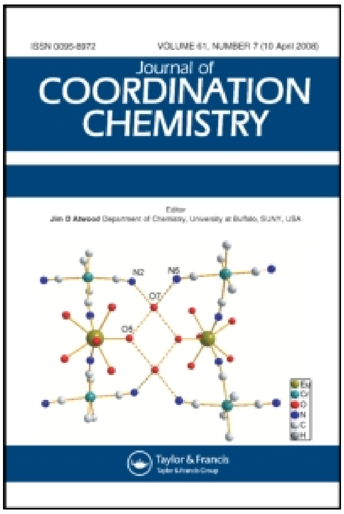

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NOVEL PLATINUM(II) AND (IV) COMPLEXES OF NAPHTHALDIMINE SCHIFF BASES

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Naphthaldimines containing N_2O_2 donor centers react with platinum(II) and (IV) chlorides to give two types of complexes depending on the valence of the platinum ion. For [Pt(II)], the ligand is neutral, $[(H_2L^1)PtCl_2]\cdot 3H_2O$ (**1**) and $[(H_2L^3)_2Pt_2Cl_4]\cdot 5H_2O$ (**3**), or monobasic $[(HL^2)_2Pt_2Cl_2]\cdot 2H_2O$ (**2**) and $[(HL^4)_2Pt]\cdot 2H_2O$ (**4**). These complexes are all diamagnetic having square-planar geometry. For [Pt(IV)], the ligand is dibasic, $[(L^1)Pt_2Cl_4(OH)_2]\cdot 2H_2O$ (**5**), $[(L^2)Pt_3Cl_{10}]\cdot 3H_2O$ (**6**), $[(L^3)Pt_2Cl_4(OH)_2]\cdot C_2H_5OH$ (**7**) and $[(L^4)Pt_2Cl_6]\cdot H_2O$ (**8**). The Pt(IV) complexes are diamagnetic and exhibit octahedral configuration around the platinum ion. The complexes were characterized by elemental analysis, UV-Vis and IR spectra, electrical conductivity and thermal analyses (DTA and TGA). The molar conductances in DMF solutions indicate that the complexes are non-ionic. The complexes were tested for their catalytic activities towards cathodic reduction of oxygen.

Keywords: Naphthaldimine; Pt(II); Pt(IV)

INTRODUCTION

There has been considerable interest in platinum complexes with symmetrical bidentate ligands. One such ligand is the naphthaldimine which typically coordinates to the metal ion by means of imino and hydroxyl groups. Platinum dimers bridged by diphenylphosphinocyclopentadienyl ligands have been prepared and characterized [1]. The *cis*- and *trans*-isomers of $Pt(NH_3)_2Cl_2$ have been studied by luminescence, absorption and magnetic circular dichroism (MCD) experiments [2,3]. The thermal decompositions of the *cis*- and *trans*-isomers of dichlorobis(pyridine)platinum(II) complex have been reported [4,5], and the reactivity of the $[Pt(CO)_2Cl_2]$ with an asymmetric acetylene investigated [6]. The limited information available on platinum complexes of Schiff bases prompted us to undertake a systematic examination in this field. In the present work, platinum(II) and (IV) complexes of naphthaldimines were prepared and characterized by elemental analysis, UV-Vis and IR spectra, conductivity and thermal analyses. Electrochemical measurements were conducted to test the catalytic activity of some complexes towards cathodic reduction of oxygen. The data show that the reduction process takes place irreversibly.

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EXPERIMENTAL

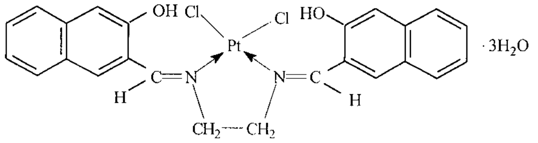
Reagent grade chemicals were used. Platinum(II) and (IV) chlorides were obtained from Johnson Matthey Ltd. Elemental analyses for C, H, N and Cl were determined at the Analytical Unit of Cairo University, Egypt. A gravimetric method was used for determining the platinum content. All complexes were dried in vacuo over P_4O_{10}. The IR spectra were measured as KBr discs using a Perkin-Elmer 681 spectrophotometer (4000–200 cm^{-1}). Electronic spectra in the 200–900 nm region were recorded as nujol mulls on a Perkin-Elmer 550 spectrophotometer. Molar conductances were measured on a Tacussel-type CD_6NG conductivity bridge using 10^{-3} M DMF. Thermal analyzes (DTA and TGA) were carried out in air on a Shimadzu DT-30 thermal analyser from 27 to 700°C. Current–voltage curves were recorded on a Hewlett-Packard model 7440AX-Y recorder. The buffers used for the electrochemical study were the universal Britton–Robinson acetate, phosphate and borate of pH 2–12, using 20% ethanol to aid the dissolution of the complexes. TLC (silicia gel/CH_3OH, 100%) of all the complexes confirmed their purity.

