

Molybdenum Complexes. 3.¹ Bis(hydroxamates) of Dioxomolybdenum(VI) and Their Reactions: Control of Redox Activity by Substituent Effects, Protic Equilibria, and Oxaziridine Formation

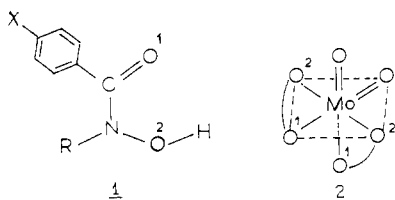
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The synthesis, characterization, and spectra (¹H NMR, IR, and UV) of a group of molybdenum hydroxamates of type MoO₂(RX)₂ (**2**) are reported (RX = RN(O⁻)C(=O)C₆H₄X R = H, Me, Ph; X = OMe, Me, H, Cl, NO₂). These exist in only one isomeric form in which the MoO₂ group is cis and the carbonyl oxygen is trans to a terminal oxo function. The CO stretching frequency of **2** is low due to the presence of hydroxamate-hydroximate resonance in metal-bound RX. The Mo(VI)-Mo(V) redox activity of **2** is systematically examined by using cyclic voltammetry at the mercury electrode. In acetonitrile the reduction peak (*E*_{pc}) is readily seen but the corresponding oxidation peak (*E*_{pa}) is absent except in MoO₂(HX)₂⁻ (rapid decomposition of MoO₂(PhX)₂⁻ and MoO₂(MeX)₂⁻). For a given X, *E*_{pc} decreases as R changes in the order H > Ph > Me. For a given R, *E*_{pc} values, which decrease with X as NO₂ > Cl > H > Me > OMe, correlate linearly with Hammett constants. The reaction of MoO₂(PhX)₂ with *p*-YC₆H₄NHOH (Y = H, Cl, Me) yields a red-orange solution thought to contain MoO(YC₆H₄NO)(PhX)₂, whose *E*_{pc} is ~300 mV lower than that of MoO₂(PhX)₂. A span of more than 1 V is covered by the *E*_{pc} values (-0.60 to -1.64 V vs. SCE) of the various complexes. The complex MoO₂(HH)₂ undergoes proton dissociation in aqueous media (p*K*₁ = 3.45 ± 0.05 and p*K*₂ = 5.85 ± 0.05), and the current corresponding to *E*_{pc} progressively diminishes with increasing pH. This effect, which is reversible, is shown to arise from MoO₂(HH)₂ alone being electroactive while [MoO₂(H)(HH)]⁻ and [MoO₂(H)₂]²⁻ are inactive.

Introduction

There is current interest²⁻⁶ in the chemistry and structure of transition-metal hydroxamates, some of which are biochemically significant.⁷ As part of our program^{1,8} on molybdenum complexes we have undertaken a study of the hydroxamates of this metal. In the present work we describe the synthesis and the spectral characterization of a sizable group of complexes derived from the general hydroxamic acid **1**, which is abbreviated as HRX. Here H refers to the OH



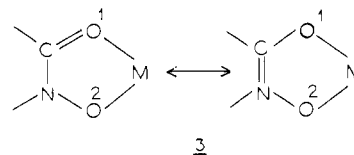
proton, which dissociates on complex formation; R is Ph, Me, or H, and X is OMe, Me, H, Cl, or NO₂. The complexes prepared are of the general type MoO₂(RX)₂ (**2**). The redox activity of the whole group of complexes is examined electrochemically. The effects of several factors on the molybdenum(VI)-molybdenum(V) couple are studied. Thus the variation of X and R is found to provide a large control on the redox potential. The possibility of a further control via the in situ reaction of **2** with hydroxylamines, yielding molybdooxaziridines,^{9,10} is explored. Finally the acidity of the NH proton in complexes of type MoO₂(HX)₂ and the role of as-

sociated protic equilibria in modifying the redox response are examined. The redox activity of molybdenum complexes has the special interest of being biochemically relevant.¹¹

Results and Discussion

Synthesis, Spectra, and Structure. The complexes (Table I) were obtained as shining crystals in different shades of yellow by reacting Na₂MoO₄·2H₂O with HRX in aqueous acidic media.¹² The free hydroxamic acids were synthesized¹³⁻¹⁵ from appropriate acid chlorides and hydroxylamines in alkaline solution. All complexes except¹² MoO₂(HH)₂ and MoO₂(HCl)₂ are new.

Selected spectral data are in Table I. In **2** the ν_{Mo=O} doublet, characteristic of *cis*-MoO₂, appears in the range 880-940 cm⁻¹. In oxygen donor chelates the Mo-O stretches usually occur^{1,16} within the interval 550-650 cm⁻¹. Two or more bands systematically appear in this region in **2**. The assignments of IR bands shown in Table I were arrived at after careful comparison of the spectrum of each complex with that of the corresponding ligand. A case is illustrated in Figure 1. One notable feature of the IR spectra is the substantial decrease in ν_{C=O} in going from HRX (1600-1650 cm⁻¹) to MoO₂(RX)₂ (1480-1550 cm⁻¹). This is attributed to the chelate resonance **3**.



