Displacement of Cu(II) by Ag(I) in Solvated Metal Sulfides. A DFT and AIM Computational Study

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The substitution of Cu^{2+} by Ag^+ in hydrated $Cu^{II}S$ and $(Cu^{II})_3S_3$ was modeled computationally by density functional theory quantum theory of atoms in molecules, and solvent field methods. The coordination, first-shell and partly second-shell molecular structures, and thermochemical data for solvated Cu^{2+}, Ag^+, $Cu^{II}S$, $(Cu^{II})_3S_3$, $AgCu_2S_3$ and their reactions were obtained. The thermochemical data showed that displacement of Cu^{2+} and Cu^+ from $Cu^{II}S$ and $(Cu^{II})_3S_3$ by Ag^+, while unfavorable in the gas phase, is facilitated in an aqueous environment. Several covalently bonded species were examined as intermediates in the substitution reactions.

Introduction

Copper and silver ions and their sulfide complexes play a range of roles in biochemical reactions of living species. For example, Cu^IS clusters serve as catalytic centers in biologically important reactions of charge transfer, ligand exchange, and oxidative degradation.[1−3] Free or weakly bound Cu(I) and Ag-(I) ions are highly toxic to aquatic animals even at low concentrations.[4−7] At the same time, complexation of a metal by sulfide substantially suppresses its toxicity,[8,9] yet investigations of the role of metal sulfides in biochemical reactions are often complicated by the lack of knowledge about the degree of coordination and the strength and nature of the of the interactions in solvated species. The relative stabilities of solvated metal sulfide complexes could differ from the relative stabilities of those determined in the gas phase. For example, experimental atomization energies of $(Cu^I)_2S$ and $(Ag^I)_2S$ in the gaseous phase are 135.9 ± 5 and 107.6 ± 5 kcal mol^{-1}, respectively.[10] The gas-phase dissociation energy (DE) of CuS also is larger than the DE of the diatomic AgS, indicating that the Cu−S bond is stronger than Ag−S bond,[10] yet Cu^{2+} of $Cu^{II}S$ can be displaced by Ag^+ in aqueous solution.[11] In addition, $Ag_2S(xl)$ is less soluble than $Cu_2S(xl)$.[12] We previously investigated the coordination, bonding, and stability of $[(Cu^I)_2S]_n$ and $Cu_xS_y^-$ clusters in the gaseous phase[13,14] as well as the complexation of Cu^+ and Ag^+ and their sulfides with water and showed that Cu(I)−S and Cu(I)−O bonds are stronger than the corresponding Ag−S and Ag−O analogues in gas phase and in aqueous solution.[15] We also demonstrated that coordination of Cu^+ and Ag^+ in water is very similar. These findings, however, contrast the observation that Cu^{2+} of CuS can be displaced by Ag^+ in aqueous solution.[11]

The purpose of this study was to investigate possible pathways for substituting Cu^{2+} by Ag^+ in solvated sulfides by calculating thermochemical data and studying the nature of the bonding in hydrates. Varying levels of solvation were considered in the density functional theory (DFT) calculations. Quantum theory of atoms in molecules (QTAIM) calculations were used to study the molecular structures of hydrated Cu^{2+}, $Cu^{II}S$, their Ag analogues, and several potential intermediates for the substitution reactions involving $Cu^{II}S$ and $(Cu^{II})_3S_3$. The results are presented and discussed in this paper.

Computational Methods

The hydration of Cu(II) and Ag(I) sulfides was modeled by investigating complexes with varying numbers of water molecules. The first and partly second water solvation shells were considered explicitly at the DFT level. Equilibrium optimized geometries and wave functions of hydrates were obtained at the B3PW91 level[16] as implemented in Gaussian 98.[17] Selected internuclear distances are given in Table 1. The 6-311+G(d) basis set was used for all elements except Ag. Gaussian 98 does not provide medium-sized all-electron basis sets for atoms beyond Kr, yet AIM analyses require all-electron wave functions. Consequently, we use the DZVP basis set for Ag originally developed for the DeMon program.[18] It includes 6s, 5p, and 3d functions with contraction (633321/53211*/531+) along with polarization and diffuse functions. We showed previously that calculated gas-phase dissociation energies of $[Ag(H_2O)_n]^+$ hydrates with this basis set correlated well with experimental values,[15] thereby validating the use of the DeMon basis set. Optimization of weakly bound complexes such as $Cu^{II}S(H_2O)_n$, $(Cu^{II})_3S_3(H_2O)_n$, and $AgCu_2S_3(H_2O)_n$ with numerous hydrogen bonds required up to 120 steps because the calculation of forces for noncovalent interactions was close to the limit of precision for DFT calculations. Nevertheless all optimizations converged. Selected internuclear distances are given in Table 1. Vibration analyses were performed for all complexes in order to confirm that all species were minima on the potential energy surfaces and to obtain enthalpies of formation of $[Cu(H_2O)_6]^{2+}$ and $[Ag(H_2O)_4]^+$ at 298.13 K used in the calculation of the heats of formation of the ions in solution (entries 11 and 22 of Table 2). Zero-point-energy-corrected total energies (E_o) are displayed in column two of Table 2, and the uncorrected total energies E_{elec} are included as Supporting

TABLE 1: Interatomic Distances (Å) and Values of Electron Density (e Å^{-3}) at Bond Critical Points

