A New Nickel(II) Cyclam (Cyclam = 1,4,8,11-Tetraazacyclotetradecane) Complex Covalently Attached to Ru(phen)$_3^{2+}$ (phen = 1,10-Phenanthroline). A New Candidate for the Catalytic Photoreduction of Carbon Dioxide

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Received May 19, 1992

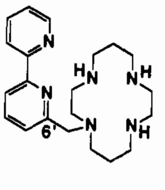
A bifunctional supramolecular complex Ru(phen)$_2$(phen-cyclam-Ni)(ClO$_4$)$_4$ (**6**) (phen-cyclam = 1-(1,10-phenanthrolin-5-ylmethyl)-1,4,8,11-tetraazacyclotetradecane) has been newly synthesized, and its spectroscopic, redox properties, and catalytic behavior in the photoreduction of CO$_2$ have been examined. The new binuclear complex **6** is shown to be an interesting hybrid molecule composed of a Ru(phen)$_3^{2+}$ (phen = 1,10-phenanthroline) subunit, which acts as a photosensitizer, and a Ni(cyclam)$^{2+}$ catalytic reduction site.

Introduction

Activation and reduction of CO$_2$ is one of the major targets in artificial photosynthesis. Appreciable efforts[1,2] have been devoted to the design of catalytic systems incorporating a photosensitizer (e.g. Ru(bpy)$_3^{2+}$, bpy = 2,2′-bipyridine), an electron donor (e.g. ascorbic acid), and a transition-metal complex for the CO$_2$ reduction site. However, to date, only modest success has been achieved.[3,4]

The system using Ru(bpy)$_3^{2+}$ with Co^{2+} ion as a homogeneous combination catalyst for the photoreduction of CO$_2$ to CO (accompanied by H$_2$ evolution) was reported by Hawecker et al.[4a] Grant et al. reported another system using Ru(bpy)$_3^{2+}$ and Ni(cyclam)$^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane), and ascorbate as the sacrificial electron donor agent.[4c] However, this photosensitizer molecule cannot sustain long irradiation due to decomplexation, i.e. the loss of a bpy ligand from Ru(bpy)$_3^{2+}$. These systems also generate a considerable amount of H$_2$ as a side reduction product from water.

Recently, we communicated[5] a hybrid molecule Ru(bpy)$_2$(bpy-cyclam-Ni)$^{4+}$ (**3**), in which the CO$_2$ reduction site Ni(cyclam)$^{2+}$ is covalently attached to a photosensitizer Ru(bpy)$_3^{2+}$. Its X-ray crystal structure and multi-redox properties have been characterized. Our aim was to improve the catalytic efficiency by combining the two different functions into one molecule (Scheme I). However, **3** does not exhibit much catalytic activity in photochemical CO$_2$ reduction mainly due to the unusual configuration of the Ni(cyclam)$^{2+}$ subunit.[5] In addition, the Ru(bpy)$_3^{2+}$ subunit was found to dissociate readily on irradiation.[6]



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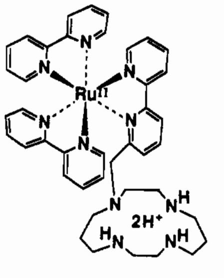

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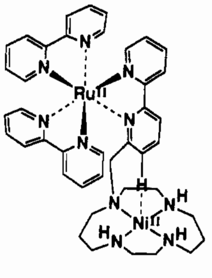

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(6) An aqueous solution of **3** containing 1 M ascorbic acid readily experienced absorption spectral changes from λ_{max} 450 nm to 485 nm with an isosbestic point at 465 nm under photoirradiation, indicating the changes in the coordination sphere around Ru.

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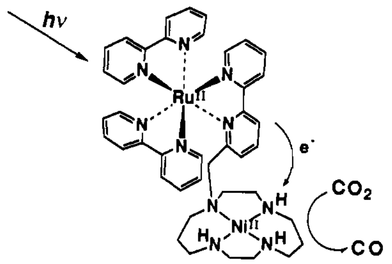
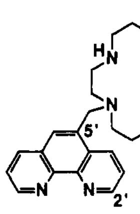
Scheme I



In tris(polypyridine)ruthenium complexes, a substituent (e.g. methyl group) introduced at a sterically crowded position (e.g. 6′-position of bpy (see **1**) or 2′-position of phen (see **4**)) often serves to reduce the photoenergy absorption, emission quantum yields, and/or emission lifetimes.[7] The increase in the Ru–N bond length as seen in **3**, as evidenced by the X-ray structure,[5] facilitates the internal conversion to the low-energy ligand field state (^{3}LF) of Ru.[8] In addition, the very short emission lifetime due to the energy transfer to Ni ion[8] may also cause less catalytic reactivity.

