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

V.E. Matulis*, A.S. Mazheika, O.A. Ivashkevich

Research Institute for Physical Chemical Problems of the Belarusian State University,
14 Leningradskaya Street, 220050 Minsk, Belarus

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.

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-mercaptotetrazoles 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 и 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-mercaptotetrazolium and 1-phenyl-5-mercaptotetrazolium 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-mercaptotetrazolium anion with silver nanoparticle should pass through one of the mentioned atoms. We also considered the method of interaction shown in Fig. 3.
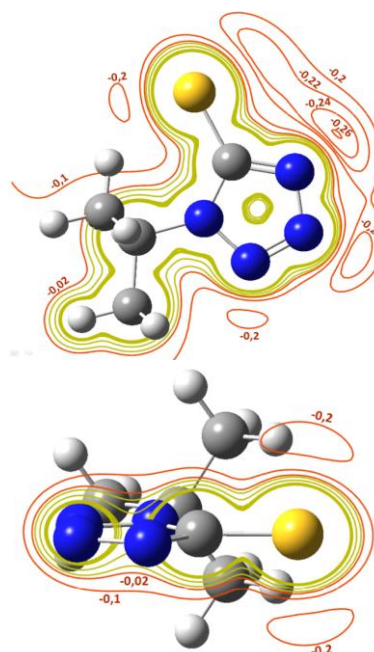

Fig. 1 – B3LYP/6-31G(d) calculated plots of molecular electrostatic potential of 1-*tret*-butyl-5-mercaptotetrazolium anion

---

* vitaly_matulis@mail.ru

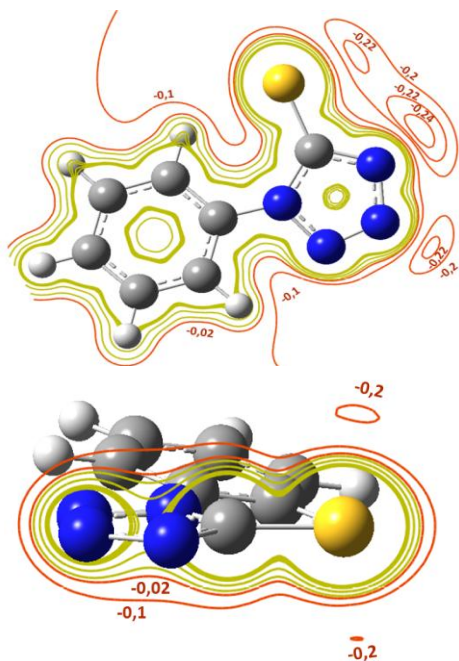**Fig. 2** – B3LYP/6-31G(d) calculated plots of molecular electrostatic potential of 1-phenyl-5-mercaptotetrazolium anion
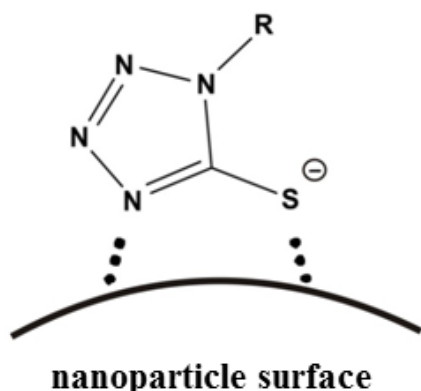

Fig. 3 – The proposed method of interaction of 1-R-5-mercaptotetrazolium anion with silver nanoparticle

The B3LYP/6-31G(d) calculations of the total energy of complexes of 1-substituted-5-mercaptotetrazolium with Ag$^+$ and Ag$_3^+$ 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-mercaptotetrazolium and 1-phenyl-5-mercaptotetrazolium 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-mercaptotetrazolium 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-mercaptotetrazolium 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-mercaptotetrazolium 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-mercaptotetrazolium anions with Ag$^+$
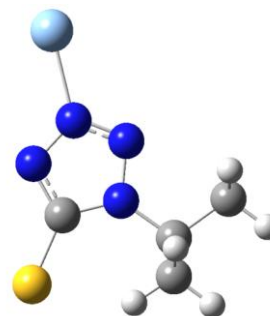
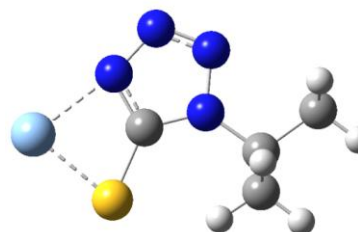| Structure	E, Hartree	ΔE, kcal/mol
1c	-958.85249	27.4
1b	-958.89618	0.0
2c	-1032.64200	27.5
2d	-1032.68584	0.0
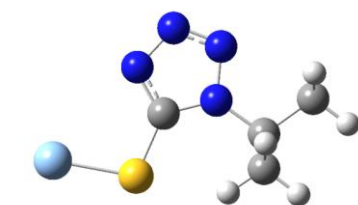
1a
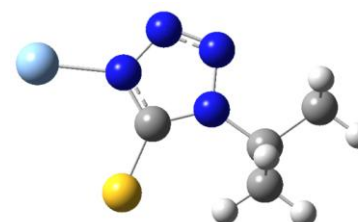
1b

