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Synthesis of Molybdenum Acid-containing Chelates and Their Usage in Broiler Feeding

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A B S T R A C T

Synthesis conditions are established and molybdenum chelate compounds are synthesized with general formulas $[(H_2MoO_4)x\cdot gl]\cdot nH_2O$, (where x=1-3; gl-glutamine acid, n=2; 3) (I) and $[(H_2MoO_4)x\cdot Mt]\cdot nH_2O$ (where x=1;2; n=1; 2 Mt-methionine). The composition, individuality, and qualitative solubility in different solvents of the synthesized compounds are determined. Thermal analysis determines the nature of the thermal decomposition of the compounds. The degree of dissociation of chelates and the dissociation constants are determined based on the conductometric study. An experiment was conducted on a broiler to study biological activity. Dynamics of broiler live mass, absolute live weight gain, daily weight gain, fowl keeping, feeding expenditure for 1 kg. weight gain, broiler growth efficiency. It has been established that the use of chelate molybdenum in broiler feeding had a positive effect on all the above parameters and the optimal dose of chelate is 100-150 mcg. on one wing.

Key words: molybdenum, chelate, premix, broiler, glutamine acid, methionine.

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The actuality of the Issue

The role and importance of micronutrients as well as organic substances (amino acids, oxyacids, vitamins, etc.) in the normal growth and development of agricultural poultry and animals are now widely recognized. Micronutrients in bird premixes can be incorporated into two forms: both inorganic and chelate. In the inorganic form, salts are characterized by high toxicity, low degree of absorption, and efficiency, which is due to the formation of compounds that are difficult to dissolve and difficult to assimilate in the gastrointestinal tract of animals and birds. In the chelate form, micronutrients have low toxicity, high absorption capacity, and consequently, an increased degree of efficiency when used in small doses, which in turn contributes to the ecological safety of the use of micronutrients in this form. It should be noted that in 2003, European countries passed a law on the maximum allowable doses of trace elements in the manure of agricultural poultry and animals: manganese, zinc, iron, cobalt, and copper. The solution to this problem, as already mentioned, is possible only by using the chelate form of these micronutrients. This fact is confirmed by the results of research conducted by foreign scientists [1-6] and results of research conducted by us over the years [17-23]. These advantages explain the increase in the production scale of premixes containing micronutrients in the form of chelates compared to non-chelated ones, which is increasing. Nowadays, micronutrients Mn, Zn, Fe, Co, Cu, and I are included in the premixes according to the detailed norms of nutrition. However, the number of vital (essential) micronutrients that can not be replaced by other micronutrients and in the absence or deficit of which the likelihood is much higher, that the body can not grow normally and end the life cycle normally. Among these trace elements, our focus has been on molybdenum.

Molybdenum is characterized by low toxicity compared to other trace elements and is included in the enzymes xanthine oxidase, sulfite oxidase, and aldehyde oxidase. Has pronounced antioxidant properties, provides the breakdown and expulsion of toxic substances in the body, has a positive effect on the intestinal microflora, and actively participates in the synthesis of amino acids and vitamins (especially vitamin C). Has the ability to capture fluoride in the body, which ensures the maintenance of tooth tissue and gums in normal conditions and prevents caries. Molybdenum facilitates the absorption of iron by the body, which helps prevent anemia. Molybdenum deficiency contributes to the development of anabolic processes, weakening the immune system.

Georgia is an endemic center of molybdenum deficiency, however, as we have already mentioned, it is not included in the premixes, and in the composition of fertilizers it is used in the form of inorganic salts; This circumstance is explained by the fact that as a trace element in the composition of anions, it is characterized by a lower tendency to form compounds of the chelate form. According to the modern view of the ability to form complex microelements, which implies the use of a base nature chelate agent [27, 28], it is possible to synthesize molybdenum-containing chelates. Taking into account these factors, our work aimed to synthesize molybdenum-containing chelate compounds, physical-chemical research, and determine its impact on fowl growth and development, productivity, and physiological condition.

Aim and Objectives of the Research

The study aimed to study and establish the role of molybdenum, a micronutrient necessary for life, in broiler productivity, its impact on growth intensity, food compensation, organism viability, meat quality, and taste, and some morphological and biochemical parameters of the blood.

The study aimed to determine the optimal dose of molybdenum, a micronutrient necessary for life, in broiler nutrition.

