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Original Russian Text © M.I. Ul'yanova, S.A. Baskakova, T.V. Aksenova, P.A. Slepukhin, A.V. Pestov, 2015, published in Koordinatsionnaya Khimiya, 2015, Vol. 41, No. 4, pp. 213–219.

The Second Example for a Cubane-Like Copper(II) Complex in a Series of *N*-Hydroxyalkyl β-Alanine Derivatives

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Abstract—A new tetranuclear cubane-like copper(II) complex $[Cu_4(HL^1)_4]$ based on *N*-(1,1-dihydroxymethyl)ethyl-βalanine (H_3L^1) is synthesized. Its structure is studied by X-ray diffraction analysis (CIF file CCDC 1020735). In the crystal structure of the complex, the copper atoms are joined into tetrahedra with the distances Cu···Cu 3.139–3.456 Å supplemented to cubanes by the μ_3-bridging oxygen atoms of the hydroxymethyl groups. The coordination environment of each metal center is a distorted octahedron. The $(HL^1)^{2-}$ ligand is doubly protonated and performs the hexadentate chelate-(μ_3-bridging) function to form the alkoxocarboxylate chelate of copper(II).

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INTRODUCTION

The synthesis of polynuclear complexes is urgent due to the modern necessity to prepare from them units of molecular electronics [1–4], catalysts [5–8], and biomimetic enzymatic centers [9–12]. The methodology for the targeted synthesis of these coordination structures is very valuable, because makes it possible to predict the dimensionality and structure of the polynuclear framework from an analysis of the structure and properties of the ligand. The first attempts to accomplish this approach in a series of *N*-derivatives of β-alanine allow one to supplement the classical Chugaev rule: six-membered chelates are less stable than five-membered cycles but are more favoring the formation of polynuclear coordination structures [13, 14]. In particular, in a series of amino alcohols, the formation of the polynuclear copper(II) complexes is provided by ligands with a dentatity of three or four, including those with OH dentatity, or with equivalent higher steric hindrances [13, 14].

This work continues the systematic studies on the purposeful synthesis of polynuclear copper(II) complexes by the predictive design of the organic ligand structure.

EXPERIMENTAL

Synthesis of *N*-(1,1-dihydroxymethyl)ethyl-β-alanine (H_3L^1). A mixture of 2-methyl-2-aminopropanediol-1,3 (8.4 g, 0.08 mol), acrylic acid (5.48 mL, 0.08 mol), water (24 mL), and hydroquinone (5 mg) was refluxed for 12 h with a reflux condenser. Then water was distilled off, and methanol (20 mL) was added. The crystals formed were filtered off and dried at room temperature to a constant weight. The yield was 50% (mp = 161–163°C).

For $C_7H_{15}NO_4$			
anal. calcd., %:	C, 47.45;	H, 8.47;	N, 7.90.
Found, %:	C, 47.36;	H, 8.51;	N, 7.77.

IR, ν, cm^{-1}: 3377 ν(NH), 3231 ν(OH), 1597 ν_{as}(C=O), 1426 ν_s(C=O).

^1H NMR, δ, ppm: 1.28 s (CH_3), 2.59 t (CH_2COO), 3.22 t (CH_2NH), 3.69 m (CH_2COH).

Synthesis of tetrakis(*N*-(1-hydroxymethyl-1-hydroxylatomethyl)ethyl-β-alaninatocopper(II)) $[Cu_4(HL^1)_4]$ (I). A mixture of acid **I** (1.06 g, 6 mmol), $CuCO_3 \cdot Cu(OH)_2$ (1.6 g, 7.2 mmol), and water (20 mL) was stirred at room temperature for 48 h. A precipitate was filtered off, and crystals precipitated from the filtrate upon slow evaporation.

For $C_{28}H_{52}N_4O_{16}Cu_4 \cdot 2H_2O$				
anal. calcd., %:	C, 33.87;	H, 5.64;	N, 5.64;	Cu, 25.80.
Found, %:	C, 33.24;	H, 6.06;	N, 5.34;	Cu, 25.58.

IR, ν, cm^{-1}: 3255 ν(OH), 1563 ν_{as}(C=O), 1457 ν_s(C=O).

Analyses to C, H, and N were carried out on an automated analyzer (PerkinElmer), and copper was determined by atomic emission spectroscopy on an Optima 4300 DV spectrometer. IR reflectance spectra were recorded on a Spectrum-One spectrometer (PerkinElmer).

