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冠醚的空腔及其与希土硝酸盐配合物结构的关系

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本文计算了五十多种希土硝酸盐冠醚配合物中冠醚的空腔直径 D_c 及希土离子直径(D_i)与 D_c 之比值(D_i/D_c)．冠醚的空腔受许多因素影响，诸如希土元素的离子半径，希土离子与冠醚之间的结合力，冠醚环上的取代基等．D_i/D_c 数值所处的范围与所形成的配合物结构类型密切相关，遵循下列四个近似规则：(1) 如 $D_i/D_c>1.4$，所形成的配合物结构中三个阴离子占据冠醚的同一侧（结构类型Ⅰ)；(2) 若 $0.8<D_i/D_c<0.9$，配合物中金属离子被包围在冠醚空腔中，三个阴离子占据冠醚环的两侧（结构类型Ⅱ)；(3) 如 $D_i/D_c<0.8$，配合物中冠醚分子一般与配位水分子以氢键相连（结构类型Ⅲ)；(4) 若 $0.9<D_i/D_c<1.4$，配合物一般为结构类型Ⅲ，在某些情况下也可为结构类型Ⅳ，它由几个配位阴离子及一个多硝酸根配阴离子形成．

关键词：　冠醚腔径　D_i/D_c 比值　计算　近似规则

CAVITY OF THE CROWN ETHER AND ITS RELATIONSHIP WITH THE STRUCTURE OF RARE EARTH NITRATE COMPLEXES

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Cavity diameters of the crown ether (D_c) and ratios of rare earth ionic diameter (D_i) to D_c (D_i/D_c) for over fifty rare earth nitrate complexes have been calculated. The crown cavity is affected by many factors, such as the ionic radius of the rare earth element, the bonding force between the crown ligand and the RE(Ⅲ) ion, the substitutes on the crown ring, et al. The range of the D_i/D_c value is closely related to the type of complex formed. Four approximate rules hold: (1) if $D_i/D_c>1.4$, the complex formed has a structure in which three anions occupy the same side of the crown ether (struct. type I); (2) if $0.8<D_i/D_c<0.9$, the metal ion in the complex isolated is most possibly encapsulated in the crown cavity with three anions residing on the two opposite sides of the crown ether (struct. type Ⅱ); (3) if $D_i/D_c<0.8$, the crown ligand in the complex is probably hydrogen bonded with the coordinated water molecules (struct. type Ⅲ); (4) if $0.9<D_i/D_c<1.4$, the structure of complex generally belongs to struct. type Ⅲ, in

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some cases it can be of struct. type Ⅳ which is composed of complex cations and a polynitrato anionic species.

Keywords: **crown ether cavity diameter** **D_i / D_c ratio** **calculation** **approximate rule**

Introduction

Rare earth crown ether complexes are of special intersct to chemists because they display various metal / ligand (M / L) ratios and a number of unusual structures. For the lanthanide nitrate complexes, M / L ratios of 1 : 1, 1 : 2, 2 : 1, 2 : 3, 3 : 2 and 4 : 3 have been reported [1]. These complexes generally belong to four types of structures which are shown in Figs. 1,2,3 and 4 respectively [2-4]. In 1987, an approximate rule was put forward by Bunzli which delt with the relation between D_i / D_c and M / L ratio [1]. However, due to the negligence of the facts that the cavity diameter (D_i) of a crown ether may change along the lanthanide contraction and complexes with a same M / L ratio may have various types of structures as well as the inadaquate structure data available, his rule could not fully rationalize the relation between D_i / D_c and the composition of complexes. We think the M / L ratio and the structure of complexes depend on many factors. By studying over 30 crystal structures of rare earth nitrate complexes with the crown ethers recently accomplished in our laboratory and related structures in literatures, we have calculated cavity diameters of the crown ethers in their complexes (D_c), studied the factors that affect the crown cavity and rationalized several approximate rules that govern the relation between D_i / D_c ratios and the structural types of lanthanide nitrate complexes.

