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SYTHESIS OF RUTHENIUM(II) COMPLEXES WITH CARBOXAMIDE DERIVATIVES: SPECTROSCOPIC CHARACTERISATION AND STUDIES ON DNA AND BSA INTERACTION

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ABSTRACT

Two new mononuclear ruthenium(II) complexes of two new carboxamide derivatives formulated as $[Ru(bpy)2(L^7)](ClO_4)_2$ (**1**) and $[Ru(bpy)2(L^8)](ClO_4)_2$ have been isolated as pure materials from the reaction of H**L**^{7} and H**L**^{8} [where H**L**^{7}= *N*-(furan-2-ylmethyl)-2 pyridinecarboxamide and H**L**^{8} = *N*-(thiophen-2-ylmethyl)-2-pyridinecarboxamide] with $Ru(bpy)_2Cl_2$. All the complexes were characterized by physico-chemical and spectroscopic tools. The interaction of the complexes with calf thymus DNA (CT-DNA) using absorption, emission spectral and viscosity studies have been used to determine the binding constant, K_b and the linear Stern-Volmer quenching constant, K_{SV}. The results indicate that the ruthenium(II) complexes interact with CT-DNA strongly in a groove binding mode. The interactions of bovine serum albumin (BSA) with the complexes were also investigated with the help of absorption spectroscopy tools. Absorption spectroscopy proved the formation of a ground state BSA-$[Ru(L)(bpy)_2](ClO_4)_2$ complex.

Keywords: Ruthenium Complex, Carboxamide Derivative, BSA, CT- DNA.

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INTRODUCTION

Coordination chemistry of metal complexes derived from the ligands containing carboxamide (-CONH-) nitrogen donors has received considerable current attention.[1-7] Especially the last few decades have witnessed a remarkable interest in pyridine–N containing carboxamide complexes in various fields of biological relevance like asymmetric catalysis,[8,9] dendrimer preparation,[10] molecular receptor synthesis[11] and also in the synthesis of compounds with possible anti-tumor properties.[12-16] Carboxamide [–C(O)NH–], a key moiety of the primary structure of proteins, represents an important ligand in coordination chemistry, since its chelating rigid nature imparts a unique balance of stability versus reactivity, and allows for developments in catalytic transformations. There are several roles exhibited by carboxamide nitrogen in the chemistry of different coordination complexes. For example, cobalt and iron centers present in the enzyme nitrile hydratase (NHase) are bound through carboxamido nitrogen atoms [17-19]. This amido nitrogen possessing trans effect is also found to be important for the coordination and photolability of nitric oxide (NO).[20-23] Collins and coworkers[5,6] have extensively studied the coordination chemistry of metal complexes derived from the macrocyclic ligands containing four carboxamido nitrogen donor centers.

Among the transition metals, the chemistry of ruthenium is currently receiving a lot of attention, primarily because of the fascinating electron transfer, photochemical and catalytic properties displayed by the complexes of this metal[24]. Ruthenium complexes containing heterocyclic nitrogenous ligands use as building blocks for supramolecular assemblies, photophysical properties, directional electron and energy transfer, DNA intercalation, and potential antitumor activity.[25-28] A wide range of ruthenium compounds have been used in the synthesis of potential anticancer drugs.[29-31] Because of the spectroscopic and redox

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properties of ruthenium(II) complexes with heterocyclic N-donor ligands, the study of their interaction with proteins, DNA and lipids have received considerable attention due to the possible application in biochemistry and clinical diagnosis.

In this paper, an account of the synthesis, characterization, DNA and BSA binding study of two ruthenium(II) complexes of nitrogen heterocyclic ligands, furan-2-ylmethyl-amide (H**L**^{7}) and thiophen-2-ylmethyl-amide (H**L**^{8}) derived from pyridine-2-carboxylic acid have been described. The binding constants K_b (derived from UV-vis study) and the quenching constant K_{sv} (obtained from fluorescence displacement experiments using ethidium bromide) have been determined in order to establish the binding mode of these complexes to double-helix DNA. Moreover the binding of these ruthenium(II) complexes with bovine serum albumin (BSA) was studied by means of absorption spectroscopy tools.

