



PREPARATION AND STUDY OF MIXED-LIGAND COMPLEXES OF CHROMIUM WITH ACETYLACETONE AND ACETAMIDE

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ABSTRACT

Recently, great importance has been attached to the study of the synthesis, composition, structure, and properties of complex compounds with heteroligands. It is important to determine the centers of coordination, to determine the geometric structure, composition and properties of compounds with heteroligands. In this article, methods for the synthesis of complex compounds with mixed heteroligands formed by chromium salts with acetamide and acetylacetone are studied.

INTRODUCTION

Many scientists are studying complex formation reactions, establishing reaction mechanisms, studying complex compounds in solutions and isolating them in solid form.

At the same time, attention is growing to the synthesis and study of complex compounds of transition metals with oxygen-containing heteroligands. The presence of two carbonyl groups in the acetylacetone molecule provides high coordination [1]. The structure of complex compounds formed by transition metals with acetylacetone is the subject of many works, in which the structural features of such complexes were studied, which are determined by various factors, including the nature of the metal, the presence of a substituent in the ligand, and its type. These properties of acetylacetone allow the synthesis of complex compounds with different structures and physicochemical properties [2].

Currently, complex compounds with heteroligands are used in medicine, polymers, analytical chemistry, photosensitive materials, production of corrosion inhibitors, plant growth accelerators, and radiochemistry. Based on the above information, it is important to study the formation of complexes with ligands, to give a scientific justification for their composition, structure and properties [3].

The study of mixed-ligand complexes suggests the need to introduce a number of refinements to the fundamental concepts of coordination chemistry. This is due to the fact that such complexes play an important role in redox processes, participate in physiological processes and enzymatic reactions of various biological systems [4]. In this case, the individuality of complexing elements often manifests itself, which, in turn, opens up prospects for increasing the selectivity and sensitivity of identification, separation and concentration of components [5].

The stability of mixed-ligand complexes is usually compared with the stability of the corresponding binary complexes, since it allows one to determine the type of coordination, the coordination number of the metal ion, the nature of the ligands involved in the formation of coordination compounds, etc. [6].

Mixed-ligand complexes in solutions were studied mainly by spectrophotometric, spectrographic methods and potentiometric titration. To determine the stability constants of mixed-ligand complexes, the Irving-Rossotti method is used, as well as the methods of Berrum, Thompson and Loraas to determine the stepwise formation constants [7]. A fundamentally new approach to determining the stability constants of complexes - the method of potentiometric surfaces proposed by Lefebvre deserves special attention, it can be applied to systems where two different ligands are simultaneously attached to a complexing ion. The most complete information on the formation of mixed-ligand metal complexes is provided by the method of mathematical modeling [8].

Currently, mixed-ligand complexes are widely studied, in which the main ligand is a complexone, and additional ligands can be different. In complexes of transition elements with mixed ligands, the coordination number of metals is 6, and the denticity of ligands is less than 6 [9].

Binary complexes of d-elements contain water molecules $MA \cdot nH_2O$, which can be replaced by a second ligand without changing the structure of the main complex during the formation of mixed-ligand complexes. The formation of complex compounds of d-metals, the coordination sphere of which contains two different complexones, can be carried out in two ways: during the formation of the complex, the main more stable complex is not destroyed when the remainder of the second complexone is added, or two ligands interacting with the d-metal ion have approximately the same ability form a complex, and the composition of the complex is determined by the ratio of the concentration of ligands [10].

Crystal hydrates of chloride, acetate, chromium (III) nitrate of "chemically pure" grade and the corresponding organic solvents subjected to purification and drying according to known methods were used in the work [11].

EXPERIMENTAL

Complex compounds were synthesized according to the known method [12]. According to it (0.01 mol) 0.59 g of acetamide (AA), (0.01 mol) 1 g of acetylacetonone (AcAc) and chromium (III) chloride 1.585 g (0.01 mol) were mixed in a mortar. When mixed, the color of the mixture was dark green. The mixture was dissolved in 50 ml of ethanol and refluxed for 30 minutes, then left to crystallize. After 3 days small crystals formed, which were filtered off and washed several times with ethanol. The yield was 65%.

