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A Set of Homologous Quadruply Bonded Molecules of Dichromium(II), Dimolybdenum(II), and Ditungsten(II) with the Ligand 2,4-Dimethyl-6-hydroxypyrimidine

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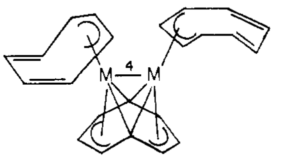
The hexacarbonyls of chromium, molybdenum, and tungsten react with 2,4-dimethyl-6-hydroxypyrimidine, Hdmhp, in refluxing diglyme to give the $M_2(dmhp)_4$ molecules. These crystallize from diglyme solution in two crystal forms. Form I crystals, obtained within the first 12 h, have the composition $M_2(dmhp)_4\cdot{}^1/_2$(diglyme) and belong to space group $P2_1/n$ with the following unit cell dimensions, where values for the Cr and W compounds are given in that order: a = 14.655 (4), 14.783 (3) Å; b = 14.881 (4), 14.929 (3) Å; c = 14.415 (4), 14.521 (4) Å; β = 90.43 (2), 90.00°. It was not possible to refine the disordered solvent molecules in these crystals. Form II crystals, obtained over a longer period of time, have the composition $M_2(dmhp)_4$·diglyme. These belong to the space group $P2_1/c$ and have the following unit cell dimensions, where values for the Cr, Mo, and W compounds are given in that order: a = 11.502 (3), 11.538 (1), 11.544 (3) Å; b = 9.702 (2), 9.739 (1), 9.742 (2) Å; c = 31.372 (8), 31.659 (4), 31.583 (8) Å; β = 98.55 (2), 98.22 (1), 98.18 (2)°. These form II structures were refined to R_1 values of 0.073, 0.049, and 0.043 for the Cr, Mo, and W compounds, respectively. The metal-metal distances are Cr–Cr = 1.907 (3) Å, Mo–Mo = 2.072 (1) Å, and W–W = 2.163 (1) Å. The $M_2(dmhp)_4$ molecules have virtual D_{2d} symmetry, although there is no crystallographically imposed symmetry since there is one entire molecule in the asymmetric unit.

Introduction

Within the past two years two of the most remarkable developments that have occurred in the field of metal-to-metal multiple bonds are (1) the discovery[1] that certain ligands promote the formation of extremely short $\mathrm{Cr}\overset{4}{-}\mathrm{Cr}$ bonds (≤1.90 Å) and (2) that very stable compounds containing $\mathrm{W}\overset{4}{-}\mathrm{W}$ quadrupole bonds can be made.[2,3] While the number of ligands pertinent to point (1) is large,[4] and they are of diverse types, there have still been only three reported cases of stable $\mathrm{W}\overset{4}{-}\mathrm{W}$ containing compounds, namely, those of types **1**,[2] **2**,[3] and **3**.[5] For each of these types Cr and Mo homologues are also known. However, only for types **2** and **3** do the chromium compounds contain exceedingly short bonds.

In this paper we report another type of compound for which the complete set of Cr, Mo, and W compounds has been obtained. In this set we again have a rather stable tungsten compound with a $\mathrm{W}\overset{4}{-}\mathrm{W}$ bond and a chromium compound with a $\mathrm{Cr}\overset{4}{-}\mathrm{Cr}$ bond that is, within experimental error, on the threshold of being in the extremely short range, nominally bounded by 1.90 Å.



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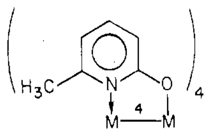

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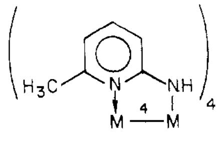

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Experimental Section

Preparation. These compounds are best made with an excess of the metal carbonyl; otherwise there is a considerable amount of unreacted ligand. In a typical reaction, 15 mmol of Hdmhp (2,4-dimethyl-6-hydroxypyrimidine) and 10 mmol of the metal carbonyl are refluxed in 75 mL of distilled diglyme, bis(2-methoxyethyl) ether, for 12–16 h. In the case of the chromium compound, it is necessary

Table I. Crystal Data[a]

	form I, $M_2O_4N_8C_{24}H_{28}\cdot{}^1/_2O_3C_6H_{14}$		form II, $M_2O_4N_8C_{24}H_{28}\cdot O_3C_6H_{14}$		
	Cr	W	Cr	Mo	W
mol wt	663.62	927.33	730.71	818.60	994.42
a, Å	14.655 (4)	14.783 (3)	11.502 (3)	11.538 (1)	11.544 (3)
b, Å	14.881 (4)	14.929 (3)	9.702 (2)	9.739 (1)	9.742 (2)
c, Å	14.415 (4)	14.521 (4)	31.372 (8)	31.659 (4)	31.583 (8)
β, deg	90.43 (2)	90.00 (2)	98.55 (2)	98.22 (1)	98.18 (2)
V, Å^3	3143.5	3204.7	3462.0	3520.9	3515.7
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Z	4	4	4	4	4
d_{calcd}, g cm^{-3}	1.42	1.94	1.40	1.54	1.88
μ, cm^{-1}	7.76	76.56	7.14	7.58	69.88
data with $I > 3\sigma(I)$	1971	1472	1553	3358	3044
R_1	0.119	0.055	0.073	0.049	0.043
R_2	0.213	0.078	0.089	0.073	0.056
esd(observn of unit wt)	4.12	1.53	1.58	1.66	1.12

[a] Figures in parentheses following some numbers are esd's occurring in the least significant digit.

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr_2(dmhp)_4$, Form I[a]

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr(1)	0.3450 (3)	0.1824 (3)	0.4426 (2)	1.8 (1)	2.2 (2)	1.7 (1)	0.0 (2)	−0.2 (1)	0.2 (2)
Cr(2)	0.3383 (3)	0.3094 (3)	0.4311 (2)	2.3 (2)	2.1 (2)	2.0 (1)	−0.2 (2)	−0.3 (1)	−0.1 (2)
O(1)	0.406 (1)	0.178 (1)	0.565 (1)	3.3 (8)	2.8 (8)	2.4 (7)	0.0 (7)	−0.7 (6)	−0.1 (7)
O(2)	0.216 (1)	0.328 (1)	0.485 (1)	2.0 (7)	3.7 (9)	3.0 (7)	1.0 (7)	0.1 (6)	−0.6 (7)
O(3)	0.287 (1)	0.149 (1)	0.324 (1)	3.5 (8)	1.7 (7)	2.3 (6)	−0.1 (7)	−0.8 (6)	−0.3 (6)
O(4)	0.458 (1)	0.329 (1)	0.374 (1)	3.6 (8)	3.0 (9)	2.4 (7)	−1.1 (7)	0.3 (7)	0.7 (6)

	x	y	z	B, Å^2		x	y	z	B, Å^2
N(1)	0.399 (1)	0.331 (1)	0.557 (1)	2.6 (4)	C(23)	0.052 (2)	0.181 (2)	0.576 (2)	4.6 (7)
N(2)	0.220 (1)	0.181 (1)	0.506 (1)	3.6 (5)	C(24)	0.181 (2)	0.102 (2)	0.538 (2)	4.0 (6)
N(3)	0.280 (1)	0.301 (1)	0.303 (1)	2.3 (4)	C(25)	−0.044 (3)	0.168 (2)	0.612 (2)	6.8 (9)
N(4)	0.470 (1)	0.179 (1)	0.375 (1)	3.1 (4)	C(26)	0.236 (2)	0.016 (2)	0.529 (2)	5.0 (7)
N(13)	0.458 (2)	0.419 (2)	0.679 (1)	3.9 (5)	C(31)	0.265 (2)	0.217 (2)	0.270 (2)	2.7 (5)
N(23)	0.094 (2)	0.101 (2)	0.574 (2)	4.3 (5)	C(32)	0.225 (2)	0.205 (2)	0.181 (2)	2.9 (5)
N(33)	0.217 (1)	0.366 (1)	0.169 (1)	2.8 (4)	C(33)	0.201 (2)	0.280 (2)	0.133 (2)	2.7 (5)
N(43)	0.591 (2)	0.102 (2)	0.314 (2)	4.7 (6)	C(34)	0.258 (2)	0.371 (2)	0.249 (2)	2.4 (5)
C(11)	0.423 (2)	0.255 (2)	0.603 (2)	2.9 (5)	C(35)	0.161 (2)	0.274 (2)	0.039 (2)	4.3 (7)
C(12)	0.466 (2)	0.257 (2)	0.692 (2)	3.6 (6)	C(36)	0.277 (2)	0.463 (2)	0.292 (2)	3.9 (6)
C(13)	0.478 (2)	0.341 (2)	0.725 (2)	3.6 (6)	C(41)	0.505 (2)	0.258 (2)	0.353 (2)	2.8 (5)
C(14)	0.418 (2)	0.409 (2)	0.595 (2)	2.9 (5)	C(42)	0.592 (2)	0.267 (2)	0.308 (2)	3.5 (6)
C(15)	0.519 (2)	0.355 (2)	0.824 (2)	5.6 (8)	C(43)	0.630 (2)	0.183 (2)	0.292 (2)	4.5 (7)
C(16)	0.386 (2)	0.495 (2)	0.542 (2)	4.1 (6)	C(44)	0.512 (2)	0.101 (2)	0.353 (2)	3.1 (6)
C(21)	0.174 (2)	0.262 (2)	0.511 (2)	2.5 (5)	C(45)	0.725 (3)	0.182 (3)	0.243 (3)	7.6 (10)
C(22)	0.085 (2)	0.264 (2)	0.547 (2)	3.6 (6)	C(46)	0.468 (2)	0.015 (2)	0.369 (2)	5.4 (8)

