RJC

RASĀYAN *J. Chem.*
Vol. 10 | No. 3 |981 - 989 | July - September | 2017
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

THE GROUND STATE Cu^{2+}ION AFFINITIES OF GLYCINE, ALANINE AND CYSTEINE IN GAS AND AQUEOUS PHASE: A DFT BASED COMPUTATIONAL STUDY

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ABSTRACT

A detailed study of Cu^{2+}ion affinities of the amino acids namely Glycine (Gly), Alanine (Ala) and Cysteine (Cys) and their Cu^{2+}complexes have been investigated using density functional theory. Interactions of a Cu^{2+} ion with oxygen, nitrogen, and sulfur (for cysteine) of the selected amino acids have been optimized. The results show that complex formation reactions are exothermic in both gas and aqueous phase and the neighboring stereochemical nature of Cu^{2+}ion is more or less same in all amino acids. The computed Cu^{2+} affinity for both O-Cu^{2+} and N-Cu^{2+} interaction in the gas phase is in this order $\Delta E_{Cys}>\Delta E_{Ala}>\Delta E_{Gly}$. In aqueous phase, Cu^{2+}ion affinity for O-Cu^{2+} interaction follows the same order as above, whereas in N-Cu^{2+} interaction it differs as $\Delta E_{Ala}\geq\Delta E_{Cys}>\Delta E_{Gly}$. In N-$Cu^{2+}$ interaction Zwitterterionic complexes (Cu^{2+} bind with both nitrogen and carbonyl oxygen atom) have been formed. The optimization energies are estimated to be lower relative to the other interactions and the Cu^{2+} ion affinities have been predicted more. The results have been well supported by the natural population analysis (NPA) of the atoms and hardness parameters. The charge, energetics, geometrical and electronic properties of the complexes signify that the interaction between the Cu^{2+} with the carbonyl oxygen and the amino nitrogen of free amino acids is predominantly a covalent interaction in the gas phase and which becomes more ionic in the aqueous phase.

Keywords: B3LYP DFT; Gaussian; Amino acids; Gas phase

INTRODUCTION

Glycine, alanine, and cysteine have important roles as model systems due to the small in structure compared to the other amino acids. They contain a carboxyl group (COOH), an amino group (NH_2) and a side group(R). The side group increases gradually from glycine (R=H) to alanine (R=CH_3) and to cysteine (R=CH_2SH). Copper ion is responsible for oxidation, dioxygen transport, and charge transfer.[1] It also plays an important role in many biochemical processes. The metal binding affinity to the biological fragments has remarkable attention from both experimental[2-6] and theoretical[7-11] points of view. The role of a metal ion in the biochemical process can be known from thermodynamic properties of metal ion-protein interaction.[12] In gaseous phase, binding energies for Cu^{+}ion-amino acid complexes have been studied earlier. The Cu^{+} ion affinities for glycine, serine, and cystein also have been studied theoretically by Hoyau.[13] The metal ions(Mg^{2+}, Ca^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) effect, ion affinities for arginine complexes were reported by Remko[14] where arginine showed the strongest affinity by a Cu^{2+} cation. Interaction of Cu^{+} and Cu^{+2} ions with theα-alanine system has been reported by Nino Russo.[15]

The metal complex stability and preferable binding sites are different, based on the nature of the metal ion. In general, open-shell system $Cu^{2+}(d^9)$ is less stable than $Cu^{+}(d^{10})$ system, but this is not always true. However, in aqueous phase Cu^{+} ion disproportionate to $Cu^{2+}$with an unusual oxidation state and become

http://dx.doi.org/10.7324/RJC.2017.1031798

less stable than Cu^{2+}state. Different theoretical studies on amino acids–copper complexes were found in the literature.[16,17] So far, detailed, systematic comparative studies on the interactions between Cu^{2+} with glycine or alanine or cysteine are rather scarce.

To the best of our knowledge, no more theoretical works have been performed on Cu^{2+} – amino acid complexes in the gas phase as well as in aqueous phases together. A systematic study on metal ion-amino acid complexation is important for better understanding of metal-protein binding mechanism in living systems. Therefore, in order to explore the nature of binding interactions ofCu^{2+} ion with three amino acids glycine, alanine, and cysteine and to find some quantitative thought about comparative Cu^{2+} ion affinities, we have performed a DFT study on the Cu^{2+}– glycine, Cu^{2+}– alanine and Cu^{2+}– cysteine complexes. The conformational behavior of amino acids is necessary to recognize their vibrant role in protein formation. Though, amino acids have a zwitterionic structure in the solid state, subsequently, to get the neutral structure of amino acids, studies are required in gas and aqueous phases. Solvent effect on the energetics and geometries of the complexes has been observed carefully in the present work. We have also focused our attention on the binding sites of the amino acid withCu^{2+} ion and on the optimized geometrical structure of the complexes.

