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Synthesis, Structure, and Fungicidal Activity of Mono- and Binuclear Mixed-Ligand Copper Complex with *p*-Nitrobenzoic Acid and Monoethanolamine

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Abstract—Mixed-ligand metal complexes based on ethanolamines and simple monosubstituted benzoic acids, in particular, mono- and binuclear copper complexes with monoethanolamine (MEA) and *p*-nitrobenzoic acid (PNBA), $[Cu^{2+}((PNBA)_2^-(MEA)_2)]$ (**I**) and $[2Cu^{2+}((PNBA)_4^-(MEA)_2(H_2O)_2)]$ (**II**), were prepared for the first time. The structures of the complexes were characterized by FT IR spectroscopy and X-ray diffraction (CIF files CCDC no. 1497849 (**I**) and no. 1497848 (**II**)). The doubly charged copper ions are coordinated at the vertices of octahedra, which are highly distorted due to the Jahn–Teller effect. In the crystals of the mononuclear complex **I**, the molecules are joined into columns, whereas in the binuclear compound **II**, a three-dimensional framework is formed owing to intermolecular H-bonds involving the nitro group. Fungicidal activities were found for compounds **I**, **II**, MEA, PNBA, previously obtained single-ligand copper complexes with MEA and PNBA, and MEA- and PNBA-based organic salt. The biological activity gradually increases in the series: ligand, single-ligand metal complex, organic salt, mono- and binuclear mixed-ligand complex, i.e., some ligands and copper ions show a synergistic effect.

Keywords: *p*-nitrobenzoic acid, monoethanolamine, Cu complex, molecular and crystal structure, X-ray diffraction, fungicidal activity

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INTRODUCTION

Deterioration of the environmental situation in the world results in a gradual loss of agricultural crops due to the action of phytopathogenic microorganisms. Therefore, for the control of agricultural pests, researchers continue to develop new highly efficient agents (fungicides) with a complex structure [1, 2]. However, fungicides can also be prepared by boosting the biological activity of known chemically simple compounds via the formation of supramolecular complexes and coordination compounds [3, 4]. A fairly promising approach is design of compounds possessing both fungicidal and growth-stimulating action. Examples of such compounds are chemically simple, cheap, and commercially available benzoic acids [5] and ethanolamines [6], which are widely used for technological and industrial applications and exhibit moderate growth-stimulating [7, 8] and antimicrobial [9, 10] activities.

Therefore, we are engaged in systematic research into the formation of supramolecular compounds (organic salts) and metal complexes from simple monosubstituted benzoic acid and ethanolamine derivatives [11, 12]. Of particular interest are mixed-ligand metal complexes, as they may provide higher biological activity due to both synergism of the ligands and the toxicity of metal ion. It is equally important to elucidate the details of coordination of these ligands by determining the exact molecular structure of the complexes. However, analysis of the Cambridge Crystallographic Data Centre (CCDC) [13] demonstrated that no mixed-ligand metal complexes of monosubstituted benzoic acid or ethanolamine derivatives have yet been deposited in the database. Therefore, we obtained mixed-ligand metal complexes of 4- or *p*-nitrobenzoic acid (PNBA) with triethanolamine [14] and 2-nitrobenzoic acid with diethanolamine [15].

As a continuation of these studies, we synthesized two forms of mixed-ligand copper complex with PNBA and monoethanolamine (MEA), mononuclear and binuclear ones, $[Cu^{2+}((PNBA)_2^-(MEA)_2)]$ (**I**) and $[2Cu^{2+}((PNBA)_4^-(MEA)_2(H_2O)_2)]$ (**II**). This communication is devoted to the preparation and study of the structures and fungicidal activities of these complexes.

EXPERIMENTAL

All compounds and solvents were commercial chemicals and were used as received. Elemental analysis for C, H, and N was performed on a German Elementar Vario EL instrument. The experimental X-ray diffraction data were collected at room temperature on a Xcalibur-R CCD diffractometer (CuK_α radiation, graphite monochromator, ω-scan mode). The IR spectra were measured on a FTIR Nicolet iS50 instrument (Thermo Scientific, USA) in the 400–4000 cm^{-1} range.

