

## Metal Complexes of Cyclic Diamines, Dissociation Kinetics of Bis(1,5-diazacyclo-octane)nickel(II) in Acidic and Basic Solution, and Electrochemical Studies

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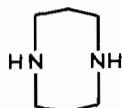
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The preparation of the planar yellow  $[\text{Ni}([\text{8}]\text{-aneN}_2)_2](\text{ClO}_4)_2$  is described. The complex dissociates in basic solution, with rate  $= k_{\text{OH}}[\text{NiL}][\text{OH}^-]$  ( $L = 1,5\text{-diazacyclo-octane}$ ). At  $25^\circ\text{C}$ ,  $k_{\text{OH}} = 4.5 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  and the corresponding activation parameters are  $\Delta H^\ddagger = 69.2 \text{ kJ mol}^{-1}$  and  $\Delta S_{298}^\ddagger = -38.6 \text{ J K}^{-1} \text{ mol}^{-1}$ . Acid catalysed dissociation is quite slow even in strongly acidic solutions. The kinetic data in this case can be fitted to the expression  $k_{\text{obs}} = k_0 + k_{\text{H}}[\text{H}^+]$ , where  $k_0$  relates to a solvolytic pathway and  $k_{\text{H}}$  to the acid catalysed pathway. At  $60^\circ\text{C}$ ,  $k_0 = 2 \times 10^{-5} \text{ s}^{-1}$  and  $k_{\text{H}}$  is  $2 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ . Possible mechanisms for these reactions are considered.

The  $\text{Ni(II)/Ni(III)}$  redox couple for  $\text{NiL}^{n+}$  is irreversible on Pt using MeCN as solvent.

### Introduction

The extremely stable square planar complexes of nickel(II) and copper(II) with 1,5-diazacyclo-octane ( $[\text{8}]\text{aneN}_2$ ) (I) were first described by Musker and Hussain [1] in 1966. The formation constant for the planar yellow nickel(II) complex is much higher than for the bis complexes of ethylenediamine and its derivatives ( $\log \beta_2 = 18.68$  at  $25^\circ\text{C}$  compared with  $\log \beta_2 = 14.08$  for ethylenediamine) [1]. The nickel(II)



(I)

complex is also extremely kinetically inert. Thus decomposition of the nickel(II) complex was not observed at room temperature on solution in 12 M hydrochloric acid and only slow decomposition was apparent in EDTA solutions [1]. However, addition of cyanide led to immediate decomposition of

the complex. Bis(1,5-diazacyclooctane)nickel(II) displays many features of the kinetic inertness of metal complexes of 14-membered macrocyclic tetraaza-ligands [2–4].

The present paper discusses the acid and base hydrolysis of  $[\text{Ni}([\text{8}]\text{aneN}_2)_2]^{2+}$ . Murphy and Zompa [5] have recently reported on the acid catalysed dissociation of the two nickel complexes  $[\text{Ni}([\text{9}]\text{-aneN}_3)]^{2+}$  and  $[\text{Ni}([\text{12}]\text{aneN}_3)]^{2+}$  ( $[\text{9}]\text{aneN}_3 = 1,4,7\text{-triazacyclononane}$ ;  $[\text{12}]\text{aneN}_3 = 1,5,9\text{-triazacyclododecane}$ ). The analogous copper(II) complexes have recently been studied by Graham and Weatherburn [6].

### Experimental

The ligand 1,5-diazacyclooctane was prepared by reacting the disodium salt of ditosyl 1,3-diaminopropane with 1,3-dibromopropane in DMF solution using the general cyclisation procedure reported by Richman and Atkins [7]. The ditosylate of 1,5-diazacyclooctane was detosylated using sulphuric acid by a previously reported procedure [8], and the free base converted to the dihydrochloride salt.

The complex  $[\text{Ni}([\text{8}]\text{aneN}_2)_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  was prepared by heating an aqueous solution of the ligand dihydrochloride with an excess of basic nickel carbonate (water bath). After filtration of the hot solution and volume reduction, addition of sodium perchlorate gave yellow crystals of the perchlorate salt. *Anal.* Calcd: for  $\text{C}_{12}\text{H}_{28}\text{N}_4\text{O}_8\text{Cl}_2\text{Ni} \cdot 2\text{H}_2\text{O}$ ; C, 27.61; H, 6.2; N, 10.7. Found: C, 27.42; H, 6.1; N, 10.54%.

### Kinetics

Base catalysed dissociation of the complex was monitored using the absorbance decrease at 240 nm. Measurements were made in a Gilford 2400S spectrophotometer interfaced with an Apple II

TABLE I. Base Catalysed Dissociation of Bis(1,5-diazacyclo-octane)nickel(II) at 25 °C and I = 0.1 M (NaClO<sub>4</sub>).

