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Heteroligand Copper(II) Complexes with Hydroxyethyleneiminodiacetic Acid and Bidentate Nitrogen-Containing Ligands: Structures and Properties

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Abstract—Procedures were proposed for the synthesis of the heteroligand copper(II) complexes with N-(2-hydroxyethyl)iminodiacetic acid (H_2Heida) and 2-aminoethanol and ethylenediamine ligands. The optimal parameters of solutions for the isolation of ternary complexes were found. Heteroligand complexes Cu(Heida)En · $3H_2O$ (**I**) and Cu(Heida)Mea (**II**) (En is ethylenediamine, and Mea is 2-aminoethanol) were examined by X-ray diffraction analysis. The thermal properties of complexes **I** and **II** and their thermodynamic stability in aqueous solutions were studied.

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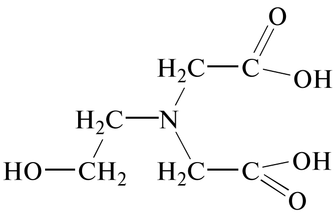
INTRODUCTION

Aminopolycarboxylic acids of medium dentate mode are of significant practical interest along with theoretical significance, since they are relatively cheap and efficient chelating agents that can be used for the synthesis of biologically active Cu, Zn, Mn, and Fe complexes. The latter deliver necessary microelements for plants [1]. One of the promising complexones for the formation of biologically active compounds is N-(2-hydroxyethyl)iminodiacetic acid (H_2Heida), being an organic ligand that can be classified as a complexone with a medium (3–4) dentate mode [2].



The participation of the hydroxy group in the coordination by the cation remained disputable for a long time. Systematic X-ray diffraction studies showed that the character of the cation and the metal to ligand ratio can change, indeed, the coordination mode. It was found for Cu(Heida) · $2H_2O$ [3] that the 3*d* cation coordinates the hydroxyethyl group CH_2CH_2OH, nitrogen atom, water molecule, and two oxygen atoms of the carboxy group of its Heida molecule. The coordination is supplemented by the carbonyl oxygen atom of one of the carboxy groups of the adjacent similar fragment. Chains $[M(H_2O)Heida]_\infty$ are formed in the solid phase due to the bidentate-bridging function of the carboxy group. The hydroxyethyl group can be replaced by the monodentate ligands and remained uncoordinated in the dicomplexes [4].

Polydentate ligands can also form heteroligand copper(II) complexes with Heida. So, the copper complex with Heida and bipyridine was studied and characterized by X-ray diffraction analysis. In this complex, the complexone molecule performs the tetradentate function, exhibiting the noticeable coordination flexibility, and the bipyridine molecule supplements the coordination mode to octet [5]. The formation of the heteroligand copper(II) complexes with benz- and ethylimidazoles was also characterized [6]. In these structures, the Heida molecule is also tetradentate and imidazole manifests itself as a monodentate ligand.

In the course of studying the formation and properties of heteroligand copper complexes of medium dentate mode, we synthesized and examined by X-ray diffraction analysis the heteroligand copper(II) complexes with Heida and potentially bidentate nitrogen-containing ligands, namely, ethylenediamine and 2-aminoethanol. The structures of the formed complexes were determined in order to reveal the structural functions of the complexone and bidentate ligand during heteroligand complex formation.

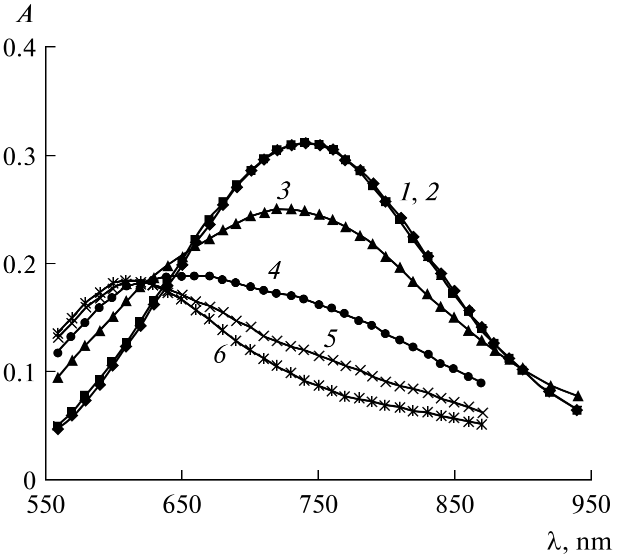


Fig. 1. Absorption spectra of the Cu^{2+}–Heida–En system at different values of pH: (*1*) 3.02 (*2*) 4.99, (*3*) 5.97, (*4*) 6.50, (*5*) 6.96, and (*6*) 8.02; $c_{Cu^{2+}} = 0.005$, $C_{Na_2Heida} = 0.005$, and $c_{EnSO_4} = 0.005$ mol/L.