Synthesis of Ligands

The naphthaldimines were prepared as previously described [7].

Preparation of Complexes 1, 2, 3 and 4

Complexes were prepared by reacting $PtCl_2$ (0.01 mol, 2.7 g) in ethanol (30 mL) with purified ligand in the same solvent (50 mL), (0.01 mol, 3.92 g, (H_2L^1)), [(H_2L^1)



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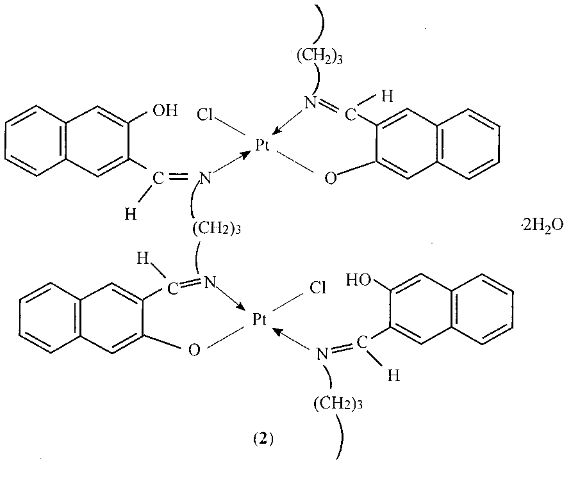

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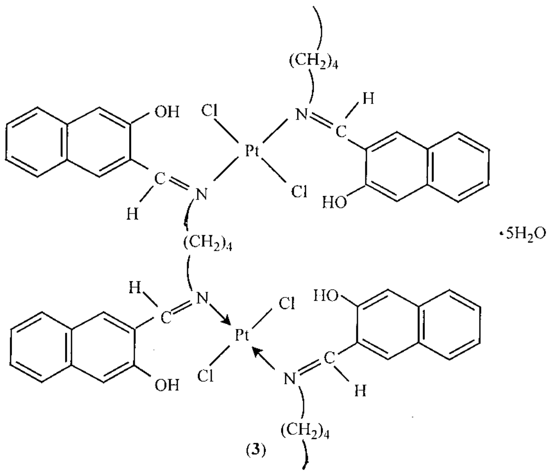

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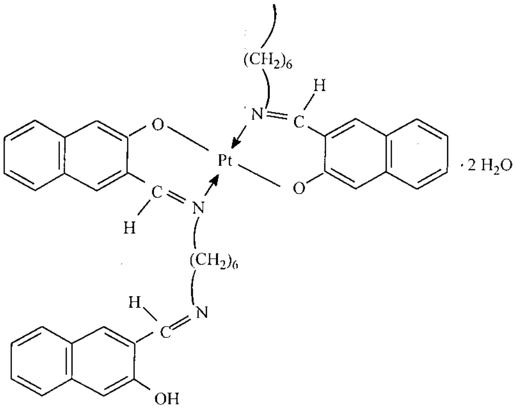


(4)

$PtCl_2]\cdot 3H_2O$ (**1**), (0.01 mol, 4.06 g, (H_2L^2)), $[(HL^2)_2Pt_2Cl_2]\cdot 2H_2O$ (**2**), (0.01 mol, 4.2 g, (H_2L^3)), $[(H_2L^3)_2Pt_2Cl_4]\cdot 5H_2O$ (**3**) and (0.01 mol, 4.5 g, (H_2L^4)), $[(HL^4)_2Pt]\cdot 2H_2O$ (**4**). The reaction mixture was stirred under reflux for 3 h and the colored precipitates removed by filtration, washed several times with hot ethanol and ether, then dried in a vacuum desiccator over P_4O_{10} for three days. The analytical data are given in Table I.

