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Steric Control of Coordination Number: A Series of Mo(VI) Dioxo Diaryloxide Complexes Bearing 4-, 5-, and 6-Coordinate Environments

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The design, synthesis, and structure determination of a series of Mo(VI) dioxo diaryloxide complexes have been reported. By varying the steric bulk of the aryloxide ligand, control of the coordination number around the Mo(VI) center was achieved. All the complexes are characterized by analytical and spectroscopic techniques. Preliminary reactivity tests indicate that the 4-coordinate compound is the most stable and the 6-coordinate compound is the least stable.

Introduction

Molybdenum is a versatile transition element possessing a large number of stable and accessible oxidation states. A variety of chemical reactions such as hydrodesulfurization,[1] oxygen transfer reactions (e.g., olefin epoxidation),[2] and olefin metathesis[3] are catalyzed by molybdenum coordination complexes. The useful role of molybdenum is not restricted to industrial catalysis alone: nature has also incorporated the molybdenum center in various redox enzymes such as xanthine oxidase and DMSO reductase.[4,5] In all of these industrial and biological reactions, molybdenum plays the role of a catalytic redox site.

High oxidation state molybdenum oxo compounds are dominated by monooxo and *cis*-dioxomolybdenum species. The *cis*-dioxo compounds display catalytic activities,[6] are models for enzymes,[7,8] and are useful material precursors.[9] Catalytic activity is frequently linked to coordinative unsaturation, and the active sites in various molybdenum oxidation catalysts are believed[2,10,11] to contain coordinatively unsaturated molybdenum centers. For the *cis*-dioxo moiety, however, the most common structural varieties found are octahedral and pseudooctahedral. There are reports of a few 6-coordinate nonoctahedral compounds and also a few 5-coordinate compounds.[12−14] Tetrahedral 4-coordinate $MoO_2(OR)_2$ complexes are rare. To the best of our knowledge, the only example of a structurally characterized 4-coordinate $MoO_2(OR)_2$ compound (R = alkyl or aryl) known to date is the $MoO_2(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_2\cdot HO\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3$ molecule from our group.[15] One structurally characterized siloxy-ligated MoO_2^{2+} complex, $MoO_2(OSiPh_3)_2$, was reported by DeKock et al.[16]

In this article, we shall describe the synthesis and characterization of a series of 4-, 5-, and 6-coordinate *cis*-dioxomolybdenum compounds including their X-ray struc-

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tural analysis. We shall also demonstrate the control of the coordination number about the Mo(VI) center by using different bulky aryloxide ligands.

Experimental Section

General. All reactions and workups were performed inside a glovebox under nitrogen atmosphere. Mo(VI) dichloride dioxide, *n*-butyllithium (2.0 M solution in pentane), tri-*n*-butylphosphine, tri-*n*-butylphosphine oxide, 2,6-dimethylphenol, 2,6-diisopropylphenol, and 2,4,6-tri-*tert*-butylphenol were obtained from Aldrich and were used as received. Commercial pyridine was distilled from CaH_2, THF was freshly distilled from Na/benzophenone, and benzene was filtered through activated alumina and Cu-based oxygen absorbent as described by Grubbs et al.[17] Aldrich anhydrous acetonitrile, diethyl ether, and pentane were bubbled with N_2 gas before introducing them inside the glovebox. All these solvents and pyridine were stored inside the glovebox over 4 Å molecular sieves for 48 h before use. NMR solvents (C_6D_6 and THF-d_8) were degassed and dried with CaH_2. THF-d_8 was vacuum transferred from Na/benzophenone, and C_6D_6 was filtered through activated alumina inside the glovebox prior to use.

The melting points of the compounds were observed in sealed capillary tubes on a Mel-Temp apparatus (Laboratory Devices, Cambridge, MA). ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 300 or Unity Inova 400 spectrometer. IR spectra were obtained with an Infinity Gold TM FTIR spectrometer. UV/vis spectra were recorded on a Agilent 8453 UV−visible spectrophotometer. Mass spectra were recorded at UT Austin (CI) or UC Berkeley (EI) mass spectrometry facilities.

Preparation of Compounds. All the lithium aryloxides were prepared following a standard[18] procedure. The preparation for the compound **1a** is described below.

