Synthesis, Structural, and Antibacterial Studies of Some Transition Metal Complexes Derived from Thiosemicarbazone and Semicarbazone

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A series of metal complexes of Pd(II), Pt(II), Rh(III), Ir(III), and Ru(III) with thiosemicarbazone and semicarbazone of 2-acetyl thiophene have been synthesized. Their structures were determined on the basis of elemental analyses; molar conductance; magnetic susceptibility measurements; and IR, ^1H NMR, and electronic spectral studies. On the basis of molar conductance, the complexes may be formulated as $[M(L)_2]Cl_2$ and $[M'(L)_2Cl_2]Cl$ [where $M = Pd(II)$, $Pt(II)$ and $M' = Rh(III)$, Ir(III), and Ru(III)] due to their 1:2 and 1:1 electrolytic nature. On the basis of IR, ^1H NMR, and electronic spectral studies, an octahedral geometry has been assigned for Rh(III), Ir(III), and Ru(III), while square planar geometry has been assigned for the Pd(II) and Pt(II) complexes. The synthesized ligands and their complexes have been screened for bactericidal activity against several bacterial species (i.e., B. macerans, A. aureus, E. coli), and it is shown that the metal complexes act as more active antimicrobial agents than the uncomplexed ligands from which they derive.

Keywords Biological screening; semicarbazone; thiosemicarbazone; transition metal complexes

INTRODUCTION

Thiosemicarbazones and their metal complexes are widely known as having a large range of biological applications such as antiviral, antifungal, antibacterial, antimalarial, and anticancer agents.[1−7] The activity of these compounds is strongly dependent upon the nature of the heteroaromatic ring and the position of attachment to the ring, as well as the form of the thiosemicarbazone moiety.[8,9] Thiosemicarbazones and semicarbazones usually react with metallic cations, giving complexes in which the ligand behaves as a chelating agent bonding coordination through the hydrazine nitrogen and sulfur/oxygen atoms.[10]
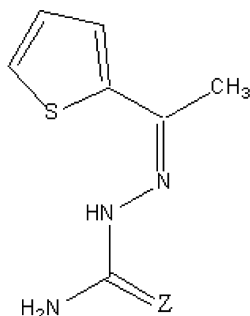
Z =S, for L^1

Z =O, for L^2

FIGURE 1 Suggested structure of the ligands.

After the discovery of the chemotherapeutically active platin complexes of thiosemicarbazide derivatives,[11] many thiosemicarbazone compounds showing biological activity were synthesized. There are only a few reports of palladium and platinum complexes of thiosemicarbazones.[12–14] It is well known that several metal ions enhance the biological activities of thiosemicarbarbazones; the new metals to add to such a list are ruthenium and rhodium.[15,16] Much attention has been drawn towards the chemistry of ruthenium and rhodium in different coordination spheres.[17,18] Due to the different oxidation states of ruthenium and rhodium, their reactivity depends upon the stability of the oxidation states. Due to the growing interest of thiosemicarbazones of palladium, platinum, ruthenium, and rhodium metal ions, here we report the synthesis, characterization, and biological activities of Pd(II), Pt(II), Rh(III), Ir(III), and Ru(III) complexes of 2-acetyl thiophene thiosemicarbazone and semicabazone (Figure 1).

RESULTS AND DISCUSSION

A systematic study of the reactions of metal chlorides with ligands in a 1: 2 molar ratio has been carried out. The reactions can be represented by the following reactions:

$$L_2 + MCl_2 \xrightarrow{\text{Reflux}} ML_2Cl_2$$

$$L_2 + M'Cl_3 \xrightarrow{\text{Reflux}} M'L_2Cl_3$$
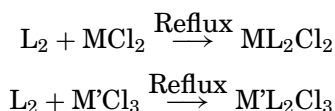
where L=L^1, L^2, M=Pd(II), Pt(II), and M'= Rh(III), Ir(III) and Ru(III).

On the basis of elemental analysis, the complexes were assigned to possess the composition as shown in Table I. The Pd(II) and Pt(II) complexes are 1:2 electrolytes with conductance values of 202–212 $\Omega^{-1}cm^2mol^{-1}$. However, the molar conductance data of the Rh(III), Ir(III), and Ru(III) complexes lies in the range 92–102 $\Omega^{-1}cm^2mol^{-1}$ indicating a 1:1 electrolytic nature. Thus these complexes may be formulated as $[M(L)_2]Cl_2$ and $[M'(L)_2Cl_2]Cl$ [where L= $L^1$and L^2, M = Pd(II), Pt(II) and M'= Rh(III), Ir(III), and Ru(III)].

