Background

Earlier potentiometric and $^{13}$C-NMR studies have shown that at $H_2L / Hg(II) > 2$ and in alkaline pH, Hg(II) forms:

- $[Hg(Cys)_{2}]^{2-}$ and $[Hg(Cys)_{3}]^{4-}$ with cysteine
- $[Hg(Pen)_{2}]^{2-}$ and $[Hg(Pen)_{3}]^{4-}$ with penicillamine

No structural information was available!

Synthesis

$Hg(ClO_4)_2 + n \xrightarrow{Ar} Hg(ClO_4)_{2-n}$

$Hg(II)$ complex formation with thiol-containing ligands of biochemical interest

Structural determination of $Hg(II)$ complexes with $L$-cysteine and $D$-penicillamine formed in aqueous solution

$Hg(ClO_4)_2 + n \xrightarrow{Ar} Hg(ClO_4)_{2-n}$

$Hg(II)$ complex formation with thiol-containing ligands of biochemical interest

Structural determination of $Hg(II)$ complexes with $L$-cysteine and $D$-penicillamine formed in aqueous solution

Hg L$_3$-edge X-ray absorption spectrum

Why XAS?

1) Element specific
2) Measurement on any physical state of sample
3) Dilute samples

Information

1) Bond distances (accuracy: $\pm 0.02 \, \text{Å}$)
2) Coordination number
3) Type of neighboring atom
4) Debye-Waller parameter (displacement from the mean distance)
Hg(II)-cysteine complex formation

Hg L$_3$-edge EXAFS C$_{Hg(II)}$ ~ 0.1 M pH = 11

<table>
<thead>
<tr>
<th>H$_2$Cys / Hg(II) ratio</th>
<th>C.N.</th>
<th>Hg-S (Å)</th>
<th>$\sigma^2$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid Hg(HCys)$_2$</td>
<td>2 fix</td>
<td>2.34</td>
<td>0.0028</td>
</tr>
<tr>
<td>Solutions ($S_o^2 = 0.9$ fix)</td>
<td>2.2</td>
<td>2.05</td>
<td>2.36</td>
</tr>
<tr>
<td></td>
<td>3.3</td>
<td>2.13</td>
<td>2.39</td>
</tr>
<tr>
<td></td>
<td>4.3</td>
<td>2.73</td>
<td>2.44</td>
</tr>
<tr>
<td></td>
<td>5.3</td>
<td>3.40</td>
<td>2.50</td>
</tr>
<tr>
<td></td>
<td>10.1</td>
<td>3.48</td>
<td>2.50</td>
</tr>
</tbody>
</table>

Solutions (pH = 11)

$\delta(^{199}$Hg) = 0 ppm
HgCl$_2$ in D$_2$O $\delta(^{199}$Hg) = -1550 ppm

Hg(II)-cysteine complex formation

199Hg NMR C$_{Hg(II)}$ ~ 0.1 M pH = 11

Possibility of formation of [Hg(Cys)$_4$]$^{2-}$ when:
$[\text{H}_2\text{Cys}] / [\text{Hg}^{2+}] > 5$
if $[\text{Hg}^{2+}] ~ 0.1$ M and
Free $[\text{Cys}^2-] > 0.1$ M and pH > 9

Hg(II)-cysteine complex formation

Structure of [Hg(Cys)$_2$]$^{2-}$ in solution (pH = 11)
based on the EXAFS of solution with H$_2$Cys / Hg(II) = 2.2

$\delta(^{199}$Hg) = 0 ppm
HgCl$_2$ in D$_2$O $\delta(^{199}$Hg) = -1550 ppm
Distribution of $[\text{Hg(Cys)}_n]^{2-2n}$ ($n = 2 - 4$) in alkaline aqueous solutions

1) Simulation of EXAFS oscillations for: $[\text{Hg(Cys)}_2]^2-$, $[\text{Hg(Cys)}_3]^4-$ and $[\text{Hg(Cys)}_4]^{6-}$

2) Linear combination fitting of these simulated oscillations to the Fourier-filtered EXAFS spectra of Hg-cysteine solutions

De-convolution of EXAFS spectra:

