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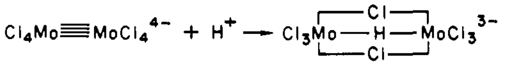
Kinetic Studies of Metal–Metal Bonded Species: Protonation of $Mo_2Cl_8^{4-}$ and Hydrogen Evolution from $Mo_2Cl_8H^{3-}$[1]

Steven S. Miller and Albert Haim*

Contribution from the Department of Chemistry, State University of New York, Stony Brook, New York 11794. *Received February 2, 1983*

Abstract: The reaction between octachlorodimolybdate(II,II) and protons to produce the triply bridged species $Cl_3MoCl_2HMoCl_3^{3-}$ was studied at 25 °C with [HCl] = 6–12 M. The reaction is first order in $Mo_2Cl_8^{4-}$ and obeys a linear dependence with respect to the acidity function H_0. The hydrido-bridged complex $Cl_3MoCl_2HMoCl_3^{3-}$ decomposes in hydrochloric acid solutions with [HCl] < 3 M to yield hydrogen and the dihydroxy-bridged dimer $Mo_2(OH)_2Cl_x^{(x-4)-}$. Kinetic studies at 25 °C and ionic strength 3.0 M are compatible with the rate law $a[Mo_2Cl_8H^{3-}]/(b + [H^+][Cl^-])$, where $a = (5.75 \pm 0.48) \times 10^{-3}$ M^{-2} s^{-1} and $b = 0.44 \pm 0.06$ M^{-2}. When [HCl] < 0.5 M, a relatively rapid equilibrium is reached, prior to the evolution of hydrogen, between $Mo_2Cl_8H^{3-}$ and an intermediate of composition $Mo_2Cl_7(OH)H^{3-}$. The mechanism of these reactions is discussed in some detail.

A great deal of synthetic and structural work has been carried out during the last 20 years in the significant and novel area of metal–metal bonded complexes,[2] but it is only recently that reactivity patterns for these compounds have been studied systematically.[3] In the present paper we report detailed kinetic studies of two reactions. First, we examine the protonation of octachlorodimolybdate(II,II) in strong hydrochloric solutions (eq 1).



$$Cl_4Mo{\equiv}MoCl_4^{4-} + H^+ \rightarrow Cl_3Mo(\mu\text{-}Cl)_2(\mu\text{-}H)MoCl_3^{3-} \qquad (1)$$

This interesting reaction represents the addition of a proton across a molybdenum–molybdenum quadrupole bond and results in the two-electron reduction of the proton, the breaking of the multiple bonding between the molybdenum centers, and the formation of chloride bridges. The second reaction is the decomposition of the hydride complex formed in eq 1 according to eq 2.[4,5] This reaction

$$Mo_2Cl_8H^{3-} + 2H_2O \rightarrow Mo_2(OH)_2Cl_x^{(x-4)-} + H_2 + (8 - x)Cl^- + H^+ \qquad (2)$$

illustrates the importance of hydride intermediate species[6] in reactions that result in the evolution of hydrogen.

Experimental Section

Materials. Trifluoromethanesulfonic acid (Eastman) was purified by distillation at reduced pressure. Lithium trifluoromethanesulfonate monohydrate was prepared by mixing stoichiometric amounts of the purified acid and lithium carbonate. The resulting neutral solution was boiled with activated charcoal. After removal of the charcoal, the resulting solution was evaporated to dryness at 100 °C. Lithium chloride was recrystallized from purified water. The purification of *p*-toluenesulfonic acid was achieved by dissolution of the Eastman product in boiling dichloromethane containing activated charcoal. After removal of the charcoal and upon cooling, fine white needles separated from the solution. The house-distilled water was purified by allowing it to pass through a Barnstead ion-exchange demineralizer followed by distillation in a modified (all glass) Corning Model 1 B apparatus. All other chemicals were reagent grade. Argon was utilized to deaerate all the solutions used in the measurements. $K_4Mo_2Cl_8$ and $Cs_3Mo_2Cl_8H$ were synthesized by literature[7,8] methods and were stored in an argon-filled desiccator.

