HETEROCYCLIC COMPLEXES OF PALLADIUM (II) : TEMPLATE SYNTHESIS, SPECTROSCOPIC STUDIES AND BIOCHEMICAL ASPECTS

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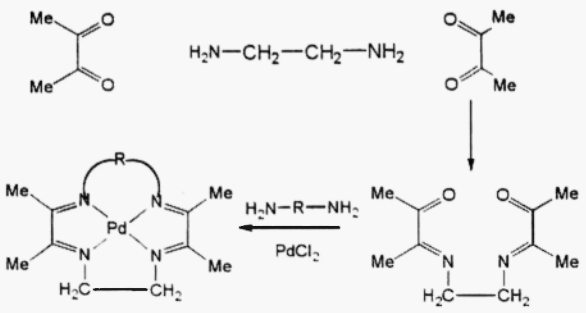
Abstract : Synthesis and spectroscopic studies of new heterocyclic unsymmetrical tetraazamacrocyclic complexes of palladium (II) have been reported. These new complexes were prepared by the template process using 3,8-dimethyl-4,6-diazadecane - 3,7 - diene - 2,9-dione (L^1H) and 3,9 dimethyl - 4,8-diazaundecane - 3,8-diene - 2,10 dione (L^2H) as ligands. The organic ligands L^1H and L^2H react with $PdCl_2$ and different diamines in 1:1:1 molar ratio. The geometry and the mode of bonding of the resulting complexes have been inferred from chemical analysis, IR, ^1H NMR, ^{13}C NMR, mass and electronic spectra and X-ray diffraction studies. Square planar geometry around the palladium ion is suggested for the complexes. Based on molecular weight determinations and conductivity measurements, their monomeric and electrolytic nature has been confirmed. All the complexes along with their ligands have been screened for their antifungal and antibacterial activities.

Introduction

The chemistry of heterocyclic compounds having metal-nitrogen bonding occupy an important position amongst the recent developments related to bioinorganic systems. Metal ion recognition is of fundamental importance to broad areas of both chemistry and biochemistry[1-4]. The importance of metal ion in biological systems as macrocyclic compounds is well established because of their catalytic behaviour in a number of redox reactions of biological significance. Heterocyclic polyamines have attracted increasing attention because of their unique property, namely to form very stable chelates with various heavy metal ions[5]. Increasing attention has recently been focussed on the concept of preparing low valent transition metal complexes. A review on macrocycles had revealed the importance of macrocyclic complexes in biological processes such as photosynthesis and dioxygen transport, and their catalytic properties[6]. It was, therefore, considered of interest to synthesize and characterize unsymmetrical heterocyclic organic ligands and their macrocyclic complexes with palladium (II), the references of which are not available in the literature.

Results and Discussion

The elemental analysis and analytical data of the prepared hetero organic ligands and their complexes suggested 1:1 metal to ligand stoichiometric ratio in methanol and may be represented by the scheme 1. Similar reactions were take place with 1,3-diaminopropane in place of 1,2-diaminoethane. All the resulting solids are soluble in DMF and DMSO. The Rast Camphor method for determinations of molecular weights showed them to be monomeric in nature. These complexes behave as electrolytes in DMF at the room



Where, R = 1,2-C_6H_4, 2,6-C_5H_3N, 1,2-C_4H_6N and 1,8-$C_{10}H_6$

Scheme 1

temperature as the value of molar conductance lie in the range 210-240 ohm^{-1} cm^2 mol^{-1}. Tentative structures have been proposed on the basis of IR, ^{1}HNMR, ^{13}CNMR, electronic, mass and X-ray diffraction studies. The physical properties and analytical data are given in Table 1.

Table 1. Physical properties and analytical data of ligands and their complexes.

Compound	Colour	M.P. (°C)	Analysis (%) Found (Calcd.)			Mol. Wt.
			Pd	N	Cl	Found (Calcd.)
$C_{10}H_{16}N_2O_2$	Wine Red	156	-	14.22	-	168.05
				(14.27)		(196.25)
$[Pd(C_8H_{10}N_2)_2]Cl_2$	Reddish Brown	205	23.60	12.36	15.33	423.65
			(23.88)	(12.57)	(15.9)	(445.67)
$[Pd(C_{15}H_{19}N_5)_2]Cl_2$	Reddish Brown	110	23.27	15.11	15.26	419.71
			(23.83)	(15.68)	(15.87)	(446.65)
$[Pd(C_{14}H_{25}N_5)]Cl_2$	Yellow	116 (d)	23.67	15.69	15.51	417.13
			(24.15)	(15.89)	(16.09)	(440.69)
$[Pd(C_{10}H_{11}N_2)_2]Cl_2$	Coke	143	21.20	11.09	13.72	472.95
			(21.47)	(11.30)	(14.30)	(495.73)
$C_{11}H_{18}N_2O_2$	Reddish Brown	168	-	13.11	-	186.23
				(13.32)		(210.28)
$[Pd(C_{17}H_{22}N_4)]Cl_2$	Dark Brown	>300	22.87	11.95	15.64	435.46
			(23.15)	(12.18)	(15.42)	(459.69)
$[Pd(C_{16}H_{23}N_5)]Cl_2$	Reddish Brown	123	22.88	15.01	14.81	436.31
			(23.10)	(15.20)	(15.39)	(460.67)
$[Pd(C_{15}H_{27}N_5)]Cl_2$	Brown	141	21.58	19.93	13.88	462.09
			(21.86)	(20.14)	(14.56)	(486.77)
$[Pd(C_{21}H_{24}N_4)]Cl_2$	Light Brown	155 (d)	20.60	10.78	13.33	485.19
			(20.88)	(10.99)	(13.91)	(509.75)

