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# Mixed-ligand Ru(II) complexes with 2,2'-bipyridine and tetradentate Schiff bases auxiliary ligands: Synthesis, physico-chemical study, DFT analysis, electrochemical and Na<sup>+</sup> binding properties<sup> $\frac{1}{3}$ </sup>

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#### Abstract

*cis*-Bis(2,2'-bipyridyl)dichlororuthenium(II)dihydrate complexed with Schiff bases salen  $(L^1H_2)$  and salophen  $(L^2H_2)$  provides complexes of compositions  $[Ru(L^1)(bpy)_2]$  **1** and  $[Ru(L^2)(bpy)_2]$  **2**, respectively with cavity. The structure of these complexes characterized by spectroscopic studies were supported by their optimized geometries based on DFT calculations. Complexes **1** and **2** were then allowed to interact with methanolic solution of sodium perchlorate separately providing corresponding complexes **3** and **4** with the compositions **1**·NaClO<sub>4</sub> and **2**·NaClO<sub>4</sub>, respectively. The formation constants were then evaluated by monitoring the changes in their UV–visible spectral features upon addition of different amount of sodium salts in the presence of a fixed concentration of the ruthenium complexes at a wavelength 294 nm. Emission (solution), luminescence microscopic and cyclic voltammetric studies of these complexes have also been made.

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Keywords: Salen and salophen; Ruthenium bipyridyl complexes; Optimized structures; Cyclic voltammetric studies; Binding property

# 1. Introduction

Highly organized supramolecular complexes obtained by the self-assembly of polydentate ligands assisted by metal ions are of current interest. They often provide binding sites and cavity for other cations, anions or organic molecules [1]. Recently, we have studied the crystal structure of Schiff base N,N'-bis(salicylidene)benzidine [2] and compared its structure with that of N,N'-bis(salicylidene)-p-phenylenediamine reported earlier [3]. The packing of molecules in the crystal structure are found to be dictated by intermolecular interactions. Involvement of these ligands in the development of metal complexes of catalytic importance [4,5] as well as in the self-assembled triple-decker and tetra-decker luminescent materials [6] put them in high demand. Additionally, the chemistry of ruthenium polypyridyl complexes has become competitive because of their

diverse applications in photophysical processes owing to long lived excited states [7] of parent complex tris-bipyridyl Ru(II). With this background, incorporation of ruthenium polypyridyl in the structural frame of salen and salophen ligands was thought to be worthy as its exploitation may enable monitoring of changes in the optical signals upon binding with the guest molecules as reported earlier [8,9]. Thus, initially synthesized salen and salophen ligands were complexed with *cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (bpy = 2,2'-bipyridine) in anticipation that the two donors (deprotonated OH groups) from the tetradentate Schiff bases may be coordinate leaving two additional binding sites for further coordination by guests fitting in the cavity provided by the resulting complexes.

# 2. Experimental

# 2.1. Materials and methods

RuCl<sub>3</sub> purchased from Sigma–Aldrich was converted into *cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O using reported procedure [10], where as salen and salophen were prepared and characterized by

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reported procedure [4,5]. Elemental analysis, FAB mass spectra and sodium (%) were recorded on Carbo-Erba elemental analyzer 1108, JEOL SX-102 mass spectrometer and Perkin-Elmer 2130 AAS, respectively. IR spectra in the 400–4000 cm<sup>-1</sup> range were recorded as KBr pellets on a JASCO FT-IR 5300 spectrometer, <sup>1</sup>H NMR spectra were recorded on a JEOL AL 300 MHz spectrometer using CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub> as solvents and TMS as internal reference, UV–visible and luminescence measurements in the range of 200–800 nm were recorded on Shimadzu UV-1601 and Perkin-Elmer LS-45 Luminescence spectrophotometers, respectively. Cyclic voltammetric data were recorded on EG&G instruments (model–Versastat). Formations constant were evaluated by the method as used earlier [11].

