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SYNTHESIS AND SPECTRAL STUDIES OF COMPLEXES BETWEEN PALLADIUM AND SOME THIOSEMICARBAZONES

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SUMMARY

This paper reviews the synthesis and spectral studies of some complexes of palladium with thiosemicarbazones: Pd(L¹)NH₃ (L¹: pyruvic acid thiosemicarbazone) and Pd(Lⁱ)₂, (i: 2-4, thiosemicarbazone of: acetophenone (L²), benzaldehyde (L³), p-dimethylaminobenzaldehyde(L⁴)). The ligands and complexes are characterized by means of chemical analysis, thermal analysis, IR, ESI-MS and ¹H-NMR spectroscopy. The obtained data show that in Pd(L¹)NH₃, three coordinate sites are realized by S, N(1) and O-atoms of L¹ and the fourth coordinate site by NH₃-group; in Pd(Lⁱ)₂ complexes, Lⁱ acts as anionic bidentate ligands, two coordinate bonds realize through S and N(1) atoms. Especially, the obtained data ¹H-NMR spectrum of Pd(L³)₂ indicate that this complex exists in two isomers, supposed to be cis and trans, in DMSO solutions.

Keywords: thiosemicarbazone; palladium complex.

I - INTRODUCTION

Thiosemicarbazones and their complexes with transition metals are widely known as having a large range of biological applications, such as antiviral, antibacterial, antimalarial, antifungal, anti HIV and especially antitumor activities [1 - 3]. The compound p-acetamidobenzaldehyde thiosemicarbazone (thiacetazone) has been long time employed in the treatment of tuberculosis [4]. The biological activities of the compounds have been found that they depend not only on thiosemicarbazones but also on the nature of the metal ions [5, 6]. Most of metal complexes have higher activities than the free ligand, especially in case of precious metal complexes [7, 8]. In view of the above application, it is highly desirable to synthesize and characterize as many as possible the complexes and investigate their structures and properties.

In this paper, we report the synthesis and

characterization of Pd(II) complexes with some thiosemicarbazones derived from pyruvic acid (L¹), acetophenone (L²), benzaldehyde (L³), and p-dimethylaminobenzaldehyde (L⁴).

II - EXPERIMENT

Experimental work was carried out in air atmosphere. Solvents were distilled prior to use. All the chemicals used were of AnalR and were obtained from Aldrich. Metal salt were purchased from Merck and was used as received.

1. Analysis and physical measurements

¹H-NMR of the synthesized ligands and complexes were recorded in d₆-DMSO solvent at 500 MHz using Bruker Av500 equipment. The chemical shifts, δ, were given in ppm relative to TMS. Mass spectra were obtained by Electrospray Ionization (ESI) method using LC-MSD Trap SL instrument. The IR spectra were

recorded on a Nicolet Impact 410 spectrophotometer using KBr pellets. Thermal behaviors of the complexes when heating in air were studied from 30 to 1200°C using LabSys TG/DSC Sataram system. Metal contents were determined gravimetrically by precipitating palladium ion with dimethylglyoxime.

2. Synthesis of the ligands

The ligands were formed by reaction between thiosemicarbazide and a corresponding carbonyl compound in acidic (pH = 2 - 4) aqueous solution.

a) Synthesis of pyruvic acid thiosemicarbazone (H_2L^1)

0.91 g (0.01 mol) of thiosemicarbazide was first dissolved in water. Solution of HCl 0.1M was slowly added to increase solubility of thiosemicarbazide and to adjust pH of solution. To this solution, 0.69 ml of pyruvic acid in 30 ml water was added. The mixture was heated to 50°C for 3 hr. A pale yellow precipitate settled down on cooling, which was collected by filtration, washed with water and dried in desiccators to constant weight.

b) Synthesis of acetophenone thiosemicarbazone (HL^2)

20 ml hot ethanolic solution of 1.17 ml (0.01 mol) acetophenone was mixed with hot aqueous solution of 0.91 g (0.01 mol) of thiosemicarbazide. The contents were kept at 50°C for about 1 h in a water bath. After cooling, a yellow colored compound separated out. Precipitate was filtrated, washed with the solution 50% (by volume) of ethanol, then with diethyl ether and dried in desiccators.

c) Synthesis of benzaldehyde thiosemicarbazone (HL^3); *p*-dimethylaminobenzaldehyde thiosemi-carbazone (HL^4)

The same procedures were followed, as for HL^2 but heating the mixture under reflux with stirring for 3-4 hours. In these syntheses, the molar ratios between thiosemicarbazide and the carbonyl compound were remained as 1:1.

