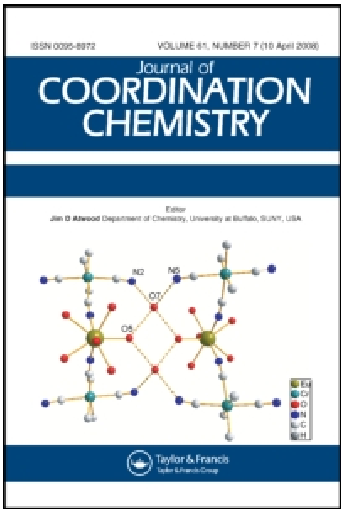

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ULTRASONIC RELAXATION KINETICS OF PLANAR:OCTAHEDRAL EQUILIBRIA OF A NICKEL MACROCYCLIC COMPLEX

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The equilibrium between the diamagnetic, planar nickel(II) macrocyclic complex known as $NiCR^{2+}$ (CR is 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15pentaene) and its paramagnetic, six-coordinate dimethanol adduct has been examined in methanol solution as the tetrafluoroborate salt. From the temperature dependence of the electronic absorption spectrum, thermodynamic parameters of $\Delta H^\circ_{46} = -4.35$ kcal mol^{-1} and $\Delta S^\circ_{46} = -8.72$ cal deg^{-1} mol^{-1} were determined. From the excess ultrasonic absorption a relaxation frequency of 15 MHz was observed from which rate constants of k_{46} of 8.6×10^7 s^{-1} and k_{64} of 7.9×10^6 s^{-1} were calculated. The rate constant k_{46} is nearly the same as the rate constant for solvent exchange which had previously been determined by NMR. This implies that the solvent exchange is effected by the octahedral-planar equilibrium and that a two-step mechanism with a five-coordinate intermediate can be eliminated.

KEYWORDS: nickel macrocyclic complex, kinetics, ultrasonic relaxation, planar-octahedral equilibria

INTRODUCTION

Planar, diamagnetic nickel(II) complexes can add solvent molecules to give six-coordinate paramagnetic species.[1] This structural interconversion was one of the earliest examples of the 'anomalous' properties of nickel complexes and of 'spin-equilibrium' between states of different spin multiplicity.[2] There have been few kinetics studies of such reactions, however, in part because the processes are extremely rapid. In one of the first such experiments, McGarvey and co-workers[3] used a neodymium laser to photochemically perturb equilibrium (1) (where 2,3,2-tet is N,N'-bis(2-aminoethyl)-1,3-propanediamine).

$$[Ni(2,3,2\text{-tet})]^{2+} + 2\ H_2O \rightleftharpoons [Ni(2,3,2\text{-tet})(H_2O)_2]^{2+} \qquad (1)$$

Creutz and Sutin[4] then confirmed that the observed spectral change was due to perturbation of the thermal equilibrium (1) and not to a photochemical reaction by studying the same reaction with the laser temperature-jump technique. The relaxation time observed in both experiments was about 300 ns. These results were interpreted with a two-step mechanism, equations (2) and (3), where L denotes the tetradentate macrocycle, S denotes a solvent molecule and charges are omitted for clarity:

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$$\mathrm{NiL + S} \underset{k_{54}}{\overset{k_{45}}{\rightleftharpoons}} \mathrm{NiLS} \tag{2}$$

$$\mathrm{NiLS + S} \underset{k_{65}}{\overset{k_{56}}{\rightleftharpoons}} \mathrm{NiLS_2} \tag{3}$$

With the assumption that the five-coordinate intermediate, NiLS, is paramagnetic, McGarvey assigned the rate determining step to reaction (2), the interconversion of the four- and five-coordinate species, on the grounds that the step involving a spin state change between diamagnetic and paramagnetic is likely to be rate determining.[3] The same mechanism was assumed for the addition of two water molecules to the planar α, β, γ, δ-tetra(4-*N*-methylpyridyl)porphinatonickel(II) complex ion, which was observed by the laser Raman temperature-jump method.[5]

This mechanism leads immediately to the prediction that the rate of solvent relaxation by the paramagnetic $\mathrm{NiLS_2}$ complex should be more rapid than the planar-octahedral interconversion. This follows because the more rapid reaction (3) provides a mechanism for the interchange of solvent molecules between the diamagnetic bulk solvent environment and the paramagnetic coordination sphere of the octahedral $\mathrm{NiLS_2}$ complex.

