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Supplementary Material Available: Listings of anisotropic thermal parameters for the non-hydrogen atoms, positional and isotropic thermal parameters for the hydrogen atoms, torsion angles, least-squares planes and deviations, and all bond distances and angles (12 pages); a listing of the observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

Diphenyl(2,2′-bipyridyl)dioxomolybdenum(VI) and -tungsten(VI): A Comparative Study

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Summary: The structures of $(C_6H_5)_2Mo(O)_2(bpy)$ (**1**) and of the newly prepared tungsten analogue $(C_6H_5)_2W(O)_2(bpy)$ (**2**), where bpy = 2,2′-bipyridyl, are reported. The molybdenum complex **1** exists as two isomers in the same crystal. The orthorhombic unit cell *Pbca* contains 16 molecules in 8 asymmetric pairs of the isomers **1A** and **1B**, which differ primarily with respect to the orientations of the phenyl rings. In **1A**, interactions of the aromatic π-electron systems with one Mo=O bond are maximized; one phenyl ring is almost coplanar with one Mo=O bond and the dihedral angle between the phenyl rings is 20.5°. In **1B**, the phenyl groups adopt a configuration minimizing repulsive interactions with the $Mo(O)_2(bpy)$ moiety; the smallest Mo=O/phenyl dihedral angle is 23°, and the phenyl groups are in a near-orthogonal configuration with a dihedral angle of 75.5°. The combined presence of both modifications allows an especially close-packed molecular arrangement in the crystal. The tungsten complex **2** crystallizes in a monoclinic unit cell with only one type of molecule present, whose structure is intermediate between these of **1A** and **1B**. One phenyl ring is coplanar with a W=O bond; the dihedral angle between the phenyl rings is 46.7°. In solutions of **2** and of the additionally prepared complexes $(4\text{-}CH_3C_6H_4)_2W(O)_2(bpy)$ (**3**) and $(4\text{-}CH_3OC_6H_4)_2W(O)_2(bpy)$ (**4**) evidence for π-type electronic interactions between the aryl substituents and the W=O bond(s) was obtained by UV-vis spectroscopic measurements.

The chemistries of molybdenum and tungsten show striking similarities as well as differences that are still largely unexplained. One approach toward the understanding of these differences is the comparison of chemically analogous compounds of the two elements. In a previous paper[1] we reported comparisons of dialkyl derivatives of the type $R_2Mo(O)_2(bpy)$, where bpy = 2,2′-bipyridyl, with newly prepared analogous complexes of tungsten. We have now extended our studies to the diaryl derivatives of the two elements. Although the synthesis of $(C_6H_5)_2Mo(O)_2(bpy)$ (**1**) and of several substituted derivatives thereof have been described,[2] thus far the structure of only the bis(4-methoxyphenyl) derivative could be determined, as isolation of single crystals of these compounds is difficult. However, we have now succeeded in obtaining single crystals of **1** and completed an X-ray crystallographic structure determination, which produced an unexpected result. In addition, we report the structure of the newly prepared tungsten derivative $(C_6H_5)_2W(O)_2(bpy)$ (**2**). Although the structures of **1** and **2** are different, interactions between the aromatic π electrons and the Mo=O or W=O bonds were observed in both complexes. Furthermore, spectroscopic evidence for similar interactions in solution was also obtained for **2** and the additionally prepared $R_2W^{VI}(O)_2(bpy)$ complexes with R = $4\text{-}CH_3C_6H_4$ (**3**) and $4\text{-}CH_3OC_6H_4$ (**4**).

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 1330 infrared spectrometer. NMR spectra were measured on a GE QE-300 instrument at 300 MHz (^1H) and on a EM 390 instrument at 90 MHz. UV-vis spectra were measured on a Beckman DU-40 spectrophotometer.

Reagents and Chemicals. Complex **1** was prepared as described in ref 2 and recrystallized from CH_2Cl_2/C_2H_5OH. Anal. Calcd for $C_{22}H_{18}MoN_2O_2$: C, 60.28; H, 4.14. Found: C, 59.75; H, 4.25. Mass spectrum (^{96}Mo; *m/z* (relative intensity, assignment)): 439 (3, M^+); 362 (12, $M^+ - Ph$). $W(O)_2Br_2(bpy)$ (**6**)[3] was dried for 24 h at 100 °C prior to use. Anal. Calcd for $C_{10}H_8Br_2N_2O_2W$: Br, 30.0; W, 34.6. Found, Br, 30.6; W, 34.2. Solutions of the arylmagnesium halides in tetrahydrofuran (THF) were prepared by the usual methods; all aryl bromides were dried over $MgSO_4$ and distilled prior to use.

