

Theoretical studies on the formation of mercury complexes in solution and the dissolution and reactions of cinnabar

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ABSTRACT

Expanding upon our previous studies of the properties of Au complexes, we present calculations for several Hg^{2+} species in aqueous solution and for molecular models for cinnabar. Hydration effects are treated with a combination of "supermolecule" calculations containing several explicit water molecules and polarizable continuum calculations. We focus upon the following problems: (1) calculation of the stabilities of HgL_2 , $L = \text{F}^-$, Cl^- , OH^- , SH^- , and CN^- and HgCl_n^{2-n} $n = 1-4$; (2) development of a molecular model for cinnabar of the form $\text{Hg}_3\text{S}_2(\text{SH})_2$; and (3) dissolution or adsorption reactions using this cinnabar model. The absolute and relative formation enthalpies of the HgL_2 species can be satisfactorily reproduced at the Hartree-Fock plus Moller-Plesset second order correlation correction level using relativistic effective core potential basis sets if the hydration of neutral HgL_2 is explicitly taken into account. Evaluating the energetics for the series of complexes HgCl_n^{2-n} is more difficult, because great accuracy is needed in the large hydration energies and some of the species are highly nonspherical. The $\text{Hg}_3\text{S}_2(\text{SH})_2$ species shows an equilibrium structure very much like that in cinnabar. The relative energetics for dissolution of cinnabar by H_2O , H_2S , SH^- , and $\text{SH}^- + \text{elemental S}$ are correctly reproduced using this model molecule. Calculations on $\text{Hg}_3\text{S}_2\text{ClI}$ provide a model for understanding the adsorption of I^- ions on cinnabar surfaces in the presence of Cl^- .

INTRODUCTION

The speciation of metal cations in aqueous solution strongly influences mineral dissolution and precipitation processes (Drever 1997) and the bioavailability of the metal (Mason et al. 1996). Partly because of the significance of Hg as an environmental pollutant, its speciation in natural waters is of great interest. The solubilities of Hg containing minerals in various solutions and the concentrations of Hg^{2+} ions in equilibrium with various ligands have been studied experimentally to deduce Hg speciation. These studies generally used methods that determine the total concentrations of Hg containing species in solution or the concentration of the Hg^{2+} hydrated cation. Such studies have serious limitations: (1) the speciation models are often ambiguous, with different researchers obtaining apparently different sets of species and formation constants, and (2) the participation of chemical components whose activities or concentrations cannot be varied experimentally are indeterminate, e.g., the participation of water in such species cannot be determined in aqueous solution. Spectral studies could, in principle, determine which species were present, as well as their concentrations if relative spectral intensities for the different species could be assessed. However, in many cases the species concentrations are so low that no usable spectra can be obtained. Although Hg speciation has been studied for years (Schwarzenbach and Widmer 1963; Barnes et al. 1967; Shikina et al. 1981) new results continue to emerge. For example, Paquette and Helz (1995, 1998) established that cinnabar has a higher solubility in solutions containing both elemental sul-

fur and bisulfide than in those containing bisulfide alone and identified a new Hg polysulfide species as the cause of this enhanced solubility.

Recently, we have matched spectral properties calculated quantum mechanically for various As, Sb, and Au species (Tossell 1995, 1996a, 1997; Helz et al. 1995) with experimental spectral data to determine the predominant species present. We have also calculated reaction energetics for these species, but the low accuracy of our energetics prevented their use as the main criterion to determine speciation. Rather the energetic calculations were offered as further confirmation of the assignments made on spectral grounds. For example, for the As hydroxides Tossell (1997) identified a trimeric species $\text{As}_3\text{O}_5(\text{OH})_3$ existing in concentrated solutions primarily on the basis of its Raman spectrum, but noted that its high calculated thermodynamic stability provided additional, weaker evidence for its existence. Quantum mechanical methods were also used to model the structures, energetics, and spectral properties of certain "molecular" minerals, e.g., realgar, As_4S_4 (Tossell 1996b). For strongly covalent sulfides with small coordination numbers, such molecular approaches yielded accurate results for structures, vibrational spectra, and energetics.

This paper focuses more upon the energetics of reactions in solution, to determine how well we can distinguish the stabilities of different complexes and the energetics for various dissolution reactions. Structural and spectral results are presented which may prove useful in characterizing the complexes. Two different types of reactions are considered: (1) complex formation, in which I start with isolated hydrated ions and form (hydrated) complexes, and (2) dissolution reactions, in which I start with a molecular model for the solid mineral and consider

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the dissolution caused by species in solution. Each type of reaction presents its own problems for quantum mechanical calculation. In the association reactions the gas-phase reactants and products are fairly simple and can be treated at a high quantum mechanical level. The much more serious problem is the description of the hydration processes. For dissolution reactions, particularly where solids produce neutral solution species, the hydration problem is less serious, but studying a sufficiently large molecular model for the solid may not be computationally feasible. In general, small molecular models of solids represent the real solid more accurately if the solid shows small coordination numbers and substantial covalency. Such an approach is therefore feasible for HgS, cinnabar, a helical chain structure with two-fold-coordinated Hg (1950) and for HgCl₂, which is basically a molecular crystal with twofold-coordinated Hg (Wells 1975). As discussed by Kaupp and von Schnering (1994a) and more qualitatively by Tossell and Vaughan (1981), the small coordination numbers observed in Hg compounds are a consequence of relativistic effects. The impact of relativistic effects on the structures of heavy element compounds has also been discussed by Pyykko (1988). Other researchers have recently studied Hg complexes (Stromberg et al. 1991; Swerdtfeger et al. 1993; Kaupp and Schnering 1994), establishing the importance of relativistic effects and calculating structures and energetics at a fairly high quantum mechanical level.

COMPUTATIONAL METHODS

We use Hartree-Fock based techniques (Hehre et al. 1986). The basis sets used are of the relativistic effective core potential type, as implemented by Stevens, Basch, and Krauss (SBK) (Stevens et al. 1992). Polarization functions of d type only are added to each of the non-H atoms. We used the programs GAMESS (Schmidt et al. 1993) and GAUSSIAN94 (Frisch et al. 1994). In addition to the Hartree-Fock calculations we have utilized the Moller-Plesset 2nd order perturbation theory method (MP2) (Pople et al. 1976) for evaluation of the bond distances and energetics of many of the molecules studied, particularly those containing a single Hg atom. For most of the molecules considered we have also calculated the Hessian matrix to establish that we have found an equilibrium geometry and to determine the vibrational spectrum, allowing determination of the zero-point vibrational energy.

