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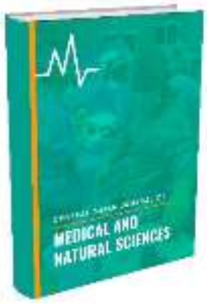

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STUDY THE COMPLEX FORMATION OF MOLYBDENUM (V) WITH DIETHYLETHYLENE DISULFIDE

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ABSTRACT: The results of the study of the synthesis of complex compounds of molybdenum (V) with diethylethylene disulfide are presented. A method for the synthesis of complex compounds of molybdenum (V) with (C2H5)2SC2H4 was developed. Chloride and bromide analogs of molybdenum (V) complexes with the indicated ligand were synthesized. On the basis of physicochemical research methods, it has been proved that the compounds prepared have a constant qualitative and quantitative composition.

KEYWORDS: synthesis, ligand, complex, coordination, bond, potential, spectrum.

INTRODUCTION

Coordination compounds of molybdenum are widely used as catalysts in the chemical industry, as well as in various biochemical processes [1]. Chemically conversion of coordination compounds and their ligands underlie on the basis of many biocatalytic processes. In some cases, the catalysts based on coordination compounds of transition metals allow working under much milder conditions than classical heterogeneous catalysts [2].

The interaction of molecules in the course of chemical reactions is usually considered from the point of view of electrostatics. Such simplification of the interpretation of chemical processes makes it possible, in a number of cases, to determine the reaction centers of interacting molecules [3, 4]. In the course of chemical reactions, a redistribution of electron density and a change in the mutual arrangement of the nuclei of the reacting molecules occur. The result of redistribution is judged on the molecular structure of the final reaction products in comparison with the structure of the reagents [5]. The greatest difficulties arise in interpreting the stages of a chemical process, i.e. the mechanism of electronic redistribution [6].

At present, various coordination compounds of molybdenum with organic bioactive ligands are widely used in medicine as medicines. It is known that, being a polyvalent metal, molybdenum in various degrees of oxidation can form mono, bi- and polynuclear coordination compounds with various classes of organic ligands, exhibiting enzymatic properties.

On the other hand, it is known that the coordination compounds of molybdenum (V) with nitrogen-, sulfur-, oxygen- and phosphorus-containing organic ligands are structural models of the active centers of metal-enzyme, are included in the composition of active of vitamins and hormones, and participate in many biochemical processes in a living organism [1]. An example is the coordination compound of molybdenum (V) with bis-β-phenyl-α-alanine dioxide, which is used in veterinary medicine to treat liver cirrhosis in animals [2]. In this regard, the synthesis and study of the properties of complex compounds of molybdenum (V) with organic ligands is urgent.

The purpose of this research is to study the complex-formation of molybdenum (V) with diethylethylenedisulfide, study the physicochemical characteristics of the obtained compounds and their quantum-mechanical calculation [3].

EXPERIMENTAL PART

As the starting compounds were chosen molybdenum (V) oxopentahologenides, which were prepared by the reduction of $(NH_4)_2[MoO_4]$ with ammonium iodide in 6 mol/l solution of hydrochloric acid.

$$2(NH_4)_2MoO_4 + 2NH_4I + 12HCl = 2(NH_4)_2[MoOCl_5] + I_2 + 2NH_4Cl + 6H_2O,$$

where Г-Cl^-; Br^-

The resulting solution was boiled until the iodine vapor was completely removed, then the solution was cooled, and a concentrated solution of hydrochloric acid (ρ = 1.19 g/cm^3) was added. The formed crystals were filtered off, washed with 6 M HCl solution, and dried in a vacuum desiccator over 98% H_2SO_4 solution until constant weight. The product yield is 90-92%.

By a similar procedure an ammonium salt of the composition $(NH_4)_2[MoOBr_5]$ was obtained in a 7 M solution of hydrobromic acid.

The synthesized compounds are partially soluble in water, mineral acids, dimetylformamide, acetone, ethyl alcohol and insoluble in benzene, toluene and chloroform.

According to their crystal-optic characteristics, they belong to the rhombic system, are biaxial, optically negative. Refractive indices are equal to $N_g = 1.618$, $N_p = 1.708$.