Research Materials and Methods

Microelement analysis - to determine the composition of molybdenum chelate compounds

Determination of melting temperature and diffractogram study - To determine the individuality of the chelates

Determination of solubility - to study the qualitative solubility of chelate compounds in different solvents

Conductometric research - determination of dissociation constant and dissociation quality of solutions containing solutions of chelate compounds

Thermographic analysis - to study the thermal stability of chelate compounds and the study the sequence of the thermolysis process

Weighing method - to determine the weight gain of the broiler

Accounting method of food consumption - to determine the conversion of food and consumed nutrients (protein, energy).

Research Results under Production Conditions

To obtain molybdenum chelate compounds with general formulas $[(H_2MoO_4)x\cdot gl]\cdot nH_2O$, (where x = 1-3; gl-glutamine acid, n = 2; 3) (I) and $[(H_2MoO_4)x\cdot Mt]\cdot nH_2O$ (Where x = 1; 2; n = 1;2 Mt-methionine). In the case of (I) molybdenum and glutamine acid are taken separately with 1:1; 1:2 and 1:3 molar ratios, and in the case of (II), also separate molybdenum acid and methionine are taken with 1:1 or 1:2 molar ratios. Each of them dissolves in a minimum volume of water under conditions of intense stirring and heating. To the chem solutions of glutamine acid and methionine is added ammonia up to a weak alkaline range (pH = 8). Chem solutions of molybdenum acid and glutamine acid and molybdenum acid and methionine are mixed in the above-mentioned sequence, filtered, and each of them is kept at room temperature. After a few days, the obtained compounds are filtered, washed with water, and ether, and dried at room temperature.

The composition and individuality of the obtained compounds are determined. Melting point is defined on the device melting point /SMP10 (Table 1), And it ranges from 190-240^{0}C temperature range.

Table 1.

Some Physical Characteristics of the compounds containing Molybdenum Acid and Glutamine Acid

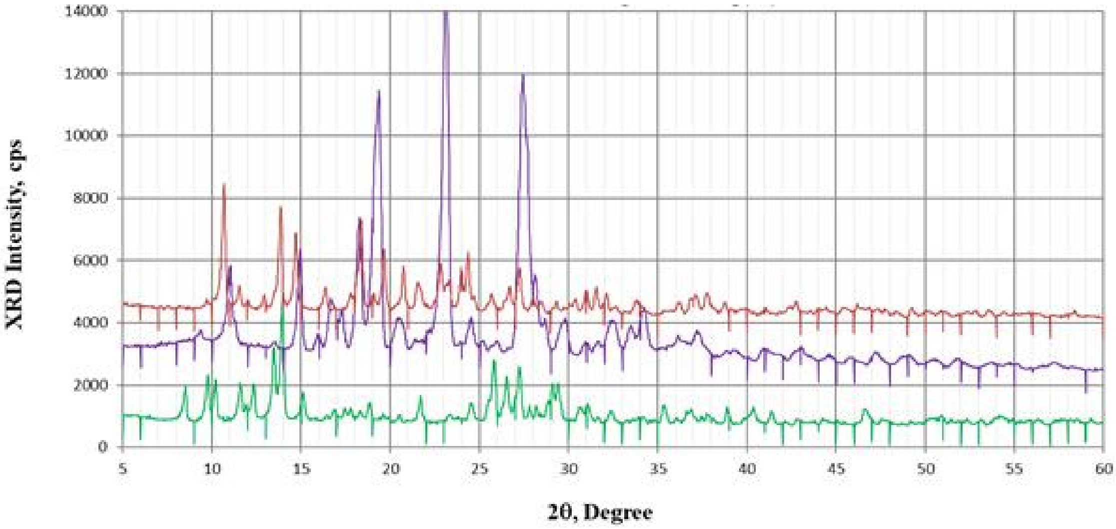
#	The formula of the Compound	Mol Mass	Melting $t\,^0c$	Solubility				Conductometric Survey Results		
				Water	Alcohol	Acetone	Dmf	α Average	R^2	K
1	$[H_2MoO_4 \cdot gl]\cdot 2H_2O$	345.10	190	+	+ t	+ t	+	0.8010	0.8615	0.0604
2	$[(H_2MoO_4)_2 \cdot gl]\cdot 2H_2O$	507.04	220	+	+ t	+	+	0.8012	0.9514	0.0342
3	$[(H_2MoO_4)_3 \cdot gl]\cdot 3H_2O$	686.96	240	+	+ t	+ t	+	0.7315	0.9118	0.0261
4	$[H_2MoO_4Mt]\cdot 2H_2O$	347.19	210	+	+ t	+	+ t	0.7810	0.8820	0.0397
5	$[(H_2MoO_4)_2\, Mt\cdot H_2O$	491.12	230	+	+ t	+ t	+	0.8075	0.9078	0.0271

