

# The Chemical Dynamics of 1,4,8,11-Tetraazacyclotetradecane Nickel(II) Perchlorate with Several Solvents.

## I. Thermodynamics of Base Adduct Formation

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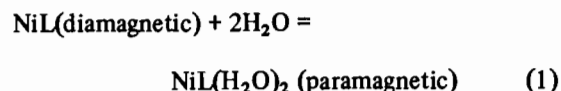
*A solvent adduct study of 1,4,8,11-tetraazacyclotetradecane nickel(II) perchlorate with the coordinating solvents acetonitrile, N,N-dimethylformamide (DMF), methyl sulfoxide (DMSO), and water by optical and nmr techniques is reported. The thermodynamic parameters  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $K_{eq}$  for adduct formation are given for each solvent system. At 25 °C, the stability order is found to be  $DMF > CH_3CN > DMSO > H_2O$ . A comparison of the observed stability order and stabilities predicted by single optical measurements and solvent donicity is presented.*

### Introduction

Metal complexes with synthetic tetraaza macrocyclic ligands have received much attention since the early studies of Busch and Curtis [1–5]. Moreover, new preparation methods for tetraaza ligand complexes have been developed recently promoting interest in these complexes for study as biological models [3, 4, 6, 7]. Solid state and solution studies of the complexes have shown the metal ion to be four-, five-, and six-coordinated [1, 3, 4, 7–12].

Four-coordinate complexes of nickel with tetraaza macrocyclic ligands may exist as either square-planar or distorted complexes depending upon the ring size and substitution of the macrocycle [1, 3, 11, 12]. For ionic nickel(II) tetraaza macrocycles whose anions are weakly binding (perchlorate, nitrate, etc.), the nickel(II) remains four-coordinate. Five-coordinate complexes may be prepared using coordinating anions (chloride, thiocyanate, etc.) or by attaching an 'arm' to the ligand ring which has a functional group capable of coordinating to one of the open sites on the nickel(II) complex [9, 13–16]. Six-coordinate nickel(II) complexes are formed by the coordinating of two monodentate anions, a bidentate anion, or two 'arm' functional groups. Alternately,

the two remaining nickel(II) sites may be occupied by coordinating solvent molecules. Numerous spectroscopic and magnetic studies have shown that in coordinating solvents such as water, the nickel(II) complexes may exist in an equilibrium between the square-planar and the tetragonally distorted octahedral ( $O_h$ ) species [1, 3, 8, 13, 14–22] as shown in eqn. (1):



Busch has discussed the chemical and biological significance of ligand or solvent coordination to open positions on metal macrocyclic complexes [23]. However, only two systematic thermodynamic studies of solvents interacting with metal macrocyclic complexes<sup>1</sup> have been previously reported [17, 19]. Such thermodynamic studies, which evaluate stability contributions from both enthalpic and entropic effects are necessary for a thorough understanding of the chemical and biological function of the metallo-macrocyclic complexes.

Thus, we propose to study the thermodynamics of base adduct formation of several coordinating solvents of varying donor properties with 1,4,8, 11-tetraazacyclotetradecane nickel(II) perchlorate (NiL). In a future work the kinetics of exchange of these solvents coordinated to the NiL will be reported.

### Experimental

#### Synthesis

1,4,8,11-tetraazacyclotetradecane nickel(II) perchlorate (Ni(II) cyclam perchlorate) was prepared by a modified literature method [24]. The ligand was obtained from Strem Chemicals, Inc. The C,H,N data are in excellent agreement with the predicted values; Found, C 26.11, N 12.15, H 5.36; Calculated, C 26.20, N 12.23, H 5.28.

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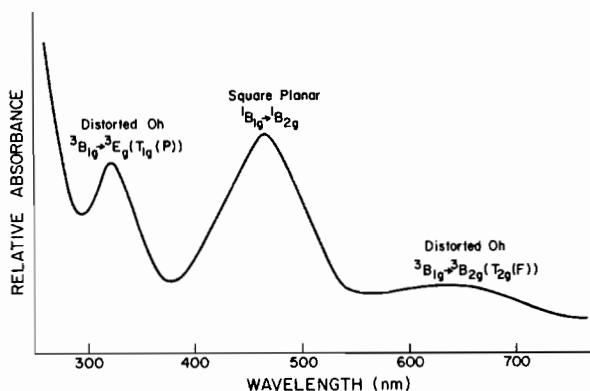


Fig. 1. Optical spectrum of 1,4,8,11-tetraazacyclotetradecane nickel(II) perchlorate dissolved in methyl sulfoxide at 25 °C.

