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Structural and spectral studies of palladium(II) and platinum(II) complexes derived from *N*,*N*,*N*,*N*-tetradentate macrocyclic ligands

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Abstract

Palladium(II) and platinum(II) complexes having the general composition $[M(L)] X_2$ {where M = Pd(II) and Pt(II), L = 3,4,12,13-tetraphenyl-2,5,11,14,19,20-hexaaza tricyclo [13.3.1.1.⁶⁻¹⁰] cosa-1(19), 2,4,6,8,10,(20),11,13,15,17-decaene (L₁); 3,4,13,14-tetraphenyl-2,5,12,15-tetraaza tricyclo [11,0,0,⁶⁻¹¹] cosa-1(16),2,4,7,9,6(11),12,14,17, 19-decaene (L₂); 2,3,8,9-tetraphenyl-1,4,7,10-tetraaza cyclododeca-1,3,7,9-tetraene (L₃) and X = Cl⁻} have been synthesized. The ligands were characterized on the basis of elemental analyses, IR, ¹H NMR and EI mass spectral studies while that of the complexes were characterized on the basis of elemental analyses, molar conductance measurements, magnetic susceptibility measurements, IR, and electronic spectral techniques. All the complexes were found to be diamagnetic. The structures consist of monomeric units in which the Pd(II) and Pt(II) atoms exhibit square planar geometry.

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1. Introduction

The intense interest in synthetic macrocycles and their metal complexes depends on the fact that they mimic naturally occurring macrocyclic molecules in their structure and functional features and on their rich chemical behaviour [1–4]. In addition, the study of metal complexes of macrocyclic ligands appears to be interesting in view of the possibility of obtaining coordinating compound of unusual structure and stability. The formation of macrocyclic complexes depends on the size of the macrocycles, on the nature of its donor atoms and on the complexing behaviour of the anions involved in coordination [5-7]. Macrocyclic ligands are also of theoretical interest since they are capable of furnishing an environment of controlled geometry and ligand field strength [8]. Moreover, macrocyclic Schiff base nitrogen donor ligands have received special attention because of their mixed hard-soft donor character [9,10] and versatile coordination behaviour [11–14].

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Palladium(II) complexes have been found to cleave proteins selectively in high yield [15]. It has been well established that Platinum and Palladium complexes are of biological importance due to their carcinostatic activity and interest in biological chemistry [16]. The carcinostatic action of the drugs is due to their interaction with nuclear DNA [17]. Charlson et al. [18] have reported that cesium *cis*-dichloroserineto palladate(II) induces filament growth in *E. coli*. The complexes of palladium(II) with amino acids like glycine, serine, and glutamine have also been reported [19,20], to be active against certain tumors. Palladium(II) and platinum(II) complexes of some Schiff base ligands derived from S-alkyl esters of dithiocarbazic acid have been found to exhibit marked cytotoxicity against leukaemia [21] and the human ovarian cancer (Caov-3) cell lines [22].

In view of the above applications, in the present paper we report the synthesis and characterization of Pd(II) and Pt(II) complexes with nitrogen donor $[N_4]$ macrocyclic ligands L_1 , L_2 and L_3 (Fig. 1).

2. Experimental

All the chemicals used were of AnalaR grade and procured from Sigma–Aldrich and Fluka. Metal salts were obtained from commercial sources (E. Merck) and used without further

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Fig. 1. Structure of ligands.

purification. All solvents used were purified according to standard procedures.

2.1. Synthesis of macrocyclic ligands

To a hot ethanolic (20 mL) solution of benzil (4.2046 g, 0.02 mol), a hot ethanolic (20 mL) solution of corresponding diamines, i.e. 2,6-diaminopyridine (2.1826 g, 0.02 mol), *o*-phenylenediamine (2.1628 g, 0.02 mol) and ethylene diamine (1.2000 g, 0.02 mol) was added dropwise with constant stirring. This solution was refluxed at 70–75 °C for 8 h in presence of few drops of concentrated hydrochloric acid. On cooling coloured product was precipitated out. It was filtered, washed several times with cold EtOH, and dried under vacuum over P_4O_{10} .

