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Efficient Photocatalytic CO₂ Reduction by a Ni(II) Complex Having Pyridine Pendants through Capturing a Mg²⁺ Ion as a Lewis-Acid Cocatalyst

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ABSTRACT: We have synthesized a new Ni(II) complex having an S_2N_2 -tetradentate ligand with two non-coordinating pyridine pendants as binding sites of Lewis-acidic metal ions in the vicinity of the Ni center, aiming at efficient CO production in photocatalytic CO₂ reduction. In the presence of Mg^{2+} ions, enhancement of selective CO formation was observed in photocatalytic CO₂ reduction by the Ni complex with the pyridine pendants through the formation of a Mg^{2+} -bound species, as compared to the previously reported Ni complex without the Lewis-acid capturing sites. A higher quantum yield of CO evolution for the Mg^{2+} -bound Ni complex was determined to be 11.1%. Even at lower CO₂ concentration (5%), the Ni complex with the pendants exhibited comparable CO production to that at the CO₂-saturated concentration (100%). The Mg^{2+} -bound Ni complex was evidenced by mass spectrometry and ¹H NMR measurements. The enhancement of CO₂ reduction by the Mg^{2+} -bound species should be derived from cooperativity between the Ni and Mg centers for the stabilization of Ni–CO₂ intermediate by a Lewis-acidic Mg^{2+} ion captured in the vicinity of the Ni center, as supported by DFT calculations. The detailed mechanism of photocatalytic CO₂ reduction by the Ni complex with the pyridine pendants in the presence of Mg^{2+} ions is discussed based on spectroscopic detection of the intermediate and kinetic analysis.

INTRODUCTION

Converting CO₂ by solar energy into valuable chemicals and fuels is one of the important scientific challenges toward a sustainable society.^{1,2} Many researchers have devoted their enormous efforts to developing catalysts for efficient and selective photocatalytic CO2 reduction.³⁻¹⁰ Among the reported catalysts, homogeneous molecular catalysts of metal complexes have merits on the freedom in selection of metals and ligands, enabling us to design superior catalysts for efficient CO₂ reduction.¹¹ In earlier reports, noble metal complexes such as Re and Ru complexes have been demonstrated to perform efficient catalysis on photocatalytic CO₂ reduction.¹²⁻¹⁷ To avoid the use of noble metals, molecular catalysts based on earth abundant metals (Mn,¹⁸⁻²⁰ Fe,²¹⁻²² Co,²³⁻²⁵ and Ni²⁶⁻²⁸) have been also explored for photocatalytic CO2 reduction. However, the catalytic performance by non-noble metal complexes is relatively less impressive as compared to that by noble metal complexes. Strategies to enhance catalytic activity of non-noble metal complexes should be important for further development of low-cost and efficient catalysts for photocatalytic CO₂ reduction. Efforts to improve catalytic performance in the reaction using non-noble metal ions as catalytically active sites have been largely limited to tuning coordination environments,²⁹ functional groups,³⁰ and immobilizing them on solid surfaces of metal oxides.31

In nature, RuBisCo (Ribulose bisphosphate carboxylase/oxygenase) known as an enzyme for CO_2 fixation uses a Mg^{2+} ion as a Lewisacidic active site for efficient CO_2 fixation.³² It should be noted that RuBisCo carries out CO_2 fixation under low CO_2 concentrations (atmospheric CO_2 level of 0.04%). In addition, [NiFe] CODH (carbon monoxide dehydrogenase) enzyme has also been known to catalyze CO_2 to produce CO. In the active site of the enzyme, one Ni and four Fe centers form a sulfur-bridged cluster to facilitate CO_2 coordination at the carbon to the sulfur-coordinated Ni center to form a $[Ni^{2+}-C(O)O-Fe^{2+}]$ intermediate.^{33,34} In this intermediate, the cooperativity between the Ni and Lewis-acidic Fe centers to activate the CO_2 molecule is indispensable for the efficient reduction of the carbon-coordinated CO_2 at the nickel center.

Involvement of Lewis-acidic metal ions into electrochemical CO2 reduction has been explored in recent years to enhance the reaction.³⁵⁻⁴⁰ The size of alkali metal cations in electrolytes have been known to exert influence on the efficiency of electrochemical CO₂ reduction and the effects have been elucidated to be a decrease of the pKa of hydrolysis of the cations near the working cathodes.³⁷ Several molecular catalysts in electrochemical CO2 reactions have been also reported to exhibit improved catalytic performance by adding external Mg²⁺ ions.³⁸⁻⁴⁰ Savéant and coworkers have proposed that a Mg²⁺ ion forms a complex with negatively charged oxygen atoms of CO2 that coordinates to Fe⁰ porphyrins with the carbon atom to accelerate electrochemical reduction of CO2.³⁸ Kubiak and coworkers have also suggested that a similar intermediate involving a Mg²⁺ ion coordinated to a CO2-derived ligand is formed to facilitate reductive disproportionation of CO2 to afford CO and MgCO3 during electrochemical CO2 reductions.⁴⁰ Although the positive effect of Mg²⁺ ions

has been demonstrated in electrochemical CO_2 reduction in previous works, the origin of the positive effects of the Mg^{2+} ion in the CO_2 reduction have yet to be clearly elucidated due to the complexity of the heterogeneous catalysis on electrodes.

