Inorg. Chem. **1992**, *31*, 5555–5560 **5555**

NMR Study of the Kinetics of Ligand-Exchange Reactions of Ethylenediamine with Tetrakis(ethylenediamine)lanthanide(III) Complexes

John H. Forsberg,* Theodore J. Dolter, Ann M. Carter, Deepak Singh, Steven A. Aubuchon, Aaron T. Timperman, and Ali Ziaee

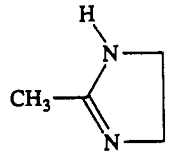
Department of Chemistry, Saint Louis University, St. Louis, Missouri 63103

Received July 10, 1991

The kinetics of the exchange reactions of N-deuterated ethylenediamine with paramagnetic $Ln(en\text{-}d_4)_4^{3+}$ (Ln^{3+} = Pr^{3+}, Nd^{3+}, Eu^{3+}, Er^{3+}, Yb^{3+}) complexes in deuterated acetonitrile were investigated over the temperature range 233–343 K using ^1H NMR. The data were analyzed by line shape analysis using the equation for a two-site exchange. The mean ligand residence times, τ_m, were observed to increase across the lanthanide series. The erbium and ytterbium systems demonstrated both the slow- and fast-exchange limits over this temperature range on both the 300- and 100-MHz time scales; however, exchange involving complexes of the larger metal ions revealed coalescence of the coordinated and free ligand peaks even at the lowest temperature studied (233 K). A linear dependency of $1/\tau_m$ on the concentration of free ligand was observed for complexes derived from the larger ions (Pr^{3+}, Nd^{3+}, Eu^{3+}), corresponding to a rate law that is first order in ethylenediamine concentration. The mechanism proposed for these reactions is discussed in terms of a nine-coordinate intermediate. At 298 K: $k'' = (1.9 \pm 0.2) \times 10^6$ (Pr), $(2.0 \pm 0.2) \times 10^6$(Nd), $(1.5 \pm 0.15) \times 10^6$ M^{-1} s^{-1} (Eu); $\Delta H^{\ddagger} = 9.7 \pm 1$ (Pr), 16 ± 1 (Nd), 11 ± 1 $kJ{\cdot}mol^{-1}$ (Eu); $\Delta S^{\ddagger} = -92 \pm 9$ (Pr), -71 ± 5 (Nd), -91 ± 8 $J{\cdot}K^{-1}{\cdot}mol$ (Eu). For complexes of the smaller ions (Ln^{3+} = Er^{3+}, Yb^{3+}), $1/\tau_m$ was nearly independent of the ethylenediamine concentration at higher temperatures and revealed a nonlinear dependency on ethylenediamine concentration at lower temperatures. Parallel I_d and D exchange mechanisms are proposed to be operating in these systems. At 298 K: $k_D = (3.6 \pm 0.4) \times 10^4$ (Er), $(1.3 \pm 0.1) \times 10^4$ s^{-1} (Yb); $\Delta H^{\ddagger} = 53 \pm 5$ (Er), 53 ± 5 $kJ{\cdot}mol^{-1}$ (Yb); $\Delta S^{\ddagger} = 17 \pm 5$ (Er), 12 ± 5 $J{\cdot}K^{-1}{\cdot}mol$ (Yb).

Introduction

Previously we reported that catalytic quantities of $Ln(CF_3SO_3)_3$ salts catalyze a reaction between ethylenediamine and acetonitrile with formation of **1**.[1] This reaction was surprising to us since we had previously used acetonitrile as the solvent to prepare high-coordinate lanthanide complexes, $Ln(en)_4X_3$ (X = NO_3^-, ClO_4^-, Cl^-, Br^-), derived from ethylenediamine.[2] More recently, Smith and Raymond reported the isolation of $[La(en)_4CF_3SO_3](CF_3SO_3)_2{\cdot}CH_3CN$ from the same solvent.[3] The molecular structure of the latter complex confirmed bidentate ligation of the ethylenediamine molecules in the solid state as well as unidentate coordination of one triflate ion. Moreover, the $Ln(en)_4^{3+}$ chelates are thermodynamically stable in acetonitrile, as evidenced by the large exothermic ligational enthalpy changes (−241 to −277 kJ/mol).[4] Whereas the formation of **1** is carried out under reflux using a 1:1 en:CH_3CN mole ratio with 2 mol % Ln^{3+} (50:1 en:Ln^{3+} mole ratio), the syntheses of the complexes were carried out either at ambient temperatures or under reflux using a stoichiometric (4:1 en:Ln^{3+} mole ratio) amount or slight excess of ligand. We have shown that the rate of formation of **1** is negligible (<0.001 turnover/(h·mol of Ln^{3+})) under the latter conditions.[1] A prerequisite to the formation of **1** is activation of the nitrile molecule through coordination to the Ln^{3+} ion. The ability of the Ln^{3+} ions to activate the nitrile in the presence of a large excess of a strongly coordinating amine was attributed to the labile nature of the $Ln(en)_4^{3+}$ chelates in solution. This proposal prompted us to study the ligand-exchange kinetics of the $Ln(en)_4^{3+}$ chelates in CD_3CN.