3. Synthesis of the complexes

The complexes were formed when aqueous solution of tetraammine palladium(II) chloride is mixed with ethanolic solution of a corresponding thiosemicarbazone. Aqueous solution of tetraammine palladium (II) chloride was obtained by exceed addition of NH_3 10% to solution of palladium (II) chloride.

a) Synthesis of $Pd(L^1)NH_3$

To a round-bottom-flask containing 0.16g (1mmol) of H_2L^1 in 20 ml ethanol, was added a solution of 1mmol tetraammine palladium (II) chloride. After 3h of stirring at room temperature, the yellow precipitates were filtered off and washed with 50% ethanol-water mixture. The products were dried in desiccators. Anal. %Pd Calc. 37.7%, Found 37.1%.

b) Synthesis of $Pd(L^2)_2$

Firstly, dissolve 0.38 g thiosemicarbazone HL^2 (2 mmol) in 30 ml of hot ethanol. Then add to this solution 20 ml of tetraammine palladium (II) chloride solution (1 mmol in $PdCl_2$). The obtained mixture was stirred for 2 - 3 hours at room temperature. On cooling, light yellow colored compound precipitated. The complex was filtered, washed with 50% ethanol-water mixture, diethyl ether then allowed to dry in vacuum desiccators. Anal. %Pd Calc. 21.7%, Found 20.9%.

c) Synthesis of $Pd(L^3)_2$; $Pd(L^4)_2$

These complexes were prepared in the same way, as above, but the reaction mixtures were refluxed for 3 h before cooled down to obtained complexes as precipitants. Anal. %Pd in $Pd(L^3)_2$: Calc. 23.0%, found 22.7%; in $Pd(L^4)_2$: Calc. 19.4%, found 20.6%;

III - RESULTS AND DISCUSSION

1. Thermal behavior of synthesized complexes

Thermal behaviors of palladium complexes of thiosemicarbazones were studied from 30 to 1200°C. In the present study, the TG lines remain unchanged when samples are heating from ambient temperature to 200°C, that indicates water is absent in complex molecules.

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In thermal analysis diagram of Pd(L¹)NH₃, endothermic peak in DTA curve was observed at near 250°C with the weight loss from the TG curve suggests that there is one molecule NH₃ in complex, which is further substantiated by qualitative analyses and NMR studies.

At higher temperature, in region of 300 - 700°C range, there are some broad exothermic peaks in DTA, accompanying with weight loss are observed in the TG curve. These peaks correspond to the simultaneous elimination and

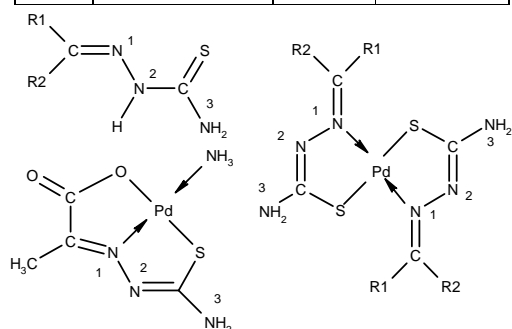
oxidation of organic ligands. The ultimate decomposition residues were found to correspond to palladium metal by X-Ray diffraction. The residues were weighed and compared to the theoretical value if the residue was metal, good agreement was found.

2. IR spectrum of the ligands and complexes

The most important bands and their tentative assignment in the IR spectra of the ligands and their complexes are presented in table 2.

