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Synthesis, characterization, antimicrobial and insecticidal activity of some new ruthenium (III) complexes with Schiff bases of amino acids

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ABSTRACT

Hexa-coordinated ruthenium (III) complexes of the type $[RuCl_2(L)_2]$ where L = anion of the Schiff base, have been prepared by reacting $RuCl_3.3H_2O$ with monofunctional bidentate Schiff bases in 1:2 molar ratio using benzene as reaction medium. Schiff bases are synthesized by condensing 2-acetylflourene or 4-acetylbiphenyl with amino acids (glycine, alanine, valine, leucine, isoleucine and tryptophan) in methanol. All of the new complexes have been characterized by elemental analysis and I.R. spectral data. An octahedral structure has been proposed for the newly synthesized complexes. These complexes are evaluated for their antibacterial, antifungal and insecticidal activities and their results are encouraging.

KEYWORDS

Ruthenium (III) complexes;
Bidentate ligands;
2-Acetylflourene;
4-Acetylbiphenyl;
Antibacteria.

INTRODUCTION

The condensation of an aldehyde or ketone with primary amine leads to formation of the Schiff base ligands and has played an important role in the development of coordination chemistry. They readily form stable complexes with most of transition metals through imine nitrogen and another group. Transition metal complexes containing a Schiff base are used in the biological[1] and catalytic activity in many reactions[2-4]. Transition metal Schiff base chelates have been found to be excellent homogeneous catalyst[5] in the reactions such as hydrogenation[6], isomerization[7], oxidation[8], dehydrogenation[9] and carbonylation[10] of various organic substrates.

Ruthenium Schiff base complexes, particularly those containing oxygen and nitrogen as donor atoms were found to be very efficient catalysts in the oxidation of alcohols and alkenes[11-12]. Several transition metal Schiff base complexes have been found to possess interesting biological properties, such as antibacterial, antifungal[13-14] and insecticidal activity. It has been observed that Schiff bases with ruthenium complexes showed better biological activity than the free Schiff bases.

The preparation of ruthenium (III)complexes of general formula $[RuCl_2L_2]$ where L=bidentate Schiff base, derived from the condensation of 2-acetylfluorene or 2-acetylbiphenyl and amino acids (glycine, alanine, valine, leucine, isoleucine and tryptophan) and $RuCl_3.3H_2O$ in 1:2 molar ratio in benzene medium are reported here. The general structure of Schiff base ligands used in this investigation is depicted in Figure 1.

EXPERIMENTAL

Materials and methods

Commercially available $RuCl_3.3H_2O$ was used as

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supplied. All the reagents used were chemically pure and of ARgrade. Solvents were purified and dried according to standard procedure. The reactions were carried out under strictly anhydrous conditions. Carbon and hydrogen analyses were carried out on a coleman 5612 analyser of CDRI, Lucknow. Nitrogen was estimated by Kjeldahl's method[15]. The IR spectra were recorded on a FTIR spectrometer using Shimadzu-Japan 8400S in the range 4000–200 cm^{-1} using KBr optics. Molecular weight determinations were carried out by the Rast method.

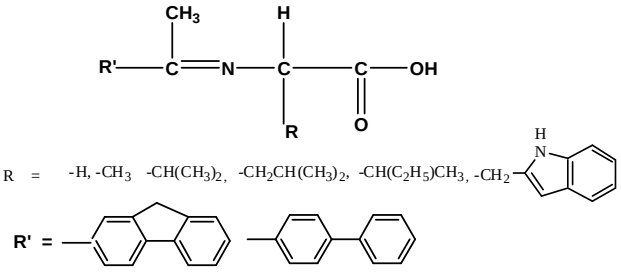

Figure 1: Structure of ligand

Synthesis of ligands

Azomethines were synthesized by the condensation of 2-acetylfluorene and 4-acetylbiphenyl with amino acids (glycine, alanine, valine, leucine, isoleucine and tryptophan) in 1:1 molar ratio using methanol as reaction medium. The solution was refluxed on a water bath for 5 to 7 h and then allowed to cool at room temperature. On cooling, crystals of schiff bases separated out which were washed with methanol, dried and purified by recrystallization with the same solvent. The physical properties and analytical data are recorded in TABLE 1.

