Bull. Chem. Soc. Jpn., **72**, 725—731 (1999)

Synthesis and Photochemical Properties of Ruthenium–Cobalt and Ruthenium–Nickel Dinuclear Complexes

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(Received October 26, 1998)

Three dinuclear colmplexes, two Ru(II)–Co(III) and one Ru(II)–Ni(II) polypyridyl complexes, were prepared by the use of ethylene- and pentamethylene-linked bisphenanthroline as the bridging ligands. Their photochemical and electrochemical properties were examined. Each metal complex component was shown to be electronically insulated. Since the roles of the Ru(II) as a photosensitizer and the Co(III) or Ni(II) moiety as an electron acceptor were expected, a photocatalytic CO_2 reduction experiment was carried out. The catalytic ability of the Ru(II)–Co(III) system was shown to be almost the same as the corresponding intermolecular systems with the improved CO/H_2 selectivity, showing that the Co(III) polypyridyl complex was as effecticve as the Co(II) species for a catalytic center.

Photochemically active polypyridyl complexes have attracted much attention recently.[1] Especially, $[Ru(bpy)_3]^{2+}$ [bpy: 2,2′-bipyridine] has been widely studied because of its long-lived metal-to-ligand charge transfer (MLCT) excited state and the ability to cause an easy electron transfer reaction.[2] Polynuclear systems incorporating the $Ru(bpy)_3{}^{2+}$ moiety are of interest since they construct efficient intramolecular electron or energy transfer systems[3] and many kinds of multicomponent systems (often called 'supramolecular species') have been designed and studied in terms of their photo and/or redox properties.[4] For example, Barigelletti et al. reported the photophysical properties of rodlike dinuclear Ru/Ru and Ru/Os complexes.[5] Other heteronuclear complexes such as Ru/Co, Ru/Rh, Ru/Ir, Ru/Mn, or Ru/Pt complexes also have been investigated by several research groups.[6] Most studies have focused on their basic photophysical or photochemical properties.[7] Recently these polynuclear complexes have been used for functional materials[8] such as photochemical molecular devices[9] or metallopolymers containing the $Ru(bpy)_3{}^{2+}$ moiety,[10] however, there are few reports on the photochemical reactions using these systems so far.

On the other hand, many studies on the use of two-component systems composed of a photosensitizer and a catalyst for photochemical reactions have been reported.[11] Especially, considerable effort has been devoted to develop effective catalysts for reduction of CO_2 in view of the use of light energy.[11d,11e,11f] Lehn et al. have reported the systems of $[Ru(bpy)_3]^{2+}$ as a photosensitizer and Co^{2+} salts or complexes as a catalyst for photoreduction of CO_2 to CO (accompanied by H_2 evolution) for the first time.[12]

Although there are some reports on the mechanism and kinetics of photochemical CO_2 reduction by metal complexes,[13] there seems to be great room for improvement of efficiency and lifetime of the catalyst from the practical viewpoint. Recently, a few dinuclear complexes, in which there is interesting intramolecular electron transfer from the photosensitizer to the catalytic site, have been proposed to increase the reaction efficiency.[6c,14] Kimura et al. reported a hybrid molecule $[Ru(bpy)_2(bpy\text{-}cyclam\ Ni)]^{4+}$, [cyclam: 1,4,8,11-tetraazacyclododecane] in which the CO_2 reduction site, $[Ni(cyclam)]^{2+}$, was covalently attached to a photosensitizer $[Ru(bpy)_3]^{2+}$.[14b] They concluded that the hybrid complex may be a more useful photocatalyst than the separate system in the long run. However the effectiveness of such systems on the photoreduction of CO_2 is still controversial.[13] For example, Fujita et al. implied that a difunctional polynuclear complex may not be effective for the photoreduction of CO_2 because the chemical reduction process is much slower than the photo-absorption or the electron-transfer process.[13a] Furthermore, polynuclear complexes containing a Co component, which seems more effective than Ni complex as a photocatalyst,[12,13a,14,15] have not been reported.

To further investigate the validity of polynuclear complexes as photocatalytic systems for CO_2 reduction, we designed novel Ru–Co and Ru–Ni dinuclear complexes covalently connected by bisphenanthroline ligands. Catalytic features of the monomeric Co and Ni bipylidine complexes on CO_2 photoreduction have been studied.[11b,12] Here, we report the synthesis of the heterodinuclear complexes and studied their photochemical and electrochemical properties. The photoreduction of CO_2 using these complexes was also investigated.

