$[C_2H_5SFe(NO)_2]_2$ (for which the observed Fe–Fe bonding distance of 2.72 A is compatible with the electron-spin pairing)[26] and for $[BrMn(CO)_4]_2$ (for which a molecular D_{2h} configuration with a nonbonding intramolecular Mn···Mn distance of 3.74 A was found).[59] However, the geometrical consequences of the metal–metal bonds in these two dimeric systems are apparent from stereochemical considerations. The dimeric cobalt nitrosyl complexes no doubt will retain a similar symmetrical configuration to the one ascertained in the known mercaptoiron nitrosyl dimer (in which the two NO groups and two S atoms form a tetrahedral-like environment about each iron atom) except for a longer nonbonding metal–metal distance of magnitude 3.3–3.4 A (together with normal bridging ligand angles of approximately 100°). Similarly, outside of the expected decrease in metal–metal distance to a single bond value of 3.0 A (as found in the related bridging complex $[C_5H_5CrS_2C_4F_6]_2$ for which a proposed chromium–chromium single bond is in agreement with the observed diamagnetism),[60] the $[XCr(CO)_4]_2$ species should remain invariant in its general shape relative to that of $[BrMn(CO)_4]_2$. Structural work is in progress to verify these deductions.

Acknowledgments. We are extremely grateful to Dr. Roy Hayter for furnishing us with samples of these two complexes and for his interest in this work. We also are pleased to acknowledge the Air Force Office of Air Research and Development Command for their financial support of this research. The use of the CDC 1604 and 3600 computers at the University of Wisconsin Computing Center was made possible by partial support of N.S.F. and W.A.R.F. through the University Research Committee.

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Aminopolycarboxylic Acid Ligand-Exchange Kinetics of Selected Alkaline Earth Ions[1]

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Abstract: The ligand-exchange kinetics of the strontium–ethylenediaminetetraacetic acid system and the calcium–N′-(2-hydroxyethyl)ethylenediamine-N,N,N′-triacetic acid system have been evaluated in aqueous solution using proton nmr line-broadening techniques. Exchange occurs by both first-order dissociation of the metal–ligand species and second-order processes involving free ligand and metal–ligand species. The pH dependence of the rate was used to evaluate the rate constants for the individual exchange steps. From comparison of the rate constants in these and other systems, mechanisms of the second-order exchange reactions are proposed, and the structure of the protonated metal–ligand species is concluded to be such that only one iminodiacetate segment of ethylenediaminetetraacetate is metal coordinated.

Despite the importance of the alkaline earth metal ions and the extensive thermodynamic data available on their complexes, only meager kinetic information on such complexes is available. This circumstance results from the rapid reaction rates involving these ions and eliminates the possibility of employing conventional techniques for rate studies. In an earlier paper, the ligand-exchange kinetics in the calcium–ethylenediaminetetraacetic acid (EDTA) system were studied using proton nuclear magnetic resonance (nmr) line-broadening techniques.[2] In the present paper we have studied the exchange kinetics of two related systems in an attempt to elucidate the mechanisms of aminopolycarboxylic acid ligand exchange with the alkaline earth ions. One of these systems is strontium and EDTA, which can be described by the same pH-dependent rate expression as calcium and EDTA, suggesting that exchange occurs by similiar mechanisms in both systems. The second system is calcium and N′-(2-hydroxyethyl)ethylenediamine-N,N,N′-triacetic acid (HEEDTA).[3] The latter ligand, while structurally related to EDTA, is capable of only pentadentate coordination to metal ions. Although the rates in the present investigation are generally greater than the corresponding rates found in the CaEDTA study, they are still within the time limits accessible to nmr line-broadening measurements. Advantage has been taken of the extensive pH range available with the alkaline earth ions to isolate the various pH-dependent rate processes. The lower pH limit is approximately 4 because of dissociation of the chelates, but there is no upper pH limit because metal–(hydroxy)–ligand species do not exist.

