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An Investigation of the Stereochemistry of some Nickel(II) Tetraamines in Acetonitrile Solution

GERALD S. VIGEE and CHARLES L. WATKINS*

Department of Chemistry, University of Alabama at Birmingham, Birmingham, Ala. 35294, U.S.A.

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Abstract

The equilibria of adduct formation between several nickel(II) tetraamine complexes and acetonitrile were determined from −40 to 80 °C in acetonitrile solution by the Evans NMR magnetic susceptibility method. The stability order for adduct formation of the paramagnetic complex in terms of the ligand was found to be: 2,2,2-tet, 3,3,3-tet > 3,2,3-tet > 2,3,2-tet > cyclam. This order parallels that found in previous studies in aqueous solution. However, in this study, enthalpic factors were found to be dominant whereas enthalpic and entropic factors have been reported to be comparable in magnitude in aqueous solution. Optical studies from 200–1500 nm were conducted on 0.01 M acetonitrile solutions of the complexes from 25–65 °C. Only small changes in the intensity and position of the optical bands were observed with temperature except for the 2,3,2-tet (468 nm), 3,2,3-tet (450 nm), and cyclam (460 nm) complexes. These indicated bands increase with increasing temperature, which can be explained by assuming a square-planar (diamagnetic)–octahedral (paramagnetic) equilibrium in agreement with the magnetic susceptibility data. Band assignments were made for the *cis*- and *trans*-octahedral isomers for each of the complexes. The order of *cis*-octahedral character for the complexes was found to be 2,2,2-tet, 3,3,3-tet > 2,3,2-tet > 3,2,3-tet > cyclam in agreement with previous studies in aqueous, DMSO, and DMF solutions.

Introduction

There has been considerable interest for several years in the study of the properties of metal complexes containing cyclic multidentate ligands [1–6]. These complexes have served as biological models for naturally occurring macrocyclic molecules. In addition, the chemical properties of these complexes have been found to be unusual compared to their linear analogs. For example, cyclic tetraamines form more stable metal complexes than their linear counterparts. The term 'macrocyclic effect' has been introduced to describe the additional thermodynamic and kinetic stability imparted to the cyclic complexes [7]. Extensive studies have been reported relating to the origin of this effect [8–16].

In solution, nickel(II) complexes of tetraamines may be four-, five- or six-coordinate [10, 17–22]. In the four-coordinate, or yellow form, the nitrogen atoms are coplanar, yielding a square-planar geometry, resulting in a Ni–N bond distance of approximately 1.9 Å. The complex is diamagnetic. Solvation of the nickel(II) four-coordinate complex leads to either a five- or six-coordinate complex, both of which are paramagnetic, or high-spin. The Ni–N bond distance increases to approximately 2.1 Å [6, 11, 12, 18, 23–26] in the high-spin, or blue form. Numerous studies have indicated that in solution in coordinating solvents, an equilibrium is established between the diamagnetic (four-coordinate) and paramagnetic (six-coordinate) forms of a given NiL complex [6, 10, 18, 21–25, 27–37]:

$$\text{NiL(diamagnetic)} + 2\ \text{Solvent} \rightleftharpoons \text{NiL(Solvent)}_2\text{(paramagnetic)} \qquad (1)$$

Nickel(II) complexes of noncyclic tetraamines exist primarily in the blue form in aqueous solution at 25 °C, while the cyclic complexes favour the yellow form. Factors which seem to affect the position of diamagnetic–paramagnetic equilibrium include temperature, presence of electrolyte in aqueous solution, relative stability of the cyclic ligand complex due to its hole size, solvent, and the size of the linear tetraamine and its sequence of chelate rings. Jϕrgensen, in 1957, first reported that an increase in temperature and/or addition of an inert electrolyte shifted the equilibrium to the left (see eqn. 1) favoring the yellow form for nickel(II) triethylenetetraamine ions in aqueous solution [32]. Subsequently, Fabbrizzi *et al.*, [24, 25] demonstrated the same phenomenon for several nickel(II) tetraamine complexes in aqueous solution. The stability order for octahedral solvent adduct formation was: 3,3,3-tet > 2,2,2-tet > 3,2,3-tet > 2,3,2-tet > cyclam (see 'Experimental' for nomenclature). Interestingly, this

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*Author to whom correspondence should be addressed.

