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Synthesis, Spectral Characteristics and DFT Studies of the [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$]

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***Abstract*—[Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$] was obtained. The geometry optimization of this molecule was done by Density Functional Theory (DFT/B3LYP) method with 6-31G(d,p) basis in gas and in water phase. The experimental infrared spectrum was compared with calculated and complete vibrational assignment was provided. The bond orders and the electronic properties of the molecule were calculated. The calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) with frontier orbital gap were presented. The electrostatic potential was calculated in order to investigate the reaction properties of the molecule.**

Keywords—[Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$]; quantum chemical calculations; geometry optimization; electronic properties

I. INTRODUCTION

The protection of metal surfaces against corrosion is an important industrial and scientific topic. Inhibitors are one of the practical mean of preventing corrosion, particularly in acidic media. Inhibitors can adhere to a metal surface to form a protective barrier against corrosive agents in contact with metal.

Organic compounds which can donate electrons to unoccupied d orbitals of metal surface to form coordinate covalent bonds and can also accept free electrons from the metal surface by using their antibond orbitals to form feedback bonds constitute excellent corrosion inhibitors. The most effective corrosion inhibitors are those compounds containing heteroatoms like nitrogen, oxygen, sulfur and phosphorus as well as aromatic rings. The inhibitory activity of these molecules is accompanied by their adsorption to the metal surface. Free electron pairs on heteroatoms or p electrons are readily available for sharing to form a bond and act as nucleophile centers of inhibitor molecules and greatly facilitate the adsorption process over the metal surface, whose atoms act as electrophiles.

Inhibitors have been selected mainly by using empirical knowledge based on their macroscopic physicochemical properties. Quantum chemical methods are ideal tool for investigating these properties. Triazole-type compounds, which are also environmentally acceptable, are considered to be effective corrosion inhibitors in HCl solutions [1,2]. Recently, Cruz et al. [3] reported an experimental and theoretical study of the anticorrosive properties of amino-triazole and amino-thiazole as inhibitors for mild steel in hydrochloric acid. Later studies [4–7] have been oriented to investigations of various triazole derivatives with the aim of finding more effective and environmental friendly inhibitors.

The aims of this publication is to report the synthesis, characterizaton of Cu(II) adducts with 3-Amino-1,2,4-triazole. Using quantum chemical calculations to determine the geometric and electronic structure of [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$]. Quantum chemical parameters, such as highest occupied and lowest unoccupied molecular orbital energy levels, energy gap, ionization potential, atomic charges and electron-density distribution, have been calculated at the B3LYP/6-31G(d,p) level of theory. In particular, reactive behavior of [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$] has been investigated on the basis of electronegativity, global hardness, global softness, electron-donating ability and fraction of an electron transferred from the inhibitor molecule to the metal atom. The local reactivity has been studied by the Fukui indices approach, to predict both the reactive centers and their electrophilic or nucleophilic behavior. Also considered the effect of water as a solvent on the calculated parameters, since corrosion commonly occurs in the liquid phase.

II. EXPERIMENTAL

The [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$] was prepared as follows. An aqueous solution of $CuSO_4.5H_2O$ (0,50 g in 3 ml of water) was mixed with an aqueous solution of Amino-triazole, $C_2H_4N_4$ (0,50 g in 2 ml of water). After kept overnight, it was filtered slowly, washed with water, and dried over P_2O_5 in vacuum. The infrared spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer in the 4000 – 400 cm^{-1} range, with the samples embedded in KBr matrixes.

III. COMPUTATIONALS METHODS

The full optimization of [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$] was carried out by Density Functional Theories (DFT) method using Gaussian 03 software [8]. It was used Becke's three parameter hybrid exchange functional with Lee–Yang–Parr correlation functional (B3LYP) [9-11] with added polarization functions 6-31G(d,p). All calculations were converged to 10–8 a.u. The absence of imaginary frequencies in the calculated vibrational spectrum confirms that the structure corresponds to minimum energy.

