

**Figure 5.** Chelating effects of Cys-X-Y-Cys sequences with NH...S hydrogen bonding and restricted rotation of the Fe-S torsion angles.

for  $[\text{Fe}(\text{S}_2\text{-}o\text{-xyl})_2]^{2-}$  in  $\text{Me}_2\text{SO}$ . The Fe(II) complexes of Cys-X-Y-Cys peptides showed remarkably shifted redox potentials in  $\text{Me}_2\text{SO}$ . For example,  $[\text{Fe}(\text{Z-cys-Pro-Leu-cys-OMe})_2]^{2-}$  has a 2-/1- couple at -0.5 V vs. SCE. One of the important factors of the positive shift has been proposed to be a NH...S hydrogen

bond that forms between Cys(1) S and Cys(4) NH or Y NH groups of the chelating Cys(1)-X-Y-Cys(4) ligand, as shown in Figure 5. Elongation of the Fe-S bond with the NH...S hydrogen bond and the chelation effect provide for conditions that give ionic character to the Fe-S bond. In general, an Fe(III) ion with four thiolato ligands, such as  $[\text{Fe}(\text{SR})_4]^-$ , is thermodynamically unstable and is readily decomposed by dissociation of the ligand ( $\text{RS}^-$  or  $\text{RS}^*$ ). However, native rubredoxin is stable with Fe at this oxidized state (Fe(III)). Another important factor for the shift can be proposed: the distortion around Fe(III) by the variation of Fe-S torsion angles in a chelating Cys-X-Y-Cys.

In conclusion, the conformational restriction of the Cys-X-Y-Cys chelating peptides in rubredoxin and its peptide model complexes induces a  $C_2$  distortion around Fe(III). The distortion can successfully explain the characteristic CD and MCD extrema. Further work is under way to investigate the contributions of the distortion to thermodynamic stability and electrochemical properties.

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## Dissociation Kinetics of 1,10-Diaza-4,7,13,16-tetraoxacyclooctadecane-*N,N'*-diacetic Acid Complexes of Lanthanides

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The dissociation kinetics of 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N,N'*-diacetic acid (K22DA) complexes of lanthanide(III) ions were studied in perchloric acid and other media, over the concentration range  $5 \times 10^{-4}$  to  $7.5 \times 10^{-3}$  M and at a constant ionic strength of 0.1 M ( $\text{LiClO}_4$ ). 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-dependent and acid-independent pathways in a manner similar to those of  $\text{LnCyDTA}^-$  complexes ( $\text{CyDTA}^- = \text{trans-1,2-diaminocyclohexane-}N,N,N',N'\text{-tetraacetate ion}$ ). Unlike lanthanide (Ln) complexes of 1,7-diaza-4,10,13-trioxacyclopentadecane-*N,N'*-diacetic acid (K21DA),  $\text{LnK22DA}^+$  complex dissociation rates are independent of [anion] and [electrolyte]. There is also no general-acid catalysis. The overall results are compared with those of complexes that are structural analogues such as  $\text{LnK21DA}^+$ ,  $\text{LnMEDTA}$  ( $\text{MEDTA} = N\text{-methyl-ethylenediamine-}N,N,N'\text{-triacetate ion}$ ), and  $\text{LnCyDTA}^-$ . A rationalization is given to account for similarities and differences with respect to observed kinetic characteristics. A number of postulates concerning the relationship between thermodynamic and kinetic stabilities and the detailed reaction mechanisms of lanthanide complexes of polyamino polyacetate ligands are proposed.

The study of solution thermodynamic complex formation and kinetic (both formation and dissociation) stabilities of lanthanide complexes have been of interest for a number of years because of their significant implications in analytical, biological, and other chemical applications.<sup>1-7</sup> In general, it is observed that the ligand topology can affect the thermodynamic and kinetic stabilities of lanthanide complexes. Ligand characteristics such as the charge, cavity size, number of donor atoms, and stereochemical constraints imposed are all found to be important. Thus, it is believed that by varying these factors, one might be able to develop ion selective reagents for an individual or a group of metal ions.

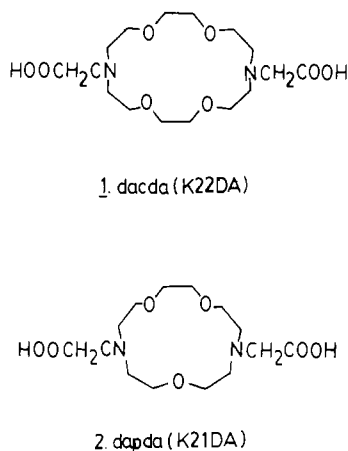
In order to develop lanthanide ion selective reagents, we have initiated a systematic study of lanthanide complexes of two

macrocyclic compounds with ionizable pendant functional groups, i.e., 1,7-diaza-4,10,13-trioxacyclopentadecane-*N,N'*-diacetic acid (DAPDA or K21DA) and 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N,N'*-diacetic acid (DACDA or K22DA) (Figure 1). The stability constants of lanthanide complexes of the two ligands have been previously reported.<sup>8,9</sup> Also, for the reason of convenience of study by a stopped-flow spectrophotometer, we have studied the dissociation kinetics of K21DA complexes of lanthanides.<sup>10</sup> The dissociation reaction rates together with the stability constants allow the calculation of formation rate constants, which may otherwise be difficult to obtain experimentally. Both formation and dissociation kinetic studies can afford further information concerning mechanistic details.

