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RESEARCH ARTICLE

SPECTROSCOPIC CHARACTERIZATION OF P-QUINONE WITH RUTHENIUM II COMPLEX OF 1,10-PHENANTHROLINE FAMILY OF LIGANDS.

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Abstract

Tridendate polypyridine ligands made of 1,10-phenanthroline ligands substituted at the 4,7 positions with the corresponding homoleptic Ru(II) complex have been synthesized and characterized. The complex is formulated as $[Ru(NN)_3{}^{2+}]$, (where N= 1,10 phenanthroline, 4,7-dimethyl 1.10-phenanthroline, 4,7-diphenyl 1,10-phenanthroline). In this work, electron transfer studies of quinone with $[Ru(NN)_3{}^{2+}]$ complexes were carried out using absorption spectral technique. The binding efficiency of quinone was also studied using this technique. Intrinsic binding constants (K_b) have been estimated under a similar set of experimental conditions, to probe the details of BQ binding by these complexes. The results indicated that the complex interacted with BQ. The binding efficiency was moderate and similar for all complexes with quinone. The nature of the binding seemed to be mainly an electrostatic interaction between BQ and the Ruthenium(II)complex. The possibility of electron transfer between the ruthenium(II) complex and 1,4-benzoquinone as an electron acceptor was explored by UV/Vis spectroscopy.

Introduction:-

Quinones are ubiquitous in nature. They are ET mediators between PSI and PSII, and act as anticancer drugs in medicine [1–8]. They appear to be predestined as electron acceptors in nature for a variety of reasons [9–11]. Quinones are of interest because of their relevance for natural photosynthesis, and they have been extensively used in electron transfer studies involving porphyrins and organic donors[12,13]. From a synthetic point of view, quinones are highly attractive, because they are noncharged species, and are easily functionalized, offering a wide range of redox potentials. Ruthenium (II) polypyridyl complexes have attracted attention in recent years due to their well-defined spectroscopic, photophysical, photochemical and electrochemical properties [14]. These properties are of particular use in the construction of supramolecular systems[15] and in the development of photophysically driven molecular devices[16]. In the present study, we have used 1,4- benzoquinone (BQ) as electron acceptor.

Experimental methods:-

Materials:-

Tris(1,10-phenanthroline)ruthenium(II), $Ru(phen)_3{}^{2+}$, and Tris(4,7-dimethyl-1,10-phenanthroline) ruthenium(II), $Ru(dmphen)_3{}^{2+}$ and Tris(4,7-phenyl-1,10-phenanthroline)ruthenium(II), $Ru(bathophen)_3{}^{2+}$, (as perchlorate salts) were synthesized by reacting $RuCl_3.3H_2O$ with the corresponding ligands in 1:3 equivalence by the known procedures described in the literature [17-19] and purified by means of re-crystallization from ethanol. All the complexes obtained initially as the chloride salt, were dissolved in minimum amount of water and concentrated solution of ammonium hexafluorophosphate was added to precipitate the perchlorate salt. The hexafluorophosphate salts of the complexes employed in this work have been fully characterized by UV/Visible measurements. The 1,4-benzoquinone was purified by sublimation under vacuum. Acetonitrile (CH_3CN) HPLC grade was used as the solvent. All experiments were done at room temperature (25ºC).

Details of Spectral Measurements:-

The solution of the metal complexes and the quinones were freshly prepared using acetonitrile. The absorption spectral measurements were carried out using Perkin Elmer, Lambda25, UV/VIS spectrophotometer. Quartz cuvettes with a 1cm path length were used throughout. The emission intensity measurements were recorded by JASCO/FP—6500 spectrofluorometer with a 1cm path length quartz cell equipped with a 150W xenon source, a red sensitive photomultiplier tube. All the sample solutions used for emission measurements were deareated for about 20 min by dry nitrogen gas purging and keeping the solutions in cold water to ensure that there is no change in volume of the solution. The nitrogen gas was purified by Fieser's solution to remove the oxygen present in the solution.