An effective method for studying the reaction behavior of the molecules is the measuring of their electrostatic potential [12]. The electrostatic potential of [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$] was calculated by DFT method. In order to characterize the electronic population on each atomic centre a Mulliken population analysis [13] was carried out.

To take into account the effect of the solvent by self-consistent reaction field (SCRF) the method of Onsager was used [14]. The Onsager model places the solute in a spherical cavity within the solvent reaction field. The solvent is treated as polarizable continuum with a dielectric constant - ε, instead of explicit solvent molecules. The charge distribution of the solute polarizes the solvent producing a reaction potential. The reaction potential of solvent alters the solute. This interaction is represented by Hamiltonian containing the solvent reaction potential.

The software packages HyperChem 5.0 [15] and Molekel 5.4 [16] were used for data preparation and visualization of the results.

IV. RESULTS AND DISCUSSION

A. *Geometry Optimization*

The geometric parameters of 3-Amino-1,2,4-triazole – lengths, angles, bond orders and its molecular electrostatic potential were established by DFT (at B3LYP level) method with 6-31G (d,p) basis sets and are reported [17]. It was calculated that the site most suitable for creation of a coordination bond is N4.

It is well known that DFT methods work better for systems containing transition metal atoms. For these reasons is use the B3LYP level sets for analyses of [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$].

The visualization of the optimized geometrical structure and atomic labeling of [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$] are presented in Figure 1. The optimized geometry is shown in Table 1.

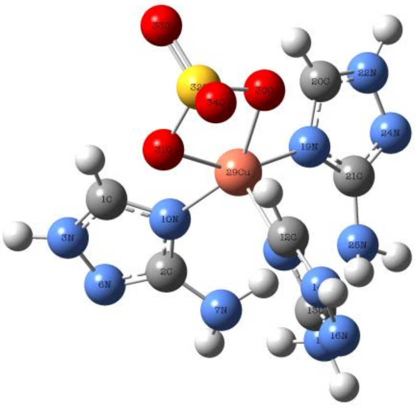


Figure 1. Optimized geometrical structure and atomic labeling of [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$]

It can be seen that the DFT method produce structural parameters for triazole ring, that are in good agreement with the experimental Rë structure analyses reported for similar compounds [18]. Despite the fact that the reference compound has either an H atom or a CH$_3$- group instead of the NH$_2$- one.

Quantum-chemical calculations provide the ability to calculate the net atomic charges (*q*), which are localized at the corresponding atoms as a result of the redistribution of the electrons in the molecule. Though they are not connected with physical properties and cannot be observed experimentally, they allow the understanding of the distribution of the electronic density in a system of connected atoms and predict some chemical properties of the molecules. The nitrogen atoms exhibit their electro negative nature as expected. The net atomic charges, calculated by Mulliken and the order of the bonds in the investigated compounds are presented in Table 2. Obviously, the triazole bond orders are in the range 1,280 – 1,676. These bond orders values suggest a relatively strong aromatic character for the five-membered ring of triazole

Table 1. Some optimized geometrical parameters of [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$]