1

Although it is well established that lanthanide(III) complexes are among the most labile, the number of ligand-exchange reactions that have been investigated remains relatively limited. Merbach et al. reported the solvent-exchange reactions of the aqua complexes $Ln(H_2O)_8^{3+}$ ($k = 55.8 \times 10^7$ s^{-1} for Tb^{3+} to 4.7×10^7 s^{-1} for Yb^{3+} at 298 K), using ^{17}O NMR,[5] and ^1H studies of the dimethylformamide complexes $Ln(dmf)_8^{3+}$.[6] An interchange associative (I_a) mechanism was proposed for the aqua ions, whereas for the $Ln(dmf)_8^{3+}$ complexes, both interchange dissociative (I_d) (Ln = Tb, Dy, Ho) and limiting dissociative (D) mechanisms were proposed ($k = 3.1 \times 10^7$ and 9.9×10^7 s^{-1} at 298 K, for Tm^{3+} and Yb^{3+}, respectively). Lincoln et al. reported that exchange of tetramethylurea (tmu) with $Ln(tmu)_6^{3+}$ (Ln = Tb, Dy, Ho, Er, Yb, Lu) proceeds through a limiting D mechanism in CD_3CN (at 298 K, $k = 1380$ s^{-1} for Tb^{3+} to 41.9 s^{-1} for Lu^{3+}).[7] Forsberg and Johnson observed that the exchange reaction of the quadridentate donor 2,2′,2″-tris(2-aminoethyl)amine (tren) with $Nd(tren)_2^{3+}$ in CD_3CN ($k = 58$ $L{\cdot}mol^{-1}{\cdot}s^{-1}$ at 298 K) occurs through an A mechanism involving a simultaneous unwrapping of the coordinated ligand and stepwise chelation of the incoming

---

[1] Forsberg, J. H.; Spaziano, V. T.; Balasubramanian, T. M.; Liu, G. K.; Kinsley, S. A.; Duckworth, C. A.; Poteruca, J. J.; Brown, P. S.; Miller, J. L. *J. Org. Chem.* **1987**, *52*, 1017.

[2] Forsberg, J. H.; Moeller, T. *Inorg. Chem.* **1969**, *8*, 883.

[3] Smith, P. H.; Raymond, K. N. *Inorg. Chem.* **1985**, *24*, 3469.

[4] Forsberg, J. H.; Moeller, T. *Inorg. Chem.* **1969**, *8*, 889.

[5] (a) Cossy, C.; Helm, L.; Merbach, A. E. *Inorg. Chem.* **1989**, *28*, 2699. (b) Cossy, C.; Helm, L.; Merbach, A. E. *Inorg. Chem.* **1988**, *27*, 1973. (c) Cossy, C.; Helm, L.; Merbach, A. E. *Inorg. Chim. Acta* **1987**, *139*, 147.

[6] (a) Pisaniello, D. L.; Helm, L.; Meier, P.; Merbach, A. E. *J. Am. Chem. Soc.* **1983**, *105*, 4528. (b) Pisaniello, D. L.; Merbach, A. E. *Helv. Chim. Acta* **1982**, *65*, 573.

[7] (a) Lincoln, S. F.; White, A. *Inorg. Chim. Acta* **1990**, *168*, 265. (b) Lincoln, S. F.; Hounslow, A. M.; Jones, A. J. *Aust. J. Chem.* **1982**, *35*, 2393.

0020-1669/92/1331-5555$03.00/0

ligand.[8] A similar mechanism was proposed for the exchange of nitrilotriacetate[9] (nta^{3-}) with $Ln(nta)_2^{3-}$ and (hydroxyethyl)-iminodiacetate[10] ($himda^{2-}$) with $Ln(himda)_2^-$ under alkaline conditions. The exchange of the bidentate donor 4,4′-dibutyl-2,2′-bipyridine (=L) with $EuL_2(NO_3)_3$ was proposed to follow a primarily dissociative path.[11]

In this paper we report the results of our ^1H NMR study of the kinetics of the ligand-exchange reactions of ethylenediamine with $Ln(en)_4^{3+}$ (Ln = Pr, Nd, Eu, Er, Yb) in deuterated acetonitrile over the temperature range 233–343 K.

Experimental Section

Variable-temperature ^1H NMR spectra were recorded on Varian Gemini (300.1 MHz) and XL-100 (100.0 MHz operating in the CW mode) spectrometers. ^{19}F (282.3 MHz) spectra were recorded on the Varian Gemini instrument. The standard Varian temperature controllers (±1 °C) were calibrated by using a digital thermometer equipped with a type J thermocouple that was emersed in deuterated acetonitrile contained in a standard NMR tube (XL-100) or from chemical shifts observed for ethanol or ethylene glycol. The XL-100 spectrometer was interfaced to a microcomputer, which allowed the spectra to be digitized and saved to floppy disks.

Anhydrous lanthanide trifluoromethanesulfonate (triflate) salts[1] and N-deuterated ethylenediamine[12] were prepared according to procedures reported in the literature. The ethylenediamine was 80–85% N-deuterated as determined by NMR integration.

NMR samples for the ligand-exchange studies were prepared by adding the required amount of en-d_4, measured using 10- or 100-μL Eppendorf pipets (1% precision), to a 0.600-mL aliquot of stock solution containing a 1:1 mole ratio of en-d_4:$Ln(CF_3SO_3)_3$ in CD_3CN. The preparation was carried out in a glovebox under a nitrogen atmosphere. The addition of en-d_4 to the stock solution was required to effect solubility of the triflate salt (erbium triflate is soluble in CD_3CN). The stock solutions were titrated (Hach digital titrator) with standard edta solution using xylenol orange as the indicator. The stock solutions derived from the larger ions (Pr^{3+}, Nd^{3+}, Eu^{3+}) had to be kept less than 0.07 M and those of the smaller ions (Er^{3+}, Yb^{3+}) less than 0.04 M to prevent crystallization of $Ln(en\text{-}d_4)_4(CF_3SO_3)_3$ in the NMR tubes. Some samples were also prepared using a 1:1 v/v CD_3CN/CD_2Cl_2 solvent mixture to allow studies at lower temperatures (193–233 K).

