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Copper(II) Complexes Based on *N*-(2-Carboxyethyl)alkanolamines

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Abstract—A comparative study of the copper metallocenter coordination sphere is carried out for a series of *N*-substituted β-alaninate ligands in condensed phase. For the elucidation of the effect of regular changes in dentate properties of a ligand on the complex structure, *N*-(bis(hydroxymethyl)methyl)-β-alanine and its copper(II) complex are specially synthesized and the complex structure is studied by the method of X-ray structural analysis. For determination of structure of the complexes in aqueous solution is applied electron spin resonance spectroscopy. Structural characteristics of β-alaninate and glycinate complexes are compared. The factors promoting formation of polynuclear complexes are considered.

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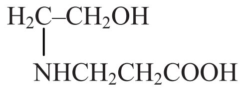
Current view on the substance require imperatively to use knowledge about coordination compound not only due to wide practical application of the latter but also owing to the possibility of solving fundamental problems of chemical structure in a great variety of structural types of coordination compounds. Despite the fact that the modern chemistry of coordination compounds is a wide and independent branch of chemical science, it embarrasses the problems that traditionally related to inorganic and organic chemistry. An independent uniting idea of the chemistry of coordination compounds is interrelations of the structure of ligands (the goal-directed synthesis of those is accessible only in organic chemistry) and that of the formed complexes (that traditionally are considered in the framework of inorganic chemistry). Search for the key regularities is unavoidable task of the general chemistry.

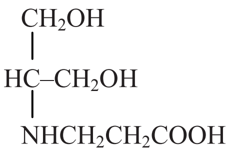
For application to such advanced areas as metallocomplex catalysis, creation of new medicine preparations and elements of molecular electronics and nonlinear optics, the coordination compound should have complicated structure and contain more than bidentate ligands (denticity over two). Only in such situation appears a possibility of multichelating that provides necessary steric arrangement of atoms and as a sequence revealing by such coordination compounds of unique properties. Thus, a study of structure of coordination compounds as a dependence on the regularly varied structure of ligands gives rise to formulation of the conclusions characterizing fundamental problems of formation of coordination compounds and the possibilities of their practical application.

Being targeted on the study of dependence of structure of copper complexes on the regularly varied structure of tridentate ligands, we synthesized *N*-[bis(hydroxymethyl)methyl]-β-alanine (**I**) and its copper(II) complex. Whole we formed a comparative series of the ligands with monotonically increased denticity in account of additional hydroxymethyl groups:



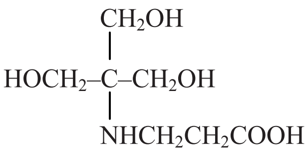
$$\begin{array}{l} H_2C\text{–}CH_2OH \\ \quad | \\ \quad NHCH_2CH_2COOH \end{array}$$

N-(2-hydroxyethyl)-β-alanine (he-ala) [1]



$$\begin{array}{l} CH_2OH \\ | \\ HC\text{–}CH_2OH \\ | \\ NHCH_2CH_2COOH \end{array}$$

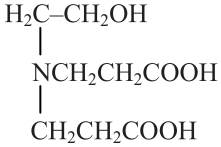
N-[bis(hydroxymethyl)methyl]-β-alanine (bis-ala)



$$\begin{array}{c} \mathrm{CH_2OH} \\ | \\ \mathrm{HOCH_2{-}C{-}CH_2OH} \\ | \\ \mathrm{NHCH_2CH_2COOH} \end{array}$$

N-[tris(hydroxymethyl)methyl]-β-alanine (tris-ala) [2]

For the change in denticity in account of carboxylic groups we synthesized *N*-(2-hydroxyethyl)iminodipropanoic acid (he-diala) [3]:



$$\begin{array}{l} \mathrm{H_2C{-}CH_2OH} \\ | \\ \mathrm{NCH_2CH_2COOH} \\ | \\ \mathrm{CH_2CH_2COOH} \end{array}$$

This wok is denoted to generalization of the dependence of composition and structure of the copper metallocenter coordination sphere on the structure of *N*-hydroxyalkyl-β-alaninate ligands by means of the X-ray structural analysis and electron spin resonance spectroscopy on the following complexes: bis{*N*-[bis-(hydroxymethyl)methyl]-β-alaninato}copper(II) (compound **II**), bis[*N*-(2-hydroxyethyl)-β-alaninato]copper(II) (compound **III**), *N*-[tris(hydroxymethyl)-methyl]-β-alaninatocopper(II) (compound **IV**) and *N*-(2-hydroxyethyl)-iminodipropanoatocopper(II) (compound **V**).

