



## *Trans*–*cis* isomerization of $[(C_6H_5)_3P]_2PtCl_2$ complex in dimethylformamide solutions <sup>☆</sup>



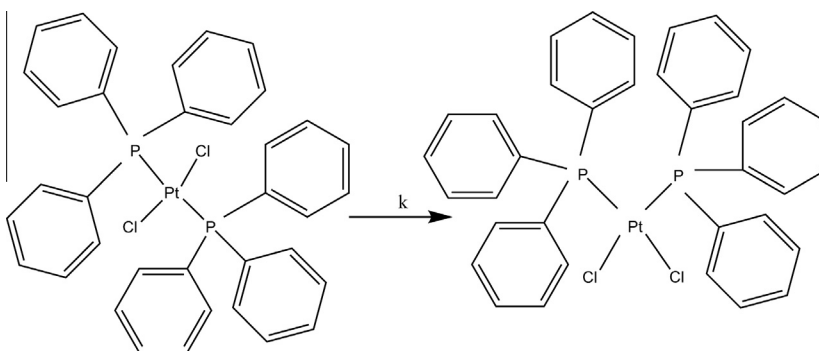
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### HIGHLIGHTS

- The isomerization reaction of  $[(C_6H_5)_3P]_2PtCl_2$  is catalyzed by metal ions.
- The rates of the isomerization reaction were determined spectrophotometrically.
- The reaction proceeds in a single step according to the dissociative mechanism.
- The kinetics of the isomerization reaction was monitored in DMF solution.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The kinetics of the *trans*–*cis* isomerization reactions of the  $[(C_6H_5)_3P]_2PtCl_2$  neutral complex catalyzed by four different metal ions:  $Be^{2+}$ ,  $Mg^{2+}$ ,  $Ca^{2+}$  and  $Sr^{2+}$  has been studied. The isomerization reactions were investigated in dimethylformamide (DMF) solutions at five temperatures in the range of 278–298 K keeping a constant concentration of metal ions  $c = 0.5$  M. The rates of the isomerization reactions were determined spectrophotometrically by monitoring the absorbance changes at the 277 nm wavelength. The spectral measurements were carried out in the UV–Vis region using the Perkin–Elmer Lambda 650 instrument with the scan accuracy of 1 nm and 1 nm slit width at the 120 scanning rate. The observable rate constants were computed using the “Glint” program based on the global analysis. The activation energies were determined using the Arrhenius equation. The differences in the structures of the obtained *cis* and *trans* geometric isomers were confirmed on the basis of their IR spectra.

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### Introduction

The *trans* effect in square complexes can be explained in terms of an addition/elimination mechanism that goes through a trigonal bipyramidal intermediate [1]. The classic example of the *trans*

effect is the synthesis of *cis*platin. Starting from potassium tetrachloroplatinate(II),  $K_2[PtCl_4]$ , the first  $NH_3$  ligand can be added to any of four equivalent positions but the second  $NH_3$  molecule could be added in the *cis* or *trans* position to the bound ammine ligand. Since the  $Cl^-$  ion has a larger *trans* effect than the  $NH_3$  molecule, the second ammine ligand preferentially substitutes *trans* to the chloride ligand, and therefore *cis* to the first ammine molecule. The *trans* effect of the halides follows the order  $I^- > Br^- > Cl^-$ , therefore the synthesis is conducted using  $[PtI_4]^{2-}$  to ensure a high yield and purity of the *cis* isomer, followed by the conversion of  $PtI_2(NH_3)_2$  into  $PtCl_2(NH_3)_2$  [2].

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Structure–activity relationships for a class of platinum coordination compounds confirm that only these with the *cis* geometry block a cell growth. The better understanding of both the chemical properties and the pharmacological action of *cisplatin* has guided the development of analogs having always the *cis* geometry but differing from *cisplatin* either for the ammine carrier ligands or for the leaving chlorides [3,4]. In general, a modification of the chloride leaving groups of *cisplatin* results in compounds with different pharmacokinetic properties, whereas a modification of the carrier ligands alters the efficacy and/or the spectrum of activity of the resulting complex. Platinum complexes effective as cytostatic agents have been introduced into a medicinal practice by the end of seventieths of the twentieth century [5,6]. *Cisplatin*, or *cis*-diamminedichloroplatinum(II), is the first of a series of square planar platinum(II)-containing chemotherapy drugs, including carboplatin and oxaliplatin [7,8]. The interaction of DNA and *cisplatin* results in 35–45° bend in the large groove in the direction of the spot within the *cis*-Pt-GG-N7, N7 chain adduct [9–12]. Moreover, many other complex compounds of platinum(II) and palladium(II) were studied in terms of the human cell lines and the ovarian fibroma hamster. These studies confirmed that the complex compounds of both Pd<sup>2+</sup> and Pt<sup>2+</sup> affected the cell apoptosis, however, the compounds of platinum(II) showed a much more potent and higher activity [13–15].

