STRUCTURE AND VIBRATIONAL ANALYSIS OF
[Al(3-AMINO-1,2,4-TRIAZOLE)_3]^{3+} BY DFT CALCULATIONS

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ABSTRACT
The pesticides contained in soil often react with metal ions. The information about the
geometry of these complexes would provide a possibility to describe pesticides propagation in
soil and subterranean water, as well as the mechanisms of their transportation in plants. The
geometry optimization of [Al(3-Amino-1,2,4-triazole)_3]^{3+} was done in gas and in water phase by
DFT using Becke’s three-parameter hybrid functional with 6-31G(d,p) and 6-311++G(d,p)
basis sets. The bond orders and the electronic properties of the complex ion were calculated.

HOMO-LUMO energies and calculated structure are shown.

Key words: [Al(3-Amino-1,2,4-triazole)_3]^{3+}, quantum chemical calculations, geometry
optimization, electronic properties

INTRODUCTION
The pesticide 3-Amino-1,2,4-triazole is the first 1,2,4-triazole to be manufactured on a large
scale from aminoguanidine formate. It is a non-selective herbicide which inhibits chlorophyll
formation and regrowth from buds. Although some derivatives are more effective for some
purposes, none of the more complex triazole derivatives has been able to displace aminotriazole as
a neutral herbicide and defoliant of cotton. The 5-membered nitrogen heterocyclic rings are
structural fragments in a number of biologically active compounds [9], pesticides [11], pigments
and other substances used in industry [5, 19]. The pesticides contained in soil often react with metal
ions. The information about the geometry of these complexes would provide a possibility to
describe pesticides propagation in soil and subterranean water, as well as the mechanisms of their
transportation in plants.

In a previous work, we have studied aminotriazole complex formation in aqueous solutions
with ions contained in soil as macrocomponents (Fe^{3+}, Al^{3+}, Ca^{2+}) and microcomponents (Cu^{2+},
Co^{3+}, Cd^{2+}, Ni^{2+}, Zn^{2+} and Hg^{2+}) [2].

The aims of the present work is using quantum chemical calculations to determine the
geometric structure of [Al(3-Amino-1,2,4-triazole)_3]^{3+} in gas and in water phase and to examine the
electronic properties of the complex ion.

COMPUTATIONAL METHODS
The full optimization of [Al(3-Amino-1,2,4-triazole)_3]^{3+} complex ion was carried out by the
Density Functional Theories (DFT) method, using Gaussian 03 software [4] at the B3LYP level
with 6-31G(d,p) basis set in gas and in water phase, and with 6-311++G(d,p) basis set in gas phase.
All calculations were converged to 10–8 a.u. Vibration frequencies were also calculated to the
structure with optimized geometry and no imaginary frequency were obtained, so the stationary
points correspond to the minima of the potential energy surface.

In order to characterize the electronic population on each atomic centre a Mulliken population
analysis [12] was carried out for [Al(3-Amino-1,2,4-triazole)_3]^{3+}.

To take into account the effect of the solvent by self-consistent reaction field (SCRF) the
method of Onsager was used [13]. 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 Hamiltonian containing the solvent reaction potential.
The software packages HyperChem 5.0 [6] and Molekel 5.4 [18] were used for data preparation and visualization of the results.

RESULTS AND DISCUSSION

1. 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 [20]. 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 metal atom. For these reasons is used the B3LYP level set for analyses of [Al(3-Amino-1,2,4-triazole)₃]³⁺ complex ion.

