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COMPLEXES OF 1-(2-ETHOXYETHYL)-4-(DIMETHOXYPHOSPHORYL)-4-HYDROXYPIPERIDINE WITH IONS OF BIOGENIC METALS: SYNTHESIS AND PROPERTIES

Abstract. The complexation of 1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine with ions of biogenic metals (Co^{+2}, Ni^{+2}, Cu^{+2}, Mn^{+2}) in the ligand : ion ratio of 2:1 had been studied. It had been turned out that cobalt and nickel ions generate stable complexes, whereas the product obtained with copper and manganese ions is basically a mixture of the ligand and the corresponding salt. By modeling with the semiempirical PM3 method, it had been shown that a complex in which the divalent metal ion forms coordination bonds with nitrogen atoms and oxygen with a double bond on phosphorus is energetically most advantageous, with the piperidine cycle being in the “boat” conformation. CoL_2Cl_2 (Kaz-10) and [MnL_2SO_4] (Kaz-11) at a concentration of 1.0.10-3% significantly stimulate the germination of barley and wheat seeds.

Key words: α-Hydroxyphosphonate, ions of biogenic metals (Co^{+2}, Ni^{+2}, Cu^{+2}, Mn^{+2}), complex, synthesis, structure, stimulator of germination of barley and wheat seeds.

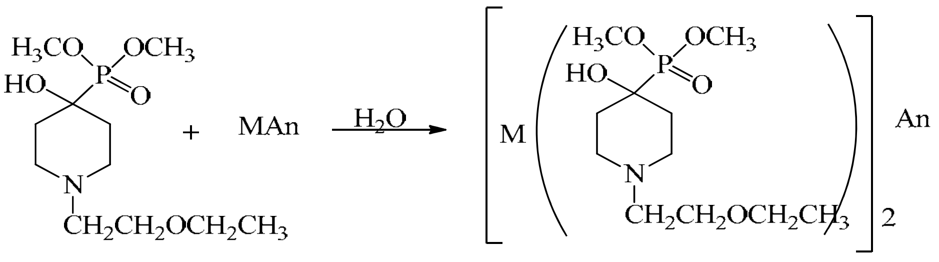
Bioregulation - an area that enables to regulate the direction and intensity of biochemical processes, which can be widely used in medicine, livestock and crop production. It is related to development of ways to restore the physiological function of the body both for the prevention and treatment of diseases and age pathologies. Complex compounds of organic ligands with ions of biogenic metals refer to promising biologically active compounds. The results of their biological effect tests showed that chemistry gives novel preparations to doctors, cattle breeders, agronomists and biologists, allowing them to actively influence the living cell, regulate the nutritional conditions, growth and development of living organisms [1-4].

Among the microelements, the content of which in the body amounts to thousands and even trillions of percent, are: iron, cobalt, manganese, copper, molybdenum, zinc, cadmium, fluorine, iodine, selenium, strontium, beryllium, lithium, etc. Despite the small quantitative content in organisms, microelements has a significant biological role in the processes of growth and development. It has been established that the excess of microelements, as well as their lack, adversely affects the plants.

α-Hydroxy- and α-aminophosphonates are of practical interest as substances with biological activity of widely spectrum and technological simplicity of their obtaining [5-9]. In addition, the ability of organophosphorus to complex formation with metal ions [10-14] contributes to the expansion and more intensive development of chemistry of this class of compounds. Complexes of aminophosphonates with lanthanides and actinides are used in medical NMR diagnostics. Using aminophosphonates, effective methods for separating gold ions, iron ions, copper ions, and also palladium extraction have been developed. Currently, there are a number of drugs based on nitrogen-containing bisphosphonates for patients with impaired calcium metabolism. Aminopolyphosphonates as complexing agents with high specificity for various cations are widely used in analytical chemistry and catalysis, in the paper and textile industries to remove trace amounts of metal ions in whitening baths, as well as in medicine to relieve metal overload in living organisms, particularly for the treatment of anemia overload of iron in the body.

The previously synthesized hydroxyphosphonate with the N-(2-ethoxyethyl)piperidine moiety [15, 16], at a concentration of $1.0\cdot10^{-3}$%, stimulates growth and increases resistance to drought of plants, and in an experiment on animals poisoned with salts of heavy metals, it treats their immune status.

