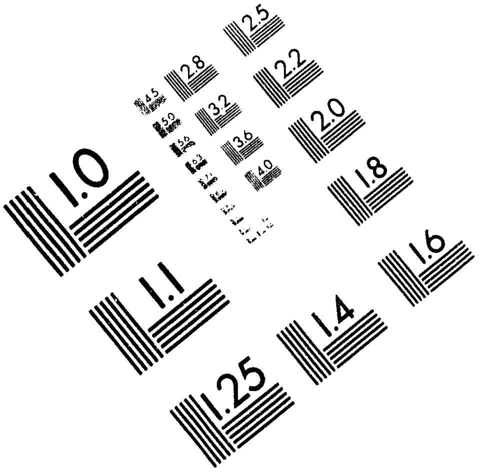
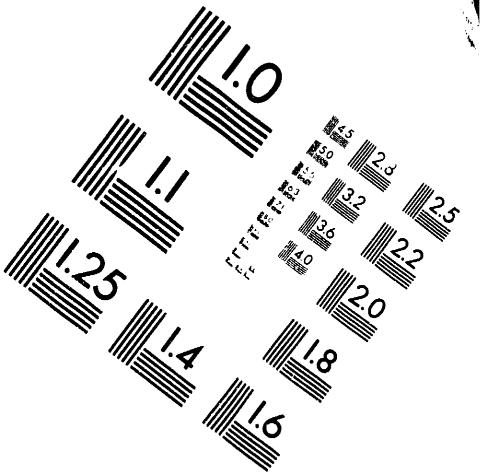


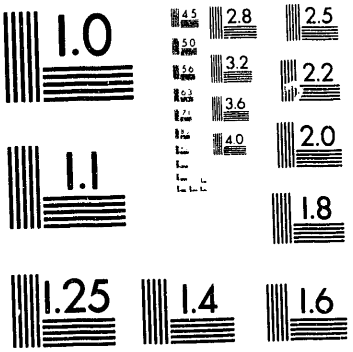
AIIM

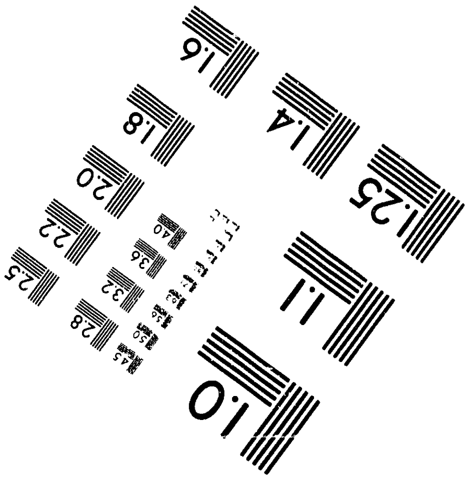
Association for Information and Image Management

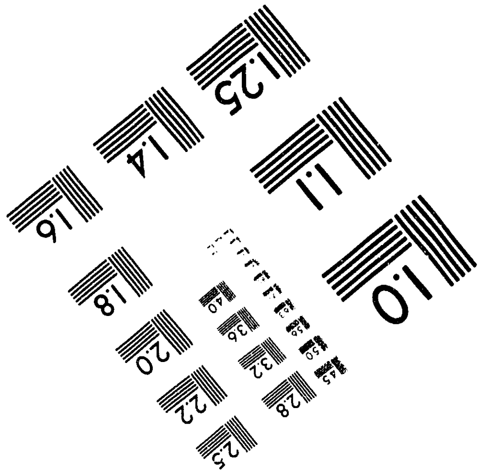
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910

301/587-8202









MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

2

Conf-9309182--1

BNL-49082

BINDING OF CARBON DIOXIDE TO METAL MACROCYCLES: TOWARD A MECHANISTIC UNDERSTANDING OF ELECTROCHEMICAL AND PHOTOCHEMICAL CARBON DIOXIDE REDUCTION