Evaluation of Binding Constants:-

The donor-acceptor complex formation in solution was analysed using UV-Visible spectrophotometric titration. These experiments were performed by maintaining a constant concentration of the quinone while varying the Ruthenium (II) complex concentration. This was achieved by dissolving an appropriate amount of the Quinone in the Ruthenium (II) complex stock solution and by mixing various proportions of the Quinone and complex solutions while maintaining the total volume constant (1 ml). This resulted in a series of solutions with varying concentrations of Ruthenium (II) complex but with a constant concentration of Quinone. The binding constants were then evaluated with the aid of Benesi-Hildebrand procedure[20]
using eq. (1),

$$[Ru(NN)_3]^{2+}] / [\mathcal{E}_a - \mathcal{E}_f] = [Ru(NN)_3]^{2+}] / [\mathcal{E}_b - \mathcal{E}_f] + 1/ K_b[\mathcal{E}_b - \mathcal{E}_f] \text{ ....(1)}$$

where $[Ru(NN)_3]^{2+}]$ is the concentration of $[Ru(NN)_3]^{2+}]$ in the base pairs. The apparent absorption coefficients $\mathcal{E}_a$, $\mathcal{E}_f$ and $\mathcal{E}_b$ correspond to A_{obsd} / [BQ], the extinction coefficient for the free BQ and the extinction coefficient for the BQ in the fully bound form respectively. The slope and Y-intercept of the linear fit of $[Ru(NN)_3]^{2+}] / [\mathcal{E}_a-\mathcal{E}_f]$ versus $[Ru(NN)_3]^{2+}]$ give $1/[\mathcal{E}_b-\mathcal{E}_f]$ and $1/ K_b[\mathcal{E}_b-\mathcal{E}_f]$ respectively. The intrinsic binding constant K_b can be obtained from the ratio of the slope to the intercept[21]. The MicroCal Origin software package was used for curve fitting the data.

Results and discussion:-

The metal complexes, $[Ru(NN)_3]^{2+}$ were synthesized and characterized. The absorption and emission spectra of Ru(II) complexes used in this study were shown in the Figs 1and 2 and the λ_{max} values were shown in the Table 1 and agree well with the literature values. The photophysical properties of the complexes were carried out and the binding constant of the metal complexes with benzoquinone was determined. These data were summarized in Table 2.

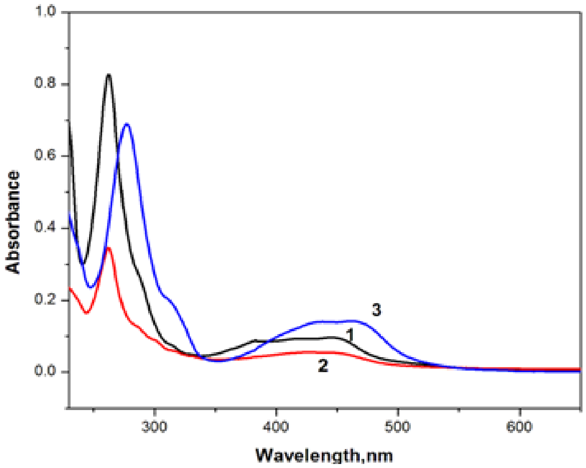

Fig. 1:- Absorption spectra of (1) $[Ru(phen)_3]^{2+}$ (2) $[Ru(dmphen)_3]^{2+}$ (3) $[Ru(bathophen)_3]^{2+}$ in acetonitrile medium.

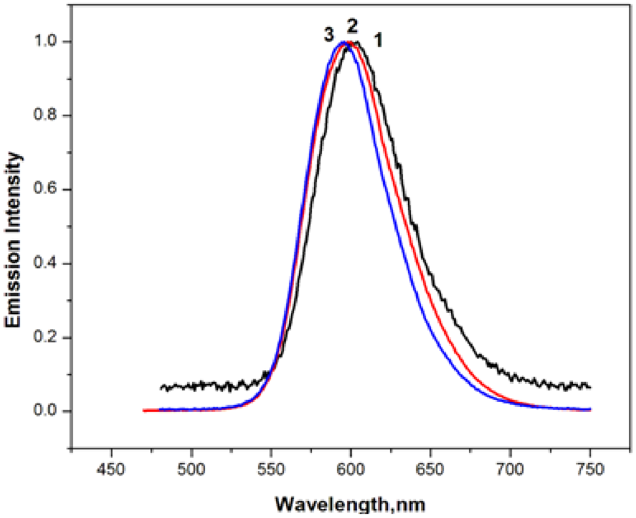

Fig. 2:- Emission spectra of (1) $[Ru(phen)_3]^{2+}$ (2) $[Ru(dmphen)_3]^{2+}$ (3) $[Ru(bathophen)_3]^{2+}$ in acetonitrile medium.

Table. 1:- The Photophysical data of Ruthenium (II) complexes in acetonitrile medium.