LiO-2,4,6-t-$Bu_3C_6H_2$ (1a): A 10.00 mL solution of 2,4,6-t-$Bu_3C_6H_2OH$ (1.5802 g, 6.0211 mmol) in THF was prepared and kept in a −35 °C freezer for 1 h. *n*-BuLi solution (3.00 mL, 6.0 mmol) was added dropwise to this cooled solution under rapid stirring over a period of 30 min, as the reaction was highly exothermic. The reaction mixture was then stirred for 3 h and the solvent removed under vacuum to obtain a white powder, which is the desired compound. ^{1}H NMR (C_6D_6): δ (ppm) 7.58 (s, 2H, m-H), 1.75 (s, 18H, o-$C(CH_3)_3$), 1.48 (s, 9H, p-$C(CH_3)_3$).

LiO-2,6-i-$Pr_2C_6H_3$ (1b): This compound was prepared by following a procedure similar to that for **1a** but using 2,6-i-$Pr_2C_6H_3$-OH (3.00 mL, 16.2 mmol) and *n*-BuLi solution (8.10 mL, 16 mmol). ^{1}H NMR (C_6D_6): δ (ppm) 7.17 (d, 2H, $J = 8$ Hz, m-H), 6.84 (t, 1H, $J = 8$ Hz, p-H), 3.68 (m, 2H, $J = 7$ Hz, i-Pr CH), 1.40 (d, 12H, $J = 7$ Hz, i-Pr CH_3).

LiO-2,6-$Me_2C_6H_3$ (1c): This compound was also prepared by a procedure similar to that for **1a** using 2,6-$Me_2C_6H_3OH$ (1.8402 g, 15.063 mmol) and *n*-BuLi solution (7.50 mL, 15 mmol). ^{1}H NMR (C_6D_6): δ (ppm) 7.07 (d, 2H, $J = 8$ Hz, m-H), 6.70 (t, 1H, $J = 8$ Hz, p-H), 2.26 (s, 6H, o-CH_3).

MoO_2(O-2,4,6-t-$Bu_3C_6H_2)_2$ (2): A solution of MoO_2Cl_2 (0.1006 g, 0.5059 mmol) in 5 mL of acetonitrile was added dropwise to a rapidly stirred solution of **1a** (0.2706 g, 1.008 mmol) in 4 mL of acetonitrile containing 1 mL of pyridine at room temperature. The mixture immediately turned dark brown-red and was allowed to stir for 3 h. ^{1}H NMR of the crude mixture showed the presence of uncoordinated pyridine in addition to compound **2**. The solvent and uncoordinated pyridine were then removed under vacuum, 10 mL of pentane was added to the dark solid, and the mixture was stirred overnight. The resulting mixture was filtered through a medium pore frit. The dark green filtrate was concentrated to 5 mL and kept at −35 °C. After 5 days the supernatant was decanted and the green crystalline compound (0.1402 g, 44% yield based on Mo) was dried under vacuum. ^{1}H NMR (C_6D_6): δ (ppm) 7.46 (s, 4H, m-H), 1.58 (s, 36H, o-$C(CH_3)_3$), 1.28 (s, 18H, p-$C(CH_3)_3$). ^{13}C NMR (C_6D_6): δ 162.5 (C−O), 145.9 (p-aryl quat), 139.1 (o-aryl quat), 122.7 (meta to O), 35.6 (p-t-Bu quat), 31.7 (o-t-Bu quat), 31.4 (o-t-Bu CH_3), 30.3 (p-t-Bu CH_3). mp: 118−120 °C. IR (cm^{-1}, C_6H_6): 2959vs, 2927s, 2871m, 1960w, 1596w, 1519w, 1482m, 1416m, 1364m, 1214m, 1189m, 1109m, 963m, 939m, 882m, 710m, 679m, 664m. UV/vis (C_6H_6) λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}): 362 (7800), 277 (6345). HRMS (EI) *m*/*e* Calcd for $C_{36}H_{58}O_4Mo$: 652.338 916 (M^+). Found: 652.339 081 (M^+). Anal. Calcd for $C_{36}H_{58}O_4Mo$: C, 66.44; H, 8.98. Found: C, 65.84; H, 8.89.

