Synthesis and Properties of Novel Ru-Ni and Ru-Cu Dinuclear Complexes

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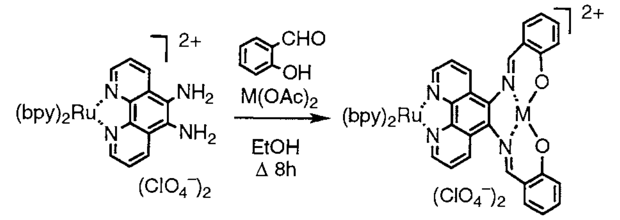
Novel Ru-Ni and Ru-Cu dinuclear complexes, in which Ru(bpy)$_2^{2+}$ (bpy = 2,2′-bipyridine) and Ni- or Cu-Schiff base unit fused together, were synthesized. The molecular structure of Ru-Ni dinuclear complex was determined by an X-ray crystal structure analysis. Photochemical studies on these complexes showed that the excited state of the Ru(bpy)$_2^{2+}$ moiety in the dinuclear complexes was quenched by intramolecularly attached metal-Schiff base unit.

Polynuclear complexes have attracted much attention in terms of effective intramolecular electron or energy transfer systems.[1] Especially, polymetallic systems incorporating Ru(bpy)$_2^{2+}$ unit, which is well known as a useful photosensitizer, have been of much interest.[2] Here, we report on the synthesis of novel Ru-Ni and Ru-Cu dinuclear complexes, in which Ru(bpy)$_2^{2+}$ and Ni- or Cu-Schiff base unit fused together. Schiff base complexes have been interested from the electrochemical point of view, since the salen type ligands are widely known to form stable complexes with a variety of redox active transition-metal ions.[3] Hence the combination of these two metal complex units was expected to exhibit interesting photochemical and electrochemical properties.

5,6-Diamino-1,10-phenanthroline was used for bridging between two metals and its Ru complex **1** was prepared by the reported method.[4] Dinuclear complexes **2a**[5] and **2b**[6] were synthesized in one pot by reacting two equivalents of salicylaldehyde with Ni or Cu acetate and **1** in ethanol and isolated as perchlorates, respectively (Scheme 1). Recrystallization of **2a** from C_2H_5OH-CH_3CN gave crystals suitable for an X-ray structure analysis. The ORTEP drawing of **2a**[7] is shown in Figure 1. The Ru center has a little distorted octahedral configuration. The bond angle of N(1)-Ru-N(2) is 78.6°, which is smaller than that of N(4)-Ru-N(5) (87.4°) with the average Ru-N bond length (2.06(1) Å) close to the normal range for [Ru(bpy)$_3$]$^{2+}$.[8] The Ni-Schiff base unit has an approximately square-planar coordination geometry. The average Ni-N and Ni-O bond lengths are 1.86(1) Å and 1.84(1) Å, which are in agreement with those of [Ni(saloph); saloph = *N*, *N′*-*o*-phenylenebis(salicylidenaminato)].[9] The spatial distance between Ru and Ni is 7.88(1) Å. The most remarkable feature of the structure of **2a** is that the Ni-Schiff base unit was distorted against the plane of phenanthroline ring due to the effect of steric repulsion between the phenanthroline ring and the Ni-Schiff base unit.



1 **2a** (M = Ni), **2b** (M = Cu)

Scheme 1. Synthesis of Ru-Ni and Ru-Cu dinuclear complexes.

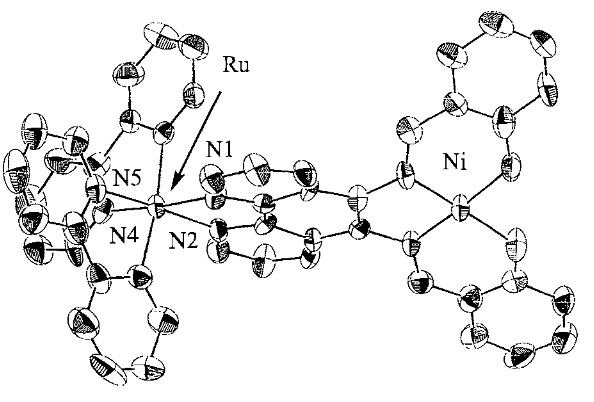


Figure 1. ORTEP drawing of **2a** (hydrogen atoms and ClO_4 are not shown for clarity).

