Research Article

Synthesis, Spectral and Antimicrobial Investigation of Some New Coordination compounds of Palladium (II) with Biologically Active Nitrogen donor Ligands

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Accepted on: 12-09-2016; **Finalized on:** 30-11-2016.

ABSTRACT

Some new Pd (II) complexes have been synthesized with biologically active nitrogen donor ligands. The ligands used in these studies are semi carbazones and thiosemicarbazones and prepared by the condensation of diketones with thiosemicarbazides and semi carbazide hydrochloride in 1:2 molar ratio using ethanol as a reaction medium. The geometry and coordination pattern of complexes were confirmed by elemental analysis, IR and NMR (^{1}H, ^{13}C) spectral studies. The metal complexes are found to be more potent than the ligands and are quite encouraging.

Keywords: Palladium(II) complexes, Coordination compounds, Semicarbazone, Thiosemicarbazone, Antimicrobial activities, Spectral studies.

INTRODUCTION

Thiosemicarbazone and semicarbazone are important classes of compounds which have long attraction owing to their remarkable biological and pharmaceutical properties such as antibacterical, antiviral, antimalarial and antineoplastic activities[1]. These compounds play significance role in numerous biological systems due to their coordinating ability with various transition metals to form organometallic compounds. The coordination chemistry of organometallic compounds has a vital role as ligands from last two decades [2,3]. Organometallic compounds containing nitrogen oxygen and sulphur donor atoms have structurally identical with natural biological systems due to presence of azomethine groups[4]. Azomethine linkage of Schiff bases plays an important role in medical field such as Antimicrobial and Anticancer activity. These activities encouraged the development of some more potent and significant compounds and metal complexes such as palladium (II) complexes.

Azomethine group (-C= N-) containing compounds typically known as Schiff bases have been synthesized by the condensation of primary amine with active carbonyls [5-10]. Schiff bases have been studies extensively as class of ligand [11-12]and are known to coordinate with metal ion through the nitrogen atom. Coordination compound are compound containing one or more coordinate bonds, which is a link between a pair of electron in which both electrons are donated by one of the atom and the donor site may be the Nitrogen of (NH_2) or (-CN) or Oxygen of (-OH) and Sulphur of (-SH). In the last few decades Schiff base ligands have received more attention mainly because of their vide application in formation of C-C, C-O, C-N and C-S bonds in the field of catalyst. Due to the higher cellular uptake and rapid hydrolysis Pd (II) complexes has greater activity for their corresponding analogues in human. Coordination compound of Pd (II) which have N/O/S donor atom have enormous biological importance [13-16], therefore its widely used for Suzuki cross coupling[17], Heck[18] reaction and Oligomerization of ethylene[19]. Antifertility and Anticancer activities of palladium (II) coordination compound have been reported earlier. Palladium (II) metal complexes continuously used in chemotherapy as well as in catalysis and it's the part of continuing interest [20].

This paper includes the synthesis, spectral studies and antimicrobial activities of semicarbazone and thiosemicarbazone moiety and their metal complexes with palladium (II).

MATERIALS AND METHODS

Chemical and instrumentation

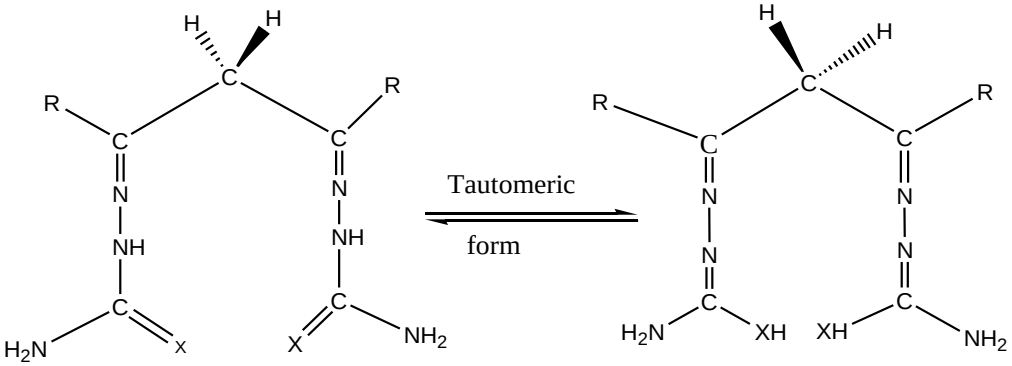
1-Phenyl butane-1,3- dione, pentane -2,4-dione, ethanedione, were purchased from HIMEDIA, palladium acetate was purchased from HIMEDIA. The solvent and chemicals used in experimental work were analytical grade and dried by standard procedure. Reactions were carried out under anhydrous condition. Molecular weight was determined by Rast camphor method[21]. The CHN elemental analysis was determined using a Thermo Finnigan CE 125 CHN analyser. Fourier Transform Infrared spectra of synthesized metal complexes were recorded on SHIMADZU FTIR spectrometer in the range of 4000-400cm^{-1} using KBr disc. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Jeol Al 300 MHz spectrometer. TMS used as reference nuclei and the solution was DMSO-d6. Nitrogen was estimated by Kjeldahl's method. Chlorine was estimated by Volhard's method. Palladium was estimated gravimetrically and sulphur was estimated by the messenger method [22]. Ultraviolet absorption spectra were measured on Perkin Elmer UV visible spectro-photometer in the range 200-600 nm.

