Ruthenium chromophores containing terpyridine and a series of polyazine bridging ligands

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Abstract

A series of monometallic Ru(II) complexes have been synthesized with the general formula $[Ru(tpy)(BL)Cl]^+$ and $[Ru(tpy)(BL)(py)]^{2+}$ and their spectroscopic, electrochemical and photochemical properties studied (where tpy = 2,2′:6′,2″-terpyridine and BL = bridging ligand). The bridging ligands utilized in these complexes were 2,3-bis(2-pyridyl)pyrazine (dpp), 2,3-bis(2-pyridyl)quinoxaline (dpq) and 2,3-bis(2-pyridyl)benzoquinoxaline (dpb). The lowest energy absorption for all six complexes is assigned as a $Ru(d\pi) \rightarrow BL(\pi^*)$ transition. This metal-to-ligand charge transfer (MLCT) transition shifts to lower energy when BL is varied from dpp to dpq to dpb. Substitution of the chloride ligand with pyridine leads to a blue shift of this transition. $[Ru(tpy)(dpp)Cl]^+$ and all $[Ru(tpy)(BL)(py)]^{2+}$ complexes emit in fluid solution at room temperature, in marked contrast to $[Ru(tpy)_2]^{2+}$. These complexes are of interest as starting materials for the preparation of multimetallic systems capable of intramolecular electron transfer. Synthetic variation has been made possible by the presence of the coordinated halide, as demonstrated by the pyridine substitution.

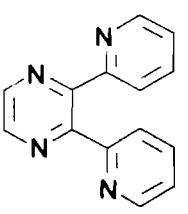
Key words: Electrochemistry; Photochemistry; Ruthenium complexes; Polydentate ligand complexes; Chromophore complexes

Introduction

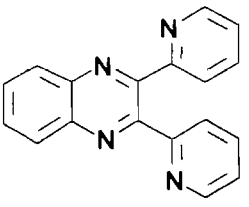
Since the recognition of the photoinduced properties of $[Ru(bpy)_3]^{2+}$ much work has concentrated on studying the properties of related Ru(II) polypyridyl complexes and their use as light absorbers in solar energy conversion schemes (bpy = 2,2′-bipyridine) [1]. In the presence of an added electron donor or acceptor, the metal-to-ligand charge transfer (MLCT) excited state can be quenched leading to either a reduced or oxidized complex. Tuning of the properties of $[Ru(bpy)_3]^{2+}$ has been accomplished through the variation of the ligands attached [1–3]. Recent work has concentrated on the incorporation of polyazine bridging ligands [2, 3]. This work is aimed at covalent attachment of other metals to construct supramolecular complexes.

The application of terpyridine complexes to photochemical schemes has been limited due to the short excited-state lifetime of $[Ru(tpy)_2]^{2+}$, less than 1 ns [4]. However, the ability of tpy to occupy three coordination sites makes it useful in the development of stereochemically controlled complexes, eliminating the Λ and Δ isomers possible in the tris-chelated systems.

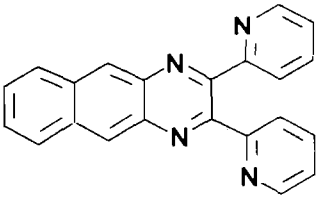
In this study we have synthesized a series of ruthenium complexes containing the tridentate ligand tpy, $[Ru(tpy)(BL)Cl]^+$. The attached bidentate bridging ligand was varied from dpp to dpq to dpb (dpp = 2,3-bis(2-pyridyl)pyrazine, dpq = 2,3-bis(2-pyridyl)quinoxaline and dpb = 2,3-bis(2-pyridyl)benzoquinoxaline).



dpp



dpq



dpb

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These complexes possess a vacant coordination site on the bridging ligands as well as an easily substituted chloride ligand on the ruthenium metal center. Substitution of this chloride by pyridine has been accomplished to yield complexes of the type $[Ru(tpy)(BL)(py)]^{2+}$ (py = pyridine). These systems are of interest as building blocks for supramolecular complexes. In this study we will clearly demonstrate that the presence of a coordinated terpyridine in a ruthenium polypyridine complex does not dictate a short excited state lifetime.

