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EXAFS Spectroscopy: Its Applications in Chemical Speciation in Solution

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Earlier potentiometric and ¹³C-NMR studies have shown that at $H_2L / Hg(II) \ge 2$ 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!







Hg(II)- Hg L ₃ -edg	c <mark>yste</mark> i je EXA	ine co FS	C _{Hg(II)} ~ 0	formation 1 M pH = 11 UNMERSITY OF CALCARY	
H ₂ Cys / Hg(II) ratio) C.N.	Hg-S (Å	A) σ ² (Å ²)	H ₂ Cys / Hg(II) ratio	
Solid Hg(HCys) ₂	2 <mark>fix</mark>	2.34	0.0028		
Solutions $(S_0^2 = 0.9 \text{ fix})$ $\approx 4.3 \text{ VVVVV}$					
2.2	2.05	2.36	0.0037	S MM	
3.3	2.13	2.39	0.0069		
4.3	2.73	2.44	0.0089	10.1	
5.3	3.40	2.50	0.0087		
10.1	3.48	2.50	0.0084	2 4 6 8 10 12 14	
				<i>k</i> (Å ⁻¹)	

Mon	omeric Hg(I 2010 survey	distances	UNIVERSITY OF CALGARY	
	Range of Hg-S (Å) R _{ave Hg-S}			
	RS—Hg—SR	2.30 – 2.34	2.33 ± 0.01	
		2.33 – 2.36	2.35 ± 0.01	
	RS-Hg SR	2.40 – 2.51	<mark>2.44</mark> ± 0.04	
		2.49 – 2.58	2.54 ± 0.02	

Hg(II)- Hg L ₃ -edç	cysteine Je EXAFS	complex for C _{Hg(II)} ~ 0.1 M	pH = 11	Y OF RY
H ₂ Cys / Hg(I ratio	I) C. <i>N.</i> Hg-	<mark>S</mark> (Å) σ ² (Å ²)		
Solutions			Possibility of formation	
2.2	2.05 2.3	6 0.0037	of [Hq(Cys) ₄]6- when:	
3.3	2.13 2.3	9 0.0069	$[H_{\alpha}Cys] / [Hq^{2+1} > 5]$	
4.3	2.73 2.4	4 0.0089	$[1, 2^{2}, 3^{2}, 1] \sim (1, 1, 1)$	
5.3	3.40 2.5	0.0087	Frop [Cyrc ² -] > 0.1 M	
10.1	3.48 2.5	0 0.0084	and pH > 9	













Hg(II)- pe Hg L ₃ -edge	enicill e EXAF	amine S p	e comp H = 11	ex formation	UNIVERSITY OF CALGARY
H ₂ Pen / Hg(II)	C.N.	Hg-S (Å	Λ) σ ² (Å ²)		
Solid Hg(HPen) ₂ Solutions (S ₀	2 <mark>fix</mark> ² = 0.9 fi	2.35 ix)	0.0036		
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		







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Distribution in alkaline a	Distribution of $[Hg(Pen)_n]^{2-2n}$ ($n = 2, 3$) in alkaline aqueous solutions				
□ ¹⁹⁹ Hg NM	R	H₂Pen/ Hg [∥]	%[Hg(Pen) ₃]4-	[Pen] ²⁻ (mM)	
H Bop (Ha(II) r	tio	1.9	0		
1.0 -619	400	2.5	20	12	
2.5 1-57	'4	3.6	54	103	
3.6	3.6 1-496		85	192	
4.9	-425	6.2	89	301	
6.3		8.0	99	469	
8.0	-394	10.0	99	675	
10.0	-394	15.4	100	1007	
15.4	-391	%[Hg(Pen) ₂] ²⁻ = 100 - %[Hg(Pen) ₃] ⁴⁻			
-700 -600 - ¹⁹⁹ Hg NMR	500 -400 -300 Chemical Shift	$[{\sf Pen}]^{2\cdot} = C_{{\sf H2Pen}} - 2 \ C_{[{\sf Hg}({\sf Pen})2]2\cdot} - 3 \ C_{[{\sf Hg}({\sf Pen})3]4\cdot}$			





Mo(V) Species in Aqueous HCI Solution











