

X-ray Absorption Edge and EXAFS Spectroscopic Studies of Molybdenum Ions in Aqueous Solution

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Received November 30, 1981

Abstract: X-ray absorption edge and EXAFS spectra have been measured for acidic-aqueous solutions containing Mo(II), Mo(III), Mo(IV), and Mo(V). The edges increase in energy according to Mo(II) << Mo(III) < Mo(IV) < Mo(V). Bond distances calculated for the binuclear species are as follows: Mo(II)/1 M CF₃SO₃H (aqueous), Mo-Mo = 2.12 Å; Mo-O(OH₂) = 2.14 Å; Mo(III)/3 M CH₃SO₃H (aqueous), Mo-Mo = 2.54 Å; Mo-O(bridging OH) = 2.06 Å; Mo-O(OH₂) = 2.20 Å; Mo(V)/3 M HCl (aqueous) (Mo₂O₄²⁺ core), Mo-Mo = 2.56 Å; Mo-O(terminal oxo) = 1.68 Å; Mo-O(bridging oxo) = 1.93 Å. The EXAFS data for Mo(IV) in 4 M methanesulfonic acid are consistent with the accepted Mo₃O₄⁴⁺ (aq) (Mo-Mo = 2.49 Å; Mo-O(μ₂) = 1.88 Å) formulation for the red ion. Estimates of the Mo-Mo Debye-Waller factors were obtained by comparison with σ = 0.0377 Å calculated for Mo₂⁴⁺ (aq). The stiffest Mo-Mo bond is in Mo₃O₄⁴⁺ (aq) (σ = 0.031 Å); σ values for Mo₂(μ-OH)₂⁴⁺ and Mo₂O₄²⁺ (aq) are 0.044 and 0.037 Å, respectively.

Molybdenum compounds play an important role in both biological and industrial catalysis, owing in part to their rich oxidation-reduction chemistry in aqueous solutions.² It is now well established that all oxidation levels from II through VI are represented by stable ionic species in the aqueous chemistry of molybdenum, and the main features of the core structures of several of these ions are known.³ Our interest in this area in recent years has centered mainly on the red species that is present in acidic-aqueous solutions of Mo(IV).³⁻⁷ Although our extended X-ray absorption fine structure (EXAFS) spectroscopic analysis showed conclusively that direct Mo-Mo interactions were present, we were not able to determine the number of molybdenums in the red ion.⁶ The correct formulation of the core of the red ion, Mo₃O₄⁴⁺, was established first by Murmann and Shelton in an elegant ¹⁸O-labeling study.⁷

More detailed solution structural information is needed for all the principal molybdenum aquo ions. With this goal in mind we have performed an extensive investigation of the X-ray absorption edge and EXAFS spectra of aqueous Mo(IV) solutions with variations in pH and added anions. We also have examined the edge and EXAFS spectra of aqueous solutions containing Mo(II), Mo(III), and Mo(V). The results and principal structural conclusions drawn from these studies are reported herein.

Experimental Section

Sample Preparation. Aqueous solutions of Mo(II) containing 1 M trifluoromethanesulfonic acid were prepared by the method of Bowen and Taube.⁸ Aqueous Mo(III) in 3 M methanesulfonic acid was prepared by Pernick's procedure and purified by column chromatography.^{5b} Red

aqueous solutions of Mo(IV) containing 4 M CH₃SO₃H were prepared by the method of Ardon and Pernick,^{5a} and lower acid concentrations were achieved by addition of solid NaOH. In certain experiments the 4 M methanesulfonic acid solution of Mo(IV) was saturated with NaCl or NaBr by addition of the solid salt. Aqueous Mo(V) in 3 M HCl was prepared by a standard procedure.⁹ All of the samples were characterized by optical absorption spectroscopy, and the oxidation levels were verified by ceric ion titrations. Solutions for the X-ray absorption experiments were typically 0.1 M Mo.