For lanthanide complexes of multidentate ligands such as polyamino polycarboxylic acids, the dissociation reactions show strong pH dependence with the rate and mechanism changing upon changes in acid strength. Two types of pH dependence have been observed, a linear dependence and a saturation kinetic dependence. Examples of the latter include those complexes of *N*-methyl-

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**Figure 1.** 1,7-Diaza-4,10,13-trioxacyclopentadecane-*N,N'*-diacetic acid (K21DA) and 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N,N'*-diacetic acid (K22DA).

ethylenediamine-*N,N,N'*-triacetic acid (MEDTA)<sup>11</sup> and the heavy lanthanide complexes of K21DA. Examples of the former are those of cyclohexylenediamine-*N,N,N',N'*-tetraacetic acid (CyDTA)<sup>12</sup> and the lighter lanthanide complexes of K21DA. From a mechanistic point of view, there are at least two pathways leading to the dissociation of these complexes. One is the self-dissociation pathway, the rate of which is independent of the concentrations of acid, base, or any coordinating anions present in the supporting electrolyte medium. The other is an acid-catalyzed path, which may show a first-order or more complex dependence on acid concentration depending on the number of basic sites available for attack, stability of the complex, etc. Certainly other pathways are also possible, e.g. a path that is catalyzed by the buffering or coordinating anions in a manner similar to acid hydrolysis but with the attack on the metal ion itself.<sup>13</sup>

Unlike in self-dissociation, steric effects could play very important roles in altering the rate of catalyzed pathways, as these reactions are associative in nature. For example, lanthanide complexes of EDTA have been shown to be susceptible to  $\text{Cu}^{2+}$  attack in metal-exchange reactions<sup>14</sup> whereas the contribution from these pathway is insignificant to the overall rate of metal exchange in lanthanide-CyDTA complexes.<sup>12</sup> This fact has been explained on the basis of rigidity of the cyclohexane backbone ring, which prevents the direct attack of  $\text{Cu}^{2+}$  on the complexed ligand.

In a continuation of our previous efforts, we have studied the kinetics and mechanism of exchange reaction of lanthanide complexes containing K22DA with  $\text{Cu}^{2+}$  ion, and the results of this investigation are reported here. It should be noted that K22DA has a 18-membered backbone ring, and its lanthanide complex stability constant is in general greater than the corresponding one of K21DA, a ligand with a 15-membered backbone ring.

### Experimental Section

**Reagents.** Reagent grade chemicals lithium acetate (Aldrich), lithium perchlorate (Aldrich), lanthanide nitrates (Aldrich/Alfa), copper nitrate (MCB), acetic acid (MCB), and perchloric acid were used as received. The ligand (K22DA) was synthesized following the method published elsewhere.<sup>15</sup>

**Instruments.** 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. Complex solutions were made by mixing appropriate amounts of lanthanide nitrate

**Table I.** Independence of Dissociation Rates of La(III), Eu(III), and Lu(III) Complexes of K22DA of the Concentration of  $\text{Cu}^{2+}$  in the Reaction Mixture<sup>a</sup>

metal	$10^3[\text{Cu}^{2+}]$ , M	$10^3k_{\text{obsd}}$ , $\text{s}^{-1}$	$10^3[\text{Cu}^{2+}]$ , M	$10^3k_{\text{obsd}}$ , $\text{s}^{-1}$
La	0.5	$3.37 \pm 0.05$	3.0	$3.21 \pm 0.12$
	1.0	$3.35 \pm 0.10$	4.0	$3.37 \pm 0.13$
	1.5	$3.41 \pm 0.13$	5.0	$3.42 \pm 0.08$
Eu	0.5	$1.86 \pm 0.18$	3.0	$1.86 \pm 0.17$
	1.0	$1.82 \pm 0.12$	4.0	$1.85 \pm 0.15$
	1.5	$1.82 \pm 0.13$	5.0	$1.86 \pm 0.12$
Lu	0.5	$4.85 \pm 0.17$	3.0	$4.80 \pm 0.13$
	1.0	$4.78 \pm 0.09$	4.0	$4.75 \pm 0.11$
	1.5	$4.70 \pm 0.10$	5.0	$4.84 \pm 0.17$