Synthesis of I. A hot ($T = 60°C$) solution of PNBA (0.167 g, 1 mmol) in 1.5 mL of methanol was added to a solution of $CuCl_2 \cdot 2H_2O$ (0.135 g, 0.5 mmol) in 4 mL of a water–methanol mixture (1 : 0.25 v/v). Then monoethanolamine (62 μL) was added dropwise. The reaction mixture was kept in an ultrasonic bath (30 kHz) for 10 min. The resulting solution was placed into a loosely closed bottle (20°C). After 8 days, prismatic crystals were formed. The yield was 60%.

For $C_{18}H_{22}N_4O_{10}Cu$ ($M = 517.55$)

anal. calcd., %:	C, 41.73;	H, 4.25;	N, 10.82.
Found, %:	C, 41.25;	H, 4.31;	N, 10.72.

IR (ν, cm^{-1}): 3600–2400 br, 3310 w ν(OH), 3237 w, 2955 m $\nu_{as}(CH_2)$, 1615 w, 1569 s ($\nu_{as}(NO_2) + \delta(NH)$), 1511 s $\nu_{as}(COO^-)$, 1459 w, 1385 s $\nu_s(COO^-)$, 1340 vs $\nu_s(NO_2)$, 1317 s δ(OH), 1160 w σ(NH), 1104 w, 1069 s ν(C–OH), 1021 m, 1009 m, 876 m, 828 w, 796 s, 721 s, 571 w, 515 vs ν(Cu–N), 442 w.

Synthesis of II. A hot ($T = 70°C$) solution of PNBA (0.167 g, 1 mmol) in 3 mL of ethanol was added to a solution of $Cu(CH_3COO)_2$ (0.095 g, 0.5 mmol) in 5 mL of a water–ethanol mixture (1 : 1 v/v). Then monoethanolamine (62 μL) was added dropwise. The reaction mixture was kept in an ultrasonic bath (30 kHz) for 5 min. The resulting solution was placed into a loosely closed bottle (20°C). After 7 days, prismatic crystals precipitated. The yield was 55%.

For $C_{32}H_{34}N_6O_{20}Cu_2$ ($M = 949.10$)

anal. calcd., %:	C, 53.95;	H, 3.58;	N, 8.85.
Found, %:	C, 54.23;	H, 3.41;	N, 8.95.

IR (ν, cm^{-1}): 3600–2400 sh, 2947 w $\nu_{as}(CH_2)$, 1558 s $\nu_{as}((NO_2) + \delta(NH))$, 1509 m $\nu_{as}(COO^-)$, 1432 w, 1402 m, 1381 m, 1340 vs $\nu_s(NO_2)$, 1320 vs $\nu_s((COO^-) + \delta(OH))$, 1161w σ(NH), 1102 m ν(C–OH), 1064 m, 1023 m, 1009 m, 877 w, 833 w, 796 s, 720 vs, 651 s, 512 s ν(Cu–N).

X-ray diffraction. The data were collected using the CrysAlisPro program package [16]. The absorption corrections were applied by the multi-scan procedure integrated in this package. The structures were solved by the direct method (SHELXS-97) [17]. All non-hydrogen atoms were refined in the anisotropic approximation by the full-matrix least-squares method (SHELXL-97) [18]. The hydrogen atom positions were revealed geometrically and refined with invariable thermal displacement parameters $U_{iso} = nU_{eq}$, where $n = 1.5$ for the hydroxyl oxygen atom and 1.2 for other non-hydrogen atoms, U_{eq} is the equivalent isotropic displacement parameter for the corresponding atoms.

The molecular graphics was constructed using the MERCURY program package [19]. The crystallographic data and structure refinement parameters for **I** and **II** are summarized in Table 1.

