Concluding Remarks

This study documents the existence of a previously unknown class of compounds that are unique in several respects. First, and most importantly, they constitute the only members of an $M_2Cl_4(LL)_2$ general class of compounds, in which there is an overall eclipsed conformation with two trans bidentate ligands (LL) that are anions of a substituted hydroxypyridine. We are working to extend this class of compounds to include examples with other transition metals. Secondly, they are the first reported examples in diosmium chemistry of an $Os_2Cl_4(LL)_2$ structural type. Finally, **1** and **2** are the first diosmium compounds that contain a neutral donor molecule as an axial ligand. Previous compounds have always possessed either one or two halides in the axial positions. The investigation of the reactivity of $Os_2Cl_4(chp)_2(L)$ (L = py, H_2O) is currently under way. These complexes, in which the Os-Os bond is supported by trans bridging ligands, may provide us with the opportunity to study substitution reactions that might otherwise (e.g., for the $Os_2Cl_8{}^{2-}$ ion) result in disruption of the dimetal unit.

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Supplementary Material Available: Full listings of bond angles, bond distances, and anisotropic equivalent displacement parameters and Figures 2 and 4 (9 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (21 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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Synthesis, Structure, and Interconversion of Polypyrazolylborate Complexes of Molybdenum(V)

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A series of oxomolybdenum(V) complexes with the hydrotripyrazolylborate ($HB(pz)_3{}^-$) ligand has been synthesized and characterized. $HB(pz)_3MoOCl_2$ (**1**) was prepared by the reaction of O_2 with $HB(pz)_3MoCl_3$. A pair of $(HB(pz)_3MoOCl)_2O$ geometric isomers (**2a**, **2b**) and $(HB(pz)_3)_2Mo_2O_2(\mu\text{-}O)_2$ (**3**) were obtained from the reaction of $MoCl_5$ and $KHB(pz)_3$ in dilute HCl. A Mo(V) tetramer, $Mo_4(HB(pz)_3)_2(O)_4(\mu\text{-}O)_4(\mu\text{-}OMe)_2(HOMe)_2$ (**4**), was synthesized from the reaction of **3** with MeOH. Compounds **1**, **2a**, **2b**, and **4** were structurally characterized by X-ray diffraction. The unit cell parameters are as follows: for **1**, $a = 15.273$ (2) Å, $b = 7.698$ (1) Å, $c = 13.442$ (2) Å, $\beta = 108.84$ (1)°, $V = 1495.9$ (6) Å^3, $Z = 4$, *Cc*; for **2a**, $a = 16.140$ (5) Å, $b = 11.163$ (2) Å, $c = 17.337$ (4) Å, $\beta = 116.18$ (2)°, $V = 2803$ (1) Å^3, $Z = 4$, $P2_1/c$; for **2b**, $a = 7.763$ (4) Å, $b = 13.128$ (4) Å, $c = 14.823$ (4) Å, $\beta = 96.61$ (3)°, $V = 1501$ (2) Å^3, $Z = 2$, $P2_1/c$; for **4**, $a = 14.763$ (6) Å, $b = 8.965$ (3) Å, $c = 14.076$ (4) Å, $\beta = 104.25$ (3)°, $V = 1806$ (2) Å^3, $Z = 2$, $P2_1/c$. Compounds **2a** and **2b**, which are geometric isomers, have the structures typical of $Mo_2O_3{}^{4+}$ dimers with linear Mo-O-Mo bridges. Compounds **2a** and **2b** provide the first example of Mo=O distortional isomers with a d^1 electronic configuration: the Mo-oxo distance in **2a** is 1.670 (4) Å while the corresponding distance in **2b** is 1.779 (6) Å. The yellow-brown colors of **2a** and **2b** with intense bands at 21 645 cm^{-1} indicate that the previous interpretations of the electronic spectra of $Mo_2O_3{}^{4+}$ complexes must be reevaluated. The chemical and crystallographic characterization of **4** indicated that it is a Mo(V) tetramer with a zigzag chain of four Mo atoms. The importance of correctly distinguishing between a coordinated alkoxide and a coordinated alcohol has been demonstrated in the structure of **4** and by the reformulation of two Mo(V) tetramers that had been previously reported in the literature as mixed-valence complexes.

Introduction

Molybdenum serves an important role in certain metalloproteins and in heterogeneous catalysts. In both cases sulfur and oxygen ligands are particularly important. The biochemistry of the molybdenum-containing enzymes[2] has provided much of the inspiration for the extensive development in the coordination chemistry of molybdenum with sulfur and oxygen ligands.[3-6] More recently, the widespread industrial use of molybdenum oxides and molybdenum sulfides as oxidation and hydroprocessing catalysts[7,8] has also begun to suggest research problems in molybdenum coordination chemistry.[9] One of our research goals has been to synthesize molybdenum cluster complexes with oxygen and sulfur donor ligands that would contain structural features found in the solid-state molybdenum oxides and sulfides. This paper describes some of our efforts in this area. In this, and our related publications,[10-12] we have been making use of the tridentate polypyrazolylborate ligand to control three of the coordination sites of the molybdenum center.

Experimental Section

All organic solvents were dried by standard procedures. Unless otherwise noted, reactions were carried out under a nitrogen atmosphere by using Schlenk glassware and vacuum-line procedures. ^1H NMR spectra were obtained with a Varian HFT-80 spectrometer.

$HB(pz)_3MoOCl_2$ (1). $HB(pz)_3MoCl_3$[10] (1.0 g, 2.4 mmol) was dissolved in dry CH_2Cl_2 (90 mL); dioxygen (27 mL, 1.2 mmol) was added, and the reaction was stirred for several hours. After filtration to remove

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Table I. Crystallographic Data for X-ray Diffraction Studies

	1	**2a**	**2b**	**4**
formula	$MoCl_2ON_6C_9BH_{10}$	$Mo_2Cl_2O_3N_{12}C_{18}B_2H_{20}$	$Mo_2Cl_2O_3N_{12}C_{18}B_2H_{20}$	$Mo_4O_{12}N_{12}C_{22}B_2H_{34}$
fw	395.9	736.85	736.85	1063.97
a, Å	15.273 (2)	16.140 (5)	7.763 (4)	14.763 (6)
b, Å	7.698 (1)	11.163 (2)	13.128 (4)	8.965 (3)
c, Å	13.442 (1)	17.337 (4)	14.823 (4)	14.076 (4)
β, deg	108.84 (1)	116.18 (2)	96.61 (3)	104.25 (3)
V, Å^3	1495.9 (6)	2803 (1)	1501 (2)	1806 (2)
Z	4	4	2	2
space group	Cc	$P2_1/c$	$P2_1/c$	$P2_1/c$
cryst size, mm	0.63 × 0.32 × 0.17	0.5 × 0.3 × 0.2	0.25 × 0.25 × 0.45	0.5 × 0.35 × 0.25
density (calcd), g cm^{-3}	1.756	1.746	1.63	1.957
density (measd), g cm^{-3}		1.75	1.63	1.90
temp, ±3 °C	23	23	23	23
radiation (λ, Å)	Cu (1.54184)	Mo (0.71073)	Mo (0.71073)	Mo (0.71073)
monochromator		graphite	graphite	graphite
scan mode	θ–2θ	θ–2θ	θ–2θ	θ–2θ
max 2θ, deg	78	46	45	56
abs coeff, cm^{-1}	108.4	11.15	10.41	14.07
reflcns measd	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$
no. of reflcns measd	1764	4304	2253	4800
no. of data used ($\|F_o\|^2 > 3\sigma\|F_o\|^2$)	1273	2846	1134	3151
final no. of variables	179	352	178	204
final R	0.049	0.037	0.046	0.038
final R_w	0.066	0.050	0.059	0.048
esd of unit wt observn	1.507	1.189	1.230	1.117

a yellow precipitate, the solvent was removed from the filtrate. The residue was washed with hexane and dried under vacuum to yield the product as a green powder (66% yield). The product may be recrystallized from hot toluene; however, the green powder was pure enough for use in further synthesis. Electronic spectrum: (CH_2Cl_2) 670 nm (ϵ = 44 M^{-1} cm^{-1}), 460 nm ϵ = 45) (sh), 350 nm (ϵ = 3100) (sh), 272 nm (ϵ = 7800).

HB(3,5-Me$_2$pz)$_3$MoOCl$_2$. This compound was prepared in the same manner as $HB(pz)_3MoOCl_2$ and was recrystallized from chlorobenzene. Electronic spectrum: (CH_2Cl_2) 690 nm (ϵ = 58), 450 nm (sh), 340 nm (ϵ = 1800) (sh), 280 nm (ϵ = 7900) (sh).

