

A Triad of Homologous, Air-Stable Compounds Containing Short, Quadruple Bonds between Metal Atoms of Group 6

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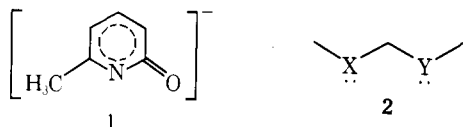
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Abstract: Each of the metals chromium, molybdenum, and tungsten forms a compound of molecular formula $M_2(\text{mhp})_4$, where mhp represents the anion of 2-hydroxy-6-methylpyridine, Hmhp (6-methylpyridone). These compounds, which are yellow, orange, and red, respectively, are all stable toward dry air as solids and can be easily and quickly prepared in large quantities from readily available starting materials. $\text{Cr}_2(\text{mhp})_4$ is stable toward even humid air and appears to be more chemically and physically stable than any other chromium(II) compound. The Cr and Mo compounds were prepared by reactions of $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$ or $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ and $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, respectively, with the sodium salt of the ligand; $\text{W}_2(\text{mhp})_4$ was obtained by reaction of $\text{W}(\text{CO})_6$ with Hmhp in refluxing diglyme. All three compounds are volatile and give definitive mass spectra. The Raman spectra have M–M stretching frequencies ($\pm 3 \text{ cm}^{-1}$) at 556, 425, and 295 cm^{-1} , for the Cr, Mo, and W compounds, respectively. All three give crystals of composition $M_2(\text{mhp})_4(\text{CH}_2\text{Cl}_2)$ which are isomorphous; each structure has been determined by x-ray crystallography, revealing the M–M distances to be Cr–Cr, 1.889 (1) Å; Mo–Mo, 2.065 (1) Å; W–W, 2.161 (1) Å. The compounds form monoclinic crystals (space group $P2_1/n$ with $Z = 4$) with unit cell dimensions at $22 \pm 2^\circ \text{C}$ as follows, where the values for the Cr, Mo, and W compounds are given in that order for each: a (Å) = 12.792 (2), 12.959 (1), 12.924 (1); b (Å) = 16.985 (3), 16.948 (2), 16.948 (2); c (Å) = 12.904 (2), 13.064 (2), 13.010 (2); β (deg), 104.42 (1), 104.90 (1), 104.78 (1).

Introduction

Since 1964, when the existence of quadruple bonds was first recognized,^{1,2} the chemistry of compounds containing such bonds, as well as related chemistry of compounds containing double^{3,4} and triple^{5–9} bonds¹⁰ between metal atoms, has developed rapidly and broadly.^{7–9} Throughout this period one of the persistent sources of puzzlement—and frustration—has been the nearly complete absence of quadruple bonds between tungsten atoms, despite many attempts to prepare compounds that might contain them.^{11–15} Only two such ditungsten entities, that have been shown conclusively to contain W–W quadruple bonds, are presently recorded in the literature. The first to be characterized were the $\text{W}_2(\text{CH}_3)_8^{4-}$ ion^{16,17} and the related mixed ligand complex, $[\text{W}_2(\text{CH}_3)_x\text{Cl}_{8-x}]^{4-}$ ($x \approx 3$), which are extremely unstable thermally and acutely reactive; they are, therefore, difficult subjects for further experimentation. Somewhat more recently the $\text{W}_2(\text{C}_8\text{H}_8)_3$ molecule was structurally characterized.¹⁸ This is rather stable, but the $\text{M}_2(\text{C}_8\text{H}_8)_3$ compounds appear to be electronically somewhat different from most other quadruply bonded species. Thus, until now there have been only two complete triads of quadruply bonded compounds, viz., those containing the $\text{M}_2(\text{CH}_3)_8^{4-}$ ions and the $\text{M}_2(\text{C}_8\text{H}_8)_3$ set, both containing the group 6 metals Cr, Mo, and W.

We have now prepared and thoroughly characterized a new set of compounds that (a) comprise a complete triad, (b) are electronically in the “mainstream” of quadruply bonded compounds, (c) have unprecedented thermal and chemical stability, especially for the tungsten compound, and (d) are easy to make and handle. They are of the composition $\text{M}_2(\text{mhp})_4$, where mhp represents the anion, **1**, of 2-hydroxy-6-methylpyridine. This ligand is a member of the same class of bidentate ligands, represented in the most general way by **2**, that we have discussed in some detail in a recent paper.¹⁹



Experimental Section

Materials and Methods. $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$ were prepared according to established procedures. $\text{W}(\text{CO})_6$ was purchased from Pressure Chemical Co. 2-Hydroxy-6-methylpyridine (Hmhp) was purchased from Aldrich Chemical Co., Inc. Sodium methoxide was obtained from Fisher Scientific Co. All other compounds and solvents were of reagent grade or better from commercial sources. Carbon, hydrogen, and nitrogen analyses were performed at the Center for Trace Characterization, Texas A&M University.

Preparation of $\text{Cr}_2(\text{mhp})_4$. All reactions were performed under nitrogen using air-tight glassware. All solvents were dried over molecular sieves and deoxygenated prior to use. In a typical reaction, 0.54 g (10 mmol) of NaOCH_3 was dissolved in 75 mL of absolute ethanol. To this was added 1.09 g (10 mmol) of Hmhp. After the ligand had completely dissolved, 0.94 g (2.5 mmol) of $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$ was added with vigorous stirring. The mixture was stirred for 4 h at room temperature after which a yellow, crystalline product was present. The compound was filtered, washed with 50 mL of 2-propanol, and dried under vacuum at room temperature for 3 h. The product was found to have the composition $\text{Cr}_2(\text{mhp})_4 \cdot \text{H}_2\text{O}$. Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{N}_4\text{O}_5\text{Cr}_2$: C, 51.99; H, 4.69; N, 10.11. Found: C, 52.1; H, 4.92; N, 10.1. The compound can be dehydrated by heating at 100°C under vacuum for 2 h. Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{N}_4\text{O}_4\text{Cr}_2$: C, 53.73; H, 4.48; N, 10.45. Found: C, 53.9; H, 4.55; N, 10.5. Dehydration causes no change in the physical appearance of the complex, and there is no tendency to rehydrate upon standing. Crystals suitable for x-ray analysis were grown by slowly evaporating a dichloromethane solution under nitrogen. The crystals thus obtained were found (vide infra) to contain solvent of crystallization.

Preparation of $\text{Mo}_2(\text{mhp})_4$. A similar procedure was used in the preparation of the molybdenum compound. Using $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ as the starting material, one obtains an orange, unsolvated, crystalline product, $\text{Mo}_2(\text{mhp})_4$. Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{N}_4\text{O}_4\text{Mo}_2$: C, 46.15; H, 3.85; N, 8.97. Found: C, 45.7; H, 4.11; N, 8.49. Crystals of this compound were also obtained from dichloromethane, and were also subsequently found to contain a molecule of solvent per molecule of complex.

