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Synthesis and Structure of Mono- and Polynuclear Cu(II) Complexes with α-(*N*-Benzoxazolin-2-one)acetic Acid

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Abstract—Two compounds with the α-(*N*-benzoxazolin-2-one)acetic acid ligand (L) were synthesized: $[Cu(L)_2(NH_2C_2H_4OH)_2]$ (**I**) and $[Cu(L)_2(H_2O)_2]_n$ (**II**), viz., mono- and polynuclear complexes, respectively. According to X-ray diffraction data (CIF files CCDC no. 1008795 (**I**) and 1008794 (**II**)), the coordination polyhedron of the metal atom in **I** is an extended tetragonal bipyramid with four heteroatoms of two monoethanolamine molecules in the equatorial plane. The carboxyl oxygen atoms of two ligands L occupy the apical positions. In complex **II**, a tetragonal bipyramid is also formed, having two O atoms of the carboxyl groups of the L molecule and two water O atoms in the equatorial plane. Two oxygen atoms of the carboxyl groups of the L molecule occupy apical positions. Complex **II** is a 2D polymer (polymerization involves four O atoms of the carboxyl group) with the $[CuL_2(H_2O)_2]$ unit.

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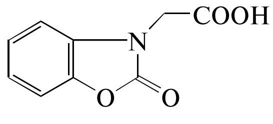
INTRODUCTION

Benzoxazolin-2-one was isolated from rye seedlings [1] and the derivatives, 6-methoxy- and 6,7-dimethoxybenzoxazolin-2-ones, were isolated from the *Coix lacryma-jobi* [2] and *Scoparia dulcis* roots [3], which have been used in folk medicine from long ago. The presence of benzoxazolin-2-one derivatives accounts for the resistance against some diseases of a number of crops [2, 4, 5]. Benzoxazolin-2-one derivatives are used as fungicides for agricultural plants [6, 7].

A benzoxazolin-2-one derivative, α-(*N*-benzoxazolin-2-one)acetic acid (HL), contains exocyclic active sites prone to form intra- and intermolecular hydrogen bonds. Also, exocyclic active sites stimulate the formation of complexes with transition elements. The introduction of vitally important metals into biologically active compounds not only reduces the toxicity but also, in most cases, enhances the biological activity, and new biological properties often appear.

The complex species formed depend on the nature of the substrate, the solvent, and the reacting salt. Previously, we synthesized the transition metal complexes ($M = Co^{2+}, Cu^{2+}, Zn^{2+}$) with L and proved their isomorphic structure to be $[M(L)_2(H_2O)_4]$. In these complexes, the coordination polyhedron of the M atom is an extended tetragonal bipyramid with four water molecules in the equatorial plane; the oxygen atoms of the carboxyl groups of the two ligands L occupy the apical positions [8, 9]. These complexes were prepared under the conditions described in [9].

However, a change in the conditions of synthesis of the complexes, in particular, the use of a solution of $CuCl_2$ and other active solvents resulted in the synthesis of two more complexes with the ligand L (see Experimental). This communication presents the results of synthesis of the mono- and polynuclear complexes $[Cu(L)_2(NH_2C_2H_4OH)_2]$ (**I**) and $[Cu(L)_2(H_2O)_2]_n$ (**II**). Data on the spatial and crystal structures of the complexes determined by X-ray diffraction are reported.



(HL)

EXPERIMENTAL

Synthesis of I. A hot ethanolic solution of HL (0.1 g, 0.52 mmol) was added to a solution of $CuCl_2 \cdot 2H_2O$ (0.044 g, 0.26 mmol) in a 1 : 1 water–ethanol mixture (3 mL). Monoethanolamine (32 μL) was added dropwise to the reaction mixture with continuous stirring. The reaction mixture was kept in an ultrasonic bath (30 kHz) for 10 min. The resulting solution was placed (25°C) into a non-tightly closed sample bottle. After 6 days, prismatic crystals formed. Among them, a single crystal for X-ray diffraction was selected after numerous attempts (due to poor quality).

