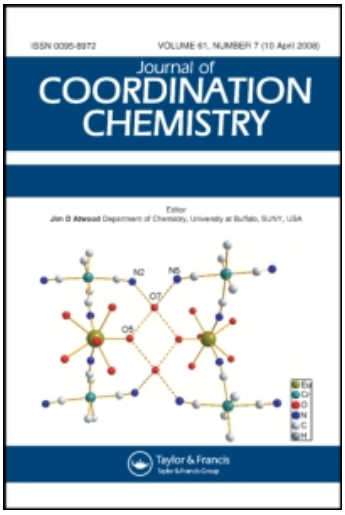

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Encapsulation of Pd(II) by N_4 and N_2O_2 macrocyclic ligands: their use in catalysis and biology

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Encapsulation of Pd(II) by N_4 and N_2O_2 macrocyclic ligands: their use in catalysis and biology

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New macrocyclic Schiff base Pd(II) compounds were synthesized by treating N_4 and N_2O_2 macrocycles with palladium chloride in a 1 : 1 ratio. The resulting macrocyclic compounds were characterized by elemental, IR, ^{1}H-NMR, ^{13}C-NMR, mass, molar conductance, magnetic susceptibility, electronic spectra, and thermal analysis. These compounds were used as catalysts in the development of an efficient catalytic method for reduction of organic substrates having nitro, olefinic, acetylenic, and aldehyde groups under mild reaction conditions. The biological activities of all the macrocycles and macrocyclic Pd(II) compounds have been tested against gram positive (*Bacillus subtilis* and *Staphylococcus aureus*) and gram negative (*Escherichia coli* and *Klebsiella pneumonia*) bacteria and found to be more active than commercially available antibacterial drugs like Streptomycin and Ampicillin.

Keywords: Encapsulation of Pd(II); N_4 and N_2O_2 macrocyclic ligands; Catalysis; Biology

1. Introduction

The chemistry of macrocyclic ligands and their complexes have been extensively studied in recent years [1–3]. Dramatic progress has been achieved in macrocyclic chemistry with various applications in catalysis and biology [4–6]. Pd(II) Schiff-base complexes [7–9] are of interest in catalysis and bioinorganic chemistry. Schiff-base complexes have been used as antimicrobial [10], genotoxicity [11], and anti-inflammatory agents [12]. Furthermore, Pd(II) catalysts are compatible with environmentally friendly water. Palladium complexes are versatile catalysts used for hydrogenation reactions [13–17]. Most existing orthophthalaldehyde based macrocyclic metal compounds were synthesized by template method from *o*-phthalaldehyde (OPA), diamine, and metal salts [18–21]. To the best of our knowledge, there are no reports on the synthesis of macrocyclic Pd(II) compounds derived from *o*-phthalaldehyde. We have synthesized and characterized Pd(II) macrocyclic Schiff-base complexes. The present article deals

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with the striking structural features, synthesis, catalysis, and appreciable biological applications of these complexes.

2. Experimental

2.1. *Physical measurements*

The melting points of all the macrocyclic Pd(II) compounds were obtained on a Buchi-510 melting point apparatus. The percentages of carbon, hydrogen, and nitrogen in macrocyclic Pd(II) compounds were determined using a Perkin–Elmer 2400 CHN analyzer. IR spectra were recorded in KBr/CsBr pellets on a Perkin Elmer-283 spectrophotometer. Bruker WH 300 (200 MHz) and Bruker WH 270 (67.93 MHz) spectrometers were used for ^{1}H-NMR and ^{13}C-NMR spectra. An electrospray ionization mass spectrometer was used for mass spectra. UV-Visible spectra were recorded with a Shimadzu UV-160A double beam spectrophotometer with matched quartz cells of path length 1 cm.