IR Spectra : The IR spectra of the ligands and their complexes were recorded and their comparative study confirmed the formation of unsymmetrical heterocyclic complexes with the proposed coordination pattern. The infrared spectra of the ligands show strong absorption in the region 1660-1690 cm^{-1} corresponding to

υ(C=O) vibration. The bands observed in the region 3430-3350 cm^{-1} attributed to stretching and deformation vibrations of the -NH_2 group, in case of starting material (diamine). Both of these bands (>C=O and NH_2) disappeared in case of all the complexes, confirming the cyclization of ligands and characteristic bands of imine groups υ(C=N) occur in the range 1592-1620 cm^{-1} are the major changes observed in the IR spectra of the macrocyclic complexes. All the NH_2 and >C=O groups have been condensed into >C=N bonds. Two distinct bands, characteristic of methyl moiety are observed at 3019 cm^{-1} $\upsilon_{as}(CH_3)$ and 2805 cm^{-1} $\upsilon_s(CH_3)$ in the IR spectra of all the complexes. IR spectra of metal complexes show strong and sharp bands at *ca* 2831 and 1439 cm^{-1} corresponding to C-H stretching and bending vibrations, respectively. Stretching bands are present at 1635, 1552 and 1478 cm^{-1} due to aromatic ring of 1,2-phenylene, pyridine and naphthalene ring. The spectra of complexes do not show any changes in the pyridine and 2,2'-diaminodiethylamine which clearly indicate that in these complexes the nitrogen atoms of the diamines do not participate in coordination

^{1}HNMR Spectra : The mode of bonding and the geometry of these complexes have been established with the help of proton NMR spectra of the ligands and their complexes which were recorded in DMSO-d_6. Chemical shift values (δ, ppm) are given in Table 2.

Table 2. ^{1}H NMR Spectral data (δ, ppm) of ligands and their complexes.

S.No.	Compound	>CH_2	-R		-CH_3
1.	$C_{10}H_{16}N_2O_2$	3.09 (bs)	-	-	1.29 (s)
2.	$[Pd(C_8H_{10}N_2)_2]Cl_2$	3.39 (bs)	8.36 ($H_{2,5}$d)	7.37 ($H_{3,4}$d)	1.83 (s)
3.	$[Pd(C_{15}H_{19}N_5)_2]Cl_2$	3.44 (bs)	8.9 ($H_{2,4}$s)	7.42 (H_3d)	1.19 (s)
4.	$[Pd(C_{14}H_{25}N_5)]Cl_2$	3.18 (bs)	-	-	1.36 (s)
5.	$[Pd(C_{10}H_{11}N_2)_2]Cl_2$	3.32 (bs)	8.20 (H_2-bs)	7.43($H_{4,5}$d)	1.52 (s)
6.	$C_{11}H_{18}N_2O_2$	3.17 (bs)	-	-	1.21 (s)
7.	$[Pd(C_{17}H_{22}N_4)]Cl_2$	3.58 (bs)	8.18($H_{2,5}$d)	7.39 ($H_{3,4}$d)	1.48 (s)
8.	$[Pd(C_{16}H_{23}N_5)]Cl_2$	3.19 (bs)	8.24 ($H_{2,4}$s)	7.30 (H_3d)	1.56 (s)
9.	$[Pd(C_{15}H_{27}N_5)]Cl_2$	3.23 (bs)	-	-	1.62 (s)
10.	$[Pd(C_{21}H_{24}N_4)]Cl_2$	3.70 (bs)	8.32 (H_2-bs)	7.41 ($H_{3,6}$d) 7.34 ($H_{4,5}$d)	1.51 (s)