Experimental

Materials

The materials were reagent grade and used without further purification. Ruthenium trichloride was received from the Johnson Matthey precious metal loan program. The UV grade acetonitrile and dimethylformamide solvents (Burdick and Jackson) used in the spectroscopic and electrochemical studies were dried over activated molecular sieves. The supporting electrolyte (tetrabutylammonium hexafluorophosphate) used for electrochemical measurements was prepared by a metathesis reaction of tetrabutylammonium bromide with potassium hexafluorophosphate. Purification was achieved through repeated recrystallization from ethanol. This was dried in a vacuum oven and stored in a dessicator prior to use.

Syntheses

The ligands 2,3-bis(2-pyridyl)pyrazine (dpp) and 2,2′:6′,2″-terpyridine (tpy) were purchased from Aldrich Chemical Company. 2,3-Bis(2-pyridyl)quinoxaline (dpq) [5a] was synthesized according to the published method of Goodwin and Lions reacting *o*-phenylenediamine and 2,2′-pyridyl in ethanol. Similarly, 2,3-bis(2-pyridyl)benzoquinoxaline (dpb) [5a–c] was synthesized substituting 2,3-diaminonaphthalene for *o*-phenylenediamine. The ligands dpq and dpb were purified through repeated recrystallization from hot ethanol. Trichloro(2,2′:6′,2″-terpyridine)ruthenium(III) [6] was prepared according to literature methods.

(2,3-Bis(2-pyridyl)pyrazine)chloro(2,2′:6′,2″-terpyridine)ruthenium(II) hexafluorophosphate

$[Ru(tpy)(dpp)Cl](PF_6)$ was prepared by adding solid $Ru(tpy)Cl_3$ (0.824 g, 1.87 mmol) to a solution of the ligand dpp (0.599 g, 2.56 mmol) in 100 ml of 2:1 ethanol/deionized water mixture with 8 ml of triethylamine as a reducing agent. The solution was heated near reflux for *c.* 5 h under argon. The complex was precipitated by the addition of saturated, aqueous KPF_6 (20 ml) and separated by vacuum filtration. Purification was achieved by column chromatography on adsorption alumina in 3:2 (vol./vol.) toluene/acetonitrile. The red product was the first one to elute. This band was collected, concentrated by rotary evaporation, and precipitated by addition to diethyl ether (100 ml). The precipitate was separated by vacuum filtration and dried under vacuum. A typical yield was 79%.

(2,3-Bis(2-pyridyl)quinoxaline)chloro(2,2′:6′,2″-terpyridine)ruthenium(II) hexafluorophosphate

$[Ru(tpy)(dpq)Cl](PF_6)$ was synthesized as described above for $[Ru(tpy)(dpp)Cl]^+$ substituting the ligand dpq (0.820 g, 1.86 mmol) for the ligand dpp. Purification was as described above. The product was the first to elute and was purple. A typical yield was 65%.

(2,3-Bis(2-pyridyl)benzoquinoxaline)chloro(2,2′:6′,2″-terpyridine)ruthenium(II) hexafluorophosphate

$[Ru(tpy)(dpb)Cl](PF_6)$ was prepared as above for $[Ru(tpy)(dpp)Cl](PF_6)$ substituting the ligand dpb (0.863 g, 2.58 mmol) for the ligand dpp. A 2:1 toluene/acetonitrile eluent was used and the product band was blue. A typical yield was 63%.

(2,3-Bis(2-pyridyl)pyrazine)pyridine(2,2′:6′,2″-terpyridine)ruthenium(II) hexafluorophosphate

$[Ru(tpy)(dpp)(py)](PF_6)_2$ was prepared by adding 1 ml of pyridine to a stirring solution of $[Ru(tpy)(dpp)Cl](PF_6)$ (0.117 g, 0.156 mmol) in 20 ml of 1:1 ethanol/distilled water. This mixture was heated at reflux under argon for *c.* 20 h. The complex was precipitated by the addition of a saturated, aqueous KPF_6 solution (20 ml) and separated by vacuum filtration. Purification was performed as described for the chloride substituted complexes. The desired product was the orange band which eluted second, after unreacted starting material. A typical yield was 85%.

(2,3-Bis(2-pyridyl)quinoxaline)pyridine(2,2′:6′,2″-terpyridine)ruthenium(II) hexafluorophosphate

$[Ru(tpy)(dpq)(py)](PF_6)_2$ was prepared as described above substituting $[Ru(tpy)(dpq)Cl](PF_6)$ (0.113 g, 0.142 mmol) for the analogous dpp complex. The desired product eluted second and was red in color. A typical yield was 82%.