RESULTS AND DISCUSSION

The IR absorption spectra of the compounds were studied in the range of 400–3800 cm^{-1} using a pelleted sample with KBr 7 mm in diameter on an IRAffinity-1S Shimadzu spectrophotometer (Japan).

Complex compounds were identified using an XRD-6100 powder diffractometer (Shimadzu, Japan). It was carried out under the influence of $CuK\alpha$ radiation (β -filter, Ni, $\lambda=1.54178\text{\AA}$, current and voltage in the X-ray tube 30 mA, 30 kV). In this case, the constant rotation speed of the detector was 4 deg/min with a step of 0.02°, and the scanning angle varied from 4° to 80°. The results of derivatography were analyzed to determine the thermal stability of complex compounds and the presence of water molecules in the complex. The composition and structure of complex compounds of metal salts were studied using thermal analysis.

Color, product yield, melting point and results of elemental analysis of complex compounds are presented in Table. 1, and the solubility of complex compounds in various solvents - in table. 2.

Table 1.

Characterization of the ligand and synthesized complex compounds

Substance	Color	Yield %	Melting point °C	% elemental composition			formula
				C	N	M	
[Cr(Acac) ₂ (AA) ₂]	Brown	75	235-240	45,65	7,6	14,13	C ₁₄ H ₂₄ O ₁₆ N ₂ Cr
[Cr(Acac)(AA) ₂]	White	65	199-201	39,25	6,5	26,17	C ₁₄ H ₂₄ O ₁₆ N ₂ Cr

Table 2.

Solubility of synthesized mixed-ligand complex compounds

Substance	Water	Ethanol	Acetic acid	Benzene	DMF	DMSO
[Cr(Acac) ₂ (AA) ₂]	I	I	S	I	S	S
[Cr(Acac)(AA) ₂]	H	I	H	I	S	S

S. – soluble; H. –hardly soluble, I– insoluble

In the IR spectrum of the complex compound containing [Cr(AcAc)₂(AA)₂], the frequencies of symmetric and asymmetric vibrations of the carbonyl group in the acetamide molecule appear in the region of 1742 and 1690 cm⁻¹. In addition, absorption lines appeared in the low-frequency range at 591 cm⁻¹, corresponding to the νN→M stretching vibrations, which indicates the coordination of the acetamide molecule through the nitrogen atom of the amino group. In the region of 678 cm⁻¹ of the spectrum, M-O stretching vibrations appeared, where the bond is formed through the oxygen atom in acetylacetone. As a result of the connection of one of the 2 oxygen atoms in the acetylacetone molecule with the metal atom through an ionic bond, and the other through a coordination bond, the double bonds of the oxygen atoms open, which leads to delocalization of the bond in the resulting chelate.

The EPR spectra of the synthesized complex compounds were determined in the X-band (λ=3 sm, ν = 9500 MGs, Ho =3400 e).

The formation of a mixed ligand complex by EPR spectroscopy has been little studied. This is due to the fact that the mathematical processing of the obtained experimental data is rather complicated. Interpretation of the EPR spectra is difficult because the signals of complexes of different composition strongly overlap, since the parameters of the spectra - the linewidth and position of the signals - are little sensitive to changes in coordination.

The complexes with a square planar structure studied by us have isotropic EPR spectra in solutions similar to the spectra of previously studied compounds and characteristic of bihedral chromium(III) complexes.

