expected to be equal to the averages of the mean M–O and M–N distances, respectively, in **1** and **3** because of the disorder of the metal atoms. This is precisely so for the M–O distance in **2**, 2.063 (9) Å, which is only 0.001 Å different from the average of M–O distances in **1** and **3**. The M–N distance in **2**, 2.156 (19) Å, is 0.015 Å closer to the Mo–N distance in **1**, but it is within 1σ of the average of the Mo–N and W–N distances in **1** and **3** and cannot, therefore, be considered significantly different from the average.

No other bond lengths or angles in MoW(mhp)$_4$·CH$_2$Cl$_2$ differ significantly from those found in Mo$_2$(mhp)$_4$·CH$_2$Cl$_2$ and W$_2$(mhp)$_4$·CH$_2$Cl$_2$.[4] Tables III and IV list bond lengths and selected bond angles for MoW(mhp)$_4$·CH$_2$Cl$_2$.

Raman Spectrum. A strong band in the Raman spectrum at 384 (3) cm^{-1} can be identified as the "M–M stretching mode" for MoW(mhp)$_4$. On the basis that the observed frequency gives a good measure of the *intrinsic* "M–M" frequency,[4,7] a force constant of 5.45 mdyn/Å is calculated using the harmonic-oscillator approximation, in the same way as was done previously for the homonuclear M$_2$(mhp)$_4$ molecules. This force constant is significantly higher than those calculated for Mo$_2$(mhp)$_4$ and W$_2$(mhp)$_4$, 5.10 and 4.71 mdyn/Å, respectively. The larger force constant for MoW(mhp)$_4$ is another indication that the bond between metal atoms in the heteronuclear compound is stronger than either of those in the related homonuclear compounds.

Table III. Bond Distances (Å) for MoW(mhp)$_4$·CH$_2$Cl$_2$

M(1)-M(2)	2.091 (1)	C(24)-C(25)	1.38 (2)
M(1)-O(2)	2.060 (8)	C(25)-C(26)	1.51 (2)
M(1)-O(3)	2.068 (7)	C(25)-N(2)	1.38 (2)
M(2)-O(1)	2.067 (8)	O(3)-C(31)	1.28 (1)
M(2)-O(4)	2.058 (8)	C(31)-N(3)	1.36 (1)
M(1)-N(1)	2.163 (9)	C(31)-C(32)	1.44 (2)
M(1)-N(4)	2.140 (9)	C(32)-C(33)	1.33 (2)
M(2)-N(2)	2.157 (9)	C(33)-C(34)	1.40 (2)
M(2)-N(3)	2.163 (9)	C(34)-C(35)	1.36 (2)
O(1)-C(1)	1.29 (1)	C(35)-N(3)	1.40 (2)
C(1)-N(1)	1.36 (2)	C(35)-C(36)	1.51 (2)
C(1)-C(2)	1.43 (2)	O(4)-C(41)	1.29 (1)
C(2)-C(3)	1.38 (2)	C(41)-N(4)	1.37 (1)
C(3)-C(4)	1.39 (2)	C(41)-C(42)	1.40 (2)
C(4)-C(5)	1.37 (2)	C(42)-C(43)	1.42 (2)
C(5)-N(1)	1.35 (1)	C(43)-C(44)	1.42 (2)
C(5)-C(6)	1.50 (2)	C(44)-C(45)	1.34 (2)
O(2)-C(21)	1.28 (1)	C(45)-N(4)	1.40 (2)
C(21)-N(2)	1.35 (2)	C(45)-C(46)	1.50 (2)
C(21)-C(22)	1.41 (2)	C(100)-Cl(1)	1.75 (2)
C(22)-C(23)	1.39 (2)	C(100)-Cl(2)	1.82 (2)
C(23)-C(24)	1.40 (2)		

