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Complexation Behavior of Guanine with Th^{4+}, UO_2^{2+}, and Ce^{3+} at Various Temperatures

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The complexation of guanine with Th^{4+}, UO_2^{2+}, and Ce^{3+} was investigated using the potentiometric method at a constant ionic strength of $I = 0.10$ mol·dm^{-3} (KCl) in aqueous solutions at elevated temperatures. For each metal ion, stability constants were obtained from the pH-metric data using the program HYPERQUAD2006. The formation of monomeric and polymeric species was taken into consideration for each ion at (25, 37, and 45) °C. The thermodynamic parameters for the formation of the guanine complexes were calculated. In conclusion, it is indicated that the values of the stability constants change at various temperatures.

Introduction

The metal complexes of the purine and pyrimidine bases play a dominant role in many biochemical systems. DNA (deoxyribonucleic acid) and RNA (ribonucleic acid), the most common nucleic acids, are found in all living cells. Nucleotides are monomers of nucleic acids. Guanine, a purine base found in both DNA and RNA, forms a derivative called guanosine, when combined with the sugar ribose. Guanosine can be phosphorylated with one to three phosphoric acid groups, yielding the three nucleotides GMP (guanosine monophosphate), GDP (guanosine diphosphate), and GTP (guanosine triphosphate). Of these phosphorylated structures, GTP acts as a coenzyme in carbohydrate metabolism and in the biosynthesis of proteins.[1]

Complex formation between metal ions and bioligands such as nucleobases or nucleotides may serve as models for metal−enzyme reactions in biological systems. The determination of stability constants of the formed complexes also provides valuable information in understanding the specific and selective interactions that take place in many biochemical processes. The interaction of metals with purine and pyrimidine nucleobases and their derivatives play an important role in many biochemical systems.[2−4] The complexes of various metal ions with nucleobases, nucleosides, nucleotides, and other ligands have been a subject of many studies.

As well as the behavior of actinides and lanthanides in nuclear waste processing, their cations with various oxidation states are important in biological systems. For instance, uranyl, UO_2^{2+}, has a nephrotoxic effect on the kidney. Depending on isotopic composition and dosage, UO_2^{2+} is also chemically toxic and carcinogenic in bone.[5] Thorium, Th^{4+}, reacts with in vivo proteins, amino acids, and nucleic acids to form stable complexes which are deposited in the body.[6] Also cerium, Ce^{3+}, is a subject of increasing interest in bioinorganic and coordination chemistry.[7]

Many studies have been aimed at designing ligands to remove actinides and lanthanides not only from nuclear waste but also from biological systems. Also the importance of metal ion−nucleic acid interactions is well-known and applied in medicinal chemistry. Thus, studies of the formation of metal complexes of purine bases are of considerable interest. The complexes of various metal ions with nucleobases, nucleosides, nucleotides, and other ligands have been reported by several workers.[1,3,4,8] But, limited literature is reported on the complexation of guanine with actinides and lanthanides.

The present paper reports studies of the stability constants of complexes of guanine with metal ions, UO_2^{2+}, Th^{4+}, and Ce^{3+}, potentiometrically at elevated temperatures in KCl medium. The stability constants of the complexation species of guanine with these metal ions were simulated using the HySS program and were computed with the aid of the Hyperquad2006 computer program. Furthermore, thermodynamic data on the complexation of actinides at elevated temperatures are mandatory to gain an understanding of the coordination chemistry of actinides and lanthanides. Therefore, thermodynamic parameters were derived and discussed by utilizing these data.[9]

Experimental Section

Materials and Solutions. Guanine was purchased from the Sigma-Aldrich Chemical Co. (Germany). All other chemicals of analytical grade were supplied by the Merck Chemical Co. (Germany). Bidistilled water was obtained from a Millipore (Milli-Q gradient A-10, USA) water purification instrument. Solutions of Th^{4+}, UO_2^{2+}, and Ce^{3+} were prepared from their nitrate salts ($UO_2(NO_3)_2 \cdot 6H_2O$, $Th(NO_3)_4 \cdot 6H_2O$, and $Ce(NO_3)_3 \cdot 6H_2O$). Stock solutions of 0.1 M NaOH and 0.1 M HCl were prepared in CO_2-free bidistilled water and standardized by a literature method.[10] KCl (1 M) was used to adjust the ionic strength of the media.

