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Van der Waals Complexes of Cu, Ag, and Au with Hydrogen Sulfide. The Bonding Character

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The electronic and structural features of the Cu$\cdots$$SH_2$, Ag$\cdots$$SH_2$, and Au$\cdots$$SH_2$ complexes are investigated by using the spin-adapted restricted open-shell HF coupled cluster CCSD(T) method combined with the second-order spin-free Douglas−Kroll−Hess (DKH) relativistic approach. M$\cdots$$SH_2$ complexes are nonplanar with bonding energies −5.99, −1.99, and −9.08 mHartree, respectively. Comparison with analogous M$\cdots$$OH_2$ and M$\cdots$$NH_3$ complexes allows us to establish general features of the bonding between coinage metal atoms and ligand molecules with the participation of their lone electron pairs. Consistent interpretation of the interaction effects can be obtained by using the molecular orbital picture of the M$\cdots$L region. The bonding character is explained by stressing the importance of the charge transfer from the lone pair of the ligand to the metal atom. Relativistic changes of the metal element electron affinity and polarizability facilitate the understanding of major trends in the pattern of interactions between the coinage metal atoms and different lone pair donating ligands.

I. Introduction

Interactions between open-shell metals and closed-shell atoms[1−3] and molecules[4−8] lead to weak van der Waals complexes whose electronic and structural features reveal different aspects of the interaction mechanism. The study of such complexes is usually focused on the long-range part of the interaction potential and can be interpreted in terms of permanent multipole moments and polarizabilities of the interacting subsystems. The long-range models, however, have been found to be insufficient, *e.g.*, in the case of complexes involving coinage metal atoms and ligand molecules which contribute lone electron pairs.[8]

The failures of the long-range model have been discussed in the context of our earlier studies of the coinage metal (M) complexes with different ligands.[4,8] It has been pointed out that in the case of the M$\cdots$$NH_3$ and M$\cdots$$OH_2$ complexes[8] a consistent interpretation of the interaction effects can be obtained by assuming certain charge transfer from the lone pair carrier L to the coinage metal atom. This *partial* charge-transfer means that a molecular orbital picture needs to be used to interpret the trends in M$\cdots$L interactions in which the coinage metal atoms interact with selected ligands.

According to the classical molecular orbital interpretation of the charge redistribution in M$\cdots$L systems the transfer of the electronic charge to M will depend on the ionization potential (IP) of the lone pair electron in L and the electron affinity (EA) of M. The importance of these factors has been discussed in our earlier paper.[8] The molecular orbital picture requires also that there is certain overlap between the electron donor (lone pair) orbital of L and the electron acceptor (valence *n*s) orbital of M. This requirement makes the interaction pattern symmetry-dependent and is the main cause of the distinction between the geometric structure of the M$\cdots$$NH_3$ and M$\cdots$$OH_2$ complexes.[8]

In the axially symmetric M$\cdots$$NH_3$ system both the *n*s orbital of M and the lone pair orbital of NH_3 belong to the fully symmetric representation of the C_{3v} group, and this facilitates the formation of the bonding−antibonding pair of molecular orbitals of the M$\cdots$N region. Because the canonical lone pair orbital of the water molecule is essentially the 2pπ orbital of oxygen, this mechanism is absent in the case of the planar (axially symmetric) M$\cdots$$OH_2$ complex. Thus, to obtain a nonzero *n*s−2pπ overlap requires some out-of-plane deformation. This simultaneously diminishes the role of induction interactions, which favor the planar structure. Hence, depending on the magnitude of the induction (and dispersion) interactions and the relation between the lone pair ionization potential of the planar ligand L and the electron affinity of M, the complex will be either planar or nonplanar. In the former case its structure and energetics will be determined primarily by induction and dispersion forces with essentially no charge transfer. For low enough IP of the lone pair donor and/or high enough EA of M the “molecular” picture will prevail and leads to nonplanar M$\cdots$L complexes.

In the present paper the validity of this interpretation of the origin of the nonplanarity in interactions between coinage metal atoms and planar ligands will be analyzed in terms of the computed structural and energy data for M$\cdots$$SH_2$ complexes. On comparing the electron donating ability of the hydrogen sulfide with the isovalent H_2O molecule, one can expect that certain structural features of the M$\cdots$$OH_2$ complexes should be

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further enhanced in M···SH_2 interactions. One should note that the first (lone pair) IP of H_2S[9] is 2.14 eV lower than that of H_2O.[10] This should facilitate the partial charge transfer toward the coinage metal atom.

