

## Polyaza Cavity-shaped Molecules.

## VIII. Ruthenium(II) Complexes with 3,3'-Annulated Derivatives of 2-(2'-Pyridyl)-quinoline and 2-(2'-Pyridyl)-1,8-naphthyridine

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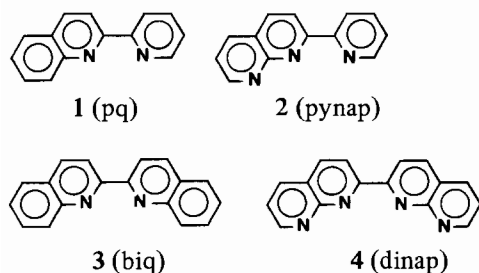
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## Abstract

Mixed ligand complexes of the type  $\text{Ru}(\text{bpy})_2\text{L}^{2+}$  have been prepared where L is a 3,3'-polymethylene bridged derivative of 2-(2'-pyridyl)-quinoline or 2-(2'-pyridyl)-1,8-naphthyridine. In the electronic absorption spectra for these species the long wavelength band associated with the MLCT state shows two components whose separation increases with increasing delocalizing ability of the ligand L. This same interpretation may be invoked to explain a shift of the first reduction wave to more positive potential. Both of these features do not vary appreciably as a function of the polymethylene bridge length.

A great deal of recent attention has been focussed on the properties of the  $\text{Ru}(\text{bpy})_3^{2+}$  cation. The role which this complex plays in photosensitized electron transfer processes has made it a prime target for a wide range of photophysical and electrochemical studies [1]. Modifications of the bipyridine ligands have been investigated with the intent of modifying and hopefully optimizing the efficiency with which the complex functions as a photocatalyst.

The annulation of a benzo- or a pyrido-ring in the 5,6-position of one or both of the pyridine rings of 2,2'-bipyridine would lead to the ligands 1 to 4.



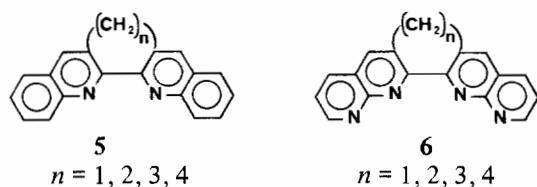
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The additional annulated aromatic rings would be expected to assist in the delocalization of charge with the more electronegative pyridine ring being more effective than a benzo ring in this respect. Thus delocalization should increase along the series 1 to 4. Examination of the ultraviolet absorption spectra of this series of molecules bears out this premise in that the absorption maximum of the long wavelength band shifts to lower energy in a regular fashion as one progresses from 1 to 4.

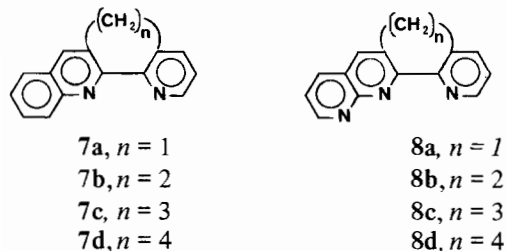
Seddon and coworkers have shown that for the mixed ligand ruthenium complex  $\text{Ru}(\text{bpy})_2(\text{pq})^{2+}$ , the electronic absorption spectrum shows two independent charge transfer transitions [2]. These bands are poorly resolved, centering around 450 nm and their intensities approximate a weighted superimposition of the absorption maxima for the  $\text{Ru}(\text{bpy})_3^{2+}$  and the  $\text{Ru}(\text{pq})_3^{2+}$  complexes. Similar behavior has been observed by Belser and von Zelewsky for the complex  $\text{Ru}(\text{bpy})_2(\text{biq})^{2+}$  where much better resolution of the two visible absorption bands is obtained [3]. A long wavelength band at about 535 nm is attributable to the metal-to-ligand charge transfer (MLCT) state involving the 2,2'-biquinoline ligand while the band at approximately 440 nm is associated with the MLCT state involving the two bipyridines. Interestingly, the intensity of the 535 band is greater than that of the 440 band and thus represents more than a proportional contribution of the biquinoline ligand in metal-to-ligand charge transfer. A third, less well resolved, example of this same type of behavior was observed by Rillema and coworkers for the complex  $(\text{Ru}(\text{bpy})_2(\text{bpyrz}))^{2+}$  where bpyrz represents 2,2'-bipyrazine [4].

