

Theoretical studies on metal thioarsenites and thioantimonides: synergistic interactions between transition metals and heavy metalloids

J. A. Tossell

Department of Chemistry and Biochemistry, University of Maryland, College Park MD 20742, USA

Received 15th April 2000, Accepted 5th May 2000
Published on the Web 15th May 2000

Article

Recently we established that the ternary complex, $\text{CuAsS}(\text{SH})(\text{OH})$ has an unusually high stability and makes a large contribution to the total concentrations of both Cu and As in sulfidic solutions equilibrated with Cu and As sulfide minerals. This ternary complex has an unusual structure, containing a bond which is formally $\text{Cu}(\text{I})\text{--As}(\text{III})$, along with a broken As–S bond. We have now found that complexes with similar structures exist for Au^+ and Tl^+ coordinated to $\text{AsS}(\text{SH})(\text{OH})^-$. However, such a direct metal–metalloid bond is not a requirement for stability. In fact, $\text{TlAsS}(\text{SH})(\text{OH})$ is unstable while $\text{AuAsS}(\text{SH})(\text{OH})$ is highly stable (compared to the aquo ion). Zn^{2+} , Cd^{2+} , Hg^{2+} and Pb^{2+} also form bonds to the As of $\text{AsS}(\text{SH})(\text{OH})$, but without breaking any As–S bonds, and $\text{HgAsS}(\text{SH})(\text{OH})^+$ and $\text{PbAsS}(\text{SH})(\text{OH})^+$ are particularly stable complexes. Calculated structures are shown for these complexes, gas-phase energies are calculated, and formation constants in aqueous solution are estimated. The $\text{SbS}(\text{SH})(\text{OH})^-$ ion forms analogous complexes, with similar stabilities. However, the Au^+ complex of $\text{SbS}(\text{SH})(\text{OH})^-$ is slightly less stable than the Cu^+ complex, opposite to the order found for the $\text{AsS}(\text{SH})(\text{OH})^-$ ligand. The Au^+ and AuSH complexes of $\text{AsSSH}(\text{OH})^-$ or $\text{AsS}(\text{SH})_2^-$ may be implicated in "invisible gold" in arsenian pyrites. Vibrational frequencies are given for the $\text{AuAsS}(\text{SH})_3^-$ complex and the XANES energies of this complex and $\text{Au}(\text{SH})_2^-$ are compared. The existence of such strong complexes may explain the many correlations observed between the concentrations of coinage metals and metalloids.

Introduction

In determining the solubilities of minerals in solution one generally examines the mineral by itself in contact with a solution which contains only noncoordinating ions.¹ However, in nature minerals do not occur in isolation. Rather, it is common to have suites of minerals occurring together, such as various combinations of metal sulfides. Mineral associations containing combinations of heavy transition metal sulfides and metalloid sulfides are well known.^{2,3} In such situations there may be interactions between the different minerals that can modify the solubility of each, by creating a ternary (*i.e.*, metal plus metalloid plus sulfide) species in solution. Studying such systems is difficult experimentally and arriving at a coherent set of solution species and stability constants is even more difficult. Recently it was shown that when As and Cu sulfide minerals were equilibrated together with aqueous solution the solubility of both As and Cu was dominated by contributions from a metal–thiometalate (or metal–metalloid) species⁴ $\text{CuAsS}(\text{SH})(\text{OH})$. Quantum mechanical calculations⁵ confirmed the stability of this species and characterized its structure and some of its properties.

In this work we systematically explore the complexes formed between the thiometalate ligand $\text{AsS}(\text{SH})(\text{OH})^-$ (and some closely related ligands) and a number of late transition metal ions, including Cu^+ , Ag^+ , Au^+ , Zn^{2+} , Cd^{2+} , Hg^{2+} , Tl^+ and Pb^{2+} . We use the same quantum mechanical methods which have previously proven successful for both the thioarsenite⁵ and the simpler complexes of Cu^+ . Accurate energies are determined for the formation of such complexes in the gas phase and reaction energies in solution are estimated, using a simple scheme for approximating the hydration enthalpies of the ions. This allows us to determine which complexes should

be of greatest stability in aqueous solution and suggests targets for more accurate computational studies and for experimental studies.

Computational methods

We use mainly the techniques of Hartree–Fock theory and many-body perturbation theory. The theoretical foundations and capabilities of these techniques are discussed in several reference texts.^{6,7} Recent studies have established that accurate calculation of reaction energies requires consideration of the instantaneous correlations between electron motions,⁸ using the techniques of configuration interaction, many-body perturbation theory, coupled cluster theory or density functional theory. This is particularly important for transition metal compounds, for which even structural properties are sensitive to electron correlation.⁹ We have calculated energy-optimized structures for all molecules using the simplest version of Möller–Plesset many-body perturbation theory¹⁰ (2nd order or MP2, since the sum of the 0th and 1st orders is simply the Hartree–Fock result). The MP2 method is now routinely used for calculations on both main-group and transition-metal organometallic compounds. It is very efficient and reliable, failing to give a better description than the Hartree–Fock only for some pathological open-shell systems. However, recent studies have shown that it can give poor results for some transition metal systems, producing substantial overbonding, *i.e.*, bonds that are too short and too strong, which can be corrected¹¹ by going to higher levels of theory, such as coupled cluster approaches. For the complexes $\text{Cu}(\text{OH})_2^+$, $\text{Cu}(\text{SH})_2^-$ and $\text{CuAsS}(\text{SH})(\text{OH})$ we have therefore also carried out geometry optimizations at the 4th order Möller–Plesset level (MP4) and coupled cluster with double

