

Preparation and Characterization of Platinum(IV)-N2O2 Schiff Base Complexes Their Catalytic and Biological Activities.

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Summary. A series of platinum(IV)-A[^]O[^] Schiff base complexes are prepared and characterized by elemental and thermal analyses as well as IR, electronic, HNMR spectra, molar conductance and magnetic measurements. The investigated complexes were also subjected to polarographic and cyclic voltammetric studies; The structural formulae, the mode of bonding, and geometry of the complexes were elucidated. The catalytic effect of these complexes on the cathodic reduction of oxygen and their bioactivity are as well studied.

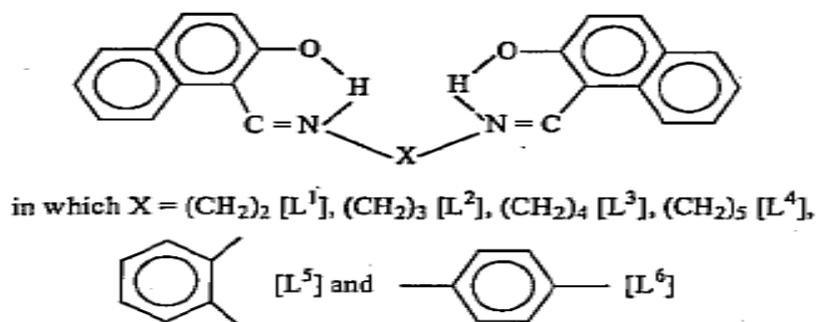
Introduction

A variety of metal complexes of Schiff bases having nitrogen and oxygen donating centers were found to play important roles in biological systems essentially a models for metallo enzymes which can catalyze the reduction of di-nitrogen and di-oxygen compounds. Also some metal Schiff base complexes act as catalysts I photosynthesis and for oxygen transfer in some respiratory systems. In the present work the preparation and characterization of some platinum (IV)-1 Schiff base complexes were shown. The reactivity of these complexes towards catalytic oxygen reduction and their bioactivity are investigated. The ligands used have the structural formulae represented in Scheme .

Experimental

All compounds and solvents used in the present study were pure grade chemicals obtained from BDH, Aldrich or Sigma and were used as provided.

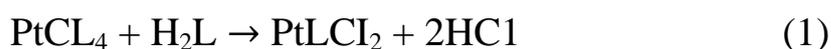
The ligands used for the preparation of the Pt (IV)-complexes under investigation (Scheme 1) were prepared using the common method for the condensation of primary diamines with 2-hydroxy-1-naphthaldehyde.



Scheme 1. The structure of the prepared ligands

Preparation of the platinum (IV)-Schiff base complexes:

The ligand (10 mmole) was suspended in 50 mL ethanol and refluxed for 10 min., a solution of sodium acetate (20 mmol in 50 mL ethanol) was then added and the mixture was further refluxed for 30 min. An ethanolic solution of PtCl₄ (10 mmole) in 30 mL water-ethanol mixture (50% v/v) was added drop-wise to the stirred ligand-sodium acetate mixture. The reaction mixture was refluxed for 24 h. The precipitates were filtered off, recrystallized and dried in a vacuum desiccator. The addition of sodium acetate to the reaction mixture was necessary to enhance the reaction according to the following equations:



Apparatus used

Elemental analysis of the Pt(IV)-complexes was carried out at the Microanalytical Unit Laboratory, Tanta University, Tanta, Egypt. The thermo-gravimetric (TGA) and differential thermal analyses (DTA) of the solid complexes were performed using a TG-50 thermo gravimetric analyzer (Shimadzu) and DTA-50 differential thermal analyzer (Shimadzu) in the temperature range 25-800°C with 10°C min heating rate using nitrogen as atmosphere. IR spectra of were recorded as KBr using a Perkin Elmer 1430 spectrophotometer within the range 4000-200 cm⁻¹ ranges. The

¹HNMR spectra were carried out on a Bruker AC spectrometer operating at 300 MHz in d₆-DMSO as a solvent using TMS as internal standard. Electronic spectra in Nujol mull and DMF were determined using a Shimadzu UV-visible 240 spectrophotometer. The magnetic measurements were carried out at room temperature by Gouy method; the apparatus being calibrated with mercury tetrathiocinato cobaltate (II). Diamagnetic corrections were made using Pascal's constants' Conductivity measurements were made at 25°C using conductance bridge of the type" 523 conduct meter. The studies of DC polarography and cyclic voltammetry went carried out as described previously. The catalytic activity of the complexes] towards cathodic reduction of oxygen at a glassy carbon electrode was studied using' Oxford rotating disc system within speed range 0 to 3,000 rpm.