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

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for $W_2(dmhp)_4$, Form I[a]

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	0.3443 (1)	0.17464 (9)	0.44589 (9)	2.64 (7)	2.28 (5)	2.42 (5)	0.24 (8)	−0.67 (5)	0.16 (7)
W(2)	0.3378 (1)	0.31840 (9)	0.43445 (9)	2.88 (7)	2.51 (5)	2.61 (6)	0.16 (9)	−0.72 (5)	−0.21 (8)
O(1)	0.409 (2)	0.184 (2)	0.575 (1)	4 (1)	4 (1)	3.3 (9)	−3 (1)	−1.9 (9)	2 (1)
O(2)	0.216 (2)	0.332 (2)	0.489 (2)	4 (1)	3 (1)	3 (1)	−2 (1)	−0.2 (9)	2 (1)
O(3)	0.285 (2)	0.153 (2)	0.318 (1)	5 (1)	2 (1)	3.5 (9)	−1 (1)	−1.2 (9)	1.0 (9)
O(4)	0.459 (2)	0.331 (1)	0.375 (1)	8 (2)	0.9 (8)	3 (1)	−0 (1)	−1 (1)	1.6 (9)

	x	y	z	B, Å^2		x	y	z	B, Å^2
N(1)	0.401 (2)	0.334 (2)	0.566 (2)	2.4 (6)	C(23)	0.050 (4)	0.183 (3)	0.580 (3)	5.1 (11)
N(2)	0.214 (2)	0.180 (2)	0.511 (2)	3.8 (7)	C(24)	0.165 (3)	0.100 (3)	0.543 (3)	3.4 (10)
N(3)	0.278 (2)	0.306 (2)	0.306 (2)	2.5 (7)	C(25)	−0.042 (4)	0.168 (4)	0.622 (3)	6.1 (13)
N(4)	0.470 (2)	0.180 (2)	0.377 (2)	2.8 (6)	C(26)	0.220 (3)	0.014 (3)	0.531 (3)	4.9 (9)
N(13)	0.466 (3)	0.423 (2)	0.685 (2)	4.3 (8)	C(31)	0.261 (3)	0.221 (2)	0.267 (3)	3.2 (9)
N(23)	0.076 (3)	0.101 (3)	0.581 (3)	4.5 (10)	C(32)	0.217 (3)	0.209 (3)	0.184 (3)	3.7 (9)
N(33)	0.214 (3)	0.375 (2)	0.165 (2)	3.7 (8)	C(33)	0.195 (3)	0.287 (3)	0.137 (3)	4.5 (10)
N(43)	0.601 (3)	0.106 (3)	0.306 (3)	6.3 (12)	C(34)	0.255 (3)	0.381 (3)	0.251 (3)	2.6 (8)
C(11)	0.426 (3)	0.259 (3)	0.611 (2)	2.4 (8)	C(35)	0.156 (3)	0.283 (3)	0.040 (3)	5.2 (11)
C(12)	0.466 (2)	0.260 (3)	0.700 (2)	2.5 (7)	C(36)	0.268 (3)	0.465 (3)	0.295 (3)	3.6 (9)
C(13)	0.488 (3)	0.347 (3)	0.731 (3)	2.8 (9)	C(41)	0.515 (2)	0.263 (2)	0.353 (2)	1.5 (6)
C(14)	0.420 (3)	0.418 (3)	0.605 (3)	3.4 (8)	C(42)	0.596 (3)	0.265 (2)	0.310 (2)	2.9 (8)
C(15)	0.533 (4)	0.347 (4)	0.828 (4)	7.8 (15)	C(43)	0.642 (3)	0.189 (3)	0.286 (3)	3.9 (10)
C(16)	0.394 (3)	0.497 (3)	0.551 (3)	3.7 (11)	C(44)	0.515 (4)	0.099 (3)	0.350 (3)	4.9 (11)
C(21)	0.175 (3)	0.269 (3)	0.518 (2)	2.5 (8)	C(45)	0.736 (4)	0.178 (3)	0.239 (3)	5.1 (11)
C(22)	0.085 (3)	0.260 (4)	0.555 (3)	5.1 (10)	C(46)	0.472 (3)	0.010 (3)	0.368 (3)	5.3 (11)

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

to push sublimed $Cr(CO)_6$ on the condenser back into the flask two or three times during the course of the reaction. After the required time, the flask is cooled to room temperature, the reaction mixture is immediately filtered through a medium frit, and the filtrate is left undisturbed overnight. The crystals present at this point are designated form I and analyze for about one-half molecule of diglyme per dimer. Anal. Calcd for $W_2(dmhp)_4\cdot 0.5(diglyme)$: C, 34.95; H, 3.77; N, 12.08. Found: C, 34.12; H, 3.69; N, 11.93.

If these crystals are filtered off and the filtrate is left undisturbed for 4 or 5 days, a different type of crystal is formed, designated form II. These crystals analyze for one molecule of diglyme per molecule of dimer. Anal. Calcd for $Mo_2(dmhp)_4\cdot$diglyme: C, 44.01; H, 5.13; N, 13.69. Found: C, 43.30; H, 5.04; N, 13.38. Both crystalline forms tend to lose solvent readily.

Crystals of form I were made and studied crystallographically for both the Cr and W compounds, and difficulties were encountered in refinement of their structures. In the meantime, the existence of form II crystals had been discovered, and it was found that the molybdenum compound in this form gave a very satisfactory structure. Therefore, the Cr and W compounds were also crystallized in form II and their structures determined. Since there was no reason to study the crystal structure of form I of the Mo compound, this was not done.

Crystallographic Studies. All of the crystals examined were grown from solutions of bis(2-methoxyethyl) ether (diglyme). Crystals of both forms were mounted in glass capillaries with epoxy cement and examined on a Syntex $P\bar{1}$ four-circle automated diffractometer. Intensity data were collected with graphite-monochromated Mo Kα radiation and the θ–2θ scan technique. Three standard reflections

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr_2(dmhp)_4 \cdot O_3C_6H_{14}$[a]

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr(1)	0.2520 (2)	0.2541 (3)	0.13031 (8)	2.90 (9)	1.72 (9)	2.6 (1)	−0.3 (1)	−0.01 (8)	0.1 (1)
Cr(2)	0.1634 (2)	0.0985 (3)	0.10678 (8)	2.9 (1)	1.8 (1)	2.6 (1)	−0.3 (1)	0.09 (9)	−0.2 (1)
O(1)	0.3822 (9)	0.158 (1)	0.1661 (3)	3.3 (5)	1.1 (5)	4.1 (6)	−0.3 (4)	−0.2 (5)	0.0 (4)
O(2)	0.2350 (9)	0.073 (1)	0.0550 (3)	3.0 (5)	2.9 (6)	3.5 (5)	−0.6 (5)	0.4 (4)	−0.9 (5)
O(3)	0.1505 (9)	0.402 (1)	0.1023 (3)	2.5 (4)	3.3 (5)	4.2 (5)	−0.9 (5)	−0.6 (4)	0.2 (5)
O(4)	0.0634 (9)	0.071 (1)	0.1520 (3)	3.8 (5)	2.3 (5)	3.2 (5)	−1.1 (5)	−0.6 (4)	−0.7 (5)
N(1)	0.2853 (11)	−0.036 (1)	0.1391 (4)	3.5 (6)	0.8 (5)	3.3 (6)	−0.2 (5)	−0.2 (5)	−0.7 (5)
N(2)	0.3476 (9)	0.255 (2)	0.0805 (4)	2.0 (5)	2.8 (6)	3.7 (6)	0.4 (7)	0.7 (5)	−0.1 (7)
N(3)	0.0384 (9)	0.224 (1)	0.0725 (4)	2.1 (5)	2.1 (7)	3.1 (6)	−0.8 (5)	−0.4 (5)	1.1 (5)
N(4)	0.1647 (9)	0.260 (1)	0.1831 (3)	2.8 (5)	2.2 (5)	2.1 (5)	0.8 (6)	0.8 (4)	0.6 (6)