The bonding−antibonding orbitals of the M···S region will be mostly due to the overlap of the 3pπ lone pair orbital of sulfur and the valence *n*s orbital of the metal atom. Thus, one expects that the M···SH_2 systems should exhibit stronger nonplanarity than the corresponding M···OH_2 complexes. The relativistic increase of the electron affinity in the Cu, Ag, Au series should also enhance the weak M···L bonding. The consequences of the fact that the lone pair IPs of NH_3 and SH_2 are close to each other and by about 2 eV lower than the IP of H_2O should be also manifested in energetics of their M···L complexes. Once the importance of the charge-transfer bonding mechanism in M···L is accepted,[8] the interaction pattern for M···SH_2 and M···NH_3 complexes should be similar and simultaneously quite different from that for M···OH_2 complexes.

The electronic and structural features of the M···SH_2 complexes are investigated in this paper by using high-level-correlated methods of the electronic structure theory in both relativistic and nonrelativistic approximations. The present results will be compared with those obtained earlier[8] for M···OH_2 and M···NH_3 systems. The main goal of this study is the understanding of the origin of the weak bonding between coinage metal atoms and ligand molecules with the participation of their lone electron pairs. However, one should mention the related interest which follows from spectroscopy of weak M···L van der Waals complexes.[6,11−13] Additionally, the understanding of the mechanism of the M···S interaction may also prove useful in devising new routes to the synthesis of self-assembling monolayers.[14] Not surprisingly the coinage metal interactions with various ligands attract a great deal of attention among both experimentalists and theoreticians.[6,11−13,15−20]

II. Methods and Computations

All calculations for M···SH_2 complexes reported in this paper have been carried out at the level of the coupled cluster (CC) approximation with the restricted open-shell Hartree−Fock (ROHF) reference function.[21] The contribution of all single and double excitations (CCSD) is evaluated iteratively and the noniterative correction due to triple excitation terms (CCSD(T)) is added perturbatively. The ROHF CCSD(T) method[22,23] employed in the present study uses only a partial spin adaptation. However, this computationally less demanding approach has been found to give satisfactory agreement of the corresponding CCSD energies with those calculated by fully spin-adapted method.[24] In all calculations the number of electrons explicitly correlated at the level of the CCSD(T) approximation is equal 25 with 8 of them corresponding to the valence shell of H_2S. The other 17 electrons refer to the valence (*n*s) and subvalence ($(n-1)p^6(n-1)d^{10}$) shells of M.

The present study follows to a large extent the methodology of our earlier investigations of M···OH_2 and M···NH_3 complexes.[4,8] However, in the present ROHF CCSD(T) calculations the energy denominators have been expressed in terms of orbital energies rather than in terms of the corresponding diagonal elements of the Fock matrix.[22,23] This difference only negligibly affects the calculated interaction energies and comparisons between the earlier and present results are essentially independent of this change.

The metal atoms in the studied complexes are heavy enough to make the relativistic effects important for the evaluation of interaction energies. The relativistic contribution has been included by using the scalar second-order Douglas−Kroll−Hess (DKH) formalism.[25,26] Most of the important features of the studied complexes follow from interactions between the *n*s electron of M and valence electrons of H_2S. Hence, they should be primarily sensitive to the scalar relativistic shrinkage of the *n*s orbital of the metal atom. The role of the spin−orbit (SO) coupling is uncertain and can be revealed only by the corresponding four-component Dirac−Fock CCSD(T) studies in which both the SO splitting of *n*d orbitals and the electron correlation effects are taken into account. The *a posteriori* treatment of the SO contribution,[27] which does not modify the orbitals obtained in the scalar approximation, suggests that the doublet ground state will be SO-coupled to quartet states of the system. These, however, lie high enough to make their contribution of secondary importance.

The basis sets used in the present calculations are the PolX (for nonrelativistic calculations) and PolX_dk (for relativistic DKH calculations) contracted Gaussian type orbitals (CGTO).[28,29] The GTO/CGTO basis set size for the H and the S atom, respectively, is [6s4p/3s2p] and [13s10p4d/7s5p2d]. The basis sets for Cu, Ag, and Au atoms are [16s12p6d4f/9s7p3d2f], [19s15p9d4f/11s9p5d2f], and [21s17p11d9f/13s11p7d4f], respectively. All these basis sets are available on our web page, http://bradlo.fns.uniba.sk/. These basis sets have been designed for calculations of basic molecular electric properties and are also suitable for the calculation of interaction energies. Obviously, the accuracy of the absolute values of the interaction energy may be affected by the relatively small size of PolX basis sets. However, this does not influence the pattern of the relative interaction energy data for a series of similar systems.

