ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2014, Vol. 40, No. 10, pp. 718–721. © Pleiades Publishing, Ltd., 2014.
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Heteroligand Zinc(II) and Copper(II) Complexes with Naphthylacetic Acid and Monoethanolamine: Syntheses and Crystal Structures

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Received February 2, 2014

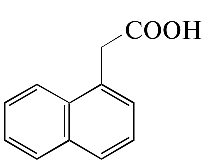
Abstract—New heteroligand Cu(II) and Zn(II) complexes with the α-naphthylacetic acid anion (NAA) and monoethanolamine (MEA), $[M(NAA)_2(MEA)_2]$ ($M = Cu^{2+}$, (**I**), Zn^{2+} (**II**)), are synthesized. The crystal structures of the obtained complexes are determined by X-ray diffraction analysis (CIF files CCDC 984097 (**I**) and 930946 (**II**)). The crystals are monoclinic, for **I**: $a = 18.8140(9)$ Å, $b = 4.82500(14)$ Å, $c = 16.0360(7)$ Å, $\beta = 115.135(6)°$, $V = 1317.87(11)$ Å^3, space group $P2_1/c$, $Z = 2$; for **II**: $a = 32.9760(14)$ Å, $b = 5.0911(3)$ Å, $c = 15.7994(10)$ Å, $\beta = 94.418(5)°$, $V = 2644.6(3)$ Å^3, space group $C2/c$, $Z = 4$. In the structure of complex **I**, the Cu^{2+} ion arranged in the symmetry center is coordinated at the vertices of the distorted octahedron by the oxygen atoms of two NAA molecules (Cu–O(2) 2.019(4) Å) and two MEA molecules. The latter is the bidentate-chelating ligand and coordinates the metal through the O and N atoms to form the five-membered metallocycle (Cu–O(3) 2.457(5), Cu–N(1) 1.986(5) Å). In complex **II**, the Zn atom (on axis 2) is coordinated at the vertices of the distorted tetrahedron by the oxygen atoms of two NAA molecules (Zn–O(2) 1.976(4) Å) and the nitrogen atoms of two MEA molecules (Zn–N 2.034(6) Å). The character of the interaction of coordinated NAA and MEA ligands and methods for packing complexes **I** and **II** are considered on the basis of the structural data.

DOI: 10.1134/S1070328414100017

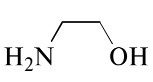
INTRODUCTION

α-Naphthylacetic acid (NAA) is widely used as a regulator of plant growth. Heteroligand complexes of a series of metals with NAA anions were also studied and characterized [1–3]. The study of systems containing a metal, a complexone, and an additional ligand is an important scientific practical problem, because mixed complex formation increases the biological activity of the metal ion [4]. Monoethanolamine (MEA) containing nitrogen and oxygen atoms was chosen as an additional ligand. Attention to these compounds is caused by their ability to change the dentate character depending on the reaction conditions and to form both mononuclear and polynuclear complexes. In particular, the MAA-based complexes are characterized by the high anticancer activity and bactericidal, fungicidal, and antiphytoviral effects.

In this work, heteroligand complexes of the composition $[M(NAA)_2(MEA)_2]$ (M = Cu (**I**), Zn(**II**)) were synthesized for the first time, and their molecular and crystal structures were determined by X-ray diffraction analysis.



(NAA)



(MEA)

EXPERIMENTAL

Synthesis of complex I. A hot solution of NAA sodium salt (0.5 mmol, 0.104 g) in 4 mL of a water–ethanol mixture (1 : 1 vol/vol) was added to a solution of $CuSO_4 \cdot 5H_2O$ (0.25 mmol, 0.062 g) in 4 mL of the same mixture. MEA (0.5 mmol) was added dropwise to the obtained mixture with continuous stirring. The reaction mixture was kept in an ultrasonic bath (30 kHz) for 10 min. The obtained solution was placed in a not tightly closed box at 25°C. Prismatic crystals were formed in 6 days, and a single crystal for X-ray diffraction analysis was selected.

Synthesis of complex II. A hot solution of NAA sodium salt (1 mmol, 0.208 g) in 6 mL of a water–ethanol (1 : 1 vol/vol) mixture was added to a solution of $ZnCl_2$ (0.5 mmol, 0.068 g) in 4 mL of the same mixture. MEA (1 mmol) was added dropwise to the obtained mixture with continuous stirring. The reaction mixture was kept in an ultrasonic bath (30 kHz) for 15 min. Then the solution was placed at 25°C in a not tightly closed box. Prismatic crystals were formed in 7 days, and a single crystal for X-ray diffraction analysis was selected.

