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Thermodynamic Stabilities of Ni(II), Cu(II), Co(II), Fe(III), AND U(II) Complexes of the Oximated Derivative of P-Tert-Butylcalix[6]Arene

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**THERMODYNAMIC STABILITIES OF Ni(II), Cu(II), Co(II),
Fe(III), AND U(II) COMPLEXES OF THE OXIMATED
DERIVATIVE OF P-TERT-BUTYLCALIX[6]ARENE**

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ABSTRACT

The stability constant ($\log K$) of Ni(II), Cu(II), Co(II), Fe(III) and U(II) complexes with the oximated derivative of p-tert-butylcalix[6]arene were determined at different ionic strengths (0.012, 0.023 and 0.032 M) and at different temperatures (20°, 24°, 28° and 32°C). For each metal-ligand system at each temperature, thermodynamic stability constant, $\log K^\circ$, was obtained graphically at zero ionic strength from the plot of $\log K$ vs ionic strength. The order of thermodynamic stability of the complexes is as follows: U(II) > Fe(III) > Ni(II) > Cu(II) > Co(II). The stability constants were found to be proportional with the ionic strength and inversely proportional to temperature. Thermodynamic parameters such as ΔH° , ΔS° were derived from the plot of $\log K^\circ$ vs T^{-1} and ΔG was calculated for each temperature. Based on the negative values of ΔG and ΔH° suggest that the metal-ligand interaction is exothermic.

INTRODUCTION

We aimed to determine the thermodynamic stabilities of some metal complexes of oximated derivative of p-tert-butylcalix[6]arene in this study. We used spectrophotometric method to determine the thermodynamic stability constant and other parameters. Calixarene esters exhibit high affinity of complex formation with metal cations [1-7]. Calixarene was prepared by applying standart procedure [8]. The tetraester of the calixarene was isolated by reacting calixarene with p-nitrobenzoyl chloride in a high yield [9]. The nitro groups of tetraester compound was reduced to tetraamino groups by $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and, tetrakis[(4-aminoglyoxime-benzoyl)oxy]-bis(dihydroxy)-p-tert-butylcalix[6]arene (abbreviated as $\text{I}_6\text{-(NH-VD)}_4$) was obtained by treating the macrocyclic compound with monochloroglyoxime.

EXPERIMENTAL

Instruments

Orion Model 720 pH/ISE meter, a Schimadzu UV-160 A spectrophotometer with 1.0 cm quartz constant-temperature cell holder and equipped with Julabo U3-7A circulator were used for the measurements in the experiments.

Reagents

$\text{I}_6\text{-(NH-VD)}_4$ was prepared as described in the literature [9]. A solution of $\text{I}_6\text{-(NH-VD)}_4$ was prepared in an 90:10 (v/v) acetone-water mixture. For each experiment a freshly prepared solution was used. Stock solution of metal chlorides of Cu(II), Co(II), Ni(II), Fe(III) and uranyl acetate were prepared in 75:25 (v/v) acetone- water and standardized according to the conventional methods. The acetic acid-sodium acetate buffer (0.2 M, pH 4.0) and 0.12 M KCl solution were prepared. The stock metal solutions of 0.05 M were prepared by diluting the standard solution with buffer. The stock solution of 75:25 (v/v) acetone-water was also prepared to be used as a solvent in

experiments. All the reagents were of analytical grade. Double distilled, CO₂-free water was used for all experiments.

Procedure

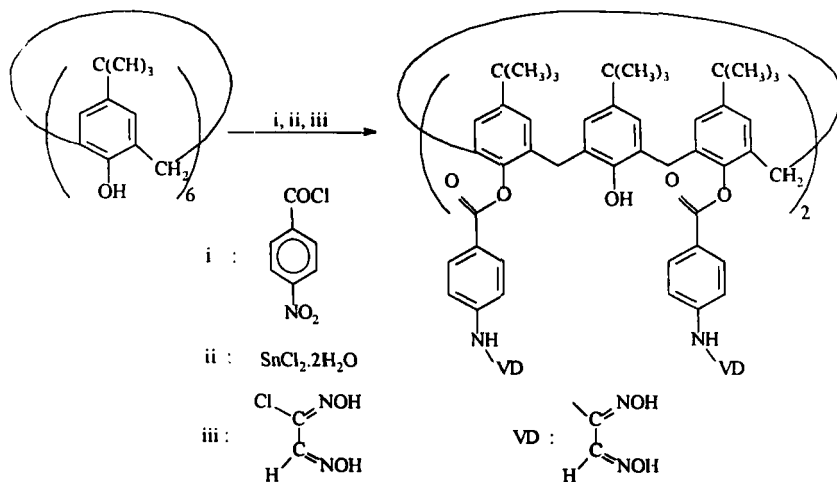
A spectrophotometer was used for absorbance measurements. Molar absorption coefficients and stability constants were determined as described below [10].