The DKH interaction energies, optimized M···S distances and the out-of-plane angles of the M···SH_2 complexes obtained with PolX_dk sets have been checked against the DKH values computed with larger and more flexible HyPolX_dk basis sets.[29] All interaction energy data presented in this paper are corrected for the basis set superposition contribution (BSSE) by using the usual counterpoise correction.[30]

Because the interaction between metal atoms and H_2S is very week, its geometry has been assumed to be frozen in all calculations. The experimental values[31] of the S−H bond distance ($r_{SH} = 2.523919$ au) and the bond angle ($\angle$H−S−H $= 92.12°$) are assumed for all studied complexes. Under the assumption of the fixed geometry of H_2S one is left with three geometry parameters that characterize the structure of the complex. These can be chosen as the M···S distance (R), the in-plane angle ϕ between the M···S direction and the C_2 symmetry axis of H_2S, and the out-of-plane angle θ between the M···S direction and the plane of the molecule. The sampling of ϕ and θ has indicated that all minimum energy structures correspond to the out-of-plane ($\theta \neq 0°$) deformation, which preserves the C_s symmetry of the complex. Hence, the final optimization of the complex geometry could have been limited to only two parameters, R and θ. The planar complex structure with M facing the sulfur atom corresponds to $\theta = 0°$ whereas the $\theta = 180°$ geometry features the interaction of M oriented toward hydrogens of H_2S.

All results reported in this paper have been calculated by using computer codes of the Molcas 6.0 suite of quantum chemistry programs.[32] The ROHF CCSD(T) code of the Bratislava Group[22,23] is a part of this software.

III. Results and Discussion

A. Structure and Interaction Energies. The main results of this study, as summarized in Table 1, include the interaction

TABLE 1: Interaction Energies (ΔE, in mhartrees) and Optimized Structure Parameters (R_e in au, θ_e in Degrees) of the M···SH_2 Complexes (Nonrelativistic (NR) and Relativistic (DKH) Results with BSSE Correction)

	Cu···SH_2		Ag···SH_2		Au···SH_2	
	NR	DKH	NR	DKH	NR	DKH
			Fully Optimized Structures			
ΔE	−4.526	−5.985 (−8.461)	−1.533	−1.991 (−3.413)	−1.404	−9.075 (−13.376)
R_e	4.76	4.60 (4.50)	6.30	5.90 (5.58)	6.72	4.87 (4.74)
θ_e	81.8°	79.9°	91.0°	89.7°	93.3°	81.1°
			Planar Structures ($\theta = 0°$)[b]			
ΔE		−0.55		−0.64		−0.87
R_e		7.3		7.7		7.2
			Planar Structures ($\theta = 180°$)[b]			
ΔE		−0.74		−0.84		−1.11
R_e		8.0		8.2		7.2

[a] The numbers in parentheses correspond to DKH calculations with the HyPolX_dk basis sets.[29] [b] See section II.

energies and structural data computed in different approximations. These numbers are supplemented in Figures 1−3 by a series of graphical data. Plots in Figure 1 show the R-dependence of the Cu···SH_2 complex energy at the value of the out-of-plane angle, $\theta_e = 79.3°$, which is close to different optimized values given in Table 1. Potential energy curves for Ag···SH_2 and Au···SH_2 are analogous.

The validity of our assumption of the frozen SH_2 geometry in the complex was verified by considering as an example the strongest Au···SH_2 complex. At the optimized Au···S distance and the out-of-plane angle, θ_e, we have reoptimized the HSH bond angle and the SH bond distance in the SH_2 ligand. The resulting values, 92.0° and 2.586 bohr, respectively, do not differ significantly from the frozen H_2S experimental geometry (92.12° and 2.524 bohr, respectively). Such a change can hardly affect any essential features of the bonding parameters of our complexes. Moreover, our aim was to study the trends within the series of different ligands interacting with the metal atom by their lone pair rather than obtaining very accurate interaction energies. Because the ligands considered in our earlier calculations of M···L complexes[8] were also frozen at their respective experimental geometries the present study follows the same assumption.

Figure 1 demonstrates the importance of the BSSE corrections in DKH calculations with PolX_dk basis sets at the level of the ROHF, ROHF/CCSD, and ROHF/CCSD(T) approximations. These results show that all ROHF curves are essentially repulsive with very small attractive (induction) contribution in the long-range region. Hence, one concludes that a simple model based on dipole−induced-dipole interactions cannot account for the binding of the coinage metal atoms to the sulfur atom of H_2S. The importance of the electron correlation effects including triple excitations is clearly visible from Figure 1. The plots in Figures 2 and 3 illustrate the relativistic effect on the structure and energetics of all investigated complexes.

It can be seen from the data of Table 1 and Figure 2 that for all studied complexes the energy minimum is obtained at the cost of the out-of-plane deformation. This structural feature of the M···SH_2 complexes arises in both nonrelativistic and relativistic DKH calculations. Moreover, for all these complexes, at least at the relativistic DKH level, the energy minimum occurs on the sulfur side of the H_2S molecule. This suggests that the directional features of the interaction are mostly due to the shape of the electron density distribution in the H_2S molecule.

