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Computing the Properties of the Copper Thioarsenite Complex, CuAsS(SH)(OH)

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In aqueous solutions in equilibrium with the mineral assemblage CuS (covellite)−$Cu_{1.8}S$ (digenite)−Cu_3AsS_4 (enargite), a copper thioarsenite species, CuAsS(SH)(OH), makes major contributions to both Cu and As solubility (Clarke, M. B.; Helz, G. R. *Environ. Sci. Technol*. **2000**, *34*, 1477−1482. The structure and energetics of this complex have been calculated quantum mechanically (Tossell, J. A. *Environ. Sci. Technol*. **2000**, *34*, 1483−1488), confirming its high stability and establishing the presence of a novel direct bond between Cu (formally Cu(I)) and As (which is formally As(III) and retains its lone pair). To provide further evidence for the existence of this complex, it would be desirable to concentrate it and to measure its spectral properties. To assist in the confirmation of its identify, we have calculated a number of different spectral properties for this complex, including its vibrational, visible/UV, X-ray absorption near edge (XANES), and Cu and As NMR spectra. The visible/UV spectrum has been calculated using both Hartree−Fock and density functional theory based methods, which have been tested against the known properties of the gas-phase CuCl molecule. We calculate distinctive stretching vibrations of the three-membered Cu−As−S ring around 440−500 cm^{-1}, an absorption in the visible at around 2.4 eV, and an absorption at low energy in XANES (compared to that calculated for $Cu(SH)_2^-$). The calculated Cu and As NMR properties of CuAsS(SH)(OH) are also distinctive, but both Cu and As are quadrupolar nuclides and their calculated quadrupole coupling constants in CuAsS(SH)(OH) are very large, so their NMR signals may not be observable. Mulliken population analyses, natural bond orbital analyses, and contour plots of HOMO and LUMO electron densities are also used to characterize the bonding within the copper thioarsenite complex. We have also calculated the hydration energy of the complex using polarized dielectric continuum methods, confirming its low degree of stabilization in water.

Introduction

Determining the chemical species present in aqueous solutions in equilbrium with minerals or mineral assemblages is often a difficult task. In most cases one hypothesizes possible complexes, writes equations for their formation, establishes the dependence of their concentrations upon other concentration variables through the equilbrium constant expressions for the assumed reactions, and then measures the total concentration of one or more of their constituent elements in solution for various values of the ligand concentrations. Plots of total element concentration vs ligand concentrations can often be interpreted to give the empirical formulas for the complexes.[1] Two problems commonly arise using this approach: (1) the participation of ligands whose concentrations cannot be readily varied cannot be determined, e.g., H_2O in aqueous solution, and (2) there are often several sets of complexes which can yield equally good fits to the concentration data, given the lack of independent constraints on the complex formation constants. The identity of the complexes present can sometimes be confirmed using spectroscopic data, such as that from IR-Raman or NMR, since the spectral signatures of these complexes in well-defined environments, such as crystalline solids, may be known. However, in most cases no “fingerprint” spectral data exist. In a number of recent theoretical studies the properties of complexes (usually their Raman or NMR spectra) have been calculated and matched against experiment to confirm the identity of the complex.[2]

In a study of the solubility of Cu and As in sulfidic solutions in equilibrium with a CuS (covellite)−$Cu_{1.8}S$ (digenite)−Cu_3AsS_4 (enargite) assemblage, Clarke and Helz[3] found that the total Cu solubility as a function of sulfide concentration could only be fitted accurately if a complex with stoichiometry CuH_2AsOS_2, with a large formation constant, was included in the set of complexes considered. We subsequently studied this species theoretically[4] at high quantum mechanical levels, characterizing its structural formula as CuAsS(SH)(OH) and verifying its large formation constant. The calculated structure of this complex is shown in Figure 1a. The complex also bonds a single water molecule fairly strongly (as discussed in ref 4), producing the analogue hydrated complex shown in Figure 1b. Although its concentration never exceeds the 10^{-7} M range in the study of ref 3, this is sufficient to produce total As concentrations higher than the proposed US drinking water standard.

