Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 99 (2012) 211–217

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Supramolecular and structural modification on conformational by mixed ligand

A.Z. El-Sonbati *, M.A. Diab, A.A. El-Bindary, M.K. Abd El-Kader

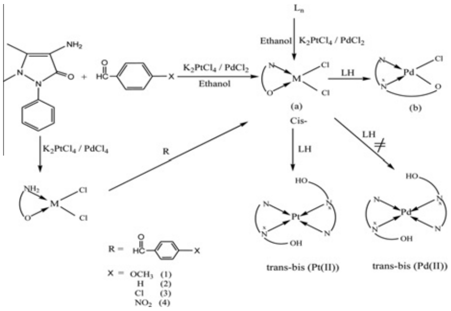
Chemistry Department, Faculty of Science, Damietta University, Damietta, Egypt

HIGHLIGHTS

- On the basis of these studies a square planar geometry has been proposed.
- The infrared data indicate the bidentate nature of ligands in all complexes.
- Molar conductance measurements indicated the complexes to be electrolytes.
- Various ligand and nephelouxetic parameter have been calculated for the complexes.
- The thermal decomposition for complexes was studied.

GRAPHICAL ABSTRACT

The formation of [Pd(L_n)(L)Cl] shows that upon the addition of [Pd(L_n)Cl_2] to a solution of LH, the ligand rearranges itself into the formation of an imine appended with Pd(II) and 4-derivatives benzaldehyde-4-aminoantipyrine (L_n).



ARTICLE INFO

Article history:
Received 23 July 2012
Received in revised form 30 August 2012
Accepted 9 September 2012
Available online 21 September 2012

Keywords:
Pt(II)/Pd(II) supramolecular structure of Schiff base
Spectral studies

ABSTRACT

A novel series of platinum(II) and palladium(II) complexes have been synthesized by template condensation of 4-methoxybenzaldehyde, benzaldehyde, 4-chlorobenzaldehyde and 4-nitrobenzaldehyde, with appropriate 4-aminoantipyrine (4-AAP) in the presence of K_2PtCl_4/$PdCl_2$ to form complexes of the type [M(L_n)Cl_2](where M = Pt(II) or Pd(II)). The corresponding Schiff base complexes mixed ligand were prepared by condensation of [M(L_n)Cl_2] with ethanolamine (LH). The complexes have been characterized with the help of elemental analysis, IR, ^{1}H and ^{13}C NMR, electronic spectra, conductance measurements, magnetic susceptibilities and thermal analysis. On the basis of these studies, it is clear that ligands coordinated to metal atom in a mononuclear (NO) in (**1**–**6**), Schiff base complexes (NN*) in (**7**–**9**) and monobasic tridentate Schiff base complexes (NN*O) in (**10**–**12**). Thus, suitable square planar geometry for tetradentated state has been suggested for the metal complexes. Various ligand and nephelouxetic parameter have been calculated for the complexes. The thermal decomposition for complexes was studied.

Introduction

Interest in coordination chemistry is increasing continuously with the preparation of organic ligands containing a variety of donor groups and it is multiplied manifold when the ligands have biological importance [1]. The number and diversity of nitrogen and oxygen chelating agents used to prepare new coordination and organometallic compounds has increased rapidly during the past few years [2–4]. The field of pyrolozone chemistry of metals is developing very rapidly because of its importance in the area of coordination chemistry [5]. Template condensation is one of the most highlighted methods. Metal template condensation often provides selective route towards the products that are not obtainable in absence of metal ion [6]. The preparation of Schiff bases containing >C=O and >C=N groups with potential ligating ability has drawn a lot of attention because of their use as chelating agents, analytical reagents, metal indicators in complexometric

---

* Corresponding author. Tel.: +20 1060081581; fax: +20 752403867.
E-mail address: elsonbatisch@yahoo.com (A.Z. El-Sonbati).

1386-1425/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.saa.2012.09.016

titrations and calorimetric reagents, in addition to biochemical research [7]. The behavior of the >C=N bond is strongly dependent on the structure of the amine moiety, which in turn controls the efficiency of the conjugation and may incorporate structural elements able to modulate the steric crowding around the coordination [8].

Cisplatin, cis-[$PtCl_2(NH_3)_2$], is one of the most effective chemotherapeutic agents currently used for the treatment of ovarian, bladder, and testicular cancer [9,10]. The drug has to be administered intravenously, however, and has dose-limiting side effects such as severe renal toxicity, neurotoxicity, and emesis, arising, in part, from the low solubility of cis-platin in water. These problems, along with the observation that cancer cells treated with cis-platin acquire resistance to the drug, have provided an impetus for research focused on the development of a more effective platinum drug that can be administered orally and with reduced side effects.

Our interest in this area is focused for a considerable time on the investigation of coordination chemistry of transition metal with using pyrazolone based ligand. To gain information about the structure and stereochemistry of such type of complexes. Therefore, in continuation of our earlier work on structural characterization of mixed ligand transition metal complexes containing rhodanine ligand [11–15], here we report the synthesis and characterization of M(II) complexes and Schiff base complexes derived from the condensation of 4-aminoantipyrine (4-AAP) with 4-derivatives benzaldehyde (L_n). The complexes prepared were characterized particularly by elemental analysis, conductance, magnetic measurements and spectral studies (IR, UV–vis and ^{1}H NMR). Thermal stabilities of the complexes have also been discussed.

In view of these facts and prosecute the research programs in the field of template coordination chemistry, we report here the synthesize cis-dichloro(pyrazolone derivatives) M(II) complexes and Schiff bases complexes (Scheme 1).

