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Metal Complex Formation with 1,10-Diaza-4,7,13,16-tetraoxacyclooctadecane-*N*,*N'*-diacetic Acid. An Approach to Potential Lanthanide Ion Selective Reagents

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The principles of designing lanthanide (Ln) ion selective macrocyclic reagents are discussed. Factors such as the size of the metal ion, the cavity size of the ligand, the stereochemical constraint imposed on the ligand, and the overall coordination number of the multidentate ligand are considered. On the basis of these principles, the macromonocyclic ligand 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N*,*N'*-diacetic acid (dacda) has been prepared and characterized. The stability constants of dacda complexes of various metal ions are reported. Except for a few metal ions such as copper(II), lead(II), and cadmium(II), dacda shows unique selectivity toward lanthanide ions as a group. Also, for the first time in aqueous solution for a multidentate ligand, the stability constants for Ln–ligand complexes decrease with increasing atomic number for heavy lanthanides and remain roughly unchanged for the lighter lanthanides. These data are discussed, and the structures of the complexes are proposed.

Recently the study of metal ion specific organic reagents has gained momentum. The study of iron transport using simple models of various siderophores has led Raymond and his co-workers to a biomemetic design and synthesis of actinide-specific sequestering agents[1,2] as well as gallium- and indium-imaging agents.[3] The study of ionophoric antibiotics and their structural analogues, namely crown ethers, led to Cram's host–guest complexation concept[4] and Lehn's study of macromolecular inclusion complexes of cryptands.[5] The use of macrocyclic compounds as models of alkali and alkaline earth metal ion transport mediators and other applications have been summarized.[6,7] Also, a series of studies of the potential for transition metal ion recognition by some mixed-donor (N, O, S) macrocyclic compounds have been reported.[8] Other examples of novel calcium[9] and uranyl[10] ion selective reagents have been recently published.

We are interested in the lanthanide ion selective reagents for two principal reasons. From a theoretical point of view, it is hoped that a better understanding of their coordination properties as well as stereochemistry can be achieved. From a practical point of view, we wish to synthesize several selective reagents useful for analytical, hydrometallurgical, and pharmaceutical applications. It should be noted that although many studies on the lanthanide complex binding properties have been reported, both for classical noncyclic polyamino polycarboxylic acids and β-diketones[11] as well as several crown ethers,[12] it appears that no reagent has been reported to be ion selective in nature.

The most unique properties of lanthanide ions are the common +3 oxidation state and the "lanthanide contraction"—the gradual but small decrease in ionic size with increasing atomic number. In coordination chemistry, the lanthanides in general prefer oxygen donor atoms rather than nitrogen and the coordination numbers are usually 8 or 9.[11] The bonding of lanthanide complexes is mainly electrostatic with possibly minor covalent modification due to the influence of inner-shell f orbitals. In summary, the bonding is similar to that of main group metal ions but different from those of transition metal ions, which involve a great deal of covalent character. In addition, the thermodynamic parameters of complex formation between lanthanides and classical ligands such as polyamino polycarboxylic acids and β-diketones consist of favorable negative ΔH and positive $T\Delta S$ terms in most cases.[13] However, these are different from the latest findings for lanthanide–crown ether complexes. In general, lanthanide–crown ether complexation involves a favorable positive $T\Delta S$ contribution and an unfavorable positive ΔH contribution.[14] For example, for La(III)–18-crown-6 complex in methanol, $\Delta H°$ is 2.81 kcal/mol and $T\Delta S°$ is 7.30 kcal/mol. This differs from the alkali and alkaline earth metal ion–crown ether reactions, in which favorable negative $\Delta H°$ contributions are observed.[15]

In this paper, we discuss, first, the principles for the design of lanthanide ion selective reagents and, second, the stabilities of some lanthanide ion complexes with 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N*,*N'*-diacetic acid (dacda; Figure 1) as compared with those of other representative metal ions.