# 2.2. Preparation of Ru(II) bipyridyl complexes with salen and salophen

L<sup>1</sup>H<sub>2</sub> and L<sup>2</sup>H<sub>2</sub> were prepared and characterized by reported procedure [4,5] by condensing salicylaldehyde (4.2 ml) in each case with corresponding solutions of ethylenediamine (1.3 ml) and *o*-phenylenediamine (2.2 g) in ethanol. The solids thus obtained were characterized as L<sup>1</sup>H<sub>2</sub> mp 126 °C; Yield: 80%; IR (KBr pellet, cm<sup>-1</sup>): 1635 ( $\nu_{HC=N}$ ), 1219 ( $\delta_{O-H \text{ phenolic}}$ ), 2901 ( $\nu_{C-H \text{ phenyl}}$ ); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  (ppm) = 13.2 (s, 2H; OH), 8.3 (s, 2H; HC=N), 7.4 (m, 8H; aromatic), 3.9 (s, 4H; -CH<sub>2</sub>-CH<sub>2</sub>-) and L<sup>2</sup>H<sub>2</sub>. mp 144 °C; Yield: 92%; IR (KBr pellet, cm<sup>-1</sup>): 1616 ( $\nu_{HC=N}$ ), 1236 ( $\delta_{O-H}$  phenolic), 2922 ( $\nu_{C-H}$  phenyl); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  (ppm) = 13.1 (s, 2H; OH), 8.6 (s, 2H; HC=N), 7.4 (m, 8H; aromatic), 7.1 (m, 4H; aromatic), respectively.

# 2.3. Preparation of complex 1

The complex 1 was prepared by adding a solution of cis- $Ru(bpy)_2Cl_2 \cdot 2H_2O$  (0.260 g, 0.5 mmol) in DMF (10 ml) to a solution of  $L^1H_2$  (0.134 g, 0.5 mmol) in DMF (10 ml) with gentle heating, followed by the addition of few drops of Et<sub>3</sub>N, while stirring. The corresponding mixture was then heated with stirring on water bath  $(70 \,^{\circ}\text{C})$  for 14 h. Upon cooling in a refrigerator; black-brown crystalline solid isolated by filtration was washed with distilled water, methanol followed by diethyl ether. Its solution in acetonitrile was then purified using a column with alumina as support and acetonitrile as eluent. Eluate thus obtained was evaporated and dried, which decomposed at >220 °C; Yield: 35% with satisfactory elemental analysis. The FAB mass spectrum gave peak at m/z = 679 $[M]^+$ , 413  $[M-L_1]^+$ ; IR (KBr pellet, cm<sup>-1</sup>): 1635 ( $v_{\text{HC}=N}$ ), 1604 ( $v_{bpy}$ ), 731 ( $v_{bpy}$ ); <sup>1</sup>H NMR (DMSO- $d_6$ , 300 MHz):  $\delta$ (ppm) = 3.94 (s, 4H; -CH<sub>2</sub>-CH<sub>2</sub>-), 8.36 (s, 2H; HC=N). Additional peaks observed between  $\delta$  6.8–9.2 ppm were assigned to phenyl protons overlapped with bipyridyl protons; UV/vis (DMSO,  $10^{-4}$  M):  $\lambda_{\text{max}}$  (nm) ( $\varepsilon \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) 521 (6.7), 389 (10.5), 347 (11.9), 294 (32.0); emission excited at 450 nm (DMSO,  $10^{-4}$  M):  $\lambda_{max}$  (nm) (intensity in a.u.) 512 (36.0);  $\Lambda_{M}$  $(DMSO, 10^{-3} \text{ M}) 31.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}.$ 