To enhance the stimulating growth of plants there is set to study complexation of 1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine (ligand, L) with certain ions of biogenic metals - Co^{+2}, Mn^{+2}, Cu^{+2} and Ni^{+2}. To prepare the complexes ligand and chlorides of cobalt, nickel, copper and manganese sulfate are taken with the ratio (metal ion : L) = 1: 2.



$M = Co^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}$;

$An = 2Cl^-$ or SO_4^{2-}

To obtain the complexes, the salt and ligand are separately dissolved in the solvent, then the solutions are drained and stirred at room temperature for 2 hours. The reaction mixture is then dried at 50 ° C until the solvent evaporates completely. Moreover, various solvents have been used to prepare the target complexes: ethanol, methylene chloride, acetonitrile, benzene, acetone and water. The best results were obtained using ethanol or methylene chloride.

The synthesized complexes are crystalline products, some have different colors (Co^{+2} - dark blue, Ni^{+2} - yellow-green, Cu^{+2} - light blue), but only the complex of the ligand with Mn^{+2} is white crystals.

In the IR spectrum of the ligand (figure 1), an intense absorption band is observed at 1037.5 cm^{-1}, which is characteristic of C-N stretching vibrations, the band at of 1226.2 cm^{-1} is attributed to the absorption of P=O group, 3269.5 cm^{-1} -

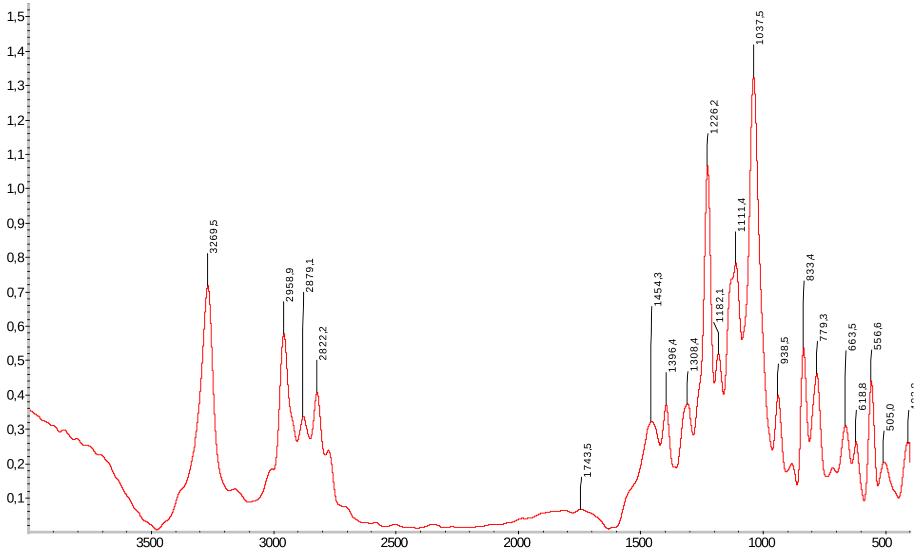


Figure 1 – IR spectrum of 1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine (L)

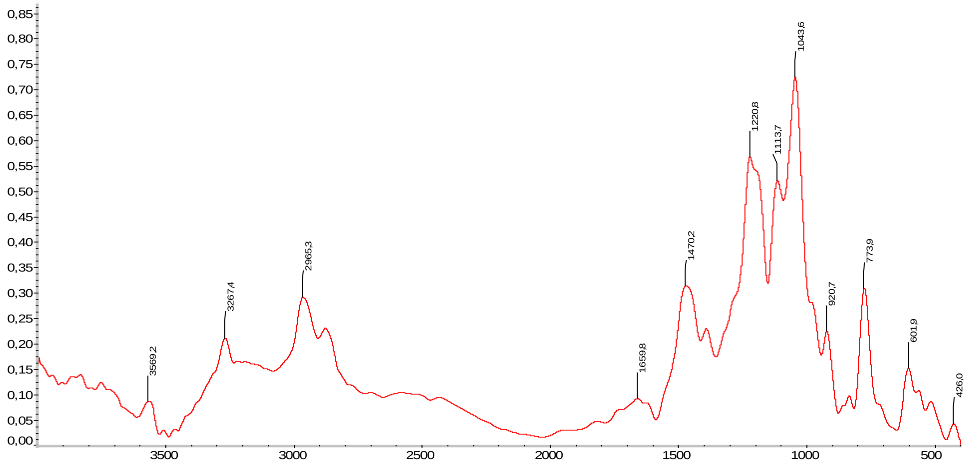


Figure 2 – IR spectrum of CoL_2Cl_2

to the uptake of O-H, 1182.1 cm^{-1} – ($-CH_2-O-CH_2-$), 1454.3 cm^{-1} - $P-OCH_3$, and also several absorption bands of $C_{sp2}-C_{sp2}$ (2822.2 cm^{-1}, 2879.1 cm^{-1}, 2958.9 cm^{-1}).