The atom coordinates and other parameters for **I** and **II** are deposited with the Cambridge Crystallographic Data Centre (nos. 1497849 and 1497848, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

The fungicidal activity was determined using two pathogenic test microorganisms: *Fusarium oxysporum* and *Aspergillus niger*, which are responsible for the loss of agricultural crops in Uzbekistan. In particular, *F. oxysporum* substantially damages the cotton plant, which is the major commercial crop, while *Aspergillus niger* is one of the main pests of fruit and vegetables during storage. The tests were performed on solid culture media in well plates [20]. DMSO was used as the control. Inoculated Petri dishes were incubated for 3–4 days in a thermostat at 30°C and then the pathogen growth inhibition zone was measured (mm).

RESULTS AND DISCUSSION

A comparative examination of the IR spectra of monosubstituted benzoic acids (including PNBA), their Na salts, and Cu complexes was reported [21]. The IR spectra of ethanolamines incorporated in various metal complexes have been discussed [22]. The papers [21, 22] served for band assignment in the spectra of **I** and **II**.

In the Na salt, PNBA occurs in the benzoate form with symmetric and asymmetric carboxylate stretching bands being located at 1408 and 1525 cm^{-1} [21]. These bands are found in the spectrum of **I** at lower wavenumbers (1385 and 1511 cm^{-1}) as strong peaks, which can be indicative of the coordination to copper ions. One more piece of evidence for this statement is the presence of very strong symmetric and antisymmetric NO_2 stretching modes at 1340 and 1569 cm^{-1}, which are recorded at 1353 and 1543 cm^{-1} in the spectrum of PNBA [21].

Table 1. Principal crystallographic data and structure refinement details for structures **I** and **II**

Parameter	Value	
	I	**II**
System	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a, Å	4.781(5)	6.80268(12)
b, Å	21.252(5)	21.6950(4)
c, Å	10.701(5)	12.8350(3)
β, deg	97.375(5)	94.441(2)
V, Å^3	1078.3(13)	1888.56(7)
Z	2	2
ρ(calcd.), g/cm^3	1.595	1.670
μ, mm^{-1}	1.077	2.219
Crystal size, mm	0.08 × 0.16 × 0.40	0.10 × 0.18 × 0.36
θ Range, deg	3.9–50.2	4.0–76.2
Region of h, k, l	$-5 \le h \le 5, -25 \le k \le 24, -11 \le l \le 12$	$-5 \le h \le 8, -26 \le k \le 27, -15 \le l \le 16$
Number of collected reflections	7618	13809
$R_{\rm int}$	0.034	0.042
Number of reflections with $I > 2\sigma(I)$	1540	2981
GOOF (F^2)	1.08	1.02
R_1, wR_2 ($I > 2\sigma(I)$)	0.0601, 0.1956	0.0432, 0.1249
$\Delta\rho_{\rm max}/\Delta\rho_{\rm min}$, e/Å^3	−0.56/0.48	−0.64/0.51

The bands corresponding to the OH stretching modes of the C–OH group and NH bending modes of MEA occur at 3450, 1120, and 1576 cm^{-1}, respectively [22]. In the spectrum of **I**, these bands are located at lower wavenumbers (3310, 1069, and 1569 cm^{-1}), which is indicative of chelation by the MEA molecule. This is also confirmed by the strong band at 515 cm^{-1} in the spectrum of **I**, which is characteristic of the Cu–N bond. However, the denticity of PNBA coordinated through the carboxylate group cannot be derived from the IR data alone; meanwhile, the results of elemental analysis attest to the occurrence of two molecules of each ligand in the copper coordination sphere. This composition of the coordination sphere (with C.N. of 6, which is usual for Cu(II)) is achieved via bidentate coordination of two MEA molecules and monodentate coordination of two PNBA molecules.

The IR spectrum of compound **II** exhibits a broad low-intensity band in the high-frequency region (3600–2400 cm^{-1}). The stretching modes of the MEA and water hydroxyl groups are not resolved and are also located in this region. The spectrum exhibits the same major peaks as in compound **I**. A similar consideration leads to the conclusion that compound **II** is also a mixed-ligand copper complexes.

In the crystals of **I**, the Cu^{2+} ion located at the inversion center is chelated by two MEA molecules via nitrogen and oxygen atoms (Fig. 1a). Two PNBA molecules are attached in the monodentate fashion via the oxygen atom of the carboxyl group, which occurs as the carboxylate anion to counterbalance the positive charge of copper ions. The carboxylate group is not coplanar with the benzene ring, the corresponding dihedral angle being 25.28°. The nitro group is rotated with respect to the aromatic ring through 11.51°.