Electronic Spectra : The electronic spectra of the ligands and their metal complexes were recorded in distilled DMSO. The absorption maxima appears at 410 nm in the case of ligands can be assigned to the n-π* electronic transitions. However, the position of these transitions in the complexes remains almost same as that of the ligands. The electronic spectra of these complexes show d-d spin allowed transitions. These are

corresponding to the transitions from the three lower lying 'd' level to the empty $d_{x^2-y^2}$ orbitals. The ground state is ^1A_1g and excited states corresponding to the above transitions are ^1A_1g, ^1B_1g and ^1Eg in order of increasing energy. Three d-d bands are observed in the regions 545-570 nm, 485-495nm and 440-460 nm. These bands are attributed to $^1A_1g \rightarrow {}^1A_2g$, $^1A_1g \rightarrow {}^1B_1g$ and $^1A_1g \rightarrow {}^1Eg$ transitions, respectively. The electronic spectra of these complexes indicate the square planar geometry and the values obtained correspond to those reported earlier for the square planar complexes.[7]

^{13}CNMR Spectra : The ^{13}CNMR spectra of the ligands and their complexes were recorded in DMSO. The signal observed at δ121.22- 135.72 ppm have been assigned to phenyl carbons attached to nitrogen atoms. Carbon atoms which have a distance from nitrogen atoms show upfield shift. A signal observed at δ 163.92 - 169.34 ppm may be assigned to carbonyl (>C=O) carbons in the ligands which disappears in the complexes. Similarly a band appeared in the range δ 153.28-164.39 ppm due to >C=N bands in the complexes, indicates cyclisation of ligand. Signals observed for these carbons have also been assigned in the ligands and their complexes, recorded in Table 3.

Table 3. ^{13}C NMR Data (δ, ppm) of the organic ligands and their complexes.

S.No.	Compound	>C=O	>N-CH_2	>C=N	-CH_3	-R	-CH_2
1.	$C_{10}H_{16}N_2O_2$	169.34	40.74	163.53	12.32	-	-
2.	$[Pd(C_8H_{10}N_2)_2]Cl_2$	-	46.53	158.32	16.32	$C_{1,6}$129.97, $C_{2,5}$127.43, $C_{3,4}$125.02	28.59
3.	$[Pd(C_{15}H_{19}N_5)_2]Cl_2$	-	43.89	162.61	12.29	$C_{1,5}$135.72, $C_{2,4}$128.18, $C_3$121.22	37.13
4.	$[Pd(C_{14}H_{25}N_5)]Cl_2$	-	39.81	153.28	19.09	-	26.02
5.	$C_{11}H_{18}N_2O_2$	163.92	42.39	164.39	11.38	-	33.52
6.	$[Pd(C_{17}H_{22}N_4)]Cl_2$	-	40.59	160.13	18.88	$C_{1,6}$134.14, $C_{2,5}$129.42, $C_{3,4}$124.41	35.03

Mass Spectra : The fast atom bombardment mass spectrum of one complex is consistent with the presence of 1:1 (metal to ligand) stoichiometry. In the mass spectrum the molecular ion peak of the complex $[Pd(C_{15}H_{19}N_5)]Cl_2$, appeared at m/z 447 $[M]^+$ Some other peaks appeared at m/z 419, 391, 388, 370, 341 and 339 correspond to the $[Pd(C_{13}H_{15}N_3)]^+Cl_2$, $[Pd(C_{13}H_{15}N_3)]^+Cl_2$, $[Pd(C_{11}H_7N_5)]^+Cl_2$, $[Pd(C_{10}H_{16}N_4)]^+Cl_2$, $[Pd(C_{10}H_{16}N_2)]^+Cl_2$ and $[Pd(C_7H_7N_5)]^+Cl_2$, species, respectively, which resulted from the loss of the C_5H_4, $C_2H_3N_2$, C_4H_{12}, C_5H_3N, $C_5H_3N_3$ and C_8H_{12} fragments from the parent compound, respectively. Two peaks appeared at m/z 413 and 378 are due to the loss of one chlorine atom and two chlorine atoms, respectively.

X-ray Powder Diffraction Spectra : The X-ray powder diffraction studies of the finally powdered sample of the compound $[Pd(C_{14}H_{25}N_5)]Cl_2$, has been carried out in order to have an idea about the lattice dynamics of the compounds. The data suggest a 'tetragonal' lattice to this derivative having unit cell dimensions; a =

25.600 A°, b = 17.220 A°, c = 10.600 A° and the miller indices h, k, l and a, b, c are recorded in (Table 4).

Table 4. X-ray powder diffraction data of $[Pd(C_{14}H_{24}N_4)]Cl_2$

Peak	2θ (deg.)	d-spacing	h	k	l
1.	34.90	3.230	2	4	2
2.	35.00	3.221	2	4	2
3.	35.00	3.152	5	4	1
4.	35.70	3.014	8	1	1
5.	38.40	2.945	2	3	3
6.	40.80	2.779	0	6	1
7.	48.56	2.356	4	2	4
8.	49.80	2.301	6	4	3
9.	58.20	1.992	2	7	3
10.	59.30	1.958	5	0	5
11.	60.30	1.929	12	2	2