species	M1^a–S1	M2–S1	Cu2–S2	Cu3–S2	Cu3–S3	M1–S2	M1–S3	M1–O1*	M1–O2*	Cu2–O2	Cu3–O3	Cu3–O4	O4–H2	O5–H1	H4–S1
CuS	2.091														
	0.711^b														
Ag$_2$S	2.384	2.384													
	0.491	*0.491*													
[Cu(H$_2$O)$_4$(H$_2$O)$_2$]$^{2+}$								1.925	1.929				1.728	1.809	
								0.591	*0.577*				*0.285*	*0.236*	
[Cu(H$_2$O)$_4$]$^{2+}$								1.977	1.960						
								0.507	*0.531*						
[Cu(H$_2$O)$_6$]$^{2+}$								2.005	2.265						
								0.462	*0.278*						
[Ag(H$_2$O)$_2$(H$_2$O)$_2$]$^+$								2.177	2.177				1.731		
								0.453	*0.453*				*0.270*		
[Ag(H$_2$O)$_4$]$^+$								2.410	2.409						
								0.270	*0.270*						
CuS(H$_2$O)$_4$	2.119							2.062	2.083				1.713		2.376
	0.680							*0.433*	*0.417*				*0.300*		0.139
CuS(H$_2$O)$_6$	2.118							2.186	2.367				1.670	1.747	2.205
	0.683							*0.346*	*0.239*				*0.327*	*0.279*	*0.198*
Cu$_3$S$_3$	2.176	2.198	2.198	2.176	2.177		2.177								
	0.619	*0.593*	*0.593*	*0.619*	*0.617*		*0.617*								
AgCu$_2$S$_3$	2.520	2.161	2.172	2.171	2.160		2.521								
	0.404	*0.640*	*0.623*	*0.623*	*0.640*		*0.403*								
[AgCu$_3$S$_3$]$^+$	2.650	2.234	2.164	2.160	2.223	2.634	2.610	2.318		2.401	2.189	2.303	1.936	1.742	
	0.300	*0.547*	*0.625*	*0.629*	*0.560*	*0.304*	*0.325*	*0.333*		*0.219*	*0.326*	*0.268*	*0.175*	*0.263*	
[Cu$_3$S$_3$(H$_2$O)$_6$]	2.202	2.190	2.211	2.225	2.231		2.195	2.034		2.062	2.310	2.174			
	0.585	*0.602*	*0.577*	*0.559*	*0.563*		*0.592*	*0.465*		*0.432*	*0.260*	*0.336*			
[AgCuS(H$_2$O)$_8$]$^+$	2.490	2.103						2.399	2.283					1.909	
	0.421	*0.705*						*0.280*	*0.363*					*0.191*	
[Ag$_2$CuS(H$_2$O)$_{12}$]$^{2+}$	2.461	2.515		2.133				2.354	2.553		2.248	2.020		1.946	
	0.437	*0.397*		*0.657*				*0.320*	*0.211*		*0.298*	*0.473*		*0.174*	
[AgCu$_2$S$_3$(H$_2$O)$_6$]	2.521	2.173	2.189	2.189	2.166		2.550	2.489		2.210	2.032		1.682	1.743	2.333
	0.392	*0.618*	*0.600*	*0.595*	*0.619*		*0.375*	*0.238*		*0.320*	*0.477*		*0.318*	*0.278*	*0.141*
[Ag$_2$S(H$_2$O)$_8$]	2.457	2.458						2.523	2.341					1.825	
	0.450	*0.449*						*0.226*	*0.325*					*0.236*	

^{a} M1 and M2 Cu or Ag. ^{b} Electron density (e Å^{-3}) at bond critical point in italics.

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TABLE 2: Thermochemical Data for Various Species in the Gas Phase and the Water Solvent Field

species	E_o	$\Delta E_{hyd(cu)}$ (counterpoise-uncorrected)	$\Delta E_{hyd(cc)}$ (counterpoise-corrected)	E_{sf}
Cu^0	−1 640.426 590			
Cu^+	−1 640.136 904			
S^0	−398.078 156			
S^{2-}	−398.006 372			
Cu^{2+}	−1 639.375 164			
CuS	−2 038.603 225			
Cu_3S_3	−6 116.026 493			
H_2O	−76.391 540			
$[Cu(H_2O)_4]^{2+}$	−1 945.437 098	−311.1	−294.3	−224.8
$[Cu(H_2O)_4(H_2O)_2]^{2+}$	−2 098.316 578	−371.6	−354.5	−196.0
$[Cu(H_2O)_6]^{2+}$	−2 098.301 746	−362.3	−339.4	−204.7
				547.1[a] (calc)
				507.4[b] (exp)
$CuS(H_2O)_4$	−2 344.257 815	−55.5	−49.3	−18.6
$CuS(H_2O)_6$	−2 497.071 715	−74.8	−68.4	−19.3
$Cu_3S_3(H_2O)_6$	−6 574.441 382	−41.2	−28.0	−33.9
$[Cu(H_2O)_2(H_2O)_2]^+$	−1 945.892 230	−118.7	−111.0	−53.4
$[Cu(H_2O)_4]^+$	−1 945.877 093	−109.2	−94.4	−68.1
Ag^0	−5 199.523 643			
Ag^+	−5 199.258 847			
Ag_2S	−10 797.277 838			
$AgCu_2S_3$	−9 675.084 083			
$[Ag(H_2O)_2(H_2O)_2]^+$	−5 504.962 057	−86.0	−80.1	−54.5
$[Ag(H_2O)_4]^+$	−5 504.960 104	−84.8	−72.7	−69.9
				144.3[a] (calc)
				116.6[b] (exp)
$[Ag_2S(H_2O)_8]$	−11 408.564 516	−96.9	−86.2	−32.4
$[AgCuS(H_2O)_8]^+$	−7 849.278 327	−132.9	−119.8	−59.9
$[Ag_2CuS(H_2O)_{12}]^{2+}$	−13 354.209 599	−242.8	−223.1	−244.7
$[AgCu_3S_3(H_2O)_8]^+$	−11 926.659 943	−116.1	−91.8	−94.4
$AgCu_2S_3(H_2O)_6$	−10 133.512 994	−50.0	−33.3	−18.0

[a] Enthalpy of formation calculated as $\Delta H_{hydr} + E_{sf}$. [b] Experimental enthalpy of formation from ref 36.

Information. The counterpoise-uncorrected ($\Delta E_{hyd(cu)}$) and counterpoise-corrected ($\Delta E_{hyd(cc)}$) hydration energies based on ZPE-corrected total energies E_os are listed in columns three and four of Table 2. Counterpoise calculations were carried out to evaluate the basis set superposition error (BSSE) according to a procedure described elsewhere.[19] Bulk-solvent polar effects were modeled with standard single-point solvent field calculations on the hydrates at the IPCM level using the water dielectric constant of 78.4. The E_{sf} values for embedding hydrates in the water solvent field are listed in column five. AIM 2000 was used for QTAIM analyses and to obtain molecular graphs.[20] Selected $\rho(\mathbf{r}_c)$ values at bond critical points are collected in Table 1.

Results and Discussion

Phillips and Kraus[11] showed experimentally that Ag^+ replaces Cu^{2+} of $Cu^{II}S$ in aqueous solution and proposed the simple reaction 1 for their experimental findings. We studied the

$$CuS + 2Ag^+ \rightleftharpoons Cu^{2+} + Ag_2S \tag{1}$$
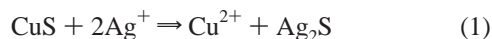
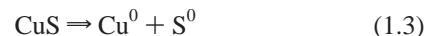feasibility of this gas-phase reaction in a stepwise fashion by calculating ΔE_o ($E_o = E_{elec} + ZPE$) for the reaction. The optimized geometrical parameters and thermochemical data are given in Tables 1 and 2, respectively. The entries in italics listed in Table 1 indicate the values of the electron density $\rho(\mathbf{r}_c)$ at bond critical points (BCPs)—often used as a measure of the bond strength for similar types of bonds[21,22]—obtained with AIM 2000.[20] Reaction 1 is highly endothermic ($\Delta E_o = 293.3$ kcal mol^{-1}) and therefore impossible in the gas phase. We split reaction 1 into two steps—reactions 1.1 and 1.2—in order to understand its high endothermicity. The first step (1.1) that involves the dissociation of CuS into ions requires 767.2 kcal