The copper coordination polyhedron is an octahedron highly distorted due to the Jahn–Teller effect. The equatorial plane contains two PNBA oxygens and two MEA nitrogens (bond lengths ~2.000 ± 0.03 Å), while the apical positions are occupied by the MEA

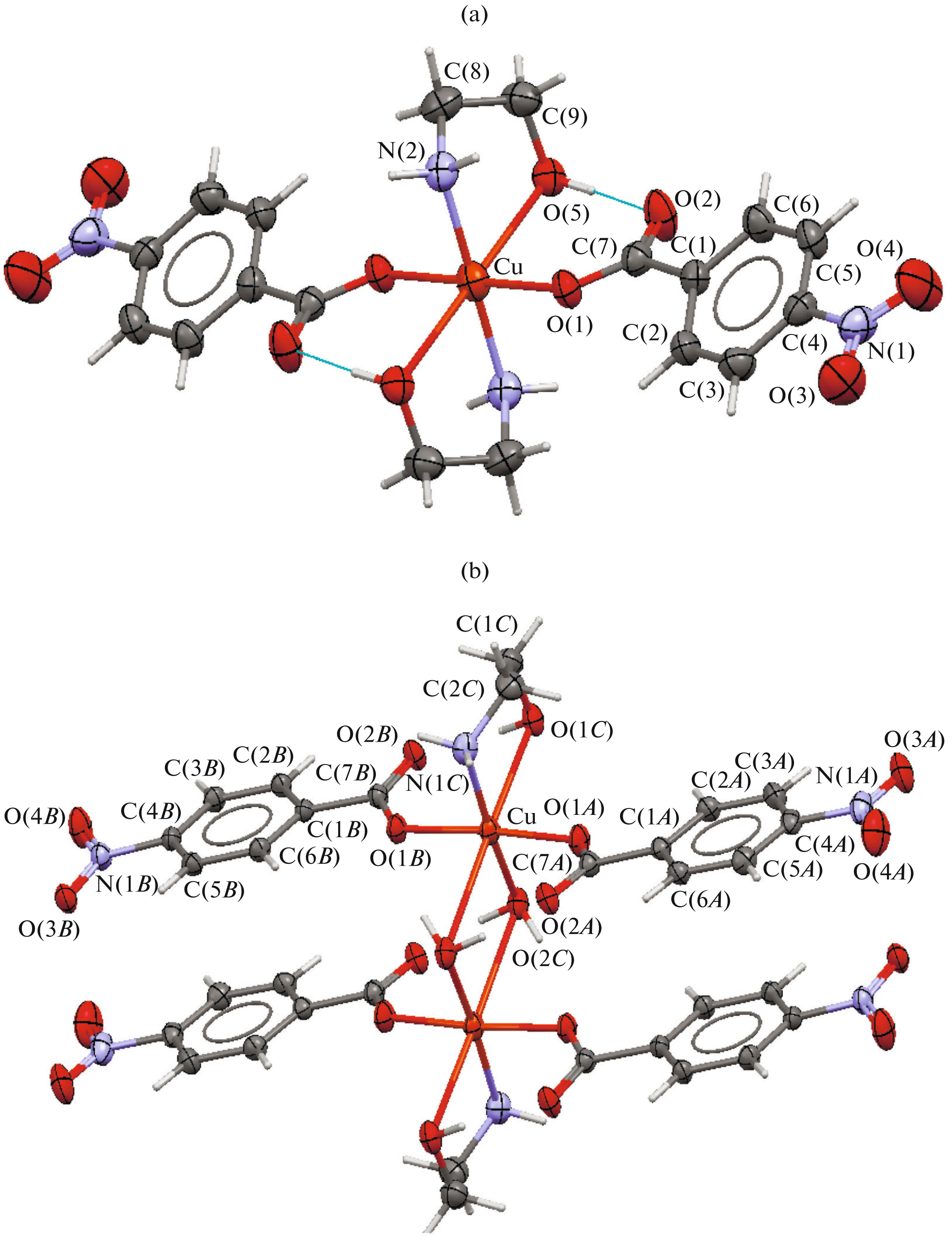

Fig. 1. Structure of the complex molecule in compounds (a) **I** and (b) **II**. Thermal ellipsoids of non-hydrogen atoms are shown at 50% probability level.

