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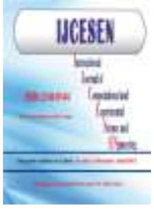

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Research Article

Retarding Effect of the Mediating Sulfane (-S-) Group on Chelation Efficacy of Thiolic-Sulfur Toward Mercury in 2-(2-Mercaptothiazol-5-yl) acetic acid Derivative. DFT-Theoretical Study.

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Abstract:

Mercapto-containing chelates: 2-(2-mercapto-4-methyl-2,3-dihydrothiazol-5-yl) acetic acid **(AS$_2$NHM),** 2-(2-mercapto-4-methylthiazol-5-yl) acetic acid **(AS$_2$NM),** 2-(2-mercapto-5-methyl-3H-pyrrol-4-yl) acetic acid **(ACSNM),** 2-(5-mercapto-3-methylthiophen-2-yl) acetic acid **(AS$_2$CM),** 2-(2-mercaptothiazol-5-yl) acetic acid **(AS$_2$N)** and 4-ethylthiazole-2-thiol **(S$_2$NM)** were studied using DFT method of calculation employing B3LYP/LanL2DZ level of theory. Computational results have showed that mediating groups (*Sulfane -S- and imine =N-*) along with the attached substituents (*methyl -CH$_3$ and carboxylic -COOH*) surprisingly have a dramatic effect on charge density localization/delocalization on thiolic-sulfur as a donor atom and thus on its capability of binding the mercuric divalent ion.Responses for modifications brought by in all simulates were tracked by calculating the charge density on thiolic-sulfur and atoms in proximity. Related changes in geometrical parameters, namely, bond lengths and bond angles in the neighborhood of thiolic-sulfur were also monitored to hopefully provide us with more insights about the effect of the performed modifications. Images of HOMO-LUMO orbitals and charge density distribution surfaces are also presented. Effects of Sulfane (-S-) mediating group on electron density enrichment of thiolic-sulfur, thus its chelation effectiveness for mercuric ion have been investigated. This is in order to deep understand the chelation weakness of 2-(2-Mercaptothiazol-5-yl) acetic acid (AS$_2$NM) toward mercury(II) ions in particular, which has been encountered in earlier experimental research work.Findings of the study, have clarified the drawbacks of AS$_2$NM that lay behind its failure in stabilizing the divalent mercuric ion through effective coordination. Nevertheless, it was able of developing stronger binding with Hg metal ions compared to the other chelates, this was attributed to softness close matching with Hg ion.

1. Introduction

Owing to the harmful effects of toxic heavy metallic ions (*Mercuric ion in specific*) on environmental livings [1-3], their capturing and removal from contaminated areas, still acquire a serious attention from researchers [4-7] who are interested in this field. Despite of existence a wide range of techniques known for removal of these heavy metal contaminants [8-11], the use of suitable chelating agents, still considered the most convenient technique [12-15]. This is due to having many advantages over other removal techniques from which; simplicity, efficiency, low cost and availability of chemical reagents [16, 17]. Basically, these agents (*commonly called chelators*) are organic molecules with one or more electron rich atoms that would offer the incoming metal species sufficient electron density necessary for its stabilization. Among other parameters, electronegativity and amount of electron density localized on the donor atom were proven to determine its efficiency when acting as a binding site for the targeted metal ion [18-23].

It is worthy to mention that, many of these chelating agents, and in many occasions, have been recruited to medically treat heavy metal poisoning [24-26]. Previously, and in a related research work [14, 27], it was observed that similar chelating agents containing sulfur *(such as thiols)*, nitrogen *(amines)* and oxygen *(hydroxyls or carboxylates)*, tend to vary in their preferences toward binding the divalent Hg ion. In these reports [14, 27] for example, sulfur- and nitrogen-based chelates were noticed to preferentially bind mercuric ions when co-existed with other ions in an aqueous solution matrix. However, oxygen-based chelates [13, 28] were observed to show weak preference toward Hg ion in the same media. In these referred reports, the variation in chelation preference toward mercury, was attributed to the degree of softness/hardness matching between the interacted Hg ion and the involved chelates [14, 27, 29].

In a one unique late study, when the chelate: 2-(2-mercapto-4-methylthiazol-5-yl)acetic acid (*abbreviated as* AS_2NM) was interacted with Hg(II) ions [27] an unexpected finding was witnessed. This chelate AS_2NM was found to bind mercuric ion in an optimum chelation percent below 70%. Moreover, when AS_2NM was immobilized on surface of silica nanoparticles, this percent chelation was not changed. At that time, we have struggled explaining this finding, and noticeably, has raised an important wondering about how, the aspects of coordination should be understood and interpreted when the metal interacts with a given chelate. Eventhough, AS_2NM having two available binding sites (*carboxylic oxygen and sulfur of thiol*), its overall binding effectiveness was seen to be independent on oxygen of the carboxylic group. At that time, this finding was not fully understood, therefore was attributed to the softness matching parameter between the two; Hg(II) ion and the thiolic-sulfur of AS_2NM. As a consequence, the fact of participation of the hard carboxylic oxygen in the binding competition, was therefore excluded. Since that time, this finding has caught my attention and kept in mind for further future investigation. From my perspective, this experimental observation, deserves to re-considered again and to acquire special interest to be deeply figured out.

In this current study, a carefully chosen simulated chelates *(shown in Figure 1)* that resemble our controversy chelate (AS_2NM, *simulate B*) in structure were proposed. As seen, all of the proposed simulates have thiol group in common. Although having; thiol (-SH) and ($-CH_2COOH$) as main interactive groups, all simulates (*except E*) have one methyl ($-CH_3$) group attached to the thiazole cyclic moiety. Furthermore, all simulates (*except C*), have acetic acid ($-CH_2COOH$) and thiol (-SH) groups placed alternatively in one side of the parent molecule and separated by the Sulfane (-S-) functionality. In simulate (*C*), the same two groups (*acetic acid;* $-CH_2COOH$ *and thiol; -SH*) are separated by (-C-) functionality instead of sulfane (-S-).Considering the structures of simulates shown in Figure 1, we have the following notes;

(i) The proposed simulates, enable studying the binding effectiveness of (-SH) when ($-CH_2COOH$) is attached alternatively to the thiazole cyclic moiety and separated by either (-S-) or (-C-) functionalities, Figure 1.

(ii) In addition, those simulates having methyl group attached to thiazole ring, would enable studying the binding effectiveness of (-SH) group under the circumstances in which ($-CH_2COOH$) is co-existed with the ($-CH_3$) group. Knowing that, ($-CH_3$) is an electron donating group, thiazole ring in these simulates is anticipated to receive more electron density and becomes more enriched in effect.

(iii) Simulate (*A*) has the same structural features as others in the list, however, it differs in having -NH- mediating group situated in place of -N= group. This simulate would allow investigating the role of -N= group on electronic enrichment of (-SH), and thus on its binding effectiveness. This is owing to the believe that, mediating group would somehow interfers with the amount of electron density delocalizes toward (-SH) group.

(iv) Simulate (*C*) is very similar to chelate (*B*) in structure, however it differs in the aspect of having $-CH_2-$ in place of -S- as a mediating group. This formulation is assumed to give insights about the role of -S- group on switching on/off the influx of electronic density toward (-SH) and therefore how far, it can control the electronic enrichment of (-SH). This is hopefully, be deduced by replacing the -S- group by -C- group and see how the amount of electronic density was affected while crossing in the direction of (-SH) group.

(v) Simulate (*E*) and by applying the same argument as pointed in (ii), is having the same structural features as in other chelates, but with no methyl group being attached to thiazole ring. This simulate is actually, hoped to allow investigating the binding effectiveness of (-SH) as co-existed with ($-CH_2COOH$) group, but under the situation, where no extra electron density flowing from $-CH_3$ into the thiazole ring as has been proposed in other simulate.