The IR spectrum of the cobalt complex (figure 2) suggests the formation of a complex. Thus, the shift of the absorption bands of the P=O group into the region 1220.6 cm^{-1} and $P-OCH_3$ - at 1470.2 cm^{-1} indicates the participation of the phosphonate fragment in the formation of the Co^{+2} - ligand bond, and also the C-N bonds with 1037.5 cm^{-1} to 1043.5 cm^{-1}. Absorption of the bonds of the hydroxyl group remains almost unchanged (C-O alcohol - 1037.5 cm^{-1}, 3267.4 cm^{-1} - O-H). The IR spectrum of the nickel complex looks similar.

The average values of the absorption bands of the bonds of the P-OCH_3, P=O, C-N of ligand and its complexes are presented table 1.

Table 1 – IR spectra of the ligand and its complexes with ions Co^{+2}, Ni^{+2}, Cu^{+2}, Mn^{+2}

Compound	IR spectrum, cm^{-1}		
	P-OCH_3	P=O	C-N
Ligand (L)	1454	1226	1037
CoL_2Cl_2	1466	1200	1043
NiL_2Cl_2	1456	1188	1049
$[CuL_2Cl_2]$	1454	1226	1038
$[MnL_2SO_4]$	1453	1226	1037

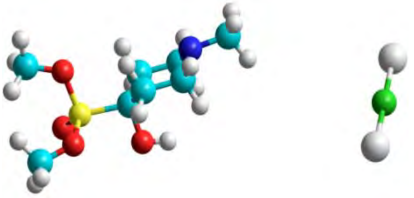
Infrared spectra of copper and manganese complexes are characterized by the presence of absorption bands of the above groups both in the ligand itself, which indicates that the resulting samples contain mainly the initial ligand. However, judging by some changes in the reaction solution (color, gradual dissolution of the precipitate of the salt), a complex is formed. Apparently, the technique used is not entirely suitable for the preparation of complexes with copper and manganese ions.

The NMR spectra of the obtained complexes due to the strong magnetic field of the metal ions turned out to be unsuitable for decoding and, accordingly, it is impossible to determine the structure of the complex. To solve this problem, the possibilities of computer chemistry are involved. The modeling was carried out using the semiempirical PM3 method. To accelerate the optimization of ligand structures and its complexes, its structure is simplified by replacing the substituent at the nitrogen of piperidine ring by the methyl group, while the extension of this substituent is assumed to have a slight effect on the heat of complex formation. As the complex-forming model compound, chloride of bivalent copper is taken. The accuracy of the optimization (gradient) is set to 0.01 kcal/mol.

To estimate the heat of formation of the copper ligand-chloride system, calculations were carried out for two conformational states of the heterocyclic ring ("*chair*" and "*boat*"), and the distance between the ligand and copper chloride was not less than 7A in order to avoid convergence and the formation of coordination bonds during optimization. Since the possibility of forming coordination bonds of three groups or fragments of the ligand was taken into account, four more probable structures (figure 3) of the complex were calculated.

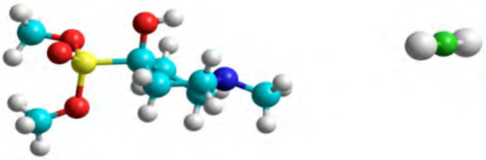
After optimization of the most probable structures of the complex, the heat of formation was estimated. Calculations show that the formation of complex 4 (HF = -267.960 kcal/mol) is most profitable energetically. The main points for the generation of coordination bonds between the ligand molecule - 1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine, and the bivalent copper ion are nitrogen and oxygen with a double bond on phosphorus, which have the

Initial system
(ligand "*chair*")



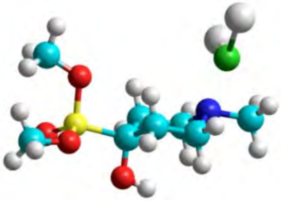
Heat of formation
HF = -200.893 kcal/mol

Initial system
(ligand "*boat*")



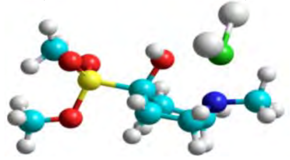
Heat of formation
HF = -202.286 kcal/mol