2.2. *Materials*

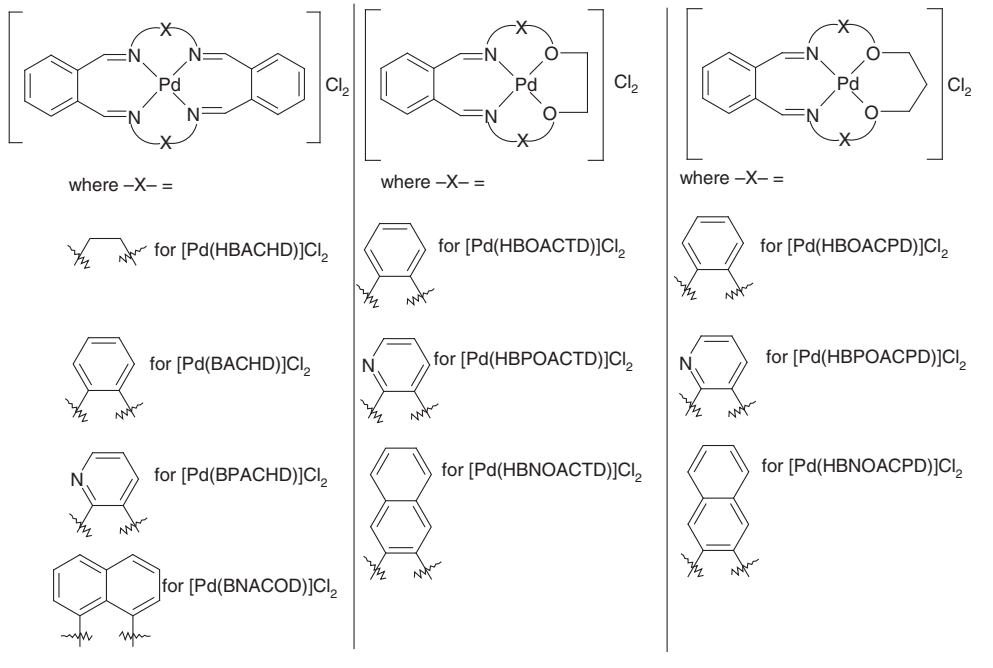
Palladium chloride (Merck), methanol, diethyl ether, and dichloromethane (Qualigens) were used as supplied. Ten macrocyclic ligands *viz*. 7,8,17,18-tetrahydrodibenzo[f,n][1,4,9,12]tetraazacyclohexadecine [HBACHD], tetrabenzo[b,f,j,n][1,4,9,12]tetraazacyclohexadecine [BACHD], dibenzo[f,n]dipyrido[2,3-b:3,2-j][1,4,9,12]tetraazacyclohexadecine [BPACHD], dibenzo[g,p]dinaphtho[1,8-bc:1,8-kl][1,5,10,14]tetraazacyclooctadecine [BNACOD], 6,7-dihydrotribenzo[e,i,m][1,4,7,12]dioxadiazacyclotetradecine [HBOACTD], 13,14-dihydro-12H-tribenzo[b,f,j][1,12,4,9]dioxadiazacyclopentadecine [HBOACPD], 6,7-dihydrobenzo[i]dipyrido[3,2-e:2,3-m][1,4,7,12] dioxadiazacyclotetradecine [HBPOACTD], 13,14-dihydro-12H-benzo[f]dipyrido[3,2-b:2,3-j][1,12,4,9]dioxadiazacyclopentadecine [HBPOACPD], 21,22-dihydrobenzo[i]dinaphtho-[2,3-e:2,3-m][1,4,7,12]-dioxadiazacyclotetradecine [HBNOACTD], and 15,16-dihydro-14H-benzo[f]binaphthol[2,3-b:2,3-j][1,12,4,9]dioxadiazacyclopentadecine [HBNOACPD] were reported previously [22]. The hydrogenation unit consists of three-necked, double-walled glass drain, which in turn is connected to a double-walled hydrogen burette through which water at the desired temperature from a thermostat is circulated. *Bacillus subtilis* (MTCC–619), *Staphylococcus aureus* (MTCC–96), *Escherichia coli* (MTCC–722), and *Klebsiella pneumonia* (MTCC–109) from IMTECH, Chandigarh, were used for antimicrobial studies.

2.3. *Synthesis of macrocyclic Pd(II) compounds*

In a round bottom flask of 100 mL, 20 mL of $PdCl_2$ (1.062 g in 40 mL 0.1M HCl and 40 mL methanol) and 30 mL of ligand solution (0.003 mol, *viz*. 0.948 g of HBACHD, 1.236 g of BACHD, 1.242 g of BPACHD, 1.536 g of BNACOD, 1.026 g of HBOACTD, 1.068 g of HBOACPD, 1.032 g of HBPOACTD, 1.074 g of HBPOACPD, 1.326 g of HBNOACTD, or 1.368 g of HBNOACPD in methanol) were mixed with continuous

stirring. The resulting solution was concentrated to 5 mL under reduced pressure and a few milliliter of diethylether was added to initiate crystallization. The resulting precipitate was separated by suction filtration, washed with diethylether, vacuum dried to obtain a crystalline compound and recrystallized using dichloromethane and diethylether solvent mixture. The physical and analytical data are in agreement with the proposed molecular formula *viz*. $[Pd(L)]Cl_2$ {L = tetradentate macrocyclic ligand} (scheme 1).

