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Homologous Chromium, Molybdenum, and Tungsten Compounds with Very Short Quadruple Bonds

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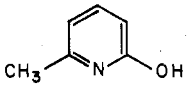
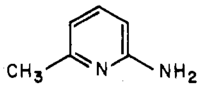
By reactions of the acetates $M_2(O_2CCH_3)_4$ with the lithium salt of 2-amino-6-methylpyridine (Hmap) the compounds $M_2(map)_4$, M = Cr or Mo, have been prepared. The tungsten analogue has been made by a similar reaction with tetrakis(2-hydroxy-6-methylpyridine)ditungsten. Their structures have been determined X-ray crystallographically. They form isomorphous crystals with the composition $M_2(map)_4 \cdot 2THF$ belonging to the space group $P2_1/c$, with $Z = 4$. Unit cell dimensions (Å, degrees) for the Cr, Mo, and W compounds, in that order, are the following: $a = 10.123$ (2), 10.202 (2), 10.200 (1); $b = 16.520$ (5), 16.676 (3), 16.642 (2); $c = 20.553$ (3), 20.617 (4), 20.547 (3); $\beta = 106.66$ (1), 106.73 (2), 106.86 (1). The $M_2(map)_4$ molecules have idealized D_{2d} symmetry and the M–M bond lengths are Cr–Cr = 1.870 (3) Å, Mo–Mo = 2.070 (1) Å, and W–W = 2.164 (1) Å. These are among the shortest of their kind. The M–M′–N angles are all essentially the same (95.1–96.7°) although the two kinds of M–N distances differ by ca. 0.05 Å, those to the ring atoms being longer. There are no axial metal–ligand bonds.

Introduction

A recent study[1] has shown that a group six triad of quadruply bonded compounds can be formed from the ligand 2-hydroxy-6-methylpyridine, Hmhp, **1a**. This ligand is unusual in that it produces very stable compounds with short metal–metal bonds. It was of interest to vary the ligand slightly in terms of the donor atoms and determine what changes in bond lengths and stability would result if a stronger ligand with the same steric constraints was used. Such a ligand is the corresponding amino compound 2-amino-6-methylpyridine, Hmap, **1b**. We have prepared and characterized the entire set of chromium, molybdenum, and tungsten compounds, $M_2(map)_4$.



1a



1b

Experimental Section

Materials. $Mo_2(O_2CCH_3)_4$ and $Cr_2(O_2CCH_3)_4$ were prepared according to established procedures. $W_2(mhp)_4$ was prepared from $W(CO)_6$ and 2-hydroxy-6-methylpyridine in refluxing diglyme.[1] 2-Amino-6-picoline (or 2-amino-6-methylpyridine, Hmap) and *n*-butyllithium were purchased from Aldrich Chemical Co., Inc. All other compounds and solvents were of reagent grade or better from commercial sources. All solvents were dried over molecular sieves and deoxygenated prior to use. Reactions were performed under nitrogen using airtight glassware.

Preparation of $Cr_2(map)_4$ and $Mo_2(map)_4$. In a typical reaction, 1.62 g (15 mmol) of Hmap was dissolved in 50 mL of THF. The solution was cooled to 0 °C and 15 mmol of *n*-BuLi in hexane was added very slowly with stirring. The mixture was allowed to warm to room temperature and 3.75 mmol of $Cr_2(O_2CCH_3)_4$ or $Mo_2(O_2CCH_3)_4$ was added. After 6 h, the reaction mixture was filtered through a medium frit into a tubular flask approximately 1.5 inches in diameter. Very gently, 40 mL of hexane was added through a syringe so as to maintain a THF/hexane interface. After 1 or 2 days, slow diffusion of hexane into the THF solution produced yellow ($Cr_2(map)_4$) or red ($Mo_2(map)_4$) crystals. These were quickly filtered and dried under a stream of nitrogen. X-ray analysis showed the crystals to be solvated with the general formula $M_2(map)_4 \cdot 2THF$ where M is Cr or Mo. Larger crystals can be formed by initially mixing the hexane into the THF and allowing the solution to remain undisturbed overnight.

Preparation of $W_2(map)_4$. In a similar procedure, 3.0 g (3.75 mmol) of $W_2(mhp)_4$ was added to 15 mmol of Li(map) in 50 mL of THF. After 8 h, the reaction mixture was filtered through a medium frit into a flat-bottom flask. Slowly, 40 mL of hexane was added to the THF solution and the mixture shaken. The flask was then set aside overnight. The flask was observed to contain dark crystals of $W_2(map)_4$ together with a white precipitate of Li(mhp). These solids were separated by filtration and dried in a stream of nitrogen. On exposure to air, the tungsten compound decomposed when in contact with Li(mhp). However, a few crystals remaining in the flask were dislodged and found to be of suitable quality for X-ray analysis.

X-ray Crystallography. The crystals used were those obtained by slow diffusion of a hexane layer into a THF solution of the compound. To prevent loss of solvent from the crystals they were sealed in a layer of epoxy in a glass capillary. The data were collected on a Syntex $P\bar{1}$ four-circle, automated diffractometer. Unit cell constants were obtained by a least-squares fit to the setting angles for 15 strong reflections.

Intensity data were collected using graphite-monochromated Mo Kα radiation and a variable θ–2θ scan rate of 4 to 24°/min. The range of 2θ was 0–45° for each crystal. Background measurements were made at both limits of each scan. The data were monitored by measuring three standard reflections every 97 reflections. Only the reflections having intensities, I, greater than $3\sigma(I)$ were retained as observed and, after correction for Lorentz and polarization effects, were used to solve and refine the structures. 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.[2] 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 calculations required for data reduction and refinement of the structures[2] were carried out using the Enraf-Nonius structure determination package on a PDP 11/45 computer operated by Molecular Structure Corp., College Station, Texas.

