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Research Article

SYNTHESIS, CHARACTERIZATION, ANTIMICROBIAL ACTIVITIES AND DNA–BINDING STUDIES OF SOME Ru (III) COMPLEXES OF SCHIFF BASES

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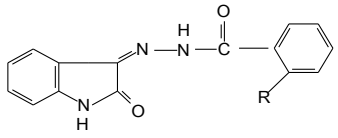
ABSTRACT : A new ruthenium (III) Schiff base complexes of the type $[RuX_2(PPh_3)_2(L)]$ (where X = Cl or Br; L = monobasic bidentate Ligand) have been synthesized. All the complexes were characterized by analytical, IR, electronic and EPR spectral studies. An octahedral geometry has been tentatively proposed to all the new complexes. Further the ligands and complexes were subjected to antimicrobial activity studies. The new complexes have been tested to find out the DNA – binding by electronic spectral studies and anti cancer effect.

Keywords: Monobasic bidentate Schiff bases, ruthenium(III) complexes, spectral studies, antimicrobial activities, DNA binding and anticancer studies.

INTRODUCTION

In recent days, Schiff base ligands have received much attention because of their application in the fields of synthesis and catalysis. A considerable research effort is devoted to the synthesis of new Schiff base complexes with transition metal ions, to further develop applications in the area of catalysis (Leung et al., 1996, Wong et al., 2002) material and pharmaceutical chemistry (Ramesh and Maheswaran 2003, Prabhaharan et al., 2004). A recent report reveals that phosphine ligands play a key role in many reactions catalyzed by transition metals (Pignolet,1983, Simpson et al., 1996, Cornils and Herrmann, 1996). Triphenylphosphine complexes of ruthenium have been employed as catalysts for various organic transformations such as oxidation (Sheldon et al., 2002), hydrogenation (Doucet et al., 1998), C–C couplings (Barrata et al., 2000), hydroformylation (Ahn et al., 1999), isomerisation (Seron et al.,1997), polymerization (Ando et al.,2000), racemisation (Persson et al., 1999) etc. Ruthenium complexes areefficient inDNA binding (Shilpa et al., 2010). As a part of our continuing efforts to synthesis and characterize ruthenium chelates using simple and inexpensive Schiff base ligands, in this paper we describe the synthesis, characterization and DNA binding studies of stable ruthenium (III) complexes. The general structure of the Schiff base ligands used in this study is shown in Fig. 1.



R = H, Cl, NH_2

HL1 : H, HL2 : Cl, HL3:NH_2

Fig. 1. General structure of the Schiff base ligands

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Stable ruthenium (III) complexes of general formula $[RuX_2(PPh_3)_2(L)]$ (X = Cl or Br;L = monobasic bidentate Schiff base ligands) have been prepared by the reaction of equimolar amounts of $[RuX_3(PPh_3)_3]$ and Schiff base in benzene.

$$[RuX_3(PPh_3)_3] + HL \xrightarrow[\text{Reflux, 6h}]{\text{Benzene}} [RuX_2(PPh_3)_2(L)] + HX + PPh_3$$

EXPERIMENTAL

Material and methods

$RuCl_3.3H_2O$, purchased from Loba-Chemie, was used as supplied. All chemicals were of analytical grade. Solvents were purified according to standard procedures (Vogel, 1989).The starting complexes $[RuCl_3(PPh_3)_3]$ (Poddar et al., 1974), and $[RuBr_3(PPh_3)_3]$ (Natarajan et al., 1977) were prepared by reported literature methods. The Schiff base ligands were prepared according to published procedures (Sammaiah et al., 2008).

Physical measurements

Elemental analysis was performed at SAIF- Cochin. IR spectra were recorded in KBr pellets with PerkinElmer Spectrophotometer in the 4000- 450 cm^{-1} range. Electronic spectra were recorded in CH_2Cl_2 solution with Systronic spectrophotometer in the 800 – 200 nm range. EPR spectra of powered samples were recorded with a Jeol TEL-100 instrument at X-band frequencies at room temperature. Melting points were recorded on Boetius micro heating table and were uncorrected.

Preparation of new ruthenium(III) complexes, $[Ru(X)_2(PPh_3)_2(L)]$.

