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THERMODYNAMICS OF METAL COMPLEXES WITH LIGAND–LIGAND INTERACTION. MIXED COMPLEXES OF COPPER(II) AND ZINC(II) WITH ADENOSINE 5′-TRIPHOSPHATE AND L-PHENYLALANINE OR L-TYROSINE

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ABSTRACT

Thermodynamic parameters for the formation of copper(II) and zinc(II) mixed complexes with ATP and L-phenylalanine or L-tyrosine were determined by means of potentiometric and calorimetric measurements at $t = 25°C$ and $I = 0.1$ mol dm^{-3} (KNO_3) in aqueous solution. ΔG^0, ΔH^0 and ΔS^0 values for the binary systems of the two amino acids were also determined under the same experimental conditions. On the basis of the obtained results, the occurrence of solvophobic and of other non-covalent interactions between the non-coordinating side-chain moieties of the bonded ligands has been ascertained in the investigated zinc(II) mixed complexes. For copper(II) mixed complexes, ΔG^0, ΔH^0 and ΔS^0 values do not allow a straightforward assessment of the occurrence of stacking interaction. The origin of this difference in behaviour of the two metal ions is also discussed.

INTRODUCTION

It is well established that the stacking affinity of the nucleobases, rather than the hydrogen bonding, represents the major contribution to the free energy sustaining the nucleic acid secondary structure [1,2]. Furthermore, the selective recognition of particular mononucleotides by certain proteins or enzymes involves direct or indirect interactions between the nucleotides and individual amino acyl residues [3,4]. The participation of amino acyl side-chains in localized electrostatic or hydrogen-bonding interactions with nucleic acid components is much better understood [5,6], to date, than their involvement in delocalized phenomena such as hydrophobic or base stacking interactions [7].

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Indirect interaction between proteins and nucleic acids may be mediated through a third component, in particular metal cations, which are required for many enzymatic reactions [8–11]. Interactions between negatively charged polypeptides and polynucleotides have been shown to take place in ternary complexes involving zinc(II) or copper(II) ions [12].

Recently, model systems for the above mentioned biological systems have been investigated by means of spectroscopic and thermodynamic measurements, as reported in some recent reviews [13,14].

In our laboratory, we have been using the calorimetric approach to establish the presence of a solvophobic [15] (or according to more classical denominations, hydrophobic or stacking [16,17]) interaction between two ligands bound to the same metal ion [18,19], between the aromatic or aliphatic side chains of protonated dipeptides [20] and of their complexes with copper(II) [21].

We report here all the thermodynamic functions involved in the formation of ternary complexes of copper(II) or zinc(II) with ATP (ATP = adenosine 5′-triphosphate) and L-phenylalanine or L-tyrosine, bearing in mind that tyrosine and related phenol derivatives have been shown to interact with purine nucleotides in aqueous solution [22–24].

Moreover, we have carried out a detailed potentiometric and calorimetric study of copper(II) and zinc(II) simple complexes of the two amino acids under the same conditions used for the mixed complexes, i.e., $t = 25°C$ and $I = 0.1$ mol dm^{-3} (KNO_3). The thermodynamic parameters pertinent to the ATP complexes had already been determined under the same experimental conditions [18].

EXPERIMENTAL

L-Tyrosine and L-phenylalanine (C. Erba, RPE) were used without further purification. Their purity, checked by titration with CO_2-free standard KOH, was always > 99.5%. Metal nitrate stock solutions were standardized by EDTA titrations according to Flaschka [25]. All the standard solutions were prepared by using twice-distilled water. The ionic strength of measurement solutions was kept at 0.1 mol dm^{-3} by adding KNO_3.

The potentiometric measurements were carried out by means of an Orion potentiometer (using Metrohm glass and saturated calomel electrodes). The calibration of the electrode couple, in $-\log C_H$ units, was achieved by titrating HNO_3 (4–8 mmol dm^{-3}) with KOH standard, at $I = 0.1$ mol dm^{-3} (KNO_3).