MoO_2(py)(O-2,6-i-$Pr_2C_6H_3)_2$ (3): A solution of MoO_2Cl_2 (0.1003 g, 0.5044 mmol) in 5 mL of acetonitrile was added dropwise to a rapidly stirred solution of **1b** (0.1909 g, 1.036 mmol) in 4 mL of acetonitrile containing 1 mL of pyridine at room temperature; the mixture turned orange-red. The solution was allowed to stir for 3 h. The solvent and excess pyridine were then removed under vacuum, 10 mL of pentane was added to the dark solid, and the mixture was allowed to stir overnight. The resulting solution was filtered through a medium pore frit. The orange-red filtrate was concentrated and kept inside the freezer at −35 °C for 3 days to produce needle-shaped, pentane-solvated orange crystals. The supernatant was decanted, and the solvated crystals were dried under vacuum with loss of pentane (0.1106 g, 40% yield based on Mo). ^{1}H NMR (C_6D_6): δ (ppm) 8.26 (d, 2H, $J = 7$ Hz, py o-CH), 6.54 (t, 1H, $J = 8$ Hz, py p-CH), 6.22 (t, 2H, $J = 8$ Hz, py m-CH), 7.02 (d, 4H, $J = 8$ Hz, m-CH), 6.91 (t, 2H, $J = 7$ Hz, p-CH), 3.85 (m, 4H, i-Pr CH), 1.29 (d, 24H, $J = 8$ Hz, i-Pr CH_3). ^{13}C NMR (THF-d_8): δ 162.0 (C−O), 150.9 (ortho to N, py), 141.0 (aryl quat), 138.9 (para to N, py), 126.9 (para to O), 124.7 (meta to O), 124.4 (meta to N, py), 28.9 (i-Pr CH), 24.9 (i-Pr CH_3). mp: 67−69 °C (dec). IR (cm^{-1}, C_6H_6): 3066m, 2963vs, 2927s, 2866s, 1970w, 1854w, 1597m, 1580m, 1528w, 1435vs, 1383w, 1361m, 1327s, 1253vs, 1193vs, 1154w, 1112m, 1069m, 1016w, 991w, 938vs, 915vs, 899vs, 870s, 793w, 752vs, 710m, 657m, 601m, 513w, 405m. UV/vis (C_6H_6) λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}): 374 (5690), 277 (8830). HRMS (CI) *m*/*e* Calcd for $C_{29}H_{39}O_4NMo$: 563.193 314 (M^+). Found: 563.192 559 (M^+). Anal. Calcd for $C_{29}H_{39}O_4NMo$: C, 62.03; H, 7.00; N, 2.49. Found: C, 62.22; H, 6.55; N, 2.39.

$MoO_2(py)_2$(O-2,6-$Me_2C_6H_3)_2$ (4): During preparation of this compound, an improvement in yield was observed when ether was used as solvent instead of acetonitrile. A solution of MoO_2Cl_2 (0.1007 g, 0.5064 mmol) in 5 mL of ether was added dropwise to a rapidly stirred solution of **1c** (0.1302 g, 1.016 mmol) in 4 mL of ether and 1 mL of pyridine at room temperature. The mixture turned deep orange-red. The solution was allowed to stir for 4 h. The solution was filtered through a medium pore frit. The orange-red filtrate was evaporated under vacuum to remove the solvent and excess pyridine to produce a dark-red solid (0.1089 g, 37% yield based on Mo). A concentrated solution of the compound in ether was able to produce X-ray quality crystals at −35 °C on standing for 7 days. ^{1}H NMR (C_6D_6): δ (ppm) 8.40 (d, 4H, $J = 4$ Hz, py o-CH), 6.37 (t, 4H, $J = 6$ Hz, py m-CH), 6.68 (t, 2H, $J = 8$ Hz, py p-CH), 6.83 (d, 4H, $J = 7$ Hz, m-CH), 6.70 (t, 2H, $J = 8$ Hz, p-CH), 2.41 (s, 12H, o-CH_3). ^{13}C NMR (THF-d_8): δ 163 (C−O), 151.8 (ortho to N, py), 140.1 (para to N, py), 129.9 (meta to O),

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Table 1. Comparison of Important Bond Lengths (Å)

	Mo=O	Mo−O(aryloxy)	Mo−N(py)
	4-Coordinate		
2	1.682(2)	1.850(2)	
A[15]	1.703(2)	1.857(2)	
	1.706(2)	1.861(2)	
$MoO_2(OSiPh_3)_2$[16]	1.692(7)		
	5-Coordinate		
3	1.701(4)	1.912(4)	2.292(5)
	1.705(4)	1.909(4)	
$MoO_2(OSiPh_3)_2(PPh_3)$[16]	1.688(7)		
	1.678(7)		
	6-Coordinate		
4	1.697(5)	1.964(4)	2.421(5)
B[29]	1.71(1)	1.95(1)	
	1.718(9)	1.91(1)	
$MoO_2(OSiPh_3)_2(Py)_2$[30]	1.695(2)		2.404(4)

Table 2. Comparison of Important Bond Angles (deg)