Etsuko Fujita
Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA

Introduction

A great deal of effort has been devoted to finding effective catalysts for photochemical and electrochemical reduction of CO_2. Metal complexes with 14-membered tetraazamacrocyclic ligands, $[CoL_5(H_2O)](ClO_4)_2$ (L_5 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) and $NiL_{10}Cl_2$ (L_{10} = 1,4,8,11-tetraazacyclotetradecane), have been used as successful electrocatalysts[1-3] for the reduction of CO_2 in H_2O or aqueous CH_3CN. The total yields of CO and H_2 are ~1 in most cases and the CO/H_2 production ratio is ~1 for $[CoL_5(H_2O)](ClO_4)_2$ [1]and >100 for $NiL_{10}Cl_2$.[1] Beley et al. suggested that the large selectivity for the electroreduction of CO_2 compared with water is related to the size of the macrocyclic ligand and to the presence of N-H groups in $NiL_{10}Cl_2$. Despite the successful electrochemical reduction of CO_2 by metal macrocycles, photochemical reduction of CO_2 by these macrocycles showed a very low quantum yield for CO_2 reduction and the undesired competitive evolution of H_2, along with the HCO_2^- and CO production. Tinnemans et al.[2] have reported the use of cobalt macrocyclic complexes as electron mediators for the $Ru(2,2'\text{-bipyridine})_3^{2+}$-catalyzed photochemical reduction of CO_2 to yield a CO/H_2 ratio of ~0.3. Grant et al.[4] investigated the electron mediation of a NiL_{10} complex for the same photosensitized CO_2 reduction and found quantum yields of 10^{-4} to 10^{-3} and a CO/H_2 ratio of ~0.2. Both groups proposed the insertion of CO_2 into the M-H bond in the reaction mechanisms.

In order to find an effective and selective photochemical CO_2 reduction system, we are elucidating the factors controlling excited-state lifetimes, electron-transfer rates to mediators/catalysts, properties of reduced mediators, the binding of small molecules to reduced mediators, and the reactivity of the mediators to yield the desired products. Here we describe some of our results of binding on CO_2 to metal macrocycles.

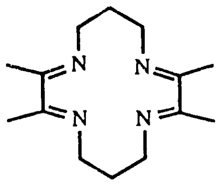
Nature of Reduced Mediators.

Most $Co^{II}L$ and $Ni^{II}L$ complexes studied here can be reduced to the metal(I) oxidation state by Na-Hg reduction in CH_3CN.[5,6] These metal(I) complexes are unstable in water, forming $M^{III}L\text{-}H^-$ complexes, which produce H_2 by reacting with protons. Various properties of CoL_5 ($E_{1/2}$ -1.34 V vs SCE), NiL_5 ($E_{1/2}$ -1.22 V vs SCE), and NiL_{13} ($E_{1/2}$ -1.32 V vs SCE) in CH_3CN are shown in Table I. Since the structure of the Ni^IL_{10} complex, a well known catalyst, has not been determined, the results[6,7 8] for NiL_5 and NiL_{13} are also shown here. These metal(I) complexes have very strong MLCT bands in the visible region and react with carbon monoxide to form square pyramidal CO adducts. Although the Co-N bond distances are not significantly changed by reduction, the Ni-N distances of nickel(I) complexes increase quite dramatically compared to the nickel(II) complexes. Although the coordination geometry varies from square planar to elongated octahedral, and the spin varies from low to high in these nickel(II) complexes, the bond length differences between the Ni(II) and Ni(I) complexes remain about 0.1 Å. Such a bond length difference may cause a 2- or 3-order-of-magnitude slower electron transfer between the Ni(II) and Ni(I) species than that between the Co(II) and Co(I).

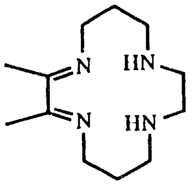
Table I. Properties of Cobalt and Nickel Complexes in CH_3CN.