The crystallographic data for the three compounds are summarized in Table I. Details specific to the solution and refinement of each individual structure are as follows.

$Cr_2(map)_4 \cdot 2THF$. This compound crystallizes in the space group $P2_1/c$ with one dimer per asymmetric unit. The structure was solved by direct methods and refined to convergence using anisotropic thermal parameters for the Cr and N atoms and isotropic thermal parameters for the O and C atoms. Two THF molecules were found to make up the rest of the asymmetric unit. There is no chemical interaction between the THF molecules and the chromium dimer. A final difference map had no peaks with intensity greater than 0.5 e/Å^3. No effort was made to locate hydrogen atoms.

$Mo_2(map)_4 \cdot 2THF$. This compound is isomorphous to the chromium compound. Refinement was commenced immediately using atomic parameters from the chromium structure and carried to convergence with anisotropic thermal parameters for the Mo and N atoms and isotropic thermal parameters for the O and C atoms. A final difference map had no peaks with intensity greater than 1 e/Å^3.

$W_2(map)_4 \cdot 2THF$. This compound is isomorphous to the chromium and molybdenum analogues. The data were corrected for absorption using an empirical procedure based on ψ scans at $\chi = 90°$. Five sets of ψ-scan data were collected, each set consisting of a measurement every 10° in ψ from 0 to 350°. The range of normalized transmission factors was from 1.0000 to 0.3569. Refinement was begun using

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Table I. Crystallographic Data for $M_2(map)_4 \cdot 2THF$

Parameters[a]	Cr_2N_8-$C_{24}H_{28} \cdot 2C_4H_8O$	Mo_2N_8-$C_{24}H_{28} \cdot 2C_4H_8O$	W_2N_8-$C_{24}H_{28} \cdot 2C_4H_8O$
mol wt	676.75	764.64	940.38
a, Å	10.123 (2)	10.202 (2)	10.200 (1)
b, Å	16.520 (5)	16.676 (3)	16.642 (2)
c, Å	20.553 (3)	20.617 (4)	20.547 (3)
β, deg	106.66 (1)	106.73 (2)	106.86 (1)
V, Å^3	3293	3359	3338
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
d_c, g cm^{-3}	1.365	1.512	1.851
Z	4	4	4
μ, cm^{-1} (for Mo Kα)	7.323	7.774	73.421
data with $I > 3\sigma(I)$	1617	2663	2431
R_1	0.083	0.059	0.055
R_2	0.103	0.080	0.065
esd(observn of unit wt)	1.932	1.624	1.242

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

atomic parameters from the molybdenum structure and carried to convergence with anisotropic thermal parameters for the W and N atoms and isotropic thermal parameters for the O and C atoms. A final difference map had one peak of intensity 1.77 e/Å^3 which was about halfway between C(11) and C(12). The second highest peak, of intensity 1.25 e/Å^3, was very close to W(2). All remaining peaks had intensities less than 1.47 e/Å^3 and were located between atoms in the pyridine rings of the ligands.

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

Results and Discussion

Chemistry. As in the case of the mhp compounds, reaction of the lithium salts of the ligand with chromium or molybdenum acetates gives the desired product. However, Hmap is much less acidic than Hmhp and a stronger base is required to deprotonate it. Also, it is not possible to use the hydrated chromium(II) acetate as a reactant. $M_2(map)_4$ compounds appear to be much more soluble than the corresponding mhp compounds. Isolation from THF affords solvated crystals that lose THF rather easily. The unsolvated compounds, readily obtained by mild heating under vacuum, are quite stable thermally and chemically. They do not appear to decompose in dry air, but they are more sensitive to moisture than are the mhp analogues, presumably because of the more basic nature of the map$^-$ ion.

Since no authenticated $W_2(O_2CR)_4$ compound is available as a starting material, it was necessary to prepare the tungsten compound in a different manner. The preparation of $W_2(mhp)_2$ from $W(CO)_6$ and Hmhp provided the first example of a quadruply bonded W_2 compound obtained from $W(CO)_6$.[1] Reaction of $W(CO)_6$ and Hmap in refluxing diglyme produced a dark solution, but no product could be isolated. Probably the acidity of Hmap is so low that it cannot react as did Hmhp. We find that reactions of Hmap with $Mo(CO)_6$ and $Cr(CO)_6$ were similarly unproductive. However, the stability of $W_2(mhp)_4$ and its ease of synthesis led us to consider it as a starting material for the preparation of other tungsten compounds. Since map is expected to be a stronger ligand than mhp, we felt that it should be possible to perform the pertinent ligand replacement reaction.

Initial trials of the reaction of $W_2(mhp)_4$ with Li(map) appeared to be successful. Whereas $W_2(mhp)_4$ is almost insoluble in THF, reaction with Li(map) produced a dark solution with very little insoluble material. However, in contrast to our experience with $Cr_2(map)_4$ and $Mo_2(map)_4$, it proved very difficult to obtain a precipitate upon addition of hexane. Several solutions were discarded before it was realized that precipitation would occur only after prolonged periods. Unfortunately, a considerable amount of Li(mhp) also precipitates. This contaminates the compound and causes it to be extremely sensitive to atmospheric conditions. Further effort will be required to find an efficient procedure for the

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr_2(map)_4 \cdot 2THF$[a]