EXPERIMENTAL

DFT calculations were performed at the B3LYP level with 6-311G(d,p) internal basis set for all atoms using the Gaussian 09W program[18] package. In order to understand the structural behavior of the free amino acids and different Cu^{2+} complexes, we carried out PCM[19] (polarizable continuum model) geometry optimization process at the same level of theory. Water was used as a solvent. Both natural population analysis (NPA) and Mulliken population analysis[20] were applied to determine equivalent charges on atoms of the free bases and their metal complexes. The calculated NPA charges help to analyze the nature of the bonding of Cu^{2+}-amino acids complexes.

It has been found earlier that, the DFT method gives almost accurate results for several transition metal-containing systems.[21-23] Hence this method is suitable for studying metal ion complexes. Unrestricted open shell methods have been used to compute the Cu^{2+}systems. Equilibrium geometries for all amino acids and their Cu^{2+} complexes were completely optimized devoid of any symmetry restrictions. In order to minimize basis set super position error (BSSE), final energetic were obtained at 6-311G (d,p) basis set level.

Use of 6-311G (d,p) basis set ensures that the magnitude of the computed BSSE values is small, it is (2.0 to 2.5 kcal / mole) for complexes. Since this is a comparative study and energetic values discussed in this paper are relative to a particular species. Therefore errors occurred in the results will be canceled and does not affect more on Cu^{2+} affinities of the complexes and stability order as well. Thus we neglected this in our study.

RESULTS AND DISCUSSION

We have studied the interaction of Cu^{2+}ion with N atom of the amino group (Cu^{2+} directly bonded with N in initial input) and O atom of the carbonyl group (Cu^{2+} directly bonded with carbonyl O in initial input) of each amino acid. In addition to N–Cu^{2+} and O–Cu^{2+} interactions, we have studied the interaction of Cu^{2+} with S atom of CH_2SH side group in cysteine. The optimization energy is found to be lowest in Zwitterionic cases compared to O–Cu^{2+} or S–Cu^{2+} complexes. The highest Cu^{2+} ion affinity to nitrogen indicates that Cu^{2+} ion preferably binds with – NH_2 group of amino acids to form stable complexes. This is because of the lone pair of nitrogen is loosely bind and a lone pair of carbonyl oxygen atom is more tightly bound, then Cu^{2+} ion interacts more easily with amino N atom. The stability of coordinated complexes depends on the hard-soft nature of metal and ligand (according to HSAB theory).Being borderline acid, Cu^{2+} ion forms a most stable complex with borderline donor nitrogen. This is exactly seen in our study. Results obtained from S–Cu^{2+} complexes of cysteine are not discussed widely, because comparatively lower minimum optimization energies are found from O–Cu^{2+}, N–Cu^{2+} optimization process. Computed total energies(Hartree) of the free amino acids(B) and their complexes(B–Cu^{2+}) and the computed Cu^{2+} ion affinities (ΔE, kcal/mole) are tabulated in Table-1. In both phases, ΔE values are higher for N-Cu^{2+}–O complexes than that of O–Cu^{2+}complexes. The ΔE values are increased by –

20.269,–14.872, –19.603 kcal/mole in the gas phase and it is –6.275, –38.027,–26.293kcal/mole in the aqueous phase for glycine, alanine and cysteine respectively.

The computed net charge on carbonyl O (>C = O) atom and N atom of the amino group of the free amino acids and their complexes in their ground state in gas and aqueous phases are summarized in Table-2. It also reports the net Mulliken charge on Cu^{2+}at the ground state of Cu^{2+} complexes in both phases. The net Mulliken charges on the Cu^{2+} vary from 0.9187eto 1.0637ein the gas phase, on solvation, the values are slightly increased and they are in the range of 1.2918 to 1.3654 e. The values of the atomic charges on Cu in O-Cu^{2+} complexes indicate some shifting of electron density to the metal ion. Similarly, for N-Cu^{2+}-O complexes, the net charge on the Cu varies within 1.1708 to 1.3805e in gas and it ranges from 1.4932 to 1.5099 e in the aqueous phase. This shifting of electron density is not local; it originates from an entire molecule which is obvious from the estimated net charge on O and N atom of the Cu^{2+}complexes. The carbonyl O atom and amino N still carries a negative Mulliken charge, which is increased compared to the amino acids in both phases.