Preparation of $\text{W}_2(\text{mhp})_4$. In an air-tight flask, 3.52 g (10 mmol) of $\text{W}(\text{CO})_6$ and 2.20 g (20 mmol) of Hmhp were added to 150 mL of freshly distilled diglyme. The reactants were stirred and gently refluxed under nitrogen for 6 h during which time they became dark red in color. The reaction mixture was then allowed to cool slowly to room temperature overnight, whereupon a red, crystalline precipitate was observed in the dark red solution. The product was filtered, washed

Table I. Crystallographic Data for the Three $M_2(mhp)_4 \cdot CH_2Cl_2$ Compounds

parameter ^a	metal		
	Cr	Mo	W
<i>a</i> , Å	12.792 (2)	12.959 (1)	12.924 (1)
<i>b</i> , Å	16.985 (3)	16.948 (2)	16.948 (2)
<i>c</i> , Å	12.904 (2)	13.064 (2)	13.010 (2)
β , deg	104.42 (1)	104.90 (1)	104.78 (1)
<i>V</i> , Å ³	2715.4	2772.7	2755.4
<i>d</i> _{calcd.} , g cm ⁻³	1.520	1.699	2.134
<i>Z</i>	4	4	4
formula wt, g mol ⁻¹	536.48	624.36	885.11
approx crystal size, mm	0.7 × 0.6 × 0.5	0.5 × 0.4 × 0.2	0.7 × 0.3 × 0.08
μ cm ⁻¹	16.689	11.189	90.726
range of 2θ	0–45°	0–45°	0–50°
no. unique data	3564	3639	4884
data with $I > 3\sigma(I)$	2783 ^b	2418	3650
<i>R</i> ₁	0.077	0.057	0.082
<i>R</i> ₂	0.106	0.083	0.098
esd, obs of unit wt	2.28	1.80	2.165

^a Figures in parentheses following some numbers are esd's occurring in the least significant digit. ^b $I > 2\sigma(I)$.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr_2(mhp)_4(CH_2Cl_2)_4$ ^a

atom	<i>X</i>	<i>Y</i>	<i>Z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr(1)	0.764 01 (9)	0.939 02 (7)	0.174 02 (9)	0.003 74 (7)	0.002 01 (4)	0.004 03 (7)	0.000 21 (9)	0.0018 (1)	–0.000 21 (9)
Cr(2)	0.819 20 (9)	0.838 68 (7)	0.222 04 (9)	0.003 97 (7)	0.002 06 (4)	0.004 06 (7)	0.000 44 (9)	0.0023 (1)	0.000 35 (9)
Cl(1)	0.6153 (3)	0.9532 (3)	0.6097 (3)	9.7 (1)					
Cl(2)	0.5940 (4)	0.7871 (3)	0.5581 (4)	11.0 (1)					
O(1)	0.6882 (4)	0.7920 (3)	0.2507 (4)	0.0052 (3)	0.0024 (2)	0.0059 (3)	–0.0008 (4)	0.0042 (5)	0.0007 (4)
O(2)	0.7917 (4)	0.9941 (3)	0.3118 (4)	0.0058 (3)	0.0025 (2)	0.0053 (3)	0.0002 (4)	0.0025 (6)	–0.0020 (4)
O(3)	0.7165 (4)	0.9173 (3)	0.0185 (4)	0.0046 (3)	0.0022 (2)	0.0038 (3)	0.0002 (4)	0.0008 (5)	0.0001 (4)
O(4)	0.9674 (4)	0.8532 (3)	0.2090 (4)	0.0043 (3)	0.0024 (2)	0.0057 (3)	0.0007 (4)	0.0029 (5)	0.0007 (4)
N(1)	0.6120 (4)	0.9085 (4)	0.1900 (4)	0.0038 (4)	0.0027 (2)	0.0043 (4)	0.0008 (5)	0.0021 (6)	–0.0002 (5)
N(2)	0.8658 (5)	0.8784 (4)	0.3785 (5)	0.0046 (4)	0.0027 (2)	0.0045 (4)	0.0001 (5)	0.0028 (6)	0.0006 (5)
N(3)	0.7757 (4)	0.7939 (3)	0.0683 (5)	0.0045 (4)	0.0018 (2)	0.0052 (4)	–0.0002 (5)	0.0031 (6)	–0.0002 (5)
N(4)	0.9114 (4)	0.9771 (4)	0.1555 (4)	0.0043 (4)	0.0023 (2)	0.0044 (4)	–0.0009 (5)	0.0022 (6)	0.0005 (5)
C(1)	0.6020 (6)	0.8360 (4)	0.2285 (6)	2.9 (1)					
C(2)	0.5035 (7)	0.8095 (5)	0.2450 (7)	4.0 (2)					
C(3)	0.4137 (8)	0.8605 (6)	0.2170 (8)	5.1 (2)					
C(4)	0.4257 (7)	0.9344 (5)	0.1741 (7)	4.3 (2)					
C(5)	0.5253 (6)	0.9580 (5)	0.1654 (6)	3.2 (1)					
C(6)	0.5466 (7)	1.0393 (5)	0.1263 (7)	4.0 (2)					
C(21)	0.8414 (6)	0.9532 (5)	0.3954 (6)	3.0 (1)					
C(22)	0.8661 (7)	0.9867 (5)	0.4979 (7)	4.4 (2)					
C(23)	0.9222 (9)	0.9397 (6)	0.5831 (9)	5.9 (2)					
C(24)	0.9489 (8)	0.8633 (6)	0.5647 (8)	5.0 (2)					
C(25)	0.9186 (7)	0.8335 (5)	0.4635 (7)	4.0 (2)					
C(26)	0.9405 (8)	0.7475 (6)	0.4369 (8)	5.1 (2)					
C(31)	0.7315 (6)	0.8462 (4)	–0.0100 (6)	2.7 (1)					
C(32)	0.6991 (6)	0.8219 (5)	–0.1172 (6)	3.5 (2)					
C(33)	0.7140 (7)	0.7446 (5)	–0.1420 (7)	4.3 (2)					
C(34)	0.7606 (7)	0.6903 (5)	–0.0619 (7)	4.4 (2)					
C(35)	0.7904 (6)	0.7169 (5)	0.0422 (6)	3.6 (2)					
C(36)	0.8399 (8)	0.6635 (6)	0.1365 (7)	4.8 (2)					
C(41)	0.9918 (6)	0.9209 (4)	0.1780 (6)	2.9 (1)					
C(42)	1.0959 (6)	0.9410 (5)	0.1677 (6)	3.7 (2)					
C(43)	1.1162 (7)	1.0156 (5)	0.1347 (7)	4.1 (2)					
C(44)	1.0320 (7)	1.0714 (5)	0.1143 (7)	3.8 (2)					
C(45)	0.9326 (6)	1.0510 (5)	0.1245 (6)	3.1 (1)					
C(46)	0.8383 (7)	1.1073 (6)	0.1040 (7)	4.4 (2)					
C(100)	0.6200 (13)	0.8861 (10)	0.5109 (13)	10.0 (4)					

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

with 50 mL of deoxygenated hexane, and dried under vacuum for 4 h. Crystals for x-ray and chemical analysis were obtained as above from dichloromethane. Anal. Calcd for $C_{25}H_{26}N_4O_4W_2Cl_2$: C, 33.90; H, 2.94; N, 6.33. Found: C, 33.7; H, 2.86; N, 6.22.

Crystallographic Studies.²⁰ The crystals used were grown by slow evaporation under nitrogen of methylene chloride solutions. A crystal of the chromium compound was lodged in a capillary; a crystal of the

molybdenum compound was cemented to the end of a glass fiber and coated with epoxy resin; a crystal of the tungsten compound was cemented to the end of a glass fiber but not covered.

The crystals were examined on a Syntex PT four-circle automated diffractometer. Both rotation photographs and ω scans were used to judge the quality of the crystals. Lattice parameters were obtained by a least-squares fit to the setting angles of 15 strong reflections.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for Mo₂(mhp)₄(CH₂Cl₂)^a