Dmf* - Dimethyl formamide;

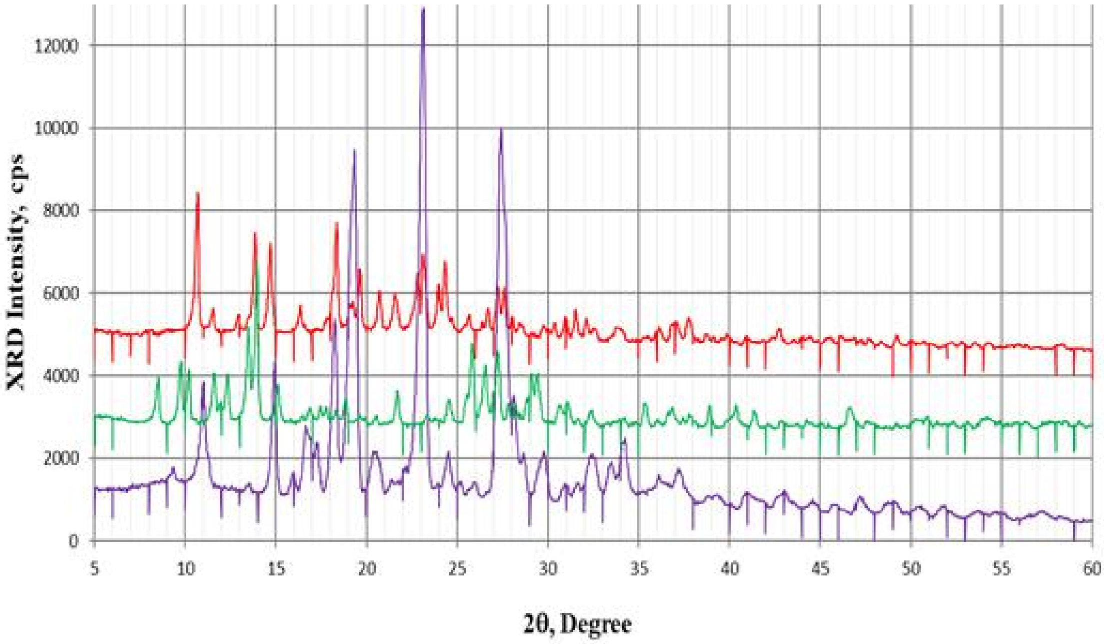
The qualitative solubility of compounds in different solvents is determined, according to which they are characterized by good solubility in water and dimethylformamide, and relatively poor solubility in alcohol and acetone (Table 1).

To determine the degree of dissociation and dissociation constant of molybdenum chelate compounds, a conductometric study was performed on the device pH and Conductivity Sensor LE703. For compounds for this purpose: $[H_2MoO_4\cdot gl]\cdot 2H_2O$; $[(H_2MoO_4)_2\cdot gl]\cdot 2H_2O$; $[(H_2MoO_4)_3\cdot gl]\cdot 3H_2O$; $[H_2MoO_4Mt]\cdot 2H_2O$; $[(H_2MoO_4)_2\, Mt\cdot H_2O$ solutions were prepared in the concentration range from 0.025N to 0.00065N. The experiment was conducted on a thermostat at 25^0C. The results of the experiment are presented in Table 1. $\mathbf{R^2}$ - (Determination coefficient), is called the approximation reliability coefficient, which shows how close the experimental data is to the corresponding function of the graph. As can be seen from the table it is quite high and ranges from 0.8615-to 0.9514. The degree of dissociation, which is a variable, increases with dilution. As for the values of the dissociation constant, it does not depend on the dilution of the solution, is the constant value, as shown in the table, is quite low and ranges from 0.0261-to 0.0604.