For Cu and Ag complexes the relativistic treatment within the scalar DKH approximation does not lead to major differences in interaction energy. Upon including the scalar relativistic effects, the value of the interaction energy ΔE becomes more negative. However, the magnitude of the relativistic effect remains small with respect to the basis set truncation effects which are exemplified by the comparison of the interaction energy values obtained with PolX_dk and HyPolX_dk basis sets. The relativistic effects in Cu and Ag complexes lead also to the shortening of the corresponding M···S distances whereas the value of θ_e remains almost unchanged.

For the "most relativistic" system, the Au···SH_2 complex, the relativistic effects become the major factor which determines the interaction energy. On passing from the nonrelativistic to the relativistic approximation the interaction energy changes by almost an order of magnitude and makes this complex well bound. The calculated energy minimum is further lowered by using the HyPolX_dk basis set. These interaction energy changes in Au···SH_2 are accompanied by the very large relativistic effect on the Au···S distance. Compared to the nonrelativistic result its value is reduced by about 2 au in relativistic DKH calculations. Even in Au···SH_2 the equilibrium angle θ_e appears to be essentially insensitive to the relativistic treatment. One can see, however, that neglecting the relativistic effects leads to a very flat potential energy curve with respect to the out-of-plane angle θ. Consequently, in the nonrelativistic (NR) case the curves for Ag···SH_2 and Au···SH_2 complexes are almost overlapping each other (see Figure 2). Although the calculated relativistic and nonrelativistic equilibrium values of θ are very similar, the depth of the minimum is significantly affected by relativistic effects. Clearly, the large relativistic enhancement of the Au electron affinity supports the charge transfer from the lone pair of SH_2 to Au and this leads to much deeper minimum of ΔE with respect to the angle θ.

Surprisingly enough, the interaction energy value obtained for Ag···SH_2 is less negative than that for Cu···SH_2. Invoking the change in the induction and dispersion contributions to the interaction energy would not help because the DKH CCSD(T) polarizabilities of Cu (46.5 au) and Ag (52.5 au) are almost the same.[33] Moreover, the very negative relativistic value of ΔE for Au···SH_2 would clearly contradict the interpretation based on induction and dispersion forces because the DKH CCSD(T) polarizability of Au is much smaller (36.1 au[33]) than those of Cu and Ag. Furthermore, for all planar structures with the metal atom facing the sulfur side of SH_2 ($\theta = 0°$, C_{2v} symmetry), the binding energy is very small and of almost the same magnitude for all M···SH_2 complexes (see Table 1). The same applies to structures of C_{2v} symmetry at $\theta = 180°$. A little is gained by the (bifurcated) M···H_2 interaction, though some traces of the bonding of hydrogens to the metal atom are obviously present.[4]

The structural data for the studied complexes and in particular for their out-of-plane equilibrium configurations definitely show that the increase of their stability upon the out-of-plane bending does not arise from polarization forces. There must be another mechanism that leads to differences in the M···SH_2 interaction in the investigated complexes. The possibility of the complex stabilization due to a partial charge transfer from the ligand molecule to M has been discussed in our earlier papers.[4,8] We shall return to this point in section IIIC.

Another set of plots showing the R-dependence of nonrelativistic and DKH potential energy curves at the optimized out-of-plane angle θ_e is presented in Figure 3. One finds that both the interaction energies and minima of these curves are considerably influenced by the relativistic treatment. Already

