

# Thermodynamics of Nickel(II) N-Alkyl-Substituted Diamino Diamides in Aqueous Solution

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The equilibria occurring in aqueous solutions of 4-methyl-4,7-diazadecanediamide (4-Me-L-2,2,2), 4,7-dimethyl-4,7-diazadecanediamide (4,7-N,N'-Me<sub>2</sub>-L-2,2,2), 4-ethyl-4,7-diazadecanediamide (4-Et-L-2,2,2), and 4-methyl-4,8-diazaundecanediamide (4-Me-L-2,3,2) with protons and nickel(II) ions as well as the deprotonation reactions of the nickel(II) complexes of these four ligands have been studied by calorimetry at T=25.0 and  $\mu=0.10\text{M}(\text{KCl})$ . The enthalpy changes and the entropy changes for these reactions are reported and discussed.

## INTRODUCTION

Polyurethanes (PUs) are multiblock copolymers usually consisting of hard segments and polyether or polyester soft segments. These materials have been used to separate oxygen from air.<sup>1-5</sup> The gas permeability of metal-containing PU membranes were significantly improved as compared to pure PUs.<sup>6-8</sup> The complexation of PU polymers was generally obtained by incorporating a chain extender containing diol or diamine of low molecular weight. These diamino diamides, 4-methyl-4,7-diazadecanediamide (4-Me-L-2,2,2), 4,7-dimethyl-4,7-diazadecanediamide (4,7-N,N'-Me<sub>2</sub>-L-2,2,2), 4-ethyl-4,7-diazadecanediamide (4-Et-L-2,2,2), and 4-methyl-4,8-diazaundecanediamide (4-Me-L-2,3,2), can be used as chain extenders for the preparation of polyurethane-urea polymer and then complexed with nickel chloride or cupric chloride. All metal-containing polyurethane-urea polymers can be used in many fields, such as the separation of oxygen from air. The above projects are under investigation in our laboratory.

Previously we have reported the equilibrium constants of the following reactions, and the complexation kinetics of these nickel (II) complexes at 25.0 and  $\mu=0.10\text{M}(\text{KCl})$ <sup>9-11</sup> (equations 1-5).



Where  $\text{M}^{2+}$  represents  $\text{Ni}^{2+}$ ; L represents the N-alkyl-substituted diamino diamides depicted in Chart I; and the three complexes  $\text{ML}^{2+}$ ,  $\text{MH}_{-1}\text{L}^+$ , and  $\text{MH}_{-2}\text{L}$  are depicted in Chart II. This paper concerns the thermodynamic functions  $G^\circ$ ,  $H^\circ$ , and  $S^\circ$  of these reactions.

## EXPERIMENTAL

### Reagents

The ligands, 4-Me-L-2,2,2, 4,7-N,N-Me<sub>2</sub>-L-2,2,2, 4-Et-L-2,2,2, and 4-Me-L-2,3,2 were the same as those reported previously.<sup>10-14</sup> All other chemicals used were of GR grade from Merck or Fluka.

### Measurements

For pH measurements a Radiometer PHM 64 equipped with a GK 2401 B combined electrode was used. The pH was standardized with NBS buffers. The hydrogen ion and hydroxide ion concentrations at 25.0 °C and  $\mu = 0.10 \text{ mol dm}^{-3}$  KCl were calculated from  $-\log[\text{H}^+] = \text{pH} - 0.11$  and  $k_w = 10^{-13.78}$ .<sup>15-17</sup>

Appropriate aliquots of standard solutions of the ligand or acid were titrated with a standard CO<sub>2</sub> free sodium hydroxide solution. The concentrations of Ni Cl<sub>2</sub> solution were determined by atomic absorption.

For calorimetric measurements a Parr 400 solution calorimeter equipped with a temperature difference ( $\pm 0.001$  °C) recorder attachment was used. This calorimeter was calibrated with aminotris (hydroxyl-methyl) methane.<sup>18-20</sup> All measurements were carried out at  $25.0 \pm 0.1$  °C. The enthalpy changes were obtained by a linear least-squares fit for the data by using microcomputer.