Table 1 Calculated energies (in hartree, H) for formation of the complexes MAsS(SH)(OH) and M(SH)₂⁻ in the gas phase from M(OH₂)₂⁺ and ligand(s), obtained from polarized SBK MP2 equilibrium geometries and energies, for complexes of Cu⁺, Ag⁺, Au⁺, Zn²⁺, Cd²⁺, Hg²⁺, Tl⁺ and Pb²⁺

Cation	Complex	
	MAsS(SH)(OH)	M(SH) ₂ ⁻¹
Cu ⁺	-0.1886	-0.3168
Ag ⁺	-0.1638	-0.3007
Au ⁺	-0.2120	-0.3470
Zn ²⁺	-0.3866	-0.7285
Cd ²⁺	-0.3705	-0.6987
Hg ²⁺	-0.3960	-0.7487
Tl ⁺	-0.0746	-0.0941
Pb ²⁺	-0.4045	-0.4805

excitations (CCD) levels (see ref. 7 for a description of these methods), considerably more demanding approaches which recover a very large fraction of the energy arising from electron correlation, establishing that these methods yielded results similar to our MP2 results.⁵

The basis sets used for the calculations were of the relativistic effective core potential type, as implemented by Stevens, Basch and Krauss¹² (designated SBK, neglecting core electrons but properly describing their effect upon the valence electrons, with the incorporation of relativistic effects. Additional basis functions of d-type (polarization functions) are added to each of the non-H atoms to better account for the polarization of the electron density during bond formation. We employed the programs GAMESS¹³ and GAUSSIAN94.¹⁴ We have tested our results for the related compounds Ag₂S and Au₂S against those recently obtained by Bagatur'yants, *et al.*¹⁵ Our polarized SBK MP2 results are very similar to their next to best results, obtained using coupled cluster methods, small core pseudopotentials and uncontracted, doubly polarized basis sets.

The calculation of hydration effects upon chemical reactions is currently a very active area within quantum chemistry, with a number of different approaches being employed by various researchers.¹⁶ To evaluate hydration enthalpies we use a multipart approach. For monatomic ions, such as Cl⁻, and for the common small polyatomics, such as OH⁻ or SH⁻, we use "experimental" hydration energies from the tables of Rashin and Honig.¹⁷ Of course, the hydration energy of a neutral compound cannot be uniquely divided into contributions from cation and anion, but if we choose the hydration energy of one particular species as a reference, we can define almost all other hydration energies with respect to it, obtaining quite consistent values. For the large polyatomic ions we determine the hydration energy by using the reformulated Born model of Rashin and Honig, approximating the effective Born radius by adding an effective OH or SH radius to the calculated radius of the molecule, or by calculating the volume enclosed within an isodensity surface with electron density equal to 0.001 electrons bohr⁻³. For the diaquo ions we employ both the Born model described above and the isodensity polarized continuum (IPCM) method,¹⁶ as implemented in GAUSSIAN94. The

Table 2 Estimated hydration enthalpies (in H) of M(OH₂)₂⁺

Cation	R(M-O)+1.49/Å	Born term with RH radii	a ₀ from GAUSSIAN volume	SCRF monopole term	IPCM	exp. ΔH-ΔE _{M(H₂O)₂}
Cu ⁺	3.38	-0.079	3.48	-0.076	-0.1006	-0.092
Ag ⁺	3.75	-0.071	3.42	-0.078	-0.0989	-0.093
Au ⁺	3.68	-0.074	3.47	-0.077	-0.1112	-0.042 ^a
Zn ²⁺	3.36	-0.316	3.29	-0.323	-0.535	-0.486
Cd ²⁺	3.62	-0.294	2.89	-0.368	-0.485	-0.466
Hg ²⁺	3.60	-0.296	3.07	-0.346	^b	-0.452

^aBased on estimated experimental hydration enthalpy (see ref. 23). ^bIPCM calculation did not converge.

Table 3 Estimated enthalpies (in kJ mol⁻¹) for formation of the complexes MAsS(SH)(OH) and M(SH)₂⁻ in aqueous solution from M(OH₂)₂⁺ and ligand, obtained from polarized SBK MP2 equilibrium geometries, for Cu⁺, Ag⁺, Au⁺, Zn²⁺, Cd²⁺, Hg²⁺, Tl⁺ and Pb²⁺. Hydration enthalpies of ions are estimated using effective radii calculated from M-L bond distances

Cation	Complex	
	MAsS(SH)(OH)	M(SH) ₂ ⁻¹
Cu ⁺	-115	-89
Ag ⁺	-71	-52
Au ⁺	-189	-173
Zn ²⁺	-13	-1055
Cd ²⁺	-28	-1003
Hg ²⁺	-89	-1129
Tl ⁺	+140	+459
Pb ²⁺	-177	-483

IPCM avoids an estimate of the Born radius by employing an electron density criterion for defining a surface, not necessarily spherical, enclosing the species.

