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Spectroscopic and electrochemical investigations and antibacterial activity of binuclear Pd(II) and Pt(IV) complexes of newly synthesized tridentate heterocyclic compounds

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ABSTRACT

New Pd(II) and Pt(IV) binuclear complexes with two heterocyclic Schiff base ligands of type ONO derived from condensation of salicylaldehyde with 4-aminoantipyrine have been synthesized and characterized using elemental analysis, IR, electronic absorption spectra, magnetic moments. It has been found that the stoichiometric ratio is metal:ligand (2:2) with Pd(II) or Pt(IV) ions forming binuclear complexes. The electrochemistry of the Pt complexes for Pt(IV)/Pt(II) redox couple was investigated by cyclic voltammetry. According to molar conductance, the complexes may be formulated as $[Pd_2(L1)_2]$, $[Pt_2(L1)_2(H_2O)_4]Cl_2$, $[Pd_2(L2)_2]Cl$, and $[Pt_2(L2)_2(H_2O)_4]Cl_3$. On the basis of the magnetic moments, square planar geometry is suggested for Pd(II) complexes and octahedral geometry is suggested for Pt(IV) complexes. The antibacterial activity of the ligands and complexes were assessed against Gram-positive bacteria *B. subtilis* and *S. aureus* and Gram-negative bacteria *S. typhi* and *Salmonella spp.*

1. Introduction

Metal complexes of Schiff bases occupy a central role in coordination chemistry for analytical, physical, and biochemical purposes [1-10]. Heterocyclic phenazone and their derivatives (4-aminoantipyrine) are known to act as bidentate or tridentate ligands when coordinated to metal ion and can form mononuclear and binuclear complexes [11-14].

Characterization and theoretical treatment of palladium and platinum complexes as well as their use in medicinal purposes are reported [15-20].

In this paper, we are reporting the synthesis and characterization of the binuclear Pd(II) and Pt(IV) complexes of two heterocyclic Schiff base ligands containing 4-amino antipyrine.

2. Experimental

All the chemicals and solvents used for the synthesis were reagent grade and procured from (BDH chemicals or Sigma-Aldrich or Fluka). Anhydrous palladium(II) chloride (59%, Merck) and anhydrous platinum(IV) chloride (57.5%, Merck) were used as received. All solvents were dried and purified before used.

Elemental analyses were determined at the Micro-analytical Centre, Cairo University, Egypt. IR spectra were recorded on Perkin Elmer (Spectrum 1000) FT-IR spectrometer using KBr pellets at National Research Center. Electronic absorptions were recorded on a Shimadzu UV-240 automatic spectrophotometer. Determination of all metals percentage by atomic absorption spectrophotometry on AA-680G (Shimadzu).

Cyclic voltammograms were obtained at room temperature using a VersaSTAT3 potentiostat from Princeton Applied Research accompanied by the V_3 Studio software. A three electrode system was used comprising a glassy carbon electrode as the working electrode, a Pt wire as the auxiliary electrode, and Ag/AgCl (aqueous, saturated NaCl) electrode as the reference electrode. Samples were prepared as 2 mmol solutions in DMF with 0.1 M $(n\text{-Bu}_4N)PF_6$ as the supporting electrolyte. Reported values are peak potentials of the irreversible reduction using a scan rate of 100 mV/s.

Molar conductance (S. m^2/mol), at 25 °C of freshly prepared (0.001 mol/L) metal chelates in DMF was determined using a YSI-32 model conductometer. Magnetic measurements were done on solid complexes using the Gouy method. Melting points were recorded on a Gallenkamp apparatus and are uncorrected.

