660 *Inorg. Chem.* **1981**, *20*, 660–664

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Molybdenum Complexes. 1. Acceptor Behavior and Related Properties of $Mo^{VI}O_2$(tridentate) Systems

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Received March 12, 1980

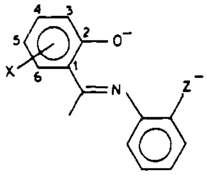
Molybdenum(VI) complexes of the type $MoO_2(L)$, where L is a tridentate dianionic Schiff base ligand, are reported. Infrared data suggest oligomerization via a $Mo{=}O{\rightarrow}Mo$ bridge which is cleaved by a wide variety of donors (D): aldehyde, amide, amine, *N*-oxide, sulfoxide, phosphine oxide, water, alcohol, and phosphine-producing $MoO_2(L)(D)$. The tendency of adduct formation by the molybdenyl systems increases in a particular way as L is changed. $MoO_2(L)(D)$ usually shows two IR absorptions attributable to *cis*-MoO_2 stretches, and on the average, species with oxygen donors vibrate at higher frequencies than those with nitrogen donors. On the basis of ligand displacement reactions D binding increases in the order CH_3CHO < C_6H_5CHO < EtOH < *p*-anisaldehyde < dmf < pic < Me_2SO < im < py-*N*-O. On being heated, $MoO_2(L)(D)$ is readily converted to $MoO_2(L)$ in a single endothermic step. Thermal analysis data together with NMR data support the weak binding of the D ligands. The electron transfer characteristics of a number of the $MoO_2(L)$(dmf) species are studied with use of voltammetric techniques. In general two to three reduction waves are observed, all located at potentials more negative than −0.9 V vs. SCE. The chemistry and electrochemistry of a dinuclear molybdenum(V) species resulting from hydrazine reduction of one $MoO_2(L)$ is also briefly described.

Introduction

Several redox enzymes are dependent on variable-valence molybdenum cofactors.[1-3] Oxygen, nitrogen, and sulfur donors are implicated as ligands. In this background we undertook a project to generate relatively simple molybdenum species with one binding site which is more labile than others allowing binding and displacement of various substrate molecules. The present report mainly concerns Mo(VI) systems. Since MoO_2^{2+} usually attaches four donor atoms to produce a grossly octahedral geometry around molybdenum, planar tridentate ligands were utilized to engage three coordination positions, leaving the fourth site available for substrate binding. A preliminary report has appeared.[4]

Results and Discussion

A. Ligands and Complexes. The dianionic Schiff base ligands **1** and **2** were used. When the substituent X is H, it is not explicitly stated; e.g., H-sap is written simply as sap. The general abbreviations for all ligands of type **1** and **2** will be L and for monodentate ligands D. Other abbreviations are as follows: acac, acetylacetonate anion; dmf, dimethylformamide; Me_2SO, dimethyl sulfoxide; Ph_2SO, diphenyl sulfoxide; im, imidazole; pic, γ-picoline; py, pyridine; sal, salicylaldehydato anion; tppo, triphenylphosphine oxide.



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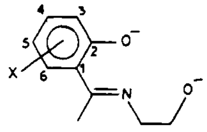
z = o : x-sap
z = s : x-sapt



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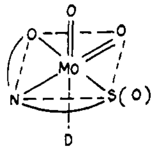
x-sae



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The complexes are prepared by reacting respective ligands with $MoO_2(acac)_2$, $MoO_2(sal)_2$, or molybdate. Depending on the ligands, molybdenum precursor, and reaction conditions the initially isolated complexes are of type $MoO_2(L)$, $MoO_2(L)(EtOH)$, or $MoO_2(L)(H_2O)$. By reaction of these with D ligands, the $MoO_2(L)(D)$ species result. A complete listing of the complexes which form yellow to brown crystals is given in the Experimental Section. Various Schiff base complexes of molybdenum are known.[5-7] Except for a brief mention of one or two compounds these reports do not pertain to systems of the type under consideration here.

B. $MoO_2(L)(D)$ Species. (a) Structural Characterization and Reactivity. Water, alcohol, aldehyde, amide, *N*-oxide, phosphine oxide, amine, and phosphine ligands are used as D. Analytical data and extensive physicochemical studies are in agreement with the $MoO_2(L)(D)$ formulation and exclude the possibilities of Mo_2O_3 and Mo_2O_5 core structures.[8] All results support structure **3** in which the tridentate ligand spans three meridional positions. Isomeric facial spanning is sterically excluded by the ligand planarity.

