Mechanisms of *in Situ* Macrocyclic Ligand Synthesis, 2. [1]
Kinetics and Mechanism of Formation of a Nickel(II) Complex Containing an N₄ Donor Macrocyclic Ligand [2]

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The rate of reaction of [3,3'-[Ethylenebis(nitrilo-methylidyne)] di-2,4-pentanedionato(2-)] nickel(II) with ethylenediamine has been studied in tetrahydrofuran-ethanol solution. The rate is first order in nickel complex, second order in ethylenediamine and first order in added base (hydroxide or ethoxide ion) concentration. The enthalpy of activation, $\Delta H^{\neq}$, is 41 ± 3 kJ mol^{-1} and the entropy of activation, $\Delta S^{\neq}$, is -180 ± 20 J mol^{-1} K^{-1}. A multistep mechanism is proposed for the reaction in which initial coordination of two molecules of ethylenediamine is followed by nucleophilic attack of the deprotonated amine at a coordinated CO group of the ligand and rapid ring closure to produce a macrocyclic ligand with N₄ donor atoms. The role of the metal ion in the in situ macrocyclic ligand synthesis is discussed.

Introduction

Many recently reported complexes containing macrocyclic ligands have been synthesized by *in situ* methods in which a complex containing a tetradentate ligand undergoes reaction with a difunctional reagent [3]. The first deliberate synthesis of a new macrocyclic ligand was based on this approach; the complex 2,3-pentanedionebis(mercaptoethylimino)nickel(II) was shown to react with α,α'-dibromo-o-xylene to give a nickel(II) complex containing a macrocyclic ligand with N₂S₂ donor atoms [4]. A study of the kinetics of this reaction was subsequently reported; the proposed mechanism provided evidence for the kinetic template effect [5]. Many macrocyclic ligand formation reactions involve condensations between amines and carbonyl-containing compounds. Jäger has described a variety of reactions between diamines and complexes containing tetradentate ligands with *cis*-oriented CO groups. For example, reactions between ethylenediamine and the β-ketoiminato complexes *1*, M = Ni, Cu, in the absence of solvent were shown to give complexes *2* containing a macrocyclic ligand with an N₄ donor atom set [6].

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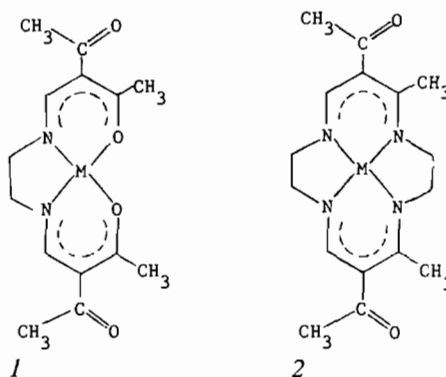
Following this report, several complexes of nickel(II) and copper(II) containing similar macrocyclic ligands were synthesized under forcing conditions in the absence of solvent [7]. Few investigations of the kinetics and possible mechanisms of *in situ* formation of N₄ macrocyclic ligands have been carried out in spite of the extensive number of reported syntheses for complexes containing these ligands. In part 1 of this series we reported a study of the kinetics of the reaction between 1,3-propanediamine and a nickel(II) complex containing a ligand derived from benzilmonohydrazone with N₂O₂ donor atoms in solution [1]. The amine reacts with one CO group of the coordinated ligand to give a non-macrocyclic ligand. A mechanism for this reaction based on the kinetic template effect was proposed and related to the *in situ* formation of the macrocyclic ligand derived from the same nickel(II) complex and ethylenediamine. In a previous publication we measured the rate of interchange between coordinated and uncoordinated acetyl groups for *1*, M = Ni, in solution and conclusions concerning the possible site of attack of a diamine with *1* to give a coordinated macrocyclic ligand were presented [8]. In this paper we report, as part of our program concerning mech-

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anisms of *in situ* macrocyclic ligand synthesis, a study of the reaction between *1*, M = Ni abbreviated Ni-(enp) and ethylenediamine to give *2*, abbreviated Ni-(Me$_2$Ac$_2$[14]-tetraenatoN$_4$)* or Ni(enp-en) in tetrahydrofuran-ethanol solution.

