

Kinetic Study on 1,10-Phenanthroline Reaction with Cis-[Pt(*p*-FC₆H₄)₂(SMe₂)₂] Complex

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Abstract To determine the rate constants and kinetic parameters on the reaction between 1,10-Phenanthroline, as a bidentate ligand and cis-[Pt(*p*-FC₆H₄)₂(SMe₂)₂] complex in acetone and benzene solvents, the reactions were monitored by UV-Vis spectrophotometer. The pseudo-first-order rate constants ($k_{obs}=k_1+k_2[phen]$) of the reaction were derived, and the values of the first and second order rate constants (k_1 and k_2) calculated using standard equations. The reactions were carried out in the range of 20 to 50 °C. The second-order rate constant dependency on the temperature was in agreement with the Arrhenius equation, providing the relevant plots to calculate the activation energy of all the reactions. The ΔH^\ddagger (KJ.mol⁻¹) and ΔS^\ddagger (J.mol⁻¹.K⁻¹) were obtained 28.677 and -165.9 respectively in benzene. These values were 56.723 and -72.2 respectively, in acetone. The product synthesizing was confirmed using elemental (CHN) and spectral (IR) analysis.

Keywords Pt(II) Complex, Substitution, UV-Vis Spectrophotometry, Activation Parameters, Kinetics

1. Introduction

Ligand substitution reactions on monomeric square planar platinum (II) complexes have been extensively studied.^{1,2} These complexes have shown low rates in their reactions comparing with other d⁸ square planar complexes of palladium, nickel, rhodium, iridium and gold. This property is particularly important in cancer chemotherapy of platinum (II) complexes, since this allows binding to cellular DNA before inactivation of the Pt (II) center by extra cellular binding sites such as S-donor residues.³ Some researchers have investigated and focused on the kinetics and mechanism of the interaction of platinum (II) complexes and bio-molecules with the aim of developing new family of metallo-pharmaceuticals.^{4,5} The ionic complexes [M(Ph₂PC₂H₄P(Ph)₂C₂H₄PPH₂)X]Cl have been obtained in substitution reaction of related chloro-complexes with 1 equivalent of KX (X=I, CN).⁶ There has been a great interest in ligand substitution reactions of organoplatinum (II)

complexes containing one or more Pt-C bonds,⁷⁻¹⁰ e.g. the ligand substitution or ligand exchange on organometallic substrates of the type cis-[PtR₂L₂] (R=Ph or Me; L=thioethers or dimethylsulfoxide). Rashidi et al. have studied widely about the kinetics and mechanism of ligand substitution reactions involving binuclear dimethylplatinum(II) complex containing N-donor ligands.^{11,12} Kinetics and mechanism of substitution and ring opening reaction of some platinum(II) complexes with N-heterocyclic bases have been studied by UV-Vis spectrophotometry.¹³ There is evidence for a dissociative mechanism as well as associative in ligand exchange and substitution at platinum(II) complexes.¹⁴ Neutral monodentate ligands such as pyridine, 4-Me-pyridine and thiourea have been substituted with a SMe₂ ligand in the first step of reaction in trans-[PtClMe(SMe₂)₂] complex, as confirmed by ¹H NMR spectroscopy and kinetic data.¹⁵ It has been proven that ligand substitution processes trans to a carbon atom are extremely rapid due to the high trans effect of these ligands.¹⁶ In addition to the large trans effect of σ -carbon ligands, it is also well known that these ligands exert an appreciable trans influence by weakening the metal-ligand bond opposite on it. In this regard, we are interested in studying about the kinetic of the systems containing α -carbon trans directing ligand. Details of our findings in a comprehensive study of the substitution rates in the cis-[Pt(*p*-FC₆H₄)₂(SMe₂)₂] complexes^{12,17} reactions with 1,10-Phenanthroline, as a neutral bidentate ligand are reported in this paper.