1c

1d

Fig. 4 – The initial structures of complexes of 1-*tret*-butyl-5-mercaptotetrazolium 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-mercaptotetrazolium anion with respect to Ag_3^+ 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.
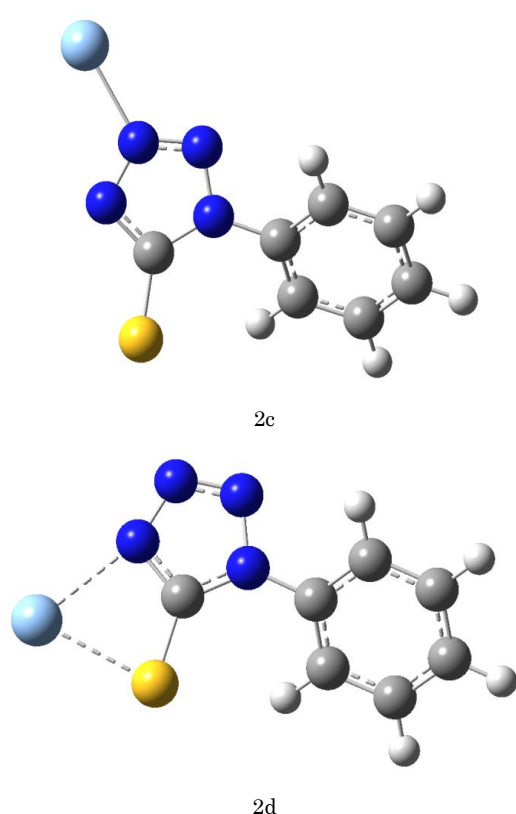

2c

2d

Fig. 5– B3LYP/6-31G(d) optimized structures of complexes of 1-phenyl-5-mercaptotetrazolium anion with Ag⁺

The structure **3c** turned to structure **3b** during the geometry optimization. The results of calculations of total, relative and binding energy for complexes of 1-*tret*-butyl- and 1-phenyl-5-mercaptotetrazolium anion with Ag_3^+ are given in Table 2.

Table 2 – B3LYP/6-31G(d) calculated total (*E*), relative (Δ*E*) and binding (E_b) energy for complexes of 1-*tret*-butyl- and 1-phenyl-5-mercaptotetrazolium anions with Ag_3^+

Structure*	*E*, Hartree	Δ*E*, kcal/mol	E_b, kcal/mol
3a	-1250.51199	13.4	131.0
3b	-1250.53328	0.0	144.4
4a	-1324.30185	13.4	126.8
4b	-1324.32317	0.0	140.2

* - in the case of 1-phenylsubstituted tetrazole derivatives the same structures as for 1-tret-butyl-5-mercaptotetrazolium (Fig. 6) are denoted as 4a and 4b.

It can be seen from Table 2 that the structures **3b** and **4b** are indeed the most stable for both 1-*tret*-butyl- and 1-phenyl-5-mercaptotetrazolium anions complexes with Ag_3^+.

The calculations of interaction of Pd_3^+ cluster with 1-phenyl-5-mercaptotetrazolium anion have been carried out based on reported above results. The ground state geometry of cationic palladium trimer is ⁴B₂ 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).
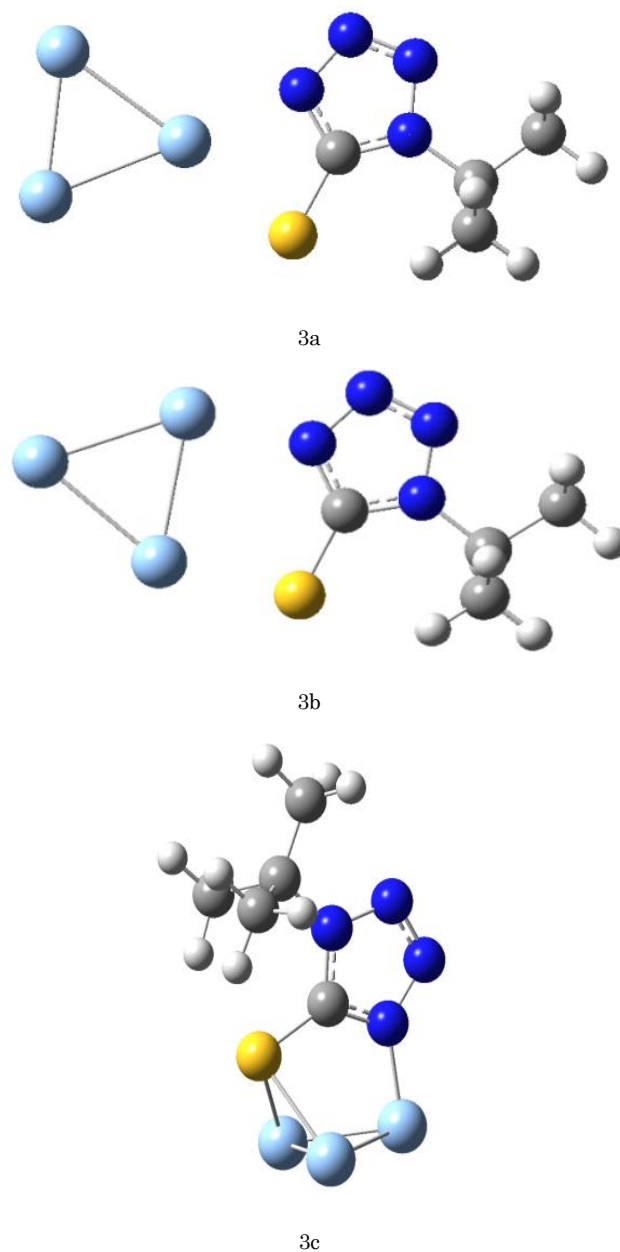