The important component of the valence interaction is the charge transfer (CT). We have used this quantity to determine the degree of valance interaction in the present cation-dipole complexes (B-Cu^{2+}). The calculated atomic charges and the net amount of CT from the base to $Cu^{2+}$are given in Table-3. We have seen that the degree of CT increases from gas phase to aqueous phase. We also observed that, for the N–Cu^{2+}-O complexes, the degree of CT is more than that of O–Cu^{2+}complexes. The results revealed that theN-Cu^{2+}interactions are more ionic.

The partial NPA charges on metal ion in all the metal-amino acid complexes and ligand to metal charge transfer (Q_{CT}) in both gas and aqueous phases are summarized in Table-4. The results show that, there is a significant charge transfer from ligand to the metal ion. A good correlation between the extent of charge transfer and complex stability were observed. In both phases, the extent of charge transfer in both complexes follows the decreasing order as cysteine > alanine > glycine. This is well supported by the computed Cu^{2+} affinity values.

We are to find out the possibility of the existence of a correlation with a single global parameter of the entire molecule through our investigation. We have selected the hardness (η) as the global parameter, $\eta = (I - A)/2 = (\varepsilon_{LUMO} \sim \varepsilon_{HOMO})/2$ reported in Table-7. In both phases, hardness values of glycine and alanine are almost same and it is found to be slightly less for cysteine. Obtained η values clear that, a good correlation between η and Cu^{2+}ion affinity values of the amino acids could be made. In this series, glycine has the highest η value whereas its Cu^{2+} ion affinity is the lowest.

It also shows that both pre- and post-complex correlations with local charge densities in the immediate vicinity of the complex formation site are weak. Therefore it can be predicted that the Cu^{2+} ion affinities of these amino acids cannot be modeled or described by local properties of the carbonyl moiety of the carboxyl group and amino group of the amino acids only. At this level of calculation, while not perfect, a nice linear correlation between the charge on oxygen and nitrogen atom of the studied amino acids and their Cu^{2+}affinity values can be established. Still, it has to shape strongly by distant atom contribution besides to the contribution from the carbonyl and amino group respectively.

In Table-5 and Table-6 we have highlighted some important optimized geometrical parameters of the free amino acids and their complexes. The neighboring stereochemical nature at or around the carbonyl moiety of carboxyl group and $–NH_2$ group of amino acids are almost same in both phases. The C–O bond length is found to be almost same for all the amino acids. The <C–C–O bond angles for free amino acids are very nearly identical, which are reported in the range of 122.666^0 to 125.148^0 and 123.189^0 to 125.5^0 in gas and aqueous phases respectively. In both phases, the C–O and the C-N bond length is increased upon Cu^{2+} ion complex formation relative to the free amino acids. The O–Cu^{2+} bond length is found to be almost same for all the complexes. In O–Cu^{2+} complexes (where carbonyl oxygen directly involved in the bonding with Cu^{2+} ion) the O–Cu^{2+} bond distance decreased a little bit (0.027 to 0.047Å) from gas to aqueous phase. Similarly, the N–Cu^{2+} bond distance in N–Cu^{2+}–O complexes (where nitrogen directly involved in the bonding with Cu^{2+} ion) also decreased by 0.06 to 0.19Å from gas to aqueous phase. The<C–C–O bond angles are also found to be almost identical in each complex. In the same way, the torsion angle τ(C–C–O–Cu^{2+}) is nearly identical for Cu^{2+}complexes of glycine and alanine and these are –

178.611^0 and -179.998^0showing loss of planarity. Forcys–Cu^{2+} complex the τ value is 174.860^0 which reveal its planar structure. Exactly reverse cases are observed in the aqueous phase. The carbonyl chromospheres of carboxyl group near invariant stereochemistry around the complexation site of each amino acid tend to imply that, the entire contribution to Cu^{2+}ion affinity cannot be modeled accurately without considering the contribution from far-off centres is taken into account. We observed from the geometrical structures of corresponding Cu^{2+} complexes of three amino acids, they form mono-coordinated species when Cu^{2+} ion directly bonded with carboxyl oxygen in gas as well as in aqueous phase. We also observed, bicoordinated (with N and O atom) optimized geometries are formed in aqueous phase when the Cu^{2+} ion is directly bonded with amino nitrogen in the initial input. Optimized geometries in the gas phase and aqueous phase of the studied amino acids and their different Cu^{2+}complexes are shown in Fig.-1.From Table-1weobservedthat,gas phase ΔE values of the amino acids in O–Cu^{2+}interactions vary in the range–205.948 to –226.342 kcal/mole and in the aqueous phase, it (ΔE value) varies in the range of–67.143 to –78.689 kcal/mole. For N–Cu^{2+}interactionsΔE values are in the range of–226.217 to –245.983 kcal/mole and –73.418 to–107.115 kcal/mole in gas and aqueous phase respectively. From Table-1, it is also clear that the amino acids and their complexes are stabilized in water. The dipole moment of the amino acid is increased in water indicating that the charge separation is higher in water as is expected for a polar molecule. This is supported by the data tabulated in Table-2. It has been found that the charge density on O-atoms and N-atoms are much more increased than that in the gas phase. The ΔE values clear the fact that,O–$Cu^{2+}$and N–Cu^{2+}–O complexation reactions in both phases are turns to be exothermic. Table-2 shows that the charge densities on the carbonyl oxygen atom and amino nitrogen atom before the complex formation are almost similar. In the complexes, the charge density on carbonyl oxygen atom (q_{O^-}) and an amino nitrogen atom (q_{N^-}) has been increased for all the amino acids in both phases. A number of charges on O and N atom of the complexes signifythatinteractionof$Cu^{2+}$with the carbonyl oxygen atom and an amino nitrogen atom in the ground state is predominantly a covalent interaction in the gas phase. It clears that both pre- and post-complex correlations with local charge densities in the immediate vicinity of the complexation site are not strong. The Cu^{2+} ion affinities should be modeled strongly by distant atom contribution additionally to the contribution from carbonyl and amino group.