Data Collection. The solutions were loaded into Lucite cuvettes with 1-mm-thick Lucite windows at 5- or 10-mm path lengths. Because the Mo(II) and Mo(III) samples are air sensitive, they were stored over zinc amalgam and loaded into the cuvettes in an anaerobic glovebox just prior to data collection. Spectra were recorded at the Stanford Synchrotron Radiation Laboratory.

Data Analysis. The spectra were calibrated by using the Mo foil edge inflection as 20003.9 eV, and the EXAFS was processed by using standard procedures of preedge subtraction, spline removal, and Fourier filtering.¹⁰ The curve-fitting analysis of the EXAFS data depends upon the assumption of phase shift and amplitude transferability among compounds of similar chemical structure.^{10,11} The standard used for Mo-O interactions was MoO₄²⁻; K₂[Mo₃O₄(ox)₃(H₂O)₃] (prepared by a procedure analogous to that employed¹² for Cs₂[Mo₃O₄(ox)₃(H₂O)₃]·4H₂O·0.5H₂O) was the reference for Mo-Mo; K₃MoCl₆¹³ and (N-H₄)[MoOBr₄(H₂O)]¹⁴ were used for Mo-Cl and Mo-Br functions.

The curve-fitting program simulated the EXAFS, as follows:

$$\chi(k) \approx \sum_b \frac{N_b A_{ab}(k) e^{-2\sigma_{ab}^2 k^2}}{k R_{ab}^2} \sin(2k R_{ab} + \alpha_{ab}(k)) \quad (1)$$

where k is the photoelectron wavenumber, R_{ab} is the distance of a group of N_b backscatterers to molybdenum, σ_{ab} is the root-mean-square deviation of R_{ab} , and $\alpha_{ab}(k)$ is the total phase shift. The amplitude function $A_{ab}(k)$ depends not only on the electron-atom backscattering amplitude for the particular scattering atom but also on the properties of the particular X-ray absorbing species.¹⁵

Definition of $A_{ab}(k)$ for a given Mo-X pair requires knowledge of the appropriate Debye-Waller factor for a simple standard compound. For the Mo-O amplitude the σ of 0.0411 Å for MoO₄²⁻ calculated from the vibrational spectrum was used.¹⁶ The Mo-Mo amplitude originally

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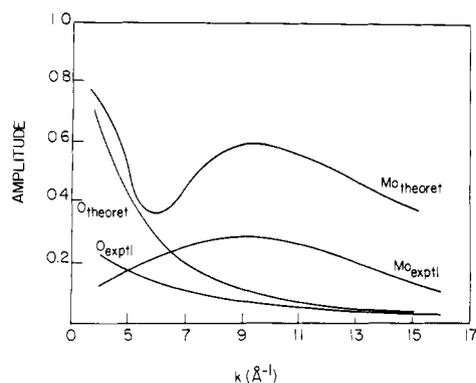


Figure 1. Theoretical O and Mo electron-atom backscattering amplitudes (see ref 19) compared to experimental Mo-O and Mo-Mo EXAFS amplitudes.

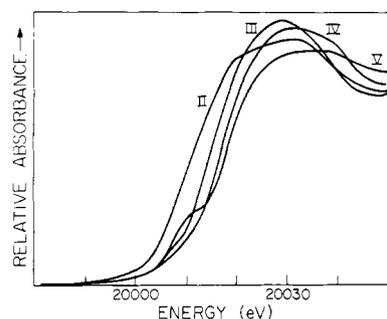


Figure 2. Absorption edge spectra for aqueous molybdenum ions: Mo(II) in 1 M trifluoromethanesulfonic acid; Mo(III) in 3 M methanesulfonic acid; Mo(IV) in 4 M methanesulfonic acid; Mo(V) in 3 M HCl. The spectra were scaled to yield the same amplitude at 20000 eV.

obtained from the $K_2[Mo_3O_4(ox)_3(H_2O)_3]$ spectrum was calibrated by using the Mo-Mo stretching frequency for $Mo_2^{4+}(aq)$ (344.7 cm^{-1})¹⁷ and eq 2:¹⁸

$$\sigma_{\text{vib}} = \left[\frac{h}{8\pi^2\mu c\omega} \coth \frac{hc\omega}{2kT} \right]^{1/2} \quad (2)$$

thereby giving $\sigma = 0.0377\text{ \AA}$ (μ is the reduced mass, and ω is the vibrational frequency in cm^{-1}).