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr(1)	0.1847 (3)	0.6751 (1)	0.2289 (1)	4.2 (1)	2.8 (1)	3.9 (1)	0.3 (1)	1.00 (9)	−0.4 (1)
Cr(2)	0.0422 (2)	0.6520 (1)	0.1504 (1)	3.6 (1)	2.5 (1)	4.0 (1)	0.2 (1)	1.10 (9)	−0.2 (1)
N(1)	0.066 (1)	0.6608 (7)	0.2952 (5)	6.0 (7)	3.1 (6)	1.8 (5)	0.4 (6)	0.9 (5)	0.5 (5)
N(2)	−0.107 (1)	0.6360 (8)	0.1968 (6)	4.9 (6)	4.0 (6)	3.5 (6)	0.1 (5)	1.7 (5)	−0.1 (5)
N(3)	0.145 (1)	0.7955 (7)	0.2294 (6)	4.2 (6)	3.7 (6)	3.5 (6)	−0.1 (5)	1.0 (5)	0.9 (5)
N(4)	−0.022 (1)	0.7728 (8)	0.1303 (6)	3.3 (6)	5.1 (7)	4.7 (6)	1.2 (6)	1.3 (5)	0.8 (6)
N(5)	0.334 (1)	0.6971 (7)	0.1776 (6)	3.2 (6)	3.1 (6)	4.7 (6)	0.4 (5)	1.0 (5)	−0.2 (5)
N(6)	0.159 (1)	0.6614 (8)	0.0846 (6)	5.1 (6)	4.0 (7)	5.5 (6)	1.4 (6)	1.9 (5)	0.1 (6)
N(7)	0.254 (1)	0.5604 (8)	0.2475 (6)	4.2 (6)	4.3 (7)	4.1 (6)	−0.1 (6)	0.6 (5)	−0.8 (6)
N(8)	0.073 (1)	0.5272 (7)	0.1558 (6)	4.9 (7)	3.3 (6)	5.0 (6)	−0.2 (6)	1.7 (5)	−0.1 (6)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
O(1)	0.444 (2)	0.494 (1)	0.6477 (9)	12.3 (5)	O(2)	0.388 (2)	0.600 (1)	0.8870 (10)	14.7 (7)
C(1)	−0.067 (2)	0.6416 (10)	0.2640 (8)	4.4 (4)	C(17)	0.471 (1)	0.7167 (8)	0.2098 (7)	5.2 (3)
C(2)	−0.164 (2)	0.6261 (11)	0.3060 (8)	5.3 (4)	C(18)	0.509 (1)	0.7274 (9)	0.2857 (7)	6.3 (4)
C(3)	−0.108 (2)	0.6364 (11)	0.3758 (8)	5.6 (4)	C(19)	0.180 (1)	0.4964 (7)	0.2091 (6)	3.6 (2)
C(4)	0.029 (2)	0.6565 (11)	0.4062 (8)	5.7 (4)	C(20)	0.203 (1)	0.4117 (8)	0.2179 (7)	5.1 (3)
C(5)	0.113 (2)	0.6689 (10)	0.3633 (8)	5.1 (4)	C(21)	0.122 (1)	0.3581 (8)	0.1760 (7)	5.2 (3)
C(6)	0.260 (2)	0.6914 (12)	0.3921 (9)	6.2 (5)	C(22)	0.015 (1)	0.3857 (8)	0.1192 (6)	4.7 (3)
C(7)	0.047 (2)	0.8269 (10)	0.1810 (7)	4.1 (4)	C(23)	−0.006 (1)	0.4677 (7)	0.1106 (6)	4.0 (3)
C(8)	−0.001 (2)	0.9084 (11)	0.1746 (9)	5.5 (4)	C(24)	−0.119 (1)	0.5032 (9)	0.0539 (7)	5.3 (3)
C(9)	−0.103 (2)	0.9300 (11)	0.1178 (9)	5.9 (5)	C(25)	0.349 (2)	0.5645 (13)	0.6567 (9)	9.5 (5)
C(10)	−0.165 (2)	0.8760 (11)	0.0653 (9)	6.0 (5)	C(26)	0.271 (2)	0.5822 (13)	0.5849 (10)	10.2 (6)
C(11)	−0.122 (2)	0.7958 (10)	0.0750 (8)	4.3 (4)	C(27)	0.377 (2)	0.5627 (13)	0.5480 (10)	9.5 (5)
C(12)	−0.176 (2)	0.7326 (11)	0.0229 (9)	5.7 (5)	C(28)	0.477 (2)	0.4996 (14)	0.5860 (11)	11.5 (6)
C(13)	0.291 (2)	0.6839 (10)	0.1103 (8)	4.4 (4)	C(29)	0.536 (3)	0.6060 (18)	0.9250 (14)	15.5 (9)
C(14)	0.383 (2)	0.6953 (11)	0.0667 (9)	6.1 (5)	C(30)	0.600 (2)	0.5368 (14)	0.9028 (11)	11.0 (6)
C(15)	0.514 (2)	0.7230 (12)	0.1013 (9)	6.5 (5)	C(31)	0.503 (3)	0.5062 (17)	0.8429 (13)	14.3 (8)
C(16)	0.563 (1)	0.7315 (9)	0.1733 (7)	6.1 (3)	C(32)	0.370 (2)	0.5374 (16)	0.8392 (13)	13.3 (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 $Mo_2(map)_4 \cdot 2THF^a$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	0.1896 (1)	0.67542 (6)	0.23409 (5)	3.45 (4)	2.61 (4)	3.64 (4)	−0.04 (4)	0.72 (3)	−0.25 (4)
Mo(2)	0.0342 (1)	0.65053 (6)	0.14671 (5)	3.27 (4)	2.46 (4)	3.28 (4)	0.18 (4)	0.87 (3)	−0.04 (4)
N(1)	0.0577 (10)	0.6577 (5)	0.2990 (4)	5.6 (5)	2.1 (4)	3.8 (4)	−0.1 (4)	1.8 (3)	−0.2 (3)
N(2)	−0.1125 (9)	0.6312 (5)	0.2002 (5)	4.3 (4)	2.7 (4)	4.3 (4)	0.7 (4)	1.6 (3)	0.7 (4)
N(3)	0.1395 (10)	0.7996 (6)	0.2302 (5)	4.5 (4)	2.9 (4)	5.0 (5)	−0.5 (4)	1.0 (4)	−0.2 (4)
N(4)	−0.0265 (8)	0.7761 (6)	0.1312 (4)	3.5 (4)	3.7 (4)	4.7 (4)	0.3 (4)	2.3 (3)	0.6 (4)
N(5)	0.3379 (9)	0.6957 (6)	0.1771 (5)	2.8 (4)	3.4 (4)	5.9 (5)	−0.3 (4)	1.3 (3)	−0.2 (4)
N(6)	0.1650 (10)	0.6657 (6)	0.0829 (5)	5.3 (4)	3.7 (5)	4.3 (4)	1.1 (4)	2.3 (3)	0.5 (4)
N(7)	0.2518 (10)	0.5521 (6)	0.2500 (5)	4.1 (4)	3.3 (4)	4.0 (5)	−0.0 (4)	0.6 (4)	−0.3 (4)
N(8)	0.0713 (9)	0.5222 (5)	0.1544 (4)	3.7 (4)	2.4 (4)	3.8 (4)	−0.2 (3)	1.3 (3)	−0.7 (3)
atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O(1)	0.450 (1)	0.500 (1)	0.6513 (7)	11.8 (4)	O(2)	0.389 (2)	0.601 (1)	0.8886 (9)	15.9 (6)
C(1)	−0.076 (1)	0.6369 (7)	0.2676 (6)	3.7 (2)	C(17)	0.466 (2)	0.7189 (10)	0.2112 (8)	4.8 (4)
C(2)	−0.169 (1)	0.6216 (8)	0.3081 (6)	4.8 (3)	C(18)	0.500 (2)	0.7299 (11)	0.2853 (9)	5.8 (5)
C(3)	−0.120 (1)	0.6328 (9)	0.3766 (7)	6.1 (3)	C(19)	0.183 (2)	0.5032 (9)	0.2094 (7)	3.7 (3)
C(4)	0.014 (1)	0.6571 (9)	0.4079 (7)	5.7 (3)	C(20)	0.206 (2)	0.4180 (10)	0.2187 (8)	5.2 (4)
C(5)	0.102 (1)	0.6686 (8)	0.3684 (6)	4.6 (3)	C(21)	0.122 (2)	0.3647 (11)	0.1772 (8)	5.4 (4)
C(6)	0.247 (1)	0.6923 (9)	0.3962 (7)	6.0 (3)	C(22)	0.012 (2)	0.3929 (11)	0.1215 (9)	5.8 (5)
C(7)	0.041 (1)	0.8294 (7)	0.1806 (5)	3.5 (2)	C(23)	−0.009 (2)	0.4748 (9)	0.1128 (7)	4.0 (4)
C(8)	−0.006 (1)	0.9116 (8)	0.1743 (7)	5.2 (3)	C(24)	−0.122 (2)	0.5070 (11)	0.0546 (9)	5.9 (5)
C(9)	−0.103 (1)	0.9358 (9)	0.1203 (7)	5.8 (3)	C(25)	0.342 (3)	0.5594 (16)	0.6542 (12)	10.7 (7)
C(10)	−0.173 (1)	0.8804 (8)	0.0679 (7)	5.1 (3)	C(26)	0.274 (2)	0.5787 (15)	0.5831 (12)	9.9 (7)
C(11)	−0.128 (1)	0.8030 (7)	0.0758 (6)	4.1 (3)	C(27)	0.371 (3)	0.5618 (17)	0.5454 (12)	11.0 (8)
C(12)	−0.189 (1)	0.7409 (8)	0.0226 (7)	5.2 (3)	C(28)	0.473 (3)	0.4973 (17)	0.5883 (13)	11.0 (8)
C(13)	0.297 (1)	0.6869 (8)	0.1106 (6)	4.2 (3)	C(29)	0.522 (3)	0.5972 (17)	0.9301 (13)	11.7 (8)
C(14)	0.391 (1)	0.6988 (9)	0.0711 (7)	6.1 (3)	C(30)	0.598 (3)	0.5358 (16)	0.9024 (13)	11.2 (8)
C(15)	0.519 (2)	0.7219 (10)	0.1036 (8)	6.9 (4)	C(31)	0.496 (3)	0.5084 (20)	0.8378 (15)	14.1 (10)
C(16)	0.557 (2)	0.7319 (12)	0.1709 (9)	6.5 (5)	C(32)	0.367 (3)	0.5370 (19)	0.8385 (14)	12.6 (9)

