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## Study of ruthenium (III), rhodium (III), palladium (II), platinum (II, IV), osmium (VIII) complexes with $\beta$ -naphthaldehyde-4-benzamido thiosemicarbazone

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### Abstract

In this paper, we studies on the complexes of  $\beta$ - Naphthaldehyde-4-benzamido thiosemicarbazone/p-acetomido benzaldehyde-4-benzamido thiosemicar-carbazone with Ru (III), Rh (III), Pd (II), Pt (II) (IV) and OS (VIII).

**Keywords:** Ruthenium (III), rhodium (III), palladium (II), platinum (II, IV), osmium (VIII)

### Introduction

We have been interested in studying the coordinating properties of thioamide group containing compounds. The interactions of thioamide group containing compounds. The interaction of different metal ions with diversely Substituted amides have been intensively investigated [1-5].

Metal complexes with  $\beta$ -Naphthaldehyde-4-benzamido thiosemicar-bazone (NBTSC) and p-acetamido benzaldehyde-4-benzamido thiosemicarbazone (ABBTSC) of the type  $M.L.Cl_2$ ;  $[M^I L_2 Cl_2] Cl_2$ ,  $[M^{II} L_2 Cl_2] Cl$ ;  $M^{III} L_2 Cl_4$ : where  $M = Pd (II)$ ,  $Pt (II)$ ;  $M^I = Pt (IV)$ ,  $M^{II} = Ru^{+3}/Rh^{+3}$ ,  $M^{III} = OSO_2$ , and  $L = (C_{19}H_{16}N_4OS) / (C_{17}H_{17}N_2O_2S)$  have been isolated and characterised using different physico-chemical methods.  $Pd (II) / Pt (II)$  - complexes have square planar geometry while other platinum metals have octahedral geometry as revealed by magnetic and electronic spectral studies. Both are neutral ligands having  $-CH=N$  and  $>C=S$  as the coordinating sites.

### Materials and Methods

The metal salt (2m mol) (Chloride in case of Ru (III), Rh (III), Pd (II), Pt (II), Pt (IV) osmic acid in case of osmium (VIII) was dissolved in 20-30 ml of methanol ( $PdCl_2$  was dissolved in water). To this 4 m mol of ligand (NBTSC) / (ABBTSC) in methanol (20 ml) was added slowly with constant stirring and the mixture was refluxed for 3-hour. On concentration, evaporation and standing over night yielded colored mass which were filtered, washed and dried.

The metal chlorides (Arora Matthey) were purified by evaporating with concentrated hydrochloric acid several times before use. The ligand  $\beta$ -naphthaldehyde - 4 - benzamido thiosemicarbazone ( $C_{19} H_{16} N_4 OS$ ) / p-acetamido benzaldehyde-4-benzamido thiosemicarbazone ( $C_{17} H_{17} N_2 O_2 S$ ).

### Discussion of the Results

The analytical and physical data of the compounds under study are present in Table 1.

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**Table 1:** Analytical data of the platinum metal complexes