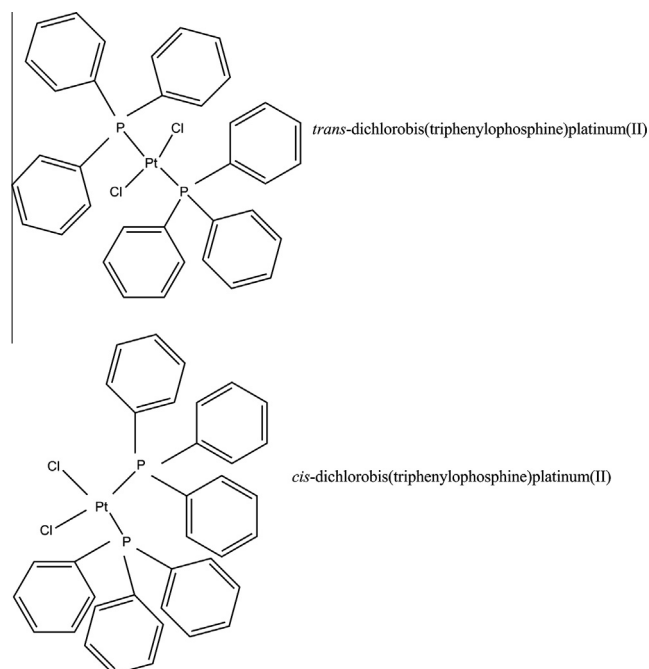
There are two main reasons to be interested in the isomerization reactions of the platinum complexes. Firstly, as mentioned above, the platinum complexes play very important roles in our body and our life. Therefore the knowledge of the kinetics of isomerization reactions of this class of compounds is of big importance. The ability to isomerize of the compounds, especially in the presence of other individuals (such as metal ions) that are capable to catalyze the processes of structure transformation has a great impact on their biological properties. Furthermore, due to the dependence of the pharmacokinetics of platinum compounds on the substituted ligand type it seems to be reasonable to perform the kinetic stability study of interesting class of platinum coordination compounds which are *trans*-/*cis*-[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>PtCl<sub>2</sub> isomers. Secondly, in the literature one can find insufficient data concerning this type of reactions in both aqueous, and especially, non-aqueous solutions. Consequently, it is possible to find only few kinetic studies concerning the *trans*-*cis* isomerization reactions of metal complex compounds in non-aqueous solvents [16,17] such as tetrahydrofuran, dimethyl sulfoxide or dimethylformamide. Moreover, there is a lack of consistent data on the influence of metal ions as catalysts on the kinetics of the *trans*-*cis* isomerization reactions in solutions. Thus, the present work is needed to supplement the information on the kinetic stability of platinum(II) complexes in non-aqueous solutions in the presence of different metal cations. Besse and Johnson [18] have stated that the racemization of tris(oxalate)chromate(III) is dependent upon a large number of different cations, including magnesium, whereas Schlafer and co-workers [19] have reported that the rate of the *trans*-*cis* isomerization is independent on the added magnesium ion.

Due to the lack of data and the described discrepancies in the findings it seemed worthwhile to investigate the catalytic effect of metal ions such: Be<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and Sr<sup>2+</sup> on the *trans*-*cis* isomerization of [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>PtCl<sub>2</sub> in the dimethylformamide (DMF) solutions. The non-aqueous solvent had to be used owing to the fact that the both isomers studied were not soluble in water.

## Experimental section

### Reagents

The *cis*- and *trans*-dichlorobis(triphenylphosphine)platinum(II) were bought from Sigma Aldrich. The molecular weight of both



**Fig. 1.** Structures of the *trans*-[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>PtCl<sub>2</sub> and *cis*-[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>PtCl<sub>2</sub>.

complexes is 790.56. The melting point equals to 300 °C. Elemental analysis data for the isomers are as follows: *cis*-[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>PtCl<sub>2</sub>: C, 54.51, H, 38.02; for *trans*-[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>PtCl<sub>2</sub>: C, 54.62, H, 38.14, whereas the theoretical composition for both isomers is as follows: C, 54.71, H, 38.23.

Fig. 1 shows the structures of *trans*-[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>PtCl<sub>2</sub> and *cis*-[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>PtCl<sub>2</sub> complex compounds.

The solubility of tested complex compounds is inversely proportional to the increasing value of the dielectric constant of the solvent. Thus, the compounds studied are insoluble in water, slightly soluble in DMSO, and completely soluble in DMF.

### Kinetic measurements

The isomerization reactions were investigated in dimethylformamide (DMF) solutions at five temperatures: 278 K, 283 K, 288 K, 293 K and 298 K. The stock solutions containing the metal cations used as catalysts were prepared using the nitrate salts of the cations which were soluble in dimethylformamide (DMF) – all metals of the second group of the periodic table except for the salt of barium, namely Be<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and Sr<sup>2+</sup>. The stock solutions of cations were 0.5 M. 2 ml of such solution was placed in a cuvette, which was thermostated at the snap of temperature control (Peltier system) with the option of mixing and water circulation. Then the solution was added to the cuvette with the pure, finely grounded complex, *trans*-[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>PtCl<sub>2</sub>, stirred until the dissolution of the sample. Subsequently, the *trans*-*cis* isomerization reaction of the complex studied was monitored spectrophotometrically. The rates of reactions studied were measured at the wavelength equal to 277 nm.

### IR spectra

IR spectra were recorded as the Nujol mulls using the Bruker IFS 66 spectrophotometer.

### Potentiometric measurements

The potentiometric measurements were carried out using an ion-selective electrode (SCHOTT Instruments Ag 6280). The

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