## RESULTS AND DISCUSSION

The experimental conditions and the results of the calorimetric measurements of 4-Me-L-2,2,2 are given in Tables 1-2; the other ligands show a similar behavior. The calculation of the composition of the solutions at equilibrium, before and after the

reaction, was carried out using a program similar to that reported by Paoietti.<sup>21,22</sup> The values of all the equilibrium constants used in the calculation were the same as those reported previously.<sup>10</sup>

Table 3 shows the values of the thermodynamic functions  $G^\circ$ ,  $H^\circ$ , and  $S^\circ$  for the stepwise protonation reactions of these ligands. Table 4 shows the values of the thermodynamic functions  $G^\circ$ ,  $H^\circ$ , and  $S^\circ$  for the formation reactions of the nickel(II) complexes of these ligands and the deprotonation reactions of these complexes.

## Protonation Reactions of N-Alkyl-Substituted Diamino Diamides

The first protonation reactions of these N-alkyl-substituted diamino diamides are characterized by the negative  $H_1^\circ$  values and the positive  $S_1^\circ$  values. Both the enthalpy and the entropy factors promote the protonation reactions of these ligands. The negative enthalpy change for the first protonation reaction,  $-H_1^\circ$ , varies in the order 4,7-N,N'-Me<sub>2</sub>-L-2,2,2 < 4Me-L-2,2,2 < 4-Et-L-2,2,2 < 4Me-L-2,3,2. This sequence can satisfactorily be explained by the inductive effects of the substituents and the distance between the amino group and the substituent. The methyl group and ethyl group are base-strengthening; -NMR, -OH, and -CONH<sub>2</sub> are base-weakening. These effects fall off rapidly with distance in saturated hydrocarbons, decreasing by a factor of about 0.4 across each -CH<sub>2</sub>-, so that the base-weakening effect of -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHR is only about two fifths as great as that of -CH<sub>2</sub>CH<sub>2</sub>NHR. The large positive  $S_1^\circ$  is mainly due to the positive contribution of the entropy of desolvation of the proton.

The second protonation reaction of each of these ligands is characterized by a large negative  $H_2^\circ$  value and an extremely small  $S_2^\circ$  value. The protonation of HL<sup>+</sup> is virtually promoted by the enthalpy factor. The negative enthalpy change for the second protonation reaction,  $-H_2^\circ$ , varies in the order 4,7-N,N'-Me<sub>2</sub>-L-2,2,2 < 4-Me-L-2,2,2 < 4-Et-L-2,2,2 < 4-Me-L-2,3,2. The most important factor affecting this sequence is the base-weakening effect of the protonated amino group. This effect is attenuated rapidly with increasing chain length. Thus the values of  $-H_2^\circ$  for the reactions of 4-Me-L-2,2,2,4-Et-L-2,2,2 and 4,7-N,N'-Me<sub>2</sub>-L-2,2,2 are smaller than those of 4-Me-L-2,3,2. The sequence 4-Me-L-2,2,2 < 4-Et-L-2,2,2 is due to the base-strengthening effect of the ethyl substituent; the sequence 4,7-N,N'-Me<sub>2</sub>-L-2,2,2 < 4-Me-L-2,2,2 is due to the base-weakening effects of the tertiary amine substituent. The extremely small  $S_2^\circ$  value is a sum of a small positive solvation effects and a small negative statistical effect.

For each of these diamino diamides  $-H_1^\circ$  is slightly larger than  $-H_2^\circ$ . This

small difference can be described as a result of two positive contributions; the inductive effect and the electrostatic effect, and a negative contribution; the solvation effect. The base-weakening effect of the protonated amino group is much larger than that of the unprotonated amino group.<sup>23</sup> In addition, the electrostatic effect also hinders the second stage of protonation. On the other hand, the large solvation enthalpy of  $H_2L^{2+}$  promotes the protonation of  $HL^+$ ; therefore  $-H_1^\circ$  is only slightly smaller than  $-H_2^\circ$ . The difference  $(-G_1^\circ) - (-G_2^\circ)$  is mainly due to the entropy factor. The large difference  $S_1^\circ - S_2^\circ$  can be described as a sum of two positive factors, i.e. the solvation and the statistical effects.

