

The Kinetics of the Exchange Reaction of β, β', β'' -Triaminotriethylamine with Bis(β, β', β'' -triaminotriethylamine)neodymium(III)

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The exchange kinetics of β, β', β'' -triaminotriethylamine (tren) with Nd(tren)₂³⁺ in acetonitrile have been measured using the nuclear magnetic resonance line-broadening technique in the slow-exchange region (20–80°). The data indicate that the intermolecular exchange reaction is first order with respect to both the complex and ligand. The proposed mechanism for the bimolecular reaction involves the simultaneous partial attachment of free ligand and partial unwrapping of coordinated tren from the metal ion. Transition-state parameters for the reaction at 25° are $\Delta H^\ddagger = 10.6 \pm 1.3$ kcal mol⁻¹, $\Delta S^\ddagger = -15.0 \pm 4.0$ cal deg⁻¹ mol⁻¹, and $k = 58.2 \pm 17.0$ l. mol⁻¹ sec⁻¹.

Introduction

Recent studies have established that neutral nitrogen donors such as ethylenediamine,¹ diethylenetriamine,² and β, β', β'' -triaminotriethylamine (tren)³ form high-coordinate, thermodynamically stable complexes with lanthanide ions in acetonitrile. As part of a further characterization of these chelates in solution, we have investigated the kinetics of the ligand exchange reaction involving tren and the eight-coordinate complex Nd(tren)₂³⁺.

Although numerous kinetic studies of ligand exchange reactions involving d-type transition metal complexes have been published, relatively few studies involving lanthanide complexes have been reported. The majority of these studies involve the kinetics of complex formation and dissociation in aqueous solution and verify quantitatively the labile nature of lanthanide complexes.⁴ The only exchange study reported⁵ in nonaqueous medium involves the nitrogen donor 4,4'-di-*n*-butyl-2,2'-bipyridine (L) and the europium complex EuL₂(NO₃)₃. This exchange was found to be first order, indicative of a dissociative mechanism.

The kinetic parameters in the present study were obtained by the nmr line-broadening technique in the slow-exchange region. The rate law governing the exchange was determined and a mechanism consistent with the rate law is proposed.

Experimental Section

Materials.—Neodymium oxide, 99.9% purity, was obtained from the American Potash and Chemical Corp. Anhydrous neodymium perchlorate was prepared according to methods previously described.^{1a} Reagent grade acetonitrile and deuterated acetonitrile (Diaprep Corp.) were dried and purified by distillation from phosphorus(V) oxide. Thiophene-free benzene was dried by refluxing over calcium hydride and distilled. β, β', β'' -Triaminotriethylamine was extracted as the hydrochloride salt from technical grade triethylenetetramine as previously described.³

Nuclear Magnetic Resonance Spectra.—Variable temperature ¹H nmr spectra were obtained using a Varian HA-100 spectrometer, equipped with the standard Varian variable tempera-

ture accessory. Tetramethylsilane was used as an internal lock. The variable temperature accessory was calibrated using methanol (-40 to +40°) and ethylene glycol (40 to 80°). Double-resonance experiments were performed utilizing an external Hewlett-Packard Model 200 AB audio oscillator for spin saturation.

Solutions.—All solutions were prepared and transferred in an inert atmosphere glove box. An aliquot of a standardized deuterated acetonitrile solution of anhydrous neodymium(III) perchlorate was measured with a 2.000 ml Gilmont micrometer syringe. The calculated amount of tren was then added using the syringe, and the resulting solution was diluted to the appropriate volume. The solution was transferred to a precision nmr tube containing TMS. The tube was sealed with a double ring plastic cap, wrapped with Parafilm, and stored in liquid nitrogen until use.

Metal concentrations studied were 0.05, 0.08, and 0.14 M. Ligand:metal ion mole ratios were varied from 2:1 to 10:1. Spectra were recorded in 10° intervals from -40 to +80°.

Results and Discussion

The pmr spectrum³ of a deuterated acetonitrile solution containing a 4:1 ligand:metal ion mole ratio shows resonances corresponding to both free (CH₂, A₂X₂ pattern centered at 2.65 ppm; NH₂, 1.54 ppm) and coordinated ligand (CH₂, 3.48 ppm, 7.41 ppm; NH₂, not observed) at ambient probe temperature (*ca.* 31°). The downfield positions of the equally intense methylene resonances of the coordinated ligand result from an isotropic shift caused by interaction with the paramagnetic neodymium ion. The NH₂ resonance of the coordinated ligand could not be observed, presumably due to effective relaxation by the paramagnetic ion.