Within the framework of *cis*-MoO₂ geometry MoO₂(RX)₂ can have three isomeric structures. If we number the oxygen

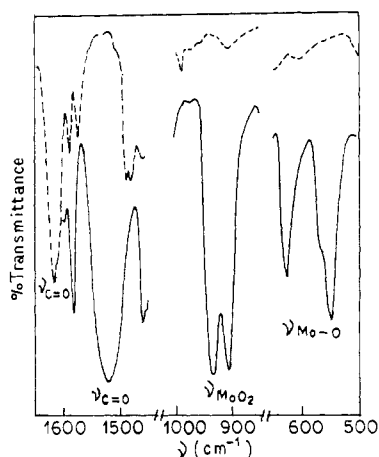
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- (13) The statement¹⁴ that the synthesis of hydroxamic acids is difficult is unclear to us. The authors¹⁴ used the reaction¹⁵ of oxidoperoxo(hexamethylphosphoramide)molybdenum(VI) with amides to obtain hydroxamates of the metal. In our opinion the direct method of synthesis from HRX and molybdate is straightforward and provides much synthetic flexibility.
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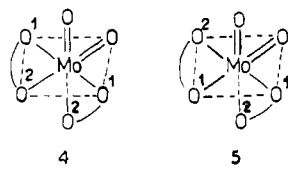
Table I. Selected Spectral Data of MoO₂(RX)₂

complex		IR ^a frequencies, cm ⁻¹			UV ^b λ _{max} , nm (ε, M ⁻¹ cm ⁻¹)	
R	X	ν _{C=O}	ν _{Mo=O}	ν _{Mo-O}	RX → Mo	intraligand
Ph	H	1520	905, 935	550, 630	330 ^c (42 000), 272 (9000)	220 (20 800)
Ph	Me	1510	900, 930	540, 610	272 (16 000)	224 (40 500)
Ph	OMe	1500	900, 925	550, 610	280 (21 000), 260 (22 000)	218 (30 000)
Ph	Cl	1520	900, 930	564, ^d 627 ^e	270 (17 000)	228 (34 000)
Ph	NO ₂	1530	910, 935	561, ^f 617 ^g	300 ^c (16 000), 256 (33 000)	230 (32 000)
Me	H	1550	890, 930	545, 590	324 ^c (3000), 268 (4000)	224 (12 000)
Me	Me	<i>h</i>	900, 935	580, 600	274 (19 000)	240 (42 000)
Me	OMe	<i>h</i>	900, 925	550, 580	328 ^c (5000), 270 (16 000)	220 (21 000)
Me	Cl	<i>h</i>	900, 930	550, 590	324 ^c (4000), 272 (11 000)	230 (27 000)
Me	NO ₂	<i>h</i>	905, 930	540, 580	290 ^c (9000)	240 (14 000)
H	H	1525	880, 935	545	320 ^c (8000), 276 (11 000)	230 (35 000)
H	Me	1520	890, 935	540, 620	272 ^c (10 000)	238 (18 000)
H	OMe	1485	895, 940	540, 620	272 ^c (21 000)	240 (24 000)
H	Cl	1555	890, 930	550, 580	328 ^c (9000), 284 ^c (16 000)	230 (37 000)
H	NO ₂	1550	880, 930	550, 580	344 ^c (13 000), 256 (40 000)	230 (42 000)

^a In KBr disk. ^b In acetonitrile. ^c Shoulder. ^d Center of doublet peaks occurring at 558 and 570 cm⁻¹. ^e Center of doublet peaks occurring at 622 and 632 cm⁻¹. ^f Center of doublet peaks occurring at 555 and 568 cm⁻¹. ^g Center of doublet peaks occurring at 612 and 622 cm⁻¹. ^h A number of overlapping bands occur in the range 1600-1400 cm⁻¹, making the identification of ν_{C=O} difficult.

Figure 1. Infrared spectra of MoO₂(PhH)₂ (—) and HPhH (---).

atoms as in **1** and take the pairs (from two ligands) O¹, O¹ and O², O², the three possible isomers are cis-trans (**2**), trans-cis (**4**), and cis-cis (**5**). The complexes as prepared have



sharply defined ¹H NMR spectra (Table II); only one isomer is present in each case. The data also exclude structure **5**, which requires the two rings to be nonequivalent. While our work was in progress, two reports^{10,14} on the X-ray structures of some hydroxamates of molybdenum(VI) appeared. On the strength of these, the complexes reported here are given the cis-trans structure **2**, in which the weakly donating O¹ atoms are trans to a terminal oxo function. X-ray data^{2,3,10,14} are also in accord with the ring resonance **3**.

The electronic spectra of the complexes convey little structural information. One or two shoulders are seen above 250 nm probably due to RX → Mo charge transfer (Table I). Free ligands have bands only below 240 nm.

Redox Activity. The electron-transfer behavior of **2** was examined in acetonitrile (0.1 M in tetraethylammonium perchlorate, TEAP) at the hanging mercury drop electrode (HMDE) with use of voltammetric techniques. All potentials were measured at 298 K and are referenced to the saturated calomel electrode (SCE).

Table II. ¹H Chemical Shifts^a of MoO₂(RX)₂

complex		δ ^b	
R	X	Me	aromatic
Ph	Me	2.30	7.00 ^c
Ph	OMe	3.76	7.00 ^c
Me	H	3.58	7.51
Me	Me	2.60 ^d , 3.60 ^e	(7.58, 7.43, 7.28, 7.15) ^h
Me	OMe	3.58 ^f , 3.83 ^g	(7.86, 7.63, 7.45, 7.40) ^h
Me	Cl	3.58	(7.76, 7.58, 7.28, 7.36) ^h
Me	NO ₂	3.56	(8.40, 8.20, 8.00, 7.80) ^h
H	H		7.56
H	Me	2.33	(7.76, 7.66, 7.36, 7.23) ^h
H	OMe	3.83	(7.83, 7.61, 7.40, 7.00) ^h
H	Cl		(7.86, 7.73, 7.63, 7.50) ^h
H	NO ₂		(8.44, 8.30, 8.16, 8.02) ^h

^a For the first seven complexes measurements are made in CDCl₃ and the other five in (CD₃)₂SO (due to solubility reasons).

