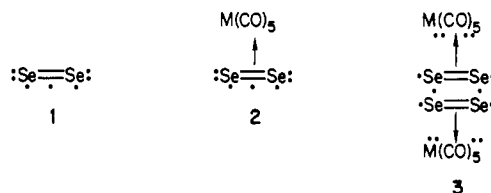


photons from a green 5145-Å source. Use of a red source results in rapid decomposition of the compound even at low temperature. Magnetic measurements of the solid by the Gouy method show the compound to be diamagnetic.

**Bonding.** The  $\text{Se}_2^+$  ion can be described as having the electron configuration  $(\sigma p_x)^2(\pi p_y)^2(\pi p_z)^2(\pi p_z^*)^1$ , assuming that the interaction of the  $\pi p^*$  orbital with the metal atom raises its energy above that of the  $\pi p^*$  orbital.<sup>36</sup> We can then assume that the pair of electrons in the  $\pi p_y$  orbital is donated to  $\text{M}(\text{CO})_5$  to complete its 18-electron count, thus forming a 3-center-2-electron bond. This would result in the Se-Se bond having a resultant order of somewhere between 1.5 and 2.5, depending on the strength of the interaction with the metal atom, and probably slightly less than 2.0. Interaction of the  $p_z$  and  $p_z^*$  orbitals of two  $\text{M}(\text{CO})_5\text{Se}_2^+$  monomers then leads to the formation of a 4-center-6-electron bond.<sup>6</sup> MNDO calculations<sup>37</sup> on the related  $\text{S}_6\text{N}_4^{2+}$  ion have shown that the interaction of the four  $p_z$  orbitals leads to the formation of four molecular orbitals ( $a_g, b_{1u}, a_{1u}$ , and  $b_g$ ), with the six electrons occupying one bonding and two nonbonding orbitals of this set, thus giving rise to relatively weak bonding between two monomers. Alternatively, the bonding in  $\text{Se}_2^+$ ,  $\text{M}(\text{CO})_5\text{Se}_2^+$ , and  $[\text{M}(\text{CO})_5\text{Se}_2]_2^{2+}$  can be described in valence bond terms by structures 1-3, respectively. In terms of this description the Se-Se bond order in 1 is 2.5, and in 2 and 3 it is  $\sim 2$ .



The recently reported  $\text{I}_4^{2+}$  cation consists of two  $\text{I}_2^+$  monomers bonded together in a manner similar to that in the  $[\text{M}(\text{CO})_5\text{Se}_2]_2^{2+}$  dimer.<sup>38</sup> The formation of  $\text{I}_4^{2+}$  results in only a very small increase in the length of the I-I bond, which has an order of 1.5, from 2.557 Å in the monomer to 2.578 Å in the dimer. Presumably, therefore, the formation of the  $[\text{M}(\text{CO})_5\text{Se}_2]_2^{2+}$  dimer also results in only a very small increase in the Se-Se bond length from what it would be in the monomer. So the short Se-Se bond in the dimer can be regarded as having a bond order of  $\sim 2$  in agreement with its length of only 2.21 Å.

**Acknowledgment.** This work was supported by a grant from the Natural Science and Engineering Research Council.

**Registry No.** Ia, 101935-11-9; Ib, 101935-13-1; Id, 101935-14-2; W(CO)<sub>6</sub>, 14040-11-0; Mo(CO)<sub>6</sub>, 13939-06-5; Cr(CO)<sub>6</sub>, 13007-92-6; Se<sub>4</sub>(AsF<sub>6</sub>)<sub>2</sub>, 53513-64-7; Se<sub>2</sub>(AsF<sub>6</sub>)<sub>2</sub>, 52374-78-4; Se<sub>10</sub>(SbF<sub>6</sub>)<sub>2</sub>, 72827-63-5.

**Supplementary Material Available:** Listings of anisotropic thermal parameters and mean least-squares planes (3 pages). Ordering information is given on any current masthead page.

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## Dissociation Kinetics of 1,7-Diaza-4,10,13-trioxacyclopentadecane-*N,N'*-diacetic Acid Complexes of Lanthanides

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Received February 12, 1986

The dissociation kinetics of 1,7-diaza-4,10,13-trioxacyclopentadecane-*N,N'*-diacetic acid (K21DA) complexes of lanthanide(III) ions were studied in acetate-acetic acid buffer medium, over the acid concentration range of  $8.4 \times 10^{-6}$ – $2.5 \times 10^{-4}$  M and at a constant ionic strength of 0.1 M (LiClO<sub>4</sub>). Copper(II) was used as the scavenger of free ligand, and the rates of dissociation of these complexes have been found to be independent of  $[\text{Cu}^{2+}]$ . All the complexes exhibit acid-independent and acid-dependent pathways. Lighter lanthanide complexes display a first-order dependence upon  $[\text{H}^+]$  in the pH range studied. The complexes of heavier lanthanides show  $[\text{H}^+]$  dependence at low acid concentrations but become acid-independent at high acid concentrations. Influence of acetate content in the buffer and total electrolyte concentration on the rate of dissociation has also been investigated. The observed rate constants for erbium, ytterbium, and lutetium complexes do not show a significant dependence on acetate concentration, but lanthanum and europium complexes do exhibit a first-order dependence on [acetate]. All the complexes under study respond similarly with change in electrolyte concentration; i.e., the rate constants decrease with increase in [electrolyte]. Activation parameters for both self-dissociation and acid-catalyzed dissociation pathways have been obtained for lanthanum, europium, erbium, and lutetium complexes, from the temperature dependence of rate constants in the 15–45 °C range. The results are compared with those of the lanthanide-polyamino polycarboxylate systems, and possible mechanisms are discussed.