EXPERIMENTAL

We used H_2Heida synthesized according to a known procedure [7]. Crystalline copper hydroxide was precipitated from an ammoniate solution, and the starting reagents were analytical grade.

Synthesis of Cu(Heida)(En) (I). Solid H_2Heida (5.1 g, 0.029 mol) was added to a suspension of crystalline copper hydroxide $Cu(OH)_2$ (2.8 g, 0.029 mol) in water (50 mL). The reaction mixture was stirred and left to stand for 30 min until copper hydroxide dissolved completely. Ethylenediamine ($\omega = 92\%$, $\rho = 0.915$ g/mL) (2.1 mL, 0.03 mol) was added to the obtained solution to pH 8.6. To isolate the complex, the solution was evaporated to 1/2 volume at 60°C and the complex was precipitated with ethanol (40 mL). Fine bright blue needle-like crystals with metallic luster that formed were filtered off on a paper filter, washed with ethanol, and dried in a drying box at room temperature to a constant weight.

Synthesis of Cu(Heida)(Mea) (II). Solid H_2Heida (9.1 g, 0.051 mol) was added to a suspension of crystalline copper hydroxide $Cu(OH)_2$ (5 g, 0.05 mol) in water (60 mL), and the reaction mixture was stirred to the complete dissolution of copper hydroxide. 2-Aminoethanol (3.1 g, 0.05 mol) was added to the obtained solution. To isolate the complex, the solution (pH 8.0) was evaporated by 1/3 volume on heating and kept at room temperature for 32 h. The obtained bright blue crystalline precipitate was filtered off, washed with distilled water, squashed on a paper filter, and dried in air at room temperature to a constant weight.

The color of a solution of the complexonate changed upon the addition of ethylenediamine to solutions of the complex. In a series of experiments with solutions simultaneously containing copper ions, the complexone, and the second ligand (ethylenediamine), a change in the position of the absorption maximum of the solutions was observed at different pH, which can correspond to the incorporation of the ligand into the coordination sphere of the copper(II) ion (Fig. 1). Based on these data, we chose the pH of the concentrated solutions to isolate the formed heteroligand complex **I**.

The values of pH were controlled with a pH-150MA ionometer with an ESK10601/7 combined electrode.

The IR spectra of the complexes were recorded on a Specord 75IR spectrophotometer in a range of 400–4000 cm^{-1} (KBr pellets).

Thermal analysis was conducted on a Termoskan-2 instrument (OOO Analitpribor, St. Petersburg, Russia) using a ceramic crucible, weighed samples of 0.015 g each, and a heating rate of the sample of 10 deg/min.

X-ray analyses of complexes **I** and **II** were carried out on an Xcalibur3 automated single-crystal diffractometer (Oxford Diffraction Ltd.) ($\lambda(MoK_\alpha)$ radiation, graphite monochromator, Sapphire-3 CCD detector). The structures were solved and refined using the SHELX-97 program package. An X-ray absorption correction was applied by equivalent reflections. Hydrogen atoms were revealed from the difference synthesis and refined by the riding model with the total isotropic thermal correction. The structures were examined and the figures were constructed using the WinGX program. The main crystallographic data and the results of structure refinement are given in Table 1. Selected bond lengths and bond angles are listed in Table 2. The characteristics of hydrogen bonds in the structures are presented in Table 3. The structures of complexes **I** and **II** are shown in Fig. 3. The coordinates of atoms with anisotropic thermal corrections and the refinement results for structures **I** and **II** were deposited with the Cambridge Crystallographic Data Centre (nos. 838045 (**I**) and 837957 (**II**); deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

As can be seen from Fig. 2a, the copper complex with the hydroxyethyliminodiacetate anion (L^1) and ethylenediamine (L^2) forms an isolated unit in which the L^1 ligand occupies four coordination sites and the L^2 ligand occupies two *cis* positions around the copper atom. The latter is hexacoordinated. The Cu–O and Cu–N distances differ appreciably. So, the Cu–N and Cu(1)–O(2) distances range from 1.973 to 2.055 Å (the N(1), N(2), N(3), and O(2) atoms form a slightly distorted square), whereas the Cu(1)–O(4) and Cu(1)–O(5) distances are considerably longer, and the O(4)Cu(1)O(5) angle differs substantially from 180° (Table 2). Thus, an elongated square bipyramid is

Table 1. Crystallographic data and the experimental and refinement characteristics for complexes **I** and **II**

