Asian Journal of Chemistry; Vol. 27, No. 12 (2015), 4505-4509

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.19198

Synthesis, Spectral and Thermal Studies of Mixed Ligand Complexes of Rh^{3+} with Nucleobase and Amino Acid

R. ILAVARASI

Department of Chemistry, Kalasalingam University, Krishnankoil-626 126, India

Corresponding author: E-mail: ilavarasi_chidu@yahoo.com; r.ilavarasi@klu.ac.in

Received: 24 March 2015; *Accepted*: 6 May 2015; *Published online*: 29 August 2015; AJC-17498

Mixed ligand complexes of rhodium with nucleobases and amino acid have been synthesized. The complexes have been characterized on the basis of analytical data, thermogravimetric studies, IR, NMR, electronic and XPS studies. The magnetic measurements suggest that all the complexes are diamagnetic as expected for octahedral rhodium(III) complexes. From the infrared spectral studies, it is inferred that in adenine derivatives (ade, amp and $C_6H_5CH_2$-ade) N7 atoms is involved in coordination and in guanine derivatives (Cl-gua and S-gua) both N1 and N7 atom are involved in coordination. The studies suggest that adenine derivatives (amp, C_6H_5 CH_2-ade) gave mononuclear complexes and guanine derivatives (Cl-gua, S-gua) lead to binuclear complexes.

Keywords: Mixed ligand complexes, Rhodium(III), Nucleobases, Aminoacid, Nucleobase sugars.

INTRODUCTION

Depending upon the donor atom and pK values exhibited by the group present in the ligands, it is expected that each donor atom will bind to its own preferred metal ions[1]. The chemistry of metal ions with nucleic acids and their derivatives has been extensively studied[2,3] as it relates to the understanding of the mechanism of action of the anticancer platinum complexes. With d^6 configuration Rh(III) favours diamagnetic complexes. In the complex $[Rh(NH_2CH_2CH_2COO)_3]\cdot 2H_2O$, the ligand 3-aminopropanoic acid is bidentate and coordinated through the N and O atoms[4]. The adenosine triphosphate rhodium complexes were reported and N7 of purine is bound to the metal. Synthesis and properties of rhodium complexes with nitrogen ligands of type $[RhCl_n(Hpz)_m]$ have been studied for cytostatic activity against HCV29T tumor cells and the cytostatic activity of the isolated complexes is greater than that of cisplatin[5]. A rhodium(III) complex, *rac*-$[Rh(bpy)_2phzi]^{3+}$ (bpy, 2,2′-bipyridine; phzi, benzo[*a*]phenazine-5,6-quinone diimine) has been designed as a sterically demanding intercalator targeted to destabilized mismatched sites in double-helical DNA. This mismatch-specific targeting, offers a potential strategy for new chemotherapeutic design[6]. Synthesis of complexes of the type *trans*-$[RhL_4X_2]Y$ (L = 3 or 4-substituted pyridine, 3,5-disubstituted pyridine, isoquinoline, pyrimidine, pyrazole, thiazole, X = Cl, Br and Y = univalent anion) are described and the characterization of the formed complexes is studied[7].

EXPERIMENTAL

Rhodium(III) chloride (1.0 mmol) and N6-benzyladenine (1 mmol) are suspended in methanol solution. The contents were stirred for 24 h and left overnight. The resultant brown precipitate formed is filtered, washed with acetone and air-dried. The ligand amp required refluxion. Synthesis of $RhCl_3(C_6H_5$-CH_2-ade$)(H_2O)_2$, $RhCl_3(amp)(H_2O)_2$, $Rh_2Cl_6(H_2O)_4$(Cl-gua), $Rh_2Cl_6(H_2O)_4$(S-gua) was done.

$Rh_2Cl_5(H_2O)_3$(Cl-gua)(cys): $Rh_2Cl_6(H_2O)_4$(Cl-gua) (1 mmol) and cysteine (1 mmol in 15 mL of water) are suspended in ethanol and refluxed for 2 h. The resulting clear solution is neutralized with KOH (1 mmol) and the resultant yellow precipitate obtained on stirring is filtered and weighed with acetone and dried.

