

# Complexes of Palladium with Tetramethylethylenediamine and their Properties

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## ABSTRACT

Depending on the reaction conditions of palladium with tetramethylethylenediamine, first obtained and studied individual and mixed ligands with different composition and structure. Depending on the process conditions, one or two molecules of the tetramethylethylenediamine bidentate coordinated and form a five-star *metalchelate cycle*. In another obtained cation - anion complex ligand protonated in type of doubly charged cation and organizes the outer sphere of the complex. In the mixed ligands complex of 4 amino pyridine are having the effect of trans influence occurs forced cis-coordination. The study of the biological activity of the synthesized complexes has yielded positive results.

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## Introduction

The Correlation between structure and biological activity of the complexes have long attracted the attention of researchers [1–4]. Obtaining complexes with the predictable structure and composition is a complex and multistep process. Recently, obtaining and study of complexes of platinum-group metal with cis - structure has had great significance from the medical and biomedical point of view [4, 5]. Investigation of the biological activity of the complex compounds such as diamine type based on platinum and palladium has proven that they exhibit resistance to malignant tumors, possess antihypoxic, radioprotective and other biological properties [5–8].

One of the methods for the preparation of cis-diamine type complexes is using ligands containing only 2 nitrogen donor atoms and through their ability to chelate. In this regard, tetramethylethylenediamine (TMEDA)– $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$  was used as a potential bidentate ligand which has the feature of chelation and properties of the obtaining complexes was studied.

## Experimental

### Synthesis of the complex – $[(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{PdCl}_2]$

0.4117 g (1.4033 mmol) of  $\text{K}_2[\text{PdCl}_4]$  are dissolved in 20 ml of water and heated to  $80^\circ\text{C}$ , and then the warm solution was filtered through filter paper. In the same order, the ligand  $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ , was dissolved in 0.1682 g (1.4493 mmol) 15 ml of water (is taken on 15% more) is heated to  $80^\circ\text{C}$  and filtered. Both solutions are mixed in the heat form and the pH of the mixture was reduced to 12. At this time, the reaction mixture becomes colorless. The resulting mixture was evaporated in a water bath at  $60^\circ\text{C}$  to 10 mL of volume. To the warm syrupy mass was added 10 mL of methanol and treated. Excess amount of solvent in the cooled mass is distilled in vacuum, thus the cotton-like precipitate slightly yellow color falls.

The resulting complex is washed several times with cold methanol, and dried in vacuum over  $\text{CaCl}_2$  to constant weight. Yield: 0.3182 g (86%).

For formula  $\text{C}_6\text{H}_{16}\text{N}_4\text{PdCl}_2$

Found, %: Pd – 36.41; Cl – 24.34; N – 9.70; C – 24.70; H – 5.63

Calculated, %: Pd – 36.26; Cl – 24.16; N – 9.54; C – 24.56; H – 5.45

### Synthesis of the complex

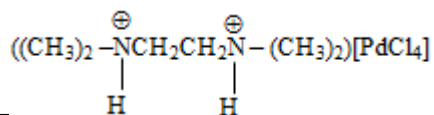
#### $[(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{Pd}]\text{Cl}_2$

The complex  $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$  in an amount of 0.4007 g (1.6335 mmol) was dissolved in 20 ml of a mixture water: DMSO (1:1). TMEDA ligand in quantity 0.3791 g (3.2664 mmol) is added to the finished mixture, which then dissolved in 20 ml of water. The reaction mixture was transferred to a round-bottom flask 50 ml of volume equipped with reflux condenser and heated at the temperature of  $160^\circ\text{C}$  for 17 hours. pH of the reaction mixture is kept constant in the range of 7.5–8 using a solution of  $\text{NH}_4\text{OH}$ . After color change of the reaction mixture is completed, it is cooled and treated with cold methanol. Afterwards, vacuum distillation of excess amount of solvent, slightly yellow-white color crystals precipitated. The precipitate obtained after the completion of the precipitation, filtered through a glass filter and washed with cold methanol and water, then ether. The complex is dried in vacuum over  $\text{CaCl}_2$  to constant weight. Yield: 0.6687 g (91%).