For the compound $(NH_4)_2[MoOCl_5]$, IR spectra were recorded, in which absorption bands appeared, 265 (m), 510 (m), 780 (m), 965 (m), 1080 (m) and 3250 (pts).) cm^{-1}, the IR absorption spectra of $(NH_4)_2[MoOBr_5]$ revealed absorption bands at 447 (m), 518 (m), 767 (m), 1053 (m), 3050 (m), 3270 (m) cm^{-1}

Ammonium oxochloromolybdate (V) is a green crystal, with its bromide analogue - dark red shiny crystals, easily hydrolyzed in humid air. To prevent the obtained compounds from moisture in the air and exposure to light, they were stored in an airtight container.

The individuality and purity of the synthesized compounds were controlled by the method of chemical analysis. The content of molybdenum in the composition of the synthesized complex compounds was determined by its precipitation from solution in the form of a poorly soluble precipitate $PbMoO_4$ [3,4]. The molybdenum content was calculated using the formula:

$$\% \ Mo = (0.295m_1 / m_2) * 100$$

where: m_1 is the mass of the precipitate formed, g; m_2 - weight of a complex compound, g; 0.2956 recalculation factor for molybdenum.

The content of halogens in the composition of the coordination compounds was determined by the gravimetric method [5]. The chlorine and bromine contents were calculated using the formula.

$$\% \text{ Hal} = (aF / \text{в}) * 100,$$

where *a* is the precipitate mass, g; в - the complex weight, g; Hal - ions of Cl^-, Br^-, F^- recalculation factor: for chlorine - 0, 2470, for bromine - 0.4272.

Determination of the sulfur content in complex compounds was carried out by the high-speed method according to Scheniger [6]. The analyses for carbon and hydrogen were carried out by combustion of a substance in oxygen according to the standard procedure [7].

In this work, complex compounds of molybdenum (V) with diethylethylene disulfide (DEDS) $C_2H_5SC_2H_4SC_2H_5$ were synthesized.

Diethylethylene disulfide is a colorless liquid with a pungent odor that does not mix with water, but dissolves well in an organic solvent [8].

By the preliminary experiments it was found that the interaction of a solution of ammonium oxopentachloromolybdate in hydrochloric acid with deethylethylene disulfide at 0°C and constant stirring first forms an oily substance, which turns into a crystalline substance after 8-10 hours [9].

A change in the ratio of the reacting components in the range from 1: 1 to 1: 5, as well as an increase in temperature up to 40°C affects the yield, but their composition remains constant.

The optimal synthesis conditions are as follows: to 100 ml of 0.2 M hydrochloric acid solution at 0°C and constant stirring, the ligand was added dropwise up to the ratio of complex : ligand 1:3. Initially, as the ligand is added, an oily compound is formed, which, with prolonged stirring for some time, transforms into fine-crystalline state. The resulting precipitate was filtered off, washed with a small amount of cold hydrochloric acid, carbon tetrachloride and ether. The resulting compounds were dried in a thermostat at 110°C. The results of the analyses carried out for molybdenum, sulfur, chlorine, carbon and hydrogen in Table 1 show that when $(NH_4)_2MoOCl_5$ interacts with diethylethylene disulfide (L), a complex of the $MoOCl_3$ type is formed in all cases. It is colored light green, does not dissolve in water and most organic solvents (ethanol, ether, benzene, tetrachloride, carbon) [10].

Table 1.Results of elemental analysis of complex compounds of molybdenum (V) with dietlethylene disulfide (L)

Compound	Found %						Calculated %					
	Mo	Hal	N	S	C	H	Mo	Hal	N	S	C	H
$(NH_4)_2[MoOCl_5]$	50.10	53.70	9.02	-	-	-	29.49	54.53	8.61	-	-	2.17
$(NH_4)_2[MoOBr_5]$	16.85	71.93	4.85	-	-	-	17.51	72.93	5.10	-	-	-
$MoOLCl_3$	25.95	28.00	-	17.01	19.45	3.55	26.05	28.90	-	17.36	19.54	3.80
$MoOLBr_3$	18.95	48.00	-	12.50	14.12	2.65	19.12	47.80	-	12.75	14.34	2.79
$Mo_2O_3L_2Cl_4$	28.00	20.69	-	18.54	20.10	4.02	28.15	20.82	-	18.76	21.11	4.10
$Mo_2O_3L_2Br_4$	28.15	37.01	-	14.95	16.50	3.15	22.32	37.21	-	14.88	16.74	3.25

When the synthesized compound is recrystallized in acetone, two different forms of crystals are formed - acicular and lamellar.