Kinetic Measurements. The desired amount of the molybdenum complex was weighed on a microbalance and then transferred to a 2-cm spectrophotometric cell equipped with a removable glass stopcock. The cell was purged of air by a stream of argon and then placed in the thermostated cell compartment of a Cary 17 spectrophotometer. A solution containing the desired concentrations of chloride and hydrogen ions and of background electrolyte was placed in a constant temperature bath and deaerated by flushing the solution with argon. After temperature equilibration was reached, 6.0 mL of the solution was added anaerobically (syringe technique) to the cell. The cell was shaken rapidly to achieve dissolution of the solid. The cell was then returned to the compartment of the spectrophotometer and a recording of absorbance vs. time was obtained. The wavelengths of observation were 520 and 420 nm for $Mo_2Cl_8^{4-}$ and $Mo_2Cl_8H^{3-}$, respectively. At the completion of each run, the solutions were analyzed for hydrogen and chloride ions by titration with standard sodium hydroxide and silver nitrate (Mohr's method) solutions, respectively. In the case of reaction 1, data were collected for 8–10 half-lives. First-order rate constants (k_{obsd}) were obtained from least-squares fits of ln $(A_t - A_\infty)$ to time. Values of A_t and A_∞, the absorbances at time t and at the completion of the reaction, respectively, were obtained by utilizing a digitizer interfaced to a Hewlett-Packard 9820 calculator. A somewhat different procedure was utilized for reaction 2 because the initial reaction product undergoes further reaction at long times, and a reliable value of A_∞ cannot be obtained experimentally. Values of A_t were obtained as above (2–3 half-lives), and an iterative least-squares procedure was utilized. An initial estimate of A_∞ was incremented so the A_t vs. t data gave the best fit to the equation $\ln (A_t - A_\infty) = \ln (A_0 - A_\infty) - k_{obsd}t$, and the least-squares value of k_{obsd} was then calculated.

Table I. Observed First-Order Constants for the Protonation of $Mo_2Cl_8^{4-}$ at 25.0 °C[a]

[HCl], M	$k \times 10^4$, s^{-1}	[HCl], M	$k \times 10^4$, s^{-1}
5.78	0.227	9.79	10.8
5.89	0.154	9.91	11.7
7.98	1.77	9.94	13.1
8.03	1.86	11.66	36.3
8.91	4.53	11.85	42.9

[a] $[Mo_2Cl_8^{4-}] = (3-5) \times 10^{-4}$ M; oxygen-free solutions.

Results and Discussion

Protonation of $Mo_2Cl_8^{4-}$ (Eq 1). When $K_4Mo_2Cl_8$ is allowed to dissolve in hydrochloric acid solutions with [HCl] > 6 M, the pink color of the $Mo_2Cl_8^{4-}$ ion is gradually replaced by the yellow color of $Mo_2Cl_8H^{3-}$. The reaction stoichiometry is very clean: the characteristic absorption maximum of $Mo_2Cl_8^{4-}$ near 520 nm[9] decreases while the absorbance at 420 nm, characteristic of $Mo_2Cl_8H^{3-}$,[10] increases, isosbestic points being maintained throughout the reaction at 474 and 665 nm. At the completion of the reaction (12 M HCl), the absorbance at 420 nm is within 5% of that calculated for quantitative formation of $Mo_2Cl_8H^{3-}$.

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[1] (a) This work was supported by Grants CHE-7909253 and CHE-8203887 from the National Science Foundation. (b) Presented at the Second Chemical Congress of the North American Continent (180th National Meeting of the American Chemical Society), Las Vegas, NV, Aug 25–26, 1980, Paper INOR 196.

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[5] Bino, A.; Ardon, M. *J. Am. Chem. Soc.* **1977**, *99*, 6446.

[6] Trogler, W. C.; Erwin, D. K.; Geoffroy, G. L.; Gray, H. B. *J. Am. Chem. Soc.* **1978**, *100*, 1160.

[7] Brencic, J. V.; Cotton, F. A. *Inorg. Chem.* **1970**, *9*, 351.

[8] Bennett, M. J.; Brencic, J. V.; Cotton, F. A. *Inorg. Chem.* **1969**, *8*, 1060.