Experimental Section

Materials and Standard Solutions. The ligand 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N*,*N'*-diacetic acid (dacda, H_2L) was prepared according to the method of Kulstad and Malmsten with minor modifications.[16] One gram of kryptofix 22 (1,10-diaza-4,7,13,16-tetraoxacyclooctadecane, Parish Chemical Co.), 1.42 g of ethyl bromoacetate, and 1.54 g of triethylamine in 20 mL of absolute ethanol were refluxed for 24 h. The solution was then concentrated with a rotary evaporator and poured into 20 mL of water and extracted four times with 25 mL of chloroform. The chloroform extracts were evaporated to dryness, and 25 mL of water was added to the solid residue. The mixture was then refluxed for 18 h. The hydrolyzed mixture was extracted with two portions of 35 mL of chloroform to

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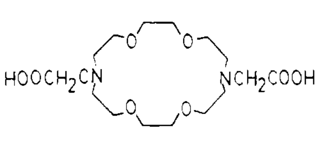

Figure 1. Structure of 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N*,*N*′-diacetic acid (dacda).

remove unwanted materials; the aqueous layer was rotary evaporated to almost dryness, and 30 mL of absolute ethanol was added and homogenized. The white precipitate was collected by filtration and recrystallized in 80% ethanol–water solution. The yield was 0.70 g (37.7% overall).

The IR spectrum of the zwitterion form of the crown ether amino acid shows a broad peak at 1620 cm^{-1}. The NMR spectrum in D_2O shows a sharp singlet at 3.72 ppm, another singlet at 3.85 ppm, and a multiplet in the region of 3.50–3.80 ppm, which is in contrast to that reported previously.[16] Recrystallization of the compound in ca. 4 M HCl ethanolic solution yields the crystalline dihydrochloride salt, which shows a sharp characteristic carbonyl absorption band at 1715 cm^{-1} indicating the presence of protonated carboxylic acid groups. The NMR peaks also shift to low field as a result of protonation, i.e. 3.72 (singlet), 4.15 (singlet), and 3.60–3.90 ppm (multiplet). Anal. Calcd for $C_{16}H_{30}N_2O_8{\cdot}2HCl{\cdot}2H_2O$: C, 39.43; H, 7.44; N, 5.75. Found (Galbraith): C, 39.44; H, 7.49; N, 5.72.

A 7×10^{-3} M ligand stock solution was prepared and standardized by standard tetramethylammonium hydroxide solution in the presence of equimolar calcium chloride. Carbonate-free tetramethylammonium hydroxide solution (0.05 M) was prepared by diluting a 20% $(CH_3)_4NOH$ methanol solution from Aldrich Chemical Co. The aqueous $(CH_3)_4NOH$ solution was standardized by using potassium hydrogen phthalate. The standard metal salt solutions having concentrations of about 0.01 M were prepared from reagent grade nitrates (K, Ca, Sr, Ba, Cu, Zn, Pb, Ce, Pr, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), chlorides (La, Nd, Ni), or sulfate (Sm). The metal solutions were standardized by edta complexometric titrations using xylenol orange (all lanthanide ions), murexide (Cu and Ni), and eriochrome black T (Ca, Zn, and Pb) as indicators. A 1 M solution of $(CH_3)_4NCl$ was prepared and determined by passing aliquots of the solution into a cation-exchange (Dowex 50W-X8 resin) column in the H^+ form and by titrating the displaced H^+ ions with standard KOH solution.