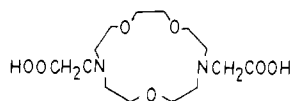
### Introduction

The majority of investigations concerning lanthanide complexes have been on their synthesis and structural studies,<sup>1-7</sup> thermodynamics of complexation,<sup>8-12</sup> analytical applications in separation of lanthanide ions,<sup>13-16</sup> and biological applications of metal-enzyme or protein bindings.<sup>17-19</sup> Comparatively very few studies have been devoted to their kinetics and reaction mechanisms<sup>20-22</sup> despite their significance in (i) improving the existing methods of lanthanide ion separations by ion exchange, solvent extraction, and other methods and (ii) understanding lanthanide metal ion exchange reactions in enzymes and proteins. The monodentate

ligands in general are far too weak complexing agents<sup>23</sup> and, consequently, too labile to deduce a detailed reaction mechanism.

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**Figure 1.** 1,7-Diaza-4,10,13-trioxacyclopentadecane-*N,N'*-diacetic acid (K21DA).

So, the bulk of the mechanistic information regarding formation or dissociation reactions is obtained from polydentate ligands. Although parallel reaction pathways such as direct metal ion attack, anion catalysis, and acid-independent pathways have been shown to exist, the acid-catalyzed pathway dominates in the isotope/metal exchange or dissociation reactions of lanthanide complexes of polyamino polycarboxylic acids such as ethylenediaminetetraacetic acid (EDTA),<sup>24</sup> *N*-methylethylenediaminetriacetic acid (MEDTA),<sup>25</sup> *N*-hydroxymethylethylenediaminetriacetic acid (HEDTA),<sup>26</sup> cyclohexylenediaminetetraacetic acid (CyDTA),<sup>27</sup> and diethylenetriaminepentaacetic acid (DTPA).<sup>28</sup> Virtually nothing is known about the kinetic behavior of complexes with the class of ligands possessing a macrocyclic structure.<sup>29</sup>

In the previous communications from this laboratory, we have reported the thermodynamic stabilities of lanthanide complexes of two closely related ligands,<sup>30,31</sup> 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N,N'*-diacetic acid (K22DA or DACDA) and 1,7-diaza-4,10,13-trioxacyclopentadecane-*N,N'*-diacetic acid (K21DA). In a continuation of this work, we have studied the kinetics and mechanism of exchange reaction of lanthanide complexes containing the latter ligand (Figure 1) with  $\text{Cu}^{2+}$  ion, and the results of this investigation are discussed here.

## Experimental Section

**Reagents.** Reagent grade lithium acetate (Aldrich), lithium perchlorate (Aldrich), lanthanide nitrates (Aldrich/Alfa), copper nitrate (MCB), acetic acid (MCB), and perchloric acid (Fisher) were used as received. The ligand (K21DA) was synthesized by following a procedure published elsewhere<sup>32</sup> and was found to be analytically and spectroscopically pure.

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**Table I.**  $[\text{Cu}^{2+}]$  Independence of Ln-K21DA Dissociation Kinetics<sup>a</sup>

metal	$10^3 \times$		metal	$10^3 \times$	
	$[\text{Cu}^{2+}]$ , M	$k_{\text{obsd}}$ , s <sup>-1</sup>		$[\text{Cu}^{2+}]$ , M	$k_{\text{obsd}}$ , s <sup>-1</sup>
La	0.5	$7.74 \times 10^{-2}$	Lu	0.5	$2.57 \times 10^{-2}$
	1.5	$7.84 \times 10^{-2}$		1.5	$2.59 \times 10^{-2}$
	2.5	$7.88 \times 10^{-2}$		2.5	$2.64 \times 10^{-2}$
	5.0	$7.93 \times 10^{-2}$		5.0	$2.66 \times 10^{-2}$
	10.0	$7.90 \times 10^{-2}$		10.0	$2.66 \times 10^{-2}$
Eu	0.5	$2.92 \times 10^{-3}$			
	1.5	$2.92 \times 10^{-3}$			
	2.5	$2.92 \times 10^{-3}$			
	5.0	$2.93 \times 10^{-3}$			
	10.0	$2.96 \times 10^{-3}$			

<sup>a</sup>  $[\text{H}^+] = 4.52 \times 10^{-5}$  M,  $[\text{acetate}] = 2.5 \times 10^{-3}$  M,  $T = 25$  °C,  $\mu = 0.1$ .

