

COMPLEX COMBINATIONS OF TRANSITIONAL METALS WITH MIXED LIGANDS

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abstract: This paper describes synthesis and characterization of ternary complex combinations of Zn(II) and Co(II) with Tyrosine and Cysteine as primary ligands and 2,2'-bipyridyl as secondary ligands. The type of complex combinations form depends on pH. Complex combinations were characterized through IR-spectroscopy, electronic spectra, thermogravimetrycal analysis, electrical conductivity and elemental analysis. Analyzing the result we were able to determine the geometry of complex combinations that we obtained.

Introduction

Complex combinations of metal ions with aminoacids are important because of their biological applications. In 1965 Szazuchin O. and his team studied the synthesis of complex combinations of Zn(II) and Ni(II) with aminoacids: D-Penicilamine and L-Cysteine. These complex combinations have biological and therapeutical activities [1].

In 1970 Final I.L.describes the importance of biological applications of ternary complexes with transition metals using as primary ligand imidazol and as secondary ligand Hystidine [2].

From literature we know that aryl-azobenzimidazol, barbituric acid and their derivatives are important in biochemistry because their imidazolic and barbituric parts are contained in enzymes, proteins and nucleic acids [3,4]. In literature [5,6] are described the biological and therapeutical activities of ternary complex combinations using different amino acids as primary ligand and imidazol as secondary ligand. Those complex combinations were found in biological medium and influence the interaction between drugs and biomolecules [7,8]. It's presumed that the presence of metal ions in biological fluids influences the therapeutical action of drugs.

It is well known that carboxylic acids and their derivatives from Py: e.g. N-(2-acetamido)-iminodiacetic acid and amino acids have biological activities [9] and ternary complex combinations of these ligands with transition metals are important in biological medium, because enzymes are activated by metal ions.

Bunel S. and his team [10] have synthesized ternary complex combination with Zn (II) using 1,10-phenantroline as primary ligand and amino acids: L-Alanine, L-Serine, L-Threonine, L-Proline, L-Valine and L-Leucine as secondary ligands. He proved that the

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volume of the ligands influences the geometry of complex combinations. Many biological studies showed that Zn (II) is more efficient because it inhibits the elimination of histaminic parts from base cell or in elimination of histaminic parts in extra cellular fluids [11]. Zn (II) can be used to diminish pharmacological effects of histamine after its elimination from the base cells. These effects can be used for treating anaphylactic and anafilactidic shocks. It was, also, observed that Zn (II) is capable of inhibition the physiological activity of neurotransmission injected into the sanguine flow (circuit) compared with other metals ions that have the opposite effects [12]. Taking in consideration biological activity of Zn(II) and ternary complex combinations, Kahn F. and his team prepared ternary complex combination with amino acids: α -Alanine, L-Leucine, L-Valine, L-Glutamine, L-Asparagine, L-Lisine, L-Ornithine, L-Threonine, L-Serine, L-Phenylglycina, L-Phenylalanine as primary ligands and as secondary ligands used: acetic and propionic acids [13,14].

Amrallah A.H. and his team proved that in complex combinations of Zn (II), Cu (II) and Cd (II) with imidazol, its derivatives and amino acids the imidazolic part as primary ligand is involved into coordination to metal ions. This interaction was attributed ability to form σ and π bonds [15]. This paper describes synthesis and characterization of some ternary complex combinations of Zn (II) and Co (II) with Tyrosine and Cysteine as secondary ligand depending on pH.

Experimental

a) Synthesis of complex combination using Zn (II), L-Tyrosine (Tyr) and 2, 2'-Bipyridil (Bipy).

An amount of Bipy (0.156g) was dissolved in 10 ml of HCl 0.2M. This solution was added to a solution of ZnSO₄H₂O (0.287g) in 10 ml of HCl 0.2M. The mixture was stirred up for 15 minutes, heating the solution at 65÷70°C. After cooling under energetic stirring, a solution of 0.145 g Tyr in 5ml solution of NaOH 1M was added.

The pH of the solution was adjusted to 4.5 using HCl 0.2 M. It was observed the formation of a grey precipitate that changes the colour to yellow-green after 24 hours. The precipitate was filtered, washed with methanol and dried out.

b) Synthesis of complex combination using Zn (II), L-Cysteine (Cys) and 2,2'-Bipyridil (Bipy).