Results and Discussion

Elemental analysis

The data of elemental analysis are in satisfactory agreement with those calculated! from the suggested formula [PtLCl₂). This supports the structural formulae given and denotes that all the ligands reacted with PtCL₄ to give Pt(IV)-Schiff base complexes, as a dibasic acid according to equation (1).

Thermal analysis

The TGA and DTA curves show that, all complexes are thermally stable up to at least 200 °C which is a good evidence that the complexes are free from both hydrated and coordinated water molecules(IOJ and are in satisfactory agreement .with the data of elemental analysis.

The TGA curves of all complexes display two thermal decomposition steps within; the temperature ranges 250-360 and 396-441 DC. The first step can be assigned to loss of the two chloride ions (most probably as HCl) and partial degradation of the," chelating agent in case of complexes (1-4) and removal of the two chloride ions (as , HCl) in case of complexes (5 and 6). The second step corresponds to the complete thermal decomposition of the organic ligand in all cases leading to PtO₂ as final product.

The DTA curves of Pt(IV)-complexes (1-4) showed two exothermic peaks due to partial pyrolysis of the ligand molecule and complete thermal decomposition of the complex, the first peak lied within temperature range 200-260°C and the second one within the range 360-3820C (Table 1). For complexes (5) and (6), DTA curves showed an endothermic peak at 200 and 265°C, respectively resulting from the thermal liberation of the coordinated chloride ions and another exothermic peak at 370 and 480°C corresponding to the thermal decomposition of the whole complex within formation of PtO₂ as final product (Table 1). The observations in the DTA results were confirmed by the TGA weight losses.

IR spectra

A comparison of the IR. spectra of the Pt(IV)-Schiff base complexes with those of the free ligands (Table 2) reveals the following points: Table 1. DTA peaks of the Pt(IV)-complexes and then: assignments.

Com. No.	DTA peak (°C)		Assignment
	Step	Endo Exo	
(1)	A	260	Partial pyrolysis of the ligand molecule
	B	377	Thermal decomposition of the chelates rings and formation of Pt(CO ₃)
(2)	A	245	Partial pyrolysis of the ligand molecule
	B	382	Thermal decomposition of the chelates rings and formation of Pt(CO ₃) +PtO ₂
(3)	A	240	Partial pyrolysis of the ligand molecule
	B	360	Thermal decomposition of the chelates rings and formation of PtO ₂
(4)	A	200	Partial pyrolysis of the ligand molecule
	B	380	Thermal decomposition of the chelates rings and formation of PtO ₂
(5)	A	200	Thermal liberation of chloride ions
	B	370	Thermal decomposition of the whole complex and formation of PtO ₂
(6)	A	265	Thermal liberation of chloride ions
	B	480	Thermal decomposition of the whole complex and formation of PtO ₂

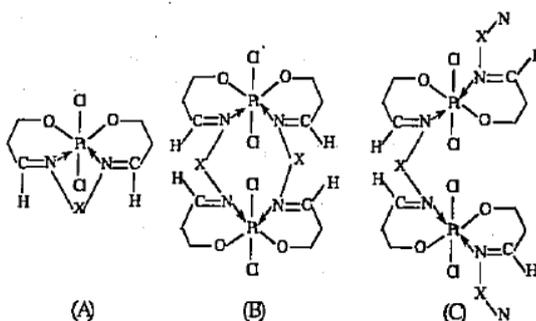
1) The disappearance of all bands due to the various modes of OH vibrations [$\nu(\text{OH})$ 3250-3200, $\delta(\text{OH})$ at 1358-1347, $\nu(\text{C-OH})$ at 1190-1160 and $\gamma(\text{OH})$ at 850-820 cm^{-1}] This denotes the displacement of the protons of OH-groups through the metal ions and the bonding of Pt(IV) ions to the phenolic oxygen through a covalent bond.

2) The shift of $\nu(\text{C=N})$ band at 1630-1616 cm^{-1} in the spectra of the ligands to higher wave numbers by 19-10 cm^{-1} . These shifts besides showing the coordination of the azomethine nitrogen to the Pt(IV) ions indicates the bonding of the Schiff I molecule as tetradentate N₂O₂ ligand to Pt(IV) ion.

