Electronic Supplementary Material

Mercury(II) Complex Formation with *N*-Acetylcysteine

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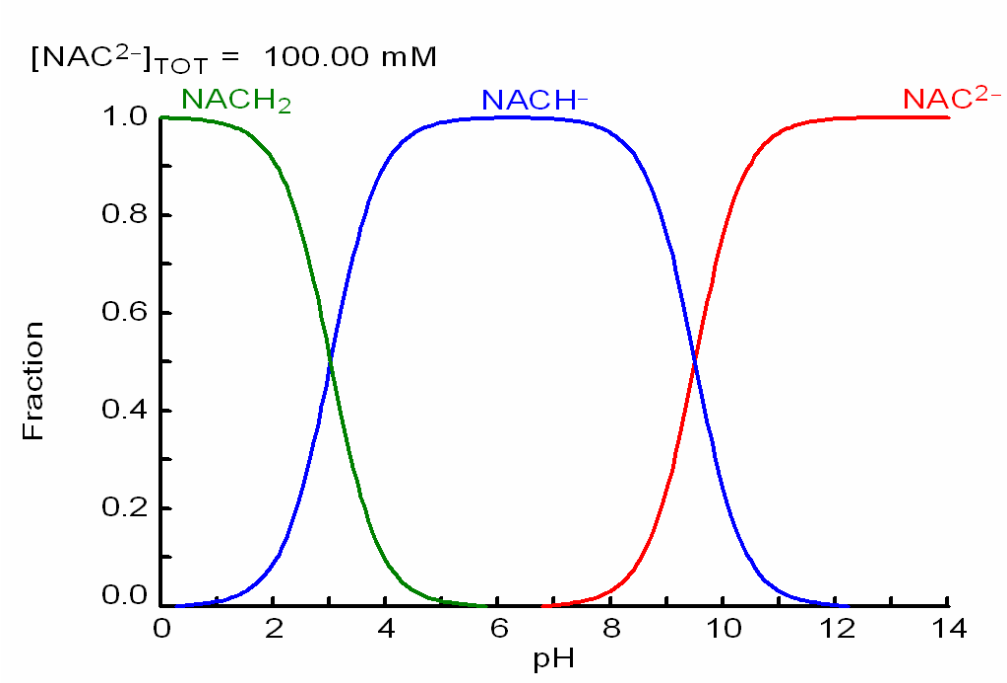


Figure S-1. Distribution diagram showing the pH dependence of *N*-acetylcysteine protonated forms (H_2NAC, $HNAC^-$ and NAC^{2-}), considering the acid dissociation constants $pK_1 = 3.31$ and $pK_2 = 9.85$ (*Ref.* 23)