The former are highly soluble in acetone, while the latter are practically insoluble in acetone.

According to the elemental analysis data (see table 1), needle crystals have the composition $MoOLCl_3$, and lamellar crystals have the composition $Mo_2O_3L_2Cl_4$.

We have suggested that the latter is the hydrolysis form of the former. The hydrolysis process can be represented by the following scheme

$$2MoOLCl_3 + H_2O \rightarrow Mo_2O_3L_2Cl_4 + 2HCl$$

The addition of a few drops of water to the acetone solution contributed to an increase in the yield of lamellar crystals, and upon recrystallization from absolute acetone, up to 90% of the yield of needle crystals was obtained. These results confirm the above scheme of the hydrolytic process. The dimeric nature of the hydrolysis form is also indicated by its low solubility in most solvents.

The synthesis of the bromide complex of molybdenum with diethylethylene disulfide was carried out by replacing the chloride ions in the complex with the bromide ion by the influence of 6 N hydrobromic acid.

The optimal synthesis conditions are as follows: a weighed portion of $MoOLCl_3$ was dissolved in acetone and a 6 N HBr solution was immediately added. As the acid was added, precipitates formed from the acetone solution, which are insoluble in HBr. The precipitate was filtered off, washed with hydrobromic acid, redissolved in acetone, and the precipitation was repeated. The resulting compound was dried to constant weight at 105°C.

According to the analysis results, the synthesized compound has the composition $MoOLBr_3$ (see table. 1). On analogy with chloride, the hydrolysis form of the bromide complex with the composition $Mo_2O_3L_2Br_4$ was prepared, the elemental analysis data of which are given in Table 1.

All syntheses of complexes of molybdenum (V) with diethylethylene disulfide were repeated at least 4-5 times.

To determine the type of electrolyte in the chemistry of complex compounds, the method for determining the molecular electrical conductivity in aqueous solutions is widely used [8].

However, the molybdenum (V) complexes obtained in this work are either insoluble in water or hydrolyzed. Among organic solvents, dimethylformamide and acetone are the most suitable, since the solutions of the complexes in these solvents are quite stable.

Due to the fact that there are practically no data in the literature on the values of the molar conductivity of complex ions in dimethylformamide, we carried out measurements for complex electrolytes and electrolytes of the 1: 1, 1: 2 type.

The resistance of the solutions of the complexes under study was measured at various concentrations using an MP513 conductometer. Molecular conductivity was calculated by the formula

$$\mu = (K * 1000) / CR, \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1},$$

where K is the cell constant, R is the resistance of the solution (ohm), C is the molar concentration (mol/l).

The data on the determination of molecular electrical conductivity are given in Table 2. As it can be seen from the table, when water is replaced with dimethylformamide, the molar electrical conductivity of solutions decreases slightly, but the difference in the values corresponding to their different types of electrolytes remains big. As it can be seen from the data in Table 2, all studied compounds are not electrolytes.

Table 2. Molecular conductivity of molybdenum complexes (V)

№	Compound	Ligand (L)	Solvent	C *mol/l*	*μ, ohm^{-1} sm^{-1} mol^{-1}*	Dissociation type
1	$MoOLCl_3$	$C_2H_5SC_2H$	Acetone	16,5; 7,8; 5,2.	1,7; 4,2; 5,6	

2	$MoOLBr_3$			15,6; 6,8; 4,4	1,8; 3,4; 5,3	non-electrolyte
3	$Mo_2O_3L_2Cl_4$		DMPh	14,0; 7,0; 4,7	5,6; 9,2; 11,5	
4	$Mo_2O_3L_2Br_4$			22,0; 11,0; 7,3	5,5; 7,3; 9,5	

We have studied the IR spectra of the synthesized molybdenum (V) complexes of both $MoOLX_3$ monomers and $Mo_2O_3L_2Hal_4$ dimers, where L is $C_2H_5SC_2H_4SC_2H_5$, Hal- is Cl^-, Br^-.