Apparatus and Procedure. pH-metric titrations were performed in a 100 mL jacketed cell (Metrohm, thermostat jacket, 6.1418.250) that has two ports for electrodes, a port for titrant addition, and a port for purging with inert gas. The titrations were carried out at (25 ± 0.1) °C, (37 ± 0.1) °C, and (45 ± 0.1) °C by circulating water from a thermostat (Nüve-BM 302). Metrohm autoburets (Titraprocessor 686 and Dosimat 665) with a glass electrode (Metrohm 6.0262.100) were used for pH measurements. To avoid any side effects that could come from oxygen, argon gas (ultrahigh purity, 99.99 %) was bubbled through the solution before and during the pH measurements in all titrations. The pH meter was calibrated with standard

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Table 1. Summary of Titration Data at $I = 0.10\ \text{mol}\cdot\text{dm}^{-3}$ KCl

metal ion[a]	initial total metal ion	ligand:metal molar ratio	temperature		
M^{n+}	$\text{mmol}\cdot\text{dm}^{-3}$	L:M	25 °C	37 °C	45 °C
				pH range	
Th^{4+}	0.5	1:1	2.80 to 4.22 (57 data)	2.79 to 5.68 (65 data)	2.82 to 5.31 (63 data)
		2:1	2.80 to 3.99 (76 data)	2.70 to 3.47 (72 data)	2.72 to 3.56 (70 data)
UO_2^{2+}	0.37	1:1	3.14 to 5.92 (98 data)	3.74 to 6.05 (72 data)	3.72 to 5.96 (73 data)
		2:1	3.60 to 6.92 (65 data)	3.51 to 7.35 (64 data)	3.55 to 7.65 (61 data)
Ce^{3+}	0.5	1:1	3.58 to 10.33 (139 data)	3.63 to 10.36 (178 data)	3.62 to 10.18 (170 data)
		2:1	3.51 to 11.00 (110 data)	3.50 to 10.21 (89 data)	3.59 to 10.09 (102 data)

[a] Concentration of guanine was in the range (0.4 to 1.0) $\text{mmol}\cdot\text{dm}^{-3}$ in the pH range 2.80 to 10.57 (for 110 data) at 25 °C, 2.86 to 9.54 (for 111 data) at 37 °C, and 2.84 to 9.48 (for 120 data) at 45 °C.

Table 2. Proton−Ligand Stability Constants of Guanine and Literature Data

t (°C)	log K_1/log β	data type[a]	ref
25	9.36 ± 0.01 12.65 ± 0.04	pt	16[b]
25	9.25 ± 0.01 12.20 ± 0.03	pt	1[c]
35	9.13 ± 0.07 11.80 ± 0.02		
45	8.80 ± 0.08 11.84 ± 0.07		
25	9.21 ± 0.02	pt	4[d]
25	9.28 ± 0.28 12.75 ± 0.63	pt	this work
37	8.59 ± 0.15 12.12 ± 0.26		
45	8.38 ± 0.22 11.59 ± 0.85		

[a] pt: potentiometric. [b] Medium: 0.1 M NaNO_3. Titration data of experiments were analyzed by the Newton−Gauss equation. [c] Medium: 0.1 M NaNO_3. Titration data of experiments were analyzed by p^{KAS} and Best. [d] Medium: 0.1 M KNO_3. Titration data of experiments were analyzed by Superquad.

Table 3. Results of Potentiometric Measurements of Guanine Complexes with Th^{4+} at $I = 0.10\ \text{mol}\cdot\text{dm}^{-3}$ KCl

initial total $[\text{Th}^{4+}] = 0.5\ \text{mmol}\cdot\text{dm}^{-3}$				
	$-\log \beta$			
	(p, q, r)			
t (°C)	(1, 0, 1)	(1, 0, 3)	(1, −2, 2)	(1, −3, 1)
25	10.63 ± 0.42		13.32 ± 1.07	−0.39 ± 0.20
37	10.50 ± 0.26		13.15 ± 0.41	−0.27 ± 0.21
45	10.10 ± 0.30	28.19 ± 0.88	12.03 ± 0.75	−0.54 ± 0.19

buffer solutions (pH 4 and pH 7; HC607673 and OC516474, respectively) before the pH measurements.

The results of strong acid versus alkali titrations were analyzed using a computer program named GLEE (glass electrode evaluation). The program GLEE has been developed as part of the HYPERQUAD suite of programs for stability constant determination. The values of $\mathrm{p}K_\mathrm{w}$ were confirmed using GLEE[11] ($\mathrm{p}K_\mathrm{w} = 13.78$ at 25 °C, 13.46 at 37 °C, and 13.16 at 45 °C). The ionic strength (I) of all of the titration mixtures was adjusted to 0.1 by adding the requisite volume of 1 M KCl stock solution, and a constant volume was maintained at 100 mL. Before performing the titrations, the titration conditions were simulated using the HySS2006 computer program.[12] The potentiometric titrations in aqueous solution were carried out and evaluated as described previously for proton−ligand and metal−ligand stability constants.[9]

Titrations for Proton−Ligand Stability Constants. The protonation constants of guanine were determined by titrating 100 mL of aqueous solution in the presence of an appropriate amount of guanine with 0.1 M NaOH. The pH measurements were done automatically using the MET program of Titroprocessor 686 by recording the pH measurements at suitable time intervals for guanine. A summary of the titrations used in the numerical analysis for the three temperatures is given in Table 1.

