

Production of Hydrogen by Ultraviolet Irradiation of Binuclear Molybdenum(II) Complexes in Acidic Aqueous Solutions. Observation of Molybdenum Hydride Intermediates in Octahalodimolybdate(II) Photoreactions

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Abstract: Irradiation (254 nm) of $\text{Mo}_2(\text{SO}_4)_4^{4-}$ in aqueous H_2SO_4 at 25 °C yields 0.5 mol of H_2 and $\text{Mo}_2(\text{SO}_4)_4^{3-}$. The disappearance quantum yield for this photoreaction (0.17 ± 0.02) is independent of acid concentration (0.001–5 M H_2SO_4). Similar irradiation of $\text{Mo}_2(\text{aq})^{4+}$ in 1 M HO_3SCF_3 produces 1 mol of hydrogen and $\text{Mo}_2(\mu\text{-OH})_2(\text{aq})^{4+}$. The quantum yield for this process is 0.035 (254-nm excitation). When $\text{Mo}_2\text{Cl}_8^{4-}$ is irradiated at 254 nm in 3 M HCl, $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$ is formed with a quantum yield of 0.13. In a subsequent step, $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$ thermally decomposes to yield 1 mol of hydrogen gas and $\text{Mo}_2(\mu\text{-OH})_2(\text{aq})^{4+}$. A similar reaction occurs for $\text{Mo}_2\text{Br}_8^{4-}$ in 3 M HBr ($\Phi_{254} = 0.043$). At 313 nm the quantum yields for $\text{Mo}_2\text{X}_8\text{H}^{3-}$ formation from $\text{Mo}_2\text{X}_8^{4-}$ in 3 M HX are 0.008 (X = Cl) and 0.007 (X = Br). It is proposed that $\text{Mo}_2\text{X}_8\text{H}^{3-}$ (X = Cl, Br) is formed from the reaction of H_2O with a ligand to metal charge transfer (LMCT) excited state of $\text{Mo}_2\text{X}_8^{4-}$. No reaction is observed when $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4^{4+}$ in 0.25 M HCl is subjected to UV irradiation.

Introduction

Photooxidation reactions have been observed for a variety of metal ions in aqueous media.^{1–3} Frequently, molecular hydrogen is one product of the photoredox reaction. For example, ultraviolet excitation of $\text{Cr}(\text{aq})^{2+}$, $\text{Fe}(\text{aq})^{2+}$, $\text{Eu}(\text{aq})^{2+}$, and $\text{Ce}(\text{aq})^{3+}$ results in a one-electron oxidation of the metal center along with formation of molecular hydrogen.¹ Recently, we reported⁴ the first examples of analogous reactions involving binuclear Mo(II) and Rh(I) complex ions. In order to test the generality of this process for binuclear Mo(II) complexes, we have examined the photochemistry of $\text{Mo}_2(\text{aq})^{4+}$, $\text{Mo}_2\text{X}_8^{4-}$ (X = Cl, Br), and $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4^{4+}$ in acidic aqueous solutions.

Although photooxidation reactions in aqueous media are often loosely described as the result of charge transfer to solvent (CTTS) excitation, solvated electron production has only been established for those complex ions where independent spectroscopic studies also indicate a low-lying CTTS absorption (e.g., $\text{Cr}(\text{aq})^{2+}$, $\text{Fe}(\text{CN})_6^{4-}$, $\text{W}(\text{CN})_8^{4-}$, and $\text{Mo}(\text{CN})_8^{4-}$).^{1–3} This should be compared with the fact that solvated electrons have not been observed subsequent to flash photolysis of aqueous ferrous solutions.³ Mechanistic studies⁵ have implicated the presence of H atoms during photolysis of $\text{Fe}(\text{aq})^{2+}$. Kinetic evidence⁶ for the photooxidation reaction is consistent with a mechanism involving hydrogen evolution from a FeH^{2+} species, the latter presumably being formed from the reaction⁷ of H and $\text{Fe}(\text{aq})^{2+}$. Herein we present direct evidence that the production of hydrogen by ultraviolet irradiation of acidic aqueous solutions of octahalodimolybdate(II) ions occurs via intermediate hydride complexes.

