



EXAFS Spectroscopy:
Its Applications in Chemical Speciation in Solution

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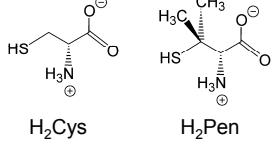
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Hg(II) Complex Formation with Thiol-containing Ligands of Biochemical Interest

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



*H*₂Cys *H*₂Pen



Background

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

- $[\text{Hg}(\text{Cys})_2]^{2-}$ and $[\text{Hg}(\text{Cys})_3]^{4-}$ with cysteine
- $[\text{Hg}(\text{Pen})_2]^{2-}$ and $[\text{Hg}(\text{Pen})_3]^{4-}$ with penicillamine

No structural information was available!



Synthesis

$\text{Hg}(\text{ClO}_4)_2 + n \begin{cases} \text{H}_2\text{Cys} \\ \text{or} \\ \text{H}_2\text{Pen} \end{cases} \xrightarrow[\text{[Hg}^{2+}\text{ (aq)} \sim 0.1 \text{ M}]{\text{Ar}} \begin{cases} \text{Hg}(\text{HCys})_2 \text{ solid} \\ \text{or} \\ \text{Hg}(\text{HPen})_2 \end{cases}$

$n = 2 - 10 \text{ for cysteine}$
 $2 - 15 \text{ for penicillamine}$

$\downarrow \text{pH} = 11$
Clear solution

Hg L₃-edge X-ray absorption spectrum



Why XAS?

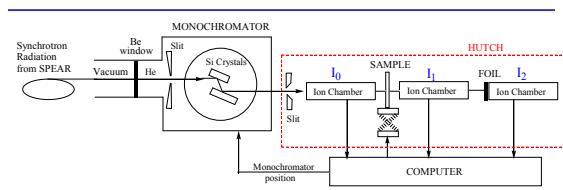
- 1) Element specific
- 2) Measurement on any physical state of sample
- 3) Dilute samples