Compound **1**: Yield 81%; cream; reaction time: 55 min; Anal. found (%): C 48.61, H 4.01, N 11.40, Pd 21.50; Calcd for $C_{20}H_{20}Cl_2N_4Pd$: C 48.64, H 4.05, N 11.34, Pd 21.56%. Compound **2**: Yield 76%; blackish white; reaction time: 70 min; Anal. found (%): C 57.10, H 3.41, N 9.36, Pd 18.09; Calcd for $C_{28}H_{20}Cl_2N_4Pd$ (%): C 57.00, H 3.39, N 9.50, Pd 18.05. Compound **3**: Yield 71%; light brown; reaction time: 75 min; Anal. found (%): C 52.61, H 3.09, N 14.46, Pd 18.05; Calcd for $C_{26}H_{18}Cl_2N_6Pd$ (%): C 52.75, H 3.04, N 14.20, Pd 17.99. Compound **4**: Yield 78%; cream; reaction time: 95 min; Anal. found (%): C 63.01, H 3.30, N 8.15, Pd 15.36; Calcd for $C_{36}H_{24}Cl_2N_4Pd$ (%): C 62.66, H 3.48, N 8.12, Pd 15.43. Compound **5**: Yield 78%; brown; reaction time: 80 min; Anal. found (%): C 50.92, H 3.52, N 5.23, Pd 20.42; Calcd for $C_{22}H_{18}Cl_2N_2O_2Pd$ (%): C 50.82, H 3.46, N 5.39, Pd 20.48. Compound **6**: Yield 81%; light green; reaction time: 95 min; Anal. found (%): C 51.86, H 3.61, N 5.31, Pd 20.01; Calcd for $C_{23}H_{20}Cl_2N_2O_2Pd$ (%): C 51.74, H 3.74, N 5.24, Pd 19.94. Compound **7**: Yield 83%; cream; reaction time: 90 min; Anal. found (%): C 46.08, H 3.01, N 10.85, Pd 20.51; Calcd for $C_{20}H_{16}Cl_2N_4O_2Pd$ (%): C 46.02, H 3.06, N 10.74, Pd 20.40. Compound **8**: Yield 78%; light brown; reaction time: 105 min; Anal. found (%): C 46.98, H 3.40, N 10.55, Pd 20.03; Calcd for $C_{21}H_{18}Cl_2N_4O_2Pd$ (%): C 47.06, H 3.36,



Scheme 1. Structures of macrocyclic Pd(II) compounds.

N 10.45, Pd 19.87. Compound **9**: Yield 72%; ash; reaction time: 180 min; Anal. found (%): C 57.95, H 3.68, N 4.58, Pd 17.09; Calcd for $C_{30}H_{22}Cl_2N_2O_2Pd$ (%): C 58.12, H 3.55, N 4.52, Pd 17.17. Compound **10**: Yield 75%; light brown; reaction time: 180 min; Anal. found (%): C 58.96, H 3.71, N 4.53, Pd 16.51; Calcd for $C_{31}H_{24}Cl_2N_2O_2Pd$ (%): C 58.73, H 3.78, N 4.42, Pd 16.79.

2.4. *Catalytic hydrogenation*

Hydrogen gas was saturated in dimethylformamide–water solution and then 0.01 mmol of catalyst was added. The catalyst dissolves and the reaction system was evacuated and flushed with hydrogen for few minutes. Then 0.01 mmol of substrate in DMF was injected. Hydrogen absorption begins as soon as the shaking is started. The process was continued for 2 h. The resulting mixture was cooled and extracted with chloroform; the organic layer was separated, washed with water, dried over magnesium sulphate, and evaporated to give the reduced product. The procedure is repeated by changing the palladium catalyst.