In Table 1 some experimental details of potentiometric measurements are reported.

The calorimetric measurements were carried out by an LKB Model 8700 precision calorimeter. The titrations were performed in a 100 cm^3 calorimet-

ric vessel by adding metal nitrate (0.25 mol dm^{-3}) to the solution containing a) L-tyrosine or L-phenylalanine (15–20 mmol dm^{-3}) neutralized at 80–90% (for L-tyrosine, OH group not taken into account), b) L-tyrosine or L-phenylalanine (10–20 mmol dm^{-3}) and ATP (20–30 mmol dm^{-3}) both neutralized up to 80–90%. The protonation heats were measured by adding HNO_3 0.25 mol dm^{-3} to the solution containing the deprotonated amino acids (10–20 mmol dm^{-3}). The reaction heats, corrected for the dilution heats determined in separate experiments, were calculated considering 1 cal = 4.184 J. The calculations were performed by means of least squares computer programs ACBA [26] (protonation constants and ligand purity), MINIQUAD [27] (formation constants), DOEC [28] (enthalpy changes). Throughout the paper, errors are expressed as three times the standard deviation or as "range" (maximum deviation from the mean). Other experimental and calculation details are as previously reported [19].

RESULTS AND DISCUSSION

Simple Complexes

Table 2 shows the log β, ΔG^0, ΔH^0 and ΔS^0 values for the reaction of hydrogen ion and copper(II) or zinc(II) with L-phenylalaninate (phalaO$^-$) or L-tyrosinate (HtyrO$^-$).

The species found in the H^+–M^{2+}–phenylalaninate system were: [phala], $[Hphala]^+$, $[M(phalaO)]^+$ and $[M(phalaO)_2]$, which is in agreement with literature findings [29].

The species found in the H^+–M^{2+}–tyrosinate system were $[H_2tyr]$, $[H_3tyr]^+$, $[M(HtyrO)]^+$, $[M(HtyrO)_2]$ and $[M(HtyrO)(tyrO)]^-$; the protonation of the OH group was neglected, (log k = 10.2), since our measurements

TABLE 1

Some experimental details of potentiometric measurements at 25°C and I = 0.1 mol dm^{-3} (KNO_3) [Titrant = 0.25 mol dm^{-3} KOH]

Metal	Ligand	C_M^0 [a]	C_{ATP}^0 [a]	C_L^0 [a]	pH
Cu^{2+}	L-tyrosine	2–4	0	2–8	3–8.5
Cu^{2+}	L-tyrosine	1.5–3.5	3.8–5.8	1.5–3.4	3–8
Zn^{2+}	L-tyrosine	2–4	0	2–8	3–8.6
Zn^{2+}	L-tyrosine	2.2–3.5	4.9–5.9	2.1–3.5	3.5–8.1
Cu^{2+}	L-phenylalanine	2–4	0	2–8	3–7
Cu^{2+}	L-phenylalanine	4–8	8–20	4–8	3–7
Zn^{2+}	L-phenylalanine	2–4	0	2–8	3–7
Zn^{2+}	L-phenylalanine	5–9.8	10–25	8–14	3–7

[a] Initial analytical concentrations in mmol dm^{-3}; initial volume 50 cm^3.

TABLE 2

Thermodynamic parameters [a] for complex formation of H^+, Cu^{2+} and Zn^{2+} with L-phenylalanine and L-tyrosine at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3)