Titrations for Metal−Ligand Stability Constants. The titrations for the evaluation of metal−ligand procedures including the calculations were the same as before. For the determination of stability constants, a few preliminary titrations were performed to investigate the effects of experimental variables such as the time interval between consecutive titration readings and varying concentrations of relevant metal ions at appropriate pH ranges and at desired temperatures. First, the metal−ligand titration conditions were simulated considering the hydrolytic behavior of the relevant metal ions, reported before, using the HySS2006 computer program, and then the pH measurements were done using the MET program of Titroprocessor 686 by recording the pH measurements at suitable time intervals for each metal ion.[9] Finally, the potentiometric results were transferred to the HYPERQUAD2006 computer program, and stability constants were computed for the relevant metal ions.[13]

Titration for Thorium. For the complex with Th^{4+}, the ligand-to-metal ratios were 1:1 and 2:1. An aqueous solution of 0.5 $\text{mmol}\cdot\text{dm}^{-3}$ Th^{4+} in the range (0.4 to 1.0) $\text{mmol}\cdot\text{dm}^{-3}$ guanine was used.

Titration for Uranium. The stability constants of the guanine complexes with UO_2^{2+} at ligand-to-metal ratios ranging between 1:1 and 2:1 were determined by titrating an aqueous solution of 0.37 $\text{mmol}\cdot\text{dm}^{-3}$ UO_2^{2+}, in the range of (0.4 to 1.0) $\text{mmol}\cdot\text{dm}^{-3}$ guanine.

Titration of Cerium. The same procedure was applied to Ce^{3+} for the titration of an aqueous solution of 0.5 $\text{mmol}\cdot\text{dm}^{-3}$ Ce^{3+} at the same ligand-to-metal ratios, in the range (0.4 to 1.0) $\text{mmol}\cdot\text{dm}^{-3}$ guanine.

Each set of titrations was carried out using an appropiate amount of 0.1 M HCl stock solution with 0.1 M NaOH automatically.

A summary of the titrations used in the numerical analysis for guanine and its complexation with metal ions is given in Table 1. Each set of titrations were repeated at least three times at (25, 37, and 45) °C for each metal ion concentration.

Calculations. The data from each titration were imported into the program Hyperquad and treated by nonlinear least-squares refinement.[13]

The beta (β) values of proton−ligand and metal−ligand species for each metal given in Tables 2 to 5 are the average values of logarithms. The weights of the titrant were input directly into the HYPERQUAD2006 program as independent variables and the emf (electromotive force) or pH values as the dependent variables. While log β for the proton−ligand or metal−ligand species is calculated for acceptable conditions in the solution, others worsen the statistical parameters and are

Table 4. Results of Potentiometric Measurements of Guanine Complexes with UO_2^{2+} at $I = 0.10\ mol \cdot dm^{-3}$ KCl

	initial total $[UO_2^{2+}] = 0.37\ mmol \cdot dm^{-3}$			
	$-\log \beta$			
	(p, q, r)			
t (°C)	(1, 0, 1)	(1, 1, 1)	(1, 2, 1)	(1,−2, 1)
25	8.56 ± 0.44	13.27 ± 0.28	17.13 ± 1.01	−3.32 ± 1.17
37	8.22 ± 0.36	12.87 ± 0.36	16.72 ± 0.65	−3.55 ± 1.08
45	8.06 ± 0.22	12.60 ± 0.46	16.40 ± 0.92	−3.67 ± 1.05

Table 5. Results of Potentiometric Measurements of Guanine Complexes with Ce^{3+} at $I = 0.10\ mol \cdot dm^{-3}$ KCl

	initial total $[Ce^{3+}] = 0.5\ mmol \cdot dm^{-3}$			
	$-\log \beta$			
	(p, q, r)			
t (°C)	(1, 1, 1)	(1, 2, 1)	(1,−1, 1)	(1,−2, 1)
25	12.83 ± 0.51	17.53 ± 0.32	−2.03 ± 0.23	−9.80 ± 0.26
37	13.00 ± 0.07	17.48 ± 0.40	−1.17 ± 0.16	−10.30 ± 0.03
45	13.32 ± 0.51	16.78 ± 0.19	−0.98 ± 0.18	−8.36 ± 0.26

Table 6. Thermodynamic Parameters of Guanine

		thermodynamic parameters		
		ΔH	ΔG	ΔS
t (°C)	(p, q)	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$J \cdot mol^{-1}$
25	1, 1	−94.4 ± 19.0	−53.8 ± 1.6	−136.1 ± 60.3
	1, 2	−39.1 ± 3.6	−69.9 ± 1.0	103.4 ± 15.6
37	1, 1		−50.9 ± 1.0	−140.3 ± 62.3
	1, 2		−71.8 ± 1.1	105.7 ± 15.2
45	1, 1		−51.3 ± 1.4	−135.4 ± 60.0
	1, 2		−71.8 ± 1.4	103.0 ± 15.6

rejected as being negative or excessive by the Hyperquad program. Errors in fixed values are not introduced in Hyperquad, so that error propagation is not considered in optimizing the protonation constants. Statistical data refer to protonation constants: N = total number of experimental data points used, χ^2 = observed statistical parameter based on weighted residuals of the emf or pH readings (values < 12.6 indicate a confidence level > 95 %), and σ = ratio of the root-mean-square of the weighted residuals to the estimated error in the actual working conditions (σ_V and σ_E).[9]