2.2. Synthesis of complexes

Table 1

The complexes were prepared by dissolving corresponding metal salts (0.001 mol) in ethanol and then an ethanolic solution of respective ligand (0.001 mol) was added to this solution in 1:1 molar ratio. The solution was stirred and the mixture was

heated under reflux over 8–11 h at 70–75 $^{\circ}$ C. On cooling up to 4 $^{\circ}$ C a coloured precipitate formed, was collected by filtration. The resulting solid was finally washed with cold EtOH and dried in vacuum.

3. Physical measurements

Elemental analyses of C, H, and N were performed on a Carbo-Erba EA 1106 analyser, the nitrogen contents of the complexes were determined using Kjeldahl's method. Molar conductance was measured on an ELICO (CM 82T) conductivity bridge. Magnetic susceptibility was measured at room temperature on a Gouy balance using CuSO₄·5H₂O as a callibrant. Electron impact mass spectra were recorded on JEOL. JMS, DX-303 mass spectrometer. The ¹H NMR (300 MHz) spectra were recorded on a Bruker Advance DPX-300 spectrometer using CDCl₃ as solvent. Chemical shifts are given in ppm relative to tetramethylsilane. IR spectra were recorded as KBr pellets on a FT-IR spectrum BX-II spectrophotometer. The electronic spectra were recorded in DMF on Shimazdu UV mini-1240 spectrophotometer.

| Elemental analyses data of the ligands and Pd(II) and Pt(II) complexes | | | | | | | | | |
|--|------------|--------------|-------------|-----------|---|---------------|-------------|---------------|--|
| Ligands/complexes | M.W. found | Color | M.P. (0 °C) | Yield (%) | Elemental analysis found (calculated) % | | | | |
| | | | | | М | С | Н | Ν | |
| $L_1 = C_{38}H_{26}N_6$ | 567 | Cream | 65 | 62 | _ | 80.19 (80.50) | 4.66 (4.50) | 15.12 (14.80) | |
| [Pd(L1)]Cl2 PdC38H26N6Cl2 | 744 | Green | 84 | 52 | 14.24 (14.31) | 61.29 (61.33) | 3.49 (3.50) | 11.26 (11.29) | |
| [Pt(L1)]Cl2 PtC38H26N6Cl2 | 833 | Green | 85 | 60 | 23.40 (23.43) | 54.74 (54.80) | 3.10 (3.12) | 10.08 (10.09) | |
| $L_2 = C_{40}H_{28}N_4$ | 563 | White | 85 | 67 | - | 85.40 (85.1) | 5.16 (4.90) | 9.82 (9.91) | |
| $[Pd(L_2)]Cl_2PdC_{40}H_{28}N_4Cl_2$ | 740 | Mehendi | 110 | 62 | 14.32 (14.30) | 64.86 (64.74) | 3.78 (3.77) | 7.56 (7.55) | |
| [Pt(L2)]Cl2 PtC40H28N4Cl2 | 829 | Orange | 98 | 68 | 23.52 (23.49) | 57.90 (57.83) | 3.38 (3.37) | 6.77 (6.75) | |
| $L_3 = C_{32}H_{28}N_4$ | 470 | Light yellow | 64 | 62 | - | 81.82 (82.01) | 6.03 (5.91) | 10.35 (11.09) | |
| $[Pd(L_3)]Cl_2PdC_{32}H_{28}N_4Cl_2$ | 647 | Brown | 90 | 60 | 16.38(16.43) | 59.35 (59.93) | 4.32 (4.34) | 8.65 (8.68) | |
| $[Pt(L_3)]Cl_2PtC_{32}H_{28}N_4Cl_2$ | 736 | Brown | 95 | 50 | 14.40 (14.44) | 52.17 (52.31) | 3.80 (3.81) | 7.60 (7.62) | |

