Theoretical Study of the Hg^{2+} Recognition by 1,3-Diphenyl-Thiourea

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We have studied the electronic and structural properties responsible for the molecular recognition that the 1,3-diphenyl-thiourea ionophore (L) experiences by the Hg^{2+} cation. The theoretical data was obtained for the bare L and for the $[L-HgOH]^+$ and $[L-Hg-L]^{2+}$ coordination compounds involved in the reaction mechanism in reported sensors. Calculations were performed with the Gaussian-98 program at the B3LYP/6-31G** level. A LANL2DZ pseudopotential was used for Hg. The calculated electrostatic potential of the ionophore has a maximum on the S atom and, with less intensity, on the Z-phenyl group; consistently, high negative charges occur on those sites. The two highest occupied molecular orbitals are also mainly located on the sulfur-Z-phenyl atoms. Thus, this region defines the active site. These results account for the softness of the S atom that is bonded to Hg^{2+} in the complexes. The metal−sulfur interaction is key in the observed selectivity of Hg^{2+} by L. However, a significant Z-phenyl-Hg^{2+} bonding was also found. This rather unexpected result suggests that Z-phenyl is crucial in the recognition of Hg^{2+}. In fact, in $[L-Hg-L]^{2+}$, two S atoms and two Z-phenyl groups carry the Hg^{2+} ion.

1. Introduction

Every day, significant amounts of heavy metal ions, such as Pb^{2+}, Cd^{2+}, and Hg^{2+}, are emitted into the environment as a result of human activities ranging from large industrial enterprises up to home activities. The release of these pollutant ions leads to a chemically complex environment whose characterization needs to be determined quantitatively to know its effects. In fact, the presence of these ions, even at trace levels, may be critical for human life, because most of them are toxic or poisonous elements. For instance, mercury is one of the most toxic of the metals, producing serious irreversible neurological damage.[1] A quantitative determination of the concentration of those species implies the design of devices able to detect them in a highly sensitive and selective way. For instance, this is currently achieved through the use of ion selective electrodes (ISE) showing a high selectivity for a given metallic cation, which usually is present in natural complex samples. Carrier-based ISE are well-established analytical tools that are used routinely to on line-measure, in real time, the in situ concentration in a wide variety of different ions in complex samples. These types of devices are commonly applied in the monitoring of environmental pollution and in the control of several chemical processes.[2−5]

The ISE membrane contains a compound, the ionophore or ion carrier, which is able to recognize the target ion. The recognition depends, ultimately, on the nature of the chemical bond that is formed between the ionophore and the metallic ion. However, little is known about the bonding originated from the interaction of heavy metal ions with ionophores. As it was mentioned, the key feature of the sensitive sensor membrane is the incorporated carrier, which recognizes the target ion with an appropriate sensitivity and selectivity, giving an adequate electrochemical response. In the past years, various research groups have synthesized a large variety of neutral selective carriers for cations.[3] The selectivity behavior of the carrier to the analyzed ion has been explained on the molecular recognition basis.[6−12] Within this framework, several ideas and models have been proposed to understand the mechanism of the membrane response.[2−7] It depends on several electrochemical and interface equilibria, which are influenced by the easiness of formation of the ionophore-ion adduction as well as on the transport through the membrane. However, at molecular level, the mechanism by which the recognition of the metallic ion by the ionophore is carried out is not yet completely known.

Some of us have reported thiourea derivatives as ionophores for heavy metal ISE.[13−18] In particular, we succeeded in the design of a high performance Hg^{2+} ISE,[16,17] which is reliable at two pH values, 7 and 4, with the required time life and high selectivity and sensitivity. This ISE showed a different calibration slope value for each pH: for the pH 7, it recognizes the $[Hg(OH)]^+$ cation with a monovalent ion calibration slope, whereas at pH 4, it recognizes the Hg^{2+} cation. The used ionophore in the membrane was the well-known and cheap 1,3-diphenylthiourea (L). It was found that, because this thiourea derivative is a less reactive ionophore, it yields a high selective sensor. Other derivatives such as 1-furoyl-3-phenylthiourea, 1-furoyl-3-bencyl-3-phenylthiourea, and 1-furoyl-3-hydroxyethylthiorea were found to be highly reactive toward all soft cations; they are not really selective, due to their high reactiv-

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TABLE 1: Bond Lengths, in Å, for the Optimized Structures of L, $[L-Hg]^{2+}$, $[L-HgOH]^{+}$, and $[L-Hg-L']^{2+}$ [a]

bond	L exp[b]	L calc	$[L\text{-}Hg]^{2+}$	$[L\text{-}Hg-OH]^{+}$	$[L\text{-}Hg\text{-}L']^{2+c}$	$[L\text{-}Hg\text{-}L']^{2+d}$
C1−N7	1.434	1.416	1.420	1.443	1.450	1.447
N7−C8	1.336	1.380	1.343	1.342	1.335	1.336
H17−N7	0.860	1.011	1.018	1.013	1.015	1.014
C8−S10	1.681	1.681	1.752	1.746	1.753	1.751
C8−N9	1.349	1.364	1.344	1.341	1.342	1.342
H18−N9	0.860	1.014	1.018	1.018	1.019	1.019
N9−C11	1.436	1.415	1.440	1.436	1.434	1.433
S10−Hg			2.630	2.550	2.553	2.553
Hg−O				2.075		
Hg−S10′					2.535	2.554
S10′−C8′					1.680	1.751
N7′−C8′					1.349	1.342
N9′−C8′					1.326	1.336
N9′−C11′					1.443	1.433

[a] The labeled prime values are for the bond lengths of the ligand L′. [b] Experimental values from ref 24. [c] Higher energy state. [d] Ground state.