In the current study, the proton−ligand constants for the overall reaction, β_n, are described as:

$$\beta_n = K_1 \cdot K_2 ... K_n = \frac{[H_nL]}{[H]^n[L]} \tag{1}$$

For metal−ligand complexation, formation constants, β_{pqr}, are generally represented by the following eq 2:

$$pM^{n+} + qH^+ + rL^{m-} \leftrightarrow M_pH_qL_r^{(np+q-mr)} \tag{2}$$

The equilibrium constants for the overall reaction are described as:

$$\beta_{pqr} = \frac{[M_pH_qL_r]}{[M]^p[H]^q[L]^r} \tag{3}$$

where $M^{n+} = Th^{4+}$, UO_2^{2+}, or Ce^{3+} (in this study).

Results and Discussion

The numerical values for protonation and complexation species of guanine with metal ions have been evaluated pH metrically at (25, 37, and 45) °C and are summarized in Table 1. The mean values of the protonation constants (the log values) obtained from this study for guanine including literature data are given in Table 2. The guanine complexes of each metal ion with the associated experimental parameters are given in Tables 3 to 5.

Also, thermodynamic parameters of guanine and complexation species of guanine with Th^{4+}, UO_2^{2+}, and Ce^{3+} have been calculated and summarized in Tables 6 and 7, respectively. In addition, percent distributions of complexation species of guanine with Th^{4+}, UO_2^{2+}, and Ce^{3+} at certain temperatures are shown in Figures 1 to 3. These figures were drawn using the IUPAC Stability Constants Database (SC-Database).[14,15]

Relationships among metal concentrations and other variables were analyzed by multivariate statistics using the SPSS 16 program (univariate variance analyses and (Chicago, IL) Pearson correlation). The correlation is significant at $p < 0.01$ for 99 % confidence level. While log β values were chosen as dependent variables, the independent variables were temperature and concentration for each metal ion.

Proton−Ligand Stability Constants for Guanine. The average proton−ligand values (log K_1, log β) obtained at (25, 37, and 45) °C are listed in Table 2. The results agree with reported values at given temperatures.[1,8,16] The proton binding sites of the purine bases have been established between N1 and N7 for guanine. Guanine has two acidic groups so dissociation takes place in two steps as seen in Figure 4. As reported by other workers, in this study the first deprotonation occurs from the N1-H side, and the second deprotonation occurs from the N7-H side or vice versa due to the tautomeric structures of guanine.[1,4,8]

Taking into account the results of the definite concentration range, there is a significant correlation between log β values and temperature of guanine as seen in Table 2. Statistical results showed that log K_1 ($p < 0.01$, $r^2 = 0.75$) and log β ($p < 0.05$, $r^2 = 0.37$) correlated well with temperature.

Also thermodynamic parameters for guanine and its complexes have been calculated using the Gibbs and van't Hoff equations and are summarized in Table 6.

Metal−Ligand Stability Constants for Guanine. The hydrolysis constants of relevant metal ions that were reported previously were used in the calculation of the metal−ligand stability constants.[9]

Complex Formation of Guanine with Th^{4+}. The guanine complexes with thorium at (25, 37, and 45) °C have been calculated from the data obtained by potentiometry in the definite pH range given in Table 1. The ratio of the ligand-to-metal ion, 1:1 and 2:1, was carried out. As with all titrations the ligand protonation constants and thorium hydrolysis constants were held constant.

In the current study, except for the hydrolyzed thorium species, while log β_{101} was found at all temperatures, log β_{103} was defined only at 45 °C represented as ThL_3. In addition, log $\beta_{1\text{-}22}$ and log $\beta_{1\text{-}31}$ values which are hydrolyzed thorium complexes in solution were computed from the imported potentiometric data to HYPERQUAD2006. They are represented by $M(OH)_2L_2$ and $M(OH)_3L$. The log β values for guanine with Th^{4+} are summarized in Table 3.

The analysis of the species distribution curves reveals the existence of the free metal and metal−ligand systems in solution at various pH values.[1] Depending upon the chelation processes, the formation of various stable complex species in the solution was altered.

In the current study, Figure 1 shows the distribution of possible Th-guanine species in solution depending upon pH. Stability constant data revealed the relative stability order of metal−ligand complexation as Th-L > ThOHL.

