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Copper(II) Complexes of Oxyphosphonates: Synthesis, Spectroscopic Characterization and Plant Growth-Stimulating Activity

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Abstract

Coordination compounds of Cu(II) ions with some oxyphosphonates were synthesized in ethanol using ultrasonic activation. The complexes were isolated as blue crystalline powders in yields of 72–87%. Complex formation was confirmed by IR spectroscopy and thermal analysis. The shift of the ν(P=O) band to lower frequencies indicates the involvement of the phosphoryl oxygen in coordination with the Cu(II) ion. Changes in melting points compared to the initial ligands indicates a rearrangement of the crystal structure. For the piperidine based complex, the N,O coordination type was observed by the appearance of a Cu–N absorption band at 661 cm^{-1}. The biological activity of the synthesized compounds was evaluated using a wheat seed germination model. It was found that the oxyphosphonates and their complexes stimulate seedling development, leading to increased shoot and root lengths compared to the control. The most pronounced effect was observed for compounds containing phenyl and piperidine moieties, with root length increases reaching 74.8% and shoot length by 18.7%, relative to the control. In addition, the copper complexes suppressed the growth of mold microflora on treated seeds, exhibiting antimicrobial activity. These results demonstrate the potential of phosphorus-containing Cu(II) coordination compounds as potential agrochemicals with growth-promoting and antimicrobial properties.

1. Introduction

Copper is a vital micronutrient that plays a crucial role in the biochemical processes of living organisms. Owing to the ability of Cu(II) ions to participate in oxidation-reduction reactions, copper is a component of numerous enzymes and metalloproteins that regulate cellular respiration, iron metabolism, photosynthetic processes, and antioxidant defense [1, 2]. In plant, copper influences enzymatic processes, growth, development, and resistance to environmental stresses. Copper coordination compounds, especially with organic ligands, are attracting particular attention due to their broad spectrum of biological properties, including antibacterial, antitumor, antioxidant, and immunomodulatory activities [3]. Their activity is determined by both the nature of the metal ion and the properties of the organic ligands. Furthermore, organic ligands can modify the biological and physicochemical properties of the resulting complexes [4].

Phosphonates and their derivatives are promising ligands for the production of biologically active metal complexes. The presence of a phosphoryl group with pronounced donor properties ensures effective coordination with transition metal ions,

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and the diversity of biological effects of phosphonates enables their application in medicine, agriculture, and materials science [5–7]. Among the phosphonate ligands, α-hydroxyphosphonates (oxyphosphonates), containing both hydroxyl and phosphoryl group, are of particular interest. The presence of multiple donor centers facilitates the formation of stable coordination structures, ranging from molecular complexes to multidimensional coordination networks with diverse functional properties [8, 9]. The ability of copper ions to interact effectively with phosphonate ligands significantly influences the chemical and biological properties of the resulting compounds [10]. Moreover, the field of environmentally friendly phosphonate chemistry is actively developing, highlighting the relevance of this area [11, 12].

We have previously demonstrated that oxyphosphonates and their complexes with biogenic metal ions exhibit growth-promoting activity in agricultural plants [13]. However, the influence of the structural features of oxyphosphonate ligands on the properties and biological activity of the resulting complexes remains an important issue. Therefore, the synthesis of new copper coordination compounds with structurally diverse oxyphosphonates and the study of their effects on seed germination and plant development are of scientific interest.

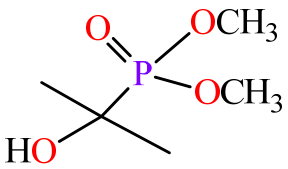
The aim of this work is to synthesize Cu(II) complexes with oxyphosphonate ligands of various natures, to establish their coordination features using IR spectroscopy, and to evaluate the influence of ligand structure on growth-promoting activity.