Given the low concentration of this complex, direct determination of its properties is difficult. However, its neutral charge suggests that it may partition into solvents of low dielectric constant, raising the possibility that it can be concentrated sufficiently for spectral analysis. We have therefore calculated

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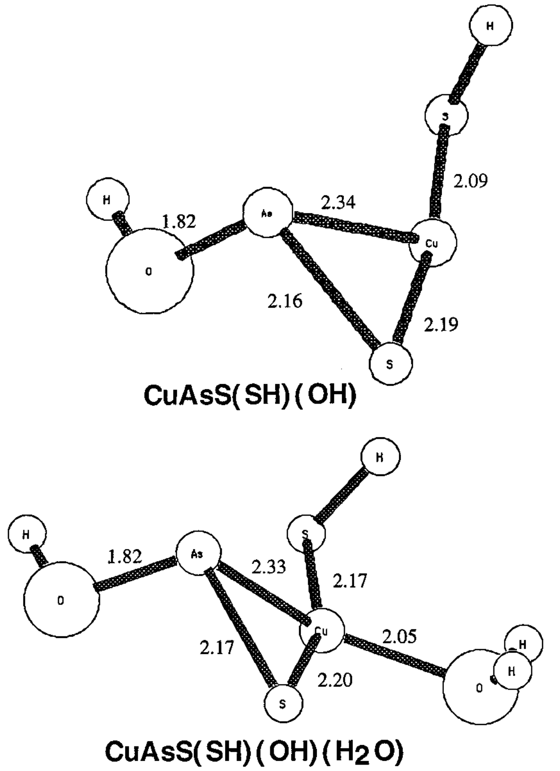

CuAsS(SH)(OH)

CuAsS(SH)(OH)(H_2O)

Figure 1. Geometries calculated for (a) CuAsS(SH)(OH) and (b) CuAsS(SH)(OH)(H_2O) at the polarized SBK MP2 level.

a range of spectral properties for this complex which may be useful in its identification in solution. Finally, some aspects of its electronic structure which are not actually quantum mechanical observables (e.g., charges), and thus cannot be measured, have nonetheless been calculated to help in assessing the nature of the bonding in the complex.

There are two general areas of research within quantum chemistry related to this work. One consists of numerous collaborations between experimentalists and theoreticians, in which a new compound has been prepared experimentally and characterized spectroscopically and its stoichiometry and structure have been confirmed by matching quantum mechanically calculated properties with those measured.[5] A second, more speculative, area involves quantum mechanical studies of possible new, unusual stable compounds,[6] carried out with the hope that experimentalists might be encouraged to attempt the synthesis of the compounds. In the present case the impetus for the work came from experimentalists who postulated the stoichiometry of the new species but, due to the low concentrations involved, were unable to obtain spectral data to further characterize it.

The spectral data most commonly used to identify species in solution are IR-Raman, visible/UV, and NMR spectra, and we have calculated all these for CuAsS(SH)(OH) (and in some cases for related well-characterized compounds to test our methodology or other compounds expected to occur in the same solution, such as $Cu(SH)_2^-$). Unfortunately, none of the nuclides in CuAsS(SH)(OH) except ^1H is a particularly good NMR nuclide—all the others have nonzero quadrupole moments and so can (for low symmetry geometries) give broad lines even in solution due to rapid quadrupolar relaxation. However, for completeness and to help in understanding the electronic structure of CuAsS(SH)(OH), we present their calculated NMR shieldings and electric field gradients at the nuclei. Solvation energies have also been estimated using a simple polarized continuum method.

Computational Methods

We use the methods of Hartree−Fock theory and density functional theory.[7] For both the related simple gas-phase molecule CuCl and for CuAsS(SH)(OH) itself we have done a very complete study of both geometry and visible/UV spectra, utilizing geometries calculated with a number of different methods and basis sets (as well as that taken from experiment for CuCl), along with several more flexible basis sets and different theoretical methods to determine the visible/UV spectrum. The visible/UV absorption spectrum is well characterized for gas-phase CuCl, and the lowest energy features have been confidently assigned based on large basis set MCSCF-MRCI calculations.[8] Comparison of the energies calculated using different approaches with each other and with experiment allows us to isolate the effects of geometry, basis set, and method upon the calculated visible/UV spectra.

