Copper(II) complexes with *N*-(2-carboxyethyl)anthranilic acid H_2CEAnt. Synthesis and crystal structure of $[Cu(CEAnt)(H_2O)] \cdot H_2O$

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Protolytic equilibria and complexation of *N*-(2-carboxyethyl)anthranilic acid (H_2CEAnt) with copper(II) ions in aqueous solutions were studied by UV spectroscopy and pH potentiometry. The H_2CEAnt compound has no zwitterionic structure, and the protons are localized on the carboxy groups. The acid ionization constants of H_3CEAnt^+ ($T = 25$ °C, $I = 0.1$ *M* KNO_3) are $pK_0 = 1.3 \pm 0.2$ ($=NH_2^+$), $pK_1 = 3.88 \pm 0.02$ (Alk—COOH), and $pK_2 = 5.28 \pm 0.02$ (Ar—COOH). The model of complexation of H_2CEAnt with copper(II) ions involves two deprotonated complexes $[Cu(CEAnt)]$ and $[Cu(CEAnt)_2]^{2-}$ ($\log\beta = 6.31 \pm 0.04$ and 8.0 ± 0.2, respectively). The $[Cu(CEAnt)(H_2O)] \cdot H_2O$ complex was synthesized by the reaction of H_2CEAnt with $(CuOH)_2CO_3$, and its structure was established by X-ray diffraction. The coordination polyhedron of Cu is intermediate between the tetragonal pyramid and trigonal bipyramid. The $CEAnt^{2-}$ ligand serves as a tetradentate chelating bridging ligand (Cu—O, 1.944(3) and 1.950(3) Å; Cu—O′, 2.195(4) Å; Cu—N, 2.016(5) Å), and the fifth position of the polyhedron is occupied by a water molecule (Cu—O_w, 1.976(4) Å).

Key words: *N*-(2-carboxyethyl)anthranilic acid, β-alanine, aza-Michael reaction, acid ionization constants, copper(II) complexes, crystal structure.

The present study is part of systematic investigation of the coordination ability of *N*-substituted aromatic β-amino acids[1—5] and is aimed at investigating the acid-base equilibria, compositions, stability, and structures of the complexes of *N*-(2-carboxyethyl)anthranilic acid (H_2CEAnt) with copper(II) ions in aqueous solutions and in the crystalline state.

The new ligand contains anthranilic acid as the main structural fragment. This acid has long been used for the spectrophotometric[6—8] and potentiometric[9] determination of various metals. Anthranilic acid by itself is not a selective agent, and selectivity of analytical reactions is achieved by performing determination under specific conditions (preseparation, masking, pH, *etc.*). Complexes of anthranilic acid with copper(II) ions possess biological activity. For example, although anthranilic acid exhibits no antiinflammatory activity, it acquires the ability to exhibit activity due to specific binding of copper(II) ions at inflammatory sites.[10,11]

Earlier,[1,5,12] the introduction of β-carboxyethyl groups into aromatic amines has been demonstrated to enhance, on the whole, the selectivity of complex formation with copper(II) ions and increase the stability of the resulting complexes. Hence, one would expect H_2CEAnt, which is produced by carboxyethylation of anthranilic acid, to react with copper(II) ions more selectively than the starting anthranilic acid.

Experimental

The ^1H NMR spectra were recorded on an Avance DRX-400 spectrometer (DMSO—CCl_4) operating at 400 MHz with Me_4Si as the internal standard. The UV-Vis absorption spectra were measured on Shimadzu UV-3101PC and SF-46 spectrophotometers. Elemental analysis was carried out on a Carlo Erba EA 1108 automated analyzer at the Institute of Organic Synthesis of the Ural Branch of the Russian Academy of Sciences.