The procedure for the preparation of this complex is the same with the except that a solution of 0.24 g Cys in 5 ml solution of NaOH 0.1 M was used. pH of the solution was adjusted to 4.5÷5 using HCl 0.2 M. The mixture was allowed to stand at room temperature and after 48 hours an orange precipitate was formed. The precipitate was filtered, washed with methanol and dried out.

c) Synthesis of complex combination using Cu (II), L-Tyrosine (Tyr) and 2, 2'-Bipyridil (Bipy).

An amount of 0.290 g Co(NO₃)₂6H₂O and 0.156 g of Bipy in molar ratio 1:1, were dissolved separate into 10 ml solution of HCl 0.2 M. After the entire amount was dissolved,

the two solutions were mixed under energetic stirring and heated at 60°C, that lead to homogeneous solution. Over the mixture, after cooling and under energetic stirring, it was added a solution of 0.145 g Tyr in 5 ml NaOH 1M.

The mixture was divided in two parts.

To one part the *pH* was adjusted to 5.5 using HCl 0.2 M. A grey precipitate was formed and its colour changed to pink after 24 hours. The precipitate was filtered, washed with methanol and dried.

To the other part *pH* was adjusted to 4÷4.5 and allowed to stand at room temperature for five days. The green precipitate resulted was filtered, washed with methanol and dried.

d) Synthesis of complex combination using Co (II), L-Cysteine (Cys) and 2,2'-Bipyridil (Bipy).

The procedure is the same as we described at c), but it was used 0.24 g Cys in 5 ml NaOH 0.1 M. the *pH* was adjusted to 4.5÷5 using HCl 0.2 M. The mixture obtained was coloured brown light and after 48 hours a precipitate red-brown was formed. The precipitate was filtered, washed and dried.

For the characterization of complex combinations obtained were used: electronic spectra performed with spectrophotometer VSU-2P diffuse reflectance technique (using MgO), IR spectra (KBr) using Spekord M-80 Carl Zeiss Jena spectrometer, in the range 4000÷400 cm⁻¹, elemental analysis for C,N using a Carlo-Erba LA 118 analyser, and AAS-1N Carl-Zeiss-Jena spectrometer for Zn(II) and Co(II), thermo gravimetric analysis using MQ-1500 derivatograph and molar conductance in nitrobenzene solution on Consort C-533 conductometer.

Results and Discussion

The results of elemental analysis, molar electrical conductivity determined for the 10⁻¹M solutions of complex combination in nitrobenzene and *pH* values of solution that lead to the complex combination are given in Table 1.

Table 1. Data for elemental analysis, molar electrical conductivity and *pH*.

Compound	Colour	<i>pH</i>	C(%) calc. det.	N(%) calc. det.	M(%) calc. det.	Λ ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)
[Co(Tyr) ₂ (Bipy)]	Pink	5.5	58.43 59.62	9.82 8.80	10.26 9.96	11
[Co(Tyr)(Bipy)(H ₂ O) ₂](NO ₃)	Green	4÷4.5	46.81 47.30	11.08 10.50	12.11 11.86	24
[Zn(Tyr)(Bipy)] ₂ SO ₄	Yellow-green	4.5	50.77 51.82	9.35 8.76	11.67 11.20	57
[Co ₂ (Cys)(Bipy) ₂ (H ₂ O) ₂](NO ₃) ₂	Brown-red	4.5÷5	37.68 38.71	13.52 12.91	14.25 13.92	53
[Zn ₂ (Cys)(Bipy)]SO ₄	Orange	5	30.80 31.56	9.00 8.21	20.90 20.35	27

From the experimental date obtained through electrical conductivity resulted that complex combination $[\text{Co}(\text{Tyr})_2(\text{Bipy})]$ has a character of nonelectrolyte and the other two are electrolytes.

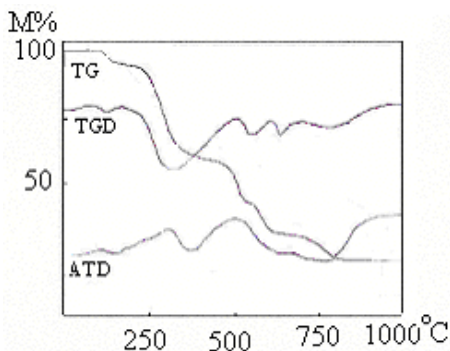


Fig. 1: Curve of thermal analysis for complex combination $[\text{Co}_2(\text{Cys})(\text{Bipy})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$.

