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The Molybdenum–Molybdenum Triple Bond. 6.[1] Bis(2-oxy-6-methylpyridine)tetrakis(dimethylamido)dimolybdenum

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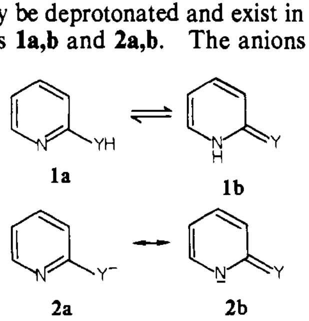
$Mo_2(NMe_2)_6$ reacts in hydrocarbon solvents with 2-hydroxy-6-methylpyridine (2 equiv) to give the title compound as dark red crystals. In the solid state, each molybdenum atom is coordinated to two amido nitrogen atoms and an oxygen and nitrogen atom of the anionic ligand generated by proton loss from 2-hydroxy-6-methylpyridine. These ligands form cis bridges across the molybdenum–molybdenum triple bond which has a bond distance equal to 2.211 (2) Å. The molecule has virtual C_2 symmetry and avoids the eclipsing of the Mo–N bonds of the dimethylamido groups. The Mo–N distances to the pyridine nitrogen atoms are long (2.325 (10) Å) relative to the Mo–N distances (1.98 Å averaged) associated with the dimethylamido ligands. The Mo–O bond distances (2.08 Å averaged) are longer than those found in molybdenum alkoxides but are comparable to those found in bridging carboxylates. ^1H NMR studies reveal the presence of two isomers in solution. The spectra associated with the major isomer are consistent with the structure found in the solid state. The minor isomer is not bridged and maintains an apparent C_2 axis of symmetry, but beyond this, its structure is uncertain. Above 70 °C, isomerization is rapid on the NMR time scale. Crystal data for $Mo_2C_{20}H_{36}N_6O_2$ are as follows: space group *Pbca*; $Z = 8$; $a = 14.402$ (5), $b = 21.746$ (7), $c = 15.358$ (5) Å; $V = 4810$ (1) Å^3. Further addition of 2-hydroxy-6-methylpyridine to the title compound yields a brown hydrocarbon-insoluble compound which is formulated as $Mo_2(NMe_2)_2(2\text{-}O\text{-}6\text{-}Mepy)_4$ on the basis of analytical data and mass spectral data.

Introduction

An extensive chemistry is emerging for dinuclear compounds of molybdenum and tungsten containing the $(M\equiv M)^{6+}$ unit.[2,3] The ethane-like M_2X_6 molecules, where X = CH_2SiMe_3, NMe_2, and O-*i*-Pr, provide examples of extremely unsaturated metal complexes since the formation of a metal-to-metal triple bond and three M–X σ bonds leads to only 12-metal valence-shell electrons. Ligand-to-metal π bonding can occur when X = NR_2 and OR but not when X = alkyl. Consequently, we anticipate that these complexes should be labile to a number of modes of reaction involving an increase in the coordination number and valence-shell electron count of the metal atoms. Lewis base association has been observed for the alkoxides of molybdenum[5] and tungsten,[6] but not for the alkyls or dialkylamides. In order to compare the Lewis acidity of molybdenum and tungsten toward specific donor groups as a function of X and M (Mo vs. W), we decided to prepare a series of compounds of general formula $M_2X_4(YL)_2$, where X = CH_2SiMe_3, NMe_2 and O-*i*-Pr and YL is a uninegative and potentially bidentate ligand.

The 2-YH-substituted pyridine molecules contain acidic protons that may be deprotonated and exist in tautomeric and resonance forms **1a,b** and **2a,b**. The anions may act as bidentate ligands and have been found to be capable of bridging dimetal complexes.[7] We report here the preparation and characterization of the $Mo_2(NMe_2)_4(2\text{-}O\text{-}6\text{-}Mepy)_2$ (2-O-6-Mepy = 2-oxy-6-methylpyridine) molecule, which is a member of the $M_2X_4(YL)_2$ class of compounds.



1a **1b**

2a **2b**

Results and Discussion

Synthesis. $Mo_2(NMe_2)_6$, in toluene, reacts rapidly with 2-hydroxy-6-methylpyridine to give a deep red solution of $Mo_2(NMe_2)_4(2\text{-}O\text{-}6\text{-}Mepy)_2$ and dimethylamine. Deep red crystals of the title compound were obtained from hexane solutions.

Analytical, IR, and ^1H NMR data are reported in the Experimental Section.

Solid-State Structure. In the crystalline state, the compound is composed of discrete $Mo_2(NMe_2)_4(2\text{-}O\text{-}6\text{-}Mepy)_2$ molecules. Final atomic positional parameters are given in Table I and bond distances and bond angles are given in Tables II and III, respectively. An ORTEP view of the molecule giving the atomic numbering scheme is shown in Figure 1, and Figure 2 shows a view of the molecule down the Mo–Mo axis.