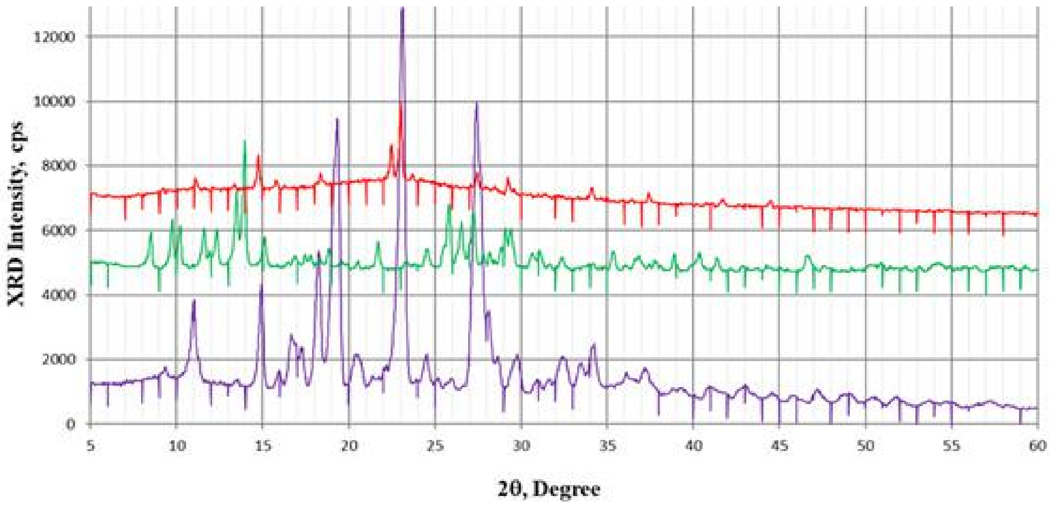
For compounds $[H_2MoO_4\cdot gl]\cdot 2H_2O$, $[(H_2MoO_4)_2\cdot gl]\cdot 2H_2O$, and $[(H_2MoO_4)_3\cdot gl]\cdot 3H_2O$ X-ray diffractometric study was performed using ДРОН-4 $Cu_{k\alpha}$(λ=0.154184nm) output. During the exposure, the samples were rotated on their plane by a special device - ГП-13. Starting reactants Molybdenum acid and glutamine acid diffractograms were also taken for comparison. As can be seen from the analysis of diffractograms (Fig. 1-3), the location and intensities of the diffraction maximum characteristic of the obtained chelate compounds differ from the location and intensities of the diffraction maximum of the reactant compounds in other words do not contain characterizing diffraction maximums of the initial compounds (molybdenum acid and glutamine acid). This indicates that new individual compounds are being formed.



[H_2MoO_4(gl])]·$2H_2O$; H_2MoO_4; gl
Fig.1



[$(H_2MoO_4)_2$· gl]·$2H_2O$; H_2MoO_4; gl
Fig.2



[$(H_2MoO_4)_3$· gl]·$3H_2O$; H_2MoO_4; gl
Fig.3

To study the thermal stability and sequence of the thermolysis process of the synthesized molybdenum chelate compounds $[H_2MoO_4{\cdot}gl]{\cdot}2H_2O$; $[(H_2MoO_4)_2{\cdot}gl]{\cdot}2H_2O$; $[H_2MoO_4Mt]{\cdot}2H_2O$; $[(H_2MoO_4)_2{\cdot}Mt{\cdot}H_2O$, a thermographic test was performed on the instrument: NETZSCH STA2500 the heating rate of the sample is 10 degree/min (Table 2). As it became clear from the thermographic test, each thermogram is characterized by several exogenous and endogenous effects and with corresponding effects on the curve (Table 2).

Table 2.

Results of a thermographic study of molybdenum acid and glutamine acid-containing compounds