**Table II.** Effect of Acetate Concentration on Ln-K21DA Dissociation Kinetics<sup>a</sup>

metal	$10^2 \times$		metal	$10^2 \times$	
	[acetate], M	$k_{\text{obsd}}$ , s <sup>-1</sup>		[acetate], M	$k_{\text{obsd}}$ , s <sup>-1</sup>
La	1.25	$6.75 \times 10^{-2}$	Yb	1.25	$1.09 \times 10^{-2}$
	2.0	$8.57 \times 10^{-2}$		2.0	$1.11 \times 10^{-2}$
	3.75	$12.2 \times 10^{-2}$		3.75	$1.12 \times 10^{-2}$
	5.0	$15.0 \times 10^{-2}$		5.0	$1.12 \times 10^{-2}$
Eu	1.25	$2.80 \times 10^{-3}$	Lu	1.25	$1.66 \times 10^{-2}$
	2.0	$3.48 \times 10^{-3}$		2.0	$1.78 \times 10^{-2}$
	3.75	$4.93 \times 10^{-3}$		3.75	$1.75 \times 10^{-2}$
	5.0	$5.83 \times 10^{-3}$		5.0	$1.65 \times 10^{-2}$
Er	1.25	$4.48 \times 10^{-3}$			
	2.0	$4.47 \times 10^{-3}$			
	3.75	$4.49 \times 10^{-3}$			
	5.0	$4.47 \times 10^{-3}$			

<sup>a</sup>  $[\text{H}^+] = 1.54 \times 10^{-5}$  M,  $T = 25$  °C,  $\mu = 0.1$ ,  $[\text{Cu}^{2+}] = 1.0 \times 10^{-3}$  M.

**Equipment.** A Durrum-Dionex stopped-flow spectrophotometer interfaced with an OLIS data collection system was used for kinetic measurements. pH measurements were done on a Fisher Accumet selective-ion analyzer (Model 750) with a Fisher combination electrode.

**Solutions.** All solutions were made in deionized water. Complexes were made in situ by mixing appropriate amounts of lanthanide nitrate and ligand (slight excess) and adjusting the pH to about 7 with  $(\text{C}_2\text{H}_5)_4\text{NOH}$ . The complex concentration in the reaction mixtures was kept at ca.  $5 \times 10^{-5}$  M. The buffer solutions were made by using a constant acetate ion concentration and varying the [acetic acid]. The reaction mixtures generally contained  $5 \times 10^{-3}$  M acetate unless stated otherwise. The ionic strength was adjusted to 0.1 M with  $\text{LiClO}_4$ , for acid as well as acetate dependence studies. Hydrogen ion concentrations were calculated from the pH measurements by the expression  $-\log [\text{H}^+] = \text{pH} - 0.11$ .<sup>26</sup>

**Kinetic Runs.** As the lanthanide complexes do not show appreciable absorption in the near-ultraviolet or visible region, copper(II) was used as the scavenger of free ligand and the reaction kinetics were followed by monitoring the growth in absorbance due to the copper complex at 270 nm. Although the rates observed are independent of  $[\text{Cu}^{2+}]$ , a pseudo-first-order (20-fold) excess of  $\text{Cu}^{2+}$  ( $1 \times 10^{-3}$  M) was used in reaction mixtures.

The solutions in the drive syringes of the stopped-flow spectrophotometer, one containing complex solution and the other containing buffer,  $\text{LiClO}_4$ , and  $\text{Cu}^{2+}$ , were preequilibrated at the required temperature, which was maintained to  $\pm 0.2$  °C with a Lauda-Brinkman (Model K-2/RD) refrigerated water bath and a heat exchanger. Reactions were generally followed up to 3–5 half-lives. Plots of  $\log (A_\infty - A_t)$  vs. time were linear for at least 3 half-lives of reaction. Rate constants quoted represent the average values of at least three kinetic runs and were reproducible within  $\pm 5\%$ .

## Results and Discussion

Since the stability of  $\text{CuK21DA}$  ( $\log K = 16.02$ ) is much greater than that of corresponding lanthanide complexes<sup>31</sup> ( $\log K = 10.11$ – $11.85$ ), the exchange reaction



will be complete under the experimental conditions (20-fold excess

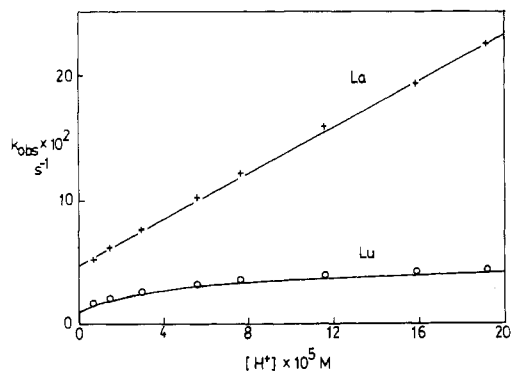


Figure 2. Plots of observed rate constants vs.  $[H^+]$  for La and Lu complexes of K21DA.

of  $Cu^{2+}$ ). The experimental data fit pseudo-first-order kinetics with respect to complex.