Potentiometric titration was carried out on a Crison MicropH 2002 pH-meter equipped with glass (Russel SWL/S7) and silver-chloride (Orion 90-02-00) electrodes under nitrogen (free of CO_2 and O_2) at an ionic strength $\mu = 0.1$ *M* KNO_3 and at 25.0 ± 0.1 °C. The pH-meter was connected to a PC through an RS232C interface. The parameters of the system were controlled

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using a program written in QuickBasic (Microsoft Corporation, version 7.0). The electrode system was calibrated against the proton concentration using buffer solutions with an ionic strength of 0.1 (KNO_3 additive) according to recommendations.[13] A carbonate-free 0.1 *M* KOH solution was used as the titrant. The acid ionization constants were determined from the titration curves of $5 \cdot 10^{-3}$ *M* H_2CEAnt solutions containing an equimolar amount of nitric acid (0.1000 *M* HNO_3, E. Merck 9964). The stability constants were determined by titration of $5 \cdot 10^{-3}$ *M* H_2CEAnt solutions, the $Cu(NO_3)_2$ concentration (0.1000±0.0005 *M* solution, Orion 942906) being varied in the CEAnt : Cu ratio range from 2 : 1 to 1 : 2. The acid ionization constants and the complexation constants were calculated using the SUPERQUAD program.[14]

Synthesis of the ligand.[15] Anthranilic acid of analytical grade (8.22 g, 0.06 mol), acrylic acid (E. Merck 8.00181) (8.6 mL, 0.12 mol), acetonitrile of reagent grade (70 mL), and hydroquinone of analytical grade (~0.1 g) were placed in a 500 mL round-bottom flask equipped with a reflux condenser. The reaction mixture was refluxed for 12 h. After one day, a gray powdered precipitate was obtained in a yield of 6.0 g (48%). The precipitate was filtered off and twice recrystallized from water, m.p. 182 °C (DTA). According to the results of pH-metric titration, the percentage of the acid was at least 98%. Found (%): C, 57.42; H, 5.35; N, 6.71. $C_{10}H_{11}NO_4$. Calculated (%): C, 57.41; H, 5.30; N, 6.70. ^{1}H NMR (DMSO—CCl_4), δ: 2.53 (t, 2 H, —CH_2COOH, J = 6.7 Hz); 3.44 (t, 2 H, —NH—CH_2—, J = 6.7 Hz); 3.82 (s, 1 H, =NH); 6.52 (m, 1 H, H(4)); 6.69 (d, 1 H, H(6), J = 7.9 Hz); 7.31 (m, 1 H, H(5)); 7.78 (dd, 1 H, H(3), J_{AB} = 7.9 Hz, J_{AX} = 1.7 Hz); 7.92 (br.s, 1 H, Ar—COOH); 12.15 (br.s, 1 H, Alk—COOH).

Synthesis of the [Cu(CEAnt)(H_2O)]·H_2O complex (1). A weighed sample (1 g) of H_2CEAnt was dissolved in water (30 ml) on heating, and then an excess of $(CuOH)_2CO_3$ was added until carbon dioxide ceased to evolve. Green crystals of Cu(CEAnt)·$2H_2O$ precipitated from the solution. Found (%): C, 39.57; H, 4.49; N, 4.54. $C_{10}H_{13}NO_6Cu$. Calculated (%): C, 39.15; H, 4.27; N, 4.57.

Table 1. Crystallographic data and details of X-ray diffraction study

Parameter	Characteristic
Molecular formula	$C_{10}H_{13}CuNO_6$
Molecular weight	306.75
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	11.8629(11)
b/Å	13.3850(18)
c/Å	7.3569(7)
β/deg	104.869(7)
V/Å^3	1129.0(2)
Z	4
d_{calc}/g cm^{-3}	1.805
μ/mm^{-1}	1.955
Scan range/deg	1.78—24.96
Number of measured reflections (R_{int})	2150 (0.0356)
Number of reflections with $I \geq 2\sigma(I)$	1108
Number of parameters in refinement	179
R_1 ($I \geq 2\sigma(I)$)	0.0345
wR_2 (based on all reflections)	0.0666

X-ray diffraction analysis. X-ray diffraction data were collected from a single crystal of complex **1** (green platelet of dimensions 0.35×0.30×0.05 mm) on an automated four-circle Nonius CAD4 diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, 293 K, θ/2θ scanning technique). The crystallographic data and details of structure refinement are given in Table 1. No absorption correction was applied because of the low absorption coefficient. The structure was solved by direct methods and refined by the full-matrix least-squares method. The nonhydrogen atoms were refined first isotropically and then anisotropically. The H atoms were refined isotropically. The positions of the hydrogen atoms were located from difference electron density maps and refined with geometric constraints. All calculations were carried out with the use of the SHELX97 program package.[16]