General Synthesis of Complexes $(aryl)_2W(O)_2(bpy)$ (2–4). To stirred suspensions of 2.5 g (4.7 mmol) of **6** in 5 cm^3 of dry THF was added 10.5 mmol of the respective arylmagnesium halide in 7 cm^3 of THF dropwise under argon at 0 °C over a period of 30 min. The reaction mixtures were warmed to room temperature and were subsequently stirred for 12 h. The brown-black heterogeneous reaction mixtures were treated with 100 cm^3 of cold, saturated aqueous NH_4Cl followed by 100 cm^3 of CH_2Cl_2 and were vigorously shaken in air until the CH_2Cl_2 layer was bright yellow. The CH_2Cl_2 phases were collected, repeatedly washed with water, and dried with $MgSO_4$. The complexes were isolated as pale yellow crystalline solids by evaporating the CH_2Cl_2 solutions to volumes of 5 cm,[3] adding 10 cm^3 of *n*-hexane, and cooling to 0 °C. The yields ranged from 60 to 70%, based on **6**. Analytical data are summarized in Table I. Mass spectrum for **2** (^{184}W; *m/z* (relative intensity, assignment)): 527 (4, M^+); 449 (14, $M^+ - Ph$).

Properties. Complexes **2–4** are air-stable and have higher thermal decomposition points than the corresponding molybdenum compounds (see Table I). On thermolysis at 250 °C, biphenyl and the corresponding biaryls were detected as the main soluble thermolysis products (identified by ^1H NMR spectra and melting points).

Structural Analyses. Crystals of **1** and of **2** as obtained from CH_2Cl_2 were suitable for X-ray structural analysis. The structures were solved by conventional Patterson and difference Fourier techniques. Crystallographic data and data collection parameters are given in Table IV. Crystals of approximate sizes given in

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(3) Hull, C. G.; Stiddard, M. H. B. *J. Chem. Soc. A* **1966**, 1633.

(4) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

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Table I. Analytical Data for Complexes 2–4

			anal. calcd, %				anal. found, %			
no.	mp (dec), °C	compositn	C	H	W	mol wt	C	H	W	mol wt
2	232	$C_{22}H_{18}WN_2O_2$	50.21	3.34	34.94	526.25	49.64	3.38	35.60	530
3	240	$C_{24}H_{22}WN_2O_2$	52.01	4.00	33.17	554.30	52.35	4.27		
4	247	$C_{24}H_{22}WN_2O_4$	49.17	3.78	31.36	586.30	49.00	3.85	31.57	

Table II. Optical and IR Spectral Data of Complexes 1–5[a]

no.	R	M	UV-vis (CH_2Cl_2) λ_{max}, nm (ϵ)				IR (Nujol) $\nu_{W=O}$, cm^{-1}
1	C_6H_5	Mo	328 (6272)	309 (20 100)	301 (20 300)	249 (22 910)	928, 898
2	C_6H_5	W	331 (4900)	310 (14 469)	304 (13 930)	250 (14 471)	944, 896
3	$C_6H_4CH_3$	W	342 (5120)	312 (14 988)	303 (13 113)	254 (13 394)	945, 897
4	$C_6H_4OCH_3$	W	365 (3718) 328 (5978)	318 (15 112)	305 (12 980)	253 (13 350)	943, 894
5	$C_6H_4OCH_3$	Mo	360 (5643)	309 (23 785)	302 (18 486)	252 (22 390)	924, 889

[a] Data for complexes 1 and 5 from ref 2.

Table III. Summary of ^{1}H NMR Data for Complexes 2–4

	chem shift, ppm[a]		
proton type	**2**	**3**	**4**
aromatic	7.40 (6)^m 6.90 (4)^m	7.28 (4)^m 6.73 (4)^m	7.30 (4)^m 6.46 (4)^m
CH_3		2.04 (6)^s	3.58 (6)^s
bpy			
H1,10	10.04	10.04	10.01
H2,9	8.02	7.99	8.04
H3,8	8.06	8.05	8.02
H4,7	7.74	7.70	7.70

[a] Relative to $CDHCl_2$ (intensities in parentheses) in CD_2Cl_2 solution. Superscripts denote signal multiplicities, where observable (m, multiplets; d, doublets; s, singlets).