Table-1: Computed total energies (Hartree) of the free amino acids and their Cu^{2+} complexes (BCu^{2+}) and a Cu^{2+} ion affinities [ΔE] in Hartree unit for both gas and aqueous phase at the equilibrium geometry of the ground state. E_{Cu2+}(gas)=–1639.3973 Hartree, E_{Cu2+} (aqueous) = –1639.9410 Hartree. 1 Hartree = 627.5095 Kcal/ mole.

Molecule	Gas phase			Aqueous Phase		
	Total energy(hartree)		ΔE	Total energy(hartree)		ΔE
	B	BCu^{2+} (O–Cu^{2+})	(kcal/mole)	B	BCu^{2+} (O–Cu^{2+})	(kcal/mole)
Glycine	–284.5149	–1924.2404	–205.948	–284.5248	–1924.5728	–67.143
Alanine	–323.8334	–1963.5781	–217.996	–323.8466	–1963.8977	–69.088
Cysteine	–722.0495	–2361.8075	–226.342	–722.0621	–2362.1285	–78.689
Molecule	B	BCu^{2+} (N–Cu^{2+}-O)	ΔE	B	BCu^{2+} (N–Cu^{2+}-O)	ΔE
Glycine	–284.5149	–1924.2727	–226.217	–284.5248	–1924.5828	–73.418
Alanine	–323.8334	–1963.6018	–232.868	–323.8466	–1963.9583	–107.115
Cysteine	–722.0495	–2361.8388	–245.983	–722.0621	–2362.1704	–104.982
Molecule	B	BCu^{2+} (S–Cu^{2+})	ΔE	B	BCu^{2+} (S–Cu^{2+})	ΔE
Cysteine	–722.0495	–2361.7997	–221.761	–722.0621	–2362.1184	–72.351

Table-2:Computed net Mulliken charge (unit 'e') on O-atom (q_{O^-}) and charge on N-atom (q_{N^-})of free amino acids and their Cu^{2+} complexes and the computed net charge on Cu^{2+}ion (q_{Cu2+}) of B-$Cu^{2+}$and also dipole moment, μ(Debye) of amino acids for both gas phase and aqueous phase in the equilibrium ground state.

Molecule	q_{O^-}(Gas Phase)		q_{O^-}(Aq. Phase)		Gas phase	Aq. Phase	μ in gas phase	μ in aq. phase
	B	BCu^{2+}(O–Cu^{2+})	B	BCu^{2+}(O–Cu^{2+})	q_{Cu2+}	q_{Cu2+}	B	B
Glycine	–0.3369	–0.4859	–0.3772	–0.4730	1.0637	1.3654	2.0037	2.9458

Alanine	–0.3171	–0.4949	–0.3631	–0.5039	1.0237	1.2918	4.1481	5.9648
Cysteine	–0.3162	–0.4747	–0.3634	–0.4998	0.9187	1.3368	2.0393	2.7745
Molecule	q_{N^-}(Gas Phase)		q_{N^-}(Aq.Phase)		Gas phase	Aq. Phase	μ in gas phase	μ in aq. phase
	B	BCu^{2+} (N–Cu^{2+}-O)	B	BCu^{2+} (N–Cu^{2+}-O)	q_{Cu2+}	q_{Cu2+}	B	B
Glycine	–0.4534	–0.7200	–0.4632	–0.6904	1.3805	1.5099	3.2456	5.3375
Alanine	–0.4513	–0.7038	–0.4623	–0.6770	1.3654	1.5019	4.8014	6.6653
Cysteine	–0.4215	–0.6728	–0.4317	–0.6821	1.1708	1.4932	4.0578	13.2029