	x	y	z	B, Å^2		x	y	z	B, Å^2
O(100)	0.243 (1)	0.135 (1)	0.3547 (4)	6.3 (3)	C(31)	0.059 (1)	0.364 (2)	0.0782 (5)	2.8 (3)
O(101)	0.308 (1)	−0.119 (2)	0.3215 (4)	6.5 (3)	C(32)	−0.022 (1)	0.458 (2)	0.0540 (5)	2.7 (3)
O(201)	0.300 (1)	0.466 (2)	0.4054 (4)	6.7 (4)	C(33)	−0.121 (1)	0.401 (2)	0.0290 (5)	3.9 (4)
N(13)	0.355 (1)	−0.260 (2)	0.1587 (4)	3.8 (3)	C(34)	−0.058 (1)	0.179 (2)	0.0471 (5)	3.7 (4)
N(23)	0.493 (1)	0.342 (1)	0.0421 (4)	3.2 (3)	C(35)	−0.215 (1)	0.493 (2)	0.0037 (6)	4.0 (4)
N(33)	−0.137 (1)	0.263 (2)	0.0252 (4)	3.5 (3)	C(36)	−0.079 (1)	0.023 (2)	0.0447 (5)	3.8 (4)
N(43)	0.123 (1)	0.348 (1)	0.2493 (4)	3.4 (3)	C(41)	0.081 (1)	0.157 (2)	0.1847 (5)	3.2 (4)
C(11)	0.377 (1)	0.025 (2)	0.1652 (5)	3.3 (4)	C(42)	0.021 (1)	0.150 (2)	0.2201 (5)	2.8 (3)
C(12)	0.465 (1)	−0.062 (2)	0.1892 (5)	2.7 (3)	C(43)	0.046 (1)	0.251 (2)	0.2508 (5)	3.3 (3)
C(13)	0.448 (1)	−0.206 (2)	0.1834 (5)	3.4 (4)	C(44)	0.180 (1)	0.349 (2)	0.2157 (5)	2.4 (3)
C(14)	0.277 (1)	−0.177 (2)	0.1377 (6)	3.8 (4)	C(45)	−0.018 (1)	0.253 (2)	0.2906 (5)	4.2 (4)
C(15)	0.536 (1)	−0.301 (2)	0.2075 (5)	3.6 (4)	C(46)	0.272 (1)	0.461 (2)	0.2111 (5)	3.7 (4)
C(16)	0.176 (1)	−0.233 (2)	0.1067 (5)	3.8 (4)	C(101)	0.194 (2)	0.005 (2)	0.3649 (7)	6.5 (6)
C(21)	0.320 (1)	0.157 (2)	0.0488 (5)	3.1 (4)	C(102)	0.190 (2)	−0.080 (2)	0.3234 (6)	5.6 (5)
C(22)	0.380 (1)	0.146 (2)	0.0134 (5)	2.5 (3)	C(103)	0.323 (2)	−0.199 (3)	0.2847 (8)	8.3 (7)
C(23)	0.467 (1)	0.244 (2)	0.0121 (5)	3.3 (3)	C(201)	0.247 (2)	0.236 (3)	0.3903 (6)	6.8 (5)
C(24)	0.435 (1)	0.348 (2)	0.0742 (5)	2.6 (3)	C(202)	0.291 (2)	0.369 (2)	0.3717 (7)	6.2 (5)
C(25)	0.544 (2)	0.240 (2)	−0.0237 (5)	4.8 (4)	C(203)	0.334 (2)	0.601 (3)	0.3926 (7)	7.4 (6)
C(26)	0.460 (2)	0.453 (2)	0.1085 (6)	4.7 (5)					

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table V. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Mo_2(dmhp)_4 \cdot O_3C_6H_{14}$, Form II[a]

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	0.25815 (6)	0.25665 (6)	0.13126 (2)	2.61 (3)	1.61 (2)	2.65 (3)	−0.33 (2)	−0.21 (2)	−0.06 (2)
Mo(2)	0.16082 (6)	0.08958 (6)	0.10590 (2)	2.54 (2)	1.80 (2)	2.61 (3)	−0.46 (2)	−0.04 (2)	−0.16 (2)
O(1)	0.3887 (4)	0.1405 (5)	0.1668 (2)	2.8 (2)	1.8 (2)	3.6 (2)	−0.1 (2)	−0.7 (2)	−0.0 (2)
O(2)	0.2435 (4)	0.0712 (5)	0.0523 (2)	3.0 (2)	3.1 (2)	3.5 (2)	−0.9 (2)	0.5 (2)	−0.9 (2)
O(3)	0.1455 (4)	0.4044 (5)	0.1009 (2)	3.1 (2)	2.4 (2)	3.4 (2)	−0.2 (2)	−0.3 (2)	0.1 (2)
O(4)	0.0611 (4)	0.0726 (5)	0.1553 (2)	3.4 (2)	3.0 (2)	3.0 (2)	−0.9 (2)	0.4 (2)	−0.4 (2)
N(1)	0.2887 (5)	−0.0471 (6)	0.1400 (2)	3.3 (3)	1.4 (2)	3.6 (3)	−0.2 (2)	0.4 (2)	−0.3 (2)
N(2)	0.3544 (5)	0.2547 (6)	0.0779 (2)	2.9 (3)	2.2 (3)	2.9 (3)	−0.2 (2)	−0.3 (2)	0.1 (2)
N(3)	0.0335 (5)	0.2260 (6)	0.0716 (2)	2.4 (3)	2.6 (3)	2.7 (3)	−0.4 (2)	−0.3 (2)	−0.2 (2)
N(4)	0.1622 (5)	0.2567 (6)	0.1852 (2)	3.4 (3)	2.1 (3)	2.8 (3)	−0.4 (2)	0.1 (2)	−0.4 (2)

	x	y	z	B, Å^2		x	y	z	B, Å^2
O(100)	0.2402 (6)	0.1352 (8)	0.3538 (2)	6.5 (2)	C(31)	0.0530 (6)	0.3625 (8)	0.0760 (2)	2.9 (1)
O(101)	0.3067 (6)	−0.1236 (8)	0.3213 (2)	6.5 (2)	C(32)	−0.0257 (7)	0.4583 (9)	0.0533 (3)	3.5 (2)
O(201)	0.3002 (6)	0.4561 (8)	0.4054 (2)	6.3 (2)	C(33)	−0.1234 (7)	0.4063 (9)	0.0282 (3)	3.8 (2)
N(13)	0.3577 (6)	−0.2733 (7)	0.1592 (2)	3.6 (1)	C(34)	−0.0622 (7)	0.1850 (8)	0.0457 (3)	3.4 (2)
N(23)	0.5030 (6)	0.3397 (7)	0.0401 (2)	3.6 (1)	C(35)	−0.2160 (8)	0.4965 (10)	0.0036 (3)	4.7 (2)
N(33)	−0.1416 (6)	0.2688 (7)	0.0234 (2)	3.9 (1)	C(36)	−0.0857 (7)	0.0321 (9)	0.0424 (3)	3.9 (2)
N(43)	0.1241 (6)	0.3483 (7)	0.2513 (2)	3.9 (1)	C(41)	0.0799 (6)	0.1576 (8)	0.1872 (2)	2.9 (1)
C(11)	0.3805 (6)	0.0089 (8)	0.1657 (2)	2.7 (1)	C(42)	0.0194 (7)	0.1484 (8)	0.2221 (2)	3.3 (2)
C(12)	0.4651 (7)	−0.0745 (8)	0.1885 (3)	3.5 (2)	C(43)	0.0426 (7)	0.2458 (8)	0.2537 (3)	3.8 (2)
C(13)	0.4519 (7)	−0.2168 (9)	0.1849 (3)	3.6 (2)	C(44)	0.1806 (7)	0.3474 (8)	0.2183 (2)	3.1 (2)
C(14)	0.2825 (7)	−0.1872 (8)	0.1376 (2)	3.2 (2)	C(45)	−0.0193 (8)	0.2488 (10)	0.2928 (3)	5.0 (2)
C(15)	0.5367 (8)	−0.3161 (10)	0.2083 (3)	4.3 (2)	C(46)	0.2713 (7)	0.4565 (9)	0.2152 (3)	3.9 (2)
C(16)	0.1790 (8)	−0.2447 (9)	0.1078 (3)	4.4 (2)	C(101)	0.1889 (10)	0.0051 (11)	0.3624 (3)	6.0 (2)
C(21)	0.3277 (7)	0.1568 (8)	0.0477 (2)	3.1 (2)	C(102)	0.1872 (10)	−0.0813 (11)	0.3242 (4)	6.4 (3)
C(22)	0.3892 (7)	0.1472 (9)	0.0121 (3)	3.6 (2)	C(103)	0.3200 (12)	−0.2008 (15)	0.2840 (5)	8.9 (4)
C(23)	0.4766 (7)	0.2425 (8)	0.0098 (3)	3.9 (2)	C(201)	0.2434 (9)	0.2279 (11)	0.3882 (3)	5.8 (2)
C(24)	0.4424 (7)	0.3435 (8)	0.0719 (2)	3.2 (2)	C(202)	0.2904 (11)	0.3586 (14)	0.3705 (4)	7.5 (3)
C(25)	0.5487 (8)	0.2391 (10)	−0.0258 (3)	5.0 (2)	C(203)	0.3345 (11)	0.5904 (14)	0.3929 (4)	8.3 (3)
C(26)	0.4691 (8)	0.4518 (10)	0.1060 (3)	4.4 (2)					