Reaction	log β	$-\Delta G^0$ (kcal mol^{-1})	$-\Delta H^0$ (kcal mol^{-1})	ΔS^0 (cal K^{-1} mol^{-1})
$H^+ + phalaO^- \rightleftarrows phala$	9.08(2)	12.39(3)	11.22(10)	3.7(5)
$2H^+ + phalaO^- \rightleftarrows Hphala^+$	11.32(5)	15.45(7)	12.7(4)	8.7(2)
$H^+ + HtyrO^- \rightleftarrows H_2tyr$	9.04(4)	12.33(5)	10.1(2)	7(1)
$2H^+ + HtyrO^- \rightleftarrows H_3tyr^+$	11.32(7)	15.4(1)	10.3(2)	17(1)
$Cu^{2+} + phalaO^- \rightleftarrows [Cu(phalaO)]^+$	7.77(5)	10.60(7)	5.5(3)	17(2)
$Cu^{2+} + 2phalaO^- \rightleftarrows [Cu(phalaO)_2]$	14.65(13)	20.0(2)	12.5(5)	25(3)
$Zn^{2+} + phalaO^- \rightleftarrows [Zn(phalaO)]^+$	4.38(5)	5.97(7)	1.2(3)	16(2)
$Zn^{2+} + 2phalaO^- \rightleftarrows [Zn(phalaO)_2]$	8.25(15)	11.3(2)	2.2(5)	31(3)
$Cu^{2+} + HtyrO^- \rightleftarrows [Cu(HtyrO)]^+$	7.84(5)	10.69(7)	6.0(4)	16(2)
$Cu^{2+} + 2HtyrO^- \rightleftarrows [Cu(HtyrO)_2]$	14.82(7)	20.2(1)	12.7(6)	25(3)
$[Cu(HtyrO)_2] \rightleftarrows [Cu(HtyrO)(tyrO)]^- + H^+$	−9.4(1)	−12.8(2)	−6(1)	23(4)
$Zn^{2+} + HtyrO^- \rightleftarrows [Zn(HtyrO)]^+$	4.21(5)	5.74(7)	2.2(5)	12(2)
$Zn^{2+} + 2HtyrO^- \rightleftarrows [Zn(HtyrO)_2]$	8.3(1)	11.3(2)	4.8(6)	22(3)
$[Zn(HtyrO)_2] \rightleftarrows [Zn(HtyrO)(tyrO)]^- + H^+$	−8.9(2)	−12.1(3)	−8(1)	14(4)

[a] 3σ in parentheses.

were performed at pH < 9. This speciation is in partial agreement with the one recently proposed by Pettit et al. [30]. These authors found also the species [M(tyrO)] and $[M(tyrO)_2]^{2-}$ that, however, under our experimental conditions, (i.e., at pH < 9), are negligible. The thermodynamic parameters are in agreement with literature findings [31,32], if differences in ionic strength are taken into consideration.

The results in Table 2 show that copper(II) as well as zinc(II) form complexes of comparable stability with both amino acids. The fact that ΔH_2^0 is larger than ΔH_1^0 while ΔS_1^0 is much more positive than ΔS_2^0 has been ascribed [33] to the large difference in hydrational energies of the Cu_{aq}^{2+} and CuL_{aq}^{+} species. ΔH^0 and ΔS^0 values give no useful information towards the understanding of the difference shown by the ΔG^0 values of the first and second complexation step of copper(II) ion with $HtyrO^-$ and $phalaO^-$ compared to $alaO^-$ [32,34].

On the basis of our calorimetric data, it is not possible to infer the presence of either an interaction of the metal ion with the aromatic side ring of the two amino acids or the solvophobic interaction between side chains in the bis-complexes. The above interactions have been hypothesised to explain thermodynamic [34–36] and spectroscopic [37,38] results concerning simple and mixed complexes of copper(II) with aromatic or hetero-aromatic amino acids in elucidating the mechanism of certain oxidase enzymes [39–41].