X-Ray diffraction analyses of complexes I and II. Sets of reflections 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 [5]. An absorption correction was applied by the multi-scan method in the CrysAlisPro program package. The structures were solved by a direct method (SHELXS-97) [6] and refined by full-matrix least squares (SHELXL-97) [7]. All non-hydrogen atoms were localized in difference electron density syntheses and refined for F_{hkl}^2 in the anisotropic approximation. Positions of all hydrogen atoms were calculated geometrically and included into the refinement in the isotropic approximation. The molecular graphics was constructed using the XP program in the SHELXTL-Plus program package [8]. The crystallographic data and refinement parameters for structures **I** and **II** are given in Table 1.

The atomic coordinates and other parameters of the compounds were deposited with the Cambridge Crystallographic Data Centre (CCDC 984097 (**I**), 930946 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 1. Main crystallographic data and the refinement results for structures **I** and **II**

Parameter	Value	
	I	**II**
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a, Å	18.8140(9)	32.9760(14)
b, Å	4.82500(14)	5.0911(3)
c, Å	16.0360(7)	15.7994(10)
β, deg	115.135(6)	94.418(5)
V, Å^3	1317.87(11)	2644.6(3)
Z	2	4
ρ_{calcd}, g/cm^3	1.401	1.401
μ, mm^{-1}	1.545	1.663
Crystal sizes, mm	0.41 × 0.25 × 0.18	0.52 × 0.38 × 0.2
2θ range (min, max), deg	5.2–75.9	5.4–76.0
Range of indices h, k, l	$-21 < h < 23$ $-6 < k < 6$ $-20 < l < 13$	$-40 < h < 24$ $-6 < k < 6$ $-19 < l < 19$
Collected reflections	8920	10283
Independent reflections	2692	2736
R_{int}	0.052	0.049
Reflections with $I > 2\sigma(I)$	2018	1699
Number of refined parameters	171	178
Goodness-of-fit (F^2)	1.08	1.04
R_1, wR_2 ($I > 2\sigma(I)$)	0.0797, 0.2908	0.0655, 0.2174
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e/Å^3	–0.36, 0.58	–0.31, 0.56

RESULTS AND DISCUSSION

Heteroligand complexes of Cu(II) and Zn(II) containing NAA and MEA anions were synthesized under specified conditions. The crystal structures of complexes **I** and **II** are based on discrete mononuclear molecules (Fig. 1). In the presence of the same amounts of NAA and MEA, cations Cu(II) and Zn(II) form complexes with the coordination numbers 6 and 4, respectively. In complex **I** MEA is coordinated through the bidentate mode, and its coordination in complex **II** is monodentate.

The Cu atom in complex **I** is in the symmetry center. Its coordination polyhedron is a slightly distorted octahedron N_2O_4 formed by two oxygen atoms of the carboxy groups of NAA in the axial positions and by two oxygen atoms and two nitrogen atoms of two MEA molecules in the equatorial positions (Fig. 1a). The Cu–O(NAA), Cu–N, and Cu–M(NAA) bond lengths are 2.457(5), 1.986(5), and 2.019(4) Å, respectively. In complex **I**, the O,N-donor amino alcohol acts as a bidentate cyclic ligand and forms five-membered metallocycles. The latter have an envelope conformation, and the C(13) (C(13*A*)) atoms shift by 0.628 Å from the planes of other four (coplanar within 0.039 Å) atoms. The intracyclic OCuN angles are 78.38(18)°. The angular distortions of the metal polyhedra are due to the presence of five-membered metallocycles. The square structure of the central node CuN_2O_2 is similar to that found in the earlier studied compounds [9]. The difference in C–O distances (0.063 Å) is due to the coordination of the carboxy groups by only one oxygen atom (O(2)). The dihedral angle between the planes of the carboxy group and naphthyl fragment is 87.61°.

The strong intermolecular hydrogen bond O(3)–H(3)···O(1) (O···O 2.583(8) Å) is formed in complex **I** between the O(1) atoms of the carboxy group and the hydroxy groups of MEA. The six-membered pseudoheterocycles with the graph-set $S(6)$ is formed in the structure due to this hydrogen bond. In crystals both oxygen atoms of the carboxy groups are involved in the formation of the intermolecular hydrogen bond with the coordinated oxygen atom N(1)–H(1*B*)···O(2) ($-x$, $1 - y$, $1 - z$) (H···O 2.41 Å) and the free O(1) atom C(11)–H(11*B*)···O(1) (x, $1 + y$, z) (H···O 2.48 Å). The fragment of the crystal structure with the formation of centrosymmetrical motifs along the direction [001] is shown in Fig. 1b. The linear and angular parameters characterizing hydrogen bonds in structures **I** and **II** are given in Table 2.