The calculation of hydration effects upon chemical reactions is currently a very active area within quantum chemistry, with a number of different approaches being used by various researchers (Wiberg et al. 1996; Cramer and Truhlar 1994). To evaluate hydration enthalpies we use a multipart approach. For monatomic ions, such as Hg²⁺ and Cl⁻, and for the common small polyatomics, such as OH⁻ or SH⁻, we use "experimental" hydration energies from the tables of Rashin and Honig (1985). Of course the hydration energy of a neutral compound cannot be uniquely divided into contributions from cation and anion, but by choosing the hydration energy of one particular species as a reference, most all other hydration energies can be defined with respect to it, obtaining quite consistent values. For neutral molecules, we evaluate hydration enthalpies by performing quantum mechanical supermolecule calculations with as many as 6 water molecules surrounding the solute molecule. The

choice of six water molecules is somewhat arbitrary and is dictated in part by computational considerations and in part by the coordination numbers commonly observed for cations using solution X-ray diffraction or EXAFS. For a few of the species considered, e.g., Hg²⁺ and HgCl₂, we have considered complexation with four, six, and eight water molecules, and have established that the greatest stability occurs for complexation with six water molecules. For polyatomic ions we evaluate the first hydration sphere contribution to the hydration energy by performing such a supermolecule calculation and determine the longer range contribution by performing a self-consistent-reaction-field (SCRf) calculation (Wiberg et al. 1996) for the supermolecule immersed in a polarizable continuum with a dielectric constant equal to that in bulk H₂O. The Born radius needed for the SCRf calculation is determined using the Rashin and Honig (1985) semiempirical prescription (not an essentially arbitrary electron density surface criterion as in Wiberg et al. 1996). The use of the RH effective Born radius value, rather than the radius calculated from the molecular volume by GAUSSIAN, is potentially significant because of the large magnitude of the Born term. In the GAUSSIAN94 implementation of the SCRf scheme only the dipole term is included, so that for a supermolecule with zero dipole moment, e.g., Hg(OH₂)₆²⁺ or HgCl(OH₂)₆²⁺, the Born term is the only non-zero term. Other potentially more accurate methods, such as the isodensity polarized continuum method (IPCM), are not yet implemented for the case of effective core potentials.

The general procedure of combining a supermolecule calculation with a Born model or SCRf calculation is simple and intuitively appealing and has been used by a number of different researchers (e.g., Claverle et al. 1978; Freitas et al. 1992; Parchment et al. 1996) at various levels of sophistication. It basically relies upon the idea that there should be a smooth convergence of the local hydration energy for a cluster of solvent molecules to the bulk solvation energy as the number of solvent molecules is increased. Coe (1994) has demonstrated that this is approximately true, although the change in solvation energy with number of solvent molecules may not be completely continuous.

It may be worthwhile to describe in detail the procedure used for the cases of Hg²⁺, Cl⁻, HgCl⁺, and HgCl₂. First, for Hg²⁺ and Cl⁻ we use the hydration energies of -0.700 and -0.136 Hartrees (H), respectively, tabulated by Rashin and Honig (1985). An alternative would be to calculate these directly using our combined supermolecule, Born model approach. For the formation of Hg(OH₂)₆²⁺ for free Hg²⁺ and six H₂O molecules we calculate an energy change of -0.420 H, using the HF method and the polarized SBK basis and correcting for basis set superposition error (Boys and Bernardi 1970). The calculated Hg-O distance in Hg(OH₂)₆²⁺ is 2.428 Å (T_h symmetry assumed), consistent with the experimental X-ray value of 2.40 Å obtained by Johansson (1971). Adding the Rashin and Honig value of 1.495 Å for the "O-H" bond radius to the calculated Hg-O distance we get a radius for the Born model calculation of 3.92 Å, giving a Born energy of -0.271 H, for a total hydration energy of -0.691 H, certainly in good agreement with the RH value of -0.700 H. For the case of Cl⁻ the formation energy

for $\text{Cl}(\text{OH}_2)_6^{-1}$, is -0.091 H (after basis set superposition correction), and the Cl-O distance has a range from 3.17 to 3.60 Å and an average value of 3.54 Å. This gives a Born energy of -0.053 H, for a total hydration energy of -0.144 H, fairly close to the the RH "exp." value of -0.136 H. Note that in our calculations we have required the Cl^- to lie at the center of the cluster, which is apparently not its lowest energy position with a small cluster (Caldwell and Kollman 1992; Coe 1994) but is appropriate for bulk solution. However, we emphasize that the reaction energies (below) are not based upon such calculated hydration energies for the monotomic and small ions, but utilize the RH experimental values.

For ions such as HgCl^+ no tabulated hydration energies are available, so we utilize the combined supermolecule, SCRF model approach. We first calculated energies for formation of $\text{HgCl}(\text{OH}_2)_n^+$, $n = 4-6$, from HgCl^+ and H_2O , establishing that the most stable species had $n = 5$. This species is shown in Figure 1. The calculated Hg-O distances are 2.34, 2.60, 2.60, 2.64, and 2.64, while the Hg-Cl distance is 2.38 Å. Adding the RH radii of 1.94 and 1.495 Å for Cl^- and OH^- , respectively, we get radii along the bond directions of 3.84, 4.10, 4.10, 4.14, 4.14, and 4.32 Å, for an average of 4.11 Å. This average radius gives a Born energy of -0.0647 H. The SCRF calculation as implemented in GAUSSIAN94, gives an additional polarization energy of -0.0134 from interaction of the dipole moment of $\text{HgCl}(\text{OH}_2)_5^+$ with the solvent polarizable continuum, for a total hydration energy of -0.251 H. For the HgCl_2 case, six H_2O molecules attach with an energy of -0.0475 H (four H_2O molecules give a supermolecule formation energy of -0.0375 H). There is no Born energy because the species is neutral and there is no SCRF polarization energy because the dipole term is zero for $\text{HgCl}_2(\text{OH}_2)_6$. The neglect of higher multipole terms probably systematically underestimates the stability of such symmetric species. However, using an average Born radius and treating lower symmetry species such as $\text{HgCl}(\text{OH}_2)_5^+$ within a spherical approximation may also systematically underestimate their stability.