Geometries have been calculated using SBK effective core potential bases[9] and 6-31G* and 6-311G(2d,p) bases.[10] The basis sets used to calculate excitation energies are generally either LANL2DZ effective core potential bases,[11] with d polarization functions and diffuse functions added, or all-electron 6-311+G* bases. For the hydrated CuAsS(SH)(OH) complex we have also evaluated excitation energies using the 6-311+G(2d,p) basis. To evaluate excitation energies, we use either the configuration-interaction singles (CIS),[12] the time-dependent Hartree−Fock,[13] or the time-dependent density functional[14] method. The density functional theory (DFT) studies have been done with the hybrid B3LYP potential.[15] An analysis of these different methods for calculating excitation energies is given in ref 14a,b. Basically, CIS describes the excited-state wave function at a level comparable to Hartree−Fock (HF), using single excitations from the HF determinant. The time-dependent (TD) HF method (also called the random phase approximation, RPA) includes some double excitations, giving a slightly correlated description of both ground and excited states, while TD DFT includes additional electron correlation through the exchange correlation potential. Bauernschmitt and Ahlrichsin in ref 14a found for several different molecules that TD DFT using the hybrid B3LYP potential gave the best agreement with experiment,

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Table 1. Calculated Cu−Cl Bond Distance (in Å) in CuCl (Gas Phase), as a Function of Method and Basis Set

basis set	method	R(Cu−Cl)
LANL2DZ + Cl 3d	HF	2.182
	BLYP	2.114
	B3LYP	2.115
	MP2	2.128
	MP4(SDQ)	2.126
	CCD	2.144
	QCISD	2.135
polarized SBK	HF	2.168
	MP2	2.065
3-21G*	HF	1.961
	MP2	1.941
6-31G*	HF	2.109
	MP2	1.985
6-311(2d,p)	HF	2.167
	MP2	2.044
large basis	HF (ref 8)	2.22
large basis	CASSCF (ref 8)	2.059
expt (quoted in ref 8)		2.052

consistently giving excitation energies intermediate between those from TD HF and those from TD DFT with pure DFT potentials.

To describe the CuAsS(SH)(OH) species in aqueous solution, we use a microsolvation approach, in which only one or two explicit water molecules are bonded to the solute. An alternative is to use polarizable continuum solvation models, but these seem to generally underestimate the change in UV energy in an aqueous environment[16] compared to the gas phase or a noncoordinating solvent (the so-called solvatochromic shift). However, such methods give fairly accurate results for lower polarity, non-hydrogen-bonding solvents. Better results are obtained for aqueous environments if a “mixed” approach is used, employing both microsolvation and a polarizable continuum.[17] However, in the studies done so far the number of water molecules used has been very small, usually only one or two coordinating to the chromophoric group of the molecule, e.g., the C═O in acetone.

The calculations were performed using GAMESS[18] and Gaussian 98[19] software. Molecular geometries and MO electron densities were displayed using MacMolplot software.[20]

Results

Calculated bond distances in CuCl using a range of methods and basis sets are shown in Table 1. Note that the bond distance does not change much from its MP2 value as further correlation is introduced in the higher level methods. The SBK effective core potential bases also give results quite similar to those of 6-31G*, while the LANL2DZ and 3-21G* results seem a little aberrant. The LANL2DZ (large core, Cu 3p in the core) effective core potential bases always give bond distances substantially longer than those for the SBK (small core, Cu 3s and 3p as valence) effective core potential bases.

Calculated bond distances about Cu in CuAsS(SH)(OH), obtained using a range of different basis sets and methods, are given in Table 2. We find that a direct bond between Cu and As does not exist at the Hartree−Fock level, no matter what the basis set used, but that this bond does appear at *all* correlated levels (as seen in the calculated Cu−As distances), whether the correlation is introduced by density functional theory, Møller−Plesset perturbation theory, or coupled cluster theory. Calculated Cu−As distances at correlated levels range from 2.23 Å for 6-31G* MP2 to 2.55 for the LANL2DZ BLYP calculation. The polarized SBK MP2 optimized geometry is shown in Figure 1a. As discussed in ref 4, this molecule bonds a single H_2O moderately strongly, with an interaction energy of about −61 kJ/mol at the polarized SBK MP2 level, but without much change in bond distances. Its interaction energy with a second water molecule is only −37.5 kJ/mol, less than the hydration energy of a water molecule within liquid water. This suggests that the singly hydrated species is probably the best zero-order representation of this molecule in aqueous solution.

