

*J. Serb. Chem. Soc.* 77 (9) 1211–1222 (2012)  
JSCS–4346

Journal of  
the Serbian  
Chemical Society

JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

UDC 542.913+66.095.252:547.53–304.9+  
547.496.3:546.742'982

Short communication

SHORT COMMUNICATION

## Synthesis of thiadiazolobenzamide, *via* cyclization of thioxothiurea, and its Ni and Pd complexes

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(Received 11 September 2011, revised 28 February 2012)

**Abstract:** In this study, a compound, *N*-(3-methyl-4-oxo-4*H*-[1,3,4]thiadiazolo[2,3-*c*][1,2,4]triazin-7-yl)benzamide, was obtained *via* two different reactions: 1) reaction of 4-amino-6-methyl-3-(methylthio)-1,2,4-triazin-5(4*H*)-one with benzoyl isothiocyanate under removal of methanethiol and 2) reaction of 4-amino-3,4-dihydro-6-methyl-3-thioxo-1,2,4-triazin-5(2*H*)-one with benzoyl isothiocyanate under elimination of hydrogen sulfide. In both reactions, a new bond between sulfur and nitrogen atoms was formed and a five-membered ring was created. The oxo thiadiazolo benzamide was characterized by IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy, and mass spectrometry. X-Ray crystallography was used to shed light on the structure of this new compound. Two new complexes could be generated by coordination of the oxo thiadiazolo benzamide to Pd(II) and Ni(II) ions. These complexes were analyzed by IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy, conductometry and thermal gravimetry (TGA). The theoretical QM calculation GIAO was also applied to predict the structure of the Pd complex.

**Keywords:** nucleophilic addition reaction; Pd complexes; QM calculations; GIAO.

### INTRODUCTION

The chemistry of isocyanates and isothiocyanates have been greatly investigated.<sup>1,2</sup> Isocyanate and isothiocyanate compounds undergo two kinds of reactions: cycloaddition,<sup>3–5</sup> such as [2+2],<sup>6,7</sup> [3+2],<sup>8,9</sup> [4+2],<sup>10,11</sup> [2+2+2],<sup>12,13</sup> and nucleophilic addition, such as to thiosemicarbazide,<sup>14</sup> thiosemicarbazone,<sup>15</sup> urea<sup>16</sup> and thiourea.<sup>17</sup> The nucleophilic addition of an amine group to an isothiocyanate results in the formation of thiourea, thiosemicarbazide and, in some cases, to

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doi: 10.2298/JSC110911052A

benzamide derivatives.<sup>18</sup> Properties such as cytotoxic and antibacterial have been reported for some of these compounds.<sup>19–21</sup> These compounds, as neutral or anionic ligands, can also connect to metal cations and form numerous complexes.<sup>22–24</sup>

In this study, the compounds produced by the nucleophilic addition reaction of benzoyl isothiocyanate with two thiotriazine derivatives were analyzed. In addition, these compounds were used as ligands to produce their nickel(II) and palladium(II) complexes. The biological activities of the obtained complexes were also investigated. The prepared compounds and complexes were analyzed by different techniques and quantum mechanical calculations were employed to confirm additionally the experimental data.

#### EXPERIMENTAL

4-Amino-6-methyl-3-(methylthio)-1,2,4-triazin-5(4*H*)-one (AMMSTO) and 4-amino-3,4-dihydro-6-methyl-3-thioxo-1,2,4-triazin-5(2*H*)-one (AMTTO) were prepared according to literature procedures.<sup>25</sup> Benzoyl isothiocyanate and the solvents were purchased from Fluka and Merck. All chemicals were used without further purification.

Ultrasonic (Elmasonic S) and microwave (CEM MDS-2000) radiation were applied in the experiments. Melting points were determined using an Electro Thermal IA 9000 instrument. The infrared spectra (on a Nicolet 55XC employing the KBr disk technique, 4000–400  $\text{cm}^{-1}$ ) and  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra (on a Bruker Advance 500 spectrometer using  $\text{DMSO-}d_6$  and TMS as the internal reference) were recorded at room temperature.