Results and Discussion

Synthesis of the Dinuclear Complexes. The synthetic route of the bridging ligands and their complexes is summa-

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rized in Scheme 1. Two bridging ligands, bisphenanthroline **1** were prepared by the reported method.[15] An excess of bisphenanthroline ligands **1** were reacted with $[RuCl_2(bpy)_2]$ in MeOH. After removing the unreacted ligand and the homodinuclear complex by alumina column chromatography, mononuclear Ru complex **2** were obtained and characterized by NMR and FAB-Mass or ES-Mass spectroscopies. For example, the ^{1}H NMR spectrum of **2b** in CD_3CN showed two sets of doublets at 9.1 and 8.9 ppm, which were assigned to the aromatic protons at the 2- and 9-positions of the uncoordinated, 'free', phenanthroline moiety.

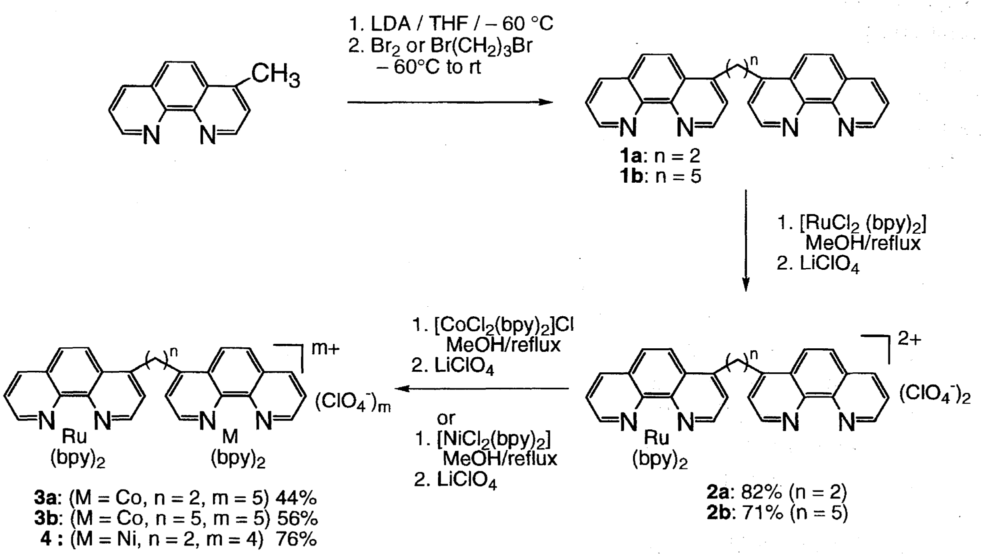
These mononuclear Ru complexes, which have an open chelating site, are useful synthetic intermediates for heterodinuclear complexes. Starting from **2**, we synthesized of the Ru–Co or Ru–Ni dinuclear complexes **3** and **4**. In the case of the Ru–Co dinuclear system, we isolated **3** as the Ru(II)–Co(III) complexes because Co(II) polypyridyl complexes are unstable and are difficult to characterize due to their paramagnetic character.

Though Lehn et al. used some Co(II) species as catalysts in the intermolecular CO_2 photoreduction experiments, they suggested that the Co(I) species formed by electron transfer from the excited $[Ru(bpy)_3]^{2+}$ reduces CO_2 to CO and the oxidation state of Co changes to Co(III). Then it is reduced back to Co(I) via Co(II) by an unknown reduction process to complete the catalytic cycle.[12] Furthermore, in the case of using the cyclam-Co as a photocatalyst, it was also reported that the Co(I) species was the intermediate.[13b] Based on this hypothetical catalytic cycle, we thought that a Co(III) species should be usable as the catalytic site of **3**. The dinuclear complexes **3** and **4** were prepared by the reaction of **2** with $[CoCl_2(bpy)_2]Cl$[16] or $[NiCl_2(bpy)_2]$,[17] respectively. They were purified by alumina column chromatography.

The ^{1}H NMR spectra of **3** and **4** were rather complicated because of containing some diastereomers, however, the spectra assigned to aromatic protons of free phenanthroline moiety of **2** disappeared and the spectra of the bridging methylene protons became more simple than those of **2**. In the FAB-Mass spectrum on Ru–Ni dinuclear complex **4**, the sequential loss of ClO_4 counterion was observed while the dinuclear framework was kept intact. In contrast, neither Ru–Co dinuclear complexes **3** gave similar fragmentation, and the spectra were almost the same as those of mononuclear complexes **2**. However, from the Es-Mass spectroscopy, we did observe the fragmentations due to the loss of ClO_4. These facts indicated that Ru–Co dinuclear complex was thermally less stable than Ru–Ni one.

Absorption and Emission Studies. The absorption and emission spectra of the complexes were recorded in CH_3CN and their data are summarized in Table 1. All spectra showed the metal-to-ligand charge-transfer (MLCT) bands in the visible region as seen for $[Ru(bpy)_3]^{2+}$. The lowest-energy charge-transfer bands, attributable to the Ru–bpy transition, were little affected by the intramolecularly attachment of a Co(III) or Ni(II) moiety, which indicated that the Ru(II) and the Co(III) or Ni(II) have no electronic interaction. No absorption band due to the Co(III) nor Ni(II) moiety was observed, so their molar absorption coefficients were negligible compared with that of the $Ru(bpy)_3{}^{2+}$ moiety.