We have recently synthesized a series of 3,3'-annulated derivatives of 2,2'-biquinoline (5) [5] and 2,2'-bi-1,8-naphthyridine (6) [6]. A variety of ruthenium complexes of the type  $\text{RuL}_3^{2+}$  and  $\text{Ru}(\text{bpy})_2\text{L}^{2+}$  were also prepared [7].

The mixed ligand complexes exhibit similar behavior to what was reported by earlier workers for the non-bridged systems. To complete this series of mixed ligand ruthenium complexes of



annelated derivatives of the series 1 to 4, we prepared the ligands 7 and 8 [8] and in this paper report the preparation and properties of their  $\text{Ru}(\text{bpy})_2\text{L}^{2+}$  complexes.



The tris-complexes of 2-(2'-pyridyl)-quinoline (1) [9] and 2-(2'-pyridyl)-1,8-naphthyridine (2) [10] with ruthenium have been previously reported. In both instances the authors ignore the stereochemical consequences of octahedral tris-coordination of unsymmetrical ligands such as 1 or 2. In the case of a symmetrical ligand having a C-2 axis such as 2,2'-bipyridine, octahedral coordination can lead to a pair of enantiomers. For the unsymmetrical ligand

1, two geometric isomers (A and B) are possible each of which can give rise to a pair of enantiomers. This situation is illustrated in Fig. 1 where P represents the coordinated pyridine ring of 1 and Q represents the coordinated quinoline ring. The purified chemical yield was 87% for  $\text{Ru}(\mathbf{1})_3(\text{PF}_6)_2$  and 88% for  $\text{Ru}(\mathbf{2})_3(\text{PF}_6)_2$ . If one assumes that these materials represent a pure stereoisomer A or B, it appears that formation of one isomer A or B is preferred. No definitive evidence was presented in either case regarding the structure of these tris complexes. We discovered that the bridged ligands 7 and 8 also formed tris complexes but due to the difficulties associated with assigning stereochemistry, we limited our study to complexes of the type  $\text{Ru}(\text{bpy})_2\text{L}^{2+}$  where no ambiguity exists.

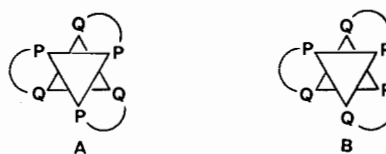


Fig. 1. Geometric isomers of 1.

The mixed ligand complexes (I–VIII) were formed by the reaction of the appropriate ligand with *cis*-(bpy)<sub>2</sub>RuCl<sub>2</sub>·2H<sub>2</sub>O (see Table III) later and were characterized by the appearance of a predominant parent ion in the thermospray interfaced mass spectrum. Detailed interpretation of the NMR spectra was complicated by the fact that all the aromatic

TABLE I. Ultraviolet Absorption Data for  $\text{Ru}(\text{bpy})_2\text{L}^{2+}$  Complexes ( $\text{CH}_3\text{CN}$ )