Parameters	In gas phase B3LYP/6-31G(d,p)	In water phase B3LYP/6-31G(d,p)	Exp.[3]
Bond length (Å)			
$N^{3(14,22)}$–$N^{6(16,24)}$	1.369	1.366	1,359
$N^{6(16,24)}$–$C^{2(13,21)}$	1.324	1.324	1,323
$C^{2(13,21)}$–$N^{10(11,19)}$	1.372	1.377	1,359
$N^{10(11,19)}$–$C^{1(12,20)}$	1.334	1.333	1,324
$C^{1(12,20)}$–$N^{3(14,22)}$	1.333	1.333	1,331
$C^{2(13,21)}$–$N^{7(17,25)}$	1.386	1.381	–
$N^{10(11,19)}$–Cu	2.090	2.040	–
Cu–$O^{30(31)}$	1.975	1.993	–
S–$O^{30(31)}$	1.575	1.567	–
S–$O^{33(34)}$	1.470	1.472	–
Bond angle (degree)			
$N^{3(14,22)}$–$N^{6(16,24)}$–$C^{2(13,21)}$	101.9	102.2	102,1
$N^{6(16,24)}$–$C^{2(13,21)}$–$N^{10(11,19)}$	114.0	113.7	114,6
$C^{2(13,21)}$–$N^{10(11,19)}$–$C^{1(12,20)}$	103.7	103.8	103,0
$N^{10(11,19)}$–$C^{1(12,20)}$–$N^{3(14,22)}$	108.8	108.9	110,1
$C^{1(12,20)}$–$N^{3(14,22)}$–$N^{6(16,24)}$	111.4	111.4	110,2
$N^{6(16,24)}$–$C^{2(13,21)}$–$N^{7(17,25)}$	122.8	122.9	–
$C^{2(13,21)}$–$N^{10(11,19)}$–Cu	140.0	139.2	–
O^{30}–Cu–O^{31}	73.1	72.2	–
Dihedral angle(degree)			
$N^{6(16,24)}$–$C^{2(13,21)}$–$N^{10(11,19)}$–Cu	172.9	173.0	–
$C^{1(12,20)}$–$N^{10(11,19)}$–Cu–$N^{11(10,11)}$	119.4	121.1	–
C^{12}–N^{11}–Cu–O^{30}	31.6	30,6	–
C^{1}–N^{10}–Cu–O^{31}	22.2	23.7	–
C^{20}–N^{19}–Cu–O^{30}	30.7	33.8	–

Table 2. Mulliken atomic charges and bond orders of [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$]

Atom	Mulliken atomic charges	Bond	Bond order
$N^{3(14,22)}$	–0.336	$N^{3(14,22)}$–$N^{6(16,24)}$	1.343
$N^{6(16,24)}$	–0.347	$N^{6(16,24)}$–$C^{2(13,21)}$	1.676
$C^{2(13,21)}$	0.625	$C^{2(13,21)}$–$N^{10(11,19)}$	1.342
$N^{10(11,19)}$	–0.587	$N^{10(11,19)}$–$C^{1(12,20)}$	1.536
$C^{1(12,20)}$	0.370	$C^{1(12,20)}$–$N^{3(14,22)}$	1.489
$N^{7(17,25)}$	–0.704	$C^{2(13,21)}$–$N^{7(17,25)}$	1.280
Cu	0.781	$N^{10(11,19)}$–Cu	0.257
S	1.393	Cu–$O^{30(31)}$	0.258
$O^{30(31)}$	–0.707	S–$O^{30(31)}$	0.637
$O^{33(34)}$	–0.583	S–$O^{33(34)}$	0.920

B. *Molecular Electrostatic Potential Analysis*

The molecular electrostatic potential is a property that the electrons and nuclei of a molecule create at each point an electrical potential in the surrounding space [12]. Electrostatic potential provides very useful information to explain hydrogen bonding, reactivity and structure–activity relationship of molecules and correlates with dipole moment, electronegativity, net atomic charges and site of chemical reactivity of the molecule. It gives a visualization to understand the relative polarity of a molecule.