Synthesis of ligand I and molecular structure of compound II. Among various practical applications of compound **I** there is an application for binding TcO_4^{2-} ions for introducing technetium into a living organism as radioactive label, that is disclosed by patent [4]. But examples of this patent do not include a description of the synthesis of compound **I**. The commonly used method for the synthesis of such compounds consists in addition of acrylonitrile followed by hydrolysis of nitrile fragment to carboxyl. We propose a one step method of synthesis, by direct addition of acrylic acid.

At the formation of copper(II) complex the two tetradentate ligands **I** form oxtahedral environment at the metallocenter and thus bear tridentate function closing two chelate rings conjugated through Cu–N bond: six-membered β-alaninate and five-membered ethanolaminate (Fig. 1). The values of some bond lengths and bond angles are listed in Table 1. The ligands in this complex are monodeprotonated and have meridianal conformation that provides a possibility of formation of chiral center for the metallocenter. Earlier such possibility has been established on an example of *N*-(2-hydroxyethyl)-β-alanine [5]. Actually, in structure **II** coexist two crystallographically independent stereoisomers while the whole crystal is a racemic mixture of these stereoisomers (Fig. 2).

Comparison of the complexes II–IV. Comparison of coordination sphere of the presented complexes shows that increase in denticity by means of introduction of hydroxymethyl or 2-ethoxycarbonyl

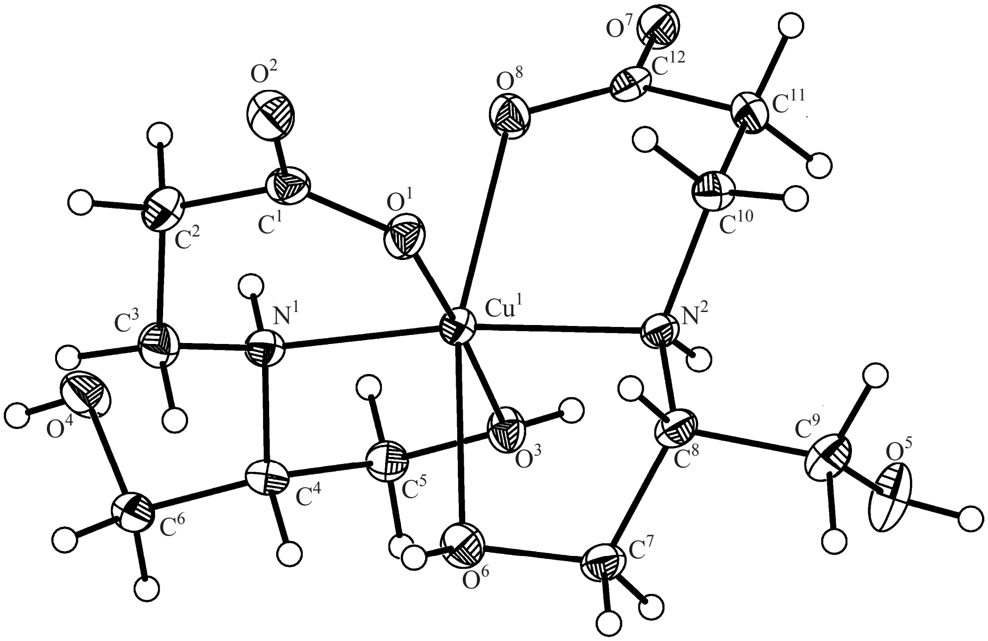


Fig. 1. Structure of the coordination sphere of metallocenter in the complex **II**.