The emission spectra were measured for the complexes **2**, **3**, and **4** in CH_3CN together with the reference complexes, $[Ru(bpy)_3]Cl_2$ and $[Co(bpy)_3](ClO_4)_3$[18] $[Ni(bpy)_3](ClO_4)_2$.[18] They were excited at 450 nm, which was the MLCT absorption maximum observed by the absorption measurement for the Ru complexes. Though $[Co(bpy)_3]^{3+}$ and $[Ni(bpy)_3]^{2+}$ did not show emission since it did not absorb the light in this wavelength range, other complexes containing the $Ru(bpy)_3{}^{2+}$ moiety gave emissions around 610 nm as $[Ru(bpy)_3]^{2+}$. The relative emission intensities of the dinuclear complexes, **3a**, **3b**, and **4**, were reduced to 30—47% of those of mononuclear complexes, **2a** and **2b**, respectively. Though the excited state of the $Ru(bpy)_3{}^{2+}$ moiety in **3** should have been quenched by the intramolecularly attached $Co(bpy)_2{}^{3+}$ and $Ni(bpy)_2{}^{2+}$ moieties as observed by



Scheme 1.

Table 1. Absorption and Emission Spectral Data for Complexes in CH_3CN[a)]

Compound	Absorption λ_{max}/nm ($\varepsilon/10^4$ M^{-1} cm^{-1})			Emission[b)] λ_{max}/nm
$[Ru(bpy)_3]Cl_2$	451 (1.51)	286 (8.20)		615
$[Co(bpy)_3](ClO_4)_3$[18)]		319 (2.54)	307 (3.46)	c)
$[Ni(bpy)_3](ClO_4)_2$[18)]		306 (4.10)	297 (4.52)	c)
2a	452 (1.80)	285 (8.40)	268 (7.80)	613
2b	450 (1.66)	286 (7.15)	265 (9.18)	618
3a	451 (1.86)	284 (10.1)	268 (8.92)	614
3b	451 (2.05)	284 (11.3)	266 (11.0)	618
4	451 (1.87)	287 (10.1)	269 (12.5)	616

a) All experiments were carried out using 1×10^{-5} M of complexes at room temperature.
b) Excitiation wavelength was 450 nm. c) No emission was observed.

some research groups,[6a,19)] our dinuclear complexes were not quenched completely. On the other hand, the emission due to the Co(III) or Ni(II) moiety was negligible in this range (500—800 nm) as neither of them absorbed light around 450 nm. The reason for this incomplete quenching phenomenon could be that the observed emission spectra were caused by the Ru(II) species produced by the dissociation of $Co(bpy)_2{}^{3+}$ and $Ni(bpy)_2{}^{2+}$ species from **3** and **4** due to the unstability of these complexes under irradiation.

Electrochemical Studies. The electrochemical data for all the complexes studied in CH_3CN (0.1 M TBAP) are shown in Table 2 (1 M = 1 mol dm^{-3}). A cyclic voltammogram of **3b** is shown in Fig. 1. Three redox potentials were observed at -1.39, -0.10, and $+0.85$ V ($E_{1/2}$, vs. Fc/Fc$^+$) for the Co(II)/Co(I), Co(III)/Co(II), and Ru(III)/Ru(II) couples, which corresponded to those of $[Co(bpy)_3](ClO_4)_3$ and $[Ru(bpy)_3]Cl_2$, respectively. The reduction peaks at -1.78 and -1.91 V were assigned to ligand-localized reduction.[20)] A desorption spike was also observed at -1.70 V and these redox behaviors were similar to those of $[Ru(bpy)_3]Cl_2$[20)] and the mononuclear complex **2**. The other dinuclear complex **3a** also afforded a similar result as **3b**. Thus, comparison of the redox and electronic properties of the dinuclear complex **3** with those of the component complexes described above gave no evidence of interaction between the ruthenium and the cobalt moieties of **3** in the ground state.