Data Analysis

Line shape analysis was carried out using the equation for a two-site exchange (eq 1),[13] where $g(\omega)$ is the intensity of the spectrum at frequency

$$g(\omega) = -\omega_1 M^{\circ}\{P[1 + \tau(P_M/T_{2M} + P_L/T_{21})] + Q[R + \tau(1/T_{2L} - 1/T_{2M})(\delta\omega/2)]\}/\{P^2 + [R + \tau(1/T_{2L} - 1/T_{2M})(\delta\omega/2)]^2\}$$

$$P = \tau[(1/T_{2M})(1/T_{2L}) - (\Delta\omega)^2 + (\delta\omega/2)^2] + P_M/T_{2M} + P_L/T_{2L}$$

$$Q = \tau[\Delta\omega - (\delta\omega/2)(P_M - P_L)]$$

$$R = \Delta\omega[1 + \tau/T_{2M} + \tau/T_{2L}] + (\delta\omega/2)(P_M - P_L)$$

$$\Delta\omega = {}^1/_2(\omega_M + \omega_L) - \omega \qquad \delta\omega = \omega_M - \omega_L \qquad \tau = \tau_M\tau_L/(\tau_M + \tau_L) \tag{1}$$

ω (rad/s), ω_M and ω_L are the chemical shifts, T_{2M} and T_{2L} are the transverse relaxation times of the coordinated and free ligand, respectively, P_M and P_L are the mole fractions, and τ_M and τ_L are the mean lifetimes of the coordinated and free ligand. The intrinsic chemical shifts and line widths ($1/T_2 = \pi(\Delta\nu)^{1/2}$) required for line shape analysis were obtained as described below. A complete list of parameters used in the analysis is given in Table S1 of the supplementary data. Simulated spectra were fit to the observed spectra by varying τ_M. The best fit of 100-MHz data was taken as that which minimized the value of R defined by

$$R = \sqrt{\frac{\sum_{\omega}[g^c(\omega) - g^o(\omega)]^2}{\sum_{\omega}(g^o(\omega))^2}} \tag{2}$$

where $g^o(\omega)$ and $g^c(\omega)$ are the normalized spectral intensities of the observed and calculated lines at frequency ω, respectively. Simulated spectra were fit to spectra recorded at 300 MHz by comparing line widths and chemical shifts. Line shape distortion due to the presence of a solvent peak and phase shifts of the free and coordinated ligand precluded reliable simulations of 300-MHz spectra of the erbium and ytterbium systems in regions where the coordinated- and free-ligand peaks merged (ca. 283–303 K).

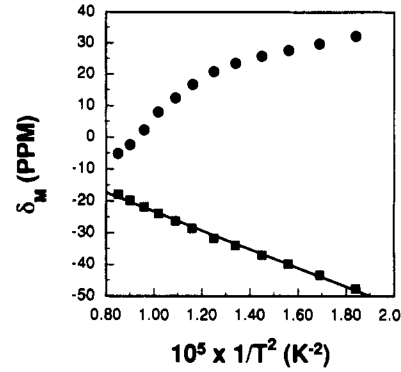


Figure 1. Chemical shifts (referenced to TMS) of $Yb(en\text{-}d_4)_4^{3+}$ (●) and $Yb(en\text{-}d_4)_3^{3+}$ (■) as a function of temperature.

Intrinsic Chemical Shifts

The NMR spectra (100 and 300 MHz) of solutions of $Ln(en)_4(CF_3SO_3)_3$ in CD_3CN (233–343 K) and 1:1 v/v CD_3CN/CD_2Cl_2 (193–233 K) revealed single peaks for both the CH_2 and NH_2 groups as observed previously for the series of perchlorate salts, $Ln(en)_4(ClO_4)_3$.[14] The chemical shifts of protons on the coordinated ligand (δ_M) are dictated by the magnitude of the isotropic shift induced by the paramagnetic lanthanide ions (LIS). Plots of δ_M vs T^{-2} for the triflate salts of the tris complexes in deuterated acetonitrile appear linear, whereas the plots for the tetrakis complexes appear linear at lower temperatures but deviate from linearity at higher temperatures, as shown for the representative ytterbium system (Figure 1). In each case, the observed shift deviates in the direction of the LIS observed for the tris complex, suggesting that partial dissociation of the tetrakis complex[15] is occurring at higher temperatures, with rapid exchange of ethylenediamine between the tris and tetrakis complexes. For this reason, the values of δ_M required to simulate spectra recorded above 273 K were obtained by extrapolating plots (δ_M vs T^{-2}) of the low-temperature data (193–273 K).[16] In the region of

---

(8) Johnson, M. F.; Forsberg, J. H. *Inorg. Chem.* **1972**, *11*, 2683.

(9) Gfeller, Y.; Merbach, A. *Inorg. Chim. Acta* **1978**, *29*, 217.

(10) Chastellain, F.; Merbach, A. E. *Helv. Chim. Acta* **1975**, *58*, 1.

(11) (a) Hart, F. A.; Newberry, J. E.; Shaw, D. *Chem. Commun.* **1967**, 45. (b) Hart, F. A.; Newberry, J. E.; Shaw, D. *Nature* **1967**, 261.

(12) Sabatini, A.; Califano, S. *Spectrochim. Acta* **1960**, *16*, 677.

(13) (a) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228. (b) Williams, K. C.; Brown, T. L. *J. Am. Chem. Soc.* **1966**, *88*, 4134.

(14) Birnbaum, E. R.; Stratton, S. *Inorg. Chem.* **1973**, *12*, 379.