Table 2. Calculated Bond Distances (in Å) in CuAsSSHOH and Calculated Formation Energy (in kJ/mol) from Bare Cu^+ and $AsSSHOH^-$ as a Function of Method and Basis Set

method	R(Cu−As)	R(Cu−S)	R(Cu−SH)	ΔE
LANL2DZ				
HF	3.17	2.48	2.53	−615.7
BLYP	2.55	2.24	2.36	−790.0
MP2	2.49	2.22	2.34	−723.6
MP4	2.54	2.21	2.34	−743.8
CCD(SD)	2.45	2.15	2.24	−666.1
polarized SBK				
HF	3.07	2.33	2.52	−658.2
MP2	2.34	2.09	2.19	−847.8
6-31G*				
HF	2.73	2.24	2.34	−683.9
MP2	2.23	2.06	2.14	−992.7
6-311G(2d,p)				
HF	2.52	2.19	2.29	−572.6
MP2	2.30	2.07	2.13	−826.2

It is clear from the data in Table 2 that both basis set and treatment of correlation have substantial effects upon the Cu−As bond length, suggesting that it is a relatively weak bond. By contrast, the effects of basis set and methodology on the Cu−S and Cu−SH bond distances (and the Cu−Cl distance in Table 1) are much smaller. The energy for formation of CuAsS(SH)(OH) from Cu^+ and $AsS(SH)(OH)^-$ (also given in Table 2) also varies substantially with basis set and method. A more relevant quantity for assessing the stability of the complex is the energy for formation of CuAsS(SH)(OH) from $Cu(OH_2)_2{}^+$ and $AsS(SH)(OH)^-$, with loss of two molecules of water. In ref 4 we calculated energies for such reactions in the gas phase and then corrected them for hydration effects for a large number of different ligands, to show the unique stability of the $AsS(SH)(OH)^-$ complex. Our calculated energy for this reaction at the polarized SBK MP2 level was −487 kJ/mol, while our present MP2 results using 6-31G* and 6-311(2d,p) bases are −474 and −416 kJ/mol. Thus, the results are not changed greatly in going from effective core potential bases to all electron bases.

Vibrational frequencies calculated at the MP2 level for CuAsS(SH)(OH) with polarized SBK and 6-31G* basis sets are fairly similar, as shown in Table 3. The Cu−As distance is slightly shorter for the 6-31G* basis and the vibrations with Cu−As stretching character consequently occur at higher wavenumber. Many of the vibrations are those which might occur in a simpler species such as $Cu(SH)_2{}^-$ (for which we calculate Cu−S symmetric and asymmetric stretches at 320 and 444 cm^{-1}). However, the vibrations calculated at 441 and 506 cm^{-1} (polarized SBK basis) are distinctive stretching vibrations of the Cu−As−S three-membered ring. They are unusual in their high frequency and thus could be diagnostic. These are

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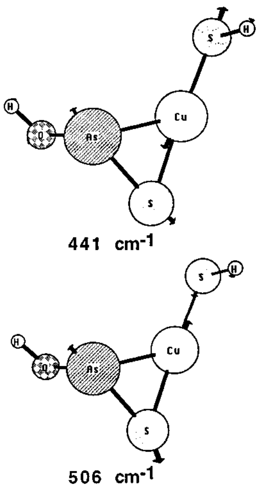

Figure 2. Calculated vibrational normal modes for Cu−As−S ring stretching in CuAsS(SH)(OH), obtained at the polarized SBK MP2 level.