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

![Optimized geometrical structure and atomic labeling of [Al(3-Amino-1,2,4-triazole)₃]³⁺](image)

**Table 1. Optimized geometrical parameters of [Al(3-Amino-1,2,4-triazole)₃]³⁺**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>In gas phase (B3LYP/6-31G(d,p))</th>
<th>In water phase (B3LYP/6-31G(d,p))</th>
<th>In gas phase (B3LYP/6-311++G(d,p))</th>
<th>Exp.[1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond length (Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₁(14,24) – N₆(16,26)</td>
<td>1.359</td>
<td>1.359</td>
<td>1.357</td>
<td>1.359</td>
</tr>
<tr>
<td>N₁(16,26) – C₁(13,23)</td>
<td>1.302</td>
<td>1.302</td>
<td>1.297</td>
<td>1.323</td>
</tr>
<tr>
<td>C₁(13,23) – N₁(10,22)</td>
<td>1.344</td>
<td>1.345</td>
<td>1.344</td>
<td>1.324</td>
</tr>
<tr>
<td>N₁(10,22) – N₄(14,24)</td>
<td>1.336</td>
<td>1.336</td>
<td>1.334</td>
<td>1.331</td>
</tr>
<tr>
<td>C₁(13,23) – N₃(17,27)</td>
<td>1.431</td>
<td>1.431</td>
<td>1.431</td>
<td>–</td>
</tr>
<tr>
<td>N₁(10,21) – Al</td>
<td>1.984</td>
<td>1.981</td>
<td>1.985</td>
<td>–</td>
</tr>
<tr>
<td>N₇(17,27) – Al</td>
<td>2.189</td>
<td>2.195</td>
<td>2.188</td>
<td>–</td>
</tr>
<tr>
<td>Bond angle (grad)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₁(14,24) – N₆(16,26) – C₁(13,23)</td>
<td>101.4</td>
<td>101.4</td>
<td>101.7</td>
<td>102.1</td>
</tr>
<tr>
<td>N₁(16,26) – C₁(13,23) – N₁(10,22)</td>
<td>115.1</td>
<td>115.1</td>
<td>115.0</td>
<td>114.6</td>
</tr>
<tr>
<td>C₁(13,23) – N₁(10,22) – N₄(14,24)</td>
<td>103.7</td>
<td>103.7</td>
<td>103.7</td>
<td>103.0</td>
</tr>
<tr>
<td>N₁(10,22) – N₄(14,24) – N₆(16,26)</td>
<td>107.0</td>
<td>107.0</td>
<td>107.0</td>
<td>110.1</td>
</tr>
<tr>
<td>C₁(13,23) – N₁(10,21) – Al</td>
<td>112.8</td>
<td>112.8</td>
<td>112.6</td>
<td>110.2</td>
</tr>
<tr>
<td>N₃(17,27) – N₁(10,21) – Al</td>
<td>95.8</td>
<td>96.0</td>
<td>95.6</td>
<td>–</td>
</tr>
<tr>
<td>N₇(17,27) – Al – N₁(10,21)</td>
<td>67.2</td>
<td>67.1</td>
<td>67.1</td>
<td>–</td>
</tr>
<tr>
<td>Dihedral angle (grad)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₁(14,24) – C₁(13,23) – N₄(14,24) – Al</td>
<td>178.6</td>
<td>178.5</td>
<td>178.7</td>
<td>–</td>
</tr>
<tr>
<td>C₁(13,23) – N₁(10,21) – Al – N₁(14,24)</td>
<td>86.1</td>
<td>85.6</td>
<td>86.1</td>
<td>–</td>
</tr>
</tbody>
</table>
Analysis of the coordination modes of $[\text{Al}(3\text{-Amino-1,2,4-triazole})_3]^{3+}$ indicates that 3-Amino-1,2,4-triazole is bonded to Al$^{3+}$ through two nitrogen atoms yielding a highly stable system.

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 [8]. 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 compound are presented in Table 2. Obviously, the triazole bond orders are in the range $1.125 - 1.780$. These bond orders values suggest a relatively strong aromatic character for the five-membered ring of triazole.

2. HOMO-LUMO Analysis

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the main orbitals that plays an important role in chemical stability. The HOMO exhibits the ability to donate an electron and LUMO as an electron acceptor serves the ability to obtain an electron. The HOMO and LUMO energy calculated by B3LYP/6-31G (d,p) level of theory show the energy gap which reflects the chemical activity of the molecule.