2. Experimental

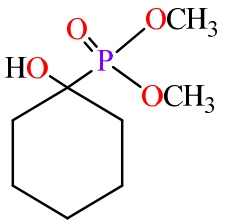
The progress of the reactions was monitored by thin-layer chromatography (TLC) on Al_2O_3. IR spectra were recorded using a Nicolet 5700 FT-IR spectrometer (Madison, USA). Samples were prepared as KBr pellets. Elemental analyses (C and H) were performed using a FlashSmart Elemental Analyzer (Thermo Fisher Scientific Inc., Waltham, USA). Biological experiments were conducted in a LAC-475-N climate chamber (Hangzhou Boyn Instrument Co., Ltd., Hangzhou, China).

2.1. Synthesis of oxyphosphonates and their coordination compounds

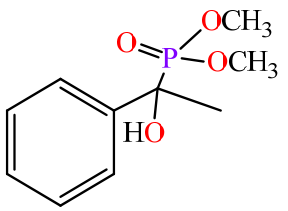
2-Dimethoxyphosphoryl-2-hydroxypropane, 1-dimethoxyphosphoryl-1-hydroxycyclohexane, dimethyl-1(1-hydroxy-1-phenylethane)phosphonate, and 1-(2-ethoxyethyl)-4-hydroxypiperidin-4-yl) phosphonate were synthesized according to the Abramov reaction [14–15] (Fig. 1).



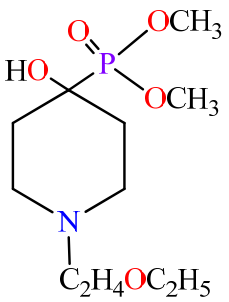
2-dimethoxyphosphoryl-2-hydroxypropane (**AcOP**) [15]



1-dimethoxyphosphoryl-1-hydroxycyclohexane (**CHOP**) [15]



dimethyl-(1-hydroxy-1-phenylethane)phosphonate (**APhOP**) [16]



1-(2-ethoxyethyl)-4-hydroxypiperidin-4-yl)phosphonate (**PipOP**) [17]

Fig. 1. Structure of synthesized oxyphosphonates.

General procedure for the preparation of coordination compounds. Oxyphosphonate (0.1 mmol) and a copper(II) acetate monohydrate (0.054 mmol; Labkhimprom LLP, Almaty, Kazakhstan) were placed in a flask of an ultrasonic reactor. Ethanol was added before the tip of the ultrasonic probe was immersed in the reaction mixture. The mixture was sonicated until complete dissolution, maintaining the reaction temperature below 50 °C. During this process, the color of the reaction mixture changed from deep blue to light blue, and a pale blue precipitate gradually formed. The reaction mixture was then left for 12 h. The liquid phase and precipitate were separated by centrifugation and dried separately in Petri dishes. The products were obtained as blue crystalline powders.

Copper complex of 2-dimethoxyphosphoryl-2-hydroxypropane. 1.34 g (87% yield) of copper di(2-dimethoxyphosphoryl-2-hydroxypropane) acetate was obtained with a melting point of 113 °C.

Calculated, %: C 32.41; H 6.19. $CuC_{14}H_{32}O_{12}P_2$. Found, %: C 32.43; H 6.18.

IR spectrum, cm^{-1}: 1199 ($\nu_{Me\text{-}P=O}$); 3477 ($\nu_{O\text{-}H}$); 1601 ($\nu_{C=O}$).

Copper complex of 1-dimethoxyphosphoryl-1-hydroxycyclohexane. 1.19 g (82% yield) of copper di(1-dimethoxyphosphoryl-1-hydroxycyclohexane) acetate was obtained with a melting point of 107–108 °C.

Calculated, %: C 40.10; H 6.71. $CuC_{20}H_{40}O_{12}P_2$. Found, %: C 40.13; H 6.69.

IR spectrum, cm^{-1}: 1227 ($\nu_{Me\text{-}P=O}$); 3295 ($\nu_{O\text{-}H}$); 1593 ($\nu_{C=O}$).

Copper complex of dimethyl(1-hydroxy-1-phenylethyl)phosphonate. 1.19 g (72% yield) of copper di(dimethyl-(1-hydroxy-1-phenylethyl)phosphonate) acetate was obtained with a melting point of 105–106 °C.