Preparation of Complexes 5, 6, 7 and 8

The complexes were obtained from $PtCl_4$ (0.01 mol, 3.4 g) in ethanol (30 mL) and (0.01 mol, 3.92 g, (H_2L^1)), $[(L^1)Pt_2Cl_4(OH)_2]\cdot 2H_2O$ (**5**), (0.01 mol, 4.06 g, (H_2L^2)), $[(L^2)Pt_2Cl_{10})]\cdot 3H_2O$ (**6**), (0.01 mol, 4.2 g, (H_2L^3)), $[(L^3)Pt_2Cl_4(OH)_2]\cdot C_2H_5OH$ (**7**) and (0.01 mol, 4.5 g, (H_2L^4)), $[(L^4)Pt_3Cl_6]\cdot H_2O$ (**8**), in the same solvent (50 mL). Complexes (**5**) and (**7**) were prepared in the presence of KOH (1.18 and 1.26 g, respectively). The reaction was carried out as described above. The precipitated complex was filtered off, washed with hot ethanol and ether, then dried in a vacuum desiccator over P_4O_{10} for three days. The analytical data are given in Table I.

TABLE I Analytical and physical data of Pt(II) and (IV) complexes.

Complex no/ suggested formulation	*Color*	*Yield* (%)	*M.P.* (°C)	*Molar conductance* (Ω^{-1} cm^2 mol^{-1})	*Found (Calc)* (%)				
					C	*H*	*N*	*Cl*	*Pt*
1 $[(H_2L^1)PtCl_2]\cdot 3H_2O$	Yellowish green	68	> 300	12	41.8	3.6	4.0	10.1	28.0
$(C_{24}H_{20}N_2O_2PtCl_2\cdot 3H_2O)$					(41.8)	(3.7)	(4.1)	(10.3)	(28.3)
2 $[(HL^2)_2Pt_2Cl_2]\cdot 2H_2O$	Yellow	65	> 220	10	46.2	4.1	4.2	5.3	30.0
$(C_{25}H_{21}N_2O_2ClPt\cdot 2H_2O)$					(46.3)	(3.9)	(4.3)	(5.5)	(30.0)
3 $[(H_2L^3)_2Pt_2Cl_4]\cdot 5H_2O$	Yellowish green	70	> 300	13	41.1	4.4	3.5	9.2	25.2
$(C_{26}H_{26}N_2O_2Cl_2Pt\cdot 5H_2O)$					(41.0)	(4.4)	(3.6)	(9.3)	(25.0)
4 $[(HL^4)_2Pt]\cdot 2H_2O$	Yellow	70	220	13	57.6	4.8	4.6	–	22.2
$(C_{24}H_{40}N_3O_3Pt\cdot 2H_2O)$					(57.9)	(5.0)	(4.8)	–	(22.4)
5 $[(L^1)Pt_2Cl_4(OH)_2]\cdot 2H_2O$	Yellowish brown	58	> 300	11	29.6	2.6	2.6	14.5	39.8
$(C_{24}H_{20}N_2O_4Cl_4Pt_2\cdot 2H_2O)$					(29.8)	(2.5)	(2.8)	14.7	(40.0)
6 $[(L^2)Pt_3Cl_{10}]\cdot 3H_2O$	Black	55	> 300	15	21.4	2.3	2.2	25.6	42.3
$(C_{25}H_{20}N_2O_2Cl_{10}Pt_3\cdot 3H_2O)$					(21.8)	(2.0)	(2.0)	(25.8)	(42.6)
7 $[(L^3)Pt_2Cl_4(OH)_2]\cdot C_2H_5OH$	Yellowish brown	60	215	17	33.5	3.2	2.5	14.0	38.3
$(C_{26}H_{24}N_2O_4Cl_4Pt_2)\cdot C_2H_5OH)$					(33.3)	(3.0)	(2.7)	(14.1)	(38.8)
8 $[(L^4)Pt_2Cl_6]\cdot H_2O$	Deep brown	58		11	33.0	3.0	2.7	20.7	37.0
$(C_{28}H_{26}N_2O_2Cl_6Pt_2\cdot H_2O)$					(32.8)	(2.7)	(2.7)	(20.4)	(37.4)

RESULTS AND DISCUSSION

Platinum(II) and (IV) complexes with ligands which have the general structural formula shown in Fig. 1 have been prepared and characterized. The analytical and physical data (Table I) and spectral data (Tables II and III) are compatible with the suggested structures (Fig. 2). The complexes are colored, stable at room temperature and have high melting points. The complexes are insoluble in non-polar solvents such as benzene and toluene, partly soluble in methanol and ethanol, and soluble in polar solvents such as DMF and DMSO. The low molar conductances imply that they are non-ionic [8].

