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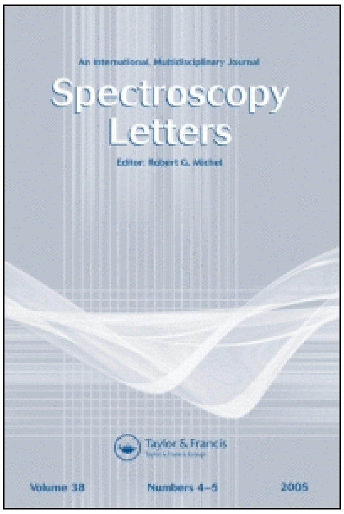

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A Study on the Spectra Characterization of Ruthenium(Ii) Complexes

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A STUDY ON THE SPECTRA CHARACTERIZATION OF RUTHENIUM(II) COMPLEXES

Key words: ruthenium(II) complexes, NMR spectroscopy, Ruthenium(II) complex
Coordination Electronic spectra

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ABSTRACT

A series of Ru(II) complexes have been synthesized, and their electronic spectra and NMR spectroscopy properties were characterized. The chemical shifts of aromatic protons of $[Ru(bpy)_3](PF_6)_2$, $[Ru(phen)_3](ClO_4)_2$ and $[Ru(bqdi)_3](PF_6)$ move downfield, but the resonance peaks of cis-$Ru(bpy)_2Cl_2$ shift upfield. Within the visible spectra of the ruthenium(II) complexes appear a relatively high oscillator strength which is referred to as the $\pi(Ru)\rightarrow\pi^*$(ligands) transition.

INTRODUCTION

A number of recent studies on ruthenium complexes have focused on the synthesis, electrochemistry, electronic spectra, and nuclear magnetic resonance spectroscopy[1-3]. There has been considerable interest in the complexes $Ru(LL)_3^{2+}$ (LL=bpy, phen, bqdi, see **Scheme 1**) in recent year because of its unique combination of spectral,

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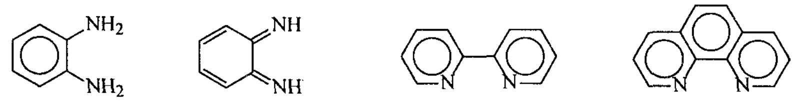
photochemical, and biochemical properties[4-8]. One of the goals of this research is the characterization of nuclear magnetic resonance spectroscopy, which can be very well



1,2-diaminobenzene (dabz) o-benzoquinone diimine (bqdi) 2,2'-bipyridine (bpy) 1,10-phenanthroline (phen)

Scheme 1

applied to the investigation of Ru(II) complexes. This is due to the change of electron density on the aromatic ring after coordinating between ligands and ruthenium. Visible spectroscpy is also useful in studying the electronic spectra because of the strong visible absorptions from metal to ligands charge transfer transition in rutherium complexes.

EXPERIMENTAL

Synthesis of substances

The $RuCl_3{\cdot}3H_2O$ was purchased from Johnsen Matthey Company; 2,2'-bipyridine(bpy) from Fisher Scientific Company; hexafluorophosphate from Aldrich Company; 1,10-phenanthroline(phen), and 1,2-diaminobenzene(dabz) from Shanghai Chemical Reagents Company. All were used without further purification.

Ruthenium Complexes $[Ru(bpy)_3](PF_6)_2$

A round flask equipped with a magnetic stirrer, a thermometer, a 0.383 mmol sample of $RuCl_3{\cdot}3H_2O$, and 1.160 mmol of bpy were dispersed into 15 mL of methanol, and heated under nitrogen for 8h at 100°C. During this time, three portions of 20 mg of zinc powder each, were added. After the solution had reached room temperature, the residual zinc powder was filtered. A solution containing 3 mg of hexafluorophosphate in 10 mL water was added, as soon as the small red-brown crystals were precipitated. The solution containing the solid was placed in an ice cold water bath overnight, and then filtered using Büchner funnel, washed with a cold mixture of water and acetone several times. The product obtained was recrystallized with 20 mL of methanol, and dried *in vacuo*. Yield: 71.4%

Cis-Ru(bpy)$_2$Cl$_2$·2H$_2$O

$RuCl_3 \cdot 3H_2O$(29.8mmol), bpy(60.0mmol), and LiCl(2.0 mmol) were refluxed for 6-8 h under nitrogen in 15 mL of dimethylformamide (DMF) at 150°C. During this time, the mixture was magnetically stirred. The solution was evaporated (reduced) to approximately one-third volume, and 50 mL of acetone was added. The resulting solution was then set aside for 12 h in an ice water bath. The product was precipitated as fine red-brown crystals, which were washed with a generous amount of ice-cold water/methanol three times, and dried *in vacuo*. The yield was 51%.