The redox potential of the excited state *Ru(II) in **3b** can be calculated on the basis of the ground state redox potential and the MLCT excitation energy. The dinuclear complex **3b** has 2.02 eV of the MLCT excited energy calculated from the wavelength of the emission maxima (618 nm) in CH_3CN. As a result, $E_{1/2}$ for *Ru(II)/Ru(III) becomes $E_{1/2}$ (*Ru(II)/Ru(III)) = $E_{1/2}$ (Ru(II)/Ru(III)) $-E_{MLCT} = -1.17$ V vs. Fc/Fc$^+$. The excited state *Ru(II), the oxidation potential of which is -1.17 V as estimated above, is likely to reduce the $Co(bpy)_2{}^{3+}$ part ($E_{1/2}$(Co(III)/Co(II)) = -0.10 V vs. Fc/Fc$^+$). From the electrochemical data and the quenching experiments, it was concluded that photo irradiation of this Ru(II)–Co(III) intramolecular system (**3**) excites the Ru side and the excited energy could be passed to the Co side by electron transfer to change the original oxidation states of Ru(II) and Co(III) to Ru(III) and Co(II), respectively.[6a,19)]

Table 2. Electrochemical Data for Complexes

Complex	$E_{1/2}$ vs. Fc/Fc$^+$ Ru(III)/(II)	Co(III)/(II)	Co(II)/(I)
$[Ru(bpy)_3]Cl_2$	+0.87		
$[Co(bpy)_3](ClO_4)_3$[18)]		−0.09	−1.39
2a	+0.87		
3a	+0.86	−0.07	
2b	+0.84		
3b	+0.85	−0.10	−1.39
4	+0.86		

Potentials were measured in 0.1 M TBAP acetonitrile solutions with carbon electrode. Sweeprate = 100 mV s^{-1}.

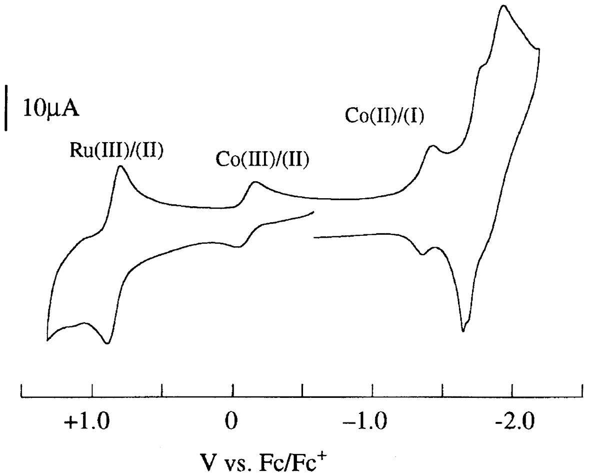


Fig. 1. Cyclic voltammogram of **3b** (1 mM) in CH_3CN (0.1 M TBAP) at a glassy carbon electrode vs. Fc/Fc$^+$ internal reference. Scan rate = 100 mV s^{-1}.

Photoreduction of CO_2. Lehn et al. reported that CO_2 was reduced to CO photochemically by some Co complexes in DMF in the presence of $[Ru(bpy)_3]^{2+}$, although the quantum yield was not as high.[12)] In order to investigate the validity of the intramolecular system, we irradiated our complexes (**2**—**4**) with visible light under similar conditions to those in the literature[12)] and the results are summarized in Table 3. The two component intermolecular systems were also examined by our experimental system for comparison.

Table 3. Generation of CO and H_2 by Photoreduction of CO_2 after 29 h

Run	Catalyst/ Photosensitizer	CO µmol	H_2 µmol	CO/H_2	HCO_2H µmol
1[a]	$CoCl_2/[Ru(bpy)_3]Cl_2$	26	25	1.0	350
2[a]	$[Co^{III}(bpy)_3](ClO_4)_3$[18] $/[Ru(bpy)_3]Cl_2$	130	240	0.6	420
3[a]	$[Co^{III}(phen)_3](ClO_4)_3$[18] $/[Ru(bpy)_3]Cl_2$	81	33	2.5	410
4[a]	$[Ni^{II}(bpy)_3](ClO_4)_2$[18] $/[Ru(bpy)_3]Cl_2$	30	8	3.7	[g]
5[b]	**2a**/$CoCl_2$	86	16	5.4	470
6[c]	**3a**	49	18	2.7	460
7[b]	**2b**/$CoCl_2$	74	24	3.1	480
8[c]	**3b**	77	20	3.8	510
9[c]	**4**	29	29	1.0	[g]
10[d]	$[Co^{III}(bpy)_3](ClO_4)_3$[18] $/[Ru(bpy)_3]Cl_2$	5	23	0.22	85
11[e]	$CoCl_2/[Ru(bpy)_3]Cl_2$	23	47	0.5	
12[f]	$CoCl_2/[Ru(bpy)_3]Cl_2$	27	49	0.6	
13[e]	$[Co^{II}(bpy)_3]Cl_2$ $/[Ru(bpy)_3]Cl_2$	177	127	1.4	

a) 5.0×10^{-4} M of $[Ru^{II}]$ and $[Co^{II}]$ or $[Co^{III}]$, b) 5.0×10^{-4} M of $[Ru^{II}]$ and $CoCl_2$, c) 5.0×10^{-4} M of the catalyst, d) Blank experiment without CO_2, e) Ref. 12: 4.7×10^{-4} M of $[Ru^{II}]$ and 1.5×10^{-3} M of $[Co^{II}]$, f) Ref. 12: 4.7×10^{-4} M of $[Ru^{II}]$ and 1.5×10^{-3} M of $[Co^{II}]$, 3 equiv of bpy ([Ru]/bpy = 1/3) was added, g) Not determined.

