

## Kinetics of the Formation and Dissociation of Nickel(II) Complexes of Diamino Diamides

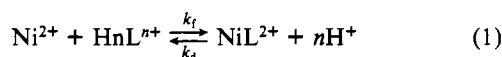
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The basicity constants of *N,N'*-bis( $\beta$ -carbamoylethyl)ethylenediamine (BCEN), *N,N'*-bis( $\beta$ -carbamoylethyl)trimethylenediamine (BCTN), *N,N'*-bis( $\beta$ -carbamoylethyl)-1,2-propylenediamine (BCMEN), and *N,N'*-bis( $\beta$ -carbamoylethyl)-2-hydroxytrimethylenediamine (BCHTN) as well as the stability constants of nickel(II) complexes of these diamino diamides have been determined potentiometrically in 0.10 M NaClO<sub>4</sub> at 25.0 °C. The formation and dissociation kinetics of these nickel(II) complexes have been studied by using the stopped-flow technique. The possible pathways for the reactions of nickel(II) with these ligands are discussed. It is proposed that these diamino diamides react with the nickel(II) ion by the stepwise formation of coordinate bonds, where the rate-determining step is the formation of the first nickel–nitrogen bond and the subsequent bonding is rapid. Similarly, the dissociation mechanism proposed involves the preequilibration of intermediately bonded species, with the second nickel–nitrogen bond breakage as the rate-determining step. The reactivity order for the dissociation reaction is [Ni(BCHTN)]<sup>2+</sup> > [Ni(BCTN)]<sup>2+</sup> > [Ni(BCEN)]<sup>2+</sup>, [Ni(BCMEN)]<sup>2+</sup>. The important factors determining the reactivity of these complexes are considered.

### Introduction

A previous paper has dealt with the thermodynamic behavior of nickel(II) complexes of four closely related diamino diamides.<sup>1</sup> In the present study we are concerned with the kinetics of the formation and dissociation of nickel(II) complexes of these four diamino diamides in aqueous solution:



where L represents the quadridentate diamino diamide *N,N'*-bis( $\beta$ -carbamoylethyl)ethylenediamine (BCEN), *N,N'*-bis( $\beta$ -carbamoylethyl)trimethylenediamine (BCTN), *N,N'*-bis( $\beta$ -carbamoylethyl)-1,2-propylenediamine (BCMEN), or *N,N'*-bis( $\beta$ -carbamoylethyl)-2-hydroxytrimethylenediamine (BCHTN). These four ligands are depicted in Chart I.

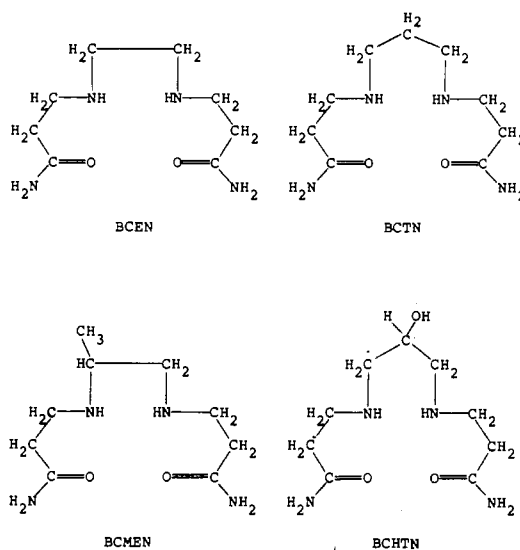
### Experimental Section

**Reagents.** The ligands BCEN, BCTN, BCMEN, and BCHTN were the same as those reported previously.<sup>1-4</sup> All other chemicals used were of GR grade from Merck or Fluka.

**Measurements.** For pH measurements a Radiometer PHM64 instrument equipped with a GK2401B combined electrode was used. The pH was standardized with NBS buffers. The hydrogen ion and hydroxide ion concentrations in 0.10 M NaClO<sub>4</sub> were calculated from  $-\log[\text{H}^+] = \text{pH} - 0.11$  and  $K_w = 10^{-13.78}$ .<sup>5</sup> Appropriate aliquots of standard solutions of ligand or ligand and metal were titrated with a standard sodium hydroxide solution. In all titrations the ionic strength was maintained relatively constant by using 0.10 M NaClO<sub>4</sub> as supporting electrolyte. The solutions were protected from air by a stream of humidified prepurified nitrogen and were maintained at 25.0 ± 0.1 °C during measurements. The methods of calculations are the same as reported previously.<sup>3</sup> The equilibrium constants were obtained by a linear least-squares fit of the data on the CDC Cyber-172 computer.

Standard solutions of ligands, borate–mannitol buffers, and sodium perchlorate were prepared by weight. Nickel(II) ion concentration was determined gravimetrically as the DMG complex. The kinetics of the nickel(II) complex formation reactions with BCEN, BCTN, BCMEN, and BCHTN were studied spectrophotometrically at 363, 372, 364, and 369 nm, respectively, with a Union Giken RA-401 stopped-flow spectrophotometer equipped with a Union RA-415 rapid-scan attachment. For the spectrophotometric experiments the pH was controlled with a borate–mannitol buffer<sup>6</sup> that was also incorporated into the reference solution. Recrystallized NaClO<sub>4</sub> was used to maintain constant ionic

Chart I



**Table I.** Protonation Constants of Diamino Diamides and Stability Constants of Their Nickel(II) Complexes at 25.0 ± 0.1 °C and  $\mu = 0.10$  M (NaClO<sub>4</sub>)

	BCEN	BCTN	BCMEN	BCHTN
$\log K_1^{\text{H}}$	8.78 ± 0.04	9.22 ± 0.06	8.84 ± 0.05	8.53 ± 0.06
$\log K_2^{\text{H}}$	5.82 ± 0.03	6.98 ± 0.04	5.54 ± 0.04	6.60 ± 0.06
$\log K_f$	7.90 ± 0.06	6.82 ± 0.08	7.95 ± 0.06	6.43 ± 0.07

strength at  $\mu = 0.10$  M in all solutions. Kinetic studies were carried out under pseudo-first-order conditions by using at least a 10-fold excess of ligand.