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

were monitored after every 97 reflections to check for decay. Lattice parameters were obtained by a least-squares fit of 15 strong reflections in the 2θ range 20–30°.

All data were corrected for Lorentz and polarization effects. The function minimized during refinement was $\sum w(|F_o| - |F_c|)^2$ where $p = 0.07$ was used in the previously defined expression of weights.[6]

Table VI. Positional and Thermal Parameters and Their Estimated Standard Deviations for $W_2(dmhp)_4 \cdot O_3C_6H_{14}$, Form II[a]

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	0.26017 (5)	0.25980 (6)	0.13188 (2)	2.29 (2)	1.60 (2)	2.58 (2)	−0.39 (2)	−0.02 (2)	−0.07 (2)
W(2)	0.15875 (5)	0.08540 (6)	0.10535 (2)	2.29 (2)	1.79 (2)	2.55 (2)	−0.51 (2)	0.14 (2)	−0.18 (2)
O(1)	0.3887 (9)	0.1432 (9)	0.1671 (3)	3.4 (5)	1.3 (4)	4.0 (5)	−0.8 (4)	−0.9 (4)	0.3 (4)
O(2)	0.2430 (8)	0.0717 (11)	0.0521 (3)	2.3 (4)	3.0 (4)	3.2 (4)	−0.9 (4)	0.3 (4)	−1.0 (4)
O(3)	0.1450 (9)	0.4030 (11)	0.1008 (3)	4.4 (5)	2.7 (4)	2.6 (4)	−0.7 (5)	−0.7 (4)	0.3 (4)
O(4)	0.0625 (9)	0.0729 (10)	0.1552 (3)	3.2 (5)	2.2 (4)	3.1 (4)	−1.2 (4)	0.3 (4)	−0.2 (4)
N(1)	0.286 (1)	−0.044 (1)	0.1394 (4)	2.2 (5)	1.0 (4)	2.9 (5)	−0.8 (4)	0.1 (4)	−0.2 (4)
N(2)	0.355 (1)	0.255 (1)	0.0778 (3)	2.5 (5)	2.6 (5)	1.8 (4)	−0.7 (5)	−0.2 (4)	0.8 (4)
N(3)	0.033 (1)	0.222 (1)	0.0714 (3)	3.2 (6)	1.9 (5)	1.9 (5)	−1.2 (5)	−0.0 (4)	−0.0 (4)
N(4)	0.163 (1)	0.258 (1)	0.1859 (4)	2.3 (5)	2.4 (5)	2.9 (5)	−0.1 (5)	0.1 (4)	0.4 (5)

	x	y	z	B, Å^2		x	y	z	B, Å^2
O(100)	0.241 (1)	0.134 (1)	0.3548 (4)	5.7 (3)	C(31)	0.052 (1)	0.363 (2)	0.0765 (5)	3.0 (3)
O(101)	0.307 (1)	−0.122 (2)	0.3216 (4)	6.4 (3)	C(32)	−0.026 (1)	0.455 (2)	0.0542 (5)	2.9 (3)
O(201)	0.302 (1)	0.455 (1)	0.4062 (4)	5.9 (3)	C(33)	−0.123 (1)	0.403 (2)	0.0278 (5)	3.4 (3)
N(13)	0.355 (1)	−0.272 (1)	0.1590 (4)	3.0 (2)	C(34)	−0.063 (1)	0.182 (2)	0.0458 (5)	2.7 (3)
N(23)	0.502 (1)	0.341 (1)	0.0404 (4)	3.3 (3)	C(35)	−0.214 (2)	0.494 (2)	0.0030 (6)	4.4 (4)
N(33)	−0.141 (1)	0.265 (2)	0.0236 (4)	4.1 (3)	C(36)	−0.087 (2)	0.027 (2)	0.0426 (6)	4.0 (4)
N(43)	0.124 (1)	0.348 (1)	0.2519 (4)	3.3 (3)	C(41)	0.080 (1)	0.158 (1)	0.1875 (4)	2.3 (3)
C(11)	0.380 (1)	0.008 (1)	0.1661 (4)	2.1 (3)	C(42)	0.018 (1)	0.150 (2)	0.2228 (5)	3.1 (3)
C(12)	0.465 (1)	−0.076 (2)	0.1884 (5)	3.3 (3)	C(43)	0.042 (1)	0.249 (2)	0.2533 (5)	3.7 (3)
C(13)	0.450 (1)	−0.217 (2)	0.1852 (5)	2.9 (3)	C(44)	0.182 (1)	0.348 (2)	0.2186 (5)	3.1 (3)
C(14)	0.285 (1)	−0.193 (2)	0.1365 (5)	3.2 (3)	C(45)	−0.021 (2)	0.255 (2)	0.2922 (6)	4.6 (4)
C(15)	0.536 (2)	−0.314 (2)	0.2072 (5)	3.9 (4)	C(46)	0.276 (2)	0.457 (2)	0.2150 (5)	3.6 (3)
C(16)	0.178 (1)	−0.245 (2)	0.1088 (5)	3.5 (3)	C(101)	0.188 (2)	0.006 (2)	0.3635 (6)	5.4 (5)
C(21)	0.327 (1)	0.155 (1)	0.0475 (4)	2.4 (3)	C(102)	0.188 (2)	−0.079 (2)	0.3244 (6)	5.4 (4)
C(22)	0.389 (1)	0.148 (2)	0.0128 (5)	3.6 (3)	C(103)	0.314 (3)	−0.201 (3)	0.2838 (9)	8.9 (7)
C(23)	0.478 (1)	0.242 (2)	0.0093 (5)	3.4 (3)	C(201)	0.245 (2)	0.230 (2)	0.3892 (6)	5.1 (4)
C(24)	0.444 (1)	0.344 (2)	0.0721 (5)	2.9 (3)	C(202)	0.293 (2)	0.362 (3)	0.3709 (8)	7.1 (6)
C(25)	0.549 (2)	0.238 (2)	−0.0257 (6)	5.0 (4)	C(203)	0.333 (3)	0.597 (3)	0.3923 (9)	9.6 (8)
C(26)	0.472 (1)	0.451 (2)	0.1066 (5)	3.4 (3)					

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table VII. Bond Distances (Å) for $M_2(dmhp)_4$, Form I