The molecule has a virtual C_2 axis of symmetry. There are two types of NMe_2 groups, those trans to oxygen atoms and those trans to nitrogen atoms of the 2-oxy-6-methylpyridine ligand having long and short Mo–N distances, respectively. The Mo–O distances (2.08 Å (average)) are comparable to those found[8] for the bridging carbamate ligands in $W_2(O_2CNMe_2)_6$ and $W_2Me_2(O_2CNEt_2)_4$ and much shorter than the Mo–N distances (2.325 (10) Å) associated with the coordinated pyridine moiety. A comparison of bond distances for the 2-oxy-6-methylpyridine ligand bridging two molybdenum atoms in the title compound and in $Mo_2(2\text{-}O\text{-}6\text{-}Mepy)_4$, which contains a $M\overset{4}{-}M$ bond,[7] is shown in Figure 3. The Mo–N(py) distances found in the title compound, though very long by comparison to those found in $Mo_2(2\text{-}O\text{-}6\text{-}Mepy)_4$, are comparable to the tungsten–pyridine nitrogen distances in $W_2(O\text{-}i\text{-}Pr)_6(py)_2$ $(W\equiv W)$.[6] In the latter compound, it is fair to correlate the long W–N(py) bonds with weak W–N bonds since the pyridine molecules dissociate slowly in solution and rapidly upon heating in vacuo. It would appear reasonable to suppose that in $Mo_2(NMe_2)_4(2\text{-}O\text{-}6\text{-}Mepy)_2$, the Mo–py bonding is weak and, as is shown later, may dissociate in

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Table I. Fractional Coordinates for $Mo_2(NMe_2)_4(2\text{-}O\text{-}6\text{-}Mepy)_2$[a,b]

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Mo(1)[c]	1651.9 (7)	3535.4 (4)	871.6 (6)	8
Mo(2)[c]	2797.0 (7)	4205.6 (5)	734.1 (7)	9
O(3)	3384 (6)	4027 (4)	1947 (5)	13 (1)
C(4)	2922 (9)	3724 (5)	2530 (8)	13 (2)
N(5)	2050 (7)	3536 (4)	2339 (6)	10 (2)
C(6)	1535 (9)	3223 (6)	2926 (8)	13 (2)
C(7)	542 (9)	3056 (6)	2730 (9)	12 (2)
C(8)	1917 (9)	3057 (6)	3738 (8)	12 (2)
C(9)	2809 (10)	3237 (6)	3929 (8)	16 (3)
C(10)	3311 (10)	3580 (6)	3361 (8)	15 (2)
O(11)	688 (6)	4151 (4)	1376 (5)	13 (2)
C(12)	986 (8)	4657 (5)	1739 (7)	9 (2)
N(13)	1877 (7)	4828 (5)	1612 (6)	12 (2)
C(14)	2164 (9)	5378 (5)	1920 (7)	12 (2)
C(15)	3173 (10)	5537 (7)	1745 (10)	17 (3)
C(16)	1592 (9)	5762 (6)	2395 (8)	16 (2)
C(17)	684 (10)	5583 (6)	2553 (10)	18 (3)
C(18)	372 (10)	5019 (6)	2235 (9)	17 (3)
N(19)	2261 (7)	2703 (4)	965 (6)	9 (2)
C(20)	3140 (9)	2546 (7)	1335 (9)	16 (3)
C(21)	1600 (10)	2189 (6)	1045 (8)	13 (2)
N(22)	1051 (7)	3500 (5)	−271 (6)	11 (2)
C(23)	99 (10)	3255 (7)	−301 (9)	16 (2)
C(24)	1345 (10)	3660 (7)	−1150 (9)	17 (3)
N(25)	2370 (7)	4795 (4)	−164 (6)	12 (2)
C(26)	1431 (11)	5020 (8)	9692 (10)	20 (3)
C(27)	3041 (11)	5174 (8)	9441 (9)	20 (3)
N(28)	3807 (7)	3785 (5)	102 (7)	11 (2)
C(29)	3827 (10)	3269 (6)	−467 (9)	14 (2)
C(30)	4733 (10)	4046 (7)	212 (10)	17 (3)
H(31)	28 (9)	340 (6)	273 (8)	22
H(32)	50 (9)	289 (6)	217 (9)	22
H(33)	36 (9)	269 (6)	305 (8)	22
H(34)	167 (9)	286 (6)	404 (8)	21
H(35)	301 (9)	314 (6)	427 (9)	25
H(36)	396 (9)	373 (6)	350 (8)	26
H(37)	317 (9)	566 (6)	117 (9)	26
H(38)	320 (10)	592 (7)	187 (9)	26
H(39)	355 (9)	517 (6)	202 (8)	26
H(40)	191 (9)	614 (6)	247 (9)	27
H(41)	25 (10)	568 (6)	286 (8)	30
H(42)	987 (10)	487 (6)	235 (9)	25
H(43)	333 (9)	210 (6)	112 (8)	26
H(44)	353 (10)	280 (7)	125 (8)	26
H(45)	325 (9)	252 (6)	210 (8)	26
H(46)	102 (9)	228 (5)	69 (8)	23
H(47)	190 (8)	188 (6)	74 (8)	23
H(48)	164 (9)	206 (6)	163 (9)	23
H(49)	−26 (10)	354 (6)	−49 (8)	27
H(50)	2 (8)	285 (6)	−64 (8)	27
H(51)	−5 (10)	325 (6)	27 (9)	27
H(52)	138 (9)	329 (6)	−155 (9)	26
H(53)	93 (10)	397 (6)	−137 (9)	26
H(54)	184 (10)	388 (6)	−118 (9)	26
H(55)	141 (9)	540 (6)	−5 (9)	27
H(56)	140 (9)	502 (6)	921 (10)	27
H(57)	85 (11)	488 (6)	−16 (9)	27
H(58)	370 (10)	502 (6)	−55 (9)	28
H(59)	301 (10)	524 (7)	−112 (10)	28
H(60)	299 (9)	556 (7)	−53 (9)	28
H(61)	320 (10)	307 (6)	−58 (8)	25
H(62)	409 (9)	336 (6)	−114 (8)	25
H(63)	409 (10)	293 (6)	−29 (8)	25
H(64)	510 (10)	371 (6)	39 (8)	27
H(65)	488 (10)	412 (7)	−26 (9)	27
H(66)	477 (10)	429 (6)	55 (9)	27