Table 1. Crystallographic data and the experimental and refinement parameters for the structure of complex **I**

Parameter	Value
FW	1099.02
Crystal system	Orthorhombic
Space group	*Pbca*
Z	8
a, Å	16.0285(8)
b, Å	15.2037(5)
c, Å	36.1110(18)
V, Å^3	8800.0(7)
ρ_{calcd}, g/cm^3	1.659
μ, mm^{-1}	1.995
F(000)	4576
Crystal sizes, mm	0.21 × 0.15 × 0.06
Data collection θ range	$2.68 < \theta < 26.38$
Ranges of reflection indices	$-10 \le h \le 20$, $-9 \le k \le 19$, $-45 \le l \le 44$
Measured reflection	40013
Independent reflections	8963
Reflections with $I \ge 2\sigma(I)$	4822
Number of refined parameters	541
R_1, wR_2 ($I > 2\sigma(I)$)	0.0383, 0.0777
R_1, wR_2 (all reflections)	0.0829, 0.0814
GOOF (all reflections)	1.001
Residual electron density (max/min), e/Å^3	1.221/–0.548

X-ray diffraction analysis. The experimental data for complex **I** were obtained on an Xcalibur 3 automated diffractometer (CCD detector, MoK_α, graphite monochromator, T = 135(2) K). The crystallographic data and experimental and refinement characteristics for structure **I** are presented in Table 1. An absorption correction was applied analytically by the polyhedral crystal model [15]. The structure was solved and refined using the SHELX program package [16]. All nonhydrogen atoms were determined by a direct method and refined in the anisotropic approximation. Hydrogen atoms were placed in the geometrically calculated positions and included into refinement in the riding model with dependent thermal parameters. The coor-

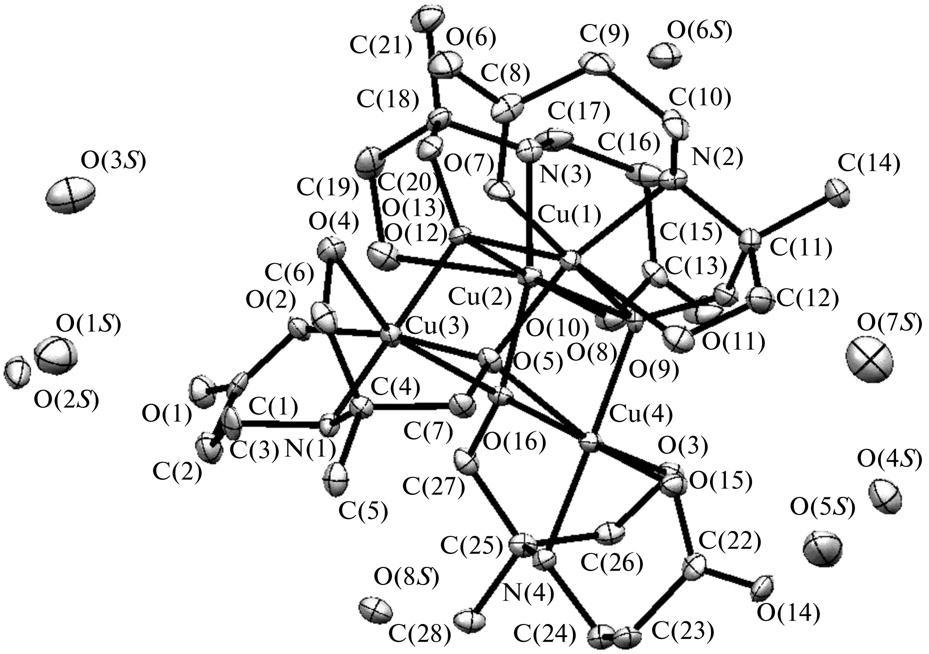
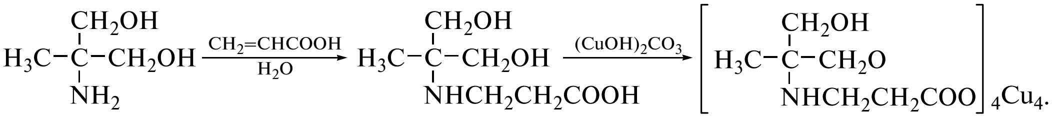


Fig. 1. Molecular structure of complex **I** in 50% probability thermal ellipsoids (hydrogen atoms are omitted).

dinates of atoms and the values of thermal parameters were deposited with the Cambridge Crystallographic Data Centre (CCDC 1020735, deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

Molecule H_3L^1 was obtained according to the earlier developed approach to the synthesis of *N*-derivatives of β-alanine [13, 17, 18] by the direct addition of the amine to acrylic acid in water



$$H_3C-\underset{NH_2}{\overset{CH_2OH}{C}}-CH_2OH \xrightarrow[H_2O]{CH_2=CHCOOH} H_3C-\underset{NHCH_2CH_2COOH}{\overset{CH_2OH}{C}}-CH_2OH \xrightarrow{(CuOH)_2CO_3} \left[H_3C-\underset{NHCH_2CH_2COO}{\overset{CH_2OH}{C}}-CH_2O\right]_4Cu_4.$$

(H_3L^1) **(I)**

Complex **I** with the composition $[Cu_4(HL^1)_4]$ was synthesized by the reaction of basic copper(II) carbonate and compound H_2L.