Experimental

[3,3'-[Ethylenebis(nitrilomethylidyne)]di-2,4-pentanedionato(2-)]nickel(II), Ni(enp), was prepared as previously reported [9]. Ethylenediamine, (en), was twice distilled from sodium hydroxide under dry nitrogen and stored in a dry nitrogen atmosphere. Tetrahydrofuran (THF) was dried by refluxing over calcium hydride and then stored over molecular sieves (Linde, type 5A). Absolute ethanol was used as provided. The ethanolic sodium hydroxide was prepared by dissolving (with small additions) reagent grade sodium hydroxide pellets in ice cold deaerated absolute ethanol under a flow of dry N$_2$. After several hours, undissolved solid was removed by filtration and the solution stored in a dark Nalgene bottle in a refrigerator. Ethanolic sodium ethoxide was prepared in a similar manner by dissolving freshly cut sodium metal in cold deaerated absolute ethanol. The sodium hydroxide and sodium ethoxide solutions were standardized by titration against dried (110°) potassium hydrogen phthalate with phenolphthalein as the indicator.

Kinetics Data

All reactions were carried out in a 100 ml round bottom flask fitted with a thermometer port and a sidearm with stopcock. The exit from the stopcock was fitted with a rubber septum cap. A weighed quantity of Ni(enp) was placed into the flask, then THF, absolute ethanol, and standardized base (ethanolic sodium hydroxide or ethoxide) were added via pipet. The flask was fitted with a thermometer and reflux condenser on to which was placed a drying tube containing Drierite and Mallcosorb (to absorb water and carbon dioxide, respectively). The stirred solution was brought to reflux and the ethylenediamine added via pipet. When the solution came to reflux again (less than 30 seconds) the timer was started. Samples were withdrawn through the sidearm by means of a microliter syringe fitted with a Chaney adaptor. The sample aliquot was injected into a 10 ml or a 25 ml volumetric flask containing absolute ethanol at room temperature and the solution diluted to the mark with ethanol. Aliquot sizes were chosen so that the total concentration of nickel complexes after dilution was about 3×10^{-5} M. The absorbances of the diluted solutions were measured at 296 and 342 nm with a Beckman model DB-GT or a Beckman

*[6,13-Diacetyl-7,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,12,14-tetradeca-4,6,12,14-tetraenato(2-)]nickel. For the macrocyclic ligand abbreviation system used see reference 3, p. 6.

Acta MVII spectrometer. For kinetics data obtained at temperatures other than reflux a thermostated oil bath was used; reaction temperature was controlled to ±0.2 °C, and a continuous flow of dry nitrogen gas was maintained over the solution. The rest of the procedure was identical to that used for obtaining data at reflux temperature. The absorbance/time data obtained at 296 and 342 nm correspond to the rate of loss of starting material, Ni(enp), and the rate of formation of product, Ni(enp–en), respectively. All kinetics data were obtained under pseudo-first order conditions, (base in excess and not consumed in the reaction and ethylenediamine in large excess), and were treated with KINFIT, a non-linear curve fitting program [10], with the Michigan State University CDC 6500 or the Virginia Commonwealth University IBM 370/158 computer. The following equation was used to fit the data:

$$(A_t - A_\infty) = (A_0 - A_\infty)e^{-k_{obs}t}$$

A_t, A_0, and A_∞ are the absorbances at time equal to t, zero, and infinity respectively, t is the elapsed time in seconds and k_{obs} is the pseudo-first order rate constant. The equation was solved by an iterative method for A_0, A_∞, and k_{obs}. The rate constants, k_{obs}, reported here are the averaged values of the rate constants, k_{296} and k_{342}, calculated from the absorbance/time data obtained at the two wavelengths. Generally, the values of k_{296} and k_{342} agreed within 5%. The slopes and intercepts reported in the results were obtained by the method of least squares.

Dielectric constants were obtained at 25 °C with a Wissenschaftlich-Technische Werkstätten Dipolmeter Type DM-01, as previously described [1].