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order is exactly the opposite of that found for the stabilities of formation of the respective nickel(II) tetraamine complexes [12, 38, 39]. The strength of adduct formation between 1,4,8,11-tetraazacyclotetradecane nickel(II) perchlorate and four Lewis base solvents has been reported [30, 33]. The order of adduct formation was DMF > CH_3CN > DMSO > H_2O. This stability order is not predicted by either optical assignments (d–d transitions) or Lewis base donor number arguments [30].

An additional complicating feature of the solution chemistry of the octahedral complexes is that they may exist as *cis* or *trans* isomers. Also, there may be interconversion between the *trans* and the two *cis* forms [34, 37, 40, 41]. In certain cases, the *cis/trans* isomer ratio can be determined from the position and intensity of the d–d transitions in the optical spectrum and has been found to depend on both the tetraamine ligand and solvent.

In the present study the equilibria of adduct formation between several nickel(II) tetraamine complexes and acetonitrile have been determined from −40 °C to 80 °C in acetonitrile solution by the Evans NMR magnetic susceptibility method [42] in order to ascertain the effect of variation of the ligand on adduct formation. The series of tetraamine ligands employed was chosen to study chelate effects arising from various combinations of five- and six-membered rings as well as a direct comparison of macrocyclic and linear analogs. The electronic absorption spectra (200–1500 nm) of the nickel(II) complexes in acetonitrile solution (25–60 °C) have been utilized to determine the presence of *cis* and/or *trans* isomers as well as to determine the individual maxima for the diamagnetic and paramagnetic species present. A comparison of the thermodynamic parameters obtained in this study is contrasted with previously reported results in aqueous solution [24, 25].

Experimental

The ligands used in this study are: L(I) = 1,4,7,10-tetraazadecane (2,2,2-tet); L(II) = 1,4,8,11-tetraazaundecane (2,3,2-tet); L(III) = 1,5,8,12-tetraazadodecane (3,2,3-tet); L(IV) = 1,5,9,13-tetraazatridecane (3,3,3-tet); L(V) = 1,4,8,11-tetraazacyclotetradecane (cyclam); and L(VI) = bis-ethylenediamine (bis-en).

The 1:1 nickel(II) complex of each ligand was prepared as the perchlorate salt in order to minimize anionic interactions. The nickel(II) complexes of L(II), L(III), and L(V) were prepared by standard methods [10, 30, 43]. The bis(ethylenediamine)-nickel(II) perchlorate was prepared by dissolving stoichiometric amounts of ethylenediamine and $Ni(ClO_4)_2 \cdot 6H_2O$ in a minimal amount of ethanol. After mixing, the solvent was removed by vacuum. The yellow–orange complex was washed with cold ethanol and dried under vacuum. Satisfactory C, H, N analyses were obtained for the L(II), L(III), L(V) and L(VI) nickel(II) complexes (see 'Supplementary material'). The nickel(II)–L(I) and –L(IV) complexes were not isolated due to their hygroscopic nature. Acetonitrile solutions of the nickel(II)–L(IV) complex were prepared by addition of a stoichiometric amount of a concentrated anhydrous $Ni(ClO_4)_2$ solution to the ligand in acetonitrile. Solutions of the nickel(II)–L(I) complex were prepared by addition of the concentrated $Ni(ClO_4)_2$ solution to acetonitrile solutions of the dimeric $Ni_2L(I)_3(ClO_4)_4$ complex, prepared by the method of Curtis [44].

The stability constants for the diamagnetic–paramagnetic equilibria as shown in eqn. 1 were determined between −40 °C and 80 °C for several concentrations of each nickel(II) complex in acetonitrile solution by magnetic susceptibility measurements using the Evans NMR method, as previously described [30, 42]. In each case, the magnetic moment of the fully coordinated complex was determined and is given in Table I.

Optical measurements were performed on 0.01 M acetonitrile solutions of each complex from 25 °C to 60 °C over a range of 200–1500 nm on a Cary model 17 spectrophotometer. The temperature inside the thermostatted cell was measured directly by using a Bailey Instruments digital thermometer equipped with a microprobe.

TABLE I. Thermodynamic Data for Base Adduct Formation in Acetonitrile Solution

Compound	μ_0(BM)	ΔH^a	ΔS^b	% Paramagnetic	
				25 °C	60 °C
L(I)	3.18			100	100
L(II)	3.05	−32.422	−82.01	100	97.4
L(III)	3.14	−36.894	−92.47	100	98.7
L(IV)	3.18			100	100
L(V)	3.10	−28.727	−76.15	91.8^c	76.9^d
L(VI)	3.14			100	100

^{a}kJ/mol. ^{b}J/mol K. $^cK_{eq}$ = 11.3. $^dK_{eq}$ = 3.33.