2.5. *Antimicrobial testing by agar diffusion*

Antimicrobial testing was done by the cup plate method [23]. Molten agar (27 mL) was added into sterile petri dishes and allowed to solidify for 1 h. Then 50 mL of the 24 h culture of a test organism was spread evenly on the agar plate with a sterile cotton swab. Six-millimeter wide bores were made on the agar using a borer. The solutions of the macrocyclic metal compounds were added to each of the bores using a sterile tip with micropipette. A similar plate was prepared by replacing macrocycle by Streptomycin sulphate as a standard against bacteria. These dishes were then incubated at 37°C for 24 h and zones of growth inhibition were measured. The activities of the compounds were interpreted as either active or inactive. The minimum inhibitory concentration required was also found when a series of dilutions were tested.

2.6. *Determination of minimum inhibitory concentration (MIC)*

The minimum inhibitory concentration [24] was determined by liquid dilution method. Stock solutions of Pd(II) complexes with 2.5 μg mL^{-1}, 5 μg mL^{-1}, 10 μg mL^{-1}, 20 μg mL^{-1}, 50 μg mL^{-1}, and 100 μg mL^{-1} concentrations were prepared with appropriate solvent; solutions of standard drugs like Streptomycin, Ampicillin, and Rifampicin were also prepared in the same concentrations. Inoculum of the overnight culture was prepared. To a series of tubes containing 1 mL each of macrocyclic Pd(II) complex solution with different concentrations, 0.2 mL of the inoculum was added. Further 3.8 mL of sterile water was added to each of the test tubes. These test tubes were incubated for 24 h and checked for turbidity. The absorbance of the suspension of the inoculum was detected by using a spectrophotometer at 550 nm. This method was repeated by changing Pd(II) complexes with drugs like Streptomycin, Ampicillin, and Rifampicin as references.

3. Results and discussion

Ten new macrocyclic Pd(II) compounds have been prepared by treating palladium chloride with macrocyclic ligands.

3.1. *Infrared spectral analysis*

Infrared spectra of the free ligands were compared to those of the macrocyclic Pd(II) compounds to assess coordination (table 1). Characteristic bands of the macrocyclic ligands, skeleton vibrations in the range of 1630–1608 cm^{-1}, 1600–1560 cm^{-1}, 1208–1141 cm^{-1} and the out-of plane band at 810–860 cm^{-1}, were observed [25–27]. These bands were absent in macrocyclic palladium(II) complexes and four new bands were observed in the region of 1607–1582, 1560–1530, 1180–1110, and 780–720 cm^{-1}. According to Ivanova *et al.* [25, 26] and Koleva *et al.* [27], the first two maxima correspond to mixed $\upsilon_{C=N}$ and $\upsilon_{C=C}$ vibrations of the imino-form and third maximum corresponds to υ_{C-O-C} vibrations of the macrocyclic palladium(II) complexes. That the ligands coordinate through nitrogens of C=N group and oxygens of C–O–C is further supported by appearance of a lower-intensity band in the 530–503 cm^{-1} and 430–410 cm^{-1} regions assignable to υ_{M-N} [18, 28] and υ_{M-O} vibrations [19].

3.2. *NMR spectral data*

The ^{1}H-NMR spectra of macrocycles were compared to Pd(II) complexes to assess the binding. In all the ligands, signals due to CH=N protons appeared in the range of

Table 1. Infrared spectroscopic data and molar conductance values of macrocyclic Pd(II) compounds.

Sl. No.	Macrocyclic Pd(II) compound	Selected IR bands (cm^{-1})				Λ_M ($\Omega^{-1}\,cm^2\,mol^{-1}$)
		$\upsilon_{C=N}$	υ_{C-O-C}	υ_{Pd-N}	υ_{Pd-O}	
1	[Pd(HBACHD)]Cl_2	1590	–	510	–	54.0
L-1	HBACHD	1618	–	–	–	–
2	[Pd(BACHD)]Cl_2	1595	–	515	–	53.5
L-2	BACHD	1620	–	–	–	–
3	[Pd(BPACHD)]Cl_2	1607	–	516	–	55.6
L-3	BPACHD	1630				
4	[Pd(BNACOD)]Cl_2	1586	–	530	–	58.2
L-4	BNACOD	1610	–	–	–	–
5	[Pd(HBOACTD)]Cl_2	1600	1110	520	410	58.8
L-5	HBOACTD	1622	1141	–	–	–
6	[Pd(HBOACPD)]Cl_2	1592	1145	515	422	60.3
L-6	HBOACPD	1620	1171	–	–	–
7	[Pd(HBPOACTD)]Cl_2	1598	1160	508	430	59.6
L-7	HBPOACTD	1625	1206	–	–	–
8	[Pd(HBPOACPD)]Cl_2	1590	1170	503	425	52.4
L-8	HBPOACPD	1620	1200	–	–	–
9	[Pd(HBNOACTD)]Cl_2	1585	1125	512	428	56.8
L-9	HBNOACTD	1608	1158	–	–	–
10	[Pd(HBNOACPD)]Cl_2	1582	1180	522	415	60.2
L-10	HBNOACPD	1610	1208	–	–	–