Calculated, %: C 53.55; H 4.70. $CuC_{34}H_{36}O_{12}P_2$. Found, %: C 53.54; H 4.73.

IR spectrum, cm^{-1}: 1198 ($\nu_{Me\text{-}P=O}$); 3284 ($\nu_{O\text{-}H}$); 1618 ($\nu_{C=O}$).

Copper complex of dimethyl(1-(2-ethoxyethyl)-4-hydroxypiperidin-4-yl)phosphonate. 1.15 g (76% yield) of copper di(dimethyl(1-(2-ethoxyethyl)-4-hydroxypiperidin-4-yl)phosphonate) acetate was obtained with a melting point of 100–101 °C.

Calculated, %: C 41.96; H 7.31. $CuC_{26}H_{54}O_{14}N_2P_2$. Found, %: C 42.00; H 7.27.

IR spectrum, cm^{-1}: 1225 ($\nu_{Me\text{-}P=O}$); 3271 ($\nu_{O\text{-}H}$); 1599 ($\nu_{C=O}$); 661 ($\nu_{Me\text{-}N}$).

2.2. Methodology for determining growth stimulating activity

The growth-promoting activity of the obtained compounds was studied using the wheat variety "Steklovidnaya 24" in accordance with GOST 12038-84, "Agricultural seeds. Methods for determination of germination" [18]. Simultaneously, the accompanying microflora was assessed using a biological method in accordance with GOST 12044-93, "Agricultural seeds. Methods for determining disease infection" [19], employing a visual scoring scale to determine the degree of seed damage. The seeds were soaked for 12 h in solutions of the free oxyphosphonate and its complex at a concentration of 10^{-3}%. The seeds were then planted on filter paper in closed Petri dishes and placed in a climate chamber at 23 °C and 55% relative humidity. Distilled water served as a control. To prevent dehydration, the seeds were moistened daily.

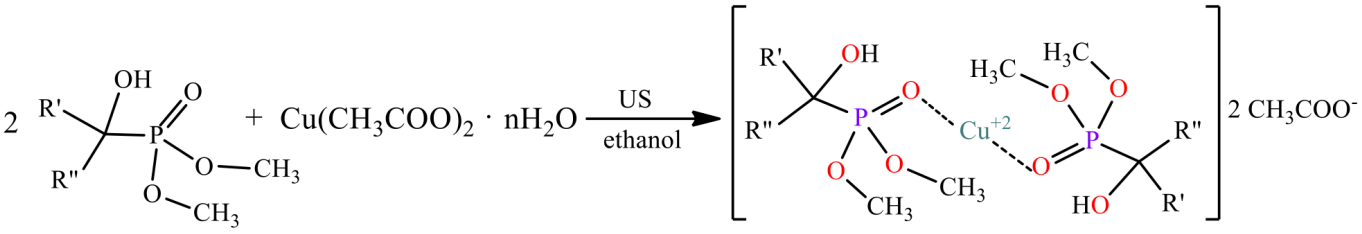
The growth-promoting effect was assessed by measuring shoot and root lengths on the eighth day. The experiment was performed three times, and the results were expressed as mean values.

3. Results and Discussion

Acetone, cyclohexanone, acetophenone, and 1-(2-ethoxyethyl)-4-hydroxypiperidone were used as starting substrates for the synthesis of organic ligands. The corresponding oxyphosphonates were prepared under Abramov reaction conditions by reacting the aforementioned ketones with dimethyl phosphite in hexane in the presence of sodium methylate [14–15].

The molecular structures of the obtained compounds include a phosphoryl group (P=O) and a hydroxyl fragment, which serve as donor sites for coordination with transition metal ions. The structural diversity of the synthesized ligands is ensured by the presence of aliphatic, unsaturated, and heterocyclic fragments in their molecules.

Complexation of the ligands with Cu(II) ions was carried out in an ethanol medium using ultrasound, which intensified the dissolution and diffusion of the reactants, increasing the reaction efficiency (Scheme 1). The resulting crystalline powders were blue in color, which is characteristic of Cu(II) compounds.