**Independence of  $k_{obsd}$  on  $[Cu^{2+}]$ .** The rates of dissociation are zero order in copper(II) concentration (Table I), suggesting no appreciable copper ion attack on the lanthanide complexes in the pH range studied. Such an independence of  $[Cu^{2+}]$  in the dissociation kinetics of lanthanide-CyDTA<sup>27</sup> and lanthanide-MEDTA<sup>25</sup> complexes was reported by other workers. Presumably, the copper ion is unable to attack ligand nitrogen(s) to form a binuclear intermediate due to steric constraints imposed by the macrocyclic ring when a lanthanide ion is already present in its cavity.

**Acetate Catalysis.** Table II shows that the acetate ion concentration does not significantly affect the rates of dissociation of heavier lanthanide (Er, Yb, and Lu) complexes. However, when observed rate constants of lanthanum as well as europium complexes are plotted against acetate concentration, straight lines are obtained with appreciable slopes. The enhanced rate of dissociation of these complexes in the presence of higher acetate concentration can be attributed to the acetate ion complexation. The incoming acetate ion may attack a vacant coordination site or replace a coordinated water molecule. The parent complexes are positively charged, and by the introduction of a negatively charged acetate ion into the coordination sphere they become neutral and become labilized with respect to hydrogen ion attack.<sup>26</sup> The relative insensitivity of the heavier lanthanide complexes to acetate catalyses may be due to their different solution structures or strong binding of coordinated water molecules, which acetate ion finds difficult to displace. The ligand offers 7 coordination sites, and a more common coordination number of lanthanide ions is either 8 or 9.<sup>33</sup> As the title complexes form 9-coordinate ternary complexes with  $\beta$ -diketonates,<sup>34</sup> it is more likely that they contain at least two coordinated water molecules in solution. Evidence for tight binding of coordinated water by later lanthanide complexes comes also from the pH titration curve of the Yb complex, in which coordinated water could be detected. Laser fluorescence studies of the Eu complex also indicate the same.<sup>35</sup>

**Acid-Independent and Acid-Dependent Pathways.** The observed rate constants for reaction 1, the temperature at which they were measured, and the concentration of hydrogen ion are given in Table III. All complexes exhibit two reaction pathways: (1) an acid-independent pathway and (2) an acid-dependent pathway. When the observed rate constants are plotted against hydrogen ion concentration (Figure 2), the lighter lanthanide complexes yield straight lines whereas the heavier lanthanides show saturation curves with limiting rate constants at higher acid concentrations. However, in all plots appreciable intercepts are obtained that correspond to acid-independent or self-dissociation rate constants ( $k_d$ ). The proposed mechanisms are shown in Figure 3. The

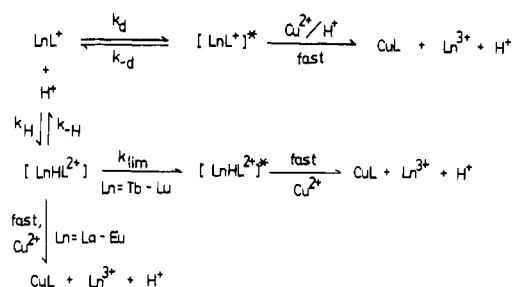


Figure 3. Proposed mechanisms for dissociation of Ln-K2DA complexes (coordinated water molecules omitted for clarity).

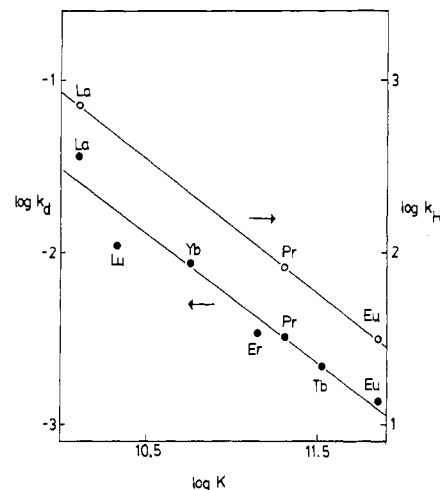


Figure 4. Plot of  $\log k_d$  (●) and  $\log k_H$  (○) against  $\log K$  for Ln-K21DA complexes.

observed rate constants for the lighter lanthanide complexes obey the rate law<sup>36</sup>

$$k_{obsd} = k_d + k_H[H^+] + k_{AC}[\text{acetate}] \quad (2)$$

and for heavier lanthanides the rate law assumes the form<sup>36</sup>

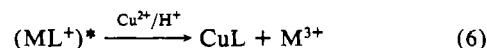
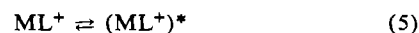
$$k_{obsd} = k_d + \frac{K'k_{lim}[H^+]}{1 + K[H^+]} \quad (3)$$

The values of acid-independent rate constants ( $k_d$ ), the acid-catalyzed rate constant ( $k_H$ ), the limiting rate constant for the protonated complexes of heavier lanthanides ( $k_{lim}$ ), and the equilibrium constant ( $K'$ ) for the reaction



are resolved by an unweighted least-squares analysis and are listed in Table IV. The regular decrease in  $k_d$  values in going from lanthanum to europium followed by a monotonic increase up to lutetium reflects the trend in their thermodynamic stability. A plot of  $\log K$  against  $\log k_d$  is shown in Figure 4.