TABLE 2: Bond Angles, in Degrees, for the Optimized Structures of L, $[L-Hg]^{2+}$, $[L-HgOH]^{+}$, and $[L-Hg-L']^{2+}$ [a]

bond angles	L exp[b]	L calc	$[L\text{-}Hg]^{2+}$	$[L\text{-}Hg-OH]^{+}$	$[L\text{-}Hg\text{-}L']^{2+c}$	$[L\text{-}Hg\text{-}L']^{2+d}$
C1−N7−C8	127.72	131	131	125	125	125
C1−N7−H17	116.13	117	115	118	118	117
H17−N7−C8	116.14	112	114	116	117	117
N7−C8−S10	120.77	119	114	116	116	116
N7−C8−N9	117.11	114	121	118	118	118
S10−C8−N9	122.11	127	125	126	126	126
C8−N9−C11	123.81	131	124	128	129	129
C8−N9−H18	118.03	115	117	115	115	115
H18−N9−C11	118.16	113	118	117	117	116
C8−S10−Hg			104	105	105	106
S10−Hg−O				177	-	-
S10−Hg−S10′					168	172
Hg−S10′−C8′					103	105

[a] The labeled prime values are for the bond angles of the ligand L′. [b] Experimental values from ref 24. [c] Higher energy state. [d] Ground state.

ity.[19] Coming back to the high selective sensor of 1,3-diphenylthiourea, the scanning electron microscopy (SEM) study of membranes activated at both pH values was performed.[18] The presence of two different Hg^{2+} coordination compounds into the corresponding activated membrane was demonstrated: $[L-HgOH]^{+}$ at pH 7 and $[L-Hg-L]^{2+}$ at pH 4.

For the purpose of the present research, it is important to point out that the ISE membrane was prepared with a hydrophobic, low dielectric constant, plastizer-solvent. Thus, solvation effects due to water toward the complexes are expected to be minimal. This is why we did not consider them in the calculations, see below. Indeed, $[L-Hg-L']^{2+}$ and $[L-HgOH]^{+}$ were detected as solid cumulus inside the sensor membrane,[18] not in solution. The $[L-HgOH]^{+}$ compound was formed when the membrane was conditioned in a $Hg(NO_3)_2$ solution in neutral or slightly basic media. The most abundant $[HgOH]^{+}$ ion is formed in water solution,[16] but it is coordinated with the ionophore in the membrane, where the response of the ISE is carried out. A similar behavior occurs for $[L-Hg-L']^{2+}$, but these cumulus are formed when the membrane is conditioned at acidic pH values.[16]

The goal of this contribution is to obtain a deeper understanding, at molecular level, of the Hg^{2+} and $[HgOH]^{+}$ recognition by 1,3-diphenyl-thiourea as ionophore. This is accomplished through a theoretical study of the L, $[L-Hg]^{2+}$, $[L-HgOH]^{1+}$, and $[L-Hg-L]^{2+}$ systems. As quoted, $[L-HgOH]^{+}$ and $[L-Hg-L]^{2+}$ are present in the membrane of the ISEs.[18] It should be mentioned that the observed cumulus have the appropriate stoichiometry corresponding to the proposed structures that may occur within the membrane.[18] Thus, the chosen structures represent appropriate minimal models for the performance of a theoretical analysis of the ionophore-ion systems. This type of approach gives valuable information for the understanding of the electronic and structural aspects determining the recognition properties that are exhibited by these types of selective carriers. This point of view could facilitate the prediction of the fitness of the molecular recognition capability of the proposed ionophores, needed for the specific sensors, saving time and many trial and error experiments in the design of this kind of devices.

2. Computational Procedure

Calculations for 1,3-diphenyl-thiourea and for the $[L-Hg]^{2+}$, $[L-HgOH]^{1+}$ and $[L-Hg-L]^{2+}$ compounds were performed by means of the Gaussian-98 program.[20] The exchange-correlation was treated at the B3LYP[21,22] level of theory. 6-31G** orbital basis sets were employed for the C, N, O, S, and H atoms. A LANL2DZ[23] effective core potential was used for the Hg atom. First, the 1,3-diphenyl-thiourea molecule was fully optimized. Further, this L geometry was used as input for the $[L-Hg]^{2+}$, $[L-HgOH]^{1+}$ and $[L-Hg-L]^{2+}$ geometry optimizations. In Tables 1−3 are reported the calculated equilibrium bond lengths, bond angles, and dihedral angles for the lowest energy states of the studied systems, respectively. The charge distribution analysis was done by the Mulliken approach, and the results are shown in Table 4. In Table 5, the energies of the frontier molecular orbitals are reported, namely the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), and the HOMO-1 to HOMO-3 energies are also indicated. The 1,3-diphenyl-thiourea molecule was analyzed before by some of us, using a lower level of theory.[19] There, a local functional was used jointly with DZVP orbital basis sets.[19] In this paper, the use of the (B3LYP) generalized gradient approximation of the density functional theory and the use of bigger basis sets (of 6-31G** quality)

TABLE 3: Dihedral Angles, in Degrees, for the Optimized Structures of L, $[L-Hg]^{2+}$, $[L-HgOH]^{+}$, and $[L-Hg-L']^{2+}$ [a]

dihedral angles	L exp[b]	L calc	$[L\text{-}Hg]^{2+}$	$[L\text{-}Hg-OH]^{+}$	$[L\text{-}Hg\text{-}L']^{2+c}$	$[L\text{-}Hg\text{-}L']^{2+d}$
C3−C1−N7−C8	108.49	139	−158	−116	−96	−115
C2−C1−N7−C8	74.7	−44	25	66	86	67
C2−C1−N7−H17	−105.27	141	−152	−117	−95	−116
C3−C1−N7−H17	71.54	−36	25	61	83	61
C1−N7−C8−S10	−178.44	175	−159	−175	−175	−175
C1−N7−C8−N9	2.06	−7	18	5	5	5
N7−C8−N9−C11	−175.66	177	−180	−174	−174	−172
H17−N7−C8−N9	−177.97	169	−164	−172	−175	−172
H17−N7−C8−S10	1.53	−9	19	9	6	8
S10−C8−N9−C11	4.85	−5	−3	5	6	7
S10−C8−N9−H18	−175.19	167	−174	−175	−176	−176
C8−N9−C11−C12	101.16	155	84	67	70	71
H18−N9−C11−C14	99.91	160	76	64	67	68
N7−C8−S10−Hg			−144	−156	−162	−163
C8−S10−Hg−O				151		
C8−S10−Hg−S10′					174	123
S10−Hg−S10′−C8′					−14	−70
Hg−S10′−C8′−N7′					−46	−157

[a] The labeled prime values are for the dihedral angles of the ligand L′. [b] Experimental values from ref 24. [c] Higher energy state. [d] Ground state.