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Inspired by the Ni active center of [NiFe]CODH, we previously reported that a Ni^{II} complex bearing an S₂N₂-type tetradentate ligand, [Ni(bpet)(MeCN)₂](ClO₄)₂ (**1**•(ClO₄)₂) (bpet = bis(2-pyridylmethyl)-1,2-ethanedithiol) as shown in Figure 1, exhibited CO₂ reduction to produce CO exclusively (> 99%) in a photocatalytic system using [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine) as a photosensitizer.⁴¹ The rate-determining step of the photocatalytic CO₂ reduction by **1** was revealed to involve coordination equilibrium of CO₂ to the reduced Ni center; therefore, almost no catalytic activity was observed under low CO₂ concentrations.⁴¹ Thus, it should be required to stabilize a CO₂-coordinated intermediate for the promotion and enhancement of CO₂ reduction even under low concentrations of CO₂ as observed in CODH. Toward this goal, we have introduced two pyridine pendants to **1** as a Lewis-acid binding site.

Herein, we report a novel Ni complex with two pyridine pendants Lewis-acid binding sites, [Ni(bpetpy₂)(H₂O)₂](ClO₄)₂ as $(2 \cdot (ClO_4)_2)$ (bpetpy₂ = bis(2-pyridyl-3-pyridylmethyl)-1,2ethanedithiol, Figure 1), as an efficient catalyst for photocatalytic CO2 reduction. We have evaluated the photocatalytic CO2 reduction in the presence of Mg²⁺ ions as a Lewis acid by using complexes 1 and 2 as catalysts, $[Ru(bpy)_3]^{2+}$ as a photosensitizer and 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH) as a reductant. Selective CO production was observed in the photocatalytic system. The TONs (turnover numbers) of CO evolution for the Ni complexes are increased in the present of Mg²⁺ ions. Complex 2 having the pyridine pendants showed higher TON and higher quantum yield in the photocatalytic CO2 reduction in the presence of Mg^{2+} ions as compared to 1 without the arms. In particular, the enhancement was remarkable for 2 under low CO₂ concentrations. The use of other Lewis acids has also enhanced the CO evolution in the photocatalytic CO₂ reduction by 2. In this work, we have gained insights into enhancing effects of Lewis acids on visible-light-driven CO₂ reduction using **2** as a homogeneous catalyst on the basis of spectroscopic detection of reaction intermediates and kinetic data.



Figure 1. Molecular structure of complexes 1 and 2.

RESULTS AND DISCUSSION

Synthesis and Characterizations of Ni Complexes. The synthesis of complexes 1⁴¹ and **2** was made as described in the Experimental Section. ¹H NMR spectrum of **2** exhibits paramagnetic shifts as observed for **1**, indicating the Ni center of **2** is in a six-coordinate high-spin Ni^{II} state (Figure S1). ESI-TOF-MS measurement in MeCN has demonstrated that the structure of **2** is maintained in solution (Figures S2). Unfortunately, a number of attempts to obtain a single crystal of **2** have yet to be successful. Elemental analysis (EA) and IR

spectroscopy have been applied to confirm the formula of **2** (Experimental Sections and Figure S3). The IR spectrum of **2** in a KBr pellet showed a strong absorption due to the Cl-O stretching for ClO_4^- at 1120 and 1093 cm⁻¹ (Figure S3), indicating that the ClO_4^- ions do not bind to the Ni^{II} center but reside in the outer sphere as counter ions. Thus, on the basis of the EA result, we propose that **2** should be $[Ni(bpet-py_2)(H_2O)_2](ClO_4)_2$. Note that the crystal structure of **1** was revealed to include two CH₃CN molecules as ligands (Figure 1) and two ClO_4^- ions as counter anions.⁴¹

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) of **2** was performed in the presence or absence of Mg^{2+} ions under CO₂ atmosphere (Figure S4). Two reduction waves of **2** was observed at –1.23V and –1.39 V (vs Fc/Fc⁺) in the absence of Mg^{2+} , indicating that the Ni^{II} center was reduced to Ni¹ and Ni⁰ stepwisely. Almost no difference of reduction potentials (–1.21 V and –1.36 V vs Fc/Fc⁺) was observed in the CV and DPV in the presence of Mg^{2+} . This suggests that Mg^{2+} ions do not affect the reduction processes of **2**. The catalytic current observed for **2** in the presence of Mg^{2+} ions exhibited only a slight improvement in contrast to the case of [Mn(mesbpy)(CO)₃(MeCN)](OTf) (mesbpy = 6,6'-dimesityl-2,2'-bipyridine) with Mg^{2+} ,⁴⁰ where the catalytic current was increased by adding more than 10-fold excess of Mg^{2+} ions. The results indicate that the electrochemical CO₂ reduction by complex **2** is not influenced by Mg^{2+} ions.

Photocatalytic CO_2 Reduction by Complexes 1 and 2 in the Absence of Mg²⁺ Ions. By using complexes 1 and 2 as catalysts, we conducted photocatalytic CO2 reduction in the absence of Mg2+ ions to evaluate their intrinsic reactivity. The reaction was initiated by visible-light irradiation (λ = 450 nm) of a DMA/H₂O (9:1 vol%) solution containing a catalyst (1 or 2), $[Ru(bpy)_3]^{2+}$ as a photosensitizer, and BIH as a reductant. The obtained gaseous products were quantified by gas chromatogram (GC). CO was selectively formed in the photocatalytic systems and a slight amount of H₂ was detected as displayed in Figure 2. No formation of formic acid was observed in GC-MS measurements for reaction mixtures in both cases. Complexes 1 and **2** exhibited a similar CO evolution rate in the absence of Mg²⁺ ions. The result indicates that the Ni-S2N2 moieties of 1 and 2 should have almost the same reactivity in the reaction and the pyridine arms in 2 exert no influence on the photocatalytic CO₂ reduction in the absence of Mg²⁺ ions. Therefore, both 1 and 2 perform CO₂ reduction through the formation of Ni⁰ intermediates that are derived from electron transfer (ET) from [Ru(bpy)₂(bpy⁻)]⁺ that should be formed through photoinduced ET from BIH to the triplet excited states of [Ru(bpy)₃]²⁺ (³{[Ru(bpy)₃]²⁺}*).⁴¹



