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Synthesis, characterization and biological properties of ruthenium(III) Schiff base complexes derived from 3-hydroxyquinoxaline-2-carboxaldehyde and salicylaldehyde

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Ruthenium(III) complexes of the Schiff bases derived from 3-hydroxyquinoxaline-2-carboxaldehyde and *o*-phenylenediamine, *o*-aminophenol or 2-aminobenzimidazole (qpd, qap and qab, respectively) and the Schiff bases derived from salicylaldehyde and *o*-phenylenediamine, *o*-aminophenol or 2-aminobenzimidazole (salpd, salap and salab, respectively) have been prepared and characterized by elemental, spectral (FT IR, UV-vis, EPR and FAB mass), thermogravimetric, conductance and magnetic moment analyses. The complexes exhibit the following molecular formulae: $[Ru_2(qpd)Cl_4(H_2O)_2].2H_2O$, $[Ru_2(qap)_2Cl_2(H_2O)_2].H_2O$, $[Ru_2(qab)_2Cl_4(H_2O)_2].3H_2O$, $[Ru_2(salpd)_3Cl_2(H_2O)_2]$, $[Ru_2(salap)_4Cl_2].H_2O$ and $[Ru(salab)(H_2O)_4]Cl_2.H_2O$. An octahedral structure has been tentatively proposed for all the new complexes. The synthesized ligands and complexes have been tested for *in vitro* growth inhibitory activity against gram positive bacteria *Klebsiella pneumoniae*, gram negative bacteria *Escherichia coli* and *Pseudomonas aeruginosa*. The complexes are active while the ligands are inactive towards the bacteria under study.

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The growing interest of the chemists in the study of ruthenium complexes[1-4] is due to their interesting electron-transfer properties. Change in coordination environment around ruthenium plays an important role in modulating the properties of the complexes. The presence of nitrogen and oxygen donor atoms tunes the properties of the complexes to a great extent as effective and stereo specific catalysts for oxidation, reduction and hydrolysis[5-7]. These types of complexes are also reported to have carcinostatic, antitumour, antiviral and antibacterial activity[8] and are known to serve as models for biologically important species, which contain metal ions in macrocyclic environment. Schiff bases and their metal complexes are reported to posses important biological[9,10] applications. We report herein the synthesis and characterization of new Schiff base complexes of ruthenium having biological and catalytic activity.

Experimental

o-Phenylenediamine (Loba Chemie), sodium pyruvate (Loba Chemie) bromine, glacial acetic acid, precipitated $CaCO_3$ (Merck), sodium bicarbonate (Merck), sodium chloride (Merck), salicylaldehyde (Merck), 2-aminobenzimidazole (Merck), 2-amino-phenol (Merck) and $RuCl_3.3H_2O$ (Merck) were used. All materials used were of the highest purity available and used without further purification. Solvents employed were either of 99% purity or purified by known laboratory procedures. CHN analyses of the ligands and complexes were done using Elementar model Vario EL III. The metal (%) present in the complexes was determined using ICP-AES spectrometer (Thermo Electron, IRIS Intrepid II XSP DUO). Magnetic susceptibility measurements were done on a PAR model 155 Vibrating Sample Magnetometer. Electronic spectra of complexes in methanolic solution were recorded on a Varian Cary 5000 UV-Vis-NIR spectrophotometer. IR spectra were recorded as KBr pellets (Schimadzu 8000, Japan). The far infrared spectra were recorded in the region 100-500cm^{-1} on a Nicolet Magna 550 FTIR instrument. FAB mass spectra were recorded at room temperature in thioglycerol matrix on a JEOL SX 102/DA-6000 mass spectrometer using argon/xenon (6 kv,10 mA) as the FAB gas. The EPR spectra were recorded operating at 100 KHz field modulation at liquid nitrogen temperature (Bruker EMX X band). Thermogravimetric analyses were done on a Perkin Elmer, Diamond TG/DTA analyzer at a heating rate of 10°C min^{-1} in nitrogen atmosphere. The molar conductance of the simple complexes were determined at room temperature in methanol (10^{-3} *M*) using a Cenutry CC 601 digital conductivity meter with a dip type cell and a platinum electrode.