To a solution of $[RuB_3(PPh_3)_3]$ [B= Br or Cl;] 0.1 g, (0.1 – 0.13 mmol) in benzene ($25cm^3$),was added the appropriate Schiff base (0.021 – 0.051g,0.1- 0.13 mmol) (molar ratio of ruthenium complex: Schiff base was 1:1). The solution was heated under reflex for 6 h. Then, it was concentrated to ca.3 cm^3, cooled and new complexes were separated upon addition of small quantity (6 cm^3) of light petroleum (60-80^oC). The products were filtered, washed with light petroleum, recrystallised from CH_2Cl_2/light petroleum mixture and dried in vacuo (yield: 70-80%). All the complexes are brown color and soluble in most of the common organic solvents. Their purity was checked by thin-layer chromatograph.

Antibacterial Activity Studies

Pathogenic microbials namely *Bacillus subtilis, Pseudomonas aeruginosa, Staphylococcus aureus, Streptococcus aureus and Escherichia coli* were used to test the biological potential of the ligands and their complexes of ruthenium(III). The antibacterial activities of the complexes were determined by disc diffusion method. The bacteria were cultured in nutrient agar medium in petriplates and used inoculums for the study. The complexes to be tested were dissolved in DMSO to a final concentration of 0.5% and 1% and soaked in filter paper disc of 5 mm diameter and of 1 mm thickness. The disc were placed on the previously seeded plates and incubated at 35 ± 2^oC for 24 hrs. The diameter of inhibitory zone around each disc was measured after 24 hrs. *Streptomycin* was used as a standard.

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RESULTS AND DISCUSSION

Analytical Studies

The analytical data of the new ruthenium complexes agree very well with the proposed molecular formula. (Table.1.) In all the above reactions, the Schiff base behaves as mononegativebidentate ligands.

I.R. Spectra

The IR spectra of the free ligands were compared with those of the new complexes in order to confirm the coordination of ligands to the ruthenium metal. The IR spectra of the free ligands showed a band in the absorption due to ν(C=N) appears in the 1620 – 1624 cm^{-1} region undergoes reduction in frequency due to lowering of electron density upon coordination. In the spectra of all the new complexes, this band is shifted to the region of 1593 – 1579 cm^{-1} indicating the coordination through nitrogen atom (Karvembu et al., 2003). A strong band which appeared in the spectra of ligands around 1248 -1273 cm^{-1} due to ν(C-O) completely disappeared and a new band was observed around 1340 -1352 cm^{-1}. This may be due to the enolisation and subsequent coordination through deprotonated oxygen atom (Viswanathamurthy et al., 1998). In addition to above, the characteristic bands due to PPh_3 or $AsPh_3$ were also present in the expected region (Ramesh and Sivagamasundari, 2003). (Table.2.).

Table 1.Analytcial data of new Ru (III) Complexes.

Complex	Mp (°C)	Yield (%)	Calculated(found)%		
			C	H	N
[RuCl2(PPh3)2(L1)]	129	80	63.75(63.68)	4.16(4.18)	4.37(4.30)
[RuBr2(PPh3)2(L1)]	222	75	57.25(57.21)	3.74(3.70)	3.92(3.89)
[RuCl2(PPh3)2(L2)]	142	75	61.56(61.50)	3.92(3.87)	4.22(4.18)
[RuBr2(PPh3)2(L2)]	215	70	55.48(55.51)	3.53(3.50)	3.80(3.82)
[RuCl2(PPh3)2(L3)]	198	80	62.77(62.73)	4.20(4.23)	5.74(5.71)
[RuBr2(PPh3)2(L3)]	206	75	56.45(56.40)	3.78(3.81)	5.16(5.20)

Electronic Spectra

The electronic spectra showed three to four bands in the 408 – 246 nm region. (Table.2.).The ground state of ruthenium(III) is $^2T_{2g}$ and the first excited doublet levels, in order to increasing energy are $^2A_{2g}$ and $^2T_{1g}$ which arises from $t^5_{2g}\ e^1_g$ configuration (Ballhausen, 1962). In the most of the ruthenium(III) complexes the electronic spectra (Fig.2). showed only charge transfer bands (Lever, 1984). The band in the 403 – 350 nm region have been assigned to the d-d transition, which is in conformity with assignments made for the similar ruthenium(III) complexes (Natarajan and Agarwala, 1976, Jayakumar and Natarajan, 1992). Other bands in the 315-246 nm region have been assigned to the charge transfer transitions (Balasubramanian et al., 2006). In general the electronic spectra of the all the complexes are characteristic of an octahedral environment around ruthenium (III) ions.