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(1) (a) This work was supported by a grant (GP 4423) from the National Science Foundation and by a National Institute of Health Predoctoral Fellowship (D. L. R.); (b) presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

(2) R. J. Kula and G. H. Reed, *Anal. Chem.*, 38, 697 (1966).

(3) In this paper L^{3-} is used to designate the trianion of HEEDTA and HL^{2-} the monoprotonated anion; Y^{4-} represents the EDTA tetraanion and HY^{3-} the monoprotonated anion; M^{2+} represents either Ca^{2+} or Sr^{2+}.

Experimental Section

Chemicals. Analytical reagent grade anhydrous strontium nitrate, calcium nitrate tetrahydrate, ethylenediaminetetraacetic acid, and N′-(2-hydroxyethyl) ethylenediamine-N,N,N′-triacetic acid (Geigy Chemical Co.) were used without further purification. Solutions were prepared using triply distilled water for all formation constant measurements and rate measurements. Weighed amounts of metal nitrate and fully protonated ligands were mixed to give the concentrations desired, and potassium hydroxide was added to bring the solutions to the desired pH.

Potentiometric Titrations. Determinations of formation constants and dissociation constants were carried out as described previously.[2] The ionic strength was maintained with potassium nitrate, and titrations were performed at 25°.

Nmr Measurements. The nmr data were obtained on a Varian A-60 spectrometer operated at 32 ± 1 and at 25 ± 1°. The general techniques have been described earlier.[2]

Rate Measurements. In both the SrEDTA and CaHEEDTA systems containing excess ligand, averaged, exchange-broadened resonances located between the positions of the free and the complexed ligand resonances were observed. The ligand exchange rates were such that slow exchange on the nmr time scale could not be achieved. The mean lifetime, τ_{complex}, of a given metal–ligand species between events which lead to exchange of a ligand between free and complexed forms was calculated from the width of the averaged resonances using the rapid exchange approximation[4]

$$\frac{1}{\tau_{\text{complex}}} = \frac{4\pi P_{\text{free}}{}^2 P_{\text{complex}}(\delta_{\text{complex}} - \delta_{\text{free}})^2}{w_{\text{obsd}} - (P_{\text{complex}} w_{\text{complex}}) - (P_{\text{free}} w_{\text{free}})}$$

where P is the fractional population of ligand in free or in complexed forms ($P_{\text{free}} + P_{\text{complex}} = 1$), δ is the chemical shift in cps of free and complexed ligand resonances in the absence of exchange (determined from a solution of the free ligand and from a 1:1 solution of the metal–ligand complex at the appropriate pH), and w_{obsd}, w_{complex}, and w_{free} are the resonance line widths at half-height (measured in cps) of the averaged resonance, the complex resonance in the absence of exchange, and the free ligand resonance in the absence of exchange, respectively.

The reciprocal of the mean lifetime of the metal–ligand complex can be related to the exchange rate, $-\text{d}[\text{complex}]/\text{d}t$, by

$$\frac{1}{\tau_{\text{complex}}} = \frac{-\text{d}[\text{complex}]}{\text{d}t} \frac{1}{[\text{complex}]}$$

The total rate expression contains terms which are either zero order or first order in free ligand so that the exchange rate equation can be expressed as

$$\frac{-\text{d}[\text{complex}]}{\text{d}t} = k_{\text{A}}[\text{complex}] + k_{\text{B}}[\text{complex}][\text{ligand}]_{\text{free}}$$

The reciprocal of the mean lifetime of the metal–ligand species is then

$$\frac{1}{\tau_{\text{complex}}} = k_{\text{A}} + k_{\text{B}}[\text{ligand}]_{\text{free}}$$

and k_{A} and k_{B} can be obtained from the intercept and slope, respectively, of plots of $(\tau_{\text{complex}})^{-1}$ *vs.* free ligand concentration at constant pH values. Such plots at different pH values indicate that both k_{A} and k_{B} are pH dependent. From the potentiometrically determined equilibrium constants, concentrations of the various species present were calculated. Alternatively, the concentrations of unprotonated and monoprotonated ligand were determined from the chemical shift *vs.* pH curves for solutions of free ligand. From this information the appropriate pH and concentration conditions were chosen so that k_{A} and k_{B} could be resolved into the rate constants for each of the pH dependent processes.

