

- (2) In a typical reaction, degassed **1** (8 mL) and CpCo(CO)₂ (2.15 g) were added to refluxing nitrogen-flushed **1** (74 mL) over a period of 100.5 h using a syringe pump. After additional refluxing (24 h), excess **1** was removed by vacuum transfer and the products were chromatographed on Woelm neutral alumina (grade II) eluting in consecutive fractions (pentane) **2** (540 mg), **3** (1.44 g), **4** (80 mg), and (pentane-ether, 19:1) **5** (7 mg).
- (3) Satisfactory analytical and spectral data were obtained for all new compounds.
- (4) Compound **2**: pale yellow crystals; mp 103–104 °C; *m/e* 340.1881 (calcd 340.1894, M⁺, 70%), 237 (M – Me₃Si, 74%), 179 (M – Me₃Si, –Me₄Si, 75%), 73 (Me₃Si, 100%); τ (CCl₄) 9.83 (s); ¹³C NMR (parts per million from Me₄Si, in C₆D₆) δ 0.54, 157.17, 207.03; ν_{C=C} 1536, ν_{Me₃Si} 1245 cm⁻¹; UV λ_{max} (95% EtOH) 209 (log ε 4.60), 282 (4.30), 298 (4.58). **4**: orange crystals; mp 83.5–86.5 °C; *m/e* 488.1609 (calcd 488.1617, M⁺, 100%), 318 (M – Me₃SIC₂SiMe₃, 6%), 294 (M – Me₃SIC₄SiMe₃, 61%); τ (CCl₄) 5.22 (s, 5 H), 9.77 (s, 18 H), 9.86 (s, 9 H), 9.92 (s, 9 H); IR ν_{C=O} 2125, ν_{Me₃Si} 1250 cm⁻¹. **5**: dark purple crystals; mp 188–189.3 °C; *m/e* 566 (M⁺, 20%), 370 (3%), 247 (7%), 189 (Cp₂Co, 100%); τ 5.77 (s, 15 H), 9.27 (s, 9 H), 9.51 (s, 9 H); IR ν_{C=O} 2070, ν_{Me₃Si} 1240 cm⁻¹.
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- (12) The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the average value.
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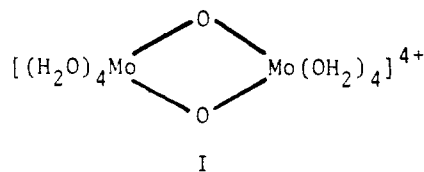
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The Nature of Molybdenum(IV) in Aqueous 4 M HCl Solution. Structure Analysis by EXAFS

Sir:

The structure of Mo(IV) in acidic aqueous media has occasioned much speculation¹⁻⁵ since its first synthesis in relatively pure form in 1966.¹ The solution structure of the red ion was originally proposed¹ as MoO(OH)⁺, but Ardon and Pernick,⁴ on the basis of ion-exchange column elution behavior (4 M HPTS) and redox titrations, postulated a dinuclear structure (I). Their conclusion was challenged by Ramasami et al.,⁵ whose kinetics data were interpreted in terms of a mononuclear MoO²⁺ or Mo(OH)₂²⁺ structure. However, Ardon and co-workers⁶ performed cryoscopic experiments that rule strongly in favor of a dinuclear formulation such as I; what is more, the results of recent electrochemical studies⁷ are entirely consistent with some type of dimeric structure for Mo(IV)_{aq}.



X-ray absorption spectroscopy has recently been developed as a probe of molecular structure capable of identifying the type, number, and distances of atoms in the environment of a particular X-ray absorber.^{8,9} Analysis of the extended X-ray absorption fine structure (EXAFS) of a variety of Mo compounds has demonstrated an accuracy of ±0.02 Å in the determination of Mo–X distances, along with a capacity for identifying the type and number of X atoms.¹⁰ In this communication we present X-ray absorption data for Mo(IV) in 4 M HCl that (1) conclusively rule out mononuclear formulations and strongly suggest a dinuclear structure; (2) indicate the absence of multiply bound oxo groups; and (3) provide the first quantitative structural information about Mo–Mo and Mo–O bond lengths in this Mo(IV) complex.