[a] The isotropic thermal parameters listed for those atoms refined anisotropically are the isotropic equivalent. [b] Numbers in parentheses in this and all following tables refer to the error in the least significant digits. [c] Anisotropic thermal parameters for the two molybdenum atoms are given in the supplementary data.

solution to form an isomer having a central gauchelike $Mo_2N_4O_2$ skeleton.

Table II. Bond Distances (Å) for the $Mo_2(NMe_2)_4(2\text{-}O\text{-}6\text{-}Mepy)_2$ Molecule

A	B	dist	A	B	dist
Mo(1)	Mo(2)	2.211 (2)	N(22)	C(23)	1.472 (17)
Mo(1)	O(11)	2.078 (8)	N(22)	C(24)	1.457 (16)
Mo(1)	N(5)	2.325 (9)	N(25)	C(26)	1.455 (18)
Mo(1)	N(19)	2.017 (9)	N(25)	C(27)	1.408 (18)
Mo(1)	N(22)	1.958 (9)	N(28)	C(29)	1.423 (16)
Mo(2)	O(3)	2.082 (8)	N(28)	C(30)	1.460 (17)
Mo(2)	N(13)	2.325 (10)	C(4)	C(10)	1.428 (17)
Mo(2)	N(25)	1.980 (10)	C(6)	C(7)	1.507 (17)
Mo(2)	N(28)	1.973 (10)	C(6)	C(8)	1.410 (17)
O(3)	C(4)	1.296 (14)	C(8)	C(9)	1.375 (18)
O(11)	C(12)	1.306 (14)	C(9)	C(10)	1.356 (18)
N(5)	C(4)	1.352 (15)	C(12)	C(18)	1.409 (17)
N(5)	C(6)	1.352 (15)	C(14)	C(15)	1.517 (18)
N(13)	C(12)	1.350 (15)	C(14)	C(16)	1.383 (17)
N(13)	C(14)	1.350 (15)	C(16)	C(17)	1.386 (18)
N(19)	C(20)	1.428 (16)	C(17)	C(18)	1.394 (19)
N(19)	C(21)	1.472 (15)			

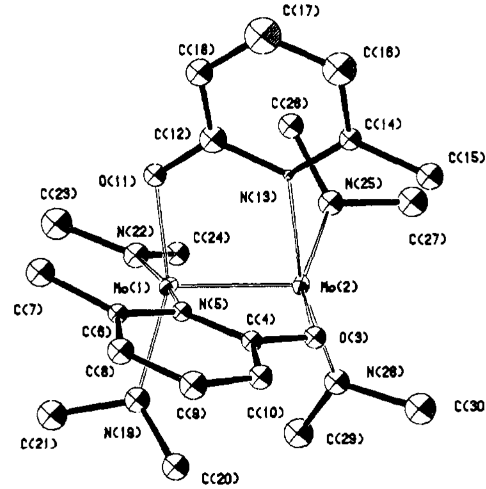

Figure 1. ORTEP view of the $Mo_2(NMe_2)_4(2\text{-}O\text{-}6\text{-}Mepy)_2$ molecule showing atomic numbering scheme used in the tables.

