pyridines, which have both bonding and antibonding π orbitals, may, depending on other circumstances, lead either to a larger or smaller crystal field splitting than would be observed with a (hypothetical) ligand which is otherwise similar but incapable of π bonding. Since the direction of the spectral effects resulting from π interaction cannot be simply predicted, the effect of removing such interaction is likewise in doubt.

For the 4-cyanopyridine derivative, the reduction path is not simple. Disappearance of Co(III) is not clearly first order in Co(III), as is observed with the other complexes. This system, in which reduction of the ligand may compete with reduction of Co(III),[2,9] is the subject of investigation now in progress.

Water Exchange between Solvent and Aquoethylenediaminenickel(II) Complexes

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Abstract: Water exchange rates with $Ni(H_2O)_6^{2+}$ (pH 6), $Ni(H_2O)_4(en)^{2+}$, and $Ni(H_2O)_2(en)_2^{2+}$ are reported. The k_1 (25°, sec^{-1}) values for a particular water molecule are 4.4 ($\pm$0.2) $\times 10^4$, 4.4 ($\pm$0.2) $\times 10^5$, and 5.4 ($\pm$0.3) $\times 10^6$, respectively. The corresponding ΔH^* values are 10.3 $\pm$ 0.5, 10.0 $\pm$ 0.5, and 9.1 $\pm$ 0.5 kcal mole^{-1}. Scalar coupling constants (A/h) in the same order are 2.2 ($\pm$0.4) $\times 10^7$, 2.2 ($\pm$0.2) $\times 10^7$, and 2.3 ($\pm$0.2) $\times 10^7$ cps. T_{1e} for $Ni(H_2O)_2(en)_2^{2+}$ is *ca.* 2.5 $\times 10^{-12}$ sec. Some discussion of the effects of water substitution on lability of the remaining water is given.

The studies reported here are in continuation of investigations of the effects on water exchange rates caused by substitution in the aquonickel(II) ion.[2–4] Using ^{17}O nmr, direct measurements of these effects can be made. In addition to interest in the effects themselves, comparisons with substitution rates in these ions may shed further light on the substitution mechanisms. The ethylenediamine complexes of nickel(II) are reasonably well characterized and lend themselves well to such studies.

Experimental Section

The nmr equipment previously described[5] was used with the important modification that a Varian 24.6-kG magnet with a field inhomogeneity of *ca.* 0.05 G was employed. The ^{17}O resonance was ordinarily observed at 14.19 MHz. Sample temperatures were controlled to $\pm$0.10° using an ethanol circulation system below 50° and to $\pm$0.3° above 50° using a thermostated air flow. Signal enhancement was obtained using a Fabri-Tek LSH 1024 point signal averager.

The water used was enriched to 7 atom % ^{17}O (56.3% ^{18}O and normal H content) and made by YEDA R & D Co. Ltd., Rehovoth, Israel. It was distilled *in vacuo* for reuse. Other reagents used were Mallinckrodt AR $Ni(NO_3)_2 \cdot 6H_2O$, Baker Analyzed ethylenediamine (en) (99.6%), and B & A reagent HNO_3.

Solutions were prepared from measured amounts of all reagents. The ionic strength was fixed by the nickel salt, and nitric acid concentrations and varied from 0.51 to 0.53 *M*. Measurements of pH were made using a Beckman Research Model meter. Solution composition calculations were done using the known starting amounts of all reagents. The measured pH's were only used to obtain estimates of species concentrations for use in the computer program based on SECANT 1620.[6] Values used for acid dissociation constants of enH^+, enH_2^{2+}, and the nickel(II)–en complex constants were those of Basolo and Murmann[7] at μ = 0.5. Effects of temperature change on the various K_{eq} values were calculated from the calorimetric enthalpy values (assumed independent of temperature) of Holmes and Williams[8] at μ = 0.3. Results of the computations indicated that solution compositions were essentially constant ($\pm$1%) over the temperature range used. The relative amounts of the various nickel species are given in Table I for the solutions used.