^b Downfield from tetramethylsilane. ^c Center of complex pattern.

^d For X = Me. ^e For R = Me. ^f For X = OMe. ^g For R = Me.

^h AB pattern with *J* = 8-10 Hz.

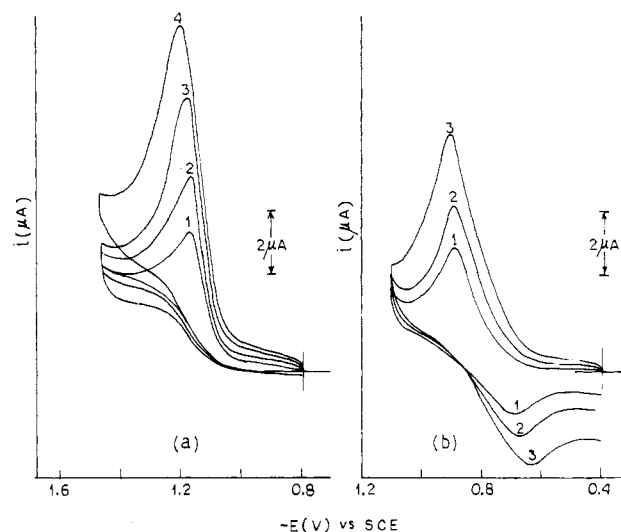


Figure 2. Cyclic voltammograms at HMDE in MeCN (0.1 M in TEAP, 298 K): (a) MoO₂(PhH)₂; (b) MoO₂(HH)₂. Scan rates (mV s⁻¹) are as follows: (1) 50; (2) 100; (3) 200; (4) 500.

The cyclic voltammogram of a representative member, viz., MoO₂(PhH)₂, is shown in Figure 2 at several scan rates (*v*). A well-defined cathodic response with a peak potential (*E*_{pc}) of ~-1.20 V is observed; the peak height increases in proportion to *v*^{1/2}. Coulometry at potentials more negative to

Table III. Voltammetric Molybdenum(VI)-Molybdenum(V) Reduction Potentials^{a, b} in Complexes

A. MoO ₂ (RX) ₂						
complex			complex			
R	X	E _{pc} , V	R	X	E _{pc} , V	
Ph	H	-1.23	H	H	-0.78 (180), ^c -0.69 ^d	
Ph	Me	-1.27	H	H	-0.42 ^{e, f}	
Ph	OMe	-1.33	H	Me	-0.83 (200), ^c -0.71 ^d	
Ph	Cl	-1.15	H	Me	-0.46 ^e	
Ph	NO ₂	-0.92	H	OMe	-0.89 (250), ^c -0.76 ^d	
Me	H	-1.29	H	OMe	-0.49 ^e	
Me	Me	-1.34	H	Cl	-0.73 (200), ^c -0.63 ^d	
Me	OMe	-1.44	H	Cl	-0.37 ^e	
Me	Cl	-1.24	H	NO ₂	-0.61 (240), ^c -0.49 ^d	
Me	NO ₂	-0.99	H	NO ₂	-0.30 ^e	

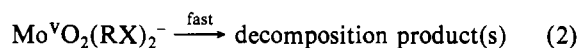
B. MoO(YC ₆ H ₄ NO)(PhX) ₂						
complex			complex			
X	Y	E _{pc} , V	X	Y	E _{pc} , V	
H	H	-1.50	OMe	H	-1.64	
H	Cl	-1.61	Cl	H	-1.43	
H	Me	-1.28	NO ₂	H	g	
Me	H	-1.55				

^a Meaning of symbols as in text. ^b Conditions of measurements are as follows: electrode, HMDE; concentration of complex, 10⁻³ M. Unless otherwise stated, all measurements are made in acetonitrile with 0.1 M TEAP as supporting electrolyte at a scan rate of 100 mV s⁻¹. ^c Peak-to-peak separation in mV. ^d Formal potentials, E^o₂₉₈, calculated as the average of the cathodic and anodic peak potentials. ^e In 80:20 water-dioxane solution (1 M in sodium chloride). ^f Reduction potential in pure water (1 M NaCl) is -0.40 V. ^g E_{pc} could not be determined due to interference by reduction of the NO₂ group.

E_{pc} did not give meaningful results due to continuous accumulation of coulombs arising from unknown reactions. However, by a comparison of the cathodic peak current with those of authentic one-electron reactions^{1,17,18} the reduction peak of MoO₂(PhH)₂ is found to involve only one electron. When *v* is increased, E_{pc} becomes more negative (Figure 2), showing that the reduction process is quasi-reversible in the electrochemical sense.