##### *Synthesis of N-(3-methyl-4-oxo-4H-[1,3,4]-thiadiazolo[2,3-c][1,2,4]triazin-7-yl)benzamide (1)*

Benzoyl isothiocyanate (0.156  $\text{cm}^3$ , 1 mmol) was gradually added to a solution of 4-amino-6-methyl-3-(methylthio)-1,2,4-triazin-5(4*H*)-one (AMMSTO) (0.2 g, 1 mmol) in acetonitrile (15  $\text{cm}^3$ ). The mixture was stirred for 7 h at 70–80 °C. The milky precipitate of **1** was filtered, washed with methanol and dried in an oven at 80 °C. Yield: 76 %. The reaction was repeated with the same reactant ratio under other conditions: 1) microwave 360 W, 15 min; 600 W, 3 min in solvent and 600 W, 2 min without solvent, 2) ultrasonic 75 °C, 2 h. The maximum yield of about 81 % was obtained by using microwave 600 W and without solvent.

##### *Synthesis of N-[(2,5-dihydro-6-methyl-5-oxo-3-thioxo-1,2,4-triazin-4(3H)-yl)amino]thioxomethylbenzamide (2)*

Benzoyl isothiocyanate (0.156  $\text{cm}^3$ , 1 mmol) was gradually added to a solution of 4-amino-3,4-dihydro-6-methyl-3-thioxo-1,2,4-triazin-5(2*H*)-one (AMTTO) (0.158 g, 1 mmol) in ethanol (15  $\text{cm}^3$ ). The mixture was stirred for 6 h at 70–80 °C. The white precipitate of **2** was filtered, washed with methanol and acetone, and dried in an oven at 80 °C. Yield: 36 %. This reaction was also repeated with the same reactant ratio under the other conditions. The highest yield of 42 % was afforded using microwave 360 W radiation for 15 min and solvent-free.

##### *Synthesis of the Pd and Ni complexes*

*Synthesis of the palladium complex with N-(3-methyl-4-oxo-4H-[1,3,4]-thiadiazolo[2,3-c][1,2,4]triazin-7-yl)benzamide (1), complex C1.* Complex **C1** was synthesized from palladium(II) chloride (0.04 g, 0.2 mmol) and **1** (0.105 g, 0.3 mmol) in 8  $\text{cm}^3$  acetonitrile. After 1 hour, 1  $\text{cm}^3$  methanol was added and the mixture was stirred under reflux for 4 h. The ob-

tained brown precipitate was filtered, washed with methanol and dried in a vacuum oven. The yield was 82 %. With the same ratio of reactants in DMSO under the other employed conditions, microwave 180 W radiation for 15 min afforded the highest yield of 92 %.

*Synthesis of the nickel complex with N-}[(2,5-dihydro-6-methyl-5-oxo-3-thioxo-1,2,4-triazin-4(3H)-yl)amino]thioxomethyl}benzamide (2), Complex C2.* Complex C2 was synthesized from nickel(II) acetylacetonate (0.051 g, 0.20 mmol) and **2** (0.064 g, 0.20 mmol) in 4 cm<sup>3</sup> ethanol. The mixture was stirred gently at 70 °C for 10 h. The obtained green precipitate was filtered, washed several times with methanol and dried in a vacuum oven. Repetition of the reaction under the other conditions had no effect on the yield.

#### *Thermal gravimetric analysis and conductivity*

Thermal analysis and conductivity of complexes were measured by Module STA 1500 and Metrohm, respectively.

The conductivity of 0.20–0.80 M solutions of complexes in *N,N*-methylformamide was measured at room temperature. No conductivity has been detected. Thermal analysis was performed in air within 100–950 °C temperature range; the heating rate was 40 °C min<sup>-1</sup>.

#### *X-Ray crystallography*

Suitable single crystals of compounds **1** and **2** were obtained by dissolving the corresponding precipitate in a mixture of methanol and acetonitrile (1:1) or methanol and *N,N*-dimethylformamide (1:1), respectively. The data collection for the crystal was realized on a Bruker AXS SMART diffractometer at room temperature using MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) monochromatized by a graphite crystal. Data reduction was completed using the Bruker AXS SAINT and SADABS software packages. The structure of compounds **1** and **2** were solved by direct methods and refined by full-matrix least-squares calculation using SHELX-97. An empirical absorption correction ( $\Psi$ -scan) was applied. All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were calculated corresponding to their geometric conditions and refined using the riding model. Isotropic displacement parameters of hydrogen atoms were derived from the parent atoms.