(HB(pz)$_3$MoOCl)$_2$O, "C_2 Dimer" (2a). A solution of $KHB(pz)_3$ (5.04 g, 20 mmol) in 12 mL of water at 0 °C was added under N_2 to a $MoOCl_5^{2-}$ solution at 0 °C prepared by dissolving $MoCl_5$ (1.35 g, 5.0 mmol) in 12 mL of 3 M HCl. The mixture was stirred for 5–10 min with the temperature maintained at 0 °C. The pH was adjusted to 2–3 by adding 6 M NaOH in air. The yellow-brown precipitate that formed was filtered off in air and washed with H_2O. CH_3OH (70 mL) was added to the filtrate; the solution was degassed and allowed to stand under N_2 for about 1 week until green-black crystals formed (yield 10%). ^1H NMR δ ($CDCl_3$): ring 3,5-positions, 7.46 (1 H, d), 7.57 (1 H, d), 7.69 (1 H, d), 8.18 (1 H, d), 8.42 (2 H, m); ring 4-position, 5.7 (1 H, t), 6.18 (1 H, t), 6.32 (1 H, t). Mass spectrum: found, *m/e* 737; calcd, *m/e* 737. Electronic spectrum: (CH_2Cl_2) 698 nm (ϵ 485), 460 nm (ϵ 9000), 350 nm (ϵ 590) (sh), 270 nm (ϵ 9200); (KBr) ca. 690 nm (sh), 470 nm (intense). IR (Nujol mull): 966 cm^{-1} (Mo=O).

(HB(pz)$_3$MoOCl)$_2$O, "C_i Dimer" (2b). H_2O (40 mL) was added to a CH_2Cl_2 (150 mL) solution of $HB(pz)_3MoCl_3$[10] (3.24 g, 7.8 mmol) in air. The stirred reaction mixture was heated on a hot plate for 2 days during which time the mixture turned brown. The CH_2Cl_2 layer was drawn off and dried with Na_2SO_4. The CH_2Cl_2 was removed and the brown residue dissolved in warm CH_3CN. The resulting solution was allowed to crystallize by slow evaporation in air, yielding dark crystals that were suitable for study by X-ray diffraction (yield 50%). This compound was also prepared from the $MoCl_5/KHB(pz)_3$/dilute HCl reaction (see the preparation of **2a** above) when the reaction was done at one-tenth scale and the reaction mixture was allowed to warm to room temperature. The crude precipitate was washed with a small amount of CH_3OH and then dissolved in CH_3CN. Evaporation of the CH_3CN filtrate in air gave beautiful crystals of **2b** in 60% yield. ^1H NMR spectrum δ ($CDCl_3$): ring 3,5-positions, 7.64 (1 H, d), 7.78 (1 H, d), 7.81 (1 H, d), 8.13 (1 H, d), 8.46 (1 H, d), 8.70 (1 H, d); ring 4-position, 6.27 (1 H, t), 6.41 (1 H, t), 6.44 (1 H, t). Mass spectrum: found, *m/e* 737; calcd, 737. Electronic spectrum: (CH_2Cl_2) 676 nm (ϵ = 496), 460 nm (ϵ = 9350), 350 nm (ϵ = 690) (sh), 245 nm (ϵ = 9300) (sh). IR (Nujol mull): 960 cm^{-1} (Mo=O).

(HB(pz)$_3$)$_2$Mo$_2$(O)$_2$(μ-O)$_2$ (3). This compound was prepared in a manner similar to that described for **2a**, but the reaction mixture was allowed to warm to room temperature. The precipitate that formed at pH ~2 was washed with H_2O. The precipitate was washed further with 25 mL of CH_3OH and dried under vacuum. The bright yellow powder, which was obtained in 30% yield, can be recrystallized from $CHCl_3$. Mass spectrum: found, *m/e* 682; calcd, *m/e* 682. Electronic spectrum: (CH_2Cl_2) 310 nm (ϵ = 3320) (sh), 244 nm (ϵ = ca. 7000) (sh).

Mo$_4$(HB(pz)$_3$)$_2$(O)$_4$(μ-O)$_4$(μ-OMe)$_2$(HOMe)$_2$ (4). When the crude filter cake of **3** was treated with methanol, platelike orange-red crystals of the product formed from the mixture after 2 days. The reaction reached completion after 3–4 weeks, resulting in crystals that were of sufficient size for an X-ray crystal structure determination. ^1H NMR spectrum (Me_2SO-d_6) ring 3,5-positions, 8.07 (4 H, d), 7.80 (2 H, d); ring 4-position, 6.35 (3 H, m), OCH_3 3.30 (3 H, s), *H*OMe 4.05 (1 H, q (J = 7 Hz)), HOCH_3 3.17 (3 H d (J = 7 Hz).

X-ray Structure Determination. Compounds **1**, **2a**, **2b**, and **4** were characterized by single-crystal X-ray diffraction studies. Suitable crystals of these compounds were mounted on glass fibers and examined on an Enraf-Nonius CAD4A automated diffractometer under control of a PDP 11/45 computer. The unit cells and space groups were determined, data sets were collected, and the structures were solved and refined by using the programs of the Enraf-Nonius structure determination library. Lattice parameters were derived from a least-squares fit of the setting angles of 25 of the strongest high-angle reflections. Other pertinent crystal data for the individual compounds are given in Table I. Atomic scattering factors were calculated by standard procedures.[48] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[48] All of the structures were solved by Patterson methods, followed by cycles of refinement and difference Fourier methods. Full-matrix least-squares refinements minimized the function $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o)$. $R = \sum||F_o| - |F_c||/\sum|F_o|$, and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

HB(pz)$_3$MoOCl$_2$ (1). Data for this crystal were collected by using Cu radiation. The intensities of the reflections were corrected for absorption. The systematic absences were consistent with either space group *C*2/*c* or *Cc*. The structure was successfully refined with the latter space group. Since the top three peaks of the first difference Fourier map indicated three nearly equivalent atoms in the primary coordination sphere of molybdenum, the molecule was suspected of containing a disorder of the chloride and oxo ligands. Three chlorine atoms were refined with a multiplicity of 0.666. After all of the atomic positions of the $HB(pz)_3$ ligand were located and refined, the multiplicites of the "chlorine" atoms were refined, indicating an unequal distribution over the three positions (0.88, 0.86, 0.71). The sum of the refined multiplicites was 2.45, which is equivalent to the total number of electrons in two chlorines and one oxygen atom. The position containing the lowest chlorine multiplicity (0.71) also displayed the shortest bond distance from Mo (2.07 Å) and hence was considered to be the site containing the greatest percentage of oxygen character. However, a model using positions calculated for partial oxygen and chlorine atoms at reasonable distances from the metal could not be successfully refined. The two partial atoms converged to an equilibrium distance of 2.090 Å from the Mo and could not be maintained as separable atoms. Final least-squares refinement was carried out by using three chlorine atoms with multiplicities 0.88, 0.86, and 0.71, all non-hydrogen atoms with anisotropic thermal parameters. Calculated positions of the hydrogen atoms were included in the structure

Table II. Positional Parameters for $HB(pz)_3MoOCl_2$ (**1**)

atom	*x*	*y*	*z*
Mo	−0.2500 (0)	0.0195 (1)	−0.2500 (0)
Cl1	−0.3350 (2)	−0.0928 (6)	−0.4102 (3)
Cl2	−0.3222 (3)	0.2715 (6)	−0.2742 (3)
Cl3	−0.3229 (4)	−0.1036 (8)	−0.1643 (4)
N1	−0.1465 (5)	0.122 (1)	−0.1136 (6)
N2	−0.1506 (6)	−0.194 (1)	−0.2240 (7)
N3	−0.1498 (5)	0.124 (1)	−0.3259 (6)
N11	−0.0528 (6)	0.109 (1)	−0.0957 (6)
N21	−0.0574 (5)	−0.172 (1)	−0.1898 (6)
N31	−0.0582 (5)	0.109 (1)	−0.2822 (6)
C11	−0.0095 (8)	0.191 (2)	−0.0074 (9)
C12	−0.0673 (10)	0.258 (2)	0.0359 (8)
C13	−0.1540 (7)	0.213 (2)	−0.0327 (8)
C21	−0.0157 (7)	−0.325 (1)	−0.1740 (8)
C22	−0.0828 (10)	−0.451 (1)	−0.1999 (9)
C23	−0.1679 (9)	−0.366 (1)	−0.2300 (9)
C31	−0.0173 (7)	0.179 (1)	−0.3452 (8)
C32	−0.0804 (8)	0.251 (2)	−0.4299 (8)
C33	−0.1646 (8)	0.208 (2)	−0.4170 (9)
B	−0.0172 (8)	0.012 (1)	−0.1765 (9)