Parameter	Value	
	I	**II**
Formula	$C_8H_{23}N_3O_8Cu$	$C_8H_{16}N_2O_6Cu$
FW	352.83	299.77
Temperature, K	290(2)	
Wavelength, Å	0.71073	
Crystal system, space group	Monoclinic, $P2_1/c$	Orthorhombic, $Pna2_1$
Cell parameters:		
a, Å	9.6378(7)	7.1281(5)
b, Å	11.9248(10)	16.1438(11)
c, Å	13.0853(9)	19.7298(12)
β, deg	96.524(7)	
V, Å^3	1494.1(2)	2270.4(3)
Z	4	8
ρ_{calcd}, g/cm^3	1.569	1.754
$\mu(MoK_\alpha)$, mm^{-1}	1.501	1.944
$F(000)$	740	1240
Crystal sizes, mm	0.80 × 0.07 × 0.03	0.20 × 0.07 × 0.01
θ scan range, deg	3.02–30.0	3.12–32.50
Index ranges	$-11 \le h \le 13, -16 \le k \le 16, -18 \le l \le 16$	$-8 \le h \le 10, -23 \le k \le 23, -23 \le l \le 29$
Reflections:		
measured	9422	22417
independent (R_{int})	4306 (0.0318)	6768 (0.0979)
observed ($I > 2\sigma(I)$)	3098	3187
Transmission coefficients T_{max}/T_{min}	0.9564/0.3798	0.9808/0.6972
Completeness, %	98.6	98.9
Parameters	214	317
S	0.949	0.937
R factors ($I > 2\sigma(I)$)	$R_1 = 0.0342$, $wR_2 = 0.0643$	$R_1 = 0.0470$, $wR_2 = 0.0553$
R factors for all reflections	$R_1 = 0.0607$, $wR_2 = 0.0702$	$R_1 = 0.1416$, $wR_2 = 0.0713$
$\Delta\rho_{min}/\Delta\rho_{max}$, e/Å^3	−0.305/0.370	−0.362/0.367

Table 2. Bond lengths (Å) and bond angles (deg) in structures **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
I			
Cu(1)–O(2)	1.9733(9)	O(5)–C(5)	1.4157(14)
Cu(1)–N(2)	1.9879(10)	N(1)–C(4)	1.4704(13)
Cu(1)–N(3)	2.0265(11)	N(1)–C(2)	1.4817(15)
Cu(1)–N(1)	2.0554(9)	N(1)–C(6)	1.4940(14)
Cu(1)–O(4)	2.3903(8)	N(2)–C(7)	1.4724(18)
Cu(1)–O(5)	2.4629(8)	N(3)–C(8)	1.4735(16)
O(1)–C(1)	1.2429(14)	C(1)–C(2)	1.5198(15)
O(2)–C(1)	1.2589(14)	C(3)–C(4)	1.5182(15)
O(3)–C(3)	1.2536(13)	C(5)–C(6)	1.5070(15)
O(4)–C(3)	1.2470(13)	C(7)–C(8)	1.493(2)
II			
Cu(1)–O(2)	1.939(2)	O(10)–C(13)	1.253(4)
Cu(1)–O(5)	1.983(2)	O(10)–Cu(1)$^{\#2}$	2.688(3)
Cu(1)–N(2)	1.993(2)	O(11)–C(13)	1.311(4)
Cu(1)–N(1)	2.015(3)	O(12)–C(16)	1.359(5)
Cu(1)–O(3)	2.459(2)	N(1)–C(2)	1.434(4)
Cu(1)–O(10)$^{\#1}$	2.688(3)	N(1)–C(6)	1.513(4)
Cu(2)–N(4)	1.917(3)	N(1)–C(4)	1.519(4)
Cu(2)–O(8)	1.953(2)	N(2)–C(7)	1.426(4)
Cu(2)–O(11)	1.961(2)	N(3)–C(10)	1.435(4)
Cu(2)–N(3)	1.994(3)	N(3)–C(12)	1.459(5)
Cu(2)–O(9)	2.482(3)	N(3)–C(14)	1.549(4)
Cu(2)–O(1)	2.695(2)	N(4)–C(15)	1.526(4)
O(1)–C(1)	1.206(4)	C(1)–C(2)	1.634(4)
O(2)–C(1)	1.240(4)	C(3)–C(4)	1.463(5)
O(3)–C(3)	1.440(4)	C(5)–C(6)	1.469(4)
O(4)–C(5)	1.302(4)	C(7)–C(8)	1.466(5)
O(5)–C(5)	1.235(4)	C(9)–C(10)	1.602(5)
O(6)–C(8)	1.463(4)	C(11)–C(12)	1.532(5)
O(7)–C(9)	1.171(4)	C(13)–C(14)	1.406(5)
O(8)–C(9)	1.315(4)	C(15)–C(16)	1.578(5)
O(9)–C(11)	1.429(4)		
Angle	ω, deg	Angle	ω, deg
I			
O(2)Cu(1)N(2)	90.69(4)	C(2)N(1)C(6)	110.99(8)
O(2)Cu(1)N(3)	173.92(4)	C(4)N(1)Cu(1)	109.31(6)
N(2)Cu(1)N(3)	84.28(4)	C(2)N(1)Cu(1)	105.82(6)
O(2)Cu(1)N(1)	85.37(3)	C(6)N(1)Cu(1)	109.58(7)
N(2)Cu(1)N(1)	171.78(4)	C(7)N(2)Cu(1)	110.77(8)
N(3)Cu(1)N(1)	99.18(4)	C(8)N(3)Cu(1)	105.61(8)
O(2)Cu(1)O(4)	92.02(3)	O(1)C(1)O(2)	124.21(10)
N(2)Cu(1)O(4)	113.10(4)	O(1)C(1)C(2)	117.98(10)
N(3)Cu(1)O(4)	93.09(4)	O(2)C(1)C(2)	117.76(10)
N(1)Cu(1)O(4)	74.32(3)	N(1)C(2)C(1)	113.44(9)
O(2)Cu(1)O(5)	87.98(3)	O(4)C(3)O(3)	125.49(10)
O(4)Cu(1)O(5)	152.37(3)	O(4)C(3)C(4)	117.83(9)
O(5)Cu(1)N(1)	78.14(3)	O(3)C(3)C(4)	116.66(9)
O(5)Cu(1)N(2)	94.53(4)	N(1)C(4)C(3)	111.50(9)
O(5)Cu(1)N(3)	89.01(3)	O(5)C(5)C(6)	108.56(9)
C(1)O(2)Cu(1)	114.97(7)	N(1)C(6)C(5)	111.98(9)
C(3)O(4)Cu(1)	109.13(7)	N(2)C(7)C(8)	109.76(10)
C(4)N(1)C(2)	110.20(9)	N(3)C(8)C(7)	107.72(12)
C(4)N(1)C(6)	110.81(8)		