(15) log K_4 values for the series of $Ln(en)_4^{3+}$ chelates at 23 °C are in the range 3.0–3.8, corresponding to ca. 17–7% dissociation at this temperature at the concentration level used in this study.[4] The percent dissociation is suppressed to less than 1% at this temperature on the addition of free ligand.

(16) The contact contribution[17] to the LIS is a function of T^{-1}, whereas the dipolar contribution is reported to vary as T^{-2} [18] or T^{-1}.[19] Over the temperature range in our study, however, apparent linearity was obtained when δ_M was plotted versus T^{-1} or T^{-2}. The δ_M values obtained from extrapolation of the T^{-2} plots were used in the simulations, since these values gave better agreement for the shifts observed at coalescence ($\delta_{obsv} = P_M\delta_M + P_L\delta_L$) than those values obtained from the T^{-1} plots. The probable error in δ_M values obtained by extrapolation is estimated at ±5%, resulting in an error of ca. 10% in τ_M; e.g., for the erbium system at 50 °C using $P_M = 0.470$ and $\delta_L = 768$ Hz, $\tau_m = (2.05 \pm 0.2) \times 10^{-5}$ s for $\delta_M = 6680 \pm 330$ Hz.

(17) Reuben, J.; Fiat, D. J. *J. Chem. Phys.* **1969**, *51*, 4909.

(18) Bleaney, B. *J. Magn. Reson.* **1972**, *8*, 91.

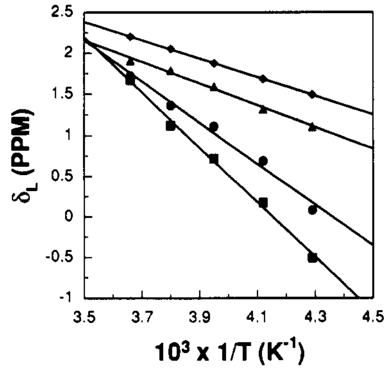


Figure 2. Chemical shifts (referenced to TMS) of the free-ligand methylene resonance in the ytterbium system (100 MHz) as a function of temperature and concentration of free en-d_4. [en-d_4] = 0.06 M (■), 0.12 M (●), 0.36 M (▲), 0.61 M (◆) ([Yb^{3+}] = 0.03 M).

coalescence, the values of δ_M obtained by extrapolation agreed with those calculated from eq 3. In the case of the erbium and

$$\delta_{obsv} = P_M\delta_M + P_L\delta_L \qquad (3)$$

ytterbium systems, δ_M was observed to be dependent on the concentration of free ligand in the region of slow exchange. The largest variations were observed in the erbium system at 300 MHz; e.g., at 253 K, δ_M ranged from 16 070 to 17 100 Hz as the en:Ln^{3+} ratio was varied from 6:1 to 24:1. Nevertheless, the values of δ_M obtained by extrapolating plots of the 4:1 en:Ln^{3+} data (δ_M vs T^{-2}) for use in simulating spectra in the region of coalescence agreed with those values obtained from eq 3.

In the erbium and ytterbium systems, in the region of slow exchange, the values of δ_L are displaced up to 2 ppm from the chemical shift values observed for free ethylenediamine in acetonitrile (δ 2.62 ppm at 233 K to 2.58 ppm at 343 K). The magnitude of the shift depends on the concentration of free ligand and varies with temperature as shown for the representative ytterbium system in Figure 2. The displacement of the shifts is presumed to be dipolar in origin, resulting from certain preferred orientations of ethylenediamine groups in the secondary coordination sphere.[20] However, no such displacements were observed for δ_L in systems derived from the larger metal ions (Pr^{3+}, Nd^{3+}, Eu^{3+}) in 1:1 v/v CD_2Cl_2/CD_3CN solutions in the region of slow exchange (<233 K). Thus, for complexes derived from the larger Ln^{3+} ions, simulations were carried out using the chemical shift values observed for free ethylenediamine, whereas in studies involving erbium and ytterbium, δ_L was estimated by extrapolating graphs such as shown in Figure 2 (δ_L was assumed to be the free-ligand values above 313 K). A probable error of ±10 Hz in δ_L leads to an uncertainty of less than 1% in τ_M.

Intrinsic Line Widths

Transverse relaxation times are usually obtained by measuring the line widths at half-height ($\pi(\Delta\nu)^{1/2} = 1/T_2$) of the complexes in solution in the absence of free ligand. Paramagnetic lanthanide ions induce relaxation (LIR) of protons on the coordinated ligand, resulting in line broadening. Plots of ln $((\Delta\nu)^{1/2})$ vs $1/T$ for solutions containing 1:1 and 4:1 en:Yb^{3+} mole ratios (100-MHz data) are shown in Figure 3 and are typical of all the systems studied. The linear plot observed for each 1:1 system is characteristic of an LIR dominated by a dipolar relaxation process following Arrhenius behavior.[21] However, the line widths of the 1:1 complexes measured at 300 MHz were approximately twice those measured at 100 MHz, indicating the presence of a Curie contribution (field dependent) in addition to the standard dipolar contribution to the LIR.[22] In addition to an explicit T^{-2} dependency, the Curie contribution to line broadening is also a function of the rotational correlation time, τ_r, which has a T^{-1} dependency. Thus the linear plot observed for the 1:1 complexes is probably fortuitous. In contrast to the linear plots observed for the 1:1 complexes, plots for the tetrakis complexes reveal a maximum at intermediate temperatures. In this case, the plot is characteristic of a species involved in exchange, presumably with traces of free ligand and the tris complex resulting from dissociation (see above). Line broadening due to exchange precludes direct measurement of the intrinsic line widths of protons on the $Ln(en)_4^{3+}$ complexes in CD_3CN over the temperature range of this study (233–343 K). However, the low-temperature range was extended to 193 K by using the mixed solvent 1:1 v/v CD_2Cl_2/CD_3CN. The ln $((\Delta\nu)^{1/2})$ vs $1/T$ plots for the tetrakis complexes were linear (300-MHz data) over the relatively limited range of 193–223 K, allowing $(\Delta\nu)^{1/2}{}_M$ to be estimated by extrapolation ($(\Delta\nu)^{1/2}{}_{Pr}$ = 55–25 Hz, $(\Delta\nu)^{1/2}{}_{Nd}$ = 51–22 Hz for T = 233–273 K; $(\Delta\nu)^{1/2}{}_{Eu}$ = 39–11 Hz for T = 233–293 K; $(\Delta\nu)^{1/2}{}_{Er}$ = 803–132 Hz for T = 243–343 K; $(\Delta\nu)^{1/2}{}_{Yb}$ = 178–48 Hz for T = 253–343 K). Fortunately, errors associated with $(\Delta\nu)^{1/2}{}_M$ lead to large uncertainties in τ_M^{-1} values only in the limits of fast or slow exchange. Thus simulations were limited to the temperature ranges given above.[23] In the 100-MHz studies, the $(\Delta\nu)^{1/2}{}_M$ values of the tetrakis complexes were assumed to be the same as those measured for the mono complexes. That this approximation is reasonable within the uncertainties reported for τ_M^{-1} values (Table S1) is reflected in the self-consistency of simulating line widths corresponding to both the coordinated- and free-ligand peaks in the region of slow exchange (Figure 4).