A comparison of the experimental amplitudes with theoretical backscattering amplitudes¹⁹ is shown in Figure 1. Since it is possible that the Fourier filtering and fitting procedure eliminated some of the low k structure in the Mo-Mo amplitude and phase shift, the fits were always begun at $k = 6\text{ \AA}^{-1}$.

In a given fit, there were two variables optimized per Mo-X component. One variable was always the Mo-X distance (R), whereas the other was either the number of X atoms (N) or the Debye-Waller factor (σ). The correlation between N and σ made it unreliable to vary both simultaneously in multishell fits.

Results and Discussion

The aqueous molybdenum samples yielded a remarkable diversity of edge and EXAFS spectra. The edge region often provides useful information about the electronic structure of the X-ray absorbing atom.²⁰ Because of lifetime broadening, molybdenum K edges have a natural line width of about 6 eV,²¹ about equal to the spectrometer resolution; as a result, the sharp structure associated with the edges of lower Z elements is not observed. Nevertheless, it is clear that the edges move progressively to higher energy as the Mo oxidation state is raised (Figure 2). The largest

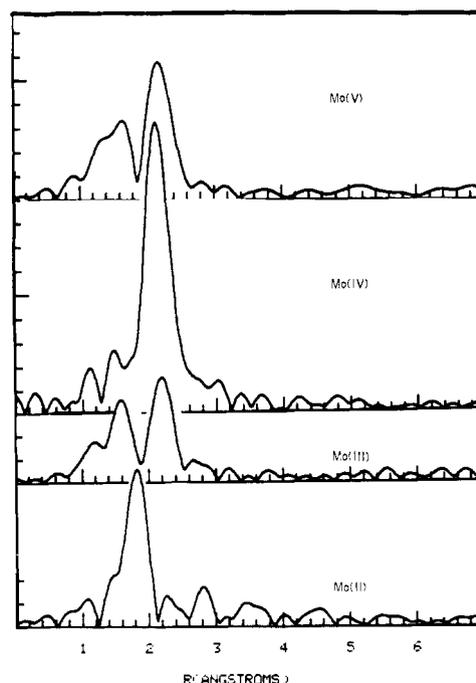


Figure 3. EXAFS Fourier transforms for aqueous molybdenum ions. Range: $4\text{--}15\text{ \AA}^{-1}$, k^3 weighting.

Table I. EXAFS Fourier Transform Analysis of Mo-Mo Interactions in Aqueous Molybdenum Ions^a

sample	calcd Mo-Mo/ Å	calcd no. of Mo neighbors
$K_2[Mo_3O_4(ox)_3(H_2O)_3]$ ^b	2.49	2
Mo(V)/3 M HCl (aq)	2.51 (4)	0.89 (20)
Mo(IV)/4 M CH_3SO_3H (aq)	2.48 (4)	2.0 (4)
Mo(IV)/4 M CH_3SO_3H /satd/NaCl (aq)	2.48 (4)	2.1 (4)
Mo(IV)/4 M CH_3SO_3H /satd/NaBr (aq)	2.48 (4)	2.0 (4)
Mo(IV)/ CH_3SO_3H /pH 1.6 (aq)	2.49 (4)	1.8 (4)
Mo(IV)/ CH_3SO_3H /pH 1.8 (aq)	2.46 (4)	1.6 (3)
Mo(IV)/5 M NaOH (aq)	2.51 (4)	1.5 (3)
Mo(III)/3 M CH_3SO_3H (aq)	2.56 (4)	0.75 (15)
Mo(II)/1 M CF_3SO_3H (aq)	2.12 (4)	0.79 (15)