## Complexation Reactions of Nickel(II) Ion with N-Alkyl-Substituted Diamino Diamides

The complexation reactions of nickel(II) ions with these ligands are characterized by the negative  $H_3^\circ$  values and the positive  $S_3^\circ$  values. Both the enthalpy and the entropy factors promote the formation reactions of these complexes. The negative enthalpy change for the complexation reaction,  $-H_3^\circ$ , varies in the order 4-Me-L-2,3,2 < 4,7-N-N'-Me<sub>2</sub>-L-2,2,2 < 4-Me-L-2,2,2 < 4-Et-L-2,2,2. There are two important factors influencing this sequence. The most important factor is the steric strains among the three linked chelate rings. For the nickel(II) complex with an alternating sequence of six- and five- membered rings, the N-Ni-O bond angles are close to 180° and the NiN<sub>2</sub>O<sub>2</sub> group is almost planar. Consequently, the N<sub>2</sub>O<sub>2</sub> donor set in this complex nearly matches the symmetry properties of the Ni(II) orbitals; on this basis, a large  $-H_3^\circ$  is expected and found in the reaction of nickel(II) ions with 4-Me-L-2,2,2 or 4-Et-L-2,2,2. For Ni(4-Me-L-2,3,2)<sup>2+</sup>, the extremely large steric strains among three linked six-membered chelate rings strongly disfavor the formation of these complexes. The other important factor influencing the value of  $-H_3^\circ$  is the inductive effect of the substituent. The sequence of  $-H_3^\circ$ , 4,7-N,N'-Me<sub>2</sub>-L-2,2,2 < 4-Me-L-2,2,2 is due to the base-weakening effect of the substituent; the sequence of  $-H_3^\circ$ , 4-Me-L-2,2,2 < 4-Et-L-2,2,2 is due to the base-strengthening effect of the ethyl substituent.

A positive  $S_3^\circ$  is typical for the reaction of nickel(II) ions with neutral quadridentate ligands to form a complex with five- and six- membered chelate rings.<sup>24</sup> As shown in Table 4, the value of  $S_3^\circ$  for the formation of the complex with the 6,5,6-membered ring system is larger than that with the 6,6,6-membered ring system. The internal rotational entropy of 4-Me-L-2,3,2 is larger than that of 4-Me-L-2,2,2, 4-Et-L-2,2,2 or 4,7-N,N'-Me<sub>2</sub>-L-2,2,2. Thus the loss of internal rotational entropy in the reaction of 4-Me-L-2,3,2 is larger than that of 4-Me-L-2,2,2 or 4-Et-L-2,2,2.

## Deprotonation Reactions of Nickel(II) complexes

The deprotonation reactions of these complexes are characterized by the positive  $H_4^\circ$  and  $H_5^\circ$  values and the negative  $S_4^\circ$  and  $S_5^\circ$  values. Both the enthalpy and the entropy factors strongly disfavor these reactions. The negative entropy change is mainly due to the strong solvation of  $H^+$ . The value of  $H_4^\circ$  or  $H_5^\circ$  for the complex with tertiary amine ring systems is smaller than that with secondary amine ring systems. As pointed out above, the four donor atoms in the nickel(II) complex with a secondary ring system are almost planar. The larger steric constraints in the tertiary amine chelate rings for the complex with a tertiary amine ring system distort the planar structure, therefore the crystal field stabilization energy (C.F.S.E) for the nickel(II) complex with secondary amine ring system is larger than that with a tertiary amine system. For each of these diamino diamides, the C.F.S.E of the nickel(II) complex increases in the order  $NiL^{2+} < NiH_1L^+ < NiH_2L$ . Thus, the effect attributed to the distortion from a square-planar structure on the C.F.S.E of the nickel(II) complex increases in the order  $NiL^{2+} < NiH_1L^+ < NiH_2L$ . Therefore, the values of  $H_4^\circ$  and  $H_5^\circ$  for the reactions of the nickel(II) complexes containing secondary amine rings are larger than those for the complexes containing tertiary amine.

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Key Word Index – Thermodynamics; Nickel(II) Complexes.