### Magnetic Susceptibility Measurements

The Evans method was used for the determination of the magnetic moment of the NiL complex in solutions of water, 0.1 molar aqueous sodium perchlorate, acetonitrile, methyl sulfoxide (DMSO), and *N,N*-dimethylformamide (DMF) [25]. The equilibrium constant for base adduct formation at a given temperature (eqn. (1)) may be calculated from the observed solution magnetic moment and the magnetic moment of the fully coordinated complex [26]. The magnetic susceptibility studies were performed on a Varian EM-390 nmr spectrometer. Temperature calibration was achieved using the method of Van Geet [27]. Corrections were made for variation of solvent density with temperature.

### Optical Measurements

The optical studies were conducted on NiL solutions of the four solvents using Beckman model 26 and Cary model 17 spectrophotometers.

### Results and Discussion

The visible spectrum of NiL in DMSO is shown in Fig. 1. This spectrum is representative of the NiL solution spectra for the solvents acetonitrile, DMF, and water. Three optical bands can be identified in the spectrum which are indicative of the square-planar–distorted octahedral equilibrium as shown in eqn. (1). Their assignments are as follows:  $\lambda(325 \text{ nm}) - {}^3B_{1g} \rightarrow {}^3E_g(T_{1g}(P))$ ;  $\lambda(465 \text{ nm}) - {}^1B_{2g} \rightarrow {}^1B_{1g}$ ; and  $\lambda(650 \text{ nm}) - {}^3B_{1g} \rightarrow {}^3B_{2g}(T_{2g}(F))$ . Thus, the transitions at 325 and 650 nm arise from the tetragonal complex while the transition at 465 nm results from the square-planar species. A fourth band, occurring in the near ir at 1080 nm, not shown in the spectrum, is assigned to the  ${}^3B_{1g} \rightarrow {}^3E_g(T_{2g}(F))$  transition. It should be noted that these assignments may only be considered as approximate because of the following complications which may occur in the

optical spectrum. There may be a small contribution to the optical spectrum from five-coordinated Ni(II) tetraaza macrocyclic species present in solution, which are found to absorb at approximately 670, 430, and 380 nm [16]. These peaks could add to or reduce the intensities of the three peaks observed, thus causing some error in optical assignments. Additionally, although the peak at 650 nm for the DMSO solution was assigned to the  ${}^3B_{1g} \rightarrow {}^3B_{2g}$  transition, there is another possible transition at approximately the same energy in the tetragonally distorted Ni(II) complex ( ${}^3B_{1g} \rightarrow {}^3A_{2g}$ ). The energies of the two above transitions for the same NiL complex ion will vary with different axial ligands. Of lesser importance but of some consideration is the fact that the NiL in the square-planar configuration shows only one transition in the visible spectrum, usually assigned as  ${}^1B_{1g} \rightarrow {}^1B_{2g}$ . In fact, the additional transitions  ${}^1B_{1g} \rightarrow \{{}^1A_{2g}, {}^1E_g\}$  and  ${}^1B_{1g} \rightarrow {}^1E_g$  may appear in the spectrum from crystal field considerations. The possible occurrence of these additional transitions may introduce significant error in energy assignments, in the calculation of molar absorptivities, and in the analytical use of these transitions. However, we do feel that in the solvents chosen for this study, the two main species involved in the equilibrium in solution are the square-planar and the tetragonal complexes of NiL, and the observed spectra result primarily from these complexes.

The  ${}^3B_{1g} \rightarrow {}^3B_{2g}$  transition, referred to as the  $D_q^{xy}$  transition, is significant in terms of Ni(II)–nitrogen bonding [22]. It may be taken as a measure of the ability of the Ni(II) to bond in the  $N_4$  matrix of the macrocyclic ring. This transition is obviously influenced by bonding between the axial ligand (solvent molecule) and the Ni(II). Thus, the value of  $D_q^{xy}$  would increase in energy with a decrease in the axial bonding of a ligand since the  $N_4$  group forces more electron density onto the Ni(II) with an increase in  $D_q^{xy}$ . Based on the energy of this transition the stability order for solvent adduct formation would be  $H_2O$  (670 nm) > DMSO (650 nm) > DMF (645 nm) >  $CH_3CN$  (625 nm). From similar considerations, the  ${}^3B_{1g} \rightarrow {}^3E_g$  transition in the near ir could be used to infer a stability order for solvent adduct formation by considering it to be  $D_q^{z^2}$  in nature. The analogous predicted stability order would be DMSO (1080 nm) >  $H_2O$  (1070 nm) > DMF (1060 nm) >  $CH_3CN$  (1030 nm), and is in disagreement with that order based on  $D_q^{xy}$  assignments.