Results and Discussion

Protolytic equilibria of H_2CEAnt in aqueous solution

N-(2-Carboxyethyl)anthranilic acid H_2CEAnt has amphoteric properties and is involved in the following equilibria in solution:

$$CEAnt^{2-} + H_3O^+ \overset{K_{1H}}{\rightleftharpoons} HCEAnt^- + H_2O,$$

$$HCEAnt^- + H_3O^+ \overset{K_{2H}}{\rightleftharpoons} H_2CEAnt + H_2O,$$

$$H_2CEAnt + H_3O^+ \overset{K_{3H}}{\rightleftharpoons} H_3CEAnt^+ + H_2O.$$

The protonation constants determined from pH-potentiometric titration are given in Table 2 in comparison with the constants of related compounds, *viz.*, benzoate ($Benz^-$),[17] anthranilate (Ant^-),[10] *N*-(carboxymethyl)anthranilate ($CMAnt^{2-}$),[18] and *N*-(2-carbamoylethyl)anthranilate ($CmEant^-$).[19]

To relate these protonation constants to the corresponding constants of the functional groups of the ligand, we additionally used the UV spectrophotometric method. The characteristic spectra of CEAnt at different acidities are shown in Fig. 1. One of the pH dependences of absorbance at a fixed wavelength is presented in Fig. 2 (curve *1*). The presence of two steps in the latter curve allowed us to determine only two (of three possible) constants characterizing protonation of the amino and carboxylate groups directly conjugated with the benzene chromophore. The calculated protonation constants are given in Table 2.

A comparison of the constants evaluated by two methods shows that the constant K_{2H} was not determined by spectrophotometry. Hence, this constant presumably corresponds to protonation of the aliphatic carboxylate group. Taking into account that the constant $\log K_{1H}$ of $CEAnt^{2-}$ is similar to the corresponding constants of benzoate, anthranilate, and *N*-(2-carbamoylethyl)anthranilate (see Table 2), it can be assigned to protonation of the aromatic

Table 2. Equlibrium constants for $p\ Cu^{2+} + q\ H^+ + r\ L \rightleftharpoons Cu_pH_qL_r$

Ligand L	*p*	*q*	*r*	logβ_{pqr}	logK_{pqr}	*T*/°C	μ/mol L^{-1}	Method[a]	References
CEAnt^{2-}	0	1	1	5.28±0.02	5.28	25	0.1 KNO_3	PM	[b]
	0	2	1	9.16±0.02	3.88				
	0	3	1	10.5±0.2	1.3				
	1	0	1	6.31±0.04	6.31				
	1	0	2	8.0±0.2	1.7				
CEAnt^{2-}	0	1	1		5.23±0.06	20	0.1 KCl	SP	[b]
	0	3	1		1.5±0.10				
	1	0	1	6.44	6.44±0.15				
Benz$^-$	0	1	1	4.210	4.210	25	0.1 KNO_3	PM	17
Ant$^-$	0	1	1	4.679	4.679	37	0.15 NaCl	PM	10
	0	1	2	6.865	2.186				
	1	0	1	3.696	3.696				
	1	1	1	6.36	1.68				
	1	0	2	6.45	2.76				
CMAnt^{2-}	0	1	1	4.90	4.90	25	0.1 KNO_3	PM	18
	0	2	1	8.20	3.30				
	1	0	1	6.65	6.65				
CmEAnt$^-$	0	1	1	4.623	4.623	25	0.1 KNO_3	PM	19
	0	2	1	5.8—6.5	1.2—1.9				
	1	0	1	4.02	4.02				
	1	0	2	6.02	2.00				

[a] PM is potentiometry and SP is spectrophotometry.
[b] The present study.

