Spin-Conversion Reaction of Muonium with Nickel Cyclam

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Abstract: Muonium atoms in aqueous solution were made to interact with nickel cyclam in two spin states, interchanged merely by altering the ionic strength of the solution by addition of an inert salt. The results show that "triplet" muonium interacts with the paramagnetic ion (octahedral coordination) at about the diffusion-limited rate (2×10^{10} M^{-1} s^{-1}), but with the diamagnetic ion (square-planar coordination only) about 100-fold slower. This strongly implies that the interaction with the paramagnetic state is an electron spin conversion (either spin-exchange or spin-flip). It demonstrates the potential of using the "triplet" to "singlet" conversion of muonium, as followed by the muon spin-rotation technique, as a probe of paramagnetism and as a monitor of spin-exchange interactions.

Introduction

Muonium atoms in aqueous solution undergo many of the same reactions with added solutes as do their much heavier isotope, the hydrogen atom. Thus one observes redox reactions with reducible additives, addition to vinyl bonds, abstraction of hydrogen or halogen atoms, and even acid-base reactions with OH^-.[1-3] However, with paramagnetic solutes which are unreactive toward H, such as $Ni^{2+}{}_{aq}$ or $Fe^{2+}{}_{aq}$, there is also a very fast (often diffusion-limited) interaction observed for muonium by the muon spin rotation (μSR) technique.[4,5] This is attributed to an electron spin-conversion process, which gives rise to an observed loss of muonium signal, because this technique monitors only those muonium atoms which remain in the "triplet" state (parallel electron and muon spins). Any conversion to "singlets" (antiparallel spin states) corresponds to an observed net loss of coherent triplet muonium states.

Such electron-spin exchange (or, possibly, spin-flip) interactions of muonium were first reported by Hughes and his co-workers in the mid 1960's[6-8] in gas-phase studies of muonium formed in Ar reacting with added O_2 and NO. Although fast addition reactions are possible with these additives, the authors concluded from the magnetic field dependence that spin exchange was the dominant process. For the liquid-phase studies involving paramagnetic solutes,[4] the reaction was assigned to spin conversion on the basis of the comparison with H-atom reactions. Thus Fe(II) in a low-spin complex (diamagnetic $Fe(CN)_6{}^{4-}$) reacted with muonium at $\sim 10^8$ M^{-1} s^{-1}, whereas in a high-spin state (paramagnetic $Fe^{2+}{}_{aq}$) it reacted at $\sim 10^{10}$ M^{-1} s^{-1}.[4] Also, in the comparison between Ni^{2+} and Zn^{2+}, neither of which is reduced by H (nor, therefore, expected to be reduced by Mu), the paramagnetic Ni^{2+} caused loss of triplet muonium with a rate constant of $\sim 10^{10}$ M^{-1} s^{-1}, whereas the diamagnetic Zn^{2+} had no observable effect (i.e., $\leq 10^7$ M^{-1} s^{-1}). For the case of dissolved O_2 in water,[5] there was no basis for deciding whether the high rate constant for loss of triplet muonium was due to spin conversion or chemical reaction (addition or reduction).

In this paper we present data on the reaction of muonium with a metal complex that contains the same metal ion, in the same oxidation state, and with essentially the same ligands, in two spin states. Thus nickel cyclam (1,4,8,11-tetraazacyclotetradecane)-nickelate(II)) exhibits the rare quality of switching from an octahedral (paramagnetic, d^8) configuration to a square-planar (diamagnetic) structure simply by the addition of an inert salt,[9] $NaClO_4$ and Na_2SO_4 in this study. It therefore provides an excellent system with which to unambiguously test the spin-conversion mechanism of muonium.

The muonium atom (Mu) is formed when a positive muon, μ^+, abstracts an electron from the surrounding medium and forms a bound state. High-energy (24.4 MeV) "backward" muons and low-energy (4.1 MeV) "surface" muons are products of pion (π^+) decay and can be obtained from the M20 channel at TRIUMF (the Tri University Meson Facility on the campus of the University of British Columbia). The muons have an intrinsic lifetime of 2.2 μs, while the muonium atoms in pure water have a chemical lifetime of at least 4 μs. Because the Bohr radius and the ionization potential of Mu are very nearly equal to the values found for H, this radioactive atom can be used as a hydrogen-like probe to study hydrogen-atom reaction rates and kinetic isotope effects.[6] It has a mass equal to $^1/_9$th the mass of H.

