Theoretical Investigation of Interaction of 1-R-5-Mercaptotetrazoles with Silver and Palladium Particles

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The molecular electrostatic potential (MESP) distribution for 1-R-5-mercaptotetrazolium anions, as well as total energy of complexes of 1-R-5-mercaptotetrazoliums ions with silver and palladium particles has been calculated using DFT approach. Based on the results of quantum-chemical calculations, coordination mode of the ligands under their binding with surfaces of nanoparticles was proposed.

Keywords: Anion, nanoparticle, 1-phenyl-5-mercaptotetrazolium.

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1. INTRODUCTION

Recently, tetrazole derivatives were proposed as capping agents for stabilization of metal and semiconductor nanoparticles. It was shown that easily available 1-R-5-mercaptotetrazoles (R = alkyl, phenyl) can be used for chemical synthesis of cadmium sulphide [1] and gold [2] nanoparticles. Interest in these novel capping agents was determined by their thermally induced decomposition leading to a high percentage of gaseous products which is an interesting feature for future applications in coatings, since the removal of capping agents provides great opportunity to improve catalytic properties of the NPs and their assemblies.

Due to the presence of multiple donor centers in 1-R-5-mercaptotetrazoles, there are several possibilities of bonding between metal nanoparticles and capping ligands. In coordination compounds 5-mercaptotetrazoliums are known to act as monodentate (S or N) or bidentate (N,N or N,S) ligands depending mostly on the nature of the metal ions [3,4]. In the present paper we report of investigation of the coordination of adsorbed 1-R-5-mercaptotetrazolium ion with respect to silver and palladium nanoparticles.

2. COMPUTATIONAL DETAILS

All calculations have been carried out within density functional theory with B3LYP functional [5] and 6-31G(d) basis set [6] for H, C, N and S atoms. LANL2DZ basis set [7] has been used for Ag and Pd atoms. For all considered structures the full geometry optimization without symmetry constrains has been performed, force constants have been calculated to verify that optimized structures are minima on potential energy surface.

3. RESULTS AND DISCUSSION

Two different models have been used to predict the orientation of the adsorbed 1-R-5-mercaptotetrazolium ion with respect to silver nanoparticle: the model based on molecular electrostatic potential distribution and the model based on comparison of values of total energy calculated for different complexes of 1-R-5-mercaptotetrazolium anions with silver ions.

The B3LYP/6-31G(d) calculated plots of molecular electrostatic potential for 1-tret-butyl-5-mercaptopentetrazolium and 1-phenyl-5-mercaptopentetrazolium anions are given in Fig. 1 and Fig. 2 respectively. It can be seen from Fig. 1 and Fig. 2 that the most negative areas of molecular electrostatic potential are located in plain of tetrazolium ring near N(4)-, N(3)- and S-atoms. So, we can suppose that the favorable interaction of 1-R-5-mercaptopentetrazolium anion with silver nanoparticle should pass through one of the mentioned atoms. We also considered the method of interaction shown in Fig. 3.

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The B3LYP/6-31G(d) calculations of the total energy of complexes of 1-substituted-5-mercaptopotetrazolium with Ag⁺ and Ag₃⁺ cations have been performed to verify the proposed methods of coordination of tetrazole derivatives relative to silver nanoparticle. The following possible structures of complexes of 1-tret-butyl-5-mercaptopotetrazolium and 1-phenyl-5-mercaptopotetrazolium anions with Ag⁺ have been considered: the structures where silver ion interacts with sulfur atom a, N(4) b and N(3) c; the bridged structure d, where Ag⁺ interacts both with S and N(4).

The initial structures of complexes of 1-tret-butyl-5-mercaptopotetrazolium anions with Ag⁺ chosen for the geometry optimization are given in Fig. 4. The structures a and b turned to bridged structure d during the geometry optimization. So, the only two stable structures have been found. The same results have been obtained during the geometry optimization of complexes of 1-phenyl-5-mercaptopotetrazolium anions with Ag⁺ (see Fig. 5).

The results of calculations of total and relative energies of stable structures c and d are given in Table 1. It can be seen from Table 1 that the bridged structure is the most stable for both 1-tret-butyl- and 1-phenyl-5-mercaptopotetrazolium anions complexes with Ag⁺.

### Table 1 – B3LYP/6-31G(d) calculated total (E) and relative (ΔE) energy of complexes of 1-tret-butyl- and 1-phenyl-5-mercaptopotetrazolium anions with Ag⁺

<table>
<thead>
<tr>
<th>Structure</th>
<th>E, Hartree</th>
<th>ΔE, kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1c</td>
<td>-958.85249</td>
<td>27.4</td>
</tr>
<tr>
<td>1b</td>
<td>-958.89618</td>
<td>0.0</td>
</tr>
<tr>
<td>2c</td>
<td>-1032.64200</td>
<td>27.5</td>
</tr>
<tr>
<td>2d</td>
<td>-1032.68584</td>
<td>0.0</td>
</tr>
</tbody>
</table>

![Fig. 2 – B3LYP/6-31G(d) calculated plots of molecular electrostatic potential of 1-phenyl-5-mercaptopotetrazolium anion](image1)