It is useful to consider what accuracy we might expect to attain in evaluating the energetics of the Cu complexes. As described in ref. 8, even an extremely accurate method such as the composite G2 approach of Pople and coworkers, which incorporates electron correlation at a very high level and effectively extrapolates to the infinite basis set limit, cannot obtain reaction energies to better average accuracy than about 6 kJ mol⁻¹, resulting in equilibrium constant errors at room temperature of about a factor of 10. Most of the compounds in the G2 test set are also smaller than those considered here and G2 is a considerably more accurate theory than the polarized SBK MP2 approach we employ. Nonetheless, we have found that *relative* complex formation enthalpies, within this series of related compounds, can be evaluated with an accuracy which is useful at least for exploratory purposes. Invariably, many serious approximations need to be made for calculations on such systems to be feasible. We believe we have developed a computationally feasible model and method to describe the relative energetics of such complexes. It is important that the method also be simple enough computationally that we can apply it to a wide range of cations and ligands, so as to identify stable species for further more detailed theoretical or experimental study. The accuracy of the gas-phase reaction energies depends only upon the accuracy of the quantum mechanical method, which can be continuously refined to give more reliable results. The more problematic terms in the reaction energies in solution involve our approximations for the hydration energies and our inclusion of only a small and finite number of atoms in our models for the reactive species.

Results

Energetics of complex formation

We have evaluated energies for reactions of type (1) and (2) below in both the gas-phase and aqueous solution. Results are given in Tables 1-3.

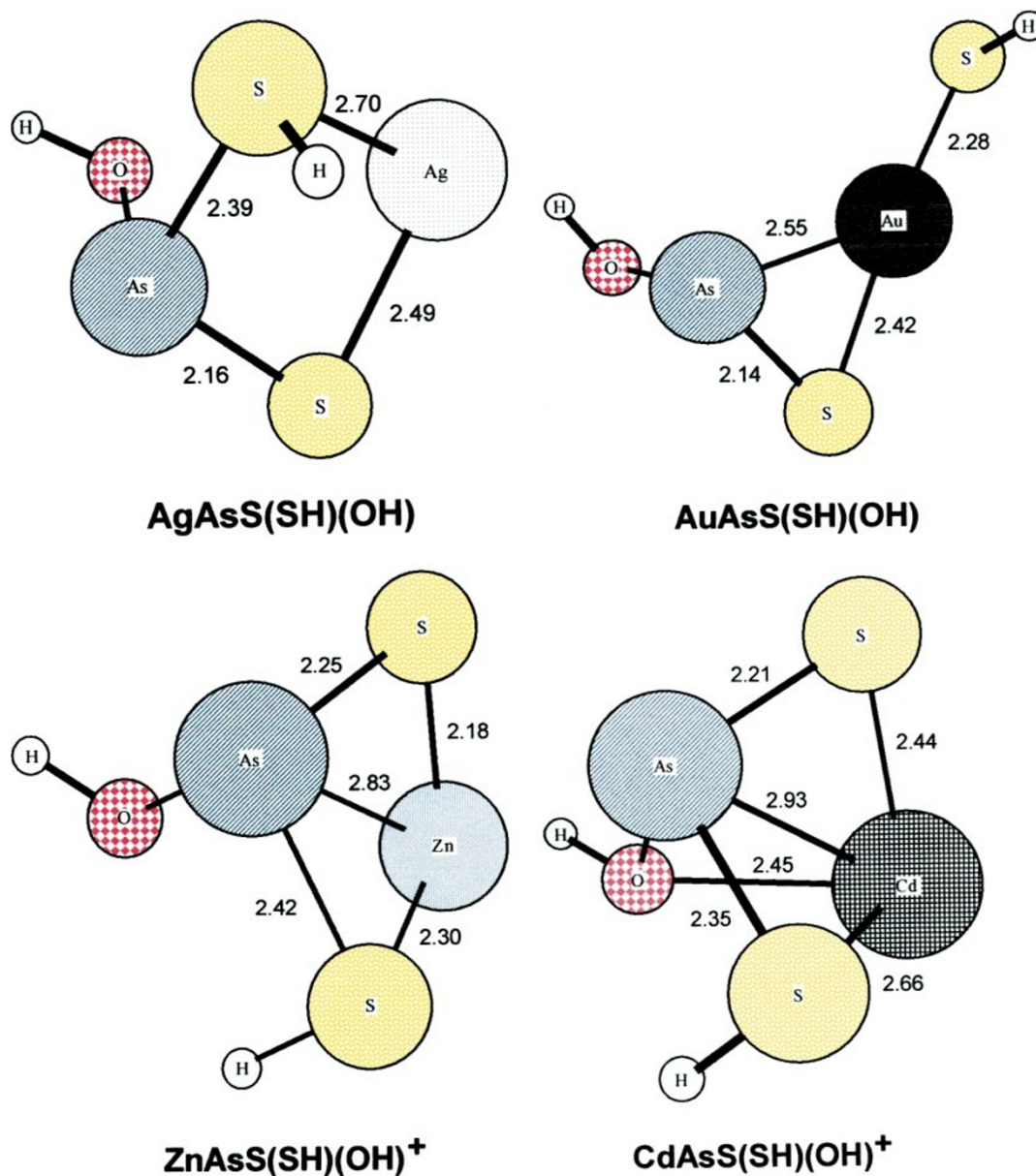
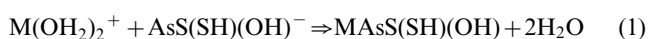