Muon spin rotation (μSR) and muonium spin rotation (MSR) are the techniques used to observe the rotation and decay of free muons (and other diamagnetic muonic species) and paramagnetic triplet muonium, respectively. These techniques monitor the spin precession frequencies and signal amplitudes of the species present under transverse magnetic fields. Since the Larmor frequency for triplet Mu (1.3. MHz/G) is some 102 times faster than the precession frequency of the diamagnetic species and free muons (13.6 kHz/G), Mu can be easily distinguished from muons in other spin states. More detailed descriptions of the μSR and MSR methods have been reported elsewhere.[10,11]

It has been observed that Mu undergoes relatively slow depolarization reactions in such pure liquids as water,[1-3] alcohols,[2] and hydrocarbons.[12] These pure liquids, therefore, can be used as muonium-producing solvents for the examination of various solutes of interest. As free triplet Mu reacts chemically with the solute, the atom's signal at the characteristic precession frequency is damped so that a muonium decay constant, λ, can be obtained. From these decay constants and the corresponding solute concentrations, the bimolecular rate constant, k_M, can be calculated.

Prior to 1977 aqueous solutions of $Ni(cyclam)^{2+}$ were considered to be completely diamagnetic in nature, exhibiting typical square-planar nickel complex spectral characteristics.[13] In 1977 Anichini et al.[9] reported that in 0.1 M $NaClO_4$ solution $Ni(cyclam)^{2+}$ existed as a mixture of 71% "yellow" diamagnetic and 29% "blue" paramagnetic. Increasing the inert salt concentration

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(1) P. W. Percival, H. Fischer, M. Camani, F. N. Gygax, W. Ruegg, A. Schenck, H. Schilling, and H. Graf, *Chem. Phys. Lett.*, **39**, 333 (1976).

(2) P. W. Percival, E. Roduner, and H. Fischer, *Chem. Phys.*, **32**, 353 (1978).

(3) Y. C. Jean, J. H. Brewer, D. G. Fleming, D. M. Garner, R. J. Mikula, L. C. Vaz, and D. C. Walker, *Chem. Phys. Lett.*, **57**, 293 (1978).

(4) Y. C. Jean, J. H. Brewer, D. G. Fleming, and D. C. Walker, *Chem. Phys. Lett.*, **60**, 125 (1978).

(5) Y. C. Jean, D. G. Fleming, B. W. Ng, and D. C. Walker, *Chem. Phys. Lett.*, **66**, 187 (1979).

(6) V. W. Hughes, *Annu. Rev. Nucl. Sci.*, **16**, 445 (1966).

(7) R. M. Mobley, J. M. Bailey, W. E. Cleland, V. W. Hughes, and J. E. Rothberg, *J. Chem. Phys.*, **44**, 4354 (1966).

(8) R. M. Mobley, Ph.D. Thesis, Yale University, 1967.

(9) A. Anichini, L. Fabbrizzi, P. Paoletti, and R. M. Clay, *Inorg. Chim. Acta*, **24**, L21 (1977).

(10) J. H. Brewer and K. M. Crowe, *Annu. Rev. Nucl. Part. Sci.*, **28**, 239 (1978).

(11) D. G. Fleming, D. M. Garner, L. C. Vaz, D. C. Walker, J. H. Brewer, and K. M. Crowe, *Adv. Chem. Ser.*, No. 175, 279 (1979).

(12) Y. Ito, B. W. Ng, Y. C. Jean, and D. C. Walker, *Can. J. Chem.*, **58** 2395 (1980).

(13) L. Fabbrizzi, *Inorg. Chem.*, **16**, 2667 (1977).

