Supplemental Information: The Molecular Structure of Aqueous Hg(II)-EDTA as Determined by X-ray Absorption Spectroscopy

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Determination of S_0^2

Crystalline powdered Hg(II) acetate was purchased from Sigma Aldrich and analyzed to determine the S_0^2 parameter, where S_0^2 is the passive electron reduction factor. Previously reported crystallographic information for Hg(II) acetate[1] was used to fit the experimental data with the program Artemis.[2] We were able to reproduce the major spectral features by including seven single and multiple scattering paths, and the fit parameters and fit results are included in Tables S3 and S4 respectively. We obtained an S_0^2 of 0.99 ± 0.07 and a ΔE_0 of 6.61 ± 0.52 for each path. Plots of the fitted k^2-weighted EXAFS and FT of the EXAFS are included in Figure S4. Due to an uncorrectable glitch in the spectrum, the data range in k-space was kept narrow at 2.7 – 9.0 $Å^{-1}$, and the fit range in R-space was 1.2 – 5 Å.

Coordination number of Hg^{2+}

Two recent studies have assessed the coordination of $Hg^{2+}_{(aq)}$ with contradicting results. The first combined quantum mechaniscs/molecular dynamics calculations with XAS to conclude that Hg^{2+} is sevenfold coordinated with C_2 symmetry.[3] The more recent and in depth study examined aqueous Hg^{2+} with EXAFS and large-angle X-ray scattering and determined that $Hg^{2+}_{(aq)}$ is hexacoordinated with distorted octahedral geometry.[4] We fit a single Hg-O shell to our aquired EXAFS of $Hg^{2+}_{(aq)}$ with four variables: the amplitude ($N*S_0^2$), ΔE_0, ΔR, and σ^2 (Figure S5). We obtained an amplitude ($N*S_0^2$) of 5.5 ± 0.3, a ΔE_0 of -1.77 ± 0.53, an average bond distance (R) of 2.30 ± 0.01, and a σ^2 of 0.018 ± 0.001. The fit range of the EXAFS was 2.1 – 9.8 $Å^{-1}$, and the fit range of the F.T. of the k^2-weighted EXAFS was 1.0 – 2.6 Å. Considering the S_0^2 value of 0.99 that was obtained for Hg(II) acetate, we can deduce that the coordination number of $Hg^{2+}_{(aq)}$ is six, which agrees with the most recent study of $Hg^{2+}_{(aq)}$. We acknowledge that our $Hg^{2+}_{(aq)}$

sample contains ~2% $HgNO_3^+$, which will slightly decrease the average coordination number of Hg compared to a sample of pure $Hg^{2+}_{(aq)}$.

References

1. R. Allmann, *Z Kristallogr* 1973, **138**. 366-373.

2. B. Ravel, M. Newville, *J Synchrotron Radiat* 2005, **12**. 537-541.

3. G. Chillemi, G. Mancini, N. Sanna, V. Barone, S. Della Longa, M. Benfatto, N. V. Pavel, P. D'Angelo, *J Am Chem Soc* 2007, **129**. 5430-5436.

4. I. Persson, L. Eriksson, P. Lindqvist-Reis, P. Persson, M. Sandstrom, *Chem-Eur J* 2008, **14**. 6687-6696.

Supporting Tables

Table S1: Description of fit paths[a]