^{1}H NMR Spectra

The ^{1}H NMR spectra of the free ligands show three singlets at δ 3.40–3.46, 11.91–11.95, and 8.01–8.09 ppm due to -NH_2 proton, -NH proton, and azomethane proton (CH=N-), respectively. The -NH_2 proton and -NH proton gives the same singlet in the complexes, which indicates that these groups are involved in coordination. The azomethane proton signal shows a change as a downfield shift in the complexes, indicating involvement of nitrogen in coordination (Table II).

IR Spectra

The IR spectra of the free ligands display two sharp bands at *ca* 3432 and 3357 cm^{-1}, assignable to asymmetric and symmetric NH_2 groups, respectively, which remain at almost the same positions in the metal complexes, suggesting that amino group is not involved in the coordination. The bands at 1592 and 1579 cm^{-1} in ligands L^1 and L^2, respectively, due to $\nu(C=N)$ are shifted to lower wave numbers in the metal complexes, suggesting coordination through the azomethane nitrogen.[19,20] The strong bands at 756 cm^{-1} and 1670 cm^{-1} are due to $\nu(C=S)$ and $\nu(C=O)$ groups, respectively. Upon complex formation, the position of these bands is shifted towards the lower side, indicating coordination of the sulfur and oxygen atom to the central metal atoms.[21,22] Bands at *ca* 454–475, 308–318, and 411–420 cm^{-1} can be assigned to $\nu(M=N)$, $\nu(M=S)$, and $\nu(M=O)$, respectively. The appearance of these bands further supports the bonding of the ligands to the metal through the nitrogen, sulfur, and oxygen atoms of $\nu(C=N)$, $\nu(C=S)$, and $\nu(C=O)$ groups respectively (Table III).

TABLE I Analytical Data for Ligands (L^1 and L^2) and Their Metal Complexes

Compound	Empirical formula	Yield (%)	M.P. (°C)	Color	Analysis found (Calcd.) %				Molar Cond.[a] ($\Omega^{-1}cm^2\,mol^{-1}$)
					C	H	N	M	
L^1	$C_7H_9N_3S_2$	70	160	White	42.25 (42.21)	4.50 (4.52)	21.13 (21.11)	—	—
$[Pd(L^1)_2]Cl_2$	$PdC_{14}H_{18}N_6S_4Cl_2$	66	212	Light Yellow	29.20 (29.22)	3.10 (3.13)	14.59 (14.61)	18.40 (18.43)	Diamagnetic
$[Pt(L^1)_2]Cl_2$	$PtC_{14}H_{18}N_6S_4Cl_2$	70	215	Shiny Yellow	25.34(25.30)	2.68(2.71)	12.60 (12.65)	29.42 (29.37)	Diamagnetic
$[Rh(L^1)_2Cl_2]Cl$	$RhC_{14}H_{18}N_6S_4Cl_3$	62	225	Brown	31.23 (31.26)	3.39 (3.35)	15.60 (15.63)	12.76 (12.78)	Diamagnetic
$[Ir(L^1)_2Cl_2]Cl$	$IrC_{14}H_{18}N_6S_4Cl_3$	74	230	Brown	28.10 (28.16)	2.27 (3.02)	14.05 (14.08)	21.40 (21.45)	Diamagnetic
$[Ru(L^1)_2Cl_2]Cl$	$RuC_{14}H_{18}N_6S_4Cl_3$	65	235	Light Brown	31.30 (31.34)	3.32 (3.35)	15.62 (15.67)	12.56 (12.60)	1.86
L^2	$C_7H_9N_3OS$	68	193	White	45.87 (45.90)	9.80 (9.84)	22.93 (22.95)	—	—
$[Pd(L^2)_2]Cl_2$	$PdC_{14}H_{18}N_6O_2S_2Cl_2$	64	220	Yellow	30.90 (30.94)	3.28 (3.31)	15.42 (15.47)	19.49 (19.52)	Diamagnetic
$[Pt(L^2)_2]Cl_2$	$PtC_{14}H_{18}N_6O_2S_2Cl_2$	65	227	Yellow	26.52 (26.58)	3.01 (2.85)	13.31 (13.29)	30.89 (30.85)	Diamagnetic
$[Rh(L^2)_2Cl_2]Cl$	$RhC_{14}H_{18}N_6O_2S_2Cl_3$	58	232	Black	29.19 (29.22)	3.15 (3.11)	14.56 (14.61)	17.87 (17.91)	Diamagnetic
$[Ir(L^2)_2Cl_2]Cl$	$IrC_{14}H_{18}N_6O_2S_2Cl_3$	64	218	Dark Brown	25.34 (25.30)	2.68 (2.71)	12.67 (12.65)	28.90 (28.92)	Diamagnetic
$[Ru(L^2)_2Cl_2]Cl$	$RuC_{14}H_{18}N_6O_2S_2Cl_3$	55	225	Light Brown	29.27 (29.32)	3.00 (3.14)	14.71 (14.66)	17.60 (17.63)	1.84