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

Parameter	Value	
	I	**II**
System	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a, Å	7.181(4)	16.3872(7)
b, Å	9.090(5)	7.3898(3)
c, Å	9.721(8)	7.5875(3)
α, deg	72.77(6)	90
β, deg	78.12(5)	90.627(4)
γ, deg	88.22(4)	90
V, Å^3	592.8(6)	918.78(6)
Z	1	2
ρ(calcd.), g/cm^3	1.597	1.749
μ, mm^{-1}	1.889	2.282
Crystal size, mm	0.2 × 0.10 × 0.08	0.7 × 0.2 × 0.1
Scan range, θ, deg	4.9–35.5	5.4–63.7
Region of h, k, l	$-5 \le h \le 5$, $-3 \le k \le 6$, $-7 \le l \le 7$	$-19 \le h \le 19$, $-8 \le k \le 7$, $-8 \le l \le 8$
Reflections collected	982	4510
Independent reflections collected	522	1505
R_{int}	0.061	0.067
Reflections with $I > 2\sigma(I)$	440	952
GOOF (F^2)	1.01	0.95
R_1, wR_2 ($I > 2\sigma(I)$)	0.0537, 0.1377	0.0467, 0.1098
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e/Å^3	–0.33, 0.20	–0.26, 0.59

Synthesis of II. A hot solution of HL (0.46 g, 0.088 mmol) in a 1 : 1 water–ethanol mixture (4 mL) was added to a solution of $CuCl_2 \cdot 2H_2O$ (0.044 g, 0.23 mmol) in the same solvent mixture (3 mL). The reaction mixture was kept in an ultrasonic bath (30 kHz) for 10 min. The solution was placed into a non-tightly closed sample bottle and, after 4 days, blue-colored plate crystals formed.

X-ray diffraction analysis of I and II. The sets of reflections were measured at 293 K on a Xcalibur R Oxford Diffraction automated diffractometer (CuK_α radiation, λ = 1.54184 Å, ω scan mode, graphite monochromator). The experimental data were collected using CrysAlisPro software [10]. The absorption corrections were applied by the multi-scan method within the CrysAlisPro program package. The structures were solved by the direct method (SHELXS-97) [11] and refined by the full-matrix least-squares method (SHELXL-97) [12]. All non-hydrogen atoms were located in the difference electron density maps and refined on F^2_{hkl} in the anisotropic approximation. No high-quality crystals of **I** for X-ray diffraction analysis could be selected. Therefore, the full set of reflections was not collected from the crystal. For this reason, DFIX restraints had to be used in the benzene ring at the final stages of refinement. The hydrogen atoms were specified geometrically and refined with fixed isotropic parameters $U_{iso} = nU_{equiv}$, where $n = 1.5$ for methyl carbon atoms and $n = 1.2$ for other atoms, and U_{equiv} is an equivalent isotropic displacement parameter for the corresponding carbon atoms. The coordinates of hydrogen atoms of the water molecule in **II** were determined experimentally from the difference electron density maps and refined isotropically.

Molecular graphics was based on the XP program included in the SHELXTL-Plus program package [13]. The crystallographic data and structure refinement parameters for compounds **I** and **II** are summarized in Table 1.

The atom coordinates and other parameters of **I** and **II** are deposited at the Cambridge Crystallographic Data Centre (nos. 1008795 and 1008794, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

According to X-ray diffraction data, the complexes have the composition $[Cu(L_2)(MEA)_2]$ (**I**) and $[Cu(L_2)(H_2O)_2]_n$ (**II**). The ligands L^- in complexes **I** and **II** are planar, except for the carboxyl group; the bicyclic structure with *exo*-bond is planar to an accu-

