

## Molybdenum(V) Complex Formation in Aqueous HCl Solutions

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### Introduction

In different concentrations of HCl acid solutions, Mo(V) exhibits distinct color changes from emerald green in 9.4 M to opaque brown in 6 M and amber yellow in 2 M. Magnetic studies show that these color changes are associated with the conversion of paramagnetic to diamagnetic properties, respectively corresponding to mononuclear Mo(V) with  $4d^1$  electronic configuration ( $> 7$  M HCl), and  $\text{Mo}_2\text{O}_4$  dimeric species ( $< 2.5$  M) where the electron on each metal center pair.

To better understand the structures of the different Mo(V) species formed in HCl solutions between 1.7-9.4 M concentrations, Mo K- and  $L_{2,3}$ -edge as well as Raman spectroscopic characterizations were carried out.[1]

### Experimental Procedure

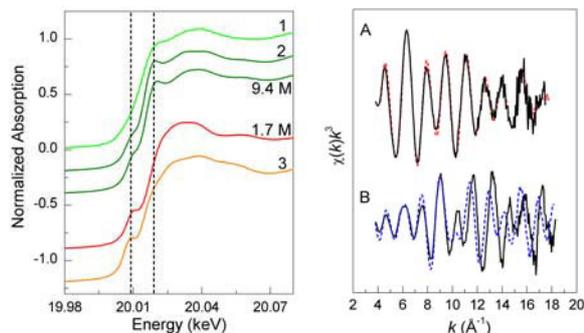
The 0.2 M Mo(V) solutions were prepared by dropwise addition of the corresponding HCl (1.7-9.4 M) to  $\text{MoCl}_5$  in an ice bath under Ar.  $(\text{HPPH}_3)_2[\text{MoOCl}_5]$  (**1**),  $(\text{pyH})[\text{MoOCl}_4(\text{OH}_2)]$  (**2**) and  $(\text{pyH})_2[\text{Mo}_2\text{O}_4\text{Cl}_4(\text{trans-OH}_2)_2]$  (**3**) solids with known crystal structures were compared with species formed in solution. Mo K- and  $L_{2,3}$ -edge and Raman spectra were measured for the Mo(V) solutions and solids. Mo K-edge spectra were measured on BL 10-B at the Photon Factory (PF) of the High Energy Accelerator Research Organization. Least-squares curve fitting of Mo K-edge EXAFS data was used to derive structural parameters, where the coordination numbers were fixed and the amplitude reduction factor, bond distances and Debye-Waller parameters were allowed to float.

### Results and Discussion

The shift in the  $\nu(\text{Mo}=\text{O})$  Raman band showed that depending on the HCl concentration, three different species: mononuclear, mono-oxo and dioxo-bridged Mo(V) complexes are formed. [1]

Mo K-edge XANES spectra of Mo(V) in 7.4-9.4 M HCl overlap and closely resemble the spectrum of solid **2**, while noticeable differences are observed compared with solid **1** (Figure 1, left). This provides evidence for the formation of  $\text{MoOCl}_4(\text{OH}_2)^{1-}$  rather than the previously suggested  $\text{MoOCl}_5^{2-}$  complex at high HCl concentrations. Although at slightly different energies, the XANES features of Mo(V) in  $< 4.5$  M HCl are similar to that of solid **3**, indicating that a dioxo-bridged dinuclear species is formed as the HCl concentration is reduced.

The EXAFS oscillations of Mo(V) in 9.4 M HCl and **2** overlap very well (Figure 1, right). EXAFS curve fitting for Mo(V) in 9.4 M HCl provided mean bond distances of 1 Mo=O 1.66(2) Å, 4 Mo-Cl 2.38(2) Å and 1 Mo-OH<sub>2</sub> 2.30(2) Å for the  $\text{MoOCl}_4(\text{OH}_2)^{1-}$  complex.



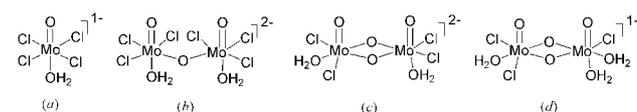
**Figure 1.** (left) Mo K-edge XANES for **1** and **2** compared to Mo(V) in 9.4 M HCl, and **3** to Mo(V) in 1.7 M HCl; (right) Mo K-edge EXAFS of: A) Mo(V) in 9.4 M HCl (—) and **2** (---); B) Mo(V) in 1.7 M HCl (—) and **3** (---).[1]

Clear phase shifts were observed for overlapped EXAFS of **3** and Mo(V) in 1.7 M HCl (Figure 1, right). The EXAFS of the solution fitted well to 1 Mo=O 1.67(2) Å, 2  $\mu$ -Mo-O 1.93(2) Å, 2 Mo-Cl 2.47(2) Å, 1 Mo-OH<sub>2</sub> 2.15(2) Å and 1 Mo-Mo 2.56(2) Å. This somewhat differs with the distances obtained for **3**, most notably 2 Mo-OH<sub>2</sub> at 2.31(2) Å and 1 Mo-Mo at 2.60(2) Å. The short Mo-OH<sub>2</sub> distance of 2.15(2) Å for Mo(V) in 1.7 M HCl suggests that at least one of the aqua ligands is equatorial in position, whereas both aqua groups are axial in **3**.

The Raman spectra of Mo(V) solutions in 2.7 M  $< [\text{HCl}] < 7.4$  M, show that mixtures of three different Mo(V) complexes are formed. However, from Principle Component Analysis (PCA) of EXAFS spectra for 10 solutions, only two different groups of Mo(V) species could be differentiated. This indicates that the EXAFS oscillation for the mono-oxo bridged binuclear Mo(V) complex is very similar to that of the mononuclear species.

### Conclusion

Mononuclear  $\text{MoOCl}_4(\text{OH}_2)^{1-}$  and dinuclear species  $[\text{Mo}_2\text{O}_4\text{Cl}_4(\text{OH}_2)_2]^{2-}$  and  $[\text{Mo}_2\text{O}_4\text{Cl}_3(\text{OH}_2)_3]^{1-}$  dominate in 9.4 M and 1.7 M HCl, respectively. In intermediate HCl concentrations, a third mono-oxo bridged Mo(V) species is formed with a non-linear Mo-O-Mo entity. The EXAFS oscillation of this complex (without a Mo-Mo bond) is very similar to that of  $\text{MoOCl}_4(\text{OH}_2)^{1-}$  (Figure 2).



**Figure 2.** Dominant Mo(V) complexes formed in (a) 6.3-9.4 M HCl, (b) 4.9-5.9 M HCl, (c) and (d) 1.7-4.5 M HCl.

### Reference

[1] F. Jalilehvand *et al.*, *Inorg. Chem.* 46 (2007) 4430.

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