Table IV. Crystal Data and Data Collection Parameters of Complexes 1 and 2

	1	2
space group	*Pbca*	$P2_1/c$
a, Å	18.416 (3)	14.261 (3)
b, Å	17.017 (3)	9.860 (2)
c, Å	24.163 (4)	14.990 (3)
β, deg		112.88 (2)
V, $Å^3$	7572 (2)	1942 (1)
T, K	296	296
ρ, g/cm^3	1.538 (2)	1.800 (2)
Z	16	4
fw	438.3	526.3
cryst size, mm	0.1 × 0.2 × 0.4	0.1 × 0.2 × 0.2
abs cor	empirical scan	
range of transmissn	0.92–1.00	0.861–0.997
total no. of observns	4372	3377
no. of indep observns	3907	3035
no. of indep observns above 2σ	2776	2171
no. of variables	487	244
λ, Å (Mo Kα)	0.7107	0.7107
μ, cm^{-1}	6.93	60.9
scan width (θ)	$0.55 + 0.35 \tan \theta$	$0.70 + 0.35 \tan \theta$
scan speed	variable, to maintain 3% counting statistics to max of 90 s/scan	
max 2θ, deg	41.5	45
$R(R_o)$	0.028	0.026
$R_w(F_o)$	0.034	0.032
S	1.13	1.10
max resid peak, e/$Å^3$	0.55	0.75

Table IV were mounted on an Enraf-Nonius CAD4 automated diffractometer for data collection. Unit cell dimensions were determined by a least-squares fit of reflections obtained by automatic centering on the diffractometer. Intensity data (295 K) were measured by a θ–$2J$ step scan technique with Mo Kα radiation (λ = 0.710 73 Å) from a graphite monochromator. No noticeable decomposition occurred during data collection. Orientation of the crystals was checked after every 200 reflections.

Table V. Positional Parameters and Their Estimated Standard Deviations for $(C_6H_5)_2Mo(O)_2(bpy)$ (1)

atom	x	y	z	B, $Å^2$
Mo1	0.62162 (3)	0.21064 (4)	0.52187 (3)	2.34 (1)
Mo2	0.90422 (3)	0.19850 (4)	0.68672 (3)	2.49 (1)
O1′	0.9960 (3)	0.1959 (3)	0.6790 (2)	3.9 (1)
O1	0.5294 (3)	0.2134 (3)	0.5255 (2)	3.5 (1)
O2′	0.8649 (3)	0.2397 (3)	0.6298 (2)	4.0 (1)
O2	0.6592 (3)	0.2396 (3)	0.5834 (2)	3.6 (1)
N1′	0.9198 (3)	0.1459 (3)	0.7743 (2)	2.6 (1)
N1	0.6131 (3)	0.1672 (3)	0.4308 (2)	2.3 (1)
N2	0.7365 (3)	0.1910 (3)	0.4827 (2)	2.5 (1)
N2′	0.7947 (3)	0.1870 (3)	0.7329 (2)	2.6 (1)
C1	0.5481 (4)	0.1534 (4)	0.4078 (3)	3.1 (2)
C1′	0.7320 (4)	0.2075 (5)	0.7079 (3)	3.5 (2)
C2	0.5398 (4)	0.1215 (5)	0.3559 (3)	4.0 (2)
C2′	0.6676 (5)	0.2096 (5)	0.7362 (4)	4.6 (2)
C3	0.6010 (5)	0.1033 (5)	0.3260 (4)	4.8 (2)
C3′	0.6662 (5)	0.1897 (5)	0.7907 (4)	5.3 (2)
C4′	0.7299 (5)	0.1678 (5)	0.8170 (4)	4.5 (2)
C4	0.6689 (4)	0.1195 (5)	0.3484 (4)	4.1 (2)
C5	0.6736 (4)	0.1522 (4)	0.4008 (3)	2.7 (2)
C5′	0.7936 (4)	0.1672 (4)	0.7870 (3)	2.8 (2)
C6′	0.8644 (4)	0.1434 (4)	0.8100 (3)	2.7 (2)
C6	0.7418 (4)	0.1727 (4)	0.4289 (3)	2.5 (2)
C7′	0.8746 (4)	0.1192 (5)	0.8648 (4)	4.1 (2)
C7	0.8084 (4)	0.1737 (5)	0.4020 (3)	3.5 (2)
C8	0.8698 (4)	0.1931 (5)	0.4313 (4)	4.2 (2)
C8′	0.9437 (5)	0.0968 (5)	0.8807 (4)	5.4 (2)
C9	0.8646 (4)	0.2090 (5)	0.4865 (4)	4.2 (2)
C9′	1.002 (5)	0.0964 (5)	0.8440 (4)	5.0 (2)
C10′	0.9860 (4)	0.1212 (5)	0.7915 (3)	3.8 (2)
C10	0.7972 (4)	0.2080 (4)	0.5110 (3)	3.4 (2)
C11′	0.8785 (4)	0.0751 (4)	0.6691 (3)	3.0 (2)
C11	0.6402 (4)	0.3202 (4)	0.4754 (3)	2.5 (2)
C12′	0.8507 (4)	0.0154 (5)	0.7023 (3)	3.6 (2)
C12	0.5874 (4)	0.3485 (5)	0.4398 (3)	3.6 (2)
C13	0.5939 (5)	0.4222 (5)	0.4154 (4)	4.4 (2)
C13′	0.8420 (4)	−0.0614 (5)	0.6837 (4)	4.1 (2)
C14′	0.8666 (5)	−0.0796 (5)	0.6302 (4)	4.8 (2)
C14	0.6532 (5)	0.4688 (5)	0.4260 (4)	4.3 (2)
C15	0.7058 (4)	0.4419 (5)	0.4617 (3)	3.9 (2)
C15′	0.8933 (5)	−0.0220 (5)	0.5959 (4)	4.9 (2)
C16	0.6999 (4)	0.3682 (4)	0.4863 (3)	3.3 (2)
C16′	0.8991 (4)	0.0549 (5)	0.6150 (3)	3.9 (2)
C17	0.6387 (4)	0.0843 (4)	0.5345 (3)	2.4 (2)
C17′	0.8981 (4)	0.3068 (4)	0.7373 (3)	2.7 (2)
C18	0.5972 (4)	0.0254 (4)	0.5103 (3)	3.6 (2)
C18′	0.8467 (4)	0.3633 (5)	0.7236 (3)	3.5 (2)
C19′	0.8478 (5)	0.4374 (5)	0.7475 (4)	4.6 (2)
C19	0.6014 (4)	−0.0519 (5)	0.5280 (3)	4.0 (2)
C20	0.6461 (4)	−0.0728 (5)	0.5710 (3)	3.6 (2)
C20′	0.9003 (5)	0.4569 (5)	0.7857 (4)	4.7 (2)
C21	0.6881 (4)	−0.0162 (5)	0.5950 (4)	4.3 (2)
C21′	0.9513 (5)	0.4015 (5)	0.8006 (4)	4.6 (2)
C22′	0.9500 (4)	0.3269 (4)	0.7768 (3)	3.6 (2)
C22	0.6848 (4)	0.0616 (5)	0.5771 (3)	3.6 (2)