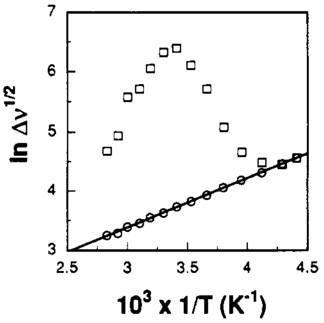


Figure 3. Line widths of the methylene peaks (100 MHz) as a function of temperature for 0.03 M solutions of $Yb(en\text{-}d_4)^{3+}$ (○) and $Yb(en\text{-}d_4)_4^{3+}$ (□) in CD_3CN.

Results and Discussion

The spectra (300 and 100 MHz) of systems derived from the larger metal ions (Pr^{3+}, Nd^{3+}, Eu^{3+}) revealed coalescence of the coordinated- and free-ligand resonances at the lowest temperature studied in CD_3CN (233 K), whereas the limits of both slow and fast exchange (Figure 4) were observed in the spectra of systems derived from the smaller ions (Er^{3+}, Yb^{3+}). For the smaller ions, the coalescence temperature is essentially independent of the free-ligand concentration and at 300 MHz was observed at 308 and 315 K in the erbium and ytterbium systems, respectively, whereas at 100 MHz, the corresponding coalescence temperatures were 298 and 305 K. In order to ensure sufficient broadening of the coalesced resonance due to chemical exchange, τ_M values for

---

(19) Horrocks, W. D. *J. Magn. Reson.* **1977**, *26*, 333.

(20) (a) Eaton, D. R. *Can. J. Chem.* **1969**, *47*, 2645. (b) Eaton, D. R.; Ohorodnyk, H. O.; Seville, L. *Can. J. Chem.* **1971**, *49*, 1218.

(21) Alsaadi, B. M.; Rossotti, F. J. C.; Williams, R. J. P. *J. Chem. Soc., Dalton Trans.* **1980**, 2147.

(22) (a) Kemple, M. D.; Ray, B. D.; Lipkowitz, K. B.; Prendergast, F. G.; Rao, B. D. N. *J. Am. Chem. Soc.* **1988**, *110*, 8275. (b) Burns, P. D.; LaMar, G. N. *J. Magn. Reson.* **1982**, *46*, 61.

(23) To estimate the effect of uncertainties in $(\Delta\nu)^{1/2}{}_M$, consider the praseodymium system, which demonstrated the fastest ligand-exchange rate. At 273 K, the highest temperature for which τ_m^{-1} values are reported, $P_M = 0.435$, δ_M = 2554 Hz, δ_L = 756 Hz, $(\Delta\nu)^{1/2}{}_M$ = 25 Hz, $(\Delta\nu)^{1/2}{}_{obsv}$ = 140 Hz (observed line width of the coalesced peak), and $\tau_M = 2.30 \times 10^{-5}$ s. An uncertainty of ±25 Hz (±100%) in $(\Delta\nu)^{1/2}{}_M$ gives $\tau_M = (2.30 \pm 0.15) \times 10^{-5}$ s.