Table 1. Principal bond lengths (*d*, Å) and and bond angles (ω, deg) in complex **II**

Bond	*d*, Å	Angle	ω, deg	Angle	ω, deg
Cu^1–O^1	1.9666(16)	$O^1Cu^1O^3$	176.09(7)	$O^2C^1O^1$	122.9(2)
Cu^1–O^3	2.0008(16)	$O^1Cu^1N^1$	95.47(7)	$CNCu^a$	105.04(13)
Cu^1–N^1	2.003(2)	$O^1Cu^1N^2$	90.65(7)		113.66(15)
Cu^1–N^2	2.0450(19)	$N^1Cu^1N^2$	172.06(8)	CCC^a	109.33(18)
Cu^1–O^6	2.3702(17)	$O^1Cu^1O^8$	91.91(7)		116.28(18)
Cu^1–O^8	2.3199(17)	$N^1Cu^1O^8$	98.48(7)	$O_{OH}CC^a$	106.29(18)
O_{COO}–C^a	1.245(3)	$O^1Cu^1O^6$	91.35(7)		113.66(18)
	1.273(3)	$N^1Cu^1O^6$	94.39(7)	$O_{COO}CC^a$	117.5(2)
O_{OH}–C^a	1.415(3)	$O^8Cu^1O^6$	166.35(6)		119.6(2)
	1.439(3)	$C^{12}O^8Cu^1$	122.62(14)	NCC^a	105.75(17)
N–C^a	1.474(3)	$C^5O^3Cu^1$	112.40(12)		114.90(18)
	1.494(3)	$C^{10}N^2C^8$	113.54(18)		
C–C^a	1.509(3)	$C^3N^1C^4$	114.55(18)		
	1.529(3)	$O^7C^{12}O^8$	123.5(2)		

[a] Minimal and maximal values of interatomic distances and bond angles of the same type are given.

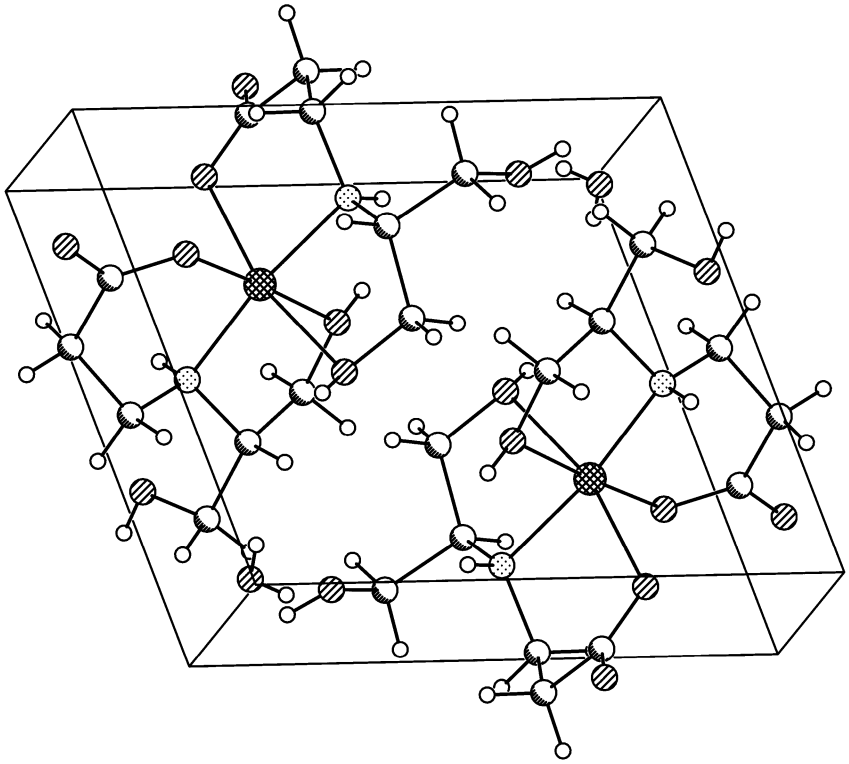


Fig. 2. Molecular structure of two enantiomeric structures of complex **II**.