$RhCl(ade)(NH_3)_4]Cl_2H_2O$: To the rhodium chloride (1 mmol) in water was added NH_4Cl (1 mmol) and ammonium carbonate (7 mmol). The mixture is allowed to stand for 4 h. It is then cooled and allowed to crystallize. The golden yellow precipitate is collected to crystallize and the product is collected. It is extracted with 100 mL of boiling HCl and H_2O (2:1 by volume). The precipitate is then refluxed with adenine to get the desired complex.

RESULTS AND DISCUSSION

The reactions of rhodium(III) with nucleobases is shown in Fig. 1. The analytical and conductivity data of all the

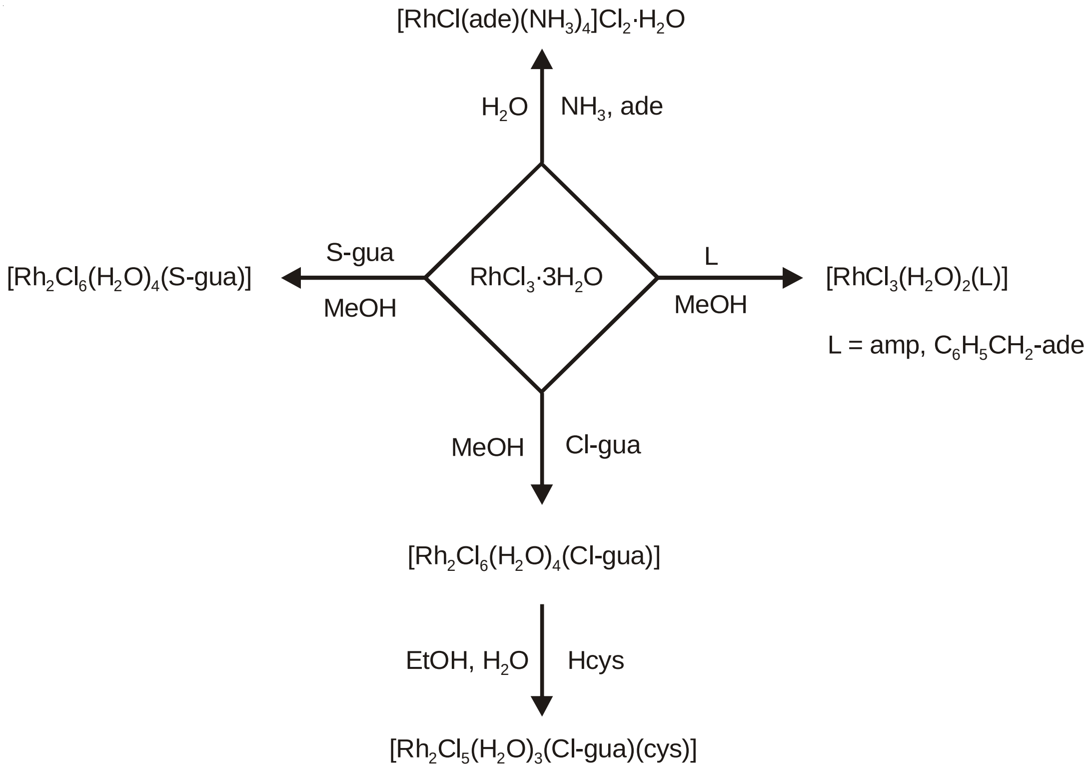

Fig. 1. Reactions of $RhCl_3$ with nucleobases

TABLE-1
ANALYTICAL AND CONDUCTIVITY DATA OF Rh(III) COMPLEXES

Complexes	Elemental analysis (%): Found (calcd.)					*Molar conductance (ohm^{-1} cm^2)
	C	H	N	Cl	Rh	
$RhCl_3(C_6H_5\text{-}CH_2\text{-ade})(H_2O)_2$	30.38 (30.63)	3.49 (3.21)	15.41 (14.89)	22.96 (22.60)	22.43 (21.87)	4.2
$RhCl_3(amp)(H_2O)_2$	19.05 (19.67)	1.73 (2.31)	11.83 (11.47)	17.36 (17.42)	16.81 (16.86)	–
$Rh_2Cl_6(H_2O)_4(Cl\text{-gua})$	8.53 (9.20)	2.4 (1.83)	11.21 (10.61)	32.42 (32.22)	30.22 (31.18)	3.8
$Rh_2Cl_6(H_2O)_4(S\text{-gua})$	8.63 (9.13)	1.87 (1.99)	10.65 (10.65)	31.97 (32.34)	32.09 (31.29)	–
$Rh_2Cl_5(H_2O)_3(Cl\text{-gua})(cys)$	16.49 (15.89)	2.50 (2.80)	10.92 (11.12)	28.12 (28.14)	26.73 (27.23)	4.2
$[RhCl(ade)(NH_3)_4]Cl_2H_2O$	13.62 (13.95)	4.00 (3.98)	29.11 (29.30)	24.72 (24.71)	24.41 (23.91)	120

*10^{-3} M in DMSO