(2,3-Bis(2-pyridyl)benzoquinoxaline)pyridine(2,2′:6′,2″-terpyridine)ruthenium(II) hexafluorophosphate

$[Ru(tpy)(dpb)(py)](PF_6)_2$ was prepared as described above substituting $[Ru(tpy)(dpb)Cl](PF_6)$ (0.127 g, 0.150 mmol) for the analogous dpp complex. The desired product eluted second as a purple band. A typical yield was 81%.

Electrochemistry

Cyclic voltammograms were performed on a Bio-Analytical Systems 100B electrochemical analyzer. The three electrode system utilized in this study consisted of a platinum working electrode, a platinum wire auxiliary electrode and a silver/silver chloride reference electrode (0.286 V versus SHE). The platinum electrode was cleaned prior to each scan. The solvent used was a high purity acetonitrile or dimethylformamide dried over activated molecular sieves. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. Prior to each scan, the solutions were deoxygenated by bubbling with argon for 20 min and blanketed with argon during each scan.

Spectroscopy

Absorption spectra were recorded in acetonitrile solutions at room temperature on a Hewlett Packard 8452A diode array spectrophotometer (resolution 2 nm).

Emission spectra were recorded at room temperature in deoxygenated acetonitrile solution and obtained on a PTI alpha scan fluorimeter modified to detect red shifted emissions utilizing a thermoelectrically cooled Hamamatsu R666S photomultiplier tube.

The configuration for excited-state lifetime measurements has been reported in detail elsewhere [8]. Deoxygenated solutions were prepared employing the freeze–pump–thaw degassing method, repeating the process five times. The glass tubes were then sealed under vacuum. Upon returning to room temperature, the samples were ready for lifetime measurements.

Results and discussion

Electrochemistry

The ligands used in this study have been characterized previously [5, 7]. All the bridging ligands are easier to reduce than tpy. In addition, the ligands become easier to reduce within the series dpp, dpq, dpb. This is a result of the addition of the fused phenyl ring giving rise to a stabilization of the π^* lowest-occupied molecular orbital (LUMO). The electrochemical data for all six ruthenium complexes are summarized in Table 1. These systems display one reversible metal based oxidative and two reversible ligand localized reductive couples. Each complex has a reversible oxidation corresponding to an Ru(II)/Ru(III) couple that occurs at a similar potential in the three complexes within each series. The first reductive process varies as a function of the bridging ligand shifting to more positive potential on going from dpp to dpq to dpb supporting its assignment as being BL based. The magnitude of this shift is essentially independent of the formulation of the complex, i.e., Cl^- or py in the sixth coordination site. The change from dpp to dpq results in a 300 mV shift for the Cl^- series and 290 mV for the py series. The substitution of dpb for dpq gives a 160 mV shift for both the Cl^- and py system.

TABLE 1. Cyclic voltammetric data for a series of Ru(II) complexes of the general formula $[Ru(tpy)(BL)Cl]^+$ and $[Ru(tpy)(BL)(py)]^{2+}$ where BL = dpp (2,3-bis(2-pyridyl)pyrazine), dpq (2,3-bis(2-pyridyl)quinoxaline) and dpb (2,3-bis(2-pyridyl)benzoquinoxaline), and tpy = 2,2′:6′,2″-terpyridine

Complex	$E_{1/2}$[a] (V)	Assignment
$[Ru(tpy)(dpp)Cl]^+$	+1.04	Ru^{II}/Ru^{III}
	−1.07	dpp/dpp^-
	−1.27	tpy/tpy^-
$[Ru(tpy)(dpq)Cl]^+$	+1.06	Ru^{II}/Ru^{III}
	−0.77	dpq/dpq^-
	−1.27	tpy/tpy^-
$[Ru(tpy)(dpb)Cl]^+$	+1.02	Ru^{II}/Ru^{III}
	−0.61	dpb/dpb^-
	−1.25	tpy/tpy^-
$[Ru(tpy)(dpp)(py)]^{2+}$	+1.42	Ru^{II}/Ru^{III}
	−1.04	dpp/dpp^-
	−1.35	tpy/tpy^-
$[Ru(tpy)(dpq)(py)]^{2+}$	+1.41	Ru^{II}/Ru^{III}
	−0.75	dpq/dpq^-
	−1.34	tpy/tpy^-
$[Ru(tpy)(dpb)(py)]^{2+}$	+1.44	Ru^{II}/Ru^{III}
	−0.59	dpb/dpb^-
	−1.34	tpy/tpy^-

[a]Potentials reported in CH_3CN solution with 0.1 M TBAH and reported vs. Ag/AgCl (0.286 V vs. SHE).