	O=Mo=O	Mo−O−C(aryloxy)
	4-Coordinate	
2	105.4(2)	171.9(2)
A[15]	106.5(1)	170.3(2)
		174.2(2)
$MoO_2(OSiPh_3)_2$[16]	106.4(5)	
	5-Coordinate	
3	110.3(2)	141.6(4)
		134.4(4)
$MoO_2(OSiPh_3)_2(PPh_3)$[16]	110.0(4)	
	6-Coordinate	
4	103.9(3)	124.5(4)
B[29]	109.2(6)	
$MoO_2(OSiPh_3)_2(Py)_2$[30]	104.5(1)	

128.3 (aryl quat), 126.4 (meta to N, py), 123.5 (para to O), 18.2 (CH_3). mp: 62−63 °C. IR (cm^{-1}, C_6H_6): 3065w, 2948m, 2858w, 2291w, 1974w, 1854w, 1778w, 1606s, 1580s, 1529w, 1446vs, 1377w, 1264vs, 1204vs, 1153w, 1094m, 1069s, 1032m, 990m, 939vs, 919vs, 897vs, 877vs, 815w, 764vs, 746s, 719s, 638m, 572m, 543w, 405w. UV/vis (C_6H_6) λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}): 378 (3585), 278 (6490). HRMS (EI) Calcd for $C_{16}H_{18}O_4Mo$: 372.025 914 ($M^+ - 2py$). Found: 372.025 809 ($M^+ - 2py$). Anal. Calcd for $C_{26}H_{28}O_4N_2Mo$: C, 59.09; H, 5.34; N, 5.30. Found: C, 57.20; H, 5.33; N, 5.20. Elemental analysis was unsatisfactory, possibly due to the extreme air sensitivity of this compound and/or the presence of paramagnetic impurities. A ^1H NMR spectrum of the compound has been deposited as Supporting Information.

Reaction of 2 with $ZrCp_2Me_2$. Cp_2ZrMe_2 was prepared from Cp_2ZrCl_2, obtained from Aldrich, following a reported[19] procedure. Compound **2** (0.0506 g, 0.0777 mmol) was dissolved in 3 mL of C_6D_6, forming a bright green solution. Cp_2ZrMe_2 (0.0182 g, 0.0723 mmol) was dissolved in another 2 mL of C_6D_6, forming a colorless solution. The Cp_2ZrMe_2 was added dropwise to the rapidly stirred C_6D_6 solution of **2**, and the green color of the solution was intensified. A ^1H NMR experiment was performed within 5 min of mixing the two compounds.

The same procedure was followed in the reaction of **3** and **4** with Cp_2ZrMe_2. In both cases the orange C_6D_6 solutions of **3** and **4** turned brown colors of different intensities.

Reaction of 4 with (n-Bu)$_3$P. Compound **4** (0.0503 g, 0.0951 mmol) was dissolved in 5 mL of ether to form an orange solution. To this rapidly stirred solution was added (n-Bu)$_3$P (0.0192 g, 0.0948 mmol) dropwise. The solution became dark orange-brown. The solution was stirred for 5 days at room temperature as it gradually changed to light green. A new ^{31}P NMR peak at 46.38 ppm ((n-Bu)$_3$PO) was observed in addition to a less intense peak at −30.85 ppm (unreacted (n-Bu)$_3$P). The IR spectrum of the mixture in benzene solution also supported the formation of (n-Bu)$_3$PO. There was no indication of the formation of (n-Bu)$_3$PO when compounds **2** and **3** were reacted with (n-Bu)$_3$P under the same conditions.

X-ray Structure Determination. The crystal data of compounds **2**, **3**, and **4** are collected in Table 3. In the cases of **2** and **4**, suitable crystals of the compounds were placed in a small amount of oil and transferred from the drybox in a closed vial. Oil-coated crystals were placed on a cooled glass slide and attached to a glass fiber with epoxy resin. The samples were transferred to the diffractometer and cooled to −60 °C. All X-ray data were collected on a BRUKER SMART 1000 CCD-based diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.710 73 Å). A total of 1800 frames were collected at 10 s per frame. The frames were intregated with the SAINT software package[20] using a narrow frame algorithm, and the structures were solved using the SHELXTL program package.[21] Statistics strongly indicated a noncentric space group for both compounds, and the structures were solved in *Cc* and *C*2, respectively. Compound **4** could also be solved in *P*1 but not in $P\bar{1}$. Platon[22] analyses indicated both structures probably belonged to *C*2/*c*. Neither structure could be solved directly in *C*2/*c*; however, transformation of the coordinates led to satisfactory refinement. SADABS was used to evaluate the range of observed reflections and to apply an absorption correction. The program Mercury 1.1.2[23] was used to generate the X-ray structural diagrams shown in the table of contents.