Experimental

Materials

4-Aminoantipyrine, $PdCl_2$, K_2PtCl_4 and various aldehydes were purchased from Aldrich, and the other chemicals were of analytical grade quality.

Preparation of ligands (L_n)

Ethanolic solutions of 4-aminoantipyrine (0.1 mol) and 4-derivatives benzaldehyde (0.1 mol) were refluxed together for 4 h over a steam bath. The excess solvent was removed by evaporation and the concentrated solution was cooled in an ice bath with stirring. The Schiff base (L_n) which separated out as a colored powder and then recrystallized from ethanol. The purity of ligands was checked by TLC. Our synthetic route of Schiff base ligands is shown in Fig. 1. The color, yield %, M.P. °C and analytical data given in Table 1.

Preparation of Pt(II)/Pd(II) salt, complexes

The complexes were prepared by the template condensation of 4-aminoantipyrine with 4-methoxybenzaldehyde, benzaldehyde, 4-chlorobenzaldehyde and 4-nitrobenzaldehyde in the presence of K_2PtCl_4 and/or $PdCl_2$.

*Preparation of cis-dichloro(4-derivatives benzaldehyde pyrazolone) platinum(II) (**1–3**)/palladium(II) (**4–6**) (Scheme 1a)*

A weight amount of methanolic solution of 4-derivatives benzaldehyde (10 mmol) 50 mL was mixed with the methanolic solution of 4-aminoantipyrine (10 mmol) in the presence of $K_2PtCl_4/PdCl_2$ (10 mmol) in 1:1:1 molar ratio. After addition of all the reagents, the contents were stirring for 6–7 h. The reaction mixture was concentrated to half of its volume by removing the solvent and kept in desiccators at room temperature. The complexes obtained as solids, were washed with methanol and dried under vacuo.

*Preparation of cis-dichloro(4-derivatives benzaldehyde pyrazolone) platinum(II) (**1–3**)/palladium(II) (**4–6**) (Scheme 1a)*

The metal complexes were prepared by the addition of hot solution of the appropriate metal chloride ($PdCl_2$, K_2PtCl_4) (10 mmol) in ethanol (25 mL) to the hot solution of L_n (10 mmol) in the same solvent (25 mL). The resulting mixture was stirred under reflux for 1 h whereupon the complex precipitated. They were collected by filtration, washed thoroughly with ethanol and dried in vacuum.

*Preparation of Schiff base complexes (**1–6**)*

The Schiff base complexes were prepared by 1:1 interaction of complexes (**1–6**) (Scheme 1a).

To the complexes of Pd(II)/Pt(II) (Scheme 1d) (1 mmol) 25 mL methanol was added 4-derivatives benzaldehyde (R) (1 mmol). Solution was allowed to stand for 10 min at room temperature and then refluxed for 6–7 h on a water bath. The solution was reduced to 1/3 volume and kept in a desiccator as solids, were washed with methanol and dried under vacuo.

*Trans-Pt(II) Schiff base complexes (**7–9**) (Scheme 1b)*

A solution of [$Pt(L_n)Cl_2$] (**1**–**3**) (1 mmol) in DMF (10 mL) was added to a solution of LH (ethanolamine) (1 mmol) in DMF/ethanol (v/v%). The resulting mixture was stirred whilst heating on a water bath for ~5 h. The solid obtained after the addition of an aqueous solution of ethanol was filtered, washed with distilled water and followed by diethyl ether and dried in vacuo as [$Pt(L_n)_2(LH)_2$]Cl_2 (Scheme 1b).

*Preparation of Pd(II) Schiff base complexes (**10–12**) (Scheme 1c)*

Pd(II) Schiff base complexes (**10–12**) have also been prepared using a method similar to that adopted for complexes (**7–9**) by the addition of a solution of [$Pd(L_n)Cl_2$] (**4–6**) (1 mmol) in DMF (10 mL) to a solution of LH (1 mmol) in DMF. The product, after heating on a sand bath for ~4–5 h with stirring, was isolated after the addition of H_2O to the reaction mixture. It was then filtered and washed with distilled water and methanol followed by diethyl ether. The product was then dried in vacuo as [$Pd(L_n)(L)Cl$] (Scheme 1c).

