broken by nitrogen; otherwise, decomposition of $Mo_2(O_2CCH_3)_4$ will occur, giving a brown solution. To the suspension was added CF_3SO_3H (0.17 mL, 1.92 mmol). An intensely purple solution formed immediately (use of more than 2 equiv of CF_3SO_3H still leads to isolation of **1** with the possibility of solvent decomposition). Removal of solvent left a dark purple solid, which was dissolved in the minimum amount of acetonitrile (~2 mL), and the mixture was filtered. Addition of toluene (5 mL) to the resulting solution led to formation of a dark purple precipitate after 1 h. Filtration afforded 0.5 g of **1**. Anal. Calcd for $[Mo_2(O_2CCH_3)_2(CH_3CN)_4](CF_3SO_3)_2$: C, 21.77; H, 2.35; N, 7.25; S, 8.30; F, 14.76; Mo, 24.84; O, 20.72. Found: C, 21.83; H, 2.38; N, 7.56; S, 8.28; F, 15.10; Mo, 24.00; O (by difference), 20.85.

Bis(acetato)pentakis(acetonitrile)dimolybdenum(II) Bis(trifluorohydroxyborate) (2). $Mo_2(O_2CCH_3)_4$ (0.71 g, 1.66 mmol) was suspended in acetonitrile as above. To this was added $HBF_4{\cdot}Et_2O$ (0.8 mL, ~6 mmol). An intensely magenta solution formed immediately (excess acid is needed to dissolve most of the $Mo_2(O_2CCH_3)_4$). Removal of solvent left a magenta solid, which was dissolved in acetonitrile (4 mL), and the mixture was filtered. A small amount of yellow needle crystals of unreacted $Mo_2(O_2CCH_3)_4$ remained. Addition of Et_2O (5 mL) to the solution led to rapid formation of a magenta precipitate. Filtration afforded 0.9 g of **2**. The compound was recrystallized from 1:1 toluene–acetonitrile. Anal. Calcd for $[Mo_2(O_2CCH_3)_2(CH_3CN)_5](BF_3OH)_2$: C, 24.55; H, 3.38; N, 10.23; F, 16.65; Mo, 28.02. Found: C, 23.79; H, 3.32; N, 10.02; F, 17.03; Mo, 27.36.

Anion Exchange. $(n\text{-Bu})_4NBF_4$ (1 g, 3.0 mmol) was dissolved in acetonitrile (5 mL). Complex **2** (0.3 g, 0.44 mmol) was added to the solution. Toluene (5 mL) was then added, leading to formation of a magenta precipitate. This procedure was repeated twice. IR spectroscopy showed a greatly diminished OH stretch and the other bands unchanged. Anal. Calcd for $[Mo_2(O_2CCH_3)_2(CH_3CN)_5](BF_4)_2$: C, 24.41; H, 3.07; N, 10.17; F, 22.06; Mo, 27.86. Found: C, 24.49; H, 3.29; N, 11.77; F, 19.16; Mo, 28.13. Thus, this exchange method is reasonably effective and helps to confirm the anion formulation in **2** as BF_3OH^-.

