

## Electrocatalytic Reduction of Carbon Dioxide with Iron, Cobalt, and Nickel Complexes of Terdentate Ligands

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### Introduction

There has been, in the recent past, much interest in the design of electrocatalysts for the reduction carbon dioxide<sup>1-4</sup> to useful fuel products. These reactions are particularly difficult to catalyze since they not only involve multiple electron transfers but also are often coupled with chemical steps such as protonation. Furthermore, there can be multiple and competing reaction pathways giving rise to a variety and distribution of reaction products.

A number of transition-metal complexes, both in solution and on electrode surfaces, have been shown to be effective in the electrocatalytic reduction of carbon dioxide.<sup>1-6</sup>

We have previously shown that electropolymerized layers of  $[\text{Co}(\text{v-terpy})_2]^{2+}$  (v-terpy is 4'-vinyl-2,2':6',2''-terpyridine) are electrocatalytically active in the reduction of carbon dioxide to formic acid and of oxygen to water and hydrogen peroxide.<sup>7,8</sup> This reactivity was attributed to the generation of empty coordination sites on the cobalt. In addition, there was evidence for cooperativity effects between adjacent metal complexes within the polymeric film.

We also prepared the 7-coordinate vinylquinquepyridine (v-qpy) (v-qpy is 4',4''-divinyl-2,2':6',2''':6'',2''':6''',2''''-quinquepyridine) derivative  $[\text{Co}(\text{v-qpy})\text{Cl}_2]$ .<sup>9</sup> Analogous to the v-terpy complex, this material could be easily electropolymerized to give rise to electrodes modified with electroactive polymeric films of the complex. Unfortunately, such modified electrodes only exhibited modest electrocatalytic activity.

These findings prompted us to take a closer look at various transition-metal complexes and to try to determine what aspects, in terms of coordination, dictate electrocatalytic activity. In essence, we wished to determine if terdentate coordination, especially around first-row transition metals, favored such electrocatalytic activity.

With this objective in mind, we have prepared a wide variety of first-row transition-metal complexes that incorporate bis(terdentate) coordination around the metal center. The ligands used

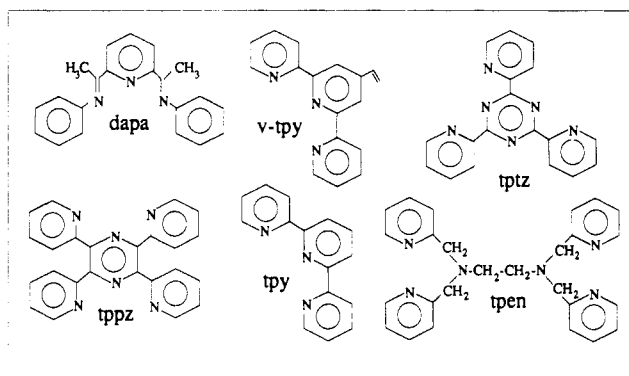


Figure 1. Terdentate ligands employed.

are presented in Figure 1, and the complexes prepared are presented in Table I. Consistent with the above-mentioned arguments, we find that all of these materials exhibit some degree of electrocatalytic activity in the reduction of  $\text{CO}_2$ . We describe below our preliminary observations and point to some future directions.

### Experimental Section

The ligands tppz,<sup>10</sup> dapa,<sup>11</sup> and tpen<sup>12</sup> were prepared according to literature methods. The ligands terpyridine and tripyridyltriazine were purchased from Aldrich Chemical Co. and were used without further purification. v-tpy was prepared as previously described.<sup>13</sup> The metal complexes were prepared by combining the appropriate molar ratios of the ligand and the metal chloride salt in ethanol/water (1:1) and heating at reflux and under  $\text{N}_2$  for 3 h. The products were isolated by precipitation upon addition of a concentrated aqueous solution of ammonium hexafluorophosphate. The resulting product was collected and washed with water and ether. Purification was effected by recrystallization from acetone/toluene. All new compounds were characterized by elemental analysis and/or FAB mass spectrometry and satisfactory results were obtained in all cases (this information is available as supplementary material).

