

Synthesis, Physico-Chemical Properties, Structure of Acetamide and Dimethyl Sulfoxide Coordination Compounds

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Abstract. This article describes the synthesis of acetamide compounds in ethanol and dimethyl sulfoxide by isothermal solubility technique at 25°C. Physicochemical properties of synthesized coordination compounds, IR absorption spectra and thermal stability were studied. Decomposition kinetics of coordination compounds $\text{CoCl}_2 \cdot 4\text{CH}_3\text{CONH}_2$, $\text{NiCl}_2 \cdot 4\text{CH}_3\text{CONH}_2$ were characterized. Geometric structures of $\text{MnCl}_2 \cdot \text{CH}_3\text{CONH}_2 \cdot (\text{CH}_3)_2\text{SO}$ complex compounds were optimized by quantum-chemical calculation.

Keywords: Synthesis, Physico-chemical properties, Acetamide, Dimethyl sulfoxide, Coordination compounds, Derivatogram

1. INTRODUCTION

In recent years, the chemistry of metals coordination compounds [1-3] with various classes of organic and inorganic ligands [4, 5] has been intensively developed, since many fundamental and applied problems are solved within the framework of complex formation theory [6]. Among the various organic ligands, nitrogen and sulfur containing compounds of Acetamide (AA) have reactive ligands [7].

The presence of three active centers in its molecule, the oxygen atom of carbonyl group, the nitrogen atom of amino group with single electrons pairs and hydrogen atoms capable of forming hydrogen bonds and, in addition, the molecules high polarity determines reactivity of acetamide with both organic components and inorganic salts [8-10]. Acetamide and its compounds are widely used as insectofungicides, plant growth stimulants, feed additives, polymers and resins, cathode materials in chemical current sources.

There are many known compounds of acetamide with inorganic salts, which synthesized in aqueous solutions [11]. Some of these compounds obtained by the preparative method in alcoholic medium.

It is known that metal ions complex formation ability depends significantly on the solvents properties. Solvents shift the reaction equilibrium, strongly influence the reaction mechanism and act not only as a medium but also as a direct participant in chemical equilibrium. Consequently, the study of interaction between acetamide with inorganic salts in non-aqueous protic and aprotic solvents [12], i.e. in ethyl alcohol and dimethyl sulfoxide (DMSO) is of particular interest.

Ethyl alcohol belongs to protolytic donor solvents and is widely used in chemical and pharmaceutical industries for the synthesis of complex compounds and drugs [13]. DMSO is of considerable interest in the chemistry of coordination compounds due to the presence of two electron-donating atoms in the molecule O, S as an active complexing ligand and possesses a wide range of biological and therapeutic activities.

Consequently, the synthesis and study of new biologically active complex compounds of metals with AA and DMSO, elucidation of the effect of solvents, as well as the mutual influence of the nature of ligands in the process of complexation is an urgent task.

Research purpose and objectives in this work are aimed to systematically study interaction of acetamide with inorganic salts in non-aqueous solvents by solubility method, as well as the physicochemical properties of new formed coordination compounds.

In this regard, the following tasks were set: 1) determination of compositions and compounds amount formed in heterogeneous systems, inorganic salt - acetamide - ethyl alcohol and inorganic salt - acetamide - DMSO, the nature of their dissolution, concentration limits of their crystallization from saturated solutions, identification of as synthesized coordination compounds by chemical, physical and physicochemical methods and application of new acetamide compounds. This research was carried out in Chemical Technologies laboratory in the Kyrgyz Academy of Sciences on topic "Study of bioactive ligands interaction with inorganic salts in aqueous and water-organic systems to obtain stimulants and plant growth, regulators. The scientific novelty in this work is related to the study of solubility at 25 °C in 12 three-component systems containing acetamide, chlorides of

manganese, cobalt, nickel, magnesium, zinc, cadmium and ethyl alcohol and acetamide, chlorides of manganese, cobalt, nickel, magnesium, zinc, cadmium and DMSO, in which formation of 12 complex compounds of various stoichiometric compositions were established;

Patterns in mutual influence of ligands nature, the influence of solvents of studied 3 component systems, the nature of dissolution of the resulting compounds were studied;

Physicochemical characteristics of 12 compounds performed by methods of chemical, IR spectroscopic, thermal analyzes, for some obtained compounds, areas of their practical application have been found.