 Table 2

 Molar conductance and Electronic spectral data of the complexes

| S. no. | Complexes | Molar conductance $(\Omega^{-1} \operatorname{cm}^2 \operatorname{mol}^{-1})$ | $\lambda_{max} \ (cm^{-1})$ |
|--------|-----------------|---|-----------------------------|
| 1 | $[Pd(L_1)]Cl_2$ | 198 | 18622, 27397, 34247 |
| 2 | $[Pd(L_2)]Cl_2$ | 206 | 20747, 27933, 36764 |
| 3 | $[Pd(L_3)]Cl_2$ | 208 | 30674, 37174 |
| 4 | $[Pt(L_1)]Cl_2$ | 210 | 27397, 34364 |
| 5 | $[Pt(L_2)]Cl_2$ | 200 | 21413, 29155, 37037 |
| 6 | $[Pt(L_3)]Cl_2$ | 195 | 18621, 29412, 36364 |

4. Result and discussion

The physical properties and analytical data of ligands and complexes are given in Table 1. The molar conductance measurements in dimethylformamide/nitrobenzene indicate that the complexes are of 1:2 electrolytic nature [23] (Table 2).

4.1. IR spectra

The IR spectra of ligands do not show any band at $1700 \,\mathrm{cm}^{-1}$ $(\nu C=0)$, 3380 cm⁻¹ $(\nu_{as}NH_2)$ and 3250 cm⁻¹ (ν_sNH_2) corresponding to carbonyl group and free primary amine [24], which suggest the complete condensation of amino group with keto group. A band corresponding to ν (C=N) (azomethine linkage) appears at $1650-1660 \text{ cm}^{-1}$ in the ligands (Fig. 2a). On complex formation, the IR band due to azomethine group shifts to the lower wave number $(20-30 \text{ cm}^{-1})$ which indicates that the nitrogen atom of azomethine groups are coordinated to the metal atom (Fig. 2b and c). The band in the $360-390 \,\mathrm{cm}^{-1}$ region may be assigned to ν (M–N) vibrations. In ligand L₁ the bands due to pyridine ring deformation, in-plane-ring deformation and out-of-plane-ring deformation [25] appear at 1593, 642 and $420 \,\mathrm{cm}^{-1}$, respectively. These bands are unaffected in complexes suggesting that pyridine nitrogen is not coordinated to the metal atom. On the basis of above discussion a four coordinated structure is proposed for all the complexes in which the ligands coordinate via four azomethine nitrogens (N,N,N,N-donor, tetradentate).

4.2. ¹H NMR

The ¹H NMR spectra (300 MHz) of the ligands were recorded in dueterated chloroform at room temperature. The peak positions of the different protons of the ligands are given as:

- Two signals at ca. δ 8.0 ppm (d,2H,2H) and δ 7.66 ppm (t,H,H) appear in the spectrum of ligand L₁ due to the two types of pyridine ring protons (Fig. 3a).
- Spectrum of the ligand L_2 shows the two doublet of doublet signals at ca. δ 7.77 ppm (dd,2H,2H) and δ 8.18 ppm (dd,2H,2H) corresponding to the two types of non-equivalent aromatic protons (Fig. 3b).
- The ligand L_3 gives a ¹H NMR singlet at ca. δ 3.70 ppm (S,4H,4H) due to the ethylinic protons (Fig. 3c).



Fig. 2. IR spectra of (a) ligand (L_1) , (b) $[Pd(L_1)]Cl_2$, and (c) $[Pt(L_1)]Cl_2$.

 In addition, a multiplet appears in the spectra of ligands at ca. δ 7.22–7.40 ppm (m,5H,5H,5H,5H) equivalent to the four phenyl groups protons [26].

4.3. Mass spectra

The electron impact mass spectra confirm the proposed formulae of ligands L_1 , L_2 , and L_3 . The fragmentation patterns of the ligands are discussed below.



Fig. 3. ¹H NMR spectra of ligands (a) L_1 , (b) L_2 , and (c) L_3 .