S. No.	Complex	Color	% Found (Calculated)								$\mu$ -eff. Magnetic Moment (B.M.)	$\Omega$ M (mho $\text{cm}^2 \text{mol}^{-1}$ )
			C	H	N	S	X	Metal				
1.	$\text{Pd}(\text{C}_{19}\text{H}_{16}\text{N}_4\text{OS})\text{Cl}_2$	Orange	41.0 (41.37)	2.95 (3.04)	10.31 (10.63)	6.01 (6.07)	13.10 (13.51)	20.01 (20.23)	0.52	62.14		
2.	$\text{Pd}(\text{C}_{17}\text{H}_{17}\text{N}_5\text{O}_2\text{S})\text{Cl}_2$	Orange	38.01 (36.31)	3.07 (3.17)	13.03 (13.14)	6.97 (6.01)	12.98 (13.32)	19.02 (19.95)	0.64	57.6		
3.	$\text{Pt}(\text{C}_{19}\text{H}_{16}\text{N}_4\text{OS})\text{Cl}_2$	Reddish	37.02 (37.12)	2.52 (2.60)	7.01 (7.11)	5.01 (5.21)	11.40 (11.56)	31.10 (31.76)	0.40	60.30		
4.	$\text{Pt}(\text{C}_{17}\text{H}_{17}\text{N}_5\text{O}_2\text{S})\text{Cl}_2$	Reddish	32.12 (32.82)	2.64 (2.71)	11.01 (11.25)	5.02 (5.15)	11.0 (11.48)	30.79 (31.41)	0.30	55.14		
5.	$[\text{Pt}(\text{C}_{19}\text{H}_{16}\text{N}_4\text{OS})_2\text{Cl}_2]\text{Cl}_2$	Reddish	44.0 (44.13)	3.04 (3.07)	10.63 (10.84)	6.13 (6.19)	13.60 (13.74)	18.22 (18.88)	0.24	58.11		
6.	$[\text{Pt}(\text{C}_{17}\text{H}_{17}\text{N}_5\text{O}_2\text{S})_2\text{Cl}_2]\text{Cl}_2$	Reddish	38.83 (38.94)	3.76 (3.24)	13.18 (13.35)	6.05 (6.11)	13.44 (13.54)	18.20 (18.63)	0.34	50.34		
7.	$[\text{Ru}(\text{C}_{19}\text{H}_{16}\text{N}_4\text{OS})_2\text{Cl}_2]\text{Cl}$	Grey	50.10 (50.46)	3.46 (3.54)	12.23 (12.37)	7.0 (7.08)	11.60 (11.78)	11.01 (11.16)	1.91	31.4		
8.	$[\text{Ru}(\text{C}_{17}\text{H}_{17}\text{N}_5\text{O}_2\text{S})_2\text{Cl}_2]\text{Cl}$	Grey	44.10 (44.46)	3.56 (3.70)	15.10 (15.25)	6.70 (6.95)	11.43 (11.60)	10.95 (11.01)	1.90	30.2		
9.	$[\text{Rh}(\text{C}_{19}\text{H}_{16}\text{N}_4\text{OS})_2\text{Cl}_2]\text{Cl}$	Brown	50.24 (50.34)	3.45 (3.53)	12.10 (12.35)	6.95 (7.06)	11.60 (11.76)	11.25 (11.36)	0.25	30.0		
10.	$[\text{Rh}(\text{C}_{17}\text{H}_{17}\text{N}_5\text{O}_2\text{S})_2\text{Cl}_2]\text{Cl}$	Brown	44.25 (44.37)	3.55 (3.67)	15.08 (15.22)	6.70 (6.94)	11.40 (11.58)	11.04 (11.19)	0.16	33.32		
11.	$[\text{OSO}_2(\text{C}_{19}\text{H}_{16}\text{N}_4\text{OS})_2\text{Cl}_2]\text{Cl}_4$	Chocolate Brown	42.66 (43.01)	2.94 (3.01)	9.83 (10.54)	5.88 (6.03)	12.31 (13.37)	–	0.20	103.2		
12.	$[\text{OSO}_2(\text{C}_{17}\text{H}_{17}\text{N}_5\text{O}_2\text{S})_2]\text{Cl}_4$	Chocolate Brown	37.76 (37.98)	3.01 (3.16)	12.75 (13.03)	5.82 (5.93)	12.74 (13.21)	–	0.15	108.0		

The analytical results are in good agreement with the proposed compositions of the ligand and the metal complexes. The IR-spectrum of the ligand exhibit absorption peak as  $1635\text{cm}^{-1}$  and  $1050\text{cm}^{-1}$  which are assigned to  $(-\text{CH}=\text{N})$  and  $\nu(\text{C}=\text{S})$  mode respectively. A comparison of the spectra of the free ligand and its metal complexes indicate that the frequencies of  $-\text{CH}=\text{N}$ , and  $(\text{C}=\text{S})$  modes get shifted to lower wavenumbers by  $10\text{-}40\text{cm}^{-1}$  and  $30\text{-}40\text{cm}^{-1}$  respectively. Such a negative shift in the frequencies indicate the participation of these groups to chelation. This observation is in conformity with the bidentate coordination of the ligand. The magnetic moment values of the complexes studied are presented in table. The

$\text{Pd}(\text{II})$ ,  $\text{Pt}(\text{II,IV})$ ,  $\text{OS}(\text{VIII})$ ,  $\text{Rh}(\text{III})$  complexes were found to be diamagnetic while all the  $\text{Ru}(\text{III})$  complexes are paramagnetic with magnetic moment values close to the spin only values. The magnetic moment values of  $\text{Ru}(\text{III})$  and  $\text{Rh}(\text{III})$  complexes are indicative of an octahedral structure of these metal ions