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Table1 Calorimetric results for the system 4-Me-L-2,2,2+HCl in 0.1 mol dm<sup>-3</sup> KCl at 25.0

Run	In ampoule HCl(m moles)	In Dewar <sup>a</sup> vessel 4-Me-L-2,2,2(m moles)	pH value before reaction	pH value after reaction	Q(J) <sup>b</sup>	Qco <sup>c</sup> (J)
1	1.538	1.452	10.11	6.78	57.23	56.28
2	1.682	1.452	10.11	6.54	59.75	58.32
3	1.714	1.452	10.11	6.32	69.41	68.71
4	1.846	1.452	10.11	5.96	78.78	77.03
5	2.032	1.452	10.11	5.58	86.11	84.65
6	2.156	1.452	10.11	5.31	88.87	87.88
7	2.385	1.452	10.11	5.02	90.92	89.10
8	2.524	1.452	10.11	4.56	94.68	93.34
9	2.713	1.452	10.11	4.34	104.06	102.13
10	2.901	1.452	10.11	4.02	110.00	108.10

a. For all measurements the volumes of the solution in the Dewar flask were 100.0 and 103.5 mL before and after the reaction.

b. These values are corrected for the heat of dilution of HCl.

c. Values corrected for the side-reaction  $H^+ + OH^- \rightarrow H_2O$ ;  $H^0 = -55.794$  kJ/mole.

 Table2 Calorimetric results for the system 4-Me-L-2,2,2+NiCl<sub>2</sub> in 0.1 mol dm<sup>-3</sup> KCl at 25.0

Run	In ampoule NiCl <sub>2</sub> (m moles)	In Dewar vessel <sup>a</sup>		pH value after reaction	Q(joule) <sup>b</sup>
		4-Me-L-2,2,2 (m moles)	NaOH (m moles)		
1	1.638	1.639	0.486	7.48	95.65
2	1.638	1.639	0.983	8.16	103.85
3	1.638	1.639	1.346	8.28	108.62
4	1.638	1.639	1.734	8.41	113.47
5	1.638	1.639	1.916	9.06	124.93
6	1.638	1.639	2.214	9.32	128.20
7	1.638	1.639	2.536	9.43	133.55
8	1.638	1.639	2.948	10.02	137.49
9	1.638	1.639	3.121	10.42	138.57
10	1.638	1.639	3.296	11.01	141.17

a. For all measurements the volumes of the solution in the Dewar flask were 100.0 and 103.5 mL before and after the reaction.

b. These values are corrected for the heat of dilution of nickel chloride in 0.10 mol dm<sup>-3</sup> KCl.

Table 3 Thermodynamic functions of protonation reactions at 25.0 °C in aqueous KCl solution (0.10 mol dm<sup>-3</sup>)

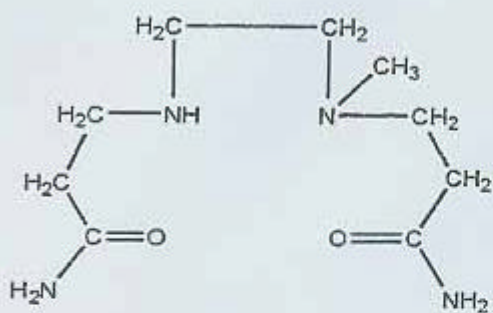
Reaction	L	G kJ mol <sup>-1</sup>	H <sup>o</sup> kJ mol <sup>-1</sup>	S <sup>o</sup> JK <sup>-1</sup> mol <sup>-1</sup>
H <sup>+</sup> +L ? HL <sup>+</sup>	4-Me-L-2,2,2	-52.08 ±0.23	-35.78 ±0.24	54.7 ±0.14
	4-Et-L-2,2,2	-49.70 ±0.29	-36.03 ±0.32	45.9 ±2.0
	4-Me-L-2,3,2	-54.39 ±0.34	-38.95 ±0.28	51.8 ±2.1
	4-7-N,N'-Me <sub>2</sub> -L-2,2,2	-46.69 ±0.34	-27.38 ±0.32	64.8 ±2.2
H <sup>+</sup> +HL <sup>+</sup> ? H <sub>2</sub> L <sup>2+</sup>	4-Me-L-2,2,2	-35.24 ±0.17	-33.01 ±0.20	7.54 ±1.2
	4-Et-L-2,2,2	-34.98 ±0.23	-33.26 ±0.15	5.8 ±1.2
	4-Me-L-2,3,2	-40.58 ±0.23	-37.96 ±0.32	8.8 ±1.8
	4-7-N,N'-Me <sub>2</sub> -L-2,2,2	-27.85 ±0.34	-24.61 ±0.20	10.9 ±1.8