For Formula  $\text{C}_{12}\text{H}_{32}\text{N}_4\text{PdCl}_2$

Found, %: Pd – 26.17; Cl – 17.49; N – 13.81; C – 35.38; H – 7.96

Calculated, %: Pd – 35.98; Cl – 17.31; N – 13.67; C – 35.20; H – 7.81



#### Synthesis of complex –

25 g of TMEDA neutralized with 20% HCl, constantly mixing in a magnetic stirrer. The reaction mixture was transferred to a porcelain cup and evaporated on a water bath at 50°C until a thick syrup and then cooled. 30 ml of cold ethanol added on the cold mass and then treated. As a result, white crystals are formed. The resulting precipitate was filtered using a glass filter and washed with cold ethanol, then dried to constant weight.

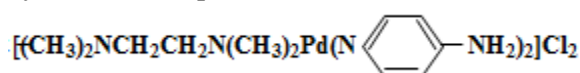
Synthesized according to a special procedure tetramethylethylenediamine-bichloride –  $(\text{CH}_3)_2\text{NH}^+\text{CH}_2\text{CH}_2\text{NH}^+(\text{CH}_3)_2$  in an amount 3662 g (3,1552 mmol) and taken in a stoichiometric ratio of 1:1 in an amount of 0.5594 PdCl<sub>2</sub> g (3,1552 mmol) were mixed dry, and benzene was added in an amount of 50 ml. The reaction mixture was stirred at a temperature of 45–50°C for 2 days, dust-like precipitate a reddish-yellow color drops from the solution. The precipitate was filtered off the glass filter, washed with benzene and then with ether of them. The complex was dried in vacuum over CaCl<sub>2</sub> to constant weight. Yield: 1.0168 g (88%).

For formula C<sub>6</sub>H<sub>18</sub>N<sub>4</sub>PdCl<sub>4</sub>

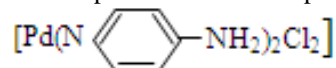
Found, %: Pd – 29.22; Cl – 38.89; N – 7.81; C – 19.80; H – 6.09

Calculated, %: Pd – 29.05; Cl – 38.71; N – 7.64; C – 19.67; H – 4.91

#### Synthesis of complex



Suspension of the complex



compound synthesized by a well-known method in quantity of 0.4271 (1,1688 mmol) is prepared in 15 ml of water at a temperature of 60°C [10]. Tetramethylethylenediamine ligand (TMEDA) is calculated in a stoichiometric ratio of 1:1, and is taken with excess of 20% and dissolved in (1,1688 mmol) 10 ml of warm water. Then, at continuous stirring, the solutions were mixed and the reaction temperature was raised to 80°C. At this temperature, pH of medium support equals to 8 for 3-hours. After the cooling, clear solution drops light-yellow colored flat crystals. Full precipitation is completed for 24 hours at the temperature of + 60°. The resulting crystal was filtered in a glass filter, washed with cold water, then with ethanol and ether, and after everything dried over CaCl<sub>2</sub> in vacuum to constant weight. Yield: 0.4163 g (74%).

For formula C<sub>16</sub>H<sub>28</sub>N<sub>4</sub>PdCl<sub>2</sub>

Found, %: Pd – 22.27; Cl – 14.90; N – 17.56; C – 40.09; H – 5.97

Calculated: Pd – 22.09; Cl – 14.72; N – 17.44; C – 39.91; H – 5.81

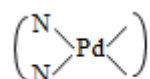
#### Results and Discussion

Platinum and palladium complexes of the di- and tetraamine types from the biological and nanotechnology point of view represents a great interest [11–13]. Chelating ligands play an important role in the formation of models of biological systems. Triple aliphatic amines in addition to those that have important donor centers differ in tendency to protons. Tetramethylethylenediamine (TMEDA) is a potential bidentate chelating ligand containing a nitrogen donor atom and can form complexes of the di- and tetraamine types.