Table 2. (Contd.)

Angle	ω, deg	Angle	ω, deg
II			
O(2)Cu(1)O(5)	163.37(9)	C(2)N(1)C(6)	116.1(2)
O(2)Cu(1)N(2)	93.64(9)	C(2)N(1)C(4)	109.6(3)
O(5)Cu(1)N(2)	97.61(9)	C(6)N(1)C(4)	111.9(2)
O(2)Cu(1)N(1)	84.48(9)	C(10)N(3)C(12)	106.6(3)
O(5)Cu(1)N(1)	84.12(9)	C(10)N(3)C(14)	113.3(3)
N(2)Cu(1)N(1)	178.05(9)	C(12)N(3)C(14)	115.8(3)
O(2)Cu(1)O(3)	87.69(8)	O(1)C(1)O(2)	129.3(3)
O(5)Cu(1)O(3)	102.52(8)	O(1)C(1)C(2)	116.1(3)
N(2)Cu(1)O(3)	98.97(9)	O(2)C(1)C(2)	114.6(3)
N(1)Cu(1)O(3)	81.47(9)	N(1)C(2)C(1)	110.4(3)
O(2)Cu(1)O(10)$^{\#1}$	80.62(8)	O(3)C(3)C(4)	109.7(3)
O(5)Cu(1)O(10)$^{\#1}$	86.15(8)	C(3)C(4)N(1)	115.3(3)
N(2)Cu(1)O(10)$^{\#1}$	95.35(9)	O(5)C(5)O(4)	122.5(3)
N(1)Cu(1)O(10)$^{\#1}$	83.86(9)	O(5)C(5)C(6)	121.2(3)
O(3)Cu(1)O(10)$^{\#1}$	162.04(8)	O(4)C(5)C(6)	116.3(3)
N(4)Cu(2)O(8)	97.74(11)	C(5)C(6)N(1)	109.9(2)
N(4)Cu(2)O(11)	93.27(11)	N(2)C(7)C(8)	115.2(3)
O(8)Cu(2)O(11)	164.18(10)	O(6)C(8)C(7)	111.2(3)
N(4)Cu(2)N(3)	178.30(13)	O(7)C(9)O(8)	129.1(4)
O(8)Cu(2)N(3)	82.82(10)	O(7)C(9)C(10)	119.1(3)
O(11)Cu(2)N(3)	86.50(10)	O(8)C(9)C(10)	111.8(3)
N(4)Cu(2)O(9)	97.31(11)	N(3)C(10)C(9)	109.9(3)
O(8)Cu(2)O(9)	103.07(9)	O(9)C(11)C(12)	112.9(3)
O(11)Cu(2)O(9)	86.67(9)	N(3)C(12)C(11)	110.6(3)
N(3)Cu(2)O(9)	81.00(10)	O(10)C(13)O(11)	121.9(3)
N(4)Cu(2)O(1)	94.50(11)	O(10)C(13)C(14)	119.0(3)
O(8)Cu(2)O(1)	86.47(8)	O(11)C(13)C(14)	119.1(3)
O(11)Cu(2)O(1)	81.36(9)	C(13)C(14)N(3)	114.9(3)
N(3)Cu(2)O(1)	87.13(10)	N(4)C(15)C(16)	110.3(3)
O(9)Cu(2)O(1)	163.63(8)	O(12)C(16)C(15)	113.8(3)

* Symmetry transforms for obtaining equivalent atoms: $^{\#1}$ $x + 1, y, z$; $^{\#2}$ $x - 1, y, z$.

