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Coordination Chemistry of Palladium(II) and Platinum(II) Complexes with Bioactive Schiff Bases: Synthetic, Spectral, and Biocidal Aspects[1]

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Abstract—The Schiff bases, 5-nitro-indol-2,3-dionehydrazinecarboxamide (HSCZ[1]) and 7-nitro-indol-2,3-dionehydrazinecarboxamide (HSCZ[2]), have been synthesized by the condensation of 5-nitro-indol-2,3-dione and 7-nitro-1H-indol-2,3-dione with semicarbazide hydrochloride, respectively. The palladium(II) and platinum(II) complexes have been prepared by mixing palladium chloride and platinum chloride in 1 : 2 molar ratios with monobasic bidentate Schiff bases. The ligands and complexes of palladium and platinum have been characterized by elemental analyses, melting point determinations, conductance measurements, molecular weight determinations, and IR, ^{1}H NMR, and UV spectral studies. These studies showed that the ligands coordinate to the metal atoms in a monobasic bidentate mode, coordinating through oxygen and nitrogen donor systems. Thus, a tetracoordinated environment around the metal atom has been proposed. Both the ligands and their complexes have been screened for their biological activity on several pathogenic fungi and bacteria and were found to possess appreciable fungicidal and bactericidal properties. Plant growth regulating activity of one of the ligands and its complexes has also been recorded on gram plant, and results have been discussed.

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INTRODUCTION

The chemistry of coordination compounds with heterocyclic ligands containing oxygen and nitrogen as donor atoms has attracted increasing attention in recent years. It is well known that such ligands coordinate to a metal atom in different ways in different media. Transition metal ions are essential in many biological systems in nature [1]. These metal complexes with bidentate and tetradentate ligands containing both hard and soft donor groups have been used extensively in coordination and organometallic chemistry [2]. The chelating properties of Schiff bases display manifold applications in medicine, industry, and agriculture [3].The metal complexes of thiosemicarbazones and semicarbazones have aroused considerable interest in view of their industrial and biological applications [4, 5]. Metal semicarbazones are reported to be active against small pox, viral diseases, and certain kind of tumours [6]. Heterocyclic compounds like indole-3-acetic acid and naphthyl-1-acetic acid are the plant growth auxins found to affect the growth of plants [7]. The transition metal complexes of Schiff bases have exhibited fungicidal and bactericidal activities including regulating the growth of plants [8]. It is known that chelation of metal ions with organic ligands acts synergistically to increase its effect [9].

The coordination chemistry of the square planar palladium(II) and platinum(II) complexes of nitrogen and sulfur/oxygen donor ligands have gained enormous importance because of their antitumour [10], anticancer [11], and catalytic activities [12]. Antimicrobial aspects [13] and antifertility activity [14] of coordination compounds of palladium(II) and platinum(II) also reported in recent years. Earlier studies from our laboratory [15, 16] on biological activity of Schiff bases derived from isatins and their metal complexes showed significant enhancement of antibacterial and antifungal activity of the isatin derivative on complexation. Keeping this in mind and in continuation of our previous studies, in the present contribution we report the synthesis and characterization of some palladium(II) and platinum(II) complexes with monobasic bidentate ligands, 5-nitro-indol-2,3-dione semicarbazone (**HSCZ[1]**) and 7-nitro-indol-2,3-dione semicarbazone (**HSCZ[2]**), and effect of complexation on antimicrobial and plant growth regulating activity.

EXPERIMENTAL

Analytical methods and physical measurements. Palladium and platinum salts, $PdCl_2$ and $PtCl_2$, *p*-nitroaniline, and *o*-nitroaniline were purchased from Lancaster and used as such. 5-Nitroisatin and 7-nitroisatin were prepared by the literature method in the laboratory [15]. All the solvents were dried and distilled before

[1] The article is published in the original.

use. Molecular weights were determined by the Rast Camphor method. Pd(II) and Pt(II) were estimated gravimetrically. Nitrogen was estimated by Kjeldahl's method, and sulfur was estimated by Messenger's method [17].

Conductivity measurements were made with a conductivity bridge (Systronics model 305). Infrared spectra of the ligands and their complexes were recorded with the help of a Nicolet-Megna FT-IR 550 spectrophotometer using KBr pellets. The electronic spectra were recorded on a Varian-Cary/2390 spectrophotometer at RSIC, I.I.T., Chennai. ^{1}H NMR spectra were recorded on a Hitachi Perkin Elmer spectrometer in DMSO-d_6 at 300 MHz using TMS as the internal standard at the Delhi University (New Delhi).