TABLE 4: Mulliken Population Analysis for the Optimized Geometries[a]

atom	L	$[L\text{-}Hg]^{2+}$	$[L\text{-}Hg-OH]^{+}$	$[L\text{-}Hg\text{-}L']^{2+b}$	$[L\text{-}Hg\text{-}L']^{2+c}$
S10	−0.29	0.12	−0.03	−0.02	−0.03
N9	−0.61	−0.49	−0.50	−0.48	−0.48
C8	0.34	0.28	0.32	0.32	0.31
N7	−0.59	−0.48	−0.51	−0.50	−0.50
C1	0.26	0.24	0.13	0.09	0.12
H17	0.29	0.34	0.32	0.33	0.32
H18	0.27	0.33	0.31	0.32	0.31
Hg		0.64	0.64	0.46	0.47
O			−0.66		
S10′				0.00	−0.03
N9′				−0.48	−0.49
C8′				0.29	0.30
N7′				−0.51	−0.49
C11	0.31	0.16	0.12	0.11	0.14
C12	−0.13	−0.03	−0.10	−0.10	−0.09
C13	−0.10	−0.08	−0.10	−0.10	−0.09
C14	−0.07	−0.17	−0.07	−0.07	−0.10
C15	−0.10	−0.11	−0.07	−0.09	−0.08
C16	−0.08	−0.06	−0.05	−0.07	−0.06

[a] The labeled prime values are for the atoms of the ligand L′. [b] Higher energy state. [c] Ground state.

allow a more accurate description of the ion carrier and of its complexes. We have found that this chosen methodology is appropriate for an accurate study of the bonding interactions that occur during the recognition process of Hg^{2+} by the ionophore.

3. Results and Discussion

3.1. The 1,3-Diphenyl-thiourea Ionophore. *3.1.a. Geometrical Features.* The optimized geometry of 1,3-diphenyl-thiourea is shown in Figure 1. The experimental structure of this compound, as reported in the Cambridge Structural Data Base,[24a] was determined by Peseke et al.[24b] Some calculated bond lengths and bond angles are quoted in Tables 1 and 2, respectively, and the corresponding experimental values are also indicated, for comparative purposes. A good agreement is found between theory and experiment. In particular, high accuracy is reached for the structural parameters of the thioureido group, which, as will be shown below, plays a crucial role in the recognition properties of the ion carrier. For example, the calculated C8−S10 distance, 1.681 Å, is the largest one and matches with the experimental value.[24] The shortest distances, 1.380 and 1.364 Å, occur for the C−N bonds. It is interesting

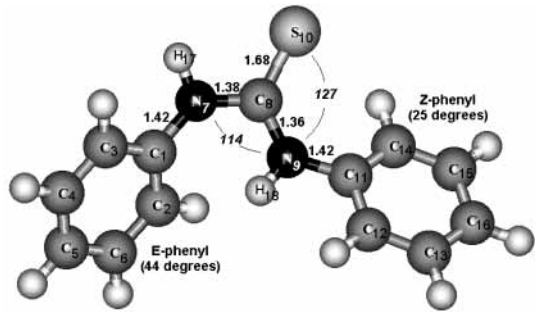

Figure 1. Optimized structure of 1,3-diphenyl-thiourea. Some bond lengths, in Å, and bond angles, in degrees, are indicated.

to observe that C8−N9, through which the thioureido is bonded to the Z-phenyl ring (nearest to the S atom), is shorter than C8−N7, through which the thioureido is bonded to the E-phenyl ring (farthest to the S atom). The small difference of these two C−N bonds is consistent with the appearance of an E, Z conformer as the ground state for 1,3-diphenyl-thiourea. In the experimental geometry,[24] the C−N bonds also are different, but C8−N7 is the shortest one (see Table 1). With respect to the experiment, our C−N values have small overestimations of 0.02−0.04 Å, which are mainly due to the fact that the geometric optimization was done in the gas phase, while the experiment records the structure in a crystal lattice; see lines below for details. Up to here, the calculated S−C distance is between the average for double, S=C = 1.56 Å, and single, S−C = 1.75 Å, bonds.[25] Similarly, the C−N distances fall in the regime of a typical single formamide, C−N = 1.36 Å, bond.[25] Despite their E or Z position, N9−C11 and N7−C1 have, essentially, the same bond length, 1.415−1.416 Å, and are only 0.015 Å shorter than the experimental value.[24] It will be very important to follow the changes of the S−C and N−C bonds through coordination of the ionophore with Hg^{2+}. The observed and calculated N−H distances differ significantly, because in X-ray determinations, the proton bond lengths have some uncertainty. The calculated E, Z conformer of 1,3-diphenyl-thiourea is consistent with X-ray[24] and NMR[26] determinations, which indicates the accuracy of the theoretical results. Indeed, the estimated bond lengths differ by at most 0.01−0.04 Å from the experiment. The computed S10−C8−N9 and C8−N9−C11 bond angles, 127 and 131°, agree well with the experimental values; see Table 2. The E and Z phenyl rings are not coplanar with the thioureido unit, but the observed structure has the most

TABLE 5: Orbital Energies, in eV, for LUMO and HOMO to HOMO − 3 of L, $[L-Hg]^{2+}$, $[L-HgOH]^{+}$, and $[L-Hg-L']^{2+}$. The Electro-negativity, χ, in eV, the Hardnes, η, in eV, and the Softnes, σ, in eV^{-1} Also Are Indicated.