(vi) In contrast to simulate (*E*), simulated chelate (*F*), is having the same structural features as others, however, no ($-CH_2COOH$) group being attached to the thiazole ring. This simulate is proposed to investigate the -SH chelation readiness in absence of ($-CH_2COOH$) group.

(vii) The purpose of attaching or /eliminating the methyl group to the thiazole ring, is to deep investigate the effect of ($-CH_2COOH$) on reactivity of (-SH) group under two conditions: (a) when ($-CH_2COOH$) is enforced by existence of an electron releasing group; methyl ($-CH_3$) in our case and (b) when ($-CH_2COOH$) works independently and no support for the electron density from other groups.

The six simulates shown in Figure 1, where chosen carefully to serve as modulated structures to conduct the *Ab-initio* calculations in two themes; (*free modes*), means no complexation with Hg(II) ion, and *(complexation mode*) where, Hg(II) is incubated by the chelate. The various theoretical calculations are performed using Gaussian 09 program, employing (*Density Functional Theory (DFT*), *TD-SCF and LANL2DZ/B3LYB basis set*), where our focus was on parameters include: (*Optimization energy, Bond lengths, Bond angles, Occupation of the frontier orbitals HOMO and LUMO, Charge distribution over donor atoms, Atomic hardness of donor atoms and total hardness of the whole chelate*).

Throughout such theoretical studies, we are trying to achieve two important goals: (*One*) determining the electronic effect of the secondary group(s) on the donation efficacy of the principal donating group when both co-existed within the same chelate (*for example -CH_2COOH on (-SH) in our case).* By applying this scope, we look forward to build better understanding of the role of these secondary groups (*whether they are enforcing or retarding*) and how the principal donating group would be maximally optimized to effectively bind the targeted metal ion(s). (*Two*) determining the geometrical effect of the secondary group(s) on the binding effectiveness of the principal coordinating site. This is assumed to be accomplished by positioning these secondary groups on variable positions with respect to the principal donating group. The geometrical parameters (*bond angles, bond distances and distribution surfaces of electron density*) are the ones that are proposed to be measured. These parameters are no doubt interrelate among each other when they practice their effect on the electronic environment of the principal binding group. In results, findings of this study, are hoped to provide more insights toward recruiting chelates as effective binders for metal ions.

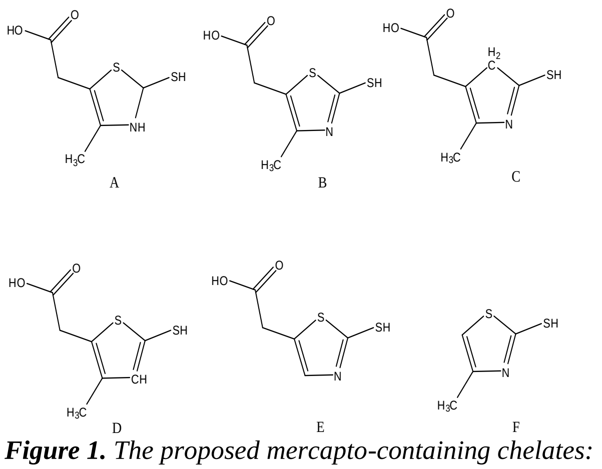

Figure 1. *The proposed mercapto-containing chelates: (A) 2-(2-mercapto-4-methyl-2,3-dihydrothiazol-5-yl)acetic acid **(AS_2NHM)** (B) 2-(2-mercapto-4-methylthiazol-5-yl)acetic acid **(AS_2NM)** (C) 2-(2-mercapto-5-methyl-3H-pyrrol-4-yl)acetic acid **(ACSNM)** (D) 2-(5-mercapto-3-methylthiophen-2-yl)acetic acid **(AS_2CM)** (E) 2-(2-mercaptothiazol-5-yl)acetic acid **(AS_2N)** (F) 4-methylthiazole-2-thiol **(S_2NM).***

2. Computational details

Density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations at B3LYP level [30-35] using the basis set; LANL2DZ [30-32, 36, 37] were performed to simulate the molecular structures and to calculate the vibrational frequencies along with the charge density distribution. The wide use of LANL2DZ in theoretical investigations involving inorganic complexes and related ligands is behind its employment as a basis set for our calculations [38-44]. The NBO-Model [45-48] has been utilized to assign and evaluate the partial charge on donor atoms of parent chelate derivatives. Herein, we adopt the NBO-approach since it is considered the most reliable for our purposes in this investigation, especially when it comes to investigate the charge density localization/delocalization on atoms.

In addition, when charges on thiolic-sulfur was evaluated by this model, they were found to vary according to a reasonable trend that was easy to follow and explain.

The number of excited state-electronic configurations used in TDDFT was 80, and only singlet excitations were considered. Structures of complexes were optimized with no symmetry constraints. The same functional and basis sets were employed for TDDFT calculations to simulate the charge density surfaces and the electronic images of the frontier HOMO orbital of these complexes.

All calculations were carried out using the Gaussian 09 program [49] on *Toshiba- Satellite i5 Dual Core, Equipped with windows7*. Geometry optimization is one of the most important steps in the theoretical calculations of TDDFT and vibrational spectra. All geometries converged perfectly, and vibrational frequencies and intensities were computed at the same theoretical levels as those used in geometry optimization. Excluding the six parent compounds (*chelates A-F, Figure 1*), six simulates were proposed to represent the type of complexations with the Hg in the divalent oxidation state. In each case, the investigated chelates were complexed with the indicated metal ion in a bidentate fashion via two donor atoms (*thiolic-sulfur/carboxylic oxygen or thiolic-sulfur/nitrogen of -N=*).

Table 1. *Calculated optimum energy and NBO-partial charge of (S of SH, O of OH, -S-, and -N=) in free chelates*

No	**Compound**	**Optimum Energy (Atomic unit)**	**Charge on S-atom (a.u)**	**Charge on O-atom (a.u)**	**Charge on hetero atom -S- (a.u)**	**Charge on hetero atom =N- (a.u)**
1	**ACSNM**	- 487.36804956	+ 0.059	- 0.744	-C- (-0.480)	- 0.191
2	**AS$_2$NHM**	- 458.72512944	+ 0.052	- 0.780	+ 0.359	- 0.721-NH
3	**AS$_2$NM**	- 458.16330277	+ 0.060	- 0.780	+ 0.411	- 0.518
4	**AS$_2$CM**	- 442.12604611	+ 0.047	- 0.782	+ 0.424	-----
5	**AS$_2$N**	- 418.84809077	+ 0.062	- 0.778	+ 0.414	- 0.504
6	**S$_2$NM**	- 230.31584668	+ 0.054	----	+ 0.377	- 0.523

Table 2. *Calculated Optimum Energy and bond lengths of C-S, C=C and C=N bonds in the free chelates*

No	Compound	Optimum Energy (Atomic unit)	Bond Length C-S (^{0}A)	Bond Length C=C (^{0}A)	Bond Length C=N (^{0}A)
1	ACSNM	- 487.36804956	1.81180	1.36613	1.30628
2	AS$_2$NHM	- 458.72512944	1.83309	1.36796	1.41472
3	AS$_2$NM	- 458.16330277	1.81262	1.37851	1.30601
4	AS$_2$CM	- 442.12604611	1.82194	1.38305	1.37448
5	AS$_2$N	- 418.84809077	1.81140	1.37359	1.30897
6	S$_2$NM	- 230.31584668	1.81283	1.37395	1.30639

Table 3. *Calculated optimum energy and NBO-partial charge of (S of SH and Hg-Metal ion) in mercury complexes with the six chelates*

