RELATIONS BETWEEN ^{13}C NMR SPECTRA AND OXIDATION POTENTIALS OF RUTHENIUM(II) POLYPYRIDINE COMPLEXES

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Comparative study on electrochemistry and NMR has been carried out on a series of $\text{Ru}(\text{bpy})_2\text{L}^{n+}$ and $\text{Ru}(\text{phen})_2\text{L}^{n+}$. Linear relations were found between the ^{13}C chemical shifts and E_{ox} for these mixed ligand ruthenium(II) complexes.

^{13}C NMR chemical shift, ruthenium(II) complex, oxidation potential

$\text{Ru}(\text{II})$ polypyridine complexes have attracted much attention because of their excellent catalytic and photosensitive properties[1]. The reversible half-wave potentials of these complexes have been extensively studied from the viewpoint of the valence electronic energies of metal complexes[2,3]. For a series of ruthenium complexes with mixed ligands including bipyridine and β -diketone, $[\text{Ru}(\text{bpy})_3-x\text{L}_x]^{n+}$ ($x = 0, 1, 2, 3$, $n = 2, 1, 0$), we have found that the reversible oxidation potentials are additive with respect to ligand variation. Based on these ligand additivities, we have proposed the ligand parameter, P_L , which is a measure of the donor/acceptor ability of the bidentate ligands[4].

In the present report, electrochemical and NMR data have been obtained on a series of $\text{Ru}(\text{bpy})_2\text{L}^{n+}$ ($n = 2, 1, 0$) and $\text{Ru}(\text{phen})_2\text{L}^{n+}$ ($n = 2, 1, 0$) and the results compared to clarify a correlation between oxidation potentials and micro electronic states of complexes.

Ruthenium(II) complexes, $\text{Ru}(\text{bpy})_2\text{L}^{n+}$ ($n = 2, 1, 0$) and $\text{Ru}(\text{phen})_2\text{L}^{n+}$ ($n = 2, 1, 0$) were prepared according to the procedures in the literature[5,6]. ^1H and ^{13}C NMR spectra of the complexes were measured with a Jeol JNM-FX 200 NMR spectrometer.

^{13}C NMR spectrum of $\text{Ru}(\text{bpy})_3^{2+}$ in Fig. 1A consists of 5 peaks, which correspond to the five pairs of carbon atoms (3,3', 5,5', 4,4', 6,6' and 2,2') in the bipyridine ligands. In the spectrum of $\text{Ru}(\text{bpy})_2(\text{acac})^+$, each of the five peaks splits into two peaks as shown in Fig. 1B. The peaks of the 4,4' carbon atoms of the bipyridine ligand of $\text{Ru}(\text{bpy})_2\text{L}^{n+}$ shift to the upperfield or the downfield depending to the donor/acceptor property of ligand L compared to bipyridine. With donor ligands such as β -diketones, the peaks of the 4,4' carbon atoms of the bipyridine ligand are observed at the upperfield, while with acceptor ligands such as bipyrazine the peaks shift to the downfield. This shows that the electron densities of carbon atoms in bpy of $\text{Ru}(\text{II})$ complex vary with the donor/acceptor property of ligand L relative to bipyridine. Linear relations between the difference of chemical shifts of 4,4'-carbon atoms, $\Delta\delta_{4,4'}$ ($= \delta_{\text{bis},4,4'} - \delta_{\text{tris},4,4'}$), and E_{ox}^r are found with $\text{Ru}(\text{II})$ bis bipyridine system as shown in Fig. 2.

Figure 1. ^{13}C NMR spectrum of Ru(II) bipyridine complexes in CD_3CN
A: $\text{Ru}(\text{bpy})_3^{2+}$, B: $\text{Ru}(\text{bpy})_2(\text{acac})^+$

Similar relations are found with Ru(II) phenanthroline complexes.

The parameters of these linear relations are given in Table 1.

This result shows that reversible oxidation potentials, E_{ox}^{r} , of Ru(II) polypyridine complexes reflect both the HOMO energies and micro electronic state of these complexes.

Table 1. The parameters for linear relations between $\Delta\delta_{\gamma,\gamma'}$ and E_{ox}^{r} of $\text{Ru}(\text{bpy})_2\text{L}^{\text{n}+}$ and $\text{Ru}(\text{phen})_2\text{L}^{\text{n}+}$

Complex	$\Delta\delta_{\gamma,\gamma'}$ C	$\Delta\delta_{\gamma,\gamma'} = a \cdot E_{\text{ox}}^{\text{r}} + b$		r^*
		a	b	
$\text{Ru}(\text{bpy})_2\text{L}^{\text{n}+}$	γ	2.38	-2.79	0.99
	γ'	4.42	-5.58	0.99
$\text{Ru}(\text{phen})_2\text{L}^{\text{n}+}$	γ	2.71	-3.08	0.91
	γ'	5.32	-6.38	0.97

*Correlation coefficient

Figure 2. Relation between E_{ox}^{r} and $\Delta\delta(\delta_{\text{bis}} - \delta_{\text{tris}})$ for 4,4' carbon in the bipyridine ligand of $\text{Ru}(\text{bpy})_2\text{L}^{\text{n}+}$ complexes

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