Path[b]	R (Å)	N_{degen}	Amp[c] (%)	ΔR_i (Å)	σ^2_i (Å^2)	ΔR_i (Å)	σ^2_i (Å^2)
Measurement temperature				298 K		193 K	
$Hg \rightarrow O_{eqW}$	2.30	1	100.0	ΔR_{1a}	σ^2_1	ΔR_{1b}	σ^2_3
$Hg \rightarrow O_{eq1}$	2.49	1	52.9	ΔR_{2a}	σ^2_2	ΔR_{2b}	σ^2_4
$Hg \rightarrow N_{eq}$	2.49	2	100.0	ΔR_{2a}	σ^2_2	ΔR_{2b}	σ^2_4
$Hg \rightarrow O_{ax}$	2.65	2	90.0	ΔR_{3a}	σ^2_2	ΔR_{3b}	σ^2_4
$Hg \rightarrow C_1$	2.83	1	32.6	ΔR_4	σ^2_2	ΔR_4	σ^2_4
$Hg \rightarrow C_{3,4,7,8,9,10}$	3.21	6	100	ΔR_5	σ^2_2	ΔR_5	σ^2_4
$Hg \rightarrow C_2$	3.28	1	15.7	ΔR_6	σ^2_2	ΔR_6	σ^2_4
$Hg \rightarrow N_{eq} \rightarrow C_{3,4,8,10}$	3.59	8	23.1	$\Delta R_{2a} + \Delta R_5$[c]	$1.3 \times \sigma^2_2$	$\Delta R_{2b} + \Delta R_5$	$1.3 \times \sigma^2_4$
$Hg \rightarrow O_1$	4.02	1	9.9	ΔR_7	$1.3 \times \sigma^2_2$	ΔR_7	$1.3 \times \sigma^2_4$
$Hg \rightarrow O_1 \rightarrow C_1$	4.03	2	25.3	$\Delta R_4 + \Delta R_7$	$1.3 \times \sigma^2_2$	$\Delta R_4 + \Delta R_7$	$1.3 \times \sigma^2_4$
$Hg \rightarrow C_1 \rightarrow O_1 \rightarrow C_1$	4.05	1	16.2	$\Delta R_4 + \Delta R_7$	$1.3 \times \sigma^2_2$	$\Delta R_4 + \Delta R_7$	$1.3 \times \sigma^2_4$
$Hg \rightarrow O_{2,3}$	4.41	2	14.8	ΔR_8	$1.3 \times \sigma^2_2$	ΔR_8	$1.3 \times \sigma^2_4$
$Hg \rightarrow O_{2,3} \rightarrow C_{7,9}$	4.42	4	38.6	$\Delta R_5 + \Delta R_8$	$1.3 \times \sigma^2_2$	$\Delta R_5 + \Delta R_8$	$1.3 \times \sigma^2_4$
$Hg \rightarrow C_{7,9} \rightarrow O_{2,3} \rightarrow C_{7,9}$	4.43	2	24.8	$\Delta R_5 + \Delta R_8$	$1.3 \times \sigma^2_2$	$\Delta R_5 + \Delta R_8$	$1.3 \times \sigma^2_4$
Measurement temperature				100 K		29 K	
$Hg \rightarrow O_{eqW}$	2.30	1	100.0	ΔR_{1c}	σ^2_5	ΔR_{1d}	σ^2_7
$Hg \rightarrow O_{eq1}$	2.49	1	52.9	ΔR_{2c}	σ^2_6	ΔR_{2c}	σ^2_8
$Hg \rightarrow N_{eq}$	2.49	2	100.0	ΔR_{2c}	σ^2_6	ΔR_{2c}	σ^2_8
$Hg \rightarrow O_{ax}$	2.65	2	90.0	ΔR_{3b}	σ^2_6	ΔR_{3b}	σ^2_8
$Hg \rightarrow C_1$	2.83	1	32.6	ΔR_4	σ^2_6	ΔR_4	σ^2_8
$Hg \rightarrow C_{3,4,7,8,9,10}$	3.21	6	100	ΔR_5	σ^2_6	ΔR_5	σ^2_8
$Hg \rightarrow C_2$	3.28	1	15.7	ΔR_6	σ^2_6	ΔR_6	σ^2_8
$Hg \rightarrow N_{eq} \rightarrow C_{3,4,8,10}$	3.59	8	23.1	$\Delta R_{2c} + \Delta R_5$	$1.3 \times \sigma^2_6$	$\Delta R_{2c} + \Delta R_5$	$1.5 \times \sigma^2_8$
$Hg \rightarrow O_1$	4.02	1	9.9	ΔR_7	$1.4 \times \sigma^2_6$	ΔR_7	$1.5 \times \sigma^2_8$
$Hg \rightarrow O_1 \rightarrow C_1$	4.03	2	25.3	$\Delta R_4 + \Delta R_7$	$1.4 \times \sigma^2_6$	$\Delta R_4 + \Delta R_7$	$1.5 \times \sigma^2_8$
$Hg \rightarrow C_1 \rightarrow O_1 \rightarrow C_1$	4.05	1	16.2	$\Delta R_4 + \Delta R_7$	$1.4 \times \sigma^2_6$	$\Delta R_4 + \Delta R_7$	$1.5 \times \sigma^2_8$
$Hg \rightarrow O_{2,3}$	4.41	2	14.8	ΔR_8	$1.4 \times \sigma^2_6$	ΔR_8	$1.5 \times \sigma^2_8$
$Hg \rightarrow O_{2,3} \rightarrow C_{7,9}$	4.42	4	38.6	$\Delta R_5 + \Delta R_8$	$1.4 \times \sigma^2_6$	$\Delta R_5 + \Delta R_8$	$1.5 \times \sigma^2_8$
$Hg \rightarrow C_{7,9} \rightarrow O_{2,3} \rightarrow C_{7,9}$	4.43	2	24.8	$\Delta R_5 + \Delta R_8$	$1.4 \times \sigma^2_6$	$\Delta R_5 + \Delta R_8$	$1.5 \times \sigma^2_8$

