^{99}Ru-NMR Spectroscopy of Ruthenium(II) Tris-Polypyridine Complexes

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The ^{99}Ru-NMR spectra of a series of tris-polypyridine ruthenium(II) complexes were studied in acetonitrile solution. The spectroscopic results indicate that the ^{99}Ru-NMR chemical shifts of these complexes are sensitive to the environment around the metal center. The correlation between the ^{99}Ru-NMR chemical shifts and the energy of metal-to-ligand charge transfer, E_{MLCT}, was discussed.

The ruthenium(II) polypyridine complexes are attracting much attention because of their extensive prospects of application to energy conversion and photoinduced electron transfer. Over the past decades quite a large amount of data of the ^{1}H and ^{13}C-NMR for the ruthenium polypyridine complexes has been accumulated.[1-4] On the other hand, there are relatively fewer reports about the ^{99}Ru-NMR spectroscopy, especially for the ruthenium polypyridine complexes.[3-7] The ^{99}Ru-NMR spectroscopy is very important to understand the electronic interaction between the central metal ion and ligands because the ruthenium chemical shifts can sensitively reflect the electronic and geometrical changes around the metal core. We have examined the ^{99}Ru-NMR spectra of a series of ruthenium tris-polypyridine complexes. A correlation between the electronic spectra and electronic structures of the complexes has been analyzed.

The ruthenium tris-polypyridine complexes were synthesized by microwave irradiation which has been described previously.[8] ^{99}Ru-NMR spectra were recorded at 293±2 K on a JEOL JEM-GX200 spectrometer equipped with a broad-band probe. Typically the parameters used for the acquisition of the FT spectra were spectral width 40000 Hz, acquisition time 0.1 s, delay time 1ms, and pulse width 10μs. Saturated solution of Ru(II) complexes in acetonitrile was used. The chemical shifts reported refer to $K_4Ru(CN)_6$, which resonates at 9.19013 MHz. In order to evaluate energies of metal-to-ligand charge transfer (E_{MLCT}), the UV/VIS spectra were also obtained on a Hitachi U-2000 spectrophotometer.

^{99}Ru-NMR chemical shifts of various ruthenium(II) tris-polypyridine complexes are shown in Table 1 along with the energies, E_{MLCT}. For all the ruthenium tris-polypyridine complexes studied in this work, the ^{99}Ru-NMR chemical shifts range from ca. 4000 to 6500 ppm, showing their high sensitivity to the environment around the metal center. It has been proved that the electronic donation or acceptance of ligands obviously change the spectral and electrochemical properties of the complexes, because it changes the energy of the HOMO t_{2g} and the LUMO π*orbital.[9] The basicity of the ligand dpk-oxime (dipyridyl ketoneoxime) enhances the donation more than that of other ligands. So the ^{99}Ru -NMR chemical shift of the complex **1** is the highest field among all ones detected in the present work. In contrast, the acidic ligand Hdpa (dipyridylamine) leads the complex **13** to the lowest field ^{99}Ru-NMR chemical shift. Those of the bpy or phen derivative complexes lie in a relatively narrow range. In bpy and phen derivative ligands, the difference of donation or acceptor abilities should be small due to the presence of their large π conjugated systems.

Table 1. ^{99}Ru-NMR chemical shifts (δ), wave lengths of MLCT(λ_{MLCT}) and energy of MLCT (E_{MLCT}) for ruthenium tris-polypyridine complexes in acetonitrile

No.	Complex	δ/ppm	κ_{MLCT} /nm	E_{MLCT}/eV
1	$Ru(dpk\text{-}oxime)_3^{2+}$	3998	490	2.53
2	$Ru(df\text{-}bpy)_3^{2+}$ [a]	4541	457	2.71
3	$Ru(bpy)_3^{2+}$ [b]	4546	451	2.75
4	$Ru(bpy)_3^{2+}$	4580	450	2.76
5	$Ru(bpz)_3^{2+}$	4586	450	2.77
6	$Ru(2,9\text{-}dmphen)_3^{2+}$	4601	448	2.77
7	$Ru(4,4'\text{-}dmbpy)_3^{2+}$	4615	460	2.70
8	$Ru(5\text{-}Me\text{-}phen)_3^{2+}$	4657	450	2.76
9	$Ru(5\text{-}phyl\text{-}phen)_3^{2+}$	4666	450	2.76
10	$Ru(phen)_3^{2+}$	4685	448	2.77
11	$Ru(5\text{-}Cl\text{-}phen)_3^{2+}$	4706	448	2.77
12	$Ru(5\text{-}NO_2\text{-}phen)_3^{2+}$	4709	449	2.76
13	$Ru(Hdpa)_3^{2+}$	6532	375	3.31

[a] df-bpy = 4,4′-di-(trifluoromethyl)-2,2′-bipyridine.
[b] in aqueous solution.