Table 2. Principal bond lengths (Å) in copper complexes

Complex[a]	Cu–O_{COO}	Cu–O_{OH}	Cu–N	References
$[Cu(\beta\text{-ala})_2(H_2O)_2]$	2.085	–	2.093	[13]
$[Cu(\text{he-ala})_2]\cdot 2.5\,H_2O$	1.968	2.473	2.017	[1]
$[Cu(\text{bis-ala})_2]\cdot H_2O$	equatorial: 1.966 axial: 2.319	equatorial: 2.001 axial: 2.370	average: 2.024	This work
$[Cu_4(\text{tris-ala})_4]\cdot 11.25\,H_2O$	1.947	2.465; 1.947[b]	1.992	[2]
$[Cu(\text{he-diala})]$	1.941	2.211	1.991	[3]
$[Cu(\text{he-ida})]\cdot H_2O$	1.942	2.351	2.004	[14]
$[Cu(\text{deg})_2]$	1.949	2.384	2.062	[15]
$K_2[Cu(\text{ida})_2]\cdot H_2O$	equatorial: 1.960 axial: 2.441	–	1.973	[16]
$[Cu(\text{ea})_2(OH)_2]\cdot 2\,H_2O$	–	2.369	2.064	[17]
$[Cu(\text{pro-ea})_2](SCN)_2$	–	2.441	2.054	[18]
$[Cu_4(\text{pro-ea'})_4](NO_3)_4\cdot 2\,H_2O$	–	1.942[b]	2.012	[19]

[a] (he-ida) is *N*-(2-hydroxyethyl)iminodiacetic acid, (deg) is *N,N*-bis(2-hydroxyethyl)aminoacetic acid, (ida) is iminodiacetic acid, (ea) is 2-aminoethanol, (pro-ea) is *N*-(3-aminopropyl)-aminoethanol, (pro-ea') is *N*-(3-aminopropyl)-aminoethoxide. [b] Alkoxyl Cu–O bond.

group in the crystal state leads to oligomerization or polymerization of the formed complexes.

Monotonic increase in the number of hydroxymethyl groups left coordination number unchanged (octahedral environment), hydroxy group is located in axial position. In each complex are formed two equal chelate ring: six-membered β-alaninate and five-membered ethanolaminate, that immediately equalizes the complexes by strength. Ligand **I** is rather a stranger. It reacts like *N*-(2-hydroxyethyl)-β-alanine, but the ligand conformation for no reason is altered. As a result, in the complex **II** the equatorial plane is formed by one ligand and nitrogen atom of another ligand whose hydroxy and carboxylic groups occupy axial positions. In complexes **III** and **IV** their equatorial positions are occupied by nitrogen atom and carboxylic groups. On the other hand, if ligand **I** is similar to *N*-[tris(hydroxymethyl)methyl]-β-alanine, the analogous cubane-like tetrameric structure nevertheless is not formed, for incomprehensible reasons.

In all likehood, the observed change in the complex formation can be explained by entropy factor. Introduction of next hydroxymethyl group decreases entropy of environment. Therefore in accordance with the universal law of an increase in the entropy of spontaneous processes formation of the complexes should lead to increase in entropy. Thus, introduction of one hydroxymethyl group leads to the possibility of formation of one complex in the case of **III** instead of two enantiomers of **II**. Introduction of the second hydroxymethyl group in the structure **IV** allows formation of even 18 geometric isomers, of whose one is formed in the case of copper.

Comparison of essential bond lengths in the copper(II) complexes with the considered ligands is given in Table 2. As seen, N-substitution in β-alanine molecule leads to decrease in Cu–O_{COO} and Cu–N bond lengths attesting strengthening of the complexes. In comparison with the parent 2-aminoethanol (Table 2) the bond Cu–N is shortened while Cu–O_{OH} remains little changed.

Increase in denticity in account of the groups with higher acidity leads to pentagonal environment [3]. Therewith, hydroxy and carboxylic groups occupy axial positions, like in complex **II**.