[9] The wavelength of the absorption maximum and the molar absorbance at the maximum are functions of the hydrochloric acid concentration: for [HCl] = 3, 6, and 12 M, values of λ_{max} in nm (ϵ, M^{-1} cm^{-1}) are 514 (8.5×10^2), 520 (8.8×10^2), and 527 ($\sim 1 \times 10^3$), respectively. These rather modest changes suggest that the protonation according to eq 3 is unfavorable even in 12 M HCl.

[10] Values of the absorption maximum and molar absorbance for $Mo_2Cl_8H^{3-}$ appear to be independent of hydrochloric acid concentration; for [HCl] = 6 and 12 M, values of λ_{max} in nm (ϵ, M^{-1} cm^{-1}) are 420 (1.68×10^3) and 420 (1.65×10^3), respectively.

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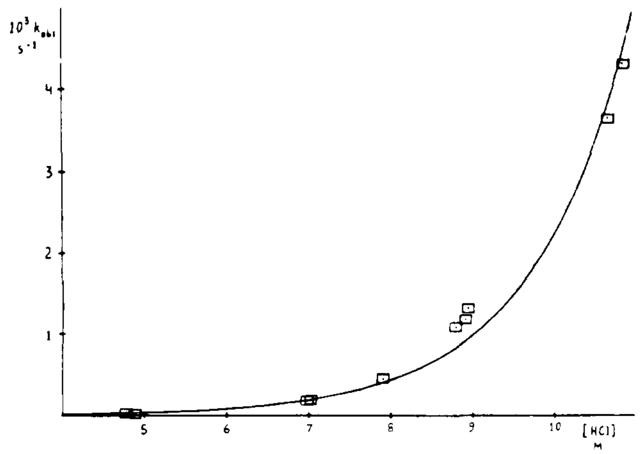
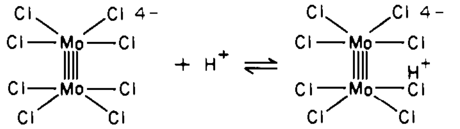


Figure 1. Rate constants for protonation of $Mo_2Cl_8^{4-}$ vs. concentration of hydrochloric acid. Squares: experimental points. Solid line: calculated from $k_{obsd} = 10^{(-6.54-H_0)}$.

Reaction 1 was studied as a function of hydrochloric acid concentration in the range 5.78–11.85 M. Because of the high concentration of acid needed to obtain measurable rates, no attempts were made to maintain ionic strength constant. The reaction follows excellent first-order kinetics up to 90% reaction. Observed rate constants, listed in Table I, exhibit a 7.5-order dependence with respect to hydrochloric acid concentration. The logarithms of the observed rate constants exhibit a first-order dependence with respect to the Hammett acidity function H_0.[11] The latter result will be seen in Figure 1 where the observed rate constants are plotted vs. [HCl] and the solid line represents the best fit to the equation $k_{obsd} = 10^{(-6.54-H_0)}$.

The dependence of k_{obsd} upon H_0 is consistent with the two-step A-1 mechanism.[11] In the first step, protonation of the quadrupole bond obtains according to eq 3, and this is followed by the rearrangement of the protonated species to the hydrido-bridged product as in eq 4.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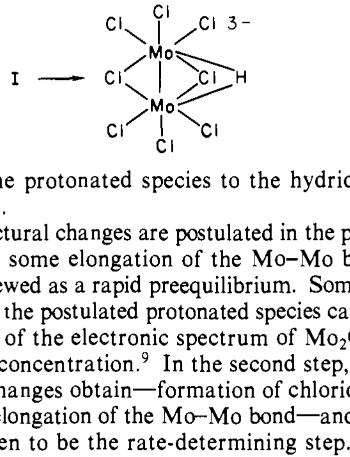
(4)

Little or no structural changes are postulated in the protonation reaction—perhaps some elongation of the Mo–Mo bond—and therefore eq 3 is viewed as a rapid preequilibrium. Some evidence for the existence of the postulated protonated species can be found in the dependence of the electronic spectrum of $Mo_2Cl_8^{4-}$ upon hydrochloric acid concentration.[9] In the second step, eq 4, profound structural changes obtain—formation of chloride and hydride bridges and elongation of the Mo–Mo bond—and therefore this process is taken to be the rate-determining step.