mol^{-1}, while the second reaction (1.2) that yields Ag_2S is highly exothermic (473.9 kcal mol^{-1}). One could consider reaction 1.1 as a two-step process involving homolytic dissociation of CuS

$$CuS \rightleftharpoons Cu^{2+} + S^{2-} \tag{1.1}$$

$$S^{2-} + 2Ag^+ \rightleftharpoons Ag_2S \tag{1.2}$$
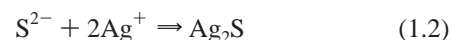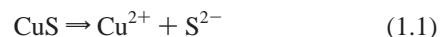
into Cu^0 and S^0 followed by double ionization of Cu^0 and reduction of S^0 to S^{2-}. We calculated (Table 2) a homolytic

$$CuS \rightleftharpoons Cu^0 + S^0 \tag{1.3}$$

$$Cu^0 \rightleftharpoons Cu^{2+} + 2e^- \tag{1.4}$$

$$S^0 + 2e^- \rightleftharpoons S^{2-} \tag{1.5}$$

dissociation energy of 62.4 kcal mol^{-1} for reaction 1.3 that is very close to the experimental value of 64.7 kcal mol^{-1} for $Cu^{II}S$.[10] Our computed ionization energy for reaction 1.4 was 659.8 kcal mol^{-1}, close to the experimental value (645.9 kcal mol^{-1}).[12] The gas-phase reduction of S^0 to S^{2-} (1.5) required 45.0 kcal mol^{-1} (Table 2). The formation of Ag_2S (reaction 1.2) involving formation of two Ag–S bonds is highly exothermic (473.9 kcal mol^{-1}); the main energy cost of reaction 1.1 comes from the ionization of Cu^0 to Cu^{2+} over $2Ag^0$ to $2Ag^+$.

Solvation could dramatically affect ΔE for reaction 1. In our previous study of hydrated copper(I) and silver(I) sulfides, we showed that ΔE could be substantially decreased in going from the gas phase to water when first and second hydration shells are included explicitly and long-range bulk-solvent polar effects are modeled by embedding the hydrates in a solvent field.[15,23] In fact, the hydration of Ag^+ has been studied experimentally.[24−26]
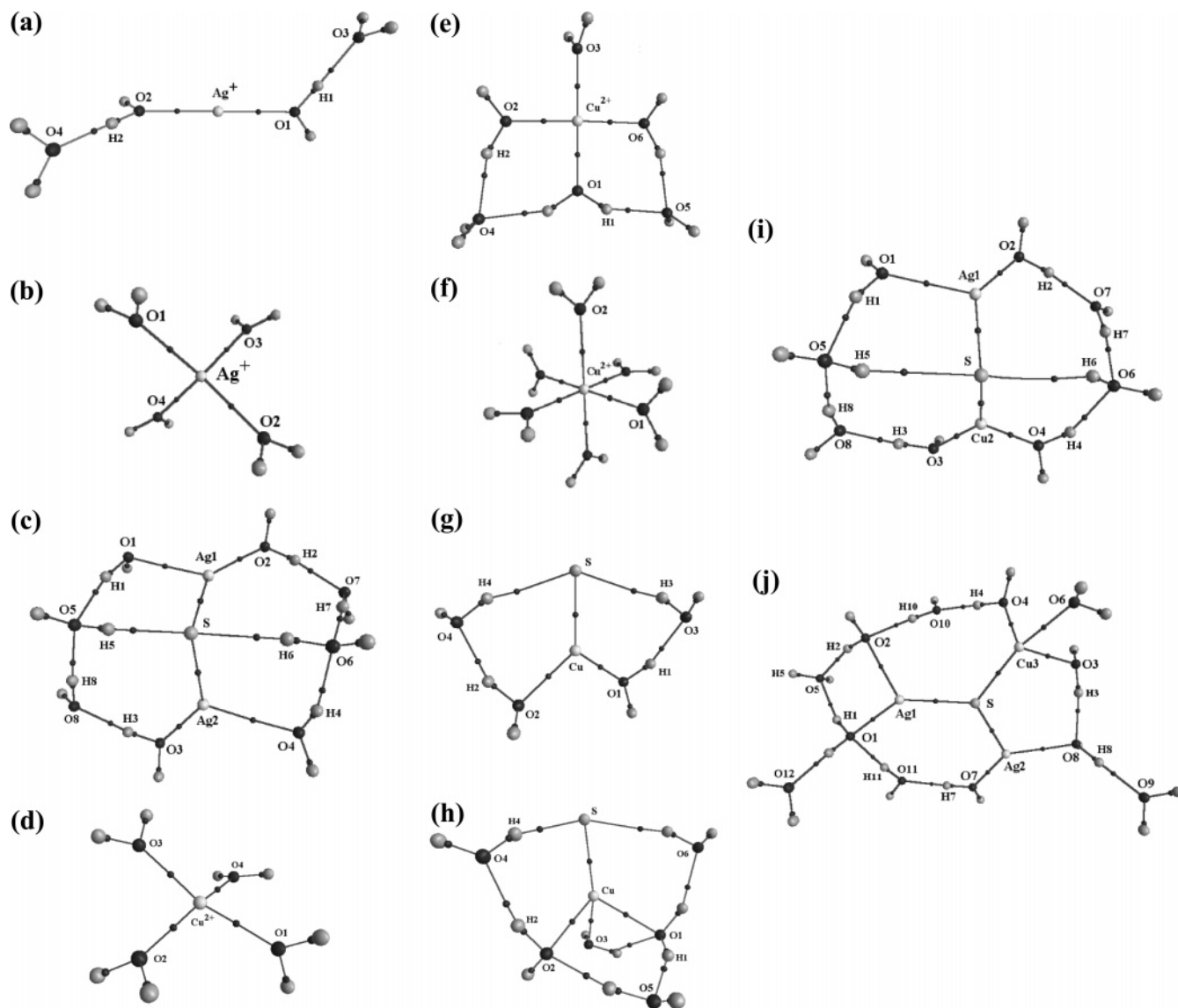
Figure 1. Molecular graph of (a) $[Ag(H_2O)_2(H_2O)_2]^+$ (the small black spheres are bond critical points), (b) $[Ag(H_2O)_4]^+$, (c) $[Ag_2S(H_2O)_8]$, (d) $[Cu(H_2O)_4]^{2+}$, (e) $[Cu(H_2O)_4(H_2O)_2]^{2+}$, (f) $[Cu(H_2O)_6]^{2+}$, (g) $[Cu(II)S(H_2O)_4]$, (h) $[Cu(II)S(H_2O)_6]$, (i) $[AgCuS(H_2O)_8]^+$, and (j) $[Ag_2CuS(H_2O)_{12}]^{2+}$.

