CH/π Interaction in Linkage Isomers of Bis(2,2'-bipyridine)ruthenium(II) Complexes with Pyrimidine-2-thione and Related Ligands

Kazuaki Yamanari,* Tsuyoshi Nozaki, Akira Fuyuhiro, and Sumio Kaizaki
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

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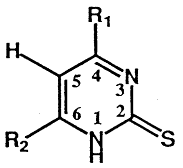
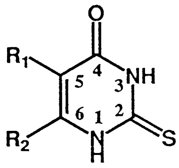
Ruthenium(II) complexes containing nine pyrimidine-2-thione $[Ru(L\text{-}N,S)(bpy)_2]^+$ (HL = pyrimidine-2-thione; bpy = 2,2'-bipyridine) are prepared and characterized. Two linkage isomers exist for most of the complexes with unsymmetrical ligands. The isomeric ratios are interpreted by CH/π attractive interaction between the 4- or 6-alkyl group of the thione ligands and the π-system of bpy.

Pyrimidine-2-thione (Hpymt) acts as a bidentate-N,S ligand. For the complexes with an unsymmetrical ligand, two linkage isomers are possible. Our recent investigations of bis(ethylenediamine) type cobalt(III) complexes have revealed that only one linkage isomer exists in each system and a substituent group in the 4-position of pymt plays an essential role in their stereochemistries.[1-4]

Here we describe the preparation of nine bis(bipyridine) ruthenium(II) complexes containing five pyrimidine-2-thione [Hpymt = pyrimidine-2-thione, H4mpymt = 4-methylpyrimidine-2-thione, Hdapymt = 4,6-dimethylpyrimidine-2-thione, H4apymt = 4-aminopyrimidine-2-thione and Hdapymt = 4,6-diaminopyrimidine-2-thione] and four 2-thiouracil ligands [H_2tuc = 2-thiouracil, $H_2$5mtuc = 5-methyl-2-thiouracil, $H_2$6mtuc = 6-methyl-2-thiouracil and $H_2$6ptuc = 6-propyl-2-thiouracil] (Chart 1). It is quite interesting to compare the stereochemistries of the d^6 complexes of cobalt(III) and ruthenium(II). The ruthenium(II) complexes are characterized by elemental analyses, UV-vis absorption spectra and ^1H and ^{13}C NMR spectra.



	R_1	R_2
Hpymt	H	H
H4mpymt	CH_3	H
Hdmpymt	CH_3	CH_3
H4apymt	NH_2	H
Hdapymt	NH_2	NH_2



	R_1	R_2
H_2tuc	H	H
$H_2$5mtuc	CH_3	H
$H_2$6mtuc	H	CH_3
$H_2$6ptuc	H	$n\text{-}C_3H_7$

All of the pyrimidine-2-thione ligands (Aldrich) were used without further purification. The general preparation procedure was as follows: The pyrimidine-2-thione ligand (0.5 mmol) was suspended in 50% aqueous methanol (50 cm^3) and the pH adjusted to 8-9 by adding aqueous NaOH. To the above solution was added *cis*-$[RuCl_2(bpy)_2]\cdot0.5H_2O$ (0.25 g, 0.5 mmol)[5] and the mixture was refluxed for 2-4 h to give the brownish purple solution. By adding $LiClO_4$ and evaporating the solution, the brown perchlorate $[Ru(L)(bpy)_2]ClO_4$ was obtained and recrystallized from water and methanol. The yields were 70-90%.

The complexes $[Ru(L)(bpy)_2]^+$ were prepared in good yields by refluxing *cis*-$[RuCl_2(bpy)_2]$, pyrimidine-2-thione ligand HL and NaOH (mole ratio = 1:1:1) in water-methanol. In cases of 2-thiouracil derivatives H_2L, free ligands were used without neutralizing by NaOH. The elemental analyses indicate that the complexes have the composition of $[Ru(L\text{ or }HL)(bpy)_2]ClO_4$.

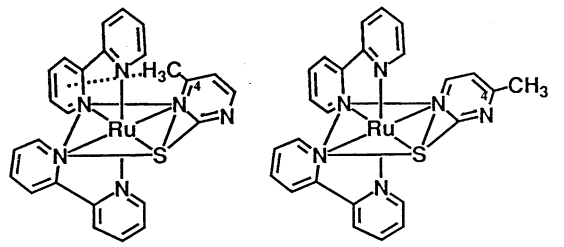


Figure 1. Two linkage isomers of $[Ru(4mpymt)(bpy)_2]^+$.

All complexes show similar UV-vis absorption spectra. There are mainly four peaks at 500-520, 335-345, 280-290 and ca. 240 nm. The first two peaks are assignable to Ru 4dπ→bpy π* metal-to-ligand charge-transfer (MLCT) transitions.[6] The sharp peak at 280-290 nm is assigned to an intraligand π→π* transition of bipyridine.[6]

In the ^{13}C NMR spectrum of $[Ru(dmpymt)(bpy)_2]^+$, twenty-six signals, six signals [δ 182.5(C^2), 166.8 and 165.5(C^4 and C^6), 114.5(C^5) and 23.2 and 19.8(CH_3)] in the dmpymt chemical shift region and twenty signals [δ 158.04-123.3] in the bpy region were observed. The result is consistent with the above formulation $[Ru(dmpymt\text{-}N,S)(bpy)_2]^+$.