Determination of molar absorption coefficients: 0.5 mL of 0.05 M metal solution, X mL of 0.12 M KCl, and Y mL of 0.00475 M I₆-(NH-VD)₄ were pipetted into 25 mL volumetric flasks; where X=1 mL, X=2 mL and X=3 mL for each Y = 2.5, 5.0, 7.5 and 10.0 mL, respectively. Each flask was filled up to the mark with solvent. Then 1, 3, 5, 7 and 9 mL of each solution were pipetted into tubes and filled with solvent to a final volume of 10 mL. The mixtures were heated for 15 min. at 20 ± 0.1°C. 5 mL of each solution were transferred to the constant-temperature cell thermostated at 20 ± 0.1°C and the absorbance changes at peak wavelength of ligand were recorded and the molar absorption coefficients were calculated. The experiments were performed at various temperatures i.e. 24°, 28° and 32°C.

Determination of stability constants: 0.5 mL of 0.05 M metal solution, 1 mL of 0.12 M KCl, and Y mL of 0.00475 M I₆-(NH-VD)₄ were pipetted into 25 mL volumetric flasks (Y = 2.5, 5.0, 7.5 and 10.0 mL). Each flask was filled up to the mark with solvent and allowed to stand for 10 min. at 20 ± 0.1°C in the thermostatic bath. The absorbances were recorded in the same way as described for determination of ε. Each experiment was performed in triplicates. The experiments were performed at various ionic strengths (2 mL and 3 mL of 0.12 M KCl) and at various temperatures (24°, 28° and 32°C).

RESULTS AND DISCUSSION

The tetra ester of I₆ have been obtained by the action of p-nitrobenzoyl chloride as esterification agent on the lower rim of I₆ according to 1-methylimidazole procedure in CH₃CN for 30 min. at room temperature in



Scheme I

high yield as soon as 80-85% [9]. When $\text{I}_6\text{-(NO}_2)_4$ reacts $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in ethyl alcohol, tetranitro groups of tetraester reduced to tetraamino groups by refluxed for 4 h. The oximated derivatives of $\text{I}_6\text{-(NH}_2)_4$ obtained by monochloroglyoxime in CH_2Cl_2 at room temperature for 16-20 h (Scheme I).

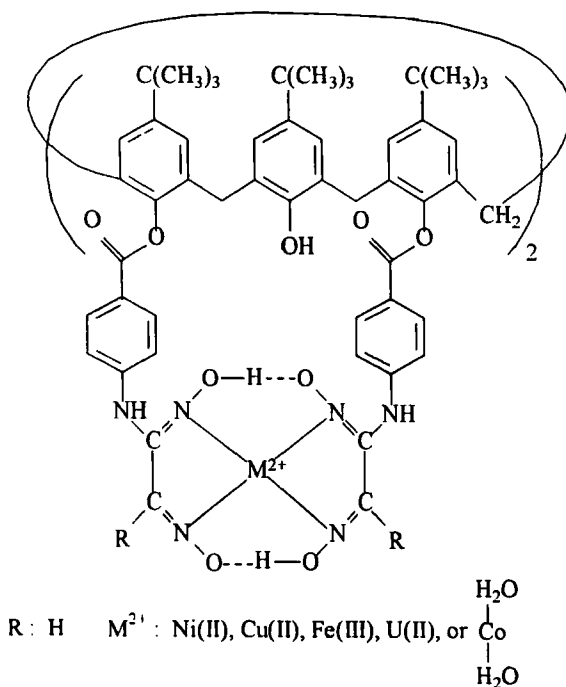
The complexes occur between two glyoxime groups and one metal ion (Scheme II). In each complex of macromolecular compounds the ligand-metal ratio is 1:1. This can be formulated as follows:



