Inorg. Chem. **2005**, *44*, 3046–3056

Inorganic Chemistry
Article

Concentration of Carbon Dioxide by Electrochemically Modulated Complexation with a Binuclear Copper Complex

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Received January 7, 2005

The reactions of bicarbonate ion with a series of binuclear Cu(II) complexes in buffered aqueous solution have been studied, and effective binding constants for bicarbonate have been determined at pH 7.4 for the complexes $[Cu_2(taec)]^{4+}$ (taec = *N*,*N*′,*N*′′,*N*′′′-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane) and $[Cu_2(tpmc)(OH)]^{3+}$ (tpmc = *N*, *N*′,*N*′′,*N*′′′-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane). $[Cu_2(o\text{-xyl-DMC}_2)]^{4+}$ (*o*-xyl-DMC$_2$ = α,α'-bis(5,7-dimethyl-1,4,8,11-tetraazacyclotetradecan-6-yl)-*o*-xylene) did not react with bicarbonate ion in an aqueous solution buffered at this pH. The complexes were reduced by controlled-potential electrolysis, and the stability of the Cu(I) derivatives in aqueous solution and their affinity for bicarbonate/carbonate ion were investigated. On the basis of these fundamental studies, $[Cu_2(tpmc)(\mu\text{-OH})]^{3+}$ has been identified as an air-stable, water-soluble carrier for the capture and concentration of CO_2 by electrochemically modulated complexation. The carrier binds to the carbonate ion strongly in its oxidized, Cu(II) form and releases the ion rapidly when reduced to the Cu(I) complex. In small-scale electrochemical pumping experiments designed to demonstrate the feasibility of this approach, CO_2 has been pumped from an initial 10% CO_2/N_2 mixture up to a final concentration of 75%.

Introduction

Separation technologies for the removal and concentration of CO_2 have many known and potential applications, including the recovery of CO_2 from pre- or postcombustion gas streams used in power production from fossil fuels, purification of gas streams for ammonia synthesis, and upgrading natural gas streams from gas wells rich in CO_2.[1] Current methods for carbon dioxide capture include carbonate formation,[2,3] the use of different amines to form either carbamates or ammonium bicarbonate salts,[4,5] and membrane separations.[6a] A particular interest of our laboratories is the development of electrochemical methods for pumping CO_2. Electrochemical cycles are not Carnot-limited, and such an approach in the long term may offer advantages in efficiency for CO_2 recovery from dilute CO_2 streams. A number of electrochemical methods for CO_2 recovery have been proposed, including molten carbonate fuel cells,[6b,c] proton pumps,[7] doped alkaline earth carbonates,[8] and electrochemically modulated complexation (EMC).[9,10] The last approach uses a redox-active carrier molecule that has a strong affinity for CO_2 in one oxidation state and a weak affinity upon either oxidation or reduction of the carrier molecule.

Recently, our laboratories reported the concentration of carbon dioxide in a batch experiment from 0.5% in N_2 to nearly 100% using 2,6-di(^{t}butyl)benzoquinone as an electrochemically modulated CO_2 carrier in propylene carbonate.[10] Figure 1 shows the essential features of this process. In its reduced, dianionic form, 2,6-di-(^{t}butyl)-catecholate strongly binds to carbon dioxide to form a carbonate complex

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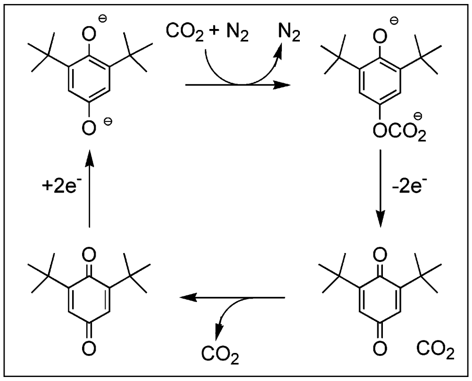

Figure 1. Cycle for the electrochemical concentration of carbon dioxide using 2,6-di-^{t}butyl-benzoquinone as the redox-active carrier.

($K = 10^{15}$), and upon oxidation to the quinone, the carbon dioxide is released.[9] Although this compound can effectively pump CO_2 from very low to atmospheric pressure, a potential drawback is that the reduced carrier is oxygen-sensitive, and the presence of oxygen in the feed stream can decrease the pumping efficiency or degrade the carrier. Oxygen sensitivity in the exit stream should not be an issue because this will be pure CO_2 in a well-designed system.

We have begun a project to explore the use of air-stable, water-soluble transition-metal complexes as redox-active carriers in the electrochemical pumping of CO_2. Water is an advantageous solvent because it is inexpensive, benign, and has a low vapor pressure that will minimize solvent loss during the carbon dioxide extraction process. Additionally, carbon dioxide has a lower solubility in water than in organic solvents at atmospheric pressure.[10,11] The lower solubility gives increased efficiency in EMC because dissolved CO_2 (or hydrated forms) is simply recycled rather than released in the pumping experiment. It follows that an effective pumping experiment requires that the solubility of the carrier molecule be significantly greater than that of the pumped molecule.

We have recently reported our studies of the reactions of bicarbonate ion with known Ni(II) complexes containing a series of related chelating, macrocylic, or binucleating ligands.[12] In agreement with earlier studies with other anions,[13] the binuclear complexes showed a higher affinity for bicarbonate than mononuclear derivatives. For example, $[Ni_2(taec)](BF_4)_4$ (see Figure 2 for ligand structures) reacted rapidly with bicarbonate ion in buffered aqueous solution at pH 7.4, and log K_B was determined to be 4.39. In comparison, no bicarbonate binding was observed for the related mononuclear complex, $[Ni(2,3,2\text{-tetraamine})](BF_4)_2$, under identical conditions.

The structure and flexibility of the binucleating ligand was also an important factor. $[Ni_2(o\text{-xyl-DMC}_2)](ClO_4)_2$ does not react with bicarbonate ion in aqueous solution, although a μ-CO_3 adduct does form in mixed or nonaqueous solvents. All of these nickel−carbonate adducts exhibit very negative reduction potentials (more cathodic than −2 V vs Fc). This property limits their utility in electrochemical pumping applications because of complications upon reduction such as solvent breakdown, increased carrier reactivity, and competing reactions.

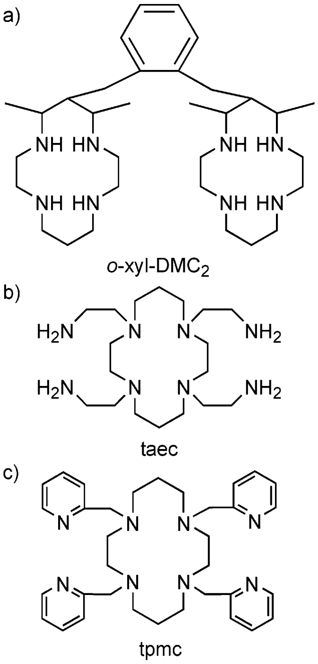

Figure 2. Binucleating ligands used in this study.

In this paper, we report our studies of the reactions of bicarbonate ion with related binuclear copper complexes. Effective binding constants of copper(II) derivatives for the anion in buffered aqueous solution have been determined and compared, and the reduction behavior of the complexes has been studied. Our studies have led to the identification of an effective air-stable, water-soluble carrier and the demonstration of its viability in the electrochemical concentration of carbon dioxide.

Experimental Section

Instrumentation. ^1H NMR spectra were acquired with a Varian Inova 400- or 500-MHz instrument. Electrospray ionization (ESI) mass spectra were collected using an HP 59987A electrospray with an HP 5989B mass spectrometer. MALDI mass spectra were collected using a PerSeptive Biosystems Voyager-DE STR instrument using a 2,5-dihydroxybenzoic acid (DHB) matrix and a 1:1 acetonitrile/water solution for sample deposition. Electronic spectra were collected on an Agilent 8453 UV−visible spectrometer. Conductivity measurements were performed on a Yellow Springs Instrument Co. model 31 conductivity bridge using a model 3403 conductivity cell. Elemental analyses were carried out by Desert Analytics Laboratory in Tucson, Arizona.

Cyclic voltammograms were obtained using a Cypress Systems model CS-1200 computer-aided three-electrode electrolysis system. Data were acquired using a glassy carbon disk as a working electrode and a glassy carbon rod as a counter electrode. The reference electrode was separated from the main compartment by a Vycor disk ($^1/_8$ in. diam) obtained from Bioanalytical Systems,

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Inc. For the aqueous cyclic voltammograms, an SCE was used as the reference electrode, and the potentials are reported versus SCE. For cyclic voltammograms in acetonitrile, the samples were dissolved in 0.3 M tetraethylammonium tetrafluoroborate in distilled acetonitrile, and a silver chloride-coated silver wire was used as a pseudoreference. Ferrocene was employed as an internal reference, and all of the potentials in nonaqueous solutions are reported versus the ferrocene/ferrocenium couple.

The bulk electrolysis experiments for the EMC CO_2 concentration experiments were carried out with an EG&G Princeton Applied Research model 173 potentiostat/galvanostat with a model 179 digital coulometer. Experiments were performed with a working electrode constructed from a reticulated vitreous carbon rod with a diameter of 1.3 cm and a length of 2.0 cm (60 pores per in.) obtained from the Electrosynthesis Co., Inc. The counter electrode was a platinum electrode, and a silver chloride-coated silver wire was used as a pseudoreference.