Table III. Positional Parameters for $[HB(pz)_3MoOCl]_2O$ (**2a**)

atom	*x*	*y*	*z*
Mo1	0.14044 (3)	0.07799 (4)	0.16323 (3)
Mo2	0.34306 (2)	−0.11724 (5)	0.28309 (3)
Cl1	0.1680 (1)	0.0520 (2)	0.04230 (9)
Cl2	0.2964 (1)	−0.2461 (2)	0.16302 (10)
O1	0.0524 (2)	−0.0134 (4)	0.1471 (2)
O2	0.4304 (2)	−0.0416 (4)	0.2791 (2)
O3	0.2434 (2)	−0.0198 (4)	0.2265 (2)
N1	0.1339 (3)	0.1540 (4)	0.2749 (3)
N2	0.0492 (3)	0.2241 (4)	0.0923 (3)
N3	0.2419 (3)	0.2376 (4)	0.1998 (3)
N4	0.3672 (3)	−0.0384 (5)	0.4053 (3)
N5	0.4306 (3)	−0.2649 (4)	0.3561 (3)
N6	0.2482 (3)	−0.2270 (5)	0.3250 (3)
N11	0.1209 (3)	0.2732 (5)	0.2825 (3)
N21	0.0515 (3)	0.3343 (4)	0.1283 (3)
N31	0.2209 (3)	0.3477 (5)	0.2192 (3)
N41	0.3840 (3)	−0.1035 (5)	0.4767 (3)
N51	0.4460 (3)	−0.2877 (5)	0.4382 (3)
N61	0.2794 (3)	−0.2711 (5)	0.4055 (3)
C11	0.1131 (4)	0.2915 (7)	0.3560 (4)
C12	0.1229 (4)	0.1829 (7)	0.3965 (4)
C13	0.1348 (4)	0.0997 (6)	0.3432 (4)
C21	−0.0169 (4)	0.4000 (6)	0.0712 (4)
C22	−0.0644 (4)	0.3364 (6)	−0.0025 (4)
C23	−0.0218 (4)	0.2253 (6)	0.0137 (4)
C31	0.2927 (5)	0.4204 (7)	0.2392 (5)
C32	0.3620 (4)	0.3577 (7)	0.2327 (5)
C33	0.3276 (4)	0.2446 (7)	0.2085 (4)
C41	0.3906 (4)	−0.0300 (7)	0.5403 (4)
C42	0.3796 (5)	0.0854 (7)	0.5103 (4)
C43	0.3649 (4)	0.0774 (6)	0.4249 (4)
C51	0.5155 (5)	−0.3674 (7)	0.4730 (5)
C52	0.5468 (5)	−0.3960 (7)	0.4142 (5)
C53	0.4914 (4)	−0.3317 (6)	0.3409 (4)
C61	0.2102 (4)	−0.3243 (6)	0.4157 (4)
C62	0.1328 (4)	−0.3181 (6)	0.3389 (4)
C63	0.1595 (4)	−0.2565 (6)	0.2828 (4)
B1	0.1239 (5)	0.3656 (7)	0.2171 (5)
B2	0.3781 (5)	−0.2390 (8)	0.4736 (4)

Table IV. Positional Parameters for $[HB(pz)_3MoOCl]_2O$ (**2b**)

atom	*x*	*y*	*z*
Mo1	0.4461 (1)	0.09753 (7)	0.08346 (6)
Cl1	0.1652 (4)	0.1177 (2)	0.0107 (2)
O2	0.5457 (8)	0.2089 (5)	0.0449 (4)
O1	0.5000 (0)	0.0000 (0)	0.0000 (0)
N1	0.677 (1)	0.0652 (6)	0.1771 (6)
N2	0.360 (1)	0.1754 (6)	0.2000 (5)
N3	0.354 (1)	−0.0352 (6)	0.1644 (6)
N11	0.672 (1)	0.0500 (6)	0.2680 (6)
N21	0.401 (1)	0.1459 (6)	0.2866 (6)
N31	0.390 (1)	−0.0405 (6)	0.2575 (6)
C11	0.838 (2)	0.0423 (9)	0.3096 (8)
C12	0.948 (1)	0.0534 (8)	0.2451 (9)
C13	0.845 (1)	0.0664 (8)	0.1651 (8)
C21	0.340 (1)	0.2136 (9)	0.3424 (8)
C22	0.254 (1)	0.2906 (9)	0.2930 (8)
C23	0.271 (1)	0.2626 (8)	0.2024 (7)
C31	0.321 (1)	−0.1267 (8)	0.2886 (8)
C32	0.238 (1)	−0.1758 (8)	0.2131 (9)
C33	0.261 (1)	−0.1174 (7)	0.1397 (8)
B	0.498 (2)	0.045 (1)	0.3090 (9)

Table V. Positional Parameters for $Mo_4(HB(pz)_3)_2(O)_4(\mu\text{-}O)_4(\mu\text{-}OCH_3)_2(HOCH_3)_2$ (**4**)

atom	*x*	*y*	*z*
Mo1	0.76482 (2)	0.43867 (4)	0.31365 (2)
Mo2	0.92268 (2)	0.37578 (4)	0.42891 (2)
O1	0.7116 (2)	0.2726 (4)	0.3128 (2)
O2	0.8858 (2)	0.4012 (4)	0.2880 (2)
O3	0.8205 (2)	0.4896 (4)	0.4510 (2)
O4	0.9040 (2)	0.1973 (4)	0.4547 (3)
O5	1.0654 (2)	0.2941 (4)	0.4199 (2)
O6	0.9912 (2)	0.4303 (3)	0.5724 (2)
N1	0.7796 (2)	0.6924 (4)	0.2834 (3)
N2	0.7097 (2)	0.4553 (4)	0.1546 (3)
N3	0.6333 (2)	0.5440 (5)	0.3285 (3)
N11	0.7097 (3)	0.7699 (4)	0.2223 (3)
N21	0.6441 (3)	0.5584 (5)	0.1123 (3)
N31	0.5792 (2)	0.6284 (5)	0.2570 (3)
C11	0.7287 (4)	0.9149 (6)	0.2308 (4)
C12	0.8116 (4)	0.9358 (6)	0.2964 (4)
C13	0.8413 (3)	0.7939 (5)	0.3273 (3)
C21	0.6213 (4)	0.5371 (7)	0.0153 (4)
C22	0.6709 (4)	0.4184 (7)	−0.0059 (4)
C23	0.7249 (4)	0.3712 (6)	0.0826 (4)
C31	0.5034 (3)	0.6740 (7)	0.2871 (4)
C32	0.5083 (3)	0.6177 (7)	0.3776 (4)
C33	0.5907 (3)	0.5372 (7)	0.4014 (4)
C1	1.0986 (4)	0.1444 (7)	0.4168 (4)
C2	0.9498 (3)	0.3889 (6)	0.6500 (3)
B	0.6192 (3)	0.6889 (7)	0.1723 (4)

factor calculations but were not refined. The final coordinates for the non-hydrogen atoms are listed in Table II. Refinement of the enantiomorph resulted in higher values of R and R_w.

In an attempt to obtain a more satisfying result, the crystal structure of $HB(3,5\text{-}Me_2pz)_3MoOCl_2$ was investigated. This compound crystallizes from toluene solution in the monoclinic space group $P2_1$ with a = 8.878 (2) Å, b = 18.650 (4) Å, c = 8.045 (4) Å, β = 100.84 (3)°, V = 1308 (1) Å^3, and Z = 2. The results of the structure determination were unfortunately quite similar to those described for **1**.

$[HB(pz)_3MoOCl]_2O$ (2a). This structure was solved and refined in a straightforward manner. The positions of all 20 hydrogen atoms were clearly revealed in a difference Fourier map. The hydrogen positions were fixed, and all hydrogen atoms were assigned an isotropic temperature of 6 Å^3. Final refinement gave R and R_w equal to 0.037 and 0.050, respectively. Final atomic parameters are given in Table III.

$[HB(pz)_3MoOCl]_2O$ (2b). The experimentally determined density for **2b** was in excellent agreement with the calculated density. Similar good agreement between the measured and calculated densities was also observed for **2a**. The difference in the densities of **2a** and **2b** explains the slight but significant differences in unit cell volume per dimer in the isomeric compounds. Since this structure contained an unusually long Mo═O bond length, a second data set was collected on a new crystal taken from a different synthetic batch of crystals. The refined position of the atoms for this second structure determination gave bond distances and angles in close agreement with the first structure. The atomic parameters from the first structure are given in Table IV.

$Mo_4(HB(pz)_3)_2(O)_4(\mu\text{-}O)_4(\mu\text{-}OCH_3)_2(HOCH_3)_2$ (4). The structure was solved by normal Patterson and Fourier methods. All non-hydrogen atoms were refined anisotropically, and a difference Fourier map then revealed the location of all 17 hydrogen atoms. Subsequent refinement cycles included positional and anisotropic thermal parameters for non-hydrogen atoms and positional and isotropic thermal parameters for the H atoms. The position of H2 was redetermined from a difference Fourier map and its position and isotropic temperature factor was fixed in the two final cycles of full-matrix least-squares refinement. The position of H2 could be refined; however, the position obtained from the difference map was slightly more reasonable. The atomic positional parameters are given in Table V.

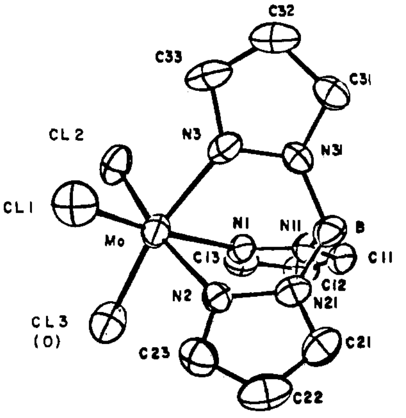

Figure 1. ORTEP diagram of [HB(pz)$_3$MoOCl$_2$] (1).