[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 IV. Positional and Thermal Parameters and Their Estimated Standard Deviations for $W_2(map)_4 \cdot 2THF^a$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	0.19249 (9)	0.67515 (5)	0.23560 (5)	3.73 (4)	3.05 (3)	3.47 (4)	−0.06 (3)	0.63 (3)	−0.35 (4)
W(2)	0.02938 (9)	0.64910 (5)	0.14402 (5)	3.56 (3)	2.87 (3)	3.20 (4)	0.19 (3)	0.84 (3)	−0.15 (3)
N(1)	0.058 (2)	0.6573 (9)	0.2981 (9)	8 (1)	2.7 (7)	3.6 (9)	0.7 (8)	1.6 (8)	−0.1 (7)
N(2)	−0.114 (2)	0.6329 (9)	0.1976 (9)	4.2 (7)	2.8 (7)	3.9 (8)	0.4 (6)	1.4 (6)	0.8 (6)
N(3)	0.144 (2)	0.7984 (10)	0.2323 (10)	4.9 (8)	4.0 (8)	4.4 (9)	0.0 (7)	1.4 (7)	−0.6 (8)
N(4)	−0.031 (2)	0.7738 (9)	0.1310 (9)	3.1 (7)	3.9 (7)	2.9 (8)	−0.5 (7)	−0.2 (7)	1.2 (7)
N(5)	0.334 (2)	0.6952 (10)	0.1767 (10)	3.0 (7)	3.6 (7)	6 (1)	−0.4 (7)	1.7 (7)	0.5 (8)
N(6)	0.159 (2)	0.6637 (10)	0.0821 (9)	4.7 (8)	4.3 (8)	3.7 (8)	0.5 (7)	1.5 (6)	−0.3 (7)
N(7)	0.250 (2)	0.5538 (10)	0.2489 (11)	3.2 (7)	4.1 (8)	6 (1)	−0.7 (7)	0.1 (8)	0.3 (8)
N(8)	0.075 (2)	0.5215 (10)	0.1538 (9)	4.3 (7)	3.3 (7)	5.6 (9)	0.7 (7)	2.4 (7)	−0.7 (7)
atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O(1)	0.450 (2)	0.498 (2)	0.648 (1)	12.0 (8)	O(2)	0.395 (3)	0.603 (2)	0.884 (2)	17.4 (12)
C(1)	−0.079 (2)	0.637 (1)	0.266 (1)	4.1 (5)	C(17)	0.470 (2)	0.716 (1)	0.209 (1)	4.8 (5)
C(2)	−0.167 (2)	0.620 (1)	0.307 (1)	4.3 (5)	C(18)	0.508 (3)	0.727 (2)	0.284 (1)	6.6 (7)
C(3)	−0.115 (2)	0.633 (1)	0.376 (1)	5.7 (1)	C(19)	0.180 (2)	0.495 (1)	0.207 (1)	3.3 (4)
C(4)	0.010 (2)	0.655 (1)	0.407 (1)	5.5 (6)	C(20)	0.206 (2)	0.414 (1)	0.220 (1)	5.6 (6)
C(5)	0.101 (2)	0.667 (1)	0.366 (1)	4.8 (5)	C(21)	0.123 (2)	0.360 (1)	0.173 (1)	4.6 (5)
C(6)	0.248 (3)	0.691 (2)	0.396 (1)	6.6 (7)	C(22)	0.016 (2)	0.386 (1)	0.117 (1)	4.2 (5)
C(7)	0.042 (2)	0.828 (1)	0.180 (1)	4.3 (5)	C(23)	−0.006 (2)	0.468 (1)	0.111 (1)	4.7 (5)
C(8)	−0.004 (2)	0.912 (1)	0.176 (1)	5.1 (6)	C(24)	−0.122 (2)	0.500 (1)	0.054 (1)	5.1 (5)
C(9)	−0.105 (2)	0.934 (1)	0.119 (1)	5.7 (6)	C(25)	0.347 (4)	0.563 (2)	0.652 (2)	10.0 (10)
C(10)	−0.169 (2)	0.880 (1)	0.067 (1)	5.1 (6)	C(26)	0.272 (4)	0.582 (2)	0.581 (2)	11.0 (11)
C(11)	−0.128 (2)	0.802 (1)	0.074 (1)	3.5 (4)	C(27)	0.379 (4)	0.561 (3)	0.544 (3)	14.0 (15)
C(12)	−0.191 (2)	0.741 (1)	0.019 (1)	5.8 (6)	C(28)	0.478 (4)	0.499 (3)	0.585 (2)	12.4 (12)
C(13)	0.288 (2)	0.684 (1)	0.108 (1)	4.6 (5)	C(29)	0.532 (5)	0.611 (3)	0.931 (3)	14.0 (15)
C(14)	0.382 (3)	0.697 (2)	0.067 (1)	6.4 (7)	C(30)	0.593 (4)	0.535 (3)	0.903 (3)	14.4 (15)
C(15)	0.510 (3)	0.719 (2)	0.100 (2)	6.8 (7)	C(31)	0.498 (5)	0.497 (3)	0.843 (3)	14.7 (15)
C(16)	0.560 (2)	0.732 (2)	0.171 (1)	6.0 (6)	C(32)	0.372 (4)	0.539 (3)	0.838 (2)	13.6 (14)