The broad hydrogen-bonded OH stretch near 2700 cm^{-1} present in the free ligands is absent in the complexes. Formation of Mo–O bonds with organic ligands result in the appearance of a few medium to strong stretching frequencies in the 550–650-cm^{-1} region.[8,9] All complexes reported herein display[10] up to three such bands (absent in ligand) in the above region. The most persistent feature is a sharp medium to strong band at 630 ± 15 cm^{-1}. In the X-sap and X-sapt complexes a strong band in the region 1598–1610 cm^{-1} and a medium band in the region 1540–1550 cm^{-1} are assigned[10] respectively to $\nu_{C=N}$ and aromatic ν_{CO}. In X-sae complexes the frequencies are $\nu_{C=N} \approx 1640$; aromatic $\nu_{CO} \approx 1550$, and aliphatic $\nu_{CO} \approx 1040$ cm^{-1}.

The hard acid Mo(VI) binds to sulfoxides and dmf at the oxygen end as is evident from shifts of ν_{S-O} and $\nu_{C=O}$, respectively, to lower frequencies compared to free D values. The ν_{P-O} and ν_{N-O} frequencies in phosphine oxide and *N*-oxides also

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Table I. Infrared Spectral[a] (cm^{-1}) and Thermal Analysis Data for Selected Complexes

complex						Δ*m*, %	
L	D	$\nu_{MO=O}$[b]	selected D vibrations	T_i, °C	T_f, °C	calcd	found
sap	nil	937,[c] 909, 815[d]					
	EtOH	931, 909	3380 (m, br),[e] 1030 (m)[f]	90	110	12.0	12.1
	MeOH	928, 903	3400 (m, br),[e] 1010 (w)[f]	98	125	8.6	8.5
	tppo	928, 901	1152 (s),[g] 750 (s)				
	PhCHO	927, 902	1650 (m)[h]				
	dmf	924, 900	1645 (s),[h] 684 (m)[i]	132	180	17.5	17.7
	Me_2SO	924, 892	1010 (s)[j]	185	240	18.6	18.9
	p-anisaldehyde	921, 905	1653 (s)[h]				
	Ph_2SO	918, 898	970 (s)[j]				
	py-*N*-O	912, 888	1208 (m),[k] 842 (m)[l]	230	265	21.8	21.7
	$MeNH_2$	920, 892	3300 (s),[m] 3360 (s),[m] 1640 (m)[n]				
	py	918, 897	1441 (s), 1210 (m), 1117 (m), 1036 (m), 840 (m)	154	210	18.9	18.8
	pic	918, 893	1450 (s), 1220 (m), 1123 (m), 1022 (m), 830 (m)	160	230	21.4	21.5
	im	917, 901	3330 (m, br),[m] 1062 (s)	210	290	16.5	16.6
	aniline	915, 890	3500 (s),[m] 3400 (s)	120	160	21.4	21.2
	PPh_3	930, 905	1150 (m), 740 (s), 490 (s)				
5-Me-sap	nil	935, 908, 815[d]					
	Me_2SO	924, 903	1005 (s)[j]	188	260	18.1	18.3
	aniline	915, 885	3288 (s),[m] 3230 (s),[m] 3140 (s),[m] 740 (s)				
3-*t*-Bu-sap	H_2O	922, 900	3400 (m, br),[e] 1620 (m),[o] 840 (m)	115	135	4.3	4.5
	pic	918, 896	1420 (m), 1055 (w), 1008 (m), 860 (m)				
5-*t*-Bu-sap	nil	943, 830[d]					
	dmf	930, 901	1635 (s),[h] 735 (m)[i]				
	im	916, 896	3310 (m),[m] 3130 (m),[m] 1060 (s)				
5,6-bz-sap	nil	938, 830[d]					
	MeOH	932, 908	3200 (m, br),[e] 1015 (m)[f]	120	140	7.6	7.4
	Me_2SO	910, 890	990 (s)[j]	180	220	15.7	15.9
	aniline	922, 892	3340 (m),[m] 3265 (m),[m] 740 (s)				
sapt	nil	915, 780[d]					
	tppo	928, 899	1152 (s),[g] 535 (s)				
	py	921, 891	1455 (s), 1068 (m), 1035 (m), 1012 (m)				
5-*t*-Bu-sapt	Me_2SO	918, 890	987 (s)[j]				
	pic	916, 890	1460 (m), 1012 (m), 830 (m)				
	PPh_3	930, 896	1120 (s), 740 (s), 535 (s)				
sae	nil	933, 920, 900, 815[d]					
	H_2O	933, 925, 890	3300 (s, br)[e]	105	125	5.8	5.7
	pic	932, 912, 890	1415 (m), 1122 (m), 1010 (m)	155	205	24.2	24.5
5-Me-sae	Me_2SO	930, 920, 902	1005 (s)[j]	185	230	20.3	20.6
	pic	929, 920, 900	1455 (m), 825 (s)	170	230	23.4	23.6
5-*t*-Bu-sae	H_2O	930, 920, 898	3300 (s, br)[e]	165	185	4.9	5.1
	pic	924, 918, 903	1435 (m), 1105 (m)				