Table 1: Ligand, complex structures and notations

R1	R2	Ligands	Comp. For.
- CH ₃	- COOH	H ₂ L ¹	Pd(L ¹)NH ₃
- CH ₃	- C ₆ H ₅	HL ²	Pd(L ²) ₂
- H	- C ₆ H ₅	HL ³	Pd(L ³) ₂
- H	-p C ₆ H ₄ N(CH ₃) ₂	HL ⁴	Pd(L ⁴) ₂



The positions of these bands provide significant indications regarding the bonding sites of the ligand molecules when complexes to Pd(II). In principle, the ligands can exhibit thione-thiol tautomerism since they contain thioamide NH-C-S functional group. The ν(S-H) bands at about 2600 - 2800 cm⁻¹ are absent from the IR spectra of schiff bases indicating that in the solid state the ligands remain as the thione isomer [9]. The bands appearing at about 830 cm⁻¹, ν(CS) [10, 11] in the spectrum of ligands are shifted to lower wave number, indicating that thione sulfur behaves as a donor group [12].

In other hand, strong bands observed at about 1500 cm⁻¹ can be assigned to ν(C=N) [11, 12]. This bands, except for Pd(L⁴)₂, shift towards lower wave number (Table 2) in the spectra of all metal complexes, suggesting the coordination of the azomethine groups to the central metal ion.

In addition, coordination via the nitrogen of the azomethine groups is indicated by a shift towards higher side of bands corresponding to δ(CNN) at about 1300 - 1400 cm⁻¹ [12].

Table 2: IR spectral data (cm⁻¹) of the ligands and complexes

Compounds	H ₂ L ¹	Pd(L ¹)NH ₃	HL ²	Pd(L ²) ₂	HL ³	Pd(L ³) ₂	HL ⁴	Pd(L ⁴) ₂
ν(OH)	3405	-	-	-	-	-	-	-
ν(C=N)	1512	1498	1527	1495	1540	1517	1516	1525
δ(CNN)	1340	1360	1295	1300	1372	1367	1363	1367
ν(C=S)	858	787	845	825	870	810	814	813

The absorb band at 3405 cm^{-1} in the IR spectrum of H_2L^1 was assigned for $\nu(\text{OH})$ [13] and disappeared in the spectrum of complex. That indicates the deprotonation of the ligand and O-hydroxyl atom bonded to metal ion.

3. Mass spectra of the ligands and complexes

ESI mass spectra of the ligands confirm the proposed formulas by showing the peaks corresponding to molecules ion $\text{M}^+ + 1$: H_2L^1 at 162 amu ($\text{C}_4\text{H}_7\text{N}_3\text{SO}_2$ calculated molecular mass 161 amu); HL^2 at 194 amu ($\text{C}_9\text{H}_{11}\text{N}_3\text{S}$ -193 amu); HL^3 at 180 amu ($\text{C}_8\text{H}_9\text{N}_3\text{S}$ -179 amu) and HL^4 at 223 amu ($\text{C}_{10}\text{H}_{14}\text{N}_4\text{S}$ - 222 amu). The abundance of molecular peaks in range of $10^4 - 10^6$ indicates that the synthesized ligands were stable at recording condition. $\text{M}+2/\text{M}$ ratios in spectra of all ligands vary from 4.5/100 to 6.0/100, as can be seen from MS data file, suggested that ligand molecules consist of one S atom, in another way, each ligand molecule contains only one thiosemicarbazide moiety.

The synthesized complexes were first subjected to Electron Impact ionization MS method, the peak abundance in range of 10 - 1000, were not high enough to be of consideration. That indicates, due to their poor in sublimation ability, these complexes are not suitable to be studied by EIMS. When using ESI MS, good mass spectra were obtained. Mass spectra of the complexes confirm the proposed formulas by showing the peaks corresponding to the molecules ion ($\text{M}^+ + 1$).

Complex $\text{Pd}(\text{L}^1)\text{NH}_3$: molecules ion ($\text{M}^+ + 1$) is found at 283 amu ($\text{PdC}_4\text{H}_8\text{N}_4\text{SO}$ calculated molecular mass 282 amu) (Fig. 1). Beside the molecular peaks, there existed many other peaks which may be attributed to fragments (267, 209, 192, 151 and 134 amu) formed by electrospray ionization process. Complex $\text{Pd}(\text{L}^2)_2$: molecular ion peak stands at 491 amu ($\text{PdC}_{18}\text{H}_{20}\text{N}_6\text{S}_2$ calculated molecular mass 490 amu). The peaks due to the various fragments are found at 361, 303 and 128 amu.