GC analyses were carried out using a 100/120 Carbosieve S-II stainless steel column with a length of 10 feet and a diameter of $^1/_8$ in. purchased from Supelco. A thermal conductivity detector was used, and the oven and detector temperatures were set to 175 °C. Argon was used as the carrier gas with a flow rate of 30 mL/min.

Materials. Reagents were purchased commercially and used without further purification unless otherwise specified. Acetonitrile and methanol were distilled from calcium hydride where noted. Cyclam was prepared by a procedure similar to that reported by Hervé et al.[14] The ligand taec·HBr was synthesized by slight modification of the procedure of Kida and co-workers by the reaction of cyclam with tosylaziridine.[15] Tosylaziridine was prepared from ditosylethanolamine[16] by slight modification of the procedure of Martin, Ford, and Bulkowski.[17] Synthesis of the *N*,*N*′,*N*′′,*N*′′′-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tpmc) ligand followed the procedure reported by Alcock et al.[18] in which cyclam was reacted with 2-(chloromethyl)pyridinium chloride (also named 2-picolyl chloride hydrochloride). The latter reagent was purchased from Aldrich.

Aqueous solutions for UV−vis titrations and CV measurements were prepared using 18-MΩ water from a Millipore Milli-Q plus water system. The aqueous solutions were buffered using HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid, $pK_a = 7.5$) or MES (2-(4-morpholino)ethanesulfonic acid, $pK_a = 6.15$). Buffers were purchased commercially and used without further purification with the exception of HEPES sodium salt. (Commercially purchased material appeared to contain halide contaminants.) HEPES sodium salt was isolated from the reaction of HEPES (32.00 g, 0.134 mol) with sodium hydroxide (5.73 g, 0.143 mol) in 640 mL of absolute ethanol and 100 mL of methanol. The mixture was heated to 60 °C, filtered, and placed in the freezer (−15 °C) overnight. The crystalline solid was collected by filtration, washed first with 1:1 ethanol and diethyl ether and then with diethyl ether, and dried under vacuum to give 23.94 g of product (68%).

Synthesis of α,α′-Bis(5,7-dimethyl-1,4,8,11-tetraazacyclotetradecan-6-yl)-*o*-xylene, (*o*-xyl-DMC$_2$). Details of the free-ligand synthesis have not been reported previously. $[Ni_2Cl_2(o\text{-xyl-DMC}_2)](ClO_4)_2$[19] (0.920 g, 0.971 mmol) was dissolved in 300 mL of water by heating. The pH was adjusted to 10 by addition of NaOH, and 50 mL of ethanol was added. NaCN (0.479 g, 9.76 mmol) was added to this solution, and the solution was refluxed until a pale-pink precipitate appeared. After the addition of 200 mL of ethanol, NaCN (∼2 g) was added until the precipitate dissolved. The ethanol was removed by rotary evaporation, and concentrated aqueous NaOH was added. The solution was extracted with chloroform, and the organic layer was dried with Na_2SO_4 and evaporated to give an oily product. The product was dissolved in ethanol and filtered through a fine frit, and the solvent was removed by rotary evaporation to give 0.103 g of a white powder. ^{13}C NMR in $CDCl_3$ agrees with the previously reported data.[20]

Synthesis of $[Cu_2(o\text{-xyl-DMC}_2)](X)_4$, X = BF_4 or ClO_4. The *o*-xyl-DMC$_2$ ligand (0.10 g, 0.18 mmol) was dissolved in 10 mL of acetone, and a solution of $Cu(BF_4)_2 \cdot 4.8\ H_2O$ (0.232 g, 0.717 mmol) in 5 mL of acetone was added. A purple precipitate formed immediately and was isolated by filtration. Yield: 0.120 g, 64%. Diffusion of diethyl ether into an acetonitrile solution of the purple solid resulted in the deposition of a microcrystalline solid. MS (*m*/*z*, ESI positive ion): 946 ($[Cu_2(o\text{-xyl-DMC}_2)](BF_4)_3^+$), 429 ($[Cu_2(o\text{-xyl-DMC}_2)](BF_4)_2^{2+}$), 257 ($[Cu_2(o\text{-xyl-DMC}_2)](BF_4)^{3+}$), 172 ($[Cu_2(o\text{-xyl-DMC}_2)]^{4+}$). Λ_M, $\Omega^{-1}\ mol^{-1}\ cm^{-1}$ (CH_3CN): 324. (The value indicates between three and four ions in solution.[21]) Vis spectrum, nm (propylene carbonate): 526 (223 $M^{-1}\ cm^{-1}$). CV, E_P, *V* versus SCE (aqueous solution with 0.3 M $NaBF_4$): −0.92 (irr); −1.1 (irr). A large anodic stripping wave was observed at ca. 0 V. CV, $E_{1/2}$, *V* versus ferrocene (acetonitrile): −1.27 ($\Delta E_p = 65$ mV); $E_p = -1.42$ (irr).

A similar procedure with $Cu(ClO_4)_2 \cdot 6H_2O$ was used to synthesize $[Cu_2(o\text{-xyl-DMC}_2)](ClO_4)_4$. Slow diffusion of methylene chloride into an acetonitrile solution of the purple solid resulted in the formation of purple needles. MS (*m*/*z*, ESI positive ion): 984 ($[Cu_2(o\text{-xyl-DMC}_2)](ClO_4)_3^+$), 442 ($[Cu_2(o\text{-xyl-DMC}_2)](ClO_4)_2^{2+}$), 261 ($[Cu_2(o\text{-xyl-DMC}_2)](ClO_4)^{3+}$). Λ_M, $\Omega^{-1}\ mol^{-1}\ cm^{-1}$ (H_2O): 416, four ions in solution.[21] Anal. Calcd for $C_{32}H_{62}N_8Cu_2Cl_4O_{16}$: C, 35.46; H, 5.77; N, 10.34. Found: C, 35.46; H, 5.61; N, 10.07.

Synthesis of taec. The octahydrobromide salt of taec (taec·HBr)[15] was deprotonated using Dowex-22 anion-exchange resin in the hydroxide form. The resulting yellow oil was collected in quantitative yield. It was dissolved in absolute ethanol to give a 5% stock solution (by mass), which was used thereafter for the syntheses of the metal taec complexes.

Synthesis of $Cu_2(taec)(BF_4)_4$. $Cu(BF_4)_2 \cdot 4.8H_2O$ (1.71 g, 5.3 mmol) was dissolved in 41 mL of acetonitrile and filtered, and 11.88 g of the 5% taec solution was added (0.59 g taec, 1.6 mmol). The blue-purple mixture was stirred for 30 min, and then 120 mL of absolute ethanol was added. The resulting precipitate was collected by filtration, washed with ethanol and diethyl ether, and then crystallized by diffusion of diethyl ether into an acetonitrile solution to give deep-purple crystals. Yield: 0.84 g, 62%. Anal. Calcd for $C_{18}H_{44}N_8B_4F_{16}Cu_2$: C, 25.53; H, 5.24; N, 13.23. Found: C, 25.21; H, 5.45; N, 12.90. MS (*m*/*z*, MALDI positive ion): 497 ($[Cu_2(taec\text{-}H)]^+$), 535 ($[Cu_2(taec)Cl]^+$). Λ_M, $\Omega^{-1}\ mol^{-1}\ cm^{-1}$ (18-MΩ water): 470, indicating between four and five ions in solution;[21] (CH_3CN): 375, four ions in solution. Vis spectrum, nm (aqueous solution with 0.5 M HEPES buffer at pH 7.4): 572 (315

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M^{-1} cm^{-1}). CV, $E_{1/2}$, V versus SCE (aqueous solution with 0.5 M HEPES buffer at pH 7.4): −0.37 V (ΔE_p = 144 mV) at 50 mV/s.

Synthesis of $Cu_2(\mu\text{-}CO_3)(taec)(BPh_4)_2$. The carbonate adduct of $Cu_2(taec)(BF_4)_4$ was isolated as the tetraphenylborate salt after many unsuccessful isolation attempts as the tetrafluoroborate salt. $Cu_2(taec)(BF_4)_4$ (0.30 g, 0.36 mmol) and sodium bicarbonate (0.90 g, 1.1 mmol) were dissolved in water (30 mL), filtered, and added slowly to a solution of sodium tetraphenylborate (0.71 g, 2.1 mmol) in water (15 mL). The resulting blue suspension was centrifuged, and the precipitate was washed with 30 mL of water. The blue solid was recrystallized by diffusion of diethyl ether into an acetone/water (15:1) mixture. Yield: 44 mg, 10%. Anal. Calcd for $Cu_2(\mu\text{-}CO_3)(taec)(BPh_4)_2 \cdot 4H_2O$, $C_{67}H_{92}N_8O_7B_2Cu_2$: C, 63.35; H, 7.30; N, 8.82. Found: C, 63.77; H, 6.83; N, 9.32. MS (*m*/*z*, ESI positive ion): 879 ($[Cu_2(\mu\text{-}CO_3)(taec)(BPh_4)]^{1+}$). Λ_M, Ω^{-1} mol^{-1} cm^{-1}, (acetone) 177, three ions in solution.[21] IR (KBr): new bands observed at 1360, 1345, and 1327 cm^{-1}. Other bands may be obscured by BPh_4 absorptions. The CV in aqueous solution was obtained by the addition of 4 equiv of $NaHCO_3$ to $Cu_2(taec)(BF_4)_4$. $E_{1/2}$, *V* versus SCE (aqueous solution with 0.5 M HEPES buffer at pH 7.4): −0.41 V (ΔE_p = 193 mV) at 50 mV/s.