Fig. 1a Geometries calculated at the polarized SBK MP2 level for several metal–thiometalate complexes, with bond distances given in Å.



In each case we use a two-coordinate aquo species as our reactant, allowing it to react with either $\text{AsS}(\text{SH})(\text{OH})^-$ or two SH^- . Results for several other species reacting with the Cu^+ aquo species were given previously.⁵

The results in Table 1 show some interesting trends. For both the Cu^+ and Zn^{2+} families the formation energies are least negative for the intermediate members (Ag and Cd) and most negative for the heaviest members (Au and Hg). This immediately suggests that Au^+ and Hg^{2+} form the strongest complexes, a result in general agreement with experiment for a wide range of ligands. We find also that the formation energy for the Tl^+ complex is quite small, probably a consequence of Tl^+ 's small tendency to bind with S (*i.e.*, Tl^+ is a relatively hard cation, preferring O over S). On the other hand, Pb^{2+} has very negative formation energies with these S-containing ligands. Calculated equilibrium geometries for several of these complexes are shown in Fig. 1.

Calculation of the gas-phase energies for eqns. (1) and (2) is relatively straightforward. Evaluation of the hydration enthal-

pies needed to determine reaction energies in aqueous solution is much more difficult. There are a number of methods currently available for calculating such hydration energies, but none of them is particularly accurate in a first-principles, unparameterized form. We must therefore be content with a reasonably simple and consistent approach which will treat the different complexes with the same level of accuracy. Using the reformulated Born model of Rashin and Honig¹⁷ with their prescription for evaluating effective Born radii gives the results for the Cu series diaquo ions shown in the second column of Table 2.

Since the RH model is based on a spherical cavity containing the solute, and since the diaquo ions are linear and so not space filling, it seems probable that hydration energies calculated in this way would systematically underestimate the experimental results. If we calculate the volume inside an isodensity surface of 0.001 electrons bohr^{-3} and estimate the effective radius from that we obtain the values in the fourth column. The Born energies for these effective radii are given in the fifth column. Clearly the values from the two approaches are similar, but do not show the same trends down the groups. We can also use a full SCRF or IPCM calculation, which will contain a