Results and Discussion

The magnetic susceptibility of each nickel(II) complex in acetonitrile solution was determined as a function of temperature from −40 °C to +80 °C by the Evans NMR method. Variation in the density of the solvent with temperature was taken into account as previously described [30, 42]. The magnetic moment in Bohr magnetons was calculated from the corrected molar magnetic susceptibility value in each case by use of the standard formula $\mu(\text{BM}) = 2.828\,(\chi_m T)^{1/2}$. Plots of μ(BM) *versus* temperature for the complexes indicate that the L(I), L(IV) and L(VI) nickel(II) complexes exist exclusively in the high-spin or blue form over the investigated temperature range. The magnetic moments of these fully coordinated complexes, μ_o, are given in Table I. However, there is considerable curvature in the μ(BM) *vs.* *T* plots for the nickel(II) complexes of L(II), L(III), and L(V) as shown in Fig. 1. For these three complexes a measurable diamagnetic–paramagnetic equilibrium exists which is a function of temperature. However, at a sufficiently low temperature, μ(BM) reaches a limiting value for each complex, which may be considered to be the μ_o value for the fully coordinated complex (Table I). The equilibrium constant may be calculated at the different temperatures from the μ(BM) data by use of the following equation [30]:

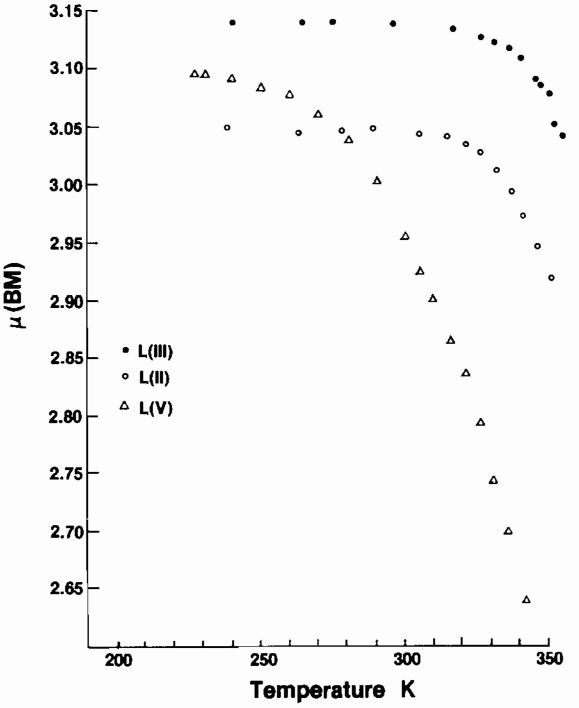

Fig. 1. A plot of the magnetic moment (BM) *vs.* *T*(K) for the nickel(II) complexes of L(II), L(III), and L(V) in acetonitrile solution: (○) L(II) complex; (●) L(III) complex; (△) L(V) complex.

$$K_{eq} = \frac{(\mu/\mu_o)^2}{1 - (\mu/\mu_o)^2} \tag{2}$$

Van't Hoff plots (ln K_{eq} *vs.* $1/T$) exhibit excellent linearity, the correlation coefficients obtained by linear regression analysis being 0.9985, 0.995, and 0.999 for the L(II), L(III), and L(V) complexes, respectively. The resulting ΔH° and ΔS° values are listed in Table I. Also given in Table I is the calculated percentage of each complex in the paramagnetic form at 25 and 60 °C.

Several conclusions can be obtained by examination of the above data in comparison with the previously reported equilibrium data on the nickel(II) macrocyclic complexes in aqueous solution [24, 25]. The stability order for formation of the paramagnetic complex is in this case L(I), L(IV) > L(III) > L(II) > L(V). This order parallels that found in the previous studies in aqueous solution although acetonitrile is a much stronger Lewis base than water toward the nickel(II) tetraamine complexes. The position of singlet–triplet equilibrium is dependent on both enthalpic and entropic factors. ΔH° is exothermic for the formation of the coordinated complex, and its magnitude demonstrates the same trend as the stability order for the L(II), L(III), and L(V) complexes (Table I). Previous analyses [6, 24, 25] have indicated that ΔH° is actually composed of two terms, an exothermic term (which is dominant in this case) arising from the formation of two Ni–N bonds from the bonding of two acetonitrile solvent molecules; and an endothermic term which reflects the energy required for the increase in the in-plane ligand Ni–N bond lengths in going from the singlet (low-spin) to the triplet (high-spin) state.