2. Experimental

2.1. Materials and Instrumentation

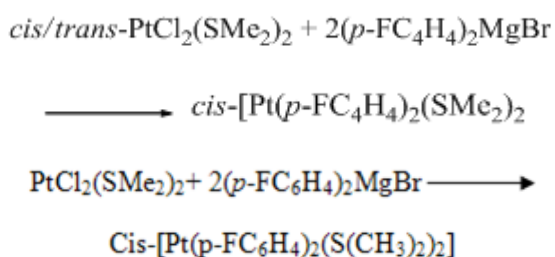
The ligand, 1,10-phenanthroline, was a Merk product. Acetone and benzene, used as the solvents were purchased from the Merk or Fluka Company. All UV-Vis spectra were recorded in a Shimadzu double beam spectrophotometer machine, UV-Vis 2550. Sartorius analytical balances with accuracy 0.0001, a micro syringe 500 μ L, and a screw cap cuvette made by American Hellma Company, were used for

experiments. In all measurements, a circulator Ayat 83 was used for controlling the temperature.

The infrared spectrum was recorded on a Shimadzu Prestige 8400 FT-IR spectrometer as KBr disks. CHN analysis was performed using a Heraeus CHN-O-FLASH EA 1112 elemental analyzer.

2.2. Synthesis of Platinum Complexes

In order to synthesis of the first complex, FC₆H₄MgBr was used as reported.^{12, 17} The reaction between (*p*-FC₆H₄)₂MgBr and [PtCl₂(SMe₂)₂] was occurred and led to synthesis of Cis-[Pt(*p*-FC₆H₄)₂(S(CH₃)₂)₂]. Related reaction is appeared in following:



All properties such as ¹HNMR chemical shifts of this precursor were similar to be reported.

In a substitution reaction which is shown in Figure 1, two dimethyl sulfide ligands are substituted slowly by a bidentate 1, 10-Phenanthroline, ligand.

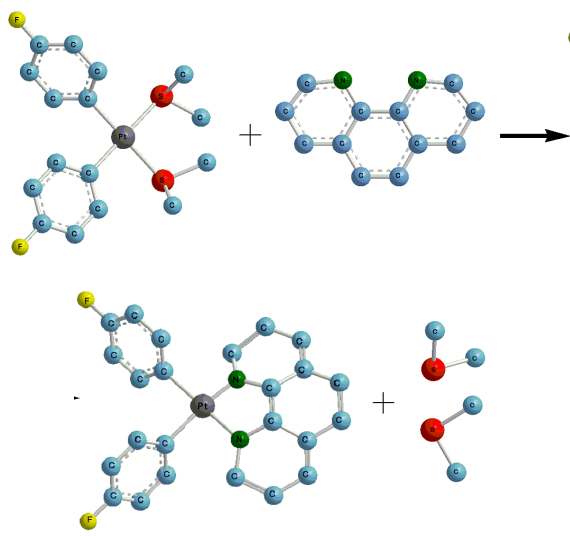


Figure 1. Substitution reaction of 1,10-Phenanthroline with [Pt(*p*-FC₆H₄)₂(SMe₂)₂]

A solution of 1,10-phenanthroline (5 mmol, 0.9 g) in 50cc acetone was added to a solution of Cis-[Pt(*p*-FC₆H₄)₂(SMe₂)₂] complex (5 mmol, 2.55 g) in 50 ml of the same solvent. The mixed solution was stirred for 72h in a closed flask. Immediately, after opening the flask, smell of the released SMe₂ was distinguished. The yellowish precipitate was filtered, washed with ether (3×5 ml) and dried in vacuum.

CHN analysis for C₂₄H₁₆F₂N₂Pt (%): C, 50.98; H, 2.85; N,

4.95. Found: C, 50.12; H, 2.34; N, 4.75. Significant IR bonds (KBr, cm⁻¹): 3421.5 s (ν C-H), 1625.9 w (ν C=N), 1473.5 s (ν C=C), 1384 s (ν C-N), 1203.5 s (ν C-F), 842.8 m, 813.9 m (ν C-H), 582.5 w (ν Pt-C), 518.8 w (ν Pt-N).