No.	**Compound**	**Coord-ination sites**	**Optimum Energy (a.u)**	**S of SH Atomic charge (a.u)**	**Metal Atomic charge (a.u)**
1	**ACSNM-Hg**	S-, O-	- 528.94143825	- 0.207	+ 1.157
		S-, N-	- 529.53873003	- 0.154	+ 0.487
2	**AS$_2$NHM-Hg**	S-, O-	-500.34633818	- 0.104	+ 0.589
		S-, N-	-500.34202373	- 0.146	+ 0.484
3	**AS$_2$NM-Hg**	S-, O-	-499.67923819	- 0.178	+ 1.098
		S-, N-	-500.34202377	- 0.146	+ 0.484
4	**AS$_2$CM-Hg**	S-, O-	-483.64632127	- 0.173	+ 1.032
5	**AS$_2$N-Hg**	S-, O-	-460.36349760	- 0.172	+ 1.103
		S-, N-	-461.02733688	- 0.143	+ 0.493
6	**S$_2$NM-Hg**	S-, N-	-272.49444933	- 0.149	+ 0.485

Table 4. *Calculated structural parameters; bond lengths (C-S, C=C, C=N, and Hg-S) and bond angles (S-Hg-O or S-Hg-N) for mercury complexes with the six chelates.*

No	**Compound**	**Coord-ination sites**	**Bond length C-S**	**Bond length C=C**	**Bond length C=N**	**Bond length Hg-S**	**Bond angle S—Hg—O or S---Hg---N**
1	**ACSNM-Hg**	S-, O-	1.68017	1.48565 single C-C	1.42435 single C-N	4.55279	80.94509
		S-, N-	1.77503	1.37030	1.33112	2.86302	59.51773
2	**AS$_2$NHM-Hg**	S-, O-	1.69865	1.36799	1.38063 -NH-	8.54233	47.25998
		S-, N-	1.78569	1.37691	1.32891 -NH-	2.83437	59.74113
3	**AS$_2$NM-Hg**	S-, O-	1.84645	1.38300	1.30389	2.63869	144.15861
		S-, N-	1.78569	1.37691	1.32892	2.83435	59.74190
4	**AS$_2$CM-Hg**	S-, O-	1.83348	1.38364	---	2.65939	144.05565
5	**AS$_2$N-Hg**	S-, O-	1.84424	1.37878	1.30684	2.64016	143.57603
		S-, N-	1.78403	1.37181	1.33150	2.83667	59.72381
6	**S$_2$NM-Hg**	S-, N-	1.78658	1.37217	1.32951	2.83970	59.86821

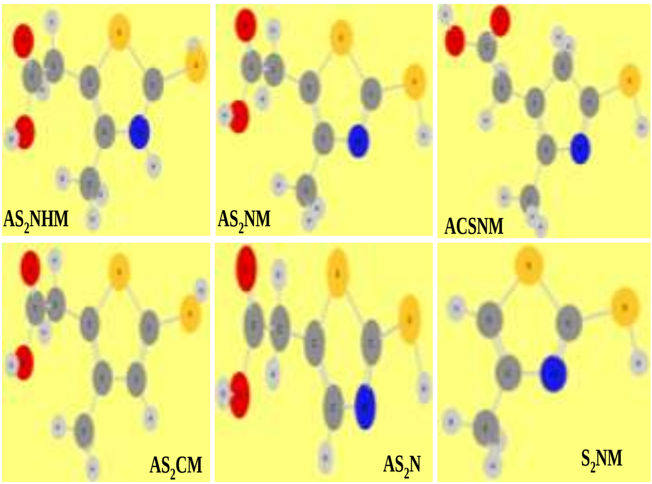

Figure 2. *The fully optimized geometries of the six mercapto-containing chelates: AS_2NHM, AS_2NM, ACSNM, AS_2CM, AS_2N and S_2NM*

3. Results and Discussions

The calculated optimum energy and NBO-partial charges on (*Sulfur of SH, Oxygen of OH, -S-, and -N=*) in the free Mercapto-containing chelates: (A) 2-(2-mercapto-4-methyl-2,3-dihydrothiazol-5-yl)acetic acid **(AS_2NHM)** (B) 2-(2-mercapto-4-methylthiazol-5-yl)acetic acid **(AS_2NM)** (C) 2-(2-mercapto-5-methyl-3H-pyrrol-4-yl)acetic acid **(ACSNM)** (D) 2-(5-mercapto-3-methylthiophen-2-yl)acetic acid **(AS_2CM)** (E) 2-(2-mercaptothiazol-5-yl)acetic acid **(AS_2N)** (F) 4-methylthiazole-2-thiol **(S_2NM)** which have been schematically shown as chelates (A–F) in Figure 1, are tabulated in Table 1. Furthermore, the calculated bond lengths of carbon-sulfur (C-S) bond, carbon-carbon double bond (C=C) and carbon-nitrogen double bond (C=N) for all indicated chelates are included in Table 2. The calculated optimum energy and NBO-partial charge of (S of SH and metal ion) in mercury complexes with the six chelates are all included in Table 3. The fully optimized geometries of mercapto-containing chelates listed in Table 1, are again shown in Figure 2. The calculated structural parameters; bond lengths (C-S, C=C, C=N, and Hg-S) and bond angle (S-Hg-O or S-Hg-N) for mercury complexes with the six chelates are included in Table 4.

As noted from data in Table 1 and Table 3, all simulated complexes of the six chelates with mercury, show higher stabilization energy than the parent chelates, indicating that more stability was gained when both (*chelates from one side and Hg-metal ion from the other side*) engaged in the event of complexation.

Amongst all, the highest optimum energy is recorded for the simulated complex ACSNM-Hg, Table 3. In this simulate, the complexation interaction involves the free chelate ACSNM (*Table 1 and Figure 2*), where by close looking at the structure of the mentioned chelate, we easily see it differs from the others in the fact of having $-CH_2$ group in place of the sulfane (-S-) mediating group in the thiazol ring. Therefore, optimum energy (*stability*) observed for this chelate, is believed to arise in result of this modification. In other words, this means that, $-CH_2$ group compared to sulfane (-S-) mediating group enhances the delocalization within the thiazol ring. In consequence, more relaxation in the whole structure of the chelate is attained and therefore more stabilization (*higher negative optimum energy values*) is observed in cause of this effect.On the other side, this aforementioned delocalization, is no doubt lowering the abundance of electron density assumed to localize on substituents attached to thiazole ring, particularly, -SH group. This is observed in data of Table 3, where S of SH in ACSNM-Hg has the highest electronegative charge value.

AS_2NHM-Hg complexation, in contrast to ACSNM or AS_2NM, has shown a noticeable electron density lowering on thiolic-sulfur. This simply can be explained based on the same argument made a head for ACSNM. In AS_2NHM, and compared to ACSNM, -S- and -NH- groups are installed in place of $-CH_2-$ and -N= groups within the thiazole ring. Based on values of the calculated atomic charge densities *(Table 3)*, the mediating groups -S- and -NH- have together worked better and promoted more electron density sweeping toward the complexed Hg than was observed for ACSNM which have $-CH_2-$ and -N= couple (*as mediating groups*) and AS_2CM which have $-CH_2-$ and -S- couple (*as mediating groups*) or the other chelates having -S- and -N= couple (*as in AS_2NM, AS_2N and S_2NM*). Again, and in terms of charge density, this explains the decrease in negative charge density (- 0.104) developed on S of -SH after complexation). This simple comparison between chelates in terms of their electronic donation to Hg, has actually assisted exploring the retarding effect of the mediating coupled group -S- and –N= on availability of electronic density on -SH donor site. On the other hand, if we again established a second comparison between AS_2CM and AS_2NM, we further ensure the conclusion reached previously. Which is, $-CH_2-$ in AS_2CM versus -N= in AS_2NM was better translating the electronic density (*better electronic delocalization enhancer*) toward the attached terminal groups and across the thiazole ring.

At this moment, it is important to look at the other factors that may interfere with the electronic delocalization across the thiazole ring in free chelates (*simulates*). Whether enhancing or inhibiting, these factors would at the end, exert their effect on the tethered terminal groups, -SH group in particular. Building up a connection between charge density numbers in case of free chelates (*before complexation*) with those of the coordinated chelates *(after complexation)*, would hopefully, enable better understanding of the map of electronic charge distribution over various atoms within the chelate system in general and over donor atoms in particular, this is either before or after complexation with Hg. For example, and as a result of the enhanced electronic delocalization in ACSNM, we would not expect thiolic-sulfur to be rich in charge density (*charge density on S of SH = + 0.059*). In contrast, in chelates like AS_2CM, where no similar effective electronic delocalization, we find the electronic density on thiolic-sulfur is more localized and therefore more electron rich sulfur atom (*charge density of on S of SH = + 0.047*).