Double-resonance experiments, depicted in Figure 1, establish transfer of spin saturation^{6a} (TOSS^{6b}) indicating an intermolecular exchange reaction of the type Nd(tren)₂³⁺ + tren' ⇌ Nd(tren)(tren')³⁺ + tren. Thus saturating the free-ligand methylene resonances (spectrum A) results in diminution of both coordinated methylene resonances (TOSS effect). However, saturation of either coordinated methylene resonance (spectra B and C) causes partial collapse of the free-ligand resonance but leaves the other coordinated methylene resonance unaffected. This behavior is consistent with the assignment of the two downfield peaks to the chemically nonequivalent methylene groups present in the tren molecule, since these two groups cannot be related by an inter- or intramolecular exchange process. That only two resonances are observed is indicative of rapid intramolecular exchange and/or rapid chelate ring inversion.

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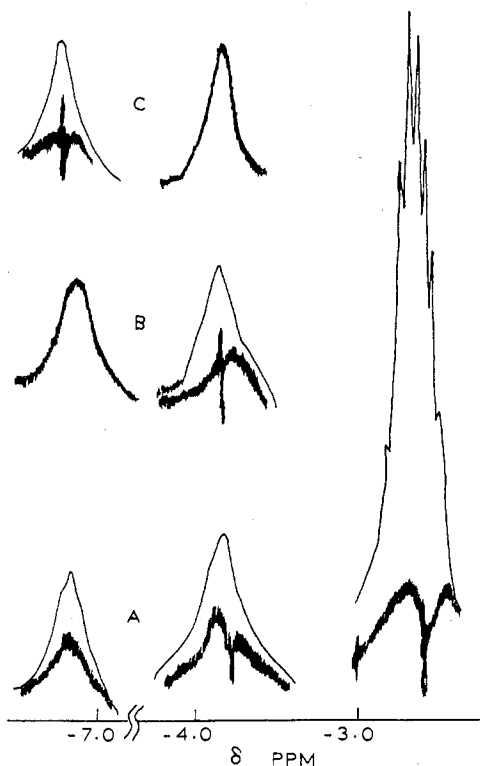


Figure 1.—Transfer of spin saturation for a solution containing $\text{Nd}(\text{tren})_2^{3+}$ and excess ligand. Bold traces were observed under conditions of double resonance.

The ligand exchange reaction occurs in the slow exchange region (nmr time scale) over the temperature ($20\text{--}80^\circ$) and concentration ranges studied. Kinetic data were obtained by applying the line-broadening technique to the downfield methylene resonance of the coordinated ligand. In the slow-exchange region, under conditions of slow passage, line broadening due to exchange (τ_M^{-1}) is given by the equation⁷

$$\tau_M^{-1} = \pi [(\Delta\nu_{1/2})_M^{\text{obsd}} - (\Delta\nu_{1/2})_M] \quad (1)$$

where $(\Delta\nu_{1/2})_M^{\text{obsd}}$ and $(\Delta\nu_{1/2})_M$ are the full line widths (Hz) at half-height of a coordinated ligand resonance in respectively an exchanging system and a system with no exchange. This equation is valid until the coordinated- and free-ligand resonances begin to overlap. Since τ_M represents the mean lifetime of the ligand in the coordination sphere, it is related to the rate law governing the exchange by the expression⁸

$$\text{rate} = a[\text{ML}_a]\tau_M^{-1} = k[\text{ML}_a]^m[\text{L}_f]^n \quad (2)$$

In eq 2, m and n represent the order of the reaction with respect to the concentration of the complex, ML_a , and free ligand, L_f , respectively.

A plot of $\log (\Delta\nu_{1/2})_M^{\text{obsd}}$ vs. $1/T$ (Figure 2) is similar to those observed for ligand exchange systems involving paramagnetic transition metal ions. In transition metal systems, the natural line width $(\Delta\nu_{1/2})_M$ is usually obtained by extrapolation of the linear portion of this curve from the region where exchange is stopped (low temperature) into the exchange region (high temperature). However, in the Nd^{3+} -tren system, such treat-

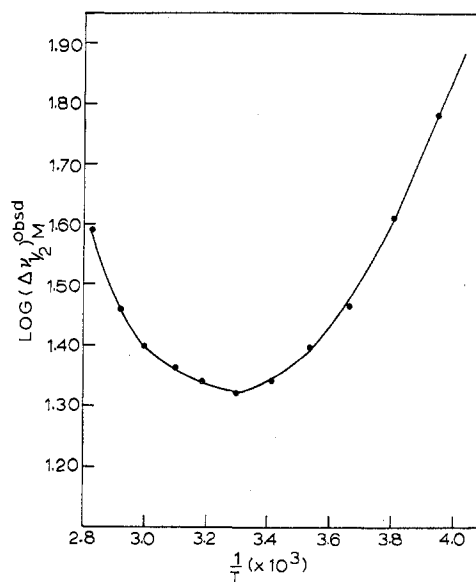


Figure 2.—Temperature variation of observed line width for a 3:1 ligand:metal ion mole ratio, $[\text{Nd}^{3+}] = 0.14 \text{ M}$.