Table VI. Selected Bond Distances (Å) and Angles (deg) for HB(pz)$_3$MoOCl$_2$ (1)[a]

Mo–Cl1	2.294 (3)	Mo–N1	2.149 (7)
Mo–Cl2	2.203 (4)	Mo–N2	2.190 (9)
Mo–Cl3	2.072 (5)	Mo–N3	2.244 (7)
Cl3–Mo–Cl1	96.1 (2)	Cl1–Mo–N3	88.3 (2)
Cl3–Mo–Cl2	98.7 (2)	Cl2–Mo–N1	89.8 (2)
Cl3–Mo–N1	94.2 (2)	Cl2–Mo–N2	166.9 (2)
Cl3–Mo–N2	92.1 (3)	Cl2–Mo–N3	90.0 (2)
Cl3–Mo–N3	169.8 (3)	N1–Mo–N2	82.0 (3)
Cl1–Mo–Cl2	95.1 (2)	N1–Mo–N3	80.5 (3)
Cl1–Mo–N1	167.8 (2)	N2–Mo–N3	78.6 (3)
Cl1–Mo–N2	91.1 (2)		

[a] In the disordered HB(pz)$_3$MoOCl$_2$ molecule the ligand with the largest O multiplicity is Cl3.

Results and Discussion

Synthesis and Characterization. Monomers. HB(3,5-Me$_2$pz)$_3$MoOCl$_2$ was obtained, a number of years ago, by Trofimenko by alumina treatment of the uncharacterized red solution that he obtained from the reaction of [HB(3,5-Me$_2$pz)$_3$Mo(CO)$_3$]$^-$ with thionyl chloride.[13] The red solution has since been characterized as containing HB(3,5-Me$_2$pz)$_3$MoCl$_3$,[10] and it was found that the oxidation of this compound with dioxygen gave a good yield of the yellow-green crystalline complex HB(3,5-Me$_2$pz)$_3$MoOCl$_2$. HB(pz)$_3$MoOCl$_2$ (1) was made in an analogous manner. These monomers are paramagnetic, as expected for a d^1 system.

X-ray Structure of HB(pz)$_3$MoOCl$_2$. The X-ray crystal structure (Figure 1, Table VI) revealed that the molecule was disordered by a noncrystallographically imposed pseudo-C_3 axis passing through the molybdenum and boron atoms. No refinement of individual position or occupancy of the oxygen and the chlorine atoms was successful; it was necessary to settle for a model in which three ligands were each hybrid atoms. Although one of the three Mo–O(Cl) bond distances is distinctly shorter than the other two, indicating the greatest percent occupancy of the oxygen, all of the observed Mo–O(Cl) distances (2.294 (3), 2.203 (4), 2.072 (5) Å) tend toward the mean of the Mo–Cl and Mo–O$_t$ bond lengths found in the dimers **2a** and **2b** and in the HB(pz)$_3$TcOCl$_2$ monomer.[15] The three distinct Mo–O(Cl) bond lengths and the multiplicity refinement of the three "chlorine" atoms suggest an unequal distribution of occupancy by oxygen over the three sites (23% (Cl1), 27% (Cl2), 50% (Cl3)). The differences in the Mo–N bond distances in **1** reflect the disorder of the trans-effecting oxo ligand. The shortest Mo–N distance (Mo–N1 = 2.149 Å) is trans to the longest Mo–Cl bond. The Mo–N3 bond, which is opposite the O(Cl3) position, which has the greatest oxo character, has the longest distance (2.244 (7) Å). The usually strong trans effect is somewhat masked in **1** by the threefold disorder. The crystal structure of HB(3,5-Me$_2$pz)$_3$MoOCl$_2$ was also attempted; a similar disorder was found to be present in this compound.

A disorder similar to that found in HB(pz)$_3$MoOCl$_2$ has also been observed in MoOCl$_3$(PPh$_3$O)$_2$, WOCl$_3$(PPh$_3$O)$_2$, and WSCl$_3$(PPh$_3$O)$_2$ by Garner, Mabbs, and co-workers.[14] These authors have noted that this tendency to disorder is often seen in molecules containing a combination of larger bulky ligands with smaller, more equal, oxygen and chlorine ligands where the molecules are held together only by weak van der Waals forces. There is no such disorder in the structure of the closely related HB(pz)$_3$TcOCl$_2$; the larger trans effect of the Tc=O bond is apparently sufficient to remove the threefold disorder in the HB(pz)$_3$ ligand.[15]

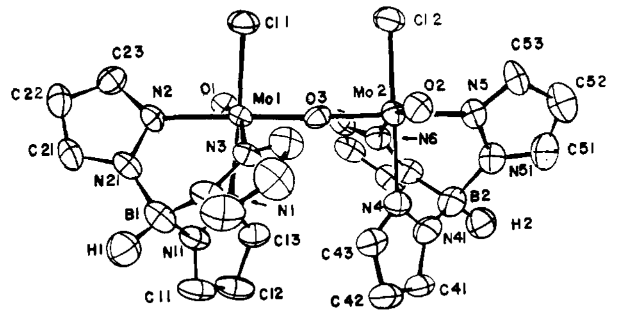

Figure 2. ORTEP diagram of [HB(pz)$_3$MoOCl]$_2$O (**2a**).

Dimers. Mo$_2$O$_4$(HB(pz)$_3$)$_2$ (3) was the major product obtained from the reaction of KHB(pz)$_3$ with solutions of [MoOCl$_5$]$^{2-}$ in aqueous HCl solution (pH ~2) according to a modification of a synthetic procedure developed by Melby for similar Mo$_2$O$_4$$^{2+}$ complexes.[16] This bright yellow compound has been characterized by its ^{1}H NMR, IR, and mass spectra. The IR spectrum of **3** possesses bands characteristic of the terminal (960 cm^{-1}) and bridging oxo's (750, 733, and 460 cm^{-1}). Compound **3** is easily converted to the mono μ-oxo-bridged species **2a** with HCl, which is a characteristic reaction of Mo$_2$O$_4$$^{2+}$ complexes.[3]

The two geometrical isomers of [HB(pz)$_3$MoOCl]$_2$O, **2a** (10% yield) and **2b** (60% yield), are obtained from the same reaction of KHB(pz)$_3$ and MoCl$_5$ in dilute HCl. Isomer **2b** may also be obtained by treating HB(pz)$_3$MoCl$_3$ with water in air (50% yield). The electronic spectrum of **2a** follows Beer's law, which indicates that it does not take part in the disproportionation reaction (Mo$_2$O$_3$$^{4+}$ = MoO$_2$$^{2+}$ + MoO^{2+}) that is common for several Mo$_2$O$_3$$^{4+}$ complexes.[17] The peak positions and relative intensities of a solid-state spectrum of **2a** in a KBr pellet are similar to the solution spectra, indicating that the complex is stable in solution. The electronic spectrum of **2a** in CH$_2$Cl$_2$ or THF shows transitions at 698 nm (ϵ = 485), 462 nm (ϵ = 9000), 350 nm (sh), (ϵ = 600), and 270 nm (sh) (ϵ = 9000). The electronic absorption spectrum of **2b** has the same intense 462-nm band as that of **2a**; however, the lowest energy band is shifted to 676 nm. The ^{1}H NMR spectra of **2a** and **2b** are different; however, when **2a** remains in solution (CDCl$_3$) for more than 30 min, the spectrum obtained is a combination of **2a** and **2b**. Under the same conditions there is no change in the spectrum of **2b**.

X-ray Structures of the [HB(pz)$_3$MoOCl]$_2$O Geometric Isomers. Figure 2 shows a perspective view of dimer **2a** with the labeling scheme; interatomic distances and angles of the metal–ligand coordination are given in Table VII. The dimer possesses no crystallographically imposed symmetry, but it has an approximate C_2 axis and will be referred to as the "C_2 dimer" to distinguish it from its geometrical isomer, **2b**. The crystal structure displays

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Table VII. Selected Distances (Å) and Angles (deg) for $[HB(pz)_3MoOCl]_2O$ (**2a**)

Mo1-Cl1	2.346 (2)	Mo2-N4	2.164 (5)
Mo2-Cl2	2.364 (2)	Mo1-N2	2.178 (5)
Mo1-O1	1.670 (4)	Mo2-N5	2.176 (5)
Mo2-O2	1.671 (4)	Mo1-N3	2.311 (5)
Mo1-O3	1.883 (4)	Mo2-N6	2.315 (5)
Mo2-O3	1.829 (4)	Mo1-Mo2	3.710 (1)
Mo1-N1	2.158 (4)		
Mo1-O3-Mo2	177.3 (2)	Cl2-Mo2-N6	87.5 (1)
O1-Mo1-O3	102.2 (2)	O3-Mo1-N1	94.9 (2)
O2-Mo2-O3	103.7 (2)	O3-Mo2-N4	91.1 (2)
O1-Mo1-Cl1	104.9 (2)	O3-Mo1-N2	165.0 (2)
O2-Mo2-Cl2	102.6 (2)	O3-Mo2-N5	162.7 (2)
O1-Mo1-N1	90.9 (2)	O3-Mo1-N3	87.2 (1)
O2-Mo2-N4	92.6 (2)	O3-Mo2-N6	86.3 (2)
O1-Mo1-N1	92.9 (2)	O3-Mo1-Cl1	89.0 (1)
O2-Mo2-N5	93.6 (2)	O3-Mo2-Cl2	91.5 (1)
O1-Mo1-N3	164.7 (2)	N1-Mo1-N2	85.6 (2)
O2-Mo2-N6	165.4 (2)	N4-Mo2-N5	87.0 (2)
Cl1-Mo1-N1	162.6 (1)	N1-Mo1-N3	76.1 (2)
Cl2-Mo2-N4	163.6 (1)	N4-Mo2-N6	76.5 (2)
Cl1-Mo1-N2	86.3 (1)	N2-Mo1-N3	78.4 (2)
Cl2-Mo2-N5	85.6 (2)	N5-Mo2-N6	76.5 (2)
Cl1-Mo1-N3	87.1 (1)		