Data presented in Table 4 (*namely the bond length and bond angles*) are actually calculated to serve tracking the variation of charge density in vicinity of thiolic- sulfur donor atom as a function of structural modification. Wise reading the data in the indicated table, would provide insights of how charge density is distributed on donor atoms; (*S of -SH and O of -OH)* as mother simulate is subjected to this modification. Furthermore, studying the proceeded variables around sulfur in specific, is believed to be helpful in mapping the charge density (*localization/delocalization*) around this atom and how structural changes made on mother chelate interfere with the donation ability (*whether enforced or weakened*). This, of course, is considered as a consequence of dispersing or/accumulating the charge density around the donor atom itself or in the close proximity.Therefore, we would relate the structural modifications performed on the engineered simulates to the quantity of NBO-charge gathered on sulfur for each case. The key in establishing this relationship between the two; bond geometries and charge density on sulfur is based on the fact that, mobilizing electrons through a bond, affects its force constant and thus force adopting certain bond geometries. As basically known, electrons when added to the bond, higher bond order (*bond strengthening*) arises, and vice versa happened to the bond, if electrons are withdrawn from the bond. This kind of effects, would in result appears as a change in bond parameters (*bond distance shortening/lengthening*) or as (*bond angle shrinking/opening*) in other situations. Therefore, our focus will be on calculating these variables for carbon-sulfur bond and other bonds in proximity, particularly Hg-S bond. Figure 3 below, provides us with an over simplified graphical representation showing the variation in bond lengths (Hg-S, C-S) as a function of charge density variation on both Hg and S of -SH which has been left behind after complexation.

As shown in the Figure, the amount of charge density left behind on thiolic-sulfur and on Hg metal ion after complexation in structure B is decreased from -1 to
- 0.146 for sulfur and from + 2.0 to + 0.480 for Hg, this is compared to -1 to - 0.178 for sulfur and from + 2.0 to + 0.109 for Hg in structure A. In addition, the bond distance of C-S in B ($1.78A^0$) is shorter than that in A ($1.84A^0$), while the bond distance of Hg-S in B ($2.83A^0$) is longer than that in A($2.63A^0$). All these introduced measures in Figure 3, indicate that coordination of Hg through Sulfur/ Oxygen couple is more favored and effective compared to coordination via Sulfur/ Nitrogen couple as donor atoms. This is no doubt is clear when we compare the bond length of Hg-S in B relative to that in A. Involvement of oxygen along with sulfur in the coordination interaction with mercuric ion is more competing and thus more effective in stabilizing the

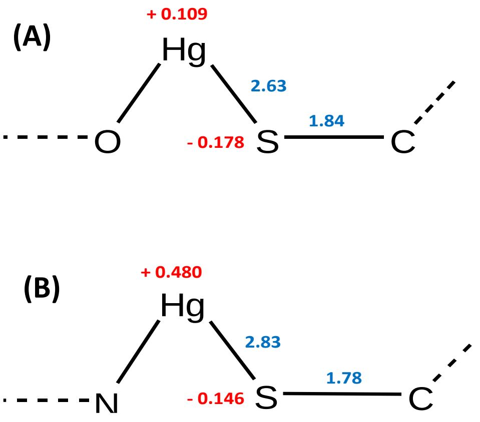

Figure 3. *An over simplified graphical representation showing bond lengths (Hg-S, C-S) and charge densities of (S of SH and Hg metal in the complex AS_2NM-Hg) variations in two situations: when (A) Hg is S-, O-bonded and (B) Hg is S-, N-bonded. Note (data included in the figure are extracted from Table 4.*

Hg ion than nitrogen does when involved in bonding in place of oxygen. In effect and for the rest of this article, only the case of Sulfur/ Oxygen coordination with Hg, will be considered throughout the discussion part.

3.1 Analyses of bond lengths and angles.

Data presented in Table 1-3 are calculated to correlate the variation in charge density in vicinity of thiolic-sulfur as a donor atom with respect to the position of the mediating groups (-S-) or (=N-), Figures 1 and 2. This kind of correlation, would be deduced from the bond distance and bond angle variations. Therefore, we would focus on the carbon-sulfur (C-S) bond length and Sulfur-Mercury-Oxygen (S-Hg-O) and Sulfur-Mercury-Nitrogen (S-Hg-N) bond angles in proximity.

Data presented in Table 2, reveals that:

Case (1) for mercury-complexations through (*thiolic-sulfur/carboxylic oxygen),*

Metal-Sulfur (M-S) bond length (8.54 ^{0}A) is the longest for AS$_2$NHM-Hg complex, and is the shortest for AS$_2$NM-Hg and AS$_2$N-Hg (*both have 2.64 ^{0}A bond distance value*). As numbers revealed, AS$_2$NHM chelation was not effective enough, this is when compared to chelation effectiveness observed for AS$_2$NM and AS$_2$N, where both have recorded lower bond distance value compared to that for AS$_2$NHM. It is clear that, -S- (a*long with* -NH-) as a mediating groups in AS$_2$NHM-Hg, are not functioning reasonably in motivating thiolic-sulfur toward strong chelation of mercuric ion.

However, in AS$_2$NM-Hg and AS$_2$N-Hg, -S-functionality (a*long with* -N=) as mediating groups, are forming a good couple in motivating thiolic-sulfur toward strong chelation with mercuric ion. Another observation worthy mentioned, is that, no significant role is seen for the -CH$_3$ group in enhancing thiolic-sulfur toward mercury chelation. This is obvious, when we compare AS$_2$NM-Hg with AS$_2$N-Hg, (*the later has no -CH$_3$ group*), where both have shown comparable values of Metal-Sulfur (M-S) bond lengths. Similar to AS$_2$NHM-Hg, the complex ACSNM-Hg *(where -S- is accompanied with -CH$_2$- as mediating group partners and* (*M-S bond distance = 4.55 ^{0}A*) is not providing a better evidence for effective chelation between thiolic-sulfur and mercuric ion.

Case (2) for mercury-complexation through (*thiolic-sulfur/ nitrogen of -N=*),

the Metal-Sulfur (M-S) bond length is very similar as observed in all cases of complexations (*it is 2.84 ^{0}A on average*), Table 4. This clearly indicates that, this kind of chelation satisfies higher degree of independence on structural variations within the ligand than the case of chelation through (*thiolic sulfur/ oxygen*). This complexation behavior witnessed for (*thiolic-sulfur/ nitrogen of -N=*) donor sites toward mercury, can be attributed to the close matching in electronegativities for sulfur/nitrogen couple than for sulfur/oxygen couple.

Again for the case of (*thiolic-sulfur/carboxylic oxygen)* bonding and based on the aforementioned discussed trends in Hg-S bond distances observed for the proceeded six chelates with mercury (*which was, AS$_2$NHM-Hg (8.54A^0) > ACSNM-Hg (4.55A^0) > AS$_2$CM-Hg (2.66A^0) > AS$_2$NM-Hg ≈ AS$_2$N-Hg (2.63A^0)*), we may deduce more about the role of the mediating groups (-S-) and (=N-) on the charge density influx toward -SH group. This can be attained, if we correlated the Hg-S bond distances to the amount of interaction between the approached positively charged mercuric ion and the electronegative sulfur atom. As known, the amount of attraction between the two is basically related to the polarizability of mercury from one side and to the electronegativity of sulfur from the other side. Accordingly, we find ourselves obligated to broaden the image, and look at the hardness parameter of chelates rather than focusing only on negativity of the donation site. This actually, enable resetting a new connection between chelate characteristics and its chelation effectiveness. Data in Table 5, present this in hands and therefore, would allow tying up this connection, where as shown in Table 5, the total hardness of chelates is estimated as the measure of the gap between HOMO and LUMO molecular orbitals of the chelate. According to data in Table 5, AS$_2$NHM has an increased total hardness value (η = 3.13), AS$_2$NM ≈ AS$_2$N has little lower total hardness (η = 3.06), however, ACSNM has recorded the lowest value of total hardness (η = 1.02). If we recalled that, AS$_2$NM and AS$_2$N, both have shown shortest Hg-S bond length compared to that for AS$_2$NHM and ACSNM, Table 2, we may conclude that, mercuric is favoring interaction with chelates of moderate hardness rather than those extremely (*hard/ or soft*). Meaning that, mercuric ion (*at least in this study*) is neither acting as hard nor as soft metal ion.