On scan reversal no anodic peak is observed. Evidently the product of reduction is unstable and does not survive to undergo reoxidation. The free ligand (HPhH) displays irreversible and relatively ill-defined reductions only below -1.80 V. Similar reductions are also seen in MoO₂(PhH)₂ at low potentials. These are not considered any further here. The process occurring near -1.20 is thus ascribable to a one-electron reduction of the metal. The instability of the bis chelates of the Mo^{VO}₂ moiety is well-documented in the literature.^{1,19} The Mo^{VO}₂(PhH)₂⁻ complex formed on reduction is no exception.

The cyclic voltammograms of the remaining MoO₂(PhX)₂ species and all the MoO₂(MeX)₂ complexes are qualitatively similar to those of MoO₂(PhH)₂. Peak potential data are collected in Table III. We thus have the general reactions 1 and 2 (R = Ph or Me). The thiohydroxamate analogue of



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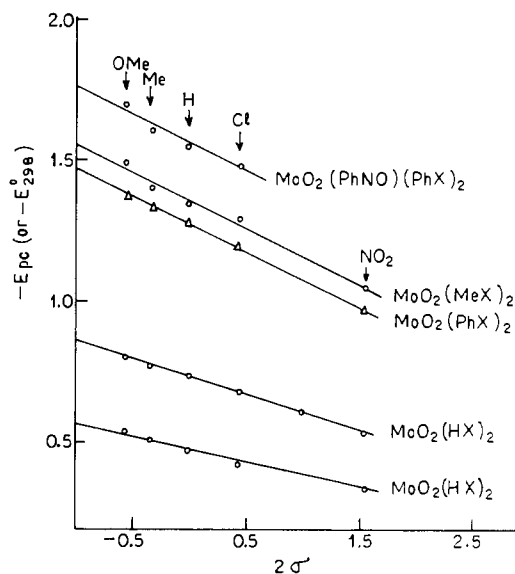


Figure 3. Least-squares plots of *E* vs. 2σ . The solvent is MeCN in all cases except for the bottom line, for which the solvent is 80:20 water-dioxane solution.

MoO₂(MeMe)₂ is reported¹⁹ to display an one-electron reduction peak at -1.18 V (in CH₂Cl₂), which also has no anodic counterpart.

The MoO₂(HX)₂ group behaves slightly differently from the other two groups. Here the one-electron reduction peak occurs near -0.70 V and the corresponding anodic peak is observable, though with diminished height (Figure 2). The peak-to-peak separation (ΔE_p) is ~200 mV. Evidently MoO₂(HX)₂⁻ is more stable than MoO₂(RX)₂⁻ (R = Me or Ph). The formal potential E^o₂₉₈ of the quasi-reversible couple (3) is calculated as the average of cathodic and anodic peak



potentials (Table III). In this group of complexes a second reduction peak of unknown origin is observed near -1.0 V.

Linear Substituent Effects. The E_{pc} values of the various electrode processes of types 1 and 3 are sensitive to X and R. The relatively remote groups on the ligand observably influence the reducibility of the metal. The E_{pc} values of our complexes span a range of more than 800 mV: -0.61 to -1.44 V. We wish to note that while systematic studies of substituent effects on metal redox activity in coordination compounds are numerous,^{17,20} very few reports concern molybdenum as the active metal center^{1,8,21,22} or HRX as the substituent-bearing ligand.⁴ The present results are significant on both counts.

For a given X, the E_{pc} values decrease in the order of R H > Ph > Me as excepted from the order of electron-donating power. For a given R, reduction becomes progressively more difficult as X becomes more electron donating: E_{pc} decreases as NO₂ > Cl > H > Me > OMe. For each group of complexes (given R) eq 4 holds. Here ΔE_{pc} is the shift of E_{pc} from

$$\Delta E_{pc} = 2\sigma\rho \quad (4)$$

that of the standard complex (X = H), 2σ is the total Hammett substituent constant for the two ligands, and ρ is the reaction constant, which measures the susceptibility of the electron-transfer process to polar effects.^{17,20,23,24} In the case

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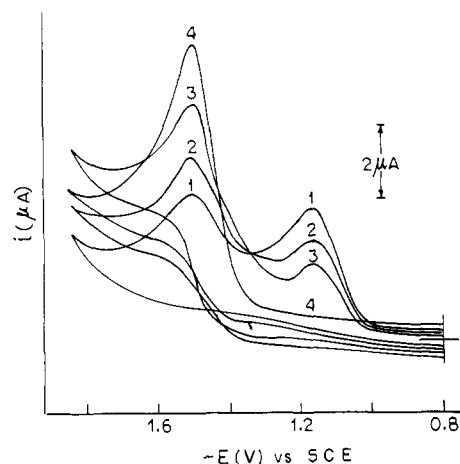
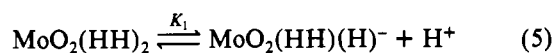


Figure 4. Cyclic voltammograms at HMDE in MeCN (0.1 M TEAP at 298 K, scan rate 100 mV s^{-1}) of a mixture of $\text{MoO}_2(\text{PhH})_2 + \text{PhNHOH}$ (initial mole ratio 1:10) as a function of time: (1) 15 min; (2) 2 h; (3) 3 h; (4) 6 h.

of $\text{MoO}_2(\text{HX})_2$ it is appropriate to replace ΔE_{pc} by ΔE°_{298} in eq 4. The excellent linear $E_{\text{pc}} (E^{\circ}_{298})$ vs. 2σ plots for process 1 (3) are shown in Figure 3.