	$Co^{II}L_5$	Co^IL_5	$Ni^{II}L_5$	Ni^IL_5	$Ni^{II}L_{10}$	Ni^IL_{10}	$Ni^{II}L_{13}$	Ni^IL_{13}
Spin	d^7	d^8	d^8	d^9	d^8	d^9	d^8	d^9
	low	low	low		high		high	
Coord. number	6 or 5	4	4	4	6	6	6	4
UV-vis $\lambda_{max}(\varepsilon)$	440(125)	678(18000)	438(90)	600 sh	445(42)	560(150)		384(6200)
				468(4120)		382(6500)		
K_{CO} M^{-1}	—	2.3×10^8	—	5.6×10^4	—	2.8×10^5	—	3.4×10^5
K_{CO_2} M^{-1}	—	6×10^4	—	<0.2	—	a	—	a
ν_{CN}, cm^{-1}	1661	1571	1660	1635	—	—	—	—
$M\text{-}N_{amine}$, Å (soln)	b	b	1.93^c	2.06^c	1.99^d	2.10^d	b	b
$M\text{-}N_{imine}$, Å (soln)	b	b	1.93^c	1.94^c	—	—	—	—
$M\text{-}N_{amine}$, Å (solid)	1.967^e	1.957^f	1.914^g	2.066^c			1.959^d	2.068^d
$M\text{-}N_{imine}$, Å (solid)	1.927^e	1.911^f	1.907^g	1.984^c	—	—	—	—
Geometry (solid)	sq. pyr.	sq. pl.	sq. pl.	sq. pl.			sq. pl.	sq. pl.
							low spin	

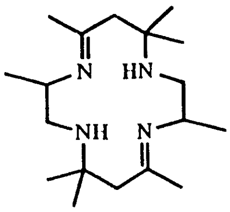
[a] $Ni^IL_{13}^+$ reacts with CO_2 in CH_3CN to form a pale yellow solution. Study of the product is in progress. [b] EXAFS study of these solutions are in progress. [c] ref. 6. [d] ref. 8. [e] ref. 19. [f] ref. 5. [g] ref. 7.



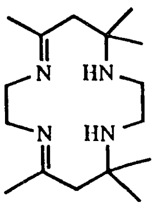
L_1



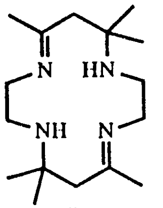
L_2



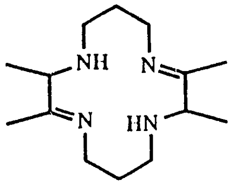
L_3



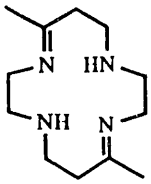
L_4



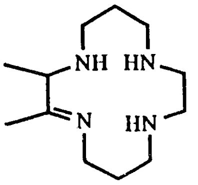
L_5



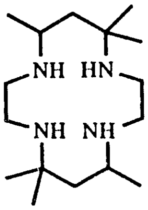
L_6



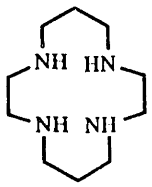
L_7



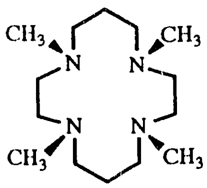
L_8



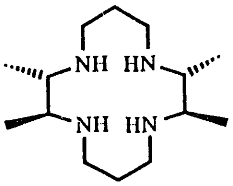
L_9



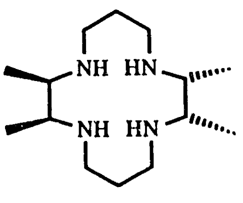
L_{10}



L_{11}



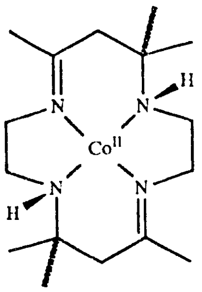
L_{12}



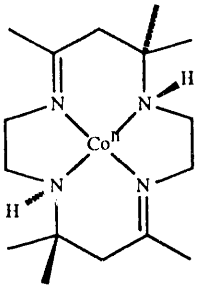
L_{13}

Binding and Reduction of Carbon Dioxide.