2. RESEARCH METHODS AND MATERIALS

The interaction of AA with inorganic salts in ethyl alcohol and DMSO studied by isothermal solubility method at 25 ° C. When identifying the obtained compounds, the methods of physicochemical analysis were used such as pycnometry, IR spectroscopy and thermogravimetry.

Infrared absorption spectra (4000-200 cm^{-1}) of complex compounds recorded on a Specord-75 IR spectrometer and a Bruker "IFS-113B" Fourier spectrometer. Samples were prepared in the form of suspensions in liquid paraffin in the form of tablets with potassium bromide. Thermal analysis was performed on system derivatograph F. Paulik, I. Paulik, L. Erdey at a heating rate of 5 °, 10 °C/min up to 1000 °C in air, inside standard platinum crucibles.

3. RESULTS AND DISCUSSIONS

3.1. The system manganese chloride - acetamide - ethyl alcohol at 25 ° C. The solubility diagram of $\text{MnCl}_2\text{-CH}_3\text{CONH}_2\text{-C}_2\text{H}_5\text{OH}$ system shown in **Fig. 1** consisting of four crystallization branches. The first branch corresponds to the precipitation of manganese chloride solvate $\text{MnCl}_2\cdot 3\text{C}_2\text{H}_5\text{OH}$ crystal. It should be noted that addition of acetamide increases solubility of manganese chloride. The second branch is a crystallization of new compound $\text{MnCl}_2 \cdot 2\text{CH}_3\text{CONH}_2$ from equilibrium saturated solutions. A further increase in acetamide concentration leads to formation of second compound $\text{MnCl}_2\cdot 4\text{CH}_3\text{CONH}_2$ corresponding to the third crystallization branch. The fourth branch of crystallization corresponds to separation of pure acetamide crystals from the solution. Both compounds dissolve in ethyl alcohol congruently.

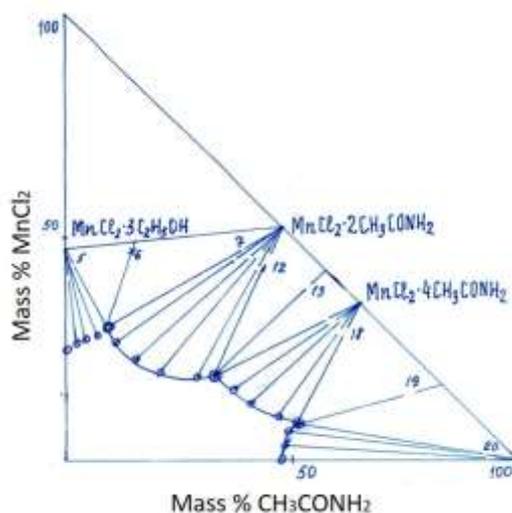


FIGURE 1

SOLIBILITY DIAGRAMM FOR SYSTEM MANGANESE CHLORIDE - ACETAMIDE - ETHYL ALCOHOL AT 25 °C.

3.2. Systems chlorides of cobalt (nickel, magnesium) - acetamide - ethyl alcohol 25 °C. Solubility isotherms in systems (CoCl_2 , NiCl_2 , MgCl_2)- $\text{CH}_3\text{CONH}_2\text{-C}_2\text{H}_5\text{OH}$ are similar, they were characterized by presence of three crystallization branches. As an example, **Fig. 2** shows the isotherm of the $\text{CoCl}_2\text{-CH}_3\text{CONH}_2\text{-C}_2\text{H}_5\text{OH}$ system. The initial branches of solubility isotherms indicate the separation of crystals of solvates $\text{CoCl}_2\cdot 3\text{C}_2\text{H}_5\text{OH}$ ($\text{NiCl}_2\cdot 3\text{C}_2\text{H}_5\text{OH}$, $\text{MgCl}_2\cdot 6\text{C}_2\text{H}_5\text{OH}$) from solutions.

The second branches of the solubility isotherms of the systems correspond to the saturation of solutions with the formed compounds of the composition: $\text{CoCl}_2\cdot 4\text{CH}_3\text{CONH}_2$, $\text{NiCl}_2\cdot 4\text{CH}_3\text{CONH}_2$, $\text{MgCl}_2\cdot 4\text{CH}_3\text{CONH}_2$.

The third branch of solubility isotherms corresponds to separation of pure acetamide crystals from saturated solutions.