Generation of CO and H_2 was observed in each of the experiments. Comparison between Run 1 and the literature data (Run 11)[12] shows the reliability of our photoreaction experiments. Some amount of HCO_2H (about 400—500 µmol) was detected in every experiment and even with no cobalt catalyst (only $[Ru(bpy)_3]Cl_2$ was used). This result is in accord with the literature[22] that a $[Ru(bpy)_2]^{2+}$ complex produced by partial photodecomposition of $[Ru(bpy)_3]^{2+}$ can act as a catalyst of the photoreduction of CO_2 to HCO_2H. The blank experiment without CO_2 gave exclusively H_2 and a trace of CO, which might be generated by decomposition of DMF (Run 10).[21]

Runs 2 and 3 clearly demonstrate that the Co(III) species had comparable CO_2 reduction ability with Co(II) (Runs 1, 11—13) as we expected. This result indicated that the catalytic efficiency did not depend on the valence of the cobalt ion.

On the other hand, in the case of our new complexes **2** and **3** (Runs 5—8), the amount of evolved CO was almost the same with the two component system of $[Ru(bpy)_3]Cl_2$ and $[Co(phen)_3](ClO_4)_3$ (Run 3). At the same time, generation of H_2 due to reduction of H_2O decreased. As a result, the CO selectivity was slightly improved for the dinuclear complexes. The time dependence of CO and H_2 generation is shown in Fig. 2 for $[Co(phen)_3](ClO_4)_3$ (Run 3) and **3b** (Run 8). It turned out that the catalytic efficiencies of **3b** and $[Co(phen)_3](ClO_4)_3$ were almost the same and no marked effects of polynuclear complexes on the generation of CO were observed.

As mentioned above, the quenching of the excited state of the dinuclear complexes **3** was observed from their emission spectra. However the intermolecular quenching was not observed at all for the two-component system of Ru(II) and Co(III) at the same concentration. From this difference in electron transfer efficiency between the intra- and the intermolecular systems, almost the same CO generation of these catalyst systems was unexpected.

Fujita et al. pointed out that the rate-determining step of CO_2 photoreduction by Co complexes was the binding of CO_2 to Co(I)[13] and this process was much slower than the photoinduced electron transfer from excited Ru(II) to a Co(II) complex. Moreover, the concentration of the metal complexes was much higher for the photoreaction experiments than that of the emission spectral measurements due to the low catalytic activity of Co complexes. Under such concentrated conditions, the intramolecular electron transfer must be less important and the slow CO_2 reduction process determines the efficiency of CO generation for both the inter- and intramolecular systems. More diluted conditions or a multi-electron transfer system are necessary to observe the effect of intramolecular electron transfer on polynuclear complexes.

It was reported that the kind of polypyridine ligand of Co(II) affected the CO/H_2 ratio and the CO selectivity was higher for $[Co(phen)_3](ClO_4)_2$ than $[Co(bpy)_3](ClO_4)_2$.[12] The ligands are supposed to affect the coordination site around Co(II) and control its reactivity. In the case of our dinuclear system, the number of bipyridine ligands of **2** and **3** is less than that of $[Co(bpy)_3](ClO_4)_3$ because of having the bridging bisphenanthroline ligand. This might have reduced the generation of H_2. However, we cannot discuss this further in detail since the critical intermediates have not yet been characterized. Comparing the results of Runs 5—8, the

