

# Crystal Structure of 4,4-Bipyridine-Containing Complexes of Copper(II) Nitrate with 1-[(2-Hydroxyethylimino)methyl]naphthalen-2-ol and 2-[(2-hydroxyethylimino)methyl]phenol

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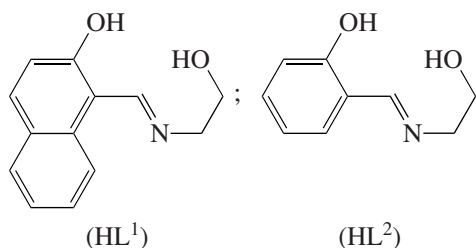
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Received October 23, 2008

**Abstract**—The crystal structures of  $(\mu$ -4,4'-bipyridine)-di(nitrato-1-[(2-hydroxyethylimino)methyl]naphthalen-2-olcopper) (**I**) and catena-di( $\mu$ -4,4'-bipyridine){di( $\mu$ -4,4'-bipyridine)-di(nitrato-2-[2-(hydroxyethylimino)methyl]phenolcopper)} diaquacopper(II) nitrate (**II**) were determined. In the crystal of **I**, each of the two copper atoms coordinates a singly deprotonated tridentate azomethine molecule, a nitrate ion, and bipyridine, which functions as a bridge between the central atoms. The copper coordination polyhedron is a slightly distorted tetragonal pyramid with the base formed by the imine and bipyridine nitrogen atoms and the phenol and alcohol oxygen atoms. The axial site in the pyramid is occupied by the oxygen atom of the monodentate nitrate groups. In the trinuclear structure **II** with  $C_2$  crystal chemical symmetry, the terminal coordination unit is composed through copper coordination of monodeprotonated 2-[2-(hydroxyethylimino)methyl]phenol, bipyridine, and the nitrate anion. In the crystal, the trinuclear molecules form infinite ribbons along the  $z$  axis in which the pyridine molecules perform the bridging function. The central copper atom has an octahedral configuration formed by the nitrogen atoms of four 4,4'-bipyridine molecules and oxygen of two water molecules.

DOI: 10.1134/S1070328409070070

The amine-containing copper(II) complexes with 2-[2-(hydroxyethylimino)methyl]phenol have been studied in considerable detail [1]. They were mainly synthesized using pyridine and picolines as the starting compounds. Therefore, it was of interest to find out how the composition, structure, and the properties of coordination compounds would change upon replacement of these monoamines by an aromatic diamine. Therefore, we synthesized  $(\mu$ -4,4'-bipyridine)-di(nitrato-1-[(2-hydroxyethylimino)methyl]naphthalen-2-olcopper) [ $(NO_3)(L^1)Cu(4,4'-Bipy)Cu(L^1)(NO_3)$ ] (**I**) and catena-di( $\mu$ -4,4'-bipyridine){di( $\mu$ -4,4'-bipyridine)-di(nitrato-2-[2-(hydroxyethylimino)methyl]phenolcopper)} diaquacopper(II) nitrate [ $Cu_3(H_2O)_2(4,4'-Bipy)_3(L^2)_2(NO_3)_2(NO_3)_2$ ] (**II**) and studied the structural features of these complexes by X-ray diffraction.



## EXPERIMENTAL

**Synthesis of I.** A solution containing 2-hydroxy-1-naphthaldehyde (10 mmol), monoethanolamine (10 mmol), and 4,4'-bipyridine (5 mmol) in ethanol (30 ml) was added with continuous magnetic stirring and heating (50–55°C) to a solution containing copper(II) nitrate trihydrate (10 mmol) in ethanol (20 ml). The reaction mixture was heated at reflux for 55–60 min. On cooling, dark green crystals precipitated; these were collected on a glass filter, washed with small amounts of ethanol and ether, and dried in air. The yield of the complex was 76%. It was readily soluble in dimethylformamide and dimethyl sulfoxide, sparingly soluble in water and alcohols, and almost insoluble in ether. The composition of **I** was determined from the data of elemental analysis.