Magnetic moments

The magnetic moments for some of the complexes have been measured at room temperature using a vibration sample magnetometer. The values obtained in the 1.90 – 1.96 BM range corresponding to one unpaired electrons, suggesting a low spin t^5_{2g} configuration for ruthenium(III) ion in pseudo – octahedral environment (Figgis, 1966).

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Table.2. IR and UV – Vis Spectral data of ligands and new Ru(III) Complexes.

Ligand/Complex	ν (C=N)	ν (C –O)	Λmax
HL1	1624	1273	-
[RuCl2(PPh3)2(L1)]	1601	1343	246, 320,360
[RuBr2(PPh3)2(L1)]	1580	1345	248, 316, 368, 393
HL2	1623	1270	
[RuCl2(PPh3)2(L2)]	1600	1347	246, 315, 368
[RuBr2(PPh3)2(L2)]	1591	1342	248, 316, 363, 390
HL3	1604	1248	
[RuCl2(PPh3)2(L3)]	1600	1341	248, 318, 350
[RuBr2(PPh3)2(L3)]	1578	1345	246, 313, 369, 408

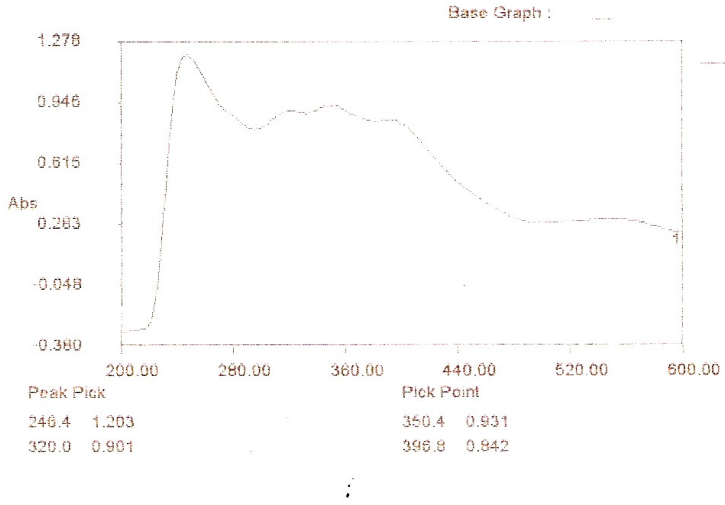

Fig. 2. Electronic spectra of $[RuCl_2(PPh_3)_2(L_1)]$

EPR Spectra

The room temperature spectra of powdered samples were recorded at X-band frequencies. The g values of the complexes are listed in Table.3.show that the complexes exhibit spectra with a $g_{\perp}$at 1.99 – 2.05 and $g_{\parallel}$ at 1.99 – 2.6. Fig. 3.The presence of two g values is an indication of an octahedral field with tetragonal distortion ($g_x = g_y \neq g_z$) and also points out an axial symmetry for the complexes and hence Trans positions are assigned to PPh_3 groups. The nature and pattern of the EPR spectra suggests an almost perfect octahedral environment around the ruthenium ion in these complexes (Manivannan et al.,. 2007, Kim et al., 1996).

Table.3. EPR Speectral data of new Ru(III) Complexes.

Complex	gx	gy	gz	<g>a
[RuCl2(PPh3)2(L1)]	1.99	1.99	1.85	1.94
[RuBr2(PPh3)2(L1)]	2.18	2.18	1.96	2.18
[RuCl2(PPh3)2(L2)]	2.12	2.12	2.01	2.07
[RuBr2(PPh3)2(L2)]	2.05	2.05	1.91	2.00
[RuCl2(PPh3)2(L3)]	2.08	2.08	1.92	2.03
[RuBr2(PPh3)2(L3)]	2.05	2.05	1.96	2.02