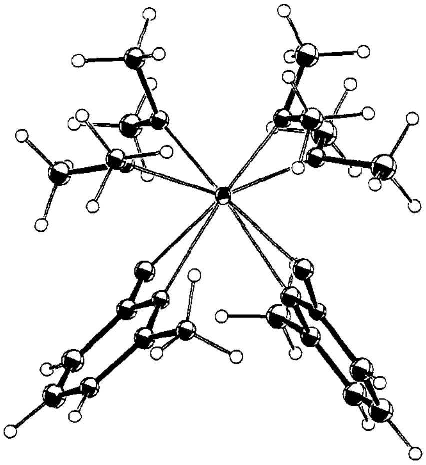

Figure 2. ORTEP view of the $Mo_2(NMe_2)_4(2\text{-}O\text{-}6\text{-}Mepy)_2$ molecule viewed down the metal–metal axis.

It is interesting to note that in the solid state, the molecule avoids adopting an eclipsed geometry (see Figure 2) despite the presence of two bridging ligands. This is achieved in the following manner. (1) The $Mo_2(NC_2)_4$ unit adopts a skew geometry as is evident from the N–Mo–Mo–N torsional angles

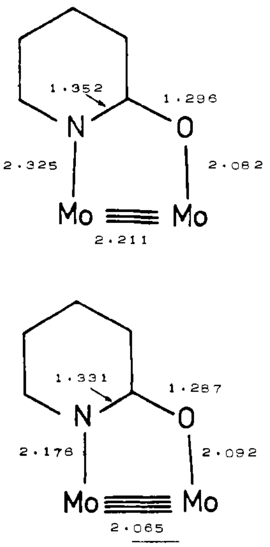

Figure 3. Comparison of the coordination of the 2-oxy-6-methylpyridine ligand to the $(\mathrm{M{\equiv}M})^{6+}$ unit (this work) and the $(\mathrm{M}\overset{4}{-}\mathrm{M})^{4+}$ unit as seen in ref 7.

given in Table III. (2) The blades are twisted away from their prefered orientation which places them in their respective Mo–Mo–N planes.[9] The average dihedral angle between the Mo–NC_2 planes and the Mo–Mo–N planes, which contain the same Mo and N atoms, is 22°. (A listing of these dihedral planes is given in MSC Report 7961. See paragraph at end of paper regarding supplementary material.) (3) The pyridine nitrogen shows a small pyramidal distortion in coordinating to the molybdenum atom. This is seen by the fact that the molybdenum atom lies 0.5 Å (average) out of the plane containing the pyridine atoms. This type of distortion in the coordination of pyridine N donors has been observed previously[10] and can occur without any apparent significant destabilization of the py–M bond.

^1H NMR Studies. The ^1H NMR spectra obtained in toluene-d_8 and 100 MHz in the temperature range −70 to +70 °C reveal the presence of the isomers A and B. The concentration ratio A:B is approximately 5:1 as judged by integration. The ^1H NMR spectra of A are entirely consistent with a structure akin to that found in the solid state. At −70 °C there are four *N*-methyl resonances corresponding to the proximal and distal *N*-methyls of the two types of $MoNMe_2$ groups. Upon raising of the temperature, these start to collapse in a pairwise manner as is typical of molecules of the type 1,2-$M_2X_2(NMe_2)_4$ which have C_2 symmetry. The methyl resonance of the 6-methyl-substituted pyridine ligand appears at δ 1.72 which is upfield by δ 0.6 from that found in the free ligand. This again is expected since this methyl group is aligned along the Mo–Mo axis in a distal position and should experience shielding by the diamagnetic anisotropy of the Mo≡Mo bond.[11]

The minor isomer, B, also shows four *N*-methyl resonances at low temperatures consistent with the existence of a C_2 axis of symmetry, and upon raising of the temperature, these too coalesce in a pairwise manner. The methyl signal of the 6-methylpyridine ligand occurs at a position similar to that of the free ligand.