The electronic spectra of  $\text{Ru}(\text{III})$  complexes are generally complicated with eight transition from  ${}^2\text{T}_{2g}$  ground state. Present complexes shows number of bands in the vicinity of  $16300\text{-}17540$ ,  $20300\text{-}21700$ ,  $24800\text{-}28030$ ;  $29060\text{-}32520$  and  $33010\text{-}42200\text{cm}^{-1}$  which are assigned to  ${}^2\text{T}_{2g} \rightarrow {}^2\text{A}_{2g}$ ;  ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$  and  ${}^2\text{T}_{2g} \rightarrow {}^2\text{A}_{1g}$ ; in order of increasing energy having octahedral geometry, as shown in table-2

**Table 2:** Electronic spectral data and relevant ligand field parameters of rh (III) complexes.

S. No.	Compound	Observed Bands $\text{cm}^{-1}$	Assignments	$\nu_2/\nu_1$	B	$\Delta$	$\beta$	L.F.S.E.K. Cals per mole	F	$\text{gx}10^3$	K	K
1.	$[\text{Rh}(\text{C}_{19}\text{H}_{16}\text{N}_4\text{OS})_2\text{Cl}_2]\text{Cl}$	13780 21890 30860 41860	${}^1\text{A}_{1g} \rightarrow {}^3\text{T}_{1g}$ $\rightarrow {}^1\text{T}_{1g}(\nu_1)$ $\rightarrow {}^1\text{T}_{1g}(\nu_2)$ Charge Transfer	1.40	560	15506	0.77	17.71	0.55	27.0	0.74	0.30
2.	$[\text{Rh}(\text{C}_{17}\text{H}_{17}\text{N}_5\text{O}_2\text{S})_2\text{Cl}_2]\text{Cl}$	14000 22220 32040 40000	${}^1\text{A}_{1g} \rightarrow {}^3\text{T}_{1g}$ $\rightarrow {}^1\text{T}_{1g}(\nu_1)$ $\rightarrow {}^1\text{T}_{1g}(\nu_2)$	1.44	613.75	16.41	0.83	18.42	0.57	27.0	0.55	0.30

$\text{Ru}(\text{III})$  complexes exhibit three bands at  $14000$ ,  $22000$  and  $32000\text{cm}^{-1}$  assignable to  ${}^1\text{A}_{1g} + {}^3\text{T}_{1g}$ ;  ${}^1\text{A}_{1g} + {}^1\text{T}_{1g}(\nu_1)$  and  ${}^1\text{A}_{1g} + {}^1\text{T}_{2g}(\nu_2)$  transitions respectively indicating octahedral geometry of  $\text{Rh}(\text{III})$  compound. Various ligand field parameters such as inter electronic repulsion energies or Racah inter electronic repulsion parameter B-C., Dq- and L.F.S.E. were evaluated. The value. Than the free ion value indicating orbital overlap and delocalization of d-orbitals.  $\beta$ -values obtained are less than unity suggesting considerable amount of character of the metal-ligand bonds. Three transitions are expected for square planar  $\text{Pt}(\text{II})$  complexes. But most of the reported (Mishra and Jha)  $\text{Pt}(\text{II})$  complexes do not show all these bands. The  $\text{Pt}(\text{II})$  complexes of NBTSC and ABBTSC show two and one band respectively alongwith one charge transfer band.

Electronic spectra of the platinum (IV) complexes exhibit number of bands which have been anticipated to  ${}^1\text{A}_{1g} \rightarrow {}^3\text{T}_{1g}$ ;  ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$ ;  ${}^1\text{A}_{1g} \rightarrow {}^1\text{E}_g$ ;  ${}^1\text{A}_{1g} \rightarrow {}^2\text{T}_{2g}$  and  ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1u}$  transitions in order of increasing energy in the range of  $19000\text{-}19370$ ,  $27000\text{-}27640$ ,  $31300\text{-}31630$ ,  $34150\text{-}35530$  and  $37200\text{-}38150\text{cm}^{-1}$  respectively. The bands noticed at  $27100$  and  $31130\text{cm}^{-1}$  are the split of  ${}^1\text{T}_{1g}$  levels which has been predicted at  $28700\text{cm}^{-1}$  in other octahedral complexes. The splitting is due to the lowering of symmetry from octahedral to  $\text{D}_{4h}$ -symmetry.

## Conclusion

It may be concluded that all the platinum metals have octahedral stereochemistry except bivalent  $\text{Pt}$ - and  $\text{Pd}$ , which have square : planar geometry and the coordinating sites of the ligands are  $>\text{C}=\text{S}$  and  $-\text{CH}=\text{N}$  respectively.

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