Table 3. Geometric parameters of hydrogen bonds in structures **I** and **II***

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
I				
O(5)–H(5O)···O(4)$^{\#1}$	0.82	1.88	2.6873(11)	168
O(6)–H(6OA)···O(1)$^{\#2}$	0.82	2.1318(11)	2.9396(10)	169
O(6)–H(6OB)···O(3)$^{\#1}$	0.82	1.9734(12)	2.7836(10)	170
O(7)–H(7OA)···O(6)	0.82	1.9580(10)	2.7741(9)	174
O(7)–H(7OB)···O(8)$^{\#3}$	0.82	1.9724(13)	2.7604(9)	161
O(8)–H(8OA)···O(7)	0.82	2.0168(12)	2.7665(9)	152
O(8)–H(8OB)···O(3)$^{\#2}$	0.82	1.9828(14)	2.7760(12)	163
N(2)–H(2NA)···O(7)	0.88	2.235(13)	3.0218(12)	149
N(2)–H(2NB)···O(3)$^{\#1}$	0.87	2.085(13)	2.9451(12)	168
N(3)–H(3NA)···O(1)$^{\#4}$	0.86	2.324(13)	3.0692(13)	145
N(3)–H(3NB)···O(1)$^{\#5}$	0.84	2.586(13)	3.3742(13)	156
N(3)–H(3NB)···O(2)$^{\#5}$	0.84	2.653(15)	3.4199(14)	152
II				
O(3)–H(3C)···O(7)$^{\#3}$	0.83	1.811(9)	2.624(3)	167
O(6)–H(6C)···O(3)$^{\#1}$	0.82	2.08	2.851(3)	156
O(12)–H(12C)···O(9)$^{\#1}$	0.82	2.01	2.789(4)	159
N(2)–H(1N2)···O(12)	0.90	2.18	3.008(3)	153
N(2)–H(2N2)···O(11)$^{\#1}$	0.90	2.15	2.975(3)	151
N(4)–H(1N4)···O(2)	0.90	2.16	2.993(4)	153
N(4)–H(2N4)···O(6)$^{\#2}$	0.90	2.25	3.061(3)	149
O(9)–H(9)···O(4)$^{\#4}$	0.83	1.939(18)	2.653(3)	144

* Symmetry transforms for obtaining equivalent atoms: $^{\#1}\,-x + 2, y - 1/2, -z + 1/2$; $^{\#2}\,x + 1, y, z$; $^{\#3}\,-x + 3, -y + 2, -z + 1$; $^{\#4}\,-x + 2, y + 1/2, -z + 1/2$; $^{\#5}\,x, -y + 3/2, z - 1/2$ (**I**) and $^{\#1}\,x + 1, y, z$; $^{\#2}\,x - 1, y, z$; $^{\#3}\,-x + 1, -y + 1, z - 1/2$; $^{\#4}\,-x +\ \ + 1, -y + 1, z + 1/2$ (**II**).

the coordination polyhedron of copper in this complex.

In crystal, molecules of **I** are packed in layers in the (100) planes. Hydrogen bonds N(3)···O(1) ($2 - x, y + 1/2, 1/2 - z$) 3.069,O(5)···O(4) ($2 - x, y - 1/2, 1/2 - z$) 2.687, N(2)···O(3) ($2 - x, y - 1/2, 1/2 - z$) 2.945, N(3)···O(1) ($x, 3/2 - y, z - 1/2$) 3.374, N(3)–H(3NB)···O(2) ($x, 3/2 - y, z - 1/2$) 3.420 Å are formed between the adjacent molecules in a layer along the direction [010] (Table 3). Other hydrogen bonds are formed between molecules of the complex and water of crystallization, which are not in the coordination sphere of the copper atoms, and between different molecules of water of crystallization. The molecules of water of crystallization also form layers arranged between the layers of the molecules of the complex (Fig. 3a).