Table-3:Computed atomic charges (unit 'e') in the complexes and the amount of charge transfer (CT)

BCu^{2+}(O–Cu^{2+}) Gas phase	q_{Cu2+}	q_{O^-}	q_{CT}	BCu^{2+}(O–Cu^{2+}) Aq. Phase	q_{Cu2+}	q_{O^-}	q_{CT}
Glycine	1.0637	–0.4859	0.5778	Glycine	1.3654	–0.4730	0.8924
Alanine	1.0237	–0.4949	0.5288	Alanine	1.2918	–0.5039	0.7879
Cysteine	0.9187	–0.4747	0.4440	Cysteine	1.3368	–0.4998	0.8370
BCu^{2+} (N–Cu^{2+}-O)	q_{Cu2+}	q_{N-}	q_{CT}	BCu^{2+} (N–Cu^{2+}-O)	q_{Cu2+}	q_{N-}	q_{CT}
Glycine	1.3805	–0.7200	0.6605	Glycine	1.5099	–0.6904	0.8195
Alanine	1.3654	–0.7038	0.6616	Alanine	1.5019	–0.6770	0.8249
Cysteine	1.1708	–0.6728	0.4980	Cysteine	1.4932	–0.6821	0.8111

Table-4:Natural net charges (Units e) on Cu^{2+} ion (q_{Cu2+}),Oxygen atom(q_{O^-}) and Nitrogen atom (q_{N^-}) and ligand to metal charge transfer (Q_{CT}) of O-Cu^{2+} complexes and N-Cu^{2+}-O complexes (Zwitterionic)in gas and aqueous phase respectively obtained from NPA analysis.

O–Cu^{2+} Complex	Gas phase			Aqueous phase		
	q_{Cu2+}	q_{O^-}	Q_{CT}	q_{Cu2+}	q_{O^-}	Q_{CT}
Glycine	0.6347	-0.3483	1.365	0.9453	-0.3049	1.054
Alanine	0.5932	-0.3540	1.40	0.8656	-0.3336	1.134
Cysteine	0.4800	-0.3504	1.52	0.9149	-0.2885	1.085
N–Cu^{2+}-O complex	Gas phase			Aqueous phase		
	q_{Cu2+}	(q_{N^-})	Q_{CT}	q_{Cu2+}	(q_{N^-})	Q_{CT}
Glycine	1.041	- 0.3634	0.959	1.143	-0.3543	0.857
Alanine	1.022	-0.3642	0.978	1.132	-0.3525	0.868
Cysteine	0.795	-0.4093	1.205	1.120	-0.3512	0.88

Table-5:Geometrical features of the free amino acids and their Cu^{2+} complexes in gas phase (length in Å , bond angle and torsion angle (τ) in degree).

Molecule	B		BCu^{2+} (O–Cu^{2+})			
	r (C-O)	<C-C-O	r(C-O)	r (O-Cu^{2+})	<C-C-O	τ <C-C-O-Cu^{2+}
Glycine	1.204	125.148	1.230	1.927	119.931	–178.611
Alanine	1.199	123.519	1.233	1.922	120.052	–179.998
Cysteine	1.200	122.666	1.227	1.906	119.748	174.860
Molecule	B		BCu^{2+} (N–Cu^{2+}-O)			
	r (C-N)	<C-C-N	r(C-N)	r (N-Cu^{2+})	<C-C-N	τ <C-C-N-Cu^{2+}
Glycine	1.45	110.154	1.47	1.9556	105.867	–0.1428
Alanine	1.44	108.346	1.52	1.9586	106.555	200.6756
Cysteine	1.449	112.398	1.50	2.0262	111.944	–151.1961

Table-6: Geometrical features of the free molecule and their Cu^{2+} complexes in the aqueous phase(Bond length in Å, bond angle and torsion angle (τ) in degree).

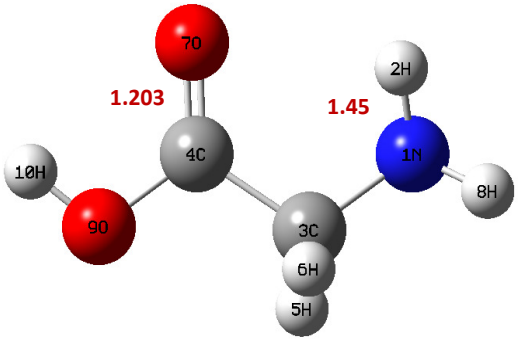
Molecule	B		BCu^{2+}			
	r (C-O)	<C-C-O	r(C-O)	r (O-Cu^{2+})	<C-C-O	τ<C-C-O-Cu^{2+}
Glycine	1.207	125.500	1.224	1.880	121.861	179.921