Table 7. Thermodynamic Parameters for Complexation of Guanine with Th^{4+}, UO_2^{2+}, and Ce^{3+}[a]

			thermodynamic parameters		
			ΔH	ΔG	ΔS
metal ion	t (°C)	(p, q, r)	$kJ\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	$J\cdot mol^{-1}$
Th^{4+}	25	1, 0, 1	−72.1 ± 1.9	−62.7 ± 0.1	−31.6 ± 6.6
		1, −2, 2	−153.0 ± 4.6	−81.2 ± 0.9	−240.7 ± 18.3
	37	1, 0, 1		−63.4 ± 0.1	−28.0 ± 6.7
		1, −2, 2		−76.0 ± 0.6	−248.1 ± 12.7
	45	1, 0, 1		−61.8 ± 0.2	−32.2 ± 6.6
		1, −2, 2		−76.8 ± 1.6	−239.4 ± 19.2
UO_2^{2+}	25	1, 0, 1	−105.8 ± 46.9	−51.7 ± 3.1	−181.4 ± 14.7
		1, 1, 1	76.5 ± 13.1	−75.3 ± 1.1	−4.1 ± 0.4
		1, 2, 1	−177.6 ± 17.5	−105.5 ± 1.5	−242.0 ± 53.6
		1, −2, 1	−53.8 ± 19.2	12.6 ± 1.5	−222.6 ± 59.3
	37	1, 0, 1		−48.6 ± 2.1	−184.2 ± 14.4
		1, 1, 1		−76.0 ± 0.8	−1.6 ± 0.4
		1, 2, 1		−101.3 ± 2.6	−246.2 ± 48.1
		1, −2, 1		16.2 ± 1.1	−225.8 ± 58.4
		1, 0, 1		−48.2 ± 0.1	−180.9 ± 14.7
	45	1, 1, 1		−75.1 ± 0.3	−4.5 ± 0.4
		1, 2, 1		−100.8 ± 0.1	−241.3 ± 54.5
		1, −2, 1		16.8 ± 0.3	−222.1 ± 59.5
Ce^{3+}	25	1, 1, 1	59.9 ± 6.6	−88.0 ± 1.3	496.0 ± 18.2
		1, 2, 1	40.8 ± 15.4	−121.9 ± 1.8	545.6 ± 45.7
		1, −1, 1	68.7 ± 5.9	−2.5 ± 1.4	238.8 ± 24.6
		1, −2, 1	101.4 ± 8.8	50.0 ± 1.3	172.4 ± 29.8
	37	1, 1, 1		−90.7 ± 0.9	485.7 ± 23.7
		1, 2, 1		−123.2 ± 2.0	528.9 ± 56.3
		1, −1, 1		−4.5 ± 0.1	236.1 ± 19.1
		1, −2, 1		50.1 ± 0.2	165.5 ± 28.9
	45	1, 1, 1		−98.4 ± 1.2	497.7 ± 17.3
		1, 2, 1		−133.7 ± 1.5	548.4 ± 43.9
		1, −1, 1		−7.4 ± 2.2	239.2 ± 25.5
		1, −2, 1		46.2 ± 1.7	173.6 ± 30.0

[a] Initial total [Gua] = 0.4 $mmol\cdot dm^{-3}$, [Th^{4+}] = 0.5 $mmol\cdot dm^{-3}$, [UO_2^{2+}] = 0.37 $mmol\cdot dm^{-3}$, and [Ce^{3+}] = 0.5 $mmol\cdot dm^{-3}$ at $I = 0.10$ $mol\cdot dm^{-3}$ KCl.

To our knowledge, there are no experimental results that exist to compare log β values for guanine complexes with thorium. There are many studies of thorium with other related ligands. For instance, Xu et al. examined the complexation of Th(IV) ion with three bidentate isomers of hydroxypyridinonates (HOPO) by potentiometry. They have explored log β values of the (140), (13−1), and (12−2) species for PR-1,2-HOPO, (140), (130), (13−1), and (12−2) species for PR-Me-3,2-HOPO, and (140), (130), (120), and (110) species for PR-3,4-HOPO-N isomers.[6] They concluded that the different acidities of these ligands lead to significantly different complexation behavior as a function of pH. Rao et al. studied the complexation of thorium with desmethyldesferrithiocin using potentiometric, spectrophotometric, and NMR data. They reported that three protonation constants of the ligand assigned to the phenolate group, the nitrogen at the hydroxypyridine ring, and the carboxylate group. Therefore, it is reasonable to assume that desmethyldesferrithiocin forms a similar tridentate complex with thorium involving the same groups.[17]

Taking into account the results of the definite concentration range, there is no significant correlation between log β values and temperature of thorium−guanine complexes.

Table 7 displays the thermodynamic data calculated from log β values of complexes formed by guanine with thorium. All species show exothermic behavior as seen in Table 7.

Complex Formation of Guanine with UO_2^{2+}. As with all titrations, the ligand protonation constants and uranyl hydrolysis constants were held constant at the ratios of the ligand-to-metal ion, 1:1 and 2:1. Then, stability constants of guanine complexes with UO_2^{2+} at (25, 37, and 45) °C were calculated from the imported data to the program HYPERQUAD2006.

It was found that a mononuclear complex formed, represented as ML, and its value is shown by log β_{101}. In addition, log β_{111} and log β_{121} values were found that represent the formation of two protonated uranyl complexes with guanine such as MHL and MH_2L. Also, a metal−ligand complex has been hydrolyzed in the medium by assuming the formation of $M(OH)_2L$. The calculated log $\beta_{1\text{-}21}$ value represents this complex in Table 4.