For  $C_{36}H_{32}Cu_2N_6O_{10}$  (**I**)

anal. calcd, %: C, 51.74; H, 3.86; Cu, 15.21; N, 10.06.

Found, %: C, 51.50; H, 3.58; Cu, 15.00; N, 9.85.

IR ( $\nu$ ,  $cm^{-1}$ ): 3290–3275  $\nu(OH)_{alc}$ , 1600  $\nu(C=N)$ , 1530  $\nu(C-O)_{phen}$ , 1045  $\nu(C-O)_{alc}$ , 515 and 430  $\nu(Cu-N)$ , 470  $\nu(Cu-O)$ . Absorption bands of the inner-



**Table 1.** Crystal data, X-ray experiment details, and structure refinement parameters for structures **I** and **II**

Parameter	Value	
	<b>I</b>	<b>II</b>
<i>M</i>	833.74	1269.59
Crystal system, space group; <i>Z</i>	Orthorhombic; <i>Pca</i> 2 <sub>1</sub> ; 4	Orthorhombic; <i>Fdd</i> 2; 8
<i>a</i> , Å	22.957(5)	26.196(5)
<i>b</i> , Å	5.244(1)	35.384(7)
<i>c</i> , Å	28.417(6)	11.073(2)
<i>V</i> , Å <sup>3</sup>	3421.0(1)	10264(4)
ρ(exp), g/cm <sup>3</sup>	1.619	1.643
μ, cm <sup>-1</sup>	21.37	13.20
<i>T</i> , K	293(2)	293(2)
Sample size, mm	0.1 × 0.11 × 0.24	0.15 × 0.13 × 0.25
Scan mode	ω–2θ	ω–2θ
θ <sub>max</sub> , deg	70.03	25.00
(Limits of reflection indices	–27 ≤ <i>h</i> ≤ 9, –6 ≤ <i>k</i> ≤ 0, –34 ≤ <i>l</i> ≤ 34	0 ≤ <i>h</i> ≤ 31, 0 ≤ <i>k</i> ≤ 42, 0 ≤ <i>l</i> ≤ 13
The number of reflections: Independent ( <i>N</i> <sub>1</sub> ) with <i>I</i> > 2σ( <i>I</i> ) ( <i>N</i> <sub>2</sub> )	3266/1121	2339/816
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0696P)^2]$ , $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1448P)^2 + 31.00P]$ , $P = (F_o^2 + 2F_c^2)/3$
The number of refined parameters	487	374
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> for <i>N</i> <sub>1</sub>	0.1905/0.1685	0.2314/0.0969
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> for <i>N</i> <sub>2</sub>	0.065/0.1328	0.0659/0.0711
<i>S</i>	0.792	0.721
Δρ <sub>min</sub> /Δρ <sub>max</sub> , e Å <sup>-3</sup>	–0.317, 0.428	–0.639, 0.510

onal pyramid (TP) or trigonal bipyramid (TBP) was solved using the index  $\tau$  [6]:  $\tau = (\beta - \alpha)/60$ , where  $\alpha$  and  $\beta$  are the greatest angles between the bonds formed by the central atom. If  $\tau = 0$ , the metal coordination is described as ideal TP; when  $\tau = 1$ , as ideal TBP. For Cu(1) and Cu(2) atoms in **I**,  $\tau = 0.01$ , i.e., their coordination polyhedra are nearly ideal TP having volumes of 6.190 and 6.405 Å<sup>3</sup>, respectively. The base of the coordination polyhedron is formed by the imine and bipyridine nitrogen atoms and phenol and alcohol oxygen atoms. The displacements of these atoms from their mean planes in the Cu(1) and Cu(2) polyhedra are 0.024 (0.020), 0.020 (0.017), –0.022 (–0.018), and –0.0215 (–0.019) Å, respectively, and the deviation of the copper atom from this plane is –0.053 (–0.050) Å. The axial sites in the TP are occupied by the O(1N1) (O(1N2)) atoms of the monodentate nitrate groups.