atom	X	Y	Z	β ₁₁	β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃
Mo(1)	0.762 46 (7)	0.943 38 (5)	0.171 70 (7)	0.004 09 (5)	0.001 94 (3)	0.004 17 (6)	0.000 52 (8)	0.0015 (1)	-0.000 28 (9)
Mo(2)	0.822 37 (7)	0.833 45 (5)	0.223 80 (7)	0.004 45 (5)	0.001 99 (3)	0.004 07 (6)	0.000 65 (7)	0.0021 (1)	0.000 45 (9)
Cl(1)	1.1166 (5)	0.5458 (3)	0.1071 (5)	11.6 (2)					
Cl(2)	1.0942 (4)	0.7108 (4)	0.0587 (5)	12.0 (2)					
O(1)	0.6801 (5)	0.7909 (4)	0.2506 (6)	0.0052 (4)	0.0024 (3)	0.0069 (6)	-0.0012 (6)	0.0049 (8)	0.0027 (7)
O(2)	0.7988 (5)	0.9948 (4)	0.3209 (6)	0.0055 (5)	0.0029 (3)	0.0062 (6)	0.0011 (6)	0.0024 (9)	-0.0030 (8)
O(3)	0.7145 (5)	0.9127 (4)	0.0112 (5)	0.0054 (4)	0.0020 (2)	0.0033 (5)	0.0002 (6)	0.0013 (7)	-0.0004 (6)
O(4)	0.9754 (5)	0.8560 (4)	0.2072 (5)	0.0047 (4)	0.0021 (3)	0.0052 (5)	0.0006 (6)	0.0028 (8)	0.0009 (7)
N(1)	0.6064 (6)	0.9095 (5)	0.1906 (6)	0.0040 (5)	0.0032 (4)	0.0037 (6)	-0.0006 (7)	0.0002 (9)	-0.0015 (9)
N(2)	0.8695 (6)	0.8788 (5)	0.3845 (7)	0.0044 (5)	0.0036 (4)	0.0043 (6)	0.0006 (8)	0.0019 (10)	0.0016 (9)
N(3)	0.7747 (6)	0.7886 (5)	0.0623 (7)	0.0052 (5)	0.0019 (3)	0.0046 (6)	-0.0002 (7)	0.0032 (9)	0.0006 (8)
N(4)	0.9150 (6)	0.9789 (5)	0.1523 (7)	0.0042 (5)	0.0020 (3)	0.0046 (6)	-0.0008 (7)	0.0016 (9)	0.0009 (8)
C(1)	0.5993 (8)	0.8379 (6)	0.2299 (9)	3.5 (2)					
C(2)	0.4975 (9)	0.8099 (7)	0.2456 (10)	4.6 (3)					
C(3)	0.4112 (9)	0.8612 (7)	0.2188 (10)	4.7 (3)					
C(4)	0.4225 (9)	0.9357 (7)	0.1757 (10)	4.4 (3)					
C(5)	0.5200 (8)	0.9583 (6)	0.1666 (9)	3.2 (2)					
C(6)	0.5416 (9)	1.0410 (7)	0.1275 (10)	4.2 (3)					
C(21)	0.8459 (8)	0.9534 (6)	0.4018 (9)	3.4 (2)					
C(22)	0.8688 (9)	0.9882 (7)	0.5029 (10)	4.7 (3)					
C(23)	0.9265 (10)	0.9393 (8)	0.5887 (11)	5.7 (3)					
C(24)	0.9553 (10)	0.8630 (8)	0.5712 (11)	5.4 (3)					
C(25)	0.9253 (9)	0.8344 (7)	0.4717 (10)	4.8 (3)					
C(26)	0.9463 (9)	0.7462 (7)	0.4476 (10)	5.1 (3)					
C(31)	0.7295 (7)	0.8415 (6)	-0.0145 (8)	2.8 (2)					
C(32)	0.6964 (8)	0.8174 (6)	-0.1234 (9)	3.4 (2)					
C(33)	0.7127 (9)	0.7411 (8)	-0.1480 (10)	4.9 (3)					
C(34)	0.7595 (9)	0.6866 (7)	-0.0685 (10)	4.1 (3)					
C(35)	0.7892 (8)	0.7116 (6)	0.0344 (9)	3.3 (2)					
C(36)	0.8400 (9)	0.6579 (8)	0.1296 (10)	4.9 (3)					
C(41)	0.9974 (7)	0.9249 (6)	0.1756 (8)	2.9 (2)					
C(42)	1.1000 (8)	0.9435 (7)	0.1659 (9)	3.6 (2)					
C(43)	1.1200 (9)	1.0184 (7)	0.1323 (10)	4.6 (3)					
C(44)	1.0348 (8)	1.0770 (7)	0.1112 (9)	3.9 (2)					
C(45)	0.9349 (8)	1.0545 (6)	0.1211 (9)	3.3 (2)					
C(46)	0.8446 (8)	1.1105 (7)	0.1013 (9)	4.1 (3)					
C(100)	1.1317 (15)	0.6195 (12)	0.0121 (17)	10.7 (6)					

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

Intensity data were collected using graphite-monochromated Mo K α radiation and θ -2 θ scan rates varying from 4 to 24°/min depending on the intensity of the reflection. Background measurements were made at both limits of each scan. Three standard reflections were measured after every 97 data points. Data used were corrected for Lorentz and polarization effects. The function minimized during refinement was $\sum w(|F_o| - |F_c|)^2$ where a value of $\rho = 0.07$ was used in the previously defined expression of weights.²⁰ The discrepancy indexes used were

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$R_2 = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2}$$

The data reduction and structure refinement were carried out using the Enraf-Nonius structure determination package on the PDP 11/45 computer owned by Molecular Structure Corp.

The crystallographic data for all three compounds are summarized in Table I. The solution and refinement of each structure proceeded as follows.

Cr₂(mhp)₄·CH₂Cl₂. This structure was solved by conventional heavy-atom methods and refined to convergence using anisotropic thermal parameters for the Cr, O, and N atoms and isotropic thermal parameters for the C and Cl atoms. A final difference map had no peaks with intensity greater than 1 e/Å³. No effort was made to locate hydrogen atoms.

Mo₂(mhp)₄·CH₂Cl₂. Data were collected in the space group $P2_1/c$ but when it was recognized that the compound was isomorphous to the chromium compound, the structure of which had already been solved, a transformation was made to $P2_1/n$. There was a slight linear decline in the intensities of the standards (reaching about 15%) and a correction was made to all the data for this. Refinement was com-

menced immediately using atomic parameters from the chromium structure and carried smoothly to convergence with anisotropic thermal parameters for Mo, O, and N atoms only. Again the structure was verified by the absence of peaks exceeding 1 e/Å³ in a final difference map, and hydrogen atoms were omitted.

W₂(mhp)₄·CH₂Cl₂. The crystal used was lath-like but irregular and an absorption correction was applied using the empirical procedure based on ψ scans at $\chi \approx 90^\circ$. Nine sets of ψ -scan data were collected, each set consisting of a measurement every 10° from 0 to 350°. The range of normalized transmission factors was from 1.000 to 0.3995. Refinement was commenced directly, using the atomic positions already found for the chromium and molybdenum atoms; the remaining atoms were located in difference maps and all atoms were then refined anisotropically. The parameter $\beta(22)$ for N(1) persistently converged to a negative value so this atom was restricted to an isotropic thermal parameter. We attribute this behavior as well as the presence of 15 peaks with densities of 1–6 e/Å³ within 1.5 Å of the tungsten atoms to inaccuracies in the absorption correction. Hydrogen atoms were omitted.

The atomic positional and thermal parameters are given in Tables II–IV for the Cr, Mo, and W compounds, respectively. Tables of observed and calculated structure factors are available as supplementary material.

Spectra. Raman spectra were measured on a Cary Model 82 Raman spectrophotometer equipped with a Coherent Radiation Laboratory Model 53 argon ion laser. Samples were mixed with KBr and placed in a rotating sample holder. Most spectra were recorded using the 5145-Å line for excitation. Mass spectra were obtained on a CEC21-110B high-resolution mass spectrometer. The sample probe was maintained at 300 °C and the ionizing electron beam was at 70 eV. The calculated isotopic distribution patterns were obtained using a program provided by Dr. M. W. Extine of this laboratory.

