

## Quantum chemical study on $\text{Me}^{2+}$ -3-Amino-1,2,4-Triazole complexes ( $\text{Me} = \text{Ca}, \text{Zn}, \text{Cu}, \text{Co}, \text{Ni}, \text{Cd}$ and $\text{Hg}$ )

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**Abstract.** The geometry optimization of 3-Amino-1,2,4-Triazole and  $\text{Me}^{2+}$ -3-Amino-1,2,4-Triazole complexes ( $\text{Me} = \text{Ca}, \text{Zn}, \text{Cu}, \text{Co}, \text{Ni}, \text{Cd},$  и  $\text{Hg}$ ) was done in water-phase with HF and DFT quantum chemical methods with 6-31G(d,p) and LANL2DZ basis sets. The bond orders and the electronic properties of complexes were calculated. It was found that the stability constants of complexes correlate well with the calculated dipole moments.

**Key words:**  $\text{Me}^{2+}$ -3-Amino-1,2,4-Triazole complexes, quantum chemical calculations, geometry optimization, electronic properties

### INTRODUCTION

The 5-membered nitrogen heterocyclic rings are structural fragments in a number of biologically active compounds [11], pesticides [12], pigments and other substances used in industry [9, 2]. The pesticides contained in soil often react with metal ions. The information about the geometry and stability constants of such complexes would provide a possibility to describe pesticides propagation in soil and subterranean water, as well as the mechanisms of their transportation in plants.

One of the interesting pesticides is 3-Amino-1,2,4-Triazole (Amitrol). In a previous work, we have studied Amitrol complex formation in aqueous solutions with ions contained in soil as macrocomponents ( $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ) and microcomponents ( $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$ ) [10].

The aims of the present work is using quantum chemical calculations to determine the geometric and electronic structure of  $\text{Me}^{2+}$ -3-Amino-1,2,4-Triazole complexes ( $\text{Me} = \text{Ca}, \text{Zn}, \text{Cu}, \text{Co}, \text{Ni}, \text{Cd}$  and  $\text{Hg}$ ) in water-phase and determine the relationship between the stability constants of complexes and their electronic properties.

### COMPUTATIONAL METHODS

The full optimization of 3-Amino-1,2,4-Triazole was carried out by the Hartree-Fock (HF) and Density Functional Theories (DFT) methods, using Gaussian 03 software [1] at the B3LYP level with 6-31G(d,p) basis set for all calculations and LANL2DZ basis set with effective core potential for the metals Cu, Co, Cd, Ni и Hg in complexes. All calculations were converged to  $10^{-8}$  a.u. Vibration frequencies were also calculated to the structures with optimized geometry and no imaginary frequency were obtained, so the stationary points correspond to the minima of the potential energy surface.

An effective method for studying the reaction behavior of molecules is the measuring of their electrostatic potential. The electrostatic potential of 3-Amino-1,2,4-Triazole was calculated by DFT method at the B3LYP level with 6-31G(d,p) basis sets. The electrostatic potential is widely used in studies on biological systems to predict the reactivity of numerous chemical systems in electro- and nucleophilic reactions [7].

In order to characterize the electronic population on each atomic centre a Mulliken population analysis [5] was carried out for 3-Amino-1,2,4-Triazole.

To take into account the effect of the solvent by self-consistent reaction field (SCRF) the method of Onsager was used [6]. 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 -  $\epsilon$ , 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 a Hamiltonian containing the solvent reaction potential. All calculations are for complexes at ratio  $\text{Me} : \text{L} = 1 : 1$ .

The software packages HyperChem 5.0 [3] and Molekel 5.4 [8] were used for data preparation and visualization of the results.

## RESULTS AND DISCUSSIONS

The visualization of the optimized geometrical structure and atomic labeling of 3-Amino-1,2,4-Triazole are presented in Fig. 1.