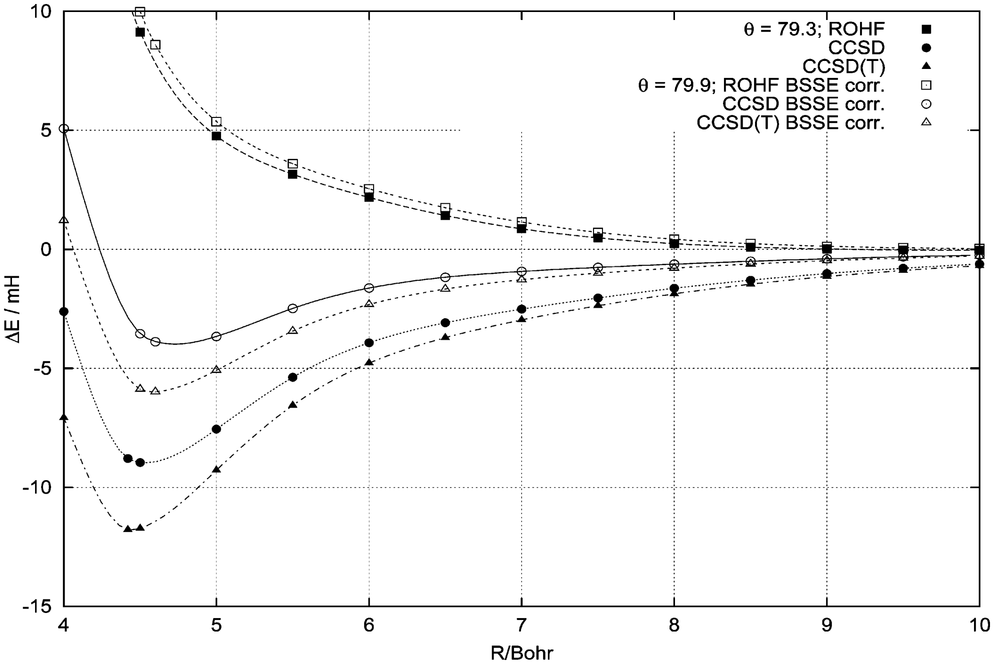

Figure 1. Plain (uncorrected) and BSSE corrected ROHF, CCSD, and CCSD(T) interaction energies for Cu···SH_2 complexes as a function of the Cu···S distance, *R*, at the optimized value of the out-of-plane angle *θ*. See Table 1 and text. DKH relativistic energies using the PolX_dk basis sets.

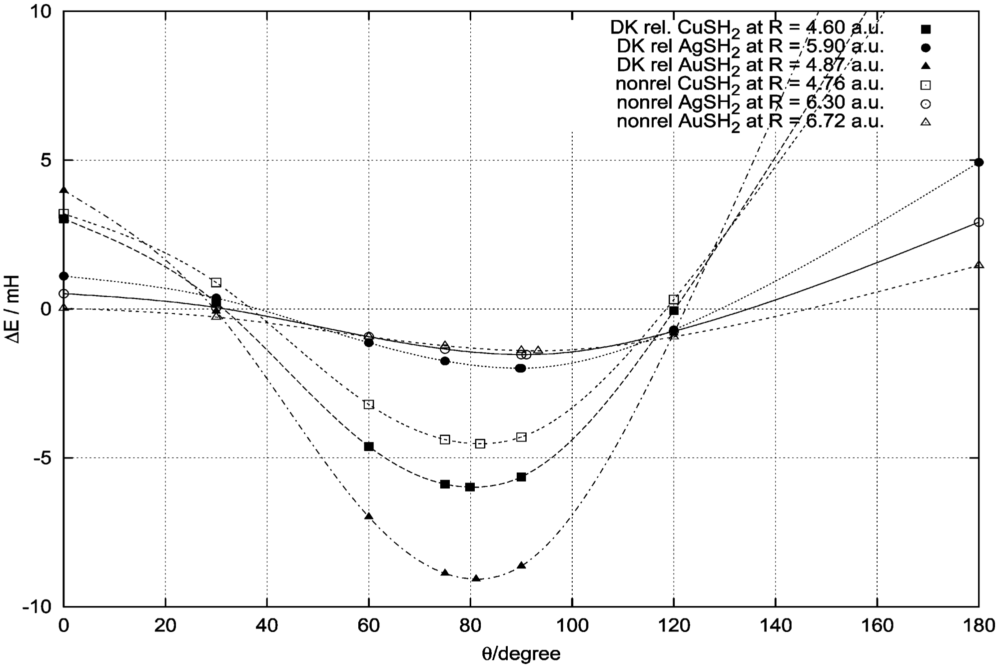

Figure 2. Nonrelativistic (open symbols) and DKH relativistic (full symbols) BSSE-corrected CCSD(T) interaction energies for M···SH_2 complexes as a function of the out-of-plane angle *θ* at optimized M···S distances. See Table 1 and text.

for the lightest and the “least relativistic” system, Cu···SH_2, this difference is quite visible and considerably increases with the nuclear charge of a heavy atom.

The present data show that for all M···SH_2 complexes the energy minima correspond to nonplanar structures and this finding is almost independent of the relativistic effects. Simultaneously, the depth of the energy minima significantly depends on the relativistic treatment of the complex. Although the relativistic effect should increase with the nuclear charge of the metal atom, no such regularity is observed among the computed interaction energies. The explanation of this finding will be attempted in terms of a simple molecular orbital picture, which assumes that a weak polarized bond is formed between M and sulfur.