Figure 2. Time course of products obtained from the photocatalytic reaction by irradiation (λ = 450 nm) of a DMA/H₂O solution (4.0 ml, 9:1

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vol%) containing a catalyst (**1** or **2**, 30 μ M), [Ru(bpy)₃]²⁺ (0.50 mM) and BIH (0.10 M) in the absence of Mg(ClO₄)₂ under CO₂ atmosphere at 298 K.

Evidence of Mg²⁺ Binding to 2. We have performed several experiments to prove the capture of Mg^{2+} ions by the pyridine arms of 2. When excess $Mg(ClO_4)_2$ was added into a MeCN solution containing 2, we successfully detected a Mg²⁺-bound species of 2 by ESI-TOF-MS as shown in Figure 3. According to the MS spectrum, one Mg^{2+} ion is assumed to coordinate to the pyridine arms of **2** in the solution. In addition, the interaction of Mg²⁺ with 2 was also supported by ¹H NMR spectroscopy in CD₃CN: The addition of Mg²⁺ ions into a solution containing 2 allowed us to observe peak shift for paramagnetically shifted signals of 2 (Figure S5). The binding constant between Mg²⁺ and **2** was obtained to be 146 ± 32 M⁻¹ that was calculated on the basis of a plot of chemical shift change in ¹H NMR spectra versus Mg²⁺ concentration in CD₃CN (Figure S6). On the other hand, we didn't observe any Mg²⁺-bound species of 1 in the MS spectrum or any spectral change of ¹H NMR spectrum of **1** in the presence of excess Mg²⁺ ions in CD₃CN (Figure S7). These results indicate that the pyridine arms introduced to 2 are indispensable for the Mg²⁺ binding.



Figure 3. (a) A proposed structure of Mg^{2+} -bound **2**. (b) ESI-TOF-MS spectrum of **2** (0.56 mM) in the presence of $Mg(ClO_4)_2$ (84 mM) in MeCN. Simulated (c) and observed (d) MS spectra of Mg^{2+} -bound **2**.

Photocatalytic CO₂ Reduction in the Presence of Mg²⁺ ions. On the basis of the result shown in Figure 3, we examined photocatalytic CO₂ reduction under the conditions where Mg²⁺ ions should bind to **2**. We found that the presence of Mg^{2+} ions can afford considerable amount of CO in the presence of $[Ru(bpy)_3]^{2+}$ under the reaction conditions. Thus, the net amount of CO formed by **2** with Mg²⁺ ions was determined by subtracting that of the control experiment without a catalyst in the presence of Mg²⁺ ions from the apparent amount of CO formed in the photocatalysis using **2** in the presence of Mg²⁺ ions (Figure S8). The net amount of CO evolved was increased in the photocatalytic CO2 reduction in comparison with that obtained by **2** in the absence of Mg^{2+} , as shown in Figure 4. Note that the time courses of CO formation did not show apparent saturation, indicating that each catalytic component is persistent for at least 4 h reaction time. The highest amount of CO evolved was obtained when the concentration of Mg²⁺ ions was 5.0 mM with use of 30 μ M of 2 as a catalyst (Figure S9). A negligible amount of H₂ was also formed in the presence of Mg^{2+} ions (Figure S10); the selectivity of CO evolution was determined to be over 99% for **2** in the photocatalytic system, as comparable to that of **1** under the same conditions. For both **1** and **2**, formation of formic acid was not observed in GC-MS measurements for reaction mixtures. The CO evolution rates in the presence of Mg^{2+} ions (5.0 mM) were determined to be 0.086 µmol min⁻¹ for **1** and 0.17 µmol min⁻¹ for **2**, which were higher than those without Mg^{2+} ions (0.043 µmol min⁻¹ for **1** and 0.042 µmol min⁻¹ for **2**). The addition of Mg^{2+} ions was revealed to accelerate the CO evolution rates by greater than 2 times for **1** and 4 times for **2** as compared with those in the absence of Mg^{2+} ions. The activity difference in the CO evolution between **1** and **2** should be derived from the Mg^{2+} ion captured by the pyridine arms in the vicinity of the Ni center of **2**.



Figure 4. (a) Time courses of CO evolution obtained from the photocatalytic reaction by irradiation (450 nm) of a DMA/H₂O solution (4.0 mL, 9:1 v/v) containing a catalyst {(a) for **1** and (b) for **2** (30 μ M)}, [Ru(bpy)₃]²⁺ (0.50 mM), and BIH (0.10 M) in the absence of Mg(ClO₄)₂ and in the presence of Mg(ClO₄)₂ (5.0 mM) under CO₂ atmosphere at 298K.