Experimental Section

The compounds $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$,⁸ $(\text{NH}_4)_4\text{Mo}_2\text{Br}_8$,⁹ $\text{K}_4\text{Mo}_2(\text{SO}_4)_4$,¹⁰ $\text{Rb}_3\text{Mo}_2\text{Cl}_8\text{H}$,^{11,12} and $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$,¹³ were prepared by published methods. Solutions of $\text{Mo}_2(\text{aq})^{4+}$ in 1 M HO_3SCF_3 were prepared as described by Bowen and Taube.¹⁴ Constant-boiling HBr was purified by distillation from red phosphorus at reduced pressure. Although binuclear Mo(II) compounds are air stable for short (3 h) to long (1 year) periods of time in the solid state, they are exceedingly oxygen sensitive in solution. The following procedures were adopted to minimize sample decomposition. Solids were stored under N_2 prior to use. Solution spectra were measured in special evacuable cells. The apparatus consisted of

a 1.0- or 0.1-cm quartz cuvette attached to a Pyrex tube, which in turn was connected to a Teflon needle valve and a 10-mL Pyrex bulb. A 24/20 ground glass joint after the needle valve allowed attachment to a vacuum line. Solid samples, weighed in room atmosphere, were transferred to the cuvette side arm and the appropriate solvent was added to the Pyrex bulb. The cell was then sealed, attached to the vacuum line, and freeze-pump-thaw degassed for three to four cycles; at this point the solution was mixed with the solid in the side arm. For H_2SO_4 , HCl, and HBr solutions, 5 mL of the acid mixture was pipetted into the 10-mL bulb. Solutions of $\text{Mo}_2(\text{aq})^{4+}$ were transferred in a nitrogen-filled glovebag. Extinction coefficients were determined in 0.1-cm cells so that a sufficiently large amount (0.02 g) of material could be used for an accurate weighing. No correction for sample volume was made, as it is an insignificant source of error. Molar extinction coefficients were reproducible to $\pm 5\%$ and are believed to be precise within $\pm 10\%$.

Irradiations at 546, 505, and 436 nm were obtained from the output of a 1000-W Hg-Xe arc lamp that was collimated before passing through the appropriate interference filter. For some 546-nm irradiations, light from a 450-W Hanovia medium-pressure Hg lamp was passed through a Corning 4-102 glass filter combination. A 30-W low-pressure Hg lamp (Hanovia Germicidal) with a Vycor envelope was used as a source of 254-nm radiation. Owing to competing thermal side reactions, it often was vital to have an intense source of 254-nm radiation. Therefore, the output of the low-pressure Hg lamp was not filtered. The only other spectral line of appreciable intensity is at 578 nm.¹⁵ In each instance we have shown that the compounds examined are not photoactive in this spectral region. The sample temperature was maintained at 25.0 ± 1.0 °C in all photochemical experiments.

Quantum yields were determined at 254 nm employing the ferrioxalate actinometer.¹⁵ The procedure was modified to adopt the precautions recently suggested by Bowman and Demas.¹⁶ Quantum yields for the binuclear Mo(II) compounds were obtained by monitoring the decrease in intensity of the lowest energy visible absorption band. Aqueous solutions of binuclear Mo(II) ions often decompose thermally.^{11,12,14} Correction for these thermal background reactions was necessary for the quantum yield determinations. This was accomplished by alternating periods of time with and without irradiation for each sample. In most instances this correction was less than 5–10%. No corrections for inner filter effects were applied, as the quantum yields were obtained for less than 10% photolysis. Typically, three measurements were obtained, with an internal consistency of $\pm 5\%$. Except in those cases where the thermal correction was large (i.e., the photochemical reactions in 0.001 M H_2SO_4 and 6 M HCl), reproducibility of the quantum yields was $\pm 15\%$.

Hydrogen evolution was measured for photolyzed samples in vacuum-tight 1-cm spectrophotometer cells. The amount of evolved H_2

Table I. Disappearance Quantum Yields for Photooxidation Reactions of Binuclear Mo(II) Complexes in Aqueous Acids (254-nm Excitation) at 25 °C