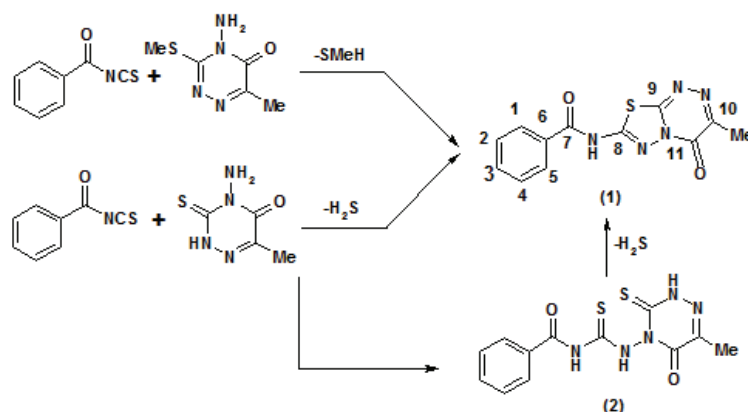
## RESULTS AND DISCUSSION

On reaction of AMMSTO with benzoyl isothiocyanate, methanethiol was released,<sup>26</sup> a five-membered ring was formed and finally *N*-(3-methyl-4-oxo-4*H*-[1,3,4]-thiadiazolo[2,3-*c*][1,2,4]triazin-7-yl)benzamide (**1**) was afforded. *N*-}[(2,5-dihydro-6-methyl-5-oxo-3-thioxo-1,2,4-triazin-4(3*H*)-yl)amino]thioxomethyl}-benzamide (**2**) was synthesized directly through the reaction of AMTTO with benzoyl isothiocyanate (Scheme 1).

#### *Spectral data for the synthesized compounds and complexes*

*N*-(3-methyl-4-oxo-4*H*-[1,3,4]-thiadiazolo[2,3-*c*][1,2,4]triazin-7-yl)benzamide (**1**). Decomposed at 300 °C. FTIR (KBr, cm<sup>-1</sup>): 3212 (NH stretching), 3109 (CH stretching of aromatic ring), 2921 (CH stretching of aliphatic group), 1702 (C=O stretching), 1673 (C=O stretching), 1598, 1566 (NH bending), 1529 (C=N and C=C stretching), 1487 (C=N and C=C stretching), 1296 (C–N– stretching), 1252 (N–N stretching), 1068 (C–N stretching), 713 (C–S stretching). <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  / ppm): 2.42 (3H, *s*, CH<sub>3</sub>), 7.58 (2H, *t*,  $J = 7.3$  Hz, C2H and

C4H), 7.70 (1H, *t*,  $J = 7.3$  Hz, C3H), 8.14 (2H, *d*,  $J = 7.35$  Hz, C1H and C5H), 13.76 (1H, *s*, NH).  $^{13}\text{C}$ -NMR (125 MHz, DMSO- $d_6$ ,  $\delta$  / ppm): 17.29 (CH<sub>3</sub>), 128.51 (C2 and C4), 128.77 (C1 and C5), 130.41 (C3), 133.70 (C6), 147.92 (C9), 152.97 (C11), 153.57 (C7), 157.42 (C8), 166.89 (C10). MS ( $m/z$ , (relative abundance, %)): 211 (C<sub>6</sub>H<sub>4</sub>N<sub>5</sub>O<sub>2</sub>S<sup>+</sup>+1, 75), 105 (C<sub>6</sub>H<sub>5</sub>CO<sup>+</sup>, 100), 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 88), 51 (C<sub>4</sub>H<sub>3</sub><sup>+</sup>, 30). Scheme 1 indicates the C numbering.



Scheme 1. Reaction pathways of the reactants to **1** and **2**. The C atom numbering is indicated.

*N*-{[(2,5-di-hydro-6-methyl-5-oxo-3-thioxo-1,2,4-triazin-4(3*H*)-yl)amino]-thioxomethyl}benzamide (**2**). Decomposed at 330 °C. FTIR (KBr,  $\text{cm}^{-1}$ ): 3328 (NH stretching), 3169 (CH stretching of aromatic ring), 2956 (CH stretching of aliphatic group), 1713 (C=O stretching), 1698 (C=O stretching), 1599 (NH bending), 1519 (C=N and C=C stretching), 1490 (C=N and C=C stretching), 1376 (C=S stretching), 1324 (C=S stretching), 1297 (C–N stretching), 1269 (N–N stretching), 1094 (C–N stretching).  $^1\text{H}$ -NMR (500 MHz, DMSO- $d_6$ ,  $\delta$  / ppm): 2.43 (3H, *s*, CH<sub>3</sub>), 7.59 (2H, *t*,  $J = 7.3$  Hz, C2H and C4H), 7.71 (1H, *t*,  $J = 7.3$  Hz, C3H), 8.14 (2H, *d*,  $J = 7.3$  Hz, C1H and C5H), 13.71 (1H, *s*, NH).  $^{13}\text{C}$ -NMR (125 MHz, DMSO- $d_6$ ,  $\delta$  / ppm): 17.00 (CH<sub>3</sub>), 128.49 (C2 and C4), 128.77 (C1 and C5), 130.28 (C3), 133.74 (C6), 147.90 (C9), 153.00 (C11), 153.44 (C7), 157.39 (C8), 166.79 (C10). MS ( $m/z$ , (relative abundance, %)): 321 (C<sub>12</sub>H<sub>11</sub>N<sub>5</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup>, 14.5), 287 (C<sub>12</sub>H<sub>9</sub>N<sub>5</sub>O<sub>2</sub>S<sup>+</sup>, 8.5), 158 (C<sub>4</sub>H<sub>5</sub>N<sub>4</sub>OS<sup>+</sup>+1, 36.5), 105 (C<sub>6</sub>H<sub>5</sub>CO<sup>+</sup>, 100), 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 83), 51 (C<sub>4</sub>H<sub>3</sub><sup>+</sup>, 23). Scheme 1 indicates the C numbering.