EXPERIMENITAL

Reagents and Measurements

All chemicals and reagents were obtained from commercial sources and used as received. Solvents were distilled from an appropriate drying agent. $RuCl_3.3H_2O$ (Aldrich) was used without further purification. $[Ru^{II}(bpy)_2Cl_2].2H_2O$ was synthesized according to the literature method[32]. Tetra-n-butylammonium perchlorate (TBAP) was prepared by addition of sodium perchlorate (taking the usual precaution of handling perchlorate salts!) to a hot solution of tetra-n-butylammoniumbromide (Aldrich).

The C, H, N elemental analyses were performed on a Perkin Elmer model 2400 elemental analyzer and ruthenium analyses were carried out by means of a Varian atomic absorption spectrophotometer (AAS) model-AA55B, GTA using graphite furnace. Electronic absorption spectra were recorded on a JASCO UV-Vis/NIR spectrophotometer model V-570 in the range of 1100-200 nm. Molar conductances (Λ_M) were measured in a Systronics conductivity meter (model 304) in acetonitrile with ~10^{-3} mol L^{-1} complex concentration. The measurement of pH of the reaction mixture was done with a systronics digital pH meter (Model 335). The fluorescence spectra of complexes bound to DNA were obtained at an excitation wavelength of 522 nm with the Fluorimeter Hitachi-4500.

Preparation of the Ligands

N-(furan-2-ylmethyl)-2-pyridinecarboxamide (H**L**^{7}) and N-(thiophen-2-ylmethyl)-2-pyridinecarboxamide] (**HL**^{8}) A common synthetic procedure has been followed to obtain H**L**^{7} and **HL**^{8}. To a pyridine solution of pyridine-2-carboxylic acid (1.231 g, 10 mmol), furfurylamine (0.9712 g, 10 mmol) for H**L**^{7} or 2-thiophenemethyl amine (1.1312 g, 10 mmol) for H**L**^{8} was added with stirring. Then tri-phenylphosphite (3.101 g, 10 mmol) was added to this mixture and heated in an oil bath at 80 °C for 6 h. The resulting orange solution was allowed to evaporate for a few days to collect a white crystalline solid after washing with methanol and water thoroughly. The crystalline material dried in vacuo over silica gel was used for characterization by using physico-chemical and spectroscopic tools.