It was shown that the first-shell coordination of the hydrated Ag^+ varies from 2 to 4 depending on the temperature and pressure and whether the solute is solvated in the liquid or saturated vapor phase.[24] We carried out a computational study with a limited number of water molecules in the gas phase and found that the two-coordinate hydrate $[Ag(H_2O)_2(H_2O)_2]^+$ (Figure 1a) with two water molecules in the first shell is more stable than the four-coordinate species (Figure 1b).[15] That the hydrate is two-coordinate in the gas phase is nicely in accord with the experimental findings that there is a decrease in the first-shell coordination in going from the liquid phase to the gas phase.[25,26] In our earlier computational study[15] we also found that each Ag atom of Ag_2S is two-coordinate in the first shell (Figure 1c). The thermochemical data for the two- and four-coordinate hydrates of Ag^+ and Ag_2S from our previous work are given in Table 2.[15]
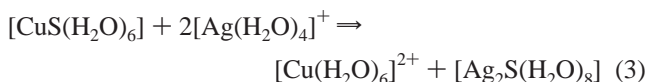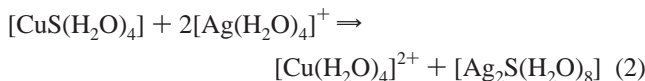
The hydration of Cu^{2+} has been investigated experimentally and computationally.[24,27−31] The first-shell coordination ranged from four to six water molecules in solution and four water molecules in the gas phase.[24,31] The lower Cu^{2+} coordination in gaseous phase found by Berces and co-workers[31] was explained by the fact that a limited number of solvent molecules

was used and that the calculations slightly overestimated the of strength of the hydrogen bonds. We studied $[Cu(H_2O)_4]^{2+}$, $[Cu(H_2O)_4(H_2O)_2]^+$, and $[Cu(H_2O)_6]^{2+}$—the molecular graphs are displayed as Figure 1d−f, respectively—and found that the four-coordinate hydrate $[Cu(H_2O)_4(H_2O)_2]^+$ (Figure 1e) that has two hydrogen-bonded water molecules in the second shell was more stable than the six-coordinate hydrate $[Cu(H_2O)_6]^{2+}$ (Figure 1f) by 9.3 kcal mol^{-1} (Table 1). The molecular structures we obtained for $[Cu(H_2O)_4]^{2+}$ and $[Cu(H_2O)_6]^{2+}$ are similar to the geometrical structures reported by Berces and co-workers.[31]

However, there is a paucity of data on $Cu^{II}S$. Luther and co-workers suggested that each Cu atom in solvated $Cu^{II}S$ is coordinated to two water molecules on the basis of molecular mechanics calculations.[32] We obtained optimized geometries of the four- (Figure 1g) and six-water (Figure 1h) hydrates of CuS. The first-shell coordination to Cu in CuS varies slightly depending on the number of water molecules available for hydration. In case of hydration of $Cu^{II}S$ by four H_2Os, the metal atom was coordinated to two water molecules and two others formed hydrogen bonds to the S atom. For the six-H_2O hydrate, three water molecules coordinated to Cu, and two water molecules are hydrogen-bonded to S; one H_2O was hydrogen-

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bonded to the two H_2Os coordinated to Cu. On the basis of these results for $Cu^{II}S(H_2O)_6$, the maximum coordination to Cu of CuS in the gas phase is three. From the data in Table 1 it is seen that lower coordination to Cu of $Cu^{II}S(H_2O)_4$ leads to shorter and stronger Cu−O bonds than in the case of $Cu^{II}S$-$(H_2O)_6$.

Having data for the hydrates in hand, we examined reaction 2 and reaction 3.

$$[CuS(H_2O)_4] + 2[Ag(H_2O)_4]^+ \Longrightarrow$$
$$[Cu(H_2O)_4]^{2+} + [Ag_2S(H_2O)_8] \quad (2)$$

$$[CuS(H_2O)_6] + 2[Ag(H_2O)_4]^+ \Longrightarrow$$
$$[Cu(H_2O)_6]^{2+} + [Ag_2S(H_2O)_8] \quad (3)$$

On the basis of the E_o values listed in Table 2, reaction 2 (110.7 kcal mol^{-1}) and reaction 3 (78.9 kcal mol^{-1}) are endothermic in the gas phase, but not nearly to the same extent as reaction 1 (293.3 kcal mol^{-1}). The main reason for this significant decrease in ΔE_o is the exothermicity of the hydration of Cu^{2+}. The counterpoise-uncorrected ($\Delta E_{hyd(cu)}$) and counterpoise-corrected ($\Delta E_{hyd(cc)}$) hydration energies (HEs) of $[Cu(H_2O)_4]^{2+}$ and $[Cu(H_2O)_6]^{2+}$ are substantially larger than the values for $[CuS(H_2O)_4]$, $[CuS(H_2O)_6]$, and $[Ag_2S(H_2O)_8]$ and three times the HE of $[Ag(H_2O)_4]^+$.

That the H_2O-Cu^{2+} covalent interactions are stronger than in the other hydrates is seen in the higher values of $\rho(\mathbf{r}_c)$ at the BCPs and shorter interatomic distances. For example, the values of $\rho(\mathbf{r}_c)$ for the Cu−O bond in $[Cu(H_2O)_6]^{2+}$ are larger (four BCPs have a $\rho(\mathbf{r}_c)$ of 0.462 e A^{-3} and two have a value of 0.278 e A^{-3}) than the values of the Ag−O bonds of $[Ag(H_2O)_4]^+$ ($\rho(\mathbf{r}_c) = 0.270$ e A^{-3}) even though the first shell coordination of $[Cu(H_2O)_6]^{2+}$ is higher than that of $[Ag(H_2O)_4]^+$. The values of $\rho(\mathbf{r}_c)$ differ even more for the hydrates $[Cu(H_2O)_4(H_2O)_2]^{2+}$ and $[Ag(H_2O)_4]^+$ that have the same first-shell coordination. The hydrates $[Cu(H_2O)_4]^{2+}$ and $[Cu(H_2O)_4(H_2O)_2]^{2+}$ with the similar coordination exhibit very similar values of $\rho(\mathbf{r}_c)$ and Cu−O bond lengths. Larger values of $\rho(\mathbf{r}_c)$ and correspondingly shorter interatomic distances are also observed for Cu(II)−O bonds relative to the Cu(I)−O ones; the $\rho(\mathbf{r}_c)$ values for $[Cu(H_2O)_4(H_2O)_2]^{2+}$ vary from 0.577 to 0.591 e A^{-3}, whereas those in $[Cu(H_2O)_4(H_2O)_2]^+$ range from 0.380 to 0.382 e A^{-3}, [15] indicating a stronger Cu−O interaction in the former case. Comparing $\rho(\mathbf{r}_c)$ values for Cu(II)−O bonds in $[Cu(H_2O)_6]^{2+}$ and Cu(I)−O in $[Cu(H_2O)_6]^+$,[15] one might argue that that their bond strengths are similar, although the HE for $[Cu(H_2O)_6]^{2+}$ is substantially larger than the HE for $[Cu(H_2O)_6]^+$. In fact, $[Cu(H_2O)_6]^{2+}$ has four strong bonds with $\rho(\mathbf{r}_c) = 0.462$ e A^{-3} and two relatively weak bonds ($\rho(\mathbf{r}_c) = 0.278$ e A^{-3}), whereas $[Cu(H_2O)_6]^+$ has only two strong bonds with $\rho(\mathbf{r}_c) = 0.436$ e A^{-3} and four very weak bonds with ($\rho(\mathbf{r}_c)$ ranging between 0.153 and 0.192 e A^{-3}). Thus, the larger values of $\rho(\mathbf{r}_c)$ for the Cu(II)−O bonds as well the larger first-shell hydration energy of Cu^{2+} demonstrate dominance of the interaction of Cu^{2+} with water molecules with respect to that of singly charged and neutral species. This is the main reason for the dramatic decrease in the endothermicity of reaction 2 relative to reaction 1.