Molybdenum Trifluoromethanesulfonate Complex. To $Mo_2(O_2CCH_3)_4$ (0.2 g, 0.47 mmol) was added CF_3SO_3H (10 mL). After the mixture was heated at 100 °C with stirring for 1 h, all the solid dissolved. The acid was removed under vacuum, leaving a red solid which presumably corresponds to the $Mo_2(O_3SCF_3)_4(CF_3SO_3H)$ complex described by Abbott et al.[27] Further pumping with heating at 150 °C led to formation of a tan solid.[38] These intermediates were not isolated or characterized. Addition of acetonitrile (10 mL) led to formation of a bright blue precipitate. Elemental analysis of this compound was not satisfactory, although it appears to be a $CF_3SO_3^-$ salt of a molybdenum(II) acetonitrile complex. IR spectroscopy indicated strong CN and OH stretches as well as bands corresponding to uncoordinated $CF_3SO_3^-$ and residual acetate bands at 1615 cm^{-1} ($\nu_{asy}(CO_2)$) and 675 cm^{-1} ($\delta(CO_2)$). A band at 415 cm^{-1} may be $\nu(Mo_2)$. Slow evaporation of the filtrate obtained above resulted in formation of purple crystals of what is most likely **1**. The IR spectrum corresponded to **1** as did the elemental analysis, although the precipitate may have been contaminated with species such as $[Mo_2(O_2CCH_3)(CH_3CN)_x](CF_3SO_3)_3$, giving higher % S, % F, and % O. Anal. Calcd for $[Mo_2(O_2CCH_3)_2(CH_3CN)_4](CF_3SO_3)_2$: See above. Found: C, 21.33; H, 2.10; N, 6.23; S, 9.48; F, 15.48; Mo, 21.47; O (by difference), 23.91.

Experimental Methods. Elmental analyses were performed by the microanalytical laboratory of the University of Illinois. EPR spectra were recorded on a Varian E-9 instrument. $^{13}C\{^1H\}$ Fourier-transforming NMR spectra were recorded on a Varian Associates XL-100 FT spectrometer operating at 25.2 MHz. The ^{13}C chemical shifts were measured with respect to the nitrile carbon of CD_3CN (118.2 ppm relative to Me_4Si). ^1H NMR spectra were recorded on a Varian HR-220 NMR spectrometer equipped with a Nicolet Instrument Corp. TT-220 Fourier-transform accessory. Precision-grade tubes were used for the 220-MHz spectra so as to reduce spinning sidebands. All ^1H chemical shifts were measured relative to Me_4Si. Infrared spectra were recorded on a Perkin-Elmer 599B instrument. UV-vis spectra were recorded on a Cary 14 spectrometer with matched quartz 1.0-cm cells.

Registry No. 1, 89746-57-6; 2, 89746-59-8; $Mo_2(O_2CCH_3)_4$, 14221-06-8; $Rh_2(butyr)_4$, 56281-34-6; $Rh_2(butyr)_2^{2+}$, 89746-60-1; $[Mo_2(O_2CCH_3)_2(CH_3CN)_5](BF_4)_2$, 89746-61-2; $Rh_2(O_2CCH_2CH_2CH_3)_2S$, 89746-62-3; Mo, 7439-98-7; Rh, 7440-16-6.

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[38] Subsequent to the submission of this paper, a report appeared (Mayer, J. M.; Abbott, E. H. *Inorg. Chem.* **1983**, *22*, 2774) in which this tan solid was reformulated as $[Mo_2(H_2O)_4(CF_3SO_3)_2](CF_3SO_3)_2$ synthesized under slightly different conditions. Addition of acetonitrile to this species led to isolation of a blue complex formulated as $[Mo_2(CH_3CN)_8](CF_3SO_3)_4$. The blue complex described in this work is most likely impure $[Mo_2(CH_3CN)_8](CF_3SO_3)_2$.

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Nickel(II) Complexes of Diamino Diamides in Aqueous Solution

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Received June 16, 1983

The basicity constants of *N,N'*-bis(β-carbamoylethyl)ethylenediamine, *N,N'*-bis(β-carbamoylethyl)trimethylenediamine, *N,N'*-bis(β-carbamoylethyl)-1,2-propylenediamine, and *N,N'*-bis(β-carbamoylethyl)-2-hydroxytrimethylenediamine were determined potentiometrically in 0.10 M $NaNO_3$ at 25.0 °C. The formation of nickel(II) complexes of these ligands and the Ni–O to Ni–N bond rearrangements at the two amide sites of these complexes were investigated quantitatively by potentiometric and spectrophotometric techniques under the same conditions. Electronic spectra of the nickel(II) complexes of these ligands and their deprotonated species formed in aqueous solution were measured and discussed.