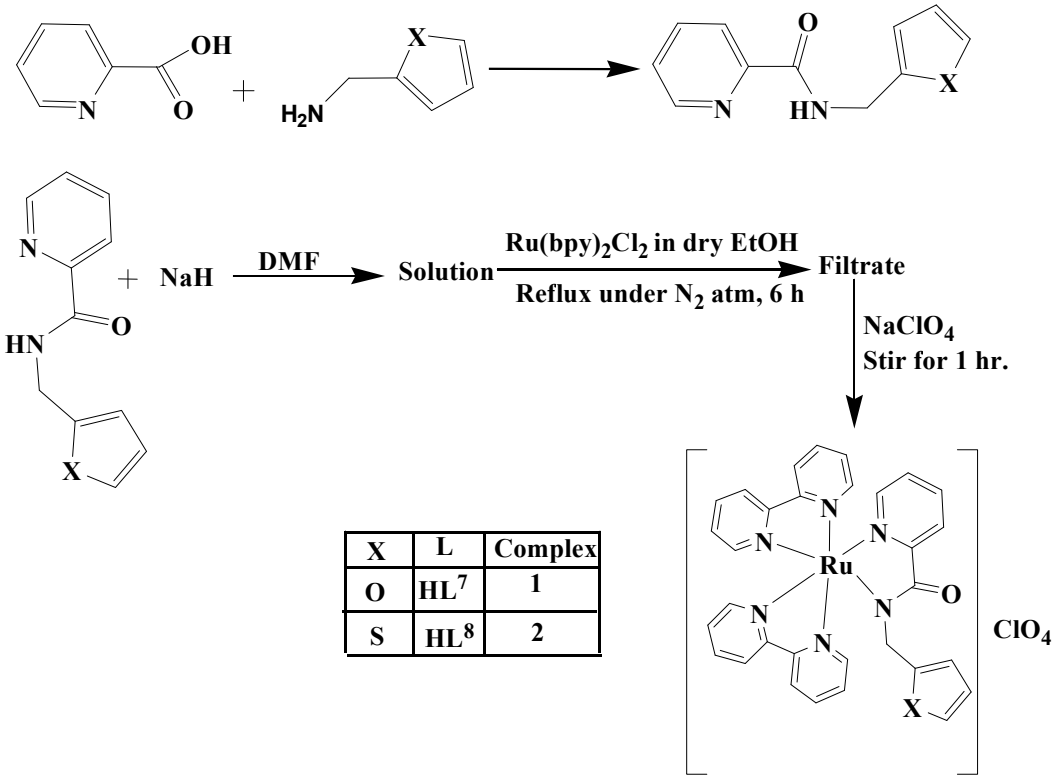
Preparation of $[Ru(L^7)(bpy)_2](ClO_4)_2$ (1) and $[Ru(L^8)(bpy)_2](ClO_4)_2$ (2)

Syntheses of the complexes were performed following a common procedure as shown in Scheme-1.A solution of HL^7 (0.202 g, 1.0 mmol) in case complex **1** or HL^8 (0.218 g, 1.0 mmol) in case complex **2** was prepared in 10 mL of N,N′-dimethylformamide and to it was added solid NaH (1.1 mmol, 0.0264 g) to obtain a light yellow solution of deprotonated ligand. This mixture was added slowly to a hot solution of $[RuCl_2(bpy)_2]$ (bpy = bipyridyl) (0.484 g, 1 mmol) in dry EtOH (20 mL) previously purged with N_2 was added dropwise and the resulting solution was refluxed for ~ 6 h under N_2 atmosphere. The solvent of the resulting solution was reduced to one-third of the total volume, and water solution of $NaClO_4$ (0.140 g 1mmol) was added in stirring condition. The resulting mixture was stirred for ~2 h and then by filtering a red solid mass was obtained. The product was dissolved in the minimum amount of dichloromethane and chromatographed over a silica gel column prepared in dichloromethane. Only one band was obtained**.** Yield: 70-75 %.

DFT Calculation

Full geometry optimization was performed by using the density functional theory method at the B3LYP level for **1** and **2** [33]. All elements except Ru were assigned the 6-31G(d) basis set. The SDD basis set with

effective core potential was employed for the Ru atom. The vibrational frequency calculations were done to ensure that the optimized geometries represent the local minima and there are only positive eigen values. All calculations were performed with Gaussian 03 program package. Vertical electronic excitations based on B3LYP optimized geometry was computed using the time-dependent density functional theory (TD-DFT) formalism in acetonitrile using conductor-like polarizable continuum model (CPCM). Gauss Sum [34] was used to calculate the fractional contributions of various groups to each molecular orbital.