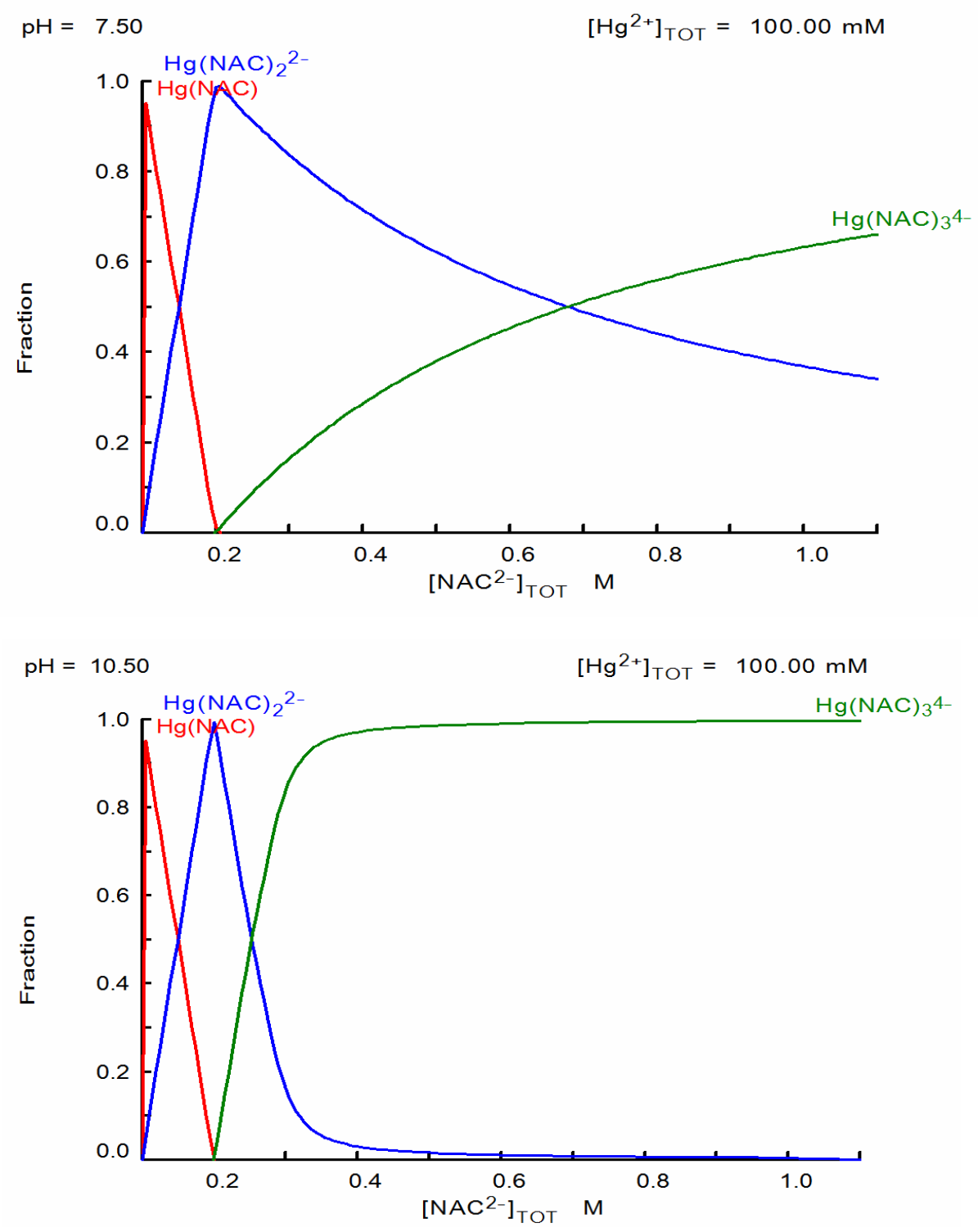


Figure S-2. Distribution diagrams for Hg(II) *N*-acetylcysteine complexes as a function of C_{H_2NAC} at pH = 7.5 (*top*) and 10.5 (*below*) in aqueous solution containing $C_{Hg(II)}$ = 0.1 M, based on the reported stability constants in *Ref.* 24. No stability constant has been reported for the $Hg(NAC)_4^{6-}$ complex identified in the current study.

The above diagrams were calculated with MEDUSA program (http://www.kemi.slu.se/medusa)

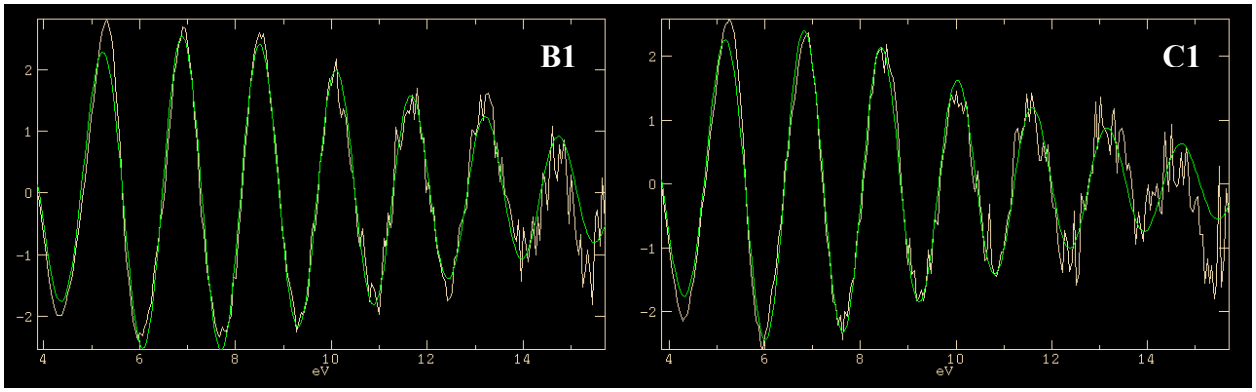
Input file for MEDUSA program:

```
  3,  13,  1,  0   /MEDUSA, t= 25 C, p= 1
H+
Hg 2+
NAC 2-
NACH -              ,   9.69    1  0  1
NACH2               ,   12.7    2  0  1
Hg(NAC)             ,   34.61   0  1  1
Hg(NAC)2 2-         ,   41.81   0  1  2
Hg(NAC)2H -         ,   45.37   1  1  2
Hg(NAC)2H2          ,   47.83   2  1  2
Hg(NAC)3 4-         ,   44.37   0  1  3
OH-                 ,  -14.0    -1  0  0
Hg(OH)2             ,  -6.097   -2  1  0
Hg(OH)3-            ,  -21.1    -3  1  0
Hg2OH 3+            ,  -3.33    -1  2  0
Hg3(OH)3 3+         ,  -6.42    -3  3  0
HgOH+               ,  -3.4     -1  1  0
Hg(OH)2(c)          ,  -2.601   -2  1  0
EH, Hg 2+, NAC 2-,
LA, -10.5
T,  0.1
TV,  0.1    2.0
```