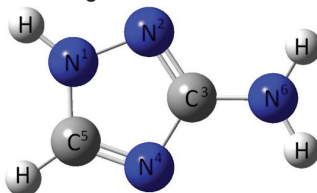


Fig. 1 Optimized geometrical structure and atomic labeling of 3-Amino-1,2,4-Triazole

To choose suitable calculation method, geometric optimization of 3-Amino-1,2,4-Triazole (ATR) carried out and the results were compared with the experimentally obtained results (Table 1). It can be seen that the HF and DFT methods produce structural parameters that are in good agreement with the experimental R $\ddot{e}$  structure analyses reported for similar compounds [4]. Despite the fact that the reference compound has either an H atom or a CH<sub>3</sub>- group instead of the NH<sub>2</sub>- one, the average bond length divergence between theoretical and experimental data are much better for B3LYP.

Table. 1. Optimized geometrical parameters of 3-Amino-1,2,4-Triazole.

Para- meters	HF/6- 31G(d,p)	B3LYP/6- 31G(d,p)	Exp.[4]	Para- meters	HF/6- 31G(d,p)	B3LYP/6- 31G(d,p)	Exp.[4]
Bond length (Å)				Bond angle (grad)			
N <sup>1</sup> -N <sup>2</sup>	1,361	1,373	1,359	N <sup>1</sup> -N <sup>2</sup> -C <sup>3</sup>	101,8	101,1	102,1
N <sup>2</sup> -C <sup>3</sup>	1,300	1,332	1,323	N <sup>2</sup> -C <sup>3</sup> -N <sup>4</sup>	115,2	115,6	114,6
C <sup>3</sup> -N <sup>4</sup>	1,359	1,372	1,359	C <sup>3</sup> -N <sup>4</sup> -C <sup>5</sup>	102,4	102,4	103,0
N <sup>4</sup> -C <sup>5</sup>	1,300	1,322	1,324	N <sup>4</sup> -C <sup>5</sup> -N <sup>1</sup>	110,9	110,5	110,1
C <sup>5</sup> -N <sup>1</sup>	1,319	1,344	1,331	C <sup>5</sup> -N <sup>1</sup> -N <sup>2</sup>	109,7	110,5	110,2
C <sup>3</sup> -N <sup>6</sup>	1,355	1,364	-	N <sup>2</sup> -C <sup>3</sup> -N <sup>6</sup>	123,7	123,1	-

Fig. 2 shows the molecular electrostatic potential of 3-Amino-1,2,4-Triazole calculated by DFT method with 6-31G(d,p) basis sets. The red colored surface areas show the most negative molecular electrostatic potential while dark blue areas – the most positive one. As can be seen, the region around N<sup>4</sup> is rich in electrons. Since the electrostatic potential there has the most negative values, the metal ion coordinates with this atom.

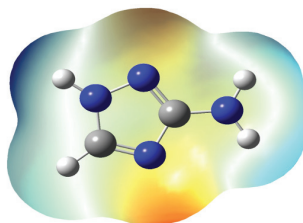


Fig.2 Calculated electrostatic potential on the molecular surface of ATR

The quantum chemical calculations provide possibility to estimate the net atomic charges –  $q$ , localized at the corresponding atoms as a result of the redistribution of the electrons in the molecule. Despite that they are neither experimentally observed nor related to some physical property, they allow revealing the distribution of electron density in a system of

interconnected atoms and predicting some chemical properties of the molecule. The net atomic charges values were obtained by the Mulliken population analysis [6] with Hartree-Fock (HF) and Density Functional Theories (DFT) methods with 6-31G(d,p) basis sets.

Table 2. Mulliken atomic charges of 3-Amino-1,2,4-Triazole.

atom	HF/6-31G(d,p)	B3LYP/6-31G(d,p)	atom	HF/6-31G(d,p)	B3LYP/6-31G(d,p)
N <sup>1</sup>	-0.443	-0.329	N <sup>4</sup>	-0.619	-0.503
N <sup>2</sup>	-0.414	-0.367	C <sup>5</sup>	-0.365	0.296
C <sup>3</sup>	0.774	0.629	N <sup>6</sup>	0.366	-0.676

The net atomic charges of the heteroatoms (Table 2) show that the N<sup>1</sup>, N<sup>2</sup>, N<sup>4</sup> and N<sup>6</sup> centers of triazole have negative charge values of -0,329, -0,367, -0,503 and -0,676, respectively.