^a Transform range: $4\text{--}15\text{ \AA}^{-1}$, k^3 weighting. ^b Reference standard (solid sample).

shift is between Mo(II) and Mo(III); the smallest is between Mo(IV) and Mo(V). If the edge position is taken as a semi-quantitative indicator of the charge on the X-ray-absorbing atom, then these data indicate an increasing amount of covalency as the formal oxidation state is raised. It should be noted that only the Mo(V) sample exhibits a low-energy shoulder in its edge spectrum; this feature is attributed to terminal oxomolybdenum coordination.^{20,22}

EXAFS Fourier Transforms. Fourier transformation of the EXAFS data yields a pattern that is qualitatively similar to a radial distribution function.²³ The transforms for all samples are dominated by a peak corresponding to the Mo-Mo interaction (Figure 3). Distances (Mo-Mo) and Mo-neighbor numbers are set out in Table I. As expected, the Mo(II)-Mo(II) distance is significantly shorter than those found for the higher Mo oxidation states.

At distances shorter than the Mo-Mo bond lengths, the transforms of the Mo(III), Mo(IV), and Mo(V) EXAFS contain features due to Mo-O interactions. Relative to the Mo-Mo peak, these features are strongest for Mo(III), somewhat weaker for

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Table II. EXAFS Curve-Fitting Analysis for Aqueous Molybdenum Ions^a

sample	Mo-Mo			Mo-O			Mo-O'			F ^b
	no.	R/Å	σ/Å	no.	R/Å	σ/Å	no.	R/Å	σ/Å	
Mo(II)/1 M CF ₃ SO ₃ H (aq)	0.77	2.117								0.502
	0.90	2.123		1.5	2.14					0.332
	1	2.119	0.0377 ^c	4	2.14	0.10				0.327
Mo(III)/3 M CH ₃ SO ₃ H (aq)	0.6	2.54								3.160
	0.7	2.54		2.2	2.06					0.858
	0.8	2.54		3.6	2.05		2.2	2.24		0.426
	1	2.54	0.044	3	2.06	0.041	3	2.20	0.076	0.365
Mo(IV)/4 M CH ₃ SO ₃ H (aq)	1.9	2.493								1.612
	2.0	2.493		1.2	1.88					0.851
	2.0	2.493		2.1	1.89		1.8	2.05		0.192
	2	2.493	0.031	2	1.88	0.031	4	2.04	0.077	0.234
	2.0	2.488		1.2	1.92					1.653
K ₂ [Mo ₃ O ₄ (ox) ₃ (H ₂ O) ₃] ^d	2.0	2.488		2.1	1.92		1.5	2.07		0.510
	2.0	2.488		2	1.91	0.042	4	2.05	0.090	0.430
	2.0	2.488	0.031	2	1.91	0.042	4	2.05	0.090	0.430
	2	2.488	0.031	2	1.91	0.042	4	2.05	0.090	0.430
Mo(V)/3 M HCl (aq)	0.87	2.56								2.983
	0.87	2.56		1.9	1.93					1.289
	0.88	2.56		1.8	1.93		1.1	1.68		0.280
	1	2.562	0.037	2	1.93	0.042	1	1.68	0.038	0.232
	1	2.562	0.037	2	1.93	0.042	1	1.68	0.038	0.232

^a Debye-Waller factors for the standards (MoO₄²⁻; [Mo₃O₄(ox)₃(H₂O)₃]²⁻) were assumed for the fits with variable coordination numbers; statistical errors are less than the least significant figure quoted. Systematic errors are larger (see text): Mo-Mo number (±25%), R (±1%), σ (±15%); Mo-O number (±100%), R (±2%), σ (±50%). ^b $(\sum(\chi_{\text{obsd}} - \chi_{\text{calcd}})^2 k^6)/N$, where N is the number of data points. ^c Calculated from $\nu_{\text{Mo-Mo}}$. ^d Solid sample.