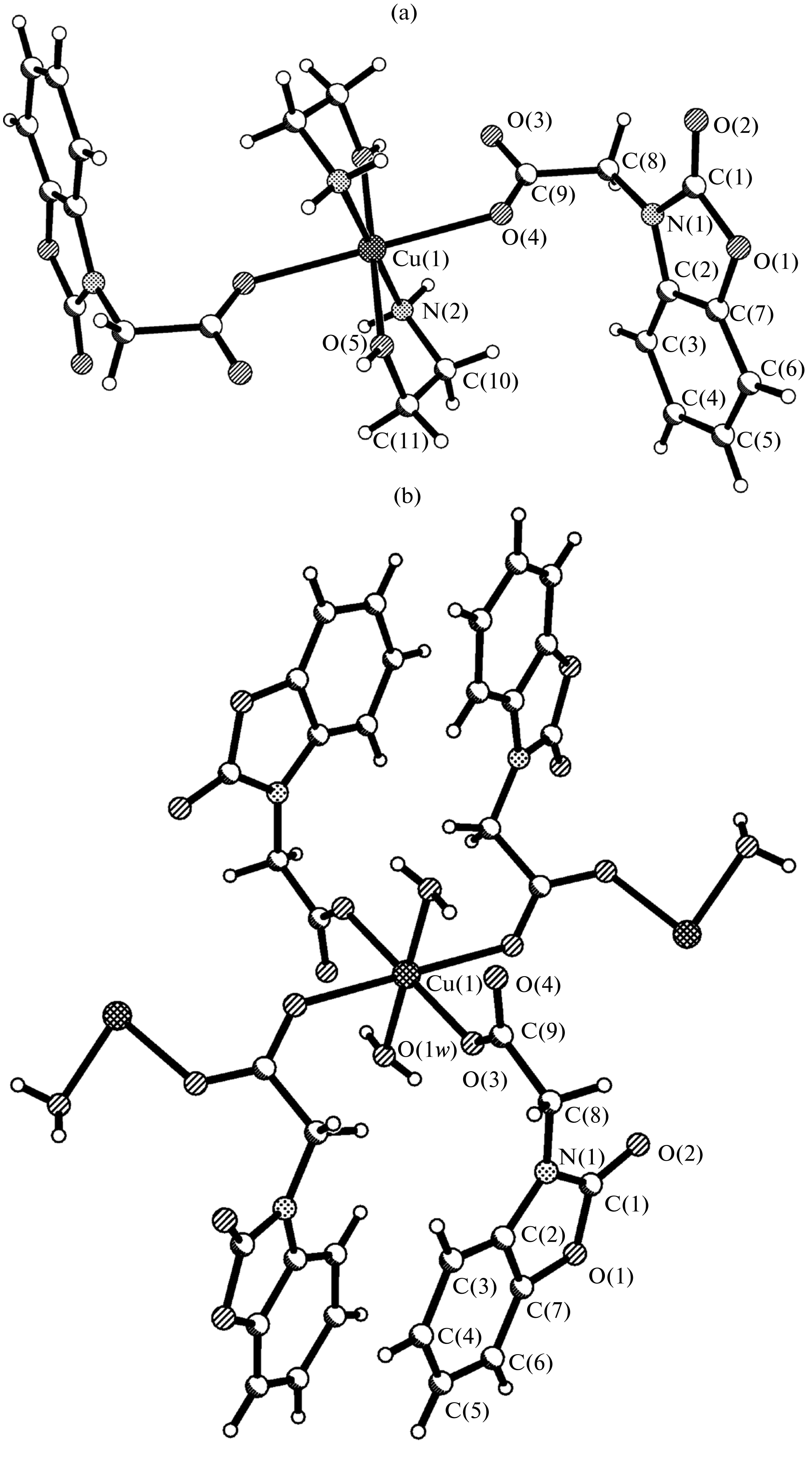


Fig. 1. Structure of the (a) discrete **I** and (b) polynuclear **II** complexes (the atoms of the asymmetric part of the molecules are numbered).

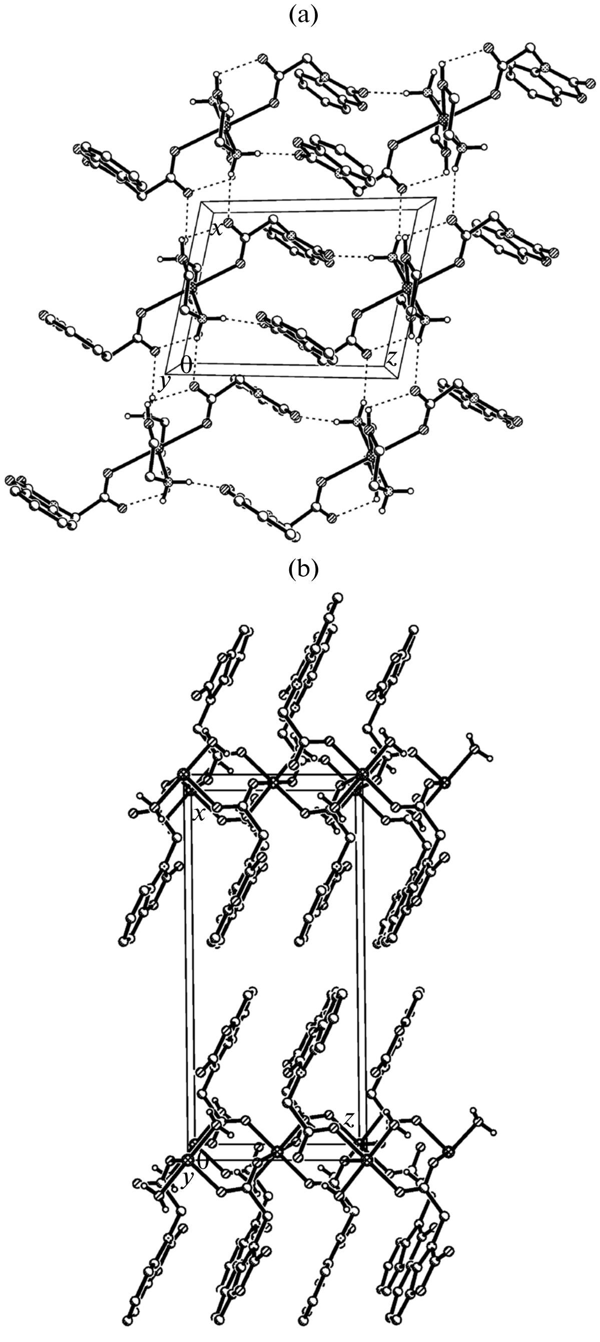


Fig. 2. Molecular packing in the crystals of (a) **I** and (b) **II**.