TABLE II ^{1}H NMR Spectral Data (δ ppm) of the Ligands and Their Metal Complexes

Compounds	-NH$_2$	-NH	HC=N
L^1	3.46	11.91	8.09
[Pd(L^1)Cl$_2$]	3.44	11.90	8.28
[Pt(L^1)Cl$_2$]	3.45	11.92	8.32
[Rh(L^1)$_2$Cl$_2$]Cl	3.46	11.92	8.29
[Ir(L^1)$_2$Cl$_2$]Cl	3.47	11.91	8.30
L^2	3.40	11.95	8.01
[Pd(L^2)Cl$_2$]	3.41	11.94	8.22
[Pt(L^2)Cl$_2$]	3.41	11.93	8.25
[Rh(L^2)$_2$Cl$_2$]Cl	3.42	11.95	8.20
[Ir(L^2)$_2$Cl$_2$]Cl	3.40	11.96	8.23

Magnetic Moments and Electronic Spectra

Pd(II) and Pt(II) Complexes

All the complexes are diamagnetic as expected for square planar d^8 metal complexes. The electronic spectra of Pd(II) and Pt(II) complexes show three d-d spin-allowed transitions. These correspond to the transitions from the three lower lying "d" levels to the empty d$_{x^2-y^2}^2$ orbital. The ground state is $^1A_{1g}$ and excited states corresponding to the $^1A_{2g}$, $^1B_{1g}$, and ^1E_g transitions in order of increasing energy.[23,24] Two d-d transitions are observed in the range of 18760–21276 cm^{-1} and 20811–25310 cm^{-1}. These bands are attributed to $^1A_{1g} \rightarrow {}^1A_{2g}(\nu_1)$ and $^1A_{1g} \rightarrow {}^1B_{1g}(\nu_2)$ transitions, respectively. The electronic spectra of these complexes indicate the square planar geometry around the Pd(II) and Pt(II) ion.

By assuming a value of $F_2 = 10F_4 = 600$ for Slater-Condon interelectronic repulsion parameters for both Pd and Pt , it is possible to calculate the value of Δ_1 (Table IV) from the first spin-allowed d-d transition. The splitting parameter increases in the expected order Pt>Pd.

Rhodium(III) and Iridium(III) Complexes

All of the formed complexes have been found to be +3 oxidation state. All the complexes are diamagnetic. Rhodium(III) complexes exhibit in the electron spectra with transitions at 17550–17600 cm^{-1}, 20210–20280 cm^{-1}, and 27170–27400 cm^{-1}. These bands resemble those of reported transitions for other hexacoordinated rhodium complexes[25] and may be assigned $^1A_{1g} \rightarrow {}^3T_{1g}$, $^1A_{1g} \rightarrow {}^1T_{1g}$, and $^1A_{1g} \rightarrow {}^1T_{2g}$, respectively, which agree with an octahedral geometry. The B and Dq values

TABLE III Infrared Absorption Frequencies (cm⁻¹) of Ligands and Their Metal Complexes