The second reductive process occurs at a relatively constant potential within each series. This supports the assignment of the second reduction as being tpy based. It is interesting to note that this tpy based reduction shifts to more negative potential upon substitution of pyridine for the chloride within this framework while the BL based reductions shift to more positive potential. The difference in the response of these two ligands to substitution of the Cl^- by pyridine could be a result of the stereochemistry of the system. Namely, the BL is *trans* to the ligand being substituted while the tpy is *cis* to the site of substitution. Similar stereochemical effects on redox potentials of polyazine ligands have been observed in the past [8].

Substitution of the chloride ligand with pyridine to produce complexes of the type $[Ru(tpy)(BL)(py)]^{2+}$ results in complexes that are harder to oxidize by *c.* 400 mV consistent with the decreased σ donating and increased π accepting ability of the pyridine ligand. In all of these systems the highest-occupied molecular orbital (HOMO) is a ruthenium based $d\pi$ orbital and the lowest-unoccupied molecular orbital (LUMO) is a bridging ligand based π^* orbital.

Absorption spectroscopy

The ligands used in this study have been characterized previously [5, 7]. These spectra consist of high energy n–π^* and π–π^* intraligand transitions. These transitions shift to lower energy on going from dpp to dpq to dpb. Figure 1 summarizes the electronic absorption data for this new series of complexes. The spectra consist of ligand localized n–π^* and π–π^* transitions in the UV and a series of metal to ligand charge transfer (MLCT) transitions in the visible. The relative energy of the lowest lying excited states in both of these series is dominated by the shift in the bridging ligand based π^* LUMO [3, 5, 7]. The addition of the fused benzene ring to the bridging ligand extends the aromatic system and stabilizes the π^* orbital thus shifting the transition to lower energy as dpq and dpb are substituted for dpp. Substitution of the chloride with pyridine results in a stabilization of the Ru(dπ) orbitals, leading to a blue shift of the Ru→BL MLCT.