We characterized the reversible binding of CO_2, CO and H^+ to *meso*- and *racemic*-$[Co(I)L_5]^+$ in H_2O[9,10] and in CH_3CN.[5,11] The CO_2 binding constant for the *racemic* isomer is about one-hundred times greater than for the *meso* isomer in both solvents. The difference seems due to steric and hydrogen-bonding interactions between the bound CO_2 and the macrocycle. We also characterized[11] a binuclear species containing the Co-C(OH)-O-Co moiety (in which hydrogen bonding exists between the bound CO_2H and amine hydrogens of the macrocycle) and studied a CO_2 reduction pathway involving two cobalt centers which takes place during the slow decomposition of the $[Co(I)L_5CO_2]^+$ complex to $Co(II)L_5^{2+}$, CO, H_2, HCO_2^- and HCO_3^- in CH_3CN.



N-rac-Co^{II}L^{2+}



N-meso-Co^{II}L^{2+}

We have extended our work by using various 14-membered cobalt macrocycles to investigate factors affecting CO_2 and CO binding, catalytic activity and kinetics of thermal decomposition of CO_2 complexes. The electronic absorption spectra and other physical properties of the Co^{I}L, Co^{I}L-CO_2 and Co^{I}L-CO complexes were measured. The CO_2 and CO binding constants were determined by spectroscopic and/or electrochemical methods. As can be seen from Table II, the binding constants range from 5×10^4 to $\geq 3 \times 10^8$ M^{-1} for CO and from ≤ 0.5 to $> 10^6$ M^{-1} for CO_2 at 25 °C. The binding constants increase as the Co$^{II/I}$ reduction potentials become more negative.

Table II. CO_2 and CO Binding Constants and Carbonyl Vibrational Frequencies for Cobalt Macrocycles in CH_3CN at 25 °C

Macrocycle	$E_{1/2}$ V *vs* SCE	K_{CO_2}(Elec) M^{-1}	K_{CO_2}(Spec) M^{-1}	K_{CO} M^{-1}	$\nu_{C\equiv O}$ cm^{-1}
L_1	-0.37	<0.5		5×10^4	2007
L_2	-0.82	<0.5		1.4×10^5	1959
L_3	-1.28	1.7±0.5	4.0±1.3	1.1×10^8	1912
L_4	-1.34	25±6	26±8	1.9×10^8	1918
meso-L_5	-1.34	190±9			
rac-L_5	-1.34	$(6\pm2)\times10^4$	$(1.2\pm0.5)\times10^4$	2.3×10^8	1916
L_6	-1.41	$(9\pm3)\times10^4$		$\geq3\times10^8$	1910
L_7	-1.51	$(7\pm3)\times10^5$		$\geq3\times10^8$	1915
L_8	-1.65	$(3\pm2)\times10^6$		$\geq3\times10^8$	1912,1895

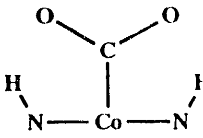
The CO_2 complexes studied here are 1:1 complexes in which the CO_2 is presumably bound η^1-C to an axial metal coordination site *(i.e.*, Co-C(O)O). It appears that, depending on the complex and the conditions, the cobalt center in the CO_2 complex may be either five coordinate, like the CO-adduct, or six coordinate. The CO_2 adduct of Co^IL_5 is thermochromic, evidently existing in a five-coordinate form at higher temperatures and in a six-coordinate form at low temperatures.

$$Co^IL_5\text{-}CO_2^+ + S \rightleftharpoons CoL_5(CO_2)S^+ \tag{1}$$

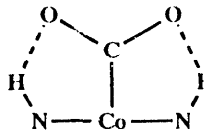
$$K_s = [CoL_5(CO_2)S^+] / [Co^IL_5\text{-}CO_2^+] \tag{2}$$

