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2-Anilinopyridine Complexes of Dimolybdenum(II) and Ditungsten(II)

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The reaction of $Mo_2(O_2CCH_3)_4$ with the lithium salt of 2-anilinopyridine in tetrahydrofuran has led to the formation of $Mo_2(PhNpy)_4$ (**9**). The tungsten analogue (**10**) was prepared by the reduction of WCl_4 with 2 equiv of sodium amalgam in tetrahydrofuran followed by the addition of a slight excess of LiPhNpy. Their structures have been determined by X-ray crystallography. The dark red dimolybdenum complex crystallizes in the monoclinic space group $P2_1/c$ with the following cell dimensions: $a = 19.867$ (1) Å, $b = 9.763$ (1) Å, $c = 20.082$ (1) Å, $\beta = 100.4$ (1)°, $V = 3831$ (2) Å^3, $Z = 4$. The average of the two crystallographically independent Mo–Mo quadruple bond lengths is 2.071 (2) Å. The black-red ditungsten analogue, which crystallizes with two THF molecules per unit cell in the $P\bar{1}$ space group, shows the following cell dimensions: $a = 10.535$ (2) Å, $b = 19.194$ (3) Å, $c = 18.598$ (3) Å, $\alpha = 107.4$ (1)°, $\beta = 99.7$ (1)°, $\gamma = 103.6$ (1)°, $V = 3369$ (3) Å^3, $Z = 3$. The average W–W quadruple bond length is 2.165 (2) Å (average for three independent molecules per asymmetric unit, located on inversion centers at 0, 0, 0; $^1/_2$, 0, $^1/_2$; and $^1/_2$, $^1/_2$, $^1/_2$). The average M–N(py) and M–N$_a$ bond lengths are 2.156 (8) and 2.141 (8) Å, respectively, for the dimolybdenum complex and 2.144 (14) and 2.123 (8) Å, respectively, for the ditungsten complex. The M–M′–N angles lie in the range 91.4–93.0°. Electronic absorption bands that we assign to the $\delta \rightarrow \delta^*$ transitions were observed at 467 nm for **9** and 520 nm for **10**. In **9** there is also a band at 440 nm that is possibly due to a $\delta \rightarrow \pi^*$ transition. Compound **9** in THF displays two one-electron quasi-reversible oxidative responses at 0.00 V ($\Delta E_p = 200$ mV) and +0.475 V ($\Delta E_p = 150$ mV) vs. Ag–AgCl at 100 mV s^{-1} with tetrabutylammonium perchlorate as the supporting electrolyte. The oxidation processes are due to successive removal of two electrons from the δ level:

$$(\sigma)^2(\pi)^4(\delta)^2 \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} (\sigma)^2(\pi)^4(\delta)^1 \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} (\sigma)^2(\pi)^4(\delta)^0$$

The ditungsten analogue undergoes a one-electron oxidation at −0.067 V ($\Delta E_p = 130$ mV) due to the couple

$$(\sigma)^2(\pi)^4(\delta)^2 \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} (\sigma)^2(\pi)^4(\delta)^1$$

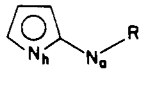
and the one-electron reduction at −0.84 V ($\Delta E_p = 140$ mV) may be due either to the couple

$$(\sigma)^2(\pi)^4(\delta)^2 \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} (\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1$$

or to a ligand reduction. The relationships between the observed $\delta \rightarrow \delta^*$ transitions and the formal potentials are discussed.

Introduction

Although a wide variety of quadruply bonded compounds are reported in the literature,[1] only a few are reported[2-8] in which all eight coordinated ligand atoms are nitrogen atoms. Most of those that have been crystallographically characterized contain bridging ligands, **1–4**. Structural data for complexes of the type $M_2(N_aN_h)_4$ or $M_2(N_aN_a)_4$, where N$_a$ and N$_h$ are, respectively, the amine and heterocyclic nitrogen atoms of the bridging ligand, are given in Table I. The number is limited to three in the case of W–W quadruply bonded complexes, of which two are mixed-ligand complexes. There are only five Mo–Mo quadruply bonded complexes known to have the structure **5**.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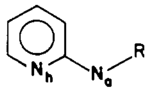
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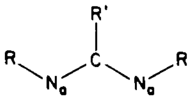
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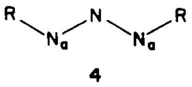
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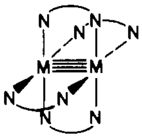
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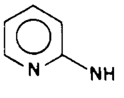
Previous attempts[2] were made to synthesize compounds of the general formula $M_2(ap)_4$ (ap = the anion of 2-aminopyridine). When the 2-aminopyridine anion **6** was used, noncrystalline, insoluble polymeric species were obtained, but when the anion of 6-methyl-2-aminopyridine **7** was used crystalline products were obtained and characterized. The formation of polymeric species with **6** may be attributed to intermolecular bridging, which is, presumably, prevented by the 6-methyl group in **7**. In the present study, we similarly find that when the 2-anilinopyridine anion **8** is used, well-defined molecular products, **9** and **10**, can be obtained.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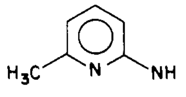
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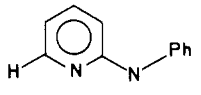
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We report here the synthesis and structures of two new compounds $Mo_2(PhNpy)_4$ (**9**) and $W_2(PhNpy)_4$ (**10**). Structural parameters of **9** and **10** have been compared with other reported $Mo\overset{4}{-}Mo$ and $W\overset{4}{-}W$ compounds with N—C—N and N—N—N bridges. We have recently reported[9] the ligational behavior of this ligand (**8**) toward ruthenium(II)

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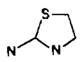
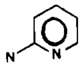
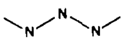
(1) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.
(2) Cotton, F. A.; Niswander, R. H.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3541.
(3) Cotton, F. A.; Inglis, T.; Kilner, M.; Webb, T. R. *Inorg. Chem.* **1975**, *14*, 2023.
(4) Cotton, F. A.; Ilsley, W. H.; Kaim, W. *Inorg. Chem.* **1979**, *18*, 3569.
(5) Cotton, F. A.; Ilsley, W. H.; Kaim, W. *Inorg. Chem.* **1981**, *20*, 930.
(6) Cotton, F. A.; Ilsley, W. H. *Inorg. Chem.* **1981**, *20*, 572.
(7) Cotton, F. A.; Rice, G. W.; Sekutowski, J. C. *Inorg. Chem.* **1979**, *18*, 1143.
(8) Cotton, F. A.; Ilsley, W. H.; Kaim, W. *Inorg. Chem.* **1980**, *19*, 1450.
(9) Chakravarty, A. R.; Cotton, F. A.; Shamshoum, E. S. *Inorg. Chim. Acta* **1984**, *86*, 5.