The stability constants for the Hg(II)-NAC system were obtained from Kõszegi-Szalai et al (*Ref.* 24). The formation constant of the Hg(NAC) complex, *i.e.* log β (HgNAC) = 38.4, given by Basinger et al. (*Ref.* 25) is evidently too high; it gives a too small calculated fraction of the $Hg(NAC)_2^{2-}$ complex (log β = 41.81) , when comparing with our investigations.

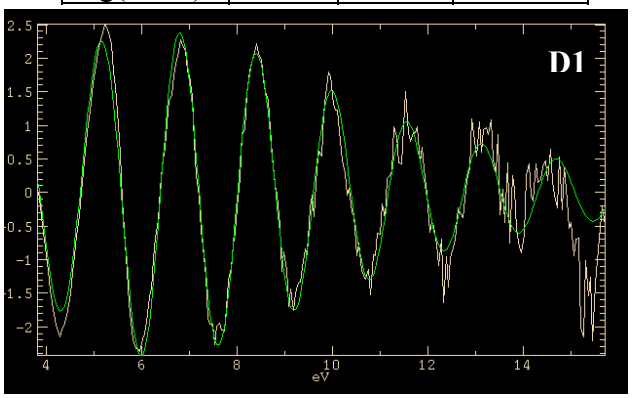
For a consistent estimate of the formation constant of the Hg(NAC) complex, i.e. logβ (HgNAC), we assume that the log *K* (HgL_2) = 7.2 from *Ref.* 25 can be used to estimate the relative amount of the Hg(NAC) complex relative to the $Hg(NAC)_2^{2-}$ complex. We therefore use the formation constant log β (HgNAC) = 41.81 – 7.2 = 34.61 in our calculations, to make the constant comparable with the set of Kõszegi-Szalai et al..

In the above input file, we have also included the solid phase $Hg(OH)_2(c)$.

