

Theoretical Study for the Site Exchange Mechanism of Anionic 5-Coordinate Pt(II) Complexes with Halide, $[\text{PtX}(\text{hfac})_2]^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$, hfac = hexafluoroacetylacetonate)

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DFT calculations of the intra molecular site exchange process in square pyramidal five coordinate complexes, $[\text{PtX}(\text{hfac})_2]^-$ (hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate, $\text{X} = \text{Cl}, \text{Br}, \text{I}$), were performed. The calculation reproduces well the X-ray molecular structures and the trigonal bipyramidal transition state energies of three possible paths, two of which actually seem to function, show that the order of the *trans* effect of halide ligands is $\text{Cl} < \text{Br} < \text{I}$, and that of the *cis* effect is $\text{Cl} > \text{Br} > \text{I}$, which is in accordance with the experimental results.

Keywords: DFT calculations, 5-Coordinate Pt(II) complex, Site exchange, *trans* effect, *cis* effect

1 Introduction

The exchange rates of aqua ligand in water have been reported for a variety of metal complexes[1]. In the case of mixed complexes these are affected by the supporting ligands, the so-called *cis* and *trans* effects. The order of the *trans* effect of halide ligands is well known to be $\text{I} > \text{Br} > \text{Cl} > \text{F}$, but few reports about the *cis* effect have been presented[2]. For example, however, the water exchange rate constant in $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$ was reported to be of the order of 10^{-4} s^{-1} using ^{195}Pt nmr[3] and ^{17}O nmr[4] spectroscopy, while that in $[\text{PtX}(\text{H}_2\text{O})_3]^+$ ($\text{X} = \text{halide}$), which contains two exchange routes, is unknown. One question is to what degrees halide ligands activate the water exchange reaction in the *cis* and *trans* positions, and the other question is what are the orders of the *cis* and *trans* effects of halide ligands, respectively? The answers of these problems are important to understand the biochemistry of Pt(II). Since it is difficult to determine separately the water exchange rates of the *trans* position to X ligand and the *cis* position, we chose the $[\text{PtX}(\text{hfac})_2]^-$ (X

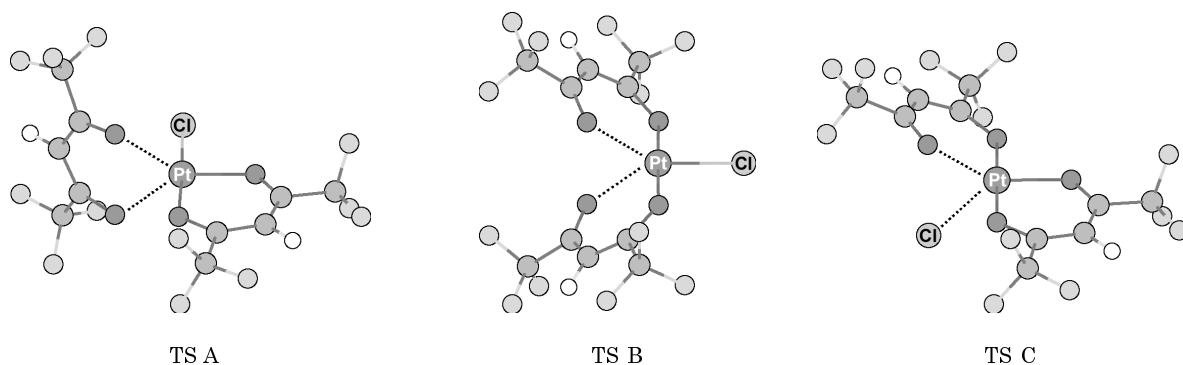
= Cl, Br, I; hfac = hexafluoroacetylacetonate) system as a model, which has a 5-coordinate distorted square pyramidal structure[5]. This structure is maintained in solution and the fast dynamic site exchange process has been observed in the temperature variable ^1H and ^{19}F NMR spectra. One of the oxygen donors occupies an apical position in the apically wounded hfac chelate; O_{ap} has four possibilities to assault the positions in the square plane, X, O_{cis-1} , O_{cis-2} and O_{trans} . Considering the coalesce mode of the ^1H and ^{19}F signals with temperature variation, it was found that two independent site exchange paths occur, in which O_{ap} assaults the positions of O_{cis-2} and O_{trans} , respectively. The line shape analyses were performed qualitatively, and the orders of *cis* and *trans* effects were determined as follows; *cis* effect; $\text{Cl} > \text{Br} > \text{I}$, and *trans* effect; $\text{I} > \text{Br} > \text{Cl}$. It is very interesting that the order of the *cis* effect is the reverse of that of the *trans* effect. In this paper the ab initio calculations to determine the optimal structures of $[\text{PtX}(\text{hfac})_2]^-$ and the trigonal bipyramidal transition state energies of each path are reported.