<sup>a</sup> [Complex] =  $5.0 \times 10^{-5}$  M,  $T = 25^\circ\text{C}$ ,  $[\text{H}_3\text{O}^+] = 2.50 \times 10^{-3}$  M, and  $\mu = 0.10$ .

and ligand (slight excess) and adjusting the pH of solution to about 7 with  $\text{Me}_4\text{NOH}$ . The complex concentration in the reaction mixtures was kept at  $\sim 5 \times 10^{-5}$  M. The acid solutions were made by diluting a  $\text{HClO}_4$  stock solution. The ionic strength was adjusted to 0.1 M with  $\text{LiClO}_4$  for acid- as well as anion-dependence studies. The hydrogen ion concentration was calculated from the pH measurements by using the expression<sup>7</sup>

$$-\log [\text{H}^+] = \text{pH} - 0.11$$

**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 copper complex at 270 nm. Although the rates observed are independent of  $[\text{Cu}^{2+}]$  a 20-fold excess of copper nitrate solutions ( $1 \times 10^{-3}$  M) was used in reaction mixtures.

The solutions in the drive syringes of stopped-flow spectrophotometer, one containing complex solution and the other containing buffer,  $\text{LiClO}_4$  and  $\text{Cu}^{2+}$ , were pre-equilibrated at the required temperature, which was maintained to  $\pm 0.2^\circ\text{C}$  by using a Lauda-Brinkman (Model K-2/RD) refrigerated water bath and a heat exchanger. Reactions were generally followed up to 3–5 half-lives and were found to be first-order in complex. 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

**Independence of  $k_{\text{obsd}}$  on  $[\text{Cu}^{2+}]$ .** Table I shows that under identical experimental conditions other than  $[\text{Cu}^{2+}]$  the rates for some representative lanthanide complexes are independent of  $[\text{Cu}^{2+}]$  for the exchange reaction



for which at least a 10-fold excess of  $\text{Cu}^{2+}$  is present. This suggests that the copper ion is unable to attack the ligand to form a rate-determining intermediate due to steric constraints imposed by the macrocycle ring when a lanthanide ion is already present in its cavity. This independence of  $[\text{Cu}^{2+}]$  in the dissociation kinetics is also observed for lanthanide complexes of K21DA,<sup>10</sup> CyDTA,<sup>12</sup> and MEDTA.<sup>11</sup> It should be noted that  $\text{CuK22DA}$  ( $\log K = 14.5$ ) is at least 2 orders of magnitude more stable than the corresponding lanthanide complexes ( $\log K = 10.8\text{--}12.2$ );<sup>8</sup> reaction 1 is essentially completed under the experimental conditions.

**Acid-Independent and Acid-Dependent Pathways.** The observed rate constants for reaction 1, the temperature at which they were measured, and the concentrations of hydrogen ion are given in Table II. In all cases, the plots of  $k_{\text{obsd}}$  vs.  $[\text{H}^+]$  give straight lines, similar to those of  $\text{LnCyDTA}^-$  complexes and the lighter lanthanide complexes of K21DA. This linear plots together with the absence of anion and general-acid catalysts (see below) suggest the simple rate law

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

The values of the acid-independent rate constants ( $k_d$ ) and the acid-catalyzed rate constants ( $k_H$ ) are resolved by a weighted least-squares analysis and are listed in Table III. The precision

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**Table II.** Kinetic Data ( $10^3 k_{\text{obsd}}$ , s<sup>-1</sup>) for the H<sub>3</sub>O<sup>+</sup>-Catalyzed Dissociation of Lanthanide K22DA Complexes<sup>a</sup>

metal	T, °C	10 <sup>3</sup> [H <sub>3</sub> O <sup>+</sup> ], M						
		0.5	1.0	1.95	2.5	3.75	5.0	7.5
La	25	1.01 ± 0.04	1.59 ± 0.14	2.77 ± 0.05	3.40 ± 0.10	4.93 ± 0.07	6.56 ± 0.24	9.45 ± 0.32
	35	1.45 ± 0.03	2.29 ± 0.10	5.83 ± 0.19	6.91 ± 0.23	9.60 ± 0.43	13.1 ± 0.85	20.4 ± 0.51
	45	3.06 ± 0.09	5.27 ± 0.21	10.1 ± 0.32	13.2 ± 0.89	19.9 ± 1.05	26.1 ± 1.85	38.7 ± 1.94
Pr	25	0.36 ± 0.01	0.63 ± 0.04	1.14 ± 0.04	1.40 ± 0.04	2.10 ± 0.03	2.82 ± 0.08	4.12 ± 0.13
Eu	25	0.68 ± 0.03	1.22 ± 0.03	1.39 ± 0.02	1.83 ± 0.03	2.65 ± 0.07	3.51 ± 0.10	4.51 ± 0.54
	35	0.96 ± 0.03	1.56 ± 0.17	2.14 ± 0.06	2.94 ± 0.09	3.50 ± 0.06	5.01 ± 0.25	6.65 ± 0.28
	45	1.64 ± 0.06	2.40 ± 0.14	3.36 ± 0.10	4.10 ± 0.13	5.52 ± 0.32	7.25 ± 0.33	10.2 ± 0.37
Yb	25	1.14 ± 0.03	2.02 ± 0.10	3.21 ± 0.07	3.88 ± 0.25	5.82 ± 0.06	7.16 ± 0.08	10.5 ± 0.26
Lu	25	1.34 ± 0.09	2.34 ± 0.02	3.65 ± 0.05	4.73 ± 0.05	6.79 ± 0.21	8.71 ± 0.16	12.6 ± 0.83
	35	1.57 ± 0.07	2.99 ± 0.26	5.32 ± 0.08	6.84 ± 0.12	9.69 ± 0.36	13.2 ± 0.80	18.8 ± 1.00
	45	1.97 ± 0.15	3.70 ± 0.34	7.92 ± 0.53	9.76 ± 0.64	15.4 ± 0.45	19.9 ± 1.21	29.1 ± 1.00