complexes are presented in Table-1. The complexes **2** and **4** are found to be insoluble in DMSO, water and common organic solvents and all the other complexes (**1**, **3**, **5** and **6**) are soluble in DMSO. The molar conductance of $[RhCl(NH_3)_4(ade)]Cl_2$ is 120 ohm^{-1} cm^2 characteristics of 1:2 electrolytes[8] and other rhodium complexes show a molar conductance of around 4 ohm^{-1} cm^2 suggesting them to be non-ionic. The magnetic measurements suggest that all the complexes are diamagnetic as expected for octahedral rhodium(III) complexes.

Thermonalytical studies: The TG and DTA plots of the rhodium(III) complexes are given in Figs. 2 and 3. The thermoanalytical data are presented in Tables 2 and 3.

TABLE-2
THERMONALYTICAL DATA OF Rh(III) COMPLEXES

Complexes	Dehydration				Decomposition			
	Temp. range (°C)	Weight loss (%)		DTA peak (°C)	Temp. range (°C)	Weight loss (%)		DTA peak (°C)
		Found	Calcd.			Found	Calcd.	
$RhCl_3(C_6H_5\text{-}CH_2\text{-ade})(H_2O)_2$	100-135	6.9	7.65	-120	145-200	22.9	22.60	-160
$RhCl_3(amp)(H_2O)_2$	110-130	6.1	5.90	-120	150-200	17.1	17.42	-160
$Rh_2Cl_6(H_2O)_4(Cl\text{-gua})$	110-140	10.1	10.91	-125	190-260	32.0	32.25	-200
$Rh_2Cl_6(H_2O)_4(S\text{-gua})$	110-140	10.1	10.95	-130	200-250	31.7	32.34	-200
$Rh_2Cl_5(H_2O)_3(Cl\text{-gua})(cys)$	110-130	6.9	7.14	-115	190-225	26.3	28.14	-190
$[RhCl(ade)(NH_3)_4]Cl_2.H_2O$	70-150	35.0	36.44 (NH_3, H_2O & Cl_2)	-85 -140	180-200	9.1	8.23	-180

(-): Endotherm

TABLE-3
THERMONALYTICAL DATA OF Rh(III) COMPLESES

Complexes	Formation of Rh_2O_3			DTA peak (°C)
	Temp. range (°C)	Weight loss (%):		
		Found	Calcd.	
$RhCl_3(C_6H_5\text{-}CH_2\text{-ade})(H_2O)_2$	220-410	73.6	73.02	+280, +375
$RhCl_3(amp)(H_2O)_2$	220-410	56.2	55.95	+290, +380
$Rh_2Cl_6(H_2O)_4(Cl\text{-}gua)$	265-415	62.7	61.55	+300, +385
$Rh_2Cl_6(H_2O)_4(S\text{-}gua)$	270-410	60.2	61.41	+325, +390
$Rh_2Cl_5(H_2O)_3(Cl\text{-}gua)(cys)$	270-400	66.0	66.42	+320, +395
$[RhCl(ade)(NH_3)_4]Cl_2.H_2O$	230-400	70.9	70.51	+320