3) The bonding of the Pt(IV) ions to the oxygen of the hydroxy group and the azomethine nitrogen is supported by the appearance of two new bands at 640-590 and 593-454 cm^{-1} which can be assigned to the $\nu(\text{Pt-O})$ and $\nu(\text{Pt-N})$, respectively.

4) The low intensity new bands at 355-308 cm^{-1} in the spectra of the complexes can be assigned to the $\nu(\text{Pt-Cl})$ vibration denoting the coordination of the chloride ions to the Pt(IV) ions.

Based on these results, the Pt(IV) ions would be bonded to the Schiff base molecules] by two covalent bonds with the phenolic oxygen and two coordination bonds with the* azomethine nitrogen's. These four centers can be provided from one and the same molecule in case of ligands L1, L2 and L5 (A) whereas for ligands L3, L4 and L6, this is not possible and the four bonding centers can only be given by two ligand molecules. This is achieved through dimer (B) or polymer (C) formation (Scheme 2).



Scheme 2

Table 2. IR spectral data of the Pt (IV) – complexes:

Com. No.	V(C=N) (ligand)	V(C=N) Complex	V (C-O)	V (Pt-O)	V (Pt-N)	V (Pt-Cl)
(1)	1627 (br,s)	1640 (w)	1106 (s)	592 (m)	464(w)	324 (w)
(2)	1628 (br,s)	1640 (w)	1108 (m)	586 (m)	530 (s)	308 (m)
(3)	1618 (br,s)	1635 (w)	1035 (s)	605 (m)	530 (s)	355 (m)
(4)	1630 (br,s)	1640 (w)	1038 (s)	619 (w)	454 (s)	321 (m)
(5)	1618 (br,s)	1630 (w)	1035 (m)	640 (m)	480 (s)	340 (m)
(6)	1616 (br,s)	1635 (w)	1028 (s)	626 (w)	583 (s)	333 (w)

br = broad, s = strong, m = medium, w = weak

HNMR spectra

The ¹H NMR Spectra of the Pt(TV)-complexes (1, 5 and 6) compared to those of the free ligands(4'n) show me disappearance of the signal due to the hydrogens of the OH : groups at 4.3-4.7 ppm. The signals due to the azomethine hydrogen (CH=N) exhibit a " down field shift of 0.06-0.35 ppm; also the signals of the N-CH₂ groups in case of complex (1) shows a down field shift of 0.3 ppm. The signals due to the hydrogens of the aromatic rings exhibit varied down filed shifts (0.04-0.51 ppm). The down filed shifts of the different signals of CH=N, CH₂ or ph-hydrogens are mainly due to the de-shielding of such hydrogens under the effect of the Pt(IV) ion having a high positive field and acting as electron acceptor from the Schiff base ligands.

Uv/Vis absorption spectra and magnetic measurements

The electronic absorption spectra of the Pt(TV)-complexes under study as nujol mull and DMF solutions display the same spectral pattern with slight shift in band position revealing that the geometry of the complexes is the same in all cases. The band observed at 270-290 nm is due to intra-ligand $\pi - \pi^*$ transition while the other bands are due to d-d transitions within the Pt(IV) ion. The bands at 320-420 ($^1A_{1g} \rightarrow ^3T_{1g}$), 410-460 ($^1A_{1g} \rightarrow ^2T_{1g}$) and 480-560 nm ($^1A_{1g} \rightarrow ^1T_{1g}$) correspond to electronic transitions in octahedral geometry of a d⁶ system Four of the required bonding sites will be provided by the organic ligands and two by the chloride ions since all the Pt(IV) complexes are deprived of water molecules.

All complexes were found to be diamagnetic hence do not exhibit unpaired d-electrons and being of low spin type.

Conductance measurements

The molar conductance values of the Pt(XV)-Schiff base complexes lie with the range ($2.5-3.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) which indicate that these complexes have nonionic nature. This supports the participation of the chloride ions in the coordinate sphere.