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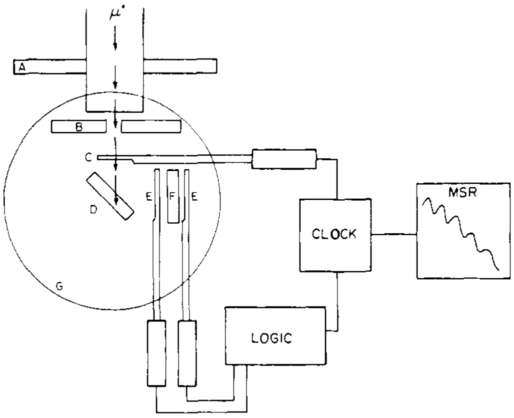

Figure 1. Schematic diagram of the μSR apparatus. A and B are lead shielding and collination for the muon beam. C is a thin muon (start) counter. D represents the sample, a thin-walled cell containing the aqueous solutions being deoxygenated by continuous bubbling with pure helium. E and E, separated by carbon absorber F, represent a positron telescope, providing a stop signal when the decay positron is emitted in their direction. G indicates a pair of Helmholtz coils which provide a magnetic field perpendicular to the plane of the paper, so that the muon's spin precesses in the plane of the paper.

caused a reduction in the octahedral spectral lines at 337 and 666 nm, resulting in an increase in the square-planar absorption band at 447 nm. At 6 M $NaClO_4$ only the square-planar diamagnetic form exists in solution,[13] for which a maximum extinction coefficient limit, ϵ_{limit}, of 64.5 M^{-1} cm^{-1} is reported.[9,13] Using this the authors calculate an equilibrium constant for eq 1, $K = \epsilon/(\epsilon_{\text{limit}} - \epsilon) = 2.47$ in 0.1 M $NaClO_4$ at 25 °C.

$$[\mathrm{Ni(cyclam)\cdot 2L}]^{2+} \underset{K}{\overset{\substack{\text{inert}\\ \text{salt}}}{\rightleftharpoons}} [\mathrm{Ni(cyclam)}]^{2+} + 2\mathrm{L} \qquad (1)$$

The ligands, L, in eq 1 are presumed to be H_2O molecules. Their removal by high concentrations of inert salts results in the conversion from a distorted (elongated) octahedral complex to a square-planar one in which the $d_{x^2-y^2}$ orbital is unoccupied. However, during the course of these experiments it was found necessary to add a slightly stronger nonionic ligand than H_2O to shift the equilibrium to the octahedral structure. Aqueous ammonia was chosen for this purpose as it reacts negligibly with Mu and seems to bind with about the correct tenacity. $\mathrm{Ni(cyclam)}^{2+}$ was thus selected for these studies and offers an ideal complex in which to study the spin state without changing the oxidation state of the central ion or the identity or number of the principal tetradentate ligand.

Experimental Section

A. Chemicals. 1,4,8,11-Tetraazacyclotetradecane (cyclam) and the Ni(II) salt, $[\mathrm{Ni(cyclam)}]\cdot 2\mathrm{PF}_6$, were both obtained from Strem Chemicals Inc. and used without further purification. NH_4PF_6, Na_2SO_4, and $NaClO_4$ were obtained in reagent grade quality, and the NH_4OH solution came from North American Scientific Chemicals Co. The water used was initially deionized, then distilled from chromic acid and potassium permanganate solutions. This water is known to provide a medium in which Mu can be formed with a chemical lifetime of at least 4 μs.[3-5]

B. Spectral Analysis. A Cary 17D spectrophotometer and 10-cm cylindrical cells were used to determine the percentages of the paramagnetic "blue" and diamagnetic "yellow" species present in each solvent system studied. At the concentrations of $\mathrm{Ni(cyclam)}^{2+}$ used it was not possible to observe the reported 666-nm band, and the 337-nm band absorbed only weakly. Therefore, the square-planar 447-nm absorption band only was utilized, together with the assumptions that (i) only the square-planar configuration exists in 6 M $NaClO_4$ and that (ii) the observed extinction coefficient limit, ϵ_{limit} = 63 M^{-1} cm^{-1}, for $\mathrm{Ni(cyclam)}^{2+}$ in 6 M $NaClO_4$ could be used for the square-planar absorptions in any solute system to calculate the fractions of the two configurations in our solutions.