Table VIII. Selected Distances (Å) and Angles (deg) for $[HB(pz)_3MoOCl]_2O$ (**2b**)

Mo-Cl	2.334 (3)	Mo-N2	2.178 (7)
Mo-O2	1.779 (6)	Mo-N3	2.277 (8)
Mo-O1	1.861 (1)	Mo-Mo′	3.722 (1)
Mo-N1	2.179 (8)		
Mo-O1-Mo′	180.0	Cl-Mo-N3	89.8 (2)
O2-Mo-O1	102.3 (2)	O1-Mo-N1	93.3 (2)
O2-Mo-Cl	100.1 (2)	O1-Mo-N2	164.4 (2)
O2-Mo-N1	90.5 (3)	O1-Mo-N3	86.1 (2)
O2-Mo-N2	93.1 (3)	O1-Mo-Cl	92.29 (8)
O2-Mo-N3	166.6 (3)	N1-Mo-N2	83.8 (3)
Cl-Mo-N1	166.6 (2)	N1-Mo-N3	78.5 (3)
Cl-Mo-N2	87.5 (2)	N2-Mo-N3	78.3 (3)

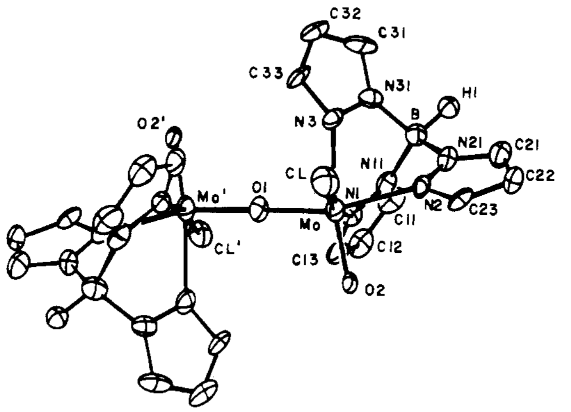

Figure 3. ORTEP diagram of $[HB(pz)_3MoOCl]_2O$ (**2b**).

the well-known $Mo_2O_3^{4+}$ bridging structure found in many earlier structures.[18] The present structure is distinctive in two ways. In the previous structures where the terminal oxo ligands are trans to one another, this relationship has been rigorous due to a center of symmetry that is crystallographically imposed. The structure of **2a** contains a nearly linear Mo-O-Mo bridge (177.3 (2)°) with trans oxo ligands but no center of symmetry. The second distinctive facet is the observed value of 13.5° for the dihedral angle between the two planes defined by the $Mo(O_t)O_b$ atoms. The largest value previously reported is 4.5° (in a structure containing cis oxo ligands).[18a] Compound **2a** is diamagnetic in the solid state and in solution (as indicated by sharp unshifted resonances in the NMR spectrum). No ESR spectrum was observed at room temperature or at 77 K. The diamagnetism of **2a** is consistent with the analysis of Cotton,[18a] who pointed out that there could be significant deviation from planarity in the $Mo_2O_3^{4+}$ unit without affecting the coupling of the Mo(V) d^1 electrons through the oxo three-center bond. The observed bond distances in **2a** are similar to those reported for the other $Mo_2O_3^{4+}$ complexes:[18] the short Mo-O_t distances (1.670 (4) and 1.671 (4) Å) and the structural trans effect experienced by the ligands trans to the oxo group (Mo1-N3 = 2.311 (5) Å and Mo1-N6 = 2.315 (5) Å vs. the four Mo-N_{cis} distances of 2.158-2.178 Å). The difference in the distances Mo1-O3 (1.883 (4) Å) and Mo2-O3 (1.829 (4) Å) is 13σ, which may indicate this asymmetry in the Mo-O-Mo bridge is real. Other crystallographically significant distortions in the coordination sphere of the $HB(pz)_3MoO_tCl(O_b)$ unit are found in isomer **2b**.

The X-ray structure determination of **2b** (Figure 3, Table VIII) revealed it to be a geometrical isomer of **2a**. Compound **2b** has a crystallographically imposed center of symmetry (i.e. the C_i dimer); the oxo groups as well as the other ligands are trans to one another. The center of symmetry also requires that the dihedral angle between the two $Mo(O_t)O_b$ planes be equal to 0°. A rotation about the Mo-O-Mo unit does not interconvert the isomers; the interconversion of **2a** and **2b** requires a bond-breaking mechanism. A striking structural difference between the two isomers is that the C_i dimer, **2b**, contains a Mo-O_t bond length of 1.779 (6) Å. This distance is substantially longer than the corresponding Mo-O_t length of 1.671 (4) Å found in isomer **2a** and is outside the range of 1.61-1.74 Å found in other structures containing $Mo^V{=}O$ groups.[3,4,6,18,19] No other metrical value in the structure can be considered unusual. The Mo-N3 bond, which is trans to the terminal oxo ligand, is 2.277 (8) Å in **2b** and 2.313 Å in **2a**. Thus, the trans nitrogen experiences a greater trans effect in isomer **2a**, which possesses the shorter Mo-O_t, as would be expected. The other Mo-ligand distances are comparable in the two isomers; the Mo-O_b distance (1.861 (1) Å) is not significantly different from the average Mo-O_b distance in **2a**.

The explanation for the long oxo bond distance is not the result of intermolecular forces. There is no evidence for a hydrogen-bonding interaction with this oxygen; moreover, none of the hydrogens of the pyrazolylborate ligands can be considered likely to hydrogen bond to the oxo group since they are bonded only to carbon and boron atoms. A unit cell diagram of **2b** (supplementary material) does not reveal any obvious packing strains. The closest intermolecular distances between the terminal oxygen atoms in **2b** and H31 and H21 from an adjacent molecule are 2.55 and 2.65 Å, respectively. The long metal-metal distance resulting from the linear oxo bridge also rules out any steric interactions of the two monomers across the bridge.

The importance of the nonbonded repulsions between donor atoms as a determining factor in the irregular stereochemistry of oxomolybdenum compounds has been previously recognized.[20]

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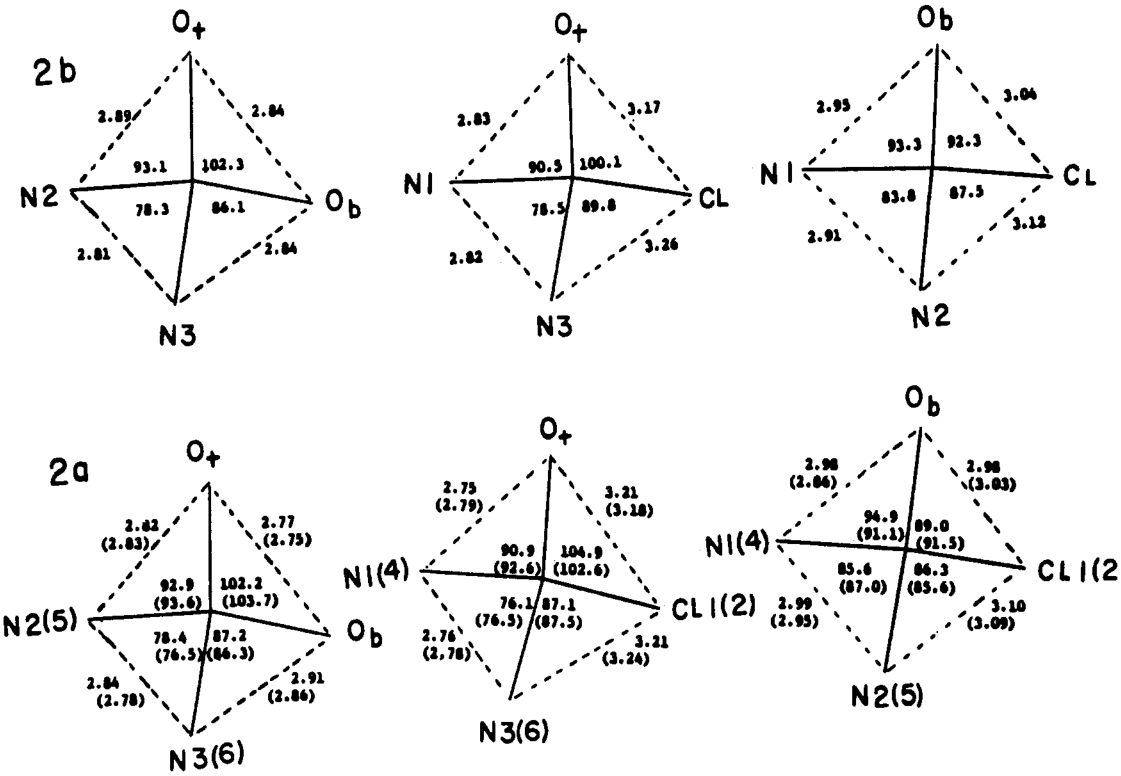

Figure 4. Structure diagrams that compare the L–Mo–L bond angles and the ligand–ligand nonbonding distances in **2a** and **2b**.