oxygens (C–O, 2.552(4) Å). The most pronounced deviation from 90° is found for the O(5)CuN(2) (76.20(13)°) and O(5)CuN(2) (103.80(13)°) angles (Table 2). The analysis of bond lengths and bond angles by the MOGUL program integrated into the MERCURY package [19] attests to the absence of unusual geometric parameters.

There is a strong intramolecular H-bond between the coordinated hydroxy group of MEA and free oxygen atom of the PNBA carboxylate group (Table 3); this bond closes a six-membered H-ring with the graph set $S_1^1(6)$ [23].

Thus, compound **I** is a mixed-ligand mononuclear 1 : 2 : 2 Cu(II) complex with PNBA and MEA rein-

Table 2. Bond lengths and bond angles of metal atoms in compounds **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
I			
Cu–O(1)	2.024(4)	Cu–O(1)$^{\text{i}}$	2.024(4)
Cu–N(2)	1.969(4)	Cu–O(5)$^{\text{i}}$	2.552(4)
Cu–O(5)	2.552(4)	Cu–N(2)$^{\text{i}}$	1.969(4)
II			
Cu–O(1*A*)	1.9288(18)	Cu–O(2*C*)	1.998(2)
Cu–O(1*B*)	1.9294(19)	Cu–O(2*C*)$^{\text{i}}$	2.714(2)
Cu–O(1*C*)	2.558(2)	Cu–N(1*C*)	2.007(3)
Angle	**ω, deg**	**Angle**	**ω, deg**
I			
O(1)CuO(5)	88.15(11)	O(5)CuN(2)	76.20(13)
O(1)CuN(2)	88.64(14)		
II			
O(1*A*)CuO(1*C*)	90.23(8)	O(1*B*)CuN(1*C*)	90.07(10)
O(1*A*)CuO(2*C*)	89.46(9)	O(1*B*)CuO(2*C*)$^{\text{i}}$	83.77(7)
O(1*A*)CuN(1*C*)	90.78(10)	O(1*C*)CuO(2*C*)	97.08(8)
O(1*A*)CuO(2*C*)$^{\text{i}}$	90.22(8)	O(1*C*)CuN(1*C*)	76.57(9)
O(1*B*)CuO(1*C*)	95.83(8)	O(2*C*)CuO(2*C*)$^{\text{i}}$	79.30(8)
O(1*B*)CuO(2*C*)	90.36(9)	O(2*C*)$^{\text{i}}$CuN(1*C*)	107.04(9)

* Symmetry codes: $^{\text{i}}$ 1 – *x*, 1 – *y*, –*z* (**I**); $^{\text{ii}}$ 2 – *x*, –*y*, 1 – *z* (**II**).

Table 3. Geometric parameters of the H-bonds in the crystals of compounds **I** and **II***

D–H···A	Distance, Å			DHA angle, deg	Coordinates of A atom
	D–H	H···A	D···A		
I					
O(5)–H(5)···O(2)	0.82	1.81	2.591(6)	160	1 – *x*, 1 – *y*, –*z*
N(2)–H(2*A*)···O(5)	0.89	2.09	2.942(6)	160	1 + *x*, *y*, *z*
N(2)–H(2*B*)···O(1)	0.89	2.37	3.033(6)	131	1 + *x*, *y*, *z*
II					
O(1*C*)–H(1*C*)···O(2*B*)	0.82	1.87	2.652(3)	160	
O(2*C*)–H(2*CB*)···O(2*A*)	0.86	1.82	2.664(3)	169	2 – *x*, –*y*, 1 – *z*
N(1*C*)–H(1*CA*)···O(3*B*)	0.89	2.51	3.303(3)	149	5/2 – *x*, –1/2 + *y*, 3/2 – *z*
N(1*C*)–H(1*CA*)···O(4*B*)	0.89	2.38	3.216(3)	157	5/2 – *x*, –1/2 + *y*, 3/2 – *z*
N(1*C*)–H(1*CB*)···O(4*A*)	0.89	2.29	3.161(4)	166	5/2 – *x*, –1/2 + *y*, 3/2 – *z*