Table 2. Selected bond lengths (Å) and bond angles (deg) in the coordination node of complex **I**

Bond	*d*, Å	Angle	ω, deg
Cu(1)–O(5)	1.940(3)	O(5)Cu(1)O(7)	93.64(11)
Cu(1)–O(7)	1.954(3)	O(5)Cu(1)O(8)	88.00(11)
Cu(1)–O(8)	1.954(3)	O(7)Cu(1)O(8)	172.67(12)
Cu(1)–O(9)	2.506(3)	O(5)Cu(1)N(2)	166.66(12)
C(1)–N(2)	1.978(3)	O(7)Cu(1)N(2)	95.24(12)
Cu(1)–O(13)	2.524(3)	O(8)Cu(1)N(2)	84.45(12)

In crystal **I**, the copper atoms are joined into tetrahedra (Cu···Cu 3.139–3.456 Å) supplemented to cubanes by the μ_3-bridging oxygen atoms of the hydroxylate groups of ligands $(HL^1)^{2-}$ (Fig. 1). The coordination environment of each metal center is a distorted octahedron (Fig. 2), whose equatorial plane is formed by the nitrogen atom of the amino group and the oxygen atoms of the carboxylate and hydroxylate groups and the bridging hydroxylate group of the adjacent ligand. The oxygen atoms of the hydroxyl group and the bridging hydroxylate group of the third ligand lie on the axial axis. The main characteristics of one of the coordination nodes are given in Table 2. The minimum and maximum values of the corresponding bond lengths in one molecule of complex **I** are listed in Table 3.

Thus, each organic ligand $(HL^1)^{2-}$ is tetradentate with respect to the "intrinsic" copper atom (Fig. 2) and forms three equatorial bonds and one axial bond.

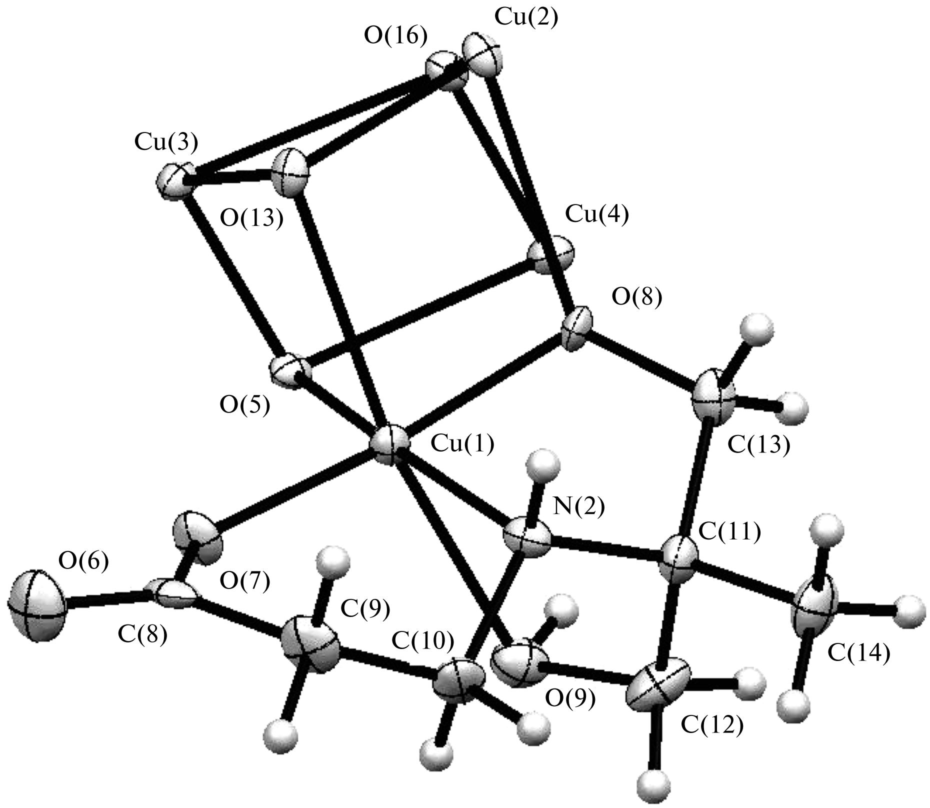
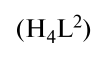


Fig. 2. Coordination environment of the Cu atom in complex **I** in 50% probability thermal ellipsoids.