	Assignments					
Compound	ν (C=N)	ν(C=S)	ν(C=O)	ν(M—S)	ν(M—O)	ν(M—N)
L^1	1592	756	—	—	—	—
$[Pd(L^1)_2]Cl_2$	1578	732	—	308	—	460
$[Pt(L^1)_2]Cl_2$	1582	740	—	312	—	472
$[Rh(L^1)_2Cl_2]Cl$	1570	738	—	318	—	465
$[Ir(L^1)_2Cl_2]Cl$	1576	729	—	315	—	468
$[Ru(L^1)_2Cl_2]Cl$	1580	745	—	310	—	458
L^2	1579	—	1670	—	—	—
$[Pd(L^2)_2]Cl_2$	1567	—	1659	—	-411	475
$[Pt(L^2)_2]Cl_2$	1560	—	1650	—	418	454
$[Rh(L^2)_2Cl_2]Cl$	1554	—	1647	—	404	462
$[Ir(L^2)_2Cl_2]Cl$	1562	—	1645	—	416	470
$[Ru(L^2)_2Cl_2]Cl$	1550	—	1664	—	420	465

were calculated from the positions of their electronic bands using the following equations:

$$\nu_1 = 10 \text{ Dq} - 4B + \frac{86(B)^2}{10 \text{ Dq}},$$

$$\nu_2 = 10 \text{ Dq} + 12B + \frac{2(B)^2}{10 \text{ Dq}}.$$

The B values are 55–62% of the free ion value. The decrease in B values from the free ion value suggests that there is a considerable orbital overlap with strong covalency in the metal ligand σ bond.[26] Jorgensen has demonstrated that the decreasing the value of β is associated with a reduction in the positive charge of the cation and with the tendency to be reduced to the next lower oxidation state.

The electronic spectra of the iridium(II) complexes under study display bands in the range of 30800 and 34000–34250 cm⁻¹, which may be assigned to $^1A_{1g} \rightarrow {}^1T_{1g}(\nu_1)$ and $^1A_{1g} \rightarrow {}^1T_{2g}(\nu_2)$ transitions in order of increasing energy. The two transitions ν_1 and ν_2 have been used to evaluate the ligand field parameters (Table IV). The values of these ligand field parameters are compared with those reported for other iridium(III) complexes involving similar donors.[27]

Ruthenium(III) Complexes

The ground state of ruthenium(III) is $^2T_{2g}$ and the first excited doublet levels in order of increasing energy are $^2A_{2g}$ and $^2T_{2g}$, which

TABLE IV Electronic Spectral Bands (cm^{-1}) and Ligand Field Parameters

Complex	λ_{max} (cm^{-1})	Dq (cm^{-1})	B (cm^{-1})	C (cm^{-1})	β	υ_2/υ_1	Δ_1 (cm^{-1})
[Pd(L^1)$_2$]Cl$_2$	18639, 20811	–	–	–	–	–	20439
[Pt(L^1)$_2$]Cl$_2$	21276, 25310	–	–	–	–	–	23376
[Rh(L^1)$_2$Cl$_2$]Cl	17600, 20210, 27170	2195	435	1740	0.60	1.15	–
[Ir(L^1)$_2$Cl$_2$]Cl	30800, 34000	3160	200	800	0.33	1.10	–
[Ru(L^1)$_2$Cl$_2$]Cl	13500, 17260, 23550	2738	470	2882	0.75	1.28	–
[Pd(L^2)$_2$]Cl$_2$	18760, 22565	–	–	–	–	–	20560
[Pt(L^2)$_2$]Cl$_2$	20080, 24815	–	–	–	–	–	22180
[Rh(L^2)$_2$Cl$_2$]Cl	17550, 20280, 27400	2206	445	1780	0.62	1.15	–
[Ir(L^2)$_2$Cl$_2$]Cl	30800, 34250	3085	212	850	0.32	1.11	–
[Ru(L^2)$_2$Cl$_2$]Cl	14000, 17850, 23600	2725	475	2705	0.76	1.27	–

are known to arise from $T_{2g}^4 e_g^1$ configuration.[28] The ruthenium(III) complexes display electronic spectra with transitions at 13500–14000 cm^{-1}, 17260–17850 cm^{-1}, and 23550–23600 cm^{-1}. These bands may be assigned due to $^2T_{2g} \rightarrow {}^4T_{1g}$, $^2T_{2g} \rightarrow {}^4T_{2g}$, and $^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$ in