Synthesis of 3-hydroxyquinoxaline-2-carboxaldehyde

3-Hydroxy-2-methyl quinoxaline was prepared by mixing *o*-phenylenediamine (0.1 mol, 10.8 g) dissolved in hot water (250 mL) with sodium

pyruvate (0.1 mol, 11.0 g) in 250 mL water acidified by adding conc. HCl (~11 mL). The precipitated yellow compound (0.1 mol, 16.2 g) in glacial acetic acid (200 mL) was stirred with 10% (*v/v*) bromine in acetic acid (110 mL) in sunlight for 1 h. It was then diluted to 1 L and the precipitated dibromo derivative was filtered, washed with water and purified by crystallization from 50% alcohol (yield: 95%, m.pt. 246°C). The dibromo compound (5.0 g) was mixed with precipitated calcium carbonate (20.0 g). This mixture was treated with water (1.5 L) in a 3 L RB flask and heated over water bath for 2 h. As the aldehyde formed is soluble in water, the solution was filtered hot. The yellow aqueous solution thus obtained is very stable and the entire solution is used for the preparation of each Schiff base.

Synthesis of the ligands

N,N′-Bis(3-hydroxyquinoxaline- 2- carboxalidene)-*o*-phenylenediamine (qpd) and 3-hydroxy-quinoxaline-2-carboxalidene-2-aminobenzimidazole (qab) were prepared by adding a solution of *o*-phenylenediamine (2.0 g in 20 mL water) or 2- aminobenzimidazole (1.5 g in 20 mL hot water) to an acidified solution of the aldehyde (0.025 molar with respect to HCl). Hydroxyquinoxaline-2-carboxalidene-*o*-aminophenol (qap) was obtained by adding a solution of *o*-aminophenol (2.0 g in 20 mL of water) to the aldehyde solution. Each of the precipitated compound was filtered, washed with methanol and dried *in vacuo* over anhydrous phosphorus(V) oxide.

The ligands N,N′-bis(salicylaldimine)-*o*-phenylene-diamine (salpd), salicylaldimine-o-aminophenol (salap) and salicylaldimine-2-aminobenzimidazole (salab) were prepared by refluxing the methanolic solutions of *o*-phenylenediamine (2.0 g), *o*-aminophenol (2.0 g) or 2-aminobenzimidazole (1.5 g) with salicylaldehyde (4.8 g) for 30 min. The volume of the solution was reduced by distillation. The Schiff bases which precipitated on cooling were washed with methanol and dried over anhydrous phosphorous(V) oxide.

Synthesis of the metal complexes of qpd, qap and qab

Ruthenium(III) chloride trihydrate (1 mmol; 0.261 g) was dissolved in methanol (10 mL) and added to a refluxed solution of qpd (0.5 mmol; 0.210 g) in methanol (10 mL). This mixture was refluxed for 24 h, concentrated by evaporation and cooled. Precipitated complex was filtered, washed with dichloromethane and dried *in vacuo* over anhydrous calcium chloride. The qap and qab complexes were prepared in a similar manner by using $RuCl_3.3H_2O$ (1 mmol: 0.261 g) and qap (1 mmol: 0.265 g) or qab (1 mmol; 0.289 g).

Synthesis of metal complexes of salpd, salap and salab

Ruthenium(III) chloride trihydrate (0.5 mmol; 0.131 g) was refluxed with a solution of salpd (0.75 mmol; 0.237 g) in methanol (20 mL) for 8 h. The solution was concentrated, cooled and stirred with petroleum ether (60-80°C). The resultant solid was separated, washed with dichloromethane and dried *in vacuo* over anhydrous calcium chloride. The salap and salab complexes were prepared in a similar way by refluxing $RuCl_3.3H_2O$ (1 mmol: 0.261 g) with salap (2 mmol; 0.426 g) or with salab (1 mmol; 0.237 g).