#	Formula	Melting T^0 C	Mass loss,%		Broken-off Molecule, Mol	Solid Product of Decomposition
			Practical	Theoretical		
1	$[H_2MoO_4{\cdot}\ gl]{\cdot}2H_2O$	100 130 240 280 310	3.01 7.87 23.71 30.84 10.86	2.61 8.04 23.80 31.24 11,12	$0.5H_2O$ $1.5H_2O$ 0.5gl 0.5gl H_2O	$[H_2MoO_4{\cdot}\ gl]{\cdot}1.5H_2O$ $[H_2MoO_4{\cdot}\ gl]$ $[H_2MoO_4{\cdot}\ g_{0.5}]$ H_2MoO_4 MoO_3
2	$[(H_2MoO\ _4)_2{\cdot}gl]{\cdot}2H_2O$	100 120 230 250 300	4.0 3.79 15.93 18.21 11.51	3.55 3.68 15.62 18.51 11.12	H_2O H_2O 0.5gl 0.5gl $2H_2O$	$[(H_2MoO\ _4)_2{\cdot}gl]{\cdot}H_2O$ $[(H_2MoO_4)_2\ {\cdot}\ gl]$ $[(H_2MoO_4)_2\ {\cdot}\ g_{0.5}]$ H_2MoO_4 $2MoO_3$
3	$[H_2MoO_4Mt]\ {\cdot}2H_2O$	90 110 240 270 320	2.74 8.21 24.23 30.87 10.99	2.59 7.99 23.98 31.54 11.12	$0.5H_2O$ $1.5H_2O$ 0.5Mt 0.5Mt H_2O	$[H_2MoO_4Mt]{\cdot}.5H_2O$ $[H_2MoO_4Mt]$ $[H_2MoO_4Mt_{0.5}]$ H_2MoO_4 MoO_3
4	$[(H_2MoO_4)_2\ Mt{\cdot}\ H_2O$	110 260 280 310	3.21 15.23 18.14 11.43	3.67 15.77 18.72 11.12	H_2O 0.5Mt 0.5Mt $2H_2O$	$[(H_2MoO_4)_2{\cdot}Mt$ $[(H_2MoO_4)_2{\cdot}Mt_{0.5}$ $2H_2MoO_4$ $2MoO_3$

Thermogravimetric analysis of the chelate compound $[H_2MoO_4{\cdot}gl]{\cdot}2H_2O$ shows that I endo effect (100^{0}C) corresponds to a 0.5 mol H_2O breaking off (mass loss: practical 3.01%, theoretical 2.61%), at next endo effect (130^{0}C) the remaining Mol H_2O is broken off (mass loss: practical 7.87%, theoretical 8.04%). As the analysis shows, at the next endo effect (240^{0}C) there is an oxidation of 0.5 mol glutamine acid (mass loss: practical 23.71%, theoretical 23.80%) and it ends at 280^{0}C (mass loss: practical 30.84%, theoretical 31.24%). The thermal decomposition of molybdenum acid corresponds to a strong exogenous effect at 310^{0}C (mass loss: practical 10.86%, theoretical 11.12%) and the final product of thermolysis is molybdenum oxide MO_3, which was confirmed by qualitative and quantitative analysis of thermolysis residue.

The compound $[(H_2MoO_4)_2{\cdot}gl]{\cdot}2H_2O$ on the thermogravimetric graph shows three endo and one strong exogenous effect. The first endo effect at 100^{0}C corresponds to the break-off of 1 mol of water (mass loss: practical 4.00%, theoretical 3.55%), at the next endo effect (120^{0}C) the second water molecule is broken-off (mass loss: practical 3.79%, theoretical 3.68%), at the third endo effect (230^{0}C) oxidation of 0.5 mol glutamine acid takes place (mass loss: practical 15.93%, theoretical 15.62%). At the next endo effect (250^{0}C) the oxidation of glutamine acid ends (mass loss: practical 18.21%, theoretical 18.51%). A strong exogenous effect (300^{0}C) corresponds to the thermal decomposition of molybdenum acid (mass loss: practical 11.51%, theoretical 11.12%) and the formation of MO_3 molybdenum oxide. The obtained result was confirmed by qualitative and quantitative analysis of the residue.

The compound $[H_2MoO_4Mt]{\cdot}2H_2O$ thermogravimetric graph is characterized by several endos and one strong exogenous effect, indicating that it is decomposed in stages. In particular, the first endo effect at 90^0C corresponds to the loss of 0.5 mol of water (mass loss: practical 2.74%, theoretical 2.59%). At the second endo effect at 110^0C, there is a breakage of the remaining 1.5 mol water molecule (mass loss: practical 8.21%, theoretical 7.99%). The third endo effect at 240^0C corresponds to oxidation of 0.5 mol **Mt** (mass loss: practical 24.23%, theoretical 23.98%). At the next endo effect at 270^0C, methionine oxidation ends (mass loss: practical 30.87%, theoretical 31.54%). Thermal decomposition of molybdenum acid corresponds to a strong exogenous effect at 320^0C (mass loss: practical 24.23%, theoretical 23.98%). The final product of thermolysis is molybdenum oxide MO_3. The obtained result was confirmed by qualitative and quantitative analysis of the thermal residue.