$10^2 [\text{NaOH}]$ (M)	$10^4 k_{\text{obs}}$ (s <sup>-1</sup> )	$10^2 k_{\text{obs}}/[\text{OH}^-]$ (M <sup>-1</sup> s <sup>-1</sup> )
1.0	4.27	4.27
1.5	6.54	4.36
2.0	8.74	4.37
3.0	13.24	4.41
4.0	17.28	4.32
6.0	25.96	4.33
9.0	40.48	4.49

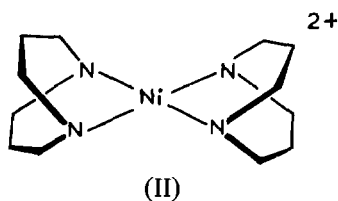
$k_{\text{OH}} = (4.5 \pm 0.06) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$

computing system. Acid catalysed dissociation was monitored similarly.

Electrochemistry was carried out using a PAR 170 electrochemistry system. The complex was  $1 \times 10^{-3}$  M with a Pt working electrode and an SCE reference electrode. The solvent employed was acetonitrile with 0.1 M tetra n-butylammonium perchlorate as the supporting electrolyte.

## Results and Discussion

The complex  $[\text{Ni}([\text{8}] \text{aneN}_2)_2](\text{ClO}_4)_2$  was isolated as a yellow dihydrate,  $\lambda_{\text{max}}$  448 nm,  $\epsilon = 112.5$ ) (lit. [1]  $\lambda_{\text{max}}$  444 nm,  $\epsilon = 115$ ). The compound is a 2:1 electrolyte in aqueous solution ( $\Lambda_{\text{M}} = 217 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  for a  $10^{-3}$  M solution). The crystal structure of  $[\text{Ni}([\text{8}] \text{aneN}_2)_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  establishes that it consists of  $[\text{Ni}([\text{8}] \text{aneN}_2)_2]^{2+}$  cations, perchlorate anions and water molecules; the water molecules and the perchlorate oxygens are too far removed from the nickel for any form of coordination to be considered [9]. The stereochemistry of the complex cation is shown in (II). The complex has a twin 'butterfly' shape, the actual conformation of the eight-membered ring is best described as a planar eight-membered ring folded across the 1,5-axis (N,N axis).



The protons on C<sub>3</sub> and C<sub>7</sub> provide some shielding of the axial sites so that octahedral coordination may be prevented by steric factors. This point is seen more

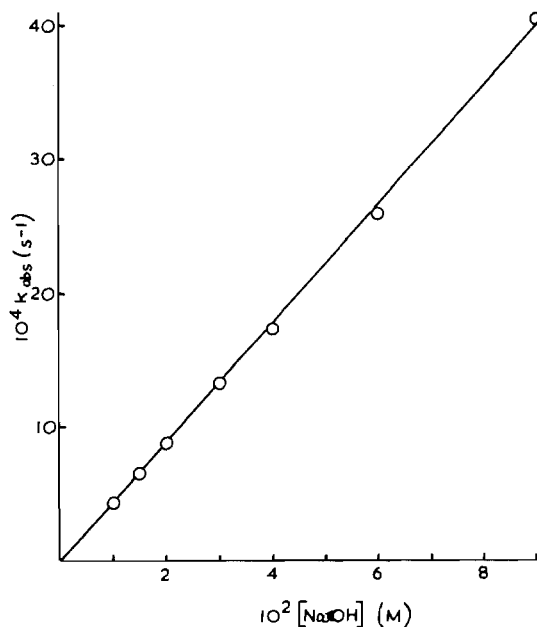
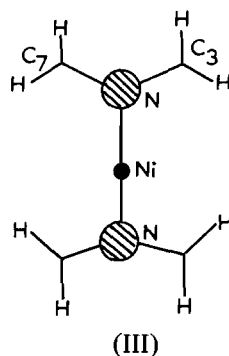


Fig. 1. Base catalysed dissociation of  $[\text{Ni}([\text{8}] \text{aneN}_2)_2]^{2+}$  at 25 °C and I = 0.1 M (NaClO<sub>4</sub>).

clearly if the molecule is viewed along the N–N axis (III):



### Base Catalysed Dissociation

The complex dissociates in basic solution and this reaction was monitored kinetically by recording the decrease in absorbance at 240 nm. Values of  $k_{\text{obs}}$ , the observed first order rate constant at various concentrations of sodium hydroxide, are summarised in Table I.