Complex $\text{Pd}(\text{L}^3)_2$: The presence of ESI mass spectral peak at 463 amu confirms the proposed formula ($\text{PdC}_{16}\text{H}_{16}\text{N}_6\text{S}_2$ calculated molecular mass 462 amu). A set of peaks observed in the range 384, 360, 316 and 288 amu are assigned to various fragments.

Complex $\text{Pd}(\text{L}^4)_2$: Molecular ion peak is found on spectral at 549 substantiated the proposed complex formula ($\text{PdC}_{20}\text{H}_{26}\text{N}_8\text{S}_2$ calculated molecular mass 548 amu). Other peaks found at 267, 209, 151, 134 and 76 amu may be distributed to complex fragments. The scheme below shows the simulated fragmentation pattern of this complex.

The relative peak abundance in molecular ion peak set was compared with theoretically calculated peak abundance. Theoretical calculations were done using Isotope Distribution Calculator software which is available online. Good agreement between experiment and calculation substantiates the proposed formulas of these complexes.

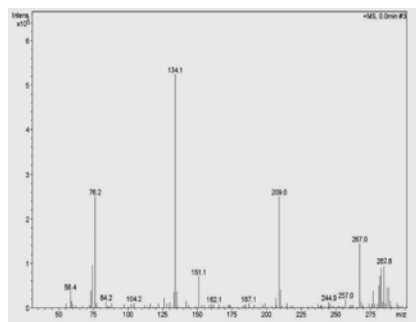
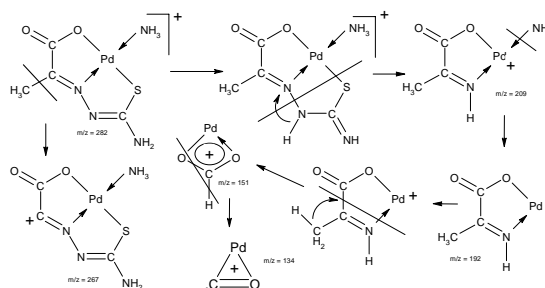


Fig. 1: ESI-MS spectrum of $\text{Pd}(\text{L}^1)\text{NH}_3$



Scheme 1: Simulated fragmentation patterns of $\text{Pd}(\text{L}^1)\text{NH}_3$

4. NMR spectra of complexes, the existence of two isomers in case of Pd(L²)₂ complex

Table 3 lists the selected ¹H-NMR chemical shifts for the synthesized ligands and complexes. Spectra of all the ligands show N(2)H- signals in range from 10.54 - 11.56 ppm, indicate that the ligands exist in thione isomer in DMSO solution. The relative positions of the resonances are in agreement with the

lower acidity of N(2)H for a keto thiosemicarbazone (H₂L¹; HL³) compared to an aldo thiosemicarbazone (HL²; HL⁴) [14]. However, these signals are absent in spectra of all complexes, that indicates the N(2)H deprotonation when the ligands coordinated to metal ion. This is in accordance with the coordination behavior of thiosemicarbazones [9, 11, 15].

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Table 3: ¹H-NMR spectral data (δ, ppm) of synthesized ligands and complexes

Compounds	OH	N(2)H	N(3)H ₂	CH=N	H _{ph}	NH ₃	CH ₃
H ₂ L ¹	12.06(1,s)	10.65(1,s)	8.68(1,s); 8.60(1,s)	-	-	-	2.08(3,s)
Pd(L ¹)NH ₃	-	-	7.61(2,s)	-	-	3.21(3,s)	1.94(3,s)
HL ²	-	10.20(1,s)	8.27(1,s); 7.92(1,s)	-	7.38- 7.93	-	2.30(3,s)
Pd(L ²) ₂	-	-	7.89(4,s)	-	6.38- 7.56	-	1.69(6,s)
	-	-	7.97(4,s)	-	6.57- 7.56	-	2.50(6,s)
HL ³	-	11.41(1,s)	8.18(1,s); 7.97(1,s)	8.05	7.38- 7.81	-	-
Pd(L ³) ₂	-	-	6.76(4,s)	7.34(2,s)	8.39- 7.84	-	-
HL ⁴	-	11.14(1,s)	7.96(1,s); 7.73(1,s)	7.93(1,s)	6.70- 7.73	-	3.00(3,s)
Pd(L ⁴) ₂	-	-	7.45(4,s)	7.32(2,s)	6.39- 6.60	-	2.97(6,s)