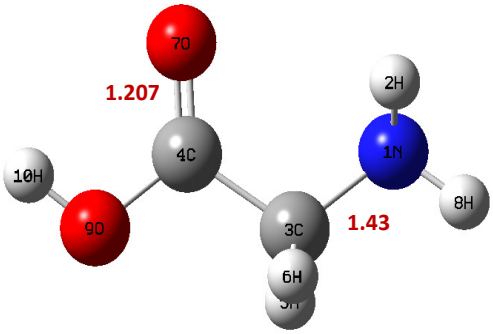
Alanine	1.204	124.560	1.232	1.895	119.226	179.149
Cysteine	1.206	123.189	1.243	1.879	122.140	–177.736
Molecule	B		BCu^{2+} (N–Cu^{2+}-O)			
	r (C-N)	<C-C-N	r(C-N)	r (N-Cu^{2+})	<C-C-N	τ<C-C-N-Cu^{2+}
Glycine	1.43	110.919	1.44	1.949	109.001	–0.1818
Alanine	1.42	108.896	1.50	1.939	106.595	–23.124
Cysteine	1.426	112.796	1.48	1.879	122.140	–149.853

Gas phase

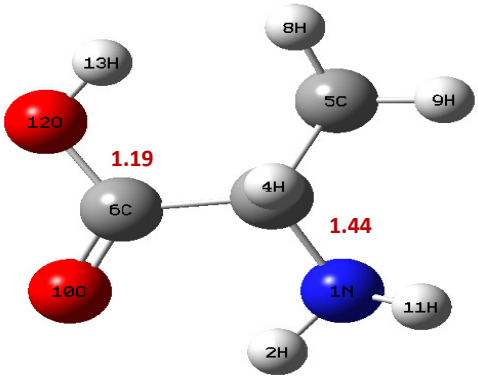
Aqueous phase

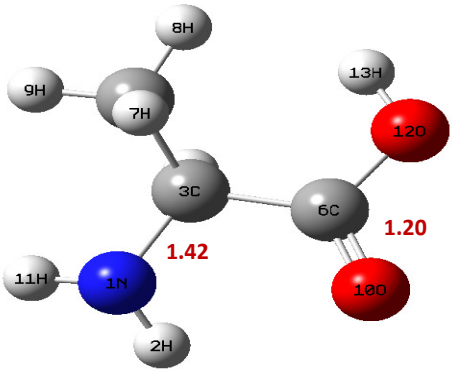
Glycine



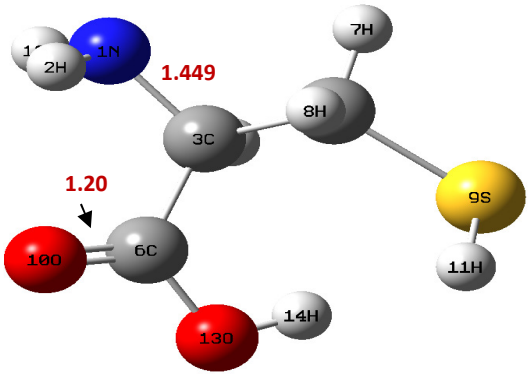