0020-1669/84/1323-4216$01.50/0

Table I. Comparison of Structural Parameters for Quadruply Bonded Mo and W Compounds[a] with N-C-N and N-N-N Bridges

	av bond angles, deg					bond dist, Å		
					M–M'–N	$M\overset{4}{-}M$	M–N	ref
$Mo_2(map)_4 \cdot 2THF$		117.8 (9)			92.9 N_h		2.18 (1) N_a	2
					93.1 N_a	2.070 (1)	2.14 (1) N_h	
$W_2(map)_4 \cdot 2THF$		117.0 (2)			91.2 N_h		2.160 (8) N_h	2
					92.5 N_a	2.164 (1)	2.100 (8) N_a	
$Mo_2(PhC(NPh)_2)_4$			117.0 (1)		92.4 N_a	2.090 (1)		3
$W_2(dmhp)_2[(PhN)_2CCH_3]_2 \cdot 2THF$			115 (1)		89.0 N_h	2.174 (1)	2.17 (1) N_h	4
					91.6 N_a	2.174 (1)	2.11 (1) N_a	
$Mo_2[(PhN)_2CCH_3]_3(CH_3COO)$			115.7 (5)		92.5 N_a	2.082 (1)	2.143 (5) N_a	5
$Mo_2[[(2,6\text{-xylyl})N]CCH_3]_2\text{-}(CH_3COO)_2 \cdot 4THF$			117.4 (5)		92.3 N_a	2.107 (1)	2.161 (5) N_a	5
$Mo_2(ambt)_3(CH_3COO) \cdot 2THF$	125 (2)				91.4 N_h		2.22 (2) N_h	6
					95.3 N_a	2.093 (3)	2.33 (2) N_a	
$Mo_2(ambt)_4 \cdot THF$	123.5 (8)				93.1 N_h		2.206 (7) N_h	6
					93.1 N_a	2.103 (1)	2.137 (7) N_a	
$Mo_2(acbt)_4 \cdot 2THF$	121.7 (4)				92.4 N_h		2.203 (3) N_h	6
					93.0 N_a	2.117 (1)	2.133 (4) N_a	
$Mo_2[(PhN)_2N]_4$				112.9 (5)	93.7 N_a	2.083 (2)	2.045 (5) N_a	7
$W_2(dmhp)_2[(PhN)_2N]_2 \cdot 2THF$				111.9 (7)	89.0 N_h		2.153 (7) N_h	8
					90.3 N_a	2.169 (1)	2.103 (7) N_a	
$Mo_2(PhNpy)_4$		114.9 (5)			93.0 N_h		2.156 (8) N_h	
					92.9 N_a	2.071 (2)	2.141 (8) N_a	this work
$W_2(PhNpy)_4 \cdot {}^2/_3THF$		115.0 (2)			91.4 N_h		2.144 (14) N_h	
					91.7 N_a	2.165 (2)	2.123 (8) N_a	this work

[a] Abbreviations: Hmap, 2-amino-6-methylpyridine; Hdmhp, 2,4-dimethyl-6-hydroxypyridine; Hambt, 2-amino-4-methylbenzothiazole; Hacbt, 2-amino-4-chlorobenzothiazole; THF, tetrahydrofuran; PhNHpy, 2-anilinopyridine; N_h, N_a, heterocyclic and amine nitrogens, respectively.

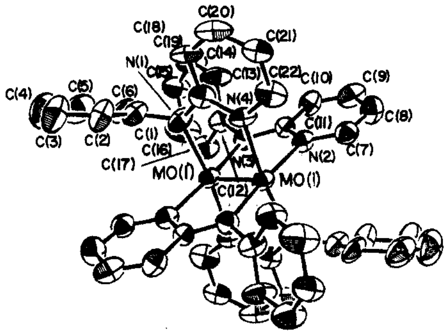


Figure 1. ORTEP drawing of one of the two $Mo_2(PhNpy)_4$ molecules. The other one is very similar, and atoms in it are labeled similarly, i.e., beginning with N(5) and C(23).

Table II. Crystallographic Parameters

formula	$Mo_2(PhNpy)_4$	$W_2(PhNpy)_4 \cdot {}^2/_3C_4H_8O$
fw	868.71	1049.33
space group	$P2_1/c$	$P\bar{1}$
syst abs	$0k0$, $k = 2n$; $h0l$, $l = 2n$	none
a, Å	19.867 (1)	10.535 (2)
b, Å	9.763 (1)	19.194 (3)
c, Å	20.082 (1)	18.598 (3)
α, deg		107.4 (1)
β, deg	100.4 (1)	99.7 (1)
γ, deg		103.6 (1)
V, Å^3	3831 (2)	3369 (3)
Z	4	3
d_{calcd}, g/cm^3	1.51	1.54
cryst size, mm	0.2 × 0.2 × 0.20	0.3 × 0.2 × 0.2
μ(Mo Kα), cm^{-1}	6.8	97.2
data collcn instrum	CAD-4	Syntex $P\bar{1}$
radiation (monochromated in incident beam)	Mo	Cu
orientation reflcns range (2θ), deg	8–31	40–60
temp, °C	25	5
scan method	ω–2θ	ω–2θ
data collcn range (2θ), deg	5–50	6–115
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	2976	4861
no. of parameters refined	487	725
transmissn factors (max, min)	no abs cor	99.3, 46.5
R[a]	0.060	0.067
R_w[b]	0.062	0.084
quality-of-fit indicator[c]	1.371	1.715
largest shift/esd, final cycle	0.03	0.46
largest peak, e/Å^3	0.8	3.3

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma(|F_o|^2)$. [c] Quality of fit = $[\Sigma w(|F_o| - |F_c|^2/(N_{observns} - N_{parameters})]^{1/2}$.

in affording two stable isomers of formula $Ru(PPh_3)_2(PhNpy)_2$, in which the ligand forms a stable four-membered chelate ring.