Table 1. Redox properties (V vs. Fc/Fc$^+$)^a

	$E_{1/2}$(Ru$^{III/II}$)	$E_{1/2}$(Ni$^{III/II}$)	E_pCu$^{II/I\,b}$	E_pNi$^{II/I\,b}$
2a	+0.87	+0.52		-1.38
2b	+0.94		-1.14	
[Ru(bpy)$_3$]Cl$_2$	+0.88			
[Ni(saloph)]		+0.55		-1.82
[Cu(saloph)]			-1.57	

^{a}The cyclic voltammetry was conducted with glassy C, Pt and Ag/Ag$^+$ as working, counter and reference electrodes, respectively, under N_2 atmosphere. The concentration was kept at 1 mM in CH_3CN with 0.1 M TBAP. Scan rate = 100 mV/s. ^{b} Peak potential.

Table 1 summarizes the electrochemical properties. **2a** showed quasi-reversible redox wave at + 0.87 V vs. Fc/Fc$^+$ for Ru(II)/Ru(III), which corresponded to that of [Ru(bpy)$_3$]Cl$_2$, though that of **2b** was observed more positive (0.94 V). The Ni(II)/Ni(III) redox potential for **2a** was +0.52 V, which was almost same as that of [Ni(saloph)][10]. Reduction potentials, both of the Ni(II)/Ni(I) for **2a** (-1.38 V) and Cu(II)/Cu(I) for **2b** (-1.14 V), were observed more positive than those of [Ni(saloph)][10](-1.82 V) and [Cu(saloph)][11](-1.57 V). The reason of this phenomenon might be presumed to be a conventional substituent inductive effect upon coordinated metal potentials. Thus, the positively charged Ru(bpy)$_2^{2+}$ moiety should exert a substantial electron-withdrawing effect,[12] making reduction of Ni(II)/Ni(I) and Cu(II)/Cu(I) easier and thereby shifting $E_{1/2}$ in the positive direction.

The absorption and emission spectral data are summarized in Table 2. The MLCT absorption bands for the Ru component in both of complexes **2a, b** are almost same as that of [Ru(bpy)$_3$]Cl$_2$ (Figure 2). However, their excition coefficients increased since absorption bands for MLCT of Ni- and Cu-Schiff

Table 2. Absorption and emission data of complexes

	Absorption[a] λ_{max}/nm(ε/10^4 $M^{-1}cm^{-1}$)	Emission[b] λ_{max}/nm	Φ_{ref}[d]
2a	449 (2.8)	620	0.02
2b	458 (4.1)	614	0.02
$[Ru(bpy)_3]Cl_2$	450 (1.5)	618	1
[Ni(saloph)]	474 (0.6)	[c]	
[Cu(saloph)]	419 (2.2)	[c]	

[a] MLCT absorption measured in CH_3CN at room temperature. [b] Emission spectra excited at 450 nm were recorded in CH_3CN at room temperature. The concentration of all measured samples were 1.0 x 10^{-5} M. [c] No emission was observed. [d] Φ_{ref} Values are relative emission intensities based on that of $[Ru(bpy)_3]Cl_2$ complex.

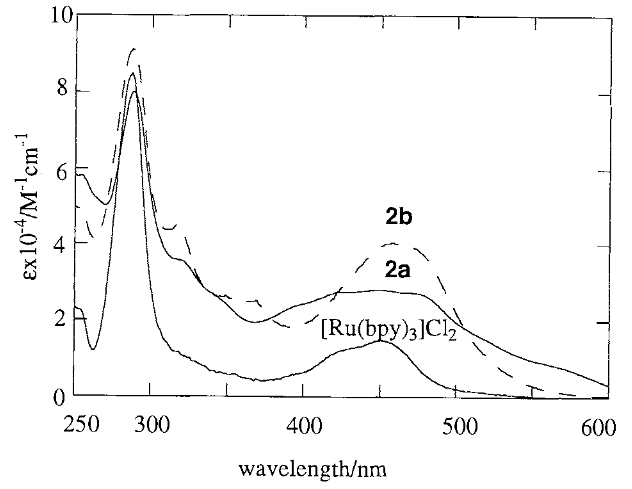


Figure 2. Absorption spectra of **2** and $[Ru(bpy)_3]Cl_2$ in CH_3CN.