Treatment of Data and Results

The complexities of the solutions and the nmr phenomena involved required a moderately involved treatment of the data. Detailed basic considerations have been given previously.[5,9,10] The observed line-broadening data were treated in terms of the quantity $T_{2p}' \equiv 2M(Ni)/\gamma\Delta'$ where M(Ni) refers to total nickel concentration, γ is the magnetogyric ratio for ^{17}O (3628 G^{-1} sec^{-1}), and $\Delta' = W_{obsd} - W_0$, where W_{obsd} is the full nmr line width at half-maximum absorption (absorption curve) for solutions containing Ni(II) and W_0 is the same quantity for the appropriate blank not containing Ni(II). The observed width of the blank varied from 0.16 to 0.26 G as a function of temperature. The data are listed in Table II and plotted as $\log T_{2p}'$ *vs.* $10^3/T$ in Figure 1. Measured chemical shifts are treated in terms of the quantity $Q(\text{obsd}) = TSM(H_2O)/M(Ni)$, where T is the absolute temperature, S is the chemical shift in parts per million relative to the $H_2{}^{17}O$ blank, and the molarities refer to total concentrations. Values

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[1] To whom inquiries should be addressed. This work supported by U.S.A.E.C., Contract No. AT(54-1)-2040, and is Report No. RLO-2040-9.

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Table I. Solution Compositions

Solution	Total Ni(II), *M*	Total en, *M*	HNO_3 added, *M*	pH obsd	pH calcd	% Ni-$(H_2O)_6^{2+}$	% Ni-$(H_2O)_4en^{2+}$	% Ni-$(H_2O)_2(en)_2^{2+}$	% Ni(en)$_3^{2+}$
I	9.72×10^{-2}	0.216	0.240	5.59	5.75	19.0	64.3	16.3	0.4
II	9.57×10^{-2}	0.260	0.237	5.85	6.04	3.9	48.4	46.3	1.4
III	9.42×10^{-2}	0.303	0.233	6.32	6.38	0.3	17.0	71.9	10.8
IV	1.98×10^{-1}	. . .	. . .	6.20	. . .	100.0	. . .	. . .	. . .

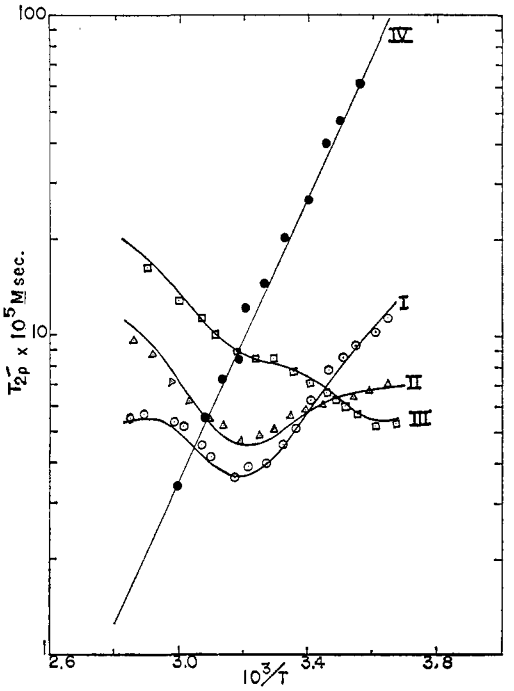

Figure 1. Semilogarithmic plot of T_{2p}' vs. $10^3/T$ for solutions I-IV. Solid lines are calculated from determined parameters.

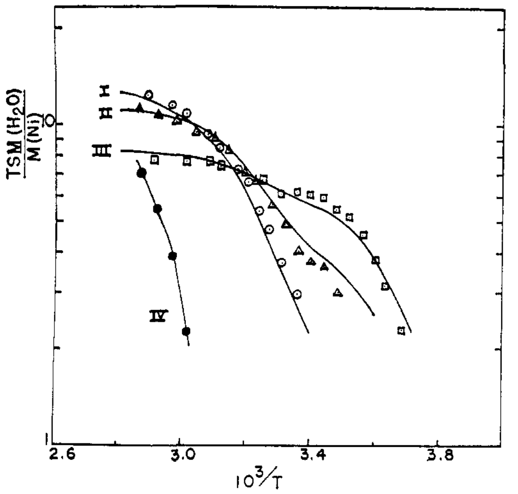

Figure 2. Semilogarithmic plot of $TSM(H_2O)/M(Ni)$ vs. $10^3/T$ for solutions I-IV. Solid lines are calculated from determined parameters.

