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Study of a Copper Microelement Compound Formed in Ammophosis Pulp

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Abstract. The results of physicochemical analyzes of the compound $CuNH_4 PO_4 \cdot H_2O$ isolated from ammophos pulp at pH 6.58 obtained by neutralization of phosphoric acid containing copper sulfate as a trace element with gaseous ammonia are presented. The compound was found to have the formula $[Cu (NH_3) (H_2O) HPO_4]$. The parameters of the N–H bond for the coordinated amino group were calculated: force constant, bond angle, and interatomic distance. In the transition from the electronic spectrum of the reflection of copper hydrophosphate monohydrate to the spectrum of copper ammonium phosphate monohydrate, a hypochromic shift of a maximum of 74 nm is observed, which indicates the entry of an ammonia molecule into the composition of copper monoaquahydrophosphate with the formation of copper monoaquaaminehydrophosphate. This is confirmed by the absence of an intense wide band at 3100-2900 sm^{-1} characteristic of the ammonium cation in the IR spectrum.

1 Introduction

For normal growth and development of plants, various nutrients are needed. According to modern data, there are about 70 such elements, without which plants cannot complete the development cycle and which cannot be replaced by others [1].

It has been proven that there is not a single important biochemical process, not a single physiological function in a living organism and in a plant that would be carried out without the participation of one or another microelement. Trace elements increase the resistance of plants to adverse environmental factors, some infectious and non-infectious diseases, increase the rate of development of plant organisms and maturation of seeds [2].

Studies in different soil and climatic zones in Uzbekistan and Southern Kazakhstan, with different amounts of available trace element compounds in the soil, have shown that the yield of raw cotton does not increase even under conditions of increased dosage of

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cotton due to the lack of individual trace elements in the soil nitrogen and phosphorus fertilizers and other agricultural practices.

At present, the physiological and biochemical role of zinc, copper, molybdenum, manganese, boron, and cobalt, for which a role in plant metabolism has been quite clearly established, has been most studied. They participate in the synthetic processes of the cell, and consequently, in the growth and development of plants, and also determine the speed and direction of reactions in the body. With a lack of them, the synthesis of organic compounds of phosphorus and nitrogen is disrupted, the speed and direction of the main metabolic processes in the plant cell are reduced [3].

In the life of plants, each microelement performs a specific function [4]. In particular, copper and molybdenum are involved in redox reactions associated with plant respiration, photosynthesis, nitrogen and phosphorus metabolism, as well as in the biosynthesis of amino acids, chlorophyll and molecular nitrogen fixation [5].

With a lack of copper in plant nutrition, the activity of enzymes decreases, the normal formation of chlorophyll, nucleic acids, and protein biosynthesis are disturbed; as a result, the productivity of plants decreases [6].

With intensive growth and development and against the background of high doses of nitrogen fertilizers, the need of plants for copper and zinc increases, which play an important role in phosphorus and nitrogen metabolism and promote the assimilation of these elements from the soil [7].

Trace elements cannot replace the main nutrients of mineral fertilizers, but only supplement their action. Plants use nitrogen, phosphorus and potash fertilizers much more efficiently if the content of microelements in the soil is sufficient. They play an important role in the metabolism directly or as part of biocatalysts and other physiologically active substances, and participate in almost all major biochemical reactions occurring in plant organisms [8-10].

The deficiency of one or another element is reflected in almost all organs of the plant. The action of each trace element in redox processes is specific. Copper is involved in the photosynthesis of carbohydrates and the formation of proteins and vitamins, increases the resistance of plants to fungal diseases. Zinc is part of the molecule of the pancreatic hormone - insulin, copper is required for the processes of photosynthesis and respiration. Cobalt is a component of vitamin $B12_,$ the absence of which leads to anemia [11].

In the case of cotton cultivation in Central Asia, the most effective micronutrients are copper, zinc, cobalt, molybdenum, manganese, which are closely related to nitrogen and phosphorus metabolism. The use of these trace elements in cotton improves the absorption and conversion of nitrogen and phosphorus into high-molecular organic compounds, thereby having a positive effect on yield [12].