Accordingly, we have redesigned a new hybrid molecule phen-pendant cyclam **4** (phen = 1,10-phenanthroline) and its supramolecular RuNi complex **6**. In ligand **4**, cyclam links with phenanthroline at the 5′-position. The new RuNi complex **6** was found to be photochemically much more stable than Ru(phen)$_3^{2+}$ complex on irradiation, exhibiting improved photocatalytic activity in the reduction of CO_2 over **3** and the intermolecular combination of Ru(phen)$_3^{2+}$/Ni(cyclam)$^{2+}$. Herein we report the synthesis and spectroscopic and electrochemical properties as well as the photocatalytic behavior of this new hybrid ligand and its RuNi dinuclear complex.



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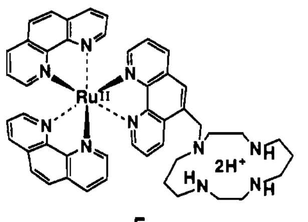

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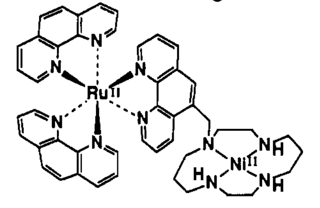

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Experimental Section

General Methods. All the starting materials for synthesis were obtained commercially and used without further purification unless otherwise stated. Gases of analytical grade were employed. ^{1}H NMR spectra were recorded on a JEOL GX-400 spectrometer (400 MHz, 25 °C, in D_2O, with 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid, sodium salt, as an internal reference). IR was taken on a Shimadzu FTIR-4200. For TLC analysis, Merck precoated TLC plates (silica gel 60 F_{254}) were used. Ru(bpy)$_2$(bpy-cyclam-Ni)(ClO$_4$)$_4$·2H$_2$O (**3**) (bpy-cyclam = 1-(2,2′-bipyridin-6-ylmethyl)-1,4,8,11-tetraazacyclotetradecane),[5] cyclam,[9] and Ru(phen)$_2$Cl$_2$[10] were synthesized according to the literature. *N*-Bromosuccinimide (NBS) was recrystallized from distilled water. All the other reagents used in CO_2 reduction experiments or other analyses were of analytical grade.

Warning! All the perchlorate salts used in this study may be explosive and are potentially hazardous.

Synthesis of 1-(1,10-Phenanthrolin-5-ylmethyl)-1,4,8,11-tetraazacyclotetradecane (4, phen-cyclam). 5-Methyl-1,10-phenanthroline (**7**, 385 mg, 2 mmol), NBS (356 mg, 2 mmol), and azobis(isobutyronitrile) (AIBN, 20 mg) were dissolved in 20 mL of CCl_4. The resulting reaction mixture was heated at reflux for 3 h. After filtration and evaporation, the residue was redissolved in H_2O and extracted with several portions of CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$ and evaporated to dryness to obtain 5-(bromomethyl)-1,10-phenanthroline (**8**) as a colorless solid. A solution of the crude product in 20 mL of deoxygenated dimethyl formamide (DMF) was added dropwise to a solution of cyclam (600 mg, 3 mmol) in 30 mL of DMF at 90 °C. The resulting reaction mixture was heated at 90 °C for 5 h under Ar. Unreacted cyclam precipitated and was filtered off and the filtrate evaporated to dryness. The residue was purified by column chromatography on silica gel (Wakogel C-300) by eluting with CH_2Cl_2/CH_3OH/28% *aqueous* NH_3(50:7:1). The obtained free form of **4** as an oil was transformed into its crystalline pentahydrochloride salt by treating it with a slight excess of concentrated HCl in C_2H_5OH (230 mg, 24%). ^{1}H NMR (D_2O): δ 1.74 (2H, quintet), 2.05 (2H, quintet), 2.78–3.24 (16H, m), 4.19 (2H, s), 7.86 (1H, s), 7.88–7.91 (1H, m), 7.94–7.98 (1H, m), 8.51 (1H, d, *J* = 8.3 Hz), 8.66 (1H, d, *J* = 8.3 Hz), 9.10–9.11 (1H, m), 9.14–9.15 (1H, m). IR (KBr pellet): 3435, 2963, 2787, 2501, 1618, 1597, 1543, 1471, 1456, 727 cm^{-1}. Anal. Calcd for $C_{23}H_{32}N_6$·5HCl·3H$_2$O: C, 43.93; H, 6.89; N, 13.36. Found: C, 43.79; H, 6.83; N, 13.17.