	L	$[L-Hg]^{2+}$	$[L-Hg-OH]^{+}$	$[L-Hg-L']^{2+\,a}$	$[L-Hg-L']^{2+\,b}$
LUMO	−1.08	−11.97	−5.71	−8.80	−8.51
HOMO	−5.59	−13.00	−10.11	−11.71	−11.77
HOMO − 1	−5.73	−13.43	−10.29	−11.74	−11.80
HOMO − 2	−6.07	−14.52	−10.43	−11.80	−11.83
HOMO − 3	−6.88	−14.67	−10.56	−11.92	−11.84
χ	3.34	12.48	7.91	10.25	10.14
η	2.26	0.52	2.20	1.45	1.63
σ	0.44	1.92	0.45	0.69	0.61

[a] Higher energy state. [b] Ground state.

orthogonal position of them (Figure 1 and Table 3). In our calculations, the Z-phenyl is near in plane to the thioureido group, because their dihedral angle is 25°, while the E-phenyl is 44° out of the plane. Note that as the coordination of the ionophore increases, as in L−Hg−L′ (see section 3), the orientation of the phenyl rings and the C8−N9 and C8−N7 distances are very similar to those of the experimental geometry, where these structural parameters, particularly the former ones, reflect some effects of the lattice. The three-dimensional E, Z geometry of the ionophore has important consequences for its coordination with Hg^{2+}.

3.1.b. Electronic Structure. The charge distribution around the thioureido region of 1,3-diphenyl-thiourea is as follows: The S atom has a population of −0.23 electrons (e), while the N7 and N9 sites have bigger contributions of −0.63 and −0.61 e, respectively (see Table 4). So, the thioureido group is rich in electrons, which are available for donations in reactions where the group behaves as a Lewis base against positive moieties or cations. At first sight, the N atoms could be more reactive than the S center. However, aside from the charge distribution, the most external or frontier orbitals are also involved in the reactivity behavior. Indeed, both HOMO and HOMO − 1 play an important role in the nucleophilic response of this ion carrier toward soft cations. The LUMO is delocalized around the whole molecule (Figure 2). However, the HOMO orbital is mainly located on the C−S bond with a bigger weight on the sulfur site, suggesting that the S atom is the most favorite reactive site. Aside from HOMO, HOMO − 1 has also strong contributions on the S site reinforcing the sulfur reactivity. Also, note the contributions in HOMO and HOMO − 1, particularly those located around the C12−C11−C14 region arising from the Z-phenyl ring, which could also participate in the nucleophilic response. In fact, we have found that the Z-phenyl group plays a very important role in the coordination of the ionophore with Hg^{2+}. Note the absence of any contribution from the E-phenyl group in HOMO, while small orbital contributions of this group appear in HOMO − 1 (Figure 2). Even more, in terms of the soft acids and bases (HASB) scheme,[27] the calculated softness, σ, which involves the LUMO−HOMO energy separation, see Table 5, has the appropriate value of 0.44 to react with the soft,[27] $\sigma = 0.13$, Hg^{2+} cation. This softness fitting accounts for the fact that this ionophore produces a good sensor of Hg^{2+}.[19] To summarize this thought, both HOMO and HOMO-1, which are very close in energy, see Table 5, suggest that the sulfur-Z-phenyl region is the most favored reactive site. That is, an orbital type control, aside or instead of a charge one, may be important in the ionophore−ion complex formation. This could partially explain the molecular recognition of Hg^{2+} by 1,3-diphenyl-thiourea.

These orbital features are confirmed by the nature of the electrostatic potential, which shows clearly a maximum around the sulfur region and, to a lesser extent, around the Z-phenyl ring(Figure 3).

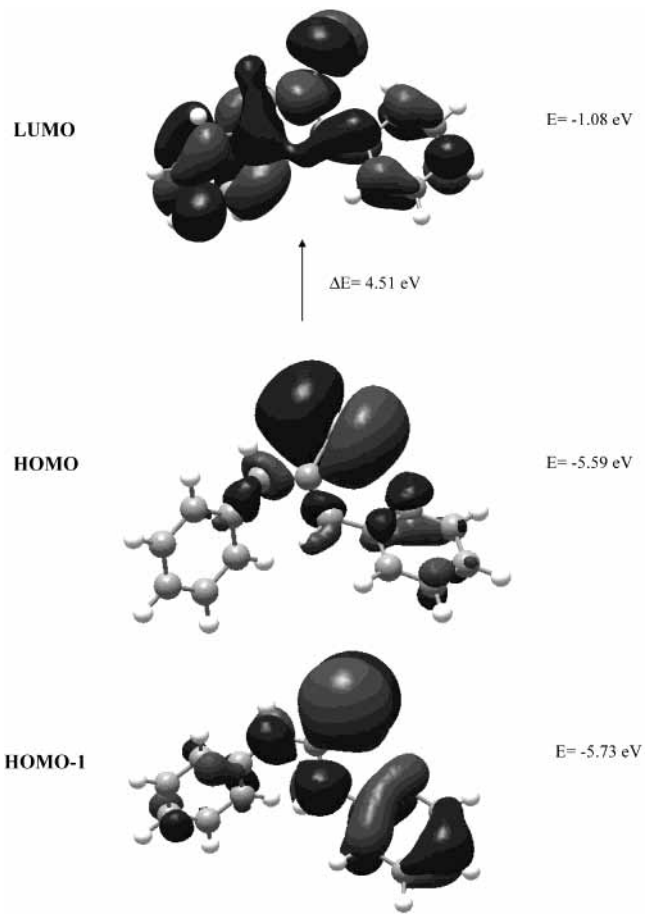

Figure 2. LUMO, HOMO, and HOMO − 1 contour plots of 1,3-diphenyl-thiourea.