According to agropages.com, the micronutrient market reached $8.81 billion by the end of 2022 with a CAGR of 8.60%. According to estimates, the market capacity has reached almost 2 million tons. It has been substantiated that more than 70% of microfertilizers should be supplied as part of complex NRK fertilizers, as an economically viable method. The introduction of microelements into the composition of the components of NPK fertilizers can lead to their interaction with the formation of various compounds.

2 Materials and methods

Earlier, when studying the behavior of copper sulfate, as well as copper oxide and copper extracted from spent industrial catalysts, in phosphoric acid solutions, depending on the degree of neutralization with gaseous ammonia, the formation of copper hydrogen phosphate monohydrate $CuHPO_4*H_2O$ was established in the pH range 1.6-2, 0 and copper ammonium phosphate monohydrate - $CuNH_4$ PO_4*H_2O. Copper ammonium phosphate monohydrate is formed at pH above 6.0 in phosphate solutions. To confirm chemical analyzes and identify this compound and establish the true formula, physical and chemical studies were carried out using X-ray phase, IR- spectroscopic and thermogravimetric methods of analysis.

3 Results and Discussion

The The derivatogram of copper ammonium phosphate monohydrate shows endothermic effects at 170 and 340°C (Figure 2). At 170°C, the mass loss is due to the loss of a water molecule. Complete removal of water and ammonia ends at 500°C. In this case, the total mass loss is 22.3, which corresponds to the calculated content of water and ammonia in the compound. Chemical analysis of the compound obtained at 500°C showed the presence of copper and phosphorus and the complete absence of nitrogen.

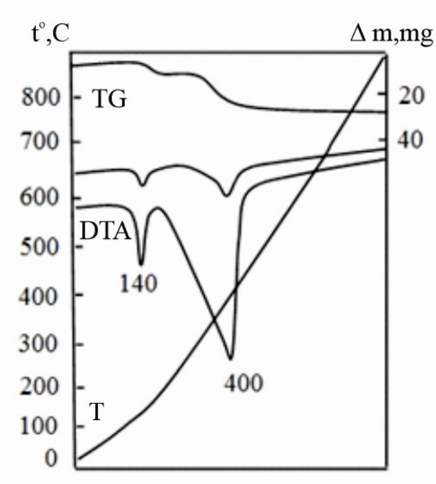

Fig. 1. Derivatogram compounds $CuHPO_4{\cdot}H_2O$ formed in ammophos pulp at pH 1.8.

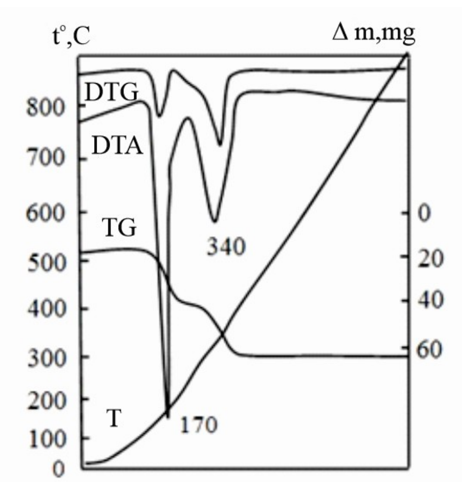

Fig. 2. Derivatogram $CuNH_4\,PO_4 \cdot H_2O$, formed in ammophos pulp at pH 6.58.

Based on the data obtained, the process that occurs during the dehydration of Cu (NH_3) (H_2O) HPO_4 can be represented by the following scheme:

$$2Cu\ (NH_3)\ (H_2O)\ HPO_4 \rightarrow Cu_2P_2O_7 + 2NH_3\uparrow + 3H_2O\uparrow \quad (1)$$

To check, the samples of the compound were kept under isothermal conditions for 60 min at various temperatures, followed by the determination of weight loss and chemical composition. As can be seen from Table 1, the results obtained confirm the data of the derivatogram.

Table 1. Results of chemical analysis of heat treatment products copper ammonium phosphate.