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

isolation of $W_2(map)_4$, but the important thing for the present is that we know it is a stable compound and we have been able to determine its structure.

If the methyl group is not present on the aminopyridine ligand, compounds with the general formula $M_2(ap)_4$ can be formed where ap is 2-aminopyridine. These compounds are noncrystalline, insoluble substances which appear to be polymeric. A similar observation was made with the 2-hydroxypyridine complexes. Intermolecular ligand bridging is one possible explanation, since this type of bonding cannot occur when methyl groups are present blocking the axial positions.

Solutions of the $M_2(map)_4$ compounds absorb CO_2 to give noncrystalline precipitates, but attempts to isolate and

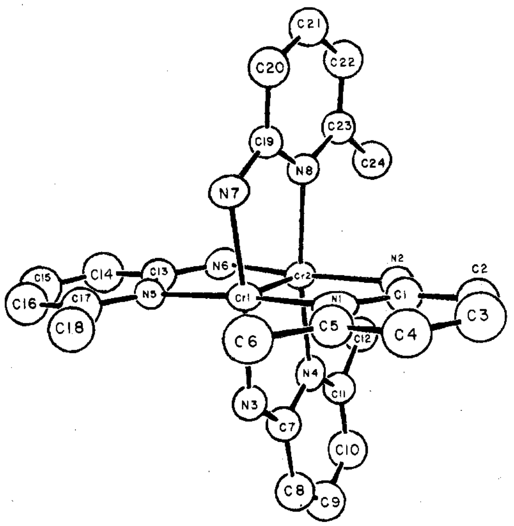


Figure 1. An ORTEP drawing of the $Cr_2(map)_4$ molecule in which each atom is represented by the projection of its ellipsoid or sphere of thermal vibration scaled to enclose 50% of the electron density. The atom numbering scheme shown also applies to the Mo and W compounds.

characterize these resulted in their decomposition with concomitant evolution of CO_2. It is likely that the initial reaction with CO_2 leads to formation of relatively labile carbamato compounds which readily decompose.

