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Direct Evidence of Coordination on the Endocyclic Nitrogen Atom in the Adducts of 2-Aminoazoles and 2-Aminoazines with Copper(II) Acetate

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Abstract

The coordinative bond has been shown by X-ray structure analysis to be localized at the endocyclic nitrogen atom of pyridine type in the adducts of copper(II) acetate of the composition $[Cu(CH_3COO)_2L]_2$ where L = 2-aminopyridine or 2-aminothiazole and $Cu(CH_3COO)_2 \cdot 2L$ where L = 2-amino-1-methylbenzimidazole or 2-amino-1-heptylbenzimidazole.

The lowering of the stretching vibration frequencies of the primary amino group in the IR spectra of complex compounds with Lewis acids used earlier as a test for coordination on the exocyclic nitrogen atom is actually caused by the realization of intra- and intermolecular hydrogen bonds in the compounds studied.

Introduction

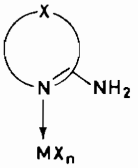
The problem of the pattern of coordinative bond localization in the complex compounds of 2-aminoderivatives of five- and six-membered heterocycles is open to discussion up to now. Although the metal binding to the endocyclic nitrogen atom of the heterocycle (**I**) is considered to be the most real process [1–7], the possibility of a coordination on the amino group nitrogen atom (**II**) [8–12] or other nucleophilic centers (**III**) [13, 14] has not been excluded.

The IR spectral test is usually applied as an evidence for the pattern of localization of the coordinative bond (**I**–**III**). The lowering of the frequencies of amino group stretching vibrations (3200–3500 cm^{-1}) in the complexes in comparison with the free ligands is considered as sign of participance of the primary amino group in the coordination (**II**). The raising or the constancy of the position of these frequencies often serves as the basis for the conclusion in favour of the localization of the coordinative bond on the endocyclic nitrogen atom (**I**) or on another nucleophilic center of the heteroring (**III**). However, as will be shown later, the IR spectral test is not reliable and is connected with some other effects. The origin of these and the pattern of the coordination bond localization have been elucidated by us with the aid of a comparison of the IR spectral data and the results of an X-ray structure analysis of the series of 2-amino heterocycles in their adducts with copper(II) acetate.

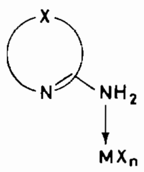
Results and Discussion

The complexes between 2-aminoderivatives of azines and azoles (**IV**, **V**, **VI**) and copper(II) acetate have been synthesised in methanol or ethanol media and have the compositions $[Cu(CH_3COO)_2L]_2$ (L = **IV**, **V**) and $Cu(CH_3COO)_2 \cdot 2L$ (L = **VI**).

Dimeric complexes (L = **IV**, **V**) are characterized by antiferromagnetic interaction typical of the majority of copper(II) acetate adducts [15, 16] (parameter of exchange interaction is equal to 250



I



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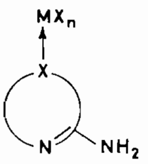

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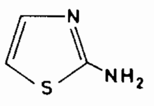

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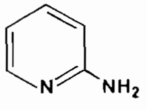
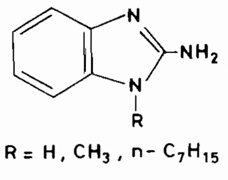


V



VI

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TABLE 1. Position of amino group stretching vibration frequencies in 2-aminoheterocyclic ligands (L = IV, V, VI) and complexes (the LiF prism region)

Ligand	Frequencies (cm^{-1})	Complex	Frequencies (cm^{-1})
IV	3179, 3306, 3451	$Cu_2(OAc)_4 \cdot 2L$	3212, 3315, 3400
V	3181, 3311, 3445	$Cu_2(OAc)_4 \cdot 2L$	3220, 3311, 3487
VI, R = H	3172, 3321, 3451	$Cu(OAc)_2 \cdot 2L$	3219, 3330, 3479
VI, R = CH_3	3225, 3460	$Cu(OAc)_2 \cdot 2L$	3289, 3431
VI, R = C_7H_{15}	3164, 3339	$Cu(OAc)_2 \cdot 2L$	3098, 3241

cm^{-1} for L = IV and 298 cm^{-1} for L = V), the monomeric ones have the near spin values of effective magnetic moments (see 'Experimental').