[a] The simultaneous fit of 4 spectra at different temperatures used 23 variables and the data contained ~61 independent points.
[b] The atom positions from each path are explained in Figure 3 (main text).
[c] Amplitude ratio relative to first path, calculated by FEFF6.
[d] The ΔR parameter for the multiple scattering paths is written as a sum of the ΔR parameter for associated single scattering paths as an approximation so that no new parameters are introduced.

Table S2: Cartesian coordinates of Hg-EDTA$_{(aq)}$ molecular model

Atom	x	y	z
Hg	0.000	0.000	0.000
N	0.000	2.490	0.000
N	2.457	0.405	0.000
O	-2.452	0.431	0.000
O	0.000	-2.300	0.000
O	0.000	0.601	-2.581
O	0.593	0.098	2.581
O	2.396	0.395	3.684
O	-3.378	2.174	0.000
O	5.646	-1.664	0.000
O	5.691	0.527	0.000
O	0.000	2.428	-3.684
C	2.603	1.878	0.000
C	1.429	2.874	0.000
C	-1.402	2.965	0.000
C	-2.244	1.724	0.000
C	3.536	-0.607	0.000
C	5.036	-0.607	0.000
C	0.000	2.874	-1.429
C	0.000	1.911	-2.579
C	2.836	0.468	1.429
C	1.886	0.311	2.579

Table S3: Description of fit paths for Hg(II) acetate

Path[a]	R (Å)	N_{degen}	N_{leg}	ΔR_i (Å)	σ^2_i (Å^2)
Hg→O_1	2.07	2	2	ΔR_1	σ^2_1
Hg→O_2	2.73	2	2	ΔR_2	σ^2_2
Hg→C_1	3.04	2	2	ΔR_2	σ^2_2
Hg→O_1→C_1	3.24	4	3	$\Delta R_1 + \Delta R_2$	σ^2_2
Hg→O_2→C_1	3.25	4	3	$2 \times \Delta R_2$	σ^2_2
Hg→O_1→Hg→O_1	4.14	2	4	$2 \times \Delta R_1$	σ^2_2
Hg→O_3	4.45	2	2	$2 \times \Delta R_1$	σ^2_2