TABLE V Antibacterial Activity Data of Ligands and Their Metal Complexes

Compounds	Diameter of Inhibition Zone (mm)(conc.in μgml^{-1})					
	B. macerans		*A. aureus*		*E.coli*	
	250	500	250	500	250	500
L^1	9	11	10	13	12	14
[Pd(L^1)$_2$]Cl$_2$	13	21	14	23	16	27
[Pt(L^1)$_2$]Cl$_2$	12	19	12	17	15	24
[Rh(L^1)$_2$Cl$_2$]Cl	11	14	11	15	13	18
[Ir(L^1)$_2$Cl$_2$]Cl	9	13	10	12	14	20
[Ru(L^1)$_2$Cl$_2$]Cl	10	19	11	16	14	22
L^2	6	9	7	8	9	12
[Pd(L^2)$_2$]Cl$_2$	11	17	12	19	13	20
[Pt(L^2)$_2$]Cl$_2$	9	14	11	16	12	18
[Rh(L^2)$_2$Cl$_2$]Cl	7	12	9	15	10	16
[Ir(L^2)$_2$Cl$_2$]Cl	8	14	7	11	9	13
[Ru(L^2)$_2$Cl$_2$]Cl	9	15	8	13	11	14
Streptomycin (standard)	14	24	16	25	19	34

increasing order of energy. The B, C, and 10 Dq parameters were calculated using the following equations[29]:

$$^2T_{2g}(t^5) = 0,$$

$$^4T_{1g}(t^4\,e) = 10\,Dq - 5B\;4C,$$

$$^4T_{2g}(t^4\,e) = 10\,Dq + 5B - 4C,$$

$$^2A_{2g}, {}^2T_{1g}(t^4\,e) = 10\,Dq - 2B - C.$$

The values of these ligand field parameters are comparable to those reported for other trivalent ruthenium complexes involving nitrogen and sulfur donor molecules. The considerable decrease in Racah interelectronic repulsion parameter, B, suggests the presence of strong covalent bonding between the donor and metal ions. The overall effect will be an increase in the observed Dq value; high Dq values are usually associated with considerable electron delocalization.[30]

On the basis of spectral studies, the following structure may be suggested for the complexes (Figure 2).

EXPERIMENTAL

All the chemicals used were of Anala R grade and procured from Sigma-Aldrich and Fluka. Metal salts were purchased from E. Merck and were used as received. All solvents used were of standard/spectroscopic grade. C, H, and N were analyzed on a Carlo-Erba 1106 elemental analyzer. Molar conductance was measured on the ELICO (CM82T) conductivity bridge. Magnetic susceptibility was measured at room temperature on a Gouy balance using $CuSO_4.5H_2O$ as a calibrant. ^1H NMR spectra were recorded at room temperature on a Bruker Avance DPX-300 spectrometer using DMSO-d_6 as a solvent. IR spectra (KBr) were recorded on a FTIR spectrum BX-II spectrophotometer. The electronic spectra were recorded in DMSO on a Shimadzu UV mini-1240 spectrophotometer.

The Synthesis of Ligands

Ligands L^1 & L^2 were prepared, and the methods of their preparation are given below.

Ligand L^1

A hot ethanolic (20 mL) solution of thiosemicarbazide (0.91 g, 0.01 mol) and an ethanolic (20 mL) solution of 2-acetyl thiophene (1.26 g,
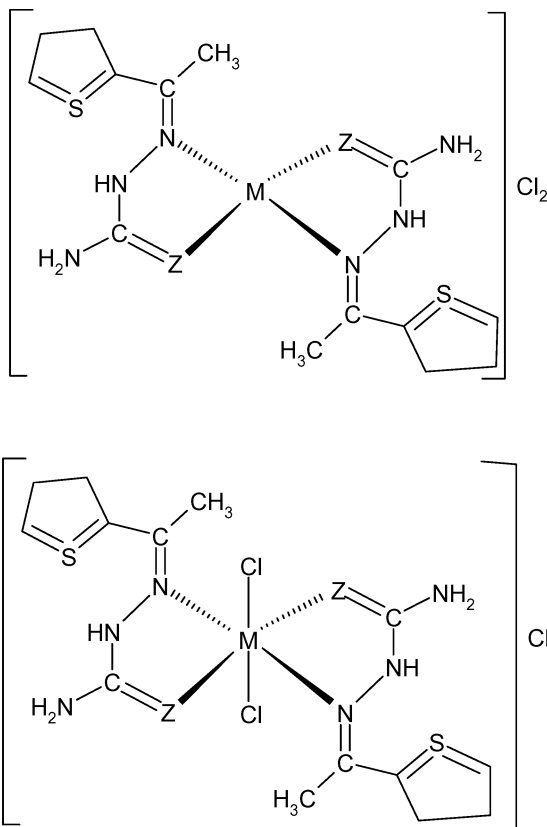
[where M= Pd(II) and Pt(II), M'= Rh(III), Ir(III), Ru(III)Z= S /O]

FIGURE 2 Suggested structure of the complexes.