Synthesis of complex

For the synthesis of ruthenium (III) complexes, the requisite amount of $RuCl_3.3H_2O$ was added to the appropriate Schiff base in 1:2 molar ratio in dry benzene and the mixture was stirred for 6 h at room temperature. The complex was precipitated by the addition of a small quantity of petroleum ether, recrystallised from petroleum ether and dried under vacuum. The purity of the compounds was checked by TLC using silica gel-G as an adsorbent. The physical properties and analysis of these complexes are enlisted in TABLE 2.

Biological activity

Antibacterial activity

All the synthesized ligands and their corresponding ruthenium (III) complexes were screened in vitro for their antibacterial activity against two Gram-negative (*Escherichia coli* and *Proteus milamilis*) and two Gram-positive (*Bacillus thuringiensis* and *Staphylococcus aureus*) bacterial strains, using paper disc plate

TABLE 1 : Physical properties and Elemental analysis of monofunctional bidentate ligands of amino acids

S. No.	Ligands	Colour & State	Molecular wt. Found (Calcd.)	M.P. (C)	(%) Analysis: Found (Calcd.)		
					C Found (Calcd.)	H Found (Calcd.)	N Found (Calcd.)
1.	$C_{17}H_{15}NO_2$ 2-Acetylfluorene glycine	Cream Powdery Solid	267.67 (265.31)	123	77.09 (76.96)	5.87 (5.67)	5.45 (5.27)
2.	$C_{18}H_{17}NO_2$ 2-Acetylfluorene alanine	White Powdery Solid	280.98 (279.33)	132	77.59 (77.40)	6.19 (6.13)	5.18 (5.01)
3.	$C_{20}H_{21}NO_2$ 2-Acetylfluorene valine	Shining cream Crystal Solid	305.97 (307.40)	138	77.87 (78.14)	6.57 (6.89)	4.13 (4.56)
4.	$C_{21}H_{23}NO_2$ 2-Acetylfluorene leucine	White shining Crystal Solid	320. 98 (321.43)	119	78.01(78.47)	7.09 (7.21)	4.23 (4.36)
5.	$C_{21}H_{23}NO_2$ 2-Acetylfluorene isoleucine	Shining cream Crystal Solid	320. 98 (321.43)	135	78.01 (78.47)	7.09 (7.21)	4.23 (4.36)
6.	$C_{26}H_{22}N_2O_2$ 2-Acetylfluorene tryptophan	White Solid	394.47 (393.59)	128	79.16 (79.01)	5.62 (5.53)	7.10 (6.98)
7.	$C_{16}H_{15}NO_2$ 4-Acetylbiphenyl glycine	Shining cream Powdery Solid	255.76 (253.30)	114	75.97 (75.87)	6.03 (5.97)	5.68 (5.53)
8.	$C_{17}H_{17}NO_2$ 4-Acetylbiphenyl alanine	White Solid	268.98 (267.32)	126	76.58 (76.38)	6.52 (6.41)	5.69 (5.24)
9.	$C_{19}H_{21}NO_2$ 4-Acetylbiphenyl valine	Off White Crystal Solid	296.97 (295.37)	106	78.19 (77.25)	7.20 (7.17)	4.77 (4.74)
10.	$C_{20}H_{23}NO_2$ 4-Acetylbiphenyl leucine	Dull off White Solid	307.33 (309.413)	99	77.59 (77.64)	7.39 (7.49)	4.38 (4.53)
11.	$C_{20}H_{23}NO_2$ 4-Acetylbiphenyl isoleucine	White Solid Powdery Solid	307.33 (309.413)	108	77.59 (77.64)	7.39 (7.49)	4.38 (4.53)
12.	$C_{25}H_{22}N_2O_2$ 4-Acetylbiphenyl tryptophan	Dull off White Solid	382.56 (382.12)	120	78.51(78.39)	5.80 (5.69)	7.32 (7.19)

TABLE 2 : Physical properties and analysis of ruthenium(III) complexes with amino acids schiff bases