The molybdenum K-absorption edge of Mo(IV) in 4 M aqueous HCl is shown in Figure 1a.¹¹ The principal inflection point occurs at 2001.49 ± 0.5 eV, which is within experimental error of the 2001.54 ± 0.5 eV value previously found for

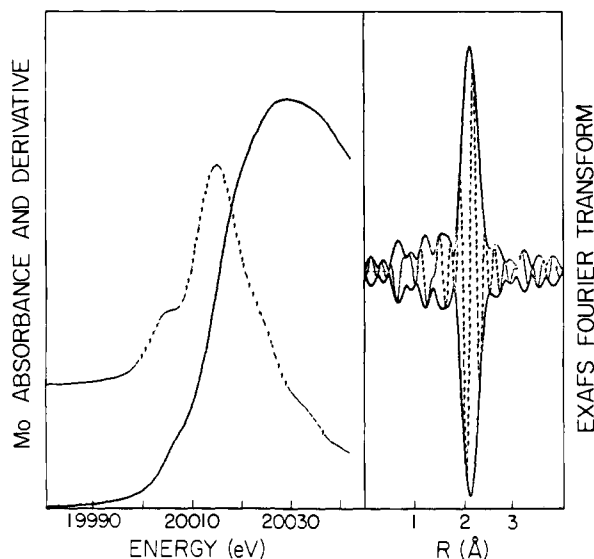


Figure 1. (a) Mo(IV) (4 M HCl) absorption edge (---) and derivative (---). (b) Mo(IV) (4 M HCl) EXAFS Fourier transform: range, 4–16 Å⁻¹; scaling, k^3 ; magnitude (---) and imaginary part (---).

MoO₂.¹² For comparison, Mo(V) and Mo(VI) compounds with all oxygen-donor ligands typically have edge inflection points 3–5 eV higher.¹³

In the low-energy foot of the absorption edge there is a weak bound-state transition, which is primarily $1s \rightarrow 4d$ in character, and which is best seen as an inflection in the derivative curve. It has been shown previously that the presence of multiply bound oxo groups, i.e., Mo=O, results in a substantial enhancement of the low-energy bound-state transitions at the Mo edge.¹² Thus, as the number of oxo groups is increased from 1 to 4, a characteristic low-energy feature grows from a shoulder to a well-resolved peak.¹³ In all cases examined to date, the presence of Mo=O bonds resulted in a bound-state transition substantially stronger than observed in the present case. Thus we conclude on the basis of the edge shape alone that a Mo=O unit is not present under the conditions of our experiment. Similar arguments have been used to exclude the presence of Mo=O bonds in the nitrogenase Mo-Fe protein¹² and to confirm their presence in the molybdenum enzyme sulfite oxidase.¹⁴

The EXAFS of Mo(IV) (4 M HCl) is depicted in Figure 2a along with the best three-wave fit. The Fourier transform of these data reveals only a single major peak (Figure 1b), the position and size of which agree with a MoMo assignment. Similar transforms for oxo and sulfido-bridged Mo dimers have been obtained previously,¹⁰ and comparison of the Mo(IV) (4 M HCl) peak position with the [Mo₂O₂O₂cys₂]²⁻ standard indicates an Mo–Mo distance of 2.52 Å in the former.

Curve-fitting analysis of the EXAFS itself, according to previously published procedures,¹⁰ began with a single-shell fit using empirical MoMo phase shift and amplitude functions. This two-parameter fit predicted an Mo–Mo distance of 2.510 Å, with a normalized MoMo component amplitude 1.5 times that obtained for the dinuclear Mo(V) complex [Mo₂O₂O₂cys₂]²⁻. Extra waves were then added for various Mo–O distances. A medium Mo–O distance was found at ~1.95 Å, which is reasonably assigned to the bridging oxygens in structure I, whereas a longer Mo–O distance observed at ~2.15 Å probably represents an average bond length for a relatively disordered set of water ligands.