Distribution of $[\text{Hg(Cys)}_n]^{2-2n}$ ($n = 2 - 4$) in alkaline aqueous solutions

Combination of EXAFS, Raman and $^{199}$Hg NMR

Estimation of Stability Constants Hg(II)-Cysteine Complex Formation

Hg(II)- penicillamine complex formation

Hg L$_3$-edge EXAFS

Hg(II)- penicillamine complex formation

$^{199}$Hg NMR

A possible structure for $[\text{Hg(Pen)}_3]^{4-}$ in aqueous solution (pH = 11)

B. Leung, F. Jalilehvand, V. Mah, Dalton Trans. 2007, 4666-4674
Distribution of $[\text{Hg(Pen)}_n]^{2-2n} (n = 2, 3)$ in alkaline aqueous solutions

$^{199}\text{Hg NMR}$

<table>
<thead>
<tr>
<th>$\text{H}_2\text{Pen} / \text{HgII}$ ratio</th>
<th>%$[\text{Hg(Pen)}_2]^{2-}$</th>
<th>%$[\text{Hg(Pen)}_3]^{4-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>619</td>
<td>394</td>
</tr>
<tr>
<td>2.5</td>
<td>506</td>
<td>490</td>
</tr>
<tr>
<td>4.9</td>
<td>317</td>
<td>435</td>
</tr>
<tr>
<td>6.2</td>
<td>364</td>
<td>89</td>
</tr>
<tr>
<td>8.0</td>
<td>394</td>
<td>85</td>
</tr>
<tr>
<td>10.0</td>
<td>469</td>
<td>100</td>
</tr>
<tr>
<td>12.0</td>
<td>469</td>
<td>100</td>
</tr>
<tr>
<td>15.4</td>
<td>469</td>
<td>100</td>
</tr>
</tbody>
</table>

$^{199}\text{Hg NMR}$ Chemical Shift

Mo(V) Species in Aqueous HCl Solution

MoCl$_5$ shows different colors in 3-10 M HCl.

Saccini, J. Am. Chem Soc. 1954, 76, 4239

Diamagnetic in 3 M HCl
Paramagnetic in 10 M HCl

Mo(V) Species in Aqueous HCl Solution

Proposed structures from magnetic and UV-vis. data:

$[\text{MoCl}_5]^{2-}$ $[\text{MoCl}_4(OH_2)]^{-}$ $[\text{Mo}_2\text{O}_2(\mu-O)_2\text{Cl}_4(OH_2)_2]^{2-}$

Counter ions eliminated for clarity
Mo(V) Species in Aqueous HCl Solution

Mo Cl₅ in 7.4 M, 8.5 M and 9.4 M HCl

a) MoCl₅ in 7.4 M, 8.5 M and 9.4 M HCl
b) Solid [MoOCl₅]²⁻ (—)
Solid [MoOCl₄(OH₂)]⁻ (—)
c, d) MoCl₅ in 9.4 M HCl (—) compared with the above two solids

Mo(V) Species in Aqueous HCl Solution

Mo K-edge EXAFS $C_{\text{Mo(V)}} \sim 0.2$ M

MoCl₅ in 7.4 M - 9.4 M HCl

b) Solid [MoOCl₅]²⁻ (—)
Solid [MoOCl₄(OH₂)]⁻ (—)

c, d) MoCl₅ in 9.4 M HCl (—) compared with the above two solids

Mo(V) Species in 1.7 M HCl Solution

Combined results from Mo K-edge EXAFS data analysis, Mo L₂,3-edge XANES and ADF calculations showed:

Possible Mo(V) species in 1.7 M HCl

(b and d = major species)


Mo(V) Species in 3.7 – 6.3 M HCl Solution


Acknowledgement

- Co-workers
  Bonnie Leung
  Maryam Izadifard
  Vicky Mah

- Funding
  Natural Science and Engineering Research Council of Canada (NSERC); NSERC UFA
  Canadian Foundation for Innovation (CFI); Province of Alberta; Alberta Synchrotron Institute
  University of Calgary

- Beam time
  Photon Factory (Japan)
  Stanford Synchrotron Radiation Lab (SSRL, US) - US Dept. of Energy (DOE)