Hydrogen Evolution from $Mo_2Cl_8H^{3-}$ (Eq 2). When $Cs_3Mo_2Cl_8H$ is allowed to dissolve in solutions containing 2–3 M HCl, the yellow color of the initial solution gradually changes to green. The characteristic absorption of $Mo_2Cl_8H^{3-}$ at 420 nm decreases whereas maxima develop at 650, 610, and 372 nm, and concomitantly hydrogen is evolved. Isosbestic points are maintained for about 1 h at 700, 556, and 390 nm, but these shift slightly during the next 3 h. The relatively stable product that is attained in about 4–5 h has molar absorbances 8.4 × 10^2, 1.1 × 10^2, and 1.1 × 10^2 at 372, 610, and 650 nm, respectively. Our observations, in excellent agreement with literature results,[5,6] demonstrate that the reaction product is the dihydroxy-bridged molybdenum(III) dimer[12] in which a certain number of water molecules in the inner coordination shell have been replaced by chloride ions.[13] A total of 52 kinetic runs pertaining to the hydrogen evolution reaction (eq 2) were performed at 25 °C and ionic strength 3.0 M. In one set (18 experiments), $[Cl^-] = 3.0$ M, $[H^+] = 0.11$–2.0 M, $[Li^+] = 2.89$–1.0 M. In the second set (17 experiments), $[H^+] = 3.0$ M, $[Cl^-] = 0.50$–2.0 M, $[CF_3SO_3^-]$ or $[p\text{-}CH_3C_6H_4SO_3^-] = 2.5$–1.0 M. In the third set, $[H^+] = 0.28$–1.70 M, $[Cl^-] = 0.28$–2.0 M, with the remaining ionic strength being made up by Li^+ and $CF_3SO_3^-$. Finally, one set of four experiments had $[H^+] = [Cl^-] = 3.0$ M. Observed rate constants for all the experiments were fitted to the empirical rate law given by eq 5. The nonlinear

$$k_{obsd} = \frac{a}{b + [H^+][Cl^-]} \tag{5}$$

least-squares values of a and b are (5.75 ± 0.48) × 10^{-3} M^{-2} s^{-1} and 0.44 ± 0.06 M^{-2}, respectively. It will be seen in Figure 2 by comparing the experimental points with the curve calculated from eq 5 that the rate law describes reasonably well the dependence of observed rate coefficients upon hydrogen and chloride ion concentrations in the range studied. However, it must be admitted that additional, small contributions by terms containing inverse square dependences upon $[Cl^-]$ and/or $[H^+]$ cannot be ruled out.

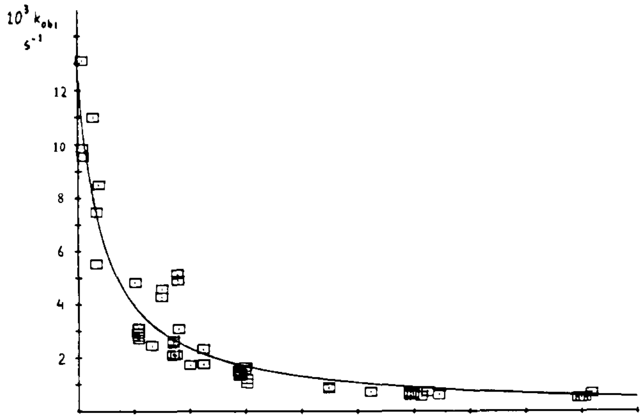

Figure 2. Rate constants for hydrogen evolution from $Mo_2Cl_8H^{3-}$ vs. $[H^+][Cl^-]$. Squares: experimental points. Solid line: calculated from $k_{obsd} = 5.75 \times 10^{-3}/(0.44 + [H^+][Cl^-])$.

Additional evidence for the importance of the inverse $[H^+][Cl^-]$ pathway comes from earlier observations[5] and from kinetic measurements at low hydrochloric acid concentrations. When $Cs_3Mo_2Cl_8H$ is allowed to dissolve in solutions containing relatively low concentrations of hydrochloric acid at ionic strength 3.0 M (<0.5 M), a very rapid (a few seconds at room temperature) formation of a pink intermediate[5] (maximum absorption at ~515 nm with molar absorbance ~80 M^{-1} cm^{-1}) is observed.[14] The intermediate then decays (isosbestic point at 485 nm) to the dihydroxy-bridged dimer with concomitant hydrogen evolution.