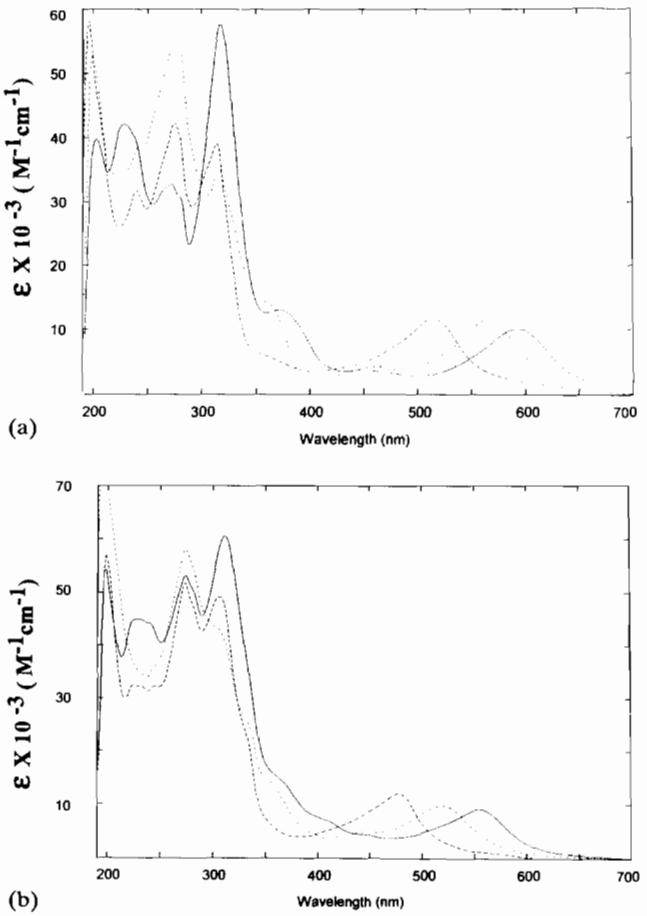

Fig. 1. Electronic absorption spectra in acetonitrile for a series of ruthenium terpyridine complexes : (a) $[Ru(tpy)(BL)Cl]^+$ – – – dpp, – · – dpq, —— dpb; (b) $[Ru(tpy)(BL)(py)]^{2+}$ – – – dpp, – · – dpq, —— dpb (where BL = dpp (2,3-bis(2-pyridyl)pyrazine), dpq (2,3-bis(2-pyridyl)quinoxaline) and dpb (2,3-bis(2-pyridyl)benzoquinoxaline), and tpy = 2,2′:6′,2″-terpyridine).

Emission spectroscopy and excited state lifetimes

$[Ru(tpy)(dpp)Cl]^+$ and all $[Ru(tpy)(BL)(py)]^{2+}$ systems emit in fluid solution at room temperature. The dpq and dpb based chloride systems may display red shifted emissions beyond the detection limit of our system. The emission of our complexes is in marked contrast to $[Ru(tpy)_2]^{2+}$ which has an excited state lifetime of less than 1 ns and does not display an emission under our conditions [4]. The short lifetime of $[Ru(tpy)_2]^{2+}$ at room temperature has been attributed to a thermally accessible ruthenium based ligand field excited state that decays rapidly [4c]. The presence of more stabilized π^* orbitals on our bridging ligands gives rise to a lowering of the energy of the MLCT state preventing thermal population of the ligand field state. The Ru(dπ)→BL(π^*) MLCT excited state emissions occur at 760 nm (20 ns) for $[Ru(tpy)(dpp)Cl]^+$, 700 nm (80 ns) for $[Ru(tpy)(dpp)(py)]^{2+}$, 800 nm (28 ns) for $[Ru(tpy)(dpq)(py)]^{2+}$ and 860 nm (<20 ns) for $[Ru(tpy)(dpb)(py)]^{2+}$ (lifetimes given in parentheses).

Correlation of spectroscopic and electrochemical results

A correlation can be drawn between the spectroscopic and electrochemical energy gap within similar complexes if the same orbitals are involved in both of these processes [1, 9]. A plot of the energy of the lowest lying spectroscopic transition (E_{abs} in eV) versus the difference in redox potentials between the first oxidation and the first reduction, $\Delta E_{1/2} = E_{1/2}(Ru^{II}/Ru^{III}) - E_{1/2}(BL/BL^-)$, for the six ruthenium complexes gave a linear correlation. A linear least-squares analysis of this plot yielded:

$$E_{abs} = 1.08 + 0.609\ \Delta E_{1/2}$$

with a correlation coefficient of 0.974. This linear relationship supports our assignment of the lowest energy absorption in the six ruthenium complexes as MLCT in nature involving BL based acceptor orbitals.

Conclusions

In this study a series of complexes of the type $[Ru(tpy)(BL)Cl]^+$ and $[Ru(tpy)(BL)(py)]^{2+}$ were synthesized and investigated using electrochemistry, emission spectroscopy, excited state lifetime measurements and electronic absorption spectroscopy. It was found that $[Ru(tpy)(dpp)Cl]^+$, $[Ru(tpy)(dpp)(py)]^{2+}$, $[Ru(tpy)(dpq)(py)]^{2+}$ and $[Ru(tpy)(dpb)(py)]^{2+}$ all emit in fluid solution at room temperature. These complexes clearly show that ruthenium terpyridine systems can be designed which have reasonable excited state lifetimes. These complexes are useful in that tpy is a tridentate ligand therefore eliminating Λ and Δ stereoisomers. This will control the stereochemistry in

multimetallic systems incorporating these new light absorbers. It has been illustrated that the chloride ligand provides a site for synthetic modification within this framework. This establishes that the covalent attachment of electron donors or acceptors is possible. These substituted complexes can then be used in the synthesis of multimetallic systems capable of intramolecular electron transfer. Recently the incorporation of pyridylphenathiazine into this framework has been accomplished [10]. Work is in progress to use these chromophores and related systems in the construction of a variety of supramolecular complexes [10, 11].

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