X	L	Complex
O	HL^7	1
S	HL^8	2

Scheme-1: Synthetic Procedure of Ruthenium(II) Complexes Synthesis

DNA Binding Experiments

The tris-HCl buffer solution (pH 7.2) used in all the CT-DNA experiments was prepared using deionized and sonicated HPLC grade water (Merck). The CT-DNA used in the experiments was sufficiently free from protein as the ratio of UV absorbance of DNA solution in tris-HCl at 260 and 280 nm (A260/A280) was 1.9. The concentration of DNA was estimated by using the extinction coefficient (6600 M-1 cm-1) at 261 nm and the stock solution of DNA was stored at 4 °C. The interaction of the complexes with CT-DNA was studied by dissolving each complex in 2 mL of DMSO and diluting with tris-HCl buffer to get the required concentration for all the experiments. Absorption spectral titration experiments were performed by maintaining the complex concentration constant and varying the CT-DNA concentration. To eliminate the absorbance of DNA itself, an equal amount of CT-DNA was added to the reference solution.

In the ethidium bromide (EB) fluorescence displacement experiment, 5.0 μL of the EB Tris-HCl solution (1.0 mmol L^{-1}) was added to 1.0 mL of DNA solution (at saturated binding levels) and stored in the dark for 2.0 h. Then the solution of the complex was titrated into the DNA/EB mixture and diluted with tris-HCl buffer to 5.0 mL to get the appropriate complex/CT-DNA mole ratio in solution. Before measurements, the mixture was shaken and incubated at room temperature for 30 min. The fluorescence spectra of EB bound to DNA were obtained with an λ*ex* of 522 nm.

To ascertain the binding mode (groove/intercalative) of the complexes with DNA, the viscosity measurement method was used by employing an Ostwald's viscometer. Titrations were carried out in the viscometer by adding the complex (0.5-3.5 μM) to the CT-DNA solution (5.0 μM). The viscosity value of the solutions was calculated from the observed flow time of CT-DNA-containing solution corrected from

the flow time of buffer alone (t_0), $\eta = t\text{-}t_0$. The obtained data were used to plot the $(\eta/\eta_0)^{1/3}$ versus the ratio of the concentration of complex to CT-DNA, where η is the viscosity of the CT-DNA solution in the presence of complex and η_0 is the viscosity of the CT-DNA solution only.

Protien (Bovine Serum Albumin) Binding Experiments

Samples for spectroscopic measurements were prepared by dissolving bovine serum albumin in water and administering the appropriate concentration of the Ru(II) complexes. The samples were carefully degassed using pure nitrogen gas for 15 min. Quartz cells with high vacuum Teflon stopcocks were used for degassing.

RESULTS AND DISCUSSION

Characterization

The formulation of the ligands was established using spectroscopic and physico-chemical tools. These organic moieties act as bidentate N,N chelators. The complexes **1** and **2** are soluble in DCM, acetonitrile, methanol, and DMF. Microanalytical data (Table-1) confirms the formulation of complexes **1** and **2**. The conductivity measurements indicate that both the ruthenium (II) complex species are non-electrolytes in methanolic solution.

Table-1: Microanalytical Data of the Ruthenium (II) Complexes (1 and 2)

Compounds	Elemental Analysis Found (Calcd.)				Conductance (Λo)[a]
	C	H	N	Ru	
$[Ru(L^7)(bpy)_2]ClO_4$ (1)	52.14 (52.11)	3.50 (3.44)	11.77 (11.71)	14.15 (14.09)	87
$[Ru(L^8)(bpy)_2]ClO_4$ (2)	50.99 (50.93)	3.43 (3.38)	11.51 (11.45)	13.85 (13.80)	93

DFT Computations for Explanation of Spectral and Redox Properties

DFT calculations were performed using Gaussian-09 software over a Red Hat Linux IBM cluster to clarify the configurations of **HL**[7] and **HL**[8] and their respective complexes (**1** and **2**). Molecular level interactions between ligands and the Ru(II) complexes were studied using DFT with the B3LYP/6-31G (d, p) functional model. Theoretical calculations shows that it may be deduced that both the HOMO and LUMO of the L–Ru complex were better stabilized than those of ligands (**Fig. 1**). It can easily be deduced that the greater electronic charge density in HOMO over the carboxamide unit from the energy optimization of the HOMO and LUMO of the L–Ru complex. In the case of ligand, the electron density resides mainly on half of the furan or thiophene moiety, with some electron density on the pyridine moiety.