C. MSR: Muonium Spin Rotation Measurements. Low-energy, 4.1 MeV, muons were provided through the M20 channel at the TRIUMF facility. The muon beam was made to strike a Mylar-windowed Teflon target containing approximately 80 mL of sample, D in Figure 1. As the range of these muons is 0.15 g cm^{-2}, almost all of the incident muons were stopped in the sample. Magnetic coils mounted traverse to the muon beam and centered on the target provided a field of 8 G, giving a muonium precession frequency of 11.1 MHz. All samples were bubbled with high-purity He previous to and during the run to remove dissolved oxygen. In the cases of the ammonia-solvent samples, the prebubblers contained aqueous ammonia in the same concentration as the target sample to minimize loss through volatilization.

Table I. Spectral Data at 447 nm for 0.50 × 10^{-3} M $\mathrm{Ni(cyclam)}^{2+}$ in Various Aqueous Solutions[a]

solution	absorbance[b]	F_D[c]	F_P[d]	K^1
6 M $NaClO_4$	0.315	1.0	0	~10^2
1 M $NaClO_4$	0.283	0.90	0.10	9
0.5 M Na_2SO_4	0.242	0.77	0.23	3.4
pure water	0.220	0.70	0.30	2.3
0.8 M NH_3	0.119	0.38	0.62	0.61
6 M NH_3	0.019	0.06	0.94	0.06

[a] These data are then used to evaluate the fractions present as diamagnetic (F_D) and paramagnetic (F_P) complexes, and the equilibrium constant K^1 of eq 4. [b] Average values from several measurements. [c] It is assumed that the complex is some 99% in the diamagnetic form in 6 M $NaClO_4$, as in ref 9 and 13. F_D was then calculated from the absorbance using $A = \epsilon bc$, with ϵ = 63 M^{-1} cm^{-1} (Figure 3), b = 10-cm path length, and c(total) = 0.5 × 10^{-3} M. [d] $F_P = 1 - F_D$.

The MSR data histograms were computer analysed using a χ^2-minimization fitting program (MINUIT) which, after removal of background and muon decay, uses eq 2. In this equation A_D and A_M are the muon

$$A(t) = A_D \cos(\omega_D t + \phi_D) + A_M \exp(-\lambda t) \cos(\omega_M t - \phi_M) \qquad (2)$$

and muonium signal amplitudes, ω_D and ω_M are their precession frequencies, ϕ_D and ϕ_M are their initial phases, and λ is the muonium decay constant. Figure 2 shows typical data histograms. From λ the bimolecular rate constant, k_M, for the reaction between Mu and the solute of concentration [S] can be calculated using eq 3. The decay constant for

$$\lambda = \lambda_0 + k_M[\mathrm{S}] \qquad (3)$$

the solvent, λ_0, has several values in this study. For pure water at TRIUMF, λ_0 has been found to be (2.4 ± 0.6) × 10^5 s^{-1},[3-5] using one frequency fit and no coils to compensate for external fields. Because NH_3(aq), Na_2SO_4, and $NaClO_4$ were added to the solutions to shift the paramagnetic-diamagnetic equilibrium, decay constants for these solvent systems were also determined. In addition, the background Mu decay rate (λ_0) was obtained for PF_6^- and for uncomplexed cyclam itself. Ni^{2+} in NH_3 solution was also studied for comparison purposes.

Each experiment yields two histograms, for the right and left positron detectors. These independent histograms each yield a λ, and both of these were normally plotted against solute concentration in order to obtain the best value for k_M. The slope of the best straight line is taken to be k_M. It was found that for ClO_4^- solutions more concentrated than 1 M, Mu reacted so rapidly that λ_0 dominated the measurement. Therefore, it was not possible to study nickel cyclam at 6 M $NaClO_4$ where it should be 100% diamagnetic. Na_2SO_4 was found to be much less reactive toward Mu, and it was used in place of $NaClO_4$ in some experiments.