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations for $W_2(\text{mhp})_4(\text{CH}_2\text{Cl}_2)^a$

atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W(1)	0.238 90 (6)	0.054 22 (5)	0.830 18 (5)	0.004 50 (4)	0.001 20 (2)	0.003 74 (4)	0.000 55 (6)	0.000 57 (7)	-0.000 04 (6)
W(2)	0.175 95 (6)	0.169 17 (5)	0.775 24 (5)	0.004 97 (4)	0.001 26 (2)	0.003 60 (4)	0.000 60 (6)	0.001 06 (7)	0.000 48 (5)
Cl(1)	0.383 (1)	0.0439 (7)	0.3909 (9)	0.022 (1)	0.0067 (5)	0.0139 (8)	-0.003 (1)	0.006 (2)	-0.004 (1)
Cl(2)	0.405 (1)	0.2105 (8)	0.4400 (9)	0.024 (1)	0.0074 (6)	0.0152 (9)	0.004 (1)	0.006 (2)	-0.006 (1)
O(4)	0.0270 (9)	0.1446 (8)	0.7946 (9)	0.0048 (7)	0.0019 (5)	0.0038 (6)	0.002 (1)	0.002 (1)	0.0027 (9)
O(3)	0.2842 (10)	0.0865 (7)	0.9862 (9)	0.0056 (8)	0.0013 (4)	0.0032 (7)	0.001 (1)	0.000 (1)	-0.0009 (9)
O(2)	0.2002 (10)	0.0043 (8)	0.6830 (9)	0.0066 (9)	0.0014 (4)	0.0039 (7)	0.003 (1)	0.001 (1)	0.0005 (10)
O(1)	0.3155 (10)	0.2068 (8)	0.7480 (9)	0.0059 (8)	0.0020 (5)	0.0045 (7)	0.002 (1)	0.003 (1)	0.0006 (11)
N(3)	0.224 (1)	0.2132 (10)	0.936 (1)	0.0057 (10)	0.0017 (6)	0.0053 (10)	0.001 (1)	0.001 (2)	0.000 (1)
N(2)	0.130 (1)	0.1261 (10)	0.618 (1)	0.0056 (10)	0.0024 (6)	0.0026 (7)	0.000 (1)	0.001 (1)	0.002 (1)
N(4)	0.388 (1)	0.0862 (8)	0.809 (1)	0.0048 (9)	0.0008 (5)	0.0028 (7)	0.001 (1)	0.001 (1)	0.000 (1)
N(1)	0.089 (1)	0.020 (1)	0.848 (1)	2.4 (3)					
C(1)	0.005 (2)	0.076 (1)	0.828 (1)	0.005 (1)	0.0043 (10)	0.0019 (9)	-0.001 (2)	-0.001 (2)	0.000 (2)
C(2)	-0.099 (2)	0.056 (1)	0.835 (2)	0.006 (1)	0.0037 (10)	0.0048 (11)	0.000 (2)	0.003 (2)	0.001 (2)
C(3)	-0.120 (2)	-0.021 (1)	0.867 (2)	0.008 (2)	0.0029 (9)	0.0061 (14)	-0.002 (2)	0.002 (2)	0.000 (2)
C(4)	-0.034 (2)	-0.075 (1)	0.888 (2)	0.007 (1)	0.0020 (8)	0.0058 (13)	-0.001 (2)	0.000 (2)	0.002 (2)
C(5)	0.064 (1)	-0.054 (1)	0.877 (1)	0.006 (1)	0.0016 (7)	0.0035 (10)	-0.001 (2)	0.000 (2)	0.001 (1)
C(6)	0.159 (2)	-0.111 (1)	0.901 (2)	0.008 (2)	0.0016 (7)	0.0127 (19)	0.002 (2)	0.007 (3)	0.003 (2)
C(21)	0.269 (1)	0.159 (1)	1.012 (1)	0.004 (1)	0.0020 (7)	0.0037 (10)	-0.002 (1)	0.001 (2)	0.001 (1)
C(22)	0.302 (2)	0.183 (1)	1.123 (1)	0.006 (1)	0.0027 (8)	0.0036 (11)	0.000 (2)	-0.001 (2)	-0.001 (2)
C(23)	0.288 (2)	0.260 (1)	1.147 (2)	0.011 (2)	0.0029 (10)	0.0057 (12)	-0.002 (2)	0.006 (2)	-0.002 (2)
C(24)	0.239 (2)	0.314 (1)	1.066 (2)	0.014 (2)	0.0016 (8)	0.0053 (12)	0.000 (2)	0.006 (2)	-0.001 (2)
C(25)	0.209 (2)	0.289 (1)	0.962 (2)	0.007 (1)	0.0016 (7)	0.0089 (15)	-0.001 (2)	0.004 (2)	0.002 (2)
C(26)	0.165 (2)	0.345 (1)	0.871 (2)	0.012 (2)	0.007 (6)	0.0055 (13)	0.000 (2)	0.002 (3)	0.002 (2)
C(31)	0.155 (2)	0.046 (1)	0.601 (1)	0.008 (1)	0.0024 (8)	0.0031 (9)	0.000 (2)	0.004 (2)	-0.001 (1)
C(32)	0.130 (2)	0.014 (1)	0.496 (2)	0.009 (2)	0.0028 (9)	0.0059 (13)	-0.002 (2)	0.004 (2)	-0.004 (2)
C(33)	0.076 (2)	0.060 (2)	0.412 (2)	0.012 (2)	0.0054 (13)	0.0043 (14)	-0.002 (3)	-0.005 (3)	0.003 (2)
C(34)	0.046 (2)	0.140 (2)	0.428 (2)	0.013 (2)	0.0037 (11)	0.0048 (14)	-0.001 (3)	0.000 (3)	0.000 (2)
C(35)	0.078 (2)	0.167 (2)	0.531 (2)	0.007 (2)	0.0040 (11)	0.0054 (14)	0.000 (2)	0.001 (2)	0.000 (2)
C(36)	0.054 (2)	0.252 (1)	0.555 (2)	0.012 (2)	0.0027 (9)	0.0041 (12)	0.004 (2)	0.000 (3)	0.002 (2)
C(41)	0.401 (1)	0.163 (1)	0.769 (1)	0.005 (1)	0.0026 (8)	0.0044 (11)	-0.002 (2)	0.001 (2)	0.000 (2)
C(42)	0.499 (2)	0.188 (1)	0.753 (2)	0.007 (1)	0.0033 (9)	0.0072 (14)	-0.003 (2)	0.005 (2)	-0.002 (2)
C(43)	0.588 (2)	0.140 (2)	0.779 (2)	0.008 (1)	0.0051 (12)	0.0097 (17)	-0.001 (2)	0.007 (2)	-0.002 (3)
C(44)	0.576 (2)	0.064 (1)	0.823 (2)	0.006 (1)	0.0034 (10)	0.0071 (14)	0.003 (2)	0.004 (2)	-0.001 (2)
C(45)	0.478 (2)	0.041 (1)	0.833 (2)	0.006 (1)	0.0028 (9)	0.0055 (12)	0.000 (2)	0.002 (2)	-0.002 (2)
C(46)	0.461 (2)	-0.041 (1)	0.872 (2)	0.007 (2)	0.0020 (8)	0.0082 (17)	0.002 (2)	-0.001 (3)	-0.001 (2)
C- (100)	0.379 (3)	0.112 (2)	0.489 (2)	0.031 (3)	0.0173 (19)	0.0130 (21)	-0.036 (4)	0.026 (4)	-0.023 (3)

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

Results and Discussion

Preparation and General Properties. For the chromium and molybdenum compounds, which were prepared first, we chose the obvious method of ligand displacement, using an mhp salt, from compounds already containing the Cr_2 and Mo_2 units, namely, the readily available acetates. In the chromium case the hydrated acetate, $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$, is more conveniently obtained and handled than the anhydrous compound and reacts quite well to give a product that retains 1 mol of H_2O per mole of dinuclear product. This water can be expelled by heating in vacuo at 100 °C without change in the color of the compound, and the anhydrous compound can be prepared directly using anhydrous dichromium tetraacetate. We believe that these water molecules are interstitial, like the CH_2Cl_2 molecules which are incorporated when each of the three compounds is recrystallized from dichloromethane, and not coordinated to the chromium atoms. As the structure shows, the axial positions of the $\text{M}_2(\text{mhp})_4$ molecules are blocked by the methyl groups of the ligands.

The molybdenum compound is obtained directly in unsolvated form employing $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ as starting material, but upon recrystallization from dichloromethane $\text{Mo}_2(\text{mhp})_4\cdot\text{CH}_2\text{Cl}_2$ is obtained.