The repulsion between the multiply bonded oxo ligand and its cis ligands results in the O_t–Mo–L_{cis} angles being in general greater than 90°. The resultant nonbonded repulsion between these cis ligands and the ligand trans to the oxo causes the increase in the M–L_{trans} bond length. Figure 4 schematically compares the ligand–ligand distances and their effect on the L–M–L angles in **2b** and **2a**. The $[HB(pz)_3MoOCl]_2O$ dimers are composed of two highly strained distorted octahedra, with the $HB(pz)_3$ tridentate ligand imposing its own geometric constraints in addition to that resulting from the dominant molybdenum–oxo bond. Adjustment of ligand–Mo–ligand angles and the Mo–O_t bond length to achieve a balance of ligand–ligand repulsive forces and metal–ligand bonding forces apparently allows two stable isomers with differing Mo–O_t bond lengths. The interligand distances between O_t and three of its four cis ligands (N2, O_b, and N1) increase in going from **2a** to **2b** (i.e. as the Mo–O_t bond distance increases). Although the O_t–Cl distance is slightly shorter in **2b**, the O_t–Mo–Cl angle has become significantly less distorted from 90° in **2b**. All these changes are small (and barely crystallographically significant); however, they indicate that the increase in the Mo–O_t distance in **2b** may result from an attempt to decrease the nonbonded repulsions with its cis ligands. In a manner consistent with the structural results, the Mo=O stretch in the IR spectrum of **2a** (966 cm^{-1}) is found at higher energy than the corresponding peak in **2b** (960 cm^{-1}). A detailed study of the vibration spectra of compounds **2a** and **2b** and also of **1** is in progress in an attempt to further monitor the changes in the metal–ligand bonding in these compounds.[21]

Analogies to the structural phenomena observed in **2a** and **2b** can be found in a series of Mo^{IV}=O complexes and isoelectronic Re^V≡N complexes. Chatt et al. synthesized a series of Mo(IV) oxo complexes of the type $MoOX_2L_3$ (X = halide or pseudohalide; L = tertiary phosphine), some of which were blue and some of which were green.[22] Initially, the blue and green forms were thought to have different arrangements of the halide atoms; however, X-ray crystal studies of $MoOCl_2(Et_2PPh)_3$ (green) and $MoOCl_2(Me_2PPh)_3$ (blue) showed both to possess the same basic arrangement of the ligands.[23] However, the green isomer displays a long Mo–oxo bond (1.802 (11) Å) while the blue form possesses a short Mo–O bond length of 1.676 (7) Å. More recently, the green isomer of $MoOCl_2(Me_2PPh)_3$ was structurally characterized and found to have a long Mo–O bond of 1.80 (2) Å.[24] Completely analogous observations have been found for the rhenium compound: $ReNCl_2(Me_2PPh)_3$ has an anomalously long Re–N bond length (1.788 (11) Å) while the Re–N distance (1.660 (8) Å) in $ReNCl_2(Et_2PPh)_3$ lies in the normal range. Chatt recommended the term "distortional isomers" for this phenomenon.[23] Another example of such isomers has been found in two crystalline forms of $[MoO(OH_2)(CN)_4]^{2-}$.[26] The observation of this phenomenon in compounds **2a** and **2b** extends this unusual type of isomerism to a d^1 Mo(V) metal center; the previous examples have been found in d^2 (Mo(IV) and Re(V)[27]) metal complexes. The monomeric units of dimers **2a** and **2b** (i.e. $(HB(pz)_3Mo(O_t)(Cl)(O_b-))$ can be described as distortional isomers of one another. In addition to their distortional differences, **2a** and **2b** are true geometric isomers. Although there is no completely satisfying explanation for the existence of distortional isomers, their occurrence is becoming more common.

Electronic Spectra of 2a and 2b. The electronic spectra of the linear bridged $[HB(pz)_3MoOCl]_2O$ dimers **2a** and **2b** are unique among those reported for $Mo_2O_3^{4+}$ complexes of known structure in that they do not possess a 19000-cm^{-1} band and are not purple. In the past, the intense band at ca. 19000 cm^{-1} and the associated

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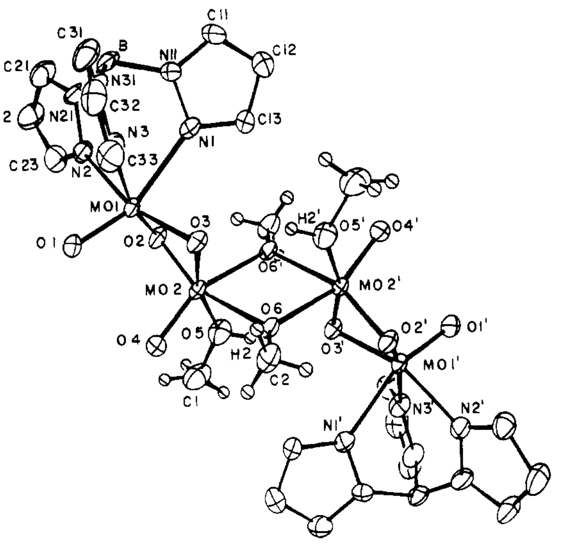

Figure 5. ORTEP diagram of $[Mo_4(HB(pz)_3)_2(O)_4(\mu\text{-}O)_4(\mu\text{-}OCH_3)_2(CH_3OH)_2]$ (**4**). The hydrogen atoms of the $HB(pz)_3$ ligand have been omitted.

deep (usually purple) color have been considered to be characteristic of a linear (Mo═O)—O—(Mo═O) bridged dimer, and in fact, compounds lacking this band were deemed suspect.[28] The apparent lack of ligand dependence on the position of this band led to its suggested assignment as a transition involving the Mo–O–Mo bridging unit.[28] Complexes **2a** and **2b** are yellow-brown in solution with an intense band at 21 645 cm^{-1}. It now appears that the rigid criterion of a ca. 19 000-cm^{-1} band in $Mo_2O_3^{4+}$ complexes may have been established for a set of compounds with too small a variation of donor ligands. The $Mo_2O_3^{4+}$ compounds that have been the most extensively studied have sulfur ligands. In any case the existence of complexes **2a** and **2b** shows the danger of using the 19 000-cm^{-1} band as a criterion for a linear oxo-bridged $Mo_2O_3^{4+}$ complex and reveals the band in this region to be more ligand-dependent than was previously suspected. In contrast to the intense study of oxo Mo(V) monomers,[29] the electronic structure and electronic spectra of $Mo_2O_3^{4+}$ complexes have not been adequately studied.

Mo_4 Tetramer. Further evidence of the well-known tendency of Mo(V) to dimerize and polymerize is seen in the formation of the tetramer $Mo_4(HB(pz)_3)_2(O)_4(\mu\text{-}O)_4(\mu\text{-}OCH_3)_2(HOCH_3)_2$ (**4**). Compound **4** is obtained from the treatment of $(HB(pz)_3)_2Mo_2O_4$ (**3**) with methanol. Figure 5 shows a perspective view of **4** obtained by an X-ray crystallographic study; selected bond distances and angles are listed in Table IX. The basic structure of the molybdenums and their ligating oxygen and nitrogen atoms can be envisioned as an oligomer of four MX_6 octahedra joined together by edge sharing. It is a fragment of the zigzag chain structure found in many MX_4 solid-state structures such as $ZrCl_4$ and monoclinic $MoOCl_3$.[30] In the idealized zigzag chain the metal atoms are coplanar and the M–M–M angles are 120°; in **4** the Mo1–Mo2–Mo2′ angle is 126.55 (2)°.

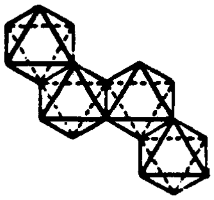

Table IX. Selected Bond Distances (Å) and Angles (deg) for $Mo_4(HB(pz)_3)_2(O)_4(\mu\text{-}O)_4(\mu\text{-}OCH_3)_2(HOCH_3)_2$ (**4**)