The  $k_d$  values and characteristic water-exchange or complexation rate constants for the lanthanide complexes indicate that the self-dissociation of the complex does not occur in one step but involves a rate-determining distortion of the complex to yield an intermediate that is rapidly scavenged by hydrogen ion or copper ion to give products. The reaction sequence may be written as



The water-exchange rate constant<sup>37</sup> for erbium ion and the formation rate constant for its oxalate complex<sup>38</sup> are  $1.0 \times 10^7$  and

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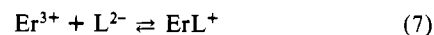
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Table III. Dependence of Dissociation Kinetics<sup>a</sup> ( $k_{\text{obsd}}$ , s<sup>-1</sup>) of Ln-K21DA Complexes on [H<sup>+</sup>]

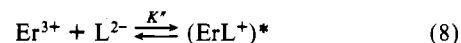
metal	temp, °C	10 <sup>5</sup> [H <sup>+</sup> ], M									
		0.84	1.85	3.76	4.55	7.07	9.66	14.73	19.36	20.37	24.66
La	15	3.65 × 10 <sup>-2</sup>	4.15 × 10 <sup>-2</sup>	6.36 × 10 <sup>-2</sup>	7.81 × 10 <sup>-2</sup>	10.4 × 10 <sup>-2</sup>	12.6 × 10 <sup>-2</sup>	15.2 × 10 <sup>-2</sup>			
	25	4.93 × 10 <sup>-2</sup>	5.98 × 10 <sup>-2</sup>	10.0 × 10 <sup>-2</sup>	11.9 × 10 <sup>-2</sup>	15.7 × 10 <sup>-2</sup>	19.1 × 10 <sup>-2</sup>	22.2 × 10 <sup>-2</sup>			
	35	6.62 × 10 <sup>-2</sup>	8.08 × 10 <sup>-2</sup>	13.7 × 10 <sup>-2</sup>	16.8 × 10 <sup>-2</sup>	22.1 × 10 <sup>-2</sup>	26.9 × 10 <sup>-2</sup>	31.6 × 10 <sup>-2</sup>			
	45	8.81 × 10 <sup>-2</sup>	10.9 × 10 <sup>-2</sup>	19.0 × 10 <sup>-2</sup>	23.1 × 10 <sup>-2</sup>	31.0 × 10 <sup>-2</sup>	38.3 × 10 <sup>-2</sup>	48.0 × 10 <sup>-2</sup>			
Pr	25	4.36 × 10 <sup>-3</sup>	5.62 × 10 <sup>-3</sup>	10.2 × 10 <sup>-3</sup>	12.4 × 10 <sup>-3</sup>	16.5 × 10 <sup>-3</sup>	20.3 × 10 <sup>-3</sup>	24.4 × 10 <sup>-3</sup>			
	45	1.21 × 10 <sup>-3</sup>	1.41 × 10 <sup>-3</sup>	2.27 × 10 <sup>-3</sup>	2.78 × 10 <sup>-3</sup>	3.61 × 10 <sup>-3</sup>	4.47 × 10 <sup>-3</sup>	5.39 × 10 <sup>-3</sup>			
Eu	15	1.89 × 10 <sup>-3</sup>	2.30 × 10 <sup>-3</sup>	4.06 × 10 <sup>-3</sup>	4.88 × 10 <sup>-3</sup>	6.49 × 10 <sup>-3</sup>	8.05 × 10 <sup>-3</sup>	9.33 × 10 <sup>-3</sup>			
	25	2.84 × 10 <sup>-3</sup>	3.55 × 10 <sup>-3</sup>	6.07 × 10 <sup>-3</sup>	7.00 × 10 <sup>-3</sup>	9.10 × 10 <sup>-3</sup>	11.2 × 10 <sup>-3</sup>	13.0 × 10 <sup>-3</sup>			
	35	4.04 × 10 <sup>-3</sup>	4.78 × 10 <sup>-3</sup>	8.54 × 10 <sup>-3</sup>	10.4 × 10 <sup>-3</sup>	13.9 × 10 <sup>-3</sup>	17.8 × 10 <sup>-3</sup>	20.3 × 10 <sup>-3</sup>			
	45	2.56 × 10 <sup>-3</sup>	2.90 × 10 <sup>-3</sup>	4.72 × 10 <sup>-3</sup>	5.60 × 10 <sup>-3</sup>	6.55 × 10 <sup>-3</sup>	7.59 × 10 <sup>-3</sup>	8.43 × 10 <sup>-3</sup>			
Tb	15	2.00 × 10 <sup>-3</sup>	2.21 × 10 <sup>-3</sup>	3.09 × 10 <sup>-3</sup>	3.35 × 10 <sup>-3</sup>	3.74 × 10 <sup>-3</sup>	4.03 × 10 <sup>-3</sup>	4.35 × 10 <sup>-3</sup>			
	25	3.82 × 10 <sup>-3</sup>	4.49 × 10 <sup>-3</sup>	6.69 × 10 <sup>-3</sup>	7.38 × 10 <sup>-3</sup>	8.45 × 10 <sup>-3</sup>	9.12 × 10 <sup>-3</sup>	9.89 × 10 <sup>-3</sup>			
	35	6.27 × 10 <sup>-3</sup>	7.54 × 10 <sup>-3</sup>	11.7 × 10 <sup>-3</sup>	13.3 × 10 <sup>-3</sup>	15.3 × 10 <sup>-3</sup>	17.0 × 10 <sup>-3</sup>	18.4 × 10 <sup>-3</sup>			
	45	9.07 × 10 <sup>-3</sup>	11.1 × 10 <sup>-3</sup>	18.4 × 10 <sup>-3</sup>	21.8 × 10 <sup>-3</sup>	26.8 × 10 <sup>-3</sup>	29.4 × 10 <sup>-3</sup>	31.8 × 10 <sup>-3</sup>			
Yb	25	0.98 × 10 <sup>-2</sup>	1.10 × 10 <sup>-2</sup>	1.48 × 10 <sup>-2</sup>	1.59 × 10 <sup>-2</sup>	1.74 × 10 <sup>-2</sup>	1.84 × 10 <sup>-2</sup>	1.94 × 10 <sup>-2</sup>			
	45	0.92 × 10 <sup>-2</sup>	1.07 × 10 <sup>-2</sup>	1.53 × 10 <sup>-2</sup>	1.65 × 10 <sup>-2</sup>	1.78 × 10 <sup>-2</sup>	1.83 × 10 <sup>-2</sup>	1.91 × 10 <sup>-2</sup>			
Lu	15	1.46 × 10 <sup>-2</sup>	1.84 × 10 <sup>-2</sup>	2.95 × 10 <sup>-2</sup>	3.31 × 10 <sup>-2</sup>	3.78 × 10 <sup>-2</sup>	4.02 × 10 <sup>-2</sup>	4.11 × 10 <sup>-2</sup>			
	25	2.40 × 10 <sup>-2</sup>	2.90 × 10 <sup>-2</sup>	4.82 × 10 <sup>-2</sup>	5.49 × 10 <sup>-2</sup>	6.52 × 10 <sup>-2</sup>	7.22 × 10 <sup>-2</sup>	7.73 × 10 <sup>-2</sup>			
	35	3.59 × 10 <sup>-2</sup>	4.49 × 10 <sup>-2</sup>	7.66 × 10 <sup>-2</sup>	9.11 × 10 <sup>-2</sup>	10.9 × 10 <sup>-2</sup>	12.5 × 10 <sup>-2</sup>	13.6 × 10 <sup>-2</sup>			
	45	5.66 × 10 <sup>-2</sup>	6.66 × 10 <sup>-2</sup>	1.11 × 10 <sup>-1</sup>	1.26 × 10 <sup>-1</sup>	1.46 × 10 <sup>-1</sup>	1.61 × 10 <sup>-1</sup>	1.74 × 10 <sup>-1</sup>			