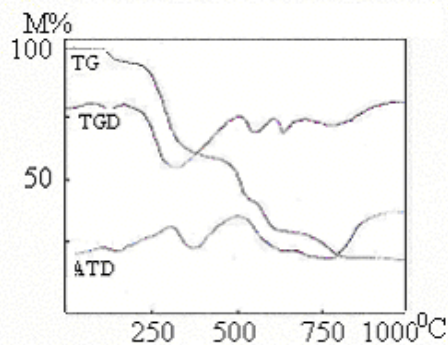


Fig. 2: Curve of thermal analysis for complex combination $[\text{Zn}_2(\text{Cys})(\text{Bipy})]\text{SO}_4$.

Curve of the loss of weight TG and TGD for Co(II) complex: $[\text{Co}(\text{Tyr})(\text{Bipy})(\text{H}_2\text{O})_2]\text{NO}_3$ green and $[\text{Co}_2(\text{Cys})(\text{Bipy})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ brown-red indicate a loss of weight from $130^\circ\div 140^\circ\text{C}$ corresponding to 2 molecules of water per mol of complex combination. Between $220^\circ\div 360^\circ\text{C}$ the loss of weight is 32.20% with a maximum of temperature at 305°C for complex combination $[\text{Co}(\text{Tyr})(\text{Bipy})(\text{H}_2\text{O})_2]\text{NO}_3$ and 38.18% with a maximum of temperature at 294°C for $[\text{Co}_2(\text{Cys})(\text{Bipy})(\text{H}_2\text{O})_2](\text{NO}_3)_2$. For the green combination we observed the third loss of weight 37.30% with a maximum of temperature at 610°C corresponding of one mol of complex. For the brown-red combination between $494^\circ\div 635^\circ\text{C}$ we have a loss of weight of 28.10% in two steps that indicates the elimination of one mol of Cys from two molecule of complex combination. We can presume that S-S bond is broken from Cys molecule and elimination of the two fragments took place in two steps. The final step of loss of weight $690^\circ\div 800^\circ\text{C}$, $694^\circ\div 810^\circ\text{C}$ suggests that NO_3^- is eliminated and the residue corresponds to Co_2O_3 . In Fig. 1 is presented the loss of weight (TG and TGD) and the curve of differential analysis (ATD) which indicates the effect endo-exothermic that accompanies the loss of weight for complex combination: $[\text{Co}_2(\text{Cys})(\text{Bipy})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$.

The curve of thermo analysis for $[\text{Co}(\text{Tyr})_2(\text{Bipy})]$ doesn't indicate the elimination of water molecules or NO_3^- groups.

Curve for loss of weight TG and TGD for complex combination of Zn(II): $[\text{Zn}(\text{Tyr})(\text{Bipy})_2]\text{SO}_4$ yellow-green $[\text{Zn}_2(\text{Cys})(\text{Bipy})]\text{SO}_4$ are characterized by three steps in the same ranges of temperature.

For complex combinations $[\text{Zn}_2(\text{Cys})(\text{Bipy})]\text{SO}_4$ the loss of weight between $480^\circ\div 644^\circ\text{C}$ took place in two steps. In Fig. 2 are presented the curve of weight loss (TG and TGD) and differential thermal analysis (ATD) corresponding to the loss of weight for $[\text{Zn}_2(\text{Cys})(\text{Bipy})]\text{SO}_4$ complex.

The absorption bands corresponding to stretching and bend frequencies for ligands and for the complex combinations prepared are given in Table 2. For the spectral data of complex combinations were attributed signals corresponding to atoms or group of atoms involved in coordination and the signals corresponding to the groups not involved in coordination.

So, the bands from 3107 cm^{-1} , 1602 cm^{-1} , 1513 cm^{-1} corresponding to stretching and bend frequencies (δ -amino acid I, δ -amino acid II) can be attributed to $-\text{NH}_2$ from Tyr are shifted to higher wave numbers in complex combination spectrum. This proves that the group $-\text{NH}_2$ is involved in coordination.