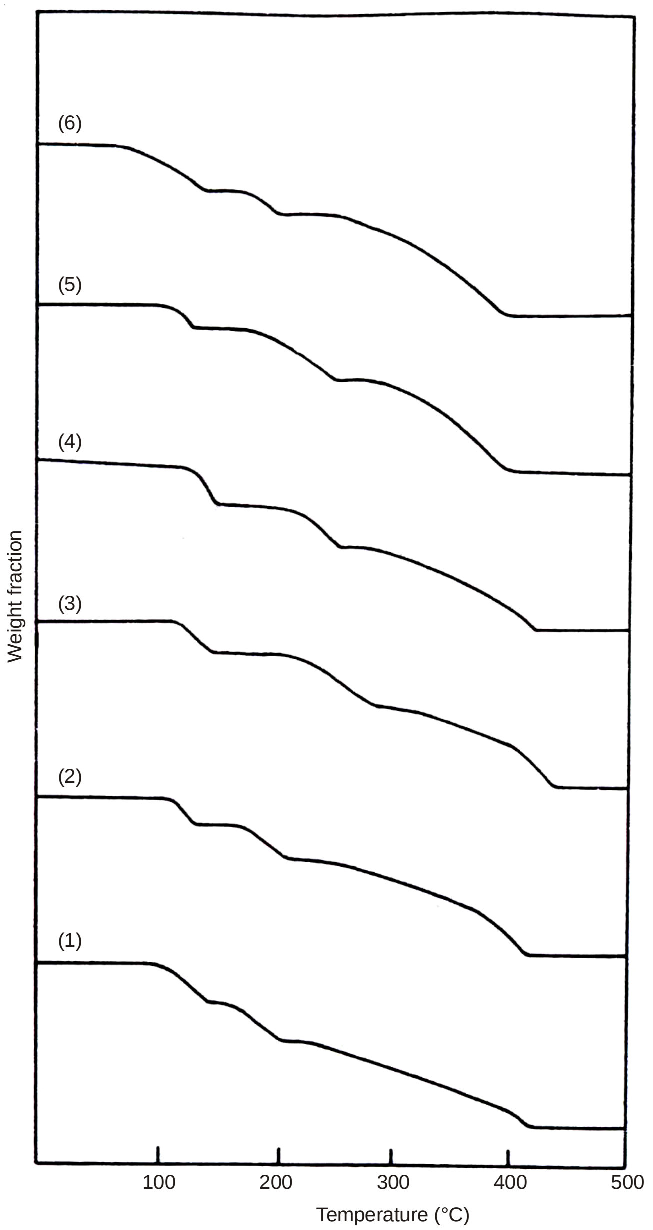

Fig. 2. TG curves of $RhCl_3L(H_2O)_2$, L = (1) $C_6H_5CH_2$-ade (2) amp; $Rh_2Cl_6(H_2O)_4L$, L = (3) Cl-gua (4) S-gua (5) $Rh_2Cl_5(H_2O)_3$(Cl-gua)(cys) (6) $[RhCl(ade)(NH_3)_4]Cl_2\cdot H_2O$