Characterization of complexes with the use of electron spin resonance spectroscopy. Earlier for many times has been shown [6–8] that at dissolving crystals of complexes in water the nearest environment of copper(II) complexes does not alter noticeable. Only in the copper(II) carboxylate complexes the place of carbonyl oxygen of the bridgehead carboxylic group often occupies solvent molecule. Therefore the data of ESR spectroscopy of frozen solutions (low temperature glasses) can be analyzed proceeding from the structure of coordination shell of metallocenter known from X-ray structural data [9, 10]. Also it has been established [11, 12] that strengthening in the binding of copper(II) ions along the axial axis of stretched bipyramid leads to increase in *g*-factor and decrease in superfine coupling constant of the copper ion.

The spin Hamiltonian parameters determined for the frozen at 77 K aqueous solutions of copper(II) bis-β-alaninate hexahydrte **VI** are listed in Table 3 [7]. The X-ray structural analysis of crystals **VI** showed [13] that its metallocenter is coordinated in the equatorial plane of stretched tetragonal bipyramid with two oxygen and two nitrogen atoms of β-alaninate molecules that are mutually in *trans* positions (the bond lengths are given in Table 2), and two oxygen atoms belonging to water molecues are located on the axial axis (bond length Cu–O = 2.485 Å) and thus complete coordination. In structure **III** the copper(II) complex has screwed bipyramidal-tetragonal geometry (4+2) with the metallocenter in the inversion center. β-Alaninate chelate rings of two he-ala molecules occupy coordination sites of copper in equatorial plane, therewith the oxygen and nitrogen atoms are mutually in *trans* positions (the bond lengths are listed in Table 2). The angle between ethanolaminate and β-alaninate chelate rings is almost exactly 90°.

From comparison of structure of the complexes **VI** and **III** follows that besides certain shortening of the copper bonds with equatorial ligands in complex **III** due to formation of chelate ring also occurs shortening and strengthening of the bond with the oxygen atoms located on the axial axis. As a result, the $g_{\|}$ value for this complex increases while $A_{\|}$ decreases (Table 3), in correspondence with the established regularities.

Even more significant shortening and strengthening of the bonds of copper ion with axial oxygen atoms is observed in complex **II**. In distinct to complex **III**, in this complex the ligand occupies meridianal position, that is, both β-alaninate and ethanolaminate chelate rings of each of two bis-ala molecules lie in the same plane (Fig. 1, the bond lengths in Table 2). As a result, the oxygen atoms of carboxylic and one hydroxyl groups are axial.

Table 3. ESR spectral parameters of copper(II) complexes with aminoacetate and aminopropionate ligands

Ligand	Complex composition	$g_{II} \pm 0.005$	$(A_{II} \pm 3)\times10^4$, T	References
β-ala	CuL_2	2.243	130	[7]
he-ala	CuL_2	2.257	117	This work
bis-ala	CuL_2	2.271	124	
he-ida[a]	CuL	2.305	158	[9]
	CuL_2	2.270	170	
he-diala	CuL	2.295	152	This work
	CuL_2	2.261	134	
ida[b]	CuL	2.303	156	[9]
	CuL_2	2.271	167	
deg[c]	CuL	2.331	148	
	CuL_2	2.274	170	

[a] (he-ida) is *N*-(2-hydroxyethyl)-iminodiacetic acid. [b] (ida) is iminodiacetic acid. [c] (deg) is *N,N*-bis(2-hydroxyethyl)amino-acetic acid.

The growth of $g_{\|}$ in the series **VI**, **III** and **II** of the complexes first of all is connected with shortening and strengthening of bonds of copper with axial oxygen atoms. The value $A_{\|}$ in a greater extent than $g_{\|}$ is connected with the changes in the copper coordination in equatorial plane (bond lengths, bond angles and solid angles). The deviations from right figure (square, parallelogram) in the equatorial plane of the studied complexes are great and are quite individual in each complex. We suggest that just by this reason occurs distortion of a regularity in the variations of this value. It turned out that although $A_{\|}$ in **II** is less than in **VI**, it nevertheless a bit larger than in **III** (Table 3).