R' = R" = CH_3; R' + R" = C_6H_{10}; R' = CH_3, R" = Ph; R'+R" = $C_5H_8N(C_2H_4OC_2H_5)$

Scheme 1. Synthesis of copper(II) coordination compounds with oxyphosphonate ligands.

The formation of the Cu(II) coordination compounds was confirmed by thermal analysis and IR spectroscopy.

Complexation is accompanied by a change in the melting points of the resulting compounds compared to those of the starting ligands (Table 1). In most cases, a decrease in melting point is observed, due to the disruption of the intermolecular hydrogen bond system and the formation of a new coordination structure involving the copper ion. It should be noted that all synthesized complexes are characterized by a narrow melting range (1–2 °C), which indicates their individuality and high degree of purity. An exception is the Cu(II)AcOP complex, for which the melting point increases from 71–73 to 113 °C, which is explained by the formation of a more rigid coordination structure with an increased molecular weight, which facilitates the formation of a more stable crystal lattice.

The main absorption bands of the synthesized compounds are presented in Table 2. In the spectra of all copper complexes, the ν(P=O) stretching band is shifted to lower frequencies relative to the corresponding bands of the free ligands (Fig. 2), indicating the involvement of the phosphoryl oxygen atom in coordination with Cu(II). Additional confirmation of coordination is provided by bands in the region of 400–600 cm^{-1}, attributed to vibrations of the Cu–O bond. The spectra of the copper complexes also exhibit bands near 1600 cm^{-1} corresponding to the stretching vibrations of the carboxylate group (COO^-) of acetate, indicating the incorporation of acetate ions into the inner coordination sphere of Cu(II). For the Cu(II)CHOP, Cu(II)APhOP, and Cu(II)PipOP complexes, the formation of Cu–O bonds leads to a change in the packing of molecules in the crystal and a decrease in the lattice energy, which is consistent with the observed decrease in melting points.

Table 1. Physicochemical characteristics of the synthesized Cu(II) complexes

Compound	Yield, %	Reaction time, h	m.p., °C (initial oxyphosphonate)	m.p., °C	Molecular formula
Cu(II)AcOP	87	2	71–73	113	$CuC_{14}H_{32}O_{12}P_2$
Cu(II)CHOP	82	2	110–112	107–108	$CuC_{20}H_{40}O_{12}P_2$
Cu(II)APhOP	72	2	132–134	105–106	$CuC_{34}H_{36}O_{12}P_2$
Cu(II)PipOP	76	2	107–109	100–101	$CuC_{26}H_{54}O_{14}N_2P_2$

Table 2. Main IR absorption bands of oxyphosphonates and their Cu(II) complexes

Compound	ν(P=O), cm^{-1}	Shift, cm^{-1}	ν(Cu–N), cm^{-1}
AcOP	1238	39	–
Cu(II)AcOP	1199		–
CHOP	1229	3	–
Cu(II)CHOP	1227		–
APhOP	1230	32	–
Cu(II)APhOP	1198		–
PipOP	1228	3	–
Cu(II)PipOP	1225		661