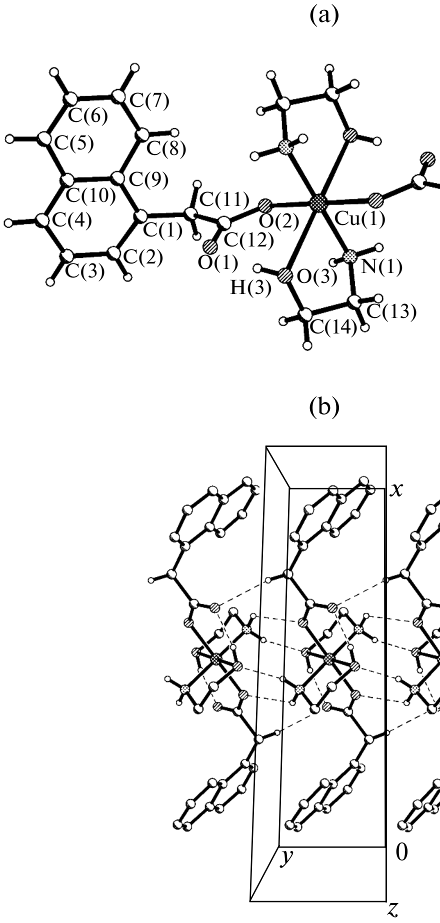


Fig. 1. Structure of compound **I**: (a) structure of the complex and (b) crystal packing. Hydrogen atoms, except for those involved in hydrogen bonding, are omitted for clarity. Hydrogen bonds are shown by dash.

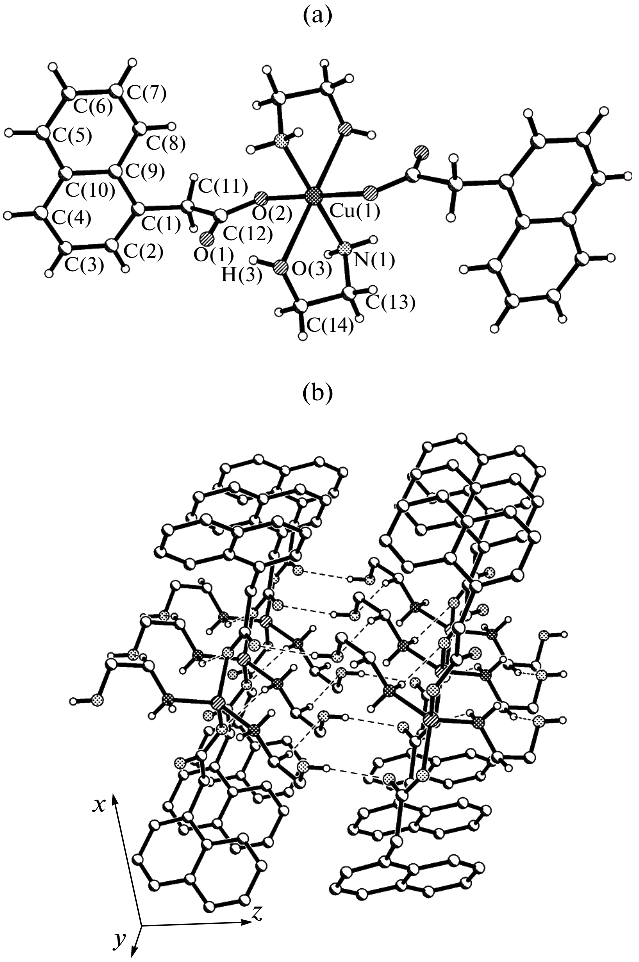


Fig. 2. Structure of compound **II**: (a) neutral complex and (b) crystal packing. Hydrogen atoms, except for those involved in hydrogen bonding, are omitted for clarity. Hydrogen bonds are shown by dash.