For comparison: in the case of *N*-(2-hydroxyethyl) iminodiacetic acid is formed a coper(II) complex of 1:1 composition where the ligand is tetradentate [14]. The copper(II) complex geometry is axially elongated screwed tetragonal bipyramid with two aminoacetate chelate rings in its equatorial plane (the bond lengths are listed in Table 2). The fourth position, *trans* to the nitrogen atom occupies water molecule (Cu–O bond length 1.907 Å). The oxygen of the ligand hydroxy group is axial. At dissolving the crystal in water the opposite axial position in the complex becomes occupied probably by water molecule rather than by carbonyl oxygen of the bridgehead carboxylic group of another ligand molecule. The ESR spectral parameters of this complex are listed in Table 3. The sharp growth in $g_{\parallel}$ vaue for this complex as compared with the above considered complex with the ratio copper(II) : ligand = 1:2 reflects the decrease to unity of the number of nitrogen atoms in the nearest environment of the metallocenter [9]. The same regularity is well traced (Table 3) at the comparison of spectral parameters of the complexes of 1:1 and 1:2 composition.

In the structure of complex **V** the coordination sphere of the copper metallocenter is a screwed trigonal bipyramid with he-diala molecule as a tetradentate ligand, like the above considered he-ida. The fifth coordination site occupies carbonyl oxygen of neighboring chelate that converts the crystal structure to polymer. At dissolving in water this bond breaks, and vacant position in the copper(II) complex occupies water molecule. Not excluded that the complex is completed with second water molecule and is converted in solution into elongated trigonal bipyramid. Anyway, parameters of this complex are close (although a bit below) to those of analogous complex [Cu(he-ida)] and other complexes of 1:1 composition with various aminoacetate ligands (Table 3).

There is no published X-ray structural data on the copper(II) complexes of 1:2 composition with he-ida and he-diala ligands. Therefore we can not compare directly structures of these complexes and their ESR spectral parameters. However, judging from the closeness of spectral parameters of 1:2 copper(II) complexes with he-ida, *N*-bis(2-hydroxyethyl)aminoacetic (deg) and iminodiacetic (ida) acids (Table 3) we suggest that their structures are in much similar. For the complexes with the two last ligands there are structural data. In the case of deg [15] the coordination environment of the metallocenter is elongated tetragonal bipyramid in which each ligand molecule is tridentate, the glycinate rings are located in equatorial plane and oxygen of one of alcohol hydroxyl is axial. The nitrogen atoms of the ligands are *trans* to each other (for bond lengths see Table 2). In the copper(II)–ida complex the coordination environment of the metallocenter is elongated octahedron with two tridentate ligands filling inner sphere of the copper ion with the nitrogen atoms in equatorial plane in mutual *trans* positions (bond lengths in Table 2) [16].

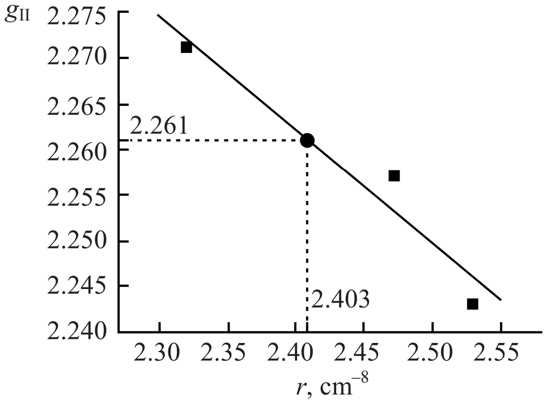


Fig. 3. Plot $g_{\parallel}$ of respective complexes vs. distance r from copper to axially located oxygen atoms in the copper complexes of 1:2 composition with aminopropionate ligands.

From the comparison of the ESR spectral parameters of copper(II) complexes with he-ida and he-diala (Table 3) of 1:2 composition follows that $g_{\parallel}$, and $A_{\parallel}$ of the second complex are much less that for the first one. On the other hand, these parameters are quite consistent with all the data in Table 3 for the ligands with propanoate groups. Using the given above analysis of relations between $g_{\parallel}$ and axial Cu–O bond length for the copper(II) complexes with amonopropanoate ligands of 1:2 composition (Fig. 3) one can predict the probable value of this distance in the copper complexes with he-diala. The value of 2.40 Å is quite consistent with the given above distances in [Cu(deg)$_2$] and [Cu(ida)$_2$]$^{2-}$ complexes determined by the method of X-ray structural analysis.