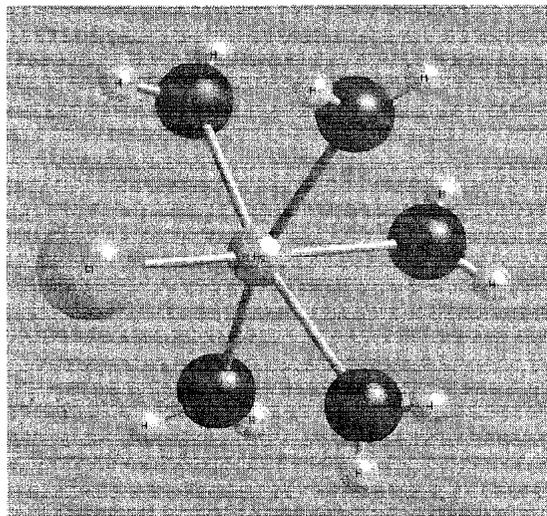


FIGURE 1. Calculated structure for $\text{HgCl}(\text{OH}_2)_5^+$, a model for HgCl^+ and its first hydration sphere.

RESULTS

Structures and vibrational spectra

As is generally observed for Hg compounds (Kaupp and Schnering 1994b) calculated bond distances (Table 1) are substantially longer than experiment at the Hartree-Fock level (even when relativistic effects are included) but are considerably improved by MP2, although they are still a bit too long. The errors are similar in magnitude for the neutral species HgCl_2 and $\text{Hg}_3\text{S}_2(\text{SH})_2$ but seem somewhat larger for the HgCl_4^{2-} anion. If we add the Born hydration energy in aqueous solution for HgCl_4^{2-} to the HF energy of the free anion the equilibrium distance is somewhat reduced, because shorter Hg-Cl distances give a larger Born stabilization. The calculated equilibrium distance drops from 2.63 to 2.58 Å, giving better agreement with experiment (although the experimental values is for a different condensed-phase environment). For HgS our $\text{Hg}_3\text{S}_2(\text{SH})_2$ model reproduces not only the Hg-S bond distance, but S-Hg-S and Hg-S-Hg angles, and the helical structure of HgS, cinnabar, as shown in Figure 2. Note that the calculations on the trimeric model $\text{Hg}_3\text{S}_2(\text{SH})_2$ are already extremely demanding, so that we have not considered any larger oligomers.

Vibrational frequencies calculated at the HF level (Table 2) are similar to those of Kaupp and Schnering (1994b) and establish that unscaled HF values reasonably fit experiment for neutral molecules or ions with small charges. That is, for these heavy element compounds the Hartree-Fock method with conventional basis sets does not give the systematic underestimation of bond distances and overestimation of vibrational frequencies observed for light element compounds (Hehre et al. 1986). For the case of HgCl_4^{2-} , the calculated frequencies are seriously underestimated, presumably for the same reason that the bond distance was overestimated for free HgCl_4^{2-} , compared to the condensed-phase experimental data. The spectrum of the molten HgCl_2 , KCl system is rather complicated (Janz and James 1963) and some of the spectral assignments may be in error. An extremely demanding calculation on the vibrational spectrum of $\text{HgCl}_4^{2-} \cdot 6\text{H}_2\text{O}$ yielded no significant change in the calculated frequencies, indicating that explicit consideration of the Born model term would probably be a better approach.

TABLE 1. Comparison of calculated and experimental Hg-X distances (in Å)

Molecule	Calculated		Experimental
	HF	MP2	
HgCl_2	2.33	2.30	2.25, gas phase*
$(\text{HgCl}_2)_2$	2.33, 2.36	2.25×2	
	3.31	—	$3.34 \times 2, 3.63 \times 2$, solid HgCl_2^*
HgCl_4^{2-}	2.63 (2.58§)	2.58	2.50, solid*
$\text{Hg}(\text{OH}_2)_6^{2+}$	2.43	—	2.40, aqueous solution†
HgS	2.36	2.27	cinnabar‡
$\text{Hg}_2\text{S}(\text{SH})_2$	2.39	2.36	2.36
$\text{Hg}_3\text{S}_2(\text{SH})_2$	2.39-2.41		
	<S-Hg-S=179°		<S-Hg-S=172°
	<Hg-S-Hg=96 - 104°		<Hg-S-Hg=105°

* Wells (1975).

† Johansson (1971).

‡ Aurivillius (1950).

§ With Born correction.

TABLE 2. Comparison of calculated and experimental vibrational frequencies (in cm^{-1})

Molecule	HF calculation				Experiment*			
HgCl ₂		+	+			+	+	
	90	342	394	107	348			405 (gas phase)
HgCl ₃	a ₁	a ₂	e'	e'	a ₁	a ₂	e'	e'
	278	82	266	67	273	13	263	100, (molten salt)
HgCl ₄ ²⁻	a ₁	e	t ₂	t ₂	a ₁	e	t ₂	t ₂
	225	62	185	85	267	280	276	192, (molten salt)

* Janz and James (1963).

Energetics

Crystalline HgCl₂ is reasonably soluble in water. Although the dissolution of HgCl₂ is difficult to describe quantitatively, a simple molecular model explains qualitatively why the material dissolves. Each HgCl₂ unit within the solid interacts weakly with four other units, to give a 2 + 4 coordination about each Hg, i.e., two short Hg-Cl bonds and four much longer Hg-Cl bonds. Calculations by Kaupp and Schnering (1994a) give a dimerization energy for HgCl₂ (at their highest level of calculation) of about 5.8 kcal/mol. It seems reasonable to conclude that the total stabilization of the HgCl₂ unit in the molecular crystal can be no more than $4 \times 5.8 = 23.2$ kcal/mol, because such effects would be expected to saturate. However, the HgCl₂ molecule in solution is coordinated by at least four H₂O molecules, for which we calculate a stabilization energy of 23.5 kcal/mol. Including six H₂O molecules raises the calculated stabilization to 29.8 kcal/mol. Our supermolecule calculations are not performed at the same level as the dimer calculations of Kaupp and Schnering (1994b), but it seems clear that the stabilization of the HgCl₂ units in solid and solution are comparable.