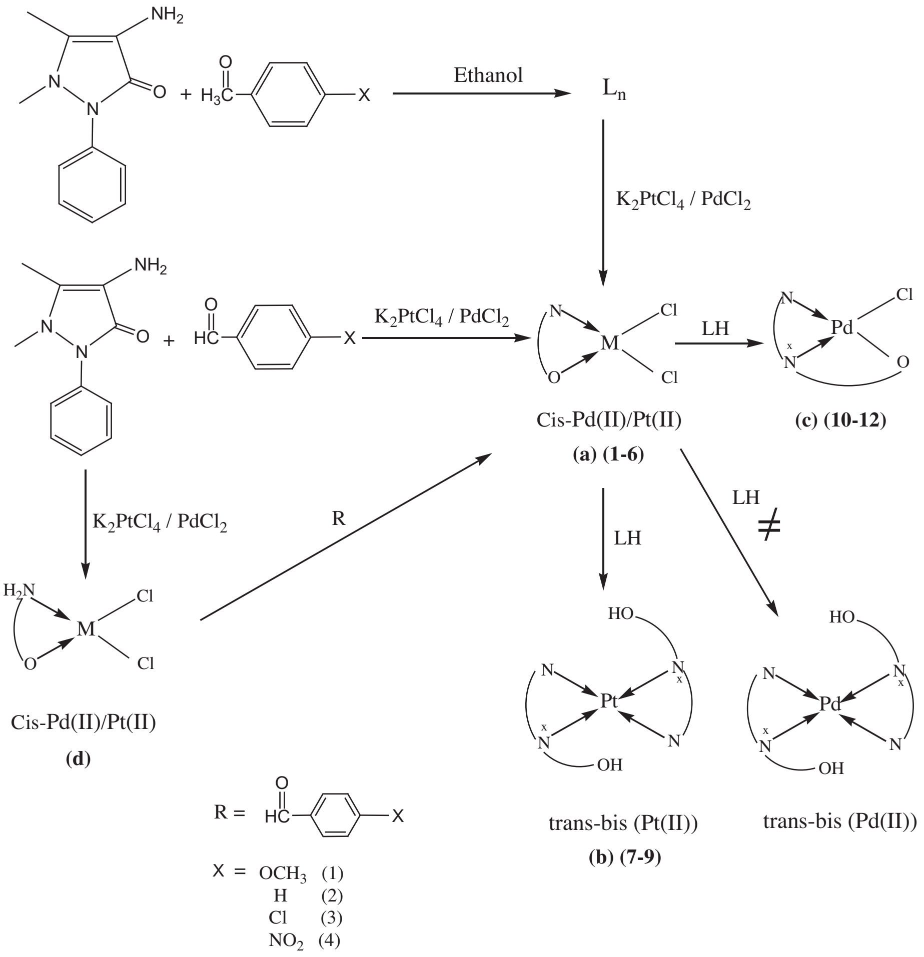
This indicates that the Pd(II) complex did not follow the same reaction pattern as is followed by the Pt(II) complex.

All the complexes were recrystallization from 1:1 molar ratio solution of methanol and benzene. The purity of the complexes was checked by thin layer chromatography (TLC). The yield of complexes = ~55–75%.

The template synthesis of the complexes may be represented in Scheme 1.

Analytical and physical measurements

Elemental microanalyses of the separated ligands and solid chelates for C, H, and N were performed in the Microanalytical Center, Cairo University, Egypt. The analyses were repeated twice to check the accuracy of the analyzed data. The ^{1}H NMR spectrum was obtained with a JEOL FX90 Fourier transform spectrometer with DMSO-d_6 as the solvent and TMS as an internal reference. Infrared spectra were recorded as KBr pellets using a Pye Unicam SP 2000 spectrophotometer. Ultraviolet–visible (UV–vis) spectra of the compounds were recorded in solution using a Unicom SP 8800



Scheme 1. The structures of the complexes.

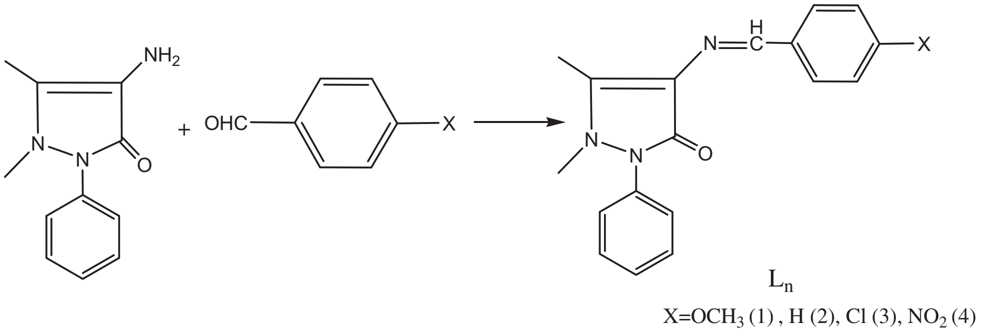


Fig. 1. Synthetic route of Schiff base ligands.

spectrophotometer. The magnetic moment of the prepared solid complexes was determined at room temperature using the Gouy's method. Mercury(II) (tetrathiocyanato)cobalt(II), $[Hg\{Co(SCN)_4\}]$, was used for the calibration of the Gouy tubes. Diamagnetic corrections were calculated from the values given by Selwood [16] and Pascal's constants. Magnetic moments were calculated using the equation, $\mu_{\text{eff.}} = 2.84\ [T_{\chi\mathrm{M}^{\text{coor.}}}]^{1/2}$. TG measurements were made using a Du Pont 950 thermobalance. Ten milligram samples were heated at a rate of 10 °C/min in a dynamic nitrogen atmosphere (70 mL/min); the sample holder was boat-shaped, 10 × 5 × 2.5 mm deep; the temperature measuring thermocouple was placed within 1 mm of the holder. The halogen content was determined by combustion of the solid complex (30 mg) in an oxygen flask in the presence of a $KOH—H_2O_2$ mixture. The halide content was then determined by titration with a standard $Hg(NO_3)_2$ solution using diphenylcarbazone indicator. The conductance measurement was achieved using Sargent Welch scientific Co., Skokie, IL, USA.

Results and discussion

The ligand

In the present investigations, the ligands (L_n) were prepared by stirring an appropriate amount of reactive 4-derivatives benzaldehyde with the corresponding 4-aminoantipyrine in ethanol. Schiff

Table 1
Elemental analysis (C, H, N)[a], color, yield (%) and melting point (°C) of derivatives (L_n).

Compound[a]	Color	Yield%	M.P. °C	Calc. (exp.)%		
				C	H	N
L_1	Yellow	46.7	173	71.03 (71.17)	5.92 (5.99)	13.08 (13.37)
L_2	Pale yellow	52.2	195	74.23 (74.42)	5.84 (5.93)	14.43 (14.59)
L_3	Yellow	56.5	237	66.36 (66.45)	4.92 (5.13)	12.90 (13.21)
L_4	Pale yellow	67	261	64.29 (64.37)	4.76 (4.88)	16.67 (16.88)

[a] The excellent agreement between calculated and experimental data suggests the assignment suggested in the present work.

base ligands (L_n) were light yellow in color and it is soluble in common organic solvents. The Schiff bases formed were characterized with respect to its composition by elemental and spectral analysis. The physical and analytical data given in Table 1, ^{1}H NMR (Table 2) and IR spectra (Table 3). Elemental analysis data of the ligand (L_n) show good agreement with theoretical values.