The antifungal activity was evaluated against *Alternaria alternata* and *Fusarium oxysporum* using Czapek's agar medium having the composition: glucose 20 g, starch 20 g, agar-agar 20 g, and distilled water 1000 ml. To this medium was added a requisite amount of the compounds after being dissolved in dimethylformamide so as to get a certain concentration (50, 100, and 200 ppm). The medium then was poured into Petri plates, and the spores of fungi were placed on the medium with the help of inoculum's needle. These Petri plates were wrapped in polythene bags containing a few drops of alcohol and were placed in an incubator at 30 ± 2°C. The controls were also run, and three replicates were used in each case. The linear growth of the fungus was recorded by measuring the diameter of the fungal colony after 96 h, and the percentage inhibition was calculated by the equation:

$$\% \text{ Inhibition} = (C - T) \times 100\ C^{-1},$$

where C and T are the diameters of the fungal colony in the control and the test plates, respectively [18].

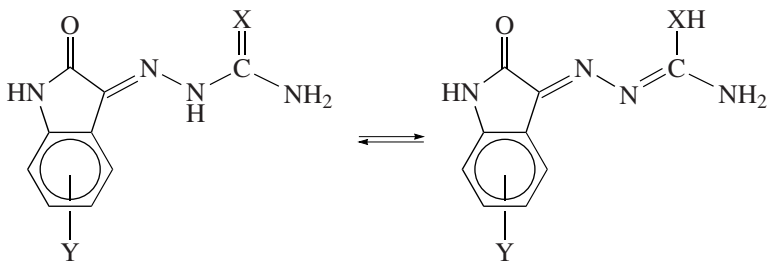
Antibacterial activity was tested against *Eschirichia coli* and *Pseudomonas cepacicola* using the paper disc plate method [19]. The nutrient agar medium (peptone, beef extract, NaCl, and agar–agar) and 5 mm diameter paper discs of whatman filter paper no. 1 were used. The compounds were dissolved in methanol for obtaining concentrations of 500 and 1000 ppm. The filter paper discs were soaked in these solutions, dried, and then placed in the Petri plates previously seeded with the test organisms. The plates were incubated for 24 h at 28 ± 2°C, and inhibition zone around each disc was measured.

Plant growth regulating activity. One of the ligands, HSCZ[1], and its complexes were tested for their plant growth regulating activity against gram plant. Two types of experiments were conducted.

In the first experiment, seeds were treated with an aqueous solution of the synthesized complexes by the following germination test method. The germination was followed by the Towel Paper method. Two brown-colored towel papers of equal size (46 × 27 cm) for each test were jointly soaked in different concentrations (1, 5, 10, and 25 ppm) of the ligand and its complexes for treated experiments and in water for controlled experiment for 4 h and placed over a butter paper (39 × 25 cm). One hundred seeds were placed at an equal distance over the towel papers, which were subsequently covered by another moist towel paper (46 × 27 cm). Then the towel paper was rolled up, two ends of the towel paper tied lightly with a rubber band and placed in a germination chamber at 25 ± 1°C. One hundred seeds were used for each sample. The observations for percent germination and normal seedling were recorded on the 4th and 8th days. The seedlings, which possessed the ability to develop into fully normal and healthy plants, were considered as normal seedlings.

In the second experiment, the seeds were treated with physiologically active concentration of the plant growth regulators solution for 6 h at room temperature and drying them to the original moisture level by a hot air circulating oven. After that, uniform size seeds were placed on whatman no. 1 filter paper lying in the glass petri plates. Each petri plate has 15 seeds placed at equidistance. The filter papers were moistened with fresh solutions of required concentrations. The concentrations of the plant growth regulators used were 1, 5, 10, and 25 ppm.

Synthesis of the ligands. The ligands HSCZ[1] and HSCZ[2] were prepared by the condensation of semicarbazide hydrochloride with 5-nitro-indol-2,3-dione and 7-nitro-indol-2,3-dione in the presence of sodium acetate in a 1 : 1 molar ratio in ethanol. The reaction mixture was then refluxed over a water bath for 3–4 h, and allowed to stand overnight. The products were recrystallized from the solvent ethanol and dried *in vacuo*. Their physicochemical properties and analytical data of the ligands are given in Table 1. The parent ligands exist in the tautomeric forms:



X = O; Y = HSCZ[1] and HSCZ[2].