Syntheses of Ru(phen)$_2$(phen-cyclam-H$_2$)(ClO$_4$)$_4$·3H$_2$O (5) and Ru(phen)$_2$(phen-cyclam-Ni)(ClO$_4$)$_4$·2H$_2$O (6). An C_2H_5OH (50 mL) solution of the free form of **4** (393 mg, 1 mmol), obtained through Amberlite IRA 400 ion exchange treatment, was added dropwise to a solution of Ru(phen)$_2$Cl$_2$ (532 mg, 1 mmol) in 25 mL of H_2O under Ar. The resulting reaction mixture was heated at reflux for 5 h. The reaction was monitored by TLC (Merck No. 5567, eluent 10% NaCl/CH_3OH/28% *aqueous* NH_3 = 10:2:1, R_f = 0.54, bright orange color). After filtration and evaporation, the resulting red residue was poured into H_2O and adjusted to ~pH 3 with $HClO_4$ aqueous solution. Upon the addition of an excess amount of $NaClO_4$, an orange powder immediately precipitated, to which acetone was added to dissolve it. The solvent was partially removed by slow evaporation to obtain Ru(phen)$_2$(phen-cyclam-H$_2$)(ClO$_4$)$_4$·3H$_2$O (**5**) as red needles (800 mg, 60%). ^{1}H NMR (D_2O): δ 1.71–1.81 (2H, m), 2.10–2.30 (2H, m), 2.70–3.40 (16H, m), 4.35 (1H, d, *J* = 15.2 Hz), 4.56 (1H, d, *J* = 15.2 Hz), 7.63–7.78 (6H, m), 8.11–8.18 (6H, m), 8.23–8.28 (5H, m), 8.60–8.66 (5H, m), 8.83 (1H d, *J* = 9.0 Hz). IR (KBr pellet): 3441, 3119, 2963, 1630, 1427, 1121, 1100, 1090, 845, 721, 625 cm^{-1}. Anal. Calcd for $C_{47}H_{56}N_{10}O_{19}Cl_4Ru$: C, 43.16; H, 4.32; N, 10.71. Found: C, 43.39; H, 4.41; N, 10.81.

For the preparation of Ni^{II} complex **6**, NiCl$_2$·6H$_2$O (238 mg, 1 mmol) was added to a solution of the free form of **5** in 10 mL of CH_3OH, obtained as described above. The reaction mixture was heated at reflux for 30 min. The reaction was monitored by TLC (Merck No. 5567, eluent 10% NaCl/CH_3OH/28% *aqueous* NH_3 = 10:2:1, R_f = 0.70, dark orange color). After filtration, about 10 equiv of $NaClO_4$ was added to the filtrate to obtain an orange precipitate, which was collected and purified by recrystallization from H_2O–CH_3CN (or H_2O–acetone) (740 mg, 55%). The ^{1}H NMR spectrum in D_2O showed no distinct signal for the cyclam-original protons probably due to the high-spin nature of Ni^{II} ion in the cyclam cavity. IR (KBr pellet): 3427, 3074, 2939, 1630, 1427, 1141, 1121, 1109, 1091, 847, 721, 625 cm^{-1}. Anal. Calcd for $C_{47}H_{52}N_{10}O_{18}Cl_4RuNi$: C, 41.92; H, 3.89; N, 10.40. Found: C, 41.85; H, 3.80; N, 10.51.

Potentiometric Titration. Aqueous solution (50 mL) of **4**·5HCl·2H$_2$O (1.00 × 10^{-3} M) was titrated with carbonate-free 0.100 M NaOH aqueous solution at 25.00 ± 0.05 °C. pH values were read with an Orion 811 digital pH meter and ionic strength was adjusted to 0.10 with $NaClO_4$. The solution was carefully protected from air by a stream of humidified Ar. The electrode system was calibrated with pH 6.86 standard buffer solution and checked by the duplicate theoretical titration curves of 4.00 × 10^{-3} M HCl with a 0.100 M NaOH solution at 25 °C and *I* = 0.10 M ($NaClO_4$) in low- and high-pH regions.

Electrochemical Measurements. Cyclic voltammetric measurements were performed with a Yanako P-1100 polarographic analyzer at 25.00 ± 0.05 °C in CH_3CN with 0.10 M tetrabutylammonium hexafluorophosphate ((TBA)PF$_6$) or tetrabutylammonium perchlorate ((TBA)-

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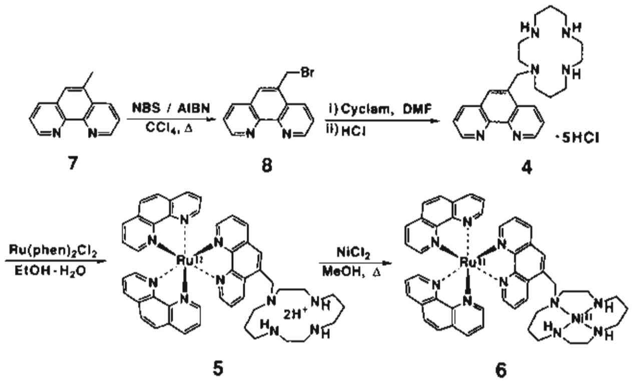
Scheme II



ClO_4) as a supporting electrolyte, and the solution was bubbled with pure Ar gas presaturated with CH_3CN. A three-electrode system was employed: a Pt disk as the working electrode, a Pt wire as the counter electrode, and a Ag/AgCl electrode (Bas Co.) as the reference electrode. The cyclic voltammograms, with a scan rate of 200 mV/s, were evaluated graphically. All of the solutions were kept at 1.0 mM.