Synthesis of $Cu_2(tpmc)(NO_3)_4$. $Cu(NO_3)_2 \cdot 3H_2O$ (0.24 g, 1.0 mmol) was dissolved in 10 mL of absolute ethanol and added to solid tpmc (0.28 g, 0.5 mmol). The resulting mixture was stirred overnight, and the blue precipitate was collected by filtration, washed with diethyl ether, and air dried to give pure product. Yield: 0.45 g, 96%. Anal. Calcd for $C_{34}H_{44}N_{12}O_{12}Cu_2$: C, 43.45; H, 4.72; N, 17.88. Found: C, 43.56; H, 4.61; N, 17.51. MS (*m*/*z*, ESI positive ion): 407 ($[Cu_2(tpmc)(NO_3)_2]^{2+}$), 689 ($[Cu_1(tpmc)(NO_3)]^{1+}$), 814 ($[Cu_2(tpmc)(NO_3)_2]^{1+}$) (mixed valence $Cu^{I}Cu^{II}$), 876 ($[Cu_2(tpmc)(NO_3)_3]^{1+}$). Λ, Ω^{-1} mol^{-1} cm^{-1}, (18-MΩ water): 445, between four and five ions in solution.[21] Vis spectrum, nm (aqueous solution at 0.5 M ionic strength at pH 7.4): 698 (230 M^{-1} cm^{-1}). CV, $E_{1/2}$, *V* versus SCE (aqueous 0.3 M sodium nitrate): −0.12 (ΔE_p = 188 mV) and −0.33 (ΔE_p = 127 mV) at 50 mV/s.

Synthesis of $[Cu_2(tpmc)(\mu\text{-}CO_3)](BPh_4)_2$. $Cu_2(tpmc)(NO_3)_4$ (0.20 g, 0.21 mmol) and cesium carbonate (0.21 g, 0.64 mmol) were stirred in 10 mL of distilled acetonitrile for 1.5 h to give a green solution and pale precipitate. Sodium tetraphenylborate (0.22 g, 0.63 mmol) was added, and the mixture was stirred for 30 min and then filtered. Water (1.0 mL) was added to the filtrate, causing the solution to change from green to blue-green. Methanol diffusion into the solution resulted in the formation of blue-green crystals, which were collected by filtration, washed with water and methanol, and dried under vacuum to give a green solid. Yield: 0.16 g, 52%. Anal. Calcd for $Cu_2(tpmc)(\mu\text{-}CO_3)(BPh_4)_2 \cdot H_2O$, $C_{83}H_{86}N_8O_4B_2Cu_2$: C, 70.79; N, 6.15; H, 7.96. Found: C, 70.75; N, 6.18; H, 8.21. MS (*m*/*z*, ESI positive ion): 1071 ($[Cu_2(\mu\text{-}CO_3)(tpmc)(BPh_4)]^{+}$), 750 ($[Cu_2(\mu\text{-}CO_3)(tpmc)]^{+}$) (mixed valence $Cu^{I}Cu^{II}$). IR (KBr): new bands observed at 1446, 1319, and 1327 cm^{-1}. Λ_M, Ω^{-1} mol^{-1} cm^{-1}, (acetone): 170, indicating three ions in solution.[21] The CV in aqueous solution was obtained by adding 4 equiv of $NaHCO_3$ to $[Cu_2(tpmc)](NO_3)_4$. $E_{1/2}$, *V* versus SCE (aqueous 0.3 M sodium nitrate): −0.41 (ΔE_p = 204 mV) at 50 mV/s.

Characterization of $Cu_2(tpmc)(PF_6)_2$.[22] $[Cu(CH_3CN)_4]PF_6$ (0.022 g, 0. 059 mmol) and tpmc (0.016 g, 0.028 mmol) were mixed in CD_3CN under nitrogen to yield an air-sensitive yellow solution of the Cu(I) complex. NMR data have not been reported previously. ^1H NMR (CD_3CN, 400 MHz): δ ∼2.15 (br s, 7.4 H), 2.51 (br s, 4.3 H), 2.75 (br s, 7.3 H), 3.56 (br s, 8.0 H), 7.37 (br s, 8.0 H, Py***H***), 7.86 (br s, 4.0 H, Py***H***), 8.42 (br s, 3.9 H, Py***H***).

Electrochemical Reductions of the Copper Complexes. Cu_2(*o*-xyl-DMC$_2$)]$(BF_4)_4$. The copper dimer (0.053 g, 0.051 mmol) was dissolved in 20 mL of 0.3 M tetraethylamonium tetrafluoroborate in acetonitrile. The solution was reduced at −1100 mV versus a permethylferrocene/permethylferrocenium reference for 1 h, passing 25.8 C. The resulting solution was clear, and copper metal was deposited on the working electrode. Attempts to reoxidize the material at +1000 mV were unsuccessful.

$Cu_2(taec)(BF_4)_4$. In a typical experiment, $Cu_2(taec)(BF_4)_4$ (0.062 g, 0.073 mmol) was dissolved in 24 mL of 0.5 M HEPES buffer solution at pH 7.4 and reduced at −0.57 V, approximately 125 mV negative of the peak of the reduction wave. The reaction resulted in passing 29.9 C, whereas 14.2 C was expected for a one-electron reduction of each copper. Multiple attempts were made to reduce the complex in aqueous solution, but all of them resulted in the formation of copper(0), which was observed as a metallic deposit in the cell.

Electrochemical reduction of $Cu_2(taec)(BF_4)_4$ (0.062 g, 0.073 mmol) in a 0.3 M solution of *N*-tetraethylammonium tetrafluoroborate in acetonitrile resulted in the passing of 13.9 C (13.7 C expected). The initially blue solution formed a pale-green solution without any copper(0) being observed. A similar reduction was run in a 1:1 mixture of acetonitrile and water, and again no copper(0) was formed.

$Cu_2(tpmc)(NO_3)_4$. Electrochemical reduction of $Cu_2(tpmc)(NO_3)_4$ in aqueous 0.3 M sodium nitrate under nitrogen resulted in a stable complex with no visible formation of copper(0). $Cu_2(tpmc)(NO_3)_4$ (62 mg, 0.066 mmol) was dissolved in 20 mL of a nitrogen-purged electrolyte solution (0.31 M $NaNO_3$ in 18-MΩ water). The blue solution was reduced at approximately −0.47 V versus SCE, 80 mV negative of the peak of the second reduction wave. A current drop was observed after 12.7 C of charge was passed (the charge expected for a one-electron reduction of each copper). The solution was a yellow-green color with a pale precipitate. The precipitate was collected by cannula filtration under nitrogen and analyzed by ^1H NMR spectroscopy in CD_3CN. The NMR data for the precipitate matched that of independently synthesized $Cu_2(tpmc)(PF_6)_2$ (see above).

The cyclic voltammogram of the reduced complex was found to be identical to that of the copper(II) starting material. Coulometric experiments were carried out on the Cu(I) product to avoid the problems noted above of product precipitation and a small background current observed in the controlled-potential electrolysis of the Cu(II) complex. Controlled-potential electrolysis at ca. 0.0 V versus SCE resulted in the passage of 0.94 electrons per copper ion with no significant background current.

The reduction of $Cu_2(tpmc)(NO_3)_4$ was repeated in the presence of sodium bicarbonate. $Cu_2(tpmc)(NO_3)_4$ (123 mg, 0.13 mmol) and $NaHCO_3$ (87 mg, 1.0 mmol) were dissolved in 20 mL of a nitrogen-purged electrolyte solution (0.30 M $NaNO_3$ in 18-MΩ water). The cyclic voltammogram of the blue-green solution was characteristic of $[Cu_2(tpmc)(\mu\text{-}CO_3)]^{2+}$. The solution was reduced at approximately 80 mV negative of the peak of the reduction wave. The solution became a yellow-green color with a pale precipitate, and a total of 29.2 C of charge was passed (25.3 C would be expected for the one-electron reduction of each copper in this complex). Again, the precipitate was isolated by filtration and analyzed by ^1H NMR (CD_3CN). The spectrum matched that of $Cu_2(tpmc)(PF_6)_2$.