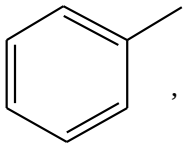
Synthesis of ligands

Schiff bases were synthesized by the condensation of 1-phenyl butane-1,3-dione, ethanedial and pentane 2,4-dione with thiosemicarbazide and semicarbazide hydrochloride in the presence of sodium acetate. The reactions were carried out in 1:2 molar ratio using ethanol as reaction medium. The solution was refluxed on a water bath for 2h and then allowed to cool at room temperature. The crystalline solids were separated out and purified by recrystallization [23]from the same solvent[24-26] and dried over anhydrous calcium chloride under vacuum. Physical properties and analysis of ligands are recorded in Table1.

Synthesis of metal complexes

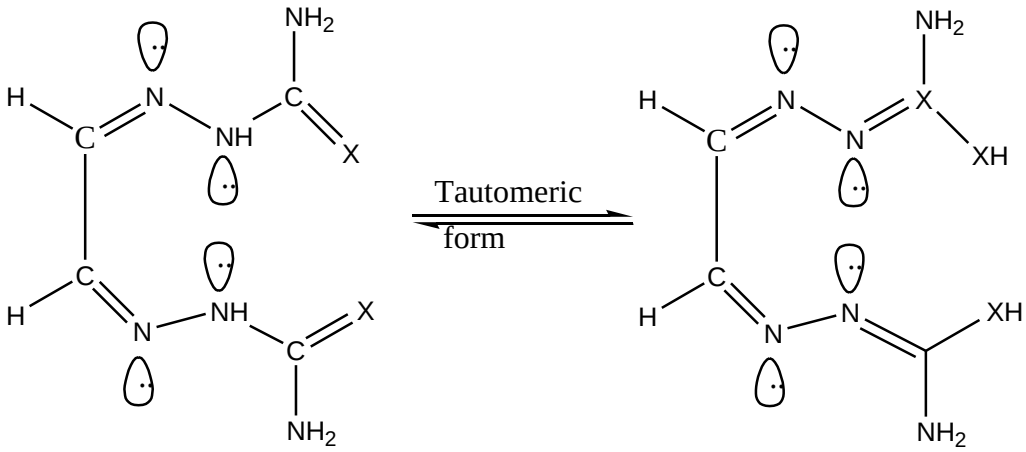
All new complexes were prepared in 1:1 [M:L] molar ratio by the addition of palladium acetate and ligands in acetonitrile solution. The reactions were carried out in round bottom flask for 5-6 hours. The mixture was refluxed on a fractional column. The resulting derivatives were recovered by filtration, washed with same solvent and dried in vacuum. The purity of the compounds was checked by TLC using silica gel-G as an adsorbent. The physical properties and analytical data of complexes are listed in table 2.



X= O, S 1. R =  ,

2. —CH_3

[Semicarbazone and thiosemicarbazone of acetylacetone and benzoylacetone]