Table IV. Selected Bond Angles (deg) for MoW(mhp)$_4$·CH$_2$Cl$_2$

M(1)-M(2)-O(1)	94.3 (2)	O(4)-M(2)-N(3)	89.8 (3)
M(2)-M(1)-O(2)	94.7 (2)	N(1)-M(1)-N(4)	178.7 (4)
M(2)-M(1)-O(3)	94.9 (2)	N(2)-M(2)-N(3)	179.5 (3)
M(1)-M(2)-O(4)	94.6 (2)	M(2)-O(1)-C(1)	120.5 (8)
M(2)-M(1)-N(1)	90.4 (3)	O(1)-C(1)-N(1)	117.5 (1.1)
M(1)-M(2)-N(2)	89.8 (2)	O(1)-C(1)-C(2)	121.0 (1.2)
M(1)-M(2)-N(3)	89.7 (3)	N(1)-C(1)-C(2)	121.5 (1.1)
M(2)-M(1)-N(4)	90.3 (3)	C(1)-C(2)-C(3)	115.6 (1.3)
O(1)-M(2)-O(4)	171.1 (3)	C(2)-C(3)-C(4)	122.5 (1.5)
O(2)-M(1)-O(3)	170.4 (3)	C(3)-C(4)-C(5)	118.7 (1.4)
O(1)-M(2)-N(2)	89.7 (3)	C(4)-C(5)-C(6)	121.8 (1.2)
O(1)-M(2)-N(3)	90.2 (3)	N(1)-C(5)-C(6)	116.8 (1.1)
O(2)-M(1)-N(1)	88.8 (3)	C(4)-C(5)-N(1)	121.4 (1.2)
O(2)-M(1)-N(4)	90.1 (3)	M(1)-N(1)-C(1)	117.3 (8)
O(3)-M(1)-N(1)	90.9 (3)	M(1)-N(1)-C(5)	122.4 (8)
O(3)-M(1)-N(4)	90.0 (3)	C(1)-N(1)-C(5)	120.3 (1.0)
O(4)-M(2)-N(2)	90.3 (3)		

Conclusions. Three separate lines of evidence lead to the conclusion that the M–M′ bond in MoW(mhp)$_4$ is inherently stronger than the M–M bonds in the analogous homonuclear compounds Mo$_2$(mhp)$_4$ and W$_2$(mhp)$_4$. (1) There is chemical evidence, in the sense that reaction of Mo(CO)$_6$, W(CO)$_6$, and Hmhp leads to the preferred production of MoW(mhp)$_4$; that is, 74% of MoW(mhp)$_4$ is formed but only 22 and 4% of Mo$_2$(mhp)$_4$ and W$_2$(mhp)$_4$ are formed. (2) There is structural evidence, since the Mo–W bond in the crystal, 2.091 (1) Å, is 0.022 (2) Å shorter than the average of the corresponding Mo–Mo and W–W bonds. (3) There is spectral evidence in the form of the Raman spectrum in which the high M–M stretching frequency, 384 (3) cm^{-1}, leads to the calculation of a force constant for the M–M stretch of 5.45 mdyn/Å, the largest yet observed[7-10] for a metal-to-metal bond. Further evidence concerning the metal-to-metal bonding can, of course, be otained from electronic absorption spectra and photoionization spectra, and such studies will be reported in a future paper.

Acknowledgment. We thank the National Science Foundation for financial support. Raman spectra were provided by Professor Jaan Laane and his co-workers. Mass spectra were obtained by Larry Birchfield of the Texas A&M Center for Trace Characterization. We thank Dr. J. C. Sekutowski for help with the refinement of the crystal structure.

Registry No. $MoW(mhp)_4{\cdot}CH_2Cl_2$, 67577-07-5; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0.

Supplementary Material Available: A table of calculated and observed structure factors (11 pages). Ordering information is given on any current masthead page.

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Two Bis(diphenylphosphinomethane) (DPPM) Complexes of Quadruply Bonded Dimolybdenum(II): $Mo_2(DPPM)_2X_4$, X = Cl, NCS

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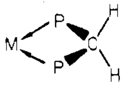
Received June 5, 1978