Temperature,°C	Mass loss, %	Cu,%	N, %	P_2O_5, %	H_2O%
20-25	-	32.0	7.4	36.6	9.5
100-110	0.03	32.1	7.4	36.8	9.3
200-210	10.2	36.0	5.5	40.2	3.2
300-320	14.2	40.1	2.3	42.6	-
500-520	22.3	42.2	-	41.3	-

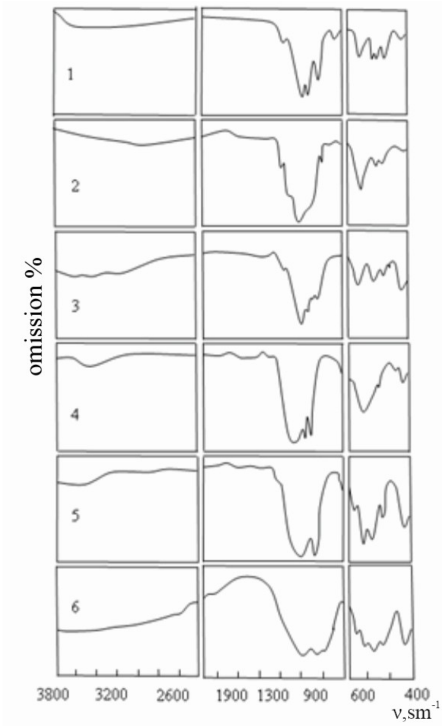

Fig. 3. IR spectra of $CuHPO_4 \cdot H_2O$ (1) and products of its heating: 2-200°C; 3-300 about C; 4-500 about C; 5-750 about C; 6-900 about C.

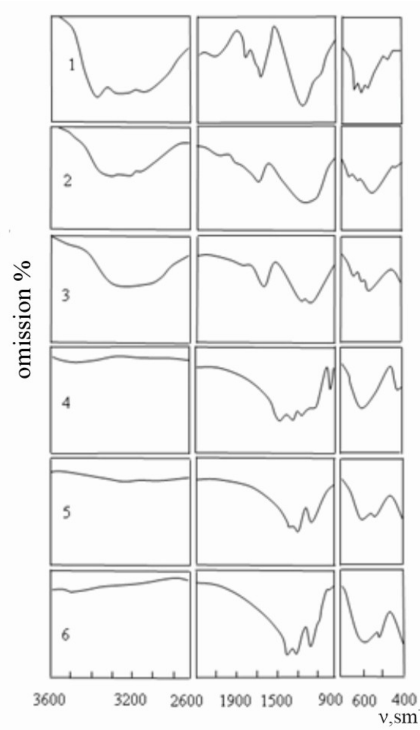

Fig. 4. IR spectra of $CuNH_4 PO_4 \cdot H_2O$ (1) and products of its heating: 2-200°C; 3-300 about C; 4-500 about C; 5-750 about C; 6-900 about C.

At a temperature of 200–210°C, the weight loss is 10.2%. The water content is 3.2% and nitrogen is 5.5%. At 300-320°C nitrogen (2.3%). At a temperature of 500°C, the weight loss is 22.3% (23.0% according to the derivatogram, 22.6% according to the calculation).

To establish the true formula of copper ammonium phosphate monohydrate, the IR spectra and electronic spectra of the compounds $CuHPO_4 \cdot H_2O$ and $CuNH_4 PO_4 \cdot H_2O$ were studied. ν,sm $^{-1}$

If an ammonia molecule enters into the composition of copper (II) monoaquahydrophosphate with the formation of copper (II) monoaquaamine hydrogen phosphate $[Cu(NH_3)(H_2O)HPO_4]$, then upon passing from the electronic spectrum $[Cu(H_2O)HPO_4]$ to the spectrum of the compound $[Cu(NH_3)(H_2O)HPO_4]$ there should be a hypsochromic shift of the Cu(II) absorption band, which is associated with the transition from the ground state (4F) to the component (4P) level. This is due to the fact that in the spectrochemical series, ammonia is located to the left of the water molecule and has a greater field strength than water. To confirm this version, the reflection spectra in the visible region from 400 to 750 nm were studied (Figure 4). As seen from figure 5, maximum for connection copper (II) monoaquahydrophosphate is at 698 nm, and for copper (II) monoaquaamine hydrogen phosphate - 624 nm.

Thus, for the second compound, there is a hypsochromic shift of the maximum at 74 nm, which indicates the incorporation of the ammonia molecule into the composition of copper monoaquahydrophosphate. (II) with the appearance of an N–Cu bond and with the formation of copper (II) monoaqua amine hydrogen phosphate.

