

Study on the Intramolecular Aromatic-Ring Stacking Interaction in the Ternary Calcium Complexes (VII)

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Abstract : The stability constants of the ternary mixed-ligand complexes of $\text{Ca}(\text{NTP})(\text{HRB})^n$ ($n = 2$ or 3) have been determined by potentiometric pH titration in aqueous solution ($I = 0.1 \text{ mol/L}$ KNO_3 ; 25°C) , where NTP refers to adenosine 5'-triphosphate (ATP) and uridine 5'-triphosphate (UTP) ; HRB refers to 1,10-phenanthroline (phen) , 2,2'-bipyridyl (bpy) , and L-tryptophane (trp) . The stability difference between the ternary complexes and the binary complexes has been compared and discussed. The increased stability in the ternary mixed-ligand complexes was attributed to the cooperative effect of $\pi_A - \pi_B$ and the intramolecular ligand-ligand aromatic-ring stacking interaction. The extent of the intramolecular aromatic-ring stacking interaction in the ternary calcium complexes was calculated , which is in accord with the size of the aromatic rings forming stacks.

Key words ternary mixed-ligand complex ; calcium ; nucleotide ; aromatic-ring stacking

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0 Introduction

The intramolecular ligand-ligand interaction in the ternary complexes have received considerable attention in recent years^[1]. The study on this field has been extended to a large amount of ligands such as nucleotides , xanthosines , amino acids , a series of aromatic carboxylic acids and so on^[2-5]. It is also relevant to medical effects in biological system^[6]. Because nucleotides are the essential substances in energy transferring in living things , more and more bioinorganic chemists have been attracted to the study on stacking interaction and one review has been given out recently^[1]. The aromatic-ring stacking interactions among the ternary complexes of nucleotides with $\text{Cu}(\text{II})$, $\text{Zr}(\text{II})$, and $\text{Mg}(\text{II})$ have been studied^[3]. Similar stacking also exists in the ternary mixed-ligand complexes composed of calcium(II) and it seems to more practicable because of important roles of calcium in biological systems. The author studied the ternary calcium-heterocyclic ring base HRB(HRB refers to 1,10-phenanthroline (phen) , 2,2'-bipyridyl (bpy) , and DL-tryptophane (trp))-nucleotides NTP(NTP are adenosine 5'-triphosphate and uridine 5'-triphosphate) systems. Their stability constants of the binary and ternary complexes have been determined and the percentages of the stacked isomers in the ternary mixed-ligand $\text{Ca}(\text{HRB})(\text{ATP})^n$

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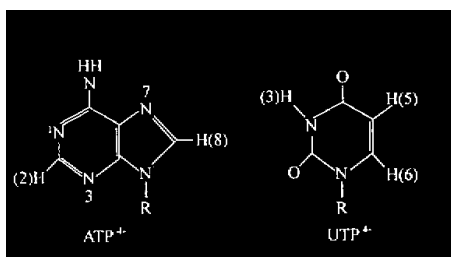
complexes have been calculated.

1 Experimental

The disodium salt of adenosine 5'-triphosphate($\text{Na}_2\text{H}_2\text{ATP}\cdot 3\text{H}_2\text{O}$) and trisodium salt of uridine 5'-triphosphate($\text{Na}_3\text{HUTP}\cdot 2\text{H}_2\text{O}$) were purchased from Sigma Chemical Co. of USA. $\text{Ca}(\text{NO}_3)_2$, phen, bpy, and trp were all of A.R. grade from Shanghai Factory of Chemical Reagent. The concentration of the solution of HRB was measured by accurate weighing. Caborate-free sodium hydroxide as standard solution was measured with potassium hydrogenphathlate. The concentration of the stock solution of $\text{Ca}(\text{NO}_3)_2$ was determined with EDTA. The stock solution of NTP was always freshly prepared. The exact concentration of NTP solution was analysed by potentiometric pH titration with standard solution of sodium hydroxide. The pH titrations were carried out with a pHS-3c meter made in Shanghai Factory of Analytical Instrument with an accuracy of $\pm 0.02\text{pH}$. The pH meter accompanied with glass electrodes was calibrated with standard buffer solutions before and after each titration. Both the determination of pH and calibration were carried out in the double-layer titrating-cell at a constant temperature of $(25 \pm 0.1)^\circ\text{C}$ under an atmosphere purified with N_2 . Ionic strength was adjusted to 0.1 mol/L with KNO_3 . All the experiments were carried out as described in detail recently^[7]. All of dissociation constants of NTP and the stability constants of the binary and ternary complexes were measured by at least three independent titrations.