Thermal decomposition of the compound $[(H_2MoO_4)_2\ Mt{\cdot}\ H_2O$ begins at the end effect by breaking off 1 mol of water at 110^0C (mass loss: practical 3.21%, theoretical 3.67%). At the next endo effect (260^0C) the oxidation of the methionine molecule begins (mass loss: 15.23%, theoretical 15.77%). The endo effect at 280^0C corresponds to the oxidation of the remaining 0.5 mol of methionine (mass loss: practical 18.14%, theoretical 18.72%). As in all other cases the thermal decomposition ends at a strong exogenous effect with the decomposition of molybdenum acid at 310^0C and the formation of MO_3 molybdenum oxide (mass loss: practical 11.43%, theoretical 11.12%). The obtained result was confirmed by qualitative and quantitative analysis of the residue.

To determine the biological activity of the molybdenum chelate compound containing methionine acid, the effect of chelate on the broiler's productivity was studied. The experiment was conducted according to the following scheme:

Table 3.

Test scheme

#	Test Group	Number of Fowls	Rearing Period	Molybdenum Dose per 1 Wing (mcg)
1	Group 1	100	35	-
2	Group 2	100	35	50
3	Group 3	100	35	100
4	Group 4	100	35	150

We experimented on a meat cross "Ross 308" at "Roster" Ltd. located in the village of Teleti, Gardabani district, where we studied the effect of methionine-containing molybdenum chelate on the growth and development of broiler and meat quality. For the experiment, we took 400 wings of a 1-day-old chicken, which was divided into 4 groups (100-100 wings). One for control and three for trial.

During the experimental period, broiler rearing in all four groups was carried out with the same technological parameters, on deep bedding, and fully complied with the technological parameters set for broiler rearing.

During the experimental period, we studied the growth and development of a broiler with live mass dynamics. The broiler was weighed at 1,14,28 and 35 days of age, by individual weighing. We have studied the absolute gain in different periods of weighing. We also studied maintenance and food consumption per 1 kg. weight gain. Feed coefficient as well as feed reimbursement, which means the ratio of spent feed to broiler weight gain.

The results of the experiment showed that the mass of one-day-old chicken was almost the same in all groups and ranged from 38.4 to 38.9 g. The relatively low live weight compared to the standard weight of one-day-old chickens (42g) is explained by the fact that they are obtained from the eggs of a relatively young mother hen's team (30 weeks) whose incubation egg weight is 52-54 g. The relatively low mass of a one-day-old broiler negatively affected its growth and development of the broiler. It has been scientifically established that the correlation between one-day-old chicken mass and final live weight is quite high at 0.7-0.75.

Table 4.

Broiler live weight dynamics

#	Test Group	Age, Day			
		1	14	28	35
1	Group 1	38.5	457.9	1361.1	1793.0
2	Group 2	38.4	464.2	1383.8	1829.5
3	Group 3	38.9	473.8	1396.2	1866.8
4	Group 4	38.9	487.8	1426.3	1880.3

The highest live weight at 14 days of age was given to the fourth experimental group of broilers - 487.8 in which the dose of the molybdenum added to feed was 150 mcg. This mass was 6.5% higher than the control group (P≥0.001). During this period, the broiler of the second and third experimental groups, where the dose of molybdenum was 50-100 mcg per wing, exceeded the control group by 1.4 and 3.3%, although the difference is uncertain.

At 28 days of age, the difference between the live weight of the fourth experimental group broiler and the same characteristic of the control group broiler was reduced to 4.8%, although even in this case the difference was uncertain (P≥0.001). And the difference between the live weights of the second and third experimental groups and the broiler live weights of the control groups was also reduced to 1.7 / 2.6%. The difference is uncertain.

At 35 days, respectively at the age of slaughter, the highest live weight - 1880 kg was in the fourth experimental group and exceeded the control group by 4.9% (the difference is uncertain P≥0.001)

As can be seen from the live weight dynamics, the live weight in all groups in all age groups was almost 200-250 grams behind the Ross standards, the reason for which, as mentioned above, is the low initial live weight of one-day-old chickens.

Table 5.