Potentiometric Titration. All titrations were carried out at constant ionic strength of 0.10 M $(CH_3)_4NCl$. Boiled deionized water was used for all experiments. A Model 750 Fisher Acument selective ion analyzer in conjunction with a Fisher combination electrode was employed to monitor the pH (±0.001 pH unit). The sample solution was prepared by pipeting exact amounts of each stock solution into a titration vessel so that the final mixture is 7×10^{-4} M in both the ligand and the metal salt. An additional amount of standardized HCl was also added into the titration mixture so that the final ligand would be in the triprotonated form, $H_2L{\cdot}HCl$. The water-jacketed titration vessel with a 50-mL capacity was purchased from Brinkmann together with a five-hole cover. Electrode, buret, and temperature probe were fitted into these holes. The vessel was always kept at 25.0 ± 0.1 °C by using a constant-temperature circulating bath from Van Waters and Rogers. Prior to each titration, the pH meter was standardized at pH 4.00 and 7.00 ± 0.02 pH unit with Fisher buffer solutions. $(CH_3)_4NOH$ solution was delivered from a 5-mL buret with a reading accuracy of ±0.01 mL. All titrations were performed two to three times, and reproducible results were obtained. Oxygen-free nitrogen gas was bubbled through the titrate solution on several occasions, and no significant difference was found if the step is neglected. All equilibrium calculations were performed with use of computer programs described elsewhere.[17] Data points in the metal buffer region of 20–80% metal complexation were employed for the calculation of stability constants. The averaged values are presented together with the standard deviations calculated from those valid data points.

Results and Discussion

Principles for the Design of Lanthanide Ion Selective Reagents. At least four factors should be considered in the design of metal ion selective reagents: (1) the nature of ligand donor atoms and metal receptors, i.e., electronic vs. covalent and hard vs. soft; (2) the structure and size, i.e., the sizes of metal ion and the cavity of the ligand as well as the stereochemical constraints imposed on the ligand; (3) the charge of metal ion and ligand; (4) the number of chelate rings formed and the coordination number of the resulting complex.

Several additional comments should be noted. First, Leppkes and Vogtle have recently pointed out the concept of "donor stereology", i.e. the metal-complexing ability for a ligand can be varied if its donor functionalities are bonded to various anchor groups that impose stereochemical constraints.[18] Second, full or partial charge neutralization normally increases the stability of complex formation presumably due to a favorable increase in the $T\Delta S$ term. For example, it is found that the complexes of the ligand triethylenetetraamine-N^2,N^3-diacetate with Ni(II) and Zn(II) are more stable than those of *N*,*N*,*N*′,*N*′-tetrakis(β-aminoethyl)ethylenediamine, its structural analogue.[17] Also, it has been shown that the crown ether carboxylic acids exhibit metal ion extraction efficiencies and selectivities that surpass those of neutral crown ethers.[19]

The effective ionic radii for lanthanide ions range from 0.98 Å for Lu^{3+} to 1.16 Å for La^{3+} for a coordination number of 8[20] which is on average smaller than those of alkali and alkaline earth metal ions and greater than those of first-row transition metal ions. To make lanthanide ion selective reagents that do not prefer first-row transition metal ions, the crown ether family seems to be the choice because it is known that crown ethers, generally, do not bind first-series divalent transition metal ions appreciably. In order to differentiate lanthanide ions from alkali and alkaline earth metal ions if a certain crown ether is chosen, it is necessary to derivatize the crown ether with additional ionizable functional groups such as carboxylic acid so that enhanced binding with the lanthanide is observed. For our present purpose, we have selected the diaza crown ether, 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane, as the anchor backbone for an easier acetic acid derivatization reaction and ease of study in aqueous solutions. The final ligand, dacda, is very soluble in aqueous solution but insoluble in most organic solvents.

Ligand Protonation Constants. The ligand potentiometric titration curve (L of Figure 2) shows two buffer regions: one from pH 2.9 to pH 5, which corresponds to the dissociation of the acetic acid proton; another from pH 5 to pH 9, which corresponds to the two simultaneous dissociation of protons attached to nitrogen atoms. The two calculated pK_a values, 8.45 ± 0.02 and 7.80 ± 0.02, for the nitrogen protons correspond well with the published ones for the nonderivatized macrocycle[21] and the same diaza crown with nonionizable pendent groups.[22] The values are also consistent with those of the dipropionic acid derivative.[23] The third protonation constant with a value of 2.90 ± 0.10 is estimated from the titration data.