#### 2.4. Preparation of complex 2

Complex **2** was also prepared using the same procedure in ~53% yield. mp >240 °C with satisfactory elemental analysis and mass at  $m/z = 727 \ [M]^+$ , 413  $[M-L_2]^+$ ; IR (KBr pellet, cm<sup>-1</sup>): 1616 ( $\upsilon_{\text{HC}=N}$ ), 1606 ( $\upsilon_{\text{bpy}}$ ), 760 ( $\upsilon_{\text{bpy}}$ ); <sup>1</sup>H NMR (DMSO- $d_6$ , 300 MHz):  $\delta$  (ppm) = 8.6 (s, 2H; HC=N). Phenyl and bipyridyl protons overlapped between  $\delta$  6.4–9.2 ppm; UV/vis (DMSO,  $10^{-4}$  M):  $\lambda_{\text{max}}$  (nm) ( $\varepsilon \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup>) 535 (5.5), 362 (13.6), 292 (40.0); emission excited at 450 nm (DMSO,  $10^{-4}$  M):  $\lambda_{\text{max}}$  (nm) (intensity in a.u.) 518 (56.0);  $\Lambda_{\text{M}}$  (DMSO,  $10^{-3}$  M) 27.0  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

# 2.5. Isolation of Na<sup>+</sup> complexes (3 and 4)

Methanolic solution of NaClO<sub>4</sub> was added to the corresponding solutions of complexes **1** and **2** separately in DMF. After stirring for 4 h, solutions were left in a refrigerator overnight and filtered. Solids thus obtained were washed with methanol followed by diethyl ether. The corresponding solutions in excess of acetonitrile were purified as reported for their parent complexes **1** and **2** dried in vacuo, which shows high melting temperature (>240 °C).

Mass pattern of complex 3 gave peaks at  $m/z = 801 [M]^+$ , 702  $[M-ClO_4^-]^+$ , 679  $[M-NaClO_4^+]^+$ , 413  $[M-L^1-Na^+-ClO_4^-]^+$ fitted with the composition  $Ru(bpy)_2(L^1)(Na) \cdot ClO_4$  whereas complex 4 with the similar composition  $Ru(bpy)_2(L^2)(Na) \cdot ClO_4$ 748  $[M-ClO_4^- - 2]^+$ , gave m/z = 849 $[M]^+,$ 727  $[M-Na^+-ClO_4]^+$ . Estimation of sodium as Na (%) gave values as 2.87 and 2.68 for complexes 3 and 4, which fit well with the values calculated from their compositions as 2.87 and 2.70%, respectively. Additional data also supported their compositions as for complex **3**: IR KBr pellet,  $cm^{-1}$ ): 1635  $(\upsilon_{\text{HC=N}})$ , 1599  $(\upsilon_{\text{bpy}})$ , 754  $(\upsilon_{\text{bpy}})$ , 987  $(\upsilon_{\text{CIO4}}^{-})$ ; <sup>1</sup>H NMR (DMSO- $d_6$ , 300 MHz):  $\delta$  (ppm) = 3.98 (s, 4H; -CH<sub>2</sub>-CH<sub>2</sub>-), 8.40 (s, 2H; HC=N);  $\delta = 6.2-9.6$  (aromatic + bipyridyl); UV/vis (DMSO,  $10^{-4}$  M):  $\lambda_{\text{max}}$  (nm) ( $\varepsilon \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup>) 496 (5.0), 348 (8.0), 294 (28.7), 260 (17.8); emission excited at 450 nm (DMSO,  $10^{-4}\,\text{M})$ :  $\lambda_{max}$  (nm) (intensity in a.u.) 517 (186.0);  $\Lambda_{\rm M}$ (DMSO, 10<sup>-3</sup> M) 136  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

As well as for complex **4**: IR (KBr pellet, cm<sup>-1</sup>): 1616 ( $\upsilon_{\text{HC=N}}$ ), 1585 ( $\upsilon_{\text{bpy}}$ ), 750 ( $\upsilon_{\text{bpy}}$ ), 970 ( $\upsilon_{\text{CIO4}}^{--}$ ); <sup>1</sup>H NMR (DMSO- $d_6$ , 300 MHz):  $\delta$  (ppm) = 8.36 (s, 2H; HC=N),  $\delta$  = 6.8–9.2 (aromatic + bipyridyl); UV/vis (DMSO, 10<sup>-4</sup> M):  $\lambda_{\text{max}}$  (nm) ( $\varepsilon \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) 515 (2.0), 321 (13.8), 290 (22.8); emission excited at 450 nm (DMSO, 10<sup>-4</sup> M):  $\lambda_{\text{max}}$ (nm) (intensity in a.u.) 514 (121.0);  $\Lambda_{\text{M}}$  (DMSO, 10<sup>-3</sup> M) 109  $\Omega^{-1} \text{ cm}^{2} \text{ mol}^{-1}$ .