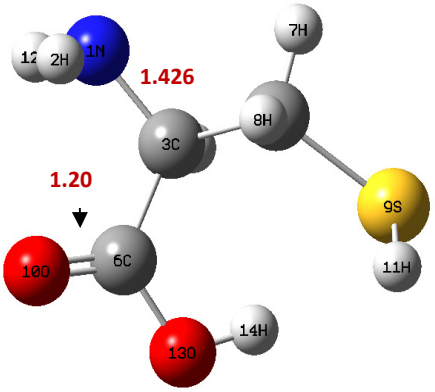
Alanine

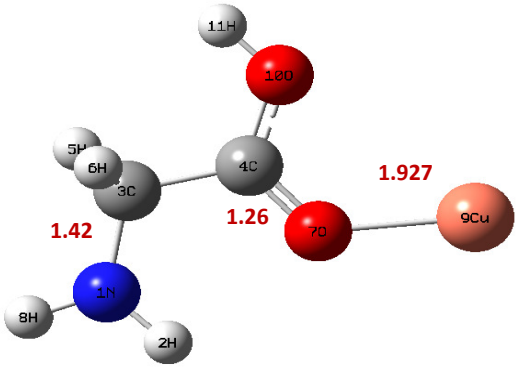
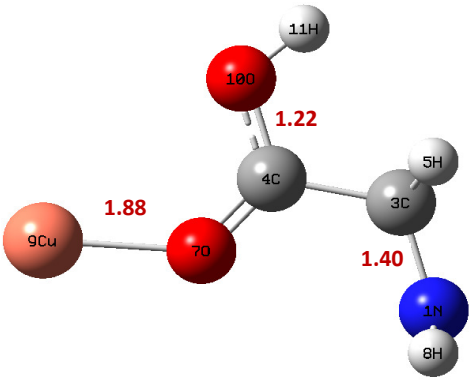
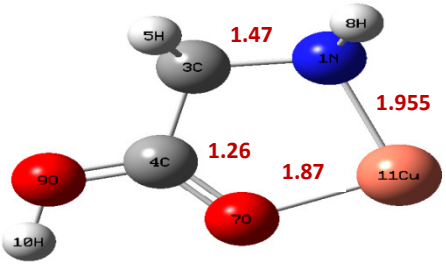
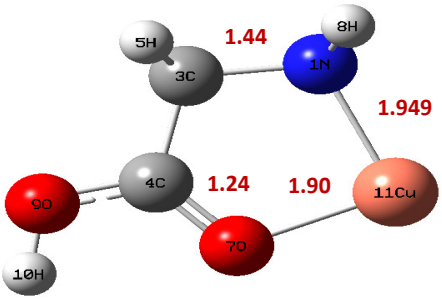
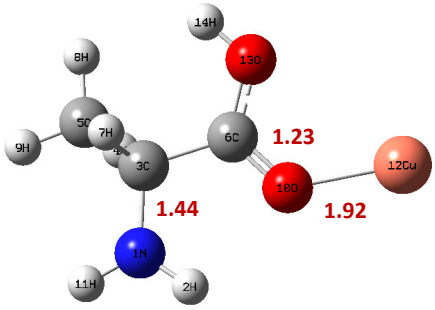
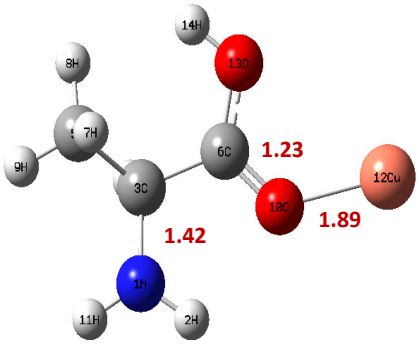
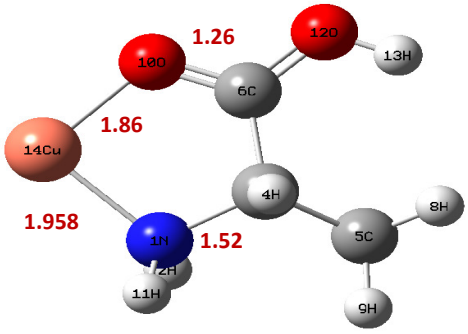
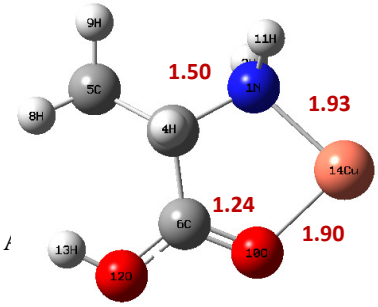




Cysteine





	Gas phase	Aqueous phase
Glycine (O-Cu^{2+})		
Glycine (N-Cu^{2+}-O)		
Alanine (O-Cu^{2+})		
Alanine (N-Cu^{2+}-O)		