	M = Cr	M = W		M = Cr	M = W
M(1)–M(2)	1.898 (3)	2.155 (2)	C(23)–N(23)	1.34 (2)	1.28 (5)
–O(1)	1.974 (8)	2.11 (2)	–C(25)	1.51 (2)	1.51 (6)
–O(3)	1.965 (8)	2.08 (2)	N(23)–C(24)	1.34 (2)	1.42 (5)
–N(2)	2.05 (1)	2.15 (4)	C(24)–N(2)	1.38 (2)	1.47 (5)
–N(4)	2.08 (1)	2.11 (4)	C(24)–C(26)	1.52 (2)	1.53 (5)
M(2)–O(2)	1.976 (9)	1.98 (3)	O(3)–C(31)	1.32 (1)	1.30 (3)
–O(4)	1.960 (9)	2.01 (3)	C(31)–N(3)	1.34 (1)	1.41 (4)
–N(1)	2.04 (1)	2.14 (2)	–C(32)	1.41 (2)	1.38 (4)
–N(3)	2.038 (9)	2.07 (2)	C(32)–C(33)	1.37 (2)	1.38 (4)
O(1)–C(11)	1.29 (1)	1.25 (4)	C(33)–N(33)	1.40 (1)	1.40 (4)
C(11)–N(1)	1.35 (2)	1.35 (4)	–C(35)	1.47 (2)	1.52 (5)
–C(12)	1.42 (2)	1.43 (3)	N(33)–C(34)	1.29 (1)	1.38 (4)
C(12)–C(13)	1.35 (2)	1.41 (4)	C(34)–N(3)	1.34 (1)	1.42 (4)
C(13)–N(13)	1.37 (2)	1.36 (4)	–C(36)	1.53 (2)	1.42 (5)
–N(15)	1.56 (2)	1.55 (5)	O(4)–C(41)	1.31 (2)	1.33 (4)
N(13)–C(14)	1.35 (1)	1.35 (4)	C(41)–N(4)	1.33 (2)	1.45 (4)
C(14)–N(1)	1.31 (1)	1.39 (4)	–C(42)	1.44 (2)	1.35 (4)
–C(16)	1.55 (2)	1.47 (4)	C(42)–C(43)	1.39 (2)	1.37 (5)
O(2)–C(21)	1.23 (1)	1.19 (4)	C(43)–N(43)	1.36 (2)	1.41 (5)
C(21)–N(2)	1.38 (2)	1.46 (4)	–C(45)	1.56 (2)	1.55 (6)
–C(22)	1.40 (2)	1.45 (5)	N(43)–C(44)	1.30 (2)	1.42 (6)
C(22)–C(23)	1.39 (2)	1.30 (6)	C(44)–N(4)	1.34 (2)	1.43 (5)
			–C(46)	1.45 (2)	1.50 (6)

The discrepancy indices used were

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$$

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

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

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

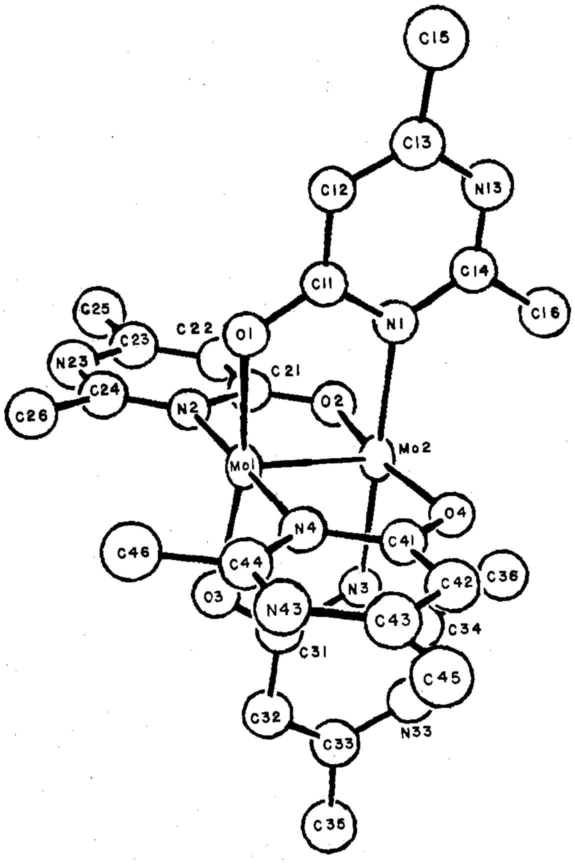


Figure 1. ORTEP drawing of the $Mo_2(dmhp)_4$ molecule, form II. The orientation of ligands and numbering scheme are the same for all five compounds.

Table VIII. Bond Angles (deg) for $M_2(dmhp)_4$, Form I

	M = Cr	M = W		M = Cr	M = W
M(2)–M(1)–O(1)	97.7 (3)	91.3 (7)	N(1)–C(11)–C(12)	122 (1)	122 (3)
–O(3)	98.8 (2)	93.8 (6)	C(11)–C(12)–C(13)	113 (1)	113 (3)
–N(2)	90.3 (3)	87.6 (9)	C(12)–C(13)–N(13)	126 (1)	124 (3)
–N(4)	91.8 (3)	88.0 (9)	–C(15)	120 (1)	112 (3)
O(1)–M(1)–O(3)	163.4 (3)	174.7 (9)	N(13)–C(13)–C(15)	114 (1)	124 (3)
–N(2)	90.3 (4)	91 (1)	C(13)–N(13)–C(14)	115 (1)	120 (3)
–N(4)	91.2 (4)	91 (1)	N(13)–C(14)–N(1)	124 (1)	120 (3)
O(3)–M(1)–N(2)	90.0 (4)	91 (1)	–C(16)	118 (1)	122 (3)
–N(4)	87.8 (4)	87 (1)	N(1)–C(14)–C(16)	118 (1)	117 (3)
N(2)–M(1)–N(4)	177.2 (4)	175 (1)	O(2)–C(21)–N(2)	116 (1)	120 (4)
M(1)–M(2)–O(2)	98.8 (3)	96.6 (7)	–C(22)	124 (1)	132 (4)
–O(4)	98.0 (3)	94.8 (7)	N(2)–C(21)–C(22)	120 (1)	107 (4)
–N(1)	93.2 (3)	91.2 (8)	C(21)–C(22)–C(23)	115 (1)	123 (5)
–N(3)	92.1 (3)	89.9 (8)	C(22)–C(23)–N(23)	128 (1)	136 (5)
O(2)–M(2)–O(4)	163.1 (4)	168.5 (8)	–C(25)	123 (1)	127 (5)
–N(1)	90.8 (4)	91 (1)	N(23)–C(23)–C(25)	109 (1)	97 (4)
–N(3)	85.6 (4)	89 (1)	C(23)–N(23)–C(24)	115 (1)	106 (4)
O(4)–M(2)–N(1)	88.0 (4)	89 (1)	N(23)–C(24)–N(2)	122 (1)	124 (3)
–N(3)	90.0 (4)	90 (1)	–C(26)	121 (1)	123 (4)
N(1)–M(2)–N(3)	174.6 (4)	179 (1)	N(2)–C(24)–C(26)	118 (1)	112 (4)
M(1)–O(1)–C(11)	115.6 (8)	121 (2)	O(3)–C(31)–N(3)	117 (1)	115 (3)
M(2)–O(2)–C(21)	117.7 (8)	121 (3)	–C(32)	122 (1)	121 (3)
M(1)–O(3)–C(31)	115.2 (7)	120 (2)	N(3)–C(31)–C(32)	121 (1)	123 (3)
M(2)–O(4)–C(41)	117.3 (8)	126 (2)	C(31)–C(32)–C(33)	117 (1)	116 (3)
M(2)–N(1)–C(11)	114.4 (8)	117 (2)	C(32)–C(33)–N(33)	121 (1)	126 (3)
–C(14)	126.4 (9)	123 (2)	–C(35)	121 (1)	121 (3)
C(11)–N(1)–C(14)	119 (1)	120 (2)	N(33)–C(33)–C(35)	117 (1)	112 (3)
M(1)–N(2)–C(21)	116.9 (9)	114 (3)	C(33)–N(33)–C(34)	117 (1)	114 (3)
–C(24)	122 (1)	123 (3)	N(33)–C(34)–N(3)	126 (1)	124 (3)
C(21)–N(2)–C(24)	121 (1)	122 (3)	–C(36)	119 (1)	122 (3)
M(2)–N(3)–C(31)	116.7 (8)	121 (2)	N(3)–C(34)–C(36)	115 (1)	114 (3)
–C(34)	125.2 (8)	123 (2)	O(4)–C(41)–N(4)	117 (1)	108 (3)
C(31)–N(3)–C(34)	118 (1)	116 (2)	–C(42)	121 (1)	130 (3)
M(1)–N(4)–C(41)	116.1 (9)	123 (2)	N(4)–C(41)–C(42)	123 (1)	122 (3)
–C(44)	122 (1)	121 (3)	C(41)–C(42)–C(43)	110 (1)	123 (4)
C(41)–N(4)–C(44)	121 (1)	116 (3)	C(42)–C(43)–N(43)	125 (1)	117 (4)
O(1)–C(11)–N(1)	119 (1)	119 (2)	–C(45)	116 (1)	130 (4)
–C(12)	119 (1)	118 (3)	N(43)–C(43)–C(45)	118 (1)	113 (4)
			C(43)–N(43)–C(44)	120 (1)	123 (4)
			N(43)–C(44)–N(4)	120 (1)	119 (4)
			–C(46)	119 (1)	122 (4)
			N(4)–C(44)–C(46)	121 (1)	120 (5)