Calculated energetics for both gas-phase and aqueous solution reactions of Hg²⁺ plus two X⁻ to give HgX₂ (Table 3) show that formation of the complexes is somewhat more favorable at the MP2 level but that trends from one complex to the other are the same for HF and MP2. Using tabulated values for heats of hydration and lattice energies (Christensen et al. 1965) one can obtain values for these reaction energies in the gas phase, as shown for HgCl₂ and Hg(CN)₂ in Table 3. However, these are only estimates because the tabulated lattice energies are based upon a simple ionic model—experimental energies for the direct process of vaporization of the solid to ions are not measurable. Nonetheless, the estimated values and those calculated quantum mechanically are the same to within about 3% and show

the right trend. To obtain the solution energies we must add the hydration energies for the Hg²⁺ and X⁻ ions from the tabulated values of Rashin and Honig (1985) and the first coordination sphere stabilization energies for HgX₂ from our supermolecule calculations. We also add the vibrational zero-point energies of the HgX₂ species and the thermal energy corrections needed to generate enthalpy difference values for the gas phase reaction. We are therefore evaluating the difference between the enthalpy of the products and that of the reactants at 298 K in solution. We do not add entropic corrections from the gas phase reaction. The $-T \Delta S$ term for the gas phase reaction will be positive, because the number of particles decreases in going from reactants to products so ΔS is negative. But the experimental values of $-T \Delta S$ in solution for such reactions are usually negative, because the entropy of the solvent increases when the ions combine to form neutral molecules. This point has been discussed by Marcus (1986). It would therefore be completely inappropriate to use the gas-phase entropies to estimate solution effects. An important result (Table 3) is that the energy for the gas phase reaction is always highly negative (-1 H) and the change in hydration energy is always highly positive ($+1$ H) so that the solution phase reaction energy has a very small magnitude (less than 0.1 H). Accuracy in the solution reaction energy then requires either very high accuracy in both gas-phase and hydration energy components or compensating errors.

Our results can be compared with the limited experimental data on the thermodynamics of such processes tabulated in Smith and Martell (1976), as shown in Table 4. Comparing the results in Tables 3 and 4, we see that we correctly reproduce the fact that the HgF₂ complex is not observed, because we calculate its formation to be endothermic. Second, we reproduce the high stability of the Hg(CN)₂ complex and correctly obtain Hg(SH)₂ as considerably more stable than HgCl₂. However, we do find

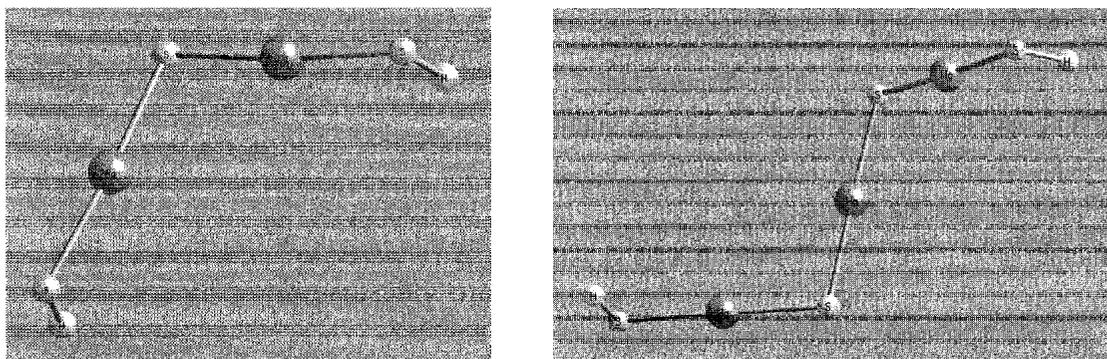
**FIGURE 2.** Calculated structures for Hg₂S(SH)₂ and Hg₃S₂(SH)₂, models for HgS, cinnabar.

TABLE 3. Components of the energy and total energy for the formation of HgX_2 complexes in the reaction: $\text{Hg}^{+2} + 2 \text{X}^- \rightarrow \text{HgX}_2$

Complex	E_{HF} (Hartrees)	E_{MP2} (Hartrees)	H_{hyd} ions (kcal/mol)	H_{hyd} neutrals (kcal/mol)	Gas-phase E_{ZPE} (kcal/mol)	Gas-phase thermal correction $H_{298} -$		H_{total} (2) + (3) + (4) + (5) + (6) H kcal/mol
						E_{ZPE} (kcal/mol)	$H_{298} -$ (kcal/mol)	
HgCl_2	-0.8775	-0.9400 (-0.969)*	0.975	-0.0475	0.0021	-0.0016	-0.0120	-7.5
$\text{Hg}(\text{SH})_2$	-0.9304	-0.9968	0.970	-0.0235	0.0061	-0.0027	-0.0469	-29.4
$\text{Hg}(\text{OH})_2$	-1.0282	-1.0901	1.059	-0.0290	0.0092	-0.0036	-0.0545	-34.2
$\text{Hg}(\text{CN})_2$	-0.9060	-0.9681 (-1.001)*	0.964	-0.0568	0.0062	-0.0020	-0.0567	-35.6
HgF_2	-0.9652	-1.0191	1.080	-0.0595	0.0035	-0.0022	+0.0027	+1.7

* Values estimated by Christensen et al.(1965) for gas-phase reaction from tabulated heats of hydration and lattice energies.

that $\text{Hg}(\text{OH})_2$ is more stable than $\text{Hg}(\text{SH})_2$, which seems inconsistent with the available G values, although there are no available H values for $\text{Hg}(\text{SH})_2$. It should be noted that the experimental entropic terms for the various HgX_2 complexes seem inconsistent. According to Marcus (1986) the hydration entropies of Cl^- and CN^- are very similar, so it is difficult to understand the large difference in the experimental $-T \Delta S$ terms for the formation of aqueous HgCl_2 and $\text{Hg}(\text{CN})_2$. Both HgCl_2 and $\text{Hg}(\text{CN})_2$ are linear molecules, which are of similar size and (according to our calculations) interact with water in very similar ways, suggesting similar entropic effects.