Electrochemical experiments and techniques were as previously described.<sup>8</sup> All potentials are referenced to the sodium saturated calomel electrode (SSCE) without regard for the liquid junction.

The production of formic acid was assessed using the chromotropic acid spot test.<sup>14</sup> This involves reaction of an aliquot of the reaction mixture with 2 N HCl (1 drop), and magnesium is added until no more gas is evolved. Sulfuric acid (12 N, ca. 1 mL) is added, and the reaction mixture is incubated at 60 °C for 10 min. The presence of formic acid is evidenced by the generation of a violet-pink solution with strong absorbances at 482 and 584 nm. These absorbances were referenced to solutions electrolyzed in the absence of carbon dioxide. The amount of formic acid generated was determined from a calibration curve made with solutions of known concentrations of formic acid.

### Results and Discussion

**Electrochemical Characterization.** In general, all of the complexes investigated were electrochemically well behaved and exhibited both metal-localized as well as ligand-localized redox processes. Values for the formal potentials (or peak potentials in the case of irreversible processes) as well as  $\Delta E_p$  (difference in peak potential values) for all the complexes studied are presented in Table I. For the iron complexes, typically one metal-based redox process was observed whereas the cobalt and nickel complexes, as anticipated, exhibited two metal-based redox processes.

- (10) Goodwin, H. A.; Lyons, F. J. *Am. Chem. Soc.* **1959**, *81*, 6415.
- (11) Aleya, E. C.; Merrel, P. H. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4* (6), 535.
- (12) Mandel, J. B.; Maricondi, C.; Douglas, B. E. *Inorg. Chem.* **1988**, *27*, 2990.
- (13) Potts, K. T.; Usifer, D.; Guadalupe, A.; Abruña, H. D. *J. Am. Chem. Soc.* **1987**, *109*, 3961.
- (14) Feigl, F. *Spot Tests in Organic Analysis*; Elsevier: Amsterdam, 1956; p 451.

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- (1) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: New York, 1988.
- (2) Ayers, W. M., Ed. *Catalytic Activation of Carbon Dioxide*; ACS Symposium Series No. 363; American Chemical Society: Washington, DC, 1988.
- (3) Abruña, H. D. *Coord. Chem. Rev.* **1988**, *86*, 135.
- (4) Abruña, H. D. *Electrode Modification with Polymeric Reagents*. In *Electroresponsive Molecular and Polymeric Systems*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1988; Vol. 1, Chapter 3.
- (5) (a) Lieber, C. M.; Lewis, N. S. *J. Am. Chem. Soc.* **1984**, *106*, 5033. (b) Christensen, P. A.; Hamnett, A.; Muir, A. V. G. *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *241*, 361.
- (6) (a) Cabrera, C. R.; Abruña, H. D. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *209*, 101. (b) Sullivan, B. P.; Bolinger, C. M.; Conrad, D.; Vining, W. J.; Murray, R. W.; Meyer, T. J. *J. Chem. Soc. Chem. Commun.* **1985**, 1416.
- (7) (a) Guadalupe, A. R.; Usifer, D. A.; Potts, K. T.; Hurrell, H. C.; Mogsstad, A.-L.; Abruña, H. D. *J. Am. Chem. Soc.* **1988**, *110*, 3462. (b) Potts, K. T.; Usifer, D. A.; Guadalupe, A. R.; Abruña, H. D. *J. Am. Chem. Soc.* **1987**, *109*, 3961.
- (8) Hurrell, H. C.; Mogsstad, A.-L.; Usifer, D. A.; Potts, K. T.; Abruña, H. D. *Inorg. Chem.* **1989**, *28*, 1080.
- (9) Gheysen, K. A.; Potts, K. T.; Hurrell, H. C.; Abruña, H. D. *Inorg. Chem.* **1990**, *29*, 1589.