Electrochemical reduction

The DC polarograms and cyclic voltammograms for the reduction of the Pt(IV)SB complexes under study were carried out in 0.01 M KCl containing 40% (v/v) DMF at 25 °C. The polarograms exhibit two waves of almost equal heights; the first one with $E_{1/2}$ within the range from -0.21 to -0.42 volt corresponds to the reduction of Pt (IV) while the second wave at more negative potentials mostly joins the wave due to the reduction of IT ions. The $E_{1/2}$ shift to less negative potentials as the length of the aliphatic chain increases, but is shifted to more negative values for SB derived from aromatic diamines.

Analysis of the waves showed that the reduction of Pt(IV) proceeds irreversibly; the most probable values of the transfer coefficient (α) obtained from the slope of the logarithmic analysis amount to 0.41-0.48 for $n_a = 2$. This denotes that the rate-determining step in the electro-reduction of Pt(IV) comprise two electrons. The effect of Hg-pressure at the dropping electrode gave a slope for the plot of $\log i$ vs $\log h$ amounting to (0.55-0.7) denoting that the electrode reduction is governed by diffusion with partial adsorption contribution.

The cyclic voltammograms of the complexes gave one cathodic peak with $E_p = 0.37-0.45$ volt at scan rate of 50 mV s^{-1} but no anodic peaks were observed. The absence of anodic peaks confirms the irreversible nature of the electrode process. **Catalytic effect of Pt(IV)-Schiff base complexes on the cathodic reduction of oxygen**

The catalytic effect of the Pt(IV)-complexes on the cathodic reduction of oxygen at a glassy carbon electrode was studied in 1.0 M phosphoric acid. The solution was saturated with air by bubbling

a fine stream of air for 30 min. The cathodic reduction of oxygen was carried out, then increasing volumes (0.2-4.0 mL) of 2×10^{-4} M solution of the Pt(IV)-SB complexes were added and the voltamogram was recorded. The reduction of oxygen gave a single cathodic peak with $E_p = -1.10$ volt vs. Ag/AgCl electrode in the absence of catalysts but no anodic ones are observed denoting that the reduction proceeds irreversibly. The addition of the Pt(IV)-SB complexes causes a shift of E to less negative potentials and the peak current (i_p) increased to some extent. These changes increased with increasing the concentrations of the catalyst. The shift in E_p reached 300 mV using Pt(IV)-complexes under investigation while using SB. complexes of the first transition series the shift in E_p did not exceed 190 mV.(15) The shift of E_p to less negative potential in presence of Pt(IV)-complexes denotes that these complexes catalyze the oxygen reduction by decreasing the activation energy of the electrode reaction. The increase in i_p values can be ascribed to increasing the amount of oxygen transferred to the electrode surface; under conditions in which Pt(IV)-SB complexes act as oxygen carrier.

Biological activity of platinum (IV)-complexes

In this section, experiments were carried out to study the effect of the Pt(IV)-complexes (1-6) as antibacterial agents against gram positive [*Bacillus subtilis* NRRL-B-4378 (A), *Serratia marcescens* (B) and *Staphylococcus aureus* NRRL-B-767(C)] and gram negative [*Escheria coli* NRRL-B-3704 (D), *Salmonella typhosa* (E) and *Pseudomonas aeruginosa* (F)] bacteria. The minimum inhibitory concentration (MIC) of Pt(IV)-SB complexes was defined as the lowest concentration of the Pt(IV)-SB complex that inhibited visible bacterial growth and was determined by the recommended method.

The MIC of the different Pt(IV)-complexes was found to be 25, 25, 25, 50, 50, and 100 $\mu\text{g ml}^{-1}$ for Pt(IV)complex(1), 100,25,12.5, 6.25 and 25 $\mu\text{g ml}^{-1}$ for Pt(IV)-complex (2), 100, 25,100, 25, 50 and 50 $\mu\text{g ml}^{-1}$ for Pt(IV)-complex (3), 100, 50,25, 50, 50 and 25 $\mu\text{g ml}^{-1}$ for Pt(IV)-complex (4), 6.25,12.5, 12.5,25, 50 and 12.5 $\mu\text{g ml}^{-1}$ for Pt(IV)-complex (5) and 100, 50, 50, 100, 25 and 50 $\mu\text{g ml}^{-1}$ for Pt(IV)-complex (6) in case of different types of bacteria from (A) to (F), respectively. These results indicate that all Pt(IV)-SB complexes under study show antibacterial activity against both Gram positive and Gram negative Also, the Pt(IV)-SB complexes (2 and 5) and the most efficient as antibacterial agents.

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