[a] As KBr disks. [b] All the absorptions are very strong. [c] One more band is present at 923 cm^{-1}. [d] Strong and broad band due to Mo=O→Mo bridging. [e] ν_{OH}. [f] ν_{C-O}(alkyl). [g] ν_{PO}. [h] $\nu_{C=O}$. [i] δ_{NCO}. [j] ν_{SO}. [k] ν_{NO}. [l] δ_{NO}. [m] ν_{NH}. [n] δ_{NH_2}. [o] δ_{H_2O}.

display similar shifts (Table I). The strong binding of PAr_3 is somewhat unexpected. The $MoO_2(L)(PAr_3)$ species are stable and do not get converted to phosphine oxide species (vide infra). In relation to aldehyde oxidase models it is significant that *monodentate* aldehydes are found to bind to the molybdenum center. This binding in, e.g., $MoO_2(sap)(C_6H_5CHO)$ results in the shift of $\nu_{C=O}$ to 1650 cm^{-1} from the free-ligand value of 1680 cm^{-1}. Binding of the aldehyde function to molybdenum(VI) in chelated ligands is well documented as in[5] $MoO_2(sal)_2$. Xanthine because of its insolubility could not be attached to $MoO_2(L)$, but imidazole readily forms (via tertiary nitrogen) $MoO_2(L)(im)$ (Table I). Attempts to bind ammonia to $MoO_2(L)$ always resulted in hydrolysis of the complex to molybdate ion and free ligand.

The complexes undergo substitution reactions of the type $MoO_2(L)(D) + D' \rightarrow MoO_2(L)(D') + D$, where D and D′ are different donor molecules. On addition of a little ethanol to $MoO_2(C_6H_5CHO)$, $MoO_2(EtOH)$ was immediately formed. On addition of Me_2SO to $MoO_2(L)(EtOH)$ in ethanol, $MoO_2(L)(Me_2SO)$ is formed and can be crystallized out. From experiments of this type the following increase in qualitative order of D binding could be established: $CH_3CHO < C_6H_5CHO <$ EtOH < *p*-anisaldehyde < dmf < pic < Me_2SO < im < py-*N*-O.

The $MoO_2(L)(D)$ complexes usually display two *cis*-MoO_2 stretches in the region 880–950 cm^{-1}. However, the X-sae complexes like some other known[6] MoO_2 species have three bands in this region (Table I). Whereas the region of MoO_2 stretching frequencies for D = oxygen ligands has a zone of overlap with that of D = nitrogen ligands, quite often the latter give rise to relatively lower frequencies. The average frequencies for all complexes (23 in number) prepared by us[10] with oxygen donors are 924 and 898 cm^{-1} while the corresponding average for nitrogen donor complexes (18 in number) are 918 and 893 cm^{-1}.

Thermal analysis data for $MoO_2(L)(D)$ compounds reveal a well-defined endothermic step, the mass loss of which corresponds to the mass of D. The residue is $MoO_2(L)$. The initial (T_i) and final (T_f) temperatures and percent mass loss (Δ*m* (%)) defining the thermal conversion of $MoO_2(L)(D)$ to $MoO_2(L)$ are shown in several cases in Table I. The relatively labile binding of D in the solid state is evident. On continued heating beyond the $MoO_2(L)$ stage highly exothermic oxidative reactions set on with complete loss of organic matter, MoO_3 being the final residue.

Some $MoO_2(L)(D)$ species derived from *t*-Bu-substituted ligands have sufficient solubility in $CDCl_3$ for NMR studies (Table II).[10] The $MoO_2(L)$ species are not soluble in $CDCl_3$, suggesting that $MoO_2(L)(D)$ retains its identity in solution. The N=CH signal of L shows appreciable shift from free-ligand values. Shifts for signals pertaining to D are also present but are small. In mixtures of $MoO_2(L)(D)$ and D only one

Table II. NMR Data[a] for Complexes in $CDCl_3$

compd[b]	signal	EtOH[c]	pic[d]	aniline[d]	Me_2SO[d]	PPh_3	P(*p*-tol)$_3$
MoO_2(5-*t*-Bu-sap)	i	8.83	8.73	8.46	8.70	8.23	*e*
	ii	1.21	2.25	3.53	2.63		2.33
MoO_2(5-*t*-Bu-sapt)	i		8.83				7.93
	ii		2.26				2.30

[a] Signals for the free ligand: 5-*t*-Bu-H_2sap (i), 8.63; *t*-Bu, 1.33. Signal i corresponds to the N=CH signal of L and signal ii to the methyl group (where present) of D. Values are in ppm from Me_4Si. [b] Data for the compound MoO_2(5-Me-sae)(H_2O) in py-d_5 (i): 8.66; 5-Me, 3.21; CH_2, 3.81; CH_2, 4.70; H_2O, 5.01. [c] The chemical shift of ethanolic CH_2 is 3.63. [d] Free D ligand values for signal ii: pic, 2.33; aniline, 3.53; Me_2SO, 2.61. [e] The CH=N signal is shifted and probably buried under aromatic signals.