Reactant	Ligand	Molar ratio	Product state & colour	M.P. °C	Molecular wt. Found (Calcd)	%Analysis: Found (Calcd)				
						C	H	N	Cl	Ru
$RuCl_3.3H_2O$	$C_{17}H_{15}NO_2$	1:2	$RuCl_2C_{34}H_{28}N_2O_4$ Green crystals Solid	148	698.94 (700.56)	58.02 (58.28)	3.89 (4.02)	3.78 (3.99)	9.98 (10.12)	14.24 (14.42)
$RuCl_3.3H_2O$	$C_{18}H_{17}NO_2$	1:2	$RuCl_2C_{36}H_{32}N_2O_4$ Brown solid	120	726.89 (728.63)	59.18 (59.34)	4.31 (4.42)	3.67 (3.84)	9.57 (9.73)	13.66 (13.87)
$RuCl_3.3H_2O$	$C_{20}H_{21}NO_2$	1:2	$RuCl_2C_{40}H_{40}N_2O_4$ Reddish brown crystals solid	128	782.77 (784.73)	61.03 (61.22)	4.98 (5.13)	3.25 (3.56)	8.86 (9.03)	12.76 (12.87)
$RuCl_3.3H_2O$	$C_{21}H_{23}NO_2$	1:2	$RuCl_2C_{42}H_{44}N_2O_4$ Black solid	135	811.01 (812.79)	61.83 (62.06)	5.31 (5.45)	3.30 (3.44)	8.57 (8.72)	12.22 (12.43)
$RuCl_3.3H_2O$	$C_{21}H_{23}NO_2$	1:2	$RuCl_2C_{42}H_{44}N_2O_4$ Brown solid	122	810.95 (812.79)	61.78 (62.06)	5.24 (5.45)	3.29 (3.44)	8.53 (8.72)	12.20 (12.43)
$RuCl_3.3H_2O$	$C_{26}H_{22}N_2O_2$	1:2	$RuCl_2C_{52}H_{42}N_4O_4$ Brown solid	142	956.33 (958.89)	64.89 (65.13)	4.32 (4.41)	5.76 (5.84)	7.23 (7.39)	10.42 (10.54)
$RuCl_3.3H_2O$	$C_{17}H_{15}NO_2$	1:2	$RuCl_2C_{32}H_{28}N_2O_4$ Grey solid	135	674.65 (676.55)	56.48 (56.80)	4.01 (4.17)	4.02 (4.14)	10.27 (10.48)	14.74 (14.93)
$RuCl_3.3H_2O$	$C_{18}H_{17}NO_2$	1:2	$RuCl_2C_{34}H_{32}N_2O_4$ Brown solid	115	702.56 (704.61)	57.78 (57.95)	4.44 (4.57)	3.81 (3.97)	9.93 (10.06)	14.22 (14.34)
$RuCl_3.3H_2O$	$C_{20}H_{21}NO_2$	1:2	$RuCl_2C_{38}H_{40}N_2O_4$ Brown solid	125	758.54 (760.71)	59.77 (59.99)	5.21 (5.30)	3.56 (3.68)	9.24 (9.32)	13.11 (13.28)
$RuCl_3.3H_2O$	$C_{21}H_{23}NO_2$	1:2	$RuCl_2C_{40}H_{44}N_2O_4$ Black solid	138	786.45 (788.77)	60.79 (60.90)	5.51 (5.62)	3.42 (3.55)	8.84 (8.98)	12.68 (12.81)
$RuCl_3.3H_2O$	$C_{21}H_{23}NO_2$	1:2	$RuCl_2C_{40}H_{44}N_2O_4$ Black solid	142	786.38 (788.77)	60.74 (60.90)	5.46 (5.62)	3.40 (3.55)	8.79 (8.98)	12.62 (12.81)
$RuCl_3.3H_2O$	$C_{25}H_{22}N_2O_2$	1:2	$RuCl_2C_{50}H_{42}N_4O_4$ Black solid	145	932.33 (934.87)	64.11 (64.23)	4.39 (4.52)	5.87 (5.99)	7.45 (7.58)	10.68 (10.81)

TABLE 3 : Antibacterial screening data of amino acid ligands and their ruthenium (III) complexes

