

Complex Formation of Mercury(II) with Cysteine in Aqueous Solution

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Introduction

The toxic properties of inorganic mercury have been attributed to the high affinity of Hg(II) ions to thiol (-SH) groups of cysteine residues in proteins and peptides, damaging enzymes and disrupting membrane transport. To obtain further insight into the mechanism of this toxicity, the structure and speciation of mercury(II) complexes in aqueous solutions with the amino acid L-cysteine ($\text{HSCH}_2\text{CH}(\text{NH}_3^+)\text{COO}^-$ or H_2Cys) was studied.

Experimental

Under argon, five solutions with $[\text{Hg}^{2+}] \sim 0.09$ mol/L and $\text{H}_2\text{Cys}/\text{Hg(II)}$ molar ratios of 2.2 (A), 3.3 (B), 4.3 (C), 5.3 (D), and 10.1 (E) were prepared at pH = 11 and their ^{199}Hg NMR and Raman spectra measured. Hg L_{III} -edge EXAFS spectra were collected at BL 10-B of the Photon Factory (PF) of the High Energy Accelerator Research Organization. During the least-squares curve-fitting analysis, which provides Hg-S bond distances (R) and Debye-Waller parameters (σ^2), the amplitude reduction factor (S_0^2) was fixed to 0.9. Principle Component Analysis (PCA) applied on this series of EXAFS spectra revealed three different Hg(II)-species. A characteristic Raman band was used to obtain the concentration of the $[\text{Hg}(\text{Cys})_2]^{2-}$ complex [1].

Results and Discussion

Fourier transforms of k^2 -weighted EXAFS oscillations for solutions A – E show only one peak, corresponding to the Hg-S path. Least-squares curve-fitting analysis of the EXAFS spectra for these solutions resulted in a roughly estimated ($\pm 20\%$) coordination number varying between 2.1 (A) to 3.5 (E), and Hg-S distances of 2.36 Å (A), 2.39 Å (B), 2.44 Å (C), 2.50 Å (D) and 2.50 Å (E), with an accuracy of ± 0.02 Å. A literature survey of Hg(II)-thiolate crystals indicated that the mean Hg-S bond distance falls in the range 2.32–2.36 Å for linear $[\text{Hg}(\text{SR})_2]$ complexes, 2.42–2.44 Å for trigonal $[\text{Hg}(\text{SR})_3]^-$ and 2.52–2.54 Å for distorted tetrahedral $[\text{Hg}(\text{SR})_4]^{2-}$ complexes. By comparing the mean Hg-S distances from the EXAFS of solutions A – E with those from crystal structures, it may be concluded that in solution A, a linear $[\text{Hg}(\text{Cys})_2]^{2-}$ complex and in solution C, a three-coordinated $[\text{Hg}(\text{Cys})_3]^{4-}$ complex is dominating. However, other solutions contain mixture of three $\text{Hg}(\text{Cys})_n$ ($n=2, 3, 4$) species, as indicated by the PCA analysis. To determine the amount of each complex in solutions A – E, the EXAFS oscillations for $\text{Hg}(\text{Cys})_n$ ($n=2, 3, 4$) were generated theoretically by means of FEFF8.1, and a linear combination was fitted to the experimental data for each solution (Table 1, Figure 2).

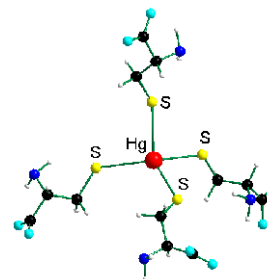


Figure 1. The proposed structure of the novel $[\text{Hg}(\text{Cys})_4]^{6-}$ species, from a simulation. The presence of this species in solutions with $\text{H}_2\text{Cys}/\text{Hg(II)} \geq 5$ was confirmed by ^{199}Hg NMR [1].

The best fits were obtained by assuming average Hg-S distances of 2.35(2), 2.44(2) and 2.52(2) Å for $\text{Hg}(\text{Cys})_2$, $\text{Hg}(\text{Cys})_3$ and $\text{Hg}(\text{Cys})_4$ species, respectively, with the corresponding Debye-Waller parameters of 0.003, 0.006 and 0.008 Å², calculated by the FEFF 8.1 program.

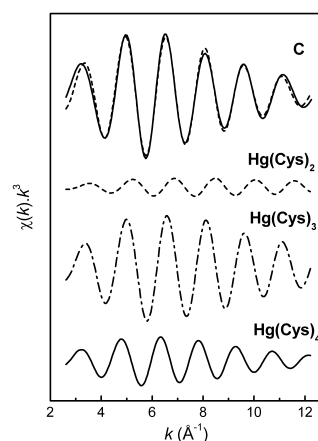


Figure 2. Hg L_{III} -edge k^3 -EXAFS oscillation of solution C fitted to linear combination of Hg-S interaction in $\text{Hg}(\text{Cys})_2$ (12%), $\text{Hg}(\text{Cys})_3$ (62%) and $\text{Hg}(\text{Cys})_4$ (26%).

Table 1. Relative amount (%) of $\text{Hg}(\text{Cys})_n$ species in solutions A – E from EXAFS, Raman and ^{199}Hg NMR.

Solution	$\text{H}_2\text{Cys}/\text{Hg(II)}$	$\text{Hg}(\text{Cys})_2$	$\text{Hg}(\text{Cys})_3$	$\text{Hg}(\text{Cys})_4$
A	2.2	94	6	
B	3.3	42	58	
C	4.3	12	62	26
D	5.3	5	22	73
E	10.1		~15	~85

Reference

[1] F. Jalilehvand et al., *Inorg. Chem.* 45 (2006) 66.

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