Spectroscopic Measurements. Emission spectra were recorded on a modified Shimadzu FR-5000 spectrophotometer. Deoxygenated solutions for emission measurements were prepared by repeated freeze–pump–thaw cycles for the solvent H_2O. UV–vis spectra were recorded on a Hitachi U-3200 double-beam spectrophotometer at 25.0 ● 0.1 °C, using matched quartz cells of 10-mm path length. The emission lifetimes were measured on Horibaa NAES-550 emission lifetime measuring equipment at room temperature using the time-correlated multiphoton counting method. A pulsed Xe lamp was used as a light source. Ar was bubbled through the solution for 20 min before measuring to deoxygenate, and the solution was kept under Ar during the measurement.

Photoreduction of CO_2. The photolysis system consisted of a Ushio xenon short arc lamp UXL500D-0 (500 W), IR cut-off filter (0.5 M $CuSO_4$ aqueous solution with 50 mm of path length), a 350-nm cut-off filter (TOSHIBA UV-35), and a photolysis vessel. The light beam was concentrated with a converging lens. The photolysis cell was custom-made in order to manipulate degassing and irradiation of the solution and analysis of the gas products. All solutions were stirred continuously and irradiated after deaerating with CO_2 for 1 h. Gas samples (0.5 mL), taken at various intervals with a gastight syringe through a septum and a valve, were analyzed for H_2 on a Shimadzu GC-8A gas chromatograph equipped with a thermal conductivity detector by using a 3 m × 2.6 mm o.d. column packed with 13X-S molecular sieves at 30 °C using N_2 as carrier gas, and for CO on a Shimadzu GC-4CMPF gas chromatograph equipped with a flame ionization detector by using the same column at 50 °C with a Shimadzu MTN-1 methanizer using N_2 as carrier gas. The conditions used in each experiment are given in Table III.

Results and Discussion

Synthesis of Ligand 4. Phen-cyclam (**4**) was synthesized by a method similar to that for bpy-cyclam (**1**) (Scheme II).[5,11] 5-(Bromomethyl)-1,10-phenanthroline (**8**), obtained by the reaction of 5-methyl-1,10-phenanthroline (**7**) with equivalent NBS in CCl_4 in the presence of AIBN, was treated with a slight excess of cyclam in DMF at 90 °C for 5 h under Ar to obtain phen-cyclam (**4**). This functionalized cyclam was purified by silica gel column chromatography with an eluent system of CH_2Cl_2/CH_3OH/28% *aqueous* NH_3 (50:7:1) and purified by further treatment with HCl in C_2H_5OH to isolate crystalline **4**·5HCl in 24% overall yield.

Protonation Constants. The protonation constants K_1–K_5 of **4** were determined by potentiometric titrations aided by spectroscopic titrations at 25 °C and $I = 0.10$ M ($NaClO_4$). The logarithmic values of protonation constants are 10.89, 8.84, 4.64, 2.10, and <1.5, respectively. From the UV absorption spectral changes at varying pH values, we assign the log K_3 value of 4.64 to the protonation of phenanthroline. The UV absorption maxima for the phenanthroline and its monoprotonated form discretely occur at 277 and 268 nm, respectively, with three isosbestic points at 240, 271, and 296 nm. The log K_3 value of 4.64 is slightly smaller than the log K value of 4.93 for the monoprotonation of 1,10-phenanthroline itself,[12] due to the influence of the proximate diprotonated cyclam.

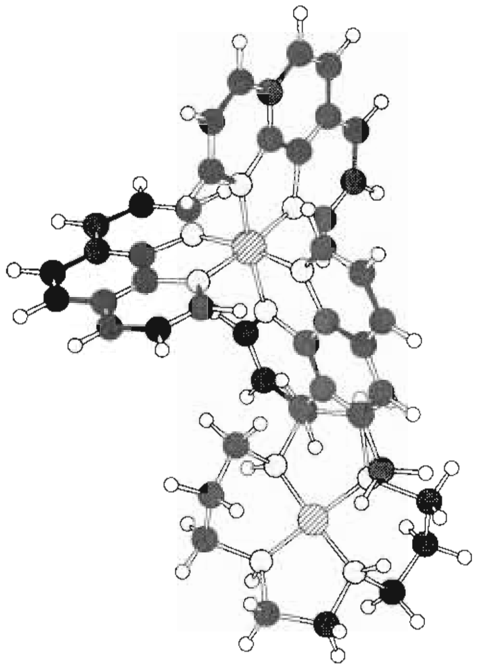


Figure 1. Speculated structure of $Ru(phen)_2(phen\text{-}cyclam\text{-}Ni)^{4+}$ (**6**).

