



New Platinum(II) Complex Containing Asymmetric Tetra Dentate Schiff Base Ligand Synthesis, Characterization and DFT Calculation

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Abstract: The tetra dentate neutral (E)-4-nitro-2-((2-(2-(pyridin-2-yl) ethylthio) ethylimino) methyl) phenol, (pytaO₂NSalH), Schiff-base ligand was synthesized using 1-(2-pyridyl)-3-thia-s-aminopentane (pyta) and 5-NO₂ salicylaldehyde. Then the related square planar Pt (II) cationic complex, [Pt (NSNO)] Cl, was synthesized using PtCl₂ (SMe₂)₂ as precursor complex. The nature of the pytaO₂NSalH and its platinum complex were determined by the elemental analysis, molar conductivity and spectrochemical (IR, UV-vis, ¹HNMR) techniques. In addition, the fully optimized geometries and vibration frequencies of them together were calculated using the ADF 2009.01 package. Structural parameters are in good agreement with the experimental data. The calculated and experimental results confirmed the suggested structures for the ligand and complex.

Keywords: Platinum(II), Schiff base, DFT, ADF.

Introduction

Chelating ligands containing N, S and O donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions. It is known that the existence of metal ions bonded to biologically active compounds may enhance their reactivities¹. Square planar substitution reaction at Pt(II) centers have been extensively studied and contributed significantly to current understanding of ligand effects and reactions mechanisms^{2,3}. Platinum is the heaviest member of the group VIII of the transition metals. Interest in the interactions of platinum metals with biologically important molecules began about 35 years ago when Rosenberg, *et al.* published their discovery that certain platinum complexes exhibit anticancer activity⁴. Cisplatin is the parent compound in this group. It is widely used for the treatment of testicular and ovarian cancers and to a lesser extent head and neck tumors. However, the efficacy of the drug is hampered by severe side effects. The number of platinum complexes that show antitumor activity is still rapidly growing because of attempts to find complexes with greater potency and less toxicity than the existing clinical drugs⁵⁻⁷.

Experimental

All the chemicals and solvents used for the syntheses were of reagent grade and were obtained commercially from Merck Company. The ligand (PytO₂NsalH) and Pt(SMe₂)₂ Cl₂ precursor were synthesized and characterized according to our previous published method^{8,9}. Reported calculations in this paper were carried out using the Amsterdam density functional (ADF) 2009.01 software¹⁰. Geometry of the ligand and complex were optimized at DZ basis set except for Pt which TZ basis sets were used. Theoretical calculations of harmonic frequencies at the fully optimized geometries of the ligand and its Pt(II) complex are performed at B3LYP level¹¹⁻¹³.

The mentioned complex was prepared by dissolving Pt(SMe₂)₂ Cl₂ (0.0316 g, 0.081 mmol), in 5 mL methanol and mixture were stirred for 30 minutes. Separately, 5 mL triethylamine was added to a solution of pytaNO₂salH ligand (0.0269 g, 0.081 mmol) and the mixture was refluxed for one hour. The mentioned solution of ligand was added drop-wise to the solution of Pt(SMe₂)₂ Cl₂ in nitrogen atmosphere, and stirred for two days. Evaporation of this solution gave an orange precipitate which filtered, washed with ether and dried. (Yield: 45.68%), FT-IR (KBr, cm⁻¹): $\nu=1608(\text{C-N})_{\text{py}}$, 1550 (C=N)_{imi}, 1321.1(C-O), 673.1(C-S), 564, 489; CHN, Cal: C, 34.26; H, 2.88; N, 7.49; Found: C, 32.79; H, 3.50; N, 6.42. M.p. complex = 210 °C (decomposed).

Results and Discussion

B3LYP optimized geometries of Ligand (left) and its Pt (II) complex, Figure 1, showed that the metal atom should bonded in a slightly distorted square planar coordination to the oxygen of the phenyl ring, sulfur, iminic and pyridinic nitrogen atoms. As an example, the C(1)-O(1), S(1)-C(5) and S(1)-C(6) bond distances in ligand calculated as 1.353 Å, 1.891 Å and 1.89 Å respectively, but changed to 1.316 Å, 1.87 Å, 1.86 Å in the complex. In the complex [Pt(pytaO₂Nsal)]Cl, Pt-O (2.101 Å□), Pt-N(1) (2.101 Å□) and Pt-N(2) (2.186 Å□) bond lengths slightly longer than related Schiff base complex¹⁴⁻¹⁹ (Table 1).