Less than supposed van der Waals' contact distances found in several crystal structure determinations [42,43] have also led to suggestions of weak attractive interactions between aromatic side chains and transition-metal ions, chelated by amino acids or peptides. The crystal structures of bis-(L-phenylalaninate) [44] and bis-(L-tyrosinate) [45] copper(II) have been determined. In the former, the copper coordination is best described as a tetragonally distorted octahedron and the conformations of both phenylalanine molecules are similar and such that the aromatic rings are pointed away from the metal coordination. In the second case the ligands are *trans*, as found for a phenylalaninate compound, and the coordination of the copper(II) ion is distorted square pyramidal, with one of the phenolic rings located beneath the base of the coordination pyramid at a distance slightly greater than 3 Å. The difference in structure between the two complexes in the solid state is not found in solution, where the thermodynamic data seem to indicate a similar kind of coordination.

Mixed Complexes

ΔG^0, ΔH^0 and ΔS^0 values of mixed-ligand complex formation of copper(II) with both the investigated amino acids are reported in Table 3. The ΔG^0 values are nearly equal to those of the $[Cu(ATP)(alaO)]^{3-}$ for which a chromophore of NO_3 type (one nitrogen and one oxygen atom from the amino acid and two oxygen atoms of β- and γ-phosphates of ATP) has been

TABLE 3

Thermodynamic parameters [a] for mixed-ligand complex formation at 25 °C and $I = 0.1$ mol dm^{-3}

	log β	$-\Delta G^0$ (kcal mol^{-1})	$-\Delta H^0$ (kcal mol^{-1})	ΔS^0 (cal K^{-1} mol^{-1})
$Cu^{2+} + ATP^{4-} + alaO^- \rightleftarrows [Cu(ATP)(alaO)]^{3-}$ [b]	12.93	17.64	2.5	51
$Zn^{2+} + ATP^{4-} + alaO^- \rightleftarrows [Zn(ATP)(alaO)]^{3-}$ [b]	9.18	12.52	−4.0	55
$Cu^{2+} + ATP^{4-} + phalaO^- \rightleftarrows [Cu(ATP)(phalaO)]^{3-}$	12.94(6)	17.66(8)	4.0(6)	46(3)
$Zn^{2+} + ATP^{4-} + phalaO^- \rightleftarrows [Zn(ATP)(phalaO)]^{3-}$	9.7(7)	13.23(10)	4.9(6)	28(3)
$Cu^{2+} + ATP^{4-} + HtyrO^- \rightleftarrows [Cu(ATP)(HtyrO^-)]^{3-}$	12.86(6)	17.55(8)	5.5(6)	40(3)
$Zn^{2+} + ATP^{4-} + HtyrO^- \rightleftarrows [Zn(ATP)(HtyrO)]^{3-}$	9.26(7)	12.64(10)	−0.4(6)	44(3)

[a] 3σ in parentheses.

[b] Ref. 19.