To establish how long-range bulk−solvent polar interactions affect ΔE, we embedded reactants, intermediates, and products in the water solvent field[23] to obtain additional thermochemical data. Generally reaction field methods and IPCM in particular are based on empirical parametrization and fitting to the set of

atomic charges or multipoles. Therefore IPCM calculations are not as accurate as the so-called explicit solvation calculations involving covalently bound first-shell water molecules of hydrates. Our goal rather was to establish trends in the effect of long-range polar interactions on substitution reactions rather than to make accurate predictions of total solvation energies. Reaction 2 that was endothermic in the gas phase (110.7 kcal
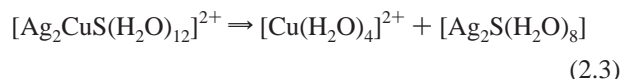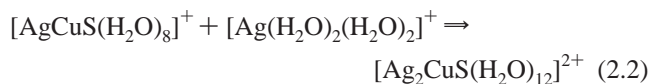
$$[CuS(H_2O)_4]_{sf} + 2[Ag(H_2O)_4]^+{}_{sf} \Longrightarrow$$
$$[Cu(H_2O)_4]^{2+}{}_{sf} + [Ag_2S(H_2O)_8]_{sf} \quad (2sf)$$
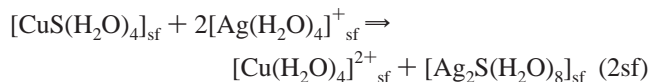
mol^{-1}) was very much less so when it was embedded in the H_2O solvent field (reaction 2sf, 11.9 kcal mol^{-1}). Reaction 3 that was also endothermic in the gas phase (78.9 kcal mol^{-1}) was marginally exothermic when embedded in the H_2O solvent field (reaction 3sf, −0.90 kcal mol^{-1}).

$$[CuS(H_2O)_6]_{sf} + 2[Ag(H_2O)_4]^+{}_{sf} \Longrightarrow$$
$$[Cu(H_2O)_6]^{2+}{}_{sf} + [Ag_2S(H_2O)_8]_{sf} \quad (3sf)$$
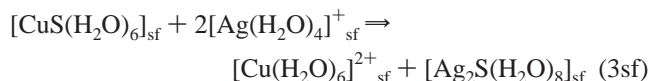
We also modeled a possible stepwise process for reaction 2 based on an electrophilc reaction of Ag^+ with CuS. We considered the formation of the intermediate $AgCuS(H_2O)_8^+$ (reaction 2.1) from CuS hydrated with four water molecules and the two-coordinate Ag^+ hydrate $[Ag(H_2O)_2(H_2O)_2]^+$. The molecular graph of the intermediate $[AgCuS(H_2O)_8]^+$ displayed

$$[CuS(H_2O)_4] + [Ag(H_2O)_2(H_2O)_2]^+ \Longrightarrow [AgCuS(H_2O)_8]^+$$
$$(2.1)$$
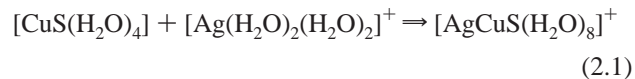
as Figure 1i is similar to the molecular graphs of $[Ag_2S(H_2O)_8]$, $[Cu_2S(H_2O)_8]$, and $[AgCuS(H_2O)_8]$.[15] As expected the HE of $[AgCuS(H_2O)_8]^+$ is higher than HEs of the neutral hydrates. Reaction 2.1 is exothermic ($\Delta E_o = -36.7$ kcal mol^{-1}). No other minimum was located during the optimization of $[AgCuS$-$(H_2O)_8]^+$. We modeled a second intermediate $[Ag_2CuS$-$(H_2O)_{12}]^{2+}$ - formed by electrophilic addition of a second unit of hydrate $[Ag(H_2O)_2(H_2O)_2]^+$ to $[AgCuS(H_2O)_8]^+$ as shown in reaction 2.2 − that, in principle, could decompose to the Ag_2S and Cu^{2+} hydrates as shown in reaction 2.3. The molecular graph of $[Ag_2CuS(H_2O)_{12}]^{2+}$ is displayed as Figure 1j. Each

$$[AgCuS(H_2O)_8]^+ + [Ag(H_2O)_2(H_2O)_2]^+ \Longrightarrow$$
$$[Ag_2CuS(H_2O)_{12}]^{2+} \quad (2.2)$$

$$[Ag_2CuS(H_2O)_{12}]^{2+} \Longrightarrow [Cu(H_2O)_4]^{2+} + [Ag_2S(H_2O)_8]$$
$$(2.3)$$

Ag is coordinated to two H_2Os and each Cu to three H_2Os. The remaining five H_2Os lie in the second solvation shell. Unlike reaction 2.1, (2.2) is endothermic ($\Delta E_o = 19.3$ kcal mol^{-1}). Reaction 2.3 is much more endothermic (130.5 kcal mol^{-1}) in the gas phase than reaction 2.2, indicating that should $[AgCuS$-$(H_2O)_8]^+$ be formed, it is unlikely to yield Ag_2S via the formation of $[Ag_2CuS(H_2O)_{12}]^{2+}$ in the gas phase. Reaction 2.1 that was exothermic in the gas phase (−36.7 kcal mol^{-1}) was more so when embedded in the H_2O solvent field (reaction 2.1sf, −49.9 kcal mol^{-1}). Reaction 2.2 that was endothermic in the

$$[CuS(H_2O)_4]_{sf} + [Ag(H_2O)_2(H_2O)_2]^+{}_{sf} \Longrightarrow$$
$$[AgCuS(H_2O)_8]^+{}_{sf} \quad (2.1sf)$$
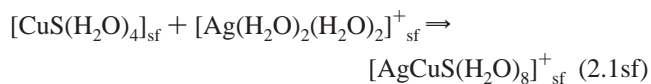
gas phase (19.3 kcal mol^{-1}) was highly exothermic in the solvent

$$[AgCuS(H_2O)_8]^+{}_{sf} + [Ag(H_2O)_2(H_2O)_2]^+{}_{sf} \rightleftharpoons$$
$$[Ag_2CuS(H_2O)_{12}]^{2+}{}_{sf} \quad (2.2sf)$$
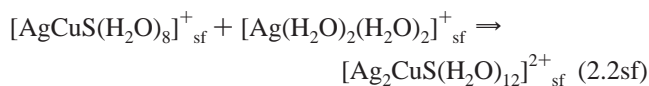
field (reaction 2.2sf, -111.0 kcal mol^{-1}) due to the enormous stabilization of $[Ag_2CuS(H_2O)_{12}]^{2+}$ in the H$_2$O solvent field. While the endothermicity of reaction 2.3 decreased marginally in the solvent field (reaction 2.3sf, 118.0 kcal mol^{-1}), it is clear that should $[AgCuS(H_2O)_8]^+$ be formed, even in solution it will not yield Ag$_2$S via $[Ag_2CuS(H_2O)_{12}]^{2+}$ even though we did not attempt to locate a transition state for reaction 2.3.