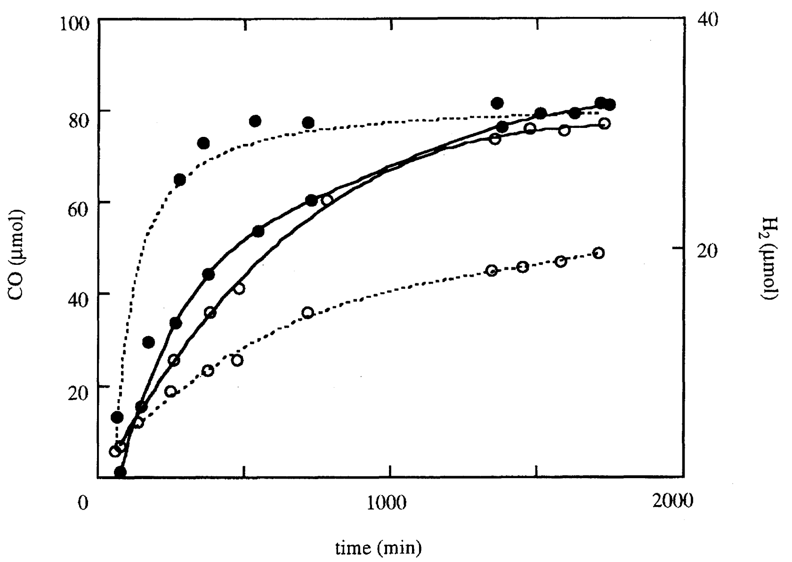


Fig. 2. Photogeneration of CO (—) and H_2 (···) as a function of time. ● 5.0×10^{-4} M of $[Co^{III}(phen)_3](ClO_4)_3$ and $[Ru(bpy)_3]Cl_2$, ○ 5.0×10^{-4} M of **3b** (n = 5), $DMF/H_2O/(HOCH_2CH_2)_3N$ (3 : 1 : 1) saturated with CO_2.

influence of the length of alkyl chain in bisphenanthroline ligands on the reaction was not observed.

We have investigated the durability of **3b** and the two component system under the same irradiation conditions by observing the change of absorption spectra (Fig. 3). Both of them showed a similar change in the MLCT absorption bands, indicating the changes in the coordination sphere around Ru. In the photoreaction mentioned above, generation of HCO_2H was observed. Lehn et al. suggested that a Ru(II) complex after dissociation of a bipyridine ligand should be the intermediate in the HCO_2H production mechanism.[22] Therefore it seems plausible to assume that the spectral change was due to the dissociation of ligands of **3b** and $Ru(bpy)_3Cl_2$ to form the active Ru species for the catalytic CO_2 reduction to HCO_2H.

In the case of the Ru–Ni dinuclear complex **4** (Run 9), the production of H_2 was increased but the amount of evolved CO was the same as that of the two-component system (Run 4) and was half of the Ru–Co system. This result is in accordance with the fact that Co complexes are a better catalyst for photochemical reduction of CO_2 than Ni complexes though the latter are excellent electrocatalysts.[13a] Nevertheless the amount of evolved CO is more than with the dinuclear complex containing cyclam–Ni complex as a catalytic center.[14b] This might be another example showing the ligand effect on CO_2 photoreduction.

In conclusion, we have succeeded in the synthesis of the novel Ru–Co and Ru–Ni dinuclear complexes (**3** and **4**) having bisphenanthroline ligands **1**, which contain a photosensitizer and allow electron transfer. In these complexes, it was found that photo irradiation caused excitation of the Ru(II) side and reduced the Co(III) or Ni(II) side, which should be the catalytic reaction site for CO_2 reduction. In this study we showed that a Co(III) complex becomes a photocatalyst as good as a Co(II) one in combination with the Ru polypyridyl complex. If it is assumed that only Co(I) is effective for CO_2 reduction,[13b] these results support the mecahnism proposed[12] that a Co(III) species is involed in the catalytic cycle.

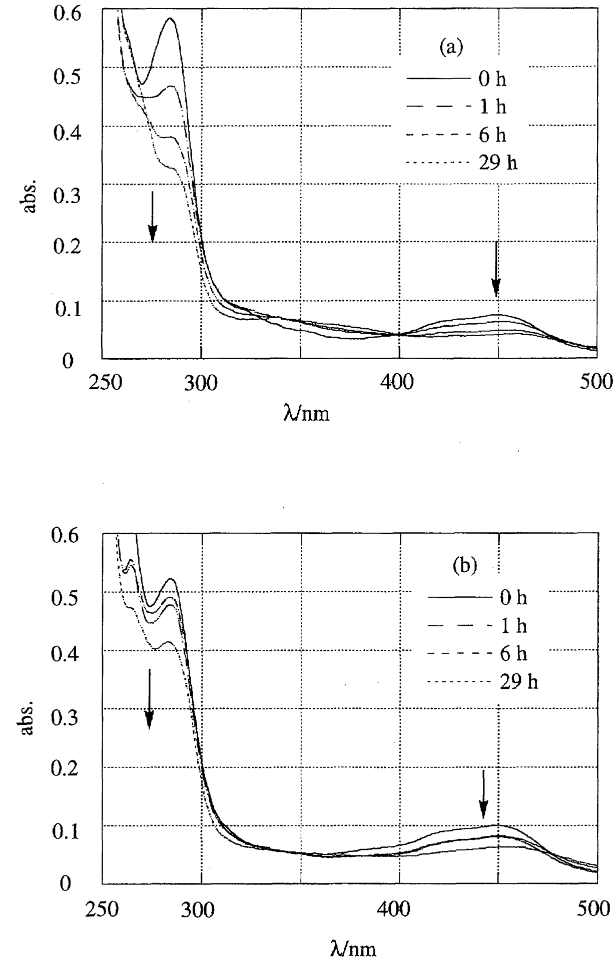


Fig. 3. The changes of absorption spectra of $[Ru(bpy)_3]Cl_2/[Co(phen)_3](ClO_4)_3$ (a) and **3b** (b) leading to generation of CO by reduction of CO_2.

