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Evidence for dissolved polymeric mercury(II)-sulfur complexes?

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Abstract

We have examined alkaline sulfidic (0.5–0.003 M Na₂S), aqueous solutions of Hg(II)-S complexes (4–370 ppm Hg(II)) by Hg *L*_{III} edge EXAFS spectroscopy at 296, 348 and 423 K. Data were collected using the ID26 High Brilliance X-ray Spectroscopy beamline at the ESRF. Analysis of these EXAFS spectra shows Hg coordinated by two S atoms at 2.30 Å; multiple scattering analyses reveal a linear [–S–Hg–S–] arrangement in the solution complex. These results are in agreement with earlier results on more concentrated solutions of these complexes. There is also evidence in the data for polynuclear sulfide complexes at 296 K and 348 K for samples with the lowest sulfide concentrations although this is complicated by multiple scattering effects.

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1. Introduction

Determination of metal speciation in aqueous systems is critical if we are to understand metal cycling at or near the Earth's surface. The lack of this knowledge inhibits accurate modelling and thus predictive capabilities. Of particular interest are the highly toxic

metals anthropogenically introduced into the biosphere and geosphere. Many of these metals are concentrated in reducing sedimentary environments where they form complexes with sulfur ligands, which is a rate controlling step in the metal cycle. Therefore to fully understand the controls on the transport and deposition of metals, their speciation with dissolved sulfide is critical. In particular, an example is the transport and toxicity of mercury in the environment (Lennie et al., 2003) for which understanding of the Hg–S system is fundamental. This is of relevance to the bioavailability of mercury and remediation of contaminated land. More comprehensive reviews of Hg speciation and transport

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Table 1
Sample details

Sample	Solvent	[Na ₂ S] M	Added solids	pH	[Hg] ppm	[Sb] ppm	Colour
b	H ₂ O	0.05	HgS	12.7	369.66	–	Purple
c	buffer	0.03	HgS	11.9	4.324	–	Pale grey
d	buffer	0.006	HgS, S	9.5	–	–	green
f	H ₂ O	0.05	HgS, Sb ₂ S ₃	12.8	270.3	554.82	clear
g	H ₂ O	0.5	HgS, Sb ₂ S ₃	12.5	82.4	2698	pink/orange
h ^a	H ₂ O	0.005	HgS	12.5	37.0	–	pale purple
i ^a	buffer	0.003	HgS	^b	0.43	–	clear

^a Sample h is sample b diluted 10 times and sample i is sample c diluted 10 times.^b pH for sample i was not measured.

in hydrothermal systems, which are controlled by sulfidic species, are given by Varekamp and Buseck (1984), Krupp (1988) and Barnes and Seward (1997).

A recent Hg *L*_{III} edge EXAFS study (Lennie et al., 2003) of the speciation of concentrated Hg in sulfidic solutions at high pH showed that Hg was coordinated by two S atoms at 2.30 Å in a linear HgS₂^{2–} complex. The Lennie et al investigation was undertaken using the ultra dilute spectroscopy beamline 16.5 at the Daresbury Synchrotron Radiation Source (SRS) and the mercury sulfide species were dissolved in the pH range 11.3–11.5, producing concentrations of 2.8–2.5 mM Hg. The solubility of Hg in sulfidic solutions is pH dependent and to investigate lower Hg concentrations, the higher SR intensity of the ID26 X-ray Spectroscopy beamline at the European Synchrotron Radiation Facility (ESRF) was used in this study. EXAFS investigations of the Hg *L*_{III} edge were again used to probe the local structural environment of Hg–S solution complexes and alkaline solutions were prepared and studied at 296, 348 and 423 K.

2. Experimental

2.1. Sample preparation

Deoxygenated aqueous solvents and a commercial pH 9.18 sodium tetraborate buffer solution (Hanna Instruments) were used in sample preparation that was undertaken in a nitrogen-filled anoxic chamber nine days prior to the XAS experiment to ensure samples had reached equilibrium. Anhydrous Na₂S was dissolved in the solvents to make five solutions (samples b, c, d, f and g) which were then saturated with cinnabar (HgS); two (samples f and g) were also saturated with stibnite (Sb₂S₃) and one (sample d) was also saturated with elemental sulfur (S). Stibnite was added to samples f and g to examine the possible formation of polymetallic “Hg–S–Sb” complexes.