Compounds	Diameter (mm) of Inhibition Zone after 24 h(conc. in ppm)							
	Staphylococcus aureus (+)		*Proteus milamilis* (-)		*Escherichia coli* (-)		*Bacillus thuringiensis* (+)	
	500 ppm	1000 ppm	500 ppm	1000 ppm	500 ppm	1000 ppm	500 ppm	1000 ppm
$C_{17}H_{15}NO_2$	6	10	6	7	6	7	4	6
$C_{18}H_{17}NO_2$	8	9	8	9	7	8	7	8
$C_{20}H_{21}NO_2$	6	8	6	8	7	9	6	7
$C_{16}H_{15}NO_2$	7	8	7	8	6	8	7	7
$C_{17}H_{17}NO_2$	5	8	6	7	5	7	6	8
$C_{19}H_{21}NO_2$	6	7	7	8	6	8	5	7
$RuCl_2C_{34}H_{28}N_2O_4$	12	12	8	9	9	11	11	11
$RuCl_2C_{36}H_{32}N_2O_4$	12	13	8	10	10	11	11	12
$RuCl_2C_{40}H_{40}N_2O_4$	11	13	9	11	11	12	10	11
$RuCl_2C_{32}H_{28}N_2O_4$	10	12	11	13	11	13	10	12
$RuCl_2C_{34}H_{32}N_2O_4$	12	13	10	12	10	12	11	12
$RuCl_2C_{38}H_{40}N_2O_4$	11	13	9	11	11	13	11	13
Streptomycin	15	17	12	15	17	18	14	16

method[16-17]. 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 for this. The compounds under investigation were dissolved in methanol to give concentrations of 500 and 1,000 ppm. The filter paper discs were soaked in these solu-

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tions, dried and then placed in petri dishes 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. The antibacterial activity displayed by various compounds is given in TABLE 3.

Antifungal activity

Antifungal activity was evaluated against *Fusarium oxysporium* and *Aspergillus niger* by the agar plate technique. Solutions of the compounds in different concentrations in DMF were then mixed with the medium. The linear growth[18] of the fungus was recorded by measuring the diameter of colony after 96 h, and the percentage inhibition was calculated as 100 (C-T)/ C[19], where C and T are the diameters of the fungus colony in the control and test plates, respectively (TABLE 4).

Insecticidal activity

Two synthesized azomethine derivatives of amino acids and their complexes have been screened for their insecticidal activity against *Helicoverpa armigera*, and results are presented in TABLE 5. The study has been conducted on the second and third instar larval stages of the said insect. Two concentrations (0.025% and 0.05%) of the test compounds were taken along with the standard check, the endosulfan 35, together with an untreated control. The mortality counts of the insect pests were recorded daily up to fourteen days.

RESULTS AND DISCUSSION

New hexa-coordinated ruthenium (III) complexes of the type $[RuCl_2(L)_2]$ where L = mono basic bidentate Schiff base ligand were prepared from $RuCl_3.3H_2O$ and the respective Schiff bases in 1:2 molar ratio in the presence of dry benzene as shown below:

$$RuCl_3.3H_2O + 2\ \text{N OH} \xrightarrow[1:2]{\text{benzene}} RuCl_2(\text{N O})_2$$

The new Schiff base ruthenium (III) complexes are bright colored solid, stable to air and light and soluble in benzene, chloroform, methylene chloride, DMF and DMSO. The analytical data for the new complexes synthesized are consistent with the empirical formula given in TABLE 2, indicating the 1:2 metal to ligand ratio. In the above reactions, the Schiff bases used investigation behave as monofunctional bidentate ligands by replacing three molecules of water and one chloride ion from the starting complexes.

TABLE 4 : Antifungal screening data of amino acid ligands and their ruthenium (III) complexes

Compounds	Percent Inhibition after 96h (conc in ppm)					
	Organism *Fusarium oxysporum*			Organism *Aspergillus niger*		
	50 ppm	100 ppm	200 ppm	50 ppm	100 ppm	200 ppm
$C_{17}H_{15}NO_2$	64	71	84	52	62	73
$C_{18}H_{17}NO_2$	51	58	72	50	69	72
$C_{20}H_{21}NO_2$	54	56	66	55	67	79
$C_{16}H_{15}NO_2$	44	65	75	58	68	69
$C_{17}H_{17}NO_2$	48	56	66	52	61	68
$C_{19}H_{21}NO_2$	53	63	69	54	68	77
$RuCl_2C_{34}H_{28}N_2O_4$	59	73	79	65	72	88
$RuCl_2C_{36}H_{32}N_2O_4$	59	71	78	54	65	71
$RuCl_2C_{40}H_{40}N_2O_4$	65	74	86	53	63	79
$RuCl_2C_{32}H_{28}N_2O_4$	56	59	71	59	68	81
$RuCl_2C_{34}H_{32}N_2O_4$	48	69	83	60	71	75
$RuCl_2C_{38}H_{40}N_2O_4$	52	71	81	55	78	78
Micostatin	72	82	96	70	91	100