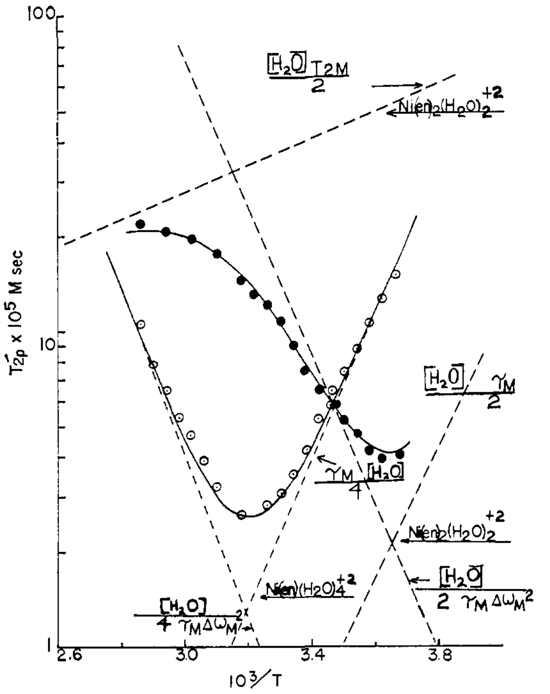

Figure 3. Semilogarithmic plot of T_{2p}' function for individual species. Dashed lines are used in the curve-fitting process. Solid lines are calculated from determined parameters.

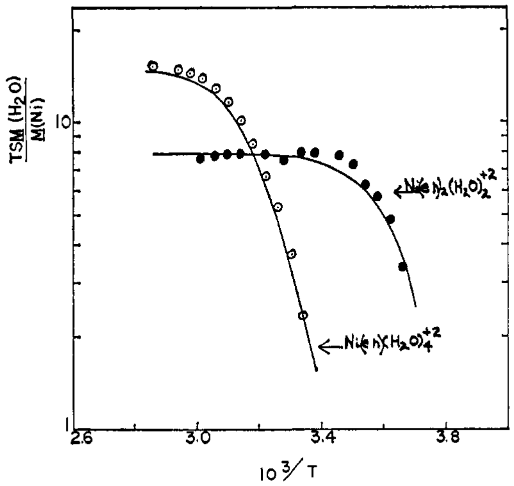

Figure 4. Semilogarithmic plot of shift function for individual species. Solid lines are calculated from determined parameters.

are given in Table II and plotted in Figure 2. The first step in treating these results was to assume that the observed line broadenings and shifts were additive; *i.e.*, $1/T_{2p}'(\text{obsd}) = X_1/T_{2p}'(1) + X_2/T_{2p}'(2) + X_3/T_{2p}'(3)$ and $S(\text{obsd}) = X_1S(1) + X_2S(2) + X_3S(3)$, where X_1 is the mole fraction of $Ni(H_2O)_6^{2+}$, X_2 is the mole fraction of $Ni(H_2O)_4en^{2+}$, X_3 is the mole fraction of $Ni(H_2O)_2(en)_2^{2+}$, $T_{2p}'(1)$ and $S(1)$ are molar line broadenings and shifts due to $Ni(H_2O)_6^{2+}$, and so on. Independent measurements showed that solutions of $Ni(en)_3^{2+}$ alone did not produce either line broadenings or shifts at the concentrations used here (0.1 *M*). Knowing the solution compositions and the independently measured values for $Ni(H_2O)_6^{2+}$, the simultaneous linear equations were solved at each temperature using a standard matrix inversion computer method. The resolved curves for the en species are shown in Figures 3 and 4. Inspec-