The speciation diagram calculated for a total guanine concentration of 0.4 $mmol\cdot dm^{-3}$ is shown in Figure 2 for species formed in solution at (25, 37, and 45) °C. While (1, 1, 1) and (1, 0, 1) are observed over a narrow pH range such as between 4 and 6, (1, 2, 1) is a dominant species at low pH. As seen, a complex of metal−ligand has been hydrolyzed in solution at pH > 5. There is no significant difference between temperature and speciation curves.

There have been some studies of the complexation of UO_2^{2+} ion with various related ligands at different experimental conditions. Rao et al. reported the formation constants and the molar enthalpies of complexation of uranium(VI) with oxidiacetate determined at various temperatures by potentiometry and calorimetry.[18]

When we discussed the effect of temperature, there is a meaningful agreement between temperature and log β values. According to multiple linear regression results, (1, 1, 1) ($p < 0.01$, $r^2 = 0.43$), and (1, 0, 1) ($p < 0.05$, $r^2 = 0.30$) correlated well with temperature.

In Table 7, the calculated enthalpy, entropy, and Gibb's energy for the complexation of the uranyl ion are given. Enthalpy values show that only the formation of (1, 1, 1) species is endothermic; the other three species have a negative enthalpy value.

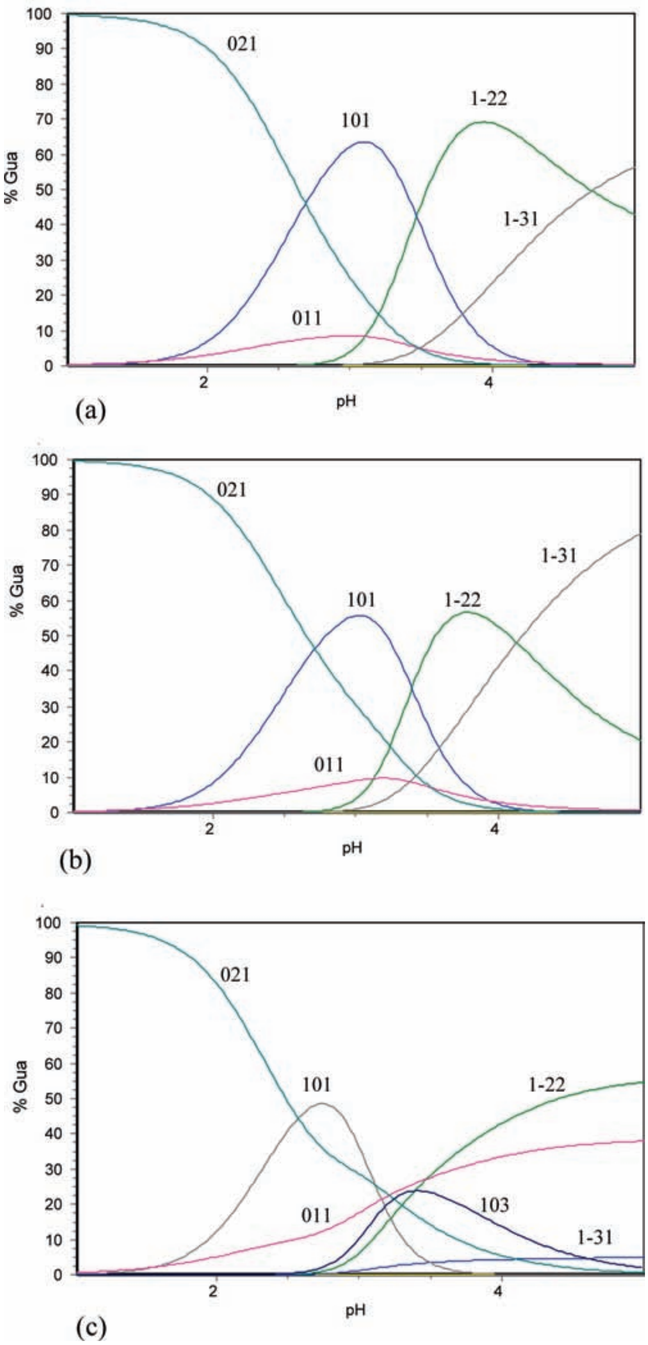

Figure 1. Percentage distribution of complexation species of guanine with Th^{4+} ([Gua] = 0.4 mmol·dm^{-3}, [Th^{4+}] = 0.5 mmol·dm^{-3}, and I = 0.10 mol·dm^{-3} KCl) (a) at 25 °C; (b) at 37 °C; (c) at 45 °C.