The data to test this prediction are available for $[\mathrm{Ni(2,3,2\text{-}tet)(H_2O)_2}]^{2+}$; the lifetime of solvent exchange is within a factor of two of the lifetime for the planar-octahedral relaxation.[6] The authors concluded that "one probably cannot say which process (of the two steps) is rate controlling for low-spin to high-spin interconversion." Some preliminary water exchange data are also available for the $[\mathrm{Ni(P)}]^{4+}$ porphyrin complex.[7] A water exchange rate constant of $4 \times 10^6\ \mathrm{s^{-1}}$ can be compared with a rate constant of $1.1 \times 10^7\ \mathrm{s^{-1}}$ calculated from the relaxation lifetime of 40 ns reported for the planar-octahedral equilibrium. In both cases the near equality of the rate constants indicates that a common mechanism is responsible for both the solvent exchange and the planar-octahedral equilibrium.

For $[\mathrm{Ni([12]aneN_4)(H_2O)_2}]^{2+}$ ($\mathrm{[12]aneN_4}$ is 1,4,7,10-tetraazacyclododecane) the relaxation time for the planar-octahedral equilibrium is 3.3 ± 0.2 ms at 25°C while the relaxation time for solvent exchange is almost 100 times shorter at 0.048 ± 0.004 ms.[8] In the octahedral complex, however, the macrocyclic ligand is believed to be folded into a *cis*-configuration. The geometric isomerization necessary between the planar complex and the presumably *cis* five-coordinate species could contribute to a large activation free energy barrier for this step and thereby reduce the rate of interconversion between the four- and five-coordinate species.

The pyridine exchange[9] from the complex $[\mathrm{Ni(bbh)(py)_2}]$ (bbh is biacetylbis-α-hydroxybenzylidenehydrazone(2-1)-$\mathrm{N^1N^{1\prime}OO'}$) occurs with almost the same rate as the octahedral-planar interconversion.[10] The latter was measured using a microwave repetitive temperature-jump technique in a dilute solution of pyridine in chlorobenzene, so that it is not strictly a solvent addition-elimination reaction. The $^{14}\mathrm{N}$ NMR solvent exchange study indicated little difference, however, between the exchange rates in neat pyridine and in 20% pyridine in chlorobenzene. The results of these studies were interpreted with the two-step mechanism in which the rate of dissociation of the ligand from the octahedral complex, k_{65}, is the rate determining step.

This interpretation is subject to some ambiguity, however, depending on whether the proposed five-coordinate species is a transition state, a paramagnetic intermediate or a diamagnetic intermediate. If the five-coordinate species is a transition state there is no need to assign a rate determining step; the mechanism coalesces to a single step with rate constants k_{46} and k_{64}.

$$\mathrm{NiL} + 2\mathrm{S} \underset{k_{64}}{\overset{k_{46}}{\rightleftharpoons}} \mathrm{NiLS_2} \tag{4}$$

If there is a paramagnetic five-coordinate intermediate then the interpretation is incorrect, for if the six-coordinate to five-coordinate step were rate determining, then the four-coordinate to five-coordinate step provides a more rapid mechanism for solvent relaxation. Diamagnetic solvent molecules could relax by reaction (2) into the paramagnetic five-coordinate species with a rate constant k_{45} which would be larger than k_{65}. Only if the five-coordinate species were diamagnetic is the two-step mechanism possibly correct.