In **I** the six-membered CuNC<sub>3</sub>O metal rings are slightly folded along the O(11)···N(11) and O(12)···N(12) lines. The dihedral angles between the planes Cu(1)O(11)N(11), O(11)C(11)C(21)C(31)N(11) and Cu(2)O(12)N(12), O(12)C(12)C(22)C(32)N(12) are 5.0° and 4.9°, respectively. In the related compounds, di(μ-O<sub>phenoxo</sub>)-bis{nitrate-2-[2-(hydroxyethylimino)methyl]phenoloimidazolecopper(II)} [7], nitrate-2-[2-(hydroxyethylimino)methyl]phenol-3-picolinecopper(II) [8], 3-hydroxypropylsalicylaldiminatocopper [9], the analogous dihedral angles are 20.6°, 14.9°, and 22.7°, respectively. In nitrate-2-[2-(hydroxyethylimino)methyl]phenolcopper [10], nitrate-2-[2-(hydroxyethylimino)methyl]phenolo-4-picolinecopper [11], 2-[2-(hydroxyethylimino)methyl]phenolcopper [12], no such folding is observed. The five-membered CuNC<sub>2</sub>O metal rings in complex **I** have an envelope conformation, the

deviation of the O(22) atom from the Cu(2)N(12)C(82)C(92) root-mean-square plane ( $\pm 0.004$ – $0.009$  Å) being equal to  $0.300$  Å and the deviation of the C(92) atom from the Cu(1)O(11)N(12)C(82) root-mean-square plane ( $\pm 0.009$ – $0.018$  Å) being equal to  $0.488$  Å.

The complexes in crystal **I** separated by translation along the *y* axis are combined by the C(9P)–H...O(1N2) hydrogen bond into infinite ribbons. The ribbons are further connected through the nitrate group by the C(82)–H...O(2N1) and C(122)–H...O(3N2) hydrogen bonds (Fig. 2, Table 3). According to the criterion proposed previously [3] ( $Cg \cdots Cg < 6.0$  Å),  $\pi$ – $\pi$  stacking interaction occurs in the ribbons between the Cu(1)O(11)N(11)C(11)C(21)C(31) and C(21)C(31)C(41)C(51)C(61)C(71) rings. The  $Cg \cdots Cg$  distance between the centroids of these fragments is  $3.747$  Å.

The structure of **II** is based on a trinuclear molecule ( $C_2$  crystallographic symmetry) incorporating two nitrate ions (Fig. 3). The terminal coordination unit (at Cu(1)) is constructed through cooper coordination of the monodeprotonated 2-[2-(hydroxyethylimino)methyl]phenol ligand ( $L^2$ ), bipyridine, and nitrate anion. The Cu(2) central atom located on a twofold axis has an extended tetragonal bipyramidal coordination ( $4 + 2$ ) by the N atoms of four 4,4'-bipyridine molecules and two O atoms of water molecules. In crystal **II**, these fragments form infinite ribbons along the *z* axis. The bipyridine molecules perform a bridging function (Fig. 4). The Cu(1)–Cu(2) distance is  $11.111$  Å, the Cu(2) atoms in the ribbon are located  $11.071$  Å apart from one another.