Complex	Concn $\times 10^3$, M	Solvent	ϵ_{\max}	Φ_{254}
K ₄ Mo ₂ (SO ₄) ₄	4.41	5.0 M H ₂ SO ₄	150 ^a	0.19
K ₄ Mo ₂ (SO ₄) ₄	3.90	2.5 M H ₂ SO ₄	207	0.17
K ₄ Mo ₂ (SO ₄) ₄	3.90	0.5 M H ₂ SO ₄	230	0.16
K ₄ Mo ₂ (SO ₄) ₄	3.72	0.05 M H ₂ SO ₄	237	0.15
K ₄ Mo ₂ (SO ₄) ₄	3.84	0.001 M H ₂ SO ₄	250	0.18
Mo ₂ (aq) ⁴⁺	2.15	1 M HO ₃ SCF ₃	337 ^b	0.035
Mo ₂ (aq) ⁴⁺	1.93	1 M HO ₃ SCF ₃ / 0.15 M CH ₃ OH	337	0.031
K ₄ Mo ₂ Cl ₈ ·2H ₂ O	1.71	3 M HCl	960 ^c	0.14
K ₄ Mo ₂ Cl ₈ ·2H ₂ O	1.06	3 M HCl	960	0.13
K ₄ Mo ₂ Cl ₈ ·2H ₂ O	0.933	6 M HCl	1050 ^d	0.092
(NH ₄) ₄ Mo ₂ Br ₈	1.23	3 M HBr	1170 ^e	0.043
Rb ₃ Mo ₂ Cl ₈ H	0.537	6 M HCl	1400 ^f	0.040

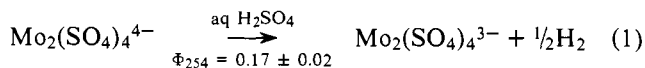
^a $\lambda_{\max} = 515$ nm. ^b Value of ϵ_{\max} taken from ref 13; $\lambda_{\max} = 505$ nm. ^c $\lambda_{\max} = 510$ nm. ^d $\lambda_{\max} = 518$ nm. ^e $\lambda_{\max} = 514$ nm. ^f $\lambda_{\max} = 419$ nm.

was determined by Toepler pumping the stirred photolyzed solution through three liquid nitrogen traps into a 12.2-mL volume and manometrically measuring the pressure. To ensure that only H₂ was collected, the gas was then passed over hot copper oxide, yielding water that was condensed in a liquid nitrogen trap, leaving only traces (<5%) of residual gas. Typically, 0.03–0.07 mmol of hydrogen gas was collected and the measurements were reproducible to ± 5 –10%.

Ultraviolet–visible absorption spectra and spectral changes were recorded utilizing a Cary 17 spectrometer.

Results

Previously, we demonstrated^{4a} that ultraviolet irradiation of Mo₂(SO₄)₄⁴⁻ in 5 M H₂SO₄ yields H₂ and Mo₂(SO₄)₄³⁻. No appreciable reaction is observed for 436-, 505-, or 546-nm excitation. At high conversion the 254-nm photoreaction is not stoichiometric. Therefore, we have measured the amount of H₂ evolved in partially photolyzed (ca. 80%) solutions; the result is that 0.49 mol of H₂ are liberated per mol of Mo₂(SO₄)₄⁴⁻ consumed. When considered together with the earlier results, the initial stoichiometry is unambiguously defined as in the equation



The quantum yield for this process is essentially independent of acid concentration from 0.001 to 5.0 M H₂SO₄ (Table I). Attempts to extend the measurements to lower acid concentrations were hampered by increasingly rapid hydrolysis. It should also be noted that a regular increase in ϵ_{\max} for the 515-nm band was observed by decreasing the acid concentrations. This may result from either partial substitution of the sulfate ligand by water or a change in the solvation structure of the Mo₂(SO₄)₄⁴⁻ ion.

Excitation (254 nm) of Mo₂(aq)⁴⁺ in 1 M trifluoromethanesulfonic acid results in the electronic absorption spectral changes shown in Figure 1. As the irradiation proceeds, the color of the solution changes from red to green, and the band at 505 nm, characteristic of Mo₂(aq)⁴⁺,¹⁴ decreases in intensity. Absorption bands attributable to product occur at 620, 570, 490, and 362 nm, and isosbestic points at 568 and 424 nm are maintained throughout the conversion. No reaction was observed under similar conditions in the dark or when the wavelength of irradiation was 366 nm. As 254-nm irradiation proceeds, small gas bubbles are formed and mass spectral analysis confirmed the presence of H₂. Measurement of the hydrogen evolved yielded 1.1 ± 0.1 mol per mol of Mo₂(aq)⁴⁺ for solutions 0.50×10^{-2} to 1.4×10^{-2} M in Mo(aq)⁴⁺. Furthermore, the absorption spectrum of the green photoproduct is identical with that of a Mo(III) species first prepared by Hartmann and Schmidt¹⁷ and formulated as a hydroxy-