**Fig. 2** – B3LYP/6-31G(d) calculated plots of molecular electrostatic potential of 1-phenyl-5-mercaptopotetrazolium anion

![Fig. 3 – The proposed method of interaction of 1-R-5-mercaptopotetrazolium anion with silver nanoparticle](image2)

**Fig. 3** – The proposed method of interaction of 1-R-5-mercaptopotetrazolium anion with silver nanoparticle

![Fig. 4 – The initial structures of complexes of 1-tret-butyl-5-mercaptopotetrazolium anion with Ag⁺ chosen for the geometry optimization](image3)

**Fig. 4** – The initial structures of complexes of 1-tret-butyl-5-mercaptopotetrazolium anion with Ag⁺ chosen for the geometry optimization
The ground state geometry of cationic silver trimer is equilateral triangle [8]. Thus, take into account our results reported above three possible orientations of 1-R-5-mercaptotetrazole anion with respect to Ag₃⁺ particle have been considered (Fig. 6): bridged structure 3a where silver atom is located between S and N(4); structure 3b where one silver atom interacts with sulfur and another atom – with N(4); structure 3c where one silver atom interacts with N(4) whereas sulfur atom interacts with two silver atoms which located near the local minima of molecular electrostatic potential (see Fig. 1 on the bottom). It should be mentioned that in the case of structure 3b the silver atoms are located in the areas of global minima of electrostatic potential (see Fig. 1 on the top), so this structure should be the most stable.

It can be seen from Table 2 that the structures 3b and 4b are indeed the most stable for both 1-tet-butyl- and 1-phenyl-5-mercaptotetrazole anions complexes with Ag₃⁺.

The calculations of interaction of Pd₃⁺ cluster with 1-phenyl-5-mercaptotetrazole anion have been carried out based on reported above results. The ground state geometry of cationic palladium trimer is \( \text{B}_2 \text{B}_2 \) which is only slightly Jahn-Teller distorted equilateral triangle [9]. As for silver trimer three starting structures have been considered for geometry optimization (Fig. 7).

**Table 2** – B3LYP/6-31G(d) calculated total \( E \), relative \( \Delta E \) and binding \( E_b \) energy for complexes of 1-tet-butyl- and 1-phenyl-5-mercaptotetrazole anions with Ag₃⁺

<table>
<thead>
<tr>
<th>Structure &amp;superscript;</th>
<th>( E ), Hartree</th>
<th>( \Delta E ), kcal/mol</th>
<th>( E_b ), kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>-1250.51199</td>
<td>13.4</td>
<td>131.0</td>
</tr>
<tr>
<td>3b</td>
<td>-1250.53328</td>
<td>0.0</td>
<td>144.4</td>
</tr>
<tr>
<td>4a</td>
<td>-1324.30185</td>
<td>13.4</td>
<td>126.8</td>
</tr>
<tr>
<td>4b</td>
<td>-1324.32317</td>
<td>0.0</td>
<td>140.2</td>
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* - in the case of 1-phenylsubstituted tetrazole derivatives the same structures as for 1-tet-butyl-5-mercaptotetrazolium (Fig. 6) are denoted as 4a and 4b.
The structure 5a turned to structure 5c during the geometry optimization. So, the only two minima on potential energy surface have been found in the case of interaction of Pd₃⁺ cluster with 1-phenyl-5-mercaptotetrazolium anion. It should be noted, that unlike the interaction with silver trimer, in the case of Pd₃⁺ the tetrazole ring and metal cluster are not in one plane for structure 5b. The corresponding dihedral angle is 125°. The results of calculations of total, relative and binding energy for complexes of 1-tret-butyl- and 1-phenyl-5-mercaptotetrazolium anion with Pd₃⁺ are given in Table 3.

Table 3 – B3LYP/6-31G(d) calculated total (E), relative (ΔE) and binding (Eₐ) energy for complexes of 1-tret-butyl- and 1-phenyl-5-mercaptotetrazolium anions with Pd₃⁺

<table>
<thead>
<tr>
<th>Structure*</th>
<th>E, Hartree</th>
<th>ΔE, kcal/mol</th>
<th>Eₐ, kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>5b</td>
<td>-1193.37627</td>
<td>7.1</td>
<td>174.8</td>
</tr>
<tr>
<td>5c</td>
<td>-1193.38766</td>
<td>0.0</td>
<td>182.0</td>
</tr>
<tr>
<td>6b</td>
<td>-1267.16563</td>
<td>7.1</td>
<td>170.3</td>
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<tr>
<td>6c</td>
<td>-1267.17690</td>
<td>0.0</td>
<td>177.4</td>
</tr>
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</table>

* · in the case of 1-phenylsubstituted tetrazole derivatives the same structures as for 1-tret-butyl-5-mercaptotetrazolium (Fig. 7) are denoted as 6b and 6c.

It can be seen from Table 3 that the structures 5c and 6c are the most stable for both 1-tret-butyl- and 1-phenyl-5-mercaptotetrazolium anions complexes with Pd₃⁺. This result differs from that obtained for complexes with silver trimer for which the structure b was found the most stable. According to our calculations complexes of 1-R-5-mercaptotetrazolium with Pd₃⁺ are characterized by higher binding energy than those ones with Ag₃⁺ (see Tables 2 and 3).

REFERENCES