#### 3. Results and discussion

Complexes 1 and 2 provide 13-membered (N<sub>2</sub>O<sub>2</sub>) macrocycles bearing flexible and rigid alkyl and aryl groups with cavity. They are found to be thermally stable and soluble in DMSO, DMF and in excess acetonitrile. The complexes are characterized by their IR spectra which shows no change in  $\nu$ HC=N peak as compared to its position in free ligands [1635 cm<sup>-1</sup> (L<sup>1</sup>H<sub>2</sub>)



Fig. 1. Optimized structure of the complexes 1 and 2.

and  $1616 \text{ cm}^{-1} (L^2 \text{H}_2)$ ]. However, the absence of  $\delta$  OH peaks in the complexes as compared to peaks observed at 1236 and  $1219 \,\mathrm{cm}^{-1}$  in the spectra of corresponding free ligands indicates that OH groups get deprotonated during coordination with the metal ion. The positions of HC=N protons at  $\delta$  8.3 and at  $\delta$  8.6 ppm in the NMR spectra of respective complexes 1 and 2, shows no change as compared to their positions in the spectra of corresponding free ligands. Thus supports that the imine groups remain uncoordinated. However, pyridyls and aromatic protons observed between  $\delta$  6 and 9 ppm could not be distinguished due to their overlapping positions. Additionally, and most important information regarding their compositions was obtained from mass data which shows peaks at m/z = 679 and 727 in complexes 1 and 2, respectively. The presence of  $[Ru(bpy)_2]^{2+}$ in both complexes is supported by peak observed at m/z = 413. Addition of one Na<sup>+</sup> ion in each complexes 1 and 2 is also supported by their corresponding mass data which shows peaks at m/z = 702 and 748 for complexes 3 and 4, respectively. IR spectra of these complexes does not show significant change for vHC=N vibration as compared to their positions in parent complexes 1 and 2. This is likely due to the closed system having pool of electrons. It is further supported by insignificant shift in the position of HC=N protons in their corresponding NMR spectra. These observations suggest that Na<sup>+</sup> ion is trapped in the cavity containing pool of electrons according to the binding pattern reported earlier by Lehn et al. [12]. Additionally, the electrical conductance of the complexes 3 and 4 measured in DMSO ( $10^{-3}$  M) is found in the range  $109-136 \Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> and suggested them to be 1:1 electrolyte as compared to their parents 1 and 2 which are neutral [13].

# 3.1. Density functional theoretical analysis

Our all-sincere attempts to get single crystals suitable for X-ray crystallography failed. However, slow diffusion of DMSO/MeOH solution of complex 1 provided single crystals but was found not suitable for diffraction. Therefore attempts have been made to optimize the structures of complexes 1 and 2 by DFT calculations in view of the reports that such calculations can be successfully employed for ruthenium polypyridyl complexes [14–21].

All density functional calculations have been performed using GAUSSIAN98/DFT [22] package. Geometrical optimizations, energy calculations and population analysis have been obtained by using B3LYP density functional method, which uses Becke's 3 parameter nonlocal exchange functional [23]