Two other vertices of the coordination environment of the metal center are occupied by the O atoms of the hydroxylate groups of ligands $(HL^1)^{2-}$ that coordinate two other copper atoms. As a result, ligand $(HL^1)^{2-}$ performs the hexadentate chelate-(μ_3-bridging) function and forms four chelates: two five-membered CuNCCO chelates (with the hydroxyl and hydroxylate groups) and two six-membered chelates: one CuOCCCO chelate common with the five-membered cycle for the hydroxyl group and the second CuNCCCO cycle formed by the 2-carboxyethyl group.

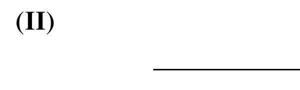
The ligands in molecules $[Cu_4(HL^1)_4]$ are additionally joined by intramolecular hydrogen bonds of two types. The first type is O–H···O and takes place between the hydroxyl group and the oxygen atom of the carboxylate group of the adjacent ligand. For the shortest bond, the H···O distance is 1.72 Å (O–H 1.01 Å, angle O–H···O 158°). The second type of intramolecular hydrogen bonds is N–H···O···H–N and is formed between the amino groups of the adjacent ligands through the water molecule. For the shortest of them, the H···O distance is 2.07 Å (N–H 0.91 Å, angle N–H···O 178°). In addition, crystal **I** includes a branched network of intermolecular hydrogen bonds due to the interactions between the oxygen atoms of the molecules of the complex and six solvate water molecules.

The closest analog of complex **I** is the coordination compound based on tris(hydroxymethyl)-β-alanine (H_4L^2), complex $[Cu_4(H_2L^2)_4]$ (**II**) [17]



$$\mathrm{HOCH_2{-}\overset{\displaystyle CH_2OH}{\underset{\displaystyle NHCH_2CH_2COOH}{C}}{-}CH_2OH}$$

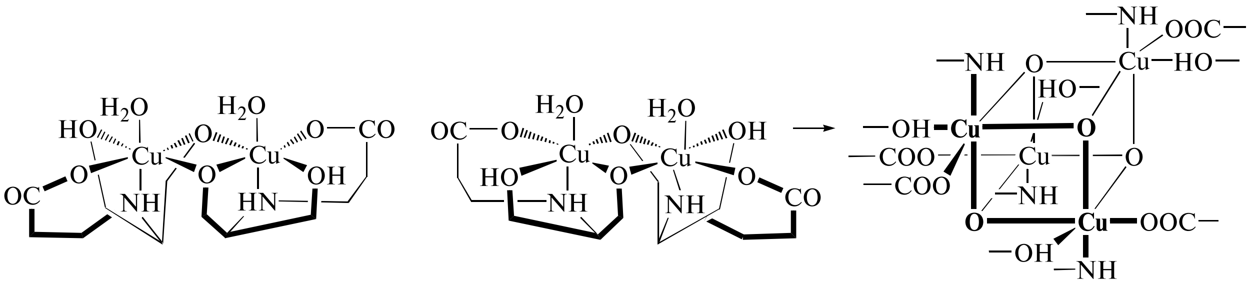
(H_4L^2)



$$\left[\mathrm{HOCH_2{-}\overset{\displaystyle CH_2OH}{\underset{\displaystyle NHCH_2CH_2COO}{C}}{-}CH_2O}\right]_4\mathrm{Cu_4}.$$

(**II**)

The absence of a hydroxyl group in ligand $(HL^1)^{2-}$ that was not involved in coordination in complex **II** results in changes in neither the structure of the coordination spheres of the metal centers, nor the structure of the whole complex. The bond lengths and interatomic distances are almost the same. Complex **I**, like complex **II**, crystallizes as a maximally symmetric cluster *cis,cis,cis,cis-P,P,M,M* of eighteen possible spatial isomers [17]



cis,cis-M,M *cis,cis-P,P* *cis,cis,cis,cis-P,P,M,M*

The basic differences in complexes **I** and **II** caused by the absence of the hydroxyl group in ligand $(HL^1)^{2-}$ concern the smaller (nearly twofold) number of solvate water molecules and, as a consequence, other values of crystallographic parameters (and different crystal systems). The appearance of the hydroxyl group in ligand $(H_2L^2)^{2-}$ compared to ligand $(HL^1)^{2-}$ decreases the symmetry from orthorhombic in crystal **I** to triclinic in crystal **II**.