### Results

The protonation constants of these four ligands and the stability constants of their nickel(II) complexes at 25.0 °C and 0.10 M NaClO<sub>4</sub> obtained in this work are listed in Table I. The values of these constants are virtually the same as those at 0.10 M NaNO<sub>3</sub> reported previously.<sup>1</sup>

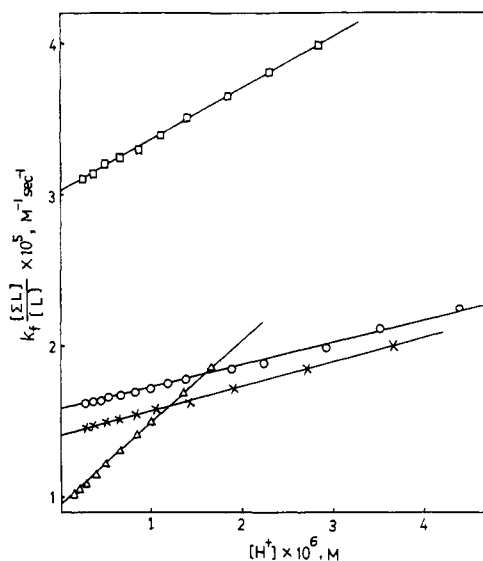
The reactions of nickel(II) and these diamino diamides were studied at 25 °C,  $\mu = 0.10$  M, and pH 5.4–6.7. Under these conditions, the complex formation reactions did not proceed to 100% completion. Kinetic studies were carried out under pseudo-first-order conditions by using at least a 10-fold excess of ligand. The observed pseudo-first-order rate constants are given in Tables II–V. Plots of  $k_{\text{obsd}}$  vs.  $[\Sigma\text{L}]$  give straight lines according to eq 2, where  $[\Sigma\text{L}]$  represents the total concentration of all species

$$k_{\text{obsd}} = k_f[\Sigma\text{L}] + k_d \quad (2)$$

- (1) Liu, S.-H.; Chung, C.-S. *Inorg. Chem.* **1984**, *23*, 1803–1806.
- (2) Wei, L.-W.; Chao, M.-S.; Chung, C.-S. *J. Chin. Chem. Soc. (Taipei)* **1979**, *26*, 145–151.
- (3) Chao, M.-S.; Chung, C.-S. *J. Chem. Soc., Dalton Trans.* **1981**, 683–686.
- (4) Liu, S.-H.; Chung, C.-S. *Polyhedron* **1984**, *3*, 559–566.
- (5) Liang, B.-F.; Margerum, D. W.; Chung, C.-S. *Inorg. Chem.* **1979**, *18*, 2001–2007.
- (6) Margerum, D. W.; Rorabacher, D. B. *Inorg. Chem.* **1963**, *2*, 667–677.

**Table II.** Experimental Observed Rate Constants for Reaction of the Nickel(II) Ion with BCEN at  $25.0 \pm 0.1$  °C and  $\mu = 0.10$  M ( $\text{NaClO}_4$ )

pH	$10^4[\text{Ni}^{2+}]$ , M	$10^3[\text{BCEN}]$ , M	$10k_{\text{obsd}}$ , $\text{s}^{-1}$	pH	$10^4[\text{Ni}^{2+}]$ , M	$10^3[\text{BCEN}]$ , M	$10k_{\text{obsd}}$ , $\text{s}^{-1}$	pH	$10^4[\text{Ni}^{2+}]$ , M	$10^3[\text{BCEN}]$ , M	$10k_{\text{obsd}}$ , $\text{s}^{-1}$
5.47	3.94	5.12	1.15	5.96	3.94	5.12	5.62	6.35	3.94	5.12	17.8
		6.30	1.41			6.30	6.92			6.30	22.0
		7.49	1.69			7.49	8.20			7.49	26.2
		8.67	1.93			8.67	9.49			8.67	30.2
		9.85	2.19			9.85	10.8			9.85	34.3
5.56	3.94	5.12	1.55	6.03	3.94	5.12	6.98	6.45	3.94	5.12	23.6
		6.30	1.89			6.30	8.57			6.30	28.9
		7.49	2.25			7.49	10.2			7.49	34.5
		8.67	2.60			8.67	11.8			8.67	39.9
		9.85	2.95			9.85	13.4			9.85	45.3
5.64	3.94	5.12	2.01	6.10	3.94	5.12	8.63	6.53	3.94	5.12	29.3
		6.30	2.46			6.30	10.6			6.30	35.6
		7.49	2.93			7.49	12.8			7.49	42.8
		8.67	3.38			8.67	14.6			8.67	49.6
		9.85	3.84			9.85	16.6			9.85	56.3
5.75	3.94	5.12	2.87	6.19	3.94	5.12	11.3	6.60	3.94	5.12	35.2
		6.30	3.53			6.30	13.9			6.30	43.3
		7.49	4.19			7.49	16.4			7.49	51.5
		8.67	4.85			8.67	19.1			8.67	59.6
		9.85	5.50			9.85	21.7			9.85	67.7
5.83	3.94	5.12	3.72	6.27	3.94	5.12	14.2			5.12	
		6.30	4.57			6.30	17.5			6.30	
		7.49	5.43			7.49	20.8			7.49	
		8.67	6.29			8.67	24.1			8.67	
		9.85	7.13			9.85	27.3			9.85	

**Figure 1.** Resolution of the formation rate constants for nickel(II) reacting with the unprotonated and monoprotonated diamino diamides at  $25.0 \pm 0.1$  °C and  $\mu = 0.10$  M ( $\text{NaClO}_4$ ). Plot of eq 5: O, BCEN;  $\Delta$ , BCTN;  $\times$ , BCMEN;  $\square$ , BCHTN.