The effectiveness of polynuclear complexes in photoreduction of CO_2 was also examined. Although effective intramolecular electron transfer was observed in the spectroscopic study of dinuclear complexes, the same effect was not seen for photoreduction of CO_2 except for the improvement of the CO/H_2 selectivity. A much higher concentration for the photoreduction experiments was expected to be the reason. At the same time production of HCO_2H was observed. The detailed mechanism that is applicable for both CO and HCO_2H generation should be further investigated.

Experimental

All the synthetic reactions were carried out under a nitrogen atmosphere. Melting points were measured on a Mettler FP62 and were uncorrected. Absorption and luminescence spectral measurements were done using a JASCO V-550 spectrometer and a Hitachi F-4500 spectrofluorimeter, respectively. ^{1}H NMR spectra were measured at 300 MHz in CD_3CN on a Varian Gemini 300 BB spectrometer, using tetramethylsilane (TMS) as an internal standard. J-values are given in Hz. High resolution, FAB, and electrospray mass spectrometry were done with a Hitachi M-80B, a JEOL JMS-DX303, and a Micromass QUATTRO II spectrometer, respectively. Elemental analysis was carried out by using a Eager 200 instrument. Unless stated, commercial grade chemicals were used without further purification.

1,2-Bis(1,10-phenanthrolin-4-yl)ethane (**1a**) was prepared by the reported method.[15)]

Preparation of 1,5-Bis(1,10-phenanthrolin-4-yl)pentane (1b). This compound was synthesized by a method similar to that for **1a** using 1,3-dibromopropane. Purification was done by recrystallization from methanol; yield 50%. Mp > 270 °C (decomp). ^{1}H NMR ($CDCl_3$) δ = 9.20 (d, 2H, J = 2.7 Hz), 9.08 (d, 2H, J = 4.5 Hz), 8.01 (d, 2H, J = 9.1 Hz), 7.79 (d, 2H, J = 9.1 Hz), 7.65 (dd, 2H, J = 4.3, 9.1 Hz), 7.62 (dd, 2H, J = 4.3, 9.1 Hz), 7.45 (d, 2H, J = 4.6 Hz), 3.16 (t, 4H, J = 7.7 Hz), 1.89 (m, 4H), 1.63 (m, 2H). HRMS Calcd for: M, 428.2000. Found: m/z 428.1983.

Preparation of Mononuclear Complex (2a). To a MeOH solution (200 ml) of 1,5-bis(1,10-phenanthrolin-4-yl)ethane (**1a**) (180 mg, 0.47 mmol) was added 50 ml of MeOH solution of $[RuCl_2(bpy)_2]\cdot 2H_2O$ (160 mg, 0.31 mmol) dropwise over 1 h. After this was refluxed for about 4 h, the resulting mixture was evaporated to give a dark red solid, which was dissolved in 50 ml of water. To this solution, dropwise addition of lithium perchlorate (99 mg, 0.93 mmol) in water produced orange precipitates, which were purified by column chromatography on alumina with CH_3CN/H_2O/sat. KNO_3 aqueous solution (v/v/v = 100/10/1) as an eluate. Orange product was obtained in 82% yield (270 mg). Mp > 300 °C (decomp). Anal. Calcd for $C_{46}H_{34}N_8O_8Cl_2Ru\cdot 2H_2O$: C, 53.39; H, 3.70; N, 10.83%. Found: C, 53.00; H, 3.51; N, 10.53%. FAB-mass: 899 $[M-ClO_4]^+$. ^{1}H NMR (CD_3CN) δ = 9.10 (dd, 1H, J = 1.7, 4.3 Hz), 8.81 (d, 1H, J = 4.5 Hz), 8.61—7.20 (m, 28H), 3.79 (t, 2H, J = 7.6 Hz), 3.69 (t, 2H, J = 7.2 Hz).

Preparation of Mononuclear Complex (2b). This compound was synthesized following the same method as that for **2a** starting from **1b**. Yield 71%. Mp > 300 °C (decomp). Anal. Calcd for $C_{49}H_{40}N_8O_8Cl_2Ru$: C, 56.54; H, 3.87; N, 10.77%. Found: C, 56.33; H, 3.90; N, 10.68%. FAB-mass: 941 $[M-ClO_4]^+$. ^{1}H NMR (CD_3CN) δ = 9.07 (dd, 1H, J = 1.7, 4.3 Hz), 8.91 (d, 1H, J = 4.5 Hz), 8.60—7.18 (m, 28H), 3.26 (t, 2H, J = 7.7 Hz), 3.20 (t, 2H, J = 7.7 Hz), 1.90—1.75 (m, 4H), 1.65—1.50 (m, 2H).