3. X= O, S [Semicarbazone and thiosemicarbazone of glyoxale]

Scheme 1

Keto- enol form of ligands

Table1: Analytical and physical data of ligands

S.N.	Compounds	Colour/ State	Mol. Wt.	Melting point	Elemental analysis (%)		
					C	H	N
1	Pentane-2,4 dione Semicarbazone (L^1H)	Milky White/solid	213.16 (214.242)	275	39.24 (38.94)	6.58 (6.34)	39.23 (39.00)
2	Pentane-2,4 dione thiosemicarbazone (L^2H)	Shiny yellow/solid	245.18 (246.362)	230	34.12 (33.98)	5.72 (5.70)	34.12 (34.10)
3	1-phenyl-butane-1,3-dione semicarbazone (L^3H)	White/solid	275.36 (276.308)	260	52.15 (52.05)	6.25 (6.02)	30.42 (30.37)
4	1-phenyl-butane-1,3-dione thiosemicarbazone (L^4H)	Slightly yellow/solid	307.38 (308.428)	210	46.72 (46.60)	5.22 (5.21)	27.25 (27.23)
5	Ethanedialsemicarbazone (L^5H)	Pale yellow/ Powder	171.15 (172.164)	280	27.90 (27.88)	4.68 (4.66)	48.82 (48.56)
6	Ethanedial thiosemicarbazone (L^6H)	Yellow/ Powder	203.28 (204.284)	235	23.51 (23.47)	3.94 (3.89)	41.14 (41.06)

Table2: Analytical and physical data of palladium (II) complexes

S.N.	Complexes	Colour/ State	Mol. Wt.	Melting point	Elemental analysis (%)			
					C	H	N	Pd
1	$C_7H_{12}O_2N_6Pd$	Brown /solid	318.482 (317.37)	280	26.39 (25.56)	3.79 (3.24)	26.37 (25.77)	33.40 (32.89)
2	$C_7H_{12}S_2N_6Pd$	yellow/ solid	350.202 (342.11)	240	24.06 (23.45)	3.45 (2.98)	23.98 (22.89)	30.38 (29.98)
3	$C_4H_6O_2N_6Pd$	Gray/solid	276.404 (275.40)	270	17.38 (16.24)	2.18 (2.01)	30.39 (29.30)	38.49 (37.57)
4	$C_4H_6S_2N_6Pd$	Chocolate/ Solid	308.524 (305.25)	220	15.57 (14.44)	1.96 (1.30)	27.22 (27.03)	34.48 (33.40)
5	$C_{12}H_{14}O_2N_6Pd$	yellow/ Powder	380.548 (377.43)	290	37.87 (36.66)	3.708 (2.56)	22.07 (21.36)	27.97 (26.46)
6	$C_{12}H_{14}S_2N_6Pd$	Dark Yellow/ Powder	412.668 (409.67)	250	34.92 (33.68)	3.66 (2.67)	20.35 (19.78)	25.78 24.98)

Biological Activity

Antibacterial Activity

Semicarbazones and thiosemicarbazonesand their corresponding Pd(II) complexes were screened in vitro for antibacterial activity against four of the test organism-Escherichia coli, B. Thurigiensis, Proteus mirabilis and staphylococcus aureus, bacterial strain using a paper disc diffusion method [27]. The nutrient agar medium and 5 mm diameter paper disc of whatman filter paper no.1were used. The compounds under investigation were dissolved in methanol to the given concentration of 500 and 1000 ppm. The filter paper soaked in these solution dried and then placed in Petri plates were incubated for 24 h at 28˚ and the inhibition zone around each disc was measured. The antibacterial activity displayed by various compounds against pathogenic bacteria is shown in table 3. The results are quite promising. It is also noted that sulphur containing ligands as well as their complexes are more active than their oxygen containing counterpart [28]. Streptomycin was used as a reference compound for antibacterial activity.

Antifungal Activity

Aspergillusflavus, AspergillusnigerFusariumoxyporum, and Rhizopusphaseolin were used for evaluate the antifungal activity of palladium (II) complexes and all synthesized ligands. For antifungal activities agar plate technique have been used. The samples were mixed with DMF and then mixed with the medium. The linear growth of the[29] fungus was recorded by measuring the

diameter of colony after 96 hours and the percentage inhibition was calculated as 100cc, where cc are the diameter of the fungus colony in the control and test plates. The data of antifungal activity was listed in table 4.

Table 3: Antibacterial activity of ligands and their corresponding complexes

S.N.	Compounds	Diameter of inhibition zone (mm)							
		Bacillus thurigiensis		*Escherichia coli*		*Proteus milamilis*		*Staphylococcus aureus*	
		500 (ppm)	1000 (ppm)	500 (ppm)	1000 (ppm)	500 (ppm)	1000 (ppm)	500 (ppm)	1000 (ppm)
1	$C_7H_{14}O_2N_6$	4	6	6	9	3	7	7	9
2	$C_7H_{14}S_2N_6$	6	10	7	10	4	8	7	10
3	$C_4H_6S_2N_6Pd$	4	8	5	8	4	7	6	8
4	$C_7H_{12}O_2N_6Pd$	9	10	11	14	7	9	12	15
5	$C_7H_{12}S_2N_6Pd$	10	14	9	14	8	15	15	16
6	$C_4H_6S_2N_6Pd$	9	12	9	13	9	12	13	15
7	Streptomycin	14	16	12	14	15	16	15	17