Table 1. Comparison of some calculated and reported vibrations.

	Reported	Calculated
Pt-O	1.976[31]; 2.005[32]; 2.006[40]	2.101
Pt-N _{imine}	1.988[31]; 1.992[32]; 2.04[33]	2.101
Pt-N _{py}	1.940, 2.002, 2.004[34];	2.186
Pt-S	2.279, 2.284 [36]; 2.336, 2.335 ,2.337[35]	2.337
C(1)-O	1.314[31]	1.316
C(3)-N(1)	1.316[31]	1.306

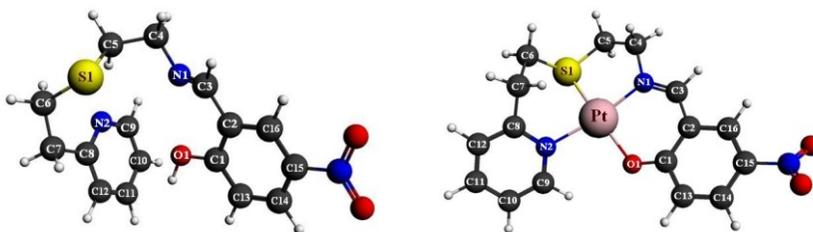


Figure 1. B3LYP optimized geometries of ligand (left) and related Pt (II) complex (right).

The absorption bands at 3446, 1284.5, 678, 1652, 1606 cm^{-1} in the IR spectrum of ligand are attributed to $\nu(\text{O-H}_{\text{phenolic}})$, $\nu(\text{C-O}_{\text{phenolic}})$, $\nu(\text{C-S})$, $\nu(\text{C=N}_{\text{pyridinic}})$, $\nu(\text{C=N}_{\text{iminic}})$ respectively. These values are in agreement with similar compounds²⁰. Theoretically IR frequencies of ligand and complex are calculated too. The important infrared spectra bands for the synthesized complex and ligand are given in Table 2.

Table 2. The selected experimental and calculated IR vibration frequencies (cm^{-1}) of the (pytaO₂NsalH) ligand and its related Pt(II) complex.

Experimental		Calculated		Vibration assignment
ligand	complex	ligand	complex	
-	-	-	641	ν (Pt-O)
-	-	-	330	ν (Pt-S)
-	-	-	489	ν (Pt-N _{py})
-	-	-	514	ν (Pt-N _{im})
678	673	624	607	ν (C-S)
1606	1550	1661	1584	(C=N) _{im}
3446	-	3328	-	ν (O-H) _{ph}

These frequencies are observed to be shifted to a lower number after complexation. The C-S bond appears at 670-770 cm^{-1} . We assigned this bond at 678 cm^{-1} in the ligand and at 673.1 cm^{-1} in complex theoretically. The observation suggests that the lone pair of the sulfur atom coordinates to platinum and causes the C-S bond shift to lower frequencies in the IR spectrum of complex. The far IR bands in the optimized structure complex show some new bands with medium to weak intensity in 530-425 cm^{-1} region, assigned to $\nu(\text{Pt-N})$ and $\nu(\text{Pt-S})$ respectively, which are in agreement with other reported works²¹. The ¹H NMR spectra of the ligand and its complex is recorded in DMSO and some data are collected in Table 3.

Table 3. Experimental chemical shifts of ligand and complex in ¹H NMR spectra.

PytaO ₂ NsalH	[PtpytaO ₂ Nsal] ⁺
14.55 (s, 1H, OH)	-
8.55 (d, 1H, pyridinic)	8.92
8.35 (s, 1H, iminic)	8.71
7.65 (t, 1H, pyridinic)	8.27
7.19 (m, 2H, aromatic)	7.77
2.83-3.10 (CH ₂ , aliphatic)	3.37

The observed pick at 14.55 ppm in the ligand spectrum is attributed to the hydroxyl proton. The absences of this proton in the complex confirm the Schiff bases coordination via oxygen of the hydroxyl group too. In all cases, there are down field shifts, which confirm coordination between the metal ion and four mentioned donor sites.