The following exchange paths are considered in the kinetic analysis of the SrEDTA system

$$\text{SrY}^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Sr}^{2+} + \text{Y}^{4-} \tag{1}$$

$$\text{SrY}^{2-} + \overset{*}{\text{Y}}{}^{4-} \overset{k_2}{\rightleftharpoons} \text{Sr}\overset{*}{\text{Y}}{}^{2-} + \text{Y}^{4-} \tag{2}$$

$$\text{SrY}^{2-} + \text{H}\overset{*}{\text{Y}}{}^{3-} \overset{k_3}{\rightleftharpoons} \text{Sr}\overset{*}{\text{Y}}{}^{2-} + \text{HY}^{3-} \tag{3}$$

$$\text{H}^+ + \text{SrY}^{2-} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \text{Sr}^{2+} + \text{HY}^{3-} \tag{4}$$

$$\text{HSrY}^- + \text{H}\overset{*}{\text{Y}}{}^{3-} \overset{k_5}{\rightleftharpoons} \text{HSr}\overset{*}{\text{Y}}{}^{-} + \text{HY}^{3-} \tag{5}$$

$$\text{H}^+ + \text{SrY}^{2-} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} \text{HSrY}^- \tag{6}$$

$$\text{HSrY}^- \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} \text{HY}^{3-} + \text{Sr}^{2+} \tag{7}$$

The resulting rate equation, applicable over the entire pH range, is

$$\frac{-\text{d}[\text{SrY}^{2-}]}{\text{d}t} = k_1[\text{SrY}^{2-}] + k_2[\text{SrY}^{2-}][\text{Y}^{4-}] + k_3[\text{SrY}^{2-}][\text{HY}^{3-}] + k_5[\text{HY}^{3-}][\text{HSrY}^-] + k_7[\text{HSrY}^-] \tag{8}$$

Above pH 8 only exchange paths 1, 2, and 3 need be considered, and a satisfactory method of treating the data to obtain the rate constants was found to be

$$\frac{1}{\tau_{\text{SrY}}} = \frac{-\text{d}[\text{SrY}]/\text{d}t}{[\text{SrY}]} = k_1 + k_2 a[\text{Y}_{\text{free}}] + k_3 b[\text{Y}_{\text{free}}] \tag{9}$$

where $a = [\text{Y}^{4-}]/[\text{Y}_{\text{free}}]$ and $b = [\text{HY}^{3-}]/[\text{Y}_{\text{free}}]$. Plots of $1/\tau_{\text{SrY}}$ *vs.* $[\text{Y}_{\text{free}}]$ at various constant pH values give straight lines whose slopes are $ak_2 + bk_3$ (analysis at different pH values yields k_2 and k_3) and whose intercepts are k_1. The CaHEEDTA system was investigated only at pH values greater than 8, and the resulting rate expression for this pH region is

$$\frac{-\text{d}[\text{CaL}^-]}{\text{d}t} = k_1[\text{CaL}^-] + k_2[\text{CaL}^-][\text{L}^{3-}] + k_3[\text{CaL}^-][\text{HL}^{2-}] \tag{10}$$

Above pH 8 the concentration of the protonated CaHEEDTA complex, known to form in acidic solutions, is negligible so that the possibility of exchange by paths analogous to (4) and (5) is not considered. The constants are evaluated experimentally using an equation analogous to eq 9.