#### *Spectral data for the prepared Ni and Pd complexes*

**Complex C1.** Decomposed at 320 °C. FTIR (KBr,  $\text{cm}^{-1}$ ): 3245 (NH stretching), 3109 (CH stretching of aromatic ring), 2956 (CH stretching of aliphatic group), 1710 (C=O stretching), 1680 (C=O stretching), 1597, 1563 (NH bending), 1492 (C=N and C=C stretching), 1460 (C=N and C=C stretching), 1297 (C–N stretching), 1254 (N–N stretching), 1099 (C–N stretching), 706 (C–S stretching).

$^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-}d_6$ ,  $\delta$  / ppm): 2.42 (3H, *s*,  $\text{CH}_3$ ), 7.58 (2H, *t*,  $J = 7.3$  Hz, C2H and C4H), 7.71 (1H, *t*,  $J = 7.3$  Hz, C3H), 8.13 (2H, *d*,  $J = 7.3$  Hz, C1H and C5H), 13.70 (1H, *s*, NH).  $^{13}\text{C-NMR}$  (125 MHz,  $\text{DMSO-}d_6$ ,  $\delta$  / ppm): 16.99 ( $\text{CH}_3$ ), 128.51 (C2 and C4), 128.78 (C1 and C5), 130.14 (C3), 133.78 (C6), 147.86 (C9), 153.02 (C11), 153.37 (C7), 157.41 (C8), 166.73 (C10). Scheme 1 indicates the C numbering.

*Complex C2*. Yield: 63 %; decomposed at 220 °C. FTIR (KBr,  $\text{cm}^{-1}$ ): 3365 (NH stretching), 3072 (CH stretching of aromatic ring), 2924 (CH stretching of aliphatic group), 1630 (C=O stretching), 1594 (C=O stretching), 1557 (NH bending), 1525 (C=N and C=C stretching), 1504 (C=N and C=C stretching), 1264 (N–N stretching), 1071 (C–N stretching), 734 (C–S stretching).  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-}d_6$ ,  $\delta$  / ppm): 2.29 (3H, *s*,  $\text{CH}_3$ ), 7.39 (3H, *s*, C2H, C3H and C4H), 8.06 (2H, *s*, C1H and C5H), 2.48 (12H, *s*,  $\text{CH}_3$ , acetylacetonate), 5.42 (2H, *s*, CH, acetylacetonate).  $^{13}\text{C-NMR}$  (125 MHz,  $\text{DMSO-}d_6$ ,  $\delta$  / ppm): 17.05 ( $\text{CH}_3$ ), 126.09 (C2 and C4), 126.69 (C1 and C5), 128.88 (C3), 136.29 (C6), 146.06 (C9), 159.85 (C11), 171.57 (C10), 15.52 ( $\text{CH}_3$ , acetylacetonate), 54.41 (CH, acetylacetonate), 196.30 (CO, acetylacetonate). Scheme 1 indicates the C numbering.

IR spectroscopy and mass spectrometry confirmed the synthesis of compound **2** as well as compound **1**. However, although **1** and **2** differed in the absorbance bands in their IR spectra and the peaks in the mass spectra differed significantly, both exhibited the same  $^1\text{H-}$  and  $^{13}\text{C-NMR}$  spectra and X-ray single crystal data. This indicated the instability of **2** in solution and its conversion to **1** by loss of hydrogen sulfide (Scheme 1). The analysis of complex **C2** showed that this conversion also occurred in this complex.