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

D–H···A	Distance, Å			Angle D–H···A, deg	Coordinates of atom A
	D–H	H···A	D···A		
			I		
N(1)–H(1*A*)···O(3)	0.90	2.1	2.977(6)	164	$x, -1 + y, z$
N(1)–H(1*B*)···O(2)	0.90	2.41	2.991(7)	122	$1 - x, -1 - y, -z$
O(3)–H(3*A*)···O(1)	0.82	1.78	2.583(8)	166	x, y, z
C(11)–H(11*B*)···O(1)	0.97	2.47	3.340(8)	149	$x, -1 + y, z$
			II		
N(1)–H(1*B*)···O(2)	0.90	2.37	3.167(7)	148	$-x, 1 + y, 1/2 - z$
O(3)'–H(3)'···O(1)	0.82	1.80	2.580(13)	159	$-x, 2 - y, 1 - z$
O(3)–H(3*A*)···O(1)	0.82	2.14	2.942(14)	164	$-x, 2 - y, 1 - z$
C(13)–H(13*A*)···O(3)	0.97	2.53	3.469(17)	163	$x, -1 + y, z$

Table 3. Selected bond lengths (Å) and bond angles (deg) in structures **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
	I		
Cu(1)–O(2)	2.019(4)	O(2)–C(12)	1.284(7)
Cu(1)–O(3)	2.457(5)	O(3)–C(14)	1.429(10)
Cu(1)–N(1)	1.986(5)	N(1)–C(13)	1.488(10)
O(1)–C(12)	1.222(7)		
	II		
Zn(1)–O(2)	1.976(4)	O(2)–C(12)	1.231(6)
Zn(1)–N(1)	2.034(6)	O(3)–C(14)	1.403(17)
O(1)–C(12)	1.239(6)	N(1)–C(13)	1.358(8)

Angle	ω, deg	Angle	ω, deg
	I		
O(2)Cu(1)O(3)	91.19(16)	O(1)C(12)O(2)	125.6(6)
O(2)Cu(1)N(1)	89.90(18)	O(1)C(12)C(11)	119.3(5)
O(3)Cu(1)N(1)	78.38(18)	O(2)C(12)C(11)	115.1(5)
Cu(1)O(2)C(12)	125.3(4)	O(3)C(14)C(13)	111.7(6)
Cu(1)O(3)C(14)	102.7(4)	N(1)C(13)C(14)	109.4(7)
Cu(1)N(1)C(13)	112.5(4)		
	II		
O(2)Zn(1)O(3)	91.19(16)	O(1)C(12)O(2)	119.3(4)
O(2)Zn(1)N(1)	89.90(18)	O(1)C(12)C(11)	120.9(4)
O(3)Zn(1)N(1)	78.38(18)	O(2)C(12)C(11)	119.6(4)
Zn(1)O(2)C(12)	125.3(4)	O(3)C(14)C(13)	115.7(6)
Zn(1)O(3)C(14)	102.7(4)	N(1)C(13)C(14)	120.8(6)
Zn(1)N(1)C(13)	112.5(4)		

The structure of compound **II** is formed of isolated complexes. The coordination mode of the Zn atom (on axis 2) is a distorted tetrahedron formed by two oxygen atoms of the carboxy groups of NAA and two nitrogen atoms of MEA (Fig. 2a). The NAA and MEA anions are monodentate ligands. The Zn–N(MEA) and Zn–M(NAA) bond lengths are 2.033(6) and 1.976(4) Å, respectively. The linear and angular parameters for structures **I** and **II** are presented in Table 3. The fragment of the naphthyl core in NAA of structure **II** is nearly planar (the maximum deviation is 0.025 Å), and the carboxy group is turned with respect to the core by 79.64°. The Zn atom in the heteroligand complex $[Zn(NAA)_2(4,4'\text{-}Bipy)]_n$ involving NAA has the coordination number 5. In the mono- and bidentate-coordinated NAA molecules, the carboxy group is turned with respect to the naphthyl fragment by 77.34° and 88.46°, respectively [10]. In the free NAA molecule, this angle is 81.31° [11]. In MEA of structure **II**, the hydroxy group is disordered over two equivalent positions.

Hydrogen bonds of the NH···O and OH···O types are formed in structure **II** by the coordinated NAA and MEA molecules. One of them, N(1)–H(1*A*)···O(1), is intramolecular, and two others, O(3)'–H(3)'···O(1) and O(3)–H(3*A*)···O(1), are intermolecular forming a polymer chain along the *z* axis (Fig. 2b).

ACKNOWLEDGMENTS

This work was supported by the Academy of Sciences of Uzbekistan, project no. F7-TO48.

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Translated by E. Yablonskaya