Structure and Properties of Diastereoisomers of a Ruthenium(II) Complex Having a Pyridylpyrazoline Derivative as a Ligand

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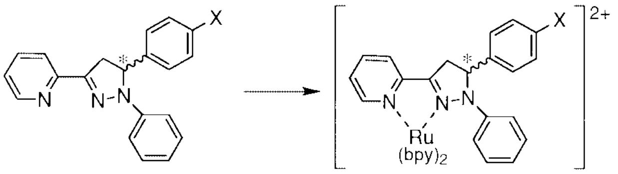
Diastereoisomers of a heteroleptic ruthenium complex, $[Ru(bpy)_2L]^{2+}$ (bpy = 2, 2'-bipyridine, L = 5-(4-nitrophenyl)-1-phenyl-3-(2-pyridyl)-2-pyrazoline) have been isolated. Two isomers have quite similar redox potentials and show MLCT absorptions in the region of 400 to 500 nm with similar absorption maxima at room temperature. By contrast, quite different emission maxima and lifetimes are observed at 77 K.

Because of their unique photophysical and photochemical properties, ruthenium(II) polypyridyl complexes have been extensively studied[1] and widely used in a number of photosensitization and photocatalytic processes. As a part of our study to develop novel Ru(II) complexes as efficient photosensitizers, we have prepared a series of *N,N'*-type bidentate ligands, 3-(2-pyridyl)-2-pyrazoline derivatives **1**[2] and their Ru(II) complexes $[Ru(bpy)_2(\mathbf{1})]^{2+}$ **2**, where bpy = 2,2'-bipyridine. Interestingly, in each of these complexes, two kinds of emissions were found to exist. Although the phenomenon of dual emission has been reported for several Ru(II) polypyridyl complexes so far,[3] it seems rather dubious whether this is the case. Because each complex **2** may exist as a mixture of four stereoisomers owing to the presence of two chiral centers, i.e., metal (Λ/Δ) and ligand (*R*/*S*). Therefore it is also plausible that the observed two kinds of emissions come from two diastereoisomers (= two enantiomeric pairs) of **2**, respectively.[4] The effect of stereoisomerizm on physical properties of the Ru(II) polypyridyl complexes has become of interest in recent years.[5] However, for simple mononuclear Ru(II) complexes, only a few examples have been known to show such a stereochemical effect.[4,6] In this study, we separated the diastereoisomers of a complex **2** and examined structure and physical properties of each isomer.



1 X = OCH_3, H, CN, NO_2 **2**

Pyridylpyrazolines **1** were prepared from the corresponding chalcones according to the reported method[7] with a slight modification. Heteroleptic Ru(II) complexes **2** were obtained from $Ru(bpy)_2Cl_2$ and 1 equivalent of **1**, and isolated as the perchlorate salts in a usual manner. The results of NMR analysis indicated that each of the obtained complexes **2** is the mixture of stereoisomers as anticipated. For a complex **2** (X = NO_2), recrystallization of the mixture sample from ethanol–acetonitrile gave one diastereoisomer **2a**.[8] And from the mother liquor, another diastereoisomer **2b**[8] was obtained. Their ^1H NMR spectra afford clear evidence for the separation of isomers.[9]

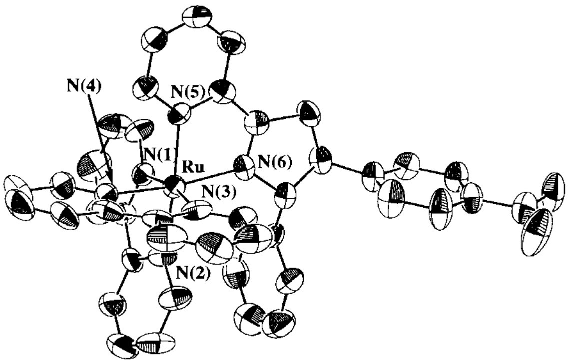


Figure 1. ORTEP drawing of isomer **2a** (hydrogen atoms and anions are omitted for clarity.).