Antibacterial studies

The synthesized ligands and complexes were screened for *in vitro* growth inhibitory activity against activity against one strain of gram positive bacteria *Klebsiella pneumoniae*, gram negative bacteria *Escherichia coli* and *Pseudomonas aeruginosa*. Nutrient agar plates were uniformly surface inoculated from the broth culture of the tested microorganisms. The impregnated disks were placed on the medium suitably placed apart and kept for 5 min for the agar surface to dry. Wells were made on the agar medium at suitable distances. Solutions (1 mg mL^{-1}) of the synthesized ligands and complexes were prepared separately in DMSO. Definite volumes of each solution (5 µL, 10 µL, 15 µL and 20 µL) were added to different wells and the plates were incubated at 37ºC for 24 h. Disc without the test solution was used as control. The diameter (in mm) of the observed inhibition zones was taken as a measure of inhibitory activity.

Results and discussion

The molar conductance values of the complexes in methanol were determined. All the complexes, except the salab complex, exhibited a value less than 60 ohm^{-1} cm^2 mol^{-1} suggesting non-electrolytic nature for the complexes. The salab complex shows molar conductance value of 144 ohm^{-1} cm^2 mol^{-1}, suggesting 1:2 electrolytic nature[11] and indicating the presence of two chloride ions outside the coordination sphere. The analytical data (Table 1) and the conductance behaviour suggest the molecular formula of the complexes as: $[Ru_2(qpd)Cl_4(H_2O)_2].2H_2O$, $[Ru_2(qap)_2Cl_2(H_2O)_2].H_2O$, $[Ru_2(qab)_2Cl_4(H_2O)_2].3H_2O$,

Table 1 — Analytical data of the ligands and the complexes

Compd	Color	M.pt. °C	Mol. weight	Found (calc.) (%) C	H	N	Metal
qpd	Reddish Brown	225	420	68.22 (68.56)	3.59 (3.84)	19.72 (19.99)	-
$Ru_2(qpd)Cl_4(H_2O)_4$	Black	>250	834	35.01 (34.55)	2.68 (2.66)	11.02 (10.07)	25.83 (24.23)
qap	Orange	140	265	67.42 (67.92)	4.53 (4.18)	16.14 (15.84)	-
$Ru_2(qap)_2Cl_2(H_2O)_3$	Black	>250	853	43.03 (42.21)	2.78 (2.83)	9.88 (9.85)	22.58 (23.68)
qab	Orange	205	289	65.87 (66.43)	4.04 (3.83)	23.59 (24.21)	-
$Ru_2(qab)_2Cl_4(H_2O)_5$	Black	>250	1010	39.11 (38.03)	3.16 (2.99)	13.84 (13.86)	22.00 (20.00)
salpd	Yellow	145	316	75.82 (75.93)	5.21 (5.10)	8.70 (8.86)	-
$Ru_2(salpd)_3Cl_2(H_2O)_2$	Black	>250	1253	56.54 (57.46)	4.15 (3.86)	7.29 (6.70)	15.43 (16.14)
salap	Orange	175	213	72.63 (73.22)	5.23 (5.20)	6.83 6.57)	-
$Ru_2(salap)_4Cl_2(H_2O)$	Black	>250	1140	53.73 (54.79)	3.75 (3.71)	5.12 (4.91)	17.24 (17.73)
salab	Lemon Yellow	200	237	70.50 (70.87)	4.63 (4.67)	17.12 (17.71)	-
$Ru(salab)Cl_2(H_2O)_5$	Black	>250	498	34.05 (33.74)	4.22 (4.05)	8.59 (8.43)	20.80 (20.28)

$[Ru_2(salpd)_3Cl_2(H_2O)_2]$, $[Ru_2(salap)_4Cl_2].H_2O$ and $[Ru(salab)(H_2O)_4]Cl_2.H_2O$. The mass spectrum of ligand qpd shows the molecular ion (M) peak at *m/z* = 420; the other important peaks are assigned as 386 (M-2OH), 263 (M-$C_9N_2H_6O$) and 107 (M- $C_{18}N_4H_{12}O_2$). The molecular ion peaks of the ligand qap, qab, salpd, salap, salab are seen at 265, 289, 316, 213, 237, respectively. They all show the same type of fragment pattern. The FAB mass spectra of the complexes give the molecular ion peak at *m/z* = 826, 840, 954, 1254, 1122 and at 497 for the qpd, qap, qab, salpd, salap and salab complexes, respectively. The FAB mass spectral fragments of the complexes are given in Table 2. The results of mass spectral analyses of all the ligands and complexes agree well with the empirical formula derived from the elemental analyses.