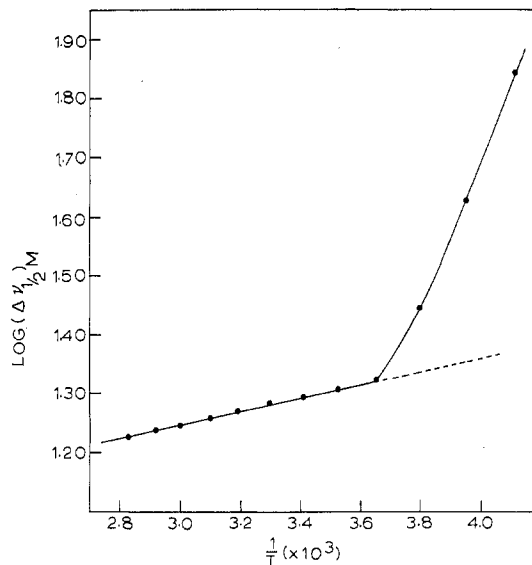


Figure 3.—Temperature variation of line width for a 2:1 ligand:metal ion mole ratio, $[\text{Nd}^{3+}] = 0.05 \text{ M}$.

ment gives smaller line widths than expected for a proton relaxation rate controlled by a Nd^{3+} ion.

The influence of the neodymium ion on the relaxation rate of a methylene proton of the coordinated ligand is observed in the high-temperature region of Figure 3. Since the solution contains only the bis complex, intermolecular exchange with free ligand is not possible. Thus relatively narrow resonance lines are observed at temperatures $> -10^\circ$, indicative of a relaxation process controlled by a neodymium ion.⁹ However, in this system as well, excessive line broadening is observed below -10° . Thus it is apparent that the metal ion is not the only factor controlling the proton relaxation rate in the low-temperature region.

The values of $(\Delta\nu_{1/2})_M$, used for the calculation of τ_M^{-1} (eq 1), were obtained from the high-temperature

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region of the plot shown in Figure 3. A plot was made for each metal ion concentration employed, but it was found that $(\Delta\nu_{1/2})_M$ values were independent of the metal ion concentration. This treatment assumes that the free ligand contributes a negligible effect to $(\Delta\nu_{1/2})_M$. Values of τ_M^{-1} are presented in Tables I and II.

TABLE I
EXCHANGE BROADENING AT CONSTANT
COMPLEX CONCENTRATIONS^a

Temp, °C	0.05 M (ML ₂) ³⁺ [L _f], M	0.08 M (ML ₂) ³⁺ [L _f], M	0.14 M (ML ₂) ⁴⁺ [L _f], M	τ_M^{-1}	τ_M^{-1}	τ_M^{-1}
40	0.05	4.1	0.16	13.5	0.07	5.7
	0.10	8.8	0.24	18.2	0.09	7.2
	0.20	18.2	0.32	27.6	0.14	8.8
	0.25	21.4	0.48	32.3	0.21	19.8
	0.40	37.1	0.64	51.2	0.28	29.2
50		0.80	59.0	0.56	33.9	
	0.05	6.0	0.16	17.0	0.07	7.5
	0.10	10.7	0.24	26.4	0.09	10.7
	0.15	21.7	0.32	35.8	0.14	15.4
	0.25	24.8	0.48	54.6	0.21	23.2
60	0.30	35.8	0.64	82.9	0.28	42.1
		0.80	111.2	0.56	53.1	
				0.84	78.8	
	0.05	7.2	0.16	32.3	0.07	8.8
	0.10	24.5	0.24	46.5	0.14	24.5
70	0.15	27.6	0.32	51.2	0.21	30.8
	0.20	35.5	0.48	88.9	0.35	44.9
	0.25	38.6			0.56	95.1
	0.30	62.2			0.84	132.8
	0.05	17.3	0.12	26.7	0.09	31.4
80	0.10	39.3	0.16	48.7	0.14	36.1
	0.15	53.4	0.24	62.8	0.21	58.1
	0.20	72.2	0.32	94.2	0.28	100.5
	0.30	102.1	0.48	158.6	0.35	114.6
	0.05	17.9	0.12	52.4	0.14	59.7
80	0.10	39.9	0.16	87.0	0.21	94.2
	0.14	60.3	0.24	120.3	0.28	128.7
	0.19	76.0		0.35	175.8	

^a τ_M^{-1} values in rad sec⁻¹.