base units are involved in those for the Ru component of **2a**, **b**. In addition, those absorption bands in visible region were more broadened than that of mononuclear complex, $[Ru(bpy)_3]Cl_2$. This result indicates that some π-conjugation of the phenanthroline ring and the Schiff base ligand of the Ni or Cu moiety is present. On the other hand, the emission intensities both of **2a**, **b** are drastically reduced to ca. 2% of that of $[Ru(bpy)_3]Cl_2$, though their emission maxima are almost identical to that of $[Ru(bpy)_3]Cl_2$ itself (excited at 450 nm; λ_{max} 620 nm).[13] This fact indicated that efficient quenching of the excited state occurs by virtue of the intramolecularly attached Ni- and Cu-Schiff base units.

In conclusion, Ru-Ni and Ru-Cu dinuclear complexes **2a**, **b** were newly synthesized, and the results of photochemical studies on these complexes implied that an efficient electron or energy transfer may happen intramolecularly. Extensive studies on the mechanism of quenching process and application for photochemical reaction are undertaken now.

References and Notes

1 F. Scandola, M. T. Indelli, C. Chiorboli, and C. A. Bignozzi, *Topics in Current Chemistry*, **158**, 73 (1990).
2 D. M. Roundhill, "Photochemistry, and Photophysics of Metal Complexes," Plenum Press, New York (1994), pp. 165-210.
3 M. D. Hobday and T. D. Smith, *Cood. Chem. Rev.*, **9**, 311, (1972).
4 E. Ishow, A Gourdon, and J. -P. Launay, *Chem. Commun.*, **1998**, 1909.
5 Selected data for **2a**: Anal. Found: C, 49.80; H, 3.22; N, 10.02%. Calcd for $C_{46}H_{32}N_8O_{10}Cl_2RuNi{\bullet}H_2O$: C,49.98; H, 3.10; N, 10.14%. ES-Mass: 987 $[M-ClO_4]^+$.
6 Selected data for **2b**: Anal. Found: C, 48.72; H, 3.14; N, 9.84%. Calcd for $C_{46}H_{32}N_8O_{10}Cl_2RuCu{\bullet}2H_2O$: C,48.97; H, 3.22; N, 9.93%. ES-Mass: 994 $[M-ClO_4]^+$.
7 Crystal data for **2a**: $C_{46}H_{32}N_8O_{10}Cl_2RuNi{\bullet}H_2O$, Mw = 1105.50, Triclinic, $P\bar{1}$, a = 9.525(2), b = 12.208(3), c = 20.436(5) Å, α = 96.69(2), β = 90.55(2), γ = 99.94(2)°, V = 2323.5(9) $Å^3$, Z = 2, D_c = 1.55 g/cm^3, MoKα, R = 0.068 and R_w = 0.108 for 8679 unique reflections with $I > \sigma 3 (I)$.
8 D. Paul and D. S. Jones, *J. Chem. Soc.,Chem. Commun.*, **1979**, 849.
9 A. Radha and M. Seshasayee, *Acta Cryst.*, **C41**, 1169, (1985).
10 F. Azeved, M. A. A. F. de C. T. Carrondo, B. de Castro, M. Convery, D. Domingues, C. Freire, M. T. Duarte, K. Nielsen, and I. C. Santos, *Inorg. Chim. Acta*, **219**, 43 (1994).
11 D. F. Rohbach, W. R. Heineman, and E. Deutsch, *Inorg. Chem.*, **18**, 2536 (1979).
12 C. B. -Brennan, P. Subramanian, M. Absi, C. Stern, and J. T. Hupp, *Inorg. Chem.*, **35**, 3719 (1996).
13 The emission intensity of $[Ru(bpy)_3]Cl_2$ under coexistence of 10 eq. of Ni(saloph) was observed to be only reduced to ca. 80% (excited at 450 nm; λ_{max} 620 nm) of that of $[Ru(bpy)_3]Cl_2$.