Because of the lack of any simple ditungsten tetracarboxylates or other convenient W_2^{4+} -containing substance to use as a starting material, the neutral ligand, Hmhp, was allowed to react with $\text{W}(\text{CO})_6$ in refluxing diglyme. This reaction is

practically quantitative (see below) in a period of 6 h to give a burgundy-red solution and much microcrystalline, deep red, solid product. It has since been found that $\text{Cr}_2(\text{mhp})_4$ and $\text{Mo}_2(\text{mhp})_4$ can also be prepared in this manner with the following order of reactivity: $\text{Cr}(\text{CO})_6 < \text{Mo}(\text{CO})_6 < \text{W}(\text{CO})_6$. Details of these reactions will be reported later upon the completion of a more general study of the reactions of metal carbonyls with Hmhp.

There is an important point to be emphasized here concerning the yield of $W_2(\text{mhp})_4$. Isolated yields are >95% and it is evident that the reaction is essentially quantitative. This is in sharp contrast to the reactions of $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ with acetic acid, either with diglyme as solvent or simply in excess of acetic acid, where only 20–80% of the molybdenum (depending on conditions) is converted to $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, and no simple dinuclear tungsten product has been found.²¹

The stabilities of all three products are remarkably high. The Cr and Mo compounds appear to be stable toward dry air at 25 °C indefinitely, though the W compound shows evidence of decomposition after 2 days. The Mo compound appears to react slowly with air that is saturated with moisture so that after 3 days superficial discoloration of the orange material is clearly evident. For the chromium compound, exposure to moisture-saturated air causes a slight greenish tinge to appear after about 10 days.

All three compounds appear to have excellent thermal stability, as shown by the fact that the mass spectra were recorded using probe temperatures of 300 °C.

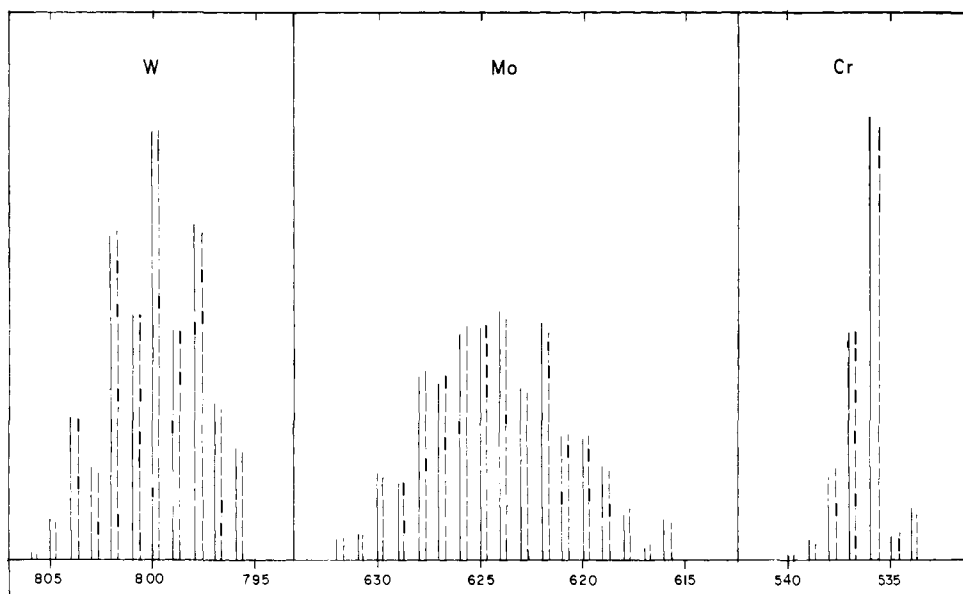


Figure 1. The observed (—) and calculated (---) parent-ion multiplets in the mass spectra of the three $M_2(\text{mhp})_4$ molecules with $M = \text{W}$ (left), Mo (center), and Cr (right). The mass numbers are given on the horizontal axis and the height of each line is proportional to the percentage of the entire multiplet intensity that it represents.

Mass Spectra. Strong parent ion multiplets, shown in Figure 1, are observed for each compound and afford conclusive evidence for the existence in the vapor phase of molecules with the proposed formulas. As shown in Figure 1, the isotopic distribution patterns observed in the parent ion peaks, as well as the mass numbers themselves, are uniquely characteristic of dinuclear species and agree perfectly with the calculated patterns.²⁵

Relatively few other fragments are observed in the mass spectra. For the Mo and W compounds doubly charged parent ion peaks are fairly prominent but for the Cr compound the corresponding peak is very weak and is overlaid by another whose pattern shows that it is derived from a singly charged Cr_2 -containing ion, the remainder of which has a principal mass number of 168. We cannot suggest any uniquely appealing formula for this. The W compound also gave a multiplet consistent with W_2O . All three compounds gave peaks corresponding to $\text{C}_6\text{H}_6\text{NO}$, the ligand radical.

Structures. Each of the three compounds was recrystallized from dichloromethane to give solvated crystals, $M_2(\text{mhp})_4 \cdot \text{CH}_2\text{Cl}_2$, which are isomorphous. The $M_2(\text{mhp})_4$ molecules reside on general positions in the unit cell and have no crystallographically imposed symmetry. However, they approximate very closely to D_{2d} symmetry, as can be seen in Figure 2, which shows the $\text{Mo}_2(\text{mhp})_4$ molecule. This figure also defines the atomic numbering scheme, which follows the same pattern for all three compounds. The bond lengths and bond angles are listed in Tables V and VI, respectively. The CH_2Cl_2 molecules are packed between the $M_2(\text{mhp})_4$ molecules, as shown in Figure 3, and do not have any significant effect on the structure or bonding within the latter.

The arrangement of the ligands in these molecules is in distinct contrast to that observed in the $M_2(\text{DMP})_4$ ($\text{DPM} = 2,6$ -dimethoxyphenyl, **3**) compounds²⁶ and several related

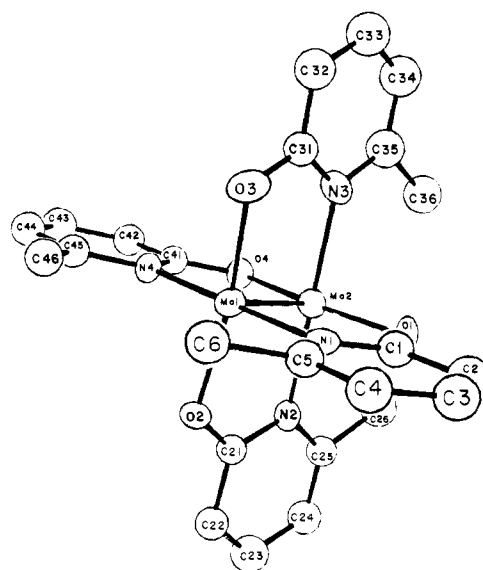


Figure 2. An ORTEP drawing of the $\text{Mo}_2(\text{mhp})_4$ molecule in which each atom is represented by its ellipsoid of thermal vibration scaled to enclose 50% of the electron density. The atom numbering scheme is shown and applies mutatis mutandis to the Cr and W compounds as well.

ones²⁷⁻³⁰ in which the ligating atoms are C and O rather than N and O . These *o*-oxophenyl ligands are arranged so that $\text{M}-\text{C}$ bonds are trans to $\text{M}-\text{O}$ bonds, thus leading to overall C_{2h} molecular symmetry, **4**, whereas in the present case the $\text{M}-\text{N}$ and $\text{M}-\text{O}$ bonds are trans to their own kind, thus leading to overall D_{2d} symmetry, **5**.

