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Water-Exchange Studies by Oxygen-17 Nuclear Magnetic Resonance on Nickel(II) Complexes with Diethylenetriamine, Triethylenetetramine, and Tetraethylenepentamine

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Oxygen-17 NMR studies were made on aqueous solutions containing $Ni(dien)(H_2O)_3^{2+}$, $Ni(trien)(H_2O)_2^{2+}$, and $Ni(tetren)(H_2O)^{2+}$. The scalar coupling constants (A/h) based on the above formulas are 2.27 ± 0.04, 2.25 ± 0.32, and 2.52 ± 0.03 × 10^7 Hz, respectively. T_{2M} values and temperature coefficients are given. The Ni–dien system shows at least two water-exchange rates which are not well resolved. Suggested parameters are as follows: two fast waters, $k_1 = 3 \times 10^6\ s^{-1}$, $\Delta H^{\ddagger} = 9$ kcal/mol, $\Delta S^{\ddagger} = 2$ eu; "slow" water, $k_1 = 4 \times 10^5\ s^{-1}$, $\Delta H^{\ddagger} = 11$ kcal/mol, $\Delta S^{\ddagger} \simeq 3$ eu. For Ni–trien only one exchange rate is seen with $k_1 = (5.7 \pm 1.6) \times 10^5\ s^{-1}$, $\Delta H^{\ddagger} = 8.2 \pm 0.9$ kcal/mol, and $\Delta S^{\ddagger} = -4.6 \pm 3.6$ eu. For Ni–tetren, $k_1 = (1.12 \pm 0.22) \times 10^7\ s^{-1}$, $\Delta H^{\ddagger} = 8.6 \pm 0.7$ kcal/mol, and $\Delta S^{\ddagger} = 2.5 \pm 2.5$ eu. Comparisons with net substitution rates are made.

Introduction

In earlier work[1] we have studied the effects of substitution of water in $Ni(H_2O)_6^{2+}$ by various ligands on the lability of the remaining water molecules. These studies are of interest for the effects themselves as well as for comparisons with net substitution reactions.[2] It seems clear[3] that the latter studies alone do not define or measure accurately the role of water lability in net chemical changes. The question of kinetic nonequivalence of water molecules is an interesting and important one which can be studied by the NMR method.[4] Furthermore, the question of ring-closure rates in multidentate ligand substitutions may be clarified by a knowledge of substitution effects on water lability.[4]

Experimental Section

The NMR spectrometer and techniques used have been described.[5] Lorentzian absorption curves for $^{17}OH_2$ are observed usually at ca. 11.5 MHz although the frequency may be varied to get more information.

Temperatures of the samples in the NMR probe are known to ca. ±0.1 °C.

The ^{17}O water was obtained from YEDA R and D Co., Ltd., Rehovot, Israel, and contains ca. 7 atom % ^{17}O (normalized in H content). The water is purified for each use by multiple distillations in vacuo.

The reagents used were Mallinckrodt Analytical reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ and Allied Chemical reagent grade nitric acid. Starting materials for purification of the ligands were Eastman Technical grade diethylenetriamine (dien) and J. T. Baker Technical grade triethylenetetramine (trien) and tetraethylenepentamine (tetren). The nickel salt was analyzed by titration of H^+ displaced from ion-exchange resin and corresponded accurately to $Ni(NO_3)_2 \cdot 6H_2O$. dien was vacuum distilled from sodium metal. A sample was analyzed by gas chromatography and showed no significant impurities. The trien was converted to the hydrosulfate which was recrystallized four times from water. The pure salt was treated with base and finally the trien was obtained by vacuum distillation. Gas chromatography confirmed the absence of water, dien, and tren (a common impurity). The tetren (linear isomer) was purified by the method of House and Garner[6] from chlorotetraethylenepentaminecobalt(III) tetrachlorozincate. After displacement of the ligand by cyanide ion, several extractions and filtrations were performed using methanol and evaporating the solutions on a steam bath before reextraction. Finally the ligand was distilled under vacuum taking a middle cut. It was not further characterized by us.