Absolute weight dynamics

#	Test Group	Absolute Gain, g			
		0-14 days	14-28 days	28-35 days	0-35 days
1	Group 1	419.35	903.2	431.9	1754.5
2	Group 2	425.80	919.6	425.7	1791.1
3	Group 3	434.9	922.4	450.6	1821.9
4	Group 4	448.9	938.5	434.0	1841.4

The calculation of the absolute gain showed that the absolute gain is different in different periods of growth. The maximum absolute gain was observed at the age of 14-28 days at 900-940 g. The highest absolute gain during this period was 938.5 in the second experimental group and exceeded the control group by 3.9%. During the same period, absolute gain in the second and third experimental groups is 1.8-2.1% higher compared to the control group.

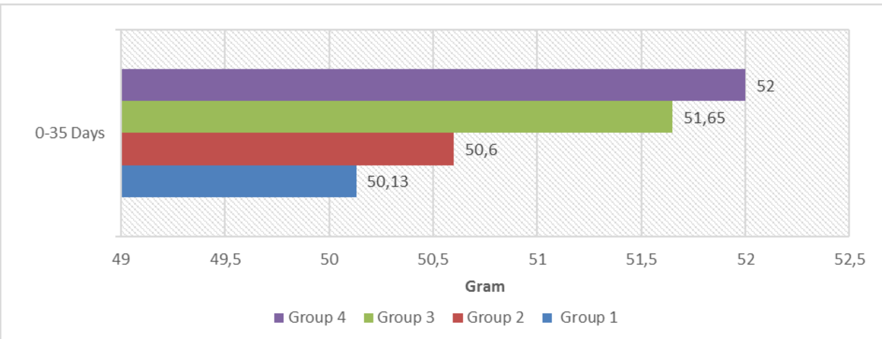


Fig.1. *Changes in daily weight gain in all groups during the rearing period (0-35 days)*

During the rearing period (0-35 days) in all groups, the daily gain varied between 50.3-52.0 g, and the highest was 52.0 grams in the fourth experimental group and the lowest in the control group - 50.13 g.

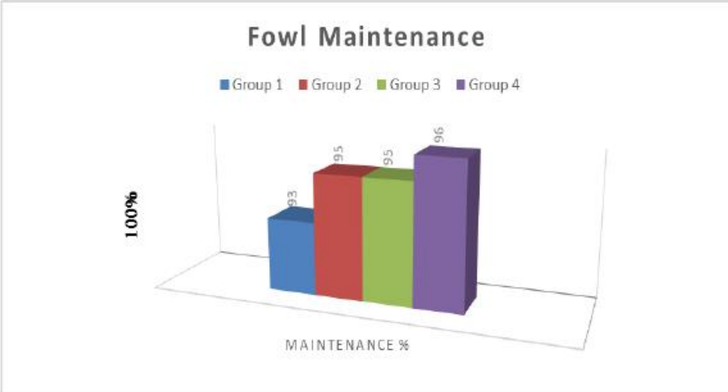


Fig.2. *Fowl Maintenance*

In the fourth test group, the maintenance is also the highest - 96%, which is 3% higher than the control group.

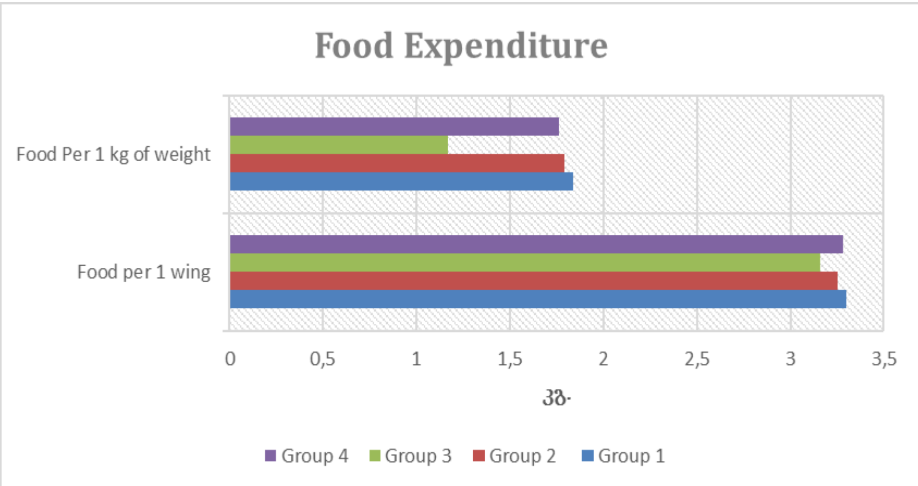


Fig.3. *Food Expenditure*

During the rearing period, the feed consumption was 3.16-3.3 kg per wing, and 1.71-1.84 kg per kilogram of weight gain. The lowest feed expenditure per 1 kg weight gain was 1.71 kg in the third experimental group. Which is 7.6% lower than in the control group. Food consumption was lower by 2.8-4.5% compared to the control in the second and fourth experimental groups per 1 kg weight gain.

