

Unusual Thermodynamic and Kinetic Properties of Lanthanide Complexes of 1,7-Diaza-4,10,13-trioxacyclopentadecane-*N,N'*-diacetic Acid

C. Allen Chang,* Ven O. Ochaya, and V. Chandra Sekhar

Department of Chemistry, University of Texas at El Paso, El Paso, Texas 79968-0513, U.S.A.

The formation constants and dissociation rate constants for 1,7-diaza-4,10,13-trioxacyclopentadecane-*N,N'*-diacetic acid complexes of lanthanide ions have been measured in water at 25 °C and the Eu^{III} complex has been found to be the most stable of all.

In an effort to develop lanthanide ion selective reagents, we have studied the thermodynamic formation constants for 1,10-diaza-4,7,13,16-tetraoxacyclo-octadecane-*N,N'*-diacetic acid complexes of lanthanide ions.¹ This ligand has shown selectivity towards the lighter lanthanides, presumably because their ionic size and charge density match well with the properties of the ligand. In order to find a selective reagent for the lanthanides in the middle of the series, we have made a ligand with a similar charge but smaller macrocyclic cavity, *i.e.* 1,7-diaza-4,10,13-trioxacyclopentadecane-*N,N'*-diacetic acid (**1**), which forms its most stable lanthanide complex with Eu^{III}.

The ligand was synthesized as its dihydrochloride salt from commercially available diaza-15-crown-5 (Kryptofix 21), by the method of Kulstad and Malmsten.² The formation constants of its complexes with lanthanide ions were determined by a potentiometric method in aqueous solution:¹ log *K* values so obtained are shown in Figure 1 as a plot against atomic number.

By virtue of a high charge density, Lu^{III} forms the most stable lanthanide complex with flexible and charged ligands such as ethylenediaminetetra-acetic acid.³ However, neutral macrocycles are known to form more stable complexes when the ring cavity matches well with the ionic size of the metal.^{4,5} As the ligand under study has a macrocyclic structure with charged carboxylate groups on the side arms, both these factors can play significant roles in determining which of the lanthanide ions forms the most stable complex. Because of its large size and low charge density, La^{III} forms the least stable complex. In spite of the high charge density on Lu^{III}, its complex attains intermediate stability, presumably because its ionic size is considerably smaller than the ligand cavity. The most stable complex in the series is formed by Eu^{III} since it is the best fit both for size and charge density.

Also plotted in Figure 1 are the observed dissociation rate constants for these complexes at 25 °C in an acetic acid-acetate buffer of pH 4.6 and ionic strength 0.1. The rates were measured on a stopped-flow spectrophotometer using Cu^{II} ion as the scavenger of free ligand and by monitoring the growth in absorbance due to the Cu^{II} complex at 270 nm. The results of the kinetic studies are in conformity with the thermodynamic data inasmuch as the plot of observed rate constants against atomic number gives a mirror image of a similar plot of log *K* vs. atomic number (Figure 1). The most stable, Eu^{III} complex exhibits the lowest dissociation rate constant. A detailed kinetic study by varying buffer pH suggests that for lighter lanthanide complexes, the kinetics obey the rate law: $k_{\text{obs.}} = k_d + k_H [\text{H}^+]$, where $k_{\text{obs.}}$ is the observed pseudo-first-order

rate constant; k_d and k_H are the rate constants for direct dissociation and acid catalysed pathways, respectively.⁶ For heavier lanthanide complexes however, saturation-type kinetics were observed with rate constants increasing with increase in acid concentration and reaching a limiting value. Irrespective of the nature of the acid dependent pathway, all plots show non-zero intercepts corresponding to the k_d values. For the lighter lanthanide complexes, it is evident that the rate determining step for the acid dependent pathway is the attack of H⁺ on the ligand. For heavier lanthanides the rate determining step for this pathway is presumably the proton migration from nitrogen to carboxylate oxygen. It is also interesting that there is an acetate catalysed pathway for complexes of La^{III} and Eu^{III}, but for the later lanthanide complexes the observed rate constants show no dependence on the concentration of acetate ion in the buffer.