Treatment of Data

I. Equilibrium Considerations and Solution Compositions. A. dien System. Known amounts of $Ni(NO_3)_2 \cdot 6H_2O$ and dien were dissolved in $^{17}OH_2$. Equilibrium constant data from the literature[7] ($\mu = 0.1$) were used to calculate the species concentrations from the known amounts of starting materials over the temperature range 0–100 °C. A computer program devised by Johnson[8] was used. While the pH changes from ca. 5.5 to 6.5 over this range, the solution's complex compositions remain constant to ±2% with $[Ni(H_2O)_3dien^{2+}]$ being calculated as 0.128 M and $[Ni(dien)_2^{2+}]$ being 0.054 M. The concentration of $Ni(H_2O)_6^{2+}$ is $\leq 4 \times 10^{-4}$ M which is negligible for our purposes. Since $\mu = 0.6$ in our run, the solution composition was checked spectrophotometrically giving a composition agreeing well with the calculations using k's valid at $\mu = 0.1$.

B. trien System. The procedure of Kolski and Margerum[9] was used to prepare the trien–Ni^{II} complex. Extinction coefficients were measured at several wavelengths. The $^{17}OH_2$ solutions were prepared by evaporation of normal water from a stock solution in vacuo, adding phosphate buffer, reevaporating, and then adding enriched water. No change in the spectrum could be detected after this procedure. Since a square-planar form of the nickel complex has been reported to be present in aqueous solutions[10] a spectrophotometric study was made in the range 25–90 °C. Using the reported molar extinction coefficient of 70 it was found that the amount of planar complex ranged from ca. 2% at 23 °C to 10% at 90 °C ($\Delta H_f = 4.12$ kcal/mol). Corrections were then applied to obtain the concentrations of the octahedral form. It was assumed that the planar form had no bound water. The composition of the solution used for the NMR studies was 0.081 M in $Ni(trien)^{2+}$, pH ~7 ([buffer] ≈ 0.01 M). The blank was the same with no nickel present.

C. tetren System. A stock solution was prepared by adding tetren to a slight excess of nickel nitrate, adding sodium hydroxide, allowing nickel hydroxide to form, and then filtering. The NMR solutions were prepared by evaporation of the stock solution in vacuo and then adding the $^{17}OH_2$. Actual concentrations of complex were obtained spectrophotometrically. Composition of the solution used was 0.147 M in Ni(tetren). The blank was pH 7 buffer. It might be noted that in all these studies the broadenings were about 1 G so that the exact nature of blank was not critical.

II. NMR Considerations. A. General Data. The line-broadening and shift data are treated essentially by the equations of Swift and Connick.[11] The basic defining equations we have used (for two sites) are[1]

$$T_{2p}' \equiv \frac{2[M]}{\gamma \Delta} = \frac{[H_2O]\tau_M[(1/T_{2M} + 1/\tau_M)^2 + \Delta\omega_M^2]}{n[1/T_{2M}^2 + 1/T_{2M}\tau_M + \Delta\omega_M^2]}$$

$$Q \equiv \frac{TS[H_2O]}{[M]} = \frac{T\Delta\omega_M}{n\omega_0\tau_M^2[(1/T_{2M} + 1/\tau_M)^2 + \Delta\omega_M^2]}$$

The symbols used have the following significance: [M] is the

Table I. NMR Exchange Parameters

Complex	$10^{-5}k_1(25\ °C)$, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu[a]	$10^{-7}A/h$, Hz	$10^6T_{2m}(25\ °C)$, s	E_a, kcal/mol
$Ni(dien)(H_2O)_3{}^{2+}$	34 ± 6 4.4 ± 0.5	9.0 ± 0.7 10.7 ± 3	1.5 ± 2.8 3.1 ± 10	2.27 ± 0.04	6.13 ± 2.56	−1.2 ± 1.1
$Ni(trien)(H_2O)_2{}^{2+}$	5.7 ± 1.6	8.23 ± 0.92	−4.61 ± 3.65	2.25 ± 0.32	4.93 ± 0.13	−2.9 ± 0.6
$Ni(tetren)(H_2O)^{2+}$	112 ± 22	8.57 ± 0.66	2.46 ± 2.60	2.52 ± 0.03	6.08 ± 0.63	−2.08 ± 0.33
$Ni(H_2O)_6{}^{2+}$ [b]	3.07 ± 0.05	14.4 ± 0.2	10.3 ± 0.6	2.16 ± 0.03	2.23 ± 0.45	2.6 ± 0.4