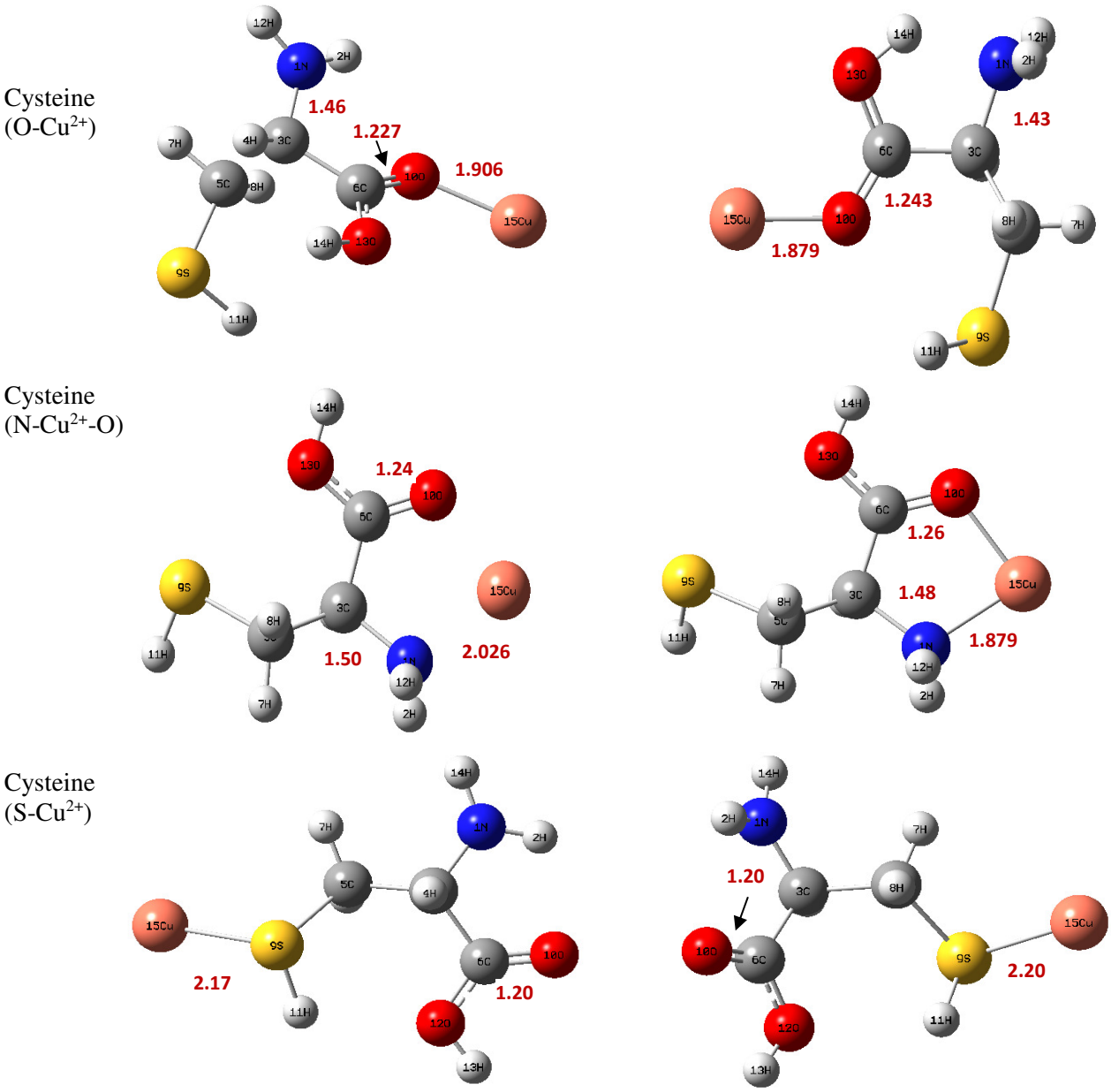


Fig.-1: Optimized structure of neutral glycine, alanine and cysteine and there different Cu^{2+}complexes in gas and an aqueous phase. (Bond distance is in angstrom (Å) unit).

Table-7: Computed hardness [hartree (h)] of the free molecules in gas and an aqueous phase.

Molecule	Gaseous phase			Aqueous phase		
	ε_{HOMO}(h)	ε_{LUMO}(h)	η(h)	ε_{HOMO}(h)	ε_{LUMO}(h)	η(h)
Glycine	–0.24567	–0.0009	0.1223	–0.2531	0.0004	0.1267
Alanine	–0.25106	–0.0067	0.1221	–0.2547	-0.0051	0.1248
Cysteine	–0.26227	–0.0192	0.1214	–0.2589	-0.0112	0.1238

CONCLUSION

From the above theoretical studies, it can be concluded that the gas phase and aqueous phase Cu^{2+}ion affinity of amino acids are spontaneous. The electronic properties of the complexes indicate that there is a

predominance of covalent and ionic interaction in gas and aqueous phases respectively. Complexes are formed (Zwitterionic) due to N–Cu^{2+}interactions are more stable than that of O–Cu^{2+} complexes in both phases. In general reactivity of the system entirely explained considering distant atom contribution besides to the contribution from the carbonyl moiety of carboxyl group and the amino group of amino acids. In the gas phase, Cu^{2+} affinity has been predicted to be more for Cysteine in both O-Cu^{2+} and N-Cu^{2+} interactions compared to glycine and alanine. Aqueous phase Cu^{2+} affinity due to O-Cu^{2+} interaction is found to be highest whereas the order of these values is slightly changed in case of N-Cu^{2+} interaction.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the laboratory (Theoretical) support of Department of Chemistry and Chemical Technology, Vidyasagar University (VU), Midnapur. We also thank Prof. B. R. De, Ex-Professor Department of Chemistry and Chemical Technology, VU, for his valuable guidance.

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[RJC-1798/2017]