The temperature dependence of the spectrum in C_3H_7CN indicates the 530-nm band diminishes in intensity and a 430-nm shoulder increases in intensity as the temperature drops. Measurements over the range -110 °C to 40 °C in C_3H_7CN yield K_s (298) = 0.08 ± 0.06, $\Delta G°$ (298) = 1.5 ± 0.4 kcal mol^{-1}, $\Delta H°$ = -6.2 ± 0.3 kcal mol^{-1} and $\Delta S°$ = -26 ± 1 cal K^{-1} mol^{-1}. A solid tan sample, obtained at -70 °C from a THF-CH_3CN mixture, shows $\nu_{C=N}$ 1653 cm^{-1}, $\nu_{C=O}$ 1558 cm^{-1}, and two kinds of $\nu_{C\equiv N}$, 2337 cm^{-1} for coordinated CH_3CN and 2272 cm^{-1} for free CH_3CN, consistent with the formation of $[CoL_5(CO_2)S](ClO_4)$ with S = CH_3CN. Furthermore, the spectrum of the low-temperature form is similar to that of *trans*-$Co(en)_2(OH_2)(CO_2)^+$, which is known to be six coordinate. From the UV-vis spectra of the CO_2-adducts, the complexes seem to fall into two classes: For L_3, L_4 and L_5, the lowest energy transition occurs at 530-540 nm, with additional bands at 400-460 nm and 310 nm. In contrast, for L_6, L_7 and L_8, the lowest energy transition is at 450-480 nm. Indeed, the room-temperature spectra of the CO_2 adducts of $Co^IL_6^+$, $Co^IL_7^+$ and $Co^IL_8^+$ resemble that of the low-temperature form of Co^IL_5-CO_2^+ and it is likely that these are also six-coordinate with a solvent molecule as an axial ligand.

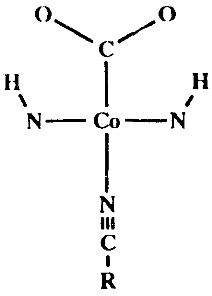
We measured the temperature-dependent FT-IR spectra of *rac*-$CoL_5(CO_2)^+$ in CD_3CN, C_3H_7CN and in a CD_3CN/THF mixture.[12] The spectra indicated the existence of four CO_2 adducts depending upon whether the solvent is coordinated or not and on whether there is hydrogen bonding between bound the CO_2 and the N-H of the ligand: a five-coordinate, non-hydrogen bonded form **A** (ν_{CO}=1710 cm^{-1}, ν_{NH}=3208 cm^{-1}), a five-coordinate intramolecular hydrogen-bonded form **B** (ν_{CO}=1626 cm^{-1}, ν_{NH}=3224 cm^{-1}), a six-coordinate non-hydrogen bonded form **C** (ν_{CO}=1609 cm^{-1}), and a six-coordinate intramolecular hydrogen-bonded form **D** (ν_{CO}=1544 cm^{-1}, ν_{NH}=3145 cm^{-1}). The binding of CO_2 *via* both its electrophilic center (carbon atom) and its nucleophilic center (oxygen atom) stabilizes the CO_2 complex at low temperature.



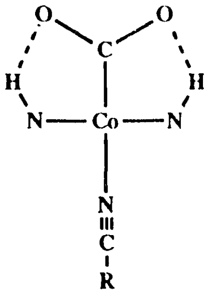
(A)



(B)



(C)



(D)

The electron distributions of CO_2 complexes are of some interest. Molecular Orbital calculations for a related complex suggests that extensive charge donation from Co(I) to CO_2 in $[Co^{I}LCO_2]^+$ results in an electronic distribution better described as $[Co^{II}L(CO_2^-)]^+$. However, there is no evidence that cobalt(II) (a d^7 metal center) is actually present. The ^1H NMR spectra of $[CoL(CO_2)]^+$ in CD_3CN at various temperatures indicate the existence of only diamagnetic CO_2 adducts. To our knowledge, low-spin, six-coordinate Co(I) has never been observed. Therefore the six-coordinate species $[Co^{I}L(CO_2)(CH_3CN)]^+$ is most reasonably formulated as a cobalt(III) complex $[Co^{III}L(CO_2^{2-})(CH_3CN)]^+$, closely related to the yellow diamagnetic complexes $[Co^{III}(en)_2(CO_2^{2-})(OH)]$ in solution and $[Co^{III}(en)_2(CO_2^{2-})]^+$ in the solid.[13] In fact, preliminary XANES (x-ray absorption near edge structure) results for $[CoL(CO_2)(CH_3CN)]^+$ in CH_3CN at 150 K indicate that the oxidation state of the cobalt center can be interpreted as Co(III).