We performed a Hg test to demonstrate the homogeneous catalysis of **2** in the presence of Mg^{2+} ions. The CO evolution rate was remained the same even when several drops of Hg were introduced into the reaction mixture as shown in Figure S11. The CO evolved in the photocatalytic CO₂ reduction by 2 was exclusively derived from CO₂ as evidenced by a ¹³CO₂ labelling experiment (Figure S12). The quantum yield (QY) of the photocatalytic CO evolution by 2 was determined to be 11.1% at 450 nm (Figure S13a) in the presence of Mg²⁺ ions (5 mM). Lowering the concentration of the photosensitizer was not effective to improve the QY. The QY obtained by Mg²⁺-bound **2** is highest among Ni complexes used for photocatalytic CO evolution from CO2. On the other hand, the QY of CO formation by 1 in the presence of Mg²⁺ ions was determined to be only 3.3 % (Figure S13b), although the value was higher than that (1.42%) in the absence of Mg²⁺ ions.⁴¹ The capture of one Mg²⁺ ion with the pyridine arms of 2 surely improved the QY of photocatalytic CO formation by 2 up to more than 3 times. Dependence of CO production and selectivity in the presence of Mg²⁺ on H₂O concentration was also examined by changing the DMA/H₂O ratio from 19:1 to 4:1. Higher concentration of H₂O suppressed the efficiency of CO formation, resulting low selectivity of CO evolution (Table S1).

Photocatalytic CO₂ Reduction under Low CO₂ Concentrations. Dependence of initial CO evolution rates on the CO₂ concentrations was also examined for **1** and **2** in the presence of Mg^{2+} ions. The time courses of CO evolution are shown in Figure S14. The CO₂ concentration dependence of the initial rate of net CO evolution is plotted in Figure 5 together with that in the absence of Mg^{2+} ions (see also Figure S15 for the CO₂ concentration dependence of the initial rate of apparent CO evolution). The initial rates exhibited saturation behavior in the photocatalytic system both with and without Mg²⁺ ions as shown in Figure 5. Notably, almost no CO evolution by 2 was observed at 5% CO₂ atmosphere without Mg²⁺ ions. In contrast, the initial rate of the CO formation by 2 with Mg²⁺ ions at 5% CO_2 atmosphere exhibited even higher as compared with that by $\boldsymbol{2}$ at 100% CO2 atmosphere without Mg2+ ions. The initial CO evolution rate for Mg²⁺-bound **2** at the low CO₂ concentration (5%) was much higher than that for 1 in the presence of Mg²⁺ ions at high CO₂ concentration (100%). The results clearly indicate the captured Mg^{2+} ions by the pyridine arms of **2** also play an important role to trap CO_2 in the vicinity of the Ni center. As a result, complex 2 can efficiently reduce CO₂ to CO even under low CO₂ concentrations probably on the basis of the cooperative manipulation of CO₂ between the Ni⁰ and Mg²⁺ to stabilize a CO₂-coordinated intermediate in the CO₂ coordination equilibrium (see below).

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Figure 5. Dependence of net CO evolution rate on CO₂ concentration for (a) **1** and (b) **2** with or without Mg²⁺ ions. The CO evolution rates were obtained from the photocatalytic reaction by irradiation (450 nm) of a DMA/H₂O solution (4.0 mL, 9:1 v/v) containing **1** or **2** (30 μ M), [Ru(bpy)₃]²⁺ (0.50 mM), BIH (0.10 M) and Mg(ClO₄)₂ (5.0 mM) under CO₂ atmosphere (5 – 100%) at 298K.

Dependence of Other Lewis Acids on CO Evolution by 2. A series of metal cations was examined as Lewis acids to investigate the effect on photocatalytic CO₂ reduction by **2**. The amounts of CO and H₂ evolved in the photocatalysis with **2** were calculated by subtracting those in the control experiments without **2** (Table S2) from those of apparent amount obtained in the photocatalytic CO₂ reduction (Table S3). The net CO evolution and TONs for **2** in Table 1 indicate that only Ca²⁺ and Zn²⁺ ions show comparable enhancement to that of Mg²⁺ ions in the photocatalytic CO₂ reduction. Comparison of the amount of CO and H₂ evolved in the presence of various Lewis acids in the photocatalytic reactions is also displayed in Figure 6. Li⁺ and Na⁺ ions showed no influence on the efficiency of the photocatalytic CO₂ reduction by **2**. On the other hand, Y³⁺ and Sc³⁺ promoted only H₂ evolution instead of CO evolution. The same tendency as **2** was observed using **1** in the presence of Lewis acids (Table S4).

Note that we could not observe any peak clusters assignable to Li^+ -, Na^+ -, Sc^{3+} - or Y^{3+} -bound species of **2** in the MS spectra under the same conditions as given in the caption of Figure 3. On the other hand, Ca^{2+} and Zn^{2+} -bound species of **2** were also observed in the ESI-TOF-MS measurements (Figure S16). This indicates that the Mg^{2+} -, Ca^{2+} - and Zn^{2+} -bound species of **2** should act as the key intermediates that enable the high efficiency in the photocatalytic CO_2 reduction to form CO selectively. Mg^{2+} -bound **2** exhibited slightly higher selectivity (99.7%) than the Ca^{2+} -bound **2** (99.0%) and the Zn^{2+} -bound **2** (98.9%) over H_2 evolution. As for Y^{3+} and Sc^{3+} ions, they can cause higher proton concentration due to the enhanced acidity of H_2O preferentially bound to the highly Lewis-acidic trivalent metal ions to facilitate H_2 evolution and rather to proceed to the CO production.