(Number of proton, s-singlet).

In addition, it is observed, as for each free thiosemicarbazone, two resonance signals for protons in NH₂ groups. Two protons in N(3)H₂ are chemically unequal due to N(3)-H...N(2) hydrogen bonding between one proton with N(2) atom. When coordinate to palladium ion, this hydrogen bonding in ligand will be broken due to the rotation about C—N² bond axis. That makes two protons in NH₂ groups become chemically equal and one resonance signal is observed for these protons as cited in table 3. NMR spectrum of H₂L¹ shows resonance signal for hydroxyl proton at 12.06 ppm. This resonance signals is absent in spectrum of corresponding complex, indicating the deprotonation from hydroxyl group.

In addition, the participation of NH₃ groups in case of Pd(L¹)NH₃ complex is demonstrated by the presence of resonance signal at 3.21 ppm. Beside that, in addition, the participation of NH₃ groups in case of Pd(L¹)NH₃ complex is demonstrated by the presence of resonance signal at 3.21 ppm. Beside that, phenyl protons in free ligands as well as in complexes are found as series of multiplets in the region of 6.38 - 8.39 ppm. Singlet signals ranging from 1.69 - 2.97 ppm in spectra of studied compounds are assigned for protons of CH₃ groups [13].

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The spectrum of Pd(L²)₂ complex is very interesting (Fig. 2). All the expected resonance signals were present but beside the main peaks there exist their "images", or in other way the

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resonance signal were duplicated. At first we thought it was impurity caused an eventually excess of ligands, but after several washing, the spectra remained as it was. The signals and their "images" signals are explained by the existence of two isomers in case of Pd(L²)₂. These isomers are supposed to be *cis* and *trans* isomers. According to NMR analysis, two isomers are supposed to be 1:2 in molar ratio. phenyl protons in free ligands as well as in complexes are found as series of multiplets in the region of 6.38 - 8.39 ppm. Singlet signals ranging from 1.69 - 2.97 ppm in spectra of studied compounds are assigned for protons of CH₃ groups [13].

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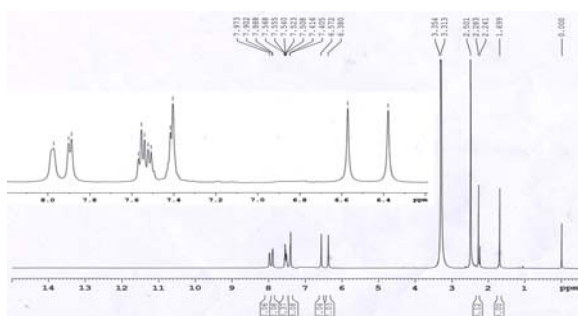


Fig. 2: NMR spectra of Pd(L²)₂

IV - CONCLUSIONS

Four new complexes of Pd were synthesized by employing the ligands pyruvic acid thiosemicarbazone, acetophenone thiosemicarbazone, benzaldehyde thiosemicarbazone, p-dimethylaminobenzaldehyde thiosemicarbazone. The complexes are characterized by means of chemical analysis, thermal analysis, IR, ESI-MS and ¹H-NMR spectroscopy. The obtained data show that in palladium complex with pyruvic acid thiosemicarbazone, three coordinate sites are realized by S, N(1) and O-atoms of ligand and the fourth coordinate site by NH₃-group; in the others Pd(L¹)₂, the ligands act as anionic bidentate ligands, two coordinate bonds realize through S and N(1) atoms.

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