Samples were filtered using “Anotop” 0.02 µm filters to remove any solid material prior to loading into the

Table 2
Results of data analyses, m.s. = multiple scattering

Sample	T/K	Scatterer	r (Å)	2σ ² (Å ²)	Data range (k)	R value
b	296				11	
Single shell, no m.s.		2×S	2.30	0.006		31.9
Single shell, +m.s.		2×S	2.30	0.006		31.2
Two shells, +m.s.		2×S	2.30	0.006		31.9
		2×Hg	3.99	0.009		
c	296				14	
Single shell, +m.s.		2×S	2.30	0.006		46.2
Two shells, +m.s.		2×S	2.30	0.006		48.9
		2×Hg	4.03	0.015		
c	348				14	
Single shell, +m.s.		2×S	2.29	0.007		43.7
Two shells, +m.s.		2×S	2.29	0.008		44.7
		2×Hg	4.00	0.015		
c	423				11	
Single shell		4×S	2.51	0.027		46.5
Two shells		4×S	2.50	0.027		45.6
		4×Hg	3.71	0.085		
f	296				14	
Single shell, +m.s.		2 S	2.31	0.004		41.8
g	296				14.5	
Single shell, no m.s.		2×S	2.30	0.005		36.8
Single shell, +m.s.		2×S	2.30	0.005		33.6
Two shells, +m.s.		2×S	2.30	0.005		34.6
		2×Hg	3.89	0.013		
g	348				13	
Single shell, no m.s.		2×S	2.30	0.006		40.0
Single shell, +m.s.		2×S	2.30	0.006		37.9
Two shells, +m.s.		2×S	2.30	0.006		38.1
		2×Hg	3.87	0.020		
g	423				12	
Single shell, no m.s.		2×S	2.30	0.009		55.5
Single shell, +m.s.		2×S	2.30	0.009		53.0
h ^a	296				11	
Single shell, no m.s.		2×S	2.28	0.006		49.6
Single shell, +m.s.		2×S	2.28	0.006		48.2
Two shells, +m.s.		2×S	2.28	0.006		46.1
		2×Hg	4.14	0.007		
h ^a	423				11	
Single shell, no m.s.		2×S	2.29	0.009		53.3
Single shell, +m.s.		2×S	2.29	0.009		51.9

^a Sample h is sample b diluted 10 times.

solution cell (Lennie et al., 2003) for the EXAFS experiment. The sample loading was undertaken under nitrogen just prior to XAS analysis. Either PEEK or BN windows were used for the cell with Kalrez high temperature O-rings. The concentration of Hg and Sb in each solution was determined by Inductively Coupled Plasma atomic emission spectroscopy (ICP-AES) in the Williamson Research Centre, University of Manchester.

Two further samples were prepared at the ESRF by dilution. Sample b was diluted 10 times then sufficient 0.05 M Na₂S was added to raise the pH to 12.5, this new sample was called sample h. Sample c was also diluted 10 times to make a sample with an Hg concentration of 0.4 ppm, this new sample was called sample i. Details of the samples are given in Table 1.

2.2. Data collection

Hg *L*_{III}-edge EXAFS spectra were measured in *k*-space mode, counting for either 1 or 2 s per point. Data were collected using a 13-element solid state Ge detector.

For the most concentrated samples (samples b and f) as few as 4 spectra were summed to give high quality data. For the most dilute sample (sample c, 4 ppm Hg) 24 spectra were summed. No useful data could be obtained for sample d thus confirming the AES result that there was no detectable Hg in solution. Data were collected at ambient temperature (296 K) for samples b, c, f, g and h. Higher temperature data were also collected at 348 K (samples c and g) and 423 K (samples c, g and h). Some precipitation of a solid phase occurred as solution c was heated. The solid accumulated on the cell window and thus dominated the EXAFS spectra. It was not possible to collect reasonable EXAFS data on sample i (sample c diluted 10 times; 0.4 ppm Hg) as the Hg EXAFS signal was extremely weak.