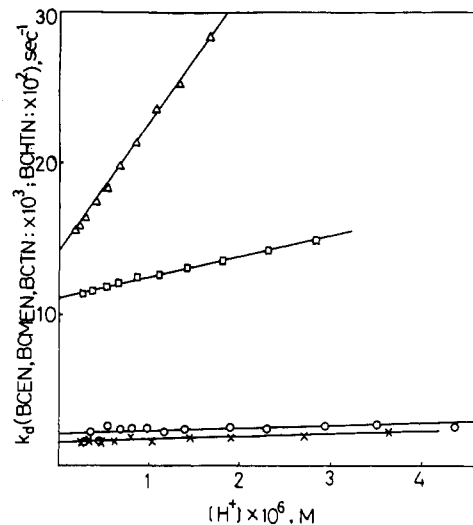
of uncomplexed ligand. The slopes give the values of the rate constants of formation, and the intercepts equal the rate constants of dissociation. These values are listed in Tables VI–IX. The equilibrium constants calculated from these rate constants by using eq 3 are in excellent agreement with those obtained by poten-

$$K = k_f/k_d \quad (3)$$

tiometric measurements under equilibrium conditions as shown in Tables VI–IX.

The kinetic data are found to conform to a reaction scheme in which it is assumed that only the unprotonated and monoprotonated ligand species react at a significant rate. Since proton transfer is very rapid compared to the other reaction steps, this scheme yields the expanded rate expression

$$d[\text{NiL}^{2+}]/dt = k_{\text{Ni}}^{\text{L}}[\text{Ni}^{2+}][\text{L}] + k_{\text{Ni}}^{\text{HL}}[\text{Ni}^{2+}][\text{HL}^+] - k_{\text{H}}^{\text{NiL}}[\text{NiL}^{2+}] - k_{\text{H}}^{\text{NiHL}}[\text{H}^+][\text{NiL}^{2+}] \quad (4)$$

**Figure 2.** Resolution of the dissociation rate constants involving proton-independent and proton-dependent terms. Plot of eq 6: O, BCEN;  $\Delta$ , BCTN;  $\times$ , BCMEN;  $\square$ , BCHTN.

Combining eq 2 and 4, it is possible to resolve the individual rate constants by plotting the expressions

$$k_f[\sum \text{L}]/[\text{L}] = k_{\text{Ni}}^{\text{L}} + k_{\text{Ni}}^{\text{HL}}K_1^{\text{H}}[\text{H}^+] \quad (5)$$

$$k_d = k_{\text{NiL}}^{\text{H}} + k_{\text{NiHL}}^{\text{H}}[\text{H}^+] \quad (6)$$

Plots of eq 5 and 6 are shown in Figures 1 and 2, respectively, and the resolved rate constants for each of these systems are listed in Table X.

#### Discussion

**Proposed Mechanisms for the Formation Reactions.** The large rate constant values obtained for the reactions of the aquonickel(II) ion with the unprotonated diamino diamides can be attributed to an internal conjugate-base mechanism in which hydrogen bond formation in the outer-sphere complex between an amino nitrogen atom and a proton of one of the coordinated water molecules increases the values of  $K_{\text{a}}$  and  $k^{\text{M-H}_2\text{O}}$ .<sup>7-9</sup> The appearance of the

(7) Taylor, R. W.; Stepien, H. K.; Rorabacher, D. B. *Inorg. Chem.* **1974**, *13*, 1282–1289.

**Table III.** Experimental Observed Rate Constants for Reaction of the Nickel(II) Ion with BCTN at  $25.0 \pm 0.1$  °C and  $\mu = 0.10$  M ( $\text{NaClO}_4$ )

pH	$10^4[\text{Ni}^{2+}]$ , M	$10^2[\text{BCTN}]$	$10^2k_{\text{obsd}}$ , $\text{s}^{-1}$	pH	$10^4[\text{Ni}^{2+}]$ , M	$10^2[\text{BCTN}]$	$10^2k_{\text{obsd}}$ , $\text{s}^{-1}$	pH	$10^4[\text{Ni}^{2+}]$ , M	$10^2[\text{BCTN}]$	$10^2k_{\text{obsd}}$ , $\text{s}^{-1}$
5.89	8.22	1.02	6.93	6.29	8.22	1.02	18.8	6.66	8.22	1.02	67.2
		1.25	7.85			1.25	22.5			1.25	82.1
		1.48	8.78			1.48	26.3			1.48	96.8
		1.71	9.71			1.71	30.1			1.71	112
		1.89	10.4			1.89	33.1			1.89	123
5.98	8.22	1.02	8.13	6.42	8.22	1.02	28.9	6.78	8.22	1.02	103
		1.25	9.39			1.25	35.0			1.25	125
		1.48	10.6			1.48	41.1			1.48	148
		1.71	11.9			1.71	47.2			1.71	171
		1.89	12.9			1.89	52.0			1.89	189
6.09	8.22	1.02	10.5	6.53	8.22	1.02	42.4	6.88	8.22	1.02	146
		1.25	12.3			1.25	51.5			1.25	178
		1.48	14.2			1.48	60.7			1.48	211
		1.71	16.0			1.71	69.9			1.71	243
		1.89	17.4			1.89	77.0			1.89	269
6.17	8.22	1.02	13.0			1.02				1.02	
		1.25	15.5			1.25				1.25	
		1.48	17.9			1.48				1.48	
		1.71	20.4			1.71				1.71	
		1.89	22.3			1.89				1.89	