Results

Figure 3 depicts the Beer-Lambert plot for $\mathrm{Ni(cyclam)}^{2+}$ in 6 M $NaClO_4$. The extinction coefficient limit, ϵ_{limit}, was calculated to be 63 M^{-1} cm^{-1}, which agrees nicely with the reported value of 64.5 M^{-1} cm^{-1}.[9] Using 63 M^{-1} cm^{-1}, the fractions of the paramagnetic and diamagnetic conformations in each solvent system were estimated and are listed in Table I, together with K^1 calculated therefrom.

Figure 2 shows examples of μSR histograms from which the values of λ reported in Table II were obtained by computer-fitting to eq 2. The listed values of λ are the average of the two histograms values obtained by the independent detectors for each concentration. Plots of λ against total Ni-complex concentration, [Ni], were made for each type of solution, with the slopes being given in the last column of Table II. It can be seen that the reaction rate increases as K^1 decreases. Data for reactions with Ni^{2+} and $\mathrm{Ni(NH_3)_4}^{2+}$ are given in Table III for comparison purposes. Both of these are paramagnetic.

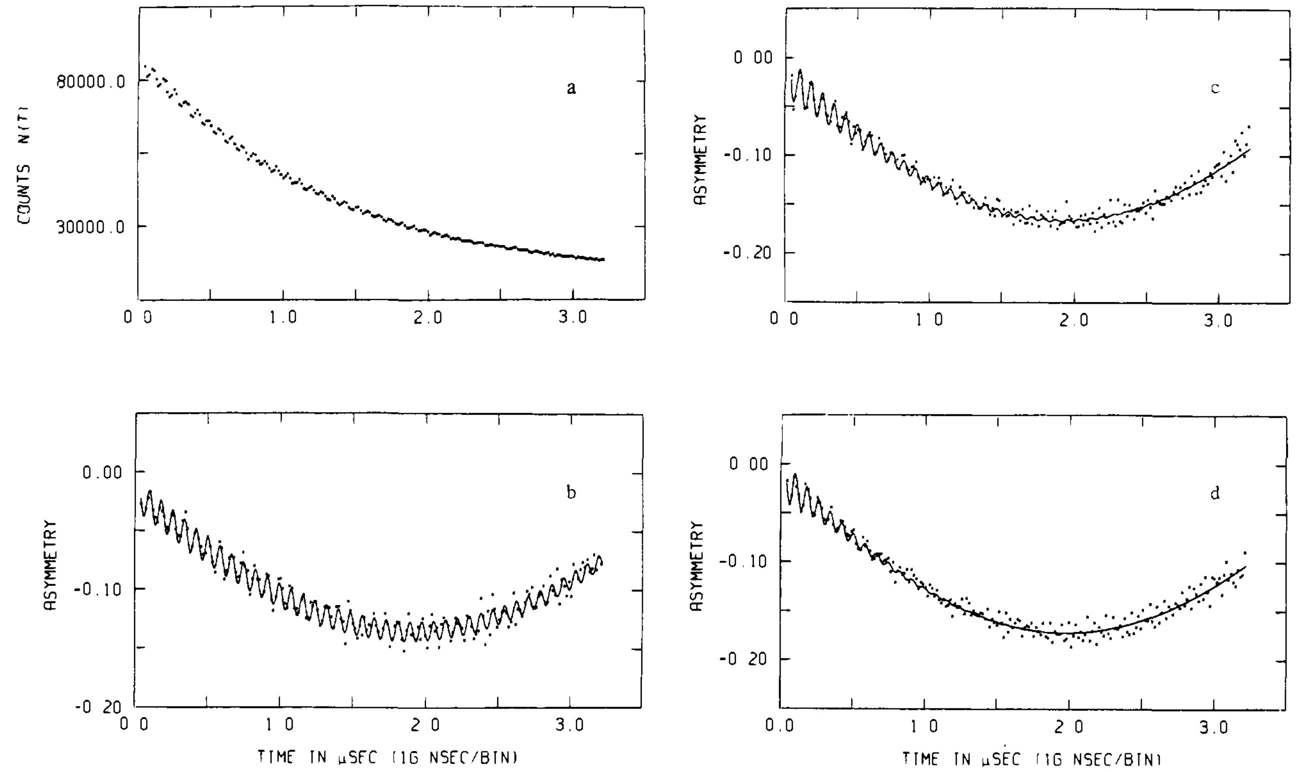

Figure 2. Typical μSR histograms: (a) raw data for pure water in an 8-G magnetic field; (b) the data of (a) fitted to eq 2; (c and d) data for 0.05 and 0.10 mM Ni(cyclam)$^{2+}$ in 6 M NH_3 solution, respectively, fitted to eq 2.