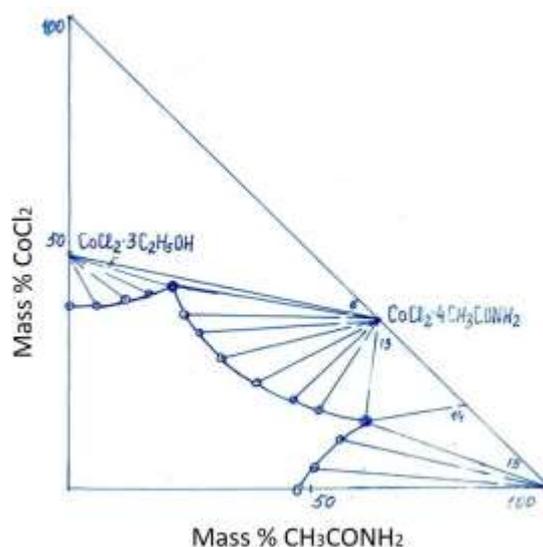


FIGURE 2

SOLIBILITY DIAGRAM FOR SYSTEM COBALT CHLORIDE - ACETAMIDE - ETHYL ALCOHOL AT 25 ° C.

3.3. System zinc chloride-acetamide-ethyl alcohol at 25 °C. The solubility diagram of the $ZnCl_2$ - CH_3CONH_2 - C_2H_5OH system consists of three crystallization branches. The crystallization branches of zinc chloride have not been identified due to high solubility of formed compounds and the solutions viscosity. When components concentration in solution reach 72.04% for $ZnCl_2$ and 14.20% for CH_3CONH_2 , crystallization begins from the solution of incongruently soluble compound $ZnCl_2 \cdot CH_3CONH_2$. The next branch corresponds to congruently soluble compound $ZnCl_2 \cdot 2CH_3CONH_2$. The last branch is pure acetamide crystals.

3.4. System cadmium chloride - acetamide - ethyl alcohol at 25 ° C. The solubility isotherm of this system consists of four crystallization branches. The two extreme branches correspond to the crystallization of the $CdCl_2 \cdot 1.5C_2H_5OH$ crystal solvate and crystals of pure acetamide. The two middle branches correspond to an evolution of an equilibrium solution of two compounds of the composition $CdCl_2 \cdot CH_3CONH_2$ and $CdCl_2 \cdot 2CH_3CONH_2$, both of these compounds dissolve incongruently in alcohol.

3.5. Systems manganese chloride (cobalt, nickel) - AA-DMSO at 25 °C. Chlorides of manganese, cobalt and nickel with acetamide in DMSO form new compounds containing both acetamide molecules and DMSO molecules. The dissolution diagrams of these systems are identical. They consist of three crystallization branches. The first branch corresponds to crystallization from a saturated solution of the crystal solvate $MnCl_2 \cdot 3(CH_3)_2SO$, $CoCl_2 \cdot 3(CH_3)_2SO$, $NiCl_2 \cdot 3(CH_3)_2SO$.

In all cases, the solubility of manganese, cobalt and nickel chlorides increases with an increase in the concentration of acetamide in DMSO, and this leads to the formation of incongruently soluble compounds of the composition $MnCl_2 \cdot CH_3CONH_2 \cdot (CH_3)_2SO$, $2CoCl_2 \cdot 3CH_3CONH_2 \cdot 2(CH_3)_2SO$, $NiCl_2 \cdot CH_3CONH_2 \cdot (CH_3)_2SO$, which corresponds to the second branch of the solubility isotherms. The third branch shows the separation of pure acetamide crystals from saturated solutions.

3.6. Systems magnesium (cadmium) chlorides - acetamide - DMSO at 25 °C. Isotherms of system $MgCl_2$ - CH_3CONH_2 - $(CH_3)_2SO$, $CdCl_2$ - CH_3CONH_2 - $(CH_3)_2SO$ belong to simple eutonic types, and consist of two crystallization branches, which correspond to the separation of crystal solvates from saturated solutions of the composition $MgCl_2 \cdot 3(CH_3)_2SO$, $CdCl_2 \cdot 3(CH_3)_2SO$ and acetamide. It should be noted that the solubility of cadmium chloride in DMSO in the presence of acetamide decreases from 34.43% to 28.61%, and the solubility of acetamide in DMSO from 44.96% to 28.57%. The solubility of magnesium chloride initially remains almost at the same level, after which increases from 4.43% to 5.40%.