IR Spectra

Important bands in the IR spectra of the complexes are presented in Table II. The bands due to the OH modes are no longer observed in the spectra of Complexes **4**–**8**, indicating that the hydroxyl protons are displaced by platinum ions. This leads to lower ν(C–O) (1348–1335 cm^{-1}). However for Complexes **1**–**3**, the ν(C–O) appears at higher frequency (1368–1355 cm^{-1}) (Table II) [9]. The ν(C=N) band (1640–1615 cm^{-1}) is shifted to lower wavenumbers (compared to that of the free ligands, 1648–1640 cm^{-1}) indicating that the nitrogen atom of the azomethine group is coordinated to the platinum ion [10]. The bonding of platinum ions to the ligand through the nitrogen and oxygen atoms is further supported by the appearance of new bands in the 540–420 and 640–605 cm^{-1} ranges due to ν(Pt–N), ν(Pt–O), respectively in the spectra of the complexes [11]. Another band was observed in the 410–320 cm^{-1} range which corresponds to ν(Pt–Cl) [6,11]. The existence of water molecules is shown by the appearance of the broad band in the 3655–3020 cm^{-1}

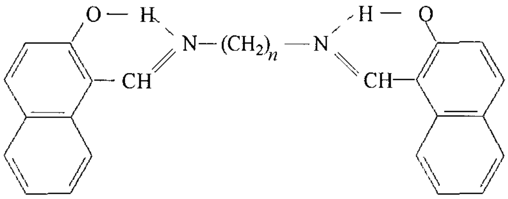


FIGURE 1 $n = 2$, [H_2L^1]; $n = 3$, [H_2L^2]; $n = 4$, [H_2L^3], $n = 6$, [H_2L^4].

TABLE II Important IR bands of Pt(II) and (IV) complexes

Complex no.	*Assignment* (cm^{-1})						
	$\nu(H_2O/H\text{-bonding})$	$\nu(C{=}N)$	$\nu(C{=}C)Ar$	$\nu(CO)$	$\nu(PtO)$	$\nu(PtN)$	$\nu(PtCl)$
1	3655–3100	1640	1618	1360	601	508	328
2	3620–3020	1640, 1625	1580	1368	615	460	330
3	3560–3040	1640	1617	1355	610	540	335
4	3600–3160	1640	1617	1340	640, 610	515, 470	–
5	3600–3200	1625	1618	1335	605	470	320
6	3500–3150	1618	1600	1338	605	470	410, 370
7	3620–3120	1639, 1632	1575	1348	605	530	355
8	3600–3100	1640, 1615	1578	1335	640	480	370, 340

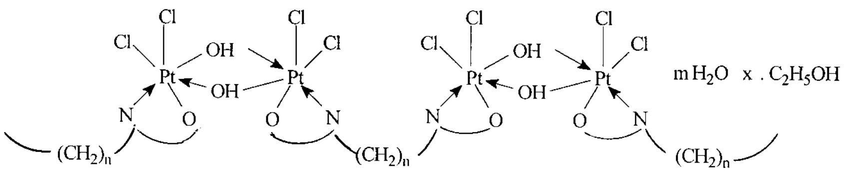
TABLE III Electronic spectra of Pt(II) and (IV) complexes in nujol mull

Complex no	λ_{max} (nm)
1	422, 370, 310, 243
2	424, 357, 310, 222
3	410, 360, 307, 225
4	420, 330, 275, 260
5	585, 510, 420, 310, 250
6	590, 515, 405, 300, 220
7	585, 510, 420, 315, 210
8	600, 510, 436, 300, 240

range, due to ν(OH) of coordinated or lattice water [12]. If the molecular geometry of the ligand does not allow formation of a stable ring involving the platinum ion, then dimeric, trimeric or polymeric complexes are formed in the solid state [13–16] as shown in Fig. 2. This behavior is comparable with that observed with other metal ions [7,9,17].