The Cu(1) coordination polyhedron in **II** is a distorted TP ( $\tau = 0.23$ ) having a volume of  $6.620$  Å<sup>3</sup>. The TP base is formed by the imine and bipyridine nitrogen atoms and the phenol and alcohol oxygen atoms. The displacements of these atoms from the mean plane are  $0.142$ ,  $0.132$ ,  $-0.135$ , and  $-0.139$  Å, respectively, and the deviation of the copper atom from this plane is  $0.196$  Å. The axial site in the TP is occupied by the O(1N1) atom of the monodentate nitrate group at a distance of  $2.278(8)$  Å. The six-membered Cu(1)NC<sub>3</sub>O metal ring in **II** is slightly folded along the O(11)–N(11) line: the dihedral angle between the Cu(1)O(11)N(11) and O(11)C(11)C(21)C(31)N(11) planes is  $3.7^\circ$ . The benzene ring lies almost in the plane of the six-membered metal ring, the angle between the corresponding root-mean-square planes being  $3.4^\circ$ . The five-membered metal ring, Cu(1)NC<sub>2</sub>N, in **II** has an asymmetric *gauche*-conformation: the deviations of C(81) and C(91) atoms from the Cu(1)O(11)N(11) plane are  $-0.37$  and  $0.21$  Å, respectively.

The coordination polyhedron of Cu(2) is an extended tetragonal bipyramid ( $4 + 2$ ) whose equatorial plane is formed by the atoms N(12), N(2P), N(22), N(2P)<sup>a</sup> ( $a = -x, -y + 1, z$ ). The apical sites in the Cu(2) coordination polyhedron are occupied by symmetrically connected O(1w) and O(1w)<sup>b</sup> atoms of water mol-

**Table 2.** Selected interatomic distances and bond angles for compounds **I** and **II**

Bond	<i>d</i> , Å	
	<b>I</b>	<b>II</b>
Cu(1)–O(11)	1.87(3)	1.954(6)
Cu(1)–O(21)	2.01(3)	2.032(6)
Cu(1)–N(11)	1.90(3)	1.918(7)
Cu(1)–N(1P)	2.03(3)	1.974(6)
Cu(1)–O(1N1)	2.42(3)	2.278(8)
O(11)–C(31)	1.37(4)	1.338(10)
O(21)–C(91)	1.35(5)	1.472(9)
N(11)–C(11)	1.28(4)	1.254(12)
N(11)–C(81)	1.48(5)	1.500(13)
C(11)–C(21)	1.44(5)	1.405(13)
C(21)–C(31)	1.42(4)	1.399(11)
C(81)–C(91)	1.500(3)	1.437(11)
Cu(2)–O(12) (–N(22))	1.94(3)	1.989(12)
Cu(2)–N(12)	1.91(3)	2.020(11)
Cu(2)–N(2P)	1.98(3)	2.032(6)
Cu(2)–O(22)	2.01(3)	
Cu(2)–O(1N2) (–O(1w))	2.46(3)	2.629(9)
O(12)–C(32)	1.30(5)	
O(22)–C(92)	1.44(4)	
N(12)–C(12)	1.31(5)	1.338(10)
N(12)–C(82)	1.46(4)	
C(12)–C(22)	1.44(6)	1.410(11)
C(22)–C(32)	1.40(5)	1.368(11)
C(82)–C(92)	1.50(3)	
Angle	$\omega$ , deg	
O(11)Cu(1)N(11)	93.1(12)	92.8(4)
C(31)O(11)Cu(1)	129.6(19)	126.3(6)
C(11)N(11)Cu(1)	123(3)	126.2(8)
C(81)N(11)Cu(1)	117(2)	111.9(7)
N(11)C(11)C(21)	132(3)	127.6(10)
C(31)C(21)C(11)	117(3)	124.4(10)
O(11)C(31)C(21)	123(3)	122.5(9)
N(11)C(81)C(91)	106(3)	107.5(8)
O(21)C(91)C(81)	113(4)	111.3(8)
N(12)Cu(2)N(2P)	173.8(16)	90.5(3)
O(12)Cu(2)O(22)	174.2(11)	
N(12)Cu(2)O(22)O(1w)	81.7(13)	87.9(5)
N(2P)Cu(2)O(22)N(22)	93.5(11)	89.5(7)
N(2P)Cu(2)O(1N2)O(1w)	86.8(13)	90.0(5)