For the series of chloride complexes HgCl_n^{2-n} the calculated properties show considerable scatter (Table 5). The hydration corrections change greatly in magnitude as the overall charge on the product ion changes and small percentage errors can greatly change the total energy for the process. The product species also change in geometry and in dipole moment, which makes modeling based on a polarizable continuum approach difficult, because the only version of the polarizable continuum model that we presently have available for Hg complexes is the Onsager SCRF that utilizes a spherical cavity and considers only the effect of the solute dipole. A more accurate treatment of hydration energies will be necessarily to reproduce the successive stabilization energies for these complexes.

Calculated energies for various cinnabar dissolution and adsorption reactions are given in Table 6. We typically present two reactions for each dissolution process—one in which the dimeric molecule $\text{Hg}_2\text{S}(\text{SH})_2$ is decomposed and one in which the trimeric molecule $\text{Hg}_3\text{S}_2(\text{SH})_2$ is decomposed. These two

molecules are shown in Figure 2. The energetics for these two types of reactions, evaluated at the HF level, are very similar, e.g. +0.0035 and +0.0033 H, respectively, for bond breaking through attack by H_2S . We are presently able to calculate correlation corrections to these reaction energies at the MP2 level only for the dimeric case, but it seems reasonable that such corrections would be almost the same for the trimer. We therefore give E_{MP2} values for the dimer reactions and make the same correlation corrections for the trimer energies, prefaced by a \approx sign. We have evaluated vibrational spectra for $\text{Hg}_2\text{S}(\text{SH})_2$, $\text{Hg}_3\text{S}_2(\text{SH})_2$, and $\text{Hg}_3\text{S}_2\text{Cl}_2$, establishing that we are at least at local minima on the energy surface for these molecules. The zero-point vibrational effects on reaction energies are found to be very small. For example, for the reaction of H_2S with $\text{Hg}_3\text{S}_2(\text{SH})_2$ to give $\text{Hg}_2\text{S}(\text{SH})_2$ and $\text{Hg}(\text{SH})_2$, the change in zero-point energy is only about 0.05 kcal/mol. We therefore ignore zero-point effects for the reactions in Table 6. In evaluating the solution energetics we include hydration energy terms only for the ions, because we cannot carry out supermolecule calculations on the very large neutral dimeric or trimeric species. In the last column we present our best estimates of the reaction energies in solution, in both H and kcal/mol.

Our results certainly indicate that the dissolution of cinnabar in H_2O is a highly unfavorable process, while dissolution in the presence of H_2S is much more favorable. If we assume that entropic and enthalpic corrections are small, then the E value of +7.1 kcal/mol for this process (reaction 3) suggests an equilibrium constant of about 10^{-5} at 298K, fortuitously close to the value of $10^{-5.36}$ from Paquette and Helz (1995). At present we have no realistic way to evaluate the entropic contributions for such reactions. According to the calculations, dissolution is more favorable in the presence of SH^- than in the presence of H_2S . Increased dissolution by SH^- compared with H_2S is consistent with the results of Paquette and Helz (1995). The calculations also indicate strong exoergicity for the reaction of the cinnabar model with HCl to form $\text{Hg}_3\text{S}_2\text{Cl}_2$ (reaction 4). Paquette and Helz (1995) also observed the apparent formation of

TABLE 4. Experimental energetics (in kcal/mol) for formation of HgL_2 complexes at 298 K (from Smith and Martell 1976)

complex	G	H	-T S
HgCl_2	-18.0	-12.8	-5.4
$\text{Hg}(\text{SH})_2$	-51.2	na	na
$\text{Hg}(\text{OH})_2$	-30.2	-16.4	-14.0
$\text{Hg}(\text{CN})_2$	-44.5	-46.6	+1.8
HgF_2	no complex observed, >0	na	na

Note: na = not available.

TABLE 5. Calculated energy components and experimental enthalpies for the formation of HgCl_n^{2-n} in the reaction: $\text{Hg}^{+2} + n \text{Cl}^- \rightarrow \text{HgCl}_n^{2-n}$

Complex	E_{HF} (H)	E_{MP2} (H)	H_{hyd} ions (H)	H_{hyd} neutrals (H)	E_{total}		H_{exp}^* (kcal)
					(H)	(kcal)	
HgCl^{+1}	-0.5506	-0.5921	0.586	-	-0.012	-7.5	-5.8
HgCl_2	-0.8775	-0.9400	0.975	-0.0475	-0.012	-7.8	-12.8
HgCl_3^{-1}	-0.9539	-1.0228	1.019	-	-0.004	-2.5	-15.0
HgCl_4^{2-}	-0.8946	-0.9648	0.943	-	-0.022	-13.8	-14.9

* Smith and Martell (1976).

TABLE 6. Calculated energetics for depolymerization of Hg-S units and for ligand replacement and addition reactions