The ρ values of the three groups of complexes are as follows: R = H, 0.13; R = Me, 0.20; R = Ph, 0.20 V. The corresponding values for the iron(III)–iron(II) couples in $\text{Fe}(\text{RX})_3$ species are⁴ 0.05, 0.07, and 0.06 V, respectively. In the dioxomolybdenum(VI) complexes the substituent effect is transmitted better than in the iron(III) tris chelates.

Protic Equilibria: Effect on Redox Activity. Complexes with R = H can be deprotonated in alkaline media. However, only $\text{MoO}_2(\text{HH})_2$ has sufficient solubility in water to permit the study of protic equilibria in this solvent. The potentiometric titration data for this complex can be rationalized in terms of equilibria 5 and 6. The $\text{p}K_1$ and $\text{p}K_2$ values (298 K, 1 M



aqueous NaCl as medium) are respectively 3.45 ± 0.05 and 5.89 ± 0.05 . The $\text{p}K$ for the dissociation of the OH proton of the free ligand is ~ 9 .²⁵ That of the NH proton is likely to be much higher. There is thus a dramatic augmentation in the acidity of the NH proton on binding of the ligand to molybdenum(VI). In fact $\text{MoO}_2(\text{HH})_2$ is a stronger acid than acetic acid. Salts of $\text{MoO}_2(\text{H})_2^{2-}$ can be isolated in the solid state, and the X-ray structure of the dicesium salt is known.¹⁰

The cyclic voltammogram of $\text{MoO}_2(\text{HH})_2$ was examined as a function of pH in aqueous media. The molybdenum(VI)–molybdenum(V) couple is again observed as in acetonitrile but only at acidic pH (Figure 4). The E_{pc} values (Table III) are however higher, and the anodic response is absent, showing that the reduced complex is unstable in water. More significantly the cathodic response diminishes in height as the pH is increased and no response is observed at all above pH ~ 5.5 (Figure 4). These changes are fully reversible: the response is reestablished to the original state simply by acidifying the solution.

The species present in aqueous solution are $\text{MoO}_2(\text{HH})_2$, $\text{MoO}_2(\text{HH})(\text{H})^-$, and $\text{MoO}_2(\text{H})_2^{2-}$. With the help of K_1 and K_2 , the formation curves for the various species are readily calculated as a function of pH. The current height (i_{pc}) for

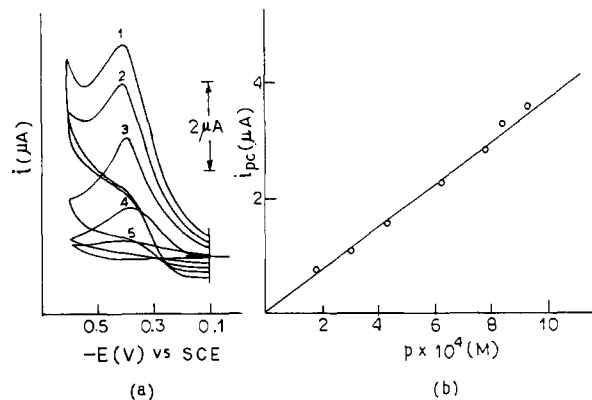


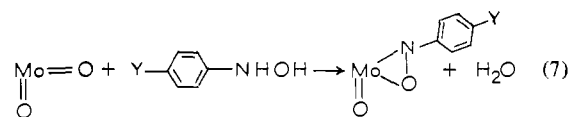
Figure 5. (a) Cyclic voltammogram of $\text{MoO}_2(\text{HH})_2$ in water (1 M in NaCl at 298 K, scan rate 100 mV s^{-1}) as a function of pH: (1) 1.80; (2) 2.26; (3) 2.80; (4) 3.80; (5) 5.85. (b) Linear variation of the cathodic peak current (i_{pc}) with concentration of $\text{MoO}_2(\text{HH})_2$ (p).

the molybdenum(VI)–molybdenum(V) reduction process is found to increase in direct proportion to the increase in the equilibrium concentration of $\text{MoO}_2(\text{HH})_2$ obtained from the relevant formation curve of this complex. Indeed the plot of i_{pc} vs. the concentration of $\text{MoO}_2(\text{HH})_2$ is excellently linear with the zero intercept (Figure 4).

We thus have the interesting and somewhat surprising result that only the fully protonated complex is electroactive near -0.4 V while the partially or completely deprotonated chelates are not. In protic media the thermodynamics of an electrode reaction can be influenced by preferential protonation of the reduced species.²⁶ In such a situation the formal potential become pH dependent. A case like the present one where proton removal blocks the electron-transfer pathway is novel in molybdenum chemistry although it is known elsewhere.²⁷

Though K_1 and K_2 for equilibria of types 5 and 6 could not be determined for the various $\text{MoO}_2(\text{HX})_2$ complexes ($X \neq \text{H}$) due to solubility reasons, the molybdenum(VI)–molybdenum(V) couple could be studied cyclic voltammetrically in 80:20 water–dioxane solution. In each case the response near -0.4 V is absent under alkaline conditions but it attains full height under acidic conditions. The behavior is qualitatively similar to that of $\text{MoO}_2(\text{HH})_2$. The E_{pc} values (Table III) obey a linear Hammett correlation (Figure 3).