2.3. Kinetic Methods

Kinetics of irreversible reaction shown in **Figure 1** was studied using UV-Vis spectrophotometry technique. Analysis of the curves were done using Excel and KaleidaGraph¹⁸ softwares. The aim of this study is the determination of kinetic parameters (ΔH[#], ΔS[#]) in acetone and benzene solvents, and we don't study the mechanism of the reaction. Following ordinary equations were used:

$$\ln(k_2/T) = \ln(k_B/h) + (\Delta S^\ddagger/R) - (\Delta H^\ddagger/RT) \text{ (Eyring equation)}$$

$$K_{\text{obs}} = k_1 + k_2 [\text{Phen}]$$

in which, *k*₁, *k*₂ and *K*_{obs} are the dissociative path (so-called solvent-assisted¹⁹), the associative and pseudo-first-order rate constants respectively. *R*, *h* and *K*_B are the ideal gas, Plank and Boltzmann constants respectively.

3. Results and Discussion

This reaction could be a pseudo-first-order one¹⁷, if we use the excess concentration for one of reagents, so the concentration of new ligand should be at least tenfold of primary complex concentration in each run. As an example, 300 μL of 1,10-Phenanthroline (0.0038538 molL⁻¹) was added to 2 ml of the starting complex at a constant temperature (35 °C) in a screw cap cuvette and the absorbance of mixed solution were recorded until the reaction was finished. The results are displayed in Figure 2.

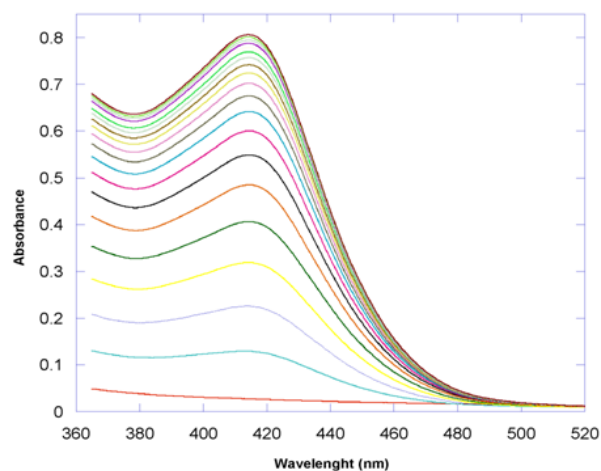


Figure 2. Absorption vs. wavelength in 35°C for adding 300 μL of new ligand in Acetone

In spite of produced complex case, the starting complex had no absorbance, so after a while, increase in absorbance was observed. After collection of the related absorption, which according to Beer-Lambert law (*A*=*ε*.*b*.*c*) should be

less than 1, the maximum wavelength, λ_{\max} , was determined in 414.3 nm (in acetone). Then, nonlinear curves of absorption against time of reaction were analyzed with pseudo-first-order method (Figure 3).

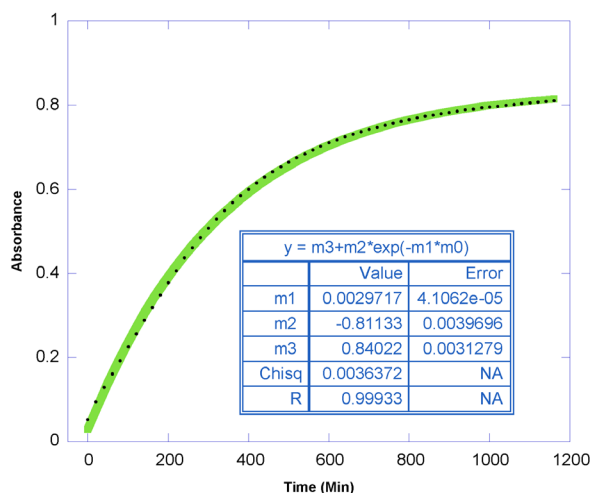


Figure 3. Absorption vs. time in 35°C for adding 300 µL of new ligand in Acetone

Pseudo-first-order rate constant of the reaction (K_{obs}) was obtained by nonlinear least-square fitting of absorption–time curve to a first order equation, $A_t = A_\infty + (A_0 - A_\infty) \cdot \exp(-K_{\text{obs}} \cdot t)$.

As it can be seen in sample curve (Figure 3), the curve fit (green) shows the good agreement with the main curve. The m_1 parameter is equal to K_{obs} , and m_2 is the difference between A_0 and A_∞ and both of them have small errors. Using other concentrations of 1,10-Phenanthroline in 35°C, similar results were obtained and gathered in Figure 4. The volumes of new ligand in this figure represent the used concentrations.