racy of ±0.02 Å in **I** and ±0.03 Å in **II**. The carboxyl group adjoining the N(3) atom can easily rotate around the N(3)–C(8) bond depending on the nature of the environment and weak interaction. The dihedral angle between the planes of the carboxyl group and the benzoxazole fragment is 98° in **I** and 75° in **II**.

The asymmetric part of the crystal of **I** contains one α-(*N*-benzoxazolin-2-one)acetate anion coordinated to the metal through the carboxyl O atom and one ethanolamine molecule chelating the metal by two heteroatoms (O,N). The Cu atoms in **I** and **II** occur in special positions at inversion centers. The coordination polyhedra of the Cu atoms in **I** and **II** are extended tetragonal bipyramids (4 + 2). The general coordination of the metal atoms in **I** and **II** does not differ from that in $[Cu(L)_2(H_2O)_4]$ [9]. The equatorial plane of the bipyramid accommodates four heteroatoms (two oxygen and two nitrogen atoms) of two bidentate ethanolamine molecules. The oxygen atoms of the carboxyl groups of two monodentate ligands L occupy the apical positions (Fig. 1a). The coordination to two heteroatoms of the ethanolamine molecule forms the five-membered metallacycle $CuOC_2N$ in the C(11)-envelope conformation.

In complex **I**, the Cu–O(5) and Cu–N(2) bond lengths are 2.053(10) and 1.963(13) Å, respectively, the length of the Cu–O(4) axial bond is 2.444(14) Å. These distances correspond to the distances in six-coordinate Cu(II) aqua complexes with the ligands L [9]. The bond angles at the Cu atom in structure **I** deviate from ideal octahedral angles by 6°–7°; the CuO(4)C(9) angle is 124(2)°.

Complex **I** has an intramolecular hydrogen bond (HB) between the ethanolamine OH group and the oxygen atoms of the carboxyl group (O···O 2.531 Å). The crystal of **I** contains also intermolecular N–H···O hydrogen bonds between the ethanolamine ligands. Figure 2a shows the packing of molecules of **I** in the crystal. The geometric parameters of the HB are given in Table 2.

In the crystal of **II** (Fig. 1b), the ligand L is involved in the coordination to the Cu atom by two oxygen atoms of the carboxyl group. The Cu coordination polyhedron is an extended tetragonal bipyramid (4 + 2) with the equatorial plane accommodating four O atoms of two water molecules and carboxyl groups of two ligands L. Other oxygen atoms of the carboxyl groups of two ligands L occupy the apical positions. The structure of **II** is 2D polymeric (polymerization involves free O atoms of four coordinated carboxyl groups). Figure 2b shows the molecular packing in the crystal of **II**.

In complex **II**, the lengths of the Cu–O(3) and Cu–O(*w*) equatorial bonds are 1.988(3) and 1.965(3) Å, respectively, and the Cu–O(4) axial bond length is 2.435(3) Å. These distances correspond to those in the structure of **I**. The bond angles at the Cu atom in **II** deviate from the ideal octahedral angles by 2°–4°. The CuO(3)C(9) angle is 128.8(1)°.

In the crystal of **II**, an intramolecular HB is present between the H atoms of the O(1*w*) water molecule and the O(4) atom of the carboxyl group. The second H(*w*)

Table 2. Geometric parameters of hydrogen bonds in **I** and **II**

D–H···A	Distance, Å			D–H···A angle, deg	Coordinates of the A atom
	D–H	H···A	D···A		
			I		
N(2)–H(2*A*)···O(2)	0.90	2.14	2.962(16)	152	$x, y, -1 + z$
N(2)–H(2*B*)···O(3)	0.90	2.10	2.973(12)	163	$2 - x, 1 - y, -z$
O(5)–H(5)···O(3)	0.85(4)	2.16(9)	2.517(12)	105(7)	$1 - x, 1 - y, -z$
			II		
O(1*w*)–H(1*wA*)···O(4)	0.84(5)	1.76(5)	2.580(5)	168(4)	$-x + 1/2, y - 1/2, -z$
O(1*w*)–H(1*wB*)···O(2)	0.74(5)	1.97(5)	2.685(5)	165.(4)	$x, -1/2 - y, 1/2 + z$

atom and the exocyclic O(2) atom are involved in the intermolecular hydrogen bonds (Table 2).

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