3.7. System zinc chloride acetamide - DMSO - at 25 ° C. The solubility isotherm of the $ZnCl_2$ - CH_3CONH_2 - $(CH_3)_2SO$ system is characterized by the presence of three crystallization branches: crystal solvate $ZnCl_2 \cdot 2(CH_3)_2SO$, a new compound $ZnCl_2 \cdot 2CH_3CONH_2$ and acetamide. The compound $ZnCl_2 \cdot 2CH_3CONH_2$ in DMSO dissolves congruently. The system turned out to be very complex due to the high solubility of the components and the formed compounds in DMSO; therefore, we have not determined the eutonic points separating the crystallization branches.

4. Physico-chemical characteristics of obtained compounds

Solubility in organic solvents. To establish individuality and select an indifferent solvent for determining the relative density of crystals of the obtained complexes, their solubility in the number of organic solvents was determined.

It was found that the complex compounds of acetamide are readily soluble in ethyl alcohol, soluble in acetone. Zinc compounds are partially soluble in benzene, toluene and chloroform. All other compounds are practically insoluble in benzene, toluene, carbon tetrachloride and chloroform. The relative density of crystals determined by the pycnometric method using benzene and carbon tetrachloride as indifferent solvents. The data obtained indicate that acetamide complexes characterized by less dense packing of crystal lattices than the initial inorganic salts.

5. Thermal study of new complex compounds

The results of studying the thermal stability show that the thermal characteristics of the obtained complexes are more complex than the initial components. Each compound characterized by its temperature ranges of transformation, which indicate the individuality of each compound. Differential thermal analysis (DTA) heating curves of the complexes characterized by several endo- and exothermic effects corresponding to the process of melting, decomposition, phase transition and oxidation of the remaining decomposition products.

Thermogravimetric studies have established that the decomposition of all complexes begins with melting. In acetamide compounds, the removal of the ligand molecule occurs in a stepwise fashion. In mixed-ligand compounds, AA and DMSO molecules contained in the compositions of the compounds decompose simultaneously in the temperature range 100-330 °C. The end product of decomposition is metal oxides. It should be noted that the thermal effects of the synthesized complexes depend on the composition, nature of the metal and the ligand of the complexes.

The thermal effects of compounds are characteristic only for a given substance, then a comparative study of the thermal stability of the synthesized compounds, crystal solvates and initial components allows one to judge the physical and chemical processes that occur when the temperature changes.

According to the derivatogram, the coordination compounds of manganese, cobalt and nickel with acetamide characterized by the presence of several thermal effects. Endoeffects up to 220-240 °C correspond to the compound melting, stepwise elimination of acetamide molecules. The mass loss of the test portions along the thermal gravimetric (TG) analysis curve is in a good agreement with the theoretically calculated data. Endoeffects in the temperature range 240-380 °C show further complex decomposition. Exothermic effects above 410 °C indicate the oxidation of intermediate decomposition products.

The derivatogram of mixed-ligand complexes $\text{MeCl}_2 \cdot \text{CH}_3\text{CONH}_2 \cdot (\text{CH}_3)_2\text{SO}$ also shows thermal effects corresponding to the melting and decomposition of the complex. Moreover, the removal of the molecules of both ligands of acetamide and dimethyl sulfoxide contained in the complex are subject to complete decomposition at 105-330 °C. A further increase in temperature leads to a phase transition and oxidation of the remaining decomposition products, mainly consisting of metal chlorides, which characterized by exothermic effects. The oxidation process ends at 720 °C. Compounds DTG curves character indicates the formation and interconversion, various oxidation states of manganese oxides, which is in good agreement with theoretical data. Residual products are metal oxides.

6. Infrared absorption spectra of compounds

The infrared absorption spectra of the compounds were studied to establish the nature and location of the bonds in the complexes. The IR spectra of the compounds contain a set of natural frequencies, an organic component, somewhat altered due to interaction with a complexing agent and under the influence of crystalline forces. The basic vibrational frequencies of the complexes and their assignment are shown in Table 1.