**Table IV.** Experimental Observed Rate Constants for Reaction of the Nickel(II) Ion with BCMEN at  $25.0 \pm 0.1$  °C and  $\mu = 0.10$  M ( $\text{NaClO}_4$ )

pH	$10^4[\text{Ni}^{2+}]$ , M	$10^3[\text{BCMEN}]$ , M	$10k_{\text{obsd}}$ , $\text{s}^{-1}$	pH	$10^4[\text{Ni}^{2+}]$ , M	$10^3[\text{BCMEN}]$ , M	$10k_{\text{obsd}}$ , $\text{s}^{-1}$	pH	$10^4[\text{Ni}^{2+}]$ , M	$10^3[\text{BCMEN}]$ , M	$10k_{\text{obsd}}$ , $\text{s}^{-1}$
5.55	3.85	4.63	1.66	6.09	3.85	4.63	7.43	6.42	3.85	4.63	17.4
		5.78	2.06			5.78	9.27			5.78	21.7
		6.93	2.47			6.93	11.1			6.93	26.0
		8.46	3.01			8.46	13.6			8.46	31.8
		9.62	3.42			9.62	15.4			9.62	36.1
5.68	3.85	4.63	2.40	6.20	3.85	4.63	9.92	6.58	3.85	4.63	25.9
		5.78	2.99			5.78	12.4			5.78	32.3
		6.93	3.57			6.93	14.8			6.93	38.5
		8.46	4.37			8.46	18.1			8.46	47.3
		9.62	4.96			9.62	20.6			9.62	53.7
5.83	3.85	4.63	3.66	6.32	3.85	4.63	13.5	6.66	3.85	4.63	31.4
		5.78	4.56			5.78	16.9			5.78	39.3
		6.93	5.47			6.93	20.2			6.93	47.0
		8.46	6.67			8.46	24.6			8.46	57.4
		9.62	7.58			9.62	28.1			9.62	65.3
5.96	3.85	4.63	5.21			4.63				4.63	
		5.78	6.51			5.78				5.78	
		6.93	7.83			6.93				6.93	
		8.46	9.56			8.46				8.46	
		9.62	10.8			9.62				9.62	

**Table V.** Experimental Observed Rate Constants for Reaction of the Nickel(II) Ion with BCHTN at  $25.0 \pm 0.1$  °C and  $\mu = 0.10$  M ( $\text{NaClO}_4$ )

pH	$10^4[\text{Ni}^{2+}]$ , M	$10^3[\text{BCHTN}]$ , M	$10k_{\text{obsd}}$ , $\text{s}^{-1}$	pH	$10^4[\text{Ni}^{2+}]$ , M	$10^3[\text{BCHTN}]$ , M	$10k_{\text{obsd}}$ , $\text{s}^{-1}$	pH	$10^4[\text{Ni}^{2+}]$ , M	$10^3[\text{BCHTN}]$ , M	$10k_{\text{obsd}}$ , $\text{s}^{-1}$
5.66	3.85	4.82	3.14	6.06	3.85	4.82	9.17	6.40	3.85	4.82	30.3
		5.86	3.49			5.86	10.9			5.86	36.6
		7.02	3.89			7.02	12.8			7.02	43.6
		8.24	4.31			8.24	14.8			8.24	50.9
		9.83	4.85			9.83	17.4			9.83	60.6
5.75	3.85	4.82	3.76	6.18	3.85	4.82	13.8	6.54	3.85	4.82	49.6
		5.86	4.26			5.86	16.6			5.86	60.1
		7.02	4.83			7.02	19.6			7.02	71.8
		8.24	5.42			8.24	22.8			8.24	84.0
		9.83	6.19			9.83	26.9			9.83	100
5.85	3.85	4.82	4.82	6.29	3.85	4.82	20.5	6.67	3.85	4.82	77.5
		5.86	5.56			5.86	24.6			5.86	94
		7.02	6.40			7.02	29.2			7.02	112
		8.24	7.27			8.24	34.1			8.24	131
		9.83	8.41			9.83	40.5			9.83	157
5.96	3.85	4.82	6.64			4.82				4.82	
		5.86	7.79			5.86				5.86	
		7.02	9.07			7.02				7.02	
		8.24	10.4			8.24				8.24	
		9.83	12.2			9.83				9.83	

**Table VI.** Rate Constants for Formation ( $k_f$ ) and Dissociation ( $k_d$ ) of  $[\text{Ni}(\text{BCEN})]^{2+}$  and Equilibrium Constants for Complexation Reactions of the Nickel(II) Ion with BCEN at  $25.0 \pm 0.1$  °C and  $\mu = 0.10$  M ( $\text{NaClO}_4$ )

