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Synthesis and Properties of the Cu(II) Complexes with Chiral Bis{(*E*)-[(1*S*,4*R*)-$\Delta^{7,8}$-1-Amino-2-*para*-Menthalidene]aminohydroxy}methane (L – a Derivative of Natural Terpenoid (*R*)-(+)-Limonene). Crystal Structure of the [Cu(L)(μ-Cl)$CuCl_3$] · *iso*-PrOH Solvate

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Abstract—The Cu_2LCl_4 complex (**I**) with chiral bis{(*E*)-[(1*S*,4*R*)-$\Delta^{7,8}$-1-amino-2-*para*-menthalidene]aminohydroxy}methane (L – a derivative of natural monoterpenoid (*R*)-(+)-limonene) is synthesized. The crystal structure of the solvate of complex **I** [Cu(L)(μ-Cl)$CuCl_3$] · *iso*-PrOH (**II**) is determined by X-ray diffraction analysis. Structure **II** is based on molecules of the [Cu(L)(μ-Cl)$CuCl_3$] binuclear complexes in which L is the tetradentate cycle-forming ligand. One Cl atom manifests the bridging function. The CuN_4Cl coordination unit is a square pyramid, and $CuCl_4$ is a distorted tetrahedron. The *iso*-PrOH molecules are localized in cavities between the layers of structure **II**. The μ_{eff} value for complex **I** is 2.56 μB and indicates the absence of an appreciable interaction between the Cu^{2+} ions in the Cu(II)–Cl–Cu(II) exchange cluster. The compound $CuLCl_2 \cdot H_2O$ (**III**) is synthesized. The μ_{eff} value for compound **III** is 1.6 μB. Complexes **I** and **III** are studied by EPR and IR spectroscopy.

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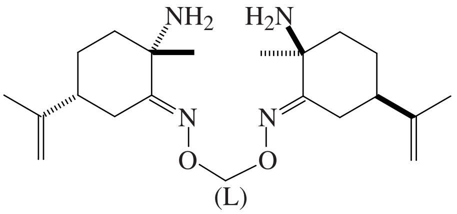
INTRODUCTION

The synthesis, structure determination, and studies of magnetic properties of polynuclear transition metal complexes are intensely developing areas of coordination chemistry [1, 2]. Considerable attention is given to the studies of magnetic exchange interactions in polynuclear compounds, particularly, in the copper(II) binuclear complexes with different exchange channels, including the Cu(II)–Cl(Br)–Cu(II) channels [1–4]. Among these copper(II) complexes, compounds with two Cl(Br) bridges are prevailing [3–12]. Several examples for the copper(II) binuclear complexes with only one Cl(Br) bridge are known [13–15]. In recent years, researchers have been interested in the synthesis and studies of the properties of chiral complexes, namely, magnetics based on chiral organic compounds [16, 17]. We synthesized the copper(II) binuclear complexes with dimethylaminooxime and morpholinooxime, namely, the 3-carene and limonene derivatives, respectively, having two Cl bridges [18, 19].

The purpose of this work is to synthesize the Cu(II) complexes with chiral bis{(*E*)-[(1*S*,4*R*)-$\Delta^{7,8}$-1-amino-2-*para*-menthalidene]aminohydroxy}methane (L), which is a derivative of natural monoterpenoid (*R*)-(+)-limonene, and to study their structures and magnetic properties. The topology of the donor heteroatomic fragments in L allowed us to hope that the tetradentate function would be manifested.



(L)

EXPERIMENTAL

(*R*)-(+)-Limonene (Fluka AG) with $[\alpha]_D^{20}$ +123; $CuCl_2 \cdot 2H_2O$ (high-purity grade), *iso*-PrOH and CH_2Cl_2 (reagent grade), and EtOH (rectified) were used for the synthesis of L and the complexes.

Synthesis of (4*R*)-1-amino-*para*-menth-7-en-2-one (*E*)-oximes (1*R*)-2 and (1*S*)-2. Anhydrous MeCN (50 ml) was saturated at room temperature with dry ammonia, and dimeric (*R*)-(+)-limonene nitrosochloride (*trans*-isomer synthesized by a standard procedure with alkyl nitrite [20]) (2.01 g, 5 mmol) was added to the resulting solution. The reaction mixture was stirred for 24 h at 16–18°C, the solvent was removed in vacuo, and the residue (yellowish oily product) was stirred with 1 M HCl (15 ml). The obtained solution was extracted with ethyl acetate (2 × 20 ml), the organic extracts were rejected, the aqueous phase was neutralized with a 25% aqueous solution of ammonia (20 ml), and the products were extracted with *tert*-butyl methyl ether (3 × 20 ml). The joined ethereal extract was washed with a concentrated aqueous solution of NaCl (5 ml) and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo, and a mixture of the (1*R*)-2 and (1*S*)-2 epimers (in the 1 : 7.5 ratio) was obtained as a colorless viscous oil. The yield was 1.60 g (8.78 mmol, 88%).

^{13}C NMR ($CDCl_3$–DMSO-d_6; δ, ppm): signals of epimer (1*S*)-2: 20.42 (C-9), 24.35 (C-3 or C-5), 25.75 (C-5 or C-3), 27.82 (C-10), 39.98 (C-6), 43.72 (C-4), 52.04 (C-1), 108.94 (C-8), 147.89 (C-7), 161.32 (C-2); signals of epimer (1*R*)-2: 20.35 (C-9), 25.55 (C-3 or C-5), 26.9 (C-5 or C-3), 26.83 (C-10), 40.59 (C-6), 43.78 (C-4), 52.90 (C-1), 108.99 (C-8), 147.67 (C-7), 161.98 (C-2).