8.02–8.83 ppm [20] and for ligands 5–10, signals in the range of 3.90–4.37 ppm [29] correspond to methylenic protons adjacent to phenolic oxygen. Coordination of nitrogen of CH=N to Pd(II) is indicated by signals slightly downfield, 8.26–8.86 ppm [21], in Pd(II) compounds. Similarly, signals with a slight upfield shift to 4.06–4.28 ppm in the spectra of Pd(II) compounds with ligands 5–10 supports coordination of these ligands through oxygen in addition to nitrogen of CH=N group. There is no appreciable change in the peak positions corresponding to aromatic protons [20].

The ^{13}C-NMR spectra of all the ligands contain signals in the range of 150.4–179.0 and 60.0–67.4 ppm [30] due to carbons doubly bonded to nitrogen and carbon and adjacent to oxygen, respectively. In spectra of macrocyclic Pd(II) compounds, a downfield shift is observed in the range of 147.5–172.0 ppm [31], indicating coordination through nitrogen. In spectra of Pd(II) compounds of ligands 5–10, a downfield shift is observed at 58.0–65.0 ppm [31], indicating that ligands 5–10 coordinate through two nitrogens and two oxygens. Appreciable changes in peak position were not observed for aryl carbons and carbons adjacent to nitrogen in pyridine. The individual ^{1}H and ^{13}C peak positions of carbon atoms of all the macrocyclic Pd(II) compounds are given in "Supplementary material".

3.3. *Mass spectral data*

The molecular ion peaks and isotopic pattern of macrocyclic Pd(II) compounds shows different m/z values with different intensities presented in "Supplementary material".

3.4. *Electronic spectroscopic data*

The UV spectra of the macrocyclic ligands show an absorption maximum at 260–290 nm due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transition of the conjugated system. Bathochromic shifts of these bands (10–15 nm) indicate coordination of Pd(II) [25–27]. Three ligand field bands are expected for square planar Pd(II) complexes in the regions 690–600, 555–450, and 410–370 nm, but are not observed in most complexes. The Pd(II) complexes show a broad d–d band in the region of 483–465 nm assignable to $^{1}B_{1g} \leftarrow {}^{1}A_{1g}$ transition typical for square planar geometry [32, 33]. A relatively strong charge transfer band has been observed in spectra of all Pd(II) complexes from 309–280 nm. Electronic spectral data and the diamagnetism are consistent with square planar geometry.

3.5. *Molar conductance, magnetic susceptibility, and thermal studies*

Molar conductance values for the Pd(II) compounds (10^{-3} M) were determined in DMF as 52.4–60.2 $\Omega^{-1}\,cm^2\,mol^{-1}$ indicating 1 : 2 electrolytes (table 1) due to the presence of two chlorides [34]. The presence of chlorides was also detected by addition of silver nitrate leading to white precipitate (AgCl). Magnetic susceptibility measurements show these compounds to be diamagnetic, confirmed by sharp signals in the ^{1}H-NMR spectra.

Thermal analysis data of the Pd(II) complexes indicate that they are stable to 210°C and hence are anhydrous. The DTA curves show no endothermic peaks to 210°C

confirming the absence of lattice or coordinated water in the complexes [35–37]. The sharp decomposition corresponding to the loss of organic moiety can be seen in the DTA curves which contained one sharp exothermic peak in the range 211–250°C. The final product of decomposition of all the complexes above 680°C corresponds to metal oxide. Taking the loss of organic moiety as the decomposition temperature, the thermal stability of the palladium(II) complexes can be represented with respect to ligands as BNACOD > BACHD > HBNOACTD > HBNOACPD > BPACHD > HBOACTD > HBOACPD > HBPOACTD > HBPOACPD > HBACHD. This order can be explained to some extent on the basis of bulkiness of the groups attached to the ligating groups, labile nature of ligand bonds, and the number of chelate rings formed by each ligand [38–40].