By varying the various physical and chemical factors and various types of individual and mixed ligand complexes

[Pd(TMEDA)Cl<sub>2</sub>], [Pd(TMEDA)<sub>2</sub>]Cl<sub>2</sub>, (H<sub>2</sub>TMEDA)<sub>2</sub>[PdCl<sub>4</sub>], [Pd(TMEDA)  $(\text{N} \text{---} \text{C}_6\text{H}_4\text{---} \text{NH}_2)_2\text{Cl}_2$ ] of palladium were synthesized for the first time. Through various physical and chemical methods, their structure and content have been identified. Comparative spectroscopic researches have been conducted. It has been filmed that IRS of the initial palladium salt and ligands for the synthesis and IRS of the obtained complexes. As a result of the comparative analysis of obtained IRS, assumptions about the structure of the complexes are made.

Due to the high information content of the IR spectra of the synthesized complexes in the 200–500 cm<sup>-1</sup>, they have been widely studied. The observed strong absorption bands at 470 and 476 cm<sup>-1</sup> in IR of complex [Pd(TMEDA)Cl<sub>2</sub>] shows that bidentate ligand coordinate to the palladium at cis position. In accordance with the selection rules C<sub>2v</sub>, if monovalent bond is accompanied with two close absorption bands, they are at deemed at cis position [14–16]. If TMEDA bidentate coordinates, then forms a metal-chelate cycle of type:

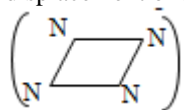


On the other hand, two absorption bands 339 and 346 cm<sup>-1</sup> attributed to ν<sub>Pd-Cl</sub> valence bond were observed at IRS of complex. Marked absorption bands correspond to the data in the literature [17,18]. If the slight variations in the synthesis process are not taken into account, bromide analogue of the complex [Pd(TMEDA)Br<sub>2</sub>] is analogous to chloride complex

[Pd(TMEDA)Cl<sub>2</sub>]. Therefore, were limited to data of IRS of this complex. Observed on the IRS of complex [Pd(TMEDA)Br<sub>2</sub>] close absorption bands at 460, 454 and 220, 206 cm<sup>-1</sup>, respectively, were correlated to the valence bonds  $\nu_{\text{Pd-N}}$  and  $\nu_{\text{Pd-Br}}$  [17, 18].

Comparative analysis of IRS bromide and chloride complexes suggests that the authenticity of the absorption bands in the IRS of complex [Pd(TMEDA)Cl<sub>2</sub>] related to the metal-metal-nitrogen and chlorine relations is not in doubt.

By changing the conditions of the process it has been synthesized tetraammine complex [Pd(TMEDA)<sub>2</sub>]Cl<sub>2</sub>. The absence of chloride ion in the inner sphere of the complex, it proved is proved by its positive reaction to AgNO<sub>3</sub> salt. Typically, in infrared spectrum of the tetraammine complex formed by amines of one force the metal-nitrogen bond characterized by a single absorption band [19, 20]. However, in infrared spectrum of the synthesized [Pd(TMEDA)<sub>2</sub>] complex, bonding of palladium-nitrogen was correlated with strong absorption band at 480 cm<sup>-1</sup> and a weak absorption at 466 cm<sup>-1</sup>. This deviation is due to the partial displacement of the coordination polyhedron of palladium as a result of electrostatic interaction of methyl groups in space

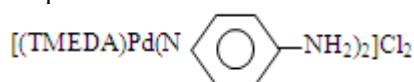


[19–21].