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[11] Rochester, C. H. "Acidity Functions"; Academic Press: New York, 1970.

[12] Ardon, M.; Pernick, A. *Inorg. Chem.* **1974**, *13*, 2275.

[13] For the bis(μ-hydroxo)octaaquomolybdenum(III,III) ion the maxima are at 360, 572, and 624 nm.[12] Substitution of one water by one chloride yields a binuclear ion that absorbs at 362, 589, and 631 nm.[12] Evidently, in the media we use, the dihydroxy-bridged dimer contains more than one chloride ion. The molybdenum dimer is a metastable intermediate under the conditions of our experiments, and after a day the solutions exhibit a pinkish color (a broad band in the 490-nm region). Presumably the dimer yields an equilibrium mixture of monomeric chloro- and aquomolybdenum(III) species. Because of the instability of the product of reaction 2, the absorbance measurements were taken only for 2–3 half-lives and values of A_∞ were adjusted assuming a first-order process.

[14] It is easily shown that the intermediate is not $Mo_2Cl_8^{4-}$ (which also has an absorption maximum near 515 nm[9]). First, $Mo_2Cl_8^{4-}$ is stable in 1 M HCl, whereas the pink intermediate has a lifetime of about 1 min. Second, when the intermediate is allowed to be formed at low [HCl] and then the concentration of HCl is rapidly increased to 6 M, the pink intermediate quantitatively produces $Mo_2Cl_8H^{3-}$ within a few seconds, whereas the time necessary to protonate $Mo_2Cl_8^{4-}$ in 6 M HCl is of the order of a day.

These observations are in excellent agreement with those reported earlier[5] by Bino and Ardon, who, in addition, carried out redox titrations of the starting yellow $Mo_2Cl_8H^{3-}$, of the pink intermediate, and of the final green dimeric product. Bino and Ardon[5] reported that the net apparent oxidation number of molybdenum in $Mo_2Cl_8H^{3-}$ and in the pink dimer is 2.5. Moreover, they found that during the conversion of the pink intermediate to the green dimer, the oxidation number of molybdenum increases from 2.5 to 3.0 as hydrogen is evolved. On the basis of these observations, Bino and Ardon[5] inferred that the intermediate pink species is a partially aquated form of $Mo_2Cl_8H^{3-}$. Our kinetic measurements of the rapid equilibration between $Mo_2Cl_8H^{3-}$ and the pink intermediate confirm the above conclusion and in addition provide information about the number of chloride ions replaced. With $[H^+] = 0.10–3.0$ M and $[Cl^-] = 3.0–0.23$ M, the pseudo-first-order rate constant for approach to equilibrium is given by $k_{obsd} = c + d/[H^+][Cl^-]$ with $c \sim 6 \times 10^{-2}$ s^{-1} and $d \sim 9 \times 10^{-3}$ M^{-2} s^{-1}.

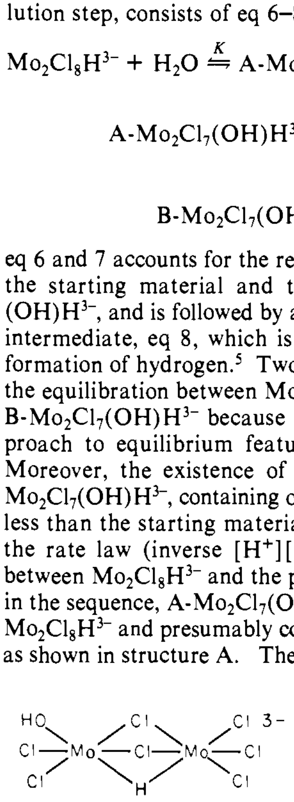
All of the above observations and measurements serve to establish quite firmly some of the key features of the mechanism. The *minimal reaction scheme demanded* by the kinetic studies of the two stages of the reaction, namely the equilibration between $Mo_2Cl_8H^{3-}$ and the pink intermediate and by the hydrogen evolution step, consists of eq 6–8. The sequence of steps given by

$$Mo_2Cl_8H^{3-} + H_2O \overset{K}{\rightleftharpoons} A\text{-}Mo_2Cl_7(OH)H^{3-} + H^+ + Cl^- \quad (6)$$