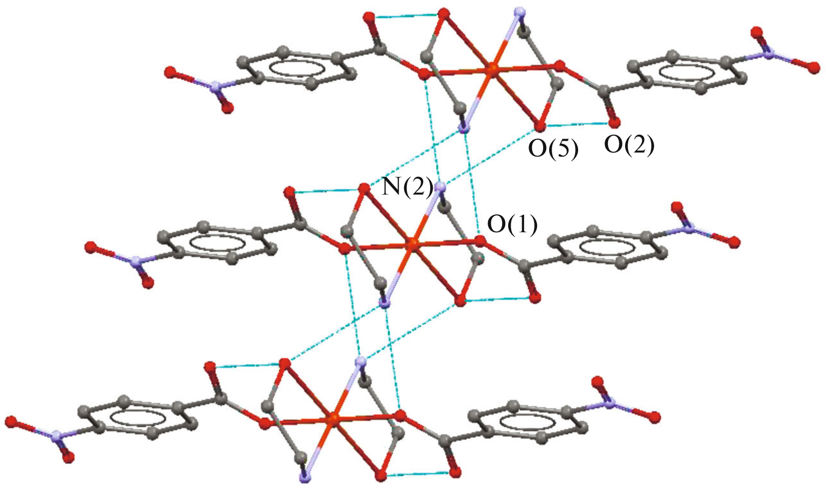

Fig. 2. Formation of columns along the *x* axis in the crystal structure of **I** (projection onto the *x*0*y* plane; H-bonds are shown by dashed lines).

forced by a strong intramolecular H-bond. The complex molecule has two donor groups for H-bonding: the O(5)–H hydroxy group and the $N(2)H_2$ amino group. The former group functions as the donor only in the intramolecular H-bond, whereas both hydrogen atoms at the MEA nitrogen atom are involved in intermolecular H-bonds with the O(1) and O(5) atoms of the complex molecule obtained from the initial molecule by translation along the *x* axis (Table 3). The nitro-group oxygen atoms do not participate in the H-bonds. The rather long distance (4.781 Å) between the centroids of the parallel aromatic rings attests to the absence of noticeable stacking interaction. The crystal packing is mainly determined by the pair of centrosymmetric H-bonds of the MEA amino group giving rise to columns parallel to the *x* axis (Fig. 2).

Compound **II** is a centrosymmetric binuclear mixed-ligand Cu(II) complex; its structure has much in common with that of mononuclear complex **I**. The site of one chelating MEA molecule is occupied in **II** by two water molecules linking the two copper ions (Fig. 1b). Each copper ion is chelated by one MEA molecule and monodentately coordinated to two PNBA molecules.

The PNBA molecules occur in the benzoate form to counterbalance the positive charge of the copper ions. The nitro and carboxylate groups are almost coplanar with the benzene ring in type A molecules (the dihedral angles are 1.39° and 1.66°) and are somewhat rotated in the type B molecules (8.89° and 8.26°).

The molecular conformation is stabilized by four H-bonds of two types. The first-type bonds are similar to the intramolecular H-bond in mononuclear complex **I** between the coordinated OH group of MEA and uncoordinated carboxylate-group oxygen atom of PNBA molecule of type B (Table 3). This bond closes a six-membered H-ring with the graph set $S_1^1(6)$. The intramolecular H-bond of the second type formed by the uncoordinated carboxylate-group oxygen of PNBA molecule of type A and by the coordinated water molecule also closes a six-membered H-ring with graph set $S_1^1(6)$ [23].