Experimental Section

$Mo_2(O_2CCH_3)_4$ was prepared by refluxing $Mo(CO)_6$ in acetic acid and acetic anhydride.[10] WCl_4 was prepared by refluxing $W(CO)_6$ with 2 equiv of WCl_6 in chlorobenzene. All reactions were done under an argon atmosphere.

Preparations. Tetrakis(2-anilinopyridine)dimolybdenum, $Mo_2(PhNpy)_4$ (9). A weighed amount of PhNHpy (171 mg, 9.83 mmol) was dissolved in 20 mL of THF. *n*-Butyllithium (6.14 mL, 9.83 mmol) was added to it via a syringe, and the solution was then stirred for 30 min. The lithium salt of the ligand was then transfered to another flask containing 1.0 g (2.34 mmol) of $Mo_2(O_2CCH_3)_4$ in 75 mL of THF. The reaction mixture was stirred at room temperature overnight and then filtered into a Schlenk tube and covered with a layer of hexane. Dark red crystals were obtained in about 75–85% yield.

Tetrakis(2-anilinopyridine)ditungsten, $W_2(PhNpy)_4$ (10). A weighed amount of WCl_4 (2.0 g, 6.2 mmol) was dissolved in 75 mL of THF. At −40 °C, 0.284 g (12.4 mmol) of Na in 6 mL of Hg was added to it and then stirred for 30 min, until the temperature reached −20 °C. At this temperature, 2.28 g (13.0 mmol) of LiPhNpy in 40 mL of THF was transferred to the THF solution. The reaction mixture was allowed to warm slowly to room temperature and then stirred at this temperature overnight. The solution was then filtered into a three-neck flask and concentrated to a volume of 30 mL. A 5-mL

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(10) Lawton, D.; Mason, R. *J. Am. Chem. Soc.* **1965**, *87*, 921.

Table III. Table of Positional Parameters and Their Estimated Standard Deviations for $Mo_2(PhNpy)_4$ (**9**)

atom	x	y	z	B,[a] Å^2	atom	x	y	z	B,[a] Å^2
Mo(1)	0.00935 (5)	0.0321 (1)	0.05001 (4)	2.93 (2)	C(19)	−0.1014 (5)	0.380 (1)	−0.0620 (5)	4.1 (3)
Mo(2)	0.51546 (5)	0.0946 (1)	0.98524 (5)	3.64 (2)	C(20)	−0.0981 (6)	0.483 (1)	−0.0150 (6)	5.3 (3)
N(1)	−0.0652 (4)	0.1477 (9)	−0.0854 (4)	3.6 (2)	C(21)	−0.0645 (5)	0.459 (1)	0.0531 (5)	4.1 (3)
N(2)	0.1068 (4)	0.1228 (9)	0.0431 (4)	3.1 (2)	C(22)	−0.0347 (5)	0.333 (1)	0.0705 (5)	4.5 (3)
N(3)	−0.0852 (4)	−0.0550 (9)	0.0683 (4)	3.3 (2)	C(23)	0.4181 (6)	0.248 (1)	0.8718 (6)	5.3 (3)
N(4)	−0.0378 (4)	0.2284 (8)	0.0235 (4)	3.1 (2)	C(24)	0.3591 (7)	0.269 (2)	0.8251 (6)	6.5 (4)
N(5)	0.4252 (4)	0.1267 (9)	0.9087 (4)	3.8 (2)	C(25)	0.6948 (6)	−0.165 (2)	1.1862 (6)	6.4 (4)
N(6)	0.4609 (4)	0.2010 (9)	1.0536 (4)	3.8 (2)	C(26)	0.6852 (6)	−0.041 (2)	1.1499 (6)	5.9 (3)
N(7)	0.5641 (4)	0.011 (1)	0.9075 (4)	3.9 (2)	C(27)	0.6233 (5)	−0.025 (1)	1.0990 (5)	4.0 (3)
N(8)	0.6075 (4)	0.0855 (9)	1.0594 (4)	3.9 (2)	C(28)	0.4534 (5)	0.338 (1)	1.0522 (6)	4.1 (3)
C(1)	−0.1098 (6)	0.137 (1)	−0.1485 (5)	4.2 (3)	C(29)	0.4191 (6)	0.413 (1)	1.0958 (6)	4.9 (3)
C(2)	0.0812 (6)	−0.097 (1)	0.2053 (5)	4.5 (3)	C(30)	0.6085 (6)	−0.331 (1)	0.8559 (6)	4.7 (3)
C(3)	0.1265 (7)	−0.073 (1)	0.2657 (6)	6.2 (4)	C(31)	0.6039 (5)	−0.196 (1)	0.8535 (6)	4.4 (3)
C(4)	−0.1986 (8)	0.082 (2)	−0.2716 (6)	7.5 (4)	C(32)	0.5691 (5)	−0.126 (1)	0.9023 (5)	3.5 (3)
C(5)	−0.2248 (7)	0.119 (2)	−0.2153 (7)	6.9 (4)	C(33)	0.5790 (5)	0.101 (1)	0.8550 (5)	3.5 (2)
C(6)	−0.1813 (6)	0.145 (1)	−0.1533 (6)	5.5 (4)	C(34)	0.6251 (6)	0.206 (1)	0.8755 (6)	5.1 (3)
C(7)	0.1497 (6)	0.177 (1)	0.0982 (5)	3.8 (3)	C(35)	0.6383 (7)	0.303 (1)	0.8242 (6)	6.8 (3)
C(8)	0.2121 (6)	0.232 (1)	0.0951 (5)	4.5 (3)	C(36)	0.6054 (7)	0.285 (1)	0.7578 (7)	6.6 (4)
C(9)	0.2345 (6)	0.230 (1)	0.0305 (6)	5.1 (3)	C(37)	0.5618 (6)	0.177 (2)	0.7396 (6)	7.0 (4)
C(10)	0.1931 (6)	0.177 (1)	−0.0248 (5)	4.2 (3)	C(38)	0.5462 (6)	0.080 (2)	0.7881 (6)	6.3 (4)
C(11)	0.1277 (5)	0.120 (1)	−0.0179 (5)	2.8 (2)	C(39)	0.6568 (6)	0.189 (1)	1.0577 (5)	4.2 (3)
C(12)	−0.0967 (5)	−0.065 (1)	0.1365 (5)	3.7 (3)	C(40)	0.6384 (6)	0.324 (1)	1.0664 (6)	5.0 (3)
C(13)	−0.1049 (6)	0.056 (1)	0.1707 (6)	4.5 (3)	C(41)	0.6841 (7)	0.432 (1)	1.0578 (6)	5.7 (4)
C(14)	−0.1127 (8)	0.046 (1)	0.2386 (6)	7.0 (4)	C(42)	0.7472 (6)	0.405 (1)	1.0407 (6)	5.4 (3)
C(15)	−0.1115 (7)	−0.080 (1)	0.2710 (5)	5.2 (3)	C(43)	0.7670 (6)	0.269 (1)	1.0343 (6)	5.9 (4)
C(16)	−0.1023 (7)	−0.196 (1)	0.2371 (6)	5.7 (3)	C(44)	0.7230 (6)	0.159 (1)	1.0417 (6)	5.4 (3)
C(17)	−0.0959 (6)	−0.192 (1)	0.1669 (5)	5.1 (3)					
C(18)	−0.0705 (5)	0.254 (1)	−0.0423 (5)	3.5 (3)					