$$A\text{-}Mo_2Cl_7(OH)H^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B\text{-}Mo_2Cl_7(OH)H^{3-} \quad (7)$$

$$B\text{-}Mo_2Cl_7(OH)H^{3-} \xrightarrow{k_2} \text{products} \quad (8)$$

eq 6 and 7 accounts for the relatively rapid equilibration between the starting material and the pink intermediate, B-$Mo_2Cl_7(OH)H^{3-}$, and is followed by a relatively slow reaction of the pink intermediate, eq 8, which is the rate-determining step for the formation of hydrogen.[5] Two steps are necessary to account for the equilibration between $Mo_2Cl_8H^{3-}$ and the pink intermediate B-$Mo_2Cl_7(OH)H^{3-}$ because of the finding that the rate of approach to equilibrium features an inverse $[H^+][Cl^-]$ term.[15] Moreover, the existence of two isomeric species, A- and B-$Mo_2Cl_7(OH)H^{3-}$, containing one hydroxide more and one chloride less than the starting material $Mo_2Cl_8H^{3-}$ is also demanded by the rate law (inverse $[H^+][Cl^-]$ term)[15] for the equilibration between $Mo_2Cl_8H^{3-}$ and the pink intermediate. The first isomer in the sequence, A-$Mo_2Cl_7(OH)H^{3-}$, is in rapid equilibrium with $Mo_2Cl_8H^{3-}$ and presumably contains a terminal hydroxide ion[16,17] as shown in structure A. The second isomer is the observed pink intermediate, which can return to the first isomer (reverse of eq 7) or undergo a rate-determining process (eq 8) that produces H_2. Since the pink intermediate, B-$Mo_2Cl_7(OH)H^{3-}$ exists in substantial concentrations even at relatively high $[H^+]$ (as long as $[Cl^-]$ is low), it is almost certain that the hydroxide group occupies a bridging position, a formulation adopted in the proposed structure B.



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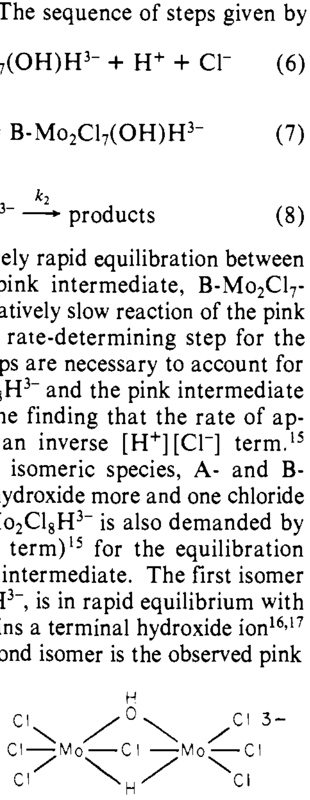

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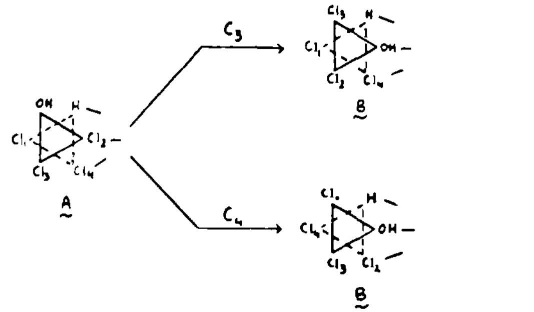

Figure 3. Rotation about pseudo-C_3 and C_4 axes of $Mo_2Cl_7(OH)H^{3-}$. Only one molybdenum atom is shown. The C_3 axis is perpendicular to the OH, Cl_2, and Cl_3 planes. The C_4 axis is collinear with the Mo–H bond.