In the low pH region (below pH 8) all possible exchange reactions, except eq 2, are considered. Exchange according to a path found to be first order in H^+ and first order in SrY^{2-} may be represented by step 4, but because HMY^- entities are known to exist, this exchange path might be equally well represented by protonation of SrY^{2-} (step 6) and subsequent dissociation according to step 7. This consideration enables the calculation of k_4 from the observed k_7 using the acid-dissociation constant of step 6. In such a case the proton-exchange rate of step 6 must be assumed to be rapid relative to the first-order dissociation rate of HSrY^-. If some dissociation proceeds through step 4, the value calculated for k_7 is too large and may be considered as an upper limit. The next to the last term in eq 8 corresponding to step 5 was found to be first order in H^+, SrY^{2-}, and HY^{3-}. Knowing the acid dis-

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[4] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 222.

Table I. Potentiometrically Determined Equilibrium Constants[a]

	CaEDTA[b]		SrEDTA		CaHEEDTA		HEEDTA		EDTA	
Ionic strength, M	0.16	1.6	0.16	1.6	0.16[c]	1.6	0.16[c]	1.6	0.16[c]	1.6
Log K_{f1}	10.6	9.4	8.6	7.4	8.1	7.65				
Log K_{f2}	3.5	2.4	1.9	1.3	1.4	1.5				
Log K_a	−3.2	−2.8	−3.6	−3.7		−3.6				
Log K_1							9.9	9.7	10.1	9.8
Log K_2							5.4	5.4	6.2	6.2

[a] At 25°. [b] See ref 2. [c] See L. G. Sillén and A. E. Martell, Special Publication No. 17, The Chemical Society, London, 1964.

sociation constant for $HSrY^-$, the second-order rate constant for ligand exchange through an $HSrY^-$ intermediate has been obtained.

In order to utilize a graphical evaluation of these rate constants, eq 8 has been rearranged to give eq 11, where K_{f1}, K_{f2}, and K_1 are

$$\frac{\left(\frac{1}{\tau_{\mathrm{SrY}}} - k_1 - k_3b[\mathrm{Y}_{\mathrm{free}}]\right)K_{f1}}{K_{f2}K_1[\mathrm{H}^+]} = k_7 + k_5b[\mathrm{Y}_{\mathrm{free}}] \quad (11)$$

defined in eq 12, 13, and 15, respectively. Experimentally, a solution containing equal concentrations of SrY^{2-} and Y_{free} was studied from pH 6.5 to 5.5, and the left-hand side of eq 11 was plotted against $b[Y_{free}]$.

In the exchange reactions studied, k_1, k_2, k_3, k_5, and k_7 have been determined directly from the nmr data, whereas k_{-1} and k_{-7} have been calculated from the reverse rate constants and the appropriate equilibrium constants.

The errors involved in using the rapid exchange approximation to calculate lifetimes were determined by evaluating the lifetime using the complete expression first given by Gutowsky and Holm.[5] The experimental chemical shift and population parameters were used in the complete expression, and the average lifetime of the SrEDTA complex was varied. The theoretical line width was calculated and plotted *vs.* lifetime. From these plots the experimental lifetimes were determined by interpolation employing the experimental line widths. When the rapid exchange approximation is used to evaluate the rate constants, those constants for processes zero order in free ligand are within 20% and those first order in free ligand are within 10% of those determined using the complete theoretical expression. Our results suggest that the errors in measuring k_2, k_3, and k_5 experimentally are somewhat greater than these percentages (about 20%), whereas the error in measuring k_1 is of the order of 30%. The error in k_7 and k_{-7} is governed by the uncertainty in K_{f2} (an order of magnitude number for values so small compared to K_{f1}). This analysis also indicated that under conditions where the populations of the free and the complexed ligand are quite different, a large change in lifetime results in only a small change in line width. A small error in the experimental line width then leads to a large error in the calculated rate constants. Solution conditions have been adjusted so that the populations do not differ significantly, and this source of error is minimized.