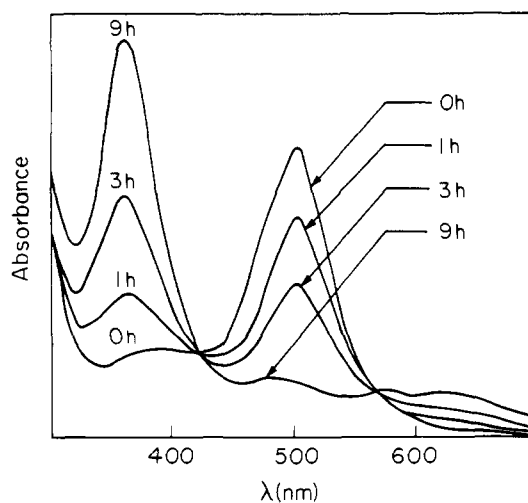
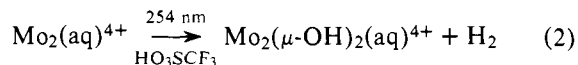


Figure 1. Electronic absorption spectral changes during 254-nm irradiation of Mo₂(aq)⁴⁺ in 1 M HO₃SCF₃ solution at 25 °C. Spectral changes were observed to be more complex for concentrations of HO₃SCF₃ less than 0.1 M.

bridged dimer by Ardon and Pernick.¹⁸ The overall photochemical reaction may be formulated as in the equation



The disappearance quantum yield for Mo₂(aq)⁴⁺ at 254 nm is 0.035.

Concentrated HCl solutions of the Mo₂Cl₈⁴⁻ ion are readily oxidized to Mo₂Cl₈H³⁻.^{11,12} The rate of this reaction is dramatically decreased in dilute HCl solutions. For example, in 3 M HCl at ambient temperature, only 15% reaction occurs over a period of 18 h. Irradiation (254 nm) of Mo₂Cl₈⁴⁻ in 3 M HCl¹⁹ induces the electronic absorption spectral changes shown in Figure 2. As the reaction proceeds the color of the solution changes from red to green; however, there are no isosbestic points. The first absorption band attributable to a product appears at 415 nm. Upon further irradiation, this peak grows slightly, a new band appears at 369 nm, and bubbles of gas are evolved. The 369-nm band also grows in if a photolyzed solution that exhibits the 415-nm absorption is allowed to stand in the dark. If an authentic sample of Rb₃Mo₂Cl₈H is dissolved in 3 M HCl, an absorption band is initially observed at 415 nm (Figure 3). Subsequently, the intensity of this band decreases at the same time a new band appears at 369 nm. Cotton and Kalbacher¹² have shown that the reaction of Mo₂X₈H³⁻ with D₂O yields HD. We have found that 0.92 mol of H₂ are evolved

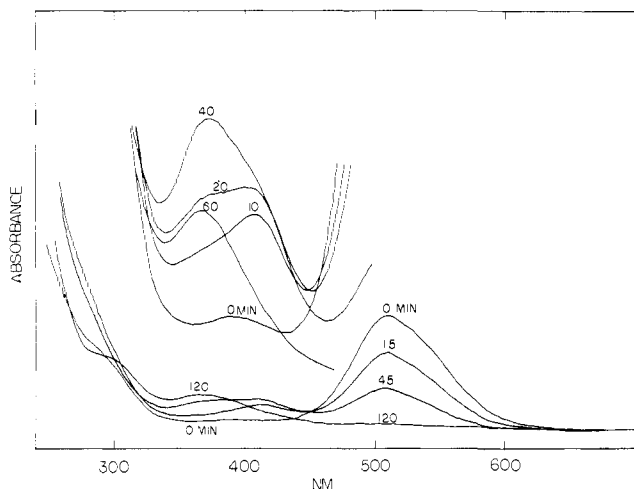
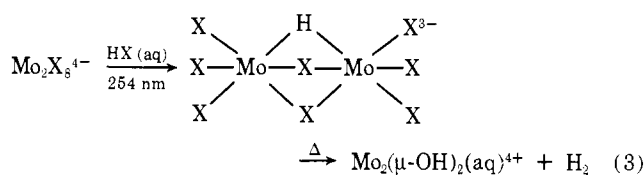