3.2. The $[L-Hg]^{2+}$ and $[L-HgOH]^{+}$ Systems. *3.2.a. Geometrical Features.* First, we have calculated the lowest energy structure for $[L-Hg]^{2+}$. Although this complex is not a final product of the reaction of 1,3-diphenyl-thiourea with Hg^{2+}, it represents the smallest system where it is possible to study some important structural and electronic aspects involved in the recognition of Hg^{2+}. The structure of $[L-Hg]^{2+}$ is shown in Figure 4. As it was mentioned, during the membrane ISE sensing process of Hg^{2+} in neutral pH aqueous media, the $[L-HgOH]^{+}$ compound is proposed to be formed,[18] because the ISE detects a monovalent cation in these conditions. The computed structure of $[L-HgOH]^{+}$ is shown in Figure 5. Some representative equilibrium bond lengths for these Hg complexes are reported in Table 1. As discussed above, the sulfur-Z-phenyl region mainly defines the reactivity of the ionophore. The S−Hg distance of 2.63 Å for $[L-Hg]^{2+}$, but more clearly the shorter value of 2.55 Å for $[L-HgOH]^{+}$, indicates the formation of an S−Hg bond. Indeed, these estimates are slightly longer, by about 0.1−0.2 Å, than the experimental S−Hg bond lengths, 2.41−

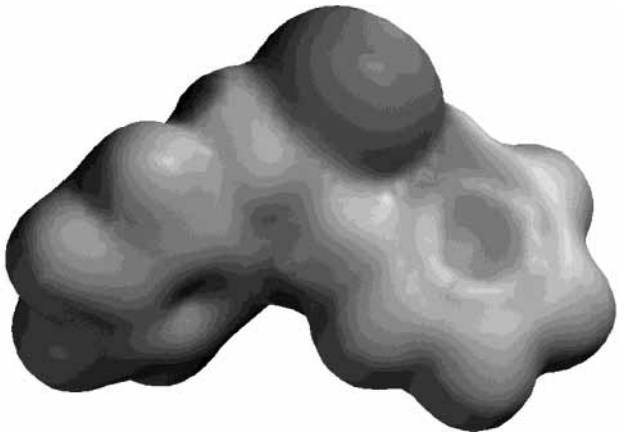

Figure 3. Electrostatic potential map of 1,3-diphenyl-thiourea, the electron rich region is red, the electron poor region is blue.

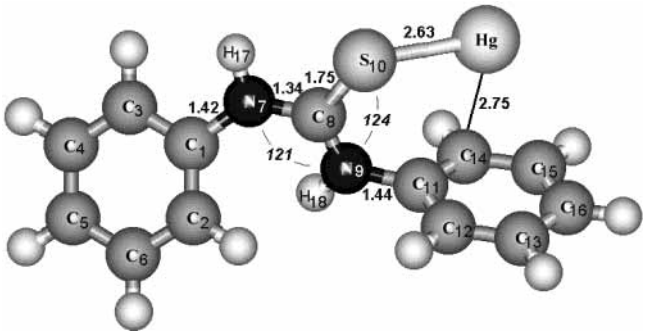

Figure 4. Lowest energy structure of [1,3-diphenyl-thiourea $-Hg]^{2+}$. Some bond lengths, in Å, and bond angles, in degrees, are indicated.

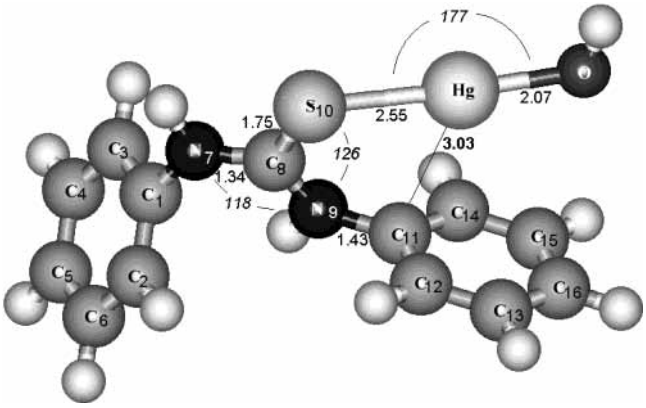

Figure 5. Lowest energy structure of [1,3-diphenyl-thiourea-Hg$-OH]^{+}$. Some bond lengths, in Å, and bond angles, in degrees, are indicated.

2.49 Å,[28−30] reported for Hg compounds of the cyclic thiourea 3-ethyl-2-thione-imidazolidine. The occurrence of a weaker ionophore(sulfur)$-Hg^{2+}$ bond in $[L-Hg]^{2+}$ and in $[L-HgOH]^{+}$ is in line with the required sensitivity that 1,3-diphenyl-thiourea possesses by the soft Hg^{2+} and $(HgOH)^{+}$ cations.

A remarkable feature is that, both in $[L-Hg]^{2+}$ and in $[L-HgOH]^{+}$, the Z-phenyl ring is also bonded to Hg^{2+}. As shown in Figures 4 and 5, the Hg^{2+} ion is located over the Z-phenyl group, making a favorable bonding interaction between them. For $[L-Hg]^{2+}$, the Hg−C14, Hg−C11, and Hg−C15 distances are 2.75, 3.09, and 3.02 Å, respectively. While for $[L-HgOH]^{+}$, the distances between Hg and the C-phenyl atoms are 3.03 Å for C11, 3.25 Å for C14, and 3.31 Å for C12. These shortest $Hg-C_{phenyl}$ separations are consistent with the appearance of coordination between Hg^{2+} and the Z-phenyl ring. In fact, theoretical studies for the $Hg(C_6H_6)_n(AlCl_4)_2$ complexes[31,32] yield 2.81−2.87 Å for the shortest interatomic $Hg-C_{phenyl}$ distances, suggesting the coordination between Hg and the C_6H_6 phenyl group. Moreover, in an X-ray-determined structure for an organometallic cluster compound containing two Hg atoms, a η^6 coordination was reported between each Hg with a phenyl ring. The experimental X-ray $Hg-C_{phenyl}$ distances range from 2.56 to 3.19 Å.[33] These reported results confirm that in our calculated structures the Hg^{2+} ion is truly coordinated with the Z-phenyl ring. The Hg−C distances are longer in $[L-HgOH]^{+}$ than in $[L-Hg]^{2+}$, indicating a weaker Hg^{2+}−Z-phenyl bond in $[L-HgOH]^{+}$. However, obeying the Bond Order Conservation Principle,[34,35] the last compound presents a stronger S−Hg bond (because the S−Hg distance is shorter), as well as a strong Hg−O bond. These features reveal the formation of a stable S-Hg−O adduct, which is quasi-linear, since its bond angle is equal to 177°.