An additional factor affecting the results is the temperature of the nmr measurements (32°). This factor was evaluated by measuring k_1, k_2, and k_3 at 25°, and the results were found to agree with those at 32° within the experimental errors discussed above. All the other rate constants were obtained at the higher temperature, and it is assumed that the temperature factor here is also less than the experimental errors involved.

In the SrEDTA system the acetate resonance of EDTA was used for the kinetic measurements as suggested previously.[2] In the CaHEEDTA system, the acetate resonance was also used, but the error in this case is larger. At certain pH values, the two acetate protons on the ethyl alcohol end of the molecule are not equivalent to those on the other end, and two lightly separated (~0.5 cps) resonances are observed for both the free ligand and for the 1:1 complex. (The pH-dependent nmr spectra for HEEDTA can be found elsewhere.[6]) When excess HEEDTA is present, this separation is not observed in the exchange-broadened average resonance, but the lines are somewhat broader than expected because they are a superposition of the two slightly different acetate resonances.

Results

The potentiometrically determined equilibrium constants are summarized in Table I. These constants correspond to the following equilibria in the EDTA system

$$K_{f1} = \frac{[\mathrm{MY}^{2-}]}{[\mathrm{M}^{2+}][\mathrm{Y}^{4-}]} \quad (12)$$

$$K_{f2} = \frac{[\mathrm{HMY}^{-}]}{[\mathrm{M}^{2+}][\mathrm{HY}^{3-}]} \quad (13)$$

$$K_a = \frac{[\mathrm{H}^+][\mathrm{MY}^{2-}]}{[\mathrm{HMY}^{-}]} \quad (14)$$

$$K_1 = \frac{[\mathrm{HY}^{3-}]}{[\mathrm{H}^+][\mathrm{Y}^{4-}]} \quad (15)$$

$$K_2 = \frac{[\mathrm{H}_2\mathrm{Y}^{2-}]}{[\mathrm{H}^+][\mathrm{HY}^{3-}]} \quad (16)$$

Analogous equilibria apply to the HEEDTA system.

The equilibrium constants obtained under high ionic strength conditions (similar to the ionic strength of solutions employed in the nmr studies) differ by as much as an order of magnitude from the constants obtained under low ionic strength conditions. Because several of the rate constants are calculated from the equilibrium data, it is necessary that the high ionic strength constants be utilized.

Rate data obtained in the high pH region for the SrEDTA and CaHEEDTA systems are presented in Table II. Analysis of the rate data in the low pH region for the SrEDTA system utilizing eq 11 is shown in Figure 1. The rate constants determined for the SrEDTA and CaHEEDTA systems are presented in

Table II. Nmr Rate Data for High pH Region[a]

pH	Slope	Intercept	*a*	*b*
		SrEDTA		
9.90	660	20	0.56	0.44
9.50	465	31	0.34	0.66
9.00	283	39	0.14	0.86
		CaHEEDTA		
8.00	230	35	0	1.0
9.20	395	25	0.18	0.82
9.45	480	23	0.28	0.72

[a] At 32°; [metal] = 0.20 M, [ligand] = 0.20 to 0.40 M.

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(5) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).
(6) J. L. Sudmeier and C. N. Reilley, *Anal. Chem.*, **36**, 1698 (1964).