Introduction

In previous studies of copper(II) complexes of *N,N'*-bis(β-carbamoylethyl)ethylenediamine, BCEN, and *N,N'*-bis(β-carbamolyethyl)trimethylenediamine, BCTN,[1,2] it was noted that copper(II), after complexation with each of these ligands, can induce ionization of the amide protons, and the Cu–O to Cu–N bond rearrangements at the two amide sites occur with an increase in pH. We now report an extension of the previous investigations to include a study of the interactions of four closely related diamino diamides, depicted in Chart I, with nickel(II). Like copper(II), nickel(II) can also induce ionization of the amide protons after combination with each of these ligands. The detailed stepwise reactions which follow the formation of the nickel(II) complex with each of these ligands and the Ni–O to Ni–N bond rearrangements at the two amide sites have now been studied by potentiometric and

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[1] Wei, L.-W.; Chao, M.-S.; Chung, C.-S. *J. Chin. Chem. Soc.* (*Taipei*) **1979**, *26*, 145.

[2] Chao, M.-S.; Chung, C.-S. *J. Chem. Soc., Dalton Trans.* **1981**, 683.

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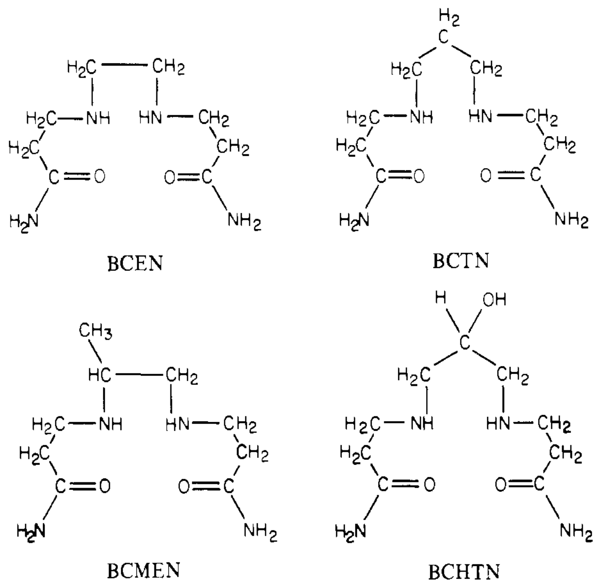
Chart I


BCEN

BCTN

BCMEN

BCHTN

spectrophotometric techniques.

Experimental Section

Reagents. The ligands BCEN and BCTN were the same as those reported previously.[1,2] The ligand BCHTN was prepared from 2-hydroxytrimethylenediamine (18.0 g; 0.2 mol) and acrylamide (28.4 g; 0.4 mol) in acetonitrile (100 mL) by heating the mixture under reflux for 2 h. The solution was cooled and the product filtered off, washed with cold chloroform, recrystallized from chloroform, and dried in air; mp 141–142.5 °C. Anal. Calcd for $C_9H_{20}N_4O_3$: C, 46.54; H, 8.68; N, 24.12. Found: C, 45.95; H, 8.80; N, 23.72. The compound was 99.9% pure as determined by titration with standard base. The ligand BCMEN was prepared from 1,2-propylenediamine (17.1 mL; 0.2 mol) and acrylamide (28.4 g; 0.4 mol) in acetonitrile (100 mL) by heating the mixture under reflux for 2 h. The solution was cooled and the product filtered off, washed with cold *N*,*N*-dimethylformamide, recrystallized from *N*,*N*-dimethylformamide, and dried in air; mp 124–126 °C. Anal. Calcd for $C_9H_{20}N_4O_2$: C, 49.98; H, 9.32; N, 25.90. Found: C, 50.00; H, 9.20; N, 25.55. The compound was 99.9% pure as determined by titration with standard base. All other chemicals used were of GR grade from Merck or Fluka. Nickel was determined gravimetrically as the DMG complex.

Measurements. For pH measurements a Radiometer PHM 64 equipped with a GK 2401B combined electrode was used. The pH was standardized with NBS buffers. The hydrogen ion and hydroxide ion concentrations in 0.1 M $NaNO_3$ were calculated from $-\log [H^+] = pH - 0.11$ and $K_w = 10^{-13.78}$.