TG data of all the complexes were recorded. All the complexes, except the salpd complex, exhibit three stages of decomposition. The mass loss occurring in the range 50-100°C for the qpd, qap, qab, salap and salab complexes agree well with the removal of lattice water molecule. The mass loss in the decomposition range 120-170ºC is in agreement with the removal of coordinated water molecule. The final stage of decomposition, which is observed above 280ºC, might be due to the decomposition of ligands.

Table 2 — FAB mass spectral data of the complexes

Compd	Fragment ions	*m/z* Found	Calc.
$Ru_2(qpd)Cl_4(H_2O)_4$	$Ru_2(qpd)Cl_4(H_2O)_4$	826	834
	$Ru_2(qpd)Cl_4$	766	762
	$Ru_2(qpd)Cl$	658	656
	Ru(qpd)Cl	554	554
	qpd-2H	418	418
$Ru_2(qap)_2Cl_2(H_2O)_2$	$Ru_2(qap)_2Cl_2(H_2O)_2$	840	836
	$Ru_2(qap)_2Cl_2$	804	800
	$Ru_2(qap)Cl.\ H_2O$	516	518
$Ru_2(qab)_2Cl_4(H_2O)_2$	$Ru_2(qap)_2Cl_4(H_2O)_2$	954	956
	$Ru_2(qab)_2Cl_2$	848	849
	$Ru_2(qab)Cl$	426	424
$Ru_2(salpd)_3Cl_4(H_2O)_2$	$Ru_2(salpd)_3Cl_2\ (H_2O)_2$	1254	1254
	$Ru\ (salpd)_2Cl\ H_2O$	784	780
	$Ru_2(salpd)Cl\ H_2O$	571	572
	salpd	316	317
	$Ru_2\ Cl_2$	273	273
$Ru_2(salap)_4Cl_2(H_2O)$	$Ru_2(salap)_4Cl_2$	1122	1125
	$Ru_2(salap)_3Cl_2$	910	910
	$Ru_2(salap)_2Cl_2$	684	683
	$Ru\ (salap)_2Cl_2$	597	597
	Ru (salap)	311	311
$Ru(salab)Cl_2(H_2O)_5$	$Ru\ (salab)\ Cl_2(H_2O)_5$	497	498
	$Ru\ (salab)\ Cl_2(H_2O)_4$	482	480
	$Ru\ (salab)\ Cl_2$	413	409

The IR spectra of the Schiff bases showed a strong band in the region 1630-1660 cm^{-1}, which is characteristic of the azomethine (C=N) group. In all the synthesized Schiff base complexes, the $\nu_{C=N}$ band is slightly shifted to lower frequency indicating coordination of the Schiff bases through azomethine nitrogen atom[12]. Presence of coordinated water in all complexes is indicated by spectral band in the region 810-860 cm^{-1}. The bands around 310 and 145 cm^{-1} indicate the presence of bridged chlorine in the complexes[13]. However, these bands are absent in salab complex, which exhibits a spectral band at 370 cm^{-1} indicating the presence of terminal chlorine.