Table 1 Selected geometrical parameters for complexes 1 and 2

	B3LYP (complex 1)	B3LYP (complex 2)
Bond distances (Å)		
Ru-O1	2.103	2.107
Ru–O2	2.125	2.123
Ru–N1	2.082	2.071
Ru–N2	2.085	2.078
Ru–N3	2.074	2.092
Ru–N4	2.076	2.086
01–C1	1.309	1.302
O2–C8	1.327	1.325
C3-N5	1.280	1.288
C6-N6	1.283	1.292
Bond angle (°)		
N1-Ru-N2	78.244	78.215
N3-Ru-N4	78.189	78.088
O1-Ru-O2	87.673	87.180
O1-Ru-N4	93.634	165.196
O2-Ru-N2	90.608	89.307
N1-Ru-N3	174.668	99.112
C2-C3-N5	127.181	127.538
N6-C6-C7	122.276	120.951
N5-C4-C5	114.153	120.392
C4-C5-N6	120.698	124.711
Dihedral angles (°)		
N1-C9-C10-N2	1.251	-0.096
N3-C11-C12-N4	-1.371	-0.937
N5-C4-C5-N6	-65.952	-1.086

Table 2a								
Bonding energy (BE) and Wiberg bond indices (WBI) of the complexes 1 and 2								
Ground-state energy in Hartrees	WBI							
	Ru–O1	Ru–O2	Ru–N1	Ru–N2	Ru–N3	Ru-		

		Ru–O	l Ru–O2	Ru–N1	Ru–N2	Ru–N3	Ru–N4	O1–C1	O2–C8	C3–N5	C6-N6
Complex 1	-1962.68	0.3793	0.3676	0.4305	0.4417	0.4372	0.4548	1.1982	1.1402	1.8065	1.8044
Complex 2	-2115.22	0.3701	0.3617	0.4239	0.4555	0.4377	0.4485	1.2343	1.1419	1.6993	1.6800
Table 2b											
Calculated c	harge distribution on sele	ected atoms									
	sharge distribution on sere										
	Ru	N1	N2		N3		N4		01		02

	Ru	N1	N2	N3	N4	01	02
Complex 1	0.7644	-0.4126	-0.4090	-0.4093	-0.3968	-0.7092	-0.7577
Complex 2	0.7376	-0.4116	-0.4037	-0.4245	-0.4071	-0.6862	-0.7538

Table 3

Cyclic voltammetric data of the complexes

Complex	Ru(II)–(I)							
	$\overline{E_{\rm pc}}$ (V)	$E_{\rm pa}\left({\rm V}\right)$	$E_{\rm f}\left({\rm V}\right)$	$\Delta E_{\rm p}~({\rm mV})$				
1	-0.652	-0.710	-0.676	58				
2	-0.530	-0.720	-0.625	190				
3	-0.308	-1.150	-0.729	842				
4	-0.566	-1.099	-0.833	533				

mixed with the exact (Hartee–Fock) exchange functional and Lee–Yang–Parr's nonlocal correlation functional [24] and the standard 6-31G(d) basis sets [25,26] for N, C, H elements and LANL2DZ [27–29] for Ru which combines quasi-relativistic effective core potentials with a valence double-basic set.

The structure of the complexes **1** and **2** computed by geometry optimization are shown in Fig. 1. The selected bond lengths, bond angles and dihedral angles at B3LYP are presented in Table 1. As evident from the structure both complexes deviate from their regular geometry. The Ru–N(bpy) distances vary from 2.074 to 2.085 in complex **1** and 2.071 to 2.092 in complex **2**, the Ru–O distances vary between 2.103–2.125 and 2.107–2.123 in complexes **1** and **2**, respectively. The imine HC=N distances lies in the range 1.280–1.283 (complex **1**) and 1.288–1.292 (complex **2**). These parameters correlate well with the reported values in literature [30,31].



Fig. 2. Cyclic voltammogram of the representative complexes 1 and 3.

A perusal of bond angles and dihedral angles reveals that both structures lack symmetry to different extent as substantiated by their dipole moment values (12.82 and 14.23 D in complexes 1 and 2, respectively). Though complex 1 is more unsymmetrical as compared to complex 2 as expected due to presence of flexible hydrophobic  $-CH_2-CH_2-$  unit in complex 1 (N5–C4–C5–N6 dihedral angle of -65.952) while rigid structure in complex 2 (N5–C4–C5–N6 dihedral angle of -1.086) yet little lesser value of dipole moment observed for complex 1 could be considered in view of electronically insulating nature of alky groups. The two pyridyl rings in bipyridyls are found to be almost coplanar to each other (N1–C9–C10–N2 and N3–C11–C12–N4 dihedral angle 1.251 and -1.371 in complex 1 whereas -0.096 and -0.937 in complex 2).