Results

The reaction of Ni(enp), *1*, M = Ni with ethylenediamine in the presence of hydroxide or ethoxide ion in tetrahydrofuran-ethanol solution proceeds smoothly to the macrocycle, *2*, Ni(enp–en), which is the exclusive product. Fig. 1 shows a series of spectra obtained during the reaction; spectrum 1 was obtained at zero time and is that of Ni(enp) and the
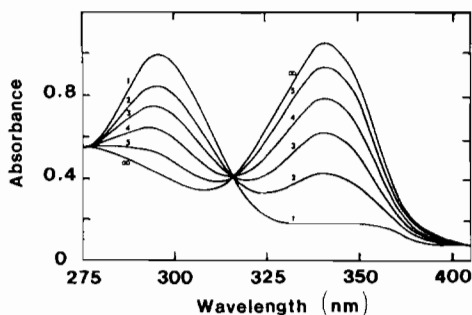

Fig. 1. Absorption spectra obtained during reaction of Ni(enp) with ethylenediamine.

spectrum marked ∞ was obtained after completion of the reaction and is identical to the spectrum obtained from an authentic sample of Ni(enp-en). The isosbestic point at 316 nm indicates the presence of significant concentrations of only two uniquely absorbing species and that detectable concentrations of intermediates or decomposition products do not occur during the course of the reaction. The results of experiments in which the effects of various factors on the rate of reaction were investigated are given below.

Ni(enp)

The reaction is first order with respect to Ni(enp). The data fit the pseudo-first order rate equation well with a standard deviation of less than 5%, in most cases. Results of experiments in which the concentration of Ni(enp) was varied are shown in Table I. Since k_{obs} does not change, the reaction is first order in Ni(enp).

TABLE I. Dependence of the Rate on the Concentration of Ni(enp)[a].

[Ni(enp)] $\times 10^3$, M	$k_{obs} \times 10^4$, s^{-1}
2.51	1.43 ± 0.04
5.02	1.38 ± 0.06
7.50	1.49 ± 0.07

[a][en] = 1.0 M; [OH⁻] = 4.05 $\times 10^{-2}$ M; temperature = 69.0 ± 0.2 °C.

Base

The rate of the reaction was found to be dependent upon the concentration of added base. The dependence was found to be first order with respect to both added sodium hydroxide and added sodium ethoxide. In the absence of added base no formation of Ni(enp—en) occurs. The results of the experiments in which the concentration of base was varied are shown in Table II and a plot of k_{obs} vs concentration of base [OR⁻], R = H, Et, is shown in Fig. 2. The slope is 3.4 ± 0.1 $\times 10^{-3}$ M^{-1} s^{-1} and the intercept is zero (0.8 ± 7 $\times 10^{-6}$ s^{-1}).

Ethylenediamine

The reaction is second order in ethylenediamine. Results of experiments in which the concentration of ethylenediamine was varied are shown in Table III and a plot of k_{obs} vs the square of the ethylenediamine concentration is shown in Fig. 3. This plot is a straight line with a slope of 7.5 ± 0.5 $\times 10^{-5}$ M^{-2} s^{-1} and an intercept of 1.5 ± 1.9 $\times 10^{-5}$ s^{-1}. A plot of log k_{obs} vs log[en] is a straight line with a slope of 1.98.

Solvent

The rate of the reaction varies with the composition of the solvent. As the relative amount of ethanol

TABLE II. Dependence of the Rate on the Concentration of Added Base[a].

[OR⁻] $\times 10^2$, M	$k_{obs} \times 10^4$, s^{-1}
(a) Hydroxide	
1.88	0.73 ± 0.08
3.71	1.25 ± 0.08
5.66	1.85 ± 0.09
6.54	2.27 ± 0.06
7.52	2.41 ± 0.08
8.43	2.97 ± 0.08
9.30	3.26 ± 0.09
(b) Ethoxide	
2.0	0.80 ± 0.1
3.0	1.23 ± 0.1
5.0	1.95 ± 0.2
8.0	2.93 ± 0.2

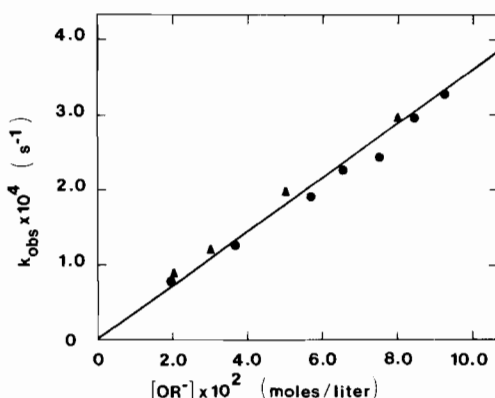[a][Ni(enp)] = 4.71 $\times 10^{-3}$ M; [en] = 0.94 M; temperature = 68.7 ± 0.3 °C.