An analysis of the known cubane-like tetranuclear copper(II) complexes shows that among all ligands all 2-aminoethanol derivatives favor the formation of the structures in which the oxygen atom of the ligand performs the μ_3-bridging function [17, 19–30]. Single examples of 3-aminopropanol-1 [31] and 2-aminoethanethiol [32] derivatives are also known. In other cases, the μ_3-bridging oxygen atom is not included in the chelate cycle [33–36].

Table 3. Minimum and maximum bond lengths (Å) in the coordination nodes of one molecule of complex **I**

Bond	*d*, Å
Cu–O(CH_2O)	1.936(3)–1.971(3)
Cu–O(COO)	1.942(3)–1.954(3)
Cu–N	1.978(3)–2.002(3)
Cu–O (axial)	2.524(3)–2.600(3)
Cu(1)–O(CH_2OH)	2.506(3)–2.557(3)

A comparative analysis of the cubane-like tetranuclear copper(II) complexes in a series of 2-aminoethanol derivatives shows (Table 4) that an increase in the dentatity of the latter by the introduction of donor functional groups (Brönsted acids) increases the coordinating ability of both functional groups of the amino alcohol. This favors the formation of cubane-like tetranuclear copper structures. Steric hindrances of the amino group in 2-aminoethanol appear similarly. The larger the size of the ligand molecule, the longer the distance between the metal centers.

Thus, this study confirms the earlier formulated regularity [13, 14] that an increase in the dentatity and steric hindrances of the amino group in the series of the *N*-hydroxyalkyl β-alanine derivatives favors the formation of oligonuclear coordination compounds. As a result, *N*-derivatives of 2-aminoethanol and β-alanine are urgent and potentially useful due to their advantages: a simple chemical structure of these compounds and the possibility of using simple methods of organic synthesis for their preparation. This provides commercial availability of the compounds and a possibility of the simple directed variation of the ligand structure for the synthesis of necessary complicated coordination compounds.

ACKNOWLEDGMENTS

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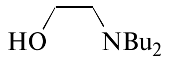
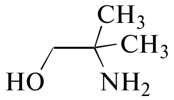
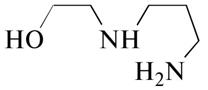
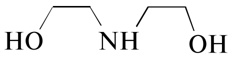
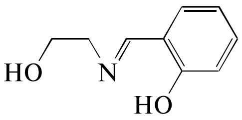
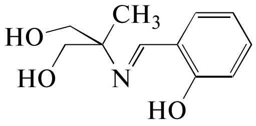
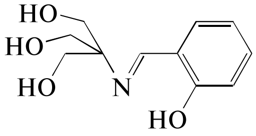
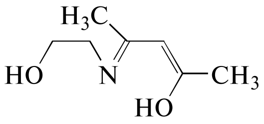
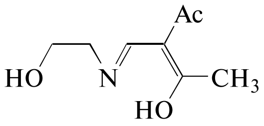
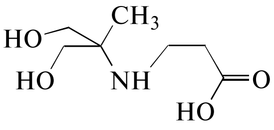
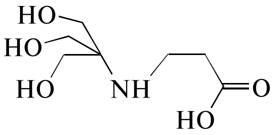
Table 4. Characterization of the cubane-like tetranuclear copper(II) complexes in the series of 2-aminoethanol derivatives

Formula of ligand	Bond length, Å*		Distance Cu···Cu, Å*	Literature
	$Cu{-}O_{alkoxyl}$	Cu–N		
	1.935 1.949	2.058 2.071	3.135 3.478	[19]
	1.969	1.983	3.036 3.302	[20]
	1.937 1.965	2.012 2.029	3.222 3.442	[21]
	1.943 1.947	2.022 2.032	3.213 3.340	[22]
	1.960 1.972	1.925 1.945	3.112 3.346	[23]
	1.912 1.960	1.921 1.948	3.144 3.522	[24]
	1.928 1.956	1.925 1.935	3.090 3.470	[23]
	1.949 1.983	1.916 1.941	3.065 3.311	[25]
	1.956 1.977	1.901 1.910	3.100 3.344	[26]
	1.936 2.002	1.978 1.954	3.139 3.456	This work
	1.934 1.952	1.987 1.997	3.193 3.458	[17]

* The minimum and maximum values are presented.

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