It can be seen from the calculations of the electrostatic potential and the atomic charges carried out that the site most suitable for creation of a coordination bond is N<sup>4</sup>.

It is well known that DFT methods work better for systems containing transition metal atoms. For these reasons, we have decided to use the B3LYP level with 6-31G(d,p) orbital basis sets for analyses of 3-Amino-1,2,4-Triazole complexes.

The visualization of the optimized geometrical structure and atomic labeling of Me<sup>2+</sup> - 3-Amino-1,2,4-Triazole are presented in Fig. 3.

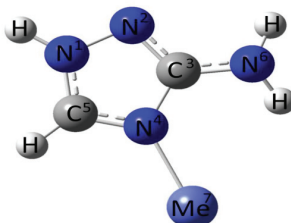


Fig. 3 Optimized geometrical structure and atomic labeling of Me<sup>2+</sup> - 3-Amino-1,2,4-Triazole complexes in water-phase

The optimized geometries of Me<sup>2+</sup>-3-Amino-1,2,4-Triazole complexes are shown Table 3.

Table 3. Optimized geometrical parameters of Me<sup>2+</sup> – ATR complexes in water-phase.

Parameters	Ca-ATR	Zn-ATR	Cu-ATR	Co-ATR	Ni-ATR	Cd-ATR	Hg-ATR
Bond length (Å)							
N <sup>1</sup> -N <sup>2</sup>	1,361	1,363	1,313	1,313	1,317	1,360	1,362
N <sup>2</sup> -C <sup>3</sup>	1,320	1,301	1,374	1,375	1,359	1,311	1,318
C <sup>3</sup> -N <sup>4</sup>	1,370	1,376	1,392	1,391	1,405	1,371	1,366
N <sup>4</sup> -C <sup>5</sup>	1,332	1,341	1,324	1,323	1,339	1,357	1,333
C <sup>5</sup> -N <sup>1</sup>	1,343	1,335	1,370	1,370	1,355	1,339	1,342
C <sup>3</sup> -N <sup>6</sup>	1,424	1,441	1,319	1,318	1,320	1,430	1,424
N <sup>4</sup> -Me	2.601	1,942	2,022	2,099	1,893	2,279	2,453
Bond angle (grad)							
N <sup>1</sup> -N <sup>2</sup> -C <sup>3</sup>	101,5	101,6	102,8	102,6	103,0	101,8	101,8
N <sup>2</sup> -C <sup>3</sup> -N <sup>4</sup>	114,7	114,2	112,5	112,7	111,8	114,1	113,9
C <sup>3</sup> -N <sup>4</sup> -C <sup>5</sup>	103,7	104,6	103,4	103,2	103,9	104,5	104,9
N <sup>4</sup> -C <sup>5</sup> -N <sup>1</sup>	108,2	106,4	109,3	109,4	107,8	107,1	107,1
C <sup>5</sup> -N <sup>1</sup> -N <sup>2</sup>	111,9	113,1	112,1	112,1	113,4	112,5	112,3
N <sup>2</sup> -C <sup>3</sup> -N <sup>6</sup>	128,9	133,3	119,8	119,8	121,7	130,7	130,2
C <sup>3</sup> -N <sup>4</sup> -Me	99,6	92,1	133,9	134,5	130,0	96,1	96,5
Dihedral angle (grad)							
N <sup>2</sup> -C <sup>3</sup> -N <sup>4</sup> -Me	180,0	180,0	180,0	180,0	159,1	180,0	179,8

The calculated bond orders are reported in Table 4. Obviously, the triazole bond orders are in the range 1,110 – 1,782. These bond order values suggest a relatively strong aromatic character for the five-membered ring of triazole.

Table. 4. Bond orders of  $\text{Me}^{2+}$ - 3-Amino-1,2,4-Triazole.