where M, L and ML represent the metal, the ligand and the complex, respectively. Stability constant is

$$K = \frac{[\text{ML}]}{[\text{L}][\text{M}]} = \frac{[\text{ML}]}{([\text{L}]_0 - [\text{ML}])([\text{M}]_0 - [\text{ML}])}$$

where $[\text{M}]_0$, $[\text{L}]_0$ are initial concentrations of the metal and ligand respectively.



Scheme II

If $[M]_0 \gg [L]_0 > [ML]$ and $[ML] = X$, then stability constant can be computed as follows:

$$K = \frac{X}{([L]_0 - X)([M]_0 - X)} \cong \frac{X}{[M]_0([L]_0 - X)}$$

$$K = \frac{X}{[M]_0[L]_0 - [M]_0 X}$$

$$K[M]_0[L]_0 = X(1 + K[M]_0)$$

$X = [L]_0 - [L]$ because of $[L] = [L]_0 - X$ and $[L]$ can be written as A/ϵ according to the Lambert-Beer law. finally, the relationship between A/ϵ and $[L]_0$ can be

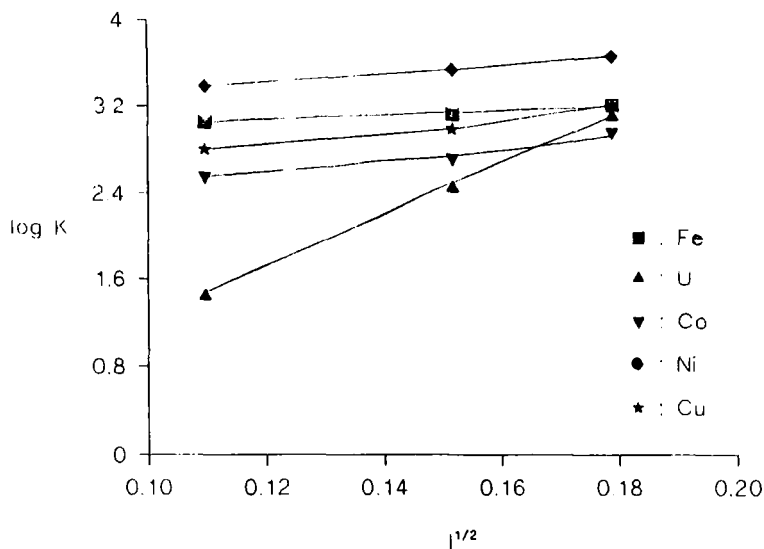


Figure 1 The plot of $\log K$ versus $I^{1/2}$ for each metal-ligand complex system.

written as follows:

$$\frac{A}{\varepsilon} = \frac{1}{1 + K [M]_0} [L]_0$$

For each temperature, the values of stability constants were determined from the slope of the curve plotted between A/ε and the initial concentrations of ligand, $[L]_0$. The average values of $\log K$ were then plotted as a function of ionic strength for complex systems, and the curves were extrapolated to zero ionic strength in order to obtain the thermodynamic stability constants ($\log K^\circ$) which was shown in Figure 1 (Table 1).

For each metal-ligand system at defined temperature, $\log K^\circ$ values were plotted against T^{-1} . For the calculation of the heat of complexation, the least

TABLE 1 Overall stability constants, log K, at different temperatures and ionic strengths (I, mol.dm⁻³) and thermodynamic parameters

Sistem	T °C	log K		
		I=0.012	I=0.023	I=0.032
Fe-L	20	3.051	3.123	3.210
	24	3.100	3.173	3.246
	28	3.162	3.226	3.289
	32	3.201	3.297	3.327
U-L	20	1.443	2.673	3.101
	24	2.436	2.692	3.218
	28	3.097	3.150	3.412
	32	4.421	3.540	3.789
Co-L	20	2.558	2.691	2.961
	24	2.611	2.732	3.041
	28	2.646	2.761	3.095
	32	2.715	2.816	3.201
Ni-L	20	3.486	3.418	3.664
	24	3.550	3.526	3.693
	28	3.605	3.507	3.710
	32	3.579	3.578	3.750
Cu-L	20	2.801	2.985	3.208
	24	2.812	3.083	3.370
	28	2.821	3.149	3.476
	32	2.835	3.279	3.691

square method was used for plotting $\log K^\circ$ versus T^{-1} to obtain a linear fit which was shown in Figure 2.