The log k_d values for La^{III}, Eu^{III}, and Lu^{III} complexes are also plotted in Figure 1, which parallel the trend shown by $k_{\text{obs.}}$ values. The formation rate constants, k_f , calculated using the relation $k_f = K \times k_d$, lie in the 10⁸–10⁹ mol⁻¹ dm³ s⁻¹ range, which is in excellent agreement with formation rate constants

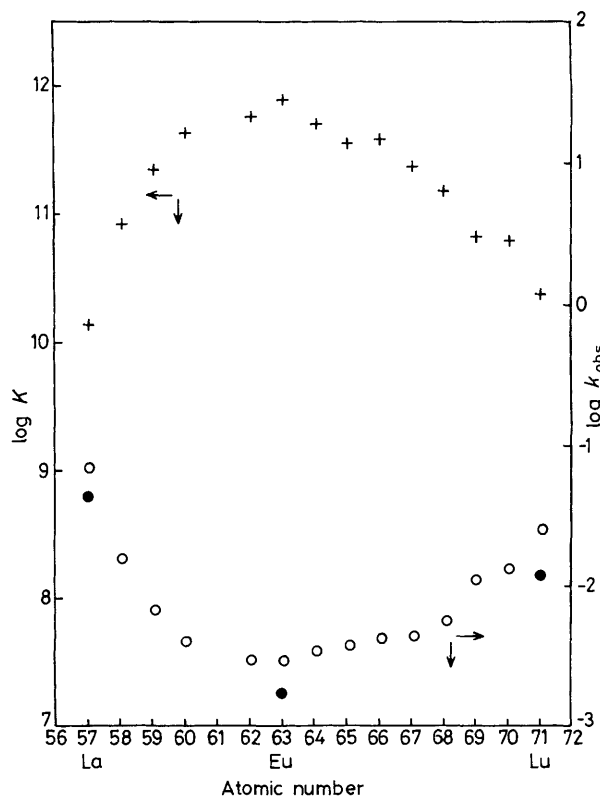
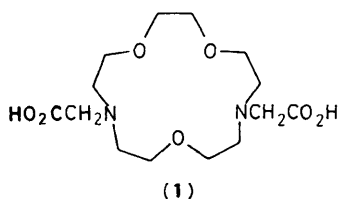


Figure 1. Plots of logarithmic formation constants (log *K*, +) and observed dissociation rate constants (log $k_{\text{obs.}}$, O; log k_d , ●) for the lanthanide complexes of (1) vs. atomic number.

with murexide and also with water exchange rate constants for hydrated lanthanide ions.⁷

In summary, it is demonstrated that by varying the type and number of donor atoms, rigidity, cavity size, and charge on the ligand, one should be able to develop selective reagents for a closely related group of metal ions such as the lanthanides.

Acknowledgement is made to the Department of Energy for financial support of this research. The initial support of this project by the Research Corporation is also appreciated.

Received, 10th July 1985; Com. 981

References

- 1 C. A. Chang and M. E. Rowland, *Inorg. Chem.*, 1983, **22**, 3866.
 - 2 S. Kulstad and L. A. Malmsten, *Acta Chem. Scand., Ser. B*, 1979, **33**, 469.
 - 3 T. Moeller, D. E. Martin, L. C. Thompson, R. Ferrus, G. Reistel, and W. U. Randell, *Chem. Rev.*, 1965, **65**, 1.
 - 4 J. M. Lehn and J. P. Sauvage, *J. Am. Chem. Soc.*, 1975, **97**, 6700.
 - 5 R. M. Izatt, J. D. Lamb, J. J. Christensen, and B. L. Haymore, *J. Am. Chem. Soc.*, 1977, **99**, 8344.
 - 6 G. A. Nyssen and D. W. Margerum, *Inorg. Chem.*, 1970, **9**, 1814.
 - 7 G. Geier, *Ber. Bunsenges. Phys. Chem.*, 1969, **69**, 617; *Helv. Chim. Acta*, 1968, **51**, 94.
-