[a] Starred atoms were refined isotropically. Anisotropically refined atoms in this and the following tables are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

portion of this solution in a Schlenk tube was mixed with 10 mL of toluene, and the mixture was covered with 15 mL of hexane. Black-red crystals were obtained in ca. 70–80% yield.

X-ray Crystallographic Procedures. The structures of single crystals containing **9** and **10** were determined by applying the general procedures that we have already described elsewhere.[11,12] A detailed description is available as supplementary material. The crystal parameters and basic information pertaining to data collection and structure refinement for both compounds are summarized in Table II. Tables III and IV list the atomic coordinates of **9** and **10**, respectively. Tables V and VI list bond distances and angles of **9** while Tables VII and VIII list bond distances and angles for **10**. Complete tables of anisotropic thermal parameters and structure factor data are available as supplementary material. Figures 1 and 2 show the structures and atom-numbering schemes.

Other Measurements. Tetra-*n*-butylammonium perchlorate (TBAP), used as a supporting electrolyte, was obtained from Aldrich Chemicals, Inc. Electrochemical measurements were made with use of a Bioanalytical Systems, Inc., Model BAS100 electrochemical analyzer instrument in connection with a Bausch & Lomb, Houston Instruments Model DMP 40 digital plotter. All experiments were done on tetrahydrofuran solutions containing 0.2 M TBAP. In a three-electrode cell system, a platinum disk, Model BAS MF 2032, and a platinum wire were used as working and auxiliary electrodes and a BAS MF 2020 Ag–AgCl cell was used as reference electrode (against which ferrocene is oxidized at $E_{1/2}$ = +0.515 V). All potentials are referenced to the Ag–AgCl electrode at 22 ± 2 °C and are uncorrected for junction potentials. All voltammetric measurements were made on THF solutions under a dry argon atmosphere. Electronic spectra were obtained from THF solutions of the compounds by using a CARY 17D spectrophotometer. Spectral measurements were done under a dinitrogen atmosphere. Solutions were prepared in thoroughly deoxygenated, dry solvents. Like other quadruply bonded tungsten compounds, **10** is extremely sensitive in solution and was observed to decompose in the quartz cell even when sealed with a rubber septum in presence of a strong flow of dry dinitrogen. The dimolybdenum compound **9** was also sensitive. Thus, we could not calculate the extinction coefficients because concentrations were not accurately known.

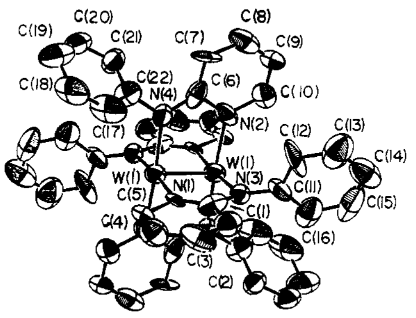

Figure 2. ORTEP drawing of one of three $W_2(PhNpy)_4$ molecules. The others are virtually identical and numbered in a similar way.

Results and Discussion

The dimolybdenum compound, $Mo_2(PhNpy)_4$ (**9**), was conveniently prepared by the reaction of $Mo_2(O_2CCH_3)_4$ with LiPhNpy in THF. It is soluble in many common organic solvents but not in hexane, and well-crystallized material was obtained by slow diffusion of hexane into a THF solution. The solutions were red, which is consistent with the absorption spectrum shown in Figure 3, in which the band at 467 nm is presumably due to the $\delta \rightarrow \delta^*$ transition. Several other Mo_2^{4+} compounds in which all eight coordinated atoms are nitrogen atoms have been structurally characterized and are listed in Table I along with important dimensions that can be compared with those in **9**.

For the W_2^{4+} unit the only previously reported compound with a set of eight coordinated nitrogen atoms is $W_2(map)_4 \cdot 2THF$, which is listed in Table I. This was prepared by the reaction of Li(map) in THF with $W_2(mhp)_4$, which in turn was prepared from $W(CO)_6$. We have prepared **10** more straightforwardly by reaction of Li(PhNpy) with a Na/Hg

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(11) (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227. (c) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Difr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

(12) Calculations were done on the VAX-11/780 computer at Department of Chemistry, Texas A & M University, College Station, TX, with VAX-SDP software package.