The slope was $\Delta H^\circ.R^{-1}$ [11,12]. $\Delta S^\circ.R^{-1}$ was determined by graphical extrapolation of the curves at intercept where $T^{-1} = 0$. The changes in free energy for each metal-ligand system were calculated from the equation $\Delta G = -2.303 RT \log K^\circ$. A program written in a QBASIC was used for all

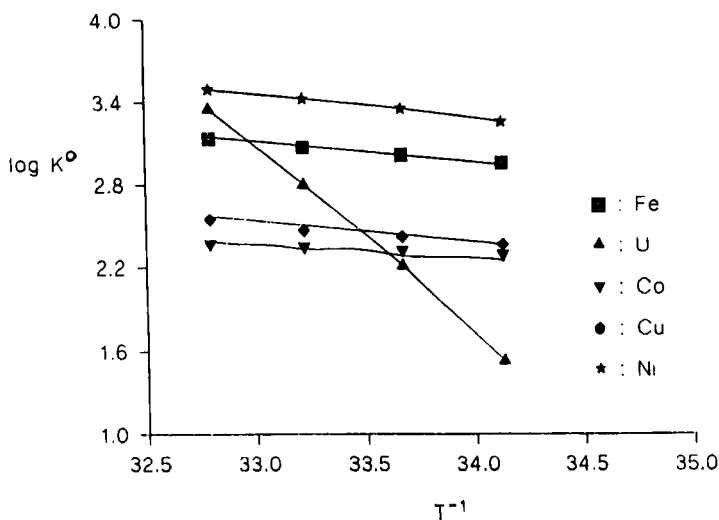


Figure 2. The plot of $\log K^\circ$ versus T^{-1} for each metal-ligand system at different temperature.

calculations at stability constants and thermodynamic parameters. The results were shown in Table 2.

Average values of overall stability constant of the metal-ligand complexes were found to be proportional to the ionic strength and inversely proportional to the temperature. In all cases the linear character of $\log K^\circ$ vs T^{-1} plots indicated that ΔC_p° values were equal to zero and independence of heat of complexation to temperature.

The negative values of ΔH° indicate the exothermic character of the metal-ligand interactions. Sufficiently large negative values of ΔG has also indicated the spontaneous formation of the complexes and the values followed the order of $U(II) > Fe(III) > Ni(II) > Cu(II) > Co(II)$ for metal ions. The highest value of the thermodynamic stability constant and ΔG was calculated for $U(II)$ complex of the large charge on the central metal atom.

TABLE 2 Some thermodynamic parameters of the metal-ligand complex systems.

Sistem	T, °C	log K ^o , l.mol ⁻¹	-ΔG ^o kJ mol ⁻¹	-ΔH ^o kJ mol ⁻¹	+ΔS ^o kJ mol ⁻¹ K ⁻¹
Fe-L	20	2.951	69.656	26.563	0.147
	24	3.010	70.244		
	28	3.084	70.832		
	32	3.132	71.420		
U-L	20	0.530	770.168	382.917	1.321
	24	1.921	775.452		
	28	2.876	780.736		
	32	3.178	786.021		
Co-L	20	2.293	36.914	12.055	0.0848
	24	2.323	37.253		
	28	2.342	37.593		
	32	2.380	37.932		
Ni-L	20	3.252	72.799	24.426	0.146
	24	3.408	67.810		
	28	3.381	68.394		
	32	3.450	68.978		
Cu-L	20	2.546	92.524	39.757	0.181
	24	2.467	93.244		
	28	2.419	93.964		
	32	2.314	94.684		

The spontaneous formation of the complex and the anionic complexed species of the ligand were further confirmed by the positive values of ΔS° . The positive entropy change for the present complexation reactions indicates that complexes are entropically favoured.

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