

## Studies of Bicarbonate Binding by Dinuclear and Mononuclear Ni(II) Complexes

Rachel Newell, Aaron Appel, D. L. DuBois,<sup>†</sup> and M. Rakowski DuBois\*

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

Received June 18, 2004

Bicarbonate ion reacts with the dinuclear nickel(II) complex containing the taec ligand (taec = *N,N',N'',N'''*-tetrakis-(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane) in buffered aqueous solution to form the  $\mu\text{-}\eta^2,\eta^2$ -carbonate complex with a large effective binding constant for bicarbonate ion,  $\log K_B = 4.39$  at pH = 7.4. In contrast, the dinuclear nickel(II) complex containing the *o*-xyl-DMC<sub>2</sub> ligand (*o*-xyl-DMC<sub>2</sub> =  $\alpha,\alpha'$ -bis(5,7-dimethyl-1,4,8,11-tetraazacyclotetradecan-6-yl)-*o*-xylene) does not react with bicarbonate or carbonate ion in aqueous solution. In propylene carbonate, the reaction of  $[\text{Ni}_2(\text{o-xyl-DMC}_2)]^{4+}$  with bicarbonate proceeds rapidly to form the  $\mu\text{-}\eta^1,\eta^1$ -carbonate complex. The structure of this carbonate complex has been determined by an X-ray diffraction study that confirms the  $\mu\text{-}\eta^1,\eta^1$ -carbonate binding mode. A mononuclear analogue of  $[\text{Ni}_2(\text{taec})]^{4+}$ ,  $[\text{Ni}(2,3,2\text{-tetraamine})]^{2+}$  does not form a detectable mononuclear or dinuclear product with bicarbonate ion in aqueous solution, but  $[\text{NiDMC}]^{2+}$  (DMC = 5,7-dimethyl-1,4,8,11-tetraazacyclotetradecane) reacts slowly with carbonate ion in aqueous solution to form a 2:1 complex.

### Introduction

The controlled binding and release of CO<sub>2</sub> or one of its aquated forms is important for developing new strategies for CO<sub>2</sub> separation and recovery for various applications. Current processes for carbon dioxide removal include wet scrubbing technologies, dry regenerable sorbents, membranes, cryogenics, and pressure and temperature swing adsorption.<sup>1–3</sup> A particular interest of our laboratories is the development of electrochemical methods for pumping CO<sub>2</sub>. Electrochemical cycles are not Carnot limited, and such an approach may offer advantages in the long term for CO<sub>2</sub> recovery from dilute CO<sub>2</sub> streams. A number of electrochemical methods for CO<sub>2</sub> recovery have been proposed, including molten carbonate fuel cells,<sup>4</sup> proton pumps,<sup>5</sup> doped alkaline earth carbonates,<sup>6</sup> and electrochemically modulated complexation.<sup>7,8</sup> The last approach uses a redox active carrier

molecule that has a strong affinity for CO<sub>2</sub> in one oxidation state and a weak affinity upon either oxidation or reduction of the carrier molecule.

In previous research, 2,6-di-*tert*-butyl-1,4-benzoquinone in propylene carbonate solution has been used as a carrier to separate CO<sub>2</sub> from a mixture with nitrogen, while pumping it from a concentration of 0.5% to nearly 100% at 1 atm.<sup>8</sup> This system, as well as other quinone carriers, have the potential for further development for dilute gas streams that do not contain oxygen. However, the reduced di-*tert*-butylbenzocatechol that binds strongly to CO<sub>2</sub> ( $K = 10^{15}$ )<sup>7</sup> is sensitive to oxygen, which is undesirable for removing CO<sub>2</sub> in certain applications.<sup>3</sup> In addition, the use of an organic solvent such as propylene carbonate has environmental and other disadvantages.

Water-soluble complexes that strongly bind the bicarbonate or carbonate anions that form when CO<sub>2</sub> dissolves in water may be developed as carriers for aqueous electrochemical pumping experiments. In this case, the carrier complex would be exposed to the feed gas stream when the complex is in its oxidized form. In order to effectively pump CO<sub>2</sub> using a

\* To whom correspondence should be addressed. E-mail: Mary.Rakowski-Dubois@Colorado.edu.

<sup>†</sup> National Renewable Energy Laboratory, Golden, Colorado.

- (1) White, C. J. *Air Waste Manage. Assoc.* **2003**, 53, 645.
- (2) (a) Bandi, A.; Specht, M.; Weimer, T.; Schaber, K. *Energy Convers. Manage.* **1995**, 37, 899. (b) Specht, M.; Bandi, A.; Maier, C. U.; Schwarz, J. *Energy Convers. Manage.* **1992**, 33, 537.
- (3) Astarita, G.; Savage, D. W.; Bisio, A. *Gas Treating with Chemical Solvents*; John Wiley & Sons: New York, 1983.
- (4) Winnick, J.; Toghaiani, H.; Quattrone, P. *AIChE J.* **1982**, 28, 103. (b) Weaver, J. L.; Winnick, J. *J. Electrochem. Soc.* **1983**, 130, 20. (c) Weaver, J. L.; Winnick, J. *Chem. Eng. Prog.* **1990**, 86, 41.
- (5) Weimer, T.; Schaber, K.; Specht, M.; Bandi, A. *Energy Convers. Manage.* **1996**, 37, 1351.

(6) Granite, E. J. Proceedings of the 20th International Pittsburgh Coal Conference, Pittsburgh, PA, 2003; Paper 29-1.

(7) DuBois, D. L.; Miedaner, A.; Bell, W.; Smart, J. C. In *Electrochemical and Electrocatalytic Reactions of Carbon Dioxide*, Sullivan, B. P., Krist, K.; Guard, H. E., Eds.; Elsevier: New York, 1993; Chapter 4. (8) Scovazzo, P.; Poshusta, J.; DuBois, D. L.; Koval, C.; Noble, R. J. *Electrochem. Soc.* **2003**, 150, D91.

bicarbonate/carbonate carrier, large bicarbonate/carbonate binding constants will be required in the oxidized form, and a very low affinity for carbonate will be required in the reduced form. One series of compounds that may function as carrier molecules is a series of metal complexes with binucleating macrocyclic ligands. Studies of these complexes have indicated that anion binding constants can be several orders of magnitude higher than for mononuclear analogues.<sup>9</sup> This effect has been attributed to the binding of the anion to two metal ions, forming an “inverse chelate ring”, as well as the hydrophobic environment around the anion.<sup>9e</sup> Many dinuclear late transition metal carbonate complexes have been reported,<sup>10</sup> and a few metal complexes containing the bicarbonate ligand have also been prepared.<sup>11</sup> However, binding constants for carbonate or bicarbonate ion have been determined for very few known binucleating systems.<sup>12</sup> In this paper, we report our studies of two known nickel complexes with binucleating ligands with the objective of understanding the structural features most likely to promote high bicarbonate/carbonate binding constants in buffered aqueous solutions. We chose nickel complexes for these initial studies, because our preliminary results indicated that

this metal exhibits high binding constants for anions, and this feature permits facile comparison of the influence of ligand structure.

## Experimental Section

**Safety Note.** *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

**Materials.** Bis-tetraethylammonium carbonate was purchased from Aldrich and was recrystallized from acetonitrile. A titration of the recrystallized material with HCl in water showed only one equivalence point, and pH determinations on aqueous solutions of the recrystallized material indicated that the material was tetraethylammonium bicarbonate (e.g., pH of 0.040 M soln = 8.37).<sup>13</sup> *N,N'*-Bis(2-aminoethyl)-1,3-propanediamine (2,3,2-tet) was prepared according to the literature method.<sup>14</sup> The perchlorate salts of  $\alpha,\alpha'$ -bis(5,7-dimethyl-1,4,8,11-tetraazacyclotetradecan-6-yl)-*o*-xylene-dinickel(II), [Ni<sub>2</sub>(*o*-xyl-DMC<sub>2</sub>)](ClO<sub>4</sub>)<sub>4</sub>, and 5,7-dimethyl-1,4,8,11-tetraazacyclotetradecane-nickel(II), [Ni(DMC)](ClO<sub>4</sub>)<sub>2</sub>, were synthesized according to the previously published procedures.<sup>15</sup> The syntheses of cyclam,<sup>16</sup> (*N-p*-tolylsulfonyl)aziridine,<sup>17</sup> and of *N,N',N'',N'''*-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (taec)<sup>18</sup> were also carried out using reported procedures.