Spectroscopic characterization

Infrared spectra

On comparing the IR spectra of the ligand as well as their corresponding ruthenium complexes, it can be concluded that the chelate formation takes place through the nitrogen and oxygen of the ligand moieties. In the infrared spectra of the ligand, medium intensity bands appearing in the region, ~3300 cm^{-1} may be assigned to the

υOH vibrations, which disappear in the resulting complexes suggesting the possible deprotonation on complexation and the formation of Ru-O bond. This fact is further supported by the increase in the absorption frequency of phenolic C-O bond from 1260-1275 cm^{-1} in the free ligands to 1285-1310 cm^{-1} in the ruthenium complexes, indicating that the other coordination site of Schiff bases is phenolic oxygen[20-21] in all the complexes

TABLE 5 : Percentage mortality of Helicoverpa armigera pest after 1, 3, 7, 10 and 14 days. Total percent mortality (concentration)

S. No.	Treatment	Percentage mortality									
		Day 1		Day 3		Day 7		Day 10		Day 14	
		a	b	a	b	a	b	a	b	a	b
1.	Compound I $RuCl_2C_{32}H_{28}N_2O_4$	40.00 (53.13)	60.00 (79.70)	100.00 (105.03)	120.00 (117.69)	140.00 (129.23)	160.00 (140.77)	180.00 (152.31)	200.00 (164.97)	240.00 (190.30)	260.00 (216.87)
2.	Compound II $RuCl_2C_{40}H_{44}N_2O_4$	60.00 (79.70)	80.00 (92.36)	100.00 (105.03)	140.00 (129.23)	160.00 (140.77)	180.00 (152.31)	220.00 (177.64)	220.00 (177.64)	260.00 (216.87)	280.00 (243.43)
3.	Compound III $C_{16}H_{15}NO_2$	20.00 (26.57)	20.00 (26.57)	60.00 (79.70)	80.00 (92.36)	100.00 (105.03)	120.00 (117.69)	140.00 (129.23)	160.00 (140.77)	180.00 (152.31)	200.00 (164.97)
4.	Compound IV $C_{20}H_{23}NO_2$	20.00 (26.57)	40.00 (53.13)	80.00 (92.36)	100.00 (105.03)	100.00 (105.03)	120.00 (117.69)	160.00 (140.77)	160.00 (140.77)	200.00 (164.97)	220.00 (177.64)
5.	Endosulfan	40.00 (53.13)		100.00 (105.03)		140.00 (129.23)		200.00 (164.97)		260.00 (216.87)	
6.	Control	0.0 (0.00)		0.0 (0.00)		0.0 (0.00)		0.0 (0.00)		0.0 (0.00)	

a = 0.025% concentration and b = 0.05% concentration, terms in parentheses are the angular transformed values

A strong band is observed in the free ligands around 1615–1620 cm, characteristic of azomethine (C=N) group[22]. In the spectra of the complexes, this band appeared on lower frequency at 1590–1605 cm^{-1}[23], indicating coordination of the azomethine nitrogen to ruthenium. Coordination of the Schiff base to the metal through azomethine nitrogen atom is expected to reduce the electron density in the azomethine link and lower the C=N absorption frequency. A bands is observed in the 1595–1650 cm^{-1} and 1390–1440 cm^{-1} regions arising from asymmetric [υ_{asy} (COO^-)] and symmetric[υ_{sym} (COO^-)] stretching of the carboxylate group. This indicates coordination of the carboxyl group to the ruthenium metal ion in the complexes

The binding of the metal to the ligand through nitrogen and oxygen atom is further supported by the appearance of new band in 460–400 cm^{-1} and 540–510 cm^{-1} ranges due to υ (Ru–N)[24] and υ (Ru–O)[25] respectively, in the spectra of all the complexes. The υ (Ru–Cl)[26-28] bands were more intense than the υ (Ru–N) bands and were observed in the region 330–335 cm^{-1}. The important IR frequencies are given in Table 6.