0.01 mol) were mixed slowly with constant stirring. This mixture was refluxed at 70–80°C for 2–3 h. Upon cooling, a white-colored compound precipitated. It was filtered, washed with cold EtOH, and dried under vacuum over P_4O_{10}. Yield: 70%, m. 159–161°C. Elemental analysis found % C 42.20, H 4.59, N 21.15 calculated for $C_7H_9N_3S_2$(molecular mass 199 amu) % C 42.21, H 4.52, N 21.10.

Ligand L²

An aqueous (20 mL) solution of semicarbazide hydrochloride(1.11 g, 0.01 mol) and an ethanolic (20 mL) solution of 2-acetyl thiophene (1.26 g, 0.01 mol) were mixed in the presence in sodium acetate (1.36g,

0.01 mol). The reaction mixture was stirred vigorously for 1 h. Upon cooling, a white compound precipitated. It was filtered, washed with cold EtOH, and dried under vacuum over P_4O_{10}. Yield 73%, mp 195–197°C. Elemental analysis found % C 46.96, H 4.87, N 22.89 calculated for $C_7H_9N_3OS$ (molecular mass 183 amu) % C 45.90, H 4.91, N 22.95.

The Synthesis of Complexes

Hot ethanolic solutions (20 mL) of the corresponding metal salts (0.01 mol) were mixed with a hot ethanolic solution (20 mL) of the respective ligands (0.02 mol). The reaction mixture was refluxed on a water bath for about 4–5 h. Upon cooling, a colored complex precipated in each case. The complex was filtered, washed with cold ethanol, and dried under vacuum over P_4O_{10}.

ANTIBACTERIAL SCREENING

The antibacterial activitity of the ligand and its metal complexes were tested by using the paper disc diffusion method[31–33] against *B. macerans*, *A. aureus*, and *E. coli.* Nutrient agar medium was prepared by using peptone, beef extract, NaCl, agar–agar, and distilled water. The test compounds in measured quantities were dissolved in DMF to give concentrations of 250 and 500 ppm of compounds. 25 mL nutrient agar media (NA) was poured into each Petri plate. After solidification, 0.1 mL of test bacteria was spread over the medium. The disc of Whatmann no. 1 filter paper of diameter 5.00 mm each containing 1.5 mg cm^{-1} of the compounds was placed at 4 equidistant places at a distance of 2 cm from the center in the inoculated Petri plates. A filter paper disc treated with DMF served as a control, and streptomycin was used as a standard drug. All determinations were made in duplicate for each of the compounds. An average of two independent readings for each compound was recorded. These Petri plates were kept in a refrigerator for 24 h for prediffusion. Finally the Petri plates were incubated for 26–30 h 28 ± 2°C. The zone of inhibition was calculated in mm.

The antimicrobial screening data show that metal chelates exhibit more inhibitory effects than the parent ligands (Table V). The increased activity of the metal chelates can be explained on the basis of chelation theory.[34] It is known that chelation tends to make the ligand act as more powerful and potent bactericidal agents, thus killing more of the bacteria than the ligand. It is observed that in the complex, the positive charge of the metal is partially shared with the donor atoms present in the ligands, and there is π-electron delocalization over the whole

chelating structure. This increases the lipophilic character of the metal chelate and favors its permeation through the lipid layer of the bacterial membranes. There are other factors that also increase the activity including solubility, conductivity, and bond length between the metal and ligand.

CONCLUSION

The present study confirmed an octahedral geometry around the Rh(III), Ir(III), and Ru(III), whereas we confirmed square planar geometry for the Pd(II) and Pt(II) complexes with bidentate ligands coordinationg through the N and O/S donors. It is also interesting to note that the sulfur-bonded ligands and their complexes are more active than the oxygen-bonded ligands and their complexes.

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