Table IV. Table of Positional Parameters and Their Estimated Standard Deviations for $W_2(PhNpy)_4 \cdot {}^2/_3THF$ (**10**)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
W(1)	−0.0551 (1)	−0.06037 (6)	−0.01985 (6)	3.99 (3)	C(37)	0.784 (2)	0.396 (1)	0.579 (1)	5.2 (7)
W(2)	0.4602 (1)	0.50063 (6)	0.55019 (6)	3.88 (2)	C(38)	0.886 (2)	0.388 (1)	0.543 (2)	6.0 (7)
W(3)	0.3946 (1)	−0.01222 (5)	0.50050 (6)	3.58 (2)	C(39)	0.892 (2)	0.407 (1)	0.473 (2)	7.1 (8)
N(1)	−0.062 (1)	0.083 (1)	0.1024 (8)	3.7 (4)	C(40)	0.787 (2)	0.438 (1)	0.448 (1)	5.6 (7)
N(2)	0.207 (2)	0.052 (1)	0.108 (1)	4.8 (5)	C(41)	0.545 (2)	0.400 (1)	0.635 (1)	4.8 (6)
N(3)	0.185 (2)	0.0420 (9)	−0.0543 (9)	3.5 (3)*	C(42)	0.518 (3)	0.442 (1)	0.704 (1)	6.3 (7)
N(4)	−0.091 (2)	0.076 (1)	−0.063 (1)	4.6 (5)	C(43)	0.451 (3)	0.401 (2)	0.748 (2)	7.9 (9)
N(5)	0.309 (2)	0.3924 (9)	0.4895 (9)	3.6 (4)	C(44)	0.425 (3)	0.322 (2)	0.724 (2)	7.9 (9)
N(6)	0.392 (2)	0.3910 (9)	0.3811 (9)	3.8 (4)	C(45)	0.459 (3)	0.280 (1)	0.654 (1)	6.4 (7)
N(7)	0.686 (2)	0.4487 (9)	0.4862 (9)	3.9 (5)	C(46)	0.518 (2)	0.321 (1)	0.609 (1)	5.6 (7)
N(8)	0.586 (2)	0.4416 (9)	0.5874 (9)	4.4 (5)	C(47)	0.626 (2)	0.637 (1)	0.703 (1)	4.4 (6)
N(9)	0.443 (1)	0.0642 (9)	0.6177 (9)	3.5 (4)	C(48)	0.747 (3)	0.632 (2)	0.748 (1)	6.6 (8)
N(10)	0.665 (2)	0.0969 (9)	0.6104 (9)	4.5 (4)	C(49)	0.246 (4)	0.341 (2)	0.168 (1)	11 (1)
N(11)	0.596 (2)	0.1044 (8)	0.4541 (9)	3.3 (4)	C(50)	0.655 (4)	0.677 (2)	0.862 (2)	11 (1)
N(12)	0.375 (2)	0.0768 (9)	0.454 (1)	4.3 (4)	C(51)	0.457 (3)	0.319 (2)	0.185 (2)	9 (1)
C(1)	−0.162 (2)	0.034 (1)	0.105 (1)	4.4 (5)	C(53)	0.528 (3)	0.659 (1)	0.734 (1)	7.2 (8)
C(2)	−0.240 (2)	0.050 (1)	0.161 (1)	5.6 (7)	C(60)	0.356 (2)	0.071 (1)	0.661 (1)	4.5 (6)
C(3)	−0.205 (3)	0.125 (2)	0.214 (1)	6.6 (8)	C(61)	0.381 (2)	0.116 (1)	0.740 (1)	5.2 (6)
C(4)	−0.093 (3)	0.184 (1)	0.213 (1)	6.2 (8)	C(62)	0.513 (2)	0.158 (1)	0.775 (1)	5.2 (6)
C(5)	−0.019 (2)	0.164 (1)	0.159 (1)	4.6 (6)	C(63)	0.615 (2)	0.156 (1)	0.735 (1)	4.5 (6)
C(6)	−0.203 (2)	0.022 (1)	−0.112 (1)	4.8 (6)	C(64)	0.579 (2)	0.1079 (9)	0.653 (1)	3.2 (5)
C(7)	0.313 (2)	−0.028 (1)	0.162 (1)	5.1 (6)	C(65)	0.711 (2)	0.146 (1)	0.443 (1)	4.7 (6)
C(8)	0.413 (2)	0.039 (2)	0.206 (1)	6.4 (8)	C(66)	0.715 (2)	0.206 (1)	0.417 (1)	4.3 (6)
C(9)	0.419 (2)	0.110 (1)	0.205 (1)	5.2 (7)	C(67)	0.587 (2)	0.224 (1)	0.406 (1)	4.4 (6)
C(10)	0.321 (2)	0.117 (1)	0.156 (1)	5.0 (6)	C(68)	0.475 (2)	0.182 (1)	0.416 (1)	4.8 (6)
C(11)	0.304 (2)	0.095 (1)	−0.041 (1)	4.9 (6)	C(69)	0.477 (2)	0.119 (1)	0.440 (1)	3.6 (5)
C(12)	0.428 (2)	0.088 (2)	−0.004 (2)	9 (1)	C(70)	0.800 (2)	0.153 (1)	0.634 (1)	4.8 (6)
C(13)	0.554 (4)	0.142 (2)	0.013 (2)	10 (1)	C(71)	0.811 (2)	0.232 (1)	0.654 (1)	5.3 (7)
C(14)	0.562 (3)	0.207 (2)	−0.000 (2)	8 (1)	C(72)	0.939 (3)	0.282 (1)	0.672 (1)	5.7 (7)
C(15)	0.440 (3)	0.221 (2)	−0.033 (2)	9 (1)	C(73)	1.056 (3)	0.262 (1)	0.670 (1)	5.8 (7)
C(16)	0.309 (3)	0.165 (2)	−0.054 (1)	7.3 (8)	C(74)	1.041 (2)	0.183 (1)	0.648 (1)	6.0 (8)
C(17)	−0.062 (3)	0.214 (1)	−0.013 (2)	7.7 (8)	C(75)	0.916 (2)	0.127 (1)	0.631 (1)	5.2 (7)
C(18)	−0.030 (4)	0.285 (2)	−0.019 (2)	11 (1)	C(76)	0.240 (2)	0.071 (1)	0.421 (1)	3.8 (5)
C(19)	0.004 (4)	0.289 (2)	−0.094 (2)	10 (1)	C(77)	0.198 (2)	0.056 (1)	0.341 (1)	4.4 (6)
C(20)	−0.002 (3)	0.225 (1)	−0.151 (1)	6.6 (8)	C(78)	0.056 (2)	0.047 (1)	0.307 (1)	4.4 (6)
C(21)	−0.040 (3)	0.155 (1)	−0.144 (1)	5.7 (7)	C(79)	−0.032 (2)	0.052 (1)	0.352 (1)	5.2 (6)
C(22)	−0.067 (2)	0.150 (1)	−0.075 (1)	5.5 (7)	C(80)	0.015 (2)	0.065 (1)	0.434 (1)	5.0 (6)
C(30)	0.776 (2)	0.642 (1)	0.476 (1)	5.1 (7)	C(81)	0.150 (2)	0.078 (1)	0.468 (1)	4.2 (6)
C(31)	0.133 (2)	0.289 (1)	0.490 (1)	5.3 (7)	O(1)	0.893 (9)	0.469 (5)	0.260 (5)	10*
C(32)	0.120 (2)	0.248 (1)	0.406 (1)	5.6 (7)	C(91)	0.910 (8)	0.411 (5)	0.263 (5)	4*
C(34)	0.209 (2)	0.280 (1)	0.370 (1)	5.2 (7)	C(92)	0.88 (1)	0.387 (7)	0.189 (7)	7*
C(35)	0.301 (2)	0.354 (1)	0.413 (1)	3.6 (5)	C(93)	0.82 (1)	0.437 (7)	0.158 (7)	7*
C(36)	0.684 (2)	0.429 (1)	0.553 (1)	4.0 (5)	C(94)	0.82 (1)	0.496 (6)	0.233 (6)	6*