Table S4: Best-fit half path distances and values of σ^2 for Hg(II) acetate

Path[a]	R (Å)	N_{degen}	R (Å)	σ^2 (10^{-3} Å^2)
Hg→O_1	2.07	2	2.08 ± 0.01	2.2 ± 1.0
Hg→O_2	2.73	2	2.80 ± 0.02	7.0 ± 2.5
Hg→C_1	3.04	2	3.11 ± 0.02	7.0 ± 2.5
Hg→O_1→C_1	3.24	4	3.32 ± 0.03	7.0 ± 2.5
Hg→O_2→C_1	3.25	4	3.40 ± 0.04	7.0 ± 2.5
Hg→O_1→Hg→O_1	4.14	2	4.16 ± 0.02	7.0 ± 2.5
Hg→O_3	4.45	2	4.47 ± 0.02	7.0 ± 2.5

Table S5: Equilibrium constants considered in speciation calculations[a]

Species	Reaction	LogK (I = 0)
$HgOH^+$	$Hg^{2+} + OH^- = HgOH^+$	10.60
$Hg(OH)_2$	$Hg^{2+} + 2OH^- = Hg(OH)_2$	21.80
$Hg(OH)_3^-$	$Hg^{2+} + 3OH^- = Hg(OH)_3^-$	20.90
$HgEDTA^{2-}$	$Hg^{2+} + EDTA^{4-} = HgEDTA^{2-}$	23.50
$HgHEDTA^-$	$Hg^{2+} + H^+ + EDTA^{4-} = HgHEDTA^-$	27.00
$HgOHEDTA^{3-}$	$Hg^{2+} + OH^- + EDTA^{4-} = HgOHEDTA^{3-}$	27.70
$HEDTA^{3-}$	$EDTA^{4-} + H^+ = HEDTA^{3-}$	10.26
H_2EDTA^{2-}	$EDTA^{4-} + 2H^+ = H_2EDTA^{3-}$	16.42
H_3EDTA^-	$EDTA^{4-} + 3H^+ = H_3EDTA^{3-}$	19.09
H_4EDTA	$EDTA^{4-} + 4H^+ = H_4EDTA$	21.08
$HgNO_3{}^+$	$Hg^{2+} + NO_3{}^- = HgNO_3{}^+$	0.19[b]
$Hg(NO_3)_2$	$Hg^{2+} + 2NO_3{}^- = Hg(NO_3)_2$	0.03[b]

[a]All constants were obtained from Stumm and Morgan (1) unless otherwise cited.
[b]Obtained from the Joint Expert Speciation System (http://jess.murdoch.edu.au/jess_home.htm).

Reference

1. Stumm, W. and J.J. Morgan, *Aquatic Chemistry: Chemical equilibria and rates in natural waters*. 3rd ed. 1996, New York: John Wiley & Sons, Inc.