Table I. Redox Potentials vs SSCE for Fe, Co, and Ni Complexes of Terdentate Ligands at a Platinum Electrode in 0.1 M TBAP

| complex  | solvent | $E^{\circ}$ (V) [ $\Delta E_p$ (mV)] |   | $E_{red(CO_2)}$ (DMF) <sup>a</sup> |
|--|---------|--------------------------------------|---|------------------------------------|
|  |         | metal based                          | ligand based                                    |                                    |
| Fe(dapa) <sub>2</sub> (PF <sub>6</sub> ) <sub>2</sub>  | ACN     | +1.43 [irrev]                        | -0.87 [60], -0.95 [70], -1.82 [irrev]           | -1.82                              |
| Co(dapa) <sub>2</sub> (PF <sub>6</sub> ) <sub>2</sub>  | DMF     | +0.59 [70], -0.37 [60]               | -1.33 [70], -1.75 [110]                         | -1.30                              |
| Ni(dapa) <sub>2</sub> (PF <sub>6</sub> ) <sub>2</sub>  | ACN     | +1.75 [80], -0.85 [60]               | -1.25 [100], -1.80 [irrev]                      | -1.25                              |
| Fe(tppz) <sub>2</sub> (PF <sub>6</sub> ) <sub>2</sub>  | ACN     | +1.35 [100]                          | -0.83 [70], -1.08 [60], -1.56 [70], -1.70 [60]  | -1.56                              |
| Co(tppz) <sub>2</sub> (PF <sub>6</sub> ) <sub>2</sub>  | ACN     | +0.41 [90], -0.39 [60]               | -0.43 [50], -0.52 [50], -0.81 [70], -1.15 [110] | -1.20                              |
| Ni(tppz) <sub>2</sub> (PF <sub>6</sub> ) <sub>2</sub>  | ACN     | +1.74 [70], -0.28 [50]               | -0.38 [40], -0.83 [130], -1.21 [60]             | -1.54                              |
| Fe(tpy) <sub>2</sub> (PF <sub>6</sub> ) <sub>2</sub>   | ACN     | +1.10 [70]                           | -1.13 [70], -1.27 [60], -1.94 [70]              | -1.15                              |
| Fe(v-tpy) <sub>2</sub> (PF <sub>6</sub> ) <sub>2</sub> | ACN     | +1.04 [80]                           | -1.19 [80], -1.32 [80]                          | -0.95                              |
| Co(tpy) <sub>2</sub> (PF <sub>6</sub> ) <sub>2</sub>   | ACN     | +0.27 [60], -0.77 [70]               | -1.66 [60]                                      | -1.53                              |
| Co(v-tpy) <sub>2</sub> (PF <sub>6</sub> ) <sub>2</sub> | ACN     | +0.26 [60], -0.79 [60]               | -1.70 [60]                                      | -0.90                              |
| Ni(tpy) <sub>2</sub> (PF <sub>6</sub> ) <sub>2</sub>   | ACN     | +1.65 [60], -1.20 [80]               | -1.38 [100]                                     | -1.20                              |
| Ni(v-tpy) <sub>2</sub> (PF <sub>6</sub> ) <sub>2</sub> | ACN     | +1.62 [110], -1.25 [80]              | -1.45 [100]                                     | -1.22                              |
| Fe(tptz) <sub>2</sub> (PF <sub>6</sub> ) <sub>2</sub>  | ACN     | -0.69 [60]                           | -0.78 [60], -1.38 [60], -1.65 [60]              | -1.38                              |
| Co(tptz) <sub>2</sub> (PF <sub>6</sub> ) <sub>2</sub>  | DMF     | +0.77 [70], -0.33 [60]               | -0.93 [60], -1.38 [70]                          | -0.93                              |
| Co(tpen)(PF <sub>6</sub> ) <sub>2</sub>                | DMF     | +0.25 [70], -1.33 [60]               | -1.98 [80]                                      | -1.51                              |
| Ni(tpen)(PF <sub>6</sub> ) <sub>2</sub>                | ACN     | +1.55 [60]                           | -1.77 [irrev]                                   | -1.80                              |
|  |         |                                      |   | -1.40 (DMSO)                       |

<sup>a</sup> Values reported represent the potential of the wave at which the current enhancement due to electrocatalytic reduction dioxide was observed.