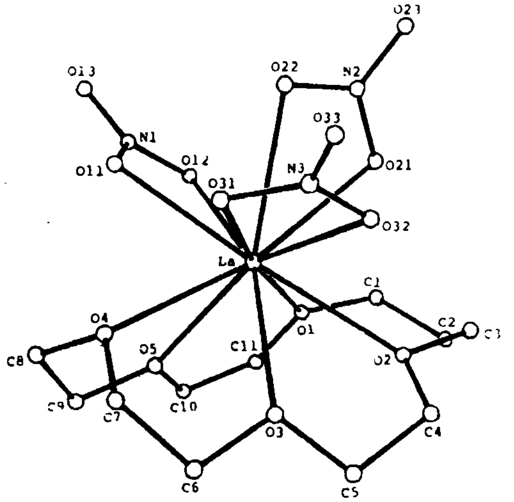

Fig.1 Structure of $La(NO_3)_3(16C5)$
(struct. type Ⅰ)

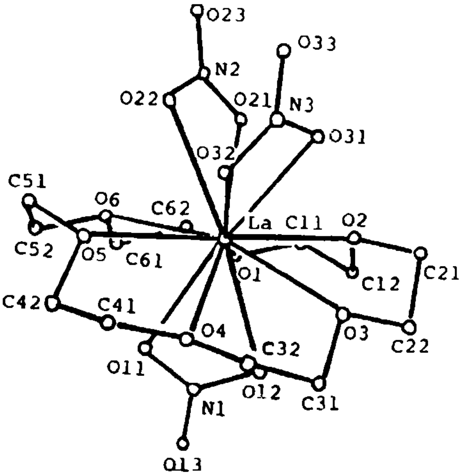

Fig.2 Structure of $La(NO_3)_3(18C6)$
(struct. type Ⅱ)

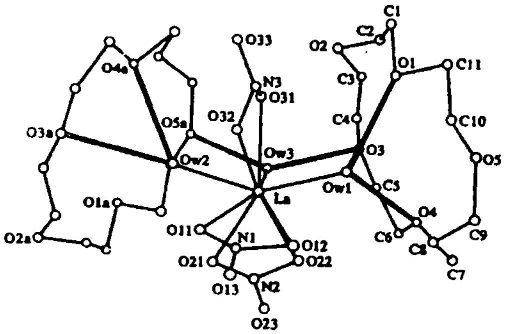

Fig.3 Structure of $[Lu(NO_3)_3(H_2O)_3]$ (16C5) (struct. type Ⅲ)

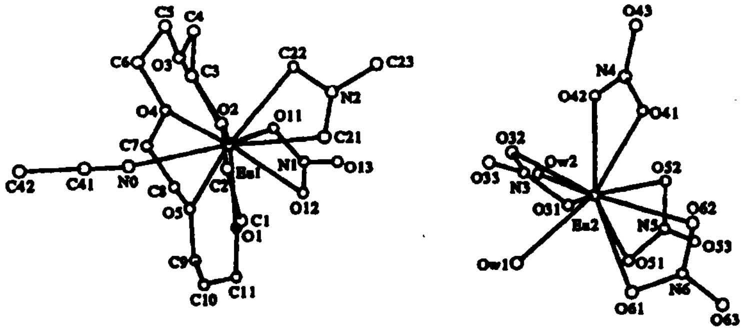

Fig.4 Structure of $[Eu(NO_3)_4(H_2O)_2][Eu(NO_3)_2(16C5)(MeCN)]$ (struct. type Ⅳ)

Theoretical Calculation

The cavity diameter of a crown ether various from one complex to another due to numerous conformations it may adopt. Most values of D_c in literatures were calculated from molecular models, thus they only have limited application to rare earth complexes. All our results were based on crystal structures of crown ethers or their complexes. D_c is calculated by the following equation:

$$D_c = \sum_{i=1}^{n}[(Dab)_i - (Ra)_i - (Rb)_i]$$

where Dab—the separation of the two non-adjacent coordination atoms a and b(for 12 or 15-membered crowns), or the distance between two coordination atoms on the crown ring of the opposite position (for 18-membered crowns).

Ra, Rb—van der Waals radius of the coordination atom, n—number of Dab.

In calculation of D_i / D_c , for struct. type Ⅰ and Ⅱ D_c is the cavity diameter of crown-coordinated complex. For struct. type Ⅲ it is the average value of crown-coordinated complexes.

Results and Discussion

1.The effect of rare earth ionic radius on the crown cavity

In the process of the interaction between rare earth ions and the crown ethers the values of D_c for isostructural complexes change along the lanthanide series and have a tendency to decrease, as indicated by Table 1. For rare earth nitrate complexes with 12–crown–4, D_c for La complex is 1.05 Å, it decreases to 0.93 Å for Yb complex.

Table 1 D_c(Å) of 12–Crown–4 in Its Complexes with Lanthanide Nitrates

RE	La	Pr	Nd	Sm	Eu	Y	Yb
D_c	1.05	0.95	0.96	0.95	1.02	0.88	0.93

Table 2 D_c(Å) of B12C4 and Cy12C4 in Their Complexes with $Ln(NO_3)_3$

Ln–B12C4	La	Ce	Nd	Gd	Lu	Ln–Cy12C4	La	Eu	Lu
D_c	0.97	0.95	0.92	0.87	0.87	D_c	1.28	1.02	0.96

For benzo substituted B12C4, because of electron–withdrawing effect of the substituent and greater rigidity of the ligand, its D_c changes very small within the lanthanide series. The difference between La and Lu complexes is only 0.10 Å (see Table 2). The cyclohexyl substituted Cy12C4 has much greater flexibility than B12C4, its D_c significantly decreases from La to Lu complexes. The difference reaches 0.32 Å.