Table 2. Calculated bond lengths (Å) and bond angles (degree) in $[\text{PtX}(\text{hfac})_2]^-$

	Calc (B3LYP)						Exp[5]	
	X = Cl (I)	X = Cl (II)	X = Br (I)	X = Br (II)	X = I (I)	X = I (II)	X = Br (II)	X = I (I)
Pt-X	2.342	2.341	2.467	2.466	2.643	2.642	2.398	2.568
Pt-O _{cis-1}	2.012	2.009	2.011	2.008	2.012	2.008	1.995	1.984
Pt-O _{trans}	2.047	2.050	2.061	2.064	2.075	2.079	2.023	2.032
Pt-O _{cis-2}	2.013	2.009	2.012	2.010	2.011	2.008	2.019	2.008
Pt-O _{ap}	2.902	2.881	2.885	2.897	2.870	2.880	2.951	2.942
X-Pt-O _{cis-1}	89.4	89.1	89.7	89.4	90.1	89.8	87.81	89.22
X-Pt-O _{trans}	178.0	177.9	177.8	177.5	177.0	177.1	176.21	176.32
X-Pt-O _{cis-2}	90.0	90.6	90.1	90.9	90.2	90.8	91.11	91.12
X-Pt-O _{ap}	101.4	107.0	101.7	108.5	104.4	110.3	100.22	90.82
O _{cis-1} -Pt-O _{trans}	92.6	92.8	92.3	92.6	92.0	92.2	94.32	94.03
O _{cis-1} -Pt-O _{cis-2}	177.1	178.0	177.5	177.2	177.9	177.4	177.62	176.63
O _{cis-1} -Pt-O _{ap}	104.1	99.9	103.6	101.8	102.6	100.8	107.12	107.02
O _{trans} -Pt-O _{cis-2}	88.0	87.5	87.9	87.0	87.7	87.1	86.72	85.63
O _{trans} -Pt-O _{ap}	78.5	73.6	79.0	72.4	77.3	71.4	82.22	90.02
O _{cis-2} -Pt-O _{ap}	78.8	82.1	78.9	80.7	79.3	81.4	75.22	76.32
X-Pt-O _{cis-2} -O _{ap}	-101.7	-107.1	-101.9	-108.6	-104.6	-110.4	-100.28	-90.58
Pt-O _{trans} -O _{cis-1} -C _{cis-1}	178.9	177.2	178.5	177.7	178.0	177.4	176.78	179.74
Pt-O _{ap} -O _{cis-2} -C _{cis-2}	-158.7	-176.2	-158.1	167.8	-158.5	170.5	147.26	-154.69

Table 3. Calculated energies of transition states for ligand exchange reactions of $[\text{PtX}(\text{hfac})_2]^-$