Table 1. Elemental analysis data and some physical properties of the ligands and their complexes

Compound	Color	Melting point, °C	Contents (found/calcd), %				Mol. wt. found (calcd)
			C	H	N	M	
$HSCZ^1$	Brown	251–254	43.74/43.38	2.54/2.83	28.36/28.10		263.32 (249.18)
$HSCZ^2$	Coke	239–241	43.86/43.38	2.56/2.83	28.30/28.10		263.34 (249.18)
$[Pd(HSCZ^1)_2]Cl_2$	Sand like	270–272	31.68/31.99	2.14/2.08	20.63/20.72	15.56/15.74	662.98 (675.69)
$[Pd(SCZ^1)_2]$	Grey	273–275	35.72/35.86	2.15/2.01	23.18/23.23	17.39/17.65	614.15 (602.70)
$[Pd(HSCZ^2)_2]Cl_2$	Grey	255–259	31.79/31.99	2.16/2.08	20.56/20.72	15.68/15.74	659.54 (675.69)
$[Pd(SCZ^2)_2]$	Brown	257–259	35.92/35.86	2.11/2.01	23.36/23.23	17.54/17.65	616.78 (602.70)
$[Pt(HSCZ^1)_2]Cl_2$	Grey	279–281	29.73/29.52	1.87/1.92	19.03/19.12	26.78/26.63	723.68 (732.35)
$[Pt(SCZ^1)_2]$	Brown	270–273	31.30/31.26	1.64/1.74	20.16/20.25	28.34/28.21	686.93 (691.43)
$[Pt(HSCZ^2)_2]Cl_2$	Purple	267–269	29.47/29.52	1.84/1.92	19.08/19.12	26.27/26.63	726.94 (732.35)
$[Pt(SCZ^2)_2]$	Brown	260–262	31.32/31.26	1.68/1.74	20.44/20.25	28.17/28.21	681.05 (691.45)

Synthesis of complexes: $[Pd(SCZ)_2]$. A methanolic solution of $PdCl_2$ was mixed with a methanolic solution of the ligands in 1 : 2 molar ratios. Aqueous NH_4OH was added dropwise to the reaction mixture until it was weakly alkaline (pH ~8.0). The mixture was then heated under reflux for about one hour. On cooling, the complexes were separated out, filtered off, washed with methanol, and dried in *vacuo*.

$[Pd(HSCZ)_2]Cl_2$. A methanolic solution of $PdCl_2$ was mixed with a methanolic solution of the ligands in 1 : 2 molar ratios. The mixture was stirred on a magnetic stirrer for 2–3 h in the presence of few drops of concentrated HCl. The resulting products were recovered by filtration, washed with methanol, and dried in *vacuo*.

$[Pt(SCZ)_2]$. These complexes were prepared by dissolving $PtCl_2$ in a 1 : 1 mixture of water and ethanol and then adding an ethanolic solution of the ligands to this solution in 1 : 2 molar ratios. Aqueous NH_4OH was added dropwise to the reaction mixture until it was weakly alkaline (pH ~8.0). The reaction mixture was heated under reflux for about one hour. On cooling, the complexes were separated out, filtered off, washed with ethanol, and dried in *vacuo*.

$[Pt(HSCZ)_2]Cl_2$. The 1 : 1 water-ethanol solution of $PtCl_2$ was mixed with an ethanolic solution of the ligands in 1 : 2 molar ratios. The mixture was stirred on a magnetic stirrer for 2–3 h in the presence of few drops of concentrated HCl. The resulting products were recovered by filtration, washed with ethanol and dried in *vacuo*.

The physicochemical properties and analytical data of these complexes are listed in Table 1.

RESULTS AND DISCUSSION

The reactions of the above ligands with $PdCl_2$ and $PtCl_2$ have been carried out in 1 : 2 molar ratios in methanol and in 1 : 1 water-ethanol solutions, respectively. The metal chloride interacts with the ligands in the presence of few drops of concentrated HCl to form complexes of the type $[M(HSCZ)_2]Cl_2$. However, complexes of the type $[M(SCZ)_2]$ were obtained when reactions were carried out in the presence of aqueous NH_4OH:

$$MCl_2 + 2HSCZ \longrightarrow [M(HSCZ)_2Cl_2],$$

$$MCl_2 + 2HSCZ + NH_4OH \longrightarrow [M(SCZ)_2] + 2NH_4Cl + 2H_2O,$$

where M = Pd(II) and Pt(II); HSCZ is the ligand molecule.