B. Origin of Nonplanarity in M···SH_2 Complexes. A hint that the M···SH_2 complexes may feature some bonding between M and sulfur comes from the out-of-plane minimum energy structure. The sole induction terms would favor a linear configuration. Because the dipole polarizability tensor of the H_2S molecule is almost isotropic,[28] the small anisotropy of the dispersion contribution would not help as well. Both these long-range models would predict the decrease of the interaction energy on passing from Cu and Ag to Au. Also the relativistic increase of the M···SH_2 interaction energy (Table 1) does not

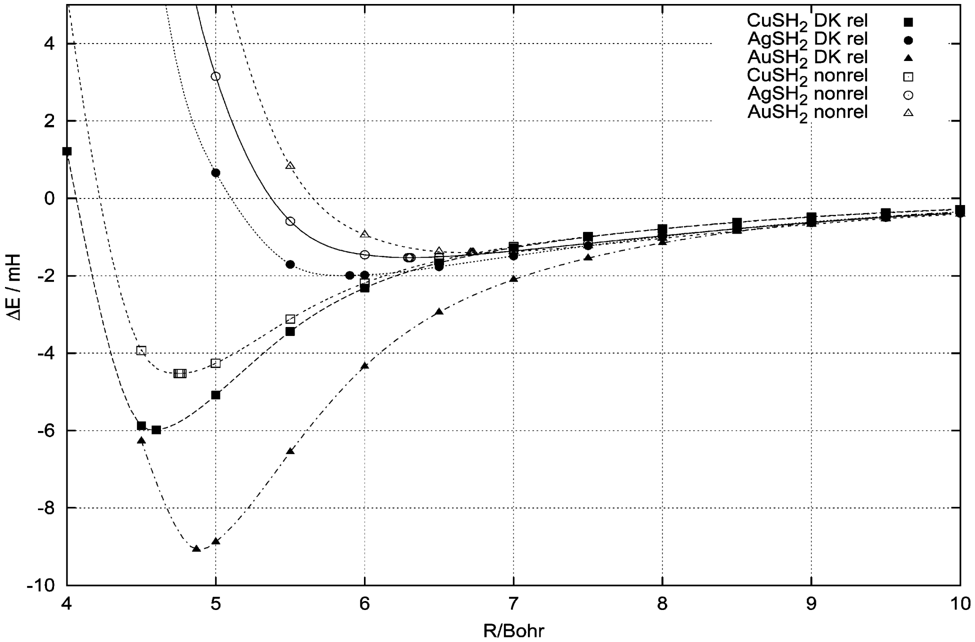

Figure 3. Nonrelativistic (open symbols) and DKH relativistic BSSE-corrected CCSD(T) potential energy curves for M···SH$_2$ complexes and the optimized values of the out-of-plane angle θ. See Table 1 and text.

parallel the relativistic effects on the dipole polarizabilities of M.[33]

A plausible explanation of the structural and energetic features of the studied complexes may follow from a simple molecular orbital picture of the M···SH$_2$ interaction. The highest occupied molecular orbital of H$_2$S represents the 3pπ lone pair localized almost solely on the sulfur atom. To form the bonding−antibonding (σ, σ^*) pair of orbitals of the M···S region, one needs to move the metal atom out of the plane of the molecule. Once the M atom is moved out of the plane of the molecule, the overlap between the *n*s(M) and the 3pπ orbital of H$_2$S becomes important. Otherwise, the only symmetry allowed valence molecular orbital of M···SH$_2$ will be that produced by a linear combination of the *n*s orbital of M and the a$_1$ orbital of H$_2$S. However, the latter is composed mainly of the 3s atomic orbital on S. Its energy (−0.5020 au, PolX_dk SCF HF calculations) is more than 0.1 au lower than that of the 3pπ (b$_2$) orbital. The large energy gap between between the a$_1$ orbital of H$_2$S and the *n*s orbital on M prohibits any significant mixing of these orbitals. Hence, the nonplanarity of the M···SH$_2$ complexes can be elucidated in terms of molecular orbitals of the M···S region that involve the 3pπ orbital on S and the *n*s orbital on M. This, however, requires the out-of-plane bending. If valid, the same model should also lead to the explanation of the relativistic increase of the interaction energy in Au···SH$_2$ and much smaller difference between the respective Cu and Ag complexes.

The nonplanarity of the valence isoelectronic M···OH$_2$ was analyzed in our earlier paper.[8] A distinctive directional (covalent) character related to structural characteristics of the thiolate sulfur−gold bond was discussed by Kröger *et al.*[19] We note that the bonding character in these compounds is related to but not identical with that discussed for complexes treated in this paper. One should also stress that the structure of metal hydrates constitutes a long-standing topic in coordination chemistry.[34] Not only neutral complexes but also the ionic monohydrates are known to be nonplanar.[35,36] The nonplanar structure of the Au···OH$_2^+$ complex is attributed to the partly covalent character of the C_s complex and the rehybridization of the ligand orbitals. Similar reasoning underlies also the recent studies by Gourlaouen *et al.*[37] and Lee *et al.*[38]