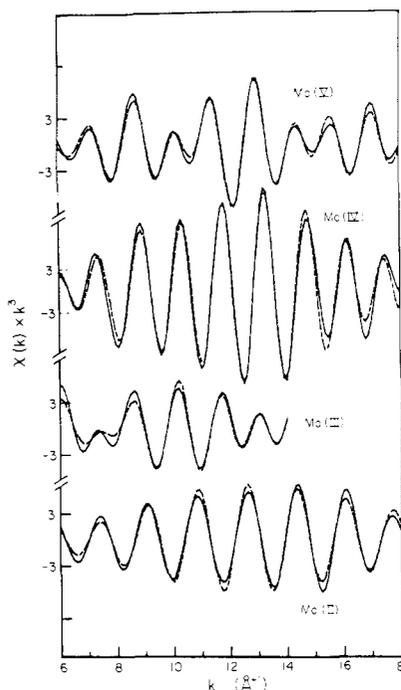


Figure 4. Fourier-filtered EXAFS (solid line) and best fits (dashed line) for aqueous molybdenum ions.

Mo(V), and smaller yet for Mo(IV). The consequence of this is evident in the curve-fitting analyses described below, where inclusion of Mo-O components significantly improves the fits for Mo(III) and Mo(V), but is less important for Mo(IV) and Mo(II). Because artifacts can arise from peak overlap and truncation effects, a quantitative analysis of the Mo-O region was not attempted on the transforms themselves.

Bond Distances from Curve Fitting. Curve fittings of the EXAFS data for the various samples are shown in Figure 4; the results are summarized in Table II and Figure 5. The optimization procedure refined two variables per shell, one being the Mo-X distance and the other being either the scatterer number or the Mo-X Debye-Waller factor. In the fits using integral scattering numbers, the number of oxygen donors was constrained to be consistent with the known structural chemistry for that oxidation state, whereas in the fits with variable scatterer numbers, the Debye-Waller factors were constrained to the values found for

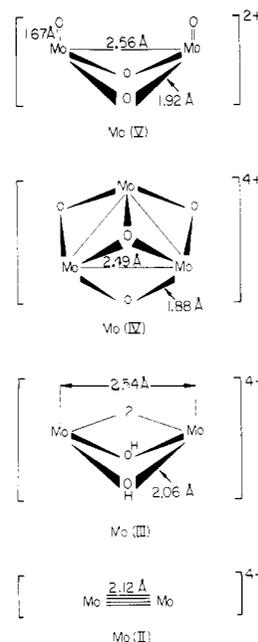


Figure 5. Core structures of aqueous molybdenum ions in different oxidation states; bond distances are from the EXAFS fits.

Mo-O in MoO₄²⁻ or Mo-Mo in the trinuclear oxalate complex.

Mo(II). An excellent fit was obtained with a single Mo-Mo interaction at 2.12 Å; slight improvement resulted from adding a Mo-O component at 2.14 Å. The short Mo-Mo distance is consistent with multiple Mo-Mo bonding in the binuclear species (it is similar to the 2.11-Å value found for Mo₂(O₂CCH₃)₄²⁴ and K₄Mo₂(SO₄)₄·2H₂O²⁵). The predicted Mo-O distance of 2.14 Å is reasonable, and the large Debye-Waller factor probably indicates that the coordinated water molecules are relatively disordered in this binuclear ion.

