Synthesis and Characterization of Two New Hydrazide Palladium Complexes

S. Ghamami *, A. Lashgari, R. Ghahremani Gavineh Roudi

Department of Chemistry, Faculty of Science, Imam Khomeini International University, Qazvin, IRAN

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Abstract

The reaction between two acetohydrazide ligands that are, N-2,4-dinitrophenyl N/-3-nitrobenzylidenehydrazine, TNBH, and Tris N-2,4dinitrophenyl N/-3-phenyl allylidenehydrazine, TDPH, with PdCl₂ produced two new ionic palladium complexes. These compounds are characterized by spectroscopic techniques. The electronic and vibrational spectra of these complexes have been measured and studied.

1. 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 [1,2]. 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 [3] and biochemically relevant studies of metal complexes [4-8]. 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.

2. Experimental

2.1. Materials and Instruments

Acetonitrile (Fluka, P.A.) was distilled several times from phosphorus pentaoxide before using, thereby reducing its water content to 4 ppm. Nitrophenyl was purchased from Merck Company. PdCl₂ (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

* Corresponding Author:
E-mail, shghamami2012@yahoo.com – Tel, (+98) 2818371378 – Fax, (+91) 2813780040

spectrophotometer. The percentages of elements in compositions were obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, and Tehran.

2.2. Synthesis of [Pd(TNBH)]Cl₂

[Pd(C₁₃H₁₀N₅O₄)]Cl₂ was prepared by dissolving PdCl₂ (0.01 g, 0.05 mmol) in DMSO and adding this solution to a solution of Tris N-2,4dinitrophenyl N/-3-nitrobenzylidenehydrazine (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 (Figure 1) and IR (Figure 2) spectra were all consistent with the complex structure. Yield: 93%. m.p. 239 °C. IR (KBr): υ 3279, 3099, 1615, 1512-1330, 523 cm⁻¹.

2.3. Synthesis of [Pd(TDPH)]Cl₂

[Pd(C₁₅H₁₃N₄O₄)]Cl₂ was prepared as follow:

To a solution of PdCl₂ (0.01 g, 0.05 mmol) in acetonitrile, the solid powder Tris N-2,4dinitrophenyl N/-3-phenyl allylidinehydrazine, TDPH (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 (Figure 3) and IR (Figure 4) data were all consistent with the complex structure. m.p.: 256-258 °C. IR (KBr): $\nu$ 3279, 2925, 1620, 1504, 1336, 516 cm$^{-1}$.

3. Results and discussion

The reaction of Pd(II) salt with the, TNBH, TDPH, ligands result in the formation of [ML] for M = Pd(II). Complexes are quite stable and could be stored without any appreciable change. Complex was characterized by several techniques using UV-Visible and IR measurement. The spectral data of the complex has good relationship with the literature data.

[Pd(C$_{13}$H$_{10}$N$_5$O$_6$)]Cl$_2$ was prepared by the reaction of C$_{13}$H$_{10}$N$_5$O$_4$ and PdCl$_2$ in DMSO solvent as follows:

$$C_{13}H_{10}N_5O_6 + PdCl_2 \rightarrow [Pd(C_{13}H_{10}N_5O_4)]Cl_2$$
In the vibrational spectrum of this compound, the known bands of cation and anion were seen such as νC=N which was found at 1615 cm⁻¹ and confirmed with literature data (Table 1). There is one absorption in the TNBH ligand electronic spectrum (Table 2).

**Table 1.** The frequencies (cm⁻¹) and assignment of cation and anion of TNBH.

<table>
<thead>
<tr>
<th>ν(cm⁻¹)</th>
<th>Assignment</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₃H₁₆N₆O₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1615</td>
<td>ν(C=N)</td>
<td>(s)</td>
</tr>
<tr>
<td>3279</td>
<td>ν(N-H)</td>
<td>(w)</td>
</tr>
<tr>
<td>3099</td>
<td>ν(C-H)</td>
<td>(w)</td>
</tr>
<tr>
<td>523</td>
<td>ν(Pd-N)</td>
<td>(m)</td>
</tr>
<tr>
<td>1330, 1512</td>
<td>ν(NO₂)</td>
<td>(s)</td>
</tr>
</tbody>
</table>

[Pd(C₁₅H₁₃N₄O₄)]Cl₂ was prepared by the reaction of PdCl₂ with C₁₅H₁₃N₄O₄ in acetonitrile solvent as follows:

\[
C_{15}H_{13}N_4O_4 + PdCl_2 \rightarrow [Pd(C_{15}H_{13}N_4O_4)]Cl_2
\]

In the vibrational spectrum of produced complex the characteristic bands were seen such as νC=N which was found at 1620 cm⁻¹ along the literature data (Table 3). There are three absorption bands in the electronic spectrum of this compound (Table 4).

**Table 2.** Transitions specifications of TNBH.

<table>
<thead>
<tr>
<th>λ (nm) (ε, M⁻¹cm⁻¹)</th>
<th>λ (nm) (ε, M⁻¹cm⁻¹)</th>
<th>λ (nm) (ε, M⁻¹cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>255 (176)</td>
<td>379 (128)</td>
<td>381 (298)</td>
</tr>
</tbody>
</table>

**Table 3.** The frequencies (cm⁻¹) and assignment of cation and anion of ligand TDPH.

<table>
<thead>
<tr>
<th>ν(cm⁻¹)</th>
<th>Assignment</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₃H₁₆N₆O₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1620</td>
<td>ν(C=N)</td>
<td>(s)</td>
</tr>
<tr>
<td>3279</td>
<td>ν(N-H)</td>
<td>(W)</td>
</tr>
<tr>
<td>2925</td>
<td>ν(C-H)</td>
<td>(W)</td>
</tr>
<tr>
<td>1504, 1336</td>
<td>ν(NO₂)</td>
<td>(S)</td>
</tr>
<tr>
<td>1504</td>
<td>ν(C=C)</td>
<td>(s)</td>
</tr>
<tr>
<td>516</td>
<td>ν(Pd-N)</td>
<td>(W)</td>
</tr>
</tbody>
</table>

**Table 4.** Transitions specifications of TDPH.

<table>
<thead>
<tr>
<th>λ₁ (nm) (ε, M⁻¹cm⁻¹)</th>
<th>λ₂ (nm) (ε, M⁻¹cm⁻¹)</th>
<th>λ₃ (nm) (ε, M⁻¹cm⁻¹)</th>
<th>λ₄ (nm) (ε, M⁻¹cm⁻¹)</th>
<th>λ₅ (nm) (ε, M⁻¹cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>223 (110)</td>
<td>237 (98)</td>
<td>266 (76)</td>
<td>305 (82)</td>
<td>395 (234)</td>
</tr>
</tbody>
</table>
4. Conclusion

Two complexes of TNBH and TDPH ligands with PdCl$_2$ 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.

Acknowledgements

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References

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