^{1}H NMR ($CDCl_3$–DMSO-d_6; δ, ppm): signals of epimer (1*S*)-2: 1.20 (s, 3H, H-10), 1.42 (ddd, J = 13.5, 13.5, and 4.7 Hz, 1H, H-6_{ax}), 1.55 (m, 1H, H-5_{eq}), 1.64 (m, 2H, H-5_{ax}), 1.68 (br.s, 3H, H-9), 1.69 (m, 1H, H-6_{eq}), 1.94 (dddd, J = 11.5, 11.5, 4.0, and 4.0 Hz, 1H, H-4), 2.07 (dd, J = 13.7 and 11.5 Hz, 1H, H-3_{ax}), 3.03 (ddd, J = 13.7, 4.0, and 1.7 Hz, 1H, H-3_{eq}), 3.20 (v.br, 2H, $-NH_2$), 4.66 (m, 1H, H-8a), 4.70 (m, 1H, H-8b), 10.21 (br.s, 1H, OH); signals of epimer (1*R*)-2: 1.17 (s, 3H, H-10), 1.68 (br.s, 3H, H-9), 2.22 (ddd, J = 13.7, 4.6, and 1.4 Hz, 1H, H-6_{eq}), 2.33 (dddd, J = 10.1, 9.5, 4.6, and 4.0 Hz, 1H, H-4), 2.79 (dd, J = 13.7 and 10.1 Hz, H, H-3_{ax}), 3.20 (ddd, J = 14.3, 4.3, and 2.2 Hz, 1H, H-3_{eq}), 4.64 (m, 1H, H-8a), 4.67 (m, 1H, H-8b), 10.30 (br.s, 1H, OH).

Synthesis of L. 1-Amino-*para*-menth-7-en-2-one (*E*)-oxime (5.0 g, 0.027 mol) was dissolved in benzene (30 ml), and a 50% aqueous solution of NaOH (20 ml), a 10% aqueous solution of tetrabutylammonium hydroxide (0.5 ml), and CH_2Cl_2 (10 ml) were poured to the resulting solution. The reaction mixture was refluxed for 30 min with vigorous stirring. After the mixture was cooled down to room temperature, the organic phase was separated, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue (yellowish viscous mass) was chromatographed on a column packed with silica gel in a *tert*-butylmethyl ether–MeOH system, and L was isolated as a colorless syrupy liquid. The yield was 4.0 g (0.011 mol, 77%).

^{13}C NMR ($CDCl_3$; δ, ppm): 20.98 (C-9), 25.80 (C-3 or C-5), 26.13 (C-5 or C-3), 27.69 (C-10), 39.51 (C-6), 43.50 (C-4), 52.66 (C-1), 98.35 ($-O-CH_2-O-$), 109.80 (C-8), 147.50 (C-7), 164.83 (C-2).

^{1}H NMR ($CDCl_3$; δ, ppm): 1.27 (s, 6H, H-10), 1.47–1.54 and 1.63–1.68 (m, 12H, H-5, H-6, $-NH_2$), 1.69 (br.s, 6H, H-9), 2.07 (m, $W_{1/2}$ = 21 Hz, 2H, H-4), 2.33 (dd, J = 14.4 and 10.3 Hz, 2H, H-3_{ax}), 2.93 (dd, J = 14.4 and 4.4 Hz, 2H, H-3_{eq}), 4.71 (br.s, 4H, H-8), 5.59 (s, 2H, $-O-CH_2-O-$).

Synthesis of $[Cu_2LCl_4]$ (I). A solution of $CuCl_2 \cdot 2H_2O$ (0.07 g, 0.4 mmol) in an EtOH–*iso*-PrOH (1 : 1 vol/vol) mixture (5 ml) was added to a solution of L (0.08 g, 0.2 mmol) in the same mixture (5 ml). The resulting dark blue solution was stored at room temperature. After some time, the solution turned green. Upon the evaporation of the solvent to a minimum volume, green needle-like crystals precipitated. They were filtered off, washed with cooled *iso*-PrOH, and dried in a vacuum desiccator. The yield was 0.07 g (54%).

For $C_{21}H_{36}N_4O_2Cl_4Cu_2$ anal. calcd. (%): C, 39.1; H, 5.6; N, 8.7; Cl, 22.0.

Found (%): C, 38.5; H, 5.6; N, 8.2; Cl, 21.9.

Synthesis of $[Cu(L)(\mu\text{-}Cl)CuCl_3] \cdot$ *iso*-PrOH (II). Single crystals of solvate **II** were prepared by the slow evaporation of a solution of complex **I** in an *iso*-PrOH–CH_2Cl_2 (1 : 1 vol/vol) mixture. The single crystals were not filtered off but were taken from the solution and immediately poured with Nujol, because on drying the crystals cracked and became inappropriate for X-ray diffraction analysis.

Synthesis of $CuLCl_2 \cdot H_2O$ (III). A solution of $CuCl_2 \cdot 2H_2O$ (0.13 g, 0.74 mmol) in EtOH (5 ml) was added to a solution of L (0.28 g, 0.74 mmol) in EtOH (8 ml). The violet solution was stored at room temperature. The oil that formed upon the evaporation of the solvent was dissolved in H_2O (20 ml). The aqueous solution was filtered through a paper filter, and the filtrate was evaporated to dryness. The solid blue-violet mass was separated from the walls of the beaker and powdered. The power was dried in air. The yield was 0.33 g (87%).

For $C_{21}H_{36}N_4O_2Cl_2Cu$ anal. calcd. (%): C, 47.7; H, 7.2; N, 10.5; Cl, 13.4; Cu, 12.0.

Found (%): C, 48.0; H, 7.1; N, 9.5; Cl, 13.7; Cu, 12.1.

Microanalyses were carried out on Hewlett Packard 185 and Carlo Erba 1106 analyzers. The copper content in compound **III** was determined with a PA-2 polarograph using a chloride–ammonia buffer. The results of the analyses were calculated by the calibration curve. The samples were decomposed with aqua regia and chloric acid.