Table 1. Photocatalytic CO2 Reduction by 2 in Presence of Lewis Acids.⁴

Lewis acid b	CO, μmol	H2, µmol ^c	TON for	Selec. for	
	с		CO ^{<i>a</i>}	CO, % ^e	
Li+	1.10	0.0152	9.24	98.6	
Na^+	1.63	0.0346	13.6	97.9	
Mg^{2+}	14.4	0.0473	120	99.7	
Ca^{2+}	14.2	0.137	118	99.0	
Zn^{2+}	14.0	0.161	117	98.9	
Sc ³⁺	0	14.4	0	0	
Y ³⁺	0	14.2	0	0	
none	1.52	0.0810	12.7	94.9	
					-

^{*a*} The photocatalytic reactions were performed in a DMA/H₂O solution (4.0 ml, 9:1 v/v) containing **2** (30 μ M), [Ru(bpy)₃]²⁺ (0.50 mM), BIH (0.10 M) and a Lewis acid (5.0 mM) under CO₂ atmosphere at 298 K. ^{*b*} ClO₄⁻ salts for Mg²⁺, Ca²⁺, Zn²⁺, Li⁺ and Na⁺ and OTf⁻ salts for Y³⁺ and Sc³⁺ were used. ^{*c*} Obtained at 1h. ^{*d*} TON for CO was defined as [CO] / [**2**], at 1h. ^{*e*} Selectivity was defined as ([CO] × 100) / ([CO] + [H₂]).



Figure 6. Product yields obtained from the photocatalytic CO₂ reduction by **2** at 1h in presence of cationic Lewis acids (5.0 mM).

Kinetic Analysis of Photocatalytic CO2 Reduction by 2 in the **Presence of Mg²⁺ ions.** We have further investigated the photocatalytic CO_2 reduction by **2** in the presence of Mg^{2+} ions to reveal the effect of Mg²⁺ ions. Kinetic analysis on the CO evolution by **2** with Mg²⁺ ion was performed for gaining a mechanistic insight into the photocatalytic CO₂ reduction. We have performed the photocatalytic CO₂ reduction with various concentrations of 2 in the presence of Mg²⁺ ions (5.0 mM). The time course of CO evolution in the photocatalytic CO2 reduction with various concentrations of 2 was obtained as shown in Figure 7a (Figure S17a for the apparent CO evolution), in which the CO evolution rate was increased in proportion to the concentrations of 2. The initial rates of CO evolution are plotted against the concentrations of 2 (Figure 7b and Figure S17b for the apparent initial rates). The initial rates exhibited first-order dependence on the concentration of **2**. The TOF (turnover frequency) of **2** calculated from the slope was determined to be 1.6 min⁻¹, which is higher than that of 1 without Mg²⁺ ions by 5 time,⁴¹ and even higher

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than those reported for Fe $(0.38 \text{ min}^{-1})^{22}$ and Co $(0.37 \text{ min}^{-1})^{23}$ complexes. In addition, dependence of CO evolution rates on the CO₂ concentration exhibited saturation behavior as depicted in Figure Sb for the CO evolution by **2** with Mg²⁺ ions, indicating a coordination equilibrium between a reduced Ni intermediate and CO₂ molecule. The Mg²⁺ ion captured in **2** can stabilize a Ni-CO₂ intermediate to promote the forward reaction in the equilibrium toward CO₂ cleavage to evolve CO,⁴² affording the efficient reactivity of Mg²⁺-bound **2**.



Figure 7. (a) Time courses of net CO evolution obtained from the photocatalytic reaction by irradiation (450 nm) of a DMA/H₂O solution (4.0 mL, 9:1 v/v) containing **2** (50 μ M: yellow squares, 30 μ M: red cycles, 20 μ M: green triangles and 10 μ M: blue diamonds), [Ru(bpy)₃]²⁺ (0.50 mM), BIH (0.10 M) and Mg(ClO₄)₂ (5.0 mM) under CO₂ atmosphere at 298K. (b) The concentration dependence of **2** on net CO evolution rate in presence of Mg²⁺ ions.

Solvent kinetic isotope effect (sKIE) was also investigated to understand the influence of H_2O . Dependence of CO evolution rates on the concentration of **2** in DMA/D₂O was examined as shown in Figure S18. The TOF of CO evolution for **2** in DMA/D₂O was calculated to be 0.87 min⁻¹, giving a sKIE value of 1.8, which is defined as TOF in DMA/H₂O divided by TOF in DMA/D₂O. This indicates that H₂O molecules are involved in the CO₂ cleavage as H⁺ sources. The sKIE value observed for the Mg²⁺-bound **2** is slightly higher than that of **1** (1.2) in the previous report.⁴¹

Mechanistic Insight into the CO Evolution by 2 in the Presence of Mg^{2+} ions. We have performed reductive quenching of excited $[Ru(bpy)_3]^{2+}, {}^3{[Ru(bpy)_3]^{2+}}*$, by BIH in the presence of Mg^{2+} ions to investigate whether the rate constant of electron transfer from BIH to ${}^3{[Ru(bpy)_3]^{2+}}*$ is influenced by Mg^{2+} or not (Figure S19a). The rate constant in the presence of Mg^{2+} ions was obtained from a Stern-Volmer plot and determined to be 7.1×10^9 M⁻¹ s⁻¹ (Figure S19b). The value is almost the same as that without Mg^{2+} (7.3×10^9 M⁻¹ s⁻¹). As mentioned above, Mg^{2+} ions have not influence on the reduction potentials of **2** (Figure S4). Thus, we conclude that Mg^{2+} ions bound to **2** resides in the second-coordination sphere without exerting any influence of the structure to facilitate and assist CO₂ binding to the Ni center.