Preparation of Ru–Co Dinuclear Complex (3a). Mononuclear complex **2a** (100 mg, 0.10 mmol) was reacted with $[CoCl_2(bpy)_2]Cl$ (53 mg, 0.10 mmol)[16)] in 80 ml of MeOH. After refluxing for about 3 h, the resulting mixture was evaporated to give a dark red solid, which was dissolved in 10 ml of water. To this solution, dropwise addition of lithium perchlorate (100 mg, 1.0 mmol) in water produced red precipitates, which were purified by column chromatography on alumina with CH_3CN/H_2O/sat. KNO_3 aqueous solution (v/v/v = 100/10/1) as an eluate. A dark red product was obtained in 44% yield (74 mg). Mp > 300 °C (decomp). Anal. Calcd for $C_{66}H_{50}N_{12}O_{20}Cl_5RuCo\cdot 2CH_3OH$: C, 47.14; H, 3.37; N, 9.70%. Found: C, 47.50; H, 3.30; N, 9.25%. ES-mass: 1156 $[M-(bpy)_2-ClO_4-HClO_4]^{2+}$. ^{1}H NMR ($CD_3CN$) δ = 9.03—7.17 (m, 46H), 3.90—3.70 (bs, 4H).

Preparation of Ru–Co Dinuclear Complex (3b). This compound was synthesized following the same method as for **3a** starting from **2b**. Yield 56%. Mp > 300 °C (decomp). Anal. Calcd for $C_{69}H_{56}N_{12}O_{20}Cl_5RuCo$: C, 48.45; H, 3.30; N, 9.83%. Found: C, 48.70; H, 3.45; N, 9.33%. ES-mass: 1611 $[M-ClO_4]^+$. ^{1}H NMR (CD_3CN) δ = 9.10—7.20 (m, 48H), 3.40—3.20 (m, 4H), 1.90—1.85 (m, 4H), 1.85—1.65 (m, 2H).

Preparation of Ru–Ni Dinuclear Complex (4). This compound was synthesized following the same method as that for **3a** using **2a** and $Ni(bpy)_2Cl_2$.[17)] Yield 56%. Mp > 300 °C (decomp). Anal. Calcd for $C_{66}H_{50}N_{12}O_{16}Cl_4RuNi\cdot 2H_2O$: C, 49.40; H, 3.39; N, 10.47%. Found: C, 49.65; H, 3.28; N, 10.15%. FAB-mass: 1468 $[M-ClO_4]^+$. ^{1}H NMR (CD_3CN) δ = 8.70—7.10 (m, 46H), 4.40—3.70 (bs, 4H).

Electrochemical Measurements. Cyclic voltammetric measurements were performed with a BAS100B/W instrument in CH_3CN with 0.10 M tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte, and the solution was bubbled with pure Ar gas saturated with CH_3CN. A three-electrode system was used: a glassy carbon electrode as the working electrode, a Pt wire as the counter electrode, and an Ag/Ag^+ electrode (BAS Co.) as the reference electrode. Ferrocene was used as an internal reference. The cyclic voltammograms, with a scan rate of 100 $mV\,s^{-1}$, were evaluated graphically. The concentrations of all sample solutions were kept at 1.0 mM.

Photoreduction of CO_2. The photoreduction system consisted of an Ushio xenon short arc lamp UXL500D-O (500 W), IR (> 750 nm) and UV (< 400 nm) cut-off filters, and a gastight photolysis photoreaction vessel. The complexes were dissolved in 30 ml of the solvent ($DMF/H_2O/(HOCH_2CH_2)_3N$; v/v/v = 3/1/1). These reaction mixtures were bubbling with CO_2 for 20 min before photoirradiation. All solutions were stirred continuously during irradiation at 40 °C. Gas sample (0.2 ml), taken at various intervals with a gastight syringe through a septum, were analyzed for H_2 by a TCD detector using a Porapak Q 80/100 at 70 °C and for CO by a FID detector using an activated carbon 60/80 at the same temperature on a GL Science GC390 gas chromatograph instrument. The CO peak was identified by comparison of the retention time with that of standard CO gas (GL Sciences). CO was measured using the working curve which had been previously obtained using standard CO gas. After the photoirradiation formic acid produced was analyzed by an HPLC using an anion-exclusion column (Tosoh TSKgel SCX, 7.8 mm i.d. ×30 cm) with an aqueous phosphate solution as an eluent (2×10^{-3} M), and detection was done with a UV (λ = 210 nm) detector.[13d)] The conditions used in each experiment are given in Table 3.

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