NMR spectra were recorded on a Bruker DRX 500 instrument (^{1}H, 500 MHz; ^{13}C, 125 MHz) for solutions with a concentration of 100 mg/ml in $CDCl_3$ or in a $CDCl_3$–DMSO-d_6 (1 : 1 vol/vol) mixture at 30°C. Chemical shifts (ppm) were detected relatively to tetramethylsilane (δ_H 0.00 ppm, δ_C 0.00 ppm), and the spin-spin interaction constants J are given in Hz. The signals of the solvent were used as an internal standard: $CDCl_3$ (δ_H 7.24 ppm, δ_C 76.90 ppm) or DMSO-d_6 (δ_H 2.50 ppm, δ_C 39.50 ppm).

The magnetic susceptibility of the polycrystals of complexes **I** and **III** was measured by the Faraday method at room temperature.

EPR spectra were recorded on a Varian E-109 radiospectrometer equipped with an analog-to-digital device for signal conversion and the unique software for spectra accumulation and primary processing. The studies were carried out in the X-range at the temperature of liquid nitrogen. For the calibration of the working frequency of the instrument, the spectra of the studied compounds were recorded together with the standard samples. A magnesium oxide powder with an admixture of Mn^{2+} ions in the 1: 5000 ratio ($g = 2.003$, $a = 86.6$ G) was used as the standard. The further presented parameters of the EPR spectra were obtained by decoding the spectra and refined by theoretical spectra simulation using the Simphonia program (Bruker).

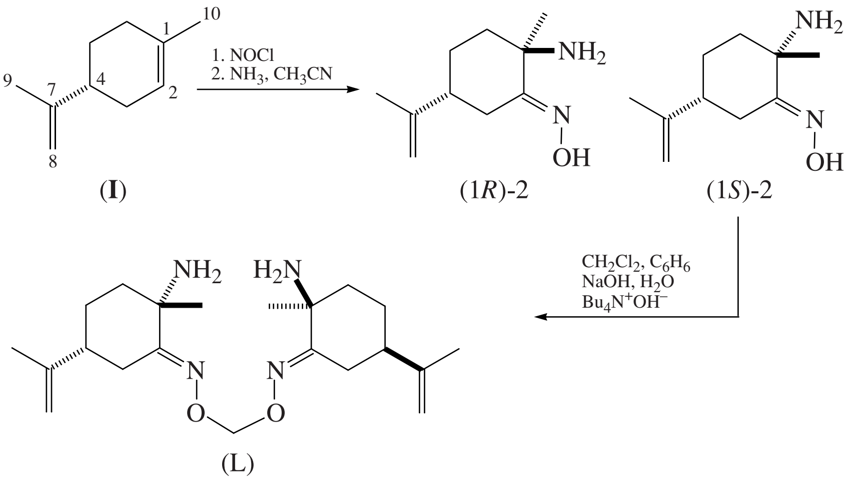
IR spectra were recorded in the 4000–80 cm^{-1} region on Scimitar FTS 2000 and Vertex 80 FT-IR spectrometers (samples were prepared as pellets pressed with KBr and polyethylene and as suspensions with Nujol).

A single crystal as a prism 0.20 × 0.12 × 0.07 mm in size was taken for the X-ray diffraction analysis of solvate **II**. The unit cell parameters and reflection intensities were measured at 150 K on a Bruker X8 Apex CCD automated diffractometer equipped with a two-coordinate detector according to a standard procedure (MoK_α radiation, graphite monochromator). The crystallographic characteristics, parameters of the X-ray diffraction experiment, and refinement details for structure **II** are presented in Table 1. The acentric space group of the crystals $P2_12_12_1$ was chosen by the analysis of extinctions in the intensity array confirmed by the calculations. The structure was solved by a direct method (SHELX-97) [21]. The refinement by the difference electron density synthesis ($\Delta\rho(xyz)$) revealed additional peaks, along with identified ones, as atoms of the $[Cu(L)(\mu\text{-}Cl)CuCl_3]$ binuclear compound. They were interpreted as atoms of the *iso*-PrOH molecules by taking into account the arrangement of the additional peaks, their values, and the starting reactants used.

The structure of solvate **II** was refined by the full-matrix least-squares method in the anisotropic approximation for all non-hydrogen atoms. The positions of hydrogen atoms were calculated geometrically and included into the refinement in the isotropic approximation. The final values of selected interatomic distances and bond angles are given in Table 2. The complete tables of atomic coordinates, bond lengths, and bond angles are deposited with the Cambridge Structural Database (no. 685326) and are also available from the authors.

RESULTS AND DISCUSSION

Ligand L was synthesized via the scheme



The initial compound was (*R*)-(+)-limonene (**1**), which was first transformed into nitrosochloride as described previously [19], and then the resulting dimeric nitrosochloride was treated with ammonia. Unlike the stereoselective reactions of limonene nitrosochloride with secondary amines [22], the reaction with ammonia under standard conditions (heating in an alcoholic solution [20]) affords an inseparable mixture of two α-aminooximes (1*R*)-2 and (1*S*)-2 epimeric by the C-1 atom in the ratio from 1 : 2 to 1 : 4[1], depending on the duration and temperature of the reaction, in a moderate yield (up to 65%). The yield of the target product can be increased (to 90%) and a higher stereoselectivity can be achieved (to 1 : 7.5) when the reaction of dimeric limonene

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[1] According to the ^{1}H and ^{13}C NMR spectral data.

nitrosochloride with ammonia is carried out in anhydrous MeCN. A mixture of the (1*R*)-2 and (1*S*)-2 epimers (to 1 : 7.5), obtained in the reaction with CH_2Cl_2 and concentrated alkali in the presence of the phase-transfer catalyst (quaternary ammonium salt), is transformed into a mixture of diastereomeric bis-esters from which the L ligand is isolated by column chromatography.