To examine these questions further we have used ultrasonic relaxation techniques[11] to measure the rates of the planar-octahedral interconversions in methanol of the complex $\mathrm{Ni(CR)^{2+}}$ (where CR is 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15 pentaene). This complex was chosen for two reasons. First, its rigid, planar structure reduces the possibility of more complex isomerism which complicates the equilibria of the $\mathrm{[Ni([12]aneN_4)(H_2O)_2]^{2+}}$ species described above and also of a closely related pyridine-containing tetra-azamacrocycle nickel(II) complex.[12] Second, there has been a thorough study of the solvent exchange rates of $\mathrm{Ni(CR)^{2+}}$ in several solvents by proton NMR[13,14] as well as a thermodynamic investigation of the planar-octahedral equilibrium in solution.[15] Only measurements of the dynamics of the planar-octahedral equilibrium are required to complete the set of kinetic and thermodynamic data.

EXPERIMENTAL SECTION

Materials

The complex salts $\mathrm{NiCRCl_2}$ and $\mathrm{NiCR(BF_4)_2}$ were prepared as described in the literature.[15,16] The chloride was recrystallized from chloroform to give olive green crystals. The tetrafluoroborate salt was recrystallized from methanol to give red crystals. The compounds were characterised by their NMR spectra in trifluoroacetic acid and their electronic absorption spectra in water and methanol.[15] The compounds were dried in vacuum over $\mathrm{P_4O_{10}}$ before use. Freshly opened Merck UVASOL methanol was used for the ultrasonics experiments.

Methods

The ultrasonic absorption of approximately 0.1 M solutions of the complexes in methanol was measured with both the pulse and cylindrical resonator techniques using the apparatus previously described.[17-19]

RESULTS

Equilibrium Spectrophotometry

Examination of the temperature dependence of the visible absorption spectrum of $NiCR(BF_4)_2$ in methanol between 5 and 45°C reveals a clearly defined isosbestic point at 650 nm. This is good evidence that at equilibrium there are only two species present. From previous work[15] these can be identified as the four- and six-coordinate complexes.

$$NiCR^{2+} + 2CH_3OH \rightleftharpoons NiCR(CH_3OH)_2{}^{2+} \qquad (5)$$

The thermodynamics of the equilibrium can be estimated from the temperature dependence of the absorption spectrum. In trifluoroacetic acid $NiCR(BF_4)_2$ is known to be completely diamagnetic;[15] an absorption band at 396 nm has a molar absorption coefficient of 1.52×10^3 M^{-1} (ε_{IV}). In methanol the absorbance at this wavelength is much lower. A study of the temperature dependence of the magnetic susceptibility in methanol indicated that the complex is at least 80% in the six-coordinate paramagnetic form at 25°C in this solvent. This is consistent with the general spectroscopic properties of nickel(II) complexes, with the planar form possessing a strong charge-transfer absorbance and the octahedral form displaying only weak *d-d* transitions in the visible region of the spectrum. If it is assumed that the absorbance of the six-coordinate complex is effectively zero at 396 nm and that the molar absorbance of the four-coordinate complex is unchanged between trifluoracetic acid and methanol, then the thermodynamics of the equilibrium can be calculated from the temperature dependence of the absorbance (A) at this wavelength according to equation (6),

$$K_{46} = (\varepsilon_{IV}C - A)/A = \exp((-\Delta H^\circ + T\Delta S^\circ)/RT) \qquad (6)$$

where C is the total concentration of the nickel(II) complex.

A plot of log K_{46} against inverse temperature is shown in Figure 1 from which values of ΔH° of -4.35 kcal mol^{-1} and ΔS° of -8.72 cal deg^{-1} mol^{-1} are obtained. These compare satisfactorily with the values obtained from NMR[15] of ΔH° of -4.09 kcal mol^{-1} and ΔS° of -12.2 cal deg^{-1} mol^{-1}.