Furthermore, the bond angle S-Hg-O order of change which following the trend

AS$_2$NM-Hg (144.16^0) > AS$_2$CM-Hg (144.06^0) > AS$_2$N-Hg (143.57^0) > ACSNM-Hg (80.95^0) > AS$_2$NHM-Hg (47.26^0), Table 4, can be explained in the light of the increased repulsion between the two negative ends; sulfur and oxygen, in connection with the Hg-S bond distance, this thought is graphically explained in Figure 4a.

To explain the trend of change in S-Hg-O bond angle observed above, we have to consider the change in Hg-S bond length and the charge density values on sulfur/oxygen mutually. For the sake of simplifying the idea, the data numbers for the two extreme complexes; AS$_2$NM-Hg and ACSNM-Hg, will be discussed. In AS$_2$NM-Hg *(the Hg-S bond distance is 2.63A^0, S-Hg-O bond angle is 144.16^0 and the S of SH charge is -0.178),* however, in ACSNM-Hg *(the Hg-S bond distance is 4.55A^0, S-Hg-O bond angle is 80.95^0 and the S of SH charge is -0.207),*

Table 4. Apparently, atomic charge on S of SH is believed to be responsible for the observed S-Hg-O bond angle opening, this is expected as a result of the developed repulsion between the two negative ends; sulfur and oxygen. In reality, and by deep looking at the values of Hg-S bond distance, we find this angle opening is no doubt significantly affected by the Hg-S bond distance variation. In effect, as the Hg-S bond distance becomes shorter, the gap separating the two negative poles (*O and S atoms*) becomes narrower, the factor which promotes more bond angle opening in results of the close distance repulsion. In corresponds, the vice versa is true where, as the Hg-S bond distance increases, the bond angle opening decreases in correspondence. This view of understanding which is graphically presented in Figure 4b, is helpful in justifying the claimed idea that, atomic charge on S of SH cann't be counted as the primary parameter responsible for the S-Hg-O bond angle variations. This can be explored by calculating the bond distance ratio to bond angle ratio for the two complexes considered in previous (*bond distance ratio = (Hg-S bond distance)$_{AS2NM-Hg}$(2.63)/(Hg-S bond distance)$_{ACSNM-Hg}$ (4.55) = 0.58*) and (*bond angle ratio = (S-Hg-O bond angle)$_{AS2NM-Hg}$ (144.16)/(S-Hg-O bond angle)$_{ACSNM-Hg}$ (80.95) = 1.78, where 1/ 1.78 ≈ 0.58*). Another important conclusion based on this finding, is that, values of S-Hg-O bond angle, reveal that change in S of SH atomic charge goes in harmony with the change in the Hg-S bond distance.

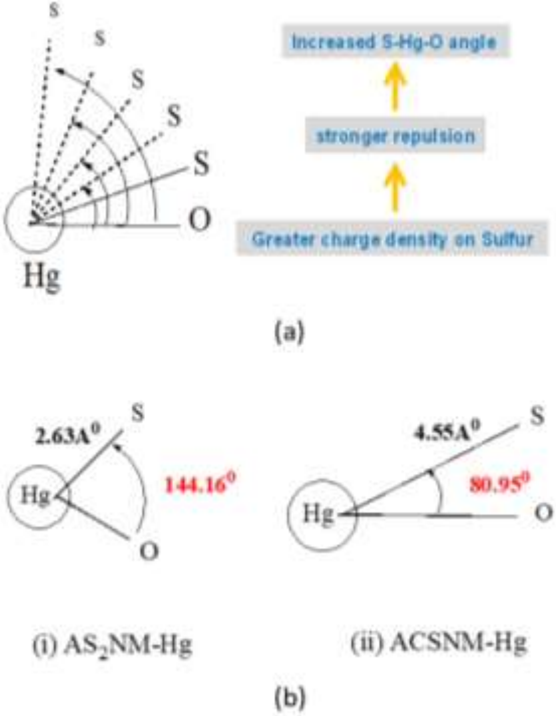

Figure 4. *(a) Graphical explanation of the view of increasing S-Hg-O bond angle as charge densities on sulfur/oxygen increases (b) S-Hg-O bond angle variation in connection with the Hg-S bond length in the two extreme complexes AS$_2$NM-Hg and ACSNM-Hg.*

Furthermore, and based on the idea of comparing the Hg-S bond distances in the formed complexes; ACSNM-Hg, AS$_2$NHM-Hg, AS$_2$NM-Hg and AS$_2$N-Hg, we may observe that, AS$_2$NM (*the chelate under investigation*) has shown a remarkable binding efficiency toward Hg cation (where *Hg-S binding distance is 2.64*, for S, O-*bonding, Table 4*) compared to its comparable chelates. The chelate AS$_2$N has recorded a similar Hg-S binding distance reading (2.64), while the chelate AS$_2$CM has recorded a little bit more increased binding distance (2.66). The other chelates (*namely ACSNM and AS$_2$NHM*) on the other hand have recorded an extremely increased bond distance. By being moderately hard (*Total Hardness (η) (eV)=3.056, Table 5*) the chelate AS$_2$NM, is looking in a better position toward building up an efficient binding interaction with Hg ion. In support of this, is the AS$_2$N which shows very close hardness value (*3.067*). Therefore, AS$_2$NM and from hardness perspective, is looking effective in respect of chelation for the Hg metal ion, this is despite of its weakness (*or failure*) in stabilizing *(through lowering the positivity)* the Hg metal ion, as have been concluded in earlier sections. The other chelates, are even further weak as chelating agents toward Hg ion, as indicated from their values of Hg-S binding distances and from their corresponding hardness values as revealed from data in Tables 4 and 5, respectively. What goes in parallel with this, is the amount of charge density left behind on thiolic-sulfur after coordination. As such, and by adopting the data in Table 2, we can establish a relationship between the amount of positive charge developed on Hg metal ion upon chelation and the negative charge left behind on thiolic-sulfur atom after chelation completion. In principle (*and as a consequence of donation to the metal ion*) as the negative charge density on sulfur donor atom goes down, the Hg metal ion positive charge density, is correspondingly dispersed more.

3.2 Analysis of charge density on S, N and O-donor atoms

Figure 5, shows the images of charge density distributions in the free chelates (AS$_2$NHM), (AS$_2$NM), (ACSNM), (AS$_2$N), (S$_2$NM) and

(AS_2CM) presented in two ways (a) distributed surfaces, and (b) distributed contours. Images in both figures, clearly show that charge density accumulation and thus probability of effective donation primarily lies on thiolic-sulfur and carboxylic-oxygen donor sites, rather than amidino (=N-) site. Plotted data in Figure 5, is supported by the values of atomic charge densities listed in Table 1.

Based on the fact that oxygen and nitrogen atoms, generally have more elevated electronegativities compared to sulfur atom, we therefore, will focus on the later, at the moment, and consider it as the principal donor site for the incoming metal ion. This consideration would be more reasonable, if we further took the property of *softness/hardness* into account.