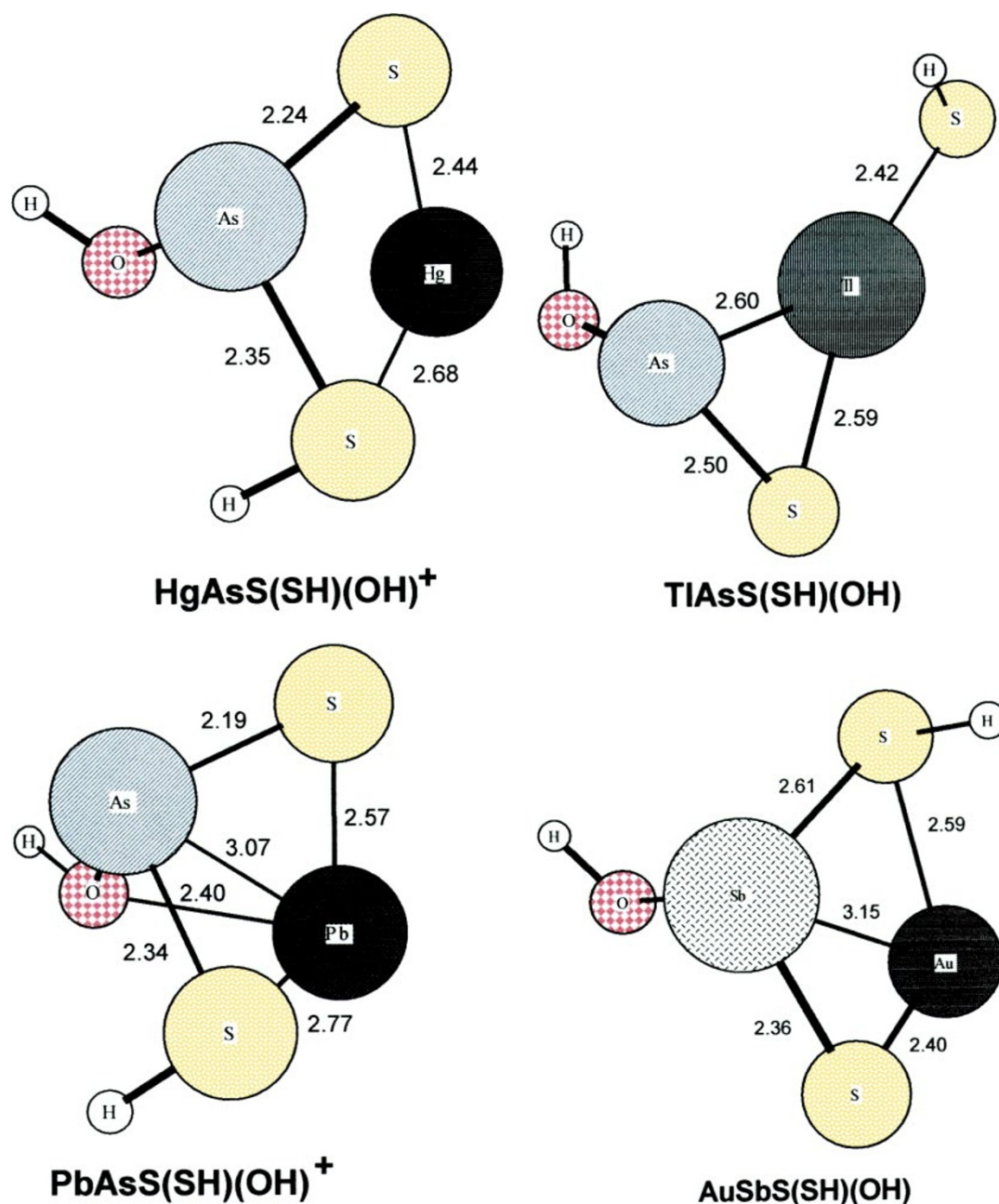


Fig. 1b Geometries calculated at the polarized SBK MP2 level for several metal–thiometalate complexes, with bond distances given in Å.

polarization energy as well as the Born (or monopole) term. These values are systematically larger in magnitude as shown in the IPCM column. We can also subtract the energy for formation of $M(\text{OH}_2)_2^{+n}$ from the experimental hydration energy of the bare cation (as obtained from various tabulations) to obtain the results shown in the last column. An apparent anomaly exists for Au^+ , but this may be a result of using an estimated hydration energy, since no experimental value is available. Otherwise these results are intermediate between the SCRF monopole and the IPCM results. Given the uncertainty in the hydration enthalpy values, we will rely upon the RH approach.

The hydration enthalpies of the other species have similar uncertainties. To be consistent with our use of a RH Born energy we will ignore hydration enthalpies for all the neutral species (even H_2O , for which the experimental value is known and sizable, about 0.015 H). For $\text{AsS}(\text{SH})(\text{OH})^-$ and SH^- we will use the RH prescription, yielding hydration enthalpies of -0.066 and -0.134 H, respectively. For $M(\text{SH})_2^-$ the RH term gives hydration enthalpies considerably smaller than those for

$M(\text{OH}_2)_2^+$, partly because of the longer M–ligand distance and partly because of the larger effective radius of the ligand. For example, the RH hydration energy of $\text{Cu}(\text{SH})_2^-$ is -0.064 H, compared to -0.079 H for $\text{Cu}(\text{OH}_2)_2^+$.

Using the RH hydration enthalpies we obtain the estimated reaction enthalpies in aqueous solution given in Table 3. Note

Table 4 Calculated energies (in hartree) for formation of the complexes $\text{MSbS}(\text{SH})(\text{OH})$ in the gas phase from $M(\text{OH}_2)_2^+$ and ligand, obtained from polarized SBK MP2 equilibrium geometries and energies, for complexes of Cu^+ , Ag^+ , Au^+ , Zn^{2+} , Cd^{2+} and Hg^{2+}

Cation	Complex $\text{MSbS}(\text{SH})(\text{OH})$
Cu^+	-0.1777
Ag^+	-0.1634
Au^+	-0.1724
Zn^{2+}	-0.3929
Cd^{2+}	-0.3728
Hg^{2+}	-0.4007

Table 5 Energies (in kJ mol⁻¹) calculated at the polarized SBK MP2 level for various reactions and hydration energies obtained from calculated volumes

Index number	Reaction	ΔE gas-phase	ΔH_{hyd}	$\Delta H_{\text{solution}}$
(1)	$\text{As}_2\text{S}_5\text{H}_4 + \text{H}_2\text{O} \Rightarrow \text{As}(\text{SH})_3 + \text{As}(\text{SH})_2(\text{OH})$	+36.5	0	+36
(2)	$\text{As}_2\text{S}_5\text{H}_4 + \text{H}_2\text{S} \Rightarrow 2\text{As}(\text{SH})_3$	+13.9	0	+14
(3)	$\text{As}(\text{SH})_3 + \text{OH}^- \Rightarrow \text{AsS}(\text{SH})(\text{OH})^- + \text{H}_2\text{S}$	-320.8	+294	-25
(4)	$\text{Au}(\text{SH}) + \text{AsS}(\text{SH})(\text{OH})^- \Rightarrow \text{AuS}(\text{SH})_2(\text{OH})$	-257	+21	-237
(5)	$\text{AuSH} + \text{AsS}(\text{SH})_2^- \Rightarrow \text{AuAsS}(\text{SH})_3^-$	-258.3	+21	-237
(6)	$\text{Au}(\text{SH})_2^- + \text{AsS}(\text{SH})(\text{OH})^- \Rightarrow \text{AuAsS}(\text{SH})_2(\text{OH})^- + \text{SH}^-$	+96.3	-147	-51
(7)	$\text{Au}(\text{SH})_2^- + \text{AsS}(\text{SH})_2^- \Rightarrow \text{AuAsS}(\text{SH})_3^- + \text{SH}^-$	+96.0	-147	-51