Table 4: Antifungal activity of ligands and their corresponding complexes

S.N.	Compounds	Diameter of inhibition zone (mm)											
		Aspergillus flavus			*Aspergillus niger*			*Fusarium oxysporum*			*Rhizopus phaseoli*		
		50	100	200	50	100	200	50	100	200	50	100	200
1	$C_7H_{14}O_2N_6$	35	40	51	36	40	60	40	46	61	53	63	70
2	$C_7H_{14}S_2N_6$	40	44	56	37	42	60	48	50	65	56	66	83
3	$C_4H_8S_2N_6$	50	51	56	52	55	57	51	55	69	66	70	83
4	$C_7H_{12}O_2N_6Pd$	30	38	51	50	48	72	44	50	63	59	64	73
5	$C_7H_{12}S_2N_6Pd$	40	45	57	53	55	67	50	48	70	57	70	75
6	$C_4H_6S_2N_6Pd$	51	52	57	61	63	60	53	56	73	70	74	89
7	Mycostatin	70	85	99	70	90	100	71	82	95	70	87	99

Insecticidal Activity

semicarbazone and thiosemicarbazone and their palladium(II) complexes have been screened for insecticidal activity against Helicoverpaarmigera. The studies have been conducted on 2nd and 3rdinstars larval stage of the insects. H. Armigera has a long history of insecticide resistance to DDT, Endosulfan, Pyrethroids, Carbonates and Organophosphates. But it is shows less resistance against[30]endosulfan. Hence it may say that this work is an active effort to make a new insecticide which show less resistance to H. Armigera like endosulfan.

RESULTS AND DISCUSSION

The metal complexes were obtained by the addition of semicarbazone and thiosemicarbazone and Pd $(OOCCH_3)_2$in 1:1 (M:L) molar ratio using acetonitrile as a reaction medium. The reaction of starting material of metal with semicarbazone and thiosemicarbazone has been shown by the following general equation.

$$Pd(OOCCH_3)_2 + L^{1\text{-}6}H \xrightarrow{\text{Acetonitrile}} [Pd(L^{1\text{-}6})] + 2CH_3COOH$$

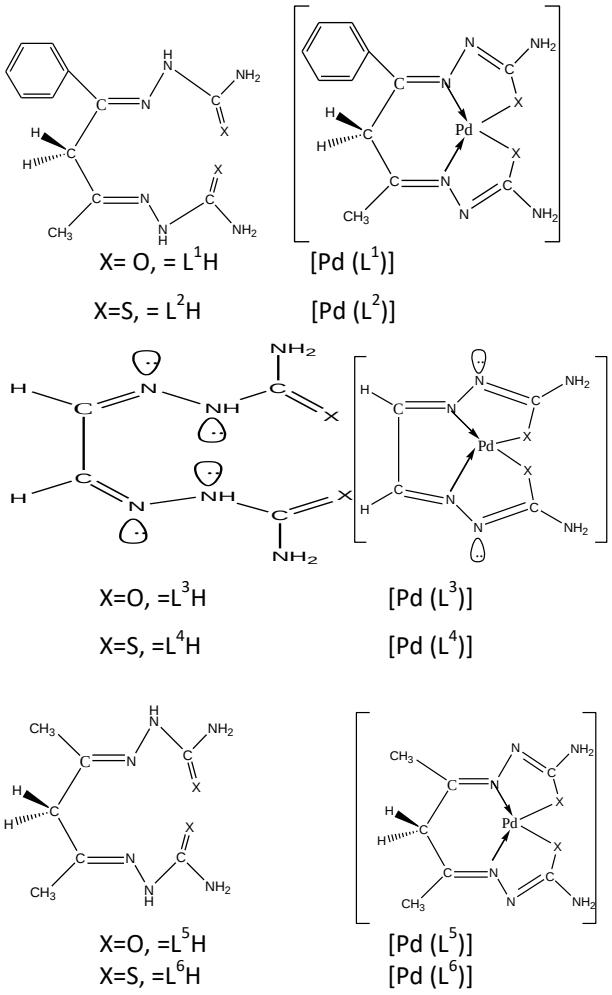
The complexes were obtained in solid form, and could be separated by filtration. The molecular weight of the newly synthesis complexes were determined by Rast camphor method showed them to be monomers. The proposed structure of ligands and metal complexes on the basis of spectral characterization are shown under scheme 2.