Table IX. Bond Distances (Å) for $M_2(dmhp)_4 \cdot O_3C_6H_{14}$, Form II

	M = Cr	M = Mo	M = W		M = Cr	M = Mo	M = W
M(1)–M(2)	1.907 (3)	2.072 (1)	2.163 (1)	C(24)–N(2)	1.38 (2)	1.367 (7)	1.380 (7)
M(1)–O(1)	1.969 (9)	2.082 (4)	2.063 (2)	–C(26)	1.48 (2)	1.510 (9)	1.51 (1)
–O(3)	1.97 (1)	2.079 (4)	2.075 (2)	O(3)–C(31)	1.26 (1)	1.300 (7)	1.290 (6)
–N(2)	2.04 (1)	2.151 (5)	2.155 (3)	C(31)–N(3)	1.39 (2)	1.352 (7)	1.396 (6)
–N(4)	2.06 (1)	2.164 (5)	2.169 (3)	–C(32)	1.44 (2)	1.422 (9)	1.383 (8)
M(2)–O(2)	1.944 (9)	2.070 (4)	2.064 (2)	C(32)–C(33)	1.40 (2)	1.380 (9)	1.388 (9)
–O(4)	1.97 (1)	2.076 (4)	2.056 (2)	C(33)–N(33)	1.45 (2)	1.361 (8)	1.373 (8)
–N(1)	2.07 (1)	2.159 (5)	2.110 (3)	–C(35)	1.53 (2)	1.51 (1)	1.51 (2)
–N(3)	2.06 (1)	2.155 (5)	2.141 (3)	N(33)–C(34)	1.33 (2)	1.348 (8)	1.326 (8)
O(1)–C(11)	1.29 (2)	1.286 (7)	1.321 (5)	C(34)–N(3)	1.34 (2)	1.339 (8)	1.341 (8)
C(11)–N(1)	1.37 (2)	1.354 (8)	1.377 (7)	–C(36)	1.53 (2)	1.51 (1)	1.53 (2)
–C(12)	1.44 (2)	1.389 (9)	1.390 (8)	O(4)–C(41)	1.31 (2)	1.301 (7)	1.310 (6)
C(12)–C(13)	1.42 (2)	1.398 (9)	1.39 (1)	C(41)–N(4)	1.39 (2)	1.362 (7)	1.369 (7)
C(13)–N(13)	1.33 (2)	1.377 (8)	1.381 (9)	–C(42)	1.39 (2)	1.390 (8)	1.408 (9)
–C(15)	1.48 (2)	1.49 (1)	1.47 (1)	C(42)–C(43)	1.37 (2)	1.378 (9)	1.366 (8)
N(13)–C(14)	1.30 (2)	1.325 (8)	1.266 (9)	C(43)–N(43)	1.30 (2)	1.381 (8)	1.352 (8)
C(14)–N(1)	1.37 (2)	1.367 (8)	1.446 (8)	–C(45)	1.54 (2)	1.52 (1)	1.51 (2)
–C(16)	1.50 (2)	1.52 (1)	1.50 (1)	N(43)–C(44)	1.32 (1)	1.308 (8)	1.327 (8)
O(2)–C(21)	1.31 (2)	1.305 (7)	1.294 (6)	C(44)–N(4)	1.33 (2)	1.363 (7)	1.350 (7)
C(21)–N(2)	1.37 (2)	1.354 (8)	1.369 (8)	–C(46)	1.53 (2)	1.504 (9)	1.532 (9)
–C(22)	1.40 (2)	1.416 (9)	1.393 (9)	O(100)–C(101)	1.44 (2)	1.44 (1)	1.43 (1)
C(22)–C(23)	1.38 (2)	1.381 (9)	1.40 (1)	–C(201)	1.48 (2)	1.41 (1)	1.43 (1)
C(23)–N(23)	1.34 (2)	1.350 (8)	1.373 (8)	O(101)–C(102)	1.42 (2)	1.45 (1)	1.46 (1)
C(23)–C(25)	1.53 (2)	1.49 (1)	1.46 (1)	–C(103)	1.42 (2)	1.43 (1)	1.43 (1)
N(23)–C(24)	1.29 (2)	1.306 (8)	1.373 (9)	O(201)–C(202)	1.41 (2)	1.45 (1)	1.43 (1)
				–C(203)	1.44 (2)	1.44 (1)	1.51 (1)
				C(101)–C(102)	1.54 (2)	1.45 (1)	1.49 (1)
				C(201)–C(202)	1.53 (2)	1.52 (1)	1.55 (2)

Table X. Bond Angles (deg) for $M_2(dmhp)_4 \cdot O_3C_6H_{14}$, Form II

	M = Cr	M = Mo	M = W
M(2)-M(1)-O(1)	99.4 (3)	95.3 (1)	94.8 (1)
-O(3)	98.9 (3)	95.5 (1)	94.0 (1)
-N(2)	91.4 (4)	90.0 (1)	89.1 (1)
-N(4)	92.1 (4)	89.8 (1)	89.2 (1)
O(1)-M(1)-O(3)	162.7 (4)	169.1 (1)	171.1 (1)
-N(2)	89.3 (4)	90.3 (2)	90.4 (1)
-N(4)	88.5 (4)	89.2 (2)	89.0 (2)
O(3)-M(1)-N(2)	90.4 (4)	90.1 (2)	90.2 (1)
-N(4)	90.7 (4)	90.4 (2)	90.6 (2)
N(2)-M(1)-N(4)	176.2 (5)	179.4 (2)	178.1 (2)
M(1)-M(2)-O(2)	98.9 (3)	95.6 (1)	94.3 (1)
-O(4)	99.4 (3)	95.7 (1)	94.1 (1)
-N(1)	91.4 (3)	89.8 (1)	88.6 (1)
-N(3)	91.6 (3)	90.2 (1)	89.7 (1)
O(2)-M(2)-O(4)	161.6 (4)	168.6 (1)	171.1 (1)
-N(1)	89.3 (4)	89.7 (2)	90.2 (1)
-N(3)	89.3 (4)	90.1 (2)	89.7 (2)
O(4)-M(2)-N(1)	89.2 (4)	89.2 (2)	89.2 (2)
-N(3)	91.1 (4)	91.0 (2)	91.1 (2)
N(1)-M(2)-N(3)	176.9 (4)	179.8 (2)	178.3 (2)
M(1)-O(1)-C(11)	116 (1)	118.8 (4)	119.3 (3)
M(2)-O(2)-C(21)	117.6 (9)	118.3 (4)	119.9 (3)
M(1)-O(3)-C(31)	117 (1)	117.9 (4)	120.3 (3)
M(2)-O(4)-C(41)	116 (9)	119.1 (4)	121.2 (3)
M(2)-N(1)-C(11)	115.3 (9)	118.1 (4)	121.4 (4)
-C(14)	126 (1)	124.1 (4)	124.7 (4)
C(11)-N(1)-C(14)	119 (1)	117.8 (5)	113.9 (4)
M(1)-N(2)-C(21)	117 (1)	118.0 (4)	118.4 (4)
-C(24)	127 (1)	125.5 (4)	124.4 (4)
C(21)-N(2)-C(24)	116 (1)	116.5 (5)	117.2 (5)
M(2)-N(3)-C(31)	114.7 (9)	117.6 (4)	118.3 (4)
-C(34)	125 (1)	124.6 (4)	124.4 (5)
C(31)-N(3)-C(34)	120 (1)	117.8 (5)	117.3 (5)
M(1)-N(4)-C(41)	115.6 (9)	118.4 (4)	118.7 (5)
-C(44)	127 (1)	124.4 (4)	123.4 (5)
C(41)-N(4)-C(44)	117 (1)	117.2 (5)	117.9 (5)
O(1)-C(11)-N(1)	118 (1)	117.8 (5)	115.8 (5)
-C(12)	123 (1)	121.6 (6)	121.8 (5)
N(1)-C(11)-C(12)	118 (1)	120.5 (6)	122.2 (6)
C(11)-C(12)-C(13)	116 (1)	118.6 (6)	118.1 (6)
C(12)-C(13)-N(13)	123 (1)	120.7 (6)	120.7 (6)
-C(15)	118 (1)	123.1 (6)	121.9 (6)
N(13)-C(13)-C(15)	119 (1)	116.1 (6)	117.2 (6)
C(13)-N(13)-C(14)	119 (1)	117.1 (6)	119.1 (6)
N(13)-C(14)-N(1)	124 (1)	125.3 (6)	125.4 (7)
-C(16)	121 (1)	119.0 (6)	121.9 (7)
N(1)-C(14)-C(16)	115 (1)	115.7 (6)	111.9 (7)
O(2)-C(21)-N(2)	115 (1)	118.0 (6)	118.2 (6)
-C(22)	123 (1)	120.8 (6)	122.2 (6)
N(2)-C(21)-C(22)	122 (1)	121.2 (6)	119.6 (6)
C(21)-C(22)-C(23)	115 (1)	116.8 (6)	119.6 (6)
C(22)-C(23)-N(23)	124 (1)	121.7 (6)	118.6 (6)
-C(25)	120 (1)	121.0 (6)	122.5 (7)
N(23)-C(23)-C(25)	116 (1)	117.3 (6)	118.9 (7)
C(23)-N(23)-C(24)	119 (1)	118.4 (6)	120.1 (6)
N(23)-C(24)-N(2)	124 (1)	125.4 (6)	124.9 (6)
-C(26)	122 (1)	119.7 (6)	119.9 (6)
N(2)-C(24)-C(26)	114 (1)	115.0 (6)	115.2 (6)
O(3)-C(31)-N(3)	118 (1)	118.8 (5)	122.5 (5)
-C(32)	124 (1)	120.7 (5)	122.5 (5)
N(3)-C(31)-C(32)	118 (1)	120.6 (6)	119.7 (5)
C(31)-C(32)-C(33)	117 (1)	117.4 (6)	119.0 (6)
C(32)-C(33)-N(33)	122 (2)	121.7 (6)	120.6 (5)
C(32)-C(33)-C(35)	121 (1)	122.9 (6)	123.1 (6)
N(33)-C(33)-C(35)	117 (1)	115.3 (6)	116.3 (6)
C(33)-N(33)-C(34)	119 (1)	117.0 (6)	117.8 (6)
N(33)-C(34)-N(3)	123 (1)	125.4 (6)	125.5 (7)
-C(36)	119 (1)	117.2 (6)	117.7 (6)
N(3)-C(34)-C(36)	117 (1)	117.3 (6)	116.8 (6)
O(4)-C(41)-N(4)	117 (1)	117.0 (5)	116.8 (5)
-C(42)	124 (1)	121.9 (6)	122.7 (6)
N(4)-C(41)-C(42)	119 (1)	121.0 (6)	120.5 (6)
C(41)-C(42)-C(43)	117 (1)	117.7 (6)	116.3 (6)
C(42)-C(43)-N(43)	124 (1)	121.4 (6)	123.5 (7)
-C(45)	120 (1)	122.8 (6)	121.6 (7)
N(43)-C(43)-C(45)	116 (1)	115.8 (6)	114.8 (7)
C(43)-N(43)-C(44)	117 (1)	117.4 (6)	117.3 (6)
N(43)-C(44)-N(4)	125 (1)	125.2 (6)	124.3 (6)
-C(46)	121 (1)	118.6 (6)	119.9 (6)
N(4)-C(44)-C(46)	114 (1)	116.2 (5)	115.7 (6)
C(101)-O(100)-C(201)	112 (1)	112.6 (7)	113.3 (8)
C(102)-O(101)-C(103)	115 (1)	114.6 (7)	111.9 (8)
C(202)-O(201)-C(203)	113 (1)	112.3 (7)	110.1 (8)
O(100)-C(101)-C(102)	104 (1)	107.7 (7)	106.0 (8)
O(101)-C(102)-C(101)	106 (1)	108.2 (7)	108.8 (8)
O(100)-C(201)-C(202)	104 (1)	103.0 (7)	103.8 (8)
O(201)-C(202)-C(201)	105 (1)	105.1 (8)	102.7 (8)

