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Note

COMPLEXATION REACTION OF METAL IONS WITH PEPTIDE SYSTEMS. PART III. STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS OF COPPER(II), NICKEL(II) AND COBALT(II) COMPLEXES WITH N-BENZOYL-L-PHENYLALANINE

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INTRODUCTION

N-Protected amino acids and peptides have been used as food supplement, herbicides, analgesics, inflammation inhibitors and antipyretics [1]. A lot of data on stability constants and thermodynamic parameters of transition metal ions with amino acids is available in the literature [2,3]. The present study reveals the formation of some metal complexes of bivalent ions like Cu(II), Ni(II) and Co(II) with ligand *N*-benzoyl-L-phenylalanine in 50% v/v dioxane—water medium at 25.0, 35.0 and 45.0°C and at 0.1 M ionic strength (KNO_3). The parameters have been calculated by the Calvin—Bjerrum titration technique [4,5] as modified by Irving and Rossotti [6]. The thermodynamic parameters have also been evaluated.

EXPERIMENTAL

N-Benzoyl-L-phenylalanine was prepared by the method described in the literature [7]. Dioxane was purified by refluxing on sodium wire for 24 h and was freshly distilled over sodium before use. The ligand solution was prepared in 50% v/v dioxane—water medium. All the metal ion solutions were prepared from B.D.H. analar samples of corresponding nitrates in doubly-distilled CO_2-free water and were standardized by conventional volumetric methods. The metal-to-ligand ratio was kept at 1 : 5.

The pH measurements were carried out in 50% v/v dioxane—water medium using Toshniwal pH meter CL 46, having a sensitivity of ±0.01 units at constant temperatures (25.0 ± 0.1°C, 35.0 ± 0.1°C and 45.0 ± 0.01°C) and ionic strength 0.1 M (KNO_3).

Three solutions containing (a) acid (2.5 ml of 1.0×10^{-2} M HNO_3); (b) ligand ("a" + 5 ml 2.5×10^{-2} M ligand); and (c) complex (mixture "b" + 2.5 ml of 1.0×10^{-2} M metal solution) were taken, and total volume raised to 50 ml. The three solutions (a), (b) and (c) were titrated separately against standard 0.05 M KOH prepared in 50% v/v dioxane—water medium. The resulting three curves from the plots of pH vs. volume of alkali added were referred to as (i) acid, (ii) ligand, and (iii) complex titration curves, respectively. The shapes of the curves were as usual.

RESULTS AND DISCUSSION

The respective metal ions in the presence of the ligand were titrated against alkali. From the shift in the pH titration curves, values of $\bar{n}_H$, $\bar{n}$ and P_L were calculated by the Irving and Rossotti [6] method. The position of the ligand curve does not shift to the left of the acid titration curve, in contrast to the observation in deprotected amino acid titrations. This indicates that the benzoyl group which protected the amino group partially removed the possibility of zwitterion formation in *N*-benzoyl-L-phenylalanine. Thus only one protonation constant ($\log P_{K_1}H$) was obtained by various computational methods [5,8], which is due to the carboxylic group present in this ligand.

The metal—ligand stability constants have been obtained by analysis of formation curves obtained by plotting $\bar{n}$ vs. P_L. These plots indicate that the value of $\bar{n}$ obtained is less than 1 for all the metal ions under study, indicating the formation of only 1 : 1 complexes. The absence of 1 : 2 chelates may be due to the steric hindrance offered by the coordinated ligand in the 1 : 1 complex to the incoming second ligand molecules. The Bjerrum half integral method [5], interpolation at various $\bar{n}$ values, and graphical method [8] were used to calculate the $\log K_1$ values. The mean values of protonation constants and stability constants are summarized in Table 1. The order of stability is Cu(II) > Co(II) > Ni(II). This order differs from the common order of Irving and Williams [9]. The reversal of the order in the case of Co(II) and Ni(II) may be attributed to the additional stabilization due to Jahn—Teller distortion present in the case of Co(II) similar to Cu(II), and to favourable entropy effect, while partial oxidation of the Co(II) complexes is not absolutely ruled out. Data showed a decrease in the values of protonation constants and stability constants with increase of temperature. The calculated error in stability constants is $\pm 0.01 \log K_1$.

TABLE 1

Values of protonation constants, stability constants and thermodynamic functions at three temperatures and $\mu = 0$ (1 M)

Metal ion	Constant	Temp. (°C)			$-\Delta G^0$ (kcal mole^{-1})			ΔH^0 (kcal mole^{-1}) at 35°C	ΔS^0 (cal mole^{-1} deg^{-1}) at 35°C
		25	35	45	25°C	35°C	45°C		
H^+	$\log P_{K_1}H$ *	5.15	5.03	4.83					
Cu(II)	$\log K_1$	3.11	2.98	2.89	4.24	4.20	4.20	—4.74	—1.75
Ni(II)	$\log K_1$	2.80	2.77	2.70	3.82	3.90	3.93	—2.20	+5.52
Co(II)	$\log K_1$	2.90	2.86	2.77	3.95	4.03	4.03	—2.85	+3.83

* Carboxylic functional group.

Table 1 also shows the values of changes in free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) which have been determined using temperature coefficients and the Gibbs—Helmholtz equation [10]. The precision of ΔG^0, ΔH^0 and ΔS^0 values are ±0.08 kcal mole^{-1}, ±0.1 kcal mole^{-1} and ±0.3 cal deg^{-1} mole^{-1}, respectively. ΔG^0 values for Ni(II) and Co(II) are more negative with increase of temperature, showing that complex formation is a spontaneous process; whereas for Cu(II) no such regular trend is observed. The enthalpy change (ΔH^0) being negative in all cases is favourable for the formation of these complexes; the enthalpy change (ΔS^0) being positive in the case of Ni(II) and Co(II) complexes is favourable, but for Cu(II) complexes, ΔS^0 being negative does not favour the formation of this complex.

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