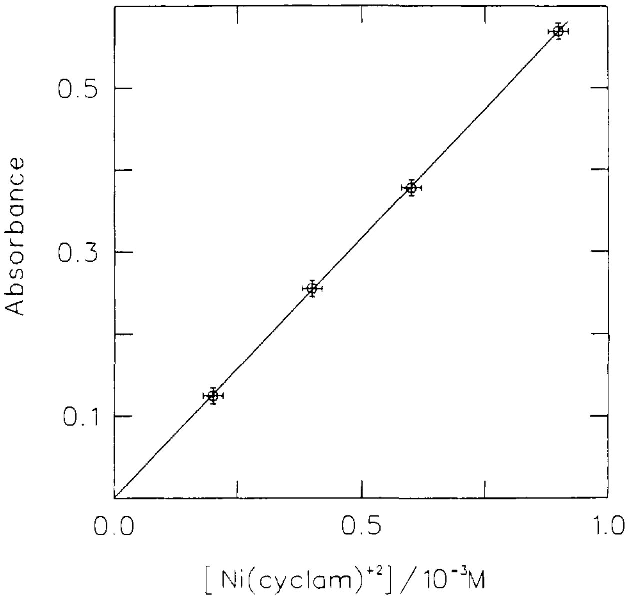

Figure 3. Beer–Lambert law plot of the Ni(cyclam)$^{2+}$ in 6 M $NaClO_4$ (all diamagnetic) at a wavelength of 447 nm, from the slope of which one obtains ϵ_{limit} = 63 M^{-1} cm^{-1}.

Table II. Kinetic Data for the Various Aqueous Solutions Studied[a]

solution	[Ni][b]/ 10^{-3} M	$\lambda/10^6$ s^{-1} [c]	$\{(\lambda - \lambda_0/[Ni]\}/10^{10}$ M^{-1} s^{-1} [d]
1 M $NaClO_4$	0	0.33 ± 0.05 (λ_0)	
	0.15	1.10 ± 0.1	
	0.30	1.62 ± 0.3	0.47
0.5 M Na_2SO_4	0	0.25 ± 0.05 (λ_0)	
	0.12	1.49 ± 0.1	
	0.24	2.53 ± 0.2	0.98
pure water	0	0.25 ± 0.05 (λ_0)	
	0.12	1.64 ± 0.2	
	0.20	3.18 ± 0.2	1.3
0.8 M NH_3	0	0.25 ± 0.05 (λ_0)	
	0.08	1.48 ± 0.2	
	0.12	2.35 ± 0.2	1.8
6 M NH_3	0	0.50 ± 0.05 (λ_0)	
	0.05	1.65 ± 0.1	
	0.10	2.45 ± 0.3	2.0

[a] The values of λ are those obtained from the μSR fits. λ_0 corresponds to values of λ when there was no complex present ([Ni] = 0). [b] [Ni] = total nickel complex concentration ([P] + [D]). [c] Statistical errors are invariably less than those given which represent the spread between left and right detectors. [d] Realistic errors are of the order of ±25%.

Table III. Kinetic Data for Ni^{2+}, $Ni(NH_3)_4{}^{2+}$, and the cyclam (no Ni) Blank

solution	$\lambda/10^6$ s^{-1}	k_M/M^{-1} s^{-1}
$NiSO_4$ (<1 mM)		1.7 × 10^{10} (ref 16)
0.3 mM $NiSO_4$ + 1 M NH_3	4.8	1.5 × 10^{10}
0.12 M cyclam (no Ni ion)	0.25	<10^7

Discussion

Not unexpectedly, the muonium rate constant was found to increase markedly as the percentage of paramagnetic species increased. But, as it was not possible to make a direct measurement of k_M in systems consisting purely of each form of the complex, it is necessary to try to estimate these limiting values from the equilibria data provided by the optical spectra.