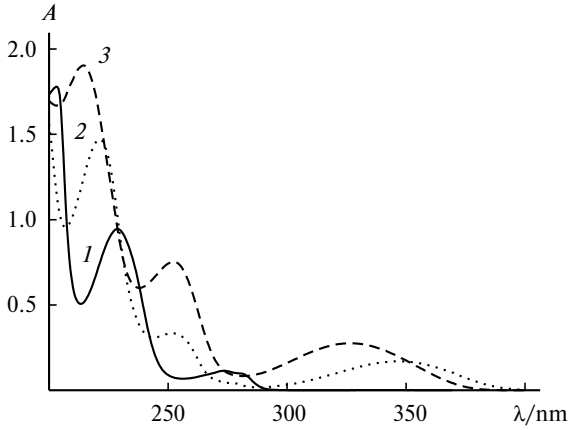


Fig. 1. UV-Vis absorption spectra of aqueous solutions of CEAnt at C_{HCl} = 1 mol L^{-1} (*1*), pH 4.0 (*2*), pH 8.0 (*3*); C_{CEAnt} = $1.0 \cdot 10^{-4}$ mol L^{-1}, *l* = 1.0 cm.

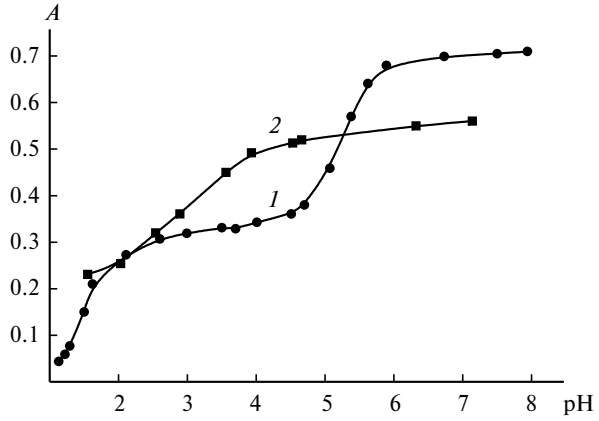


Fig. 2. Plots of absorbance of CEAnt solutions *vs.* pH in the absence (*1*) and in the presence of an equimolar amount of $CuCl_2$ (*2*); C_{CEAnt} = $1.0 \cdot 10^{-4}$ mol L^{-1}, λ = 250 nm, μ = 0.1 mol L^{-1} KCl, *l* = 1.0 cm.

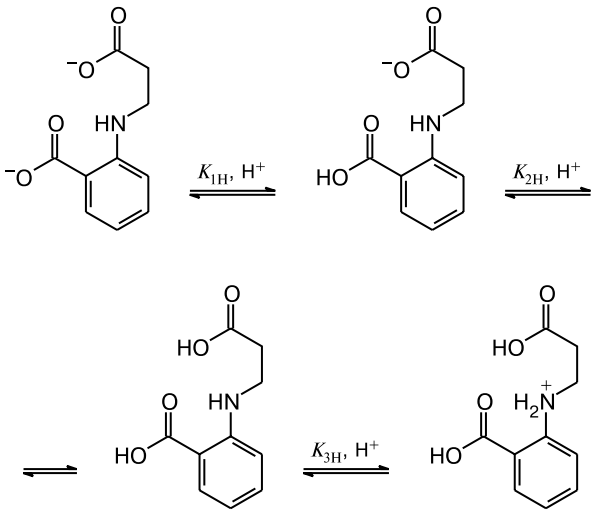
carboxylate group. Hence, it can be concluded that H_2CEAnt has no zwitterionic structure characteristic of most amino acids, the Ar—COO$^-$ is the most basic group of the ligand, and the amino group possesses the lowest basicity (Scheme 1).

The absence of the zwitterionic structure in the ligand under consideration is evidenced also by X-ray diffraction data for the crystals of anthranilic acid,[20] according to which the proton is attached to the carboxylate group and is not involved in hydrogen bonds with the amino group.