Complexes **I** and **III** with the molar ratio Cu : L = 2 : 1 and 1 : 1, respectively, were synthesized by the reaction of Cu(II) chloride with L in an alcoholic medium at different ratios of the starting reactants. When synthesizing compound **III**, we failed to select a procedure for the purification of the final product from a possible admixture of the starting substances. According to the published data, the Cu(II) complexes with the ligands, whose structure is similar to that of L, have high formation constants (β). For instance, $\log\beta_1$ of the Cu(II) complex with triethylenetetraamine is 19.31–23.26 (water–methanol) and 21.19 (water) [23, 24]. Based on this, we can assume that during the synthesis of compound **III** the initial reactants enter into the complex formation almost completely. This assumption agrees with the fact that the EPR spectra of both the solid samples and a solution of complex **III** in EtOH contain no signals that can be assigned to the starting $CuCl_2 \cdot 2H_2O$. Compounds **I** and **III** are soluble in EtOH, CH_2Cl_2, $CHCl_3$, and MeCN and are less soluble in *iso*-PrOH. Complex **I** is poorly soluble in water, whereas complex **III** is soluble. Single crystals of solvate **II** were grown from an *iso*-PrOH–CH_2Cl_2 mixture.

The X-ray diffraction study of complex **II** shows that its crystal structure is based on the [Cu(L)(μ-Cl)$CuCl_3$] binuclear complex molecules and the *iso*-PrOH solvate molecules. The structure of an acentric molecule of the binuclear complex is shown in Fig. 1.

The $Cu(1)^{2+}$ ion coordinates four N atoms of the tetradentate cycle-forming ligand L (Cu(1)–N 1.953(3)–2.003(3) Å). This results in the closure of two CuN_2C_2 five-membered chelate cycles and one CuN_2O_2C six-membered metallocycle. The coordination sphere of the $Cu(1)^{2+}$ ion also includes the Cl(1) bridging atom (Cu–Cl 2.674(1) Å). The CuN_4Cl coordination polyhedron is a distorted square pyramid, whose base is formed of the N atoms (N···N 2.569(5)···3.142(5) Å) and the Cl(1) atom occupies the axial vertex of the pyramid. The angle of the Cu(1)–Cl(1) vector with the base plane is 84.2°. The chlorine atom of the adjacent molecule, which completes the Cu(1) coordination polyhedron to the asymmetrically extended tetragonal bipyramid (4 + 1 + 1), is arranged at a longer Cu(1)···Cl(3) distance (3.200(2) Å), being considerably shorter than the sum of the van der Waals radii of Cu and Cl (3.70 Å [25]). The Cu atom shifts from the plane of the four N atoms to the Cl(1) apical atom by 0.161(2) Å (the average deviation of the N atom from the plane is 0.027(2) Å). The Cl(1)Cu(1)Cl(3) angle is 164.1°.

Unlike the $Cu(1)^{2+}$ ion, the $Cu(2)^{2+}$ ion is localized inside the Cl_4 distorted tetrahedron with three close distances Cu(2)–Cl of 2.216(1)–2.226(1) Å and an increased Cu(2)–μ-Cl(1) distance of 2.362(1) Å. The Cu···Cu distance in the binuclear complex molecule is 4.157(3) Å, and the shortest Cu···Cu distance between the molecules is 4.698(2) Å.

Table 1. Crystallographic characteristics and details of the experiment and refinement for the structure of solvate **II**

Parameter	Value
Empirical formula	$C_{24}H_{44}Cl_4Cu_2N_4O_3$
FW	705.51
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a, Å	11.1272(3)
b, Å	11.7124(5)
c, Å	23.9981(11)
V, Å^3	3127.6(2)
Z; ρ_{calcd}, g/cm^3	4; 1.498
μ_{Mo}, cm^{-1}	17.33
Crystal sizes, mm	0.20 × 0.12 × 0.07
θ range, deg	1.70–25.00
N_{hkl} measured/N_{hkl} independent	20222/5482 (R_{int} = 0.0344)
Number of refined parameters	342
Goodness-of-fit for F^2	1.035
R factor, $I > 2\sigma(I)$	$R_1 = 0.0352$ $wR_2 = 0.0851$ N_{hkl} = 4809
R factor (for all reflections)	R_1 = 0.0441 wR_2 = 0.0880
$\Delta\rho_{max}/\Delta\rho_{min}$, *e* Å^{-3}	0.545/–0.409
Absolute structure parameter	0.011(14)

The Cu(1)–N, Cu(1)–Cl, and Cu(2)–Cl distances in the coordination units of molecule **II** are consistent with those for the structures of the Cu(II) binuclear complexes [13, 15].

The both CuN_2C_2 five-membered chelate ring are almost planar (the average deviations of the atoms from their planes are 0.045(2) and 0.022(2) Å). The CuN_2O_2C six-membered metallocycle has an envelope conformation with the C(11) atom shifted from the plane of the other four atoms by 0.765(5) Å. The both six-membered carbocycles exist in the chair conformations: the C(1), C(4) and C(1a), C(4a) atoms deviate from the planes of four other C atoms by –0.533(7), 0.653(6) Å and 0.586(6), –0.665(7) Å, respectively.

Table 2. Selected interatomic distances and bond angles in the structure of solvate **II**