Complexes [a]	**Absorption Maxima,(nm)**	**Emission Maxima,(nm)**	**lifetime** [b] **τ_0(ns)**
$[Ru(phen)_3]^{2+}$	262, 443	604	460
$[Ru(dmphen)_3]^{2+}$	263, 448	600	1740
$[Ru(bathophen)_3]^{2+}$	277, 463	595	4680

[a] As PF_6^- salts; [b] Data collected from literature.

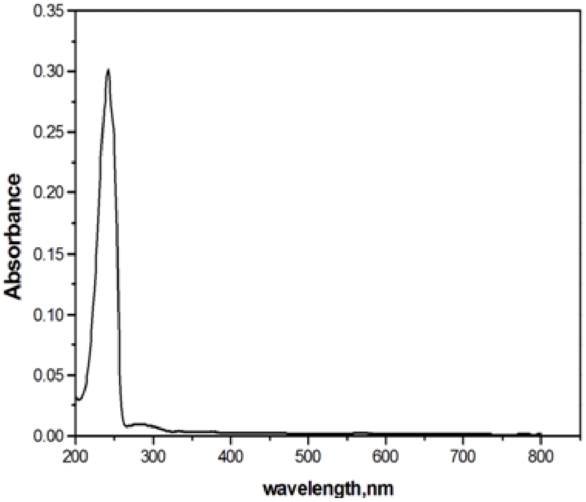

Fig. 3:- Absorption spectra of 1,4-benzoquinone(BQ) in CH_3CN.

Electronic Spectral Features:-

The UV/Visible absorption spectra of these complexes Ru(NN)$_3^{2+}$ showed intense MLCT (metal-to-ligand charge-trasnsfer) and LC (ligand-centered) transitions around 450-500 nm (ε= (1-2) x 10^4 M^{-1} cm^{-1}) corresponds to the d π- π* transition and 250-300 nm (ε = (5-10) x 10^4 M^{-1} cm^{-1}) corresponds to the π- π* transition, respectively [22-34]. The assignment of the LC transition was also confirmed by comparing the absorption spectra of free ligands. The MLCT transition involves electronic excitation from the metal orbital [dπ (Ru)] to the ligand centered acceptor π* orbitals (ligand). However, the difference in energy is so small that no separate MLCT bands can be detected. A representative spectra of Ru(NN)$_3^{2+}$ complexes in acetonitrile are shown in Fig 1 and the UV/Visible spectral data for all the three complexes investigated in this study are summarized in Table 1. The emission maxima of these complexes are observed in the range of 600-625 nm and are attributed to the decay of the ^{3}MLCT state of the ruthenium complexes. The emission spectra of these complexes are shown in the Fig 2 and the values are given in the Table 1.

Binding studies of BQ:-

Absorption titration can monitor the interaction of metal complexes with biologically molecules. So it can be used to observe the interaction of BQ with [Ru(NN)$_3$]$^{2+}$ complexes. The titrations in acetonitrile were done using a fixed BQ concentration to which increments of the [Ru(NN)$_3$]$^{2+}$ stock solution were added. Ruthenium-BQ solutions were allowed to incubate for 10 min before the absorption spectra were recorded. The absorption spectra of BQ in the absence of [Ru(NN)$_3$]$^{2+}$ is given in Fig 3. The reactions between BQ and Ru(NN)$_3^{2+}$ exhibit a significant increase in absorbtion intensity in the UV region. The changes in the absorption spectra of quinone in the presence of increasing concentrations of [Ru(NN)$_3$]$^{2+}$ complexes are shown in Figs 4,5 and 6. There is a slight change in the absorption intensity of BQ, which is sufficient for the determination of binding constant for the binding of [Ru(NN)$_3$]$^{2+}$ complexes with quinone. Moreover, increasing concentrations of the complex result in the obvious tendency of hyperchromism and shift of the absorption bands[35]. An electrostatic interaction between Ru(NN)$_3^{2+}$ complex and BQ can be predicted when it is based on the hyperchromism exhibited and shifted in absorbance of BQ.