Ultrasonic Relaxation

The excess ultrasonic absorption of an approximately 0.1 M solution of $NiCR(BF_4)_2$ in methanol was measured at 25°C between 1 and 90 MHz. The ultrasonic absorption data were fitted as α/f^2 against log f by non-linear least-squares to two relaxations. The lower frequency one was found at 0.50 ± 0.04 MHz with an amplitude of 531 ± 60 Np s^2 cm^{-1}; the higher frequency one is at 15 ± 1 MHz with an amplitude of 33 ± 1. The high frequency background was 19 ± 1 Np s^2 cm^{-1} above that of pure methanol.

The amplitude of the low frequency relaxation is very sensitive to the presence of water impurity in the methanol solvent. Addition of a few drops of water to the solvent results in a marked increase in the amplitude of this relaxation. Because only very small amounts of water produce large effects it was not possible to remove this relaxation completely. We ascribe it to the relaxation of the mixed methanol-water complex, equation (7), or possibly to the diaqua complex, equation (8).

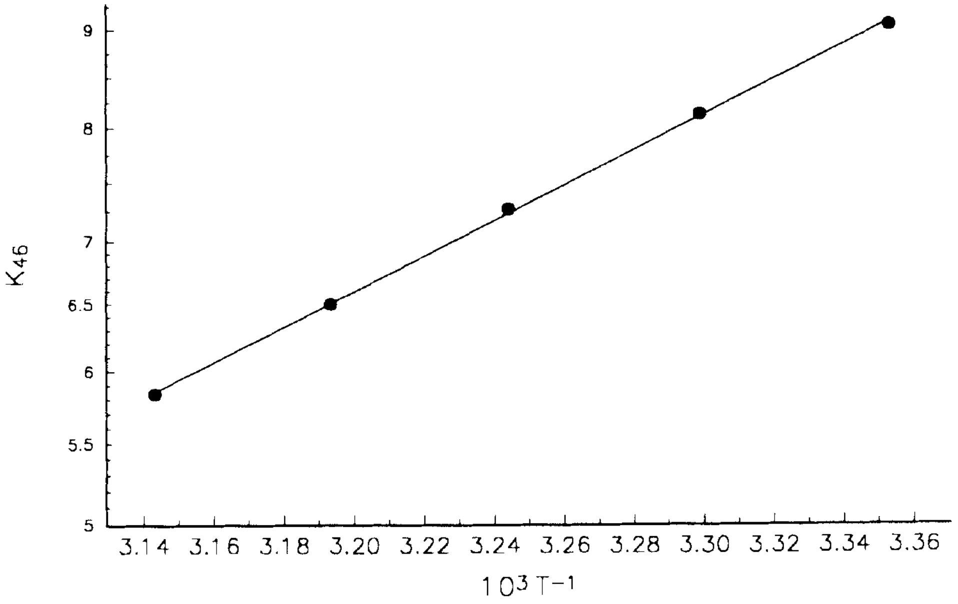

Figure 1 Logarithmic plot of equilibrium constant K_{46} against inverse temperature calculated from the temperature dependence of the absorbance at 396 nm.

$$NiCR^{2+} + CH_3OH + H_2O \rightleftharpoons NiCR(CH_3OH)(H_2O)^{2+} \tag{7}$$

$$NiCR^{2+} + 2\ H_2O \rightleftharpoons NiCR(H_2O)_2^{2+} \tag{8}$$

When the $NiCR^{2+}$ complex was examined in water as the solvent, only the beginning of excess absorption was observed at the lower frequency limit of the measurements. This implies that the relaxation time for aqua complex, equation (8), is longer than that for the methanol adduct, equation (5).

Rate Constants

With the solvent in large and constant concentration, the relaxation time for reaction (5) is given by equation (9), where f_r is the relaxation frequency.

$$2\pi f_r = \tau^{-1} = k_{46} + k_{64} \tag{9}$$

From the values of f_r of 15 MHz and K_{46} of 11, k_{46} is found to be $8.6 \times 10^7\ s^{-1}$ and k_{64} is $7.9 \times 10^6\ s^{-1}$.