Table III. Cyclic Voltammetric Peak Potential (V vs. SCE) Data[a] in dmf

compd	E_{pc}, V
MoO_2(sap)	−1.080, −1.385,[b] −1.50
MoO_2(sap)(pic)	−1.085, −1.510
MoO_2(5-*t*-Bu-sap)	−1.160[c]
MoO_2(5-*t*-Bu-sap)(im)	−1.165[c]
MoO_2(5,6-bz-sap)	−1.040, −1.425
MoO_2(sapt)[d]	−0.980, −1.170,[b] −1.445
MoO_2(5-*t*-Bu-sapt)	−1.060, −1.390
MoO_2(5-*t*-Bu-sapt)(P(*p*-tol)$_3$)	−0.980, −1.450
MoO_2(sae)	−1.400[c]
MoO_2(5-*t*-Bu-sae)	−1.490[c]
MoO_2(5,6-bz-sae)	−1.240, −1.780
Mo_2O_3(sapt)$_2$(H_2O)$_2$	−0.950, −1.170, −1.570

[a] Conditions are as follows: scan rate, 0.027 V s^{-1}; solute concentration, 3×10^{-3} M; supporting electrolyte, TEAP. The reported E_{pc} values are uncorrected for junction potentials. [b] Poorly defined peak, appears as a shoulder. [c] The alternating current polarogram of the complex dmf at the Pt electrode exhibits two peaks at −1.020 and −1.480 V vs. SCE. Conditions: amplitude, 10 mV (peak to peak); frequency, 22 Hz; scan rate, 5 mV s^{-1}.

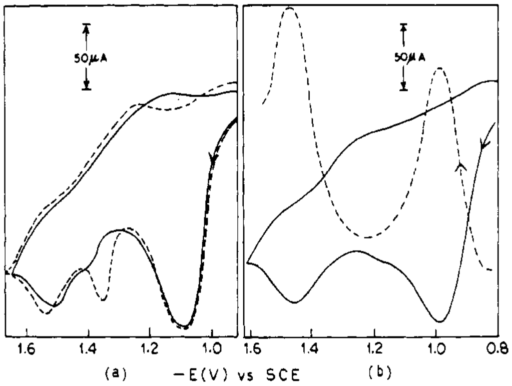

Figure 1. (a) Cyclic voltammograms (scan rate 27 mV s^{-1}) of MoO_2(sap) (—) and a mixture of MoO_2(sap) and H_2sap (---). (b) Cyclic voltammogram (scan rate 20 mV s^{-1}) of MoO_2sapt (—) and alternating current voltammogram (dc scan rate 5 mV s^{-1}, ac frequency 22 Hz, modulation amplitude 10 mV (peak to peak)) of MoO_2(sapt) (---). All measurements are in dmf (0.1M) in tetraethylammonium perchlorate (TEAP) electrolyte at 298 K.

kind of D signal is observed, showing that fast exchange of bound and free D occurs at least at room temperature.

(b) Electrochemical and Chemical Reduction. Cyclic voltammetry (CV) at the platinum electrode of a number of MoO_2(L)(dmf) species generated by dissolving MoO_2L in dmf was studied (Table III). All reductions are irreversible. The reductions for L = sap and sapt are displayed in Figure 1 which also includes the phase-sensitive alternating-current voltammogram of the sapt complex. The case of MoO_2(sap)(dmf) is considered in some detail. It displays three reduction peaks (E_{pc}) at −1.080, −1.385, and −1.535 V vs. saturated calomel electrode (SCE) all appreciably removed from the free-ligand (H_2sap) reduction peak (−1.690 V). It is believed[7,11] that at least the first reduction at −1.080 V is associated with one or two electron transfers centered on the metal. Incremental addition of H_2sap to the dmf solution of MoO_2(sap) causes an increase in the cathodic peak current at −1.385 V attended with a small anodic shift. Finally a well-defined reduction peak becomes observable at −1.340 V (Figure 1). This implies a catalytic regeneration of the species reduced at ∼−1.385 V. This may be due to interaction between MoO_2(sap) or its reduced version and H_2sap. Since the peak current at −1.385 V increases with the increase in concentration of the ligand, it is possible that there is catalytic reduction of H_2sap by the reduced molybdenum complex. A similar situation obtains in the electrochemical reduction of molybdenyl oxinate complex.[12] In several cases when experiments were also performed by dissolving MoO_2(L)(D) (D = pic, im, etc.) instead of MoO_2(L) in dmf, the voltammogram was identical with that of MoO_2(L) in dmf, suggesting that in pure dmf MoO_2(L)(D) goes over to MoO_2(L)(dmf). However, in the case of a phosphine adduct, e.g., MoO_2(5-*t*-Bu-sapt)(P(*p*-tol)$_3$), significant shifts in potentials are noticeable. Although the exact reason for this is not ascertained, it seems that the phosphine continues to remain in the vicinity of molybdenum in dmf solution.