MoO_2(O-2,4,6-t-$Bu_3C_6H_2$)$_2$ (2): Dark green crystals (0.03 × 0.07 × 0.16 mm^3) of **2** were obtained at −35 °C from a concentrated pentane solution. Data were collected at 213(2) K. Out of a total of 11 532 reflections collected, 4322 independent reflections satisfied the criteria [R(int) = 0.0397]. The structure was refined anisotropically.

MoO_2(py)(O-2,6-i-$Pr_2C_6H_3$)$_2$·0.5C_5H_{12} (3): Dark orange-red cubic crystals (0.2 × 0.2 × 0.2 mm^3) of **3** were obtained from a pentane solution of the compound kept at −35 °C. Data were collected at 150(2) K. Out of a total 26 958 reflections collected, 4975 reflections were independent [R(int) = 0.0635]. The asymmetric unit contains a highly disordered half-molecule of pentane, the recrystallization solvent, located on an inversion center. Its contribution was evaluated using the program[24] SQUEEZE, which treats the molecule as a diffuse entity without specifying atomic positions. The structure was refined anisotropically.

MoO_2(py)$_2$(O-2,6-$Me_2C_6H_3$)$_2$ (4): Orange, cubic crystals (0.34 × 0.34 × 0.12 mm^3) of **4** were produced at −35 °C from a concentrated ether solution of the compound. Data were collected at 213(2) K. The crystal decomposed during data collection, so the range of data was limited. Out of a total 5257 reflections collected, 1681 were independent reflections bearing the criteria [R(int) = 0.1491]. The structure was refined isotropically because of the limited data set.

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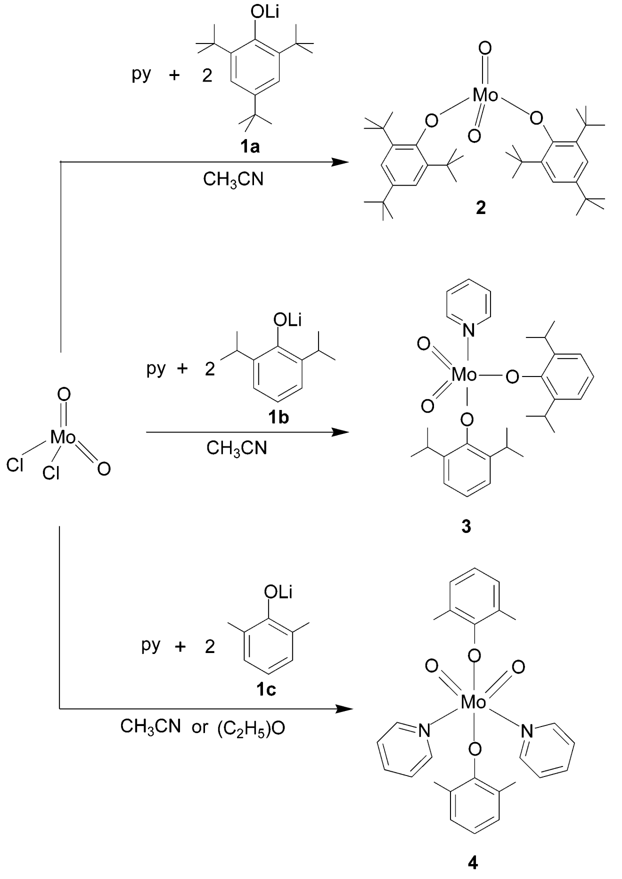
Table 3. Crystallographic Data and Summary of Data Collection and Structure Refinement

	2	3	4
formula	$MoC_{36}H_{58}O_4$	$MoC_{31.5}H_{45}NO_4$	$MoC_{26}H_{28}N_2O_4$
fw	650.72	597.62	528.44
crystal system	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*P*2(1)/*c*	*C*2/*c*
T, K	213(2)	150(2)	213(2)
a, Å	17.2709(10)	12.8628(13)	8.2854(12)
b, Å	11.7599(10)	11.0536(11)	16.596(3)
c, Å	18.5670(12)	23.076(2)	17.775(2)
α, deg	90	90	90
β, deg	108.879(2)	105.161(2)	97.342(4)
γ, deg	90	90	90
V, $Å^3$	3568.2(4)	3166.8(5)	2424.1(6)
Z	4	4	4
D_{calc}, $mg{\cdot}m^{-3}$	1.211	1.249	1.448
θ range (deg) for data collection	2.13−29.14	2.06−24.00	2.31−23.28
$N_{measured}$	11532	26958	5257
$N_{independent}$	4322	4975	1681
R	0.0410	0.0764	0.0555
ωR_2	0.1143	0.1568	0.0723
GOF	1.038	1.306	0.874
largest diff between peak and hole ($e{\cdot}Å^{-3}$)	0.904 and −0.514	0.752 and −1.752	0.586 and −0.381