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 $NaNO_3$ 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 equilibrium constants were obtained by a linear least-squares fit of the data by using the CDC Cyber-172 computer. A Cary 17 spectrophotometer with a thermostated cell compartment was used to record absorption spectra.

Calculations. The methods of calculations are the same as reported previously.[2]

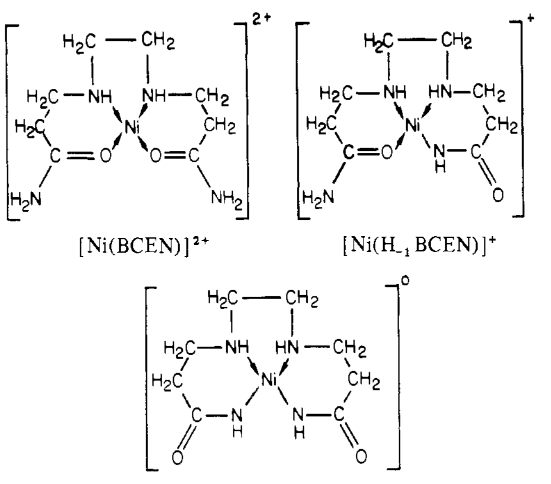
Results and Discussion

Protonation Constants. Potentiometric titration curves of the nitrate salts of diprotonated ligands BCEN and BCTN with standard base are deposited as supplemental material (Figures 1 and 2). The titration curves for BCMEN and BCHTN are similar to these curves and are submitted as supplemental material (Figures 1a and 2a). The values of the protonation constants of these four ligands obtained from these experimental data are listed in Table I.

Table I. Basicity Constants of Diamino Diamides and Equilibrium Constants of Their Nickel(II) Complexes at 25.0 ± 0.1 °C and $\mu = 0.10$ M ($NaNO_3$)

$\log K$	BCEN	BCTN	BCMEN	BCHTN
$\log K_1^H$	8.79 ±0.03	9.27 ±0.05	8.80 ±0.04	8.52 ±0.06
$\log K_2^H$	5.80 ±0.03	7.01 ±0.04	5.47 ±0.04	6.58 ±0.06
$\log K_f$	7.92	6.81	7.98	6.41
$\log K_A$	−8.46	−9.01	−8.68	−8.86
$\log K_B$	−9.69	−10.22	−9.90	−10.10

Chart II


$[Ni(BCEN)]^{2+}$

$[Ni(H_{-1}BCEN)]^+$

$[Ni(H_{-2}BCEN)]$

The values of the protonation constants of these ligands are all significantly lower than the corresponding constants of the analogous diamines[3] in accord with the base-weakening effect of the neighboring amide group.[4] For each of these ligands, the value of K_2^H is less than that of K_1^H as might have been expected on the basis of both statistical factors and electrostatic repulsion between the hydrogen ion and the protonated ligand.[5] In view of the different electrostatic distance parameters, the ratios K_1^H/K_2^H for BCEN and BCMEN are expected to be larger than those for BCTN and BCHTN. The data listed in Table I substantiate this expectation. The value of the first protonation constant, K_1^H, varies in the order BCHTN < BCEN, BCMEN < BCTN. This sequence can be related to the different inductive effects of the constituent groups in the ligands.

Composition of Nickel(II) Complexes. Job's method of continuous variations was adopted for the determination of the composition of the complex. The results indicated that nickel(II) forms a 1:1 complex with each of these four ligands.

Equilibrium Constants for the Interactions of Nickel(II) with Diamino Diamides. The complexation reactions of nickel(II) with these ligands are not fast.[6] Between $a = 0$ and $a = 2$, 1–2 h was required for the solution to reach equilibrium after each addition of titrant. Above $a = 2$, the system reacted equilibrium rapidly. During titration the color of the solutions gradually changed from pale blue to green and finally to yellow.