Table XI. Torsional Angles (deg) in $M_2(dmhp)_4$

		angles for M				
		form I		form II		
atoms in plane 1	atoms in plane 2	Cr	W	Cr	Mo	W
N(1), M(1), M(2)	M(1), M(2), O(1)	0.9	1.0	1.0	0.6	0.6
N(2), M(1), M(2)	M(1), M(2), O(2)	1.9	1.8	1.1	0.0	0.3
N(3), M(1), M(2)	M(1), M(2), O(3)	1.7	0.0	0.0	0.1	0.1
N(4), M(1), M(2)	M(1), M(2), O(4)	4.0	2.8	0.4	0.5	0.4
mean angle		2.1	1.4	0.6	0.3	0.3

Form I. Crystals of this form belong to space group $P2_1/n$ and contain one dinuclear molecule and one-half diglyme molecule per asymmetric unit. In both cases the half molecule of diglyme was severely disordered. No model which was chemically reasonable could be found to fit this disordered molecule. As the dimer molecule was the feature of most importance, refinement of both compounds was carried to convergence using only the parameters of the dimer molecule.

For $Cr_2(dmhp)_4$ in form I, the positions of the chromium atoms were found by use of direct methods while the positions of the remaining atoms were found from subsequent difference Fourier maps. Final least-squares refinement was carried out with anisotropic thermal parameters for the Cr and O atoms and isotropic thermal parameters for the remaining atoms. For $W_2(dmhp)_4$ in form I, the high absorption coefficient required an empirical absorption corrected based on ψ scans at $\chi = 90°$. Three sets of ψ-scan data were collected, each set consisting of a measurement every ten degrees from 0 to 350°. The range of normalized transmission factors was from 1.000 to 0.8274. Beginning with the positional parameters from the chromium compound, we carried refinement to convergence. Anisotropic thermal parameters for the W and O atoms and isotropic thermal parameters for the remaining atoms were used in the refinement.

Form II. Crystals of this form belong to the space group $P2_1/c$ with one dinuclear molecule and one molecule of diglyme per asymmetric unit. The solution and refinement of each structure proceeded as follows.

For $Mo_2(dmhp)_4$·diglyme the structure was solved by conventional heavy-atom methods and refined to convergence with anisotropic thermal parameters for Mo and the coordinated O and N atoms and with isotropic thermal parameters for the remaining atoms. A final difference map had no peaks with intensity greater than 1 e/Å^3.

For $Cr_2(dmhp)_3$·diglyme refinement was carried out to convergence starting with the atomic parameters from the molybdenum structure. For chromium and coordinated oxygen and nitrogen atoms, thermal parameters were anisotropic while those of the remaining atoms were isotropic. A final difference map had no peaks exceeding 1 e/Å^3.

For $W_2(dmhp)_4$·diglyme an empirical absorption correction based on ψ scans at $\chi = 90°$ was applied. Five sets of ψ-scan data were collected, each set consisting of a measurement every ten degrees from 0 to 350°. The range of normalized transmission factors was from 1.0000 to 0.6226. With the atomic parameters of the molybdenum compound, refinement was begun and carried to convergence with anisotropic thermal parameters for the W and coordinated N and O atoms. The remaining atoms were kept thermally isotropic. A final difference Fourier had no peaks greater than 1 e/Å^3.

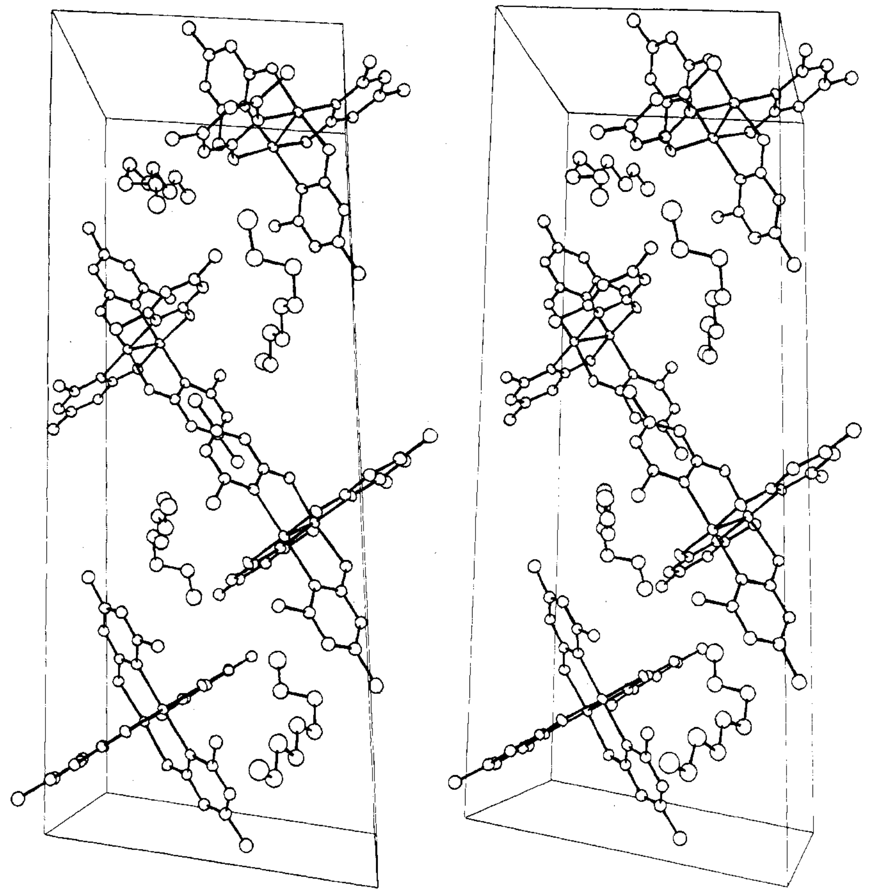


Figure 2. ORTEP stereoview of the contents of the unit cell of $Mo_2(dmhp)_4{\cdot}O_3C_6H_{14}$, form II.