$$[Ag_2CuS(H_2O)_{12}]^{2+}{}_{sf} \rightleftharpoons [Cu(H_2O)_4]^{2+}{}_{sf} + [Ag_2S(H_2O)_8]_{sf}$$
$$(2.3sf)$$
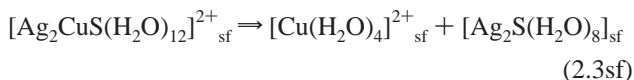
It must be kept in mind that solvent field calculations do not yield bulk solution solvation energies with the accuracy found for calculations involving explicit hydration in the gas phase.[15,33−35] In general the enthalpies of hydration for ions are overestimated when modeled with dielectric continuum calculations.[15,33] In this study, we calculated the enthalpy of formation (ΔH_f) of $[Cu(H_2O)_6]^{2+}$ and report the value for $[Ag(H_2O)_4]^+$ taken from our previous work.[15] As it was found previously in other studies,[15,33] the calculated ΔH_f for $[Cu(H_2O)_6]^{2+}$ exceeds the experimental value obtained in solution.[36] The overestimation is not large ($\sim$8%) given that such factors as the formation of a cavity in the solvent, the enthalpy of vaporization of water, and the dispersion−repulsion forces between solvent and solute are not explicitly taken into account. Martinez and co-workers[33] showed that inclusion of these corrections for hydrated Ag$^+$, calculated by empirical formulas,[37,38] improves the accuracy somewhat, but the error in the hydration enthalpy remains high, up to 31 kcal mol^{-1}. We presume that any systematic errors introduced due to cavity formation roughly cancel each other for the reactants and products. Nevertheless, the oxidation states of hydrates are different giving rise to different polar interactions with the solvent field. While one cannot rely on quantitative predictions on the basis of the solvent field calculations, significant decreases are seen in ΔE in solution due to the high heat of solvation of Cu^{2+} and the polar effect of the bulk solvent.

We also modeled a potential substitution mechanism of Cu^{2+} or Cu$^+$ by Ag$^+$ using the six-member-ring species (Cu^{II})$_3$S$_3$ that has been considered as the basic building block for aqueous Cu^{II}S clusters.[32] It was also proposed that each of the Cu atoms in Cu$_3$S$_3$ is bound to two water molecules in the first solvation shell on the basis of force field calculations on Cu$_3$S$_3$(H$_2$O)$_6$. Substitution of Cu(II) by Ag(I) in large CuS clusters—Cu$_3$S$_3$ being the model—is interesting not only because of the potential impact of a larger cluster size on the ease of substitution Cu^{2+} by Ag$^+$ but also because of the possible displacement of Cu$^+$ from Cu$_3$S$_3$ via reaction 4. We reasoned that displacement of Cu^{2+} by Ag$^+$ with the release of Cu$^+$ might occur more readily

$$Cu_3S_3 + Ag^+ \rightleftharpoons Cu^+ + AgCu_2S_3 \quad (4)$$
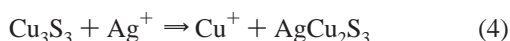
with the ionizations of Cu^0 to Cu$^+$ (178.1 kcal mol^{-1}) and Ag^0 to Ag$^+$ (174.6 kcal mol^{-1}),[12] key factors in determining ΔE_o, are similar in magnitude. In fact, in their study of the substitution of Cu^{2+} by Ag$^+$, Phillips and Kraus[11] did not provide experimental evidence that Cu^{2+} was the sole displacement product of the reaction. It is known that Cu$^+$ disproportionates to Cu^{2+} and Cu^0 in polar solvents with ΔG being -8.2 kcal mol^{-1}.[12] Disproportionation is not considered here due to its potential mechanistic complexity. The molecular graphs of optimized

Cu$_3$S$_3$ and AgCu$_2$S$_3$ are displayed as Figure 2a,b, respectively. Both six-member rings are planar; Cu$_3$S$_3$ does not possess a chairlike structure as reported previously.[32] While reaction 4 is endothermic in the gas phase, remarkably ΔE_o is only 40.7 kcal mol^{-1}, considerably smaller than ΔE_o (293.3 kcal mol^{-1}) for reaction 1. The main reason for the endothermicity of reaction 4 is that two Cu−S bonds of Cu$_3$S$_3$ are replaced by two weaker Ag−S bonds in AgCu$_2$S$_3$. This fact is supported by the larger values of $\rho(\mathbf{r}_c)$ in bond critical points for Cu−S bonds than for Ag−S bonds, shorter Cu−S interatomic distances with respect to Ag−S, and higher dissociation energy of Cu−S with respect to Ag−S.[10] Overall the energy difference is not large, making the displacement of Cu$^+$ by Ag$^+$ in solution a possibility and worthy of study computationally at the same level we used in the study on Cu^{2+}, Ag$^+$, CuS, and Ag$_2$S. Consequently, we determined the structure of the hydrates that included only first-shell H$_2$Os. As starting points we arranged two water molecules adjacent to each metal atom of Cu$_3$S$_3$—similar to the coordination proposed by Luther and co-workers[32]—and AgCu$_2$S$_3$. The molecular graphs of optimized [Cu$_3$S$_3$(H$_2$O)$_6$] and [AgCu$_2$S$_3$(H$_2$O)$_6$] are displayed as Figure 2c,d, respectively. The structures of [Cu$_3$S$_3$(H$_2$O)$_6$] and [AgCu$_2$S$_3$(H$_2$O)$_6$] are slightly different. In [Cu$_3$S$_3$(H$_2$O)$_6$], one copper atom is covalently bound to two water molecules, but the other two copper atoms coordinate to only one water each unlike what was reported by Luther and co-workers.[32] The remaining two water molecules move to the second shell and form hydrogen bonds with first-shell water molecules and sulfur rather than binding covalently to the copper atoms. The Cu$_3$S$_3$ ring remains nearly planar. In the case of [AgCu$_2$S$_3$(H$_2$O)$_6$], every metal atom is covalently bound to only one water molecule, and the remaining water molecules move to a second shell and interact with the first-shell waters and a sulfur atom via hydrogen bonds. The AgCu$_2$S$_3$ ring in hydrated [AgCu$_2$S$_3$(H$_2$O)$_6$] is distorted considerably relative to the nonhydrated gas-phase structure (Figure 2b). On the whole, the coordination and structure of [Cu$_3$S$_3$(H$_2$O)$_6$] and [AgCu$_2$S$_3$(H$_2$O)$_6$] are similar. Each metal atom, except Cu3 of [Cu$_3$S$_3$(H$_2$O)$_6$] (Figure 2c), coordinates to one water molecule, and weak hydrogen bonds are formed with sulfur atoms. The HE of [AgCu$_2$S$_3$(H$_2$O)$_6$] is slightly higher than the HE of [Cu$_3$S$_3$(H$_2$O)$_6$], a consequence of the fact that [AgCu$_2$S$_3$(H$_2$O)$_6$] has a larger number of hydrogen bonds than [Cu$_3$S$_3$(H$_2$O)$_6$]; all the water molecules in [AgCu$_2$S$_3$(H$_2$O)$_6$] but one are linked with each other, forming four intermolecular O−H hydrogen bonds. In [Cu$_3$S$_3$(H$_2$O)$_6$] only two pairs of H$_2$Os are connected by hydrogen bonds. These differences result in the HE of [AgCu$_2$S$_3$(H$_2$O)$_6$] being higher than the HE of [Cu$_3$S$_3$(H$_2$O)$_6$] even though one Cu atom in the second complex has higher coordination. On the basis of the thermochemical data $\Delta E_o = 7.1$ kcal mol^{-1} for reaction 5 so it is much more plausible than reaction 2 proposed by Phillips and Kraus.[11] Hydration facilitates reaction 4 by 33.6 kcal mol^{-1} even though two Cu−S bonds in [Cu$_3$S$_3$-