According to the mechanism given by eq 6–8, the rate constant for equilibration between $Mo_2Cl_8H^{3-}$ and the pink intermediate is equal to $k_{-1} + k_1K/[H^+][Cl^-]$, and therefore $k_{-1} \sim 6 \times 10^{-2}$ s^{-1} and $k_1K \sim 9 \times 10^{-3}$ M^{-2} s^{-1}. The rate constant for hydrogen evolution is equal to $K(k_1/k_{-1})k_2/(K(k_1/k_{-1}) + [H^+][Cl^-])$, and therefore $k_1 = 1.3 \times 10^{-2}$ s^{-1} and $Kk_1/k_{-1} = 0.44$ M^{-2}. The agreement between the values of Kk_1/k_{-1} measured by two different procedures (kinetics of equilibration according to eq 6 and 7, preliminary value of ~0.2 M^{-2}, and kinetics of hydrogen evolution, 0.44 M^{-2}) is considered acceptable.

According to the postulated structures A and B, the process of isomerization in eq 7 involves the interchange between bridging and terminal ligands, a process studied in great detail for binuclear metal carbonyl complexes containing two bridges.[18] For the isomerization A $\rightleftharpoons$ B, since the two metal centers are connected by three bridges (only one of which, the hydride, is electron deficient), the well-established[18] mechanism for carbonyl scrambling, namely, concerted opening of the two CO bridges followed by rotation about the metal–metal bond and re-formation of the bridges, is most likely not applicable. Plausible mechanisms for terminal-bridging ligand interchange in the triply bridged case involve 120° rotation about a pseudo-C_3 axis or 90° rotation about a pseudo-C_4 axis, as shown in Figure 3. The trigonal twist mechanism is somewhat more attractive since only one bridging bond is broken—in the rotation about the pseudo-C_4 axis two bonds must be broken. Moreover, in the trigonal twist mechanism a group either cis or trans to the bridging hydride can swing into a bridging position, whereas in the pseudo-C_4 rotation mechanism only groups cis to the bridging hydride can do so. If the bridging hydride, which has a structural trans effect,[16,19] also has a trans labilizing influence, then the C_3 rotation mechanism would be favored.

Finally, we consider the hydrogen evolution step. The kinetic measurements demonstrate that the pink intermediate undergoes a first-order rate-determining reaction but provide no other mechanistic information. Whether the production of dihydrogen occurs in the rate-determining step or in a subsequent fast reaction cannot be ascertained. The important finding has been reported that when $Mo_2Cl_8D^{3-}$ is allowed to decompose in H_2O, at least 95% of hydrogen evolved consists of HD.[4] Therefore, the dihydrogen must be produced by combination of the hydride in B-$Mo_2Cl_7(OH)H^{3-}$ (or a species derived from it by isomerization or hydrolysis) with the proton of a water molecule or of a hydronium ion. Unfortunately, the form of the rate law for the hydrogen evolution step does not provide an insight into this important aspect of the chemistry of $Mo_2Cl_8H^{3-}$.

Registry No. $K_4Mo_2Cl_8$, 25448-39-9; $Cs_3Mo_2Cl_8H$, 57719-40-1; H_2, 1333-74-0; H^+, 12408-02-5.

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(15) A one-step, direct equilibration between $Mo_2Cl_8H^{3-}$ and a species derived by replacement of a Cl^- by OH^- would require a rate term directly proportional to $[Cl^-][H^+]$.

(16) A terminal OH^- could be located either cis or trans with respect to the bridging hydride. In view of the trans labilizing effect of the hydride ligand, it is tempting to suggest that the trans chloride is replaced. Note that the bridging H in $Mo_2Cl_8H^{3-}$ has a substantial structural trans effect: Bino, A.; Bursten, B. E.; Cotton, F. A.; Fang, A. *Inorg. Chem.* **1982**, *21*, 3755. These authors report that Mo–Cl distances to Cl^- trans to H^- are ca. 0.1 Å longer than for Cl^- trans to Cl^-.

(17) Evidently, eq 6 represents the sum of two equilibria: the replacement of one chloride by water, $Mo_2Cl_8H^{3-} + H_2O \rightleftharpoons Mo_2Cl_7(OH_2)H^{2-} + Cl^-$, followed by proton dissociation from the bound water, $Mo_2Cl_7(OH_2)H^{2-} \rightleftharpoons Mo_2Cl_7(OH)H^{3-} + Cl^-$.

(18) Adams, R. D.; Cotton, F. A. In "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; p 489.

(19) Cotton, F. A.; Roth, W. J.; Schultz, A. J.; Williams, J. M., in press. We are grateful to Professor Cotton for a preprint of this manuscript.