Supporting Figures and Figure Legends

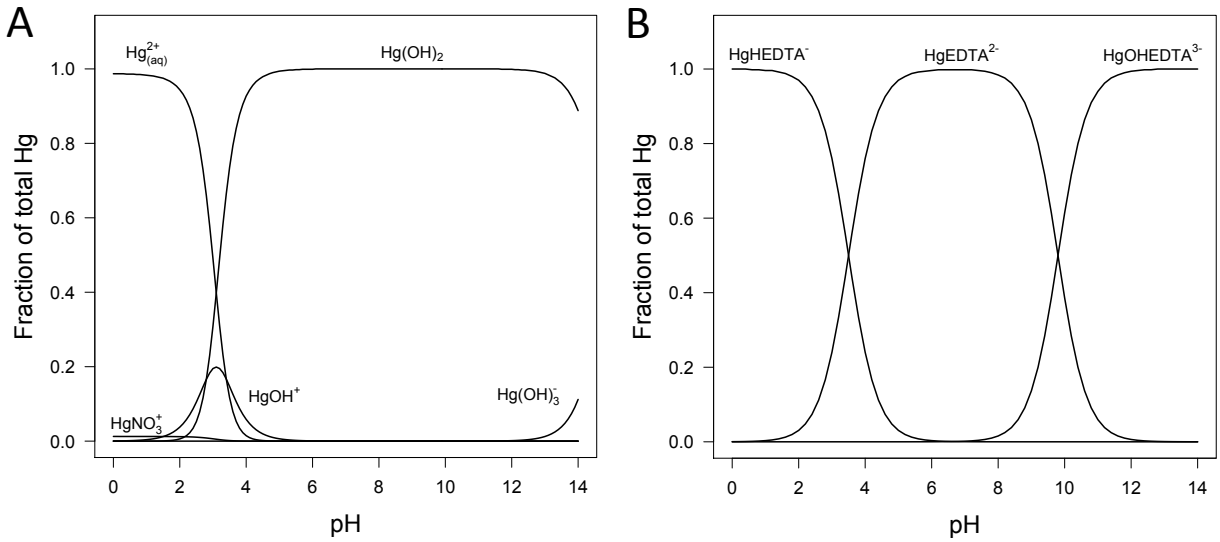

Figure S1: Hg speciation diagrams for (A) 10 mM $Hg(NO_3)_2$ dissolved in Milli-Q^R water vs. pH and (B) 50 mM $Hg(NO_3)_2$ and 250 mM Na_2H_2EDTA dissolved in Milli-Q^R water vs. pH. The equilibrium constants used to create the diagrams are presented in Table S5.

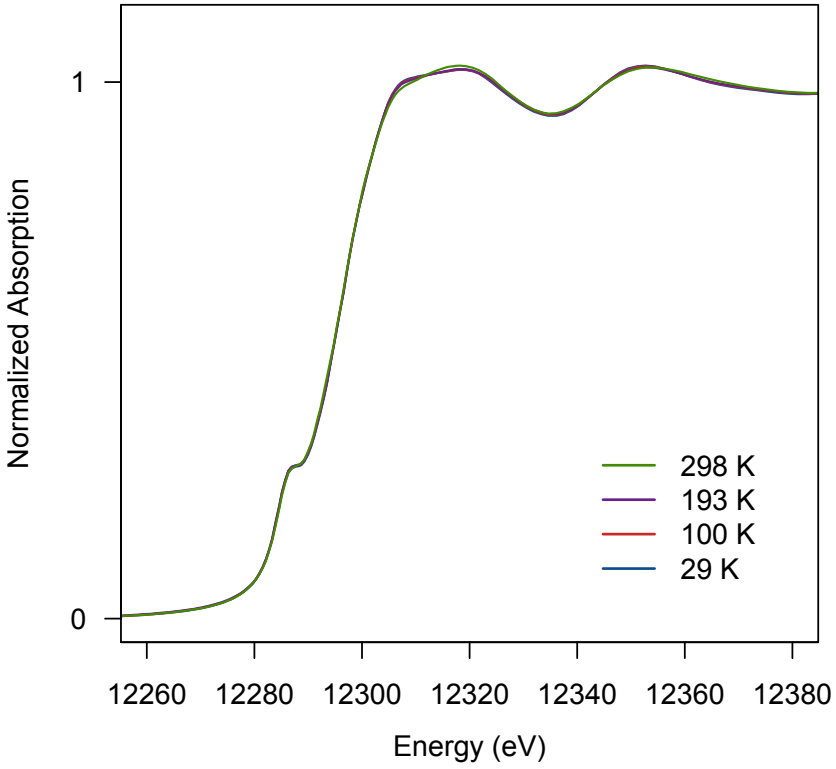

Figure S2: Superimposed Hg L_{III}-edge XANES spectra of aqueous Hg(II)-EDTA with pure Milli-Q^R as the solvent measured at different temperatures.

