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

Anthony M.T. Bell [a,*], John M. Charnock [a,b,c], George R. Helz [d], Alistair R. Lennie [c],
Francis R. Livens [b], J. Frederick W. Mosselmans [c,1],
Richard A.D. Pattrick [a], David J. Vaughan [a]

[a] School of Earth, Atmospheric and Environmental Sciences, and Williamson Research Centre for Molecular Environmental Science,
University of Manchester, M13 9PL, UK
[b] Department of Chemistry, University of Manchester, M13 9PL, UK
[c] Synchrotron Radiation Department, CCLRC Daresbury Laboratory, Warrington, WA4 4AD, UK
[d] Water Resources Research Center and Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA

Abstract

We have examined alkaline sulfidic (0.5–0.003 M Na_2S), 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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* Corresponding author. Present address: Synchrotron Radiation Department, CCLRC Daresbury Laboratory, Warrington, WA4 4AD, UK. Tel.: +441925603807; fax: +441925603124.
E-mail address: a.m.t.bell@dl.ac.uk (A.M.T. Bell).
[1] Present address: Diamond Light Source, Diamond House, Chilton, Didcot, Oxfordshire, OX11 0DE, UK.

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 HgS$_2^{2-}$ 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 Na$_2$S 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 (Sb$_2$S$_3$) 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.