pH	$k_f$ , $\text{M}^{-1} \text{s}^{-1}$	$10^3 k_d$ , $\text{s}^{-1}$	equil const, $\text{M}^{-1}$	
			kinetic <sup>a</sup>	potentiometric
5.47	22.0	2.87	$7.66 \times 10^3$	$7.77 \times 10^3$
5.56	29.7	2.69	$1.10 \times 10^4$	$1.11 \times 10^4$
5.64	38.7	2.58	$1.50 \times 10^4$	$1.51 \times 10^4$
5.75	55.6	2.42	$2.30 \times 10^4$	$2.29 \times 10^4$
5.83	72.2	2.39	$3.02 \times 10^4$	$3.06 \times 10^4$
5.96	109	2.40	$4.54 \times 10^4$	$4.82 \times 10^4$
6.03	136	2.09	$6.51 \times 10^4$	$6.11 \times 10^4$
6.10	169	2.76	$6.12 \times 10^4$	$7.68 \times 10^4$
6.19	220	2.75	$8.00 \times 10^4$	$1.02 \times 10^5$
6.27	277	2.42	$1.14 \times 10^5$	$1.30 \times 10^5$
6.35	348	2.86	$1.22 \times 10^5$	$1.66 \times 10^5$
6.45	460	1.55	$2.97 \times 10^5$	$2.21 \times 10^5$
6.53	571	2.28	$2.50 \times 10^5$	$2.76 \times 10^5$
6.60	687	1.35	$5.09 \times 10^5$	$3.34 \times 10^5$

<sup>a</sup> Kinetically determined value =  $k_f/k_d$ .**Table VII.** Rate Constants for Formation ( $k_f$ ) and Dissociation ( $k_d$ ) of  $[\text{Ni}(\text{BCTN})]^{2+}$  and Equilibrium Constants for Complexation Reactions of the Nickel(II) Ion with BCTN at  $25.0 \pm 0.1$  °C and  $\mu = 0.10$  M ( $\text{NaClO}_4$ )

pH	$k_f$ , $\text{M}^{-1} \text{s}^{-1}$	$10^3 k_d$ , $\text{s}^{-1}$	equil const, $\text{M}^{-1}$	
			kinetic <sup>a</sup>	potentiometric
5.89	4.00	2.85	$1.40 \times 10^2$	$1.42 \times 10^2$
5.98	5.48	2.53	$2.17 \times 10^2$	$2.12 \times 10^2$
6.09	7.96	2.38	$3.34 \times 10^2$	$3.46 \times 10^2$
6.17	10.7	2.12	$5.05 \times 10^2$	$4.90 \times 10^2$
6.29	16.5	1.98	$8.33 \times 10^2$	$8.24 \times 10^2$
6.42	26.5	1.82	$1.46 \times 10^3$	$1.43 \times 10^3$
6.53	39.8	1.76	$2.26 \times 10^3$	$2.26 \times 10^3$
6.66	64.3	1.64	$3.92 \times 10^3$	$3.82 \times 10^3$
6.78	99.1	1.56	$6.35 \times 10^3$	$6.12 \times 10^3$
6.88	141	1.63	$8.65 \times 10^3$	$8.93 \times 10^3$

<sup>a</sup> Kinetically determined value =  $k_f/k_d$ .**Table VIII.** Rate Constants for Formation ( $k_f$ ) and Dissociation ( $k_d$ ) of  $[\text{Ni}(\text{BCMEN})]^{2+}$  and Equilibrium Constants for Complexation Reactions of the Nickel(II) Ion with BCMEN at  $25.0 \pm 0.1$  °C and  $\mu = 0.10$  M ( $\text{NaClO}_4$ )

pH	$k_f$ , $\text{M}^{-1} \text{s}^{-1}$	$10^3 k_d$ , $\text{s}^{-1}$	equil const, $\text{M}^{-1}$	
			kinetic <sup>a</sup>	potentiometric
5.55	35.3	2.26	$1.56 \times 10^4$	$1.57 \times 10^4$
5.68	51.4	2.00	$2.57 \times 10^4$	$2.48 \times 10^4$
5.83	78.6	2.05	$3.83 \times 10^4$	$4.07 \times 10^4$
5.96	112	1.98	$5.66 \times 10^4$	$6.12 \times 10^4$
6.09	160	1.51	$1.06 \times 10^5$	$9.02 \times 10^4$
6.20	214	2.06	$1.04 \times 10^5$	$1.23 \times 10^5$
6.32	291	1.58	$1.84 \times 10^5$	$1.72 \times 10^5$
6.42	375	1.73	$2.71 \times 10^5$	$2.24 \times 10^5$
6.58	558	1.77	$3.15 \times 10^5$	$3.39 \times 10^5$
6.66	679	1.45	$4.68 \times 10^5$	$4.14 \times 10^5$

<sup>a</sup> Kinetically determined value =  $k_f/k_d$ .

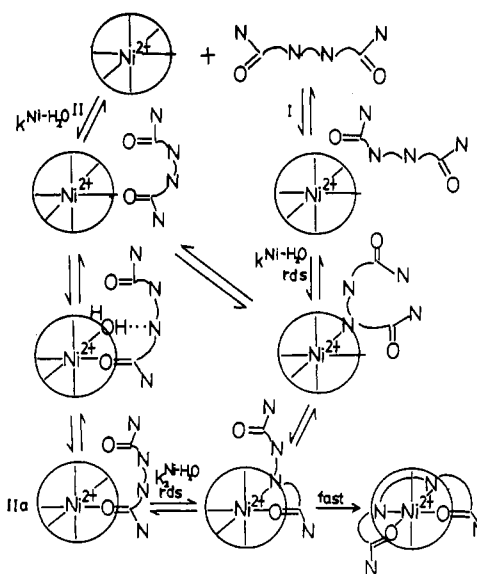
term involving monoprotonated diamino diamide in the experimental expression for the formation reaction and the fact that the rate constant values for reactions of the nickel(II) ion with unprotonated and monoprotonated BCHTN are larger than the corresponding rate constant values for the other diamino diamides indicate that the rate-determining step occurs prior to the formation of the second Ni-N bond. The stepwise reaction paths for the formation of nickel(II) complexes with unprotonated and monoprotonated BCEN, BCTN, and BCMEN are depicted