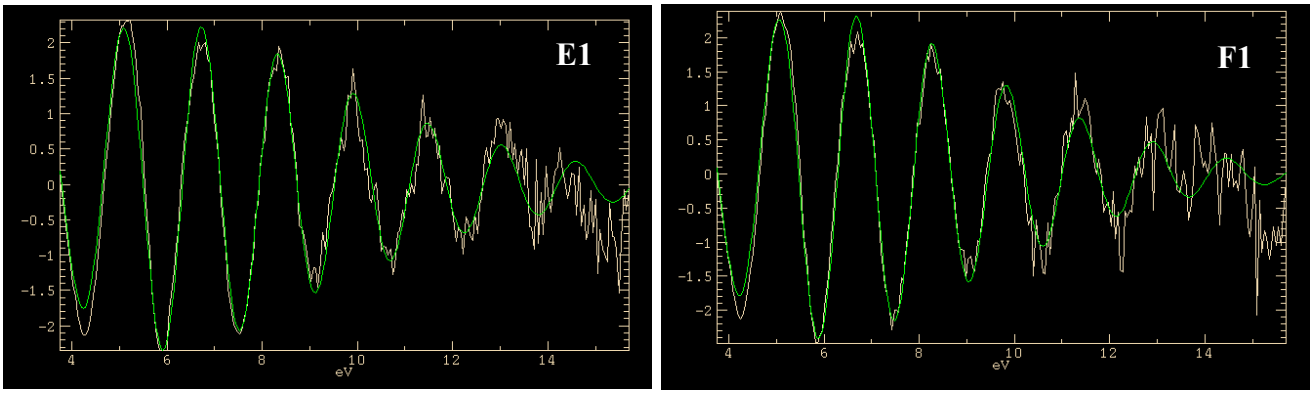


	%	R(Å)	σ^2 (Å^2)
$Hg(NAC)_2$	88	2.33	0.003
$Hg(NAC)_3$	12	2.42	0.004

	%	R(Å)	σ^2 (Å^2)
$Hg(NAC)_2$	68	2.33	0.003
$Hg(NAC)_3$	32	2.42	0.005



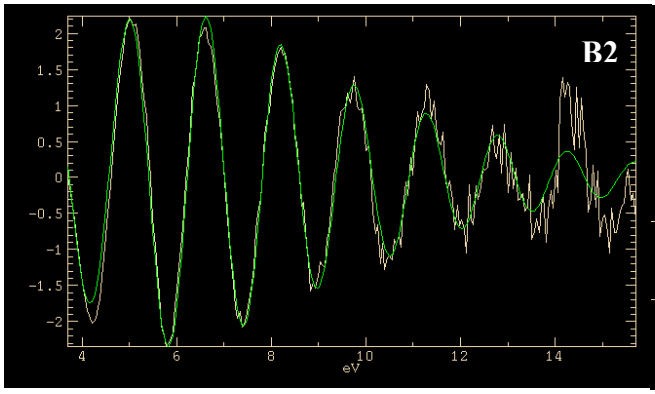
	%	R(Å)	σ^2 (Å^2)
$Hg(NAC)_2$	60	2.33	0.003
$Hg(NAC)_3$	40	2.42	0.005



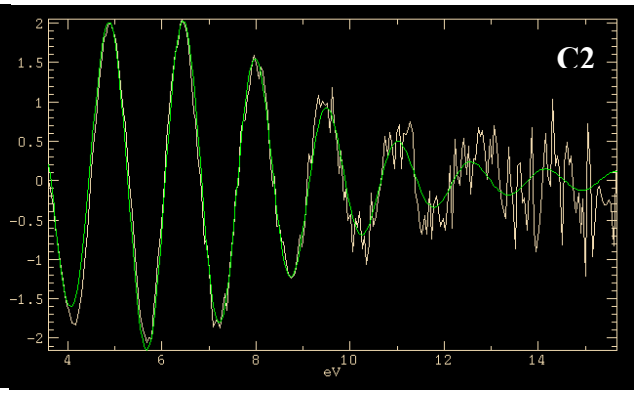
	%	R(Å)	σ^2 (Å^2)
$Hg(NAC)_2$	49	2.33	0.003
$Hg(NAC)_3$	41	2.42	0.004
$Hg(NAC)_4$	11	2.52	0.007

	%	R(Å)	σ^2 (Å^2)
$Hg(NAC)_2$	34	2.33	0.003
$Hg(NAC)_3$	58	2.42	0.005
$Hg(NAC)_4$	8	2.52	0.007

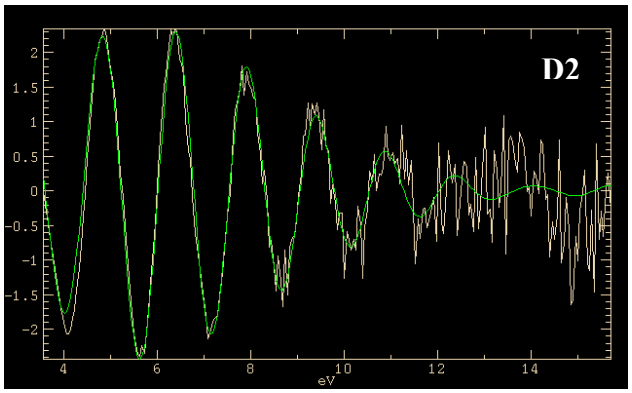
Figure S-3a. Fitting the experimental EXAFS spectra for Hg(II) *N*-acetylcysteine solutions **B1** – **F1** (pH 7.5) with linear combinations of simulated EXAFS oscillations for Hg-S single scatterings in $Hg(NAC)_2^{2-}$, $Hg(NAC)_3^{4-}$ and $Hg(NAC)_4^{6-}$ using FEFF 8.1 and DATFIT programs. ΔE_0 and S_0^2 values fixed at 11 eV and 0.9, respectively. Fits with minimum residual are shown here (see Table 4); estimated accuracy = ± 10-15%.



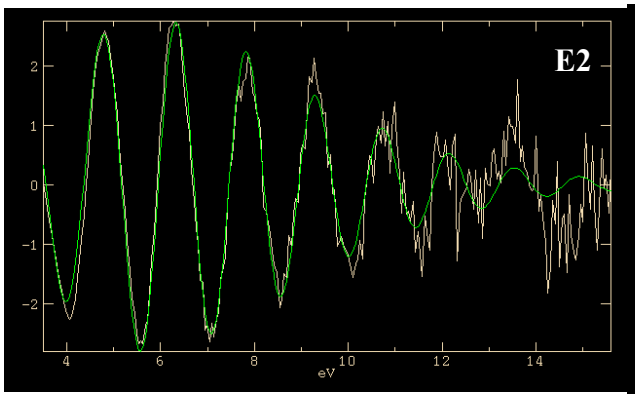
	%	R(Å)	σ^2 (Å^2)
$Hg(NAC)_2$	25	2.33	0.003
$Hg(NAC)_3$	56	2.42	0.004
$Hg(NAC)_4$	19	2.53	0.007