Presenting both parameters (*the lower electronegativity and the increased softness of sulfur relative to that of oxygen or nitrogen*) into consideration, lets thiolic-sulfur in a position of the most attractive and valuable binding site for the incoming mercuric ions in particular. According to numbers in Table 1, we find that AS_2CM has shown the richest thiolic-sulfur by recording the lowest value of electronpositivity (*charge density = + 0.047*).

On the other extreme we find AS_2N has recorded the highest value of electron positivity (*charge density = + 0.062*) on thiolic-sulfur atom, meaning that this sulfur is the poorest in charge density. If compare the structure of AS_2CM with that of AS_2N, we find both of them having $-CH_2COOH$, SH and -S- in common and differ in the fact of having -C= in place of -N= and $-CH_3$ group in place of H in AS_2CM in contrast with AS_2N. No doubt that existence of $-CH_3$ in AS_2CM but not in AS_2N and replacement of -N= in AS_2N by -C= in AS_2CM, are suspected to enrich thiolic-sulfur in AS_2CM compared to that in AS_2N. In other words, this means that, electron density furnished by $-CH_3$ group is assumed to be directed into the thiolic-sulfur through -C= moiety, the factor that would keep thiolic-sulfur rich with electron density in AS_2CM relative to that in AS_2N which lacks similar structural features.

The role of $-CH_3$ group as an electron density donating group is clear in all other chelates possessing this group (*ACSNM, AS_2CM, AS_2NM, S_2NM and AS_2NHM*). This is obvious when we compare the value of electron density on thiolic-sulfur in all of these chelates containing $-CH_3$ group compared to AS_2N chelate which lacks this group, Table 1. Similarly, existence of -C- in ACSNM compared to -S- in all other chelates included in the study, even weakly, is found to enforce enrichment of thiolic-sulfur with charge density. This is clearly seen by comparing the value of charge density on thiolic-sulfur in ACSNM (+ 0.059) with that in AS_2NM (+ 0.061).

If we turned back our attention to S_2NM chelate, where no acid group $-CH_2COOH$ attached to the thiazol ring, we deduce that existence of acid group in this chelate prohibits electronic density delocalization toward thilolic-sulfur. This again is concluded based on the values of charge density recorded for S_2NM chelate compared to that in other chelates containing $-CH_2COOH$ acid group of the same structures. For example, charge density on thiolic-sulfur in S_2NM is (+ 0.054) and is (+ 0.060) in AS_2NM, Table 1. Furthermore, and to explore the role of -N= mediating group on charge density delocalization toward thiolic-sulfur, this group -N= was replaced by -NH- in AS_2NHM. As seen, thiolic-sulfur in AS_2NHM (*charge density + 0.052*) is less electropositive than that in AS_2NM (*charge density + 0.060*), indicating that -NH- was more allowing the charge density to pass through and reaches thiolic-sulfur than -N= group permits. If we related the values of thiolic-sulfur charge density (*Table 1*) and total hardness (*Table 5*) together from one side with the Mercury-Sulfur (Hg-S) bond distance (*Table 4*) from the other side, we easily find that AS_2NM-Hg (*compared to the other chelates*) has formed the shortest Hg-S binding distances (*2.63, i.e the strongest binding through S, O-bonding*). This takes us to the fact that, both factors; charge density and chelate hardness, work together to establish stable binding for mercury.

A support for this, is coming from the complex AS_2NHM-Hg which has shown the longest Hg-S bonding distance (*8.54, Table 4, thus weakest binding for mercury*). Accordingly, AS_2NHM and by being very hard chelate (*total hardness 3.13, Table 5*) it again brought to mind, the role of softness/hardness matching with mercury and how much effective this factor in determining the final image of binding the ion. Up to this moment, and regarding this perspective, we may say that, AS_2NM was able of developing stronger binding with Hg metal ions than other chelates could have done, this (*as proceeded*) is attributed to softness close matching with Hg ion. Herein also, we may say that, charge density on thiolic-sulfur appears to have a secondary effect on the binding effectiveness of the chelate AS_2NM toward Hg ion. This understanding of the chelate/mercury binding, becomes more reasonable when we further consider the softness matching between the two; Hg ion *(as an acceptor)* and sulfur atom *(as a donor).* In corresponding, oxygen is not expected to establish such strong binding with mercury due to hardness mismatching between the two as was the case with sulfur.

Overall, *(and depending on the values of Hg-S bond distance and S-Hg-O bond angle)* AS_2NM among the comparable chelates was shown the greatest extent of effectiveness in utilizing the couple; sulfur and oxygen donor atoms in binding the incoming mercuric metal ion. Actually, mentioning this finding, should be tied with the structural layout sequence of SH, -S- and -COOH groups along with existence of -S- and –N= as the mediating groups in this chelate. This view is graphically expressed in Figure 6, where -S- functionality is mediating the path of electron density passage in the track between -COOH and SH, which is believed to have a key role in controlling the flow of electron density forth and back this line.

It is believed that, charge densities on the two heteroatoms -S- and =N- also should be taken into account and brought to discussion owing to their usefulness in explaining the variation in charge density on thiolic-sulfur and hydroxyl-oxygen of carboxylic group. By looking at charge density values in Table 1, we find -S- is showing a constancy in charge density variation (*it is around ~ 0.4 in all of the chelates containing -S- and =N- as mediating groups*). What is more interesting, is the amount of charge density on =N- group, where as seen from data in Table 1, =N- is accumulating much more electron density than -S- did. This would encourage classifying (-S-) to be a better charge density transformer than =N- and therefore would be expected to allow more charge density to cross in either direction between -SH and -COOH. In broaden, this observation is noticed for the other two chelates *(namely, AS_2N and S_2NM)* containing -S- and =N- mediating groups.

Correspondingly, the proceeded described mechanism of electron density delocalization has not furnished rich thiolic-sulfur in electron density and in results a retardation effect for chelating effectiveness of the electropositive mercuric ion, Figure 6. As such, AS_2NM as well as, all other chelates of similar structures, would not be considered a qualified chelating agents to serve as good chelators (*extractors*) for mercuric ions in concern. In reality, this interesting conclusion can be considered as the most important finding in this study. Where this can be viewed as a good example of performing theoretical calculations on systems to investigate their capability in acting as efficient chelators for specific metal ions and in explaining some experimental findings that were unjustified at the time of experimental performance[27]. Connecting the charge density values presented in Table 1 with the charge density images shown in Figure 5, in addition we find that, whenever the charge density value of a given chelate is elevated, the charge density spot around donor atoms (*specifically, sulfur and oxygen*) is larger in size and more intensified in yellowish-red color. Actually, these images, are interesting and very beneficial in providing the investigator with a clear naked eye vision of how charge density is distributed around donor atoms within the given chelate. This kind of eye looking inside the structure of the chelate, would not be realized if we just had dealt with the charge density as bare listed numbers in tables.