Values of  $k_{\text{obs}}/[\text{OH}^-]$  are constant, indicating a first order dependence on  $[\text{OH}^-]$  and the lack of any solvolytic reaction, Fig. 1. Least squares analysis of the data gives  $k_{\text{OH}} = k_{\text{obs}}/[\text{OH}^-] = (4.5 \pm 0.06) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C (corr. coef. = 0.9996). The temperature dependence of  $k_{\text{OH}}$  was studied at the additional temperatures of 30, 35 and 40 °C and the data obtained are summarised in Table II.

TABLE II. Base Catalysed Dissociation at 30, 35 and 40 °C at I = 0.1 M (NaClO<sub>4</sub>).

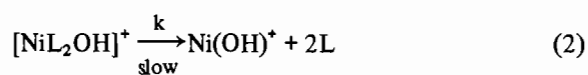
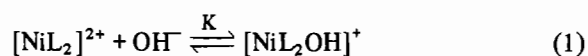
	$10^2 [\text{NaOH}]$ (M)	$10^4 k_{\text{obs}}$ (s <sup>-1</sup> )	$k_{\text{obs}}/[\text{OH}^-]$ (M <sup>-1</sup> s <sup>-1</sup> )
30 °C	1.5	10.70	7.13
	2.0	14.57	7.29
	3.0	21.37	7.12
	5.0	35.51	7.10
	6.0	43.00	7.17
			$k_{\text{OH}} = (7.1 \pm 0.05) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$
35 °C	1.0	11.42	11.42
	2.0	22.91	11.45
	4.0	45.08	11.27
	5.0	58.85	11.77
			$k_{\text{OH}} = (11.95 \pm 0.4) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$
40 °C	1.5	27.54	18.36
	2.0	39.16	19.58
	4.0	72.46	18.12
			$k_{\text{OH}} = (17.6 \pm 0.7) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$

TABLE III. Temperature Dependence of the Base Catalysed Dissociation of Bis(1,5-diazacyclo-octane)nickel(II) at I = 0.1 M.<sup>a</sup>

Temp. (°C)	$10^2 k_{\text{OH}}$ (M <sup>-1</sup> s <sup>-1</sup> )
25	4.5
30	7.1
35	11.95
40	17.6

<sup>a</sup>  $\Delta H^\ddagger = 69.2 \text{ kJ mol}^{-1}$ ;  $\Delta S_{298}^\ddagger = -38.6 \text{ J K}^{-1} \text{ mol}^{-1}$ .

Dissociation of the complex follows the rate law, rate =  $k_{\text{OH}}[\text{complex}][\text{OH}^-]$ . An appropriate reaction scheme would be,



where there is a rapid pre-equilibrium step to form the hydroxo-complex followed by a slow dissociation step. It can be readily shown that

$$k_{\text{obs}} = \frac{kK[\text{OH}^-]}{(1 + K[\text{OH}^-])} \quad (3)$$

If  $K[\text{OH}^-] \ll 1$ , then

$$k_{\text{obs}} = kK[\text{OH}^-]$$

and

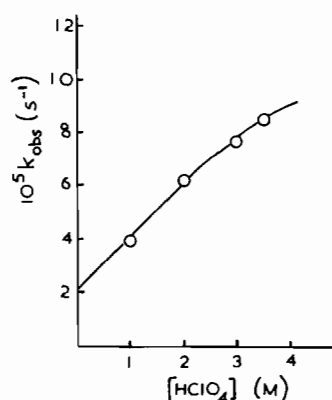


Fig. 2. Acid catalysed dissociation of  $[\text{Ni}([\text{8}] \text{aneN}_2)_2]^{2+}$  in  $\text{HClO}_4$  solutions at 60 °C. The curvature could also be due to a medium effect (see text).

$$k_{\text{OH}} = kK \quad (4)$$

Under the conditions of the present experiments  $k_{\text{OH}} = kK$  as the reaction displays a first order dependence on  $[\text{OH}^-]$  over the whole base concentration range studied. The observed activation parameters for  $k_{\text{OH}}$ ,  $\Delta H^\ddagger = 69.2 \text{ kJ mol}^{-1}$  and  $\Delta S_{298}^\ddagger = -38.6 \text{ J K}^{-1} \text{ mol}^{-1}$  thus relate to both rate and equilibrium constants, Table III.

#### Acid Catalysed Dissociation

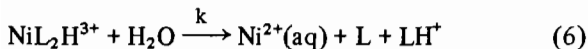
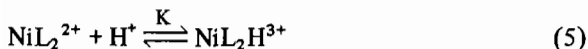
The acid-catalysed dissociation is very slow even in quite strongly acidic solutions. Acid dissociation was studied at 60 °C, and the kinetic data obtained is summarised in Table III. A plot of  $k_{\text{obs}}$  versus the hydrogen ion concentration is essentially linear with a positive intercept, Fig. 2. There is some

TABLE IV. Acid Dissociation Kinetics at 60 °C in Perchloric Acid Solutions.