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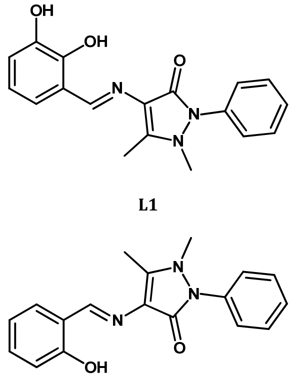
2.1. Preparation of the Schiff base ligands (L1 and L2)

The ligands (L1: 4-(2,3-dihydroxybenzylideneamino)-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one and L2: 4-(2-hydroxy benzylideneamino)-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one) were prepared by condensation of 4-aminoantipyrine with salicylaldehyde in ethanol. This preparation was performed as cited in the literature [21]. The general structures of ligands obtained from chemical analysis and spectral methods are given in Figure 1.

4-(2,3-Dihydroxybenzylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one (**L1**): Yield: 84%. M.p.: 138 °C. IR (KBr, ν, cm^{-1}): 1690 (C=O), 1625 (C=N), 1270 (C-O). UV/Vis (DMSO, λ_{max}, cm^{-1}): 26316, 28754. 34816. Anal. calcd. for $C_{18}H_{17}N_3O_3$: C, 66.86; H, 5.30; N, 13.00; O, 14.84. Found: C, 67.28; H, 5.27; N, 12.65; O, 14.98%.

4-(2-Hydroxy-benzylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one (**L2**): Yield: 88%. M.p.: 151 °C. IR (KBr, ν, cm^{-1}): 1720 (C=O), 1625 (C=N), 1290 (C-O). UV/Vis (DMSO, λ_{max}, cm^{-1}): 27184, 29411, 30769. Anal. calcd. for $C_{18}H_{17}N_3O_2$: C, 70.34; H, 5.58; N, 13.67; O, 10.41. Found: C, 69.81; H, 5.71; N, 13.50; O, 10.18%.



L1

L2

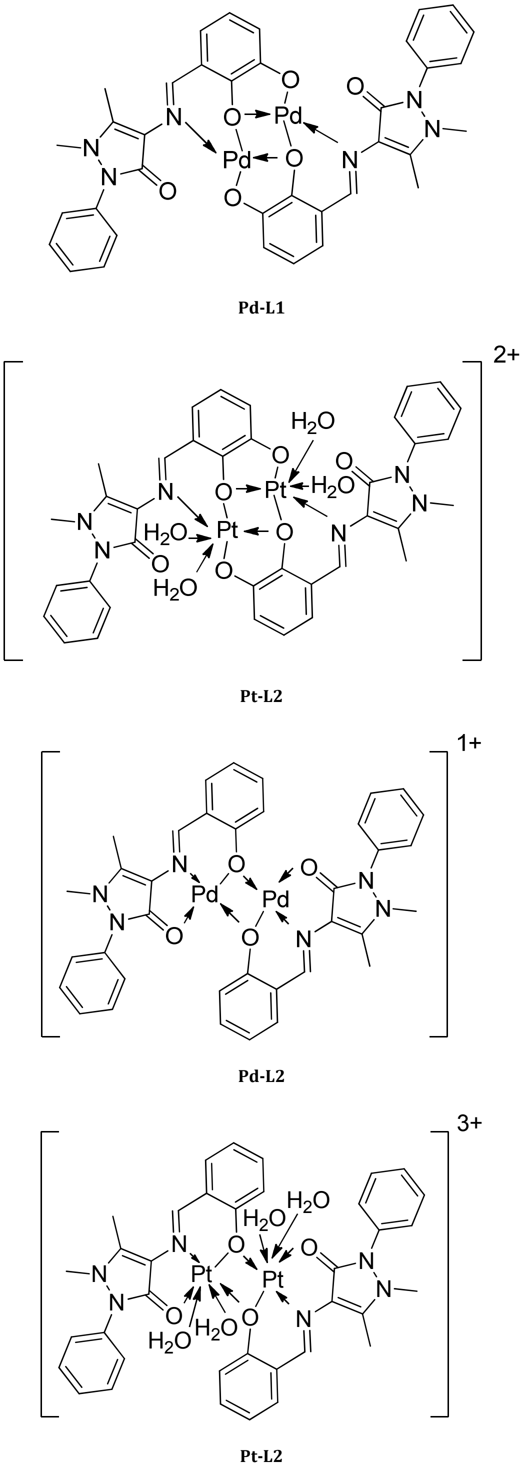
Figure 1. Structures of the ligands.