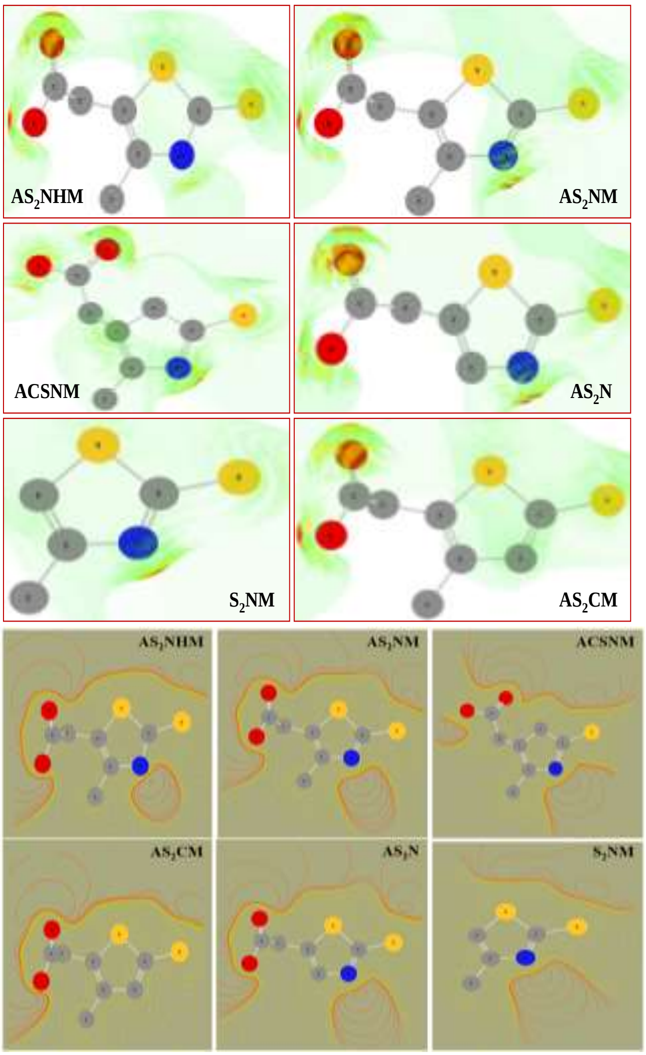

Figure 5. *Images of charge density distribution in the simulated chelates:* ***(AS_2NHM), (AS_2NM), (ACSNM), (AS_2N), (S_2NM) and (AS_2CM)*** *expressed in (a) as distributed surfaces (b) distributed contours*

The valued observations we may notice in Figure 5, are: First; in ACSNM, AS_2NHM, AS_2NM and AS_2N chelates, the charge distribution contours are clearly layout on thilolic sulfur, -S- and -COOH groups. If we looked deeply at the structure of these four chelates (*ACSNM, AS_2NHM, AS_2NM and AS_2N compared to S_2NM and AS_2N*) we see them differ in the layout sequence of -SH, -S- and -COOH functionalities, where in all of the four, -S- mediates the two groups -SH and -COOH, Figure 5. Furthermore, and as seen from the figure (*keeping in mind that, nitrogen is more electronegative than sulfur*), we find, =N- accumulates significant portion of the total molecular electron density. This withdrawn part of electron density by =N- functionality, is at the expense of electron density assumed to delocalize toward -SH or -COOH groups, the effect which lowers -SH electron density. As a consequence, readiness of -SH for donation will be inhibited in general. This point of understanding is graphically presented in the oversimplified plot shown in Figure 6.Second; tethering the methyl group to chelates included in the study, has been noticed *(even insignificant)* to enhance the electron density richness of thiolic-sulfur. This is seen, when charge density on -SH of AS_2N chelate is compared with its comparables *(ACSNM, AS_2NHM, AS_2CM, S_2NM in general and AS_2NM in particular)*, Table 4. In AS_2N, where no methyl group is attached, we find thiolic-sulfur is more electropositive (+ 0.62) compared to (+ 0.47 to + 0.60 on average) in chelates with methyl group. This in other words means that, electron density extracted from methyl group, was not fully recruited to enrich -SH as was hoping, rather, it was partitioned and swept toward oxygen of -COOH and nitrogen of =N- and little toward sulfur of -SH. We may attribute this behavior to the increased electronegativities of either oxygen or nitrogen compared to sulfur, where electron density is enforcedly directed toward oxygen and nitrogen, and beyond sulfur.Third; similarly, and to examine the effect of existence of -COOH group within the structure of the above chelates, we compare the amount of charge density accumulated on thiolic-sulfur in those containing this group (*namely; ACSNM, AS_2NHM, AS_2NM, AS_2CM and AS_2N)* to that in S_2NM chelate, which does not contain this group. Based on numbers in Table 1, and on average, all of the five chelates containing this group, are shown a more electropositive thiolic-sulfur compared to that in S_2NM chelate where no -COOH group. This simple comparison, clearly indicates the retarding effect of -COOH on chelating effectiveness of thiolic-sulfur, this is by interfering with sulfur of thiol through withdrawing a portion of charge density *(which was assumed to intensify on -SH)* due to the increased electronegtivity of oxygens of -COOH over sulfur of -SH.

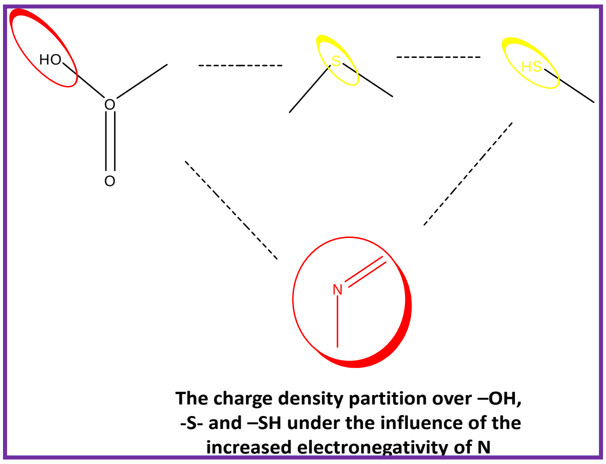

Figure 6. *Oversimplified plot showing the withdrawal effect of =N- functionality on SH richness with electron density.*

3.3. Analysis of the occupation of the frontier HOMO-molecular orbital component

Tuning the images of the highest occupied molecular orbitals (HOMOs) shown in Figure 7, with the images of charge density distribution over donor atoms in free chelates shown in Figure 5, reinforces the conclusions that have been proposed in the proceeded sections. Overall, achieved results are hoped to get us to the original aim of the study in which, we struggle to realizing how charge density could be directed toward a specific donor atom and thus be raised to act as an efficient electron donor. Achieving this goal, as in our case, would allow controlling the efficiency of thiolic-sulfur or carboxylic-oxygen as donor atoms. Therefore, studying HOMO occupation is very important, not only because of its relation to donation/acceptance activities, but also due to its emergence with the electronic properties of compounds. Computational results included in Figures 5, 8, and 9 are thus expected to be helpful and feasible in figuring out the electronic redistribution inside the simulate system. As seen in Figure 7, the free chelates; AS_2NHM, AS_2NM, AS_2CM, AS_2N and S_2NM chelates except ACSNM, all are having their HOMO orbitals localized over sulfane (-S-) orbitals, whereas, the HOMO orbital of ACSNM is localized over thiolic-sulfur. Actually, this piece of finding is considered very important since it clearly shows a strong evidence that sulfane (-S-) mediating group in AS_2NHM, AS_2NM, AS_2CM, AS_2N and S_2NM chelates is responsible for the decreased electron density on thiolic-sulfur. This is by cutting the electron density path and preventing it from flowing toward thiolic-sulfur. In ACSNM, the sulfane group -S- group is replaced by -CH_2- group, and as appears a significant portion of electron density passes through and flows toward thiolic-sulfur, the factor that kept this sulfur electron rich and mature for effective donation upon coordination with the involved metal ion, as clearly seen from HOMO image. Owing to that fact of similarity between S_2NM and AS_2NHM, AS_2NM, AS_2CM, AS_2N in having the HOMO localized on -S- atom and the fact of absence the carboxylic acid group -COOH from structure of S_2NM, we may deduce that this acid group has no proven effect on directing the HOMO

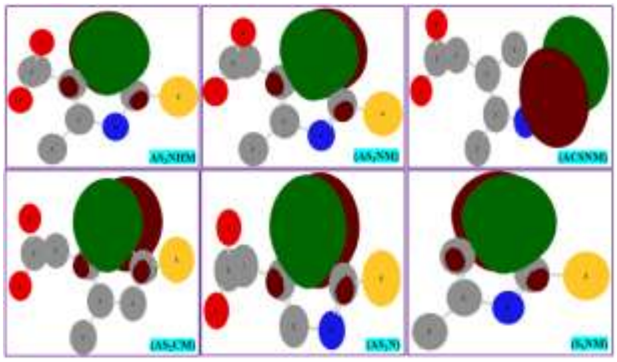

Figure 7. *Occupation of the frontier HOMO molecular orbitals of the free chelates: AS_2NHM, AS_2NM, ACSNM, AS_2CM, AS_2N and S_2NM chelates, respectively*

orbital to settle on -S- rather than on -SH group in particular. Even though, the role of carboxylic acid groups is primarily profound in; (i) withdrawing a large extent of electron density away from -SH to finally localized on -OH of -COOH *(where, charge density on oxygen is (- 0.78 on average for all chelates, Table 1)* (ii) offering the carboxylic oxygens to hold the LUMO molecular orbitals, such as in the chelates; AS_2NHM, ACSNM and AS_2CM *(where, all are not containing the mediating group couple, -S- and =N-).*

Going back to Figure 7, we see that chelates whether containing methyl group (*such as AS_2NHM, AS_2NM, AS_2CM, S_2NM rather than ACSNM*) or that does not *(namely AS_2N)* all do have the HOMO orbital laying on orbitals of the mediating -S- group and not on orbitals of -SH group. This means that, the extra electron density furnished by the methyl group, was not directed toward -SH to enrich sulfur as was assumed, rather it was crossed and contained by -S- group which is part of the thiazol ring, as seen in HOMO images.