![HOMO and LUMO](image)

$$E_{\text{HOMO}} = -1799.387 \text{ kJ/mol}; \quad E_{\text{LUMO}} = -1082.179 \text{ kJ/mol}; \quad \Delta E_{\text{LUMO-HOMO}} = 717.208 \text{ kJ/mol}$$

The atomic orbital compositions of the frontier molecular orbital are shown in Fig. 2. On the basis of HOMO-LUMO energies global reactivity descriptors, such as the energies of frontier
molecular orbitals (E\(_{\text{HOMO}}\), E\(_{\text{LUMO}}\), energy band gap (E\(_{\text{HOMO}}\)−E\(_{\text{LUMO}}\)), electronegativity (\(\chi\)), chemical potential (\(\mu\)), global hardness (\(\eta\)), global softness (\(S\)) and global electrophilicity index (\(\omega\)), which describe the electrophilic behaviour, have been calculated for [Al(3-Amino-1,2,4-triazole)]\(_3^+\) using Eqs. (2) – (6) [3, 10, 15, 16, 21]:

\[
\chi = -\frac{1}{2} \left( E_{\text{HOMO}} + E_{\text{LUMO}} \right) = 1440.783 \text{ kJ/mol} \quad (2) \quad \mu = -\chi = -\frac{1}{2} \left( E_{\text{HOMO}} + E_{\text{LUMO}} \right) = -1440.783 \text{ kJ/mol} \quad (3)
\]

\[
\eta = \frac{1}{2} \left( E_{\text{LUMO}} - E_{\text{HOMO}} \right) = 358.604 \text{ kJ/mol} \quad (4) \quad S = \frac{1}{2\eta} = 0.0014 \text{ (kJ/mol)}^{-1}
\]

\[
\omega = \frac{\chi^2}{2\eta} = 2894.357 \text{ kJ/mol} \quad (6) \quad \text{ECT} = (\Delta N_{\text{max}})_I - (\Delta N_{\text{max}})_{II}
\]

Electrophilic charge transfer (ECT) [14] is defined as the difference between the \(\Delta N_{\text{max}}\) values of interacting molecules. For two molecules I and II approaching each other (i) if ECT>0, charge flows from II to I and (ii) if ECT<0, charge flows from I to II. ECT is calculated using Eq. (7), where (\(\Delta N_{\text{max}}\)) = \(\mu/\eta\) and (\(\Delta N_{\text{max}}\)) = \(-\mu/\eta\).

From population analysis was found that coordination bond between N\(^{10-}\) Al is formed by sp (37\% s; 63\% p) hybrid orbital of nitrogen atom and sp (26\% s; 74\% p) hybrid orbital of aluminium, as 91.39\% of the bond is contributed by nitrogen atom. The same is between N\(^{11-}\) Al and N\(^{21-}\) Al.

### 3. Vibrational Spectral Analysis

The vibrational spectra of 3-Amino-1,2,4-triazole and [Al(3-Amino-1,2,4-triazole)]\(_3^+\) was calculated by DFT with B3LYP functional having extended basis sets 6-31G(d,p) and 6-311++G(d,p) using Gaussian 03 package. The experimental assignments of IR for several vibrations, IR theoretical and relative intensities were reported in Table 3.

