

Some Four Coordinated Palladium(II) Complexes of Thiosemicarbazones of 4-Aminoantipyrine

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A series of nine novel complexes of palladium(II) with nine different thiosemicarbazones derived from 4-aminoantipyrine and various aryl aldehydes have been prepared and characterized using elemental analysis, magnetic moment measurements, infrared and electronic spectroscopic techniques. The conductance values show them as 1 : 1 electrolytes. Infrared spectral studies indicate that all the nine thiosemicarbazones are neutral tridentate (N,N,S) ligands. The complexes have a square-planar structure.

Key Words: Palladium(II), Complexes, Thiosemicarbazones, Square-planar.

INTRODUCTION

Thiosemicarbazones and pyrazolone derivatives as well as their metal-coordination compounds belong to a special class of compounds which possess a wide spectrum of medicinal properties. Interest in the interaction of platinum metal with biologically important molecules began when Rosenberg *et al.*¹ published their discovery that certain platinum complexes exhibit anticancer activity. Intensive research to explain the chemistry and biochemistry of platinum complexes which behave as cytotoxic agents and to produce effective and less toxic anticancer drugs has stimulated huge scientific projects based on the chemistry of platinum complexes with many biological active ligands.^{2,3} But comparatively less is known about the platinum(II) group metal complexes of thiosemicarbazones derived from 4-aminoantipyrine.⁵ In the present work, the author presents the synthesis and characterization of palladium(II) complexes of various thiosemicarbazones of 4-aminoantipyrine, viz. 4-[N-(benzalidene)amino]antipyrine thiosemicarbazone (BAAPTS), 4-[N-(2'-hydroxybenzalidene)amino]antipyrine thiosemicarbazone (HBAAPTS), 4-[N-(4'-methoxybenzalidene)]antipyrinethio semicarbazone (MBAAPTS), 4-[N-(4'-dimethyl amino benzalidene)amino]antipyrine thiosemicarbazone (DABAAPTS), 4-[N-(2'-nitrobenzalidene)amino]antipyrine thiosemicarbazone (2'-NO₂BAAPTS), 4-[N-(3'-nitrobenzalidene)amino]antipyrine thiosemicarbazone (3'-NO₂BAAPTS), 4-[N-(4'-nitrobenzalidene)amino]antipyrine thiosemicarbazone (4'-NO₂BAAPTS), 4-[N-(4'-hydroxy-3'-methoxybenzalidene)amino]antipyrine thiosemicarbazone (HMBAAPTS) and 4-[N-(2'-hydroxy-1-naphthalidene)amino]antipyrine thiosemicarbazone (HNAAPTS).

EXPERIMENTAL

All the nine thiosemicarbazones derived from 4-aminoantipyrine were prepared in the laboratory by reported method.⁷

Synthesis of the complexes

All the palladium(II) chloride complexes of thiosemicarbazones were synthesized by the following general method. The solution of PdCl₂ (0.001 mol) and the respective ligand (0.001 mol) in ethanol containing a few drops of conc. HCl were mixed and refluxed for 1–2 h. The precipitate obtained was filtered, washed with ethanol and dried *in vacuo* over P₄O₁₀.

Physical measurements

The percentage of metal content was determined by standard methods using EDTA as titrant employing Eriochrome Black-T as indicator after decomposing the complexes with moderate concentrated sulphuric acid and hydrogen peroxide and dissolving the residue in water and by making necessary volume⁸. The Cl content was estimated by Volhard's method.⁹ The percentage of nitrogen was determined in the laboratory by Kjeldahl method. Sulphur was estimated gravimetrically as BaSO₄.

The conductivity measurements were carried out using a Toshniwal conductivity bridge type CL01/01 and dip type cell operated at 220 volts A.C. mains. All the measurements were done at room temperature in PhNO₂. The magnetic measurements on powder form of the complexes were carried out at room temperature on Gouy's balance using anhydrous copper sulphate as calibrant. The infrared spectra of the ligands and their complexes were recorded on a Perkin-Elmer infrared spectrophotometer model-521 in CsI in the range of 4000–200 cm⁻¹. Electronic spectra were recorded in Nujol mull on Perkin-Elmer 524 and Beckmann DK-2 automatic recording spectrophotometers.