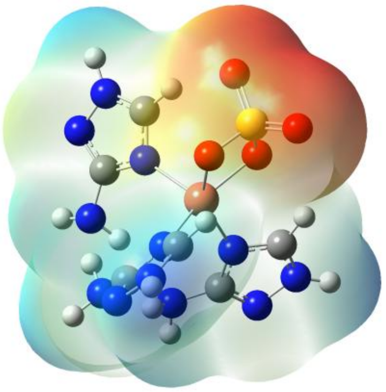


Figure 2. Molecular electrostatic potential mapped on the surface for [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$] calculated at the B3LYP/6-31G(d,p) level of DFT

The electron density isosurface for [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$] onto which the electrostatic potential surface was mapped is shown in Figure 2. The regions with negative electrostatic potential, correspond to the areas of high electron density representing a strong attraction between the proton and the points. On this molecular surface these regions are over the O^{33} and O^{34} – V_{min} = –0.09149 kcal/mol respectively. The positive valued regions, areas of lowest electron density, have deep blue color indicating the regions of maximum repulsion. The regions of most positive electrostatic potential are over the triazole rings – V_{max} = 0.07416 kcal/mol respectively. The molecular electrostatic potential is widely used as a reactivity map displaying most probable regions for the electrophilic attack of charged point – like reagents on organic molecules. The negative regions of electrostatic potential were related to electrophilic reactivity and the positive ones to nucleophilic reactivity.

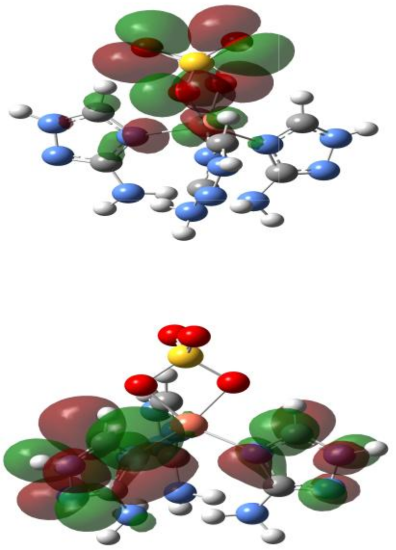
C. *HOMO-LUMO Analysis*

The frontier orbitals (highest occupied molecular orbital – HOMO and lowest unoccupied molecular orbital – LUMO) are very important in defining reactivity. The HOMO exhibits the ability to donate an electron and LUMO as an electron acceptor serves the ability to obtain an electron. The frontier orbitals (HOMO, LUMO) of [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$] calculated by B3LYP/6-31G(d,p) are plotted in Figure 3.

It can be seen that the HOMO molecular orbital is delocalized over the sulfate group while LUMO molecular orbital is over triazole rings. Energy of frontier orbitals and energy of the gap are:

$$E_{\mathrm{HOMO}} = –559.389 \text{ kJ/mol}$$
$$E_{\mathrm{LUMO}} = –49.333 \text{ kJ/mol}$$
$$\Delta E_{\mathrm{LUMO–HOMO}} = 510.056 \text{ kJ/mol}$$

High values of E_{HOMO} have a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy, empty molecular orbitals. The energy of the lowest unoccupied molecular orbital indicates the ability of the molecule to accept electrons. The lower value of E_{LUMO}, the more probable it is that the molecule would accept electrons. Consequently, concerning the value of the energy of the gap $\Delta E_{\mathrm{LUMO–HOMO}}$, larger values of the energy difference will provide low reactivity to a chemical species. Lower values of the energy difference will render good inhibition efficiency, because the energy to remove an electron from the last occupied orbital will be low. The results for the calculations of the ionization potential (I) and the electron affinity (A) by application of the Koopman's theorem [19] are shown. According to the Hartree–Fock theorem, the frontier orbital energies are given by: $I = – E_{\mathrm{HOMO}}$ = 559.389 kJ/mol; $A = – E_{\mathrm{LUMO}}$ = 49.333 kJ/mol. This theorem establishes a relation between the energies of the HOMO and the LUMO and the ionization potential and the electron affinity, respectively. Although no formal proof of this theorem exists within DFT, its validity is generally accepted. Electronegativity (χ), chemical potential (μ) and global hardness (η), their operational and approximate definitions for [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$] are: $\chi = – \mu = (I + A)/2$ = 304.361 kJ/mol; $\eta = (I – A)/2$ = 255.028 kJ/mol.