2.2. Preparation of the binuclear metal complexes

The complexes were prepared easily and in good yield from an equimolar ratio of the ligands (L1 and L2)and the metal chloride. Therefore, after the addition of (1.0 mmol, 0.178 g) of $PdCl_2$ dissolved in 20 mL ethanol and (1.0 mmol, 0.337 g) $PtCl_4$ dissolved in 20 mL acetone, to a magnetically stirred 1.00 mmol (0.548 and 0.534 g) of the ligands (L1 and L2, respectively) dissolved in 30 mL of ethanol, the mixture was stirred for 3 h. at 80 °C till the complexes precipitated. The precipitated solid was then filtered off, washed with diethyl ether, followed by cold ethanol, and dried under vacuum. The molar ratio of the complexes was determined according to the methods [22]. Proposed structures of complexes are given in Figure 2.

4-(2,3-Dihydroxybenzylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one palladium (II) (**Pd-L1**): Yield: 72%. M.p.: > 260 °C. IR (KBr, ν, cm^{-1}): 1652 (C=O), 1567 (C=N), 1262 (C-O), 534 (M-O), 458 (M-N). UV/Vis (DMSO, λ_{max}, cm^{-1}): 19494, 24630, 29411. Anal. calcd. for $C_{36}H_{30}N_6O_6Pd_2$: C, 50.54; H, 3.53; N, 9.83; O, 11.22; Pd, 24.88. Found: C, 50.81; H, 3.27; N, 10.16; O, 10.98; Pd, 24.36 %. Λ_m (S. m^2.mol^{-1}): 8.14. μ_{eff} = 0 μ_B.

4-(2,3-Dihydroxybenzylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one platinum (IV) chloride (**Pt-L1**): Yield: 68%. M.p.: > 260 °C. IR (KBr, ν, cm^{-1}): 3215 (OH), 1687 (C=O), 1576 (C=N), 1249 (C-O), 522 (M-O), 439 (M-N). UV/Vis (DMSO, λ_{max}, cm^{-1}): 20106, 33297. Anal. calcd. for $C_{36}H_{30}Cl_2N_6O_6Pt_2$: C, 39.17; H, 2.74; N, 7.62; O, 8.70; Pt, 35.35. Found: C, 39.22; H, 2.43; N, 8.56; O, 8.48; Pt, 35.17%. Λ_m (S. m^2.mol^{-1}): 126.54. μ_{eff} = 5.17 μ_B.



Pd-L1

Pt-L2

Pd-L2

Pt-L2

Figure 2. The proposed structures of the complexes.

4-(2-Hydroxybenzylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one palladium (II) chloride (**Pd-L2**): Yield: 69%. M.p.: > 260 °C. IR (KBr, ν, cm^{-1}): 1687 (C=O), 1579 (C=N), 1259 (C-O), 541 (M-O), 466 (M-N). UV/Vis (DMSO, λ_{max}, cm^{-1}): 20725, 27519, 30347. Anal. calcd. for $C_{36}H_{40}ClN_6O_8Pd_2$: C, 46.34; H, 4.32; N, 9.01; O, 13.72; Pd, 22.81. Found: C, 46.16; H, 4.43; N, 9.40; O, 13.18; Pd, 23.27%. Λ_m (S. m^2.mol^{-1}): 57.41. $\mu_{eff} = 0$ μ_B.