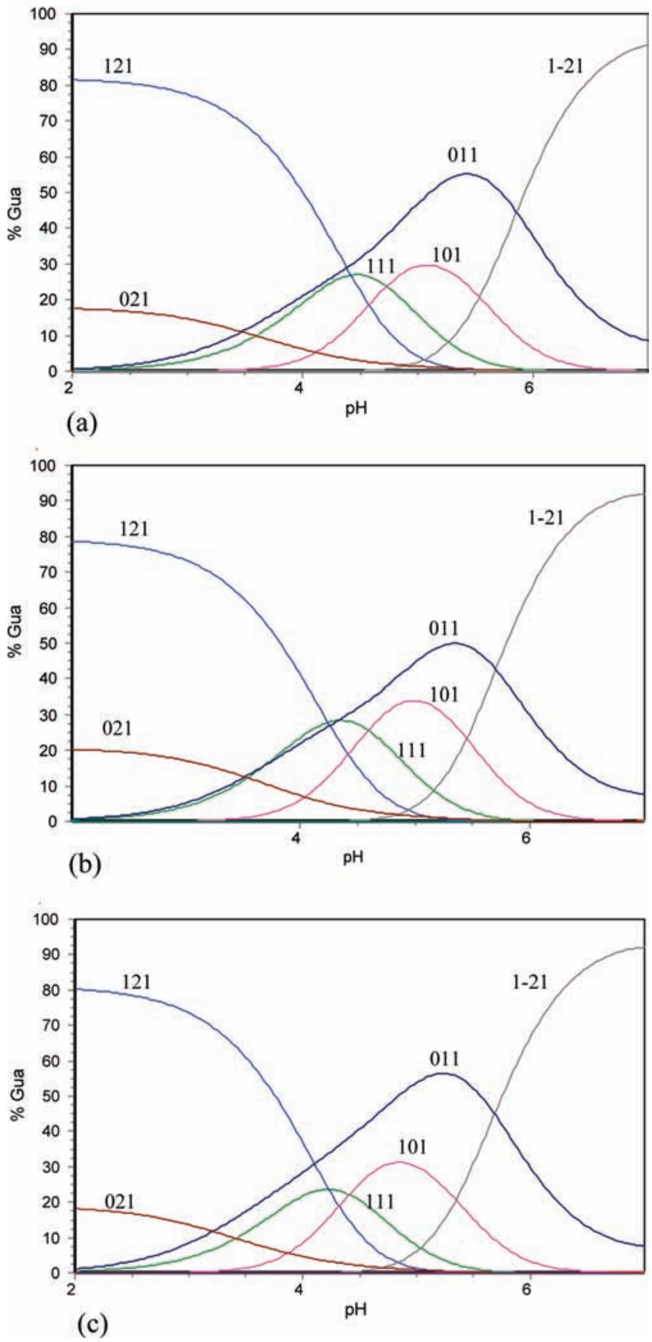

Figure 2. Percentage distribution of complexation species of guanine with UO_2^{2+} ([Gua] = 0.4 mmol·dm^{-3}, [UO_2^{2+}] = 0.37 mmol·dm^{-3}, and I = 0.10 mol·dm^{-3} KCl) (a) at 25 °C; (b) at 37 °C; (c) at 45 °C.

***Complex Formation of Guanine with Ce^{3+}*.** Stability constants of guanine complexes with cerium at (25, 37, and 45) °C were computed from the imported data by potentiometry. Ligand protonation constants and cerium hydrolysis constants were held constant for all titrations with the ratios of ligand to metal, 1:1 and 2:1. The values of log β_{111}, log β_{121}, log $\beta_{1\text{-}11}$, and log $\beta_{1\text{-}21}$ were found for species formed with guanine in solution. It is understood that log $\beta_{1\text{-}11}$ and log $\beta_{1\text{-}21}$ values correspond to the hydrolyzed species in solution represented by M(OH)L and $M(OH)_2L$. Others are protonated complexes of cerium, the MHL and MH_2L species. The log β values for guanine complexes with cerium are given in Table 5.

The stability constants of different trivalent lanthanide ion complexes formed in solution have been reported. Kostova et al. studied the complexation reaction of cerium(III) with 4-methyl-7-hydroxycoumarin by the spectrophotometric method. They found the stepwise formation of two complexes represented by CeR^{2+} and CeR_2^{+}.[7] The other study about the complexation of cerium found in the literature was carried out by Tyagi et al. at 25 °C using potentiometry. They reported that the neutral monomeric and hydrolyzed complexes exist in solution. In addition, they suggested that guanine is bonded to metal ions through N1/C6═O and N7 in its binary and ternary complexes.[1,16]

Anwar and Azab studied the interaction of nucleotides and La(III), Ce(III), Pr(III), and Eu(III) with biological buffers. They concluded that factors such as pH, temperature, and metal ion concentration affect metal−nucleotide interactions.[3] The other

