plexes with adenosine 5′-triphosphate (*ATP*) and some biofunctional ligands as L-tryptophan, histamine and L-histidine. We now report the thermodynamic properties of ternary complexes of Cu(II) and Zn(II) with *ATP* and aromatic aminoacids as phenylalanine and tyrosine.

The formation of stacking adducts has been checked by spectroscopic measurements. The thermodynamic data obtained by means of potentiometric and calorimetric measurements are compared with those of the corresponding parent complexes measured under the same experimental conditions (25 °C and 0.1 mol dm^{-3} in K[NO$_3$]). The $[\mathrm{Cu}(ATP)_2]^{6-}$ and $[\mathrm{Zn}(ATP)_2]^{6-}$ species were also found to exist; their overall stability constants were determined.

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Thermodynamics of Complex Formation: DL-Isoserine with Nickel(II) and Copper(II)

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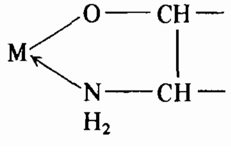
Researches in this laboratory have shown how in aqueous solution, the aminoacids, DL-4-amino-3-hydroxy-butanoic and DL-3-amino-2-hydroxypropanoic acid (isoserine) form complexes with divalent metals. The complexes contain the pentatomic chelate ring



where the alcoholic group appears to be ionized even in acidic solution [1, 2]. On the other hand the corresponding isomers, threonine and serines bind the metal *via* the α-aminoacid moiety and only in alkaline solution the hydroxyl group dissociates and is involved in chelation to the metal [3].

In order to explain the different roles of aminoethanolate and aminocarboxylate moieties in complex formation, we have now undertaken the calorimetric determination of enthalpy changes in the reactions of DL-isoserine with Ni(II) and Cu(II) in aqueous solution at 25 °C and I = 0.1 mol dm^{-3} (KCl).

The calorimetric measurements have been carried out by a modified LKB 8700-2 calorimeter. The values of the thermistor resistence in the reaction vessel were obtained by measuring the output voltage of the unbalanced Wheatstone bridge by a digital microvoltmeter HP 3455A. The e.m.f. values were printed at regular time intervals by a strip-printer HP 5150A with timer and converted to resistence values by an empirical relation.

The ΔH^0 values obtained for the protonation reaction of isoserine, $H_2NCH_2CH(OH)COOH$, H_2L, are:

HL^- $(\log K_1 = 13.2)$, $\Delta H_1^0 = -53.14$ kJ mol^{-1}
H_2L $(\log K_2 = 9.139)$, $\Delta H_2^0 = -43.60$ kJ mol^{-1}
H_3L^+ $(\log K_3 = 2.661)$, $\Delta H_3^0 = -3.70$ kJ mol^{-1}

The enthalpy changes of Ni(II) complexes are:

NiL $(\log K_1 = 9.083)$, $\Delta H_1^0 = -43.34$ kJ mol^{-1}
NiL_2^{2-} $(\log \beta_2 = 13.915)$, $\Delta H_2^0 = -55.44$ kJ mol^{-1}

The data for Cu(II) complexes are:

CuH_2L^{2+} $(\log \beta_{112} = 24.120)$, $\Delta H^0 = -53.43$ kJ mol^{-1}
Cu_2L_2 $(\log \beta_{220} = 34.568)$, $\Delta H^\circ = -118.40$ kJ mol^{-1}

The corresponding entropy changes are rather high, particularly in the copper complexes. This stands for a remarkable entropy contribution to the stability of the complexes, coming from redistribution of water molecules involved in the process.

Some hypotheses on the structure of the complexes can be put forward. They will be tested by extending the calorimetric studies to other ligands containing the aminoethanol moiety.

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