4-(2-Hydroxybenzylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one platinum (IV) chloride (**Pt-L2**): Yield: 76%. M.p.: > 260 °C. IR (KBr, ν, cm^{-1}): 3424 (OH), 1688 (C=O), 1573 (C=N), 1249 (C-O), 513 (M-O), 434 (M-N). UV/Vis (DMSO, λ_{max}, cm^{-1}): 16517, 35411. Anal. calcd. for $C_{36}H_{40}Cl_3N_6O_8Pt_2$: C, 36.60; H, 3.45; N, 7.12; O, 10.84; Pt, 33.03. Found: C, 36.16; H, 3.53; N, 7.40; O, 11.18; Pt, 33.27%. Λ_m (S. m^2.mol^{-1}): 161.82. $\mu_{eff} = 5.32$ μ_B.

2.3. Assessment of biological activity for ligands (L1 and L2) and their metal complexes

The biological activity of the ligands and their metal complexes were assessed against four selected types of bacteria, which included Gram-positive bacteria *B. subtilis* and *S. aureus*, and Gram-negative bacteria *S. typhi* and *Salmonella spp.* to be cultivated and as control for the disc sensitivity test [23]. This method involves the exposure of the zone of inhibition toward the diffusion of microorganism on agar plat. The plates were incubated for 24 hours at 37 °C, and the zone of inhibition (in mm) of bacteria growth around the disc was observed.

3. Result and discussion

The Schiff bases ligands are soluble in common organic solvents. Nevertheless, its metal complexes are soluble in DMF and DMSO. The elemental analysis of the complexes reveal that the compounds have an ion stoichiometry ratio of metal:ligand (2:2), the analytical data and other spectral analysis are in good agreement with the proposed stoichiometry of the complexes. The yields, melting points, IR, and electronic absorption spectral data of all the compounds are given in the experimental section.

3.1. Molar conductance

The molar conductance (S. m^2/mol at 25 °C) measurements of the complexes in DMSO (4.14, 46.54, 27.41 and 61.82) correspond to electrolytic nature of binuclear metal complexes. These complexes may be formulated as $[Pd_2(L1)_2]$, $[Pt_2(L1)_2(H_2O)_4]Cl_2$, $[Pd_2(L2)_2]Cl$, and $[Pt_2(L2)_2(H_2O)_4]Cl_3$, respectively.

3.2. Infrared spectral study

The most important infrared spectral bands of the investigated metal complexes in the present article are given in the experimental section. The free Schiff base ligands are characterized by strong band at 1690, 1625, and 1270 cm^{-1} for L1, 1720, 1625, and 1290 cm^{-1} for L2 which may be ascribed to the stretching vibrations of C=O, C=N (imine) and C-O (phenolic) groups, respectively. The band at 1625 cm^{-1} due to the stretching mode of the C=N group in the spectrum of the free ligands shows a remarkable blue shift with splitting in the 1579-1567 cm^{-1} region in all the complexes spectra suggesting that the coordinating azomethine nitrogen atoms of the Schiff bases are involved in the complexes formation.

In the spectra of all binuclear complexes, the phenolic (C-O) band is shifted to lower frequency (8-21 cm^{-1}) for L1 complexes and (31-41 cm^{-1}) for L2 complexes. It is suggested that the oxygen atom of the deprotonated phenolic groups are attached to the metal ions. An additional band at 3215 and 3424 cm^{-1} for Pt-L1 and Pt-L2, respectively, suggests that water molecules are coordinated to metal ion. Additional bands (541-513 cm^{-1}) of M-O and (466-434 cm^{-1}) M-N, respectively, are observed in the IR spectra of the complexes.

3.3. Electronic spectra

The electronic spectra were recorded in DMSO. In the spectrum of the ligand, the bands in the 26316-29412 cm^{-1} range are assigned to the $n \rightarrow \pi^*$ transitions of the azomethine group. During the formation of the complexes, these bands are shifted to lower wavelength, suggesting that the nitrogen atom of the azomethine group is coordinated to the metal ion. The values in the 30769-34816 cm^{-1} range are attributed to the $\pi \rightarrow \pi^*$ transition of the aromatic rings. In the spectra of the complexes, these bands are shifted slightly to lower wavelength.