Fig. 2. Dependence of the rate constant on the concentration of added base: ●, OH⁻; ▲, OEt⁻.

TABLE III. Dependence of the Rate on the Concentration of Ethylenediamine[a].

[en], M	$k_{obs} \times 10^4$, s^{-1}
1.00	0.96 ± 0.03
1.50	1.74 ± 0.03
1.75	2.74 ± 0.05
2.00	2.97 ± 0.06
2.25	3.6 ± 0.1
2.50	5.1 ± 0.1

[a][Ni(enp)] = 5.02 $\times 10^{-3}$ M; [OH⁻] = 4.03 $\times 10^{-2}$ M; temperature = 65.2 ± 0.2 °C.

to THF increases, (and thus the dielectric constant, D, increases), the rate of the reaction decreases. The experimental results are shown in Table IV, and a plot of ln k_{obs} vs 1/D is shown in Fig. 4. The slope of the straight line is 72 ± 4 and the intercept is −15.2 ± 0.4. These results are consistent with a mechanism which involves an ion-molecule reaction in the rate determining step [11].
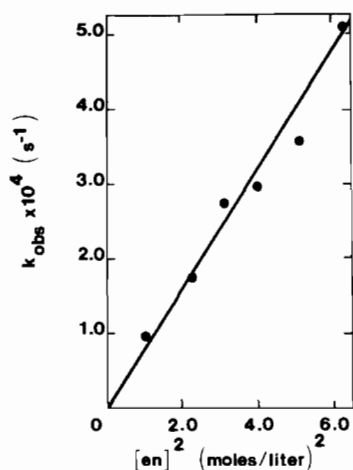
Fig. 3. Dependence of the rate constant on the concentration of ethylenediamine.

TABLE IV. Effect of Dielectric Constant, D, of the Solvent on the Rate[a].

D	$1/D \times 10^2$	$k_{obs} \times 10^4$, s^{-1}	$-\ln k_{obs}$
9.45	10.6	1.71 ± 0.09	8.68
9.65	10.4	1.43 ± 0.05	8.86
9.90	10.1	1.05 ± 0.07	9.16
10.20	9.8	0.92 ± 0.04	9.30
10.52	9.5	0.73 ± 0.05	9.52
10.81	9.2	0.57 ± 0.04	9.77

[a][Ni(enp)] = 5.02×10^{-3} M; [en] = 1.0 M; [OH$^-$] = 3.31 × 10^{-2} M; temperature = 69.0 ± 0.4 °C.
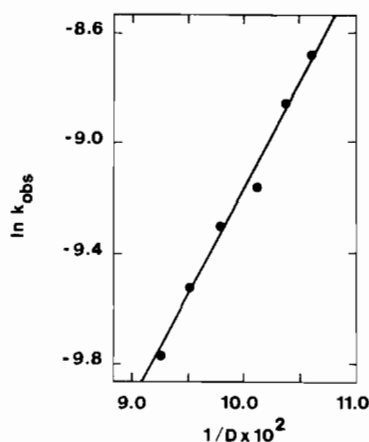

Fig. 4. Dependence of the rate constant on the dielectric constant of the medium.

Temperature

Results of the temperature dependence experiments are given in Table V and a plot of $\ln(k/T)$, where $k = k_{obs}/[en]^2[OR^-]$ versus $1/T$ is shown in Fig. 5. From this plot, the enthalpy of activation, $\Delta H^{\neq}$ is calculated to be 41 ± 3 kJ mol^{-1} and $\Delta S^{\neq}$ = −180 ± 20 J mol^{-1} K^{-1}. Since the macrocycle formation reaction is proposed to involve several steps

TABLE V. Effect of Temperature on the Rate[a].

