Spectroscopic and thermal studies of mixed ligand coordination compounds of cobalt (II) with aspartic and dicarboxylic acids

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Abstract. The synthesis of complex compounds of cobalt (II) ion in the presence of aspartic and dicarboxylic acids has been studied by thermal and spectroscopic methods. Thermal decomposition processes of these compounds are studied on the basis of thermal analysis, and endo- and exo-effects are determined. The decomposition products of the compounds were studied on the basis of mass reduction by the thermogravimetric method. Based on the results of spectroscopic studies, the structural formulas of the synthesized coordination compounds are established.

1 Introduction

The special properties of amino acids are biologically important substances, and the use of the properties of ligands in complex compounds in the field of mining and metallurgy is developing every year and the scope of its application is expanding. Especially in the field of biometallurgy, reactions involving amino acids and proteins form the basis of technological processes for processing mineral raw materials (ores) with the participation of various microorganisms and extracting basic and additional components from them. In recent years, interest in complex compounds of intermediate metal ions with biologically active ligands has sharply increased, which is explained by the fact that metal ions play an important role in many different biological processes [1-4].

Coordination compounds of biometals with amino acids exhibit activity similar in composition, structure, and properties to the active centers of many metalloenzymes [5-6].

This article is also one of the works carried out for the purpose of systematization of research in the field of coordination chemistry [7-8].

In all parts of the tree of bitter almonds (branches, shoots, roots and seeds of unripe fruits) there is mainly the substance monoglycoside prunazine, and the substance amygdalin (diglycoside) accumulates in bitter almond seeds [9-11]. Amygdalin was isolated from cyanoglycoside seeds using HPLCH, a special phase colon LC-18 (150 mm x 4.6 mm, 5 m). As a motile phase, acetonitrile:the water system (50: 50) was passed at a rate of 0.5 ml/minute and the detection was carried out at a wavelength of 215 nm. Since the linearity of the

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experiments was 0.9949, the detection limit for amygdalin was 0.88 and 2.93 mg, respectively. [12-16].

Inorganic salts of trace elements are not used in medicine because of their toxicity. The inclusion of trace elements in coordination compounds increases its biological activity and significantly reduces toxicity [17-20]. Therefore, the search for new biologically active metal complexes is very relevant.

Complexes of cobalt with aspartic acid and dicarboxylic acids in the coordination environment are not described in the literature, so the aim of this work is to synthesize and study complex compounds of cobalt(II) with aspartic acid and dicarboxylic acids. During the research work, solid compounds were synthesized and their properties and structure were studied in various ways.

2 Materials and methods

For the synthesis of coordination compounds, reagents such as cobalt(II) sulfate. $Ba(OH)_2$ (kh. ch. brand) ligands were used. Aspartic acid (Asp) and dicarboxylic acids (oxalic (OX), malonic (Mal), succinic (Suc), and glutaric (Glut), the company "REONAL" (Hungary) brand "c. f. a.").

The amount of metals in the synthesized compounds was determined by spectrophotometric and titrimetric methods [9]. Nitrogen was determined by the Kjeldahl method, and carbon and hydrogen were burned in an oxygen stream [9-10].

IR absorption spectra were recorded in the range of 400-4000 cm^{-1} on an IR Tracer-100.

Fourier spectrometer (Shumadzu) in the form of a tablet of KBr samples.

Thermal analysis was performed in derivatograph systems Paulik-Paulik-Erdiy and Lyabsys-IVO 1400 derivatographs with a speed of 10 deg / min and a sensitivity of T-900, TG-100, DTA-1/10, and DTR-1/10 galvanometers. Recording was performed at atmospheric pressure with continuous loss of gas atmosphere using a water pump. The holders were a cap less platinum crucible with a diameter of 7 mm. Al_2O_3 was used as the standart.

3 Results and discussion

For the synthesis of complex compounds of cobalt (II) ions were prepared, equimolar amounts of aspartic and dicarboxylic acids, cobalt sulfate were prepared and some amounts of $Ba(OH)_2$ were added to them for complete precipitation of SO_4^{2-} ions.

The general scheme of the chemical process as follows:

$$CoSO_4+HA+HB+Ba(OH)_2=CoAB+BaSO_4+2H_2O_2O$$

(Here HA and HB are molecules of aspartic and dicarboxylic acids)

After filtering the $BaSO_4$ precipitate, the mixture was heated in a water bath until the film was formed over the solution and the product was extracted with less polar solvents mixed with water (acetone, isopropyl alcohol). In cases of formation of hygroscopic products, the substances were dried in a desiccator over concentrated H_2SO_4 or $CaCl_2$. The results of the element analysis are presented in the table.