[Ru(phen)$_3$](ClO$_4$)$_2$

Procedures used were the same as those used for the preparation of $[Ru(bpy)_3](PF_6)_2$, except phen was substituted for bpy and $KClO_4$ was used as the precipitant. Deep green crystals were obtained, and yield was 63.4%.

[Ru(bqdi)$_3$](PF$_6$)$_2$

0.34mmol $RuCl_3 \cdot 3H_2O$ and 1.02 mmol 1,2-diaminobenzene in 15 mL of methanol were heated and refluxed under nitrogen, and the solution was vigorously stirred for 12 h. The solution was cooled slowly to room temperature and a small amount of concentrated aqueous ammonia was added and stirred for 48 h in an open beaker, the following procedure was similar to that of $[Ru(bpy)_3](PF_6)_2$, yield was 81%.

Physical Measurements

Eletronic Spectra were obtained on a 7530-G instrument. Nuclear magnetic resonance (NMR) Spectra were recorded on Varian FT-80A NMR spectrometer.

RESULTS AND DISCUSSION

^1H-NMR Spectra

Fig.1(a) shows the partial ^1H-NMR spectrum of bpy in CD_3-CN. In Figure 1(a) the lowest field peak δ8.52 ppm doublet can be assigned to the $H_{3,3'}$; the peak with a chemical shift at δ8.38 ppm double-doublet is referred to as $H_{6,6'}$; the double-triplet at δ7.78 ppm is due to $H_{5,5'}$; and the highest field δ7.27ppm corresponds to $H_{4,4'}$. The ^1H-NMR spectrum of $[Ru(bpy)_3](PF_6)_2$ is shown in Figure 1 (b), where CD_3-CN is used as the solvent. As compared with Figure 1(a), all of the chemical shifts of aromatic protons on bipyridine are shifted downfield, but the shifted values of the resonance peaks of the aromatic protons are different. The $H_{4,4'}$ display the largest shift (Δδ0.45ppm), with the

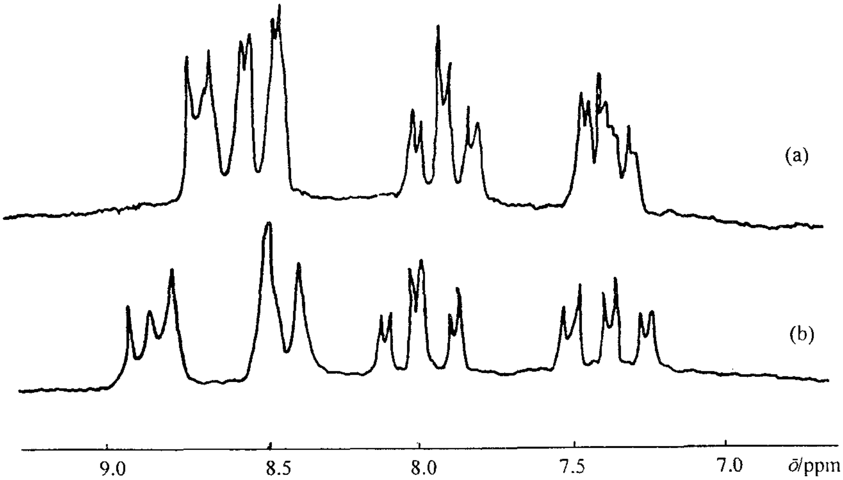


FIG. 1. ^{1}H-NMR spectra of bpy (a) and $[Ru(bpy)_3](PF_6)_2$ (b)

Table 1 ^{1}H -NMR Data of Ligands and Ru(II) Complexes (ppm)

Compounds	HDO/NH$_2$	Aromatic protons
bpy		$H_{3,3'}$(8.48~8.56), $H_{4,4'}$(7.20~7.35) $H_{5,5'}$(7.68~7.89), $H_{6,6'}$(8.33~8.43)
dabz	3.64	6.64
phen		$H_{2,9}$(8.98~9.08), $H_{3,8}$(7.78) $H_{4,7}$(8.20~8.36), $H_{5,6}$(7.54~7.70)
$[Ru(bpy)_3](PF_6)_2$		$H_{3,3'}$(8.73~8.86), $H_{4,4'}$(7.29~7.43) $H_{5,5'}$(7.97~8.17), $H_{6,6'}$(8.47~8.56)
cis-$Ru(bpy)_2Cl_2 \cdot 2H_2O$		$H_{3,3'}$(8.53~8.63), $H_{4,4'}$(7.29~7.43) $H_{5,5'}$(7.68~7.75), $H_{6,6'}$(7.95~8.15)
$[Ru(phen)_3](ClO_4)_2$		$H_{2,9}$(8.99~9.06), $H_{3,8}$(7.92) $H_{4,7}$(8.42~8.54), $H_{5,6}$(7.66~7.85)
$[Ru(bqdi)_3](PF_6)_2$	2.96	7.21