**Table IX.** Rate Constants for Formation ( $k_f$ ) and Dissociation ( $k_d$ ) of  $[\text{Ni}(\text{BCHTN})]^{2+}$  and Equilibrium Constants for Complexation Reactions of the Nickel(II) Ion with BCHTN at  $25.0 \pm 0.1$  °C and  $\mu = 0.10$  M ( $\text{NaClO}_4$ )

pH	$k_f$ , $\text{M}^{-1} \text{s}^{-1}$	$10^3 k_d$ , $\text{s}^{-1}$	equil const, $\text{M}^{-1}$	
			kinetic <sup>a</sup>	potentiometric
5.66	34.2	1.49	$2.30 \times 10^2$	$2.31 \times 10^2$
5.75	48.5	1.42	$3.42 \times 10^2$	$3.43 \times 10^2$
5.85	71.7	1.36	$5.27 \times 10^2$	$5.29 \times 10^2$
5.96	111	1.30	$8.54 \times 10^2$	$8.49 \times 10^2$
6.06	164	1.27	$1.29 \times 10^3$	$1.29 \times 10^3$
6.18	261	1.26	$2.07 \times 10^3$	$2.12 \times 10^3$
6.29	399	1.21	$3.30 \times 10^3$	$3.31 \times 10^3$
6.40	604	1.18	$5.12 \times 10^3$	$5.08 \times 10^3$
6.54	1006	1.16	$8.67 \times 10^3$	$8.60 \times 10^3$
6.67	1582	1.14	$1.39 \times 10^4$	$1.37 \times 10^4$

<sup>a</sup> Kinetically determined value =  $k_f/k_d$ .**Table X.** Resolved Rate Constant Values for Formation and Dissociation of Nickel(II) Complexes of Diamino Diamides in Aqueous Solution at  $25.0 \pm 0.1$  °C and  $\mu = 0.10$  M ( $\text{NaClO}_4$ )

ligand	$k_{\text{Ni}^{\text{L}}}$ , $\text{M}^{-1} \text{s}^{-1}$	$k_{\text{Ni}^{\text{HL}}}$ , $\text{M}^{-1} \text{s}^{-1}$	$k^{\text{NiL}}$ , $\text{s}^{-1}$	$k_{\text{H}^{\text{NiL}}}$ , $\text{M}^{-1} \text{s}^{-1}$
BCEN	$1.58 \times 10^5$	25.1	$2.09 \times 10^{-3}$	$1.73 \times 10^2$
BCTN	$9.55 \times 10^4$	33.1	$1.41 \times 10^{-2}$	$8.51 \times 10^3$
BCMEN	$1.41 \times 10^5$	23.4	$1.58 \times 10^{-3}$	$1.86 \times 10^2$
BCHTN	$3.02 \times 10^5$	102	$1.12 \times 10^{-1}$	$1.35 \times 10^4$

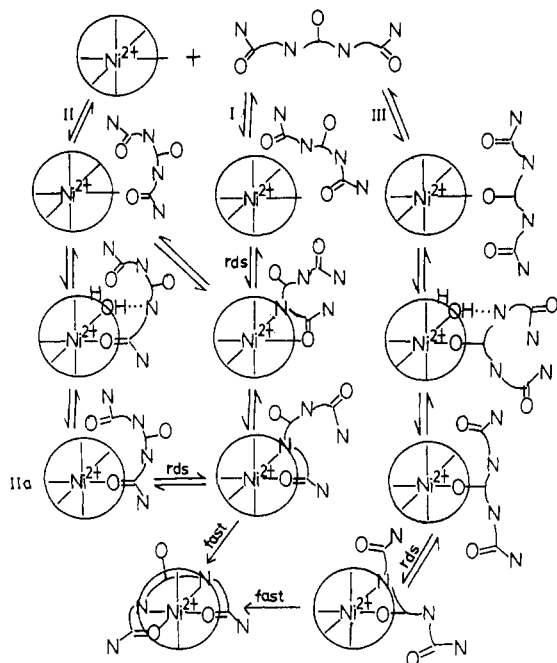
**Figure 3.** Possible pathways for the reaction of nickel(II) with BCEN, BCTN, or BCMEN. The circle represents the division between inner-sphere coordination and outer-sphere association. The position of the rate-determining step (rds) depends on which end of the ligand coordinates first.

schematically in Figure 3. For reactions of the aquonickel(II) ion with unprotonated and monoprotonated BCHTN, a third pathway, initial bonding to an alcoholic oxygen donor atom, must be taken into consideration. These three possible pathways are shown in Figure 4.

**Reaction Path I. Initial Bonding to an Amino Nitrogen Donor Atom.** For the reaction of nickel(II) with an unprotonated ligand, one of the two amino nitrogen donor atoms is presumed to hydrogen bond to a coordinated water molecule to give a strong outer-sphere complex and to labilize subsequent water exchange so that the other amino nitrogen donor atom can form an inner-sphere complex.<sup>10</sup> On the basis of proximity effect, the reaction rate via this path for the ligand containing the ethyl-

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**Figure 4.** Possible pathways for the reaction of nickel(II) with BHTN. The circle represents the division between inner-sphere coordination and outer-sphere association. The position of the rate-determining step (rds) depends on which end of the ligand coordinates first.

enediamine moiety is expected to be faster than the rate via this path for the ligand containing the trimethylenediamine moiety. The observed sequence for  $k_{\text{Ni}}^{\text{HL}}$ , BCHTN > BCEN > BCMEN > BCTN, indicates this mechanism could be a significant reaction path for the reaction of nickel(II) with BCEN, BCMEN, and BCTN but not for the reaction of nickel(II) with BHTN.

