



Trade Science Inc.

ISSN : 0974 - 746X

Volume 5 Issue 4

# Inorganic CHEMISTRY

*An Indian Journal*

*Short Communication*

ICAJI, 5(4), 2010 [202-204]

## Novel palladium (II) complexes of hydrazine ligands: Synthesis and spectral characterization

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Received: 7<sup>th</sup> October, 2010 ; Accepted: 17<sup>th</sup> October, 2010

### ABSTRACT

N-(2,4-dinitro-phenyl)-N-(3-phenyl-allylidene)-hydrazine (L<sup>1</sup>) and N-(2,4-dinitro-phenyl)-N-(3-nitro-benzylidene)-hydrazine (L<sup>2</sup>) were used as ligands for the synthesis of its palladium (II) complexes. Vibrational study in the solid state of 2,4-dinitrophenyl hydrazine derivatives and its new palladium (II) complexes was performed by elemental analysis, IR and UV-Vis spectroscopy. © 2010 Trade Science Inc. - INDIA

### KEYWORDS

Palladium complexes;  
Hydrazine ligands;  
Synthesis;  
Spectral characterization.

### INTRODUCTION

Studies of metallocyclic complexes of palladium(II) with nitrogen donor ligands are of current interest owing to their wide-range application in organic synthesis and catalysis<sup>[1,2]</sup>. Nitrogen-containing ligands such as Schiff bases and their metal complexes played an important role in the development of coordination chemistry, resulting in an enormous number of publications, ranging from pure synthetic work to physicochemical<sup>[3]</sup> and biochemically relevant studies of metal complexes<sup>[4-8]</sup>. From these points of view, it is interesting to study different types of transition metal complexes of these biologically active ligands. We have prepared two new palladium complexes from substituted hydrazide.

### EXPERIMENTAL

#### Materials and instruments

Acetonitrile (Fluka, P.A.) was distilled several times from phosphorus pentoxide before using, thereby reducing its water content to <4 ppm. Nitrophenyl was purchased from Merck company. PdCl<sub>2</sub> (Merck, p.a.) was used without further purification. Solvents were purified by standard methods. Infrared spectra were recorded as KBr disks on a Bruker Tensor model 27 spectrophotometer. The UV-Visible measurements were made on a Cam spec model 350 spectrophotometer. The percentages of elements in compositions were obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, Tehran.

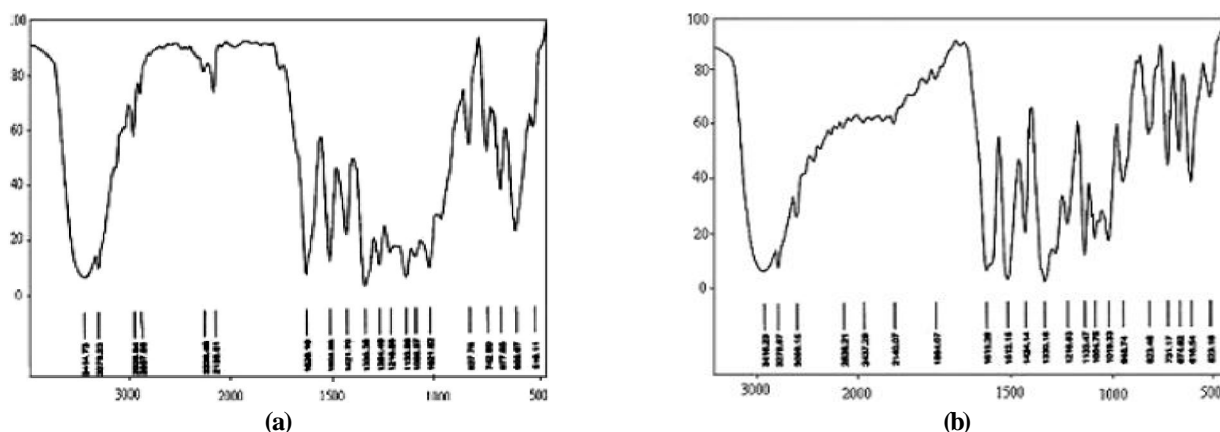


Figure 1 : IR spectra of (a)[Pd(L<sup>1</sup>)], (b)[Pd(L<sup>2</sup>)]