The electronic spectral data (Table 3) of the complexes suggest octahedral nature of the complexes. The ground state of ruthenium(III) is $^2T_{2g,}$ arising from the t_{2g}^5 configuration in an octahedral environment. The excited states are $^2A_{2g}$, $^2T_{1g}$ and ^2E_g. In the six coordinate ruthenium(III) complexes, charge transfer transition often occurs at relatively low energy. The hole in the low spin t_{2g}^5 configuration of ruthenium(III) permits relatively low LMCT bands. Since the crystal field parameter is quite large, some of the *d-d* bands are obscured by the charge transfer bands[14]. The lowest absorption corresponding to spin-forbidden $^2T_{2g} \rightarrow {}^4T_{1g}$ transition was found to occur in some cases as shoulders. Magnetic moment of the ruthenium(III) complexes (Table 3) is lower than that expected for Ru(III) low spin octahedral complexes, which might be due to the magnetic interaction between ruthenium atoms in bridged complex.

All the complexes are EPR active, which suggests that ruthenium exists in +3 oxidation state. Three *g* values are observed for $[Ru_2(qpd)Cl_4(H_2O)_2].2H_2O$ (g_1 = 2.28, g_2 = 2.11, g_3 = 1.81), $[Ru_2(qab)_2Cl_4(H_2O)_2].3H_2O$ (g_1 = 2.32, g_2 = 2.1, g_3 = 1.91) and $[Ru_2(salap)_4Cl_2].H_2O$ (g_1 = 2.12, g_2 = 2.05, g_3 = 1.89) indicating rhombohedral distortion of octahedral geometry[15]. The two *g* values of $[Ru_2(qap)_2Cl_2(H_2O)_2].H_2O$ ($g_{||}$ = 2.06, $g_{\perp}$ = 1.97), $[Ru_2(salpd)_3Cl_2(H_2O)_2]$ ($g_{||}$ = 1.84, $g_{\perp}$ = 2.34) and $[Ru(salab)(H_2O)_4]Cl_2.H_2O$ ($g_{||}$ = 2.03, $g_{\perp}$ = 1.85) indicate distorted octahedral geometry for these axial complexes. $[Ru_2(salpd)_3Cl_2(H_2O)_2]$ exhibit a reverse axial spectrum with $g_{\perp} > g_{||}$.

Table 3 — Electronic, spectral and magnetic moment data of the complexes

Compd	Absorptions (cm^{-1})	Tentative assignments	μ_{eff} (BM)
$[Ru_2(qpd)Cl_4(H_2O)_2].2H_2O$	35700	charge transfer	1.5
	31250 (sh)	$^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$	
	23500 (sh)	$^2T_{2g} \rightarrow {}^2E_g$	
	15900	$^2T_{2g} \rightarrow {}^4T_{1g}$	
$[Ru_2(qap)_2Cl_2(H_2O)_2].H_2O$	33300	charge transfer	1.4
	25000 (sh)	$^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$	
	20400	$^2T_{2g} \rightarrow {}^2E_g$	
$[Ru_2(qab)_2Cl_4(H_2O)_2].3H_2O$	31500	charge transfer	1.6
	26310 (sh)	$^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$	
	20700	$^2T_{2g} \rightarrow {}^2E_g$	
	16950 (sh)	$^2T_{2g} \rightarrow {}^4T_{1g}$	
$[Ru_2(salpd)_3Cl_2(H_2O)_2]$	35200	charge transfer	1.4
	31500	$^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$	
	20900 (sh)	$^2T_{2g} \rightarrow {}^2E_g$	
	17700	$^2T_{2g} \rightarrow {}^4T_{1g}$	
$[Ru_2(salap)_4Cl_2].H_2O$	37030	charge transfer	1.4
	30950 (sh)	$^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$	
	22800	$^2T_{2g} \rightarrow {}^2E_g$	
$[Ru(salab)(H_2O)_4]Cl_2.H_2O$	28570	Charge transfer	1.8
	26300 (sh)	$^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$	
	18200	$^2T_{2g} \rightarrow {}^2E_g$	