Complexation of Cu^{II} with CEAnt in aqueous solution

The stability constants of the complexes were determined from pH-potentiometric titration of aqueous solutions containing H_2CEAnt, $Cu(NO_3)_2$, and KNO_3. The Cu : CEAnt ratio was varied from 0.5 to 2. Since the constant K_{3H} was determined potentiometrically with insufficient accuracy, its value was included in the refinement when calculating the stability constants. The model

Scheme 1



of complexation, which is in best agreement with the experimental data, includes two mononuclear complexes, [Cu(CEAnt)] and $[Cu(CEAnt)_2]^{2-}$. The stability constants are given in Table 2 along with the constants of selected related ligands. In spite of the very low basicity of the amino group, the stability constant of the [Cu(CEAnt)] complex is rather high and is almost two orders of magnitude higher than those of analogous complexes with $Anth^-$ or $CmEAnt^-$ (see Table 2), in which only the anthranilate fragment is involved in complex formation. This indicates that the carboxyethyl group is also involved in complexation resulting in the formation of the β-alaninate chelate ring. A comparison of the stability constants of the [Cu(CMAnt)] and [Cu(CEAnt)] complexes formed by ligands of the same homologous series shows that the replacement of the five-membered glycinate chelate ring in CMAnt with the six-membered β-alaninate ring in CEAnt leads to only a slight decrease in the stability constant of the complex ($\Delta\log K_1 = 0.3$, see Table 2).

Analysis of the species distribution diagram (*vs.* pH) for the system under consideration (Fig. 3) shows that the major complex in the system is [Cu(CEAnt)]. The fraction of the $[Cu(CEAnt)_2]^{2-}$ complex (omitted in the diagram) is insignificant and is at most 10% under the titration conditions (in the presence of an excess of the ligand), which casts doubt on its presence in the system.

To obtain additional information, we recorded UV-Vis absorption spectra of aqueous solutions in the Cu^{II}—CEAnt system and the UV spectra of this system at an equimolar ratio of the components (Fig. 4). Figure 2 (curve *2*) shows one of the pH dependences at a fixed wavelength. Study of the compositions of the complexes by the method of continuous variation and the method of molar ratio demonstrated that the ratio of the components in the complex is 1 : 1. The stability constant of the

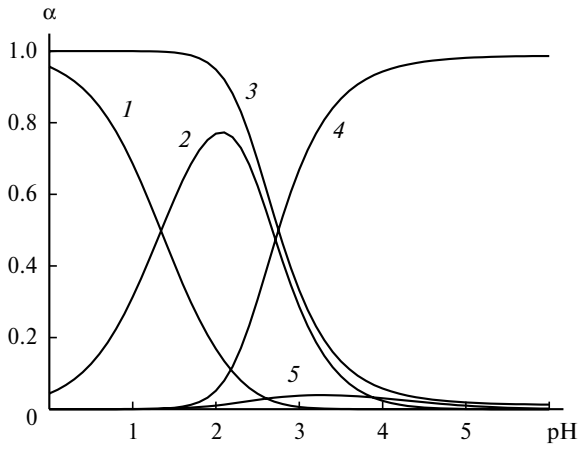


Fig. 3. Species distribution diagram as a function of pH for the Cu^{II}—CEAnt system, $C_{Cu} = C_{CEAnt} = 5 \cdot 10^{-3}$ mol L^{-1} (μ = 0.1 mol L^{-1} KNO_3, 25 °C): *1*, H_3CEAnt^+; *2*, H_2CEAnt; *3*, Cu^{II}; *4*, [Cu^{II}(CEAnt)]; 5, H_2CEAnt^-.

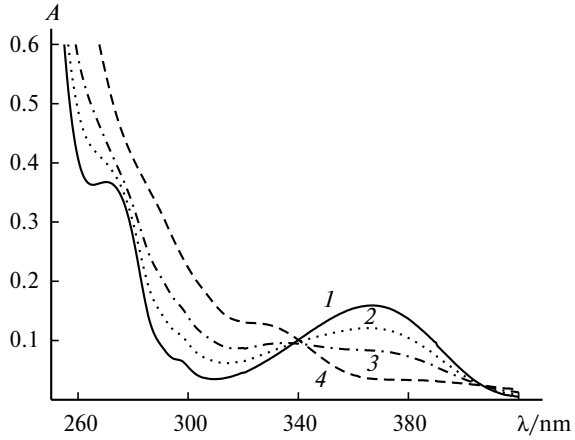


Fig. 4. UV-Vis absorption spectra of aqueous solutions containing equimolar amounts of CEAnt and $CuCl_2$, at pH 3.00 (*1*), 3.36 (*2*), 3.67 (*3*), and 5.34 (*4*); $C_{CEAnt} = 1.0 \cdot 10^{-4}$ mol L^{-1}, $l = 1.0$ cm.