Table 3. Vibrational Spectrum of CuAsS(SH)(OH) (in cm^{-1}) Calculated Using the MP2 Method and Polarized SBK or 6-31G* Basis Sets

ν		IR intensity,	
pol SBK	6-31G*	6-31G*	vibration type
216	229	2.8	As−O,Cu stretch
242	276	4.9	Cu−As, As−O asym stretch
290	304	9.7	Cu−S stretch
300	314	25.4	S−H bend
375	359	87.5	O−H bend
441	458	8.9	Cu−As−S stretch
506	521	57.8	Cu−As−S stretch
632	623	4.5	S−H bend
635	688	105.2	S−H stretch
996	1046	112.7	O−H bend
2708	2760	5.1	S−H stretch
3628	3702	148.7	O−H stretch

shown in Figure 2. In the hydrated species CuAsS(SH)(OH)(H_2O) these vibrational frequencies change slightly to 488 and 492 cm^{-1}. For main group compounds one would typically scale 6-31G* MP2 vibrational frequencies by about 0.95 to correct for the neglect of neglected correlation and for anharmonic effects. There is accumulating evidence that vibrational frequencies calculated using ECP bases on transition metal compounds should be scaled in much the same way.[21]

To test our methodology for calculating the visible/UV energies, we have applied a number of methods and basis sets to gas-phase CuCl, for which the spectrum has been well characterized both experimentally and computationally. Note that the transition energies for this diatomic are actually in the visible region of the spectrum. The two different basis sets considered (polarized plus diffuse LANL2DZ and 6-311+G*) give visible/UV excitation energies within 0.1 eV of each other (so we give only the 6-311+G* values in Tables 4 and 5), but the choice of method has a large effect upon the energies. High-level methods such as complete active space SCF plus multireference CI, as employed in ref 8, give a very accurate description of the spectrum of the molecule, but the much less computationally demanding time-dependent B3LYP hybrid method also gives results in reasonable agreement with experiment, as shown in Table 4. The TD B3LYP approach lowers the transition energies by about 1.5 eV compared to TD HF, giving much better agreement with experiment.

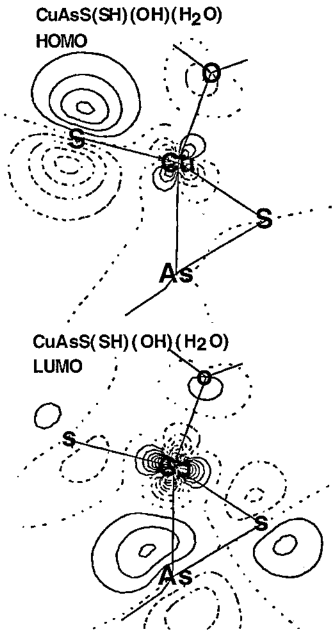

Figure 3. Plots of the HOMO and LUMO of CuAsS(SH)(OH)(H_2O) obtained at the polarized SBK Hartree−Fock level using the polarized SBK MP2 geometry.

Table 4. Calculated UV Singlet Transition Energies in CuCl for Different Methods (at Polarized SBK MP2 Geometry, Using the 6-311+G* Basis Set), Compared with More Sophisticated Calculations and Experiment

	ΔE (ev)	
method	σ	π
CIS	4.4	4.7
TD HF	4.4	5.4
TD B3LYP	3.2	2.6
MCSCF-MRCI (ref 8)	2.55	2.85
expt (from ref 8)	2.86	2.85

Table 5. Calculated UV Singlet Transition Energies in CuAsS(SH)(OH) for Different Methods (at Polarized SBK MP2 Geometry, Using 6-311+G* Basis Set)

method	ΔE (eV)
CIS	3.1, 3.4, 3.9
TD HF	2.9, 3.4, 3.8
TD B3LYP	2.1, 2.3, 2.9

Using the very cheap and efficient TD B3LYP method and the 6-311+G basis set for CuAsS(SH)(OH), we obtain a lowest optical excitation energy of 2.1 eV while in its hydrated analogue, CuAsS(SH)(OH)H_2O, the lowest calculated energy rises to 2.4 eV. The larger polarized 6-311+G(2d,p) basis set gives changes of less than 0.1 eV in the lowest excitation energies. For comparison, the same TD B3LYP methodology applied to polarized SBK MP2 geometries for $Cu(SH)_2^-$ gives an excitation energy of 3.4 eV. This suggests that CuAsS(SH)(OH) and its hydrated analogue should give absorption in the visible region of the spectrum, which will be distinct from that of $Cu(SH)_2^-$ in the near UV.