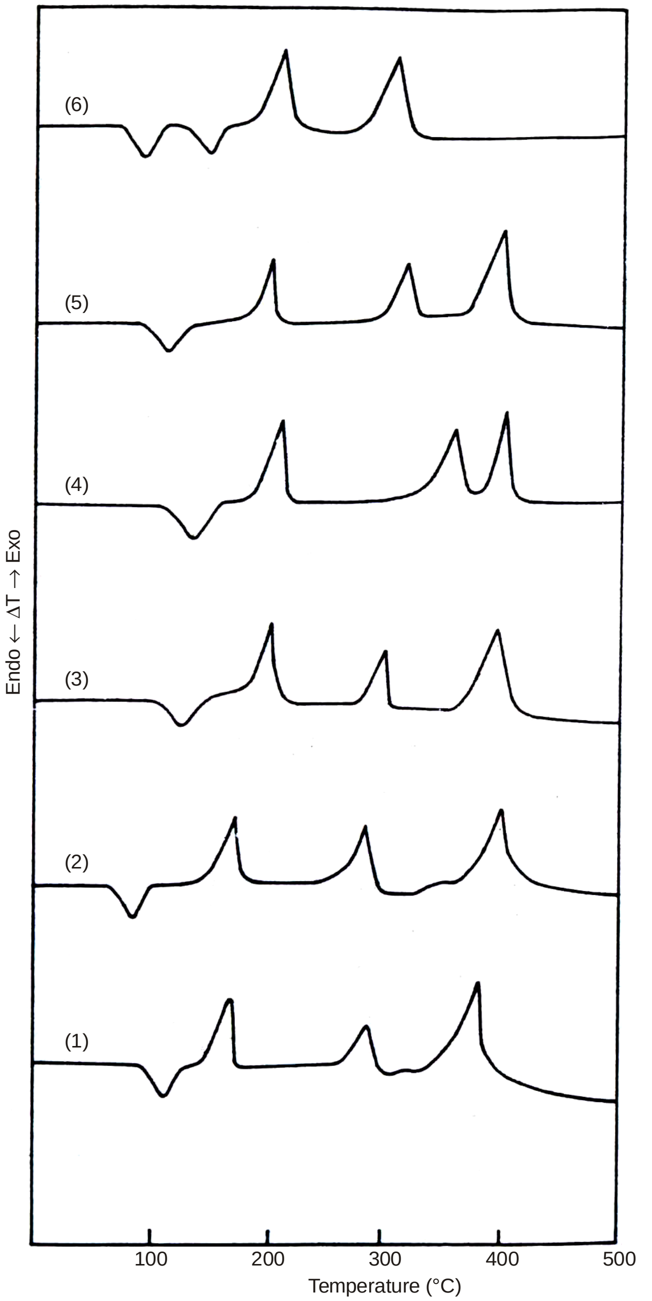

Fig. 3. DTA curves of $RhCl_3L(H_2O)_2$, L = (1) $C_6H_5CH_2$-ade (2) amp; $Rh_2Cl_6(H_2O)_4L$, L = (3) Cl-gua (4) S-gua (5) $Rh_2Cl_5(H_2O)_3$(Cl-gua)(cys) (6) $[RhCl(ade)(NH_3)_4]Cl_2\cdot H_2O$

It is seen from the plots that the complex **1** is stable upto 110 °C. The complex **1** starts losing weight above 110 °C due to the loss of coordinated water molecules. The loss in weight observed (6.9 % of the initial mass) agrees fairly well to the calculated value (7.65 %). This dehydration process is confirmed by the endothermic peak maximum observed at 120 °C in the DTA plot. The chloride ligands start getting expelled around 145 °C and goes upto 200 °C for the complex **1**. The observed loss in the weight of about 21.4 % of the initial mass agrees well with the calculated value (22.60 %). The process is characterized by the endothermic peak observed at 160 °C. The decomposition of organic moieties occur in the range 220-410 °C. The final residue obtained around 410 °C is found to be 24.9 % of the initial weight attributable to Rh_2O_3 confirmed by its X-ray powder pattern (calcd.: 26.97 %). The complex **2** also shows nearly same behaviour except that its final residue was found to be a mixture of Rh_2O_3 and Na_2HPO_4.

The complex **3** loses all of its molecules in the temperature range 110-140 °C with endothermic peak at 125 °C, its chloride around 200 °C with an endothermic peak at 200 °C and expulsion of organic moiety in the range 265 to 415 °C to leave behind Rh_2O_3 as residue[9,10]. The complexes **4** and **5** also showed a similar behaviour. The thermal studies suggest that the guanine complexes (**3, 4** and **5**) have more thermal stability compared to those of adenine complexes (**1** and **2**). It would be expected that the more basic the ligand the stronger is the metal-ligand bond. Thus, most basic nitrogen has been used in coordination towards metal in the guanine complexes and hence the decomposition of the complexes occur at higher temperature.

The complex **6** also decomposes in three stages. The onset of decomposition begins at 70 °C and about 35 % of the initial mass is lost by 150 °C. The calculated weight loss (26.44 %) suggests the loss of water. chloride and ammonia molecules. This is confirmed by the endothermic peak maxima at 85 and 140 °C In the DTA plot. The removal of coordinated chloride molecules between 180-195 °C is characterized by an endothermic peak at 180 °C. Finally the decomposition of adenine takes place between 230-400 °C with exothermic peak at 320 °C leaving behind Rh_2O_3.