Biological Screening

The antifungal activity was evaluated against *Fusarium oxysporum*, *Alternaria alternata* and *Macrophomina phaseolina* using standard Food Poisoning Technique and a procedure recommended for testing new chemicals. The linear growth of the fungus was recorded by measuring the diameter of the colony after 96 h, and the percentage inhibition was calculated as 100 (C-T)/C, where, C and T are diameters of the fungus colony in control and test plates, respectively. Antibacterial activity was tested against *Escherichia coli*, *Staphylococcus aureus* and *Pseudomonas cepacicola*.

Mode of Action

A close morphological relationship between bacteria and fungi has been reported and it has been demonstrated that complexes with antifungal and antibacterial activity also exhibit other type of activity. Due to complexity of biological systems, it is rather difficult to stipulate the exact mechanism for such type of activities. The antimicrobial activity of all these complexes may also be ascribed in term of the hydrogen linkage and some bio-receptors in the bacterial cell, which in turn blocks the synthesis of proteins in them by inhibiting the movements of ribosome along mRNA.

The results pointed out that the chelation as well as the additions of a substrate enhance the activity of the complexes. The variation in the toxicity of different microbial agents against different organisms, depends either on the impermeability of the cell or differences in ribosomes to the antimicrobial agents.

Experimental

Chemicals and solvents used were dried and purified by standard methods and moisture was excluded from the glass apparatus using $CaCl_2$ tubes. Palladium chloride was purchased from E. Merch and diamines were obtained from Fluka and used without further purification.

Synthesis of Ligands L^1H and L^2H

2,3-Butane dione was added to the calculated amount of 1,2-diaminoethane and 1,3-diaminopropane in 2:1 molar ratio in ethanol. The contents were refluxed on a column for about 10-15 hours. The resulting products was cooled and rendered free from solvents. The reddish brown compound obtained was washed repeatedly from cyclohexane (~ 15ml) and then adding petroleum ether slowly till ligand began to separated out. The ligand so formed was finally dried in vacuum for 2-3 hours.

Synthesis of the Complexes : A weighed amount of the ligand (L^1H or L^2H) was added to the diamine and palladium chloride in 1:1:1 molar ratio in methanol. The reaction mixture was refluxed for 35-40 hours. Final product obtained was cooled, transferred to an evaporating dish and set aside for a few hours. The compound thus obtained was then purified by dissolving it in a small amount of cyclohexane and dried under reduced pressure.

Molar conductance measurements were made in anhydrous DMF (10^{-3}M) on a Systronic model 305 conductivity bridge. Molecular weight determinations were carried out by Rast Camphor method. Infrared spectra were recorded on a Nicolet Megna FT – IR 550 spectrophotometer in KBr pellets. ^{1}H NMR spectra were recorded on a Jeol FX 90 Q spectrometer in DMSO –d_6 using TMS as the internal standard. The electronic spectra were recorded on a Varian Cary / 2390 spectrophotometer and magnetic measurements on a vibrating sample magnetometer model 155 at the RSIC. IIT Madras. Palladium was estimated gravimetrically. Nitrogen was estimated by the Kjeldahl's method and chlorine by Volhard's method[8].

Acknowledgement

The authors are thankful to CSIR, New Delhi for financial assistance through grant number 9/149(270)/2K-I/EMR-I.

References

1. P. Zanella, S. Tamburini, P. A. Vigato, G. A. Mazzocchin, Coord. Chem. Rev., **77**, 165 (1987).
2. M. Momemtean and C. A. Reed, Chem. Rev., **94**, 659 (1994).
3. M. A. Halcrow and G. Christon, Chem. Rev., **94**, 2421 (1994).
4. J. Atkinson, D. Black, A. J. Blake, A.Marin Becerra, S. Parsons, L. Ruiz-Ramirez and M. Schroder, Chem. Commun., **457** (1996).
5. D. Korg, L. Meng, L. Song and Y. Xie, Trans. Met. Chem., **24**, 553 (1999).
6. S. Aiman, J. R. Morrow, C. R. Lake and M. R. Cheerchill., Angew. Chem., Int. Ed. Engl., **33**, 773 (1994).
7. L. Labib, T. E. Khalil and M. F. Iskander, Polyhedron, **15**, 352 (1995).
8. K. Sharma, S. Dave and R.V. Singh, Main Group Met. Chem., **24**, 267, (2001).

Received on July 4, 2001