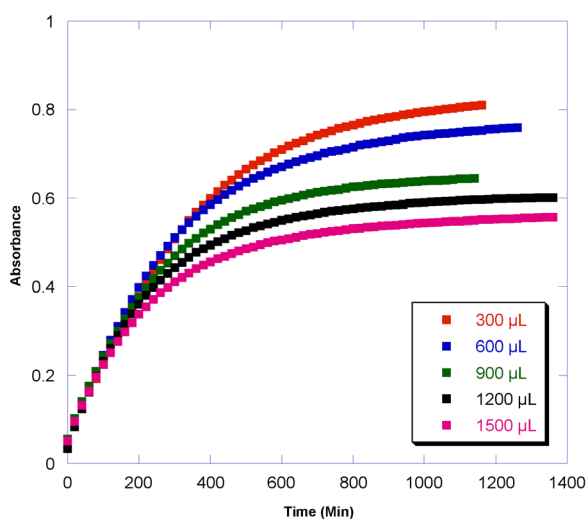


Figure 4. Overlay of absorption–time curves in Acetone, T=35°C

The concentration of the primary complex in all

experiments was 2.5×10^{-4} mol/L. The second-order rate constant (k_2) also was calculated by plotting of K_{obs} values versus concentrations of 1,10-Phenanthroline. The same method were used for other selected temperatures, including 20, 30 and 50 °C and the second-order rate constants of reactions were obtained. From Figure 5, we realize that the rate increases as temperature goes up from 20 to 50°C.

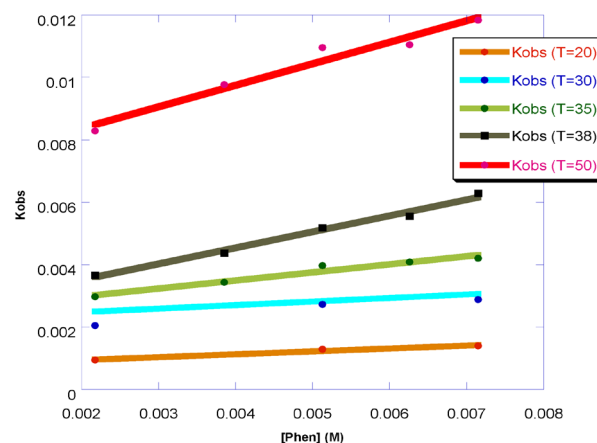


Figure 5. Overlay of K_{obs} against different concentrations of 1,10-Phenanthroline in various temperatures (in Acetone)

Table 1. First and second order rate constant in Acetone

T (Centigrade)	20	30	35	38	50
1/T (Kelvin)	0.0034	0.0033	0.0032	0.0032	0.0031
k_2	0.0928	0.1137	0.2572	0.5139	0.6903
$\ln(k_2/T)$	-8.0575	-7.8886	-7.0887	-6.4060	-6.1483
k_1	0.0008	0.0023	0.0025	0.0025	0.0070

The data shows that the values of k_2 are around 100 fold of k_1 and it means that the dissociative path is negligible in acetone.

According to the obtained data from previous curves and using Eyring equation, Figure 6 is plotted and kinetic parameters are estimated. Slope and intercept of this curve are -6822.6 and 15.076, respectively. ΔS^\ddagger and ΔH^\ddagger values were determined $-72.2 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and $56.723 \text{ KJ} \cdot \text{mol}^{-1}$ using the intercept (k_1) and slope (k_2), respectively.