that the hydration enthalpy of the reactant ligands is much more negative for eqn. (2) than for eqn. (1), since we have two SH⁻ ligands in eqn. (2) and one, larger, AsS(SH)(OH)⁻ ligand in eqn. (1). Thus hydration effects reduce the favorability of eqn. (2) compared to eqn. (1), making their energies in solution much more comparable.

We observe that some of the trends seen for the gas-phase energies in Table 1 persist in the aqueous solution energies in Table 3—in particular the intermediate members of both Cu and Zn series have the least negative enthalpies and the heaviest members have the most negative enthalpies. This suggests that the Au⁺ and Hg²⁺ complexes will be the most stable. The complexes of Tl⁺ are unstable (compared to the diaquo species) while those of Pb²⁺ are quite stable. However, our procedure may exaggerate the stability of the complexes of the divalent cations, due to the approximate nature of the hydration energy correction. Thus, the results are most reliable *within* a family, such as the Cu⁺ or the Zn²⁺ families.

Notice that the presence of a metal-metalloid bond does not necessarily mean high stability for the complex. Such a bond exists in both the AuAsS(SH)(OH) and the TlAsS(SH)(OH) complexes, but the Tl complex is actually of very low stability [*i.e.*, compared to Tl(OH)₂⁺]. There is an energy tradeoff in the formation of a direct M-As bond, since a As-S bond must be broken at the same time. The formation of direct metal-metalloid bonds, like the Cu(I)-As(III) bond characterized in CuAsS(SH)(OH), may be related to the stabilizing interactions between d¹⁰ systems, which are essentially intramolecular van der Waals (electron correlation) bonds and have been characterized as the cause of the so-called aurophilic interaction.¹⁸

In Table 4 we present calculated gas-phase energetics for the Cu⁺ family and Zn²⁺ family complexes of SbS(SH)(OH)⁻. Absolute energetics and trends are similar to those for AsS(SH)(OH)⁻, particularly for the Zn²⁺ family complexes. For the Cu⁺ family complexes we find that the Au⁺ complex has slightly less relative stability than for the AsS(SH)(OH)⁻ case. These results suggest that ternary complexes will be important for metal, Sb,S systems as well as their As analogs.

In Table 5 we give calculated energetics for the reactions which are needed to produce the AsS(SH)(OH)⁻ ligand and for the reaction of the Au complexes Au(SH) and Au(SH)₂⁻¹ with the AsS(SH)(OH)⁻ and AsS(SH)₂⁻ ligands. While depolymerization of As₂S₅H₄, a model for orpiment As₂S₃, by water is endothermic [reaction (1)], the reaction energy is small, so that As(SH)₂(OH) could be formed through this reaction. As(SH)₃ also reacts exothermically with OH⁻ to give AsS(SH)(OH)⁻. Both Au(SH) and Au(SH)₂⁻ react exothermically with AsS(SH)(OH)⁻ and AuS(SH)₂⁻ [reactions (4)–(7)]. Each of these Au complexes shows the characteristic Au-As direct bond.

The reasonably good comparison of calculated and experimental stabilities for the simple ligands previously studied⁵ supports the rather simple approach used in this study. Specifically, the gas-phase reaction energetics are evaluated at only a moderately accurate level (polarized SBK MP2), the coordination number of the metal ion is kept small and

(almost) fixed, the hydration energy of the ions is evaluated within the Born model and that of all the neutral molecules is ignored, zero-point vibrational energy effects are ignored and entropic effects are ignored.

The entropy is in fact expected to increase substantially when ions combine in solution to form a complex, leading to an increase in the formation constant. For example, for the formation of Ag(CN)₂⁻ the tabulation of Marcus¹⁹ gives an entropic contribution to log *K* at room temperature *T* of +5.9. For the formation of CuCl(aq) the same tabulation gives an entropic contribution to log *K* of about +6.2. We might therefore expect our purely enthalpic calculated log *K* values to be less positive than experiment by about 6 units.

Properties of AuAsS(SH)₃⁻

The nature of the gold present in the "invisible gold" component of metal sulfides, such as arsenian pyrite, has been studied by numerous researchers. Recently Simon *et al.*^{20(a),(b)} have studied this problem using Au X-ray absorption near edge spectroscopy (XANES). They found spectral signatures for both metallic Au⁰ and cationic Au⁺ species, with the cationic species apparently existing in both two and four-coordinate environments. The Au⁺ sulfide species present in solutions in contact with the arsenian pyrite would presumably be²¹ Au(SH) and Au(SH)₂⁻. We could envision the Au(SH) species reacting with a thioarsenite species such as AsS(SH)₂⁻ to give a AuS(SH)₃⁻ species, with Au⁺ in four-coordination. As seen from Table 4 such a reaction is predicted to be exothermic.