The preparation and structural characterization of the two compounds $Mo_2(DPPM)_2X_4{\cdot}2C_3H_6O$, where DPPM = $Ph_2PCH_2PPh_2$ and X = Cl or NCS, are reported. Their structures, though similar, show small but significant differences. Each molecule has an $MoX_2(\mu\text{-}DPPM)_2MoX_2$ type structure with the μ-DPPM units in a transoid relationship. For X = Cl, the molecule lies on a crystallographic inversion center and the rotational conformation is eclipsed. For X = NCS, no crystallographic symmetry is imposed and the rotational conformation deviates approximately 13.3° from being eclipsed. The fact that the thiocyanate ions are N bonded is notable. For the chloro compound, the main crystallographic data and some important molecular dimensions are space group $C2/c$, $a = 18.762$ (5) Å, $b = 11.701$ (4) Å, $c = 25.741$ (4) Å, $\beta = 95.44$ (2)°, $V = 5626$ Å^3, $Z = 4$, Mo–Mo = 2.138 (1) Å, and Mo–Cl = 2.39 (1) Å. For the isothiocyanato compound the important data and dimensions are space group $P2_1/c$, $a = 13.761$ (6) Å, $b = 15.806$ (6) Å, $c = 31.14$ (1) Å, $\beta = 90.78$ (3)°, $V = 6773$ Å^3, $Z = 4$, Mo–Mo = 2.167 (3) Å, and Mo–N = 2.06 (2) Å.

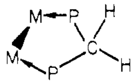
Introduction

Although well over 100 compounds containing the quadruply bonded Mo_2^{4+} unit have been reported and upward of 20 of them have been structurally characterized by X-ray crystallography,[2] there are still some questions involving both preparative and structural aspects that merit consideration. Several such questions are addressed simultaneously in the work reported here.

The DPPM ligand is capable of serving either as a chelating ligand, Ia, forming an essentially planar, four-membered ring or as a bridging ligand, Ib, forming a nonplanar, five-membered ring for which the typical conformation has the methylene carbon atom lying outside the common plane of the two metal and two phosphorus atoms. These structural studies show which role is played by DPPM in this type of molecule, namely, the bridging one.



Ia



Ib

A second question, of particular interest, has to do with the mode of attachment of the ambidentate ligand SCN^- to the Mo_2^{4+} unit. Very few thiocyanato compounds containing Mo_2^{4+} and Re_2^{6+} have been described previously,[3] and no X-ray study showing whether the ligand is thiocyanato (–SCN) or isothiocyanato (–NCS) in attachment has been made, though IR data have been interpreted[3-6] in favor of –NCS bonding.

Another interesting structural aspect of quadruply bonded M_2 systems that comes into play here is the extent to which the internal rotational conformation about the M–M bond deviates from the eclipsed one when the molecule is not constrained by any crystallographic symmetry element. Prior examples of the situation where the molecule as a whole is the asymmetric unit and is not constrained by any crystallographic plane, axis, or inversion center are remarkably few in number. The existence of the δ bond does not demand a *strictly* eclipsed conformation but only an approach thereto. Only when the surroundings of the molecule in the crystal do not impose an essentially eclipsed conformation is there a chance to see how much of a deviation can occur without loss of the δ component of the quadruple bond. A good example of such a situation is provided by the thiocyanate compound reported here.

As this work was nearing completion, the preparation of **2**, $Mo_2(DPPM)_2Cl_4{\cdot}2C_3H_6O$, as a blue-green powder containing no solvent of crystallization, was reported by Walton.[8]

Experimental Section

Materials. Methylenebis(diphenylphosphine) (DPPM) was obtained from Strem Chemicals and used without further purification. Tetrakis(methanesulfonato)dimolybdenum(II) was prepared by the method of Hochberg and Abbott.[6] All procedures were carried out under dry nitrogen using commercial Schlenk-type glassware.

Preparation of $Mo_2(NCS)_4(DPPM)_2$. A solution was prepared from $Mo_2(MeSO_3)$ (0.29 g), NH_4SCN (0.4 g), and 25 mL of methanol. A solution of 0.45 g of DPPM in 10 mL of dimethoxyethane was added dropwise. A deep green solution resulted. Dark green needles separated after ca. 12 h at 0 °C. The crystals were filtered and dried in a stream of nitrogen. They are soluble in chloroform, acetone, or benzene but insoluble in methanol, ethanol, or water. Anal. Calcd for $C_{54}H_{44}N_4P_4S_4Mo_2$: C, 54.36; H, 3.69; N, 4.69; P, 10.40; S, 10.74; Mo, 16.10. Found: C, 54.18; H, 3.67; N, 4.61; P, 10.51; Mo, 16.06.

The infrared spectrum of this compound shows $\nu(C{\equiv}N)$ at 2030 cm^{-1} and ν(C–S) at 864 cm^{-1}. Both values are in the range expected if NCS is N bonded to molybdenum,[9] as in previous cases.[3-6]

0020-1669/78/1317-3240$01.00/0