Acetonitrile was distilled from CaH<sub>2</sub> prior to use. Tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone. Reagent grade propylene carbonate was used without purification. Water (18 M $\Omega$ ) from a Millipore Milli-Q plus water system was used for the aqueous solutions. HEPES sodium salt was isolated from the reaction of HEPES (32.00 g, 0.134 mol) and 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 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. Yield, 68%.

**Instrumentation.** Electronic spectra were measured on an Agilent 8453 UV–vis spectrometer using a 1 cm cell. To eliminate complications from atmospheric CO<sub>2</sub>, measurements were performed using a sealed cell that could be evacuated and filled with nitrogen prior to adding the solution. IR spectra (KBr pellet) were recorded on an Avatar 360 FT-IR. Positive ion ESI mass spectra were measured on a Hewlett-Packard 5989B mass spectrometer that included a 59987A electrospray source. Room temperature magnetic susceptibility measurements were conducted on an Evans-Johnson Matthey magnetic susceptibility balance. Conductivity measurements on 10<sup>-3</sup> M solutions were performed using a Yellow Springs Instruments model 31 conductivity bridge and a model 3403 conductivity cell. Ion ratios were assigned according to literature values.<sup>19</sup> Elemental analyses were determined by Desert Analytics Laboratory, Tucson, AZ.

- (9) (a) Kida, S.; Murase, I.; Harada, C.; Liao, D.; Mikuriya, M. *Bull. Chem. Soc. Jpn.* **1986**, 2595. (b) Evers, A.; Hancock, R. D.; Murase, I. *Inorg. Chem.* **1986**, 25, 2160. (c) Motekaitis, R. J.; Martell, A. E.; Dietrich, B.; Lehn, J. M. *Inorg. Chem.* **1984**, 23, 1588. (d) Udugala-Ganehenge, M. Y.; Heeg, M. H.; Hryhorczuk, L. M.; Wenger, L. E.; Endicott, J. F. *Inorg. Chem.* **2001**, 40, 1614. (e) Asato, E.; Ozutsumi, D.; Ishiguro, S.; Kida, S.; Murase, I. *Inorg. Chim. Acta* **1990**, 167, 189.
- (10) (a) Palmer, D. A.; Van Eldik, R.; *Chem. Rev.* **1983**, 83, 651 and references within. (b) Kajiwara, T.; Yamaguchi, T.; Kido, H.; Kawabata, S.; Kuroda, R.; Ito, T. *Inorg. Chem.* **1993**, 32, 4990. (c) Mikuriya, M.; Murase, I.; Asato, E.; Kida, S. *Chem. Lett.* **1989**, 497. (d) Harada, H.; Koda, M.; Vuckovic, G.; Matsumoto, N.; Kida, S. *Inorg. Chem.* **1991**, 30, 1190. (e) Tyeklar, Z.; Paul, P. P.; Jacobson, R. R.; Farooz, A.; Karlin, D. K.; Zubieta, J. J. *Am. Chem. Soc.* **1989**, 111, 388. (f) Kitajima, N.; Fujisawa, K.; Koda, T.; Hikichi, S.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 1357. (g) Youngme, S.; Chaichit, N.; Kongsaree, P.; van Albada, G. A.; Reedijk, J. *Inorg. Chim. Acta* **2001**, 324, 232. (h) Youngme, S.; Pakawatchai, C.; Somjitsripunya, W.; Chinnakali K.; Fun, H. F. *Inorg. Chim. Acta* **2000**, 303, 181. (i) Fernandes, C.; Neves, A.; Bortoluzzi, A. J.; Szpogancz, B.; Schwingel, E. *Inorg. Chem. Commun.* **2001**, 4, 354. (j) Kitajima, N.; Hikichi, S.; Tanaka, M.; Hikichi, S.; Moro-oka, Y. *J. Am. Chem. Soc.* **1993**, 115, 5496. (k) Looney, A.; Han, R.; McNeill, K.; Parkin, G. *J. Am. Chem. Soc.* **1993**, 115, 4690. (l) Murase, I.; Vuckovic, G.; Koda, M.; Harada, H.; Matsumoto, M.; Kida, S. *Inorg. Chem.* **1991**, 30, 728. (m) Kruger, P. E.; Fallon, G. D.; Moubaraki, B.; Berry, K. J.; Murray, K. S. *Inorg. Chem.* **1995**, 34, 4808. (n) Escuer, A.; Mautner, F. A.; Penalba, E.; Vicente, R. *Inorg. Chem.* **1998**, 37, 4190. (o) Van den Brenk, A. L.; Byriel, K. A.; Fairlie, D. P.; Gahan, L. R.; Hanson, G. R.; Hawkins, C. J.; Kennard, C. H. L.; Moubaraki, B.; Murray, K. S. *Inorg. Chem.* **1994**, 33, 3549. (p) Allred, R. A.; McAlexander, L. H.; Arif, A. M.; Berreau, L. M. *Inorg. Chem.* **2002**, 41, 6790.
- (11) (a) Mao, Z. W.; Liehr, G.; van Eldik, R. *J. Am. Chem. Soc.* **2000**, 122, 4839. (b) Darensbourg, D. J.; Meckfessel Jones, M. L.; Reibenspies, J. H. *Inorg. Chem.* **1993**, 32, 4675. (c) Darensbourg, D. J.; Holtcamp, M. W.; Khandelwal, B.; Reibenspies, J. H. *Inorg. Chem.* **1995**, 34, 5390. (d) Baxter, K. E.; Hanton, L. R.; Simpson, J.; Vioncent, B. R.; Blackman, A. G. *Inorg. Chem.* **1995**, 34, 2795. (e) Yoshida, T.; Thorn, D. L.; Okano, T.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, 101, 4212. (f) Crutchley, R. J.; Powell, J. *Inorg. Chim. Acta* **1977**, 24, L15. (g) Massoud, S. S.; Milburn, R. M. *Inorg. Chim. Acta* **1988**, 154, 115. (h) Tsuda, T.; Chujo, Y.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, 102, 431.
- (12) (a) Barker, J. E.; Liu, Y.; Martin, N. D.; Ren, T. *J. Am. Chem. Soc.* **2003**, 125, 13332. (b) Tobey, S. L.; Jones, B. D.; Anslyn, E. V. *J. Am. Chem. Soc.* **2003**, 125, 4026. (c) Association constants of bicarbonate with aqueous metal ions: Emara, M. M.; Parid, N. A.; Bahr, M. M.; Shehata, H. A. *J. Indian Chem. Soc.* **1985**, LXII, 744. Emara, M. M.; Parid, N. A.; Shehata, H. A. *J. Indian Chem. Soc.* **1987**, LXIV, 119.
- (13) King, E. L. *Chemistry*; Painter Hopkins: Sausalito, CA, 1979; pp 576–594.
- (14) Brubaker, G. R.; Schaefer, D. P. *Inorg. Chem.* **1971**, 10, 968.
- (15) Mochizuki, K.; Kondo, T.; Manaka, S.; Kajiwara, T.; Ito, T. *J. Coord. Chem.* **1996**, 37, 205.
- (16) Herve, G.; Bernard, H.; Le Bris, N.; Yaouanc, J. J.; Handel, H.; Toupet, L. *Tetrahedron Lett.* **1998**, 39, 6861.
- (17) (a) Hope, D. B.; Horncastle, K. C. *J. Chem. Soc. C* **1966**, 1098. (b) Martin, A. E.; Ford, T. M.; Bulkowski, J. E. *J. Org. Chem.* **1982**, 47, 412.
- (18) Murase, I.; Mikuriya, M.; Sonoda, H.; Fukuda, Y.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1986**, 953.
- (19) Geary, W. J. *Coord. Chem. Rev.* **1971**, 7, 81.

All electrochemical experiments were carried out with a Cypress Systems model CS-1200 computer-aided electrolysis system using a three-electrode arrangement. Cyclic voltammetry experiments were performed using glassy carbon for the working and counter electrodes. A silver wire that had been successively dipped in concentrated nitric acid and hydrochloric acid, then rinsed with distilled water and air-dried, was used as a pseudoreference electrode. The ferrocene/ferrocenium couple was used as an internal reference,<sup>20</sup> and all potentials are reported with respect to this couple. Permethylferrocene/permethylferrocenium or cobaltocene/cobaltocenium were used as secondary references when the ferrocene/ferrocenium couple was obscured. Cyclic voltammograms were recorded under a nitrogen atmosphere in 0.3 M NEt<sub>4</sub>BF<sub>4</sub> acetonitrile solutions.