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–N(2)	1.954(3)	C(5)–C(7)	1.515(7)
Cu(1)–N(2a)	1.972(3)	C(5)–C(6)	1.561(7)
Cu(1)–N(1a)	1.991(3)	C(7)–C(8)	1.288(7)
Cu(1)–N(1)	2.002(3)	C(7)–C(9)	1.516(7)
Cu(1)–Cl(1)	2.675(1)	C(1a)–C(2a)	1.527(6)
Cl(1)–Cu(2)	2.363(1)	C(1a)–C(6a)	1.537(6)
Cl(3)–Cu(1)	3.200(2)	C(2a)–C(3a)	1.491(6)
O(1)–C(11)	1.410(5)	C(2a)–C(10a)	1.554(6)
O(1)–N(2)	1.414(4)	C(3a)–C(4a)	1.500(6)
O(1a)–N(2a)	1.404(4)	C(4a)–C(5a)	1.527(6)
O(1a)–C(11)	1.415(5)	C(5a)–C(7a)	1.516(6)
N(1)–C(2)	1.492(5)	C(5a)–C(6a)	1.528(6)
N(2)–C(3)	1.271(6)	C(7a)–C(8a)	1.314(7)
N(1a)–C(2a)	1.508(5)	C(7a)–C(9a)	1.478(7)
N(2a)–C(3a)	1.273(5)	Cu(2)–Cl(2)	2.215(1)
C(1)–C(2)	1.517(6)	Cu(2)–Cl(3)	2.219(1)
C(1)–C(6)	1.532(6)	Cu(2)–Cl(4)	2.226(1)
C(2)–C(3)	1.524(6)	C(1b)–O(1b)	1.424(5)
C(2)–C(10)	1.543(6)	C(1b)–C(3b)	1.486(7)
C(3)–C(4)	1.497(6)	C(1b)–C(2b)	1.511(7)
C(4)–C(5)	1.529(7)		
Angle	ω, deg	Angle	ω, deg
N(2)Cu(1)N(2a)	92.3(1)	O(1)N(2)Cu(1)	122.4(3)
N(2)Cu(1)N(1a)	167.8(1)	C(2a)N(1a)Cu(1)	112.7(3)
N(2a)Cu(1)N(1a)	81.4(1)	C(3a)N(2a)O(1a)	115.9(3)
N(2)Cu(1)N(1)	81.0(1)	C(3a)N(2a)Cu(1)	119.4(3)
N(2a)Cu(1)N(1)	170.2(1)	O(1a)N(2a)Cu(1)	124.6(3)
N(1a)Cu(1)N(1)	103.8(1)	O(1)C(11)O(1a)	112.5(3)
N(2)Cu(1)Cl(1)	101.3(1)	Cl(2)Cu(2)Cl(3)	104.38(5)
N(2a)Cu(1)Cl(1)	94.8(1)	Cl(2)Cu(2)Cl(4)	100.44(5)
N(1a)Cu(1)Cl(1)	89.8(1)	Cl(3)Cu(2)Cl(4)	136.03(5)
N(1)Cu(1)Cl(1)	93.5(1)	Cl(2)Cu(2)Cl(1)	114.79(5)
Cu(2)Cl(1)Cu(1)	111.07(4)	Cl(3)Cu(2)Cl(1)	98.76(4)
C(11)O(1)N(2)	108.3(3)	Cl(4)Cu(2)Cl(1)	102.96(5)
N(2a)O(1a)C(11)	110.1(3)	O(1b)C(1b)C(3b)	112(2)
C(2)N(1)Cu(1)	113.4(2)	O(1b)C(1b)C(2b)	108.8(6)
C(3)N(2)O(1)	116.1(3)	C(3b)C(1b)C(2b)	107.5(7)
C(3)N(2)Cu(1)	120.5(3)		

The molecular packing in crystal **II** is presented in Fig. 2 in the projection to the (010) plane. The binuclear complex molecules are localized in two layers bound by the 2_1 axis and parallel to the (001) plane ($z \approx 0$ and 0.5). The *iso*-PrOH molecules are arranged in large cavities between the layers. It is most likely that a possibility of filling these cavities with the *iso*-PrOH molecules favors the isolation of the solid phase of solvate **II**. The shortest contacts of the atoms of the *iso*-PrOH molecules with the layers of the binuclear molecules are at a level of the van der Waals interactions: O(1b)···Cl(4) 3.49(2), C(2b)···Cl(4) 3.51(2), and O(1b)···O(1) 3.32(2) Å. The structure of one this layer is shown in Fig. 3a. In addition to the Cu(1)···Cl(3) short contact (3.200(2) Å), structure **II** contains weaker intermolecular interactions (Cl(1)···Cl(4) 3.592(2), Cl(1)···N(1) 3.238(3), Cl(3)···N(1a) 3.404(5), Cl(3)···N(1) 3.454(4), Cl(2)···C(11) 3.490(5) Å), resulting in the formation of a supramolecular polymeric strip that lies in the above described layer and is parallel to the [100] direction. The main fragment of the polymeric strip showing the combination of the $Cu(1)N_4Cl_2$ tetragonal bipyramids and $Cu(2)Cl_4$ tetrahedra through the Cl(1) and Cl(3) common vertices is presented in Fig. 3b. A similar situation is observed for the $C_{14}H_{24}Cl_4Cu_2N_4$ structure [15]. In this structure, the Cl(2) atom of the adjacent molecule (Cu(1)···Cl(2) 3.164 Å) plays the same role as the Cl(3) atom in studied structure **II**, thus contributing to the formation of the polymeric strip parallel to the *z* axis.

The IR spectra of molecule **L** and complexes **I**–**III** exhibit the bands corresponding to vibrations of the main functional groups and fragments (Table 3). As a whole, the IR spectra of complexes **I** and **II** are similar, except for the region of the ν(OH) frequencies. This region for complex **II** contains an absorption band at 3509 cm^{-1}, which corresponds to the X-ray diffraction data indicating the presence of the *iso*-PrOH solvate molecules in the structure of this complex. The band disappears upon the storage of solvate **II** in a vacuum desiccator.

The spectrum of compound **III** exhibits absorption bands at 3405 cm^{-1} and in the region of libration vibrations (600 cm^{-1}) and the $\nu(NH_2)$ bands, which are broadened compared to those in the spectra of **L**, **I**, and **II**, indicating the presence of the H_2O molecule in the composition of complex **III**. This conclusion agrees with the elemental analysis and thermogravimetry data (a step corresponding to the loss of one H_2O molecule is observed in the curve of complex **III** at 70–130°C). In addition, the band at 404 cm^{-1} corresponding to the vibration of the Cu–O bond is observed in the low-frequency region of the IR spectrum of compound **III**.