RESULTS AND DISCUSSION

The ethanolic solution of palladium(II) chloride on reaction with thiosemicarbazones in the same solvents gave complexes of the general composition Pd(L)Cl₂, where L = BAAPTS, HBAPTS, MBAPTS, DABAPTS, 2'-NO₂ BAAPTS, 3'-NO₂BAAPTS, 4'-NO₂BAAPTS, HMBAPTS or HNAPTS. All the complexes gave satisfactory elemental analysis results (Table-1). All the complexes are quite stable and could be stored for months without any appreciable change. Most of the complexes either have sharp melting points or decomposed on heating beyond 300°C. The complexes are generally insoluble but soluble in DMF, DMSO and PhNO₂. The molar conductance values¹⁰ of the complexes correspond to 1 : 1 electrolytes and suggest that one chloro anion is present outside the coordination sphere.

TABLE-1
ANALYTICAL AND CONDUCTIVITY DATA OF Pd(L)Cl₂ COMPLEXES

Complex (Colour)	m.p. (°C)	Analysis %, Found (Calcd.)				Ω_M (ohm ⁻¹ cm ² mole ⁻¹)
		Pd	N	S	Cl	
Pd(BAAPTS)Cl ₂ (Reddish brown)	>210 d	19.38 (19.59)	15.37 (15.52)	5.84 (5.91)	13.06 (13.12)	25.2
Pd(HBAAFTS)Cl ₂ (Brown)	230	18.89 (19.03)	14.86 (15.08)	5.69 (5.74)	12.68 (12.74)	23.9
Pd(MBAAFTS)Cl ₂ (Dark brown)	210	18.42 (18.50)	14.53 (14.71)	5.54 (5.60)	12.35 (12.43)	30.3
Pd(DBAAFTS)Cl ₂ (Blackish brown)	258	18.01 (18.15)	16.59 (16.78)	5.42 (5.47)	12.07 (12.15)	26.9
Pd(2'-NO ₂ BAAPTS)Cl ₂ (Dark brown)	235	17.90 (18.08)	16.57 (16.72)	5.41 (5.46)	12.04 (12.11)	24.6
Pd(3'-NO ₂ BAAPTS)Cl ₂ (Reddish brown)	185	17.90 (18.06)	16.57 (16.72)	5.40 (5.46)	12.04 (12.11)	31.9
Pd(4'-NO ₂ BAAPTS)Cl ₂ (Blackish brown)	195	17.97 (18.08)	16.56 (16.72)	5.41 (5.46)	12.03 (12.11)	32.3
Pd(HMBAAFTS)Cl ₂ (Dark red)	240	17.90 (18.05)	14.19 (14.31)	5.40 (5.45)	12.02 (12.09)	24.9
Pd(HNAAPTS)Cl ₂ (Cherry brown)	245	17.32 (17.46)	13.69 (13.83)	5.23 (5.27)	11.63 (11.69)	25.3

All the Pd²⁺ complexes are diamagnetic and intensely coloured implying a square planar coordination of the central metal ion by the surrounding ligands. It is well known that Pd²⁺ having a d⁸ configuration favours the formation of complexes with square-planar geometry.^{11,12}

In the spectra of present complexes, two spin allowed bands in 26000–29000 cm⁻¹ region along with two charge-transfer bands have been assigned as a combination of both ¹A_{1g} → ¹A_{2g} and ¹A_{1g} → ¹E_g transitions by assuming the difference in the energies of both b_{2g}(xy) and e_g(xz, yz) levels very little. The other spin allowed bands for these complexes have been assigned to the spin allowed ¹A_{1g} → ¹B_{1g} transition. The other charge transfer bands observed have been assigned as a combination of both ¹A_{1g} → ¹A_{2u} and ¹A_{1g} → a¹E_u and ¹A_{1g} → b¹E_u transitions respectively (Table-2). The electronic spectra of these complexes are indicative of planar geometries and our data are in good agreement with the work of various authors^{13,14}. By assuming a value¹⁵ of C = 3500 cm⁻¹ and B = 500 cm⁻¹, the values of Δ₁, Δ₂ and Δ₃ have been evaluated (Table-2).