Table VI. Positional Parameters and Their Estimated Standard Deviations for $(C_6H_5)_2W(O)_2(bpy)$ (2)

atom	*x*	*y*	*z*	*B*, Å^2
W	-0.25389 (2)	0.07192 (2)	0.08901 (2)	4.358 (5)
O1	-0.1531 (3)	0.0376 (5)	0.0572 (3)	6.4 (1)
O2	-0.3628 (4)	0.0183 (5)	-0.0028 (3)	6.5 (1)
N1	-0.1469 (3)	0.1768 (5)	0.2275 (3)	4.6 (1)
N2	-0.3439 (3)	0.1547 (5)	0.1759 (3)	3.9 (1)
C1	-0.0451 (5)	0.1806 (8)	0.2515 (5)	6.4 (2)
C2	0.0177 (5)	0.2498 (9)	0.3328 (5)	8.1 (2)
C3	-0.0214 (6)	0.3179 (8)	0.3910 (5)	7.9 (2)
C4	-0.1232 (5)	0.3136 (6)	0.3670 (4)	5.8 (2)
C5	-0.1856 (5)	0.2434 (6)	0.2845 (4)	4.6 (1)
C6	-0.2977 (4)	0.2330 (6)	0.2529 (4)	4.4 (1)
C7	-0.3507 (5)	0.2988 (7)	0.3010 (4)	6.0 (2)
C8	-0.4541 (6)	0.2788 (8)	0.2667 (5)	7.4 (2)
C9	-0.5033 (5)	0.1932 (8)	0.1881 (5)	6.3 (2)
C10	-0.4445 (4)	0.1358 (7)	0.1449 (4)	5.1 (2)
C11	-0.2399 (5)	-0.0944 (6)	0.1915 (4)	4.9 (1)
C12	-0.1642 (7)	-0.1088 (8)	0.2845 (6)	8.0 (3)
C13	-0.1577 (8)	-0.2279 (8)	0.3389 (5)	9.2 (3)
C14	-0.2226 (6)	-0.3320 (8)	0.3009 (6)	9.0 (2)
C15	-0.2950 (7)	-0.3222 (9)	0.2088 (7)	10.2 (3)
C16	-0.3036 (6)	-0.2028 (8)	0.1555 (6)	7.5 (2)
C17	-0.2715 (4)	0.2875 (6)	0.0471 (4)	4.5 (1)
C18	-0.1882 (5)	0.3598 (8)	0.0476 (5)	6.0 (2)
C19	-0.1996 (6)	0.4881 (9)	0.0056 (6)	7.6 (2)
C20	-0.2940 (7)	0.5471 (8)	-0.0350 (7)	9.2 (3)
C21	-0.3785 (6)	0.4777 (9)	-0.0351 (6)	7.7 (2)
C22	-0.3680 (5)	0.3483 (8)	0.0064 (5)	6.2 (2)