Table V. Some Important Bond Distances (Å) in $Mo_2(PhNpy)_4$ (**9**)

Mo(1)-Mo(1)′	2.073 (2)	N(2)–C(7)	1.371 (12)
Mo(2)-Mo(2)′	2.068 (2)	-C(11)	1.363 (10)
Mo(1)-N(1)′	2.130 (8)	N(3)–C(11)	1.351 (11)
-N(2)	2.157 (8)	–C(12)	1.433 (11)
-N(3)′	2.152 (8)	N(4)–C(18)	1.387 (11)
-N(4)	2.156 (8)	–C(22)	1.381 (12)
Mo(2)-N(5)′	2.163 (9)	N(5)–C(23)	1.389 (13)
-N(6)	2.161 (8)	–C(27)	1.376 (13)
-N(7)′	2.138 (8)	N(6)–C(28)	1.344 (13)
-N(8)	2.142 (9)	–C(32)	1.367 (12)
N(1)–C(1)	1.414 (12)	N(7)–C(32)	1.350 (13)
-C(18)	1.370 (12)	-C(33)	1.439 (12)
		N(8)–C(27)	1.341 (13)
		-C(39)	1.409 (13)

Table VI. Some Important Bond Angles (deg) in $Mo_2(PhNpy)_4$ (**9**)

Mo(1)-Mo(1)-N(1)	93.7 (2)	Mo(1)-N(1)-C(1)	116.1 (7)
-N(2)	93.9 (2)	-C(18)	120.7 (7)
-N(3)	92.1 (2)	Mo(1)-N(2)-C(7)	122.6 (6)
-N(4)	92.1 (2)	–C(11)	118.0 (7)
Mo(2)-Mo(2)-N(5)	94.7 (3)	Mo(1)-N(3)–C(11)	120.2 (6)
-N(6)	92.2 (2)	–C(12)	119.1 (7)
-N(7)	93.8 (3)	Mo(1)-N(4)-C(18)	120.4 (7)
-N(8)	91.4 (3)	-C(22)	121.5 (7)
N(1)-Mo(1)-N(2)	86.5 (3)	Mo(2)-N(5)–C(23)	119.6 (8)
-N(3)	92.1 (3)	–C(27)	116.7 (8)
-N(4)	172.6 (3)	Mo(2)-N(6)–C(28)	122.1 (7)
N(2)-Mo(1)-N(3)	173.9 (3)	–C(32)	118.8 (7)
-N(4)	88.6 (3)	Mo(2)-N(7)–C(32)	118.9 (7)
N(3)-Mo(1)-N(4)	92.3 (3)	Mo(2)-N(7)–C(33)	119.1 (7)
N(5)-Mo(2)-N(6)	86.3 (3)	Mo(2)-N(8)-C(27)	121.7 (8)
-N(7)	87.8 (3)	–C(39)	117.6 (7)
-N(8)	173.8 (4)	N(1)–C(18)-N(4)	113 (1)
N(6)-Mo(2)-N(7)	171.9 (3)	C(1)-N(1)-C(18)	121.2 (9)
-N(8)	92.4 (3)	N(2)-C(11)-N(3)	115.7 (8)
N(7)-Mo(2)-N(8)	92.9 (3)	C(11)-N(3)–C(12)	119.8 (8)

reduced solution of WCl_4 in THF. Presumably $W_2(map)_4$ could also be prepared in this more direct way. $W_2(PhNpy)_4$ resembles its molybdenum analogue in being generally soluble in organic solvents, except hydrocarbons like hexane, and again a crystalline product was obtained by diffusion of hexane into a THF solution. However, these were very thin, dark red plates, and X-ray quality crystals were formed by diffusion of hexane into a solution in 3/1 toluene/THF. A solution in THF is purple and has a $\delta \rightarrow \delta^*$ band 520 nm (Figure 3); the solution becomes red on addition of toluene.

The $\delta \rightarrow \delta^*$ transitions for **9** and **10** (assuming that our proposed assignments are correct) show the usual energy relationship,[13,14] in accord with the weaker δ–δ overlap at the greater internuclear distance in the tungsten compound as compared to the molybdenum analogue. The spectrum of the tungsten compound also shows a shoulder at ca. 440 nm, which, as previously suggested for $W_2(O_2CC_6H_5)_4$[13] may be

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(13) Cotton, F. A.; Wang, W., submitted for publication in *Inorg. Chem.*

(14) Cotton , F. A.; Hubbard, J. L.; Lichtenberger, D. L.; Shim, I. *J. Am. Chem. Soc.* **1982**, *104*, 689.