X-ray Crystallography. A crystal of appropriate size was mounted on a glass fiber using Paratone-N oil, transferred to a Siemens SMART diffractometer/CCD area detector, centered in

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Table 1. Crystal Data for $[Cu_2(taec)(\mu\text{-}CO_3)](BPh_4)_2 \cdot 4\ H_2O$ and $[Cu_2(tpmc)(\mu\text{-}CO_3)](BPh_4)_2 \cdot CH_3CN \cdot (H_2O)_2$

ligand	taec	tpmc
formula	$C_{67}H_{84}B_2Cu_2N_8O_7$	$C_{85}H_{87}N_9O_5B_2Cu_2$
fw (amu)	1262.12	1465.58
cryst syst	triclinic	monoclinic
unit cell dimensions		
a (Å)	13.3916(5)	9.4708(4)
b (Å)	13.4574(5)	25.9130(11)
c (Å)	20.1343(7)	31.6182(13)
α (deg)	73.2260(10)	90
β (deg)	86.0700(10)	101.7900(10)
γ (deg)	64.3680(10)	90
volume, Å^c	3125.6(2)	7595.9(6)
space group	$P\bar{1}$ (no. 2)	$P2(1)/n$ (no. 14)
Z	2	4
density, calcd, mg/m^{-3}	1.341	1.316
λ(Mo Kα) (Å)	0.71073	0.71073
temp (K)	142(2)	140(2)
scan type, deg	ω scans, 0.3	ω scans, 0.3
2θ range, deg	$4.10 < \Theta < 50.06$	$3.06 < \Theta < 54.96$
independent reflns	20450 (R(int) = 0.0813)	58343 (R(int) = 0.1144)
reflns observed	10 981	17 414
abs coeff, mm^{-1}	0.741	0.619
R1 (for $F_o > 4\sigma F_o$)^a	0.0663 for 6774 data	0.1092 for 12425 data
R1, wR2 (all data)^b	0.1163, 0.1763	0.1448, 0.2643
GOF^c	0.985	1.159
largest peak, hole in final diff map, e$^-$/Å^c	0.675, −0.682	1.371, −0.709

^{a} $R = R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. ^{c} $GOF = S = [\sum[w(F_o^2 - F_c^2)^2]/(M - N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined.

the beam (Mo Kα; $\lambda = 0.71073$ Å; graphite monochromator), and cooled to −131 °C by a liquid-nitrogen low-temperature apparatus. The preliminary orientation matrix and cell constants were determined by collection of 60 10-s frames, followed by spot integration and least-squares refinement. A minimum of one hemisphere of data was collected using 0.3 °ϖ scans at 30 s per frame. The raw data were integrated and the unit cell parameters were refined using Saint. Data analysis was performed using XPREP. Absorption correction was applied using SADABS. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. Structure solutions and refinements were performed (SHELXTL-Plus V5.0) on F^2. Data collection and structure refinement information are given in Table 1.

$Cu_2(\mu\text{-}CO_3)(taec)(BPh_4)_2 \cdot 4\ H_2O$. Crystals suitable for X-ray diffraction studies were grown by diethyl ether diffusion into a 15:1 acetone/water solution at room temperature. Preliminary data indicated a triclinic cell. The structure was successfully solved and refined in the centric space group $P\bar{1}$. All non-H atoms were refined anisotropically. H atoms were placed in idealized positions and were included in structure factor calculations but were not refined. Hydrogen atoms were not placed on the oxygens of cocrystallized water.

$Cu_2(\mu\text{-}CO_3)(tpmc)(BPh_4)_2 \cdot CH_3CN \cdot (H_2O)_2$. Crystals suitable for X-ray diffraction studies were grown by methanol diffusion into a 1:10 water/acetonitrile solution at room temperature. Preliminary data indicated a monoclinic cell, and systematic absences indicated space group $P2(1)/n$. All non-H atoms were refined anisotropically with the exception of the carbonate atoms. H atoms were placed in idealized positions and were included in structure factor calculations but were not refined. Hydrogen atoms were not placed on the oxygens of cocrystallized water. The bridging carbonate was disordered into two chemically indistinguishable but opposite positions with one position occurring 74% of the time. The bonds and angles of the two carbonate positions were not restrained but were found to be nearly identical. Two cocrystallized acetonitrile molecules were found to have partial occupancies of 0.57 and 0.47.

Reactions with Anions. For $[Cu_2(taec)](BF_4)_4$, no significant changes in the values of λ_{max} (nm) and ϵ ($M^{-1}\ cm^{-1}$) in the visible spectra were observed in pure water (566, (317)), in 0.5 M $NaNO_3$ (566 (330)), or in 0.5 M NaHEPES + HNO_3 at pH 7.4 (574 (320)). For $[Cu_2(tpmc)](NO_3)_4$, maxima in the visible spectra changed from 655 (298) in pure water to 627 (320) in 0.5 M $NaNO_3$ and 698 (230) in 0.5 M HEPES buffer solution at pH 7.4. The data in the nitrate and buffer solutions correspond to those reported for $[Cu_2(tpmc)(\mu\text{-}NO_3)]^{3+}$ and $[Cu_2(tpmc)(\mu\text{-}OH)]^{3+}$, respectively.[18,23]

Titrations of the metal complexes (3 mM) with sodium bicarbonate (0.5−0.6 M) were carried out in 0.5 M aqueous HEPES sodium salt adjusted to a pH of 7.4 with concentrated HNO_3. A nearly constant 0.5 M ionic strength was maintained by addition of HNO_3 to the sodium salt of the buffer. Titrations were carried out under nitrogen in a UV−vis cell with a 1-cm path length. The temperature of the cell was not regulated but was found to be between 24.5 and 27.5 °C for all titrations. The relative effective binding constants for bicarbonate ion were determined in a least-squares approach, as described previously.[12]

To determine the binding constant of $[Cu_2(tpmc)(\mu\text{-}NO_3)](NO_3)_3$ for hydroxide ion, we titrated a 3.3 mM solution of the copper complex in 0.5 M KNO_3 with a 0.317 M solution of KOH in 10.0 μL increments, and the data were fit using Excel. The pH halfway to the equiv pt was 6.38. The value for $K_{OH} = [Cu_2(tpmc)(\mu\text{-}OH)^{3+}][NO_3^-]/[Cu_2(tpmc)(\mu\text{-}NO_3)^{3+}][OH^-] = 2.1 \times 10^7$ ($\log K_{OH} = 7.32$).

EMC Concentration of CO_2. A custom-made two-compartment cell was used for the CO_2 concentration experiments. The volumes of the working and counter compartments were 16 and 18 mL, respectively. The compartments were separated by a Rapiore cation-exchange membrane obtained from the Electrosynthesis Co., Inc. The reference electrode (AgCl/Ag pseudoreference in a glass tube with a $^1/_8$ in. Vycor disk) was inserted into the back of the working compartment and sealed in place by a septum. Working electrodes were constructed from reticulated vitreous carbon, as described above, and a platinum counter electrode was used. A pressure sensor (Omega Engineering PX139-030A4V) was attached to the cell by a 21-gauge needle through the septum at the top of the working compartment.

A 1.00 M MES buffer solution was prepared by dissolving MES (19.5 g, 0.100 mol) to a total volume of 100.0 mL with 18-MΩ water, purging the solution for 30 min with nitrogen, and then adjusting the pH to 6.37 using NaOH (~2.2 g, ~0.055 mol). The solution was filtered and then purged overnight with nitrogen.

Two bicarbonate carrier solutions were made for the working compartment. Solution 1 consisted of $Cu_2(tpmc)(NO_3)_4$ (1.89 g, 2.00 mmol) dissolved to a total volume of 10.0 mL in the MES buffer solution. Solution 2 consisted of $Cu_2(tpmc)(NO_3)_4$ (1.89 g, 2.00 mmol) dissolved in 14.0 mL of the MES buffer solution, giving an approximately total volume of 15 mL. A greater total volume was used for solution 2 to decrease the headspace in the cell. A large headspace reduces the percent of CO_2 collected by a dilution effect.

The working compartment was loaded with the carrier solution (either solution 1 or solution 2), and the counter compartment was loaded with MES buffer solution. The carrier solution was bubbled with a mixture of 10.00 ± 0.02% CO_2 in N_2, and the progress of the carrier loading was monitored by cyclic voltammetry. Once

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(23) Asato, E.; Toftlund, H.; Kida, S.; Mikuriya, M.; Murray, K. S. *Inorg. Chim. Acta* **1989**, *165*, 207−214.

there was very little change in the cyclic voltammograms, the gas purge was stopped (6 h total bubbling time), and the working compartment of the cell was sealed.

The carrier was reduced in a controlled-potential electrolysis. The potential of the working electrode was moved negative to maintain the current between 20 and 40 mA. Syringes (3 mL) were used to collect the gas evolved from the working compartment during the reduction. While the reduction was running, the pressure in the working compartment was monitored, and gas was pulled into the syringe to maintain ambient pressure.

In the electrolysis of solution 1, precipitation of the reduced carrier, $[Cu_2(tpmc)]^{2+}$, was observed after approximately two-thirds of the expected charge was passed, and this appeared to plug or coat the electrode. The total charge passed after gas evolution stopped was 238.3 C, and the current approached zero. The carrier was reoxidized using 209.4 C. The working electrode was changed to a reticulated vitreous carbon electrode with 10 pores/in., and the reduction was repeated. The current approached zero after only 135.8 C had been passed, and the carrier was reoxidized using 119.3 C. It appears that the electrode surface was still coated and passivated to further electron transfer despite the substantially more porous electrode material.

Solution 2 was loaded and reduced in the same manner as solution 1 using 60 pores/in. reticulated vitreous carbon as the electrode material. Solution 2 was made up to a greater total volume to minimize the headspace. This achieved a higher concentration of carbon dioxide during the course of the experiment. The last syringe was found to contain 74.5% carbon dioxide. In this experiment, 243.8 C was passed in the initial reduction, and 223.0 C was used to reoxidize the carrier. In a second cycle on the same solution, 168.2 C was passed in the reduction, and 165.7 C was used in the oxidation.

