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Complexes of Acetic Acid α-(*N*-Benzoxazolin-2-one) with Zn(II), Cu(II), and Co(II): Syntheses and Crystal Structures

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Abstract—The results of syntheses and X-ray diffraction analyses of mononuclear complexes $[ML_2(H_2O)_4]$ ($M = Co^{2+}$(**I**), Cu^{2+}(**II**), and Zn^{2+}(**III**)) containing water molecules and anions of acetic acid α-(*N*-benzoxazolin-2-one) ($L = C_9H_6O_4$) are presented. The crystals of complexes **I–III** are isostructural (space group $P2_1/n$, $Z = 2$) and are built of discrete neutral complex molecules. The crystallographic data are as follows: for complex **I**, $a = 6.1470(5)$, $b = 5.3310(3)$, $c = 30.5894(17)$ Å, $\beta = 95.056(6)°$, $V = 998.50(11)$ Å^3; for complex **II**, $a = 5.9661(6)$ Å, $b = 5.1414(4)$ Å, $c = 32.672(2)$ Å, $\beta = 92.395(6)°$, $V = 1001.33(14)$ Å^3; and for complex **III**, $a = 6.1404(3)$ Å, $b = 5.3476(2)$ Å, $c = 30.5865(12)$ Å, $\beta = 94.708(4)°$, $V = 1000.96(7)$ Å^3. The metal atoms (M) of the complexing agents are localized in the crystallographic symmetry centers and have a distorted octahedral environment due to two oxygen atoms of the carboxy groups of two monodentate ligands (L) and four water molecules. The M–O(1*w*)(H_2O) and M–O(2*w*)(H_2O) bond lengths for the indicated complexes are 2.088(3) and 2.118(3), 2.446(3) and 1.971(3), and 2.113(4) and 2.093(3) Å for M = Co^{2+}, Cu^{2+}, and Zn^{2+}, respectively. The crystal structures are formed due to packing of chains built of intermolecular hydrogen bonds O–H···O.

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INTRODUCTION

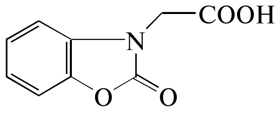
The study of transition metal complexes with molecules of biologically active compounds is one of urgent trends in the modern bioinorganic chemistry. These complexes often have useful biological properties (which are weaker or absent at all in the starting components) and serve as a basis for new drugs.

It is known that a huge part of biologically active substances used in diverse areas of national economy consists of heterocyclic compounds.

Increased interest in benzoxazolin-2-one derivatives is caused by their high biological activity and a wide spectrum of action. Benzoxazolinone and its methoxy derivatives are natural factors of resistance of some cereals to diseases and vermin. Benzoxazolinone and its derivatives possess a growth-regulating activity for plants, which is likely based on the ability of these compounds to prevent auxin binding with membrane receptors [1]. In addition, they can be used as febrifuges [2].

Investigation of the complex formation of new benzoxazolin-2-one derivatives with transition metals is of scientific and practical interest.

In this work, we synthesized complexes of acetic acid α-(*N*-benzoxazolin-2-one) (HL) with cations Co^{2+} (**I**), Cu^{2+} (**II**), Zn^{2+} (**III**) and studied their structures by X-ray diffraction analysis.



(HL)

EXPERIMENTAL

Synthesis of ligand HL. A solution of NaOH (0.6 g) in water (10 mL) was added to benzoxazolin-2-one (2 g, 15 mmol), and the mixture was stirred to complete dissolution. A mixture obtained from chloroacetic acid (1.4 g) and NaOH (1.2 g) in water (12 mL) was added to the obtained solution. After the solutions were mixed together, the reaction mixture was heated for 2.5 h and neutralized with hydrochloric acid. Acetic acid α-(*N*-benzoxazolin-2-one) (HL) was isolated in a yield of 2.44 g (80%).