In order to compare quantitatively the binding strength of the BQ, the intrinsic binding constants K_b of BQ with Ru(NN)$_3^{2+}$were obtained by monitoring the changes in absorption intensity at 241 nm for BQ, with increasing concentration of Ru(NN)$_3^{2+}$. The intrinsic binding constant of the BQ with Ruthenium (II) complex K_b was determined by using modified Benesi- Hildebrand eqn (1). From the plot (Fig 7 and 8) of [Ru(NN)$_3$]$^{2+}$] / [ε_a-ε_f] vs [Ru(NN)$_3$]$^{2+}$], the calculated binding constant K_b for phen was 4.19×10^3 while the corresponding value for dmphen was 8.7×10^3 and for bathophen is 2x 10^4. The data obtained throughout this calculation were given in Table 2

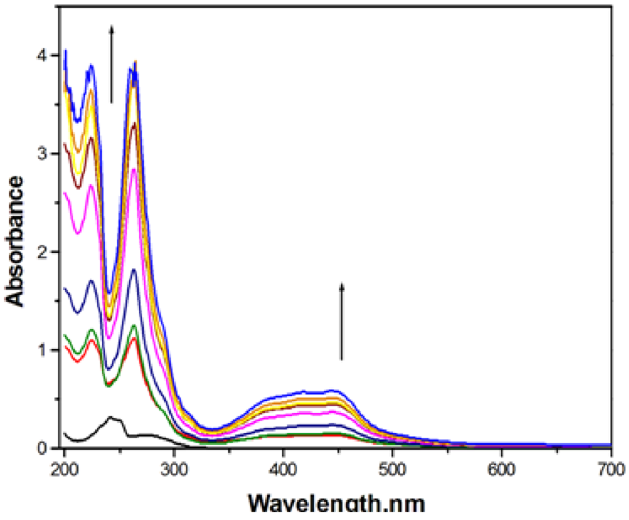

Fig. 4:- Absorption spectra of 1,4-benzoquinone with incremental addition of Ru(phen)$_3^{2+}$ in acetonitrile medium.

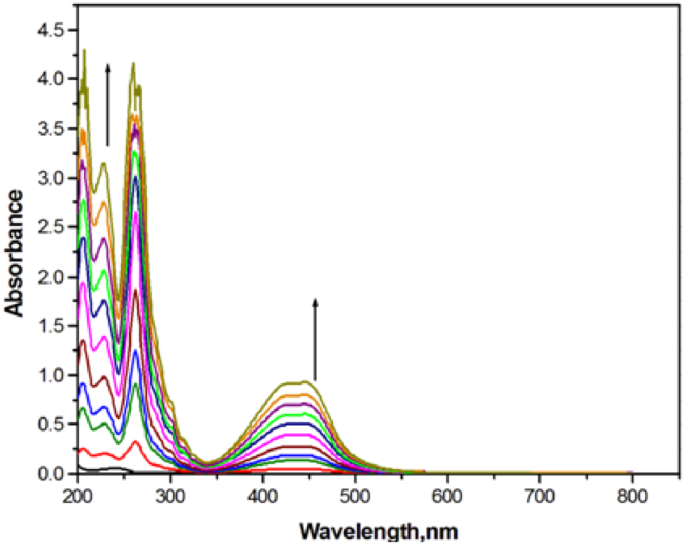

Fig. 5:- Absorption spectra of 1,4-benzoquinone with incremental addition of Ru(dmphen)$_3^{2+}$ in acetonitrile medium.

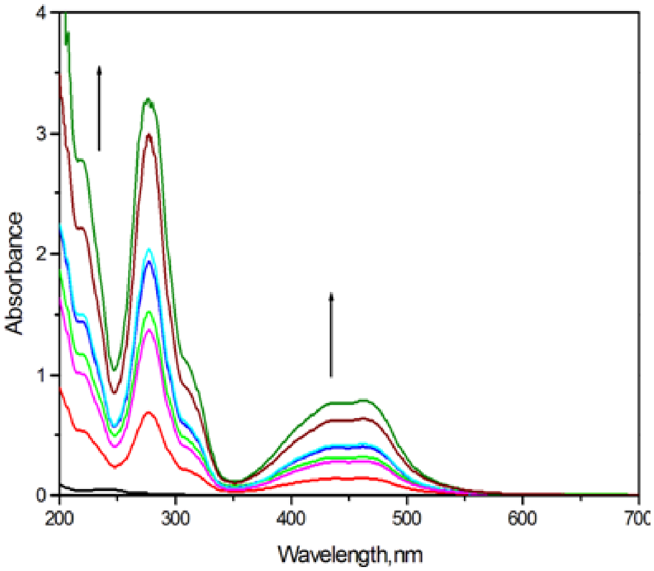

Fig. 6:- Absorption spectra of BQ with incremental addition of Ru(bathophen)$_3^{2+}$.

Table 2 Spectroscopic properties on binding to [BQ] .