Mo(III). Useful data were not obtained for k above 14 Å⁻¹. A good fit required two different Mo-O components (2.06 and 2.20 Å) as well as a Mo-Mo interaction at 2.54 Å. The Mo-Mo distance is somewhat longer than the 2.43-Å bond length in KMo₂(OH)₂(ac)(edta);²⁶ this difference most likely is due to the

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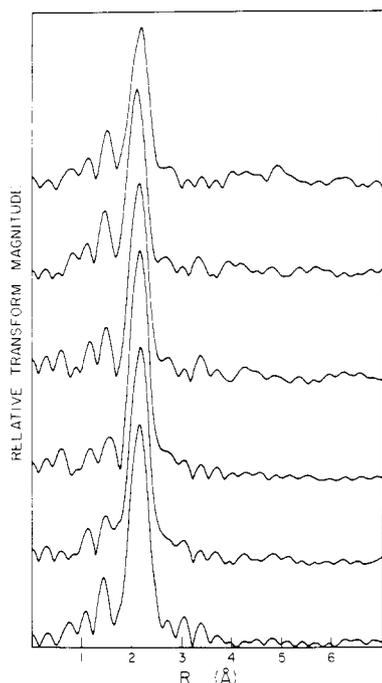


Figure 6. EXAFS Fourier transforms for Mo(IV). Top to bottom: aqueous 5 M NaOH; pH 1.8; pH 1.6; aqueous 4 M methanesulfonic acid (saturated NaCl); aqueous 4 M methanesulfonic acid; solid $K_2[Mo_3O_4(ox)_3(H_2O)_3]$. Ranges: 4–15 \AA^{-1} , k^3 weighting.

influence of the acetate bridging group in the latter complex. The 2.06- \AA Mo–O component is most reasonably assigned to bridging hydroxo groups, whereas the longer Mo–O distance is attributed to Mo–OH₂ (it is of particular interest that among the various Mo oxidation states only in the aquo Mo(III) species did Mo–OH₂ interactions make a nonnegligible contribution to the EXAFS). Thus our analysis clearly favors the $Mo_2(\mu-OH)_2^{4+}$ formulation for the core of the green Mo(III) aquo ion (over the oxo bridged alternative)³ (Figure 5).

Mo(IV). Several aqueous Mo(IV) samples were investigated. For Mo(IV) in 4 M methanesulfonic acid, the calculations gave 1.9–2.0 Mo at 2.49 \AA , an amplitude roughly twice as large as that found for Mo(II) or Mo(V). The fit was improved by using Mo–O components at 1.88 and 2.04 \AA . In our preliminary report we compared⁶ the 2.49 \AA to the Mo–Mo length in crystalline MoO_2 ,²⁷ but it is now well established that triangular- Mo_3 structures ($Mo_3O_4^{4+}$ core) also exhibit^{12,28} Mo–Mo distances that are virtually the same as found for the red Mo(IV) aquo ion. Earlier we reported⁶ a Mo–Mo amplitude of 1.4 for aquo Mo(IV), but we did not make allowance for the fact that the reference analysis consistently underestimated¹¹ oxo-bridged Mo amplitudes by about 20%. When Mo–Mo functions based on $[Mo_3O_4(ox)_3(H_2O)_3]^{2-}$ are employed as a reference, a Mo–Mo amplitude very close to 2 is obtained. Indeed, the EXAFS spectra of $K_2[Mo_3O_4(ox)_3(H_2O)_3]$ and Mo(IV)/4 M CH_3SO_3H (aqueous) are nearly identical (Figure 6). In 4 M methanesulfonic acid, therefore, Mo(IV) undoubtedly exists predominantly as a trinuclear species, $Mo_3O_4^{4+}$ (aq).²⁹

The crystal structure analysis of $Cs_2[Mo_3O_4(ox)_3(H_2O)_3] \cdot 4H_2O \cdot 0.5H_2Ox$ showed that there are three equivalent (μ_2 -O) oxo bridging groups in the $Mo_3O_4^{4+}$ core (Figure 5), with an average Mo–O distance of 1.921 \AA .¹² The EXAFS fits gave a Mo–O component at 1.88 \AA for Mo(IV) in 4 M CH_3SO_3H (aqueous) and 1.91 \AA for $K_2[Mo_3O_4(ox)_3(H_2O)_3]$. However, $[Mo_3O_4(ox)_3(H_2O)_3]^{2-}$ also has a capping (μ_3 -O) oxo ligand (Mo–O = 2.019 \AA), and for each Mo there are two oxalate oxygen atoms at 2.091 \AA and a single O(OH₂) at 2.154 \AA .¹² For this second shell of oxygen atoms the EXAFS fit for the potassium salt gave a 2.05- \AA distance with a σ of 0.09 \AA .