Synthesis of $[Co(L)_2(H_2O)_4]$ (I). A hot solution of acetic acid α-(*N*-benzoxazolin-2-one) sodium salt (0.46 mmol, 0.1 g) in a water–ethanol (1 : 1 vol/vol) mixture (4 mL) was added to a solution of $CoCl_2$ (0.23 mmol, 0.029 g) in the same mixture (3 mL). The reaction mixture was stored in an ultrasonic bath (30 kHz) for 10 min. The solution was placed in a non-tightly closed weighing bottle. After 2 days, pink platelike crystals precipitated. They were filtered off and recrystallized from ethanol. The yield of **I** was 0.12 g (83%).

Table 1. Main crystallographic data and refinement results for structures **I–III**

Parameter	Value		
	I	**II**	**III**
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	6.1470(5)	5.9661(6)	6.1404(3),
b, Å	5.3310(3)	5.1414(4)	5.3476(2)
c, Å	30.5894(17)	32.672(2)	30.5865(12)
β, deg	95.056(6)	92.395(6)	94.708(4)
V, Å^3	998.50(11)	1001.31(14)	1000.96(7)
Z	2	2	2
ρ_{calcd}, g/cm^3	1.714	1.724	1.731
μ, mm^{-1}	7.416	2.216	2.381
Crystal sizes, mm	0.51 × 0.34 × 0.18	0.52 × 0.38 × 0.2	0.5 × 0.35 × 0.2
Scan θ range, deg	5.8–75.7	5.4–66.9	5.8–66.9
Range h, k, l	$-6 \le h \le 7$, $-6 \le k \le 5$, $-38 \le l \le 37$	$-7 \le h \le 7$, $-6 \le k \le 6$, $-38 \le l \le 38$	$-7 \le h \le 7$, $-6 \le k \le 6$, $-36 \le l \le 36$
Collected reflections	6816	10216	3172
Independent reflections	2046	1776	1772
R_{int}	0.056	0.06	0.017
Reflections with $I > 2\sigma(I)$	1577	1437	1567
Goodness-of-fit (F^2)	1.06	1.12	1.05
R_1, wR_2 ($I > 2\sigma(I)$)	0.0525, 0.1370	0.0462, 0.1469	0.0353, 0.0989
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e/Å^3	–0.35, 0.35	–0.71, 0.39	–0.31, 0.64

Synthesis of [Cu(L)$_2$(H$_2$O)$_4$] (II). A hot solution of acetic acid α-(*N*-benzoxazolin-2-one) sodium salt (0.46 mmol, 0.1 g) in a water–ethanol (1 : 1 vol/vol) mixture (4 mL) was added to a solution of $CuSO_4 \cdot 5H_2O$ (0.23 mmol, 0.057 g) in the same mixture (4 mL). The reaction mixture was stored in an ultrasonic bath (30 kHz) for 15 min. The solution was placed in a nontightly closed weighing bottle. Blue plate-like crystals that precipitated in 2 days were filtered off and recrystallized from ethanol. The yield of **II** was 0.127 g (81%).

The synthesis of complex [Zn(L)$_2$(H$_2$O)$_4$] (**III**) and its X-ray diffraction characteristics were described earlier [3].

X-ray diffraction analyses of I and II. Reflection sets were obtained at 293 K on an Xcalibur R Oxford Diffraction automated diffractometer (CuK_α radiation, $\lambda = 1.54184$ Å, ω scan mode, graphite monochromator). Experimental data were collected using the CrysAlisPro program [4]. An absorption correction was applied by the multi-scan method in the CrysAlisPro program package. The structures were solved by a direct method using the SHELXS-97 program package [5] and refined by full-matrix least squares using the SHELXL-97 program [6]. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were localized from the difference synthesis and refined isotropically. The molecular drawing was plotted using the XP program in the SHELXTL-Plus program package [7]. The crystallographic data and the results of determination of structures **I–III** are given in Table 1.