**Titrations and Binding Constant Determinations.** Titrations of [Ni<sub>2</sub>(taec)](BF<sub>4</sub>)<sub>4</sub> with sodium bicarbonate, monitored by UV–visible spectroscopy, were carried out under nitrogen in aqueous solutions at a constant ionic strength buffered with 0.5 M HEPES sodium salt adjusted to pH = 7.4 with HNO<sub>3</sub>. (No change in the visible spectrum of the starting nickel complex was observed in the nitrate solutions.) The equilibrium concentration of bicarbonate at pH = 7.4 was used in the binding constant calculations. The acid dissociation constants were taken from Harris,<sup>21</sup> where the first constant is for the production of bicarbonate from dissolved carbon dioxide. The first acid dissociation constant is  $4.45 \times 10^{-7}$ , and the second is  $4.69 \times 10^{-11}$ . The temperature of the cell was not regulated, but was found to be between 24.5 and 25.5 °C for all titrations. The value of *K* was determined from five independent titrations.

Titrations of [Ni<sub>2</sub>(*o*-xyl-DMC<sub>2</sub>)](ClO<sub>4</sub>)<sub>4</sub> with sodium bicarbonate, monitored by UV–vis spectroscopy, were carried out under nitrogen in 0.20 M TRIS buffer (60%)/acetonitrile (40%) solution. This solution was prepared by dissolving the TRIS sodium salt (2.42 g, 0.02 mol) in 100 mL of water, adding concentrated HNO<sub>3</sub> until the pH was 9.26, and then adding acetonitrile (67 mL). Propylene carbonate solutions of [Ni(DMC)](ClO<sub>4</sub>)<sub>2</sub> and [Ni<sub>2</sub>(*o*-xyl-DMC<sub>2</sub>)](ClO<sub>4</sub>)<sub>4</sub> were titrated with a solution of tetraethylammonium bicarbonate in propylene carbonate at constant ionic strength (0.5 M Et<sub>4</sub>NBF<sub>4</sub>). (No changes in the visible spectra of the starting complexes were observed in the presence of high concentrations of BF<sub>4</sub> anion.)

The binding constant for the reaction of [Ni<sub>2</sub>(taec)]<sup>4+</sup> with HCO<sub>3</sub><sup>−</sup> was determined in a least-squares approach like that of Asato et al.,<sup>9c</sup> in which the absorbance is expressed as a function of the binding constant, *K*. The solver in Microsoft Excel<sup>22</sup> was used to optimize the binding constant by minimizing the sum of the square of the differences between the calculated and observed values of the absorbance at each titrant addition. The binding constant was determined using data from five titrant additions at four different wavelengths. A detailed description of calculations is provided in the Supporting Information. A similar approach was used to approximate the binding constant for the reaction of [Ni<sub>2</sub>(*o*-xyl-DMC<sub>2</sub>)]<sup>4+</sup> with bicarbonate in the mixed aqueous/acetonitrile solution. Values for the *K*<sub>a1</sub> and *K*<sub>a2</sub> of H<sub>2</sub>CO<sub>3</sub> in aqueous solution were used in this approximation.

**Synthesis of [Ni<sub>2</sub>(taec)](BF<sub>4</sub>)<sub>4</sub>.** Ni(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (2.42 g, 7.11 mmol) was dissolved in 50 mL of acetonitrile and filtered, and

**Table 1.** Crystal Data and Collection Parameters for [Ni<sub>2</sub>(*o*-xyl-DMC<sub>2</sub>)](μ-CO<sub>3</sub>)](ClO<sub>4</sub>)<sub>2</sub>·(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O·(CH<sub>3</sub>)<sub>2</sub>CO

formula	C <sub>73</sub> H <sub>140</sub> N <sub>16</sub> Ni <sub>4</sub> Cl <sub>4</sub> O <sub>24</sub>
fw	2002.65
space group	P1
temp	−131 °C
<i>a</i> (Å)	8.4384(4)
<i>b</i> (Å)	12.2522(7)
<i>c</i> (Å)	22.1306(11)
<i>V</i> (Å <sup>3</sup> )	2212.5(2)
α (deg)	80.5260(10)
β (deg)	79.9220(10)
γ (deg)	83.1770(10)
<i>Z</i>	2
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.503
λ(Mo Kα) (Å)	0.71073
scan type, deg	ω scans, 0.3
frame collection type (s)	30
reflms measured	hemisphere
2θ range (deg)	4.12–50.06
μ (cm <sup>−1</sup> )	1.040
crystal dimensions (mm <sup>3</sup> )	0.25 × 0.25 × 0.1
no. reflms measured	14501
no. observations	7794
no. params	598
<i>R</i> <sub>int</sub>	0.1012
<i>R</i> <sup>a</sup>	0.1121
<i>R</i> <sub>w</sub> <sup>b</sup>	0.2034
GOF <sup>c</sup>	1.022

<sup>a</sup> *R* = *R*<sub>1</sub> = Σ||*F*<sub>o</sub>| − |*F*<sub>c</sub>||/Σ|*F*<sub>o</sub>|. <sup>b</sup> *R*<sub>w</sub> = [Σ[*w*(*F*<sub>o</sub><sup>2</sup> − *F*<sub>c</sub><sup>2</sup>)<sup>2</sup>]/Σ[*w*(*F*<sub>o</sub><sup>2</sup>)<sup>2</sup>]<sup>1/2</sup>. <sup>c</sup> GOF = *S* = [Σ[*w*(*F*<sub>o</sub><sup>2</sup> − *F*<sub>c</sub><sup>2</sup>)<sup>2</sup>]/(*M* − *N*)<sup>1/2</sup> where *M* is the number of reflections and *N* is the number of parameters refined.

17.6 g of a 5% solution of taec in absolute ethanol (0.88 g taec, 2.4 mmol) was added. Upon addition of the ligand, the pale blue solution changed to a deep green mixture. The mixture was stirred for 30 min, and then 50 mL of absolute ethanol was added, causing increased precipitation of yellow-orange solid. The mixture was stirred for 30 min, and then the solid was collected by filtration and washed with ethanol followed by diethyl ether. The air-dried solid was dissolved in 120 mL of acetonitrile, filtered, and crystallized by vapor diffusion with 250 mL of diethyl ether. An orange crystalline solid was collected after 8 days. Yield: 1.28 g, 65%. ESI-MS (*m/z*): 749 ([Ni<sub>2</sub>(taec)(BF<sub>4</sub>)<sub>3</sub>]<sup>+</sup>), 681 ([Ni<sub>2</sub>(taec)(BF<sub>4</sub>)<sub>2</sub>F]<sup>+</sup>), 613 ([Ni<sub>2</sub>(taec)(BF<sub>4</sub>)<sub>2</sub>F<sub>2</sub>]<sup>+</sup>), 297 ([Ni<sub>2</sub>(taec)(BF<sub>4</sub>)F]<sup>2+</sup>), 192 ([Ni<sub>2</sub>(taec)(BF<sub>4</sub>)<sup>3+</sup>), 169 ([Ni<sub>2</sub>(taec)F]<sup>3+</sup>). Anal. Calcd for C<sub>18</sub>H<sub>44</sub>N<sub>8</sub>B<sub>4</sub>F<sub>16</sub>Ni<sub>2</sub>: C, 25.82; H, 5.30; N, 13.38. Found: C, 25.77; H, 5.46; N, 13.01. Other characterization data are given in Table 2.

**Synthesis of [Ni<sub>2</sub>(μ-CO<sub>3</sub>)(taec)](BF<sub>4</sub>)<sub>2</sub>.** Ni<sub>2</sub>(taec)(BF<sub>4</sub>)<sub>4</sub> (0.202 g, 0.24 mmol) and sodium bicarbonate (0.024 g, 0.29 mmol) were combined in 2.0 mL of water and 4.0 mL of acetonitrile, stirred for 20 min, and filtered. The volume of the filtrate was reduced (to remove acetonitrile), and the solution was cooled to ca. 10 °C to produce blue crystals after one or more days. Yield: 0.082 g, 47%. IR (KBr, cm<sup>−1</sup>): new absorptions at 1555 (s), 1393 (s), 841, 761. ESI-MS(*m/z*): 274 ([Ni<sub>2</sub>(μ-CO<sub>3</sub>)(taec)]<sup>2+</sup>), 635 ([Ni<sub>2</sub>(μ-CO<sub>3</sub>)(taec)](BF<sub>4</sub>)<sup>1+</sup>). Anal. Calcd for Ni<sub>2</sub>(μ-CO<sub>3</sub>)(taec)(BF<sub>4</sub>)<sub>2</sub>·1NaBF<sub>4</sub>, C<sub>19</sub>H<sub>44</sub>N<sub>8</sub>B<sub>3</sub>F<sub>12</sub>NaO<sub>3</sub>Ni<sub>2</sub>: C, 27.38; H, 5.32; N, 13.45. Found: C, 26.91; H, 5.07; N, 13.15. Other characterization data are given in Table 2.