The Mo–Mo distance of 2.51 Å exhibited by Mo(IV) (4 M HCl) is intermediate between the 2.43-Å value reported for the dinuclear Mo(III) complex [Mo₂(OH)₂(OAc)(edta)]⁻¹⁵ and the 2.54–2.57-Å distances typically found in dioxo-bridged Mo(V) complexes.^{16,17} Furthermore, it is equal to the Mo–Mo

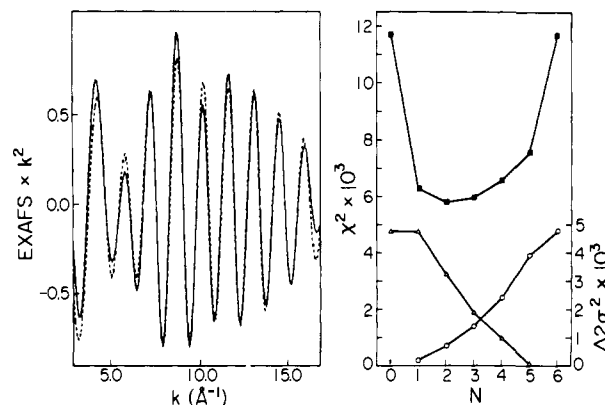


Figure 2. (a) Fourier-filtered EXAFS (---) and least-squares fit (---). (b) Variation of χ^2 (■) for three wave fits assuming 1 Mo–Mo, N Mo–O_{short} (Δ), and $6 - N$ Mo–O_{long} (O) interactions. Notice how N and $\Delta\sigma^2$ are strongly correlated.

distance observed for MoO₂.¹⁸ The 1.95-Å Mo–O distance is similar to the 1.92–1.94-Å values²⁰ reported for other di- μ -oxo groups, and significantly shorter than the 2.04-Å Mo–O bond length in the OH-bridged Mo(III) complex.¹⁵ Finally, the average Mo–O distance of 2.15 Å is between 2.10 Å reported for MoOH in MoO(OH)CN₄^{3–21} and 2.27 Å reported for MoOH₂ in MoO(OH₂)(CN)₄^{4–22}. In the latter two complexes the distances are for ligands trans to Mo=O; in view of this, 2.15 Å appears reasonable for a Mo(IV)–OH₂ distance in the absence of a bond lengthening trans effect.

Although the calculated Mo–X distances are all in agreement with structure I, the preliminary amplitudes are low for the MoO components and high for the MoMo wave. Thus, a series of fits was done in which the MoX components were fixed at integral values and the relative Debye–Waller factor was varied.²³ The best fit yields 1 MoMo (2.51 Å),²⁴ 2 short MoO (1.96 Å), and 4 long MoO (2.20 Å), thereby indicating structure I. However, several alternative structural models are compatible with the EXAFS data, because changing the relative number of short (bridging) and long (water) oxygens can be accommodated in these unconstrained fits by varying the relative Debye–Waller factor (Figure 2b). In this connection we should mention that we have found no evidence for Cl⁻ inner sphere coordination, as the Fourier transform shows no features in the region corresponding to a Mo–Cl distance, and good fits were obtained without including Mo–Cl components. Further investigation is needed both on this point as well as on the question of the numbers and types of long and short Mo–O bonds. In an attempt to provide answers to these questions we are presently engaged in an extensive series of EXAFS experiments on Mo(IV)_{aq} in methanesulfonic acid solutions.

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Supplementary Material Available: A table of calculated distances and relative Debye–Waller factors for various combinations of short and long MoO units (1 page). Ordering information is given on any current masthead page.

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The Molybdenum Site of Sulfite Oxidase. Structural Information from X-ray Absorption Spectroscopy

Sir:

Very little is known about the structures of the active sites of molybdenum enzymes. Although knowledge of the molybdenum coordination sphere is essential both for rational synthetic modeling and for determination of the catalytic mechanism, no molybdenum protein structure has yet been crystallographically determined. Recent work has shown that X-ray absorption spectroscopy is a valuable tool for the determination of metalloprotein active-site structures,¹⁻⁴ and such studies of nitrogenase have suggested that the Mo in this enzyme is present in a cluster that includes Fe and S atoms.^{5,6} However, biochemical work has shown that the "iron-molybdenum cofactor" of nitrogenase is quite different from the "molybdenum cofactor"^{8,9} common to the remainder of molybdenum enzymes (xanthine oxidase-dehydrogenase, sulfite oxidase, aldehyde oxidase, nitrate reductase, and formate dehydrogenase). We now present X-ray absorption results for sulfite oxidase, which indicate both oxo and sulfur coordination for the Mo in this enzyme.