Figure 2. Electronic absorption spectral changes during 254-nm irradiation of $\text{Mo}_2\text{Cl}_8^{4-}$ in 3 M HCl solution at 25 °C. Spectral changes upon 254-nm irradiation of a more concentrated sample are also shown in the 300–500-nm region.

per mol of $\text{Rb}_3\text{Mo}_2\text{Cl}_8\text{H}$ in 3 M HCl. When a solution of $\text{Mo}_2\text{Cl}_8^{4-}$ in 3 M HCl is photolyzed to completion, 1.16 mol of H_2 are evolved per mol of $\text{Mo}_2\text{Cl}_8^{4-}$ consumed. Similar spectral changes are observed in analogous experiments performed with $\text{Mo}_2\text{Br}_8^{4-}$ in 3 and 6 M HBr.

The electronic absorption spectrum of the green product derived from the decomposition of $\text{Rb}_3\text{Mo}_2\text{Cl}_8\text{H}$ in 3 M HCl exhibits maxima at 369 ($\epsilon \sim 820$) and 655 nm (~ 85), as well as a shoulder at 600 nm ($\epsilon \sim 75$). This spectrum is virtually identical with that of $\text{Mo}_2(\mu\text{-OH})_2(\text{aq})^{4+}$ in 2 M HCl (vide supra). The extinction coefficients given above are based on this dimeric formulation of the green product. As for $\text{Mo}_2(\text{aq})^{4+}$, the photolysis of $\text{Mo}_2\text{X}_8^{4-}$ ultimately yields 1 mol of H_2 and the hydroxy-bridged molybdenum(III) dimer, as given in eq 3:



Consistent with the observations of Cotton and Kalbacher,¹² we have found that $\text{Mo}_2\text{X}_8\text{H}^{3-}$ is stable in more concentrated acid solutions. Photolysis (254 nm) of $\text{Mo}_2\text{Cl}_8^{4-}$ in 6 M HCl initially (<5% reaction) produces only $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$, with a disappearance quantum yield of 0.092. At greater than 10% conversion, the production of $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$ levels off and then decreases upon further irradiation. This is most likely a result of secondary photolysis. In fact, $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$ in 6 M HCl disappears with a quantum yield of 0.040 when excited at 254 nm. The photoproduct in this instance possesses an intense absorption at 305 nm and a weaker band at 512 nm. An isosbestic point is maintained at 490 nm throughout the photolysis. Because $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$ absorbs more strongly than $\text{Mo}_2\text{Cl}_8^{4-}$ at 254 nm, the secondary photolysis can account for the fact that the formation of $\text{Mo}_2(\mu\text{-OH})_2(\text{aq})^{4+}$ is not quantitative at high conversions for the photolysis carried out in 3 M HCl. In fact, the development of a shoulder at 300–305 nm at long irradiation times (Figure 2) is evidence for the product of secondary photolysis.

We have also found a wavelength dependence of the quantum yield for the above reactions. No reaction can be detected when $\text{Mo}_2\text{X}_8^{4-}$ solutions in 3 M HX are irradiated at 505 nm, which is near the maximum of the $\delta \rightarrow \delta^*$ absorption. Irra-

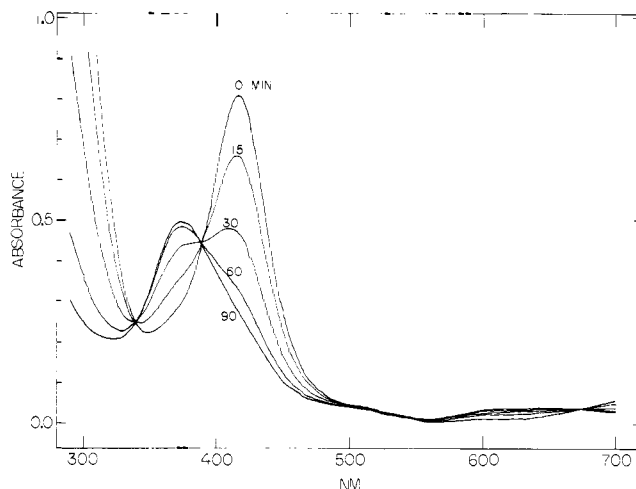


Figure 3. Electronic absorption spectral changes of a 5.84×10^{-3} M solution of $\text{Rb}_3\text{Mo}_2\text{Cl}_8\text{H}$ in 3 M HCl subsequent to mixing at 25 °C. The cell path length was 0.1 cm.