The formation of the coordinated Ni(II) cyclam complex is less favored than for any of the Ni(II) linear complexes. Thermodynamic studies on the formation of the Ni(II) tetraamine complexes themselves [12, 38, 39] show that the Ni(II) cyclam complex (four-coordinate) is more stable than its linear counterparts. (The stability order for the four-coordinated species is opposite to that of the six-coordinated species as previously mentioned). Thus, the stability of the nickel(II) low-spin cyclam complex and its inability to rearrange to the expanded form required for the triplet state as compared to the more flexible linear Ni(II) tetraamine complexes are the contributing factors to its greater diamagnetic character.

Previous studies of solvent adduct formation on these complexes in aqueous solution reported that ΔS° varied with the tetraamine ligand, the reasoning being variation in steric repulsion between the methylene groups on the ligand and the coordinating water molecules with ligand. However, in this study, ΔS° is relatively constant and has a value predicted for the complete binding of two solvent molecules in the first coordination sphere of the Ni(II) complex

[25]. These facts indicate that the acetonitrile molecule, due to its geometry and weak base character toward interaction with the N–H protons on the ligand as compared to water may more effectively enter into the first coordination sphere [33].

Comparison of the magnitudes of the ΔH° and $T\Delta S^\circ$ terms indicate that the ΔH° term is more important for the acetonitrile studies as opposed to the aqueous solution studies where ΔH° and $T\Delta S^\circ$ are more comparable in magnitude. The high-spin complexes are favored in acetonitrile solution compared to aqueous solution due to the stronger coordinating ability of the acetonitrile molecule.

Optical studies on the nickel(II) tetraamine complexes were conducted on 0.01 M solutions of each complex in acetonitrile solution as a function of temperature from 25 to 60 °C. The 200–1500 nm absorption spectra were obtained on freshly prepared solutions and after periods of time of up to one day. There was no change in any of the spectra with time. Thus, if the solid complexes were converted into spectral species which were different from those of the initially prepared complexes, then very rapid equilibria must have been established.

Only small changes in the intensity and position of the optical bands were observed with temperature, except as noted below. Most of the changes were thought to be due to normal temperature-induced (vibrational) effects. However, a thorough investigation into the nature of these effects was not undertaken. There were notable changes in the nickel(II) L(II) (468 nm), L(III) (450 nm) and L(V) (460 nm) absorption spectra with temperature, the indicated bands growing with increasing temperature. These observations can be explained by assuming an increase in the concentration of the square-planar (diamagnetic) species with increasing temperature, these results being consistent with the magnetic susceptibility data.

All the nickel(II) tetraamine complexes in this study are essentially paramagnetic in solution at 25 °C with the exception of the L(V) complex. All the absorption bands should result from octahedral (Oh) species, assuming that no five-coordinated or tetrahedral species are present. However, the difficulty in assigning the observed solution bands lies in the fact that the linear tetraamines are known to form both *cis*-octahedral(*cis*-Oh) and *trans*-octahedral(*trans*-Oh) species in solution. Additionally, separating the *cis*-Oh from the *trans*-Oh bands may be difficult because, although the molecular symmetries are obviously different, the site symmetries of the Ni^{2+} ion in the two cases may be similar enough to merge their transitions.

The observed assigned transitions for each complex in acetonitrile solution at 25 °C are listed in Table II. These data are also presented in Fig. 2 according to spectral region and arranged into two

TABLE II. Electronic Transitions of Nickel(II) Complexes in Acetonitrile Solution

Complex	Wavelength (nm)
L(I)	356, 535, 780, 870
L(II)	332, 366, 468, 500, 770, 890, 980
L(III)	336, 450, 505, 780, 977
L(IV)	353, 562, 880
L(V)	325, 468, 658, 770, 950
L(VI)	343, 536, 880