A comparison of the amino group stretching vibration frequencies in the IR spectra of complexes and the corresponding free heterocyclic amines leads to the conclusion in favour of coordination both on endo- and exocyclic nitrogen atoms (Table 1). Indeed, the lowering of NH_2 group stretching vibration frequencies in comparison with uncoordinated heterocyclic ligands takes place in the case of copper(II) acetate adducts with 2-aminobenzimidazoles (VI, R = Alk). This fact has been used for the interpretation of coordination on the exocyclic nitrogen atom [8–12]. Meanwhile, the raising of the frequencies mentioned takes place for the similar adduct of copper(II) acetate with 2-aminopyridine which is indicative of metal binding with the ring nitrogen atom. These shifts have been measured relative to the position of vibration frequencies in the 2-aminoheterocyclic ligands, whose IR spectra have been recorded in vaseline oil where the vibrations of the amino group associated by the hydrogen bond are revealed. This fact is the reason for substantial lowering of the amino group stretching vibrations. Thus, these frequencies are observed in the region 3400–

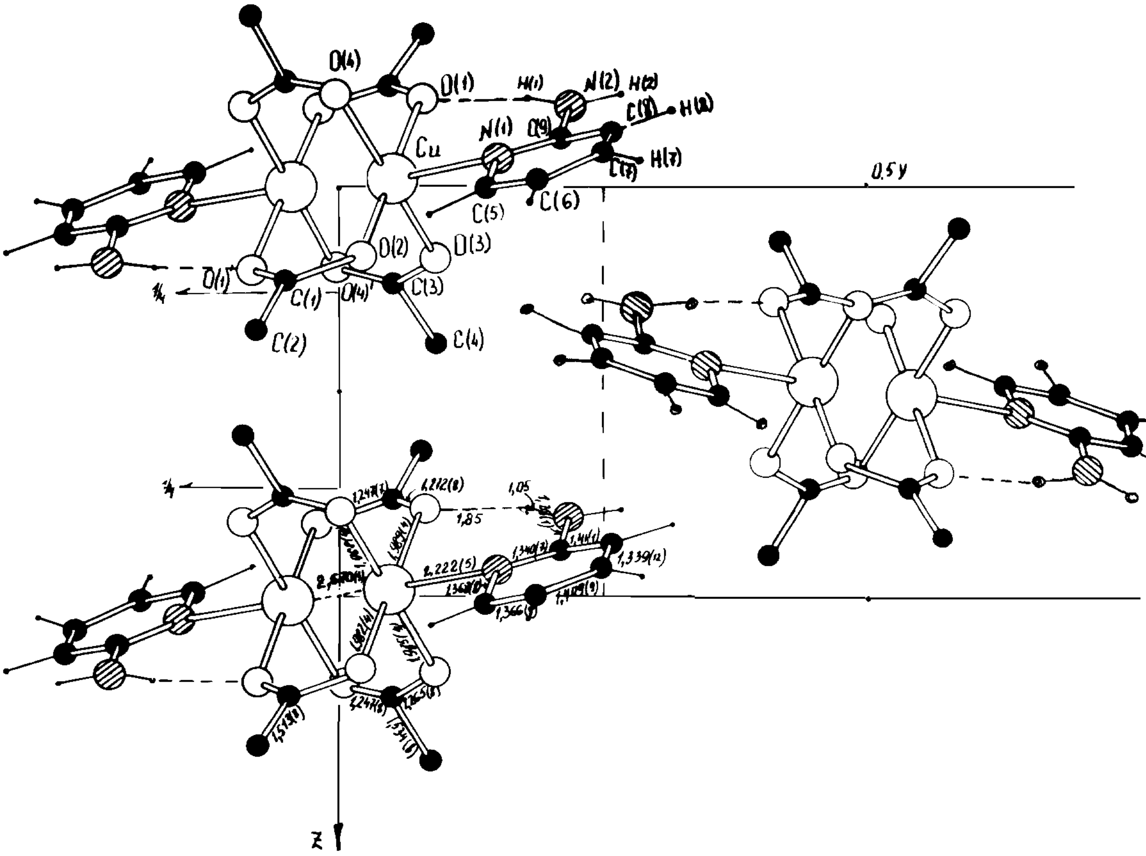

Fig. 1. Projection $\frac{1}{2}$ of the elementary cell of the structure of $[Cu(OAc)_2(NH_2{-}C_5H_4N)]_2$ along the [100] direction.