TABLE-2
ELECTRONIC SPECTRAL DATA (cm^{-1}) AND RELEVANT LIGAND FIELD
PARAMETERS OF Pd^{2+} COMPLEXES OF THIOSEMICARBAZONES

Complex	ν_1 ${}^1A_{1g} \rightarrow$ ${}^1A_{2g}, {}^1E_g$	ν_2 ${}^1A_{1g} \rightarrow$ ${}^1B_{1g}$	ν_3 $\rightarrow {}^1A_{2u'}$ $a {}^1E_u$	C.T. $\rightarrow b, {}^1E_u$	Δ_1 (cm^{-1})	Δ_2 (cm^{-1})	Δ_3 (cm^{-1})
Pd(BAAPTSCl ₂)	26100	28000	35300	47250	29600	3600	2100
Pd(MBAAPTSCl ₂)	27000	28100	35900	46350	30500	3100	1600
Pd(DBAAPTSCl ₂)	26500	28000	35700	47900	30000	3500	2000
Pd(2'-NO ₂ BAAPTSCl ₂)	27000	27800	36500	48180	30500	2800	1300
Pd(HMBAAPTSCl ₂)	26800	27900	36300	48000	30300	3100	1600
Pd(HNAAPTSCl ₂)	27300	28200	36900	48200	30800	2300	800
Pd(CAAPTSCl ₂)	26500	28000	36300	48000	30000	3500	2000

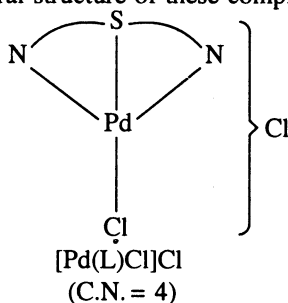
A study and comparison of infrared spectra of free ligands and their Pd^{2+} complexes (Table-3) imply that these ligands behave as neutral tridentate and the metal ion is coordinated through N and N of two azomethine groups and of S of thio-keto group. The strong bands observed at $3440\text{--}3270\text{ cm}^{-1}$ region in the free ligands have been observed due to $\nu(\text{NH})$ vibrations. Practically no effect on these frequencies after complexation precludes the possibility of complexation at this group. The absorptions at *ca.* 1600 cm^{-1} in the free ligands can be attributed to $(\text{C}=\text{N})$ stretching vibrations of imine nitrogen which is in agreement with the observations of previous workers.^{16, 17} On complexation these frequencies were observed to be shifted to lower wavenumbers (Table-3). These observations suggest involvement of unsaturated nitrogen atoms of the two azomethine groups in bonding with the metal ion. In the spectra of present ligands, the bands observed in $1300\text{--}1125\text{ cm}^{-1}$, $1120\text{--}1095\text{ cm}^{-1}$ and $840\text{--}730\text{ cm}^{-1}$ region are assigned to $[\nu(\text{C}=\text{S}) + \nu(\text{C}=\text{N}) + \nu(\text{C}-\text{N})]$, $[\delta(\text{N}-\text{C}-\text{S}) + \delta(\text{C}=\text{S})]$ bendings and $\nu(\text{C}=\text{S})$ stretchings respectively.^{18, 19} Coordination of sulphur with metal ion would result in the displacement of electrons toward the latter, thus resulting in the weakening of $(\text{C}=\text{S})$ bond. Hence, on complexation $(\text{C}=\text{S})$ stretching vibrations should decrease and that of (CN) stretching should increase.^{20, 21} In all the present complexes of Pd^{2+} , the frequencies in the range $1300\text{--}1125\text{ cm}^{-1}$ get an increase by nearly $50\text{--}60\text{ cm}^{-1}$. Similarly bending modes of $(\text{N}-\text{C}-\text{S})$ and $(\text{C}=\text{S})$ also get an increase in frequency but in lesser amount. On the other hand, on complexation the frequencies in $840\text{--}730\text{ cm}^{-1}$ are shifted to lower wavenumbers and intensity of the bands is also reduced. All these peculiar changes on complexation confidently preclude any unambiguous ascertain of metal-sulphur bond.