Table VII. Selected Interatomic Bond Angles (deg) for 1 and 2

Complex 1			
O1-Mo1-O2	110.5 (2)	Mo1-C11-C12	120.0 (4)
O1-Mo1-C11	99.1 (2)	Mo1-C11-C16	121.5 (4)
O1-Mo1-C17	99.4 (2)	Mo1-C17-C18	124.7 (4)
O2-Mo1-C11	97.8 (2)	Mo1-C17-C22	117.7 (4)
O2-Mo1-C17	95.9 (2)	Mo2-C11′-C12′	131.7 (4)
C11-Mo1-C17	151.4 (2)	Mo2-C11′-C16′	110.9 (4)
O1′-Mo2-O2′	110.1 (2)	Mo2-C17′-C18′	118.7 (4)
O1′-Mo2-C11′	99.6 (2)	Mo2-C17′-C22′	123.2 (4)
O1′-Mo2-C17′	97.7 (2)	C6′-N1′-C10′	118.7 (5)
O2′-Mo2-C11′	98.3 (2)	C1-N1-C5	118.8 (4)
O2′-Mo2-C17′	94.7 (2)	C6-N2-C10	118.9 (4)
C11′-Mo2-C17′	153.2 (2)	C1′N2′C5′	119.1 (4)
Complex 2			
O1-W-O2	108.2 (3)	Ni-W-C11	77.8 (2)
O1-W-N1	90.3 (2)	N2-W-C17	78.0 (2)
O1-W-N2	159.8 (2)	W-N1-C1	121.5 (5)
O1-W-C11	100.9 (2)	W-N1-C5	120.0 (4)
O1-W-C17	97.2 (2)	C1-N1-C5	118.5 (6)
O2-W-N1	161.1 (2)	W-N2-C6	120.0 (4)
O2-W-N2	92.0 (2)	W-N2-C10	120.7 (4)
O2-W-C11	98.0 (3)	C6-N2-C10	119.0 (5)
O2-W-C17	95.8 (2)	W-C11-C12	126.6 (6)
N1-W-N2	69.5 (2)	W-C11-C16	116.1 (6)
N1-W-C11	81.7 (2)	W-C17-C18	119.6 (5)
N1-W-C17	77.6 (2)	W-C17-C22	121.2 (5)

Recentering 25 reflections and calculating a new orientation matrix were done if any of the three were significantly off center. Empirical absorption corrections were introduced as given in Table IV.

Results and Discussion

The previously described bpy complexes of diaryldioxomolybdenum(VI) have been shown to exhibit spectroscopic properties consistent with electronic interactions of the Mo═O bonds with the aromatic π-electron systems. Specifically, the X-ray crystallographic analysis of the bis(4-methoxyphenyl) derivative $(4\text{-}CH_3OC_6H_4)_2Mo(O)_2(bpy)$ (5)[2] indicated a near-coplanar arrangement of both aromatic rings with one Mo═O bond. The structure of 1 appeared therefore to be of interest because the absence of aryl substituents should weaken the π-electronic interactions with the Mo═O bond.

Table VIII. Selected Bond Distances (Å)

Complex 1[a]			
Mo1-O1	1.701 (3)	Mo2-C17′	2.214 (5)
Mo1-O2	1.713 (4)	C5-C6	1.469 (7)
Mo1-C11	2.204 (5)	C5′-C6′	1.474 (7)
Mo1-C17	2.193 (5)	Mo1-N1	2.327 (5)
Mo2-O1′	1.701 (4)	Mo1-N2	2.342 (5)
Mo2-O2′	1.706 (4)	Mo2-N1′	2.316 (5)
Mo2-C11′	2.195 (5)	Mo2-N2′	2.313 (5)
Complex 2			
W-O1	1.715 (5)	C5-C6	1.484 (9)
W-O2	1.710 (5)	W-N1	2.290 (5)
W-C11	2.203 (6)	W-N2	2.304 (5)
W-C17	2.203 (6)		

[a] Mo1 and Mo2 refer to modifications A and B in the unit cell; primed C and N atoms refer to modification B.