A qualitative method of predicting stability depends upon the ability of the solvent (S) to form the paramagnetic complex  $NiLS_2$ . The Evans method has been used to determine the effective magnetic moment ( $\mu_{eff}$ ) of NiL in the various solvents as a function of temperature. The results are given in Fig. 2 as plots of solution magnetic moment *versus*  $10^3/T$ . Non-Curie–Weiss behavior is noted because of

TABLE I. Thermodynamic Parameters for Solvent Adduct Formation of 1,4,8,11-Tetraazacyclotetradecane Nickel(II) Perchlorate at 25 °C.

| Solvent                       | $K_{eq}$ | $\Delta G(\text{Cal/Mol})$ | $\Delta H(\text{Cal/Mol})$ | $T\Delta S(\text{Cal/mol})$ | $\Delta S(\text{EU})$ |
|-------------------------------|----------|----------------------------|----------------------------|-----------------------------|-----------------------|
| DMF                           | 27.15    | -1955                      | -8454                      | -6499                       | -21.8                 |
| CH <sub>3</sub> CN            | 8.85     | -1291                      | -6934                      | -56.44                      | -18.9                 |
| DMSO                          | 2.13     | -448                       | -4189                      | -3741                       | -12.6                 |
| H <sub>2</sub> O              | 0.43     | +500                       | -3318                      | -3818                       | -12.8                 |
| H <sub>2</sub> O <sup>a</sup> | 0.38     | +575                       | -2755                      | -3330                       | -11.2                 |

<sup>a</sup>0.10 M NaClO<sub>4</sub> solution.

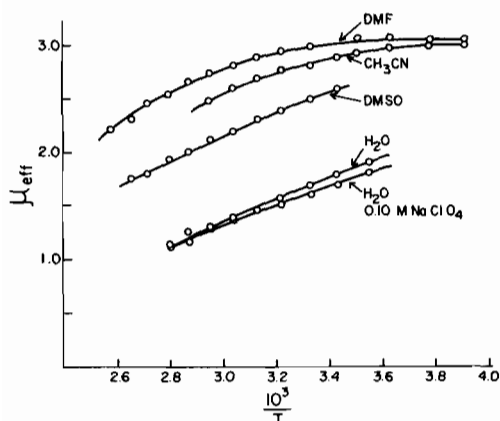


Fig. 2. The variation of magnetic moment with temperature for 1,4,8,11-tetraazacyclotetradecane nickel(II) perchlorate dissolved in several coordinating solvents.

the temperature dependence of the square-planar (diamagnetic)–distorted octahedral (paramagnetic) equilibrium. The stability order for solvent adduct formation from Fig. 2 is given as DMF > CH<sub>3</sub>CN > DMSO > H<sub>2</sub>O. These results are in disagreement with both stability orders based on optical measurements because of the previously mentioned spectroscopic complications. Conclusions about stability order drawn from spectroscopic or other parameters have been shown previously to often be in disagreement with the results from a complete thermodynamic study of the equilibrium system [26]. The advantage of doing a complete thermodynamic study is that the contribution to the stability constant from the enthalpic and entropic terms may be individually assessed.

From the data given in Fig. 2, the equilibrium constant for base adduct formation at various temperatures may be calculated using the following equation:

$$K_{eq} = (\mu_{eff}/\mu_0)^2 / (1 - (\mu_{eff}/\mu_0)^2) \quad (2)$$

$\mu_0$ , the magnetic moment for the fully coordinated complex NiLS<sub>2</sub> may be obtained directly from Fig.

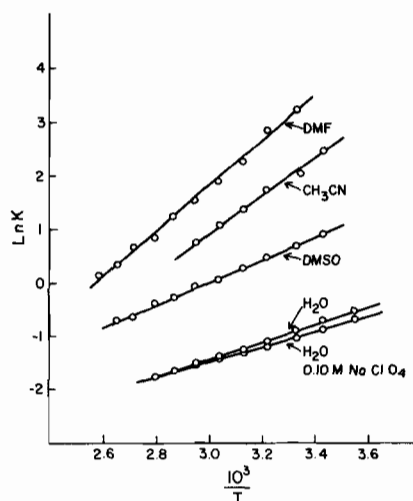


Fig. 3. Van't Hoff plots for solvent adduct formation of 1,4,8,11-tetraazacyclotetradecane nickel(II) perchlorate dissolved in several coordinating solvents.

2 for the solvents DMF (3.03 ± 0.02 BM) and acetonitrile (3.00 ± 0.01 BM) as the limiting value of  $\mu_{eff}$  at low temperature.  $\mu_0$  may be determined for the solvents DMSO (3.05 ± 0.05 BM) and water (3.10 ± 0.07 BM) by dilution of the appropriate solution with non-coordinating solvents such as nitromethane and methylene chloride which possess low freezing points. The limiting value at low temperature of  $\mu_{eff}$  is taken to be  $\mu_0$ .