The copper coordination polyhedra are distorted octahedra (due to the Jahn–Teller effect). The equatorial plane is formed by two oxygen atoms of two PNBA molecules of types A and B, the MEA nitrogen atom, and the water molecule, the bond lengths being 1.9288(18), 1.9294(19), 2.007(3), and 1.998(2) Å, respectively. The apical positions are occupied by the MEA oxygen (Cu–O 2.558(2) Å) and water molecule (Cu–O 2.714(2) Å), which modify the distorted octahedron towards a tetragonal bipyramid. The greatest deviation from 90° is found for the angles O(1*C*)CuN(1*C*) 76.57(9)° and N(1*C*)CuO(2*C*) ($2 - x$, $-y$, $1 - z$) (107.04(9)°) (Table 2). The interatomic distances and bond angles, including those with metal ions, have usual values.

As distinct from mononuclear complex **I**, in the binuclear molecule **II**, the oxygen atoms of the PNBA nitro groups are involved in H-bonds. One hydrogen atom of the amino group participates in the forked bond with the nitro-group oxygens, O(3*B*) and O(4*B*) of the $5/2 - x$, $-1/2 + y$, $3/2 - z$ molecule, while the other hydrogen atom is hydrogen-bonded to the O(4*A*) atom of the molecule obtained from the former molecule by translations along the *x* and *y* axes (Fig. 3). These H-bonds form a three-dimensional framework, which is strengthened by the moderate

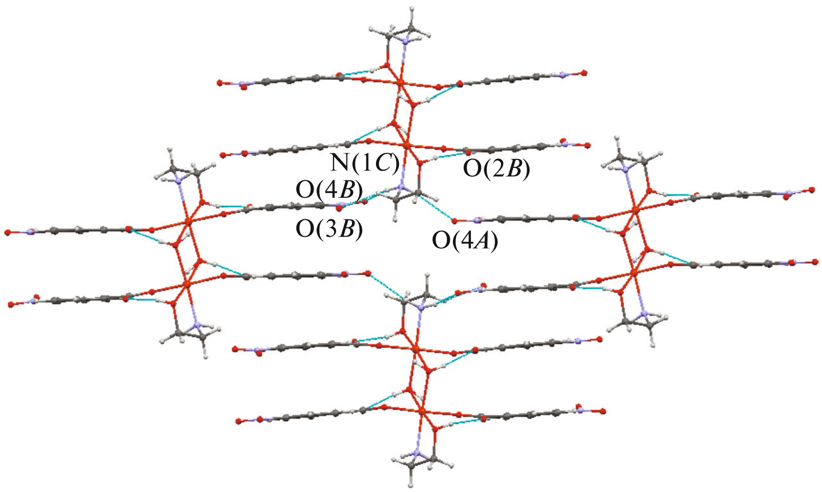

Fig. 3. Formation of the three-dimensional framework in the crystal structure of **II**. The dashed lines show the H-bonds.

stacking interaction of antiparallel benzene rings; the distances between the centroids are 3.718 Å (intramolecular) and 3.789 Å (intermolecular).

Compounds **I** and **II** were synthesized from solutions containing various copper salts, PNBA, and MEA. The same solutions can also be used to prepare compounds of a different composition such as the organic salt PNBA · MEA and the complexes Cu(PNBA) and Cu(MEA). Together with the synthesis of mixed-ligand complexes **I** and **II**, we were able to prepare and structurally characterize all of these compounds only after quite a few attempts. However, the organic salt and the single-ligand complexes prepared previously by other researchers were already present in the CCDC with the refcodes LIGZUX, AQNBCU, and ETOLCU, respectively. In order to evaluate the biological activity as a function of the ligands present in the coordination sphere, we determined the fungicidal activity of these complexes.

We found that PNBA was somewhat more active than MEA (Table 4, Fig. 4). The fungicidal action gradually increases for the single-ligand metal complexes and reaches a maximum for the mixed-ligand compounds. The binuclear mixed-ligand complex shows a higher activity than the mononuclear analog. The organic salt has an intermediate activity level between the free ligands and mixed-ligand complexes. The antimicrobial action of the test compounds is more pronounced against *Aspergillus niger*.