<sup>a</sup>[Cu<sup>2+</sup>] = 1.0 × 10<sup>-3</sup> M, [acetate] = 5 × 10<sup>-3</sup> M, μ = 0.1.

6.3 × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup>, respectively. When the maximum rate constant for the formation of ML<sup>+</sup> from {ML<sup>+</sup>}\* is allowed to be 6.3 × 10<sup>6</sup> s<sup>-1</sup>, the equilibrium constant for reaction 5 can be calculated as 3.3 × 10<sup>-3</sup>/6.3 × 10<sup>6</sup> = 5.2 × 10<sup>-10</sup>. The experimentally determined stability constant for the reaction



is 1.4 × 10<sup>11</sup> M<sup>-1</sup>, which implies that the equilibrium constant, K'', for reaction 8 should be at least 1.4 × 10<sup>11</sup> M<sup>-1</sup> × 5.2 × 10<sup>-10</sup>



= 7.28 × 10<sup>1</sup> M<sup>-1</sup> or the lower limit for log K'' is 1.9. The stability constants in log scale for the mono- and bis(acetate) complexes of erbium are 1.79 and 3.06, respectively.<sup>39</sup> Hence, it is very likely that in the active form, (ML<sup>+</sup>)\*, of the complex the metal ion is outside the ligand cavity and is bonded to at least one of the acetate moieties. The formation of copper complex is then accomplished by the fast attack of proton and/or copper ion attack at the uncoordinated ligand nitrogen(s), which explains the lack of Cu<sup>2+</sup> catalysis. By the principle of microscopic reversibility, the formation of ML<sup>+</sup> from M<sup>3+</sup> and L<sup>2-</sup> must proceed through (ML<sup>+</sup>)\*. Studies on the formation rates of these complexes were not attempted because the rate constants are expected to be much higher and would be beyond the range of a conventional stopped-flow apparatus.