$<g>^a = [1/3 (g_x^2 + g_y^2 + g_z^2)]^{1/2}$

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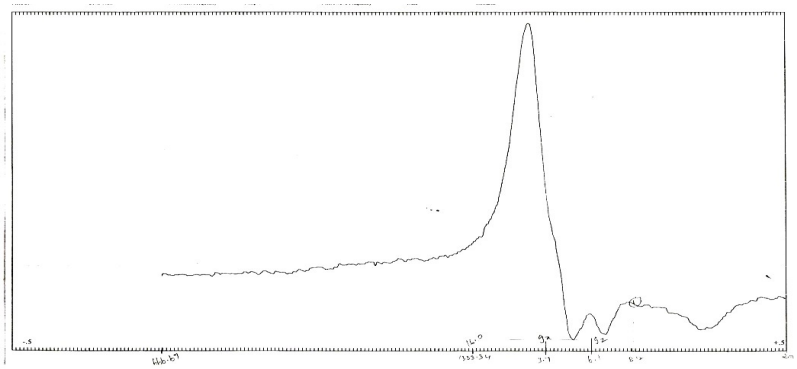

Fig. 3.EPR Spectrum of $[RuCl_2(PPh_3)_2(L_1)]$

Antibacterial Activity

The *invitro* antimicrobial screening of the new ruthenium complexes have been carried out against *Bacillus subtilis, Pseudomonas aeruginosa, Staphylococcus aureus, Streptococcus aureus, Escherichia coli* by using a nutrient agar medium by disc diffusion method (Table.4.). The toxicity increases with increasing concentration (Balasubramanian et al., 2004). The increase in the antibacterial activity of metal chelates may be due to the effect of the metal ion on the normal cell process. A possible mode of the toxicity increase may be considered in light of Tweedy's chelation theory (Tweedy, 1964). Chelation considerably reduces the polarity of the metal ion because of partial sharing of its positive charge with the donor groups and possible π-electron delocalization over the whole chelate ring. Such chelation could enhance the lipophilic character of the central metal atom, which subsequently favors its permeation through the lipid layers of cell membrane. Furthermore, the mode of action of the compounds may involve in the formation of a hydrogen bond through the azomethine (>C=N) group with the active centers of cell constituents, resulting in interference with the normal cell processes. Though the complexes possess activity, it could not reach the effectiveness of the standard drug *streptomycin.* The variation in the effectiveness of the different compounds against different organisms depends either on the impermeability of the cells of the microbes or differences in ribosome of microbial cells (Dharmaraj et al., 2001).

Table 4. Antimicrobial activity of ligands and Ru(III) complexes

Ligand /Complex	*Bacillus Subtilis*		*Pseudomonas aeruginosa*		*Staphylococcus aureus*		*Streptococcus aureus*		*Escherichia coli*	
	0.5%	1.0%	0.5%	1.0%	0.5%	1.0%	0.5%	1.0%	0.5%	1.0%
HL1	7	8	7	8	8	10	7	8	8	9
[RuCl2(PPh3)2(L1)]	7	11	9	11	8	10	8	8	9	11
[RuBr2(PPh3)2(L1)]	8	10	13	16	8	11	7	8	9	11
HL2	8	10	6	7	7	8	7	8	7	8
[RuCl2(PPh3)2(L2)]	8	9	8	9	9	11	9	10	9	10
[RuBr2(PPh3)2(L2)]	10	12	10	13	8	10	8	10	7	9
HL3	9	10	6	7	7	8	7	9	7	9
[RuCl2(PPh3)2(L3)]	13	15	14	17	7	9	9	11`	7	9
[RuBr2(PPh3)2(L3)]	-	5	6	8	10	13	9	11	8	10
Streptomycin	18	23	18	22	15	19	17	20	12	16

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Electrochemistry

Complexes were electrochemically examined at a glassy carbon electrode in dichloromethane solution using cyclic voltammetry. A representative voltammogram has been depicted in Fig.4.and the potential data are listed in Table.5.thecomplexes display the Ru(III) – Ru(II) and Ru(III) – Ru(IV) couples in the potential range -0.310 to -0.921 and 0.4 to 0.9 V respectively vs SCE. In this, the Ru(III) – Ru(II) redox couple is quasi-reversible in nature, with a peak to peak separation (ΔE_p) of 36-120 mV and the Ru(III) – Ru(IV) couple is irreversible. The reason for the irreversibility of these complexes may be oxidative degradation or the short lived oxidized state of the metal ion (Wallace et al., 1989).