In structure **II** (Fig. 2b), the second ligand is 2-aminoethanol (L^3) and each copper atom is also hexacoordinated. Two units of the complex are symmetrically nonequivalent in this structure. The coordination polyhedron of the Cu(1) atom is formed by the O(2), O(3), O(5), and N(1) atoms of the L^1 ligand, the N(2) atom of the L^3 ligand, and the O(10) atom ($x + 1, y, z$) of the adjacent L^1 ligand. Similarly, the Cu(2) atom is coordinated by the O(8), O(9), O(11), and

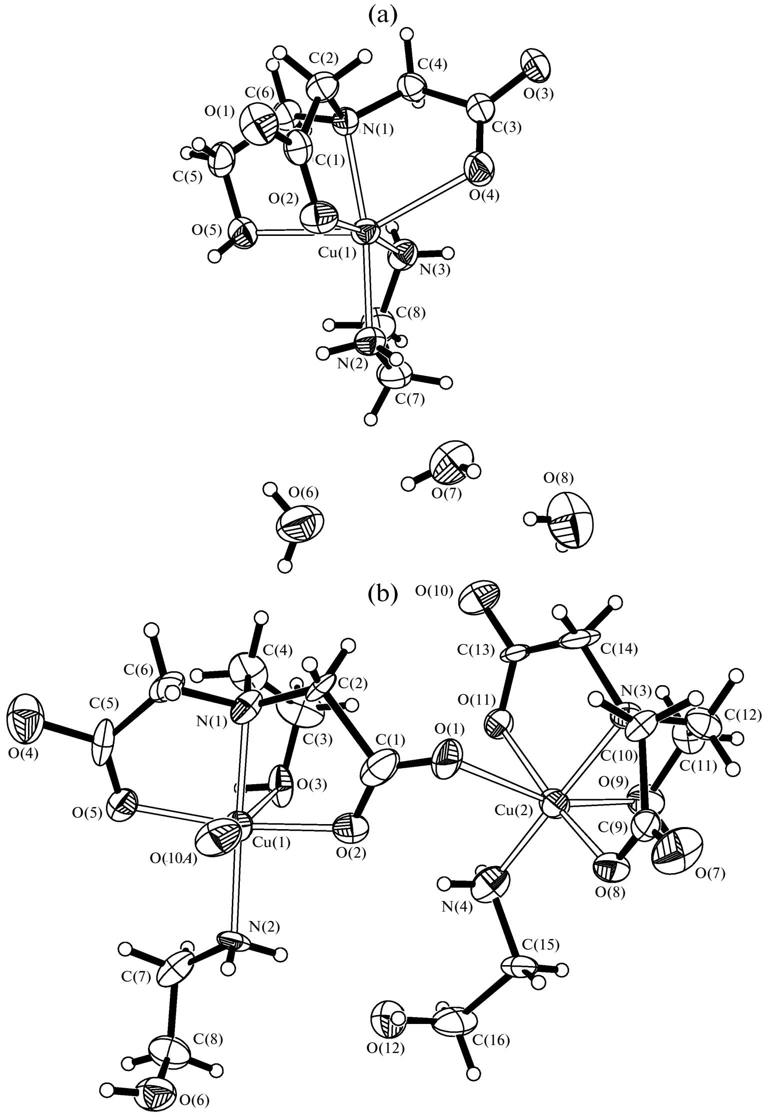


Fig. 2. Structures of complexes (a) **I** and (b) **II** in the representation of atoms by thermal displacement ellipsoids with 50% probability.

N(3) atoms of the second ligand L^1, the N(4) atom of the second basis L^3 molecule, and the O(1) atom of the first basis molecule L^1. The O(2), O(5), N(1), and N(2) atoms surrounding the Cu(1) atom and the O(8), O(11), N(3), and N(4) atoms around Cu(2) form two insignificantly distorted squares in which the Cu–O and Cu–N distances range from 1.917 to 2.015 Å, whereas the axial Cu–O distances are noticeably longer (2.469–2.695 Å, Table 2). The O(3)Cu(1)O(10) ($x + 1$, y, z) and O(9)Cu(2)O(1) angles formed by the copper atoms and axial oxygen atoms differ substantially from 180° as in structure **I**. For both copper atoms in structure **II**, an elongated square bipyramid is also the coordination polyhedron. Infinite chains extended along the [100] direction (perpendicular to the figure plane in Fig. 3b) are formed in structure **II**, unlike **I**, due to the coordination of each L_1 ligand simultaneously by two adjacent copper atoms. These chains form layers parallel to the coordinate plane (010). A system of hydrogen bonds (Table 3) is formed in the chains and between the adjacent chains in the layer. Of these hydrogen bonds, N(4)···O(2) and N(2)···O(12) are in the basis fragment (Fig. 2b) and fix the position of the ligand L_3 molecules. The O(6)···O(3) ($x + 1, y, z$), N(4)···O(6) ($x - 1, y, z$), O(12)···O(9) ($x + 1, y, z$), and N(2)···O(11) ($x + 1, y, z$) bonds are formed between the adjacent fragments along the chain, and the O(3)–H(3C)···O(7) ($-x + 1, -y + 1, z - 1/2$), O(9)···O(4) ($-x + 1, -y + 1, z + 1/2$) bonds are formed between the chains in the layer. No hydrogen bonds are observed between the layers.