<sup>a</sup>[Complex] = 5.0 × 10<sup>-5</sup> M, [Cu<sup>2+</sup>] = 2.0 × 10<sup>-3</sup> M, and μ = 0.10 (LiClO<sub>4</sub>).

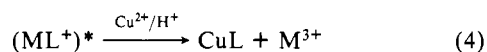
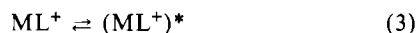
**Table III.** Acid-Independent and Acid-Dependent Rate Constants for the Dissociation Reactions of Lanthanide K22DA Complexes in Acid<sup>a</sup>

metal	T, °C	k <sub>d</sub> , s <sup>-1</sup>	k <sub>H</sub> , M <sup>-1</sup> , s <sup>-1</sup>
La	25	(3.97 ± 0.20) × 10 <sup>-4</sup>	1.21 ± 0.02
	35	(2.83 ± 0.29) × 10 <sup>-5</sup>	2.64 ± 0.32
	45	(4.42 ± 1.67) × 10 <sup>-5</sup>	5.07 ± 0.19
Pr	25	(9.14 ± 1.40) × 10 <sup>-5</sup>	(5.36 ± 0.09) × 10 <sup>-1</sup>
Eu	25	(4.31 ± 1.47) × 10 <sup>-4</sup>	(5.70 ± 0.96) × 10 <sup>-1</sup>
	35	(5.90 ± 1.29) × 10 <sup>-4</sup>	(8.39 ± 0.95) × 10 <sup>-1</sup>
	45	(1.07 ± 0.08) × 10 <sup>-3</sup>	1.22 ± 0.06
Yb	25	(5.02 ± 0.95) × 10 <sup>-4</sup>	1.37 ± 0.09
Lu	25	(5.58 ± 0.87) × 10 <sup>-4</sup>	1.64 ± 0.08
	35	(3.34 ± 0.85) × 10 <sup>-4</sup>	2.54 ± 0.09
	45	(-5.50 ± 14.7) × 10 <sup>-5</sup>	3.97 ± 0.18

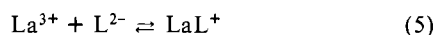
<sup>a</sup>Error limits represent one standard deviation.

of the values for the k<sub>H</sub> constants is much better than for the k<sub>d</sub> constants. In the case of Lu at 45 °C, the intercept is negative and its corresponding k<sub>d</sub> values must be taken as zero within experimental error.

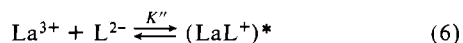
Similar to the arguments presented for LnCyDTA<sup>-</sup> and LnK21DA<sup>+</sup> complexes, the k<sub>d</sub> values of LnK22DA<sup>+</sup> complexes and characteristic water-exchange or complexation rate constants for the lanthanide complexes indicate that the self-dissociation of the complex does 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 the products. The reaction sequence may be written as



The water-exchange rate constant for lanthanum ion is roughly 1.0 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>. If this value is allowed for the maximum rate constant for the formation of ML<sup>+</sup> from (ML<sup>+</sup>)<sup>\*</sup>, the equilibrium constant for reaction 3 can be calculated as (4.0 × 10<sup>-4</sup>)/(1.0 × 10<sup>8</sup>) = 4.0 × 10<sup>-12</sup>. The experimentally determined stability constant for the reaction



is 1.6 × 10<sup>12</sup> M<sup>-1</sup> (log K = 12.21), which implies that the equilibrium constant K'' for reaction 6 should be at least 1.6 × 10<sup>12</sup>