Table VII. Some Important Bond Distances (Å) in $W_2(PhNpy)_4$ (**10**)

W(1)-W(1)′	2.164 (2)	N(3)-C(1)	1.42 (2)
W(2)-W(2)′	2.168 (2)	-C(11)	1.35 (2)
W(3)-W(3)	2.164 (2)	N(4)-C(6)	1.34 (2)
W(1)-N(1)	2.138 (14)	-C(22)	1.46 (2)
-N(2)	2.150 (15)	N(5)-C(30)	1.35 (2)
-N(3)	2.117 (13)	-C(35)	1.38 (2)
-N(4)	2.13 (2)	N(6)-C(35)	1.38 (2)
W(2)-N(5)	2.134 (14)	-C(47)	1.46 (2)
-N(6)	2.142 (13)	N(7)-C(36)	1.40 (2)
-N(7)	2.128 (15)	-C(40)	1.40 (2)
-N(8)	2.09 (2)	N(8)-C(36)	1.34 (2)
W(3)-N(9)	2.126 (14)	-C(41)	1.41 (2)
-N(10)	2.090 (14)	N(9)-C(60)	1.32 (2)
-N(11)	2.190 (13)	-C(64)	1.40 (2)
-N(12)	2.164 (14)	N(10)-C(64)	1.31 (2)
N(1)-C(1)	1.26 (2)	-C(70)	1.46 (2)
-C(5)	1.49 (2)	N(11)-C(65)	1.37 (2)
N(2)-C(6)	1.44 (2)	-C(69)	1.35 (2)
-C(10)	1.43 (2)	N(12)-C(69)	1.30 (2)
		-C(76)	1.41 (2)

Table VIII. Some Important Bond Angles (deg) in $W_2(PhNpy)_4$ (**10**)

W(1)-W(1)-N(1)	89.6 (4)	W(1)-N(2)-C(6)	119 (1)
-N(2)	93.2 (4)	-C(10)	122 (1)
-N(3)	93.0 (4)	W(1)-N(3)-C(1)	117 (1)
-N(4)	90.5 (4)	-C(11)	121 (1)
W(2)-W(2)-N(5)	93.5 (4)	W(1)-N(4)-C(6)	125 (1)
-N(6)	90.7 (4)	-C(22)	120 (1)
-N(7)	91.3 (4)	W(2)-N(5)-C(30)	123 (1)
-N(8)	92.9 (4)	-C(35)	119 (1)
W(3)-W(3)-N(9)	91.9 (4)	-N(6)-C(35)	122 (1)
-N(10)	91.9 (5)	-C(47)	119 (1)
-N(11)	92.0 (4)	-N(7)-C(36)	118 (1)
-N(12)	90.7 (4)	-C(40)	122 (1)
N(1)-W(1)-N(2)	89.6 (5)	-N(8)-C(36)	120 (1)
-N(3)	175.4 (5)	-C(41)	119 (1)
-N(4)	89.3 (5)	W(3)-N(9)-C(60)	125 (1)
N(2)-W(1)-N(3)	86.5 (5)	-C(64)	117 (1)
-N(4)	176.1 (6)	-N(10)-C(64)	121 (1)
N(3)-W(1)-N(4)	94.5 (5)	-C(70)	118 (1)
N(5)-W(2)-N(6)	175.8 (5)	-N(11)-C(65)	119 (1)
-N(7)	87.0 (5)	-C(69)	118 (1)
-N(8)	87.7 (6)	-N(12)-C(69)	122 (1)
N(6)-W(2)-N(7)	93.5 (5)	-C(76)	114 (1)
-N(8)	91.5 (6)	N(1)-C(1)-N(3)	116 (2)
N(7)-W(2)-N(8)	173.4 (6)	C(1)-N(3)-C(11)	120 (2)
N(9)-W(3)-N(10)	173.4 (6)	N(2)-C(6)-N(4)	112 (2)
-N(11)	88.1 (5)	C(6)-N(4)-C(22)	115 (2)
-N(12)	92.4 (5)	N(5)-C(35)-N(6)	115 (1)
N(10)-W(3)-N(11)	86.4 (5)	C(35)-N(6)-C(47)	119 (1)
-N(12)	92.9 (6)	N(7)-C(36)-N(8)	116 (2)
N(11)-W(3)-N(12)	177.3 (6)	C(36)-N(8)-C(41)	119 (1)
W(1)-N(1)-C(1)	124 (1)	N(9)-C(64)-N(10)	117 (1)
-C(5)	116 (1)	C(64)-N(10)-C(70)	120 (2)
		N(11)-C(69)-N(12)	118 (2)
		C(69)-N(12)-C(76)	122 (2)

assigned to a $\sigma \rightarrow L\pi^*$ transition.

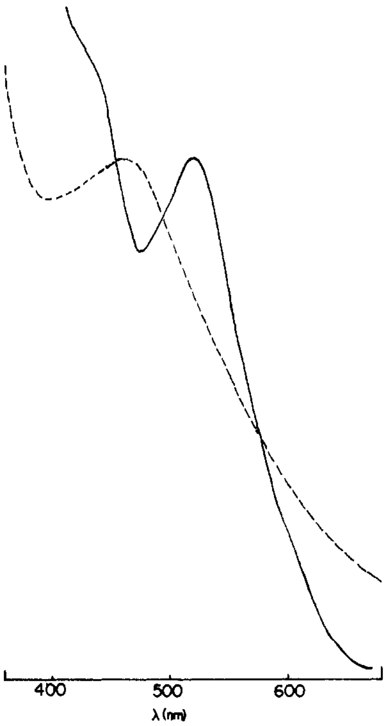

Figure 3. Visible absorption spectra of **9** (---) and **10** (—) in THF solution. The absorbance scale is arbitrary.

Molecular Structures. It is remarkable that these two homologous compounds were obtained in crystal forms that are not isotypic. The solvent systems used to obtain the X-ray quality crystals were not identical in the two cases, and this may be responsible for the difference. In the case of **9** the crystals are monoclinic with 2 molecules in the asymmetric unit while for **10** the crystals are triclinic and there are 3 molecules in the asymmetric unit, along with two molecules of THF as solvent of crystallization, per unit cell. Figures 1 and 2 show one of the molecules for **9** and **10**, respectively. The others are identical within experimental error. Both of the molecules in **9** reside on inversion centers at (0, 0, 0) and ($^1/_2$, 0, 0), and all three of the crystallographically independent molecules in **10** reside on inversion centers at (0, 0, 0), ($^1/_2$, 0, $^1/_2$), and ($^1/_2$, $^1/_2$, $^1/_2$). The averages of the crystallographically independent M–M distances are 2.070 [2] Å for molybdenum and 2.165 [2] Å for tungsten. The former is essentially identical with that in $Mo_2(map)_4$ but somewhat shorter than those in other compounds having dinitrogen bridging ligands. The mean W–W distance is close to that in the $W_2(map)_4$ molecule, and both are slightly shorter than the other W–W distances in Table I.

The various angles and M–N distances in **9** and **10** are comparable to those in the other molecules listed in Table I, and no marked trends are evident. The idealized symmetry of these centrosymmetric molecules is C_{2h}. This and the noncentric (D_{2d}) arrangement seem to be of very similar stability,[1] and there is no way to forecast which will be preferred in any given case where four unsymmetrical bridging ligands are bound to one M_2 unit.