1

2

ψ_{Homo} = 18.5% $\boldsymbol{2p_x}(O^{33})$ – 11.8% $\boldsymbol{2p_x}(O^{34})$ + 11.2% $\boldsymbol{3p_x}(O^{33})$ + 9.6% $\boldsymbol{2p_y}(O^{34})$ – 7.1% $\boldsymbol{2p_y}(O^{30})$ – 7.1% $\boldsymbol{3p_x}(O^{34})$

ψ_{Lumo} = 15.3% $\boldsymbol{2p_y}(C^{20})$ + 12.6% $\boldsymbol{3p_y}(C^{20})$ – 8.5% $\boldsymbol{2p_y}(N^{22})$ + 5.1% $\boldsymbol{2p_y}(N^{24})$ + 4.2% $\boldsymbol{2p_x}(C^{20})$ – 3.9% $\boldsymbol{2p_y}(N^{19})$

Figure 3. Electron distribution of HOMO – 1 and LUMO – 2 for [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$]

D. *Vibrational Spectral Analysis*

The vibrational spectra of [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$] was calculated by DFT with B3LYP functional having extended basis sets 6-31G(d,p). Frequencies recorded experimentally for [Cu(3-

Amino-1,2,4-triazole)$_3$SO$_4$] are compared with the calculated obtained by DFT (Figure 4).

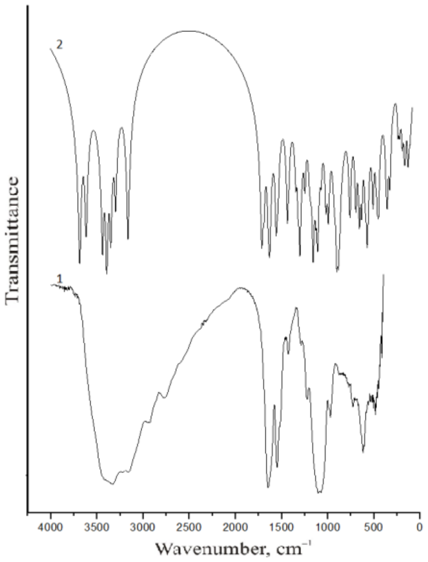


Figure 4. IR spectrum of [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$], 1 – experimental, 2 – calculated

It is well known that the harmonic frequencies by DFT calculations are usually higher than the corresponding experimental quantities due to the facts of the electron correlation approximate treatment, the anharmonicity effect and basis set deficiency, etc. [20]. In order to improve the calculated values in agreement with the experimental values, it is necessary to scale down the calculated harmonic frequencies. After scaling, the theoretical frequencies match well with the experimental ones. The experimental assignments of IR for vibrations, IR theoretical and relative intensities were reported in Table 4. These assignments are important to understand the molecular structure of the title molecule. Any discrepancies noted between the observed and the calculated wavenumbers due to the fact that the calculations were actually performed on single (isolated) molecules in the gaseous state. Thus some reasonable deviations from the experimental values seem to be justified.

Table 4. Selected experimental and calculated vibrational frequencies (cm^{-1}), IR intensity and probable assignments of 3-Amino-1,2,4-triazole and [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$]