As the pH of the medium is increased, the Mo–Mo EXAFS amplitude decreases (note the Fourier transforms, Figure 6 and Table I). The largest changes are for Mo(IV) in basic solution. Both Fourier-transform and curve-fitting analyses yield a Mo–Mo amplitude of 1.5, as opposed to 2.0 for a symmetric trinuclear species. The best fit predicts a Mo–Mo distance of 2.545 \AA and Mo–O components at 1.96 and 2.10 \AA . Clearly, a major structural change has occurred in basic solution, and one possibility is that the trinuclear ion has adopted an open structure in which a central Mo is oxo-bridged to two Mo neighbors.

The EXAFS spectra of Mo(IV)/4 M methanesulfonic acid solutions containing high concentrations of halide ions also were measured. No new peaks were observed in the Fourier transforms, and the data collected with added Br^- are virtually identical with those obtained for the original sample in methanesulfonic acid solution. However, the presence of weak X–Mo bonds in these samples cannot be ruled out.³⁰

Mo(V). Three components were required for a good fit: 2.56 \AA Mo–Mo, and 1.93 and 1.68 \AA Mo–O distances. The 2.56- \AA Mo–Mo distance observed for the aquo ion is standard for a dioxo-bridged binuclear Mo(V) complex,^{2c} and the Mo–O distances are normal (1.93 \AA , bridging; 1.68 \AA , terminal). The amplitudes are all consistent with a binuclear $Mo_2O_4^{2+}$ core, which is a common species in Mo(V) chemistry.

Concluding Remarks

By using appropriate model compounds, we have been able to distinguish binuclear and trinuclear aqueous molybdenum species in EXAFS spectroscopic experiments. The calculated Debye–Waller factors for Mo–O and Mo–Mo interactions are reasonable. The stiffest Mo–Mo bond is exhibited by trinuclear Mo(IV) ($\sigma = 0.031$ \AA); the others, in order, are dioxo-bridged Mo(V) (0.037 \AA), quadruply bound Mo(II) (0.038 \AA), and dihydroxo-bridged Mo(III) (0.044 \AA). Trends in the mean deviations of Mo–O distances also are as expected. By calculation of Debye–Waller factors from experimental amplitude functions, EXAFS analyses are improved significantly. Such improved techniques of analysis combined with the structural information now available on relatively simple aquo molybdenum ions should facilitate the structural characterization of molybdenum in the more complex environments of supported catalysts, amorphous materials, and metalloenzymes.

Acknowledgment. We thank F. C. Anson, M. Ardon, A. Bino, J. S. Najdzionek, and A. G. Sykes for helpful discussions. Research at the California Institute of Technology was supported by National Science Foundation Grant CHE80-24863. Synchrotron radiation was provided by the Stanford Synchrotron Radiation Laboratory, which is supported by the NSF through Grant DMR-77-27489, in cooperation with the Stanford Linear Accelerator Center and the Department of Energy.

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(29) Acid cryoscopic measurements by Ardon, Bino, and Yahav had indicated a binuclear formulation; however, we have made similar measurements on acidic-aqueous solutions of Mo(IV) and have found that the errors are too large ($\pm 20\%$) to pinpoint the precise state of aggregation (Eidem, P. K. Ph.D. Thesis, California Institute of Technology, Pasadena, 1981).

(30) EXAFS data on the solution with added Cl^- can be fitted by taking a Mo–Cl interaction at 2.48 \AA ; this fit is not unique, however, because Mo–Mo and Mo–Cl phase shifts are similar (modulo 2π); thus the observed changes may be accommodated entirely by Mo–Mo interaction components.