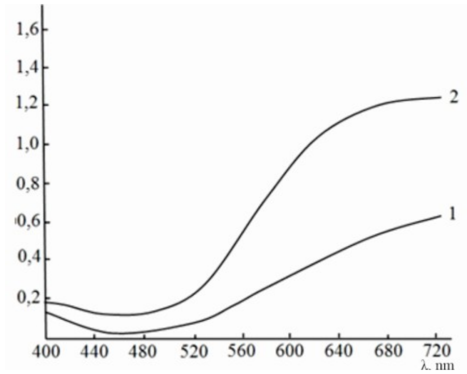

Fig. 5. λ , nm 5. Electronic diffusion reflectance spectra of compounds formed in ammophos pulp at pH 1.8 (1) and 6.5 (2).

This is also evidenced by the absence of an intense broad band at 3100-2900 sm^{-1}, characteristic of the ammonium cation, in the IR spectrum.

It should be noted that the IR spectrum of $CuNH_4\ PO_4 \cdot H_2O$ contains a band at 1280 cm^{-1} related to υP-O and characteristic of compounds containing a P-OH group. Particular attention should be paid to the absorption band of the stretching vibration of the N–H bond. υ NH ammonia molecules and υ NH ammonia complex compounds differ sharply in form and value from υ NH of the ammonium cation. These vibrations appear as a doublet with an average intensity at 3350-3220 sm^{-1}.

υ NH of the ammonium ion of solid samples has a wide intense band at 3100-2900 sm^{-1}. The IR spectrum of the compound $[Cu(NH_3)(H_2O)\ HPO_4]$ contains a doublet with an average intensity at 3350-3220 sm^{-1} corresponding to $\upsilon_{\alpha s}$ NH and υ_s NH respectively. These facts convincingly indicate that the resulting compound has the composition $[Cu(NH_3)(H_2O)\ HPO_4]$. Is of interest to elucidate the effect of nitrogen coordination to copper (II) on the N–H bond parameters in the $[Cu\ (NH_3)(H_2O)\ HPO_4]$ compound. To this end, the following N–H bond parameters for the coordinated amino group were calculated force constant *f*, bond angle θ°, interatomic distance (r) of the N –H bond.

These quantities were found by the equations:

$$f dyne/sm = 2.769\ 10^{-2}\ (\nu_{as}^2 + \nu_s^2)$$

$$\sin^2 \frac{\theta^0}{2} = 0{,}500 + 7{,}448\ \frac{\left(\nu_{as}^2 - \nu_s^2\right)}{\left(\nu_{as}^2 + \nu_s^2\right)}$$

Interatomic distance (r) of NH bonds calculated by the Badger and Douglas-Clark equations]:

$$f\,(\text{r}-0.34)^3 = 1.86;\ f \cdot \text{r}^{7.6} = 7.00$$

The values of the force constant, the bond angle, and the interatomic distance are given in Table 2. As can be seen from the table, when ammonia is coordinated to Cu (II), the force constant of the N-H bond of NH_3 in the compound decreases compared to *f* N-H bonds of NH_3 from 6.31 to 5.98 Mg/sm, and the interatomic distance increases from 1.006-1.014 to 1.018-1.021Å. These changes are more pronounced in cobalt (II) monoaquaamine hydrophosphate.

Thus, the incorporation of $_{NH3}$ into the composition of the compound led to a change in the parameters of the N-H bond in the coordination compound. This is also another piece of evidence that the compound corresponds to the formula [Cu (NH_3) (H_2O) HPO_4].

Table 2. Meaning of some communication parameters N - H.

Compound	$\nu_{as(NH)}$, sm $^{-1}$	$\nu_{s(NH2)}$, sm $^{-1}$	f NH, Mdn/ sm	θ^o H–N–H	rN - H, Å	
					Badger's formula	According to the Douglas-Clark formula
NH_3	3414	3336	6.31	110°6	1.006	1.014
[Cu(NH_3)(H_2O)HPO_4]	3350	3220	5.98	126°10	1.017	1.021

The presence of water of crystallization in the IR spectrum of copper (II)-monoaquaamine hydrogen phosphate isolated at pH 6.5 and salt heated to 300°C is characterized by absorption bands in the region of 2600 and 3400 sm^{-1} and 1600 sm^{-1} (Figure 4).