The reactions proceed easily and all the complexes are soluble in DMSO, DMF, and $CHCl_3$. The molar conductance values of 10^{-3} M solutions of $[M(SCZ)_2]$ type of complexes lie in the range 10–15 $Ohm^{-1}\ cm^2\ mol^{-1}$ in dry DMF indicating their nonelectrolytic behavior. However, the $[M(HSCZ)_2]Cl_2$ type of complexes are 1 : 2 electrolytes with conductance values of 200–220 $Ohm^{-1}\ cm^2\ mol^{-1}$. The

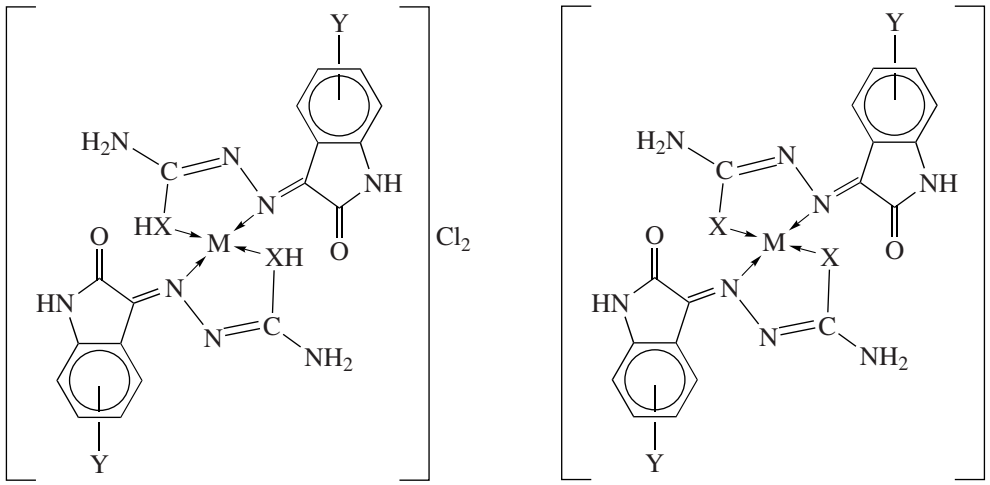
complexes are monomers as revealed by their molecular weight determinations.

The electronic spectra of the ligands and their complexes were recorded in distilled DMSO. The maximum absorption at 350 nm in the case of the ligands can be assigned to the azomethine group. The shift of this band (~20 nm) in the spectra of the metal complexes suggests the coordination of nitrogen to the metal atom. The spectra of the metal complexes show three bands due to three *d–d* spin allowed transitions. These correspond to the transitions from the three lower-lying *d* orbitals to the empty $d_{x^2-y^2}$ orbital. The ground state is $^1A_{1g}$ and excited states corresponding to the above transitions are $^1A_{2g}$, $^1B_{1g}$, and $^1E_{1g}$ in the order of increasing energy. Three *d–d* transition bands are observed in the regions 510–515, 402–410, and 335–347 nm. These bands are attributed to the $^1A_{1g} \longrightarrow {}^1A_{2g}$, $^1A_{1g} \longrightarrow {}^1B_{1g}$, and $^1A_{1g} \longrightarrow {}^1E_{1g}$ transitions, respectively. The electronic spectra of these complexes indicate the square planar geometry [20].

The IR spectra of the free ligands display two bands at 3439 and 3325 cm^{-1} due to ν_{as} and ν_s vibrations of the NH_2 group, respectively, which remain at almost the same positions in the spectra of the complexes, suggesting that the NH_2 group is not involved in chelation. The broad band in the region 3150–3245 cm^{-1} due to νNH vibrations disappears in the spectra of the $[M(SCZ)_2]$ type of complexes, indicating the deprotonation of this group on coordination with the metal atom. The band at 1610 cm^{-1} in the spectra of the free ligands due to ν(>C=N) is shifted to a higher wave number (10–20 cm^{-1}) in the metal complexes, suggesting the coordination through the azomethine nitrogen atom. The band at 1690 cm^{-1} due to >C=O is shifted toward lower frequency in the complexes, indicating coordination of oxygen to the central metal atom. The bands at 360–372, 415–426, 435–446, and 300–315 cm^{-1} can be assigned to ν(Pd←—N), ν(Pd←—O), ν(Pt←—N), and ν(Pt←—O), respectively. The appearance of these bands further support the bonding of the ligands to the metals through the nitrogen and oxygen atoms. However, no ν(M–Cl) band is observed in the spectra of the $[M(HSCZ)_2]Cl_2$ type of complexes, suggesting that the chloride is ionic in these complexes.