Index	Reaction	E		H _{hyd} ions		
		HF (M)	MP2 (M)	M	H	kcal/mol
(1)	Hg ₃ S ₂ (SH) ₂ + H ₂ O → Hg ₂ S(SH)(OH) + Hg(SH) ₂	+0.0431		0	+0.0431	27.0
(2)	Hg ₂ S(SH) ₂ + H ₂ S → 2 Hg(SH) ₂	+0.0035	0.0114	0	0.0114	7.1
(3)	Hg ₃ S ₂ (SH) ₂ + H ₂ S → Hg ₂ S(SH) ₂ + Hg(SH) ₂	+0.0033	0.0113	0	0.0113	7.1
(4)	Hg ₃ S ₂ (SH) ₂ + 2 HCl → Hg ₃ S ₂ Cl ₂ + 2 H ₂ S	-0.0258		0	-0.0258	-16.2
(5)	Hg ₂ S(SH) ₂ + SH ⁻ → Hg(SH) ₂ + HgS(SH) ⁻	-0.0297	-0.0343	+0.036	0.002	1.2
(6)	Hg ₃ S ₂ (SH) ₂ + SH ⁻ → Hg ₂ S(SH) ₂ + HgS(SH) ⁻	-0.0260	-0.0306	+0.036	0.005	3.1
(7)	Hg ₂ S(SH) ₂ + SH ⁻ + (3/8) S ₈ → Hg(SH) ₂ + HgS ₄ (SH) ⁻	-0.0767	-0.0798	0.070	-0.010	-6.3
(8)	Hg ₃ S ₂ (SH) ₂ + SH ⁻ + (3/8) S ₈ → Hg ₂ S(SH) ₂ + HgS ₄ (SH) ⁻	-0.0693	-0.0724	0.070	-0.002	-1.2
(9)	Hg ₃ S ₂ (SH) ₂ + OH ⁻ → Hg ₃ S ₂ (SH)OH + SH ⁻	-0.0486		0.044	-0.005	-3.1
(10)	Hg ₃ S ₂ (SH) ₂ + Cl ⁻ → Hg ₃ S ₂ (SH)Cl + SH ⁻	+0.0253		0.001	+0.024	+15.1
(11)	Hg ₃ S ₂ (SH) ₂ + I ⁻ → Hg ₃ S ₂ (SH)I + SH ⁻	+0.0438		-0.025	+0.019	+11.9
(12)	Hg ₃ S ₂ (SH)Cl + I ⁻ → Hg ₃ S ₂ (SH)I + Cl ⁻	+0.0185		-0.026	-0.005	-3.1
(13)	Hg ₃ S ₂ (SH)(OH) + I ⁻ → Hg ₃ S ₂ (SH)I + OH ⁻	+0.0923		-0.063	+0.029	+18.1
(14)	Hg ₃ S ₂ (SH) ₂ + I ⁻ → Hg ₃ S ₂ (SH) ₂ I ⁻	-0.0418		0.055	+0.013	+8.2

corderoite, Hg₃S₂Cl₂, in strongly acidic solutions with high chloride concentrations. This species was also observed by Hyland et al. (1990) when aqueous HgCl₂ reacted with sulfides and by Estrada et al. (1995) when aqueous HgCl₂ was reacted with films of CdSe. The presence of elemental sulfur, as in reactions 7 and 8, was also found by Paquette and Helz to enhance cinnabar solubility. The solution species we have considered, HgS₄(SH)⁻, has a structure similar to that found for Hg polysulfide complexes by Bailey et al. (1991) and is shown in Fig. 3. Of course, this complex is only one possible polysulfide. Others with larger S_n rings may well be involved. Based on the calculated energetics for reactions 3 and 8 the equilibrium constant for dissolution should be increased in the presence of S₈ by about 10⁶, while the enhancement observed experimentally using solid rhombic S is only about 10¹.

Sazarashi et al. (1994) and Balsey et al. (1996) have demonstrated experimentally the adsorption of I⁻ on the surface of cinnabar, particularly at low pH where the cinnabar surface charge is small. Balsey et al. interpreted their results as involving a surface replacement of OH⁻ by I⁻ and justified this replacement using hard and soft acid and base theory. Based on the calculated energetics for reaction 9 of Table 6, the replacement of SH⁻ by OH⁻ is favorable. However, based on the energetics shown for reaction 13, the replacement of OH⁻ by I⁻ is highly unfavorable. We favor a process in which the Cl⁻ in solution (their solutions were 0.01 M in NaCl) first replaces SH⁻ on the mineral surface (reaction 10). This reaction would be driven by the many order of magnitude concentration difference between the added Cl⁻ and the SH⁻ produced from the cinnabar dissolution. The surface Cl⁻ is then replaced by I⁻ (reaction 12), in an exoergic step. This overall process is much more favorable than the direct replacement of SH⁻ by I⁻ (reaction 11) or the replacement of OH⁻ by I⁻ (reaction 13). Another possibility is an actual adsorption process for I⁻, without any actual replacement, as in reaction 14. This process is exoergic in the gas phase but the hydration energy is difficult to estimate because it is not clear to what extent the adsorbed I⁻ would retain its hydration shell. Assuming the I⁻ loses half its hydration energy the solution process is unfavorable, but not by a large amount. Such weak coordination of additional ligands by two-coordinate Hg species is well known.

We have also considered the possible existence of Hg(I) sulfidic species in solution. Hg(I) halides have been studied

theoretically by Schwerdtfeger et al. (1993) and Kaupp and Schnering (1994b). As noted by Paquette and Helz (1999), species such as Hg₂(SH)₂ are expected to disproportionate to Hg + Hg(SH)₂. However, Pokrovskiy (1996) has presented solubility evidence for the existence of Hg₂Cl₂ in acidic chloride-bearing solutions. For the gas-phase reaction 2 Hg⁺ → Hg + Hg²⁺ we calculate at the MP2 level an energy of +0.296 H, which compares well with the experimental value of +0.306 H from tabulated thermochemical data (Hepler and Olofsson 1975). For the gas-phase reactions Hg₂L₂ → Hg + HgL₂, L = Cl⁻, SH⁻, we calculate reaction energies at the MP2 level of 0.0166 and 0.0061 H, respectively. Our value for the Cl⁻ case is close to the atomic-natural-orbital MP2 result of Kaupp and Schnering (1994b). Clearly the disproportionation reaction that is highly unfavorable for the bare Hg species in the gas phase becomes

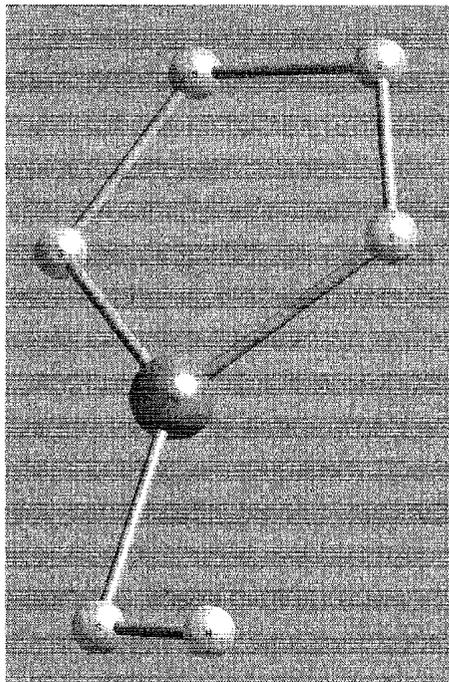


FIGURE 3. Calculated structure for HgS₄(SH)⁻, a model for the bisulfide, polysulfide species.