Electrochemical Reduction of CO_2 in Water.

We are investigating the electrocatalytic activity of cobalt macrocycle complexes in the reduction of carbon dioxide in CO_2-saturated water at the Hg electrode. CO, H_2 and a small amount of formate are the products. The influence of pH, applied potential, and the selectivity and efficiency during various times of electrolysis are currently being investigated. Unlike NiL_{10}^{2+}, the CoL_5^{2+} based system produces more H_2 from H_2O than CO from CO_2 at low pH (< 3). At 4.0 < pH < 6.0, more H_2 is produced for $E > -1.35$ V and $E < -1.60$ V vs SCE. This result can be explained by the favorable binding of H^+ to $Co(I)L_5^+$ in H_2O, previously studied by pulse radioloysis.[10] In fact, the CoL_5^{2+} complex had been used as a mediator for the photochemical reduction of H_2O with $Ru(bpy)_3^{2+}$.[14] For a reversible electron-transfer reaction followed by a fast catalytic reaction, the catalytic current of the cyclic voltammogram can be written,

$$i_c = nFA[\mathrm{CoL}](Dk[\mathrm{CO_2}])^{1/2} \qquad (3)$$

where n is number of electrons, F is the Faraday constant, D is the diffusion constant, and k is the rate constant of the catalytic reaction. The correlations of the catalytic current vs [CoL_5] and the catalytic current vs the square root of the CO_2 concentration for *rac*-CoL are linear. Therefore the reaction is first-order in [CoL_5], first-order in [CO_2], and almost independent of [H^+]. A proposed mechanism of CO_2 reduction is shown below.

$$\mathrm{CoL^{2+} + e^- \longrightarrow CoL^+} \qquad (4)$$

$$\mathrm{CoL^+ + CO_2 \longrightarrow CoL\text{-}CO_2^+} \qquad (5)$$

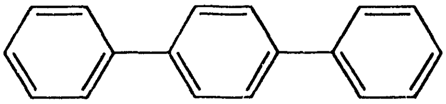
$$\mathrm{CoL\text{-}CO_2^+ + H^+ \rightleftharpoons CoL\text{-}CO_2H^{2+}} \qquad (6)$$

$$\mathrm{CoL\text{-}CO_2H^{2+} + e^- \longrightarrow \longrightarrow CoL^{2+} + CO + OH^-} \qquad (7)$$

We are extending our work to other cobalt macrocycles which differ in $Co^{II/I}$ potentials, steric hindrance of methyl groups, and position(s) of NH hydrogen(s) in order to elucidate the important factors defining an efficient electrocatalyst for CO_2 reduction. Our preliminary results indicate: (1) CoL_6 and CoL_7 seem better catalysts for the CO_2 reduction than CoL_5 in terms of selectivities and the yields. The axial methyl groups of CoL_5 may hinder an efficient binding of CO_2 and further reaction; (2) Bulk electrolysis results for *rac-* and *meso*-CoL_5 were similar, despite the of large difference in the binding constants. Isomerization may take place during the reduction; (3) All systems produced much more H_2 from H_2O than CO from CO_2 at pH 2.

Photochemical Reduction of CO_2.