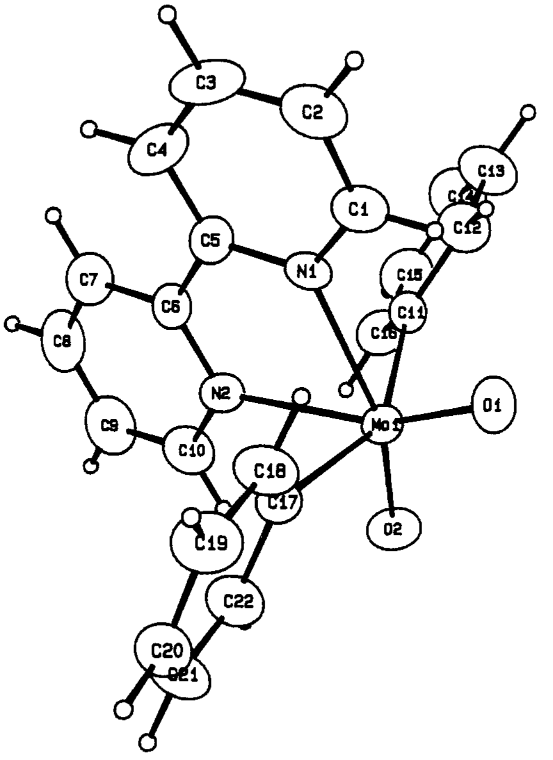

Figure 1. Perspective drawing of the structure of isomer **1A** of $(C_6H_5)_2Mo(O)_2(bpy)$ (1).

The orthorhombic unit cell of 1 (space group *Pbca*) was found to contain 16 molecules in 8 asymmetric pairs of isomeric molecules **1A** and **1B**. The isomers differ primarily with respect to the arrangements of the phenyl groups. In isomer **1A** (Figure 1), the torsion angle O2-Mo-C17-C22 of -13.21° indicates that this phenyl ring is nearly coplanar with the Mo═O2 bond and thus in a position resulting in significant π-type electronic interactions. The second ring is rotated 27.4° away from the Mo═O1 bond and 31.31° away from the Mo═O2 bond. Although the dihedral angle between the two phenyl groups is only 20.5°, the π-electronic interactions in 1 are obvious weaker than in 5, where the dihedral angle between the substituted phenyl rings is only 13.87°.[2] The C-Mo-C bond angle of 151.4° in isomer **1A** is 2° smaller than in 5, although it is not clear whether this is due to the differences in electronic interactions or to packing effects. The arrangement of the aryl groups in 5 produces stronger repulsive interactions between the ortho phenyl hydrogen atoms and the $(bpy)Mo(O)_2$ moiety, causing a distortion, for example, of the Mo-C11-C16 and Mo-

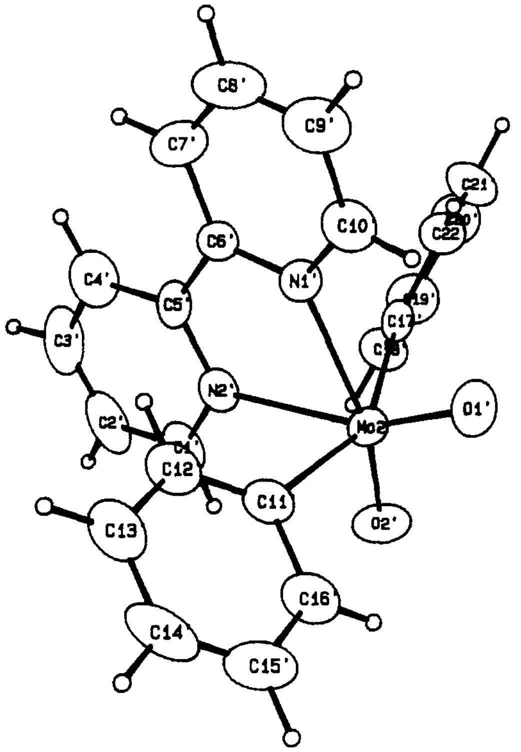

Figure 2. Perspective drawing of isomer **1B** of $(C_6H_5)_2Mo(O)_2(bpy)$ (**1**).

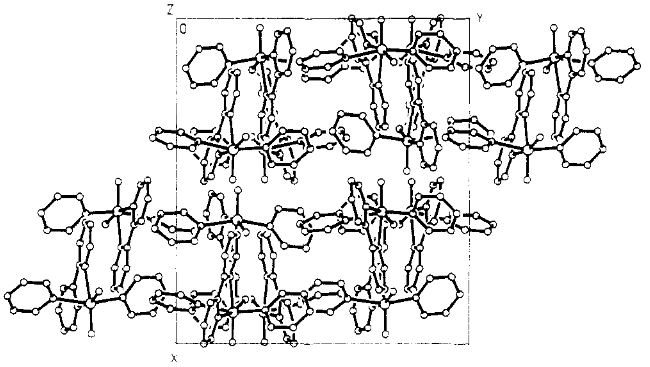

Figure 3. Perspective drawing of the unit cell of **1**.

C17–C18 angles to 130.4 and 127.7°, respectively. In **1A**, the corresponding angles of 120 and 124.7°, respectively, are close to normal.