For the four compounds (L_n) the yield %/M.P. °C of these compounds were found to be sensitive to the nature of the substituents, X, on the ligand. In case of L_4 with X = electron withdrawing NO_2, higher values (67/261) of the yield %/M.P. °C respectively are observed, whereas lowers (46.7/173) is observed for L_1 (X = OCH_3), reflects the electron donating nature of the substituent (Fig. 2).

Metal complexes and characterization

The complexes are stable in air and atmosphere. All the complexes are colored, stable at room temperature, high melting points, soluble in DMSO and DMF, but they are insoluble in some common organic solvents. Elemental analysis results for the metal complexes (Table 4) were in good agreement with calculated values showing that the complexes (**1–6**), (**7–9**) and (**10–12**) had the metal/ligand ratio of 1:1 $[M(L_n)Cl_2]$, 1:2:2 $[Pt(L_n)_2(LH)_2]Cl_2$ and 1:1:1 $[Pd(L_n)(L)Cl]$ respectively; where L_n = 4-derivatives benzaldehyde-4-aminoantipyrine; M = Pd(II) and/or Pt(II). The molar conductivity of metal complexes in DMF solution (10^{-3} M) at room temperature was measured to establish the charge of the metal complexes. The molar conductivity of (**1–6** and **10–12**) complexes indicates that they are non-electrolytes but complexes (**7–9**) indicating that they are 1:2 electrolyte type [14,15,17].

Spectral studies

^{1}H NMR and ^{13}C NMR

The absence of protons signals of free NH_2 groups in ^{1}H NMR indicates that condensation of NH_2 (of 4-aminoantipyrine) with 4-derivatives benzaldehyde has taken place.

Table 2
^{1}H NMR spectral data (δ ppm) of 4-AAP and Schiff bases (L_n).

Assignment	Compound				
	L_1	L_2	L_3	L_4	(4-AAP)
C—CH_3	2.55	2.60	2.64	2.68	2.15
N—CH_3	3.09	3.15	3.22	3.27	2.84
NH_2	–	–	–	–	2.99
ArH	6.80–7.86	7.22–7.95	7.33–8.22	7.42–8.34	7.15–7.50
CH=N	9.71	9.48	9.40	9.36	–
OCH_3	3.27	–	–	–	–

Table 3
Some selected bands of diagnostic importance from the IR spectra (cm^{-1}) of 4-AAP and ligands (L_n).

4-AAP	L_1	L_2	L_3	L_4	Assignment
3426	–	–	–	–	$\upsilon(NH_2)_{as}$
3315	–	–	–	–	$\upsilon(NH_2)s$
3175	3085	3085	3086	3088	$\upsilon(CH)_{as}$(Ar)
3087	3036	3035	3037	3038	$\upsilon(CH)_s$(Ar)
2985	2935	2930	2928	2928	$\upsilon(CH)_{as}(CH_3)$
2918	2920	2022	2924	2925	$\upsilon(CH)_s(CH_3)$
1640	1644	1648	1650	1653	C=O
–	1590	1594	1596	1598	C=N
1405	1416	1418	1420	1423	N—CH_3
1310	1360	1370	1375	1380	C—N
1200	1179	1181	1183	1185	$\delta(CH_3)$
–	1017	1020	1022	1025	γ(C=N)
730	678	680	685	687	γ(CH)ring

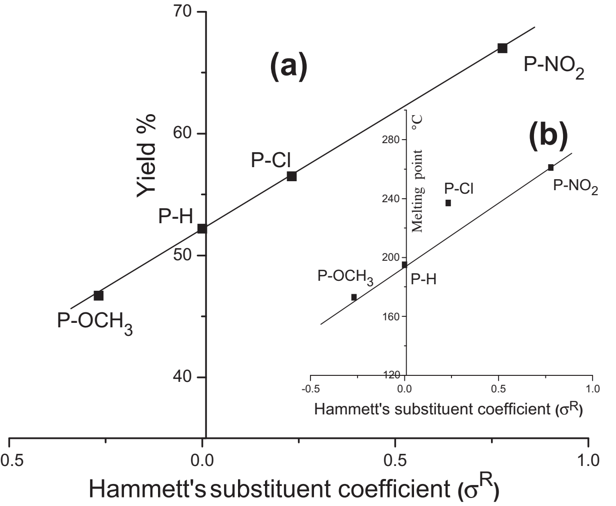


Fig. 2. The relation between Hammett's substitution coefficient (σ^R) *vs.* (a) Yield% and (b) melting point °C of ligand (L_n).

Table 4
Analytical data[a] of complexes[b].