$$[Cu_3S_3(H_2O)_6] + [Ag(H_2O)_4]^+ \rightleftharpoons$$
$$[Cu(H_2O)_4]^+ + [AgCu_2S_3(H_2O)_6] \quad (5)$$
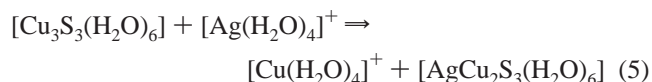
(H$_2$O)$_6$] are replaced by two weaker Ag−S bonds in AgCu$_2$S$_3$-(H$_2$O)$_6$. We used tetracoordinate [Cu(H$_2$O)$_4$]$^+$ and [Ag(H$_2$O)$_4$]$^+$ complexes, because, according to experiments results,[24,25] the first-shell coordination number of hydrated Cu$^+$ and Ag$^+$ is four. Other experiments[39] and calculations[15,40] with a limited number of water molecules in the gas phase demonstrated that the most stable Ag$^+$ and Cu$^+$ hydrates are two-coordinate complexes. If two-coordinate hydrates, [Cu(H$_2$O)$_2$(H$_2$O)$_2$]$^+$ and [Ag(H$_2$O)$_2$-

Cu(II) Displaced by Au(I) in Metal Sulfides

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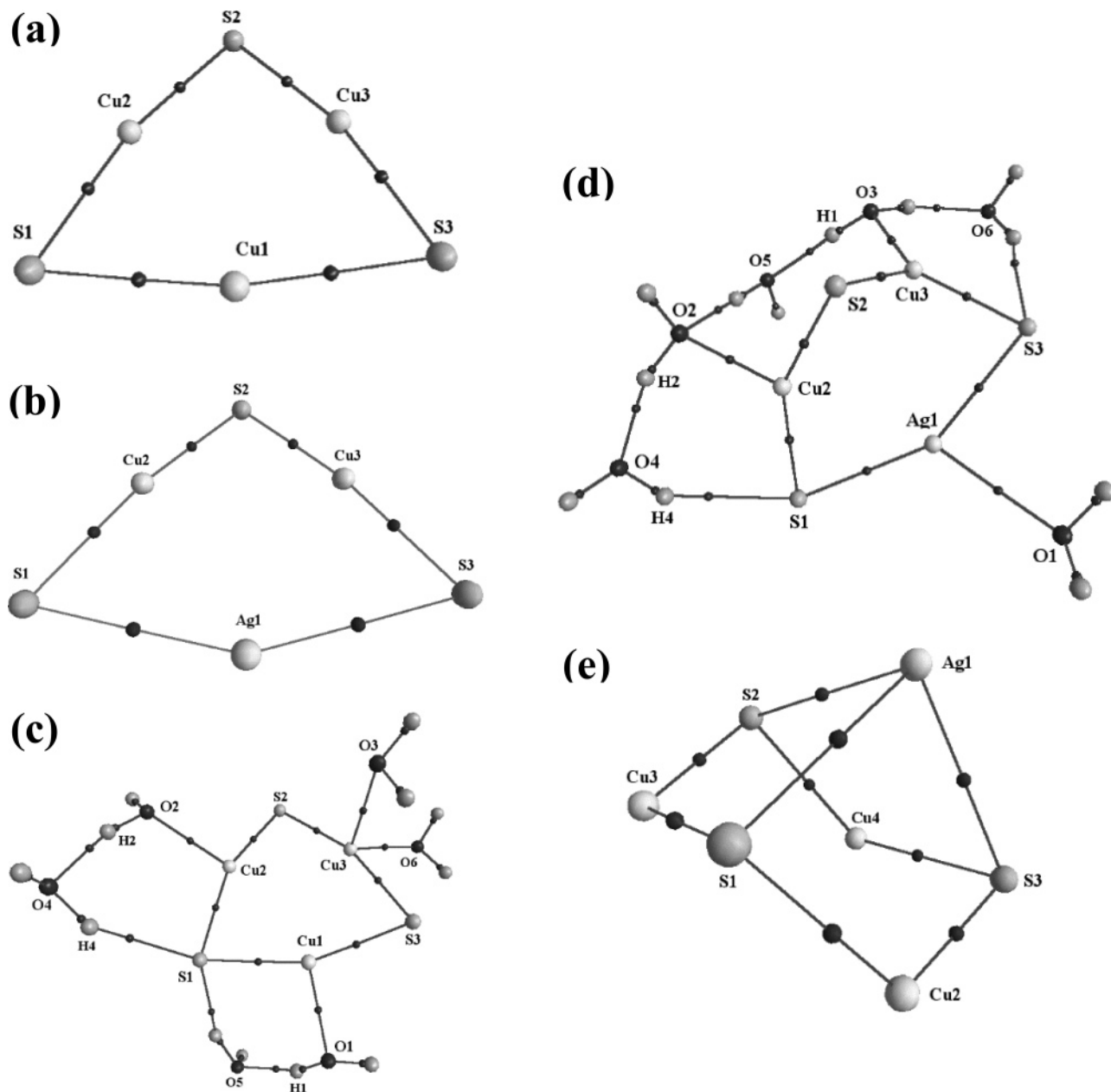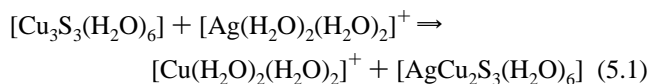**Figure 2.** Molecular graphs of (a) $(Cu^{II})_3S_3$ (the small black spheres are bond critical points), (b) $AgCu_2S_3$, (c) $[Cu(II)_3S_3(H_2O)_6]$, (d) $[AgCu_2S_3-(H_2O)_6][Cu(H_2O)_4]^{2+}$, and (e) $[AgCu_3S_3]^+$.