If one assumes that intermediate complexes of five-coordination are unimportant, then the relevant equilibria can be represented simply by eq 4, where the value of K^1 changes (from ~9 to ~0.06) with the constituents of the solution, including the presence of

$$\text{P(para)} \xrightleftharpoons{K^1} \text{D(diamagnetic)} \qquad (4)$$

the inert salts ($NaClO_4$ and Na_2SO_4). Muonium reacts with P and D with different rate constants (k_M), represented in

$$\text{Mu} + \text{P} \xrightarrow{k_P} \text{products} \qquad (5)$$

$$\text{Mu} + \text{D} \xrightarrow{k_D} \text{products} \qquad (6)$$

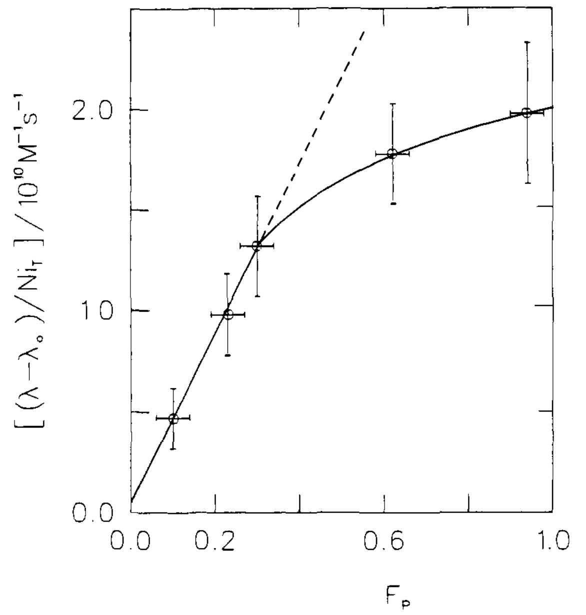

Figure 4. Plot of the observed rate constant, given as $(\lambda - \lambda_0)/[Ni]$, as a function of the fraction of nickel-complex species in the paramagnetic state (F_P). [Ni] is the total Ni complex in solution. The two highest data points were obtained in aqueous NH_3 solution, where the axial ligands will be NH_3, whereas the lower three points correspond to H_2O ligands in the axial position of the paramagnetic component.

by k_p and k_D. The rate of decay of Mu as measured by MSR is given in

$$-d[Mu]/dt = k_P[P][Mu] + k_D[D][Mu] = k^1[Mu] \quad (7)$$

where $k^1 = k_P[P] + k_D[D]$ is the overall observed pseudo-first-order decay constant of Mu, equal to $(\lambda - \lambda_0)$, for each type of solution containing the complex at total concentration [Ni]. This mechanism leads directly to

$$\lambda - \lambda_0 = k_P[Ni]F_P + k_D[Ni](1 - F_P) \quad (8)$$

where F_p is the fraction of complex ions in the paramagnetic form ($F_P = (1 + K^1)^{-1}$). Therefore, a plot of $(\lambda - \lambda_0)/[Ni]$ against F_p, as provided in Figure 4, should give k_D as its intercept and $(k_P - k_D)$ as the slope.

Unfortunately, the plot of Figure 4 is linear only over the lower third of F_P. Also the plot of the inverses of those same parameters was nonlinear. Nevertheless, the intercept of Figure 4 at $F_P = 0$ gives $k_D \leq 5 \times 10^8$ M^{-1} s^{-1}, which seems to be a reasonable value, being some 100-fold smaller than the diffusion-controlled limit. The reaction that does occur with the diamagnetic complex may be an inefficient chemical reduction of Ni(II) to Ni(I), which has a value for the H atom of 2×10^5 M^{-1} s^{-1}.[14] It is also possible that this is due to reaction with the cyclam ligand (such as abstraction of an H), since the background λ_0 in the blank cyclam solution was indistinguishable from that in pure water (2.5×10^5 s^{-1}), but with the cyclam at 5×10^{-4} M this merely indicates that $k_M < 5 \times 10^8$ M^{-1} s^{-1}.