Compound[c]	Elemental analysis calc. (exp.)%			
	C	H	N	Cl
$[Pt(L_1)Cl_2]$ (1)	38.84(38.91)	3.24(3.21)	7.15(7.43)	12.09(1223)
$[Pt(L_2)Cl_2]$ (2)	38.77(38.90)	3.05(3.15)	7.54(7.77)	12.75(12.88)
$[Pt(L_3)Cl_2]$ (3)	36.51(36.58)	2.71(2.82)	7.10(7.42)	18.00(18.33)
$[Pd(L_1)Cl_2]$ (4)	45.74(45.82)	3.21(3.32)	8.43(8.54)	14.24(14.44)
$[Pd(L_2)Cl_2]$ (5)	46.11(46.24)	3.63(3.73)	8.97(9.21)	15.16(15.35)
$[Pd(L_3)Cl_2]$ (6)	42.95(43.12)	3.18(3.28)	8.35(8.47)	21.18(21.42)
$[Pt(L_1)_2(LH)_2]Cl_2$ (7)	50.70(50.78)	4.83(4.94)	11.27(11.45)	7.14(7.44)
$[Pt(L_2)_2(LH)_2]Cl_2$ (8)	51.39(51.47)	4.71(4.89)	11.99(12.22)	7.60(7.78)
$[Pt(L_3)_2(LH)_2]Cl_2$ (9)	44.69(44.68)	3.91(3.99)	10.43(10.54)	19.83(19.89)
$[Pd(L_1)(L)Cl]$ (10)	49.91(50.05)	4.56(4.77)	11.09(11.38)	7.03(7.34)
$[Pd(L_2)(L)Cl]$ (11)	50.54(50.66)	4.42(4.54)	11.79(11.94)	7.48(7.67)
$[Pd(L_3)(L)Cl]$ (12)	47.11(47.23)	3.93(4.03)	10.99(11.23)	13.94(13.87)

[a] Microanalytical data as well as metal estimations are in good agreement with the stoichiometry of the proposed complexes.

[b] The excellent agreement between calculated and experimental data supports the assignment suggested in the present work.

[c] HL are the ligand as given in Scheme 1 and L is the anion; air-stable; no-hygroscopic; insoluble in water; soluble in coordinating solvents such as DMF and DMSO.

The ^{1}H NMR spectra of the antipyrine and Schiff bases (Table 2) were carried out at room temperature in DMSO-d_6. The spectra display two sharp signals at 2.33–2.48 and 3.09–3.16 ppm with an integration equivalent to three hydrogens corresponding to the N—CH_3 and C—CH_3 groups. The aromatic rings give a group of multi signals at 6.80–7.86 ppm. The CH=N hydrogen for L_n resonates at 9.36–9.71 ppm as a sharp singlet. The Pd(II) complexes shows a slight downfield shift of 0.3–0.6 ppm in the resonance peaks corresponding to the phenyl ring and the azomethine proton, which may be attributed to the coordination of the ligand to the Pt(II)/Pd(II) ion. ^{13}C NMR of L_{1-4} exhibited signals at 188–188.8 and 161–161.9 ppm corresponding to the carbon of C=O and C=N groups. Methyl groups were observed between 18.4 and 19.8 ppm. Also, the spectra showed peaks at 19–131 ppm corresponding to carbons of the phenyl ring. The downfield shift observed indicates the coordination of oxygen and nitrogen to M(II) ion.

The signal of O—H protons (in complexes **7–9**) at ~1.62 ppm completely disappears in the spectra of Pd(II) complexes (**10–12**) (Scheme 1c) indicating the involvement of the alcoholic oxygens in the chelation through displacement of the OH proton.

In order to get further information about the ligand at its Pd(II) complexes (**10–12**), the ^{13}C NMR spectra were investigated. In the Pd(II) complexes (**10–12**), exhibit signals at ~191 ppm (C=N*). The aliphatic carbon signals of ethyl groups showed peaks at ~55.99 and 55.87 ppm. These observations are consequence of coordination of ligand *via* (C=N), (C=N*) and alcoholic oxygen atoms.

IR spectra

Selected bands of diagnostic importance are discussed in this part (Table 5).

The IR spectra provide valuable information regarding the coordinating sites of ligands. The IR spectra of the complexes were compared with that of the free ligands to determine the changes that might have taken place during the complexation. A comparative study of the spectra of ligand and its metal complexes reveals that certain peaks are common and therefore, only important peaks, which have been either shifted or newly appeared, are discussed.

In cis-[M(L_n)Cl_2] (**1–6**) (Scheme 1a), spectra of free Schiff base ligands (L_n) showed a band of the —C=N— group in the region of 1590–1598 cm^{-1} which was shifted to lower frequencies in the spectra of all complexes (1585–1565 cm^{-1}) indicating the involvement of —C=N— nitrogen in coordination to the metal ion [14,18]. Coordination of the Schiff bases to the metal through the nitrogen atom was expected to reduce the electron density in the azomethine link and to lower the υ(C=N) vibration. All complexes showed that bands in the 1090–1100 cm^{-1} and 700–745 cm^{-1} regions which could be assigned to phenyl ring vibrations. All compounds display an intense band at 1645–1615 cm^{-1} corresponding to υ(C=O) of the antipyrine ring. The metal complexes showed a strong absorption at 1660–1690 cm^{-1} υ(C=O) (Δ = 10–20 cm^{-1}). Accordingly, all ligands act as bidentate chelating agents bonded to the platinum(II)/palladium(II) ion *via* the azomethine nitrogen and the pyrazolone ring oxygen atoms in all isolated complexes. The appearance of υ(C—H) and δ(C—H) of the methylene group at lower frequencies in the complexes compared to their positions in the free ligands could also be taken as evidence for the coordinating nature of the azomethine nitrogen.

Table 5
Important IR vibration frequencies (cm^{-1}) of complexes.