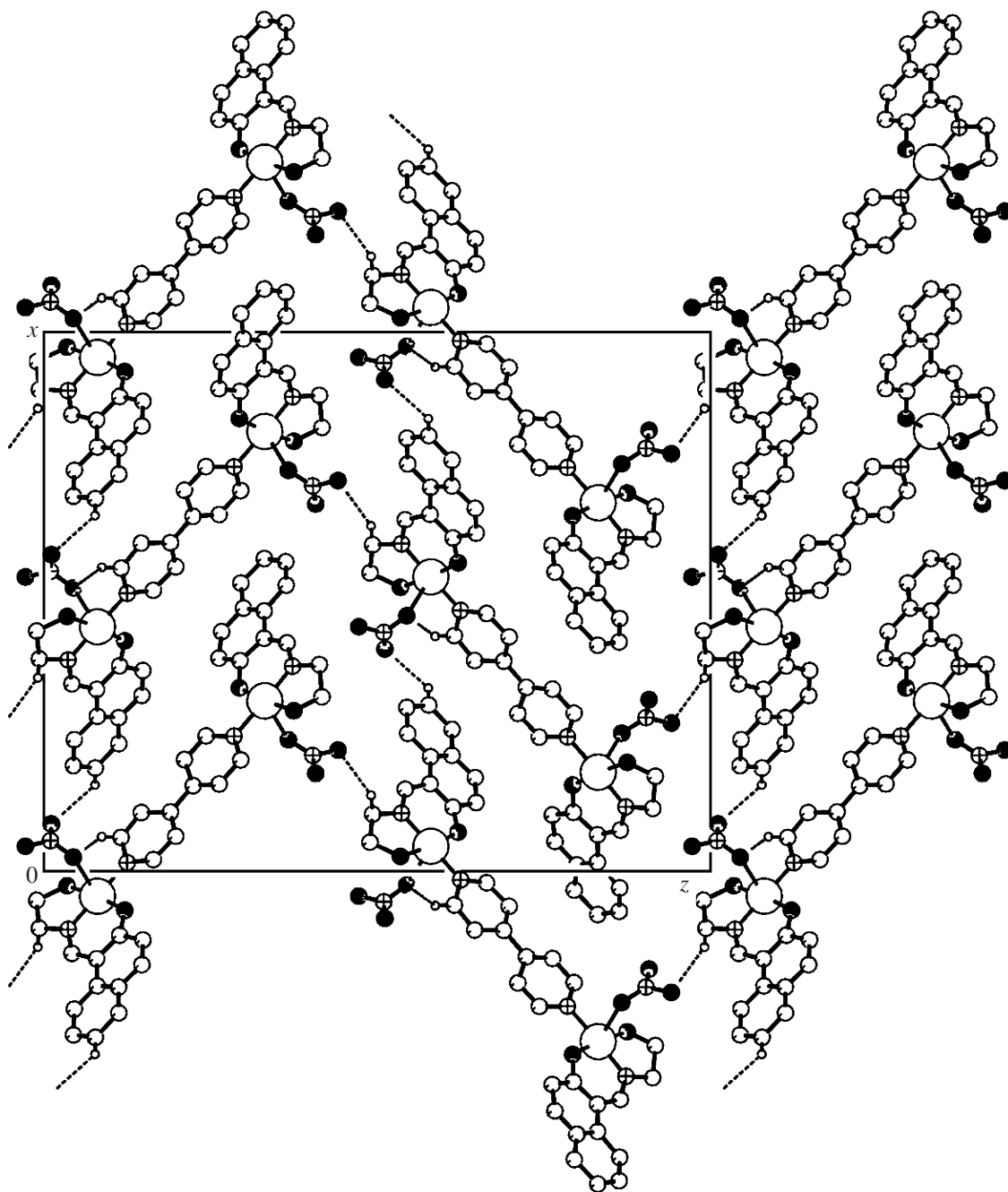


Fig. 2. Packing of structural units in crystal I.