Binding Experiments with Calf Thymus-DNA

Absorption Spectroscopy

Electronic absorption spectroscopic tool was used to find out the binding between Ru complex and DNA. Generally binding of the ruthenium (II) complex to the CT-DNA helix is examined by an increase of the absorption band (*ca.* 289 nm) of ruthenium (II) complex. This increasing value of absorbance indicates that there is the involvement of strong interactions between complex and the base pairs of DNA. The absorption spectra of the Ru (II) complex **1** in the absence and presence of CT-DNA are given in (**Fig 2**). The spectral change might be interpreted as due to the groove binding nature of the adducts since ruthenium (II) complexes containing carboxamide ligands, which likely facilitates the formation of Vander-Waals contacts or hydrogen bonds during interaction with DNA grooves. In order to further illustrate the binding strength of the Ru(II) complex with CT-DNA, the intrinsic binding constant K_b was determined from the spectral titration data using the following equation:[36,37]

$$[DNA]/(\varepsilon_a - \varepsilon_f) = [DNA]/(\varepsilon_b - \varepsilon_f) + 1/[K_b(\varepsilon_b - \varepsilon_f)]$$

Where, [DNA] represents the DNA concentration, ε_f and ε_b are the extinction coefficients for the free and fully bound ruthenium(II) complex, respectively, and ε_a the metal complex extinction coefficient during

each addition of DNA. The [DNA] / (ε_a - ε_f) plot against [DNA] gave a linear relationship. The intrinsic binding constants (K_b) for the complex **1** were calculated from the slope to intercept ratio. The value is in close agreement with those of the well-established groove binding rather than classical intercalation agent.

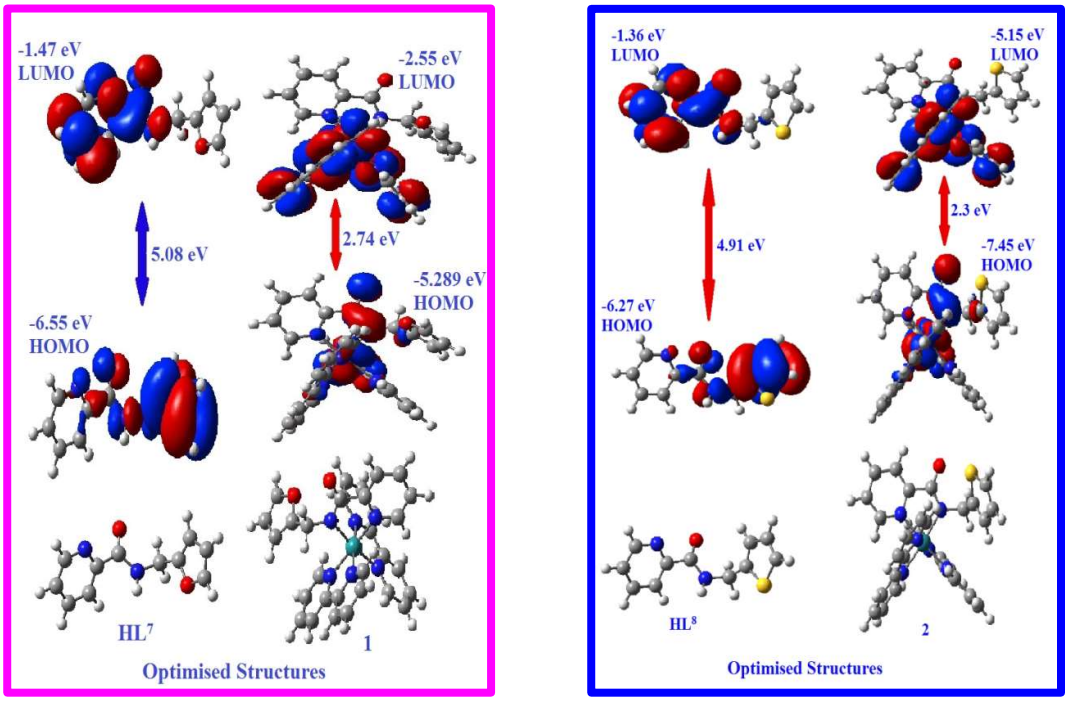


Fig.-1: Optimized Structures and HOMO and LUMO of the Organic Moieties and the Ruthenium Complexes