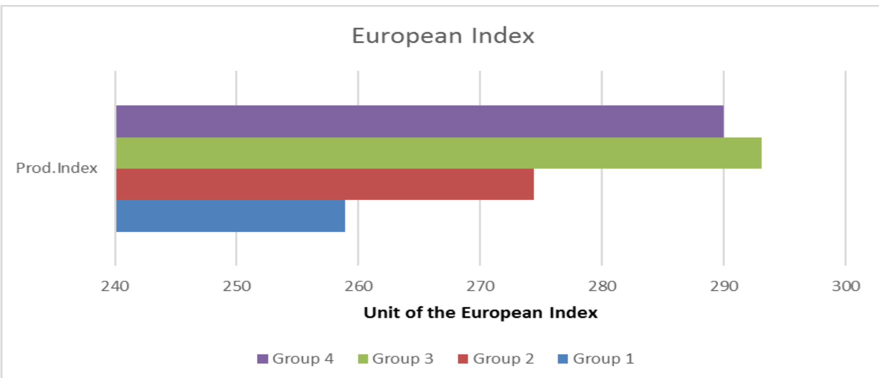


Fig.4. *European Index*

The productivity index was the highest in the third experimental group - 293.0 units, which is 34.2 units higher than the control group. The productivity index is 15-32 units higher in the second and fourth experimental groups.

At the end of the experiment, all four groups of broilers were slaughtered at 35 days of age. The half-gutted slaughtered fowl's output was 80.1% in the control group, which was 2.0% lower than in the fourth group and 1% lower than in the second and third experimental groups.

Table 6. *Slaughter results*

Poultry Meat Output				
Test Group	Group 1	Group 2	Group 3	Group 4
Number of slaughtered fowls	87	89	89	90
Live weight of the slaughtered fowls, kg	156	161	165	168
Live weight of 1 wing	1793	1809	1854	1866
Half-gutted slaughtered fowl's weight	125	131	134	138
Slaughter output %	80.1	81.4	81.2	82.1
Weight of the half-gutted 1 wing	1440	1470	1500	1530
Poultry Category				
First category wing	67	72	73	74
First category %	77.00	80.50	82.02	82.22
Second category wing	17	15	13	14
The second category %	19.50	16.85	14.60	15.55
Non-standard wing	3	2	3	2
Non-standard %	3.50	2.65	3.38	2.23

The study of the poultry meat category showed that the category I poultry meat in the fourth group was 82.12%, while the first category in the control was 77%, which is 5 percent lower. The meat of the first category was also 3% lower compared to the second and third groups by 1.0 and 2.0%.

As for non-standard poultry meat in the four groups is almost the same 2.2-3.5%. The chemical composition (water, crude protein, fat) is almost the same in all four groups. Almost identical and within the norm are some of the biochemical and morphological parameters of the blood which we have studied.

Results, Conclusion

Based on the studies conducted, the following conclusions can be made:

Synthesis conditions are established and glutamine acid and methionine-containing molybdenum chelate compounds are synthesized

The composition of synthesized compounds is determined by the microelement analysis method, and individuality - by melting temperature measurement and diffractogram method

Chelates are characterized by good solubility in water and dimethylformamide, and poor solubility in alcohol and acetone.

The degree of dissociation of compounds and the dissociation constants are determined by the method of conductometric research.

Thermal analysis has established that the thermal decomposition of compounds takes place in stages at the temperature range of 90-330^{0}C in the following sequence: I- break-off of water molecules; II- oxidizing-glutamine acid (methionine) molecule; III- Molybdenum acid is decomposed and in all cases, the final product of decomposition is molybdenum oxide MO_3.

The use of molybdenum in chelate form during the broiler rearing period has had a positive effect on both the growth and maintenance of the broiler, feed conversion, slaughter output, and poultry meat category.

The optimal dose, as the experiment shows, is 100-150 mcg on 1 wing during the full rearing period. Accordingly, 1-1.5 grams should be added to 1 ton of feed.

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