Table 2. Difference of ^{99}Ru-NMR chemical shifts(Δδ) and difference of Hammett substituent constants($\Delta\Sigma\sigma_p$). Numbers at the left side of the Table correspond to those in Table 1

No.	Ligand	Δδ/ppm	$\Delta\Sigma\sigma_p$
8	5-Me-phen	-28	-0.51
9	5-phyl-phen	-19	-0.03
10	phen	0	0
11	5-Cl-phen	21	0.69
12	$5\text{-}NO_2\text{-}phen$	24	2.34

However, for the homologues, the chemcal shift might reflect the change of the electronic configuration caused by the substituents on the ligands. Table 2 shows the change of ^{99}Ru chemical shift is sensitive to the 5-substitution of the phenanthroline. Δδ ($\Delta\delta = \delta_{com.n} - \delta_{com.10}$; **n = 8–12**) were found to be consistent with the difference of Hammett substituent constants, $\Delta\Sigma\sigma_p$, of the ligands in the corresponding complex and in complex **10.** Here positive $\Delta\Sigma\sigma_p$ value refers to an effect of inductive electron withdrawal and minus $\Delta\Sigma\sigma_p$ value to an elctron-donatating effect relative to the parent compound **10**. Our results indicate that the electronic nature dominantly affects the ^{99}Ru chemical shifts of these complexes.

For octahedral complexes, it has been demonstrated that the shielding of transition metal nuclei with singlet ground states is usually dominated by the energy separation of the π* and t_{2g} orbitals. The larger the energy

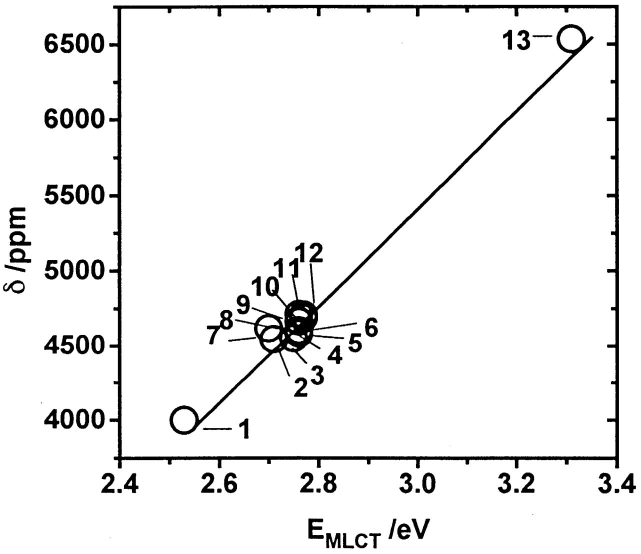

Figure 1. Plot of ^{99}Ru-NMR chemical shift vs. E_{MLCT}. The entry is the same as in Table 1.

separation, the lower the chemical shift of the central metal nucleus.[10] A correlation between the ^{99}Ru-NMR chemical shifts and the energy of metal-to-ligand charge transfer, E_{MLCT}, was found from the present results. The plot of δ vs. E_{MLCT} shown in Figure 1 reveals such a linear relationship: $\delta = 3287\ E_{MLCT} - 4409$, with a correlation coefficient, $r = 0.99$. The good coorelation and larger slope indicate that ^{99}Ru-NMR spectroscopy is a useful techniqe for getting the information about the structural or electronic variations around the metal center. Of course, it is better to further measure the ^{99}Ru-NMR spectra of some else complexes of which the chemical shifts lie the range from 5000 to 6500 ppm. However such a ruthenium tris-polypyridine complex is not available.

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