Structures. The structure of $Cr_2(map)_4$ is shown in Figure 1 and illustrates the numbering scheme for all compounds. The atomic positional and thermal vibrational parameters are given in Tables II, III, and IV for the chromium, molybdenum, and tungsten compounds, respectively. Bond distances and angles are listed in Tables V–VII. Figure 2 shows how the molecules occupy the unit cell. It is clear that the THF molecules are arranged interstitially and that there is not the slightest degree of coordination to the axial positions of the metal atoms.

The arrangment of the ligands around the M_2 units is similar to that in the $M_2(mhp)_4$ compounds. There are two ligands oriented each way with those of the same orientation trans to each other. The idealized symmetry of the $M_2(map)_4$ molecule is, therefore, D_{2d}.

The M–M quadruple bond, 4°M–M, lengths in these compounds are among the shortest that have been found.[1,3] The 4°Cr–Cr bond length of 1.870 (3) Å is 0.02 Å shorter than the distance of 1.889 (1) Å found in the analogous $Cr_2(mhp)_4$ molecule.[1] Surprisingly, however, the Mo–Mo distance is a trifle longer than the 2.065 (1) Å distance found in $Mo_2(mhp)_4$. The 4°W–W distance is again very short as in the case of $W_2(mhp)_4$.

Table V. Bond Distances (Å) in the $M_2(map)_4$·THF Molecules[a]

	M = Cr	M = Mo	M = W
M(1)–M(2)	1.870 (3)	2.070 (1)	2.164 (1)
–N(1)	2.072 (9)	2.174 (8)	2.15 (2)
–N(3)	2.029 (9)	2.129 (8)	2.11 (2)
–N(5)	2.11 (1)	2.193 (8)	2.16 (2)
–N(7)	2.02 (1)	2.149 (8)	2.10 (2)
M(2)–N(2)	2.02 (1)	2.124 (8)	2.09 (2)
–N(4)	2.10 (1)	2.181 (8)	2.16 (1)
–N(6)	2.04 (1)	2.141 (8)	2.10 (2)
–N(8)	2.08 (1)	2.170 (7)	2.17 (1)
N(1)–C(1)	1.36 (2)	1.37 (1)	1.40 (3)
N(1)–C(5)	1.35 (1)	1.38 (1)	1.35 (3)
N(4)–C(7)	1.40 (1)	1.38 (1)	1.40 (3)
N(4)–C(11)	1.34 (1)	1.38 (1)	1.38 (2)
N(5)–C(13)	1.34 (2)	1.32 (1)	1.36 (3)
N(5)–C(17)	1.36 (2)	1.38 (1)	1.40 (3)
N(8)–C(19)	1.38 (1)	1.40 (1)	1.36 (2)
N(8)–C(23)	1.34 (1)	1.36 (1)	1.35 (3)
N(2)–C(1)	1.33 (1)	1.33 (1)	1.34 (3)
N(3)–C(7)	1.30 (1)	1.31 (1)	1.35 (3)
N(6)–C(13)	1.34 (2)	1.35 (1)	1.31 (3)
N(7)–C(19)	1.30 (1)	1.40 (1)	1.36 (2)
C(1)–C(2)	1.50 (2)	1.46 (1)	1.42 (3)
C(2)–C(3)	1.39 (2)	1.37 (1)	1.39 (3)
C(3)–C(4)	1.39 (2)	1.40 (1)	1.30 (3)
C(4)–C(5)	1.41 (2)	1.39 (1)	1.44 (3)
C(5)–C(6)	1.48 (2)	1.47 (1)	1.49 (3)
C(7)–C(8)	1.42 (2)	1.45 (1)	1.46 (3)
C(8)–C(9)	1.37 (2)	1.32 (1)	1.36 (3)
C(9)–C(10)	1.40 (2)	1.44 (1)	1.39 (3)
C(10)–C(11)	1.39 (2)	1.36 (1)	1.35 (3)
C(11)–C(12)	1.48 (2)	1.51 (1)	1.52 (3)
C(13)–C(14)	1.48 (2)	1.44 (1)	1.46 (3)
C(14)–C(15)	1.38 (2)	1.34 (1)	1.34 (3)
C(15)–C(16)	1.38 (2)	1.39 (2)	1.41 (4)
C(16)–C(17)	1.42 (2)	1.38 (1)	1.40 (3)
C(17)–C(18)	1.47 (2)	1.51 (1)	1.48 (3)
C(19)–C(20)	1.43 (2)	1.43 (1)	1.38 (3)
C(20)–C(21)	1.35 (2)	1.35 (1)	1.40 (3)
C(21)–C(22)	1.42 (2)	1.43 (1)	1.41 (3)
C(22)–C(23)	1.37 (2)	1.39 (1)	1.38 (3)
C(23)–C(24)	1.50 (2)	1.51 (1)	1.51 (3)
O(1)–C(25)	1.53 (2)	1.51 (2)	1.52 (4)
O(1)–C(28)	1.34 (2)	1.45 (2)	1.40 (4)
O(2)–C(29)	1.39 (2)	1.47 (2)	1.46 (5)
O(2)–C(32)	1.41 (3)	1.44 (2)	1.40 (5)
C(25)–C(26)	1.46 (2)	1.49 (2)	1.47 (5)
C(26)–C(27)	1.44 (2)	1.52 (2)	1.55 (5)
C(27)–C(28)	1.57 (3)	1.51 (2)	1.51 (5)
C(29)–C(30)	1.48 (3)	1.46 (3)	1.58 (6)
C(30)–C(31)	1.50 (3)	1.43 (3)	1.48 (6)
C(31)–C(32)	1.39 (3)	1.44 (3)	1.44 (5)

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

The average M–N(py) and M–N(amine) distances show distinct differences. These distances are listed in Table VII.