The observed decrease in the wavelength numbers of absorbance bands of carbonyl group in the complex **C2** could be due to the dislocation of the electronic cloud in acetylacetonate and thiadiazolo benzamide. In the NMR spectrum, the resonances of the methyl groups and carbonyl groups of acetylacetonate ions appeared at 15.52 and 196.30 ppm, respectively. The sharp resonances of complexes **C1** and **C2** demonstrated that the Ni(II) and Pd(II) ions with  $d^8$  electronic configuration have diamagnetic properties.

The conductivities of the complexes were measured in *N,N*-dimethylformamide and no conductivity could be detected. The lack of conductivity certified the neutral structure of the complexes. This is evidence for the location of the ligands and the anionic parts in the inner sphere of both complexes.

#### *X-Ray diffraction analysis*

The same structures were deduced for **1** and **2**. The relevant crystallographic information on **1** is summarized in Table I and Fig. 1. In the crystal lattice, three interactions were observed between sulfur and nitrogen atoms (S1...N6, medium, 3.161 Å) and sulfur and oxygen atoms (S2...O1, strong, 2.566 Å and S2...O4,

strong, 2.602 Å). Finally, two intermolecular hydrogen bonds joined the molecules together (N5–H5···O3, strong, 2.834 Å and N10–H10A···N3, medium, 3.004 Å).

### Thermal analysis

The thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) data for complexes **C1** and **C2** are listed in Table II.

TABLE I. Crystallographic and structure refinement data of **1**

Empirical formula	C <sub>12</sub> H <sub>9</sub> N <sub>5</sub> O <sub>2</sub> S
Formula weight	287.30
<i>T</i> / K	296(2)
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> / Å	7.2750(4)
<i>b</i> / Å	26.6492(15)
<i>c</i> / Å	13.1837(7)
$\beta$ / °	100.962(4)
<i>V</i> / Å <sup>3</sup>	2509.3(2)
<i>Z</i>	8
<i>D</i> / g cm <sup>-3</sup>	1.521
$\mu$ / mm <sup>-1</sup>	0.267
% Completeness to $\theta$ , <i>R</i> (int)	97.5 ( $\theta = 34.89^\circ$ ), 0.0582
Final <i>R</i> indices ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	<i>R</i> 1 = 0.1010, <i>wR</i> 2 = 0.1329
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0471, <i>wR</i> 2 = 0.1143

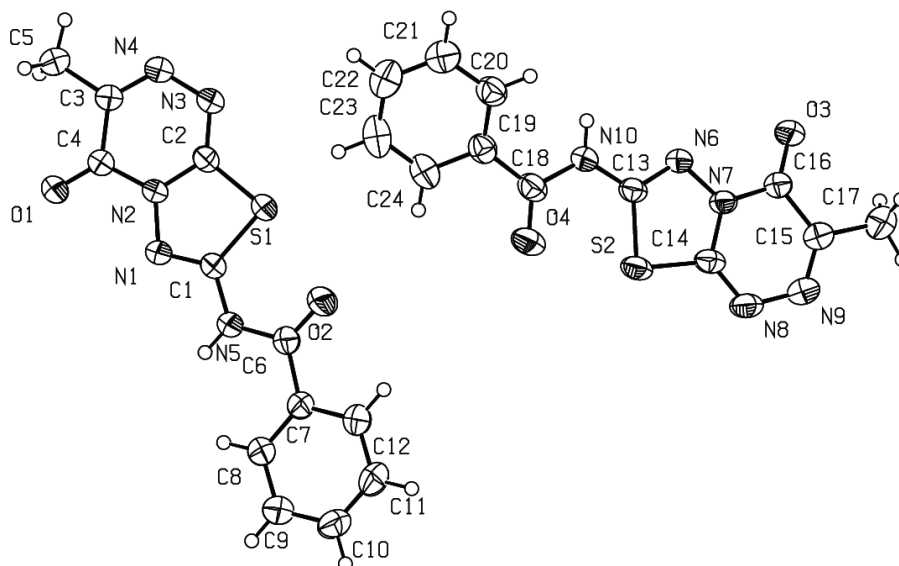


Fig. 1. Molecular structure of compound **1** (50 % probability level).

Thermal gravimetric analyses indicated different behavior of **C1** and **C2** even though both had **1** as the ligand. For both complexes, weight loss occurred in two steps. In the first step complex, **C1** lost two chloride ions above 340 °C and in the second step, compound **1** was lost above 360 °C. On the other hand, in the first step, **C2** lost compound **1** in temperature region 220–414 °C, then the two acetylacetonate ions above 420 °C. This difference could be related to the different number and kinds of bonds between compound **1** and Pd and Ni ions in complexes **C1** and **C2**.