### Synthesis of complex [N-(2,4-dinitro-phenyl)-N-(3-phenyl-allylidene)hydrazine] Pd(II) (1)

[Pd(C<sub>15</sub>H<sub>12</sub>N<sub>4</sub>O<sub>4</sub>)]Cl<sub>2</sub> was prepared as follow: To a solution of PdCl<sub>2</sub> (0.01 g, 0.05 mmol) in acetonitrile, the solid powder N-(2,4-dinitro-phenyl)-N-(3-phenyl-allylidene)-hydrazine (0.1 g, 0.33 mmol) was added under stirring at 90°C temperature until a red solid precipitate was formed. After 2 hours stirring, the mixture was filtered, washed with hexane, and dried at room temperature. UV-Visible and IR data were all consistent with the complex structure. M.p. 256-258°C. IR(KBr) vcm<sup>-1</sup>: 3414, 3279, 2925, 2887, 1620, 1504, 1421, 1335, 1264, 1210, 1133, 1088, 1021, 827, 742, 677, 606, 516.

### Synthesis of complex [N-(2,4-dinitro-phenyl)-N-(3-nitro-benzylidene)-hydrazine] Pd(II) (2)

[Pd(C<sub>14</sub>H<sub>12</sub>N<sub>4</sub>O<sub>4</sub>)]Cl<sub>2</sub> was prepared by dissolving PdCl<sub>2</sub> (0.01g, 0.05 mmol) in DMSO and adding this solution to a solution of N-(2,4-dinitro-phenyl)-N-(3-nitro-benzylidene)-hydrazine (0.1 g, 0.33 mmol) in DMSO under stirring at 90°C temperature until a brown precipitate was formed. After 2 hours stirring, the mixture was filtered, washed with hexane and dried at room temperature. UV-Visible and IR spectra were all consistent with the complex structure. M.p. 239°C. IR(KBr) vcm<sup>-1</sup>: 3416, 3279, 3099, 1615, 1512, 1424, 1330, 1216, 1133, 1064, 1019, 948, 823, 731, 674, 616, 523.

## RESULTS AND DISCUSSION

The reaction of Pd(II) salt with the L<sup>1</sup> and L<sup>2</sup> ligands

result in the formation of [ML] for M=Pd(II). The Complexes were characterized by several techniques using elemental analysis, UV-Visible and IR measurement. The complexes are stable in air and light, and are soluble in organic solvents such as HCCl<sub>3</sub> and DMSO, less soluble in methanol, and insoluble in water and n-hexane. Elemental analysis data are summarized in TABLE 1. The complexes [N-(2,4-dinitro-phenyl)-N-(3-phenyl-allylidene)-hydrazine] Pd(II) (1) and [N-(2,4-dinitro-phenyl)-N(4-methyl-benzylidene)-hydrazine] Pd(II) (2) were prepared in good yield by stirring stoichiometric amounts of PdCl<sub>2</sub> and L<sup>1</sup> and L<sup>2</sup>.

The infrared spectra of the complexes taken in the region 400-4000 cm<sup>-1</sup> were compared with those of the free ligands. There are some significant changes between the metal(II) complexes and their free ligands for chelation as expected. The IR spectra of [PdL] complexes, the ligands acts as a neutral bidentate through the azomethine nitrogen atom and carbon atom, which is meta to both the NO<sub>2</sub> groups<sup>[9]</sup>.

There are some significant changes between the metal(II) complexes and their free ligands for chelation as expected. An exhaustive comparison of the IR spectra of the ligands and complexes gave information about the mode of bonding of the ligands in metal complexes. In the IR spectra of the complexes (Figure 1) a sharp medium band at 1620 and 1615 cm<sup>-1</sup> owing to the ν(C=N) (azomethine) vibrations in the complexes (1) and (2) respectively, indicate the bonding of azomethine nitrogen atoms with the metal ions. The IR spectra of [PdL] complexes presence of a sharp band at 1504, 1512 cm<sup>-1</sup> in IR spectrum owing to the ν(C=C) (ring) vibrations in the complexes (1) and (2) respectively.