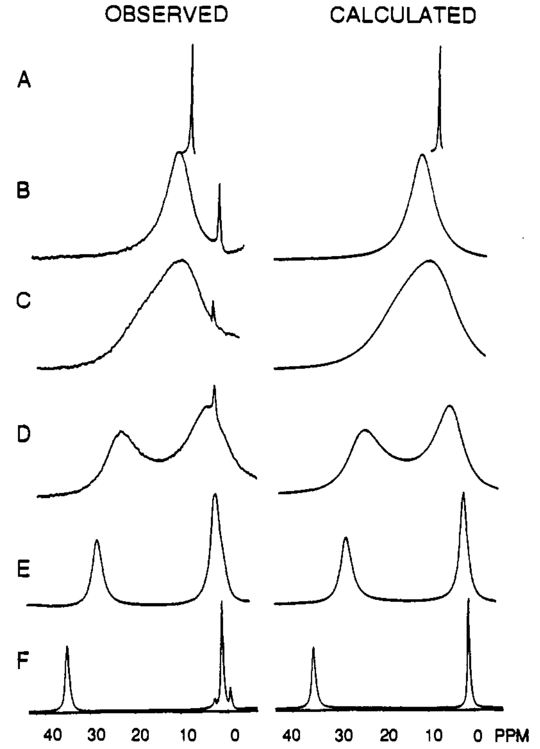


Figure 4. Calculated and observed ^{1}H NMR spectra of a solution of 0.03 M Yb(en-d_4)$_4^{3+}$ and 0.12 M en-d_4 in CD$_3$CN as a function of temperature: (A) 343 K, $\tau_m = 1.0 \times 10^{-5}$ s; (B) 313 K, $\tau_m = 1.0 \times 10^{-4}$ s; (C) 303 K, $\tau_m = 1.8 \times 10^{-4}$ s; (D) 293 K, $\tau_m = 3.9 \times 10^{-4}$ s; (E) 273 K, $\tau_m = 1.7 \times 10^{-3}$ s; (E) 243 K, $\tau_m = 1.3 \times 10^{-2}$ s. The peak at 2.52–2.54 ppm is due to residual HCD$_2$CN in the solvent. Scale is referenced to TMS.

systems derived from the larger metal ions are reported only for simulations carried out using 300-MHz data (Table S1) over the limited temperatures ranges of 233–273 K (Pr^{3+}, Nd^{3+}) and 233–293 K (Eu^{3+}).

The rate of ligand exchange is related to τ_m by the expression

$$-d[\mathrm{Ln(en)_4}^{3+}]/dt = 4[\mathrm{Ln(en)_4}^{3+}]/\tau_m \qquad (4)$$

Plots of $1/\tau_m$ vs [en] for systems derived from the larger metal ions are shown in Figure 5. The linear plots with intercepts near the origin suggest that the reactions are first order in ethylenediamine concentration and second order overall:[24]

$$-(4[\mathrm{Ln(en)_4}^{3+}])^{-1}d[\mathrm{Ln(en)_4}^{3+}]/dt = 1/\tau_m = (k''/4)[\mathrm{en}] \qquad (5)$$

In eq 5, k'' is the global rate constant for exchange of any one of the coordinated ligands[25] [$k'' = (k_bT/h)\exp(\Delta S^*/R - \Delta H^*/RT)$]. A value of k'' for each temperature was calculated from the slope of a plot of $1/\tau_m$ vs [en]. The values of k'' at 298 K (Table I) were obtained by extrapolating Arrhenius plots (ln k'' vs $1/T$) of the low-temperature data. Plots of ln (k''/T) vs $1/T$ were used to determine the activation enthalpies (ΔH^*) and entropies (ΔS^*) (Table I).

The relatively small values of ΔH^* (10–16 kJ/mol) and large negative values of ΔS^* (−70 to −90 J/(K·mol)) suggest operation of an associative (A) or interchange associative (I$_a$) mechanism (Scheme I). Although depending on the rate-determining step, the data are also consistent with an interchange dissociative (I$_d$) mechanism. According to Scheme I, following diffusion of ethylenediamine into the solvation sphere, unidentate coordination of the incoming ethylenediamine molecule results in the formation of a nine-coordinate intermediate **3**. The formation of **2** and **3** contributes to the large negative value of ΔS^*. Although the observation of first-order dependency on ethylenediamine concentration does not allow one to uniquely distinguish the rate-determining step in Scheme I, the slow step is expected to involve chelate ring opening,[26] perhaps as a concerted interchange (I$_a$) leading to formation of **4**. Assuming steady-state conditions for all the intermediates, the global rate constant for exchange in the

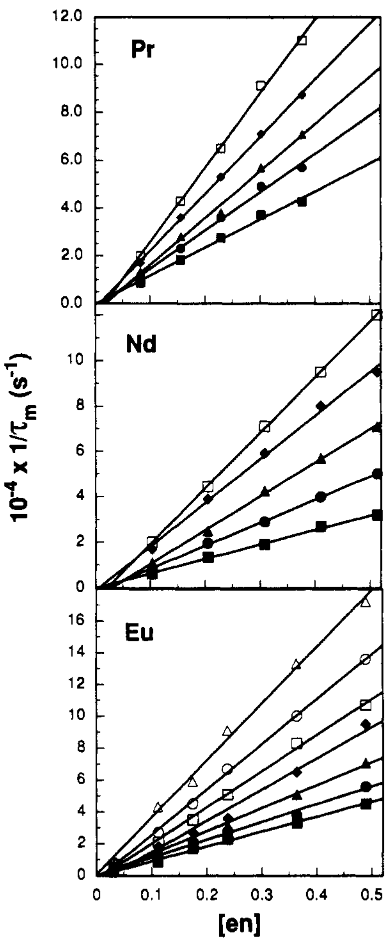


Figure 5. Dependence of $1/\tau_m$ on concentration of free ligand at various temperatures (■, 233 K; ●, 243 K; ▲, 253 K; ◆, 263 K; □, 273 K; ○, 283 K; △, 293 K) for complexes derived from the larger metal ions.

Table I. Kinetic Parameters for the Exchange Reactions of Ethylenediamine with Ln(en)$_4^{3+}$ Complexes

Ln	$10^{-6}k''$ (M^{-1} s^{-1})^a	$10^{-4}k_D$ (s^{-1})^{a,d}	ΔH^* (kJ·mol^{-1})	ΔS^* (J·K^{-1}·mol^{-1})
Pr	1.9 ± 0.2		9.7 ± 1	−92 ± 9.0
Nd	2.0 ± 0.2		16 ± 1	−71 ± 5.0
Eu	1.5 ± 0.15		11 ± 1	−91 ± 8.0
Er^b		3.6 ± 0.4	53 ± 5	17 ± 5
Er^c		4.5 ± 0.4	44 ± 4	−9.1 ± 1.0
Yb^b		1.8 ± 0.1	52 ± 5	12 ± 5
Yb^c		1.3 ± 0.1	53 ± 5	12 ± 5

[a] Values of the rate constant were extrapolated from Arrhenius plots using data obtained from the following temperature ranges given in parentheses: Pr, Nd (233–273 K); Eu (233–293 K); Er (303–343 K); Yb (313–343 K). [b] 300-MHz data. [c] 100-MHz data. [d] Values of k_D were obtained from a nonlinear least-squares fit of the experimental data to eq 8.