TABLE II. Results of TGA and DTA of **C1** and **C2**

Complex (molecular mass)	TG range, °C	Lost	Residue	Weight loss, %		Reaction pathway
				Found	Calcd.	
C1=PdLCl <sub>2</sub> (463.3)	340→358	2Cl	PdL	16	15.34	Endothermic
	360→398	L	PdO	60	62.01	Exothermic
	398→500	PdO	PdO	26	26.33	Endothermic
C2=NiL(acac) <sub>2</sub> (543)	220→414	L	Ni(acac) <sub>2</sub>	51	52.86	Exothermic
	415→498	2acac	NiO	33	36.33	Exothermic
	500→900	NiO	NiO	16	13.75	Exothermic

From the obtained results, the empirical formulas [Pd**1**Cl<sub>2</sub>] and [Ni**1**(acac)<sub>2</sub>] could be suggested for complexes **C1** and **C2**, respectively.

#### THEORETICAL SECTION

##### *Computational details*

*Ab initio molecular orbital calculation.* All calculations were performed using Gaussian 98.<sup>27</sup> The energies and geometries of compound **1** and complex **C1** were calculated and optimized with the Lee, Yang and Parr (LYP)<sup>28</sup> correlation functional, denoted B3LYP,<sup>29</sup> of which the most successful one is based on the hybrid functional method.<sup>30</sup> The spin-unrestricted version of B3LYP (UB3LYP) was used with an open-shell singlet electronic configuration of species. The 6-311G\*\* basis set was employed in the geometry optimization and energy calculations. Full optimizations of all the compounds were addressed without any symmetry constraint. Vibration frequency calculations confirmed the stationary geometries.

Solvation calculations were performed on DMSO ( $\epsilon = 46.7$ ) with the optimized geometries, using the polarized continuum (overlapping spheres) model (PCM) of Tomasi and co-workers.<sup>31</sup>

##### *Optimization of compound 1*

The structure of compound **1** was fully optimized by the B3LYP method using the 6-311G\*\* basis set with no initial symmetry restrictions and assuming C<sub>1</sub> point group.

The optimized geometry of compound **1** in the gas phase was re-optimized considering the solvent effect ( $\epsilon = 46.7$ ) using polarized continuum (overlapping spheres) model (PCM). The optimized structure of compound **1** in DMSO solvent is shown in Fig. 2. Calculations of the vibrational frequencies have confirmed stationary points with no negative eigen value observed in the force constant matrix.

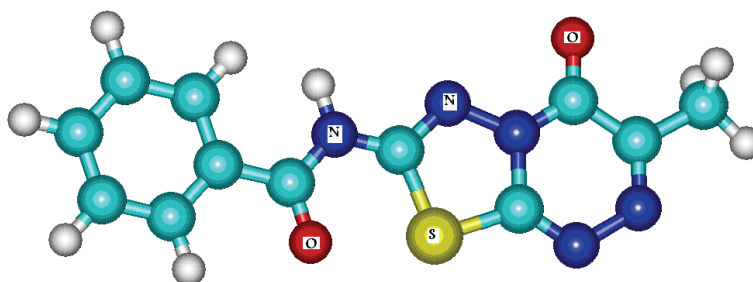


Fig. 2. The optimized structure of compound **1**.

A selection of calculated bond distances, bond angles and dihedral angles of compound **1** are compared with the X-ray data in Table III.

TABLE III. Selected bond distances, Å, and bond and dihedral angles, °, of compound **1** from X-ray analysis and DFT calculations