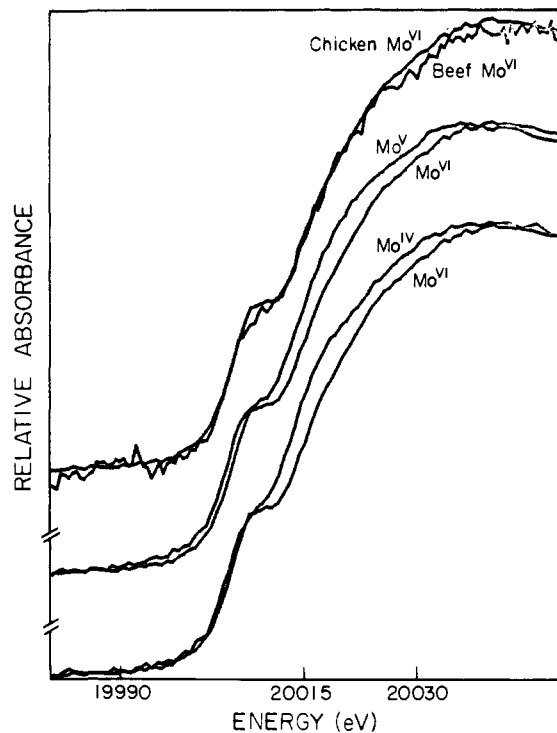


Figure 1. Molybdenum K-absorption edges for sulfite oxidase from different sources and in different states: top curves, oxidized chicken liver sulfite oxidase (CLSO) vs. oxidized beef liver sulfite oxidase; middle curves, oxidized CLSO vs. sulfite-reduced CLSO; bottom curves, oxidized CLSO vs. dithionite-reduced CLSO. All samples were run at ~100 mg/mL in 0.05 M, pH 9.2 Tris-HCl buffer. The reduced samples were prepared with a 50-fold excess of reagent.

Sulfite oxidase catalyzes the oxidation of sulfite to sulfate, using water as the source of oxygen and cytochrome *c* as the physiological electron acceptor.¹⁰ This enzyme has been observed in bacteria, plants, and in mammalian tissues, especially in the liver.¹¹ Sulfite oxidase contains two *b*-type cytochromes as well as two molybdenums, and it exists as a dimer of roughly 55 000-dalton polypeptide subunits. Several different states of sulfite oxidase have been distinguished by a combination of EPR and optical spectroscopic measurements. The protein as isolated contains Mo^{VI} and a low-spin ferric heme (Soret band at 413 nm).¹¹ In the sulfite-reduced state there is a low-spin ferrous heme with a Soret band at 423 nm, and a Mo^V EPR signal appears at *g* = 1.97.¹¹ Addition of dithionite causes loss of the Mo EPR, presumably because reduction to diamagnetic Mo^{IV} occurs.¹¹ As illustrated in Figures 1 and 2, there are significant differences in both the absorption edges and in the EXAFS of all three of these molybdenum oxidation states. By correlating the edge changes with a variety of model compounds, and by curve fitting the EXAFS with previously determined phase shift and amplitude functions,¹² a detailed structural model for the sulfite oxidase molybdenum site may be proposed.

The most prominent feature of the sulfite oxidase Mo absorption edge spectra (Figure 1) is a low-energy bound-state (1s → 4d) transition that is visible as a shoulder on the main absorption edge. Comparison with model compound spectra^{5,13} suggests that the presence of one or two Mo=O groups gives rise to this feature, since Mo complexes without Mo=O generally have a smooth, single inflection point edge,⁵ whereas those with three or four oxo groups have a resolved low-energy peak.¹³ The major inflection point for the oxidized protein falls at 20 015 eV, which for Mo^{VI} in a protein environment suggests a coordination sphere with a mix of oxygen and sulfur ligands.¹⁴ These results are in direct contrast to previous findings