Table 1. Results of elemental analysis of coordination compounds of cobalt with aspartic acid and dicarboxylic acids.

Complex connections	**Found/Calculated, %**				**t.liquef. ℃**	**λ, Cμ/m C=0.01 m**
	C	**H**	**N**	**Co**		
Co $(Asp)_2 \cdot 8H_2O$	21.41/ 20.56	4.03/ 6.00	6.01/ 6.00	12.52/ 12.62	280	91.68

Co(Asp·OX)·5H_2O	22.97/ 23.91	4.06/ 4.78	6.47/ 5.58	10.91/ 11.74	250	68.81
Co(Asp·Mal)·8H_2O	20.94/ 19.92	3.27/ 5.18	2.93/ 2.19	13.83/ 12.22	200	110
Co(Asp·Suc)·5H_2O	24.14/ 24.43	3.76/ 4.75	3.05/ 3.17	14.51/ 13.33	220	14
Co(Asp·Glut)·5H_2O	26.21/ 26.22	3.70/ 5.83	3.60/ 3.40	13.69/ 14.30	240	31

Heterolygand complexes of cobalt with dicarboxylic acids of aspartic acid were synthesized and their thermal analysis was studied. To determine the water molecules in the inner and outer spheres of complex compounds, we performed thermal analysis of these compounds in the temperature range from 10°C to 700° C.

The derivatogram of the complex compound $[Co(Asp)_2{\cdot}2H_2O]{\cdot}6H_2O$ shows an endoeffect at 107°C. With the corresponding hydration of the water molecule in the outer sphere. The mass loss occurs in the temperature range of 60-145 °C and contains 13.64%. Which corresponds to three water molecules.

At the second stage of thermal decomposition, the mass loss is 21.82% and occurs in the temperature range of 145-270 °C. The endoeffect is also observed at 250 °C, while five water molecules are released, and the final product of the thermolysis process remains Co_2O_3.

Endo- and exo-effects are also observed in the derivatogram of the $[Co(Asp^*Mal)2H_2O]6H_2O$ complex. Thermolysis of the complex occurs in the range of 175-250 °C, at which the total weight reduction is 14.79% and corresponds to the decomposition of hydrate and coordination waters. Decomposition of complex compounds continues with an exo-effect at 380°C, and the mass loss is 29.57 and 26.10%. Here, the remaining water is released, the ligands decompose, and oxide is formed as the final product.

Thus, in other complexes, the thermolysis process proceeds similarly: external-sphere and co-ordination water molecules are hydrated, and then the ligands of complex compounds are decomposed [21].

To determine the coordination of ligands to the central atom in synthesized coordination compounds by their spectroscopic analysis. In the IR spectrum of the starting substance, aspartic acid, an absorption band is observed in the following regions: 1300, 1330, 1420, 1530, 1610, 1700, 1720, 1740, 3130 cm^{-1}.

Oxalic acid has a very intense band at 1710-1690 cm^{-1}, malonic acid has two bands at 1690 and 174 cm^{-1}, succinic and glutaric acids have a clear absorption band at 1700 cm^{-1} and a weak absorption band at 1780-1800 cm^{-1}, all of these absorption bands characterize the carboxyl group [22].

It is interesting to note that in the IR spectra of malonic, succinic, and glutaric acids, the absorption bands that explain acid dimerization are observed in the range of 2750-2500 cm^{-1}, while the OH groups exhibit them as a broad band near small peaks in the range of 3000-2500 cm^{-1}. This is explained by the correlation of these vibrations with dimeric vibrations of a rather low frequency and stretching of hydrogen links.

The IR spectra of coordination compounds are fundamentally different from those of the starting materials.

In the spectrum of complex compounds $[Co(Asp)_2 {\cdot}8H_2O]$, the absorption band is observed in the following regions: 3500-2900 cm^{-1}(wide), 1630-1500 cm^{-1}, 1410, 1300, 1250, 1190, 1120, 1030(weak), 980 (weak), 890, 860, 730, 680, 620, 590, 530, 450 cm^{-1}.

Absorption bands belonging to the $–COO^-$, $–NH_2$ and H_2O functional groups, it can also be observed in the spectra of coordination compounds with heteroligands. For example, in the spectrum of the $[Co(Asp)_2{\cdot}Ox]{\cdot}5H_2O$ complex, absorption bands are observed in the following regions: 3500-2900 cm^{-1}(maximum 3000 cm^{-1}), 2720, 2670, 2500, 2340,2020 cm^{-}

^{1}(weak band), 1680, 1620, 1590, 1540, 1520, 1500, 1410, 1320, 1300, 1250, 1130, 1120, 1100, 1080(weak), 1020, 980, 890, 860, 820, 780, 740, 685, 650, 620, 590, 540, 450 cm^{-1}.