Synthesis of the Binuclear RuNi Complex 6. The binuclear RuNi complex **6** was prepared stepwise from **4** according to a method similar to that used for **3**[5] (see Scheme II). When the free form of **4** and $Ru(phen)_2Cl_2$ were heated at reflux in C_2H_5OH–H_2O (v/v = 2) for 5 h under Ar, a red material was obtained, which was identified as the N_4-diprotonated form, $Ru(phen)_2(phen\text{-}cyclam\text{-}H_2)(ClO_4)_4 \cdot 3H_2O$ (**5**), as red needles. From this mononuclear Ru complex, the heterodinuclear complex **6** was prepared by refluxing **5** with $NiCl_2 \cdot 6H_2O$ in CH_3OH for 30 min. An orange crystalline material was obtained, upon addition of $NaClO_4$, which was identified as $Ru(phen)_2(phen\text{-}cyclam\text{-}Ni)(ClO_4)_4 \cdot 2H_2O$. An analytically pure sample of **6** was obtained by recrystallization from H_2O–CH_3CN or acetone (55% yield).

The ^1H NMR spectrum of **6** revealed the absence (or extreme broadening) of the cyclam proton signals apparently due to the presence of a paramagnetic high-spin Ni^{II}. On the other hand, with the previous $Ru(bpy)_2(bpy\text{-}cyclam\text{-}Ni)^{4+}$ complex, **3**, which shows a well-dissolved NMR spectrum, Ni^{II} is in a diamagnetic low-spin state with the cyclam conformation being the square planar trans I (or *RSRS*) geometry as found by X-ray crystal analysis.[5] In CD_3CN solution, the low spin $Ni(cyclam)^{2+}$ in **3** seems to take two configurations, *RSRS* (trans I) or *RRSS* (trans III) by ^1H NMR. A molecular model for **6**, as predicted in Figure 1, suggests the most likely conformation of cyclam is trans III.[13] The proton signals of the remote phenanthroline rings in **6** are well-resolved, probably without much perturbation from the remote high-spin Ni^{II}. In the case of complex **3** with substituent at the 6′-position of the bpy ring, the steric hindrance by the 6′-methylene bridge caused the unusual trans I cyclam conformation and the distortion of the coordination sphere around Ru, which may have lowered the complex stability.[5] However, such a serious steric disadvantage may be minimized by bridging at the 5′-position in the present phenanthroline.

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Table I. Physical Properties of Ru(phen)$_2$L and Ru(bpy)$_2$L′ Complexes

		L			L′ ^{a}		
		phen	(phen-cyclam-H$_2$)$^{2+}$	(phen-cyclam-Ni)$^{2+}$	bpy	(bpy-cyclam-Ni)$^{2+}$	Ni(cyclam)$^{2+}$
UV–vis		222 (4.95)	222 (4.88)	222 (4.98)	243 (4.41)	243 (4.49)	
λ_{max}, nm (log ϵ)^b		262 (5.06)	262 (4.99)	262 (5.04)	286 (4.92)	287 (4.86)	
		421 (4.26)	419 (4.21)	420 (4.25)			
		447 (4.28)	449 (4.21)	447 (4.28)	453 (4.15)	445 (4.09)	
$E_{1/2}$, V^c	Ru	+0.99	+0.99	+1.00	+1.29	+1.39	
		−1.70^d	−1.72^d	−1.72^d	−1.33	−1.33	
		−1.83^e	−1.83^e	−1.88^e	−1.52	−1.54	
		−2.17	−2.23	−2.13	−1.78	−1.81	
	Ni			+1.26 (Ni^{III}/Ni^{II})		f	+0.73 (Ni^{III}/Ni^{II})
				−1.56 (Ni^{II}→Ni^{I})^d		−1.00 (Ni^{II}/Ni^{I})	−1.74 (Ni^{II}/Ni^{I})

^{a} Reference 5. ^{b} In H$_2$O at 25 °C. ^{c} In CH$_3$CN at 25 °C. Unless otherwise stated, all the values represent half-potentials of reversible or quasi-reversible redox waves. For Ru(phen)$_2$L and Ni(cyclam)$^{2+}$ complexes, V vs Ag/AgCl; for Ru(bpy)$_2$L′ complexes, V vs SCE. See ref 5. ^{d} The value represents the reduction peak potential. A desorption spike was observed on reversal. ^{e} The value represents the reduction peak potential. ^{f} No redox wave was observed for Ni^{III}/Ni^{II} under this condition (>1.4 V).[5]