**Synthesis of [Ni<sub>2</sub>(*o*-xyl-DMC<sub>2</sub>)](μ-CO<sub>3</sub>)](ClO<sub>4</sub>)<sub>2</sub>.** To a solution of [Ni<sub>2</sub>(*o*-xyl-DMC<sub>2</sub>)](ClO<sub>4</sub>)<sub>4</sub> (0.132 g, 0.123 mmol) in a mixture of 5 mL of acetonitrile and 5 mL of acetone was added solid Cs<sub>2</sub>CO<sub>3</sub> (0.055 g, 0.168 mmol). The suspension was refluxed for 10 min, and the solution turned purple. The solution was filtered, and anhydrous diethyl ether was added to obtain a purple precipitate that was filtered and air-dried. Yield: 0.103 g, 90%. Crystals

- (20) (a) Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854. (b) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 462. (c) Hupp, J. T. *Inorg. Chem.* **1990**, *29*, 5010.  
 (21) Harris, D. C. *Quantitative Chemical Analysis*, 5th ed.; W. H. Freeman and Co.: New York, 1991; p AP17.  
 (22) *Microsoft Excel X for Mac*, Version 10.1.0., 2002.

**Table 2.** Characterization Data for Nickel Complexes

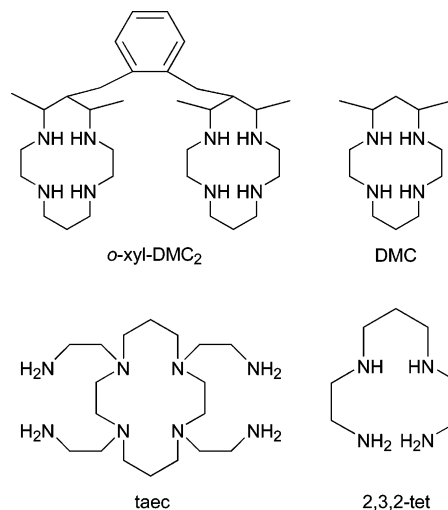
compd	UV-vis solvent, $\lambda_{\max}$ nm ( $\epsilon/\text{Ni}$ , $\text{M}^{-1}\text{cm}^{-1}$ )	CV solvent, $E_{p/2}$ ( $\Delta E$ , mV) V vs ferrocene	conductivity solvent $\Lambda_{\text{M}} \text{cm}^2/\Omega \text{mol}$ (ion ratio) <sup>19</sup>
$[\text{Ni}_2(\text{taec})](\text{BF}_4)_4$	H <sub>2</sub> O 375 (sh) 460 (45)	CH <sub>3</sub> CN -1.29 (110) <sup>a</sup> -1.50 (102) <sup>a</sup> $E_p = +1.39$ (irr) <sup>a</sup>	H <sub>2</sub> O 473 (>3:1) CH <sub>3</sub> CN 394 (3:1)
$[\text{Ni}_2(o\text{-xyl-DMC}_2)](\text{ClO}_4)_4$	PC 375 (34) 465 (80)	CH <sub>3</sub> CN -1.73 (191) <sup>b</sup> +0.69 (113) <sup>b</sup>	CH <sub>3</sub> CN 363 (~3:1)
$[\text{Ni}(\text{DMC})](\text{ClO}_4)_2$	PC 365 (17) 467 (67) 690 (2)	CH <sub>3</sub> CN -1.83 (97) <sup>b</sup> +0.62 (117) <sup>b</sup>	
$[\text{Ni}(2,3,2\text{-tet})](\text{BF}_4)_2$	H <sub>2</sub> O 447 (12)	CH <sub>3</sub> CN -1.83 (135) <sup>c</sup> +0.70 (127) <sup>c</sup>	
$[\text{Ni}_2(\text{taec})(\mu\text{-CO}_3)](\text{BF}_4)_2$	H <sub>2</sub> O 374 (33) 596 (19) 996 (15)	CH <sub>3</sub> CN -2.24 (irr) <sup>a</sup> -2.31 (irr) <sup>a</sup> +0.75 (120) <sup>d</sup> +1.62 (136) <sup>d</sup>	
$[\text{Ni}_2(o\text{-xyl-DMC}_2)(\mu\text{-CO}_3)](\text{ClO}_4)_2$	PC 347 (79) 547 (27) 953 (5)	CH <sub>3</sub> CN+0.68 (105) <sup>b</sup> +1.33 (irr) <sup>b</sup> +0.25 (irr) <sup>b,e</sup>	
$[(\text{NiDMC})_2(\mu\text{-CO}_3)](\text{ClO}_4)_2$	PC 358 (30) 561 (18) 924 (13)	CH <sub>3</sub> CN <sup>e</sup>	

<sup>a</sup> Scan rate = 50 mV/s. <sup>b</sup> Scan rate = 200 mV/s. <sup>c</sup> Scan rate = 500 mV/s. <sup>d</sup> Scan rate = 2000 mV/s. Waves were less reversible at slower scan rates and completely irreversible at 50 mV/s. <sup>e</sup> Reduction waves were not observed in this solvent.

suitable for X-ray diffraction studies were grown by slow diffusion of diethyl ether into an acetone solution of the purple solid. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3433 (br), 3257, 2931, 1712 (w), 1639, 1517, 1455, 1121 (s), 840 (w), 803 (w), 624 (s). ESI MS ( $m/z$ ): 835 [P - ClO<sub>4</sub>]<sup>+</sup>; 368 [P - 2ClO<sub>4</sub>]<sup>2+</sup>. Magnetic moment,  $\mu$  (20 °C) = 4.03  $\mu_B$  (2.0 per Ni). Anal. Calcd for  $[\text{Ni}_2(o\text{-xyl-DMC}_2)(\mu\text{-CO}_3)](\text{ClO}_4)_2 + 0.5 \text{ CsClO}_4, \text{C}_{33}\text{H}_{62}\text{N}_8\text{Cl}_{2.5}\text{O}_{13}\text{Cs}_{0.5}\text{Ni}_2$ : C, 37.70; H, 5.94; N, 10.66. Found: C, 37.77; H, 6.08; N, 10.56. Other characterization data are given in Table 2.

**Synthesis of  $[(\text{NiDMC})_2(\mu\text{-CO}_3)](\text{ClO}_4)_2$ .** To an aqueous solution containing  $[\text{Ni}(\text{DMC})](\text{ClO}_4)_2$  (0.240 g, 0.494 mmol) was added solid Na<sub>2</sub>CO<sub>3</sub> (0.157 g, 1.48 mmol). The solution was heated to reflux and turned pink. The solvent was removed by rotary evaporation, and the solid was extracted with acetone (10 mL). Slow diffusion of diethyl ether into the acetone solution resulted in deposition of feathery purple crystals. Yield: 0.090 g, 44%. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3421 (br), 3274, 3172, 2964, 2931, 2870, 1716 (s), 1635 (w), 1508, 1451, 1117, 970, 840 (s), 803, 624. ESI MS ( $m/z$ ): 733 [P - ClO<sub>4</sub>]<sup>+</sup>; 317 [P - 2ClO<sub>4</sub>]<sup>2+</sup>. Magnetic moment,  $\mu$  (20 °C): 3.21  $\mu_B$  (1.60 per nickel).  $\Lambda_{\text{M}}$  ( $\text{cm}^2/\Omega \text{mol}$  in (CH<sub>3</sub>)<sub>2</sub>CO): 194 (2:1 electrolyte). Anal. Calcd for C<sub>25</sub>H<sub>56</sub>N<sub>8</sub>Cl<sub>2</sub>O<sub>11</sub>Ni<sub>2</sub>: C, 36.04; H, 6.77; N, 13.45. Found: C, 35.78; H, 6.19; N, 11.79.