Complex	$\lambda_{\text{max}}$ (log $\epsilon$ ) (nm)
<b>I</b> $\text{Ru}(\text{bpy})_2(\mathbf{7a})^{2+}$	242(4.50)
	285(4.81)
	339(4.18)
<b>II</b> $\text{Ru}(\text{bpy})_2(\mathbf{7b})^{2+}$	345(4.14)
	356(4.23)
	445(4.07)
<b>III</b> $\text{Ru}(\text{bpy})_2(\mathbf{7c})^{2+}$	243(4.57)
	286(4.82)
	372(4.07)
<b>IV</b> $\text{Ru}(\text{bpy})_2(\mathbf{7d})^{2+}$	448(4.02)
	246(4.51)
	287(4.76)
<b>V</b> $\text{Ru}(\text{bpy})_2(\mathbf{8a})^{2+}$	250(4.49)
	287(4.79)
	328(sh, 4.30)
<b>VI</b> $\text{Ru}(\text{bpy})_2(\mathbf{8b})^{2+}$	240(4.50)
	284(4.79)
	324(sh, 4.30)
<b>VII</b> $\text{Ru}(\text{bpy})_2(\mathbf{8c})^{2+}$	334(4.28)
	341(4.27)
	351(4.26)
<b>VIII</b> $\text{Ru}(\text{bpy})_2(\mathbf{8d})^{2+}$	240(4.42)
	287(4.69)
	316(sh, 4.29)
<b>I</b> $\text{Ru}(\text{bpy})_2(\mathbf{7a})^{2+}$	339(4.18)
	345(4.14)
	356(4.23)
<b>II</b> $\text{Ru}(\text{bpy})_2(\mathbf{7b})^{2+}$	445(4.07)
	480(sh, 4.04)
	448(4.02)
<b>III</b> $\text{Ru}(\text{bpy})_2(\mathbf{7c})^{2+}$	480(sh, 3.91)
	246(4.51)
	287(4.76)
<b>IV</b> $\text{Ru}(\text{bpy})_2(\mathbf{7d})^{2+}$	250(4.49)
	287(4.79)
	328(sh, 4.30)
<b>V</b> $\text{Ru}(\text{bpy})_2(\mathbf{8a})^{2+}$	324(sh, 4.30)
	334(4.28)
	341(4.27)
<b>VI</b> $\text{Ru}(\text{bpy})_2(\mathbf{8b})^{2+}$	351(4.26)
	240(4.42)
	287(4.69)
<b>VII</b> $\text{Ru}(\text{bpy})_2(\mathbf{8c})^{2+}$	316(sh, 4.29)
	354(sh, 4.10)
	372(sh, 4.00)
<b>VIII</b> $\text{Ru}(\text{bpy})_2(\mathbf{8d})^{2+}$	330(sh, 4.32)
	230(4.54)
	285(4.77)
<b>I</b> $\text{Ru}(\text{bpy})_2(\mathbf{7a})^{2+}$	412(sh, 3.73)
	445(3.96)
	504(3.86)
<b>II</b> $\text{Ru}(\text{bpy})_2(\mathbf{7b})^{2+}$	418(sh, 3.74)
	448(3.92)
	505(3.78)

<sup>a</sup>This band appears as a poorly defined series of shoulders at 310–370 m $\mu$ .

protons were magnetically non-equivalent so that one expects 24 signals for I–IV and 23 for V–VIII. Integration of the aromatic protons *versus* the aliphatic bridge protons, however, bore out the 2:1 ratio of bipyridine to ligand 7 or 8.

### Properties

The ultraviolet absorption data for the ruthenium complexes I–VIII is given in Table I. Each complex shows bands in three regions. The shortest wavelength band consists of two components centered at 240 and 280 nm. The medium wavelength band is generally centered around 340–370 nm. The positions and intensities of these two bands correlate well with the two principal bands observed for the free ligands. The shorter wavelength absorption may be attributed to the pyridyl moiety while the medium wavelength band would be associated with the quinoline or 1,8-naphthyridine fragment. Varying the length of the annelating bridge does not greatly affect the position or intensity of the absorption although the monomethylene bridged systems, being rigid and planar, show greater resolution of vibrational fine structure.