TABLE I
THE BASIC VIBRATION FREQUENCIES IN INFRARED SPECTRUMS OF THE COMPLEX

Rate	$(\text{CH}_3)_2\text{SO}$ [cm^{-1}]	CH_3CONH_2 [cm^{-1}]	$\text{NiCl}_2 \cdot 4\text{CH}_3\text{CONH}_2$ [cm^{-1}]	$\text{NiCl}_2 \cdot \text{CH}_3\text{CONH}_2 \cdot (\text{CH}_3)_2\text{SO}$ [cm^{-1}]
$\nu_{\text{as}}(\text{NH})$		3582	3325	3400
$\nu_{\text{s}}(\text{NH})$		3464	3260	3200
$\nu(\text{C}=\text{O})$		1684	1653	1650
$\delta(\text{NH}_2)$		1589	1575	1575
$\delta_{\text{as}}(\text{CH}_3)$		1459	1460	1465
$\delta(\text{CH}_3) \nu(\text{CN})$	1435	1444	1405	1403
$\nu(\text{CN}/\text{CC})$	1405	1338		1315
$\delta(\text{CNH})(\text{OCN})$	1307		1135	1120
$\nu(\text{SO})$	1053			986
$\rho(\text{NH}_2)$	956,937	965	910	940,920,905
$\nu(\text{CC}) \nu(\text{CN})$	896 ν CS	814	885	710,630
$\tau(\text{NH}_2) \tau(\text{CO}) \nu(\text{CS})$	696	554	650,585	585
$\delta(\text{OCN}) \delta(\text{CCO})$	380,330, 302	507	525	490,460
$\delta(\text{CCN})(\text{CCO})$		434	485	415
(OCN)		423		355,320
$\tau(\text{NH}_2)$				255,220
$\delta(\text{CSO}) + \nu\text{MeO}$				
$\delta\text{MeO} + \nu \text{MeCl}$			320,240,220	

The value of stretching vibrations $\nu(\text{CO})$ in the spectra of complexes $\text{MnCl}_2 \cdot 2\text{CH}_3\text{CONH}_2$, $\text{MnCl}_2 \cdot 4\text{CH}_3\text{CONH}_2$, $\text{CoCl}_2 \cdot 4\text{CH}_3\text{CONH}_2$, $\text{NiCl}_2 \cdot 4\text{CH}_3\text{CONH}_2$ appear as an intense band in the region of 1625-1665 cm^{-1} , and in compounds $\text{MgCl}_2 \cdot 4\text{CH}_3\text{CONH}_2$, $\text{ZnCl}_2 \cdot \text{CH}_3\text{CONH}_2$, $\text{ZnCl}_2 \cdot 2\text{CH}_3\text{CONH}_2$, $\text{CdCl}_2 \cdot \text{CH}_3\text{CONH}_2$ and $\text{CdCl}_2 \cdot 2\text{CH}_3\text{CONH}_2$ in the range of 1650-1675 cm^{-1} . These bands split in the form of a doublet ($\text{CoCl}_2 \cdot 4\text{CH}_3\text{CONH}_2$), a triplet $\text{MnCl}_2 \cdot 2\text{CH}_3\text{CONH}_2$, $\text{NiCl}_2 \cdot 4\text{CH}_3\text{CONH}_2$ or with bends ($\text{MnCl}_2 \cdot 4\text{CH}_3\text{CONH}_2$) in the low-frequency region. A decrease in the frequencies of stretching vibrations $\nu(\text{CO})$ in new compounds in comparison with the frequencies $\nu(\text{CO})$ of crystalline acetamide indicates the coordination of acetamide molecules with metal ions through an oxygen atom.

The bands of bending vibrations, which appear in the region of 1575-1600 cm^{-1} , are not split and are reduced by 10-25 cm^{-1} in comparison with crystalline acetamide. Changes in HNH angles, as well as CO bonds, can cause a frequency shift $\delta(\text{NH}_2)$ when coordinated through the oxygen atom.

Stretching vibration band ν (CN) in the spectrum of new compounds manifests itself in the region 1405-1410 cm^{-1} and shifts to the high-frequency region in comparison with crystalline acetamide, thereby indicating the strengthening of CN bond. The IR spectra of obtained complexes showed four bands in the region from 340-210 cm^{-1} CN, which belong to the stretching vibrations of Me - C1, Me - O.

The change in the basic vibrational frequencies of C = O and S = O in the spectra of the complexes $\text{MnCl}_2 \cdot \text{CH}_3\text{CONH}_2 \cdot (\text{CH}_3)_2\text{SO}$, $2\text{CoCl}_2 \cdot 3\text{CH}_3\text{CONH}_2 \cdot 2(\text{CH}_3)_2\text{SO}$, $\text{NiCl}_2 \cdot \text{CH}_3\text{CONH}_2 \cdot (\text{CH}_3)_2\text{SO}$ may be due to the direct coordination of molecules around the metal AA and DMSO due to oxygen, nitrogen and sulfur atoms, as well as a result of ligands intermolecular interactions [14].