**X-ray Crystallography on  $[\text{Ni}_2(o\text{-xyl-DMC}_2)(\mu\text{-CO}_3)](\text{ClO}_4)_2$ .** Crystals suitable for X-ray diffraction studies were grown from an acetone/diethyl ether solution at room temperature. The crystals were mounted on a glass fiber using Paratone-N oil and transferred to a Siemens SMART diffractometer/CCD area detector equipped with an LT-2A low temperature apparatus operating at 142–143 K. A 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 a hemisphere of data was collected using 0.3°  $\omega$  scans at 30 s per frame. The raw data were integrated and the unit cell parameters refined using SAINT. Data analysis was performed using XPREP. Absorption correction was applied using SADABS.<sup>23</sup> 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  $F^2$ . Details of the data collection and refinement are given in Table 1.

**Chart 1**

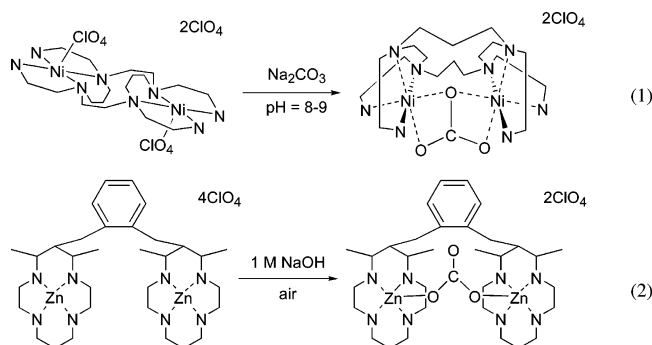
Preliminary data indicated a triclinic cell. The choice of the centric space group  $P\bar{1}$  was supported by the successful solution and refinement of the structure. All non-H atoms were refined anisotropically. All H-atoms were placed in idealized positions and were included in structure factor calculations but were not refined. Disorder of the oxygens attached to Cl(1) was modeled by allowing each oxygen to refine to three different positions with one-third occupancy and fixing the O–Cl(1) distance to approximately 1.4 Å.

## Results and Discussion

**Ligand Selection.** Two binucleating ligand types that have been previously shown to provide metal orientations for strong carbonate binding are shown on the left side of Chart 1. For example,  $[\text{Ni}_2\text{taec}](\text{ClO}_4)_4$  reacts with carbonate ion to form the structurally characterized  $\mu\text{-}\eta^2, \eta^2$  carbonate complex shown in eq 1,<sup>10c</sup> and the dinuclear Co(II)  $\mu\text{-CO}_3$  analogue with this ligand has also been characterized.<sup>10d</sup> The dinuclear zinc complex with the *o*-xyl-DMC<sub>2</sub> ligand spon-

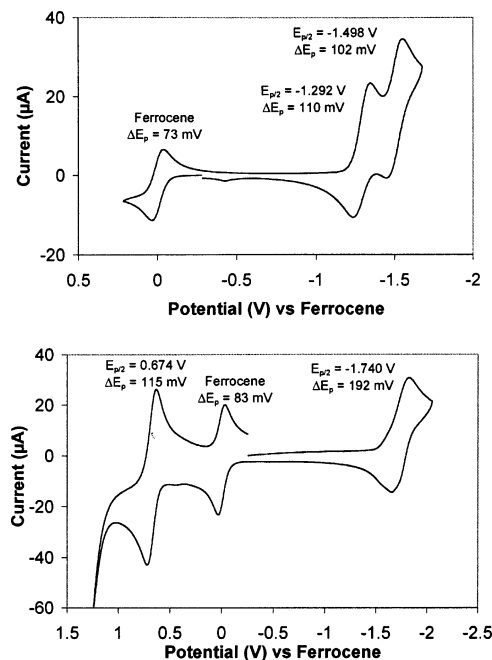
(23) Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *5*, 33.

taneously takes up carbon dioxide from air in basic solution to form the structurally characterized  $\mu$ - $\eta^1, \eta^1$ -carbonate complex, eq 2.<sup>10b</sup> Related mononuclear ligands were also chosen for study in order to provide comparisons with the binucleating systems. These include the macrocycle 5,7-dimethyl-1,4,8,11-tetraazacyclotetradecane (dimethylcyclam, DMC) and the open tetradentate ligand 1,4,8,11-tetraazaundecane (2,3,2-tet) (Chart 1, right side).



**Syntheses of Nickel Complexes.** The nickel(II) complex with each of these ligands was prepared with weakly or noncoordinating counterions.  $[\text{Ni}_2(o\text{-xyl-DMC}_2)](\text{ClO}_4)_4$  and  $[\text{Ni}(\text{DMC})](\text{ClO}_4)_2$  were synthesized by borohydride reduction of corresponding unsaturated complexes, as reported previously.<sup>15</sup> This synthetic route was shown to form primarily (>90%) the *meso* diastereomers. The new salts  $[\text{Ni}_2(\text{taec})](\text{BF}_4)_4$  and  $[\text{Ni}(2,3,2\text{-tet})](\text{BF}_4)_2$  were synthesized by procedures similar to those reported for the perchlorate analogues.<sup>18,24</sup>  $[\text{Ni}_2(\text{taec})](\text{BF}_4)_4$  shows good solubility in water and polar organic solvents, while the nickel perchlorate complexes are only slightly soluble in water, but readily soluble in polar solvents such as acetonitrile and propylene carbonate. The electronic spectral data for the complexes are summarized in Table 2. The spectra for the two binuclear nickel complexes are very similar and are consistent with a four coordinate planar geometry around nickel. Similar spectra have been reported previously for the perchlorate salts of these nickel complexes in water, and predominantly square planar geometries have been assigned.<sup>18,25</sup> In contrast, the spectrum of  $[\text{meso-Ni}(\text{DMC})](\text{ClO}_4)_2$  in propylene carbonate shows three bands of lower intensity that are characteristic of octahedral nickel, suggesting an interaction of solvent or counterions in the axial positions. Similar spectra have been observed previously for this diastereomer in water, and an octahedral structure with trans axial water molecules has been characterized by X-ray diffraction.<sup>15</sup>

Electrochemical data for the complexes, obtained in acetonitrile, are also included in Table 2. The cyclic voltammograms of  $[\text{Ni}(\text{DMC})](\text{ClO}_4)_2$  and  $[\text{Ni}_2(o\text{-xyl-DMC}_2)](\text{ClO}_4)_4$  are very similar; each shows a quasireversible one-electron reduction near  $-1.8$  V versus ferrocene. In contrast, the CV of  $[\text{Ni}_2(\text{taec})](\text{BF}_4)_4$  shows two closely spaced



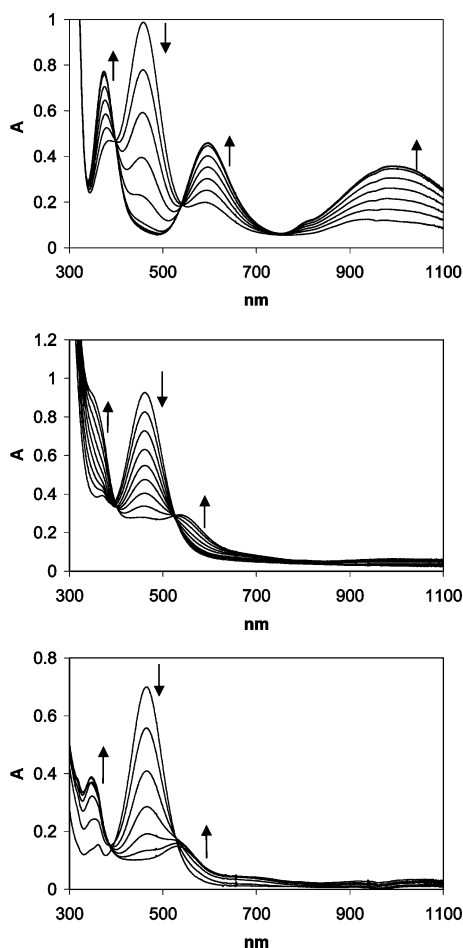
**Figure 1.** (a) Cyclic voltammogram of 8 mM  $[\text{Ni}_2(\text{taec})](\text{BF}_4)_4$  in 0.3 M  $\text{Et}_4\text{NBF}_4/\text{CH}_3\text{CN}$  at a scan rate of 50 mV/s. (b) Cyclic voltammogram of 2 mM  $[\text{Ni}_2(o\text{-xyl-DMC}_2)](\text{ClO}_4)_4$  in 0.3 M  $\text{Et}_4\text{NBF}_4/\text{CH}_3\text{CN}$  at a scan rate of 200 mV/s.

quasireversible reduction waves with  $E_{1/2} = -1.29$  V and  $E_{1/2} = -1.50$  V versus ferrocene, Figure 1. The data indicate that electronic communication between the two nickel sites is greater for  $[\text{Ni}_2(\text{taec})]^{4+}$  than for  $[\text{Ni}_2(o\text{-xyl-DMC}_2)]^{4+}$ . This could result from the presence of a bridging anion for  $[\text{Ni}_2(\text{taec})]^{4+}$ . However, the molar conductivity data for both dinuclear complexes in this solvent ( $\text{CH}_3\text{CN}$ ) are consistent with coordination of an anion (Table 2). The fact that communication between metal ions is observed in only one of these systems may be a result of the differences in ligand structure. A closer proximity of the two nickel atoms is expected to be imposed by the presence of two three-carbon atom bridges in the taec complex, compared to a single eight-carbon atom bridge in the *o*-xyl-DMC<sub>2</sub> complex. The more positive potentials observed for  $[\text{Ni}_2(\text{taec})]^{4+}$  compared to  $[\text{Ni}_2(o\text{-xyl-DMC}_2)]^{4+}$  are likely due to greater flexibility of the taec ligand compared to the macrocycle DMC. This flexibility allows for coordination sphere expansion and distortion from the planar structure, factors that would favor formation of nickel(I).