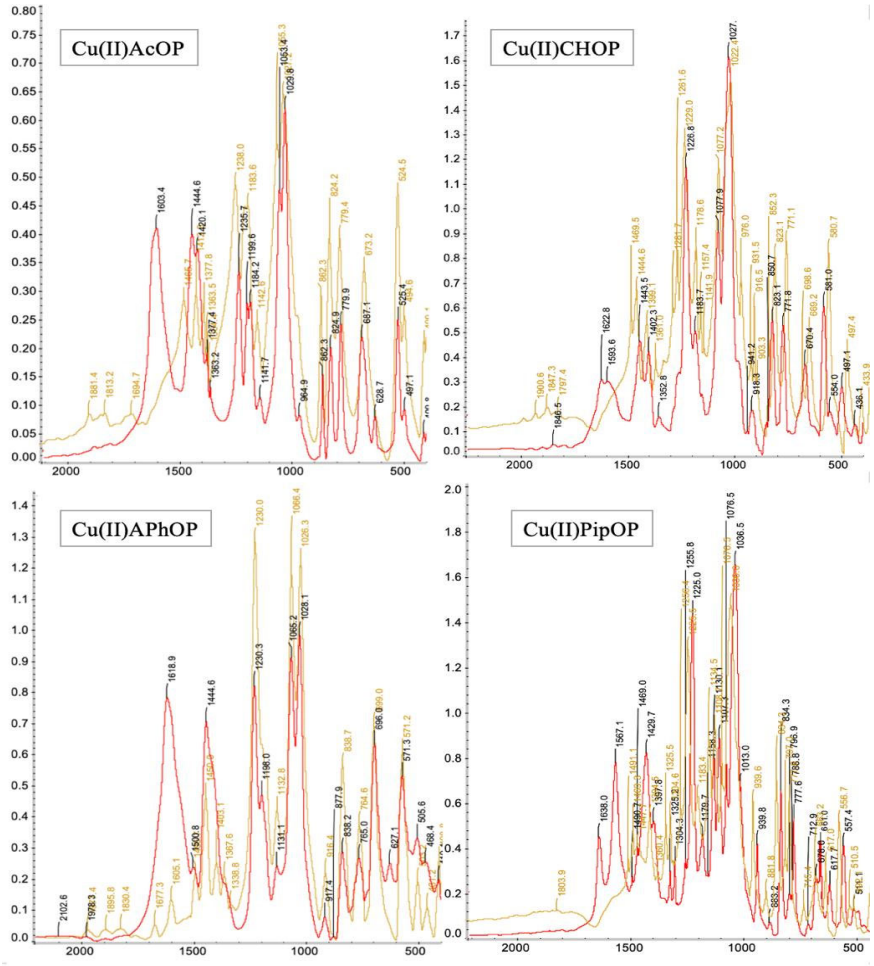


Fig. 2. IR spectra of the starting phosphonate and its Cu(II) coordination compound (yellow – parent phosphonate; red – Cu(II) complex).

For the Cu(II)PipOP complex, an additional band was detected at 661 cm^{-1}, characteristic of vibrations of the Cu–N bond, indicating the participation of the nitrogen atom of the piperidine moiety in the coordination. Thus, this ligand exhibits a mixed N,O coordination mode, while the other ligands coordinate exclusively through the oxygen atoms of the phosphoryl group (Fig. 3).

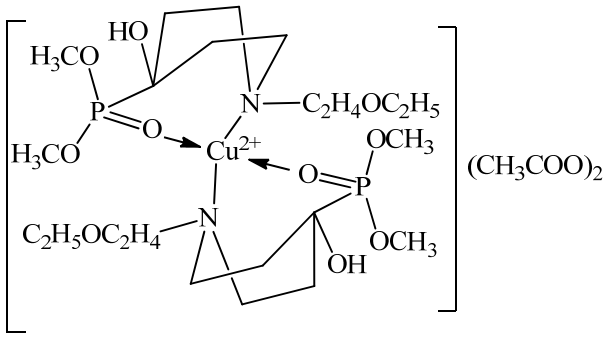


Fig. 3. The proposed structure of the complex with mixed N,O coordination mode.

The combined thermal and spectroscopic data clearly confirm the formation of new coordination compounds with different binding modes depending on the ligand structure. The structural features of the synthesized complexes are of particular interest for their biological activity, since the coordination environment of the copper ion and the nature of the organic ligand directly influence the physicochemical properties of the compounds and their interactions with biological systems. The results establish a relationship between biological activity and the structure of the organic ligand.

Evaluation of the effects of the synthesized compounds on wheat seed germination showed that most of the studied oxyphosphonates and their copper complexes stimulated seedling growth relative to the control (Fig. 4). Seed germination energy was 100% for all samples except the water control and CHOP, for which it was 97%.

In terms of shoot length, the Cu(II)PipOP complex demonstrated the greatest effect (15.26 cm), exceeding the control value (12.86 cm) by 18.7%.