Complex 1
(Cu^{+2}, N, «*chair*»)



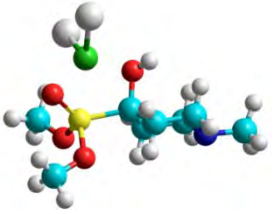
Heat of formation
HF = -258.157 kcal/mol

Complex 2
(Cu^{+2}, N, OH, «*boat*»)



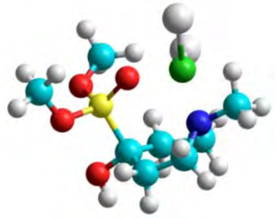
Heat of formation
HF = -261.256 kcal/mol

Complex 3
(Cu^{+2}, P=O, OH, «*chair*»)



Heat of formation
HF = -261.677 kcal/mol

Complex 4
(Cu^{+2}, N, P=O, «*boat*»)

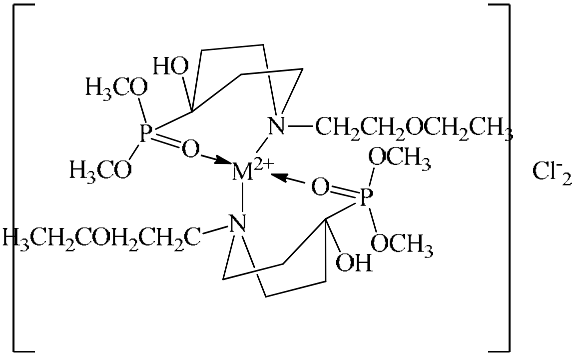


Heat of formation
HF = **-267.960** kcal/mol

Figure 3 – Probable conformation of the ligand and complexes
and the values of Heat of formation

highest electron density. The second molecule of the ligand "joins" to metal ion in the same way. The nature of the substituent at the nitrogen atom of the piperidine ring and the metal does not significantly affect the heat of formation of the complex.

Thus, the most probable structure of 1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine complex with a divalent metal ion is:



The shift in the absorption bands of the P-OCH$_3$, P=O and C-N bonds in the IR spectra of CoL$_2$Cl$_2$ and NiL$_2$Cl$_2$ compared with analogous bands of ligand testifies the formation of this complex structure.

Test studies on the germination of seeds of two complexes of 1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine with cobalt (CoL$_2$Cl$_2$) and manganese ([MnL$_2$SO$_4$]) ions were carried out on the barley variety "Arna" (elite), wheat variety "Kazakhstan-10 "(elite) and maize variety "KazNIIZR-75". Table 2 presents the results of the first 3 days after the soaking of seeds in the corresponding solutions (concentration of Kaz-10 and Kaz-11 was $1{,}0 \cdot 10^{-3}$ %).

Table 2 – Test data Kaz-10, Kaz-11 and applied plant growth stimulants (Gumi-K+Vermicai) and Baikal EM-1 for germination of barley, wheat and maize seeds in model experiments on phytotron

Preparation	The number of sprouted seeds for every 10 in the series, pcs.		
	Barley variety "Arna" (elite)	Wheat variety "Kazakhstan-10" (elite)	Maize variety "KazNIIZR-75"
Control (Water)	2,3/10	5,7/10	no
Kaz-10 (CoL$_2$Cl$_2$)	2,5/10	7,7/10	no
Kaz-11 ([MnL$_2$SO$_4$])	3,0/10	6,7/10	no
(Gumi-K+Vermicai)	2,0/10	7,3/10	no
Baikal EM-1	1,5/10	7,0/10	no

The stimulating effect of Kaz-10 and Kaz-11 and used stimulants (Gumi-K+Vermicai, Baikal EM-1) on seeds of cereal crops - barley and wheat is noted. On the seeds of maize varieties "KazNIIZR-75" during the first three days, the effect does not appear in all the solutions studied.

Thus, it had been shown that hydroxyphosphonate - 1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine, forms with the ions of biogenic metals (Co^{+2}, Ni^{+2}, Cu^{+2}, Mn^{+2}) complexes in the ratio of ligand: ion is 2 : 1. The cobalt and nickel ions generate stable complexes, whereas the product obtained with copper and manganese ions is basically a mixture of the ligand and the corresponding salt. It is energetically most advantageous a complex in which the metal ion $M^{+\ 2}$ has coordination bonds with the nitrogen and oxygen of P=O group, and the piperidine cycle is in the "*boat*" conformation. CoL_2Cl_2 and $[MnL_2SO_4]$ under laboratory ciphers Kaz-10 and Kaz-11 significantly stimulate the germination of barley and wheat seeds at a concentration of $1.0 \cdot 10^{-3}$%.