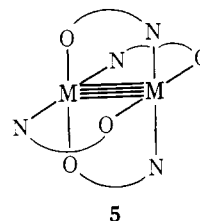
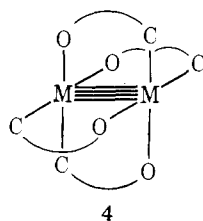
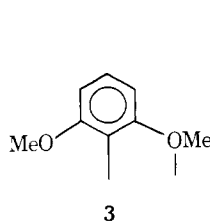


Table V. Bond Distances for the $M_2(mhp)_4 \cdot CH_2Cl_2$ Compounds (Å)

	Cr	Mo	W
M(1)-M(2)	1.889 (1)	2.065 (1)	2.161 (1)
M(1)-O(2)	1.962 (3)	2.076 (6)	2.038 (8)
M(1)-O(3)	1.982 (3)	2.093 (5)	2.036 (9)
M(2)-O(1)	1.971 (3)	2.092 (5)	2.047 (9)
M(2)-O(4)	1.960 (3)	2.084 (5)	2.028 (9)
M(1)-N(1)	2.072 (4)	2.176 (6)	2.10 (1)
M(1)-N(4)	2.062 (4)	2.143 (6)	2.09 (1)
M(2)-N(2)	2.070 (4)	2.171 (7)	2.16 (1)
M(2)-N(3)	2.064 (4)	2.177 (7)	2.11 (1)
O(1)-C(1)	1.303 (6)	1.287 (9)	1.30 (2)
C(1)-N(1)	1.347 (7)	1.33 (1)	1.42 (2)
C(1)-C(2)	1.404 (8)	1.47 (1)	1.40 (2)
C(2)-C(3)	1.412 (9)	1.39 (1)	1.42 (2)
C(3)-C(4)	1.397 (9)	1.41 (1)	1.40 (2)
C(4)-C(5)	1.365 (8)	1.36 (1)	1.36 (2)
C(5)-N(1)	1.364 (7)	1.36 (1)	1.36 (2)
C(5)-C(6)	1.519 (8)	1.54 (1)	1.53 (2)
O(2)-C(21)	1.308 (6)	1.29 (1)	1.31 (2)
C(21)-N(2)	1.340 (7)	1.33 (1)	1.36 (2)
C(21)-C(22)	1.401 (8)	1.41 (1)	1.46 (2)
C(22)-C(23)	1.402 (9)	1.44 (1)	1.37 (2)
C(23)-C(24)	1.377 (9)	1.38 (1)	1.41 (2)
C(24)-C(25)	1.363 (9)	1.35 (1)	1.38 (2)
C(25)-N(2)	1.368 (7)	1.40 (1)	1.35 (2)
C(25)-C(26)	1.543 (9)	1.57 (1)	1.51 (2)
O(3)-C(31)	1.291 (6)	1.281 (9)	1.28 (2)
C(31)-N(3)	1.359 (6)	1.36 (1)	1.43 (2)
C(31)-C(32)	1.405 (7)	1.44 (1)	1.44 (2)
C(32)-C(33)	1.376 (8)	1.36 (1)	1.38 (3)
C(33)-C(34)	1.402 (8)	1.41 (1)	1.44 (3)
C(34)-C(35)	1.378 (8)	1.37 (1)	1.38 (2)
C(35)-N(3)	1.375 (7)	1.38 (1)	1.35 (2)
C(35)-C(36)	1.523 (8)	1.55 (1)	1.53 (2)
O(4)-C(41)	1.281 (6)	1.295 (9)	1.30 (2)
C(41)-N(4)	1.381 (6)	1.380 (9)	1.43 (2)
C(41)-C(42)	1.413 (8)	1.40 (1)	1.40 (2)
C(42)-C(43)	1.381 (8)	1.39 (1)	1.38 (3)
C(43)-C(44)	1.409 (8)	1.46 (1)	1.44 (3)
C(44)-C(45)	1.356 (8)	1.39 (1)	1.36 (2)
C(45)-N(4)	1.365 (6)	1.39 (1)	1.36 (2)
C(45)-C(46)	1.510 (8)	1.48 (1)	1.51 (3)
C(100)-Cl(1)	1.72 (1)	1.81 (2)	1.74 (3)
C(100)-Cl(2)	1.85 (1)	1.78 (2)	1.85 (3)

The lengths of the M-M quadruple bonds are noteworthy, especially in the case of the tungsten compound. For $Cr_2(mhp)_4$, the distance of 1.889 (1) Å is greater than those found for $Cr_2(DMP)_4^{26}$ and related species²⁶⁻³⁰ containing *o*-oxophenyl ligands, which are in the range 1.828 (2) to 1.862 (1) Å, but it is still among the "exceedingly short" ones, the next shortest being that³¹ in $Cr_2(C_4H_8)^{4-}$, which, at 1.975 (5) Å, is nearly 0.10 Å longer. The Mo-Mo distance is essentially the same as that²⁶ in $Mo_2(DMP)_4$, 2.064 (1) Å, which is the shortest Mo-Mo bond length previously reported. The W-W distance of 2.161 (1) Å is far shorter than any previously observed W-W distance. In the $W_2(CH_3)_8^{4-}$ and $[W_2(CH_3)_x \cdot Cl_{8-x}]^{4-}$ species¹⁶ the distances are about 2.26 Å, while the numerous W-W triple bond distances^{7,8} range from 2.26 Å to 2.30 Å. The shortest known Re-Re quadruple bond distances are also longer, namely, 2.178 (1) Å in the $Re_2(CH_3)_8^{2-}$ ion³² and 2.177 (2) Å in $Re_2Cl_4(PhNCPPhNPh)_2$.³³ This W-W distance is therefore the shortest known internuclear distance between any two atoms in the third transition series.⁴²

The M-O and M-N distances observed in the chromium and molybdenum $M_2(mhp)_4$ molecules are compared with the lengths of such bonds found previously in other quadruply bonded M-M compounds in Table VII. The most striking fact

Table VI. Bond Angles for the $M_2(mhp)_4 \cdot CH_2Cl_2$ Compounds (deg)