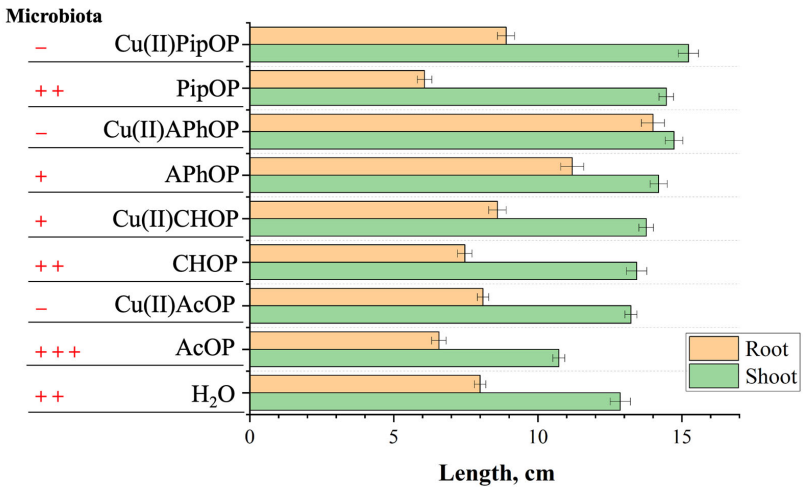


Fig. 4. Graph of results of tests on germination of wheat seeds with synthesized compounds.

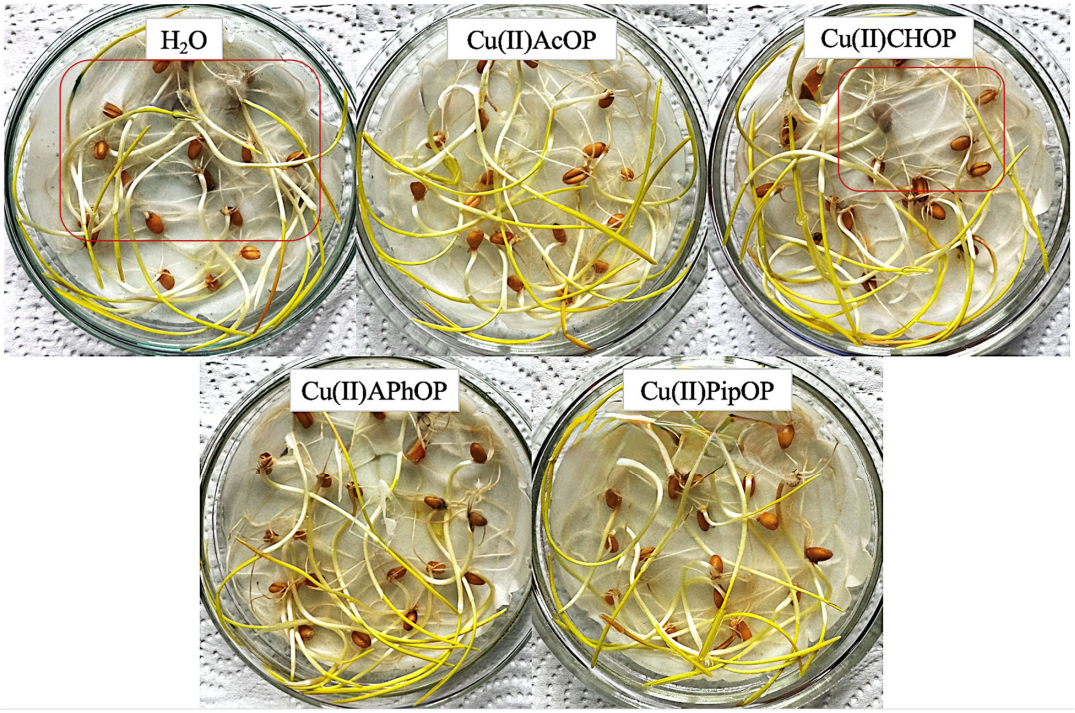


Fig. 5. Microbial contamination of test samples.