Electronic spectral studies: The electronic spectra of the rhodium(III) complexes taken in nujol medium and DMSO showed the λ_{max} around 450 nm which are normally expected for a distorted octahedral rhodium(III) complexes[11]. The intense maxima observed in the spectra of the complexes are mostly for the charge-transfer type, with contributions from $^1A_{1g} \rightarrow {}^1T_{1g}$ transition.

Infrared spectral studies: The spectral data are listed in Table-4. The spectra of the complexes are compared with those of free ligand and the characteristic bands of the nucleobase in the complexes are used for the discussion of their bonding to rhodium(III). The IR spectra of the complexes $RhCl_3(C_6H_5CH_2$-ade)$(H_2O)_2$, $RhCl_3$(amp)$(H_2O)_2$ and [RhCl(ade)$(NH_3)_4]Cl_2$-H_2O showed the non-involvement of –NH group in coordination to the metal and also the presence of hydrogen bonding with other ligands. Only in the imidazole ring frequencies (1415, 1330 and 1305 cm^{-1}), a slight reduction in wavenumbers is noticed suggesting the N7 coordination to rhodium(III). The complex [RhCl(ade)$(NH_3)_4]Cl_2 \cdot H_2O$ shows sharp and intense band at 1640cm^{-1} and assigned to the bending vibrations of NH_3 in the complex[12]. The infrared spectral characteristics of the complexes **3-5** showed shifts to 1410, 1335 and 1310 cm^{-1} indicating the coordination of N1 and N7 of nucleobases to rhodium(III).

In the mixed ligand complex, Rh_2Cl_5(Cl-gua)$(H_2O)_3$(cys), the band at 1725 cm^{-1} indicates that the carboxy1 group is not involved in bonding with the metal[13]. The absence of ν_{SH} frequency normally found at 2500 cm^{-1} suggests the deprotonation of the thiol group and hence its coordination to rhodium(III). The coordination of the NH_2 group of the aminoacid is inferred from the presence of the band at 1587 cm^{-1} due to δ_{NH_2}. Thus cysteine is acting as a bidentate chelating ligand through sulfur and nitrogen atoms.

From the infrared spectral studies, it is inferred that in adenine derivatives (ade, amp and $C_6H_5CH_2$-ade) N7 atoms is involved in coordination and in guanine derivatives (Cl-gua and S-gua) both N1 and N7 atoms are involved in coordination.

In the far IR spectra, the broad and medium intense bands at 375 and 515 cm^{-1} are assigned to V_{Rh-Cl} and V_{Rh-N}, respectively[14-16]. The band at 390 cm^{-1} is assigned to V_{Rh-s} in the mixed ligand complex with cysteine.

^{1}H NMR spectral studies: The characteristics ^{1}H NMR chemical shifts of the complexes $Rh_2Cl_6(H_2O)_4$(Cl-gua) and $Rh_2Cl_5(H_2O)_3$(Cl-gua)(cys) are given in Table-5. In the former complex, the H8 resonance is shifted downfield by 0.25 ppm compared to that of ligand and this may be attributed to the

TABLE-4
PRINCIPAL INFRARED SPECTRAL DATA (cm^{-1}) OF RHODIUM(III) COMPLEXES

Complexes	ν(NH), ν(OH)	δ(NH_2)	ν(C=C), ν(C=N)$_{Imidazole\ ring}$	ν(C=C), ν(C=N)$_{Pyrimidine\ ring}$	ν(C=O), ν(C-S)	ν(Rh-Cl)	ν(RH-N)	ν(Rh-O), ν(Rh-S)
$RhCl_3(C_6H_5$-CH_2-ade)$(H_2O)_2$	3310s 3220s	1645s	1405m, 1325m 1295m	1600s 1440m	–	375w	515m	420m
$RhCl_3$(amp)$(H_2O)_2$	3333s 3160s	1645s	1410m 1320m 1295m	1600s 1440m	–	373w	515m	425m
$Rh_2Cl_6(H_2O)_4$(Cl-gua)	3330s 3225s	1665s	1585m 1550m 1440m	1370m 1345m	–	375w	515m	420w
$Rh_2Cl_6(H_2O)_4$(S-gua)	3340s 3160s	1660s	1590m 1440m 1365m	1380m 1350m	1520m	374w	510m	420w
$Rh_2Cl_5(H_2O)_3$(Cl-gua)(cys)	3330s 3220s	1665s 1587s	1587m 1542m 1441m	1380m 1352m	1725s	375w	512w	420w 390w
[RhCl(ade)$(NH_3)_4]Cl_2H_2O$	3230s 3150s	1665s 1640s	1415m 1315m 1295m	1595m 1440m	–	370w	510w	–