The electrocatalytic activity of the metal complexes toward reduction of carbon dioxide was evaluated by comparing their voltammetric response under an atmosphere of nitrogen and carbon dioxide, respectively, and using DMF as a solvent since acetonitrile can behave as a moderately strong coordinating solvent. We find that for all of the complexes studied, the currents under an atmosphere of carbon dioxide were enhanced relative to those under an atmosphere of nitrogen, and we ascribe this enhancement to the electrocatalytic reduction of carbon dioxide. The last column of Table I lists the potential at the peak of the wave at which the current enhancement due to electrocatalytic reduction of carbon dioxide was observed for each complex. Since in most cases the onset of the current enhancement was observed prior to these peak potentials, the values given in Table I represent a lower limit for the electrocatalytic efficacy of these materials.

Although the potential at which carbon dioxide was catalytically reduced varied broadly for the various complexes, all of the complexes exhibited some degree of electrocatalytic activity. In addition, three of the complexes exhibited electrocatalytic behavior for potentials positive of -1.0 V, indicative of a very strong electrocatalytic effect since the reduction of carbon dioxide in DMF/TBAP in the absence of the complexes takes place at a potential more negative than -2.0 V.

We discuss briefly three complexes, as they are representative of the types of behavior generally found. These are Co(dapa)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub>, Ni(dapa)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub>, and Fe(v-tpy)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub>. In these complexes we will be able to compare the effects due to changes in the metal ion center while keeping the ligand (dapa) constant, as well as the effects of having the complex immobilized on the electrode surface.

1. Co(dapa)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub>. Figure 2 presents the voltammetric behavior of [Co(dapa)<sub>2</sub>]<sup>2+</sup> under an atmosphere of nitrogen and carbon dioxide in the potential range from 0.0 to -2.0 V. The inset shows the electrochemical behavior with the scan direction being reversed after each wave. The complex exhibits three well-behaved voltammetric waves with formal potentials of -0.37, -1.33, and -1.75 V (Table I). The first two processes correspond to reversible one-electron reductions whereas the last one appears to involve a two-electron transfer and, in addition, there is some chemical irreversibility associated with it. We ascribe the wave at -0.35 V to a metal-based Co(II/I) process, whereas the latter two are ligand localized. It is clear from the figure that in the presence of carbon dioxide there is a dramatic enhancement (of the order of 625%) in the current for the wave centered at -1.25 V. Preliminary studies (using the chromotropic acid test; see Experimental Section) indicate that one of the reaction products is formic acid and that the current efficiency for formic acid production is about 60%. Other potential carbon-containing