2.3. Data analysis

The data were summed in the ESRF program EXODUS and then reduced in the Daresbury program EXBROOK. The *k*³-weighted EXAFS was simulated

Fig. 1. Experimental EXAFS spectra (solid lines) and best fits (broken lines) for:—(i) sample b, 298 K, (ii) sample c, 298 K, (iii) sample c, 348 K, (iv) sample c, 423 K, (v) sample g, 298 K, (vi) sample g, 348 K, (vii) sample g, 423 K, (viii) sample h, 298 K and (ix) sample h, 423 K.

using the program EXCURV98 (Binsted et al., 1992; Binsted, 1998). Phase shifts were calculated using *ab initio* methods with Hedin–Lundquist exchange and von Barth ground state potentials. The fit index, R , quoted is defined by

$$R = \sum_i [(1/(\sigma_i))(|\text{experiment}(i) - \text{theory}(i)|)] \cdot 100\%$$

where:

$$1/(\sigma_i) = [k(i)]^3 / \left(\sum_i [k(i)]^3 \cdot |\text{experiment}(i)| \right)$$

Hg L_{III} -edge EXAFS data had previously been collected on cinnabar at the SRS, Daresbury Laboratory. These data were fitted to verify the accuracy of the analysis methods. These data were fitted to a single shell of S atoms at 2.38 (± 0.02) Å, in agreement with the crystallographic Hg–S distance for cinnabar of 2.368 Å (Rodic et al., 1996).

In the fitting of the solution data, interatomic distances, and Debye–Waller factors were refined. The shell occupancy numbers were set at 2 for most of the analyses, and a linear geometry assumed to calculate the multiple scattering. For spectra showing long Hg–S distances (2.50–2.51 Å) an integral occupancy number was chosen (Table 2).

3. Results

The results are summarised in Table 2. All samples were analysed at 296 K and these data could be modelled by a first shell in which Hg is bonded to 2 S atoms at *ca* 2.30 Å and the fits were improved significantly by multiple scattering indicating an HgS_2^{2-} species in linear geometry. No evidence for any Hg–S–Sb complexes is observed in any EXAFS spectra collected for samples f and g. Figs. 1 (EXAFS) and 2 (Fourier Transform (FT)) show respectively the observed and calculated plots at different temperatures for samples b, c, g and h.

Fig. 2. Fourier transforms of the experimental EXAFS spectra (solid lines) and best fits (broken lines) for:-(i) sample b, 298 K, (ii) sample c, 298 K, (iii) sample c, 348 K, (iv) sample c, 423 K, (v) sample g, 298 K, (vi) sample g, 348 K, (vii) sample g, 423 K, (viii) sample h, 298 K and (ix) sample h, 423 K.

The FT plots of the samples at 296 K show evidence of longer range ordered scatterers at 4.45 Å. In the region of 4–5 Å the FT show two types of shape, one with two peaks (viz sample b) and a single peak (viz sample c), with intermediate samples (sample g). The double peak in sample b is reflected in the multiple scattering fit and addition of a shell of Hg scatterers at 3.99 Å does not improve the fit (Table 2). However, the additional intensity represented in sample h can be fitted with 2 Hg atoms at 4.14 Å, even after multiple scattering of the linear S–Hg–S unit was taken into account, although the improvement in the residual is small. The FTs of sample c (296 K and 348 K) also show evidence of the additional intensity at 4–4.5 Å, but these do not demonstrate a statistically significant improvement in fit on addition of an extra shell of scatterers to the model. On heating sample h the evidence of the second shell is lost at 423 K (which could either be due to an increase in thermal vibrations or breaking up of the “cluster”). On heating sample c, there is little change in the spectrum at 348 K. However, between 348 K and 423 K the EXAFS of sample c change radically and at 423 K the best single-shell and two-shell fits both have Hg surrounded by 4 S atoms at *ca* 2.50 Å, (see Section 4.2).

4. Discussion

4.1. Linear two-fold coordination

The Hg–S bond distance of 2.30 Å seen in all samples (except sample c at 423 K) is typical of two coordinated Hg and comparable to both the Hg–S complexes in the higher concentration Hg samples studied by Lennie et al. (2003) and the Hg–S distance (2.368 Å) found in the most common HgS mineral, cinnabar (Auvray and Genet, 1973), which has –S–Hg–S– chains running through the structure. According to Barnes (1979), HgS_2^{2-} is dominant in the region above pH=8 and a Raman spectroscopy investigation (Cooney and Hall, 1966) suggests the formation of linear complexes. Other studies (Schwarzenbach and Widmer, 1963; Barnes et al., 1967) also propose a low coordination Hg–S complex at high pH, consistent with the linear HgS_2^{2-} species with Hg–S bond lengths of 2.30 Å observed here.