Results and Discussion

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

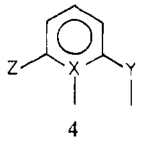
Although the two form I structures cannot be considered solved with respect to all nonhydrogen atoms, the most important feature, the dinuclear molecule, is fairly accurately defined. The bond distances and angles for the form I structures are tabulated in Tables VII and VIII, while the bond distances and angles for the form II structures are given in Tables IX and X.

Figure 1 shows the orientation of the ligands around the $Mo\overset{4}{-}Mo$ unit. The orientation and the numbering scheme are the same for all five compounds. Such an arrangement of the ligands, in which the M–N and M–O bonds are trans to their own kind, leading to overall D_{2d} symmetry, has been found previously for similar compounds.[3,5] Figure 2 shows the arrangement of molecules in the unit cells of form II. Clearly, the molecules are packed to give only nonbonding contacts, and the axial sites of the M_2 units are unoccupied. The diglyme molecules are not serving as ligands.

It is seen by comparing Tables VII and IX that the M–M bond distances are nominally shorter in form I than form II. However, the differences are not significant by the 3σ criterion. Thus, although there is one-half solvent molecule per $M_2(dmhp)_4$ in form I and one complete solvent molecule per $M_2(dmhp)_4$ in form II, there is no significant difference between the $M_2(dmhp)_4$ molecules that occur in the two forms.

One interesting feature of these molecules is that, despite the absence of any crystallographic symmetry in the molecule, they deviate very little from the eclipsed configuration. This can be seen in Table XI which compares the four independent torsional angles about the M–M bond. We have used the mean of these four angles to gauge the amount of rotation away from eclipsed configuration.[4,5,7] The mean angles here are virtually zero, indicating no significant deviation from perfectly eclipsed geometry.

It now seems clear that ligands of the general type **4** can



4

be expected to give dichromium(II) compounds with $Cr\overset{4}{-}Cr$ bonds in the range 1.83 to 1.91 Å, although they are not the only type to do so.[4] Ligands of type **4** also appear to give the most stable compounds containing $W\overset{4}{-}W$ bonds, in all of which[3,5] these bonds are far shorter (ca. 2.16 Å) than the $W\overset{4}{-}W$ bonds in other cases.[8,9]

Acknowledgment. We are grateful to the National Science Foundation for support.

Registry No. Form I (M = Cr), 69351-87-7; form I (M = W), 69351-89-9; form II (M = Cr), 69401-29-2; form II (M = Mo), 69351-91-3; form II (M = W), 69401-30-5; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0.

Supplementary Material Available: Tables of observed and calculated structure factors (51 pages) for all five compounds. Ordering information is given on any current masthead page.

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A New Compound Containing the Tetrasulfatodimolybdenum Anion with a Bond Order of 3.5

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The $[Mo_2(SO_4)_4]^{3-}$ ion has been obtained in the form of a compound with the formula $K_4[Mo_2(SO_4)_4]Cl{\cdot}4H_2O$. This compound has many advantages over the previously known $K_3[Mo_2(SO_4)_4]{\cdot}3.5H_2O$ for the study of the electronic structure and spectroscopic properties of the $[Mo_2(SO_4)_4]^{3-}$ ion. It crystallizes in the tetragonal space group $P4/mnc$ with cell dimensions $a = 11.930$ (2) Å, $c = 7.930$ (1) Å, $V = 1128$ (1) Å^3, and $Z = 2$. The $[Mo_2(SO_4)_4]^{3-}$ ions occupy special positions with $4/m$ (C_{4h}) symmetry, and the Mo–Mo axes are all precisely parallel to the crystallographic c axis. The Cl^- ions lie between $[Mo_2(SO_4)_4]^{3-}$ ions so as to form continuous, linear ···Mo–Mo···Cl···Mo–Mo···Cl··· chains with very long, 2.881 (1) Å, weak Mo to Cl interactions. The Mo–Mo distance, 2.167 (2) Å, is identical within experimental error with that found in $K_3[Mo_2(SO_4)_4]{\cdot}3.5H_2O$.

Introduction

Several years ago the first example of a metal-to-metal bond of order 3.5 based on a $\sigma^2\pi^4\delta$ configuration[1] was discovered in the form of the $Mo_2(SO_4)_4{}^{3-}$ ion.[2] This ion was obtained in the compound $K_3[Mo_2(SO_4)_4]{\cdot}3.5H_2O$ that arose by spontaneous aerial oxidation of $Mo_2(SO_4)_4{}^{4-}$. This lavender compound has since been studied electrochemically,[2b] by EPR[2b] and electronic absorption spectroscopy,[3] photochemically,[3a] by Raman spectroscopy,[4] and theoretically.[5] In view of its interesting photochemistry and its somewhat puzzling Raman and electronic absorption spectra, further study was considered worthwhile. The crystals of $K_3[Mo_2(SO_4)_4]{\cdot}3.5H_2O$ are inherently disadvantageous in several respects. First, they contain two crystallographically independent molecules. Second, there are two different, nearly perpendicular orientations of the Mo–Mo axes in the unit cell.

To facilitate more complete and unambiguous characterization of the electronic and spectroscopic properties of the $[Mo_2(SO_4)_4]^{3-}$ ion, a more advantageous crystal form was desirable. We report here a new compound, $K_4[Mo_2(SO_4)_4]Cl{\cdot}4H_2O$, which ideally fulfills our objective.

Experimental Section

Preparation of $K_4[Mo_2(SO_4)_4]Cl{\cdot}4H_2O$. A solution of $K_4Mo_2Cl_8$ (0.1 g), prepared by a literature method,[6] in 50 mL of 2 M H_2SO_4 and 0.3 M HCl was made under N_2. Three milliliters of H_2O_2 (0.025 M) was added dropwise with frequent agitation between additions. The color of the solution turned from deep red to gray-blue. KCl (0.05 g) was then added, and the solution was stirred at 0 °C for $^1/_2$ h. The blue precipitate was filtered, washed with acetone and ether, and dried under vacuum; yield 0.095 g.

Single crystals were obtained by a slow diffusion through a glass frit of the solution containing the $Mo_2(SO_4)_4{}^{3-}$ species and a solution of 0.1 M KCl.

X-ray Crystallography. A crystal of dimensions 0.1 × 0.1 × 0.1 mm was attached to the end of a glass fiber and mounted on a Syntex $P\bar{1}$ four-circle diffractometer. Mo Kα (λ 0.710730 Å) radiation, with a graphite crystal monochromator in the incident beam, was used.

Rotation photographs and ω-scans of several strong reflections indicated that the crystal was of satisfactory quality. Preliminary examination showed that the crystal belonged to the tetragonal system, space group $P4/mnc$. The unit cell dimensions were obtained by a least-squares fit of 15 strong reflections in the range $25° < 2\theta < 35°$ giving $a = 11.930$ (2) Å, $c = 7.930$ (1) Å, and $V = 1128$ (1) Å^3. With these dimensions and $Z = 2$ (for the formula $K_4Mo_2(SO_4)_4Cl{\cdot}4H_2O$; mol wt 840.05) the density is calculated to be 2.47 g cm^{-3}. The density determined by flotation in a mixture of bromoform and carbon tetrachloride was 2.50 ± 0.05 g cm^{-3}.

Data were measured by θ–2θ scans. A total of 496 reflections in the range $0° < 2\theta \leq 50°$ were collected of which 437 having $I > 3\sigma(I)$ were used to solve and refine the structure. General procedures for data collection have been described elsewhere.[7] The data were corrected for Lorentz and polarization effects. The linear absorption coefficient is 23.6 cm^{-1}; no absorption correction was applied.

The heavy-atom positions were obtained from a three-dimensional Patterson function. The structure was refined[8] in space group $P4/mnc$ to convergence by use of anisotropic thermal parameters for all the nonhydrogen atoms.

The discrepancy indices

$$R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$$

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

had final values of $R_1 = 0.035$ and $R_2 = 0.053$ with an error in an observation of unit weight equal to 1.25. The final difference map showed no peaks of structural significance. A list of the observed

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