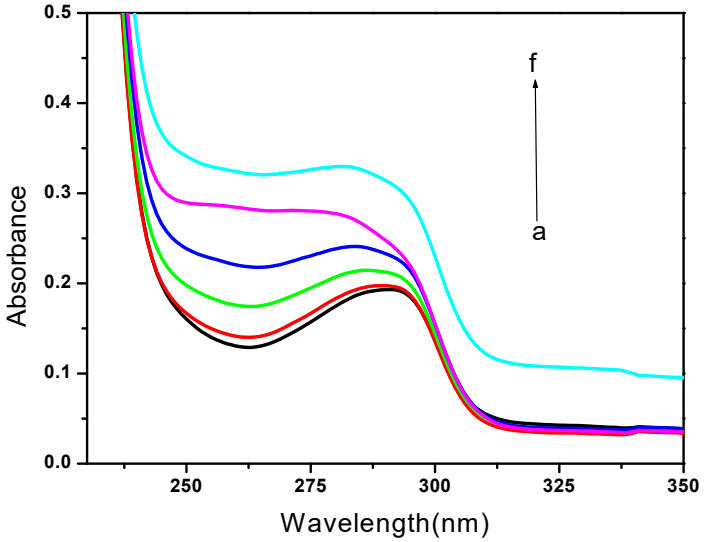


Fig.-2: Electronic Spectral of Complex **1** through Titration with CT-DNA in tris-HCl.
The increase of DNA Concentration is indicated by an arrow

Ethidium Bromide Fluorescence Displacement Experiments

Ethidium bromide (EB) fluorescence displacement experiments were also performed in order to investigate the interaction mode of the complexes with CT-DNA. In fact, the EB fluorescence intensity (at λ_{ex} = 522) will be enhanced in presence of DNA because of its intercalation into the helix, and it was quenched by the addition of another molecule that displaces EB from DNA. Here, the significant decreases of the fluorescence intensity of EB bound to DNA at around 620 nm were recorded by increasing the concentration of complex **1** as shown in Fig.-3. The observation of EB fluorescence quenching due to the releasing of some EB molecules from the EB-DNA system is supportive to the interaction of the ruthenium(II)

complexes with CT-DNA through the groove binding mode. Here, the quenching trend of EB bounded DNA by the ruthenium (II) complexes is in agreement with the linear Stern–Volmer equation:[38]

$$I_0/I = 1 + K_{SV}\,[complex]$$

Where, I_0 and I represent the fluorescence intensities in the absence and presence of quencher, respectively. K_{SV} is the linear Stern–Volmer quenching constant and [complex] the molar concentration of the quencher. From the slope of the regression line in the derived plot of I_0/I *vs* [complex] Fig.-4 the K_{SV} values for the complex was determined. This was found to be $0.2895 \cdot 10^4$ for **1** (R = 0.96665 for five points), indicating a strong affinity of ruthenium(II) complexes to CT-DNA.