In modification **1B** (Figure 2), neither phenyl group is coplanar with any of the Mo=O bonds. The smallest dihedral angle between the phenyl rings and one Mo=O bond is 23.0°. The second phenyl ring, furthermore, is rotated 50.48° away from the Mo=O bond and, with a dihedral angle of 75.5°, is in a nearly orthogonal position relative to the first. This is clearly indicative of the absence of significant π-interactions between the phenyl rings and the Mo=O moieties. Due to the close packing of the molecules of **1A** and **1B** in the crystal lattice of **1** the rotation of the phenyl groups is impaired. While one molecule of the complex can be accommodated in a fashion receiving some stabilization through π-electronic interactions, the structure of **1B** suggests that the positions of the phenyl groups are primarily governed by packing forces, although it appears that repulsive interactions with the $Mo(O)_2(bpy)$ moiety are also minimized.

Figure 3 shows the packing of the isomers **1A** and **1B** in the crystal lattice of **1**. The relative closeness between the molecules in the asymmetric unit is indicated by the closeness of the phenyl carbon atoms, e.g. 3.68 Å for C13A–C21B and 3.56 Å for C14A–C21B.

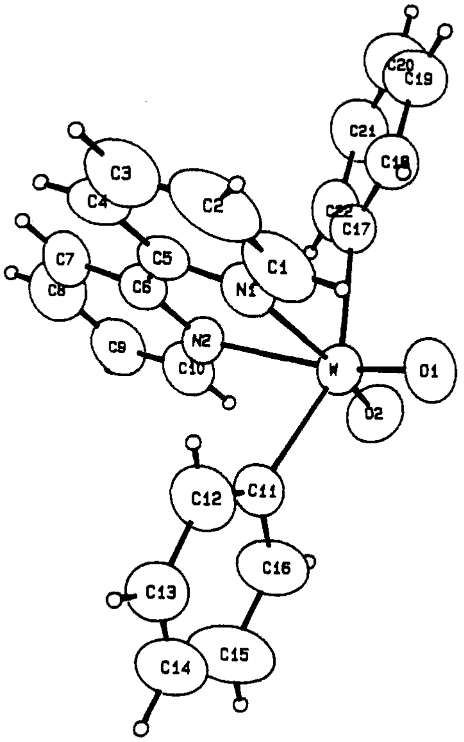

Figure 4. Perspective drawing of the structure of $(C_6H_5)_2W(O)_2(bpy)$ (**2**).

Compared to that for the corresponding molybdenum compounds, the tungsten complexes **2**–**4** show higher thermal stability (see Table I) and lower solubility in polar organic solvents. UV-vis absorption spectra in solution reveal a substituent dependence of the first low-energy absorption (Table II). This absorption is assigned to a $n_{W=O} \rightarrow \pi^*$ transition in analogy to the case for the molybdenum complexes. The $\nu_{W=O}$ absorptions in the infrared spectra suggest that the W=O bonds have a higher bond order than the Mo=O bonds, as was also observed in the dialkyl derivatives.[1] The ^1H NMR spectra indicate similar electronic environments of the aryl residues in solution.

Complex **2** crystallized in a monoclinic unit cell with only one structural modification present (Figure 4). One phenyl ring is nearly coplanar with one W=O bond; in fact, the W atom, the phenyl carbon atoms C11–C16, and O2 form a plane from which O2 deviates by only 0.16 Å. The dihedral angle between the two phenyl rings is 46.7 (4)°, and the phenyl ring with carbon atoms C17–C22 is positioned symmetrically between O1 and N1, which places it essentially parallel to the O1–O2 vector. This configuration minimizes repulsive interactions of the ortho hydrogen atoms of the phenyl ring with the $(bpy)W(O)_2$ moiety. The C–W–C bond angle of 161.0 (4)° is wider than in any similar structurally characterized tungsten or molybdenum compound. The average W=O bond length of 1.712 (5) Å is identical with the median W=O bond lengths tabulated by Mayer.[5] Since the W–N and W–C bond lengths are identical with the corresponding molybdenum bonds in analogous complexes, it follows that the structural differences between **1** and **2** are likely to be caused by small differences of the overlap integrals and energies of the mainly interacting metal orbitals and that the crystal structures of these complexes are primarily determined by packing forces.

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Acknowledgment. This work was supported by Grant CHE 84-14567 from the National Science Foundation.

Supplementary Material Available: Tables of bond distances and angles, least-squares planes, torsional angles, and general displacement parameter expressions for $(C_6H_5)_2Mo(O)_2(bpy)$ and $(C_6H_5)_2W(O)_2(bpy)$ (28 pages); listings of observed and calculated structure factors (41 pages). Ordering information is given on any current masthead page.