3500 cm^{-1} in the IR spectra of non-associated 2-aminothiazoles and -azines measured in carbon tetrachloride [17]. An analogous high-frequency shift is typical of the stretching vibrations of 2-aminothiazoles (IV) and 2-amino-1-alkylbenzimidazoles (VI) with absorption maxima at 3460 and 3470 cm^{-1}, respectively (measured by us in $C_2H_2Cl_4$).

A comparison of these frequencies and the position of amino group stretching vibrations of the complexes (Table 1) testifies to their lowering in the process of complex formation. This result being in accordance with the literature data [8, 12] seems to lead to the conclusion as to the localization of the coordinative bond at the exocyclic nitrogen atom in the complexes with copper(II) acetate.

However, this inference contradicts the X-ray structure analysis data.

The X-ray structural investigation of complexes between copper(II) acetate and 2-aminoderivatives of pyridine, thiazole and benzimidazole has shown that both dimeric complexes $[Cu(CH_3COO)_2L]_2$ (L = IV, V) and monomeric complexes (L = VI) have molecular structures. Coordination is realized at the endocyclic nitrogen atom of the heteroring in all the cases. The configuration of corresponding molecules is shown in Figs. 1–5. The ligand L is an axial one and is located at distances of 2.16–2.22 Å in dimeric complexes with 'lantern' structure. The monomeric molecules contain two benzimidazole ligands in the *cis* position with respect to each other, the distance Cu–N being 1.95–2.05 Å.

In the structures of both types the nitrogen atoms of the NH_2 fragment are oriented with respect to one of the oxygen atoms of the CH_3COO groups in such a manner that the distance N...O 2.8–2.9 Å allows us to assume the intramolecular hydrogen bond N–H...O. Indeed, one of the hydrogen atoms of the NH_2 group in the structure $[Cu(CH_3COO)_2L]_2$ (L = IV, V) (hydrogen atoms are localized on the corresponding zero Fourier syntheses) takes part in the N–H...O hydrogen bond having the following parameters: N–H 1.06 and 0.86, H...O 1.84 and 2.13, N...O 2.86 and 2.92 Å, and the NHO angle of 162 and 156° for the first and second structures, respectively. Participance of the second hydrogen atom of the NH_2 framework in an intermolecular hydrogen bond is not excluded.

Taking into account the structural data, we may infer that the lowering of the stretching vibration frequencies in the region of the primary NH_2 group