Electrochemistry. Cyclic and differential-pulse voltammetric studies on $Mo_2(PhNpy)_4$ in tetrahydrofuran show two successive one-electron oxidations. The formal potentials, $E_{1/2}$, are 0.00 and +0.475 V vs. Ag–AgCl. The separations between the anodic and cathodic peak potentials, ΔE_p, lie in the range 100–250 mV at scan rates, v, in the range 50–200 mV s^{-1}. The electron-transfer process is thus quasi-reversible. The ΔE_p value increases on increasing the scan rate (v), but i_{pa}/i_{pc}, the ratio of the anodic to the cathodic peak currents, remains virtually unity at all scan rates. The voltammetric responses are shown in Figure 4.

The experimental results at v = 100 mV s^{-1} are summarized in eq 1.

$$[\text{Mo–Mo}]^{4+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\text{Mo–Mo}]^{3+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\text{Mo–Mo}]^{2+} \quad (1)$$

$$E_{1/2} = 0.475 \text{ V} \qquad E_{1/2} = 0.0 \text{ V}$$

$$\Delta E_p = 150 \text{ mV} \qquad \Delta E_p = 200 \text{ mV}$$

Since electrochemical oxidation–reduction reactions in a transition-metal complex involve the HOMO and LUMO levels, the oxidation of a quadruply bonded dimolybdenum species (ground-state configuration $\sigma^2\pi^4\delta^2$) means the removal of electron(s) from the occupied δ-orbital (HOMO level).

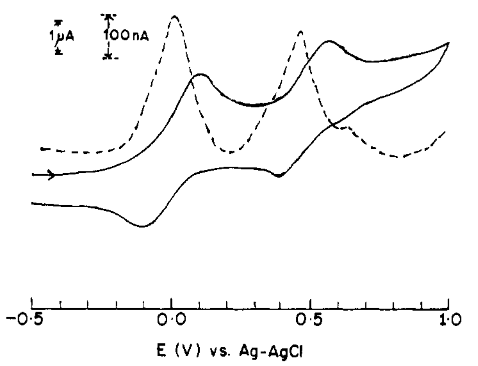

Figure 4. Cyclic (—) and differential-pulse (---) voltammograms of $Mo_2(PhNPy)_4$ in tetrahydrofuran (0.2 M TBAP) at a platinum electrode. Condition for CV: scan rate (v) = 100 mV s^{-1}. Experimental conditions for differential-pulse voltammetry: v = 10 mV s^{-1}; pulse amplitude 10 mV; pulse width 50 ms; pulse period 100 ms.

One-electron oxidation will change the electronic configuration from $\sigma^2\pi^4\delta^2$ to $\sigma^2\pi^4\delta^1$. This, in turn decreases the metal–metal bond order from 4 to 3.5. Removal of another electron leads to the electronic configuration $\sigma^2\pi^4\delta^0$ with metal–metal bond order 3.

Similar types of redox behavior were observed[15] in $Mo_2(mph)_4$, $W_2(mhp)_4$, and $MoW(mhp)_4$ complexes. The first oxidative response, which is reversible, is known[15] to appear at +0.20 and −0.35 V for Mo$\overset{4}{-}$Mo and W$\overset{4}{-}$W complexes. The second oxidation step is irreversible and occurs at +1.00–+1.15 V vs. SCE in acetonitrile ($\Delta E_{1/2}$ of SCE and Ag–AgCl is +0.04 V). Comparison between the formal potential values of the first oxidative response for **9** and $Mo_2(mhp)_4$ shows that the HOMO level in the mhp species is more stable. This is also evident from the $E_{1/2}$ values of the second oxidative response. In complexes of type $Mo_2X_4(P)_4$, where X = Cl, Br, and SCN and P = PEt_3, $P(n\text{-}Pr)_3$, $^1/_2$dppe and $^1/_2$dppm, the one-electron oxidation is known[16] to occur in the range +0.35–+0.84 V vs. SCE (in CH_2Cl_2). The $E_{1/2}$ values for the $Mo_2(O_2CC_3H_7)_4$ and $Mo_2(SO_4)_4^{4-}$ complexes are +0.39 V in CH_3CN (+0.45 V in CH_2Cl_2)[17] and +0.22 V[18] in 9 M H_2SO_4, respectively.

The ditungsten dimer, $W_2(PhNpy)_4$ (**10**), exhibits three cyclic voltammetric responses at −0.067, −0.84, and −1.31 V vs. Ag–AgCl. The first and last involve oxidation and reduction, respectively. The character of the middle one is uncertain. The compound is highly air sensitive and decomposes rapidly in the electrochemical cell. The oxidative response at −0.067 V is quasi-reversible, having ΔE_p = 130 mV at 100 mV s^{-1}. The lower value of $E_{1/2}$ compared to that of **9** indicates that the δ level in the Mo$\overset{4}{-}$Mo is more stable than that in the corresponding W$\overset{4}{-}$W analogue. This is consistent with the observed shift of the visible band in the electronic spectrum. The response at −0.84 V (ΔE_p = 160 mV at 100 mV s^{-1}) was shown to be a reduction by setting a constant potential negative to −0.84 V, where it was found the electrolysis occurs freely, while at a potential higher than the anodic peak electrolysis is not observed. In a similar way it was shown that the response at −0.067 V is due to oxidation. The reduction is most reasonably attributed to the addition of one electron to the δ^* LUMO to give an electronic configuration of $\sigma^2\pi^4\delta^2\delta^*$ and a bond order of 3.5. Such a reduction is known[19,20] in the case of $Re_2(O_2CR)_4X_2$ compounds. The reduction at −1.31 V is irreversible (at v = 100 mV s^{-1}) and might be on either the metal center or the ligand system.

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Registry No. **9**, 93110-46-4; **10**·$^2/_3C_4H_8O$, 93110-48-6; $Mo_2(O_2CCH_3)_4$, 14221-06-8; W, 7440-33-7; Mo, 7439-98-7.

Supplementary Material Available: Detailed crystallographic discussion and tables of structure factors, anisotropic thermal parameters, and bond distances and bond angles (41 pages). Ordering information is given on any current masthead page.

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