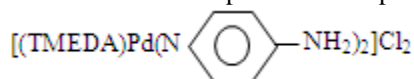
In an acidic environment, protonation of TMEDA occurs and ligand leaves the outer sphere obtained as a doubly charged cation of complex cation-anion type. Formation of tetra acid anion in the complex (H<sub>2</sub>TMEDA)[PdCl<sub>4</sub>]<sup>2-</sup> - [PdCl<sub>4</sub>]<sup>2-</sup> has been proven by result of IR spectroscopy. Registered at Infrared spectra of complex, one strong absorption band at 341 cm<sup>-1</sup> was ascribed to the valence bond  $\nu_{\text{Pd-Cl}}$  formed on the basis of symmetry 4<sub>ph</sub> of tetra acid anion. Broad absorption band in the IR at 3420–3442 cm<sup>-1</sup> is ascribed to the protonated atom. In the same way, an analog bromide complex (H<sub>2</sub>TMEDA)[PdBr<sub>4</sub>] was obtained and studied. Registered on the IR spectra of complex (H<sub>2</sub>TMEDA)<sub>2</sub>[PdBr<sub>4</sub>] and ascribed to the valence bond  $\nu_{\text{Pd-Br}}$  a strong absorption band at 236 cm<sup>-1</sup>, shows the formation of tetrachloro anion [PdCl<sub>4</sub>]<sup>2-</sup> and the same confirms the accuracy of the absorption band at 341 cm<sup>-1</sup> of tetrachloro anion [PdCl<sub>4</sub>]<sup>2-</sup> which refers to the valence bond  $\nu_{\text{Pd-Cl}}$ .

Yellow complex drops out slightly from solution when the treatment of red-yellow complex (H<sub>2</sub>TMEDA)[PdCl<sub>4</sub>] with plenty of water takes place. Physical and chemical research of obtained material shows that it corresponds to the chelate complex [Pd(TMEDA)Cl<sub>2</sub>] of diamine type. It can be concluded that deprotonation of the protonated ligand occurs in utter dilute solution and its transition into the inner sphere as well as directly coordination to the palladium is also observed. In the titration of the complex (H<sub>2</sub>TMEDA)[PdCl<sub>4</sub>] with alkaline solution of 0,1M NaNO<sub>3</sub>, 2 equivalents of alkali is consumed, which proves the neutralization of 2 protons.

In some ligands, a very strong effect of trans-influence is observed. Therefore, obtaining of their base complexes with CIS configuration is very difficult or impossible. In this case, by using the second component ligands which creates chelates with cis structure, it is possible to obtain complexes with the necessary structure. Conduct of goal-directed synthesis with the 4-aminopyridine created individual complex of TMEDA with CIS structure, while obtaining of individual complex of palladium with cis structure failed. [10]. The absorption bands at 410, 416 and 421 cm<sup>-1</sup> on the infrared spectra of synthesized mixed ligand complex



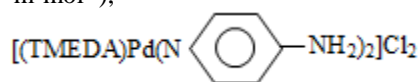
attributed to the valence bond  $\nu_{\text{Pd-N}}$ . Registration of 3 absorption bands for one valence bond is associated with the deformation of the coordination polyhedron with formation of pair conformation. 2 nitrogen atoms of TMEDA and the nitrogen atom of pyridine of 4-aminopyridine was engaged in coordination. The nitrogen atom of the exocyclic amine group doesn't participate in coordination. Amino group at the fourth position is involved in a hydrogen bond, for this reason, relating to it specific absorption band in the infrared spectra of complex is not observed. CIS structure of the complex



has been proven by a chemical process, i.e. the thiourea's [22, 23].

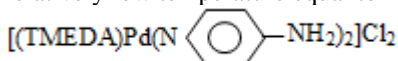
When heated for a long time of diluted solution at a temperature of 45–50°C, as expected, there is a replacement of 4-aminopyridine with water molecule accompanied with the formation of aquacomplex. It is deemed as more expedient method to use this kind of complexes in biological researches.

Molar conductivity studies were carried out in respect to the solution synthesized individual and mixed ligand complexes with concentration of 10<sup>-3</sup> mol/l at 25°C. Results of studies on the conductivity show that [TMEDAPdCl<sub>2</sub>]<sup>0</sup> (17 Om<sup>-1</sup>m<sup>2</sup>mol<sup>-1</sup>) is a nonelectrolyte, while the other three of the complex [(TMEDA)<sub>2</sub>PdCl<sub>2</sub>]Cl<sub>2</sub> (172 Om<sup>-1</sup>m<sup>2</sup>mol<sup>-1</sup>), (H<sub>2</sub>TMEDA)[PdCl<sub>4</sub>] (180 Om<sup>-1</sup>m<sup>2</sup>mol<sup>-1</sup>),



(184 Om<sup>-1</sup>m<sup>2</sup>mol<sup>-1</sup>) three-ion electrolytes. The results of the study on the conductivity and IR spectrum are mutually complementary [24–26].