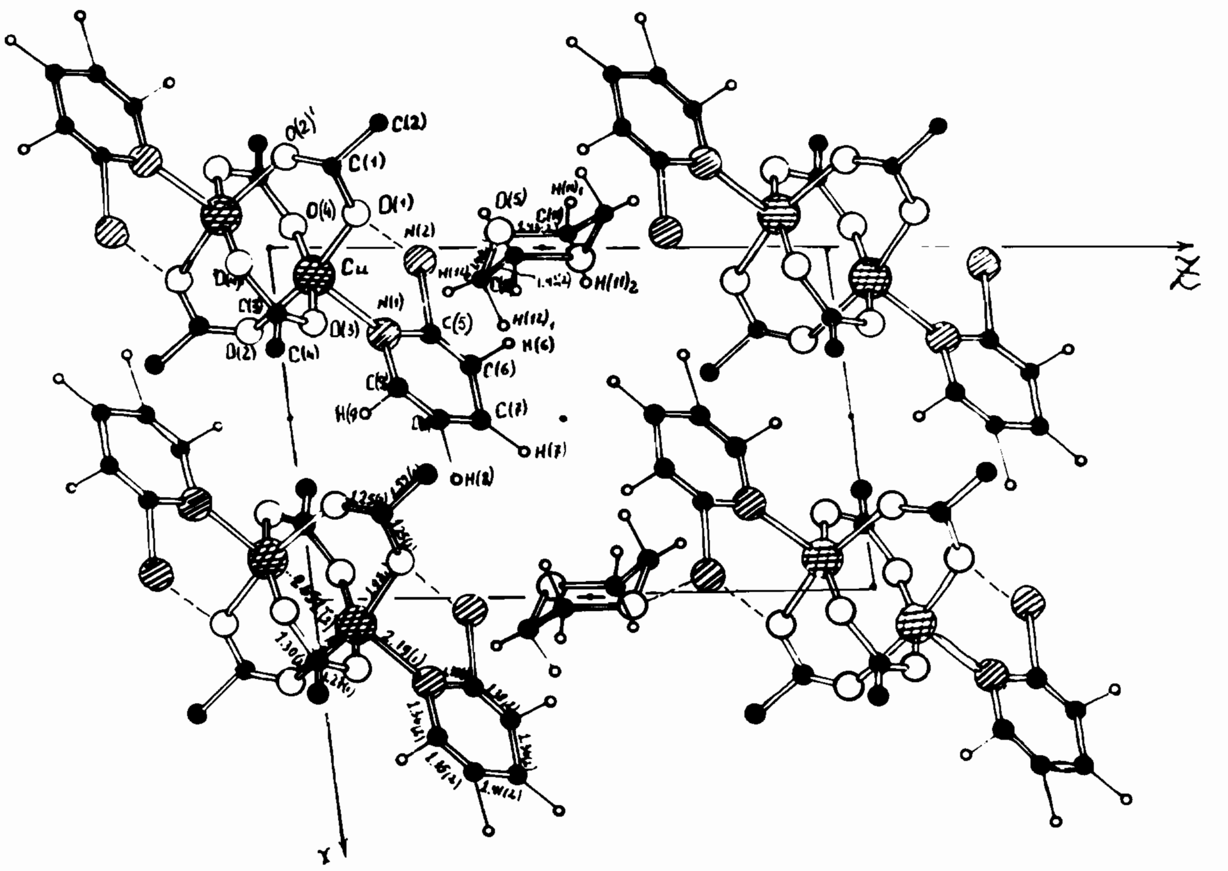

Fig. 2. Projection of the elementary cell of the structure of $[Cu(OAc)_2(NH_2{-}C_5H_4N)]_2{\cdot}0.5C_4H_8O_2$ along the [010] direction.