Bond	Ca-ATR	Zn-ATR	Cu-ATR	Co-ATR	Ni-ATR	Cd-ATR	Hg-ATR
$\text{N}^1\text{-N}^2$	1,382	1,378	1,631	1,629	1,568	1,395	1,394
$\text{N}^2\text{-C}^3$	1,725	1,782	1,391	1,391	1,429	1,752	1,732
$\text{C}^3\text{-N}^4$	1,389	1,300	1,265	1,268	1,178	1,341	1,358
$\text{N}^4\text{-C}^5$	1,591	1,486	1,636	1,645	1,531	1,543	1,568
$\text{C}^5\text{-N}^1$	1,468	1,524	1,353	1,353	1,422	1,517	1,497
$\text{C}^3\text{-N}^6$	1,175	1,110	1,620	1,623	1,603	1,163	1,169
$\text{N}^4\text{-Me}$	0,378	0,729	0,638	0,611	0,936	0,587	0,541

The calculated electronic properties of some complexes are shown in Table 5. They are the Total energies, the HOMO and LUMO energies, their energy difference and calculated dipole moments. The HOMO-LUMO gap is an important stability index. A large energy gap implies highly stable molecule. The dipole moment is another indicator of the electron distribution in a molecule and it is one of the properties used to discuss and rationalize her structure.

Table. 5. Calculated electronic properties of  $\text{Me}^{2+}$ - 3-Amino-1,2,4-Triazole in water-phase.

	$E_{\text{tot}}$ (a.u.)	HOMO (eV)	LUMO(eV)	$\Delta_{\text{LUMO-HOMO}}$	$\mu$ (D)	$\text{Lg}\beta$ [10]
Ca-ATR	-974,6900	-16,269	-9,535	6,734	15,836	1,25
Zn-ATR	-2076,0639	-17,760	-13,886	3,874	3,552	2,74
Cu-ATR	-493,0822	-16,981	-11,301	5,680	1,307	2,90
Co-ATR	-441,9887	-16,057	-14,685	1,372	0,628	2,95
Ni-ATR	-466,1593	-16,341	-15,260	1,081	0,517	2,85
Cd-ATR	-345,0242	-17,416	-13,617	3,799	3,857	2,63
Hg-ATR	-339,6826	-18,201	-14,767	3,434	1,173	3,16

The relationship between the stability constants of complexes and calculated dipole moments are shown in Fig. 4.

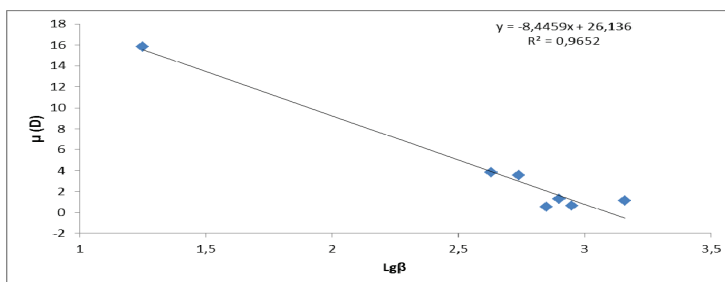


Fig. 4 Relationship between the stability constants and calculated dipole moments

It can be observed that the stability constants of complexes correlate well with the calculated dipole moments.

## CONCLUSIONS

The geometric parameters of 3-Amino-1,2,4-Triazole and  $\text{Me}^{2+}$ - 3-Amino-1,2,4-Triazole ( $\text{Me} = \text{Ca}, \text{Zn}, \text{Cu}, \text{Co}, \text{Ni}, \text{Cd}$  and  $\text{Hg}$ ) complexes – lengths, angles and bond orders in water-phase at ration  $\text{Me} : \text{L} = 1 : 1$  were established by HF and DFT (at B3LYP

level) methods with 6-31G(d,p) basis sets, for Cu, Co, Ni, Cd, Hg with LANL2DZ. The electronic properties of complexes were determined. The stability constants of complexes were found to correlate well with the calculated dipole moments.