Results and Discussion

Syntheses and Characterizations of Binuclear Copper(II) Complexes. The previously reported binucleating ligands used in this work are shown in Figure 2. Binuclear copper(II) complexes with the taec ligand have been studied extensively. An X-ray diffraction study of the perchlorate salt shows that the complex has an open structure with a single perchlorate coordinated at each copper ion (Figure 3a).[24] Several Cu(II)(taec) derivatives have been found to contain a singly charged bridging anion, including fluoride, bromide, iodide, azide, cyanate, and acetate,[15,25,26] with the generalized structure shown in Figure 3b. The binding constants of $[Cu_2(taec)]^{4+}$ with a number of the bridging anions in aqueous solution have been determined,[13,27,28] but the studies did not include bicarbonate or carbonate ions. Related structures of binuclear copper(II) tpmc complexes with bridging fluoride, chloride, hydroxide, or nitrate anions have also been reported.[18,23,29] The synthesis of $[Cu_2(tpmc)(\mu\text{-}CO_3)](ClO_4)_2$ has been mentioned, but neither binding affinities nor structural data were included in this report.[30] To our knowledge, no copper complexes with the *o*-xyl-DMC$_2$ ligand have been reported previously.[31]

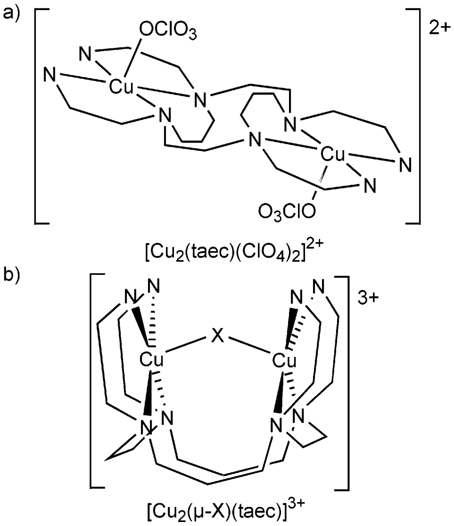

Figure 3. Structural representations of copper complexes containing the taec ligand. (a) $[Cu_2(taec)(ClO_4)_2]^{2+}$; (b) $[Cu_2(\mu\text{-}X)(taec)]^{3+}$, where X = halide.

The copper(II) derivatives, $[Cu_2(taec)](BF_4)_4$, $[Cu_2(tpmc)](NO_3)_4$, and $[Cu_2(o\text{-xyl-DMC}_2)](X)_4$ (X = BF_4 or ClO_4), were readily synthesized by reacting 2 equiv of the appropriate Cu(II) salt with the ligand in a polar solvent. These specific salts, which have not been reported previously, were characterized on the basis of spectroscopic data, cyclic voltammetry, and elemental analyses.

The electrochemical properties of these complexes are of interest because the pumping experiments described below require cycling between Cu(II) and Cu(I) oxidation states. Cyclic voltammograms for $[Cu_2(taec)](BF_4)_4$ and $[Cu_2(tpmc)](NO_3)_4$ have been recorded in aqueous solutions, and that for $[Cu_2(o\text{-xyl-DMC}_2)](BF_4)_4$ is reported for an acetonitrile solution. The latter complex showed two closely spaced reduction waves in CH_3CN at potentials of −1.27 V ($\Delta E_p = 65$ mV) and $E_p = -1.42$ V versus ferrocene (irr). The potentials are more positive than those observed for the nickel analogue (−1.8 V vs Fc).[12] The two waves are assigned to the Cu(II)−Cu(I) reduction at each of the two metal sites, indicating electronic communication between the metal ions in this complex. In contrast, the CV for $[Cu_2(taec)](BF_4)_4$ in buffered aqueous solution (pH 7.4) showed only one quasi-reversible wave at −0.37 V versus SCE ($\Delta E_p = 144$ mV).

Although chemically reversible character was observed for the reduction waves in the cyclic voltammograms, controlled-potential electrolysis of the complexes established that the Cu(I) derivatives, $[Cu_2(taec)](BF_4)_2$ and $[Cu_2(o\text{-xyl-DMC}_2)](BF_4)_2$, are unstable with respect to formation of Cu metal. Plating of copper metal was observed in aqueous solution

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(26) Mikuriya, M.; Kida, S.; Murase, I. *Bull Chem. Soc. Jpn.* **1987**, *60*, 1355−1359.

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(31) For closely related copper complexes with unsaturated macrocycles, see Udugala-Ganehenege, M. Y.; Heeg, M. J.; Hryhorczuk, L. M.; Wenger L. E.; Endicott, J. F. *Inorg. Chem.* **2001**, *40*, 1614−1625.

upon reduction of the taec derivative but not in mixed aqueous/acetonitrile (1:1) solution. Formation of copper metal was observed upon reduction of $[Cu_2(o\text{-xyl-DMC}_2)]^{4+}$ even in acetonitrile. Disproportionation of the Cu(I) complexes to Cu(0) and Cu(II) is a well-established decomposition route for formation of the metallic deposit in amino complexes of copper.

$[Cu_2(tpmc)]^{4+}$, which exists as a μ-NO_3 complex in 0.3 M aqueous $NaNO_3$ (see below), also undergoes two quasi-reversible reductions at -0.12 and -0.33 V versus SCE (ΔE_p $=$ 188 and 127 mV) in aqueous solution. These have been confirmed as one-electron waves by coulometry and by the independent synthesis of the dinuclear Cu(I) species. The quasi-reversible nature of the waves is attributed to the structural differences observed for the Cu(II) and Cu(I) complexes. The latter derivative, $[Cu_2(tpmc)]^{2+}$, has been prepared previously from the reaction of $[Cu(CH_3CN)_4]PF_6$ and the tpmc ligand in acetonitrile.[22] The crystal structure of the triflate salt of this product showed that no anions are coordinated. In fact, the ligand distorts to allow each copper ion to be three-coordinate with two pyridyl donors and only one tertiary amine. We have found that the dinuclear Cu(I) complex is stable to disproportionation in aqueous solution. Controlled-potential electrolysis of $[Cu_2(tpmc)](NO_3)_4$ in aqueous 0.3 M sodium nitrate solution under nitrogen resulted in the formation of an air-sensitive, pale yellow-green product with only moderate solubility. The precipitate that formed in the electrolysis was isolated, and the ^{1}H NMR data that were obtained for the product were identical to that obtained for independently synthesized $[Cu_2(tpmc)]^{2+}$.

Reactions with Anions in Solution. Studies were carried out to determine the nature of any coordinated counterions in the copper complexes present in buffered aqueous solution because other anions present in these solutions can compete with bicarbonate/carbonate binding during the pumping experiment. The visible spectra for $[Cu_2(taec)](BF_4)_4$ are very similar in water and in the buffered aqueous solution, which is adjusted to a pH of 7.4 by the addition of concentrated nitric acid to 0.5 M aqueous HEPES sodium salt. The spectra indicate that there is no significant interaction of $[Cu_2(taec)]^{4+}$ with the nitrate, sulfonate, or hydroxide ions under these conditions. However, the spectrum of $[Cu_2(tpmc)](NO_3)_4$ is sensitive to certain anions present in solution. In pure water, the λ_{max} for the complex is observed at 655 nm ($\epsilon = 298$ M^{-1} cm^{-1}), and this spectrum remains the same in the presence of the zwitterionic form of the HEPES buffer, indicating no significant interaction with the sulfonate anion of the buffer. A weak interaction of the dinuclear copper complex with a nitrate counterion in aqueous solution is suggested by the molar conductivity, which falls between values expected for a 4:1 and 3:1 electrolyte. In 0.5 M $NaNO_3$ solution, the absorbance shifts to 627 nm ($\epsilon = 320$ M^{-1} cm^{-1}). No further change is observed upon the addition of 4 equiv of nitric acid. The latter spectrum is assigned to $[Cu_2(tpmc)(\mu\text{-}NO_3)]^{3+}$. An X-ray diffraction study has been reported for $[Cu_2(tpmc)(\mu\text{-}NO_3)](PF_6)_3$, and the structure confirms the presence of a η^1-η^1-μ-NO_3 ligand in the solid state.[18] When $[Cu_2(tpmc)](NO_3)_4$ is dissolved in the solution buffered at pH 7.4 (see above), the spectrum closely matches that reported for $[Cu_2(tpmc)(\mu\text{-}OH)]^{3+}$ with $\lambda_{max} = 698$ nm ($\epsilon = 230$ M^{-1} cm^{-1}).[23] A pH titration was carried out with the addition of KOH to a solution of $[Cu_2(tpmc)(\mu\text{-}NO_3)](NO_3)_3$ in 0.5 M KNO_3. The log of the binding constant for hydroxide ion, log K_{OH}, defined in eq 1, was calculated from the titration curve to be 7.32.