Slow and careful addition of hydrazine hydrate to an ethanolic suspension of MoO_2(sapt) causes a vigorous reaction in which ammonia is evolved. From the reaction medium an air-unstable brownish black molybdenum(V) complex of composition Mo_2O_3(sapt)$_2$(H_2O)$_n$ ($n \approx 2$) is isolated. A strong $\nu_{Mo=O}$ at 940 cm^{-1} and a weak to medium ν_{MoOMo} band at 735 cm^{-1} are observed.[13] The complex probably has the μ-oxo-bridged constitution [(sapt)OMo–O–MoO(sapt)]. When kept in dmf solution, this is converted to MoO_2(sapt) by aerial oxidation or disproportionation followed by such oxidation. This conversion is complete in a period of 20 min. The cyclic voltammograms run immediately after making the solution in dmf display characteristic reduction peaks (Table III). However cyclic voltammograms obtained at the end of a period of 20 min are identical with that of MoO_2(sapt).

C. MoO_2L Species. Already noted is the general thermal conversion of MoO_2(L)(D) to MoO_2(L). However in some cases MoO_2(L) is directly obtained during synthesis. Thus MoO_2(sapt) separates out as such from ethanolic medium. Adducts are formed with a few strong donors (tppo, py, and Me_2SO among them) but the D ligand (except tppo) is readily lost on treatment with ethanol. MoO_2(sae) is also formed as such or as a H_2O (but not EtOH) adduct from the reaction medium. The tendency to adduct formation conspicuously increases as follows: MoO_2(sap) > MoO_2(sae) > MoO_2(sapt). This may mean that the strength of oxo bridging as described below decreases in going from MoO_2(sapt) to MoO_2(sap).

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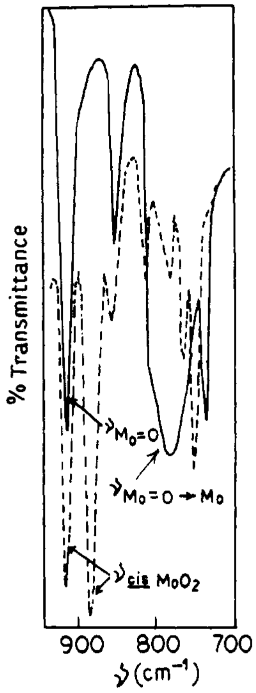
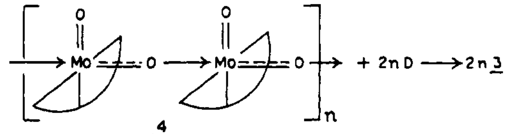


Figure 2. Mo=O stretching frequencies of MoO_2(sapt) (—) and MoO_2(sapt)(Me_2SO) (---).

All MoO_2L complexes have a characteristic strong vibration at ~800 cm^{-1} which is uniformly absent in MoO_2(L)(D). Further, in most (but not all) cases MoO_2(L) shows only a single stretch at ~930 cm^{-1} instead of the usual *cis*-MoO_2 doublet of MoO_2(L)(D) (Figure 2). These observations strongly suggest that the MoO_2L species are actually oligomeric (pseudooctahedral in Mo(VI)) via oxo bridging.[14,15] The ~930-cm^{-1} stretch is assigned to $\nu_{Mo=O}$ and the ~800-cm^{-1} stretch to the weakened $\nu_{Mo=O}$ present in the bridging $Mo\cdots O\rightarrow Mo$ moiety. Adduct formation essentially amounts to the breaking of this bridge: **4** → **3**. Significantly, the



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phenolic C–O stretching appears at nearly identical regions in MoO_2(L) and MoO_2(L)(D) (e.g.: MoO_2(sapt), 1540 cm^{-1}; MoO_2(sapt)(tppo), 1542 cm^{-1}). Oligomerization via phenolic oxygen bridging[16] in MoO_2L would be expected to result in substantial increase of the C–O stretch. It would also be difficult to understand how phenolic bridging could affect the Mo=O stretches so dramatically.