diation of 3 M HX solutions of $\text{Mo}_2\text{X}_8^{4-}$ (ca. 10^{-3} M) at 313 nm gives disappearance quantum yields of 0.008 ($\text{X} = \text{Cl}$) and 0.007 ($\text{X} = \text{Br}$). The quantum yields (Table I) markedly increase, especially for $\text{X} = \text{Cl}$, when 254-nm radiation is employed.

No spectral changes were observed when a solution of $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4^{4+}$ in 0.25 M HCl–0.3 M $\text{O}_2\text{CCH}_2\text{NH}_3$ was irradiated for 12 h with the unfiltered radiation of a 200-W Hg–Xe lamp.

Discussion

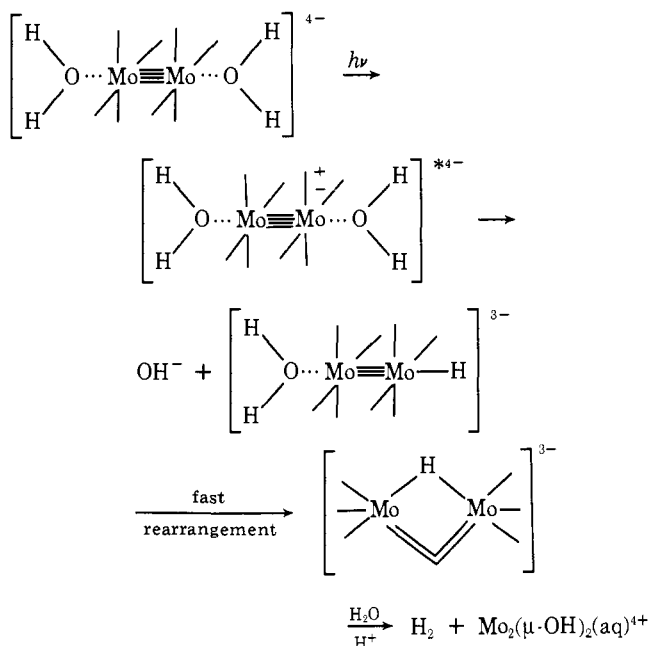
We have shown that ultraviolet irradiation of $\text{Mo}_2(\text{SO}_4)_4^{4-}$, $\text{Mo}_2(\text{aq})^{4+}$, and $\text{Mo}_2\text{X}_8^{4-}$ complexes in aqueous acidic solutions results in oxidation of the $[\text{Mo}(\text{II})]_2$ unit. In a separate study we have found²⁰ that UV excitation of $\text{Mo}_2\text{Cl}_4\text{P}_4$ ($\text{P} = \text{PEt}_3$, $\text{P}(n\text{-Bu})_3$, PEtPh_2) in chlorocarbon solvents yields trichloro-bridged dimolybdenum(III) complexes. Irradiation ($\lambda \leq 366$ nm) of $\text{Re}_2\text{Cl}_8^{2-}$ in acetonitrile solution does not result in photooxidation, however, as monomeric rhenium(III) complexes are produced.²¹ It does not appear that the excited state ReRe bond cleavage occurs by a dissociative pathway, but rather is assisted by one or more acetonitrile molecules.²² All the photooxidations and the one photocleavage observed for quadruply bonded ($\sigma^2\pi^4\delta^2$ ground state) binuclear complexes involve upper excited states, as in no case have we found any photoactivity associated with irradiation of the low-energy absorption band that is attributable to the allowed $\delta \rightarrow \delta^*$ transition (this band is in the 500-nm region in the spectra of $\text{Mo}_2(\text{SO}_4)_4^{4-}$, $\text{Mo}_2(\text{aq})^{4+}$, and $\text{Mo}_2\text{X}_8^{4-}$ complexes; see Table I for λ_{max} values).²³

The pattern of photochemical behavior that is developing for quadruply bonded binuclear complexes sharply contrasts with the prominence of dissociative photocleavage pathways^{24,25} in singly bonded species such as $\text{Mn}_2(\text{CO})_{10}$. The failure to observe dissociative photocleavage in binuclear Mo(II) complexes is not really surprising, as both theoretical calculations and experimental spectroscopic studies have established that strong metal–metal bonding persists in the low-lying $\delta\delta^*$ and $\delta\pi^*$ excited states.²³ If all the upper metal-localized excited states are converted rapidly to these low-lying inactive ones, as seems likely, then the photoactivity must be associated with charge transfer excited states, and there is no reason to believe that these would lead to dissociative metal–metal bond cleavage.