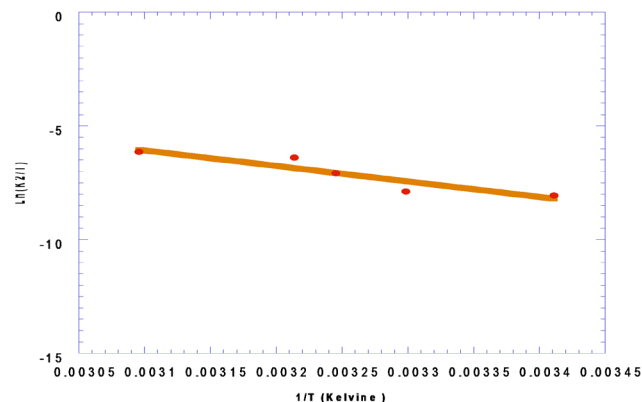


Figure 6. Plot of $\ln(k_2/T)$ against $1/T$ in Acetone as solvent

Physical and chemical characteristics of solvents can cause variations in many reactions. In fact, changing the solvent has a considerable effect on stability of the formed complex. So, to finding the solvent effect, the same experiments and computations were done for benzene, and similar curves were drawn. λ_{max} was determined in 443 nm. Some of the obtained second-order rate constants, k_2 , and their related values in benzene, are shown in Table 2.

Table 2. First and second order rate constant in Benzene

T (Centigrade)	25.5	27	30	39
1/T (Kelvin)	0.0033	0.0033	0.0033	0.0032
k_2	0.1184	0.1320	0.1857	0.2095
$\ln(k_2/T)$	-7.8328	-7.7295	-7.3977	-7.3065
k_1	0.0003	0.0003	0.0002	0.0002

According to the obtained data from previous curves and using Eyring equation, Figure 7 was plotted and kinetic parameters were estimated.

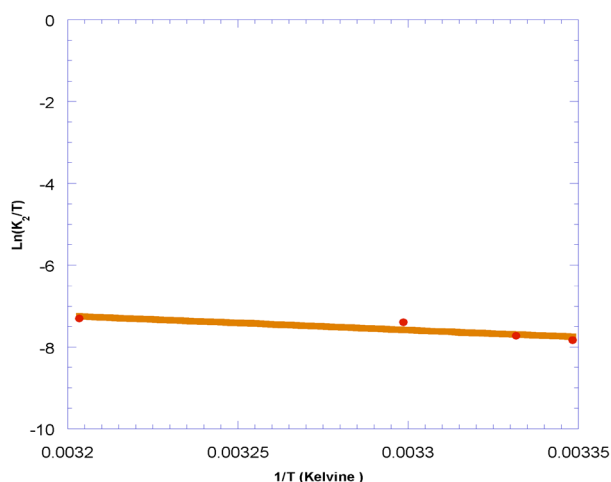


Figure 7. Plot of $\ln(k_2/T)$ against $1/T$ in Benzene as solvent

The slope and intercept of this curve were obtained -3449.3 and 3.801, respectively. ΔS^\ddagger and ΔH^\ddagger values were determined $-165.9 \text{ J.mol}^{-1}.\text{K}^{-1}$ and $28.677 \text{ KJ.mol}^{-1}$ using the intercept and slope respectively. Obtained kinetic parameters, ΔH^\ddagger and ΔS^\ddagger , for both solvents are given in Table 3.

Table 3. Kinetic parameters in benzene and acetone

Kinetic parameters	Benzene	Acetone
$\Delta S^\ddagger (\text{J.mol}^{-1}.\text{K}^{-1})$	-165.9	-72.2
$\Delta H^\ddagger (\text{KJ.mol}^{-1})$	28.677	56.723

4. Conclusion

The stability of $cis-[Pt(p-FC_6H_4)_2(1,10\text{-phenanthroline})]$ is due to the chelate effect.²⁰ Platinum is an electron-rich metal

and 1,10-phenanthroline has empty π^* orbital, so the yellow color in investigated solution could be due to the metal to ligand charge transfer (MLCT).²¹ The Pt-S is a soft-soft bond and on the other side, the Pt-C and Pt-N are soft-hard bonds. Consequently, according to the principle of symbiosis,²² the Pt-S is replaced by the Pt-N bond (Figure 8).