3a

3b

3c

Fig. 6 – Initial (3c) and B3LYP/6-31G(d) optimized (3a and 3b) structures of complexes of 1-tret-butyl-5-mercaptotetrazolium anion with Ag3+

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 Pd_3^+ cluster with 1-phenyl-5-mercaptotetrazolium anion. It should be noted, that unlike the interaction with silver trimer, in the case of Pd_3^+ 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 Pd_3^+ are given in Table 3.

Table 3 – B3LYP/6-31G(d) calculated total (E), relative (ΔE) and binding (E_b) energy for complexes of 1-*tret*-butyl- and 1-phenyl-5-mercaptotetrazolium anions with Pd_3^+

Structure*	E, Hartree	ΔE, kcal/mol	E_b, kcal/mol
5b	-1193.37627	7.1	174.8
5c	-1193.38766	0.0	182.0
6b	-1267.16563	7.1	170.3
6c	-1267.17690	0.0	177.4

* - 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 Pd_3^+. 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 Pd_3^+ are characterized by higher binding energy than those ones with Ag_3^+ (see Tables 2 and 3).

5a

5b

5c

Fig. 7 – Initial (4a) and B3LYP/6-31G(d) optimized (4b and 4c) structures of complexes of 1-*tret*-butyl -5-mercaptotetrazolium anion with Pd_3^+.

REFERENCES

1. S.V. Voitekhovich, D.V. Talapin, C. Klinke, A. Kornowski, H. Weller, *Chem. Mater.* **20**, 4545 (2008).
2. M.N. Nichick, S.V. Voitekhovich, A. Shavel, A.I. Lesnikovich, O.A. Ivashkevich, *Polyhedron* **28**, 28 (2009).
3. P.N. Gaponik, S.V. Voitekhovich, O.A. Ivashkevich, *Russ. Chem. Rev.* **75**, 507 (2006).
4. S.V. Voitekhovich, R. Syre, J. Lach, V.E. Matulis, P.N. Gaponik, O.A. Ivashkevich, B. Kersting, *Eur. J. Inorg. Chem.* **2010**, 5387 (2010).
5. A.D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
6. G. A. Petersson, M.A. Al-Laham, *J. Chem. Phys.* **94**, 6081 (1991).
7. P.J. Hay, W.R. Wadt, *J. Chem. Phys.* **82**, 299 (1985).
8. J. Yoon, K.S. Kim, K.K. Baeck, *J. Chem. Phys.* **112** No21, 9335 (2000).
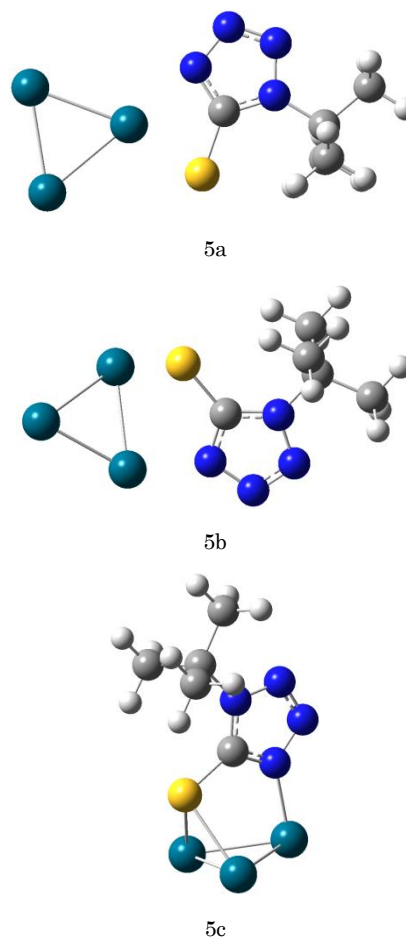9. D.G. Dai, K.K. Das, K. Balasubramanian, *Chem. Phys. Let.* **184** No5-6, 589 (1991).