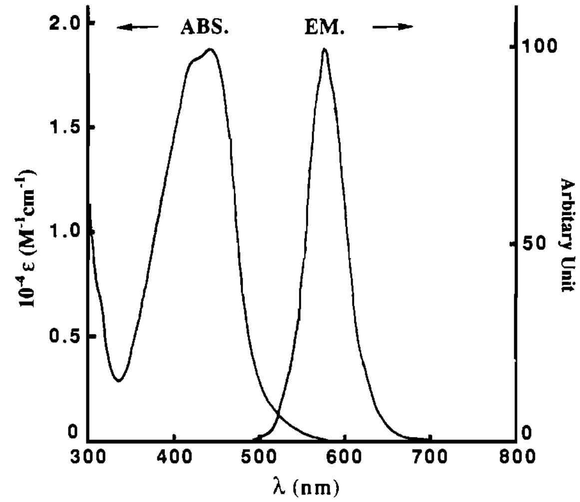

Figure 2. Charge transfer (ABS) and emission spectra (EM) of Ru(phen)$_2$(phen-cyclam-Ni)(ClO$_4$)$_4$·2H$_2$O (**6**) in H$_2$O at 25 °C.

Table II. Emission Properties of Ru Complexes in H$_2$O^a

complex	λ_{max}, nm (Φ_{rel})^b	emission lifetime, ns
Ru(phen)$_3$$^{2+}$	575 (1.0)^c	1200
5	583 (0.90)^c	1340
6	580 (0.05)^c	<10^d
Ru(bpy)$_3$$^{2+}$	625 (1.0)^e	670 (298 K)^f 1920 (165 K)^f
2	622 (0.006)^e	2 (298 K)^f 1200, 170 (165 K)^f
3	622 (0.006)^e	f 850, 54 (165 K)^f

^{a} At 25 °C. [Ru^{2+}] = 5 μM. ^{b} Excitation wavelength was 450 nm. ^{c} Φ_{rel} values are relative emission intensities based on that of Ru(phen)$_3$$^{2+}$ or Ru(bpy)$_3$$^{2+}$ complex. ^{d} The detailed emission decay was not pursued due to limitations of the detection equipment. ^{e} See ref 5. ^{f} Reference 8. In EtOH.

Absorption and Emission Studies with 6. The absorption maxima data of the present Ru complexes are listed in Table I. The absorption spectra of **5** and **6** recorded in H$_2$O at 25 °C are similar to that of Ru(phen)$_3$$^{2+}$ with metal-to-ligand charge-transfer (MLCT) bands in the visible region (Figure 2).[14] The lowest-energy charge-transfer bands [λ_{max} 449 nm (log ϵ 4.21) for **5** and λ_{max} 447 nm (log ϵ 4.28) for **6**], attributable to the Ru → phen transition, are little affected by the intramolecular attachment to a diprotonated or nickel-chelated cyclam. These spectra are also quite similar in CH$_3$CN. No absorption band due to the Ni(cyclam)$^{2+}$ was observed because its molar absorption coefficient is too small compared with that of the Ru(phen)$_3$$^{2+}$ subunit.

Table III. Generation of CO and H$_2$ in Photoreduction of CO$_2$ by the Reference System, **6**, and **3**

catalyst^a	irradiation, h	vol of CO produced, μL	vol of H$_2$ produced, μL	CO/H$_2$
Ru(phen)$_3$$^{2+}$ + Ni(cyclam)$^{2+}$	1	0.24	0.45	
	4	0.30	1.20	
	24	0.69	1.79	
	44	1.29	2.26	0.57
6	1	0.09	undetected	
	4	0.32	0.16	
	24	1.86	1.02	
	44	3.51	1.39	2.5
3	4	0.11	0.17	0.65

^{a} All experiments contain 5.0 × 10^{-4} M of [Ru^{2+}] and [Ni^{2+}], dissolved in 30 mL of CO$_2$-saturated ascorbate buffer solution (1.0 M, pH = 4). Irradiation was carried out at 25 °C. The experimental errors are within 20%.