Complex[a]	υ(C=O)	υ(C=N)	υ(OH)	υ(C—H)	υ(C—H)
1	1616	1579	–	1427, 1408	1251
2	1612	1587	–	1426, 1409	1253
3	1608	1583	–	1422, 1406	1255
4	1617	1553	–	1440, 1410	1219
5	1608	1559	–	1442, 1428	1214
6	1606	1563	–	1441, 1417	1214
7	–	1575, 1645	3515	1425, 1405	1248
8	–	1585, 1658	3516	1424, 1406	1250
9	–	1579, 1665	3518	1420, 1404	1253
10	–	1550, 1660	–	1436, 1408	1217
11	–	1555, 1678	–	1440, 1425	1212
12	–	1580, 1688	–	1438, 1415	1213

[a] Numbers as given in Table 4.

In [Pt(L_1)$_2$(LH)$_2$]Cl_2 (Scheme 1b) (**7–9**), mixed ligand (L_n and LH) behaves as a neutral bidentate coordinating *via* the υ(HC=N) and new υ(C=N*). This is confirmed by: (i) the υ(HC=N) of Pt(II) mononuclear complexes (**1–3**), (ii) the disappearance of υ(C=O) with simultaneous appearance of new bands at ~1648–1668 cm^{-1} assigned to υ(C=N*), resulting from condensation between ethanolamine and carbonyl oxygen atom of pyrazolone and (iii) the sharp band at ~3447 cm^{-1} show in ethanolamine complexes of Pt(II) Schiff bases complexes correspond to free —OH of ethanolamine. This observation is further supported by its ^{1}H NMR spectra, which shows a peak at ~δ 1.62 ppm assigned to OH protons.

In [Pd(L_1)(L)Cl] (Structure 1c) (**10–12**), this mode of complexation is confirmed by the ligands (L_n and LH) behaves as NN*O mononegative tridentate. The coordination takes place through (C—O) and C=N* groups. The IR spectra of all complexes (**10–12**) shows υ(C=N*) peak at 1648–1668 cm^{-1} and the absence of a υ(C=O) peak at ~1660–1690 cm^{-1} is indicative of Schiff's base complexes condensation. This phenomenon appears to be due to the coordination of the azomethine nitrogen (C=N*) to the metal ion [14,15,18]. Also, a broad υ(OH) band of ethanolamine at ~3435 cm^{-1} disappears on complexation. This fact is further supported by the increase in C—O stretching frequency at ~1288–1280 cm^{-1} in the complexes which indicates the other coordination of ligand to the Pd(II) ions through the charged alcoholic oxygens. Thus the IR spectra of complexes (**10–12**) indicates that the Schiff base ligands (L_n + L) (Scheme 1c) in all the complexes under investigation is tridentate and the binding sites are two azomethine nitrogens (—C=N— and —C=N*—) and oxygen of alcoholic OH atom. The square planar geometry of the palladium(II) complex is completed by chlorine atom (Scheme 1c).

The significant change in the complexing is the decrease in υ(C=N)$_{\mathrm{Schiff}}$. This shift in the spectra of the complexes suggests coordination through both nitrogens groups [19]. Recent studies [14,15,18] have shown that the s character of the nitrogen lone pair in the C=N bond increases upon coordination; this change in hybridization produces the shorter C=N bond length and greater C=N stretching force constant, relative to the free neutral Schiff bases. The variable magnitude of the shift reflects the variable Lewis acidity of the metal ions in the complexes under study.

These observations suggested that the ligand coordinate to the Pd(II) ions through the charged alcoholic oxygens and the two nitrogen atom of azomethin groups of bis-N_2O compartments in its complex. Moreover, the spectra of complexes exhibit band due to (Pd—Cl).

Thus, the formation of [Pd(L_n)(L)Cl] (Scheme 1c) (**10–12**) shows that upon the addition of [Pd(L_n)Cl_2] (Scheme 1a) (**1–6**) to a solution of LH, the ligand rearranges itself into the formation of an imine appended with Pd(II) and 4-derivatives benzaldehyde-4-aminoantipyrine (L_n) as depicted in Scheme 1 .

As mentioned above, upon the complexation of [Pt(L_n)Cl_2] (Scheme 1a) (**1–6**) with LH, a (2 + 2) condensation between the two components occurred and it resulted in the formation of a metallopyrazolone.

Although the reason for this difference in reactivity of Pd(II) and Pt(II) with the Schiff base cannot be understood accurately, it may be considered in view of the stronger Pt—N=C bond as compared to the Pd—N═C bond [20]. Theoretical calculations also support that the relativistic bond stabilization is stronger for third row transition metal complexes (Pt) than for second-row transition metal complexes (Pd) [21].

All the complexes show bands at ~1090–1100 and 700–750 cm^{-1}, assigned to phenyl ring vibrations. In the far spectra, various new bands observed are characteristic of υ(M—N) or υ(M—O) frequencies. The new bands in palladium(II) complexes at 435–460 cm^{-1} may be assigned to υ(Pd—N) while those observed at 410–465 cm^{-1} may be assigned to υ(Pd—O) vibration [14,22]. Similar bands in platinum(II) complexes observed at 345–415 cm^{-1} are well within the assignable to υ(Pt—N) mode, while those observed at 385–405 cm^{-1} may be assigned to υ(Pt—O) vibration [15,23]. These bands are consistent with the frequencies observed for square planar complexes of these metal ions.

Therefore, it is clear from these results that the data obtained from the elemental analyses, IR, and ^{1}H NMR spectral measurements are in agreement with each other.

Geometry of the Pd^{2+}—Pt^{2+} complexes

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The electronic spectral measurements are used for assigning the stereochemistries of metal ions in the complexes based on the positions and number of d–d transition peaks.

With the exception of a small number of palladium derivatives, few six-coordinate complexes of these species are known. The majority of complexes are four-coordinate and square planar. The spectra of these complexes exhibit bands characteristic of square planar palladium(II) complexes [11]. In the present studies all the complexes are found to be diamagnetic as expected for square planar d^8 complexes [24]. The geometries are supported by their electronic spectra.