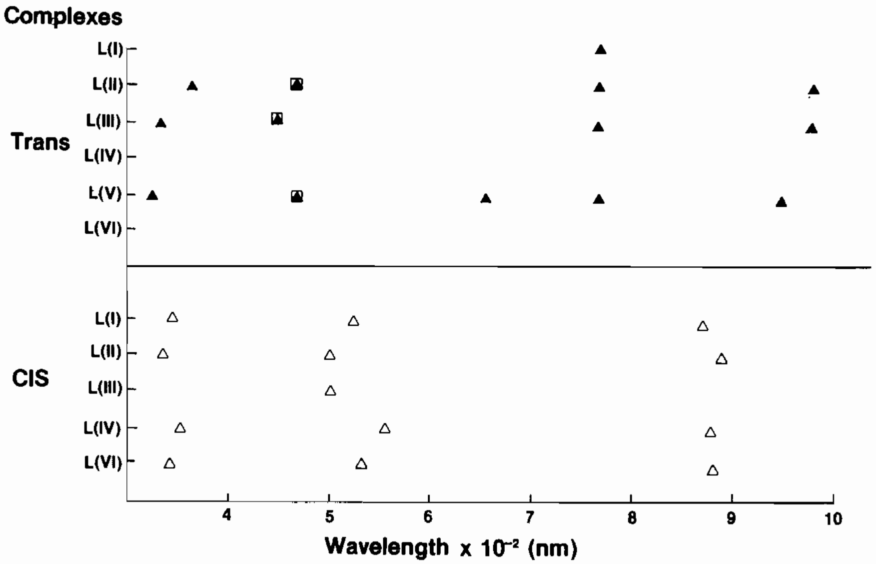

Fig. 2. Assignment of the observed optical transitions for the nickel(II) complexes in acetonitrile solution. (▣ indicates that this transition results from both *trans*-Oh and square-planar species).

groups based on whether they are *cis*-Oh or *trans*-Oh in origin. The transition energies of the cyclic L(V) complex (92% *trans*-Oh, 8% square-planar) are significantly different compared to the *trans*-Oh transition energies of the nickel(II) linear tetraamines. Assignments of the data in Table II and Fig. 2 are based on the work of Vitiello and Billo [34] and Cook and McKenzie [41]. Vitiello and Billo prepared the solid *cis*-Oh nickel(II)–L(II) complex. Then, they prepared an aqueous solution of the complex and followed the changes in the optical spectrum with time as an equilibrium mixture of *cis*-Oh, *trans*-Oh and square-planar species was obtained. In this manner, they were able to assign optical transitions to the three species. Cook and McKenzie observed a similar slow change from an initially all *trans*-Oh nickel(II)–L(II) complex in DMSO solution to an equilibrium mixture and gave spectral assignments which were appropriately in the same regions as those of Vitiello and Billo.

The optical spectral data indicate that the acetonitrile solutions of the nickel(II) complexes of the L(I), L(IV), and L(VI) are paramagnetic. There is a small indication of diamagnetic species present in each of the L(II) and L(III) solutions and somewhat more for the Ni(II)–L(V) complex as evidenced by the temperature dependence of the spectra. Unfortunately, due to overlap of the spectral bands, an analysis of the spectral data does not allow a quantitative determination of the amounts of *cis*-Oh and *trans*-Oh species for a given complex. However, the following observations can be made from an analysis of the intensities and positions of the assigned spectral bands. The L(I) complex seems to be all *cis*-Oh, but surprisingly there is one weak band present characteristic of *trans*-Oh at 770 nm. There is a dominance of *cis*-Oh species for the L(II) complex, but there is also *trans*-Oh present. The L(III) complex is nearly all *trans*-Oh in nature, while the L(IV) complex seems to exist only in the *cis*-Oh configuration. The cyclic L(V) complex is expected to exist only in the *trans*-Oh and square-planar configurations in solution. However, due to its different spectral characteristics, nickel(II) cyclam perchlorate should not be used as a model for *trans*-Oh behavior for the linear nickel(II) tetraamine complexes. The structure of the bis-(ethylenediamine)nickel(II) ion has been reported to be both *cis*-Oh [45] and *trans*-Oh [46] in aqueous solution while the perchlorate salt is thought to be *trans*-Oh in the solid state [45]. Our results indicate the L(VI) complex to be *cis*-Oh in acetonitrile solution. Our findings are complementary to those of Cook and McKenzie [40] who investigated the relative amounts of *cis*-Oh and *trans*-Oh for the L(I), L(II), and L(III) complexes in aqueous, DMSO and DMF solutions.

Supplementary Material

Analytical results are available from the Editor-in-Chief on request.

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