The titration curves for 1:1 nickel(II)–ligand (ligand = BCEN, BCTN, BCMEN, and BCHTN) show a definite break at $a = 2$ (a = number of moles of sodium hydroxide added per mole of ligand). In the first (sloping) buffer region the two protons attached to the amine groups of the ligand are dissociated by the nickel(II) ion. In the second (sloping)

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(3) Martell, A. E.; Smith, R. M. "Critical Stability Constants"; Plenum Press: New York, 1975; Vol. 2.

(4) Clark, J.; Perrin, D. D. *Q. Rev., Chem. Soc.* **1964**, *18*, 295.

(5) Chung, C.-S. *Inorg. Chem.* **1979**, *18*, 1318.

(6) Hung, T.-L. M.S. Thesis, Tsing Hua University, 1979.

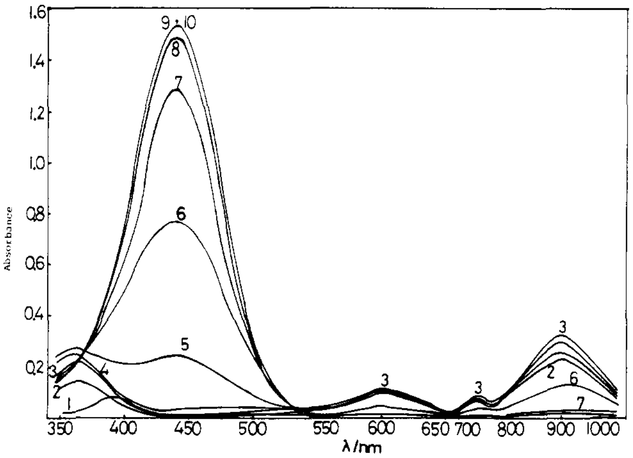

Figure 3. Visible absorption spectra of nickel(II)–BCEN solutions. All solutions contain 0.0030 M $Ni(NO_3)_2$, 0.003 M $(H_2BCEN)(NO_3)_2$ and 0.10 M sodium nitrate. The pH values of the solutions are (1) 3.72, (2) 5.15, (3) 6.88, (4) 8.48, (5) 9.15, (6) 9.82, (7) 10.55, (8) 11.31, (9) 11.80, and (10) 12.01.

buffer region the two amide protons are dissociated in overlapping steps. The equilibria (1)–(3) were found to describe

$$Ni^{2+} + L \rightleftarrows [NiL]^{2+} \qquad K_f = [NiL^{2+}]/[Ni^{2+}][L] \tag{1}$$

$$\begin{gathered}[NiL]^{2+} \rightleftarrows [NiH_{-1}L]^{+} + H^{+} \\ K_A = [NiH_{-1}L^{+}][H^{+}]/[NiL^{2+}]\end{gathered} \tag{2}$$

$$\begin{gathered}[NiH_{-1}L]^{+} \rightleftarrows [NiH_{-2}L] + H^{+} \\ K_B = [NiH_{-2}L][H^{+}]/[NiH_{-1}L^{+}]\end{gathered} \tag{3}$$

the reactions of nickel(II) with these ligands, where L represents the diamino diamide and the negative subscript to H represents the number of amide protons removed from the complex. The three complexes $[NiL]^{2+}$, $[NiH_{-1}L]^{+}$, and $[NiH_{-2}L]$ are shown in Chart II. The equilibrium constants obtained are listed in Table I.

The stability constant varies in the order $[Ni(BCMEN)]^{2+}$, $[Ni(BCEN)]^{2+} > [Ni(BCTN)]^{2+} > [Ni(BCHTN)]^{2+}$. There are two important factors influencing the stability of these nickel(II) complexes: one is the steric strains among the three linked chelate rings, and the other, the basicity of the ligand. Although the value of $K_1^{H}K_2^{H}$ for BCEN or BCMEN is much smaller than the corresponding value for BCTN, the stability constant of $[Ni(BCEN)]^{2+}$ or $[Ni(BCMEN)]^{2+}$ is much larger than that of $[Ni(BCTN)]^{2+}$ or $[Ni(BCHTN)]^{2+}$. These results indicate the girdle strains among linked consecutive chelate rings strongly disfavor the formation of nickel(II) complexes containing three linked six-membered chelate rings,[7,8] and these strains are relieved by the presence of a middle five-membered ring in the BCEN or BCMEN complex. The very low stability constant for $[Ni(BCHTN)]^{2+}$ is attributed to both the large steric strains among the three linked chelate rings and the low basicity of the ligand.