Table 4 Thermodynamic functions of formation and deprotonation reactions of nickel complexes of diamimo diamides at 25.0 °C in aqueous KCl solution (0.10 mol dm<sup>-3</sup>)

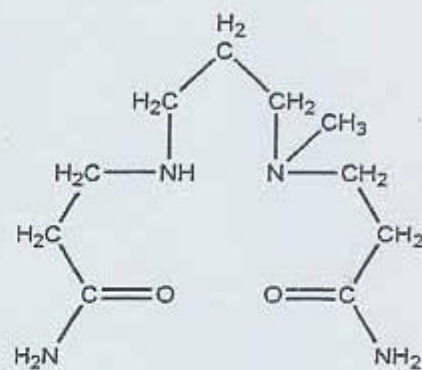
Reaction	L	G <sup>o</sup> kJ mol <sup>-1</sup>	H <sup>o</sup> kJ mol <sup>-1</sup>	S <sup>o</sup> JK <sup>-1</sup> mol <sup>-1</sup>
M <sup>+</sup> +L ? ML <sup>2+</sup>	4-Me-L-2,2,2	-39.98 ±0.40	-34.02 ±0.24	20.06 ±2.4
	4-Et-L-2,2,2	-40.78 ±0.46	-34.78 ±0.32	20.48 ±2.5
	4-Me-L-2,3,2	-31.77 ±0.46	-26.54 ±0.28	17.56 ±2.9
	4-7-N,N'-Me <sub>2</sub> -L-2,2,2	-35.18 ±0.46	-28.72 ±0.32	21.7 ±3.2
ML <sup>2+</sup> ? MH <sub>1</sub> L <sup>+</sup> +H <sup>+</sup>	4-Me-L-2,2,2	46.56 ±0.32	37.00 ±0.10	-32.0 ±0.3
	4-Et-L-2,2,2	46.53 ±0.30	36.70 ±0.24	-33.0 ±0.8
	4-7-N,N'-Me <sub>2</sub> -L-2,2,2	45.43 ±0.31	35.36 ±0.28	-33.8 ±0.9
MH <sub>1</sub> L <sup>+</sup> ? MH <sub>2</sub> L <sup>+</sup> +H <sup>+</sup>	4-Me-L-2,2,2	53.36 ±0.36	45.14 ±0.32	-34.3 ±1.1
	4-Et-L-2,2,2	55.09 ±0.37	44.64 ±0.40	-35.11 ±1.3
	4-7-N,N'-Me <sub>2</sub> -L-2,2,2	53.23 ±0.37	42.30 ±0.44	-36.7 ±1.5



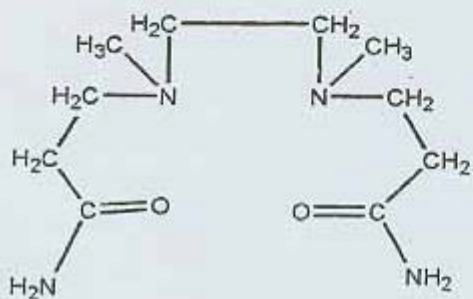
Chart I



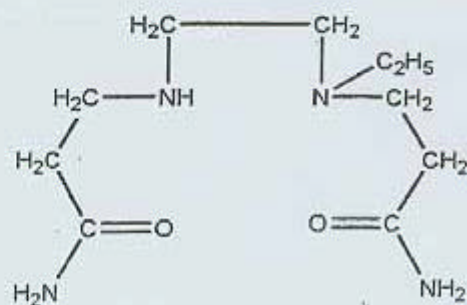
4-Me-L-2,2,2



4-Me-L-2,3,2



4,7-N,N'-Me<sub>2</sub>-L-2,2,2



4-Et-L-2,2,2

Chart II