The low energy for optical absorption in CuAsS(SH)(OH)(H_2O) is a consequence of the presence of a low energy unoccupied orbital, of Cu−As σ* character. Plots of the HOMO and LUMO of CuAsS(SH)(OH)(H_2O) (obtained at the Hartree−Fock level using the polarized SBK MP2 geometry) are shown in Figure 3. The HOMO is essentially a S 3p lone pair while the LUMO shows antibonding character between Cu and As and to a lesser extent between As and S. We have also calculated the energies for XANES transitions from the Cu 3p core, using

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Table 6. Calculated NMR Shieldings (ppm) and Electric Field Gradients (au) for CuAsS(SH)(OH) and Reference Compounds, Obtained Using the 6-311+G* Basis Set at Polarized SBK MP2 Geometries

molecule	σ^{Cu}	q^{Cu}	σ^{As}	q^{As}
CuAsS(SH)(OH)	1319.5	1.34	36.8	4.35
$Cu(SH)_2^-$	1269.6	1.76		
$Cu(SH)_2Cl^{2-}$	1359.1	0.806		
$Cu(NCH)_4^+$	1667.0	0		
$AsS(SH)(OH)^-$			589.7	4.46
AsF_6^-			1662.7	0
$As(CH_3)_4^+$			1494.4	0

the effective ionic core virtual orbital model[22] (in which Cu is replaced by its core equivalent Zn^+), for CuAsS(SH)(OH)(H_2O) and $Cu(SH)_2^-$. This method is quite crude compared to TD B3LYP or CIS but seems to give reasonable results in many cases. The lowest energy transitions calculated from the Cu 3p orbitals to the virtual orbitals are 158.9 and 161.6 eV for CuAsS(SH)(OH)(H_2O) and $Cu(SH)_2^-$, respectively (using the polarized SBK basis). This difference is consistent with, although somewhat larger than, the difference in optical excitation energies. For CuAsS(SH)(OH)(H_2O) the virtual orbital participating in the lowest energy XANES transition is the Cu−As σ^* LUMO.

We have also calculated the NMR shieldings and electric field gradients for all the atoms of CuAsS(SH)(OH) and have compared them with those calculated for some simple compounds which are thought to be prominent species in these sulfidic solutions: $AsS(SH)(OH)^-$ and $Cu(SH)_2^-$. The better characterized reference molecules $As(CH_3)_4^+$, AsF_6^-, and $Cu(NCH)_4^+$ have also been considered. Since $As(CH_3)_4^+$ and $Cu(NCH)_4^+$ are tetrahedral and have zero quadrupole coupling constants, they are good choices as reference molecules. We have previously calculated electric field gradients (EFGs) at As for a series of As sulfide minerals,[23] and As NMR shieldings have been calculated using Hartree−Fock finite perturbation theory[24] for a number of tetrahedral and octahedral As(V) compounds. Our results are shown in Table 6. The absolute shielding we calculate for the reference molecule $As(CH_3)_4^+$ is 1494.4 ppm, fairly close to the 1577 ppm value obtained in ref 24, and the shielding difference between $As(CH_3)_4^+$ and AsF_6^- is calculated to be 168 ppm, close to the experimental difference of 163 ppm (see ref 24 for representative experimental results). From the data in Table 6 we see that the As(III) ligand $AsS(SH)(OH)^-$ and the As(III) in the Cu complex are very strongly deshielded vs the As(V) in either $As(CH_3)_4^+$ or AsF_6^-. Unfortunately the calculated EFGs at As are very large in these essentially trigonal As(III) species so that the NMR lines will be broad. The conversion factor between the EFG (au) and the nuclear quadrupolar coupling constant (NQCC) (MHz) is about 60 for ^{75}As (the nuclear quadrupole moment is known to only one significant figure[25]), so our predicted NQCC for ^{75}As in CuAsS(SH)(OH) is about 260 MHz. For comparison the NQCC calculated for $AsCl_3$ using a similar method[23] was 168 MHz and an experimental value of 173 MHz has been reported for this compound.[26]