The crystal structure of diastereoisomer **2a** is depicted in Figure 1,[10] which reveals that **2a** is the racemate composed of the (Λ)-(*S*) and (Δ)-(*R*) isomers. The ruthenium center has a distorted octahedral configuration with bond angles 77.5(9)° for N(5)–Ru–N(6), 78.4(3)° for N(1)–Ru–N(2) and 79.7° for N(3)–Ru–N(4), respectively. The average bond length of Ru–N(5) and R–N(6) is about 2.06 Å which is almost same as that of $[Ru(bpy)_3]^{2+}$.[11] The 1-phenyl group is twisted out of pyrazoline plane with an angle of 82.71° to make two planes almost perpendicular. This may be caused by steric repulsion between the 1-phenyl group of **1** and two bpy ligands.

Table 1 summarizes the electrochemical data for Ru complexes **2** (X = NO_2) and $[Ru(bpy)_3]^{2+}$ as well as those for ligands. There are no significant differences in the electrochemical properties between the diastereoisomers **2a** and **2b**. Oxidation potentials of the complexes **2a**,**b** are slightly positive-shifted as compared with that of $[Ru(bpy)_3]^{2+}$. This may be due to the presence of ligand **1** having an electron-withdrawing substituent, i.e., nitro group. On the other hand, the first reduction potentials of the complexes **2a**,**b** are almost same as that of $[Ru(bpy)_3]^{2+}$. This fact is in accord with the more negative reduction potential of **1** than that of bpy and suggests the first reductions of the complexes **2a**,**b** are attributed to the reduction process at the bpy ligand.

Absorption and emission spectra of the complexes are shown in Figure 2 and their data including emission lifetimes are summarized in Table 2. In absorption spectra, each diastereoisomer shows an apparently single MLCT transition with a similar absorption maximum. Although electrochemical data suggest that first reduction of **2a,b** takes place at the bpy

Table 1. Electrochemical data for Ru(II) complexes as well as those for ligands ($E_{1/2}$/V vs Fc/Fc$^+$)^a

Compound	Oxidation	Reduction 1	Reduction 2	Reduction 3	$\Delta E_{1/2}$^{b} /eV
1 (X = NO_2)		-2.34			
bpy		-2.22^c			
2a^d	0.93	-1.73	-1.98		2.67
2b^d	0.93	-1.74	-1.99		2.66
2 (mixture)^d	0.93	-1.74	-1.99		2.67
$[Ru(bpy)_3]^{2+}$	0.87	-1.74	-1.94	-2.19	2.61

^{a}The cyclic voltammetry was conducted with glassy C, Pt and Ag/Ag$^+$ as working, counter and reference electrodes respectively under N_2 atmosphere at room temperature. The concentration of a sample solution was kept at 1.0 × 10^{-3} mol dm^{-3} in CH_3CN with 1.0 × 10^{-1} mol dm^{-3} of TBAP. Scan rate = 100 mV/s. $^b\Delta E_{1/2} = e[E_{1/2(ox)} - E_{1/2(red\ 1)}]$ ^{c}Reference 14. ^{d}Reduction of NO_2 group was also observed.

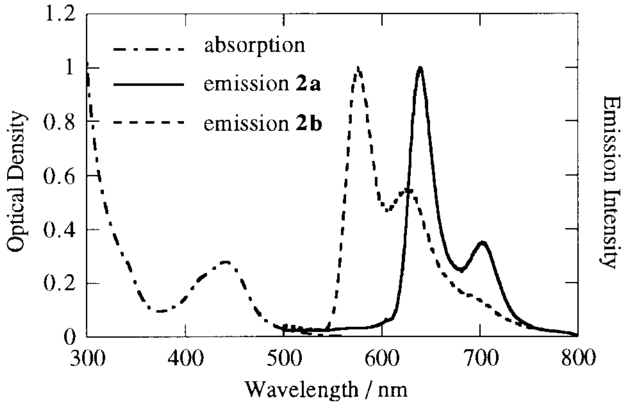


Figure 2. Absorption and emission spectra of Ru(II) complexes **2** (X = NO_2).