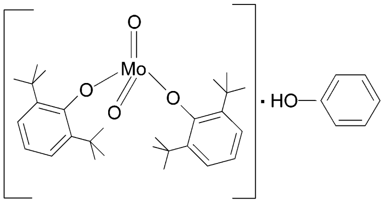
Scheme 1



Results and Discussion

MoO_2Cl_2 reacts with 2 equiv of LiOAr (Ar = 2,4,6-*t*-$Bu_3C_6H_2$ (**1a**), 2,6-*i*-$Pr_2C_6H_3$ (**1b**), and 2,6-$Me_2C_6H_3$ (**1c**)) and excess pyridine in acetonitrile (Scheme 1) to form compounds **2**, **3**, and **4** respectively.

All the reactions were fast at room temperature. In all cases**,** after 2−3 h acetonitrile and excess pyridine were stripped off and pentane was added to the residue. The concentrated pentane solution yielded X-ray quality crystals at −35 °C for compounds **2** and **3**. X-ray quality crystals of **4** were obtained at −35 °C directly from a filtered ether solution of the reaction mixture. The IR spectrum of each compound showed two medium to strong intensity peaks in the range of 915−965 cm^{-1} which are assigned to Mo═O stretching frequencies. These values fall within the range reported[15] by our group for the compound MoO_2(O-2,6-*t*-$Bu_2C_6H_3)_2{\cdot}$HO-2,6-*t*-$Bu_2C_6H_3$ (**A**) and also by other workers dealing[25,26] with the MoO_2^{2+} moiety. Other important frequency bands[27] are around 1100 cm^{-1} (O−C stretch), 2960 cm^{-1} (C−H stretch), and 1440 cm^{-1} (C−H bend). For example, for compound **2**, the O−C stretching frequency occurs at 1109 cm^{-1}, that due to the C−H bond occurs at 2959 cm^{-1}, and the C−H bending frequency occurs at 1442 cm^{-1}.



A

^1H and ^{13}C NMR data are in accordance with the structures. Due to the presence of a C_2 axis in **2**, **3**, and **4,** the two aryloxy ligands are magnetically equivalent, and in compound **4** the two pyridine ligands are also magnetically equivalent. All the peak values and assignments are reported in the Experimental Section.

Electronic spectra of the complexes in benzene display two intense bands, one of them in the 360−380 nm region and the other in the 277−278 nm region. Apart from that, only in the case of compound **2**, a broad and weak intensity

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[25] Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021−1037.

[26] DeKock, C. W.; Kim, G.; Huffman, D. *Inorg. Chem.* **1989**, *28*, 1279−1283.

[27] Kemp, W. In *Organic Spectroscopy*, 3rd ed.; The Macmillan Press Ltd.: New York, 1991; pp 60−66.

band is found at 804 nm. The intense bands are believed to be O(aryloxide) → Mo LMCT origin. For compound **A,** the corresponding bands were observed[15] at 346 and 278 nm, respectively.

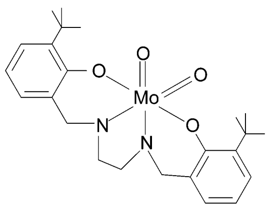
Crystal Structure and Three-Dimensional Geometry. The series of molecules **2**, **3**, and **4** demonstrates the design of MoO_2^{2+} compounds with 4-, 5-, and 6-coordinate environments by using steric hindrance as the controlling factor. A similar observation was previously reported[18] in the case of titanium aryloxide complexes. As we decrease the steric bulk of the aryloxy coligand, it results in the coordination of one or two molecules of pyridine.

Complexes **2**, **3**, and **4** display the expected geometries, though slightly distorted in each case. For example, complex **2** can be described as a slightly distorted tetrahedron. Complex **3** has a distorted trigonal bipyramidal structure, in which the two oxo atoms and one of the aryloxy ligands occupy the equatorial plane. The second aryloxy ligand and the pyridine molecule occupy the axial positions. This structural feature is unusual: generally, the aryloxy groups in MoO_2^{2+} moiety are mutually trans. Complex **4** is a distorted octahedron where the two oxo atoms are trans to the two pyridine molecules and the two aryloxy ligands are trans to each other. This structure is typical for $[MoO_2]^{2+}$ moiety containing molecules.