Mo1–Mo2	2.553 (1)	Mo2–O4	1.678 (3)
Mo1–O1	1.682 (3)	Mo2–O5	2.264 (3)
Mo1–O2	1.937 (3)	Mo2–O6	2.082 (3)
Mo1–O3	1.960 (3)	Mo2–O6′	2.156 (3)
Mo1–N1	2.335 (4)	O5–C1	1.432 (7)
Mo1–N2	2.191 (4)	O6–C2	1.426 (5)
Mo1–N3	2.215 (4)	O3–O5′	2.896 (5)
Mo2–Mo2′	3.454 (1)	H2–O5	0.86
Mo2–O2	1.937 (3)	H2–O3′	2.2
Mo2–O3	1.909 (3)		
O1–Mo1–O2	107.2 (1)	O4–Mo2–O6′	154.0 (0)
O1–Mo1–O3	107.2 (1)	O2–Mo2–O3	94.0 (1)
O1–Mo1–N1	157.8 (1)	O2–Mo2–O5	90.7 (1)
O1–Mo1–N2	89.9 (2)	O2–Mo2–L6	155.9 (1)
O1–Mo1–N3	87.7 (2)	O2–Mo2–O6′	85.1 (1)
O1–Mo1–Mo2	99.3 (1)	O3–Mo2–O5	165.0 (1)
O2–Mo1–O3	94.4 (1)	O3–Mo2–O6	86.1 (1)
O2–Mo1–N1	90.2 (1)	O3–Mo2–O6′	93.5 (1)
O2–Mo1–N2	87.0 (1)	O5–Mo2–O6	83.9 (1)
O2–Mo1–N3	164.1 (1)	O5–Mo2–O6′	72.6 (1)
O3–Mo1–N1	85.3 (1)	O6–Mo2–O6′	70.9 (1)
O3–Mo1–N2	162.3 (1)	Mo2′–Mo2–O3	89.82 (9)
O3–Mo1–N3	88.4 (1)	Mo2′–Mo2–O5	75.48 (9)
N1–Mo1–N2	77.0 (1)	Mo1–O2–Mo2	82.5 (1)
N1–Mo1–N3	74.0 (1)	Mo1–O3–Mo2	82.6 (1)
N1–Mo1–Mo2	102.69 (8)		
N2–Mo1–N3	87.4 (1)	Mo2–O5–C1	129.4 (4)
Mo1–Mo2–Mo2′	126.55 (2)	Mo2–O5–H2	128.9
Mo1–Mo2–O4	100.1 (1)	Mo2–O5–O3′	98.8 (1)
Mo1–Mo2–O6′	105.33 (7)		
O4–Mo2–O2	108.3 (2)	C1–O5–H2	96.0
O4–Mo2–O3	107.2 (2)	C1–O5–O3′	119.7 (3)
O4–Mo2–O5	84.7 (2)	O5–H2–O3′	138.4
O4–Mo2–O6	94.6 (1)		

The centrosymmetric structure is best described as a dimer of dimers with the Mo1–Mo2 units being connected by two bridging methoxides. The Mo1–Mo2 units have the typical $Mo(V)_2O_4^{2+}$ core found in many bis(μ-oxo)-bridged Mo(V) dimers.[3,6,31] The distances within the $Mo_2O_4^{2+}$ units of **4** are typical: the terminal oxo bond lengths are 1.680_{av} Å, the average Mo–O_b distance is 1.936 Å, and Mo–N1, which is trans to the oxo group, is longer than the two cis Mo–N bonds. The bonding between Mo2 and Mo2′ is not as familiar since each of the bridging methoxides is trans to a single terminal oxo group, which gives a slightly unsymmetric bridging arrangement with Mo2–O6 = 2.082 (3) Å and Mo2–O6′ = 2.156 (3) Å. A similar unsymmetric bridging arrangement due to the trans effect of a Mo(V) terminal oxo group has been observed in the polymeric complex $[MoOCl_3]_n$, which has a zigzag chain of Mo(V) atoms linked by bridging chlorine atoms (Mo–Cl_b = 2.44 (2) and 2.78 (2) Å).[32] Some precedents are provided by the large number of dialkoxide-bridged dimers that have been described by Chisholm and others.[33,34] A similar structural unit is also present as part of the structures of a series of molybdenum tetramers that will be discussed in the following section.[35-37]

The formal oxidation number of the molybdenum in **4** is +5 with a total of four electrons available for metal–metal bonding (one d_{xy} electron on each Mo when Mo1–O1 is taken as the z axis). The tetramer possessed alternating short (2.553 (1) Å), long (3.454 (1) Å), short (2.553 (1) Å) metal–metal distances in the zigzag Mo_4 chain. The short Mo1–Mo2 distance reveals the presence of a Mo–Mo single bond between Mo1–Mo2 and Mo1′–Mo2′ in each of the M_2O_4 units. This metal–metal bond is the result of direct overlap of the d_{xy} orbitals on Mo1 and Mo2, forming a two-electron covalent bond as is found in all known diamagnetic

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$Mo_2O_4^{2+}$ dimers. The long Mo2–Mo2′ distance of 3.454 (1) Å precludes metal–metal bonding between the $Mo_2O_4^{2+}$ halves of the tetramer; similar distances have been reported for dialkoxide-bridged dimers with metal–metal bond orders of 0.[33,34]

The terminal ligand on Mo2 and Mo2′ has been identified as a methanol rather than a methoxide by crystallographic and chemical evidence; this is critical since it establishes **4** as a Mo(V) tetramer rather than a mixed-valence (2Mo(V),2Mo(VI)) cluster. The long bond length of 2.264 (3) Å for Mo2–O5 reveals this ligand to be a methanol since the distance is far outside the range for terminal alkoxide ligands bound to Mo(V) (1.808–1.98 Å).[33,34] Moreover, the literature of Mo(V) complexes shows that terminal alkoxide groups have shorter bonding distances to the metal than bridging alkoxides when they are in the presence of comparable trans ligands.[33,34,38] An assignment of O5 as a methoxide would contradict this generalization. A search of an electron difference map during the solution of the crystal structure revealed the location of the methanolic hydroxyl hydrogen H2. This hydrogen is involved in a hydrogen bond with O_3', as evidenced by the short H2–O3′ distance of 2.2 Å. A structural effect of the hydrogen bond is the observed tilting of the O5′ atom toward O3; the angle Mo2–Mo2′–O5′ (75.48 (9)°) is quite acute. Quite similar hydrogen bonding has been reported in the complexes $Ti_2(OPh)_8(HOPh)_2$ and $W_2Cl_4(OCH_3)_4(HOCH_3)_2$.[39,40]

The crystallographic identification of CH_3OH as the terminal ligand on Mo2 is corroborated by chemical evidence. The mass spectrum of **4** reveals a slow continuous emission of methanol from room temperature to 60 °C. ^1H NMR spectra of **4** in acetone-d_6 and Me_2SO-d_6 gave resonances for the methanolic proton. The neutral CH_3OH ligand determines **4** to be a Mo(V) tetramer rather than a mixed-valence complex, which would be expected to be paramagnetic; **4** is clearly diamagnetic as revealed by its NMR spectra and magnetic susceptibility measurements.

In view of the known trans-labilizing effect of terminal oxo groups in Mo(V) complexes, the unsymmetric methoxide bridge structure of **4** with each of the bridging methoxides trans to a single terminal oxo group suggests the following possible retrosynthetic mechanism of formation of the tetramer **4** from $Mo_2O_4(HB(pz)_3)_2$ (**3**). The tetramer may be formed by dimerization of two $HB(pz)_3Mo_2O_4L_3$ units (L = CH_3OH or CH_3O^-). Displacement of the L ligand trans to the terminal oxo followed by dimerization leads to the formation of **4** rather than to the isomeric linear tetramer. The mild conditions (methanol, room temperature) needed for the transformation of **3** into **4** indicate the general instability of **3**. Although **3** was not crystallographically characterized, its spectroscopic properties are completely consistent with a *cis*-$Mo_2O_4^{2+}$ structure. The steric clash between the cis axial pyrazole rings is likely responsible for the ready loss of a tridentate ligand to give the $HB(pz)_3Mo_2O_4L_3$ intermediate.

The zigzag arrangement of molybdenum atoms in **4** is a more open structure than those of the Mo_4 tetramers previously reported. The tridentate $HB(pz)_3$ ligands evidently prevent **4** from collapsing into the more closely packed $Ti_4(OR)_{16}$[41] structure found in some earlier Mo_4 tetramers[35–37] or the $(MoO)_4O_4$ cubane structure found in one example.[42] The polypyrazolylborate ligand also caps off the structure of **4**, preventing further polymerization such as that found in $Mo_6O_{10}(O\text{-}i\text{-}Pr)_{12}$ and $[MoO_2(O\text{-}i\text{-}Pr)_2]_n$.[43a] The Mo_4 zigzag structure in **4** is related to the structure of the central Mo_4 unit in $Mo_6O_{10}(O\text{-}i\text{-}Pr)_{12}$; the differences in the structures of the Mo_4 units result from the difference in the coordination numbers of the molybdenums. The structural analogies between **4** and a recently reported cyclic Mo(V) octamer should also be noted.[43b]

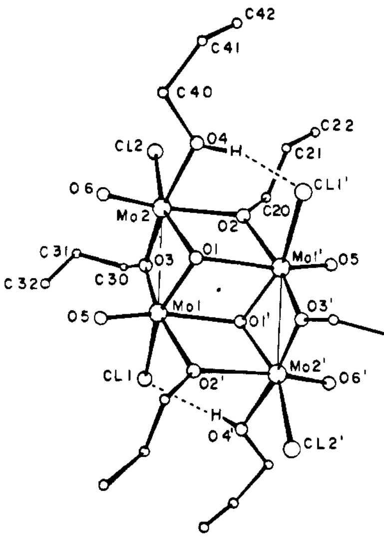

Figure 6. ORTEP diagram of **5** using the original coordinates from ref 35. The propanolic hydrogens have been drawn in the positions where they should occur on the basis of the close structural analogy to **4**.