As mentioned above, Savéant, Kubiak, and their coworkers have proposed the formation of M- $(C_2O_5\cdots Mg^{2+})$ as an intermediate in the course of electrocatalytic CO_2 reduction using Fe-porphyrin and a Mn complex as catalysts in the presence of Mg^{2+} ions.^{39,40} In the case of the Mn catalyst, it has been reported that MgCO₃ is formed as a product of reductive disproportionation to afford CO.⁴⁰ To examine the possibility of similar reaction pathway in our catalytic system, we measured IR spectra of residues obtained by the solvent evaporation followed by washing with CH₃CN of the reaction mixtures containing **2**, $[Ru(bpy)_3](ClO_4)_2$, $Mg(ClO_4)_2$ or $Ca(ClO_4)_2$, and BIH. Consequently, we could not observe any peaks derived from MgCO₃ or CaCO₃ in the IR spectra. Thus, we conclude that the present photocatalytic systems do not involve the formation of MgCO₃ and CaCO₃ derived from reductive disproportionation mentioned above.

On the basis of the investigation of the influence of Mg²⁺ ions on the photocatalytic CO₂ reduction by **2** as described above, the photocatalytic cycle is proposed as shown in Scheme 1.41 The reaction is initiated by photoexcitation of $[Ru(bpy)_3]^{2+}$, forming the triplet MLCT excited state, ${}^{3}{[Ru(bpy)_{3}]^{2+}}^{*}$, which is reductively quenched by BIH to afford [Ru(bpy)₂(bpy^{.-})]⁺ and BIH^{.+}. Another $[Ru(bpy)_2(bpy -)]^+$ is produced from the reduction of the photosensitizer by deprotonated BIH⁺⁺ (BI⁺) that is derived from the reductive quenching mentioned above. In light of the aforementioned reduction potentials of Mg²⁺-bound **2**, the two $[Ru(bpy)_2(bpy -)]^+$ can reduce the Ni^{II} center of Mg²⁺-bound 2 to form a Ni⁰ species $([Mg^{2+} \cdots LNi^0]^{2+})$. The Mg^{2+} ion coordinated to the pyridine pendants enhances the formation of a Ni^{II}-CO22--Mg2+ species $([Mg^{2+} \cdots LNi^{2+} - CO_2]^{2+})$ by stabilizing the species in the CO₂ coordination equilibrium. The C-O bond of the Ni-coordinated CO2 should be cleaved with the aid of H₂O as a proton source to afford CO. The slightly larger sKIE observed for **2** with Mg²⁺ ions than that in 1 suggests that $[Mg^{2+} \cdots LNi^{2+} - CO_2]^{2+}$ is more sensitive to the H₂O molecule as a proton source in the cleavage of a C-O bond of the coordinated CO₂ molecule to afford CO in the photocatalytic CO2 reduction by 2. This is probably due to the stabilization of the CO₂-bound Ni intermediate by Mg²⁺ to promote the forward reaction in the CO₂ coordination equilibrium (Scheme 1).

Scheme 1. Proposed Mechanism of the Photocatalytic CO_2 reduction to CO by 2 with Mg^{2+} ions.



The structure of $[Mg^{2^+} \cdots LNi^{2^+} - CO_2]^{2^+}$ was optimized by DFT calculations. The optimized structure displays that the Mg^{2^+} ion coordinated to the pyridine pendants of **2** can interact with an oxygen atom of the Ni-coordinated CO₂ molecule. The DFT calculations also suggested that the Mg^{2^+} ion captured by **2** stabilizes the CO₂-bound Ni intermediate through η^2 -O,O' coordination to the *C*-bound CO₂²⁻ ligand (Figure 8; see also Figure S20 and Table S5) in the CO₂ coordination equilibrium, resulting in the enhancement of reaction rates for the proton-assisted C-O bond cleavage to evolve CO in the photocatalytic CO₂ reduction.



Figure 8. An optimized structure of CO_2 -coordinated Mg^{2+} -bound **2** at the unrestricted B3LYP level of theory. In this model, one O-bound DMA ligand is included. Hydrogen atoms are omitted for clarity.