Relaxation Amplitude

The amplitude of an ultrasonic relaxation is given by equation (10)

$$(\alpha/f^2)_{max} = (\pi\rho v/RTf_r)\{\Delta V^\circ - (\alpha_p/\rho C_p)\Delta H^\circ\}^2\Gamma \tag{10}$$

where R, T, ΔV° and ΔH° have their usual meanings, ρ is the solution density, v is the velocity of sound in the solution in cm s^{-1}, f_r is the relaxation frequency in Hz(s^{-1}), α_p is the coefficient of thermal expansion of the solvent, C_p is the specific heat and Γ is a factor which relates to the position of the chemical equilibrium which is being perturbed. For the equilibrium of equation (5), this function Γ is given by equation (11),

$$\Gamma^{-1} = [\mathrm{NiCR}^{2+}]^{-1} + [\mathrm{NiCR(CH_3OH)_2}^{2+}]^{-1} + 4[\mathrm{CH_3OH}]^{-2} \qquad (11)$$

which under the present reaction conditions reduces to equation (12):

$$\Gamma = K_{46}[\mathrm{Ni}]_{\mathrm{total}}/(K_{46} + 1)^2 \qquad (12)$$

A measure of ΔV° can be obtained from the relaxation amplitude for the experimental values of T, f_r, ΔH° and Γ and literature values for ρ, v, α_p and C_p for the pure solvent methanol. Because of the squared relationship in equation (10), two roots are obtained, +18 and +3 cm^3 mol^{-1}. Because the equilibrium involves the coordination of two methanol molecules, the value of +18 cm^3 mol^{-1} is less physically reasonable than that of +3 cm^3 mol^{-1}.

DISCUSSION

Previous work by Rusnak and Jordan[13-15] and the present spectrophotometric observations provide good evidence that the NiCR^{2+} complex undergoes a simple equilibrium in methanol between the diamagnetic-planar and the paramagnetic-octahedral species. The observation of two relaxation processes was hence a puzzle until it was observed that the lower frequency relaxation was dependent on trace amounts of water in the solvent. We are reasonably confident, therefore, that the relaxation process observed at 15 MHz can be assigned to the dominant equilibrium involving methanol addition and elimination from the four- and six-coordinate NiCR^{2+} complexes.

The relaxation time observed for this equilibrium of 1×10^{-8} s is only slightly shorter than the relaxation times observed for the analogous equilibria of Ni(2,3,2-tet)$^{2+}$ in water[3] (3×10^{-7} s) and of a nickel porphyrin complex, also in water,[5] (4×10^{-8}s). In each case the addition and elimination of two solvent molecules is an extremely rapid process. The activation barrier for these reactions is presumably the adjustment of the nickel-nitrogen in-plane metal ligand bond lengths between the diamagnetic state, with shorter Ni-N bonds, and the paramagnetic state with longer Ni-N bonds, concomitant with the formation or dissociation of the axial Ni-solvent bonds. There is no further stereochemical change required, unlike the isomerisation which accounts for the slower relaxation of the $[\mathrm{Ni([12]aneN_4)}]^{2+}$ equilibrium.[7]

The primary purpose of this work was to compare the rate of the four-coordinate: six-coordinate equilibrium with the previously measured rate of solvent exchange.[14] The rate for the exchange of one solvent molecule is 1.1×10^7 s^{-1} at 298 K. That rate is in close agreement with the value of k_{64} of 7.9×10^6 s^{-1} found in this work. Both of these measurements are subject to considerable error, but the agreement within a factor of two is sufficient for the major point to be established. We conclude that the solvent exchange is effected by the same mechanism that leads to the ultrasonic relaxation, namely the establishment of the planar-octahedral equilibrium, equation(4).

This conclusion requires rejection of the two-step mechanism, equations (2) and (3), with the assignment of one or the other of the steps as rate-determining. It implies that any five-coordinate intermediate closely resembles a transition state and is not present as a significant reaction intermediate. It suggests that the addition and elimination of the two solvent molecules above and below the metal-ligand plane occurs as a concerted process.