Table X. Selected Distances (Å) and Angles (deg) for $Mo_4O_6Cl_4(O\text{-}n\text{-}Pr)_4(HOPr)_2$ (**5**)

Mo1–Mo2	2.669 (2)	Mo2–Mo1′	3.43
Mo2–O4	2.13 (1)	Mo1–O2′	2.05 (1)
Mo2–O3	1.98 (1)	Mo1–O3	1.98 (1)
O4–Cl1′	3.00		
Mo1′–Mo2–O4	81.5	Mo2–Mo1′–Cl1′	86.5
C40–O4–Cl1′	123.2	Mo2–O4–C40	126
		Mo2–O4–Cl1′	103.4

Table XI. Selected Distances (Å) and Angles (deg) for $[Mo_4O_8Cl_4(OEt)_2(HOEt)_2]^{2-}$ (**6**)

Mo1–Mo2	2.587 (3)	Mo1–Mo2′	3.444 (3)
Mo1–O6	2.23 (2)	Mo2–O2	2.12 (1)
Mo1–O2′	2.13 (2)	O6–Cl2′	3.08
Mo1′–Mo2–Cl2	87.5	Mo2–Mo1′–O6′	82.1
Mo1′–O6′–C18′	126.0	C18′–O6′–Cl2	117.5
Mo1′–O6′–Cl2	101.0		

Reformulation of Mixed-Valence (2Mo(V),2Mo(VI)) Tetramers. During the structural analysis of **4**, we realized that the published results of the X-ray structure of the purported mixed-valence tetramer $[Mo_4O_6Cl_4(O\text{-}n\text{-}Pr)_6]$ (**5**. Figure 6), had been misinterpreted.[35] This compound should be formulated as $[Mo_4O_6Cl_4(O\text{-}n\text{-}Pr)_4(HOPr)_2]$. Shortly after the communication of this conclusion appeared in print,[11] the structural study of a related complex, $[Mo_4O_8Cl_4(OEt)_4]^{2-}$ (**6**), was published.[36] Again, on the basis of published structural parameters, this compound should be reformulated as a Mo(V) tetrameric cluster (Figure 7). The only major difference between **5** and **6** is the replacement of two bridging alkoxides in **5** with two bridging oxides in **6**; this substitution results in the difference of two units of negative charge between the two compounds. The structural effects of the alkoxide/oxide change are completely consistent with and enhance our arguments proposing the new formulations of **5** and **6**.

The $Mo\text{–}(OR)_t$ distances assigned to the terminal alkoxide in **5** (Mo2–O4 = 2.13 (1) Å) and in **6** (Mo1–O6 = 2.23 (2) Å) are outside the observed range for terminal alkoxides in other molybdenum complexes.[33,34] The distances are also longer than some $Mo\text{–}(OR)_b$ distances in these molecules. The inconsistency in these parameters is removed if the terminal alkoxides are really terminal alcohols. Compound **5** becomes $[Mo_4O_6Cl_4(O\text{-}n\text{-}Pr)_4(HOPr)_2]$, and **6** is really $[Mo_4O_8Cl_4(OEt)_2(HOEt)_2]^{2-}$. These two clusters are, therefore, Mo(V) tetramers and are structurally related to $Mo_4O_8(py)_4(O\text{-}i\text{-}Pr)_4$ (**7**), which was reported by Chisholm.[37] This last cluster does, in fact, contain terminal alkoxides with a Mo–O

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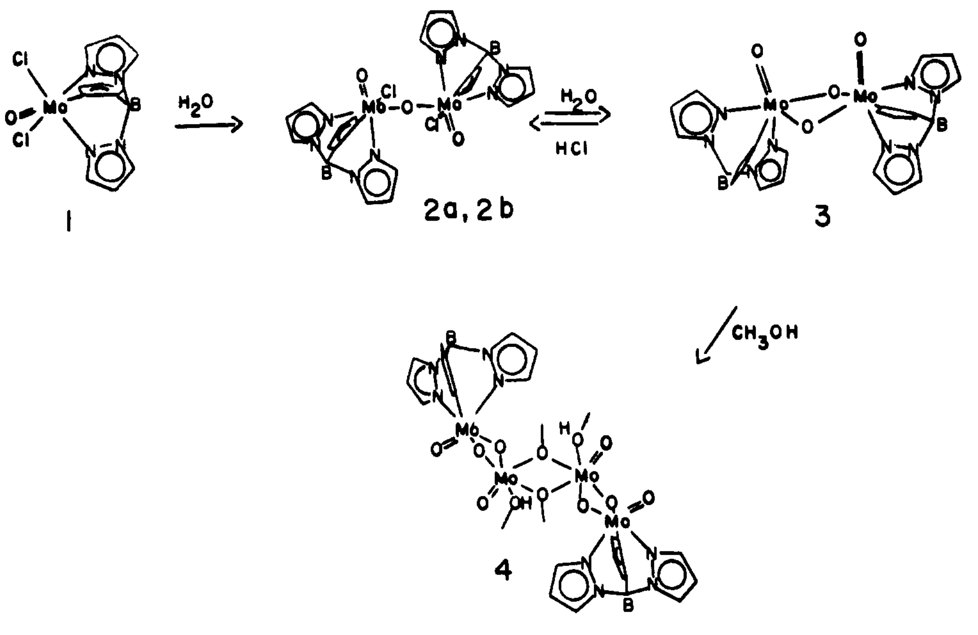
Scheme I. Synthesis of Polypyrazolylborate Mo(V) Complexes



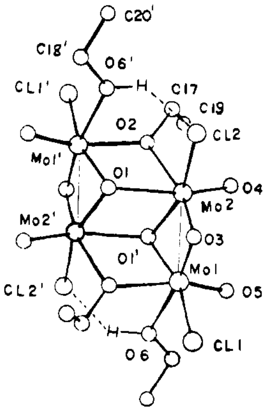


Figure 7. ORTEP diagram of **6** using the original coordinates from ref 36. The ethanolic hydrogens have been drawn in the positions where they are likely to occur.

distance of 1.945 (3) Å. The discrepancy in the Mo–(H*O*R)$_t$ distances in **5** and **6** results from their different trans-effecting ligands: a μ-oxide in **6** and a μ-alkoxide in **5**. The Mo–(H*O*Et)$_t$ distance in **6** approaches the Mo–(H*O*CH$_3$)$_t$ distance in **4** since both have similar trans ligands.

The other structural features of **5** (Table X) and **6** (Table XI) are also consistent with their formulation as Mo(V) tetramers. The Mo$_4$O$_6$ cores and the terminal oxo ligands in **6** and **7** are equivalent; the two clusters differ only in their terminal ligands. These clusters result from the dimerization of two Mo$_2$O$_4$$^{2+}$ units. The Mo–Mo single-bond distances in these units do not substantially change upon their condensation into the tetrameric clusters. The increase in this Mo–Mo distance to 2.67 Å in **5** results from its mixed oxide–alkoxide bridge rather than from the reduced bond order of $^1/_2$ that would be expected for a Mo(V)–Mo(VI) metal–metal bond. The observed distance is as one would expect: halfway between the distances found for the Mo(V)–Mo(V) dimers with two oxide[3,6,44] and with two alkoxide bridges.[38,45] Although the alcohol protons were obviously not located in the X-ray structure determinations of **5** and **6**, their positions can be confidently predicted from the geometry of the adjacent atoms. With analogy to **4**, these protons are likely engaged in hydrogen bonds with the cis axial chlorides above and parallel to the Mo–Mo vector. A structural analogy to this type of hydrogen bonding can be found in a recently reported Ni cluster complex.[46] Finally, although **5** and **6** are not mixed-valence clusters as originally described, it is considered likely that they should undergo oxidation and reduction reactions since examples of Ti$_4$(OR)$_{16}$ type clusters are known for a number of different d^n cluster electronic configurations.[47]

Summary

The chemistry presented in this paper (summarized in Scheme I) is a further demonstration of the propensity of molybdenum in the +5 oxidation state to hydrolyze with the formation of dimers and oligomers. Compounds **1**–**3** provide one of the few complete sets of well-characterized Mo(V) complexes with the same ligand that includes a MoO^{3+} monomer and Mo$_2$O$_3$$^{4+}$ and Mo$_2$O$_4$$^{2+}$ dimers. These complexes can be easily interconverted; a detailed study of the interconversions will be the subject of a later report.[21] The geometric isomers **2a** and **2b** also provide the first example of distortion isomers of Mo=O complexes with a d^1 electronic configuration.[49] The observed electronic spectra of **2a** and **2b** also indicate that previous interpretations of the electronic spectra of Mo$_2$O$_3$$^{4+}$ complexes must be reevaluated. Finally, the importance of correctly distinguishing between a coordinated alkoxide and a coordinated alcohol has been demonstrated by the structural characterization of the Mo(V) tetramer **4** and by the reformulation of two Mo(V) tetramers that had been previously reported in the literature as mixed-valence complexes.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support and Dr. M. Millar for discussions.

Registry No. **1**, 101248-28-6; **2a**, 101468-90-0; **2b**, 101248-29-7; **3**, 101347-50-6; **4**, 101347-51-7; **5**, 42844-79-1; **5** (reformulated), 101248-30-0; **6**, 85362-11-4; **6** (reformulated), 101315-85-9; HB(pz)$_3$MoCl$_3$, 101248-31-1; HB(3,5-Me$_2$pz)$_3$MoCl$_3$, 80290-66-0; HB(3,5-Me$_2$pz)$_3$MoOCl$_2$, 31371-06-9; dioxygen, 7782-44-7.

Supplementary Material Available: Tables of hydrogen atom positions, thermal parameters, additional bond distances and angles, and structure factor amplitudes for **1**, **2a**, **2b**, and **4** and a unit cell diagram of **2b** (54 pages). Ordering information is given on any current masthead page.

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