2 Results and discussion

The molecular structures of Ligands ATP and UTP are shown in Figure 1.



R = ribosyl 5'-triphosphate

Fig.1 Molecular structure of nucleotide
 ATP^{4-} and UTP^{4-}

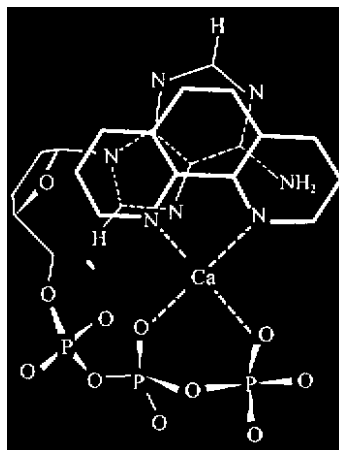


Fig.2 The simplified structure of stacked
isomer of $\text{Ca}(\text{phen})(\text{ATP})^{3-}$

The negative logarithms of dissociation constants $\text{p}K_{\text{H}_2\text{NTP}}^{\text{H}}$ and $\text{p}K_{\text{HNTP}}^{\text{H}}$, the stability constants of the binary $\text{Ca}(\text{NTP})^{2-}$ and the ternary $\text{Ca}(\text{NTP})(\text{HRB})^{0-}$ complexes, and the values of $\Delta\log K$ are presented in Table 1.

**Table 1 The dissociation constants of NTP and the stability constants
of binary complexes $\text{Ca}(\text{NTP})^{2-}$ and ternary complexes $\text{Ca}(\text{HRB})(\text{NTP})^{2-}$
in aqueous solution ($I = 0.1 \text{ mol/L}$, KNO_3 , 25°C)**

NTP	$\text{p}K_{\text{H}_2\text{NTP}}^{\text{H}}$	$\text{p}K_{\text{HNTP}}^{\text{H}}$	$\log K_{\text{Ca}(\text{NTP})}^{\text{Ca}}$	HRB	$\log K_{\text{Ca}(\text{HRB})(\text{NTP})}^{\text{Ca}(\text{HRB})}$	$\Delta\log K_{\text{Ca}}$
ATP	4.05	6.40	3.56	phen	4.20	+ 0.64
				bpy	3.75	+ 0.19
				trp	3.28	- 0.28
UTP	2.03	6.38	3.24	phen	3.62	+ 0.38
				bpy	3.44	+ 0.20
				trp	3.18	- 0.06

The common way to characterize the stability of the ternary mixed-ligand complexes of this kind here is $\Delta\log K_{\text{Ca}}$ obtained by the equation

$$\Delta\log K_{\text{Ca}} = \log K_{\text{Ca}(\text{HRB})(\text{NTP})}^{\text{Ca}(\text{HRB})} - \log K_{\text{Ca}(\text{NTP})}^{\text{Ca}}.$$

In general , $\Delta\log K_{\text{Ca}}$ is a negative value since there are more coordination sites in the binary complexes than those in the ternary complexes. The statistical value for the coordination of the two different bidentate ligands to a octahedral coordination sphere is $\Delta\log K_{\text{st}} = - 0.4^{[8]}$. It is obvious that many of these values of $\text{Ca}(\text{HRB})(\text{NTP})^{2-}$ in Table 1 are larger than expected on statistical grounds , even on the coordination of complexes with trp. This increasing stability is partly explained by $\pi_{\text{A}}-\pi_{\text{B}}$ cooperative effect^[8] by transference of π -electron on oxygen atom of NTP to empty π orbital of electron-acceptor HRB when both ligand HRB and NTP were coordinated to Ca^{2+} . Another reason for the increasing stability of the ternary complexes is the suitable aromatic-ring stacking interaction between ligand HRB and ligand NTP. It is reasonable that the stacking interaction is carried out as follows :



where K_{exp} is the equilibrium constant corresponding to Eq.(1)determined by experiments. The footnotes ‘ op ’ and ‘ st ’ stand for the species of open and stacked isomers of the ternary complexes respectively. The footnote ‘ tot ’ is the sum of the two above. K_1 is the equilibrium constants of Eq.(2)which shows the forming tendency of the stacked isomer. K_1 and % st can be calculated according to ref.[9].