## REFERENCES

- [1] Gaussian 03, Revision B.04, Frisch, M.J., G.W.Trucks, H.B.Schlegel, G.E.Scuseria, M.A.Robb, J.R.Cheeseman, J.A.Montgomery Jr., T.Vreven, K.N.Kudin, J.C.Burant, J.M.Millam, S. S.Iyengar, J.Tomasi, V.Barone, B.Mennucci, M.Cossi, G.Scalmani, N.Regga, G.A.Petersson, H.Nakatsuji, M.Hada, M.Ehara, K.Toyota, R.Fukuda, J.Hasegawa, M.Ishida, T.Nakajima, Y.Honda, O.Kitao, H.Nakai, M.Klene, X.Li, J.E.Knox, H.P.Hratchian, J.B.Cross, V.Bakken, C.Adamo, J.Jaramillo, R.Gomperts, R.E.Stratmann, O.Yazyev, A.J.Austin, R.Cammi, C.Pomelli, J.W.Ochterski, P.Y.Ayala, K.Morokuma, G.A.Voth, P.Salvador, J.J.Dannenberg, V.G.Zakrzewski, S.Dapprich, A.D.Daniels, M.C.Strain, O.Farkas, D.K.Malick, A.D.Rabuck, K.Raghavachari, J.B.Foresman, J.V.Ortiz, Q.Cui, A.G.Baboul, S.Clifford, J.Cioslowski, B.B.Stefanov, G.Liu, A.Liashenko, P.Piskorz, I.Komaromi, R.L.Martin, D.J.Fox, T.Keith, M.A.Al-Laham, C.Y.Peng, A.Nanayakkara, M.Challacombe, P.M.W.Gill, B.Johnson, W.Chen, M.W.Wong, C.Gonzalez, J.A.Pople, Gaussian, Inc., Wallingford CT, 2004.
- [2] Gilchrist T. I. Gymer G. E. 1,2,3-Triazoles. *Advances in Heterocyclic Chemistry*. 1974, 16, 33-85.
- [3] HyperChem for Windows, Release 5.1, HyperCube, Inc.
- [4] Katritzky A. R., C.W. Ress. *Comprehensive Heterocyclic Chemistry: The Structure, Reactions, Synthesis And Uses Of Heterocyclic Compounds*. Pergamon Press, New York, 1984, 5, 6, 738, 238.
- [5] Mulliken, R. S.. *Electronic Population Analysis on LCAO-MO Molecular Wave Functions*. I. *The Journal of Chemical Physics*, 1955, 23, 1833-1840.
- [6] Onsager L.. *Electric Moments of Molecules in Liquids*. *J. Am. Chem. Soc.*, 1936, 58, 1486-1493.
- [7] Politzer P, J. S. Murray. *Molecular Electrostatic Potentials and Chemical Reactivity*. *Reviews in Computational Chemistry*, K. B. Lipkowitz and D. B. Boyd, Eds., VCH Publishers, New York, 1991, 2, 273-312.
- [8] Ugo Varetto, <MOLEKEL Version>; Swiss National Supercomputing Centre: Lugano (Switzerland).
- [9] Wamhoff H.1,2,3-Triazoles and their Benzo Derivatives. *Comprehensive Heterocyclic Chemistry*, 1984, 5, 669-732.
- [10] Даварски К. А., П. Берберова, С. Манолов, Р. Янкова, Е. Момчилова. *Исследование равновесий в системе  $M^{n+}$ -3-амино-1,2,4-триазол-Н<sub>2</sub>O ( $M^{n+} = Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Hg^{2+}$ ,  $Ca^{2+}$ ,  $Al^{3+}$  и  $Fe^{3+}$ )*. *Журнал общей химии*, 1997, 67, 1, 7-10.
- [11] Ленинджер А. *Молекулярные основы структуры и функций клетчи*. Биохимия. М. Мир, 1976, 959.
- [12] Мельников Н.Н., *Пестициды: Химия, технология и применение*, "Химия", Москва, 1987.

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**This paper has been reviewed**