3.6. *Catalytic hydrogenations*

New macrocyclic palladium(II) complexes reduced unsubstituted or p-nitro aromatics at faster rates than the corresponding *o*-substituted compounds. Nitrobenzene is reduced to 96–99% when admitted with any *ortho*-substituted derivatives such as o-nitrotoluene and *o*-chloronitrobenzene. Catalytic hydrogenation of nitro aromatics leads to formation of the corresponding amines in all cases except *m*-dinitrobenzene, where the final product was the corresponding hydroxylamine [41]. Alkenes underwent simultaneous reduction and isomerization to produce alkanes and 2-alkenes. Rates of reduction of 1-hexene and 1-heptene were extremely slow. Styrene, isopropene, or cycloocta-1,5-diene, in which the >C=C< group is part of the delocalized system, were reduced more rapidly than isolated double bonds in cycloocta-1,5-diene. Hydrogenation of phenylethylene and phenylacetylene resulted only in ethylbenzene. The rate of hydrogenation of phenylethylene is higher than phenylacetylene, perhaps due to free rotation of π-electrons in the former one. Diphenylacetylene was reduced first to *cis*-stilbene and then to 1,2-diphenylethane. Diphenylacetylene was reduced at a faster rate than *cis*-stilbene due to superior coordinating capacity of the former to the metal center [42]. Catalyst **2** is more efficient than catalyst **5** for reduction of various substrates (table 2). The efficiency of **2** is due to the presence of greater metal–ligand π-electron delocalization in the complex [43]. Formation of very good yield of products under very mild reaction conditions suggests that these complexes can function as good catalysts on various substrates.

3.7. *Antibacterial activity*

Antibacterial activities of macrocyclic Pd(II) compounds were studied along with Streptomycin, Ampicillin, and Rifampicin. Preliminary screening for all the macrocyclic Pd(II) compounds was performed at $1000\,\mu g\,mL^{-1}$. All the compounds were active on two types each of gram +ve (*B. subtilis* and *S. aureus*) and gram –ve bacteria (*E. coli* and *K. pneumonia*). Out of 10 macrocyclic Pd(II) compounds, four *viz*. **3**, **4**, **7**, and **8** were very effective and based on the zone of inhibition (table 3) [44]. The activity of Pd(II) compounds is **3 > 7 > 8 > 4 > 2 > 1 = 9 > 10 > 6 > 5** for *B. subtilis* (MTCC-619), **3 > 7 > 4 > 8 > 9 > 2 > 10 > 5 = 6 > 1** for *S. aureus* (MTCC-96), **7 > 3 > 4 > 8 > 9 > 2 > 6 = 10 > 5 > 1** for *E. coli* (MTCC-722), and **4 > 3 > 7 > 8 > 10 > 9 > 6 > 5 > 1 > 2** for *K. pneumonia* (MTCC-109).

Table 2. Catalytic hydrogenation using palladium(II) compounds at 1.5 atm pressure of H_2 and 25°C in DMF.

Substrate	Catalyst (mol $L^{-1} \times 10^{-4}$)	Products	Yield (%)	
			2	**5**
Nitrobenzene	2, 5	Aniline	99	91
o-Nitrotoluene	2, 5	*o*-Toluidine	96	85
o-Chloronitrobenzene	2, 5	*o*-Chloroaniline	93	82
p-Nitrotoluene	2, 5	*p*-Toluidine	97	88
m-Dinitrobenzene	2, 5	*m*-Phenylenediamine	81	74
m-Chloronitro benzene	2, 5	*m*-Chloroaniline	94	73
Styrene	2, 5	Ethyl benzene	93	83
1-Hexene	2, 5	Hexane	71	60
2-Hexene	2, 5	Hexane	35	32
Maleic acid	2, 5	Succinic acid	95	90
Isoprene	2, 5	2-Methylbutane	92	82
1,5-Cyclooctadiene	2, 5	Cyclooctane	94	87
Phenyl acetylene	2, 5	Ethyl benzene	98	89
Diphenyl acetylene	2, 5	1,2-Diphenyl ethane	98	88
Benzaldehyde	2, 5	Benzyl alcohol	97	90

Table 3. Zones of inhibitions of macrocyclic Pd(II) compounds against four different bacteria (1000 μg mL^{-1}).