Table 2. Data of IR spectra for ligands and complex combinations prepared (cm^{-1}).

Compound	ν_{OH}	ν_{NH}	$\delta_{\text{NH(I)}}$	$\delta_{\text{NH(II)}}$	ν_{COOH}	$\nu_{\text{C-S}}$	$\nu_{\text{S-S}}$	$\nu_{\text{C-N}}$	ν_{COO} ...M
Tyr	–	3107m 2601s 2080s	1602m	1513m	1887m	–	–	–	–
[Co(Tyr) ₂ (Bipy)]	–	3440i	1620s	1580s	–	–	–	–	1634 m
[Co(Tyr)(Bipy)(H ₂ O) ₂] N O ₃	3480	3438i	1625s	1581s	1875m	–	–	–	1630 m
[Zn(Tyr)(Bipy)] ₂ SO ₄	–	3432i	1620m	1585s	–	–	–	–	1762 m
Cys	–	3037m 2570s 2078s	1650m	1486 i	1730m	667 m	532i	–	–
[Co ₂ (Cys)(Bipy) ₂ (H ₂ O) ₂] NO ₃) ₂	3487	3035m 2572s 2073s	1651m	1487m	–	636s	527m	–	1631
[Zn ₂ (Cys)(Bipy)]SO ₄	–	3030m 2570m 2071s	1650	1485	–	623 m	505s	–	1605
Bipy	–	–	–	–	–	–	–	1555i	–

The position of absorption bands corresponding to the same frequencies of Cys, from the complex combination IR spectrum, is unchanged. This behaviour indicates that, the $-\text{NH}_2$ group from amino acid is not involved in coordination. This confirms once again the information from literature [16]. If the synthesis of complex combination takes place at $\text{pH} > 4$, in coordination are involved $-\text{COOH}$ groups and atoms of sulfur.

The frequency of vibrations ν_{COOH} , attributed to the absorption bands from 1880 cm^{-1} (Tyr) and 1730 cm^{-1} (Cys) are situated in the spectrum of complex combinations, to lower wave numbers. This fact indicates amino acids coordination to metal ions through $-\text{COO}^-$ in ionized form.

The vibration frequencies $\nu_{\text{C-S}}$ and $\nu_{\text{S-S}}$ from IR spectrum of complex combination with Cys ligand are situated to lower wave numbers, indicating that the sulfur atoms are involved in the coordination, that are more polarizable than nitrogen atoms in the process of coordination.

This frequency can be attributed to ν_{OH} given by water molecules coordinated. The presence of water molecules in complex combination composition is indicated also by thermo gravimetric analysis.

From the data we presented so far we can consider that Tyr as ligand coordinates to metal ions through $-\text{COOH}$ group ionized and through $-\text{NH}_2$ group and the Cys ligand is coordinated through $-\text{COOH}$ group ionized and sulfur atoms only if the $\text{pH} > 4$.

We point out that, for all complex combination that we prepared, the band located at 1555 cm^{-1} disappears. The band from 1555 cm^{-1} , strong, is characteristic of C=N group from 2,2'-Bipyridil. This proves that nitrogen atoms from Bipyridinic unit are coordinated to metal ions.

In Table 3 are presented the type of transitions observed in electronic spectra for the ligands and their complexes.

Table 3. d-d Transitions from electronic spectra.

Compound	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	$L \rightarrow M$	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	${}^4T_{1g}(F) \rightarrow {}^4A_{1g}(F)$	Dq	B
Tyr	47393	41150	-	-	-	-	-
[Co(Tyr) ₂ (Bipy)]	46296	39270	-	21739	17699	983	1055
[Co(Tyr)(Bipy)(H ₂ O) ₂](NO ₃)	45871	38910	-	21551	17543	974	1046
[Zn(Tyr)(Bipy)] ₂ SO ₄	43668	34965	29000	-	-	-	-
Cys	45454	38461	-	-	-	-	-
[Co ₂ (Cys)(Bipy) ₂ (H ₂ O) ₂](NO ₃) ₂	44450	37735	-	22421	-	-	-
[Zn ₂ (Cys)(Bipy)]SO ₄	41152	34965	31645	-	-	-	-