hypothesised [19]. Also in the zinc(II) ternary complexes the same donor atoms should be involved in the bonding. In fact the ΔG^0 values of complex formation are quite similar to those found for the $[Zn(ATP)(alaO)]^{3-}$ complex. Furthermore, the thermodynamic parameters for the formation of the above mentioned zinc(II) complexes are different. Both the ternary complexes are more enthalpically and less entropically stabilized with respect to $[Zn(ATP)(alaO)]^{3-}$. Moreover $[Zn(ATP)(phalaO)]^{3-}$ shows a less positive entropy change and a more negative enthalpy change than that found for $[Zn(ATP)(HtyrO)]^{3-}$. Interestingly, even if the ΔG^0 value for the zinc(II) mixed ligand complex of ATP and $phalaO^-$ is lower than that of the corresponding copper(II) complexes, the enthalpy change is nearly equal to that of the zinc(II) species (Table 3). This behaviour is similar to that found for the previously studied $[M(ATP)(trpO)]^{3-}$ complexes [19] ($M = Cu^{2+}$ or Zn^{2+}, $trpO^- =$ tryptophanate). In particular, in the above systems the more favourable enthalpy and the less favourable entropy contributions accompanying the $[Zn(ATP)(trpO)]^{3-}$ complex formation ($\Delta G^0 = -13.50$ kcal mol^{-1}; $\Delta H^0 = -5.9$ kcal mol^{-1}; and $\Delta S^0 = 25$ cal K^{-1} mol^{-1}) [19] with respect to $[Zn(ATP)(alaO)]^{3-}$ (Table 3) were ascribed to the presence of a stacking interaction between the two rings of the ligands. Thermodynamic data for the solvophobic interaction of caffeine and phenylalanine.Na ($-\Delta G^0 = 0.57$ kcal mol^{-1}; $-\Delta H^0 = 4.99$ kcal mol^{-1} and $-\Delta S^0 = 14.8$ cal K^{-1} mol^{-1}) [46] provides further support for the existence of such an interaction in the $[Zn(ATP)(phalaO)]^{3-}$ complex. In the $[Zn(ATP)(HtyrO)]^{3-}$ complex it is not possible to interpret unambiguously the difference in ΔH^0 and ΔS^0 values with respect to $[Zn(ATP)(alaO)]^{3-}$ in terms of stacking interaction. While the simple complexes of zinc(II) with $alaO^-$ and $HtyrO^-$ show similar ΔH^0 and ΔS^0 values, the $[Zn(ATP)(HtyrO^-)]^{3-}$ complex formation is nearly 4 kcal mol^{-1} less endothermic with respect to the $[Zn(ATP)(alaO)]^{3-}$ complex formation, in which a "secondary bonding" cannot exist. Considering that on the basis of comparison with thermodynamic data regarding the $trpO^-$ and $phalaO^-$ ternary complexes, it is not possible to affirm the presence of the "stacking" interaction solely; the observed differences might be interpreted by hypothesizing the presence of a hydrogen bonding between the OH substituent on the amino acid ring and some basic centre on the ATP, probably the NH_2. This interaction has been found in solid compounds [48] of similar biofunctional ligands. This hypothesized hydrogen bond would put the aromatic ring of L-tyrosinate and the purine moiety of ATP in a position less favourable than in the case of L-phenylalaninate, thus altering the extent of stacking interaction between the two moieties. On the other hand, spectroscopic data [47] provide evidence for solvophobic interaction in these zinc(II) mixed complexes. It is noteworthy that both ternary copper(II) complexes studied here show a different thermodynamic behaviour with respect to the analogous $alaO^-$ compound (Table 3), while the formation of simple complexes of the three amino acids is accompanied by similar ΔH^0

and ΔS^0 values. However the results for $[Cu(ATP)(phalaO)]^{3-}$ are not as straightforward as those used in the case of the corresponding zinc(II) species to establish the presence of a solvophobic interaction. This is in agreement with spectroscopic measurements for similar systems [49] that pointed to a greater contribution to the stacking from the zinc(II) than from the copper(II). It is evident that this difference in behaviour cannot be attributed to electronic characteristics of the metal ions because the latter are not bound to the ligand moieties that interact. Also, the $[Cu(ATP)(HtyrO)]^{3-}$ is more enthalpically and less entropically stabilized with respect to the corresponding $alaO^-$ compounds. Probably, in the ternary complexes the different geometric requirements of the two metal ions place the purine and aromatic groups of ATP and $phalaO^-$ or $HtyrO^-$ in a more or less suitable arrangement which results in a variation in the extent of interaction between the two rings. Furthermore, it cannot be excluded that a different degree of solvent interaction of the copper(II) ion with respect to the zinc(II) contributes to the resulting thermodynamic parameters. An additional explanation may be the different percentage of closed and open isomers of stacked species of the two metal ions. In fact, following an approach similar to that used by Martin [50] for simple complexes, an intramolecular equilibrium between the two isomeric complexes has been proposed, determining also the percentage of mixed stacked complexes ("closed species"). From the reported data [13,14], the copper(II) compounds show a lower percentage of stacked species than the analogous zinc(II) compounds. Tentatively, considering also that those values are only estimates, it is possible to ascribe the different thermodynamic results to different percentages of stacked isomers in the zinc(II) and copper(II) complexes studied here.

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