From above discussion , it was found that the cavity of the crown ether changes with the ionic radius of the rare earth element, which was similar to "self–assembling" in biological system.

2. The effect of bonding force between crown ether and the metal ion on the crown cavity

Crown ether molecules in their rare earth complexes may coordinate to the metal ions or form hydrogen bonds with coordination water molecules, in some compounds they are held in the lattice by weak molecular interaction. From Table 3 we can see that these forces have a dramatic effect on the crown cavity. For example, 18–crown–6 has an average D_c of 2.33 Å when it coordinates to the RE(Ⅲ) ions [4-6] . It changes to 2.75 Å in hydrogen bonded complexes $[RE(NO_3)_3(H_2O)_n]$. 18–crown–6 [7] and reaches 2.91 Å when the interaction is much weaker van der Waals force as in [18–crown–6 • 2MeCN]. These different D_c values are clearly related to the different conformations of the crown ligand under various bonding forces.

Table 3 D_c(Å) of Crown Ethers under Various Interaction

	ion–dipole interaction	hydrogen bond	van der Waals force
18C6	2.33	2.75	2.88
B15C5	1.34	1.56	1.73
12C4	0.96	1.09	1.43
15C5	1.40	1.59	
16C5	1.49	2.01	
[2,2]	2.35	2.67	2.84

3.The effect of nitrate group rearrangement on the crown D_c

Another important phenomenon of rare earth crown ether complexes is that the reaction of

$Ln(NO_3)_3 \cdot nH_2O$ with some crown ether molecules can result in the rearrangement of nitrate groups and formation of complexed cation and polynitrato anionic species. Four types of rearrangement, 6∶2, 5∶2, 5∶1 and 4∶2 have been reported, as in the following reactions[8-10,5]:

$Eu(NO_3)_3 + 18C6 \longrightarrow [Eu(NO_3)_6][Eu(NO_3)_2(18C6)]_3$

$La(NO_3)_3 + Cy_218C6 \longrightarrow [La(NO_3)_5][La(NO_3)_2(Cy_218C6)]_2$

$Eu(NO_3)_3 + [2,2,2] \longrightarrow [Eu(NO_3)_5(H_2O)][Eu(NO_3)[2,2,2]]$

$Eu(NO_3)_3 + 16C5 \longrightarrow [Eu(NO_3)_4(H_2O)_2][Eu(NO_3)_2(16C5)(MeCN)]$

The formation of complexed cations decreases the coordination number of RE(Ⅲ) ion and weakens the steric interaction, thus the crown ligands have greater flexibility than that of normal complexes as illustrated by the data in Table 4.

Table 4 D_c(Å) of Complexed Cations and Corresponding Normal Complexes

normal complex	D_c	complexed cation	D_c
$Ln(NO_3)_3(18C6)$	2.47	$[Ln(NO_3)_2(18C6)]^+$	2.13
$Ln(NO_3)_3[2,2]$	2.40	$[Eu(NO_3)_2[2,2]]^+$	2.18
$La(NO_3)_3(16C5)$	1.40	$[Eu(NO_3)_2(16C5)(MeCN)]^+$	1.58

4.The effect of substituent on the crown nitrogen atom on the D_c

The D_c values for [2,2] in $La(NO_3)_3[2,2]$[11], $La(NO_3)_3(L_1)$ (L_1 = N-trizolemethyl-[2,2]) and $La(NO_3)_3(L_2)$ (L_2 = N,N-bis(benzotrizolemethyl)-[2,2]) are 2.42, 2.51 and 2.57Å respectively, which indicates that the crown cavity enlarges with the increasing number of the substitute groups. This may result from the reduction of electron density on the nitrogen atoms and weakening of the Ln(Ⅲ)/crown interaction.

5. The relationship between D_i/D_c ratios and structures of complexes

We discuss mainly complexes of struct. type Ⅰ, Ⅱ and Ⅲ. D_i/D_c ratios for these complexes are listed in Tables 5, 6 and 7 respectively. From these data four approximate rules can be rationalized:

a. if $D_i/D_c > 1.4$, the complexes formed generally belong to struct. type Ⅰ;

b. if D_i/D_c is in the range of 0.8 to 0.9, complexes of struct. type Ⅱ could be isolated;

c. if $D_i/D_c < 0.8$, the crown ether in its complexes is most propably hydrogen-bonded with the metal-coordinated water molecules (struct. type Ⅲ);

d. if $0.9 < D_i/D_c < 1.4$, the structure of complex isolated can be either type Ⅲ or type Ⅳ.