Table 2a lists the ground state energy and Wiberg bond indices (WBI) [32] on complexes **1** and **2**. The WBI values of Ru–N bond of the complexes are in the range of 0.42–0.46, Ru–O in the range 0.36–0.37 and HC=N in the range 1.68–1.80. It appears that in complexes, Ru–N and Ru–O bonds are significantly more polar



Fig. 3. UV-visible absorption spectrum of: (a) **2**  $(10^{-5} \text{ M})$ ; (b) **2**+NaClO<sub>4</sub>  $(0.2 \times 10^{-5} \text{ M})$ ; (c) **2**+NaClO<sub>4</sub>  $(0.4 \times 10^{-5} \text{ M})$ ; (d) **2**+NaClO<sub>4</sub>  $(0.6 \times 10^{-5} \text{ M})$ ; (e) **2**+NaClO<sub>4</sub>  $(0.8 \times 10^{-5} \text{ M})$ ; (f) **2**+NaClO<sub>4</sub>  $(1.0 \times 10^{-5} \text{ M})$ ; (g) **2**+NaClO<sub>4</sub>  $(1.2 \times 10^{-5} \text{ M})$ .



Fig. 4. Space filling model of complex 2 showing cavity and incorporation of Na<sup>+</sup> ion.

with a bond order less than one. Calculated charge distribution shown in Table 2b indicates that ruthenium atom carries significant positive charge while the N and O atoms are negatively charged.

# 3.2. Electrochemistry

Redox behaviour of the complexes (0.01 M in DMF) containing tetrabutyl ammonium perchlorate (TBAP) (0.1 M in DMF) as supporting electrolyte has been studied using cyclic voltammetry at Pt working electrode at scan rate of  $200 \text{ mV s}^{-1}$ . The cyclic voltammetric data are given in Table 3. A representative cyclic voltammogram is displayed in Fig. 2. Metal-based oxidation process is not visible except in cases of sodium bound complexes. Quasi reversible redox peak ( $E_{1/2}$  values) observed in -0.625 to -0.833 V has been assigned to metal-based reduction [Ru(II)/Ru(I)] in view of the data reported [33] earlier as well as in view of the report [34] that reduction of free salen and salophen Schiff bases occur in the range -1.50 to -2.58 V. However, in sodium bound complexes, the peak observed at +0.375and +0.508 V assigned to Ru(II)/Ru(III) indicates that in sodium containing complexes, oxidation of Ru(II)/Ru(III) is facilitated as normally it lies in the reported [33] range of > +1.0 V. Thus in the present ligand systems, lower oxidation state of ruthenium is gets stabilized.

# 3.3. Binding study of the complexes with Na<sup>+</sup> ion

For a deeper insight into the binding property of the complexes **1** and **2** with Na<sup>+</sup> ion, their UV–visible spectra initially recorded in DMSO solution ( $10^{-4}$  M) have been examined. They show major peaks at 521, 389, 347and 294 nm as well as 535, 362 and 292 nm, respectively. These peaks have been assigned as MLCT, [ $d\pi(M)-p\pi(bpy)$ ] transitions overlapped with d–d transitions followed by intra-ligand transitions, viz.  $\pi - \pi^*(L^1H_2/L^2H_2)$  and  $\pi - \pi^*(bpy)$ , respectively. Substantial higher energy shift in both MLCT and intra-ligand transitions are observed on binding with Na<sup>+</sup> ion ( $\lambda_{max} = 294$  nm). However  $\pi - \pi^*$  transition is shifted from 294 to 260 nm in the spectrum of complex **1**. Relatively milder shift in spectra of



Fig. 5. (a) Luminescence spectra of sodium unbound complex 2 (black) and sodium bound complex 4 (red) excited at 450 nm. (b) Comparison between the luminescence intensity ( $40 \times$  magnification) of sodium unbound (A) complex 2 and sodium bound (B) complex 4. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

complex 2 from 292 to 290 nm occurs on binding with  $Na^+$  ion.