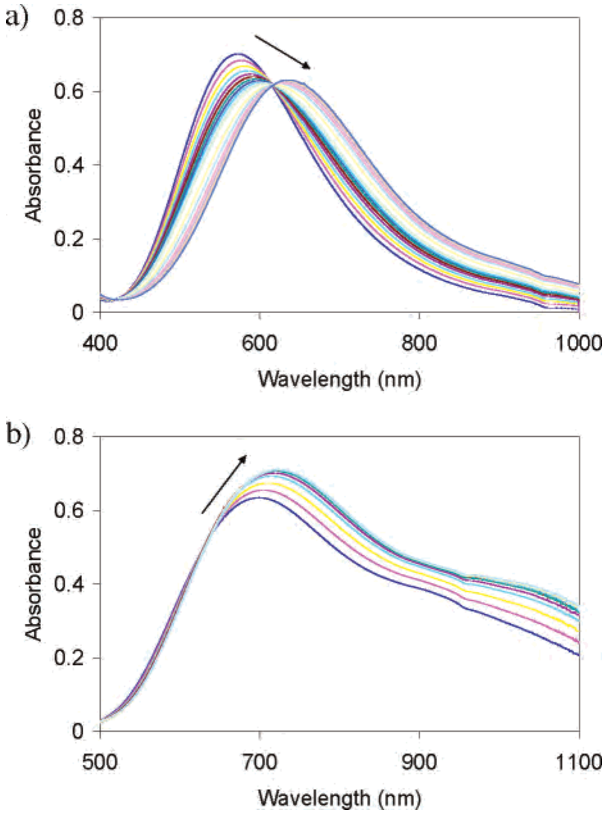

Figure 4. Visible spectra resulting from a sodium bicarbonate titration of a dinuclear copper complex in aqueous 0.5 M HEPES sodium salt adjusted to a pH of 7.4 with nitric acid: (a) $[Cu_2(taec)](BF_4)_4$; (b) $[Cu_2(tpmc)(\mu\text{-}OH)](NO_3)_3$.

$$[Cu_2(tpmc)(\mu\text{-}NO_3)]^{3+} + OH^- \overset{K_{OH}}{\rightleftharpoons} [Cu_2(tpmc)(\mu\text{-}OH)]^{3+} + NO_3^- \quad (1)$$

Titrations with Bicarbonate Ion. Both $[Cu_2(taec)](BF_4)_4$ and $[Cu_2(tpmc)(\mu\text{-}OH)]^{3+}$ reacted rapidly with sodium bicarbonate in the buffered solution, pH 7.4, and the titration curves for these complexes are shown in Figure 4. The products of bicarbonate addition have been characterized as μ-carbonate bridged complexes (see below). The effective binding constant for bicarbonate ion K_B, defined in eq 2, has been determined from the titration data for $Cu_2(taec)(BF_4)_4$, and the value of log K_B is 2.42 ± 0.05 at pH 7.4.

$$[Cu_2(taec)]^{4+} + HCO_3^- \overset{K}{\rightleftharpoons} [Cu_2(\mu\text{-}CO_3)(taec)]^{2+} + H^+ \quad (2)$$

$$K_B = \frac{K}{[H^+]} = \frac{[Cu_2(\mu\text{-}CO_3)(taec)^{2+}]}{[Cu_2(taec)^{4+}][HCO_3^-]}$$

The binding constant is similar to that reported previously for the reaction of $[Cu_2(taec)](ClO_4)_4$ with the acetate ion in unbuffered aqueous solution at 30 mM ionic strength (log $K_A = 2.12$).[27] K_B for $[Cu_2(tpmc)(\mu\text{-}OH)](NO_3)_3$ is defined in eq 3

$$[Cu_2(tpmc)(\mu\text{-}OH)]^{3+} + HCO_3^- \underset{}{\overset{K_B}{\rightleftharpoons}} [Cu_2(tpmc)(\mu\text{-}CO_3)]^{2+} + H_2O \quad (3)$$

and log K_B was found to be 4.32 ± 0.08 (assuming unit activity for the solvent). The equilibrium expression is not meant to imply a specific mechanism for the reaction. Nucleophilic attack of μ-OH metal complexes on CO_2 to form μ-CO_3 complexes in nonaqueous solution or in mixed solvents has been studied previously,[32] and a similar pathway may be occurring in the aqueous solution studied here. The binding constant for carbonate ion K_C (eq 4)

$$[Cu_2(tpmc)(\mu\text{-}NO_3)]^{3+} + CO_3^{2-} \overset{K_C}{\rightleftharpoons} [Cu_2(tpmc)(\mu\text{-}CO_3)]^{2+} + NO_3^- \quad (4)$$

can also be determined by the combination of K_B with appropriate K_A values in aqueous solution, and the value of log K_C is found to be 7.96, indicating that for this system the equilibrium constant for the formation of the μ-carbonate is favored over that for the μ-hydroxide (eq 1) by a factor of 4.4. Although these quantitative titrations were carried out under nitrogen to remove possible complications from atmospheric CO_2, the copper(II) complexes are completely stable with respect to air oxidation, and the bicarbonate binding properties of $[Cu_2(tpmc)(\mu\text{-}OH)](NO_3)_3$ have been shown to be identical when reactions are carried out in air.

When titrations of $[Cu_2(o\text{-xyl-DMC}_2)](BF_4)_4$ with sodium bicarbonate in water or with $NEt_4[HCO_3]$ in propylene carbonate were monitored by visible spectroscopy, a shift in the absorption maximum was observed, suggesting the formation of a bicarbonate or carbonate adduct. However, no reaction with bicarbonate was observed when the titration was carried out at constant pH (HEPES buffer, pH 7.4). A binding constant was therefore not determined, and further studies of the carbonate adduct were not pursued. A low affinity for bicarbonate ion in water has also been observed for the nickel(II) analogue, $[Ni_2(o\text{-xyl-DMC}_2)]^{4+}$.[12] The complexes $[Ni_2(o\text{-xyl-DMC}_2)(\mu\text{-}CO_3)]^{2+}$ and $Zn_2(o\text{-xyl-DMC}_2)(\mu\text{-}CO_3)]^{2+}$ have been prepared by other methods and characterized by X-ray diffraction.[12,33] The carbonate bridges are coordinated in a η^1,η^1-bonding mode, and the metal–metal distances expand relative to those of the nickel-chloride bridged structure described previously[19] (e.g., Ni···Ni = 6.053 Å for μ-CO_3 and Ni···Ni = 5.421 Å for μ-Cl). Nevertheless, the *o*-xyl-DMC$_2$ ligand is more rigid than the taec or tpmc ligand and less able to adjust the metal–ligand distances and coordination geometries. These factors appear to lower the affinity of this complex for the bicarbonate ion in aqueous solution, where the anion undergoes extensive hydrogen-bonding interactions.

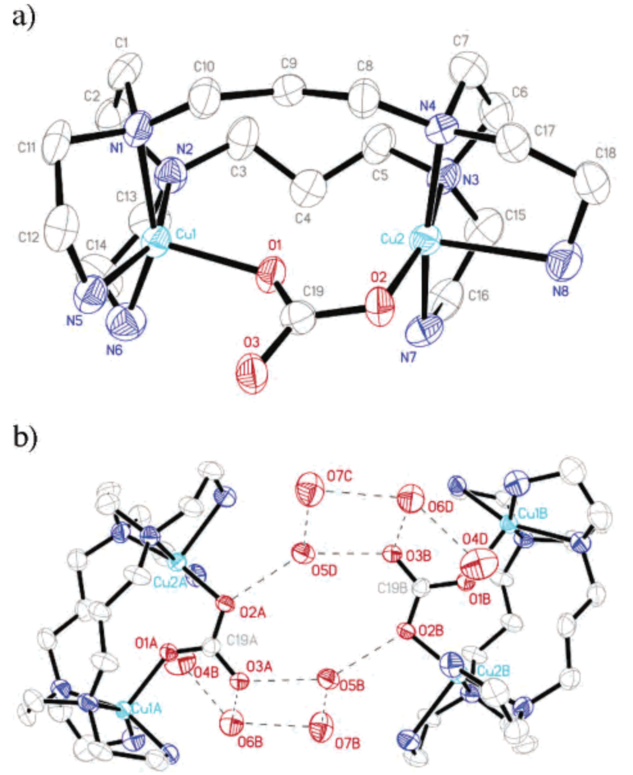

Figure 5. (a) Perspective drawing of the dication $[Cu_2(taec)(\mu\text{-}CO_3)]^{2+}$. Thermal ellipsoids are shown at the 50% probability level. (b) Perspective drawing of hydrogen-bonding interactions between $[Cu_2(taec)(\mu\text{-}CO_3)]^{2+}$ and water molecules.

Characterization of $Cu_2(\mu\text{-}CO_3)$ Complexes. $[Cu_2(taec)(\mu\text{-}CO_3)]^{2+}$, formed from the reaction of sodium bicarbonate with $[Cu_2(taec)](BF_4)_4$, was precipitated from aqueous solution by addition of sodium tetraphenylborate, whereas $[Cu_2(tpmc)(\mu\text{-}CO_3)](BPh_4)_2$ was precipitated from acetonitrile. The elemental analyses and ESI mass spectra are consistent with the formulations of the products, and molar conductivities in acetone confirm that the complexes are 2:1 electrolytes.