On the IR spectrum of the sample heated to 300°C, a weak band appears for $P_2 O_7$ at 540 sm^{-1}. At temperatures of 500, 750, and 900°C, the bands characteristic of water disappear and the bands for the pyrophosphate ion become more pronounced.

Patterns of the salts CuH $PO_4 \cdot H_2O$ and [Cu(NH_3)(H_2O) HPO_4 and the products of heating of these salts at temperatures of 200, 300, 750, and 900°C] were also taken (Figures 5 and 6).

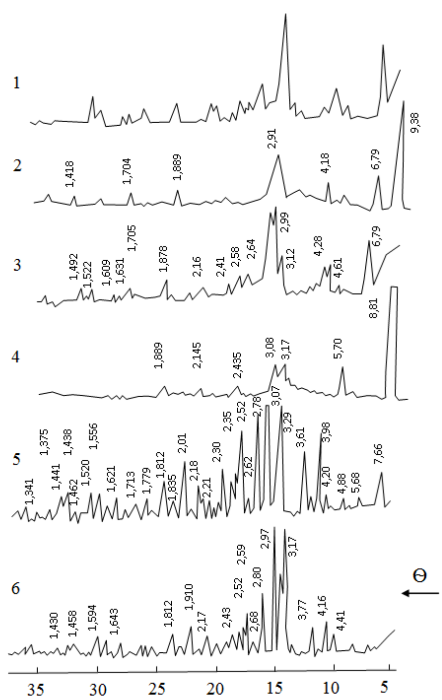

Fig. 6. X-ray patterns of the CuH $PO_4 \cdot H_2O$ compound isolated from ammophos pulp at pH 1.8 (1), and its heating products at: 2-200°C; 3-300 about C; 4-500 about C; 5-750 about C; 6-900 about C.

The data of X-ray phase analysis of compounds isolated from ammophos pulp are shown in Figures 5 and 6. From the results for the compound [Cu(NH_3)(H_2O) HPO_4, diffraction maxima are] characteristic:4.21; 3.46; 3.22; 2.92; 2.62; 2.44; 2.08; 1.61; 1.43 Å.

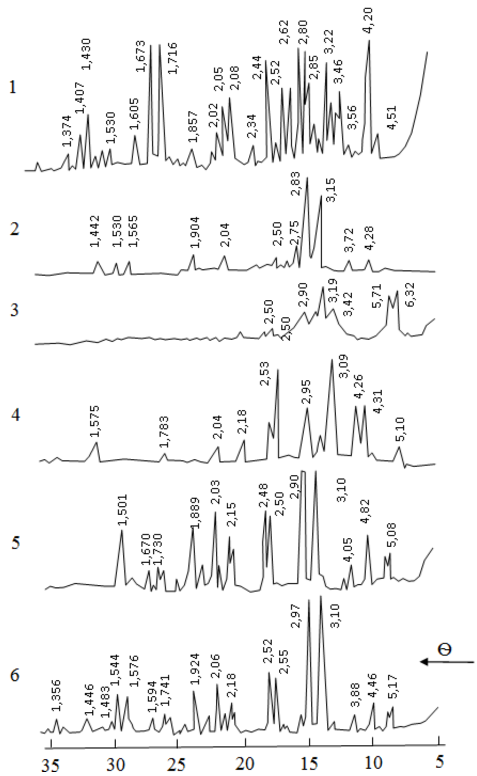

Fig. 7. X-ray patterns of the compound $[Cu(NH_3)(H_2O)\ HPO_4]$ isolated from ammophos pulp at pH 6.5 (1) and its heating products at: 2-200°C; 3-300 about C; 4-500 about C; 5-750 about C; 6-900 about C.

When manoaquaamine hydrophosphate is heated to 300–900°C, new compounds are also formed, as evidenced by the maxima of the heated sample up to 750°C: 4.32; 3.10; 2.50; 2.03; 1.88; 1.53 Å (Figure 6).

4 Conclusion

The conducted studies of the copper compound isolated from the ammophos pulp at pH 6.58 made it possible to establish the true formula of copper monoaquahydrophosphate. It is shown that the ammonia molecule enters into the composition of the copper monoaquahydrophosphate molecule with the formation of copper monoaquaaminehydrophosphate. The data of physicochemical studies confirm the individuality of the isolated compound.

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