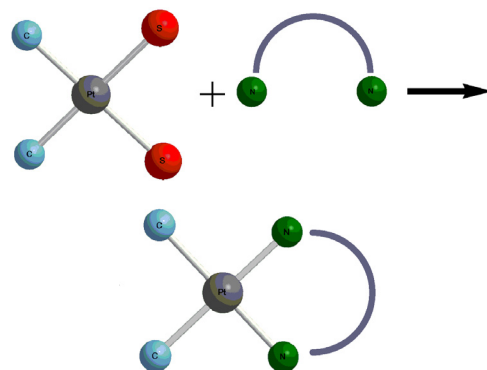


Figure 8. Principle of symbiosis for reaction of $Cis-[Pt(p-FC_6H_4)_2(S(CH_3)_2)_2]$ and 1,10-phenanthroline

Furthermore, $p-FC_6H_4$ is a π -acceptor and it can labialize the SMe_2 ligand. When such ligand forms strong π bond with Pt, the energy of the transition state is to be lower, and the activation energy is reduced.²³

As one can see, the parameters are almost the same, and in fact, although we expected more dissociative path in benzene (for substitution of bidentate ligand phenanthroline²⁴), but a negative value of ΔS^\ddagger indicates that the associative path is in current for benzene as well as acetone.

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REFERENCES

- [1] Tobe, M. L.; Burgess, J. *Inorganic Reaction Mechanism*, Longman, Essex, UK, 1999.
- [2] Richens, D.T. *Chem. Rev.* 2005, *105*, 1961-2002.
- [3] Fuertes, M.A.; Alonso, C.; Perez, J.M. *Chem. Rev.* 2003, *103*, 645-662.
- [4] Chatterjee, D.; Mitra, A.; Sengupta, A.; Basak, S. *Inorg. Chem. Acta.* 2005, *358*, 2900-2908.
- [5] Bugarcic, Z. D. et al. *Bioorg. Medicin. Chem.* 2007, *15*, 4203-4211.
- [6] Garcia-Fernandez, M. E. et al. *Inorg. Chem. Acta.* 2001, *312*, 40-52.
- [7] Romeo, R.; Grassi, A.; Scolaro, L. M.; *Inorg. Chem.* 1992, *31*,

- 4383.
- [8] Plutino, M. R.; Scolaro, L. M.; Romeo, R.; Grassi A. *Inorg. Chem.* 2000, 39, 2712-2720.
- [9] Schmulling, M.; Grove, M.; Kotten, G. Van; Eldik, R. Van; Veldman, R.; Spek, A. L. *Organometallics*. 1996, 15, 1384.
- [10] Romeo, R.; Scolaro, L. M.; Plutino, M. R.; Biani, F. F. de; Bottari, G.; Romeo, A. *Inorg. Chem. Acta*. 2003, 350, 143.
- [11] Hoseini, S. J.; Nabavizadeh, S. M.; Jamali, S.; Rashidi, M. *J. Organomet. Chem.* 2007, 692, 1990-1996.
- [12] Shafaatian, B.; Akbari, A.; Nabavizadeh, S. M.; Heinemann, F. W.; Rashidi, M. *Dalton Trans.* 2007, 4715-4725.
- [13] Banerjee P. et al. *Polyhedron*. 1999, 18, 1569-1575.
- [14] Romeo R. et al. *Inorg. Chem. Acta*. 2003, 350, 143-151.
- [15] Otto, S.; Roodt, A. *J. Organomet. Chem.* 2006, 691, 4626-4632.
- [16] Basolo, F.; Pearson, R. G. *Prog. Inorg. Chem.* 1962, 4, 381.
- [17] Akbari, A. *PhD thesis*, Shiraz University, Iran, 2005.
- [18] KaleidaGraph program, Version 3.6, Synergy Software, 2003, Reading, PA.
- [19] Miessler, G. L.; Tarr, D. A. *Inorganic Chemistry*, Third ed., Pearson Education, Michigan, 2004, p. 435.
- [20] Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*, Third ed., Harper & Row, New York, 1983, p. 527.
- [21] Shriver, D. F.; Atkins, P. W.; Lanford, C. H. *Inorganic Chemistry*, Second ed., Oxford University Press, Oxford, 1994, p. 441.
- [22] Jorgensen, C. K. *Inorg. Chem.* 1973, 12, 712-713.
- [23] Miessler, G. L.; Tarr, D. A.; *Inorganic Chemistry*, Third ed., Pearson Education, Michigan, 2004, p. 440.
- [24] Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, Second Revised ed., Wiley-VCH, New York, 1991, p. 234.