Antimicrobial activity

Antimicrobial activities of representative ligands and their complexes have been screened, which are given in TABLE 3 and 4. The results reveal that the activity

TABLE 6 : IR spectral data of the Ru(III) schiff base complexes

S.No.	Complexes	υC=N	υC-O	$\upsilon_{asy}(COO^-)$	$\upsilon_{sym}(COO^-)$	υ (Ru-O)	υ (Ru-N)	υ (Ru-Cl)
1.	$RuCl_2C_{34}H_{28}N_2O_4$	1590	1295	1595	1395	540	450	330
2.	$RuCl_2C_{36}H_{32}N_2O_4$	1600	1300	1620	1405	515	460	335
3.	$RuCl_2C_{40}H_{40}N_2O_4$	1595	1305	1635	1435	540	455	330
4.	$RuCl_2C_{42}H_{44}N_2O_4$	1605	1300	1645	1440	510	450	335
5.	$RuCl_2C_{42}H_{44}N_2O_4$	1600	1310	1610	1420	535	440	330
6.	$RuCl_2C_{52}H_{42}N_4O_4$	1590	1305	1615	1415	540	435	335
7.	$RuCl_2C_{32}H_{28}N_2O_4$	1605	1300	1600	1410	540	450	330
8.	$RuCl_2C_{34}H_{32}N_2O_4$	1600	1290	1595	1405	520	460	335
9.	$RuCl_2C_{38}H_{40}N_2O_4$	1595	1295	1650	1400	530	425	330
10.	$RuCl_2C_{40}H_{44}N_2O_4$	1595	1305	1635	1390	510	460	330
11.	$RuCl_2C_{40}H_{44}N_2O_4$	1605	1290	1645	1425	515	450	335
12.	$RuCl_2C_{50}H_{42}N_4O_4$	1600	1295	1635	1440	535	455	330

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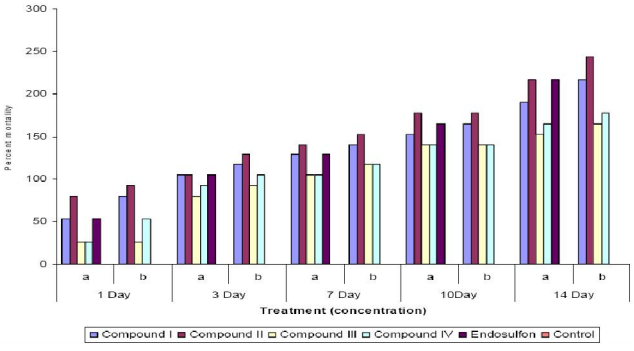
increases on complexation. The newly synthesized complexes have indeed been found to be more active in inhibiting the growth of fungi and bacteria than the precursors themselves. This may be explained by Tweedy's Theory[29], according to which the chelation reduces the polarity of the central atom mainly because of the partial sharing of its positive charge with the donor groups which enhances lipophilicity of the complexes causing breakdown of permeability of the cells. The toxicity increases with increase in the concentration of the test solution containing the new complexes.

Insecticidal activity

To study the structure-activity relationship, we have selected two azomethines of amino acids and their metal complexes where the aromatic ring was the same that is, biphenyl ring. The carbonyl moiety was also the same, but alkyl substituent was different. This study has suggested that an increase in the bulkiness of alkyl substituent and presence of the C=N moiety enhanced the bioactivity which is proved by the experimental details of the study (TABLE 5, graph 1).

Compound (I) and Compound (II) at concentrations 0.025% and 0.05% showed the best insecticidal activity, which was found to be superior to that of a standard insecticide endosulfan. Thus, the observed enhancement of activity of these complexes that were found to be more active than ligand must be due to a combination effect associated with the derivatization and complexation of the ligand and presence of the side group of the amino acid.



Based on elemental analysis and I.R spectra the following structure for ruthenium (III) complexes and is suggested and assigned a trans-position to these ligands in the complexes due to less strain in the accommadation of monofuntional bidentate ligand around the ruthenium ion.

On the basis of the data discussed above, the octahedral structure shown in the figure 2 is proposed for the ruthenium (III) complexes.