The steady-state emission maxima of **6** (λ_{max} 580 nm), when excited at 450 nm, is red-shifted only by 5 nm from 575 nm for Ru(phen)$_3$$^{2+}$ itself in vacuum-degassed H$_2$O at 25 °C (Figure 2 and Table II), indicating that a substituent at the 5′-position of phen hardly affects the coordination structure of Ru. However, the relative emission intensity of **6** is drastically reduced to ca. 1/20 of that of Ru(phen)$_3$$^{2+}$, as seen in **3**. It should be noted that the external addition of 100 equivalents of Ni(cyclam)$^{2+}$ complex did not significantly quench the emission from the MLCT excited state of Ru(phen)$_3$$^{2+}$. Comparing the diprotonated cyclam pendant effect in **5** and **2**, the former **5** only slightly quenched this emission, whereas the latter dramatically decreased the emission quantum yield. Furthermore, in an investigation of the kinetics of the emission decay in H$_2$O at room temperature (Table II), **6** showed a very short emission lifetime of a few nanoseconds (cf. two independent components **3** in EtOH at 165 K, see Table III),[8] whereas Ru(phen)$_3$$^{2+}$ had a much longer lifetime (1200 ns). Detailed analysis of the emission decay of **6** was not pursued due to the very short lifetime and to limitations of the detection equipment. In the case of **2** and **3** with very short lifetimes, the emission decay processes mainly consist of the internal conversion to ^{3}LF of Ru[8] due to the increase in the Ru–N bond length.[5] In contrast, the intramolecularly attached diprotonated cyclam in **5** does not affect the emission decay (Table III). Hence, in complexes **5** and **6** without any coordinative distortion around Ru, such an internal conversion to ^{3}LF is hardly conceivable. The quenching of the excited state of Ru(phen)$_3$$^{2+}$ subunit in **6** is due to the energy transfer to the intramolecularly attached Ni(cyclam)$^{2+}$.

The redox potential of the excited state *Ru^{2+} in **6** may be calculated on the basis of the ground state redox potentials (described later) and the MLCT excited energy: $E_{1/2}$ for *Ru^{2+}/Ru^{3+} = $E_{1/2}$(Ru^{2+}/Ru^{3+}) − E_{MLCT} = −1.15 V vs Ag/AgCl, and

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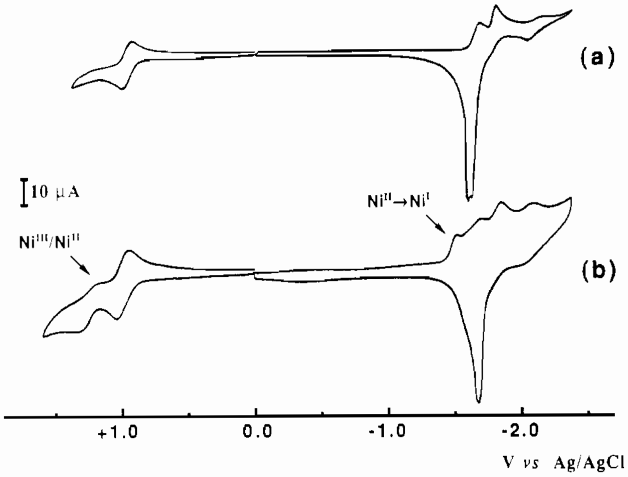

Figure 3. Cyclic voltammograms of (a) $Ru(phen)_3(ClO_4)_2$ and (b) $Ru(phen)_2(phen\text{-}cyclam\text{-}Ni)(ClO_4)_4 \cdot 2H_2O$ (**6**) in CH_3CN (0.1 M $(TBA)PF_6$) at a Pt disk electrode vs Ag/AgCl reference electrode at 25 °C. Scan rate = 200 mV/s.

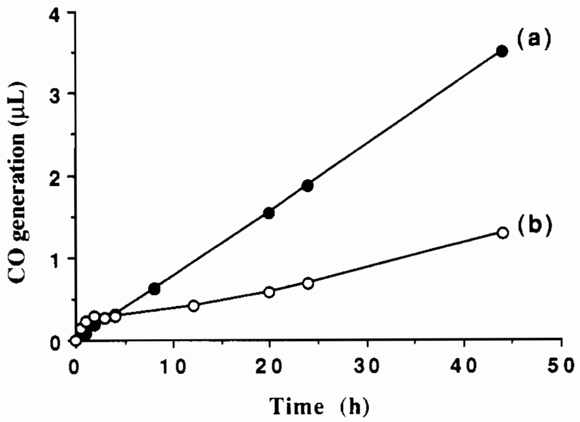

Figure 4. Time course of CO generation for (a) $Ru(phen)_2(phen\text{-}cyclam\text{-}Ni)(ClO_4)_4 \cdot 2H_2O$ (**6**) and (b) the ($Ru(phen)_3^{2+}$ + $Ni(cyclam)^{2+}$) system. Both experiments contain 5.0×10^{-4} M [Ru^{2+}] and [Ni^{2+}], dissolved in 30 mL of ascorbate buffer solution (1 M, pH = 4). The reaction mixtures were irradiated at 25 °C with a 500-W Xe lamp. The experimental errors are within 20%.

$E_{1/2}$ for $^*Ru^{2+}/Ru^+$ = $E_p(Ru^{2+} \rightarrow Ru^+) + E_{MLCT}$ = +0.42 V. Accordingly, the excited state $^*Ru^{2+}$ (its oxidation potential is −1.15 V as estimated above) is unlikely to reduce the $Ni(cyclam)^{2+}$ ($E_{1/2}$ for Ni^{2+}/Ni^+ = −1.56 V) in **6**. We thus conclude that the fast quenching observed for **6** is probably not due to an intracomplex electron transfer, but is rather due to energy transfer to the nickel ion.