[a] Calculated from k_1, the rate constant *per* H_2O. [b] G. Liu, unpublished work in this laboratory.

concentration of a particular aquo complex, γ is the magnetogyric ratio for ^{17}O (3628 G^{-1} s^{-1}), Δ is the line broadening ($\omega_{obsd} - \omega_0$) where ω_{obsd} is the full line width at half-maximum in the NMR absorption line for the paramagnetic solution and ω_0 the same quantity for the reference solution, [H_2O] is the concentration of solvent water, τ_M is the mean lifetime for exchange of a bound water molecule, n is the number of equivalent water molecules in the complex undergoing exchange, T_{2M} is the tranverse relaxation time for ^{17}O bound to the metal ion, $\Delta\omega_M = \omega_M - \omega_0$ where ω_M is the ^{17}O NMR frequency (radians/s) for a bound water and ω_0 the frequency for water in the diamagnetic reference solution (the relation is valid for dilute metal ion solutions), T is the absolute temperature, and S is the paramagnetic shift ($\omega_{obsd} - \omega_0)/\omega_0$.

If nonequivalent waters (kinetic sense) are present in a single species, we assume that the exchanges can be treated independently or in other words that the nonequivalent waters do not interconvert while bound (on an NMR time scale). The two-site approach is used for each kind of water. The data were fitted by a modified form of the program of Dye and Nicely.[12] The $T_{2p}{}^{11}$ and Q data were fitted *together* in a single process. Standard deviations are reported as given by the program. The usual Eyring equation approach was taken for k_1. For $1/T_{2M}$ an exponential temperature dependence (E_a) was assumed. The A/h values are calculated on the basis of μ_{eff} = 3.20 BM for the nickel complexes.

B. Ni–dien System. The line-broadening and shift data are shown in Figure 1. At first, attempts were made to treat these data with only a single rate of exchange, it having been shown that $Ni(dien)_2{}^{2+}$ produces no effects on $^{17}OH_2$. These attempts failed to reconcile *both* the shift and line-broadening data. Having decided that at least two rates were present, the problem of assigning them remains. The structure(s) of the complex is (are) not known in solution, facial and equatorial isomers being possible. In any case it is reasonable and simplest to assume two waters of one kind and one of another. The limiting Q value is consistent with a total of three waters undergoing rapid exchange at high temperature. We take the A/h values to be the same for all waters[1] which means $\Delta\omega_M$ is the same. Likewise T_{2M} will be the same as it is controlled by the single T_{1e} value and A/h. There will be a stoichiometric factor of 2 between the different waters which means that a decision between two "fast" rates and one "slow" rate or vice versa might be made at least in principle. With the data at hand the situation is not as clear-cut as one might hope. After much computer fitting we became convinced that the two fast–one slow case best accommodated the data and the derived parameters are given on this basis (Table I). The errors given are a reflection of the inevitable ambiguities in such a system.

C. trien System. Without a correction for the diamagnetic square-planar species the shifts observed fell off abnormally at high temperatures (consistent with a diamagnetic or nonexchanging form growing in). Upon correction, a limiting shift corresponding to two bound waters was obtained. Both the line-broadening and shift data (Figure 2) are accounted for by two equivalent water molecules. The complete Swift and Connick equations were used and the fitting is straightforward in this case. Results are given in Table I.

D. tetren System. The limiting shift value is consistent with one bound water (or a little more). The fit obtained is quite good (Figure 3); the errors in parameters reflect compensation effects among them as no clear τ_M region is present. The shift data are crucial in such cases. The T_{2p}' data at lower field