At high temperatures (>70 °C) exchange between the two isomers becomes rapid on the NMR time scale. At +90 °C the spectrum consists of only one set of ligand resonances at

Table III

Pertinent Angles (Deg) Found for the $Mo_2(NMe_2)_4$(2-O-6-Mepy)$_2$ Molecule

A	B	C	angle
Mo(2)	Mo(1)	O(11)	96.3 (2)
Mo(2)	Mo(1)	N(5)	84.7 (2)
Mo(2)	Mo(1)	N(19)	105.9 (3)
Mo(2)	Mo(1)	N(22)	105.7 (3)
O(11)	Mo(1)	N(5)	78.6 (3)
O(11)	Mo(1)	N(19)	147.4 (3)
O(11)	Mo(1)	N(22)	93.7 (4)
N(5)	Mo(1)	N(19)	79.9 (3)
N(5)	Mo(1)	N(22)	167.8 (4)
N(19)	Mo(1)	N(22)	102.7 (4)
Mo(1)	Mo(2)	O(3)	95.4 (2)
Mo(1)	Mo(2)	N(13)	84.5 (3)
Mo(1)	Mo(2)	N(25)	105.1 (3)
Mo(1)	Mo(2)	N(28)	106.9 (3)
O(3)	Mo(2)	N(13)	79.7 (3)
O(3)	Mo(2)	N(25)	150.4 (4)
O(3)	Mo(2)	N(28)	93.1 (4)
N(13)	Mo(2)	N(25)	81.4 (4)
N(13)	Mo(2)	N(28)	167.2 (4)
N(25)	Mo(2)	N(28)	100.7 (4)
Mo(2)	O(3)	C(4)	120.2 (8)
Mo(1)	O(11)	C(12)	118.8 (7)
Mo(1)	N(5)	C(4)	116.1 (8)
Mo(1)	N(5)	C(6)	120.7 (8)
C(4)	N(5)	C(6)	121.0 (10)
Mo(2)	N(13)	C(12)	117.7 (8)
Mo(2)	N(13)	C(14)	123.0 (8)
C(12)	N(13)	C(14)	119.0 (11)
Mo(1)	N(19)	C(20)	128.9 (8)
Mo(1)	N(19)	C(21)	113.9 (8)
C(20)	N(19)	C(21)	111.1 (10)
Mo(1)	N(22)	C(23)	117.0 (8)
Mo(1)	N(22)	C(24)	133.9 (8)
C(23)	N(22)	C(24)	109.1 (10)
Mo(2)	N(25)	C(26)	127.7 (9)
Mo(2)	N(25)	C(27)	117.8 (9)
C(26)	N(25)	C(27)	112.0 (11)
Mo(2)	N(28)	C(29)	133.0 (9)
Mo(2)	N(28)	C(30)	115.9 (8)
C(29)	N(28)	C(30)	111.0 (11)
O(3)	C(4)	N(5)	118.7 (11)
O(3)	C(4)	C(10)	121.8 (11)
N(5)	C(4)	C(10)	119.5 (11)
N(5)	C(6)	C(7)	120.6 (10)
N(5)	C(6)	C(8)	120.4 (11)
C(7)	C(6)	C(8)	119.1 (11)
C(6)	C(8)	C(9)	118.7 (12)
C(8)	C(9)	C(10)	121.1 (12)
C(4)	C(10)	C(9)	119.1 (13)
O(11)	C(12)	N(13)	118.9 (11)
O(11)	C(12)	C(18)	119.7 (11)
N(13)	C(12)	C(18)	121.3 (11)
N(13)	C(14)	C(15)	115.6 (11)
N(13)	C(14)	C(16)	122.5 (12)
C(15)	C(14)	C(16)	121.8 (12)
C(14)	C(16)	C(17)	119.0 (12)
C(16)	C(17)	C(18)	119.3 (13)
C(12)	C(18)	C(17)	118.7 (13)

Torsional Angles (Deg) along the Mo–Mo Bond

A	B	C	D	angle
N(5)	Mo(1)	Mo(2)	N(13)	−64.2 (3)
N(5)	Mo(1)	Mo(2)	N(25)	−143.8 (4)
N(5)	Mo(1)	Mo(2)	N(28)	109.8 (4)
O(11)	Mo(1)	Mo(2)	N(13)	13.7 (3)
O(11)	Mo(1)	Mo(2)	N(25)	−65.8 (4)
O(11)	Mo(1)	Mo(2)	N(28)	−172.3 (4)
N(19)	Mo(1)	Mo(2)	N(25)	138.3 (4)
N(19)	Mo(1)	Mo(2)	N(28)	31.9 (4)
N(22)	Mo(1)	Mo(2)	N(25)	29.8 (4)
N(22)	Mo(1)	Mo(2)	N(28)	−76.6 (4)

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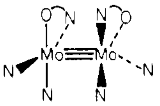
(9) This maximizes Me_2N-to-metal π bonding.

(10) Deeming, A. J.; Rothwell, I. P.; Backer-Dirks, J. D. J.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1979**, 690.

(11) See discussion in ref 2.

chemical shifts which are at weighted average values of the A and B isomer values. (Thus we are observing A $\rightleftharpoons$ B and not, say, A $\rightarrow$ B at high temperatures.) There are still two *N*-methyl signals in the ratio 1:1 which represent the averaged proximal $\rightleftharpoons$ distal signals of two types of NMe_2 ligands. Thus, isomerization does not destroy the molecular C_2 axis of symmetry associated with the $Mo_2(NMe_2)_4$ moiety.