Oxaziridine Formation: Effect on Redox Potential. The ability of hydroxylamines to convert the dioxomolybdenum(VI) group to the molybdooxaziridine function has been demonstrated in a few cases.^{9,10} We wished to examine the effect of oxaziridine formation on the molybdenum(VI)–molybdenum(V) potential. The reaction of $\text{YC}_6\text{H}_4\text{NHOH}$ ($Y = \text{H}, \text{Cl}, \text{Me}$) with $\text{MoO}_2(\text{PhX})_2$ was studied. When the reactants are mixed in CH_2Cl_2 or MeCN, an orange-red coloration develops. This indicates that reaction 7 may have occurred.^{9,10} However, crystalline oxaziridine species could not be isolated from the reaction mixture.



Cyclic voltammetry (in MeCN at the HMDE) of the orange-red solution revealed significant information. A well-defined one-electron reduction peak is observed at negative

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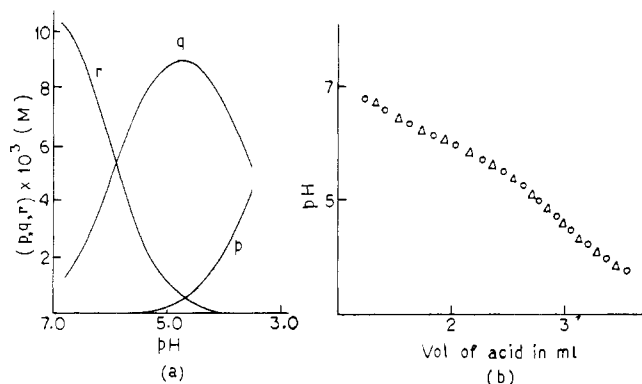


Figure 6. (a) Formation curves for protic equilibria. *p*, *q*, and *r* are respectively the equilibrium concentrations of $\text{MoO}_2(\text{HH})_2$, $\text{MoO}_2(\text{HH})(\text{H})^-$, and $\text{MoO}_2(\text{H})_2^{2-}$. (b) Titration curves of 0.01 M $\text{MoO}_2(\text{H})_2^{2-}$ vs. 0.063 M HCl at 298 K: (O) experimental curve; (Δ) calculated curve.

potentials; the anodic response is absent (Figure 5). The gross behavior of the orange-red species is thus qualitatively similar to that of the parent complex. However, the E_{pc} of the former is systematically more negative than that of the latter (Table III). The total span of E_{pc} values in Table III is more than 1 V.

The peak potentials of the orange-red species are sensitive to both X and Y substituents (Table III). Significantly the $E_{pc}-2\sigma$ line for the X substituent ($Y = \text{H}$) is parallel ($\rho = 0.20$ V) to the corresponding plot for $\text{MoO}_2(\text{PhX})_2$ (Figure 3). Thus the orange-red solution most probably contains²⁸ $\text{MoO}(\text{YC}_6\text{H}_4\text{NO})(\text{PhX})_2$.

We have examined²⁹ the cyclic voltammetry of the authentic⁹ molybdooxaziridine complexes of type $\text{MoO}(\text{YC}_6\text{H}_4\text{NO})(\text{dtc})_2$ (dtc = diethyldithiocarbamate). Here also the E_{pc} for the molybdenum(VI)–molybdenum(V) reduction is considerably (200–300 mV) more negative than that of $\text{MoO}_2(\text{dtc})_2$. Thus the oxaziridine group is a better donor than the oxo group.

Neat oxaziridine voltammograms are observed only after a solution containing an excess of $\text{YC}_6\text{H}_4\text{NHOH}$ (10 mol or more for each mole of complex) is left for several hours. If these conditions are not satisfied, the voltammogram displays cathodic responses for both $\text{MoO}(\text{YC}_6\text{H}_4\text{NO})(\text{PhX})_2$ and $\text{MoO}_2(\text{PhX})_2$ (Figure 5). The rate and equilibrium aspects of oxaziridine formation are under investigation.

Experimental Section

Materials. Water of high purity was obtained by distillation of deionized water from KMnO_4 . Sodium chloride for electrochemical and pH-metric work was recrystallized from water. The purification of solvents and preparation of supporting electrolytes for electrochemical work were done as before.¹⁷ Triple-distilled mercury was used for the HMDE. Dinitrogen was purified by bubbling it through an alkaline dithionite reducing solution. All other chemicals used for the preparative works were of reagent grade and were used without further purification.

Measurements. Spectroscopic data were obtained with use of the following instruments: electronic spectra, Cary 17D or Pye Unicam SP8-150 spectrophotometer; infrared spectra (KBr disk, 4000–400 cm^{-1}), Beckman IR-20A spectrophotometer; ^1H NMR spectra, Varian T-60 spectrometer. Voltammetric measurements were done at 298 K with a PAR 370-4 electrochemistry system as before.¹⁷ A fresh drop of mercury was used for each measurement with the HMDE.

In electrochemical measurements the pH of solutions was adjusted where required by adding hydrochloric acid or sodium hydroxide. Immediately before and after each measurement the pH was monitored accurately with the help of a Systronics Type 335 pH meter accurate to ± 0.01 pH unit. The following values²⁴ for para substituent constants (σ) were used: OMe, -0.27 ; Me, -0.17 ; H, 0.00 ; Cl, $+0.23$; NO_2 , $+0.78$.