CONCLUSIONS

We have successfully synthesized the Ni complex 2 bearing a tetradentate S2N2 ligand with two pyridine pendants in the second coordination sphere to capture Lewis acids such as Mg²⁺ ions in the vicinity of the Ni center. The capture of a Mg²⁺ ion by **2** with the arms was confirmed by the detection of Mg²⁺-bound 2 by ESI-TOF-MS and ¹H NMR measurements. Enhancement of CO production by 2 in the presence of Mg²⁺ ions was demonstrated in the photocatalytic CO_2 reduction in high selectivity and efficiency using $[Ru(bpy)_3]^{2+}$ as a photosensitizer and BIH as an electron donor, even in a low CO2 concentration (5%). The enhancement by Mg²⁺ ions was also observed by the Ni complex 1 without pyridine pendants; however, 2 with the arms exhibited a 2-fold larger enhancement in term of the CO evolution rates. The enhancement should be derived from the pyridine pendants of 2 that can capture one Mg2+ ion in the vicinity of the Ni center, as a Lewis-acid co-catalyst with strong cooperativity. The QY of the photocatalytic CO formation by Mg²⁺-bound **2** was sharply increased to 11.1%, which is the highest value for CO evolution using Ni complexes as catalysts. Other Lewis acids as such as Na⁺, Li⁺, Ca²⁺, Y³⁺and Sc³⁺ ions were also introduced in the photocatalytic CO2 reduction by 2. Only Ca2+ ions exhibited the enhancement as well as Mg²⁺ ions, indicating that Mg²⁺- and Ca²⁺-bound 2 are effective for promoting the CO evolution. Kinetic analysis together with sKIE of water have revealed the mechanism of CO evolution by Mg²⁺-bound **2**: The coordination equilibrium between Ni⁰ species and CO₂ tends to form the Ni^{II}-CO₂²⁻-Mg²⁺ intermediate (Figure 8) and a H₂O molecule can serve as a proton source to cleave the C-O bond of the Ni-coordinated CO₂ ligand. The larger sKIE of Mg^{2+} -bound **2** as compared to that of **1** suggests that the stabilized CO2-bound species should be more sensitive to the proton transfer from H₂O for the C-O bond cleavage. This work provides valuable information on the design of Ni complexes as catalysts for photocatalytic CO2 reduction, that is, the introduction of a Lewis-acid binding site in the second coordination sphere, such as the pyridine arms in 2, is effective for the enhancement of the reaction. Thus, we believe this work will contribute to the development of efficient molecular catalysts for CO2 reduction. Finally, the superiority of Mg2+ ions in CO2 reduction among other alkali and alkali-earth metal ions may imply the reason why the active site of RuBisCo contains a Mg²⁺ ion coordinated by amino-acid residues to activate a CO2 molecule toward CO formation.

EXPERIMENTAL SECTION

General. Chemicals and solvents were purchased from commercial sources and used as received unless otherwise mentioned. All synthetic reactions were performed under an argon atmosphere. Complex **1** was prepared as previously reported.⁴¹ BIH was synthesized by the reported procedure.^{41, 43} ¹H NMR measurements were performed on JEOL EX 400 and Bruker AVANCE 400 spectrometers. ESI-TOF-MS spectra were measured on a JEOL JMS-T100CS spectrometer.

5-(3-Pyridylmethyl)-2-pyridinecarboxaldehyde (L1). The title compound was synthesized in accordance with the literature procedure.⁴⁴ ¹H NMR (CDCl₃): δ 4.06 (s, 1H), 7.16 – 7.25 (m, 1H), 7.43 (t, *J* = 5.6 Hz, 1H), 7.62 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 8.42 – 8.50 (m, 2H), 8.64 (s, 1H), 10.0 (s, 1H).

5-(3-Pyridylmethyl)-2-pyridinemethanol (L2). Compound L1 (181 mg, 0.91 mmol) was dissolved in 5 mL of absolute ethanol and cooled to 0 °C, and then sodium borohydride (12.6 mg, 0.33 mmol) was added with stirring under Ar. After the reaction mixture was stirred for 25 min at 0 °C, the reaction was quenched by adding HCl aq, and NaOH aq was added to adjust the solution pH to be 11. The mixture was extracted with dichloromethane, and the organic layers were combined and dried over anhydrous Na₂SO₄. The volatiles of the filtrate were evaporated, and the residue was dried under vacuum to obtain an orange oil of L2 (128 mg, 0.64 mmol, 70% yield). ¹H NMR (CDCl₃): δ 3.56 (br s, 1H), 3.99 (s, 2H), 4.74 (s, 2H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.23 (dd, *J* = 7.5, 4.8 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 8.44 (s, 1H), 8.48 (d, *J* = 7.5 Hz, 1H), 8.49 (s, 1H).

5-(3-Pyridylmethyl)-2-chrolomethyl-pyridine (L3). Compound **L2** (130 mg, 0.65 mmol) was dissolved in 3 mL of CH₂Cl₂ and cooled to 0 °C, and a solution of thionyl chloride (0.5 mL, 6.9 mmol) in 2 mL of CH₂Cl₂ was added dropwise with stirring under Ar. After the reaction mixture was stirred at 0 °C for 1 h, and further stirred at room temperature for 20 h, and then the solvent was removed. The residual solid was washed with diethyl ether to afford a pink solid of **L3** (150 mg, 0.59 mmol, 91% yield). ¹H NMR (DMSO-*d*₆): δ 4.23 (s, 2H), 4.76 (s, 2H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.80 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.94 (t, *J* = 8.0 Hz, 1H), 8.41 (d, *J* = 8.0, 1H), 8.59 (d, *J* = 1.8 Hz, 1H), 8.78 (d, *J* = 8.0 Hz, 1H), 8.91(s, 1H).

Bis-[5-(3-pyridylmethyl)-2-pyridylmethyl]]-1,2-ethanedithiol (bpet-py₂, L4). To absolute methanol (3 mL) was added Na (4 mg, 0.17 mmol) under Ar. When all the sodium metal dissolved, 1,2ethanedithiol (3.3 μ L, 0.04 mmol) was added to the solution and the mixture was stirred at room temperature for 10 min. Then, the solution of L3 (20 mg, 0.08 mmol) in absolute methanol (2.0 mL) was added slowly to the mixture. The reaction mixture was stirred for 22 h at room temperature under Ar. After removal of the solvent, the residue was extracted with chloroform and H₂O. The organic layer was dried over anhydrous Na₂SO₄. The volatiles of the filtrate were evaporated and the residue was dried under vacuum to obtain yellow solid of L4 (23 mg, 0.05 mmol, 63% yield). ¹H NMR (CD₃CN): δ 2.66 (s, 2H), 3.78 (s, 2H), 3.98 (s, 2H), 7.26 (dd, J = 8.0, 4.7 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.53 (dd, J = 8.0, 2.2 Hz, 1H), 7.57 (dt, *J* = 8.0, 2.0 Hz, 1H), 8.39 (d, *J* = 2.2 Hz, 1H), 8.43 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.50 (d, *J* = 2.0 Hz, 1H).