Information

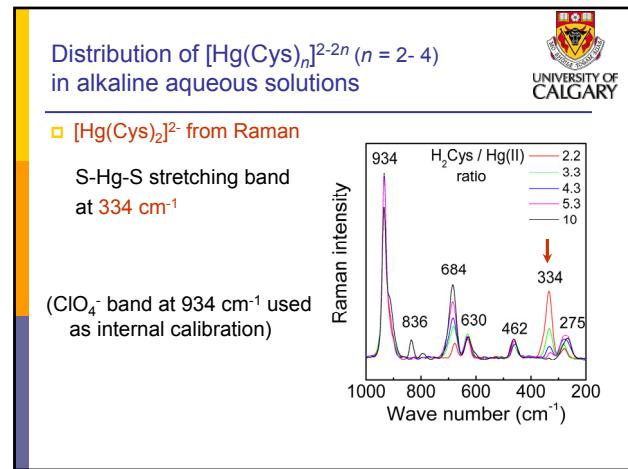
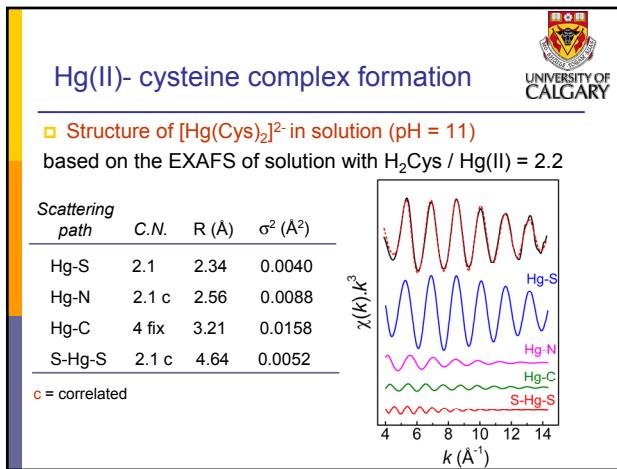
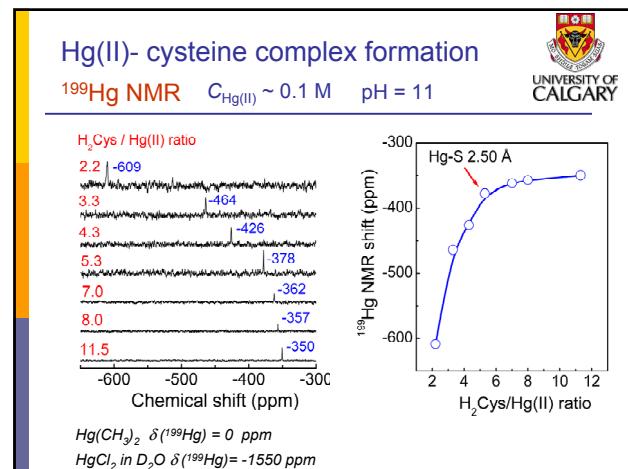
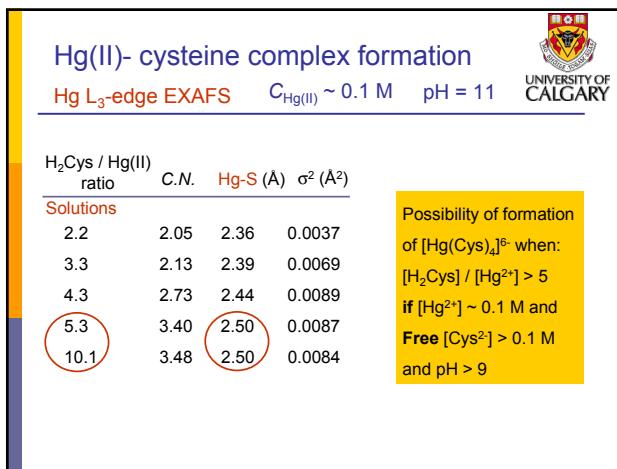
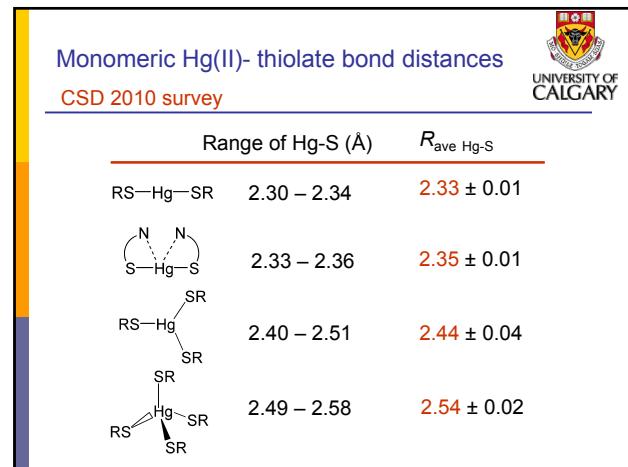
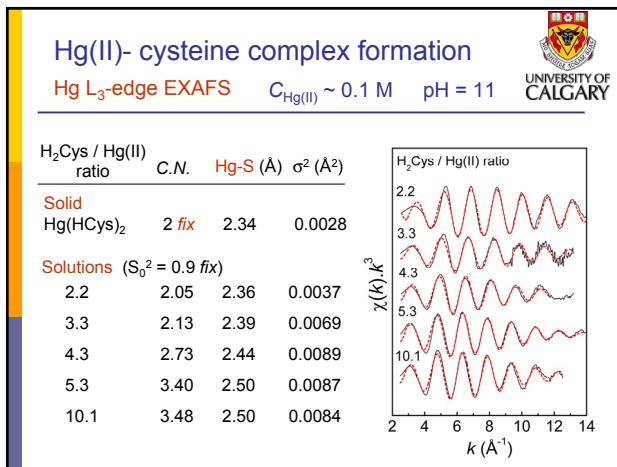
- 1) Bond distances (accuracy: $\pm 0.02 \text{ \AA}$)
- 2) Coordination number
- 3) Type of neighboring atom
- 4) Debye-Waller parameter (displacement from the mean distance)