The stability constants for copper(II) complexes of BCEN and BCTN have been reported.[1,2] For each of these ligands, the formation constants follow the expected Irving–Williams order Ni(II) < Cu(II).[9]

Like copper(II), nickel(II) can induce ionization of the amide protons, and the Ni–O to Ni–N bond rearrangements at the two amide sites occur with an increase in pH (eq 2 and 3). These reactions take place in the region a = 2–4 of the 1:1 titration curve or in the region a = 1–3 of the 1:2 titration curve. The values of the equilibrium constants for these reactions, obtained by using Schwarzenbach's method,[10] are listed in Table I. These constants indicate that the steric strains in the three consecutive six-membered rings hinder not only the formation of the complexes $[Ni(BCTN)]^{2+}$ and $[Ni(BCHTN)]^{2+}$ but also the Ni–O to Ni–N bond rearrangements at the two amide sites. Analogous steric effects were found in the reactions of copper(II) complexes of these ligands.[2]

Table II. Electronic Absorption Spectra for Nickel(II) Complexes of Diamino Diamides in Aqueous Solution

compd	transition	λ, nm	intens
$[Ni(BCEN)]^{2+}$	$^3A_{2g} \rightarrow {}^3T_{2g}$	900	21.6
	$^3A_{2g} \rightarrow {}^1E_g$	741	6.2
	$^3A_{2g} \rightarrow {}^3T_{1g}$	600	8.0
	$^3A_{2g} \rightarrow {}^3T_{1g}$	363	14.6
$[Ni(H_{-1}BCEN)]^{+}$	$^3A_{2g} \rightarrow {}^3T_{2g}$	896	18.5
	$^3A_{2g} \rightarrow {}^1E_g$	738	5.3
	$^3A_{2g} \rightarrow {}^3T_{1g}$	597	7.2
	$^3A_{2g} \rightarrow {}^3T_{1g}$	359	23.2
$[Ni(H_{-2}BCEN)]^{0}$	$^1A_{1g} \rightarrow {}^1E_g$	440	102
$[Ni(BCTN)]^{2+}$	$^3A_{2g} \rightarrow {}^3T_{2g}$	915	14.8
	$^3A_{2g} \rightarrow {}^1E_g$	750	5.2
	$^3A_{2g} \rightarrow {}^3T_{1g}$	608	6.4
	$^3A_{2g} \rightarrow {}^3T_{1g}$	372	12.6
$[Ni(H_{-1}BCTN)]^{+}$	$^3A_{2g} \rightarrow {}^3T_{2g}$	910	12.7
	$^3A_{2g} \rightarrow {}^1E_g$	748	4.4
	$^3A_{2g} \rightarrow {}^3T_{1g}$	604	5.5
	$^3A_{2g} \rightarrow {}^3T_{1g}$	367	21.7
$[Ni(H_{-2}BCTN)]^{0}$	$^1A_{1g} \rightarrow {}^1E_g$	467	100
$[Ni(BCMEN)]^{2+}$	$^3A_{2g} \rightarrow {}^3T_{2g}$	905	22.2
	$^3A_{2g} \rightarrow {}^1E_g$	745	6.3
	$^3A_{2g} \rightarrow {}^3T_{1g}$	602	7.8
	$^3A_{2g} \rightarrow {}^3T_{1g}$	364	15.2
$[Ni(H_{-1}BCMEN)]^{+}$	$^3A_{2g} \rightarrow {}^3T_{2g}$	900	19.1
	$^3A_{2g} \rightarrow {}^1E_g$	742	5.4
	$^3A_{2g} \rightarrow {}^3T_{1g}$	600	6.7
	$^3A_{2g} \rightarrow {}^3T_{1g}$	361	24.6
$[Ni(H_{-2}BCMEN)]^{0}$	$^1A_{1g} \rightarrow {}^1E_g$	442	107
$[Ni(BCHTN)]^{2+}$	$^3A_{2g} \rightarrow {}^3T_{2g}$	908	15.2
	$^3A_{2g} \rightarrow {}^1E_g$	746	5.4
	$^3A_{2g} \rightarrow {}^3T_{1g}$	604	6.8
	$^3A_{2g} \rightarrow {}^3T_{1g}$	369	13.4
$[Ni(H_{-1}BCHTN)]^{+}$	$^3A_{2g} \rightarrow {}^3T_{2g}$	902	13.1
	$^3A_{2g} \rightarrow {}^1E_g$	743	4.7
	$^3A_{2g} \rightarrow {}^3T_{1g}$	601	5.9
	$^3A_{2g} \rightarrow {}^3T_{1g}$	365	22.3
$[Ni(H_{-2}BCHTN)]^{0}$	$^1A_{1g} \rightarrow {}^1E_g$	462	103