The chelate ACSNM, solely shows the case of HOMO orbital being existed on thiolic-sulfur. By showing this ideality of localizing HOMO on -SH, this chelate in addition, has focused on and proved the critical role of the -S- mediating group in prohibiting the electron density from reaching out thiolic-sulfur. This is obvious, after installing $-CH_2-$ in place of -S- as mediating group. This finding is be claimed as the most important one in this study.

Turning our attention to the case of localization of LUMO orbitals in the six chelates, we differentiate two kinds of images in Figure 8. In the first kind; LUMO localization occurs on p-orbital of the -C=O group, this is seen in AS_2NHM, ACSNM and AS_2CM. In the second kind; LUMO localization occurs on p-orbital of -N=C-SH group, AND this is as seen in AS_2NM, AS_2N and S_2NM chelates *(which all have -S- and =N- as mediating group couple in common)*. Wise reading the two cases, we find that images of LUMO orbitals, suggest two possible sites for accommodating the electron density as it is back donated from mercury to the LUMO empty orbital of the chelate. In AS_2NHM, ACSNM and AS_2CM, this back donation fills the empty antibonding π-orbitals of -C=O, while in AS_2NM, AS_2N and S_2NM, the back donation fills electron density to the empty antibonding π-orbitals *(formed from p-orbital of nitrogen and carbon)* of -N=C-SH, Figure 8.

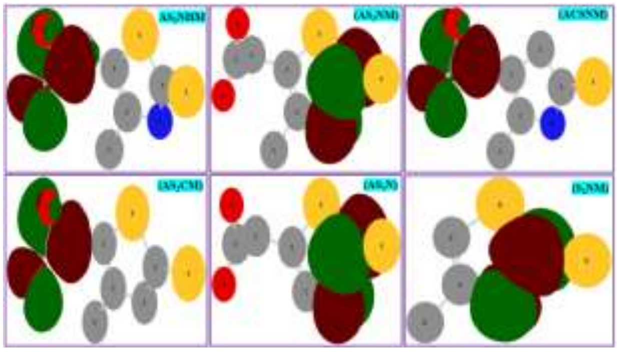

Figure 8. *Occupation of the frontier LUMO molecular orbitals of the free chelates: AS_2NHM, AS_2NM, ACSNM, AS_2CM, AS_2N and S_2NM chelates, respectively*

4. Conclusions

In summary, we have theoretically studied sex simulated chelates of the type; mercapto-containing chelates, along with their corresponding simulated complexes with Hg metal ions employing density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations at the B3LYP/LANL2DZ level of theory.

Results indicate that:

Mediating groups (*Sulfane -S- and imine =N-*) along with the substituents groups (*methyl $-CH_3$ and carboxylic -COOH*) were proved to practice important effects on charge density localization/delocalization on thiolic-sulfur as a donor atom of the proposed simulates. Where, responses for the various modifications brought by these groups in all simulates were tracked and monitored by calculating the charge density on thiolic-sulfur and atoms in proximity. Related changes in geometrical parameters, namely, bond lengths and bond angles in the neighborhood of thiolic- sulfur were also considered to hopefully provide us with more insights about the effect of the performed modifications. To figure out the distribution of charge density inside the simulate system, images of HOMO-LUMO molecular orbitals and charge density distribution surfaces are also presented.

Based on data gathered for the studied chelates, computations have showed that,

(i) Methyl introduction into thiazol ring was not beneficiary enough to enrich and enforce thiolic-sulfur with the charge density necessary for building up strong binding with mercuric ion. For example, in AS_2NM (*which is a methyl containing chelate)*, the charge density is 0.060 and in AS_2N *(which is a methyl lacking off chelate),* the charge density is 0.062, Table 1.

(ii) Among the sex chelates *(ACSNM, AS_2NHM, AS_2NM, AS_2CM, AS_2N and S_2NM)*, only AS_2CM, has possessed the richest thiolic-sulfur in charge density. This is seen from the charge density numbers, Table 1 and HOMO orbital images, Figure 7. This finding was attributed to the effect of replacement of the mediating group –N= by -CH_2-, where the later (-CH_2-) seems to allow more electron density passage toward thiolic-sulfur during the delocalization process of the electron density within the thiazol ring. This property possessed by -CH_2- compared to -N= , arises from the fact that carbon in contrast to nitrogen, is significantly lowered in electronegativity. This vision is also supported by the images of LUMO orbitals shown in Figure 8.

(iii) Whenever, the mediating groups *(sulfane -S- and imine =N-)* were replaced, by *(methylene –CH_2- or imide -NH-)* the LUMO turns to localize on orbitals of C=O moiety of the carboxylic acid group. This suggests the ease of movement of electron density through *(-CH_2- or -NH-)* compared to *(-S-)* as crossing from the side of thoilic group to the side of carboxylic group. This activity obviously occurs under the effect of the increased electronegativity of carboxylic oxygen relative to that of thiol-sulfur.

(iv) Thiolic-sulfur charge density is not the key parameter in governing the binding effectiveness toward the mercuric ion, rather, other interfering parameters were proposed to exert countable effects on the binding process. Among these factors are; electronegativity of the donor atom, nature of either the metal ion (*mercury in our case*) and the chelate used; hardness/softness matching between the two, total harness of the chelate, nature of the mediating group, layout sequence connecting the mediating groups, presence of additional subsidiary substituents such as methyl group or the carboxylic group as in our case.

(v) Geometrical parameters *(e. g. bond distance and bond angle)* were employed to show more proofs for the proposed theory of binding between the mercury ion and the involved chelate according to our understanding.

(vi) Findings of the current study, have clarified the drawback of the AS_2NM chelate in particular *(and its comparable chelates in general)* that lay behind its failure in stabilizing the divalent mercuric ion through effective coordination, as was noticed in earlier experimental work.

(vii) Existence of carboxylic group at the other end of the proposed chelates, have been found to practice prohibiting effect on the binding effectiveness in overall. This was concluded owing to the increased electron withdrawal effect exerted by oxygen atoms of the group.

(viii) The mediating group =N- group has shown an interesting behavior, where it was accumulating much more electron density than -S- has done. This refers to the fact that (-S-) would act as better charge density transformer than =N- and therefore, is expected to allow passing larger extent of charge density toward -SH or -COOH.

(ix) In results, this study has answered the critical question, why AS_2NM *(as well as, other chelates of similar structures)* are not qualified to serve as good chelating agent for mercuric ions, as was noticed in earlier experimental study. Honestly, this conclusion is considered the most important and interesting finding of this study. Furthermore, reaching this conclusion, is serving the purpose of recruiting computational chemistry in interpreting some experimental results that were not clear and unjustified at the time of conducting the experiment. This investigation is considered as a pursuing for my research work in which I am interested in recruiting the substituent modification(s) in chelates to feasibly engineer effective inorganic chelating agents. This would be attained through a wise modifications of various substituents when tethered to the mother chelate.

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