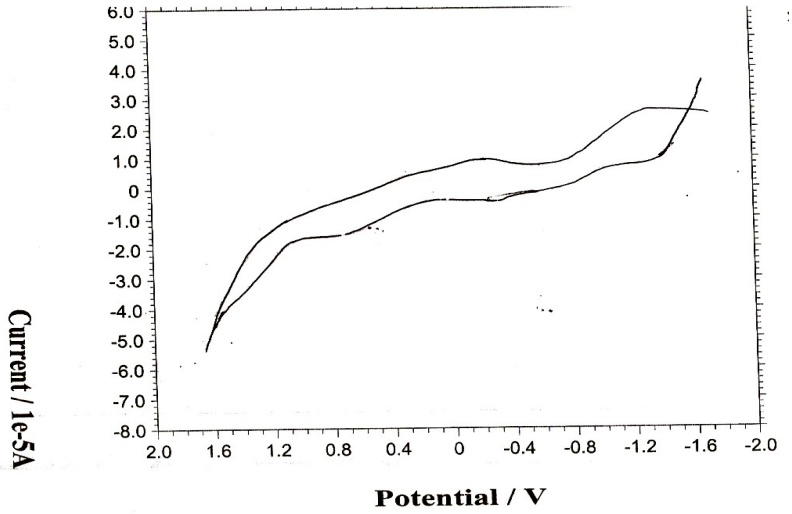

Fig. 4. Cyclic voltammogram of $[RuCl_2(PPh_3)_2(L_2)]$

DNA bindingstudies

DNA is theprimary target for most anticancer and antiviral therapies according to cell biology. Investigation ofthe interaction of DNA with small molecules is a basic study in the design of new type ofpharmaceutical molecules. When some kinds of metal complexes (Tandon and Singh, 1986) interact with DNA, they could induce the breakage of DNA strands by appropriate ways. Thus, to cancer genes, after DNA strandare cleaved by metal complexes and other cleaving agents, the DNA double strand break. In recentyears, binding studies of transition metal complexes have become very important in the developmentof DNA molecule probes and chemotherapy (Arunachalam et al., 2010, Dave et al., 1981, singh et al., 1981, Bermejo et al., 1998). These complexes can bind to DNA in non–covalent modes such as electrostatic, intercalative or groove binding. For an intercalative interactionthe planar aromatic heterocyclic group inserts and stacks between the base pair of DNA.

Electronic absorption titration

Electronic absorption spectroscopy is one of the most powerful experimental techniques for probingmetal ion–DNA interactions. Binding of the macromolecule leads to changes in the electronicabsorption spectrum of the metal complex. Base binding is expected to perturb the ligand fieldtransition of the metal complex. Intercalative mode of binding usually results in hypochromism andbathochromism due to the strong stacking interaction between an aromatic chromophore and the basepairs of DNA. The extent of hypochromism parallels the strength of intercalative binding. On theother hand, metal complexes, which bind non-intercalatively or electrostatically with DNA, mayresult inhyperchromism or hypochromism (Banbe et al., 1998, Kwiatkowski et al., 1980).

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The electronic absorption titration of complex $[RuCl_2(PPh_3)_2(L1)]$ has been carried out at a fixedconcentration of complexes (10μM) in aqueous media at 25 0C, while varying the concentration of DNA (0-50 μM).

The absorption spectra of the complex$[RuCl_2(PPh_3)_2(L1)]$ in the absence andpresence of DNA is depicted in the Figure 6,7. Addition of increasing amount of DNA resultsin an appreciable decrease in absorption intensity of LMCT band at 270 nm with insignificant shift inwavelength. The complex $[RuCl_2(PPh_3)_2(L1)]$ showed hypochromism (24%) and the Kb value is1.78×10^4 M-1. Isosbestic points are observed near 268 nm for $[RuBr_2(PPh_3)_2(L1)]$, while bindingto DNA, suggesting that the complex has a single mode of binding to DNA (Kikuta et al., 1999). Determinations ofintrinsic binding constant, Kb, based upon these absorption titrations may be made with the followingequation (Tan et al., 2007) [DNA]/ (εA-εF) = [DNA]/ (εB-εF) + 1/Kb (εB-εF)where εA, εF, and εB correspond to Aobsd/ [complex], the extinction coefficient for the free complex andthe extinction coefficient for the complex in the fully bound form, respectively. The slope and yintercept of the linear fit of [DNA]/(εA-εF) *versus* [DNA] give 1/(εB-εF) and 1/Kb(εB-εF) respectively.The intrinsic binding constant, Kb can be obtained from the ratio of slope to the intercept. The *K*bvalues observed here are lower than those observed for typical classical intercalators (ethidium-DNA,7.0 $x10^7$ M-1 in 40 mMTris-HCl buffer, pH 7.9 (Tamilselvi and Palaniandavar, 2002), and 1.4×10^6 M-1 in 40 mM NaCl-25 mMTris-HCl; proflavin with *Escherichia coli* DNA, 50% GC content, 4.1×10^5 M-1 in 0.1 M Tris-HCl)(Baba et al.,) with a proven DNA-binding mode involving the complete insertion of the planar moleculesbetween the base pairs. This is indicative of binding of the complex $[RuCl_2(PPh_3)_2(L1)]$ withDNA host with lower affinity than the classical intercalators.