	Cr	Mo	W
M(1)-M(2)-O(1)	99.1 (1)	95.3 (2)	93.6 (2)
M(2)-M(1)-O(2)	99.5 (1)	95.4 (2)	94.4 (3)
M(2)-M(1)-O(3)	99.2 (1)	95.5 (1)	94.7 (3)
M(1)-M(2)-O(4)	98.6 (1)	95.0 (1)	93.7 (3)
M(2)-M(1)-N(1)	91.4 (1)	90.3 (2)	90.4 (3)
M(1)-M(2)-N(2)	91.1 (1)	89.3 (2)	90.0 (3)
M(1)-M(2)-N(3)	91.6 (1)	90.4 (2)	89.9 (3)
M(2)-M(1)-N(4)	92.5 (1)	90.7 (2)	90.2 (3)
O(1)-M(2)-O(4)	162.3 (1)	169.6 (2)	172.7 (4)
O(2)-M(1)-O(3)	161.3 (2)	169.1 (2)	170.9 (4)
O(1)-M(2)-N(2)	90.0 (2)	90.0 (2)	89.7 (4)
O(1)-M(2)-N(3)	89.7 (2)	90.0 (2)	90.4 (4)
O(2)-M(1)-N(1)	89.5 (2)	89.9 (2)	90.1 (4)
O(2)-M(1)-N(4)	89.5 (2)	90.0 (2)	91.4 (4)
O(3)-M(1)-N(1)	89.7 (1)	90.2 (2)	88.7 (4)
O(3)-M(1)-N(4)	90.0 (2)	89.8 (2)	89.7 (4)
O(4)-M(2)-N(2)	89.6 (2)	89.8 (2)	90.9 (4)
O(4)-M(2)-N(3)	90.0 (2)	90.2 (2)	89.0 (4)
N(1)-M(1)-N(4)	176.1 (2)	179.0 (2)	178.3 (4)
N(2)-M(2)-N(3)	177.3 (2)	179.7 (2)	179.9 (5)
M(2)-O(1)-C(1)	116.1 (3)	117.1 (5)	121 (1)
O(1)-C(1)-N(1)	117.0 (4)	120.8 (8)	116 (1)
O(1)-C(1)-C(2)	121.7 (5)	118.9 (8)	122 (1)
N(1)-C(1)-C(2)	121.3 (5)	120.2 (8)	121 (1)
C(1)-C(2)-C(3)	118.0 (6)	117.3 (8)	120 (2)
C(2)-C(3)-C(4)	119.3 (6)	120.2 (9)	117 (1)
C(3)-C(4)-C(5)	119.5 (6)	119.0 (8)	121 (1)
C(4)-C(5)-N(1)	121.4 (5)	122.6 (8)	124 (1)
C(4)-C(5)-C(6)	122.7 (5)	122.6 (8)	123 (1)
N(1)-C(5)-C(6)	115.8 (5)	114.8 (7)	113 (1)
M(1)-N(1)-C(1)	116.3 (3)	116.3 (5)	118 (1)
M(1)-N(1)-C(5)	123.5 (4)	123.1 (6)	125 (1)
C(1)-N(1)-C(5)	120.2 (4)	120.6 (7)	116 (1)
M(1)-O(2)-C(21)	115.8 (3)	119.2 (5)	119 (1)
O(2)-C(21)-N(2)	117.1 (5)	117.3 (8)	121 (1)
O(2)-C(21)-C(22)	120.8 (5)	118.9 (8)	119 (1)
N(2)-C(21)-C(22)	122.2 (5)	123.7 (8)	120 (1)
C(21)-C(22)-C(23)	117.4 (6)	115.5 (9)	117 (1)
C(22)-C(23)-C(24)	120.1 (7)	121 (1)	121 (1)
C(23)-C(24)-C(25)	119.4 (7)	118 (1)	119 (1)
C(24)-C(25)-N(2)	121.8 (6)	123.5 (9)	121 (1)
C(24)-C(25)-C(26)	122.8 (6)	121 (1)	122 (1)
N(2)-C(25)-C(26)	115.4 (5)	115.5 (9)	117 (1)
M(2)-N(2)-C(21)	116.5 (3)	118.7 (6)	116 (1)
M(2)-N(2)-C(25)	124.5 (4)	123.7 (6)	123 (1)
C(21)-N(2)-C(25)	119.1 (5)	117.7 (8)	121 (1)
M(1)-O(3)-C(31)	115.6 (3)	118.1 (5)	120 (1)
O(3)-C(31)-N(3)	117.7 (4)	119.5 (8)	118 (1)
O(3)-C(31)-C(32)	121.8 (5)	120.1 (8)	122 (1)
N(3)-C(31)-C(32)	120.4 (5)	120.4 (7)	120 (1)
C(31)-C(32)-C(33)	119.1 (5)	118.6 (9)	119 (2)
C(32)-C(33)-C(34)	120.9 (6)	121 (1)	122 (2)
C(33)-C(34)-C(35)	117.9 (6)	118.8 (9)	115 (2)
C(34)-C(35)-N(3)	121.9 (5)	122.0 (8)	127 (2)
C(34)-C(35)-C(36)	122.9 (5)	124.3 (8)	119 (2)
N(3)-C(35)-C(36)	115.2 (5)	113.7 (8)	113 (1)
M(2)-N(3)-C(31)	115.8 (3)	116.5 (5)	117 (1)
M(2)-N(3)-C(35)	124.4 (3)	124.2 (6)	126 (1)
C(31)-N(3)-C(35)	119.8 (4)	119.3 (7)	117 (1)
M(2)-O(4)-C(41)	117.1 (3)	119.5 (5)	122 (1)
O(4)-C(41)-N(4)	117.4 (4)	116.6 (7)	116 (1)
O(4)-C(41)-C(42)	123.8 (5)	121.5 (7)	123 (1)
N(4)-C(41)-C(42)	118.9 (5)	121.9 (8)	121 (1)
C(41)-C(42)-C(43)	120.4 (5)	119.5 (8)	121 (2)
C(42)-C(43)-C(44)	118.7 (5)	119.2 (8)	117 (2)
C(43)-C(44)-C(45)	120.2 (5)	118.3 (8)	120 (2)
C(44)-C(45)-N(4)	121.5 (5)	122.0 (7)	125 (2)
C(44)-C(45)-C(46)	123.5 (5)	121.5 (8)	121 (1)
N(4)-C(45)-C(46)	115.1 (5)	116.5 (7)	114 (1)
M(1)-N(4)-C(41)	114.4 (3)	118.2 (5)	119 (1)
M(1)-N(4)-C(45)	125.2 (3)	122.7 (5)	126 (1)
C(41)-N(4)-C(45)	120.4 (4)	119.1 (6)	116 (1)
Cl(1)-C(100)-Cl(2)	108.4 (6)	106.3 (9)	108 (1)

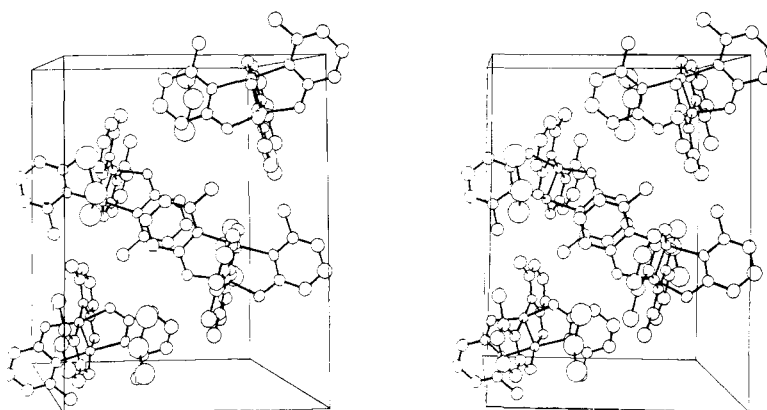


Figure 3. An ORTEP stereographic view of the unit cell of $\text{Mo}_2(\text{mhp})_4(\text{CH}_2\text{Cl}_2)$.

Table VII. Metal-Ligand Bond Lengths in Various Quadruply Bonded Dinuclear Compounds

bond	mean ^a length, Å, in			
	$\text{M}_2(\text{mhp})_4$	$\text{M}_2(\text{O}_2\text{CCH}_3)_4$	$\text{M}_2(\text{DMP})_4$	$\text{M}_2(\text{PhNCPPhNPh})_4$
Cr-O	1.969 (10)	2.011 (19) ^b	2.134 (7) ^{d,e}	
Mo-O	2.086 (8)	2.119 (13) ^c	2.269 (13) ^d	
Mo-N	2.167 (16)			2.147 (16) ^{f,g}

^a $\langle l \rangle = [(\sum l^2)/N]^{1/2}$; $\sigma \langle l \rangle = [\sum (\Delta l)^2 / (N - 1)]^{1/2}$. ^b F. A. Cotton, C. E. Rice, and G. W. Rice, *J. Am. Chem. Soc.*, **99**, 4704 (1977). ^c F. A. Cotton, Z. C. Mester, and T. R. Webb, *Acta Crystallogr., Sect. B*, **30**, 2768 (1974). ^d Reference 26. ^e For Cr-O the distances in $\text{Cr}_2(\text{TMP})_4$ as well as those in $\text{Cr}_2(\text{DMP})_4$ were averaged. ^f F. A. Cotton, T. Inglis, M. Kilner, and T. R. Webb, *Inorg. Chem.*, **14**, 2023 (1975). ^g In the recently reported $\text{Mo}_2\text{Cl}_2(\text{PEt}_3)_2(\text{C}_7\text{H}_5\text{N}_2)_2$ the mean Mo-N distance is 2.145 (14) Å. Cf. F. A. Cotton, D. G. Lay, and M. Millar, *Inorg. Chem.*, **17**, 186 (1978).

is that the M-O bonds in the $\text{M}_2(\text{DMP})_4$ compounds are distinctly longer than all the other M-O bonds. The differences between M-O bonds in the $\text{M}_2(\text{mhp})_4$ and $\text{M}_2(\text{O}_2\text{CCH}_3)_4$ compounds, 0.042 (21) and 0.033 (15) Å for the Cr and Mo pairs, respectively, are probably real, but certainly small, and there is no significant difference in the Mo-N distances in the two compounds compared. However, for the $\text{M}_2(\text{DMP})_4$ molecules the Cr-O and Mo-O distances are about 0.15 Å larger than in the other cases. Our suggestion is that the M-O and M-N distances in the $\text{M}_2(\text{mhp})_4$ molecules are normal while the M-O distances in the $\text{M}_2(\text{DMP})_4$ molecules are lengthened by the strong trans influence of the M-C bonds, as we have already suggested.²⁶

The lengths of the W-O and W-N bonds are of unusual interest. The mean W-O distance, 2.037 (8) Å, is significantly shorter, viz., 0.049 (12) Å, than the mean Mo-O distance, and the mean W-N distance, 2.115 (12) Å, is 0.052 (17) Å shorter than the Mo-N distance. It would be generally expected for Mo-X and W-X bonds, where X is some univalent, nonmetallic atom and the comparison is made using homologous compounds with identical formal oxidation numbers, that we should find $l_{\text{W-X}} \geq l_{\text{Mo-X}}$. Indeed, in a variety of common situations this is observed, although $l_{\text{W-X}}$ is generally not much greater than $l_{\text{Mo-X}}$ because of the effect of the lanthanide contraction.