Then, in these complexes, the Hg^{2+} ion is bonded both to the sulfur atom and to the Z-phenyl ring, as it was predicted from the HOMO and HOMO − 1 orbital contributions of the ion-carrier. This simultaneous interaction could be related to the observed high selectivity and sensitivity of 1,3-diphenyl-thiourea toward the Hg^{2+} cation. Note that in $[L-HgOH]^{+}$, where Hg^{2+} is more coordinated than in $[L-Hg]^{2+}$, the phenyl rings are disposed in a more orthogonal position than in the free ionophore. This is indicated by the C8−N9−C11−C12 dihedral angle (defined by the Z-phenyl ring and the thioureido group), equal to 67°; and by the C8−N7−C1−C2 dihedral angle (defined by the E-phenyl ring and the thioureido group), equal to 66° (Table 3).

As quoted above for the free ionophore, the S−C distance of 1.681 Å is between that of a double and a single S−C bond,[25] while the N−C bond lengths, 1.364 and 1.380 Å, fall closer to the single C−N bond standards.[25] In both $[L-Hg]^{2+}$ and in $[L-HgOH]^{+}$, the S−C separation increases up to about 1.75 Å, and moves to the pattern of a single[25] S−C bond. This elongation is consistent with the S−C bond lengths of 1.71−1.73 Å determined experimentally for some Hg complexes,[28−30] while both sets of the N−C distances are reduced up to about 1.34 Å, see Table 1. In this way, through enlargement and shortenings of the original S−C and N−C chemical bonds, respectively, the thioureido group responds to the bonding formation with the Hg^{2+} ion. Note that this behavior is in agreement with the Bond Order Conservation Principle.[34,35]

3.2.b. Electronic Structure. The population analysis of the Hg^{2+} complexes, reported in Table 4, reveals a significant transference of electrons from the S atom toward the Hg^{2+} ion. Indeed, the population of the S atom has decreased from −0.29 to +0.12 e for $L-Hg^{2+}$ and to −0.03 e for $[L-HgOH]^{+}$. That is, a base-acid Lewis mechanism is operative in this type of metal−ionophore interactions.

The Hg^{2+} ion noticeably perturbs the charge distribution of the Z-phenyl carbon atoms. As reported in Table 4, the carbon atoms of the Z-phenyl ring in the bare ionophore have a total population of −0.16 e, but this value is moved to −0.29 e or to −0.27 e when L is bonded to Hg^{2+} or to $(HgOH)^{+}$, respectively. In close detail for $[L-Hg]^{2+}$, a charge transfer has occurred from Hg^{2+} to the C11 and C14 atoms of the Z-phenyl ring, because both C atoms become 0.15 and 0.10 e more populated than those in the free ligand. While for $[L-HgOH]^{+}$, the C11 atom, which is nearest to Hg^{2+}, is the one that has gained more electrons. This type of charge distributions suggests a charge transfer along the S10−Hg−C14−C11−N9−C8 atoms of $[L-Hg]^{2+}$, which, as shown in Figure 4, are disposed in a twist

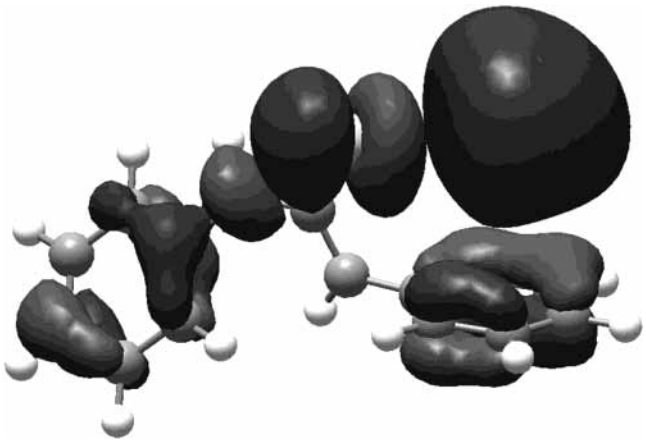

Figure 6. LUMO contour plot of [1,3-diphenyl-thiourea-Hg]$^{2+}$.

chair conformation. For [L−HgOH]$^{+}$, such charge transfer is carried out along the S10−Hg−C11−N9−C8 atoms. It is to be stressed that the uneven distribution of charge in the Z-phenyl groups reflects a strong perturbation of their aromatic π-clouds.

The [L−Hg]$^{2+}$ cation is a soft and electronegative acid. However, in comparison to the bare Hg^{2+} ion[27] (which has a hardness, η, of 7.7 eV, or $\sigma = 0.13$, and an electronegativity, χ, of 26.5 eV), [L−Hg]$^{2+}$ becomes softer, $\sigma = 1.92$, and less electronegative, $\chi = 12.48$ eV (Table 5) which is due to the type of bonding experienced between Hg^{2+} and the ionophore. The LUMO contour plot of [L−Hg]$^{2+}$ is shown in Figure 6. It is delocalized over the whole system, but a significant contribution is located on Hg^{2+}, indicating that the addition of either OH^{-} or L, to yield [L−HgOH]$^{+}$ or [L−Hg−L]$^{2+}$, may be carried out on that site.

The LUMO, HOMO, and HOMO − 1 contour plots of [L−HgOH]$^{+}$ are shown in Figure 7. The LUMO is located around the thioureido−Hg−Z-phenyl region, also showing significant contributions between Hg and the Z-phenyl ring. Both HOMO and HOMO − 1 have signatures of the bonding between Hg^{2+} and the OH^{-} ion. Additionally, in these two orbitals are also contained small contributions from the π-cloud of the Z-phenyl ring, accounting for weak bonding interactions between the Hg^{2+} ion and the Z-phenyl ring. Then, in [L−HgOH]$^{+}$, both orbitals, HOMO and HOMO − 1, which are very close in energy, play an important role in the interaction of the ion carrier with the softer $(HgOH)^{+}$ ion.