Multidentate Lewis Acids. Complex of a Macrocyclic Host with a Bidentate Guest

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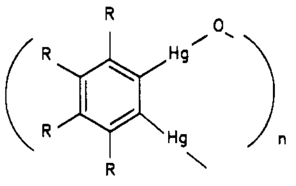
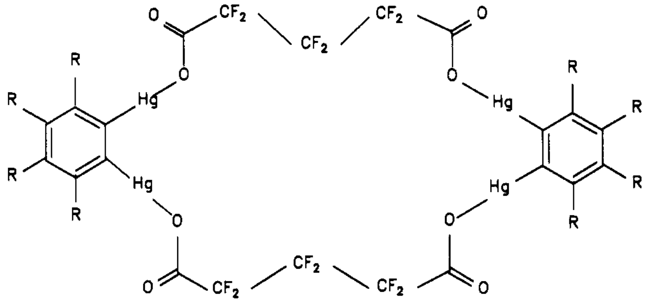
Summary: Neutralization of the mercuric oxide **1b** with hexafluoroglutaric acid in 1,2-dimethoxyethane (DME) produces the 1:4 DME adduct of macrocyclic tetradentate Lewis acid **2b** in 76% yield. An X-ray crystallographic study revealed that the macrocyclic host is approximately planar and that each 1,2-phenylenedimercury unit is associated with two molecules of DME, one above the plane and the other below. One oxygen atom from each molecule of DME bridges the two mercury atoms, and the other oxygen interacts with a single mercury. The resulting adduct is the first structurally characterized complex in which a basic guest and a multidentate Lewis acidic host share more than two bonds.

Multidentate Lewis acids with cleverly oriented electrophilic sites promise to be useful for the recognition, binding, transport, and chemical activation of complementary basic substrates.[1,2] We have shown that macrocyclic Lewis acidic hosts can be prepared by the simple expedient of neutralizing suitable organometallic oxides with perfluoro dicarboxylic acids.[1h,3] For example, treatment of (μ-1,2-phenylene)(μ-oxo)dimercury (**1a**) with an equimolar amount of hexafluoroglutaric acid in tetrahydrofuran (THF) produces a complex of the tetradentate macrocycle **2a** in high yield.[1h] In this article, we describe an extremely convenient synthesis of the octamethyl derivative **2b**, and we show how this multidentate host binds a bidentate guest.[2]



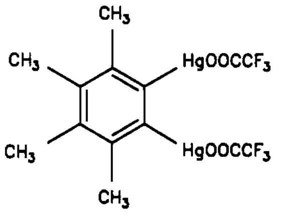
1a (R = H)

1b (R = CH_3)



2a (R = H)

2b (R = CH_3)



3

Direct bismercuration of 1,2,3,4-tetramethylbenzene ($Hg(OOCCF_3)_2$, CF_3COOH, 25 °C)[4] produced the bis(trifluoroacetate) **3** in 75% yield. Treatment of compound **3** with aqueous NaOH (0.16 N, reflux) then gave a quantitative yield of the corresponding oligomeric oxide **1b**. Neutralization of oxide **1b** with an equimolar amount of hexafluoroglutaric acid in 1,2-dimethoxyethane (DME) provided a 76% yield of crystals of a complex of macrocycle **2b** with DME. This synthesis is noteworthy because it produces a macrocyclic multidentate Lewis acid in three efficient steps from an inexpensive precursor.

Elemental analysis and ^{1}H NMR spectroscopy demonstrated that the complex contains one molecule of DME per atom of mercury. An X-ray crystallographic study revealed that the adduct has the novel structure shown in Figure 1. The macrocyclic host is approximately planar and binds two molecules of DME above the plane and two below. The two bidentate 1,2-phenylenedimercury units from which the macrocycle is built operate independently, and each binds two molecules of DME, one above the plane and the other below. One oxygen atom from each molecule of DME bridges the two mercury atoms of a 1,2-phenylenedimercury unit, and the other oxygen interacts with a single mercury. The resulting adduct is the first structurally characterized complex in which a basic guest and a multidentate Lewis acidic host share more than two bonds.

Selected interatomic distances, bond angles, and torsion angles are listed in Table I, and atomic coordinates and isotropic thermal parameters are provided in Table II. These data establish that the macrocyclic hosts in the 1:2 THF complex of hexafluoroglutarate **2a** and the 1:4 DME complex of hexafluoroglutarate **2b** have very similar

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(2) For related work on the interaction of multidentate Lewis acidic hosts with bidentate guests, see: Katz, H. E. *J. Org. Chem.* **1989**, *54*, 2179–2183.

(3) For related work on direct macrocyclizations, see: Thewalt, U.; Döppert, K.; Debaerdemaeker, T.; Germain, G.; Nastopoulos, V. *J. Organomet. Chem.* **1987**, *326*, C37–C39.

(4) For similar bismercurations, see: Sokolov, V. I.; Bashilov, V. V.; Reutov, O. A. *Dokl. Akad. Nauk SSSR* **1971**, *197*, 101–104.

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