Steric effects cause distortions from ideal angles in all three compounds. For compound **2**, the maximum angular deviation is 4° from the ideal tetrahedral value, for the angle between the two oxo ligands. Steric repulsion between the two bulky aryloxy groups apparently squeezes the angle between the two oxo groups from the ideal 109° to 105° and widens the angle between the two aryloxy groups to 111.92°. In the case of compound **3**, the angle between the two axial ligands is 171.56(18)°. The angle between the two oxo ligands in the equatorial plane is squeezed to 110.3(2)° to make room for the third ligand, which is a bulky aryloxy ligand, in the same plane. This observation is very similar to the case of the reported[16] distorted trigonal bipyramidal compound, $[MoO_2(OSiPh_3)_2(PPh_3)]$, where the corresponding angle is also squeezed to 110.0(4)° due to the presence of a bulky equatorial ligand, $-OSiPh_3$. The angles between the aryloxy ligand in the equatorial plane and the two oxo atoms are 123.3(2)° and 121.46(19)°. All the ligands in the equatorial plane are inclined toward the less bulky axial ligand, pyridine. As a result, the angles between the pyridine and the equatorial ligands (83.2(2)°, 85.1(2)°, and 79.9(17)°) are significantly smaller than those (97.2(2)°, 102.3(2)°, and 92.6(18)°) between the axial aryloxy ligand and the equatorial ligands. For compound **4**, the angle between the two cis oxo ligands is 103.9(3)°, which is considerably higher than the ideal value of 90°. The angle between the two trans aryloxy ligands is 154.2(2)°, whereas the angles between each pyridine and their respective trans oxo ligands are the same with a value of 163.9(2)°.

Our previous report[15] of complex **A** cited the short Mo−O(aryloxy) distances and large Mo−O−C(aryl) angles as plausible evidence for donation of oxygen lone pair electron density to the metal center. In the present series, as evident from Tables 1 and 2, there is a marked decrease in Mo−O−C(aryl) bond angles, increase in Mo−O(aryloxy) bond distances, and increase in Mo−N(pyridine) bond distances, as the coordination number increases. The increase in Mo−ligand distances may be due to increased steric crowding as we move from compounds **2** to **4**. Also, all three trends are consistent with a decrease of electron donation from aryloxy and the pyridine ligands to the Mo(VI) center as the coordination number increases. Such a correlation must be interpreted with caution, however, as it has been shown that the Mo−O−Ar distances and angles in early d-block transition metal aryloxides are extremely flexible parameters giving little insight into M−OAr bonding.[28]

In the case of compound **2**, the Mo−O(aryloxy) bond length is 1.8502(19) Å, which is significantly shorter than that of a previously reported[29] 6-coordinate Mo−dioxodiaryloxide molecule (**B**) (1.938(17) Å). These distances in the case of compound **3** are 1.909(4) and 1.912(4) Å, whereas the same for compound **4** is 1.964(4) Å. Similarly the Mo−N(pyridine) bond length in **3** is 2.292(5) Å. This length is noticeably shorter than the previously reported[30] value of 2.404(4) Å in a similar compound $[MoO_2(OSiPh_3)_2(Py)_2]$, and also in comparison to compound **4** where the value is 2.421(5) Å. One reason for the difference may be the strong trans influence experienced by the pyridines that are trans to terminal oxo ligands in compound **4**.



B

Finally, in the case of compound **2**, the Mo−O−C(aryl) bond angle is almost linear with a value of 171.89(15)°. This value is very close to those[15] of **A** (170.3(2)° and 174.2(2)°). In the case of compound **3**, the corresponding values are 141.6(4)° and 134.4(4)°, whereas the same for **4** is 124.5(4)°.

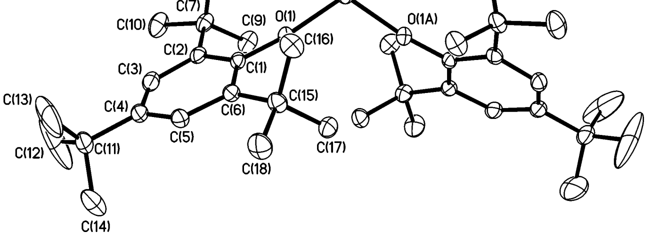


Figure 1. ORTEP view of compound **2** (30% probability). Hydrogen atoms have been omitted for clarity.