Electronic Spectra. The absorption spectra of nickel(II)–BCEN solutions are shown in Figure 3. At pH 3.72 (curve 1), practically no complex formation takes place. As the concentration of base is increased to a = 2 for the 1:1 solution (curves 2 and 3), the maxima of four bands increase in intensity. Curve 3, at a = 2, is almost entirely due to the species $[Ni(BCEN)]^{2+}$. As the base concentration is further increased beyond a = 2 for the 1:1 solution (curve 4), the four bands shift very slightly toward shorter wavelengths. Curve 5, at a = 2.5 for the 1:1 solution, is also seen to have a maximum at about 440 nm. As base concentration is further increased beyond a = 2.5 (curves 6–8), this band sharply increases in intensity. That curve 9 is identical with curve 10 confirms the potentiometric observation that no further reaction takes place between $[Ni(H_{-2}BCEN)]$ and OH^{-}.

By the use of the various equilibrium constants in Table I, the degree of formation of each nickel(II)–BCEN species in a 1:1 solution can be calculated and is shown in Figure 4. From this figure, the concentrations of all species present in

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(7) Paoletti, P.; Fabbrizzi, L.; Barbucci, R. *Inorg. Chem.* **1973**, *12*, 1861.
(8) Wang, B.; Chung, C.-S. *J. Chem. Soc., Dalton Trans.* **1982**, 2565.
(9) Irving, H.; Williams, R. J. P. *Nature (London)* **1948**, *162*, 746; *J. Chem. Soc.* **1953**, 3192.
(10) Inczédy, J. "Analytical Applications of Complex Equilibrium"; Horwood: Chichester, England, 1976.

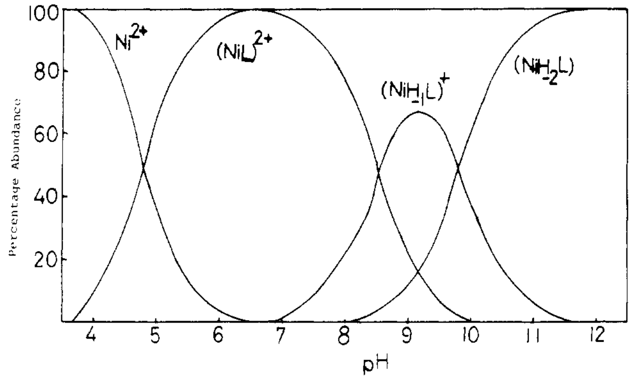

Figure 4. Degree of formation of nickel(II)-BCEN complexes in 1:1 metal-to-ligand solutions.