The IR spectrum of sample **II** exhibit bands corresponding to the C=O stretching vibrations (1600 cm^{-1}),

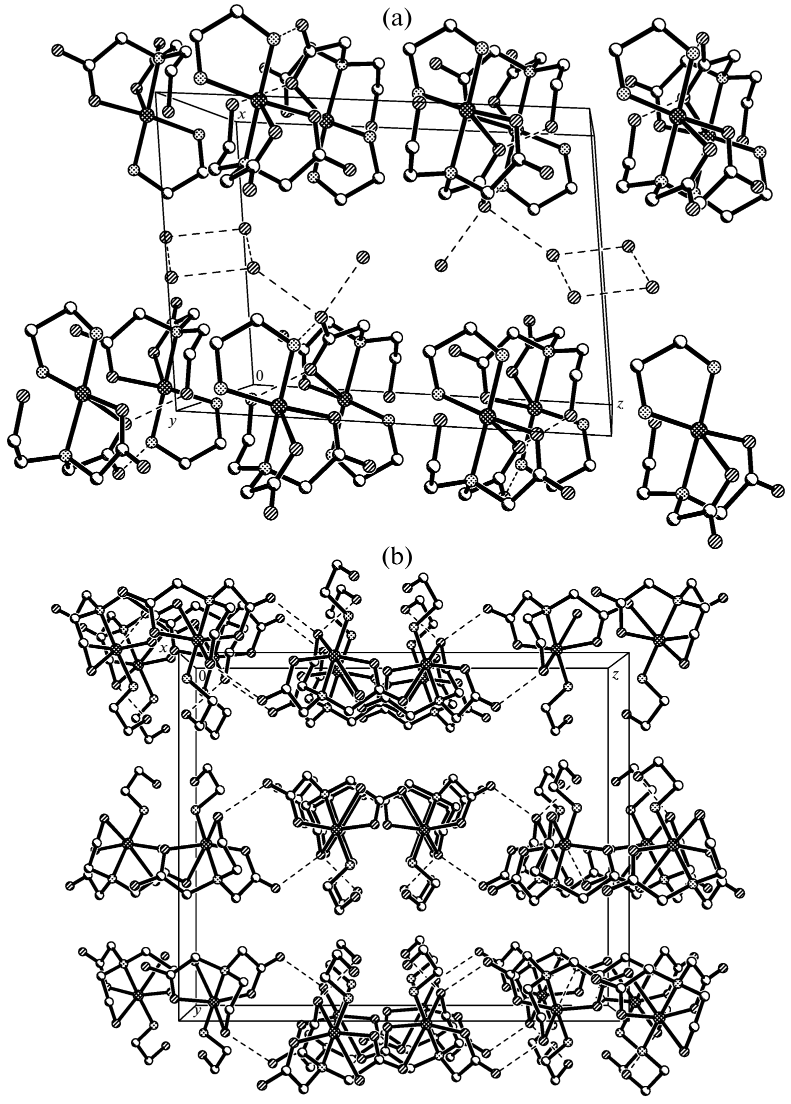


Fig. 3. Molecular packing in the crystals of compounds (a) **I** and (b) **II**.

symmetric vibrations of C–O (COO^-) (1370 cm^{-1}), and a narrow intense band of the coordinated OH group (3320 cm^{-1}), which are present in the IR spectrum of the homoligand complex [Cu(Heida)], as well as a narrow double band (3130–3220 cm^{-1}) caused by the asymmetric vibrations of the bonds. The latter indicates that the obtained crystalline complexonate includes molecules of 2-aminoethanol. The presence of this ligand in compound **II** is also indicated by the bands at 2850–3000 cm^{-1}, which are more intense than those for [Cu(Heida)] and are characteristic of C–H bonds [8].

The differential thermal analyses of the complexes confirm the presence of molecules of water of crystallization in complex **I** (an endotherm at 100–110°C) and its absence in complex **II** (Fig. 3). The pronounced endotherm at ~200°C for both compounds indicates the removal of the Heida ligands. This seems quite reasonable if taking into account that free N-(2-hydroxyethyl)iminodiacetic acid decomposes at the moment of melting (mp = 178°C [9]).

As the concentrations of ethylenediamine and 2-aminoethanol increase at an unchanged acidity of the solution, the absorbance in the absorption spectra of the solution changes, reaching its limiting value, which indicates the formation of heteroligand compounds Cu(Heida)X, where X is En and Mea, in the solution. The additional 2-aminoethanol ligand is added to the complexonate at higher pH than that for ethylenediamine.