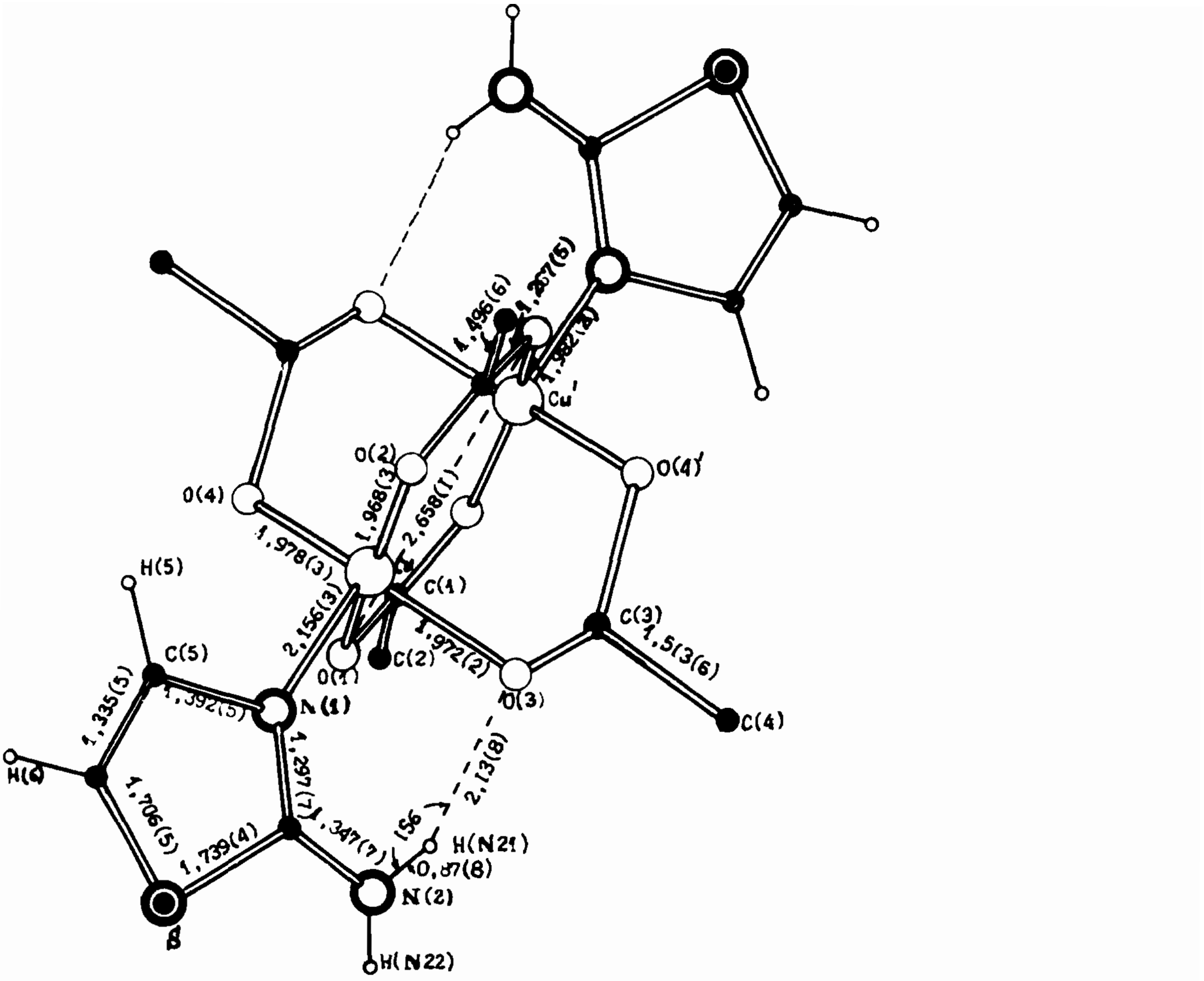

Fig. 3. Configuration of dimeric molecule $[Cu(OAc)_2(NH_2{-}C_3H_2NS)]_2$.

($3200{-}3500\ cm^{-1}$) is caused by the intramolecular (and intermolecular) hydrogen bond formed by the hydrogen atom of the NH_2 fragment and the anion of Lewis acid.

Although formation of hydrogen bonds in complex compounds of heterocyclic amines has been mentioned earlier [18, 19] and a comparison of IR and X-ray structural data has been made [20], the detailed analysis of the reasons for the lowering of amino group stretching vibration frequencies has been carried out by us for the first time (see also refs. 21–23).

The whole complex of the results testifies to the monodentate nature of 2-aminoazoles and 2-aminoazines, the metal being bonded to the endocyclic nitrogen atom.

Experimental

IR Spectra

IR spectra of complexes and corresponding heterocycles were recorded on the UR-20 Zeiss spectrometer as suspensions in vaseline oil in the region of $400{-}4000\ cm^{-1}$. Calibration of the spectrometer was made using polystyrene.

X-ray Structure

X-ray structural analysis was performed on monocrystal samples of corresponding compounds. The intensity of the reflections was measured using a Syntex $P2_1$ autodiffractometer on monochromatized Mo Kα radiation. The measurements were made by the method of $\theta/2$ scanning up to the angles $2\theta_{max}$ = 45–60°. Absorption was taken into account by azimuthal scanning of 4–5 reflections.

The structures were investigated by the heavy atom method using the analysis of Patterson and Fourier distributions. Specification has been made by the full-matrix least-squares method in isotropic and anisotropic approximations. The computations have been fulfilled using the program complex XTL-SYNTEX for the NOVA-1200 computer and the program SHELX for the ES-1060 computer.