Determination of pK Values. To a solution of $\text{MoO}_2(\text{HH})_2$ in water (1.0 M in NaCl for the maintenance of constant ionic strength) was added enough of a carbonate-free³⁰ sodium hydroxide solution (0.066 N) to make it alkaline (pH ~ 9.5). The total concentration of molybdenum was of the order $\sim 10^{-2}$ M. The solution was then titrated with standard hydrochloric acid (0.063 N) pH-metrically. Titration was continued until precipitation of $\text{MoO}_2(\text{HH})_2$ (pH ~ 3.7) occurred. A double-walled glass vessel thermostated at 298 K was used. The buret for delivering hydrochloric acid was accurate to ± 0.01 mL. The above procedure is more convenient and controllable than the direct titration of aqueous $\text{MoO}_2(\text{HH})_2$ with sodium hydroxide since the former dissolves in water only slowly and the preparation of a $\sim 10^{-2}$ M solution is not readily achieved. For equilibria 5 and 6 relation 8 holds.³¹ In the procedure adopted by us we have eq 9 defining \bar{h} .

$$\frac{\bar{h}}{2 - \bar{h}}[\text{H}^+]^2 = \frac{1 - \bar{h}}{2 - \bar{h}}[\text{H}^+]K_1 + K_1K_2 \quad (8)$$

$$\bar{h} = \frac{[\text{Na}^+] - [\text{Cl}^-]}{c} \quad (9)$$

Here Na^+ and Cl^- originate from added sodium hydroxide and hydrochloric acid, respectively, and c is the total concentration of the complex. Obviously calculations of K_1 and K_2 are possible only when $([\text{Na}^+] - [\text{Cl}^-]) \leq 2c$. The formation curves for the various species were obtained by using relations 10–12, which are readily derived

$$[\text{MoO}_2(\text{HH})_2] = c(1 + K_1/[\text{H}^+] + K_1K_2/[\text{H}^+]^2) \quad (10)$$

$$[\text{MoO}_2(\text{HH})(\text{H})^-] = [\text{MoO}_2(\text{HH})_2]K_1/[\text{H}^+] \quad (11)$$

$$[\text{MoO}_2(\text{H})_2^{2-}] = [\text{MoO}_2(\text{HH})_2]K_1K_2/[\text{H}^+]^2 \quad (12)$$

from equilibria 5 and 6 with use of the criteria of mass balance. Experimental and calculated titration data and formation curves are shown in Figure 6.

Synthesis of Compounds. Hydroxamic acids were prepared by acylation of appropriate hydroxylamines with substituted acid chlorides. $\text{MoO}_2(\text{RX})_2$ was obtained by reacting $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ with a hydroxamic acid in pH-controlled aqueous media. The procedure is essentially similar to that reported elsewhere.¹² Better methods of purification and recrystallization have however been developed. Details are given below for a representative case. The other complexes were prepared similarly.

Dioxobis(*N*-methyl-*p*-anisoylhydroxamate)molybdenum(VI), $\text{MoO}_2(\text{MeOMe})_2$. An aqueous solution (20 mL) of 0.30 g (1.24 mmol) of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ was mixed with a warm aqueous solution (20 mL) of 0.67 g (3.71 mmol) of *N*-methyl-*p*-anisoylhydroxamic acid. A light yellow color was produced. The pH of the solution was adjusted to ~ 3 by dropwise addition of 6 N HCl. The light yellow solid that separated out was filtered, washed with hot water, and dried in vacuo over P_4O_{10} . The crude product was dissolved in 40 mL of a hot acetonitrile–water mixture (1:1). When the solution cooled to room temperature, needle-shaped yellow crystals deposited. These were collected by filtration and were dried over P_4O_{10} . The yield was 70%.

On the reduction by mercury in 3 M HCl, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ gives³² a wine red solution of dioxo-bridged molybdenum(V) species. We have observed that this solution (0.05 mmol of molybdenum) rapidly reacts with hydroxamic acids (0.15 mmol) in air to produce $\text{MoO}_2(\text{RX})_2$ in very good yield. This procedure was however not pursued in detail since it offers no special advantage over the synthetic method already described.

The purity of every complex was checked by elemental analysis, and the data are collected in a table that is available as supplementary material.

(28) Molybdooxaziridine hydroxamates of a somewhat different kind are known to occur in the crystalline state, e.g. $\text{MoO}(\text{Me}_2\text{NO})(\text{HH})(\text{H})$, whose X-ray structure is known.¹⁰ The gross structure of $\text{MoO}(\text{YC}_6\text{H}_4\text{NO})(\text{PhX})_2$ is believed to be similar.

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Registry No. MoO₂(PhH)₂, 76582-00-8; MoO₂(PhMe)₂, 84927-86-6; MoO₂(PhOMe)₂, 84927-87-7; MoO₂(PhCl)₂, 84927-88-8; MoO₂(PhNO₂)₂, 84927-89-9; MoO₂(MeH)₂, 84927-90-2; MoO₂(MeMe)₂, 84927-91-3; MoO₂(MeOMe)₂, 84927-92-4; MoO₂(MeCl)₂, 84927-93-5; MoO₂(MeNO₂)₂, 84927-94-6; MoO₂(HH)₂, 67315-41-7; MoO₂(HMe)₂, 84927-95-7; MoO₂(HOMe)₂, 84927-96-8; MoO₂(HCl)₂, 84985-80-8; MoO₂(HNO₂)₂, 84985-81-9; PhNHOH, 100-65-2.

Supplementary Material Available: A listing of analytical data (1 page). Ordering information is given on any current masthead page.