Stability of Metal Chelates. Some representative metal complex formation equilibrium curves are also shown in Figure 2. All of these curves are lower in pH than that of the ligand titration without metal ion, indicating competition between metal ions and protons for binding with the ligand. For K(I), Ca(II), Sr(II), Ba(II), Ni(II), and Zn(II) ions, complexation occurs only after the acetic acid protons are removed. The

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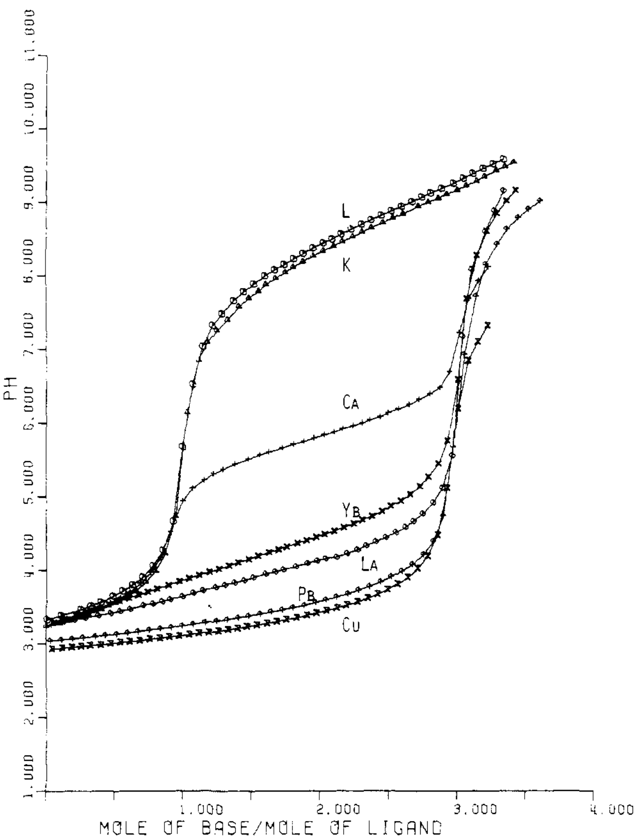

Figure 2. Potentiometric equilibrium curves for dacda ($H_2L{\cdot}HCl$) and 1:1 ratios of dacda with various metal ions ([dacda] = [M] = 7.00×10^{-4} M; 25 °C; $\mu = 0.10$ (($(CH_3)_4NCl$)).

Table I. Stability Constants of Metal Complexes of 1,10-Diaza-4,7,13,16-tetraoxacyclooctadecane-*N,N'*-diacetic Acid (dacda) and Some Ligands of Interest[a]

		log $K_{ML}{}^M$				
	ionic radii,[b] Å	dacda	kryptofix 22[c]	edda[d]	edta[d]	18-crown-6[e] (in MeOH)
K^+	1.51	3.91 ± 0.26			0.8	6.06
Ca^{2+}	1.12	8.39 ± 0.06			10.61	3.86
Sr^{2+}	1.26	8.29 ± 0.07	2.57		8.68	5.5
Ba^{2+}	1.42	7.63 ± 0.02	2.97		7.80	7.04
Ni^{2+}	0.69	7.39 ± 0.03	2.5	13.65	18.52	
Cu^{2+}	0.73	14.49 ± 0.03	6.18	16.2	18.70	
Zn^{2+}	0.74	8.42 ± 0.09	3.19	11.22	16.44	
Cd^{2+}	1.10	11.07 ± 0.03	5.25	8.99	16.36	
Pb^{2+}	1.29	13.55 ± 0.06	6.90		17.88	6.5
La^{3+}	1.160	12.21 ± 0.13	6.18	7.04	15.46	3.29
Ce^{3+}	1.143	12.23 ± 0.04		7.48	15.94	3.57
Pr^{3+}	1.126	12.22 ± 0.06		7.84	16.36	2.63
Nd^{3+}	1.109	12.21 ± 0.06		8.06	16.56	2.44
Sm^{3+}	1.079	12.12 ± 0.04		8.28	17.10	2.03
Eu^{3+}	1.066	12.02 ± 0.10		8.38	17.32	1.84
Gd^{3+}	1.053	11.93 ± 0.09		8.13	17.35	1.32
Tb^{3+}	1.040	11.70 ± 0.06		8.18	17.92	
Dy^{3+}	1.027	11.57 ± 0.04		8.31	18.28	
Ho^{3+}	1.015	11.18 ± 0.10		8.42	18.60	
Er^{3+}	1.004	11.30 ± 0.08		8.59	18.83	
Tm^{3+}	0.994	11.10 ± 0.02		8.75	19.30	
Yb^{3+}	0.985	10.90 ± 0.04		8.93	19.48	
Lu^{3+}	0.977	10.84 ± 0.02		9.09	19.80	