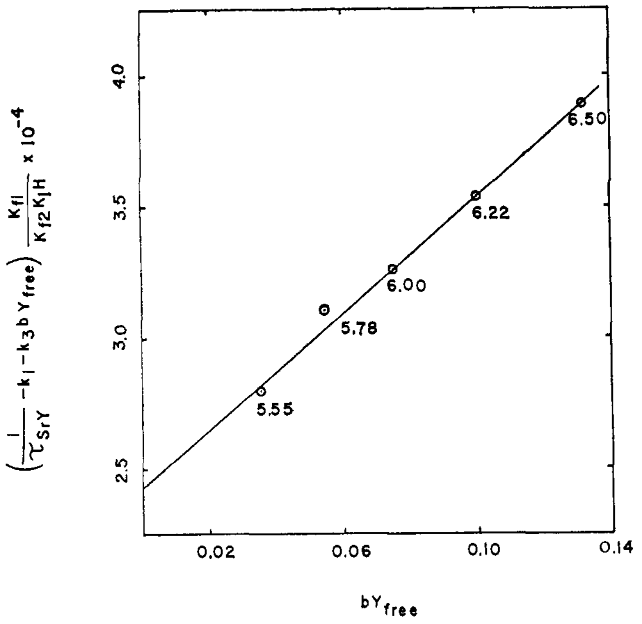

Figure 1. Nmr rate data for the SrEDTA system in the low pH region: $[Sr^{2+}] = 0.20\ M$; $[Y_{total}] = 0.40\ M$; 32°; pH values indicated by numbers beside each point.

Table III. The constants for the CaEDTA system have been included for purposes of comparison.

Table III. Experimental Rate Constants

Rate constant[a]	CaEDTA[b]	SrEDTA	CaHEEDTA
k_1, sec^{-1}	≤ 1	3×10^1	3×10^1
k_{-1}, $M^{-1}\,sec^{-1}$	$\leq 2.5 \times 10^9$	8.1×10^8	1.3×10^8
k_2, $M^{-1}\,sec^{-1}$	1.2×10^2	1.1×10^3	1.1×10^3
k_3, $M^{-1}\,sec^{-1}$	5	1.6×10^2	2.3×10^2
k_4, $M^{-1}\,sec^{-1}$	2×10^7	1×10^8	
k_5, $M^{-1}\,sec^{-1}$	2×10^5 [c]	1×10^5	
k_7, sec^{-1}	5×10^4	2×10^4	
k_{-7}, $M^{-1}\,sec^{-1}$	1×10^7	5×10^5	

[a] Ionic strength ~1.6 M. [b] See ref 2. [c] Note this value is corrected from the erroneously reported value in ref 2.

Discussion

The first-order dissociation rate constants of both SrEDTA and CaHEEDTA are greater than that for CaEDTA as might be expected from their relative thermodynamic stabilities. The values of the association rate constants are seen to approach the rate of water loss from the aquated metal ion, as determined by Eigen,[7] and are in agreement with the rates obtained by relaxation methods for the Ca^{2+} and Sr^{2+} association reactions with iminodiacetate (IDA^{2-}) (2.5×10^8 and $3.2 \times 10^8\ M^{-1}\ sec^{-1}$, respectively).[8]

The rate constants k_2 and k_3 are for ligand exchange between the free and the complexed forms by a process where the rate-determining steps involve both the free ligand and the metal-ligand complex. These processes could be one-step direct displacements of the bound ligand by an incoming ligand, no stable intermediates being formed in the exchange process. However, recent work suggests that a more plausible mechanism is a multistep displacement of the bound ligand by the incoming ligand, proceeding through intermediates in which both ligands are simultaneously bound in varying degrees to the metal ion.[9] One possible exchange path is shown in Figure 2. Water molecules are probably involved in the rupture of metal-ligand bonds but have been omitted from the proposed reaction steps. By this path intermediate structure III is symmetrical, having one iminodiacetate segment of each EDTA ligand simultaneously bound to the metal. The observed rate of ligand exchange will be one-half the rate of disappearance of this intermediate by the two identical paths, because one path goes back to the reactants and the other leads to ligand exchange. The rate of disappearance of the intermediate and the rate of ligand exchange are limited by the amount of intermediate present, which must be determined by its rate of formation. The rate-determining step in the observed ligand-exchange reaction would therefore be in the formation of the symmetrical diligand intermediate.