TABLE-5
^1H NMR DATA OF RHODIUM(III) COMPLEXES (SOLVENT-DMSO-d_6, TMS-STANDARD, δ ppm)

Complexes	Nucleobase protons (δ ppm)			Cysteine protens (δ ppm)			
	H8	NH	NH_2	SCH_2	CH	CH_2	CH_3
$Rh_2Cl_6(H_2O)_4$(Cl-gua)	8.00	12.05	7.22	–	–	–	–
$Rh_2Cl_5(H_2O)_3$(Cl-gua)(cys)	8.01	12.05	7.23	2.83	4.10	3.90	1.00

coordination of N7 to the metal. This is also deduced from the fact that N9 remains protonated, as is evidenced by the appearance of the HN9 resonance at 12.05 ppm. Also in the latter complex, similar trend has been observed[17].

X-ray photoelectron spectroscopic studies: The XPS spectra of the complex $RhCl_3(H_2O)_2(C_6H_5CH_2$-ade) in the 3*d* region of rhodium (Fig. 4a) and 2*p* region of Cl (Fig. 4b) are shown. By using the spectral deconvolution program, the binding energies corresponding to rhodium $3d_{5/2}$ and $3d_{3/2}$ are found to be at 310.5 and 315.7 ev respectively. The energy separation between the rhodium spin orbit doublet levels is 5.2 ev. The binding energy of the rhodium $3d_{5/2}$ level in $Rh(C_5H_5N)_3Cl_3$ and $K_3Rh(NO_3)_6$ are 309.9 and 310.0 ev respectively.

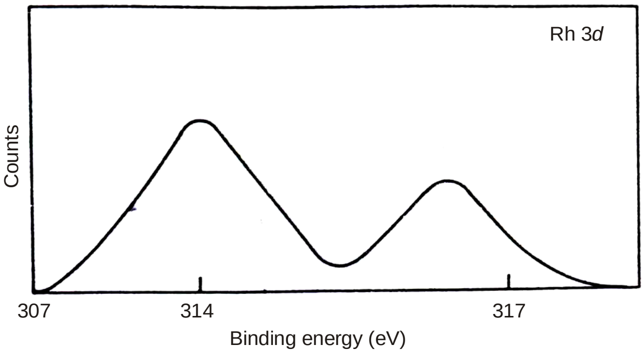

Fig. 4a. X-ray photoelectron spectra of $RhCl_3)C_6H_5CH_2$-ade)$(H_2O)_2$ Rh 3*d* region

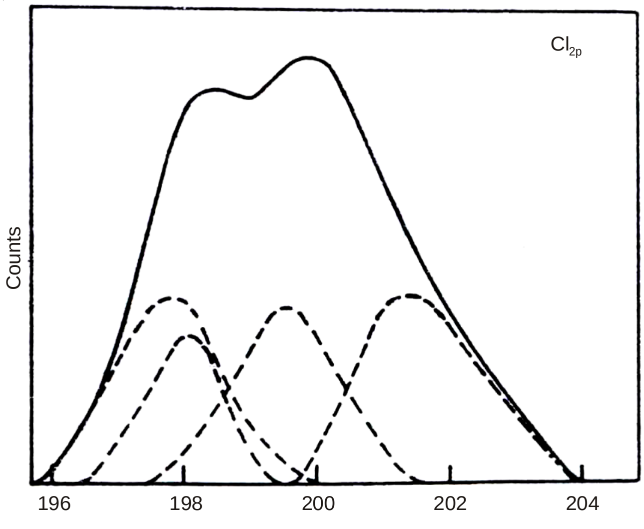

Fig. 4b. X-ray photoelectron spectra of $RhCl_3)C_6H_5CH_2$-ade)$(H_2O)_2$ Cl_{2p} region