The coordinates of atoms and other parameters for compounds **I** and **II** were deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 947612 and 947614, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The crystals of complexes **I**, **II**, and **III** are isostructural and built of discrete molecules [M(L)$_2$(H$_2$O)$_4$] (M = Co, Cu, and Zn). The coordination polyhedra of the M atoms are extended tetragonal bipyramids arranged in the crystallographic symmetry centers (Fig. 1). The oxygen atoms of four water molecules are localized in the equatorial planes of the tetragonal bipyramids, and the oxygen atoms of the carboxy groups of two ligands L occupy the apical posi-

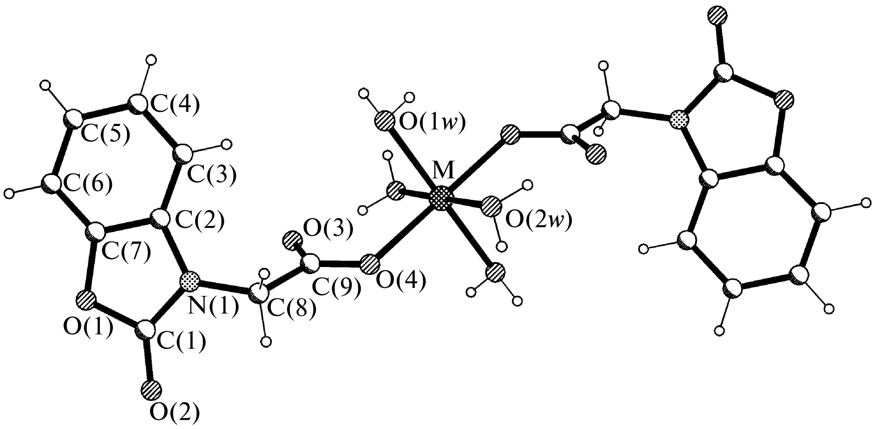


Fig. 1. Molecular structure and the numeration of atoms in complexes $[ML_2(H_2O)_4]$ ($M = Co^{2+}$, Cu^{2+}, and Zn^{2+}).

tions. In complex **I**, the Co–O(1*w*) and Co–O(2*w*) equatorial bond lengths are 2.088(3) and 2.118(3) Å, respectively, and the axial Co–O(4) bond lengths are 2.078(3) Å. These distances correspond to those found earlier in the Zn^{2+} complexes with ligands L. At the same time, the Cu–O(1*w*) equatorial bonds (2.446(3) Å) in **II** are noticeably longer than the corresponding bonds in complexes **I** and **III**.

In all three structures, the bond angles at the M atoms deviate from the ideal octahedral angles by 2.35°–2.75°. The MO(4)C(9) bond angles in complexes **I**, **II**, and **III** are equal in fact (125.5(2)°, 126.6(2)°, and 124.19(14)°, respectively). The dihedral angles between the planes of the carboxy groups and benzoxazole fragment in **I** (63.55°) and **III** (64.09°) somewhat differ from a similar value in complex **II** (65.24°).

The geometric parameters of hydrogen bonds are listed in Table 2 and shown in Fig. 2. The presence of hydrogen bonds O(2*w*)–H(2*wB*)···O(1*w*) in **II** corre-