Table 5 D_i/D_c Data for Complexes of Struct. Type Ⅰ

complex	D_i/D_c	complex	D_i/D_c
$La(NO_3)_3(12C4)(H_2O)$	2.02	$Eu(NO_3)_3(Cy12C4)$	1.86
$Pr(NO_3)_3(12C4)$	2.13	$Lu(NO_3)_3(Cy12C4)$	1.77
$Nd(NO_3)_3(12C4)$	2.07	$La(NO_3)_3(B15C5)$	1.61
$Sm(NO_3)_3(12C4)$	2.02	$Pr(NO_3)_3(B15C5)$	1.50
$Eu(NO_3)_3(12C4)$	1.86	$Sm(NO_3)_3(B15C5)$	1.46
$Y(NO_3)_3(12C4)$	2.00	$Gd(NO_3)_3(B15C5)$	1.39
$Yb(NO_3)_3(12C4)$	1.84	$La(NO_3)_3(15C5)$	1.57
$La(NO_3)_3(B12C4)(H_2O)$	2.19	$Ce(NO_3)_3(15C5)$	1.48
$Pr(NO_3)_3(B12C4)$	2.25	$Pr(NO_3)_3(15C5)$	1.41
$Gd(NO_3)_3(B12C4)$	2.17	$Nd(NO_3)_3(15C5)$	1.46
$Lu(NO_3)_3(B12C4)$	1.95	$La(NO_3)_3(16C5)$	1.52
$La(NO_3)_3(Cy12C4)$	1.66	$La(NO_3)_3(Me_216C5)$	1.51
$Pr(NO_3)_3(Me_216C5)$	1.43		

Table 6 D_i/D_c Data for Complexes of Struct. Type Ⅱ

complex	D_i/D_c
$La(NO_3)_3(18C6)$	0.86
$Ce(NO_3)_3(18C6)$	0.82
$Nd(NO_3)_3(18C6)$	0.82
$La(NO_3)_3[2,2]$	0.83
$Ce(NO_3)_3[2,2]$	0.83
$Pr(NO_3)_3[2,2]$	0.80
$Nd(NO_3)_3[2,2]$	0.79
$La(NO_3)_3(L_1)$	0.85
$La(NO_3)_3(L_2)$	0.83

Table 7 D_i/D_c Data for Complexes of Struct. Type Ⅲ

complex	D_i/D_c
$[Eu(NO_3)_3(H_2O)_3]\cdot(15C5)$	1.36
$[Sc(NO_3)_3(H_2O)_2]\cdot(15C5)$	0.97
$[Lu(NO_3)_3(H_2O)_2(MeCN)]\cdot(15C5)$	0.97
$[Lu(NO_3)_3(H_2O)_3]\cdot(16C5)$	1.27
$[Gd(NO_3)_3(H_2O)_3]\cdot(18C6)$	0.79
$[Sc(NO_3)_3(H_2O)_3]\cdot(18C6)$	0.58
$[Lu(NO_3)_3(H_2O)_3]\cdot(18C6)$	0.73

These rules may be illustrated by the characteristics of each type of complex. The rare earth ion is larger than the crown cavity in complex of struct. type Ⅰ, it resides above the crown plane and forms a pyramid with crwon oxygen atoms, thus $D_i/D_c > 1.4$ is desirable. When D_i/D_c is in the range of 0.8 to 0.9, D_i is slightly smaller than D_c, so the RE(Ⅲ) ion can be encapsulated in the crown cavity by ion–dipole interaction. If $D_i/D_c < 0.8$, the rare earth ion is too small to fit the crown cavity, struct. type Ⅱ would be unstable, however complex of struct. type Ⅲ can be formed due to the stabilizing effects of polymeric hydrogen bonding chains or networks. Complexes of struct. type Ⅰ or Ⅱ are uneasy to form if D_i/D_c is in the range of 0.9 to 1.4 due to strong steric interaction. Struct. type Ⅲ are able to form under this circumstance (see Table 4). Complexes of struct. type Ⅳ may also be crystallized for the formation of complexed cation can reduce the coordination number of the metal ion and decrease the steric crowding, for example, D_i/D_c in complex cation $[Eu(NO_3)_2(16C5)(MeCN)]^+$ is 1.20.

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