IR absorption spectra of complexes $\text{MnCl}_2 \cdot \text{CH}_3\text{CONH}_2 \cdot (\text{CH}_3)_2\text{SO}$, $2\text{CoCl}_2 \cdot 3\text{CH}_3\text{CONH}_2 \cdot 2(\text{CH}_3)_2\text{SO}$ and $\text{NiCl}_2 \cdot \text{CH}_3\text{CONH}_2 \cdot (\text{CH}_3)_2\text{SO}$ are presented in Figures 1 and 2, and the value of vibrational frequencies and their assignment are given in Table 2.

TABLE 2

BASIC VIBRATIONAL FREQUENCIES IN THE IR SPECTRA OF COMPLEX COMPOUNDS AND THEIR ASSIGNMENT (400-4000 cm^{-1}).

Assignment	$(\text{CH}_3)_2\text{SO}$ [cm^{-1}]	AA κ [cm^{-1}]	$\text{MnCl}_2 \cdot \text{CH}_3\text{CONH}_2 \cdot (\text{CH}_3)_2\text{SO}$ [cm^{-1}]	$2\text{CoCl}_2 \cdot 3\text{CH}_3\text{CONH}_2 \cdot 2(\text{CH}_3)_2\text{SO}$ [cm^{-1}]	$\text{NiCl}_2 \cdot \text{CH}_3\text{CONH}_2 \cdot (\text{CH}_3)_2\text{SO}$ [cm^{-1}]
$\nu_{\text{as}}(\text{NH})$		3582	3160	3400	3400
$\nu_{\text{s}}(\text{NH})$		3464	2990	3300,3260	3200
$\nu_{\text{as}}(\text{CH})$	2996	2990	2900	3000	3000
$\nu_{\text{s}}(\text{CH})$	2913	2987	1660,1645	2910	2960
$\nu_{\text{s}}(\text{CH})$		2885	1590	1640	2915
$\nu(\text{C}=\text{O})$		1684	1480	1590	1650
$\delta(\text{NH}_2)$		1589	1390	1470	1575
$\delta_{\text{as}}(\text{CH}_3)$	1435	1459	1316	1425,1400	1465
$\delta(\text{CH}_3)\nu$ (CN)		1444	1105	1315	1403
	1405	1363	1035,1010	1130	1315
$\delta_{\text{s}}(\text{CH}_3)$			955,930	1030	1120
			890		1015
$\nu(\text{CN}/\text{CC})$			700,640	995	986
	1307	1338	590	950	940,920,90
$\delta(\text{CNH})(\text{OCN})$			578	905,880	5
			480,430	770,718,650	710,630
$\rho(\text{CH}_3)$			395,350	590	585
$\rho(\text{CH}_3)$			290	570	490,460
$\nu(\text{SO})$		1052	265	480,430	415
$\rho(\text{NH}_2)$		1006	230	345	355,320
$\nu(\text{CC})\nu$ (CN)	1053			300	255
	956,937	965		250	220
$\tau(\text{NH}_2)\tau(\text{CO})\nu(\text{CS})$		814		230	
	896 ν CS	554			
$\delta(\text{OCN}) \delta(\text{CCO})$		507			
$\delta(\text{CCN})(\text{CCO})(\text{OCN})$		434			
	696	423			
$\tau(\text{NH}_2)$					
$\delta(\text{CSO}) + \nu\text{MeO}$					
$\delta(\text{CSC})$					
$\delta(\text{MeCl})$					
$\delta\text{MeO} + \nu \text{MeCl}$					
	380,330				
	302				

The general character of the spectra is approximately the same; there are characteristic vibration frequencies of the complexes in approximately same regions. All bands characteristic of free ligands are also found in the spectra of the complexes, somewhat altered due to the interaction with the complexing agent and the effect of crystal forces. Therefore, the preliminary assignment of frequencies can be done based on a comparison of the vibrational spectra of free and coordinated ligands / 1-3 /.

In each particular case, the primary problem in the study of dimethyl sulfoxide complexes is to identify the coordination center of DMSO (atoms S or O; respectively, S or O coordination) / 4-6 /.