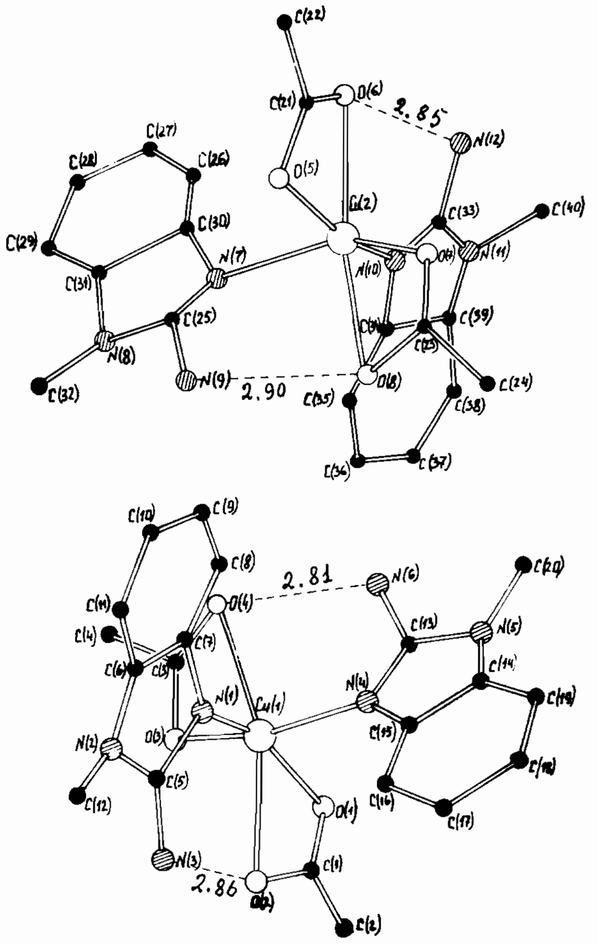

Fig. 4. Configuration of two independent molecules in the structure of $[Cu(OAc)_2(C_6H_4N_2(CH_3)C{-}NH_2)_2]$.

Bis-(2-aminopyridine)-tetraacetato-di-copper(II)

Monoclinic syngony: $a = 7.433(3)$, $b = 19.563(4)$, $c = 8.101(3)$ Å; $\beta = 114.23°$ space group $P^2I/c, Z = 2$, structural class $P2_I/c$, $Z = 2$ (I) (dimeric molecules).

Bis-(2-aminopyridine)-tetraacetato-di-copper(II) dioxane

Triclinic syngony: $a = 7.356(2)$, $b = 8.122(2)$, $c = 12.293(2)$ Å, $\alpha = 74.26(2)$, $\beta = 92.31(2)$, $\gamma = 82.88(2)°$; space group PI, $Z = 2$, structural class PI, $Z = 1$ (I) (dimeric molecules).

Bis-(2-aminothiazole)-tetraacetato-di-copper(II)

Monoclinic syngony: $a = 9.144(2), b = 8.467(2), c = 14.546(2)$ Å, $\beta = 106.91(2)°$; space group $P^2I/n, Z = 2$, structural class $P2_I/n$, $Z = 2$ (I) (dimeric molecules).

Bis-(2-amino-1-methylbenzimidazole)-diacetato-copper(II)

Monoclinic syngony: $a = 15.302(8)$, $b = 17.373(6)$, $c = 18.449(10)$ Å, $\beta = 103.06(4)°$; space group P^2I/n, $Z = 8$, structural class $P2_I(n)$, $Z = 8$ (I + I).

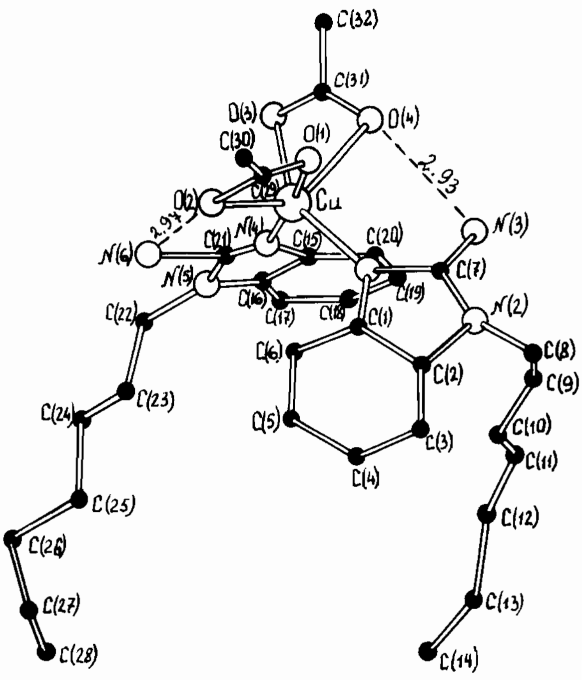

Fig. 5. Configuration of the molecule in the structure of $[Cu(OAc)_2(C_6H_4N_2(C_{17}H_{35})C{-}NH_2)_2]$.