Table 2. Photochemical data for Ru(II) complexes

Complex	Absorption^a λ_{max} / nm (ε/10^4 $M^{-1}cm^{-1}$)	Emission^b λ_{max} / nm	τ / µs
2a	441 (2.5)	645, 709	3.3^c
2b	441 (2.5)	583, 633	6.8^d
2 (mixture)	441 (2.5)	583 644 707	5.9^d 2.9^c 2.7^e
$[Ru(bpy)_3]^{2+}$	450 (1.6)	587, 630	5.2^d

^{a}Measured in CH_3CN at room temperature. ^{b} Measured in EtOH–MeOH (4 :1, v/v) at 77 K with excitation at 450 nm. The concentration of a sample solution was 1.0 × 10^{-5} mol dm^{-3}. ^{c}Measured at the 650 nm emission. ^{d}Measured at the 580 nm emission. ^{e} Measured at the 700 nm emission.

ligand in the ground state, it seems rather difficult to resolve these MLCT transitions to the particular ligands because of the small difference in the reduction potentials between **1** and bpy.

No emission was observed for both isomers **2a** and **2b** at the room temperature. However complexes **2a**, **b** show moderate emissions with quite different emission maxima in ethanol–methanol (4:1, in v/v) glasses at 77 K. Isomer **2a** has emission maxima with longer wavelength (645 and 709 nm) than those of isomer **2b** (583 and 633 nm). The results of lifetime measurements also indicate the difference between **2a** and **2b**. The values of emission maxima and lifetime for isomer **2b** are close to those for $[Ru(bpy)_3]^{2+}$ respectively, whereas emission properties of isomer **2a** are similar to those of a homoleptic ruthenium complex of **1**, $[Ru(\mathbf{1})_3]^{2+}$, which has two emission maxima at 655 and 719 nm with an emission lifetime of 1.84 µs in the case of X = H.[12] These facts imply that isomers **2a** and **2b** have different ligand-based emitting states to each other. However an alternative explanation would be also possible. Thus, in the complexes **2a,b**, the interaction between ligands through space, so-called interligand coupling, especially due to the existence of 1-phenyl group on **1** seems to be strong enough to affect energy levels.[13] Consequently the difference in the mode of the interligand interaction between **2a** and **2b** may cause the different emission properties even if both isomers have the same ligand-based emitted states. Anyhow, for further clarification of emission behavior, more detailed information on the structure and physical properties of the complexes is required. Work is in progress along this line.

References and Notes

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8 Anal. Calcd for $C_{40}H_{32}N_8O_{10}Cl_2Ru$ **2a**: C, 50.21; H, 3.37; N, 11.71% Found: C, 50.23; H, 3.29; N, 11.60%. Calcd for $C_{40}H_{32}N_8O_{10}Cl_2Ru$ **2b**·1/2H_2O: C, 49.74; H, 3.44; N, 11.60%. Found: C, 49.79; H, 3.31; N, 11.54%.

9 For example, chemical shifts of pyrazoline ring protons(CD_3CN). **2a**: δ 3.82 (dd, J =13.3, 17.5 Hz, 1H), 4.37 (dd, J = 11.0, 17.9 Hz, 1H), 5.16 (dd, J = 11.2, 13.3 Hz, 1H). **2b**: δ 3.42 (dd, J = 11.1, 18.3 Hz, 1H), 4.51 (dd, J = 12.0, 18.3 Hz, 1H), 5.30 (dd, J = 11.1, 12.0 Hz, 1H).

10 Selected crystal data for **2a**: $C_{40}H_{32}N_8O_{10}Cl_2Ru$, M_w = 956.72, Monoclinic, $P2_1$, a = 13.736(2), b = 14.378(3), c = 10.268(2) Å, β = 100.45(2) °, V = 1994.3(7) Å^3, Z = 2, D_c = 1.59 g/cm^3, T = 298 K, Mo Kα, R = 0.044, R_w = 0.035 for 4070 reflections with $I > \sigma 3(I)$.

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