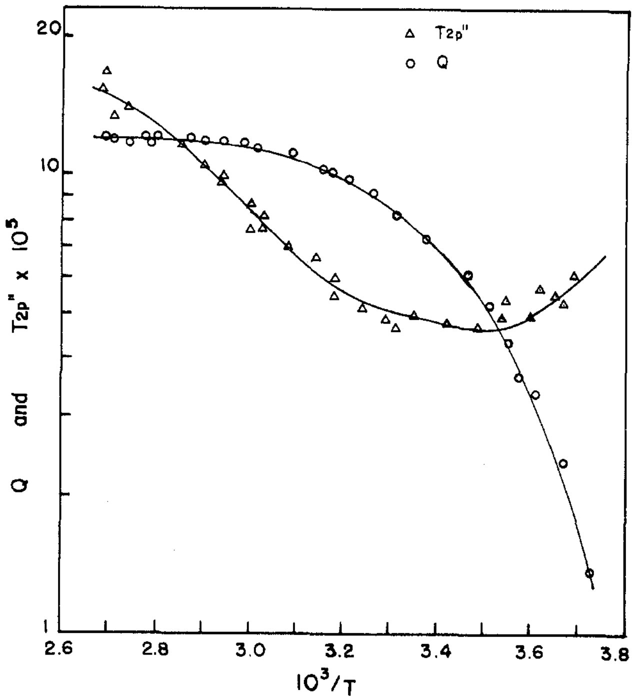

Figure 1. T_{2p}' and Q data for Ni–dien. Solid lines were calculated from computer fit.

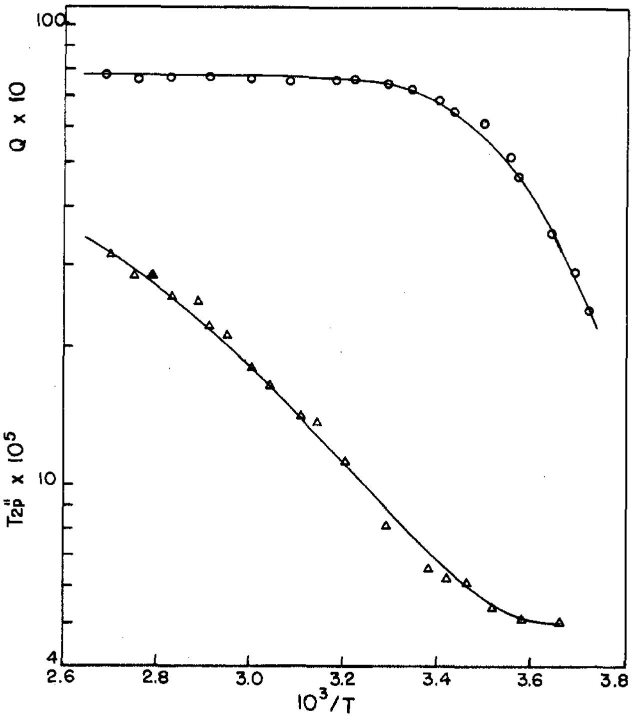

Figure 2. T_{2p}' and Q data for Ni–trien. Solid lines were calculated from computer fit.

Table II. K_{os} Values for Substitution (25 °C)

System		Substituting ligand					
		NH_3[a]	bpy[b]	phen[b]	terpy[b]	PADA[c]	Malonate(2−)[d]
Ni-dien	fast H_2O	0.013	0.0032	0.0064	0.002	0.014	2.5
	slow H_2O	0.10	0.025	0.050	0.016	0.11	19
Ni-trien		0.51 (8 °C)				0.044	>18

[a] Reference 14. [b] Reference 3. [c] Reference 15–pyridine-2-azo-*p*-dimethylaniline. [d] Reference 16.