Compound No.	Zone of inhibition (mm)			
	MTCC-619	MTCC-96	MTCC-722	MTCC-109
1	16	14	10	11
2	17	16	16	9
3	46	47	44	40
4	31	37	40	42
5	12	15	12	13
6	13	15	14	15
7	41	38	46	35
8	37	33	34	33
9	16	18	17	16
10	14	15	14	17
Streptomycin	10	12	6	6
Ampicillin	11	13	8	7
Rifampicin	51	49	48	45

In addition, the 10 compounds were effective at different dilutions. The minimum inhibitory concentration [45] of these compounds was also verified by the liquid dilution method in which the effectiveness was observed at lower concentrations. Rank orders of the relative effectiveness of these 10 compounds against gram +ve and gram −ve bacteria were obtained, in which either **3** or **7** were found to be at the top. The activities were compared with the activity of existing antibacterial drugs, Streptomycin, Ampicillin, and Rifampicin, and the new compounds were more active than the first two. The compounds **3**, **7**, and **8** show very good efficacy on clinical resistant strains. These compounds showed increased activity over corresponding ligands.

4. Conclusions

Macrocyclic Pd(II) compounds were synthesized by treating palladium chloride with 10 macrocyclic ligands. Among 10 macrocyclic Pd(II) compounds, four ligands coordinate through four N atoms and six macrocyclic ligands coordinate through two N and two O atoms to Pd(II). Square-planar geometry was assigned to these complexes based on elemental and spectral data. Catalytic hydrogenation of aromatic nitro compounds, alkenes, alkynes, and aldehydes was carried out using **2** and **5**. The macrocyclic Pd(II) compounds have significant antibacterial activity.