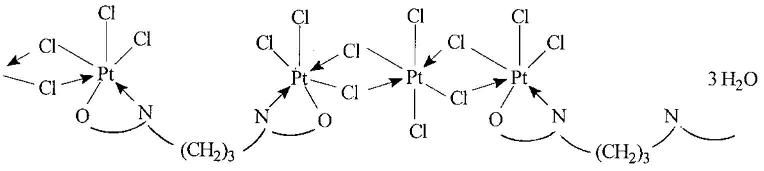
Electronic Spectra

The electronic spectra of platinum complexes as nujol mulls are summarized in Table III. Complexes **1**–**4** showed four bands: 260–222, 310–275, 370–330 and 424–410 nm ranges. The first may be attributed to intramolecular charge transfer (CT) interactions and to π–π^* internal ligand transitions. The other three bands correspond to $^1A_{1g} \rightarrow ^1E_g$, $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1A_{2g}$ transitions of Pt(II) [18,19], suggesting square-planar geometry as expected for the d^8 system. Complexes **5**–**8** show four bands: 250–210, 315–300, 436–405 and 600–585 nm ranges. The first is due to intraligand charge transfer (CT) and π–π^* internal ligand transitions. The other



n = 2, m = 4, x = 0 **(5)**

n = 4, m = 0, x = C_2H_5OH **(7)**



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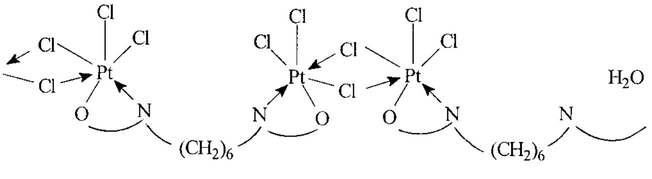


(8)

FIGURE 2 Proposed structures for Pt(II) and (IV) complexes.

bands are from $^1A_{1g} \rightarrow {}^3T_{1g}$, $^1A_{1g} \rightarrow {}^1T_{2g}$ and $^1A_{1g} \rightarrow {}^1T_{1g}$ transitions, suggesting octahedral geometry for the d^6 system [19].

Thermal Analyses (DTA and TGA)

Since the IR spectra indicate the presence of water molecules, thermal analyses (DTA and TGA) were carried out to ascertain their nature. The DTA and TGA curves in the temperature range 27–700°C for Complexes **2**, **4**, **6** and **8** show that, the complexes are thermally stable up to 60°C. Dehydration is characterized by endothermic peaks within the temperature range 60–140°C, corresponding to the loss of hydration water molecules [10,20]. Another peak was observed in the 220–370°C range, corresponding to loss of coordinated and bridged chloride atoms. The DTA curves show a peak within the 200–300°C range with no weight loss, which may be due to lattice rearrangement of the anhydrous complex or melting of the complexes. The complexes show peaks within the 410–510°C range corresponding to oxidative thermal decomposition, which proceeds slowly with a final residue at 570–650°C, assigned to platinum oxides. These observations were confirmed by TGA weight losses. The thermal decomposition of Complex **6** can be represented as follows:

$$[(L)Pt_3Cl_{10}]\cdot 3H_2O \xrightarrow{90^\circ C} [(L)Pt_3Cl_{10}] + 3H_2O$$

$$[(L)Pt_3Cl_{10}] \xrightarrow{230^\circ C} [(L)Pt_3Cl_4] + 6Cl$$

$$[(L)Pt_3Cl_4] \xrightarrow{360^\circ C} [(L)Pt_3] + 4Cl$$

$$[(L)Pt_3] \xrightarrow{480-630^\circ C} 3PtO_2 + \text{volatile organic residues}$$

The thermal stability sequence is: Complex **6** > Complex **2** > Complex **4** > Complex **8**. The results of the thermal analyses of the complexes are presented in Table IV.