**Reactions with  $\text{HCO}_3^-$ .** The reactions of the nickel complexes with bicarbonate ion were monitored by UV-vis spectroscopy. Solutions of  $[\text{Ni}_2(\text{taec})](\text{BF}_4)_4$  in water at pH = 7.4 (0.5 M HEPES buffer) were titrated with several equivalents of sodium bicarbonate. At this pH, the concentration of  $\text{HCO}_3^-$  is 1 and 2 orders of magnitude greater than that of  $\text{H}_2\text{CO}_3/\text{CO}_2(\text{aq})$  and  $\text{CO}_3^{2-}$ , respectively. As shown in Figure 2a, three new absorption bands grew in with three isosbestic points observed. The visible spectrum of the final product is consistent with the formation of an octahedral nickel complex and is identical to that reported previously for  $[\text{Ni}_2(\mu\text{-CO}_3)(\text{taec})]^{2+}$ .<sup>10c</sup> The effective binding constant for the interaction with bicarbonate ion,  $K_B$ , defined in eq 3,

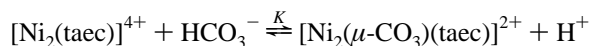
(24) Hinz, F. P.; Margerum, D. W. *Inorg. Chem.* **1974**, *13*, 2941.

(25) Kajiwara, T.; Yamaguchi, T.; Oshio, H.; Ito, T. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2130.



**Figure 2.** (a) Changes in the UV-vis spectrum of  $[\text{Ni}_2(\text{taec})](\text{BF}_4)_4$  with the addition of excess  $\text{Na}(\text{HCO}_3)$  in aqueous solution with HEPES buffer at  $\text{pH} = 7.4$ . (b) Changes in the UV-vis spectrum of  $[\text{Ni}_2(o\text{-xyl-DMC}_2)](\text{ClO}_4)_4$  with the addition of 2 equiv of  $\text{Et}_4\text{N}(\text{HCO}_3)$  in propylene carbonate at constant ionic strength of 0.5 M  $\text{Et}_4\text{NBF}_4$ . (c) Changes in the UV-vis spectrum of  $[\text{Ni}(\text{DMC})](\text{ClO}_4)_2$  with the addition of  $\text{Et}_4\text{N}(\text{HCO}_3)$  in propylene carbonate at constant ionic strength of 0.5 M  $\text{Et}_4\text{NBF}_4$ .

was calculated from the titration data as described in the Experimental Section, and  $\log K_B$  is found to be  $4.39 \pm 0.04$  at  $\text{pH} = 7.4$ .

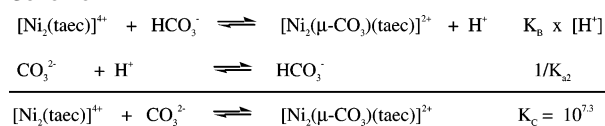


$$K_B = K/[\text{H}^+] = \frac{[\text{Ni}_2(\mu\text{-CO}_3)(\text{taec})]^{2+}}{[\text{Ni}_2(\text{taec})]^{4+}[\text{HCO}_3^-]} = 10^{4.4} \quad (3)$$

$K_B$  can also be related to the binding constant for carbonate ion ( $K_C$ ) in this system as shown in Scheme 1. The calculations give a binding constant for carbonate that is 3 orders of magnitude larger than the effective bicarbonate value at  $\text{pH} 7.4$ .

To our knowledge, only one quantitative determination of bicarbonate or carbonate binding affinity with a binuclear transition metal complex has been reported previously. In that system, bicarbonate replaced a  $\mu$ -acetate ligand in a  $\text{Cu}_2$ -18-ane $\text{N}_6$  macrocyclic complex, and the apparent association constant relative to acetate in unbuffered aqueous solution was reported to be  $160 \pm 70$ .<sup>12a</sup> Binding constants for other

#### Scheme 1

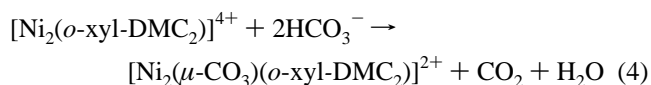


anions in aqueous solution, including acetate and halides, have been reported previously for binuclear copper complexes with the taec ligand, and binding constants on the order  $10^3$ – $10^5$  were determined in those cases.<sup>9b,e</sup>

A titration of  $[\text{Ni}(2,3,2\text{-tet})](\text{BF}_4)_2$  with sodium bicarbonate under the same conditions as described above showed no significant change in the electronic spectrum, indicating a very low affinity of this complex for bicarbonate ion in water. Comparison of the bicarbonate binding affinities for  $[\text{Ni}_2(\text{taec})]^{4+}$  and  $[\text{Ni}(2,3,2\text{-tet})]^{2+}$  confirms that in this case a significant advantage is gained by using a binuclear complex.

When a buffered aqueous solution ( $\text{pH} = 7.4$ ) of  $[\text{Ni}_2(o\text{-xyl-DMC}_2)](\text{ClO}_4)_4$  was titrated with sodium bicarbonate, no changes in absorption maxima were observed in the visible spectrum over a period of several days. Similarly, no reaction of this nickel complex was observed with sodium bicarbonate in an unbuffered aqueous solution or in a titration with sodium carbonate in an aqueous solution buffered at  $\text{pH} 9.2$ . The low affinity of this complex for bicarbonate ion in water is in marked contrast to the anion binding by  $[\text{Ni}_2(\text{taec})]^{4+}$ . Although the two binucleating ligand systems appear similar in that they both provide face-to-face square planar nickel sites, the greater flexibility of the taec ligand appears to be an important factor in determining the strength of the anion binding interaction.

Although no bicarbonate binding by  $[\text{Ni}_2(o\text{-xyl-DMC}_2)](\text{ClO}_4)_4$  was observed in aqueous solution, reactions were observed in nonprotic solvents or in mixed solvent systems where bicarbonate ion is less stabilized by hydrogen bonding. For example, when solutions of the nickel complex in propylene carbonate at constant ionic strength (0.5 M tetraethylammonium tetrafluoroborate) were titrated with 2 equiv of tetraethylammonium bicarbonate, a rapid reaction was observed. As shown in Figure 2b, absorption bands around 350 and 545 nm developed as bicarbonate associated with the nickel complex. The presence of an isosbestic point at 528 nm indicates that only one complex was formed. The product of this reaction was identified as the  $\mu\text{-CO}_3$  adduct (see below), and the reaction is therefore written as shown in eq 4:

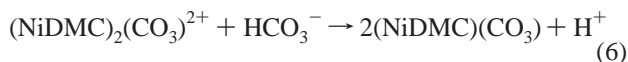


This reaction appears to be quantitative with the addition of 2 equiv of bicarbonate, and a binding constant for the reaction could not be determined.