Table 4. Inhibition zones (mm) of the ligands, the prepared complexes, and previously obtained compounds (at two concentrations) measured for two pathogens

Compound	*Fusarium oxysporum*		*Aspergillus niger*	
	0.25 mg/mL	0.50 mg/mL	0.25 mg/mL	0.50 mg/mL
PNBA	12	16	13	20
MEA		6		7
PNBA · MEA	15	24	15	25
Zn(PNBA)	10	14	11	13
Co(MEA)	8	10	9	12
I	24	28	28	30
II	28	35	30	35

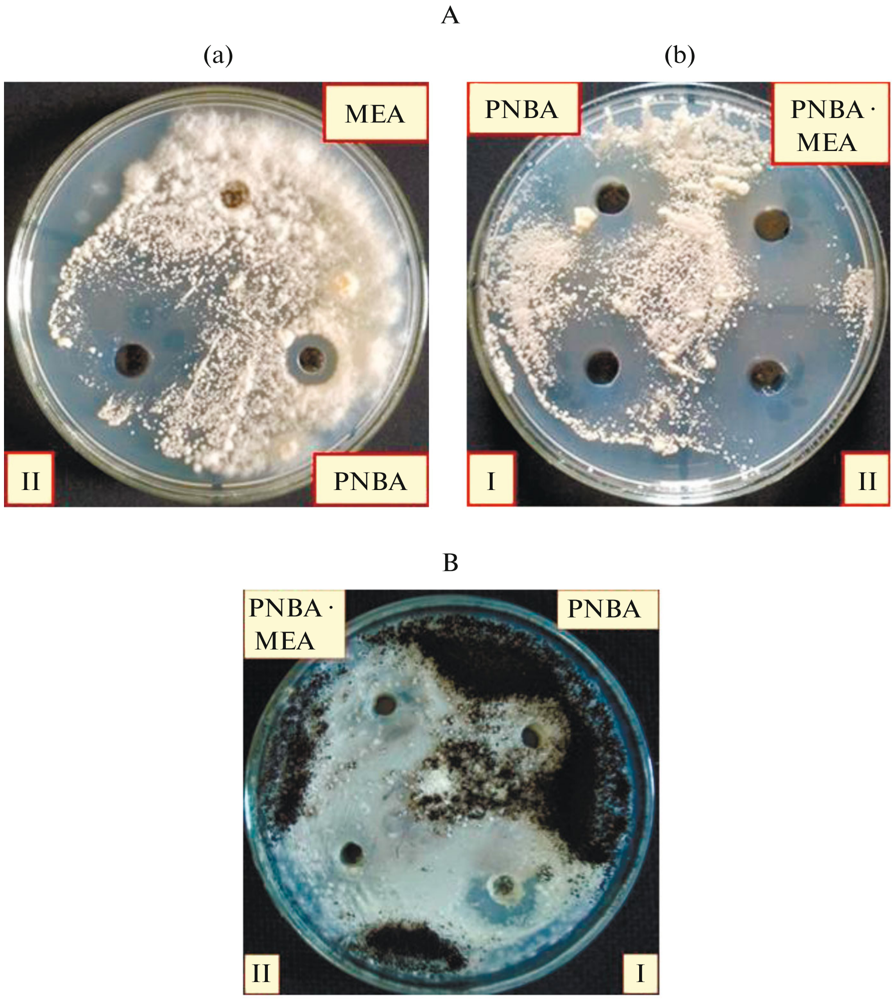

Fig. 4. Examples of experiments on the pathogen growth inhibition. (A) *Fusarium oxysporum* ((a) 0.25, (b) 0.50 mg/mL): (a) 12 (PNBA), 28 mm (**II**); (b) 16 (PNBA), 24 (PNBA · MEA), 28 (**I**), 35 mm (**II**). (B) *Aspergillus niger* (0.50 mg/mL): 20 (PNBA), 25 (PNBA · MEA), 30 (**I**), 35 mm (**II**).

Owing to the synergistic biological action of separate ligands and copper ions, the mixed-ligand complexes show the highest fungicidal activities. The results of these fungicidal activity tests can be recommended for application to other ligand pairs to boost other types of biological action. The MEA and PNBA ligands are also able to stimulate the growth of agricultural crops. Therefore, these metal complexes as rather promising dual-action compounds and can be employed for both plant protection and plant growth stimulation.

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