The long wavelength band is associated with the MLCT state and shows two principal components in most cases. A band at 438–452 nm accounts for energy transfer into the bipyridine ligands and it is uniformly present in all the mixed ligand complexes. The second component appears at longer wavelength and is associated with the MLCT state centered on the ligands 7 and 8. In the case of 7, which may be considered as a benzo-fused 2,2'-bipyridine, this second band is red-shifted only about 30 nm so that it appears as a shoulder on the bipyridine component. For 8, which is a 2-pyridyl-fused 2,2'-bipyridine, the red shift is more pronounced and for VI–VIII a

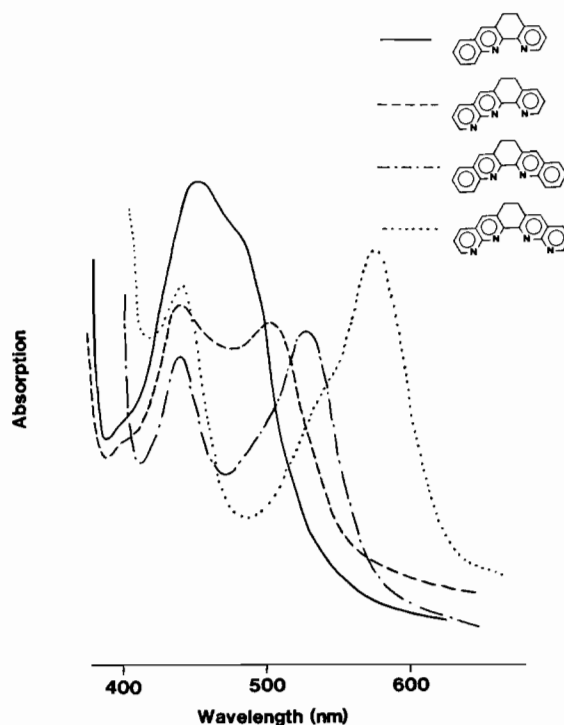


Fig. 2. Electronic absorption spectra ( $\text{CH}_3\text{CN}$ ) of  $\text{Ru}(\text{bpy})_2\text{L}^{2+}$  complexes ( $\text{L}$  = dimethylene bridged derivatives of 5–8).

clearly resolved peak at about 505 nm is observed. As we have reported earlier, the annelation of a second aromatic ring onto the other half of the bipyridine nucleus to form the ligands biq (3) and binap (4) causes even greater shifts to lower energy with the effect being most pronounced for mixed ligand complexes of 4 [7]. Figure 2 shows a comparison of the absorption spectra of  $\text{Ru}(\text{bpy})_2\text{L}^{2+}$  complexes where  $\text{L}$  is the dimethylene bridged analog of ligands 1 to 4. The increasing separation of the

TABLE II. Polarographic Half-wave Potentials for Ruthenium(II) Complexes<sup>a,b</sup>

Complex	$E_{1/2}$ , oxidation	$E_{1/2}$ , reduction			
	$\text{Ru}^{2+}/\text{Ru}^{3+}$	$\text{Ru}^{2+}/\text{Ru}^{1+}$	$\text{Ru}^{1+}/\text{Ru}^0$	$\text{Ru}^0/\text{Ru}^{1-}$	$\text{Ru}^{1-}/\text{Ru}^{2-}$
$\text{Ru}(\text{bpy})_3^{2+}$	+1.26	-1.35	-1.53	-1.78 <sup>c</sup>	
I $\text{Ru}(\text{bpy})_2(7\text{a})^{2+}$	+1.33	-1.13	-1.46	-1.71 <sup>d</sup>	-2.15 <sup>e</sup>
II $\text{Ru}(\text{bpy})_2(7\text{b})^{2+}$	+1.31	-1.11	-1.48	-1.72 <sup>d</sup>	-2.19 <sup>e</sup>
III $\text{Ru}(\text{bpy})_2(7\text{c})^{2+}$	+1.30	-1.14	-1.49	-1.72	-2.21 <sup>f</sup>
IV $\text{Ru}(\text{bpy})_2(7\text{d})^{2+}$	+1.29	-1.17	-1.49	-1.73	-2.23 <sup>f</sup>
V $\text{Ru}(\text{bpy})_2(8\text{a})^{2+}$	+1.27	-1.02	-1.51	-1.79 <sup>d</sup>	-2.06 <sup>d</sup>
VI $\text{Ru}(\text{bpy})_2(8\text{b})^{2+}$	+1.22	-0.99	-1.48	-1.76	
VII $\text{Ru}(\text{bpy})_2(8\text{c})^{2+}$	+1.22	-1.01	-1.50	-1.74 <sup>d</sup>	-2.06 <sup>e</sup>
VIII $\text{Ru}(\text{bpy})_2(8\text{d})^{2+}$	+1.22	-1.02	-1.48	-1.81	-2.06 <sup>g</sup>

<sup>a</sup>Potentials are in volts vs. SSCE.