 $[Ni(bpet-py_2)(H_2O)_2](ClO_4)_2 \cdot 0.5H_2O$ (2 · (ClO_4)_2 · 0.5H_2O). L4 (10.0 mg, 0.022 mmol) and Ni(ClO_4)_2 · 6H_2O (49.2 mg, 0.13 mmol) were mixed in CH₃OH (5 mL). The mixture was stirred at room temperature for 2 h and the filtrate was dried up under vacuum to give a pale blue solid of 2 (6.4 mg, 0.08 mmol, 64%). ESI-TOF-

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MS (CH₃CN): m/z = 615.15 (sim for [Ni(bpet-py₂) + ClO₄]⁺: 615.04). Anal. Calcd for NiC₂₆H₂₆N₄O₂S₂•2(ClO₄)•0.5H₂O: C 41.02, H 4.10, N 7.36. Found: C 41.00, H 3.85, N 7.34.

Photocatalytic CO₂ Reduction. A mixed solution of DMA/H₂O (9:1 v/v) (4.0 mL) containing **1** or **2** (10–50 μ M), a Lewis acid (0– 5 mM), BIH (0.10 M) and $[Ru^{II}(bpy)_3]Cl_2$ (0.50 mM) was purged with CO2 gas for 30 min. The solution was then irradiated with a 6 W LED lamp (λ = 450 nm) at 298 K. The power of the LED light irradiated on the vial surface was determined to be 75 mW/cm² by a photometer (Nova II, Ophir Optronics). After certain reaction time, the evolved gas in the headspace of the reaction vessel was sampled by a gastight syringe $(100 \,\mu L)$ and quantified using a Shimadzu GC-2014 gas chromatograph [GC: Ar carrier, a packed column with molecular sieves 5A (3.0 m × 3.0 mm, 60–80 mesh) at 353 K] equipped with a thermal conductivity detector (TCD). The yields of CO and H₂ formed were determined by GC; the apparent amounts of evolved CO and H2 were quantified on the basis of calibration curves prepared for various concentrations of CO and H₂. The net CO amount formed by **1** and **2** in the presence of Mg^{2+} ions in this work were obtained by subtracting the amount of CO formed in the control experiment without 1 or 2 in the presence of Mg^{2+} ions from the apparent CO amount mentioned above. GC-MS analysis was performed on a Shimadzu GCMS-QP2010 SE [He carrier, a capillary column (DB-WAX UI, 30 m × 0.32 mm × 0.25 µm)] to detect products in a solution of the photocatalytic CO₂ reduction.

Electrochemical Measurements. Electrochemical measurements were carried out on an ALS/CH Instruments Electrochemical Analyzer Model 660A. Cyclic voltammetry on **1** was carried out in a mixed solution of DMA/H₂O (9:1 v/v) containing 0.10 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as an electrolyte at 298 K under Ar or CO₂ with use of a glassy carbon as a working electrode, a platinum wire as a counter electrode, and an Ag/AgNO₃ electrode (in MeCN solution containing 0.10 M TBAPF₆ and 0.010 M AgNO₃). The potentials were calibrated by the redox potential of the ferrocene/ferrocenium (Fc/Fc⁺) redox couple as a reference.

Quantum Yield Determination. A standard actinometer (potassium ferrioxalate) was used for the quantum yield determination of the photocatalytic CO2 reduction. A mixed solution of DMA/H2O (9:1 v/v) (4.0 mL) containing 1 (30 μ M), and [Ru(bpy)₃]Cl₂ (0.50 mM) was irradiated with a monochromatized light ($\lambda = 450$ nm, MAX-303, Asahi Spectra Co.,Ltd.) at 298 K. A quantum yield (QY) of the photocatalytic CO evolution under the conditions was calculated according to the following equation; $QY(\%) = \{(R/I) \times 100\},\$ where $R \pmod{s^{-1}}$ is the CO evolution rate and $I \pmod{s^{-1}}$ is the rate of photon flux of the incident light. The amount of CO formed was monitored by GC as mentioned above. The total number of incident photons was determined by a standard method using an actinometer (potassium ferrioxalate, K₃[Fe^{III}(C₂O₄)₃], 0.18 M) in H₂O at room temperature. The rate of photon flux of the incident light (I)was determined to be 3.0×10^{-8} einstein s⁻¹ under photoirradiation with a monochromatized light at 450 nm.

Absorption and Emission Spectroscopic Measurements. UV-Vis spectroscopy was carried out on Shimadzu UV-3600 and UV-2450 spectrometers at room temperature using quartz cells (light pass length = 1.0 cm). Emission spectroscopy was carried out on a HORIBA fluomax-4 spectrofluorometer at room temperature using quartz cells (light pass length = 1.0 cm).

DFT calculations. We optimized the structure of a CO₂ complex of Mg^{2+} -bound **2** using the unrestricted B3LYP method.⁴⁵ For all atoms, we used the SDD basis sets.⁴⁶ The Gaussian 09 program package was used for all DFT calculations.⁴⁷

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Figures S1–S20 and Tables S1-S4.

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Notes

The authors declare no competing financial interest.

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