T, K	$1/T \times 10^3$, K^{-1}	$k_{obs} \times 10^4$, s^{-1}	$k \times 10^3$, M^{-3} s^{-1}	$-\ln(k/T)$
328.8	3.041	1.98 ± 0.06	1.23	12.50
333.3	3.000	2.36 ± 0.09	1.46	12.34
338.5	2.954	2.97 ± 0.06	1.84	12.12
341.3	2.930	3.6 ± 0.1	2.23	11.94

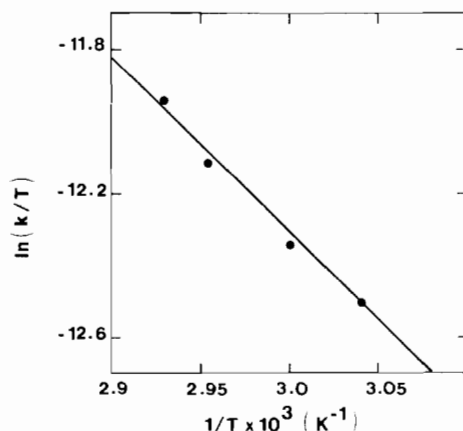[a][Nienp] = 5.02×10^{-3} M; [en] = 2.0 M; [OH$^-$] = 4.03 × 10^{-2} M.
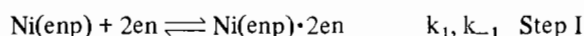

Fig. 5. Temperature dependence of the rate constant.

and the individual rate constants have not been determined (see discussion), the quoted $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values will be the sum of the values for the individual steps [12]. In spite of this limitation, it is concluded that the large negative value of $\Delta S^{\neq}$ indicates the formation of a highly ordered intermediate during the course of the reaction.
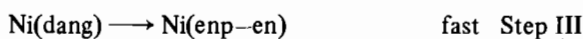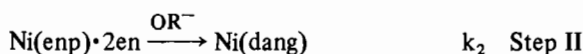
Discussion

The kinetics data obtained for the formation of Ni(Me$_2$Ac$_2$[13]tetraenatoN$_4$), Ni(enp–en), 2 M = Ni, from Ni(enp), 1, and ethylenediamine, en, in the presence of added base, OR$^-$ where R = H or Et for hydroxide or ethoxide respectively, in tetrahydrofuran–ethanol solution are consistent with the rate law:

$$d[Ni(enp\text{–}en)]/dt = -d[Ni(enp)]/dt =$$
$$k[Ni(enp)][en]^2[OR^-]$$

The reaction does not take place in the absence of added base in solution and since the rate constants for the reaction in the presence of hydroxide or ethoxide ions are the same within experimental error using similar reaction conditions, we conclude that the bases serve the same function and are not involved in the rate-determining step. The rate law is consistent with the following mechanism for the reaction:

$$Ni(enp) + 2en \rightleftharpoons Ni(enp)\cdot 2en \qquad k_1, k_{-1} \quad \text{Step I}$$

$$Ni(enp) \cdot 2en \xrightarrow{OR^-} Ni(dang) \qquad k_2 \quad \text{Step II}$$

$$Ni(dang) \longrightarrow Ni(enp-en) \qquad \text{fast} \quad \text{Step III}$$

Step I is a pre-equilibrium in which an adduct Ni-(enp)·2en is formed, Step II involves deprotonation of the coordinated amine by the base followed by the slow, rate-determining nucleophilic attack of the deprotonated amine at one CO group of the ligand to give Ni(dang) and Step III is a rapid ring closure to give the macrocyclic ligand product Ni(enp—en). Since Step III is too fast to observe, it is not possible to determine if the base participates in the final step of the ring closure reaction. The spectral data (Fig. 1) indicate the presence of only two absorbing species in significant concentrations, *viz.* Ni(enp) and Ni-(enp—en). It was discussed earlier that the presence of isosbestic points for a series of spectra will not be affected by low concentrations of highly reactive intermediates in rapid equilibration with the main components of a reaction sequence [1, 13]. Thus it is concluded that significant concentrations of the intermediates Ni(enp)·2en and Ni(dang) do not occur during the course of the reaction. If steady state conditions are applied to Ni(enp)·2en, then

$$d[Ni(enp) \cdot 2en]/dt = 0 \qquad (1)$$

which leads to

$$[Ni(enp) \cdot 2en] = \frac{k_1 [Ni(enp)][en]^2}{k_{-1} + k_2[OR^-]} \qquad (2)$$