$$K_1 = K_{\text{exp}}/K_{\text{op}} - 1 = 10^{\Delta\log K_{\text{exp}}}/10^{\Delta\log K_{\text{op}}} - 1 = 10^{\Delta\Delta\log K} - 1 \tag{3}$$

and

$$\% \text{ st} = [\text{Ca}(\text{HRB})(\text{NTP})_{\text{st}}^{2-}] / [\text{Ca}(\text{HRB})(\text{NTP})_{\text{tot}}^{2-}] = K_1 / (1 + K_1) \tag{4}$$

Though the absolute value of the dimensionless constant K_1 could not be known so for , we can assume that in the solution of the ternary $\text{Ca}(\text{HRB})(\text{UTP})^{2-}$ complexes in the Ca/HRB/UTP systems no stacked isomers were seen. Therefore the percentages of the stacked $\text{Ca}(\text{HRB})(\text{ATP})_{\text{st}}^{2-}$ isomers assembled in Table 2 were all relative values. However , it has influence neither on the existence of the stacking interaction nor on the correspondence with the order of stacking degree.

It can be seen from Table 2 that the extent of the stacked isomers of the ternary $\text{Ca}(\text{HRB})$

(ATP)ⁿ⁻ complexes increases in the order :
Ca(trp)(ATP)³⁻ < Ca(bpy)(ATP)³⁻
< Ca(phen)(ATP)³⁻ ,

which is in accordance with the order of the aromatic-ring size of ligands HRB forming stacks : trp(indole ring) < bpy(bipyridyl ring) < phen(phenanthroline ring). Thus it can be seen that in the ternary complexes the larger the size of aromatic-ring of ligands forming stacking , the more notable the intramolecular aromatic-ring stacking interaction and the higher the stability of the mixed-ligand complexes(Table 2). The simplified structure of the partly forming stacking between phen ring and purine ring of ATP in the complexes Ca(phen)(ATP)³⁻ is shown in Fig.2. The aromatic-ring stacking interaction is in essence an electron effect. Changes of resonance signal of proton on aromatic-ring before and after the stacking can be detected by means of study of ¹H NMR. Therefore the stacking interaction existing in the ternary complexes might be further expounded more powerfully. We will report the results in relation to this field later.

**Table 2 The values of K_1 and % st of the ternary
Ca(HRB)(ATP)_nⁿ⁻ complexes**

HRB	log K_{op}	log K_{exp}	$\Delta\Delta\log K$	K_1	% st
phen	3.62	4.20	0.58	2.80	74
bpy	3.44	3.75	0.31	1.04	51
trp	3.18	3.28	0.10	0.26	21

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三元钙配合物的分子内芳环堆积效应研究

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[摘要] pH 电位滴定法测定了 $\text{Ca}(\text{II})$ 与核苷酸 NTP (NTP 为腺苷 5'-三磷酸和尿苷 5'-三磷酸) 和另一芳环系列配体 HRB 形成的三元混配配合物 $\text{Ca}(\text{HRB})_n\text{NTP}^{n-}$ (HRB = phen , bpy 和 trp ; $n = 2$ 或 3) 在水溶液中的稳定常数 ($I = 0.1 \text{ mol/L}$, KNO_3 ; 25°C). 比较了二元和三元混配配合物的稳定性差异 , 认为三元混配配合物稳定性的增加可归因于 π -酸- π -碱之间的合作效应和分子内芳环配体的堆积作用 .

[关键词] 三元混配配合物 ; 钙 ; 核苷酸 ; 芳环堆积

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(上接 62 页)

Scattering of Transverse Plasma Wave by the Ultra-relativistic Electron

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Abstract : Not only the scattering probability of transverse plasma wave by the ultra-relativistic electron is given through calculation of Compton and nonlinear scattering , but also the scattering spectrum (approximate linear one) , the ratio ($2\gamma^2$) of the subsequent wave frequency to the incident one are obtained . The spectrum is different from that one of the inverse-Compton scattering of the unicolor ray by the ultra-relativistic electron in vacuum .

Key words : transverse plasma wave ; inverse-Compton scattering ; nonlinear scattering ; scattering probability

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