**Reaction Path II. Initial Bonding to an Amide Oxygen Donor Atom.** Outer-sphere association of a coordinated water molecule with the amino group speeds the replacement of the adjacent water by the amide group.<sup>11</sup> Nickel(II) bonding to an amide oxygen facilitates subsequent bonding to an amino nitrogen donor atom. For the reaction of nickel(II) with HL<sup>+</sup>, the rate of formation can be represented by

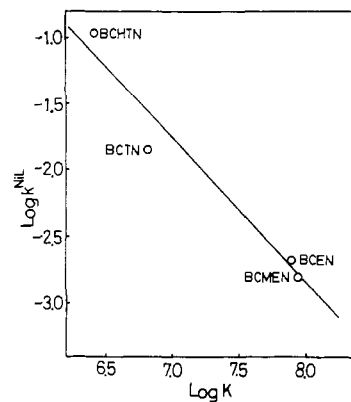
$$\frac{d[\text{NiL}^{2+}]}{dt} = \frac{K_{\text{os}} k^{\text{Ni-H}_2\text{O}} k_2^{\text{Ni-H}_2\text{O}}}{k^{\text{Ni-HL}} + k_2^{\text{Ni-H}_2\text{O}}} [\text{Ni}^{2+}] [\text{HL}^+] \quad (7)$$

where  $k^{\text{Ni-HL}}$  represents the rate constant for nickel–amide oxygen bond rupture (see Figure 3) and  $k_2^{\text{Ni-H}_2\text{O}}$  represents the rate constant for rupture of a nickel–water bond from intermediate IIa. If  $k^{\text{Ni-HL}}$  were smaller than  $k_2^{\text{Ni-H}_2\text{O}}$ , eq 7 would reduce to eq 8. However, the rate constants listed in Table X indicate that

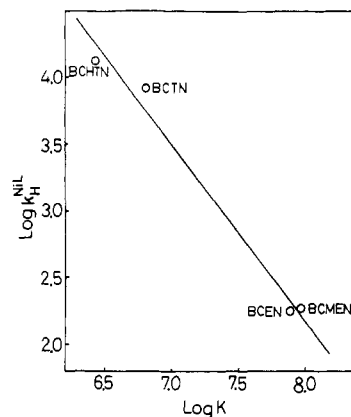
$$d[\text{NiL}]/dt = K_{\text{os}} k^{\text{Ni-H}_2\text{O}} [\text{Ni}^{2+}] [\text{HL}^+] \quad (8)$$

HL<sup>+</sup> reacts much more slowly than the rate predicted by eq 8. Therefore,  $k^{\text{Ni-HL}}$  must be greater than  $k_2^{\text{Ni-H}_2\text{O}}$  and the first chelate ring closure is the rate-determining step in this reaction path.

**Reaction Path III. Initial Bonding to an Alcoholic Oxygen Donor Atom.** For the same reason pointed out previously, the rate-determining step in this reaction path is the second bond formation, the coordination of the amine end, as shown in Figure 4. The most striking feature of this study is the relatively large rate constants for the reactions of nickel(II) with unprotonated and monoprotonated BHTN. The protonation constant for BHTN is much smaller than that for BCTN. The strength of the hydrogen bond required for the internal conjugate-base effect parallels the basicity of the ligand. If reaction path I or II predominated for the reaction of nickel(II) with unprotonated and monoprotonated BHTN, the rate constants for BHTN and



**Figure 5.** Plot of  $\log k^{\text{NiL}}$  against  $\log K$  at 25.0 °C and  $\mu = 0.10 \text{ M}$  ( $\text{NaClO}_4$ ).



**Figure 6.** Plot of  $\log k_{\text{H}}^{\text{NiL}}$  against  $\log K$  at 25.0 °C and  $\mu = 0.10 \text{ M}$  ( $\text{NaClO}_4$ ).

HBCHTN<sup>+</sup> would be smaller than those for BCTN and HBCTN<sup>+</sup>, respectively. However, the results listed in Table X clearly indicate that the rate constants for unprotonated and monoprotonated BHTN are larger than those for unprotonated and monoprotonated BCTN. Therefore, the most significant reaction path for the reaction of nickel(II) with BHTN or HBCHTN<sup>+</sup> must be path III.

**Kinetics of the Dissociation Reactions.** The increase of  $k_d$  values with decreasing pH indicates the active role of the proton in assisting the dissociation of the complex. Under the conditions used in this work, both  $k^{\text{NiL}}$  and  $k_{\text{H}}^{\text{NiL}}[\text{H}^+]$  contribute significantly to the observed  $k_d$  value. The proposed mechanism for the dissociation reaction involves the preequilibration of intermediately bonded species, with the second nickel–nitrogen bond breakage as the rate-determining step.

The relative rates of these reactions are in the order  $[\text{Ni}(\text{BCHTN})]^{2+} > [\text{Ni}(\text{BCTN})]^{2+} > [\text{Ni}(\text{BCEN})]^{2+}$ ,  $[\text{Ni}(\text{BCMEN})]^{2+}$ . This is related to two factors: (1) the girdle strains among the three linked consecutive chelate rings<sup>1,12</sup> and (2) the basicity of the ligand. Although the product of the protonation constants  $K_1^{\text{H}} K_2^{\text{H}}$  for BCEN or BCMEN is much smaller than that for BCTN, the dissociation constant for  $[\text{Ni}(\text{BCEN})]^{2+}$  or  $[\text{Ni}(\text{BCMEN})]^{2+}$  is much smaller than that for  $[\text{Ni}(\text{BCTN})]^{2+}$  or  $[\text{Ni}(\text{BCHTN})]^{2+}$ . These results indicate the girdle strains among linked consecutive chelate rings strongly favor the dissociation of nickel(II) complexes containing three linked six-membered chelate rings, and these strains are relieved by the presence of a middle five-membered ring in the BCEN or BCMEN complex.<sup>13–15</sup> The very large dissociative rate constant for [Ni-

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(BCHTN)]<sup>2+</sup> is attributed to both the large steric strains among the three linked chelate rings and the low basicity of the ligand.