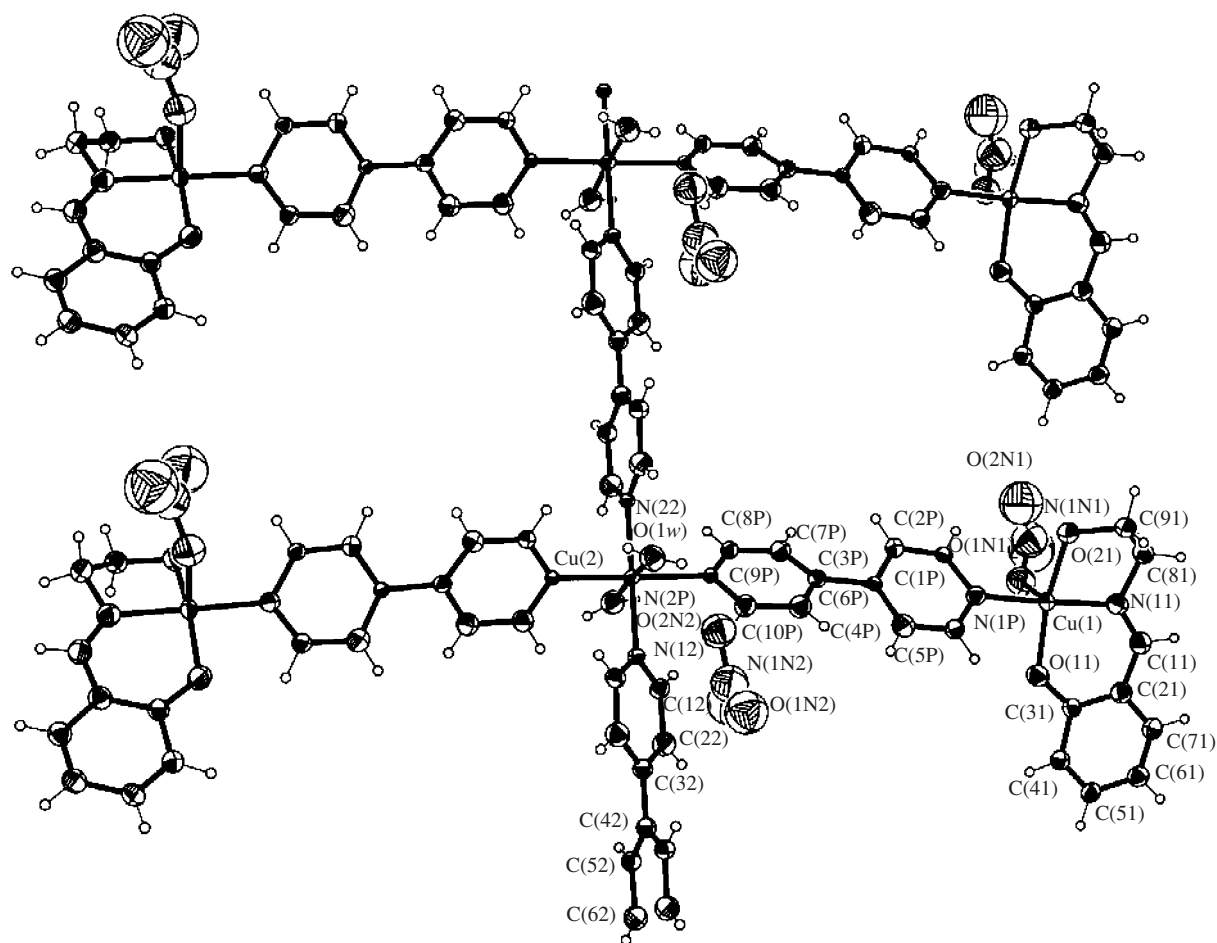
ecules ( $b = 1/2 - x, 1/2 - y, z$ ). The volume of the tetragonal bipyramid equals  $14.262 \text{ \AA}^3$ .