X	Electronic energy		Free energy	
	a.u.	ΔE (kcal mol ⁻¹)	a.u.	ΔG (kcal mol ⁻¹)
Cl (I = initial state)	-2005.339603	0	-2005.268584	0
Cl (TS A, 162.3i cm-1)	-2005.319309	12.7	-2005.248491	12.6
Cl (TS B, 121.4i cm-1)	-2005.322359	10.8	-2005.250556	11.3
Cl (TS C, 113.3i cm-1)	-2005.311376	17.7	-2005.239653	18.2
Br (I = initial state)	-2003.562026	0	-2003.493835	0
Br (TS A, 165.2i cm-1)	-2003.541174	13.1	-2003.471984	13.7
Br (TS B, 102.6i cm-1)	-2003.547199	9.3	-2003.478613	9.6
Br (TS C, 104.3i cm-1)	-2003.535663	16.5	-2003.465645	17.7
I (I = initial state)	-2001.786574	0	-2001.719318	0
I (TS A, 169.8i cm-1)	-2001.765306	13.3	-2001.696950	14.0
I (TS B, 87.9i cm-1)	-2001.774729	7.4	-2001.706538	8.0
I (TS C, 95.3i cm-1)	-2001.763129	14.7	-2001.693812	16.0

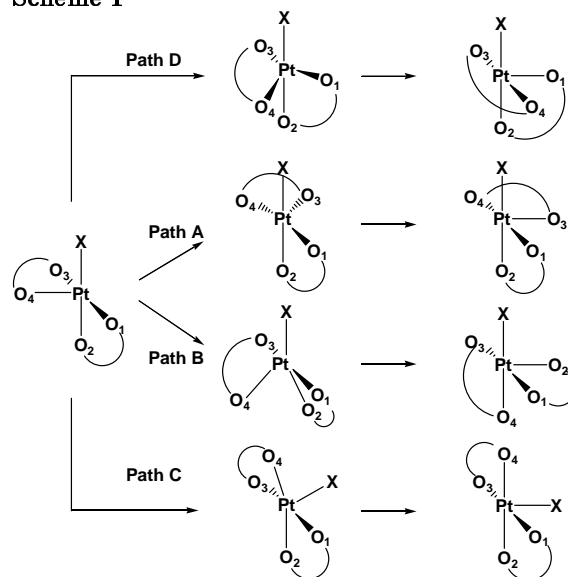
Figure 2. B3LYP optimized structures of transition states for ligand exchange reactions of $[\text{PtX}(\text{hfac})_2]^-$ (X = Cl).

There are too many optimized structure parameters for each complex. Therefore, we have summarized only some selected structural parameters in Table 2 with the corresponding experimental ones (X-ray crystal structure data). From Table 2, one can see that the agreement between the calculated values and the experimental ones is satisfactory. The calculated dihedral angles, $\text{Pt-O}_{\text{trans}}\text{-O}_{\text{cis-1}}\text{-C}_{\text{cis-1}}$ between the two planes containing $\text{Pt-O}_{\text{trans}}\text{-O}_{\text{cis-1}}$ and $\text{O}_{\text{trans}}\text{-O}_{\text{cis-1}}\text{-C}_{\text{cis-1}}$ for all complexes, are near 180° , which indicates that one hfac is almost coplanar with the coordination square plane. However the dihedral angle, $\text{Pt-O}_{\text{ap}}\text{-O}_{\text{cis-2}}\text{-C}_{\text{cis-2}}$ was calculated to be smaller than 180° , which indicates that the plane of the other hfac and the plane containing $\text{Pt-O}_{\text{ap}}\text{-O}_{\text{cis-2}}$ are bent down. From the X-ray structure it can be seen that, while this hfac plane bends away from the halogen ligand in the Br complex (Structure II), it bends toward the halogen in the I complex (Structure I). However, the following discussions associated with the effect of the halide ligand on the reaction mechanism are based on structure I as an initial state.