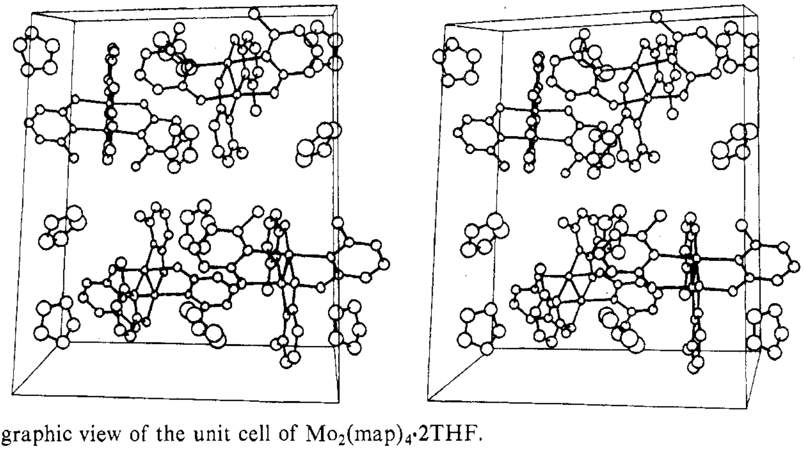


Figure 2. An ORTEP stereographic view of the unit cell of $Mo_2(map)_4$·2THF.

Table VI. Bond Angles (deg) in the $M_2(map)_4 \cdot 2THF$ Molecules[a]

	M = Cr	M = Mo	M = W
M(2)-M(1)-N(1)	95.5 (3)	93.1 (2)	91.6 (5)
N(3)	95.7 (3)	92.7 (2)	93.0 (5)
N(5)	95.1 (3)	92.2 (2)	90.8 (5)
N(7)	96.4 (3)	93.4 (2)	92.1 (5)
N(1)-M(1)-N(3)	87.6 (4)	88.4 (3)	88.2 (6)
N(5)	169.3 (4)	174.7 (3)	177.5 (7)
N(7)	90.3 (4)	89.1 (3)	89.6 (6)
N(3)-M(1)-N(5)	90.1 (4)	91.4 (3)	91.2 (6)
N(7)	167.8 (4)	173.5 (3)	174.5 (7)
N(5)-M(1)-N(7)	89.8 (4)	90.6 (3)	90.8 (6)
M(1)-M(2)-N(2)	96.7 (3)	93.2 (2)	92.7 (5)
N(4)	95.4 (3)	92.8 (2)	92.0 (4)
N(6)	96.1 (3)	93.1 (2)	92.5 (5)
N(8)	95.1 (3)	93.4 (2)	91.5 (5)
N(2)-M(2)-N(4)	89.2 (4)	90.5 (3)	88.3 (6)
N(6)	167.2 (4)	173.6 (3)	174.8 (7)
N(8)	88.1 (4)	86.9 (3)	89.4 (6)
N(4)-M(2)-N(6)	90.2 (4)	89.9 (3)	91.2 (6)
N(8)	169.4 (4)	173.3 (3)	175.9 (6)
N(6)-M(2)-N(8)	90.2 (4)	92.0 (3)	90.7 (6)
M(1)-N(1)-C(1)	113.7 (8)	116.8 (6)	118 (1)
C(5)	124.8 (8)	122.7 (7)	122 (2)
C(1)-N(1)-C(5)	121 (1)	120.5 (8)	120 (2)
M(1)-N(5)-C(13)	114.9 (8)	118.5 (7)	118 (1)
C(17)	122.0 (9)	120.9 (7)	120 (2)
C(13)-N(5)-C(17)	123 (1)	120.7 (9)	122 (2)
M(2)-N(4)-C(7)	113.7 (8)	116.8 (6)	117 (1)
C(11)	123.4 (9)	123.2 (7)	123 (1)
C(17)-N(4)-C(11)	123 (1)	120.0 (8)	119 (2)
M(2)-N(8)-C(19)	113.6 (8)	116.2 (6)	119 (1)
C(23)	123.2 (8)	123.7 (6)	121 (1)
C(19)-N(8)-C(23)	123 (1)	120.0 (8)	119 (2)
M(1)-N(3)-C(7)	119.8 (9)	121.3 (6)	120 (1)
M(1)-N(7)-C(19)	117.8 (8)	119.2 (7)	122 (1)
M(2)-N(2)-C(1)	115.7 (8)	120.2 (7)	122 (1)
M(2)-N(6)-C(13)	117.5 (9)	119.6 (7)	121 (2)
N(1)-C(1)-N(2)	118 (1)	116.7 (9)	116 (2)
C(2)	119 (1)	119.9 (9)	119 (2)
N(2)-C(1)-C(2)	122 (1)	123.4 (9)	126 (2)
C(1)-C(2)-C(3)	116 (1)	117 (1)	118 (2)
C(2)-C(3)-C(4)	123 (1)	122 (1)	125 (2)
C(3)-C(4)-C(5)	117 (1)	119 (1)	118 (2)
N(1)-C(5)-C(4)	122 (1)	121 (1)	121 (2)
C(6)	117 (1)	116 (1)	116 (2)
C(4)-C(5)-C(6)	120 (1)	123 (1)	123 (2)
N(3)-C(7)-N(4)	115 (1)	116.2 (8)	117 (2)
C(8)	128 (1)	126.2 (9)	124 (2)
N(4)-C(7)-C(8)	117 (1)	117.6 (9)	118 (2)
C(7)-C(8)-C(9)	118 (1)	121 (1)	117 (2)
C(8)-C(9)-C(10)	123 (1)	121 (1)	123 (2)
C(9)-C(10)-C(11)	116 (1)	116 (1)	118 (2)
N(4)-C(11)-C(10)	121 (1)	124 (1)	123 (2)
C(12)	116 (1)	115.6 (9)	116 (2)
C(10)-C(11)-C(12)	122 (1)	121 (1)	121 (2)
N(5)-C(13)-N(6)	116 (1)	116.6 (9)	118 (2)
C(14)	122 (1)	120 (1)	119 (2)
N(6)-C(13)-C(14)	122 (1)	123 (1)	123 (2)
C(13)-C(14)-C(15)	114 (1)	118 (1)	117 (3)
C(14)-C(15)-C(16)	122 (1)	122 (1)	125 (3)
C(15)-C(16)-C(17)	122 (1)	118 (1)	117 (2)
N(5)-C(17)-C(16)	117 (1)	120 (1)	120 (2)
N(5)-C(17)-C(18)	118 (1)	117 (1)	117 (2)
C(16)-C(17)-C(18)	125 (1)	122 (1)	123 (2)
N(7)-C(19)-N(8)	117 (1)	117.5 (9)	115 (2)
C(20)	126 (1)	124.6 (9)	123 (2)
N(8)-C(19)-C(20)	117 (1)	117.9 (9)	122 (2)
C(19)-C(20)-C(21)	120 (1)	121 (1)	116 (2)
C(20)-C(21)-C(22)	120 (1)	120 (1)	123 (2)
C(21)-C(22)-C(23)	119 (1)	118 (1)	116 (2)
N(8)-C(23)-C(22)	120 (1)	122.5 (9)	123 (2)
C(24)	119 (1)	114.7 (9)	118 (2)
C(22)-C(23)-C(24)	121 (1)	123 (1)	119 (2)
C(25)-O(1)-C(28)	112 (2)	113 (1)	112 (3)
O(1)-C(25)-C(26)	102 (2)	104 (1)	105 (3)
C(25)-C(26)-C(27)	107 (2)	102 (1)	102 (3)
C(26)-C(27)-C(28)	106 (2)	111 (1)	109 (4)
O(1)-C(28)-C(27)	105 (2)	101 (1)	104 (3)
C(29)-O(2)-C(32)	110 (2)	108 (2)	116 (4)
O(2)-C(29)-C(30)	107 (2)	106 (2)	97 (4)
C(29)-C(30)-C(31)	104 (2)	107 (2)	114 (4)
C(30)-C(31)-C(32)	107 (2)	109 (2)	103 (4)
O(2)-C(32)-C(31)	108 (2)	107 (2)	111 (4)