3-Amino-1,2,4-triazole			**[Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$]**			**Assigments^b**
Experimental frequencies	**B3LYP/6-31G(d,p)**		**Experimental frequencies**	**B3LYP/6-31G(d,p)**		
	Scaled	**I_{Abs}**		**Scaled**	**I_{Abs}**	
3717 *w*	3696	27	3423 m; 3407 m	3430	262	$v_{ass(NH)}$; (NH_2)
3688 *w*	3682	72	3381 m	3384	495	$v_{(N-H)}$
3651 *w*; 3412 *s*	3581	23	3332 m; 3329 s	3341	204	$v_{ss(NH)}$; (NH_2)
3340 *m*; 3216 *m*	3265	3	3230 m	3285	35	$v_{(C-H)}$
1643 *s*	1660	239	3179 m; 3163 m; 3159 m	3153	169	$\delta_{b(NH2)}$
1593 *s*	1598	75	1646 s	1622; 1671	103	*Rband*; $v_{(C=N)}$
1536 *s*	1530	29	1549 s	1537	134	*Rband*; $v_{(N=N)}$
1473 *m*	1490	26	1520 w	1524	25	*Rband*; $v_{(C-N)}$
1426 *s*; 1372 *s*	1399	55	1428 s	1416	93	*Rband*
1270 *s*	1304	6	1396 w	1403; 1398	17	*Rband*
1218 *s*	1199	4	1288 m	1280	278	$\delta_{r(NH2)}$; $v_{(S=O)}$
1132 *s*	1118	10	1225 m	1225	21	$\delta_{r(NH2)}$
1045*vs*	1071	49	1107 s	1106; 1134	334	$\delta_{r(NH2)})$; $v_{(N-N)}$; $v_{(S=O)}$
968 *s*	989	6	1097 m	1088	128	*Rband*
876 *s*; 826 *s*	837	13	1084 m	1085	110	$v_{(C-H)}$
812 *m*; 729 s	778	57	991 m	996	56	$\delta_{w(NH2)}$
673 *w*; 641 *m*	658	24	972 m	970	87	*Rband*
615 *w*; 593 *w*	607	248	878 m	877	365	$\delta_{w(NH2)}$
466 *m*; 434 *s*; 418 *s*	457	98	864 m	868	101	$\delta_{t(NH2)}$; $v_{(SO4)}^{2-}$
397 *s*	326	34	852 m	859	314	*Rband*; $v_{(SO4)}^{2-}$
–	–	–	843 m	847	76	$\delta_{w(NH2)}$; $v_{(SO4)}^{2-}$
–	–	–	729 w	733	43	*Rband*
			673 w	673	22	*Rband*
			625 w; 617 m	631	109	$v_{(SO4)}^{2-}$
			606 w	607	75	$\delta_{r(NH2)})$
			561 w	567	35	$v_{(SO4)}^{2-}$
			554 m	550	143	$v_{(SO4)}^{2-}$
			484 m	484	31	$\delta_{t(NH2)}$
			438 w; 414 m	436; 424	70	$\delta_{r(NH2)})$
				332; 327	34	*Rband*
				300	30	$v_{(Cu-S)}$
				210	5	$v_{(Cu-N)}$

Scale factors of 0.9613 for calculated frequencies with B3LYP/6-31G(d,p) and 0.9679 for B3LYP/6-311++G(d,p)

(a) *s* - strong; *m* - medium; *w* – weak.

(b) *v* - stretching; *ss* - symmetric; *ass* – asymmetric; δ_b – bending; δ_r – rocking; δ_w – wagging; δ_t – twisting; *Rband* – ring deformation

I_{Abs}-Theoretical infrared intensities

V. CONCLUSION

The geometry of [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$] was optimized with DFT/B3LYP methods using 6-31G(d,p) basis set in gas and in water phase. The complete molecular structural parameters of the optimized geometry of the compound were obtained. The vibrational frequencies of the fundamental modes of the compound were precisely assigned, analyzed and the theoretical results were compared with the experimental vibrations. The close agreement was observed between the experimental and scaled frequencies obtained using the basis set 6-31G(d,p). HOMO–LUMO studies reveal the intramolecular charge transfer through conjugated system. The Mulliken charges calculated by B3LYP/6-31G(d,p) method were presented. Information about the size, charge density distribution and structure–activity relationship of [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$] was obtained by mapping electron density isosurface with electrostatic potential. The present quantum chemical study may lead to the understanding of properties and activity of [Cu(3-Amino-1,2,4-triazole)$_3$SO$_4$].

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