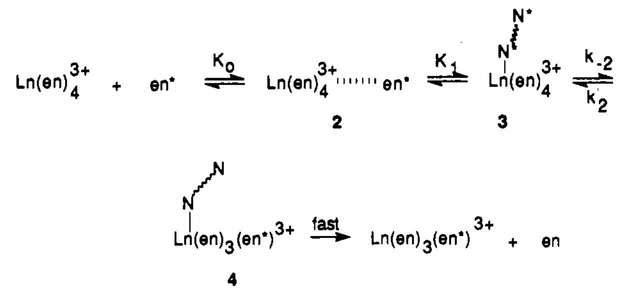
---

(24) Due to limited solubility of the Ln(en)$_4^{3+}$ complexes in the solvent, the dependency of τ_m on [Ln(en)$_4^{3+}$] was not determined and first-order dependency was assumed for each system.

(25) The factor of 4 in eqs 4 and 5 represents the number of coordinated ethylenediamine molecules in the complex.

(26) (a) Wilkins, R. G. *Acc. Chem. Res.* **1970**, *3*, 408. (b) Shamsuddin Ahmed, A. K.; Wilkins, R. G. *J. Chem. Soc.* **1959**, 3700. (c) Shamsuddin Ahmed, A. K.; Wilkins, R. G. *J. Chem. Soc.* **1960**, 2894. (d) Shamsuddin Amhed, A. K.; Wilkins, R. G. *J. Chem. Soc.* **1960**, 2900. (e) Wilkins, R. G. *J. Chem. Soc.* **1962**, 4475.

Scheme I



forward direction according to Scheme I can be shown to be

$$k'' = K_0k_1k_2/[((k_1/k_{-0}) + 1)k_2 + k_{-2} + k_{-1}] \qquad (6)$$

where $K_0 = k_0/k_{-0}$ and $K_1 = k_1/k_{-1}$, with the other terms defined in Scheme I. Making the reasonable assumptions that interchange $\mathbf{3} \rightleftharpoons \mathbf{4}$ is slow relative to the rate of loss of the incoming, unidentate ethylenediamine molecule from the inner sphere ($\mathbf{3} \rightarrow \mathbf{2}$) ($k_2$, $k_{-2} \ll k_{-1}$) and that the rate of diffusion of the incoming group back into the bulk solution is greater than the rate of $\mathbf{2} \rightarrow \mathbf{3}$ ($k_1/k_{-0} \leq 1$) leads to the expression $k'' = K_0K_1k_2$. Alternatively, if the formation of **3** via interchange (I_a) of the incoming ethylenediamine group with a solvent molecule (not shown) is rate determining, then k'' is given by eq 7 (see below), where k_I is the forward rate constant for formation of **3**. Under the limiting condition $1 \gg K_0[\text{en}]$,[28] $k'' = K_0k_I$. Finally, an A mechanism does not require the formation of the encounter complex **2**, and k'' is identical to the second-order rate constant. The mechanism proposed in Scheme I takes into account of the fact that the tetrakis(ethylenediamine) complexes of the larger lanthanides have a ninth coordination site, which in the solid state is occupied by an oxygen atom of one of the triflate ions.[3] ^{19}F NMR spectra were obtained in order to determine whether the triflate ion is coordinated in solution. Only a single peak was observed in each system, which showed relatively little variation with respect to the paramagnetic or diamagnetic character of the complex [δ in ppm relative to $CFCl_3$: -80.9 (Pr), -77.4 (Eu), -78.9 (Er), -74.6 (Yb), -78.0 (Lu)]. The variation in chemical shift is attributed to an outer-sphere rather than inner-sphere interaction. Furthermore, solutions containing 1:1 or 2:1 en:Ln^{3+} mole ratios revealed about the same chemical shifts as the tetrakis complexes. The data suggest that in solution the triflate ion is not competing successfully with ethylenediamine or the solvent for the ninth coordination site.

In contrast to those for the larger metal ions, plots of $1/\tau_m$ vs [en] in the temperature range 233–313 K are nonlinear (Figure 6), with intercepts that are not at the origin. The nonlinear dependency of $1/\tau_m$ on the concentration of ethylenediamine can be accounted for by an I_d mechanism[27] Scheme II,whereas the positive intercept suggests the simultaneous operation of a limiting dissociative D mechanism (Scheme III). It is proposed that a ninth coordination site is not available in complexes of the smaller ions due to the decrease in ionic radius across the lanthanide series. Thus, in the I_d mechanism, following rapid formation of the encounter complex **5**, a slow interchange involving chelate ring opening and coordination of one end of the incoming ethylenediamine group results in the formation of an eight-coordinate intermediate **6**. In this case, the global rate constant for exchange is given by eq 7,[27] which accounts for the nonlinear dependency of τ_m^{-1} on the concentration of ethylenediamine.