4.3.1. Ligand (L_1)

The molecular ion peak (M⁺) appears at m/z = 567 which is at highest m/z value. This peak confirms the molecular formula of ligand. Moreover a very weak peak at m/z = 568 (M⁺ + 1) also appears which corresponds to the ¹³C isotopic peak. The mass spectrum shows a most prominent peak at m/z = 77, which is the base peak and is due to phenyl cation. The other peaks at m/z = 51, 105, 206, 388, 412, and 475 are due to the different fragments and the intensities of these peaks indicate the stability of these ions [27] (Fig. 4).

4.3.2. Ligand (L2)

The peaks at m/z = 563 and 564 corresponds to the M⁺ (parental ion) and M⁺ + 1 (¹³C isotopic). The base peak appears at m/z = 77 and the other fragment ions give the peaks at m/z = 51, 105, 178, 206, 256, 282, 333, 386, 460, and 487. The peaks area provide an idea of abundance of these ions.



4.3.3. Ligand (L3)

The mass spectrum shows the peaks at m/z values 470 and 471 due to M⁺ and M⁺ + 1 and a most intense peak at m/z = 77. The various peaks appear at m/z values 14, 51, 89, 178, 206, 248, 262, 290, 314, 319, and 412 due to other fragments.

4.4. Electronic spectra

4.4.1. Palladium(II) complexes

The magnetic moment studies show that all the complexes of Pd(II) are diamagnetic with spin-paired d⁸ system, The complexes exhibit three spin allowed d–d transitions from lower



Fig. 5. Electronic spectra of complexes (a) [Pt(L₂)]Cl₂ and (b) [Pt(L₃)]Cl₂.

lying d-levels to the empty $d_{x^2-y^2}$ orbital. Although other two electronic transitions are also observed but their intensities are very weak and are neglected. The complexes show the absorptions bands at 18,622–20,747, 27,397–27,933 and 30,674 cm⁻¹ corresponding to ${}^{1}A_{2g} \leftarrow {}^{1}A_{1g}$, ${}^{1}B_{1g} \leftarrow {}^{1}A_{1g}$ and ${}^{1}E_{g} \leftarrow {}^{1}A_{1g}$ d–d transition [28], respectively. Moreover in the complexes, the high intensity charge transfer absorption bands are also observed at 34,247 and 36,764–37,174 cm⁻¹ corresponding to ${}^{1}A_{2u} \leftarrow {}^{1}A_{1g}$ and ${}^{1}E_{u} \leftarrow {}^{1}A_{1g}$ transitions, respectively (Fig. 5a). These absorption bands suggest that the complexes possess D_{4h} symmetry and square planar geometry.

4.4.2. Platinum(II) complexes

The complexes of Pt(II) are diamagnetic with low-spin d⁸ system having square planar geometry. The spin allowed d–d transitions are observed at 18,621–21,413 cm⁻¹, 27,397 cm⁻¹ and 29,155–29,412 cm⁻¹ corresponding to ${}^{1}A_{2g} \leftarrow {}^{1}A_{1g}$, ${}^{1}B_{1g} \leftarrow {}^{1}A_{1g}$ and ${}^{1}E_{g} \leftarrow {}^{1}A_{1g}$ transitions, respectively, in the complexes. The complexes show the high-energy absorption bands at 34,364 and 36,364–37,037 cm⁻¹ corresponding to charge transfer ${}^{1}A_{2u} \leftarrow {}^{1}A_{1g}$ and ${}^{1}E_{u} \leftarrow A_{1g}$ transitions, respectively (Fig. 5b). These transitions reveal that the complexes possess D_{4h} symmetry.

5. Conclusion

Our proposed structures of macrocyclic ligands on the basis of the IR, ¹H NMR, EI mass spectra have potential binding sites towards the metal ions and act as tetradentate ligands by coordinating through four azomethine nitrogens, i.e. in the N,N,N,N-fashion. The ligands form square planar complexes with Pd(II) and Pt(II) metal ions. The elemental analysis and electronic and IR spectral analysis reveal the existence of monomeric complexes.

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