The acid-dependent rate constants ( $k_{\text{H}}$ ) decreases from lanthanum to europium, corresponding to the gradual increase in stability with increase in atomic number from lanthanum to europium (Figure 4). The equilibrium constant, K', for reaction 4 increases with decrease in stability constant of parent complexes as expected, also.

**Activation Parameters.** The activation parameters (Table V) for the acid-dependent and acid-independent pathways have been obtained from the temperature dependence of rate constants. The low enthalpy of activation in combination with an unfavorably large negative entropy of activation for the self-dissociation pathway is consistent with a mechanism in which the rate-determining step is the slow distortion of complex to yield an active intermediate. The ΔH<sup>‡</sup> values for the acid-catalyzed pathway are much smaller as compared to similar values for lanthanide EDTA, CyDTA, and MEDTA complexes,<sup>26</sup> reflecting the lower thermodynamic stability of the title complexes.

**[Electrolyte] Dependence.** Finally, the effect of electrolyte concentration on the rate of dissociation has been studied and the results obtained are given in Table VI. The decrease in observed rate constants with increase in electrolyte concentration points toward the existence of ion-pair association between the cationic complexes and perchlorate ion. This is exactly the opposite trend to that shown for anionic complexes of lanthanides.<sup>40</sup> The increase in anionic concentration has been found to enhance labilization of coordinated ligands in lanthanide-polyamino polycarboxylate complexes. However, perchlorate ion is an extremely weak coordinating ligand and in our complexes it fails to enter the coordination sphere and thus is unable to cause the facilitation of leaving ligand. On the other hand, it presumably forms weak ion pairs with the complexes<sup>41</sup> and increases their thermodynamic stability, which explains the suppression of dissociation by increase in electrolyte concentration.

### Summary

The kinetics as well as mechanisms of dissociation of lanthanide K21DA complexes show certain strikingly different features from open-chain polyamino polycarboxylic acid complexes that can be attributed to the rigid macrocyclic structure of the ligand. For the majority of the systems, lanthanides as a group exhibit similar

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Table IV. Resolved Rate Constants<sup>a</sup> for Dissociation of Ln-K21DA Complexes

metal	temp, °C	$k'_d, s^{-1}$	$k_H, M^{-1} s^{-1}$	$K', M^{-1}$	$k_{lim}, s^{-1}$	$k_{AC}, M^{-1} s^{-1}$
La	15	$(3.22 \pm 0.08) \times 10^{-2}$	$(4.85 \pm 0.06) \times 10^{-2}$			2.18 ± 0.04
	25	$(4.69 \pm 0.15) \times 10^{-2}$	$(7.18 \pm 0.11) \times 10^2$			
	35	$(6.29 \pm 0.23) \times 10^{-2}$	$(1.03 \pm 0.02) \times 10^3$			
	45	$(7.66 \pm 0.51) \times 10^{-2}$	$(1.58 \pm 0.04) \times 10^3$			
Pr	25	$(4.14 \pm 0.20) \times 10^{-3}$	$(8.19 \pm 0.15) \times 10$			$(8.09 \pm 0.23) \times 10^{-2}$
	Eu	15	$(1.06 \pm 0.02) \times 10^{-3}$	$(1.75 \pm 0.01) \times 10$		
Eu	25	$(1.76 \pm 0.06) \times 10^{-3}$	$(3.11 \pm 0.04) \times 10$			
	35	$(2.83 \pm 0.12) \times 10^{-3}$	$(4.17 \pm 0.09) \times 10$			
	45	$(3.54 \pm 0.09) \times 10^{-3}$	$(6.92 \pm 0.07) \times 10$			
	Tb	25	$(2.18 \pm 0.11) \times 10^{-3}$		$(2.96 \pm 0.54) \times 10^3$	
Er	15	$(1.79 \pm 0.04) \times 10^{-3}$		$(6.41 \pm 0.58) \times 10^3$	$(4.11 \pm 0.31) \times 10^{-3}$	
	25	$(3.32 \pm 0.13) \times 10^{-3}$		$(6.64 \pm 0.85) \times 10^3$	$(1.04 \pm 0.12) \times 10^{-2}$	
	35	$(5.42 \pm 0.27) \times 10^{-3}$		$(5.69 \pm 0.83) \times 10^3$	$(2.24 \pm 0.24) \times 10^{-2}$	
	45	$(7.21 \pm 0.49) \times 10^{-3}$		$(4.82 \pm 0.72) \times 10^3$	$(4.59 \pm 0.55) \times 10^{-2}$	
Yb	25	$(8.76 \pm 0.18) \times 10^{-3}$		$(9.39 \pm 0.89) \times 10^3$	$(1.50 \pm 0.13) \times 10^{-2}$	
	Lu	15	$(7.29 \pm 0.23) \times 10^{-3}$		$(1.74 \pm 0.14) \times 10^4$	
Lu	25	$(1.08 \pm 0.06) \times 10^{-2}$		$(1.22 \pm 0.11) \times 10^4$	$(4.11 \pm 0.36) \times 10^{-2}$	
	35	$(1.95 \pm 0.04) \times 10^{-2}$		$(5.98 \pm 0.25) \times 10^3$	$(9.68 \pm 0.33) \times 10^{-2}$	
	45	$(2.91 \pm 0.11) \times 10^{-2}$		$(4.15 \pm 0.36) \times 10^3$	$(2.11 \pm 0.24) \times 10^{-1}$	