Electronic spectra of ligands and its complexes were recorded in DMF solution, the wide range bands were observed due to either the π–π^* and $n \to \pi^*$ of (C═N or C═O) chromophore or charge-transfer transition arising from π electron interactions between the metal and ligand, which involved either a metal-to-ligand or ligand-to-metal electron transfer [25]. Despite the fact that the position of the CT band is influenced by the substituent on the phenyl ring being shifted to longer wavelength with the increasing donor character of the substituent. The electronic spectra of the free ligand in DMF showed strong absorption bands in the ultraviolet region (23,530–37,460 cm^{-1}), that could be attributed to the $\pi \to \pi^*$ and $n \to \pi*$ transitions in the benzene ring or (—C═N or C═O) groups for free ligand. The absorption bands between 37,460 and 23,530 cm^{-1} in free ligands changed a bit in intensity

Table 6
Electronic absorption spectra (cm^{-1}) and ligand field parameters of complexes.

Complex[a]	Bands (cm^{-1})	Assignments	ν_2/ν_1	Δ_1	Δ_2	Δ_3
1	20,615 23,920 27,320	$d_{xy} \to d_{x2-y2}$ $d_{z2} \to d_{x2-y2}$ d_{xz}, $d_{yz} \to d_{x2-y2}$	1.160	22,715	3300	4305
2	20,150 25,250 35,150	-do-	1.251	22,250	6300	9600
3	21,133 27,039 33,187	-do-	1.28	23,233	7106	5848
4	30,050 32,240 39,550	-do-	1.073	32,150	3390	6960
5	30,150 32,180 39,500	-do-	1.067	32,250	3230	7020
6	30,250 32,280 39,600	-do-	1.067	32,350	3230	7020
7	21,800 24,900 31,000	-do-	1.142	23,900	4300	5800
8	22,900 24,800 30,100	-do-	1.083	25,000	3100	5000
9	23,000 25,000 29,100	-do-	1.09	25,100	3100	3900
10	20,100 23,500 28,500	-do-	1.169	22,200	4600	4700
11	20,900 22,100 25,650	-do-	1.069	23,000	2400	3250
12	21,050 22,300 25,400	-do-	1.059	23,150	2450	2800

[a] Numbers as given in Table 4.

and remained slightly changed for metal complexes. The absorption shift and intensity change in the spectra of the metal complexes most likely originated from the metallation, increased the conjugation and delocalization of the whole electronic system and resulted in the energy change of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the conjugated chromophore [26].

The electronic spectra of patinum(II) and palladium(II) complexes are indicative of square planar geometry (Structure 1). The absorption bands for the platinum(II) and palladium(II) complexes may be assigned to the three d–d forbidden transition expected from the three lower lying d levels to empty d_{x2-y2} orbitals. The ground state is $^1A_{1g}$ and the excited states corresponding to the above transitions are $^1A_{2g}$, $^1B_{1g}$ and ^1E_g in order of increasing energy. By assuming a value of $F_2 = 10F_4 = 600\ \text{cm}^{-1}$ for a Slater–Condon interactions repulsion parameters and subsequently the equations suggested by Cray and Ballhausen [27], it is possible to calculate the single electron parameter Δ_1, Δ_2 and Δ_3 (Table 6). The υ_2/υ_1 value lies in the 1.059–1.251 range, comparable with the values reported earlier for square planar complexes [14,15]. The values of Δ_1 for Pt(II) complexes are much higher than those observed for palladium(II) complexes but are in accordance with those required for platinum(II) square planar complexes. The values of Δ_1 lie in between those observed for cyanide (~30,000 cm^{-1}) and chloride complexes (~19,000 cm^{-1}) and are consistent with intermediate ligand field strength [28,29]. The crystal field stabilization energies for Pd(II) and Pt(II) complexes obtained from the relation: $E(\upsilon) = \Delta_1 - 35F_4^7$ [$F = 60\ \text{cm}^{-1}$ for both Pd(II) and Pt(II)]. For the Pd(II) complexes the Δ_1 values are close in value to those of $PdNOCl_2$ and PdNNOCl chromophores [30]. In the case of Pt(II) the observed values are somewhat lower than those of the $PtNOCl_2$ chromophores [27], probably due to a stronger interaction of the Cl atoms than N atoms with respect to the metal ion.

Thermal gravimetric analysis

Thermal gravimetric analysis (TGA) was used as a probe to prove the presence of associated water or solvent molecules in the coordination sphere or in the crystal lattice [14,15]. The thermal gravimetric analysis was carried out for two of the complexes $[Pt(L_1)Cl_2]$ (**1**), $[Pt(L_1)_2(LH)_2]Cl_2$ (**7**) and $[Pd(L_1)(L)Cl]$ (**10**) in the range of about 50–800 °C and it showed that the thermal decomposition of the complexes takes place in several steps. The thermal analysis data of the platinum(II) complexes indicates that they are stable up to 200 °C owing to their anhydrous nature. DTA curves show no endothermic peaks up to 200 °C confirming the absence of lattice or coordinated water molecule in the complexes [31,32]. The thermogram of complex (**7**), shows three stages of decomposition in the range 110–840 °C. The first step of decompositions within the temperature ~125 °C corresponds to the loss of 2HCl. The subsequent steps (165–840 °C) correspond to melting and partial decomposition of the ligand and the final stage is due to the decomposition of the ligand molecule, leaving metal oxide. The two complexes (**1** and **10**) show a weight loss within temperature range 225–320 °C, corresponding to the loss of coordinated chloride ions [14,15]. The decomposition of the organic ligand takes place within temperature range 245–845 °C [33]. The thermal decomposition process ended with the formation of metal oxide from complexes.