This problem is traditionally solved by the SO stretching vibration bands shift in the near IR region. Among other possible methods for determining the coordination centers of DMSO, this method occupies an essential monopoly position. However, it is inapplicable in cases where the interval of SO manifestation covered by bands of other vibrations. Attempts to clarify the situation by analyzing the spectra in region of metal - DMSO stretching vibrations manifestation (presumably M - S = 500-260, M - O = 530-380 cm), as a rule, have little success due to ambiguity in assignment and overlapping of the corresponding spectral ranges.

An analysis of the structural features and vibrational spectrum of DMSO shows that as additional arguments in favor of one or another method of DMSO coordination, the band of the bending vibration of CSO, which lies in the IR spectrum of free DMSO at 380 cm, can be used no absorption in the range 370 - 390 cm / 7-8 /.

Acetamide is also a bidentate ligand containing two donor atoms, oxygen and nitrogen, capable of forming coordination bonds with the complexing metal. The study of the IR absorption spectra of acetamide compounds with inorganic salts makes it possible to solve the question of which of the two atoms electron donors is responsible for the coordination bond.

The frequencies of stretching vibrations ν (CO) in the newly listed compounds reduced by 25-45 cm^{-1} in comparison with crystalline acetamide. This indicates that in the obtained displaced-ligand compounds, AA molecules with metal ions are coordinated through the oxygen atom of the carbonyl group. The frequencies of stretching vibrations ν (SO) in the new compounds shifted to a low-frequency region in comparison with DMSO by 35-70 cm^{-1} . The symmetric stretching vibrations bands ν (CS) shifted to the high-frequency region by 15-20 cm^{-1} compared to free DMSO. The noted shifts of the fundamental vibrational frequencies ν (SO) and ν (CS) are caused by the coordination of the ligand at the oxygen atom of the sulfoxide group.

The band of bending vibration δ (CSO), found in the region of 360-342 cm^{-1} , confirms the O-coordination of DMSO in the above compounds. The observed bands in the range of 300-320 cm^{-1} refer to stretching vibrations of Me - C1 and bending vibrations δ (CSO). The assignment of remaining vibrational frequencies in the long-wavelength region of compounds IR spectra is identical to vibrations of acetamide compounds.

7. Complexes decomposition kinetics

One of the complex tasks in chemical processes is activation energy calculation, i.e. determining the excess amount of energy that a molecule must possess at the moment of collision for a chemical reaction to begin. Such studies are very laborious and require high experimental precision. In recent years, indirect methods used to calculate the activation energy, which in their accuracy are not inferior to direct calculation methods.

In particular, to calculate the activation energy, the curves of differential thermal (DTA) thermogravimetric (TT) and differential thermogravimetric (DTG) analysis methods can be used [15]. The activation energy from the DTA, TT, DTG curve can be calculated from the Arrhenius equation.

The corresponding depths of the DTA peak are measured at a given temperature. According to the data, a graph of dependence is plotted in the coordinate's $\log \Delta t - 1/T$. The graph is a straight line, the slope of the curve that shows the activation energies.

To calculate the activation energy according to the differential thermogravimetric curve (DTG), the V_m values are determined, according to the data, a graph is plotted in coordinates $\log V_m$ (ordinate axis) $-1/T \cdot 10^{-3}$ (abscissa axis).

According to the thermogravimetric curve (TG) according to the calculated data, a graph of the dependence $(\log m - 2 \lg T) - 1/T \cdot 10^{-3}$ is plotted, in particular, the decomposition of coordination compounds $\text{NiCl}_2 \cdot 4\text{CH}_3\text{CONH}_2$.

The derivatogram of $\text{NiCl}_2 \cdot 4\text{CH}_3\text{CONH}_2$ is characterized by the presence of endothermic effects at 80, 130, 180, 250, 440 °C and exo effects at 545 °C and 705 °C. The endothermic effect at 80 °C can be attributed to compound melting. The activation energies found for DTA - 0.2679, for DTG 0.7002, for TG 0.2747 kJ/mol. Upon further heating, the complex decomposes with the gradual removal of the acetamide molecule, as evidenced by the endo-effects at 130, 180, 250 °C.