These studies allow to compare the ESR spectral parameters of copper(II) complexes with a series of ligands containing aminoacetate and aminopropanoate groups. As is found, at the same complex composition and similar structure the values of $g_{\parallel}$ and $A_{\parallel}$ of the complexes with 6-membered aminocarboxylate rings are less than the same for the complexes with 5-membered rings.

Thus, by the performed studies we established the regularities in the effect of denticity of *N*-hydroxyalkyl-β-alaninate ligands and chelate ring size on the complex structure and the ESR spectral parameters of copper(II). It is shown that increase in denticity leads to oligomerization and polymerization of the formed 1:2 complexes in crystals rather than to formation of 1:1 complexes. At the same complex composition and similarity in structure the values of $g_{\parallel}$ and $A_{\parallel}$ of the complexes with 6-membered aminocarboxylate rings are less than for the complexes with 5-membered rings.

The works on study structure of the complexes based on the β-alanine derivatives were initiated by

M.A. Porai-Koshits who was a classic in X-ray analysis. However, the necessary ligands were synthesized in many steps by adding acrylonitrile or acrylamide followed by hydrolysis, so scaled preparation and whole scope of the complexes for investigation were restricted. The modern level of development of synthetic organic chemistry allows to prepare the necessary ligands in one step that allowed to obtain in this work a series of new data that complement logically those obtained earlier.

Despite the many data on the X-ray structural analysis of complexes published recently, the problems considered in our work remain rather important. The availability of structural investigations and progress in organic chemistry led to appearance of many publications on the structure of complex compounds with the ligands of complicated chemical structure. In other words, this situation initiated development of the chemistry of complicated ligands with the purpose of creation of the complexes with new useful properties (supramolecularity, semiconductivity, soft magnetism, etc.). The ligand with relatively simple chemical structure were synthesized and used long ago while development of the chemistry of complexes, in respect of their structure in particular, is retained. However, as seen from our investigations, even small changes in the ligand structure, that is, increase in the size of carboxylate ring (glycinate and alaninate fragments) by one carbon atom changes radically the structure of the formed complex. In turn, a simple combination of electronic and steric factors (introduction of additional hydroxymethyl group) allows turning from mononuclear to the polynuclear complexes. The regularities of such changes remain in much not clear. But they can be elucidated by the application of simple models only. The systematic comparison of the data of X-ray structural analysis and ESR spectroscopy allows also to select characteristic parameters and obtain reliable data on the complex structure even when X-ray structural analysis can not be applied.

Whole should be noted that at the alaninate ligand denticity three or less the multinuclear copper complexes are formed (**III** and **VI**). The denticity equal to four or five leads to formation of multinuclear (cluster or polymer) complexes (**IV** and **V**). Bis[*N*-(bis-(hydroxymethyl)methyl]-β-alaninato)copper(II), compound **II**, firs described in this work, that has tetradentate ligand forms, however, a mononuclear complex. Thus a necessary additional condition for the formation of a polynuclear complex is bidenticity of one of coordinating functional groups: carbonyl oxygen atom in carboxylic group (complex **V**) or axial oxygen atom (complex **IV**).

We plan to continue this investigation to extend it over the complexes of other metals.

EXPERIMENTAL

Synthesis of ligand (I). To 2.72 g (0.02 mol) of 2-amino-1,3-propanediol (serinol) oxalate in 3 ml of water was added 1.11 g (0.01 mol) of $CaCl_2$, dissolved in 3 ml of water. The mixture was filtered and to the filtrate was added 1.37 ml of (0.02 mol) of acrylic acid and 1.12 g (0.02 mol) of KOH. Solution obtained was refluxed for 12 h, then solvent was removed in a vacuum at the heating in water bath, and to the residue was added 20 ml of methanol. The precipitate was filtered off and to the filtrate was added 100 ml of acetone. The residue was recrystallized from methanol. Yield 1.1 g (34 %), mp 184–186°C. Found, %: C 43.75; H 7.71; N 7.88. $C_6H_{13}NO_4$. Calculated, %: C 44.19; H 7.97; N 8.59. *M* 163.06. The ^{1}H NMR spectrum (D_2O), δ, ppm: 3.84 m (4H, HO*CH₂*), 3.38 t.t (1H, $HOCH_2C\mathit{H}CH_2OH$), 3.32 t (2H, $NH\mathit{CH_2}CH_2\cdot COOH$), 2.60 t (2H, $NHCH_2\mathit{CH_2}COOH$).