[Cu(CEAnt)] complex determined from these data (see Table 2) agrees well with the value determined by potentiometry. Since the $[Cu(CEAnt)_2]^{2-}$ complex is rather unstable, it can be detected in the presence of a large excess of the ligand only; however, the UV spectra measured for this system become noninformative because of high intrinsic absorption of CEAnt.

The visible spectrum is free of the CEAnt intrinsic absorption. Hence, the spectra allow one to estimate the environment of the central ion even in the presence of a large excess of the ligand. The spectra were recorded with the use of $CuSO_4$ solutions, because sulfate ions do not form complexes with copper(II) ions,[21] and the solution contains predominantly the hexaaqua cations $[Cu(H_2O)_6]^{2+}$. The absorption spectrum of a solution containing equimolar amounts of $CuSO_4$ and CEAnt at pH 6.0

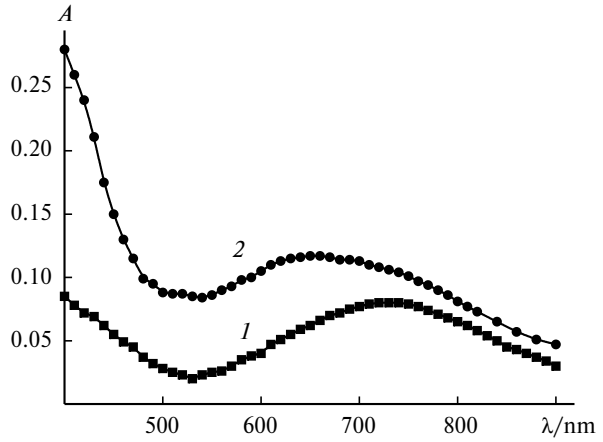


Fig. 5. UV-Vis absorption spectra of aqueous solutions containing $CuSO_4$ and CEAnt in ratios of 1 : 1 (*1*) and 1 : 100 (*2*); $C_{CuSO_4} = 2.0 \cdot 10^{-3}$ mol L^{-1}, pH 6.0, $l = 1.0$ cm.

is shown in Fig. 5 (curve *1*). Under these conditions, the 1 : 1 complex occurs as the major component. The molar fractions of the complexes calculated from the stability constants are α[Cu(CEAnt)] = 0.98 and $\alpha[Cu(CEAnt)_2]^{2-} = 0.001$. The complexation is manifested in the blue shift and hyperchromism of the d→d absorption band compared to $[Cu(H_2O)_6]^{2+}$ ($\lambda = 810$ nm, $\varepsilon = 10$ L mol cm^{-1}).[21] The blue shift and the intensity of the absorption maximum increase with increasing concentration of the ligand to the ratio Cu : CEAnt = 1 : 100 (α[Cu(CEAnt)] = 0.11, $\alpha[Cu(CEAnt)_2]^{2-} = 0.89$) (see Fig. 5, curve *2*), which is indicative of structural changes associated with the formation of a complex species with a metal : ligand ratio of 1 : 2. Therefore, in spite of low stability, the formation of a complex with an excess of the ligand is quite possible.

Crystal and molecular structure of complex 1

To reveal the coordination mode and the structure-forming role of the ligand in complex **1** when passing from solution to the solid state, we performed a single-crystal X-ray diffraction study of **1**. The crystal structure of **1** is composed of the [Cu(CEAnt)(H_2O)] complex molecules (Fig. 6) and the uncoordinated H_2O molecules in a ratio of 1 : 1. Selected bond lengths and bond angles are given in Table 3.