M<sup>-1</sup> × 4.0 × 10<sup>-12</sup> = 6.4 M<sup>-1</sup> or that the lower limit for log K'' is 0.8. In a more realistic assessment of formation rate of ML<sup>+</sup> from (ML<sup>+</sup>)<sup>\*</sup>, a value lower than 1.0 × 10<sup>8</sup> should be taken because the rates for multidentate ligand reactions are in general slower. If it is taken as 1.0 × 10<sup>7</sup>, the final log K'' value can be calculated to be 1.8. This value is very similar to that for the monoacetate complex of lanthanum (log K = 1.82), which implies that, in the active (ML<sup>+</sup>)<sup>\*</sup> form, the metal ion is probably outside

**Table IV.** Rate Parameters<sup>a</sup> for Acid-Catalyzed Dissociation of La, Eu, and Lu Complexes of K22DA

complex	ΔH <sub>H</sub> <sup>+</sup> , kcal/mol	ΔS <sub>H</sub> <sup>+</sup> , eu	ΔG <sup>+</sup> , kcal/mol
LaK22DA <sup>+</sup>	12.0 ± 0.4	14.9 ± 1.4	17.3 ± 0.6
EuK22DA <sup>+</sup>	6.5 ± 0.1	-37.7 ± 0.2	17.7 ± 0.1
LuK22DA <sup>+</sup>	7.7 ± 0.2	-31.7 ± 0.7	17.2 ± 0.3

<sup>a</sup>Error limits represent one standard deviation.

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 at the uncoordinated ligand nitrogen(s), which explains the lack of Cu<sup>2+</sup> catalysis.

A comparison of k<sub>H</sub> values indicates that the less thermodynamically stable lanthanide-K22DA complexes are kinetically more labile with respect to acid-catalyzed pathways. On the other hand, the correlation of k<sub>H</sub> values with the stability constants K does not provide a good linear relationship. This is in contrast to those Ln complexes of the open-chain, probably slightly more flexible ligands such as CyDTA for which ionic potential seems to be the dominant factor in affecting the complex stability.

Activation parameters corresponding to the acid-catalyzed pathway obtained from the temperature-dependent measurement of the rate constants are listed in Table IV. An isokinetic behavior is observed, i.e., the plot of ΔH<sub>H</sub><sup>+</sup> vs. ΔS<sub>H</sub><sup>+</sup> is linear. This implies that a common mechanism is supported.<sup>17</sup> On the other hand, except for La<sup>3+</sup>, the ΔH<sub>H</sub><sup>+</sup> values for the acid-catalyzed pathway are much smaller as compared to similar values for lanthanide complexes of EDTA and CyDTA, reflecting the lower thermodynamic stability of the title complexes.

**Lack of General-Acid and Anion Catalysis.** Tables V and VI show the observed rate constants for the dissociation of three LnK22DA<sup>+</sup> complexes in the presence of various amount of different acids and nitrate ion, respectively. In all cases, the rate constants are not varied with respect to the above-mentioned factors. The insensitivity of the LnK22DA<sup>+</sup> complexes to general-acid and anion catalysis may be due to their more compact structures, which leave little additional coordination space for other species.

The common coordination number for lanthanide complexes is eight or nine. The ligand, K22DA, has a total of eight donor atoms, which is one more than K21DA has. Indeed, for some lighter lanthanide-K21DA complexes, acetate catalysis is present. Laser fluorescence study also shows that the EuK21DA<sup>+</sup> complex has two inner-sphere coordinated water molecules but the EuK22DA<sup>+</sup> complex probably has only one.<sup>18,19</sup>

**[Electrolyte] Independence.** Table VII lists the observed rate constants for the dissociation of the specified LnK22DA<sup>+</sup> complexes, and it is observed that the rates are independent on the

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**Table V.** Observed Rate Constants for La(III), Eu(III), and Lu(III) Complexes of K22DA in the Presence of a Mixture of HClO<sub>4</sub> and General Acid<sup>a</sup>

metal	general cid	10 <sup>3</sup> k <sub>obsd</sub> , s <sup>-1</sup>
La	CH <sub>3</sub> COOH	6.50 ± 0.10
	HCOOH	6.46 ± 0.22
	ClCH <sub>2</sub> COOH	6.66 ± 0.08
Eu	CH <sub>3</sub> COOH	3.20 ± 0.10
	HCOOH	3.27 ± 0.10
	ClCH <sub>2</sub> COOH	3.36 ± 0.10
Lu	CH <sub>3</sub> COOH	8.66 ± 0.18
	HCOOH	8.57 ± 0.10
	ClCH <sub>2</sub> COOH	8.64 ± 0.25

<sup>a</sup> [Complex] = 5.0 × 10<sup>-5</sup> M, [Cu<sup>2+</sup>] = 2.0 × 10<sup>-3</sup> M, T = 25 °C, [general acid] = 1.0 × 10<sup>-2</sup> M, [H<sub>3</sub>O<sup>+</sup>]<sub>total</sub> = 5.0 × 10<sup>-3</sup> M, and μ = 0.10.