EXPERIMENTAL PART

Control over the reactions is carried out by thin layer chromatography on aluminum oxide of III degree of activity with the appearance of spots by iodine vapor. The IR spectra were recorded on a Nicolet 5700 FT-IR spectrometer in KBr tablets.

Synthesis of di[1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine]cobalt (II) chloride. To a solution of 0.25 g ($9.0 \cdot 10^{-4}$ mole) of 1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine in 5-10 ml of ethanol (or methylene chloride) was added a solution of 0.1 g (4,5.10-4 mole) of cobalt (II) chloride hexahydrate in 5-10 ml of ethanol (or methylene chloride). Then a pink mixture is placed in an ultrasonic bath for 30 min. The reaction solution is then dried at 50°C, until the solvent has completely evaporated. The complex is obtained in the form of a crystalline powder of a dark blue color with a yield of 66.7% (0.21 g), m.p. 118-128 ° C (ethanol) and 60% (1.18 g), m.p.108-135° C (methylene chloride).

Calcd., %: C 38,16; H 6,988. $CoC_{22}H_{48}N_2O_{10}P_2Cl_2$.

Found., %: C 38,49; H 6,59.

IR, cm^{-1}: 1183 ($-CH_2-O-CH_2-$); 1466 ($-P-OCH_3$); 2965, 2966, 2969 ($C_{sp2}-C_{sp2}$); 1200 (P=O); 1044 (C-OH); 3267 ($C_{arom.}$-H).

Synthesis of di[1- (2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine]nickel (II) chloride. To a solution of 0.25 g ($9.0 \cdot 10^{-4}$ mole) of 1-(2-ethoxyethyl)-4- (dimethoxyphosphoryl)-4-hydroxypiperidine in 5-10 ml of ethanol (or methylene chloride) was added a solution of 0.1 g ($4{,}5 \cdot 10^{-4}$ mole) of nickel chloride hexahydrate (II) in 5-10 ml of ethanol (or methylene chloride). The mixture is then placed in an ultrasonic bath for 1 min. The reaction solution is then dried at 50°C, until the solvent has completely evaporated. The complex is obtained as a crystalline powder of a yellow-green color with a yield of 75.2% (0.23 g), m.p. 111-161°C (ethanol) and 57.2% (1.18 g), m.p. 141-151° C (methylene chloride).

Calcd., %: C 38,18; H 6,99. $NiC_{22}H_{48}N_2O_{10}P_2Cl_2$.

Found., %: C 38,71; H 6,81.

IR, cm^{-1}: 1115 ($-CH_2-O-CH_2-$); 1456 ($-P-OCH_3$); 2971, 2972, 2973 ($C_{sp2}-C_{sp2}$); 1188 (P=O); 1048 (C-OH); 3200 ($C_{arom.}$-H).

Synthesis of di[1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine] copper (II) chloride. To a solution of 0.3 g ($7.8 \cdot 10^{-4}$ mole) of 1-(2-ethoxyethyl)-4- (dimethoxyphosphoryl)-4-hydroxypiperidine in 50 ml of ethanol (or methylene chloride) was added a solution of 0.005 g ($3.9 \cdot 10^{-4}$ mole) of copper (II) chloride in 5 ml of ethanol (or methylene chloride). The mixture is stirred for

1 h at room temperature and held for 20 min in an ultrasonic bath. The complex is obtained as a light blue crystalline powder in 75% yield (0.2 g), m.p. 107-112° C (ethanol) and m.p. 108-112 ° C (methylene chloride) (mixture of ligand, salt and complex).

Calcd., %: C 37,91; H 6,94. $CuC_{22}H_{48}N_2O_{10}P_2Cl_2$.

Found., %: C 42,54; H 7,64.

ИК спектр, $см^{-1}$: 1110 ($-CH_2-O-CH_2-$); 1454 ($-P-OCH_3$); 2821,7; 2880,6; 2959,3 ($C_{sp2}-C_{sp2}$); 1226,2 (P=O); 1037,5 (C-OH); 3269 ($C_{arom.}$-H).