If step II involves the slow, rate-determining step, then

$$d[Ni(enp-en)]/dt = \frac{k_2 k_1 [Ni(enp)][en]^2[OR^-]}{k_{-1} + k_2[OR^-]} \qquad (3)$$

or

$$d[Ni(enp-en)]/dt = \frac{k_2 K [Ni(enp)][en]^2[OR^-]}{1 + (k_2/k_1)[OR^-]} \qquad (4)$$

where $K = k_1/k_{-1}$, the equilibrium constant for the formation of Ni(enp)·2en. At low $[OR^-]$ and where $k_2 \ll k_1$, equation (4) reduces to

$$d[Ni(enp-en)]/dt = k_2 K [Ni(enp)][en]^2[OR^-] \qquad (5)$$

which is the observed rate law, where $k_2 K = k$. Under pseudo-first order conditions where [en] and $[OR^-]$ $\gg$ [Ni(enp)] and assumed to remain constant during the course of the reaction, then

$$d[Ni(enp-en)]/dt = k_{obs}[Ni(enp)] \qquad (6)$$

where

$$k_{obs} = k_2 K [en]^2 [OR^-] \qquad (7)$$

Values of the individual rate constants should be obtainable under certain conditions. For example, at high $[OR^-]$, equation (4) reduces to

$$d[Ni(enp-en)]/dt = k_1 [Ni(enp)][en]^2 \qquad (8)$$

i.e. the rate becomes independent of $[OR^-]$ and k_1 may be obtained. Over the range of alkoxide concentrations studied, the anticipated levelling effect was not observed. Experiments at concentrations higher than those used (maximum $\sim 1 \times 10^{-1}$ *M*) could not be performed due to decomposition of Ni(enp) and the precipitation of Ni(OH)$_2$, thus k_1 could not be determined. If the value of K could be obtained, k_2 could be calculated (see equation (7)). However, no spectral changes that indicate the formation of significant concentrations of Ni(enp)·2en were noted; thus the data needed to calculate K could not be obtained.

Despite the inability to calculate the specific rate constants k_1, k_{-1} and k_2, sufficient information is available to consider the nature of the intermediates and to discuss in more detail the proposed mechanism for the formation of Ni(enp—en).

In the initial step (I) the six-coordinated adduct Ni(enp)·2en is formed by reaction between the square planar Ni(enp) and two molecules of ethylenediamine coordinating as unidentate ligands in axial positions. The formation of this adduct is consistent with the second order dependence of the rate of reaction on the concentration of ethylenediamine and the large negative value of the entropy of activation $\Delta S^{\neq}$ ($- \sim 180$ J mol^{-1} K^{-1}) which indicates the formation of a highly ordered intermediate during the reaction. Similar adducts were proposed in the first step for the reaction of 1,2,8,9-tetraphenyl-3,4,6,7-tetraaza-5,5-dimethylnona-1,3,6,8-tetraen-1,9-dioxynickel(II), NiMMK, with 1,3-propanediamine [1] and ethylenediamine [14] and bis(diamine) adducts of a similar nickel(II) complex containing a tetradentate ligand with N$_2$O$_2$ donor atoms, diacetylbisbenzoylhydrazinonickel(II), have been identified and isolated [1, 15]. The formation of the six-coordinated nickel(II) complex is also consistent with the preferred stereochemistry of nickel(II) complexes (versus five-coordinated species). It should be noted here that in the reaction of *1*, M = Cu, Cu(enp) with ethylenediamine to give *2*, M = Cu, Cu(Me$_2$Ac$_2$[14]tetraenatoN$_4$), a first order dependence on [en] is observed and it has been shown that a 1:1 adduct is formed between Cu(enp) and ethylenediamine in the initial step [16]. This adduct has been characterized as a square pyramidal complex by EPR and absorption spectroscopy and its formation constant measured [17]. The formation of this and similar copper(II) complexes is consistent with the preference of copper(II) for five-coordination versus six-coordination [18]. The first step in the proposed mechanism thus results in orientation of the ethylenediamine for reaction with Ni(enp). Since detectable concentrations of the adduct do not form, it is assumed that the adduct is highly reactive; however, since the

reaction does not take place in the absence of added base in solution we conclude that the coordinated ethylenediamine is not a sufficiently strong nucleophile to react with the coordinated enp ligand.