Cobalt macrocycles mediate electron transfer in the photoreduction of CO_2 with *p*-terphenyl as a photosensitizer and a tertiary or β-hydroxylated tertiary amine as a sacrificial electron donor in methanolic acetonitrile.[15] The anion radical of *p*-terphenyl has a long lifetime (8.3 ms in TEA/THF) and is a very strong reducing reagent (-2.45 V *vs* SCE).[16] It reduces CO_2 to HCO_2^- with an apparent quantum yield of 0.072 at 313 nm in the TEA/DMF system. But *p*-terphenyl itself concurrently undergoes photo-Birch reduction within 4 turnovers of its catalytic cycle.



p-terphenyl

Mediation by certain cobalt macrocycles suppresses the degradative and competitive photo-Birch reduction of *p*-terphenyl, leading to efficient and selective formation of both CO and formate with little H_2.[17,18] The apparent total quantum yield of CO and HCO_2^- is 0.25 in the TEOA/CH_3CN/MeOH/$CoL_{10}Cl_3$ system. Structural properties such as hydrogen-bonding interactions between the bound CO_2 and N-H protons and steric repulsion by the macrocycle methyl groups to axial ligation may be responsible for the observed differences in the distribution of the reduction products – CO, formate and H_2.

Cobalt complexes with two or four C-methyl groups (L_2, L_6, L_7, and L_{10}) give comparable activity for the reduction of CO_2 and H_2 evolution. In the case of more extensively C-methylated macrocycles (L_3 and L_5), however, the activity of CO_2 reduction decreases by an appreciable amount, but not the H_2 evolution. Steric hindrance by the two pairs of geminate C-methyl groups reduces the accessibility of the metal center to approach by either CO_2 molecules or other ligands such as amines and solvent. The N-methylated complex, $Co(II)L_{11}^{2+}$, did not mediate the photoreduction of CO_2 and only a small quantity of H_2 was detected. This inactivity is due to the difficulty in attaining the six-coordinate structure of Co(III) and the very high $Co^{III/II}$ potential ($E_{1/2} > +1.2$ V vs SCE). For CoL_1 H_2 evolution dominated when TEA was used as electron donor with the tetraene complex. A proposed mechanism of CO_2 reduction is shown below.

$$\text{TP radical} + [Co^{III}L]^{3+} \longrightarrow [Co^{II}L]^{2+} + \text{TP}$$
$$\text{TP radical} + [Co^{II}L]^{2+} \longrightarrow [Co^{I}L]^{+} + \text{TP}$$
$$[Co^{I}L]^{+} + CO_2 \longrightarrow [Co^{I}L\text{-}CO_2]^{+}$$
$$[Co^{I}L\text{-}CO_2]^{+} + \text{TEA} \rightleftharpoons [Co^{III}L(CO_2^{2+})(\text{TEA})]^{+}$$
$$[Co^{III}L(CO_2^{2+})(\text{TEA})]^{+} + H^{+} \rightleftharpoons [CoL\text{-}COOH]^{2+} + \text{TEA}$$

$$[CoL\text{-}COOH]^{2+} + \text{TP radical} \longrightarrow [Co^{II}L]^{2+} + CO + OH^{-} + \text{TP}$$

Flash photolysis experiments (transient absorption) are planned to identify intermediates and determine the kinetics.

The catalytic electron mediation studies were extended to $CoCl_2$ and Ni(II), Zn(II), Fe(II), Cu(II) complexes of L_{10}. None of these complexes functioned as electron mediators for CO_2 photoreduction. The failure in the case of the NiL_{10}

complex is in marked contrast with its excellent performance as an electron mediator in the electrochemical reduction (almost 100% CO production) and with its moderate performance in photochemical reduction with $Ru(bpy)_3^{2+}$ as a sensitizer (CO/H_2 = 1/6 at pH 4). The failure with $Ni^{II}L_{10}$ and $[Co^{II}L_{11}Cl]$ in the catalytic electron mediation in the system may result from a very unstable trivalent oxidation state of the metal complexes under our conditions. Although trivalent nickel complexes have been reported, these complexes are stable only in acidic media. The CoL_{11} complex has an oxidation potential at > 1.2 V and cannot form six-coordinate species because of steric hinderance. The failure with $Ni^{II}L_{10}$ may also be due to slow electron transfer from *p*-terphenyl due to the large Ni-N bond distance change in the Ni(II) and Ni(I) states. Planned flash photolysis experiments may clarify these issues.

Concluding Remarks.