**Table 3.** Experimental and calculated vibrational frequencies (cm\(^{-1}\)), IR intensity and probable assignments of 3-Amino-1,2,4-triazole and [Al(3-Amino-1,2,4-triazole)]\(_3^+\)

<table>
<thead>
<tr>
<th>Experimental frequencies(^c) (^b)</th>
<th>3-Amino-1,2,4-triazole</th>
<th>[Al(3-Amino-1,2,4-triazole)](_3^+)</th>
<th>Assignments(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{3398 s} )</td>
<td>3696</td>
<td>57</td>
<td>3686</td>
</tr>
<tr>
<td>(\text{3326 m} )</td>
<td>3682</td>
<td>71</td>
<td>3665</td>
</tr>
<tr>
<td>(\text{3182 m} )</td>
<td>3581</td>
<td>23</td>
<td>3581</td>
</tr>
<tr>
<td>(\text{1674 vs} )</td>
<td>1660</td>
<td>239</td>
<td>1651</td>
</tr>
<tr>
<td>(\text{1590 s} )</td>
<td>1599</td>
<td>75</td>
<td>1587</td>
</tr>
<tr>
<td>(\text{1533 s} )</td>
<td>1530</td>
<td>29</td>
<td>1517</td>
</tr>
<tr>
<td>(\text{1418 s} )</td>
<td>1490</td>
<td>26</td>
<td>1473</td>
</tr>
<tr>
<td>(\text{1389 ms} )</td>
<td>1399</td>
<td>55</td>
<td>1383</td>
</tr>
<tr>
<td>(\text{1275 vs} )</td>
<td>1199</td>
<td>4</td>
<td>1296</td>
</tr>
<tr>
<td>(\text{1217 vs} )</td>
<td>1118</td>
<td>10</td>
<td>1192</td>
</tr>
<tr>
<td>(\text{1045 vs} )</td>
<td>1071</td>
<td>49</td>
<td>1064</td>
</tr>
<tr>
<td>(\text{945 vs} )</td>
<td>989</td>
<td>6</td>
<td>989</td>
</tr>
<tr>
<td>(\text{873 s} )</td>
<td>838</td>
<td>13</td>
<td>845</td>
</tr>
<tr>
<td>(\text{830 s} )</td>
<td>778</td>
<td>57</td>
<td>774</td>
</tr>
<tr>
<td>(\text{729 vs} )</td>
<td>658</td>
<td>24</td>
<td>653</td>
</tr>
<tr>
<td>(\text{608} )</td>
<td>608</td>
<td>249</td>
<td>573</td>
</tr>
<tr>
<td>(\text{421} )</td>
<td>421</td>
<td>2</td>
<td>419</td>
</tr>
<tr>
<td>(\text{317} )</td>
<td>317</td>
<td>4</td>
<td>316</td>
</tr>
<tr>
<td>(\text{304} )</td>
<td>304</td>
<td>5</td>
<td>303</td>
</tr>
</tbody>
</table>

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; \(v\) - very weak

(b) \(\nu\) - stretching; \(\delta\) - symmetric; \(\sigma\) - asymmetric; \(\delta_{\text{b}}\) - bending; \(\delta_{\text{r}}\) - rocking; \(\delta_{\text{w}}\) - wagging; \(\delta_{\text{t}}\) - twisting; \(R\) band – ring deformation

I\(_{\text{AB}}\) - Theoretical infrared intensities
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 [7].

Frequencies recorded experimentally for 3-Amino-1,2,4-triazole are compared with the calculated frequencies obtained by DFT/B3LYP methods with 6-31G(d,p) and 6-311++G(d,p) basis sets. 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 will match well with the experimental ones.

CONCLUSION

Geometry of [Al(3-Amino-1,2,4-triazole)]$_3^{3+}$ complex ion was optimized using DFT with 6-31G(d,p) basis set in gas and in water phase and with 6-311++G(d,p) basis set in gas phase. Predictive IR spectra are very useful in the absence of experimental data. The difference between the basis set frequencies values of most of the fundamentals is very small. Therefore, the assignment made at DFT higher level at theory with higher basis set with only reasonable deviations from the experimental values, seems to be correct. HOMO-LUMO analysis may serve as a useful quantity to explain hydrogen bonding, reactivity and structure–activity relationship of molecule.

REFERENCES

18. Ugo Varetto, <MOLEKEL Version>; Swiss National Supercomputing Centre: Lugano (Switzerland).