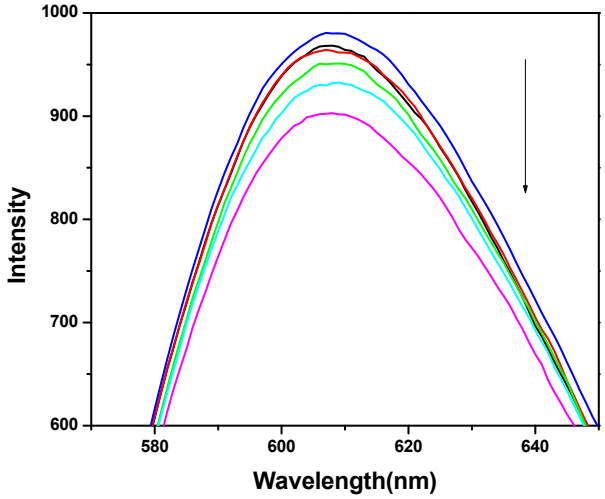


Fig.-3: Emission Spectra of the CT-DNA-EB System in tris–HCl Buffer based on the Titration of Complex. λ_{ex} = 522 nm

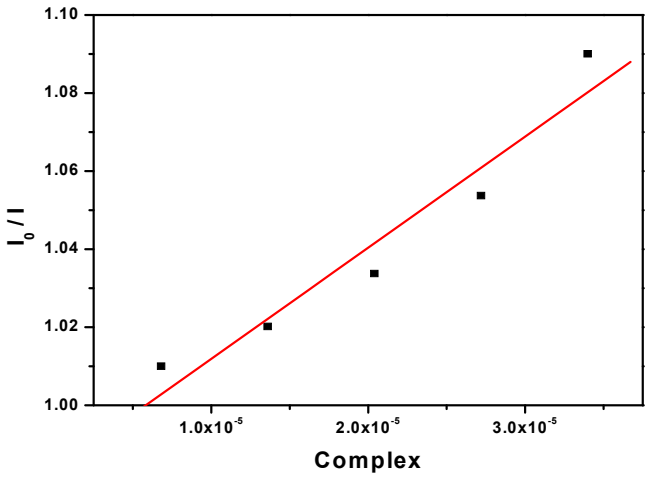


Fig.-4: Plot of I_0/I *vs* [complex] for the Titration of CT-DNA–EB System with Complex 1 using Spectrofluorimeter; Linear Stern–Volmer Quenching Constant (K_{sv}) = $0.2895 \cdot 10^4$; (R = 0.96665 for Five Points)

Protein (Bovine Serum Albumin) Binding Experiments

Absorption Characteristics of BSA–Ru(II) Complex 1

The absorption spectra of BSA in the absence and presence of Ru(II) complex **1** at different concentrations were studied (Fig.-5). From this study we observed that upon increasing the concentration of the complex the absorption of BSA increases regularly. It may happen due to the adsorption of BSA on the surface of

the complex. The apparent association constant (K_{app}) was determined of the complexes with BSA has been determined using the following equation:

$$1/(A_{obs} - A_0) = 1/(A_c - A_0) + 1/ K_{app}(A_c - A_0)[comp]$$

Where, A_{obs} is the observed absorbance of the solution containing different concentrations of the complex at 280 nm, A_0 and Ac are the absorbances of BSA and the complex at 280 nm, respectively, with a concentration of C_0, and K_{app} represents the apparent association constant.
The enhancement of absorbance at 280 nm was due to adsorption of the surface complex, based on the linear relationship between $1/(A_{obs} - A_0)$ *vs* reciprocal concentration of the complex with a slope equal to $1/K_{app}(A_c - A_0)$ and an intercept equal to $1/(A_c - A_0)$ (Fig.-6). The value of the apparent association constant (K_{app}) determined from this plot is 3.7×10^3 M^{-1}.