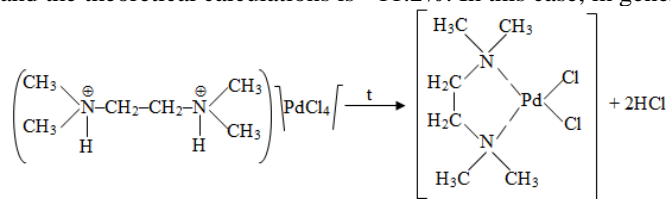
Thermal stability and mutual transformation chelates are the factors that create great interest for researchers. It is proved that the complex with two chelating ligands in the coordination sphere is less durable than a complex with a chelating ligand. For example, the complex [TMEDAPdCl<sub>2</sub>] decays completely without melting at 270°C whereas the complex [(TMEDA)<sub>2</sub>Pd]Cl<sub>2</sub> at a relatively low temperature equal to 220°C. One of the interesting facts is that mixed ligand chelate complex

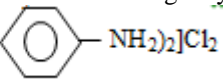


relatively durable.

In our opinion, the reason for this process is the fact that at thermal process becomes solid thermal synthesis. At relatively low temperatures the molecule of 4-amino pyridine is replaced with chloride ion from the internal sphere and formed more durable complex [TMEDAPdCl<sub>2</sub>] and at a temperature of 258<sup>0</sup>C is its decomposition.

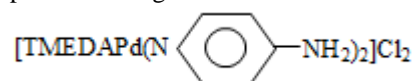
It has been studied the decomposition of the complex of cation-anion type (H<sub>2</sub>TMEDA)[PdCl<sub>4</sub>], which is interesting from the point of view of thermal analysis. On the DTA curve of this substance observed two endothermic peaks clearly showing weight loss. The first endothermic peak at 160<sup>0</sup>C was ascribed to the loss of the molecule HCl. Weight loss is 6%, and theoretical calculations are- 5.8%. The second endothermic peak at 180<sup>0</sup>C reflects the loss of a second molecule of HCl. Weight loss is 11.0% and the theoretical calculations is -11.2%. In this case, in general, the process can be described as follows:



Studying the initial biologically active of complexes [TMEDAPdCl<sub>2</sub>], [(TMEDA)<sub>2</sub>Pd]Cl<sub>2</sub>, (H<sub>2</sub>TMEDA)[PdCl<sub>4</sub>] and 

carried out in the laboratory. It was found that there are significant dependencies between the coordination types of ligand, structure of the complex, ligand environment of the central atom, and biological activity. For example, throughout coordination of one molecule of TMEDA with palladium if the resulting compound has antifungal properties, at coordination of 2 ligands the resulting compound has strong antiviral properties.

In the complex of cation- anion type (H<sub>2</sub>TMEDA)[PdCl<sub>4</sub>] ligand does not create a direct link to the central atom and the proton organizes external sphere. Along with the radioprotective properties, this complex



is also effective in treating skin diseases. It was found that the complexes



possess anti-hypoxic and adioprotective properties.

Depending on the process conditions of tetramethylethylenediamine, bidentate coordinate forms a pentagonal metal chelate cycles or two nitrogen atoms in its structure protonated as cation organize the outer sphere of the complex. In mixed ligand complex of 4-aminopyridine which yields the effect of trans-influence occurs forced cis coordination.

## Conclusion

Palladium firstly has been explored through obtaining individual and mixed complexes with Tetramethylethylenediamine. In both types of synthesized complexes Tetramethylethylenediamine forms continuous five-cored metallic cycle while coordinating at cis state. In Tetramethylethylenediamine mixture complex of palladium with 4-Aminopyridine, which has trans influence effect, the compulsory cis-coordination between nitrogen atom and pyridine. The positive results of synthesized complexes obtained through biological tests carried out in laboratory have been launched for extensive exploration.

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