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

Bond D–H···A	Distance, Å			Angle D–H···A, deg	Coordinates of atom A
	D–H	H···A	D···A		
			I		
O(1*w*)–H(1*wA*)···O(2)	0.85(3)	2.02(4)	2.792(4)	151(4)	1 + *x*, 1 + *y*, *z*
O(1*w*)–H(1*wB*)···O(3)	0.86(2)	1.84(2)	2.692(4)	177(7)	1 + *x*, *y*, *z*
O(2*w*)–H(2*wA*)···O(4)	0.85(3)	1.98(4)	2.792(4)	161(6)	1 – *x*, –1 – *y*, –*z*
O(2*w*)–H(2*wB*)···O(3)	0.85(5)	1.83(5)	2.643(4)	160(4)	1 – *x*, –*y*, –*z*
C(8)–H(8*A*)···O(3)	0.97	2.57	3.407(5)	144	*x*, –1 + *y*, *z*
			II		
O(2*w*)–H(2*wA*)···O(3)	0.85(4)	1.849(2)	2.647(5)	156.6(4)	
O(1*w*)–H(1*wA*)···O(2)	0.85(4)	2.08(4)	2.868(5)	154(5)	3 – *x*, –1 – *y*, 1 – *z*
O(2*w*)–H(2*wB*)···O(1*w*)	0.85(4)	1.96(4)	2.772(5)	159(4)	*x*, 1 + *y*, *z*
O(1*w*)–H(1*wB*)···O(3)	0.86(4)	1.94(3)	2.760(5)	161(5)	3 – *x*, –*y*, 1 – *z*
C(8)–H(8*A*)···O(3)	0.97	2.47	3.325(5)	147	*x*, –1 + *y*, *z*
C(8)–H(8*B*)···O(2)	0.97	2.55	3.484(6)	163	–1 + *x*, *y*, *z*
			III		
O(1*w*)–H(2*wA*)···O(3)	0.85(4)	1.8542)	2.702(3)	174(3)	1 – *x*, –*y*, –*z*
O(1*w*)–H(1*wB*)···O(2)	0.71(4)	2.10(4)	2.792(3)	163(4)	1 – *x*, 1 – *y*, –*z*
O(2*w*)–H(2*wA*)···O(4)	0.86(4)	1.96(4)	2.775(2)	160(3)	2 – *x*, 1 – *y*, –*z*
O(2*w*)–H(2*wB*)···O(3)	0.86(4)	1.88(4)	2.645(3)	146(4)	2 – *x*, –*y*, –*z*
C(8)–H(8*B*)···O(3)	0.97	2.59	3.419(3)	143	*x*, 1 + *y*, *z*