The Cu(I) sites in the two-coordinate $Cu(SH)_2^-$ and the three-coordinate compounds CuAsS(SH)(OH) and $Cu(SH)_2Cl^{2-}$ are deshielded by 300−400 ppm compared to that in the reference compound four-coordinate $Cu(NCH)_4^+$, and show large EFGs. Based on the nuclear quadrupole moment reported for ^{63}Cu in ref 27, the conversion factor from EFG to NQCC is about 44, giving an approximate NQCC of 60 MHz for CuAsS(SH)(OH). This is somewhat smaller than that reported[27] for three-coordinate Cu complexes with pyridine ligands, which are around 80−90 MHz. There are some experimental data on ^{63}Cu NMR shifts, mainly for tetrahedral Cu(I) species,[28] but the data are not systematic enough to allow us to establish a unique character for CuAsS(SH)(OH).

We have also evaluated both Mulliken charges and natural bond orbital[29] (NBO) charges for CuAsS(SH)(OH) and some related molecules, as shown in Table 7. As has often been noted, NBO charges correspond much more closely to our intuitive idea of charge distributions and are much more stable toward basis set expansion and change in quantum mechanical method. We see that the Cu NBO charges in CuAsS(SH)(OH) are not much different from those in $Cu(SH)_2^-$ and change little between HF and MP2. On the other hand, the Cu−As Mulliken bond overlap population (evaluated at the polarized SBK MP2 geometry) essentially doubles from HF to MP2, although even at the MP2 level it is only about one-third as large as that for the Cu−S bond (0.124 vs 0.374). This emphasizes again that the direct Cu−As bond only arises at correlated levels but that the bond is still quite weak compared to a more conventional bond.

Finally, we have estimated the hydration energies for CuAsS(SH)(OH) and related molecules using the isodensity polarized continuum method[30] (IPCM), yielding the results in Table 8. As expected the $Cu(SH)_2^-$ ion has a much more negative hydration energy than do any of the neutral compounds considered. We would therefore expect that $Cu(SH)_2^-$ and CuAsS(SH)(OH) could be separated by their different partitioning between water and nonpolar solvents.

Conclusions

Calculations at a number of different correlated levels confirm the existence of a direct Cu−As bond in CuAsS(SH)(OH). Such calculations also confirm the stability of the complex. A number of different spectral properties have been calculated to help in the identification of the complex. The calculated vibrational spectra for both CuAsS(SH)(OH) and its monohydrated form show stretching vibrations of the Cu−As−S three-membered ring around 450−500 cm^{-1}, which will not be present in conventional complexes such as $Cu(SH)_2^-$. The absorption spectrum calculated for this complex is also unusual, with its lowest energy absorption at about 2.4 eV in the singly hydrated form. This is connected with the presence of a low energy unoccupied orbital of antibonding character between the Cu and As, which also gives a low energy feature in the XANES. The Cu and As NMR spectra of the complex are also unique, but

Table 7. Calculated Mulliken Population Analysis, NBO Charges, and Dipole Moments for CuAsS(SH)(OH), $AsS(SH)(OH)^-$, and $Cu(SH)_2^-$ at Hartree−Fock and MP2 Levels Using the Polarized LANL2DZ Basis Set and the Polarized SBK MP2 Geometry

					NBO charges							
	Q_{Cu}		Q_{As}		Cu		As		Cu, As overlap populn		dipole moment (D)	
molecule	HF	MP2	HF	MP2	HF	MP2	HF	MP2	HF	MP2	HF	MP2
CuAsS(SH)(OH)	0.12	0.06	0.63	0.44	0.69	0.71	1.19	0.90	0.067	0.124	5.57	3.86
$AsS(SH)(OH)^-$			0.52	0.36			1.06	0.88			3.34	2.94
$Cu(SH)_2^-$	−0.02	−0.17			0.56	0.46					1.30	1.37

Table 8. Calculated Hydration Energies (kcal/mol) for CuAsS(SH)(OH) and Other Molecules Obtained at the IPCM Level with the 6-311G* Basis Set

molecule	IPCM hydration energy
CuAsS(SH)(OH)	−21.6
CuAsS(SH)(OH)(H_2O)	−25.3
$Cu(SH)_2^-$	−53.7
CuSH(H_2O)	−23.6

since the calculated NQCC values at both nuclei are very large the NMR signal may be broadened to invisibility.

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