The palladium chelates show two low energy weak bands and one strong high-energy band (19494, 24630, 29411cm^{-1}) for Pd-L1 and (20725, 27519, 30347 cm^{-1}) for Pd-L2. These are assigned to $^3A_2g(F) \rightarrow {}^3T_2g(F)$, $^3A_2g(F) \rightarrow {}^3T_1g(F)$ and $^3T_2g(F) \rightarrow {}^3T_1g(P)$. These three bands are expected to square planar geometry.

The electronic spectra of Pt(IV) chelates, (20106, 33297 cm^{-1}) for Pt-L1 and (16517, 35411cm^{-1}) for Pt-L2, consist of one broad low energy band, $^5E_{1g}(D) \rightarrow {}^5B_{1g}(D)$, and one strong high energy band assigned to ligand-metal charge transfer. The position of electronic spectral bands indicates that these two complexes have distorted octahedral geometry of D_{4h} symmetry. The energy level sequence will depend on the amount of tetragonal distortion due to ligand field and Jähn-Tellar distortion effect.

3.4. Cyclic voltammetry

As expected for the Pt(IV)/Pt(II) redox couple, the platinum complexes exhibit a single irreversible reduction event in the potential window of +0.4 to -1.2 V *vs.* Ag/AgCl. The peak potentials (E_p), Figure 3 for these processes obtained at a scan rate of 100 mV/s are -0.66 and -0.63 for Pt-L1 and Pt-L2, respectively. The redox potential of platinum(IV) complexes is therefore believed to be an important factor in their efficacy as antibiological agents.

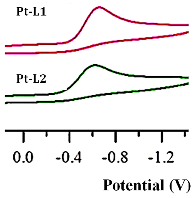


Figure 3. Cyclic voltammograms of platinum complexes.

3.5. Magnetic susceptibility measurements

On the basis of the magnetic susceptibility measurements, the Pd(II) complexes at room temperature are diamagnetic correspond to square planar geometry, whereas Pt(IV) complexes have paramagnetic character (5.17 and 5.32 μ_B) correspond to high spin octahedral geometry.

3.6. Antibacterial assessment

The ligands and their Pd(II) and Pt(IV) complexes were evaluated against different species of bacteria. The antibacterial activity on *B. subtilis*, *S. aureus, S. typhi* and *Salmonella spp.* at 25 °C was estimated by the paper disc diffusion technique [23,24]. The ligands and their metal complexes show significant antibacterial activity, Figure 4. Pt(IV) show high potency towards bacteria strains used. The antibacterial activity of Pt(IV) complexes toward *S. typhi* surpass the standard antibiotic chloramphenicol.

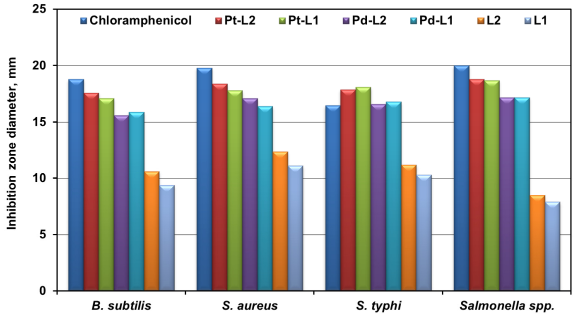


Figure 4. The effect of ligands and their metal complexes toward bacteria (Inhibition zone diameter mm (% inhibition): 6-10 (27-45%); 10-14 (45-64%); 14-18 (64-82%); 18-22 (82-100%).).

4. Conclusion

Binuclear Pd(II) and Pt(IV) complexes of tridentate Schiff base ligands were prepared and fully characterized. The antibacterial study reveals that the complexes are quite efficient towards some bacteria even more than the standards in many cases.

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