Compounds	**Absorption**[a]		**λ_{max} (nm) Δλ**	**K_b , M^{-1}**
	Free	**bound**		
BQ + Ru(phen)$_3$]$^{2+}$	241	224	17	4.19×10^3
BQ + Ru(dmphen)$_3$]$^{2+}$	241	226	15	8.7×10^3
BQ+ Ru(bathophen)$_3$]$^{2+}$	241	220	21	2.0×10^4

[a][BQ] = 1 x 10^{-6} M; all solutions in acetonitrile.

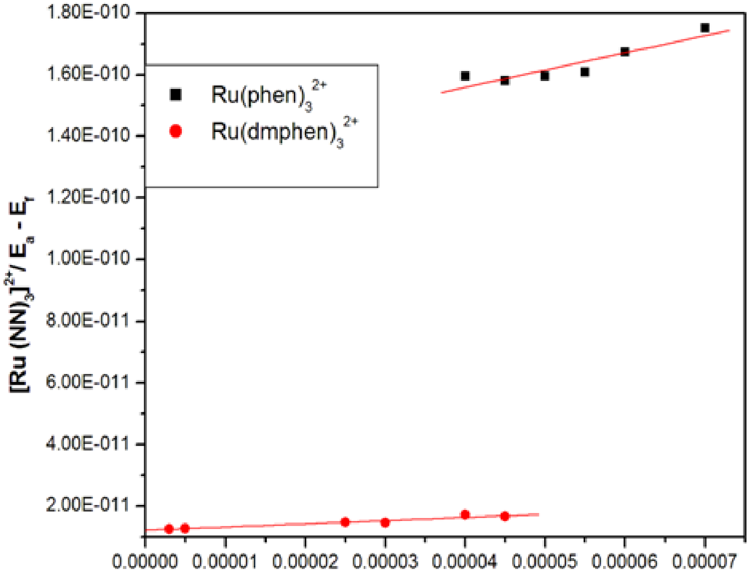

Fig. 7: Plot of $[Ru(NN)_3]^{2+}]$ / [ε_a-ε_f] vs $[Ru(NN)_3]^{2+}]$ for BQ with a) $[Ru(phen)_3]^{2+}$ b) $[Ru(dmphen)_3]^{2+}$

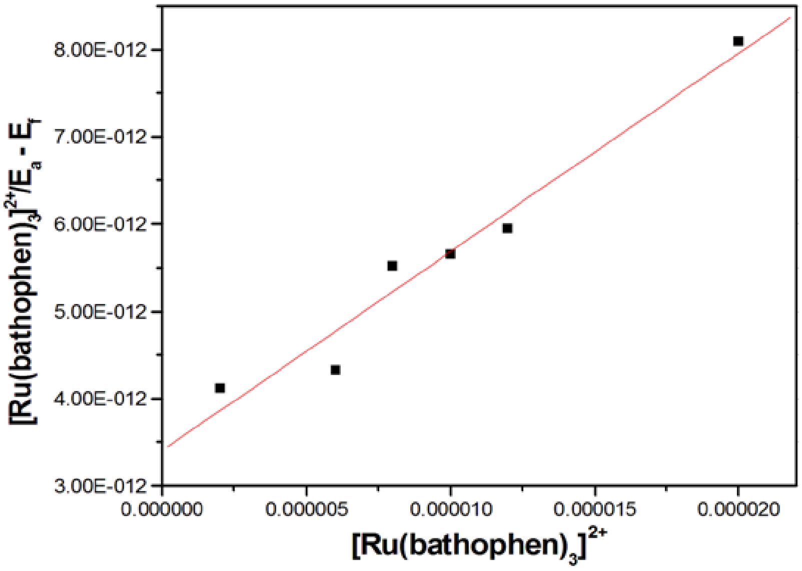

Fig. 8: Plot of $[Ru(NN)_3]^{2+}]$ / [ε_a-ε_f] vs $[Ru(NN)_3]^{2+}]$ for BQ with $[Ru(bathophen)_3]^{2+}$

Conclusion:-

In this chapter, a comprehensive study was carried out to investigate the electron transfer between BQ and Ruthenium II complexes in acetonitrile medium using UV/Vis spectrophotometer. The binding constant values obtained from absorption technique established that there is intermolecular electrostatic interaction between the BQ and Ruthenium II complexes. From the binding constant values, it can be inferred that the efficiency of binding is moderate and similar for all complexes in the range of 10^3–10^4 M^{-1}. But the interaction for Ruthenium bathophenanthroline is somewhat stronger than other two complexes, may be due to the bulky phenyl groups present.

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