Table II

(A) Line-broadening data			(B) Chemical shift data		
Temp, °C	Δ′, G	T_{2p}' × 10^5, M sec	Temp, °C	Shift, ppm	$TSM(H_2O)/M(Ni)$
		Solution I			
1.3	0.47	11.4	26.0	16.9	2.88
4.4	0.52	10.3	30.1	21.2	3.67
8.4	0.58	9.3	33.4	26.5	4.64
11.7	0.63	8.5	36.3	30.3	5.36
15.4	0.69	7.7	39.2	37.1	6.61
20.3	0.85	6.2	42.5	40.0	7.20
24.1	1.04	5.1	48.3	45.8	8.40
28.0	1.17	4.6	51.9	49.6	9.21
32.7	1.34	4.0	59.4	56.8	10.80
37.6	1.42	3.8	64.2	59.2	11.41
41.7	1.51	3.5	73.0	62.1	12.28
50.3	1.30	4.1			
51.9	1.18	4.5			
59.4	1.03	5.2			
62.0	1.02	5.2			
73.0	0.97	5.5			
77.0	0.98	5.4			
		Solution II			
1.2	0.75	7.0	12.1	14.4	2.39
5.6	0.79	6.6	15.4	17.8	2.98
10.0	0.84	6.3	18.7	21.2	3.58
13.9	0.84	6.3	22.1	21.7	3.71
17.5	0.87	6.1	25.5	23.1	4.01
21.3	0.91	5.8	29.1	27.9	4.90
25.5	0.96	5.5	33.3	31.3	5.56
30.2	1.06	5.0	37.5	46.6	6.60
35.3	1.09	4.8	41.3	38.5	7.03
40.7	1.14	4.6	46.4	44.3	8.21
45.6	1.01	5.2	51.0	47.7	8.96
50.1	0.97	5.4	56.5	49.6	9.48
56.5	0.85	6.2	62.7	53.0	10.32
62.7	0.75	7.0	69.5	54.4	10.82
69.5	0.61	8.6	76.3	54.9	11.12
76.3	0.56	9.4			
		Solution III			
−0.4	0.98	5.3	0.9	14.0	2.25
1.2	1.02	5.1	3.0	19.3	3.13
3.9	1.00	5.2	5.7	22.6	3.72
8.1	0.91	5.7	8.7	27.0	4.47
11.9	0.86	6.0	12.0	30.3	5.09
16.3	0.78	6.7	15.2	31.8	5.40
20.5	0.73	7.1	18.3	33.7	5.79
25.1	0.69	7.8	22.4	34.2	5.96
30.1	0.62	8.3	25.9	34.7	6.11
35.9	0.61	8.5	30.1	33.7	6.01
41.5	0.59	8.8	35.9	36.6	6.66
48.0	0.52	10.0	41.5	38.1	7.05
52.2	0.46	11.2	48.0	39.0	7.39
60.3	0.41	12.8	52.2	40.0	7.66
71.5	0.31	16.3	60.3	39.5	7.76
			71.5	38.5	7.86
		Solution IV			
7.6	0.18	61.5	60.2	25.3	2.23
11.9	0.23	46.3	64.5	43.4	3.87
15.9	0.28	39.1	70.0	60.3	5.46
20.8	0.41	26.6	75.3	77.2	7.10
25.3	0.54	19.9			
32.6	0.75	14.3			
38.4	0.90	12.0			
41.3	1.29	8.4			
45.8	1.52	7.1			
51.0	2.00	5.4			
60.5	3.22	3.4			

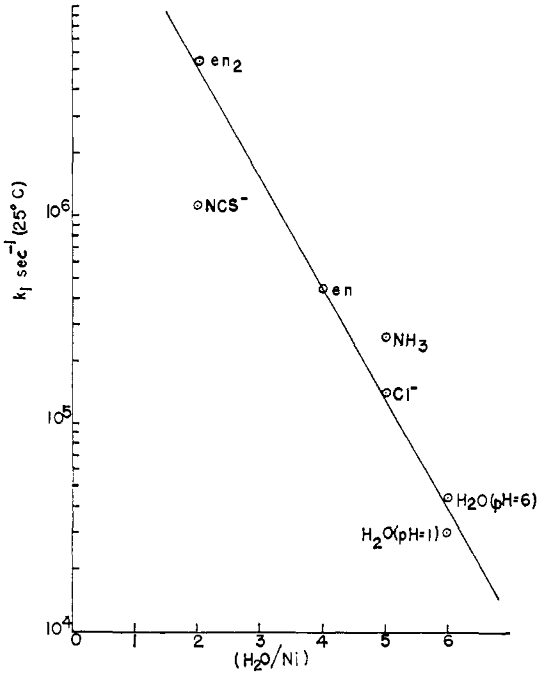

Figure 5. Semilogarithmic plot of k_1 (25°) for water exchange *vs.* H_2O/Ni in $Ni(H_2O)_x(L)_{6-x}$ species.