There are two possible structures for the minor isomer, B. A structure containing two four-coordinate molybdenum atoms connected by an unbridged triple bond or one involving three-coordinate molybdenum molybdenum atoms containing a *gauche*-$Mo_2N_4O_2$ skeleton with the pyridine nitrogens not coordinated to the metal. These are shown in **3** and **4**. The



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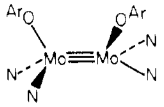

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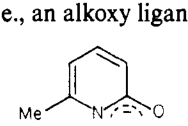
structure **3** parallels that found[12] in $W_2(NMe_2)_4(PhN_3Ph)_2$ while that of **4** corresponds to a *gauche*-$M_2(OR)_2(NMe_2)_4$ molecule. Recently we have prepared $Mo_2(OR)_2(NMe_2)_4$ compounds where R = Me, Et, *i*-Pr, and *t*-Bu and have found that the gauche $\rightleftharpoons$ anti equilibrium favors the gauche rotamer as the bulkiness of R increases.[13] Furthermore, we have prepared[14] the tungsten analogue of the title compound and find that it too shows two isomers in solution. The ^1H NMR spectra are analogous to those reported here for A and B, but the relative concentrations are in the reverse order. Crystallization yields a yellow compound, $W_2(NMe_2)_4(2\text{-}O\text{-}6\text{-}Mepy)_2$, which upon dissolution gives orange solutions. In general, we have found that M_2X_6 compounds are yellow or orange, while $M_2X_6L_2$ compounds are much more intensely colored. This can be attributed to a lifting of the degeneracy of $d_{x^2-y^2}$ and d_{xy} orbitals in the $M_2X_6L_2$ molecules.[15] Thus, we are inclined to the view that the tungsten analogue adopts a structure of type **4**, and that this is most probably the structure of B.

Finally, we note that the coordination of the 2-oxy-6-methylpyridine anion to the $(M\overset{4}{-}M)^{4+}$ is well represented by the delocalized anionic chelate shown below. The Mo–O and Mo–N bonds are of comparable length, and the system is similar to that of a chelating acetate. However, to the $(Mo{\equiv}Mo)^{6+}$ moiety and in the presence of four NMe_2 groups, the ligand more closely represents that formed from the resonance structure **2c**, i.e., an alkoxy ligand with supplementary coordination of a neighboring pyridine molecule. It remains to be established how changes in the metal (Mo vs. W) and X (alkyl, NR_2 and OR) will influence this in $(M{\equiv}M)^{6+}$ containing complexes.



2c

$Mo_2(NMe_2)_2(2\text{-}O\text{-}6\text{-}Mepy)_4$. Further addition of 2-hydroxy-6-methylpyridine to $Mo_2(NMe_2)_4(2\text{-}O\text{-}6\text{-}Mepy)_2$ in a hydrocarbon solvent yields a brown hydrocarbon-insoluble compound. Though its insolubility precluded solution characterization, the elemental analyses and mass spectral data indicate that the compound is $Mo_2(NMe_2)_2(2\text{-}O\text{-}6\text{-}Mepy)_4$. In the mass spectrometer, there is a strong molecular ion and an even stronger ion corresponding to $Mo_2(2\text{-}O\text{-}6\text{-}Mepy)_4{}^+$. Also present is a doubly charged ion, $Mo_2(2\text{-}O\text{-}6\text{-}Mepy)_4{}^{2+}$. Formation of this compound has a parallel in the formation of $Mo_2(NMe_2)_2(O_2CNMe_2)_4$ in the reaction between $Mo_2(NMe_2)_6$ and excess CO_2.[16]

Experimental Section

General procedures, including the preparation of $Mo_2(NMe_2)_6$, have been reported previously.[17] 2-Hydroxy-6-methylpyridine was purchased from Eastman Kodak Co. Elemental analyses were performed by Canadian Microanalytical Services, Ltd., Vancouver, B.C., Canada. Infrared spectra were obtained from Nujol mulls between CsI plates with a Beckman 257 spectrophotometer. ^1H NMR spectra were obtained from Varian Associates 100 and 220-MHz instruments equipped with a variable-temperature probe. Temperatures were calibrated with methanol (low temperatures) and ethylene glycol (high temperatures).