$$k = 4/\tau_m = K_0k_I[\text{en}]/(1 + K_0[\text{en}]) \qquad (7)$$

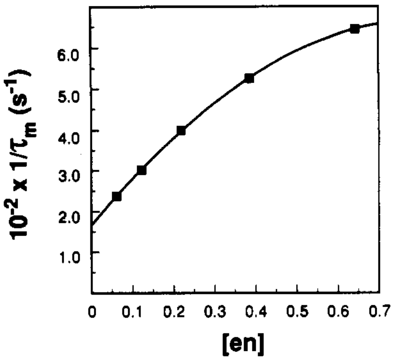
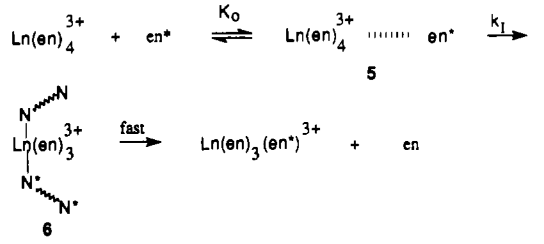
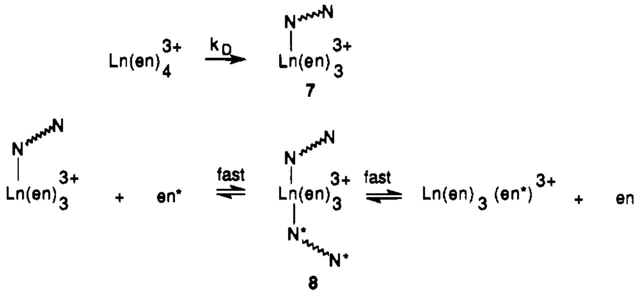


Figure 6. Dependence of $1/\tau_m$ for the $Yb(en\text{-}d_4)_4^{3+}$ system on the concentration of free ligand at 293 K.

Scheme II



Scheme III



In the limiting D mechanism, the initial (rate-determining) step involves chelate ring opening leading to formation of a seven-coordinate intermediate **7**, followed by rapid unidentate coordination of the incoming ligand, giving intermediate **8**, which has an equal probability of losing the outgoing or incoming ligand. For a parallel two-path mechanism

$$4/\tau_m = k_D + K_0k_I[\text{en}]/(1 + K_0[\text{en}]) \qquad (8)$$

where the constants are defined in Schemes II and III. A nonlinear least-squares (Marquardt method) analysis of eq 8 was carried out using k_D, K_0, and k_I as fitting parameters. Generally good agreement is observed between observed and calculated $1/\tau_m$ values (Table S1). However, since $K_0 \leq 1^{28}$, the term $K_0[\text{en}]$ is small at the concentrations of free ligand used in these studies (0.06–0.60 M). As a consequence, it was not possible to obtain reliable values of k_I, since in the limiting condition $K_0[\text{en}] \ll 1$, eq 8 becomes $4/\tau_m = k_D + K_0k_I[\text{en}]$, and only the product K_0k_I is determined. Nevertheless, reliable values of the intercept (k_D) may still be obtained (Table S1). The values of k_D at 298 K (Table I) were obtained from Arrhenius plots over the temperature range 253–343 K, using the k_D values obtained from the Marquardt analysis. Activation parameters for the smaller ions (Table I) were obtained from plots of ln (k_D/T) vs $1/T$. At higher temperatures, $1/\tau_m$ becomes nearly independent of the concentration of ethylenediamine, suggesting that the D pathway becomes more favorable than the I_d pathway as the temperature is increased. This observation may be accounted for by the reasonable assumption that the ΔS^* values for the limiting D mechanism are more positive than the corresponding values for the I_d mechanism at a given temperature.

---

[27] Langford, C. H.; Muir, W. R. *J. Am. Chem. Soc.* **1967**, *89*, 3141.

[28] In a previous NMR study of the solvation of $Gd(en)_4^{3+}$ in acetonitrile/ethylenediamine mixtures at 25 °C, we found no evidence for preferential solvation by ethylenediamine; i.e., $K_0 \leq 1$.[29]

[29] Meyer, K. E. M.S. Thesis, Saint Louis University, 1987.

The rate constants measured for ligand exchange involving complexes derived from the smaller ions are ca. 2 orders of magnitude smaller than those calculated for complexes derived from the larger ions. The observation of significantly larger ΔH^* values and more positive ΔS^* values for reactions involving complexes of the smaller ions as compared to those of the larger ions (Table I) is consistent with the proposal that the mechanism of ligand exchange is primarily dissociative for the smaller ions, but involves formation of a nine-coordinate intermediate in the case of the larger ions.

Conclusions

The mean ligand residence times, τ_m, of the series of $Ln(en)_4^{3+}$ (Ln = Pr, Nd, Eu, Er, Yb) complexes in solutions of deuterated acetonitrile containing excess ethylenediamine were observed to increase across the lanthanide series. A linear dependency of $1/\tau_m$ on the concentration of free ligand was noted for complexes derived from the larger ions (Pr^{3+}, Nd^{3+}, Eu^{3+}), corresponding to a rate law that is first order in ethylenediamine concentration. For these reactions, it is proposed that a ninth coordination site in the $Ln(en)_4^{3+}$ complexes is available for attack by the incoming ethylenediamine group. For complexes of the smaller ions, plots of $1/\tau_m$ vs [en] were nonlinear, revealing a positive intercept. Both I_d and D mechanisms were proposed to be simultaneously operating for complexes of the smaller ions, with the D pathway becoming more favorable with increasing temperature.

Acknowledgment. We thank Prof. Bruce A. Kowert for many helpful discussions throughout the course of this project. A grant to J.H.F. from the Beaumont Faculty Development Fund of Saint Louis University is gratefully acknowledged.

Supplementary Material Available: Table S1, giving the parameters used for simulating spectra and the corresponding values of τ_m (10 pages). Ordering information is given on any current masthead page.