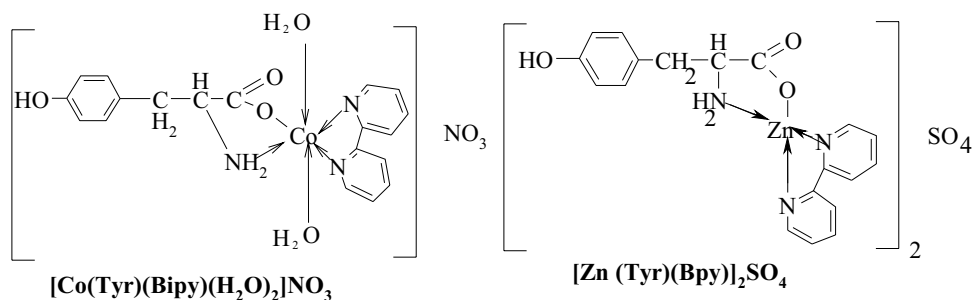
From the value of their transitions, from complex combination of Co, we determined the parameter Dq and B using the following relationships: [18]

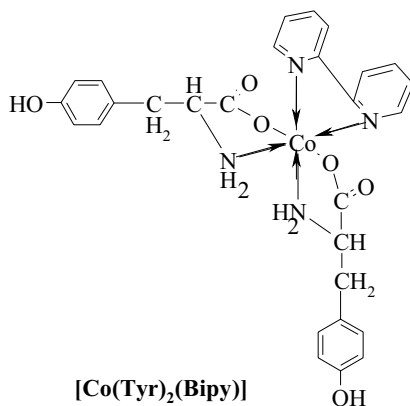
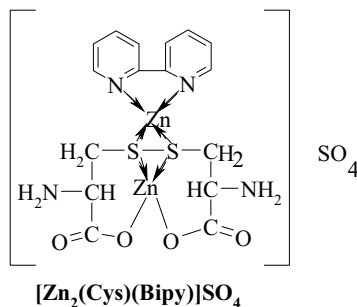
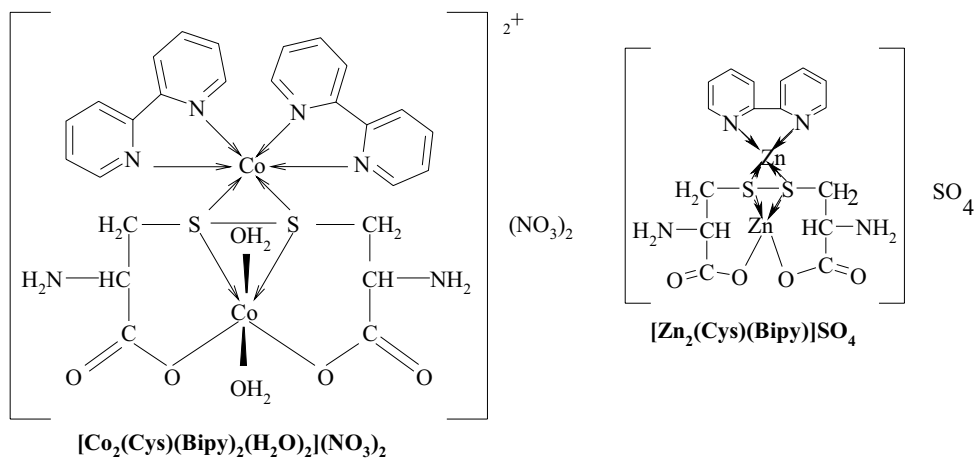
$${}^4A_{2g} \rightarrow {}^4T_{1g} = 18Dq$$

$${}^4T_{1g}(P) \rightarrow {}^4T_{1g}(F) = 6Dq + 15B$$

The calculated Dq and B values are specific to octahedral Co(II) complexes. Charge transfer bands, $L \rightarrow M$, were observed at 29000 and 31645 cm^{-1} in the UV-VIS spectra of Zn(II) complexes [18].

From experimental data we can suppose that the structures of ternary complex combination prepared are:





In conclusion, we obtained ternary complex combination with Co(II) and Zn(II) using as primary ligands amino acids L-Tyrosine and L-Cysteine and 2,2'-Bipyridil as secondary . Depending on pH value, the coordination mode of L-Cysteine is different. Probable geometry of complex combination was attributed using experimental data.

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