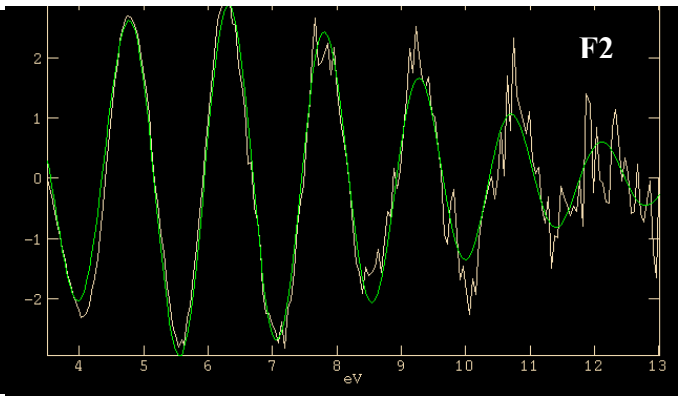


	%	R(Å)	σ^2 (Å^2)
$Hg(NAC)_2$	3	2.33	0.003
$Hg(NAC)_3$	50	2.42	0.005
$Hg(NAC)_4$	47	2.53	0.007



	%	R(Å)	σ^2 (Å^2)
$Hg(NAC)_3$	41	2.42	0.005
$Hg(NAC)_4$	59	2.53	0.007





	%	R(Å)	σ^2 (Å^2)
$Hg(NAC)_2$	4	2.33	0.003
$Hg(NAC)_3$	10	2.42	0.004
$Hg(NAC)_4$	86	2.52	0.007

	%	R(Å)	σ^2 (Å^2)
$Hg(NAC)_3$	17	2.42	0.005
$Hg(NAC)_4$	83	2.53	0.007

Figure S-3b. Fitting the experimental EXAFS spectra for Hg(II) *N*-acetylcysteine solutions **B2** – **F2** (pH 10.5) with linear combinations of simulated EXAFS oscillations for Hg-S singles scatterings in $Hg(NAC)_2^{2-}$, $Hg(NAC)_3^{4-}$ and $Hg(NAC)_4^{6-}$. Fits with minimum residual are shown here (see Tables S-1 & 4); estimated accuracy = ± 10-15%.

Table S-1. EXAFS analyses (Model II) of the relative amount of $Hg(NAC)_n$ species (n = 2, 3, 4) in solutions **A1** – **F1** and **A2** – **F2** (see Figure S-3a and S-3b) [a]

Species	% $Hg(NAC)_2^{2-}$	% $Hg(NAC)_3^{4-}$	% $Hg(NAC)_4^{6-}$	Average R [c]	% $Hg(NAC)_2^{2-}$	% $Hg(NAC)_3^{4-}$	% $Hg(NAC)_4^{6-}$	Average R [c]
Hg-S distance (Å)	**2.33**	**2.42 (σ^2 = 0.004)**	**2.53**		**2.33**	**2.42 (σ^2 = 0.005)**	**2.53**	
D1 (5.0) [b]	63	34	3	2.367	60	40		2.366
E1 (8.0)	48	41	11	2.389	44	49	7	2.388
F1 (10.0)	38	49	13	2.400	34	58	8	2.398
A2 (2.0)	100			2.330	100			2.330
B2 (3.0)	25	56	19	2.418	19	67	14	2.418
C2 (4.0)	8 [d]	42	50	2.468	3 [d]	50	47	2.469
D2 (5.0)	4 [d]	35	61	2.484		41	59	2.485
E2 (8.0)	2 [d]	18	80	2.506		22	78	2.506
F2 (10.0)		15	85	2.514		17	83	2.511

[a] Estimated accuracy is within ± 10-15%; the left and right hand sides of this table show how the assumed σ^2 value for the HgS_3 complex (0.004 $Å^2$ and 0.005 $Å^2$, respectively) affects the relative amounts of the species. [b] Numbers in brackets refer to H_2NAC / Hg(II) mole ratio. [c] The average R = Σ(% of species) x (average Hg-S distance in the species), can be compared to the average distances obtained for solutions **A1** – **F1** and **A2** – **F2** (Table 3). [d] Not observed in Raman.