Table 5.Cyclic voltammetricdata[a] for ruthenium(III) Schiff base complexes

Complex	RuIII - RuIV				RuIII - RuII			
	Epa(V)	Epa(V)	ΔEp(mV)b	E1/2 (V)c	Epa(V)	Epa(V)	ΔEp(mV)b	E1/2 (V)c
[RuCl2(PPh3)2(L1)]	0.6	--	--	--	-0.921	-0.815	106	-0.868
[RuBr2(PPh3)2(L2)]	0.7	--	--	--	-0.332	-0.223	89	-0.277
[RuBr2(PPh3)2(L3)]	0.9	--	--	--	-0.346	-0.310	36	-0.328

[a]Supporting electrolyte : $[NBu_4]ClO_4$ (0.1 M); scan rate – 100mV s^{-1}; reference electrode Ag – AgCl.

[b]$\Delta E_p = E_{pa} - E_{pc}$

[c]$E_{1/2} = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are the anodic and cathodic peak potential in volts, respectively.

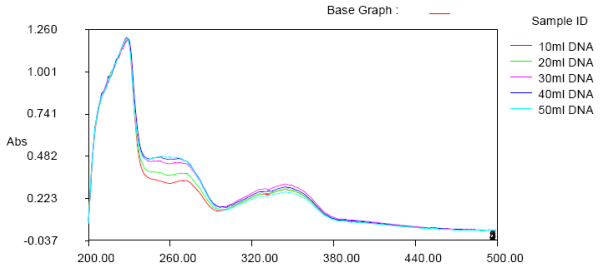

Fig. 6.Absorption spectra of $[RuCl_2(PPh_3)_2(L_1)]$ complex

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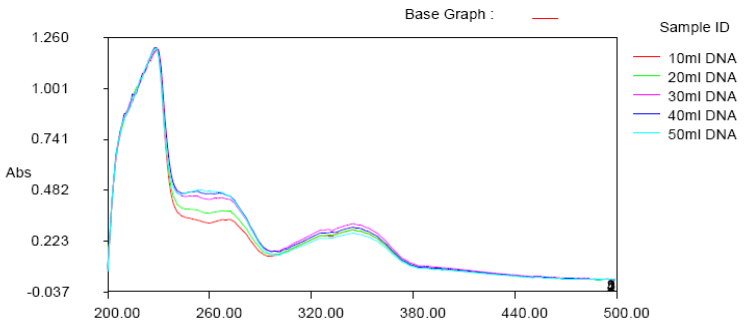

Fig.7. Absorption spectra of $[RuCl_2(PPh_3)_2(L_2)]$ complex

IN VITRO ANTI CANCER ACTIVITY

The human cervical cancer cell line (HeLa) was obtained from National Centre for Cell Science (NCCS), Pune, and grown in Eagles Minimum Essential Medium containing 10% fetal bovine serum (FBS). All cells were maintained at 37^0C, 5% CO2, 95% air and 100% relative humidity. Maintenance cultures were passaged weekly, and the culture medium was changed twice a week.(fig-8).

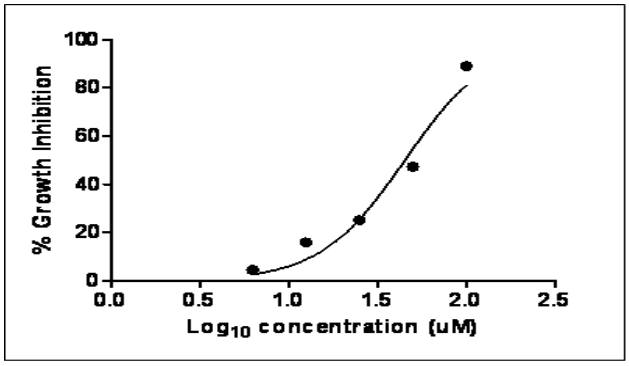

Fig. 8.Cancer cell interaction of the complex.