tion of these curves suggested that the results of $Ni(H_2O)_4en^{2+}$ could be accounted for by a $\Delta\omega$ mechanism.[9] The $Ni(H_2O)_2(en)_2{}^{2+}$ data suggested combined $\Delta\omega$ and T_{2M}[4,9] processes. The parameters of interest were obtained by a curve-fitting procedure which yielded those parameters best accounting for the independently measured shift and broadening data as a function of temperature. The equations for line broadening involved are: for $Ni(H_2O)_4en^{2+}$, $T_{2p}'(2) = [H_2O]/4(\tau_M(2) + 1/\Delta\omega_M{}^2(2)\tau_M(2))$; for $Ni(H_2O)_2(en)_2{}^{2+}$, $T_{2p}'(3) = [H_2O]/2[(\tau_M(3) + 1/\Delta\omega_M{}^2(3)\tau_M(3))/(1 + 1/T_{2M}(3)\tau_M(3)\Delta\omega_M{}^2(3))]$. Here, τ_M is the mean lifetime for exchange of a bound water molecule (n[Ni complex]/R where n is the number of water molecules in the relevant complex and R is the exchange rate), $\Delta\omega_M$ is $\omega_M - \omega_0$ where ω_M is the resonance frequency (rads/sec) for a bound water molecule in the appropriate complex and ω_0 that for solvent water, and T_{2M} is the T_2 parameter for a bound water molecule in $Ni(H_2O)_2(en)_2{}^{2+}$. Also, $\tau_M = 1/k_1$ where k_1 is the pseudo-first-order rate constant for exchange of a *particular water molecule.* Taking $k_1 = (kT/h)\cdot e^{-\Delta H^*/RT}e^{\Delta S^*/R}$ the temperature dependence is introduced. The shift equations used are: $Q(2) = 4T\cdot\Delta\omega_M(2)/\omega_0(1/[1 + \Delta\omega_M{}^2(2)\tau_M{}^2(2)])$ and $Q(3) = 2T\Delta\omega_M(3)/\omega_0(1/[1 + \Delta\omega_M{}^2(3)\tau_M{}^2(3)])$ (where $Q(2) = TS(2)\cdot M(H_2O)$, $S(2)$ is the shift produced by 1 M $Ni(H_2O)_4en^{2+}$, etc.). Using a computer program which calculated T_{2p}' (obsd) and Q(obsd), the variables $k_1, \Delta H^*, \Delta S^*, T\Delta\omega_M$, and T_{2M} were varied about graphically estimated values to give the best visual fit to the data. The solid lines in the figures show the calculated curves and can be compared with the experimental points. The treatment is remarkably successful in view of the large number of potential error sources. Table *III* gives a summary of the derived parameters for the system. The scalar coupling constants (A/h) were calculated from $A/h = (T\Delta\omega_M/\omega_0)(3k/2\Pi)(\gamma_N/S(S + 1)g_{eff}\beta)$[11] using g_{eff} values for the nickel en species consistent with $\mu_{eff} = 3.10$.[12] The shift data used here to calculate A/h for $Ni(H_2O)_6{}^{2+}$ came from separate measurements at 15 kG.

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Table III. Kinetic and Nmr Parameters

	$Ni(H_2O)_6^{2+}$	$Ni(H_2O)_4en^{2+}$	$Ni(H_2O)_2(en)_2^{2+}$
Exchange rate (25°), M sec^{-1}	2.6×10^5	1.76×10^6	1.08×10^7
k_1, sec^{-1} (25°)	$(4.4 \pm 0.2) \times 10^4$	$(4.4 \pm 0.2) \times 10^5$	$(5.4 \pm 0.3) \times 10^6$
ΔH^*, kcal $mole^{-1}$	10.3 ± 0.5	10.0 ± 0.5	9.1 ± 0.5
ΔS^*, cal $mole^{-1}$ deg^{-1}	-5.2 ± 2	10 ± 2	2.6 ± 2
A/h, cps	$(2.2 \pm 0.4) \times 10^7$	$(2.2 \pm 0.2) \times 10^7$	$(2.3 \pm 0.2) \times 10^7$
T_{1e}, sec	...	...	$(2.5 \pm 0.5) \times 10^{-12}$
E_a for T_{1e}, kcal $mole^{-1}$	...	...	$+1.9 \pm 0.5$

The quantity T_{1e} for $Ni(H_2O)_2(en)_2^{2+}$ was calculated from $1/T_{2M} = {}^2/_3 S(S + 1)(A/\hbar)^2 T_{1e}$[13] and E_a from the apparent temperature variation of T_{1e} (T_{1e} assumed equal to T_{2e}).