TABLE II
EXCHANGE BROADENING AT CONSTANT FREE-LIGAND
CONCENTRATION ([L_f] = 0.20 M)^a

Temp, °C	τ_M^{-1} , 0.05 M ML ₂ ³⁺	τ_M^{-1} , 0.08 M ML ₂ ³⁺	τ_M^{-1} , 0.14 M ML ₂ ³⁺
40	17.3	16.0	14.1
50	23.2	21.4	21.0
60	38.3	38.6	29.2
70	70.3	59.3	59.7
80	86.7	99.5	91.4

^a τ_M^{-1} values in rad sec⁻¹.

It is apparent that caution must be employed in lanthanide systems when determining $(\Delta\nu_{1/2})_M$ values by extrapolation of low-temperature data. The extensive broadening observed in the low-temperature region of the spectrum of the bis chelate appears to be indicative of an intramolecular exchange process relating two or more possible structural isomers which have been shown to be energetically favorable for eight coordination.¹⁰ Molecular models of the bis tren complex indicate that a bicapped octahedral geometry (*C_{3v}*), with the tertiary nitrogens of the two tren molecules capping opposite trigonal faces of the octahedron, is possible and may be preferred, since the configuration of the ligand in the complex is the same as that found in the crystal structure of tren·3HCl.¹¹ However, very

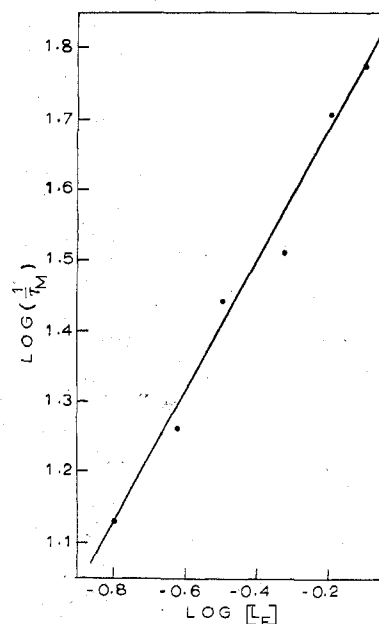


Figure 4.—Plot of $\log \tau_M^{-1}$ vs. $\log [L_f]$ at 40° for $[Nd^{3+}] = 0.08 M$.

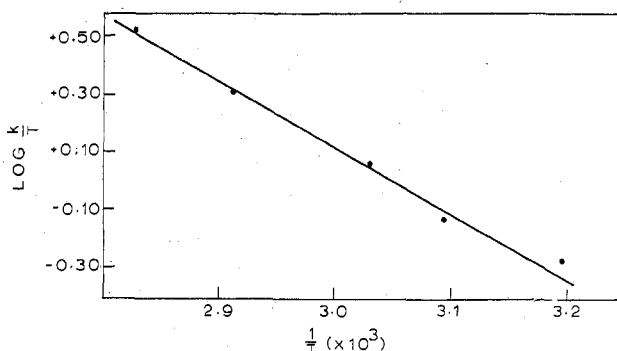


Figure 5.—Plot of $\log k/T$ vs. $1/T$.

little distortion of the tren molecule is required to produce a dodecahedral (*D_{2d}*) arrangement of nitrogen atoms about the metal ion.

The rate law governing the intermolecular exchange was determined from eq 2 using the data in Tables I and II. The slope, *n*, of a linear plot of $\log (\tau_M^{-1})$ vs. $\log [L_f]$ (data from Table I) at constant complex concentration and constant temperature gives the order of the reaction with respect to free ligand. Least-squares plots were made for each temperature and metal ion concentration. A typical plot is shown in Figure 4. The average value of the slope ($n = 1.06 \pm 0.1$) indicates the reaction is first order in free ligand.

The assumption that increasing the free-ligand concentration has no effect on $(\Delta\nu_{1/2})_M$ is borne out by the linearity of the $\log (\tau_M^{-1})$ vs. $\log [L_f]$ plots (Figure 4). If appreciable increases in $(\Delta\nu_{1/2})_M$ occurred, as found in certain transition metal systems,¹² then positive deviations from linearity should be observed with increasing $[L_f]$.