<sup>b</sup>Solutions were 0.1 M in TBAP; the solvent was acetonitrile;  $T = 25 \pm 1^\circ\text{C}$ . <sup>c</sup>Reference 3.

<sup>d</sup>Quasireversible. <sup>e</sup>Reversible at fast scan rates. <sup>f</sup>One electron wave only at fast scan rates. <sup>g</sup>Irreversible.

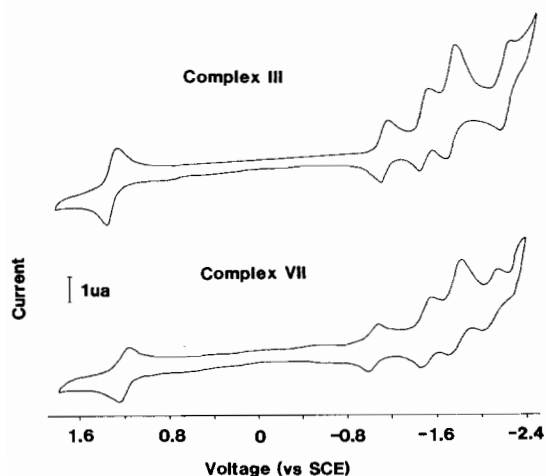


Fig. 3. Cyclic voltammograms of  $\text{Ru}(\text{bpy})_2\text{L}^{2+}$  complexes **III** and **VII**.

two MLCT states is readily apparent. It is interesting that the intensity of the lower energy state relative to the bpy centered MLCT state increases as one proceeds along the series **1** to **4**. In no case do we observe a proportionate 2:1 weighted average of the absorptions.

Table II summarizes the redox properties of the series of complexes **I–VIII**. Typical cyclic voltammograms for complexes **III** and **VII** are illustrated in Fig. 3. For all the complexes except **VI**, a fourth reduction wave is observed but is never clearly reversible. Previous workers have observed a  $\text{Ru}(-2)$  state and commented that this state was relatively unstable and readily observed only at fast potential scanning rates [11].

In comparing the potentials for **I–VIII** with those of  $\text{Ru}(\text{bpy})_3^{2+}$ , variations of 0.05 volts or less are observed for the oxidation wave and the second and third reduction waves. The first reduction wave, however, occurs at 0.18–0.35 volts more positive

potential indicating that the LUMOs for these systems are lower in energy. The effect is greater for the ligands containing a 1,8-naphthyridyl fragment than for those containing a quinoline ring. As with the shifts observed in the absorption spectra, these changes in the first reduction potential are consistent with the delocalizing ability of the ligand.

There does not appear to be any significant relationship between the redox potentials and the length of the 3,3'-annelating bridge. One interpretation of this observation would be to say that octahedral coordination of these annelated ligands with ruthenium(II) causes all of them to become planar such that electronic effects influencing the energies of the HOMO and LUMO for the members of each series ( $n = 1$  to 4) are essentially identical. Preliminary structural analysis of a related  $\text{Ru}(\text{bpy})_2\text{L}^{2+}$  complex indicates that for a tetramethylene bridged 2,2'-bipyridine, coordination with ruthenium does not necessitate coplanarity of the bridged bipyridine moiety. Where the uncomplexed tetramethylene-bridged ligand has an estimated dihedral angle of  $80^\circ$ , coordination flattens it to about  $30^\circ$ . Assuming the same approximate conformation for **7d** and **8d** in complexes **IV** and **VIII**, we may deduce that the delocalization of charge in these complexes is not dramatically influenced by modest distortion of the octahedral coordination. Further experiments are in progress to provide a better understanding of the relationship of coordination geometry to the properties of these systems.