Preparation of $Mo_2(NMe_2)_4(2\text{-}O\text{-}6\text{-}Mepy)_2$. To a solution of $Mo_2(NMe_2)_6$ (1.21 g, 2.65 mmol) in toluene (20 mL) was added 2-hydroxy-6-methylpyridine (0.58 g, 5.3 mmol). The solution immediately turned deep red and was stirred at room temperature for 30 min. The solvent was stripped, and the resulting dark-red solids were dissolved in hexane (30 mL). The solution was filtered to remove a small amount of a brown hexane-insoluble material, giving a deep red filtrate. Cooling the solution to −15 °C gave deep red crystals of $Mo_2(NMe_2)_4(2\text{-}O\text{-}6\text{-}Mepy)_2$ (0.793 g, 51% yield on the basis of Mo). Anal. Calcd for $Mo_2C_{20}H_{36}N_6O_2$: C, 41.2; H, 6.22; N, 14.4. Found: C, 41.9; H, 6.33; N, 14.2. ^1H NMR data obtained from toluene-d_8 solutions at 100 MHz and +105 °C as follows. NMe_2: δ 3.55 and 3.33 (singlets in integral ratio 1:1). Pyridine methyl: δ 1.79 (s) Pyridine hydrogens: $\delta(3, 5)$ 5.93 (d), $J = 7.0$ Hz; 6.27 (d), $J = 8.7$ Hz; $\delta(4) = 6.89$ (dd). At −70 °C isomer A: δ(N-Me) 4.43, 2.83, $T_c = -4$ °C; 4.01, 2.63, $T_c = -26$ °C; pyridine methyl δ 1.72; pyridine protons $\delta(3,5)$ 5.95 (d), $J = 7.0$ Hz, 6.59 (d), $J = 8.5$ Hz, $\delta(4)$ 6.81 (dd). Isomer B: δ(N-Me) 4.81, 2.39, $T_c = +50$ °C; 4.35, 2.73, $T_c = -20$ °C; pyridine methyl δ 2.35; pyridine hydrogens $\delta(3,5)$ 5.83 (d), $J = 7.0$ Hz; 6.19 (d), $J = 7.9$ Hz; $\delta(4) = 6.81$ (dd). δ is in ppm downfield from Me_4Si and T_c is the coalescence temperature of the preceeding proximal and distal NMe groups in °C. Relative concentration [A]/[B] = 5/1. IR data ν in cm^{-1}: 1605 vs, 1552 s, 1415 w, 1409 m, 1391 w, 1378 m, 1239 s, 1233 s, 1159 s, 1151 m, 1115 m, 1048 m, 1045 w, 1030 w, 1008 w, 1002 w, 942 vs, 875 w, 796 s, 790 s, 758 m, 753 m, 739 m, 598 m, 589 m, 579 m, 545 m, 535 m, 353 m, 285 w.

$Mo_2(NMe_2)_2(2\text{-}O\text{-}6\text{-}Mepy)_4$. Analytical data obtained on the brown hexane-insoluble precipitate formed in the above reaction were consistent with that of a compound of formula $Mo_2(NMe_2)_2(2\text{-}O\text{-}6\text{-}Mepy)_4$. Anal. Calcd for $Mo_2C_{28}H_{36}N_6O_4$: C, 47.2; H, 5.09; N, 11.8. Found: C, 46.8; H, 5.62; N, 12.42. In the mass spectrometer, the following Mo_2-containing ions were observed: $Mo_2(NMe_2)_2L_4{}^+$, $Mo_2L_4{}^+$, $Mo_2(NMe_2)L_3{}^+$, $Mo_2L_3{}^+$, $Mo_2L_2{}^+$, and $Mo_2L_4{}^{2+}$, where L = 2-oxy-6-methylpyridine. Subsequently, it was found that this brown hydrocarbon-insoluble compound is formed by further addition of 2-hydroxy-6-methylpyridine to $Mo_2(NMe_2)_4(2\text{-}O\text{-}6\text{-}Mepy)_2$.

X-ray Structural Determination. Due to difficulties encountered (vide infra), two different crystals from separate preparations were examined. Crystal I was a parallelepiped of maximum dimension 0.2 mm. The crystal possessed a slight anisotropy in the mosaicity, with ω scan widths varying from 0.30 to 0.50 at half-height. The crystal was found to be orthorhombic, space group *Pbca*, with cell dimensions at −165 °C of $a = 14.402$ (5), $b = 21.746$ (7), and $c = 15.358$ (5) Å, giving $d_{calcd} = 1.614$ g cm^{-3} for $Z = 8$. Data were collected at −165 °C, with use of a continuous θ–2θ scan with a rate of 3°/min over a range of 1.8° in 2θ plus a dispersion correction. Stationary background counts of 10-s duration were recorded at each extreme of the scan. Experimental details and data reduction formula have been previously described.[18]

A total of 3299 unique amplitudes were obtained for $6° \leq 2\theta \leq 45°$ (Mo Kα; $\lambda = 0.71069$ Å) and corrected for absorption ($\mu = 10.449$ cm^{-1}). A significant fraction (40%) of the data were

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(13) Chisholm, M. H.; Garman, J. G., results to be submitted for publication.

(14) Chisholm, M. H.; Rothwell, I. P., results to be submitted for publication.