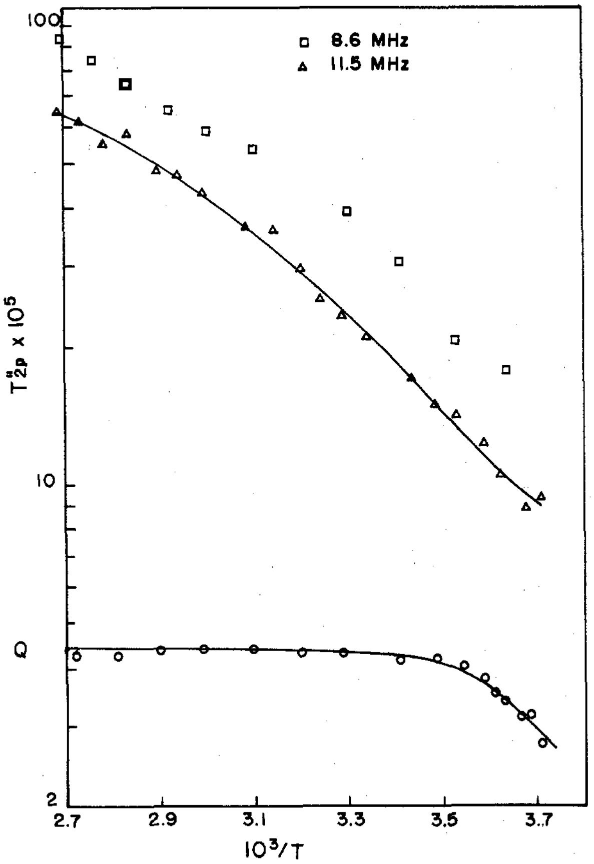

Figure 3. T_{2p}' and Q data for Ni–tetren. Solid lines were calculated from computer fit.

pretty much parallel the high-field data. The difference at low temperatures is consistent with a large contribution from the term $\Delta\omega^2\tau_M$ in the Swift–Connick equations. A larger change in field would be required to clarify the field dependence of T_{2M}.

Results and Discussion

The kinetic parameters reported earlier[1] for the dien and trien complexes differ somewhat from the current values obtained after more study. A general enhancement of the water-exchange rate constant is produced by the amine ligands but it appears to be an even less regular effect than it first seemed. For $Ni(H_2O)_6^{2+}$ our current best values give k_1(25 °C) = (3.07 ± 0.05) × 10^5 s^{-1}, $\Delta H^{\ddagger} = 14.4 \pm 0.2$ kcal/mol, and $\Delta S^{\ddagger} = 10.3 \pm 0.6$ eu in good agreement with Connick and Neely.[13] The $\Delta H^{\ddagger}$ values are considerably lowered for the amines while $\Delta S^{\ddagger}$ values are variably higher or lower.

Scalar coupling constants (A/h) are reasonably constant within the experimental errors for the three amine complexes and the aquo ion. With current more precise shift measurements, the nature of aqueous species can be more closely specified than in these studies and this should be an important contribution of the NMR studies in the future.

A lower T_{2M} value for the aquo complex relative to the ammines is expected due to a longer T_{1e}. The E_a values are reasonable.

The conclusion that $Ni(dien)(H_2O)_3^{2+}$ has at least two kinetically different kinds of water seems quite firm. The actual rate parameters, however, must be regarded as being quite uncertain. More precise data would help, but mainly limitations on the lowest available temperatures frustrate the obtaining of good parameters. It seems safe to conclude that a rate difference at 25 °C of about 10-fold is present. Substitution data for $Ni(dien)(H_2O)_3^{2+}$ are available. Using the Eigen–Wilkins[2] approach one can write that $k_f = K_{os}k_1$ where k_f is the bimolecular formation rate constant, K_{os} an outer-sphere complex constant, and k_1 the water-exchange rate constant. In Table II are shown calculated K_{os} values for various systems (no attempt to make symmetry corrections is made here). In the framework of the Eigen mechanism and *relative* K_{os} values the NH_3 substitution is fairly "normal" (allowing for a considerable spread in K_{os} values found) assuming that a "fast" water is replaced. For bpy, phen, and tren it is suggested that ring closure has been measured, with a preceding faster attachment of one end of the ligand. These aromatic ligands would not be expected to labilize remaining waters.[1] With PADA, and also with malonate, apparently the fast step is measured. Other factors may, of course, be involved in these fairly diverse systems.

For $Ni(trien)(H_2O)_2^{2+}$ all the substitution rates seem high (or K_{os} large). One might suppose that the trien complex is *trans*-diaquo and that ring closure could be slow giving a low value for PADA. Malonate seems to be anomalous on this basis. The $\Delta H^{\ddagger}$ for PADA (8.8 kcal/mol) is very similar to $\Delta H^{\ddagger}$ for H_2O exchange (8 ± 1 kcal/mol). We see no simple explanation for these observations.

With $Ni(tetren)(H_2O)^{2+}$, NH_3 substitution is too fast to measure.[14]

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Registry No. $Ni(dien)(H_2O)_3^{2+}$, 15662-52-9; $Ni(trien)(H_2O)_2^{2+}$, 15662-53-0; $Ni(tetren)(H_2O)^{2+}$, 15662-54-1; $Ni(H_2O)_6^{2+}$, 15365-79-4.

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