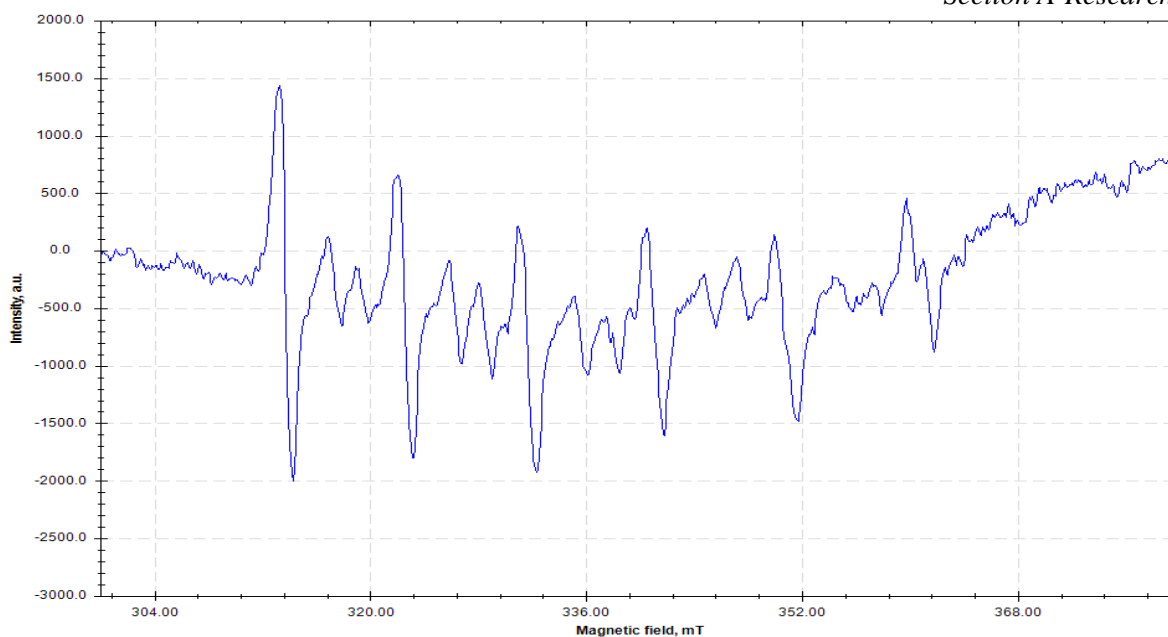


Fig. 1. EPR spectrum $[Cr(AcAc)_2(AA)_2]$

CONCLUSIONS

Based on physicochemical studies, it was concluded that the structure of the complex compound consists of acetamide, metal and acetylacetonate in a ratio of 2:1:2, and the structure of complex compounds synthesized with Cr(III) metal salts can be as follows (Fig. 2) :

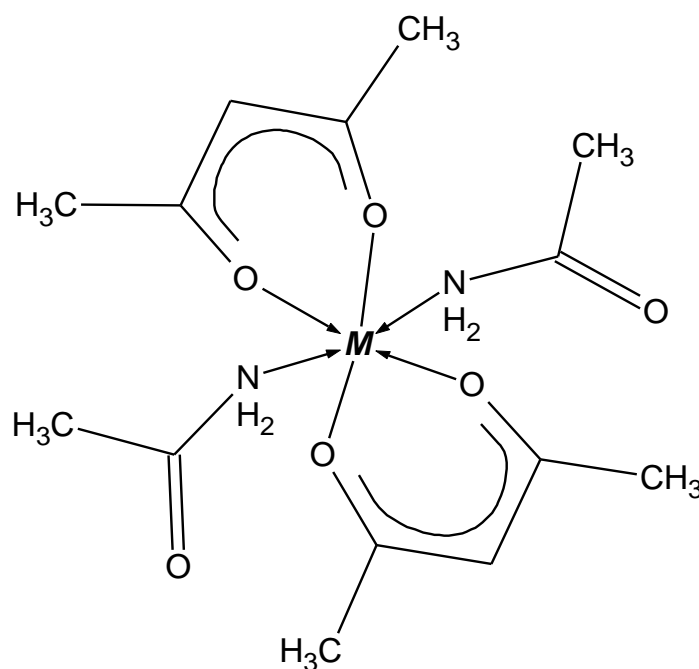


Fig. 2. Cr(III) complex compound formed by acetamide and acetylacetonate

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