In the IR spectra of oxalic acid, the absorption band is observed in the following regions: 3500-3300 (maximum 3400), 1930, 1900, 1870, 1820, 1790, 1760, 1720, 1680, 1420, 1410, 1260, 1210, 1200, 1100, 900, 790, 700 cm^{-1}.

In the IR spectra of the complex $[Co(Asp\cdot Mal)]\cdot 8H_2O$ absorption spectra are observed in the following regions: 3500-2900(wide flat band), 2720, 2660, 2500, 1320, 1240, 1130, 1100, 980, 950, 920, 890, 870, 780, 740, 710, 650, 600, 550, 450 cm^{-1}.

The following absorption bands are observed for the $[Co(Asp\cdot Ynt)\cdot 5H_2O]$ complex: 3550-2800(wide intense band), 2600, 2510, 2350, 1700-1500 (total bandwidth), 1400-1380, 1290, 1180, 1120, 1090, 890, 790,620, 540-520 cm^{-1}.

For a complex compound, the following absorption bands are observed: 3600-2800 (wide band), 2650, 2340, 1710, 1610-1540, 1400, 1300, 1250, 1140, 1050, 990, 890, 830, 800, 780, 660, 600, 550 cm^{-1}.

The absorption bands at 1930, 1900, 1870, 1820, and 1790 cm^{-1} belonging to the non-ionized carboxyl of the ligand disappear or strongly shift, and the absorption spectrum at 1680-1500 cm^{-1} appears in their place in the spectrum of the complexes^{-1}, which indicates that this group is coordinated with the central ion.

The absorption bands at 1620-1590 cm^{-1}, corresponding to asymmetric vibrations of ionized carboxyl, and the band corresponding to symmetric vibrations of the same group, are observed at 1410 cm^{-1}. The absorption band 450-540 cm^{-1} belongs to the M-O bond; this band is not detected in the ligand spectrum.

For NH_2-valence vibrations, absorption bands are observed in the region of 3000 cm^{-1}, while deformation vibrations appear at 1500 cm^{-1}. The absorption band for M-N is observed at 640 cm^{-1}. In the spectra of complex compounds, the formation of shallow broad absorption bands in the region of 3500-2900 cm^{-1} indicates the presence of water molecules in these compounds. Their strong shift to the low-frequency region and the appearance of a band at 2720, 2670, and 2500 cm^{-1} indicate the formation of hydrogen bonds [23-24].

Thus, based on the obtained data, it can be assumed that the structures of all heteroligand complexes are similar, and the ligands coordinate with the central ion in the same way.

Usually, the cobalt(II) ion has an octahedral configuration and is considered $^4T_{1g}(t_{2g})^5(e_g)^2$ or $^2E_g(t_{2g})^6(e_g)^1$. Therefore, to determine its position in coordination compounds, we studied the electronic absorption spectra in the UV and visible regions [25].

Ligands produce UV absorption bands at wavelengths of 215 nm (Asp), 225 nm (Glut), 420 nm (Suc), 210 and 275 nm (Ox), and 215 and 280 nm (Mal). These absorption bands belong to the group $\nu_{C=O}$ and correspond to the electron transition $n\rightarrow\pi^*$. Absorption bands in the spectrum of coordination compounds are observed in the UV region: 215 nm$[Co(Asp\cdot Ox)]$; 220 nm$[Co(Asp\cdot Mal)]$; 200 nm $[Co(Asp\cdot Suc)]$; 205 nm$[Co(Asp\cdot Glut)]$, which differ from the spectra of the original ligands.

In the visible region, absorption bands are observed at 510-520 nm, corresponding to the energies of the levels 19600 and 19230 cm^{-1}, and the electron transition corresponds to $^4A\rightarrow{}^4T_{1g}$ (P). Weak absorption bands are also observed in the spectra at 605 nm, corresponding ^{to} $^4T_g\rightarrow{}^4A_{2g}$ electron transitions at 16530 cm^{-1} [25]. The results of the study are consistent with the IR spectrum data.

4 Conclusion

It has been established that during thermal analysis of complex compounds of aspartic and dicarboxylic acids, hygroscopic and coordination waters (100-250°C) are first released, then the coordinated ligands decompose to form metal oxide (300-700°C).

The structure of complex compounds and coordination of ligands was determined based on spectroscopic (IR and UV spectroscopy) studies of newly synthesized compounds. The results obtained showed that the ligands are coordinated to the central ion through donor O and N atoms.

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