The infinite ribbons in the crystal of **II** are combined into a three-dimensional framework by the system of hydrogen bonds involving the coordinated water molecules and nitrate groups (Fig. 4, Table 3). According to the criterion proposed previously [3] ( $\text{Cg} \cdots \text{Cg} < 6.0 \text{ \AA}$ ),  $\pi$ - $\pi$  stacking interaction occurs in the ribbons connected by a  $2_1$  screw axis ( $1/2 - x, -y, 1/2 + z$ ) between

the  $\text{N}(2\text{P})\text{C}(6\text{P})\text{C}(7\text{P})\text{C}(8\text{P})\text{C}(9\text{P})\text{C}(10\text{P})$  and  $\text{C}(21)\text{C}(31)\text{C}(41)\text{C}(51)\text{C}(61)\text{C}(71)$  rings. The  $\text{Cg} \cdots \text{Cg}$  distance between the centroids of these fragments is  $3.669 \text{ \AA}$ . In compound **II**,  $\text{Y}-\text{X} \cdots \text{Cg}$  interaction ( $\pi$ -ring) also occurs ( $\text{X} \cdots \text{Cg} < 4.0 \text{ \AA}$ ,  $\gamma \ll 30.0^\circ$ , where  $\gamma$  is the angle between the bond vector and the normal to the aromatic ring [3]). For the interaction  $\text{N}(1\text{N}2)-\text{O}(1\text{N}2) \cdots \text{Cg}$  ( $\text{N}(12)\text{C}(12)\text{C}(22)\text{C}(32)\text{C}(12^b)\text{C}(22^b)$ ), the  $\text{O}(1\text{N}2) \cdots \text{Cg}$  distance is  $3.200 \text{ \AA}$  and the  $\gamma$  angle is  $18.9^\circ$ .

**Table 3.** Geometric parameters of hydrogen bonds for compounds **I** and **II**

Contact D–H...A	Distance, Å			DHA angle, deg	Coordinates of A atom
	D...A	H...A	D–H		
<b>I</b>					
C(9P)–H(9PA)...O(1N2)	3.31(1)	2.53	0.93	142	$x, -1 + y, z$
C(82)–H(82B)...O(2N1)	3.13(2)	2.40	0.97	132	$-x, 1 - y, -1/2 + z$
C(122)–H(122)...O(3N2)	3.26(2)	2.57	0.93	131	$-1/2 + x, 3 - y, z$
<b>II</b>					
O(1w)–H(1w1)...O(2N2)	2.90(1)	2.24	0.82	137	$1/4 + x, 1/4 - y, 1/4 + z$
O(1w)–H(1w2)...O(11)	2.95(2)	2.15	0.82	167	$1/4 + x, 1/4 - y, 1/4 + z$
C(2P)–H(2P)...O(3N2)	3.35(1)	2.54	0.93	146	$x, y, 1 + z$
C(8P)–H(8P)...O(1N1)	3.27(1)	2.43	0.93	151	$1/4 - x, 1/4 + y, 1/4 + z$
C(62)–H(62)...O(1w)	3.15(1)	2.41	0.93	136	$1 - x, 1 - y, -z$
C(91)–H(91B)...O(3N1)	3.25(1)	2.47	0.97	137	$1/4 + x, -1/4 - y, -1/4 + z$