almost thermoneutral when strongly complexing ligands such as Cl^- or SH^- are present. The more accurate configuration interaction (CI) results of Kaupp and Schnering (1994b) give a slightly negative value for this reaction energy in the Cl^- case. We would anticipate that the gas-phase reaction energy calculated at the CI level would also be negative for SH^- . We have seen that the stabilization of HgCl_2 by its first coordination sphere H_2O molecules is substantial. We would anticipate that the overall hydration energy of HgCl_2 would be greater than that for Hg_2Cl_2 , which is larger and shows smaller charge separation (i.e., it has Hg_2^{+2} rather than Hg^{+2} as cation) and that hydration effects would therefore favor the disproportionation. On the other hand, Kaupp and Schnering (1994b) have shown that the interaction energy with a single H_2O molecule is slightly larger for Hg_2Cl_2 than for HgCl_2 (probably because the single H_2O can interact with two Hg centers). At present we therefore cannot reliably evaluate the relative hydration energies of these species, but it is doubtful that hydration effects could change the overall exoergicity of the disproportionation reaction.

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REFERENCES CITED

- Aurivillius, K.L. (1950) On the crystal structure of cinnabar. *Acta Chemica Scandinavica*, 4, 1413–1436.
- Bailey, T.D., Herath Banda, R.M., Craig, D.C., Dance, I.G., Ma, N.L., and Scudder, M. L. (1991) Mercury polysulfide complexes, $[\text{Hg}(\text{S}_n)(\text{S}_m)]^{2-}$: Syntheses, 199Hg NMR studies in solution, and crystal structure of $(\text{Ph}_4\text{P})_4[\text{Hg}(\text{S}_2)_2]\text{Br}_2$. *Inorganic Chemistry*, 30, 187–191.
- Balsey, S.D., Brady, P.V., Krumhansl, J.L., and Anderson, H.L. (1996) Iodide retention by metal sulfide surfaces: cinnabar and chalcocite. *Environmental Science and Technology*, 30, 3025–3027.
- Barnes, H.L., Romberger, S.B., and Stempok, M. (1967) Ore solution chemistry II. Solubility of HgS in sulfide solutions. *Economic Geology*, 62, 957–982.
- Boys, S.F. and Bernardi, F. (1970) The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. *Molecular Physics*, 19, 553–566.
- Caldwell, J.W. and Kollman, P.A. (1992) Ab initio calculations on $\text{Cl}(\text{H}_2\text{O})_n$ clusters: comparison with the results from molecular dynamics simulation. *Journal of Physical Chemistry*, 96, 8249–8251.
- Christensen, J.J., Izatt, R.M., and Ratouph, D. (1965) Thermodynamics of metal cyanide coordination. V. Log K , H^+ , and S^0 values for the Hg^{2+} -CN $^-$ system. *Inorganic Chemistry*, 4, 1278–1280.
- Claverie, P., Dudley, J.P., Langlet, J., Pullman, B., Piazzola, D., and Huron, M.J. (1978) Studies of solvent effects. 1. Discrete, continuum and discrete-continuum models and their comparison for some simple cases: NH_4^+ , CH_3OH and substituted NH_4^+ . *Journal of Physical Chemistry*, 82, 405–418.
- Coe, J.V. (1994) Connecting cluster ions and bulk aqueous solvation. A new determination of bulk single ion solvation enthalpies. *Chemical Physics Letters*, 229, 161–168.
- Cramer, C.J. and Truhlar, D.G., Eds. (1994) *Structure and Reactivity in Aqueous Solution: Characterization of Chemical and Biological Systems*. American Chemical Society Symposium Series 568, Washington, D.C.
- Drever, J.I. (1997) *The Geochemistry of Natural Waters: Surface and Groundwater Environments*, 3rd ed. Prentice-Hall, Upper Saddle River, New Jersey.
- Estrada, C.A., Meyers, E.A., Zingaro, R.A., Dufner, D.C., Nair, P.K., and Nair, M.T.S. (1995) Electron and X-ray diffraction studies of chemically deposited thin films of cadmium selenide following reaction with mercury(II) chloride solution. *Heteroatom Chemistry*, 6, 349–354.
- Freitas, L.C.G., Longo, R.L., and Simas, A.M. (1992) Reaction-field-supermolecule approach to calculation of solvent effects. *Journal of the Chemical Society, Faraday Transactions*, 88, 189–193.
- Frisch, M.J., Trucks, G.W., Schlegel, H.B., Gill, P.M.W., Johnson, B.G., Robb, M.A., Cheeseman, J.R., Keith, T., Petersson, G.A., Montgomery, J.A., Raghavachari, K., Al-Laham, M.A., Zakrzewski, V.G., Ortiz, J.V., Foresman, J.B., Peng, C.Y., Ayala, P.Y., Chen, W., Wong, M.W., Andres, J.L., Replogle, E.S., Gomperts, R., Martin, R.L., Fox, D.J., Binkley, J.S., Defrees, D.J., Baker, J., Head-Gordon, M., Gonzalez, C.C., and Pople, J.A. and Stewart, J.P. (1994) GAUSSIAN94, Rev. B.3, Gaussian, Inc., Pittsburgh, Pennsylvania.
- Hehre, W.J., Radom, L., Schleyer, P.v.R., and Pople, J.A. (1986) *Ab Initio Molecular Orbital Theory*. Wiley, New York.
- Helz, G.R., Tossell, J.A., Chamock, J.M., Patrick, R.A.D., Vaughan, D.J., and Garner, C.D. (1995) Oligomerization in As(III) sulfide solutions: Theoretical constraints and spectroscopic evidence. *Geochimica et Cosmochimica Acta*, 59, 4591–4604.
- Hepler, L.G. and Oloffson, G. (1975) Mercury: Thermodynamic properties, chemical equilibria, and standard potentials. *Chemical Reviews*, 75, 585–602.