C. Trends in Bonding Energies in M···SH$_2$ Complexes. Comparison with M···OH$_2$ and M···NH$_3$ Complexes.. The mixing of *n*s (M) and 3pπ orbitals in nonplanar structures depends on their relative energies. Because the lone pair 3pπ orbital of H$_2$S is essentially doubly occupied, the driving force for the efficient formation of the molecular orbital of the M···S region will be characterized by the electron affinity of M. The nonrelativistic EA values for Cu, Ag, and Au, read 1.165, 1.054, and 1.161 eV, respectively.[33] The relativistic DKH CCSD(T) results,[33] 1.236, 1.254, and 2.229 eV, respectively, agree reasonably well with the corresponding experimental data (1.226, 1.303, and 2.309 eV, for Cu, Ag, and Au, respectively[39]).

The nonrelativistic EA data predict that the formation of molecular orbitals in the M···S region should be similar for all metal atoms. Hence, the sole charge transfer between the 3pπ lone pair would not explain why the *nonrelativistic* Cu···SH$_2$ interaction is much stronger than in the two other M···SH$_2$ complexes. This appears to be related to the “effective” size of the corresponding metal atoms, *i.e.*, to the interplay between the possible charge transfer from H$_2$S to M and the magnitude of the valence repulsion. In the nonrelativistic approximation the average radius of the 4s orbital of Cu is much smaller than the *n*s radii of Ag and Au. This permits a closer approach of Cu to S and increases the overlap between 4s and 3pπ orbitals. In the nonrelativistic treatment, the increase of the effective radius of *n*s orbitals in Ag and Au only weakens their interaction with sulfur.

It is also worthwhile to note that in the nonrelativistic approximation the changes of interaction energies on passing from Cu to Ag and to Au are quite smooth and do not show particular irregularities (see Table 1). Actually, this holds not only for M···SH$_2$ complexes; as shown by the data of Table 2, both M···OH$_2$ and M···NH$_3$ systems behave in a similar way. A considerably different pattern of the interaction energy changes in the M···L series is found upon including relativistic effects. Then, the absolute value of the interaction energy goes through a minimum of ΔE for Ag···SH$_2$ and Ag···NH$_3$ complexes whereas for the M···OH$_2$ series the ΔE values for Ag···OH$_2$ and Au···OH$_2$ are almost the same. They are both approximately one-half of the ΔE value calculated for Cu···

TABLE 2: Comparison of CCSD(T) DK Relativistic and Nonrelativistic Interaction Energies of M⋯SH_2 Complexes with M⋯NH_3 and M⋯OH_2 Complexes[a]

complex	ΔE_{DKH}	ΔE_{NR}	Δ_{rel}[b]	structure[c]
		$IP(NH_3) = 10.2$ eV[e]		
Cu⋯NH_3	-16.684^{d}	-14.86^{d}	−1.824	L
Ag⋯NH_3	-6.869^{d}	-6.52^{d}	−0.349	L
Au⋯NH_3	-14.642^{d}	-5.23^{d}	−9.412	L
		$IP(H_2O) = 12.6$ eV[e]		
Cu⋯OH_2	-3.784^{d}	-3.79^{d}	0.006	B
Ag⋯OH_2	-1.808^{d}	-2.13^{d}	0.322	B
Au⋯OH_2	-1.765^{d}	-1.62^{d}	−0.145	B
		$IP(H_2S) = 10.5$ eV[f]		
Cu⋯SH_2	−5.985	−4.53	−1.459	P
Ag⋯SH_2	−1.991	−1.53	−0.458	P
Au⋯SH_2	−9.075	−1.40	−7.671	P

[a] All energies (in mhartrees) are BSSE corrected. PolX_dk and PolX basis sets are used for DKH and nonrelativistic calculations, respectively. [b] Relativistic contribution to the interaction energy $\Delta_{rel} = \Delta E(\mathrm{DKH}) - \Delta E(\mathrm{NR})$. [c] Qualitative description of the main structural features. L means a linear complex, B corresponds to the bent out-of-plane structure with the θ angle far from $\pi/2$, and P stands for (almost) perpendicular structure of C_s symmetry. [d] Reference 8. [e] Reference 10. [f] Reference 9.

OH_2. As follows from the data of Table 1, not too much of the relativistic effect is seen in the case of the Cu⋯SH_2 complex. For Ag there is some relativistic increase of its EA value and the relativistic shrinkage of the 5s valence orbital. However, as indicated by the dipole polarizability data,[33] the latter effect is quite small. In consequence, the relativistic increase of the interaction energy between Ag and H_2S is small as well. Both the relativistic shrinkage of the 6s valence orbital and the relativistic increase of EA are significantly larger for Au, and both work in the same way by reducing the valence repulsion and simultaneously increasing the contribution of the 6s orbital to the molecular orbital of the Au⋯S region. Hence, the charge transfer between the two moieties of the complex will considerably increase. This makes Au⋯SH_2 into the most stable complex in the studied M⋯SH_2 series in spite of the lowest value of the dipole polarizability of Au as compared to the polarizabilities of Cu or Ag. The predicted interaction energy strongly depends on the relativistic treatment.