A slightly smaller, but still significant, stimulating effect was demonstrated by Cu(II)APhOP (14.75 cm) and APhOP (14.20 cm). It is noteworthy that in the ligand-complex series, an increase in shoot length is observed for all pairs upon moving to the copper complex, indicating an enhancement of the growth-promoting effect upon copper ion salts coordination.

Regarding root length, the most pronounced effect was observed for Cu(II)APhOP (14.00 cm), corresponding to a 74.8% increase relative to the control and representing the highest value among all samples studied. High root length values were also recorded for APhOP (11.20 cm) and Cu(II)PipOP (8.90 cm). Meanwhile, the AcOP (6.58 cm) and PipOP (6.08 cm) ligands exhibited root lengths lower than that of the control, whereas their corresponding copper complexes showed substantial improvement to 8.12 cm and 8.90 cm, respectively.

The results for the microflora index are particularly noteworthy (Figs. 4 and 5). The control sample (H_2O) showed a moderate level of microbial contamination (++), while the free AcOP ligand showed a high level (+++), indicating a lack of antimicrobial properties and, conversely, the potential for creating a favorable environment for microbial growth.

In contrast, all three copper complexes – Cu(II)AcOP, Cu(II)APhOP, and Cu(II)PipOP, demonstrated a complete absence of microbial contamination, while the corresponding free ligands were characterized by contamination at levels of "+" and "++." The Cu(II) CHOP complex also showed a reduction in microbial load to "+" compared to "++" for the CHOP ligand. Thus, the coordination of the Cu(II) ion with oxyphosphonate ligands leads to a marked suppression of microbial contamination of seeds, which is an independent and practically significant result of this study.

The observed antimicrobial effect of the copper complexes is consistent with the well-known biocidal properties of Cu(II) ions, which are realized through the generation of reactive oxygen species, disruption of the integrity of microbial cell membranes, and inhibition of pathogen enzymatic systems [3, 4]. Reduced microbial contamination of seeds likely creates more favorable conditions for germination and root development, thereby indirectly contributing to the observed growth-promoting effect of the complexes. Thus, the stimulating effect of the synthesized copper complexes is due to a combination of factors: the participation of Cu(II) ions in the regulation of plant enzyme systems, modification of the physicochemical properties of the ligand during coordination, and pronounced suppression of microbial infection of seeds.

Coordination of the Cu(II) ion consistently enhances the growth-promoting effect of oxyphosphonate ligands in all pairs studied, indicating synergism between the metal and the organic ligand. Furthermore, the Cu(II)AcOP, Cu(II)APhOP, and Cu(II)PipOP complexes completely suppressed microbial infection of seeds, creating additional favorable conditions for germination. The biological activity of the compounds is determined by the combination of the ligand structure, the physiological role of Cu(II), and changes in physicochemical properties during complexation.

4. Conclusion

In this study, coordination compounds of Cu(II) with oxyphosphonate ligands of various structures were synthesized in ethanol using ultrasonic activation in yields of 72–87%. Complex formation was confirmed by IR spectroscopy and thermal analysis. A shift of the ν(P=O) band by 3–39 cm^{-1} toward lower frequencies indicates coordination via the oxygen atom of the phosphoryl group. An additional N,O-type coordination was established for Cu(II) PipOP (the Cu–N band at 661 cm^{-1}). The change in melting point upon moving from the ligands to the complexes confirms the rearrangement of the crystal structure.

Biological testing showed that the synthesized compounds stimulate wheat seed germination. The most pronounced effect was observed for compounds with aromatic and heterocyclic fragments. Root length for Cu(II)APhOP exceeded the control by 74.8%, and shoot length for Cu(II)PipOP exceeded the control by 18.7%. In all ligand-complex pairs, copper ion coordination consistently enhanced the growth-promoting effect. Furthermore, the Cu(II) AcOP, Cu(II)APhOP, and Cu(II)PipOP complexes completely suppressed microbial contamination of seeds.

These results indicate that the biological activity of the compounds is determined by ligand structure, the physiological role of Cu(II) in plant metabolism, and changes in physicochemical properties accompanying complex formation. The synthesized compounds are promising candidates for further investigation and potential application in agrochemistry.

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