TABLE-3
PERTINENT INFRARED SPECTRAL BANDS (cm^{-1}) OF Pd^{2+} COMPLEXES OF
THIOSEMICARBAZONES

Compounds	$\nu(\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{S})$ + $\nu(\text{C}=\text{N})$ + $\nu(\text{C}-\text{N})$	$\delta(\text{NCS})$ + CS bending	$\nu(\text{N}-\text{N})$	$\nu(\text{C}=\text{S})$	$\nu(\text{Pt}-\text{N})/$ $\nu(\text{Pt}-\text{S})$
BAAPTS	3440 s 3270 s	1600 us	1330 s, 1305 s	1120 m 1095 m	1050 m	820 s, 760 us	—
$\text{Pd}(\text{BAAPTS})\text{Cl}_2$	3445 s 3270 s	1565 m	1375 s, 1330 m	1160 m, 1135 m	1065 m	765 m, 730 m	520 m 430 sh
HBAAPTS	3440 s 3270 s	1610 us	1290 s, 1260 us	1125 s, 1080 m	1050 m	840 s, 760 us	—
$\text{Pd}(\text{HBAAPTS})\text{Cl}_2$	3440 s 3275 s	1572 s	1340 s, 1283 m	1175 m, 1110 m	1065 m	805 s, 740 m	532 m, 415 w
MBAAPTS	3420 m 3310 m	1600 us	1320 s, 1195 m	1120 m, 1075 m	1060 m	840 s, 820 s	—
$\text{Pd}(\text{MBAAPTS})\text{Cl}_2$	3415 m 3315 m	1565 s	1362 s, 1242 m	1175 m, 1130 m	1072 m	770 s 752 s	515 m 425 sh
DABAAPTS	3360 s 3330 s	1600 us	1310 m, 1290 m	1115 m, 1095 m	1050 m	830 s, 730 m	—
$\text{Pd}(\text{DABAAPTS})\text{Cl}_2$	3362 s 3330 m	1565 m	1372 m 1345 m	1165 m, 1130 m, 1060 m	765 s, 710 m	525 m, 435 m	—
2'-NO ₂ BAAPTS	3442 s 3270 s	1600 us	1330 s, 1305 s	1120 m, 1098 m	1050 m	822 s, 762 us	—
$\text{Pd}(2'\text{-NO}_2\text{BAAPTS})\text{Cl}_2$	3445 s 3270 s	1572 s	1380 s, 1335 m	1165 m, 1132 m	1066 m	790 s, 705 m	525 m, 430 sh
3'-NO ₂ BAAPTS	3445 s 3272 s	1605 us	1332 s, 1305 s	1120 m, 1098 m	1052 m	820 s, 760 us	—
$\text{Pd}(3'\text{-NO}_2\text{BAAPTS})\text{Cl}_2$	3445 s 3270 m	1565 m	1370 m, 1345 m	1165 m, 1140 m	1060 m	780 s, 720 m	535 m 435 sh
4'-NO ₂ BAAPTS	3440 s 3270 s	1610 us	1315 m, 1292 m	1120 m, 1098 m	1055 m	825 s, 762 s	—
$\text{Pd}(4'\text{-NO}_2\text{BAAPTS})\text{Cl}_2$	3445 m 3272 m	1570 m	1370 m, 1340 m	1165 m, 1142 m	1065 m	772 s, 745 m	530 m 442 m
HMBAAPTS	3440 3280	1600 us	1315 s, 1185 m	1122 m, 1095 m	1040 m	840 s, 820 s	—
$\text{Pd}(\text{HMBAAPTS})\text{Cl}_2$	3440 3280	1560 s	1370 s, 1215 m	1160 m, 1135 m	1050 m	808 s, 785 m	525 m 435 m
HNAAPTS	3400 3200	1620 s	1295 s, 1265 s	1130 s, 1085 m	1045 m	840 m, 765 m	—
$\text{Pd}(\text{HNAAPTS})\text{Cl}_2$	3400 3202	1560 s	1352 m, 1285 m	1162 m, 1110 m	1060 m	792 s 720 m	520 m 430 w

The possibility of thione-thiol tautomerism $\text{H}-\text{N}-\text{C}=\text{S} \rightleftharpoons (\text{C}=\text{N}-\text{SH})$ in these ligands has been ruled out, for no band around $2700-2500 \text{ cm}^{-1}$, characteristic of thiol group is displayed in the infrared absorption.^{22, 23} In the complexes of HBAAAPS, HMBAAPTS and HNAAPTS, the stretching frequency at ca. 3400 cm^{-1} region is attributed to $\nu(\text{OH})$. In all the complexes the hydroxyl frequency appears at the same region as in the free ligands, clearly indicating that the $-\text{OH}$ group is not taking part in the coordination. In far infrared region some new bands with medium to weak intensity appear in all the complexes are tentatively assigned to $\nu(\text{Pd}-\text{N})$ and $\nu(\text{Pd}-\text{S})$ in accordance with previous reports^{11, 24}. $\nu(\text{Pd}-\text{Cl})$ is tentatively assigned in $330-300 \text{ cm}^{-1}$ region.²⁵

In conclusion, the general structure of these complexes is shown as:



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