In the IR spectra of compounds **I**–**III**, the bands caused by the $\nu(NH_2)$ vibrations are considerably shifted to the low-energy region compared to the spectrum of L. In addition, the positions of the ν(CN) bands and overlapped with them $\delta(NH_2)$ bands change (Table 3), indicating the coordination of the NH_2 groups. In the IR spectra of compounds **I** and **II**, the intense structured bands with maxima at 300 cm^{-1} were assigned to stretching vibrations of the Cu–Cl bonds. The inflections (Table 3) are related, most likely, to the difference in the Cu–Cl bond lengths (Table 2), which is due o the existence of the bridging and terminal Cl atoms. As compared

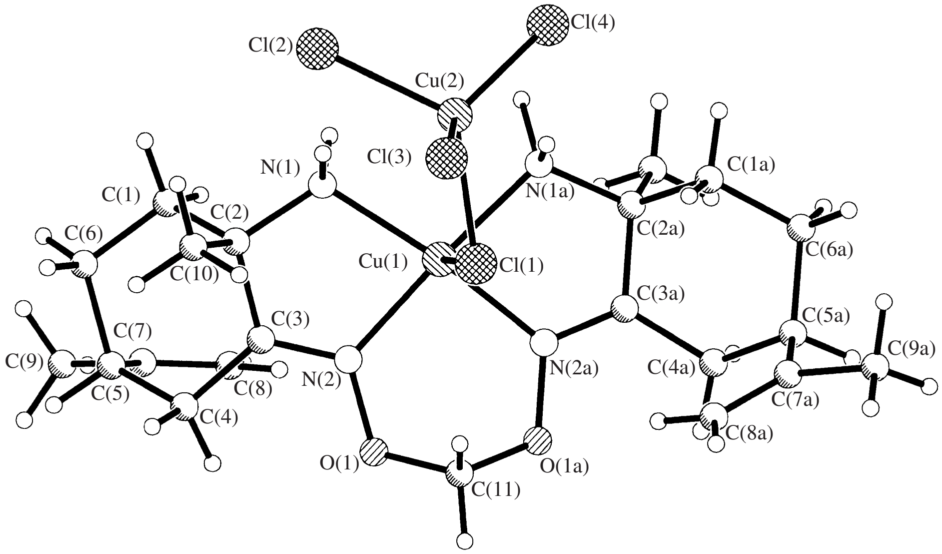

Fig. 1. Structure of the acentric molecule of the binuclear complex in crystal structure **II** with non-hydrogen atom numeration.

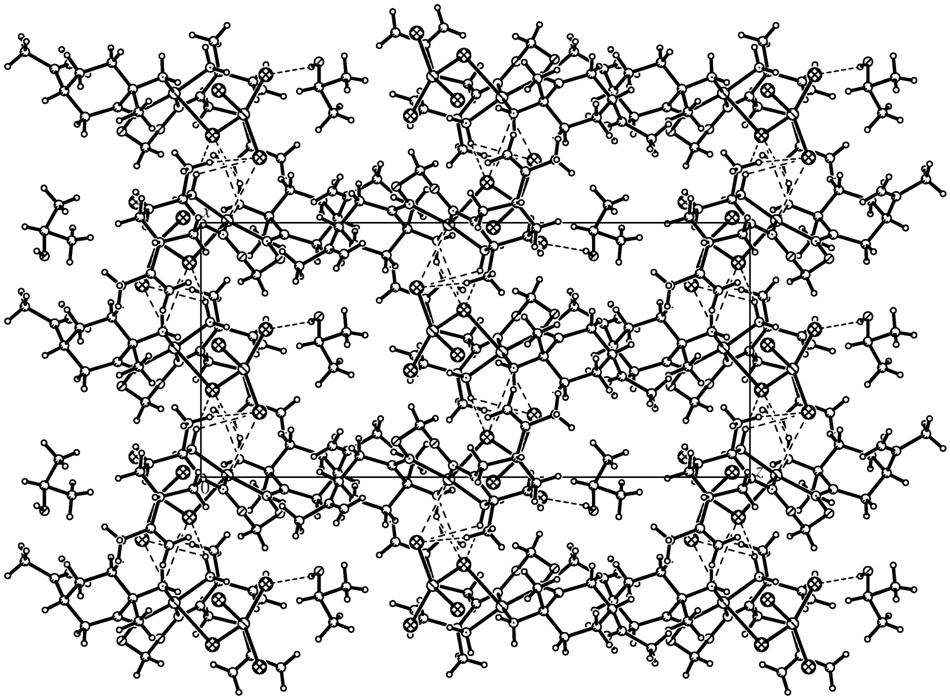

Fig. 2. Molecular packing in the structure of solvate **II** containing the [Cu(L)(μ-Cl)$CuCl_3$] binuclear complex molecules in the projection to the (010) plane.

to the spectra of complexes **I** and **II**, the IR spectrum of compound **III** contains no bands in a region of ν(Cu–Cl), indicating no Cu–Cl bonds. It should be mentioned that it was difficult to pick out the corresponding bands in a region of 500–430 cm^{-1}, where vibrations of the Cu–N bonds can appear, because this region contains the bands characteristic of L.

The data of IR spectroscopy show that complex **I** has a binuclear structure analogous to that of the complex molecule in solvate **II**. In complex **III**, the nearest coordination sphere of the Cu atom contains the N atoms of the L tetradentate ligand and, probably, the O atom of the H_2O molecule.

The EPR spectrum of the solid phase of compound **I** is not observed at room temperature. However, a single asymmetric line with a width of ~200 G and an average *g* factor of 2.13 appears with the temperature decrease to 77 K. The observed behavior can be explained, first, by