The mass loss according to TG curve was 129.00 mg, a theoretical calculation was 129.14 mg. The activation energies are equal for DTA is 1.4281 for DTG is 1.7320 for TG is 1.5670 kJ/mol. Endo effect at 440 °C and exo effect at 545 °C correspond to further decomposition of the remaining intermediate decomposition products. The remainder of the product mainly consists of NiCl_2 above 705 °C oxidized to form nickel oxide NiO. The weight loss recorded by the TG curve is 159.00 mg. The theoretical calculated NiO content is 40.82 mg. The activation energies are respectively equal for DTA was 5.6718 for DTG was 4.8390 for TG was 3.7320 kJ/mol.

The following values of the activation energy for the decomposition of the complex obtained experimentally. To calculate the activation energy DTA, TG and DTG curve the derivatograms of $\text{NiCl}_2 \cdot 4\text{CH}_3\text{CONH}_2$ were used. Derivatogram of mixed-ligand manganese complex shown in Fig. 3.

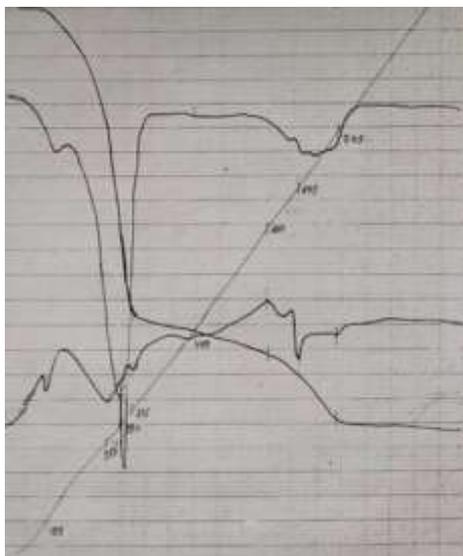


FIGURE 3
DERIVATOGRAM OF $MnCl_2 \cdot CH_3CONH_2 \cdot (CH_3)_2SO$ COMPLEX

The equilibrium configuration of the mixed-ligand complexes $[MeCl_2 \cdot (CH_3)_2SO \cdot CH_3CONH_2]$, $Me = Mn, Co, Ni, Zn$ is shown in Fig. 4. In the calculated complexes, the ligand molecules are coordinated monodentate to the central metal atom through the oxygen atom of the carbonyl group of acetamide and the sulfo group of dimethyl sulfoxide. The spatial structure of studied complexes generally characterized by tetrahedral structure. The central metal atom has a tetrahedral polyhedron formed by two chlorine atoms, as well as acetamide and dimethyl sulfoxide molecules.

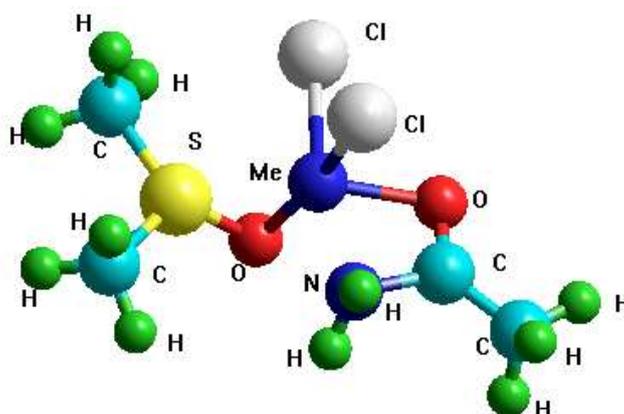


FIGURE 4
EQUILIBRIUM CONFIGURATION OF THE MIXED-LIGAND COMPLEX $[MeCl_2 \cdot CH_3CONH_2 \cdot (CH_3)_2SO]$, ($Me = Mn, Co, Ni, Zn$)

CONCLUSIONS

Based on IR spectroscopic data, the nature and place of localization of bonds in new compounds were established:

- bond in acetamide molecule with metal ions occurs through the oxygen atoms of carbonyl group;
- bond in the DMSO molecule with metal ions occurs through the oxygen atoms of the sulfoxide group;
- chlorine ions are bound in the form of a bridge between metal atoms and end bonds.

Thermogravimetric studies have established that the decomposition of all complexes begins with melting. In acetamide compounds, the removal of the ligands molecule occurs stepwise. In mixed-ligand compounds, AA and DMSO molecules contained in the compounds are decomposed simultaneously in the temperature range 10–330 °C. The end products of decomposition are metal oxides. It was found that the compounds $MnCl_2 \cdot 4 CH_3CONH_2$, $CoCl_2 \cdot 4 CH_3CONH_2$ are effective stimulators of the growth and development of sugar beet.

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