An X-ray diffraction study was carried out on a single crystal of $[Cu_2(taec)(\mu\text{-}CO_3)](BPh_4)_2$, and a perspective drawing of the dication is shown in Figure 5a, with selected bond distances and angles given in Table 2. The dication contains two square-pyramidal copper ions bridged by an asymmetrical η^1,η^1-carbonate ligand. Cu(1) lies slightly above a planar arrangement of four nitrogen donors with the carbonate oxygen, O(1), in the axial position. The Cu(1)–O(1) distance is 2.079(3) Å. Cu(2) lies in a square-planar arrangement of three nitrogen donors and the O(2) of the carbonate ligand with one aminoethyl nitrogen donor (N(8)) in the axial position of its square pyramid. The Cu(2)–O(2) bond is shorter in this case with a distance of 1.968(3) Å, whereas the axial Cu(2)–N(8) distance at 2.340(4) Å is significantly longer than the other Cu–N distances. The Cu(1)···Cu(2) distance is 4.519 Å. The

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(32) (a) Kitajima, N.; Hikichi, S.; Tanaka, M.; Moro-oka, Y. *J. Am. Chem. Soc*. **1993**, *115*, 5496 and references within. (b) Kitajima, N.; Fujisawa, K.; Koda, T.; Hikichi, S.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun*. **1990**, 1357. (c) Looney, A.; Han, R.; McNeill, K.; Parkin, G. *J. Am. Chem. Soc*. **1993**, *115*, 4690. Similar net reactions have been observed in aqueous or mixed solvent systems. See, for example, Murase, I.; Vuckovic, G.; Kodera, M.; Harada, J.; Matsumoto, N.; Kida, S. *Inorg. Chem*. **1991**, *30*, 728.

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Table 2. Selected Bond Distances and Angles for $[(Cu_2(taec)(\mu\text{-}CO_3)](BPh_4)_2$

distances, Å		angles, deg	
Cu(1)−N(1)	2.094(4)	O(1)−C(19)−O(2)	117.0(4)
Cu(1)−N(2)	2.087(4)	O(1)−C(19)−O(3)	122.7(5)
Cu(1)−N(5)	2.009(4)	O(2)−C(19)−O(3)	120.3(4)
Cu(1)−N(6)	2.029(4)	C(19)−O(1)−Cu(1)	130.9(3)
Cu(1)−O(1)	2.073(5)	C(19)−O(2)−Cu(2)	108.3(3)
Cu(2)−N(3)	2.047(4)	N(1)−Cu(1)−N(2)	85.06(16)
Cu(2)−N(4)	2.059(4)	N(1)−Cu(1)−N(5)	85.41(16)
Cu(2)−N(7)	2.007(4)	N(2)−Cu(1)−N(5)	156.16(16)
Cu(2)−N(8)	2.340(4)	N(5)−Cu(1)−N(6)	95.08(18)
Cu(2)−O(2)	1.968(3)	N(1)−Cu(1)−N(6)	153.00(17)
O(1)−C(19)	1.290(5)	N(2)−Cu(1)−N(6)	83.82(18)
O(2)−C(19)	1.312(6)	O(1)−Cu(1)−N(1)	100.99(14)
O(3)−C(19)	1.272(6)	O(1)−Cu(1)−N(2)	107.96(15)
Cu(1)···Cu(2)	4.519	O(1)−Cu(1)−N(5)	95.29(14)
		O(1)−Cu(1)−N(6)	105.82(16)

complex crystallizes as a tetrahydrate, and a perspective drawing of the crystal lattice, Figure 5b, shows a stacking arrangement of pairs of the dications mediated by hydrogen-bonding interactions between the water molecules and the carbonate oxygens.

Many examples of binculear copper complexes with a μ-η^1,η^1-carbonate ligand have been reported previously.[34] The arrangement of the taec ligand and the bridging anion in $[Cu_2(taec)(\mu\text{-}CO_3)]^{2+}$ is also very similar to that observed previously in the structure of $[Cu_2(taec)(\mu\text{-}CH_3CO_2)]^{3+}$.[25] The structure, however, differs significantly from those previously reported for $[M_2(taec)(\mu\text{-}CO_3)]^{2+}$, M = Ni or Co, in which each metal ion is octahedral with a cis η^2,η^2-coordination of the bridging carbonate ligand (Figure 6).[35,36] The structural differences between the dinuclear nickel and copper carbonate adducts are consistent with the larger binding constant observed for the nickel derivative.

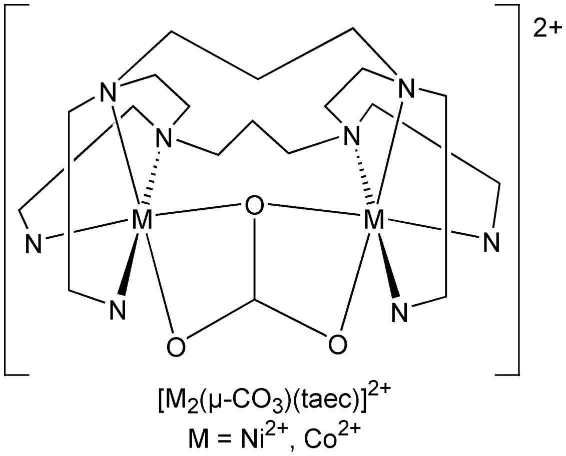

Figure 6. Structural representation of $[M_2(taec)(\mu\text{-}CO_3)]^{2+}$, where M = Ni or Co.

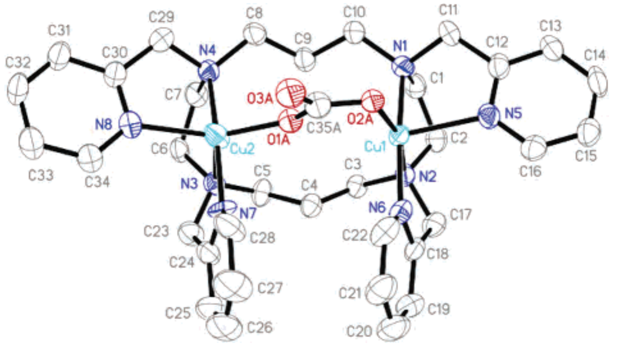

Figure 7. Perspective drawing and numbering scheme for the dication $[Cu_2(tpmc)(\mu\text{-}CO_3)]^{2+}$. Thermal ellipsoids are shown at the 50% probability level. Only one orientation (74% occupancy) of the disordered carbonate ligand is shown.

Table 3. Selected Bond Distances and Angles for $[(Cu_2(tpmc)(\mu\text{-}CO_3)](BPh_4)_2$

distances, Å		angles, deg	
Cu(1)−N(1)	2.078(5)	O(1A)−C(35A)−O(2A)	115.6(9)
Cu(1)−N(2)	2.068(5)	O(1A)−C(35A)−O(3A)	121.7(11)
Cu(1)−N(5)	2.217(5)	O(2A)−C(35A)−O(3A)	122.7(9)
Cu(1)−N(6)	1.997(5)	C(35A)−O(1A)−Cu(2)	135.8(7)
Cu(1)−O(2A)	1.950(5)	C(35A)−O(2A)−Cu(1)	114.2(5)
Cu(2)−N(3)	2.225(5)	N(1)−Cu(1)−N(2)	85.6(2)
Cu(2)−N(4)	2.073(5)	N(1)−Cu(1)−N(5)	80.88(19)
Cu(2)−N(7)	1.922(4)	N(2)−Cu(1)−N(5)	97.35(18)
Cu(2)−N(8)	2.091(5)	N(5)−Cu(1)−N(6)	95.08(18)
Cu(2)−O(1A)	1.876(6)	N(1)−Cu(1)−N(6)	168.2(2)
O(1A)−C(35A)	1.317(11)	N(2)−Cu(1)−N(6)	83.05(19)
O(2A)−C(35A)	1.279(14)	O(2A)−Cu(1)−N(1)	98.7(2)
O(3A)−C(35A)	1.271(12)	O(2A)−Cu(1)−N(2)	165.47(19)
Cu(1)···Cu(2)	4.423	O(2A)−Cu(1)−N(5)	97.05(19)
		O(2A)−Cu(1)−N(6)	93.1(2)

The structure of $[Cu_2(tpmc)(\mu\text{-}CO_3)](BPh_4)_2$ is similar to that of the taec derivative with two square-pryamidal copper ions bridged by an η^1,η^1-carbonate ligand. In this case, the carbonate ligand is disordered in two opposite but chemically equivalent orientations. A perspective drawing of the dication with one of the orientations (74% occupancy) is shown in Figure 7 (see Supporting Information for a drawing of the second orientation), and selected bond distances and angles are given in Table 3. In this structure, both of the coordinated carbonate oxygens occupy equatorial positions in the copper square pyramids, and both Cu−O distances are quite short: Cu(2)−O(1A) = 1.876(6) Å and Cu(1)−O(2A) = 1.950(5) Å. A pyridine donor occupies the axial position for Cu(1), and a tertiary amine is in the axial position of Cu(2). Both axial Cu−N distances (2.217(5) and 2.225(5) Å) are significantly longer than those in the approximate equatorial planes. Two water molecules (not shown in Figure 7) lie within hydrogen-bonding distances of the carbonate oxygens in each of the occupancies (O2A−O4A from water = 2.713 Å; O3A−O5A from water = 2.706 Å).