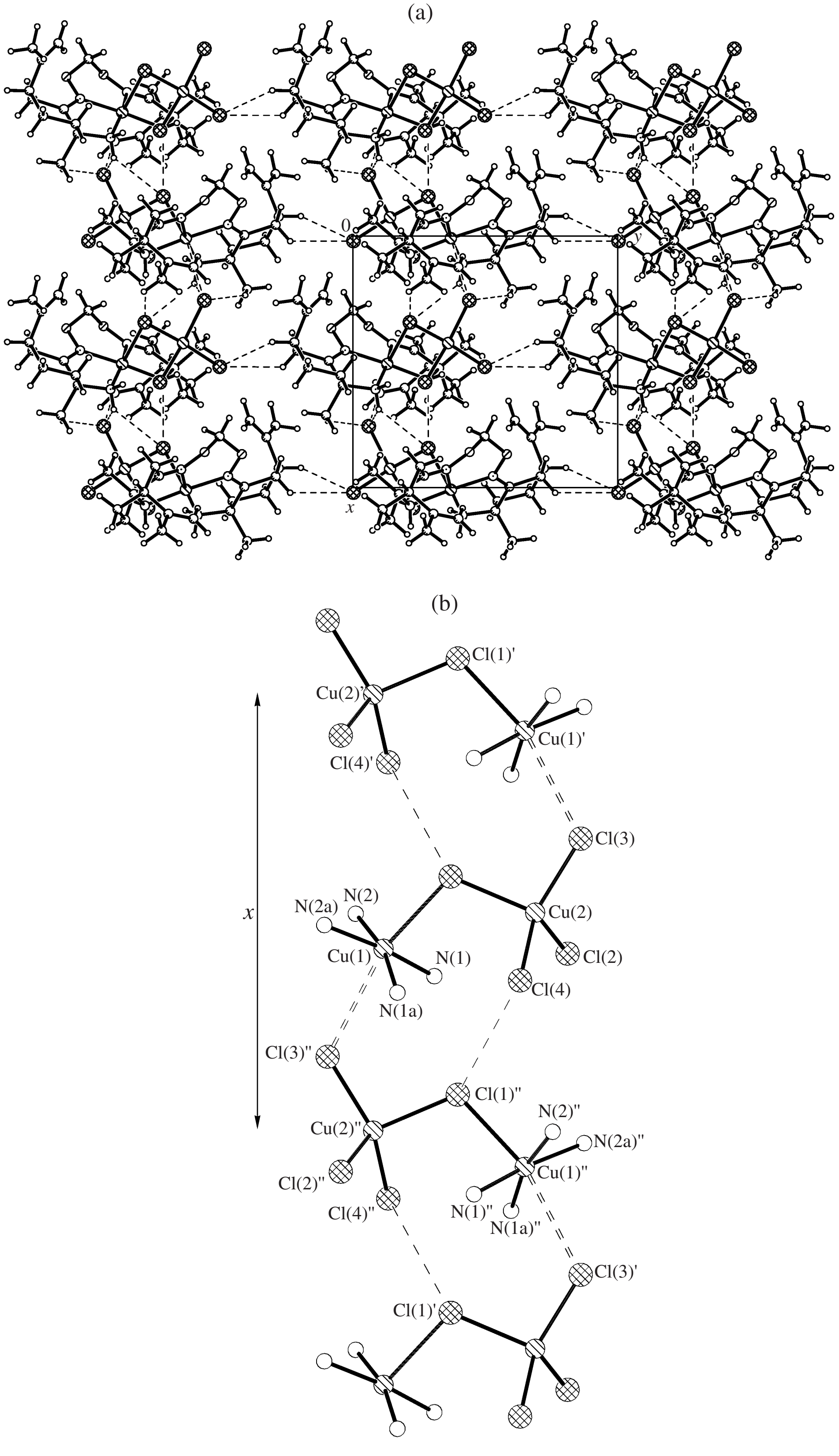

Fig. 3. (a) Structure of the layer in structure **II** containing the [Cu(L)(μ-Cl)$CuCl_3$] binuclear complex molecules in the projection to the (001) plane and (b) the main structure of the supramolecular polymeric strip in structure **II**.

the strong change in the relaxation time due to the modulation by thermal vibrations of the exchange interaction of unpaired electrons of the Cu^{2+} ions through the single bridging Cl atom. Second, considerable differences in the parameters of the spin Hamiltonian of the Cu^{2+} ions also favor the line width broadening. When the Cu(II) complexes contain two bridges, the change in the exchange via one channel can partially be compensated by the vibrations that are not synchronized via another channel, resulting in a lower temperature dependence of the line width. In the case of complex **I**, both indicated factors favor the EPR line broadening. This explanation agrees with the X-ray diffraction data for solvate **II** concerning the existence of one exchange channel Cu(II)–Cl–Cu(II). The line shape of the EPR spectrum is retained in a frozen solution of compound **I** in CH_2Cl_2, indicating the binuclear structure of the complex in the solution as well.

The parameters of the EPR spectra of compound **III** in the solid state and in the frozen ethanolic solution are similar (Table 4), indicating that the coordination polyhedron of the Cu^{2+} ion is retained upon dissolution. The values of the spectral parameters are characteristic of the environment of CuN_4A (A is the coordinated Cl or O atom) in which the N atoms of the tetradentate L ligand lie in the base of the tetragonal pyramid and the A atom occupies the axial position [25, 26]. According to the IR spectral data for complex **III**, the A atom is, most likely, the O atom of the coordinated H_2O molecule. Unlike binuclear complex **I** and solvate **II**, compound **III**, which is amorphous to X-rays, is probably mononuclear (the CuN_4O coordination site is a square pyramid).

The EPR spectra of frozen solutions of compound **I** in EtOH indicate two forms (**I-1** and **I-2**) (Fig. 4). The spectrum of form **I-1** coincides completely with the spectral parameters of an ethanolic solution of compound **III** (Table 4). It is most likely that the complex is dissolved during the dissolution of compound **I** in EtOH. In fact, upon the dissolution of green complex **I** in EtOH, the solution gains the blue color similar to that of a solution of compound **III**.

Table 3. Main vibrational frequencies (cm^{-1}) in the IR spectra of L and compounds **I–III**

Compound				Assignment
L	**I**	**II**	**III**	
		3509		ν(OH)*
			3405	$\nu(H_2O)$
3366	3210	3207	3207	$\nu(NH_2)$
3230	3116	3112	3090	
1644	1650	1650	1649	ν(CN) $\delta(NH_2)$
1601	1580	1578	1596	ν(ring)
			404	ν(Cu–O)
	301, 313 sh, 285 sh	302, 317 sh, 287 sh		ν(Cu–Cl)
	182	183	187	Lattice vibrations

* *iso*-PrOH.