A careful study of the binding energy shifts in a molecule can reveal inter- and intra molecular interactions and the XPS spectral data have been used to ascertain the intramolecular hydrogen bonding present in the complex between Cl and NH group of $C_6H_5CH_2$-ade. The photoelectron spectrum in the Cl_{2p} region indicates that there are two type of chlorine atoms. Each chlorine atom gives rise to two peaks corresponding to $2p_{1/2}$ and $2p_{3/2}$ which arise due to spin orbit coupling[18]. The peaks at higher binding energy $2p_{1/2}$ (201.3 ev), $2p_{3/2}$ (199.5 ev) are assigned to H bonded chlorine and the two peaks at low energy values $2p_{1/2}$ (198.1 ev) and $2p_{3/2}$ (197.8 ev) are assigned to the other chlorine atoms present in the complex. In view of the above discussions, the structure of the complex, $RhCl_3(H_2O)_2(C_6H_5CH_2$-ade) is described as an octahedral of rhodium(III) with three chloro ligands, two water molecules and N7 of the $C_6H_5CH_2$-ade. Further NH group of $C_6H_5CH_2$-ade is involved in hydrogen bonding with one of the chloro ligands.

Conclusion

The reaction of rhodium(III) with adenine derivatives (amp, $C_6H_5CH_2$-ade) gave mononuclear complexes which are favoured by the intramolecular hydrogen bonding between NH and Cl group and guanine derivatives (Cl-gua, S-gua) to lead to binuclear complexes.

REFERENCES

1. R.F. Carbonaro, Y.B. Atalay and D.M. Di Toro, *Geochim. Cosmochim. Acta*, **75**, 2499 (2011).
2. N. Farrell, *J. Chem. Soc. Chem. Commun.*, **21**, 1014 (1980).
3. I. Sinha, J. Kosters, A. Hepp and J. Muller, *Dalton Trans.*, **42**, 16080 (2013).
4. T.A. Ryan, *Coord. Chem. Rev.*, **41**, 251 (1982).
5. F.P. Pruchnik, P. Jakimowicz, Z. Ciunik, J. Zakrzewska-Czerwinska, A. Opolski, J. Wietrzyk and E. Wojdat, *Inorg. Chim. Acta*, **334,** 59 (2002).
6. H. Junicke, R.J. Hart, J. Kisko, O. Glebov, R. Ilan Kirsch and K.J. Barton, *Proc. Natl. Acad. Sci. USA*, **100**, 3737 (2003).
7. A.W. Addison, K. Dawson, R.D. Gillard, B.T. Heaton and H. Shaw, *J. Chem. Soc., Dalton Trans.*, **589**, (1972).
8. B.T. Khan, M.R. Somayajulu and M.M.T. Khan, *J. Inorg. Nucl. Chem.*, **40**, 1251 (1978).
9. G. Sánchez, J. García, J. Pérez, G. García and G. López, *Thermochim. Acta*, **307**, 127 (1997).
10. R. Ilavarasi, L. Muthulakshmi and S. Selvanayagam, *Chem. Sci. Transac.*, **4**, 81 (2015).
11. K.V. Sharma, S. Srivastava and A. Srivastava, *Bioinorg. Chem. Appl.*, **Article ID 68374** (2007).
12. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley Interscience, New York (1986).
13. I.P. Khullar and U. Agarwala, *Aust. J. Chem.*, **28**, 1529 (1975).
14. K.V. Sharma and A. Srivastava, *Indian J. Chem.*, **46A**, 1963 (2007).
15. M. Tyagi and S. Chandra, *Open J. Inorg. Chem.*, **2**, 19764 (2012).
16. J.R. Lusty, J. Peeling and M.A. Abdel-Aal, *Inorg. Chim. Acta*, **56**, 21 (1981).
17. J.J. Ziarek, F.C. Peterson, B.L. Lytle and B.F. Volkman, *Methods Enzymol.*, **493**, 241 (2011).
18. A.-T. Yenny, H. Lazaro and B.-B. Norah, *J. Chem.*, **Article ID 370637** (2013).