**Fig. 3.** Structure of complex **II**.

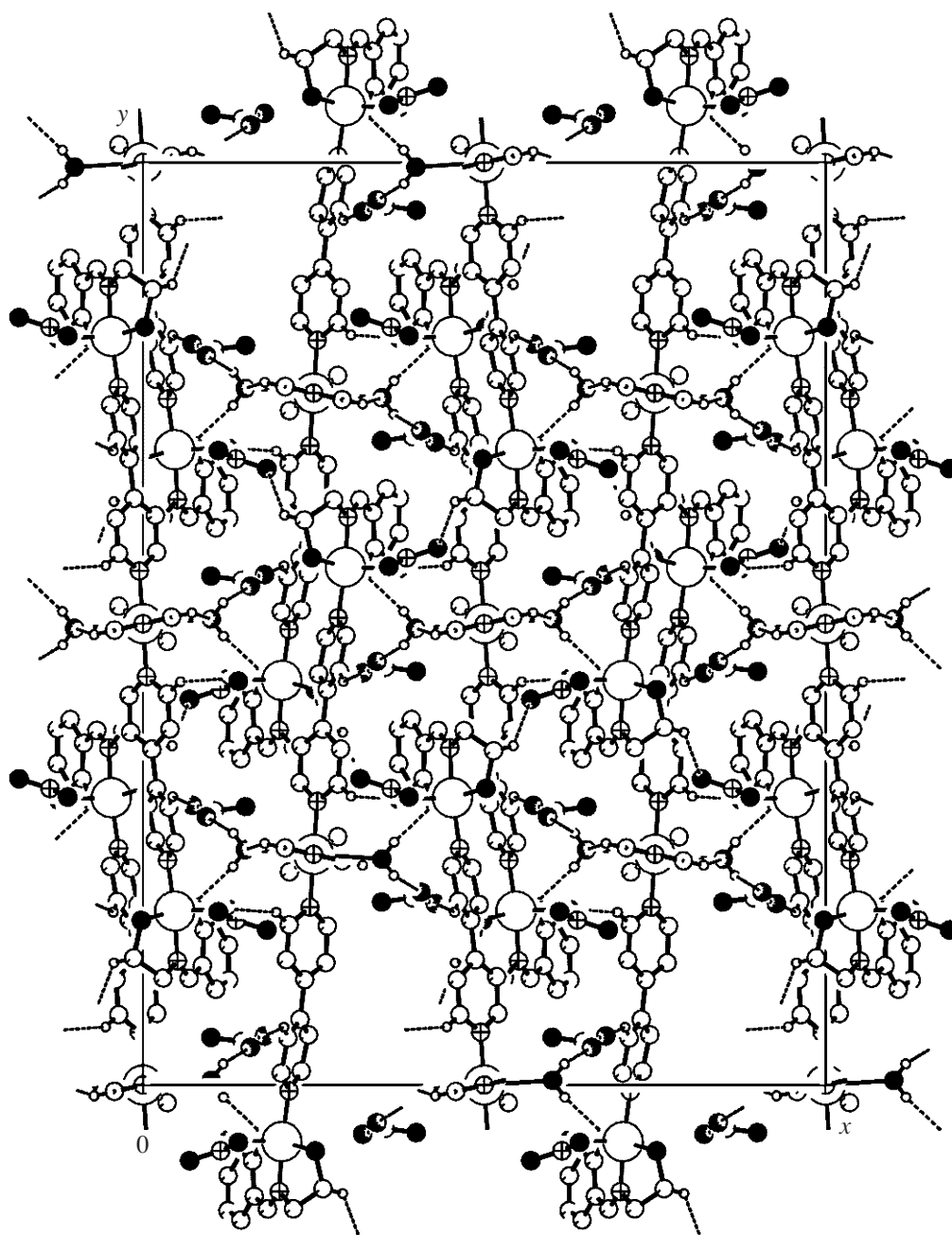


Fig. 4. Packing of structural units in crystal II.

Thus, the study showed that the replacement of pyridine or picoline by 4,4'-bipyridine in amine-containing copper(II) nitrate complexes with 1-[(2-hydroxyethylimino)methyl]naphthalen-2-ol results in the formation of only binuclear coordination compounds, while replacement of the naphthalidene fragment of azomethine by salicylidene fragment promotes the formation of coordination polymers. In all compounds studied, systems of weak contacts, H-bonds or stacking and X–Y...Cg ( $\pi$ -ring) interactions, were observed.

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