[a] $K_{ML}{}^M = [ML]/[M][L]$; ionic strength = 0.10; 25.0 ± 0.1 °C. [b] Data taken from ref 20. Coordination numbers are assumed to be 8 except for the case of Cu^{2+}, Ni^{2+}, and Zn^{2+} ions where 6 is assumed. [c] Data taken from ref 25 and 38. [d] Data taken from ref 27. [e] Data taken from ref 14 and 15.

complexation reactions for these six metal ions are best described by

$$M^{n+} + H_2L \rightleftarrows ML^{(n-2)+} + 2H^+ \qquad (1)$$

For all lanthanide ions as well as Cu(II), Cd(II), and Pb(II) ions, the stability of complex formation is greater so that the following reaction occurs:

$$M^{n+} + H_3L^+ \rightleftarrows ML^{(n-2)+} + 3H^+ \qquad (2)$$

This is demonstrated by the calculated average protonation number, $\bar{h}$, defined by eq 3.[24]

$$\bar{h} = (\text{total dissociable } [H^+] \text{ bound to ligand species})/(\text{total } [L]) \qquad (3)$$

For those ions involved in eq 2, $\bar{h}$ is always less than 2, even when no base was added. Because the complexation process must expel the two nitrogen protons from the ligand, the fact that $\bar{h} < 2$ would mean that complexation indeed occurred before any base was added. Table I lists the calculated log K values for the metal ions chosen for study together with those ligands of interest. In all cases, besides the dacda complexation, coordination of water by the final complex is not observed as noted by the absence of an inflection point corresponding to the water deprotonation.

From the values of the complex formation constants, the metals can be roughly classified into four groups. The first group includes monovalent alkali metal ions (e.g. K^+) for which the complex formations are weak but measurable.

The second group includes divalent alkaline earth metal ions (e.g. Ca^{2+}, Sr^{2+}, and Ba^{2+}) and some transition metal ions (e.g. Ni^{2+} and Zn^{2+}) that form complexes with the ligand of intermediate stability. It is interesting to observe that, for the first time, calcium, strontium, barium, nickel, and zinc all possess similar formation constants with the same ligand. A progressively slight drop of log K values for the Ca–Sr–Ba series may be related to the increase in ionic radii as well as the decrease of the charge density as the atomic number increases. On the other hand, the stabilities of the nickel and zinc complexes are mainly due to the covalent bond formation with the two nitrogen atoms. Inversion of the Irving–Williams series is also evident for Ni^{2+} and Zn^{2+} complexes.[25,26] This is not unexpected because for the smaller ions such as Ni^{2+} and Zn^{2+} with ionic radii 0.69 and 0.74 Å, respectively, special conformational changes have to be achieved in order for the ligand to complex the metal and to result in a stable configuration. It is very likely that the final zinc complex is tetrahedral and the nickel complex is either 5- or 6-coordinated. It could be that it is easier for the ligand to achieve a tetrahedral structure to fit zinc, which would give a more stable complex.