It is important to emphasize that we have identified a metal hydride, $\text{Mo}_2\text{X}_8\text{H}^{3-}$, as a key intermediate in the H_2 -pro-

ducing photoreaction involving $\text{Mo}_2\text{X}_8^{4-}$. It is our proposal that it is a ligand to metal charge transfer (LMCT) excited state of $\text{Mo}_2\text{X}_8^{4-}$ that leads to the formation of $\text{Mo}_2\text{X}_8\text{H}^{3-}$. In the case of $\text{Mo}_2\text{Cl}_8^{4-}$, the lowest $\text{Cl}(\pi) \rightarrow \delta^*$ transition is believed to fall at about 270 nm.²³ Thus irradiation at 254 nm probably produces several $\text{Cl}\delta^*$ LMCT states, which, because conversion to metal-localized states may be relatively slow,²⁶ could be responsible for the formation of $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$. From the difference in the optical electronegativities²⁷ of Cl^- and Br^- , the lowest LMCT band of $\text{Mo}_2\text{Br}_8^{4-}$ is estimated to fall at 320 nm. Thus it is probable that the shoulder at 317 nm ($\epsilon \sim 550$) (3 M HBr solution) in the spectrum of $\text{Mo}_2\text{Br}_8^{4-}$ is attributable to an LMCT transition. Our observation that the relative increase of the quantum yields at 254 nm over those at 313 nm is greater for $\text{Mo}_2\text{Cl}_8^{4-}$ than for $\text{Mo}_2\text{Br}_8^{4-}$ is consistent with the photoactive state being at lower energy in the latter complex.

A photoactive state possessing LMCT character could lead to $\text{Mo}_2\text{X}_8\text{H}^{3-}$ formation by the following mechanism:



As the $\text{X}\delta^*$ LMCT excited states possess increased electron density at the metal centers, Mo-H bond formation is a reasonable reaction pathway. Such excited-state pathways involving metal-hydrogen bond formation could provide an attractive alternative to the common CTTS routes¹⁻³ for hydrogen production, as the latter, which generate solvated electrons or hydrogen atoms, necessarily require large photon energies.

A possibly relevant observation in connection with our proposal that an LMCT state of $\text{Mo}_2\text{X}_8^{4-}$ leads to Mo-H bond formation is the lack of reactivity of $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4^{4+}$ upon ultraviolet irradiation ($\lambda \geq 200$ nm). The electronic energy levels of $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4^{4+}$ should not differ markedly from those of $\text{Mo}_2(\text{O}_2\text{CH})_4$, where both theoretical and spectroscopic studies have established²⁸ that the lowest

LMCT excited state lies above one of the metal to ligand charge transfer (MLCT) type. Following the assignment²⁸ of the electronic spectrum of $\text{Mo}_2(\text{O}_2\text{CH})_4$, the intense 300-nm absorption exhibited¹³ by $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4^{4+}$ is attributed to an MLCT transition. Ultraviolet irradiation of $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4^{4+}$ leads mainly to excitation of this MLCT state and, as electron density is decreased on the metal, it is reasonable to assume that an Mo-H bond does not form.

The lowest LMCT transitions in $\text{Mo}_2(\text{aq})^{4+}$ and $\text{Mo}_2(\text{SO}_4)_4^{4-}$ are predicted from optical electronegativities²⁷ to fall below 254 nm (190 nm, $\text{Mo}_2(\text{aq})^{4+}$, 230 nm, $\text{Mo}_2(\text{SO}_4)_4^{4-}$). Thus it is less likely that LMCT states are involved in the H_2 -producing photoreactions of these binuclear Mo(II) complexes. The nature of the photoactive state and the possible intermediacy of molybdenum hydride species in these cases are problems that will require additional study.

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