For the complexes with an unsymmetrical ligand, two linkage isomers, adjacent and remote, are possible depending upon the disposition of the C4 substituent group of pyrimidine ring as shown in Fig. 1. Since adjacent and remote is defined by the C4 substituent group, it should be noted that the 4-alkyl group is away from the two bpy chelates in a remote isomer of the pymt system (4mpymt and dmpymt) but the 6-alkyl group is close to them in a remote isomer of the tuc system (H6mtuc and H6ptuc). The existence of the linkage isomers and its isomeric ratio were determined by ^1H NMR spectra.

The complex $[Ru(dmpymt)(bpy)_2]^+$ shows two methyl signals at δ 2.28 and 1.28. In this case, the upfield signal at δ 1.28 is assigned to the methyl group at an adjacent position, whereas the signal at δ 2.28 is assigned to the methyl group in a remote position. The complex $[Ru(4mpymt)(bpy)_2]^+$ shows similar two methyl signals at δ 2.31 and 1.33 in Fig. 2: the ratio is 20% for δ 2.31 and 80% for δ 1.33 based on the signal intensities. The result means that the two linkage isomers exist in $[Ru(4mpymt)(bpy)_2]^+$ and they are composed of 20% of a remote isomer and 80% of an adjacent isomer. The linkage isomeric ratios of $[Ru(L)(bpy)_2]^+$ were determined in the same way and are collected in Table 1 as well as those of the corresponding cobalt-

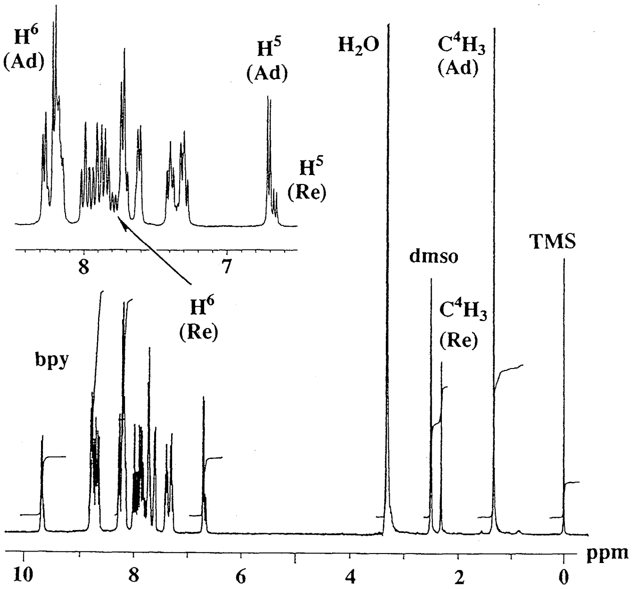


Figure 2. Proton NMR spectrum of $[Ru(4mpymt)(bpy)_2]^+$.

(III) complexes $[Co(L)(en)_2]^{2+}$.

In a case of 4apymt, only a remote isomer exists in both cobalt(III) and ruthenium(II) complexes. Since there is no attractive interaction between the amino group and the en or bpy ligand, a remote isomer is more favorable than an adjacent isomer from a steric viewpoint.

The dominant isomer is reversed drastically in the 4mpymt system. In $[Co(4mpymt)(en)_2]^{2+}$, a remote isomer is formed stereoselectively. It is reasonable to consider that the 4-methyl group is away from the en chelate ring to minimize the steric repulsion. However, an adjacent form becomes the main isomer and a remote isomer becomes minor in $[Ru(4mpymt)(bpy)_2]^+$. These facts indicate that attractive interaction exists between methyl group and the bpy ligand. Such attractive interaction between alkyl group and π system is called as CH/π interaction, and many experimental facts supporting this hypothesis have been collected from many scientific fields.[7] Thus, the drastic change of main linkage isomer in $[Co(4mpymt)(en)_2]^{2+}$ and $[Ru(4mpymt)(bpy)_2]^+$ is attributed to the existence of CH/π interaction in the latter complex. Recently we have reported similar intramolecular interaction in *mer*-$[Co(4mpymt)_3]$.[8]

Table 1. Linkage Isomer Ratio (%) in $[Ru(L)(bpy)_2]^+$ and $[Co(L)(en)_2]^{2+}$

	Ruthenium(II)		Cobalt(III)	
L	adjacent	remote	adjacent	remote
4apymt	0	100	0	100
4mpymt	80	20	0	100
Htuc	70	30	100	0
H5mtuc	65	35	100	0
H6mtuc	50	50	100	0
H6ptuc	40	60	-	-

In the Htuc system, an adjacent isomer becomes dominant in $[Ru(Htuc)(bpy)_2]^+$ as well as $[Co(Htuc)(en)_2]^{2+}$. This means that the coordination ability of the 2-S/3-N mode is higher than that of the 1-N/2-S mode. It is very interesting to know how the introduction of an alkyl group at a 5- or 6-position affects the linkage isomeric ratio. Since the changes of the isomeric ratios were not observed for the corresponding cobalt(III) series, the electronic effect by introducing the alkyl group is negligible. In $[Ru(H5mtuc)(bpy)_2]^+$, an adjacent isomer is 65% and a remote one 35%. The ratio is almost the same as that of the Htuc system and the 5-methyl group has almost no effect on the ratio. On the other hand, the isomeric ratio becomes equal in $[Ru(H6mtuc)(bpy)_2]^+$ and a remote form becomes dominant (60%) in $[Ru(H6ptuc)(bpy)_2]^+$. These results indicate that there is CH/π interaction between the 6-alkyl groups and the π system of bpy and hence the ratio of a remote isomer was increased remarkably in $[Ru(H6mtuc)(bpy)_2]^+$ and $[Ru(H6ptuc)(bpy)_2]^+$.

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