3.3. The [L-Hg-L′]$^{2+}$ System. *3.3.a. Geometrical Features.* The membrane ISE sensing process of Hg^{2+} in aqueous media, at pH = 4, involves the formation of [L−Hg−L′]$^{2+}$, as determined by SEM.[16] The lowest energy states of the many-electron [L−Hg−L′]$^{2+}$ system were also determined at the B3LYP/6-31G** level. The ground-state geometry of [L−Hg−L′]$^{2+}$ is shown in Figure 8a. In this structure, Hg^{2+} is bonded to both sulfur atoms of each ionophore, and it is also bonded to the two Z-phenyl rings, producing some type of sandwich Z-phenyl−Hg^{2+}−Z-phenyl structure, similar to that of ferrocene.[36] The state where Hg^{2+}, aside from its bonding to the S atoms, interacts with only one of the Z-phenyls is shown in Figure 8b; it was found to be 6.4 kcal/mol higher in energy. This value accounts for the type of weak bonding interactions arising between the soft Hg^{2+} ion and the Z-phenyl ring. Note that the higher energy state has a more open geometry than the ground state. Below, we will discuss only the ground state. Up to here, these results indicate the importance and the role that the thioureido and Z-phenyl groups play in the recognition of Hg^{2+} by 1,3-diphenyl-thiourea. In fact, aside from the primary

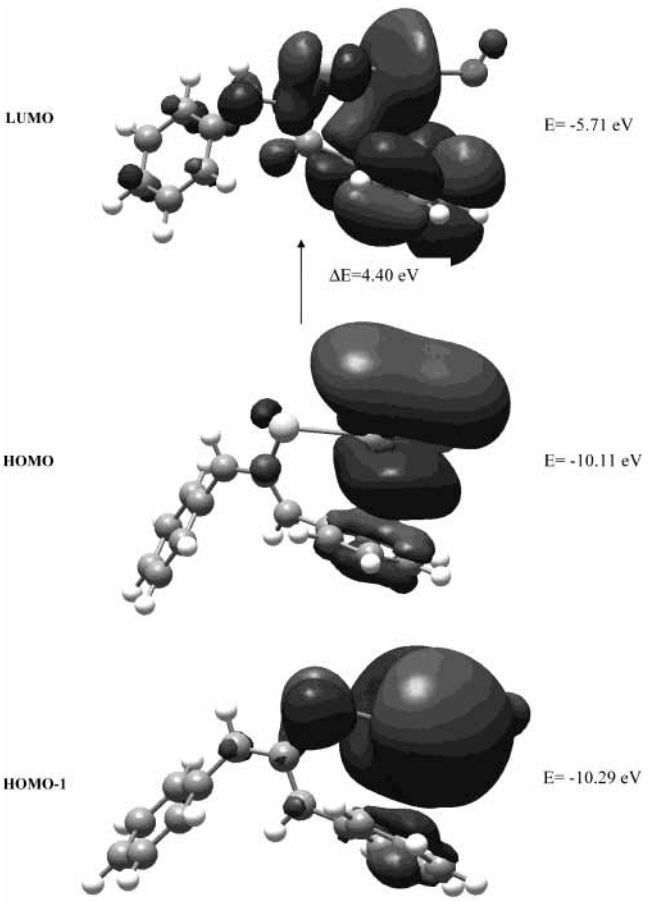

Figure 7. LUMO, HOMO, and HOMO − 1 contour plots of [1,3-diphenyl-thiourea −Hg−OH]$^{+}$.

and stronger S−Hg−S bonds, the Hg^{2+} ion is also simultaneously bonded to two Z-phenyl rings, producing a more symmetric and compact [L−Hg−L′]$^{2+}$ structure. The S_R−Hg and Hg−S_L bond lengths, where R and L stand for right and left, being equal to 2.553 and 2.554 Å, respectively, confirms the appearance of strong S−Hg bonds. Consistently, the S_R−Hg−S_L adduct is quasi-linear, with an associated bond angle of 172°. Now, the distances between Hg and the nearest C atoms of each, below (C11) and above (C11′), Z-phenyls, are equal to 3.02 and 3.05 Å, respectively. The Hg−C12(Hg−C12′) and Hg−C14(Hg−C14′) lengths fall in the 3.18−3.47 Å range. This suggests the presence of η^1−Hg−Z-phenyl coordinations, since only Hg−C11 and Hg−C11′ have the appropriate lengths for the formation of weak Hg−C bonds. As Figure 8a shows, Hg^{2+} is between two S atoms and between two Z-phenyls. That is, in [L−Hg−L]$^{2+}$, two S atoms and two Z-phenyls carry the Hg^{2+} ion.

In [L−Hg−L′]$^{2+}$, the two S−C distances are equal to 1.75 Å. The two C−N distances, for the case where the N atom of each L is bonded to the Z-phenyl ring, are both equal to 1.342 Å. The other two C−N distances, for the case where the N atom of each L is bonded to E-phenyl, are both equal to 1.336 Å. Moreover, the dihedral angles of the E-phenyl rings with their respective thioureido groups are equal to 110 and 115°. Similarly, the dihedral angles of the Z-phenyl rings with their respective thioureido units are 113° and 115°. Overall, these values indicate the high symmetry of the whole [L−Hg−L′]$^{2+}$ structure. Note that the calculated structural parameters of L, in the [L−Hg−L′]$^{2+}$ and [L−HgOH]$^{+}$ complexes, are quite close to the corresponding experimental values determined for the bare ionophore in the crystal lattice, see Tables 1−3.