The stability constants of complexes formed in the Cu–Heida–X systems, where X is En and Mea, were

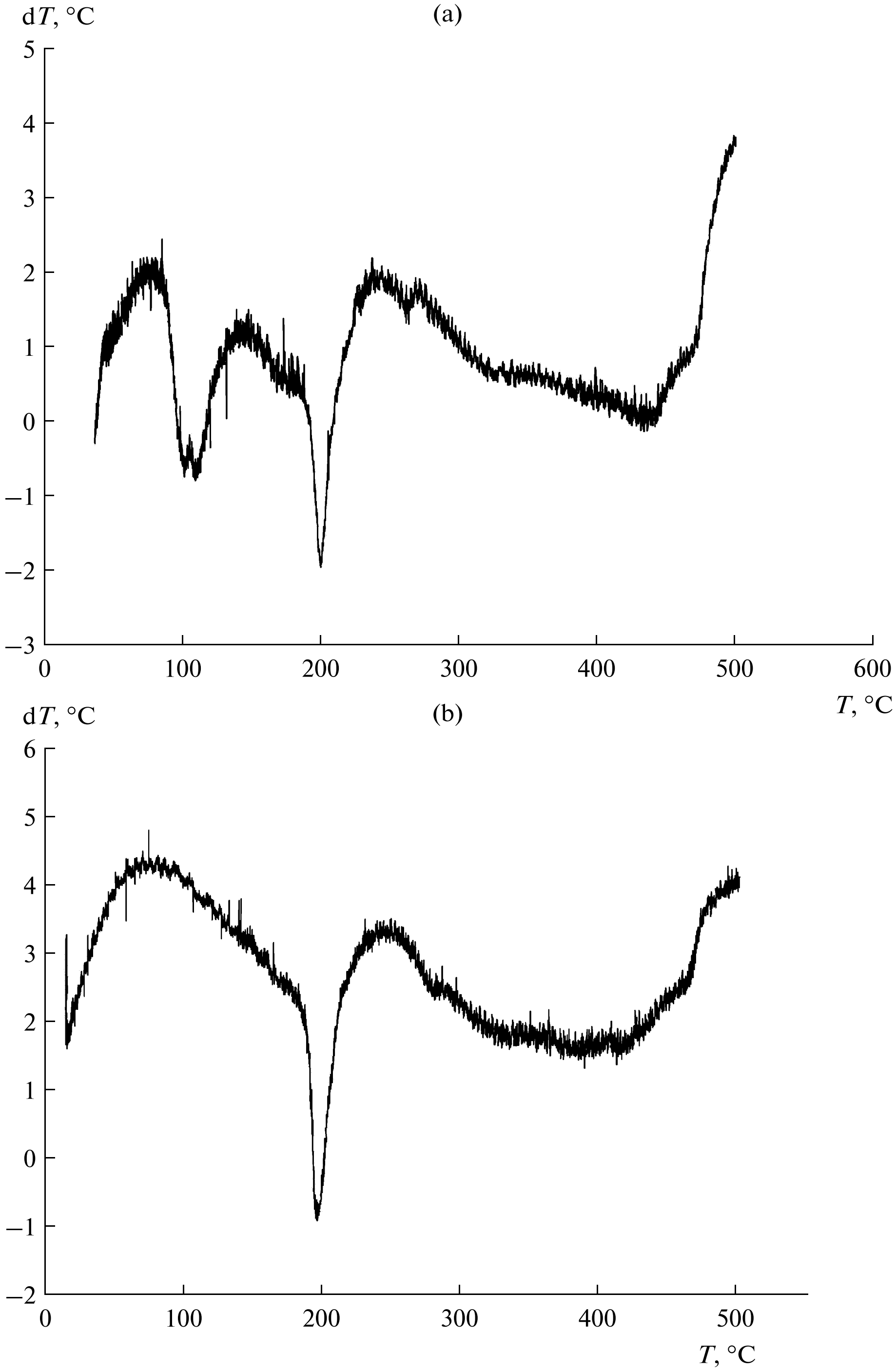


Fig. 4. Derivatograms for compounds (a) **I** and (b) **II**.

calculated according to a described procedure [10]. The logarithm of the addition constant of ethylenediamine to the complexonate is 2.79. Correspondingly, for Cu(Heida)(En), $\log K_{tot} = 11.0 + 2.79 = 13.79$; for 2-aminoethanol, $\log K_{tot} = 2.08$; and for Cu(Heida)(Mea), $\log K_{tot} = 11.0 + 2.08 = 13.08$.

According to the thermal analysis data (Fig. 4), the heteroligand (ethylenediamine for **I** and 2-aminoethanol for **II**) is the last one that leaves the complexes. Ethylenediamine is detached more slowly and at a higher temperature due to the higher addition constant.

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