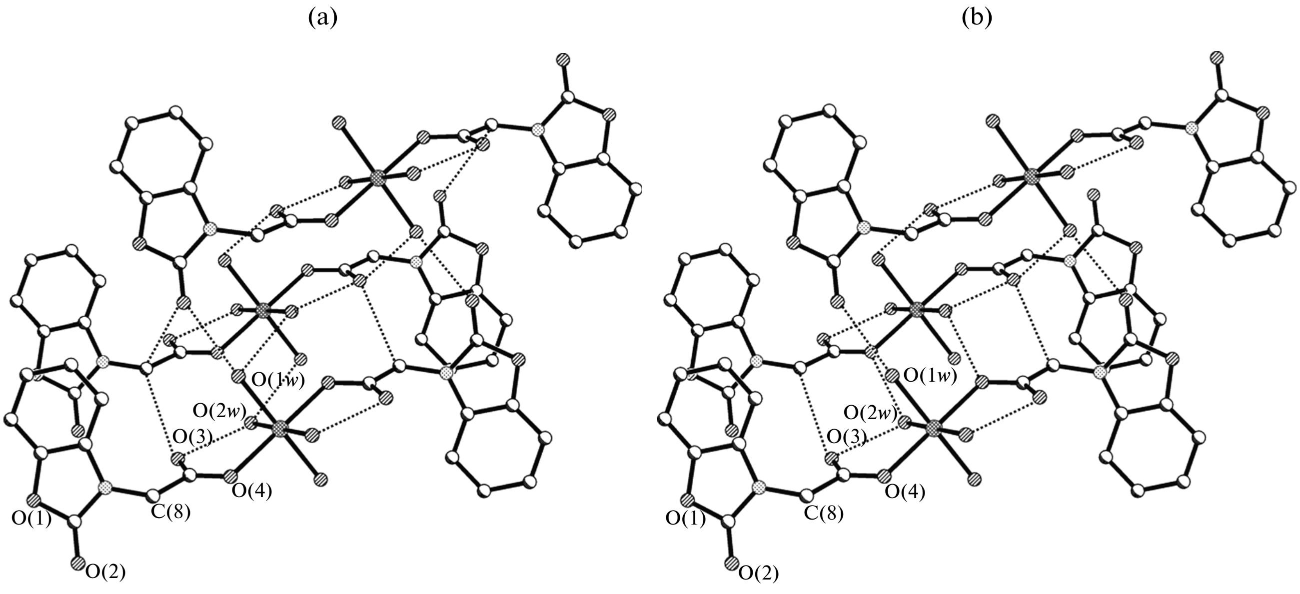


Fig. 2. Chain structures and hydrogen bonds in complexes (a) **I** and **III** and (b) **II**. Hydrogen bonds are shown by dashed lines. Hydrogen atoms are omitted.

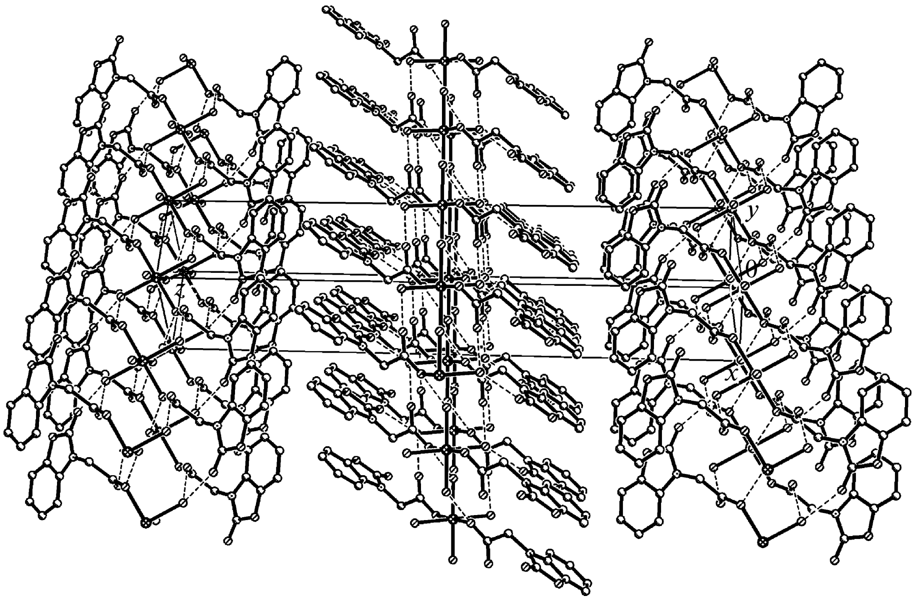


Fig. 3. Structure of the layer in complexes **I**, **II**, and **III**. Hydrogen atoms are omitted.

late with the elongation of the Cu···O(1*w*) equatorial bond and, most likely, is the main reason for the distortion of the coordination polyhedron of the Cu^{2+} atom towards the square polyhedron compared to structures **I** and **III**.

Other hydrogen bonds in the studied crystal structures are similar. The O(2*w*)–H(2*wA*)···O(4) and O(1*w*)–H(1*wB*)···O(2) hydrogen bonds cross-link the molecules bound by the inversion centers into chains extended along the *y* direction, and the O(1*w*)–H(1*wA*)···O(3) hydrogen bonds cross-link the molecules into chains along the *x* direction (Fig. 3). The molecules arranged along the *x* and *y* axes involving the hydrogen atoms of the benzene ring form a three-dimensional lattice of weak hydrogen bonds C(5)–H(5)···π. In all three structures, the intramolecular hydrogen bond O(2*wB*)–H(2*wB*)···O(3) is formed and stabilizes the complex in solution.

Thus, the X-ray diffraction analyses of the structures of the complexes of acetic acid α-(*N*-benzoxazolin-2-one) with the Co^{2+}, Cu^{2+}, and Zn^{2+} cations showed that the synthesized complexes were isostructural. The three-dimensional lattice of hydrogen bonds is formed in all three crystal structures. The hydrogen bonds in complex **II** are somewhat different compared to those in complexes **I** and **III**.

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