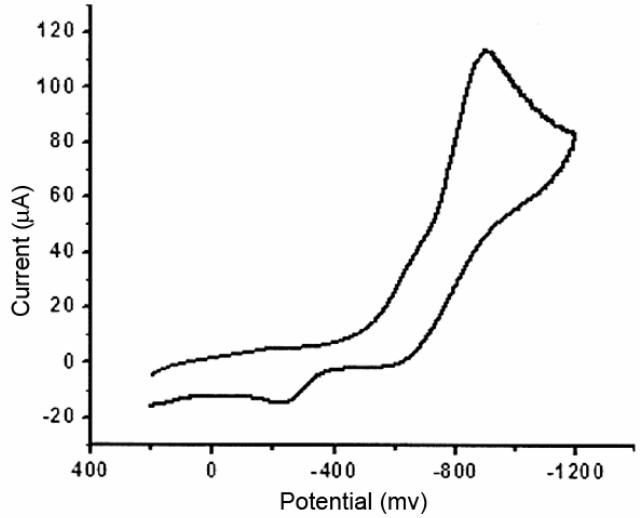


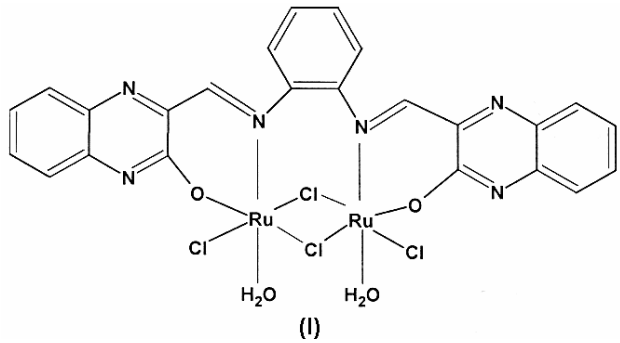
Fig. 1 — Cyclic voltammogram of $[Ru_2(salap)_4Cl_2(H_2O)]$.

The cyclic voltammogram of a representative case, $[Ru_2(salap)_4Cl_2](H_2O)$, is displayed in Fig. 1. The nature of the cyclic voltammogram is as expected for ruthenium(III) complexes. The complex shows both ruthenium(III)/(II) reduction and ruthenium(III)/(IV) oxidation peaks. However, anodic peak potential (E_{pa}) for both the redox couples could not be identified. Cathodic peak potential (E_{pc}) for the ruthenium(III)/(II) reduction is –907 mV and that for the ruthenium(III)/(IV) oxidation is -226 mV. Furthermore, nature of the curve suggest fast electron transfers, which are expected for low-spin octahedral ruthenium(III) complexes.

Based on the analytical and spectral (IR, electronic and EPR) data, an octahedral structure (**I**) is proposed for the newly synthesized ruthenium(III) Schiff base complexes.

Antibacterial screening

The Schiff bases under investigation except salab are inactive against all the bacteria. The ligand salab is found to be active against *Pseudomonas aeruginosa* in higher concentration. The ruthenium(III) complexes exhibit considerable inhibitory action on bacterial multiplication. The diameter of the inhibition zone for *Klebsiella pneumonia* was found to be in the range 5-10 mm at the concentration of ruthenium complexes of 5 ppm, 8-13 mm at the concentration of 10 ppm, 10-15 mm at the concentration of 15 ppm and 12-20 mm at the concentration of 20 ppm. The inhibition zone for the *Escherichia coli* was found to be in the range 6-18 mm at the concentration of ruthenium complexes of 5 ppm, 7-20 mm at the



(I)

concentration of 10 ppm, 9-12 mm at the concentration of 15 ppm and 11-28 mm at the concentration of 20 ppm. The inhibition zone for the *Pseudomonas aeruginosa* was found to be in the range 10-16 mm at the concentration of ruthenium complexes of 5 ppm, 14-20 mm at the concentration of 10 ppm, 18-23 mm at the concentration of 15 ppm and 22-26 mm at the concentration of 20 ppm. Thus, the effect is increased considerably with increase in concentration of the complexes, as has been observed in many cases[16-18]. The increased activity of the ruthenium complexes compared to that of the free ligands may be explained in terms of Tweedy's chelation theory[19]. According to this theory, formation of the chelate ring enhances the lipophilicity of the complexes, which breaks down the permeability barrier of the cell retarding the normal cell process.

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