The above bonding patterns are further supported by the ^1H NMR spectral studies of the free ligands and their metal complexes. The spectral data of the ligands and their complexes are listed in Table 2. The spectra of the ligands $HSCZ^1$ and $HSCZ^2$ exhibit broad signals at δ11.20 and δ11.25 ppm due to the –NH proton, which disappear in the complexes of the type $[M(L)_2]$. The absence of this signal in these complexes suggests that this proton has been lost via the ketoenolization of >C=O group and coordination of oxygen to the metal atoms has taken place. Aromatic and $–NH_2$ group protons do not take part in complexation, because their positions remain almost the same in the spectra of the ligands, as well as in the metal complexes. The broad signal in the region δ11.92–11.96 ppm due to –NH protons of the ring in the free ligands do not alter in the metal complexes, indicating the noninvolvement in coordination.

Thus, on the basis of the above discussion, the following square planar structures can be proposed for the addition (a) and substituted (b) products. These structures are given below:



where M = Pd(II) and Pt(II): X = O; Y = ($HSCZ^1$) (a) and ($HSCZ^2$) (b).

Table 2. ^{1}H NMR spectral data (δ, ppm) of the ligands and the corresponding complexes

Compound	–NH (1)*	–NH (2)*	$–NH_2$*	Aromatic protons**
$HSCZ^1$	11.20	11.92	3.41	6.75–8.15
$HSCZ^2$	11.25	11.85	3.40	6.70–8.10
$[Pd(HSCZ^1)_2]Cl_2$	11.35	11.94	3.43	6.74–8.13
$[Pd(SCZ^1)_2]$		11.96	3.45	6.73–8.14
$[Pt(HSCZ^2)_2]Cl_2$	11.29	11.90	3.42	6.72–8.08
$[Pt(SCZ^2)_2]$		11.93	3.43	6.75–8.10

Notes: * Broad signal.
** Multiplet.

Antimicrobial activity of the synthesized ligands and their corresponding metal complexes on selected fungi, *Alternaria alternata* and *Fusarium oxysporum*, and two bacteria, *Pseudomonas cepacicola* and *Escherichia coli*, were carried out. The action of the ligands and their complexes as fungicides for pathogenic fungi and as bactericides for bacteria are recorded in Tables 3 and 4, respectively. The results suggest that although the ligands have remarkable toxic property, their complexes inhibit the growth of organisms to a greater extent. Although it is difficult to make out an exact structure activity relationship between the microbial activity and the structure of these complexes, it can possibly be concluded that the chelation enhances the activity of the complexes [21]. Chelation reduces the polarity of the central ion, mainly because of the partial sharing of its positive charge with the donor groups and

Table 3. Antifungal screening data for the ligands and their complexes

Compound	Inhibition (%) after 96 h					
	Alternaria alternata			*Fusarium oxysporum*		
	50 ppm	100 ppm	200 ppm	50 ppm	100 ppm	200 ppm
$HSCZ^1$	32	35	44	40	45	50
$HSCZ^2$	30	36	42	41	42	49
$[Pd(HSCZ^1)_2]Cl_2$	39	42	53	47	59	62
$[Pd(SCZ^1)_2]$	42	41	50	43	55	60
$[Pd(HSCZ^2)_2]Cl_2$	36	43	52	50	53	62
$[Pd(SCZ^2)_2]$	40	45	53	50	61	63
$[Pt(HSCZ^1)_2]Cl_2$	50	55	59	52	59	60
$[Pt(SCZ^1)_2]$	53	60	66	52	58	64
$[Pt(HSCZ^2)_2]Cl_2$	41	46	53	48	57	53
$[Pt(SCZ^2)_2]$	40	45	52	50	58	61
Bavistin	82	100	100	86	100	100