Conclusions

Based on the above observations of the elemental analysis, molar conductivity, UV–vis, magnetic, IR, ^1H NMR spectral data it is possible to determine the type of coordination of the ligands in their metal complexes. The spectral data show that all the Schiff bases exist as neutral bidentate in mononuclear (NO)/Schiff base complexes (NN*) and monobasic tridentate (NN*O) in Schiff bases complexes. The analytical data show the presence of one metal ion per one/two ligand molecules and suggest a mononuclear structure for the complexes. The correlation of the experimental data allows assigning a square planar stereochemistry to all the above synthesized complexes as shown in Scheme 1. The present study shows the construction of a Pt(II)-based metallopyrazolone on the skeleton of a simple tridentate Schiff base which provides an electron rich cavity. The space provided by the cavity is found to be suitable for comparatively stronger binding of an electron acceptor molecule. This study also allows the difference in the reactivity of Pd(II) and Pt(II) complexes with tridentate Schiff base to be understood.

References

[1] A.K. Kulkarni, P.C. Avaji, G.B. Bagihalli, P.S. Badami, S.A. Patil, J. Coord. Chem. 62 (2009) 481.
[2] H.L. Singh, A.K. Varshney, Bioinorg. Chem. Appl. 2006 (2006) 23245.
[3] T.S. Basu Baul, Appl. Organomet. Chem. 22 (2008) 195.
[4] M.-X. Li, J. Zhouy, H. Zhaoz, C.-L. Cheny, J.-P. Wangy, J. Coord. Chem. 62 (2009) 1423.
[5] S. Ihan, H. Temel, Transit. Met. Chem. 32 (2007) 1012.
[6] S.G. Kang, J. Song, J.H. Jeong, Inorg. Chim. Acta 357 (2004) 605.
[7] K. Dey, J Sci. Ind. Res. 33 (1974) 76.
[8] J.M. Lassaletta, M. Alcarazo, R. Fernaandez, Chem. Comm. (2004) 298.
[9] E.R. Jamieson, S.J. Lippard, Chem. Rev. 99 (1999) 2467.
[10] J. Reedijk, Chem. Rev. 99 (1999) 2499.
[11] A.Z. El-Sonbati, A.A. El-Bindary, M.A. Diab, Spectrochim. Acta A 59 (2003) 443.
[12] A.Z. El-Sonbati, A.S. Al-Shihri, A.A. El-Bindary, Inorg. Organom. Polym. 14 (2004) 53.
[13] A.Z. El-Sonbati, A.S. Al-Shihri, A.A. El-Bindary, Inorg. Organom. Polym. 13 (2003) 99.
[14] A.Z. El-Sonbati, M.A. Diab, A.A. El-Bindary, Stoichiometry and Research-The Importance of Quantity in Biomedicine, Pub. by In Tech, Janeza Trdine 9, 51000 Rijeka, Croatia, 2012, pp. 147–194 (P. Cm ISBN 978-953-51-0198-7).
[15] A.Z. El-Sonbati, M.A. Diab, Physico-Chemical Studies on the Complexes, LA LAMBERT Academic Publishing GmbH, Leipzig & Co, KG, Germany, 2010, ISBN 978-3-8433-7229-9.
[16] P.W. Selwood, Magnetic Chemistry, Interscience Pub. Inc., New York, 1956.
[17] J. Cannadine, A. Hector, A.F. Hill, Organometallic 11 (1992) 2323.
[18] A.Z. El-Sonbati, R.M. Issa, A.M. Abd El-Gawad, Spectrochim. Acta A 68 (2007) 134.
[19] L.S. Gelfand, F.J. Iaconianni, L.L. Pytlewski, A.N. Speca, C.M. Mikulski, N.M. Karayannis, J. Inorg. Nucl. Chem. 42 (1980) 377.
[20] P.J. Stang, D.H. Cao, S. Saito, A.M. Arif, J. Am. Chem. Soc. 117 (1995) 6273.
[21] D.V. Deubel, J.K.-c. Lau, Chem. Commun. (2006) 2451.
[22] A.Z. El-Sonbati, A.A.M. Belal, M.A. Diab, R.H. Mohamed, Mol. Str. 99 (2011) 26.
[23] K. Sharma, R.V. Singh, N. Fahmi, Spectrochim. Acta A 75 (2010) 422.
[24] A. Garg, J.P. Tandon, Bull. Chem. Soc. Jpn. 62 (1989) 3760.
[25] M. Odabasoglu, F. Arslan, H. Olmez, O. Buyukgungor, Dyes Pigments 75 (2007) 507.
[26] Z. Chen, Y. Wu, D. Gu, F. Gan, Spectrochim. Acta A 68 (2007) 918.
[27] H.B. Gray, C.J. Ballhausen, J. Am. Chem. Soc. 85 (1963) 260.
[28] B.N. Figgis, Introduction to Ligand Fields, Wiley Eastern, New Delhi, 1976.
[29] A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1968.
[30] A.R. Latham, V.C. Hascall, H.B. Gray, Inorg. Chem. 4 (1965) 688.
[31] A.V. Nikolaev, V.A. Log Vinenkova, L.I. Myachina, Thermal Analysis, Academic Press, New York, 1969.
[32] D. Chatterjee, A. Mitra, B.C. Roy, J. Mol. Catal. A: Chem. 161 (2000) 17.
[33] M.S. Niasari, Polyhedron 28 (2009) 2321.