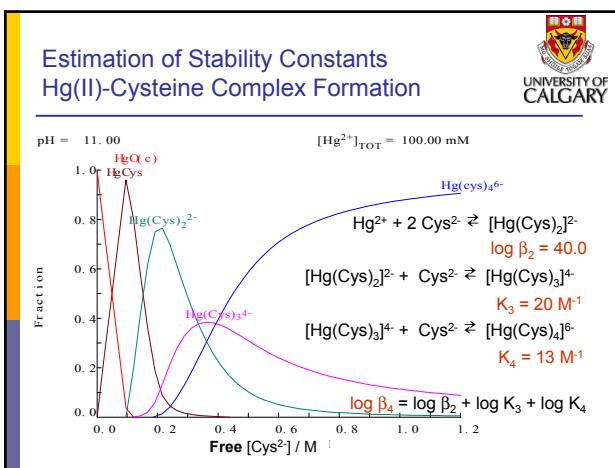
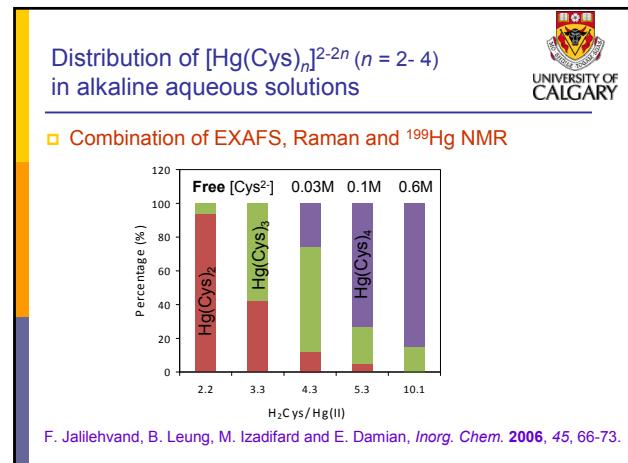
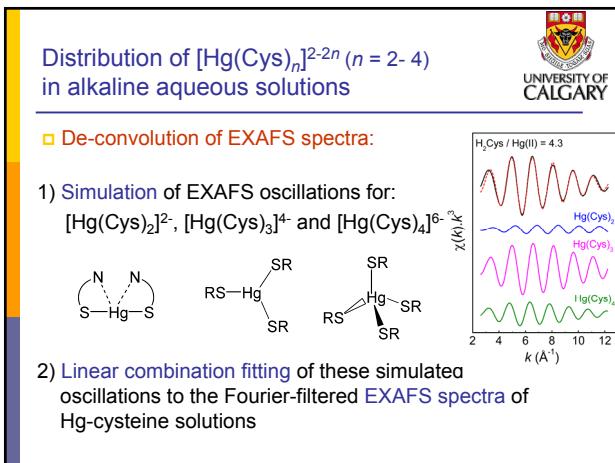


Measuring XAS Spectrum



Transmission: $\log(I_0 / I_1)$





Hg(II)- penicillamine complex formation

Hg L₃-edge EXAFS pH = 11

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$H_2Pen / Hg(II)$	C.N.	$Hg-S (\text{\AA})$	$\sigma^2 (\text{\AA}^2)$
Solid $Hg(HPen)_2$	2 fix	2.35	0.0036
Solutions ($S_0^2 = 0.9$ fix)			
1.9	2 fix	2.34	0.0037
2.5	2 fix	2.36	0.0029
3.6	2.3	2.38	0.0066
4.9	2.6	2.41	0.0072
6.2	2.7	2.42	0.0073
8.0	2.9	2.44	0.0064
10.0	3.0	2.44	0.0072
15.4	3.0	2.44	0.0061