The data in Table II indicate that τ_M^{-1} is independent of complex concentration at constant free-ligand concentration and constant temperature. According to eq 2, this behavior is expected for $m = 1$, indicating the exchange is also first order in complex concentra-

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tion. Thus the rate law for the bimolecular, second-order exchange is

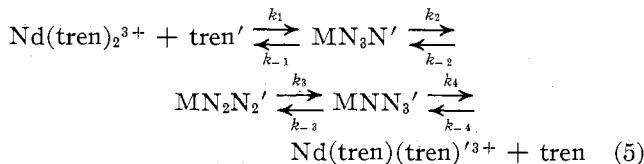
$$\text{rate} = k[\text{Nd}(\text{tren})_2^{3+}][\text{tren}] \quad (3)$$

Activation parameters were obtained from a log plot (Figure 5) of the transition state equation

$$k = \frac{k_B T}{h} \exp\left[-\frac{(\Delta H^\ddagger - T\Delta S^\ddagger)}{RT}\right] \quad (4)$$

Rate constants used in this plot were obtained from the intercepts of the $\log(\tau_M^{-1})$ vs. $\log[L_I]$ plots. The activation parameters calculated were $\Delta H^\ddagger = 10.6 \pm 1.3$ kcal mol⁻¹, $\Delta S^\ddagger = -15.0 \pm 4.0$ cal mol⁻¹ deg⁻¹, $\Delta G^\ddagger(25^\circ) = 15.1 \pm 2.5$ kcal mol⁻¹, and $k(25^\circ) = 58.2 \pm 17.0$ l. mol⁻¹ sec⁻¹. The error limits were established by regression analysis¹³ at the 95% confidence level.

The second-order kinetics observed for this reaction dictates the simultaneous attachment of incoming and outgoing ligands. However, molecular models indicate that steric repulsions would be prohibitive in a transition state with a coordination number greater than eight. Therefore, we propose a mechanism involving a stepwise dissociation of the coordinated ligand with a simultaneous stepwise coordinate bond formation by the incoming group as depicted in eq 5. In this equa-



tion, N_x and N'_{4-x} represent the number of coordinated nitrogens in each intermediate ($\text{MN}_x\text{N}'_{4-x}$) for the departing and incoming ligand, respectively. This mechanism allows simultaneous coordination of the two transitive ligands, without requiring an increase in the coordination number of an intermediate. The ligand involved must possess sufficient internal flexibility to twist out of the path of the incoming ligand upon dissociation of a coordinate bond. Molecular models indicate that an ethylamine group of tren may be effectively removed from the coordination site by rotation about the C-tertiary N bond.

According to this mechanism, the path of the exchange must pass through a symmetrical intermediate (or transition state), in which both transitive ligands are coordinated through two nitrogens ($\text{MN}_2\text{N}_2'$). Furthermore, the forward and reverse reactions (eq 5) are identical, since the reactant and product of exchange

are chemically equivalent. This suggests a symmetrical reaction profile, requiring that

$$k_1 = k_{-4}, k_2 = k_{-3}, k_3 = k_{-2}, k_4 = k_{-1} \quad (6)$$

The rate at which the symmetrical intermediate is converted into product (complete exchange) should equal the rate at which it returns to reactant (no exchange), since either transitive ligand has equal probability of dissociating in this transition state. Thus the rate of exchange is equal to half the rate of formation of the symmetrical intermediate.¹⁴

An expression for the exchange rate (eq 7), which is consistent with the observed kinetics, may be derived

$$\text{rate} = \frac{k_1 k_2}{2k_{-1}} [\text{Nd}(\text{tren})_2^{3+}][\text{tren}] \quad (7)$$

by applying the steady-state treatment to the intermediate, $\text{MN}_3\text{N}'$. The steady-state treatment is valid in this system since the kinetic measurements are made under equilibrium conditions, *i.e.*, $dC_{\text{MN}_3\text{N}'}/dt = 0$.

That second-order kinetics is exhibited by the tren exchange in contrast to the first-order kinetics observed for the 4,4'-di-*n*-butylbipyridine exchange⁵ may be due to the greater internal rigidity of the alkyl-substituted bipyridine molecule. Although a pyridine ring may rotate about the C-C bond connecting the two rings, molecular models indicate that the coordination site remains partially blocked upon such rotation following dissociation of the first coordinate bond. Thus coordination of the incoming group occurs after complete dissociation of the departing group.

Under conditions of increased intermolecular exchange rates, *i.e.*, high complex or free-ligand concentrations, a secondary reaction involving the tren molecule becomes notable, with evolution of ammonia from the solution. Further studies are presently being conducted in order to fully characterize the nature of this reaction. However, this reaction was negligible under the conditions employed in obtaining the kinetic data, as was demonstrated by lowering the temperature after each run and reproducing the spectra (line widths) previously obtained.

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