The third group includes all the lanthanide ions that form rather strong complexes with the ligand. Several observations are noted here. For the first time in aqueous solution for a multidentate ligand, the stability constants for the lighter seven lanthanides (La → Gd) are similar and they drop slightly for the heavier seven (Gd → Lu). This trend is in contrast to those classical multidentate ligands such as ethylenediaminetetraacetic acid whose lanthanide complex stability constants increase from lanthanum to lutetium due to the increase of charge density of the metal ions. Due to the presence of the macrocycle ring, both the charge density and the ionic radius

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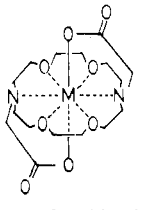

Figure 3. Possible structures of M(dacda), M = Pb^{2+} or La^{3+}.

of the metal have to be considered in order to rationalize the strength of complex formation. The lanthanum ion with a greater ionic radius fits better into the ligand cavity, but the lower charge density slightly offsets the advantage. On the other hand, samarium with a smaller ionic radius obtains its formation strength by having a greater charge density. After gadolinium, it seems that the disadvantage in complex formation due to the decrease in ionic radius cannot be compensated for by having a larger charge density; thus, the log K values drop.

The last (fourth) group includes copper(II), cadmium(II), and lead(II) ions. Lead(II) in many cases has been reported to have rather strong binding with both classical ligands as well as crown ethers and cryptands.[25,27,28] Unusual selectivity in lead transport by some crown ethers has been explained partially according to the thermodynamic stabilities of their complexes.[29] It turns out that lead, cadmium, and mercury are all very toxic metal ions and their complexation properties are similar, i.e., all bind strongly with nitrogen and carboxylic acid donors. It should be possible for detoxification using dacda by selectively separating each of the three ions from the others. The unusual stability of the copper(II) complex seems to be associated with its high enthalpy change for the copper–nitrogen bonding. However, because copper is rather small compared to the cavity of the ligand, it is highly probable that the chelate structure is quite different from those of other ions. Without diacetate derivatization, the copper(II)–kryptofix 22 complex is slightly less stable than that of the lead(II) ion,[25] which may indicate that the two acetate arms reinforce the chelate ring formation for both ions but more so for the copper(II) ion.

The published structure of [Cu(dacda)] exhibits that the Cu atom is coordinated to the two ring N atoms and the two O atoms of the two acetic acid moieties in a trans square-planar configuration.[30] In addition, the crown-ether O atoms on either side of the coordination plane are weakly bonded to the Cu atom, making an overall elongated octahedral structure. This is somewhat similar to the coordination geometry of the dichloro complex of copper(II)–kryptofix 22.[31] Thus, the extraordinary stability of the Cu–dacda complex is attributable to the ability of the ligand to form an elongated octahedral coordination. On the other hand, the structures for cadmium(II), lead(II), and lanthanide(III) complexes are very likely hexagonal bipyramidal on the basis of the structures previously determined by X-ray crystallography[32–34] or other means[35] (Figure 3).

Selectivities of Lanthanide Complexes. Comparison of the formation constants of the ligand dacda with those of edda (ethylenediamine-*N*,*N′*-diacetate ion) and edta (ethylenediamine-*N*,*N*,*N′*,*N′*-tetraacetate ion) for various metal ions indicates that (1) edta cannot differentiate among most transition metals, post transition metals, and lanthanide ions because most of these metal ions possess similarly large stability constants, (2) edda favors transition metal ions rather than lanthanide ions, and (3) the ligand dacda, in general, favors lanthanide ions rather than transition metals or alkaline earth metals. Specifically, given similar ligand donating atoms for dacda and edda (the ether oxygens have a very weak ligand field strength in aqueous solution and thus contribute much less toward the metal–ligand heat of formation), the stabilities of lanthanide complexes are at least 2–4 orders of magnitude greater for dacda than for edda. In contrast, the stabilities of transition metal complexes of dacda are 2–3 orders of magnitude less than those of edda.

The stability constants of dacoda (1,5-diazacyclooctane-*N*,*N′*-diacetate) with some transition metal ions have been determined.[36] With the eight-membered backbone cyclic ring, the Ni(II) metal complex of dacoda is forced to be 5-coordinated, square pyramidal in structure[37] and the log K value drops to 10.3 in comparison with that of its structural analogue edda. However, the log K value of Cu(II) with dacoda is 18.6, which is 2 orders of magnitude greater than that of edda. Thus, the adjustment of the backbone ring conformation of the ligand is very important in order to achieve certain selectivities toward metal ions.

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