3.2 Geometry optimization for transition state

The most interesting problem in theoretical works about the reaction mechanism is the calculation of the electronic structure and the geometry of the transition states appearing in the course of the reaction path. The coordination site exchange is attained through a pseudorotation path with minimal structural change between the square pyramidal and trigonal bipyramidal structures (see Scheme 1). There are two possible rotations, around the X-Pt-O_2 axis or the $\text{O}_1\text{-Pt-O}_3$ axis. Because there are two possible directions for each rotation, four cases in total, which correspond to the substitution of O_4 with O_1 , O_2 , O_3 or X , respectively, need to be taken into consideration (Scheme 1, path A~D). But path D can be omitted since both O_3 and O_4 belong to one hfac ligand and it would be very difficult for them to take *trans* positions relative to each other. Because the energy of the structure with an apical X (Structure III) is greater than that of the structure with a basal X (Structure I) as mentioned above, path C corresponding to the basal-apical exchange of the X ligand need not to be considered either. In path A, apical O_4 assaults the *cis*-2 position (O_3) in the same hfac and in path B, O_4 assaults the *trans* position (O_2) in the other hfac. Accordingly paths A and B are models for the substitution reaction of the square planar $[\text{PtXO}_3]$ type complex by an O-donor ligand in the *X-cis* and *X-trans* positions, respectively. The optimized structures at the transition state in paths A, B and C (TS A, B and C) for Cl complex are shown in Figure 2. From the frequency analysis it was confirmed that these transition states correspond to the ligand exchange at the *cis* and *trans* positions, respectively.

Scheme 1



The energies of the trigonal bipyramidal transition states (TS A, B and C) are shown in Table 3. The order of the relative electronic energies in TS B is $\text{Cl} > \text{Br} > \text{I}$ in accordance with the order of the *trans* effect. However, though the energy difference is not so large, the order of the energies at the transition state (TS A) is reversed, $\text{I} > \text{Br} > \text{Cl}$, which suggests that this is due to the *cis* effect. Because TS C for all halide complexes has a higher energy than the corresponding TS A or TS B, the basal-apical exchange of the X ligand should be an unfavorable energy path compared with those of oxygen donors in the hfac chelates.

4 Conclusion

From the DFT calculation based on the B3LYP/3-21G level calculations, the optimal structures of $[\text{PtX}(\text{hfac})_2]$ fit well with the crystal structures. The trigonal bipyramidal transition state energies of three possible paths, two of which actually seem to function, show that the order of the *trans* effect of halide ligands is $\text{Cl} < \text{Br} < \text{I}$, and that of the *cis* effect is $\text{Cl} > \text{Br} > \text{I}$, which is in accordance with the experimental results.

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ハライドを持つ5配位錯アニオン、 $[\text{PtX}(\text{hfac})_2]^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$, $\text{hfac} = \text{ヘキサフルオロアセチルアセトネート}$)の サイト交換機構についての理論的研究

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5配位錯アニオン、 $[\text{PtX}(\text{hfac})_2]^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$, $\text{hfac} = \text{hexafluoroacetylacetonate}$) の、溶液中における分子内配位サイト交換に関する *ab initio* 計算を行なった。まず5配位構造の最適化を、考えられる3つの構造について行なったところ、X線結晶解析されている四角錐型構造が最も安定で、計算値は構造データをよく再現することがわかった (Tables 1, 2)。次に分子内配位サイト交換運動 (Scheme 1) で考えられる3つの経路の各三角両錐型遷移状態のエネルギーを計算した。このうち、頂点位置のOドナーがXに対してシスあるいはトランス位のOドナーを置換する Path A と B とが実際に起こると予想され、Path A の速度は、 $\text{Cl} > \text{Br} > \text{I}$ 、Path B の速度は、 $\text{I} > \text{Br} > \text{Cl}$ となり、温度変化 NMR スペクトルの結果から予測された順に一致した (Table 3)。前者はハライド配位子のシス効果、後者はトランス効果の順を表すものであり、シス効果の順がトランス効果のそれと逆であることは大変興味深い。

キーワード: DFT 計算, 5配位白金 (II) 錯体, 配位サイト交換, トランス効果, シス効果