Table 4. Antibacterial screening data for the ligands and their complexes

Compound	Diameter (mm) of inhibition zone after 24 h			
	Escherichia coli		*Pseudomonas cepacicola*	
	500 ppm	1000 ppm	500 ppm	1000 ppm
$HSCZ^1$	6	7	7	8
$HSCZ^2$	8	9	8	10
$[Pd(HSCZ^1)_2]Cl_2$	10	13	12	13
$[Pd(SCZ^1)_2]$	13	15	10	12
$[Pd(HSCZ^2)_2]Cl_2$	12	13	11	13
$[Pd(SCZ^2)_2]$	11	13	12	14
$[Pt(HSCZ^1)_2]Cl_2$	13	14	12	13
$[Pt(SCZ^1)_2]$	14	13	11	12
$[Pt(HSCZ^2)_2]Cl_2$	12	14	12	13
$[Pt(SCZ^2)_2]$	11	13	11	12
Streptomycin	16	18	15	18

possible π-electron delocalization within the whole chelate ring. This chelation increases the lipophilic nature of the central atom, which favors its permeation through the lipid layer of the membrane. According to Lawrence et al. [22], the variation in the toxicity of different antibacterial agents against different organisms depends on the impermeability of the cell.

The results of the plant growth regulating activity are recorded in Tables 5 and 6. The data summarized in the Tables revealed that the ligand and its metal complexes show plant growth regulating activity only at optimum concentrations (1 ppm). On increasing the concentration of the metal complexes, the activity decreases as compared to the untreated control. The activity has been recorded in terms of a decrease in the growing period and an increase in the wet and dry length and the weight of seedling. The activity of the ligand increases on complexation with the metals due to the presence of micronutrients, which are essential for the plant growth. Singh and coworkers [23] also

Table 5. Effect of the ligand $HSCZ^1$ and its complexes on germination of gram (*Cicer aretinum*)

Compound	Growing period, h*				Wet length of seedling, cm								Wet 'wt' of seedling, gm							
					root*				shoot*				root*				shoot*			
	1	5	10	25	1	5	10	25	1	5	10	25	1	5	10	25	1	5	10	25
$HSCZ^1$	40	38	36	48	9.4	9.8	10.3	5.8	6.2	7.1	7.7	5.4	2.27	2.38	2.73	2.01	3.88	3.97	4.26	2.76
$[Pd(HSCZ^1)_2]Cl_2$	38	43	52	57	10.6	8.4	7.2	5.1	7.5	7.2	6.7	4.1	2.38	2.23	2.15	1.96	4.12	3.87	3.60	2.56
$[Pd(SCZ^1)_2]$	38	42	51	57	10.7	8.7	7.3	5.3	7.6	7.1	6.9	4.3	2.40	2.18	2.06	1.91	4.08	3.78	3.51	2.57
$[Pt(HSCZ^1)_2]Cl_2$	39	43	53	58	10.5	8.5	7.1	5.1	7.4	7.0	6.5	4.1	2.46	2.11	2.03	1.87	4.11	3.67	2.89	2.56
$[Pt(SCZ^1)_2]$	38	42	51	57	10.5	8.7	7.2	5.2	7.4	7.2	6.8	4.2	2.43	2.06	1.93	1.77	4.05	3.69	2.86	2.54

* Concentration in ppm.

Table 6. Effect of the ligand $HSCZ^1$ and its complexes on germination of gram (*Cicer aretinum*)

Compound	Dry length of seedling, cm								Dry 'wt' of seedling, gm							
	root*				shoot*				root*				shoot*			
	1	5	10	25	1	5	10	25	1	5	10	25	1	5	10	25
$HSCZ^1$	9.1	9.7	10.0	5.9	6.2	7.1	7.7	5.4	0.93	1.32	1.58	0.88	1.48	2.43	2.14	1.75
$[Pd(HSCZ^1)_2]Cl_2$	10.3	8.6	7.0	4.8	7.5	7.2	6.7	4.1	1.65	1.18	1.02	0.63	2.85	2.43	2.11	1.73
$[Pd(SCZ^1)_2]$	10.4	8.8	7.1	5.0	7.6	7.1	6.9	4.3	1.68	1.12	1.02	0.66	2.87	2.46	2.10	1.74
$[Pt(HSCZ^1)_2]Cl_2$	10.1	8.3	6.8	4.8	7.4	7.0	6.5	4.1	1.60	1.10	0.88	0.58	2.82	2.43	2.05	1.73
$[Pt(SCZ^1)_2]$	10.2	8.4	6.9	5.0	7.4	7.2	6.8	4.2	1.54	1.05	0.84	0.55	2.88	2.46	2.15	1.75
Control	8.2				5.8				0.090				1.43			

* Concentration in ppm.

obtained similar results by using synthetic plant growth regulators.

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