<sup>a</sup> From experimental data given in Tables II and III. Uncertainties correspond to standard deviations.  $k'_d = k_d + k_{AC} [5 \times 10^{-3}]$  for La, Pr, and Eu complexes;  $k'_d = k_d$  for Tb, Er, Yb, and Lu complexes.

Table V. Activation Parameters<sup>a</sup> for Self-Dissociation and Acid-Catalyzed Dissociation of Ln-K21DA Complexes

metal	$\Delta H^*_d,$ kcal/mol	$\Delta S^*_d,$ cal/(deg mol)	$\Delta H^*_H,$ kcal/mol	$\Delta S^*_H,$ cal/(deg mol)	$\Delta H^*_{lim},$ kcal/mol	$\Delta S^*_{lim},$ cal/(deg mol)
La	4.7	-49.5	6.5 ± 0.3	-23.7 ± 0.9		
Eu	6.9	-48.6	7.4 ± 0.6	-26.9 ± 2.1		
Er	7.9 ± 0.8	-43.4 ± 2.6			14.0 ± 0.3	-20.8 ± 1.1
Lu	8.0 ± 0.5	-40.5 ± 1.8			15.6 ± 0.5	-12.6 ± 1.5

<sup>a</sup> Error limits correspond to standard deviations. The values of  $\Delta H^*_d$  and  $\Delta S^*_d$  listed for La and Eu complexes are crude, and hence no error limits are quoted. They have been calculated from  $k'_d$  values (see Table IV) after subtracting the contribution from acetate catalysis. At 25 °C the acetate catalysis (0.005 M acetate) corresponds to 23% of  $k'_d$  for both La and Eu complexes, and the same percent contribution was assumed at other temperatures (15, 35, and 45 °C) as well.

Table VI. Influence of [Electrolyte] on Dissociation Kinetics<sup>a</sup> of Ln-K21DA Complexes

metal	[electrolyte], M	$k_{obsd}, s^{-1}$
La	0.05	$5.67 \times 10^{-2}$
	0.20	$5.11 \times 10^{-2}$
	0.40	$4.50 \times 10^{-2}$
	0.60	$3.84 \times 10^{-2}$
Eu	0.05	$2.17 \times 10^{-3}$
	0.20	$2.03 \times 10^{-3}$
	0.40	$1.82 \times 10^{-3}$
	0.60	$1.62 \times 10^{-3}$
Lu	0.05	$1.97 \times 10^{-2}$
	0.20	$1.75 \times 10^{-2}$
	0.40	$1.48 \times 10^{-2}$
	0.60	$1.21 \times 10^{-2}$

<sup>a</sup>  $[H^+] = 1.47 \times 10^{-5}$  M, [acetate] =  $5 \times 10^{-3}$  M,  $[Cu^{2+}] = 1.0 \times 10^{-3}$  M,  $T = 25$  °C,  $\mu = 0.1$ , [electrolyte] =  $[LiClO_4]$ .

behavior toward acid or acetate catalysis, but in our system the behavior of lighter lanthanides differs from that of their heavier counterparts. For earlier lanthanides the reactions are first order in acetate as well as acid, whereas for the later members of the

series reactions are zero order in acetate and zero to less than first order in acid. Lack of  $Cu^{2+}$  catalysis can also be explained on the basis of the rigid macrocyclic structure of the ligand, which prevents the direct attack by copper(II) ion.

It is highly desirable to extend these studies to lanthanide complexes containing macrocyclic structures with different donor atoms, ring sizes, and pendant groups in order to understand if the same reaction pathways exist in other systems or differ from one to another. Thermodynamic stability of lanthanide macrocyclic compounds has been shown to differ from one macrocycle to another with change in the size of the ring cavity,<sup>30,31</sup> and it would definitely be interesting to see how the ligand cavity affects their kinetic stability also.

**Acknowledgment.** The authors wish to thank the U.S. Department of Energy for the support of this research through Grant No. DE-FG05-84ER13292. Our thanks are also due to Dr. James E. Becvar for his valuable assistance in the operation of the stopped-flow spectrophotometer.

**Registry No.** La, 7439-91-0; Eu, 7440-53-1; Er, 7440-52-0; Yb, 7440-64-4; Lu, 7439-94-3; Tb, 7440-27-9; acetate, 71-50-1.