Cell treatment procedure (Mosmann, 1983, Monks et al., 1991)

The monolayer cells were detached with trypsin-ethylenediaminetetraacetic acid (EDTA) to make single cell suspensions and viable cells were counted using a hemocytometer and diluted with medium with 5% FBS to give final density of $1x10^5$ cells/ml. one hundred microlitres per well of cell suspension were seeded into 96-well plates at plating density of 10,000 cells/well and incubated to allow for cell attachment at 37^0C, 5% CO_2, 95% air and 100% relative humidity. After 24 h the cells were treated with serial concentrations of the extracts and fractions. They were initially dissolved in neat dimethylsulfoxide (DMSO) and further diluted in serum free medium to produce five concentrations. One hundred microlitres per well of each concentration was added to plates to obtain final concentrations of 100, 50, 25, 12.5 and 6.25 µM. The final volume in each well was 200 µl and the plates were incubated at 37^0C, 5% CO_2, 95% air and 100% relative humidity for 48h. The medium containing without samples were served as control. Triplicate was maintained for all concentrations.

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MTT assay

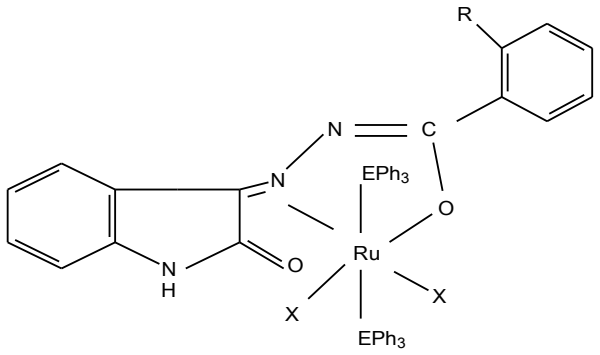
MTT is a yellow water soluble tetrazolium salt. A mitochondrial enzyme in living cells, succinate-dehydrogenase, cleaves the tetrazolium ring, converting the MTT to an insoluble purple formazan. Therefore,the amount of formazan produced is directly proportional to the number of viable cells.

After 48h of incubation, 15µl of MTT (5mg/ml) in phosphate buffered saline (PBS) was added to each well and incubated at 37^0C for 4h. The medium with MTT was then flicked off and the formed formazan crystals were solubilized in 100µl of DMSO and then measured the absorbance at 570 nm using micro plate reader. The % cell inhibition was determined using the following formula.

% cell Inhibition = 100- Abs (sample)/Abs (control) x100.

Nonlinear regression graph was plotted between % Cell inhibition and Log_{10} concentration and IC50 was determined using GraphPad Prism software. The analysis results were shown in Table. 6.

Based on the analytical, spectral and electrochemical data, an octahedral structure (Fig.5.) has been proposed for all the ruthenium (III) complexes.



X = Cl or Br, E = P or As, R = H or Cl or NH_2

Fig. 5.Structure of new Ru(III) complex

Table 6. Anticancer study of ruthenium (III) Schiff base complexes

Conc	6.25uM	12.5 uM	25 uM	50 uM	100 uM	Cont
ABS	0.503	0.437	0.391	0.27	0.052	0.533
	0.515	0.446	0.397	0.282	0.068	0.523
	0.491	0.445	0.394	0.28	0.055	0.523
Avg	0.503	0.442667	0.394	0.277333	0.058333	0.526333
Conc uM)	% Cell Inhibition					
6.25	4.433186			IC50	45.2 uM	
12.5	15.89614					
25	25.1425			R^2	0.9617	
50	47.30842					
100	88.91704					

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CONCLUSIONS

New Ru(III) complexes were prepared by using the Schiff base ligands. The complexes were characterized by spectroscopic studies. An octahedral structure was proposed. All the complexes have antibacterial activities. The new complexes were tested for DNA binding via intercalative mode. The binding constant is less. DNA – complex binding is believed to be the reaction responsible for the anticancer activity of the compounds.

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