Electrochemical Studies. Electrochemical data for all the complexes studied in CH_3CN (0.1 M $(TBA)PF_6$, at 25 °C) are shown in Table I. The cyclic voltammograms of **6** (see Figure 3b) showed two irreversible reduction waves, one quasi-reversible reduction wave, and one quasi-reversible oxidation wave arising from the Ru complex subunit. A desorption spike was also observed on reversal of the second reduction. These redox behaviors are similar to those of $Ru(phen)_3^{2+}$ (Figure 3a).[15] An additional irreversible reduction wave for Ni^{II} to Ni^{I} was observed with **6** at −1.56 V vs Ag/AgCl, being more positive than that for $Ni(cyclam)^{2+}$ ($E_{1/2}$ = −1.74 V). Similarly, the $Ni^{III/II}$ potential of **6**, +1.26 V, is 0.53 V more positive than the value of +0.73 V observed for $Ni(cyclam)^{2+}$. Both shifts are in the consistent direction expected for stabilization of a lower oxidation state of Ni by *N*-alkyl substitution,[16] but this may not necessarily reflect the electrochemical interaction between the intramolecular $Ni(cyclam)^{2+}$ and the $Ru(phen)_3^{2+}$ complex. However, these results may imply that the Ru^+ species, photochemically generated via the excited state $^*Ru^{2+}$ in the presence of electron donor, may become capable of reducing Ni^{II} to Ni^{I}.

Photoreduction of CO_2. The results of CO_2 photoreduction in CO_2-saturated ascorbate buffer solution (pH 4.0) at 25 °C catalyzed by the new complex **6**, the reference system [$Ru(phen)_3^{2+}$ + $Ni(cyclam)^{2+}$], and **3** are summarized in Table III. Irradiation of **6** for 1 h produced only 0.09 μL of CO whereas the reference system generated a higher yield of 0.24 μL. However, after prolonged (over 4 h) irradiation, the two catalytic systems became nearly equivalent in the production of CO. Thereafter, **6** yielded more CO than the reference separate system. We can clearly see such a trend in Figure 4.

We have investigated the durability of complex **6**, **3**, and the separate reference system under the same UV–vis irradiation conditions in the CO_2 reduction. The hybrid complex **6** is much more stable than either **3** or the reference system. On irradiation for 24 h, the visible absorption of **6** in the reaction mixture solution remained practically unchanged. The ^{1}MLCT absorption bands of **3** and $Ru(phen)_3^{2+}$ in the separate system readily change under irradiation.[6] With $Ru(phen)_3^{2+}$ in the separate system, the decomposition of Ru^+ generated after quenching of the excited state of Ru by an ascorbate anion is supposed to predominantly take place. On the other hand, although the probability of the ascorbate quenching in **6** is much reduced because of the effective energy transfer to Ni, the $Ru(phen)_3^{2+}$ subunit is much more robust and thus photoquenching activity lasts longer. Our new hybrid complex **6** may be a more useful photocatalyst than the separate system in the long run.

As for the selective reduction of CO_2 vs H_2O (to H_2), **6** also showed improved activity compared with the reference system (see Table III). With the latter, the ratio of [CO]/[H_2] was 0.57 in 44 h of irradiation, whereas with **6** it was 2.5.

Although **6** showed improvement, the linkage between phenanthroline and cyclam at the N position of cyclam may not be the best design. It has been known that the introduction of a methyl group in the periphery of $Ni(cyclam)^{2+}$ drastically decreases the CO/H_2 product ratio with the reference system [$Ru(bpy)_3^{2+}$ + $Ni(cyclam)^{2+}$].[2i] The $Ni(cyclam)^+$ subunit in **6** may be more crowded than anticipated, blocking the reduction of CO_2. Accordingly, we are turning to another hybrid structure in which $Ru(phen)_3^{2+}$ is linked to $Ni(cyclam)^{2+}$ through the carbon skeleton of cyclam.

Cyclam catalysts attached to a photosensitizer such as $Ru(bpy)_3^{2+}$ may have a good prospect in another application. The present new complex **6** is also of interest, because $Ru(phen)_3^{2+}$ subunit may bind intercalatively to a DNA major groove,[17] and also the pendant $Ni(cyclam)^{2+}$ may play as a reactant to modify DNA in that region.[18] The complex **6** appears to interact with DNA. In a preliminary study, we found much faster circular dichroic spectral changes of DNA upon mixing with **6** compared with $Ru(phen)_3^{2+}$ or the separate systems. This suggests that a new interaction mechanism has occurred between DNA and **6**. We are now investigating this new finding along with the photochemistry of the **6**/DNA system.

Acknowledgment. We acknowledge financial support of this work from the Nissan Science Foundation. X.B. is a recipient of a Japan Ministry of Education scholarship.

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