This description offers a reasonable mechanism in which the critical reaction coordinate parameter is the length of the in-plane nickel-ligand bonds. As these lengthen in the planar, diamagnetic state, two solvent molecules which have been solvating the planar complex move closer to occupy the axial metal coordination sites. In the reverse reaction these Ni-solvent bonds lengthen for solvent ligand dissociation as the in-plane metal-ligand bonds compress. The mechanism is concerted; the model of a single ligand dissociation in an octahedral complex is not appropriate. The results of the present work are similar to those found for the $[Ni(2,3,2\text{-tet})]^{2+}$ and the tetra(4-*N*-methylpyridyl)porphinatonickel(II) complexes. At least for these three complexes a common mechanism seems to obtain.

The volume difference between the planar and six-coordinate species is more likely to be $+3$ than $+18$ cm^3 mol^{-1}. For other complexes with water as the solvent the differences range from -1 to -10 cm^3 mol^{-1}.[20–22] The larger value for the methanol solvate may reflect a smaller volume decrease which occurs upon the coordination of methanol, in contrast with water. This decrease is opposed by the increase in volume caused by the expansion of the complex in the plane of the macrocyclic ligand.

References

1. D.H. Busch, *Adv. Chem. Ser.*, **62**, 616 (1967).
2. J.K. Beattie, *Adv. Inorg. Chem.*, **32**, 1 (1988).
3. K.J. Ivin, R. Jamison and J.J. McGarvey, *J. Amer. Chem. Soc.*, **94**, 1763 (1972).
4. C. Creutz and N. Sutin, *J. Amer. Chem. Soc.*, **95**, 7177 (1973).
5. R.F. Pasternack, N. Sutin and D.H. Turner, *J. Amer. Chem. Soc.*, **98**, 1908 (1976).
6. R.J. Pell, H.W. Dodgen and J.P. Hunt, *Inorg. Chem.*, **22**, 529 (1983).
7. S. Gower, H.W. Dodgen and J.P. Hunt, Abstracts of 185th American Chemical Society Meeting, Seattle, 1983, Abstract INORG 286.
8. J.H. Coates, D.A. Hadi, S.F. Lincoln, H.W. Dodgen, and J.P. Hunt, *Inorg. Chem.*, **20**, 707 (1981).
9. J. Sachinidis and M.W. Grant, *J.C.S. Chem. Commun.*, 157 (1978).
10. M. Cusumano, *J.C.S. Dalton Trans.*, 2133 (1976).
11. C.F. Bernasconi, *Relaxation Kinetics* (Academic Press, New York, 1976), p. 244.
12. N.W. Alcock, P. Moore and H.A.A. Omar, *J. C. S. Dalton Trans.*, 1107 (1987).
13. L.L. Rusnak and R.B. Jordan, *Inorg. Chem.*, **10**, 2686 (1971).
14. L.L. Rusnak and R.B. Jordan, *Inorg. Chem.*, **14**, 988(1975).
15. L.L. Rusnak and R.B. Jordan, *Inorg. Chem.*, **10**, 2199(1971).
16. J.L. Karn and D.H. Busch, *Nature*, **211**, 160 (1966).
17. J.K. Beattie, R.L. Binstead and R.J. West, *J. Am. Chem. Soc.*, **100**, 3044 (1978).
18. R.L. Binstead, J.K. Beattie, T.G. Dewey and D.H. Turner, *J. Am. Chem. Soc.*, **102**, 6442 (1980).
19. A.F. Godfrey and J.K. Beattie, *Inorg. Chem.*, **22**, 3794 (1983).
20. R.M. Nielson, H.W. Dodgen, J.P. Hunt, S.E. Wherland, *Inorg. Chem.*, **25**, 582 (1986).
21. J.K. Beattie, M.T. Kelso, W.E. Moody and P.A. Tregloan, *Inorg. Chem.*, **24**, 415 (1985).
22. Y. Kitamura, T. Ito and M. Kato, *Inorg. Chem.*, **23**, 3836 (1983).