There have been few other opportunities to make a similar comparison among species with multiple M-M bonds since compounds containing quadruple W-W bonds are so scarce. Indeed the $\text{M}_2(\text{CH}_3)_8^{4-}$ ions afford the only other pair and here the errors are rather large¹⁶ so that it can only be said that the two distances, 2.29 (1) Å for Mo-C and 2.32 (2) Å for W-C, are equal within a rather large uncertainty. There could be a real difference as large as 0.05 Å, either way, without exceeding 3σ.

If we turn to $\text{Mo}\equiv\text{Mo}$ and $\text{W}\equiv\text{W}$ compounds two comparisons are possible. Thus, for the $\text{M}_2\text{Cl}_2(\text{NMe}_2)_4$ the W-Cl distance,³⁴ 2.329 (5) Å, is very likely a little smaller than the

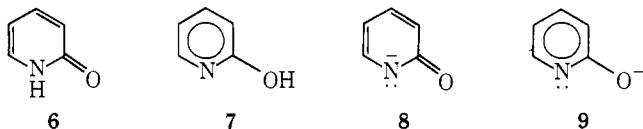
Mo-Cl distance,³⁴ 2.348 (5) Å, since the difference is 0.019 (7) Å. However, the M-C distances are indistinguishable in $\text{Mo}_2(\text{CH}_3)_2(\text{NMe}_2)_4$, 2.175 (8) Å,³⁵ and $\text{W}_2(\text{CH}_3)_2(\text{NEt}_2)_4$, 2.171 (11) Å,³⁶ though again the uncertainties are large enough to mask a small difference. It may also be noted that the M-O distances in the two $\text{M}_2(\text{O}_2\text{CCMe}_3)_4\text{Cl}_2$ compounds with M = Tc, Re are such that $l_{\text{Tc-O}} - l_{\text{Re-O}} = 0.007$ (6) Å. Thus, while there is no precedent for the relationship found here for the Mo-X and W-X bond lengths, the relationship $l_{\text{Mo-X}} - l_{\text{W-X}} \approx 0.05$ Å is not grossly out of line with the relationships seen in the few other cases available. We are dealing here with the shortest of Mo-Mo and W-W quadruple bonds (shorter by ca. 0.10 Å in comparison to the corresponding $\text{M}_2(\text{CH}_3)_8^{4-}$ species, for example) and this may well have unpredictable effects on other aspects of the stereochemistry about the Mo and W atoms.

Raman Spectra. In view of the remarkably short M-M distances, the M-M stretching frequencies, which are manifested in the Raman spectra, are of considerable interest. We shall deal with the vibrational spectra in more detail in the future, but there is no difficulty in identifying very strong lines at 556, 425, and 295 cm^{-1} (all ± 3 cm^{-1}) for the Cr, Mo, and W compounds, respectively, as the "M-M stretching modes". Previous studies of other quadruply bonded M-M compounds³⁷ have shown that the observed frequency of the normal mode gives a very good measure of the intrinsic "M-M" frequency. On this basis, using the harmonic oscillator approximation the following force constants are obtained: Cr-Cr, 4.73 $\text{mdyn}/\text{Å}$; Mo-Mo, 5.10 $\text{mdyn}/\text{Å}$; W-W, 4.71 $\text{mdyn}/\text{Å}$.

The Cr-Cr stretching frequency, 556 cm^{-1} , is by a long margin the highest metal-metal stretching frequency ever recorded, although it may be expected that even higher ones occur in the compounds, such as $\text{Cr}_2(\text{DMP})_4$, that have even shorter Cr-Cr bonds.²⁶⁻³⁰ The Mo-Mo stretching frequency, 425 cm^{-1} , is greater than the highest one previously reported,^{37a} namely, 406 cm^{-1} in $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, in keeping with the fact that the present Mo-Mo bond is some 0.03 Å shorter

than that in the acetate. The W-W stretching frequency, 295 cm^{-1} , is higher than any previously reported frequency for a quadruple Re-Re bond, for which values in the range 275–289 cm^{-1} have been found.³⁷

Bonding in the Ligand Rings. It is well known that molecules for which the two tautomeric forms **6** and **7** can be written ordinarily prefer **6**, and this is certainly true for the pyridone system itself³⁸ and its derivatives, as well as for the more elaborate but basically comparable pyrimidine bases (uracil, thymine, cytosine) that occur in nucleic acids.³⁹ However, less is known about the preferred form of the anionic species, i.e., about the relative stabilities of the two extreme forms **8** and **9** in the case of pyridone itself.



Our structural results are best accommodated by an electron distribution corresponding to a roughly equal mixture of **8** and **9**. For systems of type **6** and their pyrimidine-base relatives, C-O distances are in the range 1.21–1.24 Å with 1.215 Å being about the average.^{39,40} For aromatic alcohols a C-O distance of about 1.36 Å is typical. The average C-O distances in our compounds (Table V) are 1.296 (12), 1.29 (1), and 1.30 (2) Å for the Cr, Mo, and W compounds, respectively. These are just about halfway between the characteristic values for the extreme structures. Within the rings themselves, the C-C and C-N distances are indicative of delocalization comparable to that in pyridine itself. Only for the Cr compound are these distances accurately known. Reading around the ring in the order N-C(O), C(O)-C, . . . , C-N, we have 1.36 (2), 1.406 (5), 1.39 (2), 1.40 (1), 1.37 (1), and 1.368 (5) Å, which may be compared with the corresponding distances 1.340, 1.395, and 1.394 Å (these being the only independent ones) for pyridine⁴¹ itself.

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Supplementary Material Available: Tables of observed and calculated structure factors (39 pages). Ordering information is given on any current masthead page.

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- Beginning immediately with the isolation of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ by reaction of $\text{Mo}(\text{CO})_6$ with anhydrous acetic acid, Wilkinson (private communication) examined the corresponding reaction of $\text{W}(\text{CO})_6$ and found that there was no comparable product. Subsequently many other workers, a few of whom are listed below,¹²⁻¹⁵ have also tried in various ways to prepare and document conclusively (i.e., by crystallography) quadruply bonded W_2 species, especially the $\text{W}_2(\text{O}_2\text{CR})_4$ types, without success.
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- NOTE ADDED IN PROOF. More recent work by Brian E. Hanson has led to the preparation and characterization of $\text{MoW}(\text{mhp})_4$. The Mo-W distance, 2.091 (1) Å, makes this by far the shortest metal-metal bond in which W has been found to participate. In $\text{MoW}(\text{O}_2\text{CCMe}_2)_4(\text{CH}_3\text{CN})$ [V. Katovic, J. L. Templeton, R. J. Hoxmeier, and R. E. McCarley, *J. Am. Chem. Soc.*, **97**, 5300 (1975)], the Mo-W distance is 2.194 (2) Å. We have characterized this molecule also by its UPS spectrum (collaboration with Professor A. Cowley), Raman spectrum, and mass spectrum.