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"unobserved" by using the criteria $F^2 \geq 2.33\sigma(F^2)$, where $\sigma(F^2)$ is the estimated error based on counting statistics and an "ignorance factor" of 0.07. The large number of unobserved data is unusual for a low-temperature data set and is usually indicative of disorder.

The structure was, however, easily solved by direct methods and Fourier techniques, and full-matrix isotropic refinement converged to $R_F = 0.125$ and $R_{wF} = 0.102$. A difference Fourier synthesis based on the phases of the above refinement revealed most of the hydrogen atoms. Attempts to refine the positional parameters of the latter failed, however, so hydrogens were included as fixed atom contributors in "ideal" positions[18] in subsequent refinement. When the two molybdenum atoms were allowed to vary anisotropically, the refinement converged to $R_F = 0.094$ and $R_{wF} = 0.074$. When the remainder of the nonhydrogen atoms were allowed to vary anisotropically, little improvement was observed in the residuals and six atoms refined as nonpositive definite. A final difference Fourier synthesis was featureless, with the largest residual being 0.95 e/Å^3 near one of the molybdenum positions.

Because of the relatively high residuals and low percentage of observed data, a second crystal (II) was subsequently examined. A slightly larger crystal (0.25 × 0.30 × 0.30 mm) was used and a more extensive data set ($6° \leq 2\theta \leq 50°$) was collected with the use of a slower scan rate (2°/min; 15-s background counts). The ω scan widths of crystal II were Gaussian and nearly equal with the average width at half-height being 0.28°. While the temperature of the sample was somewhat cooler (−170 °C), no significant change was observed in cell dimensions. A total of 4314 unique amplitudes were collected and corrected for absorption (maximum and minimum absorptions 0.789 and 0.893). A careful examination of the data revealed that only 1088 (ca. 25%) had a total integrated scan count greater than the calculated background and only 2241 (52%) were "observed" by using the $F_o^2 \geq 2.33\sigma(F_o^2)$ criteria. The nonhydrogen parameters obtained from crystal I were used as starting coordinates and refinement proceeded as before.

While the refinement yielded nearly identical results, there were two notable exceptions. Only three of the nonhydrogen atoms refined to nonpositive definite anisotropic thermal parameters when all observed data were used, and, more significantly, all hydrogen atoms were easily located and their positional parameters converged to reasonable values. As in the case of crystal I, the residuals were only marginally improved when nonhydrogen atoms were refined anisotropically. A careful examination of observed and calculated structure amplitudes indicated that the relatively high residuals ($R_F = 0.088$ and $R_{wF} = 0.082$ with only molybdenum atoms anisotropic) were due in large part to statistical fluctuations in the "unobserved" data. For this reason, only the largest 2000 structure amplitudes (corresponding to approximately $F_o^2 \geq 3\sigma(F_o^2)$) were included in final refinement. Positional parameters of all atoms were varied and hydrogen thermal parameters were assigned an isotropic thermal parameter equal to $1 + B_{iso}$ of the corresponding carbon atom. Final residuals using this data set were $R_F = 0.052$ and $R_{wF} = 0.047$. Residuals based on all data and the parameters determined by the restricted set are $R_F = 0.087$ and $R_{wF} = 0.079$.

A final attempt to refine all nonhydrogen atoms anisotropically by using the restricted data set led to only one nonpositive definite thermal parameter (C(21)), and the residuals did not improve significantly ($R_F = 0.050$ and $R_{wF} = 0.044$) considering the large decrease in the ratio of observations to parameters (from 8.3:1 to 5.3:1).

An examination of the distances and angles calculated from the variance–covariance matrix revealed that nonhydrogen bond distances and angles for crystal II were within σ of each other independent of the extent of data used and were within 2σ of the parameters obtained from crystal I. A significant improvement (ca. 20–30%) was observed in the relative sigmas for bond distances and angles in crystal II. A final difference Fourier synthesis for crystal II was featureless, the largest peak being 0.62 e/Å^3. While the anisotropic behavior of several of the atoms and the high percentage of unobserved data remain a puzzle, we feel confident that no disorder is present and that the bond distances and angles are correct.

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Registry No. $Mo_2(NMe_2)_4(2\text{-}O\text{-}6\text{-}Mepy)_2$ (isomer A), 76773-07-4; $Mo_2(NMe_2)_4(2\text{-}O\text{-}6\text{-}Mepy)_2$ (isomer B), 76773-08-5; $Mo_2(NMe_2)_6$, 51956-20-8; $Mo_2(NMe_2)_2(2\text{-}O\text{-}6\text{-}Mepy)_4$, 76773-09-6.

Supplementary Material Available: Tables of anisotropic thermal parameters and observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page. The complete structural report, MSC Report 7961, is available in microfiche form only from the Indiana University Chemistry Library.