For this AuAsS(SH)₃⁻ species we have calculated the vibrational spectra and the XANES spectra, to assist in its characterization. To calculate the XANES we use the equivalent core-ion approach pioneered by Schwarz.²² Calculated energies for excitation from the Au 5s to the lowest unoccupied MO (LUMO) are given in Table 6. These are expected to match semiquantitatively the trends in Au L_{III} XANES energies. For Au(III) coordinated to Cl and Au(I) coordinated to S the XANES energies show the same trend as that calculated.

The stretching modes of the four-atom group around the Au are shown in Fig. 2.

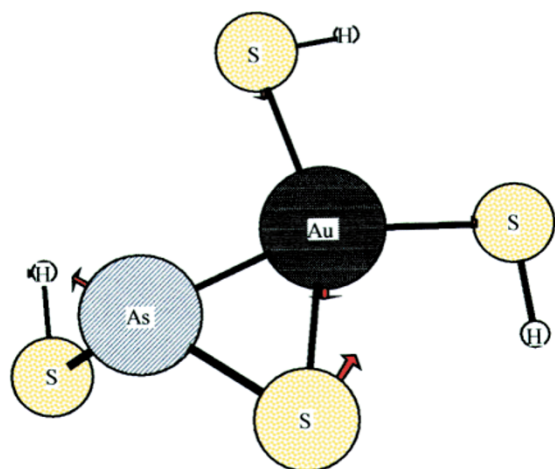
At present there is no experimental data to compare with our calculated vibrational spectra.

Conclusions

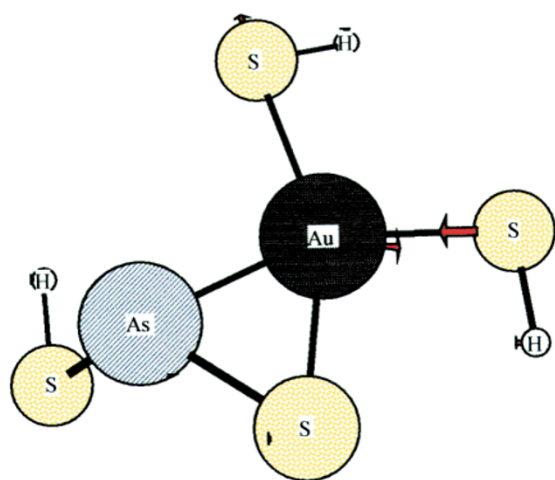
We have established that a number of complexes of AsS(SH)(OH)⁻ with late transition metals will show that

Table 6 Calculated energies (in eV) for excitation from the Au 5s orbital to the lowest energy unoccupied MO compared with Au L_{III} XANES energies [ref. 20(a)]

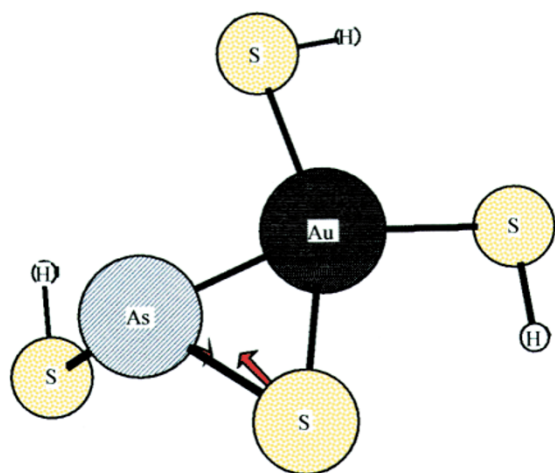
Compound	Au 5s ⇒ LUMO	Au L _{III} XANES (Au 2p ⇒ LUMO)
AuCl ₄	140.1	11 918.8 (in NaAuCl ₄)
Au(SH) ₂ ⁻	142.7	11 923 (in Na ₃ Au(S ₂ O ₃) ₂)
AuAsS(SH) ₃ ⁻	140.5	—



$\nu = 264 \text{ cm}^{-1}$



$\nu = 316 \text{ cm}^{-1}$



$\nu = 441 \text{ cm}^{-1}$

Fig. 2 Selected calculated vibrational frequencies for $\text{AuAsS}(\text{SH})_3^-$. Frequencies (in cm^{-1}) are given with plots and arrows to indicate direction and relative magnitude of motion of nuclei.

same high stability as previously seen for $\text{CuAsS}(\text{SH})(\text{OH})$. In particular, we would expect that mineral assemblages contain-

ing the sulfide pairs Au-As, Hg-As or Pb-As (and probably the corresponding Sb containing pairs) would show very stable ternary complexes. The presence of such complexes may provide part of the explanation for the element associations typically seen in sulfide deposits. That is, Hg and As sulfides may occur together not just because they are sulfides, deriving from sulfidic hydrothermal solutions, but because of specific Hg, As and S ternary complexes.