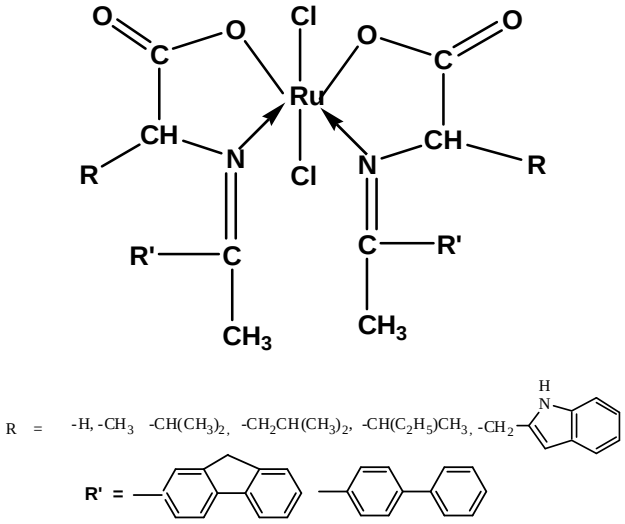


Figure 2: Structure of complex

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REFERENCES

[1] H.Singh, L.D.S.Yadav, S.B.S.Mishra; J.Inorg.Nucl. Chem., **43**, 1701 **(1981)**.
[2] P.M.Reddy, A.V.S.S.Prasad, R.Rohini, V.Ravinder; Spectrochim. Acta., **70A**, 704 **(2008)**.
[3] M.Masjedi, L.T.Yildirim, S.Özkar; J.Mol.Catal.A Chem., **355**, 186 **(2012)**.
[4] G.C.Vougioukalakis, R.H.Grubbs; J.Chem.Rev., **110**, 1746 **(2010)**.
[5] P.Viswanathamurthi, K.Natarajan; Trans.Met. Chem., **24**, 638 **(1999)**.
[6] P.Frediani, V.Pistolesi, M.Frediani, L.Rosi; Inorg.Chim.Acta., **359**, 917 **(2006)**.
[7] F.N.Haque, A.J.Lough, R.H.Morris; Inorg.Chim.Acta., **361**, 3149 **(2008)**.
[8] N.Sathya, A.Manimaran, G.Raja, P.Muthusamy, K.Deivasigamani; Trans.Met.Chem., 34, 7 **(2009)**.
[9] R.Karvembu, R.Prabhakaran, K.Senthilkumar, P.Viswanathamurthi, K.Natarajan; Reaction Kinet-

ics and Catalysis Letters, **86**, 211 **(2005)**.
[10] J.J.Byerley, G.L.Rempel, N.Takebe, B.R.James; Chem.Commun., **22**, 1482 **(1971)**.
[11] R.I.Kureshy, N.H.Khan, S.H.R.Abdi; J.Mol.Cat., **96**, 117 **(1995)**.
[12] A.M.EI-Hendawy, A.H.Alkubaisi, E.I.Ghany, A.EI-Kourashy, M.M.Shanab; Polyhedron, **12**, 2343 **(1993)**.
[13] A.Saxena, J.K.Koacher, J.P.Tandon; J.Antibact.Antifung., **9**, 435 **(1981)**.
[14] S.K.Chattopadhyay, S.Ghosh; Inorg.Chim.Acta, **131**, 15 **(1987)**.
[15] H.L.Singh, A.K.Varshney; Bioinorg.Chem.Appl., 1 **(2006)**.
[16] R.Lawrence, P.Tripathi, E.Jeyakumar; Brazilian J.Microbio., **40**, 906 **(2009)**.
[17] N.Raman, R.Jeyamurugan, A.Selvan; College Sadhana, **2**, 15 **(2009)**.
[18] Y.L.Nene, P.N.Thapliyal; Oxford & IBH Publishing Co., New Delhi, **(1993)**.
[19] J.M.Vincent, U.S.D.A.Farmer Bull; Nature, **159**, 850 **(1959)**.
[20] R.Ramesh, S.Maheswaran; J.Inorg.Biochem., **96**, 457 **(2003)**.
[21] B.Khera, A.K.Sharma, N.K.Kaushik; Polyhedron, **2**, 1177 **(1983)**.
[22] M.M.T. Khan, Z.A.Shaikh; Ind.J.Chem., **31A,** 191 **(1992)**.
[23] S.A.Ali, A.A.Soliman, M.M.Aboaly, R.M.Ramadan; J.Coord.Chem., **55**, 1161 **(2002)**.
[24] M.M.Taquikhan, R.I.Kureshy, N.H.Khan; Tetrahedron:Asymmetry, **2**, 1015 **(1991)**.
[25] K.Nakamoto; Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley-Interscience, New York, **(1971)**.
[26] M.M.Taquikhan, V.V.S.Reddy; Inorg.Chem., **25**, 208 **(1986)**.
[27] N.C.Thomas, J.Cox; Polyhedron, **7**, 731 **(1988)**.
[28] U.C.Sarma, K.P.Sarma, R.K.Poddar; Polyhedron, **7**, 1727 **(1988)**.
[29] B.G.Tweedy; Phytopathology, **55**, 910 **(1964)**.