References

[1] N.E. Borisova, M.D. Reshetova, Y.A. Ustynyuk. *Chem. Rev.*, **107**, 46 (2007).
[2] P.M. Reddy, A.V.S.S. Prasad, R. Rohini, V. Ravinder. *Spectrochim. Acta A*, **70**, 704 (2008).
[3] J. Durand, B. Milani. *Coord. Chem. Rev.*, **250**, 542 (2006).
[4] M.A. Fernández-Rodríguez, Q. Shen, J.F. Hartwig. *J. Am. Chem. Soc.*, **128**, 2180 (2006).
[5] P.M. Reddy, A.V.S.S. Prasad, V. Ravinder. *Transition Met. Chem.*, **32**, 507 (2007).
[6] M.B. Reddy, K. Shanker, P.U. Rani, R. Rohini, Ch.K. Reddy, V. Ravinder. *J. Indian Chem. Soc.*, **84**, 971 (2007).
[7] J.P. Corbet, G. Mignani. *Chem. Rev.*, **106**, 2651 (2006).
[8] S. Dastgir, K.S. Coleman, A.R. Cowley, M.L.H. Green. *Organometallics*, **25**, 300 (2006).
[9] M. Ashok, V. Ravinder, A.V.S.S. Prasad. *Transition Met. Chem.*, **32**, 23 (2007).
[10] R.S. Joseyphus, M.S. Nair. *J. Coord. Chem.*, **62**, 319 (2009).
[11] M. Tumer, E. Akgun, S. Torolu, A. Kayraldiz, L. Donbak. *J. Coord. Chem.*, **61**, 2935 (2008).
[12] N.M. Hosny, Y. Sherif, A.E. Rahman. *J. Coord. Chem.*, **61**, 2536 (2008).
[13] M.M. Dell'Anna, M. Gagliardi, P. Mastrorilli, G.P. Suranna, C.F. Nobile. *J. Mol. Catal. A*, **158**, 515 (2000).
[14] N. Kim, M.S. Kwon, C.M. Park, J. Park. *Tetrahedron Lett.*, **45**, 7057 (2004).
[15] C.A. Hamilton, S.D. Jackson, G.J. Kelly, R. Spence, D. Bruin. *Appl. Catal. A*, **237**, 201 (2002).
[16] P.U. Rani, P.M. Reddy, M. Sarangapani, V. Ravinder. *J. Indian Chem. Soc.*, **84**, 122 (2007).
[17] P.M. Reddy, K. Shanker, P.U. Rani, B.K. Rao, V. Ravinder. *J. Indian Chem. Soc.*, **85**, 411 (2007).
[18] M. Shakir, O.S.M. Nasman, S.P. Varkey. *Polyhedron*, **15**, 309 (1996).
[19] M. Shakir, S.P. Varkey, S.P. Hammed. *Polyhedron*, **30**, 1355 (1994).
[20] M. Shakir, H.T.N. Chishti, P. Chingsubam. *Spectrochim. Acta A*, **64**, 512 (2006).
[21] M. Shakir, S.P. Varkey, D. Kumar. *Synth. React. Inorg. Org. Chem.*, **24**, 941 (1994).
[22] P.M. Reddy, A.V.S.S. Prasad, Ch.K. Reddy, V. Ravinder. *Transition Met. Chem.*, **33**, 251 (2008).
[23] S. Alam. *Ind. Acad. Sci., J. Chem. Sci.*, **166**, 325 (2004).
[24] S.A. Salmon, J.L. Watts, A. Cheryal. *J. Clin. Microbiol.*, **33**, 2435 (1995).
[25] B.B. Ivanova, H. Mayer-Figge. *J. Coord. Chem.*, **58**, 653 (2005).
[26] B.B. Ivanova, M.G. Arnaudov, H. Mayer-Figge. *Polyhedron*, **24**, 1624 (2005).
[27] B.B. Koleva, E.N. Trendafilova, M.G. Arnaudov, W.S. Sheldrick, H. Mayer-Figge. *Transition Met. Chem.*, **31**, 866 (2006).
[28] S. Ilhan. *J. Coord. Chem.*, **61**, 3634 (2008).
[29] P.M. Reddy, A.V.S.S. Prasad, K. Shanker, V. Ravinder. *Spectrochim. Acta A*, **68**, 1000 (2007).
[30] A. Tzschach, K. Jurkschat, A. Zschunke, C. Mugge, B. Altenbrunn, C.P. Leopardi, G. Germain, J.P. Declercq, M.V. Meerssche. *J. Chem. Crystallogr.*, **15**, 423 (1985).
[31] Z.H. Chohan, M. Praveen. *Appl. Organomet. Chem.*, **15**, 617 (2001).
[32] S.K. Sahini, P.C. Jain, V.B. Rama. *Indian J. Chem.*, **18A**, 16 (1979).
[33] W.R. Marson, H.B. Gray. *J. Am. Chem. Soc.*, **90**, 5721 (1968).
[34] J.B. Quaglino, F. Fujta, J.A. Walmsley, G. Franz, S.Y. Tyree. *J. Am. Chem. Soc.*, **83**, 3770 (1961).
[35] A.V. Nikolaev, V.A. Logvinenkova, L.I. Myachina. *Thermal Analysis*, Vol. 2, Academic Press, New York (1969).
[36] J.R. Allan, T.M. Veitch. *J. Thermal Anal.*, **27**, 3 (1983).
[37] R.S. Bottei, D.L. Greene. *J. Inorg. Nucl. Chem.*, **30**, 146 (1968).
[38] R.S. Bottei, D. Quane. *J. Inorg. Nucl. Chem.*, **26**, 1919 (1964).
[39] V. Sheshagiri, S.B. Rao. *J. Anal. Chem.*, **262**, 175 (1972).
[40] N.R. Sheshagiri, N.R. Raghava. *Indian J. Chem.*, **15A**, 652 (1977).

[41] D.K. Mukherjee, B.K. Palit, C.R. Saha. *Indian J. Chem*., **31**, 243 (1992).
[42] M. Christopher. *Homogeneous Transition-Metal Catalysis*, p. 56, Chapman and Hall Ltd., London (1981).
[43] J.F. Knifton. *J. Org. Chem*., **41**, 1200 (1976).
[44] T.P.T. Cushine, A.J. Lamb. *Int. J. Antimicrob. Agents*, **26**, 343 (2005).
[45] M. Malue, J.M. Bastide, A. Biancard. *Int. J. Antimicrob. Agents*, **25**, 321 (2005).