The electronic spectra of the ligand and platinum complex were recorded in methanol solvent at room temperature. The relatively intense absorption at 350 nm may be assigned to charge transfer. The absorption spectrum of the entire complex is somehow similar to the ligand. This is not surprising since the d-d bands occur as a shoulder on the intense visible band which can be expected to obscure changes in the d-d band positions brought about by

small changes in the environment of the platinum atom. The Low energy band is typical of d-d transition in square planar Pt(II) complexes with the mixed coordination sphere containing nitrogen, oxygen and sulfur atoms⁸.

The absorption band of the ligand at 230-250 nm is attributed to the benzene $\pi \rightarrow \pi^*$ transition. The band around 350-360 nm is due to the $n \rightarrow \pi^*$ transition of the non-bonding electrons presented on the nitrogen of the azomethine group in the Schiff base. In the UV-vis. spectrum of the complex, the $n \rightarrow \pi^*$ transition band specified to the azomethine group again and is shifted to the higher wavelength indicating the imine nitrogen atom is involved in coordination with the metal ion. The complex of the Pt^{+2} shows a fewer intense shoulders around 480 nm, which are assigned as d-d transition of the metal ion. The spectrum of the Pt^{+2} complex shows an intense band at 350 nm, which can be assigned to charge transfer transition of square planar geometry²⁰.

Complex and ligand show several intense absorptions in the visible and ultraviolet regions. The absorption in the ultraviolet region is assignable to transitions within the ligand orbitals. Some molecular orbital data of the ligand and its complex are given in Table 4.

Table 4. Percentage composition of the lowest unoccupied and highest occupied molecular orbital (LUMO and HOMO) levels of complex.

Orbital	E(ev)	C%	N%	O%	S%	pt
HOMO ₋₁	-9.712	1.03p _x + 6.1p _z	1.37 p _z	35.43P _x + 14.27P _y + 28.06p _z	-	3.72d _z ² + 1.68d _{xz} + 1.05d _{yz}
HOMO	-9.097	1.29p _x + 3.38 p _y + 32.76p _z	4.49 p _z	17.1p _x + 27.9p _z	-	3.77d _z ² + 1.76d _{yz}
LUMO	-7.308	1.01p _y + 1.13p _z	9.64p _x + 3.59p _y + 5.12 s	1.04p _x + 7.96p _y	4.99p _x +	22.55d _{xy} + 12.06d _{yz} + 3.93d _z ² + 1.60d _{xz}
LUMO ₊₁	-6.774	1.37p _y + 16.05p _x +45.14p _z	7.67p _x + 13.58p _z	3.74p _z	-	-

In the case of the $[PtpytaO_2Nsal]^+$ complex the lowest unoccupied molecular orbital (LUMO) has major contributions from the platinum d orbital's (40.14%). The highest occupied molecular orbital (HOMO) is delocalized almost entirely on the ligand and is largely concentrated on the oxygen atom fragment (45%). Therefore, the lowest energy absorption near 350 nm is assignable to a charge- transfer transition taking place from the filled ligand orbital (HOMO) to the vacant π^* - orbital of the complex (LUMO)⁴⁰, so we can expect the charge transfer is LMCT, not MLCT here.

Conclusion

The molar conductance value of mentioned complex in methanol, 86.57 ohm⁻¹ cm² mol⁻¹, indicate that this complex to be 1:1 electrolyte and thus chloride ion should present outside of the coordination sphere. The electronic spectra of this complex can indicate the square planar geometry, and the obtained values correspond to those reported earlier for the square planar complexes²¹. The down field shifts observed in H¹ NMR spectrum of complex,

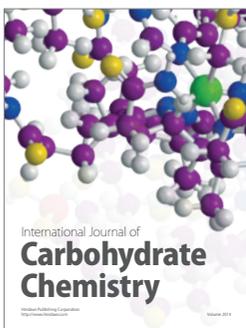
comparing the initial ligand, confirmed the coordination between the metal ion and four existing donor sites of the Schiff base. The calculated vibration frequencies are in good agreement with the experimental data. The calculated and experimental results confirmed the suggested structures for the ligand and complex.

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