Obviously, the molecular orbital picture of interactions in M⋯SH_2 complexes is highly qualitative and may not fully reveal all details of their electronic structure. This interpretation does not exclude certain importance of polarization forces that depend on polarizabilities of M and dipole moment of the ligand molecule. On combining all these interactions one obtains a consistent interpretation of the computed nonrelativistic and relativistic data.

IV. Summary and Conclusions

For better understanding of the structural features and interaction energies in M⋯L complexes with ligands that contribute a lone pair, it is worthwhile to compile the earlier data[8] for M⋯OH_2 and M⋯NH_3 and compare them with those calculated in the present study. This comparison is presented in Table 2. Of particular attention and importance are the contributions due to relativistic effects that are presented in the fourth column of Table 2. The structural features of these complexes are indicated in the last column of this table and confirm the interpretation forwarded in section IIIB.

Upon analyzing the interaction energies one can immediately recognize two distinct groups of complexes; the magnitude of the interaction energy is directly related to the ionization potential of the lone pair orbital of a ligand. An essential supporting argument for the charge-transfer contribution to the character of bonding in M⋯L complexes is given by the consideration of relativistic effects. The increase of the interaction energy primarily arises from the relativistic stabilization (shrinkage) of the valence *n*s orbital and relativistic increase of EA of the metal atom.

At the DKH relativistic level of approximation all M⋯NH_3 and M⋯SH_2 complexes, *i.e.*, the systems that belong to the mentioned first group of complexes, exhibit much stronger bonds than the corresponding complexes with water (the second group of complexes). Relativistic effects are similar for M⋯SH_2 and M⋯NH_3. They enhance the bonding. This pattern is different from that observed for M⋯OH_2 complexes. For Cu⋯OH_2 and Ag⋯OH_2 complexes one finds that relativistic contribution to the interaction energy may even have its sign opposite to that obtained for interactions of M with H_2S and NH_3. For all Au complexes the relativistic contribution to the interaction energy is negative; *i.e.*, it increases the strength of the M⋯L bond. However, for Au⋯OH_2 its value is almost 2 orders of magnitude smaller than that for Au⋯SH_2 and Au⋯NH_3.

Intuitively, one would rather expect that M⋯L complexes with H_2S and H_2O as a ligand should exhibit similar behavior. On the contrary, in terms of the interaction energy there is far more similarity between M⋯SH_2 and M⋯NH_3 complexes. Positive relativistic contributions to ΔE of Cu⋯OH_2 and Ag⋯OH_2 complexes are mainly connected with the relativistic decrease of the M polarizability. The charge-transfer mechanism is hindered by large IP of H_2O as a ligand.

The axial structure of M⋯NH_3 complexes is interpreted in terms of the overlap between the valence *n*s orbital of M with the lone pair orbital of NH_3. This favors the linear character of the weak bond formed between M and NH_3 and encourages the partial charge transfer toward the M atom. The relativistic effect in Au⋯NH_3 enhances the metal−ligand interaction. The polarization forces also favor the axial structure. Therefore complexes with NH_3 as a ligand are the most stable out of all M⋯L complexes reviewed in Table 2.

For the water complexes the symmetry arguments tell that they should be bent with the metal atom above or below the plane of the ligand molecule. For water complexes the potential energy curves with respect to the θ angle are also quite flat. The energy minima for M⋯SH_2 complexes are relatively deep. The role of polarization forces looks to be more important in water complexes because of the large dipole moment of H_2O (0.72 au). In addition, the ionization potential of H_2O is much higher than that of H_2S, thus suppressing the charge transfer from the lone pair of H_2O to M. Both these factors lead to the values of θ intermediate between 0 and 90°.

For the H_2S molecule the lower value (0.39 au[28]) of its dipole moment reduces the role of the polarization interaction. Simultaneously, the decrease of the ionization potential of H_2S favors the partial charge transfer to the *n*s orbital of the metal atom. The maximum of the overlap between the relevant orbitals leads to the dominance of “perpendicular” structures.

The interplay between polarization forces and partial charge transfer from the lone pair of the ligand molecule to the *n*s valence orbital of M provides a uniform interpretation of the present and earlier data and explains some irregularities in the relativistic effect on interaction energies and structure of the investigated systems. A similar interpretation can also be forwarded to explain the bonding and structure of complexes between ligands and heavy metal cations.[34−38]

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