Synthesis of complex (II). A mixture of 1.0 g (6 mmol) of compound **I**, 1.58 g (7.1 mmol) of $(CuOH)_2CO_3$ and 10 ml of water was stirred at room temperature for 48 h. The precipitate was removed by filtration, the filtrate was left at room temperature for slow evaporation of water. Dark blue crystals were formed. Found, %: C 35.41; H 6.85; N 6.68; Cu 15.12. $C_{12}H_{24}N_2O_8Cu\cdot H_2O$. Calculated, %: C 35.48; H 5.91; N 6.89; Cu 15.75. *M* 406.12.

The crystals of complex **II** were investigated by X-ray structural analysis.

Copper complexes bis[*N*-(2-hydroxyethyl)-β-alaninato]copper(II) [Cu(he-ala)$_2$] (**III**), *N*-[tris(hydroxymethyl)methyl]-β-alaninatocopper(II) [Cu$_4$(tris-ala)$_4$] (**IV**), *N*-(2-hydroxyethyl)iminodipropanoato-copper(II) [Cu(he-diala)] (**V**) were prepared along the procedures developed earlier [1–3].

The X-ray structural investigation. The elemental cell parameters and three-dimensional array of intensities of reflexes are obtained for the complex **II** monocrystal of the size 0.23×0.16×0.1 mm on a Xcalibur 3 diffractometer with CCD detector (MoK_α, radiation, graphite monochromator) at the temperature 105(2) K. The crystals of $C_{12}H_{26}CuN_2O_9$ ($M = 405.89$) are triclinic: $a = 8.1755(6)$ Å, $b = 9.4587(6)$ Å, $c =$

11.7994(8) Å, α = 73.845(6)º, β = 83.726(6)°, g = 68.738(7)°, V = 816.72(10) Å^3, Z = 2, ρ_{calc} = 1.65 g cm^{-3}, μ = 1.387 mm^{-1} , F(000) = 426, steric group P1. Totally was registered 7364 reflexes (θ = 2.90°–30.51°, the indices interval $-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $-8 \leq l \leq 16$), of them 4607 independent (R_{int} = 0.0167). Correction for absorption was introduced by numerical method by the crystal shape (T_{min} = 0.607, T_{max} = 0.775).

The structure is decoded by direct method with SHELXS97 program [20] and refined with SHELXL97 program [20] by least square method in anisotropic (isotropic for H atoms) approximation. The hydrogen atoms are revealed from differential syntheses and included to the refinement with the *rider* model in isotropic approximation. The final parameters of refinement are: R_1 = 0.0399, wR_2 = 0.1206 over 3864 reflexes with $I > 2\sigma(I)$, R_1=0.0496, wR_2 = 0.1260 over all reflexes (245 parameters), *GOOF* = 1.002. The maximal and minimal residual electron densities are 0.876 and –0.797 e Å^{-3} respectively. The coordinates of non-hydrogen atoms and respective temperature factors are listed in Table 1, the bond lengths and bond angles in Table 2.

The investigations by means of electron spin resonance spectroscopy. The Electron paramagnetic resonance spectra were registered on an ESR spectrometer PS 100.X produced by ADANI (Republic Belarus') in a wide temperature range. The samples for investigation were prepared by dissolving crystals of complexone in distilled water and varying pH of the mixture of aqueous solutions of copper nitrate and the complexone. The measurements were carried out using water–alcohol ($H_2O : CH_3OH$ = 1:1) solutions with the copper ion concentration 5×10^{-3} mol l^{-1} at 77 K in glassy state.

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