Discussion

It appears to us that the self-consistent results obtained justify a reasonable amount of confidence in the derived kinetic information. Our values for $Ni(H_2O)_6^{2+}$ at pH 6 are similar to those found by Connick and Fiat[14] at pH 1 (our k_1 is 4.4×10^4 compared to 3×10^4 sec^{-1} and ΔH^* is 10.3 compared to 10.8 kcal/mole). We find $k_1 = 3 \times 10^{-4}$ sec^{-1} at pH 1 also so the difference may well be real; certainly it is outside our estimated (precision) error. There appears to be a monotonic increase in k_1 (per H_2O molecule) with increasing substitution by en, ΔH^* decreasing slightly and ΔS^* increasing less regularly. The available data on water exchange in nickel complexes are shown in Table IV. Although the conditions of acidity and ionic strength are highly variable in these data, no large effects have been found upon varying these factors so that at least rough comparisons should be possible. In the series of ligands H_2O, NH_3, en, and $(en)_2$ the rate at 25° increases regularly (see Figure 5) without much change in ΔH^*. One might have expected somewhat different results (lower rates and a bend over at low H_2O/Ni) based on the studies of Margerum and Rosen.[15] These authors estimated water exchange rates from measurements on substitution reactions. Since various hard-to-test assumptions had to be made in their treatment, the lack of agreement is not surprising. The ^{17}O measurements are clearly of considerable importance in the understanding of substitution mechanisms. A comparison of the effects of charged *vs.* neutral ligands can only be roughly made as considerable uncertainty as to species exists. Often such comparisons have been made at a single temperature. That such a comparison is dubious is at least suggested by the $Ni(H_2O)_2(NCS)_4^{2-}$ and $Ni(H_2O)_2(en)_2^{2+}$ data. The k_1 values are similar, but ΔH^* certainly varies. Much more work is needed in this area.

Table IV. Comparisons of Water Rates

k_1 (25°)	System	A/h	ΔH^*
1.4×10^5	$Ni(H_2O)_5Cl^+$–7 m LiCl[a]	3.5×10^7	8 ± 1
2.6×10^5	$Ni(H_2O)_5NH_3^{2+}$[b]	...	8 ± 1
1.1×10^6	$Ni(H_2O)_2(NCS)_4^{2-}$[c]	2.0×10^7	6 ± 1
3.0×10^4	$Ni(H_2O)_6^{2+}$ pH 1[d]	1.9×10^7	10.8 ± 0.5
4.4×10^4	pH 6	2.2×10^7	10.3 ± 0.5
4.4×10^5	$Ni(H_2O)_4en^{2+}$	2.2×10^7	10.0 ± 0.5
5.4×10^6	$Ni(H_2O)_2(en)_2^{2+}$	2.3×10^7	9.1 ± 0.5

[a] Reference 3. [b] Reference 2. [c] Reference 4. [d] Reference 14.

The observation that $Ni(en)_3^{2+}$ does not produce shifts or line broadenings in $H_2{}^{17}O$ appears to rule out any stoichiometrically significant rapid processes in which one end of the ligand might come off.

Comparisons of the A/h values for ^{17}O in the various en species shows a remarkable similarity. This may suggest that the bonding to water is not greatly changed. The relatively constant values for ΔH^* may reflect this also.

The estimated T_{1e} value for $Ni(H_2O)_2(en)_2^{2+}$ (2.5×10^{-12} sec) is similar to that given by Morgan and Nolle[16] (3.2×10^{-12} sec) for $Ni(H_2O)_6^{2+}$ and our estimated value for $Ni(H_2O)_2(NCS)_4^{4-}$ (1.4×10^{-12} sec). The value given in ref 4 should be divided by 2 as a factor of 2 is missing in the T_{2M}^{-1} equation given there.

We plan to continue similar studies using other polyamines as well as charged ligands. It can reasonably be expected that some interesting details will be exposed.

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