D. Concluding Remarks. An extensive series of complexes formed by the attachment of D to MoO_2(tridentate) has been identified. The metal center becomes electrochemically more easily reducible on substitution of O by S on L. When MoO_2(L)(PPh_3) and MoO_2(L)(RCHO) were refluxed in dichloromethane, oxo abstraction resulting in $OPPh_3$ and RCOOH, respectively, did not occur.[17,18] A change of experimental conditions may bring the desired result. In the disproportionation of N_2H_4 to NH_3 and N_2 by MoO_2(sapt) and the reformation of MoO_2(sapt) from Mo_2O_3(sapt)$_2$ lies the possibility of a cyclical process. The reaction of $(NH_4)_2MoOCl_5$ with L produces crystalline, air-sensitive molybdenum(V) complexes. These are some of the aspects where investigations are continuing.

Tridentate Schiff bases of sal and amino acids such as glycine and anthranilic acid were also investigated. However, these ligands are immediately hydrolyzed in contact with the molybdate, MoO_2(acac)$_2$, etc., and a mixture containing MoO_2(sal)$_2$ along with other unidentified products was all that could be isolated.

Experimental Section

Physical Measurements. Infrared spectra were recorded on Perkin-Elmer 521 and Beckman IR-20A recording spectrophotometers. Electronic spectra were measured on Cary 14 and 17D spectrophotometers. Proton resonance measurements were obtained by using Varian T-60A and EM-390 spectrometers. A MOM derivatograph which records TG, DTG, and DTA and temperature (*T*) simultaneously by a photographic method was used for thermal analysis. The electrochemical studies were done with a three-electrode system using an MP-1502B electroanalyzer of Pacific Precision Instruments and a PAR Model 370-4 electrochemistry system. With the PAR system cyclic voltammetry was performed by using the PAR Model 174A polarographic analyzer and PAR Model 175 universal programmer. Phase-sensitive alternating-current voltammetry was performed with use of a PAR 124A lock-in-amplifier, PAR 174A polarographic analyzer, and PAR 372 ac polarography interface. In all experiments a Houston Instruments RE 0074 XY recorder was used. A Beckman Model 39273 platinum-inlay working electrode, a platinum-wire auxiliary electrode and a saturated calomel reference electrode (SCE) were used for the measurements. Controlled potential coulometry was performed by using a PAR 173 potentiostat, PAR 179 digital coulometer, and PAR 377A cell system taken in conjunction with the platinum wire gauze working electrode.

Preparation of Compounds. Standard, pure grade commercial reagents and solvents were used. Substituted salicylaldehydes were prepared in good yields from the appropriate phenols by the Duff reaction.[19] The tridentate Schiff base ligands were prepared following literature methods.[20] MoO_2(sal)$_2$ was obtained as reported.[5] MoO_2(acac)$_2$ was prepared by substantially modifying a published method.[21] A total of 1.2 g of ammonium paramolybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, was dissolved in 30 mL of water by adding 2 N HNO_3 dropwise to get a clear solution. A solution of 10 mL acetylacetone containing 1 mL of 2N HNO_3 was added immediately to it. The resulting solution was stirred for nearly 3 h. The yellow solid formed was filtered out and dried under vacuum (yield 60%).

MoO_2(sap). This was prepared by starting from three different molybdenum precursors. (a) A solution of 2.1 g of H_2sap (0.01 mol) in hot ethanol (60 mL) was added with stirring to a solution of 3.2 g of MoO_2(acac)$_2$ (0.01 mol) in hot ethanol (40 mL). Heating and stirring was continued for 50 min. The crystalline silky yellow product was then filtered and washed with alcohol. Recrystallization from boiling ethanol gave needle-shaped crystals of MoO_2(sap)(EtOH) which when dried in 100 °C under vacuum gave brown crystals of MoO_2(sap) (yield 65%). (b) A total of 1.85 g of MoO_2(sal)$_2$ (5 mmol) was taken in 40 mL of ethanol to which 1.1 g of *o*-aminophenol (10 mmol) in 10 mL of ethanol was added, and the mixture was heated at reflux for about 50 min. The yellow crystals formed were filtered, rerystallized, and dried as above (yield 70%). (c) To a suspended solution of 0.21 g of H_2sap (1 mmol) in 40 mL of distilled water was added 1.21 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (1 mmol). Concentrated HCl was added to this in drops till the pH was <1. Stirring was continued for about 50 min, and the yellow product MoO_2(sap)(H_2O) was dried under vacuum at 80 °C to form MoO_2(sap) (yield 55%).

The other molybdenyl complexes, MoO_2(5-Me-sap), MoO_2(3-*t*-Bu-sap), MoO_2(5-*t*-Bu-sap), MoO_2(5,6-bz-sap), MoO_2(sae), MoO_2(5-Me-sae), MoO_2(5-*t*-sae), MoO_2(5,6-bz-sae), MoO_2(sapt), and MoO_2(5-*t*-Bu-sapt), were obtained by similar methods or slight variations thereof. In several cases, e.g., MoO_2(5-Me-sap), MoO_2-

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(5,6-bz-sae), MoO_2(sapt), MoO_2(5-*t*-Bu-sapt), no water or alcohol adducts were formed at all during the synthesis, instead MoO_2L species resulted directly.