To look into the binding pattern of Na<sup>+</sup> ion with complexes 1 and 2, changes in peak positions of a representative complex 2 (10<sup>-4</sup> M in DMSO) at  $\lambda_{max}$  (294 nm) has been monitored by adding different concentrations of NaClO<sub>4</sub> and spectral variation is shown in Fig. 3. Binding constant as calculated using Benesi-Hilde Brand equation [35] has been found to be  $5 \times 10^5$ and shows substantial binding for Na<sup>+</sup> ion. To show the direct and clear view of binding of Na<sup>+</sup> ion, space filling model of the Na<sup>+</sup> bound and unbound complexes **4** and **2** as shown in Fig. 4 indicate the formation of the cavity of  $\sim 1$  Å radii clearly (as calculated tentatively using reported parameters of bond lengths and individual atoms covalent radii) in unbound stage which gets closed upon sitting of Na<sup>+</sup> ion in the cavity as the radii of Na<sup>+</sup> ion (0.9-1 Å) is closer to the size of cavity. To check the selective fitting of Na<sup>+</sup> ion in the cavity, the space filling models [36] of the complex 2 in presence of  $K^+$  and  $Li^+$  ions were also looked upon but binding of K<sup>+</sup> ion lead breaking of the system whereas Li<sup>+</sup> ion came out of the cavity. This behaviour suggests that the cavity of the complexes is found selective for binding of Na<sup>+</sup> ion.

To look into the effect of anions on the binding of Na<sup>+</sup>, similar experiments have been performed by the addition of different concentration of NaCl, NaBr and NaI to a fixed concentration  $(10^{-4} \text{ M})$  of the complex **2** again monitored at  $\lambda_{\text{max}} = 294 \text{ nm}$ . Binding constants thus evaluated are  $K_{\text{NaCl}}$  ( $2.94 \times 10^5 \text{ M}^{-1}$ ) >  $K_{\text{NaBr}}$  ( $2.08 \times 10^5 \text{ M}^{-1}$ ) >  $K_{\text{NaI}}$  ( $1.63 \times 10^5 \text{ M}^{-1}$ ). When compared with the binding constant for  $K_{\text{NaClO}_4}$  ( $5 \times 10^5 \text{ M}^{-1}$ ), one concludes that non-coordinating anion like ClO<sub>4</sub><sup>-</sup> supported the stabilization of the system. Positive test by anions (Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>) with aqueous solution of AgNO<sub>3</sub> support that anions are present out of the coordination sphere.

Since Ru(II)bipyridyl appended systems have intentionally been constructed owing to its luminescent nature, therefore emission spectra of Na<sup>+</sup> unbound (1 and 2) and bound (3 and 4) complexes have been recorded. To get a visible support, the fluorescent intensity of representative complexes 2 and 4 has been compared using a NIKON-ECLIPSE TS 100-F model fluorescence microscope. It was found that luminescence get enhanced upon binding with Na<sup>+</sup> ion (Fig. 5). This finding goes parallel to K<sup>+</sup>-induced enhancement in fluorescence of anthracene appended macrocycle in alkaline medium as reported earlier by de Silva et al. [37].

## 4. Conclusion

Simple metallomacrocycles bearing luminescent  $[Ru(bpy)_2]^{2+}$  unit in the structural framework of salen and salophen have been synthesized and characterized. Their binding with Na<sup>+</sup> ion has been monitored by UV/vis and emission spectra. The enhanced luminescence intensity of complex **2** upon binding with Na<sup>+</sup> ion has also been monitored by luminescence microscopic measurements.

*Caution!* Although no problems were encountered in this work, perchlorate salts are potentially explosive. They should be prepared in small quantities and handled with care.

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