Bond	X-ray	Calcd.	Bond	X-ray	Calcd.
S1–C2	1.7401(14)	1.757	N1–C1	1.2973(16)	1.297
S2–C14	1.7419(15)		N6–C13	1.2999(18)	
S1–C1	1.7440(13)	1.753	N1–N2	1.3821(15)	1.379
S2–C13	1.7465(13)		N6–N7	1.3857(14)	
O1–C4	1.2093(18)	1.212	N5–C1	1.3775(16)	1.377
O3–C16	1.2215(17)		N10–C13	1.3673(17)	
O2–C6	1.2186(17)	1.221	N5–C6	1.3798(17)	1.380
O4–C18	1.2184(18)		N10–C18	1.3835(18)	
Bond angle, °					
C2–S1–C1	87.20(6)	86.32	C1–N5–C6	122.06(11)	124.52
C14–S2–C13	86.95(6)		C13–N10–C18	122.00(12)	
C2–N2–N1	117.37(10)	117.35	N1–C1–S1	118.16(10)	117.20
C14–N7–N6	116.87(11)		N6–C13–S2	118.41(10)	
C2–N3–N4	116.55(11)	116.61	N3–C2–N2	125.55(12)	125.80
C14–N8–N9	116.48(12)		N8–C14–N7	124.98(13)	
Dihedral angle, °					
S1–C1–N5–C6	6.9(2)	0	C1–N5–C6–C7	-179.71(14)	0
N1–C1–N5–C6	-175.03(15) <sup>a</sup>	180.0	N5–C6–C7–C8	1.7(2) <sup>a</sup>	180.0
N1–C1–S1–C2	0.07(13)	0	–	–	–

<sup>a</sup>The direction of the plane was different



*Calculation of chemical shifts of compound 1*

NMR computations of the absolute shielding were performed using the GIAO method<sup>32</sup> with the DFT optimized structure in the presence of solvent. The <sup>1</sup>H- and <sup>13</sup>C-NMR chemical shifts were calculated using the corresponding absolute shieldings calculated for Me<sub>4</sub>Si at the same level of theory. The obtained calculated values together with the experimental values are given in Table IV. The impressive agreement between the experimental and theoretical chemical shifts confirmed the reliability of DFT calculations for these series of molecules and predicted theoretical results.

TABLE IV. Comparison of some experimental and theoretical <sup>1</sup>H-NMR and <sup>13</sup>C-NMR chemical shifts, ppm, of **1**

<sup>1</sup> H	Calcd.	Exp.	<sup>13</sup> C	Calcd.	Exp.
CH <sub>3</sub>	2.54	2.42	CH <sub>3</sub>	19.31	17.29
C2H and C4H	7.73	7.58	C2 and C4	129.24	128.51
C3H	7.93	7.70	C1 and C5	129.52	128.77
C1H and C5H	8.26	8.14	C3	131.25	130.41
NH	13.97	13.76	C6	134.75	133.70
			C10	149.24	147.92
			C11	154.12	152.97
			C7	154.91	153.57
			C8	158.24	157.42
			C9	168.24	166.89

*Optimization of the geometries of the Pd(II) complex with 1 in different spin states*

The geometry of the [Pd(II)ICl<sub>2</sub>] complex was estimated for two different coordination modes; complex **A** with S and O atoms coordinated to the Pd ion and complex **B** with N and O atoms coordinated to the Pd ion, Fig. 3. Both complexes were optimized in the singlet and triplet spin states with no symmetry constraint imposed and re-optimized in DMSO solvent by the PCM method. The calculated results showed that the low spin states ( $S = 1$ ) were more stable than high spin states ( $S = 3$ ) in complex **A**, 5.78 kcal mol<sup>-1</sup> and complex **B**, 6.5 kcal mol<sup>-1</sup>. Comparison of the energy values between the low spin states of the two complexes indicated **A** (with a six-membered heterocycle) is about 15.5 kcal mol<sup>-1</sup> more stable than **B** (with a five-membered heterocycle).

The calculated geometrical parameters are presented in Fig. 3 considering its optimized structure at the B3LYP/6-311G\*\* level and the solvent effect.

Given these points, the agreement between the theoretical and experimental results confirmed the suggested structure of complex **C1** and its coordination.

## CONCLUSIONS

Compounds **1** and **2** were synthesized through nucleophilic addition reactions and analyzed by IR, NMR and mass spectrometry. Compound **1** was also

characterized by quantum mechanical calculations. In addition, X-ray crystallography was used to determine the structures of compounds. This analysis indicated the inversion of compound **2** to compound **1** in solution.