- Hyland, M.M., Jean, G.E., and Bancroft, G.M. (1990) XPS and AES studies of Hg(II) sorption and desorption reactions on sulphide minerals. *Geochimica et Cosmochimica Acta*, 54, 1957–1967.
- Janz, G.J. and James, D.W. (1963) Vibrational spectra of molten halides of mercury. II. trichloro- and tetrachloromercurate ions. *Journal of Chemical Physics*, 38, 905–909.
- Johansson, G. (1971) An X-ray investigation of the hydrolysis products of mercury(II) in solution. *Acta Chemica Scandinavica*, 25, 2787–2798.
- Kaupp, M. and von Schnering, H.G. (1994a) Dominance of linear 2-coordination in mercury chemistry: Quasirelativistic and nonrelativistic ab initio pseudopotential study of $(\text{HgX}_2)_2$ (X=F, Cl, Br, I, H). *Inorganic Chemistry*, 33, 2555–2564.
- Kaupp, M. and von Schnering, H.G. (1994b) Origin of the unique stability of condensed-phase Hg_2^{2+} : An ab initio investigation of M^+ and M^{2+} species (M = Zn, Cd, Hg). *Inorganic Chemistry*, 33, 4179–4185.
- Marcus, Y. (1986) The hydration entropies of ions and their effects on the structure of water. *Journal of the Chemical Society, Faraday Transactions I*, 82, 233–242.
- Mason, R.P., Reinfelder, J.R., and Morel, F.M.M. (1996) Uptake, toxicity, and trophic transfer of mercury in a coastal diatom. *Environmental Science and Technology*, 30, 1835–1845.
- Paquette, K.E. and Helz, G. (1995) Solubility of cinnabar (red HgS) and implications for mercury speciation in sulfidic waters. *Water, Air, and Soil Pollution*, 80, 1053–1056.
- (1999) Inorganic speciation of mercury in sulfidic waters: the importance of zero-valent sulfur. *Environmental Science and Technology*, in press.
- Parchment, O.G., Vincent, M.A., and Hillier, I.H. (1996) Speciation in aqueous zinc chloride. An ab initio hybrid microsolvation/continuum approach. *Journal of Physical Chemistry*, 100, 9689–9693.
- Pokrovskiy, O.S. (1996) Measurement of the stability constant of an Hg(I) chloride complex in aqueous solutions at 20–80 °C. *Geochemistry International* 33, 83–97.
- Pople, J.A., Binkley, J.S., and Seeger, R. (1976) Theoretical methods incorporating electron correlation. *International Journal of Quantum Chemistry Symposium*, 10, 1–22.
- Pyykko, P. (1988) Relativistic effects in structural chemistry. *Chemical Reviews*, 88, 563–594.
- Rashin, A.A. and Honig, B. (1985) Reevaluation of the Born model of ionic hydration. *Journal of Physical Chemistry*, 89, 5588–5593.
- Sazarashi, M., Ikeda, Y., Seki, R., and Yoshikawa, H. (1994) Adsorption of I^- ions on minerals for ^{129}I waste management. *Journal of Nuclear Science and Technology*, 31, 620–622.
- Schmidt, M.W., Baldrige, K.K., Boatz, J.A., Elbert, S.T., Gordon, M.S., Jensen, J.H., Koseki, S., Matsunaga, N., Nguyen, K.A., Su, S.J., and Windus, T.L. (1993) General atomic and molecular electronic structure system. *Journal of Computational Chemistry*, 15, 1347–1363.
- Schwarzenbach, G. and Widmer, M. (1963) Die Löslichkeit von Metallsulfiden. I. Schwarzes Quecksilbersulfid. *Helvetica Chimica Acta*, 46, 2613–2628.
- Schwerdtfeger, P., Boyd, P.D.W., Brienne, S., McFeaters, J.S., Dolg, M., Liao, M.-S., and Schwarz, W.H.E. (1993) The mercury-mercury bond in inorganic and organometallic compounds. A theoretical study. *Inorganica Chimica Acta*, 213, 233–246.
- Shikina, N.D., Zotov, A.V., and Khodakovskii, I.L. (1981) Experimental investigation of equilibria in the $\text{HgS-H}_2\text{S-H}_2\text{O}$ system at 90 and 150 °C. *Geochemistry International* 18, no. 2, 109–117.
- Smith, R.M. and Martell, A.E. (1976) *Critical Stability Constants*. Vol. 4 *Inorganic Complexes*. Plenum, New York.
- Stevens, W.J., Krauss, M., Basch, H., and Jansen, P.G. (1992) Relativistic compact effective potentials and efficient, shared-exponent basis sets for the third-, fourth- and fifth-row atoms. *Canadian Journal of Chemistry* 70, 612–630.
- Stromberg, D., Stromberg, A., and Wahlgren, U. (1991) Relativistic quantum calculations on some mercury sulfide molecules. *Water, Air and Soil Pollution*, 56, 681–695.
- Tossell, J.A. (1995) The speciation of antimony in sulfidic solutions: a theoretical study. *Geochimica et Cosmochimica Acta*, 58, 5093–5104.
- (1996a) The speciation of gold in aqueous solution: a theoretical study. *Geochimica et Cosmochimica Acta*, 60, 17–29.
- (1996b) Theoretical studies on As and Sb sulfide molecules. *Mineral Spectroscopy: A Tribute to Roger G. Burns*, Geochemical Society Special Publication. No 5, p. 9–19.
- (1997) Theoretical studies on arsenic oxide and hydroxide species in minerals and aqueous solution. *Geochimica et Cosmochimica Acta*, 61, 1613–1623.
- Tossell, J.A. and Vaughan, D.J. (1981) Relationships between valence orbital binding energies and crystal structures in compounds of copper, silver, gold, zinc, cadmium, and mercury. *Inorganic Chemistry*, 20, 3333–3340.
- Wells, A.F. (1975) *Structural Inorganic Chemistry*, 4th ed., Clarendon, Oxford.
- Wiberg, K.B., Castejon, H., and Keith, T.A. (1996) Solvent effects: 6. A comparison between gas phase and solution acidities. *Journal of Computational Chemistry*, 17, 185–190.

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