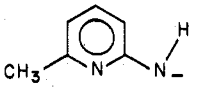
[a] Figures in parentheses following individual angles are esd's occurring in the least significant digit.

Table VII. Average Metal-Nitrogen Bond Lengths[a] in $M_2(map)_4$

bond	M = Cr	M = Mo	M = W
Mo-N(py)	2.09 (2)	2.18 (1)	2.160 (8)
Mo-N(amine)	2.027 (2)	2.14 (1)	2.100 (8)

[a] Figures in parentheses are the mean deviation of the individual values from the average.

The metal–N(amine) distance is shorter than the metal–N(py) distance in each compound, by about 0.06 Å in $Cr_2(map)_4$, 0.04 Å in $Mo_2(map)_4$, and 0.06 Å in $W_2(map)_4$. This can be understood on purely electrostatic grounds for the ligand in the form



There is nothing unusual or noteworthy in the remaining bond distances and angles for the three molecules and nothing further need be said about them.

One interesting fact about these crystalline compounds is that no crystallographic symmetry is imposed on the $M_2(map)_4$ molecules and thus there may be internal rotation away from a strictly eclipsed configuration. As a measure of the deviation from the eclipsed configuration, we calculate the four independent torsional angles about the M–M bond; these are listed in Table VIII. These angles differ from zero and each other due not only to internal rotation but also to steric distortions. Thus, an average of the torsional angles for each compound is merely an estimate of the deviation from the eclipsed configuration. We see in Table VIII that such deviation is slight in both compounds but greater in the chromium compound than in the others.

Table VIII. Torsional Angles (deg) in $M_2(map)_4 \cdot 2THF$

planes defining the angle		angle		
atoms in plane 1	atoms in plane 2	M = Cr	M = Mo	M = W
N(1), M(1), M(2)	M(1), M(2), N(2)	3.8	0.4	1.4
N(3), M(1), M(2)	M(1), M(2), N(4)	3.3	2.6	1.6
N(5), M(1), M(2)	M(1), M(2), N(6)	3.4	1.0	1.6
N(7), M(1), M(2)	M(1), M(2), N(8)	3.8	2.5	1.6
	mean angle	3.6	1.6	1.55

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

Registry No. $Cr_2(map)_4 \cdot 2THF$, 68122-29-2; $Mo_2(map)_4 \cdot 2THF$, 68122-31-6; $W_2(map)_4 \cdot 2THF$, 68122-33-8; $Cr_2(O_2CCH_3)_4$, 15020-15-2; $Mo_2(O_2CCH_3)_4$, 14221-06-8; $W_2(mhp)_4$, 67634-84-8.

Supplementary Material Available: Tables of structure factors for both compounds (30 pages). Ordering information is given on any current masthead page.

References and Notes

(1) F. A. Cotton, P. E. Fanwick, R. H. Niswander, and J. C. Sekutowski, *J. Am. Chem. Soc.*, **100**, 4725 (1978).
(2) This and other points concerning standard procedures for crystal structure determination in this laboratory have been covered often in earlier papers. See, for example, F. A. Cotton, M. Extine, and L. D. Gage, *Inorg. Chem.*, **17**, 172 (1978), and earlier references therein.
(3) See ref 1 for discussion and extensive references.