4.2. Metacinnabar precipitation

The Hg L_{III} EXAFS of sample c at 423 K contrasts with all the other data in showing the Hg atoms surrounded by 4 S atoms at *ca* 2.50 Å. This result was reproducible and in the higher concentration and

examination of the cell showed that a dark precipitate was forming in the cell window with the same (weaker) EXAFS characteristics as that recorded for the whole solution. Thus the EXAFS represent a precipitate formed at high temperatures from this solution. The bond lengths and coordination of this sample are similar to those found in the cubic amorphous metacinnabar from low temperature aqueous Hg+S precipitation (Charnock et al., 2003). The precipitation of metacinnabar from solution was also observed when sample b was heated above 423 K but no EXAFS data were collected at this temperature. This reveals that between 348 K and 423 K mercury sulfide dissolved as cinnabar precipitates from solution as metacinnabar. Metacinnabar is unstable relative to cinnabar below 590 K, so it is forming metastably here (Potter and Barnes, 1978). When samples g and h were heated to 423 K no metacinnabar precipitation was observed. Sample c was made using the buffer as solvent and the pH of this sample was measured as 11.9 at 296 K (see Table 1). The pH of sample b was measured as 12.7 and the pH for samples g and h were both measured as 12.5, higher than sample c. The solubility of Hg^{2+} cations in aqueous solutions at high temperatures is dependent on pH and sulfide concentration. However, there is no obvious pattern of metacinnabar precipitation and this destabilising of the dissolved complexes at high temperature needs further investigation.

4.3. Polynuclear species

Although there are long range peaks in the Fourier transforms of the spectra for samples b, c, g and h, only in sample h is there an indication that these are due to polynuclear Hg–S–Hg species. In the other samples fitting only a single shell of sulfur scatterers and including multiple scattering gives the best fit. The second-shell Hg–Hg interactions shown by EXAFS for sample h provide evidence for polynuclear Hg–S species, and are the first evidence of their presence in sulfidic solutions. One question that has to be addressed is the possibility that the EXAFS represent suspensions or precipitates. However, the possibility that an amorphous metacinnabar precipitate (see above) is present in these samples is discounted, because then Hg would be 4-coordinate with a first Hg–S shell distance of 2.54 Å. We also note also that the cinnabar Hg–Hg distances would be 3.79 and 4.15 Å (Charnock et al., 2003). The presence of polysulfides is another possibility to be considered. Polysulfides are common in natural sulfidic solutions and the solubility of HgS is greatly increased, especially at high pH by the presence of HgS_2^{2-} and $\text{Hg}(\text{S}_x)_2^{2-}$ (with S_x^{2-} $x=3-6$) (see Paquette and Helz, 1997; Jay et al.,

2000). Mercuric polysulfides, (formed by the availability of S^0), often involve 4 coordinate Hg and/or high S:Hg ratios forming ring structures of composition $Hg(S_6)_2^{2-}$ and $Hg(S_4)_2^{2-}$ (Muller et al., 1985) and clusters $Hg(S_4)_2^{2-}$, $Hg(S_4)(S_5)_2^{2-}$, $Hg(S_5)_2^{2-}$, $Hg(S_5)(S_6)_2^{2-}$ (Bailey et al., 1991). However, both tetrahedral HgS_4 and linear HgS_2 structures are recognized in $Na_2Hg_3S_4(H_2O)_2$, which forms chains involving Hg tetrahedra linked by ‘ring’ structures comprising two $-S-Hg-S-$ units (Banda et al., 1991). The argument against polysulfides is that they are unlikely to give the Hg–Hg distances of *ca* 4.0 Å observed in the EXAFS and that the solution chemistry involved no added S^0 . Polymeric metal species have been predicted in other metal–sulfide systems but theoretical and experimental studies (see Tossell, 1999, 2001; Barnes and Seward, 1997) all focus on monomeric Hg–S complexes. The data presented here require a re-examination of this assumption.

5. Conclusions

Hg L_{III} edge EXAFS spectra have been collected on Hg containing species in solution. By use of ID26 at the ESRF it has been possible to collect data in sulfidic solutions with Hg concentrations as low as 4 ppm.

This study confirms the previous work by showing evidence for linear HgS_2^{2-} species in solution but at significantly lower concentrations. There is also some evidence for the presence of polynuclear Hg–S species at ambient temperature but interpretation is complicated by the effect of multiple scattering in the XAS data analysis due to the linear HgS_2^{2-} species. Evidence for possible polynuclear species is only observed in data collected at 296 K and 348 K. This is not seen at 423 K and metacinnabar is seen to precipitate out from two solutions at this higher temperature.

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