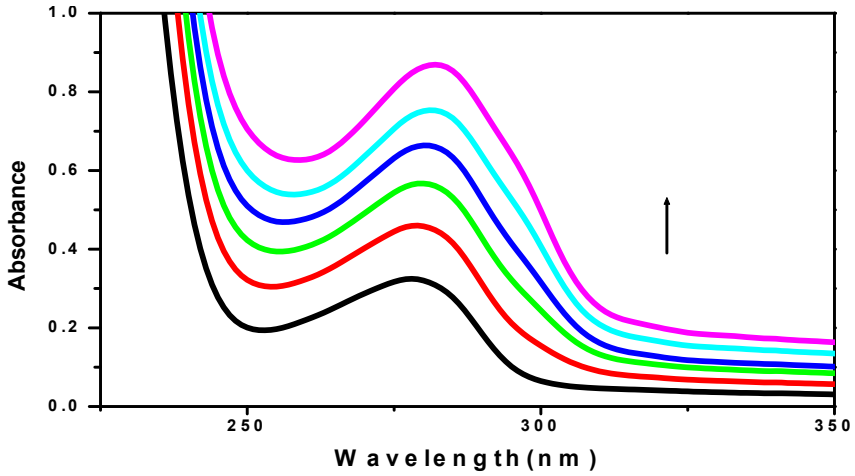


Fig.-5: Absorption Spectrum of BSA in the presence of Complex 1 in the Concentration Range 0 - 6.34×10^{-5} M

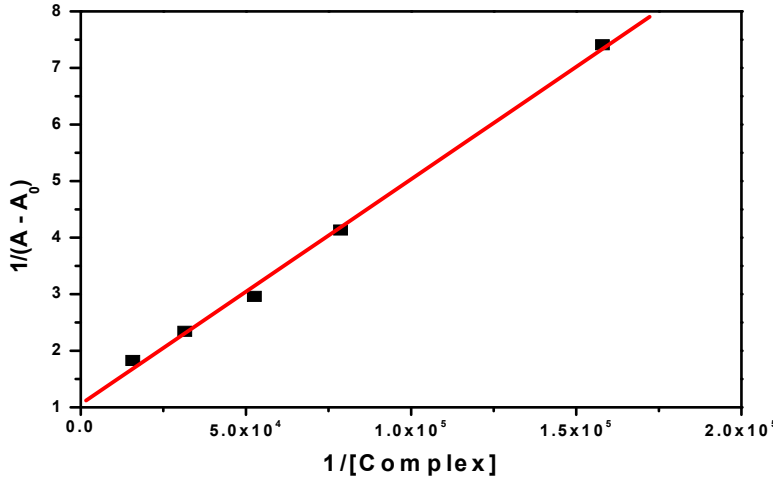


Fig.-6: Plot of $1/(A - A_0)$ *vs* 1/[Complex] for the Titration of BSA with Complex **1** in tris HCl buffer; apparent Association Constant (K_{app}) = $6.12 \times 10^3 M^{-1}$ (R = 0.99896 for four points)

CONCLUSION

In this article, two novel octahedral ruthenium (II) complexes **1** and **2** of deprotonated bidentate ligands *N*-(furan-2-ylmethyl)-2 pyridinecarboxamide and *N*-(thiophen-2-ylmethyl)-2-pyridinecarboxamide have been synthesized and characterized using various spectroscopic measurements. The aim of this research was devoted to study the interaction of the complexes with calf thymus DNA and BSA of the complexes and

the organic moieties. The interaction of the Ru (II) complexes with CT- DNA at physiological pH shows very good agreement between spectrophotometric and fluorimetric methods of measurement, the data lend support to the validity of the methods used in the experiments and all results indicate that the Ru (II) complexes bind to CT-DNA through surface or groove binding mode and it is also in accordance with the unchanged values of the viscosity of the DNA solution upon addition of complex **1**. This study clearly indicates that **1** binds to calf thymus DNA in a groove binding interaction but not in a intercalative mode like reported octahedral ruthenium (II) complexes. The absorption and emission spectroscopy tool is used to study the interaction of the complex **1** with bovine serum albumin that proves the formation of a ground state BSA-$[Ru(L^1)(bpy)_2](ClO_4)_2$ complex. The information obtained from the present work is indicative of the development of potential probes of DNA structure in future applications.

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