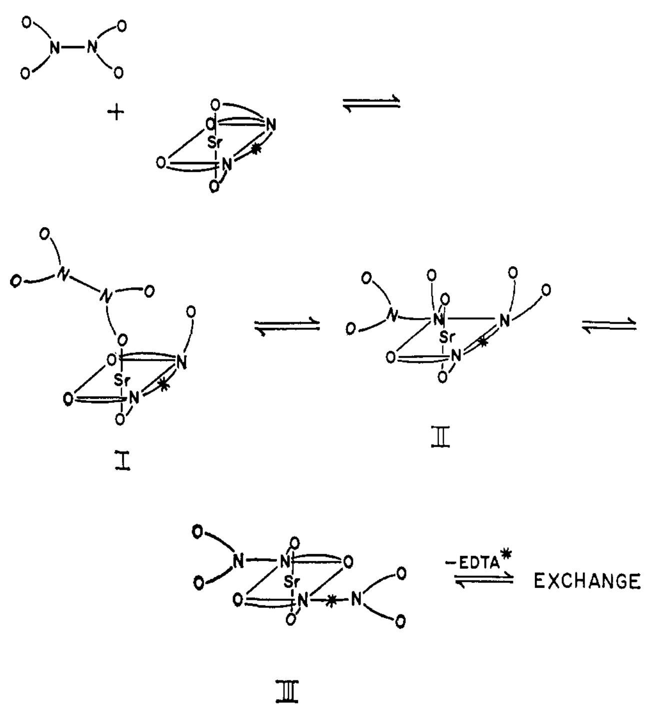

Figure 2. Proposed stepwise nature of ligand exchange for $SrY^{2-} + Y^{4-}$.

Formation of intermediate III by the proposed mechanism involves three steps: (a) displacement of one acetate arm of the bound EDTA and subsequent formation of the first metal-ligand bond with the incoming EDTA; (b) displacement and formation of the second bond (presumably a metal-nitrogen bond[10]); and (c) displacement and formation of the third bond (the second metal-carboxylate bond). If step a is rate determining, exchange reactions 2 and 3 should proceed much more rapidly for a complex in which only five sites on the metal ion are ligand coordinated. One

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(7) M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).

(8) R. K. Murmann, R. T. M. Fraser, and J. Bauman, Ed., "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 61.

(9) D. W. Margerum, D. L. Janes, and H. M. Rosen, *J. Am. Chem. Soc.*, **87**, 4463 (1965).

(10) J. L. Sudmeier and C. N. Reilley, *Inorg. Chem.*, **5**, 1047 (1966).

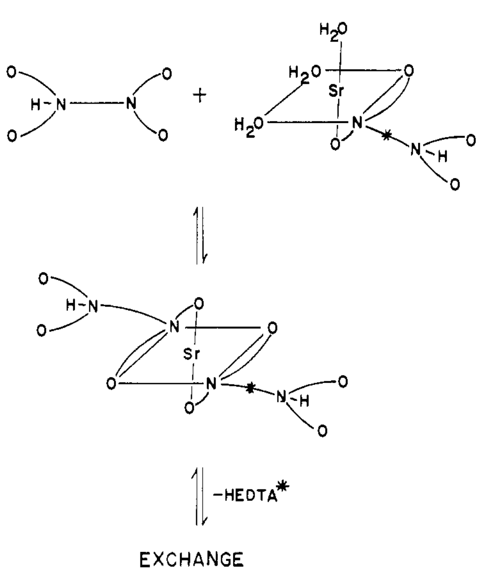

Figure 3. Proposed ligand-exchange mechanism for $HSrY^- + HY^{3-}$.

such complex is CaHEEDTA. For the HEEDTA ligand one of the acetate groups of EDTA has been replaced by an ethyl alcohol group, known to have weak coordination properties. In the CaHEEDTA system the rate of the exchange reaction corresponding to step 2 is found to increase by an order of magnitude over the rate for CaEDTA. However, the two systems differ in the electrostatic charges of the reacting species.