Similar changes in the visible spectrum were observed when excess sodium carbonate was added to  $[\text{Ni}_2(o\text{-xyl-DMC}_2)](\text{ClO}_4)_4$  in 40% acetonitrile/60% aqueous 0.2 M TRIS buffer at  $\text{pH} 9.26$  (Figure 1s). If the aqueous values for the

$K_a$ 's of  $\text{H}_2\text{CO}_3/\text{CO}_2(\text{aq})$  and  $\text{HCO}_3^-$  are used as an approximation, the binding constant ( $\log K_C$ ) for carbonate ion in this system can be calculated, and a value of  $3.5 \pm 0.1$  is obtained. Because of the  $\text{p}K_a$  approximations, the value from this calculation for the mixed solvent system cannot be directly compared to  $K_C$  for  $[\text{Ni}_2(\mu\text{-CO}_3)\text{taec}]^{2+}$ , but it is apparent that the  $[\text{Ni}_2(o\text{-xyl-DMC}_2)]^{4+}$  shows a significantly lower affinity for carbonate binding. Nevertheless, the titration data do support the conclusion that both binuclear nickel complexes have a significant binding affinity for bicarbonate/carbonate ion under appropriate conditions.

The reactivity of the mononuclear complex  $[\text{Ni}(\text{DMC})](\text{ClO}_4)_2$  with bicarbonate ion was also studied. When the complex was titrated with sodium bicarbonate in aqueous solutions buffered at pH 7.4 or 9.2, no changes in the visible spectra were observed, although the complex reacted with sodium carbonate in unbuffered aqueous solution over a period of several hours. When  $[\text{Ni}(\text{DMC})](\text{ClO}_4)_2$  was titrated with tetraethylammonium bicarbonate in propylene carbonate/0.5 M  $\text{Et}_4\text{NBF}_4$ , a rapid reaction was observed and the spectral changes are shown in Figure 2c. Deviation from the isosbestic point at more than 1 equiv of tetraethylammonium bicarbonate indicates the formation of more than one complex. A Job's method plot<sup>26</sup> of the absorbance at 544 nm had peaks at 0.35 and 0.5, indicating the initial formation of a complex with a ratio of two metals to one carbonate, followed by the formation of a 1:1 complex, eqs 5 and 6.



The 2:1 complex containing a  $\mu$ -carbonate ligand has been isolated, and characterization data are described below.

**Isolation and Characterization of Nickel Carbonate Complexes.** The product of the bicarbonate titration with  $[\text{Ni}_2(\text{taec})](\text{BF}_4)_4$  has been identified as the previously characterized cation  $[\text{Ni}_2(\mu\text{-CO}_3)(\text{taec})]^{2+}$ <sup>10c</sup> on the basis of the visible spectral data as well as the ESI mass spectrum and elemental analyses. The X-ray diffraction study of this complex has established an  $\eta^2$ -coordination of the carbonate ion to each nickel site as shown in eq 1.

The bicarbonate or carbonate adduct of  $[\text{Ni}_2(o\text{-xyl-DMC}_2)](\text{ClO}_4)_4$  has not been characterized previously. The reaction of  $[\text{Ni}_2(o\text{-xyl-DMC}_2)](\text{ClO}_4)_4$  with  $\text{Cs}_2\text{CO}_3$  in acetonitrile/acetone, followed by vapor diffusion of diethyl ether, resulted in the formation of purple crystals. The UV-vis spectrum of the isolated crystals in propylene carbonate is identical to that of the titration product in the same solvent, suggesting that the isolated product is identical to that formed in the titration. The data are summarized in Table 2. The ESI mass spectrum on the isolated crystals has peaks centered at  $m/z = 835$  and  $368$  corresponding to  $\{[\text{Ni}_2(o\text{-xyl-DMC}_2)(\mu\text{-CO}_3)](\text{ClO}_4)_4\}^+$  and  $\{[\text{Ni}_2(o\text{-xyl-DMC}_2)(\mu\text{-CO}_3)]^{2+}\}$ . In the IR spec-

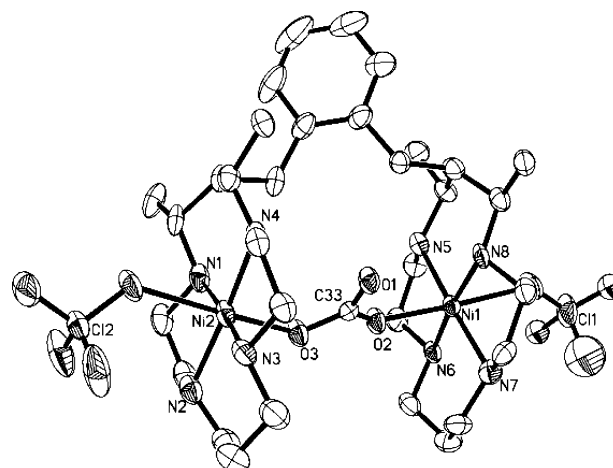


Figure 3. Perspective drawing for  $[\text{Ni}_2(o\text{-xyl-DMC}_2)(\mu\text{-CO}_3)](\text{ClO}_4)_2$ .

Table 3. Selected Bond Distances and Angles for  $[\text{Ni}_2(o\text{-xyl-DMC}_2)(\mu\text{-CO}_3)](\text{ClO}_4)_2$

distance, Å		angle, deg	
Ni(1)–O(2)	2.000(4)	O(2)–Ni(1)–N(8)	98.21(18)
Ni(1)–N(7)	2.070(5)	N(8)–Ni(1)–N(7)	86.2(2)
Ni(1)–N(6)	2.084(5)	N(8)–Ni(1)–N(5)	95.4(2)
Ni(2)–O(3)	1.998(4)	O(2)–Ni(1)–N(6)	88.38(18)
Ni(2)–N(2)	2.073(5)	N(7)–Ni(1)–N(6)	92.1(2)
Ni(2)–N(1)	2.075(6)	O(2)–Ni(1)–O(11)	173.85(19)
C(33)–O(1)	1.270(7)	N(7)–Ni(1)–O(11)	89.3(2)
C(33)–O(3)	1.307(7)	N(6)–Ni(1)–O(11)	87.96(18)
Cl(1)–O(11)	1.403(5)	O(1)–C(33)–O(3)	120.6(5)
Ni(1)–N(8)	2.068(5)	C(33)–O(2)–Ni(1)	134.1(4)
Ni(1)–N(5)	2.071(5)	O(2)–Ni(1)–N(7)	95.8(2)
Ni(1)–O(11)	2.315(5)	O(2)–Ni(1)–N(5)	88.06(19)
Ni(2)–N(3)	2.061(5)	N(7)–Ni(1)–N(5)	175.6(2)
Ni(2)–N(4)	2.075(5)	N(8)–Ni(1)–N(6)	173.31(18)
Ni(2)–O(5)	2.371(4)	N(5)–Ni(1)–N(6)	85.9(2)
C(33)–O(2)	1.286(7)	N(8)–Ni(1)–O(11)	85.56(18)
O(5)–Cl(2)	1.466(4)	N(5)–Ni(1)–O(11)	86.74(19)
Ni(1)···Ni(2)	6.053	O(1)–C(33)–O(2)	123.3(5)
		O(2)–C(33)–O(3)	116.1(5)
		C(33)–O(3)–Ni(2)	133.1(4)

trum, new absorptions were observed at 1712 (w), 1517 (m), 840 (w), and 803 (w)  $\text{cm}^{-1}$ . IR data for previously reported dinuclear complexes with bridging carbonate ligands<sup>10</sup> generally show new bands in the ranges 1500–1700 and 700–900  $\text{cm}^{-1}$ , but well-defined correlations of the frequencies with the many different bridging modes possible for this ligand were not apparent. An X-ray diffraction study was therefore carried out in order to obtain more detailed information about the structural features of the carbonate bridge.