the solution (the spectrum of which is in Figure 3) can be calculated. Then, with eq 4, the spectra in Figure 3 can be

$$A = l(\epsilon_{Ni^{2+}}[Ni^{2+}] + \epsilon_{NiL^{2+}}[NiL^{2+}] + \epsilon_{NiH_{-1}L^{+}}[NiH_{-1}L^{+}] + \epsilon_{NiH_{-2}L}[NiH_{-2}L]) \quad (4)$$

resolved into their components. The absorption characteristics of all species so obtained are given in Table II. The same method was used to obtain the absorption characteristics of nickel(II)-BCTN, nickel(II)-BCMEN, and nickel(II)-BCHTN species, and the results are listed in Table II.

The potentiometric observation shows two protons of $[NiL]^{2+}$ are dissociated as the base concentration increases beyond $a = 2$ for the 1:1 solution. The spectrophotometric results listed in Table II indicate that it is the amide protons, not those of coordinated water molecules, that are dissociated.

The electronic absorption spectra of $[NiL]^{2+}$ and $[NiH_{-1}L]^{+}$ species show the characterisitc absorptions for triplet-ground-state, tetragonally distorted, pseudooctahedral nickel(II) complexes, while the electronic absorption spectrum of each of these $[NiH_{-2}L]$ species shows a single absorption band in the characteristic 21 000–23 000-cm^{-1} region, which is assigned to the $^1A_{1g} \rightarrow {}^1E_g$ transition of singlet-ground-state, square-planar (or distorted-planar) nickel(II) complex.[11] These results agree with the tendency toward decreased coordination in the axial positions of six-coordinate nickel(II) complexes that contain strong in-plane fields.[12,13] After the Ni–O to Ni–N bond rearrangements at the two amide sites, the in-plane ligand field increases, and the extent of axial addition decreases.[14]

Comparison of the positions of the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition for $[NiH_{-1}L]^{+}$ or $[NiL]^{2+}$ indicates that the ligand field strength decreases in the order $[Ni(H_{-1}BCEN)]^{+} > [Ni(H_{-1}BCMEN)]^{+} > [Ni(H_{-1}BCHTN)]^{+} > [Ni(H_{-1}BCTN)]^{+}$ and the order $[Ni(BCEN)]^{2+} > [Ni(BCMEN)]^{2+} > [Ni(BCHTN)]^{2+} > [Ni(BCTN)]^{2+}$. Comparison of the positions of $^1A_{1g} \rightarrow {}^1E_g$ transition of $[NiH_{-2}L]$ indicates that the ligand field strength decreases in the order $[Ni(H_{-2}BCEN)] > [Ni(H_{-2}BCMEN)] > [Ni(H_{-2}BCHTN)] > [Ni(H_{-2}BCTN)]$. These orders reflect the distorted-planar structures of the nickel(II)-BCTN and nickel-BCHTN complexes. In general, the larger the degree of distortion from a square-planar structure, the smaller is the ligand field strength.[15] The distortions are mainly attributed to the large steric constraint in the three linked six-membered chelate rings. The fact that the equilibrium constants K_f, K_A, and K_B for the nickel(II)-BCHTN and nickel(II)-BCTN systems are significantly smaller than those for nickel(II)-BCEN and nickel(II)-BCMEN lends support to this view. C-Hydroxylation of a diamino diamide leads to an increase in ligand field. C-Hydroxylation of a nitrogen-oxygen-donor macrocyclic ligand complex of nickel(II) has been shown previously to result in an increase in ligand field strength.[16]

Acknowledgment. This work was supported by the Chemistry Research Center, National Science Council of the Republic of China, to which the authors wish to express their thanks. We are also grateful to Dr. Chi-Chao Wan and Yuan-Chung Hsieh for elemental analyses and for providing laboratory facilities.

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

Supplementary Material Available: Figures 1, 1a, 2, and 2a, showing titration curves for BCEN, BCMEN, BCTN, and BCHTN, respectively, in the presence and absence of Ni^{2+} at 25.0 ± 0.1 °C (4 pages). Ordering information is given on any current masthead page.

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