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(28) Steffey, B. D.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1990**, *9*, 963−968.

(29) Subramanian, P.; Spence, J. T.; Ortega, R.; Enemark, J. H. *Inorg. Chem.* **1984**, *23*, 2564−2572.

(30) Thapper, A.; Donahue, J. P.; Musgrave, K. B.; Willer, M. W.; Nordlander, E.; Hedman, B.; Hodgson, K. O.; Holm, R. H. *Inorg. Chem.* **1999**, *38*, 4104−4114.

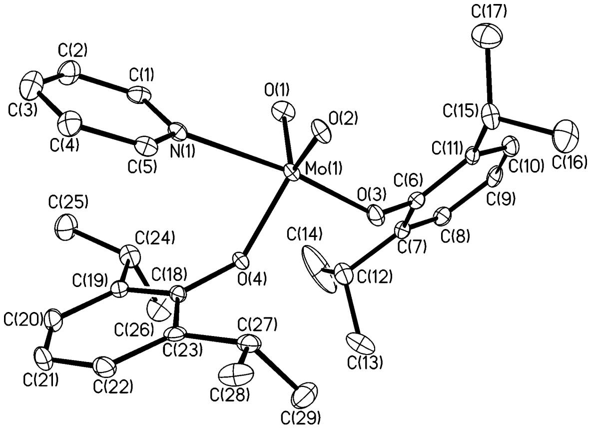

Figure 2. ORTEP view of compound **3** (30% probability). Hydrogen atoms have been omitted for clarity.

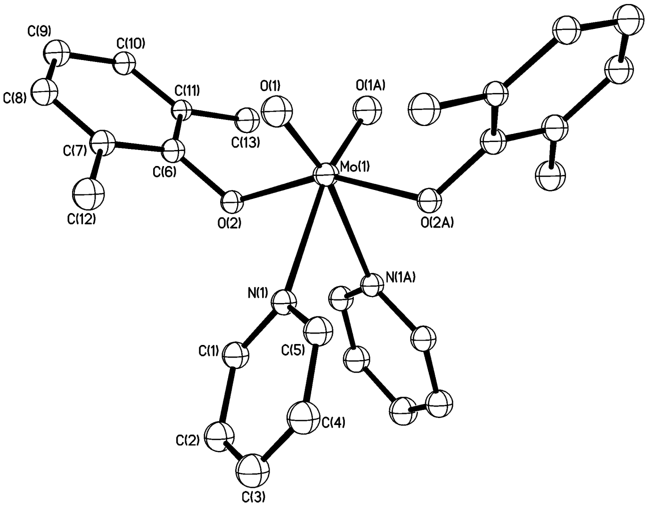

Figure 3. ORTEP view of compound **4** (30% probability). Hydrogen atoms have been omitted for clarity.

Reactivity. When (n-Bu)$_3$P was used as a substrate to probe the oxo transfer capabilities of these compounds, slow formation of (n-Bu)$_3$PO was observed only in the case of compound **4**. The formation of (n-Bu)$_3$PO was verified with ^{31}P NMR and IR spectral measurements. Under identical experimental conditions, there was no evidence of the formation of (n-Bu)$_3$PO by the other two compounds, **2** and **3**.

Cp_2ZrMe_2 is also a strong oxygen acceptor.[19] However, all three compounds decomposed upon reaction with Cp_2ZrMe_2. ^{1}H NMR experiments were carried out 5 min after mixing Cp_2ZrMe_2 with the complexes in a 1:1 ratio. Compound **4** had completely decomposed, while about 1/10 of compound **3** was present along with decomposition products. Compound **2** existed intact in the presence of Cp_2ZrMe_2. However, after 30 min compounds **2** and **3** decomposed completely. The nature of the decomposition products is yet to be identified.

Conclusion

We have reported a series of Mo(VI) dioxo diaryloxide complexes having 4-, 5-, and 6-coordinate environments. We have employed the steric bulk of different aryloxide ligands to gain control of the coordination number around the Mo(VI) center. Structural studies indicate that, with increasing coordination, Mo−O(aryloxy) bond lengths increase and Mo−O−C(aryl) bond angle decreases. Compound **3** has an unusual coordination mode where the two aryloxy groups are cis to each other. Preliminary experiments indicate that the 6-coordinate compound **4** is the most reactive among the three compounds.

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Supporting Information Available: Listing of bond lengths, bond angles, atomic coordinates, anisotropic displacement coefficients; X-ray crystallographic file for **2**, **3**, and **4** (CIF format), and ^{1}H NMR spectrum of compound **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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