The coordination polyhedron of the Cu atom in complex **1** is intermediate between the tetragonal pyramid and trigonal bipyramid. The factor $\tau = 100(\alpha - \beta)/60 = 44.9\%$ (α and β are the O(1)—Cu(1)—O(3) and O(1W)—Cu(1)—N(1) angles,[22] respectively), which characterizes the trigonal-bipyramidal distortion, has an intermediate value (0 for the tetragonal pyramid and 100% for the trigonal bipyramid). However, the polyhedron can be described as a strongly distorted tetragonal pyramid

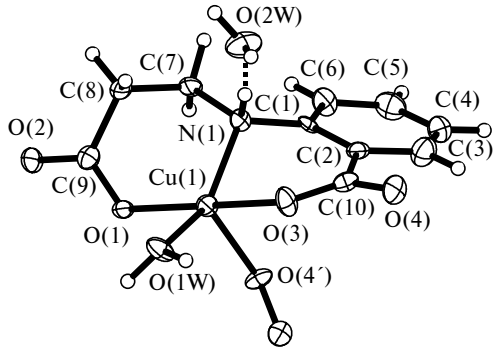


Fig. 6. Structure and the atomic numbering scheme in complex **1**.

Table 3. Selected bond lengths (*d*) and bond angles (ω) in molecule **1**

Bond	*d*/Å	Angle	ω/deg
Cu(1)—N(1)	2.016(5)	N(1)—Cu(1)—O(4)*	98.90(16)
Cu(1)—O(1)	1.944(3)	O(1)—Cu(1)—N(1)	95.40(16)
Cu(1)—O(3)	1.950(3)	O(1)—Cu(1)—O(3)	175.19(15)
Cu(1)—O(4)*	2.195(4)	O(1)—Cu(1)—O(4)*	94.19(14)
Cu(1)—O(1W)	1.976(4)	O(1)—Cu(1)—O(1W)	88.57(15)
		O(3)—Cu(1)—N(1)	87.02(16)
		O(3)—Cu(1)—O(4)*	89.52(14)
		O(3)—Cu(1)—O(1W)	87.20(15)
		O(1W)—Cu(1)—N(1)	148.24(17)
		O(1W)—Cu(1)—O(4)*	112.25(15)

* The symmetry operation: x, $3/2 - y$, $z - 1/2$.

with the basal plane formed by the O atoms of the water molecule and two carboxylate groups and the N atom of the amino group of the CEAnt ligand. The apex of the pyramid is occupied by the carbonyl O atom of the adjacent complex through which the pyramids are linked to form chains running along the [001] direction.

Therefore, the CEAnt molecule in complex **1** serves as a tetradentate chelating bridging ligand, which forms two six-membered chelate rings (β-alaninate and anthranilate) and links the complex molecules to form infinite chains through the coordination bonds between the carbonyl O atom of the anthranilate moiety and the Cu atom of the adjacent complex.

The conformation of the β-alaninate ring Cu(1)—O(1)—C(9)—C(8)—C(7)—N(1) is more consistent with the *twist* form T_{36} (notations were proposed in the study;[23] the indices are the numbers of atoms, which are not involved in distortion of the planar ring). The Cremer—Pople puckering parameters[24] are: $Q = 0.739$ Å, $\theta = 78.8°$, $\varphi = 22.8°$. The rather large value of Q is indicative of a high degree of ring puckering. This is also evidenced by the sum of the endocyclic angles (670.1°, the ideal value is 648° = 120 + (109.5 · 4) + 90), which is smaller than the value usually observed for the copper(II)

β-alaninate rings.[2] The conformation of the anthranilate ring Cu(1)—O(3)—C(10)—C(2)—C(1)—N(1) is determined by the adjacent Cu(1) and O(3) atoms deviating in the same direction from the C(10)C(2)C(1)N(1) plane by 1.268 and 0.440 Å, respectively. The ring puckering parameters are $Q = 0.620$ Å, $\theta = 118.8°$, $\varphi = 151.9°$.

In the crystal of **1**, the chains are located at two levels along the *y* axis, and their packing follows Kitaigorodskii's principle.[25] The outer-sphere H_2O molecules occupy the cavities between the chains and link the chain units as well as the chains by themselves through a hydrogen bond network (O(1)···O(2W), 2.902(6) Å; N(1)···O(2W), 2.814(6) Å; O(3)···O(2W), 3.040(6) Å).

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