MoO_2(L)(D). Generally these were prepared by treating MoO_2L, MoO_2(L)(EtOH), or MoO_2(L)(H_2O) with an excess of monodentate donor ligands (D) in ethanol medium. In the case of weak donors recrystallizations of the complexes from pure donors were done. Some selected examples are given below.

MoO_2(sap)(im). To a solution of 340 mg of MoO_2(sap)(EtOH) in 60 mL of hot ethanol was added with constant stirring a solution of 130 mg of imidazole in 10 mL ethanol. An orange-yellow microcrystalline solid started appearing immediately after the addition. The mixture was boiled on a water bath for about 50 min. The product was then filtered, washed with ethanol, and dried under vacuum over fused $CaCl_2$ (yield 70%).

MoO_2(sap)(C_6H_5CHO). A total of 400 mg of MoO_2(sap) was dissolved in 5 mL of hot benzaldehyde, and the solution was heated on a water bath for 1 h. The resulting solution was kept for 2–3 days in the refrigerator. The yellow crystals formed were filtered, avoiding too much suction. The crystals were dried by filter pressing and were kept in a desiccator over fused $CaCl_2$.

MoO_2(sap)(PPh_3). A total of 340 mg of MoO_2(sap) was taken in 30 mL of dichloromethane, and to this was added 300 mg of triphenylphosphine slowly with stirring. The solution was heated at reflux under nitrogen for about 1 h and then cooled. The yellowish brown solid was filtered, washed with the solvent, and dried in vacuo.

MoO_2(sae)(Me_2SO). A 580-mg sample of MoO_2(sae)(H_2O) was taken in 30 mL of ethanol, and to this was added a solution of 300 mg of dimethyl sulfoxide in ethanol. The resulting mixture was heated at reflux for 1 h, and the clear yellow solution was cooled slowly to room temperature. Pale yellow crystals separated out which were filtered, washed with ethanol, and dried under vacuum over fused $CaCl_2$.

MoO_2(sapt)($OPPh_3$). A total of 355 mg of MoO_2(sapt) was suspended in 25 mL of ethanol, and to this was added dimethyl formamide in drops to get a clear wine red solution. To this was added 300 mg of tppo, and the solution was heated at reflux for 50 min. To this solution was added water in drops just to get a turbid solution which was made clear by heating the solution. The resulting clear solution was kept in the refrigerator for a few days when beautiful reddish orange crystals were formed. The crystals were filtered, washed with ethanol, and dried in vacuo.

All the adduct compounds isolated during the present study are MoO_2(sap)(D) (D = EtOH, MeOH, tppo, H_2O, C_6H_5CHO, dmf Me_2SO, *p*-anisaldehyde, Ph_2SO, py-*N*-O, PPh_3, py, pic, α-picolylamine, CH_3NH_2, dimethylamine, im, and aniline), MoO_2(sapt)(D) (D = tppo, Me_2SO, py, and pic), MoO_2(sae)(D) (D = H_2O, Me_2SO, and pic), MoO_2(5-Me-sap)(D) (D = dmf, Me_2SO, py, and aniline), MoO_2(3-*t*-Bu-sap)(D) (D = H_2O, Me_2SO, and pic), MoO_2(5-*t*-Bu-sap)(D) (D = EtOH, MeOH, PPh_3, dmf, Me_2SO, pic, aniline, and im), MoO_2(5,6-bz-sap)(D) (D = EtOH, MeOH, aniline, py, and Me_2SO), MoO_2(5-*t*-Bu-sapt)(D) (D = PPh_3, P(*p*-tol)$_3$, Me_2SO, and pic), MoO_2(5-Me-sae)(D) (D = H_2O, Me_2SO, pic, and aniline), MoO_2(5-*t*-Bu-sae)(D) (D = H_2O and pic).

Mo_2O_3(sapt)$_2$(H_2O)$_n$. To a suspension of 710 mg of MoO_2(sapt) in 25 mL of absolute ethanol kept stirred under nitrogen was added in drops a 30% aqueous solution of hydrazine hydrate. A vigorous reaction occurred, and the addition was continued until the reaction subsided. The resulting solution was concentrated with use of a flash evaporator. The black powderlike solid thus formed was filtered, washed thoroughly with cold, dehydrated alcohol, and was dried in vacuo (yield 40%).

All complexes have been analyzed satisfactorily. (Analytical data are given as supplementary material.)

Acknowledgment. This work was initiated at the Indian Institute of Technology, Kanpur, India. Financial assistance received from the Department of Science and Technology, New Delhi, and the Department of Atomic Energy, Bombay, Government of India, is acknowledged.