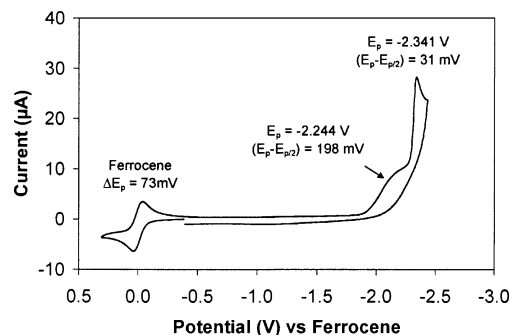
A perspective drawing of  $[\text{Ni}_2(o\text{-xyl-DMC}_2)(\mu\text{-CO}_3)](\text{ClO}_4)_2$  is shown in Figure 3, and selected bond distances and angles are given in Table 3. The complex crystallizes in the presence of one acetone and one diethyl ether molecule per unit cell that are not shown in the figure. The two cyclam rings are arranged in a face-to-face manner with carbonate acting as an  $\eta^1, \eta^1$ -bridging ligand. The two nickel ions within the molecule are crystallographically independent, but their geometries are both octahedral, with an oxygen from a perchlorate anion and the oxygen from the carbonate coordinated on either side of the plane of the nitrogens. Each nickel ion lies in the plane of the macrocyclic ligand, and

(26) Connors, K. *Binding Constants: The Measurement of Molecular Complex Stability*; John Wiley & Sons: New York, 1987; p 24.

the Ni–Ni separation is 6.053 Å. The Ni(1)–O(2) and Ni(2)–O(3) distances are equivalent within experimental error at 2.00 Å. The uncoordinated oxygen of the  $\mu$ -CO<sub>3</sub> ligand (O1) undergoes hydrogen bonding interactions with the secondary amine protons of the macrocycle [O(1)···N(4) = 2.906 Å and O(1)···N(8) = 2.924 Å]. The coordination mode of the carbonate ligand in this complex is very similar to that reported for [Zn<sub>2</sub>(*o*-xyl-DMC<sub>2</sub>)( $\mu$ -CO<sub>3</sub>)]<sup>2+</sup>,<sup>10b</sup> and similar  $\eta^1, \eta^1$ - $\mu$ -CO<sub>3</sub> complexes have been reported for many dinuclear copper systems.<sup>10e,g-i,m,o</sup> The relatively high rigidity of the ligand enforced by steric hindrance between the methyl groups on the cyclam and the xylylene group probably prevents the ring distortion necessary to accommodate bonding two of the carbonate oxygens at each metal as is seen in [Ni<sub>2</sub>( $\mu$ -CO<sub>3</sub>)(taec)](BF<sub>4</sub>)<sub>2</sub> and several other transition metal carbonate compounds.<sup>10d,f,j,l,p</sup> The difference in ligand flexibility is also reflected in the Ni···Ni distance which is >6 Å in this structure, but only 4.17 Å in [Ni<sub>2</sub>( $\mu$ -CO<sub>3</sub>)(taec)]<sup>2+</sup>.<sup>10c</sup>

Attempts to isolate a solid from the titration of [Ni(DMC)]-(ClO<sub>4</sub>)<sub>2</sub> with tetraethylammonium bicarbonate in propylene carbonate were unsuccessful. However, the dinuclear complex [(NiDMC)<sub>2</sub>( $\mu$ -CO<sub>3</sub>)](ClO<sub>4</sub>)<sub>2</sub> could be isolated as feathery purple crystals from a reaction of [Ni(DMC)](ClO<sub>4</sub>)<sub>2</sub> with 3 equiv of sodium carbonate in water. The ESI mass spectrum of this product has peaks centered at *m/z* = 733 and 316, corresponding to {[(NiDMC)<sub>2</sub>( $\mu$ -CO<sub>3</sub>)](ClO<sub>4</sub>)<sub>2</sub>}<sup>+</sup> and {[(NiDMC)<sub>2</sub>( $\mu$ -CO<sub>3</sub>)]<sup>2+</sup>. A solution of the complex in acetone has a molar conductance of 194 cm<sup>-1</sup> mol<sup>-1</sup> Ω<sup>-1</sup>, indicating that it is a 2:1 electrolyte. The electronic spectrum of the isolated crystals of [(NiDMC)<sub>2</sub>( $\mu$ -CO<sub>3</sub>)](ClO<sub>4</sub>)<sub>2</sub> in propylene carbonate shows three absorptions characteristic of octahedral nickel (see Table 2). The data are very similar to those observed for [Ni<sub>2</sub>(taec)( $\mu$ -CO<sub>3</sub>)]<sup>2+</sup>, suggesting that a similar  $\mu$ - $\eta^2, \eta^2$  binding mode of the carbonate ligand may be present. However, we were not able to obtain X-ray quality crystals of the product to confirm this tentative interpretation.

The new nickel carbonate complexes were also characterized by cyclic voltammetry in acetonitrile. As expected, cathodic shifts for the Ni(II)/Ni(I) couple were observed relative to the starting nickel complexes due to the increased charge density at the metal center provided by the coordinated anion. However, these cathodic shifts were unexpectedly large. For example, the cyclic voltammogram of [Ni<sub>2</sub>( $\mu$ -CO<sub>3</sub>)(taec)](BF<sub>4</sub>)<sub>2</sub> in acetonitrile, shown in Figure 4, shows two irreversible reduction waves with *E*<sub>p</sub> = -2.24 and -2.34 V, very near the solvent limit. Significant reduction waves were not observed in the cyclic voltammograms of [(NiDMC)<sub>2</sub>( $\mu$ -CO<sub>3</sub>)](ClO<sub>4</sub>)<sub>2</sub> and [Ni<sub>2</sub>( $\mu$ -CO<sub>3</sub>)(*o*-xyl-DMC<sub>2</sub>)](ClO<sub>4</sub>)<sub>2</sub> in acetonitrile, suggesting that reductions occurred at potentials beyond the solvent window. The very negative reduction potentials for these nickel complexes indicate that they are not suitable for electrochemical pumping applications, and the reduced nickel products were not further characterized.



**Figure 4.** Cyclic voltammogram of 6 mM [Ni<sub>2</sub>( $\mu$ -CO<sub>3</sub>)(taec)](BF<sub>4</sub>)<sub>2</sub> in 0.3 M Et<sub>4</sub>NBF<sub>4</sub>/CH<sub>3</sub>CN at a scan rate of 50 mV/s.

**Summary and Conclusions.** The binding affinities for bicarbonate ion and the reduction behaviors have been compared for two binuclear nickel complexes, and related mononuclear nickel derivatives have also been examined. Significant differences between the two binuclear complexes are attributed to distinct structural features of the binucleating ligands. Bicarbonate ion reacts with the dinuclear nickel(II) complex containing the taec ligand in buffered aqueous solution to form the  $\mu$ - $\eta^2, \eta^2$ -carbonate complex with a large effective binding constant for bicarbonate ion,  $\log K_B = 4.39$  at pH 7.4. In contrast, the dinuclear nickel(II) complex containing the *o*-xyl-DMC<sub>2</sub> ligand does not react with bicarbonate or carbonate ion in aqueous solution. In propylene carbonate, the reaction of [Ni<sub>2</sub>(*o*-xyl-DMC<sub>2</sub>)]<sup>4+</sup> with bicarbonate proceeds rapidly to form the  $\mu$ - $\eta^1, \eta^1$ -carbonate complex. The taec ligand is significantly more flexible than *o*-xyl-DMC<sub>2</sub>, and this factor is found to influence the binding mode and enhance the binding affinities for bicarbonate/carbonate ions. The greater flexibility of the taec ligand also appears to favor the formation of the nickel(I) complex, as the reduction potentials for [Ni<sub>2</sub>(taec)]<sup>4+</sup> in acetonitrile are significantly less cathodic than that for [Ni<sub>2</sub>(*o*-xyl-DMC<sub>2</sub>)]<sup>4+</sup>. A mononuclear analogue of [Ni<sub>2</sub>(taec)]<sup>4+</sup>, [Ni(2,3,2-tetraamine)]<sup>2+</sup> does not form a detectable mononuclear or dinuclear product with bicarbonate ion in aqueous solution, but [NiDMC]<sup>2+</sup> reacts slowly with carbonate ion in aqueous solution to form a 2:1 complex. Although the reduction potentials of the nickel complexes are too negative for electrochemical pumping applications in aqueous solutions, it is possible to achieve more favorable redox properties with related complexes containing other metal ions. The insights into the effect of ligand structure gained in the present work have been valuable in our continuing efforts. Recently, a binuclear copper complex with a related ligand system has been developed as an effective carrier in CO<sub>2</sub> pumping experiments in aqueous solution, and these results will be reported shortly.<sup>27</sup>

**Acknowledgment.** This work was supported by an NSF/EPA Partnership for Environmental Research Award, CTS-0124445. D.L.D. acknowledges the support of the U.S. Department of Energy, Office of Science, Chemical and

(27) Appel, A.; Newell, R.; DuBois, D. L.; Rakowski DuBois, M., submitted.



*Bicarbonate Binding by Dinuclear Ni(II) Complexes*

Biological Sciences Division, under DOE Contract DE-AC36-99GO10337. We thank S. Miller, Colorado State University, for assistance with the structural determination.

**Note Added after ASAP Publication:** The version of this paper published on the Web December 21, 2004, contained an error in Figure 2. The version published on the Web January 17, 2005, has been corrected.

**Supporting Information Available:** Tables of X-ray data collection and refinement results, complete numbering scheme, atomic coordinates, anisotropic displacement parameters, and complete bond distances and angles in CIF format; descriptions of binding constant determinations; titration data Figure 1s. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC049202C