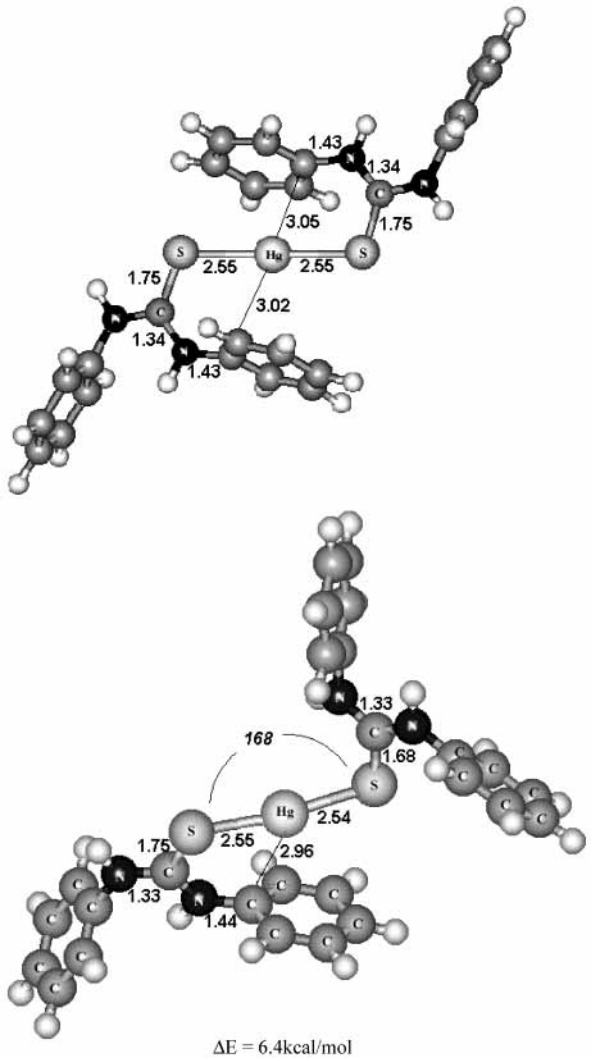

Figure 8. (top) Lowest energy structure of [1,3-diphenyl-thiourea-Hg−1,3-diphenyl-thiourea]$^{2+}$. Some bond lengths, in Å, and bond angles, in degrees, are indicated. (bottom) Higher energy structure of [1,3-diphenyl-thiourea-Hg−1,3-diphenyl-thiourea]$^{2+}$. Some bond lengths, in Å, and bond angles, in degrees, are indicated.

3.3.b. Electronic Structure. In the [L−Hg−L′]$^{2+}$ ground state, there is a transference of electrons from the two S atoms toward the Hg^{2+} ion. Indeed, from L to [L−Hg−L′]$^{2+}$, the population of both S atoms have moved from −0.29 e up to −0.03 e, yielding a less positively charged Hg cation. That is, a base-acid Lewis mechanism is operative in the L−Hg−L′ complex formation. Furthermore, a charge transfer, from Hg^{2+} to the nearest C11 and C11′ atoms, is carried out in the η^1−Hg−Z-phenyl coordinations; note that the C11 and C11′ atoms have the biggest increase in their electronic populations (Table 4).

HOMO and HOMO − 1 are quasi-degenerate and they reflect weak bonding interactions between Hg^{2+} and the (above and below) 1,3-diphenyl-thiourea moieties (Figure 9). Together, HOMO and HOMO − 1 built up some kind of envelope around the Hg^{2+} ion. On the other hand, HOMO − 2 and HOMO − 3 reflect the absence of any L−Hg bonding, despite the fact that they are also quasi-degenerate with HOMO (Table 5). So, in the [L−Hg−L′]$^{2+}$ coordination compound, the bonding between the ionophore and Hg^{2+} is mainly accounted by the HOMO and HOMO-1 orbitals as well as by the charge-transfer effects occurring from the sulfur atom to Hg^{2+} and from this ion toward the Z-phenyl rings.

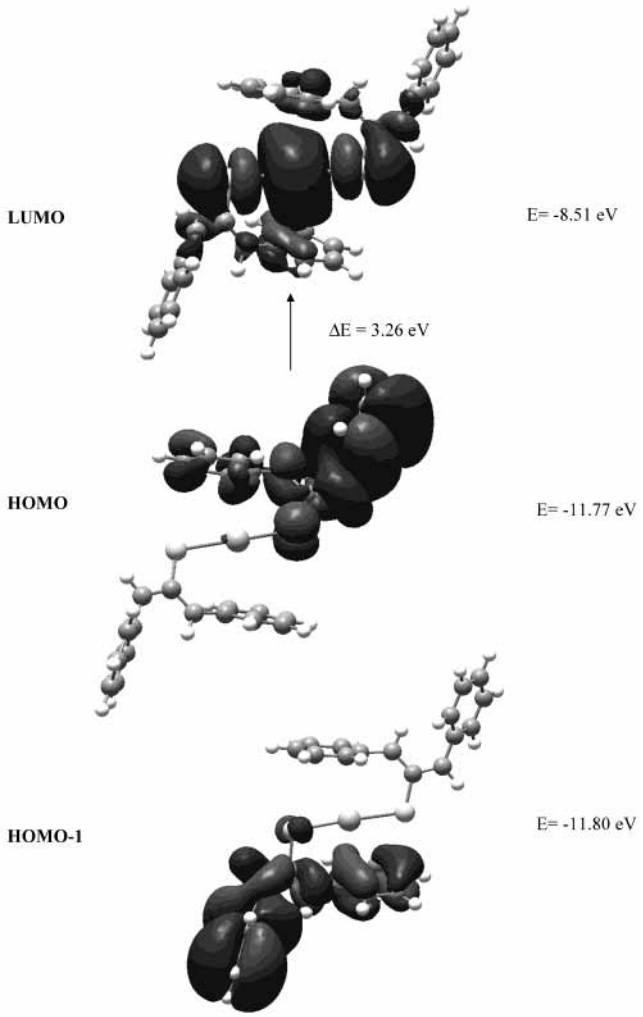

Figure 9. LUMO, HOMO, and HOMO − 1 contour plots of [1,3-diphenyl-thiourea-Hg−1,3-diphenyl-thiourea]$^{2+}$.

4. Conclusions

The lowest energy structures and electronic properties of 1,3-diphenyl-thiourea and of its [L−Hg]$^{2+}$, [L−HgOH]$^{+}$, and [L−Hg−L′]$^{2+}$ compounds were determined by means of DFT calculations. The results provide insight and rationalization of the key structural and electronic parameters involved in the recognition properties of the ion carrier; it was found that the thioureido(sulfur)-Z-phenyl region mainly defines its reactive site. The importance and the role that the S atom and the Z-phenyl groups play in the coordination with the Hg^{2+} ion were revealed. In the [L−HgOH]$^{+}$ and [L−Hg−L′]$^{2+}$ compounds formed during the sensing process one sulfur atom and one Z-phenyl ring carry the Hg^{2+} ion in the first case, while in the second compound, aside from the primary and stronger S−Hg−S bonds, the Hg^{2+} ion is also simultaneously bonded to the two Z-phenyl rings. This rather unexpected result indicates that the Z-phenyl group is crucial in the recognition properties of the ionophore.

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