References

- 1 A. E. Martell, *Determination and Use of Stability Constants*, VCH, Weinheim, 2nd edn., 1992.
- 2 H. G. Dill, T. Weisner, I. R. Bernhardt and C. R. Kilbarda, The composite gold-antimony vein deposit at Kharma (Bolivia), *Econ. Geol.*, 1995, **90**, 51.
- 3 G. A. Karpov, Complex mercury-antimony-arsenic mineralization of the Uzon-Waiotapu type in modern hydrothermal systems, *Int. Geol. Rev.*, 1991, 599.
- 4 M. Clarke and G. Helz, Metal-thiometalate transport of biologically active trace elements in sulfidic environments. 1. Experimental evidence for copper thioarsenite complexing, *Environ. Sci. Technol.*, 2000, **34**, 1477.
- 5 J. A. Tossell, Metal-thiometalate transport of biologically active trace elements in sulfidic environments. 2. Theoretical evidence for copper thioarsenite complexing, *Environ. Sci. Technol.*, 2000, **34**, 1483.
- 6 W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.
- 7 F. Jensen, *Introduction to Computational Chemistry*, Wiley, New York, 1999.
- 8 L. A. Curtiss, K. Raghavachari, P. C. Redfern and J. A. Pople, Assessment of Gaussian-2 and density functional theories for the computation of enthalpies of formation, *J. Chem. Phys.*, 1997, **106**, 1063.
- 9 H. Tractman, G. D. Markhan and C. W. Bock, Interactions of metal ions with water: ab initio molecular orbital studies of structure, bonding enthalpies, vibrational frequencies and charge distributions. 1. Monohydrates, *Inorg. Chem.*, 1998, **37**, 4421.
- 10 J. A. Pople, J. S. Binkley and R. Seeger, Theoretical methods incorporating electron correlation, *Int. J. Quantum Chem. Symp.*, 1976, **10**, 1.
- 11 S. Niu and M. B. Hall, Comparison of Hartree-Fock, density functional, Möller-Plesset perturbation, coupled cluster, and configuration interaction methods for the migratory insertion of nitric oxide into a cobalt-carbon bond, *J. Phys. Chem. A*, 1997, **101**, 1360.
- 12 W. J. Stevens, M. Krauss, H. Basch and P. G. Jansen, Relativistic compact effective potentials and efficient, shared-exponent basis sets for the third-, fourth- and fifth-row atoms, *Can. J. Chem.*, 1992, **70**, 612.
- 13 M. W. Schmidt, K. K. Baldrige, J. A. Boatz, J. H. Jensen, S. Koseki and M. S. Gordon, General atomic and molecular electronic structure system, *J. Comp. Chem.*, 1993, **14**, 1347.
- 14 Frisch *et al.*, GAUSSIAN94, Rev. B.3, Gaussian, Inc., Pittsburgh, PA, 1994.
- 15 A. A. Bagatur'yants, A. A. Safonov, H. Stoll and H.-J. Werner, Ab initio relativistic pseudopotential study of small silver and gold sulfide clusters $(\text{M}_2\text{S})_n$, $n=1$ and 2, *J. Chem. Phys.*, 1998, **109**, 3096.
- 16 J. B. Foresman, T. A. Keith, K. B. Wiberg, J. Snoonian and M. J. Frisch, Solvent effects. 5. Influence of cavity shape, truncation of electrostatics, and electron correlation on ab initio reaction field calculations, *J. Phys. Chem.*, 1996, **100**, 16098.
- 17 A. A. Rashin and B. Honig, Reevaluation of the Born model of ion hydration, *J. Phys. Chem.*, 1985, **89**, 5588.
- 18 P. Pykkö, N. Runeberg and F. Mendizabal, Theory of the d^{10} - d^{10} closed shell attraction: 1. Dimers near equilibrium, *Chem. Eur. J.*, 1997, **3**, 14512.
- 19 Y. Marcus, The hydration entropies of ions and their effects on the structure of water, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 233.
- 20 (a) G. Simon, H. Huan, J. E. Penner-Hahn, S. E. Kesler and L.-S. Kao, Oxidation state of gold and arsenic in gold-bearing arsenian pyrite, *Am. Mineral.*, 1999, **84**, 1071.; (b) G. Simon, S. E. Kesler and S. Chryssoulis, Geochemistry and textures of gold-bearing arsenian pyrite, Twin Creeks, Nevada: Implication for deposition of gold in Carlin-type deposits, *Econ. Geol.*, 1999, **94**, 405.

- 21 T. M. Seward, Thio complexes of gold and the transport of gold in hydrothermal ore solutions, *Geochim. Cosmochim. Acta*, 1972, **37**, 379.
- 22 W. H. E. Schwarz, Continuous change from valence to Rydberg type states. An example of XUV spectroscopy. *Chem. Phys.*, 1975, **9**, 157.
- 23 J. A. Tossell, The speciation of gold in aqueous solution: a theoretical study, *Geochim. Cosmochim. Acta*, 1996, **60**, 17.