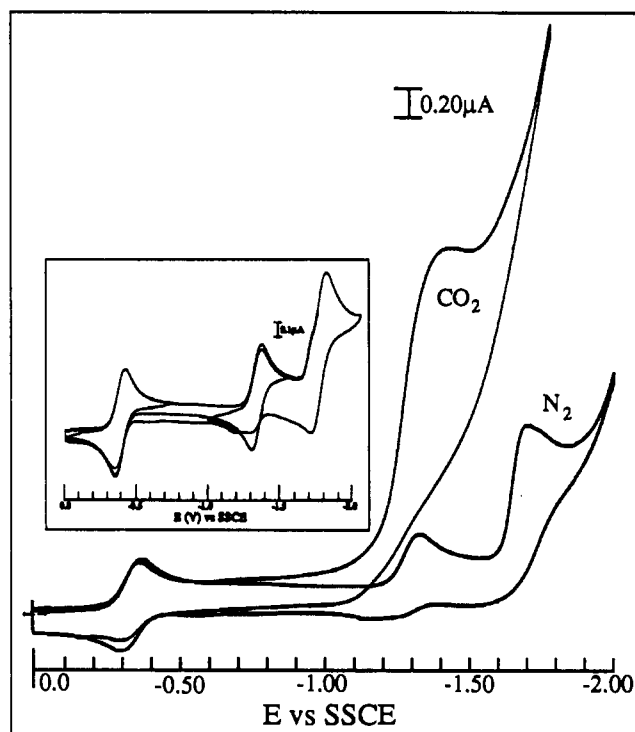
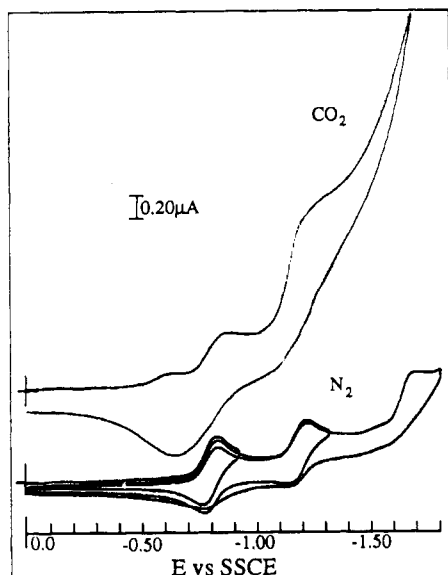


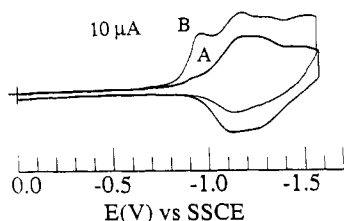
Figure 2. Electrochemical behavior of [Co(dapa)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> under nitrogen and carbon dioxide atmospheres in DMF/0.1 M TBAP. Inset: voltammetry in DMF/0.1 M TBAP and under N<sub>2</sub> and where the sweep direction is reversed after every wave.

products include CO, methanol and methane, and we are currently carrying out studies to determine if they are also produced. The production of formic acid requires the availability of protons which we believe to arise from trace water in the solvent. It should be noted that in these catalytic runs no water was deliberately added to the solutions. Although the supporting electrolyte could, in principle, serve as a source of protons, this would be most unlikely. Furthermore, if after the voltammetry in the presence of carbon dioxide the solution was again purged with nitrogen, the voltammetric response was identical to that prior to purging with CO<sub>2</sub>. We recognize the important role that a proton source may have in dictating the mechanism and/or product distribution, and we are currently investigating this aspect.

It should be mentioned that when 10% water (vol/vol) was added to the solution, the background currents (in the potential range of 0 to -2.0 V) were virtually identical to those in which no water was deliberately added and the electrochemical response



**Figure 3.** Electrochemical behavior of  $[\text{Ni}(\text{dapa})_2](\text{PF}_6)_2$  under nitrogen and carbon dioxide atmospheres in DMF/0.1M TBAP.



**Figure 4.** Cyclic voltammograms for an electropolymerized film of  $[\text{Fe}(\text{v-terpy})_2]^{2+}$  in DMF/0.1M TBAP saturated with (A)  $\text{N}_2$  or (B)  $\text{CO}_2$ .

for the complex under these conditions and an atmosphere of nitrogen was identical to that in which no water was added. These observations would strongly argue against the catalyzed evolution of hydrogen as being responsible for the observed enhanced currents. In addition, the fact that formic acid is detected unequivocally establishes that carbon dioxide is being electrocatalytically reduced.