Spectroscopic Characterization

IR Spectra

To recognize the functional group present in the ligands and metal complexes FT-IR studies have been done. A study and comparison of IR spectra of ligands and its metal complexes (Table 5) infer that the metal is coordinated through N, S or O of the ligands. In the ligands there are two bands at 3400 and 3440cm^{-} appears which are characteristic of $-NH_2$ stretching modes. Both of two bands remain unchanged in the

spectra of complexes. A broad band due to –NH vibration in the region 3100-2950cm^{-} appears in ligand but disappeared in the complexes. The absorption at 1605 cm^{-} in free ligand can be attributed to (C=N) stretching vibration of imine nitrogen[31]. The negative shift (10-20 cm^{-}) of new (C=N) bonds observed in all complexes indicates the involvement of azomethine nitrogen upon complexation. Most of the IR spectral bands appears in ligands are practically unchanged in the complexes but the appearances of new bands with medium to weak intensity in the spectra of complexes in the region 500-450 cm^{-}, 400-350 cm^{-} and 340-310 cm^{-} due to Pd-N, Pd-O and Pd-S respectively.



Scheme 2

(Ligands and their corresponding Pd (II) complexes)

^{1}H NMR Spectra

The ^{1}H NMR spectra of ligands and their corresponding metal complexes recorded in DMSO-d6. TMS was used as internal reference. A broad peak at δ7.90-7.30ppm due to -NH proton and it is disappeared in the spectra of complexes. The appearance of signal due to –NH_2 proton at the same position in the ligand and its complexes shows that this group does not involve in coordination[32]. The azomethine proton signal (H-C=N) was detected at δ8.45ppm, which appears at δ8.55ppm in the spectra of complexes due to the coordination of azomethinenitrogen to the metal atom. The NMR spectral data of ligands and their corresponding metal complexes are listed in table 6.

Table 5: IR spectral data of Ligands and their corresponding complexes (in cm^{-})

SN	Compounds	υ(C=N)	υ(M-S)	υ (M-O)	υ (M-N)
1	$C_{12}H_{14}O_2N_6$	1620	-	-	-
2	$C_{12}H_{14}O_2N_6Pd$	1625	-	360	442
3	$C_4H_6O_2N_6Pd$	1616	-	367	445
4	$C_{12}H_{14}S_2N_6Pd$	1620	315	-	448
5	$C_4H_6S_2N_6Pd$	1630	317	-	456
6	$C_{12}H_{14}S_2N_6$	1645	-	-	-
7	$C_4H_6S_2N_6$	1625	-	-	-
8	$C_4H_6O_2N_6$	1630	-	-	-

Antimicrobial Results

It has been found out that the activity of metal complexes against bacteria and fungi were more potent than their respective ligands. The activity of complexes against pathogens indicated that the complexation to metal enhance the activity of the ligand. The reason of the enhancement of activity of metal complexes is chelation and partial sharing of its positive charge with the donor groups[33]. The other factors which enhance the activity of complexes are solubility, conductivity and bond length between the metal and ligands[34]. The complexes show moderate activity as compared to standard bactericide and fungicides.

Acknowledgement: The authors are thankful to the Head of the Department of Chemistry, University of Rajasthan, Jaipur, for providing laboratory facilities. KavitaYadav is thankful to UGC for providing financial support.

Table 6: ^{1}H NMR spectral data of Ligands and their corresponding complexes in (δ ppm)

SN	Compounds	-NH_2	-CH_3	NHC=O	H-CN	Aromatic protons	=CH_2
1	$C_{12}H_{14}O_2N_6$	3.23	2.00	7.42	-	6.50-7.90	3.36
2	$C_{12}H_{14}O_2N_6Pd$	3.26	2.10	-	-	6.99-8.23	4.22
3	$C_{12}H_{14}S_2N_6$	3.10	2.05	7.30	-	7.00-8.20	3.67
4	$C_{12}H_{14}S_2N_6Pd$	3.14	2.01	-	-	6.67-8.40	3.75
5	$C_4H_6O_2N_6$	3.05	-	7.34	8.45	-	-
6	$C_4H_6O_2N_6Pd$	3.10	-	-	8.55	-	-
7	$C_4H_6S_2N_6$	2.99	-	7.30	8.30	-	-
8	$C_4H_6S_2N_6Pd$	3.08	-	-	8.50	-	-

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Source of Support: Nil, **Conflict of Interest:** None.