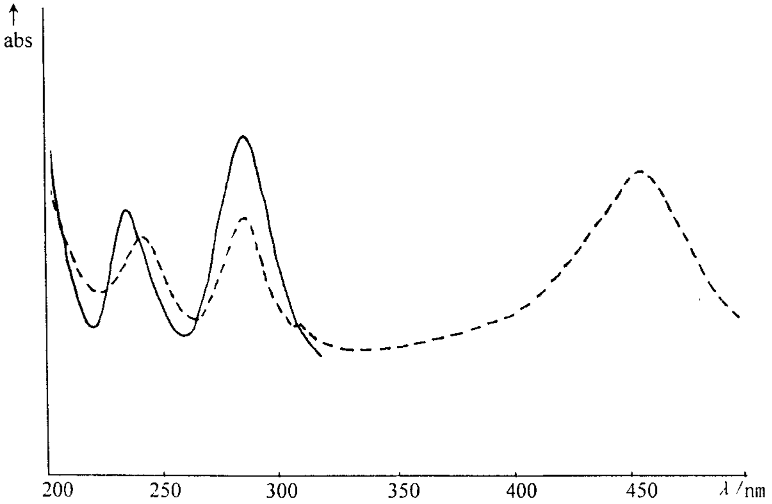


FIG. 2. The electronic spectra of bpy (—) and $[Ru(bpy)_3](PF_6)_2$ (----)

$H_{5,5'}$ ($\Delta\delta$0.30ppm), and $H_{3,3'}$ ($\Delta\delta$0.28ppm); yet the $H_{6,6'}$ ($\Delta\delta$0.13ppm) displays the smallest chemical shift changes. The results indicate that the deshielding of aromatic protons on the bipyridine causes the resonance shift downfield, while the bipyridine is coordinated with ruthenium. Furthermore, due to the effect of coordination, the nuclear spin system has also changed. The ^{1}H-NMR data for other ligands and ruthenium(II) complexes are listed in Table 1. From Table 1 it can be observed that when the ligand 1.2-diaminobenzene was substituted for bpy, the aromatic protons of $Ru(bqdi)_3^{2+}$ shift downfield by almost 0.57ppm. It is noted that the structure of the ligand dabz shows clearly a quinoid character[9,10]. However , for the cis-$Ru(bpy)_2Cl_2{\cdot}2H_2O$ complex, the resonance peaks of $H_{3,3'}$ and $H_{4,4'}$ on bpy are shift downfield; yet the $H_{5,5'}$ and $H_{6,6'}$ are upfield; this indicates that the chlorine atoms may coordinated with ruthenium[2].

Electronic Absorption Spectra

The absorption curves of bpy and $[Ru(bpy)_3](PF_6)_2$ are given in Figure 2. From the spectrum of bpy (Figure 2, solid line) it can be seen that the absorption wavelengths are less than 400 nm. These absorptions belong to the intraligand charge-transfer (LC) bands, which involve a transition from the lone-pair orbitals of nitrogen atoms to π*

Table 2 Electronic Spectra Data of Ligands and Their Ru(II) Complexes (nm)

Compd	λmax	Assgnt	Solvent
bpy	282	n →π*(bpy)	H_2O
	233	n →π*(bpy)	
phen	268	n →π*(phen)	H_2O
	230	n →π*(phen)	
dabz	290	n →π*(dabz)	H_2O
	232	n →π*(dabz)	
$Ru(bpy)_3(pF_6)_2$	452	Ru(II) →π*(bpy)	CH_3OH
	282	n (bpy)→π*(bpy)	
	242	π(bpy)→π*(bpy)	
$[Ru(phen)_3](ClO_4)_2$	455	Ru(II) →π*(phen)	CH_3OH
	263	n (phen)→π*(phen)	
	227	π(phen)→π*(phen)	
$[Ru(bqdi)_3](pF_6)_2$	554	Ru(II) →π*(bqdi)	CH_3OH
	290	n (dibq)→π*(bqdi)	
	232	π(dibq)→π*(bqdi)	

orbital (282 nm), and the band at 233 nm is referred to as the π→π* transition of bpy. The electronic spectrum of the $[Ru(bpy)_3](PF_6)_2$ complex (Figure 2, broken line) is indicated by an oscillation absorption at 452 nm, which is assigned to the characteristic absorption of Ru(II) →π* (bpy) MLCT transition. Likewise, the ultraviolet-visible absorption bands of the ligands bipyridine on $[Ru(bpy)_3](PF_6)_2$ are similar to the ligand bipyridine, but the n →π* transition dramatically shifts to a higher wavelength resulting from the coordination effect of the nitrogen donor atoms. The UV/Vis absorption spectral data for other ligands and their Ru(II) complexes are reported in Table 2. The wavelength changes depend upon the electron-contributing capacity of the ligands.

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