It is significant to note that there is a substantial difference in the relative rates of these reactions and that the order of labilities parallels the order of aqueous solution instabilities of these complexes. These data prompt further investigations to see whether

there is a simple quantitative relation between  $\log k^{\text{NiL}}$  or  $\log k_{\text{H}}^{\text{NiL}}$  and  $\log K$ . Figures 5 and 6 show such plots.

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**Registry No.** BCEN, 3216-87-3; BCTN, 34740-97-1; BCMEN, 89709-74-0; BCHTN, 89709-75-1.

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## Cobalt(I) Porphyrin Catalysis of Hydrogen Production from Water

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Cobalt complexes of three water-soluble porphyrins, *meso*-tetrakis(*N,N,N*-trimethylanilinium-4-yl)porphine chloride (CoTMAP), *meso*-tetrapyrro-4-ylporphine (CoTPyP), and *meso*-tetrakis(*N*-methylpyridinium-4-yl)porphine chloride (CoTMPyP), have been examined as catalysts of H<sub>2</sub>O reduction to H<sub>2</sub>. They have been shown to catalyze H<sub>2</sub> production via controlled-potential electrolysis (-0.95 V vs. SCE at Hg-pool electrode; 0.1 M trifluoroacetic acid) at rates approximately 10-fold greater than background and with nearly 100% current efficiency. Reversible cyclic voltammograms were observed in dry Me<sub>2</sub>SO, with Co(III)/Co(II) and Co(II)/Co(I) potentials near their expected values. Addition of water (0.5-2%) increased the cathodic peak and decreased the anodic peak at the Co(II)/Co(I) couple, consistent with electrocatalytic H<sub>2</sub>O reduction. In aqueous buffers, catalytic currents were observed for CoTMPyP, which increased with decreasing pH, but at a rate less than expected, due to porphyrin adsorption. Adsorption was more pronounced for CoTMAP, which showed no catalytic current except at very low pH. The rate of CoTMAP reaction with H<sub>2</sub>O, however, is extremely fast as shown by spectrophotometry in dry acetonitrile; a lower limit for the Co(I)-H<sub>2</sub>O reaction rate constant was estimated to be approximately 10<sup>4</sup> M<sup>-1</sup> s<sup>-1</sup>. Co(I) reactivity and cobalt hydride stability are discussed in comparison with the reactivity and stability of related compounds.

### Introduction

All schemes for storing energy by the electrochemical or photochemical reduction of water to hydrogen require catalysis of H<sub>2</sub> evolution, since the activation energy for splitting the OH bond and bringing nascent H atoms together is otherwise prohibitive. Platinum metal is an excellent catalyst for this purpose and is very widely used in studies of water splitting. Platinum is costly, however, and also can easily be poisoned by contaminants in the water, such as sulfur-containing molecules. Aside from these practical considerations, it is of interest to develop molecular catalysts for H<sub>2</sub> evolution in order to bring into clearer focus the chemical requirements for this aspect of water splitting. Cobalt(I) complexes are attractive candidates for such catalysts, since Co(I), being a powerful nucleophile, is readily protonated and the resulting cobalt hydride decomposes by proton attack or disproportionation to form H<sub>2</sub> (see Figure 1). This chemistry has been characterized for Co(I) complexes of cyanide,<sup>1-4</sup> vitamin B<sub>12</sub>,<sup>5-10</sup> dimethylglyoxime,<sup>11</sup> bipyridyl,<sup>12,13</sup> and various macrocyclic ligands.<sup>14</sup>

In this study, we examined the formation and decomposition of Co(I) porphyrins with a view toward developing an efficient electrocatalyst for H<sub>2</sub> evolution. We have been drawn to metalloporphyrins as agents for electrode modification because of their ease of deposition<sup>15-19</sup> via peripheral substituents and their favorable electron-transfer characteristics. In addition, porphyrins absorb light strongly in the visible region and offer attractive possibilities for photochemistry. In the case of Co(II) porphyrins, excitation into the allowed  $\pi-\pi^*$  transitions may be followed by electron transfer to the d<sub>z<sup>2</sup></sub> orbital, leading to transient formation of a Co(I) porphyrin radical cation. Protonation of this species might provide a pathway for photochemical H<sub>2</sub> production. Indeed Tait et al.<sup>20</sup> have interpreted the prompt photoinduced difference spectrum of cobalt(II) octaethylporphyrin as belonging to a charge-transfer state, which subsequently relaxes with a lifetime of 10-20 ps. This state is clearly too short-lived to be of any use in photochemistry, but it is conceivable that the lifetime might be increased through modifications of the porphyrin.

### Experimental Section

Free-base porphyrins *meso*-tetrakis(*N,N,N*-trimethylanilinium-4-yl)porphine chloride, *meso*-tetrapyrro-4-ylporphine, and *meso*-tetrakis(*N*-methylpyridinium-4-yl)porphine chloride were obtained from Mid-Century Chemicals (Posen, IL). These were subsequently metalated to form the corresponding Co(II) derivatives, CoTMAP, CoTPyP, and CoTMPyP, respectively, according to published protocols<sup>21-23</sup> with several

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