Synthesis of di[1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine] manganese (II) sulfate. To a solution of 0.9 g ($3.2 \cdot 10^{-3}$ mole) of 1-(2-ethoxyethyl)-4- (dimethoxyphosphoryl)-4-hydroxypiperidine in 50 ml of ethanol (or methylene chloride) was added a solution of 0.27 g ($1{,}6 \cdot 10^{-3}$ mole) manganese sulfate (II) monohydrate in 5 ml of ethanol (or methylene chloride). The mixture is stirred for 1 h at room temperature and held for 20 min in an ultrasonic bath. The complex is obtained as a white crystalline powder in 70% yield (0.18 g), m.p. 106-114°C (ethanol) and m.p. 109-113°C (methylene chloride) (mixture of ligand, salt and complex).

Calcd., %: C 33,95; H 6,78. $MnC_{22}H_{48}N_2O_{14}P_2S$.

Found., %: C 43,59; H 8,94.

IR, cm^{-1}: 1110 ($-CH_2-O-CH_2-$); 1452,7 ($-P-OCH_3$); 2957,5 ($C_{sp2}-C_{sp2}$); 1226,0 (P=O); 1038,3 (C-OH); 3267,9 ($C_{arom.}$-H).

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Резюме

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КОМПЛЕКСЫ 1-(2-ЭТОКСИЭТИЛ)-4-(ДИМЕТЕТОКСИФОСФОРИЛ)-4-ГИДРОКСИПИПЕРИДИНА С ИОНАМИ БИОГЕННЫХ МЕТАЛЛОВ: СИНТЕЗ И СВОЙСТВА

Показана возможность комплексообразования 1-(2-этоксиэтил)-4-(диметоксифосфорил)-4-гидроксипиперидина с ионами биогенных металлов (Co^{+2}, Ni^{+2}, Cu^{+2}, Mn^{+2}) в соотношении лиганд:ион = 2:1. Оказалось, что ионы кобальта и никеля образуют стабильные комплексы, тогда как полученный продукт с ионами меди и марганца представляет в основном механическую смесь лиганда и соответствующей соли. Моделированием полуэмпирическим методом РМ3 показано, что энергетически наиболее выгодно образование комплекса, в котором ион двухвалентного металла образует координационные связи с атомами азота и кислорода с двойной связью на фосфоре, при этом пиперидиновый цикл находится в конформации *ванна*. CoL_2Cl_2 и $[MnL_2SO_4]$ под лабораторными шифрами Каз-10 и Каз-11 в концентрации $1{,}0 \cdot 10^{-3}$ % заметно стимулируют прорастание семян ячменя и пшеницы.

Ключевые слова: гидроксифосфонат, ионы биогенных металлов, комплекс, синтез, структура, стимуляция прорастания семян ячменя и пшеницы.

Резюме

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1-(2-ЭТОКСИЭТИЛ)-4-(ДИМЕТЕТОКСИФОСФОРИЛ)-4-ГИДРОКСИПИПЕРИДИННІҢ БИОГЕНДІ МЕТАЛДАР ИОНДАРЫМЕН КЕШЕНДЕРІ: СИНТЕЗІ МЕН ҚАСИЕТТЕРІ

Лиганд:ион = 2:1 қатынасында 1-(2-этоксиэтил)-4-(диметоксифосфорил)-4-гидроксипиперидиннің биогенді металдардың иондарымен (Co^{+2}, Ni^{+2}, Cu^{+2}, Mn^{+2}) кешен түзу мүмкіндігі көрсетілген. Мыс пен марганец иондарынан алынған өнімдер лиганд пен сәйкес тұздың механикалық қоспасы болып табылса, ал кобальта пен никеля иондары тұрақты кешен түзетіндігі анықталды. РМ3 жартылай эмпирикалық әдісімен модельдеу арқылы, екі валентті металдың ионы азот және фосфордағы қос байланысты оттегі атомдарымен координациялық байланыс түзгенде, пиперидин циклінің *ванна* конформацияда орналасуы кешен түзілуінің энергетикалық жағынан ең тиімді екендігі көрсетілген. Каз-10 және Каз-11 зертханалық шифрлармен берілген CoL_2Cl_2 және $[MnL_2SO_4]$ $1{,}0 \cdot 10^{-3}$ % концентрациясында арпа мен бидай тұқымдарының өсуін айтарлықтай ынталандырады.

Түйін сөздер: гидроксифосфонат, биогенді металдардың иондарымен, комплекс, синтез, структура, стимуляция прорастания семян ячменя и пшеницы.