Catalytic behavior

The polarograms of 2.5×10^{-4} M solutions of dianil Compounds **6** and **8** were recorded in Britton–Robinson buffer solutions of pH 2–12. The polarograms in all solutions exhibited two waves of almost equal heights corresponding to reduction of the two C=N groups within the molecule. The total limiting current corrersponds to uptake of four electrons (two electrons transfer for each wave). On increasing the pH of the solution (Table V), the wave height decreases markedly perhaps due to the partial

TABLE IV Thermal analyses of Pt(II) and (IV) complexes

Complex no	*DTA*		*TGA wt. loss found (calcd) (%)*	*Assignment*
	°C	*Peak*		
2	60	endo	5.5 (5.5)	Dehydration
	220	endo	–	Melting point of complex
	275	endo	5.5 (5.5)	Loss of coordinated Cl as HCl
	300	endo	–	Lattice rearrangement
	410	endo	37.7(37.9)	Breaking of six-membered chelate ring
	650	exo	32.4 (32.5)	Oxidative thermal decomposition with formation of PtO
4	65	endo	4.1 (4.1)	Dehydration
	200	endo	–	Lattice rearrangement
	220	exo	–	Melting point of complex
	510	endo	33.0 (32.9)	Breaking of six-membered chelate ring
	630	exo	37.6 (37.7)	Oxidative thermal decomposition with formation of PtO
6	90	endo	4.2 (3.9)	Dehydration
	230	exo	16.4 (16.1)	Loss of coordinated Cl as HCl
	360	exo	12.8 (12.8)	Loss of bridged Cl as HCl
	480	exo	–	Oxidative thermal decomposition with formation of PtO
	600	exo	–	
	630	exo	23.2 (23.5)	
8	140	endo	1.7 (1.8)	Dehydration
	230	exo	–	Melting point of complex
	260	exo	13.8 (13.9)	Loss of coordinated Cl as HCl
	370	exo	8.3 (8.0)	Loss of bridged Cl as HCl
	570	exo	27.6 (27.9)	Oxidative thermal decomposition with formation of PtO

TABLE V DC-polarographic data of 1,3-diaminopropanedianil in buffer solutions of different pH values

PH	$E_{½}$ (V)	*Slope of analysis* (mV)	α	Δ*log I* / Δ*log h*
2.0	0.87 a	112	0.53	–
3.0	0.92 a	95.3	0.62	0.70
	1.27 b	86.9	0.68	0.72
4.0	0.95 a	95.3	0.62	–
	130 b	82.1	0.72	–
5.0	0.99 a	79.9	0.74	0.62
	1.22 b	88.2	0.67	0.65
6.0	1.02 a	89.5	0.66	–
	1.33 b	118.0	0.50	–
7.0	1.08 a	107.5	0.55	0.55
	1.50 b	115.9	0.51	0.58
8.0	1.12 a	95.3	0.65	–
	1.60 b	109.4	0.54	–
9.0	1.20 a	100.1	0.59	0.62
	1.65 b	2.1	0.72	0.65
10.0	1.28 a	100.0	0.59	–
	1.75 b	86.9	0.68	–

In column 2, *a* and *b* are XXX, respectively. *a* is the first reduction wave and *b* is the second reduction wave.

hydrolysis of these compounds at higher pH values. Also, the half-wave potential ($E_{½}$) of the polarographic waves shifts towards more negative values on increasing the pH, denoting that hydrogen ions are consumed in the reduction process. The values of $E_{½}$ range between (– 0.87 to – 1.28 V) and (– 1.27 to –1.75 V) for 1st and 2nd waves, respectively. Analysis of the polarographic waves revealed that the reduction process proceeds irreversibly. The values of the transfer coefficient (α) obtained from slopes (logarithmic analysis) ranged between 0.5 and 0.74, denoting the irreversible nature of the polarographic waves. Also, the effect of mercury height (h) on the polarographic limiting current (I) was studied in solutions of different pH. The slopes of the straight lines obtained on plotting log I *vs.* log h are between 0.55 and 0.72 denoting that the reduction process is diffusion-controlled with some adsorption contribution.

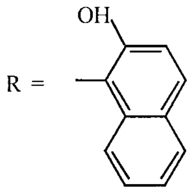
The cyclic voltammograms at a glassy carbon electrode of the two dianil Compounds **6** and **8** were recorded in solutions of different pH values covering the entire pH range. The voltammograms in all solutions show two cathodic peaks. In the reverse scan (anodic direction), the absence of any peaks denotes the irreversibility of the reduction process. The values of the transfer coefficient (α) calculated from cyclic voltammetry on plotting the peak potential (E_p) *vs.* logarithm of scan rate (lnν) are in agreement with those obtained from dc-polarography. Dc-polarographic data of 1,3-diaminopropanedianil in buffer solutions of different pH valves are presented in Table V.