**Table VI.** Lack of [NO<sub>3</sub><sup>-</sup>] Influence on Dissociation Kinetics of La(III), Eu(III), and Lu(III) Complexes of K22DA<sup>a</sup>

metal	10 <sup>2</sup> [NO <sub>3</sub> <sup>-</sup> ], M	10 <sup>3</sup> k <sub>obsd</sub> , s <sup>-1</sup>	10 <sup>2</sup> [NO <sub>3</sub> <sup>-</sup> ], M	10 <sup>3</sup> k <sub>obsd</sub> , s <sup>-1</sup>
La	2.0	3.41 ± 0.07	6.5	3.38 ± 0.10
	4.0	3.42 ± 0.06	9.5	3.43 ± 0.09
Eu	2.0	1.84 ± 0.11	6.5	1.80 ± 0.09
	4.0	1.82 ± 0.14	9.5	1.87 ± 0.04
Lu	2.0	4.62 ± 0.20	6.5	4.56 ± 0.31
	4.0	4.67 ± 0.14	9.5	4.67 ± 0.22

<sup>a</sup> [Complex] = 5.0 × 10<sup>-5</sup> M, [Cu<sup>2+</sup>] = 2.0 × 10<sup>-3</sup> M, T = 25 °C, μ = 0.10, and [H<sub>3</sub>O<sup>+</sup>] = 2.5 × 10<sup>-3</sup> M.

**Table VII.** [Electrolyte] Independence of Dissociation Rates of La(III), Eu(III), and Lu(III) Complexes of K22DA<sup>a</sup>

metal	[electrolyte], M	10 <sup>3</sup> k <sub>obsd</sub> , s <sup>-1</sup>	[electrolyte], M	10 <sup>3</sup> k <sub>obsd</sub> , s <sup>-1</sup>
La	0.05	3.25 ± 0.23	0.50	3.33 ± 0.13
	0.20	3.36 ± 0.06	0.75	3.38 ± 0.04
	0.35	3.47 ± 0.23		
Eu	0.05	1.78 ± 0.13	0.50	1.84 ± 0.08
	0.20	1.91 ± 0.11	0.75	1.80 ± 0.04
	0.35	1.81 ± 0.03		
Lu	0.05	4.50 ± 0.09	0.50	4.72 ± 0.27
	0.20	4.79 ± 0.06	0.75	4.77 ± 0.13
	0.35	4.87 ± 0.12		

<sup>a</sup> [Complex] = 5.0 × 10<sup>-5</sup> M, [Cu<sup>2+</sup>] = 2.0 × 10<sup>-3</sup> M, T = 25 °C, [H<sub>3</sub>O<sup>+</sup>] = 2.50 × 10<sup>-3</sup> M, and electrolyte = LiClO<sub>4</sub>.

electrolyte concentration. This may reflect the mutual cancellation of two opposing effects: On one hand the weak ion-pair formation between the cationic LnK22DA<sup>+</sup> and the perchlorate ion tends to stabilize the rate-determining intermediate, which slows down the reaction. On the other hand, the thermodynamic stability decreases with increasing electrolyte concentration, which tends to speed up the rate.

## Discussion

Table VIII gives a summary of a few selected kinetic characteristics for lanthanide complexes of both macrocyclic and open-chain polyamino polycarboxylic acids with different thermodynamic stabilities, structures, and electronic charges. For the

**Table VIII.** Summary of Kinetic Characteristics of Lanthanide Complexes of both Open-Chained and Macrocyclic Polyamino Polyacetate Ligands<sup>a</sup>

	LnK21DA <sup>+</sup>	LnK22DA <sup>+</sup>	LnMEDTA	LnCyDTA <sup>-</sup>
log K range	10.11–11.85	10.84–12.23	11.50–14.51	16.98–22.21
[H <sup>+</sup> ] dependence <sup>b</sup>	linear (La–Eu) saturation (Tb–Lu)	linear	saturation	linear
[acetate] dependence	yes (La–Eu) no (Tb–Lu)	no	yes	no
[electrolyte] dependence	yes	no	?	?