Step II is proposed to involve deprotonation of the coordinated NH₂ group of ethylenediamine by the base (hydroxide or ethoxide ion) followed by the slow, rate-determining nucleophilic attack of this much stronger nucleophile at the carbon atom of a coordinated CO group of the ligand. (Note that the solvent dependence data may be interpreted in terms of an ion-molecule reaction). The product, Ni(dang), is a species containing a non-macrocyclic ligand in which only one end of the ethylenediamine has undergone reaction. This species is similar to that which is produced from the reaction of NiMMK and 1,3-propanediamine [1]. It was concluded previously [8] that the coordinated rather than the uncoordinated CO group of Ni(enp) is the probable site of attack by a diamine in the formation of complexes containing macrocyclic ligands due to the polarization effect of the nickel(II) ion and the electron-withdrawing nature of the uncoordinated acetyl group. Step II is similar to that proposed by Harrowfield and Sargeson in papers describing reactions of coordinated nucleophiles [19]. These authors proposed that the intramolecular formation of coordinated imines occurs by attack of a deprotonated ammonia molecule located *cis* to a carboxylate ligand at the carbonyl center of the coordinated acid.

Step III is a rapid ring closure reaction in which the remaining amine group of the ethylenediamine residue condenses with the second coordinated CO group of the ligand to give the macrocyclic product Ni(enp—en). If this reaction is rapid compared with the initial condensation reaction, no appreciable concentration of Ni(dang) will occur during the formation of Ni(enp—en), in agreement with the observed spectral data. Blinn and Busch concluded that the final ring closure reaction in the formation of Me₂bzo[14]trieneN₂S₂* was rapid and that measurable concentrations of an intermediate were not formed [5]. These observations are in contrast to those found for the formation of Ni(Me₂Ph₄[13]-tetraenatoN₄(N₂)) where the rate of the ring closure reaction is comparable with the rate of the initial condensation reaction and detectable concentrations of an intermediate are formed [14].

The formation of the macrocyclic ligand (enp—en) from uncomplexed enpH₂ and ethylenediamine does not occur in the absence of a metal ion under comparable conditions to those used in this study, thus the metal ion plays an important role in the *in situ* macrocyclic ligand synthesis. Two functions contribute to this role. First, the nickel(II) ion serves as a center of positive charge which leads to polarization

of both the coordinated ethylenediamine and the enp ligand. Polarization of the coordinated end of the diamine allows the OR⁻ to more easily abstract a proton from the amine [20], thus forming a highly reactive nucleophilic RNH⁻ species. Polarization of the coordinated CO of the enp ligand will increase the electrophilicity (positive character) of the carbon. These combined effects make the formation of the condensation product increasingly likely. Second, the nickel(II) ion serves to orient the reactant molecules (coordinated enp and ethylenediamine) so that condensation may readily occur. The ethylenediamine is brought into the coordination sphere, and thus the reaction sphere, by complexation at the available axial sites of the nickel(II) ion. In-plane coordination of the enp ligand restricts the coordinated CO groups to the *cis* configuration necessary for the formation of a planar macrocyclic ligand. Therefore, in the final ring closure reaction the second amine group of the ethylenediamine residue and the remaining coordinated CO group of the enp are oriented such that the reaction rapidly occurs. These conclusions suggest that the kinetic coordination template effect [6, 21] is operative in the *in situ* macrocyclic ligand synthesis. The role of the metal ion is being studied further and in subsequent papers in this series the data presented here will be compared with data for the formation of Cu(enp—en) from Cu(enp) and ethylenediamine.

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