The temperature dependence of the equilibrium constant for each NiL–solvent system is shown in Fig. 3 as a plot of  $\ln K_{eq}$  versus  $10^3/T$ . The stability order for solvent adduct formation is found to be DMF > CH<sub>3</sub>CN > DMSO > H<sub>2</sub>O > 0.1 M NaClO<sub>4</sub> aqueous solution over the investigated temperature range for each solvent system. The thermodynamic parameters  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $K_{eq}$  are calculated from the plot for each solvent system and are listed in Table I. From the temperature dependence of the equilibrium constant and the data in Table I, it may be noted that an increase in temperature or an increase in the ionic strength of the solution by the

TABLE II. Observed and Predicted Stability Orders for Solvent Adducts of 1,4,8,11-Tetraazacyclotetradecane Nickel(II) Perchlorate at 25 °C.

| Stability Order | Observed                            |                         | Predicted                |                          |
|-----------------|-------------------------------------|-------------------------|--------------------------|--------------------------|
|                 | $K_{eq}$                            | $D_q^{xy}$ (nm)         | $D_q^{z^2}$ (nm)         | Gutmann (D.N.)           |
| I               | DMF(27.2)                           | H <sub>2</sub> O(670)   | DMSO(1080)               | DMSO(29.8)               |
| II              | CH <sub>3</sub> CN(8.85)            | DMSO(650)               | H <sub>2</sub> O(1070)   | DMF(24)                  |
| III             | DMSO(2.13)                          | DMF(645)                | DMF(1060)                | H <sub>2</sub> O(18)     |
| IV              | H <sub>2</sub> O(0.43)              | CH <sub>3</sub> CN(625) | CH <sub>3</sub> CN(1030) | CH <sub>3</sub> CN(14.1) |
| V               | H <sub>2</sub> O(0.38) <sup>a</sup> |                         |                          |                          |

<sup>a</sup>0.1 M NaClO<sub>4</sub>.

addition of NaClO<sub>4</sub> favors the diamagnetic form of the complex. Both effects have been previously observed [17, 18, 28]. At 25 °C, the enthalpy term contributes more to the stability of the complex than the TΔS° term for all solvents except water. With a decrease in stability in going from DMF to water as solvent, both ΔH° and TΔS° decrease in magnitude, the ΔH° term becoming less favorable and the TΔS° term becoming more favorable for solvent coordination.

A comparison of this study with a similar study by Rusnak and Jordan [19] on the paramagnetic-diamagnetic equilibrium of a Ni(II) Schiff base tetraaza complex in several solvents indicates that the thermodynamic parameters for solvent adduct formation are of comparable magnitude. However, the stability order for the various solvents is different. One previous study on Ni(II) cyclam perchlorate has been reported with the solvent being 0.1 M aqueous NaClO<sub>4</sub> [17]. The equilibrium constant at 25 °C for solvent adduct formation (0.1 M aqueous NaClO<sub>4</sub>) for the two studies agrees within experimental error. However, the ΔH° (−2.755 vs. −5.4 kcal/mol) and ΔS° (−11.2 vs. −20 eu) values are in disagreement. One reason for the deviation between the two data sets, other than the different experimental methods employed (optical versus magnetic susceptibility) is that the larger temperature range employed in this study (90 °C versus 30 °C in the previous study) allows a better statistical fitting of the data to the Van't Hoff equation.

Table II summarizes the stabilities determined by this thermodynamic study and that predicted by the optical measurements  $D_q^{xy}$  and  $D_q^{z^2}$ . The differences in these results have been previously discussed. An additional prediction of the stability order may be given by Gutmann's donor numbers (D.N.) as also shown in Table II. If the donor numbers represent relative solvent ligating ability, a direct correlation should exist between complex stability and donor number. However, from the few solvents investigated in this study, the expected correlation was not found.

## Conclusions

The optical spectrum may be used to observe the degree to which basic solvent molecules form adducts with square-planar NiLS<sub>2</sub> complexes. Since the NiLS<sub>2</sub> adducts formed are paramagnetic (while NiL is diamagnetic), a measure of the solution magnetic susceptibility can also be used to calculate the solution equilibrium constant for adduct formation. The relative stability order for solvents employed in this study was found to be DMF > CH<sub>3</sub>CN > DMSO > H<sub>2</sub>O > 0.1 M NaClO<sub>4</sub> (aqueous). This stability order is not predicted by either single optical spectral measurements or Gutmann's donor number for the solvent. Poor agreements between these techniques and a complete thermodynamic study of the base adduct formation are complex, but in general, they result from the fact that these techniques only measure a single factor (such as electronic energy) while the stability of adduct formation is a complex function of NiL-solvent entropy and enthalpy as well as solvent-solvent enthalpy and entropy contributions.

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