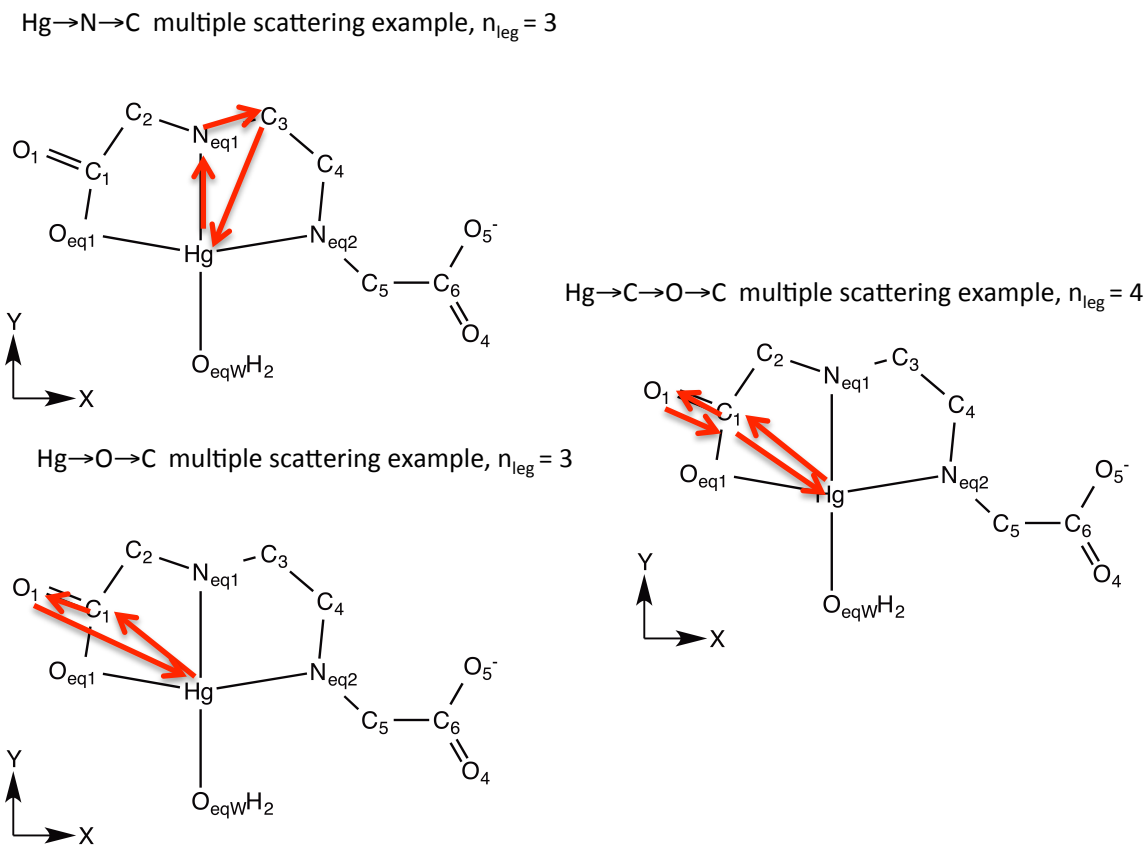

Figure S3: Schematic examples of the three types of multiple scattering paths that contribute significantly to the EXAFS signal. The degeneracy and other atoms involved in degenerate paths are presented in Table 2 as well as Table S1.