The electrode reaction of the ligands can be represented as follows:

$$\underset{\text{(i)}}{\mathrm{R{-}CH=N{-}(CH_2)_n{-}N=CH{-}R2H}} \overset{2H^+}{\rightleftharpoons} \underset{\text{(ii)}}{\mathrm{R{-}CH=NH{-}(CH_2)_n{-}{}^{+}NH=CH{-}R}}$$

$$\text{(ii)}\quad + 2e + H^+ \rightarrow \mathrm{R{-}CH_2{-}NH{-}(CH_2)_n{-}{}^{+}NH=CH{-}R}$$

$$\text{(iii)}\quad + 2e + H^+ \rightarrow \mathrm{R{-}CH_2{-}NH{-}(CH_2)_n{-}NH{-}CH_2{-}R}$$



$n = 3$ (**6**) or 6 (**8**)

The effect of platinum complexes of the dianils on the cathodic reduction of oxygen in aqueous solutions was studied at a glassy carbon electrode. These complexes can be adsorbed on the electrode surface and affect oxygen reduction owing to adsorption. The study was done by passing a stream of air into an electrochemical cell containing aqueous buffer solution (pH = 3.2) for 30 min to obtain air saturation, then the oxygen wave is recorded in the complex-free solution. A well-defined wave with peak potential ~ 1.1 V is obtained which corresponds to the reduction of oxygen. The experiment was repeated using different concentrations of Complexes **6** and **8**, 1×10^{-6}, 1×10^{-5}

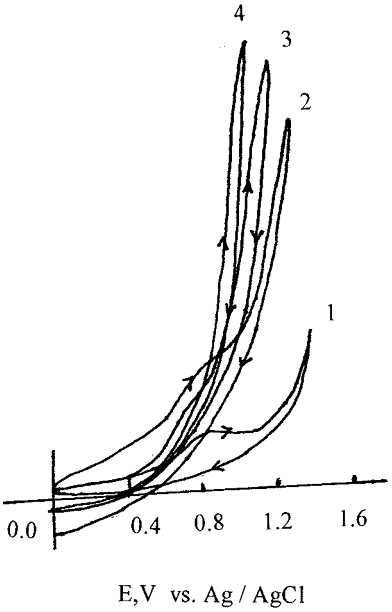


FIGURE 3 Effect of platinum(IV) Complex **8** on the oxygen reduction at pH = 3.2. (1) Oxygen wave in buffer (pH = 3.2); (2) 10^{-6} M of the complex; (3) 10^{-5} M of the complex; (4) 2×10^{-5} M of the complex.

TABLE VI Cyclic voltammogram data of Pt(II) and (IV) complexes

Complex no.	*Concentration* (M)	$\Delta E_p(O_2)$ mV	$\Delta E_p(H_2)$ mV
6	1×10^{-6}	80	70
	1×10^{-5}	132	154
	2×10^{-5}	140	160
8	1×10^{-6}	88	66
	1×10^{-5}	132	176
	2×10^{-5}	154	308

and 2×10^{-5} M, and the voltammograms were recorded. As shown in Fig. 3 for Complex **8** it is concluded that the platinum complex catalyses oxygen reduction since increasing the concentration shifted E_p to a less negative potential (Table VI). This means that adsorption of complex molecules at the electrode surface enhanced the reduction process, i.e., decreased the activation energy of the electrode process. This can be explained in two ways: (a) reduction of oxygen in the absence of platinum complexes led to the formation of a mixture of water and hydrogen peroxide by gain of four or two electrons:

$$O_2 + 2H^+ + 2e \rightarrow H_2O_2$$

However, in the presence of platinum Complexes **6** and **8**, the reaction produces water by gain of four electrons:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

or (b) the presence of the Pt–Schiff-base complex increases the current, owing to an increase in the amount of adsorbed oxygen on the electrode surface where the platinum complexes can act as oxygen carriers. The values of the reduction current and voltages change with the change of molecular structures of the complexes, as shown in Table VI.

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