**2.  $[\text{Ni}(\text{dapa})_2](\text{PF}_6)_2$ .** Figure 3 presents the voltammetric behavior of  $[\text{Ni}(\text{dapa})_2]^{2+}$  under an atmosphere of nitrogen and carbon dioxide. The complex exhibits three reductions. The first two correspond to reversible one-electron processes at formal potentials of  $-0.85$  and  $-1.25$  V, which we ascribe to metal- and ligand-localized processes, respectively. There is a third irreversible wave with a peak potential value of  $-1.80$  V, which also appears to involve the transfer of one electron and is likely ligand localized. As for the cobalt complex, there is a large enhancement in the wave at  $-1.25$  V in the presence of carbon dioxide, again implying a strong electrocatalytic effect. However, there is also an enhancement of the wave at about  $-0.85$  V, although the magnitude of the enhancement is much smaller than that at  $-1.25$  V. As for the case of the cobalt complex, we have detected formic acid as one of the products. We are currently carrying out quantitative determinations as well as determining if other products are being generated.

It is interesting to note that both of the complexes exhibit electrocatalytic activity at about  $-1.25$  which would formally correspond to a ligand-based reduction. As mentioned above,

the nickel complex also exhibits some electrocatalytic activity at  $-0.85$  V, which formally corresponds to a metal-localized process, whereas the cobalt complex does not exhibit any electrocatalytic behavior at  $-0.37$  V (which is also a metal-localized redox process). However, it should be pointed out that one should not anticipate any electrocatalytic activity at this potential since it is below the thermodynamic value for the reduction of carbon dioxide.

The electrocatalytic activity (relative current enhancement) of the cobalt complex at  $-1.25$  V is higher than that of nickel, and this might reflect an ability of the former to act as a two-electron reductant. Thus, it is clear that the metal center can play a key role. However, the fact that in the case of the nickel complex electrocatalysis was observed at  $-0.85$  V as well as at  $-1.25$  V would suggest that there might be two different mechanisms involved and that these might give rise to different products. We are currently investigating these aspects in depth.

**3.  $[\text{Fe}(\text{v-terpy})_2](\text{PF}_6)_2$ .** This complex represents the case of a complex that can be deposited on an electrode surface via electropolymerization in a way similar to that of the analogous cobalt complex which we have previously studied.<sup>7,8</sup> The complex undergoes electroreductively initiated polymerization to give rise to an electrode coated with an electroactive polymeric film of the complex with waves at formal potentials of  $-1.12$  and  $-1.28$  V, respectively (Figure 4A). During the electropolymerization process (in acetonitrile/TBAP), a new reversible wave (not present for the complex in solution) appears with a formal potential of  $-0.10$  V. This behavior is analogous to that which we previously reported for electropolymerized films of  $[\text{Co}(\text{v-terpy})_2](\text{PF}_6)_2$ <sup>7,8</sup> and which we identified in that case as being due to partial displacement of the ligand and coordination by acetonitrile. It should also be mentioned that this wave is not present for the modified electrode in DMF solution (Figure 4), again consistent with the findings for the analogous cobalt complexes.

As shown in Figure 4B, electropolymerized films of  $[\text{Fe}(\text{v-terpy})_2]^{2+}$  were also effective in the electrocatalytic reduction of carbon dioxide. The onset of electrocatalytic activity was at about  $-0.95$  V, which again represents a dramatic diminution in the activation energy by about 1 V. (Recall that reduction of  $\text{CO}_2$  in DMF takes place at potentials negative of  $-2.0$  V.)

## Conclusions

We have shown that transition-metal complexes incorporating terdentate coordination appear to be especially active in the electrocatalytic reduction of carbon dioxide. This seems to be due to a subtle balance between stability and reactivity in the reduced form which is assumed to be the one that is active in the electrocatalytic process. Since catalytic currents were observed for redox processes that correspond to metal-based as well as ligand-based processes, it is quite likely that more than one mechanism is involved. It is also clear that the metal center can also play a very significant role in dictating electrocatalytic activity. In addition, the nature of the products and their distribution may also depend on this and, as mentioned previously, on the presence of proton donors. We are continuing our investigations of these materials with emphasis on product identification and distribution.

**Supplementary Material Available:** Tables of elemental analysis and mass spectral data (3 pages). Ordering information is given on any current masthead page.

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