We are studying the properties of reduced mediators, the binding of CO_2 molecules to reduced mediators, and the reactivity of the mediators to yield the desired products. With knowledge of the properties of these complexes we are now ready to study the mechanism and kinetics of the photochemical CO_2 reduction in order to design more effecient photo-energy conversion systems.

Acknowledgment.

The author would like to acknowledge many coworkers and collaborators including Drs. C. Creutz, N. Sutin, B. S. Brunschwig, L. R. Furenlid, M. W. Renner, S. W. Feldberg, H. A. Schwarz, and J. F. Wishart of Brookhaven National Laboratory; Prof. D. J. Szalda (Baruch College); Prof. S. Yanagida, Dr. S. Matsuoka (Osaka Univ.); Mr. T. Ogata (Osaka Univ. and BNL); Prof. Horst Elias (Techniche Hochschule Darmstadt); and Ms. J. Haff (SUNY at Old Westbury and BNL). This work was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

DISCLAIMER

References

(1) Fisher, B.; Eisenberg, R. *J. Am. Chem. Soc.* **1980,** *102*, 7361.

(2) Tinnermans, A. T. A.; Koster, T. P. M.; Thewissen, D. H. M. W.; Mackor, A. *Recl. Trav. Chim. Pays. -Bas* **1984**, *103*, 288-295.

(3) Beley, M.; Collin, J. P.; Ruppert, R.; Sauvage, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 7461.

(4) Grant, J. L.; Goswami, K.; Spreer, L. O.; Otvos, J. W.; Calvin, M. *J. Chem. Soc., Dalton Trans* **1987**, 2105.

(5) Fujita, E.; Creutz, C.; Sutin, N.; Szalda, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 343.

(6) Furenlid, L. R.; Renner, M. W.; Szalda, D. J.; Fujita, E. *J. Am. Chem. Soc.* **1991**, *113*, 883.

(7) Szalda, D. J.; Fujita, E. *Acta Cryst.* **1992**, *C48*, 1767-1771.

(8) Fujita, E; Furenlid, L. R.; Renner, M. W.; Elias, H. Unpublished data.

(9) Creutz, C.; Schwarz, H. A.; Wishart, J. F.; Fujita, E.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111, 1153.*

(10) Creutz, C.; Schwarz, H. A.; Wishart, J. F.; Fujita, E.; Sutin, N. *J. Am. Chem. Soc.* **1991**, *113*, 3361-3371.

(11) Fujita, E.; Szalda, D. J.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 4870.

(12) Fujita, E.; Creutz, C.; Sutin, N.; Brunschwig, B. S. *Inorg. Chem.* **1993**, in press.

(13) Szalda, D. J.; Chou, M. H.; Fujita, E.; Creutz, C. *Inorg. Chem.* **1992**, *31*, 4712.

(14) Brown, G. M.; Brunschwig, B. S.; Creutz, C.; Endicott, J. F.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 1298.

(15) Matsuoka, S.; Kohzuki, T.; Pac, C.; Ishida, A.; Takamuku, S.; Kusaba, M.; Nakashima, N.; Yanagida, S. *J. Phys. Chem.* **1992**, *96*, 4437-4442.

(16) Matsuoka, S.; Fujii, H.; Yamamoto, K.; Pac, C.; Ishida, A.; Takamuku, S.; Kusaba, M.; Nakashima, N.; Yanagida, S. *J. Phys. Chem.* **1991**, *95*, 5802-5808.

(17) Matsuoka, S.; Yamamoto, K.; Pac, C.; Yanagida, S. **1991**, 2099-2100.

(18) Matsuoka, S.; Yamamoto, K.; Ogata, T.; Kusaba, M.; Nakashima, N.; Fujita, E.; Yanagida, S. *J. Am. Chem. Soc.* **1993**, *115*, 601-609.

(19) Szalda, D. J.; Schwarz, C. L.; Endicott, J. F.; Fujita, E.;Creutz, C. *Inorg. Chem.* **1989**, *28*, 3214.

DATE FILMED

8/24/93

END