It is clear from Figure 4 that the reaction rate constant with the paramagnetic complex (k_P) greatly exceeds k_D. Based on the initial linear slope one obtains $k_P = (4.5 \pm 0.5) \times 10^{10}$ M^{-1} s^{-1}. Perhaps the falloff in the apparent value of k_P arises from the fact that NH_3 had to be added in order to induce the transition to a paramagnetic state for the two highest F_P points on Figure 4. This would then imply that k_P with NH_3 ligands was given by extrapolation in the plateau region at $\sim 2 \times 10^{10}$ M^{-1} s^{-1}, some 2.3 times smaller than with H_2O ligands.

There is also the possibility that the break from linearity in Figure 4 arises from the presence of a five-coordinate intermediate, which, like pentacyanonickelate(II),[15] could be diamagnetic. The overall equilibrium of eq 4 covers two sequential ligand displacements as in

$$Ni(cyclam)L_2^{2+} \rightleftharpoons Ni(cyclam)L_1^{2+} \rightleftharpoons Ni(cyclam)^{2+} \quad (9)$$

with each species having a characteristic rate constant for interaction with Mu. Furthermore, if these dynamic equilibria, which involve simple loss and addition of NH_3 or H_2O ligands, occur on the timescale of a caged encounter with Mu, then the kinetics may be expected to be somewhat complicated. The caging effect of the water structure may force a typical encounter of Mu with a complex ion to last tens or hundreds of picoseconds, which may be comparable to the period of ligand exchange at molar and higher concentrations.

We are inclined to the view that k_P for the interaction of Mu with the paramagnetic complex is $\sim 4.5 \times 10^{10}$ M^{-1} s^{-1} when H_2O is the axial ligand and $\sim 2 \times 10^{10}$ M^{-1} s^{-1} for NH_3 as the axial ligand. One can see from the data of Table III that paramagnetic Ni^{2+} reacts at $>10^{10}$ M^{-1} s^{-1} by spin exchange[4,16] and that, if anything, NH_3 ligands reduce the rate. In any case these values are within a factor of 2 of the expected diffusion-controlled rates for Mu reactions in water.[16] This corroborates the conclusions inferred about spin-exchange interactions deduced from studies of different ions in various spin states.[4]

Conclusions

These results conform to our basic expectations: namely, that diamagnetic Ni(II) salts, which are not easily reducible and which contain unreactive ligands, barely react with Mu ($k_D \leq 5 \times 10^8$ M^{-1} s^{-1}). In sharp contrast to this, with the same oxidation state and virtually the same ligands, but with the nickel's d electrons making the complex paramagnetic because of the changed coordination, their reaction with Mu occurs at about the diffusion-limited rate. This strong dependence of the rate on the spin state of the complex confirms that it is an electron spin-exchange interaction of Mu, as in

$$^{T}Mu(\Uparrow\uparrow) + P(\downarrow) \rightarrow {}^{S}Mu(\Uparrow\downarrow) + P(\uparrow) \quad (10)$$

that is taking place in the presence of a paramagnetic solute. When the electrons of the solute are all spin-paired, as in diamagnetic species, then no such exchange occurs.

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Registry No. Mu, 12587-65-4; $[Ni(cyclam)]^{2+}$, 46365-93-9.

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[14] M. Anbar, Farhataziz and A. B. Ross, *Natl. Stand. Ref. Data. Ser., Natl. Bur. Stand.*, No. 51 (1975).

[15] R. A. Penneman, R. Bain, G. Gilbert, L. H. Jones, R. S. Nyholm, and G. K. N. Reddy, *J. Chem. Soc.*, 2266 (1963).

[16] B. W. Ng, Y. C. Jean, Y. Ito, T. Suzuki, J. H. Brewer, D. G. Fleming, and D. C. Walker, *J. Phys. Chem.*, **85**, 454 (1981).