<sup>a</sup> Information obtained from ref 10 for LnK21DA<sup>+</sup>, ref 11 for LnMEDTA, ref 12 for LnCyDTA<sup>-</sup>, and this work for LnK22DA<sup>+</sup>. <sup>b</sup> [H<sup>+</sup>] range: 8.4 × 10<sup>-6</sup> to 2.5 × 10<sup>-4</sup> M for LnK21DA<sup>+</sup>; 5 × 10<sup>-4</sup> to 7.5 × 10<sup>-3</sup> M for LnK22DA<sup>+</sup>; 1 × 10<sup>-5</sup> to 7 × 10<sup>-4</sup> M for LnMEDTA; 4 × 10<sup>-6</sup> to 1.4 × 10<sup>-4</sup> for LnCyDTA<sup>-</sup>.

lanthanide complexes of noncyclic multidentate ligands such as MEDTA and CyDTA, the results of rates on [H<sup>+</sup>] and [anion] dependence can be explained by their thermodynamic stabilities and charges of the complexes, respectively. A complex of greater thermodynamic stability tends to dissociate more slowly with the proton attack on the complex being rate-determining for the [H<sup>+</sup>]-dependent path. However, for a less stable complex the rate-determining step shifts to the dissociation of the protonated species. On the other hand, acetate catalysis is observed for LnMEDTA dissociation but not with LnCyDTA<sup>-</sup> because the LnMEDTA complex is neutral and steric hindrance for anion coordination is not significant.

When the rates of dissociation of lanthanide complexes of the two ionizable macrocyclic ligands are compared, a similar argument can be presented except that the relative thermodynamic stability range (in terms of log K values) for the detection of different [H<sup>+</sup>]-dependent rates (i.e., linear vs. saturation) shifts to a lower region. In particular, although the resulting macrocyclic complexes are cationic, the acetate catalysis must only occur with those complexes with available, sterically noncrowded coordination site(s).

It is also interesting to observe that the kinetic characteristics of dissociation of both LnK22DA<sup>+</sup> and LnCyDTA<sup>-</sup> complexes are very similar. They differ only in the magnitudes of rate constants. However, there are some fundamental differences in the rationalization of the kinetic event. First, the absence of acetate catalysis in LnK22DA<sup>+</sup> complexes is believed to be due to the lack of roomy coordination site in contrast to the charge barrier of LnCyDTA<sup>-</sup> complexes. Second, the ranges of both k<sub>d</sub> and k<sub>H</sub> values for LnK22DA<sup>+</sup> complexes (k<sub>d</sub>, 9 × 10<sup>-5</sup> to 6 × 10<sup>-4</sup>; k<sub>H</sub>, 0.54–1.64) are about 2 orders of magnitude smaller than the corresponding ones of LnCyDTA<sup>-</sup> complexes (k<sub>d</sub>, 1 × 10<sup>-7</sup> to 1 × 10<sup>-4</sup>; k<sub>H</sub>, 0.017–129), indicating that the stability of the latter system is mainly controlled by ionic potential whereas, for the former system, compensation effects of both ionic potential and matching of ionic radius and ligand cavity size are probably operative.

The following postulates can be made on the basis of existing kinetic information on lanthanide complexes of multidentate ligands obtained in our laboratory and elsewhere.

1. The thermodynamic stability of the lanthanide complexes is reflected in terms of slower dissociation rates as opposed to faster formation reaction rates.

2. The nature of acid attack on these complexes is dictated by the number of basic atoms on the ligand, the structure and overall charge of the complex, and its thermodynamic stability. (i) For complexes with weak metal–ligand interactions, the self-dissociation pathway probably dominates over others and the reactions may be zero-order in acid. (This is probably difficult to test due to their intrinsically faster rates.) (ii) For complexes with intermediate stability, both acid-independent and acid-dependent pathways could be important. It is possible in these reactions that the order of reaction changes from higher order to zero-order with increase in acid concentration; i.e., at sufficiently large excess of acid, reaction rates become independent of [acid]. (iii) The acid-catalyzed pathways should dominate in the case of very strong complexes. These reactions may be first-order or higher in acid. (iv) The acid-catalyzed dissociation rate constant might decrease with decrease in the anionic charge on the complex,

which means, for complexes of comparable stability, the acid-dissociation rate constant should increase in the order cationic < neutral < anionic.

3. The dissociation rates of both anionic and cationic complexes can be accelerated by coordinating anions but very weakly complexing anions can cause the reduction in rate of dissociation of cationic complexes by ion-pair formation.

4. For complexes of rigid and sterically crowded ligands such as macrocyclic compounds, the contribution from the metal-catalyzed pathway in metal-exchange reactions could be minimal. The same ligand may also prevent the anion attack on the metal center, depending on the structure of the complex.

5. The formation reaction rates of macrocyclic ligands will be considerably slower as compared to water-exchange rates of

lanthanide ions, because the rate-determining step may shift from dissociative loss of water molecule to metal ion incorporation into ligand cavity.

Further experimental testing of these postulates by careful design of thermodynamic and kinetic studies is obviously needed.

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**Registry No.** LaK22DA<sup>+</sup>, 107985-45-5; EuK22DA<sup>+</sup>, 107985-46-6; LuK22DA<sup>+</sup>, 107985-47-7; PrK22DA<sup>+</sup>, 107985-48-8; YbK22DA<sup>+</sup>, 107985-49-9.