The spectra were measured on the following devices: IR 600-1700 cm^{-1}, IR-10 400-4000 cm^{-1}, NICOLET 100-400 cm^{-1}

Wavenumbers of absorption maxima in IR spectra:

$C_2H_5SC_2H_4SC_2H_5$: 530 (w), 630 (w), 650 (w), 730 (w), 780 (w), 830 (w), 870 (w), 1060 (w), 1140 (w), 1205 (s), 1270 (w), 1380 (m), 1430 (s), 1460 (s)

$MoOLCl_3$: 650 (m), 779 (m), 846 (m), 918 (m), 979 (s), 1054 (w), 1062 (w), 1069 (w), 1241 (w)

$MoOLBr_3$: 660 (m), 690 (m), 777 (m), 845 (w), 891 (w), 917 (w), 966 (w), 973 (s), 1050 (w), 1060 (w), 1065 (w), 1267 (w)

$Mo_2O_3L_2Cl_4$: 654 (s), 704 (s), 779 (m), 849 (m), 919 (w), 966 (w), 1050 (w), 1165 (w), 1168 (w), 1172 (w), 1250 (w)

$Mo_2O_3L_2Br_4$: 659 (s) 694 (s) 710 (s) 778 (s) 850 (s) 921 (s) 967 (s) 1170 (s) 1248 (s)

In the IR spectra of the synthesized complexes of molybdenum (V) with a sulfur-containing ligand, intense absorption bands were found in the region of 950–1000 cm^{-1}, which was attributed to the stretching vibrations of the molybdenum – oxygen group. The disappearance in the spectra the sets of absorption bands at 629 cm^{-1}, characterizing the bending vibration of the C-S-C group of aliphatic sulfide, confirms the coordination of the ligand molecule with molybdenum (V) through both donor sulfur atoms.

In hydrolysis complex compounds, the Mo = 0 band is very small. In our opinion, this is due to the presence of the O-Mo-O trans-group in the complex. Both oxygen atoms use the same d-orbitals of molybdenum to form a π-bond. Therefore, when one of these bonds is stretched, the second is relatively compressed, since the d-orbitals of the metal become more accessible to it. This circumstance facilitates the antisymmetric vibration, which manifests itself in the region of lower frequencies [11].

As it can be seen from the given frequencies of the IR spectra for the hydrolysis forms of the complexes, strong bands appear in the region of 730-680 cm^{-1}, which we attributed to the vibration of O-Mo-O-Mo-O. Consequently, the hydrolysis forms are the complexes of the type $Mo_2O_3L_2Hal_4$, Mo (O) $LHal_2$-O-Mo (O) $LHal_2$ where Hal-Cl^-, Br^-, L-C_2H_5-S-C_2H_4-S-C_2H_5 [12]. The study of the complexes in the long-wave IR region is of the greatest interest [12].

In the spectra of chloride complexes there are strong absorption bands in the range of 350-380 cm^{-1}, in the case of bromide complexes such absorption is observed in the range of 250-150 cm^{-1}.

Two bands in the region of 220 cm^{-1} can be caused by the splitting of the doubly degenerated pendulum vibration of Mo-O, which is explained by the low local symmetry of the anion in the crystal lattice. The band in the area of 180 cm^{-1} is assigned to the deformation vibration δ (Cl-Mo-Cl).

In the oxobromide complex, the bands found in the region of 220 cm^{-1} are attributed to the stretching vibrations of the Mo – Br bond compared to the 217 cm^{-1} band for $MoBr_2^-$ [8]. The band in the region of 116 cm^{-1} is attributed to the deformation vibrations of Br-Mo-Br, the corresponding band of $MoBr_6^{2-}$ lies at 118 cm^{-1}.

From work [8] it is known that the absorption bands in the region of 280-360 cm^{-1} correspond to the stretching vibrations of Mo-Cl and bending vibrations of Mo-O and stretching vibrations of Mo-S 200-280 cm^{-1}. The frequencies of the stretching vibrations of Mo-Br are mixed into a longer wavelength region of 240-190 cm^{-1}.

Thus, on the basis of the literature data, it can be assumed that the absorption bands of chloride complexes of molybdenum (V) in the region of 350-280 cm^{-1} refer to the stretching vibration of the Mo-Cl bond. When chlorine is replaced by bromine, the absorption bands shift to the long-wavelength region by about 100 cm^{-1} and lie in the range of 250-190 cm^{-1}.

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