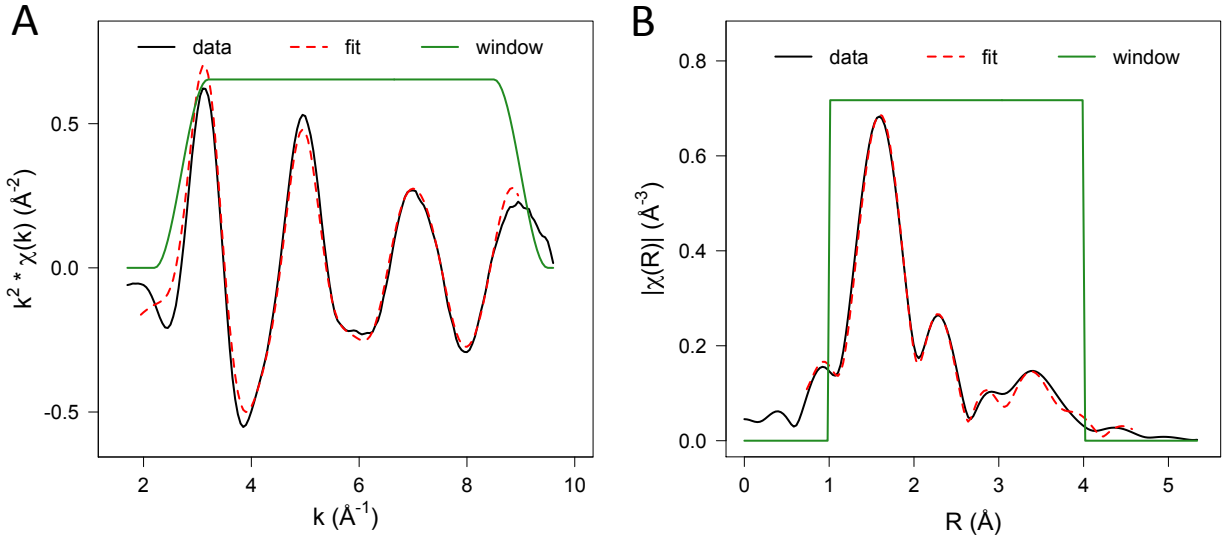

Figure S4: Results of the fit of the (A) k^2-weighted EXAFS and (B) the Fourier transform of the k^2-weighted EXAFS of crystalline Hg(II) acetate measured at 298 K.

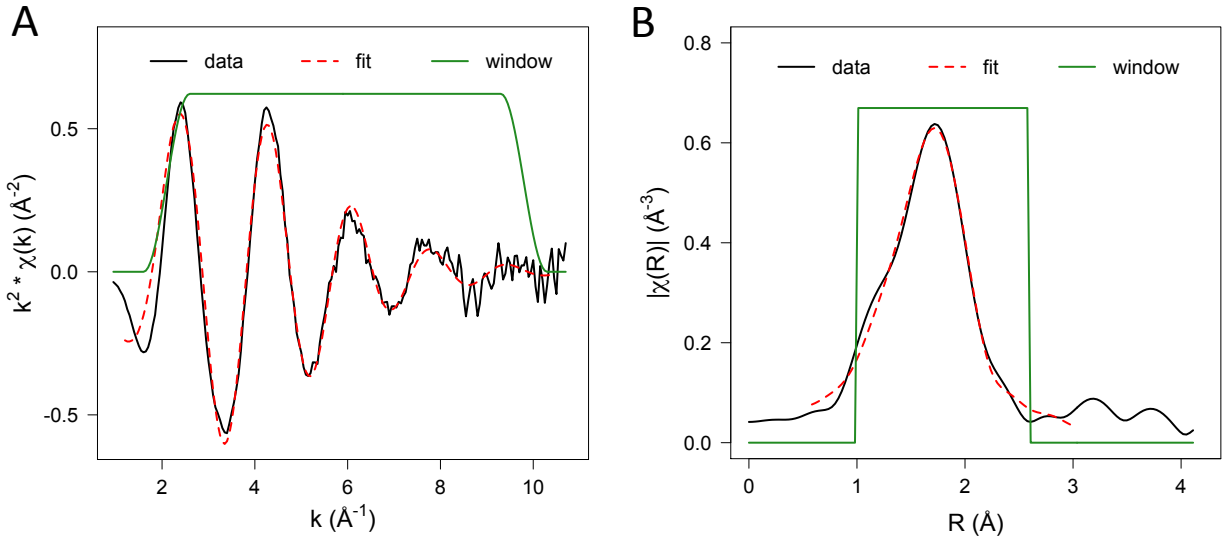

Figure S5: Results of the fit of the (A) k^2-weighted EXAFS and (B) the Fourier transform of the k^2-weighted EXAFS of $Hg^{2+}_{(aq)}$ measured at 298 K.