Registry No. MoO_2(sap), 75790-25-9; MoO_2(sap)(EtOH), 64722-32-3; MoO_2(sap)(PPh_3), 75790-24-8; MoO_2(sap)(MeOH), 75790-23-7; MoO_2(sap)($OPPh_3$), 75790-22-6; MoO_2(sap)(H_2O), 75790-21-5; MoO_2(sap)(PhCHO), 75790-26-0; MoO_2(sap)(dmf), 64973-95-1; MoO_2(sap)(Me_2SO), 64685-17-2; MoO_2(sap)(*p*-anisaldehyde), 75790-27-1; MoO_2(sap)(Ph_2SO), 75781-07-6; MoO_2(sap)(py-*N*-O), 75781-08-7; MoO_2(sap)(α-picolylamine), 75781-09-8; MoO_2(sap)(H_2NCH_3), 75781-10-1; MoO_2(sap)(HN(CH_3)$_2$), 75790-20-4; MoO_2(sap)(py), 64685-18-3; MoO_2(sap)(pic), 64685-19-4; MoO_2(sap)(im), 64669-06-3; MoO_2(sap)(aniline), 64669-05-2; MoO_2(5-Me-sap), 75781-11-2; MoO_2(5-Me-sap)(dmf), 72877-18-0; MoO_2(5-Me-sap)(Me_2SO), 75780-98-2; MoO_2(5-Me-sap)(py), 75780-99-3; MoO_2(5-Me-sap)(aniline), 75781-00-9; MoO_2(3-*t*-Bu-sap)(H_2O), 75781-01-0; MoO_2(3-*t*-Bu-sap)(pic), 75781-02-1; MoO_2(3-*t*-Bu-sap)(Me_2SO), 75781-03-2; MoO_2(5-*t*-Bu-sap), 75781-04-3; MoO_2(5-*t*-Bu-sap)(EtOH), 75781-05-4; MoO_2(5-*t*-Bu-sap)(MeOH), 75781-06-5; MoO_2(5-*t*-Bu-sap)(PPh_3), 75790-11-3; MoO_2(5-*t*-Bu-sap)(dmf), 72894-46-3; MoO_2(5-*t*-Bu-sap)(pic), 75790-12-4; MoO_2(5-*t*-Bu-sap)(aniline), 75790-13-5; MoO_2(5-*t*-Bu-sap)(im), 75790-14-6; MoO_2(5-*t*-Bu-sap)(Me_2SO), 75790-15-7; MoO_2(5,6-bz-sap), 75790-16-8; MoO_2(5,6-bz-sap)(MeOH), 75790-17-9; MoO_2(5,6-bz-sap)(aniline), 75790-18-0; MoO_2(5,6-bz-sap)(py), 75790-19-1; MoO_2(5,6-bz-sap)(Me_2SO), 75780-88-0; MoO_2(sapt), 75780-89-1; MoO_2(sapt)(Me_2SO), 75780-90-4; MoO_2(sapt)($OPPh_3$), 75780-91-5; MoO_2(sapt)(py), 75780-92-6; MoO(sapt)(pic), 75780-93-7; Mo_2O_3(sapt)$_2$(H_2O)$_2$, 75780-97-1; MoO_2(5-*t*-Bu-sapt), 75780-94-8; MoO_2(5-*t*-Bu-sapt)(PPh_3), 75780-95-9; MoO_2(5-*t*-Bu-sapt)(P(*p*-tol)$_3$), 75780-96-0; MoO_2(5-*t*-Bu-sapt)(Me_2SO), 75780-78-8; MoO_2(5-*t*-Bu-sapt)(pic), 75780-79-9; MoO_2(sae), 75780-80-2; MoO_2(sae)(H_2O), 75780-81-3; MoO_2(sae)(pic), 75780-82-4; MoO_2(sae)(Me_2SO), 75780-83-5; MoO_2(5-Me-sae)(H_2O), 75780-84-6; MoO_2(5-Me-sae)(pic), 75780-85-7; MoO_2(5-Me-sae)(Me_2SO), 75780-86-8; MoO_2(5-Me-sae)(aniline), 75780-87-9; MoO_2(5-*t*-Bu-sae)(H_2O), 75780-73-3; MoO_2(5-*t*-Bu-sae)(pic), 75780-74-4; MoO_2(5,6-bz-sae), 75780-75-5; MoO_2(5-*t*-Bu-sae), 75780-76-6; $(NH_4)_6Mo_7O_{24}$, 12027-67-7; MoO_2(acac)$_2$, 21884-95-7; MoO_2(sal)$_2$, 53062-21-8; *o*-aminophenol, 95-55-6; 5-*t*-Bu-H_2sap, 75782-85-3; MoO_2(5-*t*-Bu-sap)(P(*p*-tol)$_3$), 75780-77-7.

Supplementary Material Available: Table of analytical data for the molybdenum complexes (4 pages). Ordering information is given on any current masthead page.