The reduction chemistry of the copper carbonate adducts has also been investigated to evaluate their behavior in a pumping experiment. The cyclic voltammograms of $[Cu_2(taec)]^{4+}$ and $[Cu_2(tpmc)(\mu\text{-}NO_3)]^{3+}$ in aqueous solution undergo a cathodic shift with the addition of excess sodium

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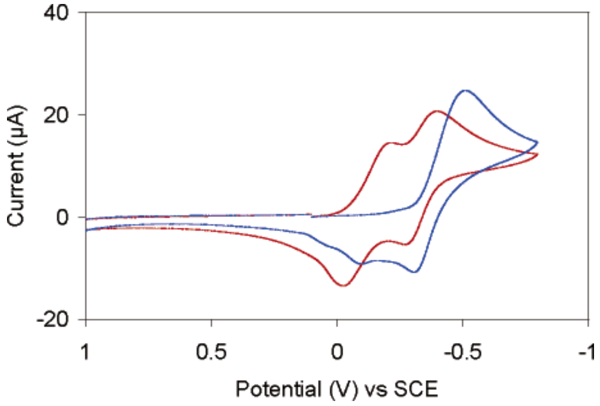

Figure 8. (a) Red: cyclic voltammogram of a millimolar solution of $[Cu_2(tpmc)(\mu\text{-}NO_3)]^{3+}$ in 0.3 M aqueous sodium nitrate at a 50 mV/s scan rate. (b) Blue: cyclic voltammogram of $[Cu_2(tpmc)(\mu\text{-}CO_3)]^{2+}$ resulting from addition of 8 equiv of $NaHCO_3$ to solution a.

bicarbonate. For the tpmc derivative, the shift, ΔE, between the average of the two waves for $[Cu_2(tpmc)(\mu\text{-}NO_3)]^{3+}$ and the reduction wave for $[Cu_2(tpmc)(\mu\text{-}CO_3)]^{2+}$ is 190 mV, as shown in Figure 8. This ΔE is much smaller than that observed for related Ni_2 and $Ni_2(\mu\text{-}CO_3)$ derivatives in acetonitrile.[12]

The cathodic shift and the quasi-reversible nature of the wave in the presence of bicarbonate indicates that a pumping experiment that cycles between the reduction of $[Cu_2(tpmc)(\mu\text{-}CO_3)]^{2+}$ and the oxidation of $[Cu_2(tpmc)]^{2+}$ could be carried out with good efficiency. To confirm that the bridging carbonate ion is released upon reduction of $[Cu_2(tpmc)(\mu\text{-}CO_3)]^{2+}$ to the Cu(I) complex, we carried out a controlled-potential electrolysis on $[Cu_2(tpmc)]^{4+}$ in the presence of ca. 8 equiv of sodium bicarbonate in aqueous solution (0.3 M $NaNO_3$). The initial CV is characteristic of $[Cu_2(tpmc)(\mu\text{-}CO_3)]^{2+}$, but as the reduction proceeded, a pale precipitate formed in the cell. This was isolated and confirmed by NMR spectroscopy to be $[Cu_2(tpmc)]^{2+}$ (see above). This result indicates a low effective bicarbonate binding constant for the Cu(I) derivative (i.e., $K_B < 2$ for Cu(I)).

Electrochemical Pumping of CO_2. On the basis of our fundamental studies of the dinuclear copper complexes described here, we conclude that $[Cu_2(tpmc)(\mu\text{-}OH)]^{3+}$ shows several characteristics that make it suitable for use as a reversible carrier of CO_2 in an electrochemical pumping experiment. The ligand can be readily prepared in moderate yield in a one-step reaction of two commercially available compounds, and the dinuclear copper complex has been synthesized on relatively large scales in near-quantitative yields. $[Cu_2(tpmc)(\mu\text{-}OH)]^{3+}$ is air-stable and shows good solubility in water (0.2 M) at near-neutral pH values, and it displays a high effective binding constant for bicarbonate ion with $\log K_B = 4.32$ at pH 7.4. $[Cu_2(tpmc)]^{4+}$ (as the $\mu\text{-}NO_3$ complex in 0.3 M aqueous $NaNO_3$) undergoes two near-reversible reductions at moderate potentials, −0.12 and −0.33 V versus SCE, and the reduction of $[Cu_2(tpmc)(\mu\text{-}CO_3)]^{2+}$ at −0.41 V shows only a modest cathodic shift relative to the starting complex. The quasi-reversible nature of this reduction wave is consistent with rapid anion binding and release. Controlled-potential electrolysis of $[Cu_2(tpmc)(\mu\text{-}CO_3)]^{2+}$ at ca. −0.5 V versus SCE in aqueous solution results in the formation of a Cu(I) derivative, $[Cu_2(tpmc)]^{2+}$, which is stable to disproportionation and shows a very low affinity for the carbonate ion. The binculear Cu(I) complex can be readily reoxidized to the binuclear Cu(II) derivative. The essential requirements for pumping of CO_2 in aqueous solution by electrochemically modulated complexation appear to be met.

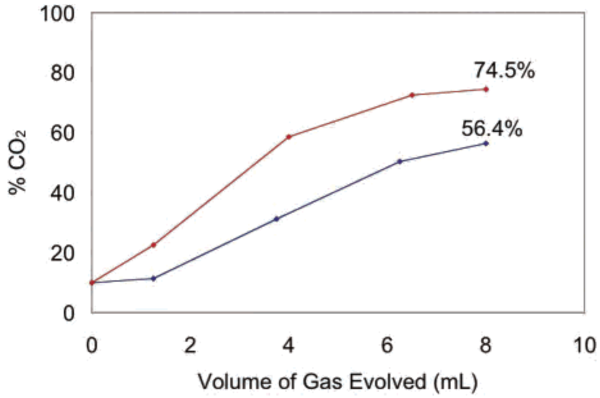

Figure 9. Percent CO_2 evolved as a function of gas collected in the pumping experiment at pH 6.4. (Blue): trial 1: 10 mL of 0.2 M solution of carrier; (red): trial 2: ca. 15 mL of a ca. 0.13 M solution of carrier.

A small two-compartment electrochemical cell was designed to demonstrate the feasibility of the pumping experiment. Working and counter compartments, each with a volume of ca. 15 mL, were separated by a cation exchange membrane, and the working compartment was equipped with a pressure sensor. An aqueous solution containing 1.0 M MES buffer at pH 6.37 was used in the counter compartment, and the same solution was used to prepare approximately 0.2 M solutions of the copper complex for the working compartment. At this pH, a mixture of $[Cu_2(tpmc)(\mu\text{-}NO_3)]^{3+}$ and $[Cu_2(tpmc)(\mu\text{-}OH)]^{3+}$ is present. Although our bicarbonate titration data were recorded at pH 7.4, the lower pH is required during the pumping experiment to limit the concentration of bicarbonate/carbonate ions in solution. The carrier solution was bubbled with a mixture of 10.00 ± 0.02% CO_2 in nitrogen, and the progress of the carrier loading was monitored by cyclic voltammetry. When the cyclic voltammograms showed little further change, the purging was stopped, and the cell was sealed. Under these conditions, the carrier loading with carbonate should be at least 75%.

The carbonate adduct, $[Cu_2(tpmc)(\mu\text{-}CO_3)]^{2+}$, was then reduced by controlled-potential electrolysis to release the carbonate ion that protonates and forms CO_2. The pressure in the working compartment was monitored during this process, and gas was pulled into a syringe to maintain ambient pressure. A total of approximately 8.6 mL of gas was collected and analyzed by gas chromatography. The concentration of CO_2 evolved versus the volume of gas collected was determined by GC analyses for two different experiments, and data are shown in Figure 9.

The first experiment yielded a final concentration of CO_2 of 56% in nitrogen. Analyses of the collected gas indicated that no significant hydrogen or carbon monoxide was produced in these experiments. In a second independent experiment, the volume of carrier solution was increased, thereby decreasing the headspace in the cell, and this adjustment resulted in an increase in the final percentage of CO_2 to 75%. The upper limit on the release pressure for these carriers depends on several factors, including the binding constant for the reduced form of the carrier (<2 for this system) and the solubility of CO_2 and HCO_3^- in solution at the release pressure and pH. In the present system, it appears that CO_2 solubility in water will limit the maximum release pressure at room temperature to approximately 1 atm.

During the reduction phase of the experiment, partial precipitation of the Cu(I) product occurred, and the current decreased to near zero after approximately two-thirds of the expected charge was passed (244 C). Nevertheless, $>90\%$ of the reduced material (223 C) was reoxidized in the next step of the experiment to reform the soluble Cu(II) complex. A second pumping cycle was carried out with the same solution. The amount of CO_2 collected per volume of gas evolved in this cycle was very similar to that in the first experiment. However, once again, precipitation of the Cu(I) complex limited the amount of current that could be passed (see the Experimental Section).

Although pumping of CO_2 in aqueous solution has been successfully demonstrated in this project, there are several ways in which chemical modifications could improve the performance of these binuclear carriers. A modification that leads to a higher effective binding constant for bicarbonate would enable the carrier to pump from lower initial CO_2 concentrations. For example, calculations indicate that a binding constant $>10^5$ would be necessary to pump from ambient CO_2 pressures in air. A higher solubility of the carrier in water would permit greater release pressures and prevent the complications that arise from electrode coating during the reduction phase in the present system. Further work to maximize the carrier properties is in progress in our laboratory.

Acknowledgment. Support of this project by an NSF/EPA Partnership for Environmental Research Award, CTS-0124445, is gratefully acknowledged. D.L.D. acknowledges the support of the U.S. Department of Energy, Office of Science, Chemical and Biological Sciences Division, under DOE contract no. DE-AC36-99G010337. We thank Professor Carl Koval, Professor John Hagadorn, and M. McNevin for helpful advice on electrochemical and X-ray diffraction studies.

Supporting Information Available: X-ray data collection, refinement results, atomic coordinates, anisotropic displacement parameters, and complete bond distances and angles in CIF format for $[Cu_2(taec)(\mu\text{-}CO_3)](BPh_4)_2$ and $[Cu_2(tpmc)(\mu\text{-}CO_3)](BPh_4)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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