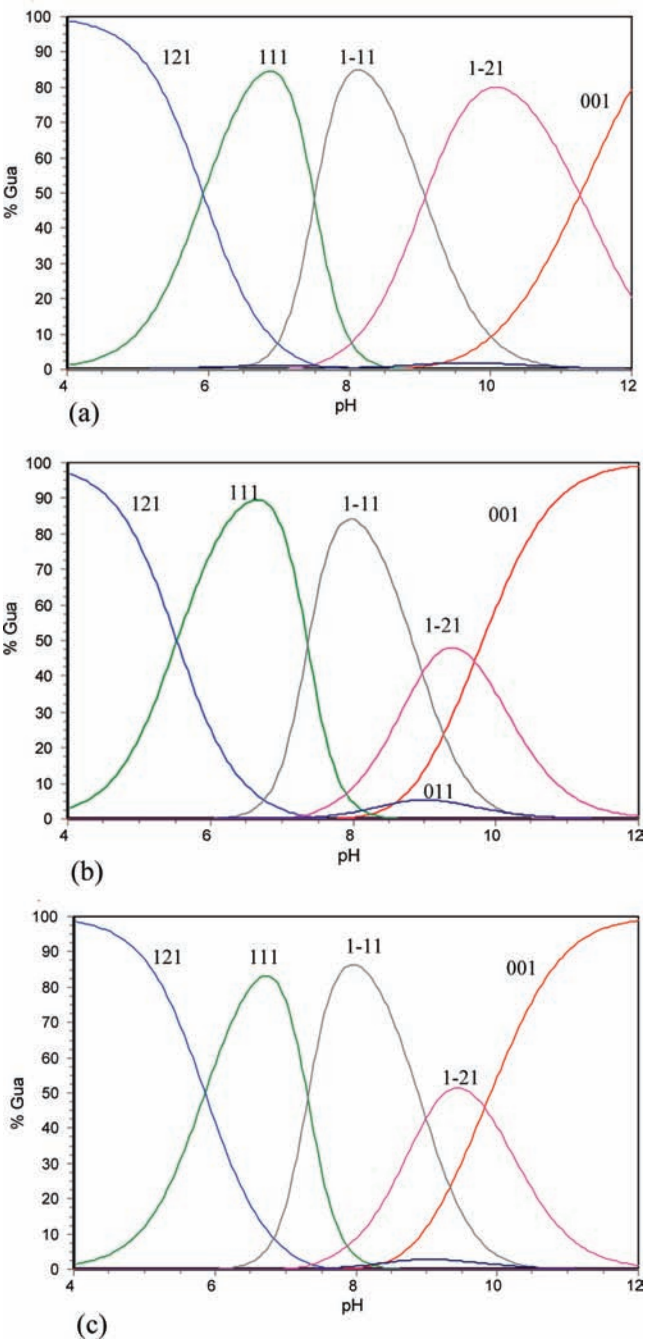

Figure 3. Percentage distribution of complexation species of guanine with Ce^{3+} ([Gua] = 0.4 mmol·dm^{-3}, [Ce^{3+}] = 0.5 mmol·dm^{-3}, and $I = 0.10$ mol·dm^{-3} KCl) (a) at 25 °C; (b) at 37 °C; (c) at 45 °C.

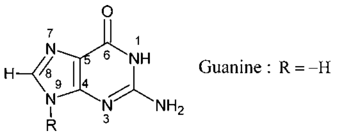

Figure 4. Structure of guanine.

study was reported to discuss complex formation of La(III), Ce(III), Th(III), and UO_2(II) with tricine. It is concluded that the stability of the formed complexes changes depending on the nature of the heavy metal cation.[19]

The percent distribution curves of Ce-guanine species versus pH were plotted for each temperature (Figure 3). As shown in the curve, the formation of metal–ligand and metal–ligand proton and hydrolyzed metal ligand species are found over a wide pH range in the solution. Also, it is considered that the % species of (1, 2, 1) and (1, 1, 1) are high at low pH. There is no significant difference between temperature and species distribution except for (1, −2, 1). As the temperature increases, the percent distribution of the (1, −2, 1) species decreases.

According to multiple linear regression results, log β values of (1, 2, 1) ($p < 0.01$, $r^2 = 0.58$), (1, −1, 1) ($p < 0.01$, $r^2 = 0.83$), and (1, −2, 1) ($p < 0.05$, $r^2 = 0.48$) correlate well with temperature. Also there is no significant correlation for log β values of (1, 1, 1).

In view of the thermodynamic data, the complexation of all cerium species is endothermic, and all species have positive entropy values at all temperatures as given in Table 7.

There are few studies on the complexation of guanine with Th^{4+}, UO_2^{2+}, and Ce^{3+}. That is why it is difficult to come across studies regarding the enthalpy of complexation. So, there are no detailed data to compare with our calculated thermodynamic data.

Conclusion

The results summarized in this study show that the metal ion and temperature effected the formation of complexes. It is concluded that experimental conditions alter the complexation behavior of lanthanides and actinides as reported by many other researchers. In this study, the calculation of metal–ligand stability constants at various temperatures and thermodynamic parameters contributes significantly to the understanding of the complexation behavior of guanine with Th^{4+}, UO_2^{2+}, and Ce^{3+}. In this respect, it could be important to gain more data about complexation related with actinide and lanthanide ions with guanine because of a widespread interest from nuclear waste to biological systems.

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