The electrostatic effect may be eliminated by reducing the experimental rate constants, k, to rate constants in media of infinite dielectric constant, k_0, using eq 17, where Z_A and Z_B are the charges of the react-

$$\ln \frac{k}{k_0} = -\frac{Z_A Z_B e^2}{\epsilon d_{AB} k T} \qquad (17)$$

ing ions, and d_{AB} is the reaction pair separation (assumed to be 7 A in our calculation), the other terms having their usual significance.[11] Using this approximation we find that the difference in rate constants for $(CaL^- + L^{3-})$ and for $(CaY^{2-} + Y^{4-})$ can be accounted for merely by the differences in electrostatic charges of the reacting ions. Consequently the formation of the first metal–ligand bond does not appear to be the rate-determining step in this exchange reaction, and the rate of formation of intermediate III (Figure 1) must be governed by either the formation of the second or third bond to the incoming ligand. Similarly eq 17 can be utilized to explain the differences in the rate constants between $(CaL^- + HL^{2-})$ and $(CaY^{2-} + HY^{3-})$ exchange reactions.

Our results show that step 5 proceeds at a rate which is first order in $HSrY^-$ and first order in free HY^{3-}. A stepwise mechanism similar to that in Figure 2 could also proceed through a symmetrical intermediate whose rate of formation would be rate determining. However, on the basis of the structure proposed by Schwarzenbach for the protonated alkaline earth–EDTA species[12] (one iminodiacetate group of EDTA metal coordinated and the other iminodiacetate nitrogen protonated), formation of the intermediate does not involve the displacement of an iminodiacetate segment of the bound EDTA. There are already three available sites on the coordinated metal ion to which the incoming HY^{3-} may coordinate to form a symmetrical $(HY\text{–}M\text{–}YH)^{4-}$ intermediate (Figure 3). This situation is analogous to the formation of SrIDA from Sr^{2+} and IDA^{2-}, in which the incoming ligand coordinates with three sites on the Sr^{2+} ion. Therefore, if the formation of a symmetrical intermediate in the HY^{3-} and $HSrY^-$ exchange is rate determining, k_5 should be comparable with the association rate constant of Sr^{2+} with IDA^{2-}.

In order to compare the Sr^{2+} and IDA^{2-} reaction with the $HSrY^-$ and HY^{3-} reaction, however, account must again be taken of the differences in electrostatic charges of the reacting species in the two systems and of the effect the proton on free EDTA has on the rate. Using eq 17, k_5 is found to be reduced to 1/1000 of the rate constant for the Sr^{2+} and IDA^{2-} association reaction because of electrostatic effects.

The effect of H^+ in HY^{3-} on the exchange rate is to decrease the availability of the ligand donor sites through internal association of these sites with H^+. The magnitude of this effect can be approximated by comparing k_2^{SrY} with k_3^{SrY}. Applying the above equation to eliminate the effects due to different charge types, Y^{4-} is calculated to be 40 times as effective at displacing the bound ligand in SrY^{2-} as is HY^{3-}. Combining this factor of 40 with the factor of 1000 because of electrostatic effects gives an over-all correction of 4×10^4 to k_5. Such a correction then makes the rate constants for SrIDA formation and for the formation of a $(HY\text{–}Sr\text{–}YH)^{4-}$ intermediate comparable. This implies that only one iminodiacetate segment of EDTA is coordinated in $HSrY^-$ and supports the mechanism in which the rate of formation of a diligand intermediate is rate determining for exchange path 5.

The low value obtained for k_7^{HSrY} compared to k_7^{HCaY} is somewhat disturbing because $HSrY^-$ should dissociate more rapidly than $HCaY^-$. However, k_7^{HSrY} is strongly dependent upon the potentiometrically determined value of K_{f2} (or alternatively, K_a). The error in k_7^{HSrY} is presumably governed by the errors in these equilibrium constants, which can be quite large because the potentiometric method is relatively insensitive to species present in such low concentrations. If a better value for K_{f2} can be obtained by some other method, the rate constants k_7, k_{-7}, and k_4 can be readily corrected.

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[11] K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, pp 211-216.

[12] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, 31, 1029 (1948).