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Reaction of Halide Ions with Tetrakis(μ -trifluoroacetato)dimolybdenum(II): Crystal Structures of (N-*n*-Bu₄)₂[Mo₂(O₂CCF₃)₄X₂] (X = Br, I) and (N-*n*-Bu₄)₂[Mo₂(O₂CCF₃)₂Br₄]

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The reaction of Mo₂(O₂CCF₃)₄ with tetra-*n*-butylammonium halides is reported. In acetone, orange solutions were obtained, which upon evaporation yielded the axial diadducts [Mo₂(O₂CCF₃)₄X₂]¹²⁻ (X = Br, I). The bromide compound crystallized in the space group *P*2₁/*n* with *a* = 16.411 (6) Å, *b* = 14.660 (7) Å, *c* = 12.313 (4) Å, β = 96.29 (3)°, *V* = 2944 (4) Å³, and *Z* = 2 while the iodo compound crystallized in the space group *P*1̄ with *a* = 13.478 (2) Å, *b* = 17.013 (2) Å, *c* = 12.638 (2) Å, α = 92.64 (1)°, β = 92.52 (1)°, γ = 78.48 (1)°, *V* = 2834 (2) Å³, and *Z* = 2. Concentrated solutions in benzene formed a gel, which upon addition of acetone yielded crystals of (N-*n*-Bu₄)₂[Mo₂(O₂CCF₃)₂Br₄], with a centrosymmetric trans anion. This compound crystallized in the space group *P*2₁/*n* with *a* = 13.379 (1) Å, *b* = 15.793 (5) Å, *c* = 13.712 (6) Å, β = 101.17 (2)°, *V* = 2842 (3) Å³, and *Z* = 2. The metal-metal distance in this compound, 2.098 (1) Å, was quite comparable to that in Mo₂(O₂CCF₃)₄ while, in the diadducts, the Mo-Mo distances, 2.134 (2) to 2.140 (2) Å, were significantly longer. The axial Mo-X distances in the diadducts were longer than when these ligands are coordinated in the equatorial plane.

Introduction

Since the discovery of dinuclear quadruply bonded molecules, the tetracarboxylate compounds have formed a cornerstone in their chemistry. The metals chromium, molybdenum, tungsten, technetium, and rhenium all form examples.¹ However, there has always been one notable difference between the compounds of molybdenum, and perhaps tungsten, and those of the other metals. In the compounds of molybdenum each metal atom is four-coordinate while the other metal atoms tend to bond to five ligands. The extra ligands occupy sites along the metal-metal bond and will be referred to as axial ligands. For technetium and rhenium the presence of axial ligands is easily explained. The M³⁺ dimers of these metals are cations. The inclusion of two anionic ligands (usually halide ions from the precursor [M₂X₈]²⁻ ions) results in a neutral complex. In the case of chromium, it is not as clear why these extra ligands are required. However, the effects of the axial ligands are important, resulting in unusually long Cr-Cr bond distances. For example, the metal-metal distance in Cr₂(O₂CCH₃)₄(H₂O)₂ is 2.362 (1) Å,² which is considerably longer than the 2.0934 (8) Å observed in Mo₂(O₂CCH₃)₄.³

When initially prepared, the dimolybdenum tetracarboxylates did not appear to have any tendency to coordinate to axial ligands. Neither the acetate nor the benzoate compounds displayed axial coordination. However, there are weak intermolecular interactions between the coordinated oxygen atoms and the axial positions of an adjacent molecule, which have important effects, at least with respect to the solid-state spectrum.³⁻⁴ On the other hand, Mo₂(O₂CCF₃)₄ displays a greater tendency to axial coordination. It was initially noted that crystals grown from solvents with donor atoms always contained molecules of solvation.⁵ Crystals of the unsolvated complex were obtained only by sublimation. In addition, the

bis(pyridine) adduct of Mo₂(O₂CCF₃)₄ was later structurally characterized.⁶ The Mo-Mo bond distance was found to be lengthened by 0.039 Å in this adduct.

In 1975, Garner and Senior reported that reacting Mo₂(O₂CCF₃)₄ with 1 or 2 equiv of tetraethylammonium bromide or iodide resulted in the formation of the mono- and diadducts.⁷ Interestingly, when the corresponding chloride was used, the only products obtained were the monoadduct or [Et₄N]₂[Mo₂(O₂CCF₃)₃Cl₃], where two chloride ions have displaced a trifluoroacetate. From the Raman spectra, these authors concluded that the Mo-Mo bonds in these axial adducts were weaker than those in the starting dimer. For this reason, it was felt that these complexes should be characterized by X-ray crystallography. In this paper we report the crystal structures of the analogous tetra-*n*-butylammonium bromide and iodide diadducts. When the bromide solutions were used, the compound (N-*n*-Bu₄)₂[Mo₂(O₂CCF₃)₂Br₄] was also isolated and structurally characterized. In addition, we discuss the solution spectrum of [Mo₂(O₂CCF₃)₄] in the presence of bromide ion. In a future paper we will report on the low-temperature polarized crystal spectra of the dibromo and diiodo adducts.

Experimental Section

All solvents used were dried by using literature methods and distilled under nitrogen prior to use. All reactions and evaporations were done under dry nitrogen.

Preparation of (N-*n*-Bu₄)₂[Mo₂(O₂CCF₃)₄Br₂]. In a typical reaction 0.5 g of Mo₂(O₂CCF₃)₄, which was prepared by the literature procedure,⁵ and 0.5 g of (N-*n*-Bu₄)Br were refluxed in benzene for 4-5

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