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## *nido*-Methylenephosphahexaboranes: R<sub>2</sub>CPB<sub>5</sub>H<sub>8</sub>

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Two routes to a new class of heteroborane clusters, the *nido*-methylenephosphahexaboranes R<sub>2</sub>CPB<sub>5</sub>H<sub>8</sub>, have been developed. (Me<sub>3</sub>Si)<sub>2</sub>CPB<sub>5</sub>H<sub>8</sub> has been prepared from the phosphoalkene (Me<sub>3</sub>Si)<sub>2</sub>C=PCl and the B<sub>5</sub>H<sub>8</sub><sup>-</sup> anion, while both R<sub>2</sub>CPB<sub>5</sub>H<sub>8</sub> compounds, where R = Me<sub>3</sub>Si or Ph, have been prepared by dehydrochlorination of the corresponding phosphino-bridged pentaborane derivatives (μ-R<sub>2</sub>CHPCl)B<sub>5</sub>H<sub>8</sub>.

### Introduction

Investigations of synthetic routes to molecular heteroborane clusters containing heteroatoms other than carbon have led to the discovery of a surprising number of new classes of cluster molecules. One synthetic approach on which we have focused is the direct insertion of heteroatoms ranging from beryllium to gallium into boron hydride clusters. Recently we have expanded our explorations to include nitrogen group elements. The initial results of these investigations are the syntheses of the first examples of phosphahexaboranes, reported below.

Prior to the present work, no examples have been reported of phosphaborane clusters containing fewer than nine boron atoms. The known phosphaboranes include C<sub>6</sub>H<sub>5</sub>PB<sub>11</sub>H<sub>11</sub>,<sup>1</sup> a phosphadodecaborane; RPB<sub>10</sub>H<sub>12</sub>,<sup>2</sup> a phosphaundecaborane; and several phosphacarboranes: 1,2- and 1,7-CHPB<sub>10</sub>H<sub>10</sub>,<sup>1,3</sup> CHP(CH<sub>3</sub>)B<sub>9</sub>H<sub>10</sub>, and the CHPB<sub>9</sub>H<sub>10</sub><sup>-</sup> anion.<sup>4</sup> Transition-metal complexes of several of these compounds have been prepared.<sup>2,4a,5,6</sup>

### Results and Discussion

**Methylenephosphahexaborane Syntheses.** Geometrical isomers of the phosphorus-bridged (μ-phosphino)pentaboranes of general formula RR'PB<sub>5</sub>H<sub>8</sub> (in which R ≠ R'), have been previously reported.<sup>7</sup> The presence of geometrical isomers led the authors

**Table I.** <sup>11</sup>B NMR Data for Isomers a and b of (μ-RPCl)B<sub>5</sub>H<sub>8</sub> Derivatives<sup>a</sup>

R	chem shift, δ					
	B(4,5)		B(2,3)		B(1)	
	a	b	a	b	a	b
CH <sub>3</sub>	-1.0	+0.2	-24.2 <sup>b</sup> (88)	-8.7 <sup>b</sup> (88)	-45.4	-46.0
C <sub>6</sub> H <sub>5</sub>	-0.1	-0.1	-21.7 (93)	-9.9 (93)	-43.7	-45.5
CH(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> , <b>1</b>	-0.5	-0.5	-21.8 (88)	-10.0 (88)	-44.8	-45.8
CH(SiMe <sub>3</sub> ) <sub>2</sub> , <b>2</b>	-0.1	-0.1	-17.4 (88)	-8.8 (96)	-44.5	-46.4

<sup>a</sup>The δ values are chemical shifts measured relative to external BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> = 0 ppm. Values in parentheses are terminal B-H coupling constants in hertz. <sup>b</sup>Apparent triplets due to <sup>31</sup>P coupling of similar magnitude to that of terminal <sup>1</sup>H. See ref 7 for details.

to suggest that the bridging phosphorus atom in these compounds is not bound to an edge of the pentaborane pyramid via a three-center-two-electron bond, as is the silicon atom in (μ-Me<sub>3</sub>Si)B<sub>5</sub>H<sub>8</sub><sup>8</sup> but that the original lone pair of electrons on phosphorus is also involved in bonding and the environment at the phosphorus is therefore approximately tetrahedral. The isomerism of these (μ-phosphino)pentaboranes result from the different environments of the two terminal substituents on phosphorus with respect to the pentaborane cluster. In the (μ-phosphino)pentaboranes, the phosphorus contributes three electrons to the cluster but is not itself a cluster atom. The five boron atom cluster is formally considered, on the basis of its electron count,<sup>9</sup> to have an arachno structure analogous to that of the isoelectronic pentaborane(11), B<sub>5</sub>H<sub>11</sub>, and (μ-Me<sub>2</sub>NCH<sub>2</sub>)B<sub>5</sub>H<sub>8</sub>,<sup>10</sup> in both of which B(2) is not expected to be within distance of B(3).

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