$(H_2O)_2]^+$, are used, reaction 5.1 holds. It is marginally exo-thermic with $\Delta E_{sf} = -1.1$ kcal mol^{-1}. We also embedded the hydrates (reaction 5.2) in the water solvent field. However, reaction 5.2 is endothermic with $\Delta E_{elec} = 24.8$ kcal mol^{-1}. The

$$[Cu_3S_3(H_2O)_6] + [Ag(H_2O)_2(H_2O)_2]^+ \Longrightarrow$$
$$[Cu(H_2O)_2(H_2O)_2]^+ + [AgCu_2S_3(H_2O)_6] \quad (5.1)$$
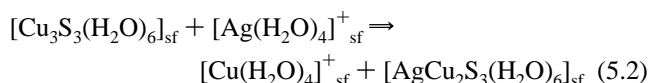
reason for this change is that while E_{sf} for $[Ag(H_2O)_4]^+$ and $[Cu(H_2O)_4]^+$ are almost equal (69.9 and 68.1 kcal mol^{-1}, respectively), the values for $[Cu_3S_3(H_2O)_6]$ and $[AgCu_2S_3-(H_2O)_6]$ differ by 15.9 kcal mol^{-1} (33.9 and 18.0 kcal mol^{-1}, respectively). When two-coordinate $[Ag(H_2O)_2(H_2O)_2]^+$ and $[Cu(H_2O)_2(H_2O)_2]^+$ were used (reaction 5.3), ΔE_{sf} became more

$$[Cu_3S_3(H_2O)_6]_{sf} + [Ag(H_2O)_4]^+_{sf} \Longrightarrow$$
$$[Cu(H_2O)_4]^+_{sf} + [AgCu_2S_3(H_2O)_6]_{sf} \quad (5.2)$$

exothermic (0.9 kcal mol^{-1}). It should be kept in mind that the

$$[Cu_3S_3(H_2O)_6]_{sf} + [Ag(H_2O)_2(H_2O)_2]^+_{sf} \Longrightarrow$$
$$[Cu(H_2O)_2(H_2O)_2]^+_{sf} + [AgCu_2S_3(H_2O)_6]_{sf} \quad (5.3)$$
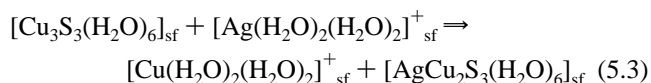
values of ΔE_{sf} obtained for reaction 5.2 and reaction 5.3 are not highly accurate.

We also considered a tricyclic species $[AgCu_3S_3]^+$ formed by the electrophilic addition of Ag$^+$ to $[Cu_3S_3]\bullet$ as a possible intermediate in reaction 4 but did not examine possible hydrates primarily because a calculation on a decahydrate $[AgCu_3S_3-(H_2O)_{10}]^+$ required in reaction 4 would be difficult. Nevertheless, tricyclic $[AgCu_3S_3]^+$ is a minimum on the PE surface, and its formation in the gas phase is highly exothermic ($\Delta E_0 = -36.0$ kcal mol^{-1}), indicating that it is a potential intermediate in reaction 4. Its molecular graph is displayed as Figure 2e. The Ag–S bond lengths range from 2.610 to 2.650 Å. On the basis of the values of $\rho(r_c)$, they are weaker than the Ag–S bonds of

AgCu$_2$S$_3$, where Ag is two-coordinate. It is the triple coordination to Ag that leads to deformation of planar Cu$_3$S$_3$ to its chairlike structure in [AgCu$_3$S$_3$]$^+$. The Cu−S bond distances differ little from the values found in Cu$_3$S$_3$. That Cu is two-coordinate and Ag is three-coordinate may facilitate the decomposition of [AgCu$_3$S$_3$]$^+$ to Cu$^+$ or Cu^{2+}.

Conclusions

The substitution of Cu^{2+} by Ag$^+$ in hydrated copper sulfides was modeled computationally by DFT, AIM, and solvent field methods. The first-shell structure, coordination and energy of hydration of Cu^{2+}, Ag$^+$, CuS, Cu$_3$S$_3$, and AgCu$_2$S$_3$ was obtained. The bonding of the solute with water molecules can be analyzed with QTAIM on the basis of the values of $\rho(\mathbf{r}_c)$ at BCPs. The Cu(I)−O and Cu(II)−O bonds in the first solvation shell of hydrates are substantially stronger than the Ag−O analogues. Consequently displacement of Cu^{2+} and Cu$^+$ from CuS and Cu$_3$S$_3$ by Ag$^+$, while unfavorable in the gas phase, is significantly facilitated in a polar solvent. The larger HE of Cu$^+$ compensates for the replacement Cu−S bonds by weaker Ag−S ones in solvated Cu$_3$S$_3$ clusters. The long-range electrostatic (polar) interactions with solvent are similar for hydrated Cu$^+$, Ag$^+$ and Cu$_3$S$_3$, AgCu$_2$S$_3$ and therefore are mutually compensating. For the substitution of Cu^{2+} in CuS, both first-shell and long-range electrostatic interactions of the metal with water are important. The long-range electrostatic (polar) effect of the solvent is more important for substitution of Cu^{2+} by Ag$^+$ than in the case of Cu$^+$

Two biological implications seem apparent from this study. First the similar stabilities of Cu−S and Ag−S complexes suggest that in nature one should expect to find multimetals as sulfide complexes, especially Group B metals such as Cu(I,II) and Ag(I). Other metals such as Hg(II), Pb(II), Cd(II), and Zn(II) may also be associated with sulfides, although we do not have corroborative data yet. Thus toxicological studies might include other Group B metals at appropriate concentrations when assessing the effects of one metal. Second Group B metals seem to be stable as relatively large molecules. This observation was made previously by Schwarzenbach and Widmer.[41] In this study convergence of our calculations and laboratory experiments suggest minimum-size molecules made up of three (Cu,Ag)−S units, but this minimum estimate is based upon the limit of our calculations so far. The seemingly large size of these complexes poses interesting considerations for trans-cellular and intercellular complexation, coordination, and transport.

Supporting Information Available: Table 3, giving uncorrected total energies of compounds at the B3PW91 level (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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