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TABLE 1 : Elemental analysis of the ligands and complexes

Compound	Empirical formula	%C		%H		%N	
		Calculated (Found)	Calculated (Found)	Calculated (Found)	Calculated (Found)		
L <sup>1</sup>	C <sub>15</sub> H <sub>12</sub> N <sub>4</sub> O <sub>4</sub>	57.69(57.86)	3.87(3.76)	17.94(18.01)			
L <sup>2</sup>	C <sub>14</sub> H <sub>12</sub> N <sub>4</sub> O <sub>4</sub>	56.00(56.14)	4.03(3.92)	18.66(18.72)			
(1)	C <sub>15</sub> H <sub>10</sub> N <sub>4</sub> O <sub>4</sub> Pd	4.07(44.12)	2.44(2.45)	11.75(11.78)			
(2)	C <sub>14</sub> H <sub>10</sub> N <sub>4</sub> O <sub>4</sub> Pd	42.38(42.41)	2.52(2.53)	12.10(12.08)			

TABLE 2 : Relevant UV data in nm for the complexes

Compound	$\lambda_1$ ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_2$ ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_3$ ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_4$ ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )
L <sup>1</sup>	270(4.67)	301(4.55)	389(4.98)	—
L <sup>2</sup>	259(4.95)	367(5.18)	—	—
(1)	237 (98)	266 (76)	305 (82)	395 (234)
(2)	255 (176)	379 (128)	381(298)	-

This precludes the possibility of coordination through the hydrazine nitrogen atom. The deformation vibration of NO<sub>2</sub> group contributes to several normal modes in the low frequency region. FT-IR spectrum absorption due to the symmetric stretching vibrations of the NO<sub>2</sub> group at 1336 and 1330 cm<sup>-1</sup> in the complexes (1) and (2) respectively. Also, the small shift to higher frequency of the band due to  $\nu$ (N–N) can be taken as additional evidence of the participation of the azomethine group in bonding. This precludes the possibility of coordination through the hydrazine nitrogen atom also supports the above coordination.

The formation of the metal(II) complexes was also confirmed by UV–Vis spectra. The main data UV–Vis solution spectra of the complexes are included in TABLE 2. The absorption spectra of the diamagnetic Pd(II) complexes were recorded as 10<sup>-4</sup> M CH<sub>3</sub>CN solutions in the range 200–800 nm using a quartz cuvette of 1 cm path length. The complexes show only the charge transfer transitions which can be assigned to charge transfer from the ligand to the metal and vice versa, no d–d transition are expected for d<sup>10</sup> Pd(II) complexes<sup>[10]</sup>. When compared complexes with the free ligands values have shifts frequency.

## CONCLUSION

Two complexes of reaction L<sup>1</sup> and L<sup>2</sup> ligands with PdCl<sub>2</sub> were simply synthesized. Electronic and vibrational spectra of these two new palladium-complexes were studied. These compounds were characterized by IR and UV-Visible, techniques. Production of these compounds shows the ability of organic compounds to addition to transition metal and main group elements compounds.

## ACKNOWLEDGEMENT

We thank Professor G. R. Rezaribehbahani and K. Ghodami for their assistances in the preparation of the compounds.

## REFERENCES

- [1] W.A.Hermann, C.Brossmer, K.Ofele, C.P.Reisinger, T.Priermeier, M.Beller, H.Fischer; *Angew. Chem.Int.Edn.Engl.*, **34**, 1844 (1995).
- [2] J.Campora, P.Palma, E.Carmona; *Coord.Chem. Rev.*, **207**, 195 (1999).
- [3] X.F.Luo, X.Hu, X.Y.Zhao, S.H.Goh, X.D.Li; *Polymer*, **44(18)**, 5285 (2003).
- [4] A.S.N.Murthy, A.R.Reddy; *Journal of Chemical Sciences*, **90(6)**, 519 (1981).
- [5] V.Razakantoanina, N.K.P.Phung, G.Jaureguiberry; *Parasitology Research*, **86(8)**, 665 (2000).
- [6] R.E.Royer, L.M.Deck, T.J.Vander Jagt; *Journal of Medicinal Chemistry*, **38(13)**, 2427 (1995).
- [7] M.R.Flack, R.G.Pyle, N.M.Mullen; *The Journal of Clinical Endocrinology & Metabolism*, **76(4)**, 1019 (1993).
- [8] R.Baumgrass, M.Weiwad, F.Erdmann; *Journal of Biological Chemistry*, **276(51)**, 47914 (2001).
- [9] Chitrapriya Nataraj, Mahalingam Viswanathan, Zeller Matthias, Natarajan Karuppanan; *Polyhedron*, **27**, 1573 (2008).
- [10] A.Majumder, G.M.Rosair, A.Mallick, N.Chattopadhyay, S.Mitra; *Polyhedron*, **25**, 1735 (2006).