The EPR spectra of dilute solutions of $CuCl_2$ in EtOH in the presence of Cl^- ion excess were recorded to identify form **I-2**. Three forms **A**, **B**, and **C** are observed in the spectra (Table 4). Upon the addition of hydrochloric acid, the solution gains the yellow-brown color characteristic of the $CuCl_4$ tetrahedra. In the case of a minor HCl concentration, form **A** has the largest fraction. The amount of form **A** decreased and the contents of forms **B** and **C** increased with an increase in the HCl concentration (Table 4). Form **A** coincides by the EPR spectral parameters with form **I-2** of the polyhedra of the Cu atom observed in an ethanolic solution of compound **I**. It is most likely that form **I-2** of the polyhedra of the Cu atom in a solution of complex **I** in EtOH can be attributed to the CuO_6 or CuO_5Cl forms, which are produced due to the solvolysis of the Cu(II) chloride complex, or to a mixture of these forms.

For freshly synthesized complex **I**, the experimental μ_{eff} value (2.56 μB) remains almost unchanged upon storing the compound for six months. According to the

Table 4. Parameters of the EPR spectra of compounds **I**, **III**, and $CuCl_2 \cdot 2H_2O$

Compound		Form	$g_\perp$	$g_\parallel$	$A_\parallel$	$W_\parallel/W_\perp$, G
I	Solid phase		2.13			200
	Solution in CH_2Cl_2		2.14			280
	Solution in EtOH	**I-1**	2.056	2.21	188	35
		I-2	2.09	2.43	110	20
III	Solid phase		2.06	2.215	180	80/70
	Solution in EtOH		2.056	2.21	188	35
$CuCl_2 \cdot 2H_2O$	Solution in EtOH in the presence of excess Cl^- ions	**A**	2.087	2.43	110	15/27
		B	2.08	2.365	133	15/27
		C	2.07	2.325	144	15/27

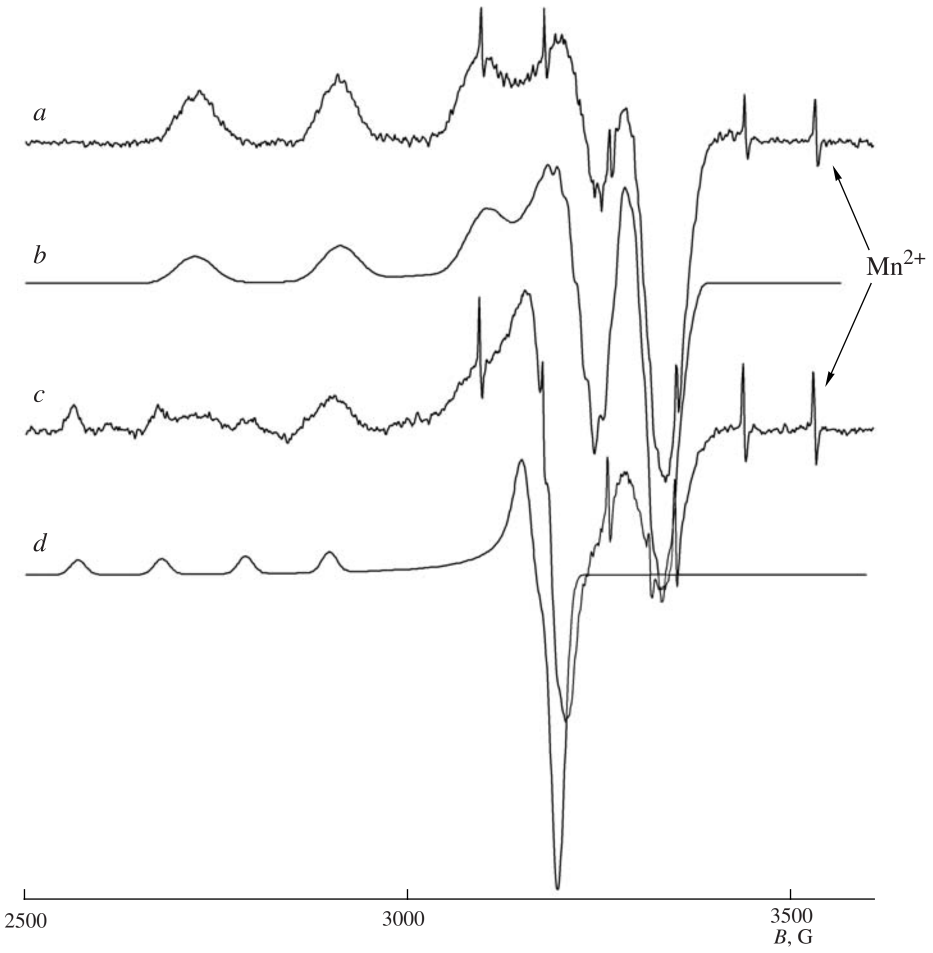

Fig. 4. EPR spectra of frozen solutions of compounds (*a*) **III** and (*c*) **I** in EtOH and the theoretical spectra of (*b*) complex **III** and (*d*) form **I-2** of complex **I**. The narrow lines in the experimental spectra refer to the Mn^{2+} ions of the side standard.

X-ray diffraction data for solvate **II** containing the $[Cu(L)(\mu\text{-}Cl)CuCl_3]$ molecule, the Cu···Cu distance in the complex is significant (4.157(3) Å) due to which only very weak exchange interaction of the Cu^{2+} ions is possible via the Cu(II)–Cl–Cu(II) exchange channel. The calculated μ_{eff} value for the system of two noninteracting Cu^{2+} ions is 2.61 μB (if $g = 2.13$). The experimental μ_{eff} value for complex **I** is close to the calculated value. This indicates that a noticeable (from the viewpoint of magnetochemistry) interaction between the Cu^{2+} ions in the Cu(II)–Cl–Cu(II) exchange cluster is absent.

For complex **III**, the μ_{eff} value (1.60 μ_B) corresponds to the electron configuration d^9.

In this work, the first binuclear Cu(II) complex with the chiral ligand (a natural terpenoid derivative) and the solvate of this complex were synthesized. A specific feature of the structures of these compounds is the formation of one exchange channel Cu(II)–Cl–Cu(II).

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