[HClO <sub>4</sub> ] (M)	10 <sup>5</sup> k <sub>obs</sub> (s <sup>-1</sup> )
1.0	3.82
2.0	6.17
3.0	7.67
3.5	8.42

evidence for a divergence from a first order dependence on [H<sup>+</sup>] at high acidities. In 3.5 M HClO<sub>4</sub>, t<sub>1/2</sub> for the dissociation at 60 °C is 130 min. The kinetic data can be fitted to the expression k<sub>obs</sub> = k<sub>o</sub> + k<sub>H</sub>[H<sup>+</sup>] where k<sub>o</sub> relates to the solvolytic pathway (the reaction will not be reversible at the acidities employed) and k<sub>H</sub> to the acid catalysed pathway. At 60 °C, k<sub>o</sub> = 2 × 10<sup>-5</sup> s<sup>-1</sup> and k<sub>H</sub> is ca. 2 × 10<sup>-5</sup> M<sup>-1</sup> s<sup>-1</sup>. A solvolytic pathway has been previously observed in the acid catalysed dissociation of nickel(II) complexes of triaza macrocycles [5] and tetraaza macrocycles [10].

It is probable that the acid catalysed pathway involves the steps

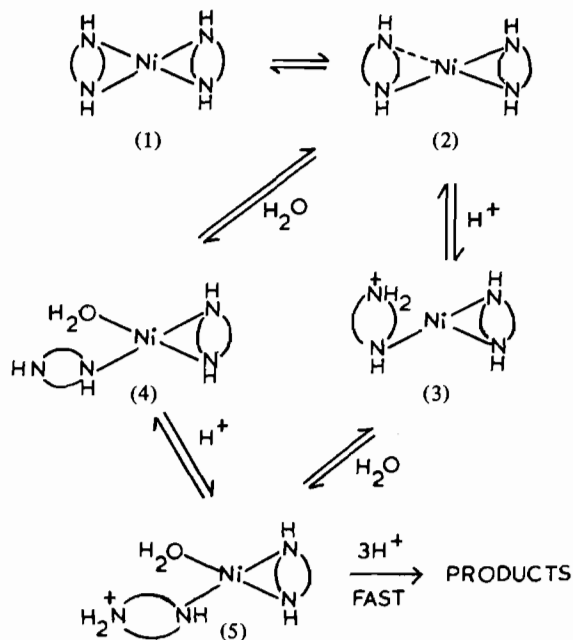


the subsequent protonation steps to give LH<sub>2</sub><sup>2+</sup> being very rapid. There is a rapid pre-equilibrium protonation step (5), followed by slow rate determining dissociation (6). The overall rate expression will take the form

$$k_{\text{obs}} = k_o + \frac{kK[\text{H}^+]}{(1 + K[\text{H}^+])} \quad (7)$$

When K[H<sup>+</sup>] ≪ 1, the reaction shows a first order dependence on [H<sup>+</sup>] with k<sub>H</sub> = kK. At high acidities where KH<sup>+</sup> ≫ 1, the reaction becomes independent of [H<sup>+</sup>] and k<sub>obs</sub> = k<sub>o</sub> + k.

A possible mechanism for the acid catalysed dissociation is summarised in the Scheme. Species (2) is a complex in which one nickel–nitrogen bond is partly broken. The acid-independent pathway involves (1) → (2) → (4) → (5) and the acid dependent pathway (1) → (2) → (3) → (5). Protonation of the partly bound nitrogen in (2) is difficult and is reflected in the small values of the equilibrium constant K in eqn. 5. At high acidities the decomposition of (3), i.e. NiL<sub>2</sub>H<sup>3+</sup>, becomes rate determining. This step is apparently several orders of magnitude faster than the corresponding reaction of the unprotonated complex where k<sub>o</sub> applies to the step (2) → (4).

Scheme. Acid catalysed dissociation of [Ni([8]aneN<sub>2</sub>)<sub>2</sub>]<sup>2+</sup>.

Cyclic voltammetry (MeCN solvent) was carried out to determine if a stable nickel(III) complex was formed on oxidation. Electrochemistry on Pt with an SCE reference and 0.1 M tetra-n-butylammonium perchlorate as supporting electrolyte showed a non-reversible oxidation at a scan rate of 100 mV s<sup>-1</sup>.

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