Bis-2(amino-1-heptylbenzimidazole)-diacetato-copper(II)

Triclinic syngony: $a = 9.782(5)$, $b = 13.557(7)$, $c = 14.188(6)$ Å, $\alpha = 100.74(4)$, $\beta = 89.90(4)$, $\gamma = 110.56(5)°$; space group PI, $Z = 2$, structural class PI, $Z = 2$ (I).

Magnetochemical Measurements

Magnetic susceptibilities (μ_{eff}) were measured by the relative Faraday method in the solid phase at 298 K and also in the temperature range 80–400 K using a magnetic balance designed and mounted in the Rostov University and in the Institute of General and Inorganic Chemistry of Academy of Sciences of the USSR. The measurements were carried out at the strength of magnetic field equal to 9000 cersted.

Synthesis

The methanol (ethanol) solution of 5 mmol of ligand in 5–10 ml of the same solvent was added to methanol (ethanol) solution containing 5 mmol of copper(II) acetate in 15 ml of the aforementioned solvents in the course of mixing. The mixture obtained was heated at 40–50 °C for 20 min, then concentrated at 65–70 °C (the volume had halved) and cooled to 5 °C. In an hour green crystals precipitated; they were filtered, washed many times with hot methanol solution and then dried in vacuum at 80 °C.

Bis-(2-aminothiazole)-tetraacetato-di-copper(II)

Green crystals (from ethanol), melting point 150 °C. *Anal.* Found: C, 30.05; H, 3.81; N, 9.77; Cu, 23.41. Calc. for $C_{14}H_{20}N_4O_8S_2Cu_2$: C, 29.78; H, 3.54; N, 9.93; Cu, 22.69%. μ_{eff} = 1.47 BM (294.6 K) and 0.44 (77.6 K) BM.

Bis-(2-aminopyridine)-tetraacetato-di-copper(II)

Green crystals (from methanol), melting point 174 °C. *Anal.* Found: C, 38.36; H, 4.29; N, 10.02; Cu, 22.56. Calc. for $C_{18}H_{24}N_4O_8Cu_2$: C, 39.11; H, 4.34; N, 10.15; C, 23.10%. μ_{eff} = 1.38 (294.2 K) and 0.39 (92.9 K) BM.

Bis-(2-amino-1-heptylbenzimidazole)diacetato-copper(II)

Green crystals (from ethanol), melting point 179 °C. *Anal.* Found: C, 59.11; H, 7.21; N, 12.89; Cu, 10.12. Calc. for $C_{32}H_{48}N_6O_4Cu$: C, 59.62; H, 7.45; N, 13.00; Cu, 9.95%. μ_{eff} = 1.89 (298.1 K) BM.

Bis-(2-amino-1-methylbenzimidazole)-diacetato-copper(II)

Green crystals (from ethanol), melting point 227 °C. *Anal.* Found: C, 50.14; H, 4.87; N, 17.69; Cu, 13.08. Calc. for $C_{20}H_{24}N_6O_4Cu$: C, 50.01; H, 5.00; N, 17.81; Cu, 13.42%. μ_{eff} = 1.86 (298.1 K) BM.

Bis-(2-aminobenzimidazole)-diacetato-copper(II)

Green crystals (from ethanol), melting point 215 °C. *Anal.* Found: C, 47.83; H, 4.41; N, 18.81; Cu, 14.91. Calc. for $C_{18}H_{20}N_6O_4Cu$: C, 48.21; H, 4.44; N, 18.75; Cu, 14.28%. μ_{eff} = 1.91 (298.1 K) BM.

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