## Experimental

The ligands were all prepared according to previously published procedures [6, 8]. The *cis*-(bpy)<sub>2</sub>- $\text{RuCl}_2 \cdot 2\text{H}_2\text{O}$  was synthesized by the method of Meyer *et al.* [12]. Tetra-*n*-butylammonium perchlorate was recrystallized from ethyl acetate/hexane

TABLE III. Experimental Details on Preparation of  $\text{Ru}(\text{bpy})_2\text{L}$  Complexes

Ligand (mg)	$\text{Ru}(\text{bpy})_2\text{Cl}_2$ (mg)	Complex (mg)	Elemental analyses (%)					
			Observed			Calculated		
			C	H	N	C	H	N
<b>7a</b> 16	31.6	<b>I</b> 46.0 (82%)	45.07	3.11	8.76	45.61	2.84	9.12
<b>7b</b> 16.5	30.3	<b>II</b> 36.5 (67%)	45.14	3.11	8.75	46.21	3.02	8.98
<b>7c</b> 18.5	29.7	<b>III</b> 52.5 (97%)	46.78	3.24	9.24	46.80	3.18	8.85
<b>7d</b> 15.9	26.0	<b>IV</b> 38.5 (80%)	47.26	3.42	8.67	47.36	3.35	8.72
<b>8a</b> 15.7	30.4	<b>V</b> 37.3 (69%)	44.41	2.92	10.28	44.26	2.73	10.63
<b>8b</b> 15.7	30.1	<b>VI</b> 39.4 (73%)	44.78	3.01	10.57	44.88	2.91	10.47
<b>8c</b> 17.3	30.3	<b>VII</b> 41.1 (74%)	45.22	3.18	10.10	45.48	3.07	10.31
<b>8d</b> 18.7	31.0	<b>VIII</b> 38.5 (66%)	45.30	3.30	9.99	46.07	3.24	10.16

and acetonitrile was distilled twice from  $P_2O_5$ . All other materials were analytical reagent grade. Elemental analyses were performed by Canadian Micro-analytical Service, Ltd., Vancouver, B.C.

The  $Ru(bpy)_2L$  complexes were prepared by the following general procedure: to a solution of 0.061 mmol of *cis*- $Ru(bpy)_2Cl_2$  in 10 ml of 1:1 ethanol-water was added 0.073 mmol of ligand and the mixture was refluxed 12–20 h. After cooling to room temperature, 40 mg of ammonium hexafluorophosphate was added. After stirring overnight, a solid precipitated which was collected by vacuum filtration and recrystallized from acetonitrile-toluene to afford the pure complex. Details regarding quantities and yields are given in Table III.

Electronic absorption spectra were obtained in acetonitrile on a Perkin-Elmer 330 Spectrophotometer. Cyclic voltammetric measurements were carried out on an IBM Instruments Model EC-225 Voltammetric Analyzer utilizing a three electrode system. The working electrode consisted of a 1 mm platinum disc connected to a 24 gauge copper wire and embedded flush at the tip of a 5 mm (o.d.) pyrex glass tube. A KCl saturated calomel electrode was used as a reference and separated from the bulk of the solution by a cracked glass bridge filled with 0.1 M TBAP in acetonitrile. The counter electrode consisted of a 20 gauge platinum wire inserted directly into the solution. Deaeration of all solutions was performed by passing high purity nitrogen through the solution for five minutes and maintaining a blanket of nitrogen over the solution while making measurements. A Hewlett-Packard X-Y Recorder was used to record the cyclic voltammograms.

Halfwave potentials ( $E_{1/2}$ ) were measured as the average of the anodic and cathodic peak potentials. Scan rates varied from 50–400 mV/s. Electrochemical reversibility was judged on the basis of the following criteria [13]:

(a) The separation of the anodic and cathodic peak potentials ( $\Delta E_p$ ) equals  $60/n$  mV where  $n$  is the number of electrons involved in the redox process.

(b) The ratio of the anodic and cathodic peak currents is unity.

### Acknowledgements

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