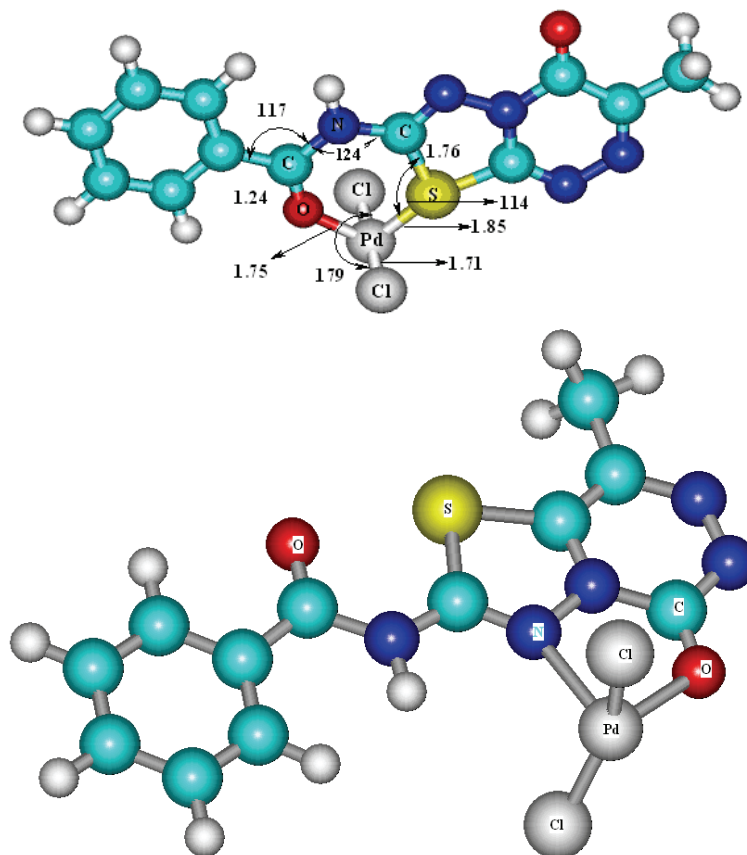


Fig. 3. The optimized structure of the complex **C1** [Pd1C12] at the B3LYP/6-311G\*\* level in DMSO for the two different possible geometries; complex **A**, O and S atoms connected to Pd, complex **B**, O and N atoms connected to Pd.

In complex **C1**, the Pd(II) ion was surrounded by compound **1** as a new non-ionic ligand and two chloride ions. During the synthesis of complex **C2** of compound **2** and Ni(II) acetylacetonate, conversion of compound **2** to compound **1** occurred, consequently complex **C2** consists also of compound **1**.

Considering the obtained experimental and theoretical data, the following structures are suggested as the most adequate for these complexes:

Complex **C1**: two chloride ions and compound **1** as the bidentate ligand are coordinated to Pd(II) ion forming a square planar complex.

Complex **C2**: a) two acetylacetonate ions and compound **1** as a monodentate ligand are coordinated to Ni(II) ions producing a square pyramidal complex, b) two acetyl acetonate ions and compound **1** as bidentate ligand are connected to Ni(II) ions constructing a distorted octahedral complex.

#### SUPPLEMENTARY MATERIAL

CCDC 758812 contains the supplementary crystallographic data. Data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033). Conductivity diagram of complexes and Crystal packing with hydrogen bonding of compound **1** are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

#### ИЗВОД

#### СИНТЕЗА ТИЈАДИАЗОЛО-БЕНЗАМИДА У РЕАКЦИЈИ ЦИКЛИЗАЦИЈЕ ТИОКСОТИОУРЕЕ И ЊЕГОВИХ Ni(II) И Pd(II) КОМПЛЕКСА

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У овом раду, једињење *N*-(3-метил-4-оксо-4*H*-[1,3,4]тијадиазоло[2,3-*c*][1,2,4]триазин-7-ил)бензамид добијено је на два различита начина: 1) у реакцији између 4-амино-6-метил-3-(метилтио)-1,2,4-триазин-5(4*H*)-она и бензоил-изотиоцијаната уз елиминацију метантиола и 2) у реакцији између 4-амино-3,4-дихидро-6-метил-3-тиоксо-1,2,4-триазин-5(2*H*)-она и бензоил-изотиоцијаната уз елиминацију водониксулфида. У овим реакцијама долази до грађења нове везе између атома сумпора и азота, при чему се формира петочлани прстен. Добијени оксотијадиазоло-бензамид је окарактерисан применом IR, <sup>1</sup>H- и <sup>13</sup>C-NMR спектроскопије, као и масене спектрометрије. Поред тога, структура новог једињења је потврђена применом рендгенске структурне анализе. Координацијом оксотијадиазоло-бензамид за Pd(II) и Ni(II) јоне настају два нова комплекса, који су карактерисани применом IR, <sup>1</sup>H- и <sup>13</sup>C-NMR спектроскопије, као и помоћу кондуктометрије и термалне гравиметрије (TGA). Поред тога, структура Pd(II) комплекса је предвиђена применом теоријских квантномеханичких (QM) израчунавања GIAO.

(Примљено 11. септембра 2011, ревидирано 28. фебруара 2012)

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